# General Discussion of Phase Diagrams

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## I. GLOSSARY

(1) **Alkemade (Van Rijn van Alkemade) Theorem:** The direction of falling temperature on the boundary curve of two intersecting primary phase areas is always away from the Alkemade line (see (2)). If the Alkemade line intersects the boundary curve, the point of intersection represents a temperature maximum on the boundary curve. If the Alkemade line does not intersect the boundary curve, then the maximum on the boundary curve is represented by that end which if prolonged would intersect the Alkemade line.

(2) **Alkemade Line:** In a ternary phase diagram a straight line connecting the composition points of two primary phases whose areas are adjacent and the intersection of which forms a boundary curve.

(3) **Boundary Line (Curve):** The intersection of adjoining liquidus surfaces in a ternary phase diagram. The area enclosed by a series of boundary lines is termed a primary phase area.

(4) **Components (of a System):** The smallest number of independently variable chemical constituents necessary and sufficient to express the composition of each phase present in any state of equilibrium. Zero and negative quantities of the components are permissible in expressing the composition of a phase.

(5) **Composition (or Compatibility) Tetrahedron:** In the phase diagram of a condensed quaternary system, the four triangular planes connecting the compositions of four solid phases which can coexist in equilibrium with liquid. The composition of the liquid is represented by a quaternary invariant point, which may lie within the composition tetrahedron (eutectic point) or outside the tetrahedron (peritectic or reaction point).

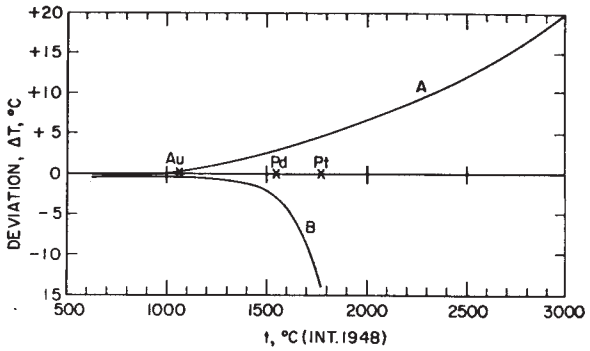


FIG. I.—Comparison of Geophysical Laboratory Temperature Scale of 1914 and International Temperature Scale of 1927 with that of the International Temperature Scale of 1948. (A) $\Delta T$ = Int. 1927—Int. 1948; (B) $\Delta T$ = Geophysical 1914—Int. 1948.

(6) **Composition (or Compatibility) Triangle:** In the phase diagram of a condensed ternary system the three joins connecting the composition points of the three primary phases whose liquidus surfaces meet at a point.

If in the diagram of a ternary system, all of the Alkemade lines (see (2)) be constructed, the ternary diagram will be divided into a number of composition triangles. If the three substances designating the vertices of any of these triangles are not miscible in the solid state, they represent the final equilibrium products of crystallization at the solidus temperature for compositions within the triangle. When crystalline solid solutions exist between any of the three substances, the final products of crystallization may be reduced in number by one or two.

(7) **Condensed System:** One in which the vapor pressures of the solid and liquid phases present are negligible or small in comparison to the atmospheric pressure. For such systems, e.g., the refractory oxide ones, as the pressure may be considered constant, one degree of freedom is lost, and the phase rule may be modified accordingly: The sum of the number of phases plus the number of degrees of freedom equals the sum of the number of components plus one (instead of two).

(8) **Congruent Melting Point:** At a specified pressure, the temperature at which a solid substance changes to a liquid of identical chemical composition.

(9) **Conjugate Phase:** One of two phases in equilibrium with each other defining a conode (see (10)).

(10) **Conode (or Tie Line):** For a particular temperature, the straight line connecting the compositions of two (conjugate) phases in equilibrium with each other.

(11) **Critical Pressure:** In a one component system, the unique pressure at which the liquid and vapor phases become identical.

(12) **Critical Temperature:** In a one component system, the unique temperature at which the liquid and vapor phases become identical. At the critical temperature the system passes from a heterogeneous state to a homogeneous phase. Above the critical temperature no liquid phase can exist however great the pressure.

(13) **Degrees of Freedom (or Variance):** "The number of intensive variables which can be altered independently and arbitrarily without bringing about the disappearance of a phase or the formation of a new one is called the number of degrees of freedom of a system."[4] Intensive variables are those which are independent of mass, such as pressure, temperature, and composition.

The number of degrees of freedom of a system may also be defined as the "number of variable factors, temperature, pressure, and concentration of the components, which must be arbitrarily fixed in order that the condition of the system may be perfectly defined."[5]

A system is termed invariant, mono-variant, bivariant, tri-variant, and so on, according to whether it possesses, respectively, 0, 1, 2, 3, etc., degrees of freedom.

(14) **Devitrification:** The formation of crystalline material from glass.

(15) **Enantiotropic Forms:** Polymorphic forms (see (43)) which possess an inversion point at which they are in reversible equilibrium, that is, they are interconvertible; for example, $\alpha$- and $\beta$-$2CaO \cdot SiO_2$ and $\alpha$- and $\beta$-quartz. In such cases the vapor-pressure curves intersect below the melting point of the highest temperature polymorphic form.

(16) **Equilibrium:** From the theoretical, thermodynamic standpoint, the conditions for equilibrium can be exactly and precisely defined; because for any reversible process, no useful energy passes from or into the system.

From the practical, experimental standpoint, however, the actual attainment of an equilibrium state within a system may be very difficult to assess. Three criteria have been used variously either singly or together: (1) The time criterion, based on the constancy of phase properties with the passage of time; (2) the approach from two directions criterion, yielding under the same conditions phases of identical properties, e.g., from undersaturation and supersaturation, or from raising and lowering the temperature to the same value; and (3) the attainment by different procedures criterion, producing phases having the same properties when the same conditions, with respect to the variants, are reached.

None of these criteria are entirely adequate for excluding metastable relationships. In silicate systems, in particular, metastable equilibrium is common and may persist for long periods of time and at high temperatures. In the final analysis, interpretation and judgment by the investigator are of prime importance.

(17) **Eutectic:** A eutectic represents an invariant (unique temperature, pressure, composition) point for a system at which the phase reaction on the addition or removal of heat results in an increase or decrease, respectively, of the proportion of liquid to solid phases, without change of temperature. At a eutectic temperature the composition of the liquid phase in equilibrium with the solid phases can always be expressed in terms of positive quantities of the solid phases.

The eutectic composition is that combination of components in a simple system having the lowest melting temperature of any ratio of the components and is located at the intersection of the two solubility curves in a binary system and of the three solubility surfaces in a ternary system.

(18) **Eutectoid:** An invariant point (see (24)) composed solely of crystalline phases, at which the phase reaction on change of heat content at constant temperature results in a change in proportions of the solid phases exactly analogous to that at a eutectic point (see (17)), in which one of the phases is liquid.

(19) **Glass:** In ceramic phase equilibria studies glass refers to supercooled liquid.

(20) **Heterogeneous Equilibrium:** A system is heterogeneous and is in heterogeneous equilibrium when it consists of two or more homogeneous portions (phases) in equilibrium with each other. In the usual consideration of the phase rule, changes in equilibrium due to electrical, magnetic, capillary, and gravitational forces are not considered; but only those changes due to temperature, pressure, and concentration.

(21) **Homogeneous Equilibrium:** A system is homogeneous and is in homogeneous equilibrium when it consists of one phase and all processes or reactions occurring within it are in reversible equilibrium. A homogeneous phase need not consist of one atomic or molecular species, e.g., in the single phase system sodium chloride solution, $Na^+$, $Cl^-$, $H_3O^+$, $OH^-$, $H_2O$, and associated molecules may all be present but the reactions involving them are at equilibrium.

(22) **Incongruent Melting Point:** At a specified pressure the temperature at which one solid phase transforms into another solid phase plus a liquid phase both of different chemical compositions than the original substance.

(23) **Indifferent Point:** In a two or more component system the special conditions where two phases become identical in composition and the system loses one degree of freedom. Typical cases include the maximum or minimum in a solid solution series and the melting point of a congruently melting compound.

(24) **Invariant Point:** The particular conditions within a system, in terms of pressure, temperature, and composition, for which the system possesses no degrees of freedom (see (13)) constitute the invariant points.

Stated differently, at an invariant point, no independent changes in the state of the system can be made.

(25) **Inversion Point:** The temperature at which one polymorphic form of a substance (see (43)) changes into another under invariant conditions.

(26) **Isobar:** The locus of all points of constant pressure.

(27) **Isofract:** For compositions within a ternary system the locus of all glasses of constant index of refraction.

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[4] F. H. MacDougall, "Thermodynamics and Chemistry," John Wiley and Sons, New York, 1939.

[5] See Alexander Findlay, A. N. Campbell, and N. O. Smith, under "Theory" in "Selected Bibliography," Part V.

(28) **Isopleth:** A line in a phase diagram of constant composition.

(29) **Isoplethal Study:** The method of considering the changes occurring in a system in which the composition variable is held constant and the temperature varied.

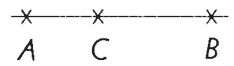
(30) **Isotherm:** In a ternary system the locus of all points on the liquidus of constant temperature.

(31) **Isothermal Study:** The method of considering the changes occurring in a system in which the temperature variable is held constant and the composition (or pressure) is varied.

(32) **Join:** The region of a phase diagram representing all mixtures that can be formed from a given number of selected compositions. A join may be binary (straight line), ternary (plane), etc., depending on the number of selected compositions, which need not be compounds. Each selected composition, however, must be incapable of formation from the others.

(33) **Le Chatelier's Theorem:** If a system in equilibrium is disturbed, a reaction tends to take place which opposes the effect of the disturbance, i.e., one by which the effect is partially annulled. The theorem of Le Chatelier is an important augment to the phase rule for it enables one to predict qualitatively the effect of external changes on the equilibrium of a system.

(34) **Lever Rule (or Center of Gravity Principle):** When a particular composition separates into only two phases, the given composition and that of the two phases are colinear; furthermore, the amounts of the two separated phases are inversely proportional to their distances from the given composition. Thus, in the adjacent figure, $A$ and $B$ represent the compositions of two phases formed from composition $C$: Amt. of $A \times$ length $AC$ = Amt. of $B \times$ length $BC$ or $A/B = BC/AC$




(35) **Liquidus:** The locus of temperature-composition points representing the maximum solubility (saturation) of a solid phase in the liquid phase. In a binary system, it is a line; and in a ternary system, it is a surface, usually curved. At temperatures above the liquidus, the system is completely liquid, and a point on the liquidus represents equilibrium between liquid and, in general, one crystalline phase (the primary one).

