IUPAC-NIST Solubility Data Series. 75. Nonmetals in Liquid Alkali Metals

Editors

Hans Ulrich Borgstedt[a)]
Forschungszentrum, Karlsruhe, Germany

Cezary Guminski[b)]
Department of Chemistry, University of Warsaw, Poland

Compilers and Evaluators

Hans Ulrich Borgstedt
Forschungszentrum, Karlsruhe, Germany

Cezary Guminski
Department of Chemistry, University of Warsaw, Poland

(Received 23 February 2001; accepted 12 April 2001)

Liquid alkali metals have several physical properties which favor their use in a number of important applications. For example, their large liquidus temperature range and their excellent heat transfer properties are important for use as heat transfer media. They are used in large nuclear reactors in which hundreds of tons of sodium are circulating, and in small parts of engines for cooling of valves. Since these metals are among the most electropositive elements, several of them (Li, Na) can be used in high specific capacity and high energy density batteries at moderately elevated temperatures. The compatibility of metallic constructional materials which are used to contain the liquid metals is strongly influenced by nonmetals present in the liquids. The physical properties of the liquid metals are also influenced by dissolved substances. Several nonmetals dissolved in alkali metals are able to form ternary compounds with components of the constructional materials. Thus, corrosion and compatibility studies have been accompanied by extensive chemical work related to the solutions of non-metallic substances in liquid alkali metals. All available solubility data of nonmetallic elements and some of their compounds in the five liquid alkali metal solvents (Li, Na, K, Rb, and Cs) are collected and compiled. Original publications with reliable data and information on the methods used to generate them are reported in individual Compilations. When numerical data are not given in a publication, the data are often read out from figures and converted into numerical data by the compilers. The precision of this procedure is indicated in the Compilations under Estimated Error. Evaluated solubility data are tabulated at the end of the Critical Evaluations: if there is agreement of at least two independent studies within the experimental error, the solubility values are assigned to the ''recommended'' category. Values are assigned as ''tentative,'' if only one reliable result was reported, or if the mean value of two or more reliable studies was outside the error limits. In the tabulation, three, two, or one significant figures are assigned for respective precisions that are better than $\pm 1\%$ and $\pm 10\%$ and worse than $\pm 10\%$. If necessary, the solubilities are recalculated into mol %. The completeness of this investigation of the literature has been confirmed and extended by studying several reviews dealing with the solution chemistry of substances in the alkali metals. Solubility data are sometimes measured under parameters, which are not standard conditions of such measurements. Frequently measurements are performed under constrained pressure. The solubility of noble gases or other gases, which do not form

[a)]Electronic mail: zlata.voss@imf.fzk.de
[b)]Electronic mail: cegie@chem.uw.edu.pl

© 2001 American Institute of Physics.

compounds with the alkali metals, depends on the gas pressures. This dependency is documented in the data sheets. Schematic phase diagrams are presented in systems for which they assist the understanding of the data and the conclusions. They are based on the most recent state of knowledge and generally presented in the Critical Evaluations. Some solubility diagrams are shown in form of a log solubility versus reciprocal temperature function. These figures illustrate the larger scatter of data for systems in which interfering reactions cause unstable behavior of solutions. While several solutes are well defined substances, other systems need still additional studies to define the equilibrium solid state compound. One should realize that estimations of the stoichiometry and thermal stability of ternary compounds are experimentally difficult, and their results are often uncertain. © *2001 American Institute of Physics.*

Key words: liquid alkali metals; noble gases; nonmetals; molten systems; solubility.

Contents

1. Preface to the Volume. 838
2. Introduction to the Solubility of Solids in Liquids. 839
   2.1. The Nature of the Project. 839
   2.2. Compilations and Evaluations. 839
      2.2.1. Compilations. 839
      2.2.2. Evaluations. 840
   2.3. Quantities and Units Used in Compilation and Evaluation of Solubility Data. 841
      2.3.1. Mixtures, Solutions and Solubilities. . . 841
      2.3.2. Physiochemical Quantities and Units. . 842
   2.4. References for the Introduction. 845
3. Solutions of Nonmetallic Substances in Lithium. . 846
   3.1 Lithium–Hydrogen. 846
   3.2 Lithium–Deuterium. 858
   3.3 Lithium–Tritium. 863
   3.4 Lithium–Boron. 866
   3.5 Lithium–Carbon. 867
   3.6 Lithium–Silicon. 872
   3.7 Lithium–Germanium. 878
   3.8 Lithium–Nitrogen. 881
   3.9 Lithium–Phosphorous. 887
   3.10 Lithium–Arsenic. 888
   3.11 Lithium–Oxygen. 888
   3.12 Lithium–Sulfur. 894
   3.13 Lithium–Selenium. 897
   3.14 Lithium–Tellurium. 899
   3.15 Lithium–Polonium. 901
   3.16 Lithium–Fluorine. 901
   3.17 Lithium–Chlorine. 902
   3.18 Lithium–Bromine. 905
   3.19 Lithium–Iodine. 906
   3.20 Lithium–Astatine. 907
   3.21 Lithium–Helium. 907
   3.22 Lithium–Radon. 908
4. Solutions of Nonmetallic Substances in Sodium. . 909
   4.1 Sodium–Hydrogen. 909
   4.2 Sodium–Deuterium. 925
   4.3 Sodium–Boron. 926
   4.4 Sodium–Carbon. 927
   4.5 Sodium–Silicon. 939
   4.6 Sodium–Germanium. 941
   4.7 Sodium–Nitrogen. 944
   4.8 Sodium–Sodium Cyanide. 945
   4.9 Sodium–Phosphorous. 951
   4.10 Sodium–Arsenic. 952
   4.11 Sodium–Oxygen. 952
   4.12 Sodium–Sodium Hydroxide. 976
   4.13 Sodium–Sodium Carbonate. 982
   4.14 Sodium–Sulfur. 986
   4.15 Sodium–Selenium. 994
   4.16 Sodium–Tellurium. 997
   4.17 Sodium–Polonium. 1001
   4.18 Sodium–Fluorine. 1002
   4.19 Sodium–Chlorine. 1003
   4.20 Sodium–Bromine. 1009
   4.21 Sodium–Iodine. 1013
   4.22 Sodium–Helium. 1020
   4.23 Sodium–Neon. 1023
   4.24 Sodium–Argon. 1023
   4.25 Sodium–Krypton. 1025
   4.26 Sodium–Xenon. 1026
   4.27 Sodium–Radon. 1028
5. Solutions of Nonmetallic Substances in Potassium. 1028
   5.1 Potassium–Hydrogen. 1028
   5.2 Potassium–Deuterium. 1034
   5.3 Potassium–Boron. 1035
   5.4 Potassium–Carbon. 1035
   5.5 Potassium–Silicon. 1037
   5.6 Potassium–Germanium. 1037
   5.7 Potassium–Nitrogen. 1039
   5.8 Potassium–Phosphorous. 1040
   5.9 Potassium–Arsenic. 1041
   5.10 Potassium–Oxygen. 1042
   5.11 Potassium–Potassium Hydroxide. 1057
   5.12 Potassium–Sulfur. 1060
   5.13 Potassium–Selenium. 1065
   5.14 Potassium–Tellurium. 1067
   5.15 Potassium–Fluorine. 1069
   5.16 Potassium–Chlorine. 1071

5.17 Potassium–Bromine. 1076
5.18 Potassium–Iodine. 1077
5.19 Potassium–Helium. 1082
5.20 Potassium–Neon, Krypton, Xenon, or Radon. 1083
5.21 Potassium–Argon. 1084
6. Solutions of Nonmetallic Substances in Rubidium. 1085
6.1 Rubidium–Hydrogen. 1085
6.2 Rubidium–Boron. 1085
6.3 Rubidium–Carbon. 1086
6.4 Rubidium–Silicon. 1086
6.5 Rubidium–Germanium. 1087
6.6 Rubidium–Nitrogen. 1089
6.7 Rubidium–Phosphorous. 1089
6.8 Rubidium–Arsenic. 1090
6.9 Rubidium–Oxygen. 1091
6.10 Rubidium–Rubidium Hydroxide. 1095
6.11 Rubidium–Sulfur. 1096
6.12 Rubidium–Selenium. 1099
6.13 Rubidium–Tellurium. 1101
6.14 Rubidium or Cesium–Polonium. 1102
6.15 Rubidium–Fluorine. 1103
6.16 Rubidium–Chlorine. 1104
6.17 Rubidium–Bromine. 1105
6.18 Rubidium–Iodine. 1106
6.19 Rubidium–Helium (Ne, Ar, Kr, Xe, Rn). . . . 1109
7. Solutions of Nonmetallic Substances in Cesium. . 1109
7.1 Cesium–Hydrogen. 1109
7.2 Cesium–Boron. 1111
7.3 Cesium–Carbon. 1112
7.4 Cesium–Silicon. 1113
7.5 Cesium–Germanium. 1114
7.6 Cesium–Nitrogen. 1115
7.7 Cesium–Cesium Amide. 1116
7.8 Cesium–Phosphorus. 1116
7.9 Cesium–Arsenic. 1117
7.10 Cesium–Oxygen. 1117
7.11 Cesium–Cesium Hydroxide. 1122
7.12 Cesium–Sulfur. 1123
7.13 Cesium–Selenium. 1125
7.14 Cesium–Tellurium. 1127
7.15 Cesium–Fluorine. 1130
7.16 Cesium–Chlorine. 1131
7.17 Cesium–Bromide. 1133
7.18 Cesium–Iodine. 1134
7.19 Cesium–Helium or Neon or Argon or Krypton or Xenon or Radon. 1137
8. System Index. 1138
9. Registry Number Index. 1138
10. Author index. 1139
11. IUPAC-NIST Solubility Data Series: Published and Forthcoming Volumes. 1157

List of Figures

1. Li–H phase diagram. 847
2. Li–B schematic phase diagram (partial). 866
3. Li–C phase diagram. 868
4. Li–Si phase diagram. 873
5. Li–Ge phase diagram (provisional). 878
6. Li–N phase diagram (partial). 881
7. Li–As phase diagram (schematic). 888
8. Li–O phase diagram (partial). 889
9. Li–S phase diagram (partial). 894
10. Li–Se phase diagram (partial). 897
11. Li–Te phase diagram (incomplete). 899
12. Li–F phase diagram. 901
13. Li–Cl phase diagram. 902
14. Li–I phase diagram. 906
15. Li–He phase diagram. 907
16. Na–H phase diagram. 910
17. Na–B phase diagram. 926
18. C–Na phase diagram (tentative). 927
19. Na–Si phase diagram (tentative). 940
20. Ge–Na phase diagram (doubtful). 941
21. Na–N phase diagram (fragmentary). 944
22. Na–NaCN phase diagram. 945
23. Na–O phase diagram. 953
24. Na–NaOH phase diagram at 0.12 MPa. 977
25. Na–Na_2CO_3 phase diagram (schematic). 983
26. Na–S phase diagram (proposed). 986
27. Se–Na phase diagram. 994
28. Te–Na phase diagram. 997
29. Na–NaF phase diagram. 1002
30. Na–NaCl phase diagram. 1003
31. Na–NaBr phase diagram. 1009
32. Na–NaI phase diagram (partial). 1014
33. Xe–Na phase diagram (schematic). 1026
34. K–H phase diagram. 1029
35. C–K phase diagram (schematic). 1035
36. K–Si phase diagram (schematic). 1037
37. Ge–K phase diagram (tentative). 1037
38. As–K phase diagram (fragmentary). 1041
39. K–O phase diagram (provisional partial). 1042
40. K–KOH phase diagram. 1057
41. K–S phase diagram. 1060
42. K–Se phase diagram (partial). 1065
43. K–Te phase diagram. 1067
44. K–F phase diagram. 1069
45. K–Cl phase diagram. 1071
46. K–Na–Cl phase diagram at 1200 K. 1071
47. K–Br phase diagram (tentative). 1076
48. K–I phase diagram at constrained pressure. 1077
49. Rb–C phase diagram (provisional). 1086
50. Rb–Si phase diagram (partial). 1086
51. Ge–Rb phase diagram. 1087
52. Rb–As phase diagram. 1090
53. Rb–O phase diagram (partial). 1091
54. Rb–RbOH phase diagram. 1095
55. Rb–S phase diagram (partly predictive). 1096
56. Rb–Se phase diagram. 1099
57. Rb–Te-phase diagram. 1101
58. Rb–F phase diagram (partial). 1103
59. Rb–Cl phase diagram. 1104

60. Rb–Br phase diagram. 1105
61. Rb–I phase diagram (tentative). 1106
62. Cs–H phase diagram. 1110
63. Cs–C phase diagram. 1112
64. Cs–Ge phase diagram. 1114
65. Cs–N phase diagram. 1115
66. Cs–O phase diagram (approximate). 1117
67. Cs–CsOH phase diagram (tentative). 1122
68. Cs–S phase diagram (predictive). 1123
69. Cs–Se phase diagram. 1125
70. Cs–Te phase diagram. 1127
71. Cs–F phase diagram. 1130
72. Cs–Cl phase diagram. 1131
73. Cs–Br phase diagram. 1133
74. Cs–I phase diagram. 1134

1. Preface

Liquid alkali metals have several physical properties, which favor them for technical application. The large temperature range of the liquid state and their excellent heat transfer properties are important for use as heat transfer media.[1,2] They are used in large nuclear reactors in which hundreds of tons of sodium are circulating, and in small parts of engines for cooling of valves. Since these metals are among the most electropositive elements, they can be used in batteries with high cell voltage, large specific energy, and at moderately elevated temperatures. Even in two-phase heat transfer systems as heat pipes, thermionic or magnetohydrodynamic devices, alkali metals are suitable working fluids at high temperatures. As alkali metals react often violently with nonmetallic elements or compounds, the solubility of nonmetals in liquid alkali metals is of importance for their technical uses.

The compatibility of metallic constructional materials, which are used in energy conversion devices with liquid alkali metals, is strongly influenced by nonmetals present in the liquids. The physical properties of the liquid metals are also influenced by dissolved substances. The knowledge of the solubility of nonmetals in the liquid alkali metals is necessary for the choice of the methods to purify them in respect to the dissolved contaminants. Several nonmetals dissolved in alkali metals are able to form ternary compounds with components of the constructional materials. Such reactions may influence the properties of the interfaces or enhance the corrosion of the materials. The high affinity of the alkali metals to form compounds with the constituents of the atmosphere is the reason for the strict exclusion of the atmosphere to the level of traces in their technical uses.

This volume contains the collection of evaluated experimental solubility data of the nonmetallic elements and some compounds of them with the five alkali metal solvents (Li, Na, K, Rb, and Cs). The systems were ordered following the (IUPAC recommended) long periodic table in respect to the solutes and following the element numbers of the solvent elements. The solubility results obtained in mixed solvents are collected together with the dominant solvent component; those for the K–Na alloy as solvent are included in the section where K is the solvent. In this way the present volume complements the previous volumes 63 and 64 of the Solubility Data Series which are devoted to *Metals in Liquid Alkali Metals*.[3]

Solubility data of nonmetallic substances in liquid alkali metals are widely spread over journals, conference proceedings and reports of several organizations in France, Germany, Japan, the UK and the US and unique literature which has appeared only in the Russian language. The first publications concerned with systems of alkali metals with nonmetals appeared in the first year of the twentieth century; and for this volume, the literature is covered inclusively up to 1999.

The majority solubility data in this volume is concerned with nonmetallic solids in liquid alkali metals since the gaseous elements as H, O, F, Cl, Br form stable compounds with the alkali metals, and such compounds act as solutes under equilibrium conditions. Only N in liquid Na, K, Rb, Cs is probably dissolved as N_2 whereas N in Li forms stable Li_3N. In the determinations gas solubilities in liquid alkali metals, no detailed pressure influences on the solubilities were investigated. There are several solubility measurements for noble gases in Li, Na, and K where pressure was one of variables, and in these cases, the editors recalculated the solubilities in mol % at the standard pressure of 0.101 MPa. For a detailed discussion on other units used for gas solubilities, the reader can consult the Introduction to *The Solubility of Gases in Liquids* published in earlier volumes of the Solubility Data Series.[4]

Chemical Abstracts, Nuclear Science Abstracts and Atom Index were used as reference sources for solubility data. The key word *solubility* was not sufficient to extract complete solubility information from the corresponding literature. Therefore, entries related to this subject were also inspected. The completeness of our investigation of the abstracts was confirmed and extended by studying several reviews dealing with the solution chemistry of substances in the alkali metals.[1,2] Since none of the mentioned reviews were sufficiently complete, we decided to collect and assess all experimental results available. If not otherwise stated, the Data Sheets were prepared directly from the original papers. Any secondary sources were used only sporadically, if original reports or thesis were not accessible, and this is always clearly indicated on the data sheets.

Solubility data are sometimes measured under parameters which are not standard conditions of such measurements. Measurements are performed under constrained pressure, since the vapor pressures of the heavier alkali metals and some of the solutes are high at elevated temperatures. The solubility of noble gases or other gases, which do not form compounds with the alkali metals, depends on the gas pressures. This dependency is documented in the data sheets.

Schematic phase diagrams are presented in systems for which they assist the understanding of the data and the conclusions. They are based on the most recent state of knowledge[5] and generally presented in the Critical Evaluations. Some solubility diagrams are presented in form of log

solubility versus reciprocal temperature functions. These figures illustrate the larger scatter of data for systems in which interfering reactions cause unstable behavior of solutions.

Compositions of equilibrium solid phases were not discussed in detail in this volume in order to avoid a repetition of the discussions in Refs. 5 and 6. While several solutes are well defined substances, other systems need still additional studies to define the equilibrium solid state compound. Several nonmetallic solutes may react with the solvent metal and the container material to form ternary compounds, which influence the solubility of the nonmetal in the alkali metal. One should realize that estimations of the stoichiometry and thermal stability of such ternary compounds are experimentally difficult, and their results are often uncertain. Thus, the presentation of the corresponding ternary phase diagrams seems to be premature in such cases.

Data Sheets contain all liquidus data extracted from individual publications. However, the evaluators generally selected the values of the solubility in the Critical Evaluations. Further recommended liquidus data may either be taken from the phase diagrams or by analyzing the corresponding Data Sheets.

Quite frequently, important solubility data are only reported graphically. From these important publications, the solubility data were determined ''visually'' by the compilers. The precision of this procedure is indicated in the data sheets under Estimated Error. Evaluated solubility data are tabulated at the end of the Critical Evaluations: if there is agreement of at least two independent studies within the experimental error, the solubility values are assigned to the ''recommended'' category. Values are assigned as ''tentative,'' if only one reliable result was reported, or if the mean value of two or more reliable studies was outside the error limits. In the tabulation, three, two, or one significant figures are assigned for respective precisions that are better than $\pm 1\%$ and $\pm 10\%$ and worse than $\pm 10\%$.

Acknowledgments

The editors gratefully acknowledge the encouraging help of the IUPAC Commission V.8 and its Editor-in-Chief, Dr. M. Salomon. Particularly, the advice and suggestions of Professor H. Gamsjäger and Professor J. W. Lorimer were fruitful. Acknowledgment is also made to the University of Warsaw, Department of Chemistry, namely Professor Z. Galus, and the Forschungszentrum Karlsruhe, Institute for Materials Research, namely Professor J. Hausselt, for permission to contribute to the Solubility Data Series and to provide the editors with library services and technical equipment for this work. The assistance of the Nucleonic Library of Warsaw and of the Central Library of the Forschungszentrum is gratefully acknowledged.

References for the Preface

[1] C. C. Addison, *The Chemistry of the Liquid Alkali Metals* (Wiley, Chichester, 1984).

[2] H. U. Borgstedt and C. K. Mathews, *Applied Chemistry of the Alkali Metals* (Plenum, New York, 1987).

[3] H. U. Borgstedt and C. Guminski, *Metals in Liquid Alkali Metals*, IUPAC Solubility Data Series (Oxford University Press, Oxford, U.K., 1996), Vols. 63 & 64.

[4] P. Scharlin, *Carbon Dioxide in Water and Aqueous Electrolyte Solutions*, IUPAC Solubility Data Series (Oxford University Press, Oxford, U.K., 1996).

[5] T. B. Massalski, Ed., *Binary Alloy Phase Diagrams* (American Society Materials, Materials Park, 1990).

[6] M. Hansen and K. Anderko, *Constitution of Binary Alloys* (McGraw-Hill, New York, 1958); R. P. Elliott, First Supplement, 950 pp. (1965); F. A. Shunk, Second Supplement, 850 pp. (1969).

H. U. Borgstedt, Karlsruhe, Germany
C. Guminski, Warsaw, Poland
October 2000

2. Introduction to the Solubility Data Series Solubility of Solids in Liquids

2.1. The Nature of the Project

The Solubility Data project (SDP) has as its aim a comprehensive review of published data for solubilities of gases, liquids and solids in liquids or solids. Data of suitable precision are compiled for each publication on data sheets in a uniform format. The data for each system are evaluated and, where data from independent sources agree sufficiently, recommended values are proposed. The evaluation sheets, recommended values, and compiled data sheets are published on consecutive pages.

2.2. Compilations and Evaluations

The formats for the compilations and critical evaluations have been standardized for all volumes. A description of these formats follows.

2.2.1. Compilations

The format used for the compilations is, for the most part, self-explanatory. Normally, a compilation sheet is divided into boxes, with detailed contents described below.

Components

Each component is listed according to IUPAC name, formula, and Chemical Abstracts (CA) Registry Number. The Chemical Abstracts name is also included if this differs from the IUPAC name, as are trivial names if appropriate. IUPAC and common names are cross-referenced to Chemical Abstracts names in the System Index.

The formula is given either in terms of the IUPAC or Hill[1] system and the choice of formula is governed by what is usual for most current users: i.e., IUPAC for inorganic compounds, and Hill system for organic compounds. Components are ordered on a given compilation sheet according to:

(a) saturating components;

(b) nonsaturating components according to chemical families; within carbon compounds, according to increasing carbon number;

(c) solvents according to chemical families; within carbon compounds, according to increasing carbon number.

In each class, ordering follows the 18-column IUPAC periodic table. The same order is followed in arranging the compilation sheets within a given volume.

Original Measurements

References are abbreviated in the forms given by Chemical Abstracts Service Source Index (CASSI). Names originally in other than Roman alphabets are given as transliterated by Chemical Abstracts. In the case of multiple entries (for example, translations) an asterisk indicates the publication used for compilation of the data.

Variables

Ranges of temperature, pressure, etc., are indicated here.

Prepared by

The names of all compilers are given here.

Experimental Data

Components are described as (1), (2), etc., as defined in the ''Components'' box. Data are reported in the units used in the original publication, with the exception that modern names for units and quantities are used; e.g., mass percent for weight percent; mol dm^{-3} for molar; etc. Usually, only one type of value (e.g., mass percent) is found in the original paper, and the compiler has added the mole fractions from calculations based on 1989 atomic weights[2] and referenced sources of densities, where necessary. Temperatures are expressed as t/°C, t/°F or T/K as in the original; if necessary, conversion to T/K are made, sometimes in the compilations, and always in the critical evaluation. However, the author's units are expressed according to IUPAC recommendations[3] as far as possible.

Errors in calculations, fitting equations, etc., are noted, and where possible corrected. Material inserted by the compiler is identified by the word ''compiler'' or by the compiler's name in parentheses or in a footnote. Details of smoothing equations (with limits) are included if they are present in the original publication and if the temperature or pressure ranges are wide enough to justify this procedure and if the compiler finds that the equations are consistent with the data.

The precision of the original data is preserved when derived quantities are calculated, if necessary by the inclusion of one additional significant figure. In some cases, compilers note that numerical data have been obtained from published graphs using digitizing techniques. In these cases, the precision of the data can be determined by the quality of the original graph and the limitations of the digitizing technique.

Method

The apparatus and procedure are mentioned briefly. Abbreviations used in Chemical Abstracts are often used here to save space, reference being made to sources of further detail if these are cited in the original paper. Several reviews on experimental methods of determining gas solubilities are given in numerous sources.[4–10]

Source and Purity of Materials

For each component, referred to as (1), (2), etc., the following information (in this order and in abbreviated form) is provided if available in the original paper: source and specified method of preparation; properties; degree of purity. The solubility is usually more sensitive to impurities in the gaseous component than in the liquid component. However, the most important source of impurities is traces of unwanted gas dissolved in the liquid. Inadequate preliminary degassing of the absorbing liquid is probably the most often overlooked serious source of error in gas solubility measurements.

Estimated Error

If estimated errors were omitted by the original authors, and if relevant information is available, the compilers have attempted to estimate errors (identified by ''compiler'' or the compiler's name in parentheses or in a footnote) from the internal consistency of data and type of apparatus used. Methods used by the compilers for estimating and reporting errors are based on Ku and Eisenhart.[11]

Comments and/or Additional Data

Compilations may include this section, in which short comments relevant to the general nature of the work or additional experimental and thermodynamic data are included which are judged by the compiler to be of value to the reader.

References

The format for these follows the format for the Original Measurements box, except that final page numbers are omitted. References (usually cited in the original paper) are given where relevant to interpretation of the compiled data, or where cross-reference can be made to other compilations.

2.2.2. Evaluations

The evaluator's task is to assess the reliability and quality of the data, to estimate errors where necessary, and to recommend ''best'' values. The evaluation takes the form of a summary in which all the data supplied by the compiler have been critically reviewed. There are only three boxes on a typical evaluation sheet, and these are described below.

Components

The format is the same as on the Compilation sheets.

Evaluator

Name and affiliation of the evaluator(s); date up to which the literature was checked.

Critical Evaluation

(a) Critical text. The evaluator checks that the compiled data are correct, assesses their reliability and quality, estimates errors where necessary, and recommends numerical values based on all the published data (including theses, reports and patents) for each given system. Thus, the evaluator reviews the merits or shortcomings of the various data. Only published data are considered. Documented rejection of some published data may occur at this stage, and the corresponding compilations may be removed.

The solubilities in comparatively few systems are known with sufficient accuracy to enable a set of recommended values to be presented, either for measurements near atmospheric pressure or at high pressures. Although many systems have been studied by at least two independent groups of workers, the range of pressures or temperatures is often sufficiently different to make meaningful comparison impossible.

Occasionally, it is not clear why two groups of workers obtained very different but internally consistent sets of results at the same temperature and pressure, although both sets were obtained by reliable methods. In such cases, a decisive assessment may not be possible. In some cases, two or more sets of data have been classified as tentative even though the sets are mutually inconsistent.

Many high pressure solubility data have been published in a smoothed form. Such data are particularly difficult to evaluate, and unless specifically discussed by the authors, the estimated error on such values can be regarded only as an ''informed guess''.

As well, many high pressure solubility data have been obtained in a more general study of high pressure vapor–liquid equilibrium. In such cases a note is included to indicate that additional vapor–liquid equilibrium data are given in the source. Since the evaluation is for the compiled data, it is possible that the solubility data are given a classification which is better than that which would be given for the complete vapor–liquid data (or vice versa). As an example, it is difficult to determine coexisting liquid and vapor compositions near the critical point of a mixture using some common experimental techniques which yield accurate high pressure solubility data. As another example, conventional methods of analysis may give results with an expected error which would be regarded as sufficiently small for vapor–liquid equilibrium data but an order of magnitude too large for acceptable high pressure gas–liquid solubility.

Sometimes it is possible to judge the reliability of data for a particular gas–liquid system by testing whether the data are consistent with the behavior of homologous gases or liquids.

(b) Fitting equations. If the use of a smoothing equation is justifiable the evaluator may provide an equation representing the solubility as a function of the variables reported on all the compilation sheets, stating the limits within which it should be used.

(c) Graphical summary. In addition to (b) above, graphical summaries are often given.

(d) Recommended values. Data are recommended if the results of at least two independent groups are available and they are in good agreement, and if the evaluator has no doubt as to the adequacy and reliability of the applied experimental and computational procedures. Data are reported as tentative if only one set of measurements is available, or if the evaluator considers some aspect of the computational or experimental method as mildly undesirable but estimated that it should cause only minor errors. Data are considered as doubtful if the evaluator considers some aspect of the computational or experimental method as undesirable but still considers the data to have some value where the order of magnitude of the solubility is needed. Data determined by an inadequate method or under ill-defined conditions are rejected. However, references to these data are included in the evaluation together with a comment by the evaluator as to the reason for their rejection.

(e) References. All pertinent references are given here, including all those publications appearing in the accompanying compilation sheets and those which, by virtue of their poor precision, have been rejected and not compiled.

(f) Units. While the original data may be reported in the units used by the investigators, the final recommended values are reported in SI units[3] when the data can be accurately converted.

2.3. Quantities and Units Used in Compilation and Evaluation of Solubility Data

2.3.1. Mixtures, Solutions and Solubilities

A *mixture*[12] describes a gaseous, liquid or solid phase containing more than one substance, where the substances are all treated in the same way.

A *solution*[12] describes a liquid or solid phase containing more than one substance, when for convenience one of the substances, which is called the *solvent*, and may itself be a mixture, is treated differently than the other substances, which are called *solutes*. If the sum of the mole fractions of the solutes is small compared to unity, the solution is called a *dilute solution*.

The *solubility* of a solute 1 (solid, liquid or gas) is the analytical composition of a saturated solution, expressed in terms of the properties of the designated solute in a designated solvent.[13]

''Saturated'' implies equilibrium with respect to the processes of dissolution and vaporization; the equilibrium may be stable or metastable. The solubility of a substance in metastable equilibrium is usually greater than that of the same substance in stable equilibrium. (Strictly speaking, it is the activity of the substance in metastable equilibrium that is greater.)

Either point of view, mixture or solution, may be taken in describing solubility. The two points of view find their expression in the reference states used for definition of activities, activity coefficients and osmotic coefficients. Note that

the composition of a saturated mixture (or solution) can be described in terms of any suitable set of thermodynamic components.

For gases, the solubility is quoted, where possible, as mole fraction of the saturating gaseous component in the liquid phase at 1 bar partial pressure of gas. The distinction between vapor–liquid equilibria and the solubility of gases in liquids is arbitrary. It is generally accepted that the equilibrium at 300 K between a typical gas such as argon and a liquid such as water is gas–liquid solubility, whereas the equilibrium between hexane and cyclohexane at 350 K is an example of vapor–liquid equilibrium.

2.3.2. Physicochemical Quantities and Units

Solubilities of gases have been the subject of research for a long time, and have been expressed in a great many ways, as described below. In each case, specification of the temperature and either partial or total pressure of the saturating gaseous component is necessary. The nomenclature and units follow, where possible, IUPAC Green Book.[3] A few quantities follow the ISO standards[14] or the German standard;[15] see a review by Cvitaš[16] for details.

A Note on Nomenclature

In the IUPAC Green Book,[3] the solute is component B and the solvent is component A. In compilations and evaluations, the first-named component (component 1) is the solute, and the second (component 2 for a two-component system) is the solvent. The reader should bear these distinctions in nomenclature in mind when comparing equations given here with those in the *Green Book*.

1. *Mole fraction* of substance 1, x_1 or $x(1)$ (condensed phases) or y_1 (gases):

$$x_1 = n_1 \Big/ \sum_{s=1}^{c} n_s \tag{1}$$

when n_s is the amount of substance of s, and c is the number of distinct substances present (often the number of thermodynamic components in the system). *Mole percent* of substance 1 is 100 x_1.

2. *Ionic mole fractions* of salt i, x_{i+}, x_{i-}: For a mixture of s binary salts i, each of which ionizes completely into v_{s+} cations and v_{s-} anions, with $v_s = v_{s+} + v_{s-}$ and a mixture of p nonelectrolytes j, of which some may be solvent components, a generalization of the definition in Ref. 17 gives:

$$x_{+i} = \frac{v_{+i} x_{+i}}{1 + \sum_{j=1}^{s} (v_j - 1) x_j}, \quad x_{-i} = \frac{v_{-i} x_{+i}}{v_{+i}} \quad i = 1 \ldots s \tag{2}$$

$$x'_j = \frac{x_j}{1 + \sum_{i=1}^{s} (v_i - 1) x_i}, \quad j = (s+1) \ldots p. \tag{3}$$

The sum of these mole fractions is unity, so that, with $c = s + p$,

$$\sum_{i=1}^{s} (x_{+i} + x_{-i}) + \sum_{i=s+1}^{c} x'_i = 1. \tag{4}$$

General conversions to other units in multicomponent systems are complicated. For a three-component system containing nonelectrolyte 1, electrolyte 2, and solvent 3,

$$x_1 = \frac{v_{2+} x'_1}{v_{2+} - (v_2 - 1) x_{2+}} \quad x_2 = \frac{x_{2+}}{v_{2+} - (v_2 - 1) x_{2+}}. \tag{5}$$

These relations are used in solubility equations for salts, and for tabulation of salt effects on solubilities of gases (see below)

3. *Mass fraction* of substance 1, w_1 or $w(1)$:

$$w_1 = g_1 \Big/ \sum_{s=1}^{c} g_s \tag{6}$$

where g_s is the mass of substance s. *Mass percent* of substance 1 is 100 w_1. The equivalent terms *weight fraction*, *weight percent* and *g(1)/100 g solution* are no longer used.

4. *Molality* of solute 1 in a solvent 2, m_1:

$$m_1 = n_1 / n_2 M_2 \tag{7}$$

SI base units: mol kg^{-1}. Here, M_2 is the molar mass of the solvent. The equivalent term *weight solubility*, C_w, is no longer used.

5. *Amount concentration* of solute 1 in a solution of volume V, c_1:

$$c_1 = [\text{formula of solute}] = n_1 / V \tag{8}$$

SI base units: mol m^{-3}. The symbol c_1 is preferred to [formula of solute], but both are used. The old terms *molarity*, *molar*, and *moles per unit volume* are no longer used.

6. *Mass concentration* of solute 1 in a solution of volume V, ρ_1 or γ_1:

$$\rho_1 = g_1 / V \tag{9}$$

SI base units: kg m^{-3}.

7. *Mole ratio*, $r_{A,B}$ (dimensionless)[15]

$$r_{A,B} = n_1 / n_2. \tag{10}$$

Mass ratio, symbol $\zeta_{A,B}$, may be defined analogously[15]

8. *Ionic strength*, I_m (molality basis), or I_c (concentration basis):

$$I_m = \frac{1}{2} \sum_i m_i z_i^2, \quad I_c = \frac{1}{2} \sum_i c_i z_i^2 \tag{11}$$

where z_i is the charge number of ion i. While these quantities are not used generally to express solubilities, they are used to express the compositions of nonsaturating components. For a single salt i with ions of charges z_+, z_-,

$$I_m = |z_+ z_-| v m_i, \quad I_c = |z_+ z_-| v c_i. \tag{12}$$

Mole and mass fractions are appropriate to either the mixture or the solution point of view. The other quantities are

TABLE 1. Interconversions between quantities used as measures of solubilities c-component systems containing c-1 solutes i and single solvent c (ρ—density of solution; M_i—molar masses of i. For relations for two-component systems, set summations to 0.)

	x_i	w_i	m_i	c_i
$x_i=$	x_i	$\dfrac{1}{1+\dfrac{M_i}{M_c}\left\{\dfrac{1}{w_i}-1+\sum_{j\neq 1}^{c-1}\left(\dfrac{M_c}{M_j}-1\right)\dfrac{w_j}{w_i}\right\}}$	$\dfrac{1}{1+\dfrac{1}{m_iM_c}+\sum_{j\neq i}^{c-1}\dfrac{m_j}{m_i}}$	$\dfrac{1}{1+\dfrac{1}{M_c}\left(\dfrac{\rho}{c_i}-M_i\right)+\sum_{j\neq i}^{c-1}\dfrac{c_j}{c_i}\left(1-\dfrac{M_j}{M_c}\right)}$
$w_i=$	$\dfrac{1}{1+\dfrac{M_c}{M_i}\left\{\dfrac{1}{x_i}-1+\sum_{j\neq i}^{c-1}\left(\dfrac{M_j}{M_c}-1\right)\dfrac{x_j}{x_i}\right\}}$	w_i	$\dfrac{1}{1+\dfrac{1}{m_iM_i}\left(1+\sum_{j\neq i}^{c-1}m_jM_j\right)}$	$\dfrac{c_iM_i}{\rho}$
$m_i=$	$\dfrac{1}{M_c\left(\dfrac{1}{x_i}-1-\sum_{j\neq i}^{c-1}\dfrac{x_j}{x_i}\right)}$	$\dfrac{1}{M_i\left(\dfrac{1}{w_i}-1-\sum_{j\neq i}^{c-1}\dfrac{w_j}{w_i}\right)}$	m_i	$\dfrac{1}{\dfrac{1}{c_i}\left(\rho-\sum_{j\neq i}^{c-1}c_jM_j\right)-M_i}$
$c_i=$	$\dfrac{\rho}{M_i+M_c\left\{\dfrac{1}{x_i}-1+\sum_{j\neq i}^{c-1}\left(\dfrac{M_j}{M_c}-1\right)\dfrac{x_j}{x_i}\right\}}$	$\dfrac{\rho w_i}{M_i}$	$\dfrac{\rho}{\dfrac{1}{m_i}\left(1+\sum_{j\neq i}^{c-1}m_jM_j\right)+M_j}$	c_i

appropriate to the solution point of view only. Conversions between some pairs of these quantities can be carried out using the equations given in Table 1 at the end of this Introduction. Other useful quantities will be defined in the prefaces to individual volumes or on specific data sheets.

In addition to these well-defined SI-based units, other units have been used to express the solubilities of gases. Units and nomenclature follow,[4,5,7,18] as modified by IUPAC recommendations.[3] The equations describing Bunsen, Kuenen, Ostwald and absorption coefficients, as well as Henry's law constants, hold for ideal gases and perfect solutions only. Corrections for nonideality should be made where possible. The corrections are less than 1% for most gases near atmospheric pressure.[5]

In much published data, the reference pressure is 1 atm =0.101 325 MPa rather than 1 bar=0.1 MPa.

9. *Bunsen coefficient* α (dimensionless): The volume of saturating gas, V_1, reduced to $T°=273.15$ K, $p°=1$ bar, which is absorbed by unit volume V_2^* of pure solvent at the temperature of measurement and partial pressure $p°=1$ bar. If the gas is ideal, Henry's law (see below) holds, and the liquid is incompressible, then

$$\alpha=\frac{V_1^\circ}{V_2^*}=\left(\frac{V_1}{V_2^*}\right)\left(\frac{T^\circ}{T}\right). \tag{13}$$

10. *Kuenen coefficient*, S:

The volume of saturating gas, $V(g)$, reduced to $T°=273.15$ K, $p°=1$ bar, which is dissolved by unit mass of pure solvent at the temperature of measurement and partial pressure 1 bar. Thus,

$$S=\frac{V_1T°}{g_2T}=\frac{\alpha V_{m,2}}{M_2} \tag{14}$$

SI base units: $m^3\,kg^{-1}$. Here, M_2 is the molar mass of the solvent. The Kuenen coefficient is proportional to the molality of the dissolved gas.

11. *Ostwald coefficient*, L (dimensionless):[18] The volume of saturating gas, V_1, absorbed by a volume V_2^* of pure solvent at the temperature and pressure of the measurement. Thus,

$$L=\frac{V_1}{V_2^*}=\left(\frac{\alpha T}{T°}\right)\left(\frac{p°}{p}\right). \tag{15}$$

The Ostwald coefficient is equal to the ratio of the amount concentrations in the gas and in the liquid.

12. *Absorption coefficient*, β (dimensionless): The most common of several definitions of absorption coefficient is the volume of gas, reduced to $T°=273.15$ K, $p°=1$ bar absorbed per unit volume of pure solvent at a total pressure of 1 bar. The absorption and Bunsen coefficients are therefore very similar, and are connected by

$$\beta=\alpha(1-p_2/p°) \tag{16}$$

where p_2 is the partial pressure of the vapor of the solvent.

13. *Henry's Law constant*, k_H:

$$K_H=\lim_{x_1\to 0}(p_1/x_1) \tag{17}$$

SI base units: Pa. Unfortunately, the definition is used often at finite mole fractions, even though this is a limiting law. The following have also been defined as Henry's Law constants:

$$K_2=p_1/c_1$$

and

$$K_c=c_1^g/c_1 \tag{18}$$

where superscript g refers to the gas phase. K_2 has SI base units: Pa $m^3 mol^{-1}$, and K_c is dimensionless. The Henry's law constant has also been called the Henry coefficient and the Henry constant. Henry's law can be used, with great caution, to convert data from the experimental pressure to 1 bar if the mole fraction of the gas in the liquid is small, and the difference in pressures is small.

The relations between the mole fraction solubility and the various quantities given above are as follows. Note again that these relations hold for ideal gaseous and perfect solution phases only.

$$x_1=\frac{1}{1+\dfrac{RT^\circ}{p_1^\circ V_{m,2}^*\alpha}}=\frac{1}{1+\dfrac{RT^\circ}{p_1^\circ M_2 S}}=\frac{1}{1+\dfrac{RT^\circ}{p_1^\circ V_{m,2}^* L}}=\frac{1}{1+\dfrac{RT^\circ}{p^\circ V_{m,2}^*\beta}}. \tag{19}$$

14. *Salt Effects on the Solubility of Gases*:[19] These are often reported as Sechenov (Setchenow, Setschenow) salt effect parameters k_{syz}, which are defined in various ways. The general semi-empirical Sechenov equation is

$$\log(z_1^\circ/z_1)=k_{syz}y \tag{20}$$

where solubility is expressed in quantities z, with superscript o designating pure solvent, and salt composition is expressed in quantities y. The quantities c_2, m_2, x_2', I_m and I_c are used for y, and the quantities c_1, m_1, x_{1+}, a, S and L for z, giving 30 definitions of k_{syz}. Here, components 1 and 2 are the gaseous solute and electrolyte, respectively. The ratios of z values are the same for $z=c_1$, α and L and for m_1 and S, respectively, leaving 15 distinct definitions. If z is the same, the definitions of k_{syz} are related simply through ten equations between pairs of c_1, m_2, x_2^*, I_m and I_c. Some relations among the definitions, in terms of k_{scc}, k_{smm} and k_{sxx}, are:

$$k_{scc}=k_{sc\alpha}=k_{scL}=\frac{m_2}{c_2}k_{smc}=\frac{x_{2'}}{c_2}k_{sxc}=\frac{I_c}{c_2}k_{sI_cc}$$

$$k_{smm}=\frac{x_{2'}}{m_2}k_{sxm}=k_{smS}=\frac{c_2}{m_2}k_{scm}=\frac{I_m}{m_2}k_{sI_mm} \tag{21}$$

$$k_{sxx}=\frac{c_2}{x_{2'}}k_{scx}=\frac{m_2}{x_{2'}}k_{smx}=\frac{I_m}{x_{2'}}k_{sI_mx}=\frac{I_c}{x_{2'}}k_{sI_cx}.$$

These relations hold when a single salt is present; note that the relations between ionic strength and either molality or concentration are simple. If more than one salt is present, the ionic strength is the only practical quantity to be used for y.

Conversions between pairs of k_{scc}, k_{smm} and k_{sxx} are more complicated and can be found using Eq. (5) and Table 1 at the end of this Introduction. For example,

$$k_{sxx}=f(m)\left(\frac{k_{smm}}{v_{2+}}+\frac{1}{m_2}\log\frac{f(m)}{f(m^\circ)}\right) \tag{22}$$

where

$$f(m)=1+(m_1+v_2m_2)M_3,\quad f(m^\circ)=1+m_1^\circ M_3. \tag{23}$$

Errors in the salt effect parameters, as defined above, can be large. If the relative standard deviation in measurement of solubility is $s(c_1)/c_1$, then the relative standard deviation in k_{scc} is

$$\frac{s(k_{scc})}{k_{scc}}=\frac{\sqrt{2}}{c_2k_{scc}\ln 10}\frac{s(c_1)}{c_1}. \tag{24}$$

For example, for $k_{scc}=0.1$ and $c_2=0.01$ mol dm^{-3}, $s(k_{scc})/k_{scc}$ is 30% when $s(c_1)/c_1=0.05\%$ and 1200% when $s(c_1)/c_1=2\%$. At $c_2=1$ mol dm^{-3}, the corresponding errors are 0.3 and 12%, respectively.

If the solubility of a gas is greater than about $x=0.01$ at partial pressure 1 bar, then several other factors must be taken into account, such as the density of the solution or the partial molar volume of the dissolved gas. In addition, corrections should be made for nonideality of the gas. See Ref. 18 for details.

In addition, the following definitions concerning density are useful in conversions between concentrations and other quantities.

15. *Density*, ρ or γ:

$$\rho=g/V \tag{25}$$

SI base units: kg m^{-3}. Here g is the total mass of the system.

16. *Relative density*, $d=\rho/\rho^\circ$: the ratio of the density of a mixture at temperature t, pressure p to the density of a reference substance at temperature t', pressure p'. For liquid solutions, the reference substance is often water at 4 °C, 1 bar. (In some cases 1 atm is used instead of 1 bar.) The term *specific gravity* in no longer used.

Thermodynamics of Solubility (Ref. 20)

Thermodynamic analysis of solubility phenomena provides a rational basis for the construction of functions to represent solubility data, and thus aids in evaluation, and sometimes enables thermodynamic quantities to be extracted. Both these aims are often difficult to achieve because of a lack of experimental or theoretical activity coefficients. Where thermodynamic quantities can be found, they are not evaluated critically, since this task would involve examination of a large body of data that is not directly relevant to solubility. Where possible, procedures for evaluation are based on established thermodynamic methods. Specific procedures used in a particular volume will be described in the Preface to that volume.

Only one thermodynamic result is mentioned here: the temperature dependence of solubility. Sometimes it is possible to fit the mole fraction solubility at various temperatures using the equation

$$\ln x_1=A+B(\mathrm{K}/T)+C\ \ln(T/\mathrm{K})+D(T/\mathrm{K}) \tag{26}$$

where A, B, C and D are constants to be determined from least-squares fitting of the data. Sometimes, to avoid singular matrices of the least-squares normal equations, T is scaled; e.g., T is replaced by $T/100$.

If the gas and the solution of the dissolved gas are ideal, the coefficients can be used to find standard thermodynamic functions for transfer of the gas from the vapor to the liquid phase at the standard pressure (1 bar) and infinitely dilute dissolved gas, as follows:

$$\Delta G^{\circ}_{m,1} M_3/R = -A(T/\mathrm{K}) - B - C(T/\mathrm{K})\ln(T/\mathrm{K}) - D(T/\mathrm{K})^2 \tag{27}$$

$$\Delta S^{\circ}_{m,1}/R = A + C\ \ln(T/\mathrm{K}) + C + 2D(T/\mathrm{K}) \tag{28}$$

$$\Delta H^{\circ}_{m,1} M_3/R = -B + C(T/\mathrm{K}) + D(T/\mathrm{K})^2 \tag{29}$$

$$\Delta C^{\circ}_{m,p} M_3/R = C + 2D(T/\mathrm{K}). \tag{30}$$

Alternatively (but equivalently), the standard state of infinitely dilute dissolved gas can be described as a hypothetical ideal dissolved gas at mole fraction $x_1=1$, $p=1$ bar.

2.4. References for the Introduction

[1] E. A. Hill, J. Am. Chem. Soc. **22**, 478 (1900).
[2] IUPAC Commission on Atomic Weights and Isotopic Abundances, Pure Appl. Chem. **63**, 975 (1989).
[3] I. Mills *et al.*, eds., *Quantities, Units and Symbols in Physical Chemistry* (The Green Book). (Blackwell Scientific Publications, Oxford, UK, 1993.)
[4] R. Battino and H. L. Clever, Chem. Rev. **66**, 395 (1966).
[5] H. L. Clever and R. Battino, in *Solutions and Solubilities (Techniques of Chemistry*, edited by M. R. J. Dack (Wiley, New York, 1975). Vol. VIII, Part 1, Chap. 7.
[6] J. H. Hildebrand, J. M. Prausnitz, and R. L. Scott, *Regular and Related Solutions* (Van Nostrant Reinhold, New York, 1970), Chap. 8.
[7] A. E. Markham and K. A. Kobe, Chem. Rev. **28**, 519 (1941).
[8] E. Wilhelm and R. Battino, Chem. Rev. **73**, 1 (1973).
[9] E. Wilhelm, R. Battino, and R. J. Wilcock, Chem. Rev. **77**, 219 (1977).
[10] A. S. Kertes, O. Levy, and G. Y. Markovits, in *Experimental Thermochemistry*, Vol. II, edited by B. Vodar and B. LeNaindre (Butterworths, London, 1974), Chap. 15.
[11] H. H. Ku, p. 73; C. Eisenhart, p. 69; in H. H. Ku, ed., Precision Measurement and Calibration, *NBS Special Publication 300*. Vol. 1 (Washington, 1969).
[12] V. Gold *et al.*, eds., *Compendium of Chemical Technology* (The Gold Book). (Blackwell Scientific Publications, Oxford, UK, 1987).
[13] H. Freiser and G. H. Nancollas, eds., *Compendium of Analytical Nomenclature* (The Orange Book) (Blackwell Scientific Publications, Oxford, UK, 1987), Sect. 9.1.8.
[14] ISO Standards Handbook, *Quantities and Units* (International Standards Organization, Geneva, 1993).
[15] German Standard, DIN 1310, *Zusammensetzungvon Mischphasen* (Beuth Verlag, Berlin, 1984).
[16] T. Cvitaŝ, Chem. Int. **17**, 123 (1995).
[17] R. A. Robinson and R. H. Stokes, *Electrolyte Solutions* (Butterworths, London, 1959), 2nd ed.
[18] R. Battino, Fluid Phase Equil. **15**, 231 (1984).
[19] H. L. Clever in *Nitrogen and Air*, edited by R. Battino, IUPAC Solubility Data Series, Vol. 10 (Pergamon, Oxford, UK, 1982), p. xxix.
[20] E. Wilhelm in *Nitrogen and Air*, edited by R. Battino, IUPAC Solubility Data Series, Vol. 10 (Pergamon, Oxford, UK, 1982), p. xii.

This section was written by:

R. Battino	H. L. Clever	P. G. T. Fogg	C. L. Young
Dayton, OH, USA	Atlanta, GA, USA	Hertford, UK	Melbourne, Australia

December, 1995

3. Solutions of Nonmetallic Substances in Lithium

3.1. Lithium–Hydrogen

Components:
(1) Hydrogen; H; [1333-74-0]
(2) Lithium; Li; [7439-93-2]

Evaluated by:
Hans Ulrich Borgstedt,
Forschungszentrum Karlsruhe,
Germany and Cezary Guminski,
University of Warsaw, Poland, June 1994

Critical Evaluation

Due to potential applications of the H isotopes–Li systems in fusion reactors and generally in energy production and storage, quite large experimental material has been found concerning phase equilibria of the Li–H, as well as Li–D and Li–T systems. Knowledge of the solubility of H isotopes in liquid Li is essential to T recovery, corrosion studies, impurity control and purification methods in nuclear technology. This evaluation is concerned only on the H–Li system which, in a different extent, was reviewed several times.[1–18] The D–Li and T–Li systems are elaborated separately later in this manuscript. Dissolution of gaseous H in liquid Li proceeds as a first order chemical reaction:

$$1/2H_2(g)+Li(l)\leftrightarrow LiH(l)\leftrightarrow LiH(s), \quad (1)$$

which is relatively slow near the melting point of Li, but increases significantly above 600 K[17] and naturally depends on the H gas pressure. Investigations of LiH could be very complex, especially at high temperatures where gaseous H is easily lost from the Li–H system through walls of a container what makes an immediate change in composition of the sample. The free volume over a sample plays a very important role in equilibrium and should be precisely taken into account. In fact, it is very difficult to prepare and investigate solid LiH of stoichiometric proportion of the elements, and liquid LiH is hardly attainable in reality since it is practically deficient in H.[19] Because the gas, liquid, and solid phases are in equilibrium, as expressed by Eq. (1), a solubility may be defined either as H concentration in liquid in dependence of the H gas pressure without presence of solid or liquid LiH, or as a maximum H concentration in the liquid being dissolved from the solid or liquid LiH. The first kind of equilibrium is named the isobaric solubility because H pressure and the corresponding H concentration are ruled by the Sieverts constant (K_s):

$$K_s=x_H p_H^{-1/2} \quad (2)$$

where x_H is the mol fraction of H in the solution and p_H is the H pressure over the solution. In fact in some publications, K_s was named simply the solubility. Dilute solutions of H in liquid Li obey the Sieverts law perfectly well up to 1 mol % H and acceptably well up to 5 mol %. The equilibrium pressures in this composition range were determined by Hill,[21] Perlow,[22] Heumann and Salmon,[26] Messer *et al.*,[16,25] Veleckis *et al.*,[33,37] Katsuta *et al.*,[27] Shpil'rain *et al.*,[20,56] Smith *et al.*,[43–46] and Simandl[42] at temperatures of 473–1273 K. Increasing the H pressure over the solution more H is dissolved and, according to Eq. (1), LiH(s) starts to precipitate. Then the pressure is independent on the melt composition till the almost stoichiometric LiH is formed. Such pressure, corresponding to the solubility limit of gaseous H, is named the equilibrium plateau pressure. The equilibrium plateau pressure (p_Hs) was measured in the above-mentioned papers, as well as by Hurd,[40] Gibb,[41] Ihle and Wu,[58] Shpil'rain,[34] Smith and Webb,[49] and Veleckis.[39] All experimental data, where the equilibrium is characterized by the monovariant three-phase equilibrium (solid LiH, saturated liquid solution and H gas), were approximated by the following equation:

$$\log(p_H s/\mathrm{Pa})=14.151-10255/(T/\mathrm{K}), \quad (3)$$

which is valid in the temperature range 454–962 K (between the eutectic and monotectic levels). Similar equations were published in numerous studies.[23,39,49] The equation reported in Katsuta *et al.*[27] differs unacceptably from the remaining works and the data of these authors seems to be charged with an experimental error. Neither this data, nor the fitting equation obtained in Ihle and Wu,[58] agree with the results of other studies. The latter results are exactly 1 order of magnitude higher than the results of Smith and Webb.[49] When two hardly miscible liquids (the Li-rich and the LiH-rich) over the monotectic temperature are in equilibrium with the gas, the corresponding vapor pressure data may be approximated by the following equation:

$$\log(p_H s/\mathrm{Pa})=11.416-7620/(T/\mathrm{K}), \quad (4)$$

which is valid at temperatures higher than 962 K. Similar equations have been reported.[2,3,4,14,20,33,34,39,49] The equations presented in Heumann and Salmon[26] and Katsuta *et al.*[27] differ unacceptably from the rest. According to Eq. (4), the standard pressure of 101 325 Pa is reached at 1189 K. Intersection of the dependencies expressed by Eqs. (3) and (4) assigns temperature of the monotectic reaction at 962 K. No such break was observed on the dependence shown in Katsura *et al.*[27] Therefore, these data are very doubtful. The temperature dependence of the Sieverts constant has been established.[2,3,7,14,20,27,33,39,42,43,44] The constant would allow one to estimate the H concentration depending on the pressure as well as the solubility in solutions more diluted than 1 mol % H. Shpil'rain,[20] taking into account the experimental K_s values from Veleckis *et al.*[33] and Smith *et al.*[43] and their own work, calculated the recommended dependence:

$$\log(K_s/\mathrm{mol\ \%\ Pa^{-1/2}})=-3.400+2769/(T/\mathrm{K}) \quad (5)$$

which is accepted in this evaluation. Equation (5) is originally valid for temperature range of 940–1180 K but it seems reasonable to assume that it is also valid at higher and lower temperatures. Similar relations have been reported,[2,3,7,14,33,39,43] but the one reported by Katsuta *et al.*[27] is unacceptably different from Eq. (5).

The complexity of the gas phase was revealed by Ihle and Wu,[38] who, in consequence of mass spectrometric–Knudsen effusion studies, observed that the gas phase over the diluted solutions of H in liquid Li contains not only H_2 but also Li_2, Li_3, LiH, Li_2H, and Li_2H_2 molecules. The authors evaluated the partial pressures and equilibrium constants for the exchange reaction among the species as function of the liquid phase composition (10^{-5}–10^{-2} mol %) and temperature (800–1600 K), specifically for D isotope.

The tabulated equilibrium data for the three isotopes were published in Shpil'rain *et al.*[20] Although the existence of gaseous hydrides does not affect the Sieverts law relationship, it leads to an increased density of H isotopes in the saturated vapors over the melts. Owing to this enrichment, it is possible to separate the isotopes from Li by fractional distillation performed at temperatures higher than 1240 K.

A solubility defined as equilibrium concentration in the liquid Li saturated with solid or liquid LiH (which is the gaseous solubility limit) was determined using various methods. Hill,[21] Perlow,[22] Heumann and Salmon,[26] Veleckis *et al.*,[33] Katsuta *et al.*,[27] Shpil'rain *et al.*,[34] Smith *et al.*,[43,45–47] and Simandl[42] measured the H pressure over the saturated solutions. Weston *et al.*[28] estimated the H solubility from a gettering coefficient and H content in a Zr getter after an equilibration of the saturated liquid with Zr wire. Messer *et al.*[23–25] and Hubberstey *et al.*[17,29] performed thermal analysis of the Li–H melts. Adams *et al.*[17,30,32] determined the H solubility with the use of resistivity measurement technique. Down[31] reported the confirmation of the results of Adams *et al.*[30] but neither method nor results obtained were specified therein. Pulham *et al.*[17] and Hubberstey *et al.*[29] observed the Li freezing point depression of 0.08 K and a eutectic point composition at 0.016 mol % H. However, their melting point of pure Li was 0.11 K below the contemporarily accepted value of Sangster and Pelton.[4] Although one may assume that the depression of 0.1±0.03 K is real, the composition of the eutectic is rather placed at 0.028 mol % H as it results from extrapolation of the solubility data from higher temperatures. A solid solubility of H in Li is not higher than 0.01 mol % H (Sangster and Pelton[4] and Hubberstey *et al.*[29]). Veleckis *et al.*[36] estimated composition of the eutectic point as 0.040 mol % H and the freezing point depression of 0.23 K; both values are too high to be accepted. The solubility data from three studies[28,30,31] near the melting point of Li show significant scatter what was connected with experimental difficulties. The solubility values from three other studies[17,30,32] form a very well linear dependence of logarithm of the solubility versus reciprocal temperature between 530 and 824 K. Two results obtained by Weston *et al.*[28] are twice higher than these obtained by Adams *et al.*[30] at 485 and 500 K with the smooth relation of Down[31] laying in between. Five results[17,30,32,28,31] are well represented by the solubility equation:

$$\log(\mathrm{soly/mol\ \%\ H})=3.527-2312\ (T/\mathrm{K}), \quad (6)$$

which is valid between the eutectic at 453.8 and about 825 K. One result of Katsuta *et al.*[27] at 623 K is three times higher than that one predicted by Eq. (6) and was neglected in the preparation of this fitting equation. (2), (3), (4), (10), (11), (13), (30) and (32) reported solubility equations similar to Eq. (6). When one would subtract the right hand sides of Eq. (6) and half of Eq. (3) one obtains temperature dependence of the Sieverts constant at temperatures below 800 K:

$$\log(K_s/\mathrm{mol\ \%\ Pa^{-1/2}})=-3.548+2815\ (T/\mathrm{K}). \quad (7)$$

Equation (7) resembles Eq. (5) and may be used for an estimation of H solubility in liquid Li with an accuracy of ±10%, if the H equilibrium plateau pressure is known. Data sheets with the plateau pressures are therefore prepared following this equation. The results of Katsuta *et al.*[27] at 813–1013 K show significantly different slope of the temperature dependence of solubility and they do not reflect the monotectic reaction at 962 K. These erroneous results might be produced by an application of the Sieverts constant in the solubility calculation; as it was mentioned above the temperature dependence of the Sieverts constant found by Katsuta *et al.*[27] was not accepted in this evaluation. Several values of Messer *et al.*[24,25] on the liquidus line between 896 K and the monotectic reaction agree well with a single result of Veleckis *et al.*[33] at 923 K. Probably due to wrong calibration of a thermoelement used, all earlier results of Messer *et al.*[23] are at 4 K lower positions than those in Messer *et al.*[24,25] The liquidus segment between 850 and 962 K is not linear in the axis of logarithm of solubility versus reciprocal temperature and should not be approximated by any linear dependence as reported in Fromm and Jehn[7] and Messer *et al.*[25] Use of a complex cubic equation by Veleckis *et al.*[2] is reasonable for the solubility prediction in this temperature range.

The monotectic temperature was established at: 954 K (Messer *et al.*[23]) and later corrected for 958 K by the same group (Messer *et al.*[25]) and 967 K by Veleckis *et al.*[2,39] Johnson *et al.*[48] and Smith and Webb[49] claimed to measure the melting point of LiH at 960 and 962 K, respectively. However, due to the decomposition of LiH they probably measured the monotectic temperature. Bredig[50] reported the melting point of LiH at 959 K without specifying the purity of the compound. The mean selected value for the monotectic was assessed to be 962 K. At this temperature the immiscibility gap extends from 19 to 49.6 mol % H. Szafranski *et al.*[51] reported the monotectic and melting point of LiH at 985 and 986 K, respectively. The experimental background for these likely erroneous values was not presented in their publication. Points on the liquidus line between the monotectic and critical miscibility temperature were measured by numerous workers.[21,22,26,33,27,34,43] A good agreement of ±0.5 mol % for the results of Perlow[22] only at 1043 K, Veleckis *et al.*,[33] Shpil'rain *et al.*,[34] and Smith *et al.*[43] was observed. The data of Hill[21] and Perlow[22] at 1098 K and Katsuta *et al.*[27] deviate by a few % from the selected liquidus line and may be neglected. The thermal analysis results of Messer *et al.*[25] seem to be 5 K too low temperature to be in agreement with Veleckis *et al.*[33] and Smith *et al.*[43] The linear solubility fitting equations proposed by Veleckis *et al.*,[2] Fromm and Jehn,[7] Messer *et al.*,[25] and Veleckis *et al.*,[33] for the temperature range (970–1170 K), are not recommended since this dependence is not linear from definition.

Parameters of the critical miscibility point were not measured experimentally. Based on various models, they were predicted by several investigators[4,5,19,26,33,51] to be between 37 and 42 mol % H and between 1218 and 1273 K. The mean parameter values 40 mol % H and 1258 K were gained from graphical extrapolation of the experimental data and proposed by Sangster and Pelton.[4] The liquidus between the critical point and the melting point of LiH is likely, as it was found by Veleckis *et al.*[33] and Smith *et al.*[43] The data of Gibb[41] at 1173 and 1273 K are in error. Due to serious difficulties in obtaining sufficiently pure LiH, its melting point was determined to be too low in earlier works.[23,25] The most contemporary determinations are: 964 K by Messer and Levy,[57] 965 K by Shpil'rain *et al.*[52] and 966 K by thermodynamic estimation of Sangster and Pelton.[4] The mean value of 965 K was selected in this assessment. Although solid LiH is predominantly ionic a small amount (<0.5 mol %) of dissolved Li seems to be experimentally detectable in it.[42]

It was found in several studies of resistivity measurements[32,53,54] and thermodynamic calculations[55] that a presence of C, N, or O in

small quantities (separately or simultaneously) makes no remarkable influence on the solubility equilibria in the H–Li system. An introduction of Na into the H–Li system caused a significant resistivity drop, thus pointing to interactions in the H–Li–Na ternary system. This is thermodynamically unjustified, since LiH is much more stable than NaH, and a formation of any stable ternary compound is hard to imagine; the effect may be only connected with influence of metallic impurities in the system investigated by Arnoldov *et al.*[53]

The partial H–Li phase diagram, constructed in agreement with this evaluation, is presented in Fig. 1. The complete liquid miscibility is reached at pressures higher than 0.1 MPa.[35]

The recommended (r) and tentative (t) values of the solubility of H in liquid Li and corresponding equilibrium H plateau pressure

T/K	Solubility/mol % H	Source	p/Pa	Source
453.7	0.028 (t) eutectic	(30),(31) extrapolated	$3.5\cdot10^{-9}$	Eq. (3) extrapolated
473	0.043 (t)	Eq. (6)	$3.0\cdot10^{-8}$	Eq. (3) extrapolated
573	0.31 (t)	(30), Eq. (6)	$1.8\cdot10^{-4}$	Eq. (3) extrapolated
673	1.2 (t)	(30), Eq. (6)	$8.2\cdot10^{-2}$	Eq. (3) extrapolated
773	3.5 (t)	(30), Eq. (6)	7.6	(49), Eq. (3)
873	9 (t)	(27),(30),(33),(42), interpolated	250	(27),(40), Eq. (3)
962	19 (t) monotectic	(33),(43) interpolated	$3.1\cdot10^{3}$	(39),(49), Eq. (3), and Eq. (4)
1073	25(r)	(33),(43)	$2.1\cdot10^{4}$	(41),(44),(39), Eq. (4)
1173	31(r)	(33),(43)	$8.3\cdot10^{4}$	(33),(41),(56), Eq. (4)
1258	40 (t) critical	(4) extrapolated	$2.3\cdot10^{5}$	Eq. (4) extrapolated

The tentative LiH-rich liquidus values of the Li–H system

T/K	Solubility/mol % H	Source
962	49.6 eutectic	(33),(43) extrapolated
1073	49.0	(33),(41),(43)
1173	46	(33)

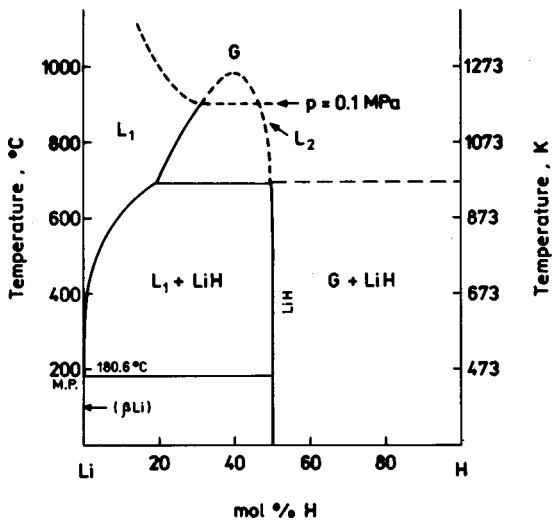

FIG. 1. Li–H phase diagram.

References

[1]C. E. Messer, *The Alkali Metals* (The Chemical Society, London, 1967), p. 183.

[2]E. Veleckis, R. M. Yonco, and V. A. Maroni, *Thermodynamics of Nuclear Materials* (IAEA, Vienna, 1980), p. 3.

[3]P. Hubberstey, *Handbook of Thermodynamic and Transport Properties of Alkali Metals*, edited by R. W. Ohse (Blackwell, Oxford, 1985), p. 885.

[4]J. Sangster and A. D. Pelton, J. Phase Equil. **14**, 373 (1993).

[5]E. Schürmann and R. Völker, Z. Metallk. **78**, 121 (1987).

[6]E. Fromm and G. Hörz, Intern. Met. Rev. **26**, 269 (1980).

[7]E. Fromm and A. Jehn, Bull. Alloy Phase Diagr. **5**, 323 (1984).

[8]K. Anderson, U.S. Atom. Energy Comm. Rep. NEPA-547 (1948).

[9]P. F. Adams, P. Hubberstey, and R. J. Pulham, J. Less-Common Met. **42**, 1 (1975).

[10]N. Rumbaut, F. Casteels, and M. Brabers, *Materials Behavior and Physical Chemistry in Liquid Metal Systems*, edited by H. U. Borgstedt (Plenum, New York, 1982), p. 437.

[11]P. Hubberstey, P. F. Adams, R. J. Pulham, M. G. Down, and A. E. Thunder, J. Less-Common Met. **49**, 253 (1976).

[12]K. M. Mackay, *Hydrogen Compounds of the Metallic Elements* (Spon, London, 1966), pp. 30, 46.

[13]P. Hubberstey, A. T. Dadd, and P. G. Roberts, *Materials Behavior and Physical Chemistry in Liquid Metal Systems*, edited by H. U. Borgstedt (Plenum, New York, 1982), p. 445.

[14]M. Hoch, J. Nucl. Mater. **120**, 102 (1984).

[15]R. E. Elson, H. C. Horning, W. L. Jolly, J. W. Kury, W. J. Ramsey, and A. Zalkin, U.S. Atom. Energy Comm. Rep. UCRL-4519 (1956).

[16]T. R. P. Gibb and C. E. Messer, U.S. Atom. Energy Comm. Rep. NYO-3957 (1954).

[17]R. J. Pulham, P. F. Adams, P. Hubberstey, G. Parry, and A. E. Thunder, U.S. Energy Res. Devel. Admin. Rep. CONF-750989-P4, p. 144 (1976).

[18]E. E. Veleckis and E. H. Van Deventer, U.S. Atom. Energy Comm. Rep. ANL-7878, p. 11 (1972).

[19]E. E. Shpil'rain and K. A. Yakimovich, High Temp.-High Pressures **13**, 597 (1981).

[20]E. E. Shpil'rain, K. A. Yakimovich, and E. A. Tsirlina, Inzh.-Fiz. Zh. **38**, 249 (1980).

[21]L. L. Hill, Ph.D. thesis, Univ. of Chicago, 1938; as cited in 24.

[22]M. R. J. Perlow, Ph.D. thesis, Univ. of Chicago, 1941; as cited in 24.

[23]C. E. Messer, E. B. Damon, and P. C. Maybury, U.S. Atom. Energy Comm. Rep. NYO-3958 (1955).

[24]C. E. Messer, U.S. Atom. Energy Comm. Rep. NYO-9470 (1960).

[25]C. E. Messer, E. B. Damon, P. C. Maybury, J. Mellor, and R. A. Seales, J. Phys. Chem. **62**, 220 (1958).

[26]F. K. Heumann and O. N. Salmon, U.S. Atom. Energy Comm. Rep. KAPL-1667 (1956).

[27]H. Katsuta, T. Ishigai, and K. Furukawa, Nucl. Technol. **32**, 297 (1977).

[28]J. R. Weston, W. F. Calaway, R. M. Yonco, and V. A. Maroni, U.S. Dept. Energy Rep. CONF-800401-P2, p. 20/1 (1980).

[29]P. Hubberstey, R. J. Pulham, and A. E. Thunder, J. Chem. Soc., Faraday Trans. I **72**, 431 (1976).

[30]P. F. Adams, M. G. Down, P. Hubberstey, and R. J. Pulham, J. Less-Common Met. **42**, 325 (1975).

[31]M. G. Down, U.S. Dept. Energy Rep. CONF-800401-P2, p. 14/16 (1980).

[32]R. J. Pulham, P. Hubberstey, A. E. Thunder, A. Harper, and A. T. Dadd, U.S. Dept. Energy Rep. CONF-800401-P2, p. 18/1 (1980).

[33]E. Veleckis, E. H. Van Deventer, and M. Blander, J. Phys. Chem. **78**, 1933 (1974).

[34]E. E. Shpil'rain, K. A. Yakimovich, and V. A. Sherevsheskii, Teplofiz. Vys. Temp. **15**, 661 (1977).

[35]C. E. Messer, R. A. Seales, and J. Mellor, U.S. Atom. Energy Comm. Rep. NYO-8021 (1957).

[36]E. Veleckis, R. M. Yonco, and V. A. Maroni, J. Less-Common Met. **55**, 85 (1977).

[37]V. A. Maroni, W. F. Calaway, E. Veleckis, and R. M. Yonco, U.S. Energy Res. Devel. Adm. Rep. CONF-760503-P1, p. 437 (1976).

[38]H. R. Ihle, H. Kudo, and C. H. Wu, *Thermodynamics of Nuclear Materials* (IAEA, Vienna, 1980), p. 31.

[39]E. Veleckis, J. Nucl. Mater. **79**, 20 (1979).

[40]C. B. Hurd and G. A. Moore, J. Am. Chem. Soc. **57**, 332 (1935).

[41]T. R. P. Gibb, U.S. Atom. Energy Comm. Rep. NEPA-1841 (1951).

[42]R. F. Simandl, U.S. Dept. Energy Rep. Y-2242 (1981).

[43]F. J. Smith, J. F. Land, G. M. Begun, and A. N. La Gamma de Batistoni, J. Inorg. Nucl. Chem. **41**, 1001 (1979).

[44]Y. Yoshimura and T. Yanagi, Techn. Rep. Osaka Univ. **31**, 191 (1981).

[45]F. J. Smith, A. M. La Gamma de Batistoni, G. M. Begun, and J. F. Land, Europ. Atom. Energy Commun. Rep. EUR-5602, p. 325 (1976).

[46]F. J. Smith, A. M. La Gamma de Batistoni, G. M. Begun, and J. F. Land, U.S. Energy Res. Devel. Adm. Rep. CONF-760631-1 (1976).

[47]F. J. Smith and J. F. Land, Trans. Am. Nucl. Soc. **21**, 167 (1975).

[48]C. E. Johnson, R. R. Heinrich, and C. E. Crouthamel, J. Phys. Chem. **70**, 242 (1966).

[49]H. M. Smith and R. E. Webb, U.S. Dept. Energy Rep. Y-2095 (1977).

[50]M. A. Bredig, J. Chem. Phys. **46**, 4166 (1967).

[51]A. W. Szafranski, E. Keller, and E. U. Franck, Ber. Bunsenges. Phys. Chem. **96**, 955 (1992).
[52]E. E. Shpil'rain, K. A. Yakimovich, V. A. Shreshevskii, and V. G. Andrianova, Teplofiz. Vys. Temp. **14**, 405 (1976).
[53]M. N. Arnoldov, M. N. Ivanovskii, A. D. Plevshivtsev, V. I. Subbotin, and B. A. Shmatko, *Teplofizicheskie Svoistva Zhidkostei*, edited by A. K. Abas-Zade and E. E. Shpil'rain (Nauka, Moskva, 1970), p. 124.
[54]P. Hubberstey, A. Harper, A. T. Dadd, D. J. Knight, and K. Maughan, U.S. Dept. Energy Rep. CONF-800401-P2, p. 18/27 (1980).
[55]H. Migge, U.S. Dept. Energy Rep. CONF-800401-P2, p. 18/9 (1980).
[56]E. E. Shpil'rain, K. A. Yakimovich, V. A. Shereshevskii, and V. G. Andrianova, Teplofiz. Vys. Temp. **6**, 1204 (1978).
[57]C. E. Messer and I. S. Levy, Inorg. Chem. **4**, 543 (1965).
[58]H. R. Ihle and C. H. Wu, J. Inorg. Nucl. Chem. **36**, 2167 (1974).

Components:
(1) Hydrogen; H; [1333-74-0]
(2) Lithium; Li; [7439-93-2]

Original Measurements:
L. L. Hill, Ph.D. thesis, Univ. of Chicago (1938); as cited in Messer.[1]

Variables:
One temperature: 973 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The limits of the liquid immiscibility gap in the H–Li system at 700 °C were estimated to be 20 and 98 mass % LiH, respectively. These values were found from a figure and recalculated by the compilers as 15.5 and 49.4 mol % H, respectively. The corresponding H dissociation equilibrium pressure was found at 35.0 mm Hg or 4670 Pa.

Auxiliary Information

Method:
Li, kept under C_4H_{10} as protective medium, was contained in a Swedish Fe capsule. The capsule was shut by means of welding.[2] It was kept at 908 K for reaction for 9 days. The product of reaction was analyzed. H_2 (Anderson[2]) was equilibrated with Li and dissociation pressures of the Li–LiH mixtures were measured at the selected temperature, which was measured with the use of Pt/Pt–Rh(10%) thermocouples. The limits of the immiscibility gap correspond to the plateau pressures observed for the same range of composition.

Source and Purity of Materials:
Li: electrolytically pure from Maywood Chemicals Works.[2]
LiH: 99.7% pure by H_2 evolution analysis.[1] It was made from commercial H_2, dried and purified by diffusion through a Pd tube at 723 K.
C_4H_{10} : unspecified.

Estimated Error:
Solubility: precision ±5% in respect to the Li content.
Temperature: nothing specified.

References:
[1]C. E. Messer, U.S. Atom. Energy Comm. Rep. NYO-9470 (1960).
[2]K. Anderson, U.S. Atom. Energy Comm. Rep. NEPA-547 (1948).

Components:
(1) Hydrogen; H; [1333-74-0]
(2) Lithium; Li; [7439-93-2]

Original Measurements:
M. R. J. Perlow, Ph.D. thesis, Univ. of Chicago (1941); as cited in Messer.[1]

Variables:
Temperatures: 1043 and 1098 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The limits of the liquid immiscibility gap in the H–Li system were determined. The values were estimated from a graph and calculated by the compilers.

t/°C	Solubility/mass % LiH[a]	Solubility/mol % H[a]	Solubility/mass % LiH[b]	Solubility/mol % H[b]
770	32	23	98	49.4
825	44	29	95	48.5

[a]Lower limit.
[b]Upper limit.

The dissociation pressures were ~153 and ~433 mm Hg (or ~20.4 and ~57.6 kPa) at 770 and 825 °C, respectively.

Auxiliary Information

Method:
Li, kept in C_4H_{10} as inert medium, was contained in a Swedish Fe capsule which was shut by means of welding.[2] It was exposed to H_2 for reaction for several days at elevated temperatures and the dissociation pressures of the Li–LiH mixtures were measured at selected temperatures. They were measured by means of a Pt/Pt–Rh(10%) thermocouple. The limits of the immiscibility gap correspond to the plateau pressures observed for some range of compositions.

Source and Purity of Materials:
LiH: 96.5% pure by H_2 evolution analysis.[1] It was made from commercial H_2, dried and purified by diffusion through a Pd tube at 723 K.
Li: electrolytically pure from Maywood Chemical Works.[2]
C_4H_{10}: unspecified.

Estimated Error:
Solubility: precision ±5% in respect to Li content.
Temperature: nothing specified.

References:
[1]C. E. Messer, U.S. Atom. Energy Comm. Rep. NYO-9470 (1960).
[2]K. Anderson, U.S. Atom. Energy Comm. Rep. NEPA-547 (1948).

Components:
(1) Hydrogen; H; [1333-74-0]
(2) Lithium; Li; [7439-93-2]

Original Measurements:
T. R. P. Gibb, U.S. Atom. Energy Comm. Rep. NEPA-1841 (1951).

Variables:
Temperatures: 1073–1273 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of H in liquid Li and the plateau equilibrium pressure were determined

t/°C	Solubility/mass % LiH	Solubility/mol % H[a]	p/Torr	p/Pa[a]
800	96±2	49.0	~160	21000
900	94±2	48.2	490±70	65200
1000	88±3	46.4	2000±50	266000

[a]Calculated by the compilers.

The melting point of LiH was observed at 680 °C (953 K). According to the author this value is probably 2 K below the correct value.

Auxiliary Information

Method:
The container used for the experiments was made of 347 type stainless steel. Proper amounts of LiH and Li were introduced into the container, which was evacuated and heated to the desired temperature in a furnace. The equilibrium H pressure was measured periodically to reach a constant value. Limits of the H plateau pressure indicate the H solubility.

Source and Purity of Materials:
LiH: 98.5% pure, prepared by reaction of the elements in a stainless steel container at 1023 K for 2 h and purified.
Li: from Maywood Chem. Works.

Estimated Error:
Solubility: precision ±0.5 mol %.
Pressure: precision better than ±15%.
Temperature: nothing specified.

Components:
(1) Hydrogen; H; [1333-74-0]
(2) Lithium; Li; [7439-93-2]

Original Measurements:
F. K. Heumann and O. N. Salmon, U.S. Atom. Energy Comm. Rep. KAPL-1667 (1956).

Variables:
One temperature: 973 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data
The limits of the immiscibility gap of the liquid Li–LiH system were reported

t/°C	p/Pa	Solubility/mol % LiH	Solubility/mol % H[a]
700	3730	26[b]	20.6[b]
700	3730	95[c]	48.7[c]

[a]Calculated by the compilers.
[b]The lower limit of the immiscibility.
[c]The upper limit of the immiscibility.

Auxiliary Information

Method:
Li was contained in a low C steel capsule with a lid being corrosion resistant. The capsule and lid were fired in H_2 at 1073 K for 1 h, degassed at 1073 K in vacuum, and stored for 24 h in an Ar dry box. A small amount of molten Li was poured on a Fe plate. A part of the solidified Li was placed in a quartz container and pumped out for several hours. The Li sample was heated to 973 K and contacted with H. Pressure readings were taken until the equilibrium pressure was reached (8–12 h). The equilibrium was approached from below and from above by the formation and dissociation of LiH. The purity of the equilibrium H_2 gas was checked by a mass spectrometer. A Chromel/Alumel thermocouple was used for the temperature measurement. Limits of the immiscibility gap were read from a plateau on the pressure–composition isotherm.

Source and Purity of Materials:
H_2: obtained from Matheson Comp., Inc.; purified by formation and subsequent decomposition of UH_3.
Li: 99.75% pure, obtained from Maywood Chem. Comp.; contained 0.02% Na, 0.05% Si, 0.03% Fe+Al, 0.06% Ca, 0.03% N, 0.003% Cl and 0.09% of other heavy metals.
Ar: purified by contact with Cu turnings at 673 K and molten Na containing Li at 448 K; finally contained (1.0–1.5) 10^{-3} % O.

Estimated Error:
Nothing specified.

Components:
(1) Hydrogen; H; [1333-74-0]
(2) Lithium; Li; [7439-93-2]

Original Measurements:
C. E. Messer, E. B. Damon, P. C. Maybury, J. Mellor, and R. A. Seales, J. Phys. Chem. **62**, 220–222 (1958).

Variables:
Temperature: 897–961 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data
The Li–LiH liquidus points were reported in the figures. The numerical results were presented in Messer *et al.*[2]
H_2 removed from the system

t/°C	H/Li at. ratio	Solubility/mol % H[a]
688	0.998	49.95
689.4	0.996	49.9
687.9	0.996	49.9
688.4	0.994	49.85
686.4	0.992	49.8
686.4	0.990	49.8
685.4	0.987	49.7
684.7	0.983	49.6
687.0	0.980	49.5
685.6	0.977	49.4
686.6	0.972	49.3
685.2	0.963	49.05
685.4	0.945	48.6
685.0	0.943	48.5
686.4	0.919	47.9
684.4	0.859	46.2
686.3	0.832	45.4
685.6	0.832	45.4
684.9	0.778	43.75
684.5	0.679	41.1
684.7	0.617	38.15
685.7	0.580	36.7
685.8	0.541	35.1
684.8	0.477	32.3
684.6	0.477	30.3
686.6	0.412	29.2
684.7	0.377	27.3

H_2 added into the system

t/°C	H/Li at. ratio	Solubility/mol % H[a]
688.1	0.993	49.8
687.0	0.989	49.7
684.6	0.648	39.3
684.4	0.420	29.6
684.3	0.370	27.0
684.2	0.364	26.7
684.0	0.312	23.8
683.6	0.312	23.8
679.0	0.242	19.5
672.1	0.215	17.7
671.1	0.215	17.7
653.3	0.180	15.25
684.0	0.174	14.8
682.9	0.174	14.8
647.4	0.170	14.5
645.9	0.170	14.5
639.2	0.155	13.4
623.7	0.137	12.1

[a]Calculated by the compilers.

The equilibrium H plateau pressure was found to be 28.8 and 27.8 Torr (3786 Pa—mean value as calculated by the compilers) at 700 °C. The stoichiometric melting point of LiH was found at 687.8±0.5 °C. The monotectic temperature was established at 684.9 ±0.8 °C. A part of the results for the H-rich range was published in Messer *et al.*[1] and Messer and Seales,[3] but all results reported therein were 4.0 K lower than reported in this paper.

Auxiliary Information

Method:

Thermal analysis of samples was performed in a bomb made of 316 stainless steel. The bomb was held in a tube furnace, equipped with a Chromel/Alumel thermocouple. It was outfitted with a valve enabling the bomb to contain Li with purified H for 15 h at 998 K and 0.101 MPa, transferred from a dry box, and a fitting to connect it to a high vacuum system. A Cu ring was used to seal the bomb. Its filling was carried out in an Ar dry box. Following the determination of the freezing point of a LiH sample by a series of cooling curves under 0.101 MPa of H, measured amounts of H were removed at 998 K, and one or more freezing curves were run after each removal. The cooling rate was 1 K/min. The process was continued until the freezing point became indistiguishable on the recorder. The sample was rehydrided until the freezing point was raised to that of original LiH, subsequently a new portion of Li was added.

Source and Purity of Materials:

H: from Linde; purified by synthesis and subsequent decomposition of UH.
Li: 99.75% pure from Maywood Chem. Works.
LiH: 99.8% pure prepared by synthesis.
Ar: nothing specified.

Estimated Error:

Solubility: precision ±0.12 mol %; change of composition during analysis ±0.02%.
Temperature: precision ±0.5 K; accuracy ±1 K.

References:

[1]C. E. Messer, E. B. Damon, and P. C. Maybury, U.S. Atom. Energy Comm. Rep. NYO-3958 (1956).
[2]C. E. Messer, R. A. Seales, and J. Mellor, U.S. Atom. Energy Comm. Rep. NYO-8021 (1957).
[3]C. E. Messer and R. A. Seales, U.S. Atom. Energy Comm. Rep. NYO-3959 (1956).

Components:

(1) Hydrogen; H; [1333-74-0]
(2) Lithium; Li; [7439-93-2]

Original Measurements:

H. R. Ihle and C. H. Wu, J. Inorg. Nucl. Chem. **36**, 2167–2170 (1974).

Variables:

Temperature: 725–800 K

Prepared by:

H. U. Borgstedt and C. Guminski

Experimental Data

Equilibrium pressure of H over the heterogeneous LiH–Li melt were measured

T/K	p/Torr	p/Pa[a]
725	0.0694	9.25
730	0.0894	11.92
740	0.1447	19.29
745	0.1745	23.26
763	0.3839	51.17
773	0.5176	68.70
790	0.9535	127.1
800	1.0301	137.3

[a]Calculated by the compilers.

The authors presented a fitting equation to describe their data. The equation was tested by the compilers but they did not confirm its validity.

Auxiliary Information

Method:

The apparatus used for these investigations was described in Ihle *et al.*[1,2] The composition of the gas phase was calculated from the measured ion current of mass spectrometry technique. A shutter was installed between the Knudsen cell and the ion source of the mass filter. The temperatures were measured with a Pt–Rh/Pt thermocouple calibrated on the melting points of Li, Ag, and Au. The Knudsen cell was made of Mo. It was heated by a generator, which was stabilized by means of a constant power stabilizer. The solutions of H in Li were prepared in an ultrahigh vacuum chamber.

Source and Purity of Materials:

H: nothing specified; probably as in Ihle *et al.*,[2] purified by formation and decomposition of UH_3.
Li: nothing specified.
Pressure: nothing specified.

Estimated Error:

Temperature: stability ±1.2 K; accuracy ±2 K.

References:

[1]H. R. Ihle and C. H. Wu, Europ. Atom. Energy Commun. Rep. EUR-4938, pp. 89–94 (1972).
[2]H. R. Ihle, H. Kudo, and C. H. Wu, *Thermodynamics of Nuclear Materials* (IAEA, Vienna, 1980), Vol. II, pp. 31–44.

Components:
(1) Hydrogen; H; [1333-74-0]
(2) Lithium; Li; [7439-93-2]

Original Measurements:
E. Veleckis, E. H. Van Deventer, and M. Blander, J. Phys. Chem. **78**, 1933–1940 (1974).

Variables:
Temperature: 926–1176 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data
Limits of the miscibility gap in the H–Li system were determined

t/°C	p/Pa	Solubility/mol % H[a]	Solubility/mol % H[b]
653	···	13.4	···
710	5130	20.1	49.6
759	11770	22.2	49.3
803	22850	24.9	48.9
847	43880	27.8	48.0
878	66680	29.5	47.0
903	87830	31.2	46.1

[a]Lower limit.
[b]Upper limit.

The results were presented graphically in Maroni *et al.*[1] and Veleckis and Van Deventer[3] and numerically in Veleckis and Van Deventer[2] and Maroni *et al.*[4]

Auxiliary Information

Method:
The experiments performed in a Sieverts' apparatus which consisted of gas purificator, gas meter, and equilibration container. Li was placed in close capsules made of Armco Fe. The capsules were heated in H and degassed at 1123–1173 K prior to the Li addition. The capsules with Li were evacuated and heated to temperature of experiments. H was added to the sample in measured portions. The equilibrium pressure was measured after 12–48 h when the equilibrium was reached. The H concentration in Li was calculated from the weight of Li before and after H addition. Temperatures were measured with three calibrated Pt/Pt–Rh(10%) thermocouples. He was used as the inert gas in glove box.

Source and Purity of Materials:
H: purified by contact with a hot Ti sponge.
Li: 99.98% pure from Foote Mineral Co.; contained $7.9–10^{-3}$ % Na, $3.5–10^{-3}$ % K; the $^{6}Li/^{7}Li$ ratio was 0.0815±0.0007.
He: purified by a silicagel getter cooled by liquid N; contained $1–10^{-4}$ % N, O.

Estimated Error:
Solubility: standard deviation ±1% on the Li-rich side and ±0.5% on the H-rich side.
Temperature: stability ±1 K.
Pressure: precision ±0.5%.

References:
[1]V. A. Maroni, E. J. Cairns, and F. A. Cafasso, U.S. Atom. Energy Comm. Rep. ANL-8001 (1973).
[2]E. Veleckis and E. Van Deventer, U.S. Atom. Energy Comm. Rep. ANL-8023, pp. 4–13 (1973).
[3]E. Veleckis and E. Van Deventer, U.S. Atom. Energy Comm. Rep. ANL-7978, pp. 4–7 (1973).
[4]V. A. Maroni, E. Veleckis, and E. H. Van Deventer, U.S. Energy Res. Devel. Admin. Rep. ERDA-50, pp. 120–32 (1975).

Components:
(1) Hydrogen; H; [1333-74-0]
(2) Lithium; Li; [7439-93-2]

Original Measurements:
P. F. Adams, M. G. Down, P. Hubberstey, and R. J. Pulham, J. Less-Common Met. **42**, 325–334 (1975).

Variables:
Temperature: 485–824 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data
The solubility of H in liquid Li was determined at several temperatures

t/°C	Solubility/mol % H
212	0.037
227	0.063[a]
257	0.140
275	0.212[a]
296	0.301
326	0.462[a]
344	0.596
361	0.753
376	0.892[a]
395	1.148
397	1.195[a]
411	1.420
441	1.930
442	1.95[b]
499	3.480
525	4.540
551	5.680

[a]Obtained by changing temperature of the sample.
[b]As reported in Pulham *et al.*[2]

A part of the results was graphically presented in Pulham *et al.*[3]

Auxiliary Information

Method:
The apparatus was constructed from AISI 321 stainless steel. It contained a reservoir, a neck, two loops with electromagnetic pumps (one loop with a capillary for a continuous resistance measurement), and a winding device for addition and removal of gettering metals Ti and Y. The vessel was evacuated, the temperature raised, and the resistance measured across the empty capillary by means of a Kelvin–Wheatstone bridge at selected temperatures. The latter was gettered with Ti or Y and a fall of resistance was observed. Accurately known volumes of H gas were added to Li and resistivity changes were detected. In some cases the resistivity was measured for a fixed H concentration while changing the temperature. Breaks on the resistivity vs. concentration plots correspond to the solubility. All operations were performed in an Ar atmosphere. The apparatus was cooled and charged with Li. The Li was heated to 673 K and the temperature was measured by means of thermocouples.

Source and Purity of Materials:
H: 99.98% pure from Air Products, purified by passage through MnO at 373 K and molecular sieve as in Pulham.[1]
Li: 99.98% pure from Koch–Light, gettered with Ti or Y at 673 K.
Ti: 99.9% pure from Koch–Light.
Y: 99.9% pure from Koch–Light.
Ar: nothing specified; probably 99.999% pure from Air Products.[1]

Estimated Error:
Solubility: nothing specified; precision of a few % (by the compiler).
Temperature: stability ±0.5 K; precision ±0.05 K.

References:
[1]R. J. Pulham, J. Chem. Soc., A, 1389–93 (1971).
[2]R. J. Pulham, P. Hubberstey, A. E. Thunder, A. Harper, and A. T. Dadd, U.S. Dept. Energy Rep. CONF-800401-P2, p. 18/1 (1980).
[3]R. J. Pulham, P. F. Adams, P. Hubberstey, G. Parry, and A. E. Thunder, U.S. Energy Res. Devel. Admin. Rep. CONF-750989-P4, p. 144 (1976).

Components:
(1) Hydrogen; H; [1333-74-0]
(2) Lithium; Li; [7439-93-2]

Original Measurements:
P. Hubberstey, R. J. Pulham, and A. E, Thunder, J. Chem. Soc., Faraday Trans. I **72**, 431–435 (1976).

Variables:
Temperature: 453.56–453.63 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

A part of the H–Li liquidus was determined. The values were read from a figure by the compilers.

t/°C	Solubility/mol % H	t/°C	Solubility/mol %
180.48	0.004	180.43	0.011
180.46	0.008	180.42	0.015
180.45	0.008	180.41	0.016

At higher H concentrations up to 0.082 mol % all thermal arrests were recorded at 180.41±0.01 °C (the eutectic temperature). The melting point of Li was found at 180.49 °C. A solid solubility of H in Li at the eutectic temperature was estimated to be 0.002 mol %. The results were graphically reported in Pulham *et al.*[2]

Auxiliary Information

Method:
The apparatus was made of AISI 321 stainless steel. It contained a reservoir, a thermocouple pocket, a small electromagnetic pump in a side loop and a winding device (in a neck) for addition and removal of Y getter. A Chromel/Alumel thermocouple, calibrated against the NPL thermometer, was used to measure temperature. The apparatus was cleaned, dried and charged with Li in an Ar atmosphere glove box. The temperature was raised to 673 K for gettering with Y. After Y removal the melting point of Li was determined from cooling curves (at a rate of 15 K/h). Successive H volumes were introduced into Li. The gas reacted instantly with Li at 673 K, and the reaction product dissolved. No detectable reaction of the melt with the apparatus was observed. The solutions were subject to controlled cooling being recorded.

Source and Purity of Materials:
H: 99.98% pure from Air Products, purified by passing through MnO at 373 K (as reported in Pulham[1]).
Li: 99.98% pure from Koch–Light, gettered with Y at 673 K during Li circulation for 12 h.
Y: 99.9% pure from Koch–Light.
Ar: nothing specified, probably 99.999% pure from Koch–Light.[1]

Estimated Error:
Solubility: nothing specified; reading out procedure ±0.001 mol %.
Temperature: precision ±0.01 K, but accuracy ±0.1 K (the latter by the compilers).

References:
[1]R. J. Pulham, J. Chem. Soc., A 1389 (1971).
[2]R. J. Pulham, P. F. Adams, P. Hubberstey, G. Parry, and A. E. Thunder, U.S. Energy Res. Devel. Admin. Rep. CONF-750989-P4, p. 144 (1976).

Components:
(1) Hydrogen; H; [1333-74-0]
(2) Lithium; Li; [7439-93-2]

Original Measurements:
H. Katsuta, I. Ishigai, and K. Furukawa, Nucl. Technol. **32**, 297–303 (1977).

Variables:
Temperature: 813–1013 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

Changes of the equilibrium H pressure with temperature are shown in a figure. The data are read from the figure and recalculated to the solubilities by the compilers.

T/K	t/°C	p/Pa	Solubility/mol % H
813	540	67	6.8
825	552	75	7.4
874	601	265	8.8
890	617	369	9.4
914	641	859	11.8
931	658	928	12.5
962	689	2020	13.4
997	724	4090	15.9
1013	740	4583	15.8

Auxiliary Information

Method:
Samples of Li containing 47 or 70 mol % LiH were placed in Mo crucibles in an Ar atmosphere. The crucibles were set into a quartz vessel at constant Ar pressure of 106.4 kPa and equilibrated at selected temperature. The partial pressure of H in Ar was measured by a gas chromatograph. To maintain uniform H concentration in Ar, the gas was circulated through the vessel and sampling tube of the chromatograph by a diaphragm pump. The temperature difference between the surface and the bottom was several degrees. The authors calculated the solubility from the Sieverts constant using the equilibrium pressures measured over the heterogeneous system LiH–Li.

Source and Purity of Materials:
LiH: unspecified purity, from Metallgesellschaft A.G.
Li: 99.8% pure from Lithium Corp. of America.
Ar: nothing specified.

Estimated Error:
Solubility: nothing specified; reading-out procedure ±0.2 mol %.
Temperature: stability ±3 K; reading-out procedure ±3 K.

Components:
(1) Hydrogen; H; [1333-74-0]
(2) Lithium; Li; [7439-93-2]

Original Measurements:
E. E. Shpil'rain, K. A. Yakimovich, and V. A. Shereshevskii, Teplofiz. Vys. Temp. **15**, 661–664 (1977).

Variables:
One temperature 1042 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of H in liquid Li was determined to be 32.06 mol % LiH or 24.2 mol % H at 1042 K. It is the Li-rich boundary of the miscibility gap of the system. The pressure over the melt was 14.9 kPa. The equilibrium vapor pressures of H_2 over the heterogeneous LiH–Li mixtures were measured.

t/K	p/Torr	p/Pa
981.7	40.3	5372
963.3	28.6	3812
1006.0	62.0	8265
1015.0	70.2	9358
1015.8	71.2	9491
1088.4	230.2	30690
1088.6	234.7	31290
1088.4	234.3	30700
1087.8	230.3	30700
1160.0	623.0	83050
1159.8	622.8	83020
1159.8	623.2	83070
1122.8	382.0	50920
1053.0	137.2	18290
984.6	42.5	5665
968.8	31.2	4159
1001.0	57.8	7705
1035.2	104.2	13890
1070.6	181.5	24190
1106.6	304.7	40620
1142.0	493.1	65730
1178.2	783.1	104400
1196.0	976.5	130200
1196.2	970.5	129400
1028.8	93.2	12420

Auxiliary Information

Method:
Li was heated under vacuum in a stainless steel ampoule up to 1042 K. Gaseous H was proportionated into it by volume under isothermal conditions. The equilibrium pressure of H over the melt was measured through a membrane by a mercury manometer with a cathetometer reading. The temperature was measured and controlled with the use of a Chromel/Alumel thermocouple, previously calibrated. The equilibrium was typically reached within 1 h. The concentration of the saturated solution was determined from the beginning of the plateau pressure.

Source and Purity of Materials:
H: contained $5\cdot10^{-7}$ vol % O and the sum of O, CO_2, N, H_2O and C_2H_2 of $1.6\cdot10^{-3}$ vol %, according to Shpil'rain *et al.*[1]
Li: 99.8% pure, contained 0.13% Na, $5\cdot10^{-3}$ % K, N, 0.02% Ca, Mg, $3\cdot10^{-3}$ % Al, Fe, $1\cdot10^{-3}$ % Mn, and $6.5\cdot10^{-3}$ % SiO_2.

Estimated Error:
Solubility: precision ±0.1 mol %.
Temperature: accuracy ±2 K; stability ±0.5 K.

References:
[1]E. E. Shpil'rain, K. A. Yakimovich, V. A. Shereshevskii, and V. G. Andrianova, Teplofiz. Vys. Temp. **14**, 405–7 (1976).

Components:
(1) Hydrogen; H; [1333-74-0]
(2) Lithium; Li; [7439-93-2]

Original Measurements:
H. M. Smith and R. E. Webb, U.S. Dept. Energy Rep. Y-2095 (1977).

Variables:
Temperature: 736–1028 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

Equilibrium pressures of H_2 gas over the heterogeneous LiH–Li mixtures were measured

t/°C	p/Pa
755	9937
738	7362
727	5940
701	3754
692	3232
652	1131.85
658	1325.28
643.5	867.80
580	168.92
529	20.81
472.5	2.27
497	6.17
549	45.17
609	313.17
644	888.3
606.5	298.1
562	72.07
532	27.86
522	16.93
505.5	8.83
486	3.57
658.5	1347.9
679	2357
686.5	2836.3
700	3683.2
696.2	3439.7
694	3323.5
704	3966.8
726	5930.8
736	7182
755	9899
727	5969
721	5381
700	3702
650	1015.04
657	1280.93
660	1356.92
632	623.12
571	94.71
515.5	13.04
463	1.45
507.5	9.60
560	89.17
618.5	421.0

654	1178.2
607	297.0
565	78.34
536	28.45
513	11.84
499	6.68
472	2.19
668.5	1721.6
673	1977
683.5	2668
698.5	3599.7
695	3364.5
694	3335.5
716.2	4926
726	5946.6
736	7186
752.3	9343
727	5849
721	5405
694	3345
651	1050.77
657	1282.06
643.5	867.18
616	385.60
553.5	52.70
506	9.25
488	4.00
523	17.16
583.5	143.13
619	423.7
653	1148.8
582	143.9
565	78.07
522	16.99
514	12.17
500	6.67
676	2197.0
681.5	2549.0
674	2033
683.5	2662
698	3562.8
694.5	3242.1
704	3986.3
716.5	4942
725.5	5880.9
746	8450
743.5	7939
727	5898
710	4480
692	3269
651.5	1056.74
658	1362.31
643.5	868.12
602	252.38
539.5	32.13
485	4.04
487	3.93
534	26.90
596	213.00
633	635.7
653	1146.0
584	143.1
551	48.42
521.5	16.72
504	8.57
483.5	3.32
666	1649.1
681.5	2541.0
691	3179
701.5	3831.7
697.5	3511.4
694	3335.7
704.5	4010.3
725	5870.7
7102.0	
746	8413

The authors proposed a fitting equation for solid and liquid LiH, respectively:

$$\log p/\mathrm{Pa} = 14.243 \pm 0.022 - (10355 \pm 15)\ (T/\mathrm{K})^{-1}; \quad \log p/\mathrm{Pa} = 11.456 \pm 0.031 - (7675 \pm 30)\ (T/\mathrm{K})^{-1}$$

The intersection of these equations at 688.6 °C (961.8 K) is the monotectic temperature of the H–Li system. The authors incorrectly treated this temperature as the melting point of LiH.

Auxiliary Information

Method:

The experiments were performed using a vacuum system made of 304 stainless steel. The equilibrium pressure was measured by means of a calibrated differential capacitance manometer. Samples of LiH were contained in a Nb–Zr(1%) alloy tube, being impermeable to liquid Li and LiH, but more permeable to H. The equilibrium was established in less than 12 h at 723 K, less than 4 h at 923 K, and about 1 h at 1023 K. The actual temperature was measured using a Chromel/Alumel thermocouple. The tubes were loaded with LiH, welded in an Ar atmosphere and etched in 46% HNO_3–8% HF solution to remove oxide films from the sample. The tube was placed in a reactor vessel and the vessel was evacuated at 673 K for 24 h. LiH was partly decomposed to H_2 and liquid Li. The equilibrium pressures were measured at changing temperature.

Source and Purity of Materials:

LiH: contained $9.5 \cdot 10^{-3}$ % Na, $4.8 \cdot 10^{-3}$ % K, $< 1.0 \cdot 10^{-3}$ % Ca, and 0.28% O.
Li: nothing specified.
Ar: nothing specified.

Estimated Error:

Pressure: precision ±1%.
Temperature: stability ±0.5 K.

Components:
(1) Hydrogen; H; [1333-74-0]
(2) Lithium; Li; [7439-93-2]

Original Measurements:
F. J. Smith, J. F. Land, G. M. Begun, and A. M. La Gamma de Batistoni, J. Inorg. Nucl. Chem. **41**, 1001–1009 (1979).

Variables:
Temperature: 973–1223 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The limits of the miscibility gap and the equilibrium pressures for the LiH–Li heterogeneous system were reported

t/°C	Solubility/mol % LiH[a]	Solubility/mol % H[a,c]	Solubility/mol % LiH[b]	Solubility/mol % H[b,c]
700	24	19	98	49.5
750	28	22	97	49.2
800	33	25	96	49.0
850	39	28	92	47.9
900	46	31	⋯	⋯

t/C	p/Torr	p/P[a,c]
700	28[d]	3730
750	74	9860
800	165[d]	22 000
850	340	45 300
900	650	86 600
950	>800	>10 660

[a]Lower limit.
[b]Upper limit.
[c]Calculated by the compilers.
[d]30 and 164 Torr at 700 and 800 °C as reported in Smith *et al.*[4] and Smith and Land.[5]

The results at 800 °C and 700, 800, 900 °C were presented in a graphical form in Smith *et al.*[1,3] and Smith *et al.*,[2] respectively.

Auxiliary Information

Method:
Equilibrium pressures of H were measured using the modified Sieverts apparatus. Samples of Li were sealed under vacuum in a thin wall capsule (Fe or Ni) permeable for H and the equilibrium was established both inside and outside the capsule. The capsule was placed in a quartz envelope. The envelope was connected to the rest of the system and its volume calibrated. The system was evacuated at ambient temperature and then at 1173 K down to a pressure of 0.013 Pa. The temperature was adjusted at a selected value. H gas was admitted to the system. Finally the valves to the quartz envelope were opened and the change in pressure with time was recorded until the equilibrium was reached.

Source and Purity of Materials:
H: "high purity"; further purified by passage through a hot Pd–Ag membrane.
Li: from Foote Mineral Comp., further purified by treating with Zr in a Ti crucible at 1073 K for >100 h and filtering through a 5 μm filter at ~573 K, contained $<6.2\cdot10^{-3}$ % O.

Estimated Error:
Solubility: nothing specified.
Temperature: nothing specified.

References:
[1]F. J. Smith, A. M. La Gamma de Batistoni, G. M. Begun, and L. F. Land, Eur. Atom. Energy Commun. Rep. EUR-5602, pp. 325–328 (1976).
[2]F. J. Smith, J. F. Land, J. B. Talbot, and J. T. Bell, U.S. Energy Res. Devel. Admin. Rep. CONF-750989-P3, pp. 539–53 (1975).
[3]F. J. Smith, A. M. La Gamma de Batistoni, G. M. Begun, and F. J. Land, U.S. Energy Res. Devel. Admin. Rep. CONF-760631-1 (1976).
[4]F. J. Smith, F. J. Land, G. M. Begun, and J. T. Bell, U.S. Energy Res. Devel. Admin. Rep. ORNL-5111, p. 267 (1976).
[5]F. J. Smith and F. J. Land, Trans. Am. Nucl. Soc. **21**, 167–8 (1975).

Components:
(1) Hydrogen; H; [1333-74-0]
(2) Lithium; Li; [7439-93-2]

Original Measurements:
E. Veleckis, J. Nucl. Mater. **79**, 20–27 (1979).

Variables:
Temperature: 903.8–1131.5 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

Equilibrium pressures of H gas over the heterogeneous mixtures of LiH–Li were measured

t/°C	p/Torr	p/Pa[a]
858.3	380.9	50770
841.2	300.1	40000
839.6	295.8	39430
820.3	223.8	29830
818.9	217.8	29030
800.0	166.8	22230
785.4	129.2	17220
768.8	100.6	13410
755.5	81.0	10800
743.1	65.74	8763
731.5	54.24	7230
718.5	43.84	5844
716.7	42.18	5623
704.6	34.09	4544
694	27.8	3706
693.5	27.65	3686
682.9	20.80	2773
669.5	14.96	1994
657.3	10.76	1434
647.4	7.97	1062
630.6	5.16	688

[a]Calculated by the compilers.

The results were presented graphically in Veleckis *et al.*[2] and numerically in Veleckis.[3] The results were represented by equations for solid and liquid LiH, respectively:

$$\log(p/\mathrm{Pa}) = 14.067 - 10154\ (T/\mathrm{K})^{-1}$$
$$\log(p/\mathrm{Pa}) = 11.392 - 7565\ (T/\mathrm{K})^{-1}$$

The monotectic temperature was estimated from intersection of the above dependencies to be 694 °C (967 K).[1]

Auxiliary Information

Method:

A Li spherule was placed in an Armco Fe capsule that had thin walls (permeable to gaseous H), a thick bottom with a re-entrant thermocouple well. The capsule was closed (by He arc welding) with a lid connected via a hollow Fe stem and a glass-to-metal seal, to a closed glass stopcock. The apparatus for the pressure measurements was made of two concentric tubes: the outer one of stainless steel and the inner one of fused silica. The tubes were joined at the top via a graded seal. The capsule was placed in the silica tube, connected to the equilibration apparatus and evacuated at ~1123 K for several days. The Li reacted with a portion of H to produce 55–70 mol % LiH solution in Li. The equilibrium pressures were measured after >4 h of equilibration. The temperatures were measured with the use of a Chromel/Alumel thermocouple.

Source and Purity of Materials:

H: 99.995+% pure from Air Products and Chemicals, Inc.; purified by absorption in a hot Ti sponge, evacuation of impurities from the cooled sponge and extraction H_2 by reheating.

Li: 99.9+% pure from Lithium Corp. of Amer.; purified by dripping of the molten Li from a Ta funnel onto a stainless steel chill plate. The Li spherules contained ~0.02% N and ~0.06% O.

Estimated Error:

Pressure: precision ±1.3 Pa.

Temperature: nothing specified; precision ±0.1 K (by the compilers).

References:

[1]V. A. Maroni, W. F. Calaway, E. Veleckis, and R. M. Yonco, U.S. Energy Res. Devel. Admin. Rep CONF-760503-P1, pp. 437–445 (1976).

[2]E. Veleckis, R. M. Yonco, and V. A. Maroni, *Thermodynamics of Nuclear Materials* (IAEA, Vienna, 1980), pp. 3–30.

[3]E. Veleckis, U.S. Energy Res. Devel. Admin. Rep. ANL-76-106, p. 5 (1976).

Components:

(1) Hydrogen; H; [1333-74-0]

(2) Lithium; Li; [7439-93-2]

Original Measurements:

J. R. Weston, W. F. Calway, R. M. Yonco, and V. A. Maroni, U.S., Dept. Energy Rep. CONF-800401-P2, 20/1-8 (1980).

Variables:

Temperature: 454 and 483 K

Prepared by:

H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of H in liquid Li was determined. The values were read from a figure and recalculated to mol % by the compilers.

T/K	t/°C	Solubility/mass % H	Solubility/mol % H
454.5	181.3	$5.3\cdot10^{-3}$	$3.6\cdot10^{-2}$
483.1	209.9	$1.00\cdot10^{-2}$	$6.9\cdot10^{-2}$

Auxiliary Information

Method:

The principal tool for this research was the Li processing test loop. The loop was constructed mainly from 304 stainless steel. It contained a Zr- packed getter trap. The Zr wires were exposed to the flowing Li saturated with H at selected temperature for up to 10 000 h. H was gettered by Zr. The amount of H dissolved in liquid Li was estimated from the gettering coefficient and the H content in Zr wire found with the use of micro-metallurgical analysis.

Source and Purity of Materials:

H: nothing specified.

Li: nothing specified; purified by gettering with Zr wire.

Estimated Error:

Solubility: nothing specified; reading out procedure ±3%.

Temperature: nothing specified; reading out procedure ±1 K.

Components:
(1) Hydrogen; H; [1333-74-0]
(2) Lithium; Li; [7439-93-2]

Original Measurements:
R. F. Simandl, U.S., Dept. Energy Rep. Y-2242, (1981).

Variables:
Temperature: 823–923 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of H in liquid Li was determined. The solubilities were read from figures relating the H equilibrium plateau pressure to the composition.

T/K	Solubility/mol % H	p/Pa
823	5.2	61.2±1.0
873	8.7	303±7
923	14	1237±23

The validity of the Sieverts law at low H concentrations was confirmed at each temperature.

Auxiliary Information

Method:
The experiments were performed using a double-walled quartz chamber connected to a vacuum system made of Type 304 stainless steel. The H pressure in the outer quartz jacket of the chamber was kept at the same level. A Cu heat ballast surrounding the chamber secured the stability of temperature, which was controlled by a high precision Pt resistance thermometer. Li was placed in a Nb–Zr(1%) container in an Ar atmosphere. The container was previously washed in a mixture of HNO_3–HF–H_2O (23:4:23), rinsed in distilled H_2O and CH_3OH, and dried under vacuum. The container was electron beam welded under 0.133 mPa. The samples were outgassed at 1073 K for >4 days under vacuum of 13.3 μPa. After these preparing steps the container with Li was inserted into the chamber, and Li was hydrided by introduction of H in small increments and equilibrated up to 16 h. A procedure of thermal cycling was applied: heating to 973 K, H addition and cooling to the desired temperature. The equilibrium pressure was measured. The solubilities were read from breaks on the pressure versus composition isotherms.

Source and Purity of Materials:
H: from UH_3 by its thermal decomposition at ≈673 K.
Li: from Oak Ridge National Lab., 6Li/7Li=0.0238±0.0002, contained <0.01% Th, W, Ca, $<6\cdot10^{-3}$ % Na, Ir, $<4\cdot10^{-3}$ % Cs, Rb, As, Hf, Ta.
Ar: contained $<1\cdot10^{-4}$ % H_2O.

Estimated Error:
Solubility: nothing specified; reading-out procedure ±0.2 mol % H.
Temperature: stability ±1 K.

3.2. Lithium–Deuterium

Components:
(1) Deuterium; D; [7782-39-0]
(2) Lithium; Li; [7439-93-2]

Evaluated By:
Hans Ulrich Borgstedt, Forschungszentrum Karlsruhe, Germany and Cezary Guminski, University of Warsaw, Poland, June 1994

Critical Evaluation

The D–Li system is qualitatively identical to the H–Li system and some features of both are not distinguishable experimentally. The D–Li system was investigated less extensively, since D is more precious than H.

Pulham *et al.*[1] found a 20% higher activation energy of the first step of the reaction:

$$1/2D_2(g)+Li(l)\leftrightarrow LiD(l)\leftrightarrow LiD(s) \quad (1)$$

with regard to the analogical LiH formation. The absolute value of the activation energy was not confirmed by Ihle and Wu.[2] The Li(l) and LiD(l) are only partly miscible. As gas, liquids, and solid are in equilibrium, a solubility of D in liquid Li may be defined in two ways depending on saturating component. According to the first step of the reaction in Eq. (1), a concentration of LiD in liquid Li is proportional to the D pressure over the solution. The dependence is ruled by the Sieverts law:

$$K_s=X_D/p_D^{1/2}, \quad (2)$$

K_s is named by some authors simply the solubility. The dilute solutions of D in liquid Li obey the Sieverts law well up to a few mol % D. The equilibrium pressures for such solutions were determined by Heumann and Salmon,[3] Veleckis,[4] McCracken *et al.*,[5] Ihle and Wu,[6,7] and Smith *et al.*[8] Increasing the D pressure LiD starts to precipitate, and the D pressure is no longer composition dependent until stoichiometric LiD is formed. This pressure, which is reached with the exceeding of the solubility limit, is named the equilibrium plateau pressure.

The equilibrium plateau pressure (p_D^s) was measured in the above listed works and by Smith and Webb.[9] All experimental data, where the equilibrium is characterized by the monovariant three-phase equilibria (solid LiD, its saturated liquid solution in Li and D gas), were expressed by the fitting equation:[3]

$$\log(p_D^s/\mathrm{Pa})=14.306-10256\ (T/\mathrm{K})^{-1} \quad (3)$$

valid between the eutectic (454 K) and the monotectic temperature (960 K). The p_D^s values of Smith and Webb[9] are a few % lower than other studies.[3,4,9,10] Equations similar to Eq. (3) were established in many studies.[4,9–12] When two hardly miscible liquids, the Li-rich and LiD-rich ones, are in equilibrium with the D gas, the corresponding vapor pressure data may be approximated by the following fitting equation:

$$\log(p_D^s/\mathrm{Pa})=11.414-7476/(T/\mathrm{K})^{-1}, \quad (4)$$

which is valid at temperatures higher than 963 K. Similar equations have been reported.[3,4,9,10,12] The equation presented by Heumann and Salmon[3] differs unacceptably from those placed in the other papers. The values p_D^s obtained by Smith and Webb[9] are generally a few percent lower than those of others.[3,4,8,10] Intersection of Eq. (3) and Eq. (4) points on the monotectic reaction at 960 K. The Sieverts law dependence was investigated by many.[4–7,14,8,13,10] Shpil'rain *et al.*,[12] taking into account their own and all the mentioned results, proposed a fitting equation of temperature dependence the K_s constant:

$$\log(K_s/\mathrm{mol\ \%\ Pa^{-1/2}})=-3.3119+2588\ (T/\mathrm{K})^{-1}, \quad (5)$$

which is accepted in this evaluation. Equation (5) is originally valid for temperature range of 940–1180 K but it seems reasonable to assume that it is also valid at higher and lower temperatures if the solutions are more diluted than 1 mol % D. Similar relations have been reported,[4,8,10,11,14–16] but the one reported by Hoch[17] differs unacceptably from Eq. (5).

The complexity of the gas phase was revealed by Ihle and Wu[6,7,14] who performed mass spectrometric-Knudsen effusion studies of the vapor phase and observed that it is composed of not only D but also of Li_2, Li_3, LiD, Li_2D, and Li_2D_2 molecules. The authors evaluated partial pressures and equilibrium constants for the exchange reaction among the species as function of the liquid phase composition (10^{-5}–10^{-2} mol % D) and temperature (800–1600 K). The corresponding data are tabulated in Hubberstey.[11] The existence of the gaseous deuterides does not affect the Sieverts law relationship, it leads to an increased content of D in the saturated vapor over the D–Li melt. It is possible this way to separate the H isotopes from Li by fractional distillation performed at temperatures higher than 1240 K.

The solubility of solid LiD in liquid Li was determined by measuring D vapor pressure over the saturated solution (it corresponds to the gaseous solubility limit),[3,4,8] chemical analysis of the saturated samples,[18] thermal analysis,[18] and resistivity measurements.[19] Adams *et al.*[19] observed Li freezing point depression of 0.075 K at composition of 0.013 mol % D, however, their melting point of pure Li was 0.11 K below the contemporary accepted value.[20] Although it may be assumed that the depression of 0.1±0.03 K is real, the corresponding composition is placed at about 0.03 mol % D but not at 0.013 mol % D as suggested by Adams *et al.*[19] Extrapolation of the data of Ihle *et al.*[14] is preferred to the extrapolation of the data of Adams *et al.*,[19] since the values of Ihle *et al.*[14] show a similar temperature dependence of the solubility to the data of H solubility in liquid Li, whereas the values of Adams *et al.*[19] do not. A solid solubility of D in Li seems to be not higher than 0.01 mol % D by analogy to the Li–H system. Veleckis *et al.*[18] and Maroni *et al.*[23] estimated the composition of the eutectic point as 0.035 and 0.028 mol % D and the corresponding freezing point depression of 0.20 and 0.15 K, respectively; all these numbers seem to be too high.

The D solubility data of Veleckis *et al.*[18] and Adams *et al.*[19] agree between 625 and 690 K but especially at lower temperatures the

discrepancy is systematically larger. Most probably some residual content of D or H in Li could simulate a premature indication of the saturation. However, Hubberstey *et al.*[22] refuse such explanation. Veleckis *et al.*[15,18] related the solubility and temperature between 454 and 960 K with the help of cubic equation but it seems rational to express the results of Veleckis *et al.*[18] up to 825 K by the following simple equation:

$$\log(\text{soly/mol \% D}) = 3.375 - 2222\ (T/\text{K})^{-1}. \tag{6}$$

This equation was formulated by Veleckis *et al.*[15] and was tested by the evaluators. Hubberstey *et al.*[22] reported quite similar equation to Eq. (6). The published solubility fitting equations[11,19,23] are not recommended since they either base on questionable data or contain an error in calculations. If one would subtract the right hand sides of Eq. (6) and half of Eq. (3), one obtains temperature dependence of the Sieverts constant at temperatures below 800 K:

$$\log(K_s\ /\text{mol \% Pa}^{-1/2} = -3.774 + 2906\ (T/\text{K})^{-1}. \tag{7}$$

The significant difference between Eqs. (5) and (7) points out that the D solubility relation on temperature should be experimentally confirmed. A use of the results of Adams *et al.*[19] to formulate an equation analogical to Eq. (7) would lead to much larger difference between Eqs. (7) and (5).

The monotectic temperature was established at: 959±5 K,[25] 961 K,[9] 963 K,[10,15,23] and 960 K in this evaluation. Smith and Webb[9] claimed to measure the melting point of LiD but due to decomposition of this compound they measured in fact the monotectic temperature. The selected monotectic temperature was assessed at 960 K. At this temperature the miscibility gap extends from 19 to 49.5 mol % D. Much narrower range given by Heumann and Salmon[3] seems to be in error. Points on the liquidus line, between the monotectic and critical miscibility temperature, have been measured by numerous workers.[3,4,6,8,13,24] A good agreement of the results of Veleckis[4] and Smith *et al.*,[8] within ±0.5 mol %, is observed. The data of Ihle and Wu[6] deviate by a few mol % from all other data and are not recommended. The linear solubility fitting equation [as Eq. (6) for example] proposed by Smith and Webb,[9] Veleckis *et al.*,[15] and Fromm and Jehn[16] is not recommended since the log(soly) versus $1/T$ dependence ought not to be linear in this composition range. Parameters of the critical miscibility point were not measured experimentally. One may expect that this temperature should be a few K lower than that predicted for the H–Li system. The melting point of LiD was reported by Smith *et al.*[24] to be 959±5 K. By analogy to the difference between the monotectic and melting temperatures for LiH, LiD should melt congruently at 963 K. The D–Li phase diagram is practically the same as of the H–Li system and only small differences in temperatures and compositions of phase transitions are observed.[21]

The recommended (r) and tentative (t) solubility and D plateau pressure values of D in liquid Li

T/K	Solubility/mol % D	Source	p/Pa	Source
453.7	0.03 (t) eutectic	(17) extrapol	$5.2\cdot10^{-9}$	Eq. (3) extrapol.
473	0.05 (t)	(17)	$4.2\cdot10^{-8}$	Eq. (3) extrapol.
573	0.3 (t)	(17) interpol	$2.6\cdot10^{-4}$	Eq. (3) extrapol.
673	1.2 (r)	(17),(18)	0.117	Eq. (3) extrapol.
773	3.2 (t)	(17)	11	(9)
873	8 (t)	(8),(17) interpol	350	(9)
960	18 (t)	(4)	4300	(9),(10) mean value
1073	25 (r)	(8),(10)	29 000	(10), Eq. (4) interpol
1123	30 (t)	(10)	61 000	(10)
~1250	40 critical	predicted ≈300 000	Eq. (4), predicted	

The tentative LiD-rich liquidus values of the D–Li system

T/K	Solubility/mol % D	Source
960	49.6 eutectic	(8)
1073	49.0	(8)
1123	48	(8)

References:

[1]R. J. Pulham, P. F. Adams, P. Hubberstey, G. Parry, and A. E. Thunder, U.S. Energy Res. Devel. Admin. Rep. CONF-750989-P4, p. 144 (1976).

[2]H. R. Ihle and C. H. Wu, Europ. Atom. Energy Commun. Rep. EUR-5602, p. 329 (1976).

[3]F. K. Heumann and O. N. Salmon, U.S. Atom. Energy Comm. Rep. KAPL-1667 (1956).

[4]E. Veleckis, J. Phys Chem. **81**, 526 (1977).

[5]G. M. McCracken, D. J. H. Goodall, R. T. P. Whipple, and G. Long, Nucl. Fusion, Spec. Suppl., p. 439 (1974).

[6]H. R. Ihle and C. H. Wu, *Proceedings Second International Congress on Hydrogen in Metals* (Pergamon, New York, 1977).

[7]H. R. Ihle and C. H. Wu, Europ. Atom. Energy Commun. Rep. EUR-5182C, p. 787 (1974).

[8]F. J. Smith, J. F. Land, G. M. Begun, and A. M. La Gamma de Batistoni, J. Inorg. Nucl. Chem. **41**, 1001 (1979).

[9]H. M. Smith and R. E. Webb, U.S. Dept. Energy Rep. Y-2095 (1977).

[10]E. Veleckis, J. Nucl. Mater. **79**, 20 (1979).

[11]P. Hubberstey, *Handbook of Thermodynamic and Transport Properties of Akali Metals*, edited by R. W. Ohse (Blackwell, Oxford, 1985), p. 885.

[12]E. E. Shpil'rain, K. A. Yakimovich, and E. A. Tsirkina, Inzh.-Fiz. Zh. **38**, 249 (1980).

[13]F. J. Smith and J. F. Land, Trans. Am. Nucl. Soc. **21**, 167 (1975).

[14]H. R. Ihle, H. Kudo, and C. H. Wu, *Thermodynamics of Nuclear Materials* (IAEA, Vienna, 1980), p. 31.

[15]E. Veleckis, R. M. Yonco, and V. A. Maroni, *Thermodynamics of Nuclear Materials* (IAEA, Vienna, 1980), p. 3.

[16]E. Fromm and H. Jehn, Bull. Alloy Phase Diagr. **5**, 324 (1984).

[17]M. Hoch, J. Nucl. Mater. **120**, 102 (1984).

[18]E. Veleckis, R. M. Yonco, and V. A. Maroni, J. Less-Common Met. **55**, 85 (1977).

[19]P. F. Adams, P. Hubberstey, R. J. Pulham, and A. E. Thunder, J. Less-Common Met. **46**, 285 (1976).

[20]J. Sangster and A. D. Pelton, J. Phase Equil. **14**, 373 (1993).

[21]P. Hubberstey, P. F. Adams, R. J. Pulham, M. G. Down, and A. E. Thunder, J. Less-Common Met. **49**, 253 (1976).

[22]P. Hubberstey, A. T. Dadd, and P. G. Roberts, *Material Behavior and Physical Chemistry in Liquid Metal Systems*, edited by H. U. Borgstedt (Plenum, New York, 1982), p. 445.

[23]V. A. Maroni, W. F. Calaway, E. Veleckis, and R. M. Yonco, U.S. Energy Res. Devel. Admin. Rep. CONF-760503-P1, p. 437 (1976).

[24]F. J. Smith, G. M. Begun, J. F. Land, and J. T. Bell, U.S. Energy Res. Devel. Admin. Rep. ORNL-5111, p. 26 (1976).

[25]C. E. Messer, U.S. Atom. Energy Comm. Rep. NYO-9470 (1960).

Components:
(1) Deuterium; D; [7782-39-0]
(2) Lithium; Li; [7439-93-2]

Original Measurements:
F. K. Heumann and O. N. Salmon, U.S. Atom. Energy Comm. Rep. KAPL-1667 (1956).

Variables:
Temperature: 973–1073 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data
Limits of the liquid immiscibility gap of the Li–LiD system were reported

t/°C	p/Pa	Solubility/mol % LiD[a]	mol % D[a,c]	Solubility/mol % LiD[b]	mol % D[b,c]
700	5990	28	22	94	48.5
750	13200	36	26	92	48
800	33700	38	28	90	47.5

[a]Lower limit.
[b]Upper limit.
[c]Calculated by the compilers.

Auxiliary Information

Method:
Li was enclosed in a low C steel capsule with a lid. The parts were corrosion resistant. They were fired in H at 1073 K for 1 h, degassed at 1073 K in vacuum and left for 24 h in an Ar dry box. A small amount of molten Li was poured on an Fe plate. A part of the solidified Li was placed in the capsule. The lid was hammered into the capsule and welded in vacuum. The capsule was placed in a quartz container, pumped out for several hours. Li was heated to 973 K and contacted with D and pressure readings were taken until the equilibrium pressure was obtained after 8–12 h. The equilibrium was reached from below and above by the formation and dissociation of LiD. The purity of the equilibrium gas was checked by a mass spectrometer. A Chromel/Alumel thermocouple was used for temperature measurements. Limits of the immiscibility gap were read from the plateau on the pressure–composition isotherm.

Source and Purity of Materials:
D: 99.5% pure from Stuart Oxygen Comp.; purified by formation and subsequent decomposition of UD_3, it finally contained a small amount of H.
Li: 99.75% pure obtained from Maywood Chem. Comp.; contained 0.02% Na, 0.015% Si, 0.03% Fe+Al, 0.06% Ca, 0.03% N, 0.003% Cl and 0.09% heavy metals.
Ar: purified by contact with Cu turnings at 673 K and molten Na containing Li at 448 K; finally contained (1.0–1.5). 10^{-3} % O.

Estimated Error:
Nothing specified.

Components:
(1) Deuterium; D; [7782-39-0]
(2) Lithium; Li; [7439-93-2]

Original Measurements:
P. F. Adams, P. Hubberstey, R. J. Pulham, and A. E. Thunder, J. Less-Common Met. **46**, 285–289 (1976).

Variables:
Temperature: 453.6–729 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data
The solubility of D in liquid Li was determined

t/°C	Solubility/mol % D
180.48	0.004[a,b]
280.44	0.009[a,b]
180.415	0.013[b]
76.0	0.12
305.0	0.23
328.0	0.33
349.5	0.49
364.5	0.69
375.0	0.77
397.0	0.99
401.5	1.10
417.0	1.39
451.0	2.35
456.0	2.63

[a]Read from a figure by the compilers.
[b]From thermal analysis.

The melting point of Li was found at 180.490 °C. A part of the results was graphically presented in Pulham *et al.*[2]

Auxiliary Information

Method:
The apparatus was constructed from AISI 321 stainless steel.[1] It consisted of a reservoir, a neck, a thermocouple pocket, a side loop with a small electro-magnetic pump, and a winding device (in the neck) for introduction and removal of an Y getter. A Chromel/Alumel thermocouple, calibrated against the NPL thermometer, was used to record the temperature. The clean and dry apparatus was charged with Li in an Ar atmosphere. The temperature was raised to 673 K for the gettering with Y. After Y removal the melting point of Li was determined from cooling curves at a rate of 10 K/h. Successive D volumes were introduced into Li and the freezing point determination repeated. For solubility measurements the Li was circulated through a capillary loop bridged by two circular discs between the resistance was measured. After successive additions of the gaseous D the resistivity was measured. Saturation was indicated by an abrupt leveling of the resistivity. The measurements were performed changing the temperature or the D content in the melt.

Source and Purity of Materials:
D: 99.5% pure.
Li: 99.98% pure, purified by gettering with Y sponge at 673 K for 12 h during Li circulation.
Ar: nothing specified.

Estimated Error:
Solubility: nothing specified; ±0.001 mol % in thermal analysis, ±0.01 mol % in resistivity studies (by the compilers).
Temperature: precision ±0.01 K, accuracy ±0.1 K (by the compilers).

References:
[1]P. F. Adams, M. G. Down, P. Hubberstey, and R. J. Pulham, J. Less-Common Met **42**, 325–34 (1975).
[2]R. J. Pulham, P. F. Adams, P. Hubberstey, G. Parry, and A. E. Thunder, U.S. Energy Res. Devel. Admin. Rep. CONF-750989-P4, pp. 144–57 (1976).

Components:
(1) Deuterium; D; [7782-39-0]
(2) Lithium; Li; [7439-93-2]

Original Measurements:
H. R. Ihle and C. H. Wu, *Proceedings Second International Congress on Hydrogen in Metals* (Pergamon, New York, 1977).

Variables:
One Temperature: 973 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of D in liquid Li and the equilibrium plateau pressure of D at 700 °C were determined. The values read from a figure are 0.26 mol fraction of LiD and 44 Torr; the values recalculated by the compilers are 20 mol % D and 5900 Pa.

Partial pressures of Li_2, Li_3, Li_2D, LiD, Li_2D_2, D_2, and LiD_2 were determined as functions of temperature.

Auxiliary Information

Method:
The apparatus used for the investigations consisted of a Mo Knudsen cell heated by a generator serving as the source of the molecular beam, a quadrupole mass filter and a gas purification and delivery system. The cell temperature was measured by an optical pyrometer. A Pt/Pt–Rh thermocouple was calibrated on the melting points of Li, Ag, and Au. Solutions of D in Li were prepared by reaction of Li with known amount of D gas. The shutter between the orifice of the cell and the ion source was used to distinguish between residual background and signals due to molecules effusing from the cell. The vapor pressure of Li was used as the standard for pressure calibration. The saturation composition was estimated from a break on the isotherm pressure versus composition.

Source and Purity of Materials:
D: purified by formation and thermal decomposition of UD_3.
Li: "pure"; the temperature of melting was used for the calibration of the thermocouple.

Estimated Error:
Solubility: accuracy ±1%; reading-out procedure ±3%.
Pressure: reading-out procedure ±3%.

Components:
(1) Deuterium; D; [7782-39-0]
(2) Lithium; Li; [7439-93-2]

Original Measurements:
E. Veleckis, J. Phys. Chem. **81**, 526–531 (1977).

Variables:
Temperature: 962–1144 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

Limits of immiscibility in the LiD–Li system were determined

t/°C	p/Pa	Solubility/mol % LiD	mol % D[a,c]	Solubility/mol % LiD	mol % D[b,c]
689	···	21.3	17.6	···	···
705	6530	22.8	18.6	98.0	49.5
756	15410	28.0	21.9	97.2	49.3
805	32550	33.2	24.9	95.3	48.8
840	53350	37.7	27.4	93.1	48.2
871	80570	41.1	29.1	90.5	47.5

[a]Lower limit.
[b]Upper limit.
[c]Calculated by the compilers.

The melting point of LiD was found at 692.4 °C. The data were partly reported in Veleckis *et al.*[2,3] and in full in Maroni *et al.*[4] and Veleckis.[5]

Auxiliary Information

Method:
The procedure was the same as in Veleckis *et al.*[1] The experiments were carried out in a Sieverts' apparatus which consisted of a gas purificator, an equilibration container and a gas meter. Li was placed in closed capsule made of Armco Fe. The capsules were heated in H and degassed at 1123–1173 K prior to the Li addition. The capsules with Li were evacuated and heated to the temperature of experiments. D was added to the sample in measured portions. The equilibrium pressure was measured after 12–48 h, when equilibrium in the system was reached. The D concentration in Li was calculated from the weight of Li before and after D addition. The temperature was measured with the use of three calibrated Pt/ Pt–Rh (10%) thermocouples. He was used as the inert gas in the glove box.

Source and Purity of Materials:
D: 99.99% pure from Air Products and Chemicals Inc. D was absorbed in a Ti sponge. Required amount of D was evolved by heating. Content of HD: 1.1%±0.2%.
Li: 99.9+% pure from Lithium Corp. of America; further purified by filtration of the molten metal through 5 μm filter at 673 K.
He: purified by a silicagel getter cooled by liquid N; contained $1 \cdot 10^{-4}$ % N, O.

Estimated Error:
Solubility: precision ±1% on the Li-rich side and ±0.5% on the LiD-rich side.
Temperature: stability ±1.5 K.
Pressure: precision ±0.5%.

References:
[1]E. Veleckis, E. H. Van Deventer, and M. Blander, J. Phys. Chem. **78**, 1933–1940 (1974).
[2]E. Veleckis and R. M. Yonco, U.S. Energy Res. Devel. Admin. Rep. ANL-76-106, pp. 8–11 (1976).
[3]E. Veleckis, U.S. Atom. Energy Comm. Rep. ANL-8123, pp. 5–6 (1974).
[4]V. A. Maroni, E. Veleckis, and E. H. Van Deventer, U.S. Energy Res. Devel. Admin. Rep. ERDA-50, pp. 120–132 (1975).
[5]E. Veleckis, U.S. Energy Res. Devel. Admin. Rep. ANL-75-50, pp. 17–22 (1975).

Components:
(1) Deuterium; D; [7782-39-0]
(2) Lithium; Li; [7439-93-2]

Original Measurements:
E. Veleckis, R. M. Yonco, and V. A. Maroni, J. Less-Common Met. **55**, 85–92 (1977).

Variables:
Temperature: 472–771 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data
The solubility of D in liquid Li was measured at several temperatures

t/°C	Solubility/mol % D
198.9	0.0514
221.1	0.0767
246.3	0.122
271.5	0.181
303.6	0.321
322	0.50[a]
323.3	0.425
351.0	0.629
375	0.84[a]
375.1	0.859
397.2	1.13, 1.16
451	2.30[a]
451.4	2.04
498.0	3.21

[a]Preliminary results reported in Veleckis and Maroni.[1]

LiD is the solid equilibrium phase. These data were also reported in Veleckis and Yonco.[2]

Auxiliary Information

Method:
Li spherules were placed in an Armco Fe vessel, which was connected to an Hetmosphere glove box. The vessel was covered with a flange that had feed-throughs for a stirrer, a sampling shaft funnel and dropping through a pinhole, a thermocouple and a leading to D or H in the funnel bottom into stainless cylinders and vacuum pumps. A Ni tube was connected to the sampling shaft with a pressed 10 μm porous Ni frit. The Li–D mixtures were prepared by reacting molten Li with a measured volume of D at temperatures 573–823 K. The melt was cooled down, an excess of D was pumped out, and the vessel refilled with He. The melt was brought to the desired sampling temperature and the samples were taken by reducing the He pressure. The sample tube was withdrawn and allowed to cool. The samples were individually sealed in thin-walled Fe capsules by electron beam welding in vacuo. Each capsule was placed in a silica tube, connected to a pump and heated at 1113 K for ~10 days. The evolved gas was analyzed for its D content by a mass spectrometer. The Li content was determined by titration with standard HCl after the sample dissolution in H_2O.

Source and Purity of Materials:
D: 99.99+5% pure from Air Products and Chemicals Inc.
Li: 99.9+% pure from Lithium Corp. of America; purified by melting in a Ta steel chill plate; finally contained $2.2 \cdot 10^{-2}$ % N and $6 \cdot 10^{-2}$ % O.
He: contained $< 10^{-4}$ % H_2O, O.

Estimated Error:
Solubility: precision ±3%.
Temperature: stability ±1 K.

References:
[1]E. Veleckis and V. A. Maroni, U.S. Energy Res. Devel. Admin. Rep. CONF-750989-P3, pp. 458–69 (1975).
[2]E. Veleckis and R. M. Yonco, U.S. Energy Res. Devel. Admin. Rep. ANL-76-106, pp. 8–11 (1976).

Components:
(1) Deuterium; D; [7782-39-0]
(2) Lithium; Li; [7439-93-2]

Original Measurements:
F. J. Smith, J. F. Land, G. M. Begun, and A. M. La Gamma de Batistoni, J. Inorg. Nucl. Chem. **41**, 1001–1009 (1979).

Variables:
Temperature: 973–1173 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data
Limits of the immiscibility gap in the LiD–Li system were determined

t/°C	p/Pa	Solubility/mol % LiD	mol % D[c,d]	Solubility/mol % LiD	mol % D[d,e]
700	6130	24	19	98	49.5
750	15300	28	22	97	49.2
800	33900[a,b]	33	25	96	49.0
850	61500	39	28	92	48
900	>107000	46	31	···	···

[a]38 260 Pa as reported in Smith *et al.*[3]
[b]41 190 Pa as reported in Smith and Land.[4]
[c]Lower limit.
[d]Calculated by the compilers.
[e]Upper limit.

The results at 700 and 800 °C were graphically presented in Smith *et al.*[1,2,5]

Auxiliary Information

Method:
Equilibrium pressures of D gas were measured using the modified Sieverts apparatus. Samples of Li were sealed under vacuum in a thin walled capsule (Fe or Ni) permeable for D. The equilibrium was established inside as well as outside the capsule. The capsule was placed in a quartz envelope. The envelope was connected to the system, and its volume was calibrated. The system was evacuated at ambient temperature and subsequently at 1173 K down to a pressure of 0.013 Pa. The temperature was adjusted at selected values. D gas was admitted to the system. Finally the valves to the quartz envelope were opened and the change in pressure with time was recorded until the equilibrium was reached.

Source and Purity of Materials:
D: "high purity", further purified by passage through a hot Pd–Ag membrane.
Li: unspecified; from Foote Mineral Comp., further purified by contact with Zr in a Ti crucible at 1073 K for >100 h and filtering through a 5 μm filter at ~573 K, contained $< 6.2 \cdot 10^{-3}$ % O.

Estimated Error:
Solubility: nothing specified.
Temperature: nothing specified.

References:
[1]F. J. Smith, J. F. Land, J. B. Talbot, and J. T. Bell, U.S. Energy Res. Devel. Admin. Rep. CONF-750989-P3, pp. 539–53 (19756).
[2]F. J. Smith, A. M. La Gamma de Batistoni, G. M. Begun, and J. F. Land, U.S. Energy Res. Devel. Admin. Rep. 760631-1, (1976).
[3]F. J. Smith, G. M. Begun, J. F. Land, and J. T. Bell, U.S. Energy Res. Devel. Admin. Rep. ORNL-5111, pp. 26–7 (1976).
[4]F. J. Smith and J. F. Land, Trans. Am. Nucl. Soc. **21**, 167–8 (1975).
[5]F. J. Smith, A. M. La Gamma de Batistoni, G. M. Begun, and J. F. Land, Eur. Atom. Energy Commun. Rep. EUR-5602, pp. 325–8 (1976).

Components:
(1) Deuterium; D; [7782-39-0]
(2) Lithium; Li; [7439-93-2]

Original Measurements:
E. Veleckis, J. Nucl. Mater. **79**, 20–27 (1979).

Variables:
Temperature: 911–1124 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

Equilibrium plateau pressures of D gas over the heterogeneous LiD–Li mixtures were measured

t/°C	p/Torr	p/Pa[a]
850.6	461.2	61480
827.5	337.7	45015
799.7	225.6	30070
774.5	155.0	20660
762.1	127.1	16940
751.6	109.9	14650
738.7	88.15	11750
726.9	71.10	9478
712.3	56.50	7531
702.3	47.40	6318
692.0	38.78	5169
690 b	37.9	5052
677.5	27.37	3648
666.4	20.64	2751
653.1	13.94	1858
641.9	10.35	1380
627.7	7.00	933

[a]Calculated by the compilers.
[b]Monotectic temperature.

The results were reported graphically in Veleckis *et al.*[1] and numerically in Veleckis.[2] The results were represented by equations for solid and liquid LiD, respectively:

$$\log(p/\mathrm{Pa}) = 14.342 - 10245\ (T/\mathrm{K})^{-1}; \quad \log(p/\mathrm{Pa}) = 11.310 - 7327\ (T/\mathrm{K})^{-1}.$$

The monotectic temperature was estimated from intersection of the above dependencies to be 690 °C (963 K).

Auxiliary Information

Method:
A Li spherule was placed in an Armco Fe capsule that had thin walls (permeable to gaseous D), a thick bottom with a reentrant thermocouple well. The capsule was closed (by He arc welding) with a lid connected via a hollow Fe stem and a glass to metal seal, to a closed glass stopcock. The apparatus for the pressure measurements was made of two concentric tubes: the outer one of stainless steel and the inner one of fused silica. The tubes were joined at the top via a graded seal. The capsule was placed in the silica tube, connected to the equilibrium apparatus and evacuated at ~1123 K for several days. The Li reacted with a portion of D to produce 55–70 mol % LiD solution in liquid Li. The equilibrium pressures were measured after more than 4 h of equilibration. Temperatures were measured by means of a Chromel/Alumel thermocouple.

Source and Purity of Materials:
D: 99.99+% pure from Air Products and Chemicals, Inc.; purified by absorption in a hot Ti sponge, evacuation of impurities from the cooled sponge and extraction D by reheating. Li: 99.9+% pure from Lithium Corp. of America; purified by dripping of the molten Li from a Ta funnel onto a stainless steel chill plate. The Li spherules contained ~0.02% N and ~0.06% O.

Estimated Error:
Temperature: nothing specified;
Pressure: precision ±1.3 Pa.

References:
[1]E. Veleckis, R. M. Yonco, and V. A. Maroni, *Thermodynamics of Nuclear Materials* (IAEA, Vienna, 1980), pp. 3–30.
[2]E. Veleckis, U.S. Energy Res. Devel. Admin. Rep. ANL-76-106, p. 5 (1976).

3.3 Lithium–Tritium

Components:
(1) Tritium; T; [12028-17-8]
(2) Lithium; Li; [7439-93-2]

Evaluated by:
Hans Ulrich Borgstedt, Forschungszentrum Karlsruhe, Germany and Cezary Guminski, University of Warsaw, Poland, August 1999

Critical Evaluation

General features of the T–Li system are experimentally hardly distinguishable from those of the H–Li and D–Li systems. Some properties of the system show small quantitative differences. If the sequence of activation energies of the first step of reaction:

$$1/2\ T_2(g) + Li(l) \leftrightarrow LiT(l) \leftrightarrow LiT(s) \tag{1}$$

increases from H to T, kinetics of this reaction should be slower than of the analogous reactions with H or D. Both liquids Li and LiT show limited miscibility. When the gas, liquids, and solid are in equilibrium, a solubility of T in liquid Li may be defined in two ways, depending on the state of the saturating component. According to the first step of the reaction expressed by Eq. (1), a concentration of LiT in liquid Li is dependent on the T pressure over the solution. For the diluted solution a ratio of T concentration to square root of its gas pressure is constant, fulfilling the Sieverts' law:

$$K_s = x_T / p_T^{1/2}, \tag{2}$$

K_s is simply named solubility by some authors. Equation (2) is valid at constant temperature up to a few mol % T. The T equilibrium pressures over the diluted solutions were determined by Heumann and Salmon,[1] Veleckis,[2] and Smith *et al.*[3] All investigators used T of purity lower than 99 vol % and corresponding corrections of measurements for a hypothetically pure T were done. The temperature dependence of K_s was determined by Smith *et al.*[3] and the results were expressed by the equation:

$$\log(K_s/\mathrm{mol\ \%\ Pa^{-1/2}}) = -3.069 + 2.208\ (T/\mathrm{K})^{-1}. \tag{3}$$

Maroni *et al.*[8] reported a set of the K_s values (0.0356, 0.0552, 0.0931, and 0.170 mol % $\mathrm{Pa}^{-1/2}$ at 1273, 1173, 1073, and 973 K, respectively) but the data were based on a prediction. Later, the same laboratory[9] reported an equation, which does not fit to the data in Maroni *et al.*[8] Veleckis,[2] Fromm and Hoerz,[4] Hoch,[5] Shpil'rain *et al.*,[7] and Hubberstey[10] reported different dependencies of K_s versus reciprocal temperature but the one predicted in Maroni *et al.*:[9]

$$\log(K_s/\mathrm{mol\ \%\ Pa^{-1/2}}) = -3.109 + 2345\ (T/\mathrm{K})^{-1} \tag{4}$$

fits the best the influence of isotopic effect of the series H–D–T as reflected in the Sieverts constant.

The equilibrium plateau pressure of T (when the liquid is saturated with LiT) at temperatures below the monotectic is expressed with the help of relation:

$$\log(p_{Ts}/\mathrm{Pa}) = 14.229 - 10080\ (T/\mathrm{K})^{-1}, \tag{5}$$

which was originally formulated by Veleckis[2] basing on his own data. Equation (5) was confirmed by the evaluators and was also reported by Hubberstey.[10] When two hardly miscible liquids the Li rich and LiT rich are in equilibrium with T gas the corresponding vapor pressure data of Heumann amd Salmon[1] and Veleckis[2] may be approximated by the following fitting equation:

$$\log(p_{Ts}/\mathrm{Pa}) = 11.221 - 7193\ (t/\mathrm{K})^{-1}, \tag{6}$$

which is valid above the monotectic temperature. This temperature may be estimated at 959 K from the intersection of Eqs. (5) and (6). Because Veleckis[2] proposed a slightly different equation to Eq. (6) the monotectic reported by Veleckis[2] and Veleckis *et al.*[6] is therefore 2 K higher than a value found in this evaluation. Vapor pressure equations formulated by Heumann and Salmon[1] from the experiments and by Hoch[5] from a prediction differ unacceptably from Eq. (6). Veleckis *et al.*,[6] Shpil'rain *et al.*,[7] Hubberstey,[10] and Sangster and Pelton[11] repeated in their papers the equation obtained by Veleckis.[2]

Direct measurements of the solubility of solid LiT in liquid Li between the eutectic and monotectic temperature were not performed since only diluted solutions of T in Li were investigated. One could estimate the solubility by an addition of Eq. (3) and half of Eq. (5), obtaining the following equation:

$$\log(\mathrm{soly/mol\ \%\ T}) = 4.045 - 2832\ (T/\mathrm{K})^{-1}. \tag{7}$$

However, the data calculated from this equation were higher at lower temperatures and lower at higher temperatures in relation to the D solubility in liquid Li. If one would use Eqs. (4) and (5) one would get:

$$\log(\mathrm{soly/mol\ \%\ T}) = 4.005 - 2695\ (T/\mathrm{K})^{-1}. \tag{8}$$

Equation (8) gives the solubility results three times larger at 454 K and equal to the D solubility at 773 K. Thus neither Eq. (7) nor Eq. (8) are recommended to estimate the T solubility in liquid Li. According to charges of general features of the H–Li, D–Li, and T–Li systems the T solubility in liquid Li should be a few percent lower than the corresponding solubility of D. Magomedov[12] reported the melting point of LiT to be at 968±2 K and the calculated values at 967.83 and 967.90 K for ^{6}LiT and ^{7}LiT, respectively.

Heumann and Salmon[1] estimated the solubility above the monotectic temperature (961 K). However, these experimental data are doubtful since neither Veleckis[2] nor Smith *et al.*[3] confirmed them experimentally. As it was mentioned above the quantitative differences between liquidus lines of the systems of H isotopes with Li are of only a few % and the differences determined by Heumann and Salmon[1] are charged with an error. In conclusion, any numerical solubility data are not suggested in this evaluation, and it seems rational to use

the D solubility data with a diminution of 2% of those values. The T–Li phase diagram is practically the same as one presented for the H–Li system.

References

[1]F. K. Heumann and O. N. Salmon, U.S. Atom. Energy Comm. Rep. KAPL-1667 (1956).

[2]E. Veleckis, J. Nucl. Mater. **79**, 20 (1979).

[3]F. J. Smith, F. J. Land, G. M. Begun, and A. M. La Gamma de Batistoni, J. Inorg. Nucl. Chem. **41**, 1001 (1979).

[4]E. Fromm and G. Hoerz, Bull. Alloy Phase Diagr. **5**, 324 (1984).

[5]M. Hoch, J. Nucl. Mater. **120**, 102 (1984).

[6]E. Veleckis, R. M. Yonco, and V. A. Maroni, *Thermodynamics of Nuclear Materials* (IAEA, Vienna, 1980), p. 3.

[7]E. E. Shpil'rain, K. A. Yakimovich, and E. A. Tsirlina, Inzh.-Fiz. Zh. **38**, 249 (1980).

[8]V. A. Maroni, E. J. Cairns, and F. A. Cafasso, U.S. Atom. Energy Comm. Rep. ANL-8001 (1973).

[9]V. A. Maroni, W. F. Calaway, E. Veleckis, and R. M. Yonco, U.S. Energy Res. Devel. Admin. Rep. CONF-760503-P1, p. 437 (1976).

[10]P. Hubberstey, *Handbook on Thermodynamic and Transport Properties of Alkali Metals*, edited by R. W. Ohse (Blackwell, Oxford, 1985), p. 885.

[11]J. Sangster and A. D. Pelton, J. Phase Equil. **14**, 373 (1993).

[12]M. N. Magomedov, Zh. Fiz. Khim. **68**, 589 (1994).

Components:
(1) Tritium; T; [12028-17-8]
(2) Lithium; Li; [7439-93-2]

Original Measurements:
F. K. Heumann and O. N. Salmon, U.S. Atom. Energy Comm. Rep. KAPL-1667 (1956).

Variables:
Temperature: 973–1074 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

Limits of the liquid immiscibility gap of the Li–LiT system and T_2 equilibrium plateau pressures were reported

t/°C	p/Pa	Solubility/mol % LiT	mol % T[a,c]	Solubility/mol % LiT	mol % T[b,c]
700	6740	31	24	91	47.6
728	11830	···	···	···	···
755	19290	39	28	87	46.5
766	19840	···	···	···	···
771	23400	···	···	···	···
801	34900	42	30	84	45.7

[a]Lower limit.
[b]Upper limit.
[c]Calculated by the compilers.

Auxiliary Information

Method:
Li was contained in a low C steel capsule with a lid. The parts were corrosion resistant. The capsule and lid were fired in H at 1073 K for 1 h, degassed at 1073 K in vacuum, and left for 24 h in an Ar dry box. A small amount of molten Li was poured on a Fe plate. A part of the solidified Li was placed in the capsule. The lid was hammered into the capsule and welded in vacuum. The capsule was placed in a quartz container and pumped out for several hours. Li was heated to 973 K and contacted with T gas. Pressure readings were taken until the equilibrium pressure was reached after 8–12 h. The equilibrium was reached from below and above by the formation and dissociation of LiT. The purity of the equilibrium gas was checked by a mass spectrometer. A Chromel/Alumel thermocouple was used for temperature measurements. Limits of the immiscibility gap were read from the plateau of the pressure versus composition isotherms.

Source and Purity of Materials:
T: unspecified purity; probably purified by formation and subsequent decomposition of UT_3.
Li: 99.75% pure, obtained from Maywood Chem. Comp.; contained 0.02% Na, 0.015% Si, 0.03% Fe+Al, 0.06% Ca, 0.03% N, 0.003% Cl, and 0.09% of heavy metals.
Ar: purified by contact with Cu turnings at 673 K and molten Na containing Li at 448 K; finally contained $(1.0–1.5)\cdot 10^{-3}$ % O.

Estimated Error:
Nothing specified.

Components:
(1) Tritium; T; [12028-17-8]
(2) Lithium; Li; [7439-93-2]

Original Measurements:
E. Veleckis, J. Nucl. Mater. **79**, 20–27 (1979).

Variables:
Temperature: 869–1118 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

Equilibrium plateau pressures of T gas over the heterogeneous LiT–Li mixture were measured

t/°C	p/Torr	p/Pa[a]
844.4	461.4	61500
820.0	327.9	43710
792.2	221.4	29510
767.6	155.1	20670
742.2	104.3	13900
732.7	90.53	12070
720.7	71.27	9500
710.7	60.51	8066
694.0	46.70	6225
688	41.3	5505[b]
680.5	34.66	4620
667.6	24.39	3251
659.9	20.17	2689
647.6	14.16	1888
636.4	10.17	1356
621.1	6.79	905
616.6	5.92	789
611.0	4.64	659
595.8	3.28	437

[a]Calculated by the compilers.
[b]Monotectic temperature.

The results were reported graphically in Veleckis *et al.*[1] and numerically in Veleckis.[2] They were represented by equations for solid and liquid LiT, respectively:

$$\log(p/\mathrm{Pa}) = 14.228 - 10\,080\ (T/\mathrm{K})^{-1} \quad \text{and} \quad \log(p/\mathrm{Pa}) = 11.210 - 7179\ (T/\mathrm{K})^{-1}$$

The monotectic temperature was estimated from the intersection of the above dependencies at 688 °C (961 K).

Auxiliary Information

Method:
Certain modifications of the apparatus were made to assure safe experiments with radioactive T. A small Li spherule was placed in an Armco Fe capsule. The capsule had thin walls (permeable to gaseous T_2), a thick bottom with a lid connected via a hollow Fe stem and a glass to metal seal, to a closed glass stopcock. The apparatus for the pressure measurements was made of two concentric tubes: the outer one of stainless steel and the inner one of fused silica. The tubes were joined at the top via a graded seal. The capsule was placed in the silica tube, connected to the equilibrium apparatus and for several days evacuated at ~1123 K. The Li reacted with a portion of T_2 to produce 55–70 mol % LiT solution in liquid Li. The equilibrium pressures were measured after more than 4 h of the equilibration. Temperature was measured by means of a Chromel/Alumel thermocouple. Since the solute contained 89.62 mol % T the pressures measured for an isotopic mixture of T, D, and H were corrected to those for pure T based on isotopic composition of the gas phase and an assumption that each component obeys the Raoult's law in the condensed phase.

Source and Purity of Materials:
T: 89.62 mol % pure from Oak Ridge Nat. Lab., contained 1.62 mol % D and 8.67 mol % H. T concentration included 0.96 mol % T in form of tritiated CH_4. 0.6 mol % T decayed to 3He during a 40 day period between the sampling and analysis. T purified by absorption in a hot Ti sponge, evacuation of impurities from the cooled sponge and extraction of T_2 by reheating.
Li: 99.9+% pure from Lithium Corp. of America; purified by dripping of the molten Li from a Ta funnel onto a stainless steel chill plate. The Li spherules contained ~0.02% N and ~0.06% O.

Estimated Error:
Pressure: precision ±1.3 Pa.
Temperature: nothing specified.

References:
[1]E. Veleckis, R. M. Yonco, and V. A. Maroni, *Thermodynamics of Nuclear Materials* (IAEA, Vienna, 1980), pp. 3–30.
[2]E. Veleckis, U.S. Energy Res. Devel. Admin. Rep. ANL-76-106, pp. 5–8 (1976).

3.4. Lithium–Boron

Components:
(1) Boron; B; [7440-42-8]
(2) Lithium; Li; [7439-93-2]

Evaluated by:
Hans Ulrich Borgstedt, Forschungszentrum Karlsruhe, Germany and Cezary Guminski, University of Warsaw, Poland, June 1999

Critical Evaluation

In a review on the Li–B system by Okamoto,[1] no equilibrium phase diagram was proposed, since experimental observations were rich but somewhat unusual,[2–19] and they were not in accordance with general principles of phase diagram construction. Secrist and Childs[13] reported a negligible solubility of B in liquid Li, but their note had only a qualitative character, since an interaction of the melt with the steel container was observed. Although a thermal analysis of the Li–B alloys was performed in several studies,[2–4,8–10,13,14,16] only the maximal temperature values obtained by Marcac[4] may be guessed as those characterizing the quite flat liquidus of the system. These data are scattered as much as ±100 K, and they may reflect a monotectic well. The scatter could be interpreted as a susceptibility of the material samples to both overheating and undercooling. However, one should also remember that some Li–B samples in Marcac[4] were contaminated by Li_3N and LiOH. Since the lowest thermal arrests of the Li-rich alloys were observed around the endothermic melting of pure Li at 453.8 K (five studies[4,8–10,13]), it may be concluded that a solubility of B in liquid Li just above this temperature is certainly lower than 1 mol % B. Adams[14] attempted to measure the solubility of B in liquid Li at 823 K. The saturated solution of B was circulated at this temperature through the capillary tube of the resistivity apparatus for prolonged periods. No significant change in the resistivity was noticed. Thus assuming that detectivity level of the method is $1 \cdot 10^{-9}$ Ω m and B has similar resistivity coefficient as Al, the solubility of B in liquid Li may be estimated as equal or lower than 10^{-2} mol % B at this temperature.

The dissolution reaction of solid B in liquid Li at elevated temperatures was described by Wang[9] and essential stages of this process were confirmed in other studies. In the temperature range 473–573 K, B is inert to molten Li (five studies[4,8–10,14]). In the temperature range 573–723 K, B particles dissolve exothermally in the molten Li to form a metallic liquid solution.[4,8–10] Unexpectedly, between 723 and 773 K, the viscosity of the Li–B melt increases, however, it decreases again, if the temperature is lowered.[9] At about 823 K, the surface of the solid alloy changes from shiny metallic to grayish-white followed by an exothermic and irreversible formation of Li_5B_4[9,11] Li_7B_6,[3,6–8] or LiB.[10] This compound remains solid from room temperature to 1273 K.[9,10] It does not melt above 1273 K[9,10] but loses Li by vaporizing and is transferred to a nonmetallic substance (not free B), probably Li_3B_{14}.[3] It is not yet known whether Li_5B_4 and LiB_3 (formed at higher temperatures) are the equilibrium or metastable phases at temperatures between their formation and the melting point of Li.

Although stoichiometries of many Li–B compounds[1] were proposed in the literature in the B-rich composition range, only the structures of Li_5B_4(Li_7B_6), LiB_3, and Li_3B_{14} were accepted from the crystallographic point of view.[20] Li_2B_{14} (or maybe LiB_6 as found earlier) formed from Li_3B_{14} at ~1200 K is further decomposed to αB at ~1450 K.[3] Other compound compositions found as LiB_4 and LiB_6 in the B-rich range are most probably mixed phases or impurity stabilized forms, since crystals of good quality of Li_5B_4, LiB_3, and Li_3B_{14} may only be obtained at temperatures above 1200 K.[3]

Several authors[5,17,18] observed the formation of compounds LiB_{10-13} at ≈1270 K characterized by the framework of βB. Therefore, they should be treated as solid solutions of Li in B. Concerning the Li-rich composition range a formation of the Li_2B compound was suggested in electrochemical experiments,[6,7] but not confirmed by Sanchez *et al.*[19] The existence of Li_3B (Ref. 11) was not corroborated in later studies.

Meden *et al.*[16] performed exhaustive experiments on the B dissolution in liquid Li at 653–693 K and provided *ab initio* support by means of molecular orbital calculations. They concluded that the formerly postulated existence of LiB_3 in form of solvated clusters, which caused the observation as liquid, should be understood as B particles (~10 μm large) saturated with Li. During cooling and the subsequent crystallization of Li, Li atoms leave easily the B particles to be incorporated into the Li crystal lattice. Above 673 K these particles react with the excess Li to form solid Li_5B_4. Such an explanation is also in agreement with electrochemical investigations[6,7,15,19] of the Li–B composite in which Li behaves very closely to pure Li.

The purity of the materials used in the experiments plays a very important role in the investigations of the B–Li system. The very high purity of both elements is not easily attenable and a subsequent purification is a very complex task. In fact, only Mair *et al.*[4] realized the possible interactions of the container materials with B. At elevated temperatures B reacts effectively with Fe, steels, and Nb (that were mostly used as the containers) but B withstands effectively with Mo; most probably due to a protective layer of Mo boride being compactly formed on the Mo container walls. The same reservations will be valid concerning solubility determinations and thermal analysis experiments which are still needed to clarify all aspects of this intriguing system.

It seems, according to our present knowledge, that some reactions in the Li–B system are very slow, some of them are of metatectic nature, and some compounds exist in limited temperature ranges or form amorphous phases.

Only very doubtful solubility values may be suggested in this situation. The schematic and partial Li–B phase diagram may only be proposed (see Fig. 2).

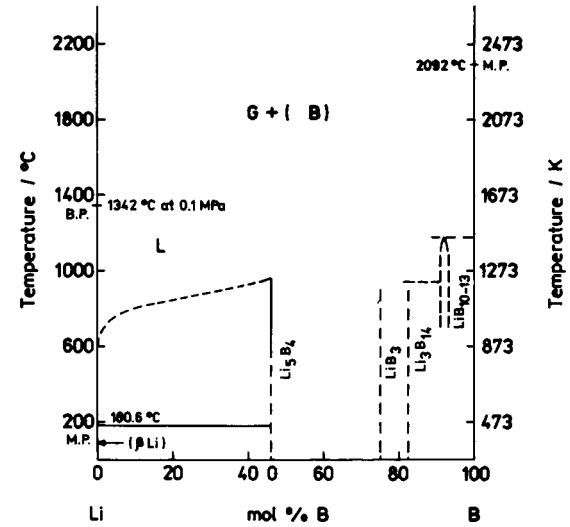

FIG. 2. Li–B schematic phase diagram (partial).

Doubtful values of the solubility of B in liquid Li

T/K	Solubility/mol % B	Source
823	$<10^{-2}$	(14)
1073	~10	(4) interpolation
1173	~33	(4)
1230	~46	(4)

References

[1] H. Okamaoto, Bull. Alloy Phase Diagr. **10**, 230 (1989).
[2] P. Sanchez and C. Belin, Compt. Rend., Ser. II **307**, 2027 (1988).
[3] G. Mair, R. Nesper, and H. G. von Schnering, J. Solid State Chem. **75**, 30 (1988).
[4] T. Marcac, P. Bukovec, and N. Bukovec, Thermochim. Acta **133**, 305 (1988).
[5] D. R. Secrist, J. Am. Ceram. Soc. **50**, 520 (1967).
[6] S. D. James and L. E. DeVries, J. Electrochem. Soc. **123**, 321 (1976).
[7] L. E. DeVries, L. D. Jackson, and S. D. James, J. Electrochem. Soc. **126**, 993 (1979).
[8] S. Dallek, D. W. Ernst, and B. F. Larrick, J Electrochem. Soc. **126**, 866 (1979).
[9] F. E. Wang, Metall. Trans., A **10**, 343 (1979).
[10] V. P. Sorokin, P. I. Gavrilov, and E. V. Levakov, Zh. Neorg. Khim. **22**, 595 (1977); Russ. J. Inorg. Chem. **22**, 329 (1977).
[11] M. A. Mitchell and R. A. Sutula, J. Less-Common Met. **57**, 161 (1978).
[12] D. R. Secrist and W. J. Childs, U.S. Atom. Energy Comm. Rep. TID-17149 (1962).
[13] D. Ernst, J. Electrochem. Soc. **129**, 1513 (1982).
[14] P. F. Adams, Ph.D. thesis, Univ. of Nottingham, UK, 1977; as reported by C.C. Addison, *The Chemistry of the Liquid Alkali Metals* (Wiley, Chichester, 1984), p. 225.
[15] A. Meden, B. Pihlar, and S. Pejovnik, J. Appl. Electrochem. **24**, 78 (1984).
[16] A. Meden, J. Mavri, M. Bele, and S. Pejovnik, J. Phys. Chem. **99**, 4252 (1995).
[17] T. I. Serebryakova, V. I. Lyashenko, and V. D. Levandovskii, Poroshk. Metall. **1/2**, 54 (1994).
[18] M. Kobayashi, I. Higashi, H. Matsuda, and K. Kimura, J. Alloy Compd. **22**, 120 (1995).
[19] P. Sanchez, C. Belin, G. Crepy, and A. De Guibert, J. Mater. Sci. **27**, 240 (1992).
[20] R. Nesper, Progr. Solid State Chem. **20**, 1 (1990).

Components:
(1) Boron; B; [7440-42-8]
(2) Lithium; Li; [7439-93-2]

Original Measurements:
T. Marcac, P. Bukovec, and N. Bukovec, Thermochim. Acta **133**, 305–310 (1988).

Variables:
Temperature: 911–1231 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

A set of differential scanning calorimetry effects was recorded for the B–Li alloys. The results are preliminary and it is not sure whether the maximal temperatures of the thermal arrests correspond to expected liquidus temperatures.

t/°C	Solubility/mol % B	Solid phases identified
900[a], 800[b]	6.0	Li_7B_6, Li, Li_3N
795[a], 802[b]	11.6	Li_7B_6, Li
903[a], 836[b]	33.5	Li_7B_6, Li, Li_3N
766[a], 836[b]	34.7	Li_7B_6, Li, Li_3N, LiOH
638[a], 823[b]	44.0	Li_7B_6, Li_3N, LiOH
958[a], 853[b]	46.0	Li_7B_6, Li, LiOH

[a]Heating curve.
[b]Cooling curve.

The thermal arrests of the melting point of Li were always found at (181±3)°C.

Auxiliary Information

Method:
Samples of the B–Li alloys were prepared from pulverized B and Li foil, pressed together, rolled, and weighed into stainless steel caps. The caps were hermetically sealed and heated at 723 K for 1 h. After cooling, two phases were separated within each sample. The phases were analyzed for their Li content. The differential scanning calorimetry (DSC) curves of both phases were recorded in a commercial equipment up to 1323 K. The solid phases were identified by powder x-ray diffraction.

Source and Purity of Materials:
B: 99.9% pure from Merck.
Li: 99.8% pure from Foote Mineral Co.
Ar: purified during the gas recirculation

Estimated Error:
Solubility: nothing specified; samples were analyzed, but they were not homogeneous.
Temperature: precision between ±3 and ±25 K.

3.5. Lithium–Carbon

Components:
(1) Carbon; C; [7440-44-0]
(2) Lithium; Li; [7439-93-2]

Evaluated by:
Hans Ulrich Borgstedt, Forschungszentrum Karlsruhe, Germany and Cezary Guminski, University of Warsaw, Poland, September, 1999

Critical Evaluation

The first study of the solubility of C in liquid Li was performed by Fedorov and Su[1] using thermal analysis and vapor pressure measurements. They observed significant solubility values, the melting point of pure Li at 448 K (5 K too low value in respect to the contemporary accepted value of 453 K [Okamoto[2]]), and 12 K depression of eutectic at the Li-rich side. The reliability of these results was therefore questioned in several reviews[2–4] and a preference was given to values presented in the subsequent studies. Pulham *et al.*[5] indicated in preliminary analyses that the solubility of C in Li should be <0.5 mol % C at 673 K and the eutectic hardly distinguishable from the melting point of pure Li. Since experimental details in Pulham *et al.*[5] were not sufficiently described, the work is not compiled. Yonco and Homa[6] determined the solubility between 477 and 908 K by analyzing the filtrate with chemical methods. Their results were 3 orders of magnitude lower than those of Fedorov and Su[1] and they were subsequently confirmed by Weston *et al.*[7,8] by cold trapping a Li processing loop.

It was further observed by Pulham *et al.*[5] that C reacts with N, if Li is contaminated by N, leading to the formation of stable Li_2NCN. This fact would explain the drastically overestimated data of Fedorov and Su,[1] who certainly did not use Li of high purity, and their experiments were performed in a contaminated Ar atmosphere. The occurrence of the reaction between C and N in liquid Li medium forced Yonco and Homa[9] to repeat the solubility experiments using still more pure Li and investigating the system after addition of some amounts of N. Their values increased smoothly with temperature from $4\cdot10^{-5}$ mol % N at 493 K to 0.4 mol % N at 1008 K. The presence of N in Li increased the C solubility at temperatures <623 K according to Yonco and Homa,[9] whereas Pulham *et al.*[5] still observed distinct elevation of concentrations of C and N which had been simultaneously dissolved at 673 K. Arnoldov *et al.*[10] equilibrated CO_2 with Li at 573 K for up to 10 h. They observed through chemical analyses and resistivity measurements that Li_2C_2 and Li_2O were finally formed in the liquid metal. The saturating concentration of C was found to be $8\cdot10^{-3}$ mol % C at this temperature. This value is one order of magnitude higher than the C solubility determined by Yonco and Homa.[9] However, one should notice that in Arnoldov *et al.*[10] Li was much more contaminated than in Yonco and Homa.[9] Natesan *et al.*[11] reported that the solubility of C in liquid Li is $4\cdot10^{-2}$ mol % at 473 K; this (much overestimated) value was not supported by experimental facts.

Contemporarily, the best estimate is represented by the solubility equation obtained by Yonco and Homa[9] and tested by the evaluators:

$$\log(\text{soly/mol \% C}) = 3.221 - 3741\ (T/\text{K})^{-1}. \quad (1)$$

The solubility equation presented in Borgstedt,[12] based on the results of Yonco and Homa,[6] is no longer valid.

It was well established in Fedorov and Su,[1] Yonco and Homa,[6] and Yonco and Homa[9] that Li_2C_2 is the solid phase of the solubility equilibrium. Interactions of C and H in liquid Li at 715 K were not detected. C_2H_2 in liquid Li decomposed into Li_2C_2 and LiH, as was concluded from resistivity measurements of Pulham *et al.*[13] Arnoldov *et al.*[10] reported the absence of any interaction in the C–H–N–O–Li system. If C is introduced into Li in form of NaCN, Li_2CO_3, graphite, carbon-black, sucrose or phthalate, it is ultimately converted into Li_2C_2 heating the reagents to ~873 K.[14] The Li_2C_2 content in Li may be analyzed by hydrolysis with quantitative evolution of H_2C_2. Another method[14] of direct combustion of all C-containing forms into CO_2 seems to be less reliable for a qualitative determination of Li_2C_2.

The thermodynamically stable Li_2C_2 may probably exist in two modifications, α-Li_2C_2 and β-Li_2C_2, as it was found by crystal structure analysis.[16,17] The corresponding transition temperature is close to 720 K,[18,19] as found in thermal analyses by Avdeev *et al.*[18] These authors showed that the plenty of thermal arrests observed by Fedorov and Su,[1] thus suggesting an existence of four forms of Li_2C_2, was rather induced by the impurities in the samples investigated. A decomposition pressure of Li_2C_2 does not reach 0.1 MPa until 1823 K.[20]

Shimp *et al.*[21] reported the formation of a series of Li–C compounds in inert solvents by chemical methods. These compounds showed increasing thermal stability in the order Li_4C, Li_4C_2, Li_4C_3 and Li_2C_2: the first three compounds were only stable up to (473–498) K. A number of the C-rich lamellar compounds (LiC_{6-72}) was formed in reactions of liquid or gaseous Li with graphite at up to 673 K, eventually also from graphite and Li powder under pressure of (1.5–2.0) GPa at room temperature.[22] Billaud *et al.*[23] demonstrated reversible electrochemical intercalation of Li into a pyrographite cathode in which LiC_6, LiC_{12}, LiC_{18}, and LiC_{27} were formed, their solubilities in liquid Li were not determined. It is still questionable if these lamellar may be considered as true equilibrium phases. All Li–C mixtures containing 45–98 mol % C were irreversibly transformed into Li_2C_2 during heat treatment between 723 and 1073 K (refer to Refs. 1, 16–19, 22). A transformation of Li_2C_2 to LiC_6 and Li due to cooling below 723 K was never observed. Fischer[24] formulated phase equilibria diagrams for intercalation compounds in the composition range above the C content of LiC_6. The thermal arrests reported by Fedorov and Su[1] were observed in the vicinity of the phase transitions of the Li lamellar compounds.[18,19,24] Further studies are needed to determine the liquidus at higher temperatures and to confirm that Li_2C_2 is the equilibrium solid phase of the Li–C system at temperatures below 723 K.

Though interaction of Li with diamond is still unknown, Li forms series of compounds with the third "allotrope" of C in form of fullerides Li_xC_{60}. On the basis of electrochemical incorporation of Li into a C_{60} electrode, Chabre *et al.*[25] found the stoichiometry coefficient x being 0.5, 2, 3, 4, and 12. Thus, $Li_{12}C_{60}$ should be the equilibrium solid phase with the saturated solution of C_{60} in liquid Li; however, nothing is known so far on the solubilities and stabilities of these interesting phases. The Li–C phase diagram based on Okamoto[2] has therefore only preliminary character (see Fig. 3).[15,23]

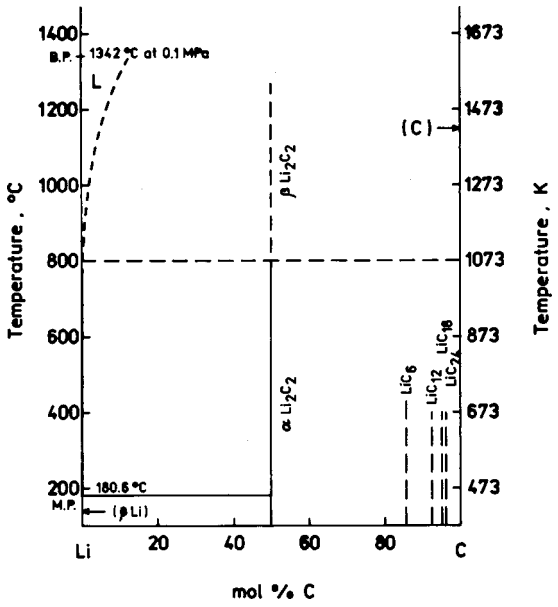

FIG. 3. Li–C phase diagram.

Tentative values of the solubility of C in liquid Li

T/K	Solubility/mol % C	Source
454	$1\cdot10^{-5}$	Eq. (1)
473	$2\cdot10^{-5}$	Eq. (1)
573	$5\cdot10^{-4}$	Eq. (1)
673	$5\cdot10^{-3}$	Eq. (1)
773	$2\cdot10^{-2}$	Eq. (1)
873	$5\cdot10^{-2}$	Eq. (1)
973	$9\cdot10^{-2}$	Eq. (1)

References:

[1]P. I. Fedorov and M. T. Su, Acta Chim. Sinica **23**, 30 (1957).

[2]H. Okamoto, Bull. Alloy Phase Diagr. **10**, 69 (1989).

[3]P. F. Adams, P. Hubberstey, and R. J. Pulham, J. Less-Common Met. **42**, 1 (1975).

[4]E. Veleckis, R. M. Yonco, and V. A. Maroni, *Thermodynamics of Nuclear Materials* (IAEA, Wien, 1980), Vol. 2, p. 3.

[5]R. J. Pulham, P. Hubberstey, M. G. Down, and A. E. Thunder, J. Nucl. Mater. **85–86**, 299 (1979).

[6]R. M. Yonco and M. I. Homa, Trans. Am. Nucl. Soc. **32**, 270 (1979).

[7]J. R. Weston, W. F. Calaway, R. M. Yonco, and V. A. Maroni, U.S. Dept. Energy Rep. CONF-800401-P2, p. 20/1 (1980).

[8]J. R. Weston, W. F. Calaway, R. M. Yonco, J. B. Hines, and V. A. Maroni, Proc. 1979 NACE Conference-Corrosion/79, Nace, Katy, 1979, paper No. 116.

[9]R. M. Yonco and M. I. Homa, J. Nucl. Mater. **138**, 117 (1986).

[10]M. N. Arnoldov, M. N. Ivanovskii, A. D. Pleshivtsev, V. I. Subbotin, and B. A. Shmatko, *Teplofizicheskie Svoistva Zhidkostei*, edited by A. K. Abas-Zade and E. E. Shpil'rain (Nauka, Moskva, 1970), p. 124.

[11]K. Natesan, C. B. Reed, and R. F. Mattas, Fusion Engin. Design **27**, 457 (1995).

[12]H. U. Borgstedt, *Handbook of Thermodynamic and Transport Properties of Alkali Metals*, edited by R. W. Ohse (Blackwell, Oxford, 1985), p. 895.

[13]R. J. Pulham, P. Hubberstey, A. E. Thunder, A. Harper, and A. T. Dadd, U.S. Dept. Energy Rep. CONF-800401-P2, 18/1 (1980).

[14]K. J. Kelly, E. W. Hobart, and R. G. Bjork, U.S. Atom. Energy Comm. Rep. CONF-650411, p. 64; E. W. Hobart and R. G. Bjork, Anal. Chem. **39**, 202 (1967).

[15]J. R. Potts and E. W. Hobart, U.S. Atom. Energy Comm. Rep. TID-7607, p. 120 (1960).

[16]R. Juza and V. Wehle, Naturwissensch. **52**, 537 (1965).

[17]D. R. Secrist and L. G. Wisnyi, Acta Crystallogr. **15**, 1042 (1962).

[18]V. V. Avdeev, A. R. Savchenkova, L. A. Monyakina, I. V. Nikolskaya, and A. V. Khvostov, J. Phys. Chem. Solids **57**, 947 (1996).

[19]A. R. Savchenkova, S. H. Kshnyakina, A. F. Mayorova, S. N. Mudretsova, L. A. Monyakina, and V. V. Ardeev, Neorg. Mater. **33**, 1305 (1997).

[20]C. E. Messer, *The Alkali Metals* (The Chemical Society, London, 1967), p. 183.

[21]L. A. Shimp, J. A. Morrison, J. A. Gurak, J. W. Chinn, and R. J. Lagow, J. Am. Chem. Soc. **103**, 5951 (1981).

[22]D. Guerard and A. Hérold, Carbon **13**, 337 (1975).

[23]D. Billaud, F. X. Henry, and P. Willmann, Mater. Res. Bull. **28**, 477 (1993).

[24]J. E. Fischer, *Chemical Physics of Intercalation*, edited by A. P. Legrand and S. Flandrois (Plenum, New York, 1987), p. 59.

[25]Y. Chabre, D. Djurado, M. Armand, W. R. Romanow, N. Coustel, J. B. McCauley, J. E. Fischer, and A. B. Smith, J. Am. Chem. Soc. **114**, 764 (1992).

Components:
(1) Carbon; C; [7440-44-0]
(2) Lithium; Li; [7439-93-2]

Original Measurements:
P. I. Fedorov and M. T. Su, Acta Chim. Sinica **23**, 30–39 (1957).

Variables:
Temperature: 438–1218 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data
The solubility of C in liquid Li was determined

t/°C	Solubility/mol % C[a]	t/°C	Solubility/mol % C[c]
595	3	945	14
410	2	920	11
407	1.5	880	8
295	1		
215	0.5		
165	0.3[b] eutectic		

[a]From thermal analysis.
[b]From extrapolation.
[c]From vapor pressure measurement.

The melting point of Li was found at 176 °C. Four forms of C_2Li_2 were postulated as the equilibrium solid phases in the temperature ranges: <410 °C, 410–440 °C, 440–560 °C, and >560 °C.

Auxiliary Information

Method:
The apparatus was based on a Fe tube with a Fe cup. C powder was added to Li in an Ar atmosphere; however, a gap between a rubber bung and a Fe stirring rod existed still. Thermal analysis cooling curves were recorded from 1073 K with the use of the Kurnakov's pyrometer. Vapor pressure at high temperatures was measured by an unspecified method. The samples were chemically analyzed after the hydrolytic decomposition. The Li content was determined by alkalimetric titration. The C content by gas analysis of CO_2 evolved after combustion of H_2C_2. The solid phases were identified by x-ray analysis.

Source and Purity of Materials:
C: "pure" graphite powder.
Li: 99.28% pure and contained 0.5% Na, 0.02% K, 0.1% Ca, 0.05% Mg, 0.01% Si, F and <0.001% Cu.
Ar: 98% pure, further purified and dried with absorptive reagents for O and H_2O.

Estimated Error:
Solubility: nothing specified; the melting point of Li was found 5 K lower than the contemporarily accepted value.
Temperature: nothing specified; accuracy not better than ±5 K (compilers).

Components:
(1) Carbon; C; [7440-44-0]
(2) Lithium; Li; [7439-93-2]

Original Measurements:
M. N. Arnoldov, M. N. Ivanovskii, A. D. Pleshivtsev, V. I. Subbotin, and B. A. Shmatko, *Teplofizicheskie Svoistva Zhidkostei*, edited by A. K. Abas-Zade and E. E. Shpil'rain (Nauka, Moskva, 1970), pp. 124–127.

Variables:
One temperature: 573 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data
The solubility of C in liquid Li at 300 °C (573 K) was found to be $1.4 \cdot 10^{-2}$ mass %, or $8 \cdot 10^{-3}$ mol % C (as calculated by the compilers).

It was proved in resistivity measurements that the reaction of CO_2 with liquid Li, though slow, leads to the formation of Li saturated with C and O in corresponding proportion.

Auxiliary Information

Method:
Li was contained in a loop made of the 1Kh18N9T stainless steel, hermetically closed and placed in a thermostat.[1] Portions of CO_2 were introduced into the liquid Li. The reaction reached equilibrium after >6 h. Measurements of the cell resistivity of the Li sample were performed by the "double bridge of constant current"; a change of the resistivity was only 0.02% compared with pure Li. Portions of the liquid Li after equilibration with CO_2 were analyzed by a chemical procedure, details of which were not reported. When Li was purified to a level of $5 \cdot 10^{-5}$ mol % C the portions of CO_2 introduced again did not change the C content ?? dissolved in Li ($8 \cdot 10^{-3}$ mol %) which was therefore taken as its solubility.

Source and Purity of Materials:
C: from CO_2, 99.9% pure (GOST-80-50-56), contained 0.1% H_2O.
Li: containing 0.01% O, N, Ba, $3 \cdot 10^{-3}$ % H, $1 \cdot 10^{-4}$ % C, 0.5% Na, $6 \cdot 10^{-3}$ % Ca, 0.03% Cr, 0.04% Si and $<3 \cdot 10^{-3}$ % Ni, Mn, Al, Be, Mg, Cu, Ti, Fe, Ag (each).

Estimated Error:
Solubility: precision of CO_2 injection ±1 vol %.
Temperature: stability ±0.05 K, accuracy ±1.5 K.

References:
[1]M. N. Ivanovskii, M. N. Arnoldov, B. A. Shmatko, A. D. Pleshivtsev, and S. K. Korotaev, Atom. Energiya **24**, 392–394 (1968).

Components:
(1) Carbon; C; [7440-44-0]
(2) Lithium; Li; [7439-93-2]

Original Measurements:
J. R. Weston, W. F. Calaway, R. M. Yonco, J. B. Hines, and V. A. Maroni, Proc. of the 1979 NACE Conf.-Corrosion/79, Nace, Katy, 1979, paper no 116.

Variables:
Temperature: 532–720 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of C in liquid Li was determined. The values were read from a figure and recalculated to mol % C by the compilers.

T/K	t/°C	Solubility/mass % C	Solubility/mol % C
532	259	$9.5\cdot10^{-4}$	$5.2\cdot10^{-4}$
552	279	$1.50\cdot10^{-3}$	$8.7\cdot10^{-4}$
613	340	$5.5\cdot10^{-3}$	$3.2\cdot10^{-3}$
720	447[a]	$1.30\cdot10^{-3}$	$7.5\cdot10^{-3}$ a

[a]It is not sure that the sample was saturated with C.

The same results were reported in Weston *et al.*[1]

Auxiliary Information

Method:
The study was performed in the Li processing test loop. The loop was constructed from 304 type stainless steel. The extraction of filtered samples from the loop was done using a bayonet contained inside a frit of porosity of 2 μm, all made of 316 type stainless steel. The samples were taken by reducing the Ar pressure inside the bayonet. After its withdrawal, the external surfaces of the bayonet were cleaned to remove adhering Li. The samples were stored in a He-filled glove box. The analyses for the C content were carried out by the C_2H_2 evolution method according to Hobart and Bjork.[2] The sample was hydrolyzed and C_2H_2 analyzed by gas chromatography.

Source and Purity of Materials:
C: nothing specified.
Li: nothing specified.
Ar: nothing specified.
He: nothing specified.

Estimated Error:
Solubility: nothing specified; reading-out procedure ±3%.
Temperature: precision ±2 K; reading-out procedure ±2 K.

References:
[1]J. R. Weston, W. F. Calaway, R. M. Yonco, and V. A. Maroni, U.S. Dept. Energy Rep. CONF-800401-P2, p. 20/1-8 (1980).
[2]E. W. Hobart and R. G. Bjork, Anal. Chem. **39**, 202–204 (1967).

Components:
(1) Carbon; C; [7440-44-0]
(2) Lithium; Li; [7439-93-2]

Original Measurements:
R. M. Yonco and M. I. Homa, Trans. Am. Nucl. Soc. **32**, 270–271 (1979).

Variables:
Temperature: 477–908 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of C in liquid Li was determined. The data were read out from the figure and recalculated to mol % by the compilers.

t/°C	Solubility/mol % C
180[a]	$1.2\cdot10^{-4}$
204	$6.9\cdot10^{-4}$
216	$2.4\cdot10^{-4}$
228	$5.8\cdot10^{-4}$
236	$6.4\cdot10^{-4}$
258	$6.1\cdot10^{-4}$
265	$5.0\cdot10^{-4}$
313	$1.3\cdot10^{-3}$
333	$3.5\cdot10^{-4}$
351	$1.8\cdot10^{-3}$
394	$4.6\cdot10^{-3}$
444	$8.1\cdot10^{-3}$
468	$2.1\cdot10^{-2}$
494	$2.4\cdot10^{-2}$
560	$3.7\cdot10^{-2}$
598	$7.5\cdot10^{-2}$
635	0.162

[a]From extrapolation.

The equilibrium solid phase was found to be C_2Li_2.

Auxiliary Information

Method:
Graphite and Li were held in an Armco Fe vessel under He atmosphere and were equilibrated at selected temperature for 20 h or more. By manipulation of the pressure in the vessel a sample of the solution was taken into a 316 stainless steel closed-end sampling tube through a 2 μm pore size filter. The excess of Li was washed from outside of the sampling tube using H_2O. The tube was returned to a glove box in which the filter was excised and discarded. The rest of the sample was sectioned and placed in a reaction vessel for analysis. The sample was hydrolyzed and titrated with a standard acid. Gases evolved from the solution were dried in H_2SO_4 and analyzed in a gas chromatograph as sum of H_2C_2, H_4C_2, H_6C_2.

Source and Purity of Materials:
C: graphite of spectrographic purity.
Li: 99.8+% pure with low Na content and ~0.13% N.
He: nothing specified.

Estimated Error:
Solubility: standard deviation ranged from 1.7% to 3.1%.
Temperature: nothing specified; reading-out procedure ±3 K.

Components:
(1) Carbon; C; [7440-44-0]
(2) Lithium; Li; [7439-93-2]

Original Measurements:
R. M. Yonco and M. I. Homa, J. Nucl. Mater. **138**, 117–122 (1968).

Variables:
Temperature: 474.3–1008.2 K;
N concentration in Li: $<2.5\cdot10^{-3}$ mol %–0.125 mol %

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The saturation concentration of C in Li was measured and the influence of N present in the solvent was determined

t/°C	Solubility/mass % C	Solubility/mol % C[b]
180.6[c]	···	$1\cdot10^{-5}$[c] eutectic
201.1[a]	$8.6\cdot10^{-5}$	$2.35\cdot10^{-4}$[a]
220.0	$8.6\cdot10^{-5}$	$4.97\cdot10^{-5}$
222.2[a]	$4.05\cdot10^{-4}$	$2.34\cdot10^{-4}$[a]
241.4[a]	$5.18\cdot10^{-4}$	$2.99\cdot10^{-4}$[a]
269.2[a]	$9.32\cdot10^{-4}$	$5.39\cdot10^{-4}$[a]
293.0	$8.49\cdot10^{-4}$	$4.91\cdot10^{-4}$
271.4	$3.46\cdot10^{-4}$	$2.00\cdot10^{-4}$
327.6	$2.00\cdot10^{-3}$	$1.16\cdot10^{-3}$
400.6	$4.93\cdot10^{-3}$	$2.85\cdot10^{-3}$
419.7	$9.05\cdot10^{-3}$	$5.23\cdot10^{-3}$
438.8	$1.77\cdot10^{-2}$	$1.02\cdot10^{-2}$
467.3	$3.12\cdot10^{-2}$	$1.80\cdot10^{-2}$
489.4	$3.73\cdot10^{-2}$	$2.16\cdot10^{-2}$
546.8	$6.66\cdot10^{-2}$	$3.85\cdot10^{-2}$
582.5	0.119	$6.88\cdot10^{-2}$
688.1	0.464	0.268
612.0	0.142	$8.21\cdot10^{-2}$
735.0	0.696	0.403

[a]N concentration in Li of 0.125 mol %.
[b]Calculated by the compilers.
[c]Estimated from extrapolation.

The equilibrium solid phase is C_2Li_2.

Auxiliary Information

Method:
Li, held in an Armco Fe vessel, was saturated with C. The solution was stirred for 24 h at each equilibration temperature before sampling. N was added to Li in form of Li_3N. The sampling was carried out with the use of a tube containing a 2 μm pore size frit, all made of 316 L stainless steel. The samples filtered into the tube were cooled down and H_2O was slowly added in a special apparatus. The resulting LiOH was titrated with a standard acid. The evolved gas was then purged from rapidly stirred solution by a He stream and trapped in a collection loop. The collected gas was analyzed in a gas chromatograph. The sum of C_2H_2, C_2H_4, and C_2H_6 was taken into account in the recalculation of the C content.

Source and Purity of Materials:
C: graphite of spectrographic purity grade.
Li: 99.8+% pure from Lithium Corp. of America, contained <0.05% Na, gettered with Y turnings for 6 days at ~1073 K.
Li_3N: nothing specified.
He: "purified".
H_2O: free of CO_2.

Estimated Error:
Solubility: precision ±7% at a confidence level of 95%.
Temperature: nothing specified.

Components:
(1) Dilithium cyanamide; Li_2NCN; [51677-22-6]
(2) Lithium; Li; [7439-93-2]

Evaluated by:
Hans Ulrich Borgstedt, Forschungszentrum Karlsruhe, Germany and Cezary Guminski, University of Warsaw, Poland, October 1993

Critical Evaluation

C and N, when introduced into Li medium, react with formation of sparingly soluble Li_2NCN. Although the mechanism of this reaction is not completely known and the formation of intermediate forms was postulated,[1] the final product of the reaction in equilibrium conditions is the same, independently of either C being introduced to N dissolved in Li or the opposite. The solid Li_2NCN was isolated from the Li solution by evaporation of Li solvent and its structural properties were studied by x-ray analysis.[2–4] It was shown in separate investigations that Li_2NCN is the most stable compound of the family of Li–C–N combinations. $LiNCN_4$, LiCN, and even LiHNCN dissociate in liquid Li forming Li_2NCN.[1,5]

The solubility of Li_2NCN in liquid Li was estimated by the evaluators from the reaction courses followed by electrical resistivity technique by Hubberstey *et al.*[5–8] As was shown in Hubberstey *et al.*,[5] only the dissolved species may change the resistivity of liquid Li solution. Therefore, Li_2NCN may be either in crystalline form or completely dissociated form in the liquid phase according to the following equation:

$$Li_2NCN(c)\leftrightarrow C(l)+2N(l)+2Li(l). \quad (1)$$

The first set of experiments was performed by addition of C to a solution of N in Li at 673 K.[3,4] The calculated solubility was found to be 0.16 mol % Li_2NCN. In the second set of experiments N was introduced to Li containing C at 750 K.[4–6] The solubility calculated was then found to be 0.07 mol % Li_2NCN.

It does not seem to be a real effect that the solubility values decrease with temperature. In the first experimental set the titration curve of N solution with C had untypical shape. Probably, the reaction rate was very slow in such conditions or an intermediate product of different stoichiometry was formed inbetween.[1] Therefore, we suggest the result from the second set of experiments be regarded as tentative, since the titration curve of C in Li by N addition does not show any complications as in the first case. The selected value in this evaluation is in agreement with the prediction of Migge[9] that the solubility of Li_2NCN should be between the solubility of C (0.015 mol %) and the solubility of N (3.1 mol %) in liquid Li at 750 K.

The tentative value of the solubility of Li_2NCN in liquid lithium is 0.07 mol % at 750 K.

References

[1]C. C. Addison, *The Chemistry of the Liquid Alkali Metals* (Wiley, Chichester, 1984), p. 179.
[2]R. J. Pulham, P. Hubberstey, M. G. Down, and A. E. Thunder, J. Nucl. Mater. **85–86**, 299 (1979).
[3]M. G. Down, M. J. Haley, P. Hubberstey, R. J. Pulham, and A. E. Thunder, J. Chem. Soc., Chem. Commun. 52 (1978).
[4]J. R. Weston, W. F. Calaway, R. M. Yonco, J. B. Hines, and V. A. Maroni, Proceedings 1979 NACE Conference—Corrosion/79, NACE, Katy, 1979, p. 11/6.
[5]P. Hubberstey, A. Harper, A. T. Dadd, D. J. Knight, and K. Maughan, U.S. Dept. Energy Rep. CONF-800401-P2, p. 18/27 (1980).
[6]R. J. Pulham, P. Hubberstey, A. E. Thunder, A. Harper, and A. T. Dadd, U.S. Dept. Energy Rep. CONF-800401-P2, p. 18/1 (1981).
[7]R. J. Pulham and P. Hubberstey, J. Nucl. Mater. **115**, 239 (1983).
[8]P. Hubberstey, Liq. Met. Engin. Technol., BNES, London, **2**, 85 (1984).
[9]H. Migge, U.S. Dept. Energy Rep. CONF-800401-P2, p. 18/9 (1980).

Components:
(1) Dilithium cyanamide; Li_2NCN; [51677-22-6]
(2) Lithium; Li; [7439-93-2]

Original Measurements:
R. J. Pulham, P. Hubberstey, M. G. Down, and A. E. Thunder, J. Nucl. Mater. **85–86**, 299–303 (1979).

Variables:
Temperature: 673 and 750 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

Li_3N dissolved in liquid Li reacts with Li_2C_2 to form Li_2NCN, which crystallizes in the resulting solution. The reaction product was identified by x-ray analysis after Li evaporation. The compilers made a tentative solubility estimation of this compound, assuming that a dissolved part of Li_2NCN dissociates completely in the liquid Li medium according to the reaction:

$$Li_2NCN(c) \leftrightarrow C(l) + 2N(l) + 2Li(l). \quad (1)$$

Since the resistivity of Li containing N and C is proportional to their concentrations, the total resistivity change of Li ($\Delta\rho_t$) being in equilibrium conditions at stoichiometric ratio is to be equal to the sum of resistivity coefficients ($d\rho/dx$) multiplied by corresponding mol % fractions of the components (x):

$$\Delta\rho_t = x \cdot d\rho_C/dx + 2x \cdot d\rho_N/dx. \quad (2)$$

Equation (2) was solved for two cases. The addition of C to the N solution (0.82 mol %) resulted in the resistivity of the heterogeneous solution at stoichiometric ratio at 673 K of $2.2 \cdot 10^{-8}$ Ω m as was read out from the figure. The $d\rho_N/dx$ is $7.0 \cdot 10^{-8}$ Ω m(mol %)$^{-1}$. Due to the very small C solubility at this temperature ($6 \cdot 10^{-3}$ mol % C) and an unknown value of $d\rho_C/dx$, the first term on the right hand in Eq. (2) is assumed to be zero. Solution of Eq. (2) leads to x value of 0.16 mol % which is the solubility of Li_3N in liquid Li at 673 K.

The addition of N at 750 K to the heterogeneous solution of C (0.32 mol %) changed the resistivity of the resulting solution to the constant value around the stoichiometric point of $1.1 \cdot 10^{-8}$ Ω m (Pulham and Hubberstey[2]). The $d\rho_N/dx$ is then $7.3 \cdot 10^{-8}$ Ω m (mol %)$^{-1}$ and the term concerning C in Eq. (2) has again been neglected. Solution of Eq. (2) leads to the value of Li_2NCN solubility in liquid Li of 0.07 mol % at 750 K.

Auxiliary Information

Method:
The method of preparation of solutions of N in liquid Li was probably the same as in Hubberstey and Dadd.[1] C was added in portions to the N solution or aliquots of gaseous N were absorbed by heterogeneous solutions of C. The resistivity of the resulting solutions was measured in an apparatus made of stainless steel. The metallic solution was held in a reservoir attached to a loop of capillary across which the resistance was measured by a Wheatstone bridge. An electromagnetic pump made circulation of the solution through the capillary. The apparatus was enclosed in an oven through which air was forced. All operations were performed in an Ar atmosphere.

Source and Purity of Materials:
C: "elemental", no longer specified.
N: probably as in Hubberstey and Dadd,[1] 99.98% pure, further "purified".
Li: probably as in Hubberstey and Dadd,[1] 99.98% pure, further purified by gettering with Y sponge at 673 K for 72 h.
Ar: 99.99% pure from Air Products, further "purified".

Estimated Error:
Solubility: precision ±20% (by the compilers).
Temperature: nothing specified.

References:
[1]P. Hubberstey and A. T. Dadd, J. Phys. Colloque C8 **41**, 531–534 (1980).
[2]R. J. Pulham and P. Hubberstey, J. Nucl. Mater. **115**, 239–250 (1983).

3.6 Lithium–Silicon

Components:
(1) Silicon; Si; [7440-21-3]
(2) Lithium; Li; [7439-93-2]

Evaluated by:
Hans Ulrich Borgstedt, Forschungszentrum Karlsruhe, Germany and Cezary Guminski, University of Warsaw, Poland, July 1999

Critical Evaluation

The solubility of Si in liquid Li below 700 K was determined by Fedorov and Yoffe[1] and Dadd and Hubberstey.[2,3] The results from both investigations show rough agreement. The values found by Hubberstey[2,3] were obtained in equilibrium conditions using precise resistivity measurements and purer chemicals; therefore they are preferred. The authors proposed a solubility equation (tested by the evaluators):

$$\log(\text{soly/mol \% Si}) = 4.408 - 2941\ (T/\text{K})^{-1}, \quad (1)$$

which is valid up to 700 K.

The liquidus line above 700 K was investigated in several papers.[1,4–9] The authors[1,4–8] struggled with compatibility problems, since the Si–Li melts were quite aggressive to Mo, Fe, Ni, steels, Ti–Zr–Mo alloy, and alumina containers. SiC (Pell[5]), Ta and W (van der Marel *et al.*[9]) were found to be the most resistive materials for such investigations. Therefore, the liquidus data reported by van der Marel *et al.*[9] seems to be the mostly recommended for the Si-richer alloys. Although most of the liquidus data are scattered within a band of ±20 K the results of Jesseman *et al.*[4] in the Li-rich range and of van der Marel *et al.*[9] in the Si-rich range deviate for 200–300 K. The liquidus line characterizing the Si-rich alloys was predicted by models of the regular solution[5] and the subregular solution.[10] The liquidus line was also thermodynamically assessed by Braga *et al.*,[11] who did not come to perfect agreement with experiments. These calculations showed very good agreement with the extrapolated results of van der Marel *et al.*,[9] whereas the data of Böhm[6] and Obinata *et al.*[7] are placed at much higher and at much lower temperatures, respectively. A solubility of Li in solid Si does not exceed 0.014 mol % Li at 860 K (Fuller[12]).

In a review on the Si–Li system, Okamoto[10] accepted the existence of four Si–Li compounds: Si_5Li_{22} (peritectically formed), Si_4Li_{13} (congruently formed), Si_3Li_7 (congruently formed), and Si_7Li_{12} (peritectically formed) treating other formula proposed in the literature as questionable. Nesper and von Schnering[13] corrected the formula of Si_5Li_{22} to Si_5Li_{21} . Evers *et al.*[14] discovered that SiLi, easily formed at high pressure, is also stable at normal pressure. However, kinetics of its formation in this case is extremely slow. SiLi is thermodynamically unstable above 743 K. Nesper, and von Schnering[13] persisted on the formation of $SiLi_2$ and Migge[16] constructed the Si–Li phase diagram with syntectic formation of Si_7Li_{12} and peritectic formation of the three other accepted compounds. The Si–Li phase diagram (see Fig. 4), is a compromise of the most reliable experimental results.

In the case of contamination of the system by N, a formation of hardly soluble Li_5SiN_3 (Dadd and Hubberstey[17]) was observed.[15]

Tentative values of the solubility of Si in liquid Li

T/K	Solubility/mol % Si	Source
473	0.015	Eq. (1)
573	0.20	(3)
673	1.1	Eq. (1)
773	5	(1),(6)
873	14	(1),(6),(7)
896	16 peritectic	(6),(7) interpolation
973	21	(8),(9)
995	23.5 congruent	(1),(7),(9) mean value
980	26 eutectic	(9)
1025	30 congruent	(9)
865	43 eutectic	(5),(9)
1073	52	(9) extrapolation

Both metals are completely miscible at >1687 K at constrained pressure sufficient to keep Li as liquid.

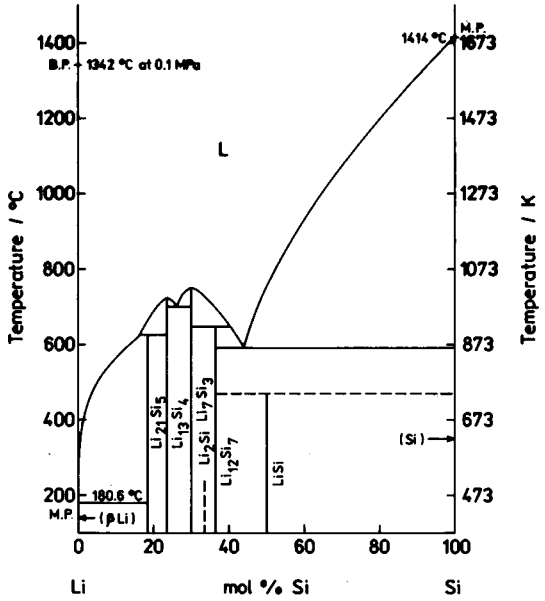

FIG. 4. Li–Si phase diagram.

References

[1]P. I. Fedorov and A. A. Yoffe, Izv. Vyssh. Ucheb. Zaved., Tsvet. Metall. **6**, 127 (1961).
[2]P. Hubberstey and A. T. Dadd, J. Phys. Colloque C8 **41**, 531 (1980).
[3]A. T. Dadd and P. Hubberstey, J. Chem. Soc., Faraday Trans. I **77**, 1865 (1981).
[4]D. S. Jesseman, G. D. Roben, A. L. Grunewald, W. S. Fleshman, K. Anderson, and V. P. Calkins, U.S. Atom. Energy. Comm. Rep. NEPA-1465 (1950).
[5]E. M. Pell, J. Phys. Chem. Solids **3**, 77 (1957).
[6]H. Böhm, Z. Metallk. **50**, 44 (1959).
[7]I. Obinata, Y. Takeuchi, K. Kurihara, and M. Watanabe, Metall **19**, 21 (1965).
[8]R. A. Sharma and R. N. Seefurth, J. Electrochem. Soc. **123**, 1763 (1976).
[9]C. Van der Marel, G. J. B. Vinke, and W. van der Lugt, Solid State Commun. **11**, 917 (1985).
[10]H. Okamoto, Bull. Alloy Phase Diagr. **11**, 306 (1990).
[11]M. H. Braga, L. F. Malheiros, and I. Ansara, J. Phase Equil. **16**, 324 (1955).
[12]C. S. Fuller, Chem. Rev. **59**, 63 (1959).
[13]R. Nesper and H. G. von Schnering, J. Solid State Chem. **70**, 48 (1987).
[14]J. Evers, G. Oehlinger, and G. Sextl, Angew. Chem. **105**, 1532 (1993).
[15]V. V. Pavlyuk, V. K. Pecharskii, and O. I. Vodak, Dopov. Akad. Nauk Ukr. SSR, Ser. B **2**, 50 (1989).
[16]H. Migge, J. Nucl. Mater. **151**, 101 (1988).
[17]A. T. Dadd and P. Hubberstey, J. Chem. Soc., Dalton Trans. 2175 (1982).

Components:
(1) Silicon; Si; [7440-21-3]
(2) Lithium; Li; [7439-93-2]

Original Measurements:
D. S. Jesseman, G. D. Roben, A. L. Grunewald, W. S. Fleshman, K. Anderson, and V. P. Calkins, U.S. Atom. Energy Comm. Rep. NEPA-1465 (1950).

Variables:
Temperature: 950 and 1216 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of Si in liquid Li was determined

t/°F	T/K[a]	Solubility/mass % Si	Solubility/mol % Si[b]
1250	950	14.43; 13.41	3.84
1730	1216	61.2; 54.9	25.5

[a]Calculated by the compilers.
[b]Mean values calculated by the compilers.

The Si samples disintegrated completely in liquid Li, while a formation of new phases occurred.

Auxiliary Information

Method:
Armco Fe capsules were used for the determinations. Si lumps were placed in the capsules and Li was added in an Ar atmosphere. After welding, the capsules were heated in a vacuum furnace on stainless steel plates characterized by an average temperature. The equilibration was continued for 24 h, then the furnace core was air cooled. The capsules were weighed and opened. The samples of the solidified Li with Si were leached out with H_2O. Si remaining undissolved was removed with the capsule, dried, and weighed as the tare to determine the amount of Li present in the capsule. The leached material was filtered, and the residue analyzed spectrographically for its Si content.

Source and Purity of Materials:
Si: nothing specified.
Li: contained 0.24% O, <0.02% N, <0.005% Na; however, the loading operation could introduce additional amounts of N and O.
H_2O: on distilled.
Ar: nothing specified.

Estimated Error:
Solubility: precision ±5% (by the compilers).
Temperature: stability ±20 K.

Components:
(1) Silicon; Si; [7440-21-3]
(2) Lithium; Li; [7439-93-2]

Original Measurements:
E. M. Pell, J. Phys. Chem. Solids **3**, 77–81 (1957).

Variables:
Temperature: 863–1023 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data
Several points on the Si–Li liquidus were determined

t/°C	Solubility/mol % Si
720	20
750	33.3
590	42 eutectic

The author calculated the liquidus line, between the eutectic and the melting point of Si (1409 °C), using the regular solution concept. The $SiLi_4$ equilibrium solid phase was identified by x-ray analysis.

Auxiliary Information

Method:
The alloys were prepared and investigated in a SiC or sapphire crucible encapsulated in a Mo container in a He atmosphere. The elements were mixed in proper amounts and melted. After the melting the sample was cooled down while recording the corresponding curve with the use of a Pt/Pt–Rh(10%) thermocouple. The composition of the samples was confirmed by chemical and x-ray analyses.

Source and Purity of Materials:
Si: probably of very high purity, surface cleaned.
Li: nothing specified, surface cleaned.
He: nothing specified.

Estimated Error:
Solubility: precision ±5 mol % for the eutectic, but much better for other samples.
Temperature: precision ±10 K; accuracy ±4 K.

Components:
(1) Silicon; Si; [7440-21-3]
(2) Lithium; Li; [7439-93-2]

Original Measurements:
H. Böhm, Z. Metallk. **50**, 44–46 (1959).

Variables:
Temperature: 768–1623 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data
The liquidus line of the Si–Li system was determined

t/°C	Solubility/mol % Si
495	5.1
540	8.0
565	11.5
580	13.1
595	14.9
630	18.6
633	19.2 peritectic
675	20.5
679	21.1
720	26.2
718	27.0
740	28.7
740	29.6
745	31.5
751	32.4
752	33.4 congruent
745	34.4
735	35.5
730	36.6
710	37.7
675	38.8
650	39.4
715	40.1
968	49.7
1260	69.0
1350	82.4

The melting points of Si and Li were found at 1412 and 179 °C, respectively. The two solid phases being in equilibrium with the saturated solutions were identified as Si_4Li_{15} and $SiLi_2$.

Auxiliary Information

Method:
The alloys were prepared in a Fe crucible by heating weighed pieces of the elements at ~1080 K for 10 min in an Ar atmosphere. Thermal analysis of the alloys was performed. A Fe crucible was used for the Li-rich alloys and a C crucible for the Si-rich alloys. A shielding tube for a thermocouple was made of Fe for Li-rich alloys and of sintercorundum for Si-rich alloys. After triple remelting of a sample in the same crucible a Fe content in the Si–Li melt was never higher than 0.3 mass % Fe. The Li content in the samples was analyzed by flame photometry in the Metallgesellschaft AG, Frankfurt.

Source and Purity of Materials:
Si: 99.24% pure.
Li: >99.0% pure with 0.5% alkali+alkaline earth metals, 0.1% N and 0.01% Cl.
Ar: nothing specified.

Estimated Error:
Solubility: precision ±2%.
Temperature: precision between ±2 and ±5 K.

Components:
(1) Silicon; Si; [7440-21-3]
(2) Lithium; Li; [7439-93-2]

Original Measurements:
P. I. Fedorov and A. A. Yoffe, Izv. Vyssh. Ucheb. Zaved., Tsvet. Metall. **6**, 127–131 (1961).

Variables:
Temperature: 507–1031 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data
A part of the Si–Li liquidus was determined

t/°C	Solubility/mol % Si
234	0.2
281	0.5
288	0.8
318	1.0
354	1.3
370	1.5
413	2.0
443	2.7
481	4.2
511	5.8
544	7.6
561	9.6
578	11.7
595	14.1
620	16.8
650	18.3
693	19.8
705	21.5
710	23.2
727	27.0
758	31.5

The melting point of Li was found at 185 °C.

Auxiliary Information

Method:
The alloys were prepared and thermally analyzed in crucibles made of Fe (with low C content). The temperature was measured with the use of the Pt/Pt–Rh thermocouple in the Kurnakov's pyrometer. The alloys containing 5.8, 9.6, 14.1, 19.8, 23.2, and 31.5 mol % Si were prepared from 99.99% pure Si and 99.8% pure Li. The alloys were analyzed for their Li contents after their decomposition with H_2O and subsequent titration with HCl. The Si content was found after decomposition of the alloys with C_2H_5OH and the resulted SiO_2 was gravimetrically analyzed. The results of the investigation using elements of different purity were received at the same temperature levels.

Source and Purity of Materials:
Si: 98.5% pure with Fe, Al, and Ca as main impurities or 99.99% pure.
Li: 98.5% pure and contained 0.8% Na, 0.2% K, Mg or 99.8% pure.
Ar: purified from traces of N and O by an unknown method.

Estimated Error:
Solubility: nothing specified.
Temperature: precision ±3 K; the melting point of Li was 4 K higher than the contemporarily accepted value.

Components:
(1) Silicon; Si; [7440-21-3]
(2) Lithium; Li; [7439-93-2]

Original Measurements:
I. Obinata, Y. Takeuchi, K. Kurihara, and M. Watanabe, Metall **19**, 21–35 (1965).

Variables:
Temperature: 758–1063 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data
A part of the Si–Li liquidus was determined

t/°C	Solubility/mass % Si	Solubility/mol % Si[a]
485	20	5.8
530	30	9.6
600	40	14
710	50	20
730	55	23
745	60	27
760	67	33.4 congruent
723	70	37
651	72	39 eutectic
695	78	47
735	80	50
760	82	53
790	85	58

[a]Calculated by the compilers.

The melting point of Li was found at 180 °C. The formation of $SiLi_2$ and $SiLi_4$ was confirmed in these studies, but the existence of $SiLi_3$ was put in question.

Auxiliary Information

Method:
The Si–Li alloys were prepared by tungsten arc melting in a Cu mould under an Ar atmosphere. The procedure was repeated many times to reach homogeneous samples. Thermal analysis of the samples was performed in a steel container after equilibration at selected temperature. The alloys were heated only up to 1100 K and the most Si-rich alloys were not investigated in order to prevent an appreciable interaction between steel container and Si. The composition of the samples was confirmed by chemical analysis after a decomposition of the samples with H_2O.

Source and Purity of Materials:
Si: 99.4% pure, contained 0.24% Fe, 0.21% Ca, 0.18% Al, 0.02% Mn, 0.005% P.
Li: 99.9% pure.
Ar: nothing specified.

Estimated Error:
Solubility: precision ±1.0%.
Temperature: precision better than ±5 K.

Components:
(1) Silicon; Si; [7440-21-3]
(2) Lithium; Li; [7439-93-2]

Original Measurements:
R. A. Sharma and R. N. Seefurth, J. Electrochem. Soc. **123**, 1763–1768 (1976).

Variables:
Temperature: 891–976 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data
Several points on the Si–Li liquidus were determined

T/K	Solubility/mol % Si
891	15.5
906	18.5
976	23.5
908	40 eutectic

The existence of the following equilibrium solid phases in the system was reported: $SiLi_2$, Si_8Li_{21}, Si_4Li_{15} (melting peritectically at 976 K) and Si_5Li_{22} (melting peritectically at 891 K).

Auxiliary Information

Method:
Mixtures of Si and Li were melted in a Ni container, cooled to room temperature and ground to a fine powder. It was further annealed at 775 K, cooled slowly to room temperature, and reground. A small portion of the powder was sealed in a small, specially designed Ni container closed nearly gas tight with a threaded cap. Differential thermal analyses of the samples were performed. All operations were performed in an inert gas atmosphere. The solid alloys were analyzed by x-ray diffraction. The temperature was measured by means of Chromel/Alumel thermocouples. The compositions of the solid phases were estimated from potentiometric studies of the cell: Li(l)LiCl–KCl eutectic\Si–Li(s).

Source and Purity of Materials:
Si: 99.999% pure in form of powder.
Li: 99.97% pure.

Estimated Error:
Solubility: nothing specified.
Temperature: precision between ±3 and ±8 K.

Components:
(1) Silicon; Si; [7440-21-3]
(2) Lithium; Li; [7439-93-2]

Original Measurements:
A. T. Dadd and P. Hubberstey, J. Chem. Soc., Faraday Trans. I **77**, 1865–1870 (1981).

Variables:
Temperature: 498–702 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data
The solubility of Si in liquid Li was determined

T/K	Solubility/mol % Si
498	0.04
530	0.07
550	0.11
561	0.14
572	0.19
574	0.20
592	0.28
608	0.37
614	0.40
632	0.53
639	0.60
650	0.72
680	1.17
702	1.65

A solubility equation for temperatures up to 700 K was proposed by the authors, also published in Hubberstey and Dadd,[1] and was tested by the compilers:

$$\log(\text{soly/mol \% Si}) = 4.408 - 2941(T/\text{K})^{-1}.$$

Auxiliary Information

Method:
The alloys were prepared from appropriately weighed amounts of both metals under Ar atmosphere. The apparatus was made of stainless steel. The resistance of the liquid alloy column was measured by means of a Wheatstone bridge. The resistance of a selected alloy was monitored as a function of temperature. The discontinuity in the resistivity versus temperature data corresponds to the Si solubility level. The temperature was measured with the use of a Chromel/Alumel thermocouple.

Source and Purity of Materials:
Si: 99.999% pure from Koch Light.
Li: 99.98% pure from Koch Light, further purified by gettering with Y sponge at 673 K for 72 h.
Ar: 99.99% pure from Air Products.

Estimated Error:
Solubility: nothing specified; precision of a few % (by the compilers).
Temperature: precision ±0.5 K.

References:
[1]P. Hubberstey and A. T. Dadd, J. Phys., Colloque C8 **41**, 531–534 (1980).

Components:
(1) Silicon; Si; [7440-21-3]
(2) Lithium; Li; [7439-93-2]

Original Measurements:
C. Van der Marel, G. J. B. Vinke, and W. Van der Lugt, Solid State Commun. **11**, 917–919 (1985).

Variables:
Temperature: 818–1038 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

Liquidus points on the partial Si–Li phase diagram were determined. They were read out from the figure by the compilers.

t/°C	Solubility/mol % Si
545	10.0
587	15.0
659	18.5
692	19.3
712	21.7
723	23.5
717	25.0
709	26.6
739	27.9
752	28.9
751	30.0
738	32.9
723	33.9[a]
683	36.9
676	37.6
643	38.9
615	41.1
606	42.0
596	43.3
624	44.1
674	45.0
722	47.4
765	50.0

[a]Obtained in the same laboratory by means of resistivity measurements.[1]

The existence of solid Si_4Li_{13} and Si_3Li_7, both melting congruently, was confirmed.

Auxiliary Information

Method:
The alloys were prepared in a W crucible inside a He glove box. The elements were melted at 1023 K and quenched on a Cu plate. After compatibility studies of the liquid Si–Li alloys with AISI 304 stainless steel, Ni, Ta, W, alumina, Ti–Zr–Mo alloy, only Ta and W were found to be resistive to corrosion by the Si–Li melt. The quenched alloy was placed in a Ta inner crucible, fitted tightly in a stainless steel crucible as supplied with the differential scanning calorimetric commercial equipment. The samples were heated (1 K/min) up to 1073 K and cooled down with the same rate.

Source and Purity of Materials:
Si: 99.99% pure from Alfa Ventron Inc..
Li: 99.9+% pure from Koch Light Inc., remelted and only internal fraction used.
He: "high purity."

Estimated Error:
Solubility: nothing specified; reading-out procedure ±0.2 mol %.
Temperature: accuracy ±2 K; reading-out procedure ±1 K; accuracy in resistivity measurements ±3 K.

References:
[1]J. A. Meijer, Univ. of Groningen, Netherland (private communication to the authors).

Components:
(1) Lithium silicon nitride; Li_5SiN_3; [67181-65-1]
(2) Lithium; Li; [7439-93-2]

Original Measurements:
A. T. Dadd and P. Hubberstey, J. Chem. Soc., Dalton Trans. 2175–2179 (1982).

Variables:
Temperature: 723 and 750 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

An interaction of Si and N, present simultaneously in liquid Li, results in the formation of solid Li_5SiN_3, as confirmed by x-ray analysis after vacuum distillation of Li excess from the product. A solubility estimation in this ternary system was done by the compilers assuming that Li_5SiN_3 precipitates in liquid Li and that a part of crystalline Li_5SiN_3 being dissolved in Li dissociates completely according to equation:

$$Li_5SiN_3 \leftrightarrow Si(l) + 3N(l) + 5Li(l). \quad (1)$$

Since the measured resistivities of the solutions of Si and N in liquid Li are proportional to their concentrations, the total change of the resistivity of Li ($\Delta\rho_t$) containing both Si and N in stoichiometric ratio should be equal to sum of resistivity coefficients ($d\rho/dx$) multiplied by corresponding mol % fractions of the components (x). An addition of Si to N solution (1.67 mol % N) as well as an addition of N to Si solution (0.50 or 1.65 mol % Si) leads to practically the same total resistivity value at the stoichiometric point (minimum at the resistivity versus concentration dependence).

$$\Delta\rho_t = x \cdot d\rho_{Si}/dx + 3 \cdot x \cdot d\rho_N/dx. \quad (2)$$

Equation (2) was solved for $\Delta\rho_t = 0.71 \cdot 10^{-8}$ Ω m (mean value read from the figures), $d\rho_{Si}/dx = 10.7 \cdot 10^{-8}$ Ω m (mol %)$^{-1}$, and $d\rho_N/dx = 7.3 \cdot 10^{-8}$ Ω m (mol %)$^{-1}$. The resulting concentration of Si equal 0.022 mol % is the solubility of Li_5SiN_3 at 750 K.

Similar calculations were performed for the analogical experiments reported in Pulham and Hubberstey[2] at 723 K. The total resistivity at stoichiometric point was read from the figure to be $0.36 \cdot 10^{-8}$ Ω m and the resistivity coefficients were $10.6 \cdot 10^{-8}$ and $7.2 \cdot 10^{-8}$ Ω m (mol %)$^{-1}$ for Si and N, respectively. The calculated solubility of Li_5SiN_3 was then 0.01 mol %. The results at both temperatures seem to be reliable. Due to the incomplete resistivity–titration curve, it is difficult to evaluate the primary result reported in Hubberstey and Dadd.[1]

Auxiliary Information

Method:
A solution of Si in liquid Li was prepared from weighed portions of the elements in an Ar atmosphere. A solution of N in liquid Li was prepared by exposing a series of small volumes of N gas to the liquid Li. The ternary solutions were obtained by mixing or by addition of the third component to the binary solutions. The apparatus used for the resistivity studies was made of the AISI 321 stainless steel. It contained a cylindrical reservoir, two independent capillary loops attached to the bottom part of the vessel. The resistivity was monitored continuously during the liquid metal circulation. To avoid interaction with the steel constituents the samples were equilibrated for 200 h in the apparatus and the concentrations of the elements were permanently monitored.

Source and Purity of Materials:
Si: 99.999% pure from Koch Light.
N: 99.98% pure from Air Products, further "purified."
Li: 99.98% pure from Koch Light, further purified by gettering with Y sponge at 673 K for 72 h.
Ar: 99.99% pure from Air Products, further "purified."

Estimated Error:
Solubility: precision ±30% (by the compilers).
Temperature: nothing specified.

References:
[1]P. Hubberstey and A. T. Dadd, J. Phys., Colloque C8 **41**, 531–534 (1980).
[2]R. J. Pulham and P. Hubberstey, J. Nucl. Mater. **115**, 239–250 (1983).

3.7. Lithium–Germanium

Components:
(1) Germanium; Ge; [7440-56-4]
(2) Lithium; Li; [7439-93-2]

Evaluated by:
Hans Ulrich Borgstedt, Forschungszentrum Karlsruhe, Germany and Cezary Guminski, University of Warsaw, Poland, July 1999

Critical Evaluation

The solubility of Ge in liquid Li was determined by Fedorov and Molochko[1] and Hubberstey and Dadd.[2,3] The results of both studies show rough agreement only at temperatures below 600 K. At higher temperatures the discrepancy increases and at 827 K[2,3] found a five times higher Ge content in the saturated solution than it had been determined by Fedorov and Molochko.[1] The solubility data of Fedorov and Molochko[1] fit well to some liquidus points reported by Pell,[4] however, the melting points of the alloys with 18.5 mol % Ge of Hubberstey and Dadd[3] and 20 mol % Ge of Pell[4] differ about 90 K, certainly a too high increase for such small difference of compositions.

Van der Marel *et al.*[5,6] performed magnetic resonance investigations of the liquid alloys between 18 and 75 mol % Ge at a temperature of 1073 K and between 15 and 55 mol % Ge at temperatures of 800–1100 K in the neighborhood of the liquidus temperatures of the system. They mentioned that an appearance of a solid Ge–Li solid phase was reflected in their measurements; corresponding liquidus data were, however, not reported therein. Nevertheless, this information demonstrates that the liquidus temperatures of Pell[4] at 20–33 mol % Ge are overestimated and the liquidus line of Fedorov and Molochko[1] at Ge-richer alloy compositions is also placed at too high temperatures. Nesper,[7] who did not give experimental details, reported the melting points of the Ge–Li intermetallic compounds with the highest value of 1000 K for Ge_4Li_{13}. Johnson *et al.*[8] performed thermal analysis of an alloy containing 20.0 mol % Ge and established the liquidus point at 963 K. These findings are in general agreement with the results of Hubberstey and Dadd[2,3] and Van der Marel *et al.*;[5,6] they disagree, however, with the data of Fedorov and Molochko[1] and Pell.[4]

Since Hubberstey and Dadd[2,3] used the most pure substances, and the system investigated was in equilibrium conditions during the resistometric measurements, the evaluators give a preference to these results. Up to 715 K the solubilities of Ge in liquid Li may be calculated from the following fitting equation which was based on the data of Hubberstey and Dadd:[2,3]

$$\log(\text{soly/mol \% Ge}) = 4.370 - 2878\ (T/\text{K})^{-1}. \quad (1)$$

The evaluators tested the equation. No influence of N present in liquid Li on the Ge–Li solubility equilibria was noticed.[2]

Phase relations of the Ge–Li system need further studies to determine precisely the liquidus and temperature ranges of existence of the solid equilibrium phases. The maximum solid solubility of Li in Ge is 0.13 mol % Li at 800 K.[9] The phase diagram reported in Drits and Zusman[10] is unfortunately erroneous, since a part of the quoted temperatures was incorrectly transformed from other original papers. The Ge–Li phase diagram in Massalski[11] is quite incomplete. According to the most recent crystallographic studies,[7,12] the following solid phases in the system are fixed: $Ge_{12}Li_7$ formed in peritectic reaction at 730 K, GeLi melting congruently at 760 K, Ge_7Li_{12} formed peritectically at 730 K, Ge_4Li_9 formed peritectically at 960 K, Ge_3Li_7 melting congruently at 990 K, Ge_4Li_{13} melting congruently at 1000 K, Ge_4Li_{15} melting congruently at 940 K, and Ge_5Li_{21} melting congruently at 860 K.[7] Pavlyuk *et al.*[12] reported Ge_2Li_7 and Ge_5Li_{22} instead of Ge_4Li_{13} and Ge_5Li_{21}, respectively. It seems impossible that the phases Ge_4Li_{13}, Ge_4Li_{15}, and Ge_5Li_{21}, situated very near to each other, all melt congruently at so many different temperatures. Therefore, it is more rational to assume that Ge_4Li_{15} and Ge_5Li_{21} phases are peritectically formed. The Ge–Li phase diagram, being a modification of one presented by Sangster and Pelton,[13] is proposed in Fig. 5; it has only provisional character.

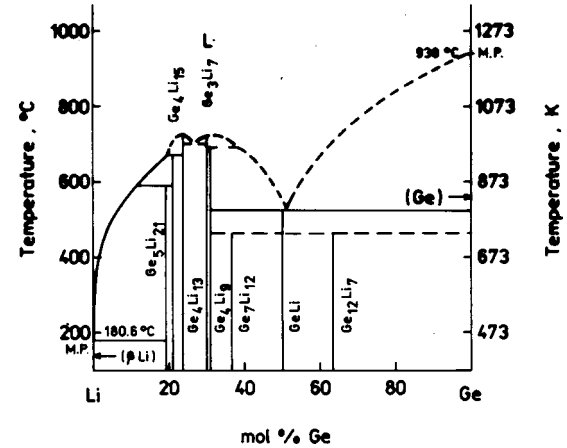

FIG. 5. Li–Ge phase diagram (provisional).

Tentative values of the solubility of Ge in liquid Li

T/K	Solubility/mol % Ge	Source
453.6	0.012 eutectic	(3), Eq. (1)
473	0.019	Eq.(1)
573	0.22	(3), Eq.(1)
673	1.24	(3)
773	5.1	(3)
873	13	(3) interpolated
934	18.5 peritectic?	(3)
963	20	(8)

The elements are completely miscible at >1212 K.

References

[1]P. I. Fedorov and V. A. Molochko, Izv. Akad. Nauk SSSR, Neorg. Mater. **2**, 1870 (1966).
[2]P. Hubberstey and A. T. Dadd, J. Phys., Colloque C8 **41**, 531 (1980).
[3]A. T. Dadd and P. Hubberstey, J. Chem. Soc., Faraday Trans. I **77**, 1865 (1981).
[4]E. M. Pell, J. Phys. Chem. Solids **3**, 74 (1957).
[5]C. Van der Marel, A. B. Van Oosten, W. Geertsma, and W. Van der Lugt, J. Phys., F **12**, 1129 (1982).
[6]C. Van der Marel, P. Heitjans, H. Ackermann, B. Bader, P. Freilander, A. Schirmer, and H. J. Stockmann, Z. Phys. Chem., N. F. **156**, 629 (1988).
[7]R. Nesper, Progr. Solid State Chem. **20**, 1 (1990).
[8]O. Johnson, G. S. Smith, and D. Wood, Acta Crystalolgr. **18**, 131 (1965).
[9]C. S. Fuller, Chem. Rev. **59**, 63 (1959).
[10]M. E. Drits and L. L. Zusman, *Splavy Shchelochnykh i Shchelochnozemlenykh Metallov* (Metallurgiya, Moskva, 1986), p. 76.
[11]*Binary Alloy Phase Diagrams*, edited by T. B. Massalski (American Society Materials, Materials Park, 1990), p. 1958.
[12]V. V. Pavlyuk, V. K. Pecharskii, and O. I. Bodak, Dopov. Akad. Nauk Ukr. SSR, Ser. B **2**, 50 (1989).
[13]J. Sangster and A. D. Pelton, J. Phase Equil. **18**, 289 (1997).

Components:
(1) Germanium; Ge; [7440-56-4]
(2) Lithium; Li; [7439-93-2]

Original Measurements:
E. M. Pell, J. Phys. Chem. Solids **3**, 74–76 (1957).

Variables:
Temperature: 798–1073 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data
Several points on the Ge–Li liquidus were determined

t/°C	Solubility/mol % Ge
750	20
800	25 congruent
730	33.3
525	49 eutectic

The liquidus line between the eutectic and the melting point of Ge (937 °C) was calculated from the regular solution concept. The equilibrium solid phases $GeLi_4$ and $GeLi_3$ were identified.

Auxiliary Information

Method:
The alloys were prepared and investigated in a SiC crucible encapsulated in a closed container made of Mo under He atmosphere. The elements were mixed in proper proportions. After their melting the sample was cooled while a thermal analysis curve was recorded by means of Pt/Pt–Rh(10%) thermocouple. The composition of the samples was confirmed by chemical and x-ray analyses.

Source and Purity of Materials:
Ge: probably of high purity, surface cleaned.
Li: nothing specified, surface cleaned.
He: nothing specified.

Estimated Error:
Solubility: precision ±5 mol % for the eutectic but much better for other samples.
Temperature: precision ±10 K; accuracy ±4 K.

Components:
(1) Germanium; Ge; [7440-56-4]
(2) Lithium; Li; [7439-93-2]

Original Measurements:
Q. Johnson, G. S. Smith, and D. Wood, Acta Crystallogr. **18**, 131–132 (1965).

Variables:
One temperature: 963 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data
The liquidus point at 20.0 mol % Ge was determined at 630 °C (or 963 K, as recalculated by the compilers). The authors found further thermal arrests with this sample at 667, 655, and 567 °C. The alloy consisted of two phases: Ge_4Li_{15} and Ge_5Li_{22}.

Auxiliary Information

Method:
4.82 g Li and 12.60 g Ge were placed in a cleaned Ta crucible. A lid of the crucible, which contained a thermocouple well was welded in place. The closed crucible was put into a DTA furnace, which could be rocked to stir the melt. A cooling curve was recorded from 1219 K within 0.5 h. All essential operations were performed in an Ar atmosphere. The solid phases were investigated by x-ray diffraction.

Source and Purity of Materials:
Ge: spectroscopically pure.
Li: 99.9% pure (reactor grade).
Ar: nothing specified.

Estimated Error:
Solubility: accuracy ±0.5% in the preparation step.
Temperature: precision ±2 K.

Components:
(1) Germanium; Ge; [7440-56-4]
(2) Lithium; Li; [7439-93-2]

Original Measurements:
P. I. Fedorov and V. A. Molochko, Izv. Akad. Nauk SSSR, Neorg. Mater. **2**, 1870–1871 (1966).

Variables:
Temperature: 541–1158 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data
The liquidus line of the Ge–Li system was determined

t/°C	Solubility/mol % Ge
268	0.21
304	0.24
368	0.35
440	0.41
460	0.64
488	0.82
504	0.99
524	1.17
544	1.52
572	1.67
600	2.33
638	2.91
644	3.28
652	3.76
662	4.50
684	42.0
628	47.0
528	50.0
680	56.0
720	60.0
805	69.0
848	76.0
865	85.0
885	91.0

The melting points of Ge and Li were found to be 934 and 186 °C, respectively. The existence of Ge_5Li_{22} and Ge_4Li_{15} was confirmed and additionally the compound $GeLi_2$ was identified by x-ray diffraction.

Auxiliary Information

Method:
The Ge–Li alloys were prepared in a Fe crucible (in the composition range of 0–4.5 mol % Ge) or graphitized corundum (in the composition range 42–100 mol % Ge) in an Ar atmosphere. After melting the alloys, they were cooled in the Kurnakov's pyrometer while recording cooling curves by means of a Pt/Pt–Rh thermocouple. Some samples were chemically analyzed to confirm the composition.

Source and Purity of Materials:
Ge: 99.99% pure.
Li: designed as Le-1, made in USSR.
Ar: nothing specified.

Estimated Error:
Solubility: nothing specified.
Temperature: precision better than ±3 K; the melting point of Li is 5 K too high.

Components:
(1) Germanium; Ge; [7440-56-4]
(2) Lithium; Li; [7439-93-2]

Original Measurements:
A. T. Dadd and P. Hubberstey, J. Chem. Soc., Faraday Trans. I **77**, 1865–1870 (1981).

Variables:
Temperature: 453.6–934 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data
The solubility of Ge in liquid Li was determined

T/K	Solubility/mol % Ge
453.6	0.012[a]
531	0.09
566	0.19
581	0.27
599	0.38
615	0.47
626	0.60
649	0.84
658	0.94
934	18.5[a]
661	1.03
674	1.24
676	1.34
680	1.42
680	1.48
693	1.60
703	1.79
700	1.79
716	2.22
728	2.75
739	3.16
749	3.71
759	4.19
767	4.64
769	5.06
786	5.83
809	7.29
827	8.72

[a]From thermal analysis.

A solubility equation valid up to 715 K was proposed by the authors and was tested by the compilers:

$$(\log \text{soly/mol \% Ge}) = 4.370 - 2878\ (T/\text{K})^{-1}.$$

The Ge_5Li_{22} equilibrium solid phase was identified by x-ray diffraction experiments. The data were also reported in Hubberstey and Dadd.[1]

Auxiliary Information

Method:
The alloys were prepared by weighing proper amounts of both metals and their mixing under Ar. The apparatus was made of stainless steel. A Wheatstone bridge was used to measure the resistance of the liquid alloy column. The resistance of a selected alloy was monitored as a function of temperature. A discontinuity in the resistivity–temperature data corresponded to the solubility level. The temperature was measured using a Chromel/Alumel thermocouple. Details concerning thermal analysis were not reported.

Source and Purity of Materials:
Ge: 99.999% pure from Koch Light.
Li: 99.98% pure from Koch Light, further purified by gettering with Y sponge at 673 K for 72 h.
Ar: 99.99% pure from Air Products.

Estimated Error:
Solubility: nothing specified; precision a few % (by the compilers).
Temperature: precision ±0.1 K at 454 K and ±0.5 K at 573 K; thermal analysis ±5 K.

References:
[1]P. Hubberstey and A. T. Dadd, J. Phys., Colloque C8 **41**, 531–534 (1980).

3.8. Lithium–Nitrogen

Components:
(1) Nitrogen; N; [7727-37-9]
(2) Lithium; Li; [7439-93-2]

Evaluated by:
Hans Ulrich Borgstedt, Forschungszentrum Karlsruhe, Germany and Cezary Guminski, University of Warsaw, Poland, September 1999

Critical Evaluation

Gaseous N reacts easily with liquid Li with the formation of stoichiometric solid Li_3N. The equilibrium between solid Li_3N and its saturated solution in the liquid Li is established at least in hours (depending on temperature). A partial pressure of N_2 over the Li_3N at its melting point should be of the order of 10^2 Pa;[1] thus practically the concentration of N in liquid Li is not diminished by N evaporation from the melt.

Bolshakov *et al.*[2] employed thermal analysis to determine the Li-rich part of the N–Li liquidus line up to the melting point of Li_3N. Hoffman[3,4] determined a solubility of Li_3N in liquid Li between 523 and 723 K using chemical analysis of the saturated solution filtrate. Arnoldov *et al.*[5,6] measured the electrical resistance of the Li_3N solutions to determine the solubility at 524–591 K. Adams *et al.*[7] used the same method for measurements performed between 473 and 723 K. Chemical analysis of the saturated solution samples was used by Yonco *et al.*[8] to determine the solubilities at 453–714 K. Weston *et al.*[9] measured the electrical resistance of a solution containing 0.3 mol % N during the decreasing of the temperature, and they found the onset of the crystallization of Li_3N at 540 K. Cheburkov and Rozanov[10] investigated the kinetics of the reaction between gaseous N and liquid Li at 568 K; they claimed to confirm Hoffmann's results,[3,4] but they did not report numerical values. Natesan *et al.*[11] reported a solubility of 0.19 mol % N at 473 K, but they did not inform on the experimental background.

The solubility values obtained by Adams *et al.*,[7] Yonco *et al.*,[8] and Weston *et al.*[9] are in excellent agreement within the experimental errors. The solubility results obtained in Hoffman[3,4] and Arnoldov *et al.*,[5,6] although being in mutual agreement between 523 and 591 K, are a few times lower and do not show any smooth temperature dependence in comparison with the selected data of Adams *et al.*[7] and Yonco *et al.*[8] It seems that N could react with the steel container used or a contamination of the system by C could lead to a decrease of the equilibrium concentration of N as quoted in Hoffman[3] and Arnoldov *et al.*[5] The liquidus data of Bolshakov *et al.*[2] above 800 K fit acceptably well to the solubility values of Adams *et al.*[7] and Yonco *et al.*,[8] but at lower temperatures the solubility values of Bolshakov *et al.*[2] seem to be slightly overestimated, probably due to an undercooling susceptibility of the system observed by Arnoldov *et al.*[5] The quite flat liquidus line near the Li_3N composition could indicate a tendency to liquid immiscibility of predominantly ionic Li_3N and metallic Li.[12]

The recommended solubility equation is derived by the compilers from the combined results of Yonco *et al.*[8] and Weston *et al.*:[9]

$$\log(\text{sol}y/\text{mol \% N}) = 3.246 - 2072(T/\text{K})^{-1} \quad (1)$$

valid up to 800 K with an uncertainty of ±3%. Very similar fitting equations have been published in reviews.[12–15] The equation proposed in Adams *et al.*,[16] as based on unreliable data of Hoffman[3,4] and Arnoldov *et al.*[5,6] is not valid.

The eutectic temperature recorded by Bolshakov *et al.*[2] at 366 K is undoubtedly erroneous concerning so low solubility values determined. Weatherford *et al.*[17,18] made observations of the lowering of the freezing point due to an addition of N into Li. They reported a repeatable temperature drop of 0.17–0.22 K at a N concentration of $(3-4)\cdot 10^{-3}$ mol % which presumably corresponded to the eutectic composition. The compositions of the samples were calculated from an unexplained, empirical formula and the melting point of pure Li was measured at 454.9 K, thus the result[18] has quite relative character. The temperature of 453.7 K was quoted as the melting point of Li in another report of the same laboratory.[17] In preliminary experiments, Creffield *et al.*[19] noticed that Li saturated with N showed a lowering of the melting point of 0.4 K; no eutectic composition was specified. Detailed measurements of the Li freezing point depression by N addition were performed by Hubberstey *et al.*[20] with the use of thermal analysis. These authors found the eutectic at 453.39 K and 0.070 mol % N; however, the melting point of Li measured in this work was 0.11 K below the contemporarily accepted value of 453.8 K.[12] Several thermal analysis measurements performed by Yonco *et al.*[8] pointed on the eutectic temperature arrests at 453.5 K; the corresponding eutectic composition was calculated to be 0.05 mol % N. The eutectic composition calculated from the recommended Eq. (1) gives a value of 0.048 mol % N and from the van't Hoff relation of 0.053 mol % N at 453.5 K. The initial slope of the liquidus in Hubberstey *et al.*[20] is practically nil. The corresponding eutectic composition is too high, although the temperature difference of the Li melting point and the eutectic point of 0.3 K seems to be accurate. The thermocouple applied by Hubberstey *et al.*[20] was perhaps improperly calibrated. However, an additional self-correction by Hubberstey[21] brought a quite rational explanation of his results in Hubberstey *et al.*[20] The stainless steel reaction vessel could slowly leach a limited amount of Li_3N (the thermal arrests at concentrations up to 0.022 mol % N were practically constant) to form a surface layer of poorly soluble Li_9CrN_5 (Cr from the steel container) and a further addition of Li_3N made the corresponding depression of the N–Li liquidus till the eutectic point was reached. Thus the liquidus curve obtained by Hubberstey *et al.*[20] should be moved to the left for 0.022 mol % N and up for 0.11 K to be in agreement with Yonco *et al.*[8] An earlier explanation of Hubberstey *et al.*[20] that solid Li dissolves as much as 0.024 mol % N at the eutectic temperature is much less probable.

As it was mentioned above, the N solubility in liquid Li may be influenced by the presence of C or Cr in the system. However, one should remember that plenty of the transition metals,[21,23] alkaline earth metals (Hubberstey and Roberts[24]) and Si (Addison[22]) interact with N with the formation of ternary and binary nitrides which may influence the N–Li solubility equilibria. The transition metals and Si decrease the apparent N solubility, the alkaline earth metals cause, however, an increase of the solubility. An interaction found by Arnoldov *et al.*[6] in the Li–Na–N system causing a decrease of the N solubility after adding up to 1 mol % Na into the Li–N solution is an apparent phenomenon, since such a reaction has no thermodynamic justification. Li_3N is much more stable than Na_3N. The added Na may contain C as well as metallic impurities which may interact with N as in pure Li as solute. The effectivity of the purification of the Li–Na alloy was not tested in Arnoldov *et al.*[6] The introduction of up to 28 mol % Li into the Na–N system increased the solubility of N spectacularly; see the corresponding data sheet for the Na–N–Li system.[25]

Interactions of N with either O or H in liquid Li were never detected either in experimental[6,26] or in theoretical studies;[27] besides Li_3N, Li_2O, and LiH are also present. A simultaneous presence of C, H, N, and O in liquid Li does not indicate mutual interactions between the dissolved elements.[6]

The melting point of Li_3N was measured to be: 1113–1118 K,[28,29] 1088 K,[2] and 1086 K.[8,30] The latter value is selected as it is the most precise determination. The phase diagram of the N–Li system, shown in Fig. 6, is partially known. The second compound in this system, LiN_3 prepared by chemical reactions, does not melt under normal pressure, but decomposes gradually between 388 and 571 K.[12] Therefore, the liquidus line and phase relations between 25% and 100% N could not be sketched.

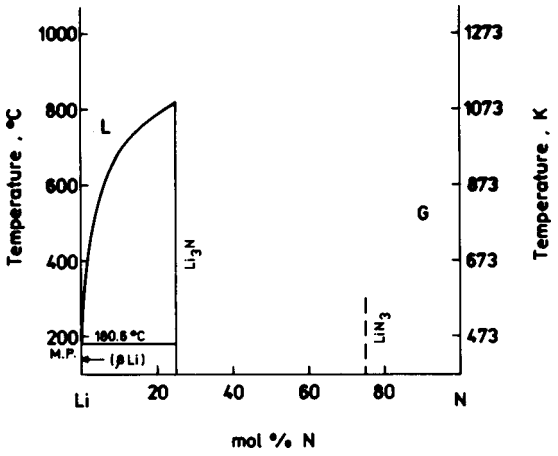

FIG. 6. Li–N phase diagram (partial).

Recommended (r) and tentative (t) solubility values of N in liquid Li

T/K	Solubility/mol % N	Source
453.5	0.05 (t) eutectic	(8), Eq. (1)
473	0.075 (t)	(8), Eq. (1)
523	0.20 (r)	(7) and (8) mean value, Eq. (1)
573	0.44 (t)	Eq. (1)
623	0.85 (t)	(7), Eq. (1)
673	1.5 (t)	(7), Eq. (1)
773	3.7 (t)	(2)
873	6 (t)	(2) interpolation
973	11 (t)	(2) interpolation
1073	21 (t)	(2)
1086	25.0 (r)	(2), (8), (9)

References

[1]H. Kimura, M. Asano, and K. Kubo, J. Nucl. Mater. **91**, 200 (1980).
[2]K. A. Bolshakov, P. I. Fedorov, and L. A. Stepina, Izv. Vyssh. Ucheb. Zaved., Tsvet. Metall. **4**, 52 (1959).
[3]E. E. Hoffman, *Newer Metals* (American Society Testing Materials, Philadelphia, PA, 1960), p. 195.
[4]E. E. Hoffman, U.S. Atom. Energy Comm. Rep. ORNL-2894 (1960).
[5]M. N. Arnoldov, M. N. Ivanovskii, and B. A. Shmatko, Teplofiz. Vys. Temp. **5**, 381 (1967).
[6]M. N. Arnoldov, M. N. Ivanovskii, A. D. Pleshivtsev, V. I. Subbotin, and B. A. Shmatko, *Teplofizicheskie Svoistva Zhidkostei*, edited by A. K. Abas-Zade and E. E. Shpil'rain (Nauka, Moskva, 1970), p. 124.
[7]P. F. Adams, M. G. Down, P. Hubberstey, and R. J. Pulham, J. Less-Common Met. **42**, 325 (1975).

[8]R. M. Yonco, E. Veleckis, and V. A. Maroni, J. Nucl. Mater. **57**, 317 (1975).
[9]J. R. Weston, W. F. Calaway, R. M. Yonco, J. B. Hines, and V. A. Maroni, Proceedings 1979 NACE Conference—Corrosion/79, NACE, Katy, 1979, paper no. 116.
[10]V. I. Cheburkov and A. N. Rozanov, Metall. Metalloved. Chist. Met. **7**, 168 (1968).
[11]K. Natesan, C. B. Reed, and R. F. Mattas, Fusion Engin. Design **27**, 457 (1995).
[12]J. Sangster and A. B. Pelton, J. Phase Equil. **13**, 291 (1992).
[13]E. Veleckis, R. M. Yonco, and V. A. Maroni, Intern. Atom. Energy Agen. Rep. SM-236/56 (1979).
[14]P. Hubberstey, A. T. Dadd, and P. G. Roberts, *Material Behavior and Physical Chemistry in Liquid Metal Systems*, edited by H. U. Borgstedt (Plenum, New York, 1982), p. 445.
[15]N. Rumbaut, F. Casteels, and M. Brabers, *Material Behavior and Physiscal Chemistry in Liquid Metal Systems*, edited by H. U. Borgstedt (Plenum, New York, 1982), p. 437.
[16]P. F. Adams, P. Hubberstey, and R. J. Pulham, J. Less-Common Met. **42**, 1 (1975).
[17]R. H. Herald and W. D. Weatherford, IEEE Trans. Aerospace **AS-1**(2), 1182 (1963).
[18]W. D. Weatherford, R. K. Johnston, M. L. Valtierra, and J. W. Rhoades, U.S. Atom. Energy Comm. Rep. ASD-TDR-63-413 (1963).
[19]G. K. Creffield, M. G. Down, and R. J. Pulham, J. Chem. Soc., Dalton Trans., 2325 (1974).
[20]P. Hubberstey, R. J. Pulham, and A. E. Thunder, J. Chem. Soc., Faraday Trans. I **72**, 431 (1976).
[21]P. Hubberstey, Liq. Met. Engin. Technol., BNES, London **2**, 85 (1984).
[22]C. C. Addison, *The Chemistry of the Liquid Alkali Metals* (Wiley, Chichester, 1984), pp. 66, 187.
[23]H. U. Borgstedt and C. Guminski, *Metals in Liquid Alkali Metals, Part I: Be to Os.; Part II: Co to Bi*, IUPAC Solubility Data Series, Vols. 63&64 (Oxford University Press, Oxford, 1996).
[24]P. Hubberstey and P. G. Roberts, *Liquid Metals Systems*, edited by H. U. Borgsted and G. Frees (Plenum, New York, 1995), p. 331.
[25]C. C. Addison and B. M. Davies, J. Chem. Soc. A, 1827 (1969).
[26]P. Hubberstey, A. Harper, A. T. Dadd, D. J. Knight, and K. Maughan, U.S. Dept. of Energy Rep. CONF-800401-P2, 18/27 (1980).
[27]H. Migge, U.S. Dept. of Energy Rep. CONF-800401-P2, 18/9 (1980).
[28]F. W. Dafert and R. Miklauz, Monatsh. Chem. **31**, 981 (1910).
[29]E. Zintl and G. Brauer, Z. Elektrochem. **41**, 102 (1935).
[30]D. W. Osborne and H. E. Flotow, J. Chem. Thermodyn. **10**, 675 (1978).

Components:
(1) Nitrogen; N; [7727-37-9]
(2) Lithium; Li; [7439-93-2]

Original Measurements:
K. A. Bolshakov, P. I. Fedorov, and L. A. Stepina, Izv. Vyssh. Ucheb. Zaved., Tsvet. Metall. **4**, 52–53 (1959).

Variables:
Temperature: 620–1088 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The liquidus of the Li_3N–Li system was determined. The data were read out and recalculated to mol % by the compilers.

t/°C	Solubility/mol % Li_3N	Solubility/mol % N
347	7	1.4
429	12	2.4
499	19	3.7
551	24	4.9
637	34	6.9
660	39	8.5
680	44	10.1
717	55	12.2
733	61	13.6
741	65	15.0
764	75	17.4
787	84	19.8
800	88	21.2
813	92	22.4
811	96	23.9
815	100	25.0

The melting point of Li was found at 185 °C.

Auxiliary Information

Method:
Li_3N was prepared by the reaction of Li with gaseous N at room temperature in a cooled container. The alloys were prepared by melting Li_3N and Li. They were chemically analyzed for their N content by an unspecified method ''used for N analysis in steels.'' The alloys were introduced into a Fe crucible and thermally analyzed by recording cooling curves with the Kurnakov's pyrometer.

Source and Purity of Materials:
N: purified from O traces.
Li: 97.85% pure and contained 0.26% K, 0.24% Na, 0.16% Mg, and 0.2% Si.
Ar: purified from O, N, and H_2O.

Estimated Error:
Solubility: nothing specified; reading-out procedure ±0.5 mol % (by the compilers).
Temperature: nothing specified; reading-out procedure ±5 K; the melting point of Li was at 4 K too high.

Components:
(1) Nitrogen; N; [7727-37-9]
(2) Lithium; Li; [7439-93-2]

Original Measurements:
E. E. Hoffman, *Newer Metals* (American Society Testing Materials, Philadelphia, PA, 1960), pp. 195–206.

Variables:
Temperature: 523–723 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of N in liquid Li was determined

t/°C	Solubility/mass % N[a]	Solubility/mol % N
250	0.04	0.02
300	0.16	0.08
350	1.19	0.59
400	1.21	0.61
450	1.31	0.65

[a]Every result is average of four determinations at the selected temperature.

Li_3N was found as the equilibrium solute. The same results were reported in Hoffman.[1]

Auxiliary Information

Method:
The solubility experiments were conducted in a sampling apparatus made of stainless steel. For each determination a sufficient amount of Li_3N was added into Li to get an N content of the bath to 5 mass %. Samples of the saturated Li were taken by forcing the Li through a 20 μm stainless steel filter after allowing the system to equilibrate at the sampling temperature for 24 h. The container was pressurized with Ar, forcing Li into a sampling tube. The samples were quenched after removal of the tube from a furnace. The tube was cut, sectioned, and submitted to chemical analysis.[2] The sample was dissolved in H_2O. The evolved NH_3 was absorbed in a solution of H_3BO_3 and determined by the conventional Nessler's method. The alkaline solution of $K_2[HgI_4]$ makes a red complex with NH_3 .

Source and Purity of Materials:
Li_3N: 99.9% pure; prepared by passing N gas over Li which was held in a Ta boat inside a stainless steel container at 1073 K.
Li: "high purity", contained $(6-33)\cdot 10^{-2}$ % N and $(3.9-19.8)\cdot 10^{-2}$ % O, further gettered by Ti sponge at 1073 K for 24 h to a level of $3.8\cdot 10^{-2}$ % N and $7\cdot 10^{-2}$ % O.
Ar: nothing specified.

Estimated Error:
Solubility: nothing specified.
Temperature: nothing specified.

References:
[1]E. E. Hoffman, U.S. Atom. Energy Comm. Rep. ORNL-2894 (1960).
[2]T. W. Gilbert, A. S. Meyer, and J. C. White, Anal. Chem. **29**, 1627–1630 (1957).

Components:
(1) Nitrogen; N; [7727-37-9]
(2) Lithium; Li; [7439-93-2]

Original Measurements:
W. D. Weatherford, R. K. Johnston, M. L. Valtierra, and J. W. Rhoades, U.S. Atom. Energy Comm. Rep. ASD-TDR-63-413 (1963).

Variables:
Temperature: difference of ~0.2 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The melting point of reactor grade Li was determined at 359.2 °F (454.9 K as calculated by the compilers). The melting point depression was recorded after subsequent addition of N into liquid Li. At the beginning even 4 °F difference was recorded but in the repeatable heating-cooling cycles the depression approached the level of 358.8–358.9 °F. The depression of the melting point, corresponding to the eutectic temperature, is 0.3–0.4 °F (0.17–0.22 K as calculated by the compilers). The authors calculated compositions of the melts from the empirical formula, the origin of which was not explained:

$$T/°F = (C_N/10^{-4}\ \text{mass}\ \% + 0.88/10^{-4}\ \text{mass}\ \%)/198.$$

Thus, the composition of the eutectic was estimated to be $(6-8)\cdot 10^{-3}$ mass % N or $(3-4)\cdot 10^{-3}$ mol % N as calculated by the compilers. The solid solubility of N in Li was estimated to be $2\cdot 10^{-3}$ mass % N ($1\cdot 10^{-3}$ mol % N as calculated by the compilers).

The same solubility equation was published in Herald and Weatherford.[1]

Auxiliary Information

Method:
The apparatus for the determination was made of 316 stainless steel. It was placed in a furnace and a Li sample was equilibrated at selected temperatures above the melting point. The apparatus was removed from the furnace and allowed to cool rapidly, while the sample temperature was monitored by an immersed thermocouple. The thermocouple was calibrated on the melting points of Sn, Zn, Al, and Cu. The sample was reheated and recooled within ±28 K in respect to the melting point. The consecutive curves were recorded. A portion of N in gaseous form reacted with Li and the melting point determinations were repeated in the same way. The solutions were equilibrated at 594–627 K. The N content in bulk Li was found by the Kjeldahl's method.

Source and Purity of Materials:
N: nothing specified.
Li: 99.98% pure (reactor grade).
Ar: 99.996% pure, further purified by bubbling through Na–K(78%) melt.

Estimated Error:
Solubility: nothing specified; precision ±20% (by the compilers).
Temperature: nothing specified; precision ±0.05 K (by the compilers).

References:
[1]R. H. Herald and W. D. Weatherford, IEEE Trans. Aerospace **AS-1**(2), 1182 (1963).

Components:
(1) Nitrogen; N; [7727-37-9]
(2) Lithium; Li; [7439-93-2]

Original Measurements:
M. N. Arnoldov, M. N. Ivanovskii, and B. A. Shmatko, Teplofiz. Vys. Temp. **5**, 380–381 (1967).

Variables:
Temperature: 524–591 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data
The solubility of N in liquid Li was determined

t/°C	Solubility/mass % N	Solubility/mol % N
251	0.04	0.02
291	0.12	0.06
318	0.25	0.12

Kinetics of the crystallization of Li_3N was investigated.

Auxiliary Information

Method:
N was introduced into Li in form of gas. The N quantity introduced was determined by chemical analysis. A tube was made of 1Kh18N9T stainless steel. It was filled with Li containing N, hermetically closed and placed in a thermostat. Measurements of the resistivity of Li, circulating in the tube loop, were performed by the "double bridge of constant current." The resistivity was monitored while changing the temperature for a given content of N in a sample. A break on a plot relating the resistivity on temperature corresponds to the solubility level of N in liquid Li.

Source and Purity of Materials:
N: nothing numerically specified, but the content of impurities was lower than in Li.
Li: containing $3\cdot10^{-2}$ % Fe, $5\cdot10^{-4}$ % Mn, $3\cdot10^{-3}$ % Mg, $2\cdot10^{-2}$ % Ca, $6\cdot10^{-3}$ % Cr, $1\cdot10^{-2}$ % Ni, $8\cdot10^{-2}$ % Na, $1\cdot10^{-2}$ % K, $5\cdot10^{-2}$ % O, and $1\cdot10^{-4}$ % C.

Estimated Error:
Solubility: nothing specified; resistivity measurements indicate changes of 10^{-4} mol % N; the compositions of the samples confirmed within the precision of their chemical analysis.
Temperature: stability and uniformity ±0.05 K; accuracy ±1 K.

Components:
(1) Nitrogen; N; [7727-37-9]
(2) Lithium; Li; [7439-93-2]

Original Measurements:
P. F. Adams, M. G. Down, P. Hubberstey, and R. J. Pulham, J. Less-Common Met. **42**, 325–334 (1975).

Variables:
Temperature: 473–748 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data
The solubility of N in liquid Li was determined

t/°C	Solubility/mol % N
200	0.086
225	0.088
250	0.207
275	0.320
300	0.416
330	0.580
340	0.700
352	0.850[a]
375	1.025
400	1.450
400	1.450[b]
425	1.940
435	2.300
450	2.770
475	2.7[c]

[a]Obtained by changing temperature of the sample.
[b]Li gettered by Y.
[c]Estimated by the compilers from experiments performed in Pulham *et al.*[1] by the same method.

The solubility equation proposed by the authors:

$$\log(\text{soly/mol \% N}) = 3.168 - 2036\ (T/\text{K})^{-1}$$

was confirmed by the compilers.

Auxiliary Information

Method:
The apparatus was constructed from AISI 321 stainless steel. It contained a reservoir, a neck, two loops with electromagnetic pumps (one loop with a capillary for continuous resistance measurement), and a winding device for addition and removal of gettering metals Y and Ti. The vessel was evacuated, the temperature raised, and the resistance measured across the empty capillary by means of a Kelvin–Wheatstone bridge at a selected temperature. The temperature was measured by means of thermocouples. The apparatus was cooled and charged with Li. The Li was heated to 673 K and gettered with Ti or Y and a decrease of the resistance was observed. Accurately known volumes of N gas were added and resistivity changes were detected. In one case the resistivity was measured for a fixed N concentration while changing temperature. The solubility corresponded to breaks on the plots of resistivity versus composition. All operations were performed in an Ar atmosphere.

Source and Purity of Materials:
N: 99.99% pure from Air Products.
Li: 99.98% pure from Koch–Light, further gettered with Ti or Y at 673 K.
Ar: nothing specified.
Ti: 99.9% pure from Koch–Light.
Y: 99.9% pure from Koch–Light.

Estimated Error:
Solubility: nothing specified; precision of few % (by the compilers).
Temperature: stability ±0.5 K; precision ±0.05 K.

References:
[1]R. J. Pulham, P. Hubberstey, A. E. Thunder, A. Harper, and A. T. Dadd, U.S. Dept. of Energy Rep. CONF-800401-P2, p. 18/9 (1980).

Components:
(1) Nitrogen; N; [7727-37-9]
(2) Lithium; Li; [7439-93-2]

Original Measurements:
R. M. Yonco, E. Veleckis, and V. A. Maroni, J. Nucl. Mater. **57**, 317–324 (1975).

Variables:
Temperature: 453.5–1086 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data
The solubility of N in liquid Li was determined

t/°C	Solubility/mol % N
180.3[a]	0.05 eutectic
194.9	0.0697
195.3	0.0616
201.0	0.0735
207.4	0.0736
221.1	0.135
221.9	0.139
226.2	0.123
252.7	0.198
252.4	0.187
279.7	0.331
279.8	0.364
309.5	0.487
310.2	0.499
376.0	1.26
376.2	1.10
376.7	1.25
376.7	1.32
377.7	1.19
378.8	1.27
440.9	2.28
440.9	2.22
813[a]	25.0

[a]From thermal analysis.

Solid Li_3N was found as the equilibrium solid phase by chemical analysis. The solubility equation valid below 723 K was proposed by the authors and confirmed by the compilers:

$$\log(\text{soly/mol \% N}) = 3.323 - 2107\ (T/\text{K})^{-1}. \quad (1)$$

The temperature dependence of the Sievert's law constant was expressed by the equation:

$$\log(K_s/10^5\ \text{Pa}^{-1/2}) = -5.99 + 6330\ (T/\text{K})^{-1}. \quad (2)$$

The same results were also presented in Veleckis and Yonco.[1]

Auxiliary Information

Method:
Li_3N was prepared by direct reaction of the elements. A mixture of Li_3N and Li was placed in an Armco Fe liner and heated Li to the desired temperature while stirring. After a 1 h equilibration, a sample tube with a porous Ni frit was lowered to a position just above the surface and preheated for 15 min. The tube was then immersed into the melt and the pressure increased. The sample tube was withdrawn and allowed to cool. The tube was cut into several sections and analyzed. N was determined by micro Kjeldahl's, Li by an alkalimetric, and Fe and Ni by a calorimetric method. The temperature was measured by means of a sheathed Chromel/Alumel thermocouple.

Source and Purity of Materials:
N: 99.995% pure from Liquid Air Inc.
Li_3N: contained ~0.2% O; the Li to N molar ratio was 3.01.
Li: 99.9+% pure from Lithium Corp. of America; contained 0.011% N and 0.03% O.
He: with less than $1 \cdot 10^{-4}$ % H_2O or O.

Estimated Error:
Solubility: precision ±4%.
Temperature: precision better than ±1 K.

References:
[1]E. Veleckis and R. M. Yonco, U.S. Atom. Energy Comm. Rep. ANL-8123, pp. 6–9 (1975).

Components:
(1) Nitrogen; N; [7727-37-9]
(2) Lithium; Li; [7439-93-2]

Original Measurements:
P. Hubberstey, R. J. Pulham, and A. E. Thunder, J. Chem. Soc., Faraday Trans. I **72**, 431–435 (1976).

Variables:
Temperature: 453.39–453.64 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data
A part of the N–Li liquidus was determined. The values were read out from the figure by the compilers.

t/°C	Solubility/mol % N
180.49	0.0057
180.49	0.0057
180.50	0.0068
180.49	0.0116
180.50	0.0134
180.49	0.0151
180.49	0.0192
180.50	0.022
180.44	0.023
180.46	0.027
180.44	0.031
180.44	0.033
180.46	0.033
180.42	0.038
180.44	0.039
180.44	0.042
180.42	0.047
180.39	0.0475
180.39	0.053
180.34	0.053
180.37	0.0545
180.32	0.059
180.32	0.061
180.27	0.064
180.32	0.063
180.24	0.068 eutectic

At higher N concentrations up to 0.11 mol % N in Li the temperature arrests were constant at 180.24±0.02 °C. The melting point of pure Li was found at 180.49±0.02 °C. A solid solubility of N in Li was estimated to be 0.024 mol % N at the eutectic temperature.

Auxiliary Information

Method:
The apparatus was constructed from AISI 321 stainless steel. It contained a reservoir, a thermocouple pocket, a small electromagnetic pump in a side loop and a winding device (in a neck) for addition and removal of Y getter. A Chromel/Alumel thermocouple, calibrated against the NPL thermometer, was used to measure the temperature. The apparatus was cleaned, dried, and charged with Li under Ar in a glove box. The temperature was raised to 673 K and Y immersed in Li. Liquid Li circulated for 12 h over the Y getter. After the removal of Y the melting point of Li was determined from cooling curves (at a rate of 15 K/h). Successive N volumes were introduced into Li. The gas reacted instantly with Li at 673 K and dissolved. Any detectable reaction of the melt with the apparatus was not observed. The solutions were subject to controlled cooling being recorded.

Source and Purity of Materials:
N: 99.99% pure from Air Products; passed through molecular sieves, MnO and liquid Na–K alloy, as in Addison *et al.*[1]
Li: 99.98% pure from Koch–Light, gettered with Y at 673 K.
Ar: nothing specified.
Y: 99.9% pure from Koch–Light.

Estimated Error:
Solubility: nothing specified; reading-out procedure ±0.001 mol %.
Temperature: precision and reading-out procedure ±0.01 K; accuracy ±0.1 K (by the compilers).

References:
[1]C. C. Addison, R. J. Pulham, and E. A. Trevillion, J. Chem. Soc., Dalton Trans. 2082–2085 (1975).

Components:
(1) Nitrogen; N; [7727-37-9]
(2) Lithium; Li; [7439-93-2]

Original Measurements:
J. R. Weston, W. F. Calaway, R. M. Yonco, J. B. Hines, and V. A. Maroni, Proceedings 1979 NACE Conference—Corrosion/79, NACE, Katy, 1979, paper no. 116.

Variables:
One temperature: 540 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of N in liquid Li at 540 K was determined to be 0.3 mol % N

Auxiliary Information

Method:
The study was performed in the Li processing test loop made of 304 stainless steel. The Li reservoir was isolated from a He-filled glove box and brought to the temperature of 760 K. The electric resistivity of the liquid Li was measured after a resistance coil was flushed. The measurements were repeated at sequentially lower temperatures, flushing the coil each time. At 540 K a sharp break of the resistance was observed suggesting the precipitation of Li_3N. Furthermore, excess resistivity calculations indicate that all excess resistivity at 540 K is due to the dissolved N in Li.

Source and Purity of Materials:
N: nothing specified.
Li: nothing specified; probably nuclear grade of purity.
He: nothing specified.

Estimated Error:
Solubility: nothing specified; precision better than ±10% (by the compilers).
Temperature: precision ±2 K.

Components:
(1) Nitrogen; N; [7727-37-9]
(2) Barium; Ba; [7440-39-3]
or Calcium; Ca; [7440-70-2]
or Strontium; Sr; [7440-24-6]
(3) Lithium; Li; [7439-93-2]

Original Measurements:
P. Hubberstey and P. G. Roberts, *Liquid Metal Systems*, edited by H. U. Borgstedt and G. Frees (Plenum, New York, 1995), pp. 331–338.

Variables:
Temperature: 473 or 673 K; Ba concentration: 2.51–13.2 mol %; Ca concentration: 5.00 mol % and Sr concentration: 5.00 and 9.27 mol %

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of N in liquid Li containing Ba, Ca, or Sr was determined

T/K	Additive	Concentration/mol %	Solubility/mol % N
473	Ba	4.75	1.5
		7.50	2.2
		13.2	6.3
673	Ba	2.51	3.06
		5.00	4.66
673	Ca	5.00	2.49
673	Sr	5.00	3.48
		9.27	5.21

Li_3N was found to be the equilibrium solid phase in these solutions. Thermal analysis was performed for the Li-rich corner of the Ba–N–Li system, and the ternary eutectic temperature was established at 368 K.

Auxiliary Information

Method:
The mixtures of Li with the alkaline earth metals were prepared from weighed amounts of the metals (Hubberstey and Roberts[1]). Aliquots of N were added to the metallic melts, and the corresponding equilibrium electric resistivity was measured in an apparatus made of AISI 316 stainless steel. The melt circulated permanently from a reservoir though a capillary by means of a pump. The temperature of the capillary was measured by means of four precalibrated Chromel/Alumel thermocouples. The solubility was found from breaks on the resistivity versus concentration dependencies. All operations were performed in an Ar atmosphere. A smaller system without a capillary was used in thermal analysis with a spontaneous cooling rate of 1.0–0.25 K/min. The solid phases were investigated by x-ray powder diffraction technique.

Source and Purity of Materials:
N: nothing specified.
Li: 99.98% pure from Koch Light, probably further purified.[1]
Ba, Ca, Sr: each 99.9% pure from Koch–Light, probably further purified.[1]
Ar: purified from O, N, and H_2O.

Estimated Error:
Solubility: nothing specified; not better than ±0.5% (by the compilers).
Temperature: stability ±0.5 K; accuracy ±1 K; as in Hubberstey and Roberts.[1]

References:
[1]P. Hubberstey and P. G. Roberts, J. Phase Equil. **15**, 473–478 (1994).

Components:
(1) Nitrogen; N; [7727-37-9]
(2) Lithium; Li; [7439-93-2]
(3) Sodium; Na; [7440-23-5]

Original Measurements:
M. N. Arnoldov, M. N. Ivanovskii, A. D. Pleshivtsev, V. I. Subbotin, and B. A. Shmatko, *Teplofizicheskie Svoistva Zhidkostei*, edited by A. K. Abas-Zade and E. E. Shpil'rain (Nauka, Moskva, 1970), pp. 124–127.

Variables:
Temperature: 573 and 623 K
Concentration of Na: 0.55 mol %

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of N in liquid Li containing 1.8 mass % Na (0.55 mol % Na) was determined

t/°C	Solubility/mass % N	Solubility/mol % N[b]
300	0.32[a]	0.16
350	0.35	0.18

[a]As read out from the figure by the compilers.
[b]Calculated by the compilers.

It was found by resistivity measurements that there is not any interaction between H and N as well as between N and O, if mixtures of these gases were introduced into the liquid Li. Na, which was added to Li, appeared to interact with N, since the measurable N concentration decreased. This can hardly be accepted from the thermodynamic point of view.

Auxiliary Information

Method:
Li was contained in a loop made of the 1Kh18N9T stainless steel, hermetically closed and placed in a thermostat.[1] Na was added to Li and the mixture was purified from nonmetallic contaminants. Portions of N gas were introduced into liquid Li at constant temperature. Measurements of the cell resistivity of the circulating Li were performed by the "double bridge of constant current." The solubility was determined from a break on the plot relating the resistivity versus N concentration. The contents of Na and N in Li were determined by an unspecified chemical analysis.

Source and Purity of Materials:
N: nothing specified.
Li: containing 0.01% O, N, Ba, $3\cdot10^{-3}$ % H, $1\cdot10^{-4}$ % C, 0.5% Na, $6\cdot10^{-3}$ % Ca, 0.03% Cr, 0.04% Si and $<3\cdot10^{-3}$ % Ni, Mn, Al, Be, Mg, Cu, Ti, Fe, Ag (each).
Na: containing $5\cdot10^{-4}$ % O, $1\cdot10^{-3}$ % H, Ca, Si, 0.05% C, $1\cdot10^{-4}$ % Li and <0.03% Ni, Mn, Al, Be, Mg, Cu, Ti, Fe, Ag (each) as in Arnoldov *et al.*[2]

Estimated Error:
Solubility: precision of N injection ±1 vol %.
Temperature: stability ±0.05 K, accuracy ±1.5 K as in Ivanovskii *et al.*[1]

References:
[1]M. N. Ivanovskii, M. N. Arnoldov, B. A. Shmatko, A. D. Pleshivtsev, and S. K. Korotaev, Atom. Energiya **24**, 392–394 (1968).
[2]M. N. Arnoldov, M. N. Ivanovskii, V. I. Subbotin, and B. A. Shmatko, *Alkali Metal Coolants* (IAEA, Vienna, 1967), pp. 479–488.

3.9. Lithium–Phosphorus

Components:
(1) Phosphorus; P; [7723-14-0]
(2) Lithium; Li; [7439-93-2]

Evaluated by:
Hans Ulrich Borgstedt, Forschungszentrum Karlsruhe, Germany and Cezary Guminski, University of Warsaw, Poland, October 1995

Critical Evaluation

Neither any solubility determination of P in liquid Li nor a part of the liquidus of the Li–P system is known so far. A formation of several Li–P compounds was reported in the literature,[1] however, only Li_3P and LiP seem to be formed by direct reaction of the elements. Probably, Li_3P is the most stable compound in the system; however, its melting point has not been determined. One may estimate this temperature as being between the melting points of Li_3N and Li_3As, in the order of ~1100 K; the thermodynamic stabilities of Li_3P and Li_3N are similar. LiP was found to be unstable in vacuum decomposing to Li_3P and P at above 873 K.[2] Li_3P_7 decomposes at 723 K.[3] LiP_5 and LiP_7 were synthesized at 773 K from the elements, in the presence of a small quantity of S.[4] Nesper[5] also reported the formation of LiP_{15} and Li_9P_{25} .

Beskorovainyi and Yakovlev[6] equilibrated Fe_3P with Li at 1073 K for 130 h. They observed the decomposition of Fe_3P; P dissolved in liquid Li and Fe precipitated at the bottom of the steel container. These authors also observed leaching of P from steels containing P. Though the P concentration in Li was not determined, the experiments suggest that it is more soluble than Fe in Li.

It seems that a solubility of P in liquid Li is not more than 1 order of magnitude different from the solubility of N in the same range of temperatures. Further experiments are needed to establish the solubility and phase diagram of the Li–P system.

References:
[1]*Binary Alloy Phase Diagrams*, edited by T. B. Massalski (American Society Materials, Materials Park, 1990), p. 2454.
[2]I. Maak and A. Rabenau, Angew. Chem. **72**, 268 (1960).
[3]V. Marinquez, W. Hönle, and H. G. von Schnering, Z. Anorg. Chem. **539**, 95 (1986).
[4]J. Sangster, A. D. Pelton, and H. Okamoto, J. Phase Equil. **16**, 92 (1995).
[5]R. Nesper, Progr. Solid State Chem. **20**, 1 (1990).
[6]N. M. Beskorovainyi and E. I. Yakovlev, Metall. Metalloved. Chist. Met. **2**, 189 (1960).

3.10. Lithium–Arsenic

Components:
(1) Arsenic; As; [7440-38-2]
(2) Lithium; Li; [7439-93-2]

Evaluated by:
Hans Ulrich Borgstedt, Forschungszentrum Karlsruhe, Germany and Cezary Guminski, University of Warsaw, Poland, November 1993

Critical Evaluation

There is no experimental study on either a solubility of As in liquid Li or a fragment of the liquidus of the As–Li system. Two compounds are formed during direct alloying of the elements: Li_3As and LiAs.[1] Li_3As melts at ~1273 K and LiAs melts at ~823 K. The high melting temperature of Li_3As points on a quite low solubility of As in liquid Li near the melting point of the latter. One may predict that the solubility of As in liquid Li should be comparable to that of N in liquid Li; see the Li–N Critical Evaluation.

A preliminary schematic As–Li phase diagram is shown in Fig. 7. The formation of As-rich compounds as Li_3As_7 cannot be excluded.[2]

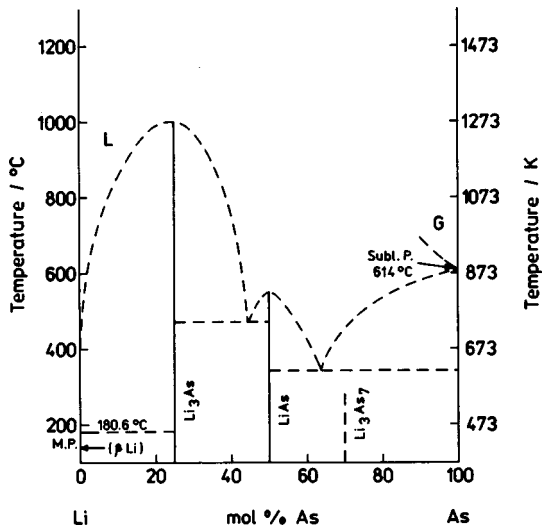

FIG. 7. Li–As phase diagram (schematic).

References:
[1]R. E. Tate and F. W. Schonfeld, Trans. AIME **215**, 296 (1959).
[2]J. Sangster and A. D. Pelton, J. Phase Equil. **14**, 238 (1993).

3.11. Lithium–Oxygen

Components:
(1) Oxygen; O; [7782-44-7]
(2) Lithium; Li; [7439-93-2]

Evaluated by:
Hans Ulrich Borgstedt, Forschungszentrum Karlsruhe, Germany and Cezary Guminski, University of Warsaw, Poland, August 1999

Critical Evaluation

Li is the only alkali metal which forms the normal oxide Li_2O during the direct reaction with gaseous O, instead of peroxide Li_2O_2 obtained only by indirect chemical processes. It is difficult to classify whether Li_2O_2 is a metastable phase or belongs to the equilibrium phase diagram Li–O. The reaction between gaseous O and liquid Li is fast, however the product Li_2O adhering to the Li surface makes irregular ceasing of the reaction rate.[1] Other Li–O compounds are certainly metastable.[2]

The melting point of Li_2O was variously reported: >1873 K,[3] 1843 K,[4] and 1700 K.[5] The value found by van Arkel *et al.*[4] is mostly recommended in Messer[1] and Sangster and Pelton[2] and was adopted in this evaluation, since it fits best with the selected solubility data.

A solubility of O in liquid Li (in fact a solubility of Li_2O in liquid Li) was investigated by several laboratories. The first results at 523–673 K were obtained by Hoffman[6,7] who performed activation analysis of the saturated filtrate. A wide scatter of all his data was observed but mean results showed a smooth temperature dependence. Two independent studies performed later in Russia by Cheburkov and Rozanov[8] at 483–908 K and by Konovalov *et al.*[9] at 455–873 K yielded higher results, being less regularly dependent on temperature than in Hoffman.[6,7] Konovalov *et al.*[9] analyzed the O content in the filtrates by activation analysis and vacuum distillation while Cheburkov and Rozanov[8] estimated the solubility from kinetic curves of the reaction between gaseous O and liquid Li. The latter procedure may be charged with uncertainty of the degree of oversaturation of the melt with Li_2O that initiates its crystallization.

Subbotin *et al.*[10] were the first to point out that the scattered values obtained in Hoffman,[6,7] Cheburkov and Rozanov,[8] and Konovalov *et al.*[9] are generally overestimated due to an ineffective separation of Li_2O solute from its saturated solution. Unfortunately, Subbotin *et al.*[10] reported only a smooth line reflecting their results obtained between 473 and 573 K; centrifuging and activation analysis was used. In another study, the same group[11] measured the O solubility at only 573 K using chemical analysis. Yonco *et al.*[12,13] applied filters with pore size of 2 μm instead of 20 μm as in the study of Hoffman[6,7] and 30–40 μm as in the study of Konovalov *et al.*[9] The results obtained by means of activation analysis of the samples[12,13] were lower than those of Hoffman,[6,7] Cheburkov and Rozanov,[8] and Konovalov *et al.*,[9] but quite similar to those of Subbotin *et al.*[10] and Arnoldov *et al.*[11] differing in the temperature dependence of the solubility.

A solubility value of $5.2 \cdot 10^{-3}$ mol % O at 529 K found in cold trapping the Li processing test loop by Weston *et al.*[14,15] agrees very well with the data of Yonco *et al.*[12,13] while the rest of data of Weston *et al.*[14,15] at other temperatures does not. Natesan *et al.*[16] reported the solubility at $4 \cdot 10^{-2}$ mol % O at 473 K, a highly overestimated value; they did not report any experimental details of their study.

The phenomenon of the large scatter of all results may be attributable to the poor crystallization properties of Li_2O. The data of Yonco *et al.*[12,13] are mostly recommended in this evaluation. Yonco *et al.*[12] presented the solubility equation:

$$\log(\text{soly/mol \% O}) = 2.628 - 2896/(T/\text{K})^{-1} \quad r = 0.997, \tag{1}$$

which was confirmed by the evaluators.

Similar assessing conclusions were formulated in reviews by Sangster and Pelton,[2] Borgstedt,[17] and Hubberstey *et al.*[18] The solubility equations proposed in Rumbaut *et al.*[19] and Adams *et al.*,[20] however, are not valid, since they were based on nonaccepted results of Hoffman,[6,7] Cheburkov and Rozanov,[8] and Konovalov *et al.*[9] As it results from resistivity measurements of Amoldov *et al.*[11] and Hubberstey *et al.*[21] and thermodynamic calculations of Migge[22] neither C, H, nor N introduced separately or simultaneously into liquid Li interact with dissolved O. A partial diagram of the Li–O system is shown in Fig. 8. The eutectic point is placed about 0.001 K below the melting point of Li at $2 \cdot 10^{-4}$ mol % O, as it was found from the van't Hoff relation and Eq. (1).

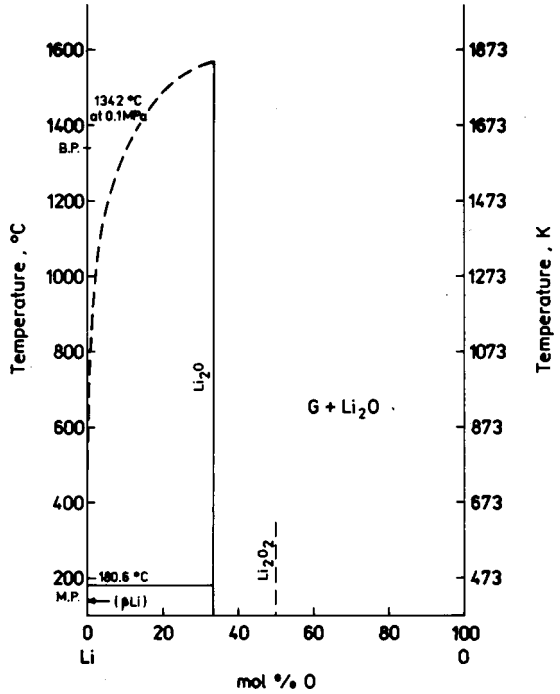

FIG. 8. Li–O phase diagram (partial).

Recommended values of the O solubility in liquid Li

T/K	Solubility/mol % O	Source
453.8	$2\cdot10^{-4}$ eutectic	Eq. (1)
473	$3\cdot10^{-4}$	Eq. (1)
573	$4\cdot10^{-3}$	Eq. (1)
673	$2\cdot10^{-2}$	Eq. (1)
773	$8\cdot10^{-2}$	Eq. (1)
873	0.2	Eq. (1)
973	0.45	Eq. (1)
1073	0.85	Eq. (1), extrapolated
1843	33.3	(4)

References:

[1]C. E. Messer, *The Alkali Metals* (The Chemical Society, London, 1967), p. 183.
[2]J. Sangster and A. D. Pelton, J. Phase Equil. **13**, 296 (1992).
[3]F. M. Jaeger and H. S. van Klooster, Proc. Roy. Acad. Amsterdam **16**, 857 (1914).
[4]A. E. van Arkel, E. A. Flood, and N. F. H. Bright, Can. J. Chem. **31**, 1009 (1953).
[5]L. Brewer and J. Margrave, J. Phys. Chem, **59**, 421 (1955).
[6]E. E. Hoffman, *Newer Metals* (American Society Testing Materials, Philadelphia, PA, 1960), p. 195.
[7]E. E. Hoffman, U.S. Atom. Energy Comm. Rep. ORNL-2894 (1960).
[8]V. I. Cheburkov and A. N. Rozanov, Matall. Metalloved. Chist. Met. **7**, 168 (1968).
[9]E. E. Konovalov, N. I. Seliverstov, and V. P. Emelyanov, Izv. Akad. Nauk SSSR, Met. **3**, 109 (1968).
[10]V. I. Subbotin, M. N. Ivanovskii, M. N. Arnoldov, and B. A. Shmatko, *Fiziko-Khimicheskie Osnovy Primenieniya Zhidkometallicheskikh Teplonositelei* (Atomizdat, Moskva, 1970), p. 57.
[11]M. N. Arnoldov, M. N. Ivanovskii, A. D. Pleshivtsev, V. I. Subbotin, and B. A. Shmatko, *Teplofizicheskie Svoistva Zhidkostei*, edited by A. K. Abas-Zade and E. E. Shpil'rain (Nauka, Moskva, 1970), p. 124.
[12]R. M. Yonco and V. A. Maroni, Trans. Am. Nucl. Soc. **26**, 166 (1977).
[13]R. M. Yonco, V. A. Maroni, J. E. Strain, and J. H. DeVan, J. Nucl. Mater. **79**, 354 (1979).
[14]J. R. Weston, W. F. Calaway, R. M. Yonco, and V. A. Maroni, U.S. Dept. Energy Rep. CONF-800401-P2, p. 20/1 (1980).
[15]J. R. Weston, W. F. Calaway, R. M. Yonco, J. B. Hines, and V. A. Maroni, Proceedings 1979, NACE Conference—Corrosion/79, NACE, Katy, 1979, paper no. 116.
[16]K. Natesan, C. B. Reed, and R. F. Mattas, Fusion Engin. Design **27**, 457 (1995).
[17]H. U. Borgstedt, *Handbook of Thermodynamic and Transport Properties of Alkali Metals*, edited by R. W. Ohse (Blackwell, Oxford, 1985), p. 901.
[18]P. Hubberstey, A. T. Dadd, and P. G. Roberts, *Material Behavior and Physical Chemistry of Liquid Metal Systems*, edited by H. U. Borgstedt (Plenum, New York, 1982), p. 445.
[19]N. Rumbaut, F. Casteels, and M. Brabers, *Material Behavior and Physical Chemistry of Liquid Metal Systems*, edited by H. U. Borgstedt (Plenum, New York, 1982), p. 437.
[20]P. F. Adams, P. Hubberstey, and R. J. Pulham, J. Less-Common Met. **42**, 1 (1975).
[21]P. Hubberstey, A. Harper, A. T. Dadd, D. J. Knight, and K. Maughan, U.S. Dept. Energy Rep. CONF-800401-P2, p. 18/27 (1980).
[22]H. Migge, U.S. Dept. Energy Rep. CONF-800401-P2, p. 18/9 (1980).

Components:
(1) Oxygen; O; [7782-44-7]
(2) Lithium; Li; [7439-93-2]

Original Measurements:
E. E. Hoffman, *Newer Metals* (American Society Testing Materials, Philadelphia, PA, 1960), pp. 195–206.

Variables:
Temperature: 523–673 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data
The solubility of O in liquid Li was determined

t/°C	Solubility $\cdot 10^{-3}$/mass % O	Solubility/mol %[a]
250	5.8; 7.4; 8.5; 9.2; 9.6; 10.1; 10.9; 12.1	$(4.0\pm1.3)\cdot10^{-3}$
300	17.6; 19.0; 19.3; 20.5; 21.2; 21.4; 21.4; 23.7; 25.3	$(9.1\pm1.2)\cdot10^{-3}$
350	34.8; 36.8; 37.4; 38.3; 39.2; 39.6	0.016±0.001
400	47.7; 52.9; 60.4; 72.9; 73.0; 76.1; 76.6	0.029±0.004

[a]Mean value calculated by the compilers.

Hoffman[1] reported the same results. Solid Li_2O is the solute.

Auxiliary Information

Method:
The solubility experiments were conducted in a sampling apparatus made of stainless steel. Sufficient amounts of Li_2O were added into Li to increase the O content of the bath to 5 mass %. Samples of the saturated Li were taken by forcing the Li through a 20 μm stainless steel filter after allowing the system to equilibrate at sampling temperature for 24 h. The container was pressurized with Ar, forcing Li into a sampling tube. The samples were quenched after removal from a furnace. The tube was cut, sectioned, and submitted to activation analysis.

Source and Purity of Materials:
Li_2O: 99.8% pure, prepared by vacuum treatment of pure grade $LiOH\cdot H_2O$ in a Ni container at 873 K.
Li: "high purity" containing $(6-33)\cdot10^{-2}$ % N, $(1.9-19.8)\cdot10^{-2}$ % O.
Ar: nothing specified.

Estimated Error:
Solubility: nothing specified; precision better than ±30% (by the compilers).
Temperature: nothing specified.

References:
[1]E. E. Hoffman, U.S. Atom. Energy Comm. Rep. ORNL-2894 (1960).

Components:
(1) Oxygen; O; [7782-44-7]
(2) Lithium; Li; [7439-93-2]

Original Measurements:
V. I. Cheburkov and A. N. Rozanov, Metall. Metalloved. Chist. Met. **7**, 168–173 (1968).

Variables:
Temperature: 483–908 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data
The solubility of O in liquid Li was determined. The values were read from a figure by the compilers.

T/K	t/°C	Solubility/mol % O
483	210	0.003[a]
594	322	0.027
629	356	0.040
633	360	0.028
641	368	0.041
670	397	0.060
719	446	0.070
720	447	0.11
761	488	0.15
776	503	0.13
782	509	0.16
799	526	0.14
819	546	0.28
829	556	0.21
886	613	0.36
908	635	0.57[a]

[a]Reported in numerical form.

Kinetics of the reaction between gaseous O and liquid Li were investigated.

Auxiliary Information

Method:
Additions of O gas into liquid Li were carried out in a specially constructed glass apparatus.[1] Kinetics of this reaction was traced by precise measurements of the O amount, which had reacted with liquid Li. The gas volume over the Li was measured with the help of a cathetometer. The liquid Li was kept in a crucible made of 1Kh18N9T stainless steel. The temperature inside the crucible was measured and stabilized by means of a Chromel/Alumel thermocouple. Kinetic curves were plotted for the samples at various temperatures and the solubility was determined from the breaking points at which the logarithmic dependence of concentration on time changed the slope.

Source and Purity of Materials:
O: obtained by controlled decomposition of $KMnO_4$; traces of H_2O, K, and Mn compounds were gettered at the temperature of liquid N; as reported in Bychkov *et al.*[1]
Li: 99% pure (designed LEI), contained 0.001% K, 0.52% Na, 0.12% Mg, 0.06% Al, 0.001% Fe, 0.008% Ca, SiO_2, 0.012% N, 0.005% Mn.
Ar: nothing specified.

Estimated Error:
Solubility: nothing specified; reading-out procedure ±5%.
Temperature: precision ±0.5 K; reading-out procedure ±2 K.

References:
[1]A. N. Rozanov, D. M. Skorov, and V. I. Cheburkov, Metall. Metalloved. Chist. Met. **2**, 78–92 (1960).

Components:
(1) Oxygen; O; [7782-44-7]
(2) Lithium; Li; [7439-93-2]

Original Measurements:
E. E. Konovalov, N. I. Seliverstov, and V. P. Emelyanov, Izv. Akad. Nauk SSSR, Met. **3**, 109–112 (1968).

Variables:
Temperature: 455–873 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of O in liquid Li at several temperatures was determined. The values were read from a figure and recalculated to mol % O by the compilers.

t/°C	Solubility/mass % Li_2O	Solubility/mol % O
182	0.026	$6.0\cdot10^{-3}$
211	0.031	$7.1\cdot10^{-3}$
214	0.032[a]	$7.4\cdot10^{-3}$[a]
287	0.037	$8.5\cdot10^{-3}$
304	0.056	$1.30\cdot10^{-2}$
365	0.102	$2.3\cdot10^{-2}$
398	0.172	$4.0\cdot10^{-2}$
493	1.07	0.25
541	1.55	0.36
600	2.53	0.59

[a]Mean value of eight determinations obtained by vacuum distillation analysis.

Auxiliary Information

Method:
An Armco Fe container was filled with Li and an excess of Li_2O was added to form the saturated solution. The container was heated and kept in an oven at constant temperature for 8 h in an Ar atmosphere. Samples of Li were filtered through two filters: a steel net and a metallo-ceramic frit with a pore size of 30–40 μm, prepared according to Shibryaev and Pavlovskaya[1]. A maximum of three samples of the filtrate were collected at selected temperature in ampoules without hermetical closure of the apparatus. The O contents in the samples were determined either by activation analysis or vacuum distillation of Li. The content of Li was analyzed by an unspecified method. The vacuum distillation was performed at ~1023 K and 10^{-2}–10^{-3} Pa for 2–3 h.[2] The residue was dissolved in H_2O. The contents of N and C were determined separately by means of the amounts of NH_3 and C_2H_2 formed. The aqueous solution was titrated with standard H_2SO_4.

Source and Purity of Materials:
Li_2O: nothing specified.
Li: nothing specified.
Ar: nothing specified.

Estimated Error:
Solubility: nothing specified; precision ±15%, sensitivity $1\cdot10^{-4}$ mol % O (2); reading-out procedure ±0.0003 mol % O at <673 K and ±0.03 mol % O at >673 K.
Temperature: accuracy ±2%; reading-out procedure ±2 K.

References:
[1]B. F. Shibryaev and E. I. Pavlovskaya, Khim. Promysl. **3**, 232 (1963).
[2]E. E. Konovalov, I. B. Dmitrieva, M. N. Arnoldov, V. P., Emelyanov, A. V. Molovidova, A. G. Karabash, and M. N. Ivanovskii, Zh. Anal. Chem. **23**, 1510–1517 (1968).

Components:
(1) Oxygen; O; [7782-44-7]
(2) Lithium; Li; [7439-93-2]

Original Measurements:
V. I. Subbotin, M. N. Ivanovskii, M. N. Arnoldov, and B. A. Shmatko, *Fiziko-Khimichaskie Osnovy Primenienia Zhidko-metallicheskikh Teplonositelei* Atomizdat, Moskva, 1970), pp. 57 and 150–152.

Variables:
Temperature: 473–573 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

A linear increase of the solubility of O in liquid Li from 0.003 to 0.011 mass % Li_2O at 200–300 °C was reported on a figure. The compilers read out these values and calculated that the solubility increased from $7\cdot10^{-4}$ to $2.5\cdot10^{-3}$ mol % O between 473 and 573 K.

In separate sedimentation experiments performed in the same laboratory 0.007–0.01 mass % O, $(1.5–2.0)\cdot10^{-3}$ mol % O—recalculated by the compilers, was found in saturated liquid Li at 473 K. This experiment shows that the latter method is less effective.

Auxiliary Information

Method:
Li was contained in a stainless steel container. An excess of Li_2O was added into Li. Samples were conditioned for 3 h at 623–673 K and then for 11 h at the selected test temperature. They were subject to centrifuging at this temperature for 10–30 min at the velocity of 50–100 rotations. The samples were then fast cooled either by air in the centrifuge or immediately after the termination of the centrifuging. The O content was found from activation analysis of the saturated Li phase. The results were not dependent on the cooling method and the centrifuging velocity. The sedimentation was performed for 6 h at 473 K.

Source and Purity of Materials:
Li_2O: "powder" of unspecified purity.
Li: nothing specified, but probably as in Arnoldov *et al.*:[1] containing 0.01% O, N, Ba, $3\cdot10^{-3}$ % H, $5\cdot10^{-4}$ % C, 0.5% Na, $6\cdot10^{-3}$ % Ca, 0.03% Cr, 0.04% Si and $<3\cdot10^{-3}$ % Ni, Mn, Al, Be, Mg, Ag, Cu, Ti, Fe each.

Estimated Error:
Solubility: nothing specified; the authors reported an almost 100% effective centrifuging separation.
Temperature: nothing specified; probable accuracy ±1 K.[1]

References:
[1]M. N. Arnoldov, M. N. Ivanovskii, V. I. Subbotin, and B. A. Shmatko, Teplofiz. Vys. Temp. **5**, 812–816 (1967).

Components:
(1) Oxygen; O; [7782-44-7]
(2) Lithium; Li; [7439-93-2]

Original Measurements:
M. N. Arnoldov, M. N. Ivanovskii, A. D. Pleshivtsev, V. I. Subbotin, and B. A. Shmatko, *Teplofizicheskie Svoistva Zhidkostei*, edited by A. K. Abas-Zade and E. E. Shpil'rain (Nauka, Moskva, 1970, pp. 124–127.

Variables:
One temperature: 573 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of O in liquid Li at 300 °C (573 K) was found to be about 0.013 mass % O or $3\cdot10^{-3}$ mol % O (as calculated by the compilers).

There is no interaction between O and N, H or C in liquid Li, as it was concluded after resistivity measurements of the corresponding solutions containing O and each of the contaminants.

Auxiliary Information

Method:
Li was enclosed in a test loop made of 1Kh18N9T stainless steel which was hermetically closed and placed in a thermostat.[1] Portions of air were introduced into the liquid Li at constant temperature. Measurements of the cell resistivity of the circulating Li were performed by the "double bridge of constant current". Changes of the resistivity agreed within 10% with the changes of resistivity of pure N dissolved in Li at the same concentration; N is much better soluble in Li than O. Portions of the Li after the equilibration were analyzed for their O content by an unspecified chemical method.

Source and Purity of Materials:
O: from air of unknown composition.
Li: containing 0.001% O, 0.01% N, Ba, 0.003% H, $1\cdot10^{-4}$ % C, 0.5% Na, 0.006% Ca, 0.03% Cr, 0.04% Si and 0.003 Ni, Mn, Al, Be, Mg, Cu, Ti, Fe, and Ag each.

Estimated Error:
Solubility: precision of the gas injection ±1 vol %.
Temperature: stability ±0.05 K, accuracy ±1.5 K.[1]

References:
[1]M. N. Ivanovskii, M. N. Arnoldov, B. A. Shmatko, A. D. Pleshivtsev, and S. K. Korotaev, Atom. Energiya **24**, 392–394 (1968).

Components:
(1) Oxygen; O; [7782-44-7]
(2) Lithium; Li; [7439-93-2]

Original Measurements:
R. M. Yonco, V. A. Maroni, J. E. Strain, and J. H. DeVan, J. Nucl. Mater. **79**, 354–362 (1979).

Variables:
Temperature: 468–1007 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of O in liquid Li was determined at various temperatures

t/°C	Solubility/mol % Li_2O	Solubility/mol % O[a]	Stand.dev. (%)
195.0	$2.70\cdot10^{-4}$	$2.70\cdot10^{-4}$	9.1
206.2	$8.40\cdot10^{-4}$	$8.40\cdot10^{-4}$	6.3
207.5	$3.76\cdot10^{-3}$	$3.76\cdot10^{-3}$	7.7
226.3	$1.25\cdot10^{-3}$	$1.25\cdot10^{-3}$	8.3
227.0	$2.48\cdot10^{-3}$	$2.48\cdot10^{-3}$	4.2
246.7	$6.67\cdot10^{-4}$	$6.67\cdot10^{-4}$	3.7
2773.	$2.27\cdot10^{-3}$	$2.27\cdot10^{-3}$	5.9
300.1	$3.66\cdot10^{-3}$	$3.66\cdot10^{-3}$	4.0
325.9	$6.23\cdot10^{-3}$	$6.23\cdot10^{-3}$	5.3
326.4	$6.00\cdot10^{-3}$	$6.00\cdot10^{-3}$	2.4
351.1	$9.67\cdot10^{-3}$	$9.67\cdot10^{-3}$	3.5
371.7	$1.40\cdot10^{-2}$	$1.40\cdot10^{-2}$	2.2
373.1	$1.31\cdot10^{-2}$	$1.31\cdot10^{-2}$	2.7
373.6	$1.14\cdot10^{-2}$	$1.14\cdot10^{-2}$	5.0
407.1	$1.97\cdot10^{-2}$	$1.97\cdot10^{-2}$	2.1
428.7	$2.94\cdot10^{-2}$	$2.94\cdot10^{-2}$	5.5
443.7	$2.85\cdot10^{-2}$	$2.85\cdot10^{-2}$	9.1
443.9	$2.12\cdot10^{-2}$	$2.12\cdot10^{-2}$	8.2
471.0	$5.01\cdot10^{-2}$	$5.01\cdot10^{-2}$	2.0
493.8	$6.56\cdot10^{-2}$	$6.56\cdot10^{-2}$	4.8
516.5	$8.09\cdot10^{-2}$	$8.09\cdot10^{-2}$	2.5
541.4	0.100	0.100	8.2
568.4	0.142	0.142	2.1
597.2	0.190	0.189	7.2
629.3	0.261	0.260	4.3
659.9	0.339	0.338	2.5
699.0	0.531	0.528	1.3
733.8	0.571	0.568	6.2

[a]Calculated by the compilers.

These results were presented graphically in Yonco.[2] The data can be represented by the fitting equation:

$$\log(\text{soly/mol \% O}) = 2.628 - 2896\ (T/\text{K})^{-1}.$$

The compilers confirmed the equation. Li_2O is the equilibrium solid phase saturating the Li.

Components:
(1) Oxygen; O; [7782-44-7]
(2) Lithium; Li; [7439-93-2]

Original Measurements:
J. R. Weston, W. F. Calaway, R. M. Yonco, J. B. Hines, and V. A. Maroni, Proceedings 1979 NACE Conference—Corrosion/79, NACE, Katy, 1979, paper no 116.

Variables:
Temperature: 529–724 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of O in liquid Li was determined. The values were read from a figure and recalculated to mol % by the compilers.

T/K	t/°C	Solubility/mass % O	Solubility/mol % O
529	256	$9.5\cdot10^{-3}$	$4.1\cdot10^{-3}$
529	256	0.0110	$4.8\cdot10^{-3}$
552	279	0.0101	$4.4\cdot10^{-3}$
592	319	0.0120	$5.2\cdot10^{-3}$
684	411	0.021	$9.1\cdot10^{-3}$
699	425	0.020	$8.7\cdot10^{-3}$
724	451	0.021	$9.1\cdot10^{-3}$

The same results were reported in Weston *et al.*[1]

Auxiliary Information

Method:
The equilibration experiments were performed in the Li processing test loop. The loop was constructed from 304 stainless steel. The extraction of filtered samples from the loop was done using a bayonet containing inside a frit of a porosity of 2 μm, all made of Ni. The samples were taken by reducing the Ar pressure inside the bayonet. After its withdrawal, the external surfaces of the bayonet were cleaned to remove adhering Li. The sample was stored in a He-filled glove box. The O content was analyzed in the ORNL by the fast neutron activation method. The empty Ni sampling tubes were H fired to reduce residual O and analyzed for the background O content.

Source and Purity of Materials:
O: nothing specified.
Li: probably nuclear grade of purity.
Ar: nothing specified.
He: nothing specified.

Estimated Error:
Solubility: nothing specified; reading-out procedure ±3%.
Temperature: precision ±2 K; reading-out procedure ±2 K.

References:
[1]J. R. Weston, W. F. Calaway, R. M. Yonco, and V. A. Maroni, U.S. Dept. Energy Rep. CONF-800401-P2, pp. 20/1-8 (1980).

Auxiliary Information

Method:
The apparatus, placed in a glove box, consisted of two concentric vessels: a container for the Li–Li_2O melt made of Armco Fe and a protector made of stainless steel filled with He. The top of the container was closed with a flange that was outfitted with a stirrer, thermocouple well, sampling shaft, and vacuum/pressure connector. Temperatures were measured with a calibrated Pt/Pt–Rh(10%) thermocouple. The Ni sampling tube contained 2 μm Ni filters. The saturated solution of Li_2O in Li was prepared by direct reaction of O gas and liquid Li. Samples of the saturated solutions were taken at selected temperatures after the solution had been stirred for at least 2 h at each temperature. The sampling tube was placed to a position just above the melt to reach the equilibrium temperature, evacuated and then lowered into the melt. The pressure in the vessel was restored to ~100 kPa, causing the tube to fill with Li. The tube was removed from the apparatus. The samples were analyzed for their O content by the fast neutron activation analysis. Their Li content was determined by dissolution in H_2O and titration with standard HCl.

Source and Purity of Materials:
O: 99.99% pure from Matheson Gas
Li: 99.8+% pure from Lithium Corp. of America, containing $<5\cdot10^{-3}$ % Na, $9.8\cdot10^{-2}$ % N.
He: containing $<1\cdot10^{-4}$ % O and H_2O.
Ni sampler: tube and sintered 201 Ni frit with 2 μm pore size, from Mott Metallurgical Corp.

Estimated Error:
Solubility: standard deviation <9%, mean deviation 4%.
Temperature: nothing specified; precision probably better than ±1 K as in Yonco *et al.*[1]

References:
[1]R. M. Yonco, E. Veleckis, and V. A. Maroni, J. Nucl. Mater. **57**, 317–324 (1975).
[2]R. M. Yonco, U.S. Energy Res. Devel. Admin. Rep. ANL-76-106, pp. 11–15 (1976).

3.12. Lithium–Sulfur

Components:
(1) Sulfur; S; [7704-34-9]
(2) Lithium; Li; [7439-93-2]

Evaluated by:
Hans Ulrich Borgstedt, Forschungszentrum Karlsruhe, Germany and Cezary Guminski, University of Warsaw, Poland, August 1996

Critical Evaluation

Quite contrastive results concerning the liquidus of the S–Li system are found in the literature. In the older work of Pearson and Robinson,[1] a composition range Li_2S–Li_2S_2 was investigated. The melting points of both compounds were found at ~1248 and 643 K, respectively. A smooth increase of the liquidus temperatures was noticed for samples with intermediate compositions. The results of Pearson and Robinson[1] were not confirmed in the independent studies by Sharma,[2] Cunningham *et al.*,[3] and Cleaver and Upton[4] who observed an almost 300 K higher melting point of Li_2S. These authors neglected the equilibrium formation of Li_2S_2 or higher polysilfides of Li. In the vicinity of the peritectic formation of Li_2S_2, as observed by Pearson and Robinson,[1] monotectic thermal arrests were concordantly observed by Sharma,[2] Cunningham *et al.*,[3] and Cleaver and Upton.[4] No doubt that the latter investigators used more pure chemicals than in Pearson and Robinson,[1] and the containers in Pearson and Robinson[1] interacted significantly with the melts. The N atmosphere in Pearson and Robinson[1] could be another reason of the discrepancies due to the formation of N–Li and eventually N–S–Li compounds. If Li_2S_2 is a metastable compound, the Li_2S–Li_2S_2 liquidus described in Pearson and Robinson[1] would reflect a metastable phase relation. Nevertheless, decisive experiments, similar to those of Pearson and Robinson[1] should be repeated to have a clear point of view in this matter.

The immiscibility curve on the S-rich side is quite unsymmetrical. This is probably connected with an existence of different polysulfide species in the S-rich melt range. Morachevskii *et al.*[5] investigated the thermodynamic features of melts containing 65.4–97.4 mol % S at 693 K and observed the existence of two immiscible liquid phases within this range of compositions. This may be considered as a qualitative confirmation of the results of Sharma,[2] Cunningham *et al.*,[3] and Cleaver and Upton.[4]

Unfortunately, no thermal effects were recorded in Sharma[2] and Cunningham *et al.*[3] in the Li-rich range. Thus the liquidus line between the melting point of Li and Li_2S is not known in details. Since Li is a metallic and Li_2S an ionic substance, a tendency to immiscibility of both forms may be manifested in the phase diagram. This composition range needs further studies. Since the temperature difference between the melting point of Li and the eutectic on the Li-rich side is the same within experimental error in Cunningham *et al.*,[3] no significant solubility of S in liquid Li is expected.

Beskorovainyi and Yakovlev[6] observed preferential leaching of S from steels containing S at 673–1273 K. The equilibration of FeS with Li at 1073 K for 130 h resulted in the dissolution of 1.72 mass % (0.37 mol % S) and the formation of a metallic deposit (probably Fe) on the bottom of the steel container. The paper is not compiled, since no more details are available, and the system is not well defined. Nevertheless, it can be concluded that the solubility of S in liquid Li should be equal or higher than 0.4 mol % S at 1073 K in agreement with expectations taking into account the melting temperature of Li_2S.

The Li–S partial phase diagram is shown in Fig. 9, it is similar to that shown in Okamoto.[7]

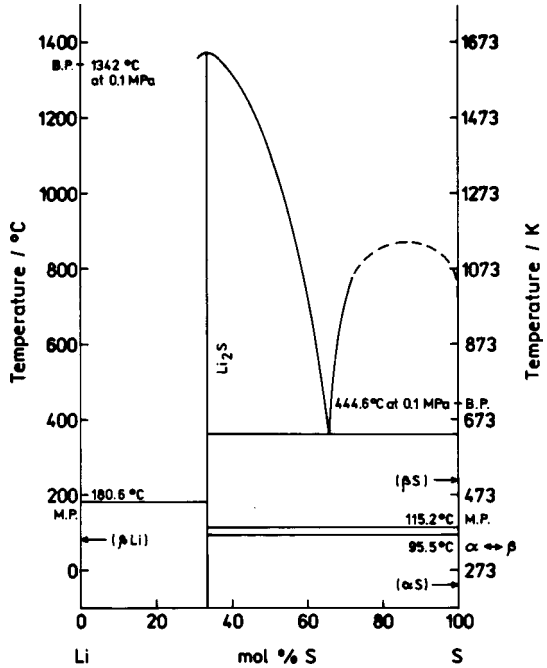

FIG. 9. Li–S phase diagram (partial).

The tentative (t) and doubtful (d) values of the solubility of S in liquid Li

T/K	Solubility/mol % S	Source
1643	33.3 (t) congruent	(2),(3),(4) mean value
638	65 (t) eutectic	(2),(3)
673	66 (d)	(2),(4) interpolated
773	67 (d)	(2) interpolated
873	69 (d)	(2) interpolated
973	70 (d)	(2) interpolated
1073	73 (d)	(2) interpolated
1133	91 (d) critical	(2)
873	99.7 (t)	(2),(3)
773	99.85 (t)	(2),(3)
673	99.97 (t)	(2),(3)

References:
[1]T. G. Pearson and P. L. Robinson, J. Chem. Soc., 413 (1931).
[2]R. A. Sharma, J. Electrochem. Soc. **119**, 1439 (1972).
[3]P. T. Cunningham, S. A. Johnson, and E. J. Cairns, J. Electrochem. Soc. **119**, 1448 (1972).
[4]B. Cleaver and S. M. Upton, Electrochem. Acta **36**, 667, 673, 679 (1991).
[5]A. G. Morachevskii, N. G. Chekov, and A. J. Demidov, Zh. Prikl. Khim. **51**, 1259 (1978); J. Appl. Chem. USSR **51**, 1208 (1978).
[6]N. M. Beskorovainyi and E. I. Yakovlev, Metall. Metalloved. Chist. Met. **2**, 189 (1960).
[7]H. Okamoto, J. Phase Equil. **16**, 94 (1995).

Components:
(1) Sulfur; S; [7704-34-9]
(2) Lithium; Li; [7439-93-2]

Original Measurements:
T. G. Pearson and P. L. Robinson, J. Chem. Soc., 413–420 (1931).

Variables:
Temperature: 643–1248 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data
A part of the Li–S liquidus was determined

t/°C	Solubility/mass % S	Solubility/mol % S[a]
975	69.5	33.3
774	74.6	38.8
765	75.0	39.4
618	77.9	43.3
520	79.6	45.8
444	81.2	48.3
369.5	82.0	50.0

[a]Calculated by the compilers.

The starting solid phases were Li_2S and Li_2S_2 ; the latter was slightly decomposed at its melting point.

Auxiliary Information

Method:
A sample of Li was dissolved in C_2H_5OH in streaming N on a water bath for the preparation of Li_2S. The solution was saturated with H_2S. After C_2H_5OH was distilled off, the dry mass was exposed to H_2S for 3 h. It was evacuated, placed in a furnace at 723 K for 4 h, regassed for several hours, and heated at 723 K for 2 h. Li_2S_2 was prepared by mixing Li_2S with an appropriate quantity of powdered S, cautiously heated, and then melted. An excess of S was removed by extraction with ice-cold CS_2 and the residue dried in vacuum. Cooling curves of the Li_2S–Li_2S_2 mixtures were performed in Pyrex glass tubes in a N atmosphere.[1] A thin-walled thermocouple sheath was made of glass or porcelain. A Chromel/Alumel up to 873 K and a Pt/Pt–Rh thermocouple above 873 K was used. Both junctions were calibrated on the melting points of H_2O, naphthalene, S, Sb, NaCl, and Ag. The samples were analyzed after the thermal treatment. The melts reacted with glass and porcelain.

Source and Purity of Materials:
S: twice recrystallized from CS_2 and dried for several hours at 373 K.
Li: electrolytic from Harrington Bros.; "visually purer parts of Li sticks were used."
C_2H_5OH: treated with quick-lime and distilled.
H_2S: from decomposition of a sulfide with an acid.
N_2 : nothing specified.

Estimated Error:
Solubility: sample composition ±0.25 mol %.
Temperature: precision between ±1 and ±10 K.

References:
[1]T. G. Pearson and P. L. Robinson, J. Chem. Soc., 1473–1497 (1930).

Components:
(1) Sulfur; S; [7704-34-9]
(2) Lithium; Li; [7439-93-2]

Original Measurements:
P. T. Cunningham, S. A. Johnson, and E. Cairns, J. Electrochem. Soc. **119**, 1448–1450 (1972).

Variables:
Temperature: 648–1245 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data
Several points on the S-rich miscibility gap were determined

t/°C	Solubility/mol % Li[a]	Solubility/mol % Li[b]	Solubility/mol % S[a,c]	Solubility/mol % S[b,c]
602	0.25, 0.29	37.3, 36.2	99.75, 99.71	62.7, 63.8
508	0.17, 0.15	37.1, 36.7	99.83, 99.85	62.9, 63.3
456	0.21, 0.20	38.5, 36.8	99.79, 99.80	61.5, 63.2
417	0.032, 0.031	36.8, 36.0	99.968, 99.969	63.2, 64.0
396	—	35.2, 33.4	—	64.8, 66.6
377	0.34	37.0	99.66	63.0
375	0.62, 0.79	36.7, 36.6	99.38, 99.21	63.3, 63.4

[a]The melting point of Li_2S determined in a Nb or vitreous graphite container was found at 1372 °C. It is the only equilibrium solid phase identified.
[b]The melting points of Li and S were found at 180.5 and 1180 °C, respectively.
[c]The eutectic point between Li_2S and S was found at ~365 °C.

Auxiliary Information

Method:
Li_2S was mixed in appropriate proportion with either Li or S. The mixtures were contained in borosilicate glass, quartz, Al for the S-rich melts and in vitreous graphite, Al, or Nb for the Li-rich melts. Normal and differential thermal analysis curves were recorded with the use of Pt/Pt–Rh(10%) thermocouples, calibrated on melting points of KNO_3 , Sn, Zn, Al, and quartz from the NBS. The melting point of Li_2S was determined in Nb or graphite crucibles. Chemical analysis was used to determine the composition of samples in which the phase separation occurred. A high-speed centrifuge was utilized to speed up the process. After the centrifuging for several hours the quartz ampoules were quenched in liquid N and separated mechanically in a glove box. Li was analyzed by flame photometry. The S content was calculated by the difference. The solid equilibrium phases were studied by x-ray diffraction.

Source and Purity of Materials:
S: 99.999+% pure from Amer. Smelting and Refining Co.
Li: 99.98% pure (reactor grade) from Foote Mineral Co.
Li_2S: 97+% pure from Foote Mineral Co.
He: "purified."
Ar: nothing specified.

Estimated Error:
Solubility: precision ±5% (analysis of Li weight).
Temperature: accuracy ±1 K; but +10 K and −5 K for Li_2S.

Components:
(1) Sulfur; S; [7704-34-9]
(2) Lithium; Li; [7439-93-2]

Original Measurements:
R. A. Sharma, J. Electrochem. Soc. **119**, 1439–1443 (1972).

Variables:
Temperature: 647–1638 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

Several points on the S–Li liquidus were determined by quenching the melts

t/°C	Solubility/mol % Li[a]	Solubility/mol % Li[b]	Solubility/mol % S[a,c]	Solubility/mol % S[b,c]
374	34.12	0.035	65.88	99.965
415	34.61	0.031	65.39	99.969
456	32.90	0.070	67.10	99.930
532	32.90	0.150	67.10	99.850
537	31.50	0.350	68.50	99.650
588	30.80	0.220	69.20	99.780
682	30.50	0.330	69.50	99.670

[a]The Li-rich solubility limit.
[b]The S-rich solubility limit.
[c]Calculated by the compilers.

Several points on the S–Li liquidus were determined by the vapor transport technique

t/°C	Solubility/mol % Li[a]	Solubility/mol % Li[b]	Solubility/mol % S[a,c]	Solubility/mol % S[b,c]
		in the liquid–liquid region		
522	···	0.055	···	99.945
620	···	0.322	···	99.678
728	29.45	···	70.55	···
776	22.74	···	77.26	···
787	···	0.597	···	99.403
809	24.40	···	75.60	···
815	21.29	···	78.71	···
843	18.60	···	81.40	···
834	···	0.642	···	99.358
838	···	4.536	···	95.464
860	9.16	9.160	90.84	90.840
		in the liquid-solid region		
376	34.70		65.30	
442	37.93		62.07	
472	38.87		61.13	
484	36.39		63.61	
497	38.83		61.17	
550	37.47		62.53	
632	39.93		60.07	
698	44.08		55.92	
791	44.67		55.33	
854	50.13		49.87	
867	46.95		53.05	
893	50.93		49.07	
983	50.73		49.27	
1365	66.66		33.34[d]	

[a]The Li-rich region.
[b]The S-rich region.
[c]Calculated by the compilers.
[d]From differential thermal analysis.

Auxiliary Information

Method:
A Kanthal-wound tubular furnace, capable of being rocked, was used to heat the mixtures. Two stainless steel containers were placed inside the uniform temperature zone which was controlled by calibrated Chromel/Alumel thermocouples. Sealed containers, made of silica (Vycor), were used for the S-rich melts and dense-graphite containers were used for the Li-rich melts. The latter containers were further enclosed in the silica capsules. The experiments were performed in a He atmosphere. Weighed amounts of Li_2S and S were mixed thoroughly in the silica capsules and kept for equilibration for 24–72 h. They were quenched at 263 K. On solidifying, the two liquid layers formed were analyzed for their Li contents by flame photometry. A similar procedure was used at higher temperature using the pairs of graphite containers. The DTA of several samples was performed in a commercial apparatus using graphite crucibles.

Source and Purity of Materials:
S: 99.999% pure.
Li_2S: "a white powder" containing 29.8% Li instead of theoretical 30.26% Li.
He: nothing specified.

Estimated Error:
Solubility: accuracy of the chemical analysis ±1%.
Temperature: precision between ±3 K (at lowest temperatures) and ±10 K (at highest temperatures).

Components:
(1) Sulfur; S; [7704-34-9]
(2) Lithium; Li; [7439-93-2]

Original Measurements:
B. Cleaver and S. M. Upton, Electrochim. Acta **36**, 667–671, 673–677, 679–687 (1991).

Variables:
Temperature: 673 and 1643 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

Several points on the S–Li liquidus were determined

t/°C	Solubility/mol % S	Comment
400[a]	66.4; 67.0	on the S-rich side, two immiscible liquids
400[a]	62	on the S-poor side, Li_2S-equilibrium solid phase
400[b]	66.7	on the S-rich side, two immiscible liquids
400[b]	63.0	on the S-poor side, Li_2S-equilibrium solid phase

[a]From equilibration studies.
[b]From electrochemical S-activity measurements.

The melting point of Li_2S was determined at 1643±20 K.

Auxiliary Information

Method:
The melting point of Li_2S was measured using an optical pyrometer. Equilibrium studies were performed in silica tubes in a glove box. The tubes were evacuated and sealed, after the Li_2S and S mixtures were dispensed into. They were equilibrated in a rocking furnace for 3 days at 723 K, 4 days at 673 K, and then transferred to a centrifuge furnace in ~5 s. After 1 h of rotation at 673 K the rotor was slowed down gradually. The samples were removed and plunged into ice water. The tubes were broken open and separated phases analyzed: Na by atomic absorption spectroscopy and S by conversion to $BaSO_4$. The S activity was measured in an electrochemical cell: Pt, Ag_2S, S–Li/Ag//Ag_2S, S, Pt. S must not pass directly from one to the other half-cell. The cells were placed in an air furnace at 673 K. The composition of the S–Li melt was changed by passing the electric charge.

Source and Purity of Materials:
Li_2S: 99.5% pure from Alfa Inorganics Inc.
S: "dry"
N: "dry and O free."

Estimated Error:
Solubility: accuracy of analysis ±1%.
Temperature: stability in electrochemical experiments ±2 K; precision of thermal analysis ±20 K.

3.13. Lithium–Selenium

Components:
(1) Selenium; Se; [7782-49-2]
(2) Lithium; Li; [7439-93-2]

Evaluated by:
Hans Ulrich Borgstedt, Forschungszentrum Karlsruhe, Germany and Cezary Guminski, University of Warsaw, Poland, September 1994

Critical Evaluation

Cunningham *et al.*[1] investigated the Li–Se system in the whole composition range, however, only a part of the equilibrium phase diagram was constructed as result of this study. It was impossible to determine any liquidus point between pure Li and Li_2Se as well as a critical miscibility temperature in the Se-rich region. Since there was no observable difference between the melting point of pure Li and the Li-rich eutectic temperature one may estimate that the solubility of Se in liquid Li at the eutectic point is lower than 0.1 mol % Se. The high value of the melting point of Li_2Se points likewise on the low solubility at low temperatures.

The partial Se–Li phase diagram reflecting our contemporary knowledge about the system is shown in Fig. 10.

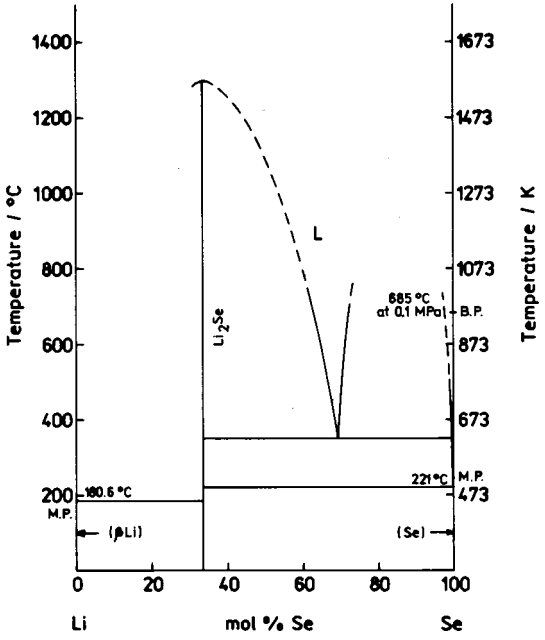

FIG. 10. Li–Se phase diagram (partial).

Tentative values of the solubility of Se in liquid Li

T/K	Solubility/mol % Se	Source
1575	33.3 congruent	(1)
973	53	(1)
623	70 eutectic	(1)
973	72	(1)
773	98.7[a]	(1)

[a]Se-rich range of the miscibility gap.

References:

[1]P. T. Cunningham, S. A. Johnson, and E. J. Cairns, J. Electrochem. Soc. **118**, 1941 (1971).

Components:
(1) Selenium; Se; [7782-49-2]
(2) Lithium; Li; [7439-93-2]

Original Measurements:
P. T. Cunningham, S. A. Johnson, and E. J. Cairns, J. Electrochem. Soc. **118**, 1941–1944 (1971).

Variables:
Temperature: 623–1575 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

Attempts to determine the whole Se–Li liquidus line were undertaken, but thermal effects were observed for a part of sample compositions

t/°C	Solubility/mol % Li[a]	Solubility/mol % Li[b]	Solubility/mol % Se[a,c]	Solubility/mol % Se[b,c]
700.0	···	27.6	···	72.4
499.5	1.32	30.2	98.68	69.8
492.0	···	33.3	···	66.7
453.2	···	29.2	···	70.8
422.0	2.23	30.1	97.77	69.9
403.5	0.45	29.9	99.55	70.1
364.0	0.54	31.9	99.46	68.1
360.5	···	30.8	···	69.2
340.5	0.18	···	99.82	···
283.0	0.50	···	99.50	···
249.8	0.80	···	99.20	···

[a]The Se-rich limit.
[b]The Li-rich limit.
[c]Calculated by the compilers.

The melting point of Li_2Se was found at 1302±5 °C. Li_2Se is the only equilibrium solid phase being identified. The melting points of Li and Se were found at 180.5±0.1 °C and 220.2 °C, respectively.

Auxiliary Information

Method:
The Li_2Se specimens prepared were mixed with appropriate amounts of the elements to obtain the desired composition of the samples. These were contained in quartz, 347 stainless steel, Al, Nb, or Ta crucibles depending on the composition and temperature range covered. The melting temperature data were obtained using normal and differential thermal analysis performed in a commercial analyzer calibrated on the NBS standards: quartz, KNO_3, Sn, Zn, and Al. Temperatures were measured with a Pt/Pt–Rh(10%) thermocouple. The melting point of Li_2Se, placed in a Nb crucible, was measured in a Mo wound resistance furnace. The composition of samples was verified by chemical analysis. Li was determined by flame photometry and Se by iodometric titration. The equilibrium solid phase was characterized by x-ray diffraction. The Se-rich samples were analyzed after several hours to several weeks of equilibration and quenching in liquid N.

Source and Purity of Materials:
Se: 99.999+% pure from Amer. Smelting and Refining Co.
Li: 99.98% pure (reactor grade) from Foote Mineral Co.
Li_2Se: prepared by reaction of molten Li and Se vapor in a Mo boat. The product had the formula
$Li_{2.05\pm0.1}Se$, it was also tested by x-ray analysis.
He: "purified".

Estimated Error:
Solubility: accuracy ±5% (determination of Li weight).
Temperature: accuracy ±1 K; precision between ±1 and ±5 K.

3.14. Lithium–Tellurium

Components:
(1) Tellurium; Te; [13494-80-9]
(2) Lithium; Li; [7439-93-2]

Evaluated by:
Hans Ulrich Borgstedt, Forschungszentrum Karlsruhe, Germany and Cezary Guminski, University of Warsaw, Poland, September 1994

Critical Evaluation

The knowledge in the Te–Li system is fragmentary. Attempts by Cunningham *et al.*[1] to determine the Li-rich liquidus part were not fruitful. Therefore, any quantitative information on the solubility of Te in liquid Li is not available. Since the eutectic temperature on the Li-rich side was decreased for 0.6 K in relation to pure Li upon an addition of Te,[1] one may evaluate that the Te content in the liquid phase at the eutectic temperature of 453 K is ~0.11 mol % Te, according to the theoretical estimation of Sangster and Pelton.[2] Cunningham *et al.*[1] observed several thermal effects at ~1085 K for the Li-rich alloys. These effects could be interpreted as a presence of either a liquid immiscibility region (8–24 mol % Te) or a corrosion product of a reaction between the Nb container and the Te sample, since such thermal arrests were not observed in the case of the W container. Anyway, a tendency of the system to limited miscibility may be observed due to the fact that Li_2Te is of rather ionic and Li of metallic nature. Without further experiments in this range one cannot suggest any solubility data in this range. The situation is more clear in the Te-rich range. A single point on the liquidus determined by Foster and Liu[3] is in good agreement with the data of Cunningham *et al.*[1] The phase relations in this part of the Te–Li diagram are not completely known which fact is reflected in Fig. 11. According to thermodynamic analysis of Sangster and Pelton[2] and Hitch *et al.*[4] and x-ray experiments of Hitch *et al.*,[4] $LiTe_3$ is unstable below 577 K; that was not observed in thermal analysis studies of Cunningham *et al.*[1]

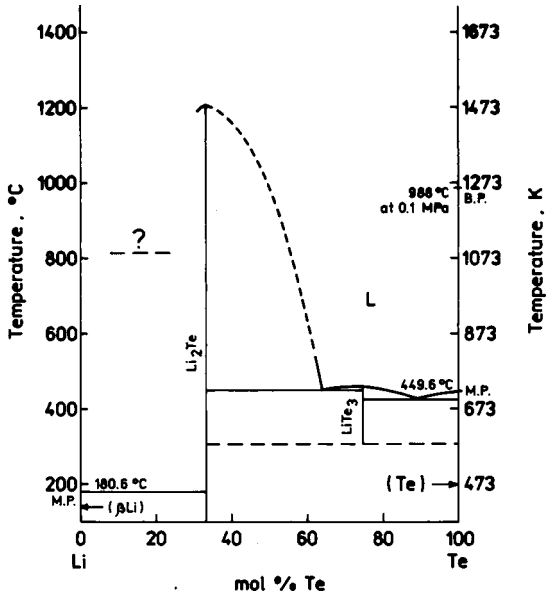

FIG. 11. Li–Te phase diagram (incomplete).

Tentative values of solubility of Te in liquid Li

T/K	Solubility/mol % Te	Source
453.2	0.1 eutectic	(3) estimation
477	33.3 congruent	(2)
798	61	(1)
722	63 eutectic	(2)
733	75 congruent	(2)
696	90 eutectic	(2)

References:

[1]P. T. Cunningham, S. A. Johnson, and E. J. Cairns, J. Electrochem. Soc. **120**, 328 (1973).
[2]J. Sangster and A. D. Pelton, J. Phase Equil. **13**, 300 (1992).
[3]M. S. Foster and C. C. Liu, J. Phys. Chem. **70**, 950 (1966).
[4]B. F. Hitch, L. M. Toth, and J. Brynestad, J. Inorg. Nucl. Chem. **40**, 31 (1978).

Components:
(1) Tellurium; Te; [13494-80-9]
(2) Lithium; Li; [7439-93-2]

Original Measurements:
M. S. Foster and C. C. Liu, J. Phys. Chem. **70**, 950–952 (1966).

Variables:
One temperature: 798 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

A point on the Te–Li liquidus was found at 798 K and 61 mol % Te. The Li_2Te solid phase was in equilibrium with the saturated solution.

Auxiliary Information

Method:
The emf of the cell: Te-Li/LiF–LiCl/Bi–Li was measured. The cell was operated in a Ta furnace under He atmosphere.[1] A Chromel/Alumel thermocouple was used to monitor the cell temperature. The electrode contacts were made of W. The Bi–Li alloy was prepared by melting both metals; only bright pieces were selected for further use. A porous BeO crucible contained the molten Te. The Te–Li alloys were prepared by coulometric addition of Li into molten Te. After each addition of Li the alloy was stirred and the cell potential recorded until it was constant to ±0.5 mV (usually ~20 min). The concentration of Li was calculated from the Coulometric charge assuming 100% current efficiency. The saturation point was found from the break point on the relation of potential versus logarithm of composition.

Source and Purity of Materials:
Te: from Amer. Smelting and Refining Co.; contained $1 \cdot 10^{-4}$ % Mg, Fe, Cu; further purified by melting and filtering under a He atmosphere.
Li: from Foote Mineral Co.; containing $3 \cdot 10^{-3}$ % Na, Cl; $3.1 \cdot 10^{-3}$ % N, and $2.8 \cdot 10^{-3}$ % K.
He: continuously purified by recirculation through an activated charcoal trap immersed in liquid N.
LiF–LiCl eutectic: reagent purity grade, further purified by passing Cl gas through the melt and the excess of Cl was removed by bubbling He through the melt.

Estimated Error:
Solubility: nothing specified.
Temperature: precision ±1 K.

References:
[1]M. S. Foster, S. E. Wood, and C. E. Crouthamel, Inorg. Chem. **3**, 1428–1431 (1964).

Components:
(1) Tellurium; Te; [13494-80-9]
(2) Lithium; Li; [7439-93-2]

Original Measurements:
P. T. Cunningham, S. A. Johnson, and E. J. Cairns, J. Electrochem. Soc. **120**, 328–330 (1973).

Variables:
Temperature: 453–1481 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The following points on the Te–Li liquidus were determined

t/°C	Solubility/mol % Te
179.9	0.1 eutectic
1201	33.3 congruent
1208	33.3 congruent
448.5	64.3 eutectic
454.0	66.9
455.6	69.0
457.6	70.2
457.5	70.6
458.0	72.1
459.3	73.1
461.0	75.0 congruent
459.2	75.0 congruent
459.2	75.0 congruent
460.1	75.0 congruent
459.0	76.2
455.2	79.6
459.0	80.0
455.5	80.3
448.5	82.5
441.6	84.9
430.7	88.0
423.4	88.8 eutectic
424.2	90.0
433.7	92.6
435.0	93.0
437.4	95.0
443.5	95.0
439.0	95.9

The melting points of Li and Te were found at 180.5±0.1 °C and 449.8±0.3 °C, respectively. It was tentatively suggested that the thermal arrests at 812±5 °C for three samples containing 9–20 mol % Te were due to a monotectic reaction of poorly miscible Li_2Te and Li. However, a possibility that these arrests were caused by a reaction of Nb container with Te could not be ruled out.

The results were also reported in Cunningham and Johnson.[1]

Auxiliary Information

Method:
The alloys were prepared from the elements in quartz, graphite, Nb, or W containers depending on the composition and maximum temperature of the experiments. Since the reaction could be quite violent, Li was added to Te in very small quantities. The solubility data were obtained by means of normal and differential thermal analysis performed in a commercial analyzer calibrated on the NBS standards: quartz, KNO_3, Sn, Zn, and Al. A Pt-wound resistance furnace was used to determine the melting point of Li_2Te (contained in a W crucible). The composition of selected samples was verified by chemical analysis. Li was determined by flame photometry and Te was found by difference. All essential operations were carried out inside a He atmosphere glove box.

Source and Purity of Materials:
Te: 99.999+% pure from Amer. Smelting and Refining Co.
Li: 99.98% pure from Foote Mineral Co.
He: "purified."

Estimated Error:
Solubility: accuracy ±0.5 mol %.
Temperature: accuracy between ±0.1 and ±7 K depending on the temperature range.

References:
[1]P. T. Cunningham and S. A. Johnson, U.S. Atom. Energy Comm. Rep. ANL-7978 (1973).

3.15. Lithium–Polonium

Components:
(1) Polonium; Po; [7440-08-6]
(2) Lithium; Li; [7439-93-2]
or Sodium; Na; [7440-23-5]
or Potassium; K; [7440-09-7]
or Rubidium; Rb; [7440-17-7]
or Cesium; Cs; [7440-46-2]

Evaluated by:
Hans Ulrich Borgstedt, Forschungszentrum Karlsruhe, Germany and Cezary Guminski, University of Warsaw, Poland, September 1994

Critical Evaluation

Information concerning either the solubility of Po in liquid Li, Na, K, Rb, or Cs or the phase diagrams of the Po–alkali metal systems has not been published so far. A similarity between the Po–alkali metal and Te–alkali metal systems is expected. The bonding of Po with Li is certainly more metallic than of Te with Li. This should lead to relatively higher solubility of Po in alkali metals than Te in alkali metals at the same temperature.

Po introduced to Na forms Na_2Po similar to the well known Na_2Te.[1,2] This compound is certainly the equilibrium solid phase, when liquid Na is saturated with Po. Na_2Po is probably the most stable compound, an existence of other compounds is possible.

References:

[1]V. G. Chlopin and E. B. Samarceva, Compt. Rend. Acad. URSS **IV**, 433 (1934).
[2]J. M. Goode, U.S. Atom. Energy Comm. Rep. MLM-677 (1952).

3.16. Lithium–Fluorine

Components:
(1) Fluorine; F; [7782-41-4]
(2) Lithium; Li; [7439-93-2]

Original Measurements:
A. S. Dworkin, H. R. Bronstein, and M. A. Bredig, J. Phys. Chem. **66**, 572–573 (1962).

Variables:
Temperature: 1180–1597 K

Prepared by:
H. U. Borgstedt and C. Guminski, September 1993

Experimental Data and Critical Evaluation

The miscibility of molten LiF and Li was measured. The results were read from Fig. 12 and recalculated to mol % F by the compilers.

t/°C	Solubility/mol % LiF	Solubility/mol % F
907	4.2[a]	4.0
1021	6.1[a]	5.7
1100	10.0[b]	9.1
1108	10.7[a]	9.7
1244	25.0	20.0
1330	···	40 c
1324	69.7[b]	41.0 LiF-rich side
1306	80.5[b]	44.6 LiF-rich side
1247	90.0[b]	47.4 LiF-rich side
1121	95.0[a]	48.7 LiF-rich side
1026	98.3[a]	49.6 LiF-rich side

[a]From sampling.
[b]From thermal analysis.
[c]Predicted by the authors.

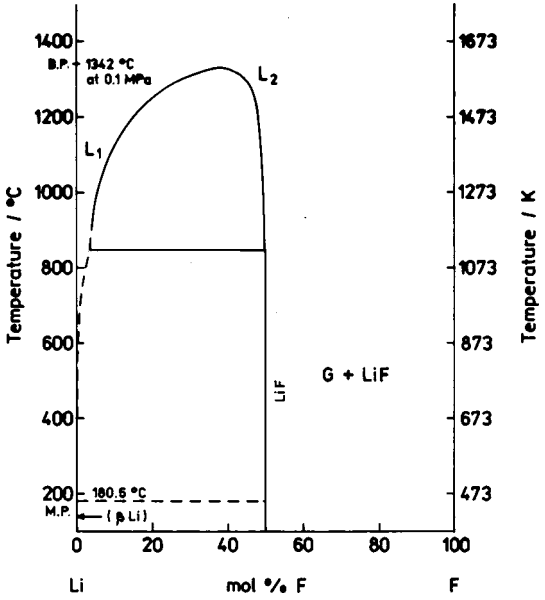

FIG. 12. Li–F phase diagram.

The monotectic temperature was found at 847 °C and the critical point was estimated to be at ~1327 °C and 37 mol % F. The melting point of LiF was determined at 848±1 °C.[3] The results of this study seem to be reliable. The Li–F phase diagram is shown in Fig. 12.

Auxiliary Information

Method:

Thermal analysis of samples (cooling curves) was performed in a stainless steel capsule placed in a Pt wound furnace. To detect small thermal effects the ratio of the container weight to the sample weight was reduced by employing thin walled tubes fitted with a bottom thermocouple well. A Pt/Pt–Rh thermocouple was used for temperature measurements.[1] At temperatures below, 1400 K and lower concentrations of LiF a separate sampling of the liquid Li-rich and LiF-rich phases were performed.[2]

Source and Purity of Materials:

LiF: "optical grade single crystal material" from Harshaw.
Li: 99.9+% pure, total content of C, N, O and other alkali metals ~0.05 mol %.
Ar: "dry."

Estimated Error:

Solubility: nothing specified; reading out procedure ±0.3 mol % for low F content and ±0.1 mol % for high F content.
Temperature: precision ±0.5 K (Johnson and Bredig[1]); reading out procedure ±3 K.

References:

[1]J. W. Johnson and M. A. Bredig, J. Phys. Chem. **62**, 604–607 (1958).
[2]M. A. Bredig, J. W. Johnson, and W. T. Smith, J. Am. Chem. Soc. **77**, 307–309 (1955).
[3]T. B. Douglas and J. L. Dever, J. Am. Chem. Soc. **76**, 4826–4828 (1954).

3.17. Lithium–Chlorine

Components:
(1) Chlorine; Cl; [7782-50-5]
(2) Lithium; Li; [7439-93-2]

Evaluated by:
Hans Ulrich Borgstedt, Forschungszentrum Karlsruhe, Germany and Cezary Guminski, University of Warsaw, Poland, October 1994

Critical Evaluation

Cl introduced into liquid Li reacts completely with this solvent and consequently LiCl and Li are the equilibrium phases in the system. Johnson[1] reported that a solubility of LiCl in liquid Li is small up to 1000 K, but experimental details were not specified. There are four independent studies of the mutual solubility of the molten (or solid) LiCl and liquid Li by Dworkin *et al.*,[2] Konovalov *et al.*,[3] Smimov *et al.*,[4,5] and Watanabe *et al.*[6–8] Dworkin *et al.*,[2] Smirnov *et al.*,[4,5] and Watanabe *et al.*[6–8] deal with the solubility of Li in molten LiCl, whereas Konovalov *et al.*[3] and Nakajima *et al.*[7] deal with the solubility of LiCl in liquid Li. Samples of saturated solutions were chemically analyzed in Refs. 2, 3, and 6–8. The Cl content in Konovalov *et al.*[3] was determined by nefelometry. Thermal analysis was performed by Dworkin *et al.*[2] and Nakajima *et al.*[7]

There is very good agreement of the data[2,4–7] concerning the solubility of Li in molten LiCl within their experimental errors. The data on the solubility of LiCl in liquid Li of Konovalov *et al.*[3] and Nakajima *et al.*[7] differ for some temperatures for more than 1 order of magnitude. Both sets of the results, when plotted as logarithm of the solubility versus the reciprocal temperature, show a curvature[7] or a wide scatter[3] of experimental points which should not occur for such dilute solutions. The correlation coefficients of fitting straight lines of both studies were found to be very poor. An extrapolation of the line representing the data of Konovalov *et al.*[3] to higher temperatures would suggest an infinitely high critical temperature for this system which would be in contrast to the other alkali metal–alkali metal halide systems. There is also no explanation for almost temperature independent solubility values obtained at lower temperatures in the measurements of Konovalov *et al.*[3] An extrapolation of the line representing the data of Nakajima *et al.*[7] to higher temperatures would suggest the critical temperature for the LiCl–Li system between 2000 and 2500 K (at elevated pressure); this seems to be a more reliable value for such case. Therefore, the evaluators give a preference to the results of Nakajima *et al.*[7] classifying them as doubtful.

The change of the slope of logarithm of the solubility versus reciprocal temperature near the monotectic temperature as found by Nakajima *et al.*[7] is unrealistic and the solubility value of 0.23 mol % Cl at 923 K is most probably in error. Also the estimation of Nakajima *et al.*[7] concerning the eutectic point (0.0022 mol % Cl at 453 K) at the Li-rich side seems to be overestimated. A composition of ~0.001 mol % Cl would be rather suggested.

A solubility of Cl in molten LiCl was elaborated in the volume concerned with the solubility of gases in salts; the solubility is low at normal pressures.[9] A partial phase diagram of the Cl–Li system is shown in Fig. 13. An asymmetrical immiscibility bow is expected with the critical point moved rather to the LiCl-rich side.

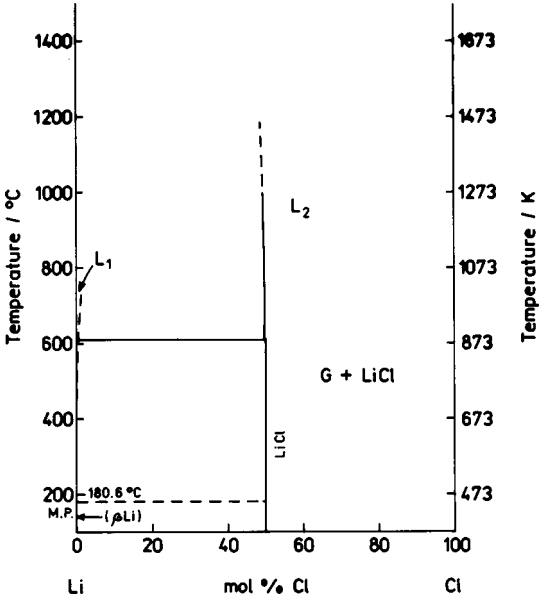

FIG. 13. Li–Cl phase diagram.

Doubtful values of the solubility of Cl in liquid Li

T/K	Solubility/mol % Cl	Source
453	~0.001	(6) extrapolation
573	~0.01	(6) interpolation
673	~0.05	(6)
773	~0.2	(6) interpolation
881	~0.3 monotectic	(6) extrapolation

Recommended (r) and tentative (t) values of the solubility of Cl in liquid Li on the LiCl-rich side of the immiscibility

T/K	Solubility/mol % Cl	Source
883	50.00 (t)	(1)
881	49.85 (t) monotectic	(3,4),(5,6) extrapolation
973	49.80 (r)	(3,4),(7) interpolation
1073	49.70 (t)	(3,4)
1173	49.60 (r)	(1),(3,4) interpolation
1273	49.49 (t)	(1)

References:

[1]C. E. Johnson, R. R. Heinrich, and C. E. Crouthamel, J. Phys. Chem. **70**, 242 (1966).
[2]A. S. Dworkin, H. R. Bronstein, and M. A. Bredig, J. Phys. Chem. **66**, 572 (1962).
[3]E. E. Konovalov, N. I. Seliverstov, and V. P. Emelyanov, Izv. Akad. Nauk SSSR, Met. **3**, 109 (1968).
[4]M. V. Smirnov and N. P. Podlesnyak, Tr. Inst. Elektrokhim. Akad. Nauk SSSR, Ural. Filial **14**, 14 (1970).
[5]M. V. Smirnov, Zh. Prikl. Khim. **43**, 1463 (1970).
[6]N. Watanabe, K. Nakanishi, and T. Nakajima, Nippon Kagaku Kaishi 401 (1974).
[7]T. Nakajima, M. Ryohei, K. Nakanishi, and N. Watanabe, Bull. Chem. Soc. Jpn. **47**, 2071 (1974).
[8]T. Nakajima, K. Hakanishi, and N. Watanabe, Bull. Chem. Soc. Jpn **49**, 994 (1976).
[9]R. P. T. Tomkins and N. P. Bansal, *Gases in Molten Salts*, Solubility Data Series, Vols. 45/46 (Pergamon, Oxford, 1990), p. 114.

Components:
(1) Chlorine; Cl; [7782-50-5]
(2) Lithium; Li; [7439-93-2]

Original Measurements:
A. S. Dworkin, H. R. Bronstein, and M. A. Bredig, J. Phys. Chem. **66**, 572-573 (1962).

Variables:
Temperature: 913 and 1273 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data
The solubility of Li in LiCl melt was determined

t/°C	Solubility/mol % Li	Solubility/mol % Cl[a]
640	0.5±0.2	49.87±0.05
1000	2.0±0.2	49.49±0.05

[a]Calculated by the compilers.

Auxiliary Information

Method:
An apparatus was built which permitted the direct sampling of the saturated solution at selected temperatures.[1] The melts were held in both Mo and stainless steel crucibles; any influence on the container material was not noticed. The apparatus had one entry port on the rotable turret. Li was introduced into the molten LiCl by means of a perforated stainless steel rod which acted both as a container for the melt and a stirrer. The basket was removed after equilibration and a sample of the melt was taken by means of a sampling device for further unspecified analysis.

Source and Purity of Materials:
LiCl: reagent grade purity; further purified by a very slow heating (just below the melting temperature) in HCl atmosphere and filtered.
Li: 99.9+% pure, total amount of C, N, O, and other alkali metals of 0.05%.
Ar: "dry."

Estimated Error:
Solubility: precision ±0.05 mol %.
Temperature: nothing specified; precision ±1 K (by the compilers).

References:
[1]M. A. Bredig and H. R. Bronstein, J. Phys. Chem. **64**, 64–67 (1960).

Components:
(1) Chlorine; Cl; [7782-50-5]
(2) Lithium; Li; [7439-93-2]

Original Measurements:
E. E. Konovalov, N. I. Seliverstov, and V. P. Emelyanov, Izv. Akad. Nauk SSSR, Met. **3**, 109–112 (1968).

Variables:
Temperature: 476–873 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of Cl in liquid Li at several temperatures was determined. The values were read from a figure and recalculated to mol % Cl by the compilers.

t/°C	Solubility/mass % LiCl	Solubility/mol % Cl
203	0.0068	0.0011
205	0.0048	0.00077
250	0.0064	0.00104
251	0.0073	0.0012
300	0.0066	0.00107
312	0.0073	0.0012
400	0.0161	0.0026
422	0.0073	0.0012
452	0.0105	0.0017
500	0.018	0.0029
600	0.065	0.0106

Auxiliary Information

Method:
An Armco Fe container was filled with molten Li. A sufficient excess of LiCl was added into the container which was kept in an oven at constant temperature for 8 h in an Ar atmosphere. Samples of Li were filtered through two filters: a steel net and a metallo-ceramic frit with pore size of 30–40 μm. The frits were prepared according to the recipe of Shibryaev and Pavlovskaya.[1] One to three samples of the filtrate were collected at selected temperature in ampoules without hermetical sealing of the apparatus. The Cl content in the samples was determined by nefelometry. The content of Li was analyzed by an unspecified method.

Source and Purity of Materials:
Nothing specified.

Estimated Error:
Solubility: nothing specified; reading out procedure ±0.0005 mol % Cl.
Temperature: accuracy ±2%; reading out procedure ±2 K.

References:
[1]B. F. Shibryaev and E. I. Pavlovskaya, Khim. Promysl. **3**, 232 (1963).

Components:
(1) Chlorine; Cl; [7782-50-5]
(2) Lithium; Li; [7439-93-2]

Original Measurements:
M. V. Smirnov and N. P. Podlesnyak, Zh. Prikl. Khim. **43**, 1463–1466 (1970); Tr. Inst. Elektrokhim. Akad. Nauk SSSR Ural. Fillial **14**, 14–16 (1970).

Variables:
Temperature: 938–1173 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of Li in molten LiCl was determined

t/°C	Solubility/mol % Li	Solubility/mol % Cl[a]
665	0.65	49.84
710	0.78	49.80
760	1.00	49.75
810	1.19	49.70
850	1.50	49.62
900	1.76	49.58

[a]Recalculated to mol % Cl in Li by the compilers.

Auxiliary Information

Method:
Measurements were performed in a hermetically closed bomb made of 1Kh18N9T stainless steel.[1] An Alundum crucible contained the LiCl melt. Temperatures were controlled by a Chromel/Alumel thermocouple sheathed by an Armco tube. Defined amounts of Li were introduced into molten LiCl by electrolysis at constant potential with the use of an Armco Fe cathode and a Cl anode in the cell with Fe cathode and Cl anode separated by the Alundum diaphragm. The electrolytic charge was measured by means of a Cu coulometer. Potentials of the cell during and after the electrolysis were monitored as function of Li concentration and temperature. Potentials of equilibrium conditions were reached for 20–30 min after the electrolysis was stopped. The saturating concentration of Li in the molten LiCl was estimated from break points on plots relating the equilibrium potential on the logarithm of the Li concentration. The experiments were performed in an Ar atmosphere.

Source and Purity of Materials:
LiCl: chemically pure, dried under vacuum for 16–20 h, melted in an Ar atmosphere, electrolyzed under controlled potential till deposition of Li on Fe cathode, treated with bubbled Cl for 2 h and then with bubbled Ar for 1 h; finally contained $\sim 5 \cdot 10^{-6}$ mol % of alkality.
Li: obtained by electrolysis of LiCl (separated by an Alundum diaphragm).
Ar: dried and purified by subsequent contact with Ca at 873 K, Ti at 1123 K, and Li at 623 K.

Estimated Error:
Solubility: nothing specified; current efficiency was 100%±1%.
Temperature: nothing specified.

References:
[1]M. V. Smirnov and N. P. Podlesnyak, Tr. Inst. Elektrokhim. Ural. Filiala Akad. Nauk SSSR **11**, 101–108 (1968).

Components:
(1) Chlorine; Cl; [7782-50-5]
(2) Lithium; Li; [7439-93-2]

Original Measurements:
T. Nakajima, R. Minami, K. Nakanishi, and N. Watanabe, Bull. Chem. Soc. Jpn. **47**, 2071–2072 (1974).

Variables:
Temperature: 567–923 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of Cl in liquid Li was determined at several temperatures

t/°C	Solubility/mol % LiCl	Solubility/mol % Cl[a]
~180	0.0022	0.0022 eutectic
294	0.007	0.007
322	0.019	0.019
394	0.069	0.069
450	0.14±0.02	0.14
540	0.21	0.21
650	0.23±0.01	0.23
656	99.34[b]	49.83[c]
662	99.34±0.10[b]	49.83[c]
678	99.3[d]	49.8[c]
750	99.00±0.02	49.75[c]
850	98.78	49.69[c]

[a]Calculated by the compilers.
[b]Reported in Watanabe *et al.*[1]
[c]LiCl-rich melt.
[d]Reported in Nakajima *et al.*[3]

The LiCl–Li system shows liquid immiscibility with the monotectic temperature found at 608 °C. Differential thermal analysis experiments performed at temperatures up to 1350 °C (slightly above the boiling point of Li). Even at this maximum temperature no critical point of the liquid miscibility was reached. When O, N, or H_2O (as contaminants) were present in the system the equilibrium was slowly reached and higher values of the apparent solubility of Li in the LiCl melt were measured and graphically presented in Watanabe *et al.*[1]

Auxiliary Information

Method:
The determinations were performed by a mutual saturation of liquid Li and LiCl. The equilibrated phases were sampled for analysis. A test cell used was made of stainless steel, as described in Watanabe *et al.*[1] The cell was loaded with LiCl and Li, sealed and placed in a closed stainless steel container equipped with a thermocouple. Samples of the melt were dissolved in H_2O. The amount of H gas was measured quantitatively. The amount of Cl was determined by the Mohr's method. Differential thermal analysis (DTA) was carried out using a Mo cell in which Li and LiCl were sealed by means of electron beam welding. The measurements were performed in a commercial micro DTA apparatus.

Source and Purity of Materials:
LiCl: 99% pure, dried under vacuum, fused in HCl atmosphere, excess of HCl removed by evaporation at elevated temperature, kept in an Ar atmosphere.[2]
Li: 99% pure, surface washed with kerosene and ethyl ether.
Ar: "dry, purified."

Estimated Error:
Solubility: precision better than ±15%.
Temperature: nothing specified; precision ±6 K or better, as reported in Watanabe *et al.*[1]

References:
[1]N. Watanabe, K. Nakanishi, and T. Nakajima, Nippon Kagaku Kaishi 401–404 (1974).
[2]H. A. Laitinen, W. S. Ferguson, and R. A. Osteryoung, J. Electrochem. Soc. **104**, 516–521 (1957).
[3]T. Nakajima, K. Nakanishi, and N. Watanabe, Bull. Chem. Soc. Jpn. **49**, 994–997 (1976).

3.18. Lithium–Bromine

Components:
(1) Bromine; Br; [7726-95-6]
(2) Lithium; Li; [7439-93-2]

Evaluated by:
Hans Ulrich Borgstedt, Forschungszentrum Karlsruhe, Germany and Cezary Guminski, University of Warsaw, Poland, October 1994

Critical Evaluation

Experimental investigations concerning the solubility of Br in liquid Li have not been performed. Bredig[1] predicted, by analogy to other alkali metal–halogen systems, that a quite limited mutual solubility of molten Li and LiBr (formed in reaction of Br and Li) should exist. The monotectic temperature should be placed at 822 K, it is 1 K below the melting temperature of LiBr at 823 K. The Br–Li phase diagram should be of the same type as those for the I–Li and Cl–Li systems.

References:
[1]M. A. Bredig, *Molten Salt Chemistry*, edited by M. Blander (Interscience, New York, 1964), p. 367.

3.19. Lithium–Iodine

Components:
(1) Iodine; I [7553-56-2]
(2) Lithium; Li; [7439-93-2]

Original Measurements:
A. S. Dworkin, H. R. Bronstein, and M. A. Bredig, J. Phys. Chem. **66**, 572–573 (1962).

Variables:
Temperature: 823 and 1223 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data
The solubility of Li in molten LiI was measured

t/°C	Solubility/mol % Li	Solubility/mol % I[a]
550	1.2±0.5	49.70±0.1
950	2.5±0.5	49.37±0.1

[a]Recalculated to mol % I by the compilers.

Attempts of the authors to perform thermal analysis above 1000 °C were not successful (see Fig. 14).

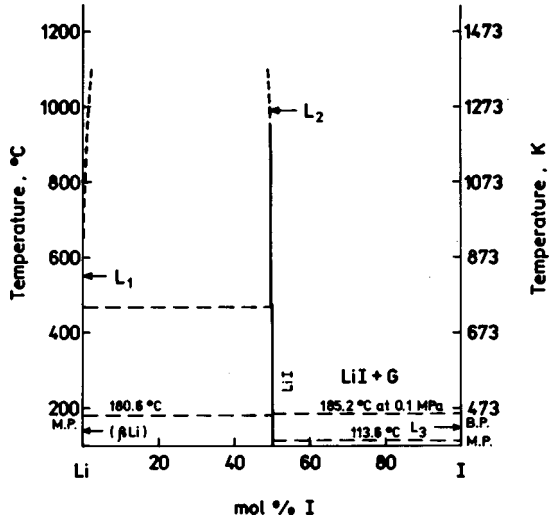

FIG. 14. Li–I phase diagram.

Auxiliary Information

Method:
An apparatus was constructed which permitted the direct sampling of the saturated solution at a selected temperature.[1] The melts were held in both Mo and stainless steel crucibles; any dependence on the container material was not noticed. The apparatus had one entry port on the rotatable turret. The Li was introduced into the molten LiI by means of a perforated stainless steel basket which was attached to a stainless steel rod and which acted both as a container for the Li and a stirrer. The basket was removed after equilibration and a sample of the melt was taken by means of a sampling device for further analysis.

Source and Purity of Materials:
LiI: reagent grade purity; purified by very slow heating in a HI atmosphere (solution just below the melting temperature), melted in an Ar atmosphere and filtered.
Li: 99.9+% pure, total amount of C, N, O, and other alkali metals of 0.05 mol %.
Ar: "dry."

Estimated Error:
Solubility: precision ±0.1 mol %.
Temperature: nothing specified.

References:
[1]M. A. Bredig and H. R. Bronstein, J. Phys. Chem. **64**, 64 (1960).

3.20. Lithium–Astatine

Components:
(1) Astatine; At; [7440-68-8]
(2) Lithium; Li; [7439-93-2]
or Sodium; Na; [7440-23-5]
or Potassium; K; [7440-09-7]
or Rubidium; Rb; [7440-17-7]
or Cesium; Cs; [7440-46-2]

Evaluated by:
Hans Ulrich Borgstedt, Forschungszentrum Karlsruhe, Germany and Cezary Guminski, University of Warsaw, Poland, October 1994

Critical Evaluation

Experimental material has not been published so far concerning any of these five systems. Due to an increase of the metallic character of At in comparison to I one should expect a better miscibility of the components in each of these binary systems with At than with I. However, a prognosis of any quantitative data would be premature.

3.21. Lithium–Helium

Components:
(1) Helium; He; [7440-59-7]
(2) Lithium; Li; [7439-93-2]

Original Measurements:
H. Slotnick, S. M. Kapelner, and R. E. Cleary, U.S. Atom. Energy Comm. Rep. PWAC-380 (1965).

Variables:
Temperature: 922–1144 K;
Pressure: 0.125–0.31 MPa

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data and Critical Evaluation

The solubility of He in liquid Li at 0.241 MPa was determined

t/°C	Solubility/mol He dm^{-3} Li atm^{-1}	Mean Solubility/mol % He Pa^{-1}[a]
649	$2.46\cdot10^{-7}$, $5.31\cdot10^{-7}$	$(5.7\pm2.0)\cdot10^{-12}$
760	$4.25\cdot10^{-7}$, $5.15\cdot10^{-7}$	$(7.0\pm0.7)\cdot10^{-12}$
871	$4.93\cdot10^{-7}$, $6.33\cdot10^{-7}$	$(8.6\pm1.0)\cdot10^{-12}$

[a]The mean value calculated by the compilers.

The authors proposed a fitting equation:

$$\log(\text{soly/mol \% He Pa}^{-1}) = -7.33 - 840\ (T/\text{K})^{-1},$$

which was tested by the compilers. There is a dimensional error in the solubility equation reported in Hubberstey.[4] The solubility of He in liquid Li at 760 °C as function of pressure was determined.

p/atm	p/MPa[a]	Solubility/mol He dm^{-3} Li	Solubility/mol % He[a]
1.23	0.125	$4.37\cdot10^{-7}$	$6.6\cdot10^{-7}$
2.38	0.241	$11.19\cdot10^{-7}$	$1.69\cdot10^{-6}$
3.06	0.310	$16.12\cdot10^{-7}$	$2.4\cdot10^{-6}$

[a]Calculated by the compilers.

The same results were previously reported in Cleary and Kapelner[1] and Kapelner and Cleary.[2] The data obtained are not very precise but reliable.

Solubilities of other noble gases in liquid Li were not investigated. The schematic Li-He phase diagram is shown in Fig. 15.

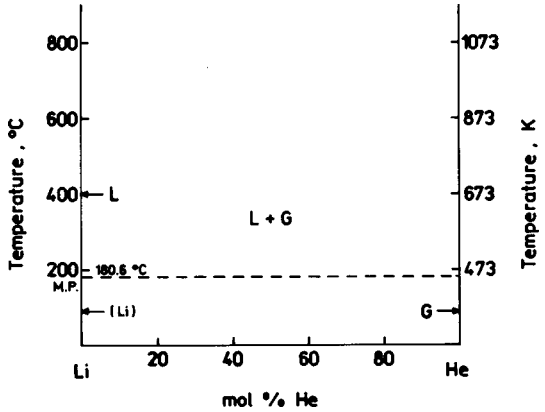

FIG. 15. Li–He phase diagram.

Auxiliary Information

Method:

The whole apparatus was constructed of 316 stainless steel. The temperature was measured and regulated by a Chromel/Alumel thermocouple. He at desired pressure was bubbled through liquid Li maintained in a dissolver at constant temperature. At saturation, which was reached after 4 h, and equilibration for 16–20 h, approximately half of the Li (measured accurately) was transferred to a stripper, which was kept at 533 K. He dissolved in Li was stripped by recirculating Ar. Aliquots of the He–Ar stripper gas were obtained in evacuated glass bulbs. To make the He enrichment, the gas was held for 1 h in cryogenic charcoal trap to permit Ar absorption. The enriched He gas, collected in sample bulbs, was analyzed in a mass spectrometer. The He content was obtained by a direct comparison with a reference sample. The volume of Li after the degassing of He was measured again.

Source and Purity of Materials:

He: purified by passage through a charcoal trap frozen by liquid N.
Li: nothing specified; probably purified by contacting with Ti at 1144 K, as in Leavenwoth and Cleary.[3]
Ar: purified by passage through activated synthetic zeolite and Ti sponge at 1116 K.

Estimated Error:

Solubility: precision not better than ±9%.
Temperature: precision not better than ±0.1 K.

References:

[1]R. E. Cleary and S. M. Kapelner, U.S. Atom. Energy Comm. Rep. BNL-756, pp. 21–33 (1962).
[2]S. M. Kapelner and R. E. Cleary, U.S. Atom. Energy Comm. Rep. CNLM-4094, pp. 3–4 (1962).
[3]H. W. Leavenwoth and R. E. Cleary, Acta Metall. **9**, 519–520 (1961).
[4]P. Hubberstey, *Handbook of Thermodynamic and Transport Properties of Alkali Metals*, edited by R. W. Ohse (Blackwell, Oxford, 1985), pp. 907–911.

3.22. Lithium–Radon

Components:

(1) Radon; Rn; [10043-92-2]
(2) Lithium; Li; [7439-93-2]
or Sodium; Na; [7440-23-5]
or Potassium; K; [7440-09-7]
or Rubidium; Rb; [7440-17-7]
or Cesium; Cs; [7440-46-2]

Evaluated by:

Hans Ulrich Borgstedt, Forschungszentrum Karlsruhe, Germany and Cezary Guminski, University of Warsaw, Poland, March 1997

Critical Evaluation

Experimental solubility data concerning these systems have not been published so far. However, taking into account the tendency that solubilities of noble gases in liquid Na decrease with their atomic number, one may safely predict that the solubilities of Rn in alkali metals are lower than the corresponding solubilities of Xe; see the Xe–Na system for comparison.

4. Solutions of Nonmetallic Substances in Sodium

4.1. Sodium–Hydrogen

Components:
(1) Hydrogen; H; [1333-74-0]
(2) Sodium; Na; [7440-23-5]

Evaluated by:
Hans Ulrich Borgstedt, Forschungszentrum Karlsruhe, Germany and Cezary Guminski, University of Warsaw, Poland, October 1999

Critical Evaluation

The knowledge on the solubility of H in liquid Na and on the H pressure over such solutions is important for Na cooled reactor technology. Plenty of work was performed on this subject, and some aspects of it were reviewed previously to different extents.[1–7] The dissolution of gaseous H in liquid Na was found in numerous studies[8–18] to be a first order process:

$$1/2\ H_2(g)+Na(l)\leftrightarrow NaH(l)\leftrightarrow NaH(s) \tag{1}$$

with moderately fast kinetics. The backward dissociation reaction is also a first order process.[12,19–23] Precipitation of NaH in Na makes that the whole reaction is controlled through diffusion. Kinetics of the crystallization and dissolution step of Eq. (1) was investigated by Fidler and Saagi.[24]

The experiments with the Na–H system are becoming more complex at higher temperatures, since gaseous H (under high pressure) can escape from a container. This effect could cause a hardly predictable change in the composition of the H–Na melt. It is therefore very difficult to prepare and investigate solid and liquid NaH of exactly stoichiometric proportions. Some authors[13,25–29] believed to measure the vapor pressure over pure NaH, but in fact they measured it over partly decomposed NaH. Since H gas takes part in the solubility equilibria, its solubility may be defined either as a H concentration in the liquid phase related to the H pressure over the liquid or as a H maximal concentration in the liquid phase being in equilibrium with solid (or liquid) NaH. The first kind of equilibrium is named isobaric solubility, since the H pressure and the corresponding H concentration are related by the Sieverts constant (K_s):

$$K_s=x_H P_H^{-1/2}, \tag{2}$$

where x_H is mol fraction of H in the solution and p_H is the H pressure over the solution. Dilute solutions of H in liquid Na obey the Sieverts law perfectly well up to 1 mol % H and 973 K. The law is obeyed acceptably well up to 5 mol % H (as reported in numerous studies[9,11,19,23,30–40]). Increasing of the H pressure over the solution causes the dissolution of more H in the molten Na solution and according to Eq. (1) NaH(s) starts to precipitate after the saturation point is reached. While the amount of NaH(s) in the melt increases, the H pressure over the melt is constant till NaH is saturated with H. The pressure, corresponding to the solubility limit of gaseous H, is named the equilibrium plateau pressure. The equilibrium plateau pressure (p_{Hs}) was measured by Pulham *et al.*,[8,9,12,19,22,31] Funada *et al.*,[32] Klostermeier and Franck,[41] Bhat and Borgstedt,[36] Dymova *et al.*,[25] Davies *et al.*,[42] Whittingham,[11] Ivanovskii *et al.*,[37–39,43] Meacham *et al.*,[20] Gibb,[44] Hérold,[13,27] McClure and Halsey,[34] Newcombe and Thompson,[21] Keyes,[26] Banus *et al.*,[45] Roy *et al.*,[46–48] Sinclair *et al.*,[33] Vissers *et al.*,[23,35,49] Compere and Savolainen,[40] Sollers and Crenshaw,[29] Skuratov *et al.*,[28] Katsuta and Furukawa,[50] Euphraim and Michel,[51] and Troost and Hautefeuille.[52] All experimental results except Hautefeuille[52] in which the equilibrium is characterized by the monovariant three-phase equilibrium (solid NaH, liquid saturated solution, and H gas), were approximated by the following fitting equation:

$$\log(p_{Hs}/\mathrm{Pa})=13.570-5925\ (T/\mathrm{K})^{-1}, \tag{3}$$

which is valid between 420 and 903 K.

All results gained between the monotectic temperature 905 and 600 K show a scatter of a few %, except those of Meacham *et al.*[20] Scatter of the pressure data below 600 K increased significantly reaching an order of magnitude at ~420 K; the results of Bhat and Borgstedt[36] deviating most negatively and the results of Katsuta and Furukawa[50] most positively in respect to Eq. (3). Similar equations were formulated in the majority of the publications mentioned and the reviews,[2,5,6,7] but in none of them such an extended temperature range was taken into account as in this evaluation. According to Eq. (3) the pressure reaches 101 325 Pa at 692 K. Above the monotectic temperature, at which two hardly miscible liquids (the Na and H rich) are in equilibrium with H gas, the corresponding dependence of H pressure on temperature may be given by the equation valid up to 1173 K:

$$\log(p_{Hs}/\mathrm{Pa})=10.840-3170\ (T/\mathrm{K})^{-1}. \tag{4}$$

The data of Arnoldov *et al.*[37] and Klostermeier and Franck[41] were used to formulate Eq. (4). An intersection of the dependencies expressed by Eqs. (3) and (4) yields the temperature of the monotectic reaction at 905 K and 10.7 MPa. These parameters are in complete agreement with Klostermeier and Franck,[41] who incorrectly specified this temperature as the melting point of NaH. Such difference, between the monotectic and the melting temperature of NaH, could be even 1–2 K but surely it is not the same temperature.

The temperature dependence of the Sievert's constant was investigated by several workers.[11,19,20,22,23,32,35,39–42,50,53,54] All results in the cited papers were in agreement, concerning the order of magnitude, but the slopes of the temperature dependence of the Sievert's constant were quite small and of different sign. The mean value estimated in this evaluation, taking into account many determinations[11,19,20,22,23,32,35,41,42,50,53,54] in the temperature range 573–973 K, is

$$K_s=x_H(P_{Hs})^{-1/2}=(9.2\pm1.0)\cdot10^{-4}\ \text{mol \% H Pa}^{-1/2}. \tag{5}$$

A very similar value was suggested by Hubberstey.[5] Four investigations[11,55,42,54] pointed to an influence of O present in Na that caused an apparent increase of K_s with increasing concentration of O. Species present in equilibrium in the gas phase were not investigated, and this phase seems to be dominated by H molecules with a small amount of Na atoms. NaH molecules should be present rather in traces at higher temperatures because the NaH molecule is not a stable one. As it was mentioned earlier, a solubility in such a system is also defined as an equilibrium H concentration in liquid Na saturated with solid or liquid NaH. In other words, it is a limit of the gaseous solubility. This solubility was measured using different experimental approaches. Williams *et al.*[56] carried out chemical analysis of filtrate of the saturated solution. Addison *et al.*[31] and Subbotin *et al.*[43] determined the H solubility with the use of the resistivity measurement technique. Savinov *et al.*[57] applied changes of the dynamic viscosity for the solubility estimation. Birault *et al.*,[58] Vissers *et al.*,[35,53] McCown and Mettler,[59] Funada *et al.*,[32] Bhat and Borgstedt,[36] Fidler and Saagi,[24] Arnoldov *et al.*,[60] and Rajan and Kale[61] determined the solubility from H meter readings. Newcombe and Thompson[21] as well as Smith and Simm[62] utilized electrochemical cells to determine the H solubility. Most frequently, the measurements of the H pressure were applied for the H solubility estimation.[9,11,19–22,34,38–42,50,63,64] Maupré[65] performed thermal analysis of the system at various pressures. The eutectic point on the Na-rich side was found to be practically degenerate of the melting point of Na (at 371.0 K). The liquid phase composition extrapolated to this temperature is $3\cdot10^{-5}$ mol % H. We selected results of many studies[9,11,55,20,66,21,22,24,31,34–36,42,43,59,63] to formulate the solubility equation; the equation was so adjusted that it goes through the monotectic point at 905 K and 4.6 mol % H (these values were obtained from an extrapolation of the data of Klostermeier and Franck[41] from the higher temperatures):

$$\log(\text{soly/mol \% H})=4.208-3210\ (T/\mathrm{K})^{-1}. \tag{6}$$

While formulating Eq. (6) we neglected several studies where the results were too low[32,53,58] as well as too high.[56,57,67] The result reported in the latter was $5.7\cdot10^{-2}$ mol % H at 473 K, but no details of the determination were available. Only a part of experimental points from Addison *et al.*[19] and Katsuta and Furukawa[50] was acceptable. One should mention that many[30,62,64,68,69] reported their results in the form of smooth equations giving no details, and only for the papers by Kozlov *et al.*[30] and Thorley and Raine[64] were the corresponding experimental details sufficiently described.

According to Naud,[15] the overestimation of the results in numerous studies[19,21,56,57] was due to the use of a glass apparatus while all the other investigators used all-metal equipment. The Pyrex glass starts to be attacked even at ~423 K and considerably at ~573 K. That attack leads to an increase of the O concentration in Na and finally of the H solubility in liquid Na. Unfortunately, there are no reliable solubility data between 673 K and the monotectic temperature. Therefore, one does not know whether Eq. (6) is justified in this temperature range. If one would subtract the right hand sides of Eq. (6) and half of Eq. (3), one should obtain the temperature dependence of the Sievert's constant (K_s) at temperatures below 905 K. The equation obtained this way,

$$\log(K_s/\text{mol \% H Pa}^{-1/2})=-2.577-247\ (T/\mathrm{K})^{-1} \tag{7}$$

is essentially different from that expressed by Eq. (5) and this suggests a slight dependence of K_s on temperature. The liquidus line between the monotectic and critical miscibility temperature was measured by Klostermeier and Franck[41] on the Na-rich side. The results may be approximated by the solubility fitting equation:

$$\log(\text{soly/mol \% H})=2.968-2089\ (T/\mathrm{K})^{-1}. \tag{8}$$

However, this relation should not be used for temperatures higher than 1173 K due to a crooking of the liquidus line near the critical point. The parameters of the critical miscibility point were not measured in experiments. Using three different procedures they were estimated by Klostermeier and Franck[41] to be $T_c=1500\pm70$ K, $x_c=39\pm4$ mol % H and $p_c=250\pm60$ MPa. According to a recent analysis of the same group (Sazafranski *et al.*[70]) the critical temperature is expected to be about 1328 K. The liquidus line between the critical point and the melting point of NaH was not systematically investigated. Klostermeier and Franck[41] reported that a solubility of Na in liquid NaH at 1173 K was found to be below 2 mol %. The melting point of NaH was first reported as 633 K (Moissan[71]) and later as higher than 1113 K (Gibb[44]). The purity of the sample for the first determination could be questionable, and experimental conditions of the second determination were not reported. Skuratov *et al.*[28] measured the melting point directly in a pressurized H atmosphere at 911±2 K at 10.7 MPa by thermal analysis cooling curves. The melting point found in Skuratov *et al.*[28] is 6 K higher than the monotectic temperature found by Klostermeier and Franck[41] but this difference, by analogy to the Li–H system, should be smaller. Maupré,[65] performing experiments similar to Skuratov *et al.*,[28] determined the melting point of NaH at 903 K and 10.97 MPa. The estimated monotectic temperature was proposed 3 K lower and the melting of NaH was proved to depend on the H pressure in the similar way as it is expressed by Eq. (3). Sazafranski *et al.*[70] reported the monotectic and the melting temperature of NaH at 904 and 905 K, respectively. The experimental basis of these results was not presented therein. Magomedov[72] calculated the melting point of NaH at 911.96 K.

Interactions of H with C and N (being simultaneously present in Na as contaminants) were not noticed at lower temperatures.[4,73] At 723–823 K, C dissolved in Na, reacted with H to form CH_4.[74] Many workers noticed an influence of O on the H solubility. Kinetics of reactions in the Na–H–O system was investigated by Naud[15] and Kozlov *et al.*[30] The corresponding equlibria were described by Myles and Cafasso.[3] Above 685 K liquid Na was in equilibrium with liquid NaOH (both species are only partly miscible), and below this temperature NaH coexisted with Na_2O in liquid Na. At lower temperatures only traces of NaOH in Na could be detected,[3,9,22] but there is no doubt that an association between H and O still occurs in liquid Na. The solubility of NaOH in liquid Na is elaborated separately. An addition of K to Na solvent makes noticeable, but not spectacular, changes of the H solubility and H equilibrium pressure.[38–40,57,60,75] The details are described in the evaluation of the K–H system. An addition of 1–4 mol % Li to the K–Na mixture considerably diminished H activity and resulted in the increased H solubility in these mixtures.[40] Most probably LiH molecules being formed in such conditions are well soluble in the K–Na medium.

The partial H–Na phase diagram is presented in Fig. 16. The complete liquid miscibility is reached at pressures significantly higher than the ambient pressure. The D–Na system is elaborated separately but no experimental material exists for the T–Na system.

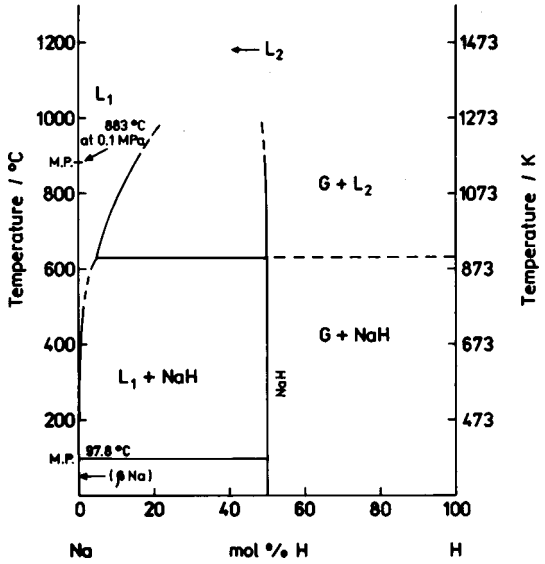

FIG. 16. Na–H phase diagram.

The recommended (r), tentative (t), and doubtful (d) values of the solubility of H in liquid Na at corresponding pressures

T/K	Solubility/mol % H	Source	p/Pa	Source
370	$3\cdot10^{-5}$ (t) eutectic	Eq. (6) extrapolated	$4\cdot10^{-3}$	Eq. (3)
473	$2.8\cdot10^{-3}$ (r)	Eq. (6)	7	Eq. (3), (50)
573	$4.0\cdot10^{-2}$ (r)	Eq. (6)	$4.8\cdot10^{4}$	Eq. (3), (26)
673	0.28 (r)	Eq. (6)	$4.8\cdot10^{4}$	Eq. (3), (9)
773	1.1 (d)	Eq. (6) extrapolated	$7\cdot10^{5}$	Eq. (3), (45)
905	4.6 (t) monotectic	(41) extrapolated	$1.0\cdot10^{7}$	(41)
973	7 (t)	(41)	$1.8\cdot10^{7}$	(41)
1073	10 (t)	(41)	$3.7\cdot10^{7}$	(41)
1173	16 (t)	(41)	$6.6\cdot10^{7}$	(41)

References:

[1]N. Rumbaut, F. Casteels, and M. Brabers, *Material Behavior and Physical Chemistry of Liquid Metal Systems*, edited by H. U. Borgstedt (Plenum, New York, 1982), p. 437.

[2]E. Fromm and H. Jehn, Bull. Alloy Phase Diagr. **5**, 323 (1984).

[3]K. M. Myles and F. A. Cafasso, J. Nucl. Mater. **67**, 249 (1977).

[4]P. Hubberstey, P. F. Adams, R. J. Pulham, M. G. Down, and A. E. Thunder, J. Less-Common Met. **49**, 253 (1976).

[5]P. Hubberstey, *Handbook of Thermodynamic and Transport Properties of Alkali Metals*, edited by R. W. Ohse (Blackwell, Oxford, 1985), p. 885.

[6]A. San-Martin and F. D. Manchester, Bull. Alloy Phase Diagr. **11**, 287 (1990).

[7]T. Gnanasekaran, J. Nucl. Mater. **274**, 252 (1999).

[8]R. J. Pulham, J. Chem. Soc., A 1389 (1971).

[9]R. J. Pulham and P. A. Simm, *Chemical Aspects of Corrosion and Mass Transfer in Liquid Sodium* (AIME, New York, 1973), p. 317.

[10]G. Naud, J. Sannier, and P. Vallet, Compt. Rend. **257**, 1276 (1963).

[11]A. C. Whittingham, J. Nucl. Mater. **60**, 119 (1976).

[12]C. C. Addison, R. J. Pulham, and R. J. Roy, J. Chem. Soc. 4895 (1965).

[13]A. Hérold, Ann. Chim. **6**, 536 (1951).

[14]P. B. Longton, U.K. Atom. Ener. Author. Rep. IGR-TN/C-435 (1957).

[15]G. Naud, Comm. Ener. Atom. (Fr.)Rep CEA-R-2583 (1964); transl. U.K. Atom. Ener. Author. Rep. TRG-Int. Ser.-522 (C) (1966).

[16]M. R. Hobdel and L. J. Newman, J. Inorg. Nucl. Chem. **31**, 1843 (1969).

[17]M. R. Hobdel and A. C. Whittingham, *Liquid Alkali Metals* (BNES, London, 1973), p. 5.

[18]V. Prohazka and M. Nedved, Coll. Czech. Chem. Commun. **38**, 2845 (1973).

[19]C. C. Addison, R. J. Pulham, and R. J. Roy, J. Chem. Soc. 116 (1965).

[20]S. A. Meacham, E. F. Hill, and A. A. Gordus, U.S. Atom. Energy Comm. Rep. APDA-241 (1970).

[21]R. J. Newcombe and J. Thompson, J. Polarogr. Soc. **14**, 104 (1968).

[22]R. J. Pulham and P. A. Simm, *Liquid Alkali Metals* (BNES, London, 1973), p. 1.

[23]D. R. Vissers, J. T. Holmes, L. G. Bartholme, and P. A. Nelson, Trans. Am. Nucl. Soc. **14**, 610 (1971).

[24]R. S. Fidler and R. Saagi, Nucl. Ener. **23**, 385 (1984).

[25]T. N. Dymova, S. I. Bakum, and U. Mirsaidov, Dokl. Akad. Nauk SSSR **216**, 87 (1976).

[26]F. G. Keyes, J. Am. Chem. Soc. **34**, 779 (1912).

[27]A. Hérold, Compt. Rend. **228**, 686 (1949).

[28]O. A. Skuratov, O. N. Pavlov, V. I. Danikin, and I. V. Volkov, Zh. Neorg. Khim. **21**, 2910 (1976).

[29]E. F. Sollers and J. L. Crenshaw, J. Am. Chem. Soc. **59**, 2724 (1937).

[30]F. A. Kozlov, E. K. Kuznetsov, G. P. Sergeev, G. L. Volchkov, and V. V. Zotov, *Trudy Fiziko-Energeticheskogo Instituta*, edited by V. A. Kuznetsov (Atomizdat, Moskva, 1974), p. 290.

[31]C. C. Addison, P. Hubberstey, J. Oliver, R. J. Pulham, and P. A. Simm, J. Less-Common Met. **61**, 123 (1978).

[32]T. Funada, I. Nihei, S. Yuhara, and T. Nakasuji, Nucl. Technol. **45**, 158 (1979).

[33]V. M. Sinclair, R. A. H. Pool, and A. E. Ross, U.S. Atom. Energy Comm. Rep. TID-7622, p. 35 (1961).

[34]D. W. McClure and G. D. Halsey, J. Phys. Chem. **69**, 3542 (1965).

[35]D. R. Vissers, J. T. Holmes, L. G. Bartholme, and P. A. Nelson, Nucl. Technol. **21**, 235 (1974).

[36]N. P. Bhat and H. U. Borgstedt, Atomkernenergie **35**, 170 (1980).