(36) **Metastable Phase:** A phase exists metastably in a system if it would not be present at final (thermodynamic) equilibrium, under unchanged conditions, and if the system is not approaching thermodynamic equilibrium at an observable rate.

(37) **Monotropic Forms:** In certain instances of polymorphism (see (43)), the vapor-pressure curves of the two forms do not meet below the melting point. They, therefore, lack a stable inversion point, and the form with the higher vapor pressure is metastable with respect to the other at all temperatures below the melting point. Such forms are called monotropic and are not interconvertible.

(38) **Peritectic Point:** An invariant point (see (24)) at which the composition of the liquid phase in equilibrium with the solid phases cannot be expressed in terms of positive quantities of the solid phases. Whereas the composition of a eutectic point always lies between or within the composition limits of the solid phases in equilibrium with liquid, the composition of a peritectic point always lies outside the composition limits.

At a peritectic point the intersecting univariant curves do not produce a minimum point on the liquidus curve as for a eutectic.

(39) **Peritectoid:** An invariant point (see (24)) composed entirely of crystalline phases, at which the phase reactions on change of heat content at constant temperature are exactly analogous to those at a peritectic point (see (38)), in which one of the phases is liquid.

(40) **Phase:** Any portion, including the whole, of a system which is physically homogeneous within itself and bounded by a surface so that it is mechanically separable from any other portions. A separable portion need not form a continuous body, as for example, one liquid dispersed in another.

A system composed of one phase is a homogeneous system; a system composed of more than one phase is heterogeneous; and inorder for the phase rule to apply, each phase must be in homogeneous as well as heterogeneous equilibrium.

(41) **Phase Rule:** For a system in equilibrium, the sum of the number of phases plus the number of degrees of freedom must equal the sum of the number of components plus two, or $P + F = C + 2$.

(42) **Piercing Point:** In a quaternary system, the intersection of a univariant curve with a ternary joint (see (32)) at a point other than a ternary invariant point. The univariant curve represents the compositions of liquids that can exist in equilibrium with three particular solid phases. The composition of these solid phases usually all lie in the plane of the ternary join if the intersection is a ternary invariant point, but they cannot all lie in that plane if the intersection is a piercing point.

(43) **Polymorphism:** The property possessed by some substances of existing in more than one crystal form, all forms being of the same chemical composition but differing in crystalline structure and physical properties, and yielding identical liquid or gaseous phases on melting or evaporating.

(44) **Primary Phase:** The only crystalline phase which can exist in equilibrium with liquid of a given composition. The primary phase is the first crystalline phase to appear on cooling a composition from the liquid state; or conversely, it is the last crystalline phase to disappear on heating a composition to melting (see, also, Boundary Line (3) and Liquidus (35)).

(45) **Primary Phase Region:** The locus of all compositions in a phase diagram having a common primary phase.

(46) **Pseudo System:** It is frequently convenient or necessary to refer to portions of a binary or ternary, etc., system which are not (true) subsystems (see (49)). In such instances the term pseudo binary, or pseudo ternary, etc., is used.

For example, in Fig. XIV, $3CaO \cdot Al_2O_3$-$2CaO \cdot SiO_2$ is a pseudo binary system and $Al_2O_3$-$CaO \cdot Al_2O_3 \cdot 2SiO_2$-$3Al_2O_3 \cdot 2SiO_2$ is a pseudo ternary system. A ternary system must consist of components and be bounded by three binary systems. In the pseudo ternary system cited, one of the boundary lines, $3Al_2O_3 \cdot 2SiO_2$-$CaO \cdot Al_2O_3 \cdot 2SiO_2$, is only a pseudo binary system, as no combination of $CaO \cdot Al_2O_3 \cdot 2SiO_2$ and $3Al_2O_3 \cdot 2SiO_2$ can yield $Al_2O_3$ which appears as a primary phase.

(47) **Solid Solution:** A single crystalline phase which may be varied in composition within finite limits without the appearance of an additional phase.

(48) **Solidus:** The locus of temperature-composition points in a system at temperatures above which solid and liquid are in equilibrium and below which the system is completely solid. In binary diagrams without solid solutions, it is a straight line, representing constant temperature, and with solid solutions, it is a curved line or combination of curved and straight lines. Likewise, in ternary systems, the solidus is represented by a flat plane or a curved surface, respectively.

(49) **Subsystem:** Any portion of a binary, ternary, etc. system which can be treated as an independent binary or ternary, etc. system. The selected substances designating the subsystem must be components for the subsystem (see (4)). In the $CaO$-$Al_2O_3$ binary system (Fig. 231), the lime-alumina compounds with congruently melting points form binary systems with each other, for example, the $CaO \cdot 2Al_2O_3$-$CaO \cdot Al_2O_3$ and the $CaO$-$CaO \cdot Al_2O_3$ systems; and in the ternary system $CaO$-$Al_2O_3$-$SiO_2$ (Fig. XIV), the binary joins, such as $CaO \cdot SiO_2$-$CaO \cdot Al_2O_3 \cdot 2SiO_2$ are true binary systems, and the three congruently melting compounds, $CaO \cdot SiO_2$, $CaO \cdot Al_2O_3 \cdot 2SiO_2$, and $2CaO \cdot Al_2O_3 \cdot SiO_2$, whose common boundary lines meet in a eutectic, constitute a true ternary system.

(50) **System:** Any portion of the material universe which can be isolated completely and arbitrarily from the rest for consideration of the changes which may occur within it under varying conditions.

The term *system* is used in two senses: the general and the specific. In the general sense, one specifies a system by naming the chosen components, for example, the binary system $CaO$-$Al_2O_3$, or the ternary system $K_2O$-$B_2O_3$-$H_2O$. In the specific sense, one may designate restricted portions of a "general" system for study or discourse. Thus one may refer to an invariant system or bi-variant system, etc. in which the restriction is based on the degrees of freedom (see (13)). One may also refer to a one phase (homogeneous) system (for example, system water vapor) or to a two phase (heterogeneous) system (for example, system calcium disilicate-liquid), etc., in which case the restriction is based on the number of phases present. Finally, one may refer to a system in which the restriction is based on chemical composition, for example, the system 20 per cent $Li_2O \cdot SiO_2$-80 percent $Li_2O \cdot B_2O_3$. The use of the term system to designate a particular chemical com position is not necessary and should be avoided.

If the definition of system be kept in mind, the varied use of the word need not be confusing and can easily be interpreted in context.

(51) **Tie Line:** See Conode (10).

(52) **Variance:** See Degrees of Freedom (13).

## II. THE PHASE RULE

### (1) Statement

The basis of all work on equilibrium diagrams is, of course, the phase rule of Willard Gibbs.[6] Its use has been greatly facilitated by the interpretations of Roozeboom,[7] Schreinemakers,[8] and others. Extensive explanations are to be found in textbooks on physical chemistry or books devoted exclusively to the phase rule (see V. Selected Bibliography, (1)).

The diagram known variously as phase diagram, equilibrium diagram, etc., is essentially a graphical expression of the phase rule. Equation (1) gives the usual mathematical form of the phase rule.

$$P + F = C + 2 \qquad (1)$$

$C$ = number of components of system.
$P$ = number of phases present at equilibrium.
$F$ = degrees of freedom (variance) of system.

The terms used in equation (1) as well as others necessary to an understanding and application of the phase rule are defined in the Glossary.

### (2) Limitations

The phase rule applies only to equilibrium states of a system, which require both homogeneous equilibrium within each phase and heterogeneous equilibrium between co-existing phases. The phase rule does not depend on the nature of the components or on the nature and amounts of the phases present, but only on their numbers; nor does it give information concerning rates of reactions.

A system in equilibrium always obeys the phase rule, but conformance, in itself, is not a sufficient test for equilibrium, because of the possible existence of nonequilibrium phases and conditions. Non-conformance with the phase rule, however, is proof that equilibrium conditions do not exist.

The phase rule provides the basis for the classification, according to number of components, of the diverse cases of chemical equilibrium. If the number of components be known, which is usually the case for a specified system, the sum of the number of phases and the number of degrees of freedom is fixed at $C$ plus 2.

The number of components plus two also represents the maximum number of phases that can coexist at equilibrium, as the degrees of freedom ($F$) can never be less than 0 (at invariant conditions).

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[6] (*a*) J. W. Gibbs, "Equilibrium of Heterogeneous Substances," *Trans. Conn. Acad. Sci.*, **3**, 108–248, 343–524 (1874–78).

(*b*) J. W. Gibbs, The Collected Works of J. Willard Gibbs, Vol. I, pp. 54–371. Longmans, Green and Co., New York, 1928.

[7] H. W. B. Roozeboom, Die heterogenen Gleichgewichte, 6 vols. F. Vieweg Co. Sohn, Braunschweig, 1911.

[8] F. A. H. Schreinemakers, "Mischkristalle in Systemendreier Stoffe," *Z. physik. Chem.*, **50** [2] 169–99: **51** [5] 547–76; **52** [5] 513–50 (1905).

## III. INTERPRETATION OF DIAGRAMS

### *(1) One-Component Systems*

The independent variables in a one-component system are limited to temperature and pressure because the composition is fixed. It follows from the phase rule that the system is bivariant if one phase is present, univariant if two phases are present and invariant if three are present. A diagram of a one-component system in which the independent variables, temperature and pressure, are the abscissa and ordinate, respectively, is shown in Fig. II. The following facts are observed:

(1) Curve *F-A* (univariant) is the sublimation curve for modification *A*.

(2) Curve *A-B* (univariant) is the sublimation curve for modification *B*.

(3) Curve *B-C* (univariant) is the vapor pressure curve for the liquid.

(4) Curve *A-D* (univariant) is the transition curve for modifications *A* and *B* and represents the change of the transition point with pressure.

(5) Curve *B-E* (univariant) is the melting curve for modification *B* and represents the change of the melting point with pressure.

(6) Point *A* (invariant) is the transition point for the two crystalline modifications. It is called a triple point since it is the point at which three phases (two solids and vapor) are in equilibrium.

(7) Point *B* is the triple point (invariant) for the equilibrium between crystalline modification *B*, liquid, and vapor.

(8) The system is bivariant in all parts not on these lines or their intersections.

In dealing with refractory substances it is at present impossible, with a few exceptions, to measure directly the vapor pressure of the solid and liquid phases. It is possible, however, to construct diagrams for refractory substances showing qualitatively the vapor pressure for the different phases if the temperature-stability relations are known because the unstable phase always has a higher vapor pressure than the stable phase even though the vapor pressure is infinitesimally small.

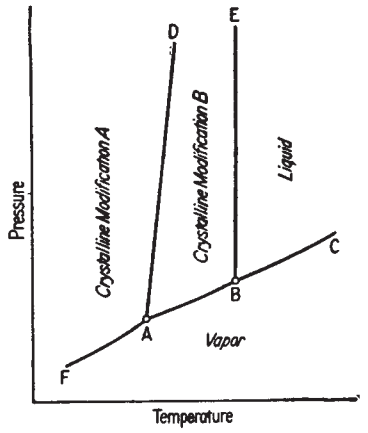


FIG. II.—Phase relations in a one-component system.