[37]M. N. Arnoldov, M. N. Ivanovskii, V. A. Morozov, S. S. Pletenets, and V. I. Subbotin, Atom. Ener. **28**, 18 (1970).

[38]M. N. Arnoldov, M. N. Ivanovskii, V. A. Morozov, S. S. Pletenets, and V. I. Subbotin, *Teplofizicheskie Svoistva Zhidkostei*, edited by A. K. Abas-Zade and E. E. Shpil'rain (Nauka, Moskva, 1970), p. 110.

[39]M. N. Ivanovskii, M. N. Arnoldov, V. A. Morozov, T. I. Moiseeva, and S. S. Pletenets, Izv. Akad. Nauk SSSR, Met. **1**, 201 (1980).

[40]E. L. Compere and J. E. Savolainen, Nucl. Sci. Engin. **28**, 325 (1967).

[41]W. Klostermeier and E. U. Franck, Ber. Bunsenges. Phys. Chem. **86**, 612 (1982).

[42]R. A. Davies, J. L. Drummond, and D. W. Adaway, *Liquid Alkali Metals* (BNES, London, 1973), p. 93.

[43]V. I. Subbotin, M. N. Ivanovskii, and M. N. Arnoldov, *Fiziko-Khimicheskie Osnovy Primeneniya Zhidkometallicheskikh Teplonositelei* (Atomizdat, Moskva, 1970), p. 235.

[44]T. R. P. Gibb, U.S. Atom. Energy Comm. Rep. NEPA-1841 (1951).

[45]M. D. Banus, J. J. Mc Sharry, and E. A. Sullivan, J. Am. Chem. Soc. **77**, 2007 (1955).

[46]D. N. Rodgers, G. D. Collins, and P. Roy, Trans. Am. Nucl. Soc. **14**, 613 (1971).

[47]P. Roy and D. N. Rodgers, Nucl. Technol. **12**, 388 (1971).

[48]P. Roy and D. N. Rodgers, Trans. Am. Nucl. Soc. **14**, 185 (1971).

[49]O. R. Vissers, L. G. Bartholme, and L. J. March, U.S. Atom. Energy Comm. Rep. ANL-7916, p. 18 (1972).

[50]H. Katsuta and K Furukawa, Nucl. Technol. **31**, 218 (1976).

[51]F. Ephraim and E. Michel, Helv. Chim. Acta **4**, 762 (1921).

[52]L. Troost and P. Hautefeuille, Compt. Rend. **78**, 807 (1874).

[53]O. R. Vissers, J. T. Holmes, P. A. Nelson, and L. G. Bartholme, Nucl. Technol. **12**, 218 (1971).

[54]H. Ullmann, K. Teske, T. Reetz, D. Rettig, F. A. Kozlov, and E. K. Kuznetsov, *Thermodynamics of Nuclear Materials* (IAEA, Vienna, 1980), Vol. 1, p. 273.

[55]A. C. Whittingham, Central Ener. Gener. Board Rep. RD/B/N-2550 (1974).

[56]D. D. Williams, J. A. Grand, and R. R. Miller, J. Phys. Chem. **61**, 379 (1957).

[57]V. B. Savinov, E. E. Konovalov, and Sh. I. Peizulaev, *Teplofizicheskie Svoistva Zhidkostei*, edited by A. K. Adas-Zade and E. E. Shpil'rain (Nauka, Moskva, 1970), p. 118.

[58]J. Birault, A. Brachet, E. Cambillard, J. Coron, L. Lannou, and C. Rault, U.S. Atom. Energy Comm. Rep. ANL-7520, Pt. I, p. 345 (1968).

[59]J. J. Mc Cown and G. W. Mettler, U.S. Energy Res. Devel. Adm. Rep. HEDL-TME-76-44, (1976).

[60]M. N. Arnoldov, M. N. Ivanovskii, S. S. Pletenets, and A. D. Pleshivtsev, Atom. Energy **32**, 234 (1972).

[61]M. Raian and R. D. Kale, *Liquid Metal Engineering and Technology* (Soc. Fr. Ener. Atom., Paris, 1988), Vol. 2, paper 604.

[62]C. A. Smith and P. A. Simm, *Liquid Metals Egineering and Technology* (BNES, London, 1984), Vol. 3, p. 103.

[63]V. I. Subbotin, F. A. Kozlov, E. K. Kuznetsov, and M. N. Ivanovskii, *Alkali Metal Coolants* (IAEA, Vienna, 1967), p. 461.

[64]A. W. Thorley and A. C. Raine, *The Alkali Metals* (The Chemical Society, London, 1967), p. 374.

[65]J. P. Maupré, Comm. Ener. Atom. (Fr.) Rep. CEA-R-4905 (1978).

[66]E. C. Kovacic and J. E. Meyers, U.S. Atom. Energy Comm. Rep. APDA-212, p. 111 (1967).

[67]Hargreaves, Atomics International; quoted by A. W. Thorley and C. Tyzack, *Thermodynamics of Nuclear Materials* (IAEA, Vienna, 1962), p. 365.
[68]V. I. Subbotin, F. A. Kozlov, Yu. I. Zagorulko, E. K. Kuznetsov, and L. G. Volchkov, U.S. Energy Res. Develop. Adm. Rep. CONF-760503, P1, 1976, p. 83.
[69]J. Rohde and M. Hissink, Centr. Techn. Inst., TNO, Apeldoorn, Netherlands (1972); cited in (35).
[70]A. W. Szafranski, E. Keller, and E. U. Franck, Ber. Bunsenges. Phys. Chem. **96**, 955 (1992).
[71]H. Moissan, Compt. Rend. **134**, 71 (1902).
[72]M. N. Magomedov, Zh. Fiz. Khim. **68**, 589 (1994).
[73]R. J. Pulham and P. Hubberstey, J. Nucl. Mater. **115**, 239 (1983).
[74]H. U. Borgstedt and S. R. Pillai, *Liquid Metal Engineering and Technology* (BNES, London, 1984), Vol. 2, p. 269.
[75]J. Reimann, R. Kirchner, M. Pfeff, and D. Rackel, *Liquid Metal Systems*, edited by H. U. Borgstedt and G. Frees (Plenum, New York, 1995), p. 233.

Components:
(1) Hydrogen; H; [1333-74-0]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
A. Hérold, Ann. Chim., Ser. 12, **6**, 536–581 (1951).

Variables:
Temperature: 423–742 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

Vapor pressures of NaH were measured by two methods. Since NaH easily decomposes to Na saturated with NaH and gaseous H_2, the pressure measured corresponds to the equilibrium H pressure over the NaH–Na system.

Dynamic method			Ni tube method[b]		
t/°C	p/Torr	p/Pa[a]	t/°C	p/Torr	p/Pa[a]
414	545	72 600	287.5	6.2	826
415.5	662	88 200	305	13.2	1760
424	838	111 700	330	36	4800
428	950	127 000	346	68	9060
439.5	1220	163 000	381	238.5	31800
450.5	1460	195 000	414	620	82600
453.5	1815	242 000			
459	1804	240 000			
461	2175	290 000			
463.5	2485	331 000			
468.5	2937	392 000			

[a]Calculated by the compilers.
[b]Also reported in Hérold[1] but all temperatures in Hérold[1] were 1 K higher than in this paper.

No solubility of NaH in liquid Na was detected at 150 °C. The melting point of Na saturated with NaOH differed from the melting point of pure Na less than 0.1 K. Kinetics of the reaction between H and Na was investigated.

Auxiliary Information

Method:
Na was placed in a glass ampoule. H was admitted into the ampoule and the ampoule was heated to 573 K. A constant pressure measured signalized an end of the reaction. In the dynamic conditions a sample of NaH, placed in an open cell, was decomposed in one part of a glass tube where temperature and pressure were higher, whereas in the other part of the tube a crystallization of NaH occurred, at lower temperature and pressure. Mean values of both parameters were assumed as the equilibrium values. The temperature was measured by means of a Chromel/Alumel thermocouple. The pressure was measured with the use of a mercury manometer. In another method a closed Ni tube containing NaH was used. H diffused through Ni walls and its equilibrium pressure was measured at constant temperature. Such equilibrium was reached after 24 h. The method to estimate the H solubility was not reported.

Source and Purity of Materials:
H: ''industrial'', further purified by passing through heated Cu and Na in a Pyrex glass apparatus.
Na: ''commercial'', further distilled. Its purity was controlled by the melting point measurement; it was in agreement within 0.2 K with the accepted temperature at that time. Cu and Zn were not detected.

Estimated Error:
Pressure: precision ±2%.
Temperature: precision better than ±1 K.

References:
[1]A. Hérold, Compt. Rend. **228**, 686 (1949).

Components:
(1) Hydrogen; H; [1333-74-0]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
D. D. Williams, J. A. Grand, and R. R. Miller, J. Phys. Chem. **61**, 379–381 (1957).

Variables:
Temperature: 525–718 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of H in liquid Na was determined. The data were read from a figure and recalculated to mol % H by the compilers.

t/°C	Solubility/mass % NaH	Solubility/mol % H
252[a]	0.005[d]	0.005
265[a]	0.003[d]	0.003
285[a]	0.013[d]	0.012
300[a]	0.04	0.04
323[b]	0.10	0.10
336[c]	0.25	0.24
352[b]	0.26	0.25
352[c]	0.37	0.35
365[b]	0.39	0.37
370[c]	0.64	0.61
379[c]	0.88	0.84
389[b]	1.00	0.94
399[b]	1.32	1.27
401[c]	1.74	1.66
411[b]	2.08	1.99
420[b]	2.40	2.30
425[b]	2.50	2.40
445[c]	4.30	4.13

[a]From the filtrate analysis.
[b]From H absorption studies.
[c]From H desorption studies.
[d]Numerical result.

NaH is the equilibrium solid phase.

Auxiliary Information

Method:
Three techniques were used for the analysis: filtration (at low temperatures), H absorption, and H desorption (at high temperatures). The apparatus for filtration was made of Pyrex glass. NaH was placed in a saturating chamber together with Na. Heat was applied to the mixture and temperature kept at desired level for proper equilibration. The solution was filtered into a sample bulb. Due to the attack of Na on the glass the solution contained also traces of Na_2O. Na was amalgamated and the rest titrated. In some runs, NaH dissolved in the saturated solution was thermally decomposed, and the amount of H gas was measured. The apparatus for absorption and desorption studies consisted of a metal saturation pot and a pressure measuring system made of Pyrex glass. For desorption, known amounts of Na and NaH were added to the saturation chamber. After evacuation, the temperature of the chamber was raised, a stopcock was opened slowly, and the excess of NaH allowed to dissociate. H gas passed into a calibrated volume cylinder for the measurement. In the absorption studies the charged pot was heated and cooled to various temperatures and the H pressure drop was recorded until no further absorption was indicated. This method was much slower than the desorption studies.

Source and Purity of Materials:
NaH: 98% pure.
Na: distilled.

Estimated Error:
Solubility: nothing specified; reading-out procedure ±0.01 mol % H.
Temperature: nothing specified; reading-out procedure ±1 K.

Components:
(1) Hydrogen; H; [1333-74-0]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
C. C. Addison, R. J. Pulham, and R. J. Roy, J. Chem. Soc., 116–121 (1965).

Variables:
Temperature: 523–603 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of H in liquid Na was determined

t/°C	Solubility/mass % H	Solubility/mol % H[a]
250	$4.2\cdot10^{-4}$	$9.6\cdot10^{-3}$
300	$2.2\cdot10^{-3}$	$5.0\cdot10^{-2}$
315	$5.2\cdot10^{-3}$	0.119
330	$1.04\cdot10^{-2}$	0.237

[a]Calculated by the compilers.

NaH is the equilibrium solid phase. The solubility values were approximated by the equation:

$$\log(\text{soly/mass \% H}) = 6.21 - 5021\ (T/\text{K})^{-1}.$$

The compilers tested the equation.

Auxiliary Information

Method:
Mixtures of NaH and liquid Na were prepared by tipping a glass vessel on its side and inserting a glass tube containing NaH until a mouth of tube almost touched Na. The tube was withdrawn and reweighed in an Ar atmosphere. The vessel was joined to a vacuum line. Na was stirred for 1 h at 383 K. A furnace containing the vessel was raised to the required temperature. A tap connected with the vessel was opened for 1 s. The gas expanded into a capillary tube and a manometer to measure the H pressure. The process was repeated at 5 min intervals. Within 1 h, the pressure was established. A part of H was pumped out making a new composition of the mixture. The pressure measurements were repeated. A break on pressure–composition isotherm corresponds to the saturation point.

Source and Purity of Materials:
H: 99.9% pure from British Oxygen Co. Ltd.; further purified.
Na: contained $8\cdot10^{-4}$ % O and 0.01% Ca (1).
NaH: prepared from the H and Na at >673 K (1) in an Ar atmosphere.
Ar: "purified."

Estimated Error:
Solubility: nothing specified; precision not better than ±1%.
Temperature: stability ±1 K.

References:
[1]C. C. Addison, R. J. Pulham, and R. J. Roy, J. Chem. Soc., 4895–4901 (1964).

Components:
(1) Hydrogen; H; [1333-74-0]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
D. W. McClure and G. D. Halsey, J. Phys. Chem. **69**, 3542–3547 (1965).

Variables:
Temperature: 536–623 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of H in liquid Na and the H plateau equilibrium pressure were determined. The solubility values were read from the figure by the compilers.

t/°C	Solubility/mol ratio	Solubility/mol % H	p/Torr	p/Pa
263.1	$1.2\cdot10^{-4}$	$2.4\cdot10^{-2}$	1.95	260
301.1	$2.2\cdot10^{-4}$	$4.8\cdot10^{-2}$	8.08	1080
350.2	···	···	⩾10	⩾1330

NaH is the equilibrium solid phase. Pressures measured for D gas over the melt were higher than for H by a factor of ~1.2.

Auxiliary Information

Method:
The functional parts of the apparatus include a cell, furnace, gas transfer system and a pressure measuring unit. The cell was made of Al with a Mo liner inside and type 347 stainless steel top. The cell was calibrated for its permeability of H and D through the top. After an introduction of Na, the cell was outgassed for 15 h. Gaseous H was introduced into the cell. To ensure equilibrium, the pressure was measured after 1 h. Pressure was measured with a manometer equipped with a cathetometer reading. Additional aliquots of H were added at 1 h intervals. The cell temperature was measured with a Chromel/Alumel thermocouple calibrated against the Pt/Rh standard.

Source and Purity of Materials:
H: "reagent grade" purchased from Air Reduction Sales Co.
Na: 99.996% pure from Baker and Adamson, outgassed for 12 h.

Estimated Error:
Solubility: nothing specified; reading-out procedure ±3%.
Temperature: stability ±0.05 K; accuracy ±1.0 K.

Components:
(1) Hydrogen; H; [1333-74-0]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
V. I. Subbotin, F. A. Kozlov, E. K. Kuznetsov, and M. N. Ivanovskii, *Alkali Metal Coolants* (IAEA, Vienna, 1967), pp. 461–478.

Variables:
Temperature: 473–615 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

Results of the solubility of H in liquid Na were presented in the figure. They were read from a figure and recalculated to mol % by the compilers.

t/°C	Solubility/mass % NaH	Solubility/mol % H
200	0.006	0.0055
235	0.012	0.0115
250	0.017	0.016
261	0.020	0.019
268	0.026	0.025
300	0.048	0.046
310	0.073	0.070
325	0.096	0.092
335	0.120	0.115
342	0.137	0.131

The results were represented by the solubility equation:

$$\log(\text{soly/mass \% H}) = 2.98 - 3209\,(T/\text{K})^{-1},$$

which was tested by the compilers. The results were reported in a graphical form in Kozlov *et al.*[2] An interaction between H and O in liquid Na was indicated.

Auxiliary Information

Method:
A method based on a H diffusion indicator was applied in this study. The pressure in a Ni chamber was measured by means of a vacuum lamp. Knowing the volume of the chamber and the time of H diffusion one may find the content of H in the Na solution being in equilibrium. The chamber was evacuated to 0.7 Pa. Gaseous H was introduced into the apparatus containing Na and the reagents were equilibrated at 673 and 723 K. Then the temperature was decreased to the desired level. Na was permanently circulated in a stainless steel loop. The pressure was measured and the amount of H saturating Na was calculated after calibration of the apparatus.

Source and Purity of Materials:
H: nothing specified.
Na: probably as in Arnoldov *et al.*[1]; contained $5\cdot10^{-4}$ % O, $1\cdot10^{-3}$ % H, Ca, Si, $5\cdot10^{-2}$ % C, 10^{-4} % Li and $3\cdot10^{-3}$ % Ni, Mn, Al, Be, Ag, Cu, Ti, and Fe, further distilled and purified by cold trapping.

Estimated Error:
Solubility: sensitivity $(2-4)\cdot10^{-3}$ mol % H; precision ±5%; reading-out procedure ±0.001 mol % H.
Temperature: nothing specified; reading-out procedure ±1 K.

References:
[1]M. N. Arnoldov, M. N. Ivanovskii, V. I. Subbotin, and B. A. Shmatko, *Alkali Metal Coolants* (IAEA, Vienna, 1967), pp. 479–488.
[2]F. A. Kozlov, E. K. Kuznetsov, G. P. Sergeev, L. G. Volchkov, and V. V. Zotov, *Trudy Fiziko-Energeticheskovo Instituta*, edited by V. A. Kuznetsov (Atomizdat, Moskva, 1974), pp. 290–308.

Components:
(1) Hydrogen; H; [1333-74-0]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
A. W. Thorley and A. C. Raine, *The Alkali Metals* (The Chemical Society, London, 1967), pp. 374–392.

Variables:
Temperature: 405–571 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of H in liquid Na was determined. The results extending from 405 to 571 K were presented graphically as a smooth line. The corresponding solubility equation in numerical form was reported in Whittingham:[1]

$$\log(\text{soly/mass \% H}) = 1.88 - 2590\ (T/\text{K})^{-1}.$$

The compilers confirmed the agreement of the graphical and numerical forms.

Auxiliary Information

Method:
The experiments were performed in a large-scale dynamic loop. Freshly distilled Na was equilibrated with NaH at different temperatures.[2] Sampling of the saturated solution was performed by means of a thin Fe crucible. The crucibles were precleaned by heating for a prolonged time under high vacuum. The Na solution was ladled into the crucible. The welded crucibles were removed and loaded into the analytical equipment. H was continuously removed from around the crucible and collected in an analytical section of defined volume. The total pressure before and after the H diffusion was compared. The solubility was calculated from the amount of H evolved.

Source and Purity of Materials:
NaH: nothing specified.
Na: purified by cold and hot trapping, finally by three-stage distillation; contained $<3\cdot10^{-4}$ % Cr, $\sim8\cdot10^{-4}$ % Fe, $6.0\cdot10^{-3}$ % K, $<5\cdot10^{-5}$ % Li, $\sim2\cdot10^{-4}$ % Ni, Pb, Ti, O, C, and $2.5\cdot10^{-5}$ % H, other metallic impurities were not detected.
Ar: "high purity," passed through activated molecular sieves, Ca turnings at 793–833 K, contained $<1\cdot10^{-4}$ vol % O and $5\cdot10^{-4}$ vol % H_2O.

Estimated Error:
Solubility: reproducibility $2\cdot10^{-5}$ mass % H at a level of $(1-5)\cdot10^{-4}$ mass % H.[3]
Temperature: nothing specified.

References:
[1]A. C. Whittingham, Centr. Ener. Gener. Board Rep. RD/B/N-2546 (1973).
[2]C. C. Addison, R. J. Pulham, and R. J. Roy, J. Chem. Soc., 116–121 (1965).
[3]J. A. Walker, E. D. France, J. L. Drummond, and A. W. Smith, *The Alkali Metals* (The Chemical Society, London, 1967), pp. 393–400.

Components:
(1) Hydrogen; H; [1333-74-0]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
J. Birault, A. Brachet, E. Cambillard, J. Coron, L. Lannou, and C. Rault, U.S. Atom. Energy Comm. Rep. ANL-7520, Pt. I, 345–373 (1968).

Variables:
Temperature: 378–434 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of H in liquid Na was determined. The results were reported in a figure; they were read from the figure and recalculated to mol % by the compilers.

t/°C	Solubility/mass % H	Solubility/mol % H
105	$1.2\cdot10^{-6}$	$2.7\cdot10^{-5}$
110	$1.3\cdot10^{-6}$	$3.0\cdot10^{-5}$
120	$1.8\cdot10^{-6}$	$4.1\cdot10^{-5}$
133	$3.2\cdot10^{-6}$	$7.3\cdot10^{-5}$
139	$4.2\cdot10^{-6}$	$9.6\cdot10^{-5}$
161	$1.46\cdot10^{-5}$	$3.3\cdot10^{-4}$

The source of H, from steam, H gas or by H diffusion through a solid metal, had no influence on the solubility results.

Auxiliary Information

Method:
The experiments were performed in a test loop made of a stainless steel. The circulation of Na was forced by an electro-magnetic pump. A Ni diaphragm detector of H connected with a mass spectrometer was used to measure the H pressure. The diaphragm was in contact with the circulating Na containing H. H was injected into Na with the use of a special apparatus. It was separately tested that the H flux was proportional to the H concentration for a fixed diaphragm temperature. The velocity of circulation of Na had no influence on the readings. The readings were dependent on diaphragm material, its thickness, and time of aging in the hot Na.

Source and Purity of Materials:
H: nothing specified.
Na: "nuclear grade" of purity.

Estimated Error:
Solubility: sensitivity $1\cdot10^{-7}$ mass % H, reading-out procedure $\pm2\cdot10^{-6}$ mol % H.
Temperature: nothing specified; reading-out procedure ±1 K.

Components:
(1) Hydrogen; H; [1333-74-0]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
R. J. Newcombe and J. Thompson, J. Polarogr. Soc. **14**, 104–108 (1968).

Variables:
Temperature: 537–564 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data
The solubility of H in liquid Na was determined by means of two methods

	H pressure			Electromotive force (emf)	
t/°C	Solubility/mol ratio	Solubility/mol % H[a]	p/Pa[c]	Solubility/mol ratio	Solubility/mol % H[a]
264.0	$1.10\cdot10^{-4}$	$2.20\cdot10^{-2}$	246	...	...
271.5	$1.87\cdot10^{-4}$	$3.54\cdot10^{-2}$	288	$1.87\cdot10^{-4}$	$3.54\cdot10^{-2}$
291.0	$3.30\cdot10^{-4}$[b]	$6.60\cdot10^{-2}$	657	$3.30\cdot10^{-4}$[b]	$6.60\cdot10^{-2}$

[a]Calculated by the compilers.
[b]The value identified by the compilers from a figure is $3.2\cdot10^{-4}$ mol ratio of H to Na.
[c]The equilibrium H plateau pressure.

Auxiliary Information

Method:
The emf experiments were performed in a cell: H(Na) saturated/alumino–silicate glass/H(Na) variable. The electrical contacts were made of molten Na with W wire. The cell was connected with an apparatus to measure H pressure over the H–Na melt. Molten Na was pipetted against a flow of N into the electrode compartments. The whole system was evacuated, the molten Na was degassed for several hours under vacuum. Then a proper H quantity was added into two compartments at 473 K. The cell was heated to the required temperature, the H pressure was measured on a manometer at time intervals >20 min, and continuous emf readings were taken. The procedure was repeated after every introduction of a new portion of H into the right half-cell. The solubility was found from a break of the dependence relating either pressure or emf on the H concentration.

Source and Purity of Materials:
H: "pure and dry."
Na: purified by filtering the molten metal through a glass sinter filter in N atmosphere.
N: "pure and dry."

Estimated Error:
Solubility: nothing specified; precision ±3% (estimated by the compilers).
Temperature: nothing specified.

Components:
(1) Hydrogen; H; [1333-74-0]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
S. A. Meacham, E. F. Hill, and A. A. Gordus, U.S. Atom. Energy Comm. Rep. APDA-241 (1970).

Variables:
Temperature: 569–674 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data
The solubility of H in liquid Na and the H equilibrium plateau pressure were determined

t/°C	Solubility/mass % H	Solubility/mol % H[a]	pH/Torr	pH/Pa[a]
295.7	$1.01\cdot10^{-3}$	$2.30\cdot10^{-2}$	3.9	520
296.7	$9.72\cdot10^{-4}$	$2.22\cdot10^{-2}$	4.5	600
318.6	$1.51\cdot10^{-3}$[b]	$3.44\cdot10^{-2}$	11.2[b]	1490
321.7	$1.56\cdot10^{-3}$	$3.56\cdot10^{-2}$	10.5	1400
400.0	$7.09\cdot10^{-3}$	$1.61\cdot10^{-1}$	23.25	3100
401.1	$6.81\cdot10^{-3}$	$1.55\cdot10^{-1}$	21.2	2800

[a]Calculated by the compilers.
[b]Reported in Kovacic and Meyers.[1]

The presence of O in Na increases slightly the H solubility in liquid Na and decreases slightly the H pressure over the melt. The solubility data were expressed by the following equation (tested by the compilers):

$$\log(\text{soly/mass \% H}) = 2.52 - 3180\ (T/\text{K})^{-1}.$$

Auxiliary Information

Method:
An elliptically shaped Ni capsule was filled with Na. The capsule wall was sufficiently thin to permit an effective H diffusion. The capsule was placed in a furnace. The temperature was controlled with the use of Cr/Al thermocouples. The capsule was heated to test conditions and degassed for 4–7 days. The vacuum system was leak tested and the free volume over the Na was determined. H gas was allowed to diffuse into the capsule and the rate of pressure decrease measured. The experiment was terminated as soon as equilibrium was attained (the pressure was not changed in three readings in 2–25 h). The solubility was found from the break point on a curve relating the square root of H pressure versus H concentration. The measured pressures were corrected for the thermal transpiration effect, the diffusion of H through the quartz parts of the apparatus, and absorption of H by Ni.

Source and Purity of Materials:
H: unspecified; purified by diffusion through the Ni capsule.
Na: from the technology loop; containing $(7-15)\cdot10^{-4}$ % O; Ca and C expected at 10^{-4} % level.

Estimated Error:
Solubility: standard deviation ±3% (in volume measurements); detectivity level of pressure 0.13 Pa; precision ±0.013 Pa.
Temperature: stability between ±0.1 and ±0.5 K.

References:
[1]E. C. Kovacic and J. E. Meyers, U.S. Atom. Energy Comm. Rep. APDA-212, p. 111 (1967).

Components:
(1) Hydrogen; H; [1333-74-0]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
V. I. Subbotin, M. N. Ivanovskii, and M. N. Arnoldov, *Fiziko-Khimicheskie Osnovy Primeneniya Zhidkometallicheskikh Teplonositelei* (Atomizdat, Moskva, 1970), pp. 235–243.

Variables:
One temperature: 623 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of H in liquid Na at 350 °C was found to be $8.6 \cdot 10^{-3}$ mass % H or 0.196 mol % H, as it was read out from a figure and recalculated by the compilers. NaH was found to be the equilibrium solid phase.

Auxiliary Information

Method:
Liquid Na circulated in a stainless steel loop. The loop was thermostated at the selected temperature with the use of a Ni/Cr thermocouple. The low content of impurities in the Na was controlled by chemical analysis. H was introduced into the liquid Na as gas and the reagents were equilibrated for a sufficient period. The electrical resistance of the liquid metallic solution in a capillary included in the loop was measured by means of a constant current bridge. The solubility of H in liquid Na corresponds to a break on the dependence relating the resistance of the alloy versus the concentration of H.

Source and Purity of Materials:
H: nothing specified.
Na: purified by cold trapping and outgassing at a high temperature.

Estimated Error:
Solubility: sensitivity $3 \cdot 10^{-5}$ % H; reading-out procedure $\pm 1 \cdot 10^{-4}$ mass % H.
Temperature: precision ±1 K; stability of the thermostat ±0.02 K.

Components:
(1) Hydrogen; H; [1333-74-0]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
V. B. Savinov, E. E. Konovalov, and Sh. I. Peizulaev, *Teplofizicheskie Svoistva Zhidkostei*, edited by A. K. Abas-Zade and E. E. Shpil'rain (Nauka, Moskva, 1970), pp. 118–120.

Variables:
Temperature: 567–668 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of H in liquid Na was determined

t/°C	Solubility/mass % H	Solubility/mol % H[a]
294	$2.1 \cdot 10^{-3}$	$4.8 \cdot 10^{-2}$
300	$4.2 \cdot 10^{-3}$	$9.6 \cdot 10^{-2}$
340	$1.3 \cdot 10^{-2}$[b]	0.30
344	$1.9 \cdot 10^{-2}$	0.42
367	$3.5 \cdot 10^{-2}$	0.79
395	$5.3 \cdot 10^{-2}$	1.19

[a]Calculated by the compilers.
[b]Numerically reported as $1.3 \cdot 10^{-3}$ mass % H, obviously an erroneous value.

Auxiliary Information

Method:
The solubility was determined by means of measurements of changes of the dynamic viscosity during the crystallization of the melt while decreasing the temperature. The viscosity was measured with the use of the torsion–pendulous method. Na was contained in a quartz ampoule closed under vacuum. H gas was introduced into liquid Na using a manometric system. The temperature was decreased with a rate 0.5 K/min. Damping of free oscillations of the ampoules was measured every 2 min. Decrements of the damping were plotted against temperature. An abrupt increase of the decrement corresponded to the temperature of the beginning of the crystallization from the supersaturated solution.

Source and Purity of Materials:
H: nothing specified.
Na: nothing specified.

Estimated Error:
Solubility: nothing specified; precision not better than ±5% (by the compilers).
Temperature: precision ±1 K (taking into account the rate of cooling and the readings).

Components:
(1) Hydrogen; H; [1333-74-0]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
D. R. Vissers, J. T. Holmes, P. A. Nelson, and L. G. Bartholme, Nucl. Technol. **12**, 218–225 (1971).

Variables:
Temperature: 429–463 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The results of the solubility of H in liquid Na were presented in a figure; they were read out and recalculated to mol % by the compilers

T/K	Solubility/mass % H	Solubility/mol % H
429	$8.5\cdot10^{-6}$	$1.9\cdot10^{-4}$
463	$4.2\cdot10^{-5}$	$9.6\cdot10^{-4}$

The same authors reported in Vissers *et al.*[1] a solubility equation and temperature dependence of the H equilibrium pressure; a source of the base of data is unknown.

$$\log(p\mathrm{H/Torr}) = 10.30 - 5633\ (T/\mathrm{K})^{-1}$$

$$\log(\mathrm{soly/mol\ \%\ H}) = 3.320 - 2842.3\ (T/\mathrm{K})^{-1}.$$

Auxiliary Information

Method:
The concentration of H in liquid Na was measured by means of a diffusion type of H-activity meter used as a leak detector in a pumped Na system at 673 K. A Ni membrane was specially designed to permit an operation under dynamic vacuum, generated by an ion pump, and also to permit a measurement of equilibrium H vapor pressure after proper valving of the apparatus. Samples of H gas were taken after various times. The amount of H in the samples was determined by gas chromatography. The concentration of H in liquid Na was calculated from the Sievert's law relationship. Na in the pumped system was cold trapped at selected temperature. The H solubility was obtained by assuming the ion-pump current to vary linearly with H activity of Na being monitored.

Source and Purity of Materials:
H: unspecified purity; purified by diffusion through a Ni membrane.
Na: cold trapped, contained $<1.6\cdot10^{-3}$ % O.

Estimated Error:
Solubility: precision ±4%; reading-out procedure ±3%.
Temperature: nothing specified; reading-out procedure ±2 K.

References:
[1]D. R. Vissers, J. T. Holmes, and P. A. Nelson, Trans. Am. Nucl. Soc. **14**, 610–611 (1971).

Components:
(1) Hydrogen; H; [1333-74-0]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
R. A. Davies, J. L. Drummond, and D. W. Adaway, *Liquid Alkali Metals* (BNES, London, 1973), pp. 93–99.

Variables:
Temperature: 423–498 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of H in liquid Na and the equilibrium H pressure were determined

t/°C	Solubility/mass % H	Solubility/mol % H[a]	p/Torr	p/Pa[a]
150	$3.5\cdot10^{-5}$	$8.0\cdot10^{-4}$	0.005; 0.005; 0.004	0.7
175	$7.7\cdot10^{-5}$	$1.76\cdot10^{-3}$	0.026; 0.024; 0.021	3.2
200	$1.28\cdot10^{-4}$	$2.9\cdot10^{-3}$	0.066; 0.071; 0.058	8.7
210	$1.83\cdot10^{-4}$	$4.2\cdot10^{-3}$	0.134; 0.138; 0.129	17.9
225	$2.09\cdot10^{-4}$	$4.8\cdot10^{-3}$	0.173; 0.181; 0.168	23.2

[a]Values calculated by the compilers.

An addition of O into the system makes a decrease of the equilibrium H pressure. The authors presented a solubility equation in their preceding publication:[1]

$$\log(\mathrm{soly/mass\ \%\ H}) = 1.835 - 2568\ (T/\mathrm{K})^{-1},$$

which does not fit to the data quoted above.

Auxiliary Information

Method:
The studies were performed in a circulating Na loop. The lower part of the loop was operated at <623 K and contained a cooler, electromagnetic pump, flowmeter, and cold trap. The upper section contained a heater and a facility for injecting H_2O or H gas. The mass of Na was measured by adding a known amount of ^{24}Na and counting the samples. Five membranes of Ni were incorporated in various sections of the circuit. Ar was used as a sweep gas. H was added to the circuit from a stainless steel bottle by diffusion through one Ni membrane. The H concentration on the other side of the membrane in Ar was measured by means of a catharometer. Equilibrium H pressure was measured after successive H additions. The H solubility in Na at cold trap temperature was calculated using Sievert's law constant determined in this work.

Source and Purity of Materials:
H: unspecified purity; purified by diffusion through Ni membrane.
Na: purified by cold trapping at 413–423 K; contained $\sim3\cdot10^{-4}$ % O.
Ar: 99.995+% pure.

Estimated Error:
Solubility: precision of Na estimation ±2%; precision of H estimation ±1%.
Temperature: precision ±5 K.

References:
[1]R. A. Davies, J. L. Drummond, and D. W. Adaway, Nucl. Engin. Intern. **16**, 493–495 (1971).

Components:
(1) Hydrogen; H; [1333-74-0]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
R. J. Pulham and P. A. Simm, *Liquid Alkali Metals* (BNES, London, 1973), pp. 1–4.

Variables:
Temperature: 623–673 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of H in liquid Na and the equilibrium plateau pressure were determined

t/°C	Solubility/mol % H	p/Torr	p/Pa[a]
350	0.1035	6.8	905
370	0.1725[b]	13.2	1760
400	0.2530[b]	35.7	4760
430	···	96	12800

[a]Calculated by the compilers.
[b]Also reported in Pulham and Simm.[1]

Kinetics of the formation and dissociation of NaH were investigated in Pulham and Simm.[1]

Auxiliary Information

Method:
The apparatus was constructed of 321 AISI stainless steel and consisted of a lower and an upper cylindrical reservoir welded together. The H pressure was measured by means of a diaphragm gauge, attached to the upper cylinder. An electromagnetic pump was used to circulate the liquid Na between the lower reservoir and the upper cylinder containing a jet. This allowed a continuous contact of the fresh metal with H gas. The apparatus was enclosed in a circulating air oven. The temperature was measured by a thermocouple. A known volume of H was expanded into liquid Na. Pressures were measured until an equilibrium value was reached. A break on a plot relating the pressure on the H concentration in liquid Na corresponds to the saturation.

Source and Purity of Materials:
H: nothing specified.
Na: purified by filtration at 383 K; it contained finally $<1.0 \cdot 10^{-3}$ % O and $<4.0 \cdot 10^{-3}$ % Ca.

Estimated Error:
Solubility: unspecified; accuracy of the pressure measurement ±2 Torr.
Temperature: precision ±1 K.

References:
[1]R. J. Pulham and P. A. Simm, *Chemical Aspects of Corrosion and Mass Transfer in Liquid Sodium* (AIME, New York, 1973), pp. 317–322.

Components:
(1) Hydrogen; H; [1333-74-0]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
D. R. Vissers, J. T. Holmes, L. G. Bartholme, and P. A. Nelson, Nucl. Technol. **21**, 235–244 (1974).

Variables:
Temperature: 401–476 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The results of the H solubility in liquid Na were presented in a figure; they were read from the figure and recalculated to mol % by the compilers

T/K	Solubility/mass % H	Solubility/mol % H
401	$7.4 \cdot 10^{-6}$; $7.5 \cdot 10^{-6}$	$1.7 \cdot 10^{-4}$; $1.7 \cdot 10^{-4}$
409	$1.05 \cdot 10^{-5}$; $1.02 \cdot 10^{-5}$	$2.4 \cdot 10^{-4}$; $2.3 \cdot 10^{-4}$
410	$1.17 \cdot 10^{-5}$	$2.7 \cdot 10^{-4}$
411	$1.17 \cdot 10^{-5}$; $1.16 \cdot 10^{-5}$	$2.7 \cdot 10^{-4}$; $2.6 \cdot 10^{-4}$
412	$1.30 \cdot 10^{-5}$; $1.28 \cdot 10^{-5}$	$3.0 \cdot 10^{-4}$; $2.9 \cdot 10^{-4}$
413	$1.29 \cdot 10^{-5}$; $1.27 \cdot 10^{-5}$	$2.9 \cdot 10^{-4}$; $2.9 \cdot 10^{-4}$
423	$1.7 \cdot 10^{-5}$	$3.9 \cdot 10^{-4}$
426	$1.8 \cdot 10^{-5}$	$4.1 \cdot 10^{-4}$
429	$2.4 \cdot 10^{-5}$	$5.5 \cdot 10^{-4}$
434	$2.9 \cdot 10^{-5}$	$6.6 \cdot 10^{-4}$
435	$3.3 \cdot 10^{-5}$; $2.4 \cdot 10^{-5}$; $2.3 \cdot 10^{-5}$	$7.5 \cdot 10^{-4}$; $5.5 \cdot 10^{-4}$; $5.3 \cdot 10^{-4}$
436	$2.5 \cdot 10^{-5}$	$5.7 \cdot 10^{-4}$
453	$5.4 \cdot 10^{-5}$	$1.23 \cdot 10^{-3}$
456	$5.8 \cdot 10^{-5}$; $5.0 \cdot 10^{-5}$; $4.9 \cdot 10^{-5}$	$1.3 \cdot 10^{-3}$; $1.14 \cdot 10^{-3}$; $1.12 \cdot 10^{-3}$
476	$9.5 \cdot 10^{-5}$; $9.4 \cdot 10^{-5}$	$2.2 \cdot 10^{-3}$; $2.1 \cdot 10^{-3}$

The authors proposed the solubility equation:

$$\log(\text{soly/mol \% H}) = 3.425 - 2880\ (T/\text{K})^{-1}$$

the validity of which was tested by the compilers. In a previous report[1] the authors presented the following numerical results; the method used was essentially the same.

t/°F	T/K[a]	Solubility/mass % H	Solubility/mol % H[a]
228	382	$3.9 \cdot 10^{-6}$	$8.9 \cdot 10^{-5}$
242	390	$4.6 \cdot 10^{-6}$	$1.05 \cdot 10^{-4}$
243	390	$5.2 \cdot 10^{-6}$	$1.19 \cdot 10^{-4}$
245	391	$5.0 \cdot 10^{-6}$	$1.14 \cdot 10^{-4}$
262	401	$7.3 \cdot 10^{-6}$	$1.67 \cdot 10^{-4}$
274	407	$9.4 \cdot 10^{-6}$	$2.2 \cdot 10^{-4}$
298	421	$1.59 \cdot 10^{-5}$	$3.6 \cdot 10^{-4}$
326	436	$2.75 \cdot 10^{-5}$	$6.3 \cdot 10^{-4}$
350	450	$4.6 \cdot 10^{-5}$	$1.05 \cdot 10^{-3}$
385	469	$8.5 \cdot 10^{-4}$	$1.94 \cdot 10^{-3}$
408	482	$1.38 \cdot 10^{-4}$	$3.2 \cdot 10^{-3}$
410	483	$1.40 \cdot 10^{-4}$	$3.2 \cdot 10^{-3}$

[a]Calculated by the compilers.

Auxiliary Information

Method:
The H level in liquid Na was measured by a diffusion type of H-activity meter. Na circulated in a test loop in which it was equilibrated with H at 723 K. The temperature of the loop was taken to be the saturation temperature. Temperature measurements were performed with a Chromel/Alumel thermocouple calibrated against a NBS Pt/Ir thermocouple. A change of H concentration in Na was monitored by a change in the H diffusion rate through a Ni membrane immersed in Na. The H partial pressure on the vacuum side of the membrane was measured by an ion pump. The H equilibrium pressures (measured at 723 K) were obtained for the cold trap temperature. The H contents were calculated using the Sievert's constant.

Source and Purity of Materials:
H: unspecified; purified by diffusion through a Ni membrane.
Na: unspecified; cold trapped in a cold trap of the loop at its coldest point.

Estimated Error:
Solubility: precision ±5%; reading out procedure ±2%.
Temperature: precision ±2 K; reading out procedure ±1 K.

References:
[1]D. R. Vissers, L. G. Bartholme, and L. J. Marek, U.S. Atom. Energy Comm. Rep. ANL-7916, pp. 18–20 (1971).

Components:
(1) Hydrogen; H; [1333-74-0]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
H. Katsuta and K. Furukawa, Nucl. Technol. **31**, 218–231 (1976).

Variables:
Temperature: 388–481 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of H in liquid Na and the H equilibrium plateau pressure were determined. The results were presented in a figure; they were read out and recalculated to mol % H and Pa by the compilers.

t/°C	Solubility/mass % H	Solubility/mol % H	p/Torr	p/Pa
115	$3.4\cdot10^{-5}$	$7.8\cdot10^{-4}$	$4.9\cdot10^{-3}$	0.65
132	$3.7\cdot10^{-5}$	$8.5\cdot10^{-4}$	$5.9\cdot10^{-3}$	0.78
140	$4.5\cdot10^{-5}$	$1.03\cdot10^{-3}$	$7.2\cdot10^{-3}$	0.96
163	$5.0\cdot10^{-5}$	$1.15\cdot10^{-3}$	$1.07\cdot10^{-2}$	1.42
178	$6.7\cdot10^{-5}$	$1.54\cdot10^{-3}$	$1.56\cdot10^{-2}$	2.1
194	$9.3\cdot10^{-5}$	$2.1\cdot10^{-3}$	$3.2\cdot10^{-2}$	4.2
194	$1.11\cdot10^{-4}$	$2.6\cdot10^{-3}$	$4.6\cdot10^{-2}$	6.1
200	$1.21\cdot10^{-4}$	$2.8\cdot10^{-3}$	$5.3\cdot10^{-2}$	7.0
208	$1.45\cdot10^{-4}$	$3.3\cdot10^{-3}$	$8.0\cdot10^{-2}$	10.6

Analogous measurements at an O concentration of $\sim3\cdot10^{-4}$ % pointed on an interaction between H and O present in liquid Na.

Auxiliary Information

Method:
A dynamic Na loop was made of 304 stainless steel. The H concentration in liquid Na was determined from the equilibrium H pressure inside a tube of thin bellow-shaped membranes (made of 316 L stainless steel) immersed in Na. The H pressure was measured with a calibrated Pirani gauge. A known quantity of H was introduced into the Na through the membrane of the H-meter tube arranged in the downstream of the Na. The change of H pressure in the liquid Na by H impregnation was measured through another tube arranged in the upstream of the Na. The Sieverts constant was obtained from the H pressure change and the impregnated H concentration. The pressure was always measured at 873 K, however, it was always related to the cold trap temperature in this part of the loop.

Source and Purity of Materials:
H: nothing specified.
Na: reactor grade, purified by cold trapping and hot trapping with Zr foil; contained $1\cdot10^{-5}$ % O.
Ar: nothing specified.

Estimated Error:
Solubility: nothing specified; precision not better than ±10% (by the compilers); reading-out procedure ±2%.
Temperature: precision ±1 K; reading-out procedure ±1 K.

Components:
(1) Hydrogen; H; [1333-74-0]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
J. J. McCown and G. W. Mettler, U.S. Energy Res. Devel. Adm. Rep. HEDL-TME-76-44 (1976).

Variables:
Temperature: 386–451 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of H in liquid Na was determined by means of two methods

t/°F	t/°C[a]	Solubility/mass % H	Solubility/mol % H[a]
		From H-meter measurements	
235	113	$6\cdot10^{-6}$; $4\cdot10^{-6}$	$1.4\cdot10^{-4}$; $9\cdot10^{-5}$
240	116	$6\cdot10^{-6}$; $4\cdot10^{-6}$; $3\cdot10^{-6}$	$1.4\cdot10^{-4}$; $9\cdot10^{-5}$; $7\cdot10^{-5}$
248	120	$4\cdot10^{-6}$	$9\cdot10^{-5}$
250	121	$4\cdot10^{-6}$; $4\cdot10^{-6}$; $7\cdot10^{-6}$	$7\cdot10^{-5}$; $7\cdot10^{-5}$; $1.6\cdot10^{-4}$
271	133	$9\cdot10^{-6}$	$2.1\cdot10^{-4}$
273	134	$5\cdot10^{-6}$; $8\cdot10^{-6}$	$1.2\cdot10^{-4}$; $1.8\cdot10^{-4}$
274	135	$7\cdot10^{-6}$; $3\cdot10^{-6}$	$1.6\cdot10^{-4}$; $7\cdot10^{-5}$
275	135	$9\cdot10^{-6}$; $1.0\cdot10^{-5}$	$2.1\cdot10^{-4}$; $2.3\cdot10^{-4}$
278	137	$9\cdot10^{-6}$	$2.1\cdot10^{-4}$
290	143	$1.3\cdot10^{-5}$	$2.4\cdot10^{-4}$
295	146	$1.4\cdot10^{-5}$; $1.0\cdot10^{-5}$	$3.2\cdot10^{-4}$; $2.3\cdot10^{-4}$
300	149	$1.4\cdot10^{-5}$	$3.2\cdot10^{-4}$
310	154	$1.9\cdot10^{-5}$; $1.7\cdot10^{-5}$; $1.3\cdot10^{-5}$	$4\cdot10^{-4}$; $4\cdot10^{-4}$; $3\cdot10^{-4}$
350	177	$3.2\cdot10^{-5}$; $3.7\cdot10^{-5}$	$7\cdot10^{-4}$; $8\cdot10^{-4}$
352	178	$3.4\cdot10^{-5}$; $4.0\cdot10^{-5}$	$8\cdot10^{-4}$; $9\cdot10^{-4}$
		From Sc-foil equilibration measurements	
235	113	$9\cdot10^{-6}$[b,c]	$2.1\cdot10^{-4}$
240	116	$1.0\cdot10^{-5}$; $7\cdot10^{-6}$	$2.3\cdot10^{-4}$; $1.6\cdot10^{-4}$
250	121	$8\cdot10^{-6}$	$1.8\cdot10^{-4}$
275	135	$1.4\cdot10^{-5}$; $1.2\cdot10^{-5}$; $1.1\cdot10^{-5}$	$3.2\cdot10^{-4}$; $2.8\cdot10^{-4}$; $2.5\cdot10^{-4}$
290	143	$2.4\cdot10^{-5}$[b]	$5\cdot10^{-4}$
300	149	$1.4\cdot10^{-5}$[b,c]	$3\cdot10^{-4}$
310	154	$1.7\cdot10^{-5}$[b];$5.6\cdot10^{-5}$[c]	$4\cdot10^{-4}$; $1.3\cdot10^{-3}$

[a]Calculated by the compilers.
[b]Sc enclosed in Ni foil.
[c]V and Fe–Mn also present in the equilibration.

Auxiliary Information

Method:
The experiments were performed in an application loop made of stainless steel. The loop was filled with Na which was forced to circulation. A H meter utilized a Ni membrane, through which H diffused from Na to the vacuum side. The H pressure was measured with the use of an ion pump and ion gauge. The H meter was calibrated and the concentration of H in liquid Na was measured at selected temperature. The equilibrium was typically reached after 1 h. In another set of experiments Sc–foil was equilibrated with liquid Na at 1023 K for 24 h. The samples were taken at cold trap temperatures. The foils were removed from the loop and analyzed for their H content by combustion followed by gas analysis.

Source and Purity of Materials:
H: nothing specified.
Na: nuclear purity, cold trapped.
Sc: nothing specified.

Estimated Error:
Solubility: precision ±30%.
Temperature: nothing specified.

Components:
(1) Hydrogen; H; [1333-74-0]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
O. V. Skuratov, O. N. Pavlov, V. I. Danilkin, and I. V. Volkov, Zh. Neorg. Khim. **21**, 2910–2913 (1976).

Variables:
Temperature: 936–1032 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The H equilibrium pressures over NaH were measured. A slight decomposition of NaH makes that the liquid phase contains the NaH–Na system.

T/K	p/MPa
936	13.15
944	14.14
964	16.76
974	18.34
980	19.31
988	20.78
1001	22.60
1004	23.11
1013	25.28
1032	28.71

The melting point of NaH was found at 911±2 K and 10.7 MPa. The melting point increased for 1.8±0.2 K at further pressure increase to 20.7 MPa.

Auxiliary Information

Method:
The preparation and investigation of NaH was performed in a high pressure autoclave. The temperature was measured by means of a Chromel/Copel thermocouple. NaH was prepared at 905–920 K and the pressure of 11.7–13.7 MPa. The reaction occurred within 2–8 min and the stoichiometric compound was obtained. The melting point of NaH was found from cooling curves. H was additionally supplied for the compensation of H loss due to its diffusion through the autoclave walls. This way, the H pressure during the melting corresponded to the equilibrium value.

Source and Purity of Materials:
H: contained $<10^{-4}$ vol % O, N; dew point 218 K.
NaH: 99.0+% pure.
Na: 99.0+% pure.

Estimated Error:
Pressure: precision ±0.4%.
Temperature: precision ±0.5 K.

Components:
(1) Hydrogen; H; [1333-74-0]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
A. C. Whittingham, J. Nucl. Mater. **60**, 119–131 (1976).

Variables:
Temperature: 610–677 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data
The solubility of H in liquid Na and the H plateau pressure over the saturated solutions was determined

T/K	Solubility/mass % H	Solubility/mol % H[a]	p/kPa
610	$3.35\cdot10^{-3}$	$7.6\cdot10^{-2}$	5.87
632	$5.35\cdot10^{-3}$	0.122	12.60
657	$8.30\cdot10^{-3}$	0.189	32.20
677	$1.10\cdot10^{-2}$	0.251	56.00

[a]Calculated by the compilers.

The same results were reported in Whittingham.[1] The equilibrium solid phase is NaH. The solubility data were approximated by the equation.

$$\log(\text{soly/mol \% H}) = (4.43\pm0.3) - (3380\pm140)\ (T/\text{K})^{-1}. \quad (1)$$

According to tests performed by the compilers, Eq. (1) overestimated values by 2%–3%.

The H equilibrium plateau pressures were approximated by the equation (confirmed by the compilers):

$$\log(p/\text{Pa}) = (13.86\pm0.2) - (6160\pm37)\ (T/\text{K})^{-1}. \quad (2)$$

Kinetics of the reaction between H and Na was studied.

Auxiliary Information

Method:
The measurements were performed in an isothermal, constant volume apparatus made of Type 316 stainless steel. The absorption of a known amount of H, equilibrated with vigorously stirred Na, was measured as pressure changes at selected temperature. The apparatus was evacuated, heated, and a capacitance manometer was calibrated with Ar. The concentration of H was calculated from the known volume and temperature of the reaction vessel. Saturation points were found from the onset of the plateau while increasing the H concentration.

Source and Purity of Materials:
H: nothing specified.
Na: filtered at ~380 K; contained $<1.0\cdot10^{-3}$ % O.
Ar: "high purity;" purified by bubbling through liquid Na at 400 K.

Estimated Error:
Solubility: precision ±7%.
Pressure: precision ±0.5%.
Temperature: nothing specified.

References:
[1]A. C. Whittingham, Centr. Electr. Gener. Board Rep. RD/B/N-2550 (1974).

Components:
(1) Hydrogen; H; [1333-74-0]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
C. C. Addison, P. Hubberstey, J. Oliver, R. J. Pulham, and P. A. Simm, J. Less-Common Met. **61**, 123–132 (1978).

Variables:
Temperature: 613–673 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data
The solubility of H in liquid Na was determined

t/°C	Solubility/mol % H
340	0.098
350	0.104
355	0.123
390	0.194

The results presented in a figure of this paper do not correspond to the numerical data of the table. A least square analysis of these results gives the following solubility equation:

$$\log(\text{soly/mol \% H}) = 4.82 - 3600\ (T/\text{K})^{-1}$$

the validity of which was tested by the compilers. NaH was the solid equilibrium phase.

Auxiliary Information

Method:
Two types of apparatus were used. The first one was given in details in Addison *et al.*[1] and served at low temperatures or saturated solutions. H was introduced in consecutive measured amounts to the liquid Na and the resulting solution was circulated continuously through a steel capillary. The electrical resistance of the solution was measured by means of a potentiometer or a Wheatstone bridge. The second construction of the apparatus was used for unsaturated solutions at high temperatures. It was made of the AISI 321 steel and comprised of a cylindrical reservoir, a second pump forcing the solution through a capillary for the resistance measurements, a valve for admitting H gas, and a diaphragm for pressure measurements. The temperature was measured by a thermocouple. The electrical resistivity was traced as a function of NaH content. A break on such dependence corresponded to the saturation point.

Source and Purity of Materials:
H: 99.98% pure from Air Products, further purified by passage through MnO at 373 K and a molecular sieve.
Na: unspecified purity; gettered by U foil at 673 K for several hours.

Estimated Error:
Solubility: nothing specified; precision of a few % (by the compilers).
Resistivity: precision ±5%.
Temperature: fluctuation ±1 K.

References:
[1]C. C. Addison, G. K. Creffield, P. Hubberstey, and R. J. Pulham, J Chem. Soc., A 1393–1396 (1971).

Components:
(1) Hydrogen; H; [1333-74-0]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
J. P. Maupré, Comm. Ener. Atom. (Fr.) Rep. CEA-R-4905 (1978).

Variables:
Temperature: 748–903 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

Thermal analyses of the NaH-Na melts and of pure NaH were performed

t/°C	p/MPa	x_{NaH} /mol % H
630	10.97	100
580	4.21	100
495	0.72	40.2
597	6.00	35.3
568	3.35	28.6
590	5.06	20.3
475	4.45	9.5

The author observed the monotectic thermal arrests at 630 °C (as read from a figure by the compilers). He reported, however, that the melting point of NaH was 3 K higher than the monotectic temperature.

Auxiliary Information

Method:
A commercial thermoanalyzer was used. Samples were placed in Ni crucibles. The crucibles were inserted into a high pressure Super–Kanthal container. The experiments were carried out in an Ar atmosphere. Pt/Pt–Rh and Ni/Ni–Cr thermocouples were used. They were placed in the bottom part of the crucibles. The thermocouples were calibrated on the melting points of In, Sn, Ag_2SO_4, K_2SO_4, K_2CrO_4, and $BaCO_3$. Cooling and heating were performed at a rate between 0.2 and 15 K/min.

Source and Purity of Materials:
NaH: 99% pure from Alfa.
Na: 99.985% pure from Pechiney.
Ar: 99.995+% pure from B.A.G.; further purified with 5 Å molecular sieves and BTS catalyzer at 383 K; finally contained $\sim 1\cdot 10^{-4}$ vol % O and $3\cdot 10^{-5}$ vol % H_2O.

Estimated Error:
Solubility: nothing specified.
Temperature: precision better than ±3 K.

Components:
(1) Hydrogen; H; [1333-74-0]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
T. Funada, I. Nihei, S. Yuhara, and T. Nakasuji, Nucl. Technol. **45**, 158–165 (1979).

Variables:
Temperature: 423–548 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of H in liquid Na was measured. The data were read out from a figure and recalculated by the compilers.

t/°C	Solubility/mass % H	Solubility/mol % H[a]
150	$1.3\cdot 10^{-5}$, $1.4\cdot 10^{-5}$, $1.5\cdot 10^{-5}$, $1.5\cdot 10^{-5}$	$3.2\cdot 10^{-4}$
175	$2.2\cdot 10^{-5}$, $2.3\cdot 10^{-5}$, $2.4\cdot 10^{-5}$, $2.6\cdot 10^{-5}$, $2.8\cdot 10^{-5}$	$5.6\cdot 10^{-4}$
200	$4.9\cdot 10^{-5}$, $5.1\cdot 10^{-5}$, $5.5\cdot 10^{-5}$, $6.0\cdot 10^{-5}$, $6.2\cdot 10^{-5}$	$1.3\cdot 10^{-3}$
225	$9.8\cdot 10^{-5}$, $1.00\cdot 10^{-4}$, $1.03\cdot 10^{-4}$, $1.10\cdot 10^{-4}$, $1.13\cdot 10^{-4}$	$2.4\cdot 10^{-3}$
250	$1.8\cdot 10^{-4}$, $1.9\cdot 10^{-4}$, $2.0\cdot 10^{-4}$	$4.3\cdot 10^{-3}$
275	$2.8\cdot 10^{-4}$, $2.9\cdot 10^{-4}$	$6.5\cdot 10^{-3}$

[a]Mean value.

The H plateau pressure over the saturated solutions was expressed by the equation:

$$\log(p/\mathrm{Torr}) = 9.515 - 5344\ (T/\mathrm{K})^{-1} \quad (1)$$

but the experimental basis for this approximation was not reported.

The temperature dependence of the Sievert's constant was expressed by the equation:

$$\log(K_s\ /\mathrm{mass\ \%\ H/Torr}^{1/2}) = -3.829 + 198.1\ (T/\mathrm{K})^{-1}. \quad (2)$$

The temperature dependence of the solubility was expressed by the equation:

$$\log(\mathrm{soly/mass\ \%\ H}) = 0.825 - 2398\ (T/\mathrm{K})^{-1}. \quad (3)$$

The compilers tested the validity of the equations.

A small influence of the presence of O or OH in Na on the solubility of H was found.

Auxiliary Information

Method:
The studies were performed in the Na exposure test loop which consisted of an electromagnetic pump, a cold trap, a gas supply and ten test pots. The cold trap contained an amount of H sufficient to saturate Na up to 548 K. Larger amounts of H could be inserted by means of an injection tube made of 304 stainless steel. A H-sensor tube made of Ni was installed inside the last pot in series. Equilibrium was reached within 15 min and the internal amount of H was measured by a chromatograph by comparison with a standard H–Ar mixture. The measurements were repeated every 15 min.

Source and Purity of Materials:
H: nothing specified; purified by diffusion through a Ni wall; considerable amounts of hydrocarbons and CO were detected at the beginning of experiments.
Na: purified in the cold trap;
Ar: 99.9999% pure.

Estimated Error:
Solubility: nothing specified; reading-out procedure ±7% (by the compilers).
Temperature: nothing specified.
Pressure: detection limit 0.13 Pa.

Components:
(1) Hydrogen; H; [1333-74-0]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
N. P. Bhat and H. U. Borgstedt, Atomkernenergie **35**, 170–174 (1980).

Variables:
Temperature: 418–443 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data
The solubility of H in liquid Na and the H equilibrium plateau pressure were determined

t/°C	Solubility/mass % H	Solubility/mol % H[a]	p/Torr	p/Pa[a]
145	$1.2\cdot10^{-5}$	$2.7\cdot10^{-4}$	$5.91\cdot10^{-4}$	$7.88\cdot10^{-2}$
150	$1.4\cdot10^{-5}$	$3.2\cdot10^{-4}$	$8.44\cdot10^{-4}$	0.1125
155	$1.7\cdot10^{-5}$	$3.9\cdot10^{-4}$	$1.182\cdot10^{-3}$	0.1576
160	$1.9\cdot10^{-5}$	$4.3\cdot10^{-4}$	$1.477\cdot10^{-3}$	0.1969
165	$2.3\cdot10^{-5}$	$5.2\cdot10^{-4}$	$2.11\cdot10^{-3}$	0.281
170	$2.5\cdot10^{-5}$	$5.7\cdot10^{-4}$	$2.532\cdot10^{-3}$	0.338

[a]Calculated by the compilers.

Auxiliary Information

Method:
A Varian diffusion type of H meter was used in connection with a chemical analytical Na loop. The main components of the H meter are: a diffusion membrane maintained at 723 K, a H sensor, and a precise pressure gauge. The H pressure over the solution after cold trapping was recorded every 2–5 minutes for 30–40 min and the equilibrium values were typically reached after 15 min. Absolute H pressure at the cold trap temperature was calculated by applying the gauge and the thermal transpiration factors. Simultaneous use of a C meter elevated the reading of the H meter due to use of H in the decarburizing gas in the C meter. If the H concentration was sufficiently high, the O concentration shown by the O meter was low due to the formation of NaOH in such conditions.

Source and Purity of Materials:
H: nothing specified.
Na: nothing specified; purified by cold trapping.
Ar: nothing specified.

Estimated Error:
Solubility: precision better than ±4%.
Temperature: nothing specified.

Components:
(1) Hydrogen; H; [1333-74-0]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
W. Klostermeier and E. U. Franck, Ber. Bunsenges. Phys. Chem. **86**, 606–612 (1982).

Variables:
Temperature: 863–1173 K;
Pressure: 4.7–65.1 MPa

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data
The solubility of H in liquid Na and the H equilibrium plateau pressure were measured

t/°C	Solubility/mol % NaH	Solubility/mol % H[a]	p/bar	p/MPa[a]
650	5.5	5.2	119	11.9
700	7.1	6.6	183	18.3
750	9.1	8.3	270	27.0
800	11.6	10.4	366	36.6
850	14.8	12.9	487	48.7
900	18.6	15.7	651	65.1

[a]Calculated by the compilers

A solubility equation, due to high contents of H, is not recommended. The solubility of Na in liquid NaH at 900 °C was found to be below 2 mol % Na; this corresponds to a composition of the liquid phase >49.5 mol % H.

The equilibrium plateau pressure of H over the NaH was measured also by an independent method.

t/°C	p/bar	p/MPa[a]	Equilibrium phase
590	47	4.7	solid NaH
598	59	5.9	solid NaH
620	78	7.8	solid NaH
636	100	10.0	solid NaH
650	122±4	12.2	liquid NaH
675	151±1	15.1	liquid NaH
700	186±2	18.6	liquid NaH
725	224±1	22.4	liquid NaH
750	270±1	27.0	liquid NaH
775	320±1	32.0	liquid NaH
800	372±6	37.2	liquid NaH
850	488±2	48.8	liquid NaH
900	651	65.1	liquid NaH

[a]Calculated by the compilers.

The pressure results between 923 and 1173 K may be approximated by the following equation, tested by the compilers:

$$\log(p/\mathrm{MPa}) = 4.501 - 3148(T/\mathrm{K})^{-1}.$$

The melting point of NaH was found at 632±2 °C and 10.6 MPa. The critical solution point was estimated at $T_c = 1500\pm70$ K, $x_H = 39\pm4$ mol %, and $p_c = 250\pm60$ MPa.

Components:
(1) Hydrogen; H; [1333-74-0]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
R. S. Fidler and R. Saagi, Nucl. Ener. **23**, 385–398 (1984).

Variables:
Temperature: 393–523 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of H in liquid Na was determined during observation of the crystallization behavior of NaH. The data were presented as either crystallization runs or a smooth solubility curve; they were read out from figures and recalculated to mol % H by the compilers.

t/°C	Solubility/mass % H	Solubility/mol % H
129[a]	$6.3\cdot10^{-6}$	$1.43\cdot10^{-4}$
196[a]	$1.13\cdot10^{-4}$	$2.58\cdot10^{-3}$
120	$5.0\cdot10^{-6}$	$1.14\cdot10^{-4}$
140	$1.45\cdot10^{-5}$	$3.3\cdot10^{-4}$
160	$2.8\cdot10^{-5}$	$6.4\cdot10^{-4}$
180	$5.5\cdot10^{-5}$	$1.25\cdot10^{-3}$
200	$1.00\cdot10^{-4}$	$2.28\cdot10^{-3}$
250	$5.9\cdot10^{-4}$	$1.35\cdot10^{-2}$

[a]From crystallization runs.

A mutual influence of both H and O on their activities in Na was established; not only the formation of OH entity but also a higher order product formation may be suggested on the experimental base.

Auxiliary Information

Method:
The experiments were performed in a Na filled loop for monitoring the purity of Na. The facility consisted of a mother loop which supplied Na to one subloop. The subloop comprised a cold trap, a plugging meter, and electrochemical meters for H and O. A H injector was located upstream of the cold trap to enable H to be dissolved in Na during circulation around the Ni diffusion membrane. The electrochemical meters were calibrated. While the plug developed, the meters monitored the changes in solute concentrations resulting from either a plug formation or a NaH dissolution. The saturation levels were measured during a stable partial plugging of the runs.

Source and Purity of Materials:
H: nothing specified.
Na: nuclear grade of purity, supplied by GEC Whetstone.

Estimated Error:
Solubility: nothing specified; reading-out procedure ±1%.
Temperature: stability ±1 K; reading-out procedure ±1 K.

Auxiliary Information

Method:
The experiments were performed in an autoclave made of the Ni-base alloy Udimet 700. A stainless steel tube was used to separate an outer and inner compartment. The H pressure in both compartments was controlled and kept equal as outside to prevent H loss during the measurements. A very pure Fe capsule containing Na was placed inside the tube. Three sheathed Chromel/Alumel thermocouples controlled the temperature of the autoclave. The apparatus was flushed with Ar. H at 1.0 MPa was introduced into and kept for several hours. Having attained the desired high temperature, the H pressure was increased, and H diffused into the Na in the capsule. The reaction of H and Na caused a reduction of pressure, correspondingly compensated by pressure reduction in the outer compartment. Stable values of pressure were recorded after several hours of equilibration. The solubility values were read out from break points on the isotherms of pressure versus composition.

Source and Purity of Materials:
H: 99.9999% pure.
Na: "carefully purified" and distilled under vacuum directly into the capsule; O content $<2.0\cdot10^{-3}$ %.
Ar: nothing specified.

Estimated Error:
Solubility: precision ±2%.
Pressure: accuracy ±0.1 MPa.
Temperature: stability ±0.5 K; accuracy ±2 K.

Components:
(1) Hydrogen; H; [1333-74-0]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
M. Rajan, and R. D. Kale, *Liquid Metal Engineering and Technology* (Soc. Fr. Energ. Aom., Paris, 1988), Vol. 3, pp. 604–1/10.

Variables:
Temperature: 393–473 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of H in liquid Na was determined. The results were read out from figures and recalculated to mol % H by the compilers.

T/K	Solubility/mass % H	Solubility/mol % H
393	$2.2\cdot10^{-6}$	$5.1\cdot10^{-5}$
418	$1.3\cdot10^{-5}$	$3.0\cdot10^{-4}$
438	$3.4\cdot10^{-5}$	$7.8\cdot10^{-4}$
458	$6.5\cdot10^{-5}$	$1.5\cdot10^{-3}$
473	$9.5\cdot10^{-5}$	$2.2\cdot10^{-3}$

The authors expressed their solubility data by the equation:

$$\log(\text{soly/mass \% H}) = 2.662 - 3126\ (T/\text{K})^{-1}.$$

Auxiliary Information

Method:
The experimental Na loop was made of stainless steel. The loop consisted of a dump tank, electromagnetic pump, cold trap, plugging indicator and a Ni tube membrane (serving as the H collecting part of the H meter). Gaseous H or Ar–H mixture was injected into the tank and the system equilibrated. The H pressure was measured on the other side of the Ni tube membrane by a quadrupole mass spectrometer working in an ultrahigh vacuum system. The H meter was calibrated. The cold point temperature of the cold trap corresponded to the saturation temperature of H in liquid Na.

Source and Purity of Materials:
H: nothing specified.
Na: nuclear grade of purity, purified by cold trapping at 383 K.
Ar: nothing specified.

Estimated Error:
Solubility: nothing specified; reading-out procedure ±3%.
Temperature: stability ±1 K; reading-out procedure ±2 K.

4.2. Sodium–Deuterium

Components:
(1) Deuterium; D; [7782-39-0]
(2) Sodium; Na; [7440-23-5]

Evaluated By:
Hans Ulrich Borgstedt, Forschungszentrum Karlsruhe, Germany and Cezary Guminski, University of Warsaw, Poland, November 1995

Critical Evaluation

The D–Na binary system seems to be qualitatively close to the H–Na system. The D–Na system was much less extensively investigated. In fact, only D equilibrium vapor pressures over the liquid D–Na melt were measured by Sollers and Crenshaw,[1] McClure and Halsey,[2] and Hackspill and Borocco.[3,4] The results of the reinvestigations agree qualitatively. No doubt that the D vapor pressure should be comparatively higher than the H vapor pressure at the same temperature. However, the twice higher D pressure than that of H as observed by Sollers and Crenshaw[1] seems to be less probable than the observation of McClure and Halsey[2] that a ratio of these pressures is ~1.2. McClure and Halsey[2] did not report experimental values. Certainly, the solubility of D in liquid Na should be higher than that of H. However, a quantitative prediction is not possible. Magomedov[5] calculated the melting points of NaD and NaT, the results were 912.66 and 912.95 K, respectively; both of the values are slightly higher than of NaH.

The D–Na phase diagram should be essentially similar to that of the H–Na system. Experiments with the T–Na system have never been performed so far.

References:
[1]E. F. Sollers and J. L. Crenshaw, J. Am. Chem. Soc. **59**, 2724 (1937).
[2]D. W. McClure and G. D. Halsey, J Phys. Chem. **69**, 3542 (1965).
[3]A. Borocco, Compt. Rend. **205**, 983 (1937).
[4]L. Hackspill and A. Borocco, Bull. Soc. Chim. Fr. **6**, 91 (1939).
[5]M. N. Magomedov, Zh. Fiz. Khim. **68**, 589 (1994).

4.3. Sodium–Boron

Components:

(1) Boron; B; [7440-42-8]
(2) Sodium; Na; [7440-23-5]

Evaluated By:

Hans Ulrich Borgstedt, Forschungszentrum Karlsruhe, Germany and Cezary Guminski, University of Warsaw, Poland, December 1995

Critical Evaluation

Moissan[1] reported that B, being produced during the reduction of B_2O_3 with Na, apparently did not dissolve in boiling Na (1156 K). A quantitative solubility limit could not be estimated on this basis. The author reported that he found a content of some Na in the B sample. Hagenmuller *et al.*[2] observed that at (1173–1273) K and 1 MPa Na reacted with B to form NaB_6. NaB_6 was transformed to NaB_{15} when further heated to 1373 K; however, observations concerning a solubility of B (or the reaction product) in liquid Na in these conditions were not reported. Mausteller and Tepper[3] carried out a reaction of Ti with B dissolved in liquid Na at 1033–1255 K for a few hours. This fact would point to a considerable solubility of B in liquid Na in this temperature range. Since the reaction product TiB_2 adhered at best to the Ti sample at 1144 K, one may deduce that the solubility of B around this temperature is certainly higher than that of Ti ($5 \cdot 10^{-4}$ mol % Ti). Astley[4] observed that a B_4C sample equilibrated with liquid Na at 1173 K was cracked and graphite was present on the sample after Na was removed. This fact would suggest that a solubility of B in liquid Na is higher than that of C in liquid Na at this temperature (~0.05 mol % C). Another proof of the relatively good solubility of B in liquid Na was found by Borgstedt *et al.*[5] who observed that flowing Na selectively leached B out of stabilized stainless steel (containing $5 \cdot 10^{-3}$ % B) at 973 K.

Adams[6] attempted to measure the solubility of B in liquid Na at 773 K. The saturated solution of B in Na was circulated through a capillary of a stainless steel apparatus for electrical resistivity measurements. No significant change of the resistivity was observed. Assuming that the detection level of the method was $1 \cdot 10^{-9}$ Ω m and B has a resistivity coefficient comparable to that of Al, the solubility of B in liquid Na may be estimated as equal or lower than 10^{-2} mol % B at 773 K. According to Adams,[6] B used in various forms (crystalline, fine powder, obtained in Ar plasma or nascent B obtained from reaction of BC_{13} with H or Na) did not react with Na in the temperature range (573–923) K. This would mean that the saturated solution of B in liquid Na is in equilibrium with practically pure B. Sorokin *et al.*[7] observed that B and Na did not form borides even at 1073 K. NaB_6 and NaB_{15} are the equilibrium phases at temperatures higher than 1073 K.

These facts are schematically reflected in the Na–B phase diagram (see Fig. 17).

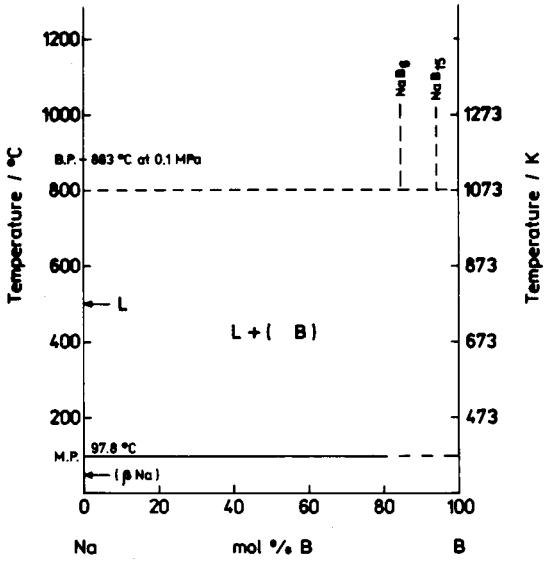

FIG. 17. Na–B phase diagram.

References:

[1]H. Moissan, Compt. Rend. **114**, 319 (1892).
[2]P. Hagenmuller, R. Naslain, M. Pouchard, and C. Cros, *The Alkali Metals* (The Chemical Society, London, 1967), p. 207.
[3]J. W. Mausteller and F. Tepper, U.S. Atom. Energy Comm. Rep. TID-7626, Pt. I, p. 146 (1962).
[4]E. R. Astley, U.S. Atom. Energy Comm. Rep. BNWL-917 (1968).
[5]H. U. Borgstedt, G. Frees, and H. Schneider, Nucl. Technol. **34**, 290 (1977).
[6]P. F. Adams, Ph. D. thesis, University of Nottingham, U.K., 1977; abstracted in C. C. Addison, *The Chemistry of the Liquid Alkali Metals* (Wiley, Chichester, 1984), p. 225.
[7]V. P. Sorokin, P. I. Gavrilov, and E. V. Levakov, Zh. Neorg. Khim. **22**, 595 (1977); Russ. J. Inorg. Chem. **22**, 329 (1977).

4.4 Sodium–Carbon

Components:
(1) Carbon; C; [7440-44-0]
(2) Sodium; Na; [7440-23-5]

Evaluated By:
Hans Ulrich Borgstedt, Forschungszentrum Karlsruhe, Germany and Cezary Guminski, University of Warsaw, Poland, December 1996

Critical Evaluation

A wide scatter of measured solubility data of C in liquid Na points on the complexity of this system.[1–27] There are several reasons of this scatter: dissolved C can exist in liquid Na as monomeric or dimeric species, the equilibrium solid phase may exist in form of finely divided particles (of graphite) which cannot be effectively separated from the saturated solution by filtration, and finally C may exist in liquid Na in different chemical forms (being bonded with traces of O, N, H, and metals as well as Na_2C_2). This way the chemical activity of C in Na is variously decreased.[24,28,29] These effects as well as the slow dissolution process of graphite in liquid Na (Longson and Thorley[16]) may alter the apparent solubility. It was found in early qualitative tests of Fredenhagen *et al.*[30,31] that C in form of soot interacted with liquid Na. These authors did not observe any dissolution of either graphite or diamond. Kelman[32] observed that graphite, placed overnight in a K–Na alloy at room temperature, was entirely broken up, however, dissolved C in the melt could not be detected. The swelling and dispersion of the graphite sample seems to be due to the formation of a K–C intercalation compound. Barker[33] established that graphite introduced into liquid Na at 811 K shows some expansion, and heat of interaction is evolved. Willhelm[34] reported that graphite showed a good corrosion resistance in liquid Na even at 1073 K. A measurable weight loss of graphite samples in liquid Na was observed by Siegel *et al.*[35] at temperatures >873 K. Belyaev and Firsonova[36] investigated the interaction of Na vapor with carboniferous materials at (673–1273) K in a vacuum chamber. Na, first adsorbed on these materials, finally penetrated interplanar spaces of the graphite lattices (existing in the materials investigated), which process caused a destruction of the materials tested. Pure graphite was most resistant in these conditions. Lyashenko and Nevzorov[37] studied C transfer through liquid Na medium, when two steel samples of different C activity were dipped in Na. In the course of such equilibration the C activity in the samples tended to equalize. Increasing O content in Na showed a negligible effect on this equilibrium but kinetics of the C transfer process significantly increased. The authors postulated that C transfer in such conditions was realized by the formation and subsequent decomposition of CO. Unfortunately the authors did not analyze the C content in Na used for these investigations. Wagner and Stearns[38] did not observe any formation of C–Na lamellar compounds; graphite expanded 1% due to irradiation, after contact with Na the expansion was found to be 6%. Thus, all these qualitative tests indicate the complexity of the C–Na system.

In the first solubility determination, Gratton[1] found $6.1\cdot10^{-3}$–0.0142 mol % C in liquid Na at 420–973 K. An increase of the O content in Na made an increase of the apparent C solubility. Anderson and Sneesby[2,3] claimed an increase of the apparent C solubility in Na upon the addition of O but no O influence on the C solution kinetics was observed. Andrews *et al.*[4] determined the C content in circulating Na filtered through 5 μm pores. The investigators did not find that the C level undergoes dramatically or systematic changes within several months, being between $4.7\cdot10^{-3}$ and $7.7\cdot10^{-3}$ mol % C at 922 K. These figures suggest a lower solubility level than that reported by Gratton.[1] Addison *et al.*[5] estimated only the upper limit of the solubility at 573 K which was almost 2 orders of magnitude lower than in Gratton[1] and Anderson and Sneesby.[2,3] Luner *et al.*[6–8] applied two methods of analysis of the saturated liquid phase. A filtration leads to results similar to those of Gratton[1] and Anderson and Sneesby,[2,3] while the use of radio isotope ^{14}C, that could be atomically dissolved from a C pellet, leads to the conclusion that at temperatures lower than 723 K the solubility of C in liquid Na was below $1\cdot10^{-5}$ mol % C. These experiments showed the uneffectivity of filtration in the case of the C–Na system. The value obtained at 923 K by Cafasso *et al.*[9–11] confirmed this conclusion. However, due to the comment of Davies,[39] it is not sure whether true saturation equilibrium was reached in the experiments of three groups[6–8] and Cafasso *et al.*[9–11] The results obtained by Gehri *et al.*[12–15] were about 3 orders of magnitude higher than those in Cafasso *et al.*[9–11] and showed a very small temperature dependence of the solubility. Weeks[40] used an amalgamation technique for the determination of C dissolved in Na; his preliminary tests gave results substantially lower than the analytical methods previously applied. Longson and Thorley[16,17] performed experiments in which atomic C diffused through a thin walled Ni can and dissolved in liquid Na up to its saturation; their results showed a much steeper temperature dependence of the solubility than in all previous works. Another temperature dependence of the solubility, being between that of Gehri *et al.*[12–15] and that of Longson and Thorley,[16,17] was observed by Salzano *et al.*[18–20] who introduced various forms of carbonaceous reagents and used C meters for the solubility determination. Johnson *et al.*[21] used Na_2C_2 as the solute to the solubility measurements. They assumed that below 800 K the rate of decomposition of Na_2C_2 is slow enough that Na_2C_2 might be treated as the solute. Their solubility results were expressed by the following equation:

$$\log(\text{soly/mol \% } Na_2C_2) = 2.326 - 4289\ (T/\text{K})^{-1}. \quad (1)$$

Using ΔG of the formation of Na_2C_2 from liquid Na and solid C, Johnson *et al.*[21] predicted a solubility equation of dissolution of graphite to monoatomic C in liquid Na in the following form:

$$\log(\text{soly/mol \% C}) = 2.99 - 5679\ (T/\text{K})^{-1}. \quad (2)$$

Similar solubility equations, as Eq. (2), were reported in Longson and Thorley,[16,17] Ainsley *et al.*,[22–24] and McKisson *et al.*;[25] the latter two groups performed own solubility tests. Longson and Thorley[16,17] and McKisson *et al.*[25] did not observe any influence of O on the solubility of C in liquid Na. Hobdell *et al.*[26] and Kozlov *et al.*[27] using C meters of various construction measured the C solubility and the results obtained were of the same order as those obtained previously by Salzano *et al.*[18–20] Hobdell *et al.*[26] confirmed the higher solubility of the dimer than monomer form of C, which was first signalized by Johnson *et al.*[21] Thompson[41] reviewed the most reliable solubility results of Longson and Thorley,[16,17] Johnson *et al.*,[21] Ainsley *et al.*,[22–24] and McKisson *et al.*[25] and proposed an average solubility equation:

$$\log(\text{soly/mol \% C}) = 3.630 - 5858\ (T/\text{K})^{-1}, \quad (3)$$

which may be applied between 750 and 1250 K, and if the solubility equilibrium consists of graphite and monomer C is dissolved in liquid Na. Different solubility equations were proposed in Rumbaut *et al.*[42] and Borgstedt.[43] It was shown by Addison *et al.*,[5] Johnson *et al.*,[21] Ainsley *et al.*,[22–24] Hobdell *et al.*,[26] Davies,[39] Borgstedt and Pillai,[44] Kelly *et al.*,[45] and Hooper *et al.*,[46] that equilibrium exists between the monoatomic and acetylide-like (C_2) species in liquid Na. The latter form is dominant at lower temperatures and higher concentrations and the former form is dominant at higher temperatures in more diluted solutions.

Therefore, lines representing Eq. (1) for Na_2C_2 and Eq. (2) for graphite as solutes, are lying above and below Eq. (3), respectively. There are no experimental proofs that Na_2C_2 is the equilibrium solid phase at lower temperatures, since graphite equilibrated with liquid Na was not covered with a Na_2C_2 deposit and freshly introduced Na_2C_2 was slowly decomposed in liquid Na. The solubility dependencies for graphite and Na_2C_2 cross at ~825 K according to Gnanasekaran[47] and at ~1600 K according to Johnson *et al.*;[21] the second temperature seems to be more reasonable, since the temperature of the first estimation is near the temperature of the decomposition of Na_2C_2. The limits of the thermal stability of Na_2C_2 were variously reported: >473 K,[5] (873–973) K,[29] >773 K,[46] (1073–1098) K,[48] <973 K,[49] (823–873) K,[50] and 1003 K.[51] The determination of Maupré[51] seems to be the most reliable. The solid phase transformation of Na_2C_2, (546±3 K) was equivocally found by several experimentalists.[21,46,50,51]

The acetylide Na_2C_2 cannot be formed by a direct reaction of C and Na and should be rather treated as the metastable phase of the C–Na system (see Fig. 18); see the corresponding phase diagram which is based on a schematic presentation of Maupré.[51] However, it is possible from the thermodynamic point of view to form a solution of Na_2C_2 in liquid Na in which the C activity is less than unity. Another group of metastable Na–C compounds is formed by graphite intercalation NaC_8, NaC_{16}, NaC_{32}, and NaC_{64};[29] however, such compounds are formed, if graphite contains O or other impurities.[52] Joncourt *et al.*[53] studied the reactivity of different C-based materials, particularly pitch-coke samples heat treated at 1073–2673 K, with Na. An uptake of Na was related to intercalation, adsorption, or capillary condensation being quite different from the NaC_8 stoichiometry.

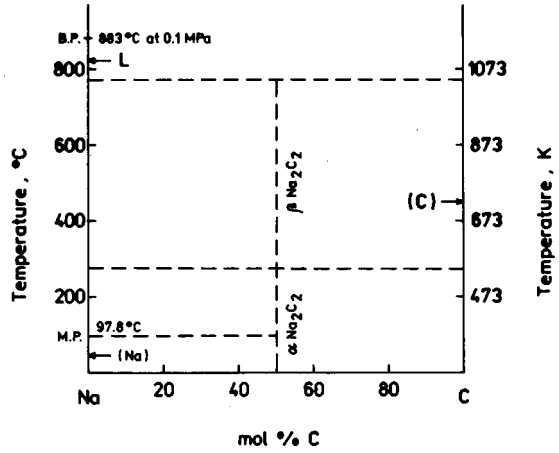

FIG. 18. C–Na phase diagram (tentative).

A distillation of slightly contaminated Na, containing dissolved C, with subsequent analysis of the residue[27,29,54] has shown the existence of the following forms, which probably were present in liquid Na: C, $Na_p(CO)_q$, M_xC_2, Na_2CO_3, M_xC_y (M=metal), NaCN,[27,54] and CaNCN.[55] C suspended in liquid Na at 723–823 K reacts with H to form CH_4.[44] Also Na_2C_2, CO, $(CN)_2$, and C_2H_2 added to liquid Na resulted in temporary changes of emf of the C meter[18] indicating complex equilibria of formation of these compounds with the C–Na system. The experimental conditions for the formation and decomposition of these specia in Na medium may be presented on the following diagram, being a modification of one shown in Konovalov *et al.*[29] Thus, below a specified temperature the apparent solubility of C in liquid Na may be the sum of concentrations (solubilities) of other contaminating elements that reacted with C to form the mentioned compounds. These reactions and the susceptibility of solid C to the formation of very small particles (≥0.1 μm), as documented by Rodgers,[56] are certainly the reason of obtaining overestimated results by Gratton,[1] Anderson and Sneesby,[2,3] and Luner *et al.*,[6–8] particularly at low temperatures. Only solubilities of Li_2C_2, Na_2CO_3, and NaCN in liquid Na were determined (see the corresponding systems) and solubilities of other substances that could be precipitated from impurities (as BaC_2, BaNCN, CsC_x) are unknown.[57,58] A new category of solubility equilibria will be expected for solutions of C_{60} in liquid Na; $Na_{10}C_{60}$ seems to be the equilibrium phase richest in Na.[59] The solubility of C_{60} has not been determined so far.

Tentative values of the solubility of C (graphite) in liquid Na

T/K	Solubility/mol % C	Source
573	$3\cdot10^{-7}$	Eq. (3), extrapolated
673	$1\cdot10^{-5}$	Eq. (3), extrapolated
773	$1.5\cdot10^{-4}$	(24), Eq. (3)
873	$1.0\cdot10^{-3}$	Eq. (3),
973	$5\cdot10^{-3}$	(16,17), (18), (27), mean value
1073	$2\cdot10^{-2}$	(16,17), mean value
1173	$5\cdot10^{-2}$	Eq. (3), extrapolated

References:

[1]J. G. Gratton, U.S. Atom. Energy Comm. Rep. KAPL-1807 (1957).
[2]W. J. Anderson and G. V. Sneesby, U.S. Atom. Energy Comm. Rep. NAA-SR-5282 (1960).
[3]W. J. Anderson, U.S. Atom. Energy Comm. Rep. TID-7626, Pt. I, p. 92 (1962).
[4]R. C. Andrews, R. H. Hiltz, L. H. Kirschler, S. J. Rodgers, and F. Tepper, U.S. Atom. Energy Comm. Rep. MSAR-65-194 (1965).
[5]C. C. Addison, M. R. Hobdell, and R. J. Pulham, *The Alkali Metals* (The Chemical Society, London, 1967), p. 270.
[6]C. Luner, A. Cosgarea, and H. M. Feder, *Alkali Metal Coolants* (IAEA, Vienna, 1966), p. 171.
[7]R. M. Adams and A. Glassner, Eds., U.S. Atom. Energy Comm. Rep. ANL-6923, p. 32 (1964).
[8]Anonymous, U.S. Atom. Energy Comm. Rep. ANL-7020, p. 78 (1965).
[9]R. M. Adams and A. Glassner, Eds., U.S. Atom. Energy Comm. Rep. ANL-7342, p. 68 (1967).
[10]F. A. Cafasso, U.S. Atom. Energy Comm. Rep. ANL-7419, p. 126 (1968).
[11]C. H. Luner, H. M. Feder, and F. A. Cafasso, U.S. Atom. Energy Comm. ANL-7520, Pt. I, p. 455 (1969).
[12]D. C. Gehri and J. B. Ott, U.S. Atom. Energy Comm. Rep. AI-AEC-Memo-12686 (1968).
[13]R. L. McKisson, R. L. Eichelberger, D. C. Gehri, and J. Guon, U.S. Atom. Energy Comm. Rep. AI-AEC-12721, p. 295 (1968).
[14]R. L. McKisson, R. L. Eichelberger, D. C. Gehri, and J. Guon, U.S. Atom. Energy Comm. Rep. AI-AEC-12744, p. 133 (1968).
[15]D. C. Gehri, U.S. Atom. Energy Comm. Rep. AI-AEC-12680, p. 158 (1968).
[16]B. Longson and A. W. Thorley, J. Appl. Chem. **20**, 372 (1970).
[17]B. Longson and A. W. Thorley, U.K. Atom. Energy Author. Rep. TRG-1906 (1970).
[18]F. J. Salzano, L. Newman, and M. R. Hobdell, Nucl. Technol. **10**, 335 (1971).
[19]F. J. Salzano and L. Newman, Nucl. Technol. **13**, 289 (1972).
[20]F. J. Salzano and L. Newman, Trans. Am. Nucl. Soc. **14**, 623 (1971).
[21]G. K. Johnson, E. H. Van Deventer, J. P. Ackerman, W. N. Hubbard, D. W. Osborne, and H. E. Flotow, J. Chem. Thermodyn. **15**, 57 (1973).
[22]R. Ainsley, L. P. Hartlib, G. Long, A. Pilbeam, and A. Thompson, *Liquid Alkali Metals* (BNES, London, 1973), p. 143.
[23]R. Ainsley, L. P. Hartlib, G. Long, A. Pilbeam, and A. Thompson, U.K. Atom. Energy Author. AERE-R-6731 (1973).
[24]R. Ainsley, L. P. Hartlib, P. M. Holroyd, and G. Long, J. Nucl. Mater. **52**, 255 (1974).
[25]R. L. McKisson, R. L. Eichelberger, D. C. Gehri, and J. Guon, U.S. Atom. Energy Comm. Rep. AI-AEC-12826 (1970); abstracted in Rep. AI-AEC-12859, p. 155 (1970).
[26]M. R. Hobdell, E. A. Trevillion, and A. C. Whittingham, U.S. Dept. Energy Rep. CONF-800401-P2, p. 18/47 (1980).
[27]F. A. Kozlov, Yu. I. Zagorulko, Yu. P. Kovalev, and V. V. Alekseev, U.S. Dept. Energy Rep. CONF-800401-P2, p. 18/54 (1980).
[28]C. K. Mathews, T. Gnanasekaran, and S. R. Pillai, Trans. Ind. Inst. Met. **40**, 89 (1987).
[29]E. E. Konovalov, A. P. Smirnov-Averin, and A. I. Lastov, Fiz.-Energ. Inst. (USSR) Rep. FEI-806, (1978).
[30]K. Fredenhagen and G. Cadenbach, Z. Anorg. Chem. **158**, 249 (1926).
[31]K. Fredenhagen and K. Such, Z. Anorg. Chem. **178**, 353 (1929).
[32]R. L. Kelman, U.S. Atom. Energy Comm. Rep. CT-3726 (1946).
[33]D. F. Barker, U.S. Atom. Energy Comm. Rep. BNWL-919, p. 3.12 (1968).
[34]C. Willhelm, Mater. Design Engin. **58**, 97 (1963).
[35]S. Siegel, R. L. Carter, F. E. Bowman, and B. R. Hayward, *Peaceful Uses of Atomic Energy* (U.N., New York, 1955), Vol. 9, p. 321.
[36]A. I. Belyaev and L. A. Firsonova, Sborn. Nauch. Tr. Moskov. Inst. Tsvet. Met. Zolota **25**, 162 (1955).
[37]V. S. Lyashenko and B. A. Nevzorov, *Corrosion of Reactor Materials* (IAEA, Vienna, 1962), p. 373; transl. U.S. Atom. Energy Comm. Rep. AEC-tr-5408 (1962).
[38]R. K. Wagner and J. D. Stearns, U.S. Atom. Energy Comm. Rep. CONF-650620 (1965).
[39]R. Davies, *Alkali Metal Coolants* (IAEA, Vienna, 1967), p. 179.
[40]J. R. Weeks, U.S. Atom. Energy Comm. Rep. BNL-5019 (1969).
[41]R. Thompson, Intern. Atom. Energy Agen. Rep. IWGFR-33 (1979).
[42]N. Rumbaut, F. Casteels, and M. Brabers, *Material Behavior and Physical Chemistry in Liquid Metal Systems*, edited by H. U. Borgstedt (Plenum, New York, 1982), p. 437.
[43]H. U. Borgstedt, *Handbook of Thermodynamics and Transport Properties of Liquid Alkali Metals*, edited by R. W. Ohse (Blackwell, Oxford, 1985), p. 895.
[44]H. U. Borgstedt and S. R. Pillai, *Liquid Metals Engineering and Technology* (BNES, London, 1984), Vol. 2, p. 269.
[45]K. J. Kelly, E. W. Hobart, and R. G. Bjork, U.S. Atom. Energy Comm. Rep. CONF-650411, p. 64 (1965); Rep. CNML-6337 (1965).
[46]A. J. Hooper, E. A. Trevillion, and A. C. Whittingham, *Liquid Metal Engineering and Technology* (BNES, London, 1984), Vol. 2, p. 255.
[47]T. Gnanasekaran, Ph.D. thesis, University of Madras, Madras, India, 1987.
[48]F. A. Kozlov, L. G. Volchkov, E. K. Kuznetsov, and V. V. Matyukhin, *Zhidkometallicheskie Teplonositeli v Yaderno Energeticheskikh Ustanovkakh* (Energoatomizdat, Moskva, 1983), p. 27.
[49]V. I. Subbotin, M. N. Ivanovskii, and M. N. Arnoldov, *Fiziko-Khimicheskie Osnovy Primeneniya Zhidkometallicheskikh Teplonositelei* (Atomizdat, Moskva, 1970), p. 66.
[50]J. P. Ackerman and J. Allen, U.S. Atom. Energy Comm. Rep. ANL-7775 (1971).
[51]J. P. Maupré, Comm. Energy Atom. (Fr.) Rep. CEA-R-4905 (1978).
[52]W. Sleppy, Inorg. Chem. **5**, 2021 (1966).
[53]L. Joncourt, M. Mermoux, P. Touzain, L. Bonnetain, D. Dumas, and B. Allard, Phys. Chem. Solids **57**, 877 (1996).
[54]Anonymous, U.S. Atom. Energy Comm. Rep. ANL-7350, p. 60 (1967).
[55]A. K. Fischer and F. A. Cafasso, Trans. Am. Nucl. Soc. **14**, 623 (1971).
[56]S. J. Rodgers, U.S. Atom. Energy Comm. Rep. ANL-7520, Pt. I, p. 25 (1969).
[57]R. J. Pulham and P. Hubberstey, J. Nucl. Mater. **115**, 239 (1983).
[58]W. S. Clough and S. W. Wade, J. Nucl. Ener. **25**, 445 (1971).
[59]T. Yildirim, O. Zhou, J. E. Fischer, N. Bykovetz, R. A. Strongin, M. A. Cichy, A. B. Smith, C. L. Lin, and R. Jellinek, Nature (London) **360**, 568 (1992).

Components:
(1) Carbon; C; [7440-44-0]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
J. G. Gratton, U.S. Atom. Energy Comm. Rep. KAPL-1807 (1957).

Variables:
Temperature: 420–973 K;
O concentration: $6\cdot10^{-3}$ and $3.7\cdot10^{-2}$ mol % O

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of C in liquid Na was determined at two O concentrations

O Concentration/mol %	t/°C	Solubility/mass % C	Solubility/mol % C[a]
$6\cdot10^{-3}$	147	$2.6\cdot10^{-3}$; $3.1\cdot10^{-3}$; $4.2\cdot10^{-3}$; $3.6\cdot10^{-3}$	$6.1\cdot10^{-3}$
		$2.5\cdot10^{-3}$; $2.7\cdot10^{-3}$; $3.0\cdot10^{-3}$; $3.0\cdot10^{-3}$; $4.0\cdot10^{-3}$	
	300	$6.2\cdot10^{-3}$; $3.8\cdot10^{-3}$; $4.5\cdot10^{-3}$; $5.0\cdot10^{-3}$	$9.2\cdot10^{-3}$
		$4.5\cdot10^{-3}$; $4.7\cdot10^{-3}$; $4.9\cdot10^{-3}$	
	500	$5.1\cdot10^{-3}$; $7.0\cdot10^{-3}$; $6.9\cdot10^{-3}$; $7.1\cdot10^{-3}$	$1.25\cdot10^{-2}$
		$7.0\cdot10^{-3}$; $7.1\cdot10^{-3}$; $5.1\cdot10^{-3}$; $6.2\cdot10^{-3}$; $7.3\cdot10^{-3}$	
	700	$7.5\cdot10^{-3}$; $8.0\cdot10^{-3}$; $8.7\cdot10^{-3}$; $8.0\cdot10^{-3}$	$1.42\cdot10^{-2}$
		$7.2\cdot10^{-3}$; $7.6\cdot10^{-3}$; $7.8\cdot10^{-3}$; $7.8\cdot10^{-3}$	
		$8.5\cdot10^{-3}$; $7.5\cdot10^{-3}$; $7.0\cdot10^{-3}$	
$3.7\cdot10^{-2}$	147	0.0116; 0.0099; 0.0112; 0.0125; 0.0118	0.022
		0.0108; 0.0114; 0.0121	
	300	0.0134; 0.0134; 0.0139; 0.0133; 0.0142	0.026
		0.0137; 0.0133; 0.0138	
	500	0.0174; 0.0168; 0.0152; 0.0179; 0.0171	0.033
		0.0170; 0.0179; 0.0176	
	700	0.0099; 0.0188; 0.0179; 0.0185; 0.0174	0.036
		0.0190; 0.0184	

[a]Mean value calculated by the compilers.

The results were approximated by two solubility equations (tested by the compilers):

$$\ln(\text{soly}/10^{-4}\ \text{mass \% C}) = 4.96 - 621\ (T/\text{K})^{-1} \quad \text{for } 6\cdot10^{-3}\ \text{mol \% O}$$

and

$$\ln(\text{soly}/10^{-4}\ \text{mass \% C}) = 5.61 - 376\ (T/\text{K})^{-1} \quad \text{for } 3.7\cdot10^{-2}\ \text{mol \% O.}$$

Kinetics of C dissolution was investigated. The solubility equilibrium was reached after 8 h.

Auxiliary Information

Method:
A reaction vessel was made of 304 stainless steel. The vessel was equipped with tubes for charging and circulation of inert gas (He), probing liquid level, withdrawing samples and with thermocouples sheaths. The vessel was surrounded by a heater and was agitated on a shaker. The temperature was determined by means of a Chromel/Alumel thermocouple. A stick of C was introduced into the vessel filled with Na. Na was sampled after various times of equilibration and at various temperature levels through a 5 μm filter. The sampling tube was immediately cooled in dry ice. Na was dissolved in H_2O. C bonded as CO_2 was evolved by acidifying the sample and heating to dryness. Acid insoluble C was oxidized with the Van Slyke mixture and CO_2 formed was measured manometrically.[1] The analysis was performed in the same manner in the case of addition of Na_2O to the Na.

Source and Purity of Materials:
C: 99.9% pure graphite from National Spectroscopic and contained $3\cdot10^{-4}$ % Mg.
Na: from Du Pont; contained $4\cdot10^{-3}$ % O, $1.2\cdot10^{-2}$ % Ca, $2.0\cdot10^{-3}$ % Co; $7.0\cdot10^{-3}$ % Si; $5.0\cdot10^{-3}$ % P; $4\cdot10^{-4}$ % Ni; $1.0\cdot10^{-4}$ % Al; and $9.0\cdot10^{-3}$ % S; Fe, Mg, B, and Cl not detected.
He: nothing specified.

Estimated Error:
Solubility: precision better than ±10%.
Temperature: nothing specified.

References:
[1]L. P. Pepkowitz and J. T. Porter, U.S. Atom. Energy Comm. Rep. KAPL-1444 (1955); Anal. Chem. **28**, 1606–1608 (1956).

Components:
(1) Carbon; C; [7440-44-0]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
W. J. Anderson and G. V. Sneesby, U.S. Atom. Energy Comm. Rep. NAA-SR-5282 (1960).

Variables:
One temperature: 922 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of C in liquid Na at (1200 °F) 922 K was found to be $7.0\cdot10^{-3}$ mass % C or $1.3\cdot10^{-2}$ mol % C, as read from a figure and recalculated to mol % C by the compilers. The authors claimed that the level of the C content in liquid Na containing O in higher concentration (0.030 mass % O) would be increased, but they did not observe any influence of O on the kinetics of the dissolution process. The same results were reported in Anderson.[1]

Auxiliary Information

Method:
The experiments were performed in a 304 stainless steel capsule. The capsule was loaded with Na, pure Fe wire, and an excess of graphite. The capsule was welded in a He-filled glove box. The capsule was held for 100 h at 922 K. The amount of C that dissolved in liquid Na, solid Fe, and in the steel was found by an unspecified chemical analysis. The solubility of C in liquid Na was found from a plot relating the C content in Na and in the steel: a plateau on such dependence starts at the saturation of liquid Na with C.

Source and Purity of Materials:
C: powdered graphite of unspecified purity.
Na: "reactor grade," contained $(1.0–1.5)\cdot10^{-3}$ % O. Only internal parts of Na blocks were utilized. Excess of O was removed by means of gettering with Zr strips.
He: nothing specified.

Estimated Error:
Solubility: nothing specified; reading-out procedure ±1%.
Temperature: nothing specified.

References:
[1]W. J. Anderson, U.S. Atom. Energy Comm. Rep. TID-7626, pp. 92–100 (1962).

Components:
(1) Carbon; C; [7440-44-0]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
R. C. Andrews, R. H. Hiltz, L. H. Kirschler, S. J. Rodgers, and F. Tepper, U.S. Atom. Energy Comm. Rep. MSAR-65-194 (1965).

Variables:
One temperature: 922 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of C in liquid Na was determined in a loop with circulating Na for several months at 1200 °F (922 K). The C content found by the measurements was $2.5\cdot10^{-3}$–$4.0\cdot10^{-3}$ mass % C, in average $3.7\cdot10^{-3}$ mass % C. The mean value of the solubility calculated by the compilers is then $7.1\cdot10^{-3}$ mol % C.

Auxiliary Information

Method:
Na (containing C) was circulated in a 316 stainless steel loop for times between 10 days and 1.5 year. Samples of Na withdrawn from the loop were filtered through a 5 μm filter into a sample tube. All steps of the analysis were performed in a He atmosphere. The filtrate was dissolved in H_2O at 273 K, acidified, and dehydrated. The dehydrated salt was combusted at 922 K in pure O atmosphere. CO_2 released during the combustion was collected at liquid N temperature in a sample tube. CO_2 was analyzed by an unspecified method which was, however, tested on C standard.

Source and Purity of Materials:
C: nothing specified.
Na: "reactor grade" from Du Pont Comp.; contained $<3\cdot10^{-3}$ % O, $<5\cdot10^{-4}$ % Ca, and $<6\cdot10^{-4}$ % Cl.
He: contained $5\cdot10^{-4}$ % H, 0.015% Ar and 4% N.

Estimated Error:
Solubility: precision ±10%; accuracy ±20% in a blank test
Temperature: nothing specified.

Components:
(1) Carbon; C; [7440-44-0]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
C. C. Addison, M. R. Hobdell, and R. J. Pulham, *The Alkali Metals* (The Chemical Society, London, 1967), pp. 270–276.

Variables:
Temperature: 373–573 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of C in liquid Na in the temperature range 100–200 °C was found to be below $1\cdot10^{-4}$ mass % C or $2\cdot10^{-4}$ mol % C (as calculated by the compilers). Qualitative observations indicated that even the C solubility at 300 °C should be lower than $2\cdot10^{-4}$ mol % C.

Auxiliary Information

Method:
The apparatus consisted of two concentric cylindrical vessels made of Pyrex glass. The entire apparatus was evacuated. The inner reservoir was filled with H_2C_2 and the outer with molten Na. The apparatus was immersed in a silicone oil thermostat. Na was vigorously stirred. H_2C_2 was introduced into the Na compartment. The formation of solid Na_2C_2 on the Na surface was completed after ~30 h at 423 K. The gaseous products H_2C_2 and H were pumped off and Na_2C_2 remained as a red film deposit on Na. The solubility limit was estimated from the mass balance of the reacting components.

Source and Purity of Materials:
H_2C_2: "purified by accepted methods."
Na_2C_2: from UKAEA; contained $(5-10)\cdot10^{-4}$ % O, $4.0\cdot10^{-3}$ % Ca.
Ar: "purified."

Estimated Error:
Solubility: nothing specified; detectivity level ~$2\cdot10^{-4}$ mol % (by the compilers).
Temperature: nothing specified.

Components:
(1) Carbon; C; [7440-44-0]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
C. Luner, A. Cosgarea, and H. M. Feder, *Alkali Metal Coolants* (IAEA, Vienna, 1967), pp. 171–179.

Variables:
Temperature: 430–728 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

Two methods of solubility determination were applied to show that Gratton's[1] results of the solubility of C in liquid Na were overestimated. The results of the first method (using a filtration) were presented in a figure; the numerical results were published briefly in Adams and Glassner[2] and in full in anonymous.[3]

t/°C	Solubility/mass % C	Solubility/mol % C[a]
157	$7.4\cdot10^{-3}$, $6.6\cdot10^{-3}$, $1.30\cdot10^{-2}$	$9.0\cdot10^{-3}$
158	$1.06\cdot10^{-2}$, $5.5\cdot10^{-3}$, $8.8\cdot10^{-3}$, $7.1\cdot10^{-3}$3, $7.2\cdot10^{-3}$, $6.3\cdot10^{-3}$	$7.6\cdot10^{-3}$
291	$6.1\cdot10^{-3}$, $8.0\cdot10^{-3}$, $4.7\cdot10^{-3}$	$6.3\cdot10^{-3}$
307	$4.1\cdot10^{-3}$, $5.6\cdot10^{-3}$, $5.7\cdot10^{-3}$, $5.8\cdot10^{-3}$	$5.3\cdot10^{-3}$
375	$5.9\cdot10^{-3}$, $1.27\cdot10^{-2}$, $9.6\cdot10^{-3}$, $1.30\cdot10^{-2}$, $4.5\cdot10^{-3}$	$9.2\cdot10^{-3}$
455	$1.01\cdot10^{-2}$, $1.16\cdot10^{-2}$, $1.08\cdot10^{-2}$	$1.08\cdot10^{-2}$

[a]Mean value calculated by the compilers.

Results of the second method (using ^{14}C) lead to the conclusion that although the total C content in liquid Na after filtration was $(9.8\pm3.2)\cdot10^{-4}$ mass % C, the true solubility of elemental C in liquid Na, however, was only $<5\cdot10^{-6}$ mass % C or $<1\cdot10^{-5}$ mol % C (as calculated by the compilers) at temperatures <723 K.

Auxiliary Information

Method:
All essential operations were performed in He atmosphere. A graphite crucible was outgassed at 1273 K (for the first method). Molten Na was filtered through a 5 μm stainless steel filter into the crucible. The melt was stirred and heated to a selected temperature. Na samples were obtained from time to time by lowering a Ta or a stainless steel tube closed by the 5 μm frit into the Na. The outer part of the apparatus was pressurized to allow a filtration of Na into the sampling tube. The samples were analyzed for total C by combustion in O gas. In the first variant the residue was heated to 1373 K in an O atmosphere. CO_2 was liberated and Na_2O reacted with SiO_2. CO_2 was determined by gas chromatography after cold trapping in liquid N. In the second variant the Na samples were burned in an alumina crucible and cooled. The residue was treated with H_2SO_4 and CO_2 released. In the second method a C pellet, containing ^{14}C, was added to liquid Na in a stainless steel container. The total C content was analyzed. The filtered samples of Na were withdrawn periodically at various temperatures over a period of 4 months from the stirred melt. The samples were analyzed for their total C and ^{14}C contents.

Source and Purity of Materials:
C: "reactor grade" ATJ graphite crucible (I method) or ^{14}C labeled pellet from New England Nuclear Corp. (II method).
Na: "high-C reagent grade" from Baker & Adamson Co. (I method) or "reactor grade" from U.S. Industrial Chem. Co., contained $(3.2\pm0.5)\cdot10^{-3}$ % C.
He: purified, contained $<1.0\cdot10^{-3}$ % O and $\sim1\cdot10^{-4}$ % H_2O.
O: "ultra high purity," further purified by passage through two furnaces containing Pt and CuO at 1223 K and 5 A molecular sieves.

Estimated Error:
Solubility: scatter of the results at selected temperature up to ±50%; accuracy of analysis ±15%.
Temperature: nothing specified; reading-out procedure ±10 K.

References:
[1]J. G. Gratton, U.S. Atom. Energy Comm. Rep. KAPL-1807 (1957).
[2]R. M. Adams and A. Glassner, Eds., U.S. Atom. Energy Comm. Rep. ANL-6923 (1964).
[3]Anonymous, U.S. Atom. Energy Comm. Rep. ANL-7020, pp. 78–82 (1965).

Components:
(1) Carbon; C; [7440-44-0]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
F. A. Cafasso, U.S. Atom. Energy Comm. Rep. ANL-7419, pp. 126–127 (1968).

Variables:
One temperature: 923 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

Na from loop tests, described in Adams and Glassner,[1] was sampled at 650 °C and analyzed for its C content. An unfiltered sample contained $1.7\cdot10^{-4}$ mass % C ($3.2\cdot10^{-4}$ mol % C), while two filtered samples contained $3\cdot10^{-6}$ mass % C ($6\cdot10^{-6}$ mol % C) and $3\cdot10^{-5}$ mass % C ($6\cdot10^{-5}$ mol % C), respectively. The discrepant results of analyses of the filtered samples, according to the authors, may be due to the existence of very fine ^{14}C-bearing particles that can pass through the filter used. Thus the lower solubility limit reported is more reliable.

Auxiliary Information

Method:
According to Adams and Glassner,[1] Na containing C circulated in a loop. C migrated from a ferritic steel (with a high C content) to an austenitic steel (with a low C content) using ^{14}C as a tracer. A cylindrical crucible and a lid were fabricated from a sheet of Fe–C alloy enriched with ^{14}C. Na was added to the crucible to immerse a 304 stainless steel coupon (suspended on a Ta wire). The crucible was welded, heated at 923 K for 150 h, cooled to room temperature, and opened for analysis. The coupon was highly enriched in ^{14}C. The total C content in liquid Na was analyzed in the unfiltered and filtered samples (through a 5 μm porosity frit into a Ni collecting tube). CO_2 was measured after combustion of C by a radio chromatograph.

Source and Purity of Materials:
C source: a ferritic steel.
Na: "reactor grade" of purity.
He: nothing specified.

Estimated Error:
Solubility: precision of order of magnitude.
Temperature: nothing specified.

References:
[1]R. M. Adams and A. Glassner, Eds., U.S. Atom. Energy Comm. Rep. ANL-7342, pp. 68–69 (1967).

Components:
(1) Carbon; C; [7440-44-0]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
D. C. Gehri and J. B. Ott, U.S. Atom. Energy Comm. Rep. AI-AEC-Memo-12686 (1968).

Variables:
Temperature: 870–1373 K; C source

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

Preliminary results of the solubility of C in liquid Na using various forms of the solute

Solute	t/°C	Time/h	Solubility/mass % C	Solubility/mol % C[a]
UC	764	4	$1.1\cdot10^{-3}$[b]	$2.1\cdot10^{-3}$
	910	4	$1.06\cdot10^{-3}$	$2.0\cdot10^{-3}$
Diamond	597	30	$1.06\cdot10^{-3}$	$2.0\cdot10^{-3}$
	601	24	$1.26\cdot10^{-3}$	$2.4\cdot10^{-3}$
	657	24	$8.0\cdot10^{-4}$	$1.5\cdot10^{-3}$
	701	24	$9.7\cdot10^{-4}$	$1.9\cdot10^{-3}$
	753	24	$9.8\cdot10^{-4}$	$1.9\cdot10^{-3}$
	764	4	$2.4\cdot10^{-3}$[b]	$4.6\cdot10^{-3}$
	815	24	$7\cdot10^{-4}$	$1.3\cdot10^{-3}$
	850	7	$1.30\cdot10^{-3}$	$2.5\cdot10^{-3}$
	917	3.5	$1.5\cdot10^{-3}$[b]	$2.9\cdot10^{-3}$
	948	4	$5\cdot10^{-4}$	$9.6\cdot10^{-4}$
	999	4	$7.9\cdot10^{-4}$	$1.5\cdot10^{-3}$
	1052	6	$1.86\cdot10^{-3}$	$3.6\cdot10^{-3}$
Graphite	698	24	$5.4\cdot10^{-4}$	$1.0\cdot10^{-3}$
commercial	901	24	$1.24\cdot10^{-3}$	$2.4\cdot10^{-3}$

[a]Calculated by the compilers.
[b]Capsule filled in glove box rather than in high vacuum chamber.

Ultimate results of C solubility in liquid Na

Solute	t/°C	Time/h	Solubility/mass % C	Solubility/mol % C[a]
Graphite	800	24	$1.5\cdot10^{-3}$[b]	$2.9\cdot10^{-3}$
Single	897	24	$1.5\cdot10^{-3}$[b]	$2.9\cdot10^{-3}$
crystal	995	24	$2.05\cdot10^{-3}$[b]	$3.9\cdot10^{-3}$
	1097	24	$1.6\cdot10^{-3}$[b]	$3.1\cdot10^{-3}$
diamond	700	24	$1.2\cdot10^{-3}$[b]	$2.3\cdot10^{-3}$
		6	$1.9\cdot10^{-3}$	$3.6\cdot10^{-3}$
	799	20	$1.35\cdot10^{-3}$[b]	$2.6\cdot10^{-3}$
	900	6	$2.35\cdot10^{-3}$	$4.5\cdot10^{-3}$
	999	6	$1.95\cdot10^{-3}$[b]	$3.7\cdot10^{-3}$
	1000	6	$2.3\cdot10^{-3}$[b]	$4.2\cdot10^{-3}$
			$2.7\cdot10^{-3}$[c]	$5.2\cdot10^{-3}$
			$2.2\cdot10^{-3}$[c]	$4.1\cdot10^{-3}$
			$1.3\cdot10^{-3}$[c]	$2.5\cdot10^{-3}$
			$2.3\cdot10^{-3}$[c]	$4.2\cdot10^{-3}$
			$1.1\cdot10^{-3}$[c]	$2.1\cdot10^{-3}$
	1100	6	$1.6\cdot10^{-3}$[b]	$3.1\cdot10^{-3}$

[a]Calculated by the compilers.
[b]Reported in McKisson *et al.*[1]
[c]Reported in McKisson *et al.*[2]

The authors proposed the following fitting equation for the results marked with (b):

$$\log(\text{soly/mass \% C}) = -2.28 - 610\ (T/\text{K})^{-1}.$$

All results were approximated by the following solubility equation:

$$\log(\text{soly/mass \% C}) = -2.45 - 360\ (T/\text{K})^{-1}.$$

The same equation was reported in (McKisson *et al.*[3]). The compilers tested the equations.

Auxiliary Information

Method:
Graphite (or another C source) sample was loaded into a Ni test capsule in He atmosphere. The capsule contained a 300 μm filter placed in the center. The capsule was outgassed at 1273 K for ~3 h at ~10^{-4} Pa. It was loaded with Na and sealed without exposing the content to the atmosphere. The sealed capsule was placed in a furnace and heated 1 h to reach a selected temperature for a proper time of equilibration. The entire furnace was inverted at the test temperature and left for 1–2 min. The capsule fell from the furnace and was quenched by blowing cold air. The solidified Na filtrate was dry combusted in a purified O–He stream for 1.5 h at 1423 K in a silica boat, placed in a quartz sleeve. The latter apparatus was fired in an O atmosphere for 4 h at 1473 K. The collected CO_2 was measured using a calibrated gas chromatograph. The C content was independently measured by G. J. Lutz (NBS) using activation analysis $^{12}C(\gamma,n)^{11}C$.[3]

Source and Purity of Materials:
C(graphite): single crystal plates from Atomics Internation, or commercial product from AGOT. Both samples were outgassed in vacuum at 2273 K for ~6 h.
UC: single crystal from EBM, broken into pieces, washed in acetone, dried, and stored in Ar.
C(diamond): industrial grade white chips from W. E. Block Co. The pieces were washed in concentrated HF, HNO_3, distilled H_2O, and acetone.
Na: unspecified; purified by double distillation and gettering with Zr foil at 923 K for ~18 h; finally contained $<5\cdot10^{-4}$ % O, $<1.0\cdot10^{-3}$ % C, and ~10^{-4} % of metallic impurities.
Ar: nothing specified.
He: nothing specified.

Estimated Error:
Solubility: precision of chemical analysis ±5%; precision of the whole determination ±30%.
Temperature: accuracy and stability ±1 K; uniformity along the capsule 3 K.

References:
[1]R. L. McKisson, R. L. Eichelberger, D. C. Gehri, and J. Guon, U.S. Atom. Energy Comm. Rep. AI-AEC-12721, pp. 295–298 (1968).
[2]R. L. McKisson, R. L. Eichelberger, D. C. Gehri, and J. Guon, U.S. Atom. Energy Comm. Rep. AI-AEC-12680, pp. 158–159 (1969).
[3]R. L. McKisson, R. L. Eichelberger, D. C. Gehri, and J. Guon, U.S. Atom. Energy. Comm. Rep. AI-AEC-12744, pp. 133–134 (1968).

Components:
(1) Carbon; C; [7440-44-0]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
C. Luner, H. M. Feder, and F. A. Cafasso, U.S. Atom. Energy Comm. Rep. ANL-7520, Pt. I, pp. 455–459 (1969).

Variables:
One temperature: 923 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The content of ^{14}C in liquid Na after equilibration of the two elements at 650 °C (923 K) was found to be $\sim 1 \cdot 10^{-5}$ mass %C or $\sim 2 \cdot 10^{-5}$ mol %C (as calculated by the compilers). It was assumed that the concentration of ^{14}C dissolved in liquid Na is the solubility of C in liquid Na in the range of experimental conditions. However, no proof was given that saturation was achieved.

Auxiliary Information

Method:
A crucible with matching lid was fabricated from the ^{14}C labeled Fe–C alloy. It was loaded with Na or Na with a 316 stainless steel coupon. The crucible was welded and closed in a second Ni or a 304 stainless steel capsule welded shut. The capsule was heated to 923 K for 120 h, cooled, and cut open. All these operations were performed in an Ar atmosphere. A Na sample (from the crucible) was dissolved in a deairated, distilled H_2O dropping from a side arm. Then H_2SO_4 was added into the solution. The evolved gases were collected in a liquid N cooled silica-gel trap. The gas was analyzed by a radio gas chromatograph. The resulting black deposit of C (left after filtration) was oxidized to CO_2 by $K_2S_2O_8$ and determined by the radio gas chromatograph.

Source and Purity of Materials:
C source: Fe (99.95+% pure) was remelted several times with amorphous C (tagged with ^{14}C) in He atmosphere and annealed at 1023 K; uniform distribution of C was tested.
Na: reactor grade purity from Industrial Chemical Co., contained $2.0 \cdot 10^{-3}$ % O and $1.0 \cdot 10^{-3}$ % C.
He: nothing specified.

Estimated Error:
Solubility: precision of the gas analysis ±3%.
Temperature: nothing specified.

Components:
(1) Carbon; C; [7440-44-0]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
B. Longson and A. W. Thorley, J. Appl. Chem. **20**, 372–379 (1970).

Variables:
Temperature: 873–1223 K;
O concentration: $1.4 \cdot 10^{-3}$–0.057 mol % O; C source

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of C in liquid Na was determined with two kinds of capsules

Silica capsules

t/°C	Time/d	C source	O Concentration in Na/mol %	Solubility/mass % C	Solubility/mol % C[a]
650	35	C-CO-CO_2	$1.4 \cdot 10^{-3}$	$1.7 \cdot 10^{-3}$	$3.3 \cdot 10^{-3}$
	70	mixture		$2.1 \cdot 10^{-3}$	$4.0 \cdot 10^{-3}$
				$2.2 \cdot 10^{-3}$	$4.4 \cdot 10^{-3}$
700	15			$2.9 \cdot 10^{-3}$	$5.6 \cdot 10^{-3}$
	21			$4.5 \cdot 10^{-3}$	$8.6 \cdot 10^{-3}$
	30			$6.0 \cdot 10^{-3}$	0.0115
800	5			$6.5 \cdot 10^{-3}$	0.0124
	28			0.0104	0.1099
	42			0.0118	0.023
	28			0.0124	0.024
				0.0101	0.0194
				$9.1 \cdot 10^{-3}$	0.0174
				$6.0 \cdot 10^{-3}$	0.0115
				$8.0 \cdot 10^{-3}$	0.0153
	17			0.0241	0.046
	21			$8.3 \cdot 10^{-3}$	0.0159
				$7.3 \cdot 10^{-3}$	0.0140
				$7.9 \cdot 10^{-3}$	0.0151
700			0.0290	$1.8 \cdot 10^{-3}$	$3.5 \cdot 10^{-3}$
				$2.6 \cdot 10^{-3}$	$5.0 \cdot 10^{-3}$
800	7		0.0570	0.0122	0.023
	14			$5.8 \cdot 10^{-3}$	0.0111
				$9.2 \cdot 10^{-3}$	0.0176

Metallic capsules; liquid Na contained $1.4\cdot10^{-3}$ mol % O

t/°C	Time/d	C source	Capsule	Solubility/mass % C	Solubility/mol % C[a]
700	49	graphite	Ni	$4.9\cdot10^{-3}$	$9.3\cdot10^{-3}$
750	21			$7.3\cdot10^{-3}$	0.0140
	84			0.0117	0.022
800	7			0.0167	0.032
	28			0.0141	0.027
	77			0.0159	0.030
				0.0206	0.039
	14			0.0207	0.040
	49			$7.1\cdot10^{-3}$	0.0137
850	3			0.0320	0.061
900	2			0.0511	0.098
	8			0.0597	0.114
950	1			0.0577	0.110
				0.0481	0.092
700	3	soot		$3.3\cdot10^{-3}$	$6.7\cdot10^{-3}$
800	2			0.0157	0.030
				0.0160	0.031
700	28	NaCN		$8.0\cdot10^{-3}$	0.0153
800	16			0.123	0.024
600	84	Steel with	Mild steel	$1.0\cdot10^{-3}$	$1.9\cdot10^{-3}$
		0.4% C		$9\cdot10^{-4}$	$1.7\cdot10^{-3}$
				$9\cdot10^{-4}$	$1.7\cdot10^{-3}$
				$1.2\cdot10^{-3}$	$2.3\cdot10^{-3}$
700	23		Cr–Mo	$5.9\cdot10^{-3}$	0.0013
				$2.8\cdot10^{-3}$	$5.4\cdot10^{-3}$
				$6.7\cdot10^{-3}$	0.0128
	56			$7.4\cdot10^{-3}$	0.0141
				$6.2\cdot10^{-3}$	0.0119
800	28			0.0113	0.022
				0.0160	0.031
	56			0.0117	0.023
				0.0111	0.021
				$9.6\cdot10^{-3}$	0.0184
				$9.8\cdot10^{-3}$	0.0188
600	112	Gettered by Zr	Ni	$1.3\cdot10^{-3}$	$2.5\cdot10^{-3}$
	28			$4\cdot10^{-4}$	$8\cdot10^{-4}$

[a]Calculated by the compilers.

The results were also published in Longson and A. W. Thorley.[1] Graphite seems to be the equilibrium solid phase. Most probably, C is dissolved in liquid Na as single atoms. Any influence of O on the C solubility was not observed.

Auxiliary Information

Method:

All glove box operations were carried out in an Ar atmosphere. The experiments were performed using two methods: two types of containment and various C sources. In the first case a metal capsule contained a C–steel, NaCN, soot or graphite suspended in Na. C diffused from an outer Na compartment through a thin walled Ni can into a pure internal Na sample. In the second case a sealed capsule contained a graphite $+CO+CO_2$ mixture to regulate the C activity in the Ni can which contained the Na sample. Both Ni cans contained alumina crucibles inside. All parts of the apparatus were cleaned by pickling and baked for 4 h at 923 K in a H atmosphere. During heat treatment, the capsules were rotated from time to time in order to expose the Ni uniformly to Na. After the heating, both types of assemblies were quenched in an oil bath. The Ni outer capsule was opened, Na dissolved in C_2H_5OH, followed by hot H_2O. In the case of the silica capsule the $CO+CO_2$ mixture was analyzed by freezing out CO_2 in liquid N and measuring the remaining gas pressure. The lids of the Ni inner cans were opened. Molten Na (after heating) was drained away leaving the alumina full of Na. Further heating leads to distillation of Na for 6 h at 873 K and a pressure of 13 Pa. The crucible from the Ni capsule was introduced into an O stream at 1473 K. The evolved CO_2 volume was measured. The C content in the Ni can was analyzed. The crucible from the silica capsule was exposed to HCl vapor and $NaCO_3$ present therein was transferred into NaCl. C, unaffected by this treatment, was burned and determined by the same method as above. The solubility results were corrected for unit C activity in relation to the various activities of C sources.

Source and Purity of Materials:

C: graphite, soot, C dissolved in a steel or Ni, NaCN; all of unspecified purity.
Na: three times distilled; contained $<1\cdot10^{-3}$ % O, $1.5\cdot10^{-3}$ % K, $8\cdot10^{-4}$ % Fe, $3\cdot10^{-4}$ % Cr, $2\cdot10^{-4}$ % Ni, $5\cdot10^{-4}$ % C, and $<3\cdot10^{-5}$ % H.
Ar: "purified."

Estimated Error:

Solubility: nothing specified; precision ±25% (by the compilers).
Temperature: nothing specified.

References:

[1]B. Longson and A. W. Thorley, U.K Atom. Ener. Author. Rep. TRG-1906 (1970).

Components:
(1) Carbon; C; [7440-44-0]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
R. L. McKisson, R. L. Eichelberger, D. C. Gehri, and J. Guon, U.S. Atom. Energy Comm. Rep. AI-AEC-12859, p. 155 (1970).

Variables:
Temperature: 973–1288 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data
The solubility of C in liquid Na was determined

t/°C	Solubility/mass % C	Solubility/mol % C[a]
700	$7.6\cdot10^{-4}$	$1.5\cdot10^{-3}$
725	$1.74\cdot10^{-3}$	$3.3\cdot10^{-3}$
750	$1.52\cdot10^{-3}$	$2.9\cdot10^{-3}$
770	$1.53\cdot10^{-3}$	$2.9\cdot10^{-3}$
780[b]	$1.68\cdot10^{-3}$	$3.2\cdot10^{-3}$
780	$2.52\cdot10^{-3}$	$4.8\cdot10^{-3}$
800	$2.18\cdot10^{-3}$	$4.2\cdot10^{-3}$
835	$2.84\cdot10^{-3}$	$5.4\cdot10^{-3}$
850	$6.37\cdot10^{-3}$	$1.22\cdot10^{-2}$
915	$6.95\cdot10^{-3}$	$1.33\cdot10^{-2}$
920	$5.11\cdot10^{-3}$	$9.8\cdot10^{-3}$
950[b]	$1.26\cdot10^{-2}$	$2.4\cdot10^{-2}$
1015	$2.80\cdot10^{-2}$	$5.4\cdot10^{-2}$

[a]Calculated by the compilers.
[b]Na contained $2.5\cdot10^{-3}$ mass % O ($2.5\cdot10^{-3}$ mol % O, by the compilers).

The authors proposed the fitting equation for their experimental results:

$$\log(\text{soly/mass \% C}) = 2.50 - 5450\ (T/\text{K})^{-1}.$$

The same results were reported in Gehri and Ott.[1]

Auxiliary Information

Method:
The experiments were performed in a closed double capsule. Na was placed in the lower half made of Ni-270 saturated with C at selected temperatures. After the equilibration of Na with C–Ni, the sampling was made by inverting the capsule and allowing the Na to run into the other half of the capsule made of Cu. The analysis of Na was accomplished by cutting off the measured length of the Cu end. The sample was combusted and the resulting CO_2 was measured using a calibrated gas chromatograph.

Source and Purity of Materials:
C: from Ni saturated with C to its saturation level.
Na: gettered and distilled from the System Quality Sodium Loop; contained finally $1.8\cdot10^{-3}$ % O and $<1.8\cdot10^{-3}$ % metallic contaminants. Two experiments were made with an O-spiked Na containing $5\cdot10^{-4}$ % C and $2.5\cdot10^{-3}$ % O.

Estimated Error:
Solubility: standard deviation ±35% according to Johnson *et al.*[2]
Temperature: probably accuracy and stability ±1 K; uniformity along the capsule 3 K.

References:
[1]D. C. Gehri and J. B. Ott, U.S. Atom. Energy Comm. Rep. AI-AEC-Memo-12826 (1970).
[2]G. K. Johnson, E. H. Van Deventer, J. P. Ackerman, W. N. Hubbard, D. W. Osborne, and H. E. Flotow, J. Chem. Thermodyn. **5**, 57–71 (1973).

Components:
(1) Carbon; C; [7440-44-0]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
F. J. Salzano, L. Newman, and M. R. Hobdell, Nucl. Technol. **10**, 335–347 (1971).

Variables:
One temperature: 923 K;
O concentration: $<1.4\cdot10^{-3}$–0.035 mol % O

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data
The solubility of C in liquid Na at 650 °C (923 K) at different O levels was determined

O Concentration/mass %	O Concentration/mol %[a]	Solubility/mass % C	Solubility/mol % C[a]	Average/mol % C[a]
$<1\cdot10^{-4}$	$<1.4\cdot10^{-4}$	$2.2\cdot10^{-3}$	$4.2\cdot10^{-3}$	$3.8\cdot10^{-3}$
		$1.7\cdot10^{-3}$	$3.3\cdot10^{-3}$	
		$1.7\cdot10^{-3}$	$3.3\cdot10^{-3}$	
		$2.1\cdot10^{-3}$	$4.0\cdot10^{-3}$	
		$2.0\cdot10^{-3}$	$3.8\cdot10^{-3}$	
		$2.2\cdot10^{-3}$	$4.2\cdot10^{-3}$	
0.01	0.014	$3.3\cdot10^{-3}$	$6.3\cdot10^{-3}$	$6.1\cdot10^{-3}$
		$3.1\cdot10^{-3}$	$5.9\cdot10^{-3}$	
0.024	0.035	$2.4\cdot10^{-3}$	$4.6\cdot10^{-3}$	$4.8\cdot10^{-3}$
		$2.6\cdot10^{-3}$	$5.0\cdot10^{-3}$	
		$2.6\cdot10^{-3}$	$5.0\cdot10^{-3}$	

[a]Calculated by the compilers.

Auxiliary Information

Method:
A C meter was based on the cell: C(graphite) in Na/Fe membrane/Na_2CO_3–Li_2CO_3 eutectic melt/C. C on the right side served as a reference electrode. The cell was placed in a Fe vessel with a Ni liner. O and C levels were reduced to lowest attainable level by gettering. The C and Fe electrodes were vacuum outgassed at 1123 K. After filling the cell with Na and C the electrolyte was added. The assembled cell was conditioned at constant temperature for 24 h. The O concentration in Na was increased by Na_2O addition. A break on relation of potential versus concentration corresponded to the saturation.

Source and Purity of Materials:
C: "high purity" from National Carbon.
Na: nuclear grade of purity, gettered at 923 K with 347 stainless steel and U rods. O content $<1\cdot10^{-4}$ %.
Na_2O: nothing specified.
Na_2CO_3, Li_2CO_3: reagent grade from Baker.

Estimated Error:
Solubility: precision better than ±10%.
Potential: precision ±0.01 mV.
Temperature: nothing specified.

Components:
(1) Carbon; C; [7440-44-0]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
F. J. Salzano and L. Newman, Nucl. Technol. **13**, 289–296 (1972).

Variables:
Temperature: 848–973 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data
The solubility of C in liquid Na was determined

t/°C	Solubility/mass % C	Solubility/mass % C[a]	Solubility/mol % C[b]
575	$(7-8)\cdot 10^{-4}$	$7\cdot 10^{-4}$	$1.3\cdot 10^{-3}$
600	$(7.5-8.2)\cdot 10^{-4}$	$8\cdot 10^{-4}$	$1.5\cdot 10^{-3}$
650	$(9-12)\cdot 10^{-4}$	$1.1\cdot 10^{-3}$	$2.1\cdot 10^{-3}$
675	$(1.3-1.4)\cdot 10^{-3}$	$1.35\cdot 10^{-3}$	$2.6\cdot 10^{-3}$
700	$(1.5-1.7)\cdot 10^{-3}$	$1.6\cdot 10^{-3}$	$3.1\cdot 10^{-3}$

[a]Mean value.
[b]Calculated by the compilers.

The results were also published in Salzano and Newman.[1] The recommended operation temperature of the apparatus is at 650 °C. The authors proposed the approximating solubility equation (tested by the compilers):

$$\log(\text{soly/mass \% C}) = -0.30 - 2440\ (T/\text{K})^{-1}.$$

The solubility of C increased to $(8.5\pm 0.5)\cdot 10^{-3}$ mass % C (0.016 mol % C) at 650 °C, if the He atmosphere was changed for N atmosphere. The results from two C meters in separate and side-by-side experiments were found to be in good agreement.

Auxiliary Information

Method:
The measurements were performed in the electrochemical cell: C(graphite) in Na/Fe barrier/Na_2CO_3–Li_2CO_3 eutectic/C. C on the right side was the reference electrode. The experimental vessel was made of a 304 stainless steel tank containing a Ni liner, filled with Na and equipped with two C meters. The cover gas was He. Known amounts of C were injected into the Na by immersing carburized Fe tabs for various times. The weight lost by the tab and the changes of emf of the cell were recorded. The solubility was calculated from the equation relating addition of C with the equilibrium potentials.

Source and Purity of Materials:
C: from a Fe tab containing dissolved C.
Na: nuclear grade of purity; contained $<1\cdot 10^{-4}$ % O and H pressure of <100 Pa.
He: "commercial" grade of purity.

Estimated Error:
Solubility: nothing specified; precision better than ±8% (by the compilers).
Temperature: nothing specified.

References:
[1]F. J. Salzano and L. Newman, Trans. Am. Nucl. Soc. **14**, 623 (1971).

Components:
(1) Carbon; C; [7440-44-0]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
G. K. Johnson, E. H. Van Deventer, J. P. Ackerman, and W. N. Hubbard, J. Chem. Thermodyn. **5**, 57–71 (1973).

Variables:
Temperature: 624–786 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The authors reported the solubility of Na_2C_2 in liquid Na which was determined in the same laboratory by a part of Ackerman *et al.*[1] The results were exclusively published in form of the solubility equations:

$$\log(\text{soly/mass \% C}) = 2.345 - 4289\ (T/\text{K})^{-1} \quad (1)$$

and

$$\log(\text{soly/mass \% } Na_2C_2) = 2.316 - 4289\ (T/\text{K})^{-1}. \quad (2)$$

It was assumed that below 800 K the rate of decomposition of Na_2C_2, according to the reaction: $2\ Na + 2C \leftrightarrow Na_2C_2$ is slow enough that the solubility of Na_2C_2 can be effectively measured. Unfortunately, the equilibration time in the experiments was not specified. The solubility equations of C in liquid Na (when graphite is dissolved to monoatomic C) was calculated from Eq. (1) and the Gibbs free energy of Na_2C_2 formation:

$$\log(\text{soly/mass \% C}) = 2.71 - 5679\ (T/\text{K})^{-1} \quad (3)$$

and

$$\log(\text{soly/mol \% C}) = 2.99 - 5679\ (T/\text{K})^{-1}. \quad (4)$$

Equation (4) was calculated from Eq. (3) by the compilers. A phase transition of Na_2C_2 occurs at 546 K.

Auxiliary Information

Method:
Finely divided powder of Na_2C_2 was stored and handled exclusively in a He-filled glove box. The solubility of Na_2C_2 in liquid Na was measured by equilibration of both components. The saturated solution was filtered out. It was analyzed by hydrolysis of Na with H_2O. The quantity of C_2H_2 in the gas phase was measured by means of a gas chromatograph.

Source and Purity of Materials:
Na_2C_2: 98.6% pure from Alpha Inorganics, Inc.; contained 0.35% $NaHC_2$, 0.31% 0, <0.005% N, 0.003% Ca, 0.002% K; x-ray diffraction patterns of the sample confirmed literature data.
Na: nothing specified; probably of reactor grade purity.
He: nothing specified.

Estimated Error:
Solubility: precision ±11% for Na_2C_2 and ±50% for C.
Temperature: nothing specified.

References:
[1]J. P. Ackerman, J. W. Allen, and F. A. Cafasso, Argonne National Laboratory (unpublished results, 1973).

Components:
(1) Carbon; C; [7440-44-0]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
R. Ainsley, L. P. Hartlib, P. M. Holroyd, and G. Long, J. Nucl. Mater. **52**, 255–276 (1974).

Variables:
Temperature: 763–1105 K;
O concentration: 0.043–0.84 mol %; N pressure: 0.10–1.8 MPa

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data
The solubility of C in liquid Na was determined

t/°C	Time/h	Solubility/mass % C	Solubility/mol % C[a]	Solubility/mol % C[b]
495	142	$8.2\cdot10^{-5}$	$1.57\cdot10^{-4}$	
500	67	$7.0\cdot10^{-5}$	$1.34\cdot10^{-4}$	
550	268	$2.0\cdot10^{-4}$	$3.8\cdot10^{-4}$	
596	100	$6.6\cdot10^{-4}$	$1.26\cdot10^{-3}$	
660	100	$1.9\cdot10^{-3}$	$3.6\cdot10^{-3}$	$3.6\cdot10^{-3}$
	100	$1.7\cdot10^{-3}$	$3.3\cdot10^{-3}$	
	95.5	$1.2\cdot10^{-3}$	$2.3\cdot10^{-3}$	
	102	$2.4\cdot10^{-3}$	$4.6\cdot10^{-3}$	
	114	$2.1\cdot10^{-3}$	$4.0\cdot10^{-3}$	
710	30	$4.9\cdot10^{-3}$	$9.4\cdot10^{-3}$	$6.5\cdot10^{-3}$
		$4.9\cdot10^{-3}$	$9.4\cdot10^{-3}$	
		$4.0\cdot10^{-3}$	$7.6\cdot10^{-3}$	
		$2.2\cdot10^{-3}$	$4.2\cdot10^{-3}$	
		$3.3\cdot10^{-3}$	$6.3\cdot10^{-3}$	
		$3.5\cdot10^{-3}$	$6.7\cdot10^{-3}$	
		$3.0\cdot10^{-3}$	$5.7\cdot10^{-3}$	
760	10	$7.8\cdot10^{-3}$	0.0150	0.0138
		$7.9\cdot10^{-3}$	0.0151	
		$6.8\cdot10^{-3}$	0.0130	
		$6.4\cdot10^{-3}$	0.0122	
		$8.1\cdot10^{-3}$	0.0154	
	30	$6.5\cdot10^{-3}$	0.0124	
810	4	0.0115	0.022	0.028
		0.0155	0.030	
	10	0.0162	0.031	
	4	0.0153	0.030	
	3	0.0132	0.025	
	4	0.0162	0.031	

[a]Calculated by the compilers.
[b]Mean value at given temperature, calculated by the compilers.

The results were approximated by the equation:

$$\log(\text{soly/mass \% C}) = 3.646 - 5970\ (T/\text{K})^{-1},$$

which was tested by the compilers. In the preceding works of the same laboratory,[1,2] the authors did not report individual results obtained with the same method as only the solubility equation:

$$\log(\text{soly/mass \% C}) = 3.82 - 6110\ (T/\text{K})^{-1}.$$

The effect of O on the C solubility in Na

t/°C	Time/h	O concentration/mol %	Solubility/mass % C	Solubility/mol % C[a]
700	30	satd	$6.6\cdot10^{-3}$	0.0126
710		0.770	$7.6\cdot10^{-3}$	0.0145
720		0.048	$2.2\cdot10^{-3}$	0.042

The effect of N on the C solubility in Na

t/°C	Time/h	N pressure/MPa	Solubility/mass % C	Solubility/mol % C[a]
710	30	0.10	0.0139	0.027
720	···	0.15	$5.0\cdot10^{-3}$	$9.6\cdot10^{-3}$
700	···	0.87	0.045	0.086
705	···	1.00	0.0252	0.048
708	···	1.80	0.032	0.062

[a]Calculated by the compilers.

Auxiliary Information

Method:
Na was contained in a Ni ampoule which itself served as the C source. A small monitor foil of Ni or Fe was immersed in the Na. The C content in the foil was analyzed to check whether the equilibrium was reached. The components were equilibrated for 3–288 h depending on temperature. The temperature of a furnace containing the ampoule was controlled using a Chromel/Alumel thermocouple. At the end of the equilibration a Na sample was removed by puncturing through the ampoule with a W spike. Na ran into a collecting silica vessel. The C content was obtained by counting the $^{14}CO_2$ produced by combustion (in an O–Ar mixture) of the sample in its silica receiver. A number of experiments was carried out to measure the change in the apparent C solubility caused by additions of O and N (introduced as NaN_3) to the Na.

Source and Purity of Materials:
C: from a Ni ampoule; the ampoule was carburized to a predetermined level with CH_4 after decarburizing in moist H and vacuum annealing at 1173 K; CH_4 was labeled with $^{14}CH_4$.
Na: reactor grade purity; gettered with Zr foil.
Ar: nothing specified.

Estimated Error:
Solubility: precision better than ±20%.
Temperature: stability ±2 K.

References:
[1]R. Ainsley, L. P. Hartlib, A. Pilbeam, and R. Thompson, *Liquid Alkali Metals* (BNES, London, 1973), pp. 143–151.
[2]R. Ainsley, L. P. Hartlib, G. Long, A. Pilbeam, and R. Thompson, U.K. Atom. Energy Author. Rep. AERE-R-6731 (1973).

Components:
(1) Carbon; C; [7440-44-0]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
M. R. Hobdell, E. A. Trevillon, and A. C. Whittingham, U.S. Dept. Energy Rep. CONF-800401-P2, pp. 18/47–53 (1980).

Variables:
One temperature: 913 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data:

The solubility of C in liquid Na in respect to graphite as solute at 640 °C (913 K) was found to be $(1.62\pm0.05)\cdot10^{-3}$ mass % C or $(3.1\pm0.1)\cdot10^{-3}$ mol % C (as calculated by the compilers) for the diatomic C_2 species in the saturated solution. For the monoatomic C species the estimated solubility is $(1.29\pm0.09)\cdot10^{-3}$ mass % C or $(2.5\pm0.2)\cdot10^{-3}$ mol % C. The authors concluded that C is dissolved in form of the diatomic species in liquid Na. It was estimated that CaC_2 has a negligible solubility in liquid Na at temperature of the experiments.

Auxiliary Information

Method:
Quantities of C (from a Fe foil) were plunged into stirred molten Na which was contained in a stainless steel crucible with an alumina liner. The dissolution test was carried out in an Ar atmosphere at the fixed temperature. The C activity was monitored by a C meter which worked with a sensing Fe membrane and molten carbonate electrolyte. The steady response values of the meter approached unity on the graphite scale. The Na contained traces of Ca which decreased the C activity due to the CaC_2 formation. The solubility of C in liquid Na was estimated from a relation between the C activity, its solubility, Ca solubility, and total C concentration.

Source and Purity of Materials:
C: from a carburized Fe foil.
Na: unspecified; filtered, gettered with 316 stainless steel at 973 K to decrease the C content; finally contained $3.5\cdot10^{-3}$ % Ca.
Ar: "purified."

Estimated Error:
Solubility: precision better than ±8%.
Temperature: nothing specified.

Components:
(1) Carbon; C; [7440-44-0]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
F. A. Kozlov, Yu. I. Zagorulko, Yu. P. Kovalev, and V. V. Alekseev, U.S. Dept. Energy Rep. CONF-800401-P2, 15/54–72 (1980).

Variables:
One temperature: 973 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The saturated solution of C in liquid Na at 700 °C (973 K) contained, as was found in two determinations, $2.7\cdot10^{-3}$ and $2.1\cdot10^{-3}$ mass % C or $5.2\cdot10^{-3}$ and $4.0\cdot10^{-3}$ mol % C, respectively (as calculated by the compilers). Elemental C, being in equilibrium with the saturated solution, had the shape of small particles of $\leqslant0.4$ μm diameter.

Auxiliary Information

Method:
Graphite powder, lamp soot, or Na_2C_2 was introduced into a nonisothermal Na loop made of stainless steel. The C concentration was determined by means of a sensor to measure the thermodynamic activity of C. The sensor was made of an Armco Fe membrane. A device dosing powder of C into the loop was isolated by means of a 50-mesh grid. The equilibration samples of Fe–Ni(8%), Fe–Mn(12%), and Kh18N9 alloy foils were placed behind the source. A mixture of 5%–19% H in Ar or He was moistened to a level of 0.5%–1% H_2O. H_2O reacted with C dissolved in the membrane of the sensor forming CO. CO was further converted to CH_4 on Ni at 693 K. The concentration of CH_4 was measured by means of gas chromatography. The sensor was calibrated on a C source of known activity. The C concentration level was measured after 20 h of Na circulation at 973–1023 K.

Source and Purity of Materials:
C: graphite, soot or Na_2C_2 of unknown purity.
Na: "industrial," contained $(3\pm2)\cdot10^{-4}$ % nonvolatile C forms, $(2\pm1)\cdot10^{-4}$ % Na_2CO_3 and $9\cdot10^{-4}$ % Na_2C_2.
H: gaseous mixture with Ar or He purified in a freezing-out trap cooled by liquid N.

Estimated Error:
Solubility: nothing specified; precision probably of $(1-2)\cdot10^{-4}$ % C (by the compilers).
Temperature: nothing specified.

Components:
(1) Carbon; C; [7440-44-0]
(2) Sodium; Na; [7440-23-5]
(3) Lithium; Li; [7439-93-2]

Original Measurements:
R. J. Pulham and P. Hubberstey, J. Nucl. Mater. **115**, 239–250 (1983).

Variables:
One temperature: 873 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data and Critical Evaluation

The authors observed a decrease of the C activity upon the addition of Li to liquid Na at 600 °C. It was assumed that in the course of the following reaction: $2\,Li(Na)+2C(Na)\leftrightarrow Li_2C_2$, the compound Li_2C_2 is precipitated in the liquid alloy. The corresponding solubility product (K_{so}) should be in the form: $K_{so}=a_{Li}^2 a_C^2$. The authors reported the Gibbs free energy values for Li_2C_2 referring the C activity to pure C graphite, and assuming a_{Li} equal to its concentration. It seems to the compilers, that one may formulate the following constant describing the equilibrium more rationally: $K'_{so}=[Li]^2[C_2]$ due to fact that C_2 dimers are dominant in the solution and the Li activity coefficient is unity. In our calculations the concentration of C_2 was found by multiplication by 0.5 of the saturating C concentration in Na at 873 K equal $1.0\cdot 10^{-3}$ mol % C (see the C–Na system) and correlated by the measured decrease of the C activity.

c_{Li} /mol %	a_C[a]	$\Delta G(Li_2C_2)$/kJ mol^{-1}	K_{so} /(mol fraction)^4[b]	c_{C2} /mol %	K'_{so}/(mol %)^3
1.14	0.177	−89.9	$4.2\cdot 10^{-6}$	$8.9\cdot 10^{-5}$	$1.16\cdot 10^{-4}$
1.43	0.149	−90.1	$4.1\cdot 10^{-6}$	$7.5\cdot 10^{-5}$	$1.53\cdot 10^{-4}$
2.07	0.126	−86.6	$6.6\cdot 10^{-6}$	$6.3\cdot 10^{-5}$	$2.6\cdot 10^{-4}$

[a]Related to activity of pure graphite equal to 1.
[b]Calculated from $\Delta G(\Delta G=RT\ \ln K_{SO})$.

As one may see, neither K_{so} nor K'_{so} is constant, a fact which may be connected with the nature of the dissolved C; a part of it is monoatomic and another part of it is diatomic in liquid Na.

Auxiliary Information

Method:
Na was contained in a Fe beaker which was decarburized prior to use by moist H at 803 K for 50 h followed by soaking in liquid Li at 873 K for 300 h. An outer stainless steel container was equipped with a Fe sheathed thermocouple pocket and couplings to accommodate the cell getter and the addition of the solutes. An electrochemical cell was dipped into the Na. The cell was filled with molten Na_2CO_3–Li_2CO_3 electrolyte. A central carburized Fe_3C electrode was immersed into the melt. The C activity was controlled by addition of either Fe_3C or 316 stainless steel as the C getter. The emf across the electrodes was measured. A steady emf was observed after ~300 h. Li was added in stages and the emf monitored continuously. The emf changes occurred over days. The decrease of C activity was found from the emf difference.

Source and Purity of Materials:
Fe_3C: as the C source of unspecified purity.
Li: gettered by Ti.
Na: filtered.

Estimated Error:
Solubility: precision ±1% (as estimated by the compilers).
Temperature: precision ±1 K.

4.5. Sodium–Silicon

Components:
(1) Silicon; Si; [7440-21-3]
(2) Sodium; Na; [7440-23-5]

Evaluated By:
Hans Ulrich Borgstedt, Forschungszentrum Karlsruhe, Germany and Cezary Guminski, University of Warsaw, Poland, December 1999

Critical Evaluation

A qualitative characterization of the solubility of Si in liquid Na exhibited different opinions[1–3] in this subject. Vigoroux[1] did not report any reaction of Si with liquid Na even at the boiling point of the latter. Pulham and Hubberstey[2] observed a spare solubility of Si in liquid Na, whereas Brush and Koenig[3] claimed that Si is soluble in liquid Na. The solubility was estimated by McCaldin *et al.*[4] at 1043 K to be between 8 and 17 mol % Si from an inspection of a Si container with Na; the method of analysis was not specified therein. More precise determinations of the solubility were performed by Yunker.[5] He analyzed (i) Na equilibrated with Si in a Ta cup and (ii) Na which circulated in a stainless steel loop containing ~0.5 mol % Si. In the first test, the concentration of the saturated solution increased from 0.0188 to 2.3 mol % Si in the temperature range 699–877 K; NaSi was found as the equilibrium solid phase. In the second test, the Si concentration found was more than 4 orders of magnitude lower and the authors observed a formation of an unstable Na–Si–O compound. Similar observations, indicating the strong interaction between Si and O in liquid Na were reported by Isaacs *et al.*[6,7] Grundy[8] reported a formula of such a phase as $Na_2Si_2O_5$. Undoubtedly, Si reacts with Na and the phase NaSi is the most stable up to 877 K, according to the experiments of Yunker.[5] This phase was not detected at 923 K and at 1043–1073 K in experiments of Hohmann[9] and McCaldin *et al.*,[4] respectively. Therefore, we tentatively assume that NaSi is stable up ~900 K in a closed system. A decomposition of NaSi in vacuum was already observed at 693 K.[9]

Several less stable Na–Si compounds were synthetically prepared: $NaSi_2$—by reduction of SiO_2 with Na,[10] Na_4Si_{23}—by thermal degradation of NaSi at ~683 K in an Ar atmosphere,[11] and $Na_xSi_{136}(3\leqslant x\leqslant 22)$—by thermal degradation at 603–733 K in vacuum.[12] Na_4Si_{23} and Na_xSi_{136} are stable up to 793 and 833 K, respectively.[11,12] A solubility of Na in solid Si is not higher than 0.02 mol % Na at 1073 K.[13,14] Von Schnering *et al.*[15] performed the thermal decomposition of NaSi under dynamic vacuum and observed the subsequent formation of Na_4Si_9, Na_6Si_{25}, Na_2Si_{11}, and $Na_xSi_{13.6}(5\leqslant x\leqslant 12)$. These facts allow us to establish a fragmentary Na–Si phase diagram, shown in Fig. 19. The diagram should be confirmed by a systematic thermal analysis. The Si–Na system was partly reviewed in Sangster and Pelton.[16]

Tentative values of the solubility of Si in liquid Na

T/K	Solubility/mol % Si	Source
673	0.01	(5) interpolated
773	0.23	(5) interpolated
873	2.2	(5) interpolated

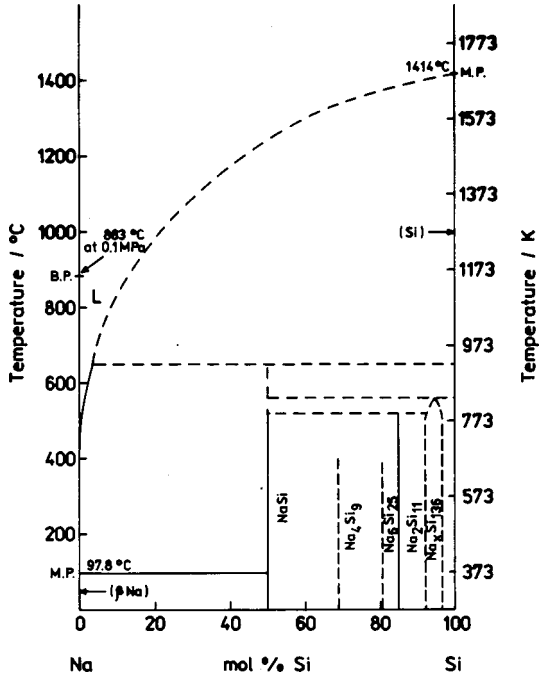

FIG. 19. Na–Si phase diagram (tentative).

References:

[1]E. Vigoroux, Compt. Rend. **123**, 115 (1896).
[2]R. J. Pulham and P. Hubberstey, J. Nucl. Mater. **115**, 239 (1983).
[3]E. G. Brush and R. F. Koenig, Corrosion [NACE] **11**, 299t (1955).
[4]J. O. McCaldin, M. J. Little, and E. E. Widmer, J. Phys. Chem. Solids **26**, 1119 (1965).
[5]W. H. Yunker, U.S. Dept. Energy Rep. CONF-800401-P2, 13/27 (1980); Rep. HEDL-SA-1897-FP (1979).
[6]H. S. Isaacs, Trans. Am. Nucl. Soc. **14**, 623 (1971).
[7]J. R. Weeks and H. S. Isaacs, Adv. Corr. Sci. Technol. **3**, 1 (1973).
[8]B. R. Grundy, *Liquid Metal Engineering and Technology* (BNES, London, 1985), Vol. 3, p. 7.
[9]E. Hohmann, Z. Anorg. Chem. **257**, 113 (1948).
[10]H. Nowotny and E. Scheil, Metallforsch. **2**, 76 (1947).
[11]P. Hagenmuller, R. Naslain, M. Pouchard, and C. Cros, *The Alkali Metals* (The Chemical Society, London, 1967), p. 207.
[12]C. Cros and J. C. Benejat, Bull. Soc. Chim. Fr. 1739 (1972).
[13]L. Svob, Solid State Electron. **10**, 991 (1967).
[14]L. Svob, Phys. Status Solidi **7**, K1 (1964).
[15]H. G. von Schnering, M. Somer, M. Kaupp, W. Carillo-Cabera, M. Baitinger, A. Schmeding, and Y. Grin, Angew. Chem. Int. Ed. **37**, 2359 (1998).
[16]J. Sangster and A. D. Pelton, J. Phase Equil. **13**, 67 (1992).

Components:
(1) Silicon; Si; [7440-21-3]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
J. O. McCaldin, M. J. Little, and E. E. Widmer, J. Phys. Chem. Solids **26**, 1119–1123 (1965).

Variables:
One temperature: 1043 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of Si in liquid Na at 770 °C (1043 K) was estimated to be between 10 and 20 mass % Si or 8.3 and 17 mol % Si (as recalculated by the compilers). Solid Si containing $3\cdot10^{17}$ cm^{-3} Na ($1.6\cdot10^{-3}$ mol %Na) was found to be in equilibrium with the saturated solution of Si in liquid Na. Na-Si intermetallics were not detected at this temperature.

Auxiliary Information

Method:
A Si container was filled with Na. Several Si specimens were placed above the Na. The assembly was contained in a quartz envelope. The envelope was placed in a furnace at the fixed temperature of 1073 K. The bottom part of the Si assembly, which contained the Na-rich liquid, was maintained ~30 K cooler. The equilibration lasted 184–188 h. At the end of the equilibration period, the envelope was lowered from the furnace and cooled in a smooth stream of air. The Na content in the specimens was measured by neutron activation analysis and the Si specimens were examined by metallographic techniques. The method of analysis of the Si content in Na was not reported.

Source and Purity of Materials:
Si: Czochralski-pulled single crystal without any dopants intentionally added.
Na: from MSA Research Corp.; contained $\sim7\cdot10^{-4}$ % Cu and $\sim1.0\cdot10^{-3}$ % Si; other elements were below the spectrochemical detection limit.
Ar: "sufficient" purity.

Estimated Error:
Solubility: nothing specified.
Temperature: stability ±5 K.

Components:	**Original Measurements:**
(1) Silicon; Si; [7440-21-3] (2) Sodium; Na; [7440-23-5]	W. H. Yunker, U.S. Dept. Energy Rep. CONF-800401-P2, 13/27-35 (1980).
Variables:	**Prepared by:**
Temperature: 699–887 K	H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of Si in liquid Na was determined by two methods. The results obtained were presented in graphical forms; they were read out from the figures and recalculated to mol % Si by the compilers.

"Laboratory data"

t/°C	T/K	Solubility/mass % Si	Solubility/mol % Si	Equilibrium solute phase
426	699	0.023	0.0188	a Na–Si compound
508	781	0.30	0.25	
604	877	2.8	2.3	

"Loop data"

t/°C	T/K	Solubility/mass % Si	Solubility/mol % Si	Equilibrium solute phase
528	801	$1.00\cdot10^{-5}$	$8.2\cdot10^{-6}$	an unstable Na–Si–O (when out of Na) compound
540	813	$1.00\cdot10^{-5}$	$8.2\cdot10^{-6}$	
555	828	$1.00\cdot10^{-5}$	$8.2\cdot10^{-6}$	
555	828	$1.95\cdot10^{-5}$	$1.60\cdot10^{-5}$	
565	838	$1.96\cdot10^{-5}$	$1.61\cdot10^{-5}$[a]	
565	838	$3.0\cdot10^{-5}$	$2.5\cdot10^{-5}$	
574	847	$3.2\cdot10^{-5}$	$2.6\cdot10^{-5}$	
577	850	$4.2\cdot10^{-5}$	$3.0\cdot10^{-5}$	
587	860	$3.3\cdot10^{-5}$	$2.7\cdot10^{-5}$	
587	860	$4.0\cdot10^{-5}$	$3.3\cdot10^{-5}$	
614	887	$6.4\cdot10^{-5}$	$5.2\cdot10^{-5}$	

[a]Numerical result.

The same results were reported in Yunker.[1] The apparent solubility of Si decreased with increasing O content in Na.

Auxiliary Information

Method:

The laboratory tests of the solubility were carried out in a Ta cup in a high vacuum cell but no other details of the technique used were reported. The loop tests were performed in a flow impedance analysis system. The primary component of this system was designed so that arrays of crystals formed would create a hydraulically roughened surface, thereby altering the sensors flow resistance. From the flow, changes in friction factor in the sensor could be determined. With this, the equilibrium and transport properties of the compound were studied *in situ*. Steel samples were introduced into the system. Na was supplied from a reservoir and circulated. Impurities were monitored and Na samples analyzed by an unknown method. Solid phases were analyzed by XRD, SAM, SEM, and ED-XRF methods.

Source and Purity of Materials:

Si: "high purity" in the laboratory tests and 300 stainless steel with ~0.5% Si in the loop tests.
Na: "high purity", contained $1.5\cdot10^{-4}$ % O and $2\cdot10^{-4}$ % H.

Estimated Error:

Solubility: nothing specified; reading-out procedure ±2%.
Temperature: stability ±3 K; reading-out procedure ±2 K.

References:

[1]W. H. Yunker, U.S. Dept. Energy Rep. HEDL-SA-1897-FP (1979).

4.6. Sodium–Germanium

Components:	**Evaluated By:**
(1) Germanium; Ge; [7440-56-4] (2) Sodium; Na; [7440-23-5]	Hans Ulrich Borgstedt, Forschungszentrum Karlsruhe, Germany and Cezary Guminski, University of Warsaw, Poland, January 1999

Critical Evaluation

Two determinations of the solubility of Ge in liquid Na in the Na-rich composition range were performed by Hubberstey and Castleman[1] using emf measurements of a cell containing the Ge–Na melt in one of electrodes, and by Hubberstey and Pulham[2] who confirmed the results of Hubberstey and Castleman[1] by means of thermal analysis and electrical resistivity measurements. The solubility equation in the temperature range 500–923 K, taking into account the results of Hubberstey and Castleman[1] and Hubberstey and Pulham[2] is:

$$\log(\text{soly/mol \% Ge}) = 2.862 - 1910(T/\text{K})^{-1} \quad r = 0.996. \tag{1}$$

Aleksandrov and Dalakova[3] analyzed solutions of Ge in liquid Na using spectral analysis after 1 h of equilibration at 973–1023 K; they characterized the solubility of Ge as small, but did not report any quantitative results. Drits *et al.*[4] investigated a larger part of the Ge–Na phase diagram by means of thermal analysis. The proposed picture of phase relations could be only partly accepted. There is quite a good agreement of the melting point of $GeNa_3$ with the extrapolated liquidus line established by Hubberstey and Castleman[1] and Hubberstey and Pulham[2] The liquidus line extrapolated to the eutectic temperature on the Na-rich side pointed on the solubility of $\sim5\cdot10^{-3}$ mol % Ge.

A depression of ~0.01 K of the melting point of Na was deduced from the enthalpy of fusion of Na. The decomposition temperature of GeNa in vacuum, observed by Hohmann[5] at 753 K and by Hagenmuller *et al.*[6] at 593–653 K, was found to be much lower than in Drits *et al.*,[4] where congruent melting of GeNa in a close capsule was recorded at 1433 K. Hohmann[5] noticed the decomposition of GeNa into elements, whereas Hagenmuller *et al.*[6] observed the subsequent formation of Ge_4Na and $Ge_{136}Na_x$ ($0\leqslant x\leqslant24$) phases, instead. Potemkin *et al.*[7] confirmed the existence of Ge_4Na and measured its melting temperature at 1419 K. According to thermogravimetric, spectroscopic, and x-ray structure analysis performed by von Schnering *et al.*,[8] the phase Ge_4Na does not exist; however, only $Ge_{17}Na_{12}$ is formed between GeNa and pure Ge. The doubtful Ge–Na phase diagram[9] is shown in Fig. 20.

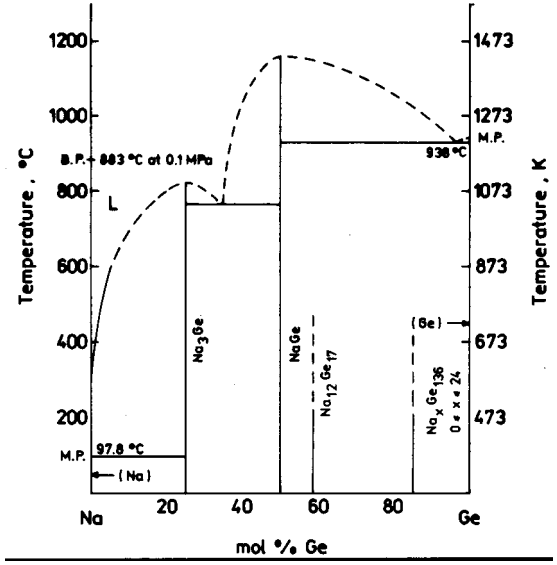

FIG. 20. Ge–Na phase diagram (doubtful).

Sangster and Pelton[9] were quite critical to plot the Ge–Na phase diagram on the basis of such unequivocal observations. Although Hubberstey and Pulham[2] reported that GeNa is the equilibrium solid phase, the saturated solution of Ge in Na (in the Na-rich region) should be in equilibrium with $GeNa_3$, according to Drits *et al.*[4] It may be that the Nb ampoules used by Drits *et al.*[4] corroded in contact with the Ge–Na melt forming a Nb–Ge compound.

Tentative values of the solubility of Ge in liquid Na

T/K	Solubility/mol % Ge		Source
371	$\sim 5\cdot 10^{-3}$	eutectic	Eq. (1), extrapolated
473	$7\cdot 10^{-2}$		Eq. (1), extrapolated
573	0.3		(1)
673	1.1		(1),(2), mean value
773	3		(1),(2)
873	5		Eq. (1), extrapolated
1100	25	congruent	(4)

References:

[1]P. Hubberstey and A. W. Castleman, J. Electrochem. Soc. **119**, 963 (1972).

[2]P. Hubberstey and R. J. Pulham, J. Chem. Soc., Dalton Trans. 1541 (1974).

[3]B. N. Aleksandrov and N. V. Dalakova, Izv. Akad. Nauk SSSR, Met. **1**, 133 (1982).

[4]M. E. Drits, V. F. Potemkin, and L. L. Zusman, Izv. Akad. Nauk SSSR, Neorg. Mater. **18**, 1148 (1982).

[5]E. Hohmann, Z. Anorg. Chem. **257**, 113 (1948).

[6]P. Hagenmuller, R. Naslain, M. Pouchard, and C. Cros, *The Alkali Metals* (The Chemical Society, London, 1967), p. 207.

[7]V. F. Potemkin, R. A. Sizov, L. L. Zusman, and M. E. Drits, Izv. Akad. Nauk SSSR, Met. **3**, 197 (1989).

[8]H. G. von Schnering, M. Baitinger, U. Bolle, W. Carrillo-Cabrera, J. Curda, Y. Grin, F. Heinemann, J. Llanos, K. Peters, A. Schmeding, and M. Somer, Z. Anorg. Chem. **623**, 1037 (1997).

[9]J. Sangster and A. D. Pelton, J. Phase Equil. **18**, 295 (1997).

Components:
(1) Germanium; Ge; [7440-56-4]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
P. Hubberstey and A. W. Castleman, J. Electrochem. Soc. **119**, 963–966 (1972).

Variables:
Temperature: 573–823 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of Ge in liquid Na was determined. The results were presented in a figure; they were read from the figure by the compilers.

t/°C	Solubility/mol % Ge
300	0.30
325	0.43
350	0.63
400	1.13
450	1.83
500	2.8
550	3.3

The authors approximated the solubility results by the equation (tested by the compilers):

$$\log(\text{soly/mol \% Ge}) = 3.154 - 2100(T/\text{K})^{-1}.$$

Auxiliary Information

Method:
An electrochemical cell: Na/Na^+ (in Pyrex glass)/Na–Ge was operated under a He atmosphere. The apparatus was made of Pyrex glass, while a stainless steel wire was applied for electrical connections. The apparatus was evacuated and baked at ~773 K for several hours. Weighed amounts of the metals were introduced into a dry atmosphere box. The cell was evacuated, sealed, and heated overnight to ~25 K above the estimated liquidus temperature. The temperature was then decreased in steps of 5 K. The Na activity became constant in the two-phase region, thus indicating the liquidus temperature. Chromel/Alumel thermocouples were used to measure and control the temperature.

Source and Purity of Materials:
Ge: "ultrapure single crystals" prepared in Brookhaven National Laboratory.
Na: 99.9% pure from J.T. Baker Comp., pipetted at ~393 K in order to reduce concentrations of nonmetals to level of $<1\cdot 10^{-3}$ %.
He: contained $<1\cdot 10^{-4}$ % O and $<1\cdot 10^{-5}$ % H_2O.

Estimated Error:
Solubility: nothing specified; reading-out procedure ±2%.
Temperature: stability ±0.5 K; reading-out procedure ±1 K.

Components:
(1) Germanium; Ge; [7440-56-4]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
P. Hubberstey and R. J. Pulham, J. Chem. Soc., Dalton Trans. 1541–1544 (1974).

Variables:
Temperature: 500–773 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of Ge in liquid Na was determined. The results were presented in a figure, they were read from the figure by the compilers.

t/°C	Solubility/mol % Ge
227	0.12
262	0.22
309	0.40
347	0.54
354	0.65
370	0.75
380	0.90
391	1.00
~500[a]	3

[a]From thermal analysis.

The melting point of Na was measured to be 97.83 °C; the Na-rich eutectic was found at the same temperature. GeNa was claimed to be the equilibrium solid phase saturating the solution.

Auxiliary Information

Method:
The apparatus for measurements of the electrical resistivity was made of stainless steel.[1] The alloys were prepared after weighing appropriate quantities of the substances under Ar atmosphere and heating them to 673 K. An electromagnetic pump served to stir and homogenize the solutions.
Simultaneous measurements of the resistance and temperature were performed during cooling the melts. The temperature, at which the saturation of Na with Ge occurred, was indicated by an abrupt change of the resistance of a sample. Details concerning the thermal analysis experiments were not reported.

Source and Purity of Materials:
Ge: 99.999% pure from Koch–Light.
Na: nothing specified, probably as in Addison *et al.*[1] containing $<4\cdot10^{-3}$ % Ca and $<1\cdot10^{-3}$ % O.
Ar: nothing specified.

Estimated Error:
Solubility: nothing specified; reading-out procedure ±0.02 mol % Ge.
Temperature: stability ±0.5 K; reading-out procedure ±1 K.

References:
[1]C. C. Addison, G. K. Creffield, P. Hubberstey, and R. J. Pulham, J. Chem. Soc., A 1482–1487 (1969).

Components:
(1) Germanium; Ge; [7440-56-4]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
M. E. Drits, V. F. Potemkin, and L. L. Zusman, Izv. Akad. Nauk SSSR, Neorg. Mater. **18**, 1148–1150 (1982).

Variables:
Temperature: 1080–1433 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

Several points on the Ge–Na liquidus were determined. They were read out from a figure by the compilers.

t/°C	Solubility/mol % Ge
826	24
828	27
807	31
846	36
1123	46
1160	51
1149	57
1132	63
1110	69
1070	77
1047	82
1027	86
982	91
950	95
930	98
953	99

$GeNa_3$ and GeNa were found as the equilibrium solid phases.

Auxiliary Information

Method:
Proper amounts of Na and Ge were placed in crucibles made of steel or Nb containing ceramic liners made of Al_2O_3 or ZrO_2. The hermeticity of every closed crucible was tested by manifold heating above 1433 K and cooling the alloy in vacuum.[1] This way the inertness of the crucibles against the liquid alloys was confirmed, if reproducible thermal arrests were recorded. Differential thermal analysis of the alloys was performed in an Ar atmosphere. The composition of some solid alloys was controlled afterwards by x-ray spectroscopy and microstructural analysis.

Source and Purity of Materials:
Ge: "semiconductor grade" of purity.
Na: 99.6+% pure.
Ar: "spectrally" pure.

Estimated Error:
Solubility: nothing specified; reading-out procedure ±0.5 mol %.
Temperature: precision ±2 K; reading-out procedure ±2 K.

References:
[1]M. E. Drits, A. S. Fridman, L. L. Zusman, and A. E. Luzik, Zavod. Lab. **3**, 299–301 (1976).

4.7. Sodium–Nitrogen

Components:
(1) Nitrogen; N; [7727-37-9]
(2) Sodium; Na; [7440-23-5]

Evaluated By:
Hans Ulrich Borgstedt, Forschungszentrum Karlsruhe, Germany and Cezary Guminski, University of Warsaw, Poland, January 1996

Critical Evaluation

N gas does not react with liquid Na even at 1073 K.[1] The N–Na compounds are known to be formed by means of chemical reactions and during electrical discharges through Na under low N pressure.[2] It seems therefore that in the absence of metallic contaminants in Na, which may react with N, the dissolution of N in liquid Na is virtually a physical process proceeding in a quite small extent. Subbotin *et al.*[3] predicted a solubility of N in Na as high as $7\cdot10^{-2}$ mol % at 573 K. Lemke[4] reported some unpublished experiments indicating that the solubility of N in liquid Na is below $8\cdot10^{-4}$ mol % N (the detectivity level of the analytical method used) at 373 K. Cafasso[5] reported a preliminary result at 573 K of $2.5\cdot10^{-7}$ volume fraction of N in liquid Na ($\sim1\cdot10^{-10}$ mol % N). Veleckis *et al.*[6] determined the solubility which increased from $1.64\cdot10^{-9}$ to $7.2\cdot10^{-9}$ mol % N in the temperature range 724–873 K. These findings are in rough agreement with the previous estimation of Cafasso.[5] However, Arnoldov *et al.* determined at 573 K as much as $2\cdot10^{-6}$ mol % N in Arnoldov *et al.*,[7] $4\cdot10^{-3}$ mol % N in Arnoldov *et al.*,[8] and 10^{-4} mol % N in Subbotin *et al.*[3] in liquid K–Na (32 mol %) eutectic alloy. Though all results were originated by the same group, the discrepancy between Arnoldov *et al.*,[7] Arnoldov *et al.*,[8] and Subbotin *et al.*[3] was not explained by the authors. It is, however, improbable that the spectacular difference of the N solubility between the results of Veleckis *et al.*[6] and Subbotin *et al.*,[3] Arnoldov *et al.*,[7] and Arnoldov *et al.*[8] could be due to the change of pure Na for the mixed K–Na solvent. Such a difference could be only possible in the case of a chemical reaction of N with Na or K, since Subbotin *et al.*,[3] Arnoldov *et al.*,[7] and Arnoldov *et al.*[8] measured the change of volume of N gas before and after the equilibration, whereas Veleckis *et al.*[6] measured the N amount (enriched in ^{15}N) being stripped with He from Na. No isotopic exchange between $^{15}N_2$ and $^{14}N_2$ molecules occurred indicating that N_2 did not dissociate in the experimental conditions. Thus a physical solubility of N was measured in Veleckis *et al.*[6] and sum of the physical solubility and a chemical interaction of N with impurities in the K–Na was measured in Subbotin *et al.*,[3] Arnoldov *et al.*,[7] and Arnoldov *et al.*[8] It could be that the metallic solvents for the experiments in these laboratories were degassed to various extents.

An influence of impurities on the solubility equilibria investigated seems to be a crucial one. Indeed, Addison *et al.*[9–13] and Fischer[14] showed that Ca, Sr, Ba, and Li react with N in molten Na medium to form the corresponding nitrides being relatively well soluble. The formation of Li_3N in liquid Na was even utilized for the growth of Li_3N single crystals. It seems rational to suppose that other metals can be nitrided in a similar way. C reacts also effectively with N at temperatures >673 K to form moderately soluble NaCN; see the Na–NaCN system. Migge[15] discussed the thermodynamic possibility of the precipitation of Na_2NCN, this was however not experimentally verified.

Ward *et al.*[16] elaborated on a method to determine nitride (Na_3N) in Na, but neither its solubility nor the form of the nitride were specified. Low contents of N in Na can be estimated by equilibration with a steel foil.[17] Certainly both the nitride (Na_3N) and azide (NaN_3) are metastable in liquid Na. Outside of the Na medium Na_3N is stable up to 423 K.[18] Further heating makes it darker and black at 573 K with a fast decomposition at 623 K.[18] NaN_3 is stable up to 548 K according to Kozlov *et al.*[18] and Belomestnykh[19] and up to 593 K according to Lutz *et al.*[20] NaN_3 undergoes a polymorphic transition at ~293 K.[17] There exists an equilibrium between Na_3N, N_2, and NaN_3 (Wattenberg[2]) but such reactions were not studied in liquid Na. A fragmentary N–Na phase diagram is shown in Fig. 21. The solubility of elemental N in liquid Na can be expressed by the equation:

$$\log(\text{soly/mol \% N}) = -5.12 - 2660\ (T/\text{K})^{-1} \qquad r = 0.996 \tag{1}$$

as calculated by the compilers from the data of Veleckis *et al.*[6] The use of this equation is finally suggested in course of this evaluation.

Tentative values of the solubility of N in liquid Na at 0.101 MPa

T/K	Solubility/mol % N	Source
773	$3\cdot10^{-9}$	(6), Eq. (1)
873	$7\cdot10^{-9}$	(6), Eq. (1)

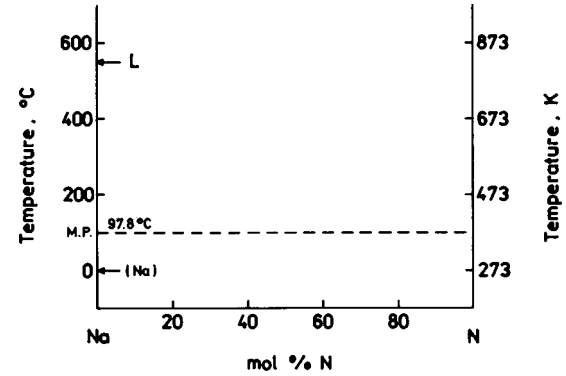

FIG. 21. Na–N phase diagram (fragmentary).

References:

[1]E. W. Guernsey and M. S. Sherman, J. Am. Chem. Soc. **47**, 1933 (1925).
[2]H. Wattenberg, Ber. Chem. Gesellsch. **63**, 1667 (1930).
[3]V. I. Subbotin, M. N. Ivanovskii, and M. N. Arnoldov, *Fiziko-Khimicheskie Osnovy Primeneniya Zhidkometallicheskikh Teplonositelei* (Atomizdat, Moskva, 1970), pp. 68, 79.
[4]E. I. Lemke, Du Pont de Nemours Co. (1958); cited in (6) in note added in proof.
[5]F. A. Cafasso, U.S. Atom. Energy Comm. Rep. ANL-7399, p. 137 (1967).
[6]E. Veleckis, K. E. Anderson, F. A. Cafasso, and H. M. Feder, U.S. Atom. Energy Comm. Rep. ANL-7520, Pt I, p. 295 (1969).
[7]M. N. Arnoldov, M. N. Ivanovskii, V. A. Morozov, S. S. Pletenets, and V. I. Subbotin, *Teplofizicheskie Svoistva Zhidkostei*, edited by A. K. Abas-Zade and E. E. Shpil'rain (Nauka, Moskva, 1970), p. 110.
[8]M. N. Arnoldov, M. N. Ivanovskii, V. A. Morozov, S. S. Pletenets, and V. I. Subbotin, Atom. Energiya **28**, 18 (1970).
[9]P. Hubberstey, *Liquid Alkali Metals* (BNES, London, 1973), p. 15.
[10]C. C. Addison, R. J. Pulham, and E. A. Trevillion, J. Chem. Soc., Dalton Trans. 2082 (1975).
[11]C. C. Addison, G. K. Creffield, H. Hubberstey, and R. J. Pulham, J. Chem. Soc., Dalton Trans. 1105 (1976).
[12]M. G. Down and R. J. Pulham, J. Cryst. Growth **47**, 133 (1949).
[13]P. Hubberstey and P. R. Bussey, *Liquid Metal Engineering and Technology* (BNES, London, 1984), Vol. 3, p. 143.
[14]A. K. Fischer, U.S. Atom. Energy Comm. Rep. ANL-7775, p. 39 (1971).
[15]H. Migge, *Material Behaviour and Physical Chemistry in Liquid Metal Systems*, edited by H. U. Borgstedt (Plenum, New York, 1982), p. 351.
[16]C. H. Ward, U.S. Atom. Energy Comm. Rep. LA-2892 (1963).
[17]H. U. Borgstedt and T. Gnanasekaran, *Analysis of Non-Metals in Metals*, edited by G. Kraft (deGruyter & Co, Berlin, 1981), p. 455.
[18]F. A. Kozlov, L. G. Volchkov, E. K. Kuznetsov, and V. A. Mtyukhin, *Zhidkometallicheskie Teplonositeli Yaderno Energeticheskikh Ustanovok* (Energoatomizdat, Moskva, 1983), p. 29.
[19]V. N. Belomestnykh, Neorg. Mater. **29**, 221 (1993).
[20]G. Lutz, D. Neil, and K. Anderson, U.S. Atom. Energy Comm. Rep. ANL-6800, p. 188 (1963).

Components:
(1) Nitrogen; N; [7727-37-9]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
E. Veleckis, K. E. Anderson, F. A. Cafasso, and H. M. Feder, U.S. Atom. Energy Comm. Rep. ANL-7520, Pt. I, pp. 295–298 (1969).

Variables:
Temperature: 724–873 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of N in liquid Na at a pressure of 0.101 MPa was determined

t/°C	Solubility/g N per 10^{12} g Na	Solubility/mol % N	Stand. dev./%	Solubility/mol % Pa^{-1}[b]
451	10	$1.64\cdot10^{-9}$	78	$1.62\cdot10^{-14}$
502	17	$2.8\cdot10^{-9}$	44	$2.8\cdot10^{-14}$
550	25	$4.1\cdot10^{-9}$	31	$4.1\cdot10^{-14}$
600	44	$7.2\cdot10^{-9}$	21	$7.1\cdot10^{-14}$

[a]The solubilities were measured at a N pressure of ~1.0 MPa and correspondingly recalculated.
[b]Calculated by the compilers.

The solute was found to exist in form of N_2 molecules in liquid Na, since not any exchange of the isotopic constitution between the molecules $^{14}N_2$, ^{14}N, ^{15}N, and $^{15}N_2$ was observed after equilibration for 96 h. The authors proposed a solubility equation, tested by the compilers:

$$\log(\text{soly/mass \% N}) = -5.18 - 2780\ (T/\text{K})^{-1}.$$

Cafasso[1] found in a preliminary experiment at 500 °C as low as $(2.5\pm1.5)\cdot10^{-7}$ vol. fraction of N in liquid Na to be soluble. Assuming that the N volume was measured at the test temperature, the N solubility in liquid Na is $\sim1.1\cdot10^{-10}$ mol % N.

Auxiliary Information

Method:
The essential parts of the apparatus were made of stainless steel. The solubility experiments were performed using N enriched in ^{15}N. In this manner, the dissolved N could be distinguished from extraneous N. Liquid Na was saturated with N at a pressure of ~1 MPa and a fixed temperature. N was stripped with He and trapped on molecular sieves at the temperature of liquid N. The sieves were transferred into a bulb and the gas was analyzed by a mass spectrometer.

Source and Purity of Materials:
N: nothing specified.
Na: "reactor grade" purity; purified by cold trapping, contained $1.6\cdot10^{-3}$ % O.
He: nothing specified.

Estimated Error:
Solubility: relative standard deviation between 21 (at 873 K) and 78% (at 724 K).
Temperature: nothing specified.

References:
[1]F. A. Cafasso, U.S. Atom. Energy Comm. Rep. ANL-7399, pp. 137–138 (1967).

4.8. Sodium–Sodium Cyanide

Components:
(1)Sodium cyanide; NaCN; [143-33-9]
(2)Sodium; Na; [7440-23-5]

Evaluated By:
Hans Ulrich Borgstedt, Forschungszentrum Karlsruhe, Germany and Cezary Guminski, University of Warsaw, Poland, February 1996

Critical Evaluation

Hobart and Bjork[1] were the first to observe a formation of NaCN in liquid Na at temperatures higher than 673 K. This fact would explain the increase of the apparent C solubility when Na contained N or was in contact with gaseous N. It seems that NaCN is stable in liquid Na up to ~970 K.[2] Cafasso[3] reported preliminary solubility results of NaCN in liquid Na without giving experimental details of a determination: $2\cdot10^{-5}$ and $3.5\cdot10^{-2}$ mol % NaCN at 773 and 823 K, respectively. This high increase of the solubility with 50 K increase of temperature appears to be unlikely. In subsequent studies of the same laboratory Veleckis *et al.*[4] established the temperature dependence of the solubility with a larger number of experimental points between 675 and 923 K and the results of Cafasso[3] were not confirmed. A single solubility determination at 688 K of Dutina *et al.*[5] and a subsequent determination of Fischer and Cafasso[6] at 863 K are in acceptable agreement with the values of Veleckis *et al.*[4] In the presence of alkali earth metals or Li and an excess of N in Na the formation of poorly soluble cyanoamides (CaNCN, SrNCN, BaNCN, Li_2NCN) may occur.[6,7] Transition metals could probably form cyanides in Na medium but this possibility needs an experimental verification. The following solubility equation for NaCN in liquid Na may be proposed by the evaluators for the temperature range 673–830 K:

$$\log(\text{soly/mol \% NaCN}) = 9.36 - 9140\ (T/\text{K})^{-1}. \quad (1)$$

Most probably, Eq. (1) may be applicable below 673 K. The Na–CN phase diagram is shown in Fig. 22. The monotectic temperature of (838±2) K (Veleckis *et al.*[4]) was found to be indistinguishable from the melting temperature of NaCN at 837 K.[8]

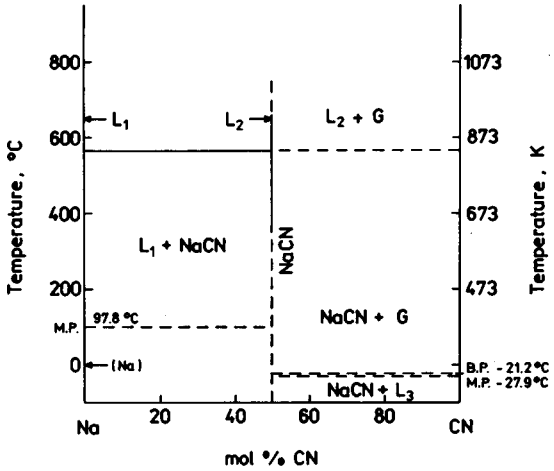

FIG. 22. Na–NaCN phase diagram.

Tentative values of the solubility of NaCN in liquid Na

T/K	Solubility/mol % NaCN		Source
673	$6\cdot10^{-5}$		(4), Eq. (1)
773	$3\cdot10^{-3}$		(4), Eq. (1)
873	$3\cdot10^{-2}$	monotectic	(4), interpolated
973	0.15		(4)

References:

[1]E. W. Hobart and R. G. Bjork, Nucl. Appl. **1**, 490 (1965).
[2]R. Ainsley, L. P. Hartlib, P. M. Holroyd, and G. J. Long, Nucl. Mater. **52**, 255 (1974).
[3]F. A. Cafasso, U.S. Atom. Energy Comm. Rep. ANL-7403, p. 124 (1967).
[4]E. Veleckis, K. E. Anderson, F. A. Cafasso, and H. M. Feder, U.S. Atom. Energy Comm. Rep. ANL-7520, Pt. I, p. 295 (1969).
[5]D. Dutina, J. L. Simpson, and R. S. Young, U.S. Atom. Energy Comm. Rep. ANL-7520, Pt. I, p. 448 (1969).
[6]A. K. Fischer and F. A. Cafasso, Trans. Am. Nucl. Soc. **14**, 624 (1971).
[7]R. J. Pulham and P. Hubberstey, J. Nucl. Mater. **115**, 239 (1983).
[8]N. N. Greenwood and A. Earnshaw, *Chemistry of Elements* (Pergamon, Oxford, 1985), p. 3395.

Components:
(1) Sodium cyanide; NaCN [143-33-9]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
E. Veleckis, K. E. Anderson, F. A. Cafasso, and H. M. Feder, U.S. Atom. Energy Comm. Rep. ANL-7520, Pt. I, pp. 295–298 (1969).

Variables:
Temperature: 675–923 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data
The solubility of NaCN in liquid Na was determined

t/°C	Solubility/mass % CN	Solubility/mol % NaCN[a]	Stand. dev./%
402	$7.0\cdot10^{-5}$	$6.0\cdot10^{-5}$	69
425	$4.2\cdot10^{-4}$	$3.7\cdot10^{-4}$	111
450	$4.2\cdot10^{-4}$	$3.7\cdot10^{-4}$	123
500	$4.0\cdot10^{-3}$	$3.5\cdot10^{-3}$	25
525	$1.00\cdot10^{-2}$	$8.8\cdot10^{-3}$	14
549	$1.08\cdot10^{-2}$	$9.6\cdot10^{-3}$	18
575	$5.0\cdot10^{-2}$	$4.4\cdot10^{-2}$	28
600	$7.8\cdot10^{-2}$	$6.9\cdot10^{-2}$	27
650	0.163	0.145	14

[a]Calculated by the compilers.

The monotectic temperature was found at 565±2 °C. The authors proposed the solubility equation valid within temperature range 673–838 K (tested by the compilers):

$$\log(\text{soly/mass \% CN}) = 9.5 - 9140\,(T/\text{K})^{-1}.$$

Auxiliary Information

Method:
An excess of NaCN was equilibrated with Na at a selected temperature in a Ta crucible under He at a pressure of 0.303 MPa. The crucible was contained in an evacuable stainless steel furnace, together with heat and vapor shields, a thermocouple well, a stirrer and a Ta sampler tube with a stainless steel filter of 5 μm porosity. For sampling, the pressure was decreased, and the sampling tube immersed into the melt. The pressure was increased in order to make filtration of the melt into the sampling tube. The melt samples were assayed spectrophotometrically after being dissolved in H_2O. Details of the thermal analysis were not specified.

Source and Purity of Materials:
NaCN: unspecified source; purified by vacuum fusion.
Na: "reactor grade" purity; purified by cold trapping; contained $1.6\cdot10^{-3}$ % O.
He: nothing specified.

Estimated Error:
Solubility: relative standard deviation between 14% and 123%.
Temperature: unspecified in the solubility tests; precision ±2 K in thermal analysis.

Components:
(1) Sodium cyanide; NaCN [143-33-9]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
A. K. Fischer and F. A. Cafasso, Trans. Am. Nucl. Soc. **14**, 623–624 (1971).

Variables:
One temperature: 863 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of NaCN in liquid Na at 590 °C (863 K) was found to be 0.0244 mass % NaCN or 0.0115 mol % NaCN (as recalculated by the compilers). An addition of 1 mass % Ca to the system made the precipitation of CaNCN.

Auxiliary Information

Method:
The experiments were performed under a N atmosphere of 0.096 MPa. Type 304 stainless steel was the material used for the apparatus and tabs which were submerged in liquid Na. The duration of the experiments was ~10 days. Absorption of N by the tabs and by the Na was analyzed by an unspecified method.

Source and Purity of Materials:
C: from Type 304 stainless steel tabs.
N: nothing specified.
Na: "reactor grade" purity.

Estimated Error:
Solubility: nothing specified; detection limit $3 \cdot 10^{-4}$ mol % NaCN.
Temperature: nothing specified.

Components:
(1) Sodium cyanide; NaCN [143-33-9]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
D. Dutina, J. L. Simpson, and R. S. Young, U.S. Atom. Energy Comm. Rep. ANL-7520, Pt I, pp. 448–453 (1969).

Variables:
One temperature: 688 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of NaCN in liquid Na at 750 °F (688 K) was found to be $(1.0 \pm 0.2) \cdot 10^{-4}$ mass % NaCN or $5 \cdot 10^{-5}$ mol % NaCN (as calculated by the compilers).