### *(2) Two-Component Systems*

Two-component systems have three independent variables, namely, temperature, pressure, and composition. In systems of importance in ceramics where the vapor pressure remains very low for large variations in temperature, the pressure variable and the vapor phase may be eliminated from consideration.

Systems with the pressure variable eliminated are called condensed systems. The reduced phase rule by which such systems may be represented is shown in equation (2) in which $P$ refers only to solid and liquid phases.

$$P + F = C + 1 \qquad (2)$$

In binary systems under these conditions three coexisting phases produce an invariant condition, two a univariant condition, and one a bivariant condition.

In representing condensed binary systems it is customary to make the ordinate the temperature scale and the abscissa the composition scale. In Fig. III, the intersection of the ordinate with the abscissa at $T_0$ represents 100 percent $S_1$ (and 0 percent $S_2$); the intersection at $T_x$ represents 100 percent $S_2$ (and 0 percent $S_1$). The scale as labeled, reading from left to right, refers to percentage of $S_2$ present; the percentage of $S_1$ represented by any point equals 100 − $S_2$. The composition variable is usually given in weight percent or mole percent, according to convenience; occasionally in weight fraction or mole fraction.

## (A) Binary Systems Without Solid Solutions

### *(a) No Compounds Present*

In Fig. III is shown a simple type of condensed binary system with (1) no intermediate compounds, (2) complete solubility in the liquid state, and (3) no solubility (i.e., no solid solution) between the solid phases. The point, $C_1$, is an invariant point of the eutectic type where two solid phases (components $S_1$ and $S_2$) and liquid (of composition 40% $S_2$, 60% $S_1$) are in equilibrium. A change in either variable will cause one or more phases to disappear. The curves $F$-$C_1$ and $G$-$C_1$ determine the position of univariant equilibrium. The coexistence of both phases (one solid and one liquid) can be maintained with change of one variable if a compensatory change is made in the other, the proportion of the two phases changing accordingly. The univariant boundary defines the quantitative relations of the variables.

In Fig. III, the vertical boundaries represent one-component systems. The solid phases, $S_1$ and $S_2$, representing these components have sharp melting points at the temperatures $F$ and $G$, respectively. Elsewhere, the $F$-$C_1$ and $G$-$C_1$ (liquidus) curves separate the one phase (liquid) region from the areas where both solid and liquid are present.

The difference between a one-phase region and a region representing two or more phases in equilibrium is a basic concept in the interpretation of phase diagrams

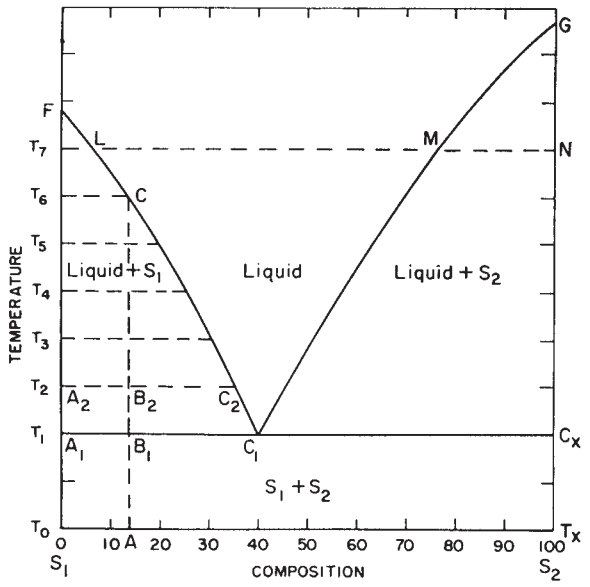


FIG. III.—Two-component system without intermediate compounds or solid solutions.

Every location within a one phase region, such as in the field designated *Liquid* in Fig. III, represents an actual state of the system, in terms of temperature and concentration variables. Locations within a two-phase region, however, do not represent actual states, but merely correspond to the overall chemical composition of two phases in equilibrium with each other, for example, points in the fields designated *Liquid* + $S_1$, *Liquid* + $S_2$, and $S_1$ + $S_2$, in Fig. III. The two-phase areas are, in effect, gaps or voids in which no single homogeneous phase can exist. To construct isobaric diagrams, it is necessary and sufficient to know the one-phase-region boundaries.[9]

*Mechanics of Crystallization:* Changes in the system illustrated in Fig. III may be followed by varying either temperature or composition. On heating, a mass of composition $C_1$ will show sharp melting at the temperature $T_1$. This is the lowest temperature in this system at which liquid is in equilibrium with solids (the eutectic temperature). Conversely, a homogeneous liquid of this composition will crystallize completely at this same temperature, on cooling, provided equilibrium conditions are maintained. Since neither of the variables, temperature or composition, can be changed without the complete disappearance of one or more phases, the point $C_1$ is an invariant point.

A liquid of composition $A$ on cooling under equilibrium conditions from a temperature above $T_6$ will behave quite differently. The substance will remain a homogeneous liquid until temperature $T_6$ is reached, when the first infinitesimal amount of the solid with composition $S_1$ will crystallize. Upon further cooling, $S_1$ will continue to crystallize while the composition of the liquid follows curve $C$-$C_1$.

[9] See J. S. Marsh, under "Theory" in Selected Bibliography, Part V.

At any temperature the composition of the liquid coexisting with the solid is represented by the point of intersection of the horizontal line corresponding to that temperature with the liquidus curve. The relative amounts of solid and liquid coexisting are represented by the relative lengths of the temperature horizontal from the composition of the initial material to intersection with the liquidus and with the vertical, $S_1$-$F$, respectively. Thus, composition $A$ at the temperature $T_2$ will consist of a solid of composition $S_1$ and a liquid of $C_2$ in the ratio of line lengths $B_2$-$C_2$/$A_2$-$B_2$.

With further cooling, solid $S_1$ will continue to crystallize until the temperature of the eutectic, $C_1$, is reached. The material will remain, because of the heat of crystallization, at that temperature until completely crystallized into a mixture of solids $S_1$ and $S_2$. The ratio of the amounts of the two solid substances can be found by the same lever rule $S_1/S_2 = A$-$S_2/A$-$S_1$.

If the two solids, $S_1$ and $S_2$ (Fig. III), are mixed in such proportion as represented by point $A$ and are heated, no reaction will take place until the temperature $T_1$, of the intersection of the isopleth and the solidus is reached. At this temperature a liquid of composition $C_1$ which contains both $S_1$ and $S_2$ is formed. The quantity of liquid $C_1$ formed at $T_1$ is measured by the line $A_1$-$B_1$ and the ratio of solid to liquid is $B_1$-$C_1$/$A_1$-$B_1$. At temperature $T_2$ the ratio of solid to liquid is $B_2$-$C_2$/-$A_2$-$B_2$, and the composition of the liquid is given at $C_2$, the intersection of the tie line $A_2$-$C_2$ with the liquidus $F$-$C_1$. As the temperature is raised, the amount of solid decreases and the liquid increases, the liquid becoming richer in $S_1$. At $dT$ below $T_6$, only a very small amount of solid remains and the composition of the liquid has changed from $C_1$ to $C$. At $T_6$, the solid is completely melted and the liquid is of composition $A$.

The relative amounts of liquid and solid $S_1$ present at various temperatures from $T_1$ to $T_6$ for the substance of composition $A$ are shown in Fig. IV. This figure serves fairly well to illustrate the use of the lever rule. The compositions, $S_1$ and $S_2$, and the composition corresponding to $C_1$ are special cases to which curves of the type of Fig. IV do not apply since melting of these compositions takes place at definite temperatures and not over temperature intervals.

The above statements regarding the crystallization of melts are true only if the rate of cooling is sufficiently slow to allow equilibrium to be attained at every instant. A rapid rate of cooling will lead to quite different results.

The liquidus boundary curve shows the effect of soluble impurities on the melting point of pure compounds. This effect can be shown by an isothermal study of the solid, $S_1$. If a charge of $S_1$ (Fig. III) is held constant at temperature $T_7$ and a small amount of $S_2$ is added, a small amount of liquid of composition $L$ will be formed. As the amount of $S_2$ is increased, the amount of liquid $L$ increases. When sufficient flux, $S_2$, has been added to bring the total composition to $L$, the solid phase, $S_1$, disappears and the charge becomes entirely liquid. Therefore, a small amount of soluble impurity lowers the melting temperature from $F$ to $T_7$.

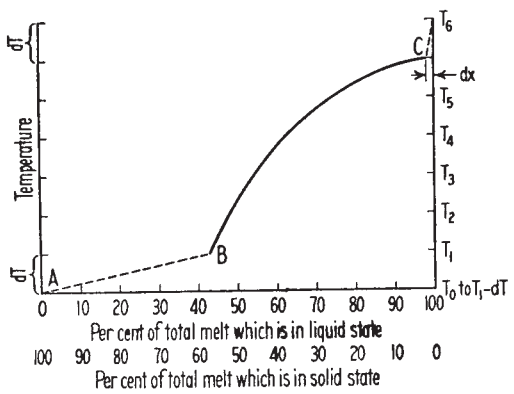


FIG. IV.—Variation in amounts of liquid and solid phase, $S_1$, upon heating composition $A$ of Fig. III from the temperature $T_0$ to $T_6 + dT$ along the isopleth $A$-$C$; $dT$ and $dx$ are infinitesimal increments in temperature and amount of solid phase, $S_1$, respectively.

Further additions of $S_2$ completely dissolve and the composition of the liquid varies until point $M$ is reached when the solid phase, $S_2$, no longer dissolves, that is, the liquid is saturated with $S_2$. Further additions of $S_2$ do not dissolve and the relative amount of liquid decreases; the mass approaches a complete solid as the total composition approaches $S_2$.

Since the curve $F$-$C_1$ represents solutions saturated with $S_1$, and the curve $G$-$C_1$, solutions saturated with $S_2$, the intersection $C_1$ (eutectic) must represent a solution saturated with both solids. The curves are, thus, solubility curves or freezing point curves.

*(b) Compounds Present*

Three types of binary diagrams with compounds, are shown in Fig. V. Figure V($A$) shows a compound, $S_1S_2$, which decomposes at $T_1$ into the solids, $S_1$ and $S_2$. Figure V($B$) shows a compound, $S_1S_2$, with an incongruent melting point; that is, it decomposes at $T_2$ into a solid, $S_2$, and liquid, $C$, neither of which has the composition of the original compound. Figure V($C$) shows a compound, $S_1S_2$, which melts congruently, that is, the liquid resulting from the melting of $S_1S_2$ is of the same composition as the solid, $S_1S_2$.