Auxiliary Information

Method:
Na circulated in a type 316 stainless steel loop, the maximum temperature of which was 900 K and the minimum temperature 650 K. All experimental operations were performed in He atmosphere. The investigated parts of the materials were cleaned before introduction of them into the loop. Samples of liquid Na were withdrawn for analysis. They were dissolved in H_2O and acidified. HCN formed, was distilled off from the acidified solution. It was determined in the distillate by means of spectrophotometric measurement of the extinction with p-phenylene diamine. The solid deposit before the hydrolysis was examined by x rays to confirm the presence of cyanide.

Source and Purity of Materials:
NaCN: formed from C and N as contaminants in the Na and the stainless steel.
Na: nuclear grade of purity; with a content of $1.0 \cdot 10^{-3}$ % O.
He: contained $< 1 \cdot 10^{-4}$ % O, H_2O.

Estimated Error:
Solubility: precision of analysis better than ±10%; standard deviation ±20%.
Temperature: nothing specified.

Components:
(1) Nitrogen; N; [7727-37-9]
(2) Barium; Ba; [7440-39-3]
(2) Sodium; Na; [7440-23-5]

Evaluated By:
Hans Ulrich Borgstedt, Forschungszentrum Karlsruhe, Germany and Cezary Guminski, University of Warsaw, Poland, February 1996

Critical Evaluation

Although N is inert towards liquid Na and its solubility is very low, an addition of Ba into Na promotes reactions and the subsequent solution of N. The process was investigated by chemical analysis of the filtrate[1] and electrical resistivity studies.[2] In the first step of the reactions Ba_4N, being soluble in Na, is formed:

$$4\ Ba+N \leftrightarrow Ba_4N. \quad (1)$$

After the bonding of the whole Ba in reaction Eq. (1) a further addition of N leads to the subsequent reaction:

$$Ba_4N+N \rightarrow 2\ Ba_2N. \quad (2)$$

The product of the reaction Eq. (2) is practically insoluble in liquid Na, certainly its solubility is lower than 0.02 mol %. The resistivity of such a solution was slightly higher than of pure Na (2), but the alloy solidified at the melting point of pure Na. The mechanism of the two-stage reaction was confirmed in kinetic studies at 573–673 K.[3] A further slow absorption of N leads finally to the formation of a typical nitride Ba_3N_2 :

$$3\ Ba_2N+N \rightarrow 2\ Ba_3N_2\,. \quad (3)$$

Hubberstey[3] proposed a qualitative figure of the Na-rich corner of the N–Ba–Na phase diagram and found that the ternary eutectic occurs at 333±1 K; the composition of this point and experimental details were not reported therein. The solubility data reported in Addison *et al.*[1] and Addison *et al.*[2] may be treated as tentative. In Na which contains 4.4 mol % Ba the apparent N solubility is 1.1 mol % N at 573 K.

References:

[1]C. C. Addison, R. J. Pulham, and E. A. Trevillion, J. Chem. Soc., Dalton Trans. 2082 (1975).
[2]C. C. Addison, G. K. Creffield, P. Hubberstey, and R. J. Pulham, J. Chem. Soc., Dalton Trans. 1105 (1976).
[3]P. Hubberstey, *Liquid Alkali Metals* (British Nuclear Energy Society, London, 1973), p. 15.

Components:
(1) Nitrogen; N; [7727-37-9]
(2) Barium; Ba; [7440-39-3]
(3) Sodium; Na; [7440-23-5]

Original Measurements:
C. C. Addison, R. J. Pulham, and E. A. Trevillion, J. Chem. Soc., Dalton Trans. 2082–2085 (1975).

Variables:
One temperature 573 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of N in liquid Na containing Ba was determined at 300 °C (573 K)

Ba concentration mol % Ba	Total N absorbed		N solubility	
	mass %	mol %[a]	mass %	mol %[a]
4.20	0	0	0.016	0.032
			0.015	0.030
4.10	0.111	0.219	0.099	0.195
			0.119	0.235
4.30	0.260	0.512	0.202	0.398
			0.272	0.536
4.40	0.425	0.837	0.360	0.709
			0.380	0.749
			0.420	0.827
4.30	0.514	1.008	0.490	0.960
			0.460	0.902
4.40	0.585	1.147	0.437	0.857
			0.481	0.943
4.40	0.633	1.24	0.393	0.770
			0.389	0.762
4.20	0.708	1.39	0.254	0.498
			0.242	0.474
			0.231	0.453
			0.222	0.435
4.40	0.851	1.67	0.221	0.433
			0.224	0.439
4.10	1.04	2.04	0.006	0.012
			0.013	0.026

[a]Calculated by the compilers.

The reaction of N with Ba lead to the formation of complex Ba_4N soluble in liquid Na. After reaching certain concentration ratio Ba_2N is precipitated. The solubility of Ba_2N in liquid Na is certainly lower than the solubility of N measured in the last experiment (see the table).

Auxiliary Information

Method:

The apparatus was constructed from AISI 321 stainless steel that allowed mixing, filtration and sampling. The sampling tube was made of Pyrex glass. The vessel was cleaned with a mixture of HCl(54%), HNO_3(5%) and H_2O, rinsed with H_2O, acetone and dried by heating in vacuum. All essential operations were carried out in an Ar atmosphere. A weighed quantity of liquid Na, drawn from a stock, was pipetted into the vessel. Ba was added into it. The temperature was raised to 573 K and Ba was dissolved during Na circulation. Ar was pumped off and immediately replaced with a known amount of N. The absorption of N was followed by its pressure changes and after completion the sampling tube was lowered to submerge the filter. On pressurizing the Ar was forced through the filter into the sampling tube. After withdrawal, the sample was cooled rapidly in an air stream. The frozen filtrate was divided into segments for analysis. The samples were dissolved in pure CH_3COOH, thus they were converted to $Ba(CH_3COO)_2$ and NH_4CH_3COO. N_2 was not produced during the solvolysis as confirmed by mass spectrometry.

Source and Purity of Materials:

N: 99.999% pure from Air products Ltd., further purified by passage through molecular sieves, MnO and liquid K–Na alloy.
Ba: 99.99% pure (according to an analysis); supplied by Koch–Light Ltd.[1]
Na: supplied by UKAEA, Culcheth,[2] contained $\leqslant 4 \cdot 10^{-3}$ % Ca, $\leqslant 1 \cdot 10^{-3}$ % O.
Ar: 99.99% pure, from Air Products Ltd., further dried by molecular sieves.[2]

Estimated Error:

Solubility: nothing specified; precision better than ±15% (by the compilers).
Temperature: nothing specified.

References:

[1]C. C. Addison, G. K. Creffield, P. Hubberstey, and R. J. Pulham, J. Chem. Soc., A 1393–1395 (1971).
[2]C. C. Addison, G. K. Creffield, P. Hubberstey, and R. J. Pulham, J. Chem. Soc., A 1482–1487 (1969).

Components:

(1) Nitrogen; N; [7727-37-9]
(2) Barium; Ba; [7440-39-3]
(3) Sodium; Na; [7440-23-5]

Original Measurements:

C. C. Addison, G. K. Creffield, P. Hubberstey, and R. J. Pulham, J. Chem. Soc., Dalton Trans. 1105–1108 (1976).

Variables:

One temperature 573 K

Prepared by:

H. U. Borgstedt and C. Guminski

Experimental Data

The dependence of the solubility of N on the Ba concentration in liquid Na at 300 °C (573 K) was determined

Ba concentration/mol %	Solubility/mol % N
0.34	0.08
2.04	0.46
2.51	0.58
2.85	0.72
3.46	0.87
4.40	1.08[a]
6.89	1.70

[a]Estimated value from a filtration and analysis experiment.[1]

N reacted with Ba dissolved in liquid Na forming soluble Ba_4N which was precipitated as Ba_2N at a critical concentration of N.

Auxiliary Information

Method:

A weighed sample of Ba was dissolved in Na in Ar atmosphere. The liquid alloy was forced continuously through a steel capillary loop by means of an electromagnetic pump and returned to a reservoir where N was metered in from vacuum frame. The returning liquid metal was injected into the N gas as a jet, thereby facilitating rapid reaction and dissolution. The electric resistance of the liquid alloy was measured by a Kelvin–Wheatstone bridge. The resistance of the empty capillary, filled with Na and filled with the alloy, were measured thus allowing the calculation of the N concentration in the saturated solution.

Source and Purity of Materials:

N: 99.99% pure from Air Products Ltd.; further purified by passage through liquid Na–K alloy and MnO.
Ba: 99.99% pure (according to an analysis) supplied by Koch–Light.[2]
Na: supplied by UKAEA, Culcheth,[3] contained $\leqslant 4.10^{-3}$ % Ca, $\leqslant 1.10^{-3}$ % O.
Ar: 99.99% pure probably as in Addison *et al.*,[1] from Air Products Ltd.; further dried by molecular sieves.[2]

Estimated Error:

Solubility: nothing specified.
Temperature: precision within a few K.

References:

[1]C. C. Addison, R. J. Pulham, and E. A. Trevillion, J. Chem. Soc., Dalton Trans. 2082–2085 (1975).
[2]C. C. Addison, G. K. Creffield, P. Hubberstey, and R. J. Pulham, J. Chem. Soc., A 1393–1395 (1971).
[3]C. C. Addison, G. K. Creffield, P. Hubberstey, and R. J. Pulham, J. Chem. Soc., A 1482–1485 (1969).

Components:
(1) Nitrogen; N; [7727-37-9]
(2) Lithium; Li; [7439-93-2]
(3) Sodium; Na; [7440-23-5]

Original Measurements:
C. C. Addison and B. M. Davies, J. Chem. Soc., A 1827–1830 (1969).

Variables:
One temperature: 673 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data and Critical Evaluation

An apparent solubility of N in liquid Li–Na mixtures was determined at 400 °C (673 K)

Li concentration/mol %	Solubility/mass % N	Solubility/mol % N[a]
16.94	11.92	2.70
16.94	2.67[b]	2.63
25.32	3.19	4.12
27.90	3.80	4.77

[a]Calculated by the compilers.
[b]The erroneous value, the correct one should be 1.87, as calculated by the compilers.

Kinetics of the reaction of N with the stirred solution of Li in liquid Na was investigated. At concentrations >13 mol % Li the reaction rate was constant and independent on the N pressure. The N absorption curves depart from linearity at the composition Li_6N and precipitation of Li_3N is believed to commence at this point. At concentrations <13 mol % Li the reaction rate changes through the reaction, consistent with continuous precipitation of Li_3N.

The solubility data have a tentative character.

Auxiliary Information

Method:
The experiments were performed in a reaction vessel made of Type 321 stainless steel. The vessel contained a steel thermometer pocket into which a Chromel/Alumel thermocouple was inserted. The vessel was cleaned with a solution of HCl (50%), HNO_3 (5%), and H_2O. It was dried in vacuum after rinsing. An electromagnetic device was used for stirring. Solutions were prepared by pipetting a known quantity of liquid Na. Pieces of Li were washed in dry ether and introduced into Na after weighing. All essential steps of the process were performed in an Ar atmosphere. The solution was mixed for 24 h at 673 K and degassed at 383 K to 0.01 Pa. No wetting of the vessel walls occurred during the experiments. The solubility was estimated from the difference of the N volume before and after the equilibration with the Li–Na alloy.

Source and Purity of Materials:
N: 99.98% pure from B.D.C.; further passed through Linde molecular sieves, MnO at 303 K to decrease contents of O, H_2O, and CO_2.
Li: 99.98% pure from Koch–Light Ltd..
Na: "high purity."
Ar: 99.99% pure from Air Products Ltd., further dried by molecular sieves (Addison *et al.*[1]).

Estimated Error:
Solubility: nothing specified; precision of a few % (by the compilers).
Temperature: nothing specified.

References:
[1]C. C. Addison, G. K. Creffield, P. Hubberstey, and R. J. Pulham, J. Chem. Soc., A 1482–1485 (1969).

Components:
(1) Nitrogen; N; [7727-37-9]
(2) Calcium; Ca; [7440-70-2]
(3) Sodium; Na; [7440-23-5]

Original Measurements:
A. K. Fischer, U.S. Atom. Energy Comm. Rep. ANL-7775, pp. 39–40 (1971).

Variables:
One temperature: 663 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data and Critical Evaluation

The introduction of 0.72 mol % N into the 1 mol % solution of Ca in liquid Na caused, due to the reaction of Ca with N, a reduction of the Ca concentration to less than $1.0 \cdot 10^{-3}$ mass % Ca ($6 \cdot 10^{-4}$ mol % Ca) in Na at 390 °C. The stainless steel used as container material did not take up any Ca or N. Thus, the concentration may be treated as the solubility limit. The solid equilibrium phase was found to be $Ca_{1.78}N$.

The solubility data appears to be of tentative character.

Auxiliary Information

Method:
A solution of Ca in liquid Na was contained in a reaction vessel made of Type 304 stainless steel. The solution was agitated under constant pressure of 720 Torr of gaseous N. The gas absorption was determined gasometrically in order to evaluate the stoichiometry of the reaction. After completion of the absorption in about 1 week a filtered sample of liquid Na was withdrawn for the determination of Ca and N (the latter by the Kjeldahl method). The stainless steel was analyzed for its content before and after the reaction with Ca in liquid Na.

Source and Purity of Materials:
N: nothing specified.
Ca: nothing specified.
Na: nuclear grade of purity.

Estimated Error:
Solubility: the measurement at the detection level.
Temperature: nothing specified.

Components:
(1) Nitrogen; N; [7727-37-9]
(2) Strontium; Sr; [7440-24-6]
(3) Sodium; Na; [7440-23-5]

Original Measurements:
P. Hubberstey and P. R. Bussey, *Liquid Metals Engineering and Technology* (BNES, London, 1984), Vol. **3**, pp. 143–149.

Variables:
One temperature: 673 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data and Critical Evaluation

An apparent solubility of N in liquid Na containing increasing amounts of Sr was determined at 400 °C (673 K)

Sr concentration/mol %	Solubility/mol % N
2.40	0.14
3.58	0.21
4.79	0.28
5.70	0.33
7.86	0.41
9.21	0.57
12.10	0.63

A soluble complex of the formula $Sr_{17-18}N$ was formed in the first step of reaction. After bonding the whole Sr in this way a further addition of N caused the precipitation of Sr_2N. The solubility data seems to have a tentative character.

Auxiliary Information

Method:
The experimental procedure was probably the same as reported in Addison *et al.*[1] A weighed sample of Sr was dissolved in Na in an Ar atmosphere. The liquid metal was pumped continuously through a steel capillary loop by means of an electromagnetic pump and returned to a reservoir into which N was metered from a vacuum frame. The returning liquid metal was injected into the gas as a jet, thereby facilitating rapid reaction and dissolution. The electric resistance of the liquid alloy was measured by a Kelvin–Wheatstone bridge. The resistance of the empty capillary, filled alternatively with Na and with the alloy investigated, was measured allowing for calculation of the N concentration in the saturated solution.

Source and Purity of Materials:
N: probably 99.99% pure, as in Addison *et al.*;[1] from Air Products Ltd.; further purified by passage through MnO and liquid K–Na alloy.
Sr: nothing specified.
Na: supplied by UKAEA, Culcheth, contained $\leqslant 4 \cdot 10^{-3}$ % Ca, $\leqslant 1 \cdot 10^{-3}$ % O.
Ar: 99.99% pure from Air Products Ltd.; further dried by molecular sieves.

Estimated Error:
Solubility: nothing specified.
Temperature: precision within few K.

References:
[1]C. C. Addison, G. K. Creffield, P. Hubberstey, and R. J. Pulham, J. Chem. Soc., Dalton Trans. 1105–1108 (1976).

4.9. Sodium–Phosphorous

Components:
(1) Phosphorous; P; [7723-14-0]
(2) Sodium; Na; [7440-23-5]

Evaluated By:
Hans Ulrich Borgstedt, Forschungszentrum Karlsruhe, Germany and Cezary Guminski, University of Warsaw, Poland, February 1996

Critical Evaluation

Since P is a constituent of many steels and some other constructional alloys, its solubility in liquid Na is of technical interest. However, solubility studies have not been reported so far. Knowledge of the Na–P system is also limited. Several investigators[1–3] found the formation of Na_3P by a direct reaction of the molten components. This compound seems to be the most stable one in this system, and it melts between 773 and 823 K (Morozova *et al.*[2]). Several compounds richer in P were obtained by chemical reactions,[4–7] but any systematic studies of the phase relations in the P–Na system have not been performed, most probably due to experimental difficulties.[3] Since Na_3P has the lowest melting temperature of all analogous compounds of As, Sb, and Bi with Na, one may postulate the highest solubility (from all these elements) of P in liquid Na.

References:
[1]G. Brauer and E. Zintl, Z. Phys. Chem., B **37**, 323 (1937).
[2]M. P. Morozova, G. A. Bolshakova, and N. L. Lukinykh, Zh. Obshch. Khim. **29**, 3144 (1959).
[3]W. Klemm, Proc. Chem. Soc. 329 (1958).
[4]M. C. Hugot, Compt. Rend. **121**, 206 (1895).
[5]E. Zintl, J. Goubeau, and W. Dullenkopf, Z. Phys. Chem., A **154**, 1 (1931).
[6]W. Hönle and H. G. von Schnering, Acta Crystall. **34**, S152 (1978).
[7]W. Wichelhaus and H. G. von Schnering, Naturwissensch. **60**, 104 (1973).

4.10. Sodium–Arsenic

Components:
(1) Arsenic; As; [7440-38-2]
(2) Sodium; Na; [7440-23-5]

Evaluated By:
Hans Ulrich Borgstedt, Forschungszentrum Karlsruhe, Germany and Cezary Guminski, University of Warsaw, Poland, February 1996

Critical Evaluation

There is no doubt that As reacts with Na at temperatures of 473–723 K.[1–4] It seems that Na_3As is the most stable compound being formed in the As–Na system. Its melting point was established at 973 K.[3] Unfortunately, systematic studies of either the phase diagram or solubility of As in liquid Na have not been performed due to experimental difficulties.[2] Other Na–As compounds (richer in As) were synthesized by chemical reactionsm[5–7] but their thermal stabilities are not known. If one assumes that Na_3As is the equilibrium solid phase being in equilibrium with the saturated solution of As in liquid Na and that solubilities of analogous compounds are proportional to their melting points, one may estimate that the solubility of As in liquid Na should be slightly higher than that of Bi in liquid Na at a corresponding temperature. Sangster and Pelton[8] estimated this $\approx 10^{-4}$ mol % As at the melting point of Na.

References:

[1]G. Brauer and E. Zintl, Z. Phys. Chem., B **37**, 323 (1937).
[2]W. Klemm, Proc. Chem. Soc. 329 (1958).
[3]M. P. Morozova, G. A. Bolshakova, and N. L. Lukinykh, Zh. Obshch. Khim. **29**, 3144 (1959).
[4]C. Hugot, Compt. Rend. **127**, 553 (1898).
[5]E. Zintl, J. Goubeau, and W. Dullenkopf, Z. Phys. Chem., A **154**, 1 (1931).
[6]W. Hönle and H. G. von Schnering, Acta Crystall., A **34**, S152 (1978).
[7]H. G. von Schnering, M. Somer, G. Kliche, W. Hönle, T. Meyer, J. Wolf, L. Ohse, and P. B. Kempa, Z. Anorg. Chem. **601**, 13 (1991).
[8]J. Sangster and A. D. Pelton, J. Phase Equil. **14**, 240 (1993).

4.11. Sodium–Oxygen

Components:
(1) Oxygen; O; [7782-44-7]
(2) Sodium; Na; [7440-23-5]

Evaluated By:
Hans Ulrich Borgstedt, Forschungszentrum Karlsruhe, Germany and Cezary Guminski, University of Warsaw, Poland, February 1997

Critical Evaluation

Very dry O does not react effectively with Na, but such a reaction may be violent in the presence of moisture.[1] Superoxide NaO_2 is initially formed in course of the reaction. NaO_2 reacts with more Na to form gradually Na_2O_2 and finally Na_2O. The latter substance is the equilibrium solid phase saturating the liquid Na. A solubility of O in liquid Na has been most frequently investigated from all nonmetals dissolved in the liquid alkali metals, since O in Na (used as a coolant in metallic tubes) has the deleterious effect on several container materials. Due to the practical importance of this solubility system it was reviewed several times[2–17] in order to make the best selection from the existing plenty of experimental data. Nearly a thousand solubility values were found so far in about 40 original papers. This indicates that not very convertible results have been obtained with the use of various determination methods in different laboratories. Grieser *et al.*[18,19] and Claxton[3] reviewed critically the usefulness of about 20 potential techniques which could be used to determine directly or indirectly the O amount present in Na. The following methods found a practical application: amalgamation of Na, leaving Na_2O undissolved in Hg (refer to Refs. 20–37), the use of the plugging indicator working on the formation of Na_2O crystals in an orifice of Na circulating loop (refer to Refs. 26, 27, 38–41), the vacuum distillation of Na leaving Na_2O precipitate (refer to Refs. 40, 42–68), the measurements of emf of a cell containing Na–O melt in one of electrodes (refer to Refs. 69–84), O gettering by V wire dipped in Na containing Na_2O (refer to Refs. 76 and 77), the photoactivation analysis (refer to Refs. 85 and 86), measurements of the electrical resistivity (refer to Ref. 87), and the use of N-butyl bromide (instead of Hg as in the amalgamation method) for a reaction with Na leaving Na_2O undissolved (refer to Refs. 88 and 89). Isaacs[90,91] and Klueh[92] worked out a process of gettering dissolved O with U or Zr, respectively. However, no one of these latter proposals was applied for the determination of the O solubility.

In some reports the solubility data were reported in numerical[93,94] or graphical[95–100] forms, but no experimental details of analysis were described. Therefore, it is difficult to judge how far the data had been original. Kolodney *et al.*[101] measured concentrations of O in liquid Na by means of potentiometry and concluded that early determinations of the solubility at lower temperatures were overestimated. Jung[102] using the same method confirmed the correctness of the solubility equation proposed by Eichelberger.[6] No solubility results were reported in Kolodney *et al.*[101] and Jung.[102] Näfe *et al.*[83] reported four smooth solubility lines based on own investigations between 383 and 483 K with slopes the temperature dependencies similar to that given in Eq. (1) (see below); they differ, however, in the pre-exponential constant within 1 logarithmic unit. The authors did not give any experimental details, and they did not prefer any of the widely scattered data. In the next report of the same laboratory[84] the solubility of 0.066 mol % O at 673 K was presented, but the report lacked of a sufficient description of the measurement; therefore, data sheets for Näfe *et al.*[83] and Näfe[84] were not prepared.

Each experimental technique was found to have its limitation and it is still rather difficult to recommend, as an absolute standard, one of the methods for the O solubility determination. At present, the vacuum distillation of Na is probably the safest procedure to get the most reproducible and reliable results. The present authors found this method to be sensitive to a level of $1\cdot 10^{-4}$ mol % O and accurate at $\pm 7\cdot 10^{-5}$ mol % O. The vapor pressure of O over Na_2O at 813 K is on the order of 10^{-5} Pa (Bagdasarov[50]) and does not practically influence the separation. The plugging indicator method gives typically overestimated results, since the precipitation process in the orifice is a rate controlled one and requires a finite concentration driving force to precipitate Na_2O in a finite time.[103,104] Other impurities may coprecipitate with Na_2O, therefore, the method is not very selective. Prach *et al.*[105] and Meacham and Hill[106] evaluated the amalgamation method. Prach *et al.*[105] found that its reproducibility within $\pm 1.4\cdot 10^{-4}$ mol % O may be achieved down to $1.4\cdot 10^{-4}$ mol % O. Meacham and Hill[106] compared the results obtained by means of this method in several laboratories and established a standard deviation of $\pm 30\%$ at a level of $1.0\cdot 10^{-3}$ mol % O and $\pm 15\%$ at level of $4.3\cdot 10^{-3}$ mol % O. Scarborough and DeVries[107] pointed out the importance of a blank correction needed, if the amalgamation process is applied; other insoluble residues collected by amalgamation (NaH, Na_2CO_3, NaOH, NaC_x, NaCl, etc.) may contribute to the measured O solubility value. In the case of the electrochemical O meter no author recommended the use of it, if a precision better than $\pm 10\%$ is needed. Although several types of such meters have been produced, the calibration of the meters does pose problems. The evaluator's experience with such meters is that they become instable at temperatures below 590 K due to insufficient ionic conductivity even in very pure Na. The correctness of this method was discussed by Näfe.[108] The V-wire equilibration method[61,77,109] is considered applicable at levels up to $2.2\cdot 10^{-3}$ mol % O with an accuracy of $\pm 15\%$. However, Hooper and Trevillon[110] concluded, after a careful analysis of the V–O system that the applicability of this technique is only up to $3\cdot 10^{-4}$ mol % O. Näfe[111] questioned the argumentation of Hooper and Trevillon.[110] The photoactivation analysis is characterized by a sensitivity of $\sim 1\cdot 10^{-4}$ mol % O and a precision not better than $\pm 5\%$. No details concerning the applicability of the electrical resistivity method are known but the method should be quite sensitive to other impurities present in Na. White *et al.*[88,89] claimed that the method using N-butyl bromide has an accuracy of ± 0.0015 mol % O and a standard deviation of 0.007 mol % O. It seems in practice that errors in the application of this method may be somewhat higher.

For the final recommendation of O solubility in liquid Na one should reject the low temperature data (at <523 K) based on the amalgamation method.[20,23–25,26–32,35] Since no phase transition in Na_2O at ~ 523 K is observed the solubility break measured in several early investigations close to this temperature may be due to other reasons, as for instance: Na attack on a glass, the blank error or other imperfections of the amalgamation method. For the same reason we should neglect the first, preliminary experiments performed by Weber and Pepkowitz[112] who found that 0.5 mol % O is equally soluble in liquid Na over the temperature range 398–698 K; ten times lower values were obtained in subsequent studies of this laboratory. One should also reject the underestimated data of the three studies.[38,75,77]

The majority of the solubility results is within a scatter band of ±50% in respect to a mean value at selected temperature. Typically the amalgamation method is characterized by the lowest temperature coefficients of the solubility, whereas the potentiometric method generates the highest slope. The vacuum distillation results are relatively different from this point of view. The correlation of Claxton[12,13] seems to be the most reliable, since it was based on the largest amount of points (about 350) selected to the correlation:

$$\log(\text{soly/mol \% O}) = 2.320 - 2372\ (T/\text{K})^{-1} \tag{1}$$

valid for the temperature range 371–850 K. The results obtained in subsequent publications[39,40,67–79,80,81,84,85] do not change the values generated by Eq. (1) for more than 3%. The authors of this evaluation realize that Eq. (1) as well as other relationships proposed in the past may not gain the general acceptance due to preferences of some and the neglect of other methods. In series of reports, Näfe[17,83,108,113,114] deliberated on the temperature dependence of the solubility, and he concluded that Henry's law is not obeyed in the solutions of O in liquid Na. Consequently, the partial enthalpy of Na_2O dissolution depends on temperature and is higher than the value hitherto known; thus, the solubility at lowest temperatures is lower than assumed. Näfe[17] proposed the equation for the O solubility with six parameters to fit the curvature of the logarithm of the solubility versus the reciprocal temperature. Precise calorimetric experiments could answer the question of an eventual instability of the partial enthalpy of the dissolution of Na_2O. Using Eq. (1) one may predict that the solubility at the eutectic temperature (371 K) is $7 \cdot 10^{-5}$ mol % O and at the monotectic temperature (~1403 K) is ~4.2 mol % O. The monotectic extends to ~32.3 mol % O.[115] The melting point of Na_2O was found to be 1406 K, with reference to the accepted melting temperature of Au at 1337 K.[116] This value was confirmed by Maupré[115] and Henry *et al.*[117] Bouaziz *et al.*[116] postulated transformations of solid Na_2O at ~1023 and ~1243 K which were not found by Henry *et al.*[117] Some weak arrests at 1203–1243 K were interpreted by Maupré[115] as corrosion effects of Ni crucibles by the Na_2O melt. Privalov[118] concluded from his calorimetric experiments that Na_2O exists in Na in molecular form.

Since O interacts with H, C, Si, many *d* and *f* metals and other elements (the interactions of which were not studied in detail), one should take into account a presence of these impurities on an apparent increase of the measured O solubility in Na. Solubilities of O-containing compounds (Na_2CO_3,NaOH) are evaluated separately. A solubility of O in the K–Na melts[24,32,37,48,119–127] is elaborated together with the O–K solubility system.

Fragments of the O–Na phase diagram were investigated by Maupré[115] between Na and Na_2O. Bunzel and Kohlmeyer[128] studied the Na_2O–Na_2O_2 system, but their diagram was not accepted by Wriedt.[16] Wriedt[16] constructed the most extensive part of the O–Na phase diagram (the shape of several fields is still unknown), and this form is reflected in Fig. 23.

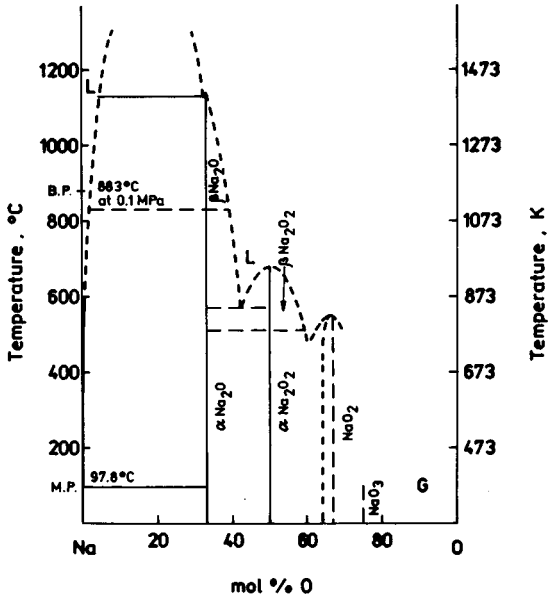

FIG. 23. Na–O phase diagram.

Recommended values of the solubility of O in liquid Na

T/K	Solubility/mol % O	Source
371	$7 \cdot 10^{-5}$ eutectic	Eq. (1), extrapolation
473	$2.0 \cdot 10^{-3}$	Eq. (1), (33), (39), (47), (52), (58), (63), (64)
573	$1.5 \cdot 10^{-2}$	Eq. (1), (33), (42), (47), (81)
673	$6 \cdot 10^{-2}$	Eq. (1), (21), (47), (64), (84)
773	0.18	Eq. (1)
873	0.4	Eq. (1), extrapolation

References:

[1]C. Tyzack and P. B. Longton, U.K. Atom. Ener. Author. Rep. R&DB(C)TN-79 (1954).
[2]C. R. F. Smith, U.S. Atom. Energy Comm. Rep. NAA-SR-Memo-2061 (1960).
[3]K. T. Claxton, J. Nucl. Energy **19**, 849 (1965).
[4]K. T. Claxton, Atom. Energy Res. Establ. Rep. R-4897 (1965).
[5]K. T. Claxton, J. Nucl. Energy **21**, 351 (1967).
[6]R. L. Eichelberger, U.S. Atom. Energy Comm. Rep. AI-AEC-12685 (1968).
[7]R. L. McKisson, R. L. Eichelberger, D. C. Gehri, and J. Guon, U.S. Atom. Energy Comm. Rep. AI-AEC-12721, p. 293 (1968).
[8]R. L. Eichelberger, Trans. Am. Nucl. Soc. **12**, 613 (1969).
[9]J. D. Noden, Centr. Ener. Gener. Board Rep. RD/B/R-2146 (1972).
[10]J. D. Noden, J. Brit. Nucl. Ener. Soc. **12**, 57, 329 (1973).
[11]O. M. Sreedharan and J. B. Gnanamoorphy, J. Nucl. Mater. **89**, 113 (1980).
[12]K. T. Claxton, U.S. Energy Res. Devel. Admin. Rep. CONF-760503-Pl, p. 407 (1976).
[13]K. T. Claxton, Junta Ener. Nucl. Rep. JEN-446 (1979).
[14]N. Rumbaut, F. Casteels, and M. Brabers, *Material Behaviour and Physical Chemistry of Liquid Metal Systems*, edited by H. U. Borgstedt (Plenum, New York, 1982), p. 437.
[15]H. U. Borgstedt, *Handbook of Thermodynamic and Transport Properties of Alkali Metals*, edited by R. W. Ohse (Pergamon, New York, 1984), p. 901.
[16]H. A. Wriedt, Bull. Alloy Phase Diagr. **8**, 234 (1987).
[17]H. Näfe, Akad. Wissensch. DDR Rep. ZfK-571, p. 29 (1985).
[18]D. R. Grieser, G. G. Cocks, E. H. Hall, W. M. Henry, and J. McCallum, U.S. Atom. Energy Comm. Rep. BMI-1538 (1961).
[19]Anonymous (Battelle Memorial Inst.) U.S. Atom. Energy Comm. Rep. TID-7626, Pt. I, p. 125 (1962).
[20]S. L. Walters, U.S. Atom. Energy Comm. Rep. NP-1955 (1950); Rep. MSA-TR-VI (1950).
[21]O. N. Salmon and T. J. Cashman, U.S. Atom. Energy Comm. Rep. KAPL-1653 (1956).
[22]L. F. Epstein, *Liquid Metal Handbook, Sodium & Na-K Supplement*, edited by C. B. Jackson (USAEC & Navy, Washington, 1955), p. 6.
[23]D. S. Oliver and J. D. Noden, U.K. Atom. Ener. Author. Rep. R&DB(C)TN-33 (1953).
[24]J. D. Noden and K. Q. Bagley, U.K. Atom. Ener. Author. Rep. R&DB(C)TN-80 (1954).
[25]A. B. McIntosh and K. Q. Bagley, Inst. Met. **84**, 251 (1955–56).
[26]I. L. Gray, R. L. Neal, and B. G. Voorhees, Nucleonics **14**(10), 34 (1956).
[27]I. L. Gray, R. L. Neal, and B. G. Voorhees, Chem. Engin. Progr., Symp. Ser. **20**, **53**, 11 (1957).
[28]W. Jahns and G. Weidmann, Nukleonik **1**, 189 (1958–59).
[29]A. D. Bogard and D. D. Williams, U.S. Naval Res. Lab. Rep. NRL-3865 (1951).
[30]A. D. Bogard and D. D. Williams, U.S. Naval Res. Lab. Rep. NRL-3895 (1951).
[31]D. D. Williams and R. R. Miller, Anal. Chem. **23**, 1865 (1951).
[32]D. D. Williams, J. A. Grand, and R. R. Miller, J. Phys. Chem. **63**, 68 (1959).
[33]R. C. Andrews and K. R. Barker, Mine Safety Appliances Rep. MSAR-67-207, p. 8 (1967).
[34]S. Dorner, U.S. Atom. Energy Comm. Rep. EUR FNR-179P (1966).
[35]H. Beisswenger and S. Dorner, J. Nucl. Mater. **23**, 297 (1968).
[36]P. Berge, C. Oberlin, and P. Saint-Paul, J. Nucl. Mater. **57**, 283 (1975).
[37]Z. S. Bannykh and G. F. Fefelova, Tr. Ural. Nauch.-Issled. Inst. **5**, 105 (1957).
[38]A. N. Hamer, J. H. Higson, J. Mathison, and R. Swinhoe, *Liquid Alkali Metals* (British Nucleus Energy Society, London, 1973), p. 59.
[39]R. S. Fidler and R. Saagi, Nucl. Ener. **23**, 385 (1984).
[40]A. W. Thorley, U.K. Atom. Ener. Author. Rep. NRL-R-1043(R) (1989).
[41]S. Siegel, R. L. Carter, F. E. Bowman, and B. R. Hayward, *Peaceful Uses of Atomic Energy* (U.N., New York, 1956), Vol. 9, p. 321.

[42]A. W. Thorley, Reactor Materials Laboratory (Culcheth, private communication to C. R. F. Smith, 1960).
[43]A. W. Thorley and A. C. Raine, *The Alkali Metals* (The Chemical Society, London, 1967), p. 374.
[44]V. M. Sinclair, R. A. H. Pool, and A. E. Ross, U.S. Atom. Energy Comm. Rep. TID-7622, p. 35 (1961).
[45]C. Tyzack, *Steels for Reactor Pressure Circuits* (The Iron & Steel Institute, London, 1961), p. 179.
[46]K. S. Bergstresser, G. R. Waterbury, and C. F. Metz, U.S. Atom. Energy Comm. Rep. LA-3343 (1965).
[47]V. I. Subbotin, F. A. Kozlov, E. K. Kuznetsov, and N. N. Ivanovskii, *Alkali Metal Coolants* (IAEA, Vienna, 1967), p. 461.
[48]F. A. Kozlov, E. K. Kuznetsov, and V. I. Subbotin, *Zhidkie Metally* (Atomizdat, Moskva, 1967), p. 324.
[49]F. A. Kozlov, E. K. Kuznetsov, G. P. Sergeev, L. G. Volchkov, and V. V. Zotov, *Trudy Fiziko-Energeticheskogo Instituta*, edited by V. A. Kuznetsov (Atomizdat, Moskva, 1974), p. 290.
[50]Yu. E. Bagdasarov, *Tekhnicheskie Problemy Reaktorov na Bystrykh Neitronakh* (Atomizdat, Moskva, 1969), p. 90.
[51]I. B. Dmitreva, F. A. Kozlov, and E. K. Kuznetsov, *Zhidkie Metally* (Atomizdat, Moskva, 1967), p. 318.
[52]J. R. Humphreys and S. B. Skladzien, U.S. Atom. Energy Comm. Rep. ANL-7518, p. 30 (1968).
[53]S. B. Skladzien, U.S. Atom. Energy Comm. Rep. ANL-7460, p. 31 (1968).
[54]V. J. Rutkauskas, U.S. Atom. Energy Comm. Rep. LA-3879 (1968).
[55]Anonymous, Los Alamos Sci. Lab., U.S. Atom. Energy Comm. Rep. LA-3524-MS, p. 50 (1966).
[56]V. J. Rutkauskas and G. E. Meadows, U.S. Atom. Energy Comm. Rep. LA-3745-MS, p. 10 (1967).
[57]V. J. Rutkauskas, *The Alkali Metals* (The Chemical Society, London, 1967), p. 401.
[58]D. L. Smith and T. F. Kassner, *Corrosion by Liquid Metals*, edited by J. E. Draley and J. R. Weeks (Plenum, New York, 1970), p. 137.
[59]D. L. Smith and R. H. Lee, U.S. Atom. Energy Comm. Rep. ANL-7891 (1972).
[60]D. L. Smith, Metall. Trans. **2**, 579 (1971).
[61]D. L. Smith, U.S. Energy Res. Devel. Admin. Rep. CONF-760503-P2, p. 631 (1976).
[62]W. H. Caplinger, G. E. Meadows, D. W. Bennett, and J. A. Yount, Trans. Am. Nucl. Soc. **14**, 611 (1971).
[63]H. U. Borgstedt, H. Schneider, and G. Wittig, Atomwirtsch. **17**, 157 (1972).
[64]G. Ilincev, Kernenergie **18**, 69 (1975).
[65]G. Ilincev, *Sostoyanie i Perspektivy Rabot po Sozdanuyu AES s Reaktorami na Bystrykh Neitronakh* (Fiziko-Energeticheskii Inst., Obnisk, 1975), p. 223.
[66]M. de la Torre Cabezas, Junta Ener. Nucl. Rep. JEN-310 (1975).
[67]R. Sridharan, T. Gnanasekaran, G. Periaswami, and C. K. Mathews, *Liquid Metal Systems*, edited by H. U. Borgstedt and G. Frees (Plenum, New York, 1995), p. 269.
[68]K. Takeda, K. Itoh, T. Mizutani, T. Wada, S. Takani, and H. Atsumo, Fall Meeting of the Atom. Ener. Soc. of Japan, 1975, Reprint D52.
[69]B. Minushkin and G. Kissel, *Corrosion by Liquid Metals*, edited by J. E. Draley and J. R. Weeks (Plenum, New York, 1970), p. 515.
[70]H. S. Isaacs and B. Minushkin, U.S. Atom. Energy Comm. Rep. BNL-50141, p. 28 (1968).
[71]D. H. Gurinsky, U.S. Atom. Energy Comm. Rep. BNL-50219 (1969).
[72]G. P. Stavropoulos and F. A. Cafasso, Trans. Am. Nucl. Soc. **14**, 621 (1971).
[73]G. P. Stavropoulos, U.S. Atom. Energy Comm. Rep. CONF-711009 (1971).
[74]C. B. Alcock and G. P. Stavropoulos, Can. Metall. Quart. **10**, 257 (1971).
[75]H. U. Borgstedt, A. Marin, Z. Peric, and G. Wittig, Atomwirtsch. **17**, 361 (1972).
[76]J. M. McKee, D. R. Vissers, P. A. Nelson, B. R. Grundy, E. Berkey, and G. R. Taylor, Nucl. Technol. **21**, 217 (1974).
[77]B. R. Grundy and D. D. Durigon, J. Nucl. Mater. **55**, 111 (1975).
[78]B. R. Grundy, E. Berkey, and G. R. Taylor, U.S. Atom. Energy Comm. Rep. WARD-3045-TI-4 (1972).
[79]H. Katsuta and K. Furukawa, Nucl. Technol. **31**, 218 (1976).
[80]C. A. Smith and P. A. Simm, *Liquid Metal Engineering and Technology* (BNES, London, 1984), p. 103.
[81]H. Sundermann and V. Schauer, Microchim. Acta, Suppl. **7**, 575 (1977).
[82]V. Schauer, Ph.D. thesis, University of Vienna, Austria, 1976.
[83]H. Näfe, H. Ullmann, and H. J. Lang, Akad. Wissensch. DDR Rep. ZfK-645, p. 30 (1988).
[84]H. Näfe, Akad. Wissensch. DDR Rep. ZfK-682, p. 130 (1989).
[85]J. S. Hislop, R. Thompson, and D. A. Wood, *Analysis of Non-Metals in Metals* (de Gruyter, New York, 1981), p. 321.
[86]J. S. Hislop, R. Thompson, and D. A. Wood, Atom. Ener. Res. Establ. Rep. M-3097 (1981).
[87]A. R. Eames, as quoted by G. W. Horsley, U.K. Atom. Ener. Author. Rep. R-3037 (1961).
[88]J. C. White, W. J. Ross, and R. Rowan, Anal. Chem. **26**, 210 (1954).
[89]W. B. Cottrell and L. A. Mann, U.S. Atom. Energy Comm. Rep. ORNL-1688, p. 67 (1953).
[90]H. S. Isaacs, U.S. Atom. Energy Comm. Rep. BNL-13078 (1968).
[91]H. S. Isaacs, U.S. Atom. Energy Comm. Rep. ANL-7520, Pt. I, p. 465 (1969).
[92]R. L. Klueh, J. Nucl. Energy **25**, 253 (1971).
[93]J. L. Phillips, U.S. Atom. Energy Comm. Rep. NP-8195 (1959).
[94]C. L. Chernick and A. Glassner, U.S. Atom. Energy Comm. Rep. ANL-7382 (1967); Rep. ANL-7399 (1967).
[95]P. A. Andreev, A. A. Kanaev, and E. D. Fedorovich, *Zhidkometallicheskie Teplonositeli Yadernykh Reaktorov* (Sudpromgiz, Leningrad, 1959), p. 92.
[96]E. G. Brush, Corrosion **11**, 299t (1955).
[97]J. Allen, Nucl. Engng. **7**, 352 (1960).
[98]F. E. Bowman and D. D. Cubicciotti, A.I.Ch.E. J. **2**, 173 (1956).
[99]I. Trocki, W. H. Bruggeman, and F. E. Crever, *Peaceful Uses of Atomic Energy* (U.N., New York, 1956), Vol. 9, p. 241.
[100]J. W. Evans, Nucl. Engng. **6**, 59 (1959).
[101]M. Kolodney, B. Minushkin, and H. Steinmetz, Electrochem. Technol. **3**, 244 (1965).
[102]J. Jung, J. Nucl. Mater. **56**, 213 (1975).
[103]C. C. McPheeters, U.S. Atom. Energy Comm. Rep. LA-3936 (1968).
[104]C. C. McPheeters and J. C. Biery, U.S. Atom. Energy Comm. Rep. LA-DC-9423 (1968); Rep. CONF-680601-9 (1968).
[105]T. E. Prach, L. Newman, and C. Auerbach, U.S. Atom. Energy Comm. Rep. BNL-50118 (1968).
[106]S. A. Meacham and E. F. Hill, U.S. Atom. Energy Comm. Rep. APDA-238 (1970).
[107]J. M. Scarborough and P. F. DeVries, Anal. Chem. **39**, 826 (1967).
[108]H. Näfe, *Liquid Metal Engineering and Technology* (BNES, London, 1984), p. 381.
[109]D. L. Smith, J. Nucl. Mater. **51**, 280 (1974).
[110]A. J. Hooper and E. A. Trevillion, J. Nucl. Mater. **66**, 88 (1977).
[111]H. Näfe, Akad. Wissensch. DDR Rep. ZfK-713, p. 18 (1990).
[112]C. E. Weber and L. F. Epstein, U.S. Atom. Energy Comm. Rep. TID-2501, p. 307 (1951); Rep. KAPL-139 (1949).
[113]H. Näfe, Akad. Wissensch. DDR Rep. ZfK-489, p. 94 (1982).
[114]H. Näfe, Akad. Wissensch. DDR Rep. ZfK-544, p. 49 (1983).
[115]J. P. Maupré, Comm. Ener. Atom. Rep. CEA-R-4905 (1978).
[116]R. Bouaziz, G. Papin, and A. P. Rollet, Compt. Rend., Ser. C **262**, 1051 (1966).
[117]J. L. Henry, S. A. O'Hare, and M. P. Krug, U.S. Atom. Energy Comm. Rep. USBM-1532 (1971).
[118]Yu. V. Privalov, Nauch.-Issled. Inst. Atom. Reakt. Rep. NIIAR-R-6 (300) (1977).
[119]S. J. Rodgers and J. W. Mausteller, U.S. Atom. Energy Comm. Rep. NP-5898 (1956).
[120]S. J. Rodgers, Mine Safety Appliances Rep. TR-47 (1956).
[121]L. R. Blake and A. R. Eames, Nucleonics **19**(5), 66 (1961).
[122]W. R. Huntley, R. E. Mac Pherson, B. Fleischer, and A. Taboada, U.S. Atom. Energy Comm. Rep. ORNL-3898 (1965).
[123]E. E. Konovalov, H. I. Seliverstov, I. B. Dmitrieva, and P. A. Sedyshkin, Atom. Energy **24**, 478 (1968).
[124]M. N. Arnoldov, M. N. Ivanovskii, S. S. Pletenets, and A. D. Plashivtsev, Atom. Energy **32**, 234 (1972).
[125]T. Sakai, M. Gunji, S. Matsumoto, and Y. Ishii, J. Nucl. Sci. Technol. **20**, 1032 (1983).
[126]D. Krishnamurthy, S. Vana Varamban, A. Thiruvengadasami, and C. K. Mathews, J. Less-Common Met. **153**, 363 (1989).
[127]M. N. Ivanovskii, V. A. Morozov, A. L. Shimkevich, and N. N. Ponomarev-Stepnoi, *Space Nuclear Power Systems*, edited by M. S. El-Genk and M. D. Hoover (Orbit Book Comp., Malabar, FL, 1992), p. 465.
[128]E. G. Bunzel and E. J. Kohlmeyer, Z. Anorg. Chem. **254**, 1 (1947).

Components:
(1) Oxygen; O; [7782-44-7]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
S. L. Walters, U.S. Atom. Energy Comm. Rep. NP-1955 (1950); Rep. MSA-TR-VI (1950).

Variables:
Temperature: 425–822 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of O in liquid Na at various temperatures was determined; as in Claxton[1]

t/°C	Solubility/mass % O	Solubility/mol % O[a]
152	$1\cdot10^{-3}$[b]	$1.5\cdot10^{-3}$
157	$1\cdot10^{-3}$	$1.5\cdot10^{-3}$
160	$3\cdot10^{-3}$	$4\cdot10^{-3}$
166	$1\cdot10^{-3}$[b]	$1.5\cdot10^{-3}$
213	$4\cdot10^{-3}$	$6\cdot10^{-3}$
232	$5\cdot10^{-3}$[b]	$7\cdot10^{-3}$
232	$5\cdot10^{-3}$	$7\cdot10^{-3}$
238	$5\cdot10^{-3}$	$7\cdot10^{-3}$
404	$5.2\cdot10^{-2}$	
413	$4.9\cdot10^{-2}$	
421	$8.0\cdot10^{-2}$	
457	0.113[b]	
502	0.150[b]	
252	$3\cdot10^{-3}$	$4\cdot10^{-3}$
277	$8\cdot10^{-3}$[b]	$1.1\cdot10^{-2}$
279	$6\cdot10^{-3}$	$9\cdot10^{-3}$
296	$5\cdot10^{-3}$	$7\cdot10^{-3}$
332	$1.8\cdot10^{-2}$[b]	$2.6\cdot10^{-2}$
341	$1.7\cdot10^{-2}$	$2.4\cdot10^{-2}$
343	$1.5\cdot10^{-2}$	$2.2\cdot10^{-2}$
377	$3.4\cdot10^{-2}$	$4.9\cdot10^{-2}$
535	0.176	0.25
538	0.198[b]	0.28
538	0.200[b]	0.29
549	0.225[b]	0.32

[a]Calculated by the compilers.
[b]Values selected by the author as preferable.

The author used the selected (b) data for the formulation of a solubility equation:

$$\log(\text{soly/mass \% O}) = 1.94 - 2150\ (T/\text{K})^{-1}.$$

The use of all data obtained leads to a different solubility equation:

$$\log(\text{soly/mass \% O}) = 1.71 - 2043\ (T/\text{K})^{-1},$$

which was tested by the compilers.

Auxiliary Information

Method:
As reported in Smith.[2] Liquid Na was introduced into an isothermal stainless steel loop. Na circulated for several hours forced by an electromagnetic pump and measured by a flowmeter, while the temperature was varied randomly between 425 and 822 K. Measured increments of Na_2O_2 were added to the Na. Samples of Na were removed under an Ar cover using a bucket-in-the-well technique. The bucket was made of Ni because of an attack on a Pyrex sampler above ~643 K. The O content in Na was found by a repeated amalgamation of Na by Hg leaving Na_2O as an insoluble precipitate. The deposit was treated with H_2O and the aqueous solution of NaOH was titrated with an acid.

Source and Purity of Materials:
Na_2O_2 : nothing specified.
Na: filtered just above its melting point.
Ar: "purified."

Estimated Error:
Solubility: precision ±10% at selected temperature.
Temperature: nothing specified.

References:
[1]K. T. Claxton, J. Nucl. Energy **19**, 849–890 (1965).
[2]C. R. F. Smith, U.S. Atom. Energy Comm. Rep. NAA-SR-Memo-2061 (1960).

Components:
(1) Oxygen; O; [7782-44-7]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
W. B. Cottrell and L. A. Mann, U.S. Atom. Energy Comm. Rep. ORNL-1688, pp. 67–69 (1953).

Variables:
Temperature: 422–755 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of O in liquid Na was determined. The data were read from a figure and recalculated to mol % O by the compilers.

t/°F	T/K	Solubility/mass % O	Solubility/mol % O
300	422	$1.0\cdot10^{-3}$	$1.4\cdot10^{-3}$
550	561	$1.1\cdot10^{-2}$	$1.6\cdot10^{-2}$
900	755	$7\cdot10^{-2}$	0.10

Na_2O is treated as the equilibrium solid phase.

Auxiliary Information

Method:
Liquid Na was held under an Ar atmosphere for at least 24 h for saturation with Na_2O at a selected temperature. The Na was filtered through a 5 μm sintered stainless steel filter. The filtrate was treated by n-butyl bromide solution in hexane. Na reacted with the reagent, while Na_2O did not. Na_2O after addition of H_2O was titrated by a standard HNO_3 acid. The experiments were performed in a glass apparatus and in an Ar atmosphere. n-butyl bromide was purified with H_2SO_4 and distilled; hexane was dried over Na and distilled; the reagents contained less than $2\cdot10^{-4}$ mass % H_2O.[1]

Source and Purity of Materials:
Na_2O: nothing specified.
Na: cold trapped at ~395 K.
Ar: purified by bubbling through a column with a K–Na melt.

Estimated Error:
Solubility: accuracy ±0.0015 mol %, stand. dev. ±0.007 mol %, reading-out procedure ±5%.
Temperature: nothing specified; reading-out procedure ±5 K.

References:
[1]J. C. White, W. J. Ross, and R. Rowan, Anal. Chem. **26**, 210–212 (1954).

Components:
(1) Oxygen; O; [7782-44-7]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
J. D. Noden and K. Q. Bagley, U.K. Atom. Ener. Author. Rep. R&D B(C) TN-80 (1954).

Variables:
Temperature: 400–813 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data
The solubility of O in liquid Na at various temperatures was determined

t/°C	Solubility/mass % O	Solubility/mol % O[b]
127	$3.2\cdot10^{-3}$	$4.6\cdot10^{-3}$
152[a]	$1.5\cdot10^{-3}$	$2.1\cdot10^{-3}$
168	$2.8\cdot10^{-3}$	$4.0\cdot10^{-3}$
177[a]	$4.0\cdot10^{-3}$	$5.7\cdot10^{-3}$
191	$4.0\cdot10^{-3}$	$5.7\cdot10^{-3}$
210[a]	$2.8\cdot10^{-3}$	$4.0\cdot10^{-3}$
218[a]	$4.4\cdot10^{-3}$	$6.3\cdot10^{-3}$
220	$4.5\cdot10^{-3}$	$6.4\cdot10^{-3}$
220	$4.2\cdot10^{-3}$	$6.0\cdot10^{-3}$
221[a]	$4.1\cdot10^{-3}$	$5.9\cdot10^{-3}$
234	$2.8\cdot10^{-3}$	$4.0\cdot10^{-3}$
240	$4.5\cdot10^{-3}$	$6.4\cdot10^{-3}$
250	$5.8\cdot10^{-3}$	$8.3\cdot10^{-3}$
251[a]	$3.9\cdot10^{-3}$	$5.6\cdot10^{-3}$
260	$6.9\cdot10^{-3}$	$9.9\cdot10^{-3}$
263	$1.05\cdot10^{-2}$	$1.51\cdot10^{-2}$
270	$5.7\cdot10^{-3}$	$8.2\cdot10^{-3}$
278[a]	$4.4\cdot10^{-3}$	$6.3\cdot10^{-3}$
278	$5.1\cdot10^{-3}$	$7.3\cdot10^{-3}$
280	$5.4\cdot10^{-3}$	$7.8\cdot10^{-3}$
281	$6.8\cdot10^{-3}$	$9.7\cdot10^{-3}$
282	$6.1\cdot10^{-3}$	$8.8\cdot10^{-3}$
284	$1.87\cdot10^{-2}$	$2.7\cdot10^{-2}$
288	0.0132	0.019
290	0.0086	0.012
292	0.009	0.013
299	0.007	0.010
300[a]	0.0248	0.036
301	0.0092	0.013
302	0.0167	0.024
302	0.023	0.033
302	0.024	0.034
303	0.0168	0.024
306	0.010	0.014
309	0.0165	0.024
320	0.0132	0.019
321	10.138	0.020
325	0.0099	0.014
332[a]	0.0188	0.027
332[a]	0.0188	0.027
380	0.0412	0.059
400	0.0716	0.103
416	0.0873	0.126
470	0.1365	0.20
511	0.2408	0.35
540	0.2742	0.40

[a]As previously reported in Oliver and Noden.[3]
[b]Calculated by the compilers.

The results were also presented in graphical form in McIntosh and Bagley.[1] The data are approximated by the solubility equations (tested by the compilers):

$$\log(\text{soly/mass \% O}) = 1.249 - 1776\,(T/\text{K})^{-1} \quad \text{for } 127\text{–}540\ ^\circ\text{C}$$

and

$$\log(\text{soly/mass \% O}) = 2.826 - 2748\,(T/\text{K})^{-1} \quad \text{for } 234\text{–}540\ ^\circ\text{C}.$$

Auxiliary Information

Method:
All essential operations were performed in an Ar atmosphere. A stainless steel apparatus consisted of a stirrer-thermocouple tube, a side arm making connection with the vacuum system, and an Ar supply, a Na containing tube with a stainless steel filter (5 μm pore size). The apparatus was connected with a glass part for chemical analysis, the lower part of which comprised a flask and a capillary tap for removal of Hg amalgam during the analysis. The Na was melted and heated to 523 K under vacuum for 30 min. An excess of O was introduced via a glass tap and Na_2O was formed. The melt was stirred. The apparatus was re-evacuated and filled with Ar. The temperature was raised to the desired level of saturation and maintained there for 30 min, while the melt was stirred (the time was sufficient). The apparatus was evacuated below the sinter causing filtration of the solution through the filter. Injected Na reacted violently with Hg. Subsequent Hg portions were added to extract Na. Na_2O left fresh on Hg was determined by alkalimetric titration.[2] It was observed that the Pyrex glass apparatus was attacked by Na above 623 K.

Source and Purity of Materials:
O: gaseous of unspecified purity.
Na: from A.E.R.E., Harwell; triple distilled.
Ar: purified over anhydrous $CaCl_2$, U turnings at 873–973 K and K–Na bubbler.

Estimated Error:
Solubility: accuracy $\pm 7\cdot10^{-4}$ mol % O.
Temperature: nothing specified.

References:
[1]A. B. McIntosh and K. Q. Bagley, J. Inst. Met. **84**, 251–270 (1955–56).
[2]D. D. Williams and R. R. Miller, Anal. Chem. **23**, 1865 (1951).
[3]D. S. Oliver and J. D. Noden, U.K. Atom. Ener. Author. Rep. R&D B (C) TN-33 (1953).

Components:
(1) Oxygen; O; [7782-44-7]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
O. N. Salmon and T. J. Cashman, U.S. Atom. Energy Comm. Rep. KAPL-1653 (1956).

Variables:
Temperature: 385–768 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of O in liquid Na was determined

t/°C	Solubility/mass % O[a]	Solubility/mass % O[b]	t/°C	Solubility/mass % O[c]
115	$(8\pm1)\cdot10^{-3}$	$(8\pm5)\cdot10^{-3}$	188	$3\cdot10^{-3}$
190	$(8\pm4)\cdot10^{-3}$	$(7\pm3)\cdot10^{-3}$	271	$9\cdot10^{-3}$
295	$(2.3\pm1.0)\cdot10^{-2}$	$(1.1\pm0.3)\cdot10^{-2}$		
395	$(4.6\pm0.7)\cdot10^{-2}$	$(4.2\pm0.7)\cdot10^{-2}$		
495	$(8.7\pm2.9)\cdot10^{-2}$	$(8.7\pm2.9)\cdot10^{-2}$		

[a]Heating sequence.
[b]Cooling sequence.
[c]Graphical results in Epstein.[1]

The smoothed values of the solubility

t/°C	Solubility/mol % O
100	$3.6\cdot10^{-4}$
200	$3.9\cdot10^{-3}$
300	$1.9\cdot10^{-2}$
400	$5.3\cdot10^{-2}$
500	$1.20\cdot10^{-1}$

The results were approximated with the solubility equation:

$$\log(\text{soly/mass \% O}) = 1.266 - 1816\,(T/\text{K})^{-1}.$$

The compilers tested the correctness of the equation. The results were graphically presented in Epstein.[1]

Auxiliary Information

Method:
The experiments were carried out in a Type 347 stainless steel container. All parts being in contact with Na were electrochemically cleaned in H_3PO_4–H_2SO_4 7:3 mixture with a current density ~6 mA/cm^2. The container was evacuated and purged with Ar three times. Na_2O_2 was added to the can through the sampling port. Molten Na at 423 K was pressurized to the can through a 5 μm stainless steel filter. An Ar blanket was maintained within the container until the sampling at different depths and different times (1, 6, and 40 h) indicated a stable and uniform composition. The samples were analyzed by the amalgamation method.[2] Na was repeatedly extracted with Hg leaving Na_2O undissolved. The aqueous solution of Na_2O was titrated with an acid. The results were corrected for the blank. When Na_2O floated on the Na surface the experiment was completed. The can was heated by a nichrome resistance furnace. Two sets of experiments were performed with increasing and decreasing temperature. 90 samples were taken for O analysis at selected temperatures for various periods. Sampling pipette devices, made of Pyrex glass and stainless steel, were used up to 573 and above 573 K, respectively.

Source and Purity of Materials:
Na_2O_2: 97.8% pure from J.T. Baker Chem. Corp. and contained $5\cdot10^{-4}$ % PO_4, Cl, $3\cdot10^{-3}$ % Fe, $2\cdot10^{-3}$ % N, $1\cdot10^{-3}$ % metals (reduced by H), $5\cdot10^{-3}$ % SiO_2.
Na: reagent grade from DuPont Comp., contained 0.025% K, 0.033% Ca, $9\cdot10^{-3}$ % Li, $5\cdot10^{-3}$ % S, $3\cdot10^{-3}$ % Cl, and $2\cdot10^{-3}$ % P.
Ar: 99.6 vol % pure from Cleveland Wire Works of General Electric and contained 0.4 vol % O and $5\cdot10^{-4}$ vol % other impurities.

Estimated Error:
Solubility: precision better than ±65%; blank test level $5\cdot10^{-3}$ mol % O.
Temperature: nothing specified.

References:
[1]L. F. Epstein, *Liquid Metal Handbook Sodium Supplement*, edited by C. B. Jackson (USAEC&Navy, Washington, 1955), p. 6.
[2]L. P. Pepkowitz and W. C. Judd, Anal. Chem. **22**, 1283–1286 (1950).

Components:
(1) Oxygen; O; [7782-44-7]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
S. Siegel, R. L. Carter, F. E. Bowman, and B. R. Hayward, *Peaceful Uses of Atomic Energy* (U.N., New York, 1965), Vol. 9, pp. 321–330.

Variables:
Temperature: 450–627 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of O in liquid Na was determined. The data were presented in a figure; they were read from the figure and recalculated to mol % O by the compilers.

t/°F	t/°C	Solubility/mass % O	Solubility/mol % O
350	177	0.0020	0.0029
400	204	0.0028	0.0040
445	229	0.0050	0.0072
470	243	0.0060	0.0086
476	247	0.0067	0.0096
527	275	0.0100	0.0144
570	298	0.0140	0.020
598	314	0.0160	0.023
670	354	0.0197	0.028

Auxiliary Information

Method:
An apparatus (with circulating Na contaminated by a known amount of Na_2O) was made of stainless steel. A method based on a plugging indicator was used. This indicator was based on the variation of the O solubility with temperature. The main cooling system was provided with a small side loop containing a plug having holes of order 0.12–0.15 mm. The temperature of the plug section was carefully controlled. The temperature of the plugging indicator was slowly lowered until a point at which the Na flow in the side tube ceased. This was the indication of the Na_2O precipitation, and reheating the plug caused redissolution. The indicator was then ready for a next determination. Most probably a mean value of plugging and unplugging temperature was ascribed to the saturation temperature.

Source and Purity of Materials:
Na_2O: nothing specified.
Na: nuclear grade of purity.

Estimated Error:
Solubility: nothing specified; reading-out procedure $\pm5\cdot10^{-4}$ mass % O.
Temperature: nothing specified; reading-out procedure ±3 K.

Components:
(1) Oxygen; O; [7782-44-7]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
Z. S. Bannykh and G. F. Fefelova, Tr. Ural. Nauch.-Issled. Khim. Inst. **5**, 105–117 (1957).

Variables:
Temperature: 376–773 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data
The solubility of O in liquid Na was determined

t/°C	Solubility/mass % O	Mean value	Solubility/mass % O
103	0.006; 0.008	0.007	0.010
104	0.001; 0.002; 0.003	0.002	0.003
106	0.005; 0.008	0.0065	0.0093
108	0.004; 0.005	0.0045	0.0064
330	0.018	0.018	0.026
340	0.015; 0.020; 0.019; 0.014; 0.016	0.017	0.024
480	0.049; 0.050	0.049	0.070
500	0.056; 0.057; 0.116; 0.069; 0.099; 0.077; 0.106; 0.079; 0.092	0.084	0.12

The compilers formulated the following solubility equation:

$$\log(\text{soly/mol \% O}) = 0.099 - 948\ (T/\text{K})^{-1} \quad r = 0.964.$$

Auxiliary Information

Method:
Measurements at ~373 K were performed in a glass container. Mixing and N supplying facilities were introduced into the container. It was thermostated in an oil bath. Na was melted and mixed for 1–5 h. It was covered with its oxide on the surface from the reaction of O traces in N gas and left at selected temperature for 0.5–2.5 h. The measurements at >473 K were performed in a stainless steel container. It was heated with an electric oven regulated by a Chromel/Copel thermocouple. The molten Na was mixed for 2–8 h. Samples of liquid Na (at <673 K) and quenched Na (at >673 K) were analyzed using the method of Na multistage extraction with Hg. Undissolved Na_2O, in this process, was treated with distilled H_2O and titrated with 0.005 mol/dm^3 HCl in the presence of phenolphthalein. Hg was treated with 1 mol/dm^3 HCl and back titrated with 1 mol/dm^3 NaOH. The solubility of O in Na was calculated from the amounts of Na_2O and Na found in the analyses.

Source and Purity of Materials:
O source: as an impurity in N.
Na: 99.7+% pure and contained ~0.01% K and <0.003% Cl, contents of Al, Mg, Ca, Fe, C, Pb, and Cu were negligible. The surface layer was cut off.
N: nothing specified.

Estimated Error:
Solubility: nothing specified; precision better than ±50% (by the compilers).
Temperature: stability between ±3 and ±10 K.

Components:
(1) Oxygen; O; [7782-44-7]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
I. L. Gray, R. L. Neal, and B. G. Voorhees, Chem. Engin. Progr., Symp. Ser. (20) **53**, 11–18 (1957).

Variables:
Temperature: 394–611 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data
The solubility of O in liquid Na was determined. The results are presented in form of a straight line on a plot of logarithm of O solubility versus reciprocal temperature; the relationship starts at 300 °F (149 °C) and ends at 1000 °F (538 °C) with the corresponding solubility values of 0.001 and 0.1 mass % O, respectively. A set of numerical values is also reported.

t/°F	t/°C	Solubility/mass % O[a]	Solubility/mol % O[a,c]	Solubility/mass % O[b]	Solubility/mass % O[b,c]
250	121	0.0006	0.0009	0.0012	0.0017
260	127	0.0007; 0.0007	0.001; 0.001	···	···
280	138	0.0008	0.0011	···	···
310	154	0.001	0.0015	···	···
345	174	0.002	0.003	0.002	0.003
375	191	0.003	0.004	0.003	0.004
380	193	0.003	0.004	0.004	0.006
390	199	0.003	0.004	0.004	0.006
400	204	0.003	0.004	0.006	0.009
410	210	0.004	0.006	0.004	0.006
420	216	0.004; 0.004	0.006; 0.006	0.004; 0.007	0.006; 0.011
425	218	0.0045	0.0065	0.0045	0.0065
430	221	0.004; 0.004	0.006; 0.006	0.004; 0.004	0.006; 0.006
440	227	0.005; 0.005	0.007; 0.007	0.004; 0.004	0.006; 0.006
450	232	0.005; 0.005	0.007; 0.007	0.006; 0.006	0.009; 0.009
455	235	0.005	0.007	0.005	0.007
460	238	0.006	0.009	···	···
465	240	0.006	0.009	0.004	0.006
470	243	0.006	0.009	0.007	0.010
480	249	0.007	0.010	···	···
490	254	0.007	0.010	0.006	0.009
500	260	0.008	0.011	···	···
510	266	0.008	0.011	···	···
520	271	0.009; 0.009	0.013; 0.013	0.008; 0.010	0.011; 0.014
580	304	0.014	0.020	0.013	0.019
585	307	0.015	0.022	0.017	0.024
590	310	0.015	0.022	0.018	0.026
615	324	0.018	0.026	0.017	0.024
640	338	0.020	0.029	0.019	0.028

[a]From plugging temperature estimation.
[b]From chemical analysis of Na.
[c]Calculated by the compilers.

A part of the results was reported in Gray *et al.*[1]

Auxiliary Information

Method:

The studies were performed in a Na loop made of Type 347 stainless steel. It consisted of a heat exchanger, electromagnetic pump, flow meter, filter, sampling device, cold trap, and perforated plate in the cold zone of the loop. The loop was operated at temperatures up to 811 K with a temperature gradient of 139 K. Na, containing various amounts of O, was circulated for a long time. Samples of Na were withdrawn for chemical analysis. Na was manifold extracted with Hg leaving Na_2O undissolved. Aqueous solution of Na_2O was analyzed by a method described in Bruggeman and Billuris.[2]

Source and Purity of Materials:

O: nothing specified.
Na: nuclear grade purity; cold trapped.

Estimated Error:

Solubility: agreement between the plug indicator and analysis ±0.001 mass % O; precision of analysis and plug indicator ±0.001 mass % O; reproducibility ±0.0005 mass % O.
Temperature: stability ±5 K.

References:

[1]I. L. Gray, R. L. Neal, and B. G. Voorhees, Nucleonics **14**(10), 34–37 (1956).
[2]W. H. Bruggeman and G. Billuris, Industr. Bull. **4**, 94 (1953).

Components:

(1) Oxygen; O; [7782-44-7]
(2) Sodium; Na; [7440-23-5]

Original Measurements:

W. Jahns and G. Weidmann, Nukleonik **1**, 189–190 (1958–59).

Variables:

Temperature: 429–679 K

Prepared by:

H. U. Borgstedt and C. Guminski

Experimental Data

The temperature dependence of the solubility of O in liquid Na was determined

t/°C	Solubility/mass % O	Solubility/mol % O[a]
156	$1.2\cdot10^{-3}$	$1.7\cdot10^{-3}$
194	$3.6\cdot10^{-3}$	$5.2\cdot10^{-3}$
	$2.1\cdot10^{-3}$	$3.0\cdot10^{-3}$
	$3.2\cdot10^{-3}$	$4.6\cdot10^{-3}$
201	$4.9\cdot10^{-3}$	$7.0\cdot10^{-3}$
240	$3.9\cdot10^{-3}$	$5.6\cdot10^{-3}$
244	$7.1\cdot10^{-3}$	$1.02\cdot10^{-3}$
246	$5.0\cdot10^{-3}$	$7.2\cdot10^{-3}$
256	$5.5\cdot10^{-3}$	$7.9\cdot10^{-3}$
276	$9.5\cdot10^{-3}$	$1.4\cdot10^{-2}$
	$1.34\cdot10^{-2}$	$1.9\cdot10^{-2}$
306	$1.35\cdot10^{-2}$	$1.9\cdot10^{-2}$
	$1.16\cdot10^{-2}$	$1.7\cdot10^{-2}$
	$1.39\cdot10^{-2}$	$2.0\cdot10^{-2}$
	$1.41\cdot10^{-2}$	$2.0\cdot10^{-2}$
	$1.53\cdot10^{-2}$	$2.2\cdot10^{-2}$
356	$2.01\cdot10^{-2}$	$2.9\cdot10^{-2}$
	$2.38\cdot10^{-2}$	$3.4\cdot10^{-2}$
	$2.76\cdot10^{-2}$	$4.0\cdot10^{-2}$
	$2.25\cdot10^{-2}$	$3.2\cdot10^{-2}$
406	$3.84\cdot10^{-2}$	$5.5\cdot10^{-2}$
	$3.83\cdot10^{-2}$	$5.5\cdot10^{-2}$
	$3.73\cdot10^{-2}$	$5.4\cdot10^{-2}$
	$3.89\cdot10^{-2}$	$5.6\cdot10^{-2}$
	$3.79\cdot10^{-2}$	$5.4\cdot10^{-2}$

[a]Calculated by the compilers.

The authors reported the solubility equation using all experimental points:

$$\log(\text{soly/mass \% O}) = 1.038 - 1682\ (T/\text{K})^{-1}.$$

For the temperature range 240–406 °C another solubility equation is valid:

$$\log(\text{soly/mass \% O}) = 1.346 - 1871\ (T/\text{K})^{-1}.$$

Auxiliary Information

Method:

Cut pieces of Na and Na_2O were introduced into a glass container being previously evacuated. The container was placed in an oil or graphite powder bath and equilibrated. The temperature was controlled with the use of a shielded thermocouple. Hg was introduced into the container in a small ampoule. The ampoule was broken, and the amalgamation of Na started. Hg with dissolved Na was filtered through a capillary at the container bottom. New portions of Hg were added and filtered that the amalgam should be unmeasurably diluted. The rest of Hg with undissolved Na_2O was treated with H_2O and titrated with 0.01 mol/dm^3 HCl. Na dissolved in Hg was determined by hydrolysis of the amalgam and titration with HCl. The determination at 679 K was performed in a stainless steel apparatus.

Source and Purity of Materials:

Na_2O: nothing specified.
Na: nuclear grade of purity; liquid metal filtered.
N: dried by blowing through molten Na–K alloy.
Hg: filtered.

Estimated Error:

Solubility: stand. dev. at <530 K ±7.2% and ±2.6% at >530 K; mean value ±4.7%.
Temperature: nothing specified.

Components:
(1) Oxygen; O; [7782-44-7]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
J. L. Phillips, U.S. Atom. Energy Comm. Rep. NP-8195 (1959).

Variables:
Temperature: 394–523 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of O in liquid Na was reported in graphical form in Grieser *et al.*[1] The values were recalculated to °C and mol % O by the compilers.

t/°F	t/°C	Solubility/mass % O	Solubility/mol % O
250	121	$3.2\cdot10^{-4}$	$4.6\cdot10^{-4}$
300	152	$7.5\cdot10^{-4}$	$1.08\cdot10^{-3}$
340	171	$1.28\cdot10^{-3}$	$1.84\cdot10^{-3}$
391	199	$2.2\cdot10^{-3}$	$3.2\cdot10^{-3}$
482	250	$5.0\cdot10^{-3}$	$7.2\cdot10^{-3}$

The results were expressed by the compiler's solubility equation:

$$\log(\text{soly/mol \% O}) = 1.5589 - 1923\ (T/\text{K})^{-1}; \quad r = 0.9985.$$

Auxiliary Information

Method:
An unknown method was used.

Source and Purity of Materials:
Nothing specified.

Estimated Error:
Solubility: stand. dev. at <530 K ±7.2% and ±2.6% at >530 K; mean value ±4.7%.
Temperature: nothing specified.

References:
[1]D. R. Grieser, G. G. Cocks, E. H. Hall, W. M. Henry, and J. McCallum, U.S. Atom. Energy Comm. Rep. BMI-1538 (1961).

Components:
(1) Oxygen; O; [7782-44-7]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
D. D. Williams, J. A. Grand, and R. R. Miller, J. Phys. Chem. **63**, 68–71 (1959).

Variables:
Temperature: 383–828 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of O in liquid Na was determined. The results were reported in graphical and in numerical form in Bogard and Williams.[1]

t/°C	Solubility/mass % O	Solubility/mol % O[a]
110	0.0026[b]	0.0037
225	0.006	0.0086
275	0.010	0.014
300	0.012	0.017
350	0.013	0.019
390	0.019	0.027
440	0.025	0.036
490	0.043	0.062
515	0.061	0.088
555	0.092	0.13

[a]Calculated by the compilers.
[b]The mean value from Williams and Miller,[2] the original value was 0.002 mass % O.

Na_2O was identified as the equilibrium solid phase. The authors formulated a solubility equation in the form:

$$\log(\text{soly/mass \% O}\cdot10^3) = -0.0535 + 0.00351\ (t/°\text{C}).$$

For the temperature range 275–555 °C, one may propose the solubility equation in the following form:

$$\log(\text{soly/mass \% O}) = 1.346 - 1871\ (T/\text{K})^{-1},$$

which was tested by the compilers.

Auxiliary Information

Method:
A Pyrex glass apparatus consisted of an oxidation and saturation chamber, O reservoir, filter, sample bulb and appropriate devices to make vacuum or a N atmosphere inside the apparatus. A stainless steel apparatus was employed at >600 K. After evacuation and filling with N, liquid Na was pipetted into the oxidation chamber. The apparatus was re-evacuated. The chamber was filled with dry O, and it reacted with Na. The apparatus was rotated to bring Na and Na_2O onto the filter. The temperature was raised to the desired level and held for 5–15 min. A slight N pressure was admitted to force the saturated Na solution through the filter into the bulb for sampling. The bulb was removed by flame sealing and the content analyzed for Na_2O by the modified amalgamation method (extraction of Na with Hg and acidimetric titration of Na_2O in aqueous solution).

Source and Purity of Materials:
Na_2O: 99.9+% pure obtained in a separate apparatus using Na and dry O.
Na: nuclear grade of purity.
N: nothing specified.

Estimated Error:
Solubility: precision of ±10%; as in Williams and Miller.[2]
Temperature: accuracy ±5 K.

References:
[1]A. D. Bogard and D. D. Williams, U.S. Naval Res. Labor. Rep. NRL-3865 (1951); Rep. NRL-3895 (1951); Rep. NRL-Memo-424 (1955).
[2]D. D. Williams and R. R. Miller, Anal. Chem. **23**, 1865 (1951).

Components:
(1) Oxygen; O; [7782-44-7]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
A. R. Eames, U.K. Atom. Ener. Author. (1961); as reported in Horsley.[1]

Variables:
Temperature: not specified

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The experimental data of the solubility of O in liquid Na were approximated by the fitting equation:

$$\log(\text{soly/mass \% O}) = 1.266 - 1816\ (T/\text{K})^{-1}$$

as reported in Horsley.[1]

Auxiliary Information

Method:
The data were obtained by means of a resistivity meter used in a Na loop with cold trap.

Source and Purity of Materials:
Nothing specified.

Estimated Error:
Nothing specified.

References:
[1]G. W. Horsley, U.K. Atom. Ener. Rep. AERE-R-3037 (1961).

Components:
(1) Oxygen; O; [7782-44-7]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
A. W. Thorley, U.K. Atom. Ener. Author., Reactor Mater. Lab. (1961), unpublished; cited by K. T. Claxton, J. Nucl. Ener. **19**, 849–889 (1965).

Variables:
Temperature: 387–565 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of O in liquid Na was determined. The numerical data were presented in Noden[1] and in a smooth graphical form in Sinclair *et al.*,[2] Thorley and Raine,[3] and Tyzack.[4]

t/°C	Solubility/mass % O[a]	Solubility/mol % O
114	$3.4\cdot10^{-4}$	$4.9\cdot10^{-4}$
144	$6.0\cdot10^{-4}$	$8.6\cdot10^{-4}$
150	$8.3\cdot10^{-4}$	$1.20\cdot10^{-3}$
175	$1.43\cdot10^{-3}$	$2.0\cdot10^{-3}$
194	$1.97\cdot10^{-3}$	$2.8\cdot10^{-3}$
242	$3.6\cdot10^{-3}$	$5.2\cdot10^{-3}$
292	$1.07\cdot10^{-2}$	$1.54\cdot10^{-2}$

[a]Average values of selected 210 values.

The solubility equation was formulated and the compilers tested the equation:

$$\log(\text{soly/mass \% O}) = (1.153\pm0.092) - (1803\pm40)\ (T/\text{K})^{-1}.$$

Auxiliary Information

Method:
Liquid Na circulated in a stainless steel loop being forced by an electromagnetic pump. A portion of Na_2O_2 was added to Na at 673 K in a glove box attached to the loop. The temperature was decreased to 383 K and again increased to 673 K. An excess of Na_2O_2 was eventually added until a flowmeter indicated a blocking of the trap. The cold trap temperature was controlled with three annealed, calibrated Pt/Pt–Rh thermocouples. The time to achieve equilibrium was on the order of 2–3 weeks. Na filtered in the cold trap was collected in Ni crucibles (previously fired in H at 1073 K). The Na_2O content in the samples was analyzed by a vacuum distillation of Na.[3] The residue left in the crucible was dissolved in H_2O, and the Na content determined by titration with an acid or flame photometry and related to the O content in the original sample on basis of the formula Na_2O.

Source and Purity of Materials:
Na_2O_2: "Analar" in a sealed can, contained $2\cdot10^{-3}$ % Cl, Pb, Cu, $3\cdot10^{-3}$ % N, $5\cdot10^{-4}$ % P, $1\cdot10^{-3}$ % S, $5\cdot10^{-3}$ % Fe, 1% Na_2CO_3.
Na: filtered, cold trapped at 393 K, hot trapped by Zr at 873 K and vacuum distilled; contained all impurities at $<2\cdot10^{-4}$ %.

Estimated Error:
Solubility: detectivity better than $1\cdot10^{-4}$ % O; stand. dev. ±10%.[3]
Temperature: accuracy ±2 K.

References:
[1]J. D. Noden, Centr. Ener. Gener. Board Rep. RD/B/R-2146 (1972).
[2]V. M. Sinclair, R. A. H. Pool, and A. E. Ross, U.S. Atom. Energy Comm. Rep. TID-7622, pp. 35–56 (1961).
[3]A. W. Thorley and A. C. Raine, *The Alkali Metals* (The Chemical Society, London, 1967), pp. 374–392.
[4]C. Tyzack, *Steels for Reactor Pressure Circuits* (The Iron and Steel Institute, London, 1961), pp. 179–195.

Components:
(1) Oxygen; O; [7782-44-7]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
K. S. Bergstresser, G. R. Waterbury, and C. F. Metz, U.S. Atom. Energy Comm. Rep. LA-3343 (1965).

Variables:
Temperature: 428–613 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data
The solubility of O in liquid Na was determined

t/°C	Solubility/mass % O	Solubility/mol % O[a]
155	$3.8\cdot10^{-4}$, $4.3\cdot10^{-4}$, $1.6\cdot10^{-4}$, $2.1\cdot10^{-4}$, $4.8\cdot10^{-4}$, $2.1\cdot10^{-4}$, $3.7\cdot10^{-4}$, $3.0\cdot10^{-4}$	$4.6\cdot10^{-4}$
240	$4.5\cdot10^{-3}$, $3.5\cdot10^{-3}$, $3.5\cdot10^{-3}$, $3.8\cdot10^{-3}$, $3.7\cdot10^{-3}$, $4.2\cdot10^{-3}$, $3.4\cdot10^{-3}$	$5.5\cdot10^{-3}$
340	$1.76\cdot10^{-2}$, $1.76\cdot10^{-2}$, $1.84\cdot10^{-2}$, $1.68\cdot10^{-2}$, $1.60\cdot10^{-2}$, $1.72\cdot10^{-2}$, $1.68\cdot10^{-2}$	$2.5\cdot10^{-2}$

[a]Mean value calculated by the compilers.

The solubility results may be expressed by the equation:

$$\log(\text{soly/mass \% O}) = 2.394 - 2518\ (T/\text{K})^{-1},$$

which was tested by the compilers.

Auxiliary Information

Method:
Ar was saturated with H_2O vapor. A measured volume of Ar in a syringe was contacted with a measured amount of Na placed in a steel container in a low pressure He atmosphere. Circulating Na was saturated with the Na_2O formed. The temperature was kept constant at a selected level for 1 week. Na was filtered through stainless steel turnings. A sample of filtered Na was withdrawn for analysis by means of a Ni crucible. The sample was vacuum distilled at ~613 K. The nonvolatile residue (Na_2O) was dissolved in dilute HCl and analyzed by flame spectrophotometry with the use of eight carefully calibrated standard solutions.

Source and Purity of Materials:
O: from H_2O vapor additions.
Na: hot and cold trapped, contained $1.3\cdot10^{-4}$ % O.
Ar: nothing specified.
He: purified by passing over anhydrous $Mg(ClO_4)_2$ and U turnings at 973 K.

Estimated Error:
Solubility: stand. dev. $5\cdot10^{-5}$ mass % O.
Temperature: stability "within a few K."

Components:
(1) Oxygen; O; [7782-44-7]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
R. C. Andrews and K. R. Barker, U.S. Atom. Energy Comm. Rep. MSAR-67-207 (1967).

Variables:
Temperature: 433–575 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data
The solubility of O in liquid Na was determined

t/°F	t/°C	Solubility/mass % O	Solubility/mol % O[a]
320	160	$3\cdot10^{-4}$	$4\cdot10^{-4}$
330	166	$1\cdot10^{-4}$, $4\cdot10^{-4}$	$3\cdot10^{-4}$
390	199	$8\cdot10^{-4}$	$1.1\cdot10^{-3}$
405	207	$1.0\cdot10^{-3}$, $1.2\cdot10^{-3}$, $1.3\cdot10^{-3}$	$1.7\cdot10^{-3}$
410	210	$1.4\cdot10^{-3}$	$2.0\cdot10^{-3}$
425	218	$1.4\cdot10^{-3}$	$2.0\cdot10^{-3}$
430	221	$1.9\cdot10^{-3}$	$2.7\cdot10^{-3}$
510	265	$6.3\cdot10^{-3}$, $7.9\cdot10^{-3}$	$1.02\cdot10^{-2}$
520	271	$7.2\cdot10^{-3}$, $8.4\cdot10^{-3}$	$1.12\cdot10^{-2}$
540	282	$5.2\cdot10^{-3}$	$7.5\cdot10^{-3}$
550	288	$6.9\cdot10^{-3}$	$9.9\cdot10^{-3}$
570	299	$9.2\cdot10^{-3}$, $1.19\cdot10^{-2}$	$1.52\cdot10^{-2}$
575	302	$1.08\cdot10^{-2}$	$1.55\cdot10^{-2}$

[a]Mean value calculated by the compilers.

The authors presented the following solubility equation:

$$\log(\text{soly/mass \% O}) = 3.108 - 3053\ (T/\text{K})^{-1},$$

which was tested by the compilers.

Auxiliary Information

Method:
The experiments were performed using a 316 stainless steel loop with circulating Na. The maximum temperature of the loop was 940 K, and the cold trap temperature was adjusted. At each operating temperature level, a minimum of three Na samples were taken from the system and analyzed for their O content by the amalgamation method. Na reacted with Hg, and Na_2O remained undissolved in Hg. It was determined by titration with an acid after dissolution in H_2O.

Source and Purity of Materials:
O: nothing specified.
Na: nuclear grade of purity.

Estimated Error:
Solubility: standard deviation ±8%.
Temperature: nothing specified.

Components:
(1) Oxygen; O; [7782-44-7]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
C. L. Chernick and A. Glassner, U.S. Atom. Energy Comm. Rep. ANL-7382 (1967); Rep. ANL-7399 (1967).

Variables:
Temperature: 440–452 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data
The solubility of O in liquid Na was determined

t/°F	t/°C[a]	Sampling	Solubility/mass % O	Solubility/mol % O[a]
333	167	Dip	$6.1\cdot10^{-4}$	$8.7\cdot10^{-4}$
333	167	Line	$4.3\cdot10^{-4}$	$6.2\cdot10^{-4}$
337	169	Line	$5.2\cdot10^{-4}$	$7.5\cdot10^{-4}$
354	179	Dip	$1.0\cdot10^{-3}$	$1.4\cdot10^{-3}$

[a]Calculated by the compilers.

Auxiliary Information

Method:
Na circulated for 2 months in a stainless steel loop. 48 runs were made with a plugging meter using two dip-tube and two line type methods of sampling. The Na samples were analyzed for their O content by an unspecified method.

Source and Purity of Materials:
O: nothing specified.
Na: nuclear grade of purity.

Estimated Error:
Solubility: nothing specified.
Temperature: nothing specified.

Components:
(1) Oxygen; O; [7782-44-7]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
V. I. Subbotin, F. A. Kozlov, E. K. Kuznetsov, and M. N. Ivanovskii, *Alkali Metal Coolants* (IAEA, Vienna, 1967), pp. 461–478.

Variables:
Temperature: 405–659 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data
The solubility O in liquid Na was presented in graphical form. It was read from a figure and recalculated by the compilers.

T/K	t/°C	Solubility/mass % O	Solubility/mol % O[a]
405	132	$3.6\cdot10^{-4}$; $5.3\cdot10^{-4}$; $6.8\cdot10^{-4}$	$5.2\cdot10^{-4}$; $7.6\cdot10^{-4}$; $9.8\cdot10^{-4}$
417	144	$1.3\cdot10^{-4}$; $3.3\cdot10^{-4}$; $5.0\cdot10^{-4}$	$1.8\cdot10^{-4}$; $4.7\cdot10^{-4}$; $7.1\cdot10^{-4}$
420	147	$5.0\cdot10^{-4}$	$7.1\cdot10^{-4}$
427	154	$4.9\cdot10^{-4}$; $6.1\cdot10^{-4}$	$7.0\cdot10^{-4}$; $8.7\cdot10^{-4}$
454	181	$7.0\cdot10^{-4}$	$1.0\cdot10^{-3}$
460	187	$4.2\cdot10^{-4}$	$6.0\cdot10^{-4}$
471	198	$5.4\cdot10^{-4}$	$7.7\cdot10^{-4}$
480	207	$1.5\cdot10^{-3}$	$2.1\cdot10^{-3}$
483	210	$1.1\cdot10^{-3}$	$1.5\cdot10^{-3}$
487	214	$1.5\cdot10^{-3}$	$2.1\cdot10^{-3}$
497	224	$9.5\cdot10^{-4}$	$1.4\cdot10^{-3}$
505	232	$1.2\cdot10^{-3}$	$1.7\cdot10^{-3}$
531	258	$3.1\cdot10^{-3}$	$4.4\cdot10^{-3}$
535	262	$2.8\cdot10^{-3}$	$4.0\cdot10^{-3}$
548	275	$3.0\cdot10^{-3}$; $5.7\cdot10^{-3}$	$4.3\cdot10^{-3}$; $8.2\cdot10^{-3}$
552	279	$3.1\cdot10^{-3}$	$4.5\cdot10^{-3}$
555	282	$7.0\cdot10^{-3}$; $7.5\cdot10^{-3}$	$1.0\cdot10^{-2}$; $1.1\cdot10^{-2}$
557	284	$6.3\cdot10^{-3}$	$9.0\cdot10^{-3}$
559	286	$4.2\cdot10^{-3}$; $5.1\cdot10^{-3}$	$6.0\cdot10^{-3}$; $7.3\cdot10^{-3}$
561	288	$7.0\cdot10^{-3}$	$1.0\cdot10^{-2}$
591	318	$1.1\cdot10^{-2}$	$1.5\cdot10^{-2}$
598	325	$1.0\cdot10^{-2}$	$1.4\cdot10^{-2}$
600	327	$8.6\cdot10^{-3}$	$1.2\cdot10^{-2}$
603	330	$7.4\cdot10^{-3}$	$1.1\cdot10^{-2}$
609	336	$9.3\cdot10^{-3}$; $7.0\cdot10^{-3}$	$1.3\cdot10^{-2}$; $1.0\cdot10^{-2}$
645	372	$1.6\cdot10^{-2}$	$2.3\cdot10^{-2}$
659	386	$1.7\cdot10^{-2}$; $2.8\cdot10^{-2}$	$2.4\cdot10^{-2}$; $4.0\cdot10^{-2}$

[a]Calculated by the compilers.

These results were represented by the solubility equation (tested by the compilers):

$$\log(\text{soly/mass \% O}) = 1.14 - 1910\,(T/\text{K})^{-1}.$$

The same results were reported in Kozlov *et al.*[3] and Bagdasarov.[5] A smoothed solubility curve and the equation were presented in Kozlov *et al.*[1]

Components:
(1) Oxygen; O; [7782-44-7]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
H. Beisswenger and S. Dorner, J. Nucl. Mater. **28**, 297–302 (1968).

Variables:
Temperature: 403–753 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data
The solubility of O in Na was determined

T/K	Solubility/mass % O	Solubility/mol % O[a]
403	$6.5\cdot10^{-4}$	$9.3\cdot10^{-4}$
413	$9.9\cdot10^{-4}$; $1.77\cdot10^{-3}$[b]	$1.42\cdot10^{-3}$; $2.5\cdot10^{-3}$
423	$1.29\cdot10^{-3}$	$1.85\cdot10^{-3}$
433	$2.04\cdot10^{-3}$	$2.9\cdot10^{-3}$
434	$2.37\cdot10^{-3}$[c]	$3.4\cdot10^{-3}$
448	$9.4\cdot10^{-4}$[c]	$1.35\cdot10^{-3}$
452	$1.74\cdot10^{-3}$[c]	$2.5\cdot10^{-3}$
453	$1.94\cdot10^{-3}$	$2.8\cdot10^{-3}$
460	$2.82\cdot10^{-3}$[c]	$4.0\cdot10^{-3}$
460	$3.32\cdot10^{-3}$[c]	$4.7\cdot10^{-3}$
460	$1.28\cdot10^{-3}$[c]	$1.8\cdot10^{-3}$
460	$2.08\cdot10^{-3}$[c]	$3.0\cdot10^{-3}$
473	$2.06\cdot10^{-3}$	$3.0\cdot10^{-3}$
477	$4.78\cdot10^{-3}$[c]	$6.9\cdot10^{-2}$
477	$3.95\cdot10^{-3}$[c]	$5.7\cdot10^{-3}$
477	$4.15\cdot10^{-3}$[c]	$1.01\cdot10^{-2}$
494	$3.10\cdot10^{-3}$; $4.56\cdot10^{-3}$[b]	$4.5\cdot10^{-3}$; $6.5\cdot10^{-3}$
523	$5.43\cdot10^{-3}$; $6.42\cdot10^{-3}$[b]	$7.8\cdot10^{-3}$; $9.2\cdot10^{-3}$
523	$5.45\cdot10^{-3}$	$7.8\cdot10^{-3}$
533	$6.82\cdot10^{-3}$	$9.8\cdot10^{-3}$
573	$1.16\cdot10^{-2}$	$1.67\cdot10^{-2}$
573	$7.89\cdot10^{-3}$	$1.14\cdot10^{-2}$
588	$1.53\cdot10^{-2}$; $1.67\cdot10^{-2}$[b]	$2.2\cdot10^{-2}$; $2.4\cdot10^{-2}$
591	$1.77\cdot10^{-2}$; $1.85\cdot10^{-2}$[b]	$2.5\cdot10^{-2}$; $2.6\cdot10^{-2}$
592	$1.74\cdot10^{-2}$; $2.00\cdot10^{-2}$[b]	$2.5\cdot10^{-2}$; $2.8\cdot10^{-2}$
673	$3.12\cdot10^{-2}$; $3.24\cdot10^{-2}$[b]	$4.5\cdot10^{-2}$; $4.6\cdot10^{-2}$
673	$3.35\cdot10^{-2}$	$4.8\cdot10^{-2}$
713	$3.62\cdot10^{-2}$	$5.2\cdot10^{-2}$
753	$6.49\cdot10^{-2}$	$9.3\cdot10^{-2}$

[a]Calculated by the compilers.
[b]Determination by means of flame photometry.
[c]Glass vial sampling.

The results were expressed by the equation:

$$\log(\text{soly/mass \% O}) = 0.908 - 1606\ (T/\text{K})^{-1}.$$

The results were also published in Dorner.[1]

Auxiliary Information

Method:
Gaseous O or Na_2O_2 were added to Na which circulated in a loop made of stainless steel. An apparatus for Na distillation (made of stainless steel) was cleaned with H_2O and C_2H_5OH; then it was flushed with Ar. The apparatus was evacuated down to 1.3 Pa at 773–823 K. Na and Na_2O were equilibrated at selected temperature.[2] A method of separation of Na_2O from Na was not specified, but most probably it was filtration. The sample of Na saturated with O was placed in the distillation apparatus in a Ni or Mo crucible. The distillation was performed under a reduced pressure at 773–873 K for 1–40 h; however, 5 h was the optimal time.[4] The deposit left after the distillation was dissolved in H_2O and the solution titrated with an acid. The amount of Na used was estimated from the weight of the distillation condensate. The authors investigated the O content by means of a plugging meter but the readings were not only specific for the O but also for the H content.

Source and Purity of Materials:
Na_2O_2 : nothing specified.[2]
Na: contained $5\cdot10^{-4}$ % O, $1\cdot10^{-3}$ % H, Ca, Si, $5\cdot10^{-2}$ % C, $1\cdot10^{-4}$ Li, and $<3\cdot10^{-3}$ % Ni, Mn, Al, Be, Ag, Cu, Ti, and Fe; further distilled and cold trapped.[2]
Ar: nothing specified.[2]

Estimated Error:
Solubility: precision between ±5% and ±30%; sensitivity $(0.4-3.4)\cdot10^{-4}$ mass % O; read-out procedure ±5%.
Temperature: accuracy ±5 K; reading-out procedure ±3 K.

References:
[1]F. A. Kozlov, E. K. Kuznetsov, G. P. Sergeev, L. G. Volchkov, and V. V. Zotov, *Trudy Fiziko-Energeticheskogo Instituta*, edited by V. A. Kuznetsov (Atomizdat, Moskva, 1974), pp. 290–308.
[2]M. N. Arnoldov, M. N. Ivanovskii, V. I. Subbotin, and B. A. Shmatko, *Alkali Metal Coolants* (IAEA, Vienna, 1967), pp. 479–488.
[3]F. A. Kozlov, E. K. Kuznetsov, and V. I. Subbotin, *Zhidkie Metally* (Atomizdat, Moskva, 1967), pp. 324–336.
[4]I. B. Dmitreva, F. A. Kozlov, and E. K. Kuznetsov, *Zhidkie Metally* (Atomizdat, Moskva, 1967), pp. 318–324.
[5]Yu. E. Bagdasarov, *Tekhnicheskie Problemy Reaktorov na Bystrykh Neitronakh* (Atomizdat, Moskva, 1969), p. 89.

Auxiliary Information

Method:

Na_2O was added to Na inside an evacuated Pyrex glass apparatus and, after equilibration at a given temperature, filtered by means of N pressure into the sample ampoules through a glass filter. At temperatures above 300 °C, a stainless steel vessel was inserted into the apparatus for the equilibration procedure. The Na samples were amalgamated in a separate vessel for the low temperature samples, while the amalgamation was included into the high-temperature apparatus. The amalgam was drained off through a capillary in order to separate the Na_2O remaining on the surface of the liquid alloy. The O content of the sample was determined by means of titration or flame photometry, and the Na content of the amalgam was measured in order to get data for corrections regarding the incomplete removal of amalgam from the oxide.[2]

Source and Purity of Materials:

Na_2O: nothing specified.
Na: nuclear grade purity.
N: nothing specified.

Estimated Error:

Solubility: accuracy $\pm 5\cdot 10^{-4}$ mol %; standard deviation $\pm 1.5\cdot 10^{-3}$ mol %.
Temperature: stability and precision ± 2 K.

References:

[1]S. Dorner, U.S. Atom. Energy Comm. Rep. EUR FNR-179P (1966).
[2]S. Dorner and K. Kummerer, Atomkernenergie **9**, 167–169 (1964).

Components:

(1) Oxygen; O; [7782-44-7]
(2) Sodium; Na; [7440-23-5]

Original Measurements:

J. R. Humphreys and S. B. Skladzien, U.S. Atom. Energy Comm. Rep. ANL-7518, pp. 30–32 (1968).

Variables:

Temperature: 394–508 K

Prepared by:

H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of O in liquid Na was determined

t/°C	Solubility/mass % O	Mean value/mass % O	Solubility/mol % O[a]
121	$3\cdot 10^{-4}$	$3\cdot 10^{-4}$	$4\cdot 10^{-4}$
127	$3\cdot 10^{-4}$	$3\cdot 10^{-4}$	$4\cdot 10^{-4}$
133	$3.2\cdot 10^{-4}$	$3.2\cdot 10^{-4}$	$4.6\cdot 10^{-4}$
208	$1.5\cdot 10^{-3}$	$1.5\cdot 10^{-3}$	$2.2\cdot 10^{-3}$
215	$2.6\cdot 10^{-3}$; $2.6\cdot 10^{-3}$; $2.6\cdot 10^{-3}$; $2.1\cdot 10^{-3}$	$2.5\cdot 10^{-3}$	$3.6\cdot 10^{-3}$
218	$2.7\cdot 10^{-3}$; $2.4\cdot 10^{-3}$; $2.6\cdot 10^{-3}$; $2.4\cdot 10^{-3}$	$2.6\cdot 10^{-3}$	$3.7\cdot 10^{-3}$
234	$3.0\cdot 10^{-3}$; $3.5\cdot 10^{-3}$; $2.9\cdot 10^{-3}$	$3.1\cdot 10^{-3}$	$4.5\cdot 10^{-3}$
235	$3.9\cdot 10^{-3}$; $3.3\cdot 10^{-3}$; $3.6\cdot 10^{-3}$; $3.5\cdot 10^{-3}$; $3.4\cdot 10^{-3}$	$3.5\cdot 10^{-3}$	$5.0\cdot 10^{-3}$
317	$6.0\cdot 10^{-3}$; $5.4\cdot 10^{-3}$; $6.0\cdot 10^{-3}$; $5.5\cdot 10^{-3}$	$5.7\cdot 10^{-3}$	$8.2\cdot 10^{-3}$

[a]Mean value calculated by the compilers.

The authors presented the solubility equation (tested by the compilers):

$$\log(\text{soly/mass \% O}) = 1.115 - 1846\ (T/\text{K})^{-1}.$$

The fitting equation was also reported in Skladzien.[1]

Auxiliary Information

Method:

The experiments were performed in a Na analytical loop made of stainless steel. The O concentration in Na was changed by adjusting the cold trap temperature. Dip samples, taken after equilibration was established (>18 h) at temperature increments, were vacuum distilled, and the residue was analyzed for Na by atomic absorption spectrometry. The O content was calculated on the basis of the entire residue being in form of Na_2O. The sampling, loading of the apparatus and distillation were performed in He atmosphere.[1]

Source and Purity of Materials:

O: nothing specified; precision better than ±8% (by the compilers).
Na: nuclear grade of purity.
He: "high purity;" recirculated continuously through a purifier to remove O and H_2O traces.[1]

Estimated Error:

Solubility: nothing specified.
Temperature: nothing specified.

References:

[1]S. B. Skladzien, U.S. Atom. Energy Comm. Rep. ANL-7460, pp. 31–33 (1968).

Components:
(1) Oxygen; O; [7782-44-7]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
V. J. Rutkauskas, U.S. Atom. Energy Comm. Rep. LA-3879 (1968).

Variables:
Temperature: 398–573 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of O in liquid Na was determined at various temperatures

t/°C	Solubility/mass % O	Mean value/mass % O	Solubility/mol % O[a]
125	$1.7\cdot10^{-4}$; $1.7\cdot10^{-4}$; $2.3\cdot10^{-4}$; $2.5\cdot10^{-4}$; $2.2\cdot10^{-4}$; $1.7\cdot10^{-4}$; $1.4\cdot10^{-4}$; $1.4\cdot10^{-4}$; $1.2\cdot10^{-4}$	$(1.8\pm0.4)\cdot10^{-4}$	$(2.6\pm0.6)\cdot10^{-4}$
150	$2.3\cdot10^{-4}$; $2.5\cdot10^{-4}$; $2.3\cdot10^{-4}$; $2.0\cdot10^{-4}$	$(2.3\pm0.2)\cdot10^{-4}$	$(3.3\pm0.3)\cdot10^{-4}$
165	$4.0\cdot10^{-4}$; $4.6\cdot10^{-4}$; $3.3\cdot10^{-4}$; $3.7\cdot10^{-4}$	$(3.9\pm0.5)\cdot10^{-4}$	$(5.6\pm0.7)\cdot10^{-4}$
175	$4.9\cdot10^{-4}$; $4.9\cdot10^{-4}$; $5.0\cdot10^{-4}$; $4.6\cdot10^{-4}$; $5.4\cdot10^{-4}$	$(5.0\pm0.3)\cdot10^{-4}$	$(7.2\pm0.4)\cdot10^{-4}$
185	$6.8\cdot10^{-4}$; $6.8\cdot10^{-4}$; $7.2\cdot10^{-4}$; $7.5\cdot10^{-4}$; $6.3\cdot10^{-4}$; $6.7\cdot10^{-4}$	$(6.9\pm0.4)\cdot10^{-4}$	$(9.9\pm0.6)\cdot10^{-4}$
200	$8.1\cdot10^{-4}$; $9.0\cdot10^{-4}$; $7.9\cdot10^{-4}$; $9.5\cdot10^{-4}$	$(8.6\pm0.8)\cdot10^{-4}$	$(1.24\pm0.11)\cdot10^{-3}$
215	$1.06\cdot10^{-3}$; $1.16\cdot10^{-3}$; $1.12\cdot10^{-3}$; $1.31\cdot10^{-3}$	$(1.16\pm0.1)\cdot10^{-3}$	$(1.67\pm0.14)\cdot10^{-3}$
225	$2.2\cdot10^{-3}$; $2.0\cdot10^{-3}$; $1.85\cdot10^{-3}$	$(2.0\pm0.2)\cdot10^{-3}$	$(2.9\pm0.3)\cdot10^{-3}$
250	$3.7\cdot10^{-3}$; $4.0\cdot10^{-3}$; $3.8\cdot10^{-3}$	$(3.8\pm0.2)\cdot10^{-3}$	$(5.5\pm0.3)\cdot10^{-3}$
265	$4.7\cdot10^{-3}$; $4.8\cdot10^{-3}$; $4.9\cdot10^{-3}$	$(4.8\pm0.1)\cdot10^{-3}$	$(6.9\pm0.2)\cdot10^{-3}$
275	$7.4\cdot10^{-3}$; $7.2\cdot10^{-3}$; $7.4\cdot10^{-3}$	$(7.4\pm0.1)\cdot10^{-3}$	$(1.06\pm0.14)\cdot10^{-2}$
300	$1.46\cdot10^{-2}$; $1.34\cdot10^{-2}$; $1.45\cdot10^{-2}$	$(1.42\pm0.06)\cdot10^{-2}$	$(2.0\pm0.1)\cdot10^{-2}$

[a]Calculated by the compilers.

The author proposed the solubility equation:

$$\log(\text{soly/mass \% O}) = 4.25 - 3499\ (T/\text{K})^{-1}.$$

The slope of this relation is too high as tested by the compilers. The recalculated equation is:

$$\log(\text{soly/mass \% O}) = 2.122 - 2395\ (T/\text{K})^{-1}.$$

The results were also published in Rutkauskas and Meadows[1] and shortly reviewed in Rutkauskas.[2] A part of the results was reported graphically.[3]

Auxiliary Information

Method

All components of the apparatus, which were in contact with Na, were constructed of Type 304 stainless steel. The facility consisted of a forced circulation Na loop and an integral vacuum distillation sampling system. Temperature sensors were located in thermocouple wells. The loop was tested for any leakage using He with mass spectrometric detection. The Na flow was established, and the temperature was raised to 673 K and maintained at this level for several hours under vacuum. The temperature of the Na reservoir was lowered to 423 K and that of the crystallizer tank to 398 K. These conditions were maintained for 2 1/2 months. Na was doped with NaOH which decomposed to Na_2O. Na_2O was equilibrated with Na for 2–3 days. Homogeneous saturated samples were taken from the crystallizer by means of a Ni sampling cup. The sample was distilled under dynamic vacuum of <0.013 Pa using an induction furnace. The residue of the distillation was dissolved in diluted HCl and analyzed for Na by flame photometry. The O concentration was calculated assuming Na_2O as the solute.

Source and Purity of Materials:

Na_2O: from decomposition of NaOH of unspecified purity at 673 K and reduced pressure.
Na: reactor grade purity containing 0.01% K, $<1\cdot10^{-4}$ % Li, Be, Cu, Mn, Sr, $<2\cdot10^{-4}$ % Al, V, Cr, Fe, Mo, Ag, In, Ba, $<5\cdot10^{-4}$ % B, Co, Ni, Cd, Sn, Au, Pb, Bi, H, $\leqslant3\cdot10^{-4}$ % N, $\leqslant1.0\cdot10^{-3}$ % C, Ca, Ti, Si, <0.02% P, Ta, W, Zn, <0.05% Hg.
He: nothing specified.

Estimated Error:
Solubility: standard deviation between 1% and 22%.
Temperature: stability ±1 K.

References:
[1]V. J. Rutkauskas and G. E. Meadows, U.S. Atom. Energy Comm. Rep. LA-3745-MS, pp. 50–51 (1967).
[2]V. J. Rutkauskas, *The Alkali Metals* (The Chemical Society, London, 1967), pp. 401–402.
[3]Anonymous, U.S. Atom. Energy Comm. Rep. LA-3524-MS, pp. 50–51 (1966).

Components:
(1) Oxygen; O; [7782-44-7]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
B. Minushkin and G. Kissel, *Corrosion by Liquid Metals*, edited by J. E. Draley and J. R. Weeks (Plenum, New York, 1970), pp. 515–522.

Variables:
Temperature: 623–823 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The results were reported graphically in form of a smooth line. The solubility equation of O in liquid Na was also reported:

$$\log(\text{soly/mass \% O}) = (2.46\pm0.11) - 2600\ (T/\text{K})^{-1}$$

for the temperature range 350–550 °C. The same results were reported in Gurinsky.[2]

The calculated (by the compilers) solubilities at 350 and 550 °C are 0.028 and 0.28 mol % O, respectively. Using the same method, Isaacs and Minushkin[3] reported the following equation:

$$\log(\text{soly/mass \% O}) = 2.52 - 2620\ (T/\text{K})^{-1}.$$

An inflection on the calibration curve at ~315 °C is probably due to the instabilities of the solid electrolyte below this temperature.

The authors suggested a phase change of Na_2O at this temperature; however, such an effect was not confirmed in more recent studies.

Auxiliary Information

Method:

emf measurements of a cell: Na, Na_2O_{satd}/ThO_2–Y_2O_3 (15 mass %)/Na–O were performed changing the O concentration in the right compartment. The solid electrolyte tube containing the reference electrode (on left) was immersed in a beaker of Na within a stainless steel tank. Provisions were made for stirring Na and introducing Na_2O or U foils into the Na through an inert gas lock. Na containing O was heated to a series of different temperatures and emf was recorded after both temperature and emf were constant for at least 1 h. Knowing the emf–temperature dependence for the cell at constant O concentration, one can solve for the constants of the solubility equation, combining it with U gettering technique for the O determination in Na.[1]

Source and Purity of Materials:

Na_2O: "high purity" pellets.
Na: reactor grade purity, filtered through 1 μm stainless steel frit and gettered by U foils.

Estimated Error:
Solubility: precision ±12%.
Temperature: nothing specified.

References:
[1]H. S. Isaacs, B. Minushkin, and F. J. Salzano, U.S. Atom. Energy Comm. Rep. ANL-7520, Pt. I, pp. 460, 465 (1969).
[2]D. H. Gurinsky, U.S. Atom. Energy Comm. Rep. BNL-50219 (1969).
[3]H. S. Isaacs and B. Minushkin, U.S. Atom. Energy Comm. Rep. BNL-50141, p. 28 (1968).

Components:
(1) Oxygen; O; [7782-44-7]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
D. I. Smith and T. F. Kassner, *Corrosion by Liquid Metals*, edited by J. E. Draley and J. R. Weeks (Plenum, New York, 1970), pp. 137–149.

Variables:
Temperature: 398–518 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The results were reported in graphical form. The solubilities of O in liquid Na were read from a figure and recalculated to mol % by the compilers.

Manual titration method			Automatic titration method		
t/°C	Solubility/mass % O	Solubility/mol % O	t/°C	Solubility/mass % O	Solubility/mol % O
124	$(1.4\pm0.2)\cdot10^{-4}$	$(2.0\pm0.3)\cdot10^{-4}$	135	$1.1\cdot10^{-4}$	$1.6\cdot10^{-4}$
125	$(9\pm3)\cdot10^{-5}$	$(1.3\pm0.4)\cdot10^{-4}$	154	$2.8\cdot10^{-4}$	$4.0\cdot10^{-4}$
135	$(1.6\pm0.3)\cdot10^{-4}$	$(2.3\pm0.4)\cdot10^{-4}$	165	$5.4\cdot10^{-4}$	$7.7\cdot10^{-4}$
140	$(3.2\pm0.3)\cdot10^{-4}$	$(4.6\pm0.4)\cdot10^{-4}$	175	$5.2\cdot10^{-4}$	$7.5\cdot10^{-4}$
146	$(1.9\pm0.3)\cdot10^{-4}$	$(2.7\pm0.4)\cdot10^{-4}$	185	$9.5\cdot10^{-4}$	$1.4\cdot10^{-3}$
153	$(2.8\pm0.4)\cdot10^{-4}$	$(4.0\pm0.6)\cdot10^{-4}$	186	$1.1\cdot10^{-3}$	$1.6\cdot10^{-3}$
178	$(6.6\pm0.3)\cdot10^{-4}$	$(9.5\pm0.4)\cdot10^{-4}$	199	$1.4\cdot10^{-3}$	$2.0\cdot10^{-3}$
187	$(1.1\pm0.1)\cdot10^{-4}$	$(1.6\pm0.1)\cdot10^{-4}$	209	$1.8\cdot10^{-3}$	$2.6\cdot10^{-3}$
198	$(1.4\pm0.1)\cdot10^{-4}$	$(2.0\pm0.1)\cdot10^{-4}$	220	$2.2\cdot10^{-3}$	$3.2\cdot10^{-3}$
199	$(1.3\pm0.2)\cdot10^{-4}$	$(1.8\pm0.3)\cdot10^{-4}$	230	$2.5\cdot10^{-3}$	$3.6\cdot10^{-3}$
204	$(1.2\pm0.2)\cdot10^{-4}$	$(1.7\pm0.3)\cdot10^{-4}$	241	$4.0\cdot10^{-3}$	$5.8\cdot10^{-3}$
205	$(1.5\pm0.1)\cdot10^{-4}$	$(2.1\pm0.1)\cdot10^{-4}$	244	$3.3\cdot10^{-3}$	$4.7\cdot10^{-3}$
208	$(1.7\pm0.1)\cdot10^{-4}$	$(2.4\pm0.1)\cdot10^{-4}$			
211	$(1.6\pm0.2)\cdot10^{-4}$	$(2.3\pm0.3)\cdot10^{-4}$			
212	$(1.5\pm0.2)\cdot10^{-4}$	$(2.1\pm0.3)\cdot10^{-4}$			
213	$(1.6\pm0.2)\cdot10^{-4}$	$(2.3\pm0.3)\cdot10^{-4}$			
220	$(1.6\pm0.2)\cdot10^{-4}$	$(2.3\pm0.3)\cdot10^{-4}$			
221	$(1.4\pm0.2)\cdot10^{-4}$	$(2.0\pm0.3)\cdot10^{-4}$			
225	$(2.5\pm0.3)\cdot10^{-4}$	$(3.6\pm0.4)\cdot10^{-4}$			

The results were approximated in Smith and Lee[1] by the equation:

$$\log(\text{soly/mass \% O}) = (3.023\pm0.095) - (2828\pm88)\ (T/\text{K})^{-1}.$$

A slightly different equation was presented in Smith:[2,3]

$$\log(\text{soly/mass \% O}) = 2940 - 2801\ (T/\text{K})^{-1}.$$

However, this equation took into account some results of other authors. An influence of H within the concentration range $1\cdot10^{-3}$–$6\cdot10^{-5}$ mass %H on the O solubility in liquid Na was not observed.

Auxiliary Information

Method:
The equilibration apparatus was constructed of Type 304 stainless steel. The O concentration in Na was controlled by its slow circulation through a cold trap with a stainless steel mesh and baffles to facilitate the attainment of the Na–Na_2O equilibrium. Samples of Na were analyzed by means of vacuum distillation of the metal. The distillation was performed for 3 h at 598 K and 0.5 h at 748 K. The remaining Na_2O was dissolved in H_2O and titrated with HCl (manually or automatically). The results were confirmed by flame photometry. All essential operations were performed in Ar atmosphere.

Source and Purity of Materials:
O: gaseous, of unspecified purity.
Na: contained $<2\cdot10^{-5}$ % Ba, Mo, $\leqslant1\cdot10^{-4}$ % Ca, Nb, Mn, N, C, H, $1\cdot10^{-5}$ % Cr, $5\cdot10^{-4}$ % Fe, $<5\cdot10^{-7}$ % Li, $<2\cdot10^{-4}$ % Mg, V, as in Smith.[3]
H_2O: "high purity," distilled; as in Smith and Lee.[1]
Ar: "dry."

Estimated Error:
Solubility: nothing specified; reading-out procedure ±5%; reading-out precision better than ±25%.
Temperature: nothing specified; reading-out procedure ±2 K.

References:
[1]D. L. Smith and R. H. Lee, U.S. Atom. Energy Comm. Rep. ANL-7891 (1972).
[2]D. L. Smith, U.S. Energy Res. Devel. Admin. Rep. CONF-760503-P2, pp. 631–637 (1976).
[3]D. L. Smith, Metall. Trans. **2**, 579–583 (1970).

Components:
(1) Oxygen; O; [7782-44-7]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
W. H. Caplinger, G. E. Meadows, D. W. Bennet, and J. A. Yount, Trans. Am. Nucl. Soc. **14**, 611–613 (1971).

Variables:
Temperature: 400–450 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of O in liquid Na was determined

t/°F	t/°C	Solubility/mass % O	Solubility/mol % O[a]
350	177	$7.6\cdot10^{-4}$	$1.09\cdot10^{-3}$
325	163	$4.8\cdot10^{-4}$	$6.9\cdot10^{-4}$
300	149	$3.8\cdot10^{-4}$	$5.5\cdot10^{-4}$
260	127	$2.1\cdot10^{-4}$	$3.0\cdot10^{-4}$

[a]Calculated by the compilers.

Auxiliary Information

Method:
Na was forced to circulate through a stainless steel loop by means of an electromagnetic pump, the loop contained also a flow meter, heater, cooler, cold trap, and a plugging device. Na samples were taken behind the cold trap section and analyzed by means of vacuum distillation of Na saturated with Na_2O. The analysis was repeated five times at each temperature.

Source and Purity of Materials:
Na_2O: nothing specified.
Na: nuclear grade of purity.

Estimated Error:
Solubility: precision between ±5% and ±16%.
Temperature: stability ±2.5 K; precision ±5 K.

Components:
(1) Oxygen; O; [7782-44-7]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
G. P. Stavropoulos and F. A. Cafasso, Trans. Am. Nucl. Soc. **14**, 621 (1971).

Variables:
Temperature: 508–848 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The authors performed solubility experiments in the temperature range 508–848 K and presented their results concerning the solubility of O in liquid Na in form of the following equation:

$$\log(\text{soly/mass \% O}) = (3.1068 \pm 0.0129) - (2876.5 \pm 21.9)\ (T/\text{K})^{-1}.$$

The corresponding solubility values at 508 and 848 K were found to be $4 \cdot 10^{-3}$ and 0.74 mol % O, respectively.

One of the authors[1,2] presented a quite similar solubility equation using the same experimental method. The authors did not comment on a very slight difference with the above equation.

$$\log(\text{soly/mass \% O}) = (3.076 \pm 0.004) - (2865 \pm 180)\ (T/\text{K})^{-1}.$$

The corresponding solubility values at the extreme temperatures are $4 \cdot 10^{-3}$ and 0.72 mol % O, respectively.

Na_2O is the equilibrium solid state.

Auxiliary Information

Method:
The measurements were carried out by means of the electrochemical cell: Sn–SnO_2/ThO_2–Y_2O_3 (15 mass %)/Na–O. The cell was housed in an all Ni apparatus. The emf was measured as function of temperature and composition. Solutions with different O concentrations were obtained by addition or removal of O by Coulometric titration or chemically. For each solution, the variation of O activity with temperature was determined. The electrode compartment was designed to prevent a loss of O and Na by vapor transport. The solubility equation was obtained taking into account the thermodynamic data of the cell reactions and assuming that the O activity coefficient is independent of its concentration up to the saturation point.

Source and Purity of Materials:
O: generated by Coulometric electrolysis.
Na: "high-purity" and contained $<1 \cdot 10^{-4}$ % H; $<6 \cdot 10^{-4}$ % C, $\sim 7 \cdot 10^{-4}$ % transition metals.
Ni: "high purity," decarburized.

Estimated Error:
Solubility: precision ±15%.
Temperature: nothing specified; better than ±2 K (by the compilers).

References:
[1]C. B. Alcock and G. P. Stavropoulos, Can. Metall. Quart. **10**, 257–262 (1971).
[2]G. P. Stavropoulos, U.S. Atom. Energy Comm. Rep. CONF-711009 (1971).

Components:
(1) Oxygen; O; [7782-44-7]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
H. U. Borgstedt, H. Schneider, and G. Wittig, Atomwirtschaft **17**, 157–158 (1972).

Variables:
Temperature: 435–492 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of O in Na was determined. The values were presented in a figure. They were read out and recalculated to mol % by the compilers.

t/°C	Solubility/mass % O	Solubility/mol % O[a]
162	$4.2 \cdot 10^{-4}$	$6.0 \cdot 10^{-4}$
162	$4.7 \cdot 10^{-4}$	$6.8 \cdot 10^{-4}$
168	$5.3 \cdot 10^{-4}$	$7.6 \cdot 10^{-4}$
173	$5.5 \cdot 10^{-4}$	$7.9 \cdot 10^{-4}$
200	$9.5 \cdot 10^{-4}$	$1.4 \cdot 10^{-3}$
200	$1.20 \cdot 10^{-3}$	$1.7 \cdot 10^{-3}$
200	$1.39 \cdot 10^{-3}$	$2.00 \cdot 10^{-3}$
212	$2.08 \cdot 10^{-3}$	$3.00 \cdot 10^{-3}$
217	$1.77 \cdot 10^{-3}$	$2.5 \cdot 10^{-3}$
219	$2.40 \cdot 10^{-3}$	$3.4 \cdot 10^{-3}$

[a]As calculated by the compilers.

The results were also expressed by the equation:

$$\log(\text{soly/mass \% O}) = 2.131 - 2362\ (T/\text{K})^{-1},$$

which was tested by the compilers.

Auxiliary Information

Method:
Molten Na in a stainless steel mold was equilibrated for several hours with O in the Ar glove box atmosphere at selected temperatures. Surface oxide skins on the liquid Na were removed mechanically. The equilibration temperature was measured by means of a calibrated thermometer. Samples of the equilibrated Na were collected in Ni crucibles, and Na was distilled off under vacuum in a closed glass container, the walls of which were covered with a layer of Na in order to keep the atmosphere inert. The distillation was performed at 0.001–0.01 Pa and 623–633 K. The residue was dissolved in H_2O and the Na_2O content was determined by means of titration with H_2SO_4. The contents of CaO, Na_2CO_3, and NaCl in the residue were below the detection limits.

Source and Purity of Materials:
O: from the box atmosphere; purified by passing Cu catalyst and molecular sieves.
Na: from Degussa; purified by keeping it just above the melting temperature in the glove box atmosphere and removal of surface skins.
Ar: contained $<10^{-4}$ vol % O.
H_2O: ultrapure.

Estimated Error:
Solubility: precision of titration analysis ±0.5 mol %; read-out procedure ±0.5 mol %.
Temperature: precision ±0.5 K; read-out procedure ±1 K.

Components:
(1) Oxygen; O; [7782-44-7]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
H. U. Borgstedt, A. Marin, Z. Peric, and G. Wittig, Atomwirtschaft **17**, 361–362 (1972).

Variables:
Temperature: 623–803 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The results were presented in a figure in the form of smooth lines. The solubility values at the extreme temperatures were read from the figure and recalculated to mol % by the compilers. The logarithm of the solubility changed linearly with the reciprocal temperature.

t/°C	Solubility/mass % O	Solubility/mol % O	Kind of cell
350	$1.16\cdot10^{-3}$	$1.67\cdot10^{-3}$	I
530	$2.5\cdot10^{-2}$	$3.6\cdot10^{-2}$	I
350	$1.71\cdot10^{-2}$	$2.4\cdot10^{-2}$	II
530	$7.1\cdot10^{-2}$	$1.02\cdot10^{-1}$	II

The following solubility equations were reported:

$$\log(\text{soly/mass \% O}) = 3.189 - 3810\ (T/\text{K})^{-1} \quad \text{for cell I}$$

and

$$\log(\text{soly/mass \% O}) = 2.429 - 2606\ (T/\text{K})^{-1} \quad \text{for cell II.}$$

Auxiliary Information

Method:
Two types of electrochemical cells were used: (I) $Na–Na_2O/ThO_2–Y_2O_3/Cu–Cu_2O$ and (II) $Na–Na_2O/ThO_2–Y_2O_3/Au$, air with $p_0 = 21.1$ kPa. The solid electrolyte tubes enclosed the reference electrodes (on the right). The sensors were immersed in a capsule made of stainless steel containing Na and Na_2O. The temperature was measured using sheathed thermocouples and controlled by a muffle furnace. The emfs of both the cells were measured by a digital voltmeter with high impedance and recorded. The saturating concentration was calculated using values for calibration of the instrument from Minushkin and Kissel.[1]

Source and Purity of Materials:
Na_2O: nothing specified.
Na: reactor grade purity.
Ar: nothing specified.
$ThO_2–Y_2O_3$: from Zircoa Corp. of America.

Estimated Error:
Solubility: nothing specified.
Temperature: nothing specified.

References:
[1]B. Minushkin and G. Kissel, *Corrosion by Liquid Metals*, edited by J. E. Draley and J. R. Weeks (Plenum, New York, 1970), pp. 515–527.

Components:
(1) Oxygen; O; [7782-44-7]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
A. N. Hamer, J. H. Higson, J. Mathison, and R. Swinhoe, *Liquid Alkali Metals* (BNES, London, 1973), pp. 59–64.

Variables:
Temperature: 433–553 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of O in liquid Na was reported graphically and in form of an equation:

$$\log(\text{soly/mass \% O}) = 0.8 - 2000\ (T/\text{K})^{-1},$$

valid between 166 and 261 °C. The corresponding solubilities at these temperatures are $2.0\cdot10^{-4}$ and $1.5\cdot10^{-3}$ mol % O, respectively, as it was read from a figure by the compilers. A single numerical result of $1\cdot10^{-4}$ mass % O ($1.5\cdot10^{-4}$ mol % O) at 160 °C (433 K) was also reported. Na which contained $7.2\cdot10^{-3}$ mass % O ($1.0\cdot10^{-2}$ mol % O) at 280 °C (553 K), according to analysis, showed evidence of a decrease of this concentration with time, a fact that indicated a supersaturation of this solution.

Auxiliary Information

Method:
Na circulated through pipework and a mixing vessel by means of a dc pump. In order to control the saturation level of impurities, a small cold trap was provided, while a sampler allowed specimens of Na to be withdrawn for subsequent analysis. Two types of plugging meters were installed. The first one gave a continuous reading of the saturation temperature, while the second one was a simple manually controlled device. The whole rig was constructed from 321 type of stainless steel. O was admitted through a removable flange attached to the sampler. Heat was applied selectively to make the reaction and dissolution of Na_2O. The temperature of the plugging meter pointed on the saturation at the temperature of the cold trap. Samples of Na were analyzed for their O content by an unspecified method.

Source and Purity of Materials:
O: nothing specified.
Na: nuclear grade of purity.
Ar: nothing specified.

Estimated Error:
Solubility: nothing specified.
Temperature: precision ±1.5 K.

Components:
(1) Oxygen; O; [7782-44-7]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
J. M. McKee, D. R. Vissers, P. A. Nelson, B. R. Grundy, E. Berkey, and G. R. Taylor, Nucl. Technol. **21**, 217–227 (1974).

Variables:
Temperature: 382–496 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of O in liquid Na was determined. The results were read from a figure and recalculated to mol % O by the compilers.

t/°C	Solubility/mass % O	Solubility/mol % O
109[a]	$4.2\cdot10^{-5}$	$6.0\cdot10^{-5}$
110[a]	$6.2\cdot10^{-5}$	$8.9\cdot10^{-5}$
121[b]	$5.4\cdot10^{-5}$	$7.8\cdot10^{-5}$
122[a]	$7.5\cdot10^{-5}$	$1.08\cdot10^{-4}$
135[a]	$8.5\cdot10^{-5}$	$1.2\cdot10^{-4}$
138[b]	$1.2\cdot10^{-4}$	$1.7\cdot10^{-4}$
148[a]	$1.5\cdot10^{-4}$	$2.2\cdot10^{-4}$
153[b]	$1.6\cdot10^{-4}$	$2.3\cdot10^{-4}$
162[a]	$3.2\cdot10^{-4}$	$4.6\cdot10^{-4}$
169[b]	$2.2\cdot10^{-4}$	$3.2\cdot10^{-4}$
175[a]	$3.6\cdot10^{-4}$	$5.2\cdot10^{-4}$
184[b]	$3.2\cdot10^{-4}$	$4.6\cdot10^{-4}$
192[a]	$6.6\cdot10^{-4}$	$9.5\cdot10^{-4}$
203[b]	$7.6\cdot10^{-4}$	$1.09\cdot10^{-3}$
208[a]	$1.01\cdot10^{-3}$	$1.5\cdot10^{-3}$
208[a]	$1.2\cdot10^{-3}$	$1.7\cdot10^{-3}$
223[b]	$1.1\cdot10^{-3}$	$1.6\cdot10^{-3}$
233[b]	$1.3\cdot10^{-3}$	$1.9\cdot10^{-3}$

[a]Oxygen meter calibrated at 482 °C.
[b]Oxygen meter calibrated at 371 °C.

Auxiliary Information

Method:
The saturating concentration of O in Na was measured with the use of an electrochemical oxygen meter. The essential part of this apparatus was the cell: Na–O/ThO_2+7.5% Y_2O_3/Pt, air. A Pt mesh in equilibrium with air acted as reference electrode. A stainless steel sheath protected the solid electrolyte tube. The temperature was measured by means of thermocouples. The O concentration was determined by means of V wire. V was equilibrated with Na at 1023 K for 4 h and cooled quickly. The Na flow was stopped and Na was displaced with Ar within 1 h. The V wires were analyzed for O by means of the vacuum fusion method after immersion in alcohol and water and anodical etching. Samples of Na were also analyzed for their O content by the amalgamation method.

Source and Purity of Materials:
Na_2O: nothing specified.
Na: nuclear grade purity.
Ar: nothing specified.

Estimated Error:
Solubility: accuracy between ±10% and 20%.
Temperature: stability ±1 K during 8 h.
Potential: stability ±1 mV during 4 h.

Components:
(1) Oxygen; O; [7782-44-7]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
P. Berge, C. Oberlin, and P. Saint-Paul, J. Nucl. Mater. **57**, 283–286 (1975).

Variables:
Temperature: 387–548 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of O in liquid Na at different temperatures was determined

t/°C	Solubility/mass % O	Solubility/mol % O[b]
114	$9.3\cdot10^{-5}$	$1.34\cdot10^{-4}$
120	$5.5\cdot10^{-5}$, $8.5\cdot10^{-5}$, $1.05\cdot10^{-4}$	$7.9\cdot10^{-5}$, $1.22\cdot10^{-4}$, $1.51\cdot10^{-4}$
122	$1.38\cdot10^{-4}$	$2.0\cdot10^{-4}$
160[a]	$5.19\cdot10^{-4}$	$7.5\cdot10^{-4}$
175[a]	$7.35\cdot10^{-4}$	$1.06\cdot10^{-3}$

[a]Filtered Na.
[b]Calculated by the compilers.

Auxiliary Information

Method:
Equilibration of Na and Na_2O was achieved in an AISI 316 stainless steel loop in >24 h. Samples of Na saturated with Na_2O were withdrawn in a He atmosphere. A pair of identical Pyrex glass containers with Teflon stop-cocks was outgassed at 433 K for 16 h at reduced pressure of 1.3 Pa. Na saturated with Na_2O was introduced into one container. Equal portions of Hg were dosed to both containers and the amalgam formed was tapped. The extraction procedure was repeated 10–12 times in both containers. Na in liquid Hg was determined by acidimetric titration. Na_2O left in the containers (the analyzed and blank test) were determined by atomic absorption spectroscopy. The solubility results were corrected for the blank test.

Source and Purity of Materials:
Na_2O: nothing specified.
Na: nuclear grade of purity, cold trapped or filtrated.
He: purified by BTS catalyzer and contained $<1\cdot10^{-4}$ vol % O.

Estimated Error:
Solubility: precision $\pm3.7\cdot10^{-4}$ mol % O.
Temperature: precision ±2 K.

Components:
(1) Oxygen; O; [7782-44-7]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
B. R. Grundy and D. D. Durigon, J. Nucl. Mater. **55**, 111–112 (1975).

Variables:
Temperature: 381–496 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of O in liquid Na at different temperatures was determined. The data were read from a figure and recalculated to mol % O by the compilers.

T/K	Solubility/mass % O	Solubility/mol % O
496	$1.20\cdot10^{-4}$	$1.7\cdot10^{-4}$
496	$1.15\cdot10^{-4}$	$1.6\cdot10^{-4}$
478	$6.6\cdot10^{-4}$	$9.5\cdot10^{-4}$
478	$5.3\cdot10^{-4}$	$7.6\cdot10^{-4}$
477	$8.3\cdot10^{-4}$	$1.2\cdot10^{-3}$
477	$7.3\cdot10^{-4}$	$1.05\cdot10^{-3}$
469	$4.3\cdot10^{-4}$	$6.2\cdot10^{-4}$
458	$3.1\cdot10^{-4}$	$4.5\cdot10^{-4}$
447	$3.0\cdot10^{-4}$	$4.3\cdot10^{-4}$
442	$2.2\cdot10^{-4}$	$3.2\cdot10^{-4}$
431	$2.4\cdot10^{-4}$	$3.4\cdot10^{-4}$
428	$1.5\cdot10^{-4}$	$2.2\cdot10^{-4}$
419	$1.15\cdot10^{-4}$	$1.66\cdot10^{-4}$
418	$1.25\cdot10^{-4}$	$1.80\cdot10^{-4}$
411	$8.6\cdot10^{-5}$	$1.20\cdot10^{-4}$
405	$8.2\cdot10^{-5}$	$1.18\cdot10^{-4}$
404	$6.2\cdot10^{-5}$	$8.9\cdot10^{-5}$
403	$1.10\cdot10^{-4}$	$1.58\cdot10^{-4}$
403	$7.3\cdot10^{-5}$	$1.05\cdot10^{-4}$
402	$6.1\cdot10^{-5}$	$8.8\cdot10^{-5}$
401	$7.1\cdot10^{-5}$	$1.02\cdot10^{-4}$
399	$9.3\cdot10^{-5}$	$1.34\cdot10^{-4}$
396	$5.3\cdot10^{-5}$	$7.6\cdot10^{-5}$
391	$6.0\cdot10^{-5}$	$8.6\cdot10^{-5}$
383	$6.0\cdot10^{-5}$	$8.6\cdot10^{-5}$
383	$4.0\cdot10^{-5}$	$5.8\cdot10^{-5}$
381	$4.1\cdot10^{-5}$	$5.9\cdot10^{-5}$
381	$3.1\cdot10^{-5}$	$4.5\cdot10^{-5}$
381	$2.7\cdot10^{-5}$	$3.7\cdot10^{-5}$

The authors reported the fitting equation of the solubility:

$$\log(\text{soly/mass \% O}) = 1.805 - 2374\ (T/\text{K})^{-1} \quad r = 0.985.$$

The compilers tested the validity of the equation. The same results were reported in Grundy and Berkey.[1]

Auxiliary Information

Method:
Na saturated with Na_2O circulated in a stainless steel loop with a cold trap compartment. The cold trap temperature was measured by a thermocouple on its exit line. Na from the cold trap was equilibrated for 4–90 h at 1023 K with a V wire to getter O from the Na. The exposure time of 4 h was sufficient to reach the equilibrium. The system was quenched. The V wire was immersed in C_2H_5OH to remove an adherent Na film, rinsed in H_2O, and anodically etched. The V wire was analyzed for its O content by means of the vacuum fusion method.

Source and Purity of Materials:
O: nothing specified.
Na: probably of nuclear grade of purity
V: contained 0.034 mass % C.

Estimated Error:
Solubility: nothing specified; precision ±20% at the 95% confidence band (by the compilers); reading out procedure ±5%.
Temperature: nothing specified; reading out procedure ±2 K.

References:
[1]B. R. Grundy, E. Berkey, and G. R. Taylor, U.S. Atom. Energy Comm. Rep. WARD-3045-T1-4 (1972).

Components:
(1) Oxygen; O; [7782-44-7]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
G. Ilincev, *Sostoyanie i Perspektivy Rabot po Sozdaniyu AES s Reaktorami na Bystrykh Neitronakh*, edited by O. D. Kazachkovskii (FEI, Obnisk, 1975), pp. 223–250.

Variables:
Temperature: 369–666 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The results of solubility measurements of O in liquid Na were presented graphically and only partly numerically. They were read out and recalculated to mol % O by the compilers.

t/°C	Solubility/mass % O	Solubility/mol % O
96	$1.3\cdot10^{-4}$	$1.8\cdot10^{-4}$
112[a]	$1.6\cdot10^{-4}$	$2.3\cdot10^{-3}$
116	$2.1\cdot10^{-4}$	$3.0\cdot10^{-4}$
118	$2.4\cdot10^{-4}$	$3.4\cdot10^{-4}$
125	$2.3\cdot10^{-4}$	$3.3\cdot10^{-4}$
149[a]	$5.6\cdot10^{-4}$	$8.0\cdot10^{-4}$
157	$9.5\cdot10^{-4}$	$1.37\cdot10^{-3}$
157	$1.4\cdot10^{-3}$	$2.0\cdot10^{-3}$
182	$1.2\cdot10^{-3}$	$1.7\cdot10^{-3}$
184	$1.9\cdot10^{-3}$	$2.7\cdot10^{-3}$
190	$1.8\cdot10^{-3}$	$2.6\cdot10^{-3}$
200[a]	$2.18\cdot10^{-3}$	$3.1\cdot10^{-3}$
213	$3.7\cdot10^{-3}$	$5.3\cdot10^{-3}$
224	$5.1\cdot10^{-3}$	$7.3\cdot10^{-3}$
227	$3.4\cdot10^{-3}$	$4.9\cdot10^{-3}$
228	$5.2\cdot10^{-3}$	$7.56\cdot10^{-3}$
238	$6.1\cdot10^{-3}$	$8.8\cdot10^{-3}$
244	$6.2\cdot10^{-3}$	$8.9\cdot10^{-3}$
250[a]	$6.6\cdot10^{-3}$	$9.6\cdot10^{-3}$
246	$7.5\cdot10^{-3}$	$1.08\cdot10^{-2}$
246	$8.5\cdot10^{-3}$	$1.22\cdot10^{-2}$
246	$9.5\cdot10^{-3}$	$1.37\cdot10^{-2}$
258	$8.2\cdot10^{-3}$	$1.18\cdot10^{-2}$
258	$9.0\cdot10^{-3}$	$1.30\cdot10^{-2}$
271	$9.2\cdot10^{-3}$	$1.32\cdot10^{-2}$
288	$2.1\cdot10^{-2}$	$3.0\cdot10^{-2}$
290[a]	$1.37\cdot10^{-2}$	$1.97\cdot10^{-2}$
292	$1.7\cdot10^{-2}$	$2.4\cdot10^{-2}$
292	$1.9\cdot10^{-2}$	$2.7\cdot10^{-2}$
297	$1.2\cdot10^{-2}$	$1.7\cdot10^{-2}$
297	$1.4\cdot10^{-2}$	$2.0\cdot10^{-2}$
326	$3.0\cdot10^{-2}$	$4.3\cdot10^{-2}$
332	$2.3\cdot10^{-2}$	$3.3\cdot10^{-2}$
332	$3.2\cdot10^{-2}$	$4.6\cdot10^{-2}$
340	$3.2\cdot10^{-2}$	$4.6\cdot10^{-2}$
340	$3.9\cdot10^{-2}$	$5.6\cdot10^{-2}$
345	$3.1\cdot10^{-2}$	$4.5\cdot10^{-2}$
345	$4.2\cdot10^{-2}$	$6.0\cdot10^{-2}$
350[a]	$3.45\cdot10^{-2}$	$5.0\cdot10^{-2}$
376	$5.3\cdot10^{-2}$	$7.6\cdot10^{-2}$
376	$5.0\cdot10^{-2}$	$7.2\cdot10^{-2}$
387	$5.0\cdot10^{-2}$	$7.2\cdot10^{-2}$
387	$5.3\cdot10^{-2}$	$7.6\cdot10^{-2}$
390	$3.7\cdot10^{-2}$	$5.3\cdot10^{-2}$
390	$6.3\cdot10^{-2}$	$9.0\cdot10^{-2}$
394	$4.3\cdot10^{-2}$	$6.2\cdot10^{-2}$
394	$4.0\cdot10^{-2}$	$5.8\cdot10^{-2}$
600[a]	0.417	0.60

[a]Numerical result.
[b]Extrapolated.

The authors proposed the solubility equation, tested by the compilers:

$$\log(\text{soly/mass \% O}) = 2.318 - 2355\ (T/\text{K})^{-1}.$$

Na_2O is the equilibrium solid phase. The same results were reported in Ilincev.[1]

Auxiliary Information

Method:
A convective Na loop, made of a stainless steel, contained heating and cooling zones, cold trap, inlet and outlet, bypass and diffusion hydrogen meter. O was introduced into the loop in form of NaOH. The latter was decomposed that Na was free of H. Na_2O formed was equilibrated with the circulating liquid Na. Samples of Na saturated with Na_2O were analyzed by distilling off the Na, contained in a Ni crucible, in an Ar atmosphere under reduced pressure. The distillation was performed at 723–753 K for 3–3.5 h; these were the most optimal conditions. The crucible with Na_2O was cooled for 1.25–1.5 h. O content was found by titration of Na_2O solution with an acid in presence of indicator changing its color at pH $=5$.

Source and Purity of Materials:
NaOH: nothing specified; decomposed in Na at high temperature.
Na: contained $(2-3)\cdot 10^{-4}$ % O.
Ar: purified from traces of O.

Estimated Error:
Solubility: precision ±10%; reading-out procedure ±3%.
Temperature: nothing specified; reading-out procedure ±2 K.

References:
[1]G. Ilincev, Kernenergie **18**, 69–75 (1975).

Components:
(1) Oxygen; O; [7782-44-7]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
K. Takeda, K. Itoh, T. Mizutani, T. Wada, S. Takani, and H. Atsumo, Fall Meeting of the Atom. Energy Society of Japan, Preprint D52 (1975).

Variables:
Temperature: 423–523 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data
The solubility of O in Na was determined. The values were presented in a figure and read out by the compilers.

t/°C	Solubility/mass % O	Solubility/mol % O[a]
150	$1.87\cdot 10^{-4}$, $2.2\cdot 10^{-4}$, $2.5\cdot 10^{-4}$, $2.6\cdot 10^{-4}$, $3.1\cdot 10^{-4}$, $3.2\cdot 10^{-4}$, $3.3\cdot 10^{-4}$, $3.4\cdot 10^{-4}$, $3.7\cdot 10^{-4}$, $4.0\cdot 10^{-4}$, $4.2\cdot 10^{-4}$, $4.8\cdot 10^{-4}$, $5.1\cdot 10^{-4}$	$(4.9\pm 1.7)\cdot 10^{-4}$
200	$7.8\cdot 10^{-4}$, $8.5\cdot 10^{-4}$, $9.3\cdot 10^{-4}$, $9.4\cdot 10^{-4}$, $1.1\cdot 10^{-3}$, $1.24\cdot 10^{-3}$, $1.29\cdot 10^{-3}$, $1.42\cdot 10^{-3}$	$(1.53\pm 0.26)\cdot 10^{-3}$
250	$3.4\cdot 10^{-3}$, $3.6\cdot 10^{-3}$, $3.9\cdot 10^{-3}$, $4.2\cdot 10^{-3}$, $4.4\cdot 10^{-3}$, $4.7\cdot 10^{-3}$	$(5.8\pm 0.6)\cdot 10^{-3}$

[a]Mean values, calculated by the compilers.

The results were also expressed by the equation:

$$\log(\text{soly/mass \% O}) = 2.118 - 2383\ (T/\text{K})^{-1}.$$

The compilers tested the equation.

Auxiliary Information

Method:
Na samples from a stainless steel loop in equilibrium with a cold trap were obtained with a dipping Ni cup through a gate valve at constant temperature. Na was distilled off from the nonvolatile Na_2O in an in-line distillation apparatus made of stainless steel. The residue of Na_2O in the crucible was dissolved in H_2O and determined by flame photometry. The sampling was performed in an Ar atmosphere and the distillation in vacuum (below 0.1 Pa) at a temperature below 773 K.

Source and Purity of Materials:
Na_2O: nothing specified, as precipitated in the cold trap.
Na: nuclear grade purity.
H_2O: nothing specified.
Ar: nothing specified.

Estimated Error:
Solubility: Reading-out procedure ±2%; standard deviation between ±10% and 30%.
Temperature: Stability and precision ±2 K.

Components:
(1) Oxygen; O; [7782-44-7]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
M. de la Torre Cabezas, Junta Ener. Nucl. Rep. JEN-310 (1975).

Variables:
Temperature: 398–573 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data
The solubility of O in Na was determined

t/°C	Solubility/mass % O	Solubility/mol % O[a]
125	$2.9\cdot10^{-4}$, $2.6\cdot10^{-4}$, $2.4\cdot10^{-4}$, $2.4\cdot10^{-4}$, $1.8\cdot10^{-4}$, $1.7\cdot10^{-4}$, $1.6\cdot10^{-4}$, $1.6\cdot10^{-4}$, $1.2\cdot10^{-4}$	$(2.9\pm0.7)\cdot10^{-4}$
150	$4.8\cdot10^{-4}$, $4.6\cdot10^{-4}$, $4.4\cdot10^{-4}$, $4.4\cdot10^{-4}$, $4.2\cdot10^{-4}$, $4.1\cdot10^{-4}$, $4.0\cdot10^{-4}$, $3.8\cdot10^{-4}$, $3.8\cdot10^{-4}$, $3.5\cdot10^{-4}$, $3.5\cdot10^{-4}$, $3.3\cdot10^{-4}$, $3.1\cdot10^{-4}$, $3.0\cdot10^{-4}$, $3.0\cdot10^{-4}$, $2.6\cdot10^{-4}$, $2.4\cdot10^{-4}$, $2.2\cdot10^{-4}$, $2.2\cdot10^{-4}$	$(5.0\pm1.0)\cdot10^{-4}$
175	$1.05\cdot10^{-3}$, $1.05\cdot10^{-3}$, $1.05\cdot10^{-3}$, $7.6\cdot10^{-4}$, $4.8\cdot10^{-4}$, $4.7\cdot10^{-4}$, $3.8\cdot10^{-4}$, $3.1\cdot10^{-4}$, $3.0\cdot10^{-4}$, $2.9\cdot10^{-4}$, $2.4\cdot10^{-4}$	$(8.3\pm5.0)\cdot10^{-4}$
200	$1.35\cdot10^{-3}$, $1.35\cdot10^{-3}$, $1.35\cdot10^{-3}$, $1.32\cdot10^{-3}$, $1.32\cdot10^{-3}$, $1.32\cdot10^{-3}$, $1.20\cdot10^{-3}$, $1.18\cdot10^{-3}$, $1.17\cdot10^{-3}$, $1.16\cdot10^{-3}$, $1.12\cdot10^{-3}$, $1.09\cdot10^{-3}$, $1.05\cdot10^{-3}$, $1.05\cdot10^{-3}$, $1.05\cdot10^{-3}$, $1.05\cdot10^{-3}$, $1.04\cdot10^{-3}$, $9.8\cdot10^{-4}$, $9.8\cdot10^{-4}$, $9.8\cdot10^{-4}$, $9.4\cdot10^{-4}$, $9.0\cdot10^{-4}$, $8.3\cdot10^{-4}$	$(1.61\pm0.22)\cdot10^{-3}$
225	$2.9\cdot10^{-3}$, $2.8\cdot10^{-3}$, $2.1\cdot10^{-3}$, $2.1\cdot10^{-3}$, $1.65\cdot10^{-3}$, $1.54\cdot10^{-3}$, $1.50\cdot10^{-3}$, $1.50\cdot10^{-3}$	$(2.9\pm0.7)\cdot10^{-3}$
250	$3.6\cdot10^{-3}$, $3.6\cdot10^{-3}$, $3.2\cdot10^{-3}$, $3.1\cdot10^{-3}$, $3.0\cdot10^{-3}$, $2.9\cdot10^{-3}$, $2.8\cdot10^{-3}$, $2.7\cdot10^{-3}$	$(4.4\pm0.5)\cdot10^{-3}$
300	$1.10\cdot10^{-2}$, $7.9\cdot10^{-3}$, $7.3\cdot10^{-3}$, $6.9\cdot10^{-3}$, $6.8\cdot10^{-3}$, $6.4\cdot10^{-3}$, $6.2\cdot10^{-3}$, $6.1\cdot10^{-3}$, $6.1\cdot10^{-3}$	$(7.1\pm1.0)\cdot10^{-3}$
300[b]	$1.21\cdot10^{-2}$, $1.38\cdot10^{-2}$, $9.2\cdot10^{-3}$, $9.2\cdot10^{-3}$, $1.04\cdot10^{-2}$, $1.44\cdot10^{-2}$, $1.35\cdot10^{-2}$, $1.55\cdot10^{-2}$, $1.55\cdot10^{-2}$, $1.32\cdot10^{-2}$, $1.66\cdot10^{-2}$, $1.66\cdot10^{-2}$, $1.06\cdot10^{-2}$, $1.66\cdot10^{-2}$, $1.38\cdot10^{-2}$, $9.7\cdot10^{-3}$, $9.5\cdot10^{-3}$	$(1.86\pm0.40)\cdot10^{-2}$

[a]Mean value calculated by the compilers.
[b]New results at this temperature.

The results were also expressed by the equations:

$$\log(\text{soly/mass \% O}) = 1.389 - 2056\ (T/\text{K})^{-1},$$

taking into account the old results at 300 °C and

$$\log(\text{soly/mass \% O}) = 2.17 - 2398\ (T/\text{K})^{-1},$$

taking into account the new results at 300 °C. Both equations were tested by the compilers. Na_2O is the equilibrium solid phase.

Auxiliary Information

Method:
The experiments were performed in a loop made of AISI 304 stainless steel through which liquid Na circulated. The loop had a hot zone, a cold trap, a container and a pump. The temperature was measured using Fe/Co thermocouples. Na was equilibrated in the cold trap compartment for 8–10 h. Na samples were vacuum distilled, and the residues were analyzed for the O contents by acid titration.

Source and Purity of Materials:
Na_2O: nothing specified, as precipitated in the cold trap.
Na: nuclear grade purity.

Estimated Error:
Solubility: standard deviation less than ±29%.
Temperature: stability and precision ±1 K.

Components:
(1) Oxygen; O; [7782-44-7]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
H. Katsuta and K. Furukawa, Nucl. Technol. **31**, 218–231 (1976).

Variables:
Temperature: 388–473 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data
The solubility of O in liquid Na was reported in a figure. The data were read from the figure and recalculated to mol % O by the compilers.

t/°C	Solubility/mass % O	Solubility/mol % O
115	$1.92\cdot10^{-4}$, $2.4\cdot10^{-4}$	$2.8\cdot10^{-4}$, $3.4\cdot10^{-4}$
118	$2.1\cdot10^{-4}$, $3.0\cdot10^{-4}$	$3.0\cdot10^{-4}$, $4.3\cdot10^{-4}$
127	$2.5\cdot10^{-4}$, $2.0\cdot10^{-4}$, $2.1\cdot10^{-4}$, $2.3\cdot10^{-4}$	$3.6\cdot10^{-4}$, $2.9\cdot10^{-4}$, $3.0\cdot10^{-4}$, $3.3\cdot10^{-4}$
130	$2.5\cdot10^{-4}$, $3.0\cdot10^{-4}$	$3.6\cdot10^{-4}$, $4.3\cdot10^{-4}$
138	$3.2\cdot10^{-4}$, $3.7\cdot10^{-4}$	$4.6\cdot10^{-4}$, $5.3\cdot10^{-4}$
140	$3.5\cdot10^{-4}$, $4.1\cdot10^{-4}$	$5.0\cdot10^{-4}$, $5.9\cdot10^{-4}$
162	$4.4\cdot10^{-4}$, $4.0\cdot10^{-4}$, $5.1\cdot10^{-4}$, $5.9\cdot10^{-4}$	$6.3\cdot10^{-4}$, $5.7\cdot10^{-4}$, $7.3\cdot10^{-4}$, $8.4\cdot10^{-4}$
182	$6.2\cdot10^{-4}$	$8.9\cdot10^{-4}$
183	$6.4\cdot10^{-4}$	$9.2\cdot10^{-4}$
184	$6.7\cdot10^{-4}$	$9.6\cdot10^{-4}$
195	$9.6\cdot10^{-4}$, $9.6\cdot10^{-4}$	$1.38\cdot10^{-3}$, $1.38\cdot10^{-3}$
200	$9.6\cdot10^{-4}$, $9.6\cdot10^{-4}$	$1.38\cdot10^{-3}$, $1.38\cdot10^{-3}$

Auxiliary Information

Method:
The determinations were performed in a Na loop made of 304 type stainless steel. The source of O was unspecified. The activity of O was measured with an electrochemical oxygen meter containing a ThO_2–Y_2O_3 (15 mass %) solid electrolyte tube with a Cu_2O/Cu reference electrode. The O activity in Na at 573 K was measured as a function of the cold trap temperature. The response of the reading to changes of the O concentration in liquid Na was proven to be reproducible and in agreement with the theoretical calculations. The solubility was calculated from equations relating the potential reading on O concentration.

Source and Purity of Materials:
O: nothing specified.
Na: reactor grade purity; purified by cold trapping and hot trapping (with Zr foil), contained $1\cdot10^{-5}$ % O.
Ar: nothing specified.

Estimated Error:
Solubility: nothing specified; reading-out procedure ±3%.
Temperature: precision ±1 K; reading-out procedure ±1 K.

Components:
(1) Oxygen; O; [7782-44-7]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
H. Sundermann and V. Schauer, Microchim.Acta, Suppl. **7**, 575–596 (1977).

Variables:
Temperature: 371–673 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of O in Na was reported in a figure as a smooth line. Temperature values for selected concentrations were read from the figure, and concentrations were recalculated to mol % O by the compilers.

t/°C	Solubility/mass % O	Solubility/mol % O
97.8	$5.5\cdot10^{-5}$ [a]	$7.9\cdot10^{-5}$
120	$1.00\cdot10^{-4}$	$1.43\cdot10^{-4}$
147	$2.5\cdot10^{-4}$	$3.6\cdot10^{-4}$
171	$5.0\cdot10^{-4}$	$7.2\cdot10^{-4}$
185	$7.5\cdot10^{-4}$	$1.08\cdot10^{-3}$
195	$1.00\cdot10^{-3}$	$1.43\cdot10^{-3}$
232	$2.5\cdot10^{-3}$	$3.6\cdot10^{-3}$
266	$5.0\cdot10^{-3}$	$7.2\cdot10^{-3}$
286	$7.5\cdot10^{-3}$	$1.08\cdot10^{-2}$
303	$1.00\cdot10^{-2}$	$1.43\cdot10^{-2}$
362	$2.5\cdot10^{-2}$	$3.6\cdot10^{-2}$
400	$5.5\cdot10^{-2}$ [a]	$7.9\cdot10^{-2}$

[a]Extrapolated.

The same results were reported in Schauer.[1] The authors proposed the following solubility equation:

$$\log(\text{soly/mass \% O}) = 2.315 - 2480\ (T/\text{K})^{-1}.$$

Auxiliary Information

Method:
Potentiometric measurements of the O concentrations in liquid Na were conducted in the cell: Ni, Na, $Na_2O/ThO_2+10\%\ Y_2O_3/Cu_2O$, Cu, Pt, after coulometric titration of O. A Ni tube was filled with the $Na–Na_2O$ mixture. The yttria doped thoria tube contained the $Cu–Cu_2O$ reference electrode. The tube was dipped into the $Na–Na_2O$ mixture which was kept under dry Ar. The reference electrode was kept under constant partial pressure of O. The temperature was measured with a sheathed Pt/Pt–Rh thermocouple. The Ni tube was heated in a furnace. Concentrations of O were changed by means of coulometric electrolysis. Potentials of saturated and unsaturated melts were recorded as function of temperature. Saturation points were determined from the intersection of the lines.

Source and Purity of Materials:
O: from electrolysis.
Na: nothing specified.
Ar: purified on BTS catalyst (from BASF) at 473 K. H_2O was precipitated in liquid air. The O partial pressure was 10^{-6} Pa.

Estimated Error:
Solubility: nothing specified; not better than ±5% (by the compilers).
Temperature: nothing specified; read-out procedure ±0.5 K.
Potential: reproducibility ±2 mV.

References:
[1]V. Schauer, PhD thesis, University of Vienna, Austria, 1976.

Components:
(1) Oxygen; O; [7782-44-7]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
J. S. Hislop, R. Thompson, and D. A. Wood, *Analysis of Non-Metals in Metals*, edited by G. Kraft (de Gruyter, Berlin, 1981), pp. 321–330.

Variables:
Temperature: 398–523 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of O in liquid Na was determined

t/°C	Solubility/mass % O	Solubility/mol % O [a]
125	$(4.4\pm2)\cdot10^{-4}$	$(6.3\pm3)\cdot10^{-4}$
150	$(7.7\pm1.7)\cdot10^{-4}$, $(16\pm2)\cdot10^{-3}$ [b]	$(1.11\pm0.24)\cdot10^{-3}$
175	$(1.15\pm0.2)\cdot10^{-3}$; $(1.27\pm0.13)\cdot10^{-3}$	$(1.74\pm0.24)\cdot10^{-3}$
200	$(2.0\pm0.2)\cdot10^{-3}$; $(1.6\pm0.16)\cdot10^{-3}$	$(2.6\pm0.2)\cdot10^{-3}$
225	$(2.74\pm0.18)\cdot10^{-3}$; $(1.75\pm0.11)\cdot10^{-3}$ [b]	$(4.0\pm0.3)\cdot10^{-3}$
250	$(5.2\pm0.5)\cdot10^{-3}$; $(4.5\pm0.5)\cdot10^{-3}$	$(6.9\pm0.5)\cdot10^{-3}$

[a]Mean value calculated by the compilers.
[b]These values were neglected in the formulation of the solubility equation by the authors.

The compilers confirmed the proposed solubility equation:

$$\log(\text{soly/mass \% O}) = (0.997\pm0.016) - (1754\pm88)\ (T/\text{K})^{-1}.$$

The results were also reported in Hislop *et al.*[1]

Auxiliary Information

Method:
An experimental Na rig was made of stainless steel. A sample container consisted of a Ni tube. After degreasing, the tube was fired at 993 K for 4 h in an Ar–H(4%) atmosphere and at 1023 K for 12 h under vacuum. The tube being connected with a syringe was attached to the apparatus. The tube was lowered into Na and the molten Na sucked into the Ni tube. The tube was withdrawn and Na allowed to solidify. Pieces of the sampling tube were irradiated in a 30 MeV accelerator for 4 min. The end portions of Na were removed using side cutters and the remaining central portion, after cutting into small pieces, was dissolved in 10 mol/dm^3 NaOH solution. ^{15}O was chemically separated by distillation and its radiation counted in a detector after 6 min from end of the irradiation.

Source and Purity of Materials:
O: nothing specified.
Na: nuclear grade of purity.
Ar: with "low O and H_2O content."

Estimated Error:
Solubility: detection limit $7\cdot10^{-5}$ mol % O; precision of ±6% to ±45%.
Temperature: nothing specified.

References:
[1]J. S. Hislop, R. Thompson, and D. A. Wood, Atom. Ener. Res. Establ. Rep. M-3097 (1981).

Components:
(1) Oxygen; O; [7782-44-7]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
R. S. Fidler and R. Saagi, Nucl. Ener. **23**, 385–398 (1984).

Variables:
Temperature: 393–523 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of O in liquid Na was determined during crystallization behavior of Na_2O. The data were presented on either crystallization runs or a smooth solubility curve; the data were read out from figures and recalculated to mol % O by the compilers.

T/°C	Solubility/mass % O	Solubility/mol % O
129[a]	$1.30\cdot10^{-4}$	$1.87\cdot10^{-4}$
120	$1.25\cdot10^{-4}$	$1.80\cdot10^{-4}$
140	$2.5\cdot10^{-4}$	$3.6\cdot10^{-4}$
160	$4.8\cdot10^{-4}$	$6.9\cdot10^{-4}$
180	$8.4\cdot10^{-4}$	$1.21\cdot10^{-3}$
200	$1.35\cdot10^{-3}$	$1.9\cdot10^{-3}$
250	$4.0\cdot10^{-3}$	$5.7\cdot10^{-3}$

[a]From the crystallization run.

The mutual influence on activity of O and H present in Na was established. A formation of OH entity or a higher order product is possible.

Auxiliary Information

Method:
The experiments were performed in a Na filled loop for monitoring the Na purity. The facility consisted of a mother loop which supplied Na to one subloop. The subloop comprised a cold trap, a plugging meter, and an electrochemical meter for O. Probably Na_2O was introduced into the loop. The temperature was raised and Na circulated isothermally at 673 K to obtain a high concentration of O. The plugging meter run started from conditions of equal flows. The electrochemical meters were calibrated. While the plug developed, the meters monitored changes in the O concentration resulting from the plug formation and dissolution. Saturation levels were measured during stable partial plugging within the subloop.

Source and Purity of Materials:
Na_2O: nothing specified.
Na: nuclear grade of purity from GEC Whetstone.

Estimated Error:
Solubility: nothing specified; reading out procedure ±1%.
Temperature: stability ±2.5 K; reading-out procedure ±1 K.

Components:
(1) Oxygen; O; [7782-44-7]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
C. A. Smith and P. A. Simm, *Liquid Metals Engineering and Technology* (BNES, London, 1984), Vol. **3**, pp. 103–109.

Variables:
Temperature: 433–598 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of O in liquid Na was measured

T/°C	Solubility/mass % O[a]	Solubility/mass % O[b]	Solubility/mol % O[b,c]
160	$1.14\cdot10^{-3}$	$1.34\cdot10^{-3}$	$1.93\cdot10^{-3}$
200	$2.5\cdot10^{-3}$	$3.3\cdot10^{-3}$	$4.7\cdot10^{-3}$
250	$5.9\cdot10^{-3}$	$7.3\cdot10^{-3}$	$1.05\cdot10^{-2}$
275	$1.08\cdot10^{-2}$	$1.26\cdot10^{-2}$	$1.81\cdot10^{-2}$
300	$1.21\cdot10^{-2}$	$1.50\cdot10^{-2}$	$2.16\cdot10^{-2}$
325	$1.92\cdot10^{-2}$	$2.22\cdot10^{-2}$	$3.2\cdot10^{-2}$

[a]Idealized solubility.
[b]True solubility.
[c]Calculated by the compilers.

The authors derived the solubility equations for the "idealized" (1), "true" (2), and cold trap experiments (3) at 393–673 K.

$$\log(\text{soly/mass \% O}) = (1.52\pm0.12) - (1940\pm65)\ (T/\text{K})^{-1}, \quad (1)$$

$$\log(\text{soly/mass \% O}) = (1.52\pm0.09) - (1900\pm45)\ (T/\text{K})^{-1}, \quad (2)$$

$$\log(\text{soly/mass \% O}) = 1.41 - 1913\ (T/\text{K})^{-1}. \quad (3)$$

The compilers confirmed the validity of the first two equations.

Auxiliary Information

Method:
The concentration of O in liquid Na was traced with the use of the oxygen meter cell: In, In_2O_3 /ThO_2–Y_2O_3(7.5%)/Na–Na_2O. Valves and the walls of the vessel in the gas spaces above Na were maintained at a temperature ~15 K higher than that of Na to prevent condensation of Na. O gas was added to Na in a special apparatus. After the reaction the vessel was maintained under vacuum through the experiments. The oxygen meter was installed in a module, containing a regenerative heat exchanger. Na was pumped through the module. Prior to the calibration the vessel was hot trapped. The Na temperature was adjusted to the required value and the hot trap isolated. The calibrations were made at selected temperatures. The emf of the cell was noted periodically to reach stable potential values within 0.1 mV for 1.5–7 h. On addition of O, the emf decreased until saturation was achieved with a constant emf value. Small deviations from the Henry's law were observed at concentrations close to the saturation and thus two solubility data could be derived: one relating to an idealized (Henrian solubility) and the other to an estimated true solubility. No details related to the cold trap experiments were reported.

Source and Purity of Materials:
O: nothing specified.
Na: nuclear purity from Culcheth Nuclear Lab., distilled and hot trapped by U and Y foil. The final O concentration $<1.10^{-5}$ mol % O.
ThO_2–Y_2O_3(7.5%): from Zircoa Division Cohart Refractories Co.

Estimated Error:
Solubility: precision better than ±30%.
Temperature: precision ±1 K.
Potential: precision ±0.1 mV.

Components:
(1) Oxygen; O; [7782-44-7]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
R. Sridharam, T. Gnanasekaran, G. Periaswami, and C. K. Mathews, *Liquid Metal Systems*, edited by H. U. Borgstedt and G. Frees (Plenum, New York, 1995), pp. 269–277.

Variables:
Temperature: 585 and 626 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of O in liquid Na was determined. The data were read from a figure and recalculated to mol % O.

T/K	Solubility/mass % O	Solubility/mol % O
585	$1.4\cdot10^{-2}$	$2.0\cdot10^{-2}$
626	$2.2\cdot10^{-2}$	$3.2\cdot10^{-2}$

In fact, Fe_2O_3 was equilibrated with liquid Na but in these experimental conditions the reaction products were Na saturated with Na_2O and Fe.

Auxiliary Information

Method:
An excess of liquid Na was equilibrated with Fe_2O_3 in a Ni container at desired temperature. A sample of Na was taken after filtration through a fine Ni filter and the Na excess was distilled off under vacuum. The Na_2O residue was analyzed for its Na content by atomic absorption spectroscopy and correlated to the concentration of dissolved O.

Source and Purity of Materials:
Fe_2O_3 : nothing specified; probably from Fisher Scientific Co. as in Sridharan *et al.*[1]
Na: nuclear grade of purity, cold trapped at ~400 K in an inert atmosphere Sridharan *et al.*[1]

Estimated Error:
Solubility: nothing specified; reading-out procedure $\pm2.10^{-3}$ mol % O.
Temperature: precision ±1 K; reading-out procedure ±2 K.

References:
[1]R. Sridharan, T. Gnanasekaran, and C. K. Mathews, J. Alloys Compd. **191**, 9–13 (1993).

4.12. Sodium–Sodium Hydroxide

Components:
(1) Sodium hydroxide; NaOH; [1310-73-2]
(2) Sodium; Na; [7440-23-5]

Evaluated By:
Hans Ulrich Borgstedt, Forschungszentrum Karlsruhe, Germany and Cezary Guminski, University of Warsaw, Poland, December 1999.

Critical Evaluation

In the first report related to this system,[1] an abnormal decrease of the NaOH solubility in liquid Na from 30.6 to 10.7 mol % Na was observed with temperature increasing from 753 to 1073 K. Williams *et al.*[2–4] measured the solubility of NaOH in liquid Na which increased from $6\cdot10^{-3}$ mol % at 383 K to $6\cdot10^{-2}$ mol % at 623 K. The authors observed that a solubility of NaOH and Na_2O mixture was slightly lower than that of pure NaOH at all experimental temperatures. The investigators demonstrated that NaOH and Na reacted at temperatures ⩾593 K (the melting point of NaOH) with formation of Na_2O and NaH:

$$2\ Na + NaOH \leftrightarrow Na_2O + NaH. \tag{1}$$

Bannykh and Fefelova[5] determined the solubility of NaOH in liquid Na contaminated with Na_2O. The solubility increased from $9\cdot10^{-3}$ to 0.138 mol % NaOH in the temperature range 373–653 K. A more detailed study of the NaOH–Na system was attempted by Mitkevich and Shikhov,[6,7] who measured the mutual solubilities of the components as well as the H pressure over the molten system and analyzed the equilibrium solid phases by chemical and x-ray diffraction analysis. The measured solubility of NaOH in Na was several times higher than measured by Williams *et al.*[2–4] The composition of the NaOH phase changed in the temperature range 681–913 K: Na_2O—from 5.1 to 15.4 mol % NaH—from 28.7 to 7.4 mol %, and NaOH—from 66.2 to 77.2 mol %. This confirmed the reaction equilibria discovered by Williams *et al.*[2–4] and formulated by Eq. (1). The H pressure over the system with less than 62.5 mol % NaOH was constant at ~26 kPa which was confirmed in the subsequent studies. Subbotin *et al.*[8–10] measured the solubility of the reaction products of H_2O with Na:

$$Na + H_2O \leftrightarrow NaOH + 1/2\ H_2\,. \tag{2}$$

The reaction expressed by Eq. (2) may be partly complicated by a subsequent reaction:

$$2\ Na + H_2 \leftrightarrow 2\ NaH. \tag{3}$$

Practically, the process described by Eq. (3) is dependent on temperature and time of conditioning but its equilibrium was never observed to be moved completely to the right side. Thus in the experimental conditions of Subbotin *et al.*,[8–10] the solubility of NaOH contaminated by NaH was measured between 497 and 593 K. In a separate experiment the authors found that at 723 K the concentration of NaOH was ~100 times lower than concentrations of Na_2O and NaH. This suggested that the equilibrium of Eq. (1) at this temperature is strongly moved to the right side. However, it was also observed by many investigators that H and O strongly interact in Na medium.[11–14] The solubility of NaOH as well as of the reaction products of H_2O with Na were measured by Kozlov *et al.*[15] in the temperature range 439–583 K. The authors experienced a large scatter of the solubility results, however the mean results at lower temperatures were lower than these observed by Williams *et al.*,[2–4] whereas at higher temperatures a reverse situation was observed. Moreover, the authors observed that, if Na and NaOH were heated to 673–723 K and subsequently cooled to the test temperature, the solubilities determined were lower than those measured without the heat treatment. This was more evidence of the NaOH decomposition at higher temperatures. Anyway, the solubility of NaOH is certainly higher than the separate solubilities of H and O in Na pointing on strong interaction between these elements in the liquid Na medium. According to thermodynamic predictions of Jansson,[16] at temperatures <683 K, the NaH and Na_2O mixture is the equilibrium solid and at temperatures >683 K, NaOH is the equilibrium solid phase with the saturated solution in liquid Na. Myles and Cafasso,[17] Privalov,[18,19] and Maupré[20] performed thermal, calorimetric, chemical, and x-ray diffraction analyses of the NaOH–Na system in the whole composition range. Plenty of thermal arrests were observed which allowed to formulate the most convincing NaOH–Na phase diagram by Privalov.[21] The following phases can exist in the Na–O–H system (of which the NaOH–Na system is the particular case): liquid Na containing dissolved NaOH, NaH, and Na_2O; liquid NaOH countering Na, NaH, and Na_2O the composition of which varies with temperature and H gas pressure; solid solutions based on NaOH, NaH, and Na_2O and gaseous H. In addition to Eqs. (1) and (3), the following reversible reactions between the components should be taken into account:

$$Na + NaOH \leftrightarrow Na_2O + 1/2\ H_2\,, \tag{4}$$

$$Na_2O + H_2 \leftrightarrow NaH + NaOH. \tag{5}$$

Whittingham[22] pointed out that a precise estimation of the boundary lines in the phase diagram is still not possible, since all mutual solubilities in these multicomponent solutions are not precisely known. Knight and Whittingham,[23] Henry *et al.*,[24] and Veleckis and Leibowitz[25] measured equilibrium pressures of H over the NaOH–Na condensed system confirming the observations of Williams[3] and Mitkevich and Shikhov[6] and formulated a supplementary pressure–temperature diagram to the composition–temperature diagram. Krasin[26] derived a theoretical equation relating the H pressure over Na–O–H melts. Privalov[21] constructed the NaOH–Na phase diagram at 0.12 MPa based on experimental data[7,18,27] and his own thermodynamic calculations. The diagram is reflected in Fig. 24. The α-NaOH↔β-NaOH phase transition was observed at 530 K;[18,24,28] the temperature is sensitive to H_2O and CO_2 as impurities).[24] Myles and Cafasso[17] and Maupré[20] proposed a similar diagram with an eutectic point on the NaOH-rich side instead of the peritectic suggested by Privalov.[21] The matter needs a clarification. Gnanasekaran[30] reviewed briefly the NaOH–Na system and plotted the projection of the phase relations in the ternary Na–O–H system at several temperatures. According to Ullmann's analysis[29] of the solubility results, the data of Williams *et al.*[2–4] are the most reliable in the temperature range 373–623 K and may be expressed by the equation:

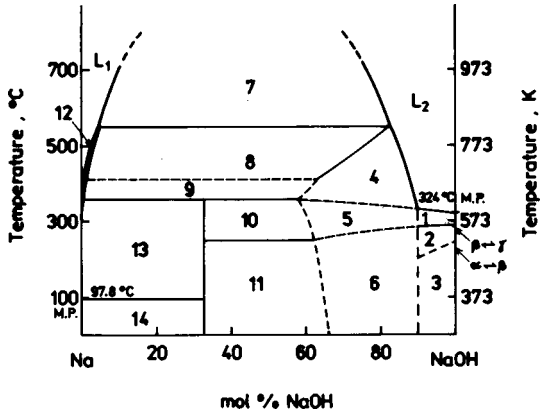

FIG. 24. Na–NaOH phase diagram at 0.12 MPa.

$$\log(\text{soly/mol \% NaOH}) = 0.74 - 1190(T/\text{K}). \quad (6)$$

At temperatures higher than 800 K the temperature dependence of the NaOH solubility in liquid Na is more steep. Kinetics of the reaction of NaOH with Na was investigated by Noud,[31] Kozlov *et al.*,[32] and Whittingham *et al.*[33]

1—(γ-NaOH), 2—(β-NaOH), 3—(α-NaOH), 4—L_2+Na_2O, 5—γ-NaOH+Na_2O, 6—β-NaOH+Na_2O, 7—L_1+L_2, 8—$L_1+L_2+Na_2O$, 9—$L_1+L_2+Na_2O$, 10—Na_2O+NaH+γ-NaOH, 11—Na_2O+NaH+β-NaOH, 12—L_1+Na_2O, 13—L_1+NaH+Na_2O, 14—(Na)+NaH+Na_2O; other details are thinner than the line thickness.

Doubtful values of the solubility of NaOH in liquid Na

T/K	Solubility/mol % NaOH	Source
373	$3\cdot10^{-3}$	Eq. (6), extrapolated
473	$1.7\cdot10^{-2}$	Eq. (6), (2–4)
573	$5\cdot10^{-2}$	Eq. (6), (2–4)
673	$9\cdot10^{-2}$	Eq. (6), extrapolated

Doubtful values of the solubility of Na in liquid NaOH

T/K	Solubility/mol % Na	Source
673	11.2	(20)
773	20.2	(20)
823	22.1	(20)

References:

[1]G. von Hevesy, Z. Elektrochem. **15**, 529 (1909).
[2]A. D. Bogard and D. D. Williams, Naval Res. Labor. Rep. NRL-3865 (1951).
[3]D. D. Williams, Naval Res. Labor. Rep. NRL-Memo-33 (1951).
[4]D. D. Williams, J. A. Grand, and R. R. Miller, J. Phys. Chem. **63**, 68 (1959).
[5]Z. S. Bannykh and G. F. Fefelova, Tr. Ural. Nauch.-Issled. Inst. **5**, 105 (1957)
[6]E. M. Mitkevich and B. A. Shikhov, Zh. Neorg. Khim. **11**, 633 (1966); Russ. J. Inorg. Chem. **11**, 343 (1966).
[7]E. M. Mitkevich and B. A. Shikhov, Zh. Neorg. Khim. **11**, 639 (1966); Russ. J. Inorg. Chem. **11**, 346 (1966).
[8]V. I. Subbotin, F. A. Kozlov, E. K. Kuznetsov, and M. N. Ivanovskii, *Alkali Metal Coolants* (IAEA, Vienna, 1967), p. 461.
[9]V. I. Subbotin, M. N. Ivanovskii, and M. N. Arnoldov, *Fiziko-Khimicheskie Osnovy Primeneniya Zhidkometallicheskikh Teplonositelei* (Atomizdata, Moskva, 1970), p. 66.
[10]Yu. E. Bagdasarov, *Tekhnicheskie Problemy Reaktorov na Bystrykh Neitronakh* (Atomizdat, Moskva, 1969), p. 107.
[11]B. Minushkin and G. Kissel, *Chemical Aspects of Corrosion and Mass Transfer in Liquid Sodium* (AIME, New York, 1971), p. 333.
[12]R. J. Pulham and P. A. Simm, *Liquid Alkali Metals* (BNES, London, 1973), p. 1.
[13]R. S. Fidler and R. Saagi, Nucl. Energy **23**, 385 (1984).
[14]H. Ullmann, K. Teske, F. A. Kozlov, and E. K. Kuznetsov, Akad. Wissensch. DDR Rep. ZfK-337, p. 16 (1977).
[15]F. A. Kozlov, E. K. Kuznetsov, G. P. Sergeev, L. G. Volchkov, and V. Zotov, *Trudy Fiziko-Khimicheskogo Instituta* (Atomizdat, Moskva, 1974), p. 290.
[16]S. A. Jansson, *Corrosion by Liquid Metals*, edited by J. E. Draley and J. R. Weeks (Plenum, New York, 1970), p. 523.
[17]K. M. Myles and F. A. Cafasso, J. Nucl. Mater. **67**, 249 (1977).
[18]Yu. V. Privalov, Akad. Wissensch. DDR Rep. ZfK-337, p. 7 (1971).
[19]Yu. V. Privalov, Nauch. Issled. Inst. Atom. Reakt. Rep. NIIAR R-6 (300), (1977); transl. Forschungszentrum Karlsruhe, Rep. KfK-tr-683 (1982).
[20]J. P. Maupré, Comm. Ener. Atom. (Fr.) Rep. CEA-R-4905 (1978).
[21]Yu. V. Privalov, Atom. Energiya **48**, 108 (1980).
[22]A. C. Whittingham, Centr. Ener. Gener. Board Rep. RD/B/N-2546 (1973).
[23]C. F. Knights and A. C. Whittingham, *Material Behavior and Physical Chemistry Systems*, edited by H. U. Borgstedt (Plenum, New York, 1982), p. 375.
[24]J.-L. Henry, S. A. O'Hare, and M. P. Krug, U.S. Atom. Energy Comm. Rep. USBM-1532 (1971).
[25]E. Veleckis and L. Leibowitz, J. Nucl. Mater. **144**, 235 (1987).
[26]V. P. Krasin, Zh. Fiz. Khim. **66**, 449 (1992).
[27]B. A. Shikhov, Zh. Neorg. Khim. **12**, 1035 (1967); Russ. J. Inorg. Chem. **12**, 545 (1967).
[28]E. M. Levin and H. F. McMurdie, *Phase Diagrams for Ceramists* (American Ceramic Society, Columbus, 1975), Vol. 3.
[29]H. Ullmann, *Material Behavior and Physical Chemistry in Liquid Metal Systems*, edited by H. U. Borgstedt (Plenum, New York, 1982), p. 375.
[30]T. Gnanasekaran, J. Nucl. Mater. **274**, 252 (1999).
[31]G. Noud, U.K. Atom. Ener. Author. Rep. TRG-Int. Ser. - 522 (C), (1966); Comm. Ener. Atom. (Fr) Rep. CEA-R-2583 (1964).
[32]F. A. Kozlov, G. P. Sergeev, A. R. Sednev, and V. M. Makarov, Atom. Energiya **44**, 88 (1978).
[33]A. C. Whittingham, C. A. Smith, P. A. Simm, and R. J. Smith, U.S. Dept. Energy Rep. CONF-800401 (1980).

Components:
(1) Sodium hydroxide; NaOH; [1310-73-2]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
G. von Hevesy, Z. Elektrochem. **15**, 529–536 (1909).

Variables:
Temperature: 753–1073 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data
The solubility of Na in liquid NaOH was measured

t/°C	Solubility/g Na in 100 g NaOH	Solubility/mol % Na	Na Solubility/mol % NaOH[a]
480	25.3	30.6	69.4
600	10.1	14.9	85.1
610	9.9	14.7	85.3
670	9.5	14.2	85.8
760	7.9	12.1	87.9
800	6.9	10.7	89.3

[a]Calculated by the compilers.

Auxiliary Information

Method:
A Fe tube was filled with NaOH and Na. The tube was closed and heated in an electric furnace up to 60 h at the desired temperature which was measured by means of a Le Chatelier thermocouple. The tube was withdrawn and quickly cooled in H_2O. The tube was then opened under petroleum. The hydroxide and metallic phases were sampled. The Na content was evaluated from a volumetric analysis of H evolved during the reaction of the metallic phase with H_2O. The amount of NaOH was determined through titration with standard HCl solution.

Source and Purity of Materials:
NaOH: dried in a Ni container in a H stream for several hours.
Na: nothing specified.

Estimated Error:
Solubility: nothing specified; several % (by the compilers).
Temperature: nothing specified.

Components:
(1) Sodium hydroxide; NaOH; [1310-73-2]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
Z. S. Bannykh and G. F. Fefelova, Tr. Ural. Nauch.-Issled. Khim. Inst. **5**, 105–117 (1957).

Variables:
Temperature: 373–653 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data
The solubility of NaOH in liquid Na was determined

t/°C	Solubility/mass % O	Mean solubility/mass % O	Solubility/mol % O[a]
100	0.007; 0.005	0.006	0.009
250	0.012; 0.008; 0.010	0.010	0.014
350	0.057; 0.060; 0.057	0.058	0.083
350[b]	0.072; 0.074	0.073	0.105
380	0.102; 0.106; 0.080	0.096	0.138

[a]Calculated by the compilers.
[b]Solid samples were analyzed.

NaOH was contaminated by Na_2O. Therefore, the results were given in mass % O.

Auxiliary Information

Method:
Measurements at ~373 K were performed in a glass container. Mixing and N supplying facilities were introduced into the container. It was thermostated in an oil bath. Na was melted and mixed for 1–5 h. It was covered with Na_2O on the surface from a reaction of O traces in N. NaOH was then added and the melt mixed for 2 h. The measurements at >473 K were performed in a stainless steel container. It was heated by an electric oven regulated by a Chromel/Alumel thermocouple. The molten Na, after NaOH addition, was mixed for 2–8 h. Samples of the liquid Na were quenched and analyzed by multistage extraction of Na by Hg. NaOH (undissolved in Hg) was treated with distilled H_2O and titrated with 0.005 mol/dm^3 HCl in the presence of phenolphthalein. Hg was treated with 1 mol/dm^3 HCl and back titrated with 1 mol/dm^3 NaOH. The solubility of NaOH (with Na_2O traces) was calculated from the amounts of Na_2O and Na found in the analyses.

Source and Purity of Materials:
NaOH: chemically pure; moisture was withdrawn by dissolution in alcohol and its evaporation; contaminated by Na_2O.
Na: 99.7+% pure and contained ~0.01% K and <0.003% Cl; contents of Al, Mg, Ca, Fe, C, Pb, and Cu were negligible. The surface layer of Na was cut off.
N: nothing specified.

Estimated Error:
Solubility: nothing specified; precision better than ±20% (by the compilers).
Temperature: stability between ±3 and 10 K.

Components:
(1) Sodium hydroxide; NaOH; [1310-73-2]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
D. D. Williams, J. A. Grand, and R. R. Miller, J. Phys. Chem. **63**, 68–71 (1959).

Variables:
Temperature: 383–623 K
Unspecified addition of Na_2O

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of NaOH in liquid Na was determined. The results were read from a figure and recalculated to mol % by the compilers.

t/°C	Solubility/mass % O	Solubility/mol % NaOH
110	$4\cdot10^{-3}$	$6\cdot10^{-3}$
150	$6\cdot10^{-3}$	$9\cdot10^{-3}$
200	0.011	0.017
250	0.022	0.032
300	0.031	0.045
350	0.042	0.060

The data were also reported in Bogard and Williams[1] and Williams.[2]

The solubility of mixtures of NaOH and Na_2O in liquid Na was determined. The data were read from a figure by the compilers. Proportions of NaOH and Na_2O were not specified.

t/°C	Solubility/mass % O	Solubility/mol % O
105	$2\cdot10^{-3}$	$3\cdot10^{-3}$
158	$8\cdot10^{-3}$	$1.1\cdot10^{-2}$
250	0.015; 0.017	0.022; 0.024
265	0.018	0.026
340	$3.2\cdot10^{-2}$	$4.6\cdot10^{-2}$
400	$4.2\cdot10^{-2}$	$6.0\cdot10^{-2}$
405	$4.4\cdot10^{-2}$	$6.3\cdot10^{-2}$
410	$4.6\cdot10^{-2}$	$6.6\cdot10^{-2}$

A comparison of the solubility results of Na_2O and Na_2O–NaOH mixtures in liquid Na pointed to a reaction of NaOH and Na with the formation of Na_2O and NaH at temperatures higher than 320 °C (the melting point of NaOH).

Auxiliary Information

Method:
Na was distilled onto NaOH contained in a solubility cell made of Pyrex. The system was heated and equilibrated at selected temperatures. Na was filtered through a filter at a slight N pressure admittance. The filtrate was analyzed by the amalgamation method (addition of Hg in portions to the melt). The residue after the Na amalgam separation was hydrolyzed and titrated with an acid. The solubility in the solute mixture was carried out in the same way.

Source and Purity of Materials:
NaOH: "pure."
Na_2O: nothing specified.
Na: nuclear grade of purity.
N: nothing specified.

Estimated Error:
Solubility: nothing specified; reading-out procedure $\pm1\cdot10^{-4}$ mol %.
Temperature: accuracy ±5 K; reading-out procedure ±3 K.

References:
[1]A. D. Bogard and D. D. Williams, Naval Res. Labor. Rep. NRL-3865 (1951).
[2]D. D. Williams, Naval Res. Labor. Rep. NRL-Memo-33 (1951).

Components:
(1) Sodium hydroxide; NaOH; [1310-73-2]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
E. M. Mitkevich and B. A. Shikhov, Zh. Neorg. Khim. **11**, 633–638 (1966); Russ. J. Inorg. Chem. **11**, 343–346 (1966).

Variables:
Temperature: 593–628 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

Melting temperatures of NaOH phase saturated with Na were determined by two techniques: Ni crucible and a stainless steel apparatus.

t/°C	Solubility/mol % Na	Solubility/mol % NaOH
320	2.0	98.0
330	18.9	81.1
336	20.8	79.2
343	21.9	78.1
340	30.0	70.0
350	33.0; 37.5; 41.1	67.0; 62.5; 58.9
355	41.5	58.5
354	46.3	53.7
350	49.6; 51.0; 58.0; 60.9; 76.4	50.4; 49.0; 42.0; 39.1; 23.6
	Ni barrels and Pyrex glass apparatus	
331	6.8	93.2
343	18.7	81.3
350	30.1	69.9
345	41.6; 50.0	58.4; 50.0
355	65.0	35.0

The melting point of NaOH was observed at 320 °C. The polymorphic transformation of NaOH was observed at 292 °C. Upon addition of Na into NaOH the temperature of transformation decreased to 250 °C. The H pressure over the system at 410–540 °C with a NaOH content lower than 62.5 mol % was constant at a level of 205±5 Torr (0.027 MPa).

Auxiliary Information

Method:
The apparatus that was used up to 973 K was made of stainless steel. NaOH and Na were placed in a Ni crucible. The apparatus that was used up to 773 K was made of Pyrex glass. NaOH and Na were placed in a Ni barrel with 20% of free volume. Normal and differential thermoanalysis were performed three times for each sample. The pressure during the heating and cooling was measured with the use of a Hg manometer. The composition of samples was analyzed by the reaction with H_2O, measuring the H volume developed and titrating the resulting solution with 1 mol/dm^3 HCl. X-ray analysis indicated the presence of Na_2O in solid NaOH.

Source and Purity of Materials:
NaOH: prepared by reaction of Na with H_2O in a N atmosphere, heated at 773 K; H_2O and Na_2CO_3 were not detected.
Na: electrolytical.
N: nothing specified.

Estimated Error:
Solubility: nothing specified; precision not better than ±0.1 mol % (by the compilers).
Temperature: nothing specified; precision better than ±5 K (by the compilers).

Components:
(1) Sodium hydroxide; NaOH; [1310-73-2]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
E. M. Mitkevich and B. A. Shikhov, Zh. Neorg. Khim. **11**, 639–643 (1966); Russ. J. Inorg. Chem. **11**, 346–349 (1966).

Variables:
Temperature: 469–978 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data
The solubility of NaOH in liquid Na was determined

t/°C	Solubility/mol % NaOH	Composition of the solute phase/mol %
196	~0.0	
284	0.1	
343	1.3	
395	0.8	
449	1.7	
520	3.1	Na_2O—10.1; NaH—12.3; NaOH—77.6
545	3.3	
566	10.4	Na_2O—12.4; NaH—9.6; NaOH—78.0
639	8.3	
640	10.7	Na_2O—15.4; NaH—7.4; NaOH—77.2
705	15.8	

It was established in supplementary experiments that the composition of the ''NaOH phase'' changed in the temperature range of 408–640 °C: Na_2O—from 5.1 to 15.4 mol %, NaH—from 28.7 to 7.4 mol % and NaOH—from 66.2 to 77.2 mol %.

Auxiliary Information

Method:
The apparatus was made of stainless steel. It contained a capsule, an internal Ni cup, a mixer, a sampling tube, and a sheath for a Chromel/Copel thermocouple. NaOH and Na were placed in the cup and heated. It was established that the equilibrium was reached within 1.5–2.0 h. Samples of both phases were withdrawn with Cu tubes containing Cu filters inside. They were cooled down and reacted with H_2O. The volume of the liberated H was measured and recalculated for the Na content. The resulting solution was titrated with 1 mol/dm^3 HCl and recalculated for the NaOH content.

Source and Purity of Materials:
NaOH: prepared from Na and H_2O, heated at 773 K.
Na: electrolytic, filtered as molten metal.

Estimated Error:
Solubility: precision in weight ±0.1 mg, corresponding to $\pm 4 \cdot 10^{-6}$ mol Na and $2 \cdot 10^{-5}$ mol NaOH, but the final scatter of results is in the order of a few mol %.
Temperature: stability ±1 K.

Components:
(1) Sodium hydroxide; NaOH; [1310-73-2]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
V. I. Subbotin, F. A. Kozlov, E. K. Kuznetsov, and M. N. Ivanovskii, *Alkali Metal Coolants* (IAEA, Vienna, 1967), pp. 461–478.