The system represented in Fig. V($C$) may conveniently be divided into two systems or subsystems, one containing $S_1$ and $S_1S_2$ as its components, the other $S_1S_2$ and $S_2$. Both may be studied in the same manner as Fig. III.

## (B) Binary Systems with Solid Solutions

*(a) Mechanics of Crystallization*

Figure VI represents the case of simple solid solution where the melting point of $A$ is depressed by $B$ and that of $B$ is raised by $A$. The composition $X$ at the temperature, $X_0$, will consist entirely of liquid. If this melt is allowed to cool along the isopleth to the temperature, $T_1$, a solid of composition $SS_1$ crystallizes out of the solution. It is apparent that the solid is richer in $A$ than is the liquid $L$. At temperature $T_2$ the liquid has a composition of $L_2$ and the solid solution a composition of $SS_2$; and the ratio of solid to liquid is $L_2$-$X$/$SS_2$-$X$.

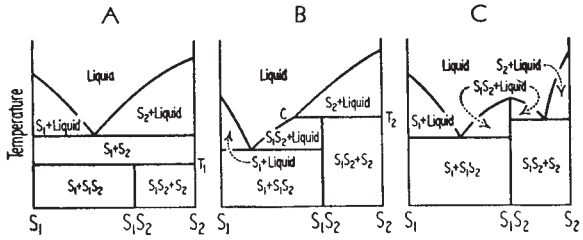


FIG. V.—Two-component systems with compounds present. ($A$), the compound, $S_1S_2$, decomposes at a temperature below the eutectic temperature; ($B$), the compound, $S_1S_2$, decomposes at a temperature above that of the eutectic; ($C$), the compound, $S_1S_2$, is stable at its melting point.

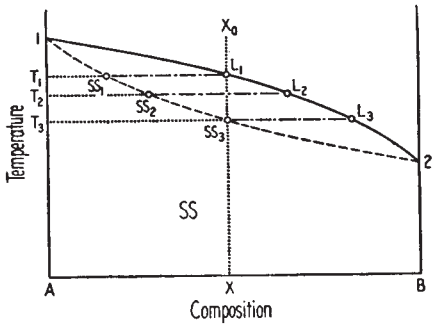


FIG. VI.—Complete solid solution without maximum or minimum in a binary system. Line 1-$L_1$-$L_2$-$L_3$-2 represents the composition of the liquid phase and is called the liquidus curve. Line 1-$SS_1$-$SS_2$-$SS_3$-2 represents the composition of the solid phase and is called the solidus curve. The tie lines, $SS_1$-$L_1$, $SS_2$-$L_2$, and $SS_3$-$L_3$, show the conjugate relation of liquid and solid phase for the three temperatures $T_1$, $T_2$, $T_3$.

As the temperature falls from $T_1$ to $T_3$ the isopleth crosses the tie lines joining compositions of solids from $SS_1$ to $SS_3$ with the compositions of liquid from $L_1$ to $L_3$. For the system to maintain equilibrium in cooling, each and every crystal of solid solution must change in composition continuously throughout its mass. There is a constant interchange of material between solid and liquid phases and a constant change in composition in all parts of the solid as cooling progresses.

The solid is thus increasing in concentration of $B$ along $SS_1$-$SS_3$ while the liquid is increasing in concentration of $B$ along $L_1$-$L_3$. Simultaneously the amount of solid is increasing and the amount of liquid decreasing, the total composition of the system, of course, remaining constant. The last drop of liquid has the composition $L_3$ and the total solid the composition $SS_3$.

Fractional crystallization can be obtained between $T_1$ and $T_3$ by removing the solid phase at any temperature between $T_1$ and $T_3$.

*(b) Types of Systems*

Figures VI, VII and VIII show types of solid-solution diagrams. In the case of binary solid solutions with a maximum or minimum (Fig. VII), the maximum or minimum point on the curve is not an invariant point, as can be seen from the following argument. In a two-component, condensed system (pressure constant), $P + F = C + 1$ and $F = 3 - P$. In order for the system to be invariant ($F = 0$), three phases must exist in equilibrium. Such a condition, however, can never exist in a solid-solution series as shown in Fig. VII, because there are never more than two phases present, i.e., solid solution and liquid solution. The system can at no point become invariant, and the equilibrium curves must be continuous, in contrast to a "true" invariant point (eutectic or peritectic) which is a point of discontinuity on the curve.

Such points designating maxima and minima, including the melting points of congruently melting compounds, at which two phases become identical in composition are known as indifferent points.[5]

Figure VIII shows two cases where two solid solutions are present. In Fig. VIII($A$) at point $c$ there are two solid solutions of compositions $a$ and $b$ and a liquid of composition $c$. This number of phases (3) present in a condensed two-component system makes the point $c$ an invariant point which satisfies the definition of a eutectic. In Fig. VIII($B$) at point $c$ there are two solid solutions of compositions $a$ and $b$ and a liquid solution of composition $c$. Point $c$ in Fig. VIII($B$) is also an invariant point, but it differs from that in VIII($A$) because there is solid in equilibrium with liquid both above and below the temperature of the invariant point. The relationship is therefore called peritectic in distinction from eutectic.

Marsh[9] has pointed out that complete insolubility in the solid state, as indicated on many hypothetical and actual binary diagrams, is highly improbable. It will be observed that this compilation shows many binary diagrams of the silicates and refractory oxides in which there is no indication of solid solubility, that is, no solid solution. In many cases solubility is so slight that evidences of it cannot be obtained or the scale of the diagram is insufficient to show it. In too many instances, however, the relations in the solid state have not been sufficiently explored. Data of this kind are important to the ceramic engineer and technologist as well as to the petrologist, and are becoming more prominent in literature.

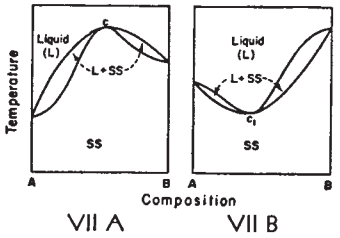


FIG. VII.—Binary systems with a single solid solution. ($A$), system with a maximum melting point at $C$, which is not a compound; ($B$), system with a minimum melting point at $C_1$, which is not a eutectic.

Handbuch der Metallphysik. Edited by Georg Masing. Vol. II, Die heterogenen Gleichgewichte, by Rudolf Vogel, p. 241. Akademische Verlagsgesellschaft, Berlin, 1937.

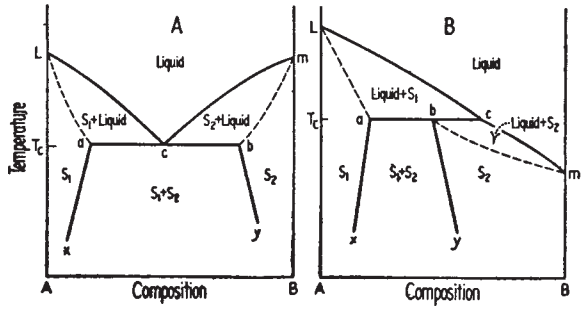


FIG. VIII.—Solid solutions showing conjugate relationships. The two solid solutions, $S_1$ and $S_2$, have a conjugate relation to each other in area $a$-$b$-$x$-$y$. The solid solutions in areas $L$-$a$-$c$ and $m$-$b$-$c$ have a conjugate relation to the corresponding liquid phases present in these areas.

## (C) Binary Systems with Immiscible Liquids

In some systems two liquid solutions can exist in equilibrium as shown by the area $a$-$b$-$c$ in Fig. IX. The extremities of the "tie line" $L_1$-$L_2$ represent the compositions of the two solutions which are in equilibrium at the temperature $T_2$. The point $c$ at temperature $T_1$ is a triple point which, in a two-component system, is an invariant point since there are two liquid phases and one solid, $A$, present. The work of Greig has shown that there are often similar conditions present in certain $SiO_2$-rich regions of silicate systems.

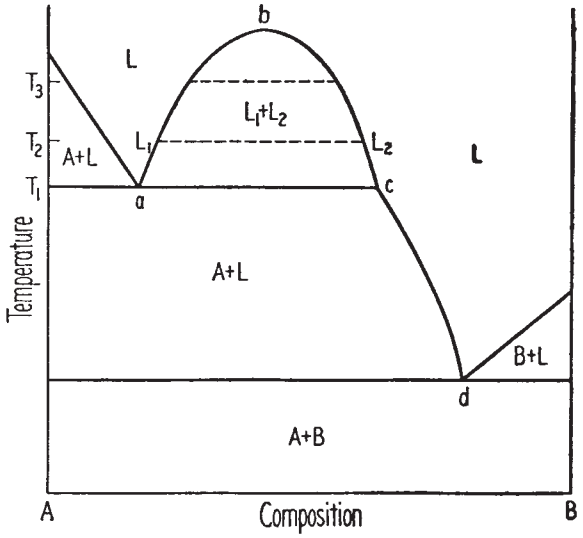


FIG. IX.—Conjugate liquid phases. The broken lines in area $a$-$b$-$c$ show the conjugate relationship of the two liquid phases for the two temperatures, $T_2$ and $T_3$.

## (D) Binary Systems of a Complex Nature

An example of a hypothetical binary diagram of considerable complexity is given in Fig. X to illustrate how the courses of crystallization under equilibrium conditions can be visualized. The two components are $A$ and $B$. Component $A$, within the temperature range of the diagram, occurs in 5 enantiotropic forms: liquid, $\alpha_1$, $\alpha_2$, $\alpha_3$, and $\alpha_4$. Component $B$ exists in only two forms within this temperature range, liquid and $\beta_1$. There is one intermediate compound, $\gamma$, which does not exist at the liquidus. In a part of the composition range two liquids, $L_1$ and $L_2$, coexist. The components, by definition, melt congruently to form liquids of their own composition.

### (a) *Crystallization Paths*

Three vertical lines of constant composition (isopleths), $C$, $D$, and $E$ will be considered.