Variables:
Temperature: 497–593 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data
The solubility of reaction products of H_2O with Na (NaOH and NaH) were determined. The data were reported in graphical form, also in Bagdasarov[1] and Subbotin *et al.*[2] They were read from a figure and recalculated to mol % NaOH by the compilers.

t/°C	Solubility/mass % O	Solubility/mol % NaOH
224	0.017	0.024
232	0.025	0.036
248	0.031	0.044
249	0.034	0.049
250	0.028	0.040
258	0.051	0.073
264	0.050	0.072
270	0.049	0.070
282	0.061	0.088
284	0.076	0.109
284	0.084	0.121
297	0.085	0.122
300	0.114	0.164
310	0.103	0.148
320	0.112	0.161

The data were approximated using the following equation (tested by the compilers):

$$\log(\text{soly/mass \% O}) = 3.63 - 2650\ (T/\text{K})^{-1} \quad (1)$$

as reported in Bagdasarov.[1] The equation reported in the original paper had the constant in Eq. (1) equal to 3.49 instead of 3.63, leading to smaller O solubility concentrations than experimentally observed. The authors reported that at 450 °C at concentrations of Na_2O and NaH of 0.017 and 0.013 mass %, respectively, the equilibrium concentration of NaOH was only $1.1 \cdot 10^{-4}$ mass % NaOH.

Auxiliary Information

Method:
An amount of O, dissolved in liquid Na and saturating it, was formed in the reaction of Na and H_2O. It was measured by the vacuum distillation method. An apparatus used for the distillation was made of stainless steel and was cleaned with H_2O, C_2H_5OH, then flushed with Ar. It was evacuated down to 1.3 Pa at 773–823 K, then filled with Na containing the reaction products and equilibrated at selected temperature. A separation of the solid from the saturated solution is not known. The sample of saturated solution in Na was placed into the distillation apparatus in a Ni or Mo crucible. The distillation was performed under reduced pressure at 773–873 K for 1–40 h. The deposit left after the distillation was dissolved in H_2O and the resulting solution titrated with an acid. The amount of the Na solvent was estimated from the weight of the distillation condensate.

Source and Purity of Materials:
NaOH: obtained in reaction of Na with H_2O; due to slow reaction rate the concentration of the byproduct NaH should be low.
Na: contained $5 \cdot 10^{-4}$ % O, $1 \cdot 10^{-3}$ % H, Ca, Si, 0.05% C, $1 \cdot 10^{-4}$ % Li and $<3 \cdot 10^{-3}$ % Ni, Mn, Al, Be, Ag, Cu, Ti, and Fe; further cold trapped.[3]
Ar: nothing specified.

Estimated Error:
Solubility: analytical sensitivity $5 \cdot 10^{-4}$ mass % O, scatter of the data less than ±15%; reading-out procedure ±5%.
Temperature: accuracy ±5 K; reading-out procedure ±3 K.

References:
[1]Yu. E. Bagdasarov, *Tekhnicheskie Problemy Reaktorov na Bystrykh Neitronakh* (Atomizdat, Moskva, 1969), pp. 107–112.
[2]V. I. Subbotin, M. N. Ivanovskii, and M. N. Arnoldov, *Fiziko-Khimicheskie Osnovy Primeneniya Zhidkometallicheskikh Teplonositelei* (Atomizdata, Moskva, 1970), pp. 66–71.
[3]M. N. Arnoldov, M. N. Ivanovskii, V. I. Subbotin, and B. A. Shmatko, B. A., *Alkali Metal Coolant* (IAEA, Vienna, 1967), pp. 479–488.

Components:
(1) Sodium hydroxide; NaOH; [1310-73-2]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
F. A. Kozlov, E. K. Kuznetsov, G. P. Sergeev, L. G. Volchkov, and V. V. Zotov, *Trudy Fiziko-Energeticheskogo Instituta* (Atomizdat, Moskva, 1974), pp. 290–308.

Variables:
Temperature: 439–583 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of NaOH in liquid Na was determined. The data were reported in graphical form. They were read from a figure and recalculated to mol % NaOH by the compilers.

t/°C	Solubility/mass % O	Solubility/mol % NaOH
166	$5.0\cdot10^{-3}$	$7.2\cdot10^{-3}$
167	$5.3\cdot10^{-3}$	$7.6\cdot10^{-3}$
228	$1.03\cdot10^{-2}$	$1.48\cdot10^{-2}$
232	$6.5\cdot10^{-3}$	$9.3\cdot10^{-3}$
232	$1.00\cdot10^{-3}$	$1.44\cdot10^{-2}$
239	$6.4\cdot10^{-3}$	$9.2\cdot10^{-3}$
239	$9.9\cdot10^{-3}$	$1.43\cdot10^{-2}$
239	$1.27\cdot10^{-3}$	$1.83\cdot10^{-2}$
244	$6.8\cdot10^{-3}$	$9.8\cdot10^{-3}$
244	$7.2\cdot10^{-3}$	$1.04\cdot10^{-2}$
247	$7.5\cdot10^{-3}$	$1.08\cdot10^{-2}$
247	$8.6\cdot10^{-3}$	$1.24\cdot10^{-2}$
248	$9.8\cdot10^{-3}$	$1.41\cdot10^{-2}$
256	$9.8\cdot10^{-3}$	$1.41\cdot10^{-2}$
258	$1.96\cdot10^{-2}$	$2.8\cdot10^{-2}$
259	$1.20\cdot10^{-2}$	$1.73\cdot10^{-2}$
260	$1.63\cdot10^{-2}$	$2.3\cdot10^{-2}$
260	$4.44\cdot10^{-2}$	$6.4\cdot10^{-2}$
266	$1.63\cdot10^{-2}$	$2.3\cdot10^{-2}$
271	$1.62\cdot10^{-2}$	$2.3\cdot10^{-2}$
272	$4.25\cdot10^{-2}$	$6.1\cdot10^{-2}$
287	$4.35\cdot10^{-2}$	$6.3\cdot10^{-2}$

The solubility of reaction products of H_2O with Na (NaOH, NaH) was determined. The data were reported in graphical form. They were read from a figure and recalculated to mol % NaOH by the compilers.

t/°C	Solubility/mass % O	Solubility/mol % NaOH
214	$3.6\cdot10^{-3}$	$5.2\cdot10^{-3}$
218	$2.7\cdot10^{-3}$	$3.9\cdot10^{-3}$
218	$3.7\cdot10^{-3}$	$5.3\cdot10^{-3}$
232	$3.7\cdot10^{-3}$	$5.3\cdot10^{-3}$
239	$4.2\cdot10^{-3}$	$6.0\cdot10^{-3}$
246	$3.9\cdot10^{-3}$	$5.6\cdot10^{-3}$
246	$5.6\cdot10^{-3}$	$8.1\cdot10^{-3}$
250	$6.0\cdot10^{-3}$	$8.6\cdot10^{-3}$
259	$8.5\cdot10^{-3}$	$1.22\cdot10^{-2}$
264	$8.8\cdot10^{-3}$	$1.27\cdot10^{-2}$
275	$1.15\cdot10^{-3}$	$1.66\cdot10^{-2}$
275	$1.20\cdot10^{-2}$	$1.73\cdot10^{-2}$
276	$1.29\cdot10^{-2}$	$1.86\cdot10^{-2}$
281	$1.79\cdot10^{-2}$	$2.6\cdot10^{-2}$
281	$2.09\cdot10^{-2}$	$3.0\cdot10^{-2}$
283	$1.05\cdot10^{-2}$	$1.51\cdot10^{-2}$
283	$1.11\cdot10^{-2}$	$1.60\cdot10^{-2}$
283	$1.79\cdot10^{-2}$	$2.6\cdot10^{-2}$
290	$1.85\cdot10^{-2}$	$2.7\cdot10^{-2}$
292	$2.09\cdot10^{-2}$	$3.0\cdot10^{-2}$
294	$1.79\cdot10^{-2}$	$2.6\cdot10^{-2}$
310	2.82×10^{-2}	4.1×10^{-2}

The data were expressed by the solubility equation (tested by the compilers):

$$\log(\text{soly/mass \% O}) = 4.0 - 3250\,(T/\text{K})^{-1}.$$

If the experimental loop was heated to 400–450 °C and then to the test temperature, the solubility of NaOH being determined approached values typical of the solubility of reaction products of H_2O with Na. Some measurements of the H pressure over NaH, NaH+Na_2O, and NaOH dissolved in liquid Na separately, showed that at temperatures <300 °C the NaOH decomposed only slightly to NaH and Na_2O.

Auxiliary Information

Method:
The experiments were performed in liquid Na circulating in a stainless steel loop. Portions of NaOH and H_2O were introduced into the loop and allowed to equilibrate for several hours. Temperatures of the beginning of crystallization were measured by means of a sample indicator. Some filtered samples were analyzed for their O content by a distillation analysis. Such analysis showed that the content of NaOH in Na was almost the same, if the reaction products of H_2O in Na were equilibrated.

Source and Purity of Materials:
NaOH: degassed at 823 K for 10 h.
Na: purified by cold trapping at temperatures <403 K.
H_2O: nothing specified.

Estimated Error:
Solubility: nothing specified; reading-out procedure $\pm2\cdot10^{-4}$ mol %.
Temperature: nothing specified; reading-out procedure ±2 K.

Components:
(1) Sodium hydroxide; NaOH; [1310-73-2]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
J. P. Maupré, Comm. Ener. Atom. (Fr.) Rep. CEA-R-4905 (1978).

Variables:
Temperature: 586–828 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data
Temperatures of the NaOH–Na liquidus fragment were reported

t/°C	Solubility/mol % Na	Solubility/mol % NaOH[a]
320	0.87	99.13
316	1.94	98.06
314	3.42	96.58
313	4.66	95.34
313	4.78	95.22
314	6.38	93.62
370	9.18	90.82
397	10.13	89.87
398	11.19	88.81
416	12.72	87.28
443	14.26	85.74
446	15.51	84.49
485	17.49	82.51
496	19.18	80.82
505	21.25	78.75
555	22.11	77.89
555	23.58	76.42

A plateau at ~555 °C was further observed between 76.5 and 11.0 mol % NaOH. At lower concentrations between 11.0 mol % NaOH and 0.6 mol % NaOH, the thermal arrests were observed at ~410 °C. Other thermal arrests were observed from 10 mol % NaOH to 75 mol % NaOH at ~355 °C and from 20 mol % NaOH to 80 mol % NaOH at ~255 °C. A precipitation of Na_2O occurred between 410 and 555 °C. The melting points of Na and NaOH were found at 98 and 319 °C, respectively. Polymorphic phase transitions were observed at 243 and 293 °C.

Auxiliary Information

Method:
A commercial thermoanalyzer was used. Samples were placed in Ni crucibles. Pt/Pt–Rh and Ni/Ni–Cr thermocouples which were placed in the bottom parts of the crucibles were used for the measurement of temperatures. The crucible was placed in a quartz container for temperatures <1273 K and a super Kanthal container for temperatures <1873 K. Thermocouples were calibrated on the melting points of In, Sn, Ag_2SO_4, K_2SO_4, K_2CrO_4, and $BaCO_3$. The rate of cooling and heating was between 0.2 and 15 K/min. The experiments were performed in an Ar atmosphere. Some samples were analyzed by x-ray diffraction and unspecified chemical analysis.

Source and Purity of Materials:
NaOH: 99% pure from Merck with 0.5% Na_2CO_3.
Na: nuclear grade of purity, 99.985% pure from Pechiney.
Ar: 99.995+% pure, purified on 5 A molecular sieves and BTS catalyzer at 383 K. Final content $\sim 1\cdot 10^{-4}$ vol % O and $3\cdot 10^{-5}$ vol % H_2O.

Estimated Error:
Solubility: nothing specified.
Temperature: precision better than ±3 K.

4.13. Sodium–Sodium Carbonate

Components:
(1) Sodium carbonate; Na_2CO_3; [497-19-8]
(2) Sodium; Na; [7440-23-5]

Evaluated By:
Hans Ulrich Borgstedt, Forschungszentrum Karlsruhe, Germany and Cezary Guminski, University of Warsaw, Poland, June 1996.

Critical Evaluation

Solutions of Na_2CO_3 in liquid Na may be either prepared by a dissolution of the solute in the liquid solvent at lower temperatures,[1–3] by a simultaneous dissolution of C and O in the solvent at higher temperature[4] or in course of the following reactions:[5]

$$Na_2O + CO_2 \leftrightarrow Na_2CO_3 \quad (1)$$

$$4\ Na + 3\ CO_2 \leftrightarrow 2\ Na_2CO_3 + C \quad \text{at } 623-773\ K \quad (2)$$

$$2\ Na + CO \leftrightarrow Na_2CO_3 + 2\ C \quad \text{at } 623-773\ K \quad (3)$$

$$3\ Na_2O + C \leftrightarrow 4\ Na + Na_2CO_3 \quad \text{at } 873-1213\ K. \quad (4)$$

Thermodynamic analyses of the stability ranges of the reagents in contact with metallic Na have been performed by Migge.[6] Na_2O and graphite (or metastable Na_2C_2) exist at low temperatures (<700 K) and low concentrations of the reagents. Na_2CO_3 can only coexist with molten Na at higher temperatures and excess concentrations of C and O. Thus, Na_2CO_3 is a metastable solute in liquid Na. An opposite opinion was formulated by Mathews *et al.*[7] who supported their conclusion by the fact that Na_2CO_3 is formed in cold traps of Na loops. According to experiments performed by Kelly *et al.*,[8] the decomposition of Na_2CO_3 in Na was not observed at ~673 K. It started obviously at ~773 K with formation of Na_2C_2 and C. The decomposition was further advanced at higher temperatures. Similar observations of Sinclair *et al.*[9] and Walker and France[10] confirmed the statement of Migge.[6] Decomposition of Na_2CO_3 to CO_2 and Na_2O was observed at temperatures >1173 K.[5] Lockhart[14] determined some CO in the products of Na_2CO_3 decomposition at ~811 K. Maupré[3] carried out thermal analysis of the Na_2CO_3–Na system. He found that Na_2CO_3 exists in three modifications (α,β,γ) stable up to 623 K, between 623 and 754 K, and between 754 and 1126 K (the melting point of Na_2CO_3), respectively. The saturated solution of Na_2CO_3 in Na is in equilibrium with γ-Na_2CO_3 between 963 and 1043 K, whereas at lower temperatures an excess of Na_2O and C in the system is needed. Thus, from the point of view of thermodynamic theory,[6] kinetic decomposition,[5–8] and thermal analysis, we observe a little different picture of the system in quantitative sense but general conclusions are similar.

The earliest attempt to measure the solubility of Na_2CO_3 in liquid Na was reported by Pepkowitz and Judd[11] who could not find any Na_2CO_3 dissolved at 673 K by an analytical method of detectivity level of $\sim 1\times 10-3$ mol % Na_2CO_3. The solubility of Na_2CO_3 in liquid Na was determined by Williams *et al.*,[1] Carmichael and Meacham,[2] and Ainsley *et al.*[4] Hill[12] described the method used by Carmichael and Meacham[2] but did not report any results except the opinion that Na_2CO_3 was virtually insoluble in the circulating Na loop at temperatures up to 723 K. Hislop *et al.*[13] tried to determine Na_2CO_3 by activation analysis, however the Na_2CO_3 was decomposed to some extent during gamma radiation. Although the results of Williams *et al.*[1] and Carmichael and Meacham[2] agree excellently at 423 K, yet further increase of temperature also makes an increase of discrepancy and at 673 K the value of Williams *et al.*[1] is 1 order of magnitude higher than of Carmichael and Meacham.[2] The data of Williams *et al.*[1] may be charged with some errors made during the analysis course, Na might react with the glass apparatus used and the chemicals were not of the highest purity. The results of Carmichael and Meacham[2] seems to be more reliable and show agreement with the single determination of Ainsley *et al.*[4] at 973 K; the flat gradient of the temperature function in Carmichael and Meacham[2] indicates that Na_2CO_3 decomposition may be superimposed on its dissolution. The relatively high concentration of Na_2CO_3 at ~423 K was qualitatively confirmed by C activity measurements.[14] Therefore we may recommend the solubility value at this temperature. Without additional investigations of the system the solubility data of Carmichael and Meacham[2] at higher temperatures may be treated as tentative. The schematic phase diagram is shown in Fig. 25.

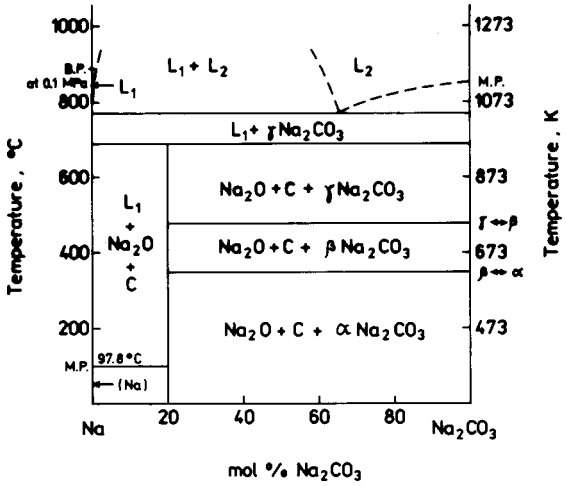

FIG. 25. Na–Na_2CO_3 phase diagram (schematic).

The recommended (r) and tentative (t) values of the solubility of Na_2CO_3 in liquid Na.

T/K	Solubility/mol % Na_2CO_3	Source	Solute
423	$4\cdot10^{-4}$(r)	(1),(2)	α-Na_2CO_3
573	$9\cdot10^{-4}$(t)	(2)	α-Na_2CO_3
673	$1.1\cdot10^{-3}$(t)	(2)	β-Na_2CO_3

References:

[1]D. D. Williams, J. A. Grand, and R. R. Miller, J. Phys. Chem. **63**, 68 (1959).
[2]H. T. Carmichael and S. A. Meacham, U.S. Atom. Energy Comm. Rep. APDA-184 (1968).
[3]J. P. Maupré, Comm. Ener. Atom. (Fr.) Rep. CEA-R-4905 (1978).
[4]R. Ainsley, L. P. Hartlib, P. M. Holroyd, and G. Long, J. Nucl. Mater. **52**, 255 (1974).
[5]E. E. Konovalov, A. P. Smirnov-Averin, and A. I. Lastov, Fiz.-Ener. Inst. (Ru.) Rep. FEI-806 (1978).
[6]H. Migge, *Material Behavior and Physiscal Chemistry in Liquid Metal Systems*, edited by H. U. Borgstedt (Plenum, New York, 1982), p. 351.
[7]C. K. Mathews, T. Gnanasekaran, and S. R. Pillai, Trans. Indian Inst. Met. **40**, 89 (1987).
[8]K. J. Kelly, E. W. Hobart, and R. G. Bjork, U.S. Atom. Energy Comm. Rep. CONF-650411 (1965); p. 64; Rep. CNLM-6337 (1965).
[9]V. M. Sinclair, J. L. Drummond, and A. W. Smith, U.K. Atom. Ener. Author. Rep. TRG-1185(D)7 (1966).
[10]J. A. Walker and E. D. France, U.K. Atom. Ener. Author. Rep. TRG-1635(C) (1968).
[11]L. P. Pepkowitz and W. C. Judd, Anal. Chem. **22**, 1283 (1950).
[12]E. F. Hill, Trans. Am. Nucl. Soc. **11**, 113 (1968).
[13]J. S. Hislop, J. R. Stevens, and D. A. Wood, J. Radioanal. Chem. **39**, 409 (1977).
[14]R. W. Lockhart, U.S. Atom. Energy Comm. Rep. GEAP-4436 (1966).

Components:
(1) Sodium carbonate; Na_2CO_3; [497-19-8]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
D. D. Williams, J. A. Grand, and R. R. Miller, J. Phys. Chem. **63**, 68–71 (1959).

Variables:
Temperature: 423–658 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of Na_2CO_3 in liquid Na was determined. The values were read from a figure and recalculated to mol % by the compilers.

t/°C	Solubility/mass % Na_2CO_3	Solubility/mol % Na_2CO_3
150	$2\cdot10^{-3}$	$4\cdot10^{-4}$
200	$5.5\cdot10^{-3}$	$1.2\cdot10^{-3}$
250	$9\cdot10^{-3}$	$1.9\cdot10^{-3}$
300	$1.6\cdot10^{-2}$	$3.5\cdot10^{-3}$
340	$2.2\cdot10^{-2}$	$4.8\cdot10^{-3}$
385	$2.7\cdot10^{-2}$	$5.9\cdot10^{-3}$

The data were also reported in Bogard *et al.*[1]

Auxiliary Information

Method:
Na was distilled into a solubility cell (made of Pyrex glass) which contained a sample of Na_2CO_3. The system was heated and equilibrated at selected temperatures. Saturated Na was filtered at a slight N pressure admittance. The filtrate was analyzed by the amalgamation method (addition of Hg to the melt in portions). The residue from the amalgam separation was titrated with an acid, using a double indicator end point (phenolphtalein and methyl orange) to ensure that the measured alkalinity was due to carbonate anions only.

Source and Purity of Materials:
Na_2CO_3: chemically pure, dried.
Na: nuclear grade of purity.
N: nothing specified.

Estimated Error:
Solubility: nothing specified; reading-out procedure $\pm1\cdot10^{-4}$ mol %.
Temperature: accuracy ±5 K; reading-out procedure ±3 K.

Reference:
[1] A. D. Bogard, D. D. Williams, J. A. Grand, and R. R. Miller, Naval Res. Labor. Rep. NRL-Memo-424 (1955).

Components:
(1) Sodium carbonate; Na_2CO_3; [497-19-8]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
H. T. Carmichael and S. A. Meacham, U.S. Atom. Energy Comm. Rep. APDA-184 (1968).

Variables:
Temperature: 423–673 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of Na_2CO_3 in liquid Na was determined

t/°C	Solubility/mass % Na_2CO_3	Mean value/mass %	Solubility/mol % Na_2CO_3[a]
150	$2.11\cdot10^{-3}$; $2.21\cdot10^{-3}$; $2.99\cdot10^{-3}$	$(2.44\pm0.48)\cdot10^{-3}$	$(5.2\pm0.1)\cdot10^{-4}$
275	$3.06\cdot10^{-3}$; $3.44\cdot10^{-3}$; $3.50\cdot10^{-3}$	$(3.79\pm0.52)\cdot10^{-3}$	$(8.2\pm0.1)\cdot10^{-4}$
	$4.15\cdot10^{-3}$; $4.28\cdot10^{-3}$; $4.30\cdot10^{-3}$		
400	$4.92\cdot10^{-3}$; $5.18\cdot10^{-3}$; $5.20\cdot10^{-3}$	$(5.10\pm0.16)\cdot10^{-3}$	$(1.11\pm0.04)\cdot10^{-3}$

[a]Calculated by the compilers.

Auxiliary Information

Method:
The solubility apparatus was constructed from Type 316 stainless steel. A Chromel/Alumel thermocouple in a stainless steel sheath was used to measure and control the stability of temperature. The entire apparatus was placed in a dry box filled with Ar. The apparatus was cleaned with HCl–H_2O mixture followed by H_2O and acetone rinses. A 5 μm filter was cleaned with toluene, acetone and H_2O. The apparatus was dried in a vacuum oven for 16 h at 423 K and a pressure of 66 Pa. The vessels were carefully cleaned, dried in the vacuum oven, and brought into the dry box. Na was equilibrated with Na_2CO_3 during stirring for 5 days and sampled through a filter. The Na_2CO_3 content was estimated by multistage amalgamation of Na. The resulting amalgam and the residue were treated with a known amount of H_2SO_4 and back titrated with NaOH to the phenolphtalein end point.

Source and Purity of Materials:
Na_2CO_3: 99.97% pure, dried for 60 h at 533 K.
Na: for ''laboratory use'' from Ethyl Corp., further distilled, contained $4\cdot10^{-5}$ % Ca.
Ar: purified by passing over Na at 473 K: contained $<1\cdot10^{-4}$ % O, H_2O.

Estimated Error:
Solubility: standard deviation between 3.1% and 19.8%.
Temperature: stability and accuracy ±10 K.

Components:
(1) Sodium carbonate; Na_2CO_3; [497-19-8]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
R. Ainsley, L. P. Hartlib, P. M. Holroyd, and G. Long, J. Nucl. Mater. **52**, 255–276 (1974).

Variables:
One temperature: 973 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of Na_2CO_3 in liquid Na at 700 °C (973 K) was estimated to be between $5\cdot10^{-3}$ and $1.0\cdot10^{-2}$ mass % C (0.010 and 0.020 mol % Na_2CO_3, as calculated by the compilers). It was found that carbonate was formed at a concentration of O of about 0.5 mass % (0.7 mol % O) and a concentration of C in Na between 0.045 and 0.075 mass % (0.09 and 0.15 mol % C). The contents of total C and Na_2CO_3 in liquid Na were determined in separate analyses.

Auxiliary Information

Method:
Na was contained in a Ni ampoule. For the addition of O, the Na filled ampoule was exposed prior to welding to the requisite amount of gaseous O at the temperature of ~473 K. The ampoule itself was the C source. A small monitoring foil of Ni or Fe was immersed in the liquid Na. The C content in the foil was analyzed to check whether the equilibrium was reached. The components were equilibrated for 30 h at the specific temperature. The temperature of a furnace containing the ampoule was controlled using a Chromel/Alumel thermocouple. Carbonate was determined by an unspecified wet analysis after quenching.

Source and Purity of Materials:
C: from a Ni ampoule; the ampoule was carburized to a predetermined level with CH_4 after decarburizing in moist H and vacuum annealing at 1173 K. CH_4 was labeled with ^{14}C.
O: nothing specified.
Na: reactor grade purity, gettered with Zr foil.
Ar: nothing specified.

Estimated Error:
Solubility: nothing specified; precision ±50% (by the compilers).
Temperature: stability ±2 K.

Components:
(1) Sodium carbonate; Na_2CO_3; [497-19-8]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
J. P. Maupré, Comm. Ener. Atom. (Fr.) Rep. CEA-R-4905 (1978).

Variables:
Temperature: 1038–1121 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data
Several points on the Na_2CO_3–Na liquidus were determined

t/°C	Solubility/mol % Na	Solubility/mol % Na_2CO_3
765	98.05	1.95
790	30.45	69.55
808	21.73	78.27
808	20.87	79.13
840	16.30	83.70
849	12.49	87.51
848	9.73	90.27

The temperature of the monotectic at ~770 °C was observed between 2 and 35 mol % Na_2CO_3. The melting points of Na and Na_2CO_3 were found at 98 and 853 °C, respectively. The $\alpha \leftrightarrow \beta$ and $\beta \leftrightarrow \gamma$ transitions of Na_2CO_3 were observed at 350 and 481 °C, respectively. A thermal arrest at ~690 °C corresponded to the reaction: $4\ Na + Na_2CO_3 \leftrightarrow 3\ Na_2O + C$.

Auxiliary Information

Method:
A commercial apparatus for thermal analysis was used. The experiments were performed in an Ar atmosphere. Samples were placed in a Ni crucible. The crucible containing Na and Na_2CO_3 was placed in a quartz container. Pt/Pt–Rh or Ni/Ni–Cr thermocouples were mounted in the bottom part of the crucibles. The thermocouples were calibrated on the melting points of In, Sn, Ag_2SO_4, K_2SO_4, K_2CrO_4, and $BaCO_3$. The rate of heating and cooling applied was between 0.2 and 15 K/min.

Source and Purity of Materials:
Na_2CO_3: 99.5% pure from Merck.
Na: 99.985% pure from Pechiney.
Ar: 99.995+% pure from B.A.G.; further purified with 5 A molecular sieves and BTS catalyst at 383 K; finally contained $\sim 1 \cdot 10^{-4}$ vol % O and $3 \cdot 10^{-5}$ vol % H_2O.

Estimated Error:
Solubility: nothing specified.
Temperature: precision better than ±3 K.

4.14. Sodium–Sulfur

Components:
(1) Sulfur; S; [7704-34-9]
(2) Sodium; Na; [7440-23-5]

Evaluated By:
Hans Ulrich Borgstedt, Forschungszentrum Karlsruhe, Germany and Cezary Guminski, University of Warsaw, Poland, March 1997.

Critical Evaluation

S introduced into liquid Na reacts with the formation of Na_2S and after further addition of S with the formation of polysulfides as Na_2S_2, Na_2S_4, and Na_2S_5. These compounds are the solid phases being in equilibrium with the liquid. Experimental information on a solubility of the Na_2S phase in liquid Na on the Na-rich side is not available. Since Na_2Te shows a tendency to limited miscibility with Na, and Na_2O with Na exhibits a quite extensive miscibility gap, it also seems that Na_2S has only limited miscibility with Na, and the solubility of S in liquid Na should not be much higher than of O in liquid Na (see the O–Na system). Investigations of the Na–S phase diagram were performed between the composition of Na_2S and elemental S. Friedrich[1] was the first to measure this composition range. He observed a formation of plenty of congruently melting polysulfides with the melting points given in parenthesis: Na_2S (1193 K), Na_4S_3 (1045 K), Na_2S_2 (718 K), Na_4S_5 (618 K), Na_2S_3 (593 K), Na_4S_7 (568 K), Na_2S_4 (528 K), Na_4S_9 (483 K), and Na_2S_5 (458 K). Eight eutectics were observed inbetween. The existence of Na_4S_3, Na_4S_5, Na_2S_3, Na_4S_7, and Na_4S_9 was not confirmed in the subsequent studies by Thomas and Rule[2] as well as by Pearson and Robinson[3] who observed a peritectic formation of Na_2S_2 and congruent formation Na_2S, Na_2S_4, and Na_2S_5. Such a situation was later confirmed in the same composition range by Rosen and Tegman[4] and Oei[5] and in fragments by Coleman and Heal,[6] Maiorova *et al.*,[7] Feher and Berthold,[8] Janz and Rodgers,[9] as well as Cleaver and Upton.[10] However, the corresponding liquidus temperatures differed between 50 K (at lower temperatures) and 200 K (at higher temperatures). The discrepancy of results is probably due to the purity of the materials, but also depends on the very strong tendency of the polysulfides melts to supercooling.[9] Since Rosen and Tegman[4] used the most pure chemicals and performed very exhaustive studies by several methods, their measurements are the most convincing. The results of Coleman and Heal[6] are most controversial. The authors observed a scatter of ±25 K for almost every composition investigated by thermal analysis. Only the melting point of Na_2S_4 at 573±5 °C is acceptable, but it is hard to explain, why Na_2S_5 melts peritectically, since the critical temperature in the limited miscibility range is at ~673 K and the melting of S is at 708±10 K. The problems were a subject of further discussion.[11]

The melting point of Na_2S, found in the earliest studies at 1193 K (Ref. 1) and 1251 K (Ref. 3) was redetermined later to be at 1453 K,[12,13] 1428 K,[14] 1446 K,[15] 1433 K,[16] 1441 K,[4] and 1448 K.[17] Following the analysis of Warnquist[18] of these results we select a value 1443±10 K; he explained that low purity and moisture in Na_2S should be the main reason for understating the results obtained in earlier studies. A transition temperature of Na_2S at 593 K reported by Ovechkin *et al.*[16] was not reported elsewhere. Böttcher *et al.*[19] identified a well documeted phase transition in Na_2S_2 at 430±20 K. There is a miscibility gap between Na_2S_5 and S which was studied in the previously mentioned[1–7,9] and other papers.[20–24] Oei,[5] Cleaver and Davies,[21] and Gupta and Tischer[24] stated that the monotectic starts at 72.1 mol % S and extends to >99.9 mol % S[4,22] at the temperature of 625 K. Morachevskii *et al.*[20] found the Na-rich border of the miscibility gap at 75 mol % S, Bikina[22] at 71.5 mol % S, Janz and Rodgers[9] at 71.8 mol % S, Janz and Rodgers[3] at <72.3 mol % S, Thomas and Rule[2] at 72.1 mol % S, and Rosen and Tegman[4] at 72.4 mol % S. The results of Thomas and Rule,[2] Oei,[5] Cleaver and Davies,[21] and Gupta and Tischer[24] are in perfect agreement, and therefore they are mostly recommended. Cleaver and Sime[25] performed thermodynamic modeling of the two-liquids region and predicted the consolute temperature at 1373–1573 K. However, the composition values of the border line (80 mol % S at 773 K and 90 mol % S at 1373 K) differ significantly from the experiments. The evaluators propose the Na–S phase diagram shown in Fig. 26.

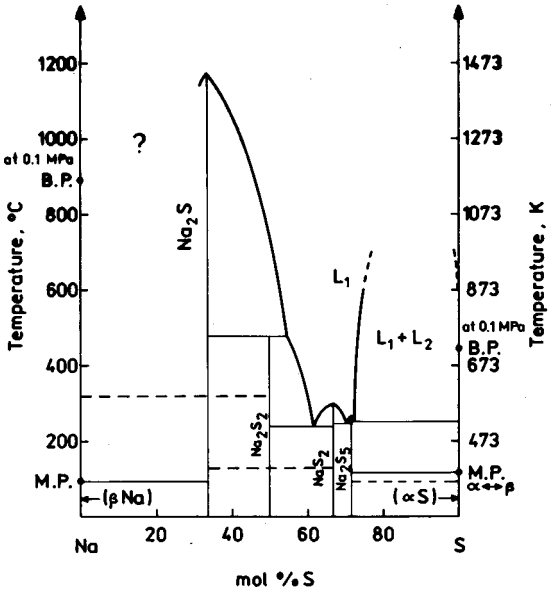

FIG. 26. Na–S phase diagram (proposed).

T/K	Solubility/mol % S	Source
	The tentative values of the solubility of S in liquid Na on the Na-rich side	
513	61 eutectic	(4)
573	60	(4)
673	57	(4)
748	54 peritectic	(4),(5),(9),(11)
873	52	(4) interpolated
973	50	(4) interpolated
1073	48	(4) interpolated
1173	46	(4) interpolated
1273	42	(4) interpolated
1373	38	(4) interpolated
1443	33.3	(4),(12),(13),(14),(15),(16),(17), mean value
	The tentative values of the solubility of S in liquid Na on the S-rich side	
558	66.7 congruent	mean value, (2),(3),(4),(5),(7),(8),(9),(24)
521	70 eutectic	(4)
531	71.4 congruent	mean value, (2),(3),(4),(5),(7),(8),(9),(24)
523	72.1 monotectic	(2),(3),(4),(23),
573	72.2 immiscible	(24)
673	72.5 immiscible	(24) extrapolated

References:

[1]K. Friedrich, Metall. Erz. **11**, 79 (1914).
[2]J. S. Thomas and A. Rule, J. Chem. Soc. **111**, 1063 (1917).
[3]T. G. Pearson and P. L. Robinson, J. Chem. Soc. 1473 (1930).
[4]E. Rosen and R. Tegman, Chem. Scrip. (Sweden) **2**, 221 (1972).
[5]D. G. Oei, Inorg. Chem. **12**, 435 (1973).
[6]D. S. Coleman and M. Heal, Inst. Min. Metall. Trans., Ser. C **83**, C258 (1974).
[7]E. A. Maiorova, N. M. Romanchenko, and A. G. Morachevskii, Elektrokhimiya **17**, 523 (1981).
[8]F. Feher and H. J. Berthold, Z. Anorg. Chem. **273**, 144 (1953).
[9]G. J. Janz and D. J. Rodgers, J. Appl. Electrochem. **13**, 121 (1983).
[10]B. Cleaver and S. M. Upton, Electrochim. Acta **36**, 673, 679 (1991).
[11]D. S. Coleman and M. Heal, Inst. Min. Metall. Trans., Ser. C **85**, C218 (1976).
[12]G. Courtois, Compt. Rend. **208**, 277 (1939).
[13]E. J. Kohlmeyer and G. Lohrke, Z. Anorg. Chem. **281**, 54 (1955).
[14]M. P. Smirnov and L. N. Strelnikova, Sbor. Nauch. Tr. Gosud. Nauch.-Issled. Inst. Tsvet. Metall. **23**, 67 (1965).
[15]N. I. Kopylov, Zh. Neorg. Khim. **13**, 529 (1968); Russ. J. Inorg. Chem. **13**, 276 (1968).
[16]E. K. Ovechkin, L. N. Shevtsova, A. E. Voitsekhovskii, and L. V. Kuznetsova, Zh. Neorg. Khim. **16**, 3156 (1971).
[17]R. Tegman and B. Warnquist, Acta Chem. Scand. **26**, 413 (1972).
[18]B. Warnquist, Thermochim. Acta **37**, 343 (1980).
[19]P. Böttcher, J. Getzschmann, and R. Keller, Z. Anorg. Chem. **619**, 476 (1993).
[20]A. G. Morachevskii, M. A. Bykova, and L. N. Gerasimenko, Zh. Fiz. Khim. **45**, 2066 (1971).
[21]B. Cleaver and A. J. Davies, Electrochim. Acta **18**, 733 (1973).
[22]G. V. Bikina, Tr. Leningrad. Politekhn. Inst. **348**, 30 (1976).
[23]B. Cleaver, A. J. Davies, and M. D. Hames, Electrochim. Acta **18**, 719 (1973).
[24]N. K. Gupta and R. P. Tischer, J. Electrochem. Soc. **119**, 1033 (1972).
[25]B. Cleaver and S. J. Sime, Electrochim. Acta **28**, 703 (1983).

Components:
(1) Sulfur; S; [7704-34-9]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
J. S. Thomas and A. Rule, J. Chem. Soc. **111**, 1063–1085 (1917).

Variables:
Temperature: 524–777 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data
A central part of the Na–S liquidus was determined

t/°C	Solubility/mass % S	Solubility/mol % S[a]
504	54.57	46.3
455	55.25	47.0
439	56.39	48.1
445	57.91	49.7
440	59.04	50.8
432	60.18	52.1
421.5	61.08	53.0
413	61.91	53.8
403.5	62.38	54.4
390	62.92	55.0
374	63.63	55.7
356.5	64.25	56.4
322	64.95	57.1
290	65.74	57.8
206	66.10	58.4
214.5	66.32	58.6
218	66.74	59.0
220	67.14	59.5
223	67.69	59.9
223.5	68.05	60.5
235.5	68.61	61.1
246	69.29	61.8
252	69.67	62.3
256	70.13	62.7
263	70.42	63.0
267.5	71.25	64.0
273	72.35	65.3
275	73.56	66.6
272.5	74.15	67.3
269	74.45	67.6
266	74.62	67.8
260.5	74.96	68.2
257.4	75.17	68.5
253.5	75.38	68.7
248.7	75.72	69.1
250	76.29	69.9
250	76.37	70.0
251	76.97	70.6
251.8	77.43	71.1
251.7	77.71	71.4
250	78.03	71.8
249.5	78.31	72.1
249.7	78.41	72.3
249.7	78.63	72.6
249.5	79.15	73.1
249.6	80.15	74.4
249.4	81.18	75.6

[a]Calculated by the compilers.

The monotectic at 249.6 °C was observed between 72.1 mol % S and practically pure S. The following equilibrium solid phases were determined Na_2S, Na_2S_2, Na_2S_4, and Na_2S_5. The melting point of S was found at 118 °C.

Auxiliary Information

Method:
Mixtures of Na_2S and S were prepared in a N atmosphere by melting proper amounts of the components in glass or porcelain containers. The solidifying points were measured with the use of a thermometer at $T<573$ K and with a pyrometer (Pt/Pt–Rh thermocouple) carefully calibrated. The melts were analyzed for the S content by precipitation of $BaSO_4$.

Source and Purity of Materials:
Na_2S: nothing specified.
S: twice recrystallized from CS_2 and heated at 373 K for several hours to remove the solvent; stored in a desicator over P_2O_5.
N: purified and dried over red-hot Cu and P_2O_5.

Estimated Error:
Solubility: nothing specified.
Temperature: accuracy of thermometer ±0.2 K and of pyrometer ±1.5 K.

Components:
(1) Sulfur; S; [7704-34-9]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
T. G. Pearson and P. L. Robinson, J. Chem. Soc. 1473–1497 (1930).

Variables:
Temperature: 524–777 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data
The S-rich part of the Na–S system was studied

t/°C	Solubility/mass % S	Solubility/mol % S[a]
978	41.00	33.3
900	47.52	39.4
766	53.80	45.6
755	54.25	46.0
560	58.00	49.8
554	58.25	50.1
534	58.51	50.3
501	58.75	50.5
472.7	60.18	52.1
470.6	60.90	52.8
457.6	62.04	54.0
445	62.75	54.8
420	63.83	55.9
407.5	64.35	56.5
385	64.95	57.1
354	65.51	57.7
356.4	65.71	57.8
350	66.18	58.5
349	66.33	58.6
353	66.55	58.8
353	66.80	59.1
343	67.17	59.5
330	67.60	60.0
321	67.77	60.2
285	68.26	60.7
275	68.39	60.8
250	68.58	61.1
247	68.59	61.1
232.1	68.77	61.3
236.1	68.99	61.5
254.0	70.40	63.0
275.0	71.99	64.9
284.8	73.00; 73.96	66.0; 67.1
283.5	74.40	67.6
267.0	75.10	68.4
262.8	75.70	69.1
249.2	76.40	70.0
252.2	76.72	70.4
254.0	77.77	71.5
252.2	77.92	71.7
251.2	78.40	72.3
251.2	80.20	74.4
251.2	89.90	86.5
250.0	94.51	92.5

[a]Calculated by the compilers.

The miscibility gap was established at 251.2 °C between 72.4 mol % S and almost pure S. These compounds are the equilibrium solid phases: Na_2S, Na_2S_2, Na_2S_4, and Na_2S_5. Na_2S_3 was found to be unstable. The melting point of S was found at 119.2 °C.

Auxiliary Information

Method:
The Na–S compounds were prepared by chemical reactions; S or Na were added if necessary. Melting was performed in test tubes of Pyrex glass or of glassed porcelain with a stirrer, a thin-walled thermocouple sheath and a delivery of N. A Chromel/Eureka thermocouple was used up to 873 K and a Pt/Pt–Rh junction above this temperature. The thermocouples were calibrated on the boiling points of H_2O, naphtalene and S and the melting points of Sb, NaCl, and Ag. Blanks were determined for all the reagents used. The tube was placed in a jacket furnace. The samples were cooled with rates of 1.5–5 K/s. After cooling to room temperature a portion of the melt was immediately analyzed. Its total S content was estimated as $BaSO_4$ after oxidation with Br and precipitation with $BaCl_2$. The remaining sample was stored in a selected tube and given to microscopic examination.

Source and Purity of Materials:
S: twice recrystallized from CS_2 and dried several hours at 373 K.
Na: from Imperial Chemical Industries Ltd., kept under dry liquid paraffin containing 1% of amyl alcohol.
N: ''dried and purified.''

Estimated Error:
Temperature: accuracy between ±0.5 and ±5 K depending on temperature.
Solubility: precision not better than ±0.1 mol % (by the compilers).

Components:
(1) Sulfur; S; [7704-34-9]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
F. Feher and H. J. Berthold, Z. Anorg. Chem. **273**, 144–160 (1953).

Variables:
Temperature: 526–763 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data
Melting temperatures of several Na–S compounds were determined

t/°C	Compound	Solubility/mol % S[a]
490	Na_2S_2	50.0
~260	Na_2S_3	60.0
286	Na_2S_4	66.7
253	Na_2S_5	71.4

[a]Calculated by the compilers

Na_2S_2, Na_2S_4, and Na_2S_5 are true compounds.

Auxiliary Information

Method:
Na_2S_2 and Na_2S_4 were prepared in absolute alcohol according to Thomas and Rule[1] or in liquid NH_3 according to Klemm *et al.*,[2] respectively. They were dried in vacuum at 423 K and at 473–573 K, respectively. Na_2S_3 was prepared by melting Na_2S_2 and Na_2S_4 or in liquid NH_3 with subsequent drying at 423–473 K. Na_2S_5 was prepared by melting of Na_2S_2 or Na_2S_4 with a stoichiometric amount of S. All operations were performed in a N atmosphere. The products were chemically analyzed. The method of the determination of the melting points was not described. Structures of the salts obtained were identified by x-ray diffraction analysis.

Source and Purity of Materials:
Na_2S: nothing specified.
S: probably as fine powder.[3]
N: dried subsequently over $Ca(OH)_2$, NaOH, KOH and molten Na.

Estimated Error:
Solubility: nothing specified; precision ±1% (by the compilers).
Temperature: nothing specified; not better than ±1 K (by the compilers).

References:
[1]J. S. Thomas and A. Rule, J. Chem. Soc. **111**, 1063–1085 (1917).
[2]W. Klemm, H. Sodomann, and P. Langmesser, Z. Anorg. Chem. **241**, 283–298 (1939).
[3]F. Feher and H. J. Berthold, Z. Anorg. Chem. **274**, 223–233 (1953).

Components:
(1) Sulfur; S; [7704-34-9]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
A. G. Morachevskii, M. A. Bykova, and L. N. Gerasimenko, Zh. Fiz. Khim. **45**, 2066–2067 (1971).

Variables:
One temperature: 673 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data
A single point on the Na–S liquidus in the range of miscibility was determined at 75 mol % S and 673 K.

Auxiliary Information

Method:
The components were molten in evacuated quartz ampoules. The melt was used to be placed in the anodic compartment of the cell: Na/Pyrex glass/Na–S. The potentials were measured at the selected constant temperature changing the composition of the melt. The phase boundary was estimated from a break on the curve relating the potential on the composition.

Source and Purity of Materials:
S: "high purity."
Na: "high purity."

Estimated Error:
Solubility: nothing specified; precision ±0.5 mol % (by the compilers).
Temperature: nothing specified.

Components:
(1) Sulfur; S; [7704-34-9]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
N. K. Gupta and R. P. Tischer, J. Electrochem. Soc. **119**, 1033–1037 (1972).

Variables:
Temperature: 508–748 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data
Several points on the liquidus Na–S were determined

t/°C	Solubility/mass % S	Solubility/mol % S[b]
475	58.1[a]	50.0
433[a]	62.5[a]	54.6
367[a]	64.2[a]	56.4
235	67.5[a]	60.0
252[a]	68.3[a]	60.7
275[a]	69.7[a]	62.3
285	73.6[a]	66.7
258	77.6	71.3
280	78.28	72.15
300	78.33	72.21
330	78.40	72.29
360	78.48	72.38
390	78.50	72.41

[a]Read from a figure.
[b]Recalculated by the compilers.

Auxiliary Information

Method:
Various compositions of the melts were prepared from Na_2S, NaS_2, Na_2S_5, and S by heating at 773 K for 4 h in a Vycor tube sealed under vacuum. The melt was cooled and the solid transferred to a cell made of Pyrex glass. One of electrodes was made of pyrolytic graphite dipped into the melt. A β-alumina tube containing molten Na which served as the solid electrolyte and a W wire was used for an electric contact. A calibrated Chromel/Alumel thermocouple was used to measure the melt temperature. The Na–S melts were introduced into the cell in a N atmosphere. The cell was evacuated and sealed. Potentials of the cell: Na/β-alumina/Na-S were stable after 24 h. The solubilities were determined from breaks on relations of potential vs. composition at selected temperatures.

Source and Purity of Materials:
S: 99.999% pure from American Smelting and Refining Corp..
Na_2S_5: synthesized by mixing Na_2S and S in the stoichiometric ratio and heating for 1 h at 773 K. The product was shaken with toluene and vacuum dried over P_2O_5.
NaS_2: from Alpha-Inorganics, purified by shaking with CS_2 and vacuum dried over P_2O_5 at 343 K for 1 week; stored under He.
Na_2S: obtained by dehydration of the hydrated salt.
Na: 99.999% pure, filtered.
N: "dry."
He: "pure."

Estimated Error:
Solubility: accuracy ±0.02 mol % in the miscibility gap region; reading-out procedure ±0.1 mol %.
Temperature: nothing specified; reading-out procedure ±1 K.

Components:
(1) Sulfur; S; [7704-34-9]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
E. Rosen and R. Tegman, Chem. Scrip. **2**, 221–225 (1972).

Variables:
Temperature: 525–1443 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data
The liquidus line between Na_2S and S was determined

t/°C	Solubility/mol % S
1162	33.3[a]
1168	33.3
1105	35.5
1117	34.4
1052	37.5
1057	37.5
997	39.4
973	41.2
977	41.2
928	42.8
884	44.4
844	44.4
760	46.0
740	47.3
765	47.3
678	48.7
657	50.0
648	50.0
560	52.4
475	54.5
475	54.5
453	56.5
351	60.0
355	60.5
314	61.1
265	61.6
276	62.9
283	63.3
291	64.0
288	64.0
288	64.9
291	65.3
296	66.1
297	66.4
295	66.7
290	67.1
287	67.7
286	67.7
282	68.0
285	68.1
277	68.6
275	69.2
273	69.7
274	69.7
265	70.4
268	70.4
254	71.0
270	71.2
269	71.4
255	74.1
252	80.3
253	86.8

257	94.0
841[b]	46.0
468	54.5
455	55.6
457	55.6
449	56.5
429	57.5
409	58.3
406	58.3
287	66.7
252	73.3
1170	33.3[c]
480	50.0
460	55.6
370	60.0
290	66.7
278	69.3
255	71.4
280	73.42[d]
300	73.53
340	73.31
400	74.40
405	74.07
465	73.96
550	74.74
565	75.41
605	75.08
525	>96.15
545	>97.66
555	>99.60
555	>99.0
370	>99.80

[a]High temperature microscopy.
[b]Thermal analysis.
[c]Differential thermal analysis.
[d]Quenching experiments.

The monotectic was observed at 253 °C between 72.8 and >99.9 mol % S. Na_2S, Na_2S_2, Na_2S_4, and Na_2S_5 were identified as solid equilibrium phases. The melting point of S was found at 118 °C.

Auxiliary Information

Method:

The mixtures were prepared by heating weighed amounts of carefully ground Na_2S and S in a Pyrex tube. The tube was evacuated and sealed. The samples were treated 10 h at 473 K and 0.5 h at 523–773 K followed by tempering at 473 K to obtain fine crystals. The compounds were analyzed for their S contents. The solid mixtures were ground and pressed into thin disks. They were placed in a high temperature microscope to directly observe the melting and solidification. The temperature was regulated and measured using a Pt/Pt–Rh(10%) thermocouple calibrated on the melting points of Sn, Al, Ag, and Au. Thermal analysis was performed with the samples placed in capillaries. The cooling rate was 0.1–1.0 K/min. Commercial equipment was used for differential thermal analysis. The quenching experiments were performed using Na_2S and S sealed in quartz ampoules and heated. The temperature of a furnace was measured and controlled with a Pt/Pt–Rh(10%) thermocouple. Heating and cooling rates were 2–5 K/min. The ampoule was rotated 4–6 h and then fixed in a vertical position for 1–2 h at the desired temperature. The ampoule was then quickly cooled in ice water. The composition of the polysulfides was determined by iodometric titration. The phases were visually examined. All essential operations were carried out in a N atmosphere.

Source and Purity of Materials:

Na_2S: obtained by dehydration of $Na_2S{\cdot}9H_2O$ (Merck's analytical purity) in vacuum at 573 K, followed by heating in a N atmosphere at 473 K; the product was 99.5+% pure.
S: spectrally pure from Johnson & Matthey Chemicals for high temperature microscopy and differential thermal analysis and analytically pure from Schuchardt for thermal analysis quenching technique.
N: "dried and purified."

Estimated Error:

Solubility: nothing specified; precision not better than ±0.1 mol % (by the compilers).
Temperature: stability ±0.2 K; accuracy ±0.5 K in high temperature microscopy; accuracy ±3 K in thermal analysis; accuracy ±5 K in quenching experiments.

Components:
(1) Sulfur; S; [7704-34-9]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
B. Cleaver and A. J. Davies, Electrochim. Acta **18**, 733–739 (1973).

Variables:
Temperature: 573 and 633 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

Two points on the S–Na liquidus were determined. The results were reported in a graphical form. They were read from a figure and recalculated to mol % S by the compilers.

t/°C	T/K	Solubility/mass % S	Solubility/mol % S
300	573	78.24	72.11
360	633	78.41[a]	72.30[a]
360	633	78.54[b]	72.46[b]

[a]Potentiometry.
[b]Transpiration experiments.

Auxiliary Information

Method:

Potentials of the following cells were measured: Na/β-alumina/Na_2S_x+S/C and C/Na_2S_x+S/C. The cells were made of glass. S was placed in an outer tube. A C rod was dipped in. A β-alumina tube filled with Na was placed inside the well containing S. A frited compartment contained a C rod dipped into the Na_2S_x+S melt. The temperature of an Al furnace was controlled and measured by means of a Chromel/Alumel thermocouple. A current was passed between the electrodes and the corresponding charge was measured by a Cu coulometer; thus the melt composition was calculated. The emf of the cell was measured. Saturation was indicated by a discontinuity on the relation between the potential and the composition of the melt. The experiments were performed in a N atmosphere. The activity of S was measured by a transpiration experiment. This allowed us to estimate the boundary of the miscibility gap between liquid Na_2S_5 and S.

Source and Purity of Materials:

Na_2S_5: prepared by reaction of Na and S in dry toluene; purity of 99.5%.[1]
Na: nothing specified.
S: nothing specified.
N: "dry."[1]

Estimated Error:

Solubility: precision ±0.5%; reading-out procedure ±0.02 mol % S.
Temperature: stability ±1 K.

References:

[1]B. Cleaver, A. J. Davies, and M. D. Hames, Electrochim. Acta **18**, 719–726 (1973).

Components:
(1) Sulfur; S; [7704-34-9]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
D. G. Oei, Inorg. Chem. **12**, 435-437 (1973).

Variables:
Temperature: 508–748 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data
A part of S–Na liquidus was determined

t/°C	Solubility/mass % S in Na_2S_2	Solubility/mol % S[a]
475	58.3	50.1
465–468	60.3	52.2
461–463	61.4	53.3
428–430	62.5	54.6
398–400	63.5	55.6
368–370	64.1	56.3
325–329	65.0	57.1
303–305	65.7	57.8
240–238	67.6	60.0
255–258	69.8	62.4
268–270	70.9	63.7
270–273	71.4	64.2
285	73.6	66.7
273–275	74.4	67.6
265–269	75.1	68.4
247–250	75.8	69.2
235–238	76.4	70.0
242–244	76.6	70.3
249–247	77.0	70.7
252–254	77.2	70.9
258	77.7	71.4

[a]Calculated by the compilers.

The monotectic was observed at 242 °C between 72.1 mol % S and almost pure S. The following equilibrium solid phases were identified NaS (Na_2S_2), NaS_2 (Na_2S_4), and Na_2S_5.

Auxiliary Information

Method:
Differential thermal analysis was performed using a commercial apparatus. Proper amounts of Na_2S_x and S were weighed and taken to prepare the mixtures. The mixtures were placed in sample tubes. Trial runs with temperature rates 10–30 K/min were conducted using reference thermocouples. The sample tubes were rotated and stirred using the thermocouples, because the mixtures exhibited a marked tendency to supercooling. The heating compartment was flushed with N.

Source and Purity of Materials:
S: spectral grade of purity from American Smelting & Refining Co.
Na_2S: prepared from $Na_2S \cdot 9\ H_2O$ from Allied Chemical by drying in vacuum at 313–343 K for 2 weeks and dehydrating at 973 K under streaming H.
Na_2S_x ($x = 2$, 4, and 5) were synthesized following Brauer's method.[1]
N: nothing specified.
H: nothing specified.

Estimated Error:
Solubility: nothing specified; not better than ±0.1 mol %.
Temperature: precision ±2 K.

References:
[1]G. Brauer, *Handbuch der Präparativen Anorganischen Chemie* (Ferdinand Enke Verlag, Stuttgart, 1960).

Components:
(1) Sulfur; S; [7704-34-9]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
G. V. Bikina, Tr. Leningrad. Politekhn. Inst. **348**, 30–34 (1976).

Variables:
One temperature: 673 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data
One point on the Na–S liquidus, in the range of the miscibility gap, was determined at 71.5 mol % S (as read from a figure by the compilers) at 673 K.

Auxiliary Information

Method:
Anhydrous Na_2S was mixed with S in various proportions, heated to 673 K and equilibrated for 2 h. After cooling the solid melt was transferred into the cell: Na/glass Na_2O/Na–S. Graphite rods were used as electric contacts to the electrodes. The potential of the cell was measured at the selected temperature and changing composition. A break on the dependence relating the potential on the composition is due to the saturation point. Samples of melt were analyzed for their Na content by flame photometry after dissolution in hot water or HNO_3 solution. All essential operations were carried out in an Ar atmosphere.

Source and Purity of Materials:
Na_2S: analytically pure $Na_2S \cdot 9\ H_2O$ was dehydrated at 323–333 K under reduced pressure and then at 423–433 K for 2 h.
S: nothing specified.
Ar: nothing specified.

Estimated Error:
Solubility: nothing specified; reading-out procedure ±0.5 mol % S.
Temperature: nothing specified.

Components:
(1) Sulfur; S; [7704-34-9]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
E. A. Maiorova, N. M. Romanchenko, and A. G. Morachevskii, Elektrokhimiya **17**, 523–527 (1981).

Variables:
Temperature: 529–662 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

Several points on the S–Na liquidus were determined. The compositions were reported numerically and temperatures were read from figures.

t/°C	Solubility/mol % S
263	70.7
274	69.8
293	66.0
283	65.3
273	65.0
256	63.5
273	60.5
310	60.0
351	59.5
335	58.7
389	58.5

The solubility gap at ~243 °C was observed between almost pure S and 72 mol % S.

Auxiliary Information

Method:
Measurements of the emf of the cell: Na/glass with 25–33 mass % Na_2O/Na–S were carried out at several temperatures. The Na–S melts were prepared in the cell by melting Na_2S and S. The content of Na was analyzed after the measurements using flame photometry. Na was contained in a capillary made of the glass; a W wire was used for electrical contact to this electrode. A graphite rod was used for contact with the second electrode. Potentials of the cell were measured for a fixed composition at changing temperature. Breaks on the dependencies correspond to the liquidus points. All essential operations were made in an Ar atmosphere.

Source and Purity of Materials:
S: "very pure."
Na_2S: obtained by a dehydration of $Na_2S \cdot 9\ H_2O$ (pure for analysis).
Ar: nothing specified.

Estimated Error:
Solubility: nothing specified.
Potential: reproducibility ±2.5 mV.
Temperature: nothing specified; reading-out procedure ± 1 K.

Components:
(1) Sulfur; S; [7704-34-9]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
G. J. Janz and D. J. Rodgers, J. Appl. Electrochem. **13**, 121–131 (1983).

Variables:
Temperature: 478–747 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

Several points on the Na–S liquidus were determined

t/°C[a]	t/°C[b]	Composition	Solubility/mol % S[c]
474	474	NaS	50.0
234	234	Na_2S_3	60.0
...	241	$Na_2S_{3.3}$	62.3
283	240	NaS_2	66.7
...	207–260	$Na_2S_{4.2}$	67.6
...	213–231	$Na_2S_{4.6}$	69.7
258	220–241	Na_2S_5	71.4
255	219–247	$Na_2S_{5.2}$	72.2
...	236–246	$Na_2S_{5.3}$	72.6
254	205–247	$Na_2S_{6.1}$	75.3
254	205–265	Na_2S_{10}	83.3

[a]First melting.
[b]Remelting.
[c]Calculated by the compilers.

The saturation solubility of S in molten Na_2S_5 was found at 0.32±0.02 mass % S, corresponding to the composition of the melt of 71.8 mol % S; the temperature was not specified. The melting point of S was found at 118.1 °C and its transition at ~95 °C. It was well proved that moisture has crucial influence on the melting behavior of polysulfides.

Auxiliary Information

Method:
The differential scanning calorimetry method with a commercial apparatus was applied. The apparatus was calibrated on the melting points of In, Sn, Pb, KNO_3, and LiCl–KCl eutectic. Cooling and heating curves were recorded at a rate of 10 K/min. Typical capsule pans were used as the reaction chambers for the preparation of the polysulfides with Na_2S and S as reactants. The substances were precisely weighed into the pans. All transfer weightings and capsule crimp seals were performed in a N atmosphere. The samples were thermally aged at ~580 K for ~1500 h and subsequently at ~473 K for ~1500 h.

Source and Purity of Materials:
S: reagent grade purity.
Na_2S: nothing specified.
N: "dried."

Estimated Error:
Solubility: accuracy of analysis ±2%.
Temperature: accuracy ±0.5 K.

Components:
(1) Sulfur; S; [7704-34-9]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
B. Cleaver and S. M. Upton, Electrochim. Acta **36**, 673–677, 679–687 (1991).

Variables:
Temperature: 503–673 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

t/°C	Solubility/mol % S
265[a]	67.8
230[a]	59.9
400[b]	73.1; 74.1 on the S-rich side, two immiscible liquids
400[b]	55.6 on the S-poor side, Na_2S_2 equilibrium solid phase
400[c]	73.2 on the S-rich side, two immiscible liquids
400[c]	57.0 on the S-poor side, Na_2S_2 equilibrium solid phase

[a]From thermal analysis.
[b]From equilibrium studies.
[c]From electrochemical S-activity measurements.

Auxiliary Information

Method:
Differential thermal analysis was performed in a self made apparatus, using heating curves only. Chromel/Alumel thermocouples were used. They were calibrated on the melting points of In, Sn, Cd, Pb, Zn, and Al. The samples were vacuum sealed into silica tubes. They were prepared by discharging a Na–S electrochemical cell with β-alumina electrolyte. Equilibrium studies were performed in silica tubes in a glove box. The tubes were evacuated and sealed, after the Na_2S and S mixtures were dispensed into. They were equilibrated in a rocking furnace for 3 days at 723 K, 4 days at 673 K, and were then transferred to a centrifuge furnace in ~5 s. After 1 h of rotation at 673 K the rotor was slowed down gradually. The samples were removed and plunged into ice water. The tubes were broken open and the separated phases analyzed: Na by atom absorption spectroscopy and S by conversion to $BaSO_4$. The S activity was measured in an electrochemical cell: Pt, Ag_2S, S–Na/Ag//Ag_2S, S, and Pt. S must not pass directly from one electrode to the other. The cells were placed in an air furnace at 673 K. The composition of the S–Na melt was changed by passing electric charge.

Source and Purity of Materials:
Na_2S: nothing specified.
S: "dry."
N: "dry and O free."

Estimated Error:
Solubility: accuracy of analysis ±1%.
Temperature: accuracy better than ±1 K at lower temperature; stability in electrochemical experiments ±2 K.

4.15. Sodium–Selenium

Components:
(1) Selenium; Se; [7782-49-2]
(2) Sodium; Na; [7440-23-5]

Evaluated By:
Hans Ulrich Borgstedt, Forschungszentrum Karlsruhe, Germany and Cezary Guminski, University of Warsaw, Poland, December 1997.

Critical Evaluation

Five compounds are formed by reactions of Se and Na: Na_2Se, Na_2Se_2 (NaSe), Na_2Se_3, Na_2Se_4 ($NaSe_2$), and Na_2Se_6 ($NaSe_3$). The first one, Na_2Se, is much more stable than the rest. The compounds are the equilibrium solid phases with saturated solution of Se in liquid Na. The compounds are stable. Thus, the Se vapor pressure over the melts is probably negligibly small. Mathewson[1] investigated the whole range of the Se–Na phase diagram. It seems that only the central part of it is correct. Due to insufficient purity of the elements, corrosion of containers used, and perhaps of undercooling effects in thermal analysis, the author was not able to measure the melting point of Na_2Se. A miscibility gap on the Se-rich side was not indicated in Mathewson.[1] According to predictions of Sangster and Pelton,[2] the melting point of Na_2Se is situated between 1173 and 1423 K and the liquidus line between 0 and 33 mol % Se should have a sigmoid shape. Works of Morachevskii *et al.*[3–6] performed by means of emf are somewhat contradictory. In Morachevskii *et al.*,[3] the liquid homogeneity range at 800 K was observed between 50 and 88 mol % Se, whereas in Maiorova and Morachevski,[4] the immiscibility was found between 80.4 and 99.1 mol % Se at 773–860 K. Maiorova and Morachevski.[5] reported a single liquidus point at 78.0 mol % Se and 800 K. The most convincing results were presented in Romanchenko *et al.*[6] in that the solubility of Se in liquid Na increases from 78.0 to 82.1 mol % Se at 523–773 K and the existence of the immiscibility gap was confirmed. The results in Morachevskii *et al.*[3–5] were not compiled because the results were either not accepted or imprecise.

The second part of the immiscibility bow on the Se-rich side was investigated conductometrically by Van der Marel and Van der Lugt[7,8] who observed a decrease of the solubility from 99.95 to 99.20 mol % Se between 546 and 734 K. Extrapolating the data of Morachevskii *et al.*[6] and Van der Marel and Van der Lugt,[7,8] one may predict the critical point for the miscibility at ~1100 K. The potentiometric experiments of Tumidajski and Toguri[9] confirmed the miscibility gap limits and the liquidus point on the Na-richer side at 621 K. The Se–Na phase diagram, reflected in Fig. 27, was compiled based on Mathewson,[1] Sangster and Pelton,[2] Morachevskii *et al.*,[6] Van der Marel and Van der Lugt,[7,8] and Tumidajski and Toguri.[9] No solubilities are suggested for the Na-rich range, since even Mathewson[1] was very critical on this part of his own investigations. It seems that the solubilities of Se in liquid Na are not more different than 1 order of magnitude from those determined for Te in liquid Na; see the Te–Na system. The solubilities in the central range of compositions may be read from Fig. 27. The suggested values for the miscibility gap are given below.

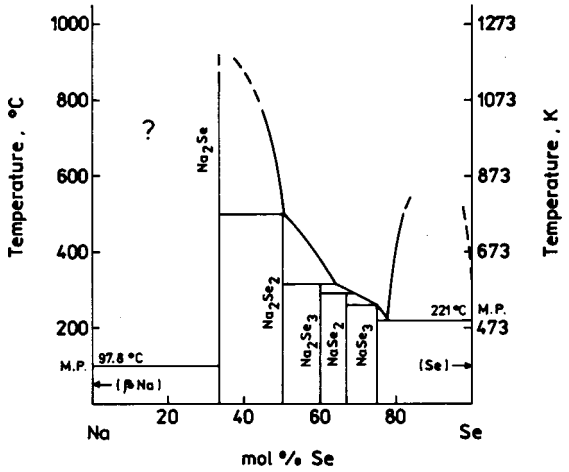

FIG. 27. Se–Na phase diagram.

Tentative values of the solubility of Se in liquid Na

T/K	Solubility/mol %	Source	Solubility/mol % Se	Source
523	78	(5)	99.98	(6,7) extrapolation
623	79	(5),(9)	99.8	(6,7),(9)
723	81	(5)	99.3	(6,7)

References:

[1]C. H. Mathewson, J. Am. Chem. Soc. **29**, 867 (1907).
[2]J. Sangster and A. D. Pelton, J. Phase Equil. **18**, 185 (1997).
[3]A. G. Morachevskii, M. A. Bykova, and T. T. Rozova, Elektrokhimiya **6**, 1065 (1970).
[4]E. A. Maiorova and A. G. Morachevskii, Elektrokhimiya **14**, 1454 (1978).
[5]E. A. Maiorova and A. G. Morachevskii, Zh. Prikl. Khim. **53**, 276 (1980).
[6]N. M. Romanchenko, E. A. Maiorova, and A. G. Morachevskii, Elektrokhimiya **17**, 750 (1981).
[7]C. Van der Marel and W. Van der Lugt, Z. Naturforsch., A **34**, 832 (1979).
[8]C. Van der Marel, Ph. D. thesis, University of Groningen, Netherland, 1981, p. 152.
[9]P. J. Tumidajski and J. M. Toguri, Can. Metall. Quart. **30**, 169 (1991).

Components:
(1) Selenium; Se; [7782-49-2]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
C. H. Mathewson, J. Am. Chem. Soc. **29**, 867–880 (1907).

Variables:
Temperature: 370–1148 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data
The following points on the Se–Na liquidus were determined

t/°C	Solubility/mol % Na	Solubility/mol % Se[a]
343	89.9	10.1
610	79.9	20.1
>875	66.7	33.3
745	56.9	43.1
593	52.0	48.0
495	50.0	50.0
469	47.5	52.5
418	44.9	55.1
368	40.0	60.0
333	37.4	62.6
306	34.0	66.0
300	32.0	68.0
286	30.0	70.0
280	27.6	72.4
276	25.0	75.0
272	20.0	80.0
253	15.1	84.9
248	8.1	91.9
226	4.0	96.0
223	2.0	98.0

[a]Calculated by the compilers.

The melting points of Na and Se were found at 97.5 and 217 °C, respectively. The following equilibrium phases were determined to decompose at Na_2Se->1148 K, Na_2Se_2-768 K, Na_2Se_3-590 K, Na_2Se_4-563 K, and Na_2Se_6-531 K.

Auxiliary Information

Method:
Small pieces of Se were added to molten Na in a tube of Jena glass. A slow flow of H circulated in the apparatus. The tube containing the alloys was transferred to a cylindrical sand bath surrounded by an asbestos mantle. The alloy was heated to melt and then cooled at a rate 0.4–0.06 K/s. The temperature was measured by a Pt/Pt–Rh (10%) thermocouple which was calibrated on the boiling point of H_2O and the melting points of Sn, Zn, and Sb. The melt was stirred during the cooling with a soft Fe wire (<673 K) or a Jena glass rod (>673 K). The apparatus glass blackened slightly but changes of composition were found to be negligible, according to chemical analysis of the samples.

Source and Purity of Materials:
Se: amorphous, purity unspecified.
Na: purified by remelting and cutting off the surface layers.[1]
H: "dry."

Estimated Error:
Solubility: precision of the preparation ±0.2 mass % as found by chemical analysis.
Temperature: accuracy ±2 K.

References:

[1]C. H. Mathewson, Z. Anorg. Chem. **46**, 94–112 (1905).

Components:
(1) Selenium; Se; [7782-49-2]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
C. Van der Marel and W. Van der Lugt, Z. Naturforsch., A **34**, 832–834 (1979).

Variables:
Temperature: 546–734 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data
Several points on the Se–Na liquidus in the miscibility range were determined

1 t/°C	*2* Solubility/mol % Na	*3* Solubility/mol % Se[a]
273	0.05	99.95
318	0.10	99.90
349	0.20	99.80
388	0.30	99.70
408	0.40	99.60
423	0.51	99.49
441	0.60	99.40
461	0.80	99.20

[a]Calculated by the compilers.

The melting point of Se was found at 219 °C. The same results were reported in Van der Marel.[1]

Auxiliary Information

Method:
A quartz vessel was carefully cleaned. Se was put into the vessel which was placed in a stainless steel tube. The vessel was evacuated to $5\cdot10^{-7}$ Torr and heated to ~433 K for 4 h. The tube was filled with He, disconnected from the vacuum system, and opened in a He glove box. The melting point of Se was measured. Stoichiometric amounts of Na and Se were placed in two ends of a quartz tube. The Se side was heated to 453 K and the Na side to 423 K. Na reacted with Se vapors to form Na_2Se within 72 h. Na_2Se was added to molten Se in a quartz–stainless steel apparatus for electrical resistivity measurements. The cell contained two Pt electrodes. The temperature was measured and regulated by means of two Chromel/Alumel thermocouples. The cell was calibrated with Cs. The temperature was decreased keeping the composition constant. Sudden breaks on the curves relating the resistivity on temperature indicate the phase separations.

Source and Purity of Materials:
Se: 99.999+% pure from Alfa Ventron; further purified.
Na: 99.93% pure from Merck, molten in a stainless steel container, surface scum removed, the liquid metal taken out by a glass pipette.
He: "high" purity, further purified and contained $1\cdot10^{-4}$ % O and $5\cdot10^{-5}$ % H_2O.

Estimated Error:
Solubility: nothing specified.
Resistivity: accuracy ±0.4%.
Temperature: precision ±1 K; stability ±1.5 K.

References:
[1]C. Van der Marel, Ph.D. thesis, University of Groningen, Netherland, 1981, pp. 152–160.

Components:
(1) Selenium; Se; [7782-49-2]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
N. M. Romanchenko, E. A. Maiorova, and A. G. Morachevskii, Elektrokhimiya **17**, 750–752 (1981).

Variables:
Temperature: 523–773 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data
Several points on the Se–Na liquidus were determined

t/°C	Solubility/mol % Na	Solubility/mol % Se[a]
250	22.0	78.0
300	21.6	78.4
350	21.0	79.0
400	20.1	79.9
450	19.1	80.9
500	17.9	82.1

[a]Calculated by the compilers.

The authors confirmed a miscibility gap on the Se-rich side of the phase diagram.

Auxiliary Information

Method:
Measurements of the emf of the cell: Na/alumino–silicate glass with 25 mass % Na_2O/Na–Se were performed at several temperatures. The Na–Se melts were prepared in the cell by melting the elements. The content of Na was analyzed after the measurements with the use of flame photometry. The Na electrode was contained in a capillary made of the Na^+ conducting glass. W wires were used for electrical contacts to the electrodes. The potentials of the cell were measured at a fixed temperature changing the concentration. Breaks on such relations correspond to phase boundary points of the liquidus. All essential operations were performed in an Ar atmosphere.

Source and Purity of Materials:
Se: "very pure."
Na: "free of oxides and other metals."
Ar: nothing specified.

Estimated Error:
Solubility: nothing specified.
Temperature: nothing specified.

Components:
(1) Selenium; Se; [7782-49-2]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
P. J. Tumidajski and J. M. Toguri, Can. Metall. Quart. **30**, 169–171 (1991).

Variables:
Temperature: 583 and 621 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The limits of the miscibility gap of Se-rich alloys were estimated from breaks on the relationships potential versus composition

T/K	Solubility/mol % Na	Solubility/mol % Se
583	21.5±0.5	78.5±0.5[a]
621	21±1	79±1[a]
···	<0.2	>99.8[b]

[a]On the Na-richer side.
[b]On the Se-richer side.

The solubility of Se in liquid Na at 621 K was estimated from the potential versus composition dependence to be 61.5±1 mol % Se.

Auxiliary Information

Method:
The experiments were performed in the electrochemical cell: Na/β-alumina/Bi–Na (5 mol %)/β-alumina/Na–Se. Na hermetically enclosed within the β-alumina tube, served as the reference electrode and the Na–Se mixture sealed in the same fashion as the working electrode. The composition of Na–Se mixtures was varied by Coulometric titration. Both half-cells were immersed to the same depth in the stirred Bi–Na alloy bath contained in a Mo crucible. The cells were loaded and operated inside an Ar filled glove box. Accurately weighed amounts of Se were loaded into the cell in small pieces. Temperatures were measured with a calibrated Pt/Pt–Rh(10%) thermocouple.

Source and Purity of Materials:
Se: 99.999% pure.
Na: 99.99% pure.
Ar: "high purity."

Estimated Error:
Solubility: precision better than ±1 mol %.
Temperature: nothing specified.

4.16. Sodium–Tellurium

Components:
(1) Tellurium; Te; [13494-80-9]
(2) Sodium; Na; [7440-23-5]

Evaluated By:
Hans Ulrich Borgstedt, Forschungszentrum Karlsruhe, Germany and Cezary Guminski, University of Warsaw, Poland, January 1997.

Critical Evaluation

Te reacts with Na forming three compounds: Na_2Te, NaTe, and $NaTe_3$. The first one is much more stable than the other two. These compounds are the equilibrium solid phases with a solution of Te in liquid Na.[1] Strong negative deviations from ideal solution rules indicate a very low Te vapor pressure over the melts. The whole range of the Te–Na phase diagram was firstly investigated by Pellini and Quercigh.[2] Only the Te-rich part of the liquidus was confirmed in subsequent studies. The Na-rich part of the liquidus suggested much higher solubilities of Te in liquid Na and only the melting point of Na_2Te at 1226 K seemed to be reasonable, because Granstaff and Thompson,[3] working at 1273 K in the vicinity of the composition Na_2Te did not observe a heterogeneity in the liquid phase. Pellini and Quercigh[2] reported an existence of a miscibility gap between 63 and 75 mol % Te. Kraus and Glass[4,5] showed that the liquidus line between 58 and 70 mol % Te should be placed lower down to 80 K and between 46 and 52 mol % Te up to 120 K higher temperatures than the data of Pellini and Quercigh.[2] No immiscibility phenomenon in the investigated composition range was observed. Walker and Pratt[6] determined a solubility of Te in liquid Na between 495 and 845 K. The solubility increased from 0.035 mol % Te to 0.264 mol % Te and was in complete disagreement with the value of Pellini and Quercigh[2] who observed at ~845 K as much as 10 mol % Te being dissolved in liquid Na. Finogenova *et al.*[7] reinvestigated the liquidus in the composition range between Na_2Te and Te. They synthesized a very pure Na_2Te (Finogenova *et al.*[8]) for the investigations. The melting point of Na_2Te was found by Finogenova *et al.*[7] at 80 K higher temperature than by Pellini and Quercigh[2] and the liquidus in Finogenova *et al.*[7] between the Na_2Te congruent point and the peritectic point at 52 mol % Te and 633 K was more steeper. Also the melting point of $NaTe_3$ in Finogenova *et al.*[7] was determined at 20 K higher temperature than in Kraus and Glass.[5] Morachevskii *et al.*[9] confirmed the liquidus line of Kraus and Glass[4,5] between 47 and 99.7 mol % Te, except one point at 621 K and 57.8 mol % Te which does not fit to the rest of the liquidus. Petric *et al.*[10] confirmed the liquidus line between 53 and 57.5 mol % Te found by Kraus and Glass[5] and modified it between 46.7 and 53 mol % Te recording ~20 K higher temperatures than Kraus and Glass[5] and Morachevskii *et al.*[9] but 30 K lower than in Finogenova *et al.*[7] The solubility equation, valid between the melting point of Na and 850 K, was proposed by Walker and Pratt[6] and is accepted in this evaluation:

$$\log(\text{soly/mol \% Te}) = 0.750 - 1282(T/\text{K})^{-1}. \quad (1)$$

A freezing point depression of Na due to the presence of $2 \cdot 10^{-3}$ mol % Te should be ~0.01 K, as estimated by Petric and Pelton.[1] The Te–Na system was reviewed by Pelton and Petric.[1] The proposed phase diagram is shown in Fig. 28. The results of Kraus and Glass,[4] Walker and Pratt,[6] Finogenova *et al.*,[7] Morachevskii *et al.*,[9] and Petric *et al.*[10] were taken into account. The existence of other solid phases was detected, but they seem (if they exist) to be nonequilibrium phases with the liquid.

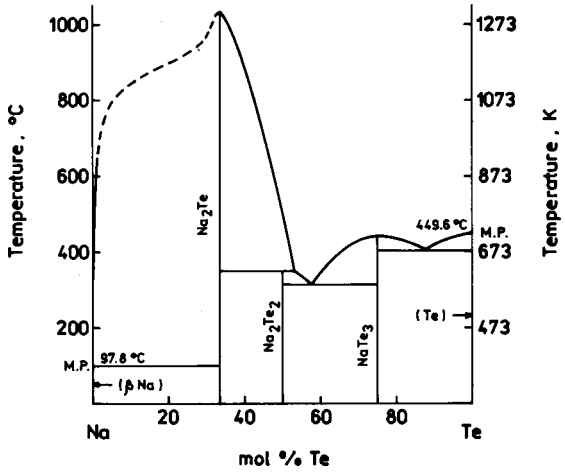

FIG. 28. Te–Na phase diagram.

Tentative values of the solubility of Te in liquid Na

T/K	Solubility/mol % Te	Source
371	$2 \cdot 10^{-3}$ eutectic	Eq. (1) extrapolation
473	0.011	Eq. (1) extrapolation
573	0.03	Eq. (1)
673	0.07	Eq. (1)
773	0.12	Eq. (1), (6)
873	0.2	Eq. (1) extrapolation
1308	33.3 congruent	(7)

For the Te-rich side see the phase diagram and the data sheets.

References:

[1]A. Petric and A. D. Pelton, Bull. Alloy Phase Diagr. **11**, 447 (1990).
[2]G. Pellini and E. Quercigh, Atti Reale Accad. Lincei **19**(Pt. 2) 350 (1910).
[3]S. M. Granstaff and J. C. Thompson, Inst. Phys. Conf. Ser. **30**, 511 (1976).
[4]C. A. Kraus and S. W. Glass, J. Phys. Chem. **33**, 984 (1929).
[5]C. A. Kraus and S. W. Glass, J. Phys. Chem. **33**, 995 (1929).
[6]R. A. Walker and J. N. Pratt, J. Nucl. Mater. **34**, 165 (1970).
[7]V. K. Finogenova, A. A. Uskov, B. A. Popovkin, and A. V. Novoselova, Vestn. Moskov. Univ. **1**, 56 (1970).
[8]V. K. Finogenova, B. A. Popovkin, and A. V. Novoselova, Zh. Neorg. Khim. **15**, 1459 (1970).
[9]A. G. Morachevskii, E. A. Maiorova, N. M. Romanchenko, and M. V. Kozlova, Zh. Prikl. Khim. **55**, 526 (1982).
[10]A. Petric, A. D. Pelton, and M. L. Saboungi, Ber. Bunsenges. Phys. Chem. **93**, 18 (1989).

Components:
(1) Tellurium; Te; [13494-80-9]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
C. A. Kraus and S. W. Glass, J. Phys. Chem. **33**, 984–994, 995–999 (1929).

Variables:
Temperature: 601–865 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data
Several points on the Te–Na liquidus were determined

t/°C	Solubility/mol % Na	Solubility/mol % Te[a]
	Measurements of the electric resistance	
430	20	80
436	25	75
405	35	65
365	40	60
	Thermal analysis	
424.7	7.5	92.5
412.5	10.0	90.0
402.5	12.5 eutectic	87.5
412.2	15	85
413.9	15	85
430.0	20	80
436.0	25	75
424.9	30	70
404.5	35	65
354.4	40	60
328.4	42	58
329.5	44	56
347.0	46	54
346.4	46	54
352.3	48	52
351.0	48	52
429.1	50	50
423.4	50	50
470.6	51	49
500.8	52	48
592.5	54	46

[a]Calculated by the compilers.

The following equilibrium solid phases were identified: Na_2Te, Na_2Te_2, and $NaTe_3$.

Auxiliary Information

Method:
Na_2Te was prepared in liquid NH_3 from Na and Te. After completion of the reaction, the NH_3 was allowed to evaporate and the necessary quantity of Te was added in order to produce an alloy of any desired composition. The tube containing the mixture was heated in N atmosphere to ~873 K and the content thoroughly stirred. A cell for conductivity measurements was made of quartz with Pt electrodes. The resistivity was measured using a Wheatstone precision bridge while stirring the melts. The temperature was measured by means of a Pt/Pt–Rh thermocouple calibrated on the boiling point of H_2O and the melting points of Sn, Zn, Pb, and Al. Thermal analysis was carried out in Pyrex tubes containing the alloy and filled with N. The thermocouple was placed in the axis. The tube was placed in a large graphite crucible in a large gas heated furnace. Temperature–time curves were obtained by means of the same thermocouples.

Source and Purity of Materials:
Te: commercial product, purified by multistage dissolution in HNO_3–HCl and precipitation as TeO_2, reduced by SO_2 to element and vacuum distilled.
Na: "freshly cut."
N: nothing specified.

Estimated Error:
Solubility: nothing specified; precision ±0.5 mol % (by the compilers).
Temperature: nothing specified; precision ±0.5 K (by the compilers).

Components:
(1) Tellurium; Te; [13494-80-9]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
V. K. Finogenova, A. A. Uskov, B. A. Popovkin, and A. V. Novoselova, Vestn. Moskov. Univ. **1**, 56–58 (1970).

Variables:
Temperature: 593–1308 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The liquidus line between Na_2Te and Te was determined. The data were read from a figure and recalculated to mol % Te by the compilers.

t/°C	Solubility/mol % Te
1035[a]	33.3
1005	35.3
919	37.9
851	39.4
777	41.1
692	42.9
598	45.4
543	47.2
481	50.0
370	52.1
320[a]	55.5
363	58.6
394	62.0
425	66.4
447	71.4
455[a]	75.0
451	76.9
438	82.8
423	86.1
425	90.9
440	95.2

[a]Numerical result.

The melting point of Te was found at 450 °C. The authors identified Na_2Te, NaTe, and $NaTe_3$ equilibrium solid phases. The melts showed a strong tendency to undercooling.

Auxiliary Information

Method:
All essential operations were performed in an Ar or He atmosphere. The melts were prepared from Na_2Te and Te taken in proper amounts. The mixtures were melted in quartz tubes. Heating and cooling curves were recorded in a commercial apparatus equipped with a Pt/Pt–Rh thermocouple. Heating and cooling rates were 10 and 5 K/min, respectively. All melts were remelted before the recordings of curves and the Na-rich melts were conditioned at 573 K for 3 weeks. The samples were gravimetrically analyzed: Te—as the element and Na—as Na_2SO_4. Selected samples were analyzed by x-ray diffraction to confirm the composition of the solid phases.

Source and Purity of Materials:
Na_2Te: from direct synthesis of Na and Te at 573 K in an evacuated quartz ampoule, 99.5+% pure.[1]
Te: 99.93% pure.
Na: 99.8+% pure.
Ar or He: dried by passing through K–Na eutectic at 423 K.

Estimated Error:
Solubility: in the preparation of the alloys ±0.3%; reading-out procedure ±0.5 mol %.
Temperature: accuracy ±5 K; reading-out procedure ±5 K.

References:
[1]V. K. Finogenova, B. A. Popovkin, and A. V. Novoselova, Zh. Neorg. Khim. **15**, 1459–1461 (1970).

Components:
(1) Tellurium; Te; [13494-80-9]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
R. A. Walker and J. N. Pratt, J. Nucl. Mater. **34**, 165–173 (1970).

Variables:
Temperature: 495.2–845.2 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of Te in liquid Na was determined at various temperatures

t/°C	Solubility/mol % Te
572.0	0.264
517.5	0.151
503.0	0.126
477.0	0.103
475.5	0.084
466.0	0.116
452.0	0.071
446.0	0.081
425.5	0.068
409.0	0.072
369.0	0.065
363.0	0.058
359.0	0.043
357.0	0.046
329.0	0.060
319.0	0.042
316.5	0.021
262.5	0.026
254.0	0.043
222.0	0.035

The data were approximated by the fitting equation (tested by the compilers):

$$\log(\text{soly/mol \% Te}) = (0.7501 \pm 0.2246) - (1281.3 \pm 154.7)\ (T/\text{K})^{-1}.$$

The solid equilibrium phase Na_2Te was identified.

Auxiliary Information

Method:
Na was equilibrated with an excess of Te in a Ni crucible which was placed and heated inside of a dry Ar box. The melt was stirred with a Ni rod for 24 h at a temperature higher than a sampling temperature. The temperature was decreased to the sampling temperature and the system equilibrated for 12 h. The solution was not mixed during the last hour of the equilibration in order to allow sedimentation of the excess of Te. Samples were withdrawn at the equilibration temperature by means of small sampler cups. The samples were removed from the dry box and dissolved in alcohol. The solution was analyzed for its content of components; Te was determined gravimetrically as pure element. The equilibrium solid phase Na_2Te was tested by x-ray diffraction analysis.

Source and Purity of Materials:
Te: 99.9999% pure, from Johnson Matthey & Co.
Na: "high" purity, from UKAEA, Harwell; distilled and finally contained $1.6 \cdot 10^{-3}$ % O.
Ar: "purified."

Estimated Error:
Solubility: standard deviation ±12%.
Temperature: nothing specified; precision not worse than ±0.5 K (by the compilers).

Components:
(1) Tellurium; Te; [13494-80-9]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
A. G. Morachevskii, E. A. Maiorova, N. M. Romanchenko, and M. V. Kozlova, Zh. Prikl. Khim. **55**, 526–529 (1982).

Variables:
Temperature: 621–810 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data
Several points on the Te–Na liquidus were determined

T/K	Solubility/mol % Na	Solubility/mol % Te[a]
722	0.3	99.7
714	2.6	97.4
698	6.3	93.7
679[b]	12.3	87.7
699	15.2	84.8
704	20.2	79.8
676	34.9	65.1
634	37.7	62.3
621	42.2	57.8
810	53	47

[a]Calculated by the compilers.
[b]From a figure; the numerical value reported at 697 K is considered to be in error.

The authors identified $NaTe_3$, NaTe, and Na_2Te as equilibrium solid phases.

Auxiliary Information

Method:
Measurements of the emf of the cell: Na/alumino–silicate glass with 33 mol % Na_2O/Na–Te were performed at several temperatures. The Na–Te melts were prepared in the cell by melting the elements.[1] The content of Na was analyzed after the measurements by means of flame photometry. The Na electrode was contained in a capillary made of the glass. W wires were used for electric contacts with the electrodes. The potentials of the cells were measured for a fixed composition varying the temperature. Breaks on such relations correspond to phase boundary points of the liquidus. All essential operations were performed in an Ar atmosphere.

Source and Purity of Materials:
Te: "very pure."
Na: free of oxides and other metals.[1]
Ar: nothing specified.

Estimated Error:
Solubility: nothing specified.
Temperature: nothing specified.

References:
[1]N. M. Romnachenko, E. A. Maiorova, and A. G. Morachevskii, Elektrokhimiya **17**, 750–752 (1981).

Components:
(1) Tellurium; Te; [13494-80-9]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
A. Petric, A. D. Pelton, and M. L. Saboungi, Ber. Bunsenges. Phys. Chem. **93**, 18–24 (1989).

Variables:
Temperature: 590–873 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data
Several points on the Te–Na liquidus were determined

t/°C	Solubility/mol % Na	Solubility/mol % Te
317 eutectic	42.5	57.5
325	42.95	57.05
338	44.7	55.3
347 peritectic	46.7	53.3
412	48.3	51.7
478	50.0	50.0
514	51.0	49.0
552	52.0	48.0
600	53.3	46.7

The equilibrium solid phases $NaTe_3$, NaTe, and Na_2Te were identified.

Auxiliary Information

Method:
The experiments were performed in a cell: Na–Te/β-alumina/Bi–Na(17%). W wires were dipped in the Na–Te and Na–Bi melts. The melts were contained in W crucibles sealed with cone-shaped Ta plugs. Both half cells were immersed in a continually stirred Bi–Na (5%) bath which served as electrical contact between the half cells and as a counter electrode used as a source/sink of Na for Coulometric titration. Compositions were varied by applying a small potential difference between the working and counter electrodes. This way the Na concentration was controlled in very precise increments. The experiments were performed either at constant temperature or constant composition. The phase boundaries were determined from the discontinuities of dependencies of potential versus temperature at constant composition. All essential operations were performed inside of a He filled glove box.

Source and Purity of Materials:
Te: "high purity," from Asarco Inc.
Na: from Coulometric titration.
He: nothing specified.

Estimated Error:
Solubility: precision ±0.3 mol %; as in Petric *et al.*[1]
Temperature: precision ±4 K; as in Petric *et al.*[1]

References:
[1]A. Petric, A. D. Pelton, and M. L. Saboungi, J. Electrochem. Soc. **135**, 2754–2760 (1988).

Components:
(1) Tellurium; Te; [13494-80-9]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
G. Pellini and E. Quercigh, Atti Reale Accad. Lincei **19**(Pt. 2) 350–356 (1910).

Variables:
Temperature: 590–1226 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data
The liquidus of the Te–Na system was determined

t/°C	Solubility/mol % Na	Solubility/mol % Te[a]
446	2	98
439	5	95
427	10	90
408	15	85
403	17	83
423	20	80
430	22.5	77.5
432	37.5	62.5
412	40	60
389	42.5	57.5
341	45	55
317	47.5	52.5
331	48.5	51.5
340	50	50
381	52.5	47.5
483	55	45
579	57.5	42.5
715	60	40
868	62.5	37.5
953	66.7	33.3
860	75	25
740	80	20
560	90	10

[a]Calculated by the compilers

The melting points of Te and Na were found at 452 and 97.5 °C, respectively.

Auxiliary Information

Method:
A quartz tube served as a container to melt the elements, since neither glass nor porcelain was sufficiently resistant to corrosion. Na was weighed in Vaseline oil, then cleaned, dried, and cut in small pieces. It was added to a known amount of Te and heated. The melting was performed in N atmosphere. The temperature during thermal analysis was recorded by means of a Pt/Pt–Rh thermocouple.

Source and Purity of Materials:
Te: "purest," in form of powder.
Na: "purest," kept under Vaseline oil.
N: "pure," additionally dried.

Estimated Error:
Solubility: nothing specified.
Temperature: nothing specified.

4.17. Sodium–Polonium

Components:
(1) Polonium; Po; [7440-08-6]
(2) Sodium; Na; [7440-23-5]

Evaluated By:
Hans Ulrich Borgstedt, Forschungszentrum Karlsruhe, Germany and Cezary Guminski, University of Warsaw, Poland, February 1997.

Critical Evaluation

There is no doubt that Po introduced to Na forms Na_2Po similar to the well known Na_2Te.[1,2] Na_2Po is certainly the equilibrium solid phase, when liquid Na is saturated with Po. Na_2Po is probably the most stable compound, an existence of other compounds is quite possible. A solubility of Po in liquid Na was not measured experimentally but due to the more metallic features of Po than Te the solubility of Po should be higher than that observed for Te in liquid Na (see the Te–Na system).

References:
[1]V. G. Chlopin and E. B. Samarceva, Comt. Rend. Acad. URSS **IV**, 433 (1934).
[2]J. M. Goode, U.S. Atom. Energy Comm. Rep. MLM-677 (1952).

4.18. Sodium–Fluorine

Components:
(1) Fluorine; F; [7782-41-4]
(2) Sodium; Na; [7440-23-5]

Evaluated By:
Hans Ulrich Borgstedt, Forschungszentrum Karlsruhe, Germany and Cezary Guminski, University of Warsaw, Poland, February 1997.

Critical Evaluation

There are two publications of Bredig *et al.*[1,2] on the mutual solubilities of NaF in liquid Na and Na in liquid NaF. The first study[1] was concerned with the Na-rich as well as the NaF-rich region and the second study[2] was rather related to the central part of the composition range. The authors applied thermal analysis and chemical analysis of equilibrated phases. This allowed us to estimate the critical miscibility and monotectic temperature; however, the solubility of F in liquid Na below 1073 K for solutions with low contents of NaF is still unknown. The partial Na–F phase diagram was sketched in Bredig[3] and the full composition range of the diagram is shown in Fig. 29.

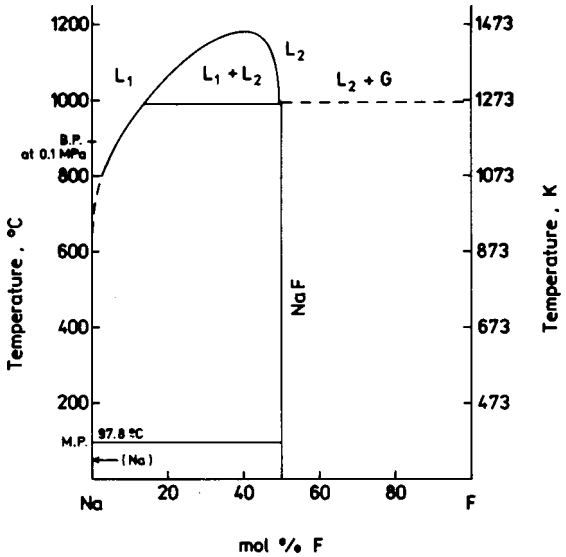

FIG. 29. Na–NaF phase diagram.

Tentative (t) and doubtful (d) values of the solubility of F in liquid Na

T/K	Solubility/mol % F	Source
1073	2.3 (t)	(1)
1173	7.5 (t)	(1)
1263	14 (t) monotectic	(1),(2) interpolated
1373	24 (t)	(2)
1453	41 (t) critical	(2) interpolated
	On the NaF-rich side	
1263	49.5 (d) monotectic	(2) extrapolated
1373	48.45 (d)	(2) extrapolated

References:
[1]M. A. Bredig, J. W. Johnson, and W. T. Smith, J. Am. Chem. Soc. **77**, 307 (1955).
[2]M. A. Bredig and H. R. Bronstein, J. Phys. Chem. **64**, 64 (1960).
[3]M. A. Bredig, *Molten Salt Chemistry*, edited by M. Blander (Interscience, New York, 1964), p. 367.

Components:
(1) Fluorine; F; [7782-41-4]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
M. A. Bredig, J. W. Johnson, and W. T. Smith, J. Am. Chem. Soc. **77**, 307–312 (1955).

Variables:
Temperature: 1074–1351 K

Prepared by:
H. U. Borgstedt & C. Guminski

Experimental Data

The solubility of NaF in liquid Na was determined

t/°C	Solubility/mol % NaF	Solubility/mol % F[a]
801	2.4[b]	2.3
849	5.3[b]	5.0
900	8.1[b]	7.5
952	10.7[b]	9.7
976	14.6[b]	12.7
983	16.4[b]	14.1
1004	17.3	14.7
1026	19.5	16.3
1048	20.0	16.7
1078	23.6	19.1

The solubility of Na in liquid NaF was determined

t/°C	Solubility/mol % Na	Solubility/mol % F[a]
979	0.19[c]	49.95[c]
983	0.96[c]	49.76[c]
1000	7.6	48.02
1001	15.8	45.7
1015	14.8	46.0

[a]Calculated by the compilers.
[b]Solid NaF is the equilibrium phase.
[c]Solid solubility of Na in NaF.

The monotectic temperature was found at 990 °C and the melting point of NaF at 995 °C.

Auxiliary Information

Method:
A container used in the tests was made of 316 Type stainless steel. Cooling and heating curves were recorded for the melting NaF and Chromel/Alumel thermocouples, placed in a well. Containers were washed in $Fe_2(SO_4)_3$(5%)–H_2SO_4(10%) mixture for 20 min at 333–343 K, then in HNO_3(15%)–HF(2%) mixture for 15 min. They were rinsed in H_2O and dried at 383 K. NaF was weighed and loaded into capsules in a dry box filled with N, and the capsules were then evacuated. A cylinder of Na was weighed under mineral oil, rinsed in hexane, placed in the capsule, and evacuated to $<1 \cdot 10^{-3}$ Torr. Gentle heating of the capsule melted Na and removed hexane. The capsules were mounted in a furnace and equilibrated while rocking 2–3 h. The bottom sample of NaF and the upper sample of Na were analyzed after the phase separation. The NaF phase was dissolved in C_2H_5OH–H_2O mixture and titrated with standard acid. Free Na was calculated from the sample weight and alkalinity. The Na phase was dissolved in H_2O–C_2H_5OH mixture. NaF was weighed directly since it was found to be insoluble in C_2H_5OH containing C_2H_5ONa. The alkalinity developed was determined by titration with HNO_3.

Source and Purity of Materials:
NaF: reagent grade, heated (<773 K) in an evacuated ($<5 \cdot 10^{-2}$ Torr) McDanel porcelain tube on a Pt boat. Ar was flushed through the tube while raising temperature 50 K above its melting point. After cooling to room temperature clear fragments of the salt stored in a desiccator over P_2O_5 were used.
Na: filtered through a sintered stainless steel filter at temperature slightly above its melting point.
Ar: "dry."
N: "dry."

Estimated Error:
Solubility: nothing specified; precision not better than ±10% (by the compilers).
Temperature: precision ±3 K in solubility experiments and ±0.5 K in thermal analysis.

Components:
(1) Fluorine; F; [7782-41-4]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
M. A. Bredig and H. R. Bronstein, J. Phys. Chem. **64**, 64–67 (1960).

Variables:
Temperature: 1205–1449 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data
The mutual liquid miscibility of NaF and Na was determined

t/°C	Solubility/mol % NaF	Solubility/mol % F[a]
1126	90.0	47.4
1175	81.0	44.7
1176	66.5	39.9
1156	50.0	33.3
1130	39.5	28.3
1130	39.2	28.2
1107	33.0	24.8
1030	21.6	17.8
932	10.0	9.1

[a]Calculated by the compilers

The monotectic temperature was found at 988±2 °C.

Auxiliary Information

Method:
Thermal analysis of samples was performed in a stainless steel capsule. The capsule was filled with proper amounts of NaF and Na, and was flushed with Ar. After that it was welded shut with a flat top and placed inside a tank made of Inconel and Ar pressurized with up to ~0.7 MPa. To detect a small thermal effect the ratio of the container weight to the sample weight was reduced by employing thin walled construction tubes. Temperatures were measured by means of a Pt/Pt–Rh(10%) thermocouple inserted in the bottom of the thermocouple well (Johnson and Bredig[1]). Cooling and heating cycles were repeated 2–4 times for each sample composition.

Source and Purity of Materials:
NaF: nothing specified; probably as in Bredig *et al.*[2]
Na: nothing specified: probably as in Bredig *et al.*[2]
Ar: "pure."

Estimated Error:
Solubility: nothing specified; precision no better than ±0.1 mol % (by the compilers).
Temperature: precision ±1 K.

References:
[1]J. W. Johnson and M. A. Bredig, J. Phys. Chem. **62**, 604–607 (1958).
[2]M. A. Bredig, J. W. Johnson, and W. T. Smith, J. Am. Chem. Soc. **77**, 307–310 (1955).

4.19. Sodium–Chlorine

Components:
(1) Chlorine; Cl; [7782-50-5]
(2) Sodium; Na; [7440-23-5]

Evaluated By:
Hans Ulrich Borgstedt, Forschungszentrum Karlsruhe, Germany and Cezary Guminski, University of Warsaw, Poland, February 1997.

Critical Evaluation

Cl introduced into liquid Na reacts spontaneously irreversibly forming NaCl, and consequently NaCl and Na are the equilibrium phases of the system. Due to practical reasons, determinations of a solubility of Na in liquid NaCl were initiated much earlier than of other halides.[1–3] Results of these investigations (being in mutual agreement) were highly overestimated, since probably impure reagents were therein used. In subsequent studies of Bredig *et al.*[4] and Adaev and Morachevskii[5] (being also in mutual agreement) comparatively smaller values of the solubility were determined. However, it seems that results of the most recent papers of Bredig and Bronstein,[6] Smirnov and Podlesnyak,[7] and Smirnov *et al.*[8] reflect best the NaCl-rich part of the Na–NaCl liquidus line. Complete miscibility of the metal and its chloride was observed at temperatures higher than 1353 K.[6,9] The monotectic was measured at 1068 K (5 K below the melting point of NaCl, which contemporarily is established at 1074 K) and was extended from 3.3 to 49.4 mol % Cl. Williams *et al.*[10] estimated that a solubility of Cl in liquid Na at 673 K is $<6\cdot10^{-4}$ mol % Cl. Bredig *et al.*[4,6] determined the solubilities at temperatures higher than 823 K. A rather significant scatter of the latter results between the monotectic temperature and 823 K does not allow for a precise extrapolation of the dependence to 673 K for a comparison with Williams *et al.*[10] A mean line drawn through these results would suggest a solubility 1 order of magnitude higher than observed by Williams *et al.*[10] The considerations of Allan,[11] based on thermodynamics, predicted the solubility of Cl in liquid Na as five times larger than for Br and I at the same temperatures. Neckel[12] predicted the liquidus and critical mixing point at 33.7 mol % Cl and 1352.7 K in very good agreement with the experimental results of Bredig and Bronstein.[6] Bredig[9] drew the Na–Cl partial phase diagram and its more complete form is reflected in Fig. 30. The phase equilibria for the mixed KCl–NaCl/Na–K system were investigated in Smirnov and Podlesnyak[13,14] and for the LiCl–NaCl/Li–Na system in Jellinek and Czerwinski.[15] Jellinek and Czerwinski[15] neglected the solubilities of the salts in the metals. The solubility of Cl in molten NaCl was critically elaborated in Tomkins and Bansal.[16]

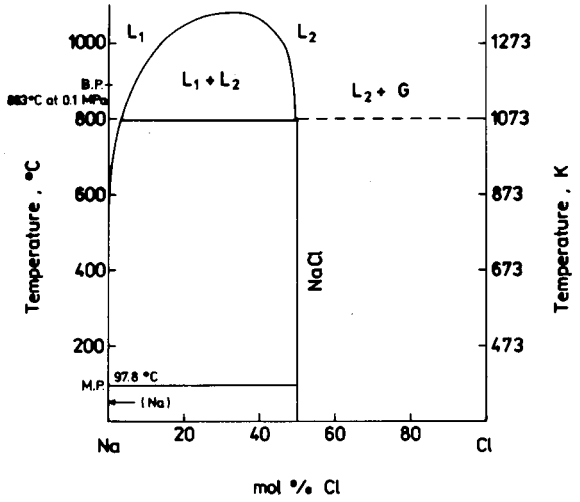

FIG. 30. Na–NaCl phase diagram.

T/K	Solubility/mol % Cl	Source
	Tentative (t) and doubtful (d) values of the solubility of Cl in liquid Na	
673	$6 \cdot 10^{-4}$ (d)	(10)
823	0.1 (d)	(4)
923	0.6 (d)	(4) interpolated
1068	3 (t) monotectic	(4),(6)
1173	8 (t)	(4) interpolated
1273	14 (t)	(6) interpolated
1353	33 (t) critical	(6)
	Tentative values of the solubility on the NaCl-rich side	
1068	49.4 (t) monotectic	(6),(7),(8) extrapolated
1173	49.0(t)	(6),(7),(8),(14) interpolated
1273	46.5(t)	(6) interpolated

References:

[1]L. Stockem, Metallurgie **1**, 20 (1904).
[2]R. Lorenz and R. Winzer, Z. Anorg. Chem. **183**, 121 (1929).
[3]N. A. Belozerskii, Tr. Gos. Inst. Prikl. Khim. **33**, 50 (1940).
[4]M. A. Bredig, J. W. Johnson, and W. T. Smith, J. Am. Chem. Soc. **77**, 307 (1950).
[5]E. I. Adaev and A. G. Morachevskii, Zh. Prikl. Khim. **38**, 2105 (1965).
[6]M. A. Bredig and H. R. Bronstein, J. Phys. Chem. **64**, 64 (1960).
[7]M. V. Smirnov and N. P. Podlesnyak, Tr. Inst. Elektrokhim. Ural. Fil. Akad. Nauk SSSR **11**, 101 (1968).
[8]M. V. Smirnov, V. V. Chebykin, and L. A. Tsiovkina, Electrochim. Acta **26**, 1275 (1981).
[9]M. A. Bredig, *Molten Salt Chemistry*, edited by M. Blander (Interscience, New York, 1964), p. 367.
[10]D. D. Williams, J. A. Grand, and R. R. Miller, U.S. Navy Res. Lab. Rep. NRL-Memo-424 (1955).
[11]C. G. Allan, *Liquid Alkali Metals* (BNES, London, 1973), p. 165.
[12]A. Neckel, Monatsh. Chem. **96**, 1617 (1965).
[13]M. V. Smirnov and N. P. Podlesnyak, Tr. Inst. Elektrokhim. Ural. Fil. Akad. Nauk SSSR **14**, 14 (1970).
[14]M. V. Smirnov and N. P. Podlesnyak, Zh. Prikl. Khim. **42**, 2454 (1969).
[15]K. Jellinek and J. Czerwinski, Z. Anorg. Chem. **139**, 233 (1924).
[16]R. P. T. Tomkins and N. P. Bansal, *Gases in Molten Salts, Solubility Data Series* (Pergamon, Oxford, 1990), Vol. 45/46, p. 118.

Components:
(1) Chlorine; Cl; [7782-50-5]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
L. Stockem, Metallurgie **1**, 20–26 (1904).

Variables:
One temperature: 1083 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of Na in liquid NaCl at 810 °C was determined in several experiments: 3.49, 3.46, 2.95, 2.79, 3.55, 3.47, and 3.39 mass % Na. The mean value calculated is 93.3±0.3 mass % Na and, as calculated by the compilers, is 47.91 mol % Cl in Na or 8.0 mol % Na in liquid NaCl.

Auxiliary Information

Method:
Na and NaCl taken in various amounts were melted together in a Ni crucible under H atmosphere. The crucible was hermetically closed in a steel container. The container was heated till Na vapor appeared. The melt was cooled down in a H stream. Both the solid phases (the salt and the metal) were mechanically isolated. The salt phase was analyzed for its Na content by an unspecified method.

Source and Purity of Materials:
NaCl: nothing specified.
Na: nothing specified.
H: dried and purified by a "known procedure."

Estimated Error:
Solubility: precision ±10%.
Temperature: nothing specified.

Components:
(1) Chlorine; Cl; [7782-50-5]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
R. Lorenz and R. Winzer, Z. Anorg. Chem. **183**, 121–126 (1929).

Variables:
Temperature: 1073 and 1123 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data
The solubility of Na in molten NaCl was determined

t/°C	Solubility/mass % Na	Solubility/mol % Na in NaCl[a]	Solubility/mol % Cl[a]
800	3.4	8.2	47.3[b]
···	5.4	12.6	
···	3.2	7.8	
···	4.3	10.3	
···	4.8	11.4	
850	15–20	31–39	39.4[b]

[a]Calculated by the compilers.
[b]Mean value of total Cl content.

The authors observed that the miscibility gap disappeared at higher temperatures.

Auxiliary Information

Method:
Molten NaCl was contained within a Jena glass tube. Na was added to the melt in portions which became colored. The melt with an excess of Na was jolted at selected temperature. Subsequently it was cooled quickly, and the metal and salt phases were separated. The amount of Na was determined by dissolution of the salt phase in H_2O and titration of the alkaline aqueous solution with 0.1 mol/dm^3 HCl.

Source and Purity of Materials:
NaCl: nothing specified.
Na: nothing specified.

Estimated Error:
Solubility: precision ±20%.
Temperature: nothing specified.

Components:
(1) Chlorine; Cl; [7782-50-5]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
N. A. Belozerskii, Tr. Gos. Inst. Prikl. Khim. **33**, 50–108 (1940).

Variables:
Temperature: 903–1083 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data
The solubility of Na in liquid NaCl was determined

t/°C	Solubility/mol % Na	Solubility/mol % Cl[a]
630[b]	1.8	49.55[b]
680[b]	3.1	49.21[b]
710[b]	4.0	48.98[b]
810	9.7	47.45

[a]Calculated by the compilers.
[b]Read from a figure as a solid solubility.

Auxiliary Information

Method:
The molten salt was introduced into a glass container. A W cathode and a graphite anode were mounted in the container. The cathodic and anodic compartments were isolated by a porcelain tube. The hermetically closed container was placed in an oven with regulated temperature. Electrolysis with a current of 2–3 A was carried out for 1–1.5 h thus saturating NaCl with Na. The two phases were cooled to room temperature and were then separated mechanically. Si, which crystallized out on the surface, was carefully removed. The NaCl phase was dissolved in H_2O. The content of Na was found from titration of the resulting solution with 0.01 mol·dm^{-3} HCl using phenolphthalein as the indicator. The apparatus was assembled in an Ar atmosphere.

Source and Purity of Materials:
NaCl: purified by blowing dry HCl through the molten salt for 2–3 h.
Na: from the electrolysis.
Ar: nothing specified.

Estimated Error:
Solubility: nothing specified; reading-out procedure ±0.1 mol % Na.
Temperature: accuracy ±10 K.

Components:
(1) Chlorine; Cl; [7782-50-5]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
M. A. Bredig, J. W. Johnson, and W. T. Smith, J. Am. Chem. Soc. **77**, 307–312 (1950).

Variables:
Temperature: 823–1274 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of NaCl in liquid Na was determined

t/°C	Solubility/mol % NaCl	Solubility/mol % Cl[a]
550	0.12[b]	0.12
649	0.75[b]	0.75
750	1.8[b]	1.75
781	2.2[b]	2.15
784	2.4[b]	2.35
790	2.9[b]	2.8
832	4.2	4.0
874	5.8	5.5
913	8.3	7.7
957	11.1	10.0

[a]Calculated by the compilers.
[b]Solid NaCl is the equilibrium phase.

The solubility of Na in liquid NaCl was determined

t/°C	Solubility/mol % Na	Solubility/mol % Cl[a]
750	0.08[b]	49.98
784	0.11[b]	49.97
790	0.15[b]	49.96
809	2.8	49.29
811	2.8	49.29
826	4.9	48.74
889	9.3	47.56
890	10.2	47.31
929	21.3	44.04
949	25.6	42.66
950	25.1	42.82
975	27.8[c]	41.93
976	32.0	40.48
1001	33.0	40.12

[a]Calculated by the compilers.
[b]Solid solubility of Na in NaCl.
[c]Equilibrated only 1 h.

The melting point of NaCl was found at 803 °C and the monotectic temperature at 794 °C.

Auxiliary Information

Method:
The container used for the tests was made of Type 316 stainless steel. Cooling and heating curves were recorded for the melting point of NaCl and the monotectic with the use of a Chromel/Alumel thermocouple placed in a well. Containers were washed in a $Fe_2(SO_4)_3$(5%)–H_2SO_4(10%) mixture for 20 min at 333–343 K, then in HNO_3(15%)–HF(2%) mixture for 15 min. They were rinsed in H_2O and dried at 383 K. NaCl was weighed and loaded into capsules in a dry box filled with N, after that the capsules were evacuated. A cylinder of Na was weighed under mineral oil, rinsed in hexane, placed in the capsule, and evacuated to $<1\cdot10^{-3}$ Torr. Gentle heating of the capsule melted Na and removed hexane. The capsules were mounted in a furnace and equilibrated, while rocking 2–3 h. The bottom sample of NaCl and the upper sample of Na were analyzed after a phase separation. The NaCl phase was dissolved in C_2H_5OH–H_2O mixture and titrated with a standard acid. Free Na was calculated from the sample weight and the alkalinity. Na sample was dissolved in a C_2H_5OH–H_2O mixture, the alkalinity developed was determined with HNO_3 and Cl as AgCl precipitate.

Source and Purity of Materials:
NaCl: reagent grade, heated (<773 K) in an evacuated (<0.05 Torr) quartz tube. Ar flushed through the tube while raising the temperature 50 K above its melting point. After slow cooling to room temperature, clear fragments of the salt stored in a desiccator over P_2O_5.
Na: filtered through a sintered stainless steel filter at a temperature slightly above its melting point.
Ar: "dry."
N: "dry."

Estimated Error:
Solubility: precision ±2% (estimated by the compilers).
Temperature: precision ±3 K in solubility experiments; precision ±0.5 K in thermal analysis.

Components:
(1) Chlorine; Cl; [7782-50-5]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
M. A. Bredig and H. R. Bronstein, J. Phys. Chem. **64**, 64–67 (1960).

Variables:
Temperature: 1117–1352 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data
The mutual miscibility of molten NaCl and Na was determined

t/°C	Solubility/mol % Na in NaCl	Solubility/mol % Cl in Na[a]
844	2.93[c]	49.26[c]
845	3.10[c]	49.21[c]
854	3.16[c]	49.20[c]
869	3.24[c,e]	49.18[c,e]
891	3.84[c]	49.02[c]
895	3.87[c]	49.01[c]
880	3.97[c,e]	48.99[c,e]
895	4.25[c]	48.91[c]
948	7.55[d]	48.04[d]
1009	14.2	46.2
1054	25.0	42.9
1068	35.0	39.4
1079	50.0	33.3
1055	75.0	20.0
946[b]	90.0	9.1

[a]Calculated by the compilers.
[b]The investigators also observed another temperature arrest at 960 °C probably connected with the precipitation of traces of Na_2O.
[c]From equilibration and analytical tests reported in Bronstein and Bredig.[3]
[d]From equilibration and analytical tests made in a capsule reported in Bredig *et al.*:[1] 10 h of shaking and with prefusing NaCl, which prevented the presence of metal phase in a sampling chamber.
[e]Not reported in Bronstein and Bredig.[3]

The monotectic temperature was found at 795±1 °C.

Auxiliary Information

Method:
Thermal analysis of samples was performed in a stainless steel capsule. The capsule was filled with known amounts of NaCl and Na and with Ar as cover gas. The capsule was welded shut with a flat top and placed inside a tank made of Inconel and Ar pressurized with up to ~0.7 MPa. The ratio of the container weight to the sample weight was reduced by employing thin walled construction tubes. Temperatures were measured using a Pt/Pt–Rh(10%) thermocouple well.[2] Cooling and heating cycles were repeated 2–4 times for each composition. Some samples of Na+NaCl were equilibrated in an Al_2O_3 single crystal crucible in an Ar atmosphere.[3] A sample of liquid NaCl with dissolved Na was withdrawn by means of a sampler. The sample was treated with C_2H_5OH–H_2O mixture under Ar atmosphere, before H_2O was added for the final dissolution The weight of the sample and alkalinity determined by titration gave the Na content.

Source and Purity of Materials:
NaCl: reagent grade, predried at 453 K for several days, further dehydrated at a temperature of 50 K below the melting point until a pressure of 2 Pa was reached.[3]
Na: contained 0.2% K and 0.1% O.[3]
Ar: "pure."

Estimated Error:
Solubility: nothing specified.
Temperature: precision ±1 K.

References:
[1]M. A. Bredig, J. W. Johnson, and W. T. Smith, J. Am. Chem. Soc. **77**, 307–312 (1955).
[2]J. W. Johnson and M. A. Bredig, J. Phys. Chem. **62**, 604–607 (1958).
[3]H. R. Bronstein and M. A. Bredig, J. Am. Chem. Soc. **80**, 2077–2081 (1958).

Components:
(1) Chlorine; Cl; [7782-50-5]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
E. I. Adaev and A. G. Morachevskii, Zh. Prikl. Khim. **38**, 2105–2107 (1965).

Variables:
Temperature: 1090–1167 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data
The solubility of Na in liquid NaCl was determined

t/°C	Solubility/mol % Na	Solubility/mol % Cl[a]
817	4.83	48.76
829	5.05	48.70
842	6.47	48.33
844	6.12	48.42
846	6.44	48.34
848	7.01	48.18
850	6.23	48.39
861	7.75	47.98
867	8.22	47.86
873	7.00	48.19
875	7.81	47.97
878	7.74	47.99
889	9.12	47.61
894	10.41	47.25

[a]Calculated by the compilers.

The authors expressed the solubilities with the equation:

$$\log(\text{soly/mol \% Na}) = 0.623 + 0.003\,83(T - 1073), \quad T \text{ in K.}$$

Such a simple equation is not recommended.

Auxiliary Information

Method:
A container, mixer, and sampling tube were made of 1Kh18N9T stainless steel. A Chromel/Alumel thermocouple was sheathed with a ceramic Al_2O_3 tube. The experiments were performed in an Ar atmosphere. The temperature of the container was regulated by means of a thermostatic furnace. Molten NaCl and Na were introduced into the container, mixed for 30 min, and equilibrated at a fixed temperature for 2–3 h. Samples of NaCl phase were withdrawn using a quartz tube. The content of Na was determined by titration of the aqueous solution with 0.1 mol·dm^{-3} HCl.

Source and Purity of Materials:
NaCl: chemically pure.
Na: from electrolysis of NaCl.
Ar: purified by blowing through K–Na eutectic liquid mixture.

Estimated Error:
Solubility: precision ±8%.
Temperature: nothing specified.

Components:
(1) Chlorine; Cl; [7782-50-5]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
M. V. Smirnov and N. P. Podlesnyak, Tr. Inst. Elektrokhim. Ural. Filala. Akad. Nauk SSSR **11**, 101–109 (1968).

Variables:
Temperature: 1093–1153 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data
The solubility of Na in liquid NaCl was determined

t/°C	Solubility/mol % Na	Solubility/mol % Cl[a]
820	2.5	49.37
835	2.6	49.34
853	2.9	49.26
880	3.8	49.03

[a]Calculated by the compilers.

The results were also reported graphically in Smirnov *et al.*[1]

Auxiliary Information

Method:
The tests were carried out in a hermetically closed bomb made of 1Kh18N9T steel which contained inside an alundum crucible. The bomb was encapsulated in a quartz container. A graphite rod for Cl electrode in alundum diaphragm (Al_2O_3) as the anode and Armco Fe as the cathode were dipped into the molten NaCl. A Chromel/Alumel thermocouple was placed in a shielding tube made of Armco Fe and positioned just above the Na melt level. The Na concentration was controlled by Coulometric electrolysis. The corresponding charge was measured with a Cu Coulometer. The experiments were performed in an Ar atmosphere. Traces of oxidants in the melt were pre-electrolyzed. The current efficiency of the electrolysis was found to be 100%±1% by a subsequent chemical analysis of the electrolyte. The redox potential between the reference anode and the indicator cathode was measured in time. Stable potential differences were observed after 20–30 min. The potential differences were linearly dependent on the logarithm of the Na concentration up to the saturation point and a further increase of the Na concentration made no effect on the potential difference.

Source and Purity of Materials:
NaCl: spectrally pure, dried, and remelted in an Ar atmosphere.
Na: from electrolysis of NaCl.
Ar: purified on Ca turnings at 873 K, Ti turnings at 1123 K, and over molten Li at 623 K.

Estimated Error:
Solubility: precision ±0.1 mol (by the compilers).
Temperature: nothing specified.

References:
[1]M. V. Smirnov and N. P. Podlesnyak, Tr. Inst. Elektrokhim. Ural. Filiala Akad. Nauk SSSR **14**, 14–18 (1970).

Components:
(1) Chlorine; Cl; [7782-50-5]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
M. V. Smirnov and N. P. Podlesnyak, Zh. Prikl. Khim. **42**, 2454–2459 (1969).

Variables:
Temperature: 1093–1173 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data
The solubility of Na in molten NaCl was determined

t/°C	Solubility/mol % Na in NaCl	Solubility/mol % Cl[a]
820	2.5	49.37
860	2.9	49.26
900	4.0	48.98

[a]Calculated by the compilers.

Auxiliary Information

Method:
The experiments were performed in a closed bomb made of 1Kh18N9T stainless steel which contained an Alundum (Al_2O_3) crucible inside. The bomb was further encapsulated in a quartz container. NaCl was placed in the crucible and melted. A chloride anode (graphite) separated by an Alundum diaphragm and an Armco Fe cathode were dipped into the melt. A Chromel/Alumel thermocouple was shielded in a tube made of Armco Fe; it was positioned just above the melt. The Na concentration was controlled by Coulometric electrolysis. The charge was measured by a Cu coulometer. Potentials between a reference electrode and an indicator cathode (Armco Fe) were measured after the electrolysis was stopped. Stable potential differences were observed after 20–30 min. The saturating Na concentrations corresponded to the break points on dependencies relating the potential versus the logarithm of the Na concentration. All essential operations were performed in Ar atmosphere.

Source and Purity of Materials:
NaCl: spectrally pure.
Na: from the electrolysis.
Ar: purified over Ti turnings at 1123 K and molten Li at 623 K.

Estimated Error:
Solubility: nothing specified; precision ±0.1% (by the compilers).
Temperature: nothing specified.

Components:
(1) Chlorine; Cl; [7782-50-5]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
M. V. Smirnov, V. V. Chebykin, and L. A. Tsiovkina, Electrochim. Acta **26**, 1275–1288 (1981).

Variables:
Temperature: 1089 and 1137 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data
The solubility of Na in liquid NaCl was determined

t/°C	Solubility/mol % Na	Solubility/mol % Cl[a]
816	2.42	49.39
864	4.06	48.96

[a]Calculated by the compilers.

Auxiliary Information

Method:
All parts being in contact with mixtures of NaCl and Na were made of a stainless steel resistant to their action at high temperatures. The pressure developed by the saturated vapors in a hermetically sealed inner part of the device was fixed with bellows manometer which had an automatic regulator for balancing the pressure of Ar in the outer, also hermetically sealed, part of the apparatus. The experimental installation was tested by means of measuring the pressure of K and Cs saturated vapors over wide temperature ranges. The measured values were in good agreement with the most reliable reference data. The mixtures were composed directly by distilling definite amounts of Na into the container filled with a known amount of NaCl. Saturation points were found from breaks in the relation of pressure versus temperature.

Source and Purity of Materials:
NaCl: "particularly pure," further recrystallized, and dried under vacuum, with the temperature being raised slowly up to 723 K until H_2O condensation in liquid N trap ceased. The alkalinity was 0.005–0.01 mol %.
Na: 99.99% pure.
Ar: nothing specified.

Estimated Error:
Solubility: precision ±3%.
Pressure: precision ±250 Pa or ±2%.
Temperature: precision ±1 K.

4.20. Sodium–Bromine

Components:
(1) Bromine; Br; [7726-95-6]
(2) Sodium; Na; [7440-23-5]

Evaluated By:
Hans Ulrich Borgstedt, Forschungszentrum Karlsruhe, Germany and Cezary Guminski, University of Warsaw, Poland, February 1997.

Critical Evaluation

Br in contact with Na reacts irreversibly with formation of NaBr and this salt is the solid equilibrium phase in the saturated liquid Na. A solubility of Br in liquid Na has been measured quite extensively by several authors between 420 and 1200 K. Clough[1] and Allan[2] performed corresponding experiments at temperatures <723 K while investigating a dissolution of NaBr deposits on stainless steel tubes. Bredig *et al.*[3,4] performed analytical determinations at temperatures >823 K and found the solubilities as well as the liquidus line in the liquid miscibility gap range. The monotectic temperature was found 7 K (Bredig[5]) below the melting point of NaBr at 1028 K. Smirnov[6] confirmed a part of the liquidus for the NaBr-rich side using of vapor pressure measurements. An extrapolation of the Bredig's data[3] to lower temperature would suggest 1 order of magnitude higher solubilities than those found by Clough[1] and Allan.[2] There are three possible explanations: (i) saturation of Na with NaBr was not reached in the experiments of Clough[1] and Allan[2] although an agreement of the results from Clough[1] and Allan[2] is observed; (ii) the solubility results of Bredig *et al.*[3] below the monotectic temperature are not sufficiently precise to be extrapolated to such low temperatures; (iii) by analogy to similar experiments performed for the Na–I system by Sagawa *et al.*[7] one may suggest that some metallic elements that could be leached from the stainless steel apparatus of Clough[1] and Allan[2] react with Br dissolved in liquid Na with a formation of precipitates, and finally the Br concentration was decreased. A single determination of the solubility of molten Na in molten NaBr was performed by Mollwo[8] at 1143 K by means of electroconductivity measurements. The content of 0.4 mol % Na in NaBr is ten times too low compared to the data of Bredig *et al.*,[3] Bredig and Bronstein,[4] and Smirnov *et al.*;[6] the result of Mollwo[8] was therefore rejected.

The solubility of Br in molten NaBr was elaborated in Tomkins and Bansal.[9] The assessed phase diagram of the Na–Br system, as partly presented in Bredig,[5] is shown in Fig. 31.

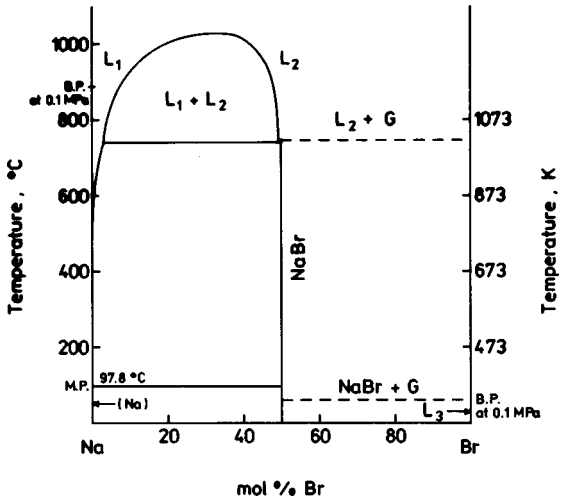

FIG. 31. Na–NaBr phase diagram.

T/K	Solubility/mol % Br	Source
	Tentative (t) and doubtful (d) values of the solubility of Br in liquid Na.	
423	$6\cdot10^{-8}$ (d)	(2)
523	$2\cdot10^{-6}$ (d)	(2)
623	$2\cdot10^{-4}$ (d)	(1)
723	$2\cdot10^{-3}$ (d)	(1)
823	0.21 (d)	(3)
923	1.0 (t)	(3) interpolated
1021	2.9 (t) monotectic	(3) interpolated
1123	5 (t)	(3) interpolated
1223	12 (t)	(3) interpolated
1299	34 (d) critical	(4) interpolated
	Tentative (t) and doubtful (d) values of the solubility on the NaBr-rich side.	
1021	49.24 (t) monotectic	(6) extrapolated
1123	48.4 (d)	(4) interpolated
1223	45.9 (t)	(4)

References:

[1]W. S. Clough, J. Nucl. Energy **25**, 417 (1971).
[2]C. G. Allan, *Liquid Alkali Metals* (BNES, London, 1973), p. 159.
[3]M. A. Bredig, J. W. Johnson, and W. T. Smith, J. Am. Chem. Soc. **77**, 307 (1955).
[4]M. A. Bredig and H. R. Bronstein, J. Phys. Chem. **64**, 64 (1960).
[5]M. A. Bredig, *Molten Salt Chemistry*, edited by M. Blander (Interscience, New York, 1964), p. 367.
[6]M. V. Smirnov, V. V. Chebykin, and L. A. Tsiovkina, Electrochim. Acta **26**, 1275 (1981).
[7]N. Sagawa, S. Miyahara, and T. Sone, *Liquid Metal Systems*, edited by H. U. Borgstedt and G. Frees (Plenum, New York, 1995), p. 321.
[8]E. Mollwo, Phys. Z. **36**, 740 (1935).
[9]R. P. T. Tomkins and N. P. Bansal, *Gases in Molten Salts*, Solubility Data Series (Pergamon, Oxford, 1990), Vol. 45/46, p. 180.

Components:
(1) Bromine; Br; [7726-95-6]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
M. A. Bredig, J. W. Johnson, and W. T. Smith, J. Am. Chem. Soc. **77**, 307–312 (1955).

Variables:
Temperature: 823–1228 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of NaBr in liquid Na was determined

t/°C	Solubility/mol % NaBr	Solubility/mol % Br[a]
550	0.21[b]	0.21
600	0.41[b]	0.41
660	1.1[b]	1.09
687	1.3[b]	1.28
721	2.4[b]	2.34
757	3.3	3.19
825	4.6	4.4
894	7.8	7.2
955	12.1	10.8

[a]Calculated by the compilers.
[b]Solid NaBr is the equilibrium phase.

The solubility of Na in liquid NaBr was determined

t/°C	Solubility/mol % Na	Solubility/mol % Br[a]
650	0.04[b]	49.99
685	0.07[b]	49.98
720	0.15[b]	49.96
750	4.6±0.1	48.82
799	6.8	48.29
849	6.4	48.35
852	7.3	48.11
909	12.2	46.75
943	14.7	46.03
953	15.0±0.3	45.94

[a]Calculated by the compilers.
[b]Solid solubility of Na in NaBr.

The melting point of NaBr was found at 1010 K and the monotectic temperature at 1013 K.

Auxiliary Information

Method:
A container used for the tests was made of Type 316 stainless steel. Cooling and heating curves were recorded for the determination of the melting point of NaBr and the monotectic. A Chromel/Alumel thermocouple was placed in a well. The container was washed in $Fe_2(SO_4)_3$(5%)–H_2SO_4(10%) mixture for 20 min at 333–343 K, then in HNO_3(15%)–HF(2%) mixture for 15 min. It was rinsed in H_2O and dried at 383 K. NaBr was weighed and loaded into a capsule in a dry box filled with N. The capsule was evacuated. Na was weighed under mineral oil, rinsed in hexane, placed in the capsule, and evacuated to $<1\cdot10^{-3}$ Torr. Gentle heating of the capsule melted Na and removed hexane. The capsule was mounted in a furnace and equilibrated while rocking 2–3 h. The bottom sample of NaBr was dissolved in a C_2H_5OH–H_2O mixture and titrated with a standard acid. Free Na was calculated from the sample weight and the alkalinity. The Na phase, upper sample was dissolved in C_2H_5OH–H_2O mixture. The alkalinity developed was determined with HNO_3 and Br as AgBr precipitate.

Source and Purity of Materials:
NaBr: reagent grade, heated (<773 K) in an evacuated (0.05 Torr) quartz tube. Ar was flushed through the tube while raising the temperature 50 K above its melting point. After slow cooling to room temperature, only clear fragments of the salt were selected and stored in a desiccator over P_2O_5.
Na: filtered through a sintered stainless steel filter at a temperature slightly above its melting point.
Ar: "dry."
N: "dry."

Estimated Error:
Solubility: precision ±2% (by the compilers).
Temperature: precision ±3 K in solubility experiments, precision ±0.5 K in thermal analysis.

Components:
(1) Bromine; Br; [7726-95-6]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
M. A. Bredig and H. R. Bronstein, J. Phys. Chem. **64**, 64–67 (1960).

Variables:
Temperature: 1070–1305 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data
The mutual miscibility of liquid NaBr and Na was determined

t/°C	Solubility/mol % Na	Solubility/mol % Br[a]
797	4.12[b]	48.95
802	4.86[d]	48.75
808	4.97[b]	48.73
811	5.20[d]	48.66
897	8.92[b]	47.67
896	9.10[b]	47.62
948	15.4[c]	45.83
1032	48.5	34.0
1013	48.8	33.9
1018	49.0	33.8
1004	74.5	20.3
1000	75.0	20.0

[a]Calculated by the compilers.
[b]Also reported in Bronstein and Bredig[1] from equilibration tests.
[c]From equilibration made in special capsule for 10 h without shaking and prefusing NaBr, thus preventing the presence of the metal phase in a sampling chamber
[d]Reported in Bronstein and Bredig[1] from equilibration tests.

The monotectic temperature was found at 741 °C (1014 K) and this temperature is probably too low due to slight Na_2O contamination, as suggested by the authors. The melting point of NaBr was found at 747 °C, 8 K lower than the contemporarily accepted value.

Auxiliary Information

Method:
Thermal analysis of samples was performed in a stainless steel capsule. The capsule was filled with known amounts of NaBr and Na, and with Ar gas over the solids. The capsule was welded shut with a flat top and placed inside a tank made of Inconel, into which Ar was pressurized with up to ~0.7 MPa. The ratio of the container weight to the sample weight was reduced by employing thin walled construction tubes. Temperatures were measured with a Pt/Pt–Rh(10%) thermocouple.[2] Cooling and heating cycles were repeated 2–4 times for each sample. Some (Na+NaBr) samples were equilibrated in a Al_2O_3 single crystal crucible in an Ar atmosphere.[1] A sample of liquid NaBr saturated with Na was withdrawn by means of a sampler. The sample was treated with C_2H_5OH under Ar atmosphere, before H_2O was added for final dissolution. The weight of the sample and the alkalinity determined by titration gave the free Na content.

Source and Purity of Materials:
NaBr: reagent grade, pre-dried at 453 K for several days, further dehydrated at temperature 50 K below the melting point until a pressure of 2 Pa was obtained.[1]
Na: contained 0.2% K and 0.1% O.[1]
Ar: "pure."

Estimated Error:
Solubility: nothing specified.
Temperature: precision ±1 K.

References:
[1]H. R. Bronstein and M. A. Bredig, J. Am. Chem. Soc. **80**, 2077–2081 (1958).
[2]J. W. Johnson and M. A. Bredig, J. Phys. Chem. **62**, 604–607 (1958).

Components:
(1) Bromine; Br; [7726-95-6]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
W. S. Clough, J. Nucl. Energy **25**, 417–423 (1971).

Variables:
Temperature: 573–723 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data
The solubility of Br in liquid Na was determined. The data were read out from a figure and recalculated by the compilers.

T/K	t/°C	Solubility/mol % Br
573	300	$9\cdot10^{-5}$
623	350	$1.7\cdot10^{-4}$
673	400	$6\cdot10^{-4}$
723	450	$1.5\cdot10^{-3}$

Auxiliary Information

Method:
Radioactive Br was introduced as a solution of ^{82}Br into the central section and dried onto the stainless steel tube before the remainder of the apparatus was assembled. The apparatus was made of stainless steel. It was evacuated and liquid Na introduced into an equilibration compartment. The temperature was raised to the chosen value. After reaching equilibrium of Na with NaBr the Na ran down into a Pyrex glass collector. The compartment was refilled and the experiment repeated with successive batches of Na. The removal of Br from the central section was recorded by a scintillation counter. The mass of Na was measured by marking the level of Na in the Pyrex collector at each stage and weighing at the end of the experiment.

Source and Purity of Materials:
NaBr: solution dried in a stainless steel oven.
Na: purified by hot and cold trapping, and distillation.

Estimated Error:
Solubility: nothing specified; reading-out procedure better than ±10%.
Temperature: nothing specified; reading-out procedure ±2 K.

Components:
(1) Bromine; Br; [7726-95-6]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
C. G. Allan, *Liquid Alkali Metals* (BNES, London, 1973), pp. 159–165.

Variables:
Temperature: 420–670 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of NaBr in liquid Na was determined. The experimental values were read from a figure and recalculated to mol % Br by the compilers.

T/K	t/°C	Solubility/mass % NaBr	Solubility/mol % Br
420	147	$2.1\cdot10^{-7}$	$4.7\cdot10^{-8}$
420	147	$2.5\cdot10^{-7}$	$5.6\cdot10^{-8}$
452	179	$4.3\cdot10^{-7}$	$9.6\cdot10^{-8}$
453	180	$5.9\cdot10^{-7}$	$1.32\cdot10^{-7}$
470	197	$1.35\cdot10^{-6}$	$3.0\cdot10^{-7}$
472	199	$1.6\cdot10^{-6}$	$3.6\cdot10^{-7}$
522	249	$7.9\cdot10^{-6}$	$1.8\cdot10^{-6}$
578	305	$2.9\cdot10^{-4}$	$6.5\cdot10^{-5}$
607	334	$3.7\cdot10^{-4}$	$8.3\cdot10^{-5}$
607	334	$5.4\cdot10^{-4}$	$1.21\cdot10^{-4}$
670	397	$1.08\cdot10^{-3}$	$2.4\cdot10^{-4}$

The solubility results of NaBr in liquid Na were represented by the author's equation (confirmed by the compilers):

$$\log(\text{soly/mass \% NaBr}) = 5.00-(5100\pm240)\ (T/\text{K})^{-1}.$$

Auxiliary Information

Method:
The experiments were performed in sealed capsules (static) or in a recirculating loop (dynamic), both made from 18-8-Ti stainless steel. In the static tests, known amounts of Na were directly filtered into capsules containing ^{87}Br labeled NaBr, as dried down deposits on the steel surface of the capsules. In the dissolution mode, the capsules were heated to the selected temperature for 16 h, and inversion of the furnace left the surface of the NaBr charge exposed. In the deposition mode, the capsules were heated to 1023 K for 16 h, inverted in the furnace, and cooled to the test temperature over up to 3 days. After 1–3 days at the final temperature the furnace was reinvented and cooled. The cold capsules were cut into two parts, and the empty end was washed out for analysis by gamma spectrometry. As the halide segregated strongly to the capsule walls on cooling, the entire Na charge was analyzed. In the dynamic experiments the labeled NaBr was introduced as dried down deposit on a Ni crucible. The crucible was immersed in circulating Na at 723 K for 24 h. The temperature of the cold trap was then reduced to 423 K in 30–50 K steps with 12 h stabilization arrests at each step. The Br distribution in the loop was established by taking Na samples for the gamma spectrometric analysis.

Source and Purity of Materials:
NaBr: labeled with ^{87}Br from the Amersham Radiochem. Center, dried over P_2O_5 in a vacuum desiccator.
Na: purified by filtration at 393 K or cold trapping; contained $(1-2)\cdot10^{-3}$ % O.
Ar: contained $<5\cdot10^{-4}$ % O and $<1.0\cdot10^{-3}$ % H_2O.

Estimated Error:
Solubility: precision ±5%; reading-out procedure ±2%.
Temperature: stability ±1 K; reading-out procedure ±1 K.

Components:
(1) Bromine; Br; [7726-95-6]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
C. G. Allan, *Liquid Alkali Metals* (BNES, London, 1973), pp. 159–165.

Variables:
Temperature: 420–670 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of NaBr in liquid Na was determined. The experimental values were read from a figure and recalculated to mol % Br by the compilers.

T/K	t/°C	Solubility/mass % NaBr	Solubility/mol % Br
420	147	$2.1\cdot10^{-7}$	$4.7\cdot10^{-8}$
420	147	$2.5\cdot10^{-7}$	$5.6\cdot10^{-8}$
452	179	$4.3\cdot10^{-7}$	$9.6\cdot10^{-8}$
453	180	$5.9\cdot10^{-7}$	$1.32\cdot10^{-7}$
470	197	$1.35\cdot10^{-6}$	$3.0\cdot10^{-7}$
472	199	$1.6\cdot10^{-6}$	$3.6\cdot10^{-7}$
522	249	$7.9\cdot10^{-6}$	$1.8\cdot10^{-6}$
578	305	$2.9\cdot10^{-4}$	$6.5\cdot10^{-5}$
607	334	$3.7\cdot10^{-4}$	$8.3\cdot10^{-5}$
607	334	$5.4\cdot10^{-4}$	$1.21\cdot10^{-4}$
670	397	$1.08\cdot10^{-3}$	$2.4\cdot10^{-4}$

The solubility results of NaBr in liquid Na were represented by the author's equation (confirmed by the compilers):

$$\log(\text{soly/mass \% NaBr}) = 5.00-(5100\pm240)(T/\text{K})^{-1}.$$

Auxiliary Information

Method:
The experiments were performed in sealed capsules (static) or in a recirculating loop (dynamic), both made from 18-8-Ti stainless steel. In the static tests, known amounts of Na were directly filtered into capsules containing ^{87}Br labeled NaBr, as dried down deposits on the steel surface of the capsules. In the dissolution mode, the capsules were heated to the selected temperature for 16 h, and inversion of the furnace left the surface of the NaBr charge exposed. In the deposition mode, the capsules were heated to 1023 K for 16 h, inverted in the furnace, and cooled to the test temperature over up to 3 days. After 1–3 days at the final temperature the furnace was reinvented and cooled. The cold capsules were cut in two parts, and the empty end was washed out for analysis by gamma spectrometry. As the halide segregated strongly to the capsule walls on cooling, the entire Na charge was analyzed. In the dynamic experiments the labeled NaBr was introduced as a dried down deposit on a Ni crucible. The crucible was immersed in circulating Na at 723 K for 24 h. The temperature of the cold trap was then reduced to 423 K in 30–50 K steps with 12 h stabilization arrests at each step. The Br distribution in the loop was established by taking Na samples for the gamma spectrometric analysis.

Source and Purity of Materials:
NaBr: labeled with ^{87}Br from the Amersham Radiochem. Center, dried over P_2O_5 in a vacuum desiccator.
Na: purified by filtration at 393 K or cold trapping; contained $(1-2)\cdot10^{-3}$ % O.
Ar: contained $<5\cdot10^{-4}$ % O and $<1.0\cdot10^{-3}$ % H_2O.

Estimated Error:
Solubility: precision ±5%; reading-out procedure ±2%.
Temperature: stability ±1 K; reading-out procedure ±1 K.

Components:
(1) Bromine; Br; [7726-95-6]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
M. V. Smirnov, V. V. Chebykin, and L. A. Tsiovkina, Electrochim. Acta **26**, 1275–1288 (1981).

Variables:
Temperature: 1027–1239 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data
The solubility of Na in liquid NaBr was determined

t/°C	Solubility/mass % NaBr	Solubility/mol % Br[a]
754	3.20	49.20
783	3.81	49.03
902	10.4	47.26
966	20.4	44.32

[a]Calculated by the compilers.

Auxiliary Information

Method:
All parts being in contact with mixtures of NaBr and Na were made of stainless steel resistant to their action at high temperatures. The pressure developed by the saturated vapors in the hermetically sealed inner part of the device was fixed by means of a bellow manometer which was equipped with an automatic regulator for balancing the pressure of Ar in the outer part of the apparatus, also hermetically sealed. The experimental installation was tested by measuring the pressures of the saturated vapors of K and Cs over wide ranges of temperature. The measured values were in good agreement with the most reliable reference data. The mixtures were composed directly by distilling definite amounts of Na into the container filled with known amounts of NaBr.

Source and Purity of Materials:
NaBr: "particularly pure;" recrystallized and dried under vacuum; the temperature was raised slowly up to 723 K until H_2O condensation in a liquid N trap ceased. The alkalinity was (0.005–0.01) mol %.
Na: 99.99% pure.
Ar: nothing specified.

Estimated Error:
Solubility: precision ±3%.
Pressure: precision ±250 Pa or ±2%.
Temperature: precision ±1 K.

4.21. Sodium–Iodine

Components:
(1) Iodine; I; [7553-56-2]
(2) Sodium; Na; [7440-23-5]

Evaluated By:
Hans Ulrich Borgstedt, Forschungszentrum Karlsruhe, Germany and Cezary Guminski, University of Warsaw, Poland, February 1997.

Critical Evaluation

I introduced into liquid Na reacts completely forming NaI. Thus, Na, NaI, and I are the equilibrium phases of the system. The NaI-rich side of the Na–I liquidus line was determined by Bredig *et al.*[1,2] and Smirnov *et al.*[3] The corresponding solubility results are in rough agreement. The higher solubilities were suggested by Bredig *et al.*,[1] the lowest by Bredig *et al.*,[2] with those of Smirnov *et al.*[3] inbetween. The results of Bredig *et al.*[2] are a part of a more exhaustive study and are selected as tentative in this evaluation. The Na-rich side of the Na–I liquidus was determined by Bredig *et al.*[1,2] in the temperature range 823–1404 K, Allan[4] in the range 419–673 K and Sagawa *et al.*[5–9] in the range 532–1080 K. Extrapolation of the data of Allan[4] to higher temperatures and of Bredig *et al.*[1] to lower temperatures are not likely to meet each other for temperatures from 623 to 823 K. The results of Bredig *et al.*[1] would suggest 1 order of magnitude higher solubilities of I in liquid Na than observed by Allan.[4] In the first study, Sagawa[5] confirmed well the values of Allan.[4] However, in subsequent determinations by Sagawa *et al.*[6–9] at temperatures higher than 614 K most of the earlier results of Bredig *et al.*[1] were confirmed. Sagawa and Miyahara[7] showed that neither local enrichment nor particle formation of NaI was observed in the system that would explain the discrepancies. Finally, Sagawa *et al.*[8,9] established in a special test that, if the I solubility is determined in a stainless steel capsule not being pretreated, more metallic components of the stainless steel are leached by the solution of I in Na. I shows a tendency to combine with the metallic elements and precipitate from the solution. Thus higher solubility values of I in liquid Na are suggested from papers of Bredig *et al.*[1] Miyahara *et al.*,[6] Sagawa and Miyahara,[7] and Sagawa *et al.*[8] In the temperature range 623–929 K (monotectic) the solubility may be expressed by the equation:

$$\log(\text{soly/mol \% I}) = 4.85 - 4550(T/\text{K})^{-1}. \quad (1)$$

Schram *et al.*[10] confirmed the correctness of the experimental solubilities of I in liquid Na (on the Na-rich side) by thermodynamic modeling. They predicted that the solubility of I, using CsI as solute, in liquid Na is very close to that of NaI as solute. The mutual solubilities in the range between NaI and I were partly evaluated by Tomkins and Bansal.[11] These evaluators mentioned a publication of Wartenberg[12] who found that molten NaI dissolves only 0.3 mol % I at 973 K, resulting in the liquidus point at 50.1 mol % I. Since gaseous I was the solute at this temperature, one should expect a higher solubility of liquid I at sufficiently increased pressure. Briggs *et al.*[13] detected a slight amount of NaI in liquid I, which gives another liquidus point at 99.7 mol % I at ≈403 K. Thus, it seems that a miscibility gap may exist between liquid NaI and I (at elevated pressure to keep I in the liquid state). Therefore, the electric conductivity measurements of Plotnikov *et al.*,[14] suggesting liquidus points at ≈97 mol % I at either 403 or 413 K, appear much less reliable; thus, the results of Plotnikov *et al.*[14] are not compiled.

Bredig[15] presented a partial phase diagram of the Na–I system. The complete range of compositions is shown in Fig. 32.

T/K	Solubility/mol % I	Source
	Tentative values of the solubility of I in liquid Na	
623	$3.5 \cdot 10^{-3}$	(6), (7), Eq. (1)
723	$3.6 \cdot 10^{-2}$	(6), (7), Eq. (1)
823	0.21	(6), (7), Eq. (1)
929	1.0 monotectic	(6), (7) mean value
1023	2.2	(6)
1123	4.5	(1) interpolated
1223	10	(1) interpolated
1306	33 critical	(1) interpolated
	The solubility values on the NaI-rich side	
929	49.55 monotectic	(2) extrapolated
1023	48.81	(2), (3) interpolated
1123	47.6	(2), (3) interpolated
1223	44.4	(2), (3) interpolated

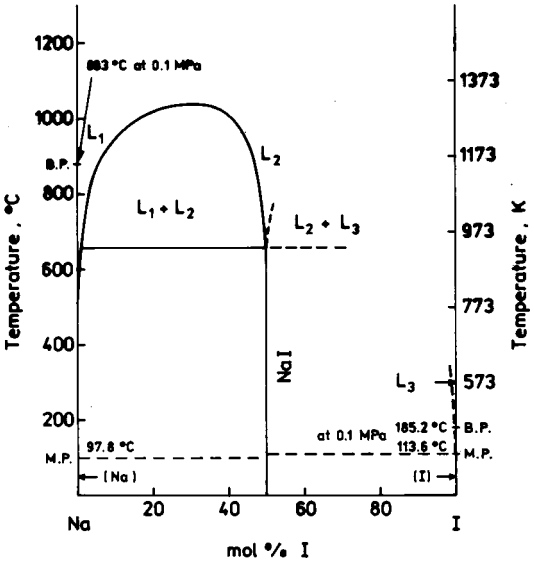

FIG. 32. Na–NaI phase diagram (partial).

References:

[1]M. A. Bredig, J. W. Johnson, and W. T. Smith, J. Am. Chem. Soc. **77**, 307 (1955).

[2]M. A. Bredig and H. R. Bronstein, J. Phys. Chem. **64**, 64 (1960).

[3]M. V. Smirnov, V. V. Chebykin, and L. A. Tsiovkina, Electrochim. Acta **26**, 1275 (1981).

[4]C. G. Allan, *Liquid Alkali Metals* (BNES, London, 1973), p. 159.

[5]N. Sagawa, J. Nucl. Sci. Technol. **28**, 305 (1991).

[6]S. Miyahara, N. Sagawa, T. Sone, T. Arakawa, and H. Hara, J. Nucl. Sci. Technol. **29**, 351 (1992).

[7]N. Sagawa and S. Miyahara, J. Nucl. Sci. Technol. **29**, 427 (1992).

[8]N. Sagawa, S. Miyahara, and T. Sone, *Liquid Metal Systems*, edited by H. U. Borgstedt and G. Frees (Plenum, New York, 1995), p. 321.

[9]N. Sagawa and S. Tashiro, IAEA/IWGFR Meeting on Evaluation of Radioactive Materials and Sodium Fires in Fast Reactors, PNC, Japan, 1996, Rep. B-4, p. 1.

[10]R. P. C. Schram, E. H. P. Cordfunke, and M. E. Huntelaar, Energy Center Netherland Rep. ECN-R-95-021, p. 1 (1995).

[11]R. P. T. Tomkins and N. R. Bansal, *Gases in Molten Salts, Solubility Data Series* (Pergamon, Oxford, 1990), Vol. 45/46, p. 187.

[12]H. U. Wartenberg, Z. Elektrochem. **32**, 330 (1926).

[13]T. R. Briggs, W. F. Geigle, and J. L. Eaton, J. Phys. Chem. **45**, 595 (1941).

[14]V. A. Plotnikov, Ya. A. Fialkov, and V. P. Tshalii, Z. Phys. Chem. A **172**, 304 (1935).

[15]M. A. Bredig, *Molten Salt Chemistry*, edited by M. Blander (Interscience, New York, 1964), p. 367.

Components:
(1) Iodine; I; [7553-56-2]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
T. R. Briggs, W. F. Geigle, and J. L. Eaton, J. Phys. Chem. **45**, 595 (1941).

Variables:
Temperature: 393–413 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of NaI in liquid I at 120–140 °C was found to be 0.29±0.14 mol % NaI. The compilers calculated on this basis the 99.7 mol % I.

Auxiliary Information

Method:
Five test mixtures of NaI and I, taken in mass ratios of about 5:1, were heated for various times (10 min–48 h). The heterogeneous liquid was filtered through a plug of glass wool and analyzed for its NaI content by the distillation method.

Source and Purity of Materials:
I: "dry."
NaI: anhydrous, finely pulverized.

Estimated Error:
Solubility: precision ±50%
Temperature: precision ±10 K.

Components:
(1) Iodine; I; [7553-56-2]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
M. A. Bredig, J. W. Johnson, and W. T. Smith, J. Am. Chem. Soc. **77**, 307–312 (1955).

Variables:
Temperature: 823–1232 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of I in liquid Na was determined

t/°C	Solubility/mol % NaI	Solubility/mol % I[a]
550	0.06[b]	0.06
584	0.28[b]	0.28
608	0.60[b]	0.60
637	0.80[b]	0.79
652	1.2[b]	1.18
699	1.5	1.48
800	2.8	2.7
882	5.7	5.4
959	10.5	9.5

[a]Calculated by the compilers.
[b]Solid NaI is the equilibrium phase.

The solubility of Na in liquid NaI was determined

t/°C	Solubility/mol % Na	Solubility/mol % I[a]
674	3.2±0.1	49.19
722	4.1	48.95
763	6.2	48.4
810	8.3	47.8
849	9.9	47.4
909	14.9	46.0
954	20.8	44.2

[a]Calculated by the compilers.

The melting point of NaI was found at 934 K and the monotectic at 929 K.

Auxiliary Information

Method:
The container used in the experiments was made of Type 316 stainless steel. Cooling and heating curves for the melting point of NaI and the monotectic were recorded with the use of a Chromel/Alumel thermocouple placed in a well. The container was washed in $Fe_2(SO_4)_3$(5%)–H_2SO_4(10%) mixture for 20 min at 333–343 K, then in HNO_3(15%)–HF(2%) mixture for 15 min. It was rinsed in H_2O and dried at 383 K. NaI was weighed and loaded into capsules in a dry box filled with N, after that the capsule was evacuated. Na was weighed under mineral oil, rinsed in C_6H_{14}, placed in the capsule, and evacuated to $<1\cdot10^{-3}$ Torr. Gentle heating of the capsule melted Na and removed C_6H_{14}. The capsules were mounted in a furnace and equilibrated while rocking for 2–3 h. The bottom sample of NaI and the upper of Na were analyzed after phase separation. The NaI phase was dissolved in C_2H_5OH–H_2O mixture and titrated by standard acid. Free Na was calculated from the sample weight and the alkalinity. The Na phase was dissolved in C_2H_5OH–H_2O mixture, the alkalinity developed was determined with standard HNO_3, and I as AgI precipitate.

Source and Purity of Materials:
NaI: reagent grade, heated (<773 K) in an evacuated (<0.05 Torr) quartz tube. Ar was flushed through the tube while raising temperature 50 K above its melting point; after slow cooling to room temperature, only clear fragments of the salt stored in a desiccator over P_2O_5, were used.
Na: filtered through a sintered stainless steel filter at a temperature slightly above its melting point.
Ar: "dry."
N: "dry."

Estimated Error:
Solubility: precision ±3% (by the compilers).
Temperature: precision ±3 K in solubility experiments; precision ±0.5 K in the thermal analysis.

Components:
(1) Iodine; I; [7553-56-2]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
M. A. Bredig and H. R. Bronstein, J. Phys. Chem. **64**, 64–67 (1960).

Variables:
Temperature: 934–1304 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The mutual miscibility of NaI and Na was determined

t/°C	Solubility/mol % Na	Solubility/mol % I[a]
661[b]	1.85	49.53
678[b]	2.02	49.49
702[b]	2.15	49.46
696[b]	2.35	49.41
704[b]	2.38	49.40
705[b]	2.47	49.37
727[b]	3.22	49.18
797[b]	6.08	48.43
803[b]	6.32	48.37
897[b]	12.15	46.77
990	29.0	41.5
998	32.0	40.5
1031	48.0	34.2
1011	74.5	20.3

[a]Calculated by the compilers.
[b]Equlibration and sampling tests.

The monotectic temperature was found at 657±2 °C, however this temperature is probably too low due to a slight Na_2O contamination, as suggested by the authors.

Auxiliary Information

Method:
Thermal analysis of samples was performed in a stainless steel capsule. The capsule was filled with known amounts of NaI and Na and then flushed with Ar over the solids. The capsule was welded shut with a flat top and placed inside a tank made of Inconel. It was pressurized with Ar up to ~0.7 MPa. The ratio of the container weight to the sample weight was reduced by employing thin walled construction tubes. Temperatures were measured using a Pt/Pt–Rh(10%) thermocouple in a well.[1] Cooling and heating cycles were repeated 2–4 times for each composition. Some samples of Na and NaI were equilibrated in an Al_2O_3 single crystal crucible in an Ar atmosphere.[2] A sample of liquid NaI saturated with Na was withdrawn by means of a sampler. The sample was treated with C_2H_5OH under an Ar atmosphere, before H_2O was added for final dissolution. The weight of the sample and the alkalinity determined by titration gave the free Na content.

Source and Purity of Materials:
NaI: reagent grade, predried at 453 K for several days; further dehydrated at temperature 50 K below the melting point until a pressure of 2 Pa was reached.[2]
Na: contained 0.2% K and 0.1% O.[2]
Ar: "pure."

Estimated Error:
Solubility: nothing specified.
Temperature: precision ±1 K.

References:
[1]J. W. Johnson and M. A. Bredig, J. Phys. Chem. **62**, 604–607 (1958).
[2]H. R. Bronstein and M. A. Bredig, J. Am. Chem. Soc. **80**, 2077–2081 (1958).

Components:
(1) Iodine; I; [7553-56-2]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
C. G. Allan, *Liquid Alkali Metals* (BNES, London, 1973), pp. 159–165.

Variables:
Temperature: 419–673 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of NaI in liquid Na was determined. The results were read from a figure and recalculated to mol % I by the compilers.

T/K	t/°C	Solubility/mass % NaI	Solubility/mol % I
419	146	$4.8\cdot10^{-7}$	$7.3\cdot10^{-8}$
421	148	$3.6\cdot10^{-7}$	$5.5\cdot10^{-8}$
467	194	$7.6\cdot10^{-6}$	$1.16\cdot10^{-6}$
467	194	$1.26\cdot10^{-5}$	$1.9\cdot10^{-6}$
470	197	$6.4\cdot10^{-6}$	$9.8\cdot10^{-7}$
470	197	$7.0\cdot10^{-6}$	$1.07\cdot10^{-6}$
484	211	$1.33\cdot10^{-5}$	$2.0\cdot10^{-6}$
501	228	$3.4\cdot10^{-5}$	$5.2\cdot10^{-6}$
503	230	$3.8\cdot10^{-5}$	$5.8\cdot10^{-6}$
519	246	$6.2\cdot10^{-5}$	$9.5\cdot10^{-6}$
521	248	$7.3\cdot10^{-5}$	$1.11\cdot10^{-5}$
552	279	$2.5\cdot10^{-4}$	$3.8\cdot10^{-5}$
566	293	$4.6\cdot10^{-4}$	$7.0\cdot10^{-5}$
574	301	$5.8\cdot10^{-4}$	$8.9\cdot10^{-4}$
576	303	$4.6\cdot10^{-4}$	$7.0\cdot10^{-5}$
579	306	$5.2\cdot10^{-4}$	$8.0\cdot10^{-5}$
580	307	$6.9\cdot10^{-4}$	$1.07\cdot10^{-4}$
585	312	$6.7\cdot10^{-4}$	$1.03\cdot10^{-4}$
615	342	$2.6\cdot10^{-3}$	$4.0\cdot10^{-4}$
625	352	$1.68\cdot10^{-3}$	$2.6\cdot10^{-4}$
631	358	$3.1\cdot10^{-3}$	$4.8\cdot10^{-4}$
639	366	$4.9\cdot10^{-3}$	$7.5\cdot10^{-4}$
645	372	$4.2\cdot10^{-3}$	$6.4\cdot10^{-4}$
673	400	$5.7\cdot10^{-3}$	$8.7\cdot10^{-4}$

The author presented his results as the solubility equation:

$$\log(\text{soly/mass \% NaI}) = 4.72-(4650\pm140)\ (T/\text{K})^{-1}.$$

The compilers tested the validity of the equation.

Auxiliary Information

Method:
The tests were performed in sealed capsules (static) or a recirculating loop (dynamic). Both the devices were made of 18-8-Ti stainless steel. In the static experiments known amounts of Na were directly filtered into capsules containing ^{131}I-labeled NaI, as dried down deposits on the steel surface of the capsules. In the dissolution mode, the capsules were heated at selected temperature for 16 h, and inversion of the furnace left the NaI charge surface exposed. In the deposition mode, the capsules were heated to 1023 K for 16 h, inverted in the furnace, and cooled to the experimental temperature over up to 3 days. After 1–3 days at this temperature the furnace was reinverted and cooled. When cold, the capsules were cut in two parts and the empty end was washed out for analysis by gamma spectrometry. As the NaI segregated strongly to the capsule walls on cooling, the entire Na charge was analyzed. Some of the wash solutions were analyzed for total I using oxidation of As(III) by Ce(IV), catalyzed by I traces. In the dynamic experiments, the labeled NaI was introduced as a dried down deposit on a Ni crucible. The crucible was immersed in circulating Na at 723 K for 24 h. The temperature of the cold trap was then reduced to 423 K in 30–50 K steps with 12 h stabilization arrests at each step. The I distribution in the loop was established by taking Na samples for gamma spectrometric and chemical analysis.

Source and Purity of Materials:
NaI: labeled with ^{131}I from the American Radiochem. Center; dried over P_2O_5 in a vacuum desicator.
Na: purified by filtration at 393 K or cold trapping; contained $(1-2)\cdot10^{-3}$ % O.
Ar: contained $<5\cdot10^{-4}$ % O and $<1.0\cdot10^{-3}$ % H_2O.

Estimated Error:
Solubility: precision ±3%; detection limit of chemical analysis $1\cdot10^{-7}$ mass % NaI; background concentration of NaI in Na $(3\pm2)\cdot10^{-7}$ mass %; reading-out procedure ±2%.
Temperature: stability ±1 K; reading-out procedure ±1 K.

Components:
(1) Iodine; I; [7553-56-2]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
M. V. Smirnov, V. V. Chebykin, and L. A. Tsiovkina, Electrochim. Acta **26**, 1275–1288 (1981).

Variables:
Temperature: 958–1168 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data
The solubility of Na in liquid NaI was determined

t/°C	Solubility/mol % Na	Solubility/mol % I[a]
685	2.64	49.33
733	4.17	48.94
767	5.17	48.67
815	8.28	47.84
831	8.38	47.81
895	14.2	46.2

[a]Calculated by the compilers.

Auxiliary Information

Method:
All parts being in contact with mixtures of NaI and Na were made of stainless steel resistant to their action at high temperatures. The pressure developed by the saturated vapor in the hermetically sealed inner part of the device was fixed with bellows to a manometer which had an automatic regulator for balancing the pressure of Ar in the outer, also hermetically sealed, part of the apparatus. The experimental installation was tested by measuring the pressures of K and Cs saturated vapors over wide temperature ranges. The measured values were in good agreement with the most reliable reference data. The mixtures were composed directly by distilling definite amounts of Na into the container filled with a known amount of NaI. The solubility was determined from a break of the pressure versus reciprocal temperature dependence.

Source and Purity of Materials:
NaI: "particularly pure," recrystallized and dried under vacuum; temperature being raised slowly up to 723 K until H_2O condensation in liquid N ceased. The alkalinity was 0.005–0.01 mol %.
Na: 99.99% pure.
Ar: nothing specified.

Estimated Error:
Solubility: precision ±3%.
Pressure: precision ±250 Pa or ±2%.
Temperature: precision ±1 K.

Components:
(1) Iodine; I; [7553-56-2]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
N. Sagawa, J. Nucl. Sci. Technol. **28**, 305–313 (1991).

Variables:
Temperature: 532–649 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data
The solubility of I in liquid Na was determined. The data were read from a figure and recalculated to mol % I by the compilers.

T/K	Solubility/mass % NaI	Solubility/mol % I
532	$1.25\cdot10^{-4}$	$1.9\cdot10^{-5}$
559	$3.0\cdot10^{-4}$	$4.6\cdot10^{-5}$
565	$2.5\cdot10^{-4}$	$3.8\cdot10^{-5}$
617	$1.8\cdot10^{-3}$	$2.7\cdot10^{-4}$
625	$2.4\cdot10^{-3}$	$3.6\cdot10^{-4}$
633	$3.2\cdot10^{-3}$	$4.9\cdot10^{-4}$
641	$7.5\cdot10^{-3}$	$1.14\cdot10^{-3}$
649	$8.0\cdot10^{-3}$	$1.22\cdot10^{-3}$

NaI is the saturating solute. The data were also reported in Sagawa *et al.*[1]

Auxiliary Information

Method:
A stainless steel capsule was loaded with Na from a supply tank and kept at 423 K. The temperature was elevated to 703 K for ~100 h for cleaning the inner capsule surface from oxides. NaI powder was introduced into the capsule and dissolved by heating at 703 K for ~100 h while turning the capsule upside down a dozen times. The capsule was installed vertically with the upper part inserted in an electric furnace. The deposition run was continued for a period of 700 h to let NaI settle on the bottom of the capsule and to establish a steady state in the I diffusion through Na in the capsule tube. The capsule was quickly cooled in oil and sectioned into samples. Core and periphery Na in the sample tube were separately dissolved in H_2O. The amount of I in the resulting solution was measured by ion chromatography with an electrochemical detector and a conductivity meter. The amount of Na was determined by acid-base titration.

Source and Purity of Materials:
NaI: nothing specified.
Na: reactor grade.
H_2O: distilled.

Estimated Error:
Solubility: nothing specified; reading-out procedure ±3%.
Temperature: nothing specified; reading-out procedure ±2 K. The capsule had a temperature gradient of 20 K/cm.

References:
[1]N. Sagawa, S. Miyahara, and T. Sone, *Liquid Metal Systems*, edited by H. U. Borgstedt and G. Frees (Plenum, New York, 1995), pp. 321–330.

Components:
(1) Iodine; I; [7553-56-2]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
S. Miyahara, N. Sagawa, T. Sone, T. Arakawa, and H. Hara, J. Nucl. Sci. Technol. **29**, 351–357 (1992).

Variables:
Temperature: 622–1080 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data
The solubility of I in liquid Na was determined

t/°C	Solubility/mass % NaI	Solubility/mol % I[a]
807	19.94	3.55
807	18.78	3.31
806	19.12	3.38
753	12.89	2.17
752	12.96	2.18
705	9.107	1.49
704	8.947	1.46
677	6.967	1.123
676	7.082	1.143
676	6.923	1.115
655	5.728	0.915
655	5.536	0.883
655	5.579	0.890
655	5.762	0.920
654	5.433	0.866
654	5.481	0.874
654	5.467	0.872
654	5.664	0.904
653	5.528	0.882
625	3.738	0.589
625	3.781	0.596
603	2.819	0.441
603	2.693	0.421
602	2.830	0.443
548	1.271	0.197
548	1.305	0.202
506	0.6027	0.0928
505	0.5774	0.0889
505	0.5991	0.0923
505	0.5871	0.0904
505	0.5930	0.0913
505	0.6088	0.0938
504	0.5956	0.0917
454	0.2586	0.0397
454	0.2421	0.0372
454	0.2517	0.0387
350	0.02596	$3.98\cdot10^{-3}$
349	0.02567	$3.94\cdot10^{-3}$

[a]Calculated by the compilers.

NaI is the saturating solute. The results were graphically reported in Sagawa *et al.*[1] The solubility data were expressed by the authors by the following equations:

$$\log(\text{soly/mass \% NaI}) = 4.46 - 3440\ (T/\text{K})^{-1} \quad \text{at} > 933\ \text{K} \tag{1}$$

and

$$\log(\text{soly/mass \% NaI}) = 5.65 - 4550\ (T/\text{K})^{-1} \quad \text{at} < 933\ \text{K}. \tag{2}$$

The compilers tested the validity of the equations.

Auxiliary Information

Method:
A "J" shaped capsule was made of Type 316 stainless steel. It permitted the decantation of a portion of equilibrated liquid Na from a base with mouth into a side arm cell. The capsule was washed with a degreasing agent and rinsed with H_2O. It was subsequently immersed for 1–2 min at 353–363 K in a mixture of HNO_3(25%)–HF(5%), rinsed with H_2O, and heated in an oven at 393 K for 2 h. NaI crystal was cracked in an Ar filled dry box and placed in the base cell. The cell was filled with Na at 313–323 K. After the Na was solidified the capsule was removed out of the glove box. The capsule was placed in an oven with uniform temperature distribution. The temperature was measured with sheathed thermocouples. A portion of liquid Na after equilibration (for 14, 10, and 7 days at 773, 923, and 1073 K, respectively) was decanted into the side arm after the oven was tilted. The tilted position was kept until the capsule had been naturally cooled to room temperature. The side cell was sectioned in the dry box. The sectioned tube was heated to melt, the Na was poured into a quartz beaker, and the tube was placed in another one. The Na was dissolved in H_2O vapor in a desiccator. The amount of I is determined by titration with a standard $KMnO_4$ solution and Na by titration with a standard HCl.

Source and Purity of Materials:
NaI: nothing specified.
Na: reactor grade.
Ar: "dry and deoxidized."
H_2O: distilled.

Estimated Error:
Solubility: accuracy of analysis ±5%; solubility equation deviation less than ±10%.
Temperature: stability ±1 K.

References:
[1]N. Sagawa, S. Miyahara, and T. Sone, *Liquid Metal Systems*, edited by H. U. Borgstedt and G. Frees (Plenum, New York, 1995), pp. 321–330.

Components:
(1) Iodine; I; [7553-56-2]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
N. Sagawa and S. Miyahara, J. Nucl. Sci. Technol. **29**, 427–435 (1992).

Variables:
Temperature: 614–909 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of I in liquid Na was determined by two methods. The results were read from a figure and recalculated to mol % I by the compilers.

T/K	Solubility/mass % NaI	Solubility/mol % I
	The short capsule method	
909	4.2	0.64
870	2.3	0.35
854	1.5	0.23
845	1.2	0.18
813	1.0	0.15
787	0.75	0.114
769	0.44	0.067
762	0.42	0.064
750	0.30	0.046
733	0.21	0.032
730	0.30	0.046
675	0.075	0.0114
	The long capsule method	
794	0.54	0.082
741	0.33	0.050
727	0.18	0.027
702	0.12	0.018
694	0.090	0.014
673	0.041	$6.2\cdot10^{-3}$
645	0.050	$7.6\cdot10^{-3}$
614	0.023	$3.5\cdot10^{-3}$

The results were also reported in (2).

Auxiliary Information

Method:
A "J" shaped capsule was made of Type 316 stainless steel. It permitted the decantation of a portion of equilibrated liquid Na from a base with mouth into a side arm cell. The capsule was washed with a degreasing agent and rinsed with H_2O. It was subsequently immersed for 1–2 min at 353–363 K in a mixture of HNO_3(25%)–HF(5%), rinsed with H_2O, and heated in an oven at 393 K for 2 h. NaI crystal was cracked in an Ar filled dry box and placed in the base cell. The cell was filled with Na at 313–323 K. After the Na was solidified the capsule was removed from the glove box. The capsule was placed in an oven with uniform temperature distribution. The temperature was measured with sheathed thermocouples. A portion of liquid Na after equilibration (for 14, 10, and 7 days at 773, 923, and 1073 K, respectively) was decanted into the side arm after the oven was tilted. The tilted position was kept until the capsule had been naturally cooled to room temperature. The side cell was sectioned in the dry box. The sectioned tube was heated to melt, the Na was poured into a quartz beaker, and the tube was placed in another one. The Na was dissolved in H_2O vapor in a desiccator. The amount of I is determined by titration with a standard $KMnO_4$ solution and Na by titration with a standard HCl.[1]

Source and Purity of Materials:
NaI: nothing specified.
Na: reactor grade.
Ar: "dry and deoxidized."
H_2O: distilled.

Estimated Error:
Solubility: accuracy of analysis ±5%; solubility equation deviation less than ±10%.
Temperature: stability ±1 K.

References:
[1]N. Sagawa, S. Miyahara, and T. Sone, *Liquid Metal Systems*, edited by H. U. Borgstedt and G. Frees (Plenum, New York, 1995), pp. 321–330.

Components:
(1) Iodine; I; [7553-56-2]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
N. Sagawa and S. Tashiro, IAEA/IWGFR Meeting on Evaluation of Radio-active Materials and Sodium Fires in Fast Reactors, PNC, Rep. B-4, pp. 1–11 (1996).

Variables:
Temperature: 567–724 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of I in liquid Na was determined

t/°C	Solubility/mass % I[a]	Solubility/mol % I[b]
294	$6.5\cdot10^{-4}$	$1.18\cdot10^{-4}$
295	$1.07\cdot10^{-3}$	$1.92\cdot10^{-4}$
443	$3.18\cdot10^{-2}$	$5.8\cdot10^{-3}$
451	$3.26\cdot10^{-3}$	$5.9\cdot10^{-3}$

[a]From a table; in figures expressed in mass % NaI.
[b]Calculated by the compilers.

It was observed that NaI and major constituents of the stainless steels used (Fe and Ni) interact in liquid Na; this interaction leads to a partial decrease of the I equilibrium concentration. Cr and Mn are insensitive to the I concentration, whereas any direct relationship with changes of the Si concentration could not be detected. Complex compounds formed between Fe (Ni), I, and Na, and probably O accumulate onto the top of the experimental capsule.

Auxiliary Information

Method:
The experiments were performed in a stainless steel capsule which was loaded with Na and NaI through nozzles. The filled capsule was installed vertically within an electrical furnace with the bottom standing on brass plates on a brick. Thus, the upper part was heated while the lower one was cooled generating a large temperature gradient. After 1300 h of equilibration the system was quickly cooled in oil. Internal parts of Na samples with the dissolved elements were taken from the sectioned capsule tube using Teflon and zirconia tools. The weighed samples were vacuum distilled. Fe was dissolved in an acid and determined by atomic absorption spectrometry. Other metals and Si were analyzed by means of induction coupled plasma mass spectrometry. Another Na sample was dissolved in vaporized H_2O and analyzed for I by ion chromatography and for Na by titration. All essential operations were performed in Ar atmosphere.

Source and Purity of Materials:
NaI: powder of unspecified purity.
Na: reactor grade purity.
Ar: nothing specified, probably dried and deoxidized as in Miyahara *et al.*[1]
H_2O: distilled.

Estimated Error:
Solubility: nothing specified; precision ±40% (by the compilers).
Temperature: nothing specified; precision not better than ±1 K (by the compilers).

References:
[1]S. Miyahara, N. Sagawa, T. Sone, T. Arakawa, and H. Hara, J. Nucl. Sci. Technol. **29**, 351–357 (1992).

4.22. Sodium–Helium

Components:
(1) Helium; He; [7440-59-7]
(2) Sodium; Na; [7440-23-5]

Evaluated By:
Hans Ulrich Borgstedt, Forschungszentrum Karlsruhe, Germany and Cezary Guminski, University of Warsaw, Poland, March 1997.

Critical Evaluation

The knowledge of the solubility of He in liquid Na is essential for the operation of Na cooled nuclear reactors. Since the experimental determination of the solubility is rather difficult and relatively small amount of data was measured, a significant effort was done on the field of the prediction of solubility data. Epstein[1] used the regular solution theory and calculated the values $1.63\cdot 10^{-12}$ and $1.48\cdot 10^{-8}$ mol % He at 505 and 755 K, respectively. Mandel[2] estimated the solubility as $6\cdot 10^{-6}$ and $6.2\cdot 10^{-5}$ mol % He at 533 and 700 K, respectively. Thormeier compared his experimental results at 573–873 K (Ref. 3) with calculations based on an improved hard sphere model;[4] the agreement was within 1 order of magnitude with steeper theoretical temperature dependence of the solubility. Independently, Veleckis *et al*. performed the solubility measurements at 623–823 K[5,6] and calculated the corresponding values[6] based on the regular solution model as in Epstein,[1] a model considering the interaction between He and Na, a model taking into account the energy of cavity formation, and a hard-sphere model. The latter three models yielded solubilities higher than those experimentally observed. Later Cafasso *et al*.[7–9] calculated the solubility using the hard-sphere model accounting the effects of conducting electrons in a liquid metal. The calculated values were lower than those observed in Veleckis *et al*.,[5,6] however they were in agreement with Thormeier[4] at 673 K but the slope of the temperature dependence of experimental results in Thormeier[4] was steeper. Fukase and Satoh[10] pointed out that taking into account the vacancy formation energy in liquid Na should improve an agreement between the experimental and theoretical solubility data; results of such modeling were not reported. Grundy and Taylor[11] found $6.9\cdot 10^{-7}$ mol % He at 611 K and 0.115 MPa which is placed between the data of Thormeier[3,4] and Veleckis *et al.*[5,6] We select in this evaluation the data of Veleckis *et al.*,[5,6] because the most pure reagents were used. The proposed solubility equation according to the latter authors, and confirmed by the compilers, is:

$$\log(\text{soly/mol \% He}) = -1.161 - 2833\,(T/\text{K})^{-1}. \quad (1)$$

The subject was briefly reviewed by Hubberstey.[12] Reed and Droher[13] considered the theoretical aspects of the solubility of noble gases in liquid alkali metals and proposed the following equation:

$$\log(\text{soly/mol \% He}) = -1.404 - 2654\,(T/\text{K})^{-1} \quad (2)$$

based on the preliminary results of Cafasso:[14] $4.5\cdot 10^{-6}$, $8.4\cdot 10^{-6}$, and $1.4\cdot 10^{-5}$ mol % He at 673, 723, and 773 K, respectively. The He–Na phase diagram should be similar to that shown for the Na–Xe system.

Arnoldov *et al*.[15,16] determined the solubility of He in liquid K–Na eutectic alloy; see details in the He–K system.

Tentative values of the solubility of He in liquid Na at 0.101 MPa

T/K	Solubility/mol % He	Source
573	$7\cdot 10^{-7}$	Eq. (1), extrapolated
673	$4\cdot 10^{-6}$	Eq. (1)
773	$1.5\cdot 10^{-5}$	Eq. (1)
873	$4\cdot 10^{-5}$	Eq. (1), extrapolated

References:

[1]L. F. Epstein, U.S. Atom. Energy Comm. Rep. KAPL-M-LFE-10 (1952).
[2]H. Mandel, U.S. Atom. Energy Comm. Rep. NAA-SR-Memo-10745 (1965); also cited by R. W. Woodruff, Trans. Am. Nucl. Soc. **10** (Suppl. 5), 5 (1967).
[3]K. Thormeier, Atomkernenergie **14**, 449 (1969).
[4]K. Thormeier, Nucl. Engin. Design **14**, 69 (1970).
[5]E. Veleckis, S. K. Dhar, F. A. Cafasso, and H. M. Feder, J. Phys. Chem. **75**, 2832 (1971).
[6]E. Veleckis, S. K. Dhar, F. A. Cafasso, and H. M. Feder, U.S. Atom. Energy Comm. Rep. ANL-7802, (1971).
[7]E. Veleckis and G. Redding, U.S. Atom. Energy. Comm. Rep. ANL-7675, p. 64 (1970).
[8]F. A. Cafasso, E. Veleckis, H. M. Feder, and H. C. Schnyders, U.S. Ener. Res. Devel. Admin. Rep. CONF-760503-P2, p. 619 (1976).
[9]H. M. Feder and H. C. Schnyders, U.S. Atom. Ener. Comm. Rep. ANL-7775, p. 107 (1971); Rep. ANL-7750, p. 90 (1971).
[10]S. Fukase and T. Satoh, Inst. Phys. Conf. Ser. **30**, 538 (1977).
[11]B. R. Grundy and G. R. Taylor, U.S. Energy Res. Devel. Admin. Rep. CONF-760503-P2, p. 782 (1976).
[12]P. Hubberstey, *Handbook of Thermodynamic and Transport Properties of Alkali Metals*, edited by R. W. Ohse (Blackwell, Oxford, 1985), p. 907.
[13]E. L. Reed and J. J. Droher, U.S. Atom. Energy Comm. Rep. LMEC-69-36 (1970).
[14]F. A. Cafasso, U.S. Atom. Energy Comm. Rep. ANL-7561, p. 68 (1969).
[15]M. N. Arnoldov, M. N. Ivanovskii, V. A. Morozov, S. S. Pletenets, and V. I. Subbotin, Atom. Energiya **28**, 18 (1970).
[16]V. I. Subbotin, M. N. Ivanovskii, and M. N. Arnoldov, *Fizikokhimicheskie Osnovy Primeneniya Zhidkometallicheskikh Teplonositelei* (Atomizdat, Moskva, 1970), p. 78.

Components:
(1) Helium; He; [7440-59-7]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
K. Thormeier, Atomkernenergie **14**, 449 (1969).

Variables:
Temperature: 573–873 K
Pressure: 0.10–0.40 MPa

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of He in liquid Na at 673 K as a function of pressure was reported in a figure. The results were read out from the figure and recalculated to mol % He by the compilers.

p/MPa	Solubility/mol % He
0.10	$2.0\cdot10^{-6}$; $2.6\cdot10^{-6}$
0.20	$4.3\cdot10^{-6}$
0.23	$5.3\cdot10^{-6}$
0.40	$8.5\cdot10^{-6}$; $9.1\cdot10^{-6}$

The solubility of He in liquid Na at 0.10 MPa as a function of temperature was reported in a figure. The results were read out from the figure and recalculated to mol % He by the compilers.

T/K	Solubility/mol % He
573	$2.5\cdot10^{-7}$
623	$6.5\cdot10^{-7}$
673	$2.2\cdot10^{-6}$
773	$1.1\cdot10^{-5}$
873	$3.2\cdot10^{-5}$

The results at 0.101 MPa were expressed by the solubility equation:

$$\log(\text{soly/mol \% He}) = -0.34 - 3595\ (T/\text{K})^{-1}.$$

The results were also reported in Thormeier.[1] No influence of O and C contents in Na on the solubility of He was found.

Auxiliary Information

Method:
The whole pressure-tight apparatus was constructed of a steel. The procedure was first tested on the air–material system.[2] He was contained in a tank. Liquid Na containing constant amounts of impurities (C and O) was pumped into the tank. The He and Na were equilibrated under constant gas pressure and temperature till saturating concentration was reached. The Na was then transferred into another tank in which it was degassed under vacuum. The quantity of the recovered gas was determined by volumetric analysis.

Source and Purity of Materials:
He: nothing specified.
Na: nuclear grade of purity; contained $(6-9)\cdot10^{-3}$ % O and $(6-9)\cdot10^{-4}$ % C.

Estimated Error:
Solubility: nothing specified; precision between ±3% and ±12% (by the compilers); reading-out procedure ±5%.
Temperature: nothing specified; reading-out procedure ±2 K.

References:
[1]K. Thormeier, Nucl. Engin. Design **14**, 69–82 (1970).
[2]K. Thormeier, Kernforschungszentrum Karlsruhe Rep. KFK-964, VII-1 (1969).

Components:
(1) Helium; He; [7440-59-7]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
E. Veleckis, S. K. Dhar, F. A. Cafasso, and H. M. Feder, J. Phys. Chem. **75**, 2832–2838 (1971).

Variables:
Temperature: 623–823 K
Pressure: 0.20–0.85 MPa

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of He in liquid Na was determined. The results were reported graphically and were read from a figure by the compilers, but numerical results appeared in Veleckis *et al.*[1]

The solubility of He in liquid Na at 773 K with varied pressure

p/MPa	Solubility/mol % He
0.20	$2.8\cdot10^{-7}$
0.21	$3.2\cdot10^{-7}$
0.28	$4.1\cdot10^{-7}$
0.30	$3.8\cdot10^{-7}$
0.40	$6.0\cdot10^{-7}$
0.41	$5.8\cdot10^{-7}$
0.51	$6.9\cdot10^{-7}$
0.53	$7.9\cdot10^{-7}$
0.62	$9.5\cdot10^{-7}$
0.64	$9.8\cdot10^{-7}$
0.66	$1.03\cdot10^{-6}$
0.67	$8.8\cdot10^{-7}$
0.75	$1.08\cdot10^{-6}$
0.87	$1.33\cdot10^{-6}$

The solubility of He in liquid Na at 0.10 MPa with varied temperature

T/K	λ (Ostwald coefficient)	Mean solubility/mol % He[a]
623	$3.3\cdot10^{-5}$, $3.4\cdot10^{-5}$, $4.0\cdot10^{-5}$, $4.0\cdot10^{-5}$	$(1.9\pm0.18)\cdot10^{-6}$
673	$7.2\cdot10^{-5}$, $8.8\cdot10^{-5}$, $9.1\cdot10^{-5}$, $1.0\cdot10^{-4}$	$(4.3\pm0.5)\cdot10^{-6}$
723	$1.5\cdot10^{-4}$, $1.5\cdot10^{-4}$, $1.6\cdot10^{-4}$, $1.7\cdot10^{-4}$, $2.0\cdot10^{-4}$	$(7.8\pm0.5)\cdot10^{-6}$
773	$3.0\cdot10^{-4}$, $3.1\cdot10^{-4}$, $3.2\cdot10^{-4}$, $3.2\cdot10^{-4}$, $3.5\cdot10^{-4}$	$(1.42\pm0.10)\cdot10^{-5}$
823	$5.3\cdot10^{-4}$, $6.2\cdot10^{-4}$, $6.2\cdot10^{-4}$	$(2.5\pm0.2)\cdot10^{-5}$

[a]Calculated by the compilers.

The results were expressed by the solubility equation at 0.101 MPa:

$$\log(\text{soly/mol \% He}) = -1.161 - 2833\ (T/\text{K})^{-1}.$$

Reed and Droher[2] expressed the same results by the equation:

$$\log(\text{soly/mol \% He}) = -1.404 - 2654\ (T/\text{K})^{-1}.$$

Auxiliary Information

Method:

Three cylindrical vessels fabricated of Type 316 stainless steel were interconnected by Na transfer lines. Separate gas circulation loops made of Type 304 stainless steel tubing were connected to the saturator and the stripper. Na was filtered into the first vessel. The He isotopic mixture was bubbled in the second vessel. The He and Na were equilibrated for overnight. Ar, used as a stripping gas, was introduced through a stainless steel dispersion disk with a 5 μm pore size at 403 K for 2 h. The vessels were heated by means of an electric furnace with Chromel/Alumel thermocouples. The gas mixture was pumped through liquid N cooled molecular sieves (5 A). Concentrations of He isotopes were determined by mass spectrometry. The isotopic composition helped to establish that He was from the dissolution–desorption process.

Source and Purity of Materials:

He: 99.5% pure ^{3}He from Mound Labor.; 99.999% pure natural He from Matheson Comp. An isotopic mixture ($\sim$30% ^{3}He) was prepared by condensing appropriate amounts of each component on activated charcoal at 4 K.
Ar: 99.999% pure from Matheson Comp.; did not contain any detectable He.
Na: reactor grade; filtered at 423 K with a content of $\sim 2 \cdot 10^{-4}$ % O.

Estimated Error:

Solubility: precision less than $\pm$4% at 95% confidence level.
Temperature: accuracy $\pm$1 K.

References:

[1]E. Veleckis, S. K. Dhar, F. A. Cafasso, and H. M. Feder, U.S. Atom. Energy Comm. Rep. ANL-7802 (1971).
[2]E. L. Reed and J. J. Droher, U.S. Atom. Energy Comm. Rep. LMEC-69-36 (1970).

Components:

(1) Helium; He; [7440-59-7]
(2) Sodium; Na; [7440-23-5]

Original Measurements:

B. R. Grundy and G. R. Taylor, U.S. Energy Res. Devel. Adm. Rep. CONF-760503-P2, pp. 782–788 (1976).

Variables:

One temperature: 611 K
One pressure: 0.115 MPa

Prepared by:

H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of He in liquid Na at 338 °C (611 K) and 0.115 MPa was found to be $1.2 \cdot 10^{-7}$ mass % He or $6.9 \cdot 10^{-7}$ mol % He (as calculated by the compilers).

Auxiliary Information

Method:

The experiments were performed in a Type 304 stainless steel sparger containing a main vessel and gas lines for He and Ar. Liquid Na was equilibrated with He. Ar bubbles were passed through the equilibrated Na in order to strip He out of the Na solution. The driving force for the sparging action is the tendency of the dissolved He to achieve its equilibrium partial pressure in the gas phase (bubbles). The gas mixture was analyzed by chromatography.

Source and Purity of Materials:

He: nothing specified.
Na: nuclear grade and contained $7 \cdot 10^{-5}$ % O and $4 \cdot 10^{-6}$ % H.
Ar: 99.999+% pure.

Estimated Error:

Solubility: detectivity $2.4 \cdot 10^{-8}$ mol % He.
Temperature: stability $\pm$10 K.

4.23. Sodium–Neon

Components:
(1) Neon; Ne; [7440-01-9]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
H. Shimojima and N. Miyaji, J. Nucl. Sci. Technol. **12**, 658 (1975).

Variables:
Temperature: 623–848 K
Pressure: 0.20–0.78 MPa

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data and Critical Evaluation

The solubility of Ne in liquid Na was determined. The results were reported in graphical form; they were read from a figure and recalculated to mol % Ne by the compilers.

The solubility of Ne in liquid Na at 470 °C (743 K) and at variant pressures

p/MPa	Solubility/mol % Ne
0.20	$2.1\cdot10^{-5}$
0.40	$4.5\cdot10^{-5}$
0.57	$5.8\cdot10^{-5}$
0.78	$1.02\cdot10^{-4}$

The solubility of Ne in liquid Na at 0.101 MPa

T/K	Solubility/mol % Ne
623	$1.8\cdot10^{-6}$; $2.0\cdot10^{-6}$; $2.3\cdot10^{-6}$
685	$3.5\cdot10^{-6}$; $4.0\cdot10^{-6}$; $4.3\cdot10^{-6}$
743	$1.1\cdot10^{-5}$; $1.2\cdot10^{-5}$; $1.0\cdot10^{-5}$; $1.3\cdot10^{-5}$
806	$1.8\cdot10^{-5}$; $2.1\cdot10^{-5}$
848	$3.2\cdot10^{-5}$; $3.6\cdot10^{-5}$; $4.0\cdot10^{-5}$

The authors formulated a solubility equation at 0.101 MPa:

$$\log(\text{soly/mol \% He}) = -1.082 - 2866\ (T/\text{K})^{-1},$$

which was confirmed by the compilers.

Compared with the solubilities of He and Ar these data seem to be overestimated for half an order of magnitude. The Ne solubility data show a similar temperature dependence as that found theoretically by Cafasso *et al.*[1] who used the hard-sphere theory taking into account the effects of the conduction electrons in liquid Na. Except for the boiling and melting points of Ne (at 24.56 and 27.14 K, respectively), the Ne–Na phase diagram is similar to the He–Na diagram.

Auxiliary Information

Method:
Details of the apparatus and the experimental procedure were announced to be reported, but the compilers could not find this information.

Source and Purity of Materials:
Ne: nothing specified.
Na: nuclear grade purity.