(i) *Crystallization along isopleth C:* At temperatures above point $k$ on the isopleth $C$, the substance is a homogeneous liquid. When the temperature drops to point $k$, separation into two liquids results, the two liquids changing in composition and in relative amounts as the temperature is lowered from $k$ to $n$. At the temperature represented by point $m$, for example, the compositions of the two liquids correspond to the intersections of the horizontal line (tie line) through point $m$ with the boundaries of the field (points $d$ and $e$) and the relative amounts of the two liquids, $L_1$ and $L_2$, are pro-

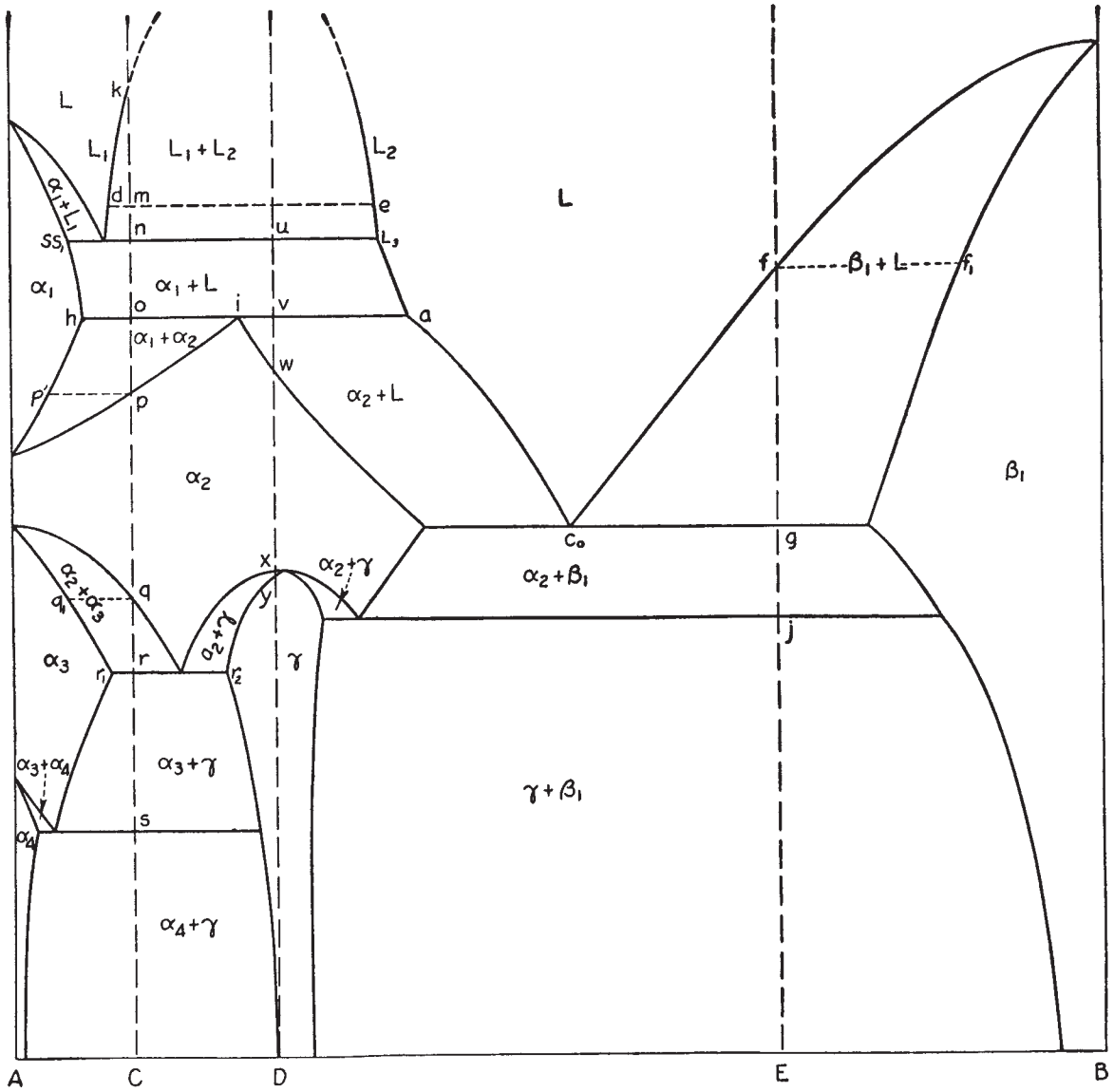


FIG. X.—Hypothetical binary diagram to illustrate possible phase changes.

portional to the lengths *m-e* and *d-m*, respectively.

At the temperature of point *n*, crystallization of the phase, $\alpha_1$, a solid solution, occurs. The coexisting solid and liquid have the compositions of the left and right extremities, $SS_1$ and $L_3$, respectively, of the horizontal line through *n*. Further temperature drop results only in changes in compositions and in relative amounts of these two phases represented by horizontal lines through the composition at the proper temperature level until point *o* is reached, at which time the compositions of solid and liquid are *h* and *a*, respectively. At the temperature of point *o*, the cooling is arrested until all of the liquid of composition *a* has crystallized to a mixture of the solid solutions, $\alpha_1$ and $\alpha_2$, $\alpha_1$ having the composition of point *h*, and $\alpha_2$ having the composition of the point *i*.[10]

Further cooling through the region from *o* to *p* results in reaction of the two phases, $\alpha_1$ and $\alpha_2$, the quantitative relations between compositions and amounts being found as before by passing horizontals through the temperature levels of the reaction to the intersections with the phase-region boundaries. Solid $\alpha_1$ changes in composition from *h* to *p'* and $\alpha_2$ from *i* to *p*. At the temperature of point *p*, continued reaction between solids $\alpha_1$ and $\alpha_2$ results in the complete disappearance of $\alpha_1$.

Solid solution $\alpha_2$ of composition *p* persists, unchanged in composition, until the temperature of point *q* is reached. At this point, there is a partial decomposition of phase $\alpha_2$ to form $\alpha_3$ of composition $q_1$ (a eutectoid decomposition). These two phases co-exist, continually changing in relative amounts and in compositions, until point *r* is reached when another eutectoid decomposition takes place. Solid $\alpha_2$ completely disappears, and the new solid solution, $\gamma$, of composition $r_2$ forms. At point *s*, $\alpha_3$ is in turn replaced by $\alpha_4$ and the two phases $\alpha_4$ and $\gamma$ exist together until the lowest temperature shown in the diagram is reached.

(ii) *Crystallization along isopleth D:* A mass of composition *D* cooled from above the temperature where it exists as a homogeneous liquid undergoes qualitatively the same changes as did sample *C* until the temperature represented by point *v* is reached. Here reaction between the solid $\alpha_1$ and liquid *L* takes place, resulting in the re-solution of $\alpha_1$ and precipitation of $\alpha_2$. The phases $\alpha_2$ and *L* coexist, changing in composition with decreasing temperature until the last bit of liquid disappears at the point *w*. From *w* to *x* only the solid phase $\alpha_2$ is present. At *x* phase $\gamma$ precipitates from $\alpha_2$, but $\alpha_2$ persists through only a very short cooling range when it reacts with (is resorbed by) phase $\gamma$, and $\gamma$ persists alone throughout the remaining cooling range shown in the diagram.

The phase $\gamma$ is a solid solution of an intermediate compound of the composition $A_xB_y$ which can take either *A* or *B* into its structure in greater than stoichiometric proportions. The compound $A_xB_y$ cannot be considered a component of a subsidiary system since it does not melt to a homogeneous liquid but instead inverts to the solid solution $\alpha_2$ on heating.

(iii) *Crystallization along isopleth E:* Cooling of composition *E* results in the crystallization of solid solution $\beta_1$ of composition $f_1$ at the temperature of point *f*. Changes in composition of the coexistent solid and liquid phases take place until the temperature of the eutectic, $C_0$, is reached. Then an arrest in the cooling takes place until reaction has caused the complete disappearance of liquid by the crystallization of phases $\alpha_2$ and $\beta_1$ in the proportion indicated by the lever principle about point *g*. Further reactions on cooling are not sufficiently different from previous descriptions to require comment.

### (3) Three-Component Systems

There are four independent variables in a ternary system, namely, pressure, temperature, and two concentration variables since a ternary solution requires a statement of its composition with respect to two components before its total composition is fixed. Five coexisting phases (a quintuple point) produce an invariant system, four give an univariant system, three, a bivariant, etc. A complete graphical representation of the ternary system is a very difficult matter. If, however, the vapor pressure is so low as to be negligible, the ternary systems may be treated as condensed systems as was the case with binary systems, the phase rule again expressed as $P + F = C + 1$.

The compositions can then be represented by triangular coordinates. This method is illustrated in Fig. XI. In this figure, each side of the equilateral triangle is divided into 100 parts, each tenth division being intersected by lines parallel to each of the other two sides. A point at the apex, *C*, is composed wholly of component *C*. A point on the base line *A-B* is composed entirely of components *A* and *B* with none of *C*. The relative distance of a point, such as *x*, from each of the three apices may be expressed in percentage and it thus may represent a percentage composition of a ternary mixture or solution in terms of components *A*, *B*, *C*. Point *X*, for example, represents a composition of 45% *A*, 20% *B*, and 35% *C*, whereas *y* represents 15% *A*, 15% *B*, and 70% *C*.

By the appropriate construction the coordinates of a point in a triangular diagram can also be read off of any one of the sides. In Fig. XI if the lines *XE* and *XF* be constructed parallel to the sides *BC* and *AB*, respectively, the length *CE* represents the percentage of *A* (45) in composition *X*, the length *AF* the percentage of *C* (35), and the length *FE* the percentage of *B* (20). By a similar construction the composition of *X*, in terms of *A*, *B*, and *C* can be read off on the sides *BC* and *AB*. The two end segments of each line represent the proportional amounts (in terms of the whole line) of the substances designated at the opposite ends; the middle segment represents the proportion of the third substance, not located on the line.

[10] Crystallization of any solid solution in equilibrium with a liquid solution or with another solid solution under changing temperature conditions requires that continual reaction takes place not only between the materials crystallizing at that instant but with all the solids already crystallized. The difficulty of the attainment of equilibrium under such conditions is obvious.

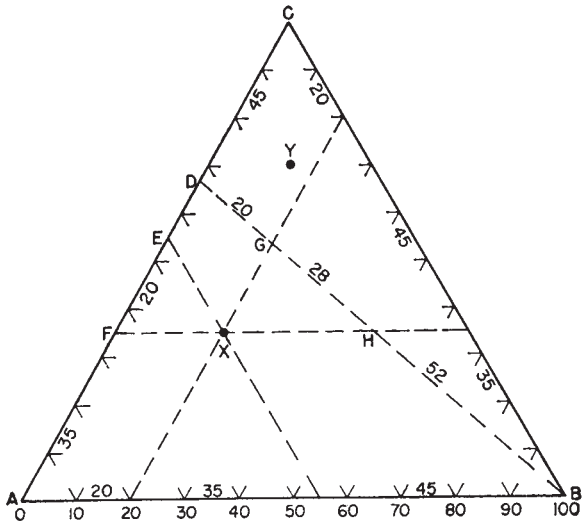


FIG. XI.—Representation of composition in a ternary system by means of triangular coordinates.

This method of expressing a composition in terms of three others by the appropriate construction, so as to designate the three proportions as segments of a line is not limited to equilateral triangles but is applicable, also, to scalene triangles. For example, point $X$ in Fig. XI can be expressed in terms of $A$, $B$, and $D$ on the line $BD$. The percentage of $B = DG \times 100/DB = 20$; the percentage of $D = HB \times 100/DB = 52$; and the percentage of $A = GH \times 100/DB = 28$. By rotating the line $XE$ until it were parallel to $BD$, the proportions of $A$, $D$, and $B$ in $X$ could be determined, similarly, on the sides $AD$ and $AB$.

As will be shown later, when dealing with subsystems or when tracing the course of crystallization of a liquid, it frequently becomes necessary to express an overall composition in terms of three others which do not form an equilateral triangle.

A triangular composition diagram also has the advantage that a series of additions of a third component to a mixture in any ratio of the other two components may be represented by a straight line from the apex of the third component. In Fig. XI for instance, additions of component $B$ to a mixture of 33% $A$, 67% $C$ (point $D$) all lie on the line $D$-$B$.

Temperatures can be represented by lengths perpendicular to the plane of the composition triangle and therefore cannot be shown directly on a two-dimensional surface, but the temperatures on one of the thermal surfaces (usually the liquidus surface) may be indicated for uniform temperature intervals by isotherms as are elevation contours on topographic maps. The actual solid diagram has an appearance like that of Fig. XII.

The liquidus surface is then a series of intersecting curved surfaces representing the primary phase fields of compounds in the system. A primary phase field of a congruently melting ternary compound is a domed surface, the highest elevation of which represents the melting point of the compound. Its field intersects that of an adjacent congruently melting compound in a sloping valley or boundary line. In the case of an incongruently melting compound the intersection of the primary phase field of the first with that of the second solid is a sloping terrace and not a valley.

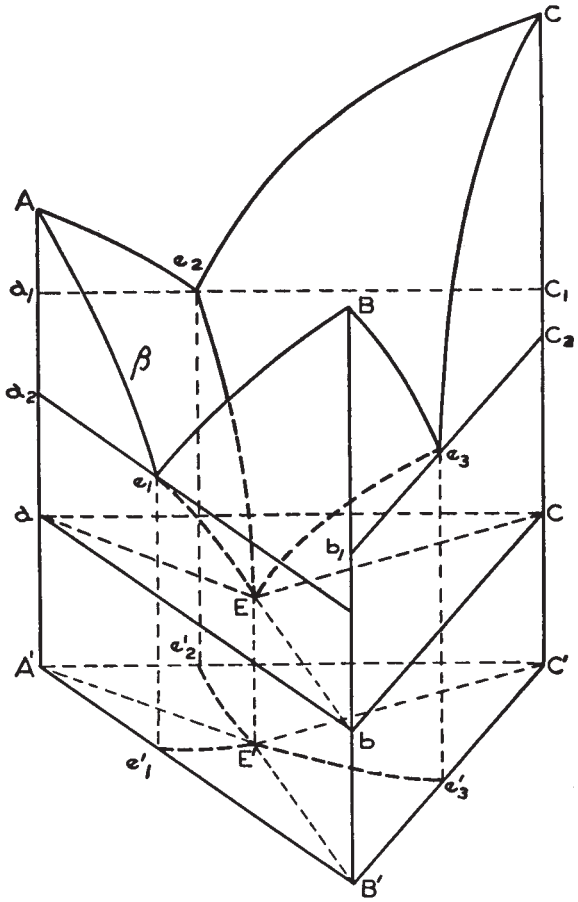


FIG. XII.—Perspective drawing of a space model of a ternary system with a simple eutectic and no ternary compound.

Modified from R. Vogel, Die heterogenen Gleichgewichte, in G. Masing, Handbuch der Metallphysik, Vol. II, Fig. 266, p. 370, 1937.

## (A) Ternary Systems Without Solid Solutions

### (a) *Typical Cases*

In Fig. XIII, six typical cases of ternary systems are shown. Figure XIII($A$) shows a system without either binary or ternary compounds present. The field 1-4-2-$C$ represents the field of stability of component $C$ in equilibrium with solution. Solid $C$ is the primary phase for this area and is the last solid to disappear when any composition within this area is heated. It is also the first solid phase to appear when liquids represented by points in this area are cooled. Points 1, 2, and 3 are binary eutectics, while point 4 is a ternary eutectic. Lines 1-4, 2-4, and 3-4 are known as boundary curves, each of which represents a condition

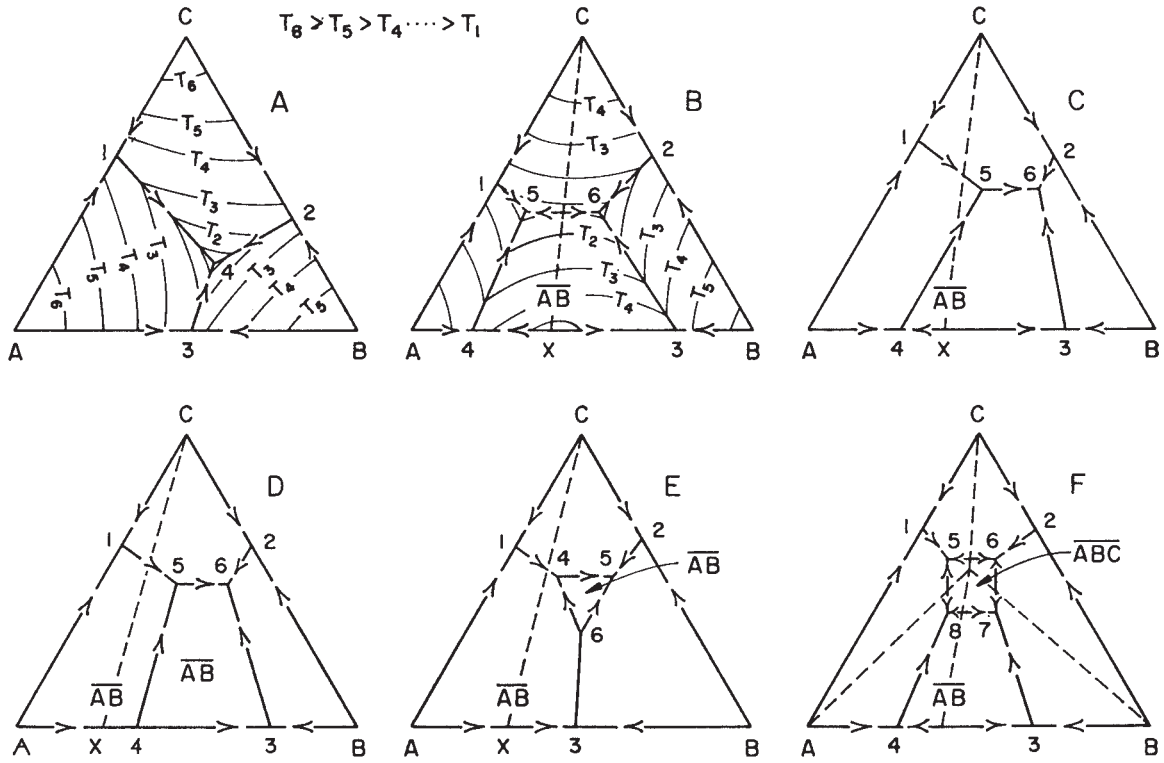


FIG. XIII.—Six typical cases of three-component systems; A and B show hypothetical isotherms. Arrows indicate the direction of falling temperatures.
G. A. Rankin and F. E. Wright, *Am. J. Sci.*, 4th Ser., **39**, 18 (1915).

of 3-phase equilibrium among two solid phases and liquid. The two solid phases at equilibrium along 1-4 are *A* and *C*, along 2-4 are *C* and *B*, and along 3-4 are *A* and *B*. Point 4 is a quadruple point in a condensed system at which solids *A*, and *B*, *C* are in equilibrium with solution.

In diagrams (*B*), (*C*), (*D*), and (*E*) of Fig. XIII an intermediate binary compound, $\overline{AB}$, is present. The straight line which joins this compound to the third component, *C*, of the ternary system is called an Alkemade line. Alkemade lines divide ternary systems into composition triangles. The final phases produced by equilibrium crystallization within one of these triangles are indicated by the apices of the triangle. For example, in diagrams of Figs. XIII(*B*), (*C*), (*D*), and (*E*), the final phases within the triangle $A$-$\overline{AB}$ $C$ are crystalline *A*, $\overline{AB}$, and *C*. In XIII(*F*), where a ternary compound is present with the binary compound, conjugation lines form four subsidiary triangles.

Figure XIII(*B*) shows a ternary system where the binary compound $\overline{AB}$ is stable at its melting point. According to the theorem of Alkemade[11] if the line *C*-*X* crosses the line 5-6, the point of intersection will be a maximum on the boundary 5-6 and the points 5 and 6 will be eutectics and each composition triangle will behave as a true ternary system. However, if *C*-*X* does not cross 5-6 but intersects 1-5 and 4-5 (as in Fig. XIII-*C*)), then only 6 will be the eutectic. In the case of Fig. XIII(*B*), the line *C*-*X* forms a true binary system with components *C* and $\overline{AB}$. It divides the ternary system *A*-*B*-*C* into two ternary systems, each of which may be treated individually. In Fig. XIII(*C*), however the line *C*-*X* crosses the primary phase field of another compound, the composition of which does not lie on this line, and therefore the line does not describe a binary system.

In Fig. XIII(*D*) the composition of the binary compound, $\overline{AB}$, lies outside the field 4-5-6-3 because it has an incongruent melting point. In the binary system *A*-*B* it dissociates at a temperature corresponding to point 4 into solid *A* and liquid. In the ternary system *A*-*B*-*C* the compound $\overline{AB}$ is the primary phase in field 3-4-5-6 and is stable in this field.

In Fig. XIII(*E*), $\overline{AB}$ dissociates into solids *A* and *B* in the binary system *A*-*B*. In the ternary system compound $\overline{AB}$ has a stable field 4-5-6.

[11] "A theorem by Van Rijn Van Alkemade serves as a very effective guide in regard to temperature changes in the interior of the triangle. If the two points in the triangle which correspond to the composition of two solid phases be connected by a line, the temperature at which these same two phases can be in equilibrium with solutions and vapor rises as the boundary curve approaches this line, becoming a maximum at the intersection though the boundary curve often ceases to be stable before this point is reached." (W.D. Bancroft, "The Phase Rule," *J. Phys. Chem.*, 1, 149 (1897))

In Fig. XIII(*F*), the system has a binary compound $\overline{AB}$ and a ternary compound, $\overline{ABC}$, each of which has a congruent melting point as their respective compositions are within or on the boundaries of the fields in which they are the primary phases.

These simple cases are also applicable to such complex systems as the one shown in Fig. XIV.