Estimated Error:
Solubility: nothing specified; reading-out procedure ±5%.
Temperature: nothing specified; reading-out procedure ±3 K.

References:
[1]F. A. Cafasso, E. Veleckis, H. M. Feder, and H. C. Schnyders, U.S Energy Res. Devel. Admin. Rep. CONF-760503-P2, pp. 619–622 (1976).

4.24. Sodium–Argon

Components:
(1) Argon; Ar; [7440-37-1]
(2) Sodium; Na; [7440-23-5]

Evaluated By:
Hans Ulrich Borgstedt, Forschungszentrum Karlsruhe, Germany and Cezary Guminski, University of Warsaw, Poland, March 1997.

Critical Evaluation

Dhar *et al.*[1,2] determined the solubility of Ar in liquid Na over the temperature range 613–753 K and the pressure range 0.34–0.91 MPa in preliminary experiments. The measured values increased with temperature from $2.3\cdot10^{-7}$ to $2.3\cdot10^{-6}$ mol % Ar at a pressure of 0.91 MPa and increased with pressure from $7.3\cdot10^{-7}$ to $2.3\cdot10^{-6}$ mol % Ar at 753 K. These data are lower than the subsequent ones from the same laboratory;[3,4] therefore, the papers of Dhar *et al.*[1,2] are not compiled. Thormeier[5,6] also performed a set of determinations in a similar temperature range and obtained slightly higher values of the solubility than Veleckis *et al.*[3,4] There are several models of the calculation of the Ar solubility[4,6–8] but the model of the hard-sphere theory adopted by Feder *et al.*[7,8] seems to be the most rational. According to this model the temperature dependence of the solubility should be less steep than measured by Thormeier[5,6] but slightly higher than the measurements of Veleckis *et al.*[3,4] We select the data of Veleckis *et al.*[3,4] as the most reliable since more pure materials were used. Their solubility equation is also accepted at a pressure of 0.101 MPa:

$$\log(\text{soly/mol \% Ar}) = -0.59 - 4221\ (T/\text{K})^{-1}. \quad (1)$$

The system was briefly reviewed by Hubberstey.[9] The Ar–Na phase diagram should be similar to that of Xe–Na differing in the boiling points of Ar and Xe.

Arnoldov *et al.*[10–12] determined the Ar solubility in liquid K–Na melt; for details see the Ar–K system.

Tentative values of the solubility of Ar in liquid Na at 0.101 MPa

T/K	Solubility/mol % Ar	Source
573	$1.1\cdot10^{-8}$	Eq. (1), (3,4)
673	$1.4\cdot10^{-7}$	Eq. (1), (3,4), (5,6)
773	$9\cdot10^{-7}$	Eq. (1), (3,4)
873	$4\cdot10^{-6}$	Eq. (1), (3,4)

References:
[1]S. K. Dhar, U.S. Atom. Energy Comm. Rep. ANL-6800, p. 183 (1963).
[2]R. C. Vogel, M. Levenson, and V. H. Munnecke, U.S. Atom. Energy Comm. Rep. ANL-6875, p. 48 (1964).
[3]E. Veleckis, R. Blomquist, R. Yonco, and M. Perin, U.S. Atom. Energy Comm. Rep. ANL-7325, p. 128 (1967).
[4]E. Veleckis, S. K. Dhar, F. A. Cafasso, and H. M. Feder, J. Phys. Chem. **75**, 2832 (1971).
[5]K. Thormeier, Atomkernenergie **14**, 449 (1969).
[6]K. Thormeier, Nucl. Engin. Design **14**, 69 (1970).
[7]H. M. Feder and H. Schnyders, U.S. Atom. Energy Comm. Rep. ANL-7775, p. 107 (1971); Rep. ANL-7750, p. 90 (1971).
[8]F. A. Cafasso, E. Veleckis, H. M. Feder, and H. C. Schnyders, U.S. Energy Res. Devel. Admin. Rep. CONF-760503-P2, p. 619 (1976).
[9]P. Hubberstey, *Handbook of Thermodynamic and Transport Properties of Alkali Metals*, edited by R. W. Ohse (Blackwell, Oxford, 1985), p. 907.
[10]M. N. Arnoldov, M. N. Ivanovskii, V. A. Morozov, S. S. Pletenets, and V. I. Subbotin, Atom. Energiya **28**, 18 (1970).
[11]M. N. Arnoldov, M. N. Ivanovskii, V. A. Morozov, S. S. Pletenets, and V. I. Subbotin, *Teplofizicheskie Svoistva Zhidkostei v Vysokikh Temperaturakh*, edited by A. K. Adas-Zade and E. E. Shpil'rain (Nauka, Moskva, 1970), p. 110.
[12]V. I. Subbotin, M. N. Ivanovskii, and M. N. Arnoldov, *Fizikokhimicheskie Osnovy Primeneniya Zhidkometallicheskikh Teplonositelei* (Atomizdat, Moskva, 1970), p. 78.

Components:
(1) Argon; Ar; [7440-37-1]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
K. Thormeier, Nucl. Engin. Design **14**, 69–82 (1970).

Variables:
Temperature: 623–873 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of Ar in liquid Na as a function of the temperature at constant pressure of 0.10 MPa was reported in a figure. The results were read from the figure and recalculated to mol % Ar by the compilers. The results were also reported in Thormeier[1] and Thormeier.[2] The experiments were originally performed in the pressure range 0.05–0.4 MPa.

T/K	Solubility/mol % Ar
623	$6.0\cdot 10^{-8}$
673	$1.5\cdot 10^{-7}$
773	$1.3\cdot 10^{-6}$
873	$5.6\cdot 10^{-6}$

The results were expressed by the following solubility equation:

$$\log(\text{soly/mol \% Ar}) = -0.26 - 4365\ (T/\text{K})^{-1}.$$

The compilers confirmed this equation. The O and C contents of Na were without any systematic influence upon the solubility of Ar.

Auxiliary Information

Method:
Ar was contained in a tank, and the whole pressure-tight apparatus was constructed of steel; the correctness of the procedure was tested on the air–water system. Liquid Na, containing constant amounts of impurities, was pumped into the tank. The Ar and Na were equilibrated under constant gas pressure and temperature until the saturation was reached. The Na was transferred into another tank where it was degassed under vacuum. The quantity of the recovered gas was determined by volumetric analysis.

Source and Purity of Materials:
Ar: nothing specified.
Na: nuclear grade of purity and distilled, contained $(6-9)\cdot 10^{-3}$ % O and $(6-9)\cdot 10^{-4}$ % C.

Estimated Error:
Solubility: nothing specified; reading-out procedure ±5%.
Temperature: nothing specified; reading-out procedure ±2 K.

References:
[1]K. Thormeier, Kernforschungszemtrum Karlsruhe Rep. KfK-964, VII-1 (1969).
[2]K. Thormeier, Atomkernenergie **14**, 449 (1969).

Components:
(1) Argon; Ar; [7440-37-1]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
E. Veleckis, S. K. Dhar, F. A. Cafasso, and H. M. Feder, J. Phys. Chem. **75**, 2832–2838 (1971).

Variables:
Temperature: 603–803 K
Pressure: 0.13–0.82 MPa

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of Ar in liquid Na was determined. The results were reported graphically; the numerical results appeared in Veleckis *et al.*[1]

The solubility of Ar in liquid Na at 753 K and changing pressure

p/MPa	Solubility/mol % Ar
0.13	$6.7\cdot 10^{-7}$
0.27	$1.3\cdot 10^{-6}$
0.34	$1.4\cdot 10^{-6}$
0.38	$2.5\cdot 10^{-6}$
0.42	$1.4\cdot 10^{-6}$
0.47	$1.4\cdot 10^{-6}$
0.58	$3.1\cdot 10^{-6}$
0.68	$3.8\cdot 10^{-6}$
0.83	$5.8\cdot 10^{-6}$

The solubility of Ar in liquid Na at 0.10 MPa and changing temperature

T/K	λ (Ostwald coefficient)	Mean solubility/mol %
603	$5.2\cdot 10^{-7}$, $6.8\cdot 10^{-7}$, $7.6\cdot 10^{-7}$, $1.2\cdot 10^{-6}$	$(4.0\pm 1.1)\cdot 10^{-8}$
654	$8.2\cdot 10^{-7}$, $8.4\cdot 10^{-7}$, $9.0\cdot 10^{-7}$, $1.1\cdot 10^{-6}$, $1.2\cdot 10^{-6}$, $2.2\cdot 10^{-6}$	$(6.0\pm 1.0)\cdot 10^{-8}$
704	$5.2\cdot 10^{-6}$, $5.5\cdot 10^{-6}$, $6.0\cdot 10^{-6}$, $6.5\cdot 10^{-6}$	$(2.7\pm 0.3)\cdot 10^{-7}$
751	$9.3\cdot 10^{-6}$, $1.1\cdot 10^{-5}$, $1.15\cdot 10^{-5}$, $1.2\cdot 10^{-5}$, $1.25\cdot 10^{-5}$, $1.4\cdot 10^{-5}$, $1.5\cdot 10^{-5}$	$(5.0\pm 1.5)\cdot 10^{-7}$
806	$4.0\cdot 10^{-5}$, $4.2\cdot 10^{-5}$, $4.3\cdot 10^{-5}$, $4.4\cdot 10^{-5}$, $5.0\cdot 10^{-5}$	$(5.0\pm 1.5)\cdot 10^{-6}$

[a]Calculated by the compilers.

The results were expressed by the solubility equation at 0.101 MPa:

$$\log(\text{soly/mol \% Ar}) = -0.59 - 4221\ (T/\text{K})^{-1}.$$

Reed and Droher[2] expressed these data by the solubility equation:

$$\log(\text{soly/mol \% Ar}) = -0.130 - 4542\ (T/\text{K})^{-1}.$$

Auxiliary Information

Method:
Three cylindrical vessels fabricated from Type 316 stainless steel were interconnected by Na transfer lines. Na was filtered in the first vessel. Separate gas circulation loops, made of Type 304 stainless steel tubing, were connected to the saturator and stripper. Ar was bubbled through Na in the second vessel. The amounts of Ar and Na were equilibrated for overnight. He was used as a stripping gas. It was introduced through a stainless steel dispersion disk with 5 μm pore size for 2 h. The vessel was heated by means of an electric furnace with Chromel/Alumel thermocouples in wells. The gas mixture was pumped through liquid N cooled molecular sieves (5 A) used as a trap. The trap was heated to 573 K and a measured portion of the desorbed gas was assayed for Ar with the use of a gas chromatograph.

Source and Purity of Materials:
Ar: 99.999% pure from Matheson Comp.; contained no detectable He.
He: 99.999% pure from Matheson Comp.
Na: reactor grade; filtered at <423 K and contained $\sim 2\cdot 10^{-4}$ % O.

Estimated Error:
Solubility: precision typically ±16% at 95% confidence level.
Temperature: accuracy ±1 K.

References:
[1]E. Veleckis, S. K. Dhar, F. A. Cafasso, and H. M. Feder, U.S. Atom. Energy Comm. Rep. ANL-7802 (1971).
[2]E. L. Reed and J. J. Droher, U.S. Atom. Energy Comm. Rep. LMEC-69-36 (1970).

4.25. Sodium–Krypton

Components:
(1) Krypton; Kr; [7439-90-9]
(2) Sodium; Na; [7440-23-5]

Evaluated By:
Hans Ulrich Borgstedt, Forschungszentrum Karlsruhe, Germany and Cezary Guminski, University of Warsaw, Poland, December 1999.

Critical Evaluation

Thormeier[1] predicted solubilities of Kr in liquid Na on the basis of an improved hard-sphere model as $1.68\cdot10^{-8}$, $3.0\cdot10^{-7}$, and $2.93\cdot10^{-6}$ mol % Kr at 673, 773, and 873 K, respectively. The temperature dependence of the solubility in Thormeier[1] was plotted in a figure. Vogel *et al.*[2] reported the first experimental studies on the solubility of Kr in liquid Na in the temperature range 473–753 K. The solubility increased in this range from $1.7\cdot10^{-10}$ to $1.1\cdot10^{-7}$ mol % Kr and could be expressed by Eq. (1) which was tested by the compilers:

$$\log(\text{soly/mol \% Kr}) = -2.188 - 3583\ (T/\text{K})^{-1}. \quad (1)$$

However, Blomquist *et al.*[3] elaborated in the same laboratory a set of solubility data at 669–826 K which were approximated by the following equation (tests by the compilers):

$$\log(\text{soly/mol \% Kr}) = -0.413 - 4374\ (T/\text{K})^{-1}. \quad (2)$$

The results of Blomquist *et al.*[3] were several times higher and their slope of the temperature dependence was steeper than in Vogel *et al.*[2] The data of Blomquist *et al.*[3] were slightly higher than those predicted in the same laboratory[4] on the basis of the hard-sphere theory. The results of this prediction were presented only in graphic form. The solubility data of Blomquist *et al.*[3] are selected for recommendation.

Except for the melting and boiling temperatures of Kr (115.76 and 119.80 K, respectively) the Kr–Na phase diagram is certainly similar to that of the Xe–Na system; see the corresponding phase diagram.

Tentative values of the solubility of Kr in liquid Na at 0.101 MPa

T/K	Solubility/mol % Ar	Source
673	$1.2\cdot10^{-7}$	Eq. (2)
773	$8\cdot10^{-7}$	Eq. (2)
873	$4\cdot10^{-6}$	Eq. (2)

References:
[1]K. Thormeier, Kernforschungszentrum Karlsruhe Rep. KFK-1166 (1970); Nucl. Engin. Design **14**, 69 (1970).
[2]R. C. Vogel, M. Levenson, and V. H. Munnecke, U.S. Atom. Energy Comm. Rep. ANL-6875, p. 48 (1964); S. K. Dhar, U.S. Atom. Energy Comm. Rep. ANL-6900, p. 125 (1964).
[3]R. A. Blomquist, F. A. Cafasso, and H. M. Feder, J. Nucl. Mater. **59**, 199 (1976).
[4]F. A. Cafasso, E. Veleckis, H. M. Feder, and H. C. Schnyders, U.S. Energy Res. Devel. Admin. Rep. CONF-760503-P2, p. 619 (1976).

Components:
(1) Krypton; Kr; [7439-90-9]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
R. C. Vogel, M. Levenson, and V. H. Munnecke, U.S. Atom. Energy Comm. Rep. ANL-6875, pp. 48–50 (1964).

Variables:
Temperature: 473–753 K
One pressure: 0.10 MPa

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of Kr in liquid Na at 0.10 MPa was measured. The data were presented in a figure; they were read out from the figure and recalculated to mol % Kr MPa by the compilers.

T/K	Solubility/mol % Kr
473	$1.8\cdot10^{-10}$, $2.1\cdot10^{-10}$
477	$2.0\cdot10^{-10}$
573	$3.8\cdot10^{-9}$, $4.9\cdot10^{-9}$
662	$2.6\cdot10^{-8}$
671	$2.8\cdot10^{-8}$, $2.9\cdot10^{-8}$
753	$7.9\cdot10^{-8}$, $1.1\cdot10^{-7}$, $1.2\cdot10^{-7}$

The data were expressed by the solubility equation:

$$\log(\text{soly/mol \% Kr}) = -2.188 - 3583\ (T/\text{K})^{-1}.$$

The compilers tested the equation. The same results were reported in Dhar.[1]

Auxiliary Information

Method:
Na was saturated with radioactive Kr by its circulation for ~3 h at selected temperature. The solution was equilibrated for several hours and transferred to a second vessel in which Kr was removed by sparging at 0.10 MPa with He containing a known amount of inactive Kr. The He–Kr mixture was circulated through a charcoal trap cooled by liquid N on which Kr and some He was adsorbed. The trap was pumped out to less than 10^{-3} Torr to remove He completely. Kr was subsequently desorbed by heating the trap and the amount of Kr dissolved in Na was calculated from the specific activity measured.

Source and Purity of Materials:
Kr: nothing specified.
Na: nuclear grade of purity.
He: nothing specified.

Estimated Error:
Solubility: precision better than ±5%; reading-out procedure ±5% (by the compilers).
Temperature: nothing specified; reading-out procedure ±2 K.

References:
[1]S. K. Dhar, U.S. Atom. Energy Comm. Rep. ANL-6900, pp. 125–127 (1964).

Components:
(1) Krypton; Kr; [7439-90-9]
(2) Sodium; Na; [7440-23-5]

Original Measurements:
R. A. Blomquist, F. A. Cafasso, and H. M. Feder, J. Nucl. Mater. **59**, 199–200 (1976).

Variables:
Temperature: 669–826 K
Pressure: ~0.7 MPa

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of Kr in liquid Na was reported in graphical form as a plot of the Ostwald coefficient versus reciprocal temperature. The results were read from the figure and recalculated to mol % Kr at 0.101 MPa by the compilers. The authors measured the solubility at ~0.7 MPa and assumed by analogy to the solutions of other noble gases in Na that Henry's law is applicable in this case.

T/K	Solubility/mol % Kr
669	$1.04\cdot10^{-7}$, $1.45\cdot10^{-7}$, $1.59\cdot10^{-7}$, $1.60\cdot10^{-7}$
675	$1.00\cdot10^{-7}$, $1.07\cdot10^{-7}$, $1.52\cdot10^{-7}$
719	$2.2\cdot10^{-7}$, $3.5\cdot10^{-7}$
725	$1.92\cdot10^{-7}$, $2.2\cdot10^{-7}$, $2.6\cdot10^{-7}$, $3.3\cdot10^{-7}$, $3.5\cdot10^{-7}$
766	$5.5\cdot10^{-7}$, $5.9\cdot10^{-7}$, $8.8\cdot10^{-7}$
772	$5.7\cdot10^{-7}$, $8.5\cdot10^{-7}$, $8.9\cdot10^{-7}$
820	$1.56\cdot10^{-6}$, $2.2\cdot10^{-6}$, $2.4\cdot10^{-6}$, $2.6\cdot10^{-6}$
826	$1.95\cdot10^{-6}$, $2.1\cdot10^{-6}$, $2.2\cdot10^{-6}$

The solubility data were expressed by the following equation at 0.101 MPa:

$$\log(\text{soly/mol \% Kr}) = -0.413 - 4374\ (T/\text{K})^{-1}.$$

The compilers confirmed this equation.

Auxiliary Information

Method:
Three cylindrical vessels fabricated from Type 316 stainless steel were interconnected by Na transfer lines.[1] Na was filtered in the first vessel. Kr was bubbled through Na in the second vessel. The Kr and Na were equilibrated overnight. He, used as stripping gas, was introduced through a stainless steel dispersion disk with 5 μm pore size for 2 h. Separate gas circulation loops, made of Type 304 stainless steel tubing, were connected to the saturator and the stripper. The mixture of Kr with the stripping gas was pumped through liquid N cooled molecular sieves (5 A), used as an absorber. The concentration of Kr was determined by means of a gas chromatograph after heating the absorber to 573 K. The vessels were heated by means of an electric furnace controlled by Chromel/Alumel thermocouples.

Source and Purity of Materials:
Kr: nothing specified but probably >99.99% pure.
Na: reactor grade, filtered at 423 K with a content of ~2.10^{-4} % O.
He: nothing specified.

Estimated Error:
Solubility: precision not better than ±7% at 95% confidence level.
Temperature: accuracy ±1 K.[1]

References:
[1]E. Veleckis, S. K. Dhar, F. A. Cafasso, and H. M. Feder, J. Phys. Chem. **75**, 2832–2838 (1971).

4.26. Sodium–Xenon

Components:
(1) Xenon; Xe; [7440-63-3]
(2) Sodium; Na; [7440-23-5]

Evaluated By:
Hans Ulrich Borgstedt, Forschungszentrum Karlsruhe, Germany and Cezary Guminski, University of Warsaw, Poland, March 1997.

Critical Evaluation

Feder *et al.*[1,2] calculated a solubility of Xe in liquid Na using the hard-sphere theory. The authors observed a good agreement of experimental data of Veleckis *et al.*[3,4] with this prediction. Mitra[5] obtained results of the solubility in earlier tests being 10^5 times higher than those in Veleckis *et al.*;[3,4] his procedure involved radiometric measurement of the quantity of Xe liberated when a frozen aliquot of Na, saturated with radioactive Xe, was remelted in an evacuated vessel. Mitra[5] is not compiled due to the rejection of the results. The temperature dependence of the Xe solubility may be expressed after Veleckis *et al.*[3,4] as:

$$\log(\text{soly/mol \% Xe}) = -1.025 - 4243\ (T/\text{K})^{-1}. \quad (1)$$

Thormeier[6] predicted the solubilities of Xe at 673, 773, and 873 K based on an improved hard-sphere model to be $1.84\cdot10^{-9}$, $4.46\cdot10^{-8}$, and $5.96\cdot10^{-7}$ mol % Xe; these values are 1 order of magnitude lower than the experimental data of Veleckis *et al.*[3,4]

The subject was briefly reviewed in Hubberstey.[7] The schematic Xe–Na phase diagram is shown in Fig. 33.

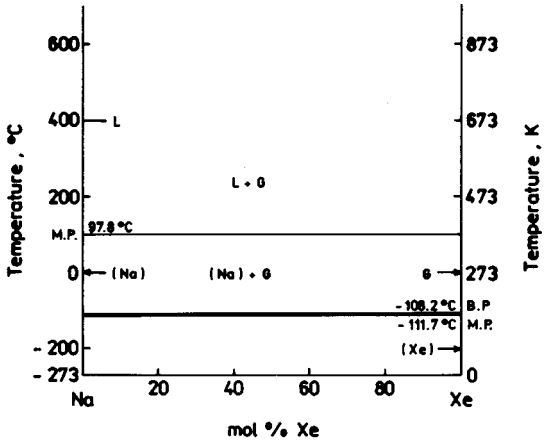

FIG. 33. Xe–Na phase diagram (schematic).

Tentative values of the solubility of Xe in liquid Na

T/K	Solubility/mol % Xe	Source
623	$1.4\cdot10^{-8}$	Eq. (1), (3,4)
673	$5.4\cdot10^{-8}$	Eq. (1), (3,4)
773	$3.1\cdot10^{-7}$	Eq. (1), (3,4)
873	$1.3\cdot10^{-6}$	Eq. (1), (3,4)

References:

[1]H. M. Feder and H. Schnyders, U.S. Atom. Energy Comm. Rep. ANL-7775, p. 107 (1971); Rep. ANL-7750, p. 90 (1971).

[2]F. A. Cafasso, E. Veleckis, H. M. Feder, and H. C. Schnyders, U.S. Energy Res. Devel. Admin. Rep. CONF-760503-P2, p. 619 (1976).

[3]E. Veleckis, F. A. Cafasso, and H. M. Feder, J. Chem. Eng. Data **21**, 75 (1976).

[4]E. Veleckis and W. A. Kremser, U.S. Atom. Energy Comm. Rep. ANL-7775, p. 40 (1971).

[5]C. Mitra, Engin. Sci. dissertation, Columbia University, N.Y., 1959; abstracted in Diss. Abstr. **22**, 100 (1961).

[6]K. Thormeier, Kernforschungszentrum Karlsruhe Rep. KFK-1166 (1970).

[7]P. Hubberstey, *Handbook of Thermodynamic and Transport Properties of Alkali Metals*, edited by R. W. Ohse (Blackwell, Oxford, 1985), p. 907.

Components:

(1) Xenon; Xe; [7440-63-3]
(2) Sodium; Na; [7440-23-5]

Original Measurements:

E. Veleckis and W. A. Kremsner, U.S. Atom. Energy Comm. Rep. ANL-7775, pp. 40–43 (1971).

Variables:

Temperature: 623–873 K
Pressure: 0.26–0.83 MPa

Prepared by:

H. U. Borgstedt and C. Guminski

Experimental Data

The pressure dependence of the solubility of Xe in liquid Na at 773 K was reported graphically. The data were read from a figure by the compilers and recalculated to mol % Xe.

p/MPa	Solubility/mol % Xe
0.26	$9\cdot10^{-7}$
0.27	$1.0\cdot10^{-6}$
0.30	$8\cdot10^{-7}$
0.40	$1.2\cdot10^{-6}$
0.41	$1.3\cdot10^{-6}$
0.53	$1.6\cdot10^{-6}$
0.54	$1.3\cdot10^{-6}$
0.55	$1.2\cdot10^{-6}$
0.67	$2.6\cdot10^{-6}$
0.70	$1.9\cdot10^{-6}$; $2.0\cdot10^{-6}$; $2.7\cdot10^{-6}$; $2.7\cdot10^{-6}$
0.71	$2.3\cdot10^{-6}$
0.82	$2.1\cdot10^{-6}$
0.83	$1.8\cdot10^{-6}$

The temperature dependence of the Xe solubility in liquid Na was reported

t/°C	Solubility/mol % Xe	Stand. dev./%	Number of tests
600	$1.59\cdot10^{-6}$	···	1
550	$6.61\cdot10^{-7}$	9	6
500	$3.00\cdot10^{-7}$	17	17
450	$1.13\cdot10^{-7}$	18	9
400	$5.36\cdot10^{-8}$	6	7
350	$1.38\cdot10^{-8}$	17	7

The same results were reported in Veleckis *et al.*[1]

Auxiliary Information

Method:

Liquid Na was saturated with Xe by prolonged bubbling at preselected temperatures and pressures. After equilibration (escaping of the excess of bubbles), a bottom portion of the solution was transferred to another container in which dissolved Xe was stripped from Na at ~423 K by sparging with He for 2 h. The stripping gas was separated by selective absorption of Xe on active silica gel at 77 K. The remaining gas was analyzed by gas chromatography after the silica gel was heated to 573 K. Xe was returned to the reservoir after each solubility experiment. The apparatus containing Na was made of Type 316 stainless steel and the tubing for gases was made of Type 304 stainless steel.

Source and Purity of Materials:

Xe: 99.995% pure from Baker Chem. Comp. and contained $1.5\cdot10^{-3}$ % N, $1.0\cdot10^{-3}$ % Kr, and $8\cdot10^{-4}$ % Ar.[1]
Na: nuclear grade of purity; periodically filtered at ~423 K.[1]
He: 99.999% pure from Mathewson Comp.[1]

Estimated Error:

Solubility: standard deviation between ±5% and ±18% at 95% confidence limits.
Temperature: accuracy ±1 K.

References:

[1]E. Veleckis, F. A. Cafasso, and H. M. Feder, J. Chem. Engin. Data **21**, 75–76 (1976).

4.27. Sodium–Radon

Components:
(1) Radon; Rn; [10043-92-2]
(2) Sodium; Na; [7440-23-5]

Evaluated By:
Hans Ulrich Borgstedt, Forschungszentrum Karlsruhe, Germany and Cezary Guminski, University of Warsaw, Poland, March 1997.

Critical Evaluation

Experimental solubility data concerning the Xe–Na system have not been published in the literature so far. However, taking into account the tendency that the solubilities of noble gases in liquid Na decrease with the increase of their atomic number, one may safely predict that the solubility of Rn in liquid Na is lower than the measured solubility of Xe in liquid Na; see the Xe–Na system for comparison.

5. Solutions of Nonmetallic Substances in Potassium

5.1. Potassium–Hydrogen

Components:
(1) Hydrogen; H; [1333-74-0]
(2) Potassium; K; [7440-09-7]

Evaluated by:
Hans Ulrich Borgstedt, Forschungszentrum Karlsruhe, Germany and Cezary Guminski, University of Warsaw, Poland, May 1997.

Critical Evaluation

H being introduced into liquid K forms KH of relative stability according to the reaction scheme:

$$1/2\ H_2(g)+K(l)\leftrightarrow KH(l)\leftrightarrow KH(s), \tag{1}$$

where the first step by analogy to Li and Na solvents is a first order process. The reaction rate is effective above 473 K,[1] Because the gas, liquid, and solid phases are in equilibrium, a H solubility may be defined either as H concentration in the liquid phase being a function of H gas pressure without presence of solid or liquid KH, or as maximum H concentration in the liquid being dissolved from the solid or liquid KH compound. The first kind of the equilibrium is the isobaric solubility where H pressure over the melt and the corresponding H concentration are ruled by the Sieverts constant K_S :

$$K_S = x_H p_H^{-1/2}, \tag{2}$$

where x_H is the mol fraction of H in the solution and p_H is the pressure of H over the solution.

Dilute solutions of H in liquid K fulfill the Sieverts law very well up to ~1 mol % H between 613 and 713 K as found by Arnoldov *et al.*[2,3] but certainly the law is valid outside the temperature range and probably up to ~5 mol % H. When the H pressure over the melt is further increased the H concentration in the liquid is also increased and finally solid KH is precipitated according to Eq. (1). Still further addition of H into the system makes the H pressure independent of the H content in the melt. Such pressure is named the equilibrium plateau pressure and the concentration at which the plateau begins is the measure of H solubility in liquid K. The equilibrium plateau pressure was measured by Troost and Hautefeuille,[4] Keyes,[5] Ephraim and Michel,[6] Sollers and Crenshaw,[7] Hérold,[8,9] Arnoldov *et al.*,[2] Dymova *et al.*,[10] Skuratov *et al.*,[11] Ivanovskii *et al.*,[3] and Kurbanov *et al.*[12] The results of Troost and Hautefeuille[4] were preliminary; irregular changes of pressure on temperature were observed and solid K_2H formation instead of KH was postulated. The rest of the pressure data were spread in a band of ±10%. The best agreement was observed for the results of Arnoldov *et al.*,[2,3] Sollers and Crenshaw,[7] and Hérold.[8,9] The proposed fitting equation relating logarithm of the H pressure versus reciprocal temperature based on the combined, selected data is:

$$\log(p_H/\mathrm{Pa}) = 13.630 - 6045\ (T/\mathrm{K})^{-1}. \tag{3}$$

Equation (3) is valid between 490 and 850 K. Other equations proposed in Arnoldov *et al.*[2,3] had slightly lower and in Dymova *et al.*[10] and Kurbanov *et al.*[12] much higher slopes of the dependence. The equation suggested in Hubberstey[13] was quoted from Arnoldov *et al.*[3] By similarity to the Li–H and Na–H systems there should be a break on the dependence of logarithm of the H pressure versus reciprocal temperature near the melting point of KH, namely at the monotectic temperature. However, this temperature range was experimentally not investigated. Skuratov *et al.*[11] investigated the H equilibrium plateau pressure for liquid KH at 932–1015 K. Their results may be expressed by the following equation:

$$\log(p_H/\mathrm{Pa}) = 11.103 - 3806\ (T/\mathrm{K})^{-1} \quad r = 0.9994. \tag{4}$$

Extrapolating Eq. (3) to higher and Eq. (4) to lower temperatures one observes their intersection at 886 K, it is 6 K lower than the melting point of KH at 892 K. We should remember the quite distant extrapolations. Magomedov[14] predicted the melting point of KH at 901.00 K, based on a thermodynamic model. Similarly to the well investigated Li–H system the difference between the melting point and the monotectic should be ~3 K. The melting point of KH determined at 10.1 MPa increased for 2.2±0.2 K,[11] Dymova *et al.*[10] found the decomposition of KH to K and H occurring at 691–711 K but the conditions were not specified.

The solubility of solid KH in liquid K was determined by Arnoldov *et al.*[2,3] from vapor pressure measurements between 603 and 713 K. The results of Arnoldov *et al.*[3] are practically the same as in Arnoldov *et al.*[2] and may expressed by the equation:

$$\log(\mathrm{soly/mol\ \%\ H}) = 4.45 - 2980\ (T/\mathrm{K})^{-1}, \tag{5}$$

which seems to be valid between the melting point of K and the monotectic temperature. Slightly different equations were suggested by Hubberstey *et al.*[15] and Fromm and Jehn.[16] The composition of the eutectic at practically the same temperature as the melting point of K was found from extrapolation with the help of Eq. (5) and is equal to $4\cdot10^{-5}$ mol % H. An extrapolation to the monotectic temperature gives ~13 mol % H dissolved in liquid K. The critical miscibility temperature was not measured but it should be a lower temperature than that predicted for the Na–H system, <1500 K.

The Sieverts constant from Arnoldov *et al.*[3] was found to be practically independent of temperature at the level of $3.3\cdot10^{-2}$ mol % H $\mathrm{Pa}^{-1/2}$. If one would subtract the right hand sides of Eq. (5) and half of Eq. (3) one obtains the following equation:

$$\log(K_S/\mathrm{mol\ \%\ H\cdot Pa^{-1/2}}) = -2.36 - 42\ (T/\mathrm{K})^{-1}, \tag{6}$$

where K_S , due to the similarity to the Na–H system, is practically temperature independent being $4.4\cdot10^{-2}$ mol % H $\mathrm{Pa}^{-1/2}$; this value is not far from that presented in Arnoldov *et al.*[3]

Influences of O, N, and C on the H solubility in liquid K were not investigated in detail but by analogy to the Na medium one should take into account the possibility of interactions between the mentioned elements and H. For example, OH is quite a stable entity in liquid K; see the K–KOH system.

The solubility of H and the H plateau pressure in the K–Na liquid alloys were frequently investigated (refer to Refs. 1, 3, 17–25) in the temperature range 373–713 K. Additional studies (refer to Refs. 1, 17–20, 25, and 21–23) investigated the solubility in the eutectic K–Na alloy.

Thorley and Tyzack[24] estimated that the H solubility in the K–Na alloy containing 80 mol % Na was at a level of 10^{-3} mol % H at temperatures between 373 and 393 K; they analyzed the alloy from a cold trap, but they did not publish therein any details of the determinations or exact data. The results of Savinov *et al.*[19] are significantly scattered, but their mean value is in agreement with the results of Subbotin *et al.*,[1] Arnoldov *et al.*,[3] and Arnoldov *et al.*[17,18] Kikin[20] used two kinds of H meters that lead them to either significantly steeper temperature dependence of the solubility (SER meter type) or too low temperature dependence of the solubility (HNPF meter type) than in subsequent studies. However, the mean results of both methods are scattered around the selected values of Subbotin *et al.*,[1] Arnoldov *et al.*,[3] and Arnoldov *et al.*[17,18] The values obtained in Arnoldov *et al.*[25] are overestimated and their temperature dependence is too steep. Arnoldov *et al.*[3] investigated the solubility at several compositions of the K–Na alloys and did not observe any spectacular changes of the solubility with the alloy composition; the solubility equations given in the corresponding data sheets are similar. The highest concentration observed at fixed temperature while changing the alloy composition is in the vicinity of the K–Na eutectic. This concentration is higher than those in pure K and Na (being for example at 673 K: 1.4, 0.95, and 0.28 mol % H in the eutectic K–Na, K, and Na, respectively). Reimann *et al.*[26] found that solid KH was precipitated from the K–Na mixed solvent containing H, whereas Arnoldov *et al.*[18] affirmed that the KH–NaH solid mixture is the equilibrium phase.

An addition of 1–4 mol % Li to the eutectic mixture of K–Na resulted in increasing H solubility.[21–23]

The partial K–H phase diagram is presented in Fig. 34. The complete miscibility is reached at pressures significantly higher than the ambient pressure. Some information on the K–D system is reported separately (see the K–D system), but experimental material was not found for the K–T system.

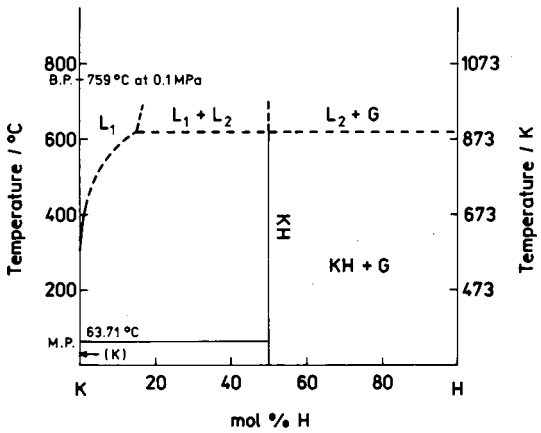

FIG. 34. K–H phase diagram.

The tentative values of the solubility of H in liquid K at corresponding pressures

T/K	Solubility/mol % H	Source	p/Pa	Source
573	0.15	Eq. (5), extrapolated	1200	Eq. (3)
673	1.0	(2), Eq. (5), interpolated	44000	Eq. (3)
773	4	Eq. (5), extrapolated	650000	Eq. (3)

References:

[1]V. I. Subbotin, M. N. Ivanovskii, and M. N. Arnoldov, *Fiziko-Khimicheskie Osnovy Primeneniya Zhidkometallicheskikh Teplonositelei* (Atomizdat, Moskva, 1970), p. 76.

[2]M. N. Arnoldov, M. N. Ivanovskii, V. A. Morozov, S. S. Pletenets, and V. V. Sitnikov, Izv. Akad. Nauk SSSR, Met. **1**, 74 (1973).

[3]M. N. Ivanovskii, M. N. Arnoldov, V. A. Morozov, T. I. Moiseeva, and S. S. Pletenets, Izv. Akad. Nauk SSSR, Met. **1**, 201 (1980).

[4]L. Troost and P. Hautefeuille, Compt. Rend. **78**, 807 (1874).

[5]F. G. Keyes, J. Am. Chem. Soc. **34**, 779 (1912).

[6]F. Ephraim and E. Michel, Helv. Chim. Acta **4**, 762 (1921).

[7]E. F. Sollers and J. L. Crenshaw, J. Am. Chem. Soc. **59**, 2015 (1937).

[8]A. Hérold, Compt. Rend. **228**, 686 (1949); **224**, 1826 (1947).

[9]A. Hérold, Ann. Chim. **6**, 536 (1951).

[10]T. N. Dymova, S. I. Bakum, and U. Mirsaidov, Dokl. Akad. Nauk SSSR 216, p. 87 (1974).

[11]O. A. Skuratov, O. N. Pavlov, V. I. Danilkin, and O. A. Volkov, Zh. Neorg. Khim. **21**, 2910 (1976).

[12]A. R. Kurbanov, A. Badalov, and U. Mirsaidov, Dokl. Akad. Nauk Tadhz. SSR **23**, 83 (1980).

[13]P. Hubberstey, *Handbook of Thermodynamic and Transport Properties of Alkali Metals*, edited by R. W. Ohse (Blackwell, Oxford, 1985), p. 885.

[14]M. N. Magomedov, Zh. Fiz. Khim. **68**, 589 (1994).

[15]P. Hubberstey, P. F. Adams, R. J. Pulham, M. G. Down, and A. E. Thunder, J. Less-Common Met. **49**, 253 (1976).

[16]E. Fromm and H. Jehn, Bull. Alloy Phase Diagr. **5**, 323 (1984).

[17]M. N. Arnoldov, M. N. Ivanovskii, V. A. Morozov, S. S. Pletenets, and V. I. Subbotin, Atom. Energiya **28**, 18 (1970).

[18]M. N. Arnoldov, M. N. Ivanovskii, V. A. Morozov, S. S. Pletenets, and V. I. Subbotin, *Teplofizicheskie Svoistva Zhidkostei v Vysshikh Temperaturakh*, edited by A. K. Abas-Zade and E. E. Shpil'rain (Nauka, Moskva, 1970), p. 110.

[19]V. B. Savinov, E. E. Konovalov, and Sh. I. Peizulaev, *Teplofizicheskie Svoistva Zhidkostei v Vysshikh Temperaturakh*, edited by A. K. Abas-Zade and E. E. Shpil'rain (Nauka, Moskva, 1970), p. 118.

[20]G. M. Kikin, U.S. Atom. Energy. Comm. Rep. NAA-SR-Memo-5472 (1960).

[21]E. L. Compere and J. E. Savolainen, Trans. Am. Nucl. Soc. **8**, 18 (1965).

[22]H. W. Savage and E. L. Compere, U.S. Atom. Energy Comm. Rep. ORNL-3898 (1965); Rep. ORNL-3789 (1965); Rep. ORNL-3591, p. 217 (1964).

[23]E. L. Compere and J. E. Savolainen, Nucl. Sci. Eng. **28**, 325 (1967).

[24]A. Thorley and C. Tyzack, *Thermodynamics of Nuclear Materials* (IAEA, Vienna, 1962), p. 365.

[25]M. N. Arnoldov, M. N. Ivanovskii, S. S. Pletenets, and A. D. Pleshivtsev, Atom. Energiya **32**, 234 (1972).

[26]J. Reimann, R. Kirchner, and D. Rackel, Fusion Engin. Design **18**, 67 (1991).

Components:
(1) Hydrogen; H; [1333-74-0]
(2) Potassium; K; [7440-09-7]

Original Measurements:
M. N. Arnoldov, M. N. Ivanovskii, V. A. Morozov, S. S. Pletenets, and V. V. Sitnikov, Izv. Akad. Nauk SSSR, Met. **1**, 74–77 (1973).

Variables:
Temperature: 613–713 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of H in liquid K and its dissociation pressure was reported in a figure. The values were read out from the figure and recalculated to mol % H by the compilers.

t/°C	p/Torr	p/Pa	Solubility/mass % H	Solubility/mol % H
340	53.4	7100	0.010	0.39
390	278	36970	0.023	0.90
405	441	58650	0.030	1.17
420	660	87780	0.037	1.45
440	1166	155100	0.047	1.81

The temperature dependence of the solubility was expressed by the equation:

$$\log(\text{soly/mol \% H}) = 4.39 - 2930\ (T/\text{K})^{-1}.$$

The dissociation pressure of over liquid K was expressed by the equation:

$$\log(p/\text{Torr}) = 11.3 - 5860\ (T/\text{K})^{-1}.$$

The compilers tested the equations.

Auxiliary Information

Method:
The apparatus was made of a metal. An amount of H was measured in a container of constant volume by means of pressure determination using a monometer. H and K were introduced into a test cell and equilibrated for 6–8 h at the selected temperature. The temperature was controlled by a Cromel/Alumel thermocouple. The H pressure was corrected for the actual K vapor pressure. A break point on the relation of the square root of the equilibrium H pressure versus the composition of the melt corresponded to the saturation of K with H.

Source and Purity of Materials:
H: from thermal decomposition of Zr–H at 973–1073 K.
K: filtered at 373–423 K through a stainless steel net with a pore size of ~50 μm. The metal was reused after such filtration.

Estimated Error:
Solubility: nothing specified; reading-out procedure $\pm 2 \cdot 10^{-4}$ mass % H.
Temperature: nothing specified; reading-out procedure ±3 K.

Components:
(1) Hydrogen; H; [1333-74-0]
(2) Potassium-sodium eutectic, $K_{68}Na_{32}$; [11147-16-3]

Original Measurements:
G. M. Kikin, U.S. Atom. Energy Comm. Rep. NAA-SR-Memo-5472 (1960).

Variables:
Temperature: 411–639 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of H in the liquid K–Na eutectic alloy (32 mol % Na) was determined using two kinds of plugging meters. The data were read from a figure and recalculated to mol % H by the compilers.

SER meter type

t/°F	T/K	Solubility/mass % H	Solubility/mol % H
410	483	$1.0 \cdot 10^{-3}$	0.034
440	500	$1.6 \cdot 10^{-3}$	0.054
460	511	$2.2 \cdot 10^{-3}$	0.075
470	516	$3.2 \cdot 10^{-3}$	0.109
480	522	$4.2 \cdot 10^{-3}$	0.143
490	528	$5.6 \cdot 10^{-3}$	0.19

These data were approximated by the compiler's solubility equation:

$$\log(\text{soly/mol \% H}) = 7.299 - 4260(T/\text{K})^{-1} \quad r = .984$$

HNPF meter type

t/°F	T/K	Solubility/mass % H	Solubility/mol % H
280	411	$1.3 \cdot 10^{-3}$	0.044
370	461	$2.3 \cdot 10^{-3}$	0.078
430	494	$3.4 \cdot 10^{-3}$	0.116
460	511	$4.4 \cdot 10^{-3}$	0.15
500	533	$5.5 \cdot 10^{-3}$	0.19
515	541	$6.5 \cdot 10^{-3}$	0.22
530	550	$7.5 \cdot 10^{-3}$	0.25
550	561	$9.0 \cdot 10^{-3}$	0.30
565	569	$1.11 \cdot 10^{-2}$	0.37
590	583	$1.25 \cdot 10^{-2}$	0.42
600	588	$1.45 \cdot 10^{-2}$	0.49
610	594	$1.65 \cdot 10^{-2}$	0.56
625	603	$1.85 \cdot 10^{-2}$	0.63
640	611	$2.0 \cdot 10^{-2}$	0.68
640	611	$2.1 \cdot 10^{-2}$	0.73
655	619	$2.3 \cdot 10^{-2}$	0.78
660	622	$2.5 \cdot 10^{-2}$	0.86
670	627	$2.7 \cdot 10^{-2}$	0.92
690	639	$3.0 \cdot 10^{-2}$	1.02

These data were approximated by the compiler's solubility equation:

$$\log(\text{soly/mol \% H}) = 2.606 - 1710(T/\text{K})^{-1} \quad r = .979$$

Components:
(1) Hydrogen; H; [1333-74-0]
(2) Potassium-sodium eutectic; $K_{68}Na_{32}$; [11147-16-3]
(3) Lithium; Li; [7439-92-2]

Original Measurements:
E. L. Compere and J. E. Savolainen, Nucl. Sci. Engin. **28**, 325–337 (1967).

Variables:
Temperature: 573–673 K;
Li concentration 0–1.16 mol %

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of H in the liquid K–Na (32 mol % Na) alloy and the equilibrium plateau pressure of H were determined

t/°C	Solubility/cm^3 H g^{-1} K–Na	Solubility/mol % H[a]	p/Torr	p/Pa[a]
300	0.42	0.16	13	1730
330	0.76	0.30	46	6130
400	2.53	1.00	517	68900

[a]Calculated by the compilers.

The solubility data were expressed by the solubility equation:

$$\log(\text{soly/mol \% H}) = 4.22 - 2900\ (T/\text{K})^{-1}$$

and the H pressure data by the equation:

$$\log(p_{\text{H}}/\text{atm}) = 13.26 - 6280\ (T/\text{K})^{-1}.$$

The compilers tested the correctness of both equations.

The solubility of H in the liquid eutectic K–Na alloy containing 1.16 mol % Li at 1100 °F (866 K) was found to be 0.012 g LiH in kg of K–Na or $5.1 \cdot 10^{-3}$ mol % H (as calculated by the compilers). Further addition of Li up to 4 mol % resulted in larger H uptake but numerical results were not reported.

The same results were also published in Savage and Compere[1] and shortly later in Compere and Savolainen.[2]

A mass action balance analysis was done by the authors to show that H, dissolved in the K–Na–Li alloy, exists largely in form of LiH molecules or ion pairs Li^+ and H^-. From the compiler's point of view, the use of the same Sieverts relationship for H in the pure K–Na and in the K–Na–Li mixture is not necessarily correct.

Auxiliary Information

Method:
A tank containing the K–Na alloy was made of Type 304 stainless steel. It was connected by loop pipes with SER and HNPF plugging meters via electromagnetic pump. A filter was placed inbetween. The system was heated by a tubular heater. H was kept in a separate gas tank made of the stainless steel. The temperature was controlled by Chromel/Alumel thermocouples in stainless steel sheaths. The apparatus was evacuated and K–Na alloy introduced, then Ar cover gas was entered. The system was heated and H addition was realized by introduction of measured amounts of H gas to the cover gas. The end of the reaction was controlled by a constant pressure inside the tank. The system was gradually cooled while observing the reaction of the plugging meters. The temperature at which a crystallization of KH started was measured.

Source and Purity of Materials:
H: "dried."
K–Na: nuclear grade of purity; further purified.
Ar: "dried."

Estimated Error:
Solubility: nothing specified; reading-out procedure $\pm 7.10^{-3}$ mol % H.
Temperature: nothing specified; reading-out procedure ± 3 K.

Components:
(1) Hydrogen; H; [1333-74-0]
(2) Potassium-sodium eutectic, $K_{68}Na_{32}$; [11147-16-3]

Original Measurements:
M. N. Arnoldov, M. N. Ivanovskii, V. A. Morozov, S. S. Pletenets, and V. I. Subbotin, *Teplofizicheskie Svoistva Zhidkostei v Vysshikh Temperaturakh*, edited by A. K. Abas-Zade and E. E. Shpil'rain (Nauka, Moskva, 1970), pp. 110–116.

Variables:
Temperature: 573–653 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of H in liquid eutectic K–Na (32 mol % Na) alloy and the equilibrium plateau pressure of H were determined. The values were read from figures and recalculated to mol % and Pa by the compilers.

t/°C	Solubility/mass % H	Solubility/mol % H	p/Torr	p/Pa
300	$6.6\cdot10^{-3}$	0.22	4.4	2580
320	$9.1\cdot10^{-3}$	0.31	6.4	5460
344	0.0122	0.41	10.0	13330
359	0.0154	0.52	12.8	21840
369.5	0.0188	0.64	15.6	32440
380	0.020	0.68	19.1	48630
380	0.022	0.75	18.4	45130

The solubility equation was reported by the authors and tested by the compilers:

$$\log(\text{soly/mol \% H}) = 3.96 - 2670\ (T/\text{K})^{-1}.$$

The same results were reported in Arnoldov *et al.*[1] and Subbotin *et al.*[2]

A mixture of KH and NaH was the equilibrium solid phase. Kinetics of the reaction between H and K–Na was investigated and a precipitation of KH–NaH was reflected therein.

Auxiliary Information

Method:
The equilibrium pressure of H gas, being in direct contact with its solution in the alloy, was measured at several temperatures. Materials used for the construction of the apparatus were not specified. The H pressure was measured by a manometer. Amounts of H in a chamber before and after the equilibration with the K–Na alloy were calculated assuming the ideal behavior of H gas. The measurements were performed in isothermal conditions till stable values of the pressure were noticed. A new temperature was established and a new portion of H gas introduced into the chamber for the next step.

Source and Purity of Materials:
H: contained <0.1 vol % N and <0.2 vol % O.
K–Na alloy: contained 78.2% K, 21.8% Na, $3\cdot10^{-4}$ % Li, In, 0.01% Mg, Zn, Cu, $1\cdot10^{-4}$ % Ag, Cd, 0.066% Fe, 0.033% Ca, Cr, Ti, $2\cdot10^{-3}$ % Sn, $1\cdot10^{-3}$ % Ba, Mo, V, Bi, Pb, Co, $3.3\cdot10^{-3}$ % Al, Mn, $9\cdot10^{-3}$ % Be, purified by decantation of solid impurities at room temperature.

Estimated Error:
Solubility: maximal deviation 10%; standard deviation 3%.
Temperature: nothing specified; precision ±0.5 K (by the compilers).

References:
[1]M. N. Arnoldov, M. N. Ivanovskii, V. A. Morozov, S. S. Pletenets, and V. I. Subbotin, Atom. Energiya **28**, 18–22 (1970).
[2]V. I. Subbotin, M. N. Ivanovskii, and M. N. Arnoldov, *Fiziko-Khimicheskie Osnovy Primeneniya Zhidkometallicheskikh Teplonositelei* (Atomizdat, Moskva, 1970), p. 79.

Auxiliary Information

Method:
A thin-walled capsule of Armco Fe contained the liquid metal. The capsule was fitted closely into a quartz jacket and was fired in H at 1313 K and then stored in a He atmosphere. The K–Na melt was injected into the capsule. H was admitted from a gasometry apparatus. The sealed capsule was put into the jacket and attached to the gasometry system. The amount of H gas was measured before and after the equilibration through the capsule walls. After the equilibration was finished at constant temperature, H was either admitted to the system, or the system was evacuated. The correctness of the method and functioning of the apparatus was tested by chemical analysis of samples.

Source and Purity of Materials:
H: "high purity," further purified by passage through a heated Pd alloy diaphragm; contained $3.2\cdot10^{-2}$ %(N+CO), $4.3\cdot10^{-2}$ % H_2O, $5.0\cdot10^{-3}$ % CO_2, $<5\cdot10^{-4}$ % O, $1.3\cdot10^{-2}$ % hydrocarbons, undetected Ar; finally purified by diffusion through the Armco Fe cell walls.
K–Na: from MSA Res. Corp. and contained ~77.6% K, $<4.6\cdot10^{-3}$ % C, $<1.0\cdot10^{-3}$ % O, $1\cdot10^{-5}$ % Li, $<2.0\cdot10^{-3}$ % Cs, $3\cdot10^{-4}$ % Rb, $<1.0\cdot10^{-3}$ % Mg, Ca, Fe, B, Co, Al, Pb, Cr, Ti, Ni, Mo, V, Zr, $<1.5\cdot10^{-3}$ % Si, $<3\cdot10^{-4}$ % Ba, $<2\cdot10^{-4}$ % Cu, $1\cdot10^{-4}$ % Mn, Sn, Be, Ag, and Sr kept in a stainless steel apparatus under He pressure and filtered before use by means of 5 μm filters.
Li: 99.88% pure from Maywood Chemical Works and contained 0.015% Na, 0.06% K, $1\cdot10^{-4}$ % Ca, $5\cdot10^{-4}$ % Al, Fe, $1\cdot10^{-3}$ Si, 0.04% Cl, 0.012% N; transferred into the K–Na alloy in an inert atmosphere.
He: "very dry," contained $\sim1\cdot10^{-4}$ % H_2O for at least 15 min in the glove box.

Estimated Error:
Solubility: precision ±5%.
Temperature: accuracy ±2.5 K; as reported in Savage and Compere.[1]

References:
[1]H. W. Savage and E. L. Compere, U.S. Atom. Energy Comm. Rep. ORNL-3591 (1964); Rep. ORNL-3789 (1965); Rep. ORNL-3898 (1965).
[2]E. L. Compere and J. E. Savolainen, Trans. Am. Nucl. Soc. **8**, 18 (1965).

Components:
(1) Hydrogen; H; [1333-74-0]
(2) Potassium-sodium eutectic, $K_{68}Na_{32}$; [11147-16-3]

Original Measurements:
V. B. Savinov, E. E. Konovalov, and Sh. I. Peizulaev, *Teplofizicheskie Svoistva Zhidkostei v Vysshikh Temperaturakh*, edited by A. K. Abas-Zade and E. E. Shpil'rain (Nauka, Moskva, 1970), pp. 118–120.

Variables:
Temperature: 581–691 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of H in the liquid eutectic K–Na (32 mol % Na) alloy was determined

t/°C	Solubility/mass % H	Solubility/mol % H[a]
308	$1.5\cdot10^{-3}$ 0.051	
337	$3.4\cdot10^{-3}$ 0.115	
378	$6.8\cdot10^{-3}$ 0.23	
385	$9.9\cdot10^{-3}$ 0.33	
397	$1.52\cdot10^{-2}$	0.51
418	$1.72\cdot10^{-2}$	0.58

[a]Calculated by the compilers.

The authors proposed the following solubility equation:

$$\log(\text{soly/mol \% H}) = 5.06 - 3670\ (T/\text{K})^{-1}.$$

The compilers tested this equation.

Auxiliary Information

Method:
The solubility was determined by means of measurements of dynamic viscosity changes during the crystallization of the melt containing various amounts of H, while decreasing temperature. The crutile-pendelous method was used. The K–Na melt was contained in a quartz ampoule closed under vacuum. H gas was introduced into the liquid alloy using a manometric system of its proportioning. The temperature during the measurement was decreased with the rate of 0.5 K/min. A damping of free oscillations of the ampoules was measured every 2 min. Decrements of damping were plotted against the temperature. An abrupt increase of the decrement corresponded to the temperature of the onset of crystallization from a supersaturated solution.

Source and Purity of Materials:
H: nothing specified.
K–Na: contained 68.1 mol % K and 31.9 mol % Na.

Estimated Error:
Solubility: nothing specified; precision not better than ±5% (by the compilers).
Temperature: precision ±1 K (multiplying the rate of cooling and the time readings).

Components:
(1) Hydrogen; H; [1333-74-0]
(2) Potassium-sodium eutectic, $K_{68}Na_{32}$; [11147-16-3]

Original Measurements:
M. N. Arnoldov, M. N. Ivanovskii, S. S. Pletenets, and A. D. Pleshivtsev, Atom. Energiya **32**, 234–235 (1972).

Variables:
Temperature: 436–562 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of H in the liquid eutectic K–Na (32 mol % Na) alloy was determined. The results were presented in a figure; they were digitized from the figure and recalculated to mol % by the compilers.

t/°C	Solubility/mass % H	Solubility/mol % H
163	$6.8\cdot10^{-4}$	0.023
167	$1.56\cdot10^{-4}$, $6.5\cdot10^{-4}$	0.0053, 0.022
170	$6.6\cdot10^{-4}$	0.022
175	$1.56\cdot10^{-4}$	0.0053
179	$3.1\cdot10^{-4}$, $6.7\cdot10^{-4}$	0.0105, 0.023
181	$3.2\cdot10^{-4}$	0.0108
189	$5.2\cdot10^{-4}$	0.0176
208	$6.7\cdot10^{-4}$	0.023
216	$6.5\cdot10^{-4}$	0.022
219	$6.5\cdot10^{-4}$	0.022
245	$1.12\cdot10^{-3}$	0.038
277	$6.3\cdot10^{-3}$; $9.1\cdot10^{-3}$	0.021, 0.031
289	$6.3\cdot10^{-3}$, $9.1\cdot10^{-3}$	0.021, 0.031

The authors proposed the solubility equation:

$$\log(\text{soly/mol \% H}) = 3.76 - 2530\ (T/\text{K})^{-1},$$

which was tested by the compilers.

Auxiliary Information

Method:
The experiments were performed in a liquid K–Na eutectic alloy circulating in a loop equipped with a purifying device, an injector of H, a sampler, and an electrochemical detector of H. After an injection of H the alloy circulated at constant temperature to get equilibrium. The concentration of H was determined by means of the detector. The solubility corresponded to the break point of the relation of the detector reading versus H concentration. Subsequent portions of H were injected and the measurement repeated.

Source and Purity of Materials:
H: nothing specified; probably contained <0.1 vol % N and <0.2 vol % O as reported in Arnoldov *et al.*[1]
K–Na: contained 68 mol % K and 32 mol % Na; purified by a cold trap.

Estimated Error:
Solubility: precision ±10%–18% at confidence level of 95%; reading-out procedure ±2%.
Temperature: nothing specified: reading-out procedure ±1 K.

References:
[1]M. N. Arnoldov, M. N. Ivanovskii, V. A. Morozov, S. S. Pletenets, and V. I. Subbotin, Atom. Energiya **28**, 18–22 (1970).

Components:
(1) Hydrogen; H; [1333-74-0]
(2) Potassium-sodium alloys; K-Na

Original Measurements:
M. N. Ivanovskii, M. N. Arnoldov, V. A. Morozov, T. I. Moiseeva, and S. S. Pletenets, Izv. Akad. Nauk SSSR, Met. **1**, 201–205 (1980).

Variables:
Temperature: 573–713 K;
Na content: 0–100 mol %

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of H in various liquid K–Na alloys and the equilibrium plateau pressure of H were determined. The values were read from a figure and recalculated to mol % and Pa by the compilers.

t/°C	Solubility/mass % H	Solubility/mol % H	p/Torr	p/Pa
330	0.0141	0.55	94	12 540
370	0.0251	0.97	392	52 300
410	0.0403	1.56	1163	155 000

The solubilities and the pressures were measured for various K–Na compositions changing temperature. The results were given in form of equations:

$$\log(\text{soly/mol \% H}) = A - B\ (T/\text{K})^{-1}.$$

and

$$\log(p/\text{Torr}) = A' - B'\ (T/\text{K})^{-1}.$$

Mass % K	Mol % Na	t/°C	A	B	A′	B′
0	100	300–400	2.54	2980	11.46	5960
43	69	330–410	3.75	2630	11.74	5960
61	52	330–410	3.94	2640	11.90	5980
69	43	330–410	4.01	2650	11.82	5940
78	32	340–380	4.07	2730	11.67	5960
100	0	340–440	4.45	2980	11.38	5960

Auxiliary Information

Method:
The alloys were prepared by mixing the corresponding volumes of the metals. The composition of these alloys was confirmed by chemical analysis. The equilibrium pressure of H gas, being in direct contact with its solution in the metallic phase, was measured in selected temperature ranges.[1] The components were equilibrated for 6–8 h. The pressure was measured using a manometer. A special valve, placed between the manometer and the container, was used to prevent the evaporation of the alloy. The temperature was measured by means of a Chromel/Alumel thermocouple.

Source and Purity of Materials:
H: prepared by decomposition of Zr–H at 973–1073 K.
K: filtered through a stainless steel filter with a pore diameter of 50 μm at 373–423 K.
Na: nothing specified

Estimated Error:
Solubility: nothing specified.
Temperature: nothing specified.

References:
[1] M. N. Arnoldov, M. N. Ivanovskii, and V. A. Morozov, Izv. Akad. Nauk SSSR, Met. **1**, 74–76 (1973).

5.2. Potassium–Deuterium

Components:
(1) Deuterium; D; [7782-39-0]
(2) Potassium; K; [7440-09-7]

Evaluated by:
Hans Ulrich Borgstedt, Forschungszentrum Karlsruhe, Germany and Cezary Guminski, University of Warsaw, Poland, May 1997.

Critical Evaluation

The D–K system is likely very similar to the H–K system, and the former was much less intensively investigated. The equilibrium vapor pressure of D over the K–D melt was measured by Sollers and Crensha[1] as well as by Borocco and Hackspill.[2,3] The data differ slightly in the slope of the temperature dependence of the gas pressure of D. No doubt that the D pressure is higher by about a factor of 2 than the H pressure over the K–H melt at the same temperature. This means that the solubility of D in liquid K should be higher than of H. Stepanov[4] measured the isotope effect and found a smaller difference between D and H in liquid K.

The K–D phase diagram is generally similar to the K–H diagram. Magomedov[5] predicted almost equal melting temperatures for KH, KD, and KT, his calculation resulted in the values 901.00, 900.86, and 900.82 K, respectively.

Experimental information was found to not concern the K–T system, which by analogy to the Li–T and Na–T systems should show a still higher solubility of T in K than D in K. Reimann *et al.*[6,7] elaborated on a method for the removal of T from K–Na melt by means of precipitation of KT in a cold trap, where the corresponding experiments were performed with H instead of T.

References:
[1] F. E. Sollers and J. L. Crenshaw, J. Am. Chem. Soc. **59**, 2015 (1937).
[2] A. Borocco, Compt. Rend. **205**, 983 (1937).
[3] L. Hackspill and A. Borocco, Bull. Soc. Chim. Fr. [Ser. 5] **6**, 91 (1939).
[4] Yu. P. Stepanov, Sov. Phys. Solid State **19**, 1561 (1977).
[5] M. N. Magomedov, Zh. Fiz. Khim. **68**, 589 (1994).
[6] J. Reimann, R. Kirchner, and D. Rackel, Fusion Engin. Design **18**, 67 (1991).
[7] J. Reimann, R. Kirchner, M. Pfeff, and D. Rackel, *Fusion Technology*, edited by K. Herschbach, W. Maurer, and J. E. Vetter (Elsevier, Amsterdam, 1995), p. 1099.

5.3. Potassium–Boron

Components:
(1) Boron; B; [7440-42-8]
(2) Potassium; K; [7440-09-7]

Evaluated by:
Hans Ulrich Borgstedt, Forschungszentrum Karlsruhe, Germany and Cezary Guminski, University of Warsaw, Poland, May 1997.

Critical Evaluation

Moissan[1] attempted to prepare B from B_2O_3 by its reduction with K. He did not observe any measurable B amount being dissolved in boiling K (1032 K), but B, obtained this way, contained some amount of K. Hagenmuller *et al.*[2] investigated the reaction between B and K in a close capsule at high temperature. They did not observe any reaction below 1373 K, and at 1423 K the reactants needed 12 h and at 1473 K 6 h of heating at 1.8 MPa for a reaction. The product had the formula KB_6 and was found to be stable up to 1023 K in vacuum ($1.33 \cdot 10^{-4}$ Pa) and to 1373 K at normal pressure. The final product of the KB_6 decomposition was B and K vapor. Adams[3] prepared KB_6 from plasma B and K at 923 K for 24 h. However, Sorokin *et al.*[4] did not observe any formation of K–B compounds during the heating of the two elements up to 1073 K. Concluding the observations of Hagenmuller *et al.*[2] and Adams,[3] no reaction between B and K occurs at temperatures <773 K and practically pure B should be in equilibrium with liquid K saturated with B.

No attempts of measuring the solubility of B or its compound in liquid K were described; it seems, however, that the solubility should not be higher than the estimated solubility of B in liquid Na ($< 10^{-2}$ mol % B at 773 K). Adams[3] assumed that solutions of B in the alkali metals contain polymeric species. The published material is not sufficient to construct even a schematic K–B phase diagram. Using K–Na alloys instead of K, Hagenmuller *et al.*[2] obtained $K_{0.14}Na_{0.86}B_6$ at 1373 and Adams[3] obtained KB_{20} at 923 K for 24 h.

References:

[1]H. Moissan, Compt. Rend. **114**, 319 (1892).

[2]P. Hagenmuller, R. Naslain, M. Pouchard, and C. Cros, *The Alkali Metals* (The Chemical Society, London, 1967), p. 207.

[3]P. F. Adams, Ph. D. thesis, University of Nottingham, U.K., 1977; abstracted in C. C. Addison, *The Chemistry of the Liquid Alkali Metals* (Wiley, Chichester, 1984), p. 225.

[4]V. P. Sorokin, P. I. Gavrilov, and E. V. Levakov, Zh. Neorg. Khim. **22**, 595 (1977); Russ. J. Inorg. Chem. **22**, 329 (1977).

5.4. Potassium–Carbon

Components:
(1) Carbon; C; [7440-44-0]
(2) Potassium; K; [7440-09-7]

Evaluated by:
Hans Ulrich Borgstedt, Forschungszentrum Karlsruhe, Germany and Cezary Guminski, University of Warsaw, Poland, June 1997.

Critical Evaluation

Chemical reactions of C and K may form K_2C_2, however, this compound is not stable in liquid K. Graphite or soot, but not diamond, react with striking readiness with molten K or its vapor. Fredenhagen *et al.*[1,2] observed that depending on temperature and pressure, different products may be obtained. The formation of KC_8 is observed in the first stage. Further heating KC_8 leads to the formation of KC_{16}, KC_{24}, KC_{36}, KC_{48}, and finally KC_{60}.[3,4] Aronson *et al.*[5] observed that KC_{10} is formed from KC_8 and KC_{24} above 593 K; this observation puts in question the existence of KC_{16}.

Fast disintegration of graphite may be wrongly estimated as good solubility of C in liquid K. In fact the solubility is low. Schwarz[6] performed analyses of liquid K from a loop sampled after cold trapping, and he found that the solubility of C in liquid K at 373 K is below $3 \cdot 10^{-4}$ mol %. The K used was relatively impure; this cannot exclude mutual interactions of C with other elements present in the liquid K medium. Aronson *et al.*[5] did not observe any difference of the emf between pure K and K–KC_8 electrodes; this observation indicates that the solubility of KC_8 in liquid K is marginal.

Kelman[7] investigated the compatibility of graphite in liquid K–Na (50 mass %) alloy at room temperature. 5 g of graphite was placed in 10 g of the K–Na alloy for ~10 h. The graphite sample was broken up, swelled ~3 times, and C particles were dispersed resulting in a sludge. No appreciable (but unspecified numerically) solubility of C in the liquid alloy was found by a chemical analysis.

A new class of solubility equilibria is expected for solutions of C_{60} in liquid K. Poirier *et al.*[8] sketched the K–C_{60} phase diagram suggesting K_6C_{60} (at lower temperatures) and K_4C_{60} (at higher temperatures) as the equilibrium sold phases in contact with the saturated solution of C_{60} in liquid K; measurements of the solubility in this system have not been performed so far. K_2CO_3 is formed by Subbotin *et al.*[9] simultaneously where the presence of C and O are in molten K. The solubility of K_2CO_3 in liquid K has not yet been measured so far. Most probably in the case of the presence of C and N in K the compound KCN may be formed.

A schematic K–C phase diagram is shown in Fig. 35. The saturated solution seems to be in equilibrium with KC_8 up to 623 K and probably with KC_{10} above this temperature.[7]

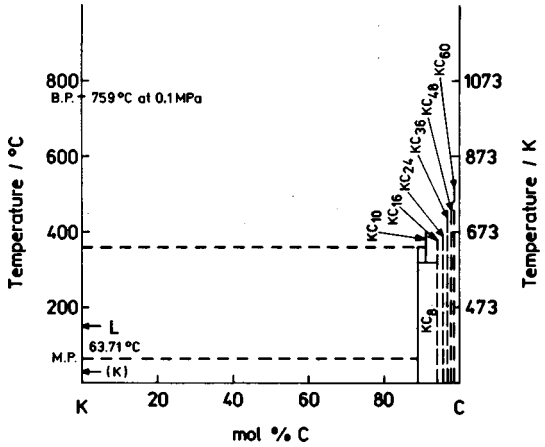

FIG. 35. The C–K phase diagram (schematic).

A doubtful value of the solubility of C in liquid K at 373 K is $< 3 \cdot 10^{-4}$ mol % C according to Schwarz.[6]

References:

[1]K. Fredenhagen and G. Cadenbach, Z. Anorg. Chem. **158**, 249 (1926).
[2]K. Fredenhagen and H. Such, Z. Anorg. Chem. **178**, 353 (1929).
[3]A. Hérold, Bull. Soc. Chim. Fr. 999 (1955).
[4]W. Rüdorff and E. Schulze, Z. Anorg. Chem. **277**, 156 (1954).
[5]S. Aronson, F. J. Salzano, and D. Bellafiore, J. Chem. Phys. **49**, 434 (1968).
[6]N. F. Schwarz, *Liquid Metal Engineering & Technology* (BNES, London 1985), Vol. 3, p. 177.
[7]L. R. Kelman, U.S. Atom. Energy Comm. Rep. CT-3726 (1946).
[8]D. M. Poirier, D. W. Owens, and J. H. Weaver, Phys. Rev. B **51**, 1830 (1995).
[9]V. I. Subbotin, M. N. Ivanovskii, and M. N. Arnoldov, *Fiziko-Khimicheskie Osnovy Primenenia Zhidkometallicheskikh Teplonositelei* (Atomizdat, Moskva, 1970), Vol. 76, p. 108.

Components:
(1) Carbon; C; [7440-44-0]
(2) Potassium; K; [7440-09-7]

Original Measurements:
N. F. Schwarz, *Liquid Metals Engineering & Technology* (BNES, London, 1985), Vol. 3, pp 177–183.

Variables:
One temperature: 373 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of C in liquid K at 100 °C (373 K) was found to be below $1 \cdot 10^{-4}$ mass % or $3 \cdot 10^{-4}$ mol % C (as calculated by the compilers). The K used was relatively impure, therefore, an interference of other elements on the solubility limit is possible.

Auxiliary Information

Method:
The solubility experiments were performed by means of chemical analysis of K sampled behind the cold trap of a high temperature stainless steel loop filled with circulating K. The apparatus contained a sampling device and a plugging meter. The cold trap temperature was fixed at 373 K. The plugging meter readings indicated the time needed to plug the orifice of the device. An unspecified analysis was performed after such purification. The C concentration in the loop was in equilibrium with the cold trap. Therefore, the concentration determined should represent the saturation limit of C in liquid K at the cold trap temperature.

Source and Purity of Materials:
C: from Incoloy.
K: nuclear grade of purity and contained 0.02% O, $1.6 \cdot 10^{-4}$ % Mn; $8 \cdot 10^{-4}$ % Fe, Cr, and $6 \cdot 10^{-5}$ % Ni.
Cover gas: purity continuously monitored.

Estimated Error:
Solubility: nothing specified
Temperature: nothing specified.

5.5. Potassium–Silicon

Components:
(1) Silicon; Si; [7440-21-3]
(2) Potassium; K; [7440-09-7]

Evaluated by:
Hans Ulrich Borgstedt, Forschungszentrum Karlsruhe, Germany and Cezary Guminski, University of Warsaw, Poland, May 1999.

Critical Evaluation

Hohmann[1] found that Si and K react easily at 923 K with the formation of KSi. Westbrook[2] reported the melting temperature of KSi at 773 K, but he did not specify the experimental conditions. Another compound, KSi_6, is formed by thermal decomposition of KSi in high vacuum. This compound decomposes to Si at ~850 K according to Schäfer and Klemm.[3] Hagenmuller *et al.*[4] decomposed KSi at 600–773 K and obtained a compound of the composition K_6Si_{46}; the stoichiometry of this compound was further corrected to K_7Si_{46} (Cros *et al.*[5]) and finally to K_7Si_{46}.[6] Von Schnering *et al.*[6] also reported the formation of $K_{12}Si_{17}$, K_6Si_{25}, and K_xSi_{136}($5 \leqslant x \leqslant 12$). The solid solubility of K in Si is not higher than 0.02 mol % K.[7] Based on this information one may sketch a fragmentary K–Si phase diagram as shown in Fig. 36.

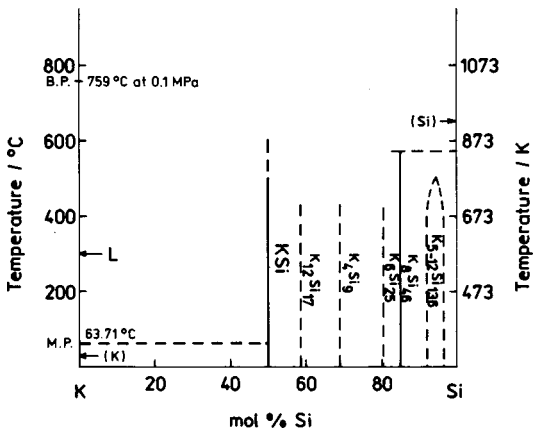

FIG. 36. K–Si phase diagram (schematic).

The solubility of Si in liquid K has not been systematically investigated. Aleksandrov and Dalakova[8] observed that after 1 h of contact of Si and liquid K at 873–923 K any dissolution of Si could not be noticed according to spectral analysis of K; the detection level of the method was not specified. Kelman[9] performed similar experiments using K–Na (50 mass % Na) alloy as the solvent at 1073 K for 6 days. The author observed that 17 g Si were dissolved in 100 cm^3 of the K–Na melt, but simultaneously Si was alloyed with the steel bomb used as the container; in this situation the numbers cannot be ascribed to only dissolution of Si, but mainly with the alloying. Analyses of this alloy at room temperature showed a Si content of $< 5 \cdot 10^{-3}$ mol % Si.

Solubility values may not be recommended.

References:

[1]E. Hohmann, Z. Anorg. Chem. **257**, 113 (1948).
[2]D. Westbrook, Metalloved. Termich. Obrabot. Met. **4**, 74 (1971).
[3]R. Schäfer and W. Klemm, Z. Anorg. Chem. **312**, 214 (1961).
[4]P. Hagenmuller, R. Naslain, M. Pouchard, and C. Cros, *The Alkali Metals* (The Chemical Society, London, 1967), p. 207.
[5]C. Cros, M. Pouchard, and P. Hagenmuller, Bull. Soc. Chim. Fr. 379 (1971).
[6]H. G von Schnering, M. Somer, M. Kaupp, W. Carrillo-Cabrera, M. Baitinger, A. Schmeding, and Y. Grin, Angew. Chem. **37**, 2359 (1998).
[7]L. Svob, Solid-State Electron. **10**, 991 (1967).
[8]B. N. Aleksandrov and N. V. Dalakova, Izv. Akad. Nauk SSSR, Met. **1**, 133 (1982).
[9]L. R. Kelman, U.S. Atom. Energy Comm. Rep. CT-3726 (1946).

5.6. Potassium–Germanium

Components:
(1) Germanium; Ge; [7440-56-4]
(2) Potassium; K; [7440-09-7]

Evaluated by:
Hans Ulrich Borgstedt, Forschungszentrum Karlsruhe, Germany and Cezary Guminski, University of Warsaw, Poland, June 1999.

Critical Evaluation

Aleksandrov and Dalakova[1] observed a low solubility of Ge in liquid K, when both metals were in contact for 1 h at 873–923 K. Numerical results of the spectral analysis of the Ge content in K were not reported therein. Drits *et al.*[2] investigated the Ge–K phase diagram. The K-rich range was not studied; therefore, solubilities could not be estimated. The authors observed the formation of KGe_4, KGe, and K_3Ge melting at 1403, 1363, and 1163 K, respectively. Earlier measurements indicated significantly lower thermal stabilities of these compounds. Hohmann[3] reported that the thermal decomposition of KGe occurred at 673–693 K, and Schäfer and Klemm[4] reported the decomposition of KGe_4 at ~773 K. Hagenmuller *et al.*[5] obtained K_8Ge_{46} by thermal decomposition of KGe at 613–653 K. Von Schnering *et al.*[6] performed thermal decomposition of KGe in dynamic vacuum and obtained evidence for the existence of following compounds: $K_{12}Ge_{17}$, $K_{12}Ge_{22}$, $K_{16}Ge_{31}$, K_4Ge_9, K_6Ge_{25}, K_8Ge_{46}, and K_xGe_{136}, ($5 \leqslant x \leqslant 12$) which are gradually formed between 700 and 900 K; the existence of the phase KGe_4 of Drits *et al.*[2] was called in question. The phase diagram proposed in Drits *et al.*[2] was also not accepted in the review of Sangster and Pelton.[7] The observations of Drits *et al.*[2] might be caused by corrosion of the Nb capsule by K–Ge alloys with the formation of an Nb–Ge compound.

The tentative K–Ge phase diagram, which takes into account parts of information from Drits *et al.*,[2] Hagenmuller *et al.*,[5] and Von Schnering *et al.*[6] is shown in Fig. 37. Since the melting point of K_3Ge is slightly higher than of Na_3Ge, one may predict the solubility of Ge in liquid K to be slightly lower than of Ge in liquid Na; see the Na–Ge system.

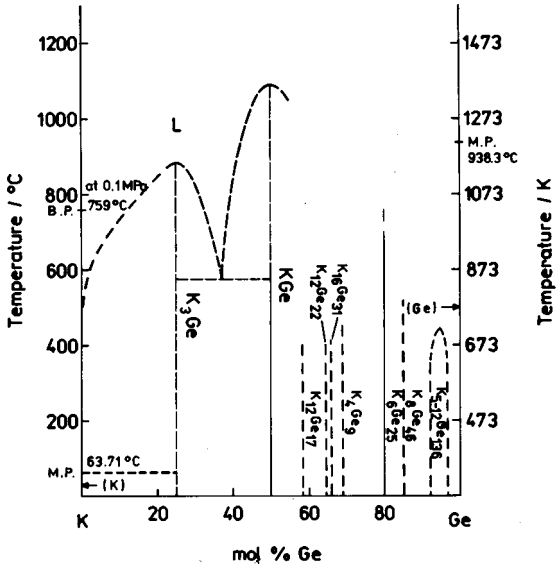

FIG. 37. Ge–K phase diagram (tentative).

A tentative value of the solubility of Ge in liquid K is 22 mol % Ge at 1138 K, according to Drits *et al.*[2]

References:

[1]B. N. Aleksandrov and N. V. Dalakova, Izv. Akad. Nauk SSSR, Met. **1**, 133 (1982).

[2]M. E. Drits, V. F. Potemkin, and L. L. Zusman, Izv. Akad. Nauk SSSR, Neorg. Mater. **18**, 1148 (1982).

[3]E. Hohmann, Z. Anorg. Chem. **257**, 113 (1948).

[4]R. Schäfer and W. Klemm, Z. Anorg. Chem. **312**, 214 (1961).

[5]P. Hagenmuller, R. Naslain, M. Pouchard, and C. Cros, *The Alkali Metals* (The Chemical Society, London, 1967), p. 207.

[6]H. G. von Schnering, M. Baitinger, U. Bolle, W. Carrillo-Cabrera, J. Curda, Y. Grin, F. Heinemann, J. Llanos, K. Peters, A. Schmeding, and M. Somer, Z. Anorg. Chem. **623**, 1037 (1997).

[7]J. Sangster and A. D. Pelton, J. Phase Equil. **18**, 287 (1997).

Components:
(1) Germanium; Ge; [7440-56-4]
(2) Potassium; K; [7440-09-7]

Original Measurements:
M. E. Drits, V. F. Potemkin, and L. L. Zusman, Izv. Akad. Nauk SSSR, Neorg. Mater. **18**, 1148–1150 (1982).

Variables:
Temperature: 942–1403 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The liquidus of the K–Ge system was determined. The experimental points were read from a figure and recalculated to mol % Ge by the compilers.

T/K	Solubility/mol % Ge
1138	22
1116	28
942	34
1350	47.5
1298	55
1129	64
1312	71
1380	75
1403	81
1385	84
1348	87.5
1292	91.5
1252	94
1225	98

The melting points of Ge and K were placed at 1247 and 337 K.

Auxiliary Information

Method:
The K–Ge alloys were synthesized by a method reported in Drits *et al.*[1] Samples of K were placed in steel or Nb crucibles which were hermetically closed in an Ar atmosphere. The crucibles contained liners made of Al_2O_3 or ZrO_2 ceramics. The tightness of the crucible was confirmed by weighing the crucibles before and after heating to ~1500 K. The thermal analysis was performed in a modified commercial apparatus. The composition of the Ge-rich alloys was quantitatively verified by spectral or microstructure analysis.

Source and Purity of Materials:
Ge: semiconductor purity.
K: 99.6+% pure.
Ar: spectrally pure.

Estimated Error:
Solubility: nothing specified; reading-out precision ±0.5 mol %.
Temperature: precision ±2 K; reading-out precision ±3 K.

References:
[1]M. E. Drits, A. S. Fridman, L. L. Zusman, and A. E. Luzik, Zavod. Labor. **3**, 299–301 (1976).

5.7 Potassium–Nitrogen

Components:
(1) Nitrogen; N; [7727-37-9]
(2) Potassium; K; [7440-09-7]

Evaluated by:
Hans Ulrich Borgstedt, Forschungszentrum Karlsruhe, Germany and Cezary Guminski, University of Warsaw, Poland, June 1997.

Critical Evaluation

N does not react with K even at high temperatures and pressures.[1] Therefore, N could be applied as cover gas in the case of manipulations with liquid K. K_3N, and KN_3 are known to be formed during electrical discharges in gaseous K–N mixtures;[2,3] KN_3 is preferentially formed at about room, while K_3N is the reaction product at elevated temperature. Both of them, K_3N (nitride) and KN_3 (azide) are not stable. KN_3 exists in two polymorphic forms. Its melting temperature was found at 616 K in Suhrmann and Clusius[4] and 623 K in Belomestnykh.[5] KN_3 decomposes at 633 K.[5]

The solubility of N in liquid K has not been determined so far. The solution process seems to be of physical nature if pure substances are used. In the presence of C in the system a formation of KCN is quite possible.[1] By analogy to the solubility of N in liquid Na, the solubility of N in liquid K is expected to be negligible, and about the same order of magnitude.

Subbotin *et al.*[1,6,7] measured the solubility of N in liquid eutectic K–Na alloy at 573 K and 0.101 MPa. The authors reported three different solubility values measured in the same conditions: $\sim 10^{-4}$ mol % N,[1] $4 \cdot 10^{-3}$ mol % N,[7] and $2 \cdot 10^{-6}$ mol % N;[6] the authors did not give any comment concerning the differences. The latter value seems to be the most reliable, since it was compared in a figure with other solubility data quoted from the literature. However, this value would suggest that the introduction of K into Na solvent would cause an increase of the solubility of N for about 4 orders of magnitude. Thus, this abnormal change of the solubility of N seems to be due to impurities present in the K–Na which might react with N. Therefore the result of Subbotin *et al.*[6] should be treated with caution.

The K–N phase diagram should be similar to that shown for the Na–N system.

References:

[1]V. I. Subbotin, M. N. Ivanovskii, and M. N. Arnoldov, *Fiziko-Khimichaskie Osnovy Primenenia Zhidkometallicheskikh Teplonositelei* (Atomizdat, Moskva, 1970), p. 76.

[2]H. Wartenberg, Ber. Chem. Gesellsch. **63**, 1667 (1930).

[3]G. J. Moody and J. D. R. Thomas, J. Chem. Educ. **43**, 205 (1966).

[4]R. Suhrmann and K. Clusius, Z. Anorg. Chem. **152**, 52 (1926).

[5]V. N. Belomestnykh, Neorg. Mater. **29**, 221 (1993).

[6]M. N. Arnoldov, M. N. Ivanovskii, V. A. Morozov, S. S. Pletenets, and V. I. Subbotin, *Teplofizicheskie Svoistva Zhidkostei v Vysshikh Temperaturakh*, edited by A. K. Abas-Zade and E. E. Shpil'rain (Nauka, Moskva, 1970), p. 110.

[7]M. N. Arnoldov, M. N. Ivanovskii, V. A. Morozov, S. S. Pletenets, and V. I. Subbotin, Atom. Energiya **28**, 18 (1970).

Components:
(1) Nitrogen; N; [7727-37-9]
(2) Potassium-Sodium eutectic; $K_{68}Na_{32}$; [11147-16-3]

Original Measurements:
M. N. Arnoldov, M. N. Ivanovskii, V. A. Morozov, S. S. Pletenets, and V. I. Subbotin, Atom. Ener. **28**, 18–22 (1970).

Variables:
One temperature: 573 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of N in liquid K–Na eutectic alloy (68 mol % K) at 300 °C was read out from a figure to be $4 \cdot 10^{-5}$ mol fract./atm or $4 \cdot 10^{-8}$ mol % N/Pa (as calculated by the compilers). The result graphically reported in Arnoldov *et al.*[1] was $1.7 \cdot 10^{-5}$ g N/1000 g K–Na or $2.0 \cdot 10^{-6}$ mol % N or $2.0 \cdot 10^{-11}$ mol % N/Pa (as calculated by the compilers). The numerical result reported in Subbotin *et al.*[2] was 10^{-4} mass % N (mol % N) or 10^{-9} mol % N/Pa (as calculated by the compilers). The discrepancies were not commented by the authors.

Auxiliary Information

Method:
Measured amounts of N were injected into the K–Na melt at normal pressure. The equilibrium pressure of N gas being in direct contact with its saturated solution was measured at constant temperature by means of a manometer. The materials used for the construction of the apparatus were not specified. The amounts of dissolved N were calculated from the difference between the amount of N being injected and being in final equilibrium assuming the ideal behavior of N gas. The pressure readings were continued until its values, stable in time, were recorded.

Source and Purity of Materials:
N: contained <0.5 % O, dew point <293 K; impurities frozen out in a liquid N trap.
K–Na alloy: contained 78.2% K, 21.8% Na, $3 \cdot 10^{-4}$ % Li, In; 0.01% Mg, Zn, Cu; $1 \cdot 10^{-4}$ % Ag, Cd; 0.066% Fe, 0.033% Ca, Cr, Ti; $2 \cdot 10^{-3}$ % Sn; $3 \cdot 10^{-3}$ % Ba, $1 \cdot 10^{-3}$ % Mo, V, Bi, Pb, Co; $3.3 \cdot 10^{-3}$ % Al, Mn; $9 \cdot 10^{-3}$ % Be; further purified by decantation of solid impurities at room temperature.

Estimated Error:
Solubility: precision unspecified; maximum relative error 50%–100%; standard deviation 15%–35%.
Temperature: nothing specified.

References:

[1]M. N. Arnoldov, M. N. Ivanovskii, V. A. Morozov, S. S. Pletenets, and V. I. Subbotin, *Teplofizicheski Svoistva e Zhidkostei*, edited by A. K. Abas-Zade and E. E. Shpil'rain (Nauka, Moskva, 1970), pp. 110–116.

[2]V. I. Subbotin, M. N. Ivanovskii, and M. N. Arnoldov, *Fiziko-Khimicheskie Osnovy Primeneniya Zhidkometallicheskikh Teplonositelei* (Atomizdat, Moskva, 1970), p. 79.

Components:
(1) Nitrogen; N; [7727-37-9]
(2) Potassium-sodium eutectic; $K_{68}Na_{32}$; [11147-16-3]

Original Measurements:
V. I. Subbotin, M. N. Ivanovskii, and M. N. Arnoldov, *Fiziko-Khimicheskie Onovy Primenenia Zhidkometallicheskikh Teplonositelei* (Atomizdat, Moskva, 1970), pp. 78, 79.

Variables:
One temperature: 573 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of N in liquid eutectic K–Na (32 mol % Na) alloy at 300 °C (573 K) was determined to be 10^{-4} mass % N or 10^{-4} mol % N (as calculated by the compilers). The gas pressure was not specified.

The same group of investigators reported graphically in Arnoldov *et al.*[1] the solubility at the same temperature equal to $4 \cdot 10^{-5}$ mol fraction N or $4 \cdot 10^{-3}$ mol % N (as read out from a figure and calculated by the compilers) and in Arnoldov *et al.*[2] $1.6 \cdot 10^{-5}$ mass % N or $2.0 \cdot 10^{-5}$ mol % N (as read out from a figure and recalculated to mol % by the compilers). Both values were reported for a pressure of 1 kg/cm^2 or 0.101 MPa. All data are different but comparing them with other data from the literature, as in Arnoldov *et al.*,[2] allows the compilers to accept the latter value as the right one.

Auxiliary Information

Method:
Materials used for the construction of the apparatus were not specified. The N gas pressure was measured with the use of a manometer. The amounts of N in a chamber before and after the equilibrium was reached, were calculated assuming ideal behavior of N gas. The N pressure was measured in isothermal conditions till its stable value was recorded.

Source and Purity of Materials:
N: contained <0.5 vol % O, dew point <273 K; further purified by freezing out in a liquid N trap.
K–Na alloy: contained 78.2% K, 21.8% Na, $3 \cdot 10^{-4}$ % Li, In, 0.01% Mg, Zn, Cu, $1 \cdot 10^{-4}$ % Ag, Cd, 0.066% Fe, 0.033% Ca, Cr, Ti, $2 \cdot 10^{-3}$ % Sn, $3 \cdot 10^{-3}$ % Ba, $1 \cdot 10^{-3}$ % Mo, V, Bi, Pb, Co, $3.3 \cdot 10^{-3}$ % Al, Mn, $9 \cdot 10^{-3}$ % Be; further purified by decantation of solid impurities floating on surface at room temperature.

Estimated Error:
Solubility: relative error 50%–100%.
Temperature: nothing specified.

References:
[1]M. N. Arnoldov, M. N. Ivanovskii, V. A. Morozov, S. S. Pletenets, and V. I. Subbotin, Atom. Energiya **28**, 18–22 (1970).
[2]M. N. Arnoldov, M. N. Ivanovskii, V. A. Morozov, S. S. Pletenets, and V. I. Subbotin, *Teplofizicheskie Svoistva Zhidkostei v Vysshikh Temperaturakh*, edited by A. K. Abas-Zade and E. E. Shpil'rain (Nauka, Moskva, 1970), pp. 110–116.

5.8. Potassium–Phosphorous

Components:
(1) Phosphorous; P; [7723-14-0]
(2) Potassium; K; [7440-09-7]

Evaluated by:
Hans Ulrich Borgstedt, Forschungszentrum Karlsruhe, Germany and Cezary Guminski, University of Warsaw, Poland, June 1997.

Critical Evaluation

Solubility determinations of P in liquid K have not been reported so far. Our knowledge about the K–P system is quite limited. P reacts directly with K, and K_3P is formed. Brauer and Zintl[1] observed two hardly miscible phases, cooling down the K–P melt in a corund crucible to room temperature from 923 K; this observation may indicate a low solubility of P (K_3P) in liquid K. Gnutzmann *et al.*[2] obtained K_3P from the elements in the gas phase. The melting temperature of K_3P has not been determined; however, this compound seems to be the most stable in the system. Hönle and von Schnering[3] also reported the formation of KP. Another, polyanionic compound K_2P_5 melts at 923 K decomposing, and KP_{10} is probably an interstitial compound the stability of which is unknown.[4] von Schnering *et al.*[5] also found K_3P_7 and K_3P_{11} ; the latter compound has a solid phase transition at 723 K. The construction of the K–P phase diagram on the basis of the few data seems to be premature.

References:
[1]G. Brauer and E. Zintl, Z. Phys. Chem. B **37**, 323 (1937).
[2]G. Gnutzmann, F. W. Dorn, and W. Klemm, Z. Anorg. Chem. **309**, 211 (1961).
[3]W. Hönle and H. G. von Schnering, Acta Crystall., A **34**, S152 (1978).
[4]W. Klemm, Proc. Chem. Soc. 329 (1958).
[5]H. G. von Schnering, M. Somer, G. Kliche, W. Hönle, T. Meyer, J. Wolf, L. Ohse, and P. B. Kempa, Z. Anorg. Chem. **601**, 13 (1991).

5.9. Potassium–Arsenic

Components:
(1) Arsenic; As; [7440-38-2]
(2) Potassium; K; [7440-09-7]

Evaluated by:
Hans Ulrich Borgstedt, Forschungszentrum Karlsruhe, Germany and Cezary Guminski, University of Warsaw, Poland, June 1997.

Critical Evaluation

Several compounds are formed in the reaction of As with K. Only the central range of K–As compositions was investigated in this system by thermal analysis.[1] The liquidus in the K-rich range may increase gradually from the melting point of K to the melting point of K_3As, but a tendency to immiscibility of K_3As and K may occur; therefore, this part of the liquidus cannot be simply predicted. Comparing this part of the K–As diagram to the K–Sb diagram, we observe a relatively small thermal stability of K_3As, whereas K_3Sb is the most stable compound in that system. KAs_2 seems to be the most stable one, whereas KSb_2 has the lowest stability. The formation of K_3As and KAs, found in Dorn *et al.*,[1] was confirmed in Hönle and von Schnering,[2] Klemm,[3] and Brauer and Zintl.[4] Dorn *et al.*[1] described a specific formation of KAs_2 which exists in two polymorphic forms, does not melt below 1033 K and sublimes without decomposition. This is a very seldom phenomenon for compounds of alkali metals with semimetals. According to the most recent study KAs_2 is probably K_3As_7 (Ref. 5) with a transition temperature of 659 K. Still another As-rich compound was identified by the authors of (Ref. 6); its formula was presented as K_3As_{11} with a transition temperature at 644 K.

The fragmentary K–As phase diagram after Sangster and Pelton[7] is shown in Fig. 38.

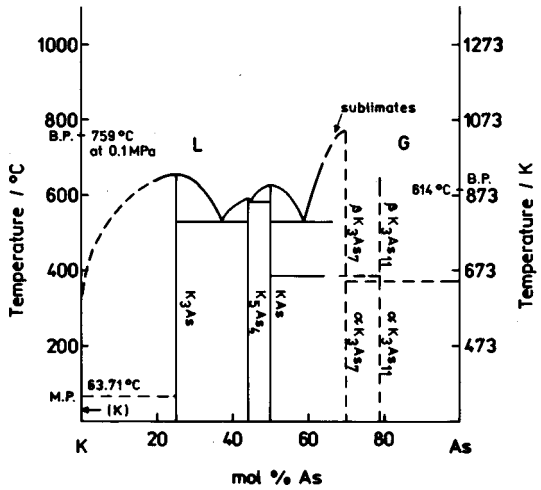

FIG. 38. As–K phase diagram (fragmentary).

Tentative values of the solubility of As in liquid K

T/K	Solubility/mol % As	Source
908	20	(1)
928	25 congruent	(1)

For the As-rich solubilities see the phase diagram.

References:
[1]F. W. Dorn, W. Klemm, and S. Lohmeyer, Z. Anorg. Chem. **309**, 204 (1961).
[2]W. Hönle and H. G. von Schnering, Acta Crystall., A **34**, S152 (1978).
[3]W. Klemm, Proc. Chem. Soc. 329 (1958).
[4]G. Brauer and E. Zintl, Z. Phys. Chem. **37**, 323 (1937).
[5]W. Hönle, H. G. von Schnering, and M. Somer, Z. Kristall. **174**, 82, 203 (1986).
[6]H. G. von Schnering, M. Somer, G. Kliche, W. Höhle, T. Meyer, J. Wolf, L. Ohse, and P. B. Kempa, Z. Anorg. Chem. **601**, 13 (1991).
[7]J. Sangster and A. D. Pelton, J. Phase Equil. **14**, 234 (1993).

Components:
(1) Arsenic; As; [7440-38-2]
(2) Potassium; K; [7440-09-7]

Original Measurements:
F. W. Dorn, W. Klemm, and S. Lohmeyer, Z. Anorg. Chem. **309**, 204–209 (1961).

Variables:
Temperature: 818–1009 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

A part of the K–As liquidus was determined

t/°C	Solubility/mol % As
635	20.0
655	25.0[a]
648	30.1
627	32.0
603	33.9
546	36.6
551	39.0
578.0	41.6
587.5	44.1
595.5	46.0
614.5	47.5
624	49.0
624.5	49.7
620	51.4
595	53.9
560	56.3
545	57.8
553	59.9
621	62.0 (?)
676	63.8
736	66.0

[a]Two determinations.

The authors reported the formation of K_3As, K_4As_5, and KAs. KAs_2 was found to have solid phase transition at 386 °C. It does not melt below 760 °C and sublimes without decomposition.

Auxiliary Information

Method:
The alloys were prepared in a quartz apparatus. The apparatus was filled with Ar, and K which was encapsulated in glass ampoules was introduced into it. K was melted. The amounts of molten K which were transferred into the apparatus were estimated from the weight difference before and after the transfer procedure. As was carefully introduced into the K samples. The apparatus was heated under an Ar atmosphere. Thermal analysis was performed by means of a Pt/Pt–Rh thermocouple. The composition of the alloys was determined by chemical analysis. The As-rich melts were investigated in a corundum vessel enclosed in a steel bomb. The prepared samples were composed from KAs, KAs_2, and As.

Source and Purity of Materials:
As: a fine As powder.
K: commercial product, purified by distillation in high vacuum.[1]
Ar: nothing specified.

Estimated Error:
Solubility: precision ±0.2%, as in Dorn *et al.*[1]
Temperature: precision ±(0.5–1.5) K; stability ±1 K at KAs_2.

References:
[1]F. W. Dorn and W. Klemm, Z. Anorg. Chem. **309**, 189–203 (1961).

5.10. Potassium–Oxygen

Components:

(1) Oxygen; O; [7782-44-7]
(2) Potassium; K; [7440-09-7]

Evaluated by:

Hans Ulrich Borgstedt, Forschungszentrum Karlsruhe, Germany and Cezary Guminski, University of Warsaw, Poland, January 2000.

Critical Evaluation

The reaction between very pure K and dry O is very slow. In the presence of moisture K reacts with O violently and the superoxide KO_2 is formed. In excess K, KO_2 decomposes gradually to K_2O_2 and finally to K_2O. A careful thermal decomposition of KO_2 leads to the formation of sesqueoxide K_2O_3.[1] K_2O is the equilibrium solid phase saturating the liquid K in the range of K-rich melts.

The solubility of O in liquid K has not been as frequently investigated as in liquid Na, and, for almost 30 years, the first results obtained by Williams *et al.*[2,3] have been treated as the only correct source. These authors found that the solubility increased from 0.20 to 1.63 mol % O in the temperature range 348–583 K. Hoffman[4] announced measurements of the O solubility between 337 and 800 K, but he did not publish any results after this information; his laboratory was able to obtain K with only $6\cdot10^{-3}$ mol % O by application of cold trapping. This indicated a much lower level of the solubility. Furthermore, Simons and Langedrost[5] reported on a decrease of the O content in K to $1.2\cdot10^{-2}$ mol % O by cold trapping at the melting point of K. This means that the value should correspond to the solubility level at the melting temperature.

Mausteller *et al.*[6] reported that a filtrate of large number of batches of K, being saturated with O at the temperature range 355–377 K, contained less than $2.5\cdot10^{-2}$ mol %. Similarly, Addison *et al.*[7] reported that they decreased the O content in K to $(2.0–2.5)\cdot10^{-2}$ mol % O by filtration of liquid K at 343 K. They did not report further details, but the value may be treated as the solubility, if the system was in equilibrium. The same authors quoted a solubility value of $3.4\cdot10^{-2}$ mol % O at 348 K from the paper of Horsley,[8] but this value was not determined by Horsley,[8] who quoted only the value from Williams *et al.*[2]

Some measurements of the O potential in liquid K by Borgstedt *et al.*[9] also indicated much lower solubilities than first reported by Williams *et al.*[2,3] This statement was confirmed in studies of Schwarz[10] who found $5.0\cdot10^{-2}$ mol % O at 373 K and of Ganesan *et al.*[11] who observed a smooth increase of the solubility from $1.7\cdot10^{-2}$ mol % O at 343 K to $7.4\cdot10^{-2}$ mol % O at 473 K. Ivanovskii *et al.*[12,13] determined as much as 3.5 mol % O being dissolved in K at 430 K. Krishnamurthy *et al.*[14] measured the O solubility in liquid K over the temperature range of 366–675 K and found an increase of the solubility from 0.164 to 0.55 mol % O. Sundermann and Schauer[15,16] published a solubility of O in liquid K in the form of an equation, valid in the range 337–673 K:

$$\log(\text{soly/mol \% O}) = 1.597\cdot1310\ (T/\text{K})^{-1}. \quad (1)$$

Recently, Borgstedt *et al.*[17] detected 0.16 mol % O at 573 K by means of an electrochemical measurement. Williams *et al.*[2,3] and Simons and Langedrost[5] employed the amalgamation method of analysis of filtrate. The vacuum distillation of K was applied by Schwarz,[10] Ganesan *et al.*,[11] and Krishnamurthy *et al.*[14] Electrochemical measurements of the cell voltages were used by Ivanovskii *et al.*,[12,13] Sundermann and Schauer,[15,16] and Borgstedt *et al.*[17] Klueh[18] elaborated a method of O determination in K by Zr gettering; however, this technique was not applied to solubility measurements.

The results of Williams *et al.*[2,3] are too high. K could have reacted with the glass container, or some K_2O particles may have passed their filters, if the pores were too large. Both effects would lead to higher O values. Lower values of the solubility, though overestimated, were obtained by Krishnamurthy *et al.*[14] whose experimental method seems to be quite convincing; they used Ni containers and a Ni frit in order to avoid the formation of ternary oxides $K_xM_yO_z$ (M is a metal). However, none of the other results (Simons and Langedrost,[5] Mausteller *et al.*,[6] Addison *et al.*,[7] Schwarz,[10] Ganesan *et al.*,[11] Sundermann and Schauer,[15,16] and Borgstedt *et al.*[17]), obtained by various methods and containers, confirms the data of Krishnamurthy *et al.*[14] and their solubility equation.

Zaezzhev *et al.*[19] reported a solubility equation for O in liquid K based on the method described in Ivanovskii *et al.*:[12,13]

$$\log(\text{soly/mol \% O}) = 2.347 - 799\ (T/\text{K})^{-1}. \quad (2)$$

They claimed that the solubility increased from 1 to 10 mol % O between 336.7 and 603 K. Although the results of Zaezzhev *et al.*[19] and Ivanovskii *et al.*[12,13] are in good agreement, they are overestimated for 2 orders of magnitude in comparison with our selection. It may be that O has not only reacted with K in their experimental equipment, or a serious source of error was within their apparatus.

An acceptable agreement is shown by the results of Simons and Langedrost,[5] Mausteller *et al.*,[6] Addison *et al.*,[7] Ganesan *et al.*,[11] and Borgstedt *et al.*[17] They fit almost perfectly a smooth solubility line which is expressed by the following equation:

$$\log(\text{soly/mol \% O}) = 0.656 - 844\ (T/\text{K})^{-1} \quad r = 0.995. \quad (3)$$

This solubility equation is similar to that published in Ganesan *et al.*[11] and has to be considered as tentative. The K-rich part of the K–O phase diagram was studied by Natola and Touzain[20] who used thermal analysis. Although their thermal arrests showed a scatter of up to ±25 K at a selected composition, it was quite obvious that K_2O exists in four polymorphic forms and displays a miscibility gap between liquid K_2O and K. In the opinion of the evaluators the liquidus line of the O-poor mixtures should be placed at higher temperatures to get a better fit to the selected solubility data, and the monotectic should extend from lower O contents than suggested by the results of Natola and Touzain.[20]

The O-richer part of the diagram was established by Byker *et al.*,[21] based on thermodynamic modeling and thermal analyses of selected compositions. The authors did not take into account the existence of the polymorphs of K_2O and KO_2; therefore, their K–O phase diagram needs further refinement. Unfortunately, the experimental data of melting points and transition temperatures of K oxides are largely dispersed[22] due to the poor purity of materials used by various laboratories. K_2O was expected to melt at ≈1370 K,[23] quoted at 1154 K,[1] 800 K,[4] and measured at 919 K;[20] the latter value was accepted in this assessment. The melting point of K_2O_2 was reported at 818 K,[22] 763 K,[23] but finally estimated at 683 K,[21] the value accepted by the evaluators. The melting temperature of KO_2 was found to be distinctly dependent on the O pressure.[21,23] The value of 845 K at 1.0 MPa was selected for plotting the phase diagram. KO_2 undergoes two phase transitions at 231 and 395 K.[22] K_2O_3, postulated earlier, does not exist in fact.[22] Since the ozonide KO_3, formed only by means of indirect reactions, decomposes above 333 K,[22] it is not further treated as an equilibrium phase. A fragmentary K–O phase diagram, based partly on Okamoto,[25] is shown in Fig. 39.[24]

The introduction of Na into liquid K solvent decreases the corresponding O solubility. According to Krishnamurthy *et al.*,[37] who investigated the whole solvent composition range from pure K to pure Na at 473 K, the solubility changed gradually for more than 1 1/2 orders of magnitude and all values were placed between the lines representing the solubility of O in liquid K as given by Krishnamurthy *et al.*,[14] and the solubility of O in liquid Na:

$$\log(\text{soly/mol \% O}) = 2.320 - 2372\ (T/\text{K})^{-1}. \quad (4)$$

The solubility results of O in liquid K–Na alloys presented in Williams *et al.*,[2,3] Mausteller *et al.*,[6] Ivanovskii *et al.*,[13] and 12 other studies[26–37] show large divergence in single values as well as temperature dependencies of the solubilities. Most of the data[6,12,13,26,27,29,31–36] were obtained for the eutectic K–Na alloy with 32 mol % Na. Noden and Bagley[30] did not specify the alloy composition.

Lower O solubility values for K-richer alloys were observed by Mausteller *et al.*[6] and Rodgers and Mausteller,[31] while opposite results were reported by Williams *et al.*[2,3] and Rodgers and Mausteller.[31] However, Williams *et al.*[2,3] did not notice any significant differences of the O solubility due to variations of the alloy composition between 22 and 82 mol % Na. Na_2O was found to be the equilibrium solid phase until the amount of Na was high enough to form the stoichiometric oxide.

A selection of the most reliable data for the mixed solvent is not quite obvious. Such data should be certainly placed between the lines corresponding to Eqs. (3) and (4), and the temperature dependencies of the solubilities should be comprised between the respective constants of these equations. Such criteria are not fulfilled by the results of several studies.[2,3,6,27,29–33,36] Thus, the most reliable results seem to be those inserted in Ivanovskii *et al.*,[12,13] Amoldov *et al.*,[26] Thorley and Tyzack,[28] and Krishnamurthy,[37] although Ivanovskii *et al.*,[12,13] Arnoldov *et al.*,[26] Thorley and Tyzack,[28] and Krishnamurthy[37] do not show any concordance of their absolute values. Extrapolating Eqs. (3) and (4) to ~1000 K, at which temperature the solubilities in Na and K are equal ~1 mol % O, one should expect that the O solubilities in the K–Na mixtures will not change with the composition of the alloys.

An influence of nonmetallic impurities on the O solubility in liquid K was not studied. However, such a possibility should be taken into account. KOH and K_2CO_3 are stable compounds in liquid K. The presence of O in liquid K enhances corrosion and solubility phenomena of many transition metals due to the formation of ternary K–M–O compounds.

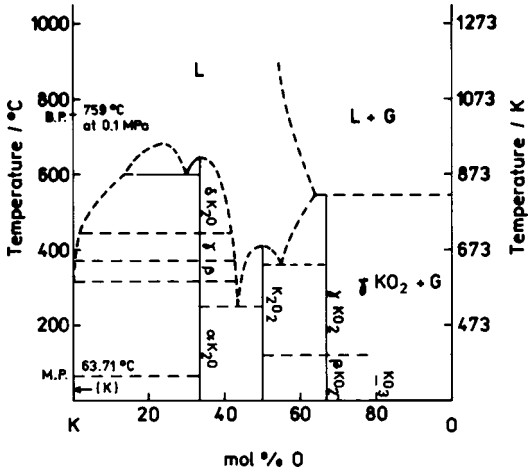

FIG. 39. K–O phase diagram (provisional partial).

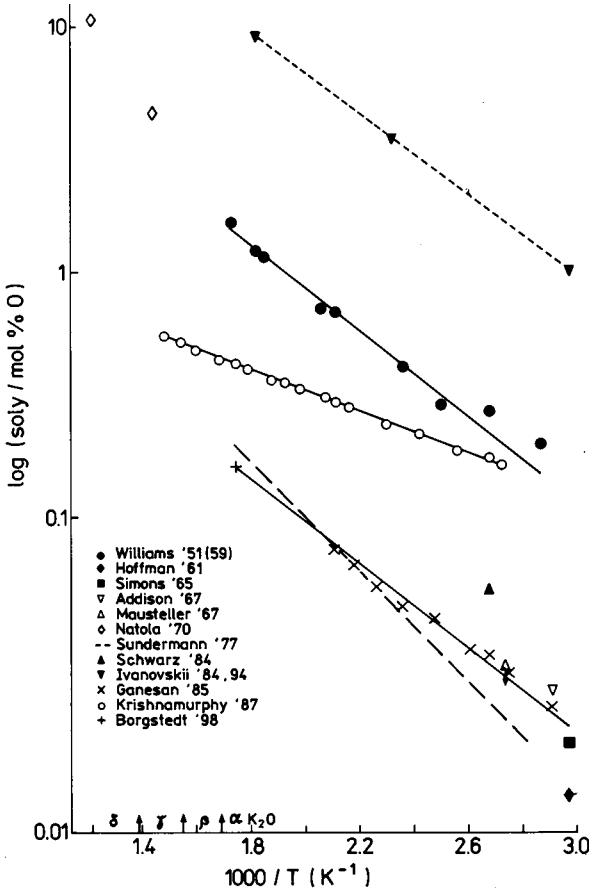

FIG. 39. —Continued.

Tentative values of the solubility of O in liquid K

T/K	Solubility/mol % O	Source
337	0.014 eutectic	(5), Eq. (1) extrapolation
373	0.025	(11), Eq. (1) interpolation
473	0.074	(11)
573	0.16	(17)

References:

[1]H. U. Borgstedt and C. K. Mathews, *Applied Chemistry of the Alkali Metals* (Plenum, New York, 1987), p. 75.
[2]D. D. Williams, Naval Res. Labor. Rep. NRL-3894 (1951).
[3]D. D. Williams, J. A. Grand, and R. R. Miller, J. Phys. Chem. **63**, 68 (1959).
[4]E. E. Hoffman, NASA Rep. TN-D-769, p. 15, 105 (1961).
[5]E. M. Simons and J. F. Langedrost, U.S. Atom. Energy Comm. Rep. CONF-650411, p. 237 (1965).
[6]J. W. Mausteller, F. Tepper, and S. J. Rodgers, *Alkali Metal Handling and System Operating Techniques* (Gordon & Breach, New York, 1967), p. 20.
[7]C. C. Addison, M. G. Barker, R. M. Lintonbon, and R. J. Pulham, *The Alkali Metals* (The Chemical Society, London, 1967), p. 460.
[8]G. W. Horsley, Atom. Ener. Roy. Establish. Rep. M/R-1371 (1954).
[9]H. U. Borgstedt, G. Frees, and H. Schneider, Ber. Bunsengesel. Phys. Chem. **80**, 740 (1976).
[10]N. F. Schwarz, *Liquid Metals Engineering and Technology* (BNES, London, 1984), Vol. 3, p. 177.
[11]V. Ganesan, C. Adelhelm, and H. U. Borgstedt, J. Less-Common Met. **113**, 253 (1985).
[12]M. N. Ivanovskii, A. A. Morozov, A. L. Shimkevich, and B. A. Shmatko, *Liquid Metals Engineering and Technology* (BNES, London, 1984), Vol. 3, p. 15.
[13]M. N. Ivanovskii, V. A. Morozov, A. L. Shimkevich, and N. N. Ponomarev-Stepnoi, *Space Nuclear Power Systems*, edited by M. S. El-Genk and M. D. Hoover (Orbit Books, Malabar, FL, 1992), p. 465.
[14]D. Krishnamurphy, A. Thiruvengadasami, N. P. Bhat, and C. K. Mathews, J. Less-Common Met. **135**, 285 (1987).
[15]V. Schauer, PhD thesis, Technical University of Vienna, Austria, 1976.
[16]H. Sundermann and V. Schauer, Microchim. Acta, Suppl. **7**, 575 (1977).
[17]H. U. Borgstedt, C. Guminski, and Hong Shunzhang, 9th International Symposium on Solubility Phenomena, Hamamet, Tunisia, 2000.
[18]R. L. Klueh, J. Nucl. Energy **25**, 253 (1971).
[19]M. V. Zaezzhev, M. N. Ivanovskii, A. G. Novikov, V. V. Savostin, and A. L. Shimkevich, Teplofiz. Vys. Temp. **32**, 749 (1994).
[20]F. Natola and P. Touzain, Can. J. Chem. **48**, 1955 (1970).
[21]H. J. Byker, J. Eliezer, R. C. Howald, and T. C. Ehlert, High Temp. Sci. **11**, 153 (1979).
[22]I. I. Volnov, *Perekisnye Soedineniya Shchelochnykh Metallov* (Nauka, Moskva, 1980), p. 54.
[23]L. L. Simmons, L. F. Lowden, and T. C. Ehlert, J. Phys. Chem. **81**, 706 (1977).
[24]M. Centnerszwer and M. Blumenthal, Bull. Acad. Polon. Sci., Cl. Sci. Math. Nat. 499 (1933).
[25]H. Okamoto, J. Phase Equil. **20**, 167 (1999).
[26]M. N. Arnoldov, M. N. Ivanovskii, S. S. Pletenets, and A. D. Pleshivtsev, Atom. Energiya **32**, 234 (1972).
[27]T. Sakai, M. Gunji, S. Matsumoto, and Y. Ishii, J. Nucl. Sci. Technol. **20**, 1032 (1983).
[28]A. Thorley and C. Tyzack, *Thermodynamics of Nuclear Materials* (IAEA, Vienna, 1962), p. 365.
[29]W. B. Cottrell and L. A. Mann, U.S. Atom Energy Comm. Rep. ORNL-1688, p. 67 (1953).
[30]J. D. Noden and K. Q. Bagley, U.K. Atom. Ener. Author. Rep. R&D B (C) TN-80 (1954).
[31]S. J. Rodgers and J. W. Mausteller, U.S. Atom. Energy Comm. Rep. NP-5898 (1956); Mine Safety Appliances Rep. TR-47 (1956).
[32]Z. S. Bannykh and G. F. Fefelova, Tr. Ural. Khim. Inst. **5**, 105 (1957).
[33]G. M. Kikin, U.S. Atom. Energy Comm. Rep. NAA-SR-Memo-5472 (1960).
[34]L. R. Blake and A. R. Eames, Nucleonics **19**(5), 66 (1961).
[35]W. R. Huntley, R. E. McPherson, B. Fleischer, and A. Taboada, U.S. Atom. Energy Comm. Rep. ORNL-3898 (1965).
[36]E. E. Konovalov, N. I. Seliverstov, I. B. Dmitreva, and P. A. Sedyshkin, Atom. Energiya **24**, 478 (1968).
[37]D. Krishnamurthy, S. Vana Varamban, A. Thiruvengadasami, and C. K. Mathews, J. Less-Common Met. **153**, 363 (1989).

Components:
(1) Oxygen; O; [7782-44-7]
(2) Potassium; K; [7440-09-7]

Original Measurements:
D. D. Williams, J. A. Grand, and R. R. Miller, J. Phys. Chem. **63**, 68–71 (1959).

Variables:
Temperature: 348–583 K;
O source: K_2O or Na_2O

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of O in liquid K was determined. The results were read from a figure; they were earlier reported numerically in Williams[1] and graphically in Miller.[2] K_2O and Na_2O were used as solutes, however Na_2O is the equilibrium solid phase in the second case.

t/°C	Solubility/mass % O	Solubility/mol % O[a]	Solute
75	0.082	0.20	K_2O
100	0.11	0.27	
128[b]	0.12	0.29	
150	0.17	0.41	
200	0.28	0.68	
212[b]	0.29	0.71	
267[b]	0.47	1.15	
275[b]	0.50	1.22	
305	0.65	1.60	
75	0.001	0.0025	Na_2O
150	0.003	0.0075	
200	0.005	0.0122	
260	0.008	0.020	
310	0.011	0.027	

[a]Calculated by the compilers.
[b]Graphical results.

Auxiliary Information

Method:
It was found in separate experiments that K_2O and Na_2O are the equilibrium solid phases in contact with saturated liquid K. The apparatus was made of Pyrex glass. It consisted of an oxidation and saturation chamber, O reservoir, filter, sample bulb, and appropriate devices to make vacuum or a N atmosphere inside the apparatus. The system was evacuated, filled with N and liquid K was pipetted into the oxidation chamber. The chamber was filled with O which reacted with K. The apparatus was rotated to bring K with K_2O onto the filter. The temperature was raised to the desired level and held for 5–15 min. A slight N pressure was admitted to force the saturated K through the filter onto a sampling bulb. The bulb was removed by flame sealing and the K_2O content analyzed by a modified amalgamation method: an extraction of K with Hg and acidimetric titration of K_2O precipitate practically undissolved in Hg. The solubility of Na_2O was carried out on an analogous way using Na_2O as the solute.

Source and Purity of Materials:
O: "dry."
Na_2O: prepared from NaOH by decomposition in high vacuum at 673 K and subsequent distilling off the excess Na.
K: nuclear grade of purity.
N: nothing specified.

Estimated Error:
Solubility: precision ±10% (by the compilers); reading-out procedure ±5%–10%.
Temperature: accuracy ±5 K; reading-out procedure ±2 K.

References:
[1]D. D. Williams, Naval Res. Labor. Rep. NRL-3894 (1951).
[2]R. R. Miller, *Liquid Metals Handbook*, edited by C. B. Jackson (AEC & NAVY, Washington D.C., 1955), p. 8.

Components:
(1) Oxygen; O; [7782-44-7]
(2) Potassium; K; [7440-09-7]

Original Measurements:
E. M. Simons and J. F. Lagedrost, U.S. Atom. Energy Comm. Rep. CONF-650411, pp. 237–271 (1965).

Variables:
One temperature: 336 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

From the analysis of the internal part of K being saturated with O one may deduce that the solubility of O at the melting point of K (336 K) is $5.0\cdot10^{-3}$ mass % or $1.2\cdot10^{-2}$ mol % O.

Auxiliary Information

Method:
Molten K was contained in a capsule made of Mo–Zr-Ti alloy, placed inside of a glove box. It was equilibrated with He containing O. Various levels of O in liquid K were detected by taking samples of liquid K at various temperatures. The samples taken at the melting temperature of K were analyzed by the amalgamation method: portions of Hg reacted with K up to its total extraction, leaving K_2O precipitate floating on the Hg surface. The amalgamation was performed in a separate apparatus. The contents of K in Hg and the amount of K_2O undissolved in Hg were analyzed by an unspecified method.

Source and Purity of Materials:
O: as impurity in He gas.
K: gettered with Zr–Ti (30%) foil at 977 K for 75–100 h and then contained $<1\cdot10^{-4}$ % Mg, $<3\cdot10^{-4}$ % Cr, $<5\cdot10^{-4}$ % Ni, Cu, Ca, Al, $1.0\cdot10^{-3}$ % Fe, Nb, Si, Zr, Pb, Ti, Mo and $1.5\cdot10^{-3}$ % O.
He: contained $<5\cdot10^{-4}$ % O and $<3\cdot10^{-4}$ % H_2O; purity continuously monitored.

Estimated Error:
Solubility: precision ±2%.
Temperature: precision ±1 K.

Components:
(1) Oxygen; O; [7782-44-7]
(2) Potassium; K; [7440-09-7]

Original Measurements:
F. Natola and P. Touzain, Can. J. Chem. **48**, 1955–1958 (1970).

Variables:
Temperature: 693–957 K;

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The K-rich part of the K–O liquidus was determined. The data were presented in a figure. They were read from the figure by the compilers.

t/°C	Solubility/mol % O
420	4.5
550	12.5
588	14.3
568	14.5
595	16.1
627	18.8
661	22.7
683, 670[a]	25.4
684	25.6
665	26.4
676, 663[a]	27.1
636	28.8
628	29.8
624	30.0
632	32.0
625	32.2
649	32.8
641	32.9
649	33.2

[a]Two arrests observed at one composition.

Polymorphic transitions in K_2O were observed at: 317, 372, and 446 °C. The melting points of K and K_2O were found at 64 °C and 646±5 °C, respectively. The immiscibility gap extended from 17 to 30 mol % O at 600 °C, and the critical point was suggested at 25 mol % O and 680 °C.

Auxiliary Information

Method:
K and K_2O were introduced into a Pyrex glass container in a N atmosphere. Differential thermal analysis of the homogenized samples was performed in glass, alumina, and Pt crucibles placed in the glass container. Pt and glass were attacked by the melt. Temperatures were measured by means of three calibrated Pt thermocouples. Changes of temperature were on the order of 8–10 K/min.

Source and Purity of Materials:
K_2O: obtained by partial oxidation of K by a known amount of O and distillation off of the excess of K.
K: probably distilled in vacuum.
N: "anhydrous."

Estimated Error:
Solubility: nothing specified; reading-out procedure ±0.2 mol %.
Temperature: precision between ±2 and ±5 K; reading-out procedure ±3 K; reproducibility better than ±25 K (by the compilers).

Components:
(1) Oxygen; O; [7782-44-7]
(2) Potassium; K; [7440-09-7]

Original Measurements:
H. Sundermann and V. Schauer, Microchim.Acta, Suppl. **7**, 575–596 (1977).

Variables:
Temperature: 336–673 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The results of measurements of the solubility of O in liquid K were reported in a figure as a smooth line. Temperature values for selected O concentrations were read from the figure, and concentrations were recalculated to mol % O by the compilers.

t/°C	Solubility/mass % O	Solubility/at % O
63.2	$1.8\cdot10^{-3}$ [a]	$4.4\cdot10^{-3}$
72	$2.5\cdot10^{-3}$	$6.1\cdot10^{-3}$
99	$5.0\cdot10^{-3}$	$1.22\cdot10^{-2}$
120	$7.5\cdot10^{-3}$	$1.83\cdot10^{-2}$
135	$1.0\cdot10^{-2}$	$2.4\cdot10^{-2}$
194	$2.5\cdot10^{-2}$	$6.1\cdot10^{-2}$
249	$5.0\cdot10^{-2}$	0.122
283	$7.5\cdot10^{-2}$	0.183
320	$1.0\cdot10^{-1}$	0.24
400	$3.0\cdot10^{-1}$ [a]	0.73

[a]Extrapolated.

The same results were reported in Schauer.[1] The authors proposed the following solubility equation:

$$\log(\text{soly/mass \% O}) = 1.209 - 1310\ (T/\text{K})^{-1}.$$

Auxiliary Information

Method:
Potentiometric measurements of the O concentrations in liquid K were conducted in the cell: Ni, K, $K_2O/ThO_2+10\%$ Y_2O_3/Cu_2O, Cu, Pt, after coulometric titration of O. A Ni tube was filled with the K–K_2O mixture. The yttria doped thoria tube contained the Cu–Cu_2O reference electrode. The yttria doped thoria tube was dipped into the K–K_2O mixture which was kept under dry Ar. The reference electrode was kept under constant partial pressure of O. The temperature was measured by means of a sheathed Pt/Pt–Rh thermocouple. The Ni tube was heated in a furnace. Concentrations of O were changed by means of Coulometric electrolysis. Potentials of saturated and unsaturated melts were recorded as function of temperature. Saturation points were determined from the intersection of the lines.

Source and Purity of Materials:
O: from electrolysis.
K: nothing specified.
Ar: purified on BTS catalyst (from BASF) at 473 K. H_2O was precipitated in liquid air. The O partial pressure was 10^{-6} Pa.

Estimated Error:
Solubility: nothing specified; not better than ±5% (by the compilers).
Temperature: nothing specified; read-out procedure ±0.5 K.
Potential: reproducibility ±2 mV.

References:
[1]V. Schauer, PhD thesis, University of Vienna, Austria, 1976.

Components:
(1) Oxygen; O; [7782-44-7]
(2) Potassium; K; [7440-09-7]

Original Measurements:
M. N. Ivanovskii, V. A. Morozov, A. L. Shimkevich, and B. A. Shmatko, *Liquid Metal Engineering & Technology* (BNES, London, 1984), Vol. 3, pp. 15–22.

Variables:
One temperature: 430 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of O in liquid K was determined to be 3.5 mol % O at 430 K as read from a figure by the compilers. The same result was reported in Ivanovskii *et al.*[1]

In a subsequent report of this laboratory,[2] the authors reported that the solubility increased from 1 to 10 mol % O with an increase of temperature from 63.5 to 330 °C. The solubility was expressed by the equation:

$$\log(\text{soly/mol \% O}) = 2.374 - 799\ (T/\text{K})^{-1}.$$

Auxiliary Information

Method:
An electrochemical cell was assembled: Mo/K–K_2O satd/$(ZrO_2)_{0.9}(Y_2O_3)_{0.1}$ /K–K_2O/Mo. The K–K_2O saturated, used as a reference system, was located in a cup made of Al_2O_3. The electrolyte test tube was loaded with K. After the cell assembling, sealing, and vacuum pumping, He gas was fed into chamber of the reference electrode. The test electrode remained in vacuum. Portions of O gas were added into the electrolyte test tube. Completeness of the reaction of O with K was recorded by a vacuum manometer. The emf steady state values were achieved after 10–30 min from the moment of O feeding. When the potential difference approached 0 the saturation of K with O was reached.

Source and Purity of Materials:
O: purified from CO_2 and moisture.
K: purified by distillation at 520 K.
He: spectrally pure.

Estimated Error:
Solubility: precision ±0.2%; reading-out procedure ±0.1 mol % O.
Temperature: accuracy ±1 K.
Potential: accuracy ±2.5 mV.

References:
[1]M. N. Ivanovskii, V. A. Morozov, A. L. Shimkevich, and N. N. Ponomarev-Stepnoi, *Space Nuclear Power Systems*, edited by M. S. El-Genk and M. D. Hoover (Orbit Books, Malabar, FL, 1992), pp. 465–469.
[2]M. V. Zaezzhev, M. N. Ivanovskii, A. G. Novikov, V. V. Savostin, and A. L. Shimkevich, Teplofiz. Vys. Temp. **32**, 749–755 (1994).

Components:
(1) Oxygen; O; [7782-44-7]
(2) Potassium; K; [7440-09-7]

Original Measurements:
N. F. Schwarz, *Liquid Metals Engineering & Technology* (BNES, London, 1984), Vol. 3, pp. 177–183.

Variables:
One temperature: 373 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of O in liquid K at 100 °C (373 K) was found to be $2.0 \cdot 10^{-2}$ mass % or $5.0 \cdot 10^{-2}$ mol % O (as calculated by the compilers). The K used was relatively impure; therefore, an interference with other elements present in the K medium is possible.

Auxiliary Information

Method:
The solubility determinations were performed by means of a cold trap of a high temperature stainless steel loop filled with K. The apparatus contained a sampling and plugging meter. The cold trap temperature was fixed at 373 K. The plugging meter readings indicated the time needed to plug the orifice of the device. Chemical analysis of K sample, taken after such purification run, was performed by vacuum distillation.[1] The concentration of O found should represent the saturating concentration at the cold trap temperature. The experiments were performed in a gas atmosphere of unspecified purity.

Source and Purity of Materials:
O: as impurity in K.
K: contained $< 1 \cdot 10^{-4}$ % C, $1.6 \cdot 10^{-4}$ % Mn, $8 \cdot 10^{-4}$ % Fe, Cr and $6 \cdot 10^{-5}$ % Ni.
Cover gas: "purity continuously monitored."

Estimated Error:
Solubility: nothing specified.
Temperature: nothing specified.

References:
[1]V. Ganesan, C. Adelhelm, and H. U. Borgstedt, J. Less-Common Met. **113**, 253–259 (1985).

Components:
(1) Oxygen; O; [7782-44-7]
(2) Potassium; K; [7440-09-7]

Original Measurements:
V. Ganesan, C. Adelhelm, and H. U. Borgstedt, J. Less-Common Met. **113**, 253–259 (1985).

Variables:
Temperature: 343–473 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data
The solubility of O in liquid K was determined. Minimum two determinations at each temperature were performed.

T/K	Solubility/mass % O	Solubility/mol % O[a]
343	$6.9\cdot10^{-3}$	0.0168
363	$9.5\cdot10^{-3}$	0.0232
373	0.0112	0.0273
383	0.0114	0.0279
403	0.0159	0.039
423	0.0176	0.043
443	0.0214	0.052
458	0.0263	0.064
473	0.0304	0.074

[a]Calculated by the compilers.

K_2O is the equilibrium solid phase which is stable in vacuum up to 623 K. The authors proposed the solubility equation, tested by the compilers:

$$\log(\text{soly/mass \% O}) = 0.1012 - 744.3\ (T/\text{K})^{-1},$$

Auxiliary Information

Method:
Liquid K was allowed to equilibrate with K_2O at desired temperature in a stainless steel bath in an Ar atmosphere. Ni crucibles were cleaned in H_2SO_4–HNO_3–H_3PO_4–CH_3COOH 1:3:1:5 mixture at 363 K for 8–10 s, poured in demineralized water and heated at 403 K. Liquid K was sampled into the Ni crucibles. The crucibles were placed in a glass vessel for vacuum distillation. The vessel, containing a film of K on its walls to avoid moisture contamination of the sample, was evacuated to $1.3\cdot10^{-3}$ Pa, and distillation was carried out at 523 K. The temperature was controlled by a sheathed thermocouple. Distilled K was deposited onto the vessel walls. The end of the distillation was manifested by a sharp rise of temperature. The Ni crucible with K_2O inside was cleaned outside from traces of K using dilute HCl. The residue inside was dissolved in 1:1 HCl. CsCl standard solution was added as an ionizing agent. The K concentration was measured on an AAS instrument previously calibrated. All essential parts of experiments were performed in an Ar filled glove box.

Source and Purity of Materials:
K_2O: nothing specified.
K: distilled and contained $\sim10^{-4}$ % Na.
Ar: contained $<1\cdot10^{-4}$ % O and H_2O.

Estimated Error:
Solubility: accuracy ±0.005% (by the compilers).
Temperature: accuracy ±1 K.

Components:
(1) Oxygen; O; [7782-44-7]
(2) Potassium; K; [7440-09-7]

Original Measurements:
D. Krishnamurthy, A. Thiruvengadasami, N. P. Bhat, and C. K. Mathews, J. Less-Common Met. **135**, 285–292 (1987).

Variables:
Temperature: 366–675 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data
The solubility of O in liquid K was determined

T/K	Solubility/mass % O	Solubility/mol % O[a]
366	0.0667	0.164
	0.0657	0.161
373	0.0720	0.176
	0.0731	0.178
391	0.0765	0.187
	0.0750	0.183
	0.0776	0.190
414	0.0882	0.22
	0.0917	0.22
434	0.1006	0.25
	0.0996	0.24
	0.0991	0.24
462	0.1124	0.27
	0.1170	0.29
	0.1121	0.27
474	0.1226	0.30
	0.1188	0.29
	0.1188	0.29
482	0.1277	0.31
	0.1277	0.31
	0.1249	0.30
504	0.1355	0.33
	0.1362	0.33
	0.1356	0.33
522	0.146	0.36
	0.144	0.35
533	0.153	0.37
	0.150	0.36
	0.149	0.36
559	0.163	0.40
	0.169	0.41
	0.167	0.40
573	0.175	0.43
	0.173	0.42
593	0.182	0.44
	0.181	0.44
	0.179	0.44
624	0.199	0.49
	0.197	0.48
	0.198	0.48
625	0.198	0.48
	0.202	0.49
650	0.213	0.52
	0.213	0.52
	0.212	0.52
675	0.222	0.54
	0.224	0.55

[a]Calculated by the compilers.

The authors formulated the solubility equation, tested by the compilers:

$$\log(\text{soly/mass \% O}) = -0.03 - 420.4\ (T/\text{K})^{-1}.$$

The equation was also reported in Mathews.[1]

Auxiliary Information

Method:
A vessel made of AISI 304 stainless steel and Ni lined was washed with diluted HNO_3, demineralized water, and acetone. The vessel was dried in vacuum for a few hours and filled with liquid K in a glove box. The assembled vessel was heated to 423 K. O gas was injected into the Ar stream in small increments to saturate the K. The vessel was equilibrated at the desired temperature for 3 h. A sample compartment was evacuated. Liquid K entered the sample chamber through a 5 μm Ni frit filter. The samples were removed for analysis by vacuum distillation at 493 K and $1.33 \cdot 10^{-3}$ Pa. Complete distillation of K was ensured by monitoring the rise in temperature of the crucible. The residue left after the distillation was dissolved in 2 mol dm^{-3} HCl. The content of K in this solution was estimated by atomic absorption spectrophotometry. The O content was calculated from the K content of the residue assuming it to be K_2O. The content of K was found from the weight difference before and after the distillation. The temperature was measured using a Chromel/Alumel thermocouple.

Source and Purity of Materials:
O: nothing specified.
K: from Heavy Water Plant, Baroda, India; K_2O present in liquid K skimmed; the metal distilled at $1.35 \cdot 10^{-3}$ Pa; finally contained $< 2 \cdot 10^{-4}$% Na.
Ar: nothing specified.

Estimated Error:
Solubility: nothing specified; precision better than $\pm 2\%$ (by the compilers).
Temperature: stability ± 1 K.

References:
[1]C. K. Mathews, High Temp. Sci. **26**, 377–394 (1988–89).

Components:
(1) Oxygen; O; [7782-44-7]
(2) Potassium; K; [7440-09-7]

Original Measurements:
H. U. Borgstedt, C. Guminski, and Hong Shunzhang, *9th International Symposium on Solubility Phenomena*, Hamamet, Tunsia, 2000.

Variables:
One temperature: 573 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of O in liquid K at 573 K was found to be $(6.53 \pm 0.95) \cdot 10^{-2}$ mass % O or 0.16 mol % O (as calculated by the compilers).

Auxiliary Information

Method:
The determination was performed by means of coulometric titration using solid electrolyte. A stainless steel vessel contained K, a Ni crucible with a mixture K and K_2O, a reference electrode, a titration electrode and a sheathed thermocouple. The electrochemical cell was: $K–K_2O/ThO_2+Y_2O_3/In–In_2O_3$. The solid thoria tube contained $In–In_2O_3$. The tube was dipped in the Ni crucible containing K and K_2O. The crucible was dipped in pure K in which the titration electrode and the thermocouples were also inserted. Mo wires were used for electrical connections. The temperature was controlled by a programmed device. The amount of O which passes the electrolyte tube was related to the electrical charge which passed the cell. Assuming applicability of Henry's law and Nernst's equation the saturating concentration of O in liquid K was calculated.

Source and Purity of Materials:
O: from the coulometric titration.
K: nuclear grade of purity.
Ar: contained $< 10^{-4}$ vol % O and H_2O.

Estimated Error:
Solubility: precision $\pm 15\%$.
Temperature: precision ± 1 K.

Components:
(1) Oxygen; O; [7782-44-7]
(2) Potassium-sodium alloy; K–Na

Original Measurements:
W. B. Cottrell and L. A. Mann, U.S. Atom. Energy Comm. Rep. ORNL-1688, pp. 67–69 (1953).

Variables:
Temperature: 533–755 K;
alloy composition unspecified

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of O in liquid K–Na mixture of unspecified composition (but probably constant) was determined. The data were read from a figure and recalculated to mol % O by the compilers assuming the eutectic composition of the alloy (32 mol % Na).

t/°F	T/K	Solubility/mass % O	Solubility/mol % O
500	533	$7\cdot10^{-3}$	$1.5\cdot10^{-2}$
700	644	$1.5\cdot10^{-2}$	$3\cdot10^{-2}$
900	755	$3\cdot10^{-2}$	$6\cdot10^{-2}$

The compilers expressed the data with the following solubility equation:

$$\log(\text{soly/mol \% O}) = 0.302 - 1144\ (T/\text{K})^{-1} \quad r = 0.998.$$

The equilibrium solid phase was treated as a mixture of Na_2O and K_2O.

Auxiliary Information

Method:
The K–Na alloy was held under an Ar atmosphere for at least 24 h for the saturation with Na_2O at selected temperature. The melt was filtered through a 5 μm sintered stainless steel filter. The filtrate was treated by N-butyl bromide solution in hexane. The K–Na alloy reacted with the reagent while the metal oxides did not. The oxides, after addition of H_2O, were titrated by an acid and the solubility calculated.

Source and Purity of Materials:
Na_2O: nothing specified.
K–Na: nothing specified.
Ar: purified by bubbling through a column of K–Na melt.

Estimated Error:
Solubility: accuracy ±0.001 mass %; reading-out procedure ±5%; standard deviation ±0.005 mass %.
Temperature: nothing specified; reading-out procedure ±5 K.

Components:
(1) Oxygen; O; [7782-44-7]
(2) Potassium–sodium alloy; K–Na

Original Measurements:
J. D. Noden and K. O. Bagley, U.K. Atom. Ener. Author. Rep. R&D B(C) TN-80 (1954).

Variables:
Temperature: 293–449 K; alloy composition probably constant being between 15 and 65 mol % Na

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of O in liquid K–Na alloy at various temperatures was determined. The composition of the alloy was not specified, it was probably constant and should be between 15 and 65 mol % Na to maintain the alloy liquid at 20 °C.

t/°C	Solubility/mass % O	Solubility/mol % O[a]
20	0.001; 0.0003; 0.000 32	0.003; 0.0007; 0.000 68
20	0.0026; 0.000 38; 0.0004	0.0055; 0.0081; 0.0085
20	0.001; 0.000 42	0.003; 0.000 89
50	0.0033	0.0070
105	0.0017	0.0036
151	0.0018	0.0038
176	0.0018	0.0038

[a]Calculated by the compilers, assuming the Na content in the solvent alloy 32 mol %.

The compilers formulated the solubility equation:

$$\log(\text{soly/mol \% O}) = -1.336 - 455\ (T/\text{K})^{-1} \quad r = 0.626.$$

Na_2O was identified as the equilibrium solid phase, after chemical analysis.

Auxiliary Information

Method:
All essential operations were performed in an Ar atmosphere. A stainless steel apparatus consisted of a stirrer-thermocouple tube, a side arm for the connection with a vacuum system and Ar supply, and a tube containing Na with a stainless steel filter of 5 μm pore size. The apparatus was connected with a glass part for chemical analysis the lower part of which comprised a flask and a capillary tap for the removal of Hg or amalgam during the analysis. Liquid K–Na alloy was distilled and poured onto the sinter. It was heated to 523 K under vacuum for 30 min. An excess of O was introduced via a glass tap and Na_2O formed. The melt was stirred. The apparatus was re-evacuated and filled with Ar. The temperature was raised to the desired level of saturation and maintained there for 30 min while the melt was stirred. The apparatus was evacuated below the sinter to enable filtration of the solution. The injected alloy reacted violently with Hg. Subsequent portions of Hg were added to extract the K–Na. Na_2O left undissolved on Hg was determined by alkalimetric titration.

Source and Purity of Materials:
O: gaseous of unspecified purity.
K–Na: distilled.
Ar: dried by an anhydrous $CaCl_2$, P_2O_5, passed over Ca turnings at 973 K and finally through a K–Na bubbler.

Estimated Error:
Solubility: accuracy $\pm 7\cdot10^{-4}$ mol % O.
Temperature: nothing specified.

Components:
(1) Oxygen; O; [7782-44-7]
(2) Potassium-sodium alloy; K–Na

Original Measurements:
S. J. Rodgers and J. W. Mausteller, U.S. Atom. Energy Comm. Rep. NP-5898 (1956); Mine Safety Appliances Rep. TR-47 (1956).

Variables:
Temperature: 566–877 K;
Na content: 32–85 mol %

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of O in liquid K–Na alloys was determined. The data were read from a figure presented in Mausteller *et al.*[1] and recalculated to mol % O by the compilers.

Alloy/mol % Na	t/°F	t/°C	Solubility/mass % O	Solubility/mol % O
85	631	333	0.017	0.027
	663	351	0.022	0.035
	840	449	0.067	0.106
	868	464	0.089	0.141
	885	473	0.097	0.154
	890	477	0.099	0.157
	888	476	0.102	0.162
68	681	361	0.018	0.032
	700	371	0.020	0.035
	760	404	0.038	0.067
	800	427	0.045	0.079
	850	454	0.052	0.091
	881	472	0.059	0.103
	888	476	0.066	0.116
	950	510	0.070	0.123
	975	524	0.076	0.133
	1100	593	0.104	0.183
	1119	604	0.113	0.198
32	560	293	0.008	0.017
	1040	560	0.055	0.117

The compilers calculated the solubility equations:

$$\log(\text{soly/mol \% O}) = 2.436 - 2431\,(T/\text{K})^{-1} \quad r = 0.999 \quad \text{for 85 mol \% Na,}$$

$$\log(\text{soly/mol \% O}) = 1.205 - 1647\,(T/\text{K})^{-1} \quad r = 0.968 \quad \text{for 68 mol \% Na.}$$

Auxiliary Information

Method:
Since the original report was not available to the compilers, details of the determinations are not known. Most probably the alloy circulated in a stainless steel loop and samples of it being saturated with O were analyzed by amalgamation method.

Source and Purity of Materials:
O: nothing specified.
K–Na: nuclear grade of purity.

Estimated Error:
Solubility: nothing specified; reading-out procedure ±0.001 mol % O.
Temperature: nothing specified; reading-out procedure ±2 K.

References:
[1]J. W. Mausteller, F. Tepper, and S. J. Rodgers, *Alkali Metals Handling and System Operating Techniques* (Gordon & Breach, New York, 1967), p. 22.

Components:
(1) Oxygen; O; [7782-44-7]
(2) Potassium–sodium alloy; K–Na

Original Measurements:
Z. S. Bannykh and G. F. Fefelova, Tr. Ural. Nauch. Issled. Khim. Inst. **5**, 105–117 (1957).

Variables:
Temperature: 377–523 K;
alloy composition: 22.6–24.1 mass % Na

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of O in liquid K–Na alloy was determined

t/°C	Alloy/mass % Na	Solubility/mass % O	Solubility/mol % O[a]
104	22.6	0.004	0.008
105	22.6	0.005	0.011
105	24.1	0.006; 0.006	0.013; 0.013
250	23.4	0.015; 0.015; 0.017	0.032; 0.032; 0.036

[a]Calculated by the compilers.

Attempts to perform experiments at 350 °C were not successful.

Auxiliary Information

Method:
The K–Na alloy was prepared by melting the metals under paraffin. The measurements at ~377 K were performed in a glass container, thermostated in an oil bath. The alloy was mixed for 2–5 h. It was covered by an oxide layer from the reaction with O traces in N as the cover gas. The melt was left for 0.5–2.5 h for equilibration. The experiment at 523 K was performed in a stainless steel container. It was heated by means of an electric oven which was regulated by a Chromel/Copel thermocouple. The alloy was mixed for 5 h. Samples of the alloy saturated with O were analyzed extracting K–Na with Hg. The undissolved oxide was treated with H_2O and titrated with HCl solution in presence of phenolphthalein. Hg was treated with HCl and back titrated with NaOH solution. The composition of the alloy was analyzed by unspecified method.

Source and Purity of Materials:
O: as the minor component in N gas.
Na: 99.7+ pure and contained <0.003% Cl; contents of Al, Mg, Ca, Fe, C, Pb, and Cu were negligible; the surface layer was cut off.
K: "thermical" of unspecified purity.
H_2O: distilled.
N: nothing specified.

Estimated Error:
Solubility: nothing specified; precision better than ±12% (by the compilers).
Temperature: stability ±3 K.

Components:
(1) Oxygen; O; [7782-44-7]
(2) Potassium–sodium alloy; K–Na

Original Measurements:
D. D. Williams, J. A. Grand, and R. R. Miller, J. Phys. Chem. **63**, 68–71 (1959).

Variables:
Temperature: 323–635 K;
alloy composition: 18–78 mass % K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of O in liquid K–Na alloy was determined. The results were read from a figure by the compilers and recalculated to mol % O assuming composition of the K–Na alloy 50:50.

t/°C	Solubility/mass % O	Solubility/mol % O
50	$1\cdot10^{-3}$	$2\cdot10^{-3}$
123	$3\cdot10^{-3}$	$6\cdot10^{-3}$
231	$6\cdot10^{-3}$	$1.2\cdot10^{-2}$
301	$1.0\cdot10^{-2}$	$2.0\cdot10^{-2}$
342	$1.3\cdot10^{-2}$	$2.6\cdot10^{-2}$
354	$1.5\cdot10^{-2}$	$3.0\cdot10^{-2}$
362	$1.5\cdot10^{-2}$	$3.0\cdot10^{-2}$

Practically the same results were obtained after changing the alloy composition from 18 to 78 mass % K. The results were previously reported in Williams.[1] The compilers formulated solubility equation:

$$\log(\text{soly/mol \% O}) = -0.360 - 754\ (T/\text{K})^{-1} \quad r = 0.996.$$

Auxiliary Information

Method:
Na_2O was found in preliminary experiments to be the equilibrium solid phase. A Pyrex glass apparatus consisted of an oxidation and saturation chamber, O reservoir, filter, sample bulb, and appropriate devices to make vacuum or N atmosphere in the apparatus. Astainless steel equipment was employed at temperatures above 600 K. After evacuation and filling with N, liquid K–Na alloy was pipetted into the oxidation chamber. The chamber was filled with O which reacted with the alloy. The temperature was raised to the desired level and held for 5–15 min. A slight N pressure was admitted to force the saturated liquid K–Na through the filter onto the sampling bulb. The bulb was removed by flame sealing and the content analyzed for O by a modified amalgamation method: extraction of K–Na with Hg and acidimetric titration of the oxides, since they are practically insoluble in Hg.

Source and Purity of Materials:
Na_2O: 99.9+% pure, obtained in a special apparatus using Na and dry O.
K–Na: nuclear grade of purity.
N: nothing specified.

Estimated Error:
Solubility: precision ±10%, as in Williams and Miller.[2]
Temperature: accuracy ±5 K.

References:
[1]D. D. Williams, Naval Res. Labor. Rep. NRL-3894 (1951).
[2]D. D. Williams and R. R. Miller, Anal. Chem. **23**, 1805 (1951).

Components:
(1) Oxygen; O; [7782-44-7]
(2) Potassium–sodium eutectic; $K_{68}Na_{32}$; [11147-16-3]

Original Measurements:
G. M. Kikin, U.S. Atom. Energy Comm. Rep. NAA-SR-Memo-5472 (1960).

Variables:
Temperature: 441–483 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of O in the liquid K–Na eutectic alloy was determined. The results were read from a figure and recalculated to mol % O by the compilers.

t/°F	T/K	Solubility/mass % O	Solubility/mol % O
335	441	$1.7\cdot10^{-3}$	$3.6\cdot10^{-3}$
350	450	$2.9\cdot10^{-3}$	$6.1\cdot10^{-3}$
360	455	$3.3\cdot10^{-3}$	$7.0\cdot10^{-3}$
365	458	$3.7\cdot10^{-3}$	$7.9\cdot10^{-3}$
370	461	$4.8\cdot10^{-3}$	$1.02\cdot10^{-2}$
380	466	$4.3\cdot10^{-3}$	$9.1\cdot10^{-3}$
380	466	$6.9\cdot10^{-3}$	$1.46\cdot10^{-2}$
390	472	$6.0\cdot10^{-3}$	$1.27\cdot10^{-2}$
400	477	$1.10\cdot10^{-2}$	$2.3\cdot10^{-2}$
410	483	$1.30\cdot10^{-2}$	$2.8\cdot10^{-2}$

The compilers expressed the data by the solubility equation:

$$\log(\text{soly/mol \% O}) = 7.556 - 4412\ (T/\text{K})^{-1} \quad r = 0.969.$$

Auxiliary Information

Method:
The tank containing the K–Na eutectic alloy was made of Type 304 stainless steel. It was connected with the loop pipes with which an O meter and an electromagnetic pump were equipped. A filter was placed inbetween. The system was heated by a tubular type of a heater. O was kept in a separate gas tank made of the stainless steel. The temperature was controlled by a Chromel/Alumel thermocouple in a stainless steel sheath. The apparatus was evacuated, the alloy introduced, and Ar cover gas entered into. The system was heated and O added in measured amounts to the cover gas. The end of the reaction was controlled by a constant pressure inside the tank. The system was gradually colled while observing the reaction of the plugging meter. The temperature at which the oxide crystallization started was determined.

Source and Purity of Materials:
O: dried.
K–Na: nuclear grade of purity; further purified.
Ar: dried.

Estimated Error:
Solubility: nothing specified; reading-out procedure $\pm 4\cdot10^{-4}$ mol % O.
Temperature: nothing specified; reading-out procedure ±3 K.

Components:
(1) Oxygen; O; [7782-44-7]
(2) Potassium–sodium alloy; $K_{65}Na_{35}$;

Original Measurements:
L. R. Blake and A. R. Eames, Nucleonics **19**(5), 66–72 (1961).

Variables:
One temperature: 393 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of O in liquid K–Na alloy (containing 24 mass % Na) at 120 °C (393 K) was found to be $1.0 \cdot 10^{-3}$ mass % or $2.1 \cdot 10^{-3}$ mol % O.

Auxiliary Information

Method:
The liquid alloy circulated in a toroidal pipe containing a rhometer for electrical resistivity measurements. This way the O content in the alloy was continuously monitored. An alloy sample from the working system was analyzed by an unspecified chemical analysis.

Source and Purity of Materials:
O: nothing specified.
Na–K alloy: nuclear grade of purity.

Estimated Error:
Solubility: nothing specified.
Temperature: stability better than ±0.1 K.

Components:
(1) Oxygen; O; [7782-44-7]
(2) Potassium-sodium alloy; $K_{20}Na_{80}$;

Original Measurements:
A. Thorley and C. Tyzack, *Thermodynamics of Nuclear Materials* (IAEA, Vienna, 1962), pp. 365–397.

Variables:
Temperature: 383–473 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of O in K–Na (80 mol %) alloy was estimated

t/°C	Solubility/mass % O	Solubility/mol % O[a]
110	$7 \cdot 10^{-4}$	$1.7 \cdot 10^{-3}$
120	$9 \cdot 10^{-4}$	$2.2 \cdot 10^{-3}$
140	$1.2 \cdot 10^{-3}$	$2.9 \cdot 10^{-3}$
200	$3.0 \cdot 10^{-3}$	$7.3 \cdot 10^{-3}$

[a]Calculated by the compilers.

The compilers found the following equation for the solubility:

$$\log(\text{soly/mol \% O}) = 0.492 - 1247\ (T/\text{K})^{-1} \quad r = 0.999.$$

Auxiliary Information

Method:
The tests were carried out in a dynamic K–Na test loop made of stainless steel. A specimen chamber was connected to the loop and was placed in a glove box filled with N. The loop contained a hot trap (with Zr foil at 873 K), a cold trap, a heater, a cooler, filters, a dump tank, and an electromagnetic pump. The samples of the K–Na alloy in equilibrium with the cold trap part were analyzed by an unspecified method.

Source and Purity of Materials:
O: nothing specified.
K–Na: nuclear grade of purity and contained $\sim 10^{-4}$ % H.
N: purified in two K–Na bubblers heated to 333–353 K and finally contained $<2 \cdot 10^{-4}$ vol % O and $<1 \cdot 10^{-3}$ vol % H_2O.

Estimated Error:
Solubility: nothing specified.
Temperature: nothing specified.

Components:
(1) Oxygen; O; [7782-44-7]
(2) Potassium–sodium eutectic; $K_{68}Na_{32}$; [11147-16-3]

Original Measurements:
W. R. Huntley, R. E. MacPherson, B. Fleischer, and A. Taboada, U.S. Atom. Energy Comm. Rep. ORNL-3898 (1965).

Variables:
Temperature: 380–566 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of O in the K–Na eutectic alloy was determined

t/°F	t/°C[a]	Solubility/mass % O	Solubility/mol % O[a]
225	107	$<1.5\cdot10^{-3}$	$<3.2\cdot10^{-3}$
250	121	$<1.9\cdot10^{-3}$	$<4.0\cdot10^{-3}$
350	177	$3.0\cdot10^{-3}$	$6.4\cdot10^{-3}$
560	293	$8.2\cdot10^{-3}$	$1.74\cdot10^{-2}$

[a]Calculated by the compilers.

A mixture of Na_2O and K_2O was detected in the solid state being in contact with the saturated solutions. The compilers formulated the following solubility equation:

$$\log(\text{soly/mol \% O}) = -0.293 - 838\,(T/\text{K})^{-1} \quad r = 0.996.$$

Auxiliary Information

Method:
The experiments were performed in a 316 type stainless steel loop. The circulation of the K–Na alloy was forced by an electromagnetic pump. Temperatures were measured with the use of a Chromel/Alumel thermocouple. Oxide level measurements were performed using a plugging indicator which reacts on a break or decrease of the liquid metal flow due to the precipitation of oxide. The samples of the alloy saturated with O from the cold trap were taken for analysis which was performed using the Hg amalgamation method. The oxide residue after the amalgamation was titrated with HCl solution. The experiments were performed in a He atmosphere.

Source and Purity of Materials:
O: nothing specified.
K–Na: from MSA Res. Corp. and contained 77.6% K, $<4.6\cdot10^{-3}$ % C, $1.0\cdot10^{-3}$ % O, $1\cdot10^{-5}$ % Li, $2\cdot10^{-3}$ % Cs, $3\cdot10^{-4}$ % Rb, $(1-10)\cdot10^{-4}$ % Mg, $(3-10)\cdot10^{-4}$ % Ca, $(10-15)\cdot10^{-4}$ % Si, $<1.0\cdot10^{-3}$ % Fe, B, Co, Al, Pb, Cr, Ti, Ni, Mo, V, Zr, $<3\cdot10^{-4}$ % Ba, $<2\cdot10^{-4}$ % Cu, $<1\times10^{-4}$ % Mn, Sn, Be, Ag, Sr.
He: contained $<1\cdot10^{-4}$ % H_2O, bubbled through the K–Na melt.
Ar: 98.9% pure and contained $8\cdot10^{-3}$ % O, 0.88% (N+CO), 0.12% H_2O and 0.05% H.

Estimated Error:
Solubility: nothing specified.
Temperature: accuracy ±2.5 K.

Components:
(1) Oxygen; O; [7782-44-7]
(2) Potassium-sodium eutectic; $K_{68}Na_{32}$; [11147-16-3]

Original Measurements:
E. E. Konovalov, Kh. I. Seliverstov, I. B. Dmitreva, and P. A. Sedyshkin, Atom. Energiya **24**, 478–479 (1968).

Variables:
Temperature: 291–494 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of O in the liquid eutectic mixture of K–Na alloy was determined. The results were read from a figure and recalculated to mol % by the compilers.

t/°C	Solubility/mass % O	Solubility/mol % O
18	$7\cdot10^{-4}$	$1.5\cdot10^{-3}$
19	$2\cdot10^{-4}$	$4\cdot10^{-4}$
43	$5\cdot10^{-4}$	$1.0\cdot10^{-3}$
68	$3\cdot10^{-4}$	$6\cdot10^{-4}$
107	$3\cdot10^{-4}$	$6\cdot10^{-4}$
153	$7\cdot10^{-4}$	$1.5\cdot10^{-3}$
199	$2\cdot10^{-3}$	$4\cdot10^{-3}$
221	$4\cdot10^{-3}$	$8\cdot10^{-3}$

According to the authors the data obtained below 100 °C may be overestimated. The compilers found the following solubility equation:

$$\log(\text{soly/mol \% O}) = -0.839 - 766\,(T/\text{K})^{-1} \quad r = 0.862.$$

Auxiliary Information

Method:
The alloy was contained in a crucible placed in a stainless steel capsule. It was saturated with gaseous O. The saturated alloy was filtered through a metal–ceramic frit with a pore size of 5–10 μm into a Ni crucible placed in the same capsule. The filtrate sample was vacuum distilled at ~800 K and ~1 Pa.[1] The remaining Na_2O was dissolved in H_2O and the alkalinity of the solution was determined by titration the results of which allowed the calculation of the solubility.

Source and Purity of Materials:
O: nothing specified.
K–Na eutectic: nothing specified.

Estimated Error:
Solubility: nothing specified; reading-out procedure ±10%.
Temperature: nothing specified; reading-out procedure ±1 K.

References:
[1]I. B. Dmitreva and E. E. Konovalov, *Metody Opredelenia Sostoyaniya Gazov v Metallakh* (Nauka, Moskva, 1968).

Components:
(1) Oxygen; O; [7782-44-7]
(2) Potassium–sodium eutectic; $K_{68}Na_{32}$; [11147-16-3]

Original Measurements:
M. N. Arnoldov, M. N. Ivanovskii, S. S. Pletenets, and A. D. Pleshivtsev, Atom. Energiya **32**, 234–235 (1972).

Variables:
Temperature: 373–548 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

Solubility results of O in liquid eutectic K–Na alloy were presented in graphical form. They were read out from the figure and recalculated to mol % O by the compilers.

t/°C	Solubility/mass % O	Solubility/mol % O
	Determinations from the saturation temperature	
100	$6\cdot10^{-4}$	$1.2\cdot10^{-3}$
118	$1.1\cdot10^{-3}$	$2.3\cdot10^{-3}$
143	$2.0\cdot10^{-3}$	$4.2\cdot10^{-3}$
151	$2.7\cdot10^{-3}$	$5.7\cdot10^{-3}$
152	$3.1\cdot10^{-3}$	$6.6\cdot10^{-3}$
157	$2.0\cdot10^{-3}$, $3.2\cdot10^{-3}$, $4.2\cdot10^{-3}$, $5.0\cdot10^{-3}$	$4.2\cdot10^{-3}$, $6.8\cdot10^{-3}$, $9.0\cdot10^{-3}$, $1.1\cdot10^{-2}$
159	$3.0\cdot10^{-3}$	$6.3\cdot10^{-3}$
165	$2.2\cdot10^{-3}$, $4.0\cdot10^{-3}$, $6.5\cdot10^{-3}$	$4.7\cdot10^{-3}$, $8.5\cdot10^{-3}$, $1.4\cdot10^{-2}$
169	$5.0\cdot10^{-3}$, $3.3\cdot10^{-3}$	$1.1\cdot10^{-3}$, $7.0\cdot10^{-3}$
172	$4.2\cdot10^{-3}$, $6.3\cdot10^{-3}$	$9\cdot10^{-3}$, $1.3\cdot10^{-2}$
197	$1.1\cdot10^{-2}$	$2.3\cdot10^{-2}$
198	$9.5\cdot10^{-3}$	$2.0\cdot10^{-2}$
200	$9.5\cdot10^{-3}$, $1.2\cdot10^{-2}$	$2.0\cdot10^{-2}$, $2.5\cdot10^{-2}$
207	$1.1\cdot10^{-2}$, $1.3\cdot10^{-2}$	$2.3\cdot10^{-2}$, $2.7\cdot10^{-2}$
212	$1.2\cdot10^{-2}$, $1.3\cdot10^{-2}$	$2.5\cdot10^{-2}$, $2.7\cdot10^{-2}$
220	$1.6\cdot10^{-2}$	$3.4\cdot10^{-2}$
224	$1.3\cdot10^{-2}$, $1.4\cdot10^{-2}$	$2.7\cdot10^{-2}$, $3.0\cdot10^{-2}$
228	$2.0\cdot10^{-2}$, $3.2\cdot10^{-2}$	$4.2\cdot10^{-2}$, $6.8\cdot10^{-2}$
235	$1.3\cdot10^{-2}$	$2.7\cdot10^{-2}$
238	$2.0\cdot10^{-2}$	$4.2\cdot10^{-2}$
240	$1.4\cdot10^{-2}$	$3.0\cdot10^{-2}$
245	$2.2\cdot10^{-2}$, $2.7\cdot10^{-2}$	$4.7\cdot10^{-2}$, $5.7\cdot10^{-2}$
247	$2.0\cdot10^{-2}$, $2.4\cdot10^{-2}$	$4.2\cdot10^{-2}$, $5.1\cdot10^{-2}$
253	$1.8\cdot10^{-2}$	$3.8\cdot10^{-2}$
260	$3.0\cdot10^{-2}$, $3.5\cdot10^{-2}$	$6.3\cdot10^{-2}$, $7.4\cdot10^{-2}$
267	$3.0\cdot10^{-2}$, $3.4\cdot10^{-2}$	$6.3\cdot10^{-2}$, $7.0\cdot10^{-2}$
271	$2.4\cdot10^{-2}$	$5.1\cdot10^{-2}$
273	$3.0\cdot10^{-2}$, $3.3\cdot10^{-2}$, $3.7\cdot10^{-2}$	$6.3\cdot10^{-2}$, $7.0\cdot10^{-2}$, $8.0\cdot10^{-2}$
275	$2.4\cdot10^{-2}$, $3.2\cdot10^{-2}$, $3.8\cdot10^{-2}$	$5.1\cdot10^{-2}$, $6.8\cdot10^{-2}$, $8.0\cdot10^{-2}$
	Determinations from chemical analysis	
110	$6.1\cdot10^{-4}$	$1.3\cdot10^{-3}$
120	$1.2\cdot10^{-3}$	$2.5\cdot10^{-3}$
160	$2.3\cdot10^{-3}$	$4.9\cdot10^{-3}$
162	$3.2\cdot10^{-3}$	$6.8\cdot10^{-3}$
165	$5.1\cdot10^{-3}$	$1.1\cdot10^{-2}$
185	$6.4\cdot10^{-3}$	$1.3\cdot10^{-2}$
200	$7.4\cdot10^{-3}$	$1.6\cdot10^{-2}$
228	$1.0\cdot10^{-2}$; $1.0\cdot10^{-2}$	$2.1\cdot10^{-2}$; $2.1\cdot10^{-2}$
268	$2.1\cdot10^{-2}$	$4.4\cdot10^{-2}$
270	$1.5\cdot10^{-2}$	$3.2\cdot10^{-2}$

All results were approximated by the authors with the solubility equation, tested by the compilers:

$$\log(\text{soly/mol \% O}) = 2.08 - 1970\,(T/\text{K})^{-1}.$$

Auxiliary Information

Method:
The solubility experiments were performed in a loop with the liquid K–Na eutectic. This was equipped with a purifier, an injector of O, a sampler, and an indicator for the determination of the saturation temperature. A known amount of O was introduced into the alloy by the injector. The Na_2O formed was equilibrated with the circulating alloy at constant temperature. The saturation temperature of the alloy with O was determined by means of a plugging indicator which measured the temperature of the alloy in the loop at its plugging with precipitated Na_2O.[1] Another set of the samples was analyzed by an unspecified chemical analysis at a temperature decrease <10 K/min. A subsequent portion of O was injected and the experiment repeated.

Source and Purity of Materials:
O: nothing specified.
K–Na alloy: purified by a cold trap.

Estimated Error:
Solubility: precision up to ±18% at confidence level of 95%; reading-out procedure ±3%.
Temperature: nothing specified; reading-out procedure ±0.5 K.

References:
[1]F. A. Kozlov, E. K. Kuznetsov, and V. I. Subbotin, *Zhidkie Metally* (Atomizdat, Moskva, 1967), pp. 324–326.

Components:
(1) Oxygen; O; [7782-44-7]
(2) Potassium–sodium eutectic; $K_{68}Na_{32}$; [11147-16-3]

Original Measurements:
T. Sakai, M. Gunji, S. Matsumoto, and Y. Ishii, J. Nucl. Sci. Technol. **20**, 1032–1038 (1983).

Variables:
Temperature: 363–483 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of O in liquid K–Na eutectic (32 mol % Na) alloy was measured

t/°C	Solubility/mass % O	Solubility/mol % O[a]
90	$2.0\cdot10^{-5}$; $2.5\cdot10^{-5}$; $3.4\cdot10^{-5}$; $3.7\cdot10^{-5}$	$6.2\cdot10^{-5}$
120	$6.6\cdot10^{-5}$; $7.4\cdot10^{-5}$; $1.16\cdot10^{-4}$, $1.54\cdot10^{-4}$; $2.1\cdot10^{-4}$	$2.6\cdot10^{-4}$
150	$1.82\cdot10^{-4}$; $2.2\cdot10^{-4}$; $2.3\cdot10^{-4}$; $2.4\cdot10^{-4}$	$6.8\cdot10^{-4}$
	$2.6\cdot10^{-4}$; $2.7\cdot10^{-4}$; $3.2\cdot10^{-4}$; $3.4\cdot10^{-4}$	
	$3.8\cdot10^{-4}$; $4.1\cdot10^{-4}$; $4.3\cdot10^{-4}$; $4.4\cdot10^{-4}$; $4.5\cdot10^{-4}$	
180	$7.6\cdot10^{-4}$; $8.7\cdot10^{-4}$; $1.00\cdot10^{-3}$; $1.16\cdot10^{-3}$; $1.36\cdot10^{-3}$	$2.2\cdot10^{-3}$
210	$1.55\cdot10^{-3}$; $1.70\cdot10^{-3}$; $1.81\cdot10^{-3}$; $2.0\cdot10^{-3}$; $2.2\cdot10^{-3}$; $3.0\cdot10^{-3}$	$4.3\cdot10^{-3}$;

[a]Mean value calculated by the compilers.

The authors formulated the solubility equation, the validity of which was tested by the compilers:

$$\log(\text{soly/mass \% O}) = 3.09 - 2795\ (T/\text{K})^{-1}.$$

Most of the residue was recognized as Na_2O equilibrium solid phase.

Auxiliary Information

Method:
The equilibration of O with the K–Na eutectic alloy was performed in a test loop made of 304 type stainless steel. A cold trap was packed with stainless steel wool. Its temperature was measured at 10 points by means of Chromel/Alumel thermocouples and the minimum temperature was assumed to be the one at which the O concentration was controlled. The sampling apparatus consisted of a sampling tank, a distillation chamber, a heating element, and vacuum/Ar lines. The distillation chamber was made of Pyrex glass. The sampling crucibles were made of Ni. The crucible was immersed in a cleaning mixture (HNO_3–H_2SO_4–H_3PO_4–CH_3COOH 3:1:1:5) at 363 K for 30 s, cleaned ultrasonically in distilled H_2O, dried in a vacuum oven, and finally baked out at 773 K under a pressure of $1.3\cdot10^{-3}$ Pa. The crucible was immersed 10 min in the K–Na alloy in an Ar atmosphere. The distillation chamber was evacuated to a pressure $<1.3\cdot10^{-2}$ Pa and heated to perform the distillation of K–Na. The end of the distillation was detected by a rapid temperature increase. The residue was dissolved in diluted HNO_3 and the amounts of Na and K were determined by atomic absorption spectrometry. The O quantity was calculated assuming that O was bounded as Na_2O or K_2O.

Source and Purity of Materials:
O: nothing specified.
K–Na: nuclear purity.
Ar: nothing specified.

Estimated Error:
Solubility: detection level of $(1.6–9)\cdot10^{-5}$ mass % O depending on the crucible volume.
Temperature: nothing specified.

Components:
(1) Oxygen; O; [7782-44-7]
(2) Potassium–sodium alloys; K–Na;

Original Measurements:
D. Krishnamurthy, S. Vana Varamban, A. Thiruvengadasami, and C. K. Mathews, J. Less-Common Met. **153**, 363–372 (1989).

Variables:
Temperature: 333–703 K;
alloy composition: 32.4–95.8 mol % Na

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of O in the liquid $K_{42}Na_{58}$ alloy was determined, mol % were calculated by the compilers

T/K	Solubility/mass % O	Solubility/mol % O
333	$3.60\cdot10^{-3}$	$6.7\cdot10^{-3}$
	$3.55\cdot10^{-3}$	$6.6\cdot10^{-3}$
338	$3.96\cdot10^{-3}$	$7.4\cdot10^{-3}$
	$3.92\cdot10^{-3}$	$7.3\cdot10^{-3}$
352	$5.24\cdot10^{-3}$	$9.8\cdot10^{-3}$
	$5.32\cdot10^{-3}$	$9.9\cdot10^{-3}$
362	$6.61\cdot10^{-3}$	$1.23\cdot10^{-2}$
	$6.69\cdot10^{-3}$	$1.25\cdot10^{-2}$
369	$7.15\cdot10^{-3}$	$1.33\cdot10^{-2}$
	$7.19\cdot10^{-3}$	$1.34\cdot10^{-2}$
386	$1.00\cdot10^{-2}$	$1.87\cdot10^{-2}$
	$9.66\cdot10^{-3}$	$1.80\cdot10^{-2}$
410	$1.45\cdot10^{-2}$	$2.70\cdot10^{-2}$
	$1.50\cdot10^{-2}$	$2.77\cdot10^{-2}$
	$1.43\cdot10^{-2}$	$2.65\cdot10^{-2}$
413	$1.53\cdot10^{-2}$	$2.84\cdot10^{-2}$
	$1.49\cdot10^{-2}$	$2.76\cdot10^{-2}$
418	$1.66\cdot10^{-2}$	$3.10\cdot10^{-2}$
	$1.58\cdot10^{-2}$	$2.92\cdot10^{-2}$
439	$2.07\cdot10^{-2}$	$3.90\cdot10^{-2}$
	$2.14\cdot10^{-2}$	$4.02\cdot10^{-2}$
465	$3.02\cdot10^{-2}$	$5.60\cdot10^{-2}$
	$3.02\cdot10^{-2}$	$5.60\cdot10^{-2}$
507	$4.65\cdot10^{-2}$	$8.7\cdot10^{-2}$
	$4.78\cdot10^{-2}$	$8.9\cdot10^{-2}$
	$4.69\cdot10^{-2}$	$8.7\cdot10^{-2}$
526	$5.58\cdot10^{-2}$	0.104
	$5.69\cdot10^{-2}$	0.106
540	$6.46\cdot10^{-2}$	0.120
	$6.35\cdot10^{-2}$	0.118
569	$8.15\cdot10^{-2}$	0.152
	$7.92\cdot10^{-2}$	0.147
	$8.20\cdot10^{-2}$	0.153
581	$9.12\cdot10^{-2}$	0.170
	$9.18\cdot10^{-2}$	0.171
621	0.1197	0.221
	0.119	0.220
	0.121	0.222
641	0.135	0.252
	0.133	0.248
670	0.164	0.302
	0.162	0.298
678	0.169	0.311
	0.169	0.311
	0.168	0.309
703	0.194	0.360
	0.195	0.362

The compilers formulated the solubility equation:

$$\log(\text{soly/mol \% O}) = 0.578 - 1101\ (T/\text{K})^{-1} \quad r = 0.999.$$

The solubility of O in the liquid $K_{68}Na_{32}$ eutectic alloy

T/K	Solubility/mass % O	Solubility/mol % O
372	$8.15\cdot10^{-3}$	$1.73\cdot10^{-2}$
	$7.25\cdot10^{-3}$	$1.54\cdot10^{-2}$
473	$3.38\cdot10^{-2}$	$7.2\cdot10^{-2}$
	$3.31\cdot10^{-2}$	$7.0\cdot10^{-2}$
	$3.31\cdot10^{-2}$	$7.0\cdot10^{-2}$
578	$8.75\cdot10^{-2}$	0.185
	$8.80\cdot10^{-2}$	0.186
673	0.163	0.351
	0.163	0.351

The compilers formulated the solubility equation:

$$\log(\text{soly/mol \% O}) = 1.150 - 1090\ (T/\text{K})^{-1} \quad r = 0.9999.$$

The solubility of O at 473 K at various K–Na alloy compositions

Mass % K	mol % K[a]	Solubility/mass % O	Solubility/mol % O[a]
7.0	4.2	$5.51\cdot10^{-3}$	$8.2\cdot10^{-3}$
		$4.69\cdot10^{-3}$	$6.9\cdot10^{-3}$
10.5	6.4	$1.34\cdot10^{-2}$	$2.0\cdot10^{-2}$
		$1.18\cdot10^{-2}$	$1.77\cdot10^{-2}$
12.1	7.5	$2.00\cdot10^{-2}$	$3.0\cdot10^{-2}$
		$1.98\cdot10^{-2}$	$3.0\cdot10^{-2}$
13.4	8.3	$2.21\cdot10^{-2}$	$3.4\cdot10^{-2}$
		$2.14\cdot10^{-2}$	$3.3\cdot10^{-2}$
23.5	15.3	$2.84\cdot10^{-2}$	$4.5\cdot10^{-2}$
		$2.77\cdot10^{-2}$	$4.4\cdot10^{-2}$
29.8	20.0	$3.25\cdot10^{-2}$	$5.3\cdot10^{-2}$
		$3.15\cdot10^{-2}$	$5.2\cdot10^{-2}$
34.7	23.8	$3.32\cdot10^{-2}$	$5.6\cdot10^{-2}$
		$3.29\cdot10^{-2}$	$5.5\cdot10^{-2}$
40.7	28.8	$3.43\cdot10^{-2}$	$5.9\cdot10^{-2}$
		$3.34\cdot10^{-2}$	$5.8\cdot10^{-2}$
55.0	42.4	$3.31\cdot10^{-2}$	$5.8\cdot10^{-2}$
78.0	67.6	$3.38\cdot10^{-2}$	$7.2\cdot10^{-2}$
		$3.31\cdot10^{-2}$	$7.0\cdot10^{-2}$
		$3.31\cdot10^{-2}$	$7.0\cdot10^{-2}$

[a]Calculated by the compilers.

Na_2O was found as the equilibrium solid phase saturating all alloys.

Auxiliary Information

Method:

The alloys were prepared in an inert atmosphere from corresponding amounts of K and Na. They were transferred to a stainless steel vessel lined with a leak-free Ni container. The assembly was connected to an inert gas manifold and heated to ~525 K. O gas was injected into the Ar stream and added in small increments. After equilibration for sufficient time at fixed temperature, the alloy was sampled through a Ni filter with the pore size 5 μm placed in the bottom of a sample holder. Three samples of the saturated alloy were simultaneously taken at each equilibrium temperature. The samples were vacuum distilled at $1.3\cdot10^{-3}$ Pa and 573 K. The residue was analyzed for the K and Na contents. The composition of the alloy was found by analysis of the distillate.

Source and Purity of Materials:

O: nothing specified.
K: from Heavy Water Plant, India.[1] The metal was melted in a stainless steel tray and maintained at 373 K for few hours. The oxide surface was skimmed off and the metal distilled under vacuum of $1.3\cdot10^{-3}$ Pa. It contained $2\cdot10^{-4}$ % Na.
Na: nuclear grade of purity.
Ar: "high purity."

Estimated Error:

Solubility: precision better than ±5% (by the compilers).
Temperature: controlled to ±1 K.

References:

[1]D. Krishnamurthy, A. Thiruvengadasami, N. P. Bhat, and C. K. Mathews, J. Less-Common Met. **135**, 285–292 (1987).

Components:

(1) Oxygen; O; [7782-44-7]
(2) Potassium–sodium eutectic; $K_{68}Na_{32}$; [11147-16-3]

Original Measurements:

M. N. Ivanovskii, V. A. Morozov, A. L. Shimkevich, and N. N. Ponomarev-Stepnoi, *Space Nuclear Power Systems*, edited by M. S. El-Genk and M. D. Hoover (Orbit Books, Malabar, FL, 1992), pp. 465–469.

Variables:

Temperature: 386–575 K

Prepared by:

H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of O in the liquid K–Na eutectic alloy (32 mol % Na). The data were read from figures and recalculated to mol % O by the compilers.

T/K	Solubility/mass % O	Solubility/mol % O
386	$6.7\cdot10^{-4}$	$1.43\cdot10^{-3}$
439	$2.8\cdot10^{-3}$	$6.0\cdot10^{-3}$
465	$4.9\cdot10^{-3}$	$1.04\cdot10^{-2}$
478	$6.8\cdot10^{-3}$	$1.45\cdot10^{-2}$
506	$1.47\cdot10^{-2}$	$3.1\cdot10^{-2}$
532	$2.0\cdot10^{-2}$	$4.3\cdot10^{-2}$
575	$4.4\cdot10^{-2}$	$9.3\cdot10^{-2}$

The compilers formulated the solubility equation:

$$\log(\text{soly/mol \% O}) = 2.681 - 2146\ (T/\text{K})^{-1} \quad r = 0.998.$$

Auxiliary Information

Method:

The K–Na–O system was studied in a loop with isothermal circulation using an electrochemical cell, plugging indicator, and distillation sampler. Portions of the liquid K–Na alloy were thermocycled in the loop in the temperature range 300–800 K with a period <200 h. Samples of the alloy saturated with O were analyzed by an unspecified method.

Source and Purity of Materials:

O: nothing specified.
K–Na alloy: initially contained $\sim3\cdot10^{-4}$ % O.

Estimated Error:

Solubility: precision ±7%; reading-out procedure ±3%.
Temperature: nothing specified; reading-out procedure ±2 K.

5.11. Potassium–Potassium Hydroxide

Components:
(1) Potassium hydroxide; KOH; [1310-58-3]
(2) Potassium; K; [7440-09-7]

Evaluated by:
Hans Ulrich Borgstedt, Forschungszentrum Karlsruhe, Germany and Cezary Guminski, University of Warsaw, Poland, July 1997.

Critical Evaluation

Although it was not investigated in detail, the simultaneous presence of H and O in liquid K leads to the formation of KOH therein. Von Hevesy[1] measured a solubility of K in liquid KOH which unexpectedly decreased with the increase of temperature from 11.5 mol % K at 753 K to 1.3 mol % K at 973 K. Such behavior cannot be explained in light of the subsequent paper of Mitkevich and Grot[2] who observed the typical increase of both the mutual solubilities of K and KOH with temperature and constructed the phase diagram of the K–KOH system. The critical miscibility temperature is ~873 K. The results of Mitkevich and Grot[2] are much more convincing than of Von Hevesy.[1] Perhaps the materials used by Von Hevesy[1] were impure and probably decomposed at high temperature.

An introduction of Na or NaOH into the K–KOH system causes changes of the equilibrium. Such a multicomponent system was first investigated by Rinck[3] who determined the equilibrium constant of the reaction:

$$KOH + Na \leftrightarrow K + NaOH. \quad (1)$$

However, Rinck[3] neglected the solubility of the hydroxide in the metallic phase and the solubility of the metals in the hydroxide phase. Independently, the system was more exactly treated by Berdichevskii and Morachevskii[4] and Mitkevich and Shikhov.[5] Even at ~773 K, at which temperature both groups performed experiments, it is difficult to compare the results of Berdichevskii and Morachevskii[4] and Mitkevich and Shikhov,[5] since Berdichevskii and Morachevskii[4] analyzed only the hydroxide phase, whereas Mitkevich and Shikhov[5] neglected the solubility of the metals in the hydroxide and opposite and took into account the partial decomposition of NaOH to Na_2O and NaH, whose possibility was otherwise neglected by Berdichevskii and Morachevskii.[4] Without further detailed studies of this multicomponent system the results of Berdichevskii and Morachevskii[4] and Mitkevich and Shikhov[5] are premature.

The K–KOH phase diagram, based on Mitkevich and Grot,[2] is shown in Fig. 40. KOH melts at 677 K and undergoes a polymorphic transition at 522 K.

Tentative values of the solubility of KOH in liquid K

T/K	Solubility/mol % KOH	Source
373	0.3	(2) extrapolated
473	1	(2) interpolated
573	3	(2)
674	14 monotectic	(2)
773	25	(2)
~873	50 critical	(2)

Tentative values of the solubility of K in liquid KOH

T/K	Solubility/mol % K	Source
674	2 monotectic	(2) interpolated
773	7	(2)

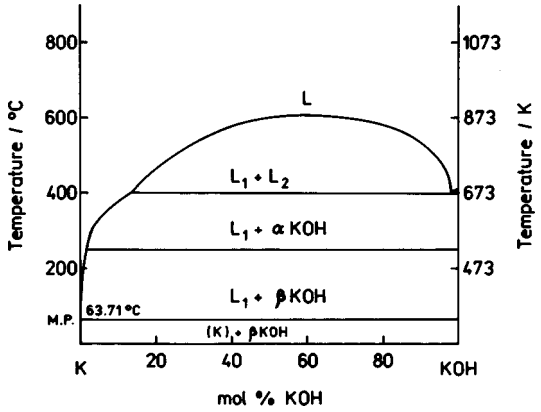

FIG. 40. K–KOH phase diagram.

References:
[1]G. von Hevesy, Z. Elekrochem. **15**, 529 (1909).
[2]E. M. Mitkevich and L. S. Grot, Zh. Neorg. Khim. **11**, 902 (1966).
[3]E. Rinck, Ann. Chim. **18**, 395 (1932).
[4]N. I. Berdichevskii and A. G. Morachevskii, Zh. Prikl. Khim. **39**, 791 (1966).
[5]E. M. Mitkevich and B. A. Shikhov, Zh. Neorg. Khim. **12**, 1041 (1967).

Components:
(1) Potassium hydroxide; KOH; [1310-58-3]
(2) Potassium; K; [7440-09-7]

Original Measurements:
G. von Hevesy, Z. Elektrochem. **15**, 529–536 (1909).

Variables:
Temperature: 753–973 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data
The solubility of K in liquid KOH was determined

t/°C	Solubility/g K in 100 g KOH	Solubility/mol % K	mol % KOH[a]
480	8.3±0.6	11.5	88.5
600	3.5±0.5	4.9	95.1
650	2.4±0.4	3.4	96.6
700	0.9±0.4	1.3	98.7

[a]Calculated by the compilers.

Auxiliary Information

Method:
A Fe tube was filled with KOH and K. It was closed and heated in an electric oven for 50 h at the desired temperature. The temperature was controlled by means of thermocouples of the Le Chatelier type. The tube was withdrawn from the oven and cooled quickly in water. The cold tube was opened under petroleum. The hydroxide and metallic phases were sampled. The content of K was analyzed from volumetric determination of H evolved during the reaction with H_2O. The amount of KOH was titrated with HCl solution.

Source and Purity of Materials:
KOH: probably dried in a Ni container in H stream for several hours.
K: nothing specified.

Estimated Error:
Solubility: precision better than ±44%.
Temperature: nothing specified.

Components:
(1) Potassium hydroxide; KOH; [1310-58-3]
(2) Potassium; K; [7440-09-7]

Original Measurements:
E. M. Mitkevich and L. S. Grot, Zhur. Neorg. Khim. **11**, 902–909 (1966).

Variables:
Temperature: 388–873 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data
The liquidus line of the K–KOH system was established by analysis of samples

t/°C	Solubility/mass % K	Solubility/mol % KOH[a]
115	99.3	0.5
300	94.8	3.7
350	88.4	8.4
360	86.8	9.6
400	80.3	14.6
410	77.5; 78.8; 78.7	16.8; 15.5; 15.4
410[b]	2.3; 2.15; 2.4;	96.7; 96.9; 96.6
450	71.5; 74.2	21.7; 19.3
450[b]	2.7; 2.9	96.2; 95.9
500	60.1; 67.3; 62.9; 58.1; 63.1	31.6; 25.3; 29.3; 33.5; 28.9
500[b]	4.9; 3.9; 5.6; 4.0	93.1; 94.2; 92.2; 94.0
550	58.5; 56.1	32.8; 35.3
550[b]	13.1; 9.6	82.2; 86.8
600	53.3; 43.8; 44.5; 49.6; 41.7	37.9; 47.2; 46.5; 41.5; 49.4
600[b]	38.4; 39.7; 40.0; 35.4; 40.8	52.8; 51.4; 51.1; 56.0; 50.2

[a]Calculated by the compilers.
[b]On the KOH rich side.

Thermal analysis was performed for ten samples in the composition range 4.2–89.2 mass % KOH. Polymorphic transition of KOH was observed at 248±3 °C and the monotectic temperature at 401±2 °C.

Auxiliary Information

Method:
Two Ni crucibles were placed in a Cu block. The block was placed in an oven. One empty crucible served as a reference. KOH was introduced into another crucible. Liquid K was dosed into the crucible from a syringe. The crucible was closed. A Chromel/Alumel thermocouple was used for recording of heating and cooling curves. Analyses of samples was performed in a container made of stainless steel. K and KOH were equilibrated for 1–5 h. Samples of both phases were withdrawn with the use of Cu tubes. After cooling, the tubes were cut into pieces and reacted with H_2O. No corrosion of tubes was observed. The samples were analyzed by reaction with H_2O (K estimated from H volume), by reaction with acid (K+KOH estimated) and by $KClO_4$ precipitation (K+KOH estimated). The experiments were carried out in a N atmosphere.

Source and Purity of Materials:
KOH: prepared from K and H_2O in a N atmosphere; the solution heated up to H_2O evaporation; deposit heated in a Ni crucible at 773 K in the N atmosphere; a small amount of K was added into; final purity 98.9+% with 0.5% K and $<0.01\%$ K_2CO_3 .
K: liquid metal filtered at 343–373 K into a container. Final purity 99.7% with 0.03%–0.05% Na.
N: ''purified and dried.''

Estimated Error:
Solubility: nothing specified; better than ±10% (by the compilers).
Temperature: stability during sampling ±2 K; precision in thermal analysis ±2 K.

Components:
(1) Potassium hydroxide; KOH; [1310-58-3]
(2) Potassium-sodium alloy; K–Na;

Original Measurements:
N. I. Berdichevskii and A. G. Morachevskii, Zh. Prikl. Khim. **39**, 791–794 (1966).

Variables:
One temperature: 773 K; initial alloy composition: 36.5–81.1 mol % Na

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

Saturating contents of metals (K+Na) in KOH–NaOH melt were determined by two methods

Content of hydroxide phase/mass %				Content of hydroxide phase/mol %			
Total		Dissolved		Components[a]			
K	Na	K	Na	K	Na	KOH	NaOH
from H evolution analysis							
39.9	30.6	11.3	10.6	10.8	19.5	20.3	49.4
49.5	15.6	9.9	3.9	3.9	17.0	11.8	67.2
39.6	26.7	8.4	4.6	4.9	15.3	23.5	56.4
37.1	29.7	6.4	6.4	6.9	11.8	25.1	56.2
19.7	49.6	1.40	9.2	11.4	2.9	47.4	38.3
19.5	49.2	0.93	6.1	7.4	1.9	52.2	38.4
21.4	49.1	2.20	3.3	4.4	3.9	53.6	38.1
16.9	52.0	1.3	4.2	5.2	2.8	59.3	32.8
21.3	45.7	0.86	4.3	5.3	1.8	50.6	42.4
15.6	52.9	0.78	4.3	5.4	1.7	61.2	31.7
from excess alkality							
39.9	30.6	11.7	11.0	11.2	20.2	20.0	48.6
49.5	15.6	9.3	3.6	3.7	16.0	12.0	68.3
39.6	26.7	8.1	4.4	4.6	14.3	23.2	57.9
37.1	29.7	6.0	6.0	6.5	11.1	25.5	56.9
19.7	49.6	1.5	9.8	11.9	3.1	47.9	37.2
19.5	49.2	1.25	8.2	10.0	2.6	49.7	37.7
21.4	49.1	2.3	3.4	4.0	4.6	53.4	38.0
16.9	52.0	1.89	6.0	7.4	4.0	57.0	31.6
21.3	45.7	0.96	4.8	5.9	2.0	50.0	42.1
15.6	52.9	1.00	5.5	6.9	2.1	59.7	31.3

[a]Calculated by the compilers.

The melting point of KOH was found at 405 °C.

Auxiliary Information

Method:
Equilibration of KOH and Na was performed in a Ni vessel which had a facility for sampling. KOH was introduced into the container in liquid state, then Na was added. The vessel was tightly closed, placed in an oven, and shaken during rotation for 1 h. It remained stable for 0.5 h in the oven to allow effective phase separation and cooled down by means of transformator oil. It was further heated to 373–393 K to melt the metallic phase. Samples of this phase were collected in glass ampoules with capillaries. Samples of the hydroxide phase were cut off as solids. The metallic phase was analyzed by flame photometry. The total alkalinity, after decomposition with H_2O, was determined by titration. The content of cations in the hydroxide phase was found by flame photometry and the total alkalinity by an acidimetric titration.

Source and Purity of Materials:
KOH: pure for analysis from Czech republic; dried in a Ni container in N atmosphere at 773–823 K for 6 h.
Na: contained <0.05% K and practically did not contain other metal impurities.
N: nothing specified.

Estimated Error:
Solubility: precision ±2%.
Temperature: stability ±5 K.

Components:
(1) Potassium hydroxide; KOH; [1310-58-3]
(2) Potassium-sodium alloy; K–Na;

Original Measurements:
E. M. Mitkevich and B. A. Shikhov, Zh. Neorg. Khim. **12**, 1041–1044 (1967).

Variables:
Temperature: 568–780 K; final alloy composition 9.5–62.2 mol % Na

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

During the equilibration of the KOH–NaOH–K–Na system additional formation of NaH and Na_2O occurs. Compositions of equilibrium phases were analyzed.

	Hydroxide phase/mol %				Metallic phase/mol %		
t/°C	NaH	Na_2O	NaOH	KOH	Na	K	KOH
300	24.7	0.9	34.4	39.9	54.3	45.7	–
415	19.3	2.1	44.9	33.7	58.9	37.6	3.5
470	12.8	4.3	52.0	31.0	62.2	33.3	4.5
120	–	–	–	–	27.4	72.6	–
295	15.1	0	29.4	56.0	26.7	70.1	3.1
396	12.7	0	34.2	53.3	31.2	62.0	6.8
467	6.4	1.1	37.3	52.2	36.4	55.8	7.8
507	5.2	5.2	38.9	50.6	–	–	–
300	–	–	–	–	10.7	85.8	3.5
–	–	–	–	–	9.5	87.3	3.2
405	3.6	2.0	23.9	70.5	11.8	80.6	7.6
490	3.5	3.5	24.7	68.3	15.2	73.5	11.2
–	3.5	3.0	25.5	68.0	15.2	71.9	12.8

Auxiliary Information

Method:
An apparatus was made of Pyrex glass. The components were placed in Ni barrels leaving 20% internal volume free. The mixtures were heated and equilibrated. Both phases (hydroxide and metallic) were filtered. The composition of the samples was analyzed by reaction with H_2O, measuring the H volume evolved by the reaction of metals. The total K content was found by means of the perchlorate method. The content of NaH was found by an unspecified method. The total alkalinity was determined by titration of the resulting solutions with 1 mol/dm^3 HCl. The composition of the phases was calculated from mass balance equations.

Source and Purity of Materials:
KOH: anhydrous, analytically pure.
NaOH: prepared from Na and H_2O in a N atmosphere, heated at 773 K; undetectable H_2O and CO_3^{2-}.
K: contained 1% Na.
Na: electrolytic.