(*b*) *Crystallization Paths*[12]

(i) *Simple systems:* Geer[12(a)] states that "the crystallization curve denotes the locus of points which represent the compositions of the solutions formed on cooling any given solution from any given temperature to the temperature (quintuple point in case of ternary systems) at which it becomes solid, under the assumption that no phase is removed during the cooling." The relations of solid phases to liquid phases of any system that does not have solid solutions are known when the liquidus of the system is determined for all compositions. The liquidus is the temperature at which the first solid (primary phase) appears on cooling under equilibrium conditions. A knowledge of the crystallization curve or the melting curve (the reverse of the crystallization curve) for any particular melt is very valuable in the study of the firing of ceramic bodies. A few types of crystallization curves will be described using the diagrams and terms given by Andersen.[12(b)]

In Fig. XV, point *m* is the ternary eutectic and all crystallization curves of this system are terminated at this point. If a liquid of composition *a* is chosen and allowed to cool, the system remains liquid until the liquidus is reached, at which temperature the solid, *A*, begins to crystallize. The course of the crystallization curve from this point to boundary *m-k* follows a straight line drawn through *A* and *a*. This is true for all crystallization curves where solid solutions are not present. As the liquid changes in composition from *a* to *b*, solid *A* crystallizes. At *b*, a second phase appears and the crystallization curve follows boundary *k-m* with phases *A* and *C* crystallizing together. At point *m*, the temperature remains constant with solid phases *A*, *B*, and *C* crystallizing together until all liquid has disappeared. The final product will be a mixture of large crystals of *A* and *C*, and small crystals (eutectic mixture) of *A*, *B*, and *C*.

The composition of the solids crystallizing at any instant along *b-m* is given at the point where the tangent to the crystallization curve intersects that side of the composition triangle representing the two solid phases coexisting. For example, at *b*, it is indicated by the intersection of the tangent to the curve *m-b-k* at the point *b* with the line *A-C* at point *b''*. The ratio of *A* to *C* is given by the lever *b''-C/b''-A*. The mean composition of the two solid phases that have crystallized between points *b* and *m* is represented by the intersection of a line drawn through *m* and *b* and the side of the composition triangle at *b'*. In this case it is a mixture of *A* and *C* in the proportion *b'-C/b'-A*. The mean composition of the total solid which separates out between *a* and *m* (before *B* begins to crystallize) is determined by drawing a line through *m* and *a* to the side of the composition triangle at *a'*.

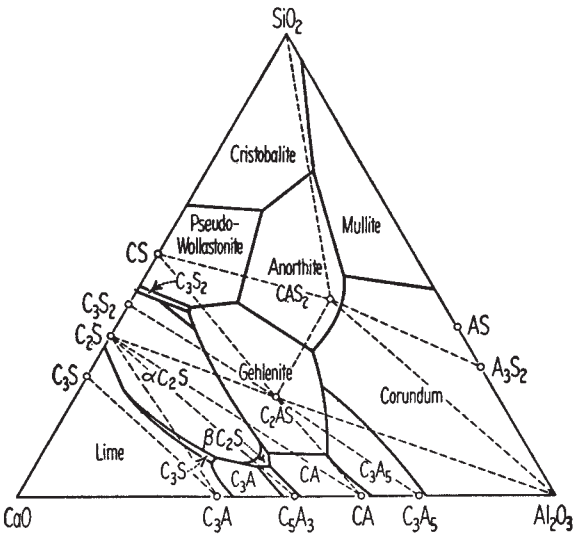


FIG. XIV.—Three-component system, $Al_2O_3$–CaO–$SiO_2$, showing (1) boundary curves as solid lines, (2) composition lines (Alkemade lines) as dashed lines. The final product of crystallization (on slow cooling) of ternary solutions of this system always consists of three solid phases whose fields of stability are adjacent. The same three solid phases will be the final product of crystallization from any solution whose composition lies within the triangle (composition triangle) formed by lines joining the compositions of these three phases. Note: In compound designations, C = CaO, A = $Al_2O_3$, S = $SiO_2$.

G. A. Rankin and F. E. Wright, *Am. J. Sci.*, 4th Ser., **39**, 52 (1915). (See Fig. 630 for revised and redrawn diagram.)

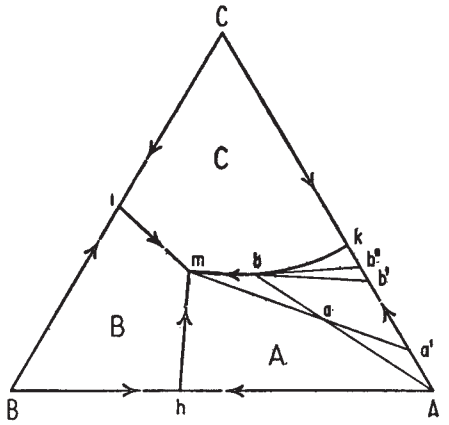


FIG. XV.—Course of crystallization in a simple ternary system

O. Anderson, *Am. J. Sci.*, 4th Ser., **39**, 427 (1915).

[12] (*a*) W. C. Geer, "Crystallization in Three-Component Systems," *J. Phys. Chem.*, **8**, 257–87 (1904).

(*b*) Olaf Andersen, "System Anorthite-Forsterite-Silica," *Am. J. Sci.*, 4th Ser., **39**, 407 (1915).

(*c*) N. L. Bowen, "Ternary System, Diopside-Forsterite-Silica," *ibid.*, **38**, 207–64 (1914).

During eutectic crystallization at $m$, the composition of the total solids changes from $a'$ to $a$, reaching the latter point as the last drop of liquid disappears.

The method of calculating the amounts of solid separating between various temperatures by the use of the lever rule as shown in the preceding paragraphs is the same as described in the case of the binary system. For example, in cooling a melt of original composition $a$ from the liquidus temperature to point $b$, the ratio of the amount of solid $A$ crystallized to the total amount of the system is equal to $a$-$b/A$-$b$ whereas the ratio of the amount of liquid of composition $b$ remaining at $b$ is equal to $a$-$A/A$-$b$. Similarly, the relative amount of solid of mean composition $a'$ crystallized between $a$ and $m$ (before $B$ has begun to crystallize) is equal to $a$-$m/a'$-$m$ and the relative amount of liquid of eutectic composition is equal to $a$-$a'/a'$-$m$.

The case of a ternary system with a binary compound stable at its melting point is discussed in connection with Fig. XIII($B$). The crystallization in each subsystem would be treated in the same manner as the above case.

(ii) *System with ternary peritectic:* In Fig. XVI the ternary eutectic point $m$ and the peritectic point, $o$, lie on the same side of the conjugation line, $C$-$\overline{AB}$, and the binary eutectic points, $h$ and $j$, lie on opposite sides. The field of $A$ ($A$-$j$-$o$-$k$) extends across the conjugation line, $C$-$\overline{AB}$, hence the system $C$-$\overline{AB}$ is not a true binary system. The temperature along line $o$-$m$ decreases according to the theorem of Alkemade toward $m$, and $o$ is not a eutectic but a peritectic.

In cooling a melt of composition $a$, solid phase $A$ crystallizes out along $a$-$b$. From $b$ to $o$, $A$ and $\overline{AB}$ crystallize together and as the total composition of the solid separated between $a$ and $o$ is given at $a'$, there must be liquid left when $o$ is reached.

The point $a$ is within the composition triangle $A$-$\overline{AB}$-$C$, and the final products of crystallization must be these three phases. It is evident from the diagram that the three phases which are in equilibrium at $o$ are $A$, $\overline{AB}$, and $C$. Therefore, the final solidification of composition $a$ must take place at $o$ and not at $m$ since $a$ lies in the composition triangle whose solid phase areas meet at $o$. During the final solidification at $o$, solid phases $C$ and $\overline{AB}$ crystallize while some of the phase, $A$, is resorbed or dissolved.

The melt, $c$, on the conjugation line $C$-$\overline{AB}$ crystallizes as follows: Along $c$-$b$, $A$ separates; along $b$-$o$, $A$ and $\overline{AB}$ separate together; at $o$, $C$ and $\overline{AB}$ separate and $A$ completely dissolves, the final products of crystallization being only $\overline{AB}$ and $C$. Crystallization at invariant points frequently involves more than physical processes and may involve chemical reactions as well. At $o$, for example, with melt $c$ the following chemical reaction must occur: $A$ (solid) + $B$ (in liquid) = $AB$ (solid).

The melt, $d$, on the left of the conjugation line in the composition triangle $B$-$\overline{AB}$-$C$, crystallizes as follows: Along $d$-$e$, $A$ separates; along $e$-$o$, $C$ and $A$ crystallize together; at $o$, $A$ dissolves and $\overline{AB}$ is formed (temperature remains constant until all of $A$ disappears); along $o$-$m$, $\overline{AB}$ and $C$ crystallize together. At $m$, the final products of crystallization are $\overline{AB}$, $B$, and $C$, which is to be expected because the point $d$ lies in the composition triangle $B$-$\overline{AB}$-$C$. The mean composition of the solid separating between $d$ and $o$ is represented by $d'$. At the moment at which all of $A$ has disappeared at $o$ and before crystallization begins to proceed along $o$-$m$, the mean composition of the solid has changed from $d'$ to $d''$ and is composed of $C$ and $\overline{AB}$. Along $o$-$m$, the mean composition of the solid changes from $d''$ to $d'''$ and during the final crystallization at $m$ from $d'''$ to $d$.

(iii) *Systems with both binary and ternary peritectics:* In Fig. XVII, the quadruple points, $h$ and $j$, and the quintuple points, $o$ and $m$, lie on the same side of the Alkemade line, $C$-$\overline{AB}$. A melt of composition $e$ crystallizes as follows: Along $e$-$b$, $A$ separates; at $b$, the compound $\overline{AB}$ begins to crystallize and $A$ to redissolve (the intersection

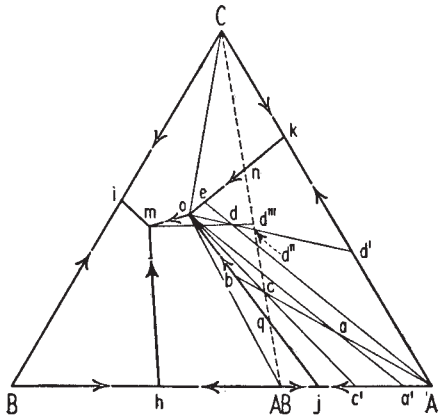


FIG. XVI.—Ternary system with a binary compound which does not form a binary system with the third component.