Estimated Error:
Solubility: precision better than ±0.5%.
Temperature: nothing specified.

5.12. Potassium–Sulfur

Components:
(1) Sulfur; S; [7704-34-9]
(2) Potassium; K; [7440-09-7]

Evaluated by:
Hans Ulrich Borgstedt, Forschungszentrum Karlsruhe, Germany and Cezary Guminski, University of Warsaw, Poland, July 1997.

Critical Evaluation

S reacts with K forming several sulfides K_2S_x ($x=1,2,3,4,5,6$) depending on the relations of the reagents used. Only Dworkin and Bredig[1] investigated the K-rich region of the K–S phase diagram. They observed a miscibility gap at 1156 K between ~21 and 31 mol % S and a solubility of K_2S in liquid K increasing from 5 to 18 mol % S at 1042–1144 K. An extrapolation of these data to the melting point of K suggests the solubility $<10^{-7}$ mol % S which seems to be a too low value.

The majority of investigators were engaged in experiments in the range between K_2S and S. There is general agreement of Thomas and Rule,[2] Pearson and Robinson,[3] Crosbie,[4] Janz and Rodgers,[5] and Feher and Berthold[6] concerning the congruent melting of K_2S, K_2S_2, K_2S_3, K_2S_4, K_2S_5, and K_2S_6. Six eutectic points are observed inbetween. The eutectic between K_2S and K_2S_2 is poorly defined, and it is possible that K_2S_2 melts peritectically. Due to a very strong tendency of these salt melts to supercooling, some fragments of the K–S phase diagram have a tentative character and are only accurate to ±15 K.

On the S-rich side, one observes a second miscibility gap and the corresponding monotectic reaction at 561 K, which should extend from >75 mol % S, since Thomas and Rule,[2] Pearson and Robinson,[3] and Janz and Rodgers[5] observed congruent melting of K_2S_6. In fact, Crosbie,[4] Morachevskii *et al.*,[7] and Maiorova[8] obtained data suggesting that the miscibility gap starts at <75 mol % S; therefore, the data of Crosbie[4] and Morachevskii *et al.*[7] should be treated as doubtful without reinvestigation of this composition range. It is also possible that K_2S_6 melts syntectically. The paper of Maiorova[8] was not available to the evaluators.

Measuring the emf of the K_2S_6–S electrolyte Crosbie[4] deduced a very slight solubility of K (K_2S_6 in fact) in liquid S; no numerical result was reported therein. The K–S phase diagram based on Sangster and Pelton[9] is shown in Fig. 41.

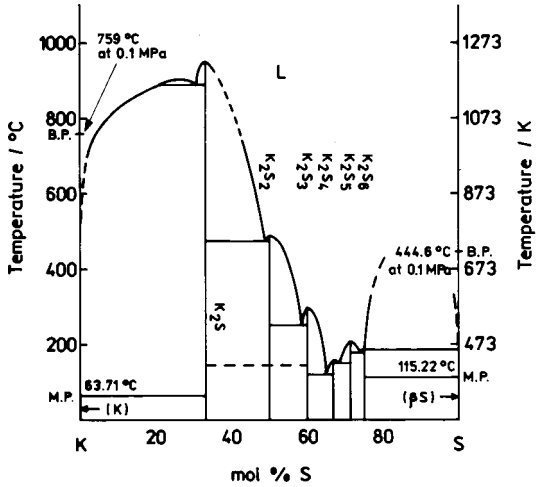

FIG. 41. K–S phase diagram.

The tentative and doubtful (d) values of the solubility of S in liquid K on the K-rich side

T/K	Solubility/mol % S	Source
973	~2	(1) extrapolated
1073	8	(1) interpolated
1156	22 monotectic	(1) interpolated
1221	33.3 congruent	(1)
1004	42 (d)	(3)
748	49 (d) eutectic	(3)
760	50 congruent	(5)

The tentative and doubtful (d) values of the solubility of S in liquid K on the S-rich side.

T/K	Solubility/mol % S	Source
524	59 eutectic	(2),(3)
575	60 congruent	(5)
~393	65 (d) eutectic	(2) extrapolated
427	66.7 congruent	(5)
~422	67.5 (d) eutectic	(2) extrapolated
479	71.4 congruent	(2),(5)
456	74 (d) eutectic	(2)
462	75 congruent	(5)
461	75.5 (d) monotectic	(2),(3) extrapolated
523	75.5 (d)	(4)
598	76.8	(4)

References:

[1]A. S. Dworkin and M. A. Bredig, J. Phys. Chem. **71**, 764 (1967).
[2]J. S. Thomas and A. Rule, J. Chem. Soc. **111**, 1063 (1917).
[3]T. G. Pearson and P. L. Robinson, J. Chem. Soc. 1304 (1931).
[4]G. M. Crosbie, J. Electrochem. Soc. **129**, 2707 (1982).
[5]G. J. Janz and D. J. Rodgers, J. Chem. Eng. Data **28**, 331 (1983).
[6]F. Feher and H. J. Berthold, Z. Anorg. Chem. **274**, 223 (1953).
[7]A. G. Morachevskii, V. S. Sharivker, E. B. Klebanov, and E. A. Maiorova, Zh. Prikl. Khim. **61**, 2311 (1988); J. Appl. Chem. USSR **61**, 2117 (1988).
[8]E. A. Maiorova, Ph. D. thesis, Leningrad, Russia, 1975; cited after Ref. 7.
[9]J. Sangster and A. D. Pelton, J. Phase Equil. **8**, 82 (1997).

Components:
(1) Sulfur; S; [7704-34-9]
(2) Potassium; K; [7440-09-7]

Original Measurements:
J. S. Thomas and A. Rule, J. Chem. Soc. **111**, 1063–1085 (1917).

Variables:
Temperature: 374–741 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data
A part of the K–S liquidus was determined

t/°C	Solubility/mass % S[a]	Solubility/mol % S[b]
467.5	44.55	49.5
468	45.66	50.5
464.5	46.89	51.7
452.5	48.09	53.0
433	49.18	54.1
390.5	50.63	55.5
360	51.97	56.9
311	53.02	57.9
251.5	54.32	59.2
251.6	55.51	60.3
238	57.06	61.8
217.4	57.78	62.6
189	58.93	63.6
160.5	59.62	64.3
101(?)	60.15	64.8
130.7	60.55	65.2
141.6	60.95	65.6
145.5	62.02	66.6
152	62.38	66.9
166	62.72	67.2
178.2	63.70	68.1
192	64.58	69.0
201.9	65.74	70.1
204.3	66.79	71.0
206.5	67.22	71.4
204.2	67.99	72.1
200	68.73	72.8
196.7	69.21	73.3
192.2	69.59	73.6
190	69.81	73.8
187	70.26	74.1
185.2	70.57	74.5
188.6	70.86	74.8
188.9	71.21	75.1
188	71.56	75.4
188.1	72.26	76.0
187.9	74.11	77.7
188.3	76.42	79.8

[a]Expressed as S in K_2S.
[b]Calculated by the compilers.

The compounds K_2S, K_2S_2, K_2S_3, K_2S_4, K_2S_5, and K_2S_6 were identified. A monotectic was observed at 188.3 °C between 75.4 mol % S and almost pure S. The S layer solidified at 117.5 °C.

Auxiliary Information

Method:
The K_2S–S mixtures were prepared from S, K_2S_5, and other compounds with less S. Melting the compounds was carried out in glass or porcelain containers in N atmosphere. The solidifying points of the melts were measured by means of a thermometer at $T<573$ K and with a carefully calibrated Pt/Pt–Rh thermocouple at $T>573$ K. The melts were analyzed for their S contents by precipitation of $BaSO_4$.

Source and Purity of Materials:
S: twice recrystallized from CS_2 and then heated at 373 K for several hours to remove the solvent; stored in a desicator over P_2O_5.
K_2S_5: prepared by reaction of S on alcoholic solutions of KHS, dried, and stored over P_2O_5.
K_2S_x: prepared by expelling S from K_2S_5 by heating in H stream.
N: purified and dried.

Estimated Error:
Solubility: nothing specified.
Temperature: accuracy of the thermometer ±0.2 K and of thermocouple ±1.5 K.

Components:
(1) Sulfur; S; [7704-34-9]
(2) Potassium; K; [7440-09-7]

Original Measurements:
T. G. Pearson and P. L. Robinson, J. Chem. Soc. 1304–1314 (1931).

Variables:
Temperature: 430–1113 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data
A part of the K–S liquidus was determined

t/°C	Solubility/mass % S[a]	Solubility/mol % S[b]
840	29.10	33.3
782	34.41	39.0
791	34.48	39.1
731	37.50	42.3
480	44.50	49.5
475	44.83	49.8
442	48.23	53.3
336	52.40	57.4
288	53.80	58.7
156.5	59.55	64.3
167.5	62.75	67.2
180.0	63.85	68.5
198.0	65.05	69.6
196.7	69.00	73.3
182.9	70.42	74.4
188.2	80.00	83.0

[a]Expressed as S in K_2S.
[b]Calculated by the compilers.

The miscibility gap was established at 188.2 °C. The following equilibrium phases were found: K_2S, K_2S_2, K_2S_3, K_2S_4, K_2S_5, and K_2S_6. A strong tendency to supercooling of the melts was noticed.

Auxiliary Information

Method:
The K_2S_x compounds were mixed in proper proportions. Their melting was carried out in test tubes made of Pyrex glass or glassed porcelain. A stirrer, thin-walled thermocouple sheath and delivery of N were introduced into the tubes. A Chromel/Eureca thermocouple was used up to 873 K and a Pt/Pt–Rh junction above this temperature. The thermocouples were calibrated for the boiling point of H_2O, naphthalene, and S, and the melting points of Sb, NaCl, and Ag. The tube was placed in a jacket furnace. The samples were cooled with rates of 1.5–5 K/s. After cooling to room temperature a portion of the melt was immediately analyzed. The remainder was stored in a sealed tube for microscopic examination.

Source and Purity of Materials:
S: twice recrystallized from CS_2 and dried several hours at 373 K.
K: from Imperial Chemical Industries Ltd.; kept under liquid paraffin, scrapped before use.
K_2S_x compounds: prepared under hot toluene by either addition of K or S to K_2S_4.
N: "dried and purified."

Estimated Error:
Solubility: precision not better than ±0.1 mol % (by the compilers).
Temperature: accuracy between ±0.5 and ±20 K, depending on the temperature level.

Components:
(1) Sulfur; S; [7704-34-9]
(2) Potassium; K; [7440-09-7]

Original Measurements:
F. Feher and H. J. Berthold, Z. Anorg. Chem. **274**, 223–233 (1953).

Variables:
Temperature: 432–793 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data
Melting temperatures of several K–S compounds were determined

t/°C	Compound	Solubility/mol % S[a]
≈520	K_2S_2	50.0
292	K_2S_3	60.0
159	K_2S_4	66.7
205	$K_2S_{4.7}$	70.1
211	K_2S_5	71.4
196	K_2S_6	75.0

[a]Calculated by the compilers.

Except $K_2S_{4.7}$, all other compounds are the equilibrium phases. Polymorphismus of K_2S_2 was not found.

Auxiliary Information

Method:
K_2S_2 was synthesized in liquid NH_3 by additions of K to dissolved S. The product loosed NH_3 upon heating up to 423 K. K_2S_3 was obtained from K_2S dissolved in absolute alcohol and S. The product was filtered off in a N atmosphere and dried in vacuum at 413 K. $K_2S_{4.7}$ was prepared in toluene and dried. K_2S_4 was prepared in NH_3 solution and dried in vacuum at 403 K. K_2S_5 was produced in alcohol and dried in vacuum at 413 K. K_2S_6 was obtained by melting K_2S_5 and S in vacuum. Melting points of the compounds prepared in these ways were determined by a Fe/Konstantan thermocouple (in the case of K_2S_2) and a mercury thermometer for the other compounds.

Source and Purity of Materials:
S: fine powder.
K: distilled in high vacuum and molten in N atmosphere.
N: dried subsequently over $Ca(OH)_2$–NaOH, KOH and molten K.

Estimated Error:
Solubility: precision ±1%.
Temperature: nothing specified; precision not better than ±1 K and accuracy ±10%.

Components:
(1) Sulfur; S; [7704-34-9]
(2) Potassium; K; [7440-09-7]

Original Measurements:
A. S. Dworkin and M. A. Bredig, J. Phys. Chem. **71**, 764–765 (1967).

Variables:
Temperature: 1042–1221 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data:
The K-rich part of the K–S liquidus was determined. The results were read from a figure and recalculated to mol % S by the compilers.

t/°C	Solubility/mol % K_2S in K	Solubility/mol % S
769	6.5	5
811	11	9
855	19	14
876	28	18
890	49	25
900	59	27
897	68	29
897	83	31
908	88	32
930	95	33

The melting point of K_2S was measured to be at 948 °C.

The monotectic temperature was found at 883 °C.

Auxiliary Information

Method:
All handling operations were performed in a He filled dry box. Inconel capsules with thermocouple wells were used as containers. A Pt/Pt–Rh(10%) thermocouple served for temperature measurements. K and K_2S were placed in the capsules which were closed by means of sealing. A rocking furnace permitted the mixing of the components before each cooling curve was run. The phase diagram was determined by thermal analysis.

Source and Purity of Materials:
S: triply sublimed, C-free.
K_2S: prepared by slowly adding S to excess of K in an inert atmosphere at 453–473 K. K excess was removed by distillation at 573–623 K under high vacuum. Final product 99+% pure with major impurities being K and K_2O.
K: contained <0.02% other metals.
He: "dry."

Estimated Error:
Solubility: nothing specified; reading-out procedure ±0.5 mol %.
Temperature: nothing specified; reading-out procedure ±1 K.

Components:
(1) Sulfur; S; [7704-34-9]
(2) Potassium; K; [7440-09-7]

Original Measurements:
G. M. Crosbie, J. Electrochem. Soc. **129**, 2707–2711 (1982).

Variables:
Temperature: 461–598 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data
Several points on the K–S liquidus were determined. They were read from figures and recalculated to mol % S by the compilers.

t/°C	Solubility/mol % S
225	74.1
275	75.0
325	76.8
250	75.3
250	62.5
310	58.8
270	60
250	61.5
220	63.6

A eutectic temperature was determined at 188 °C between the melting point of K_2S_6 and the K_2S_6–S miscibility gap. A very slight (but unspecified) solubility of K_2S_6 in liquid S was estimated.

Auxiliary Information

Method:
A β-alumina tube, containing 8.85% Na_2O and 0.75% Li_2O, was exposed to KCl vapor and rinsed in molten KNO_3 at 633 K for the replacement of Na into K. It was used as the solid electrolyte in the cell: Ni/K/K-β-alumina /K–S/C/Ni. The cell was carefully filled with S and K in N atmosphere or vacuum. The composition of the K–S phase was changed by Coulometric introduction of K into S. The open circuit voltages of the cell were measured. The solubilities were determined from breaks of the relations of the potentials versus the composition at selected temperatures. The temperature was measured using a Chromel/Alumel thermocouple in a sheath well immersed in liquid K.

Source and Purity of Materials:
S: reagent grade purity, then distilled.
K: "high purity" from Callery Chem. Comp. and contained $4.8\cdot10^{-3}$ % Si, $2.9\cdot10^{-3}$ % Na, and $1.5\cdot10^{-3}$ % Ca.
N: "dry."

Estimated Error:
Solubility: precision of Coulometric titration ±0.15%; accuracy of the composition of the melts ±0.5 mol % (by the compilers).
Temperature: nothing specified.

Components:
(1) Sulfur; S; [7704-34-9]
(2) Potassium; K; [7440-09-7]

Original Measurements:
G. J. Janz and D. J. Rodgers, J. Chem. Eng. Data **28**, 331–335 (1983).

Variables:
Temperature: 391–760 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data
Melting temperatures of several K–S compounds were determined

t/°C	Composition	Solubility/mol % S[a]
487	K_2S_2	50.0
302	K_2S_3	60.0
154	K_2S_4	66.7
205	K_2S_5	71.4
189	K_2S_6	75.0

[a]Calculated by the compilers.

Between 77.9 and 84.4 mol % S, at which temperature immiscibility of K_2S_6 and S is observed, the thermal arrests were recorded at ~118 and ~188 °C.

A solid phase transition in K_2S_2 was found at 146 °C.

Auxiliary Information

Method:
Differential scanning calorimetry using a commercially available apparatus was applied. The apparatus was calibrated on the melting points of In, Sn, Pb, KNO_3, and LiCl–KCl eutectic. Cooling and heating curves were recorded with a rate of 10 K/min. Typical capsule pans were used as the reaction chambers for the preparation of the polysulfides with K_2S_3 and S, as reactants. K_2S_3 was prepared from S and K in ethanolic solution and K_2S_2 from direct reaction of proper amounts of K_2S and K_2S_3. The substances were precisely weighed into pans. Formations of polysulfides, except K_2S_6, appeared to be slow. All transfers, weighing, and capsule crimp seals were carried out in N atmosphere. The samples were chemically analyzed.

Source and Purity of Materials:
S: "highly refined."
K: "purified" from Baker Chem. Co.
K_2S: 99.9% pure from Cerac Pure Chemicals Co. Inc.
N: "rigorously dry."

Estimated Error:
Solubility: accuracy of analysis ±2%.
Temperature: accuracy ±0.5 K.

Components:
(1) Sulfur; S; [7704-34-9]
(2) Potassium; K; [7440-09-7]

Original Measurements:
A. G. Morachevskii, V. S. Sharivker, E. B. Klebanov, and E. A. Mayorova, Zh. Prikl. Khim. **61**, 2311–2314 (1988); J. Appl. Chem. USSR **61**, 2117–2120 (1988).

Variables:
One temperature: 598 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

One point on the K–S liquidus, in the range of the S-rich miscibility gap, was determined at 598 K and 24.3 mol % K or 75.7 mol % S, as read out from a figure and recalculated to mol % S by the compilers. The same results were obtained independently on the type of solid electrolyte, glass, or a K substituted β-alumina ceramic.

Auxiliary Information

Method:
Dehydrated K_2S and S were mixed, molten in an Ar atmosphere, and conditioned at 600 K for 2 h. The K content was determined by flame photometry. The following cell: K/glass or K substituted β-alumina/K–S was established. The glass solid electrolyte had the composition: 31%–34% K_2O, 56%–58% SiO_2, and 9%–11% B_2O_3. The K-substituted β-alumina was obtained by exchange of K (from KCl vapor) in Na-β-alumina. A W wire was used for electrical contacts to the K electrode and a graphite rod was used for contact with the sulfide electrode. Potentials were measured at the fixed temperature. Breaks on curves relating potential versus composition observed for both cells correspond to the liquidus point.

Source and Purity of Materials:
S: "very pure."
K: did not contain measurable amounts of other metals.
K_2S: obtained by dehydration of $K_2S \cdot 5\ H_2O$ (pure for analysis), according to Kopylov.[1]
Ar: nothing specified.

Estimated Error:
Solubility: nothing specified; reading-out procedure ±0.5 mol %.
Temperature: nothing specified; precision probably ±1 K (by the compilers).

References:
[1]N. I. Kopylov, Zh. Neorg. Khim. **13**, 529–532 (1968).

5.13. Potassium–Selenium

Components:
(1) Selenium; Se; [7782-49-2]
(2) Potassium; K; [7440-09-7]

Evaluated by:
Hans Ulrich Borgstedt, Forschungszentrum Karlsruhe, Germany and Cezary Guminski, University of Warsaw, Poland, August 1997.

Critical Evaluation

Se reacts with K, and the following compounds are formed: K_2Se, K_2Se_2, K_2Se_3, and K_2Se_4.[1,2] K_2Se_5 is also known; but according to Klemm *et al.*[1] it may be stable below 433 K. K_2Se_6 was traced by x-ray diffraction. However, its existence was not reflected in thermal analysis.

The K-rich part of the K–Se phase diagram and the melting temperature of the probably most stable compound in this system was not determined. By analogy to similar systems one may predict the melting point of K_2Se as 1170±2000 K.[3] Due to the large scatter of thermal arrests observed by Klemm *et al.*[1] it is not clear whether K_2Se_2 melts congruently or peritectically. In the experimental conditions of Klemm *et al.*[1] the K–Se melts interacted with the quartz container.

The Se-rich part of the diagram is better defined. K_2Se_3 melts congruently and K_2Se_4 peritectically. Scheiba *et al.*[2,4] found an immiscibility region between 87.5 and 99.0 mol % Se. The upper limit seems to be underestimated, since the monotectic temperature is only 0.5 K below the melting point of Se, and the solid solubility of K in Se is negligible. Therefore, the monotectic composition calculated from the fusion enthalpy of Se is above 99.8 mol % Se.[3] Morachevskii and Maiorova[5] observed a stability of emf cells with K–Se alloys at 97.9–91.3 mol % Se in the temperature range 725–825 K. On this basis these authors postulated still the existence of two-phase liquids in this range and questioned the critical temperature of the miscibility found at 583 K and 92.5 mol % Se found by Scheiba and Wobig.[4] The evaluators favor the data of Scheiba and Wobig,[4] since Morachevskii and Maiorova[5] did not determine any solubility data.

The partial Se–K phase diagram was constructed by Sangster and Pelton[3] and is reflected in Fig. 42.

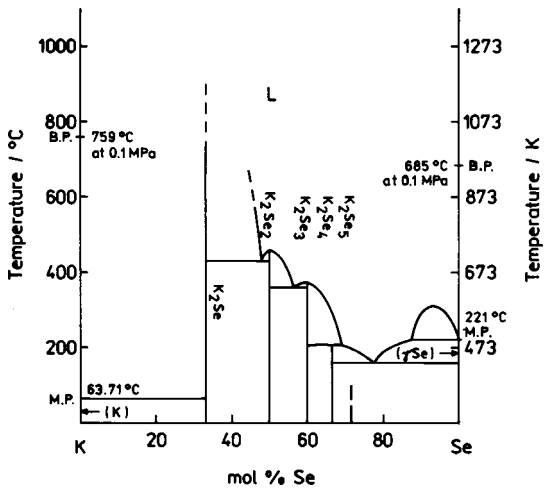

FIG. 42. K–Se phase diagram (partial).

Tentative and doubtful (d) values of the soly of Se in liquid K on the Se-rich side

T/K	Solubility/mol % Se	Source
951	38 (d)	(1)
693	48 (d) eutectic	(1)
733	50 (d) congruent	(1)
633	56 (d) eutectic	(1)
648	60 congruent	(1),(2)
573	65	(1),(2)
479	69 (d) peritectic	(1),(2)
433	78 eutectic	(1),(2)
493.5	87.5 monotectic	(2),(4)
573	89	(4) interpolation
583	92.5 critical	(4) interpolation
573	96	(4)
493.5	99.8	(3), extrapolated

References:

[1]W. Klemm, H. Sodomann, and P. Langmesser, Z. Anorg. Chem. **241**, 281 (1939).
[2]M. Scheiba, A. Tausend, and W. Wobig, Thermochim. Acta **29**, 265 (1979).
[3]J. Sangster and A. D. Pelton, J. Phase Equil. **18**, 177 (1997).
[4]M. Scheiba and D. Wobig, Z. Phys. Chem., N.F. **119**, 23 (1980).
[5]A. G. Morachevskii and E. A. Maiorova, Izv. Vyssh. Ucheb. Zaved., Tsvet. Metall. **2**, 149 (1977); A. G. Morachevskii, Zh. Prikl. Khim. **67**, 881 (1994).

Components:
(1) Selenium; Se; [7782-49-2]
(2) Potassium; K; [7440-09-7]

Original Measurements:
W. Klemm, H. Sodomann, and P. Langmesser, Z. Anorg. Chem. **241**, 281–304 (1939).

Variables:
Temperature: 433–951 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The central part of the K–Se liquidus was determined. The data were presented graphically. They were read from a figure and recalculated to mol % Se by the compilers.

t/°C	Solubility/mass % Se	Solubility/mol % Se
678	54.6	37.3
594	58.8	41.4
537	64.2	47.0
531	65.0	47.9
509	65.5	48.4
503 (459)	66.7	49.8
434	68.6	52.2
394	70.8	54.5
366	72.1	56.1
371	73.6	58.0
378	75.0	60.1
358	76.7	61.9
341	77.5	63.0
325	78.3	64.1
292	79.2	65.3
273	79.7	66.0
259	80.0	66.4
234	80.7	67.4
215	81.3	68.3
200	82.5	70.0
194	83.3	71.2
187	84.4	72.8
179	85.5	74.5
160	86.7	76.3
214	89.6	81.0
219	91.2	83.7

The following equilibrium phases were determined K_2Se, K_2Se_2, K_2Se_3, K_2Se_4, and K_2Se_5. An x-ray diffraction study indicated an existence of K_2Se_6; but its formation was not reflected in the thermal analysis. The alloys showed a tendency to supercooling.

Auxiliary Information

Method:
An apparatus was made from Jena glass or quartz (at the highest temperatures). The apparatus was filled with N and K_2Se powder and Se pieces were introduced into the mixture. The apparatus was equipped with a shielded thermocouple to record temperature. Heating and cooling curves were performed on various compositions of the melt. The authors observed a slight interaction of the melts with the container walls at high temperatures. The solid phases were analyzed by x-ray diffraction.

Source and Purity of Materials:
Se: nothing specified.
K_2Se: prepared from freshly distilled K and Se in liquid NH_3; after evaporation of NH_3, K_2Se was heated at 673–773 K under vacuum for a long time.
N: "dry."

Estimated Error:
Solubility: nothing specified; reading-out procedure ±0.2 mol %.
Temperature: nothing specified; reading-out procedure ±1 K.

Components:
(1) Selenium; Se; [7782-49-2]
(2) Potassium; K; [7440-09-7]

Original Measurements:
M. Scheiba, A. Tausend, and D. Wobig, Thermochim. Acta **29**, 265–268 (1979).

Variables:
Temperature: 435–644 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The Se-rich part of the K–Se liquidus was determined. The data were reported in a figure. They were read from the figure by the compilers.

T/K	Solubility/mol % Se
644	55.0
641	60.0
636	60.5
629	62.2
582	65.0
548	67.0
498	68.0
486	69.0
482	70.0
474	71.8
456	74.0
456	75.0
435	78.3
451	79.5
473	81.0
469	82.0
482	83.6
491	86.0

A liquid miscibility gap at 494 K was found to extend from 86 to 98 mol % Se. K_2Se_3 was detected and the existence of K_2Se_4 (formed peritectically at 479 K) is probable.

Auxiliary Information

Method:
Proper amounts of Se and K_2Se were sealed within an evacuated quartz ampoule. The ampoule was heated gradually up to 820 K and held at this temperature for 4 h. The sample was annealed at 300 K for 1 day. All subsequent preparations of samples were carried out in a glove box filled with Ar. The samples were packed in hermetically sealed pans. Differential scanning calorimetry (DSC) experiments were performed in a commercial equipment recording the heating and cooling curves.

Source and Purity of Materials:
Se: 99.999% pure from Asarco.
K_2Se: 99.9% pure from Zinsser.
Ar: 99.99% pure from Linde.

Estimated Error:
Solubility: nothing specified; reading-out procedure ±0.1 mol %.
Temperature: nothing specified; reading-out procedure ±1 K.

Components:
(1) Selenium; Se; [7782-49-2]
(2) Potassium; K; [7440-09-7]

Original Measurements:
M. Scheiba and D. Wobig, Z. Phys. Chem., N.F. **119**, 23–32 (1980).

Variables:
Temperature: 491–584 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The miscibility gap in the Se-rich melts was determined. The results were presented graphically. They were read from a figure by the compilers.

T/K	Solubility/mol % Se
491	86.1
523	87.6
508	87.8
533	87.9
543	88.0
548	88.1
553	88.1
563	88.8
573	90.0
573	90.3
582	91.0
583	91.9
583.5	93.0
583.5	93.4
581 (578)	94.0 from two figures
573	95.0
573	95.1
564	96.0
548	97.0
542	97.4
533	97.6
523	97.8
508	98.1
493.5	99.0

The immiscibility boundary was found in phase separation experiments to extend from 87.5 to 99.0 mol % Se. The lower immiscibility limit was detected at 87.7 mol % Se in DSC experiments at a monotectic temperature of 493.5 K. The critical temperature was measured at 583.5 K.

Auxiliary Information

Method:
DSC experiments were carried out in a commercial apparatus. The heating and cooling curves of samples prepared from proper amounts of K_2Se and Se were recorded. The samples were melted and annealed in a quartz tube. The K–Se alloys were quenched from the liquid state having a temperature of a few tenth of K above the melting. Two frozen layers were analyzed by AAS after dissolution in HNO_3. The AAS equipment was calibrated on standard solutions of K_2Se and Se. Electrical resistance experiments were performed in a quartz cell with six Pt electrodes. Temperatures were measured using a Ni–Cr/Ni thermocouple. The samples of melts were heated and cooled stepwise. The resistance was measured at each temperature after equilibration. The discontinuity on resistance vs. temperature dependence corresponds to the liquidus point.

Source and Purity of Materials:
Se: 99.999% pure from ASARCO.
K_2Se: 99.9% pure from Zinsser or produced at the Inst. Inorg. Chem. of Techn. Univ. of Berlin. The stoichiometry confirmed within 0.5%; no indication of the presence of H_2O.
Ar: 99.99% pure from Linde.
HNO_3: ultrapure from Merck.

Estimated Error:
Solubility: accuracy ±0.2 mol %; reading-out procedure ±0.1 mol %.
Temperature: gradient in the cell <1 K.

5.14. Potassium–Tellurium

Components:
(1) Tellurium; Te; [13494-80-9]
(2) Potassium; K; [7440-09-7]

Evaluated by:
Hans Ulrich Borgstedt, Forschungszentrum Karlsruhe, Germany and Cezary Guminski, University of Warsaw, Poland, June 2000

Critical Evaluation

The products of the reactions of Te with liquid K are the following compounds: K_2Te, K_2Te_2, K_2Te_3, depending on the stoichiometry of the amounts of elements.[1–3] Klebanov *et al.*[3] measured thermodynamic data for K_2Te_4 at 443 K and Klemm *et al.*[4] measured the magnetic susceptibility for this compound. K_2Te_4 is, however, not reflected in the emf measurements of Petric *et al.*[1] and Khabachev *et al.*,[5,6] its existence needs clarification. Another compound, K_5Te_3, was identified by Khabachev *et al.*[5,6] and Schewe-Miller.[7]

Petric *et al.*[1] investigated the liquidus of the K–Te system in the composition range 44–100 mol % Te. Khabachev *et al.*[5,6] extended the measurements into the range 33–100 mol % Te. Schewe-Miller[7] observed four liquidus points at 1075, 1039, 995, and 957 K for 37.0, 37.6, 39.1, and 39.9 mol % Te, respectively; Schewe-Miller[7] was not available and is not compiled. The results of Petric *et al.*,[1] Khabachev *et al.*,[5,6] and Schewe-Miller[7] show satisfactory agreement. According to Khabachev *et al.*,[5,6] K_2Te_2 melts incongruently in opposition to the postulation of Petric *et al.*[1] A solubility of Te in liquid K was not determined; however, Petric and Pelton[8] presented a part of the liquidus between the melting point of K and 653 K at which temperature the solubility reached 1.5 mol % Te; any experimental background for this fact was not reported. Aleksandrov and Dalakova[9] observed a dissolution of a Te sample in liquid K at 873–923 K, but numerical results were not reported in their publication.

The K–Te phase diagram according to Okamoto,[10] with the addition of the $\alpha \rightarrow \beta$ phase transition of K_2Te_2 at 487 K (11), is shown in Fig. 43.

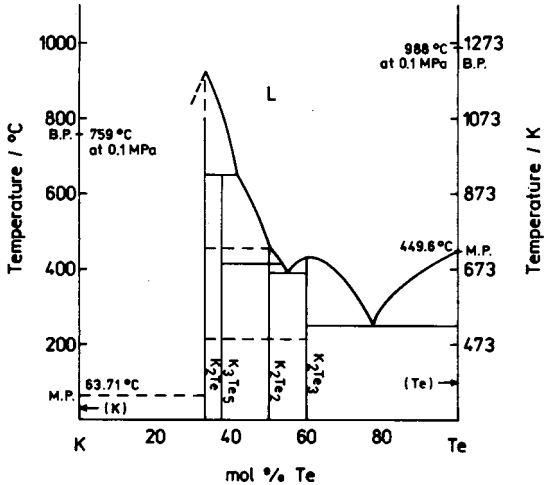

FIG. 43. K–Te phase diagram.

Tentative values of the solubility of Te in liquid K in the Te-rich range.

T/K	Solubility/mol % Te	Source
1193	33.3 congruent	(5,6)
1073	38	(5,6), (7) interpolated
973	40	(5,6), (7) interpolated
873	45	(1)
773	48	(1)
660	56 eutectic	(1), (5,6)
705	60 congruent	(1), (5,6)
525	78 eutectic	(5,6)
573	80	(5,6) interpolated
673	88	(5,6) interpolated

References:

[1]A. Petric, A. D. Pelton, and M. L. Saboungi, J. Chem. Phys. **89**, 5070 (1988).
[2]G. Brauer and V. Stein, Z. Naturforsch., B **2**, 223 (1947).
[3]E. B. Klebanov, I. I. Shibalovskaya, and A. G. Morachevskii, Izv. Vyssh. Ucheb. Zaved., Tsvet. Metall. **1**, 126 (1989).
[4]W. Klemm, H. Sodomann, and P. Langmesser, Z. Anorg. Chem. **241**, 281 (1939).
[5]M. N. Khabachev, A. G. Morachevskii, and K. A. Chuntonov, Zh. Prikl. Khim. **71**, 505 (1998).
[6]M. N. Khabachev and K. A. Chuntonov, J. Alloy Compd. **265**, 93 (1998).
[7]I. Schewe-Miller, Ph.D. thesis, University of Düsseldorf, Germany, 1990.
[8]A. Petric and A. D. Pelton, Bull. Alloy Phase Diagr. **11**, 443 (1990).
[9]B. N. Aleksandrov and N. V. Dalakova, Izv. Akad. Nauk SSSR, Met. **1**, 133 (1982).
[10]H. Okamoto, J. Phase Equil. **20**, 541 (1999).

Components:
(1) Tellurium; Te; [13494-80-9]
(2) Potassium; K; [7440-09-7]

Original Measurements:
A. Petric, A. D. Pelton, and M. L. Saboungi, J. Chem. Phys. **89**, 5070–5077 (1988).

Variables:
Temperature: 618–879 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data
A part of the K–Te liquidus was determined

t/°C	Solubility/mol % K	Solubility/mol % Te[a]
420	8.2	91.8
345	15.4	84.6
381	31.9	68.1
424	38	62
429	40	60
405	44	56
390	44.9	55.1
392	45	55
437	48	52
447	49	51
453	50	50
460	51	49
484	52	48
535	53	47
590	55	45
606	55.7	44.3

[a]Calculated by the compilers.

An invariant reaction was found at 448 °C between KTe and K_2Te.

Auxiliary Information

Method:
The experiments were performed in the electrochemical cell: K–Te/K-β-alumina/Bi–K(8%). All emf readings were referred to a cell K–Te/K–β-alumina/K using another cell for the calibration and periodical checking Bi–K(8%)/K–β-alumina/K. K–β-alumina was made by exchange from Na–β-alumina in molten KCl. The cell was loaded with the elements and operated inside a He glove box. The cell was hermetically sealed by means of a Ta cone; any Ta corrosion by Te was not observed. The K–Te compositions were varied by Coulometric titration for which 100–300 mV potential was applied between the working (the left) and the reference electrode. The emf was reproducible after 2 h from end of the electrolysis. The liquidus points were obtained from the discontinuities in plots of emf versus temperature at fixed compositions.

Source and Purity of Materials:
Te: "high purity" from Asarco, Inc., melted in an inert atmosphere, filtered, and aspired into a glass tube.
K: 99.95% pure from Callery Chem. Comp.
Bi: 99.95% pure, as in Petric *et al.*[1]
He: nothing specified.

Estimated Error:
Solubility: precision ±0.2 mol % K.
Temperature: nothing specified.

References:

[1]A. Petric, A. D. Pelton, and M. L. Saboungi, J. Phys., F **18**, 1473–1489 (1988).

Components:
(1) Tellurium; Te; [13494-80-9]
(2) Potassium; K; [7440-09-7]

Original Measurements:
M. N. Khabachev and K. A. Chuntonov, J. Alloys Compd. **265**, 95–95 (1998).

Variables:
Temperature: 618–879 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The liquidus of the K–Te system was determined. The data were read from a figure by the compilers.

t/°C	Solubility/mol % Te
413	91.9
376	89.0
366	85.3
346	84.6
322	81.8
257	77.2
324	74.9
326	72.3
382	68.9
394	65.4
437	60.0
407	57.7
417	55.6
455	50.0[a]
569	45.9
690	40.3
793	37.5[a]
920[a]	33.3[a]

[a]Numerical results.

The eutectic point was established at 252±2 °C and 78.0±0.5 mol % Te. The same results were reported in Khabachev *et al.*[1]

Auxiliary Information

Method:
The alloys were prepared from K and Te in evacuated ampoules made of Pyrex glass (at temperatures <823 K) or of quartz (>823 K). The samples were annealed at 623 K for 100 h. K_2Te was prepared from a large quantity of liquid K which was poured over Te powder in vacuum; the mixture was kept several hours at 673 K and the excess of K was distilled off at 523 K. The K_2Te powder was introduced into a quartz ampoule in an Ar atmosphere. A sample with 89% Te was centrifuged for 1 h at 723 K and the solidified ingot was used after cutting to pieces. Heating (at a rate of 10 K/min) and cooling (at a rate of 20 K/min) curves were recorded by means of a commercial apparatus. The composition of the samples was determined by a flame photometry method.

Source and Purity of Materials:
Te: 99.999% pure.
K: 99.99% pure.
Ar: nothing specified.

Estimated Error:
Solubility: nothing specified; reading-out procedure ±0.5 mol %.
Temperature: precision between ±1 and ±15 K; reading-out procedure ±1 K.

References:
[1]M. N. Khabachev, A. G. Morachevskii, and K. A. Chuntonov, Zh. Prikl. Khym. **71**, 505–506 (1998).

5.15. Potassium–Fluorine

Components:
(1) Fluorine; F; [7782-41-4]
(2) Potassium; K; [7440-09-7]

Evaluated by:
Hans Ulrich Borgstedt, Forschungszentrum Karlsruhe, Germany and Cezary Guminski, University of Warsaw, Poland, September 1997.

Critical Evaluation

F introduced into liquid K reacts violently; KF is the product of this reaction. This compound is the only equilibrium solid phase in the system. There are two publications of Bredig *et al.*[1,2] on mutual solubilities of KF in liquid K and K in liquid KF. Bredig *et al.*[2] verified the findings of Bredig *et al.*[1] and an extension of experiments to lower temperatures was made. We assume the critical miscibility and monotectic temperature of Bredig *et al.*[2] as ultimate. The solubilities of KF in liquid K below 840 K are unknown. The partial K–F phase diagram was sketched in Bredig[3] and the full composition range is shown in Fig. 44.

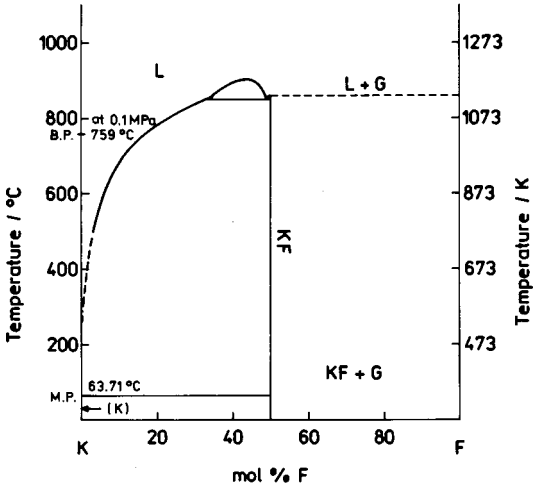

FIG. 44. K–F phase diagram.

T/K	Solubility/mol % F	Source
	Tentative values of the solubility of F in liquid K	
773	3	(2) extrapolated
873	6	(2) interpolated
973	11	(1),(2)
1073	23	(1),(2)
1122	34 monotectic	(1),(2) interpolated
1177	44 critical	(1),(2) interpolated
1131	50 congruent	(1)
	The solubility on the KF-rich side	
1122	48.7 monotectic	(2) interpolated

References:
[1]M. A. Bredig, H. R. Bronstein, and W. T. Smith, J. Am. Chem. Soc. **77**, 1454 (1955).
[2]J. W. Johnson and M. A. Bredig, J. Phys. Chem. **62**, 604 (1958).
[3]M. A. Bredig, *Molten Salt Chemistry*, edited by M. Blander (Interscience, New York, 1964), p. 367.

Components:
(1) Fluorine; F; [7782-41-4]
(2) Potassium; K; [7440-09-7]

Original Measurements:
M. A. Bredig, H. R. Bronstein, and W. T. Smith, J. Am. Chem. Soc. **77**, 1454–1458 (1955).

Variables:
Temperature: 931–1178 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data
The mutual miscibility of KF and K was determined

	Salt-rich phase		Metal-rich phase	
t/°C	Solubility/mol % KF	Solubility/mol % F[a]	Solubility/mol % KF	Solubility/mol % F[a]
658	···	···	7.6	7.1
697	···	···	12.3	10.9
750	···	···	17.7	15.0
803	···	···	30.4	23.3
832	···	···	38.4	27.7
853	···	···	48.9	32.8
862	94.0, 94.8	48.5, 48.7	49.6	33.1
863	93.7	48.4	···	···
865	92.6, 90.3	48.1, 47.5	45.0, 42.0	31.0, 29.6
865	···	···	49.0, 49.3	32.9, 33.0
865	···	···	47.0, 43.1	32.0, 30.1
877	85.6, 85.2	46.1, 46.0	···	···
881	84.4	45.8	50.8	33.7
886	82.0	45.1	49.5, 51.9	33.1, 34.2
894	78.3	43.9	56.0, 57.6	35.9; 36.5
905	69.5	41.0	54.0	35.0

[a]Calculated by the compilers.

The melting point of KF was found at 858 °C, the monotectic temperature at 849 °C. The consolute temperature was estimated to be 910 °C at 38.7 mol % F.

Auxiliary Information

Method:
The experiments were performed in a ball-check valve capsule made of 316 type stainless steel. Heating and cooling curves were recorded by means of a Chromel/Alumel thermocouple placed in a well.[1] The capsule was cleaned in $Fe_2(SO_4)_3$ (5%) and H_2SO_4 (10%) mixture for 20 min at 333–343 K, after that in HNO_3 (15%) and HF (2%) mixture for 15 min. It was rinsed in H_2O and dried at 383 K. KF was weighed and loaded into the capsule in a N-filled glove box, and it was evacuated. K was weighed under mineral oil, rinsed in hexane, and evacuated to $<1\cdot10^{-3}$ Torr. Gentle heating of the capsule melted K and removed hexane. The capsules were mounted in a furnace and equilibrated while rocking 2–3 h. The bottom sample of KF and the upper sample of K were analyzed after a phase separation. The KF phase was dissolved in C_2H_5OH–H_2O mixture and titrated with standard acid, and free K was calculated from the sample weight and the alkalinity. The K phase was dissolved in C_2H_5OH–H_2O mixture. KF was weighed directly since it was found to be insoluble in C_2H_5OH. The alkalinity developed was titrated with HNO_3. The vapor pressure measurements were performed in stainless steel containers (as a part of modified equipment) by observing boiling points of melts as function of Ar pressure.

Source and Purity of Materials:
KF: as in Bredig *et al.*,[1] anhydrous reagent grade purity, heated (≤773 K) in an evacuated ($<5\cdot10^{-2}$ Torr) McDaniel porcelain tube on a Pt boat. Temperature was raised to 50 K above the melting point in streaming Ar. After slow cooling to room temperature, clear fragments of the salt (stored in a desiccator over P_2O_5) were used.
K: contained 0.27% Na and 0.30% O.
Ar: "dry," as in Bredig *et al.*[1]

Estimated Error:
Solubility: nothing specified; not better than ±2 mol % (by the compilers).
Temperature: precision ±3 K in solubility experiments and ±0.5 K in thermal analysis.

References:
[1]M. A. Bredig, H. R. Bronstein, and W. T. Smith, J. Am. Chem. Soc. **77**, 307–312 (1955).

Components:
(1) Fluorine; F; [7782-41-4]
(2) Potassium; K; [7440-09-7]

Original Measurements:
J. W. Johnson and M. A. Bredig, J. Phys. Chem. **62**, 604–607 (1958).

Variables:
Temperature: 839–1176 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data
The mutual miscibility of molten KF and K was investigated

t/°C	Solubility/mol % KF	Solubility/mol % F[b]
565.3	4.9	4.7
565.8	5.0	4.8
622.1	8.2	7.6
658	7.6[a]	7.1
664	10.1	9.2
697	12.3[a]	10.9
750	17.7[a]	15.0
803	30.4[a]	23.3
832	38.4[a]	27.7
841	46.0	31.5
864.0	53.0	34.6
883.0	60.0	37.5
894.0	67.0	40.1
903.0	81.2	44.8
901.0	85.0	45.9
891.5	89.6	47.3
867.0	93.5	48.3

[a]Equilibration tests described in Bredig *et al.*[1]
[b]Calculated by the compilers.

The melting point of KF was found at 858 °C, the monotectic temperature at 847.6±1.6 °C.

Auxiliary Information

Method:
Thermal analysis of samples was carried out in a stainless steel capsule. The capsule was filled with known amounts of KF and K and then purged with Ar. The capsule was welded shut with a flat top and placed inside a tank made of Inconel. The tank was pressurized with Ar up to ~0.7 MPa. The ratio of the container weight to the sample weight was reduced by employing thin walled construction tubes. Temperatures were measured with a Pt/Pt–Rh(10%) thermocouple well. Cooling and heating cycles were repeated 2–4 times for each composition. The solubilities were estimated from thermal arrests.

Source and Purity of Materials:
KF: as in Bredig *et al.*,[1] reagent grade purity, heated (≤773 K) in an evacuated ($<5\cdot10^{-2}$ Torr) McDaniel porcelain tube on a Pt boat, heated 50 K above its melting point in an Ar atmosphere, slowly cooled to room temperature, clear crystals stored in a desicator over P_2O_5 were used.
K: remelted under C_6H_{14} in a stainless steel beaker, the oxidized surface removed, and stored in a desiccator.
Ar: "dry," as in Bredig *et al.*[1]

Estimated Error:
Solubility: nothing specified; not better than ±0.1 mol % (by the compilers).
Temperature: precision of readings ±0.25 K and precision of estimation ±0.05 K.

References:
[1]M. A. Bredig, H. R. Bronstein, and W. T. Smith, J. Am. Chem. Soc. **77**, 307–312 (1955).

5.16. Potassium–Chlorine

Components:
(1) Chlorine; Cl; [7782-50-5]
(2) Potassium; K; [7440-09-7]

Evaluated by:
Hans Ulrich Borgstedt, Forschungszentrum Karlsruhe, Germany and Cezary Guminski, University of Warsaw, Poland, October 1997.

Critical Evaluation

Cl reacts violently with liquid K; KCl is formed as the product of this reaction. This solid phase is in equilibrium with liquid K. Due to their technical importance the K–Na–KCl–NaCl equilibria were experimentally investigated much earlier[1] than the less complex K–KCl system. The first investigation of the solubility of KCl in liquid K was performed by Bredig *et al.*[2] In the next publication (Johnson and Bredig[3]) of the same laboratory some extended data dealing with the mutual solubility of KCl and K were reported. The critical (1063 K) and monotectic (1025 K) temperatures were determined as well as the range of the liquid miscibility gap (22–47 mol % Cl) was established. The monotectic was found 19 K below the melting point of KCl assured contemporary to be 1051 K (7 K higher than in Bredig *et al.*[2] and Johnson and Bredig[3]). The results of Bredig *et al.*[2] and Johnson and Bredig[3] were moderately scattered, and they may be treated as tentative. The solubility result of Belozerskii[4] that 8.3 mol % K dissolves in molten KCl at 1073 K is certainly erroneous, since only the liquid is present at this temperature (10 K above the critical miscibility point). Garbade and Freyland[5] investigated the K–KCl system at high pressures (up to 150 MPa). The monotectic and critical temperatures increased almost linearly with pressure within a temperature precision of ±4 K; the monotectic temperature increased more rapidly with pressure.

An addition of Na or NaCl to the K–KCl system decreases the Cl solubility in the K–Na alloy. There is a fast equilibrium between the four components:

$$\mathrm{NaCl}+\mathrm{K}\leftrightarrow\mathrm{KCl}+\mathrm{Na}. \qquad (1)$$

The equilibrium constant of this reaction was established by earlier[1,4,6–11] The authors of earlier studies (Jellinek and Tomoff,[1] Hackspill and Rinck,[6] Rinck,[7] Jellinek and Czerwinski,[8] and Alabyshev[9]) determined the reaction constant assuming that the salt phase did not contain the metals or the alloy phase did not contain the salts in measurable amounts. Therefore, their data are different from Belozerskii,[4] Neckel *et al.*,[10] and Berdichevskii and Morachevskii[11] in which a complete analysis of the salt (Belozerskii,[4] Neckel *et al.*,[10] and Berdichevskii and Morachevskii[11]) and the alloy (Neckel *et al.*[10]) phases were carried out. The reaction constant found in the latter works is recommended, though thermodynamic calculations of Berdichevskii and Morachevskii[11] and Neckel[12] suggest the value of the constant should be 2–4 times higher than in Neckel *et al.*[10] and Berdichevskii and Morachevskii.[11] The constant should be temperature dependent, which fact was not observed by Neckel *et al.*[10] A solubility of K–Na alloy in the equimolar mixture of KCl–NaCl at 963–1173 K was determined by Smirnov and Podlesnyak.[13,14] These data agree within a few mol % with the results of Neckel *et al.*[10] obtained at 1140–1243 K and of Belozerskii[4] at 873 and 953 K.

Nakajima[15] determined a solubility of Cl in molten KCl–LiCl mixture at 723–848 K; the solubility was as low as 10^{-4} mol dm^{-3}. It is a value which is 2 orders of magnitude higher than the solubility of Cl in pure KCl, as compiled by Tomkins and Bansal.[16]

Bredig[17] draw a partial phase diagram of the K–Cl system, and its extended form is shown in Fig. 45. Neckel[12] sketched the K–Na–Cl phase diagram at 1200 K, based on his thermodynamic calculations. The diagram version, proposed below in Fig. 46, takes into account the solubility results of Neckel *et al.*,[10] Berdichevskii and Morachevskii,[11] and Smirnov and Podlesnyak,[13,14] as well as the data for the Na–Cl system.

T/K	Solubility/mol % Cl	Source
	Tentative values of the solubility of Cl in liquid K	
773	0.7	(3)
873	3.1	(3)
973	10.5	(2),(3)
1025	22 monotectic	(2),(3) interpolation
1063	38 critical	(3) interpolation
	Tentative values of the solubility of Cl on the KCl-rich side	
1043	50 congruent	(3)
1025	47 monotectic	(3)
1043	45.5	(3)

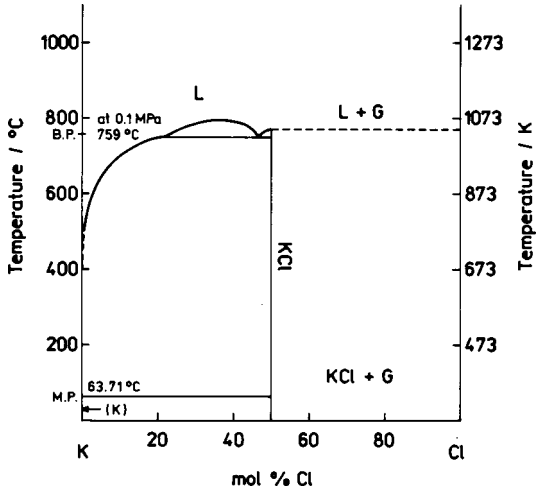

FIG. 45. K–Cl phase diagram.

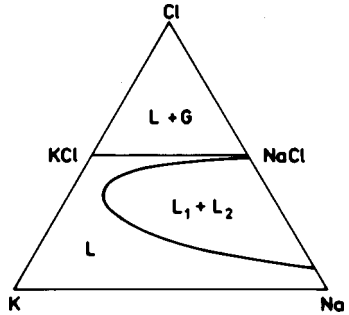

FIG. 46. K–Na–Cl phase diagram at 1200 K, after Neckel.[12]

References:

[1]K. Jellinek and G. Tomoff, Z. Phys. Chem. **111**, 234 (1924).
[2]M. A. Bredig, H. R. Bronstein, and W. T. Smith, J. Am. Chem. Soc. **77**, 1454 (1955).
[3]J. W. Johnson and M. A. Bredig, J. Phys. Chem. **62**, 604 (1958).
[4]N. A. Belozerskii, Tr. Gos. Inst. Prikl. Khim. **33**, 50 (1940).
[5]K. Garbade and W. Freyland, Ber. Bunsenges. Phys. Chem. **92**, 1131 (1988); Z. Phys. Chem. N. F. **156**, 169 (1988).
[6]Z. Hackspill and E. Rinck, Compt. Rend. **185**, 463 (1927).
[7]E. Rinck, Ann. Chim. **18**, 395 (1932).
[8]K. Jellinek and J. Czerwinski, Z. Phys. Chem. **110**, 92 (1924).
[9]A. F. Alabyshev, Tr. Gos. Inst. Prikl. Khim. **37**, 95 (1946).
[10]A. Neckel, R. Sponer, and H. Nowotny, Monatsh. Chem. **96**, 1633 (1965).
[11]N. I. Berdichevskii and A. G. Morachevskii, Zh. Prikl. Khim. **39**, 1037 (1966).
[12]A. Neckel, Monatsh. Chem. **96**, 1850 (1965).
[13]M. V. Smirnov and N. P. Podlesnyak, Zh. Prikl. Khim. **42**, 2454 (1969).
[14]M. V. Smirnov and N. P. Podlesnyak, Tr. Inst. Elektrokhim. Akad. Nauk SSSR Ural. Fil. **14**, 14 (1970).
[15]T. Nakajima, H. Imoto, K. Nakanishi, and N. Watanabe, Denki Kagaku **42**, 85 (1974); C. A. **81**, 30352 f (1974).
[16]R. P. T. Tomkins and N. P. Bansal, *Gases in Molten Salts*, Solubility Data Series (Pergamon, Oxford, 1990), Vols. **45/46**, p. 126.
[17]M. A. Bredig, *Molten Salt Chemistry*, edited by M. Blander (Interscience, New York, 1964), p. 367.

Components:
(1) Chlorine; Cl; [7782-50-5]
(2) Potassium; K; [7440-09-7] or potassium-sodium alloy; K–Na

Original Measurements:
N. A. Belozerskii, Tr. Gos. Inst. Prikl. Khim. **33**, 50–108 (1940).

Variables:
Temperature: 873–1073 K; salt composition: 26.5–85.1 mol % KCl

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of K in liquid KCl was found to be 8.3 mol % at 800 °C; the recalculated value is 47.84 mol % Cl.
The solubility of Na in KCl–NaCl mixtures was determined

	Composition of the salt phase/mol %			
t/°C	K	Na	KCl	NaCl
600	0.8	0.5	62.3	36.4
	1.1	0.6	63.7	34.6
	1.35	0.65	64.8	33.2
	2.35	0.35	86.2	11.1
	3.15	0.45	85.1	11.3
660–680	1.1	2.4	26.5	69.9
	0.85	1.7	32.8	65.7
	0.4	0.5	42.3	56.8
	1.6	0.8	65.7	31.9
	3.7	0.6	83.0	12.7

Auxiliary Information

Method:
The mixed molten salt was introduced into a glass container. A W cathode and a graphite anode were mounted in the container. The cathodic and anodic compartments were isolated by a porcelain tube. The hermetically closed container was placed in an oven with regulated temperature. Electrolysis with a current of 2–3 A was carried out for 1–1.5 h; thus, the salt mixture was saturated with K–Na. The salt and metallic phases were cooled to room temperature. They were separated mechanically. Si, which also crystallized out on the metal surface, was carefully removed. The KCl–NaCl phase was dissolved in H_2O. The contents of K and Na were found by means of titration of the resulting solution with 0.01 mol dm^{-3} HCl using phenolphthalein as the indicator and probably by photometric measurements. The apparatus was assembled and used in an Ar atmosphere.

Source and Purity of Materials:
KCl and NaCl: purified by blowing dry HCl through the molten salt for 2–3 h.
K and Na: from the electrolysis.
Ar: nothing specified.

Estimated Error:
Solubility: nothing specified.
Temperature: accuracy ±10 K.

Components:
(1) Chlorine; Cl; [7782-50-5]
(2) Potassium; K; [7440-09-7]

Original Measurements:
M. A. Bredig, H. R. Bronstein, and W. T. Smith, J. Am. Chem. Soc. **77**, 1454–1458 (1955).

Variables:
Temperature: 905–1026 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of KCl in liquid K was determined. The results were reported in a figure; they were read from the figure by the compilers and recalculated to mol % Cl.

T/K	t/°C	Solubility/mol % KCl	Solubility/mol % Cl
905	632	3.2	3.1
923	650	5.7	5.4
976	703	11.0	9.9
1026	753	26.5	20.9

The melting point of KCl and the monotectic temperature were found to be at 771 and 753 °C, respectively.

Auxiliary Information

Method:
The container used for the experiments was made of Type 316 stainless steel.[1] Cooling and heating curves were recorded by means of a Chromel/Alumel thermocouple placed in a well. The containers were washed in $Fe_2(SO_4)_3$–H_2SO_4 mixture for 20 min at 333–343 K and in HNO_3–HF mixture for 15 min. They were rinsed in H_2O and dried at 383 K. KCl was weighed and loaded into capsules in a dry box filled with N, and the capsules were evacuated. K was weighed under mineral oil, rinsed in hexane, placed in the capsule, and evacuated to $<1\cdot10^{-3}$ Torr. Gentle heating of the capsule melted K and removed hexane. The capsules were mounted in a furnace and equilibrated while rocking 2–3 h. The bottom sample of KCl and the upper one of K were analyzed after their phase separation. The KCl phase was dissolved in C_2H_5OH–H_2O mixture and titrated with a standard acid. Free K was calculated from the sample weight and the alkalinity. The K sample was dissolved in C_2H_5OH–H_2O mixture. The alkalinity developed was determined with HNO_3 and Cl as AgCl precipitate.

Source and Purity of Materials:
KCl: reagent grade, heated (773 K) in an evacuated (0.05 Torr) quartz tube. Ar flushed through the tube while raising temperature 50 K above its melting point. After slow cooling to room temperature clear fragments of the salt were used, stored in a desiccator over P_2O_5.[1]
K: filtered through a sintered stainless steel filter at temperature slightly above its melting point.
Ar: "dry"
N: "dry."

Estimated Error:
Solubility: nothing specified; reading-out procedure ±2%.
Temperature: nothing specified; reading-out procedure ±3 K.

References:
[1]M. A. Bredig, J. W. Johnson, and W. T. Smith, J. Am. Chem. Soc. **77**, 307–312 (1955).

Components:
(1) Chlorine; Cl; [7782-50-5]
(2) Potassium; K; [7440-09-7]

Original Measurements:
J. W. Johnson and M. A. Bredig, J. Phys. Chem. **62**, 604–607 (1958).

Variables:
Temperature: 769–1062 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The mutual miscibility of liquid KCl and K was investigated

t/°C	Solubility/mol % KCl	Solubility/mol % Cl[a]
496[b]	0.63–0.81	0.71
550[b]	1.40–1.61	1.49
600[b]	3.07–3.30	3.09
624[b]	3.99	3.84
650[b]	5.80–5.90	5.53
675[b]	8.30–8.90	7.92
700[b]	11.40–12.07	10.51
725[b]	16.74–17.02	14.44
735.5	20.51–20.61	17.05
743[b]	22.90–23.00	18.67
744.6	24.96–25.08	20.0
748[b]	26.89–27.14	21.3
751.6	88.47–88.67	47.0
753.3	90.64–90.94	47.6
755.8	93.29–93.49	48.3
757.9	96.39	49.08
765.3	98.33–98.46	49.60
766.4	34.31–34.46	25.6
780.5	42.58–42.66	29.9
786.7	50.43–50.57	33.6
789.1	57.04–57.14	36.3
788.7	66.82–66.93	40.1
785.6	74.14–74.23	42.6
778.4	79.40–79.50	44.3
770.5	83.17–83.24	45.4
764.0	86.02–86.09	46.3

[a]Mean value calculated by the compilers.
[b]Equilibration and sampling tests.

The melting point of KCl was found at 769.5 °C, the monotectic temperature at 751.5±1.0 °C.

Auxiliary Information

Method:
Thermal analyses of samples were performed in a stainless steel capsule. The capsule was filled with known amounts of KCl and K, and purged with Ar. The capsule was welded shut with a flat top, placed inside a tank made of Inconel, and pressurized with Ar up to ~0.7 MPa. The ratio of container weight to the sample weight was reduced by employing thin walled construction tubes. The temperature was measured by means of a Pt/Pt–Rh(10%) thermocouple well. Cooling and heating cycles were repeated 2–4 times for each composition. Some K+KCl samples were equilibrated and liquid K decanted from the solid KCl phase. The composition of both phases was analyzed by an unspecified method.

Source and Purity of Materials:
KCl: "optical grade" of purity.
K: remelted under hexane in a stainless steel beaker, the oxidized surface removed, the solid metal stored in a desiccator.
Ar: nothing specified.

Estimated Error:
Solubility: precision better than ±15%, but typically ±0.5%.
Temperature: precision of reading in thermal analysis ±0.25 K; precision of estimation ±0.05 K; stability in equilibration and sampling ±2 K.

Components:
(1) Chlorine; Cl; [7782-50-5]
(2) Sodium; Na [7440-23-5]
(3) Potassium; K; [7440-09-7]

Original Measurements:
A. Neckel, R. Sponer, and H. Nowotny, Monatsh. Chem. **96**, 1633–1638 (1965).

Variables:
Temperature: 1140–1243 K; initial composition of the melts unspecified

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data
The mutual miscibility of liquid K–Na alloy and KCl–NaCl melt was determined

	Composition/mol %							
	Na	K	NaCl	KCl	Na	K	NaCl	KCl
T/K	in the metallic phase				in the salt phase			
1243	55.0	15.9	4.2	24.9	15.5	3.1	15.8	65.5
1206	56.5	18.2	3.9	21.4	14.2	2.0	15.5	67.9
1180	69.9	15.3	3.1	11.7	10.6	2.6	15.6	71.2
1173	60.3	19.0	2.3	10.4[a]	10.5	1.0	18.6	70.1
1158	53.4	15.9	4.5	26.2	17.4	2.2	15.6	64.7
1140	51.3	13.3	6.4	29.1	13.7	3.1	19.0	64.2

[a]The sum of components is not 100 mol %.

Auxiliary Information

Method:
The container was made of carbon steel. A sampling device made of a steel was closed by a steel ball. This construction allowed a sampling of the separated liquid phases. Proper amounts of KCl and Na were introduced into the container in N atmosphere. The container was evacuated, closed and placed in an oven for 4 h. It was regularly moved during equilibration. Temperature measurements were made by means of Ni/Ni–Cr thermocouples. The sampling device was introduced into the container and samples of two phases were withdrawn and cooled down with water. Concentrations of all components in each of the phases were determined: K as K_2PtCl_6, Cl by argentometric titration and Na by the mass difference. N-propanol was used for the separation of metal and salt phases.

Source and Purity of Materials:
KCl: for analysis from Merck, further dried.
Na: free from the surface oxide.
N: dried.

Estimated Error:
Solubility: nothing specified; not better than ±0.5% (by the compilers).
Temperature: precision ±1.5 K.

Components:
(1) Chlorine; Cl; [7782-50-5]
(2) Sodium; Na; [7440-23-5]
(2) Potassium; K; [7440-09-7]

Original Measurements:
N. I. Berdichevskii and A. G. Morachevskii, Zh. Prikl. Khim. **39**, 1037–1041 (1966).

Variables:
One temperature: 1173 K; composition of both liquid phases

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data
The saturating content of the metals K–Na in KCl–NaCl melt was determined at 1173 K

Content of salt phase/mass %					Content of salt phase/mol %[a]				
Total			Dissolved		Components				
K	Na	Cl	K	Na	K	Cl	KCl	NaCl	Na/K[b]
32.7	18.6	48.2	1.10	6.09	0.9	8.8	54.0	38.3	9.4
35.8	16.9	44.6	2.04	7.44	1.8	11.1	59.0	28.1	6.2
39.0	17.2	43.4	3.30	9.25	2.8	13.5	61.5	23.3	4.62
41.1	13.9	42.6	3.33	7.73	3.0	11.6	67.1	18.3	3.95
44.8	10.6	44.4	3.57	5.92	3.2	9.0	73.5	14.3	2.82
45.7	10.8	44.0	4.88	6.50	4.3	9.8	72.9	13.0	2.27

[a]Calculated by the compilers.
[b]In the corresponding metallic phase.

The salt phase was also analyzed by Cl determination as well as by photometric estimation of K and Na. The results differed for not more than ±10%.

Auxiliary Information

Method:
The equilibrium was investigated in a tightly closed Ni container which was loaded with the salts KCl and NaCl, heated to 1173 K, and the melt was kept for 1–2 h. After cooling the metals K and Na were introduced. The free volume of the container was kept at minimum. The mixture was equilibrated by permanent shaking at 1173 K for 1 h. The melt was then kept quiet for 0.5 h to allow the separation of the liquid phases. The metallic phase was analyzed for K and Na by flame photometry; moreover the total alkalinity of the sample was measured. The contents of K and Na in the salt phase were measured by flame photometry. The total content of Cl was determined by titration with 0.05 mol dm^{-3} $Hg_2(NO_3)_2$; the alkalinity of the salt phase was found with 0.1 mol dm^{-3} HCl.

Source and Purity of Materials:
KCl: chemically pure.
NaCl: chemically pure.
K: 99.0% pure and contained ~1% Na.
Na: contained <0.05% K and practically no other metals.

Estimated Error:
Solubility: nothing specified; not better than ±1% (by the compilers).
Temperature: stability ±5 K.

Components:
(1) Chlorine; Cl; [7782-50-5]
(2) Sodium; Na; [7440-23-5]
(3) Potassium; K; [7440-09-7]

Original Measurements:
M. V. Smirnov and N. P. Podlesnyak, Zh. Prikl. Khim. **42**, 2454–2459 (1969).

Variables:
Temperature: 963–1173 K; composition of the metallic phase

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of K–Na alloy in equimolar mixture KCl–NaCl was determined

t/°C	Solubility/mol % K–Na[a]	Solubility/mol % Cl[b]
690	0.56	49.86
720	0.85	49.79
750	1.1	49.72
790	1.8	49.55
820	2.1	49.47
860	2.7	49.32
900	3.7	49.06

[a]Since the equilibrium constant of the reaction KCl+Na↔NaCl+K was not determined, the individual concentrations of K and Na could not be estimated; the authors reported individual activities, but the method of their determination was not described
[b]Calculated by the compilers.

The results were also reported in graphical form.[1]

Auxiliary Information

Method:
The measurements were performed in a hermetically closed bomb made of 1Kh18N9T steel which contained an alundum (Al_2O_3) crucible inside. The bomb was encapsulated in a quartz container. Molten KCl–NaCl mixture was placed in the crucible. A Cl electrode (on graphite) in alundum diaphragm (as anode) and Armco Fe (as cathode) were dipped in the salt melt. A Chromel/Alumel thermocouple was placed in a shielding tube made of Armco Fe. It was positioned just above the melt. The experiments were performed in an Ar atmosphere. The K–Na concentration was coulometrically controlled during electrolysis. The charge was measured with a Cu coulometer. After the electrolysis was stopped, the redox potential between the reference anode and another Armco Fe indicator electrode was measured in time. Stable potential differences were linearly dependent on the logarithm of K–Na concentration up to the saturation point and further increase of K–Na concentration made no effect on the potential readings.

Source and Purity of Materials:
KCl: spectrally pure.
NaCl: spectrally pure.
K–Na: from electrolysis.
Ar: purified over Ti turnings at 1123 K and molten Li at 623 K.

Estimated Error:
Solubility: nothing specified.
Temperature: nothing specified.

References:
[1]M. V. Smirnov and N. P. Podlesnyak, Tr. Inst. Elektrokhim. Akad. Nauk SSSR, Ural. Fil. **14**, 14–18 (1970).

Components:
(1) Chlorine; Cl; [7782-50-5]
(2) Potassium; K; [7440-09-7]

Original Measurements:
K. Garbade and W. Freyland, Ber. Bunsenges. Phys. Chem. **92**, 1131–1140 (1988).

Variables:
Temperature; 1014–1077 K;
Pressure: 0.1–150 MPa

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The liquidus temperatures were reported in graphical form; they were read from a figure and recalculated to mol % Cl by the compilers

p/MPA	t/°C	Solubility/mol % K in KCl	Solubility/mol % Cl
80	741	82.7	14.7
	766	63.1	26.9
	794	44.4	35.7
	798	33.5	40.0
	794	22.6	43.6
	774	14.5	46.1
	780	9.4	47.5
	796	0	50.0
150	755	82.7	14.7
	789	63.1	26.9
	807	44.4	35.7
	807	33.5	40.0
	797	22.6	43.6
	788	14.5	46.1
	796	9.4	47.5
	812	0	50.0

The monotectic (T_m) and critical mixing (T_c) temperatures were determined. The corresponding results were read from a figure

p/MPA	T_m/°C	T_c/°C
0.1	751	790
10	755	784
20	758	786
30	761	791
40	762	793
60	764	795
80	770	798
120	779	804
150	786	808

The same results were reported in Garbade and Freyland.[1]

Auxiliary Information

Method:
A high pressure vessel was made of 1.4122 stainless steel. It contained a volumetric cell surrounded by a heater, controlled by 3 Ni/Ni–Cr thermocouples. The cell was made of 1.4571 stainless steel and served to measure the molecular volume under pressure. The apparatus was calibrated. Fixed amounts of K and KCl were introduced into the cell and the molar volumes measured at every 10 K. Isobaric measurements were also performed at 10 and 20 MPa intervals changing temperature. Clear kinks were observed in the volumes, as the phase boundary was crossed. Approaching the phase boundary the heating rate was reduced to 1 K min^{-1}. On heating and cooling the curves showed a slight hysteresis.

Source and Purity of Materials:
KCl: 99.999% pure, cleaned and dehydrated.
K: 99.95% pure.
Ar: contained $<1\cdot10^{-4}$ % O and H_2O.

Estimated Error:
Solubility: precision ±0.2%.
Volume: precision ±1% (in calibration).
Temperature: stability ±0.5 K; homogeneity across the cell length ±3 K.
Pressure: precision ±0.2 MPa.

References:
[1]K. Garbade and W. Freyland, Z. Phys. Chem. N. F. **156**, 169–175 (1988).

5.17. Potassium–Bromine

Components:
(1) Bromine; Br; [7726-95-6]
(2) Potassium; K; [7440-09-7]

Evaluated by:
Hans Ulrich Borgstedt, Forschungszentrum Karlsruhe, Germany and Cezary Guminski, University of Warsaw, Poland, October 1997.

Critical Evaluation

KBr is the product of the reaction of liquid K with Br; this salt is the equilibrium solid phase in the system. There is practically one experimental publication on the mixing properties of liquid K and KBr published by Johnson and Bredig.[1] The determinations were performed at 875–1001 K between 5 and 50 mol % Br. The critical temperature of mixing was found at 1001 K and the monotectic extends from 24 to 45 mol % Br at 981 K. The one experimental determination of Mollwo[2] that molten KBr saturated with K at 1123 K contains 1.7 mol % K in KBr (which value corresponds to the liquidus point of 49.57 mol % Br at 1123 K) seems to be in error. Such point is in the range of complete miscibility of the components according to Johnson and Bredig;[1] therefore, this single value of Mollwo[2] should be rejected.

The solubility of KBr in liquid Br was not investigated. The solubility of Br in molten KBr at 1023 K was reported to be 0.1 mol %.[3]

Rinck[4] measured equilibrium constant of the reaction:

$$NaBr + K \leftrightarrow Na + KBr \qquad (1)$$

being equal to 28.8 at 1073 K. Unfortunately no solubilities of the salts in the alloy phase and the metals in the salt phase were taken into account. Thus, this equilibrium constant has only a qualitative character.

A partial K–Br phase diagram was presented by Bredig[5] and the more complete diagram is shown in Fig. 47.

Tentative values of the solubility of Br in liquid K

T/K	Solubility/mol % Br	Source
873	4.7	(1)
973	20	(1)
981	24 monotectic	(1)
1001	35 critical	(1)

Tentative values of the solubility of Br at the KBr-rich side

T/K	Solubility/mol % Br	Source
1007	50 congruent	(1)
981	45 monotectic	(1)
991	43	(1) interpolated

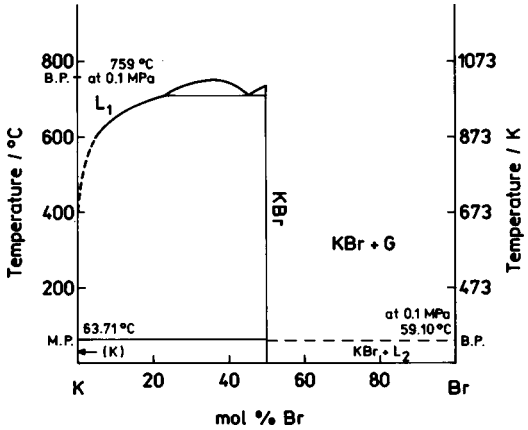

FIG. 47. K–Br phase diagram (tentative).

References:
[1]J. W. Johnson and M. A. Bredig, J. Phys. Chem. **62**, 604 (1958).
[2]E. Mollwo, Phys. Z. **36**, 740 (1935).
[3]R. P. T. Tomkins and N. P. Bansal, *Gases in Molten Salts*, Solubility Data Series (Pergamon, Oxford, 1990), Vol. 45/46, p. 181.
[4]E. Rinck, Compt. Rend. **188**, 1108 (1929).
[5]M. A. Bredig, *Molten Salt Chemistry*, edited by M. Blander (Interscience, New York, 1964), p. 367.

Components:
(1) Bromine: Br; [7726-95-6]
(2) Potassium; K; [7440-09-7]

Original Measurements:
J. W. Johnson and M. A. Bredig, J. Phys. Chem. **62**, 604–607 (1958).

Variables:
Temperature: 875–1001 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data
The mutual miscibility of KBr and K was determined

t/°C	Solubility/mol % KBr	Solubility/mol % Br[a]
602.1	4.90–5.02	4.73
647.0–647.2	9.28–9.33	8.52
677.8–678.2	14.69–14.78	12.85
694.8–695.2	19.76–19.83	16.5
701.4–701.5	24.76–24.82	19.9
709.3–709.4	83.55–84.22	45.6
711.3	87.04–87.20	46.6
716.2–716.3	91.51–91.63	47.8
725.3–725.4	96.35–96.45	49.08
715.3–715.5	34.29–34.38	25.6
723.2–723.4	42.12–42.23	29.7
728.1	49.24–49.46	33.0
728.1–728.3	50.77–50.91	33.7
726.2–726.4	54.20–54.33	35.2
726.5	59.72–59.80	37.4
726.2–726.4	65.73–65.83	39.7
721.3	73.45–73.80	42.4
714.4–714.6	77.55–77.63	43.7

[a]Mean value calculated by the compilers.

The melting point of KBr was found at 733.9 °C, the monotectic temperature at 708±1 K.

Auxiliary Information

Method:
Thermal analyses of samples were performed in a stainless steel capsule which was filled with known amounts of KBr and K and then purged with Ar. The capsule was welded shut with a flat top and placed inside a tank made of Inconel and pressurized with Ar up to ~0.7 MPa. The ratio of the container weight to the sample weight was reduced by employing thin walled construction tubes. Temperatures were measured by means of a Pt/Pt–Rh(10%) thermocouple well. Cooling and heating cycles were repeated 2–4 times for each sample composition.

Source and Purity of Materials:
KBr: "optical grade" of purity.
K: remelted under hexane in a stainless steel beaker, the oxidized surface removed, the metal stored in a desiccator.
Ar: nothing specified.

Estimated Error:
Solubility: precision better than ±0.5%.
Temperature: precision of reading ±0.25 K and precision of estimation ±0.05 K.

5.18. Potassium–Iodine

Components:
(1) Iodine; I; [7553-56-2]
(2) Potassium; K; [7440-09-7]

Evaluated by:
Hans Ulrich Borgstedt, Forschungszentrum Karlsruhe, Germany and Cezary Guminski, University of Warsaw, Poland, November 1997.

Critical Evaluation

I reacts effectively with liquid K and forms the stable compound KI. Since the formation of KI_3 in various solutions is a well known phenomenon, the question of its formation in the solid state in the K–I system was uppermost for early investigators.[1–3] Hamburger and Abegg[1] found a slight maximum on the liquidus at stoichiometry of KI_7, while Kremann and Schoulz[3] at KI_4. Later Fialkov and Kusmenko[4–6] observed a gap of a few K between the solidus and the liquidus in this composition range which was explained as a formation of two immiscible liquid phases. In fact the KI–I melts show a tendency to supercooling for several K which was reflected by such a specific sequence of thermal arrests. It was shown in subsequent and reliable papers of Briggs and Geigle[7] and Rosztoczy and Cubicciotti[8] that KI_3 or other polyiodides are not formed at ~350 K. Their formation cannot be excluded at temperatures below 320 K, but this temperature range was not investigated in detail. Old data of the melting point of KI_3 at 318 K (Ref. 9) and 311 K (Ref. 10) seem to be disturbed by the H_2O content in the materials used, since Hamburger and Abegg[1] observed the melting point of KI_3 at ~303 K, if KI_3 was recrystallized from water.

The I-rich part of the K–I phase diagram was investigated by Briggs and Geigle[7] at normal pressure and by Rosztoczy and Cubicciotti[8] in a closed container. Timmermans[2] (the paper is not compiled, since only the cryoscopic constant was reported therein) and Beckman[11] observed a depression of the melting point of I upon the addition of KI in small amounts. Wartenberg[12] reported that the solubility of I at 973 K is 0.4 mol % I in molten KI, which value was recalculated to 50.1 mol % I in common scale. This value could be treated as a content of I at normal pressure, since at this temperature KI is certainly liquid and I gaseous. A liquidus point (94 mol % I at 313 K) suggested by Plotnikov *et al.*[13] on the basis of electric conductance experiments is located above the liquidus line of other publications and is rejected. The results of numerous studies[1–8,11] show relatively good agreement. The data of Rosztoczy and Cubicciotti[8] and Beckman[11] are the most precise. Thus the eutectic at 354.7 K is placed at 89 mol % I.[1,3,4,7,8]

The K-rich part of the K–I phase diagram was investigated by Johnson and Bredig[14] and Smirnov *et al.*[15] The single result of Smirnov *et al.*[15] is placed 10 K above the liquidus line formed by data of Bredig.[14]

The K–I phase diagram at constrained pressure to keep I as liquid, is shown in the figure according to Rosztoczy and Cubicciotti.[8] The I-rich part of the phase diagram at 0.1 MPa was presented in Briggs and Geigle.[7] Hoch[16] calculated the liquidus between KI and I using his own solution model and the Schottky–Wagner disorder model; the calculated liquidus line deviates significantly from experimental observations, and the eutectic is moved for ≈10 mol % I to the KI side. Rinck[17] investigated the equilibrium of the reaction:

$$K + NaI \leftrightarrow KI + Na \quad (1)$$

and found its equilibrium constant at 973–1173 K changing from 41.2 to 75.7. The constant has only a qualitative character, since mutual solubilities of metals and salts were not taken into account.

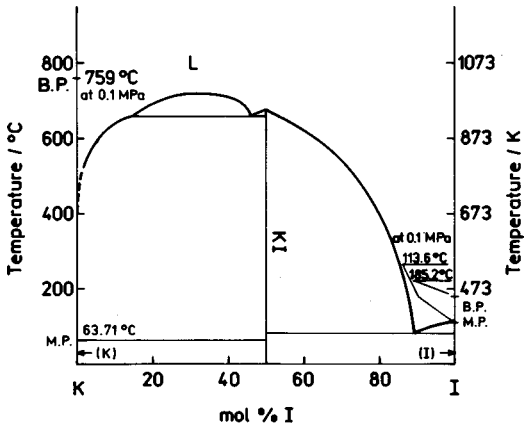

FIG. 48. K–I phase diagram at constrained pressure.

Tentative values of the solubility of I in liquid K

T/K	Solubility/mol % I	Source
773	1	(14) extrapolated
873	6	(14) interpolated
932	15 monotectic	(14) interpolated
990	33 critical	(14)

Tentative values of the solubility of I at the KI-rich side

T/K	Solubility/mol % I	Source
932	46 monotectic	(14)
953	50 congruent	(8),(14) mean value

Tentative values of the I solubility at the I-rich side

T/K	Solubility/mol % I	Source
873	63	(8) interpolated
773	74	(8) interpolated
673	80	(8)
573	84	(8)
473	87	(8) interpolated
373	89	(1),(7),(8) interpolated
354.7	89 eutectic	(8)
373	94	(1),(7),(8) interpolated

References:

[1]A. Hamburger and R. Abegg, Z. Anorg. Chem. **50**, 403 (1906).
[2]G. Timmermans, J. Chim. Phys. **4**, 170 (1906).
[3]R. Kremann and R. Schoulz, Monatsh. Chem. **33**, 1081 (1912).
[4]Ya. A. Fialkov and A. A. Kusmenko, Acta Physicichim. URSS **3**, 711 (1935).
[5]Ya. A. Fialkov and A. A. Kusmenko, Mem. Inst. Khim. Ukr. Akad. Nauk **2**, 127 (1935).
[6]Ya. A. Fialkov and A. A. Kusmenko, Zh. Obshch. Khim. **6**, 265 (1936).
[7]T. R. Briggs and W. F. Geigle, J. Phys. Chem. **34**, 2250 (1930).
[8]F. E. Rosztoczy and D. Cubicciotti, J. Phys. Chem. **69**, 1687 (1965).
[9]G. S. Johnson, J. Chem. Soc. **249** (1877).
[10]H. L. Wells, Z. Anorg. Chem. **1**, 442 (1892).
[11]E. Beckmann, Z. Anorg. Chem. **77**, 200 (1912).
[12]H. Wartenberg, Z. Elektrochem. **32**, 331 (1926).
[13]V. A. Plotnikov, Ya. A. Fialkov, and V. P. Tschalii, Z. Phys. Chem., A **172**, 304 (1935).
[14]J. W. Johnson and M. A. Bredig, J. Phys. Chem. **62**, 604 (1958).
[15]M. V. Smirnov, V. V. Chebykin, and L. A. Tsiovkina, Electrochim. Acta **26**, 1275 (1981).
[16]M. Hoch, J. Phase Equil. **14**, 296 (1993).
[17]E. Rinck, Ann. Chim. **18**, 395 (1932).

Components:
(1) Iodine; I; [7553-56-2]
(2) Potassium; K; [7440-09-7]

Original Measurements:
A. Hamburger and R. Abegg, Z. Anorg. Chem. **50**, 403–438 (1906).

Variables:
Temperature: 354–382 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data
The I-rich part of the K–I liquidus was determined

t/°C	Solubility/mol % KI in I_2	Solubility/mol % I[a]
109.1	3.9	98.0
104	8.5	95.8
100.6	10.8	94.6
100	11.1	94.3
97	12.6	93.7
84.5	18.5	90.7
87	18.5	90.7
84	19.4	90.3
81.3	22.3	88.8
80.5	24.2	87.9
81.3	25.0	87.5
81	27.3	86.3
82	28.4	85.8
82.5	31.0	84.5
82.2	32.4	83.8
82	35	82.5
80	42.6	78.7
81.9	45.7	77.1
82	50.0	75.0
83.2	53.0	73.5

[a]Calculated by the compilers.

The melting point of I was found at 112.5 °C.

Auxiliary Information

Method:
Weighed amounts of I and KI were placed in a narrow tube at the top of which a thermometer was held in place by means of an asbestos plug to prevent excessive loss of I. The assembly was heated on a sand bath and subsequently cooled, stirring the melt with the use of a Pt wire loop. Temperatures of thermal arrests were recorded three times for each sample.

Source and Purity of Materials:
I: from Kahlbaum.
KI: from Kahlbaum.

Estimated Error:
Solubility: nothing specified.
Temperature: precision ±0.1 K.

Components:
(1) Iodine; I; [7553-56-2]
(2) Potassium; K; [7440-09-7]

Original Measurements:
E. Beckmann, Z. Anorg. Chem. **77**, 200–208 (1912).

Variables:
Temperature: 386.1–386.7 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data
The depression of the freezing point upon additions of KI to I was measured

ΔT/K	T/K[a]	Solubility/g KI in 100 g I	Solubility/mol % I[b]
0.110	386.7	0.158	99.88
0.233	386.6	0.341	99.74
0.333	386.5	0.461	99.65
0.510	386.3	0.672	99.49
0.685	386.1	0.891	99.33

[a]Calculated by the compilers assuming the melting point of I at 386.8 K; the melting point measured in this work was at 387 K.
[b]Calculated by the compilers.

Auxiliary Information

Method:
A glass tube contained an entrance for a thermometer and a jacket for heating or cooling. The tube had contact with the atmosphere via another tube filled with dry $CaCl_2$. I was introduced into the main tube and melted in paraffin oil at 408 K, and crystallized by cooling to 383 K. The process was repeated. I pressed together with KI was investigated in the same way. The temperature difference from two experiments was measured by the thermometer.

Source and Purity of Materials:
I: resublimed, from Kahlbaum; stored in contact with P_2O_5.
KI: nothing specified.

Estimated Error:
Solubility: nothing specified; precision ±0.1% (by the compilers).
Temperature: nothing specified; precision ±0.01 K (by the compilers).

Components:
(1) Iodine; I; [7553-56-2]
(2) Potassium; K; [7440-09-7]

Original Measurements:
R. Kremann and R. Schoulz, Monatsh. Chem. **33**, 1081–1086 (1912).

Variables:
Temperature: 352–379 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data
The I-rich part of the K–I liquidus was determined

t/°C	Solubility/mol % I_2 in KI	Solubility/mol % I[a]
105.9	90.27	95.1
93.8	85.4	92.7
81.5	80.8	90.4
77.8	77.5	88.7
79.6	65.5	82.7
79.8	58.5	79.2
78.9	54.6	77.3

[a]Calculated by the compilers.

The melting point of I was found at 112.0 °C. The authors observed a tendency to supercooling the melts.

Auxiliary Information

Method:
The components were introduced into a large container made of glass. The container was sealed and heated to 523–573 K. The melt was conditioned for several days before cooling curves were recorded with the use of a thermocouple. The thermocouple was isolated from the melt by a glass tube.

Source and Purity of Materials:
I: "pure."
KI: "pure," in the form of fine powder.

Estimated Error:
Solubility: nothing specified; precision not better than ±0.1 mol %.
Temperature: nothing specified; precision not better than ±0.1 K.

Components:
(1) Iodine; I; [7553-56-2]
(2) Potassium; K; [7440-09-7]

Original Measurements:
T. R. Briggs and W. F. Geigle, J. Phys. Chem. **34**, 2250–2259 (1930).

Variables:
Temperature: 352–463 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data
The solubility of KI in liquid I was determined

t/°C	Solubility/mol % KI in I_2	Solubility/mol % I[b]
108.5	5	97.5
102.0	9.6	95.2
89.2	15.2	92.4
85.7	18	91.0
78.4	20	90.0
90	21.6	89.2
99	21.4	89.3
123	22.1	88.9
141	22.1	88.9
161	23.3	88.4
165	23.4	88.3
172	23.6	88.2
130	22.1	88.2
150	24.2	88.9
172	23.3	87.9
175	23.8	88.4
184[a]	10	95
188[a]	20	90
192[a]	30	85
190[a]	40	80
191[a]	50	75
190[a]	60	70
192[a]	70	65
190[a]	80	60

[a]Boiling points.
[b]Calculated by the compilers.

An increase of the KI content up to 85 mol % KI caused in the thermal analysis an arrest at 80.5±0.5 °C. The melting temperature of I was found at 113 °C, its boiling point at 182 °C.

Auxiliary Information

Method:
The eutectic mixture of KI and I was ground fine and placed in a glass tube. The tube was sealed with a thermometer preventing any serious loss of I during heating. The materials were held at 413–423 K for 2–4 h before they were allowed to cool. The cooling curves were taken in the customary way. In the solubility measurements the saturated solutions were filtered through a glass wool plug. The filtering tube below the plug was broken open when cold and the frozen liquid phase was analyzed for I and KI in the manner described in Briggs *et al.*[1] The boiling points of the solutions were determined in a glass apparatus using a thermometer.

Source and Purity of Materials:
I: "well dried," stored in a desiccator.
KI: "well dried," stored in a desiccator.

Estimated Error:
Solubility: nothing specified; not better than ±0.5 mol % (by the compilers).
Temperature: precision ±0.2 K (melting) and ±1 K (boiling).

References:
[1]T. A. Briggs, J. A. Greenwald, and J. W. Leonard, J. Phys. Chem. **34**, 1950–1955 (1930).

Components:
(1) Iodine; I; [7553-56-2]
(2) Potassium; K; [7440-09-7]

Original Measurements:
J. A. Fialkov and A. A. Kusmenko, Acta Physicochim. URSS **3**, 711–724 (1935).

Variables:
Temperature: 353–381 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data
The I-rich part of the K–I liquidus was determined. The results were reported in a figure. They were read out and recalculated to mol % I by the compilers.

t/°C	Solubility/mol % KI in I_2	Solubility/mol % I[a]
108	4	98.0
91	15	92.5
87	16	92.0
82	21 eutectic	89.5

[a]Calculated by the compilers.

Two thermal arrests at 80 and 82 °C occurred upon further addition of KI, explained as a formation of two immiscible liquid phases. The melting point of I was found at 113.36–113.20 °C. The same results were published in Fialkov and Kusmenko[1] and Fialkov and Kusmenko.[2]

Auxiliary Information

Method:
Thermal analysis of the K–I melts was performed in a glass container. A precision Hg thermometer, placed inside of the container, was used. The rates of temperature changes applied were 0.4–0.6 K/min. The container was shaken to avoid undercooling which was observed to be ~2.1 K.

Source and Purity of Materials:
I: purified by heating and dehydration.
KI: purified by heating and dehydration.

Estimated Error:
Solubility: nothing specified; reading-out procedure ±0.5 mol %.
Temperature: precision ±0.3 K; reading-out procedure ±0.5 K.

References:
[1]J. A. Fialkov and A. A. Kusmenko, Mem. Inst. Khim. Ukr. Akad. Nauk **2**, 127–139 (1935).
[2]J. A. Fialkov and A. A. Kusmenko, Zh. Obshch. Khim. **6**, 265–272 (1936).

Components:
(1) Iodine; I; [7553-56-2]
(2) Potassium; K; [7440-09-7]

Original Measurements:
J. W. Johnson and M. A. Bredig, J. Phys. Chem. **62**, 604–607 (1958).

Variables:
Temperature: 811–990 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data
The mutual miscibility of KI and K was investigated

t/°C	Solubility/mol % KI	Solubility/mol % I[a]
537.7	2.37–2.45	2.35
584.4–585.1	4.83–4.88	4.63
614.5–614.9	7.40–7.46	6.92
632.8–632.9	10.06–10.11	9.17
645.2–645.4	12.34–12.42	11.02
648.7–648.8	13.94–14.04	12.3
659.7–659.8	88.21–88.46	46.9
662.8	90.64–90.75	47.6
664.9–665.2	92.46–92.54	48.05
668.5–668.6	95.56–95.61	48.87
673.0–673.3	96.83–96.89	49.20
675.2–675.5	97.89–98.01	45.51
681.0	20.14–20.21	16.8
703.1–704.1	29.25–29.35	22.7
712.3	34.23–34.34	25.5
714.9–715.1	39.96–40.04	28.6
717.0	46.58–46.74	31.8
716.6	48.44–48.54	32.6
716.5–716.7	56.70–56.80	36.2
716.6	58.30–58.48	36.9
710.5	68.75–68.89	40.8
708.4–708.5	70.88–70.99	41.5
690.7–691.2	78.59–78.89	44.1
665.8–666.3	84.95–85.14	46.0

[a]Mean value calculated by the compilers.

The melting point of KI was determined at 680.7±0.1 °C, the monotectic temperature at 658.5±0.5 °C.

Auxiliary Information

Method:
Thermal analyses of samples were carried out in a stainless steel capsule. The capsule was filled with known amounts of KI and K and purged with Ar. The capsule was welded shut with a flat top and placed inside a tank made of Inconel, and it was then pressurized with Ar up to ~0.7 MPa. The ratio of the container weight to the sample weight was reduced by employing thin walled construction tubes. Temperatures were measured using a Pt/Pt–Rh(10%) thermocouple in a well. Cooling and heating cycles were repeated 2–4 times for each composition.

Source and Purity of Materials:
KI: "optical grade" of purity.
K: remelted under hexane in a stainless steel beaker, the oxidized surface removed, the metal stored in a desiccator.
Ar: nothing specified.

Estimated Error:
Solubility: precision better than ±0.8%.
Temperature: precision of reading ±0.25 and of estimation ±0.05 K.

Components:
(1) Iodine; I; [7553-56-2]
(2) Potassium; K; [7440-09-7]

Original Measurements:
F. E. Roszto czy and D. Cubicciotti, J. Phys. Chem. **69**, 1687–1692 (1965).

Variables:
Temperature: 355–944 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data
The I-rich part of the K–I liquidus line was determined

t/°C	Solubility/mol % KI in I_2	Solubility/mol % I[a]
112.2	1	99.5
111.8	2	99.0
107.7	6	97.0
98.2	12	94.0
86	18	91.0
83	20	90.0
81.5	22	89.0
170	24	88.0
187	26	87.0
303	32	84.0
399.9	40	80.0
448.5	45	77.5
511	55	72.5
562.2	65	67.5
619.8	80	60.0
649.0	90	55.0
660.6	94	53.0
671.1	98	51.0

[a]Calculated by the compilers.

The melting points of KI and I were found to be 113.3 and 678.5 °C, respectively.

Auxiliary Information

Method:
Cooling curves were obtained with samples in glass containers sealed under vacuum. Two types of containers were used: a medium-wall Pyrex test tube with a re-entrant thermocouple well in the bottom and a bundle of three medium-wall fused quartz tubes. Tubes of the first type were used with the I-rich solutions. Tubes of the second type were used for the KI-rich solutions. During a cooling or heating curve the samples were maintained at constant temperature above or below the temperature of the furnace.

Source and Purity of Materials:
I: resublimed crystals of ultrapure compound from Mallinckrodt.
KI: reagent grade from Allied Chemical.

Estimated Error:
Solubility: nothing specified.
Temperature: nothing specified.

Components:
(1) Iodine; I; [7553-56-2]
(2) Potassium; K; [7440-09-7]

Original Measurements:
M. V. Smirnov, V. V. Chebykin, and L. A. Tsiovkina, Electrochim. Acta **26**, 1275–1288 (1981).

Variables:
One temperature: 962 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of K in molten KI was determined to be 20.8 mol % K at 689 °C (962 K), corresponding to a solubility of 44.2 mol % I in liquid K, as calculated by the compilers.

Auxiliary Information

Method:
All parts being in contact with mixtures of KI and K were made of stainless steel, resistant to their action at high temperatures. The pressure developed by the saturated vapors in the hermetically sealed inner part of the device was fixed with bellow manometers which used an automatic regulator for balancing the pressure in Ar in the outer (also hermetically sealed) part of the apparatus. The experimental installation was tested by measuring the pressure of K and Cs saturated vapors over wide temperature ranges. The measured values were in good agreement with the most reliable reference data. The mixtures were composed directly by distilling definite amount of K into the container filled with known amount of KI. The saturated vapor pressures were measured as a function of the temperature; the break point corresponded to the solubility.

Source and Purity of Materials:
KI: "particularly pure," recrystallized, and dried under vacuum while the temperature was raised slowly up to 450 °C until H_2O condensation in liquid N ceased. The alkalinity was 0.005–0.01 mol %.
K: 99.99% pure.
Ar: nothing specified.

Estimated Error:
Solubility: precision ±3%.
Pressure: precision ±250 Pa or ±2%.
Temperature: precision ±1 K.

5.19. Potassium–Helium

Components:
(1) Helium; He; [7440-59-7]
(2) Potassium; K; [7440-09-7]

Evaluated by:
Hans Ulrich Borgstedt, Forschungszentrum Karlsruhe, Germany and Cezary Guminski, University of Warsaw, Poland, February 1998.

Critical Evaluation

The dissolution process of He in liquid K or K–Na alloy is significantly slower than of H. The solubility of He in K was measured by Slotnik *et al.*[1] at 755–977 K and between 0.125 and 0.310 MPa. The solubility data at 0.101 MPa may be expressed by the equation:

$$\log(\text{soly/mol \% He}) = -1.402 - 1536\,(T/\text{K})^{-1}, \quad r = 0.933. \tag{1}$$

An equation, which based on the same data of Slotnik *et al.*,[1] was formulated in Hubberstey,[2] however, it seems to be charged with an error.

Arnoldov *et al.*[3–5] measured the solubility of He in the eutectic K–Na mixture at 573 K. Although the publications were originated from the same laboratory and seem to describe the same experiment, three different values are reported: $1.1\cdot10^{-5}$,[3] $1.2\cdot10^{-3}$,[4] and $1\cdot10^{-5}$ mol % He.[5] Comparing these results with the figures shown in these papers we select the latter value of Arnoldov *et al.*[3] and Arnoldov *et al.*[5] as the correct one.

Reed and Droher[6] predicted the solubility equation for He in liquid eutectic K–Na alloy based on the experimental solubilities of He in Na and K, and taking into account the Na mol fraction in the alloy:

$$\log(\text{soly/mol \% He}) = -1.580 - 1517\,(T/\text{K})^{-1}. \tag{2}$$

The value calculated from Eq. (2) at 573 K is $6\cdot10^{-5}$ mol % He, which is placed above the solubility results of Arnoldov *et al.*[3] and Arnoldov *et al.*[5]

Tentative values of the solubility of He in liquid K at 0.101 MPa

T/K	Solubility/mol % He	Source
773	$4\cdot10^{-4}$	(1) interpolated
873	$7\cdot10^{-4}$	(1)
973	$1.0\cdot10^{-3}$	(1)

References:

[1]H. Slotnik, S. M. Kapelner, and R. E. Cleary, U.S. Atom. Energy. Comm. Rep. PWAC-380 (1965).

[2]P. Hubberstey, *Handbook of Thermodynamic and Transport Properties of the Alkali Metals*, edited by R. W. Ohse (Blackwell, Oxford, 1985), p. 907.

[3]M. N. Arnoldov, M. N. Ivanovskii, V. A. Morozov, S. S. Pletenets, and V. I. Subbotin, *Teplofizicheskie Svoistva Zhidkostei v Vysokikh Temperaturakh*, edited by A. K. Adas-Zade and E. E. Shpil'rain (Nauka, Moskva, 1970), p. 110.

[4]M. N. Arnoldov, M. N. Ivanovskii, V. A. Morozov, S. S. Pletenets, and V. I. Subbotin, Atom. Energiya **28**, 18 (1970).

[5]V. I. Subbotin, M. N. Ivanovskii, and M. N. Arnoldov, *Fizikokhimicheskie Osnovy Primeneniya Zhidkometallicheskikh Teplonositelei* (Atomizdat, Moskva, 1970), p. 78.

[6]E. L. Reed and J. J. Droher, U.S. Atom. Energy. Comm. Rep. LMEC-69-36 (1970).

Components:
(1) Helium; He; [7440-59-7]
(2) Potassium–sodium eutectic; $K_{68}Na_{32}$; [11147-16-3]

Original Measurements:
V. I. Subbotin, M. N. Ivanovskii, and M. N. Arnoldov, *Fizikokhimicheskie Osnovy Primeneniya Zhidkometallicheskikh Teplonositelei* (Atomizdat, Moskva, 1970), pp. 78–79.

Variables:
One temperature: 573 K;
One pressure: 0.101 MPa

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of He in liquid K–Na eutectic alloy at 0.101 MPa and 300 °C was found to be 10^{-6} mass % or $1\cdot10^{-5}$ mol % He (as calculated by the compilers). Different results, from probably the same experiments, were presented graphically in Arnoldov *et al.*[1,2] According to Arnoldov *et al.*,[1] the solubility is $1.2\cdot10^{-5}$ atom. fract. He, which corresponds to $1.2\cdot10^{-3}$ mol % He. According to Arnoldov *et al.*,[2] the solubility is $1.3\cdot10^{-5}$ g He/1000 g K, recalculation results in $1.1\cdot10^{-5}$ mol % He. Since the values differ for orders of magnitude, a comment from the authors would be helpful. The authors quoted data on the solubility of He in liquid K from literature together with their own results and on this basis we may judge that the results reported in Arnoldov *et al.*[1] are wrong.

Auxiliary Information

Method:
Unspecified materials were used for the construction of the apparatus.[1] The He gas pressure was measured with a manometer. The amounts of He in a chamber, before and after equilibration with the melt, were calculated assuming ideal behavior of He gas. The He pressure measurement was repeated till stable values were recorded.

Source and Purity of Materials:
He: contained $5\cdot10^{-4}$ vol % H, $1.3\cdot10^{-3}$ N, $4\cdot10^{-4}$ % O, $5.3\cdot10^{-3}$ % Ne, $1\cdot10^{-4}$ % hydrocarbons, dew point 213 K; the gas was frozen out in a liquid N trap.
K–Na: contained 21.8% Na; $3\cdot10^{-4}$ % Li, In; 0.01% Mg, Zn, Cu; $1\cdot10^{-4}$ % Ag, Cd; 0.066% Fe, 0.033% Ca, Cr, Ti; $3.3\cdot10^{-3}$ % Al, Mn; $2\cdot10^{-3}$ % Sn; $3\cdot10^{-3}$ % Ba; $1\cdot10^{-3}$ % Mo, V, Bi, Pb, Co; $9\cdot10^{-3}$ % Be; as in Arnoldov *et al.*[1,2]

Estimated Error:
Solubility: precision 50%–100%; reading-out procedure ±10%.
Temperature: nothing specified.

References:
[1]M. N. Arnoldov, M. N. Ivanovskii, V. A. Morozov, S. S. Pletenets, and V. I. Subbotin, Atom. Energiya **28**, 18–22 (1970).
[2]M. N. Arnoldov, M. N. Ivanovskii, V. A. Morozov, S. S. Pletenets, and V. I. Subbotin, *Teplofizicheskie Svoistva Zhidkostei v Vysokikh Temperaturakh*, edited by A. K. Abas-Zade and E. E. Shpil'rain (Nauka, Moskva, 1970), pp. 110–116.

5.20. Potassium–Neon, Krypton, Xenon, or Radon

Components:
(1) Neon; Ne; [7440-01-9]
or Krypton; Kr; [7439-90-9]
or Xenon; Xe; [7440-63-3]
(2) Potassium; K; [7440-09-7]

Evaluated by:
Hans Ulrich Borgstedt, Forschungszentrum Karlsruhe, Germany and Cezary Guminski, University of Warsaw, Poland, April 1999

Critical Evaluation

Solubilities of these noble gases have not been measured so far. According to the general tendency observed, the solubilities of Ne, Kr, Xe, and Rn in liquid K should be higher than those measured in Na. Tilton *et al.*[1] measured optical properties of solid mixtures of Kr or Xe with K at 5 K. No information concerning the phase equilibria or the miscibility of the components could be deduced from these experiments.

References:
[1]R. A. Tilton, D. J. Phelps, and C. P. Flynn, Phys. Rev. Lett. **32**, 1006 (1974).

5.21. Potassium–Argon

Components:
(1) Argon; Ar; [7440-37-1]
(2) Potassium; K; [7440-17-7]

Evaluated by:
Hans Ulrich Borgstedt, Forschungszentrum Karlsruhe, Germany and Cezary Guminski, University of Warsaw, Poland, March 1998.

Critical Evaluation

The solubility of Ar in liquid K has not been measured so far. Reed and Droher[1] predicted this solubility based on the ratio of the experimental solubilities of He in K and Na as well as the solubility of He in K. The authors proposed the following equation for the solubility of Ar in K:

$$\log(\text{soly/mol \% Ar}) = 0.261 - 3702\ (T/\text{K})^{-1} \quad (1)$$

and in eutectic K–Na alloy:

$$\log(\text{soly/mol \% Ar}) = 0.120 - 3718\ (T/\text{K})^{-1} \quad (2)$$

Arnoldov *et al.*[2–4] determined the solubility of Ar in the K–Na eutectic mixture at 573 K. The following values were reported: 10^{-5} mol % Ar in Arnoldov *et al.*,[2] $7 \cdot 10^{-4}$ mol % Ar in Arnoldov *et al.*,[3] and $8 \cdot 10^{-7}$ mol % Ar in Arnoldov *et al.*[4] Although the data seem to be obtained in the same experiment, the authors did not give any comment concerning the differences. Since the data of Arnoldov *et al.*[4] is very close to the prediction of Reed and Droher,[1] it seems to be the most reliable one. Solubilities of Ne, Kr, and Xe have not been reported in literature.

References:

[1]E. L Reed and J. J. Droher, U.S. Atom. Energy Comm. Rep. LMEC-36 (1970).

[2]V. I. Subbotin, M. N. Ivanovskii, and M. N. Arnoldov, *Fiziko-khimicheskie Osnovy Primeneniya Zhidkometallicheskikh Teplonositelei* (Atomizdat, Moskva, 1970), p. 78.

[3]M. N. Arnoldov, M. N. Ivanovskii, V. A. Morozov, S. S. Pletenets, and V. I. Subbotin, Atom. Energiya **28**, 18 (1970).

[4]M. N. Arnoldov, M. N. Ivanovskii, V. A. Morozov, S. S. Pletenets, and V. I. Subbotin, *Teplofizicheskie Svoistva Zhidkostei v Vysokikh Temperaturakh*, edited by A. K. Abas-Zade and E. E. Shpil'rain (Nauka, Moskva, 1970), p. 110.

Components:
(1) Argon; Ar; [7440-37-1]
(2) Potassium–sodium eutectic; $K_{68}Na_{32}$; [11147-16-3]

Original Measurements:
V. I. Subbotin, M. N. Ivanovskii, and M. N. Arnoldov, *Fiziko-khimicheskie Osnovy Primeneniya Zhidkometallicheskikh Teplonositelei* (Atomizdat, Moskva, 1970), pp. 78–79.

Variables:
One temperature: 573 K;
One pressure: 0.101 MPa

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of Ar in the liquid K–Na eutectic alloy at a presure of 0.101 MPa and 300 °C was determined to be 10^{-5} mass % or 10^{-5} mol % Ar. Other results from the same laboratory were presented graphically in Arnoldov *et al.*[1,2]

According to Arnoldov *et al.*,[1] the solubility is $7 \cdot 10^{-6}$ mol fraction Ar or $7 \cdot 10^{-4}$ mol % Ar. According to Arnoldov *et al.*,[2] the solubility is $9 \cdot 10^{-6}$ g Ar/1000 g K–Na or $8 \cdot 10^{-7}$ mol % Ar.

Auxiliary Information

Method:
Unspecified materials were used for the construction of the apparatus.[1,2] The Ar gas pressure was measured using a manometer. The amounts of Ar in a chamber, before and after the equilibration with the melt, were calculated assuming ideal behavior of Ar gas. Ar pressure measurement was repeated till stable values were recorded.

Source and Purity of Materials:
Ar: contained 0.01% N and $3 \cdot 10^{-3}$ % O.
K–Na: contained 21.8% Na, $3 \cdot 10^{-4}$ % Li, In, 0.01% Mg, Zn, Cu, $1 \cdot 10^{-4}$ % Ag, Cd, 0.066% Fe, 0.033% Ca, Cr, Ti, 3.3 $\cdot 10^{-3}$ % Al, Mn, $2 \cdot 10^{-3}$ % Sn, $3 \cdot 10^{-3}$ % Ba, $1 \cdot 10^{-3}$ % Mo, V, Bi, Pb, Co, $9 \cdot 10^{-3}$ % Be.

Estimated Error:
Solubility: precision 50%–100%; reading out procedure ±10%.
Temperature: nothing specified.

References:

[1]M. N. Arnoldov, M. N. Ivanovskii, V. A. Morozov, S. S. Pletenets, and V. I. Subbotin, Atom. Energiya **28**, 18 (1970).

[2]M. N. Arnoldov, M. N. Ivanovskii, V. A. Morozov, S. S. Pletenets, and V. I. Subbotin, *Teplofizicheskie Svoistva Zhidkostei v Vysokikh Temperaturakh*, edited by A. K. Abas-Zade and E. E. Shpil'rain (Nauka, Moskva, 1970), p. 110.

6. Solutions of Nonmetallic Substances in Rubidium

6.1. Rubidium–Hydrogen

Components:
(1) Hydrogen; H; [1333-74-0]
(2) Rubidium; Rb; [7440-17-7]

Evaluated by:
Hans Ulrich Borgstedt, Forschungszentrum Karlsruhe, Germany and Cezary Guminski, University of Warsaw, Poland, May 1998.

Critical Evaluation

H reacts with liquid Rb forming the compound RbH. An elevation of pressure and temperature accelerates the reaction. Solubility measurements of H in liquid Rb have not been performed so far. Expected solubility values seem to be situated between the corresponding values obtained in liquid Cs and K. However, measurements of the H vapor pressure over the Rb–H melts would point to some abnormality of the Rb–H system in comparison with the K–H and Cs–H systems. Although the equilibrium H pressure data[1–6] over Rb–H show a significant scatter, it seems that the results of Hérold[3,4] are the most reasonable. They could be expressed by the following equation:

$$\log(p_H/\mathrm{Pa}) = 13.919 - 5680\ (T/\mathrm{K})^{-1}. \quad (1)$$

The H equilibrium pressure over the Rb–H melt at 623 K is about two times higher than in the Cs–H system and about nine times higher than in the K–H system at the same temperature.

Messer *et al.*[5] observed that RbH dissociated at normal pressure before reaching its melting point. Using thermal analysis at <0.1 MPa, Dymova *et al.*[7] found a decomposition of RbH to Rb and H at 703–712 K. Skuratov *et al.*[6] performed the same kind of experiments at 1.0–3.0 MPa and determined the melting temperature of RbH at 858±2 K. An increase of the pressure to 10 MPa caused an elevation of the melting point for further 2.0±0.2 K. The Rb–H phase diagram at a pressure sufficient to keep RbH as solid up to its melting point, seems to be very similar to that of the K–H system. A monotectic at about 856 K should extend from about 10 to about 49 mol % H, according to predictions of Sangster and Pelton.[8]

The D vapor pressure over Rb–D melts was estimated to be higher than for the Rb–H. A solubility of D in liquid Rb is unknown as well. Magomedov[9] predicted the melting point of RbH, RbD, and RbT being 906.00, 905.52, and 905.42 K, respectively, suggesting that the isotope effect is small. All predicted values are higher than the experimental data for RbH.

References:

[1]F. Ephraim and E. Michel, Helv. Chim. Acta **4**, 762 (1921).
[2]L. Hackspill and A. Borocco, Bull. Soc. Chim. Fr. **6**, 91 (1939).
[3]A. Hérold, Compt. Rend. **228**, 686 (1949).
[4]A. Hérold, Ann. Chim. **6**, 536 (1951).
[5]C. E. Messer, H. Homonoff, R. F. Nickerson, and T. R. P. Gibb, U.S. Atom. Energy Comm. Rep. NYO-3955 (1953).
[6]O. A. Skuratov, O. N. Pavlov, V. I. Danilkin, and I. V. Volkov, Zh. Neorg. Khim. **21**, 2910 (1976); Russ. J. Inorg. Chem. **21**, 1605 (1976).
[7]T. N. Dymova, S. I. Bakum, and U. Mirsaidov, Dokl. Akad. Nauk SSSR **216**, 87 (1974).
[8]J. Sangster and A. D. Pelton, J. Phase Equil. **15**, 87 (1994).
[9]M. N. Magomedov, Zh. Fiz. Khim. **68**, 589 (1994).

6.2. Rubidium–Boron

Components:
(1) Boron; B; [7440-42-8]
(2) Rubidium; Rb; [7440-17-7]

Evaluated by:
Hans Ulrich Borgstedt, Forschungszentrum Karlsruhe, Germany and Cezary Guminski, University of Warsaw, Poland, May 1998.

Critical Evaluation

A reaction of B and liquid Rb at higher temperatures can be presumed by analogy to the K–B system. However, experimental material does not exist to formulate either the Rb–B phase diagram or to predict a solubility of B in liquid Rb. By comparison to the K–B and Cs–B systems, one may conclude that the solubility of B in liquid Rb should not be negligible.

6.3. Rubidium–Carbon

Components:
(1) Carbon; C; [7440-44-0]
(2) Rubidium; Rb; [7440-17-7]

Evaluated by:
Hans Ulrich Borgstedt, Forschungszentrum Karlsruhe, Germany and Cezary Guminski, University of Warsaw, Poland, October 1998.

Critical Evaluation

Graphite interacts with liquid Rb as was discovered by Fredenhagen and Cadenbach[1] and confirmed later in more detailed studies by Hérold[2] and by Salzano and Aronson.[3] Depending on temperature and pressure inside a reaction vessel, one obtains the whole series of lamellar compounds RbC_8, RbC_{10}, RbC_{24}, RbC_{36}, RbC_{48}, and finally RbC_{60}. The compound RbC_{10} is not an exactly stoichiometric phase. Higher temperature and lower pressure favors the formation of C-richer compound. No formation of acetylide Rb_2C_2 was reported.

The relatively fast disintegration of graphite may be wrongly estimated as good solubility of C in liquid Rb. The solubility seems to be rather small, however, experimental values are not available. Tepper *et al.*[4] elaborated a method of C determination in Rb, but his result indicating a content of $2.0 \cdot 10^{-2}$ mol % C in Rb is not considered as the solubility and temperature of the determination is not specified.

Metoki and Suematsu[5] performed some x-ray diffraction experiments with a mixture of RbC_8 and C-richer compounds. They established the "melting point" of RbC_8 at 776.2 K, at a Rb pressure of about 61 Pa. Moreover, they revealed the existence of a liquid between RbC_8 and RbC_{24} with a eutectic temperature of 613 K. These data are not compiled, since the results are not related to solid–liquid solubility phenomenon. Some observations of Metoki and Suematsu[5] are in contradiction to the results of Aronson *et al.*[7] who stated that the RbC_{10} phase exists above 573 K and decomposes to RbC_8 and RbC_{24} in metatectic reaction at 566 K. Ellenson *et al.*[6] reported the formation of an ordered RbC_8 phase at 708 K and a disordered phase at 747 K. Melting in the intercalation compounds occurs for Rb atoms placed between rigid graphite layers. Therefore the matter needs further experiments in this composition range. The provisional Rb–C phase diagram is shown in Fig. 49, but solubility data could not be suggested. Poirier *et al.*[8] discussed Rb–C_{60} equilibria and proposed a schematic Rb–C_{60} phase diagram similar to that of K–C_{60}. Although the solubility of C_{60} in Rb has not been investigated so far, one may expect that such a solution may be in equilibrium with Rb_6C_{60} at lower and with Rb_4C_{60} at higher temperatures; other expected phases are RbC_{60} and Rb_3C_{60}.

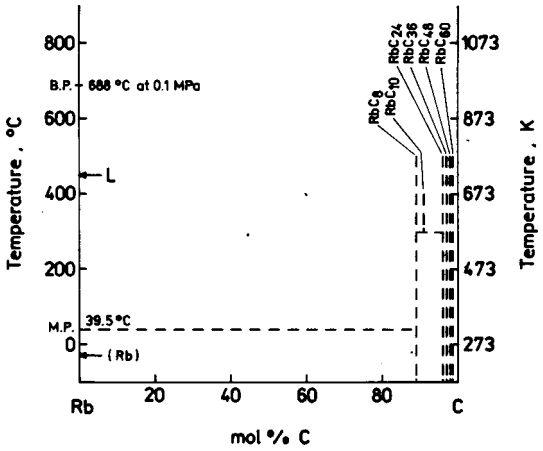

FIG. 49. Rb–C phase diagram (provisional).

References:
[1]K. Fredenhagen and G. Cadenbach, Z. Anorg. Chem. **158**, 249 (1926).
[2]A. Hérold, Bull. Soc. Chim., Fr 999 (1955); Compt. Rend. **232**, 1484 (1951).
[3]F. J. Salzano and S. Aronson, J. Chem. Phys. **45**, 4551 (1966).
[4]F. Tepper, A. Murchison, J. Zelenak, and F. Roehlich, U.S. Atom. Energy Comm. Rep. ORNL-3605, vol. 1, p. 26 (1964).
[5]N. Metoki and H. Suematsu, Phys. Rev. B **38**, 5310 (1988).
[6]W. D. Ellenson, D. Semmingsen, D. Guerard, D. G. Onn, and J. E. Fisher, Mater. Sci. Engin. **31**, 137 (1977).
[7]S. Aronson, F. J. Salzano, and D. Bellafiore, J. Chem. Phys. **49**, 434 (1968).
[8]D. M. Poirier, D. W. Owens, and J. H. Weaver, Phys. Rev. B **51**, 1830 (1995).

6.4. Rubidium–Silicon

Components:
(1) Silicon; Si; [7440-21-3]
(2) Rubidium; Rb; [7440-17-7]

Evaluated by:
Hans Ulrich Borgstedt, Forschungszentrum Karlsruhe, Germany and Cezary Guminski, University of Warsaw, Poland, June 1999.

Critical Evaluation

RbSi was prepared by Hohmann[1] by means of synthesis at 873 K in a corundum vessel enclosed in a Fe bomb. RbSi decomposes further to $RbSi_6$ at about 800 K in high vacuum as was found by Schäfer and Klemm.[2] Hohmann[1] observed this reaction at 623 K. Cros *et al.*[3] reported that the latter compound has a clathrate-like structure with the formula Rb_5Si_{46}. Chuntonov and Yatsenko[4] presented a fragment of the Rb–Si phase diagram based on Kuznetsov's thesis.[5] Since the thesis is not available to the evaluators and a figure reproduced in Chuntonov and Yatsenko[4] is rather small, we may report only qualitative conclusions from it. RbSi is poorly soluble in liquid Rb and reaches a solubility value of 4 mol % Si at 884 K. This temperature is not distinguishable from the melting point of RbSi as well as from the monotectic which extends between 4 and 50 mol % Rb. The critical temperature of the miscibility gap is 1073 K.

The partial Rb–Si phase diagram is shown in Fig. 50. Von Schnering *et al.*[6] observed several phases during the thermal decomposition of RbSi: $Rb_{12}Si_{17}$, Rb_4Si_9, Rb_6Si_{25}, Rb_8Si_{46}, and Rb_xSi_{136} ($5 \leq x \leq 12$). Solubility data cannot be suggested at the present state of research.

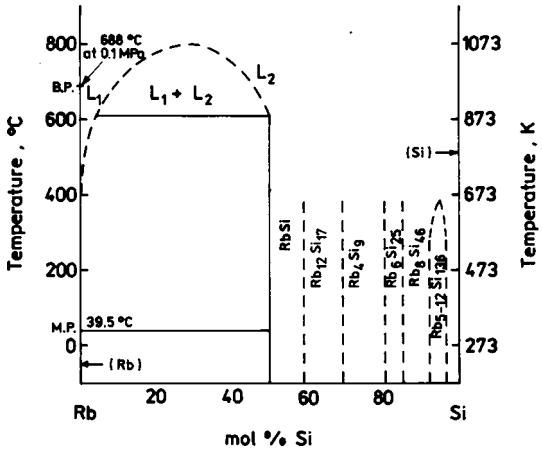

FIG. 50. Rb–Si phase diagram (partial).

The presence of O traces in the Rb–Si system leads to the formation of stable Rb_2SiO_3.[7]

References:
[1]E. Hohmann, Z. Anorg. Chem. **257**, 113 (1948).
[2]R. Schäfer and W. Klemm, Z. Anorg. Chem. **312**, 214 (1961).
[3]C. Cros, M. Pouchard, and P. Hagenmuller, Bull. Soc. Chim. Fr. 379 (1971).
[4]K. A. Chuntonov and S. P. Yatsenko, Zh. Fiz. Khim. **52**, 2145 (1978).
[5]A. N. Kuznetsov, Ph. D. thesis, Academy of Science, Sverdlovsk, Russia, 1978.
[6]H. G. von Schnering, M. Somer, M. Kaupp, W. Carrillo-Cabrera, M. Baitinger, A. Schmeding, and Y. Grin, Angew. Chem. **37**, 2359 (1998).
[7]R. Kohli, *Material Behavior and Physical Chemistry of Liquid Metal Systems*, edited by H. U. Borgstedt (Plenum, New York, 1983), p. 345.

6.5. Rubidium–Germanium

Components:
(1) Germanium; Ge; [7440-56-4]
(2) Rubidium; Rb; [7440-17-7]

Evaluated by:
Hans Ulrich Borgstedt, Forschungszentrum Karlsruhe, Germany and Cezary Guminski, University of Warsaw, Poland, June 1999.

Critical Evaluation

The literature reporting on the phase diagram of the Rb–Ge system is contradictory. Hohmann[1] discovered the formation of RbGe which probably formed $RbGe_4$ due to thermal decomposition at reduced pressure. Schäfer and Klemm[2] confirmed the findings of Hohmann.[1] According to Cros *et al.*,[3] another Ge-richer compound, Rb_xGe_{46} ($5<x<8$), of clathrate structure is formed during the thermal decomposition of RbGe in vacuum.

Yatsenko *et al.*[4,5] investigated first a major part of the Rb–Ge phase diagram. They observed the formation of RbGe and $RbGe_4$, an immiscibility gap between 15 and 50 mol % Ge at the monotectic temperature of 881 K, and in the Ge-rich range complete miscibility of the components was observed above 938 K (the melting point of Ge). $RbGe_4$ was found to be formed peritectically at 1033 K; a polimorphic transition at 438 K was stated which extends between 75 and 80 mol % Ge.

A quite different picture of the Rb–Ge phase relations was presented by Drits *et al.*[6] who reported the formation of the compounds Rb_3Ge, Rb_3Ge_2, RbGe, and $RbGe_4$, all formed congruently between 978 K (Rb_3Ge) and 1383 K ($RbGe_4$). The high melting point of $RbGe_4$ was confirmed in Potemkin *et al.*[7] Von Schnering *et al.*[8] identified $Rb_{12}Ge_{17}$ and Rb_4Ge_9; evidence was found that Rb_6Ge_{25} and Rb_xGe_{136} are also formed.

It is hard to judge whether the investigations of Yatsenko *et al.*[4,5] or of Drits *et al.*[6] and Potemkin *et al.*[7] are right. Reviewers of the Rb–Ge system (Sangster and Pelton[9]) preferred the shape of the phase diagram proposed by Yatsenko *et al.*[4,5] Drits *et al.*[6] and Potemkin *et al.*[7] used slightly purer materials and their experimental description contains more details. The experiments of Yatsenko *et al.*[4,5] were performed at a reduced pressure while the experiments of Drits *et al.*[6] and Potemkin *et al.*[7] were performed in an Ar atmosphere and normal pressure.

The phase diagram of Drits *et al.*[6] and Potemkin *et al.*[7] taking into account the observations of Cros *et al.*[3] and von Schnering *et al.*[8] is presented in Fig. 51. No solubility values could be suggested until an additional test on the Rb–Ge phase relations and the liquidus will be performed.

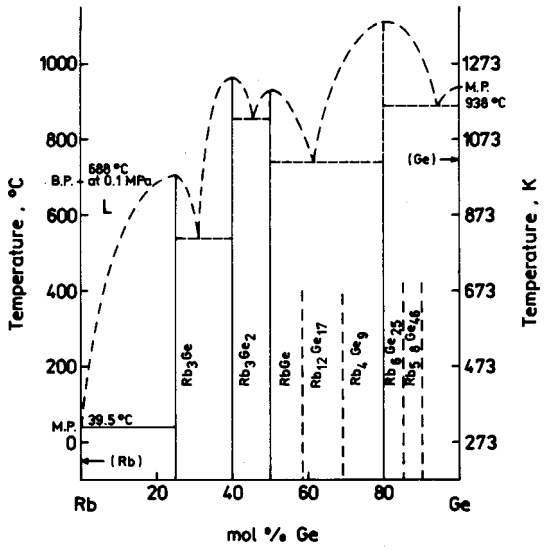

FIG. 51. Ge–Rb phase diagram.

References:

[1]E. Hohmann, Z. Anorg. Chem. **257**, 113 (1948).
[2]R. Schäfer and W. Klemm, Z. Anorg. Chem. **312**, 214 (1961).
[3]C. Cros, M. Pouchard, and P. Hagenmuller, Bull. Soc. Chim. Fr. 379 (1971).
[4]S. P. Yatsenko, A. N. Kuznetsov, and K. A. Chuntonov, Zh. Fiz. Khim. **51**, 1264 (1977).
[5]K. A. Chuntonov and S. P. Yatsenko, Zh. Fiz. Khim. **52**, 2145 (1978).
[6]M. E. Drits, V. F. Potemkin, and L. L. Zusman, Izv. Akad. Nauk SSSR, Neorg. Mater. **18**, 1148 (1982).
[7]V. F. Potemkin, R. A. Sizov, L. L. Zusman, and M. E. Drits, Izv. Akad. Nauk SSSR, Met. **3**, 197 (1983).
[8]H. G. von Schnering, M. Baitinger, U. Bolle, W. Carrillo-Cabrera, J. Curda, Y. Grin, F. Heinemann, J. Llanos, K. Peters, A. Schmeding, and M. Somer, Z. Anorg. Chem. **623**, 1037 (1997).
[9]J. Sangster and A. D. Pelton, J. Phase Equil. **18**, 298 (1997).

Components:
(1) Germanium; Ge; [7440-56-4]
(2) Rubidium; Rb; [7440-17-7]

Original Measurements:
S. P. Yatsenko, A. N. Kuznetsov, and K. A. Chuntonov, Zh. Fiz. Khim. **51**, 1264 (1977).

Variables:
Temperature: 856–1033 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

Fragments of the Rb–Ge liquidus line were determined. The numerical data were briefly reported in Kuznetsov *et al.*[1] and a small picture of the smoothed diagram in Orlov *et al.*[2]

t/°C	Solubility/mol % Ge	Characterization
608	15	monotectic
665	30[a]	critical
608	50	monotectic, syntectic
583	58[a]	eutectic
760	75[a]	peritectic

[a]As reported in Orlov *et al.*[2]

Auxiliary Information

Method:
The alloys were prepared in a small, hermetically closed Ta crucible. Filling the crucible with Rb was performed under petroleum which was subsequently washed out with ether. The remainder of ether was removed by evaporation under vacuum at room temperature. Heating and cooling curves of thermal analysis were recorded for each alloy sample with the use of a Chromel/Alumel thermocouple. The Rb content in the samples was analytically determined. The crucible was opened in anhydrous acetone and water was gradually added into. The Rb in the resulting solution was determined by alkalimetric titration.[1]

Source and Purity of Materials:
Ge: probably of semiconductor purity, as in Orlov *et al.*[2]
Rb: 99.9% pure, as in Kuznetsov *et al.*[1]

Estimated Error:
Solubility: reading-out procedure ±2 mol %
Temperature: precision ±2 K; reading-out procedure ±10 K.

References:
[1]A. N., Kuznetsov, K. A. Chuntonov, and S. P. Yatsenko, Izv. Akad. Nauk SSSR, Met. **5**, 223–225 (1977).
[2]A. N. Orlov, K. A. Chuntonov, and L. Z. Melekhov, Izv. Akad. Nauk SSSR, Met. **6**, 172–173 (1987).

Components:
(1) Germanium; Ge; [7440-56-4]
(2) Rubidium; Rb; [7440-17-7]

Original Measurements:
M. E. Drits, V. F. Potemkin, and L. L. Zusman, Izv. Akad. Nauk SSSR, Neorg. Mater. **18**, 1148–1150 (1982).

Variables:
Temperature: 948–1383 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The liquidus of the Rb–Ge system was determined. The data were reported in a figure. The values were read out and recalculated by the compilers.

T/K	Solubility/mol % Rb	Solubility/mol % Ge
1214	3	97
1168	5	95
1234	9	91
1333	15	85
1383	20	80
1343	26	74
1159	34	66
1057	39	61
1171	47	53
1175	53	47
1217	59	41
1175	63	37
948	74	26
957	77	23

The melting point of Ge, as read from the figure, is 1239 K, 27 K higher than the contemporarily accepted value. The authors identified the following phases $RbGe_4$, RbGe, Rb_3Ge_2, and Rb_3Ge.

Auxiliary Information

Method:
Weighed amounts of Ge and Rb were placed in alumina or zirkonia crucibles inserted in steel or Nb tubes. The operation was performed in a box filled with Ar. Hermeticity of every tube after closing was tested by heating in vacuum to a temperature higher than the melting point of the alloy. Reactions of the components with the containers were not observed. Multicycled thermal analysis of the samples was performed in an Ar atmosphere using a self-constructed apparatus. The composition of $RbGe_4$ was confirmed by x-ray spectral and microstructural analysis.

Source and Purity of Materials:
Ge: semiconductor purity.
Rb: >99.6% pure.
Ar: spectrally pure.

Estimated Error:
Solubility: nothing specified; reading-out procedure ±0.5 mol %.
Temperature: precision ±2 K; reading-out procedure ±3 K.

6.6. Rubidium–Nitrogen

Components:
(1) Nitrogen; N; [7727-37-9]
(2) Rubidium; Rb; [7440-17-7]

Evaluated by:
Hans Ulrich Borgstedt, Forschungszentrum Karlsruhe, Germany and Cezary Guminski, University of Warsaw, Poland, July 1998.

Critical Evaluation

Gaseous N does not react with liquid Rb. However metastable Rb_3N (nitride) and RbN_3 (azide) are known to be formed in chemical reactions.[1] Suhrmann and Clusius[2] observed the melting of RbN_3 at 594 K and its decomposition at 668 K. Belomestnykh[3] confirmed these temperatures at 590 and 668 K, respectively, and found the temperature of a phase transition in RbN_3 at 588 K. RbN_3 may be decomposed into Rb_3N and gaseous N. The thermal stability of Rb_3N is unknown.

Direct measurements of the solubility of N in liquid Rb have not been reported. Tepper *et al.*[4] analyzed Rb for the N content. If one assumes that Rb was saturated with N at its melting point and Rb_3N was formed in the course of the reaction, the result of Rb analysis performed under N cover gas could be treated as an approximate of the solubility of N in liquid Rb. Using the modified Kjehldal method, Tepper *et al.*[4] found $(2.8 \pm 1.2) \cdot 10^{-3}$ mol % N, referred to 313 K. However, this value could not be suggested as the solubility.

The Rb–N phase diagram is expected to be similar to one shown for the Na–N system differing in melting point of Rb (312.63 K).

References:

[1]G. J. Moody and J. D. R. Thomas, J. Chem. Educ. **43**, 205 (1966).
[2]R. Suhrmann and K. Clusius, Z. Anorg. Chem. **152**, 52 (1926).
[3]V. N. Belomestnykh, Izv. Akad. Nauk Rus., Neorg. Mater. **29**, 221 (1993).
[4]F. Tepper, A. Murchison, J. Zelenak, and F. Roehlich, U.S. Atom. Energy Comm. Rep. ORNL-3605, Vol. I, p. 26 (1964).

6.7. Rubidium–Phosphorus

Components:
(1) Phosphorus; P; [7723-14-0]
(2) Rubidium; Rb; [7440-17-7]

Evaluated by:
Hans Ulrich Borgstedt, Forschungszentrum Karlsruhe, Germany and Cezary Guminski, University of Warsaw, Poland, July 1998.

Critical Evaluation

By analogy to the lighter alkali metals, the formation of Rb–P compounds is expected as product of the chemical reaction between P and Rb. Since a presumed compound Rb_3P should be of a salt-like structure, one should expect a rather poor miscibility of Rb_3P with Rb as well as P. Gnutzmann *et al.*[1] did not succeed in obtaining Rb_3P by direct reaction of the components. Von Schnering *et al.*[2] reported the formation of Rb_3P_7 and Rb_3P_{11} phases; the latter one transforms into another crystallographic form at 615±5 K.

A phase diagram of the Rb–P system is not available.

References:

[1]G. Gnutzmann, F. W. Dorn, and W. Klemm, Z. Anorg. Chem. **309**, 211 (1961).
[2]H. G. von Schnering, M. Somer, G. Kliche, W. Hönle, T. Meyer, J. Wolf, L. Ohse, and P. B. Kempa, Z. Anorg. Chem. **601**, 13 (1991).

6.8. Rubidium–Arsenic

Components:
(1) Arsenic; As; [7440-38-2]
(2) Rubidium; Rb; [7440-17-7]

Evaluated by:
Hans Ulrich Borgstedt, Forschungszentrum Karlsruhe, Germany and Cezary Guminski, University of Warsaw, Poland, June 1998.

Critical Evaluation

Klemm *et al.*[1,2] reported the formation of Rb_3As, but its melting point was not determined. Kuznetsov[3] investigated the whole composition range of the Rb–As phase diagram confirming the formation of Rb_3As and of three other compounds, Rb_5As_4, RbAs, and $RbAs_2$. A small picture of the diagram in smooth form is given in Kuznetsov.[3] A larger figure reporting all experimental data from the same laboratory is shown in Yatsenko *et al.*[4] There is no exact correspondence between the figures in Kuznetsov[3] and in Yatsenko *et al.*[4] A miscibility gap between 67 and 90 mol % As is shown in Kuznetsov,[3] whereas a eutectic between $RbAs_2$ and As is placed in Yatsenko *et al.*[4] We treat the results of Yatsenko *et al.*[4] as more reliable, since they are closer to the K–As system and contain more experimental information.

Recently von Schnering *et al.*[5] reported the formation of Rb_3As_7 and Rb_3As_{11} and their transformation to plastic forms at 608 (see Ref. 6) and 689 K. It seems that the phase $RbAs_2$ reported by Yatsenko *et al.*[4] is the phase Rb_3As_7 of Hönle and von Schnering.[6] The proposed Rb–As phase diagram is shown in Fig. 52; its shape differs slightly from that one published in Sangster and Pelton.[7]

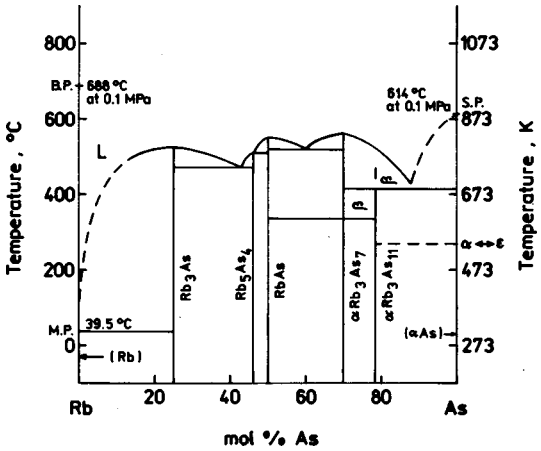

FIG. 52. Rb–As phase diagram.

Tentative values of the solubility of As in liquid Rb

T/K	Solubility/mol % As	Source
773	14	(4) extrapolated
798	25 congruent	(4)
748	40 eutectic	(4) extrapolated
783	46 peritectic	(4)
823	50 congruent	(4)
793	60 eutectic	(4)
834	66.7 congruent(4)	
703	≈88 eutectic	(4)

References:

[1]W. Klemm, Proc. Chem. Soc. 329 (1958).

[2]G. Gnutzmann, F. W. Dorn, and W. Klemm, Z. Anorg. Chem. **309**, 211 (1961).

[3]A. N. Kuznetsov, Ph.D. thesis, Akad. Nauk SSSR, Sverdlovsk, Russia, 1978; abstracted in K. A. Chuntonov and S. P. Yatsenko, Zh. Fiz. Khim. **52**, 2145 (1978).

[4]S. P. Yatsenko, B. D. Bushmanov, A. N. Kuznetsov, and K. A. Chuntonov, *V Vsesoyuznaya Konferentsiya po Khimii i Tekhnologii Redkikh Shchelochnykh Elementov* (Nauka, Moskva, 1977), p. 123.

[5]H. G. von Schnering, M. Somer, G. Kliche, W. Hönle, T. Meyer, J. Wolf, L. Ohse, and P. B. Kempa, Z. Anorg. Chem. **601**, 13 (1991).

[6]W. Hönle and H. G. von Schnering, Z. Krist. **174**, 82 (1986).

[7]J. Sangster and A. D. Pelton, J. Phase Equil. **14**, 243 (1993).

Components:
(1) Arsenic; As; [7440-38-2]
(2) Rubidium; Rb; [7440-17-7]

Original Measurements:
S. P. Yatsenko, V. D. Bushmanov, A. N. Kuznetsov, and K. A. Chuntonov, V Vsesoyuznaya Konferentsiya po Khimii i Tekhnologii Redkikh Shchelochnykh Elementov (Nauka, Moskva, 1977), p. 123.

Variables:
Temperature: 731–833 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The Rb–As liquidus was presented in a figure. The results were extracted by the compilers.

t/°C	Solubility/mol % As
506	15
518	20
525[a]	25
518	31
498	35
484	42
510[a]	46
548	49
550[a]	50
543	55
539	58
538	62
549	64
553	66
560	69
555	73
551	77
458	87

[a]Numerical result.

The following equilibrium phases were identified: Rb_3As, Rb_5As_4, RbAs, and $RbAs_2$. The eutectic temperatures between Rb_3As and Rb_5As_4, RbAs and $RbAs_2$, $RbAs_2$ and As were observed at 475, 520, and 430 °C, respectively. Peritectic decomposition of Rb_4As_5 was found at 510 °C. In the composition range 67–100 mol % As the authors found thermal arrests at 350 and 270 °C but their interpretation needs further investigations.

Auxiliary Information

Method:
The alloys were prepared in Pyrex glass tubes. The elements were introduced into the tubes, which were evacuated and heated up to the initiation of the reaction between the components. Differential thermal analysis was performed with the samples. The Rb-rich alloys were prepared in Ta tubes. X-ray diffraction analysis of the samples was performed, as in Yatsenko *et al.*[1]

Source and Purity of Materials:
As: nothing specified.
Rb: 99.9% pure, as in Yatsenko *et al.*[1]

Estimated Error:
Solubility: nothing specified; reading-out procedure ±1 mol %.
Temperature: nothing specified; reading-out procedure ±2 K.

References:
[1]S. P. Yatsenko, A. N. Kuznetsov, and K. A. Chuntonov, Izv. Akad. Nauk SSSR, Neorg. Mater. **13**, 738–739 (1977).

6.9. Rubidium–Oxygen

Components:
(1) Oxygen; O; [7782-44-7]
(2) Rubidium; Rb; [7440-17-7]

Evaluated by:
Hans Ulrich Borgstedt, Forschungszentrum Karlsruhe, Germany and Cezary Guminski, University of Warsaw, Poland, July 1998.

Critical Evaluation

Several oxides are formed as the result of reactions between O and Rb: Rb_6O, Rb_9O_2, Rb_3O, Rb_2O, Rb_2O_2, RbO_2, and RbO_3. Their mutual solubilities are larger than in the case of the K–O system. This was obvious in the first estimations of the O solubility in Rb by Weatherford *et al.*[1,2] and Tepper *et al.*[3–5] who observed a decrease of the Rb melting point upon an addition of O. Such a method is an excellent criterion of the purity of Rb metal.

Touzain and Caillet[6,7] investigated the Rb-rich part of the Rb–O phase diagram up to 33 mol % O using micro amounts of the components. Qualitative confirmation of the results of Refs. 6 and 7 was obtained by Simon[8] who reported different compositions of the equilibrium solid phases as well as the shape of the liquidus line. Experiments of Suzuki *et al.*[9,10] presented still a different course of the liquidus, however more similar to Ref. 8 than to Refs. 6 and 7. The slope of the melting point depression of Rb upon an O addition from Refs. 1 and 2 and 3–5 is closer to the slope observed in Refs. 8 and 9,10. The eutectic point at about 10 mol % O was observed by both Refs. 8 and 9,10 differing in the corresponding temperature for 7 K. Further increase of the O content causes various courses of the liquidus line, but at about 15 mol % O the lines of Refs. 8 and 9,10 coincide again. It seems that the most reliable results are originated by Suzuki *et al.*[9,10] who used the purest substances, applied the slowest heating rate and performed experiments with the highest number of samples.

At the O-rich side only stoichiometric oxides were investigated by Volnov.[11] The partial Rb–O phase diagram is shown in Fig. 53. The melting temperatures of the oxides were taken from Volnov.[11] Touzain and Caillet[7] corrected the melting point of Rb_2O found previously by Touzain.[6] However their correction is only valid, if the Rb_2O–Rb_2O_2 system is of a eutectic type, which is not yet proved in the experiments.

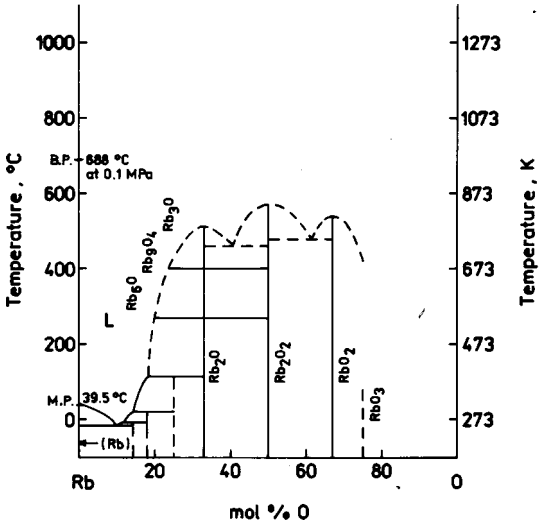

FIG. 53. Rb–O phase diagram (partial).

Tentative and doubtful (d) values of solubilities of O in liquid Rb

T/K	Solubility/mol % O	Source
259	10 (d) eutectic	(9,10)
262	12 (d) peritectic	(9,10)
293	14 (d) peritectic	(9,10)
323	15 (d)	(9,10)
389	18 (d) peritectic	(9,10)
473	23 (d)	(6)
573	26 (d)	(6)
768	33 (d) congruent	(6)
843	50 congruent	(11)
813	67 congruent	(11)
343	75 (d)	(11)

References:

[1]W. D. Weatherford, R. K. Johnston, M. L. Valtiera, and J. W. Rhoades, U.S. Air Force Rep. ASD-TDR-63-413 (1963).

[2]R. H. Herald and W. D. Weatherford, IEEE Trans. Aerospace AS-1(2), 1182 (1963).

[3]F. Tepper, *The Liquid Alkali Metals* (Chemical Society, London, 1967), p. 370.

[4]J. W. Mausteller, F. Tepper, and S. J. Rodgers, *Alkali Metal Handling and System Operating Techniques* (Gordon & Breach, New York, 1967), p. 119.

[5]S. J. Rodgers and F. Tepper, U.S. Atom. Ener. Comm. Rep. MSAR-64-108 (1964); U.S. Atom. Ener. Comm. Rep. CONF-721-10 (1964).

[6]P. Touzain, Can. J. Chem. **47**, 2639 (1969).

[7]P. Touzain and M. Caillet, Rev. Chim. Miner. **8**, 277 (1971).

[8]A. Simon, Z. Anorg. Chem. **395**, 301 (1973).

[9]T. Suzuki, S. Masuda, and Y. Tanazawa, J. Nucl. Mater. **127**, 113 (1985).

[10]T. Suzuki, S. Masuda, Y. Matsui, and Y. Nakanishi, J. Nucl. Mater. **137**, 250 (1986).

[11]I. I. Volnov, *Perekisnye Soedineniya Shchelochnykh Matallov* (Nauka, Moskva, 1980).

Components:
(1) Oxygen; O; [7782-44-7]
(2) Rubidium; Rb; [7440-17-7]

Original Measurements:
W. D. Weatherford, R. K. Johnston, M. L. Valtierra, and J. W. Rhoades, U.S. Air Force Rep. ASD-TDR-63-413 (1963).

Variables:
Temperature: 311.0–297.0 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The melting point of pure Rb and of Rb containing O additions was determined

t/°F	T/K[a]	Solubility/mass % O	Solubility/mol % O[a]
100.08	310.97	0.1	0.53
95.01	308.16	0.2	1.1
75–85	297.0–302.5	0.7	3.6

[a]Calculated by the compilers.

Hot gettered Rb (assumed to contain no measurable O concentration) melted at 102.88 °F or 312.35 K. The results were approximated by the formula: $(t_{Rb-O}-t_{Rb})/°F=(soly/mass\ \%\ O)/0.300$, where Rb_2O was found to be the equilibrium solid phase. The same results were presented graphically in Herald and Weatherford.[1]

Auxiliary Information

Method:
The apparatus for the determinations was made of 316 stainless steel. It was placed in a furnace. The Rb sample was equilibrated at selected temperature above the melting point. The apparatus was removed from the furnace and allowed to cool rapidly, while the sample temperature was monitored by an immersed thermocouple. The thermocouple was calibrated on the melting points of Sn, Zn, Al, and Cu. The sample was reheated and recooled within ±28 K in respect to the melting point. The consecutive curves were recorded in the same manner. Predeterminated quantities of gaseous O were added to Rb and equilibrated. The melting point determinations were repeated in the same way. O contents, analyzed by the butyl bromide method, were several times lower than the O amount blended into Rb.

Source and Purity of Materials:
O: gaseous of unspecified purity.
Rb: 99.9+% pure with a low Cs content, gettered with Ti–Zr (50%) chips at 930–990 K for 40 h.
Ar: 99.996% pure, further purified by bubbling through Na–K (78%) melt.

Estimated Error:
Solubility: precision ±5%.
Temperature: precision ±0.5%.

References:
[1]R. H. Herald and W. D. Weatherford, IEEE Trans. Aerospace AS-1(2), 1182–1191 (1963).

Components:
(1) Oxygen; O; [7782-44-7]
(2) Rubidium; Rb; [7440-17-7]

Original Measurements:
J. W. Mausteller, F. Tepper, and S. J. Rodgers, *Alkali Metal Handling and System Operating Techniques* (Gordon & Breach, New York, 1967), pp. 119–120.

Variables:
Temperature: 311.21–312.07 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The depression of the freezing point of Rb as a function of its O content was determined. The results were read out from a figure and recalculated to mol % by the compilers.

t/°C	Solubility/mass % O	Solubility/mol % O
38.92	0.0020	0.0107
38.86	0.0050	0.027
38.79	0.010	0.053
38.69	0.015	0.080
38.51	0.025	0.133
38.26	0.040	0.21
38.06	0.050	0.27

The melting point of Rb was found at 38.98 °C, given numerically in Ref. 1. The freezing point depression factor is 3.4 K/mol % O.

The results were also presented in Rodgers and Tepper.[2]

Auxiliary Information

Method:
Gaseous O in known quantities was added to Rb and the mixture equilibrated in an Ar atmosphere. The freezing point of the samples was measured after each O addition with a precision Beckman thermometer. Each of the experiments was duplicated after 15–20 min.

Source and Purity of Materials:
O: gaseous of unspecified purity.
Rb: 99.9% pure from the MSAR[1] and contained $3 \cdot 10^{-3}$ % Na.
Ar: nothing specified.

Estimated Error:
Solubility: detectivity $5 \cdot 10^{-4}$ mol %; reading-out procedure $\pm 1 \cdot 10^{-3}$ mol %
Temperature: precision ±0.002 K; reading-out procedure ±0.01 K.

References:
[1]F. Tepper, *The Alkali Metals* (Chemical Society, London, 1967), pp. 370–373.
[2]S. J. Rodgers and F. Tepper, U.S. Atom. Energy Comm. Rep. MSAR-64-108 (1964); U.S. Atom. Energy Comm. Rep. CONF-721-10 (1964).

Components:
(1) Oxygen; O; [7782-44-7]
(2) Rubidium; Rb; [7440-17-7]

Original Measurements:
P. Touzain, Can. J. Chem. **47**, 2639–2643 (1969).

Variables:
Temperature: 270–768 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The Rb-rich part of the Rb–O liquidus was determined. The data were presented in a figure. They were read out from the figure by the compilers.

t/°C	Solubility/mol % O
35	1.0
34	1.9
27	5.2
21	8.1
9	9.5
10	10.4
−3	14.6
−3	16.6
43	19.3
–	–
36	20.0
48	21.1
49	21.3
56	23.0
135–147	25.9
260–292	28.1
325–370	29.1
331–371	29.9
396–448	33.3
485–505[a]	33.3

[a]In Touzain and Caillet,[1] after correction for contamination of Rb_2O with Rb_2O_2.

An incongruent reaction $2\ Rb_2O \leftrightarrow Rb_2O_2 + 2\ Rb$ proceeds at ≈410 °C and $Rb_3O \leftrightarrow Rb_2O + Rb$ at ≈48 °C. The eutectic temperature was found at −10 °C. Polymorphic transitions in Rb_2O were observed at 270 and 340 °C. The same results were presented in Touzain and Caillet.[1]

Auxiliary Information

Method:
Rb was partially oxidized by introduction of a known volume of O gas into a Pyrex glass container. The composition of the melt was analyzed for its Rb content. The reaction product with water was titrated with an acid. Differential thermal analyses of the samples were performed on semimicro scale in a glass apparatus. Temperatures were measured with the use of three calibrated Pt thermocouples. The temperature changes amounted to 3–4 K/min. Cooling and heating curves were recorded after homogenization of the samples.

Source and Purity of Materials:
O: gaseous of unspecified purity.
Rb: obtained according to Hackspill[2] by Ca reduction of RbCl; the reaction product was distilled twice in vacuum.

Estimated Error:
Solubility: nothing specified; reading-out procedure ±0.2 mol %.
Temperature: precision ±2 K at low to ±5 K at high temperatures; reading-out procedure ±2 K.

References:
[1]P. Touzain and M. Caillet, Rev. Chim. Minar. **8**, 277–286 (1971).
[2]L. Hackspill, Bull. Soc. Chim. Fr. **9**, 446 (1911).

Components:
(1) Oxygen; O; [7782-44-7]
(2) Rubidium; Rb; [7440-17-7]

Original Measurements:
A. Simon, Z. Anorg. Chem. **395**, 301–319 (1973).

Variables:
Temperature: 268–317 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The Rb-rich part of the Rb–O liquidus was presented in a figure. The experimental data were read from the figure by the compilers.

t/°C	Solubility/mol % O
36.7	1.0
34.2	2.0
30.0	3.5
20.8	5.8
5.4	8.3
−4.9	9.5
3.5	10.4
13.6	11.2
21.6	11.9
30.6–31.5	12.8
44.1[a]	15.2

[a]Doubtful value according to the author.

The melting point of Rb was found at 39.37±0.01 °C. Rb_6O and Rb_9O_2 equilibrium solid phases were identified.

Auxiliary Information

Method:
Rb oxides were prepared in a glass apparatus. Small amounts of O from thermal decomposition of HgO were dosed to known amounts of Rb at reduced pressure of Ar and low temperature of environment. Samples of Rb–O melts, in glass containers, were placed in an Al block. The block was placed in a cryostat. Heating of samples was carried out with a rate of 1–60 K/h and temperature changes were recorded with the use of a Pt thermometer, previously calibrated on the melting and boiling points of H_2O. Some samples were analyzed by x-ray diffraction and chemical analysis.

Source and Purity of Materials:
O: from controlled decomposition of HgO (obtained from very pure Hg and O at 693 K, 0.45 MPa for 2 weeks; the composition of HgO confirmed by chemical analysis (99.9+% pure).
Rb: obtained from RbCl (very pure, dried at 523 K for 1 week) and Ca (nuclear purity, conditioned for 1 h in high vacuum at 1023 K) in a steel container heated up to 1203 K. Distilled Rb was collected in glass tubes.
Ar: nothing specified.

Estimated Error:
Solubility: precision ±0.1 mol %; reading-out procedure ±0.1 mol %.
Temperature: reproducibility ±0.01 K; reading-out procedure ±1 K.

Components:
(1) Oxygen; O; [7782-44-7]
(2) Rubidium; Rb; [7440-17-7]

Original Measurements:
T. Suzuki, S. Masuda, Y. Matsui, and Y. Nakanishi, J. Nucl. Mater. **137**, 250–255 (1986).

Variables:
Temperature: 260–491 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

Vessel	t/°C	Solubility/mol % O
A[a]	32	2.0
A[a]	26	4.2
B	20	5.1
A[a]	8	6.3
A[a]	−6	9.0
A[a]	−10	10.0
A	−13.5	10.0
A[a]	−7	10.9
A	−5.5	12.0
A[a]	−4	12.5
B	−1	12.5
A	2.5	13.0
C	5	13.2
A[a]	22	14.0
C	101	15.0
C	115	18.0
A[a,b]	140(?)	21.4
C	197(?)	22.0
C	218(?)	25.0

[a]Reported also in Suzuki *et al.*[1]
[b]A mixture of $Rb_{1.76}O$ and Rb was investigated.

Peritectic arrests were observed at ≈−14, −11, 20, and 116 °C.

Auxiliary Information

Method:
Three types of containers were used: (A) a Pyrex glass vessel with a reference of Type 316 stainless steel, (B) a Ni crucible in a Pyrex glass vessel, and (C) a silica vessel with a reference of Type 316 stainless steel. The containers were connected with Chromel/Alumel thermocouples sheathed by Type 316 stainless steel. A weighed quantity of Rb was loaded into a container. It was connected to a vacuum manifold having Ar and O lines, a Hg manometer, and an O reservoir. An appropriate quantity of O was slowly added to liquid Rb by controlling temperature and pressure. The vessels were back filled with Ar and the container of C type additionally sealed off. Thermal analysis was carried out using Chromel/Alumel thermocouples, an electric furnace, and a vacuum bottle containing the freezing mixture of $CaCl_2$ and ice. The phase transition temperatures were determined from repeated cooling curves of differential thermal analysis. The cooling rate was varied between 0.5 and 10 K/min. Phase changes were observed in the vessel C through a glass window.

Source and Purity of Materials:
O: 99.9+ pure.
$Rb_{1.76}O$: from Morton Thiokol Inc. was a mixture of Rb_2O, Rb_2O_2, Rb_2O_3, and RbO_2; contained 3.1% Rb_2CO_3.
Rb: from Kawecki Berylco Industries, 99.9% pure and contained <0.001% Li, Na, Ba, Si; 0.025% K; 0.073% Cs, 0.001% Al and <0.0001% Ca, Cr, Cu, Fe, Pb, Mg, Mn, and Ni.
Ar: 99.999% pure; permanently purified and contained <0.0001 vol % O, H_2O.

Estimated Error:
Solubility: nothing specified; precision no better than ±0.5 mol % (by the compilers).
Temperature: accuracy ±0.6 K.

References:
[1]T. Suzuki, S. Matsuda, and Y. Tanazawa, J. Nucl. Mater. **127**, 113–115 (1985).

6.10. Rubidium–Rubidium Hydroxide

Components:
(1) Rubidium hydroxide; RbOH; [1310-82-3]
(2) Rubidium; Rb; [7440-17-7]

Original Measurements:
P. Touzain, Compt. Rend., Ser. C **276**, 1583–1585 (1973).

Variables:
Temperature: 550–652 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data and Critical Evaluation

The liquidus line of the Rb–RbOH system was shown in a figure. The compilers read the results from the figure.

t/°C	Solubility/mol % RbOH
277	8.8
269	9.4
303	14.5
344	24.2
347	31.9
362	38.3
359	40.5
366	48.4
370	51.3
360	70.3
366	73.7
370	81.0
375	89.0
379	89.8
375	91.0
378	92.5
377	93.0
376	96.5

The melting points of Rb and RbOH were found at 39 and 382 °C, respectively. The α-RbOH↔β-RbOH transformation was observed at 235 °C. The temperature plateau observed between 48 and 81 mol % RbOH may reflect a miscibility gap with a critical temperature situated quite close to the monotectic at ≈370 °C. Although no experimental evidence was found in the literature, it seems that RbOH may be formed in liquid Rb when H and O are simultaneously present therein.

The solubility data have tentative character; the Rb–RbOH phase diagram is shown in Fig. 54.

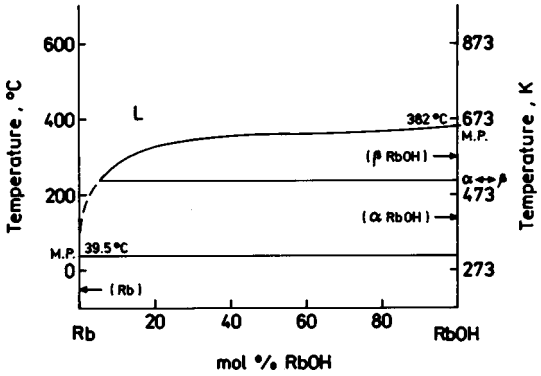

FIG. 54. Rb–RbOH phase diagram.

Auxiliary Information

Method:
All operations were performed in an Ar atmosphere. Weighed amounts of liquid dropping Rb and RbOH powder were introduced into small Ni tubes. The tubes were soldered with Ag. The samples were homogenized at 773 K. Differential thermal analysis was performed in a commercial apparatus with a heating rate of 10 K/min.

Source and Purity of Materials:
RbOH: RbOH·$2H_2O$ from Fluka was dehydrated by heating at 573 K for 3 days; contained 0.5% Rb_2CO_3 .
Rb: twice distilled.
Ar: "ultra pure."

Estimated Error:
Solubility: nothing specified; precision ±2% (by the compilers); reading-out procedure ±0.3 mol %.
Temperature: precision ±2 K; reading-out procedure ±1 K.

6.11. Rubidium–Sulfur

Components:
(1) Sulfur; S; [7704-34-9]
(2) Rubidium; Rb; [7440-17-7]

Evaluated by:
Hans Ulrich Borgstedt, Forschungszentrum Karlsruhe, Germany and Cezary Guminski, University of Warsaw, Poland, August 1998.

Critical Evaluation

S reacts with Rb with the formation of several sulfides Rb_2S_x, where $x=1,2,3,(4),5,(6)$. Biltz and Wilke-Dörfurt[1] investigated the intermediate range of the Rb–S system and established the liquidus line between 50 and 77 mol % S. The melting points of Rb_2S_2, Rb_2S_3, Rb_2S_4, Rb_2S_5, and Rb_2S_6 were confirmed in the next study from the same laboratory.[2] Feher and Naused[3] attempted to synthesize Rb_2S_2, Rb_2S_3, Rb_2S_4, Rb_2S_5, and Rb_2S_6 but only Rb_2S_2, Rb_2S_3, and Rb_2S_5 were identified as defined substances. The melting points of these compounds were determined. Kuznetsov[4] presented a small, smoothed phase diagram of the Rb–S system, based on his own and Feher's data,[3] where only Rb_2S_5 and Rb_2S were congruently melting phases; the other compounds, however, were melted under peritectic decomposition. It is more probable, by analogy to the K–S system, that all Rb–S compounds melt congruently. Bergmann[5] synthesized Rb_2S from HgS and Rb; he observed its stability up to ≈803 K under vacuum. Sangster and Pelton[6] estimated the melting point of Rb_2S under normal pressure to be 1023±200 K, by analogy to similar sulfides and selenides of other alkali metals.

The Rb-rich side of the Rb–S phase diagram was not investigated, however, by analogy to the K–S system, one may expect a miscibility gap or a tendency of the liquidus to immiscibility. A limited miscibility was also observed at the S-rich part of the diagram, but its range and critical temperature was not found experimentally. The corresponding critical temperature should be at 623±50 K. A partly predictive Rb–S phase diagram is shown in Fig. 55. Klemm *et al.*[7] confirmed the existence of Rb_2S, Rb_2S_2, Rb_2S_3, Rb_2S_4, Rb_2S_5, and Rb_2S_6 in magnetic measurements. Böttcher *et al.*[8] found the $\alpha \leftrightarrow \beta$ phase transition of Rb_2S_2 at 388±10 K; incongruent melting of β-Rb_2S_2 was observed at 728±25 K and the liquidus at 778±15 K. The compound was prepared in liquid NH_3 and was investigated by thermal analysis and x-ray diffraction; the publication did not contain more details and was not compiled, therefore.

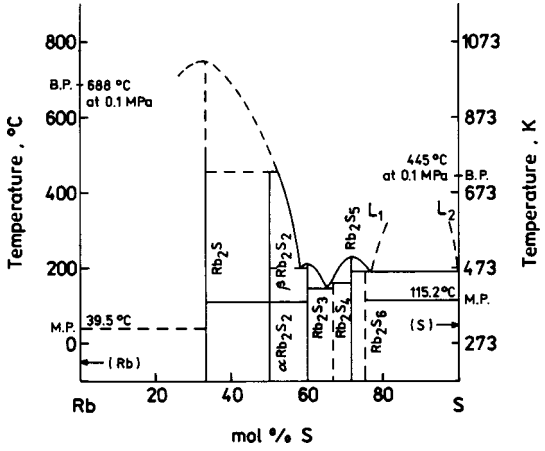

FIG. 55. Rb–S phase diagram (partly predictive).

Tentative values of the solubility of S in liquid Rb

T/K	Solubility/mol % S	Source
778	50	(8)
673	52 (1) interpolated	
473	58 eutectic	(1)
≈483	60.0 congruent	(3)
422	65 eutectic	(1)
504	71.4 congruent	(1),(3)
463	77 peritectic	(1)

References:
[1]W. Biltz and E. Wilke-Dörfurt, Z. Anorg. Chem. **48**, 297 (1906).
[2]W. Biltz and E. Wilke-Dörfurt, Z. Anorg. Chem. **50**, 67 (1906).
[3]F. Feher and K. Naused, Z. Anorg. Chem. **283**, 79 (1956).
[4]A. N. Kuznetsov, Ph. D. thesis, Akad. Nauk SSSR, Sverdlovsk, Russia, 1978; cited by K. A. Chuntonov and S. P. Yatsenko, Zh. Fiz. Khim. **52**, 2145 (1978).
[5]A. Bergmann, Z. Anorg. Chem. **231**, 269 (1937).
[6]J. Sangster and A. D. Pelton, J. Phase Equil. **18**, 97 (1997).
[7]W. Klemm, H. Sodomann, and P. Langmesser, Z. Anorg. Chem. **241**, 281 (1939).
[8]P. Böttcher, J. Getzschmann, and R. Keller, Z. Anorg. Chem. **619**, 476 (1993).

Components:
(1) Sulfur; S; [7704-34-9]
(2) Rubidium; Rb; [7440-17-7]

Original Measurements:
W. Biltz and E. Wilke-Dörfurt, Z. Anorg. Chem. **48**, 297 (1906).

Variables:
Temperature: 422–693 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data
A central part of the Rb–S liquidus was determined

t/°C	Solubility/mass % S	Solubility/mol % S
≈420	27.45	50.3
≈380	30.21	53.6
231.5	32.61	56.4
227	33.03	56.8
221.5	33.47	57.3
216	33.90	57.8
211.5	34.46	58.4
210.5	34.84	58.8
214	35.03	59.0
212	35.48	59.5
211.5	35.95	60.0
195	36.57	60.6
195	36.97	61.0
190	37.33	61.4
185.5	37.85	61.9
164.5	40.05	65.0
157	41.44	65.4
148.5	41.95	65.9
153	42.13	66.1
157.5	42.62	66.5
160.4	43.14	66.9
171.5	43.46	67.1
185.5	43.78	67.5
185	44.03	67.8
195.5	44.09	67.8
199	44.42	68.1
204.5	44.74	68.4
211.5	45.04	68.6
212	45.12	68.7
215	45.36	68.9
217.3	45.44	68.9
222	45.67	69.2
222.4	45.78	69.3
227	46.12	69.6
229	46.52	70.0
230	46.88	70.2
230	47.24	70.5
231	47.74	70.9
230	48.21	71.3
228	48.66	71.7
228	49.11	72.0
224.5	49.22	72.1
221.0	50.51	73.2
215.0	51.51	73.9
212.5	51.98	74.3
207.8	52.59	74.8
206.0	53.05	75.1
200	53.30	75.3
200	53.54	75.5
196	53.77	75.6
188	53.97	75.8
185.5	54.43	76.1
185.5	55.29	76.8
184.5	56.09	77.3

[a]Calculated by the compilers.

No appreciable solubility of Rb_2S_6 in liquid S was observed. The monotectic temperature at the S-rich side was found at 117.5 °C. The authors reported a strong tendency of the system to supercooling.

Auxiliary Information

Method:
The Rb–S mixtures were prepared from Rb_2S, Rb_2S_3, Rb_2S_5, and S. The preparations were carried out in a Durex glass apparatus filled with an inert gas. The mixtures were heated to complete melting and cooled slowly down while mixing with a glass tube. Temperatures were recorded by means of a Hg thermometer. The investigations of Rb_2S-rich melts were performed in a Jena glass apparatus. The melt was mixed with a pyrometer tube. The pyrometer was calibrated on the melting points of Zn, Pb, and Sn, and compared with the Hg thermometer. Temperature readings were made every 10 s. The experiments were performed in a H or N (at temperatures >513 K) atmosphere.

Source and Purity of Materials:
S: nothing specified.
Rb_2S: obtained from RbOH and H_2S; dried after its crystallization.
Rb_2-polysulfides: obtained from proper amounts of Rb_2S and S.
H: "pure and dry."
N: "air free and dry."

Estimated Error:
Solubility: nothing specified.
Temperature: precision of the thermometer ±0.1 K and of the pyrometer ±1 K; accuracy between ±1 and ±10 K.

Components:
(1) Sulfur; S; [7704-34-9]
(2) Rubidium; Rb; [7440-17-7]

Original Measurements:
F. Feher and K. Naused, Z. Anorg. Chem. **283**, 79–87 (1956).

Variables:
Temperature: 483–723 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data
The melting temperatures of several Rb–S compounds were determined

t/°C	Compound	Solubility/mol % S[a]
≈450	Rb_2S_2	50.0
≈210	Rb_2S_3	60.0
230–231	Rb_2S_5	71.4

[a]Calculated by the compilers.

Rb_2S_4 and Rb_2S_6 were found to have no crystal structure; therefore, they are not defined substances. No polymorphism of Rb_2S_2 was found.

Auxiliary Information

Method:
The sulfides of Rb were prepared by the reaction of stoichiometric amounts of S and Rb in liquid NH_3 in a N atmosphere. Rb was added to the S solution and corresponding crystals were precipitated. NH_3 was evaporated by heating at 373 K and later at 473 K in high vacuum for 6–10 h. The method of the determination of the melting point was not described. The solid phases were investigated by x-ray diffraction and chemical analysis.

Source and Purity of Materials:
S: "fine powder" of unspecified purity as in Feher and Berthold.[1]
Rb: distilled in high vacuum, molten in a N atmosphere.[1]
N: dried subsequently over $Ca(OH)_2$–NaOH, KOH and molten K.[1]

Estimated Error:
Solubility: precision ±1%.
Temperature: nothing specified; not better than ±1 K (by the compilers).

References:
[1]F. Feher and H. J. Berthold, Z. Anorg. Chem. **274**, 223–233 (1953).

Components:
(1) Sulfur; S; [7704-34-9]
(2) Rubidium; Rb; [7440-17-7]

Original Measurements:
A. N. Kuznetsov, Ph.D. thesis, Akad. Nauk SSSR, Sverdlovsk, Russia, 1978; abstracted in K. A. Chuntonov and S. P. Yatsenko, Zh. Fiz. Khim. **52**, 2145 (1978).

Variables:
Temperature: 439–779 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data
Melting temperatures of Rb–S compounds were read out from a figure by the compilers

t/°C	Formula	Solubility/mol % S
506	Rb_2S	33.3
435	Rb_2S_2	50.0
197	Rb_2S_3	60.0
166	Rb_2S_4	66.7
213	Rb_2S_5	71.4

Auxiliary Information

Method:
Nothing specified but probably analogous to Yatsenko *et al.*[1] The melts were investigated in thin-wall evacuated Pyrex glass tubes. Differential thermal analysis curves for the molten Rb–S mixtures were obtained using a cooling rate of 10 K/min. Temperatures were recorded by means of a Chromel/Kopel thermocouple. The solid phases were analyzed by x-ray diffraction.

Source and Purity of Materials:
S: nothing specified.
Rb: 99.9% pure, as in Yatsenko *et al.*[1]

Estimated Error:
Solubility: nothing specified; reading-out procedure ±1 mol %.
Temperature: nothing specified; reading-out procedure ±5 K.

References:
[1]S. P. Yatsenko, A. N. Kuznetsov, and K. A. Chuntonov, Izv. Akad. Nauk SSSR, Neorg. Mater. **13**, 738–739 (1977).

6.12. Rubidium–Selenium

Components:
(1) Selenium; Se; [7782-49-2]
(2) Rubidium; Rb; [7440-17-7]

Evaluated by:
Hans Ulrich Borgstedt, Forschungszentrum Karlsruhe, Germany and Cezary Guminski, University of Warsaw, Poland, September 1998.

Critical Evaluation

Se reacts with Rb with the formation of several compounds. The major part of the Rb–Se liquidus was determined by Yatsenko *et al.*[1] by thermal analysis. The authors used Ta and Pyrex glass containers for the analysis, but both the materials were sensitive to corrosion by the Rb–Se melts, particularly at higher temperatures. Bergmann[2] synthesized Rb_2Se and determined its melting temperature at 913 K in vacuum. Klemm *et al.*[3] measured magnetic susceptibilities of Rb_2Se, Rb_2Se_2, Rb_2Se_3, and Rb_2Se_4, but their thermal features were not investigated. Hoshino and Endo[4] investigated the effect of pressure on the liquid miscibility gap in the Se-rich mixtures by means of electric conductivity of the mixtures. A rough agreement between the solubility results of Yatsenko *et al.*[1] and Hoshino and Endo[4] was observed.

Sangster and Pelton[5] reviewed the Rb–Se system and proposed an assessed phase diagram which omits $Rb_{11}Se_8$ and Rb_2Se_6 phases, the existence of which was insufficiently documented by Yatsenko *et al.*[1] The compound Rb_2Se was shown to exist in two polymorphic forms with the transformation temperature being 30 K below the melting point of Rb_2Se in the diagram of Chuntonov and Yatsenko.[6] The Rb–Se phase diagram is shown in Fig. 56. The miscibility gap in the Se-rich range extends from 81 to 98 mol % Se at 486 K and the critical temperature is about 527 K.

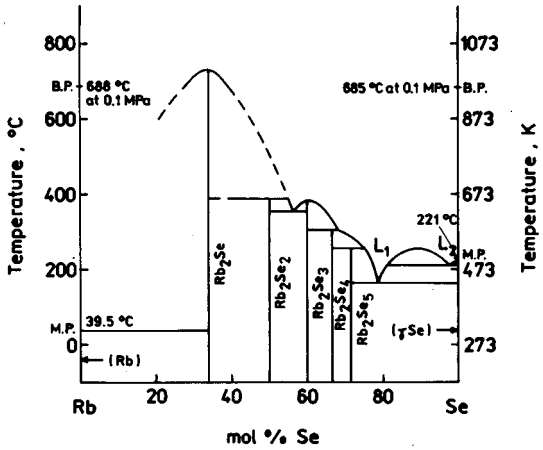

FIG. 56. Rb–Se phase diagram.

Tentative values of the solubility of Se in liquid Rb

T/K	Solubility/mol % Se	Source
≈1003	33.3 congruent	(1)
≈663	55 peritectic	(1)
≈628	56 eutectic	(1)
658	60.0 congruent	(1)
578	68 peritectic	(1)
527	75 peritectic	(1)
438	81 eutectic	(1)

References:

[1]S. P. Yatsenko, A. N. Kuznetsov, and K. A. Chuntonov, Izv. Akad. Nauk SSSR, Neorg. Mater. **13**, 738 (1977).
[2]A. Bergmann, Z. Anorg. Chem. **231**, 269 (1937).
[3]W. Klemm, H. Sodomann, and P. Langmesser, Z. Anorg. Chem. **241**, 281 (1939).
[4]H. Hoshino and H. Endo, J. Non-Cryst. Solids **117/118**, 528 (1990).
[5]J. Sangster and A. D. Pelton, J. Phase Equil. **8**, 190 (1997).
[6]K. A. Chuntonov and S. P. Yatsenko, Zh. Fiz. Khim. **52**, 2145 (1978).

Components:
(1) Selenium; Se; [7782-49-2]
(2) Rubidium; Rb; [7440-17-7]

Original Measurements:
S. P. Yatsenko, A. N. Kuznetsov, and K. A. Chuntonov, Izv. Akad. Nauk SSSR, Neorg. Mater. **13**, 738–739 (1977).

Variables:
Temperature: 508–1003 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The liquidus line of the Rb–Se system was determined. The results were presented graphically; the compilers read the results from the figure.

t/°C	Solubility/mol % Se
682[a]	27.5
730[a]	33.5
646[a]	43.5
588[a]	45.8
582[b]	45.8
561[b]	48.1
529[b]	50.5
402[b]	55.1
375[b]	57.9
385[b]	60.5
383[b]	61.8
380[b]	62.6
383[b]	63.4
305[b]	67.9
301[a]	70.0
278[b]	70.5
261[b]	75.5
228[b]	81.7
232[a]	83.2
239[b]	85.2
243[b]	89.8
235[a]	96.6

[a]In a Ta crucible; also published in Yatsenko *et al.*[1]
[b]In a Pyrex glass crucible.

The melting point of Se was found at 217 °C; this temperature is nearly the same as the monotectic temperature in the Se-rich range. The miscibility gap extends from 81 to almost 100 mol % Se. The melts interacted with Ta crucibles above 673 K and with Pyrex glass crucibles above 823 K.

Auxiliary Information

Method:
Preliminary experiments were performed in thin walled Ta crucibles. The melts containing 40–100 mol % Se were investigated in thin walled Pyrex glass crucibles being evacuated. Differential thermal analysis curves of cooling the molten Rb–Se mixtures were obtained with a rate of 10 K/min. Temperatures were recorded by means of a Chromel/Kopel thermocouple. The solid phases were analyzed by x-ray diffraction.

Source and Purity of Materials:
Se: 99.995% pure.
Rb: 99.9% pure.

Estimated Error:
Solubility: nothing specified; reading-out procedure ±0.5 mol %.
Temperature: precision between ±1 and ±5 K (at the highest temperatures); reading-out procedure ±2 K.

References:
[1]S. P. Yatsenko, K. A. Chuntonov, and A. N. Kuznetsov, Tezisy Dokladov Vsesoyuznovo Soveshchaniya po Khimii Tverdovo Tela, Sverdlovsk, Pt. IV, 1975, p. 107.

Components:
(1) Selenium; Se; [7782-49-2]
(2) Rubidium; Rb; [7440-17-7]

Original Measurements:
H. Hoshino and H. Endo, J. Non-Cryst. Solids **117/118**, 525–528 (1990).

Variables:
Temperature: 485–526 K
Pressure: 0.1–110 MPa

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The effect of pressure on the miscibility gap in the Se-rich melts of the Rb–Se system was investigated. The results were presented in graphical form. Temperatures were read out by the compilers, compositions were given in numerical form.

p/MPa	t/°C	Solubility/mol % Rb	Solubility/mol % Se
0.1	245	5.0	95.0
	253	10.0	90.0
	253	12.8	87.2
	244	15.0	85.0
18	250	10.0	90.0
50	237	5.0	95.0
	244	10.0	90.0
	241	12.8	87.2
	235	15.0	85.0
55	242	10.0	90.0
87	237	10.0	90.0
90	231	5.0	95.0
	235	10.0	90.0
	234	12.8	87.2
	229	15.0	85.0
110	233	10.0	90.0

The monotectic temperatures were reported at 212, 216, 222, 223, 229, and 229 °C for 0.1, 18, 50, 55, 87, and 90 MPa. At 106 MPa the two-phase region disappears and the critical temperature is equal to the monotectic one.

Auxiliary Information

Method:
Samples of the Rb–Se mixtures were prepared by reacting Rb and Se vapors at 673 K in a Pyrex glass tube sealed under vacuum. The region of the hardly miscible liquids was investigated by measurements of the electrical conductivity. These were made up to 110 MPa in an internally heated autoclave using a Pyrex glass cell with six electrodes made of W. Homogeneous mixtures were obtained by rocking the autoclave at 673 K. The method of pressure application to the Rb–Se system was not described.

Source and Purity of Materials:
Se: distilled.
Rb: distilled.

Estimated Error:
Solubility: nothing specified.
Temperature: nothing specified; reading-out procedure ±0.5 K.

6.13. Rubidium–Tellurium

Components:
(1) Tellurium; Te; [13494-80-9]
(2) Rubidium; Rb; [7440-17-7]

Evaluated by:
Hans Ulrich Borgstedt, Forschungszentrum Karlsruhe, Germany and Cezary Guminski, University of Warsaw, Poland, November 1998

Critical Evaluation

Bergmann[1] synthesized Rb_2Te and found that it was stable up to 963 K in vacuum. Klemm *et al.*[2] confirmed the formation of Rb_2Te; but they were not able to detect other compounds formed in the Rb–Te system.

Kuznetsov *et al.*[3,4] investigated an extended part of the system between 33 and 100 mol % Te. The authors reported the formation of seven compounds with congruently melting Rb_2Te and Rb_2Te_3, while the remaining ones (Rb_5Te_3, Rb_3Te_2, Rb_5Te_4, Rb_2Te_2, and Rb_2Te_4) were claimed to form in peritectic reactions. It seems, by analogy to the more extensively investigated system Cs–Te, that some compounds postulated in the diagram do not exist. The melting point of Rb_2Te was corrected to 1147 K, but no details were reported in Khabachev and Chuntonov.[5]

The Rb–Te diagram is shown in Fig. 57.

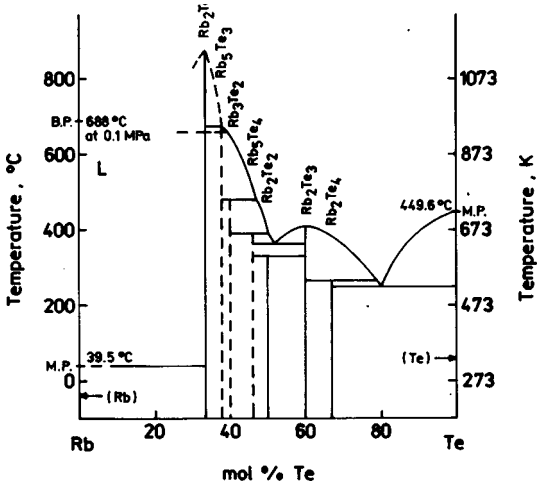

FIG. 57. Rb–Te phase diagram.

Tentative and doubtful (d) values of the solubility of Te in liquid Rb

T/K	Solubility/mol % Te	Source
1147 (d)	33.3 congruent	(3)
948	38 (d) peritectic	(3)
753	47 (d) peritectic	(3) interpolated
663	51 (d) peritectic	(3) interpolated
638	53 eutectic	(3) interpolated
681	60.0 congruent	(3)
538	78 peritectic	(3) interpolated
522	81 eutectic	(3) interpolated

References:

[1]A. Bergmann, Z. Anorg. Chem. **231**, 269 (1937).
[2]W. Klemm, H. Sodomann, and P. Langmesser, Z. Anorg. Chem. **241**, 281 (1939).
[3]A. N. Kuznetsov, K. A. Chuntonov, and S. P. Yatsenko, *Khimiya i Tekhnologiya Redkikh Shchelochnykh Elementov* (Nauka, Moskva, 1977), p. 122.
[4]A. N. Kuznetsov, Ph.D. thesis, Akad. Nauk. SSSR, Sverdlovsk, Russia, 1978; cited by K. A. Chuntonov and S. P. Yatsenko, Zh. Fiz. Khim. **52**, 2145 (1978).
[5]M. N. Khabachev and K. A. Chuntonov, J. Alloy Compd. **265**, 93 (1998).

Components:
(1) Tellurium; Te; [13494-80-9]
(2) Rubidium; Rb; [7440-17-7]

Original Measurements:
A. N. Kuznetsov, K. A. Chuntonov, and S. P. Yatsenko, *Khimiya i Tekhnologiya Redkikh Shchelochnykh Elementov* (Nauka, Moskva, 1977), pp. 122–123.

Variables:
Temperature: 528–1041 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The liquidus line of the Rb–Te system was determined. Graphical results were read from a figure by the compilers.

t/°C	Solubility/mol % Te
768[a]	33.3
675[a]	37.5
672	40
572	46
464	48
397	51
364[a]	53
396	55
406	57
408	59
407	62
399	66
385	68
332	75
255	80
329	86
347	88
386	90
425	96
448	98

[a]Numerical result.

The authors reported the formation of Rb_2Te (with polymorphic transition at 660 °C), Rb_5Te_3, Rb_3Te_2, Rb_5Te_4, RbTe, Rb_2Te_3, and $RbTe_2$ equilibrium solid phases.

Auxiliary Information

Method:
The alloys were prepared by mixing proper amounts of Te and Rb in Pyrex glass containers in vacuum. The components were heated up to their reaction initiation. After the reaction the containers were placed in an apparatus for differential thermal analysis. The analysis was performed with a cooling rate of 10 K/min.[1] The melts with <33 mol % Te were investigated in Ta containers. The solid phases were investigated by x-ray diffraction.

Source and Purity of Materials:
Te: probably semiconductor degree of purity, as in Chuntonov *et al.*[2]
Rb: probably 99.9% pure, as in Yatsenko *et al.*[1]

Estimated Error:
Solubility: nothing specified; reading-out procedure ±0.5 mol %.
Temperature: precision between ±1 K (at lowest) and ±5 K (at highest temperatures); reading-out procedure ±2 K.

References:
[1]S. P. Yatsenko, A. N. Kuznetsov, and K. A. Chuntonov, Izv. Akad. Nauk SSSR, Neorg. Mater. **13**, 738–739 (1977).
[2]K. A. Chuntonov, A. N. Kuznetsov, V. M. Fedorov, and S. P. Yatsenko, Izv. Akad. Nauk SSSR, Neorg. Mater. **18**, 1108–1112 (1982).

6.14. Rubidium or Cesium–Polonium

Components:
(1) Polonium; Po; [7440-08-6]
(2) Rubidium; Rb; [7440-17-7] or Cesium; Cs; [7440-46-2]

Evaluated by:
Hans Ulrich Borgstedt, Forschungszentrum Karlsruhe, Germany and Cezary Guminski, University of Warsaw, Poland, March 1999.

Critical Evaluation

There is no experimental material available concerning phase diagram relations and solubilities in both the systems. Since Po has more metallic character in comparison to Te one should expect lower stability (lower melting temperature) of Rb_2Po and Cs_2Po than of Rb_2Te and Cs_2Te, respectively, and consequently higher solubilities of Po than of Te in these solvent metals. It seems that several compounds may still be formed on the Po-rich sides of both systems.

6.15. Rubidium–Fluorine

Components:
(1) Fluorine; F; [7782-41-4]
(2) Rubidium; Rb; [7440-17-7]

Original Measurements:
M. A. Bredig and J. W. Johnson, J. Phys. Chem. **64**, 1899–1900 (1960).

Variables:
Temperature: 1000–1004 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data and Critical Evaluation

The solubility of F in liquid Rb was determined at two temperatures

t/°C	Solubility/mol % RbF	Solubility/mol % F[a]
787	73.1	42.2
791	79.1	44.2

The authors established the monotectic temperature at 773 °C. The monotectic was predicted to extend from 37.5 to 47.5 mol % F and the consolute point to be at 43 mol % F and 791 °C. The melting point of RbF was determined at 795 °C.

The Rb–F phase diagram should be similar to that of the Rb–Cl system, but an insufficient amount of data is known at present to define the whole liquidus as can be seen in the partial diagram shown in Fig. 58.

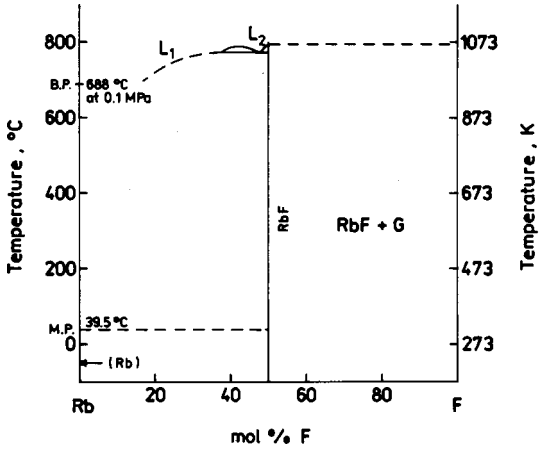

FIG. 58. Rb–F phase diagram (partial).

Auxiliary Information

Method:
Thermal analyses of mixtures were carried out in a stainless steel capsule.[1] The capsule was filled with known amounts of RbF and Rb, then purged with Ar. The capsule was shut by welding with a flat top and placed inside a tank made of Inconel and pressurized with Ar up to 0.7 MPa. The ratio of the container weight to the sample weight was reduced by employing thin walled construction tubes. The temperature was measured with a Pt/Pt–Rh(10%) thermocouple well. Cooling and heating cycles were repeated 2–4 times for each composition. The composition of the samples was analyzed by an unspecified method.

Source and Purity of Materials:
RbF: very hygroscopic, prepared in situ by reaction of Rb with CrF_2 and dried.
Rb: contained few tenths of mol % of K and Cs.
Ar: nothing specified.

Estimated Error:
Solubility: nothing specified.
Temperature: precision ±0.25 K, as in Ref. 1.

References:
[1]J. W. Johnson and M. A. Bredig, J. Phys. Chem. **62**, 604–607 (1958).

6.16. Rubidium–Chlorine

Components:
(1) Chlorine; Cl; [7782-50-5]
(2) Rubidium; Rb; [7440-17-7]

Original Measurements:
M. A. Bredig and J. W. Johnson, J. Phys. Chem. **64**, 1899–1900 (1960).

Variables:
Temperature: 881–979 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data and Critical Evaluation

The solubility of Cl in liquid Rb as a part of the Rb–Cl liquidus was determined

t/°C	Solubility/mol % RbCl	Solubility/mol % Cl[a]
608.0	9.2	8.4
664.3	22.2	18.2
685.7	33.3	25.0
701.7	49.2	33.0
705.7	65.5	39.6
704.7	73.8	42.5
697.8	88.9	47.1
699.5	93.0	48.2

[a]Calculated by the compilers.

The melting point of RbCl was reported as 715.9 °C in a table and 717 °C in a figure. The monotectic extends between 30 and 45 mol % Cl at 696 °C. The consolute point was estimated at 706 °C and 38.7 mol % Cl. The results have tentative character.

The solubility of Cl in molten RbCl was evaluated in Tomkins and Bansal.[1] The Rb–Cl phase diagram is shown in Fig. 59.

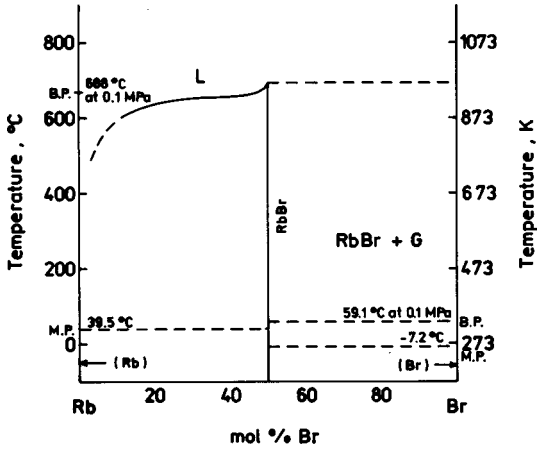

FIG. 59. Rb–Cl phase diagram.

Auxiliary Information

Method:
A stainless steel capsule was filled with known amounts of RbCl and Rb and purged with Ar.[2] The capsule was closed by welding with a flat top, placed inside a tank made of Inconel and pressurized with Ar up to 0.7 MPa. The ratio of the container weight to the sample weight was reduced by employing thin walled construction tubes. Thermal analyses of mixtures were performed with the use of a Pt/Pt–Rh (10%) thermocouple well. Cooling and heating cycles were repeated 2–4 times for each composition. The samples were analyzed by an unspecified method.

Source and Purity of Materials:
RbCl: prepared from RbBr or RbI by anion exchange reaction.
Rb: contained few tenths of mol % of K and Cs.
Ar: nothing specified.

Estimated Error:
Solubility: nothing specified.
Temperature: precision ±0.25 K, as in Johnson and Bredig.[2]

References:
[1]R. T. P. Tomkins and N. P. Bansal, *Gases in Molten Salts*, Solubility Data Series (Pergamon, Oxford, 1990), Vol. 45/46, pp. 133–135.
[2]J. W. Johnson and M. A. Bredig, J. Phys. Chem. **62**, 604–607 (1958).

6.17. Rubidium–Bromine

Components:
(1) Bromine; Br; [7726-95-6]
(2) Rubidium; Rb; [7440-17-7]

Original Measurements:
M. A. Bredig and J. W. Johnson, J. Phys. Chem. **64**, 1899–1900 (1960).

Variables:
Temperature: 857–942 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data and Critical Evaluation

The solubility of Br in liquid Rb as a part of the Rb–Br liquidus was determined

t/°C	Solubility/mol % RbBr	Solubility/mol % Br[a]
584.3	10.0	9.1
630.9	20.4	16.9
648.6	33.5	25.1
652.9	39.2	28.2
656.9	52.0	34.2
658.9	60.0	37.5
660.6	72.9	42.2
665.2	81.4	44.9
668.6	88.8	47.0

[a]Calculated by the compilers.

The melting point of RbBr was reported as 692.5 °C in a table and 693 °C in a figure. The results have only tentative character. The Rb–Br phase diagram is shown in Fig. 60. The solubility of Br in molten RbBr should be small.

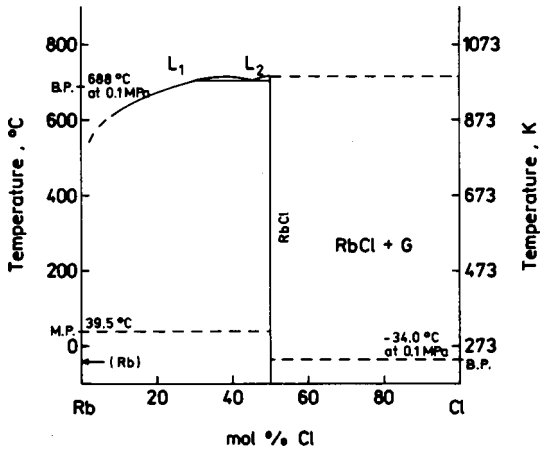

FIG. 60. Rb–Br phase diagram.

Auxiliary Information

Method:
A stainless steel capsule was filled with known amounts of RbBr and Rb and purged with Ar.[1] The capsule was welded shut with a flat top and placed inside a tank made of Inconel and pressurized with Ar up to 0.7 MPa. The ratio of the container weight to the sample weight was reduced to minimum by employing thin walled construction tubes. Thermal analyses of mixtures were performed with the use of a Pt/Pt–Rh(10%) thermocouple well. Cooling and heating curves were recorded 2–4 times for each sample. The composition of samples was analyzed by an unspecified method.

Source and Purity of Materials:
RbBr: prepared by reaction of Rb_2SO_4 with $BaBr_2$, recrystallized from aqueous solution and finally crystallized from the melt.
Rb: contained few tenths of mol % K and Cs.
Ar: nothing specified.

Estimated Error:
Solubility: nothing specified.
Temperature: precision ±0.25 K; as in Johnson and Bredig.[1]

References:
[1]J. W. Johnson and M. A. Bredig, J. Phys. Chem. **62**, 604–607 (1958).

6.18. Rubidium–Iodine

Components:
(1) Iodine; I; [7553-56-2]
(2) Rubidium; Rb; [7440-17-7]

Evaluated by:
Hans Ulrich Borgstedt, Forschungszentrum Karlsruhe, Germany and Cezary Guminski, University of Warsaw, Poland, December 1998.

Critical Evaluation

I reacts with Rb, and the stable compound RbI is formed in this reaction. The formation of the less stable RbI_3 was also observed in an excess of I. Due to the low melting point of I (458.4 K) and its relatively high vapor pressure, the I-rich part of the Rb–I phase diagram depends on pressure, and Fig. 61 shows the phase relations at the pressure of a closed container, sufficient to retain all phases in the condensed form. The mixtures show the tendency to undercooling.

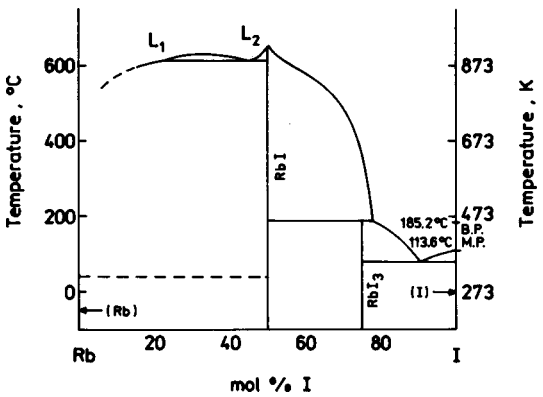

FIG. 61. Rb–I phase diagram (tentative).

The solubility of I in liquid Rb at the Rb-rich side was investigated by Bredig and Johnson[1] for higher concentrations of I in Rb and higher temperatures. A monotectic was observed in the range from 21 to 44 mol % I at 888 K, and the critical miscibility was found at 33 mol % I and 907 K. The I-rich range of compositions was much more investigated. Briggs and Patterson[2] studied this while the system was under normal pressure. This determined the boiling point of the saturated mixture with 76.9 mol % I at 512 K and a pressure of 0.101 MPa. Fialkov and Kusmenko[3–5] investigated a similar range of concentrations and confirmed the liquidus line roughly. Their eutectic point at 90.7 mol % I and 353 K was only slightly different from the parameters established previously (91.3 mol % I and 354 K) in Briggs and Patterson.[2] The temperature difference is equal to the difference of the melting point of I, observed by Briggs and Patterson[2] and by Fialkov and Kusmenko.[3–5] Plotnikov *et al.*[6] who worked at the same laboratory[3–5] observed a break at 95 mol % I and 313 K of the specific conductivity of a RbI–I melt. Treating this value as a liquidus point, it does not fit either their results or those of other investigators; the value is therefore rejected. Rosztoczy and Cubicciotti[7] performed experiments at the I-rich side using closed containers and the reagents of highest purity. Their results seem to confirm the results of Briggs and Patterson[2] rather than those of Fialkov and Kusmenko.[3–5] The temperature differences were up to 5 K. We select the data of Rosztoczy and Cubicciotti[7] as the most reliable and complete for the I-rich side and of Bredig and Johnson[1] for the Rb-rich part of the phase diagram. Hoch[8] predicted the liquidus line of the RbI–I part suggesting a eutectic which was moved more than 10 mol % to the RbI side than observed in experiments.

The combined Rb–I phase diagram (based on Rosztoczy and Cubicciotti[7]) is shown in Fig. 61.

Tentative values of the solubility of I in liquid Rb

T/K	Solubility/mol % I	Remark	Source
873	16	–	(1) interpolated
888	21 monotectic	–	(1) interpolated
907	33 critical	–	(1) interpolated
888	44 eutectic	–	(1) interpolated
920	50 congruent	–	(1)
873	56	at constrained pressure	(7) interpolated
773	69	at constrained pressure	(7) interpolated
673	74	at constrained pressure	(7) interpolated
573	76	at constrained pressure	(7) interpolated
461	78 peritectic	–	(7)
353	91 eutectic	–	(3,4,5),(7)

References:

[1]M. A. Bredig and J. W. Johnson, J. Phys. Chem. **64**, 1899 (1960).
[2]T. R. Briggs and E. S. Patterson, J. Phys. Chem. **26**, 2621 (1932).
[3]Ya. A. Fialkov and A. A. Kusmenko, Acta Physicochem. USSR **3**, 711 (1935).
[4]Ya. A. Fialkov and A. A. Kusmenko, Mem. Inst. Khim. Ukr. Akad. Nauk **2**, 127 (1935).
[5]Ya. A. Fialkov and A. A. Kusmenko, Zh. Obshch. Khim. **6**, 265 (1936).
[6]V. A. Plotnikov, Ya. A. Fialkov, and V. P. Tschalii, Z. Phys. Chem., A **172**, 304 (1935).
[7]F. E. Rosztoczy and D. Cubicciotti, J. Phys. Chem. **69**, 1687 (1965).
[8]M. Hoch, J. Phase Equil. **4**, 296 (1993).

Components:
(1) Iodine; I; [7553-56-2]
(2) Rubidium; Rb; [7440-17-7]

Original Measurements:
T. R. Briggs and E. S. Patterson, J. Phys. Chem. **26**, 2621–2624 (1932).

Variables:
Temperature: 354–513 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data
The I-rich part of the Rb–I liquidus was determined

t/°C	Solubility/mol % RbI	Solubility/mol % I[a]
108.8	5	97.5
100.0	10	95.0
87.0	15	92.5
81.8	17	91.5
81	17.44[b]	91.3
103	20	90.0
134	25	87.5
142	26.35[b]	86.8
149	30	85.0
160	32.16[b]	83.9
167	35	82.5
175	37.60[b]	81.2
178	40	80.0
185	42.5	78.8
187.2	45	77.5
195	44.71[b]	77.6
206	45.23[b]	77.4
220	45.62[b]	77.2
238.5[c]	46.23[b]	76.9

[a]Calculated by the compilers.
[b]From chemical analysis.
[c]Boiling point at ~0.1 MPa.

The melting and boiling points of I were found at 114 and 184 °C, respectively.

Auxiliary Information

Method:
The mixtures of RbI and I were ground and placed in a glass tube.[1] The tube was sealed with a thermometer in order to prevent any serious loss of I during heating. The mixtures were held at 413–423 K for 2–4 h before they were allowed to cool. The cooling curves were taken in the customary way. In the solubility measurements the saturated solutions were filtered through a glass wool plug. The filtering tube below the plug was broken open to take the frozen phase for analysis for RbI and I in the manner described in Briggs and Geigle.[1] The boiling points of the solutions were determined in a glass apparatus using a thermometer.

Source and Purity of Materials:
I: sublimed and carefully dried.
RbI: 97.8% pure from Kahlbaum, recrystallized from aqueous solution and dried.

Estimated Error:
Solubility: nothing specified; not better than ±0.5 mol % (by the compilers).
Temperature: precision ±0.2 K (in melting) and ±1 K (in boiling).

References:
[1]T. R. Briggs and W. F. Geigle, J. Phys. Chem. **34**, 2250–2259 (1930).

Components:
(1) Iodine; I; [7553-56-2]
(2) Rubidium; Rb; [7440-17-7]

Original Measurements:
Ya. A. Fialkov and A. A. Kusmenko, Acta Physicochim. **3**, 711–724 (1935).

Variables:
Temperature: 353–462 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data
The I-rich part of the Rb–I liquidus was determined. The results were reported in a figure. They were read out and recalculated by the compilers.

t/°C	Solubility/mol % RbI	Solubility/mol % I
110	3	98.5
106	4	98.0
102	5	97.5
94	10	95.0
83	14	93.0
84	16	92.0
82	19	90.5
85	20	90.0
101	21.5	89.3
107	22.5	88.8
108	24	88.0
124	27	86.5
135	28	86.0
150	30	85.0
162	32	84.0
180	37	81.5
189	44	78.0

The eutectic point was found at 18.59 mol % RbI and 79.9 °C. The melting point of I was measured at 113.20–113.36 °C. The same results were also published in Fialkov and Kusmenko.[1,2]

Auxiliary Information

Method:
Thermal analyses of RbI–I samples were performed in a glass container. A Hg precision thermometer, placed inside of the container, was used. The rate of temperature change was 0.4–0.6 K/min. The container was effectively shaken to avoid undercooling. The observed undercooling was 2.3 K.

Source and Purity of Materials:
I: nothing specified.
RbI: nothing specified.

Estimated Error:
Solubility: nothing specified; reading-out procedure ±0.5 mol %.
Temperature: precision ±0.3 K; reading-out procedure ±1 K.

References:
[1]Ya. A. Fialkov and A. A. Kusmenko, Mem. Inst. Khim. Ukr. Akad. Nauk **2**, 127–139 (1935).
[2]Ya. A. Fialkov and A. A. Kusmenko, Zh. Obshch. Khim. **6**, 265–272 (1936).

Components:
(1) Iodine; I; [7553-56-2]
(2) Rubidium; Rb; [7440-17-7]

Original Measurements:
M. A. Bredig and J. W. Johnson, J. Phys. Chem. **64**, 1899–1900 (1960).

Variables:
Temperature: 867–906 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data
A part of the Rb–I liquidus was determined

t/°C	Solubility/mol % RbI	Solubility/mol % I[a]
593.8	18.0	15.2
618.5	29.3	22.7
632.7	40.6	28.9
632.6	49.8	33.2
632.8	58.8	37.0
627.3	68.7	40.7
620.5	74.3	42.6
616.0	85.4	46.1
621.7	88.1	46.8
622.7	88.4	46.9
634.0	95.6	48.9

[a]Calculated by the compilers.

The melting point of RbI was found at 646.9 °C. The monotectic extends from 21 to 44 mol % I at 615 °C. The critical point was estimated at 33 mol % I and 634 °C.

Auxiliary Information

Method:
A stainless steel capsule was filled with known amounts of Rb and RbI and purged with Ar after filling.[1] The capsule was welded shut with a flat top and placed inside a tank made of Inconel and pressurized with Ar up to 0.7 MPa. The ratio of the container weight to the sample weight was reduced by employing thin walled construction tubes. Thermal analysis of mixtures was performed using a Pt/Pt–Rh (10%) thermocouple well. Cooling and heating cycles were repeated 2–4 times for each of the compositions. The samples were analyzed by an unspecified method.

Source and Purity of Materials:
RbI: prepared by the reaction of Rb_2SO_4 with BaI_2, recrystallized from aqueous solution and finally crystallized from the melt.
Rb: contained a few tenths of mol % of K and Cs.
Ar: nothing specified.

Estimated Error:
Solubility: nothing specified.
Temperature: precision ±0.25 K, as in Johnson and Bredig.[1]

References:
[1]J. W. Johnson and M. A. Bredig, J. Phys. Chem. **62**, 604–607 (1958).

Components:
(1) Iodine; I; [7553-56-2]
(2) Rubidium; Rb; [7440-17-7]

Original Measurements:
F. E. Roszto czy and D. Cubicciotti, J. Phys. Chem. **69**, 1687–1692 (1965).

Variables:
Temperature: 360–884 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data
The I-rich part of the Rb–I liquidus line was determined

t/°C	Solubility/mol % RbI	Solubility/mol % I[a]
108.4	5	97.5
100.6	10	95.0
88	15	92.5
87	20	90.0
121	25	87.5
145	30	85.0
181.9	40	80.0
188.0	45	77.5
448	55	72.5
518	65	67.5
578	80	60.0
611	90	55.0

[a]Calculated by the compilers.

The melting points of I and RbI were found at 113.3 and 656.0 °C, respectively.

Auxiliary Information

Method:
Cooling curves were obtained of samples in glass containers sealed under vacuum. Two types of containers were used: a medium-wall Pyrex test tube with a re-entrant thermocouple well in the bottom and a bundle of three medium-wall fused quartz tubes. Tubes of the first type were used with the I-rich solutions. Tubes of the second type were used for the RbI-rich solutions. The samples were maintained at a constant temperature difference above or below the furnace temperature during the cooling or heating cycles of the curves.

Source and Purity of Materials:
I: resublimed crystals of ultrapure substance from Mallinckrodt.
RbI: 99.9% pure from Alpha Inorganics; chemical analysis showed the I content 1.28% below the stoichiometry.

Estimated Error:
Solubility: nothing specified.
Temperature: nothing specified.

6.19. Rubidium–Helium (Ne, Ar, Kr, Xe, Rn)

Components:
(1) Helium; He; [7440-59-7]
or Neon; Ne; [7440-01-9]
or Argon; Ar; [7440-37-1]
or Krypton; Kr; [7439-90-9]
or Xenon; Xe; [7440-63-3]
or Radon; Rn; [10043-92-2]
(2) Rubidium; Rb; [7440-17-7]

Evaluated by:
Hans Ulrich Borgstedt, Forschungszentrum Karlsruhe, Germany and Cezary Guminski, University of Warsaw, Poland, February 1999.

Critical Evaluation

Experimental information on solubilities of the noble gases in liquid Rb is not available. However, the general tendency observed is that solubilities of these gases increase with the increase of atomic mass of the alkali metal solvent. Therefore, one may predict a higher solubility of them in liquid Rb than in liquid K at selected temperature. Such prediction would be also in agreement with regular solution calculation.

Tilton *et al.*[1] investigated mixtures of solid Kr and Xe with Rb at 5 K; information on the miscibility of the components in the solid state could not be deduced from the optical measurements. Phase diagrams of the whole family of systems should be similar to the Na–Xe phase diagram (shown for this solubility system) differing in melting and boiling point of Rb (312.6 and 688 K, respectively) and the corresponding noble gas.

References:

[1]R. A. Tilton, D. J. Phelps, and C. P. Flynn, Phys. Rev. Lett. **32**, 1006 (1974).

7. Solutions of Nonmetallic Substances in Cesium

7.1. Cesium–Hydrogen

Components:
(1) Hydrogen; H; [1333-74-0]
(2) Cesium; Cs; [7440-46-2]

Evaluated by:
Hans Ulrich Borgstedt, Forschungszentrum Karlsruhe, Germany and Cezary Guminski, University of Warsaw, Poland, April 1998.

Critical Evaluation

The reaction of gaseous H with liquid Cs with formation of CsH at 673 K is relatively slow but faster than the reactions of H with K or Na,[1] and the equilibrium is attained after some scores of hours.[2] Since the gas, liquid and solid phases are in equilibrium, a H solubility may be defined either as H concentration in the liquid phase being a function of H gas pressure over the melt and solid or liquid CsH is not the saturating phase, or as maximum H concentration in the liquid being dissolved from solid or liquid CsH. The first kind of the equilibrium is so named isobaric solubility. Then the H pressure over the melt and the corresponding H concentration are ruled by the Sieverts constant (K_s):

$$K_s = x_H\, p_H^{-1/2} \tag{1}$$

where x_H is the mol fraction of H in the solution and p_H is the H pressure over the solution.

Dilute solutions of H in liquid Cs fulfill the Sieverts law very well up to ~1 mol % H at 673 K, as found by Subbotin *et al.*[1] However, it seems that its validity may be extended to slightly higher temperatures and compositions. Hubberstey[3] estimated, by analogy to the K–H system, that the Sieverts constant should be practically independent on temperature.

Further increase of the H pressure causes an increase of the H concentration in Cs to such extent that solid CsH starts to precipitate from the melt which is manifested by the equilibrium plateau pressure of H. This pressure was measured by Arnoldov *et al.*[2] as well as Ephraim and Michel,[4] Hackspill and Borocco,[5] Hérold,[6,7] Messer *et al.*,[8] Skuratov *et al.*[9] and Szafranski *et al.*[10,11] Numerous measurements[2,4–8] were carried out below the monotectic temperature and of Skuratov *et al.*[9] and Szafranski *et al.*[10,11] above it. Due to significant scatter of these results it would be not precise to estimate this temperature from a break on the dependence relating the H equilibrium vapor pressure versus reciprocal temperature. The reason of the discrepancies between these results is certainly connected with impurities present in the system, particularly in older measurements. The temperature dependence of the pressure below the monotectic point seems to be best described after Hérold:[6,7]

$$\log(p_H/\mathrm{Pa}) = 13.909 - 5900\ (T/\mathrm{K})^{-1} \tag{2}$$

and above the monotectic point the best H pressure data are from Szafranski *et al.*[10,11]

$$\log(p_H/\mathrm{Pa}) = 11.153 - 3711\ (T/\mathrm{K})^{-1}. \tag{3}$$

The intersection of the lines expressed by Eqs. (2) and (3) determine the monotectic temperature at 793 K; Szafranski *et al.*,[10,11] using the same equations, reported it at 792 K.

The melting point of CsH found by thermal analysis was determined to be 801±2 K by Skuratov *et al.*[9] and 795±2 K by Szafranski *et al.*[10,11] at a pressure of 3 MPa. An increase of the H pressure to 10 MPa made an increase of CsH melting temperature for the next 2.4±0.2 K.[9] Dymova *et al.*[12] observed decomposition of CsH at 653 K and H pressure of >0.1 MPa.

According to the first information[1] on the subject of H solubility, no dissolution of CsH in liquid Cs was observed up to 423 K. The solubility of solid and liquid CsH in liquid Cs was determined by Arnoldov *et al.*[2] at 573–673 K and by Szafranski *et al.*[10,11] at 848–938 K. The data obtained by Arnoldov *et al.*[2] seem to be in the proper order of magnitude. However, the slope of the temperature dependence of the solubility as well as the H equilibrium plateau pressure data are much too low comparing them with other hydrogen alkali metal systems. An extrapolation of the results of Arnoldov *et al.*[2] to the monotectic temperature gives composition of ≈3 mol % H, whereas an extrapolation from the very extensive study by Szafranski *et al.*[10,11] points on value of 18 mol % H. The experiments of Szafranski *et al.*[10,11] were performed with the use of purer materials than in Arnoldov *et al.*[2] Therefore the results of Szafranski *et al.*[10,11] are more convincing. The critical miscibility point was determined at 938 K, 40.5 mol % H, and 15.7 MPa.[10,11]

The Cs-rich part of the Cs–H diagram was plotted by Szafranski *et al.*[10,11] The predicted form of this diagram was proposed in Sangster and Pelton.[13] The diagram shown in Fig. 62 is based on Szafranski *et al.*[10,11] D vapor pressures over the Cs–H melts were estimated to be almost twice higher than of CsH,[5] but a solubility of D in liquid Cs has not yet been measured so far. Investigations of the Cs–T system were not published. Magomedov[14] predicted melting temperatures of CsH, CsD, and CsT being 915.89, 915.19, and 914.93 K. The prediction for CsH is more than 100 K higher than the experimental observations of Skuratov *et al.*[9] and Szafranski *et al.*,[10,11] moreover, the melting temperatures show a decreasing tendency with the increase of the isotope mass, a fact which was not observed for the hydrides of Li or Na.

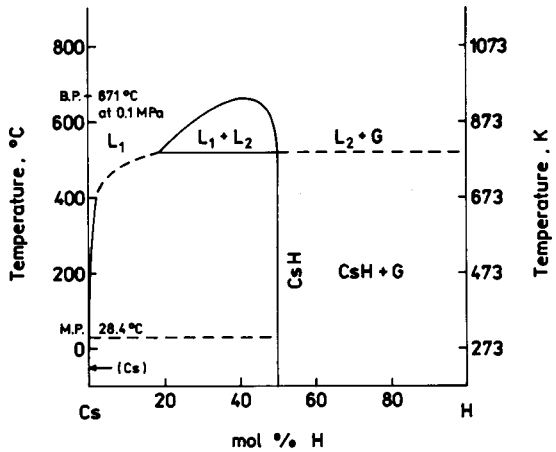

FIG. 62. Cs–H phase diagram.

The tentative and doubtful (d) values of the solubility of H in liquid Cs at corresponding pressures

T/K	Solubility/mol % H	Source	p/Pa	Source
573	1 (d)	(2)	4090	Eq. (2)
673	2 (d)	(2)	139 000	Eq. (2)
792	18 monotectic	(10,11)	2 970 000	Eq. (3)
873	28	(10,11)	7 980 000	Eq. (3)
938	40 critical	(10,11)	15 700 000	Eq. (3)

The solubility values at the CsH-rich side

T/K	Solubility/mol % H	Source
793	49.8 monotectic	(10,11)
873	48.6	(10,11)
923	46.4	(10,11)

References:

[1]V. I. Subbotin, M. N. Ivanovskii, and M. N. Arnoldov, *Fiziko-Khimicheskie Osnovy Primeneniya Zhidkometallicheskikh Teplonositelei* (Atomizdat, Moskva, 1970), p. 83.

[2]M. N. Arnoldov, Yu. V. Bogdanov, M. N. Ivanovskii, and V. A. Morozov, Izv. Akad. Nauk SSSR, Met. **4**, 30 (1976).

[3]P. Hubberstey, *Handbook of Thermodynamic and Transport Properties of Alkali Metals*, edited by R. W. Ohse (Blackwell, Oxford, 1985), p. 885.

[4]F. Ephraim and E. Michel, Helv. Chim. Acta **4**, 762 (1921).

[5]L. Hackspill and A. Borocco, Bull. Soc. Chim. Fr. Ser. [5] **6**, 91 (1939).

[6]A. Hérold, Compt. Rend. **228**, 686 (1949).

[7]A. Hérold, Ann. Chim., Ser. [12] **6**, 536 (1951).

[8]C. E. Messer, H. Homonoff, R. F. Nickerson, and T. R. P. Gibb, U.S. Atom. Energy Comm. Rep. NYO-3955 (1953).

[9]O. A. Skuratov, O. N. Pavlov, V. I. Danilkin, and I. V. Volkov, Zh. Neorg. Khim. **21**, 2910 (1976); Russ. J. Inorg. Chem. **21**, 1605 (1976).

[10]A. W. Szafranski, E. Keller, and E. U. Franck, Ber. Bunsenges. Phys. Chem. **96**, 955 (1992); E. Keller, Ph.D. thesis, University of Karlsruhe, Germany, 1985.

[11]E. Keller and E. U. Franck, Z. Phys. Chem. N.F. **156**, 195 (1988).

[12]T. N. Dymova, S. J. Bakum, and U. Mirsaidov, Dokl. Akad. Nauk SSSR **216**, 87 (1974).

[13]J. Sangster and A. D. Pelton, J. Phase Equil. **15**, 84 (1994).

[14]M. N. Magomedov, Zh. Fiz. Khim. **68**, 589 (1994).

Components:
(1) Hydrogen; H; [1333-74-0]
(2) Cesium; Cs; [7440-46-2]

Original Measurements:
M. N. Arnoldov, Yu. V. Bogdanov, M. N. Ivanovskii, and V. A. Morozov, Izv. Akad. Nauk SSSR, Met. **4**, 30–32 (1976).

Variables:
Temperature: 500–734 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of H in liquid Cs was determined. The values were read from a figure and recalculated to mol % by the compilers.

Method	t/°C	Solubility/mass % H	Solubility/mol % H
volumetric	300	$7.6\cdot10^{-3}$	1.01
	370	$1.08\cdot10^{-2}$	1.43
	400	$1.25\cdot10^{-2}$	1.66
thermal cooling	227	$4.2\cdot10^{-3}$	0.56
	251	$4.6\cdot10^{-3}$	0.61
	289	$6.5\cdot10^{-3}$	0.86
	320	$8.5\cdot10^{-3}$	1.12
	352	$1.00\cdot10^{-2}$	1.32
	423	$1.15\cdot10^{-2}$	1.52
thermal heating	245	$4.2\cdot10^{-3}$	0.56
	264	$4.6\cdot10^{-3}$	0.61
	313	$6.8\cdot10^{-3}$	0.90
	352	$8.5\cdot10^{-3}$	1.12
	461	$1.45\cdot10^{-2}$	1.88

The reaction between Cs and H is relatively slow and the equilibrium is attained after few tens of hours. The authors established that the Sieverts law in the system was fulfilled. The solubility results were expressed by the equation (tested by the compilers):

$$\log(\text{soly/mol \% H}) = 1.58 - 900\ (T/\text{K})^{-1}.$$

The H equilibrium plateau pressure versus temperature was expressed by the equation:

$$\log(p/\text{Pa}) = 7.00 - 1800\ (T/\text{K})^{-1}.$$

Auxiliary Information

Method:
Cs was contained in an ampoule made of 1Kh18N10T stainless steel. The ampoule was connected with the Cs reservoir, another container with a Ni membrane, manometer and H supply bottle. The H pressure was measured by the manometer which allowed us to define the amount of H absorbed by Cs. All elements of the apparatus were kept at stable temperature by a thermostat. The temperature was measured by means of Chromel/Alumel thermocouples. The H solubility was determined from the onset of the plateau in the relation of square root of H pressure versus H concentration. Thermal analyses of several samples of the melt were performed using a second identical ampoule as a reference.

Source and Purity of Materials:
H: purified by diffusion through a Ni membrane.
Cs: distilled.

Estimated Error:
Solubility: precision ±12%; reading-out procedure ±0.01 mol %.
Temperature: nothing specified; reading-out procedure ±2 K.

Components:
(1) Hydrogen; H; [1333-74-0]
(2) Cesium; Cs; [7440-46-2]

Original Measurements:
A. W. Szafranski, E. Keller, and E. U. Franck, Ber. Bunsenges. Phys. Chem. **96**, 955–962 (1992).

Variables:
Temperature: 792–938 K;
Pressure: 2.94–15.7 MPa

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data
The solubility of H and the H plateau pressure were determined

t/°C	p/MPa	Solubility/mol % CsH	Solubility/mol % H[a]
519[d,e] 2.94	22.6[b]	18.4[b]	
		99.2[c]	49.8[c]
550[d]	4.41	27.5[b]	21.6[b]
		98.3[c]	49.6[c]
575	5.98	32.3[b]	24.4[b]
		96.9[c]	49.2[c]
600	7.99	38.0[b]	27.5[b]
		94.7[c]	48.6[c]
625	10.49	44.2[b]	30.6[b]
		91.7[c]	47.8[c]
650	13.57	53.3[b]	34.8[b]
		86.5[c]	46.4[c]
665[f]	15.7	68	40.5

[a]Calculated by the compilers.
[b]At low H content.
[c]At high H content.
[d]Extrapolated.
[e]Monotectic.
[f]Critical point.

The results were also reported in graphical form in Keller and Franck[1] and Keller.[2] The melting temperature of CsH was determined at 522±2 °C from thermal analysis.

Auxiliary Information

Method:
The experiments were performed in an autoclave made of an austenitic Ni-base superalloy. The internal space was subdivided into two concentric compartments with equalized H pressure. The inner compartment contained a capsule of very pure Fe. The capsule was charged with a known amount of Cs through a thin stainless steel capillary under an Ar protective atmosphere. The filled capsule was evacuated and the capillary squeezed and welded. H was introduced into the outer and inner compartments of the autoclave at desired pressure. H diffused from the inner compartment through the thin steel wall into the capsule and formed CsH until its equilibrium was reached. The H pressure in the outer compartment was gradually reduced, so that the H pressure in both compartments remained equal. The H content that reacted with Cs was calculated from a proper equation of state. By stepwise increasing the H pressure the corresponding isotherms were obtained. Pressures were made by a strain gauge pressure transducer being previously calibrated. The temperature was measured and controlled with four sheathed Ni–Cr/Ni thermocouples in the autoclave wall. The solubilities were estimated from breaks on the pressure versus composition dependencies.

Source and Purity of Materials:
H: 99.999% pure from Messer–Griesheim.
Cs: 99.98% pure from Merck; main impurities were other metals and Cl, contained 10^{-2} % O.
Ar: 99.997% pure.

Estimated Error:
Solubility: precision between ±3% and ±8%.
Temperature: precision ±2 K.
Pressure: precision ±0.05 MPa.

References.
[1]E. Keller and E. U. Franck, Z. Phys. Chem. N. F. **156**, 195–204 (1988).
[2]E. Keller, Ph.D. thesis, University of Karlsruhe, Germany, 1985.

7.2. Cesium–Boron

Components:
(1) Boron; B; [7440-42-8]
(2) Cesium; Cs; [7440-46-2]

Evaluated by:
Hans Ulrich Borgstedt, Forschungszentrum Karlsruhe, Germany and Cezary Guminski, University of Warsaw, Poland, June 1998.

Critical Evaluation

Experimental material concerning the Cs–B phase diagram does not exist, and determinations of the solubility of B in liquid Cs have not been reported. Winslow *et al.*[1–3] investigated a compatibility of Nicrobraze, which contained 3.0 mass % B, with liquid Cs at 673 K for 48 or 500 h. In the short term run[1] the B content in Cs increased from $4\cdot10^{-2}$ (before the test) to 0.1 mass % B. In the triplicate long term run[2] the authors found $(1.3\pm0.1)\cdot10^{-2}$ mass % B in the liquid Cs phase. The latter value, after recalculation, is equal 0.16 mol % B. Since these experiments were no typical solubility studies, and the B source is a multicomponent material in which its chemical activity may be much below unity, the value of Winslow[2] could not be recommended as solubility; it signalizes, however, that the B solubility in liquid Cs is not negligible. Data sheets have not been prepared therefore.

References:
[1]J. H. Holley, G. R. Neff, F. B. Weiler, and P. M. Winslow, *Electric Propulsion Development*, edited by E. Stuhlinger (Academic, New York, 1963), p. 341.
[2]P. M. Winslow, Corrosion **21**, 341 (1965).
[3]P. M. Winslow, NASA Rep. SP-41, p. 243 (1964).

7.3. Cesium–Carbon

Components:
(1) Carbon; C; [7440-44-0]
(2) Cesium; Cs; [7440-46-2]

Evaluated by:
Hans Ulrich Borgstedt, Forschungszentrum Karlsruhe, Germany and Cezary Guminski, University of Warsaw, Poland, June 1998.

Critical Evaluation

Graphite reacts with liquid Cs with the formation of intercalation compounds, as it was first observed by Fredenhagen and Cadenbach.[1] The observations were confirmed by Hérold[2] and by Salzano and Aronson.[3,4] The latter authors established the existence of CsC_8, CsC_{10}, CsC_{24}, CsC_{36}, CsC_{48}, and CsC_{60}. The compounds lose Cs with the formation of the C-richer forms at increasing temperature and decreasing pressure. At very high temperatures and low Cs vapor pressures pure graphite is formed again and is even corrosion resistant to Cs vapor.[4] The CsC_{10} phase is stable above 597 K and below this temperature is decomposed in metatectic reaction to CsC_8 and CsC_{24}.[5] Caswell *et al.*[6,7] observed transformation of solid CsC_8 at 608 K. The reaction of Cs with graphite or charcoal is so effective that both forms of C may be used as a very efficient trapping device for Cs up to 873 K.[8,9]

The graphite disintegration in liquid Cs should not be taken as an evidence of good solubility of C in liquid Cs. This solubility was determined by Tepper and Greer[10,11] who performed experiments between 478 and 921 K. The authors observed almost constant C concentration of 0.013 mol % at 478 and 589 K, probably due to limits of analytical method used. The solubility increased at higher temperatures forming straight line relationship of logarithm of the solubility versus reciprocal temperature. Between 700 and 921 K the temperature dependence of the solubility may be expressed by the equation:

$$\log(\text{soly/mol \% C}) = 0.346 - 1458\,(T/\text{K})^{-1} \quad r = 0.999. \tag{1}$$

It is possible that a break on the solubility curve at about 700 K is connected with a dissociation of the Cs–C intercalation compounds (or other phase transition) and above 700 K pure graphite or an intercalate rich in C is the equilibrium solid phase. The Cs–C phase diagram is shown in Fig. 63.

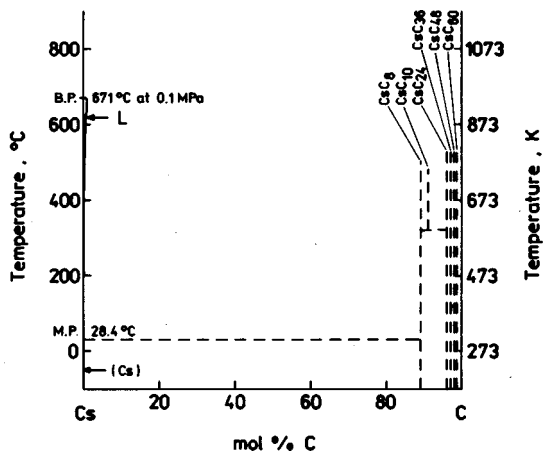

FIG. 63. Cs–C phase diagram.

C_{60} forms CsC_{60}, Cs_3C_{60}, Cs_4C_{60}, and Cs_6C_{60} with Cs. A schematic Cs–C_{60} phase diagram was constructed by Poirier *et al.*;[12] however, the solubility of C_{60} has not been measured so far.

Tentative values of the solubility of C in liquid Cs

T/K	Solubility/mol % C	Source
673	0.15	(7,8), Eq. (1) extrapolated
773	0.29	(7,8), Eq. (1) interpolated
873	0.47	(7,8), Eq. (1) interpolated
923	0.57	(7,8)

References:

[1]K. Fredenhagen and G. Cadenbach, Z. Anorg. Chem. **158**, 249 (1926).
[2]A. Hérold, Bull. Soc. Chim. Fr. 999 (1955); Compt. Rend. **232**, 1484 (1951).
[3]F. J. Salzano and S. Aronson, J. Chem. Phys. **43**, 149 (1965); **45**, 2221 (1966).
[4]F. J. Salzano and S. Aronson, Nucl. Sci. Engin. **28**, 51 (1967).
[5]S. Aronson, F. J. Salzano, and D. Bellafiore, J. Chem. Phys. **49**, 434 (1968).
[6]R. Clarke, N. Caswell, and S. A. Solin, Phys. Rev. Lett. **42**, 61 (1979).
[7]N. Caswell, Phys. Rev. B **22**, 6308 (1980).
[8]W. S. Clough and S. W. Wade, J. Nucl. Energy **25**, 445 (1971).
[9]R. P. Colburn and H. P. Maffei, U.S. Dept. Energy Rep. CONF-800401-P2, p. 13/36 (1980).
[10]F. Tepper and J. Greer, U.S. Air Force Rep. AFML-TR-64-327 (1964).
[11]F. Tepper and J. Greer, U.S. Atom. Energy Comm. Rep. CONF-650411, p. 323 (1965).
[12]D. M. Poitier, D. W. Owens, and J. H. Weaver, Phys. Rev. B **51**, 1830 (1995).

Components:
(1) Carbon; C; [7440-44-0]
(2) Cesium; Cs; [7440-46-2]

Original Measurements:
F. Tepper and J. Greer, U.S. Air Force Rep. AFML-TR-64-327 (1964).

Variables:
Temperature: 478–921 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data
The solubility of C in liquid Cs was determined

t/°F	T/K[a]	Solubility/mass % C	Solubility/mol % C[a]	Mean value[a]
400	478	0.00110, 0.00156	0.012, 0.017	0.014
600	589	0.00134, 0.00108	0.015, 0.012	0.013
		0.00115	0.013	
800	700	0.00168, 0.00176	0.018, 0.019	0.018
		0.00151	0.017	
1000	811	0.00255, 0.00352	0.028, 0.039	0.037
		0.00370, 0.00340	0.041, 0.037	
1200	921	0.00420, 0.00532	0.046, 0.059	0.056
		0.00547, 0.00524	0.060. 0.056	

[a]Calculated by the compilers.

The same results were reported in Tepper and Greer.[1] The results may be approximated by the solubility equation:

$$\log(\text{soly/mol \% C}) = 0.346 - 1458\ (T/\text{K})^{-1} \quad r = 0.999,$$

which is valid for temperature range 700–921 K.

Auxiliary Information

Method:
Graphite and liquid Cs were equilibrated in a stainless steel container at selected temperatures. Cs was filtered through a 5 μm pore size metallic filter. The extracted Cs sample was transferred to a dissolution apparatus. The sample was dissolved in distilled water at 273 K. The resulting solution was titrated with standard acid. The solution was dehydrated and the dry deposit combusted in O at 921 K. CO_2 formed was collected at liquid N temperature. The amount of CO_2 collected was measured by mass spectrometry.

Source and Purity of Materials:
C: graphite rod of spectroscopic purity kept for 72 h at 921 K.
Cs: 99.9+% pure from MSAR; contained 0.0075% Rb, 0.0040% Na, $<5\cdot10^{-4}$ % K, Cr, Co, Al, Ti, Mo, Sn, B, V, $<1.0\cdot10^{-3}$ % Fe, Pb, O, $2\cdot10^{-4}$ % Ca, $<2.5\cdot10^{-3}$ % Si, $<3\cdot10^{-4}$ % Ba, $<1\cdot10^{-4}$ % Be, $<2\cdot10^{-4}$ % N, $1.2\cdot10^{-3}$ % C as in Tepper and Greer.[2]
O: purified.

Estimated Error:
Solubility: accuracy $\pm6\cdot10^{-3}$ mol % C.
Temperature: nothing specified.

References:
[1]F. Tepper and J. Greer, U.S. Atom. Energy Comm. Rep. CONF-650411, pp. 323–333 (1965).
[2]F. Tepper and J. Greer, U.S. Air Force Rep. ASD-TDR-63-824 (1963).

7.4. Cesium–Silicon

Components:
(1) Silicon; Si; [7440-21-3]
(2) Cesium; Cs; [7440-46-2]

Evaluated by:
Hans Ulrich Borgstedt, Forschungszentrum Karlsruhe, Germany and Cezary Guminski, University of Warsaw, Poland, June 1998.

Critical Evaluation

Si reacts with Cs at elevated temperatures with the formation of CsSi as was first observed by Hohmann.[1] He further observed that CsSi is decomposed to $CsSi_8$ at about 633 K in high vacuum. Schäfer and Klemm[2] noticed that CsSi is decomposed to $CsSi_8$ during heating at about 823 K in high vacuum. Cros *et al.*[3] reported the final product of the decomposition as Cs_7Si_{136}. Melting temperatures of any of these compounds at normal pressure were not reported. Therefore, only a predictive Cs–Si phase diagram could be constructed. Such a diagram should be similar to that one reported for the Rb–Si system. The solubility of Cs in solid Si is lower than 10^{-4} mol % Cs, as measured by McCaldin and Widmer.[8]

The presence of O traces in the Cs–Si system leads to the formation of the stable compound Cs_2SiO_3.[4] There are no direct solubility studies of Si in liquid Cs. Keddy[5] observed the complete dissolution of a Si sample in Cs after 100 h contact at 773 K. Winslow *et al.*[6,7] investigated the corrosivity of Cs on Si containing alloys and ceramics. After exposure of Lucalox, alumina and sapphire to Cs vapor at 673 K for 500 h, the Si content in Cs increased to 0.03, 0.02, and 0.017 mol % Si, respectively.[7] In another test of Holley *et al.*,[6] in which several steels were kept in contact with liquid Cs at 673 K for 2 days, the Si content in the Cs phase increased from 0.2 to 0.8 mol % Si. A similar test which was performed at room temperature for 7000 h caused an increase of the Si content in Cs from $3\cdot10^{-3}$ to 5 mol % Si. Since the papers Holley *et al.*[6] and Winslow[7] are not concerned with typical solubility studies, any data sheets are not prepared and solubility values may not be suggested.

References:
[1]E. Hohmann, Z. Anorg. Chem. **257**, 113 (1948).
[2]R. Schäfer and W. Klemm, Z. Anorg. Chem. **312**, 214 (1961).
[3]C. Cros, M. Pouchard, and P. Hagenmuller, Bull. Soc. Chim. Fr. 379 (1971).
[4]R. Kohli, *Material Behavior and Physical Chemistry in Liquid Metal Systems*, edited by H. U. Borgstedt (Plenum, New York, 1982), p. 345.
[5]E. S. Keddy, U.S. Atom. Energy Comm. Rep. LAMS-2948 (1963).
[6]J. H. Holley, G. R. Neff, F. B. Weiler, and P. M. Winslow, *Electric Propulsion Development* (Academic, New York, 1963), p. 341.
[7]P. M. Winslow, Corrosion **21**, 341 (1965).
[8]J. O. McCaldin and E. A. Widmer, J. Phys. Chem. Solids **24**, 1073 (1963).

7.5. Cesium–Germanium

Components:
(1) Germanium; Ge; [7440-56-4]
(2) Cesium; Cs; [7440-46-2]

Evaluated by:
Hans Ulrich Borgstedt, Forschungszentrum Karlsruhe, Germany and Cezary Guminski, University of Warsaw, Poland, June 1998.

Critical Evaluation

In his first experiments on the dissolution of Ge in liquid Cs, Hohmann[1] observed the formation of CsGe at 873 K. CsGe heated to 663–683 K in vacuum was further transformed to $CsGe_4$, and the excess of Cs evaporated. The results of Hohmann[1] were confirmed later by Schäfer and Klemm.[2] Cros *et al.*[3] did not observe the formation of the Ge-rich clathrate compounds which were observed for lighter alkali metals and Ge. Drits *et al.*[4] performed thermal analyses of alloys containing 23–98 mol % Ge and constructed a Cs–Ge phase diagram. The authors observed the formation of Cs_3Ge, Cs_3Ge_2, CsGe, and $CsGe_4$ compounds, all of them melting congruently between 913 and 1263 K. The high melting temperature of $CsGe_4$ was confirmed in Potemkin *et al.*[5] Von Schnering *et al.*[6] claimed that $CsGe_4$ does not exist, since they found only three other compounds, $Cs_{12}Ge_{17}$, Cs_4Ge_9, and Cs_8Ge_{46}, in the Ge-rich region.

Quite a different picture of the Cs–Ge phase diagram was presented by Orlov *et al.*[7] These authors confirmed the formation of CsGe, but in the Cs-rich range they observed a miscibility gap between ≈3 and 50 mol % Ge at 934 K, instead of the compounds Cs_3Ge and Cs_3Ge_2. A critical miscibility temperature was found at ≈1093 K and ≈30 mol % Ge. It is doubtful that the melting point of CsGe in Orlov *et al.*[7] is exactly the same as the monotectic temperature at 934 K; the same phenomenon was observed for the Rb–Ge system by the same authors. Without further experimental investigation of the system in the whole composition range one cannot judge which group of the investigators presented a more correct picture of the phase relations.

In this situation solubilities of Ge in liquid Cs could not be suggested and the Cs–Ge phase diagram, shown in Fig. 64 according to Drits *et al.*,[4] should be treated with caution. Sangster and Pelton[8] preferred the phase diagram of Orlov *et al.*[7]

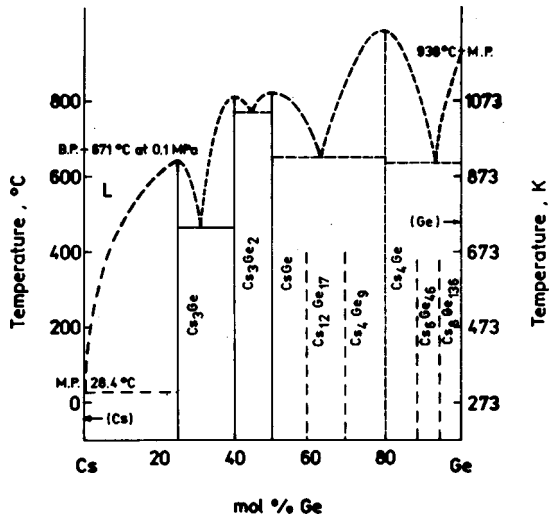

FIG. 64. Cs–Ge phase diagram.

References:
[1]E. Hohmann, Z. Anorg. Chem. **257**, 113 (1948).
[2]R. Schäfer and W. Klemm, Z. Anorg. Chem. **312**, 214 (1961).
[3]C. Cros, M. Pouchard, and P. Hagenmuller, Bull. Soc. Chim. Fr. 379 (1971).
[4]M. E. Drits, V. F. Potemkin, and L. L. Zusman, Izv. Akad. Nauk SSSR, Neorg. Mater. **18**, 1148 (1982).
[5]V. F. Potemkin, R. A. Sizov, L. L. Zusman, and M. E. Drits, Izv. Akad. Nauk SSSR, Met. **3**, 197 (1989).
[6]H. G. von Schnering, M. Baitinger, U. Bolle, W. Carrillo-Cabrera, J. Curda, Y. Grin, F. Heinemann, J. Llanos, K. Peters, A. Schmeding, and M. Somer, Z. Anorg. Chem. **623**, 1037 (1997).
[7]A. N. Orlov, K. A. Chuntonov, and L. Z. Melekhov, Izv. Akad. Nauk SSSR, Met. **6**, 172 (1987).
[8]J. Sangster and A. D. Pelton, J. Phase Equil. **18**, 284 (1997).

Components:
(1) Germanium; Ge; [7440-56-4]
(2) Cesium; Cs; [7440-46-2]

Original Measurements:
M. E. Drits, V. F. Potemkin, and L. L. Zusman, Izv. Akad. Nauk SSSR, Neorg. Mater. **18**, 1148–1150 (1982).

Variables:
Temperature: 878–1255 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The liquidus of the Cs–Ge system was determined. The data were presented in a figure. The compilers read the values from the figure.

T/K	Solubility/mol % Cs	Solubility/mol % Ge
1196	2	98
1156	13	87
1203	16	84
1255	19	81
1231	23	77
1064	47	53
1075	53	47
1079	59	41
1057	63	37
878	74	26
891	77	23

The authors identified the following phases: Cs_3Ge, Cs_3Ge_2, CsGe, and $CsGe_4$.

Auxiliary Information

Method:
Weighed amounts of Ge and Cs were placed in Al_2O_3 or ZrO_2 crucibles inserted in steel or Nb tubes. The operation was performed in a dry box filled with Ar. The hermecity of each tube after closing and resistivity of containers to a reaction with the components was tested by heating in vacuum to temperatures higher than the melting point of the alloy. Multicycled thermal analysis of the samples was performed in an Ar atmosphere in a self-constructed apparatus. The composition of $CsGe_4$ was confirmed by x-ray spectral and microstructural analysis.

Source and Purity of Materials:
Ge: semiconductor purity.
Cs: 99.6+% pure.
Ar: spectrally pure.

Estimated Error:
Solubility: nothing specified; reading-out procedure ±0.5 mol %.
Temperature: precision ±2 K; reading-out procedure ±3 K.

Components:
(1) Germanium; Ge; [7440-56-4]
(2) Cesium; Cs; [7440-46-2]

Original Measurements:
A. N. Orlov, K. A. Chuntonov, and L. Z. Melekhov, Izv. Akad. Nauk SSSR, Met. **6**, 172–173 (1987).

Variables:
Temperature: 934–1090 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

Fragments of the Cs–Ge liquidus were determined. The results were presented in a figure. The compilers read and calculated the values.

t/°C	Solubility/mol % Cs	Solubility/mol Ge	Method
661	50	50	DTA
764	54.5	45.5	DTA
791	60.0	40.0	thermomagnetic
801	60.0	60.0	DTA
811	69.3	30.7	DTA
817	69.3	30.7	thermomagnetic
795	83.5	16.5	thermomagnetic
786	89.6	10.4	thermomagnetic

The authors identified only CsGe as the equilibrium solid phase. The monotectic temperature was established at 661 °C.

Auxiliary Information

Method:
A Ta capsule was charged with a known amount of Cs and encapsulated in an evacuated Pyrex ampoule. The ampoule was opened in an Ar atmosphere and a known amount of Ge was added into the crucible. The crucible was closed by laser welding. Differential thermal analysis was carried out in the heating and cooling mode. The magnetic susceptibility of samples was measured while cooling and the temperatures of phase transitions were estimated from discontinuities.[1] A Cs–Ge alloy (19.2 mol % Ge) in a Mo container was kept 5 h at 1113 K and cooled. The excess of Cs was distilled off at 473 K in vacuum. The product was analyzed chemically and by x rays. Another experiment performed with Cs–Ge alloy (42 mol % Ge) in a sapphire vessel lead to the same results.

Source and Purity of Materials:
Ge: semiconductor purity.
Cs: 99.99% pure.
Ar: nothing specified.

Estimated Error:
Solubility: nothing specified; reading-out procedure ±0.3 mol %.
Temperature: precision ±3 K; reading-out procedure ±2 K.

References:
[1]K. A. Chuntonov, L. Z. Melekhov, A. N. Kuznetsov, A. N. Orlov, G. G. Ugodnikov, and S. P. Yatsenko, Less-Common Met. **83**, 143–153 (1982).

7.6. Cesium–Nitrogen

Components:
(1) Nitrogen; N; [7727-37-9]
(2) Cesium; Cs; [7440-46-2]

Evaluated by:
Hans Ulrich Borgstedt, Forschungszentrum Karlsruhe, Germany and Cezary Guminski, University of Warsaw, Poland, June 1998

Critical Evaluation

Gaseous N and liquid Cs do not react in normal conditions. Using indirect chemical reactions, one may obtain Cs_3N (nitride) and CsN_3 (azide) which are metastable phase,[1] CsN_3 was found to melt at 599 K and to decompose at 663 K.[2] Belomestnykh[3] confirmed both temperatures and reported that the solid compound CsN_3 is polymorphically transformed at 424 K. Cs_3N may be formed as a decomposition product of CsN_3. The melting point of the latter compound is not known. The Cs–N phase diagram is shown in Fig. 65.

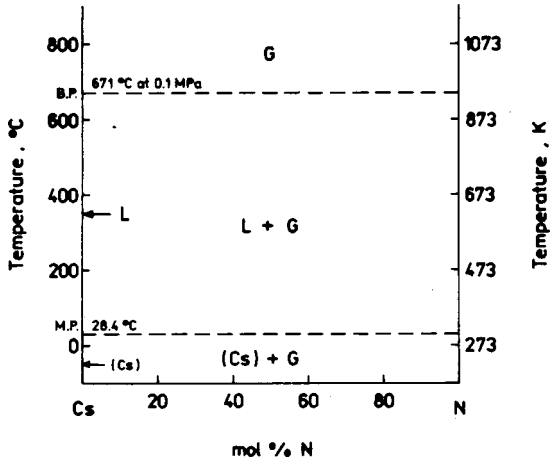

FIG. 65. Cs–N phase diagram.

Tepper *et al.*[4] analyzed Cs for its N content. If one assumes that Cs at its melting point was saturated with N and N was present in Cs in the form of Cs_3N, the Cs analysis by the Kjehldahl method indicated a N content not higher than $1.8 \cdot 10^{-3}$ mol % N (at 302 K). Since Tepper *et al.*[4] is not a solubility study, this value may be suggested as the solubility limit with reservation.

The simultaneous presence of N and H in liquid Cs may lead to the formation of $CsNH_2$; see the Cs–$CsNH_2$ solubility system (Sec. 7.7).

References:
[1]G. J. Moody and J. D. R. Thomas, J. Chem. Educ. **43**, 205 (1966).
[2]R. Suhrmann and K. Clusius, Z. Anorg. Chem. **152**, 52 (1926).
[3]V. N. Belomestnykh, Izv. Akad. Nauk Rus., Neorg. Mater. **29**, 221 (1993).
[4]F. Tepper, A. Murchison, J. Zelenak, and F. Roehlich, U.S. Atom. Energy Comm. Rep. ORNL-3605, Vol. I, p. 26 (1964).

7.7. Cesium–Cesium Amide

Components:
(1) Cesium amide; $CsNH_2$; [22205-57-8]
(2) Cesium; Cs; [7440-46-2]

Original Measurements:
S. E. Hill, Ph.D. thesis, University of Nottingham, U.K., 1979; abstracted in C. C. Addison, *The Chemistry of the Liquid Alkali Metals* (Wiley, Chichester, 1984), p. 138.

Variables:
Temperature: 355–393 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data and Critical Evaluation
The solubility of $CsNH_2$ in liquid Cs was determined

t/°C	Solubility/mol % $CsNH_2$
82	2.03
100	2.73
120	3.51

$CsNH_2$ was found to be the equilibrium solid phase. The results were obtained by a well elaborated method and they seem to be reliable.

Auxiliary Information

Method:
Solid $CsNH_2$ was added in portions to liquid Cs. Changes in the electrical resistivity of Cs were measured upon the addition of the solute. The precipitation temperature on cooling the solutions was used to determine the solubility; the resistivity change was measured during the phase separation. The apparatus was made of stainless steel. The experiments were performed in an Ar atmosphere.

Source and Purity of Materials:
$CsNH_2$: nothing specified.
Cs: nothing specified.
Ar: nothing specified, probably 99.99% pure and dried on molecular sieves, as in Ref. 1.

Estimated Error:
Solubility: nothing specified; precision not better than a few % (compilers).
Temperature: nothing specified; precision ±0.5 K (compilers).

References:
[1]A. T. Dadd, P. Hubberstey, and P. G. Roberts, J. Chem. Soc., Faraday Trans. I **78**, 2735–2741 (1982).

7.8. Cesium–Phosphorus

Components:
(1) Phosphorus; P; [7723-14-0]
(2) Cesium; Cs; [7440-46-2]

Evaluated by:
Hans Ulrich Borgstedt, Forschungszentrum Karlsruhe, Germany and Cezary Guminski, University of Warsaw, Poland, July 1998

Critical Evaluation

Cs may react with P with the formation of a salt-like Cs_3P compound, at least. A miscibility of Cs_3P with Cs seems to be quite limited. Gnutzmann *et al.*[1] attempted to synthesize Cs_3P by the direct reaction of the elements, but their results were not successful. Von Schnering *et al.*[2] reported the formation of the compounds Cs_3P_7 and Cs_3P_{11} (in two polymorphic forms). The Cs–P phase diagram is still unknown.

References:
[1]G. Gnutzmann, F. W. Dorn, and W. Klemm, Z. Anorg. Chem. **309**, 211 (1961).
[2]H. G. von Schnering, M. Somer, G. Kliche, W. Hönle, T. Meyer, J. Wolf, L. Ohse, and P. B. Kempa, Z. Anorg. Chem. **601**, 13 (1991).

7.9. Cesium–Arsenic

Components:
(1) Arsenic; As; [7440-38-2]
(2) Cesium; Cs; [7440-46-2]

Evaluated by:
Hans Ulrich Borgstedt, Forschungszentrum Karlsruhe, Germany and Cezary Guminski, University of Warsaw, Poland, July 1998

Critical Evaluation

Gnutzmann *et al.*[1] synthesized the Cs_3As phase from the elements at 673 K, but the melting point of the compound was not determined. Sangster and Pelton[2] reported in their review the formation of further phases: Cs_4As_6, Cs_3As_7 (with a polymorphic transition at ~640 K) and Cs_3As_{11} (existing in two polymorphic forms). One cannot suggest any Cs–As phase diagram or mutual solubilities of these elements on the basis of insufficient knowledge.

References:

[1]G. Gnutzmann, F. W. Dorn, and W. Klemm, Z. Anorg. Chem. **309**, 211 (1961).
[2]J. Sangster and A. D. Pelton, J. Phase Equil. **14**, 232 (1993).

7.10. Cesium–Oxygen

Components:
(1) Oxygen; O; [7782-44-7]
(2) Cesium; Cs; [7440-46-2]

Evaluated by:
Hans Ulrich Borgstedt, Forschungszentrum Karlsruhe, Germany and Cezary Guminski, University of Warsaw, Poland, August 1998

Critical Evaluation

O reacts violently with Cs with subsequent formation of several suboxides (Cs_7O, Cs_4O, Cs_7O_2, and Cs_3O) and peroxides (Cs_2O_2, CsO_2, and CsO_3) of various stability. By analogy to Rb, the compound Cs_2O_2 is the most stable oxide in the Cs–O system and the stoichiometric Cs_2O is relatively less stable.

The liquidus line of the Cs-rich range was investigated by thermal analysis,[1–7] electric resistivity,[8] vapor pressure measurements,[9] and chemical analysis of the filtrate.[10] The first investigations by Rengade[1,2] resulted in the shape of the liquidus line between Cs and Cs_2O, which was qualitatively confirmed in more recent studies.[6–8] The differences at lower temperatures are on the order of a few K, but they increase to 20–40 K between 323 and 453 K; this causes a composition difference of up to 3 mol %. The results of Brauer,[8] Simon,[6] and Knights and Phillips[7] show quite good agreement, and their values are recommended.

Tepper *et al.*[3–5] and Simon[6] measured the melting point depression of Cs upon small O additions into it. The depression factor is the same in both studies, but the melting temperature of pure Cs is 0.07 K higher in the papers of Tepper *et al.*[3–5] The liquidus results of Dmitreva *et al.*[10] do not reflect the congruent formation of Cs_7O and two eutectic points by sides are missed; therefore, their smooth solubility dependence is far from other results. The samples in Dmitreva *et al.*[10] were probably contaminated or the system was far from equilibrium state. The single result of Arnoldov *et al.*[9] at 563 K is underestimated for 3 mol % O.

Attempts of Knights and Phillips[7] to determine the Cs–O liquidus at concentrations higher than 33 mol % O were unsuccessful. The possible reasons of the shortcoming are the strong corrosive action of Cs oxides on containers made of glass as well as of metals[11] and the tendency of the system to supercooling. Touzain[11] confirmed the melting point of Cs_2O at 768 K, previously found by Rengade.[1,2] Melting temperatures of the O-rich compounds were determined by Centnerszwer and Blumenthal[12] and later reported by Volnov.[13] Berardinelli and Kraus[14] determined the melting point of CsO_2 at 723 K and did not observe any formation of solid solutions between Cs_2O_2 and CsO_2 as well as between Cs_2O and Cs_2O_2. A formation of Cs_2O_3 (melting point at 775 K) in this way, postulated in Centnerszwer and Blumenthal,[12] should be excluded from the diagram. The approximate Cs–O phase diagram, shown in Fig. 66, is constructed according to Bell[15] and Knights and Phillips.[7]

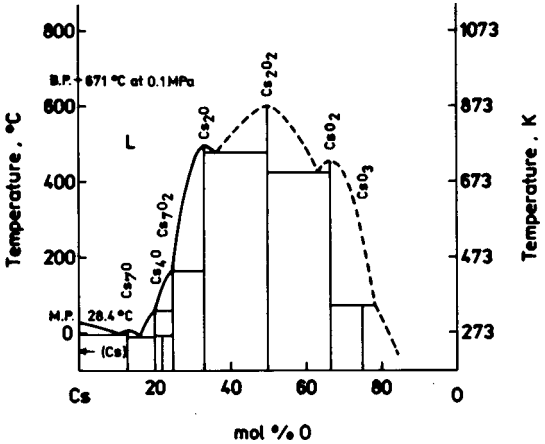

FIG. 66. Cs–O phase diagram (approximate).

Recommended and tentative (t) values of the solubility of O in liquid Cs

T/K	Solubility/mol % O	Source
271	9.0 eutectic	(1,2), (7), (8)
277	12.5 congruent	(1,2), (6), (8)
261	17 (t) eutectic	(7), (8)
326	19.5 peritectic	(6), (7)
373	21 (t)	(6), (7) interpolated
437	24 (t) peritectic	(7)
768	33.3 (t) congruent	(1,2), (11)
867	50.0 (t) congruent	(12)
723	66.7 (t) congruent	(13), (14)

References:

[1]M. E. Rengade, Compt. Rend. **148**, 1199 (1909).

[2]M. E. Rengade, Bull. Soc. Chim. Fr. **5**, 994 (1909).

[3]J. W. Mausteller, F. Tepper, and S. J. Rodgers, *Alkali Metal Handling and System Operating Techniques* (Gordon & Breach, New York, 1967), p. 119.

[4]F. Tepper, *The Alkali Metals* (The Chemical Society, London, 1967), p. 370.

[5]S. J. Rodgers and F. Tepper, U.S. Atom. Energy Comm. Rep. MSAR-64-108 (1964); U.S. Atom. Energy Comm. Rep. CONF-721-10 (1964).

[6]A. Simon, Z. Anorg. Chem. **395**, 301 (1973).

[7]C. F. Knights and B. A. Phillips, J. Nucl. Mater. **84**, 196 (1979).

[8]G. Brauer, Z. Anorg. Chem. **255**, 101 (1947).

[9]M. N. Arnoldov, M. N. Ivanovskii, G. N. Sereda, and V. V. Sitnikov, Izv. Akad. Nauk SSSR, Met. **4**, 98 (1975).

[10]I. B. Dmitreva, E. E. Konovalov, and A. I. Klentz, *Teplofizicheskie Svoistva Zhidkostei* (Moskva, Nauka, 1970), p. 117.

[11]P. Touzain, J. Thermal Anal. **9**, 441 (1976).

[12]M. Centnerszwer and M. Blumenthal, Bull. Acad. Polon. Sci., Cl. Sci. Math. Natur. Ser. A 499 (1933).

[13]I. I. Volnov, *Perekisnye Soedineniya Shchelochnykh Metallov* (Nauka, Moskva, 1980).

[14]S. P. Berardinelli and D. L. Kraus, Inorg. Chem. **13**, 189 (1974).

[15]R. L. Bell (private communication to P. E. Gregory, P. Chye, H. Sunami, and W. E. Spicer), J. Appl. Phys. **46**, 525 (1975).

Components:
(1) Oxygen; O; [7782-44-7]
(2) Cesium; Cs; [7440-46-2]

Original Measurements:
E. Rengade, Bull. Soc. Chim. Fr., Ser. [4] **5**, 994–1003 (1909).

Variables:
Temperature: 265–763 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The Cs-rich part of the Cs–O liquidus was determined. The results were read from a figure and recalculated by the compilers.

t/°C	Solubility/Cs_2O_x	Solubility/mol % O
25.5	0.02	1.0
22.7	0.05	2.4
14.1	0.10	4.8
5.9	0.15	7.0
−1.9	0.20	9.1
1.9	0.23	10.3
2.8	0.27	11.9
3.0	0.285	12.5
2.4	0.32	13.8
1.9	0.33	14.2
−0.4	0.35	14.9
−3.0	0.365	15.4
−8.0	0.39	16.3
2.5	0.405	16.8
7.2	0.42	17.4
36	0.455	18.5
70	0.475	19.2
114	0.500	20.0
142	0.52	20.6
158	0.55	21.6
169	0.59	22.8
175	0.62	23.7
179	0.64	24.2
472	0.92	31.5
482	0.96	32.4
490	1.00	33.3

The smooth liquidus line based on the same data was reported in Rengade.[1] The melting point of Cs was found at 28.25 °C. The following equilibrium phases were determined: Cs_7O, Cs_4O, Cs_2O_7, and Cs_3O.

Auxiliary Information

Method:
Cs was contained in a tube made of Jena glass. Measured volumes of O were introduced into the tube. After the reaction was completed the tube was filled with N. Cooling and heating curves were recorded with the use of a Fe/Konstantan thermocouple.

Source and Purity of Materials:
O: "pure" gas.
Cs: purified by sublimation.
N: from liquid air.

Estimated Error:
Solubility: nothing specified; reading-out procedure ±0.3 mol %.
Temperature: precision ±0.05 K up to 313 K; reading-out procedure ±0.3 K up to 313 and ±3 K at higher temperatures.

References:
[1]E. Rengade, Compt. Rend. **148**, 1199–1202 (1909).

Components:
(1) Oxygen; O; [7782-44-7]
(2) Cesium; Cs; [7440-46-2]

Original Measurements:
G. Brauer, Z. Anorg. Chem. **255**, 101–123 (1947).

Variables:
Temperature: 265–763 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The Cs-rich part of the Cs–O liquidus was determined. The temperatures were read from a figure and recalculated to mol % by the compilers.

t/°C	Solubility/CsO_x	Solubility/mol % O
22.5	0.020	2.0
12.3	0.067	6.3
−2.0[a]	0.099	9.0
4.0[a]	0.143	12.5
−8.0[a]	0.195	16.3
40	0.230	18.7
71	0.250	20.0

[a]Numerical values.

Auxiliary Information

Method:
The Cs–O mixtures were prepared in a glass apparatus. Cs was introduced into a container in ampoules. Measured O gas volumes were introduced into molten Cs during cooling the apparatus. Cs_2O prepared this way was mixed with metallic Cs. The components were melted at elevated temperature and homogenized. The composition of the melt was determined by chemical analysis. The samples were also analyzed by x-ray diffraction. The specific electric resistivity was measured in a Duran glass capillary with W electrodes as function of temperature. The liquidus points were read from breaks on resistivity versus temperature dependencies. All essential operations were performed in an Ar atmosphere.

Source and Purity of Materials:
O: gas from aqueous electrolysis, further purified at Pd-asbestos catalyzer at 673 K.
Cs: "pure" from Schering–Kahlbaum or W. Franke; further distilled.
Ar: "very pure," contained $<10^{-4}$ % O and minimal H_2O content.

Estimated Error:
Solubility: nothing specified; not better than ±0.1% (by the compilers); reading-out procedure ±0.1%.
Temperature: precision better than ±1 K; reading-out procedure ±0.5 K.

Components:
(1) Oxygen; O; [7782-44-7]
(2) Cesium; Cs; [7440-46-2]

Original Measurements:
J. W. Mausteller, F. Tepper, and S. J. Rodgers, Alkali Metal Handling and System Operating Techniques (Gordon & Breach, New York, 1967), pp. 119–120.

Variables:
Temperature: 300.09–301.70 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The freezing point depression of Cs as function of the O content was determined. The results were read from a figure and recalculated to mol % by the compilers.

t/°C	Solubility/mass % O	Solubility/mol % O
28.55	0.0010	0.0083
28.52	0.0025	0.021
28.46	0.0050	0.042
28.32	0.010	0.083
28.19	0.015	0.125
27.96	0.025	0.21
27.68	0.035	0.29
27.51	0.040	0.33
26.94	0.064	0.53

The melting point of Cs was found at 28.592 °C, as given numerically in Tepper.[1] The freezing point depression factor was found to be 2.9 K/mol % O. These results are also presented in Rodgers and Teppe.[2]

Auxiliary Information

Method:
Quantities of gaseous O were added to Cs and equilibrated in an Ar atmosphere. Freezing points of samples were measured after each O addition with a precision Beckman thermometer. Every experiment was duplicated after 15–20 min.

Source and Purity of Materials:
O: gaseous of unspecified purity.
Cs: contained up to 0.003% of alkali metals.[1]
Ar: nothing specified.

Estimated Error:
Solubility: detectivity $\pm 7 \cdot 10^{-4}$ mol %; reading-out procedure $\pm 1.5 \cdot 10^{-3}$ mol %.
Temperature: precision ±0.002 K; reading-out procedure ±0.01 K.

References:
[1]F. Tepper, *The Alkali Metals* (The Chemical Society, London, 1967), pp. 370–373.
[2]S. J. Rodgers and F. Tepper, U.S. Atom. Energy Comm. Rep. MSAR-64-108 (1964); U.S. Atom. Energy Comm. Rep. CONF-721-10 (1964).

Components:
(1) Oxygen; O; [7782-44-7]
(2) Cesium; Cs; [7440-46-2]

Original Measurements:
I. B. Dmitreva, E. E. Konovalov, and A. I. Klentz, *Teplofizicheskie Svoistva Zhidkostei* (Moskva, Nauka, 1970), pp. 117–118.

Variables:
Temperature: 309–367 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of O in liquid Cs was determined. The results were reported in a figure. The compilers extracted the values from the figure.

T/K	Solubility/mol % O
309	3.1
316	2.9
339	8.0
348	9.0
364	17.3
367	18.7

The authors expressed the data by the following solubility equation:

$$\log(\text{soly/mol \% O}) = 5.82 - 1700\ (T/\text{K})^{-1}.$$

The data shown in the figure are about 15% higher than those calculated from the equation.

Auxiliary Information

Method:
Molten Cs (contained in a glass ampoule) was saturated with O by slow oxidation. The ampoule was evacuated, sealed and placed in a device for filtration and sampling. The device was heated in an oven for 4–6 h. The ampoule was crushed inside with a special hammer and Cs filtered through a 5–10 μm pore size ceramic–metallic sinter[1] in an Ar atmosphere. The filtrate was collected in 4–6 parallel glass ampoules. The temperature of the equilibration and filtration was controlled by a Chromel/Copel thermocouple. The contents of the ampoules were analyzed by vacuum distillation.[2]

Source and Purity of Materials:
O: from air bubbled through liquid N.
Cs: nothing specified.
Ar: nothing specified.

Estimated Error:
Solubility: nothing specified; reading-out procedure ±2%.
Temperature: nothing specified; reading-out procedure ±2 K.

References:
[1]B. F. Shibraev and E. I. Pavlovskaya, Khim. Promysl. **3**, 232 (1963).
[2]E. D. Malikova, I. B. Dmitreva, E. E. Konovalov, and E. A. Desyatkina, Atom. Energiya **24**, 162 (1968).

Components:
(1) Oxygen; O; [7782-44-7]
(2) Cesium; Cs; [7440-46-2]

Original Measurements:
A. Simon, Z. Anorg. Chem. **395**, 301–319 (1973).

Variables:
Temperature: 262–439 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The Cs-rich part of the Cs–O liquidus was determined. The results were read out from a figure by the compilers.

t/°C	Solubility/mol % O
28.51	0.002
28.48	0.0035
28.46	0.005
28.45	0.007
28.44	0.009
28.43	0.012
28.42	0.017
28.40	0.025
26.9	0.5
25.8	0.9
24.4	1.6
22.5	2.4
20.0–20.9	3.3
19.9	3.6
17.6	4.4
14.5	5.4
11.3	6.3
9.3–10.9	6.9
7.3	7.7
5.8	8.0
2.0	9.0
−0.36[a]	9.4
2.0	10.1
3.0	10.7
3.0–3.3	11.0
4.0	11.5
4.3	12.3
4.33[a]	12.5
4.3	12.6
4.1	13.1
3.6	13.4
3.2	14.0
−0.2	15.1
−3.6	16.0
−10.9	17.0
38.2–39.4	18.7
46.0	19.0
62.2	20.0
92.9–94.7	20.9
113–116	21.6
117–118	21.7
138	22.6
155–156	23.7
162–166	24.4

[a]Numerical results.

The melting point of Cs was found at 28.52 °C. The author determined Cs_7O, Cs_4O, $Cs_{11}O_3$, and Cs_3O as equilibrium phases.

Auxiliary Information

Method:

The Cs–O mixtures were prepared in a glass apparatus by reaction of known amounts of the components. Ampoules with Cs were opened in an Ar atmosphere. O was introduced at reduced pressure. The Cs–O samples in glass containers were placed in an Al block and the block in a cryostat. Heating of the samples was performed with a rate of 1–60 K/h and temperature changes were recorded by means of a Pt thermometer, previously calibrated on the melting and boiling points of water. Some samples were analyzed by chemical analysis and x-ray diffraction.

Source and Purity of Materials:

O: from thermal decomposition of HgO of purity 99.9+%; HgO from direct synthesis from the elements at 633 K.
Cs: from reaction of CsCl (super pure, dried 1 week at 623 K) and Ca at 1203 K; the metal distilled at high vacuum.
Ar: nothing specified.

Estimated Error:

Solubility: precision ±0.1%; reading-out procedure $\pm 5 \cdot 10^{-4}$ mol % at low O content and ±0.1 mol % at high O content.
Temperature: reproducibility ±0.01 K; reading-out procedure ±0.01 K at low O content and ±1 K at high O content.

Components:

(1) Oxygen; O; [7782-44-7]
(2) Cesium; Cs; [7440-46-2]

Original Measurements:

M. N. Arnoldov, M. N. Ivanovskii, G. N. Sereda, and V. V. Sitnikov, Izv. Akad. Nauk SSSR, Met. **4**, 98–102 (1975).

Variables:

One temperature: 563 K

Prepared by:

H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of O in liquid Cs was determined to be 23 mol % O at 290 °C (563 K). Cs_2O was treated as the equilibrium solid phase.

Auxiliary Information

Method:

The Cs–O samples of various composition were prepared from Cs and gaseous O at a temperature <493 K in an apparatus made of unspecified material. The apparatus was composed of a container, O dosimeter, manometer, thermostat, and a valve system. The apparatus was carefully cleaned and outgassed at a temperature >643 K. The Cs vapor pressures of pure Cs and the Cs–O mixtures were measured at temperatures 555–640 K. The solubility of O in liquid Cs was estimated from a break on the dependence relating Cs vapor pressure versus composition at constant temperature.

Source and Purity of Materials:

O: gaseous of unspecified purity.
Cs: distilled.

Estimated Error:

Solubility: nothing specified; precision ±1 mol % (by the compilers).
Temperature: nothing specified.
Pressure: precision ±1.5%.

Components:	Original Measurements:
(1) Oxygen; O; [7782-44-7] (2) Cesium; Cs; [7440-46-2]	C. F. Knights and B. A. Phillips, J. Nucl. Mater. **84**, 196–206 (1979).
Variables:	**Prepared by:**
Temperature: 268–436 K	H. U. Borgstedt and C. Guminski

Experimental Data

A part of the Cs-O liquidus line was determined

t/°C	Solubility/mol % O
22.5	3.86
3.5	14.1
−3.0	15.6
−5.5	16.3
23.8	17.6
30.0	18.0
49.0	19.0
58.5	19.6
85.5	20.2
117.5	21.4
145.5	22.9
155.0	23.4
163.0	24.0
163.0	24.3

The authors established the formation of Cs_7O, Cs_4O, and Cs_3O. The melting point of Cs was found at 28.6 °C. A complete lack of temperature reproducibility was observed for mixtures with 33–57 mol % O and no corresponding data were tabulated.

Auxiliary Information

Method:

The Cs–O compositions were made by loading a weighed quantity of Cs into an Ag or Au capsule. The capsule was transferred within a Pyrex glass container to a vacuum system where an appropriate quantity of O was added. The capsule, after back filling the Pyrex container with Ar, was returned to a glove box and a lid fitted by cold welding. Temperatures of phase changes were determined with a differential scanning calorimeter calibrated on the melting points of Hg, propanoic acid, benzene, Cs, Ga, In, Sn, Pb–Ag, and Zn.

Source and Purity of Materials:

O: from bulbs with spectroscopically pure gas.
Cs: 99.9% pure from Koch Light Labor.
Ar: purified over Cu_2O at 873 K and $Mg(ClO_4)_2$ at room temperature, contained $\leqslant 2\cdot 10^{-4}$ % O and $\leqslant 1\cdot 10^{-3}$ % H_2O.

Estimated Error:

Solubility: nothing specified.
Temperature: precision between ±1 and ±4 K.

7.11. Cesium–Cesium Hydroxide

Components:	Original Measurements:
(1) Cesium hydroxide; CsOH; [21351-79-1] (2) Cesium; Cs; [7440-46-2]	P. Touzain, Compt. Rend., Ser. C **279**, 41–42 (1974).
Variables:	**Prepared by:**
Temperature: 373–605 K	H. U. Borgstedt and C. Guminski

Experimental Data and Critical Evaluation

The liquidus line of the Cs–CsOH system was presented in Fig. 67. The results were read from the figure by the compilers.

t/°C	Solubility/mol % CsOH
100	4.0
176	7.2
205	8.0
222	10.4
305	36.6
312	41.2
317	50.8
316	58.3
327	59.3
329	72.9
330	77.6
332	83.6

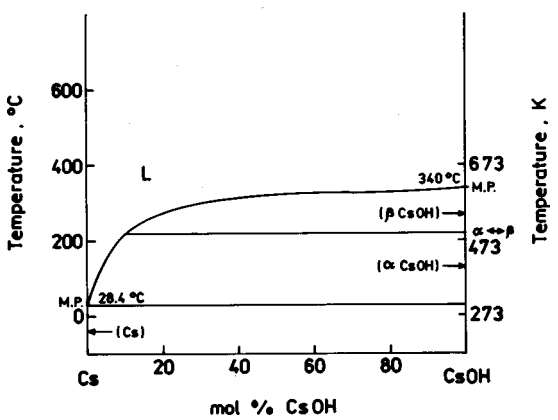

FIG. 67. Cs–CsOH phase diagram (tentative).

The melting points of Cs and CsOH were found at 28.6 and 340 °C, respectively. The α-CsOH↔β-CsOH transformation was determined at 220 °C. It seems that CsOH may be formed in liquid Cs if O and H are simultaneously present, however an experimental confirmation of this supposition was not given in literature. The solubility data have tentative character.

Auxiliary Information

Method:

The author used a previously elaborated method.[1] Weighed amounts of liquid dropping Cs and CsOH powder were introduced into small Ni tubes. The tubes were soldered with Ag. The samples were homogenized at 673 K and cooled. Differential thermal analysis was carried out in a commercial apparatus with a heating rate of 10 K/min. All essential operations were performed in an Ar atmosphere.

Source and Purity of Materials:

CsOH: $CsOH \cdot H_2O$ from Fluka was dehydrated by heating at 573 K for 3 days; the product contained 2% Cs_2CO_3 .
Cs: twice distilled.
Ar: ultrapure.[1]

Estimated Error:

Solubility: nothing specified; precision ±2% (by the compilers); reading-out procedure ±0.3 mol %.
Temperature: precision better than ±4 K; reading-out procedure ±1 K.

References:

[1]P. Touzain, Compt. Rend., Ser. C **276**, 1583 (1973).

7.12. Cesium–Sulfur

Components:

(1) Sulfur; S; [7704-34-9]
(2) Cesium; Cs; [7440-46-2]

Evaluated by:

Hans Ulrich Borgstedt, Forschungszentrum Karlsruhe, Germany and Cezary Guminski, University of Warsaw, Poland, September 1998

Critical Evaluation

The reaction between S and Cs leads to the formation of several polysulfides Cs_2S_x , where $x = 1,2,3, 4,5,6$. The intermediate range of compositions of the Cs–S system was studied by Biltz and Wilke-Dörfurt[1] who confirmed the melting points of all compounds in their subsequent determinations.[2] Bergmann[3] synthesized Cs_2S from HgS and Cs and found this phase stable up to 783–7930 K under vacuum. The melting point of Cs_2S at normal pressure was not determined, and Sangster and Pelton[4] estimated it at 1023±200 K, by analogy to similar sulfides and selenides of other alkali metals. Feher and Naused[5] attempted to synthesize all polysulfides of Cs and measured their melting points; they were not able to obtain Cs_2S_4 which was earlier defined in magnetic susceptibility measurements of Klemm *et al.*[6]

The Cs-rich part of the phase diagram was not investigated, however by analogy to the K–S system one may expect a liquidus shape showing the tendency to limited miscibility. Winslow[7] reported a good solubility of S in liquid Cs at 673 K, but he did not report any numerical results. On the S-rich side there is a liquid miscibility gap between 75 mol % S and practically pure S. The critical temperature was not determined, but by analogy to other systems it should be at 573±50 K. A partly predictive Cs–S phase diagram is shown in Fig. 68.

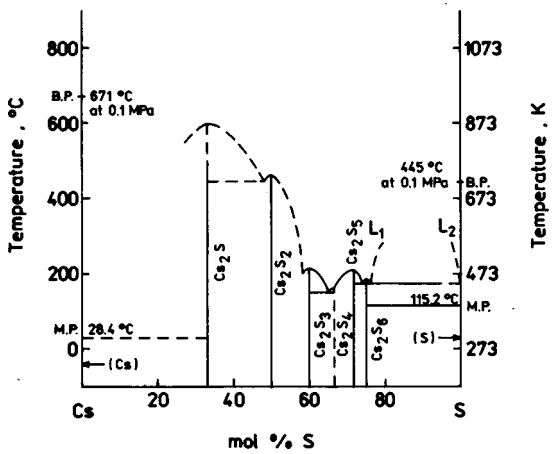

FIG. 68. Cs–S phase diagram (predictive).

Tentative values of the solubility of S in liquid Cs

T/K	Solubility/mol % S	Source
~733	50.0 congruent	(1,2), (5)
479	~58 eutectic	(1) interpolation
488	60.0 congruent	(5)
424	~65 eutectic	(1) interpolation
484	71.4 congruent	(5)
451	74 eutectic	(1) interpolation
460	75.0 congruent	(5)
446	76 eutectic	(1) interpolation

References:

[1]W. Biltz and E. Wilke-Dörfurt, Z. Anorg. Chem. **48**, 297 (1906)
[2]W. Biltz and E. Wilke-Dörfurt, Z. Anorg. Chem. **50**, 67 (1906).
[3]A. Bergmann, Z. Anorg. Chem. **231**, 269 (1937).
[4]J. Sangster and A. D. Pelton, J. Phase Equil. **18**, 78 (1997).
[5]F. Feher and K. Naused, Z. Anorg. Chem. **283**, 79 (1956).
[6]W. Klemm, H. Sodomann, and P. Langmesser, Z. Anorg. Chem. **241**, 281 (1939).
[7]P. M. Winslow, U.S. Atom. Energy Comm. Rep. CONF-650411 (1965).

Components:
(1) Sulfur; S; [7704-34-9]
(2) Cesium; Cs; [7440-46-2]

Original Measurements:
W. Biltz and E. Wilke-Dörfurt, Z. Anorg. Chem. **48**, 297–318 (1906).

Variables:
Temperature: 426–733 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data
The central part of the Cs–S liquidus was determined

t/°C	Solubility/mass % S	Solubility/mol % S[a]
~460	19.43	50.0
410	19.61	50.3
398	20.43	51.6
341	21.93	53.9
153	30.56	64.6
157.5	31.04	65.1
158.5	32.14	66.3
160	32.75	66.9
185	33.47	67.6
196	34.22	68.4
204	34.88	69.0
209	35.63	69.6
198.8	39.04	72.7
197.9	39.18	72.8
194.8	39.66	73.2
189.0	40.15	73.6
184.5	41.31	73.8
184.5	41.87	74.6
185.8	42.44	75.4
183.2	42.68	75.6
179	42.89	75.8
178	43.09	75.9
175	43.30	76.0
172.8	44.17	76.6

[a]Calculated by the compilers.

Any solubility of Cs_2S_6 in liquid S was not observed. The system showed a strong tendency to supercooling.

Auxiliary Information

Method:
The Cs–S mixtures were prepared from Cs_2S and S. The preparations were carried out in a Durax glass apparatus filled with an inert gas. The mixtures were heated to complete their melting, and then cooled down slowly while mixing with a glass tube. The temperatures were read from a Hg thermometer. The investigations of Cs_2S-rich melts were carried out in a Jena glass apparatus. The melt was mixed with a pyrometer tube. The pyrometer was calibrated on the melting points of Zn, Pb, and Sn as well as the Hg thermometer. Temperature readings were made every 10 s. The experiments were performed in a H or N atmosphere, if the temperatures were >513 K in N.

Source and Purity of Materials:
S: nothing specified.
Cs_2S: obtained from CsOH and H_2S; dried after crystallization.
H: "pure and dry."
N: "air free and dry."

Estimated Error:
Solubility: nothing specified.
Temperature: precision for the thermometer ±0.1 K and for the pyrometer ±1 K; accuracy between ±1 and ±10 K.

Components:
(1) Sulfur; S; [7704-34-9]
(2) Cesium; Cs; [7440-46-2]

Original Measurements:
F. Feher and K. Naused, Z. Anorg. Chem. **283**, 79–87 (1956).

Variables:
Temperature: 433–733 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data
Melting temperatures of several Cs–S compounds were determined

t/°C	Compound	Solubility/mol % S[a]
~460	Cs_2S_2	50.0
210–215	Cs_2S_3	60.0
160	Cs_2S_4[b]	66.7
211	Cs_2S_5	71.4
187	Cs_2S_6	75.0

[a]Calculated by the compilers.
[b]No crystal structure was identified.

Polymorphism of Cs_2S_2 was not observed.

Auxiliary Information

Method:
The sulfides of Cs were prepared by reaction of stoichiometric amounts of S and Cs in liquid NH_3 in a N atmosphere. Cs was added to the S solution in NH_3 and corresponding crystals were precipitated. NH_3 was evaporated by heating at 373 K and later at 473 K in high vacuum for 6–10 h. The method of the melting point determination was not described. The solid phases were investigated by chemical analysis and x-ray diffraction.

Source and Purity of Materials:
S: fine powder as in Feher and Berthold.[1]
Cs: probably distilled in high vacuum, molten in a N atmosphere, as in Feher and Berthold.[1]

Estimated Error:
Solubility: precision ±1%.
Temperature: nothing specified; not better than ±1 K (by the compilers).

References:
[1]F. Feher and H. J. Berthold, Z. Anorg. Chem. **274**, 223–233 (1953).

7.13. Cesium–Selenium

Components:
(1) Selenium; Se; [7782-49-2]
(2) Cesium; Cs; [7440-46-2]

Evaluated by:
Hans Ulrich Borgstedt, Forschungszentrum Karlsruhe, Germany and Cezary Guminski, University of Warsaw, Poland, October 1998

Critical Evaluation

Se dissolves well in liquid Cs at 673 K; however, the promotion of this process was not described quantitatively.[1] Bergmann[2] prepared Cs_2Se by direct reaction of the elements, the decomposition of which was observed at 933 K in vacuum. Klemm *et al.*[3] measured the magnetic susceptibility of the Cs–Se compounds and confirmed the information on Cs_2Se. The whole composition range of the Cs–Se system was investigated by Fedorov *et al.*[4] by means of thermal analysis and magnetic measurements. The existence of Cs_2Se, Cs_2Se_2, Cs_2Se_3, and Ce_2Se_5 was well documented; however, the also postulated Cs_3Se and Cs_5Se_4 phases, as untypical for this group of systems, need verification. The Cs_4Se_{16} phase, prepared by Scheldrich and Braunbeck,[5] may be stable at temperatures lower than 443 K.

The Cs–Se phase diagram, according to Sangster and Pelton,[6] is shown in Fig. 69. A miscibility gap extends from 88 to 98 mol % Se at 488 K and the critical temperature is predicted at about 547 K.

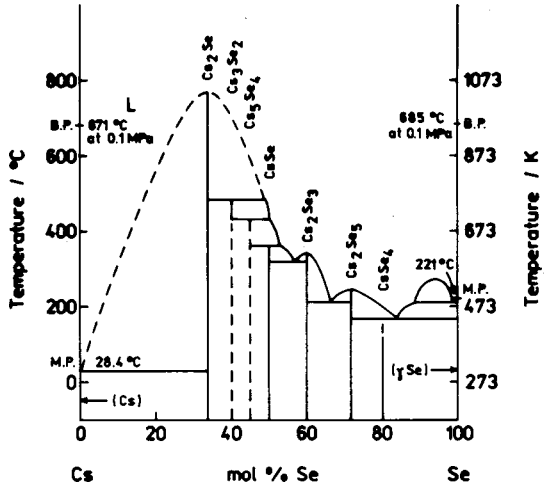

FIG. 69. Cs–Se phase diagram.

Tentative values of the solubility of Se in liquid Cs

T/K	Solubility/mol % Se	Source
773	16	(4)
1043	33.3 congruent	(4)
636	53 peritectic	(4) interpolation
593	57 eutectic	(4) interpolation
611	60.0 congruent	(4)
486	66 eutectic	(4) interpolation
515	71.4 congruent	(4)
443	84 eutectic	(4) interpolation
214	89 monotectic	(4)

References:

[1]P. M. Winslow, U.S. Atom. Energy Comm. Rep. CONF-650411 (1965).

[2]A. Bergmann, Z. Anorg. Chem. **231**, 269 (1937).

[3]W. Klemm, H. Sodomann, and P. Langmesser, Z. Anorg. Chem. **241**, 281 (1939).

[4]V. M. Fedorov, K. A. Chuntonov, A. N. Kuznetsov, G. A. Bolshakova, and S. P. Yatsenko, Izv. Akad. Nauk SSSR, Neorg. Mater. **21**, 1960 (1985).

[5]W. S. Scheldrich and H. G. Braunbeck, Z. Naturforsch., B **44**, 1397 (1989).

[6]J. Sangster and A. D. Pelton, J. Phase Equil. **18**, 173 (1997).

Components:
(1) Selenium; Se; [7782-49-2]
(2) Cesium; Cs; [7440-46-2]

Original Measurements:
V. M. Fedorov, K. A. Chuntonov, A. N. Kuznetsov, G. A. Bolshakova, and S. P. Yatsenko, Izv. Akad. Nauk SSSR, Neorg. Mater. **21**, 1960–1961 (1985).

Variables:
Temperature: 455–1043 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The liquidus line of the Cs–Se system was determined. The results were presented graphically; they were read from a figure by the compilers.

t/°C	Solubility/mol % Se
244	5[a]
333	10[a]
497	16[a]
770	33.5
586	42
579	43
557	45.5
498	47.5
391	50.5
364	53.5
337	59
338	60
293	63
255	65
239	67.5
210	69
226	70
236	71
242	71.5
208	76.5
221	78
195	82.5
182	84.5
183	86.5
237	89[a]
264	90.5[a]
271	94.5[a]
241	97.5[a]

[a]From magnetic measurements.

The monotectic was found between 89 and almost 100 mol % Se at 214 °C. The melting points of Se and Cs were found at 214±3 °C and 27.5±0.05 °C, respectively. The Cs-rich and Se-rich melts showed a strong tendency to supercooling.

Auxiliary Information

Method:

The melts were prepared in quartz or Pyrex glass ampoules by melting the elements in vacuum. Differential thermal analysis was performed. The Se-rich and Cs-rich samples were investigated by measuring the temperature at which the magnetic susceptibility changed in 3–5 K steps near a phase transition. Temperatures of the liquidus were indicated by sharp changes of the slope of the susceptibility versus temperature.[1] The equilibrium solid phases were identified by x-ray diffraction.

Source and Purity of Materials:

Se: 99.995% pure, as in Yatsenko *et al.*[2]
Cs: 99.99% pure, as in Chuntonov *et al.*[3]

Estimated Error:

Solubility: precision ±1 mol %; reading-out procedure ±0.5 mol %.
Temperature: precision between ±0.05 and ±10 K, but typically ±3 K; reading-out procedure ±3 K.

References:

[1]Sh. R. Zhakupov, K. A. Chuntonov, G. G. Ugodnikov, S. P. Yatsenko, and Kh. O. Shakarov, Zh. Fiz. Khim. **54**, 1023–1025 (1980).
[2]S. P. Yatsenko, A. N. Kuznetsov, and K. A. Chuntonov, Izv. Akad. Nauk SSSR, Neorg. Mater. **13**, 738–739 (1977).
[3]K. A. Chuntonov, A. N. Kuznetsov, V. M. Fedorov, and S. P. Yatsenko, Izv. Akad. Nauk SSSR, Neorg. Mater. **18**, 1108–1111 (1982).

7.14. Cesium–Tellurium

Components:

(1) Tellurium; Te; [13494-80-9]
(2) Cesium; Cs; [7440-46-2]

Evaluated by:

Hans Ulrich Borgstedt, Forschungszentrum Karlsruhe, Germany and Cezary Guminski, University of Warsaw, Poland, November 1998

Critical Evaluation

The first studies[1,2] of the Cs–Te system were concerned with synthesis and properties of Cs_2Te. Bergmann[1] found the melting of Cs_2Te with decomposition in vacuum at 953 K. Chuntonov *et al.*[3] investigated the whole range of compositions by thermal analysis and magnetic susceptibility for establishing the Cs–Te liquidus line. The authors observed the formation of several intermediate phases and noticed large supercooling effects, particularly at the Cs-rich side. The Cs_2Te and Cs_2Te_3 were found to melt congruently and Cs_3Te_2, Cs_5Te_4, Cs_2Te_2, Cs_2Te_5 and $CsTe_5$ peritectically. Adamson and Leighty[4] confirmed some fragments of the liquidus line of Chuntonov *et al.*[3] The melting point of Cs_2Te determined by both groups (Chuntonov *et al.*[3] and Adamson and Leighty[4]) agreed within 11 K, but the difference in the liquidus line increased at 90 mol % Te to even 60 K. The investigation of Chuntonov *et al.*[3] is more extensive and, therefore, their results are preferred.

Prins and Cordfunke[5] were not able to prepare Cs_5Te_4 and $CsTe_5$ postulated by Chuntonov *et al.*[3] The former compound was found to be only a mixture of Cs_3Te_2 and Cs_2Te_3. The formula of the latter compound was corrected for $CsTe_4$. The central part of the Cs–Te phase diagram was redetermined again by de Boer and Cordfunke[6] who found the compound Cs_5Te_3 instead of Cs_3Te_2. They also established that Cs_2Te, Cs_2Te_2 and $CsTe_4$ exist in polymorphic forms by means of high temperature x-ray diffraction analysis. Fedorov[7] redetermined the Te-rich part of the phase diagram and found that the most Te-rich phase, formed peritectically at 536 K, has a composition of $CsTe_8$.

Sangster and Pelton[8] estimated a eutectic point at 300 K and 0.4 mol % Te from thermodynamic considerations and extrapolation of the liquidus data from higher temperatures. The assessed Cs–Te phase diagram was presented by Okamoto[9] and is depicted in Fig. 70.

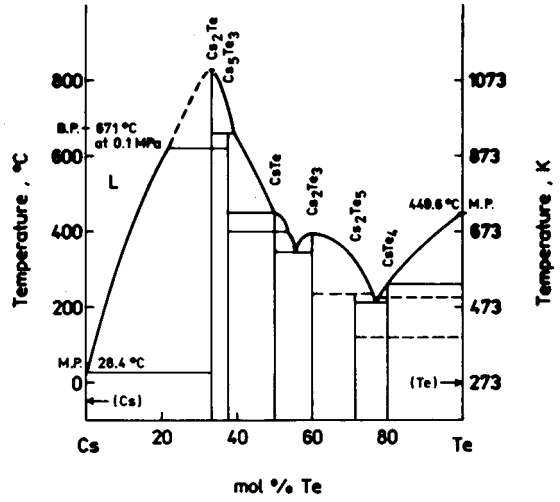

FIG. 70. Cs–Te phase diagram.

Adamson and Leighty[4] added various amounts of O to the Cs–Te system and observed a decrease of the melting point of Cs_2Te and an increase of the liquidus temperatures for the Te-richer mixtures.

Tentative and doubtful (d) values of the solubility of Te in liquid Cs

T/K	Solubility/mol % Te	Source
300	~0.4 eutectic	(3) extrapolated
473	~6	(3) interpolated
573	~9	(3) interpolated
673	~12	(3) interpolated
773	~16	(3) interpolated
895	~23 polymorphic	(6) interpolated
1104	33.3 congruent	(6)
934	38 peritectic	(3),(6) interpolated
823	45	(3),(6) interpolated
723	49 peritectic	(6)
618	55 eutectic	(6)
668	60.0 congruent	(3)
508	75 (d) peritectic	(3)
488	76 eutectic	(3)
498	77 (d) polymorphic	(4)
536	80 peritectic	(3)
623	88	(3)

References:

[1]A. Bergmann, Z. Anorg. Chem. **231**, 269 (1937).
[2]W. Klemm, H. Sodomann, and P. Langmesser, Z. Anorg. Chem. **241**, 281 (1939).
[3]K. A. Chuntonov, A. N. Kuznetsov, V. M. Fedorov, and S. P. Yatsenko, Izv. Akad. Nauk SSSR, Neorg. Mater. **18**, 1108 (1982).
[4]M. G. Adamson and J. E. Leighty, J. Nucl. Mater. **114**, 327 (1983).
[5]G. Prins and E. H. P. Cordfunke, J. Less-Common Met. **104**, L1 (1984).
[6]R. deBoer and E. H. P. Cordfunke, J. Alloy Compd. **228**, 75 (1995).
[7]V. M. Fedorov, Izv. Akad. Nauk SSSR, Neorg. Mater. **28**, 1918 (1992).
[8]J. Sangster and A. D. Pelton, J. Phase Equil. **14**, 246 (1993).
[9]H. Okamoto, J. Phase Equil. **17**, 550 (1996).

Components:
(1) Tellurium; Te; [13494-80-9]
(2) Cesium; Cs; [7440-46-2]

Original Measurements:
K. A. Chuntonov, A. N. Kuznetsov, V. M. Fedorov, and S. P. Yatsenko, Izv. Akad. Nauk SSSR, Neorg. Mater. **18**, 1108–1112 (1982).

Variables:
Temperature: 464–1094 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The liquidus line of the Cs–Te system was determined. Graphical results were read from a figure by the compilers.

t/°C	Solubility/mol % Te
191	6[a]
304	10[a]
428	14[a]
555	20[a]
821	34
749	36
660	38
650	40
626	42
547	46
481	48
416	50
386	54
358	56
372	58
395	60
390	62
370	66
354	67
352	68
292	69
276	70
265	72
225	75
215	77
252	80
280	82
306	83
316	85
342	88
373	89
392	91
420	93
422	95
424	97
439	98

[a]From magnetic susceptibility measurements.

The same results were also reported in Fedorov.[1] The melting points of Cs and Te were found at 27.5 and 445 °C, respectively. Strong undercooling effects were observed. Cs_2Te, Cs_3Te_2, Cs_5Te_4, Cs_2Te_2, Cs_2Te_3, Cs_2Te_5, and Cs_2Te_{10} equilibrium phases were identified.

Auxiliary Information

Method:

The alloys were prepared by mixing proper amounts of Te and Cs in Pyrex glass containers in vacuum. Cs was distilled from one part of the container to another where Te was placed. The reaction product was melted. Cs_2Te was prepared in a quartz ampoule. Differential thermal analysis was performed with the cooling and heating rates of 10 K/min.[2] The Cs-rich melts were investigated by magnetic susceptibility measurements changing the temperature at constant composition. Breaking points were ascribed to temperatures at which the solutions were saturated.[3] The samples were analyzed for their Cs content by means of flame photometry.

Source and Purity of Materials:

Te: semiconductor degree of purity.
Cs: 99.99% pure.

Estimated Error:

Solubility: precision better than ±2%; reading-out procedure ±0.5 mol %.
Temperature: precision ±3 K; reading-out procedure ±1 K.

References:

[1]V. M. Fedorov, Izv. Akad. Nauk SSSR, Neorg. Mater. **28**, 1918 (1992).
[2]S. P. Yatsenko, A. N. Kuznetsov, and K. A. Chuntonov, Izv. Akad. Nauk SSSR, Neorg. Mater. **13**, 738–739 (1977).
[3]Kh. O. Zhakupov, K. A. Chuntonov, G. G. Ugodnikov, S. P. Yatsenko, and Kh. O. Shakarov, Zh. Fiz. Khim. **54**, 1023–1025 (1980).

Components:

(1) Tellurium; Te; [13494-80-9]
(2) Cesium; Cs; [7440-46-2]

Original Measurements:

M. G. Adamson and J. E. Leighty, J. Nucl. Mater. **114**, 327–329 (1983).

Variables:

Temperature: 512–1083 K

Prepared by:

H. U. Borgstedt and C. Guminski

Experimental Data

Several points on the Cs–Te liquidus were determined. The results were read from a figure by the compilers.

t/°C	Solubility/mol % Te
>260	10
>540	20
810[a]	33.5
627	40
433	50
432	60
296	66.7
239	80
443	90

[a]Numerical result.

The melting points of Cs and Te were reported to be 28.5 and 450 °C, respectively. Monotectic was found at >67 mol % Te at 225±5 °C. An addition of O to the system made an increase of the liquidus temperature but a decrease of the melting point of Cs_2Te.

Auxiliary Information

Method:

The Cs–Te mixtures were prepared by mixing preweighed amounts of Cs, Cs_2Te, and Te under Ar atmosphere in alumina crucibles. The compound Cs_2Te was obtained by direct reaction of the Te with a small excess of Cs at $T>623$ K, followed by removal of the excess Cs by vacuum distillation. The composition of Cs_2Te was confirmed by chemical analysis of a corresponding sample. Thermal analysis of the samples was performed with the use of a Conax *K*-type thermocouple. The thermocouple was sheathed in an Inconel tube. It was calibrated against a NBS standard Pt–Rh (13%) thermocouple and confirmed on the melting points of Sn, Zn, Te, CsI, and KCl–LiCl eutectic. The mixtures were stirred with the thermocouple tube. The results are mean values of tests repeated several times.

Source and Purity of Materials:

Te: 99.999% pure from Cerac Inc.
Cs_2Te: stoichiometry (2.01±0.03):1; O content less than 1 mass %.
Cs: 99.9% pure from Alpha Ventron.
Ar: highly purified and contained $<2\cdot10^{-4}$ % O and $<5\cdot10^{-4}$ % H_2O.

Estimated Error:

Solubility: precision ±1.5%; reading-out procedure ±2%.
Temperature: accuracy between ±2 and ±10 K increasing with temperature; reading-out procedure ±2 K.

Components:	Original Measurements:
(1) Tellurium; Te; [13494-80-9] (2) Cesium; Cs; [7440-46-2]	R. deBoer and E. H. P. Cordfunke, J. Alloys Compd. **228**, 75–78 (1995).
Variables:	**Prepared by:**
Temperature: 621–1104 K	H. U. Borgstedt and C. Guminski

Experimental Data

The central part of the Cs–Te liquidus was determined

T/K	Solubility/mol % Te
1104	33.2
1065	34.4
1034	35.3
1013	36.3
936	37.3
926	37.4
915	40.0
837	44.4
713	49.1
621	55.0

The authors identified Cs_2Te, Cs_5Te_3, and Cs_2Te_2 equilibrium phases. They did not observe any interaction between the containers used and the samples.

Auxiliary Information

Method:

The samples were prepared by reaction of weighed amounts of Te and Cs (both contained in ampoules). The narrow ampoule with Cs was placed inside the larger one with Te. The larger ampoule was evacuated, the narrow one was broken, and the content was heated slowly to 773 K. This temperature remained constant for 16 h. The ampoule was slowly cooled to room temperature and opened in a glove box containing Ar. The reaction products were thoroughly powdered, heated to 950 K in a sealed quartz ampoule for 12 h, and finally cooled slowly to room temperature. Samples of the mixtures were analyzed by x-ray powder diffraction at room and elevated temperature in a He atmosphere. Differential scanning calorimetry was performed on every sample contained in a quartz ampoule under reduced Ar atmosphere using of a commercial apparatus. Temperatures were calibrated on melting points of In, Zn, Sb, and Ag.

Source and Purity of Materials:

Te: 99.95% pure from Cerac.
Cs: 99.95% pure from Highways.
Ar: "purified."
He: "dry."

Estimated Error:

Solubility: nothing specified.
Temperature: precision between ±2 and ±5 K.

7.15. Cesium–Fluorine

Components:	Original Measurements:
(1) Fluorine; F; [7782-41-4] (2) Cesium; Cs; [7440-46-2]	M. A. Bredig, H. R. Bronstein, and W. T. Smith, J. Am. Chem. Soc. **77**, 1454–1458 (1955).
Variables:	**Prepared by:**
Temperature: 622–965 K	H. U. Borgstedt and C. Guminski

Experimental Data and Critical Evaluation

The solubility of F in liquid Cs as a part of the Cs–F liquidus was determined

t/°C	Solubility/mol % CsF	Solubility/mol % F[a]
30	<0.001	<0.001
349	3.9	3.7
452	11.4	10.2
527	22.1	18.1
599	36.3	26.6
640	50.1	33.4
662	63.3	38.8
671	74.6	42.7
692[b]	94.0	48.5

[a]Calculated by the compilers.
[b]From thermal analysis.

The melting point of CsF was determined at 703 °C. The Cs–F diagram is shown in Fig. 71. The solubility results have tentative character.

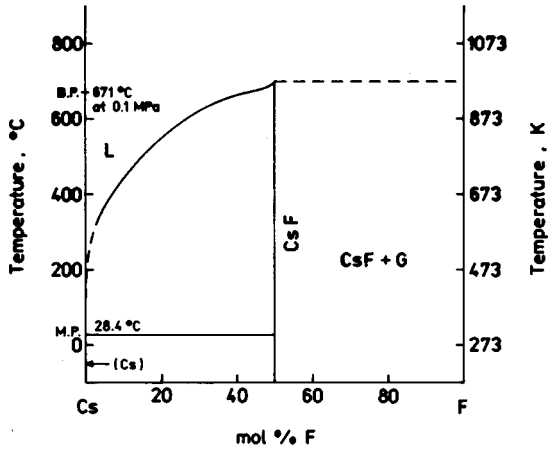

FIG. 71. Cs–F phase diagram.

Auxiliary Information

Method:

A glass ampoule with Cs was opened under hexane in an assembly with an Ar atmosphere inside. After pumping off the hexane, Cs was melted and allowed to drop into a stainless steel capsule containing the desired quantity of CsF. The capsule was evacuated and welded. The components in the capsule were equilibrated at selected temperature in a furnace. After equilibration, the furnace was tilted to another position in order to separate the liquid into two portions by decantation. If solid CsF was not found undissolved above a wire gauze, both of those positions were analyzed and the identity of their composition was taken to indicate the presence of only one liquid phase. Cs saturated with CsF was analyzed by an unspecified method. Thermal analysis was performed on one sample using the method described in Bredig *et al.*[1]

Source and Purity of Materials:

CsF: prepared from CsCl by exchange reaction with AgF in water. The reaction product was filtered, the filtrate dehydrated, and melted in a Pt container.
Cs: contained 0.01% (Rb+K).
Ar: nothing specified.

Estimated Error:

Solubility: nothing specified.
Temperature: precision ±3 K, as in Bredig *et al.*[1]

References:

[1]M. A. Bredig, J. W. Johnson, and W. T. Smith, J. Am. Chem. Soc. **77**, 307–312 (1955).

7.16. Cesium–Chlorine

Components:

(1) Chlorine; Cl; [7782-50-5]
(2) Cesium; Cs; [7440-46-2]

Evaluated by:

Hans Ulrich Borgstedt, Forschungszentrum Karlsruhe, Germany and Cezary Guminski, University of Warsaw, Poland, November 1998

Critical Evaluation

Cl reacts violently with Cs, and in the course of this reaction the compound CsCl, being the equilibrium solid phase, is formed. There are two experimental studies[1,2] on the solubility of Cl in liquid Cs, showing relatively good agreement. The differences between the two lines are a few K; however, due to the quite flat liquidus in the intermediate composition range, this causes differences in the contents of Cl of up to 10 mol %.

The solubility of Cl in molten CsCl is small; the corresponding data are collected in Ref. 3. The Cs–Cl phase diagram is shown in Fig. 72.

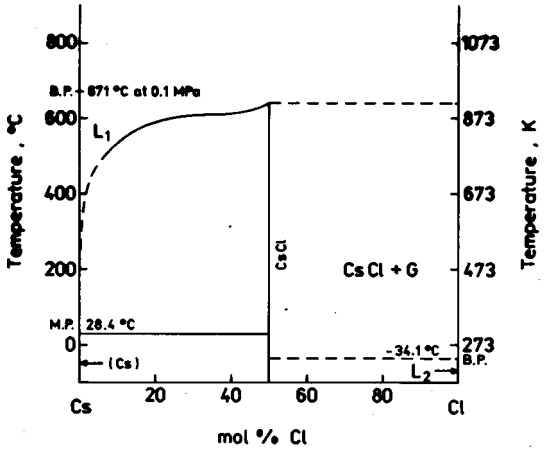

FIG. 72. Cs–Cl phase diagram.

Tentative values of the solubility of Cl in liquid Cs

T/K	Solubility/mol % Cl	Source
773	7	(1)
873	24	(1)
885	34	(2) mean value
900	47.8	(2)
910	49.3	(2)

References:

[1]M. A. Bredig, H. R. Bronstein, and W. T. Smith, J. Am. Chem. Soc. **77**, 1454 (1955).
[2]C. Hsu and N. H. Nachtrieb (1979), as reported by H. Yokokawa, O. J. Kleppa, and N. H. Nachtrieb, J. Chem. Phys. **71**, 4099 (1979).
[3]R. P. T. Tomkins and N. P. Bansal, *Gases in Molten Salts*, Solubility, Data Series (Pergamon, Oxford, 1990), Vol. 45/46, p. 136.

Components:
(1) Chlorine; Cl; [7782-50-5]
(2) Cesium; Cs; [7440-46-2]

Original Measurements:
M. A. Bredig, H. R. Bronstein, and W. T. Smith, J. Am. Chem. Soc. **77**, 1454–1458 (1955).

Variables:
Temperature: 759–894 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

The solubility of Cl in liquid Cs was determined as a part of the Cs–Cl liquidus

T/°C	Solubility/mol % CsCl	Solubility/mol % Cl[a]
486	5.9	5.6
513	8.6	7.9
549	15.5	13.4
601	32.4	24.5
611	56.1	35.9
621	78.0	43.8

[a]Calculated by the compilers.

The melting point of CsCl was determined at 640 °C (by thermal analysis).

Auxiliary Information

Method:
A glass ampoule with Cs was opened under hexane in an assembly with an Ar atmosphere above it. After pumping off the hexane, Cs was melted and allowed to drop into a stainless steel capsule containing the desired quantity of CsCl. The capsule was evacuated and welded. The components in the capsule were equilibrated at the selected temperature in a furnace. After equilibration, the furnace was tilted in order to drain the liquid from any remaining CsCl and then tilted to another position in order to separate the liquid into two portions by decantation. In cases in which no solid CsCl was found undissolved above a wire gauze, both portions were analyzed and the identity of the compositions was taken to indicate the presence of only one liquid homogeneous phase. Cs saturated with CsCl was analyzed by an unspecified method.

Source and Purity of Materials:
CsCl: chemically pure, heated at <773 K in an evacuated quartz tube. Ar flushed through the tube while raising the temperature 50 K above its melting point. After slow cooling to room temperature, clear fragments of the salt were stored over P_2O_5.[1]
Cs: contained 0.01% (Rb+K).
Ar: nothing specified.

Estimated Error:
Solubility: nothing specified.
Temperature: precision±3 K as in Bredig *et al.*[1]

References:
[1]M. A. Bredig, J. W. Johnson, and W. T. Smith, J. Am. Chem. Soc. **77**, 307–312 (1955).

Components:
(1) Chlorine; Cl; [7782-50-5]
(2) Cesium; Cs; [7440-46-2]

Original Measurements:
C. Hsu and N. H. Nachtrieb (1979); as reported by H. Yokokawa, O. J. Kleppa, and N. H. Nachtrieb, J. Chem. Phys. **71**, 4099–4107 (1979).

Variables:
Temperature: 885–915 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data

A part of the Cs–Cl liquidus was determined. The compositions were given numerically and temperatures were read from a figure by the compilers.

T/K	Solubility/mol % CsCl	Solubility/mol % Cl
915	99.00	49.75
914	98.67	49.67
910	97.23	49.30
909	96.67	49.15
903.5	93.72	48.38
900	91.60	47.81
899	89.10	47.12
896.5	88.60	46.98
896	87.45	46.65
894.5	86.36	46.34
892.5	85.54	46.10
893	82.01	45.06
892	78.17	43.87
890.5	77.16	43.55
889.5	74.53	42.70
889	73.2	42.3
890	72.88	42.16
880	67.23	40.20
888.5	66.02	39.77
888.5	63.33	38.77
887.5	59.96	37.48
885	53.06	34.67
885	49.74	33.21

Cl contents recalculated by the compilers. The melting temperature of CsCl was determined at 918 K.

Auxiliary Information

Method:
The components were mixed in Ta containers in a N atmosphere. The containers were evacuated and closed by heliarc welding. The exact amounts of the components were determined from the mass differences before and after the loading. Precise cryoscopic measurements of the mixtures were performed by an unknown method.

Source and Purity of Materials:
CsCl: from Kawecki Berylco Inc., contained 0.1% other alkali metals and 0.02% other impurities, annealed in vacuum for 2 h at 430 K.
Cs: 99.9% pure from D.E. Goldsmith Chemical & Metal Corp.
N: "high purity."

Estimated Error:
Solubility: nothing specified.
Temperature: nothing specified; reading-out procedure ±0.2 K.

7.17. Cesium–Bromine

Components:
(1) Bromine; Br; [7726-95-6]
(2) Cesium; Cs; [7440-46-2]

Original Measurements:
W. Grob and R. W. Schmutzler, Ber. Bunsengesel. Phys. Chem. **93**, 1078–1080 (1989).

Variables:
Temperature: 782–891 K

Prepared by:
H. U. Borgstedt and Guminski

Experimental Data and Critical Evaluation

The liquidus line of the Cs–Br system on the Cs side was determined

t/°C	Solubility/mol % Cs in CsBr	Solubility/mol % Br[a]
509.0	89.3	9.7
579.8	66.5	25.1
588.7	56.3	30.4
594.2	48.3	34.1
596.8	40.0	37.5
606.3	23.3	43.4
617.6	12.1	46.8

[a]Calculated by the compilers

The melting point of CsBr was determined at 630 °C. A supercooling tendency of the system was observed. The solubility of Br in CsBr should be small. The Cs–Br phase diagram is shown in Fig. 73. The solubility data have tentative character.

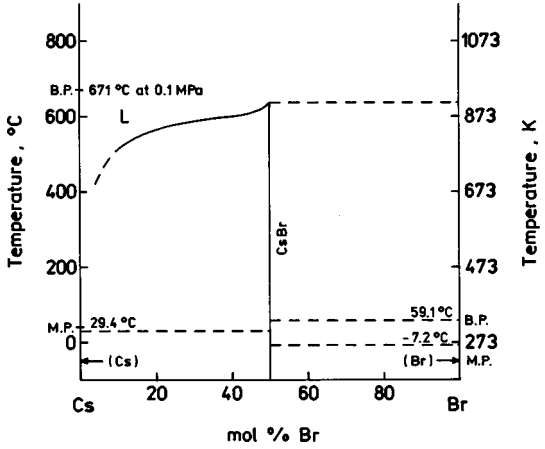

FIG. 73. Cs–Br phase diagram.

Auxiliary Information

Method:
The samples were prepared by direct mixing of precisely weighed amounts of Cs and CsBr in Mo containers tightly closed by cones to avoid Cs losses. The operations were performed in an Ar atmosphere. The liquidus temperatures were measured by differential thermal analysis. The sample cell and the reference cell were identical Mo containers. The reference cell was filled with Pb. Both cells were placed in a ceramic material (Stennan) containing 12 pairs of Pt/Pt–Rh (10%) thermocouples. One of the thermocouples was used to directly determine the temperature of the sample. The temperature of the furnace containing the ceramic block was controlled by an additional thermocouple. The container was rotated providing a possibility of sample stirring. During experimental runs a He pressure of 1 kPa was maintained in the container. The heating rate was kept at 3 K/min. The melting temperature of Pb was used for the calibration of the equipment. The liquidus temperature was carefully estimated from the heating curve.

Source and Purity of Materials:
CsBr: 99.9% pure from Ventron; dried by heating to 473 K under reduced pressure of 100 Pa for at least 6 h.
Cs: 99.98% pure from Ventron.
Ar: from Messer Griesheim, contained $<2\cdot10^{-3}$ vol % of impurities.
He: nothing specified.
Ar: nothing specified.

Estimated Error:
Solubility: nothing specified.
Temperature: accuracy ±2 K.

7.18. Cesium–Iodine

Components:
(1) Iodine; I; [7553-56-2]
(2) Cesium; Cs; [7440-46-2]

Evaluated by:
Hans Ulrich Borgstedt, Forschungszentrum Karlsruhe, Germany and Cezary Guminski, University of Warsaw, Poland, January 1999

Critical Evaluation

I reacts with Cs forming CsI (the most stable), CsI_3, and CsI_4 (the least stable) compounds. Due to the high volatility of I only the most I-rich part of the liquidus was investigated at normal pressure in Refs. 1 and 2. The data are originated from the same laboratory of Briggs; they were obtained by different methods (thermal and chemical analyses). These results show remarkable agreement within the precision of the methods used. Rosztoczy and Cubicciotti[3] performed experiments in closed containers to establish the whole Cs–I liquidus between CsI and I. Their values confirm the results obtained earlier by Ref. 1 below the boiling point of liquid I saturated with CsI (<576 K). The peritectic temperature of CsI_3 in Rosztoczy and Cubicciotti[3] was found to be 3 K higher than in Ref. 1 and the liquidus course between 414 and 488 K was more convex in Rosztoczy and Cubicciotti.[3] The authors of Ref. 1 and Rosztoczy and Cubicciotti[3] indicated an undercooling tendency of the system.

Bredig *et al.*[4] investigated the Cs-rich side of the Cs–I liquidus and noticed a tendency of the system to immiscibility as an almost plateau liquidus, but no miscibility gap was observed. The melting temperature of CsI measured by Ref. 4 was 2 K lower than by Rosztoczy and Cubicciotti.[3] The Cs–I phase diagram according to Rosztoczy and Cubicciotti[3] is shown in Fig. 74. Hoch[5] predicted a fragment of the CsI–I phase diagram which is far from the experimental findings.

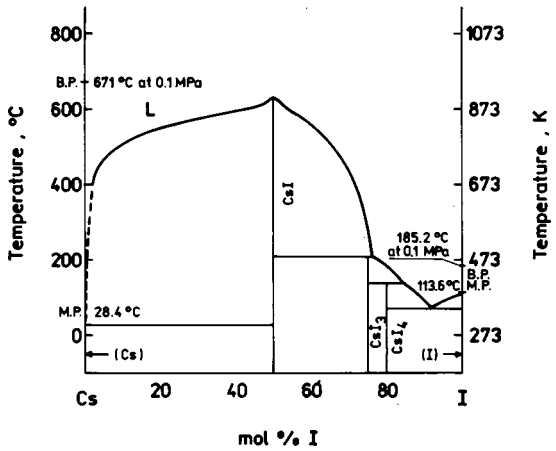

FIG. 74. Cs–I phase diagram.

Tentative values of the solubility of I in liquid Cs

T/K	Solubility/mol % I	Source
673	1.7	(4)
773	6	(4) interpolated
873	45	(4) interpolated
901	50 congruent	(3)
873	54[a]	(3) interpolated
773	67[a]	(3) interpolated
673	72[a]	(3) interpolated
573	74[a]	(3) interpolated
488	76 peritectic	(3)
414	84 peritectic	(1),(3)
343	91 eutectic	(1),(3)
373	96	(2)

[a]At constrained pressure.

References:

[1]T. R. Briggs, J. Phys. Chem. **34**, 2260 (1930).
[2]T. R. Briggs and S. S. Hubard, J. Phys. Chem. **45**, 806 (1941).
[3]F. E. Rosztoczy and D. Cubicciotti, J. Phys. Chem. **69**, 1687 (1965).
[4]M. A. Bredig, H. R. Bronstein, and W. T. Smith, J. Am. Chem. Soc. **77**, 1454 (1955).
[5]M. Hoch, J. Phase Equil. **14**, 296 (1993).

Components:
(1) Iodine; I; [7553-56-2]
(2) Cesium; Cs; [7440-46-2]

Original Measurements:
T. R. Briggs, J. Phys. Chem. **34**, 2260–2266 (1930).

Variables:
Temperature: 343–576 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data
The I-rich part of the Cs–I liquidus was determined

t/°C	Solubility/mol % CsI	Solubility/mol % I[a]
108	5	97.5
100	9	95.5
88	13	93.5
71	17	91.5
70	18	91.0
92	22.5	88.8
110	25	87.5
122	27.5	86.3
134	30	85.0
149	32.5	83.8
155	35	82.5
171	36.54	81.7
175	37.5	81.3
181	38	81.0
186	40	80.0
197	42.5	78.8
199	43	78.5
206	45	77.5
215	47.77[b]	76.1
255	48.70[b]	75.7
300	49.36[b]	75.3
303	49.40[b]	75.3

[a]Calculated by the compilers.
[b]From chemical analysis of the filtrate.

The melting point of I was found at 113 °C.

Auxiliary Information

Method:
The CsI-rich mixtures were prepared from CsI and I. They were handled in a Pyrex glass test tube. The I-rich mixtures were obtained by addition of I. Thermal analyses of the samples were performed. Thermal arrests on cooling curves were assumed as saturation points. Occasional analysis of the composition of samples was performed by an unspecified method.

Source and Purity of Materials:
I: sublimed and carefully dried.
CsI: nothing specified.

Estimated Error:
Solubility: accuracy ±0.5 mol %.
Temperature: nothing specified.

Components:
(1) Iodine; I; [7553-56-2]
(2) Cesium; Cs; [7440-46-2]

Original Measurements:
T. R. Briggs and S. S. Hubard, J. Phys. Chem. **45**, 806–822 (1941).

Variables:
Temperature: 352–484 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data
The I-rich part of the Cs–I liquidus was determined

t/°C	Solubility/mass % CsI	Solubility/mol % I[a]
104.0	8.5	95.9
100.1	10.0	95.5
94.0	12.6	93.8
86.2	14.9	92.7
79.3	17.2	91.6
140[b]	30.5	85.0
211[b]	48.3	76.1

[a]Calculated by the compilers.
[b]From inoculation technique.

Auxiliary Information

Method:
The solubility results were obtained by means of chemical analyses of CsI–I melts saturated with I. The liquid phase was filtered through a plug of glass wool and analyzed for I being dissolved by a distillation method.[1] Details of the experiments on inoculation of solutions by crystals are not described.

Source and Purity of Materials:
I: sublimed and carefully dried.
CsI: nothing specified.

Estimated Error:
Solubility: precision ±0.2 mass % Cs.
Temperature: precision ±0.5 K.

References:
[1]T. R. Briggs, W. F. Geigle, and J. L. Eaton, J. Phys. Chem. **45**, 595–613 (1941).

Components:
(1) Iodine; I; [7553-56-2]
(2) Cesium; Cs; [7440-46-2]

Original Measurements:
M. A. Bredig, H. R. Bronstein, and W. T. Smith, J. Am. Chem. Soc. **77**, 1454–1458 (1955).

Variables:
Temperature: 672–882 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data
The solubility of I in liquid Cs, as a part of the Cs–I liquidus, was determined

t/°C	Solubility/mol % CsI	Solubility/mol % I[a]
399	1.7	1.7
450	4.3	4.1
549	19.0	16.0
571	36.6	26.8
580	56.1[b]	35.9
592	72.5	42.0
609	93[c]	48.2

[a]Calculated by the compilers.
[b]No decantate was obtained and this value was accepted as the solubility value by the authors.
[c]From a cooling curve by thermal analysis.

The melting point of CsI was found at 626 °C.

Auxiliary Information

Method:
A glass ampoule with Cs was opened under hexane in an assembly filled with Ar. After pumping off the hexane, Cs was melted and allowed to drop into a stainless steel capsule containing the desired amount of CsI. The capsule was evacuated and welded. The components were equilibrated at selected temperatures in a furnace. After the equilibration, the furnace was tilted in a way as to drain the liquid from any remaining CsI and then tilted to another position in order to separate the liquid into two portions by decantation. If no solid CsI was found undissolved above a wire gauze, both portions were analyzed and the density of the composition was taken to indicate the presence of only one liquid phase. Cs saturated with CsI was analyzed by an unspecified method. Thermal analysis, as in Bredig *et al.*,[1] was carried out with one sample.

Source and Purity of Materials:
CsI: ''fragments of crystals that were optically and chemically pure'' were used.
Cs: contained 0.01% (Rb+K).
Ar: nothing specified.

Estimated Error:
Solubility: nothing specified.
Temperature: precision ±3 K; as in Bredig *et al.*[1]

References:
[1]M. A. Bredig, J. W. Johnson, and W. T. Smith, J. Am. Chem. Soc. **77**, 307–312 (1955).

Components:
(1) Iodine; I; [7553-56-2]
(2) Cesium; Cs; [7440-46-2]

Original Measurements:
F. E. Roszto czy and D. Cubicciotti, J. Phys. Chem. **69**, 1687–1692 (1965).

Variables:
Temperature: 355–885 K

Prepared by:
H. U. Borgstedt and C. Guminski

Experimental Data
The solubility of I in liquid Cs on the I-rich side of the diagram was determined

t/°C	Solubility/mol % CsI	Solubility/mol % I[a]
108.4	5	97.5
82	15	92.5
86	21	89.5
136	31	84.5
163	35	82.5
210.2	45	77.5
212.2	47	76.5
344.8	52	74.0
445.0	60	70.0
517	70	65.0
580.3	85	57.5
612.2	95	52.5

[a]Calculated by the compilers.

The melting points of I and CsI were found at 113.3 and 628.0 °C, respectively. The CsI_3 and CsI_4 equilibrium intermediate phase were identified.

Auxiliary Information

Method:
Cooling curves, performed at a rate of approximately 0.5 K/min, were obtained on samples in glass containers sealed under vacuum. Two types of containers were used: (i) a medium-wall Pyrex glass tube with a re-entrant thermocouple well and tubulation at the top, (ii) a bundle of three medium-wall fused quartz tubes. Tubes of the first type were used for the I-rich solutions and those of the second type were used for CsI-rich solutions. During cooling and heating, the sample was maintained at constant temperature above or below the furnace temperature by a differential thermocouple. The temperature was measured by a NBS calibrated Pt/Pt–Rh (10%) thermocouple. The composition of CsI_4 at room temperature was confirmed by chemical analysis with AgI precipitation.

Source and Purity of Materials:
I: ultra pure; resublimed crystals from Mallinckrodt.
CsI: 99.7% pure from Fairmont Chem. Co.; chemical analysis showed 48.92% I compared with 48.85% I as the theoretical content in CsI.

Estimated Error:
Solubility: nothing specified.
Temperature: nothing specified.

7.19. Cesium–Helium or Neon or Argon or Krypton or Xenon or Radon

Components:

(1) Helium; He; [7440-59-7]
or Neon; Ne; [7440-01-9]
or Argon; Ar; [7440-37-1]
or Krypton; Kr; [7439-90-9]
or Xenon; Xe; [7440-63-3]
or Radon; Rn; [10043-92-2]
(2) Cesium; Cs; [7440-46-2]

Evaluated by:

Hans Ulrich Borgstedt, Forschungszentrum Karlsruhe, Germany and Cezary Guminski, University of Warsaw, Poland, March 1999

Critical Evaluation

Experimental data on solubilities of He, Ne, Ar, Kr, Xe, and Rn in liquid Cs have not been found in literature. One may predict a higher solubility of Ar in liquid Cs than in liquid K at selected temperature, based on the general tendency observed that the solubilities of rare gases increase with the increase of the atomic number of the alkali metal solvent. A similar conclusion may be drawn from the regular solution calculations of solubility.

Tilton *et al.*[1] investigated optical features of mixtures of solid Kr or Xe with Cs at 5 K; it is, however, difficult to deduce a degree of equilibrium and miscibility between the components. The authors estimated that the dissolution enthalpy of Xe in liquid Cs should be similar to the dissolution enthalpy of He in liquid Li (20 kJ/mol). Since the difference of the molar volumes of Xe and Cs is smaller than of He and Li, one may expect a higher solubility of Xe in liquid Cs than He in liquid Li; see the He–Li system. Phase relations of these systems are unknown but the phase diagrams should be similar to the Na–Xe system differing in the melting and boiling point of Cs (301.5 and 671 K, respectively) as well as the corresponding rare gas.

References:

[1]R. A. Tilton, D. J. Phelps, and C. P. Flynn, Phys. Rev. Lett. **32**, 1006 (1974).

8. System Index

Argon	1023-1024, 1034, 1109, 1137
Arsenic	888, 952, 1041, 1090-1091, 1117
Astatine	907
Barium	886, 948-949
Boron	866-867, 926, 1035, 1085, 1111
Bromine	905, 1009-1013, 1076-1077, 1105, 1133
Calcium	886, 950
Carbon	867-870, 927-939, 1035-1036, 1086, 1112- 1113
Cesium	901, 907, 908, 1102, 1109-1137
Cesium amide	1116
Cesium hydroxide	1122-1123
Chlorine	902-905, 1003-1009, 1071-1075, 1104, 1131- 1132
Deuterium	858-864, 925, 1034, 1085, 1109
Dilithium cyanamide	871-872
Fluorine	901-902, 1002-1003, 1069-1070, 1103, 1130- 1131
Germanium	878-880, 941-943, 1037-1038, 1087-1088, 1114- 1115
Helium	907-908, 1020-1022, 1080-1083, 1109, 1137
Hydrogen	846-859, 863, 909-925, 985, 10268-1034, 1085, 1109-1111
Iodine	915-907, 1013, 1019, 1077-1082, 1106-1108, 1134-1136
Krypton	1025-1026, 1083, 1109, 1137
Lithium	846-908, 939, 950, 1031
Lithium silicon nitride	877
Neon	1023, 1083, 1109, 1137
Nitrogen	881-887, 944-945, 948-951, 1039-1040, 1089, 1115
Oxygen	888-893, 952-976, 1042-1056, 1091-1094, 1117- 1122
Phosphorus	887, 951, 1040, 1089, 1116
Polonium	901, 1001, 1102
Potassium	901, 907, 908, 1028-1030, 1034-1039, 1040-1048, 1057-1058, 1060-1082, 1083-1084
Potassium hydroxide	1057-1059
Potassium sodium alloy	1034, 1049-1051, 1055-0156, 1072
Potassium sodium alloy – $K_{65}Na_{35}$	1052
Potassium sodium alloy – $K_{20}Na_{80}$	1052
Potassium sodium eutectic – $K_{68}Na_{32}$	1030-1033, 1039-1040, 1051, 1053-1055, 1056, 1083
Radon	908, 1028, 1083, 1109, 1137
Rubidium	901, 907, 908, 1085-1109
Rubidium hydroxide	1095
Selenium	897-898, 994-996, 1065-1067, 1099-1100, 1125- 1127
Silicon	872-877, 939-941, 1037, 1086, 1113
Sodium	887, 901, 907, 908, 909-1028, 1074-1075
Sodium carbonate	982-985
Sodium cyanide	945-947
Sodium hydroxide	976-982
Strontium	886, 951
Sulfur	894-897, 985-994, 1060-1064, 1096-1098, 1123- 1125
Tellurium	899-901, 997-1001, 1067-1069, 1101-1102, 1127- 1130
Tritium	863-864, 925, 1034, 1085, 1109
Xenon	908, 1023, 1025-1028, 1083, 1109, 1137

9. Registry Number Index

[143-33-9]	Sodium cyanide	945-947
[497-19-8]	Sodium carbonate	982-985
[1310-58-3]	Potassium hydroxide	1057-1059
[1310-73-2]	Sodium hydroxide	976-982
[1310-82-3]	Rubidium hydroxide	1095

[1333-74-0]	Hydrogen	846-859, 863, 909-925, 985, 10268-1034, 1085, 1109-1111
[7439-90-9]	Krypton	1025-1026, 1083, 1109, 1137
[7439-93-2]	Lithium	846-908, 939, 950, 1031
[7440-01-9]	Neon	1023, 1083, 1109, 1137
[7440-08-6]	Polonium	901, 1001, 1102
[7440-09-7]	Potassium	901, 907, 908, 1028-1030, 1034-1039, 1040-1048, 1057-1058, 1060-1082, 1083-1084
[7440-17-7]	Rubidium	901, 907, 908, 1085-1109
[7440-21-3]	Silicon	872-877, 939-941, 1037, 1086, 1113
[7440-23-5]	Sodium	887, 901, 907, 908, 909-1028, 1074-1075
[7440-24-6]	Strontium	886, 951
[7440-37-1]	Argon	1023-1024, 1034, 1109, 1137
[7440-38-2]	Arsenic	888, 952, 1041, 1090-1091, 1117
[7440-39-3]	Barium	886, 948-949
[7440-42-8]	Boron	866-867, 926, 1035, 1085, 1111
[7440-44-0]	Carbon	867-870, 927-939, 1035-1036, 1086, 1112- 1113
[7440-46-2]	Cesium	901, 907, 908, 1102, 1109-1137
[7440-56-4]	Germanium	878-880, 941-943, 1037-1038, 1087-1088, 1114- 1115
[7440-59-7]	Helium	907-908, 1020-1022, 1080-1083, 1109, 1137
[7440-63-3]	Xenon	908, 1023, 1025-1028, 1083, 1109, 1137
[7440-68-8]	Astatine	907
[7440-70-2]	Calcium	886, 950
[7553-56-2]	Iodine	915-907, 1013, 1019, 1077-1082, 1106-1108, 1134-1136
[7704-34-9]	Sulfur	894-897, 985-994, 1060-1064, 1096-1098, 1123- 1125
[7723-14-0]	Phosphorus	887, 951, 1040, 1089, 1116
[7726-95-6]	Bromine	905, 1009-1013, 1076-1077, 1105, 1133
[7727-37-9]	Nitrogen	881-887, 944-945, 948-951, 1039-1040, 1089, 1115
[7782-39-0]	Deuterium	858-864, 925, 1034, 1085, 1109
[7782-41-4]	Fluorine	901-902, 1002-1003, 1069-1070, 1103, 1130- 1131
[7782-44-7]	Oxygen	888-893, 952-976, 1042-1056, 1091-1094, 1117- 1122
[7782-49-2]	Selenium	897-898, 994-996, 1065-1067, 1099-1100, 1125- 1127
[7782-50-5]	Chlorine	902-905, 1003-1009, 1071-1075, 1104, 1131- 1132
[10043-92-2]	Radon	908, 1028, 1083, 1109, 1137
[11147-16-3]	$K_{68}Na_{32}$	1030-1033, 1039-1040, 1051, 1053-1055, 1056, 1083
[12028-17-8]	Tritium	863-864, 925, 1034, 1085, 1109
[13494-80-9]	Tellurium	899-901, 997-1001, 1067-1069, 1101-1102, 1127- 1130
[21351-79-1]	Cesium hydroxide	1122-1123
[22205-57-8]	Cesium amide	1116
[51677-22-6]	Dilithium cyanamide	871-872
[67181-65-1]	Lithium silicon nitride	877

10. Author Index

Abas-Zade, A. K.	848, 868-869, 881, 887, 889, 892, 910, 916, 944, 1023, 1029, 1033, 1084
Abegg, R.	1077-1078
Ackerman, J.P.	928, 935-936,
Ackermann, H.	878
Adaev, E.I.	1003-1004, 1007
Adams, R. M.	928, 931
Adams, P.F.	846-847, 852-853, 858-860, 866, 868, 881-882, 884, 888-889, 910, 1029, 1035
Adamson, M.G.	1127-1128, 1129
Adaway, D.W.	910, 917
Addison, C.C.	866, 871, 881-882, 885, 909-910, 914, 921, 926- 928, 930, 943-944, 948-951, 1035, 1042-1043
Adelhelm, C	1043, 1046-1047
Ainsley, R.	927-928, 937, 946, 982-984
Alabyshev, A. F.	1071-1072
Alcock, C. B.	954, 968
Alekseev, V. V.	928, 938

Aleksandrov, B. N. 941-942, 1037-1038, 1067-1068
Allan, C.G. 1003-1104, 1009-1010, 1012-1014, 1016
Allard, B. 928
Allen, J. 928, 954
Allen, J. W. 936
Anderson, K. 847-849, 873, 944
Anderson, K.E. 944-946
Anderson, W.J. 927-929
Andreev, P. A. 954
Andrews, R.C. 927-928, 930, 953, 962
Andrianova, V. G. 848, 854
Anonymous 928, 931, 953-954, 966
Ansara, I. 873
Arakawa, T. 1014, 1018-1019
Armand, M. 868
Arnoldov, M.N. 848, 867-869, 881, 887, 888-889, 891-892, 910, 913, 915, 928, 944, 953, 964, 977, 1020, 1023, 1039-1030, 1032-1033, 1035, 1039-1040, 1042-1043, 1054, 1082-1084, 1109-1110, 1118, 1120
Aronson, S. 1035-1036, 1086, 1112
Astley, E. R. 926
Atsumo, H. 954, 972
Auerbach, C. 954
Avdeev, V. V. 867-868
Badalov, A. 1029
Bader, B. 878
Bagdasarov, Yu. E. 952, 954, 964, 977, 979
Bagley, K.Q. 953, 956, 1042-1043, 1049
Baitinger, M. 940, 942, 1037-1038, 1086-1087, 1114
Bakum, S. J. 910, 1029, 1085, 1110
Bannykh, Z.S. 953, 958, 976-978, 1043, 1050
Bansal, N. P. 903, 1003-1004, 1009-1110, 1013-1014, 1071- 1072, 1076, 1104, 1131
Banus, M. D. 909-910
Barker, D. F. 928
Barker, K.R. 953, 962, 1042-1043
Bartholme, L.G. 908, 917-919
Beckmann, E. 1077-1079
Begun, G.M. 847, 856, 859, 862, 864
Beisswenger, H. 953, 964
Bele, M. 866
Belin C. 866
Bell, J. T. 847, 856, 859, 862
Bell, R. L. 1117-1118
Bellafiore, D. 1036, 1086, 1112
Belomestnykh, V. N. 944, 1039, 1089, 1115
Belozerskii, N.A. 1003-1005, 1071-1072
Belyaev, A. I. 928
Benejat, J. C. 940
Bennet, D.W. 954, 967
Berardinelli, S. P. 1117-1118
Berdichevskii, N.I. 1057, 1059, 1071-1072, 1074
Berge, P. 952, 970
Bergmann, A. 1096, 1099, 1101, 1123-1126, 1127-1128
Bergstresser, K.S. 954, 962
Berkey, E. 954, 970-971
Berthold, H.J. 985-986, 989, 1060, 1062, 1098, 1125
Beskorovainyi, N. M. 887, 894
Bhat, N.P. 909-910, 923, 1043, 1047, 1056

Biery, J. C. 954
Bikina, G.V. 985-986, 992
Billaud, D. 867-868
Billuris, G. 959
Biltz, W. 1096-1097, 1123-1124
Birault, J. 909-910, 914
Bjork, R. G. 868, 928, 945-946, 983
Blake L.R. 954, 1043, 1052
Blander, M. 847, 852, 861, 1002, 1010, 1014
Blumenthal, M. 1043, 1117-1118
Blomquist, R.A. 1023, 1025-1026
Böhm, H. 872-874
Bogard, A. D. 953, 960, 977, 979, 983
Bogdanov, Yu.V. 1110
Bolle, U. 942, 1038, 1087, 1114
Bolshakov, K.A. 881-882
Bolshakova, G.A. 951-952, 1126
Bonnetain, L. 928
Borgstedt, H.U. 847, 859, 867-868, 882, 886, 888-889,909-911, 923, 926-928, 944, 953-954, 968-969, 983, 1014, 1017-1019, 1040-1043, 1046-1048, 1113
Borocco, A. 925, 1034, 1085, 1109-1110
Bottcher, P. 986, 1096
Bouaziz, R. 953-954
Bowman, F.E. 928, 953-954, 957
Brabers, M. 847, 882, 889, 910, 928, 953
Braga, M. H. 873
Brachet, A. 910, 914
Brauer, G. 951-952, 992, 1041, 1068, 1117-1119
Braunbeck, H. G. 1125-1126
Bredig, M.A. 847, 902-903, 905-906, 1003-1004, 1006-1007, 1009-1011, 1013-1015, 1060, 1063, 1069-1073, 1076-1078, 1081, 1103-1106, 1108, 1130-1132, 1134, 1136
Brewer, L. 889
Briggs, T.R. 1013-1014, 1077-1078, 1080, 11-6=11-7, 1134- 1135
Bright, N. F. H. 889
Bronstein, H.R. 902-903, 906, 1004, 1007, 1009-1011, 1013- 1015, 1069-1070, 1072-1073, 1130-1132, 1134, 1136
Bruggeman, W. H. 954, 959
Brush, E. G. 939-940, 954
Brynestad, J. 899
Bukovec, N. 867
Bukovec, P. 867
Bunzel, E. G. 953-954
Bushmanov, V.D. 1090
Bussey, P.R. 944, 951
Byker, H. J. 1042-1043
Bykova, M.A. 986, 989
Bykovetz, N. 928
Cadenbach, G. 928, 1036, 1086, 1112
Cafasso, F.A. 852, 864, 909-910, 927-928, 931, 933, 936, 944- 947, 954, 968, 976-977, 1020-1027
Caillet, M. 1091-1093
Cairns, E. J. 852, 864, 894-895, 898-900
Calaway, W.F. 859, 864, 868, 870-871, 882, 886, 889, 893
Calkins, V.P. 873
Calway, W. F. 847, 857
Cambillard, E. 910, 914
Caplinger, W.H. 954, 967
Carmichael, H.T. 982-984
Carillo-Cabrera, W. 940, 943, 1037-1038, 1084-1087, 1114

Carter, R.L. 928, 953, 957
Cashman, T.J. 953, 955
Castleman, A.W. 941-942
Casteels, F. 847, 882, 889, 910, 928, 953
Caswell, N. 1112
Centnerszwer, M. 1043, 1117-1118
Chabre, Y. 868
Cheburkov, V.I. 882, 888-890
Chebykin, V.V. 1004, 1009, 1010, 1013, 1014, 1017, 1078, 1082
Chekov, N. G. 894
Chernick, C.L. 954, 963
Childs, W. J. 866
Chinn, J. W. 868
Chlopin, V. G. 901, 1001
Chuntonov, K.A. 1067-1069, 1086-1088, 1090, 1096, 1098-1102, 1114-1115, 1126-1129
Chye, P. 1118
Cichy, M. A. 928
Clarke, R. 1112
Claxton, K. T. 9502-953, 955, 961
Cleary, R.E. 907-908, 1082
Cleaver, B. 893, 897, 985-986, 991, 994
Clough, W.S. 928, 1007-1011, 1112
Clusius, K. 1039, 1089, 1115
Cocks, G. G. 960
Colburn, R. P. 1112
Coleman, D. S. 985-986
Collins, G. D. 910
Compere, E.L. 910, 1029, 1031-1032
Cordfunke, E.H.P. 1014, 1127-1128, 1130
Coron, J. 910, 914
Cosgarea, A. 928, 931
Cottrell, W.B. 954-955, 1043, 1049
Courtois, G. 986
Coustel, N. 868
Creffield, G.K. 881-882, 921, 943-944, 948-951
Crenshaw, J. L. 909-910, 925, 1028-1029, 1034
Crepy, G. 866
Crever, F. E. 954
Cros, C. 926, 940, 942, 1035, 1037-1038, 1086-1087, 1113-1114
Crosbie, G.M. 1060, 1063
Crouthamel, C. E. 845, 900, 903
Cubicciotti, D. 954, 1077-1078, 1081, 1106, 1134, 1136
Cunningham, P.T. 894-895, 897-900
Curda, J. 942, 1038, 1087, 1114
Czerwiinski, J. 1003-1004, 1071-1072
Dadd, A. T. 847-848, 852, 859, 868, 871-873, 877-878, 880, 882, 889, 1116
Dafert, F. W. 882
Dallek, S. 866
Dalakova, N. V. 941-942, 1037, 1038, 1067-1068
Damon, E.B. 847, 850-851
Danilkin, V.I. 910, 920, 1085, 1110
Davies, A.J. 985-986, 991
Davies, B.M. 882, 950
Davies, R. 928
Davies, R.A. 909-910, 917
deBoer, R. 1127, 1130
De Gilbert, A. 866

de la Torre Cabezas, M. 954, 973
Demidov, A. J. 894
Desyatkina, E. A. 1120
DeVan, J.H. 889, 892
Dever, J. L. 902
DeVries, L. E. 866
DeVries, P. F. 954
Dhar, S.K. 1020-1-26
Djurado, D. 868
Dmitreva, I.B. 891, 954, 964, 1043, 1053, 1117, 1120
Dorn, F.W. 1040-1041, 1089-1090, 1114-1117
Dorner, S. 953, 964-965
Douglas, T. B. 902
Down, M.G. 847, 852, 859-860, 868, 871-872, 882, 884, 910, 944, 1029
Draley, J. E. 954, 966-967, 969, 977
Drits, M.E. 878, 941-943, 1038, 1087-1088, 1114
Droher, J. J. 1020, 1022, 1024, 1082, 1084
Drummond, J.L. 910, 914, 917, 983
Dullenkopf, W. 951-952
Dumas, D.
Durigon, D.D. 954, 971
Dutina, D. 945-947
Dworkin, A.S. 902-903, 905, 1060, 1063
Dymova, T. N. 909-910, 1028-1029, 1085, 1109-1110
Eames, A.R. 954, 961, 1043, 1052
Earnshaw, A. 946
Eaton, J.L. 1014, 1135
Ehlert, T. C. 1042-1043
Eichelberger, R.L. 928, 932, 935, 952-953
El-Genk, M. S. 954, 1043, 1056
Eliezer, J. 1042-1043
Ellenson, W. D. 1086
Elson, R. E. 847
Emelyanov, V.P. 889, 891, 903-904
Endo, H. 1099-1100
Ephraim, F. 909-910, 1028-1029, 1085, 1109-1110
Epstein, L. F. 953-954, 957, 1020
Ernst, D. W. 866
Evans, J. W. 954
Evers, J. 872-873
Feder, H.M. 928, 931, 933, 944-946, 1020-1027
Fedorov, P.I. 867-869, 872-873, 875, 878, 880-882
Fedorov, V.M. 1102, 1125-1129
Fedorovich, E. D. 954
Fefelova, G.F. 953, 958, 976-978, 1043, 1050
Feher, F. 985-986, 989, 1060, 1062, 1096, 1098, 1123- 1125
Ferguson, W. S. 905
Fialkov, J.A or Ya. A. . 1014, 1077-1078, 1080, 1106-1107
Fidler, R.S. 909-910, 953, 975, 977
Finogenova, V.K. 997-999
Firsonova, L. A. 928
Fischer, A.K. 928, 945-947, 950
Fischer, J. E. 868, 928
Fisher, J. E. 1086
Flandrois, S. 868
Fleischer, B. 954, 1043, 1053
Fleshman, W.S. 873

Flood, E. A. 889
Flotow, H. E. 882, 928, 935
Flynn, C. P. 1083, 1109, 1137
Foster, M.S. 899-900
France, E. D. 914, 983
Franck, E.U. 848, 909-911, 923, 1110-1111
Fredenhagen, K. 928, 1035-1036, 1086, 1112
Frees, G. 882, 886, 911, 926, 1014, 1017-1019, 1043
Freilander, P. 878
Freyland, W. 1071-1072, 1075
Fridman, A. S. 943, 1038
Friedrich, K. 985-986
Fromm, E. 847, 859, 863-864, 910, 1028-1029
Fukase, S. 1020
Fuller, C. S. 872-873, 878
Funada, T. 909-910, 922
Furukawa, K. 847, 863, 900-910, 919, 954, 973
Ganesan, V. 1042-1043, 1046-1047
Garbade, K. 1071-1072, 1075
Gavrilov, P. I. 866, 926, 1035
Geertsma, W. 878
Gehri, D.C. 927-928, 932, 935, 953
Geigle, W.F. 1014, 1077-1078, 1080, 1107, 1135
Gerasimenko, L.N. 986, 989
Getzschmann, J. 986, 1096
Gibb, T.R.P. 846-847, 849, 909-910, 1085, 1110
Gilbert, T. W. 883
Glass, S.W. 997-998
Glassner, A. 928, 931, 954, 973
Gnanamorphy, J. B. 953
Gnanasekaran, T. 910, 928, 944, 954, 976-977, 983
Gnutzmann, G. 1040, 1089-1090, 1116-1117
Goodall, D. J. H. 859
Goode, J. M. 901, 1001
Gordus, A.A. 910, 915
Goubeau, J. 951-952
Grand, J.A. 910, 912, 953, 960, 977, 983, 1004, 1043-1044, 1051
Grandstaff, S. M. 997-998
Gratton, J.G. 927-929, 1021
Gray, I.L. 953, 958-959
Greenwood, N. N. 946
Greer, J. 1112-1113
Gregory, P. E. 1118
Grieser, D. R. 952-953, 960
Grin, Y. 940, 942, 1037-1038, 1086-1087, 1114
Grob, W. 1133
Grot, L.S. 1057-1058
Guernsey, E. W. 944
Grundy, B.R. 939-940, 954, 970-971, 1020, 1022
Grunewald, A.L. 873
Guminski, C. 882, 1043, 1048
Guerard, D. 868, 1086
Gunji, M. 954, 1043, 1045
Guon, J. 928, 932, 935, 953
Gupta, N.K. 985-986, 990
Gurak, J. A. 868
Gurinsky, D. H. 954, 966

Hackspill, L. 925, 1034, 1071-1072, 1085, 1093, 1109- 1110
Hagenmuller, P. 940-942, 1035, 1037-1038, 1086-1087, 1113- 1114
Haley, M. J. 871
Hall, E. H. 953, 960
Halsey, G.D. 909-910, 913, 925
Hamburger, A. 1077-1078
Hamer, A.N. 953, 969
Hames, M. D. 986, 991
Hara, H. 1014, 1018-1019
Hargreaves 911
Harper, A. 847-848, 852, 868, 871, 884, 889
Hartlib, L.P. 928, 937, 946, 983-984
Hautefeuille, P. 909-910, 1028-1029
Hayward, B.R. 928, 953, 957
Heal, M. 985-986
Heitjans, P. 878
Heinemann, F. 942, 1038, 1087, 1114
Heinrich, R. R. 847, 903
Henry, F. X.. 868
Henry, J.-L. 953-954, 976-977
Henry, W. M. 960
Herald, R. H. 882-883, 1092
Hérold, A. 868, 909-911, 1028-1029, 1036, 1085-1086, 1109-1110, 1112
Herschbach, K. 1034
Heumann, F.K. 846-847, 850, 858-860, 863-864
Higashi, I. 866
Higson, J.H. 953, 969
Hill, E.F. 910, 915, 954, 982-983
Hill, L.L. 846-848
Hiltz, R.H. 928, 930
Hines, J.B. 868, 870-871, 882, 886, 889, 893
Hislop, J.S. 953-954, 974, 982-983
Hissink, M. 911
Hitch, B. F. 899
Hobart, E. W. 868, 870, 928, 945-946, 983
Hobdell, M.R. 910, 927-928, 930, 935, 938
Hoch, M. 847, 859, 863-864, 1077-1078, 1106, 1134
Hoerz, G. 863-864
Hoffman, E.E. 881, 883, 888-890, 1042-1043
Hohmann, E. 939-942, 1037-1038, 1086-1087, 1113- 1114
Holley, J. H. 1111, 1113
Holmes, J.T. 910, 917-918
Holroyd, P.M. 928, 937, 946, 983-984
Homa, M.I. 867-868, 870-871
Homonoff, H. 1085, 1110
Hong, Shunzhang 1043, 1048
Honle, W. 887, 951-952, 1040-1041, 1099-1090, 1116
Hooper, A. J. 927-928, 954
Hoover, M. D. 954, 1043, 1056
Horning, H. C. 847
Horsley, G. W. 954, 961, 1042-1043
Horz, G. 847
Hoshino, H. 1099-1100
Howard, R. C. 1042-1043
Hsu, C. 1131-1132
Hubard, S.S. 1134-1135
Hubbard, W.N. 928, 935-936

Hubberstey, P. 846-848, 852-853, 858-860, 863-864, 868, 871- 873, 877-878, 880-882, 884-886, 888-889, 907-908, 909-911, 921, 928, 939-944, 946, 948-951, 1020, 1023, 1036-1029, 1082, 1109-1110, 1116
Hugot, M. C. 951
Humphreys, J.R. 954, 965
Huntelaar, M. E. 1014
Huntley, W.R. 954, 1043, 1053
Hurd, C. B. 847
Ihle, H.R. 846-847, 851, 858-859, 861
Ilincev, G. 954, 971-972
Imoto, H. 1072
Isaacs, H. S. 939-940, 952, 954, 966
Ishigai, I. 847, 853
Ishii, Y. 954, 1043, 1055
Itoh, K. 954, 972
Ivanovskii, M.N. 848, 868-869, 881, 884, 887, 889, 891-892, 909- 910, 913, 916, 928, 944, 954, 963-964, 977, 980, 1020, 1023, 1029-1030, 1032-1033, 1036, 1039-1040, 1042-1043, 1046, 1054, 1056, 1082-1084, 1110, 1118, 1121
Jackson, L. D. 866
Jaeger, F. M. 889
Jahns, W. 953, 59
James, S. D. 866
Jansson, S. A. 976-977
Janz, G.J. 985-986, 992, 1060, 1064
Jehn, A. 847
Jehn, H. 859, 910, 1028-1029
Jellinek, K. 1003-1004, 1071-1072
Jellinek, R. 926
Jesseman, D.S. 872-873
Johnson, C.E. 847, 902-903
Johnson, G.K. 927-928, 935-936
Johnson, G. S. 1078
Johnson, J.W. 902, 1002-1004, 1006-1007, 1010-1011, 1014- 1015, 1069-1073, 1077-1078, 1081, 1103-1106, 1108, 1131-1132, 1136
Johnson, Q. 878-879
Johnson, S.A. 894-895, 898
Johnston, R.K. 882-883, 1092
Jolly, W. L. 847
Joncourt, L. 927-928
Judd, W. C. 957, 982-983
Jung, J. 954
Juza, R. 868
Kale, R.D. 909-910, 925
Kanaev, A. A. 954
Kapelner, S.M. 907-908, 1082
Karabash, A. G. 891
Kassner, T.F. 954, 967
Katsuta, H. 846-847, 853, 909-910, 919, 954, 973
Kaupp, M. 940, 1037, 1086
Keddy, E. S. 1113
Keller, E. 846, 90, 911, 1110, 1111
Keller, R. 986, 1096
Kelly, K. J. 868, 927-928, 982-983
Kelman, L. R. or L. R. 928, 1035-1037
Kempa, P. B. 953, 1040, 1089-1090, 1116
Keyes, F. G. 909-910, 1028-1029
Khabachev, M.N. 1067-1068, 1069, 1101

Khvostov, A. V. 868
Kikin, G.M. 1029-1030, 1043, 1051
Kimura, K. 866
Kirschler, L.H. 928, 930
Kirchner, R. 911, 1029, 1034
Kissel, G. 954, 966, 969, 977
Klebanov, E.B. 1060, 1064, ‘067-1068
Klemm, W. 951-952, 1037-1038, 1040-1041, 1065-1066, 1086-1087, 1089-1090, 1096, 1099, 1101, 1113-1114, 1116-1117, 1123-1124, 1128
Klentz, A.I.. 1118, 1120
Kleppa, O. J. 1131-1132
Kliche, G. 952, 1040-1041, 1089-1090, 1116
Klostermeier, W. 909-910, 923
Klueh, R. L. 952, 954, 1042-1043
Knight, D. J. 848, 871, 882, 889
Knights, C.F. 976-977, 1117-1118, 1122
Kobayashi, M. 866
Koenig, R. F. 939-940
Kohli, R. 1086, 1113
Kohlmeyer, E. J. 953-954, 986
Kolodney, M. 954
Konovalov, E.E. 888-889, 891, 902-904, 910, 916, 927-928, 954, 982-983, 1029, 1033, 1043, 1053, 1118, 1120
Kopylov, N. I. 986, 1064
Korotaev, S. K. 869, 887, 892
Kovacic, E. C. 910, 915
Kovalev, Yu. P. 928, 938
Kozlov, F.A. 909-911, 913, 927-928, 938, 944, 954, 963-964, 976-977, 980-981, 1054
Kraft, G. 944
Krasin, V. P. 976-977
Kraus, C.A. 997-998
Kraus, D. L. 1117-1118
Kremann, R. 1077-1079
Kremsner, W.A. 1026-1027
Krishnamurthy, D. 954, 1042-1043, 1047, 1055-1056
Krug, M. P. 953-954, 977
Kshnyakina, S. H. 868
Kudo, H. 847, 851
Kummerer, K. 965
Kurbanov, A. R. 1028-1029
Kurihara, K. 873, 875
Kury, J. W. 847
Kusmenko, A.A. 1077-1078, 1080, 1106-1107
Kuznetsov, A.N. 1086-1088, 1090, 1096, 1098-1102, 1115, 1126- 1129
Kuznetsov, E.K. 910-911, 913, 927, 944, 954, 963-964, 977, 980- 981, 1054
Kuznetsov, V. A. 910, 913
Kuznetsova, L. V. 986
La Gamma de Batistoni, A.M. 847, 856, 859, 862, 884
Lagedrost, J.F. 1042-1044
Lagow, R. J. 868
Laitinen, H. A. 905
Land, J.F. 847, 856, 859, 862
Lang, H. J. 954
Langmesser, P. 1065-1066, 1068, 1096, 1099, 1124, 1126, 1128
Lannou, L. 910, 914
Larrick, B. F. 866
Lastov, A. I. 928, 983
Leasvenworth, H. W. 908

Lee, R. H. 954, 967
Legrand, A. P. 868
Leibowitz, L. 976-977
Leighty, J.E. 1127-1128, 1129
Lemke, E. I. 944
Levendovskii, V. D. 866
Levakov, E. V. 866, 926, 1035
Levenson, M. 1023, 1025
Levin, E. M. 977
Levy, I. S. 848
Little, M.J. 940
Lin, C. L. 928
Lintonbon, R. M. 1042-1043
Liu, C.C. 899-900
Llanos, J. 942, 1038, 1087, 1114
Lockhart, R. W. 983
Lohmeyer, S. 1041
Lohrke, G. 986
Long, G. 859, 928, 937, 983-984
Long, G. J. 946
Longson, B. 927-928, 933-934
Longton, P. B. 910, 953
Lorenz, R. 1003-1005
Lowwden, L. F. 1043
Lukinykh, N. L. 951-952
Luner, C. 927-928, 931, 933
Lutz, G. 944
Luzik, A. E. 943, 1038
Lyashenko, V. I. 866
Lyashenko, V. S. 928
Maak, I. 887
MacPherson, R.E. 954, 1043, 1053
Maffei, H. P. 1112
Magomedov, M. N. 863-864, 909, 911, 925, 1028-1029, 1034, 1085, 1109-1110
Makarov, V. M. 977
Mackay, K. M. 847
Maiorova, E.A 985-986, 993-998, 1000, 1060, 1064, 1065
Mair, G. 866
Malheiros, L. F. 873
Malikova, E. D. 1120
Manchester, F. D. 910
Mandel, H. 1020
Mann, L.A. 954-955, 1043, 1049
Marcac, T. 866-867
Marek, L. J. 910, 919
Marin, A. 954, 969
Marinquez, V. 887
Margrave, J. 889
Maroni, V.A. 847, 852, 857, 859, 861-865, 868, 870-871, 882, 885-886, 889, 892-893
Massalski, T. B. 878, 887
Masuda, S. 1092, 1094
Mathews, C.K. 928, 954, 976, 982-983, 1043, 1047-1048, 1055- 1056
Mathewson, C.H. 994-995
Mathison, J. 953, 969
Matsuda, H. 866
Matsui, Y. 1092, 1094
Matsumoto, S. 954, 1043, 1055

Mattas, R. F. 868, 882, 889
Matyukhin, V. V. 928
Maupré, J.P. 909-910, 922, 927-928, 953-954, 976-977, 982- 983, 985
Mauer, W. 1034
Maughan, K. 848, 871, 882, 889
Mausteller, J.W. 926, 953-954, 1042-1043, 1050, 1092-1093, 1118-1119
Mavri, J. 866
Maybury, P.C. 847, 850-851
Mayorova, A. F. 868
McCaldin, J.O. 939-940, 1113
McCallum, J. 952-953, 960
McCauley, J. B. 868
McClure, D.W. 909-910, 913, 925
McCown, J.J. 909-910, 920
McCracken, G. M. 858-859
McIntosh, A. B. 953, 956
McKee, J.M. 954, 970
McKisson, R.L. 927-928, 932, 935, 953
McMurdie, H. F. 977
McPheeters, C. C. 954
McSharry, J. J. 910
Meacham, S.A. 909-910. 915, 954, 982-984
Meadows, G.E. 954, 966-967
Meden, A. 866
Meijer, J. A. 877
Melekhov, L.Z. 1088, 1114-1115
Mellor, J. 847, 850-851
Mermoux, M. 928
Messer, C.E. 846-851, 859, 868, 888-889, 1085, 1109- 1110
Metokj, N. 1086
Mettler, G.W. 909-910, 920
Metz, C.F. 954, 962
Meyer, A. S. 883
Meyer, T. 952, 1040, 1089-1090, 1116
Meyers, J. E. 910. 915
Michel, E. 909-910. 1028-1029, 1085, 1109-1110
Migge, H. 848, 871-873, 882, 888-889, 944, 982- 983
Miklauz, R. 882
Miller, R.R. 910, 912, 953, 956, 960, 977, 979, 983, 1004, 1043-1044, 1051
Minami, R. 903, 905
Minushkin, B. 954, 964, 969, 977
Miraidov, U. 910, 1029, 1085, 1110
Mitchell, M. A. 866
Mitkevich, E.M. 976-977, 979-980, 1057-1059
Mitra, C. 1026-1027
Miyahara, S. 1010, 1013-1014, 1017-1019
Miyaji, N. 1023
Mizutani, T. 954, 972
Moiseeva, T.I. 910
Moissan, H. 909, 911, 926, 1035
Mollwo, E. 1009-1010, 1076
Molochko, V.A. 878, 880
Molovidova, A. V. 891
Monyakina, L. A. 888
Moody, G. J. 1039, 1089, 1115
Moore, G. A. 847
Morachevskii, A.G. 985-986, 989, 993-998, 1000, 1003-1004, 1006, 1057, 1059-1060, 1064-1065, 1068-1069,

1071-1072, 1074
Morozov, V.A. 910, 944, 954, 1020, 1023, 1029-1030, 1032- 1033, 1039-1040, 1043, 1046, 1056, 1082-1084, 1110
Morozova, M. P. 951-952
Morrison, J. A. 868
Mtyukhin, V. A. 944
Mudretsova, S. N. 868
Munnecke, V.H. 1023, 1025
Murchison, A. 1086, 1089, 1115
Myles, K. M. 909-910, 976-977
Nachtrieb, N.H. 1131-1132
Nafe, H. 952-954
Nakajima, T. 902-903, 905, 1071-1072
Nakanishi, K. 903, 905, 1072
Nakanishi, Y. 1092, 1094
Nakasuji, T. 910, 922
Naslain, R. 926, 940, 942, 1035, 1038
Natesan, K. 867-868, 882, 888-889
Natola, F. 1042-1043, 1045
Naud, G. 910
Naused, K. 1096, 1098, 1123-1125
Neal, R.L. 953, 958-959
Neckel, A. 1003-1004, 1071-1072, 1074
Nedved, M. 910
Neff, G. R. 1111, 1113
Neil, D. 944
Nelson, P.A. 910, 917-918, 954, 970
Nesper, R. 866, 872-873, 878, 887
Nevzorov, B. A. 928
Newcombe, R.J. 909-910, 915
Newman, L. 927-928, 935-936, 954
Newman, L. J. 910
Nickerson, R. F. 1085, 1110
Nihei, I. 910, 922
Nikolskaya, L. V. 868
Noden, J.D. 953, 956, 961, 1042-1043, 1049
Noud, G. 977
Novikov, A. G. 1043, 1046
Novoselova, V.A. 998-999
Nowotny, H. 940, 1072, 1074
Oberlin, C. 953, 970
Obinata, I. 872-873, 875
Oei, D.G. 985-986, 992
Oehlinger, G. 873
O'Hare, S. A. 954, 977
Ohse, L. 952, 1040, 1089-1090, 1116
Ohse, R. W. 847, 864, 868, 889, 928, 953, 1110
Okamoto, H. 866-868, 873, 887, 894, 1042-1043, 1067-1068, 1127-1128
Oliver, D. S. 953, 956
Oliver, J. 910, 921
Onn, D. G. 1086
Orlov, A.N. 1088, 1114-1115
Osborne, D. W. 882, 928, 935
Osteryoung, R. A. 905
Ott, J.B. 928, 932, 935
Ovechkin, E. K. 986
Owens, D. W. 1036, 1086, 1112
Papin, G. 953-954

Parry, G. 847, 852-853, 859-860
Patterson, E. S. 1106-1107
Pavlov, O.N. 910, 920, 1085, 1110
Pavlovskaya, E. I. 891, 904, 1120
Pavlyuk, V. V. 873, 878
Pearson, T. G. 894-895, 985-986, 988, 1060, 1062
Pecharskii, V. K. 873, 878
Peizulaev, Sh. I. 910, 916, 1029, 1033
Pejovnik, S. 866
Pell, E.. M. 873-874, 878-879
Pellini, G. 997-998, 1001
Pelton, A.D. 847, 859, 863-864, 878, 882, 887-889, 899, 939- 940, 942, 952, 994-995, 997-998, 1000, 1037-1038, 1041, 1060, 1065, 1067-1068, 1085, 1087, 1096, 1099, 1109-1110, 1114, 1117, 1123-1128
Pepkiwitz, L. P. 929, 957, 982-983
Periaswami, G. 954, 976
Peric, Z. 954, 969
Perin, M. 1023
Perlow, M.R.J. 846-847, 849
Peters, K. 942, 1038, 1087, 1114
Petric, A. 997-998, 1000, 1067-1068
Pfeff, M. 911, 1034
Phelps, D. J. 1083, 1109, 1137
Phillips, B.A. 1117-1118, 1122
Phillips, J.L. 954, 960
Pihlar, B. 866
Pilbeam, A. 928, 937
Pillai, S. R. 927-928, 983
Pleshivtsev, A.D. 848, 868-869, 881, 887, 889, 892, 910, 954, 1029, 1033, 1043, 1054
Pletenets, S.S. 910, 944, 954, 1020, 1023, 1029-1030, 1032- 1033, 1039-1040, 1043, 1054, 1082-1084
Plotnikov, V. A. 1013-1014, 1077-1078, 1106
Podlesnyak, N.P. 903-904, 996-1004, 1008, 1071-1072, 1074
Poirier, D. M. 1035-1036, 1086, 1112
Ponomarev-Stepnoi, N.N. 954, 1043, 1046, 1056
Pool, R. A. H. 910, 954, 961
Popovkin, B.A. 998-999
Porter, J. T. 929
Potemkin, V.F. 941-943, 1-38, 1087-1088, 1114
Potts, J. R. 868
Pouchard, M. 926, 940, 942, 1035, 1037-1038, 1086-1087, 1113-1114
Prach, T. E. 954
Pratt, J.N. 997-999
Prins, G. 1127-1128
Privalov, Yu. V. 953-954, 976-977
Prohaazka, V. 910
Pulham, R.J. 846-847, 852-853, 858-860, 867-868, 871-872, 877, 882, 884-885, 889, 910-912, 914, 918, 921, 928, 930, 939-944, 946, 948-951, 977, 1029, 1042-1043
Quercigh, E. 997-998, 1001
Rabenau, A. 887
Rackel, D. 911, 1029, 1034
Raine, A.C. 910, 914, 954, 961
Rajan, M. 909-910, 925
Ramsey, W. J. 847
Rault, C. 910, 914
Redding, G. 1020
Reed, C. B. 868, 882, 889
Reed, E. L. 1020, 1022, 1024, 1082, 1084
Reetz, T. 910

Reimann, J. 911, 1029, 1034
Rengade, E. 117-118
Rettig, D. 910
Rhoades, J.W. 882-883, 1092
Rinck, E. 1057, 1071-1072, 1076, 1077-1078
Roben, G.D. 873
Roberts, P.G. 847, 859, 881-882, 886, 889, 1116
Robinson, P.L. 894-895, 985-986, 988, 1060, 1062
Rodgers, D.J. 985-986, 993, 1060, 1064
Rodgers, D. N. 910
Rodgers, S.J. 927-928, 930, 953-954, 1042-1043, 1050, 1092- 1093, 1118-1119
Roelich, F. 1086, 1089, 1115
Rohde, J. 911
Rollet, A. P. 953-954
Romanchenko, N.M. 985-986, 993-996, 998, 1000
Romanov, W. R. 868
Rosen, E. 985-986, 990
Ross, A. E. 910, 954-955, 961
Rosztoczy, F.E. 1077-1078, 1081, 1106, 1108, 1134, 1136
Rowan, R. 954-955
Roy, P. 909-910
Roy, R.J. 908, 910, 912
Rozanov, A.N. 882, 888-890
Rudorff, W. 1036
Rule, A. 985-987, 1060-1061
Rumbaut, N. 847, 882, 888-889, 910, 928, 953
Rutkauskas, V.J. 954, 966
Saagi, R. 909-910, 924, 953, 975, 977
Saboungi, M.L. 998, 1000, 1068
Sagawa, N. 1009-1010, 1013-1014, 1017-1019
Saint-Paul, P. 953, 970
Sakai, T. 954, 1043, 1055
Salmon, O.N. 846-847, 850, 858-860, 863-864, 953, 957
Salzano, F.J. 927-928, 935-936, 966, 1036, 1086, 1112
Samarceva, E. B. 901, 1001
Sanchez, P. 866
Sangster, J. 847, 859, 863-864, 878, 862, 887-889, 899, 939- 940, 952, 994-995, 1037, 1038, 1041, 1060, 1065, 1085, 1087, 1090, 1096, 1099, 1109- 1110, 1114, 1117, 1123-1128
San-Martin, A. 910
Sannier, J. 910
Satoh, T. 1020
Savage, H. W. 1029, 1032
Savchenkova, A. R. 8668
Savinov, V.B. 909-910, 916, 1029, 1033
Savolainen, J.E. 910, 1029, 1031-1032
Savostin, V. V. 1043, 1046
Scarborough, J. M. 954
Schafer, R. 1037-1038, 1086-1087, 1113-1114
Schauer, V. 954, 974, 1042-1043, 1045
Scheiba, M. 1065-1067
Scheil, E. 940
Scheldrich, W. S. 1125-1126
Schirmer, A. 878
Schmeding, A. 940, 942, 1037-1038, 1086-1087, 1114
Schewe-Miller, I. 1067-1068
Schmutzler, R.W. 1133
Schneider, H. 926, 954, 968, 1043

Schnyders, H. C. 1020, 1023, 1025, 1027
Schonfeld, F. W. 888
Schoulz, R. 1077-1079
Schram, R. P. C. 1013-1014
Schulze, E. 1036
Schurmann, E. 847
Schwarz, N.F. 1035-1036, 1042-1043, 1046
Seales, R.A. 847, 850-851
Secrist, D. R. 866, 868
Sednev, A. R. 977
Sedyshkin, P.A. 954, 1043, 1053
Seefurth, R.N. 876
Seliverstov, Kh. I. 8889, 891, 903-904, 954, 1043, 1053
Semmingsen, D. 1086
Sereda, G.N. 1118, 1121
Sergeev, G.P. 910, 913, 954, 964, 977, 981
Sextl, G. 873
Shakarov, Kh. O. 1127, 1129
Sharivker, V.S. 1060, 1064
Sharma, R.A. 876, 894, 896
Serebryakova, T. I. 866
Shereshevskii, V.A. 847-848, 854
Sherman, M. S. 944
Shevtsova, L. N. 986
Shibalovskaya, I. I. 1068
Shibraev, B. F. 891, 903, 1120
Shikhov, B.A. 976-977, 979-980, 1057, 1059
Shimkevich, A.L. 954, 1043, 1046, 1056
Shimojima, H. 1023
Shimp, L. A. 868
Shmatko, B.A. 848, 868-869, 881, 884, 887, 889, 891-892, 913, 964, 980, 1043, 1046
Shpil'rain, E.E. 846-848, 854, 859, 863-864, 868-869, 881887, 892, 910, 916, 944, 1023, 1029, 1033, 1084
Siegel, S. 928, 953, 957
Simandl, R.F. 847, 858
Sime, S. J. 985-986
Simm, P.A. 909-910, 918, 921, 954, 975, 977
Simmons, L. L. 1043
Simon, A. 1091-1092, 1094, 1117-1118, 1120
Simons, E.M. 1042-1044
Simpson, J.L. 946-947
Sinclair, V. M. 909-910, 954, 961, 982-983
Sitnikov, V.V. 1029-1030, 1118, 1121
Sizov, R. A. 942, 1087, 1114
Skladzien, S.B. 954, 965
Skorov, D. M. 890
Skuratov, O.A. or O. V. 909-910, 920, 1085, 1109-1110
Sleppy, W. 928
Slotnick, H. 1082
Smirnov, M.V. 902-904, 986, 1003-1004, 1008-1010, 1013- 1014, 1017, 1071-1072, 1075, 1077-1078, 1082
Smirnov-Averin, A. P. 928, 983
Smith, A. B. 868, 928
Smith, A. W. 914, 983
Smith, C.A. 909-910, 954, 975, 977
Smith, C. F. R. 953, 955
Smith, D.L. 954, 967
Smith, F.J. 846-847, 856, 858-859, 862, 863-864
Smith, G.S. 878-879

Smith, H.M. 846-847, 854, 858-859
Smith, R. J. 977
Smith, W.T. 902, 1002-1004, 1006-1007, 1010, 1014-1015, 1069-1070, 1072-1073, 1130-1132, 1134, 1136
Sneesby, G.V. 928-929
Sodomann, H. 1065-1066, 1068, 1096, 1099, 1101, 1124, 1126, 1128
Solin, S. A. 1112
Sollers, E. F. 909-910, 925, 1028-1029
Somer, M. 940, 9442, 952, 1037-1038, 1040-1041, 1086- 1087, 1089-1090, 1114, 1116
Sone, T. 1010, 1014, 1017-1018
Sorokin, V. P. 866, 926, 1035
Spicer, W. E. 1118
Sponer, R. 1072, 1074
Sreedharan, O. M. 953
Sridharan, R. 954, 976
Stavropoulos, G.P. 954, 968
Stearns, J. D. 928
Stein, V. 1068
Steinmetz, H. 954
Stepanov, Yu. P. 1034
Stepina, L.A. 881-882
Stevens, J. R. 983
Stockem, L. 1003-1004
Stocvkmann, H. J. 878
Strain, J.E. 889, 892
Strelnikova, L. N. 986
Strongin, R. A. 928
Su, M.T. 867-869
Subbotin, V.I. 848, 868-869, 881, 887-889, 891-892, 909-911, 913, 916, 928, 944, 954, 963-964, 976-977, 980, 1020, 1023, 1028-1029, 1032-1033, 1035-1036, 1039-1040, 1054, 1082-1084, 1109-1110
Such, H. 928, 1036
Suematsu, H. 1086
Suhrmann, R. 1039, 1089, 1115
Sullivan, E. A. 910
Sunami, H. 1118
Sundermann, H. 954, 974, 1042-1043, 1045
Sutula, R. A. 866
Suzuki, T. 1091-102, 1094
Swinhoe, R. 953, 969
Svob, L. 940, 1037
Szafranski, A.W. 848, 909, 911, 1109-1111
Taboada, A. 954, 1043, 1053
Takani, S. 954, 972
Takeda, K. 954, 972
Takeuchi, Y. 873, 875
Talbot, J. B. 856, 862
Tanazawa, Y. 1092, 1094
Tashiro, S. 1014, 1019
Tate, R. E. 888
Tausend, A. 1065-1066
Taylor, G.R. 954, 970-971, 1020, 1022
Tegman, R. 985-986, 990
Tepper, F. 926, 928, 930, 1043, 1050, 1086, 1089, 1091- 1093, 1112-1113, 1115, 1117-1119
Teske, K. 910, 977
Thiruvengadasami, A. 954, 1043, 1047, 1055-1056
Thomas, J. D. R. 1039, 1089, 1115
Thomas, J.S. 985-987, 1060-1061
Thompson, J. 909-910, 915

Thompson, J. C. 997-998
Thompson, R. 927-928, 937, 953-954, 974
Thorley, A.W. 910, 914, 927-928, 933-934, 954, 961, 1029, 1042-1043, 1052
Thormeier, K. 1020-1021, 1023-1027
Thunder, A.E. 847, 852-853, 859-860, 868, 871-872, 882, 884- 885, 910, 1029
Tilton, R. A. 1083, 1109, 1137
Timmermans, G. 1078
Tischer, R.P. 985-986, 990
Toguri, J.M. 994-995, 997
Tomkins, R. P. T. 903, 1003-1004, 1009-1010, 1013-1014, 1071- 1072, 1076, 1104, 1131
Tomoff, G. 1071-1072
Toth, L. M. 899
Touzain, P. 928, 1042-1043, 1045, 1091-1093, 1095, 1117- 1118, 1122-1123
Trevillon, E.A. 885, 928, 938, 944, 948-949, 952, 954
Trocki, I. 954
Troost, L. 909-910, 1028-1029
Tschalii, V. P. 1014, 1078, 1106
Tsirkina, E. A. 847, 859, 864
Tsiovkina, L.A. 1004, 1009, 1010, 1013-1014, 1017, 1078, 1082
Tumidajski, P.J. 994-995, 997
Tyzack, C. 953-954, 961, 1029, 1042-1043, 1052
Ugodnikov, G.G. 1115, 1127, 1129
Ullmann, H. 910, 954, 976-977
Upton, S.M. 894, 897, 985-986, 994
Uskov, A.A. 998-999
Vallet, P. 910
Van Arkel, A. E. 888-889
Valtierra, M.L. 882-883, 1092
Vana Varamban, S. 954, 1043, 1055
Van der Lugt, W. 873, 877-878, 994-996
Van der Marel, C. 872-873, 877-878, 994-996
Van Deventer, E.H. 847,852, 861, 928, 935-936
Van Klooser, H. S. 889
Van Oosten, A. B. 878
Veleckis, E. 846-847, 852, 856-859, 861-865, 882, 885, 893, 944-946, 976-977, 1020-1027
Vetter, J. E. 1034
Vigoroux, E. 939-940
Vinke, G.J.B. 873, 877
Vissers, D.R. 909-910, 917-919, 954, 970
Vodak, O. I. 873
Vogel, R.C. 1023-1025
Voitsekhovskii, A. E. 986
Volker, R. 847
Volchkov, L.G. 909, 911, 913, 928, 944, 954, 964, 977, 981
Volkov, I.V. 910, 920, 1085, 1110
Volnov, I. I. 1043, 1091-1092, 1117-1118
Von Hevesy, G. 977-978, 1057-1058
Von Schnering, H. G. 866, 872-873, 887, 939-941, 951-952, 1037- 1038, 1040-1041, 1086-1087, 1089-1090, 1114, 1116
Voorhees, B.G. 953, 958-959
Wada, T. 954, 972
Wade, S. W. 928, 1112
Wagner, R. K. 928
Walker, J. A. 914, 982-983
Walker, R.A. 997-999
Walters, S.L. 953, 955
Wang, F. E. 866
Ward, C. H. 944

Warnquist, B. 986
Wartenberg, H. 944, 1013-1014, 1039, 1077-1078
Watanabe, M. 873, 875
Watanabe, N. 902-903, 905, 1073
Waterbury, G.R. 954, 962
Weatherford, W.D. 882-883, 1091-1092
Weaver, J. H. 1036, 1086, 1112
Webb, R.E. 846-847, 854, 858-859
Weber, C. E. 954
Weeks, J. R. 927-928, 939-940, 954, 966-967, 969, 977
Wehle, V. 868
Weidmann, G. 953, 959
Weiler, F. B. 1111, 1113
Wells, H. L. 1078
Westbrook, D. 1037
Weston, J.R. 847-848, 857, 867-868, 870-871, 881-882, 886, 888-889, 893
Whipple, R. T. P. 859
White, J. C. 883, 952, 954-955
Whittingham, A.C. 909-910, 914, 921, 928, 938, 976-977
Wichelhaus, W. 951
Widmer, A.E. or E. E. 940, 1113
Wilke-Dörfurt, E. 1096-1097, 1123-1124
Willhelm, C. 928
Williams, D.D. 909-910, 912, 953, 956, 960, 976-977, 979, 982- 983, 1003-1004, 1042-1043, 1051
Willmann, P. 868
Winslow, P. W. 1110, 1113, 1123-1124, 1126
Winzer, R. 1003-1004
Wisnyl, L. G. 868
Wittig, G. 954, 968-969
Wobig, D. 1065-1067
Wolf, J. 952, 1040, 1089-1090, 1116
Wood, D. 878-879
Wood, D.A. 954, 974, 983
Wood, S. E. 900
Woodruff, R. W. 1020
Wriedt, H. A. 953
Wu, C.H. 846-847, 851, 858-859, 861
Yakimovich, K.A. 847-848, 854, 859, 864
Yakovlev, E. I. 887, 894
Yanagi, T. 847
Yatsenko, S.P. 1086-1088, 1090, 1096, 1098-1102, 1115, 1126- 1129
Yildirim, T. 928
Yoffe, A.A. 872-873, 875
Yokokawa, H. 1131-1132
Yonco, R.M. 847, 857, 859, 861-865, 867-868, 870-871, 881- 882, 885-886, 888-889, 892-893, 1023
Yoshimura, Y. 847
Young, R.S. 946-947
Yount, J.A. 954, 967
Yuhara, S. 910, 922
Yunker, W.H. 939-941
Zaezzhev, M. V. 1042-1043, 1046
Zagorulko, Yu. I. 911, 928, 938
Zalkin, A. 847
Zelenak, J. 1086, 1089, 1115
Zhakupov, Sh. R. 1127
Zhakupov, Kh. O. 1129
Zhou, O. 928

Zintl, E. 882, 951-952, 1040-1041
Zotov, V.V. 910, 913, 954, 964, 977, 981
Zusman, L.L. 878, 942-943, 1038, 1087-1088, 1114

IUPAC-NIST SOLUBILITY DATA SERIES

Editor-in-Chief
M. Salomon

Sub-Editor
Solid/Liquid Systems
W. Voigt

EDITORIAL BOARD

M. W. Chase (USA)
Chr. Balarew (Bulgaria)
R. Cohen-Adad (France)
J. Eysseltovà (Czech Republic)
P. G. T. Fogg (UK)
H. Gamsjäger (Austria)
M. Gaune-Escard (France)
A. Goto (Japan)
J. Hála (Czech Republic)
E. Königsberger (Austria)
J. W. Lorimer (Canada)
C. Magãlhaes (Portugal)
J. Sangster (Canada)
K. Sawada (Japan)
M.-Th. Saugier Cohen-Adad (France)
P. Scharlin (Finland)
D. G. Shaw (USA)
A. Skrzecz (Poland)
R. P. T. Tomkins (USA)
J. Vanderdeelen (Belgium)
V. M. Valyashko (Russia)
W. E. Waghorne (Ireland)

Managing Editor
M. W. Chase
National Institute of Standards and Technology

11. IUPAC-NIST Solubility Data Series: Published and Forthcoming Volumes

Volume	Author, *Title*
1	H. L. Clever, *Helium and Neon*
2	H. L. Clever, *Krypton, Xenon and Radon*
3	M. Salomon, *Silver Azide, Cyanide, Cyanamides, Cyanate, Selenocyanate and Thiocyanate*
4	H. L. Clever, *Argon*
5/6	C. L. Young, *Hydrogen and Deuterium*
7	R. Battino, *Oxygen and Ozone*
8	C. L. Young, *Oxides of Nitrogen*
9	W. Hayduk, *Ethane*
10	R. Battino, *Nitrogen and Air*
11	B. Scrosati and C. A. Vincent, *Alkali Metal, Alkaline Earth Metal and Ammonium Halides, Amide Solvents*
12	C. L. Young, *Sulfur Dioxide, Chlorine, Fluorine and Chlorine Oxides*
13	S. Siekierski, T. Mioduski and M. Salomon, *Scandium, Yttrium, Lanthanum and Lanthanide Nitrates*
14	H. Miyamoto, M. Salomon and H. L. Clever, *Alkaline Earth Metal Halates*
15	A. F. M. Barton, *Alcohols with Water*
16/17	E. Tomlinson and A. Regosch, Antibiotics: 1,β-Lactam Antibiotics
18	O. Popovych, *Tetraphenylborates*
19	C. L. Young, *Cumulative Index: Volumes 1-18*
20	A. L. Horvath and F. W. Getzen, *Halogenated Benzenes, Toluenes and Phenols with Water*
21	C. L. Young and P. G. T. Fogg, *Ammonia, Amines, Phosphine, Arsine, Stibine, Silane, Germane and Stannane in Organic Solvents*
22	T. Mioduski and M. Salomon, *Scandium, Yttrium, Lanthanum and Lanthanide Halides in Non-aqueous Solvents*
23	T. P. Dirkse, *Copper, Silver, Gold and Zinc, Cadmium, Mercury Oxides and Hydroxides*
24	W. Hayduk, *Propane, Butane and 2-Methylpropane*
25	C. Hirayama, Z. Galus and C. Guminski, *Metals in Mercury*
26	M. R. Masson, H. D. Lutz and B. Engelen, *Sulfites, Selenites and Tellurites*
27/28	H. L. Clever and C. L. Young, *Methane*
29	H. L. Clever, *Mercury in Liquids, Compressed Gases, Molten Salts and Other Elements*

30 H. Miyamoto and M. Salomon, *Alkali Metal Halates, Ammonium Iodate and Iodic Acid*
31 J. Eysseltova and T. P. Dirkse, *Alkali Metal Orthophosphates*
32 P. G. T. Fogg and C. L. Young, *Hydrogen Sulfide, Deuterium Sulfide and Hydrogen Selenide*
33 P. Franzosini, *Molten Alkali Metal Alkanoates*
34 A. N. Paruta and R. Piekos, *4-Aminobenzenesulfonamides. Part I: Non-cyclic Substituents*
35 A. N. Paruta and R. Piekos, *4-Aminobenzenesulfonamides. Part II: 5-membered Heterocyclic Substituents*
36 A. N. Paruta and R. Piekos, *4-Aminobenzenesulfonamides. Part III: 6-membered Heterocyclic Substituents and Miscellaneous Systems*
37 D. G. Shaw, *Hydrocarbons with Water and Seawater. Part I: Hydrocarbons C5 to C7*
38 D. G. Shaw, *Hydrocarbons with Water and Seawater. Part II: Hydrocarbons C8 to C36*
39 C. L. Young, *Cumulative Index: Volumes 20–38*
40 J. Hala, *Halides, Oxyhalides and Salts of Halogen Complexes of Titanium, Zirconium, Hafnium, Vanadium, Niobium and Tantalum*
41 C.-Y. Chan, I. N. Lepeshkov and K. H. Khoo, *Alkaline Earth Metal Perchlorates*
42 P. G. T. Fogg and W. Gerrard, *Hydrogen Halides in Non-aqueous Solvents*
43 R. W. Cargill, *Carbon Monoxide*
44 H. Miyamoto, E. M. Woolley and M. Salomon, *Copper and Silver Halates*
45/46 R. P. T. Tomkins and N. P. Bansal, *Gases in Molten Salts*
47 R. Cohen-Adad and J. W. Lorimer, *Alkali Metal and Ammonium Halides in Water and Heavy Water (Binary Systems)*
48 F. Getzen, G. Hefter and A. Maczynski, *Esters with Water. Part I: Esters 2-C to 6-C*
49 F. Getzen, G. Hefter and A. Maczynski, *Esters with Water. Part II: Esters 7-C to 32-C*
50 P. G. T. Fogg, *Carbon Dioxide in Non-aqueous Solvents at Pressures Less Than 200 kPa*
51 J. G. Osteryoung, M. M. Schneider, C. Guminski and Z. Galus, *Intermetallic Compounds in Mercury*
52 I. Lambert and H. L. Clever, *Alkaline Earth Hydroxides in Water and Aqueous Solutions*
53 C. L. Young, *Cumulative Index: Volumes 40–52*
54 W. E. Acree, Jr., *Polycyclic Aromatic Hydrocarbons in Pure and Binary Solvents*
55 S. Siekierski and S. L. Phillips, *Actinide Nitrates*
56 D. Shaw, A. Skrzecz, J. W. Lorimer and A. Maczynski, *Alcohols with Hydrocarbons*
57 W. Hayduk, *Ethene*
58 W. E. Acree, Jr., *Polycyclic Aromatic Hydrocarbons: Binary Non-aqueous Systems, Part I: Solvents A–E*
59 W. E. Acree, Jr., *Polycyclic Aromatic Hydrocarbons: Binary Non-aqueous Systems, Part II: Solvents F–Z*
60 A. L. Horvath and F. W. Getzen, *Halogenated Methanes with Water*
61 C.-Y. Chan, K. H. Khoo, E. S. Gryzlova and M.-T. Saugier-Cohen Adad, *Alkali Metal and Ammonium Perchlorates, Part I: Lithium and Sodium Perchlorates*
62 P. Scharlin, *Carbon Dioxide in Water and Aqueous Electrolyte Solutions*
63 H. U. Borgstedt and C. Guminski, *Metals in Liquid Alkali Metals, Part I: Be to Os*
64 H. U. Borgstedt and C. Guminski, *Metals in Liquid Alkali Metals, Part II: Co to Bi*
65 J. J. Fritz and E. Königsberger, *Copper(I) Halides and Pseudohalides*
66 J. Eysseltová and T. P. Dirkse, *Ammonium Phosphates*. JPCRD **27(5)**, 1289 (1998).
67 A. L. Horvath, F. W. Getzen and Z. Maczynska, *Halogenated Ethanes and Ethenes with Water*. JPCRD **28(2)**, 395 (1999).
68 A. L. Horvath and F. W. Getzen, *Halogenated Aliphatic Hydrocarbons C_3–C_{14} with Water*. JPCRD **28(3)**, 649 (1999).
69 A. Skrzecz, D. Shaw and A. Maczynski, *Ternary Alcohol-Hydrocarbon-Water Systems*. JPCRD **28(4)**, 983 (1999).
70 Yu. P. Yampol'skii, R. Paterson and P. G. T. Fogg, *Gases in Glassy Polymers*. JPCRD **28(5)**, 1255 (1999).
71 V. P. Sazonov, G. T. Hefter and K. N. Marsh, *Binary Nitromethane Systems*. JPCRD **29(5)**, 1165 (2000).
72 V. P. Sazonov, K. N. Marsh, and D. G. Shaw, *Ternary and Quaternary Nitromethane Systems*. JPCRD **29(6)**, 1447 (2000).
73 Chr. Balarew and T.P. Dirkse, *Metal and Ammonium Formate Systems*. JPCRD **30(1)**, 1 (2001).
74 J. Hála, *Actinide Carbonates and Carbon-Containing Compounds*. JPCRD **30(2)**, 531 (2001).
75 H. U. Borgstedt and C. Guminski, *Non-Metals in Liquid Alkali Metals*. JPCRD **30(4)**, 835 (2001).
76 P. G. T. Fogg, *Solubility of Ethyne in Liquids*. JPCRD **30(6)** (in press, 2001).

Volumes 1–53 published by Pergamon Press.
Volumes 54–65 published by Oxford University Press.
Volumes 66 and above published in the *Journal of Physical and Chemical Reference Data* (JPCRD).