O. Andersen, *Am. J. Sci.*, 4th Ser., **39**, 431 (1915).

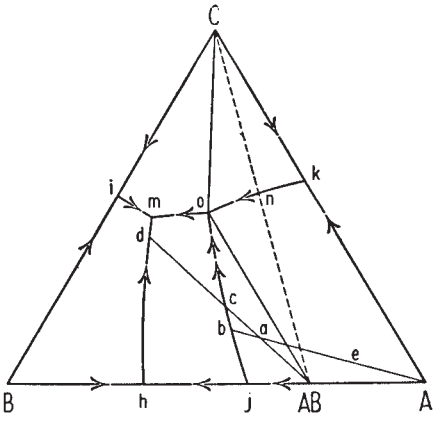


FIG. XVII.—Ternary system containing a binary compound unstable at its melting point.

O. Andersen, *Am. J. Sci.*, 4th Ser., **39**, 433 (1915).

of the tangent to line *j-b-o* intersects an extension of line *A-$\overline{AB}$*). This process continues until *o* is reached because all lines drawn through points on the curve *b-o* and point *e* intersect the line *A-$\overline{AB}$*. Final crystallization takes place when the composition of the liquid and the temperature of the system reaches *o*. In this case, *A* does not completely dissolve and the final products are *A*, $\overline{AB}$, and *C*. If the tangent to line *j-o* intersected the line *A-$\overline{AB}$* and not its prolongation, the solid *A* would tend to increase in amount along *j-o*.

A melt of composition *a* which lies in the other composition triangle will crystallize as follows: From *a* to *b*, *A* separates; between *b* and *c*, $\overline{AB}$ separates and *A* dissolves (is resorbed), and at point *c* all of *A* has disappeared (the mean composition of total solid separated between *a* and *c* is represented by $\overline{AB}$). The point of mean composition moves from *A* to $\overline{AB}$ along line *A-$\overline{AB}$* as the temperature falls from *b* to *c*. From *c*, the crystallization curve leaves the boundary *j-o* and continues across the field to *d* while $\overline{AB}$ is separating. From *d* to *m*, *B* and $\overline{AB}$ separate together, and at *m*, $\overline{AB}$, *B*, and *C* crystallize together. All melts in the field *j-o-$\overline{AB}$* pass through the field *h-m-o-j*. The line *j-o* in this case is called an alteration curve and is indicated by double arrows.

(iii) *Recurrent Crystallization:* Figure XVIII illustrates a case of recurrent crystallization. At point *c* in the crystallization of a melt of composition *a*, the phase *A* disappears and the crystallization curve follows the straight line to point *d*, at which *A* begins to separate again. Along *d-o*, *A* continues to crystallize and $\overline{AB}$ is slowly resorbed (the tangent to *d-o* intersects the extension of $\overline{AB}$-*A*). At point *o*, *A* dissolves with simultaneous separation of *C* and $\overline{AB}$, the temperature remaining constant until *A* is completely dissolved. Along *o-m*, *C* and $\overline{AB}$ separate together and the final products of crystallization at *m* are *B*, $\overline{AB}$, and *C*, as the original point lies within the composition triangle *B-$\overline{AB}$-C*.

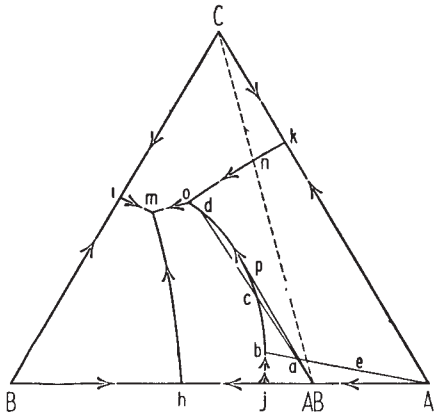


FIG. XVIII.—Recurrent crystallization in a ternary system.
O. Andersen, *Am. J. Sci.*, 4th Ser., **39**, 435 (1915).

A melt *e* crystallizes as follows: Along *e-b*, *A* separates; between *b* and *p*, $\overline{AB}$ crystallizes and *A* is partially resorbed; from *p* to *d*, the tangent to the crystallization curve, i.e., the tie line, intersects line *A-$\overline{AB}$* and not an extension of it, therefore, *A* and $\overline{AB}$ separate together; from *d* to *o*, the tangent intersects an extension of $\overline{AB}$-*A*, hence *A* crystallizes again and $\overline{AB}$ is partially resorbed; at *o*, *A* is once more partially redissolved while $\overline{AB}$ and *C* crystallize out, and the final products of crystallization are *A*, $\overline{AB}$, and *C*.

(*c*) *Summary Relating to Crystallization*[13]

(1) When a liquid is cooled, the first phase to appear is the primary phase for that part of the system in which the composition of the melt is represented.

(2) The crystallization curve follows to the nearest boundary the extension of the straight line connecting the composition of the original liquid with that of the primary phase of that field. The composition of the liquid within the primary fields is represented by points on the crystallization curve. This curve is the intersection of a plane (passed perpendicular to the base triangle and passing through the compositions of original melt and the primary phase) with the liquidus surface.

(3) At the boundary line a new phase appears which is the primary phase of the adjacent field. The two phases separate together along this boundary as the temperature is lowered.

(4) Two conditions may appear that would alter the crystallization along the boundary. In one case the first phase will increase as is the case where the tangent to the boundary curve intersects the line connecting the compositions of the two phases separating or it will decrease (be resorbed) if this tangent intersects the prolongation of this line. In the other case the crystallization curve will leave the boundary curve when the first phase has become completely resorbed leaving only the second solid phase. This may be inferred from a study of the mean composition of the solid separating between successive points on the crystallization curve.

(5) The crystallization curve always ends at the invariant point which represents equilibrium of liquid with the three solid phases of the three components within whose composition triangle the composition of the original liquid was found.

(6) The mean composition of the solid which is crystallizing at any point on a boundary line is shown by the intersection of the tangent at that point with the line joining the composition of the two solid phases which are crystallizing at the given point.

(7) The mean composition of the total solid which has crystallized to any point on the crystallization curve is found by extending the line connecting the given point with the original liquid composition to the line connecting the compositions of the phases that have been separating.

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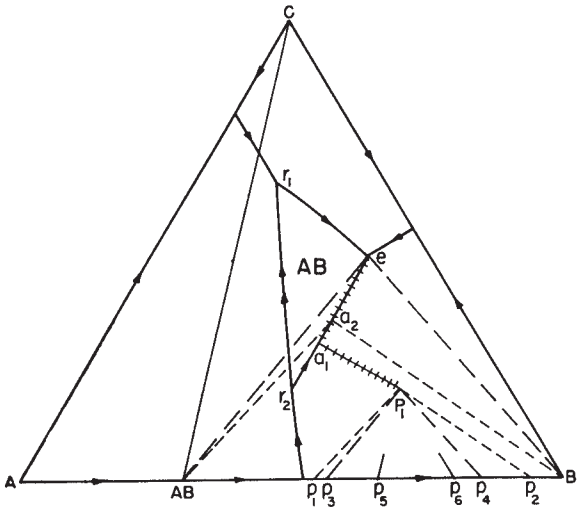
[13] See G. A. Rankin and F. E. Wright, pp. 51–69, under "Methods and Techniques, General," of Selected Bibliography, Part V. See also Andersen, reference 12(*b*).

(8) The mean composition of the solid that has separated between two points on a boundary is found at the intersection of a line passing through these two points with the line connecting the compositions of the two solid phases separating along this boundary.

### (*d*) *Alternate Method for Determining Phase Composition*

An alternate method for determining phase composition during the course of crystallization is based on the construction of similar triangles and has the advantage that the proportions of three phases in equilibrium with each other can be represented as segments of a straight line. The method has a further advantage in that it is simple and easily remembered, which is important to those who have only occasional recourse to the use of phase diagrams.

The method will be demonstrated for a system having a binary compound with a ternary field but without a binary field. Figure XIII(*E*) is such a ternary system, and the binary system containing a compound without a binary field is shown in Fig. V(*A*). In Fig. XIII(*E*), the binary compound $\overline{AB}$ decomposes into the components *A* and *B* below the eutectic (point 3); however, with addition of the third component, *C*, the liquidus values in the ternary system have been lowered to the point where the compound $\overline{AB}$ possesses a small primary field. Point 6 (Fig. XIII(*E*)) represents the unique temperature and composition at which ternary liquid can exist in equilibrium with substances *A*, *B*, and $\overline{AB}$. Point 6 is also the highest temperature at which $\overline{AB}$ can exist in equilibrium with a ternary solution.




| POINT | PHASE COMPOSITION, WT. FRACTION | | | | |
|---|---|---|---|---|---|
| | A | B | C | AB | LIQ. |
| $a_1$ | | $\frac{P_1-a_1}{B-a_1}$ | | | $\frac{B-P_1}{B-a_1}$ |
| $a_2$ | | $\frac{AB-P_1}{AB-B}$ | | $\frac{P_2-B}{AB-B}$ | $\frac{P_1-P_2}{AB-B}$ |
| e (Max. H) | | $\frac{AB-P_3}{AB-B}$ | | $\frac{P_4-B}{AB-B}$ | $\frac{P_3-P_4}{AB-B}$ |
| e (Min. H) | | $\frac{AB-P_5}{AB-B}$ | $\frac{P_5-P_6}{AB-B}$ | $\frac{P_6-B}{AB-B}$ | |

FIG. XIX.—Composition of phase assemblages for a simple crystallization path in a system having a binary compound with a ternary field but without a binary field.

The phase composition during the course of crystallization of the melt $P_1$ of Fig. XIX will now be considered. In Fig. XIX the path followed by the liquid during the process of crystallization is shown by the hatched line. From $P_1$ to $a_1$ solid *B* crystallizes; *B*, $P_1$, and $a_1$ are colinear, and the amounts of liquid and *B* at any point along the path $P_1$ to $a_1$ can be determined by the "Lever Rule," as described earlier. At point $a_1$, compound $\overline{AB}$ starts to crystallize and the composition of the liquid moves along the path $a_1$ to *e*. At any point along the path, e.g., at $a_2$, three phases are in equilibrium, namely, *B*, $\overline{AB}$, and liquid of composition $a_2$. These three phases, moreover, must be equivalent in composition to the original melt, $P_1$. Consequently, if the line $P_1$-$p_1$ be constructed parallel to the line $a_2$-$\overline{AB}$, and the line $P_1$-$p_2$ parallel to $a_2$-*B*, the proportions of the three phases are found along the line $\overline{AB}$-*B*, as $(\overline{AB}\text{-}p_1)/(\overline{AB}\text{-}B)$ of *B*, $(p_2\text{-}B)/(\overline{AB}\text{-}B)$ of $\overline{AB}$, and $(p_1\text{-}p_2)/(\overline{AB}\text{-}B)$ of liquid $a_2$.

At point *e*, at maximum heat content, that is, before any *C* has started to crystallize, the proportions of *B*, $\overline{AB}$, and liquid *e*, can be determined by constructing the line $P_1$-$p_3$ parallel to *e*-$\overline{AB}$ and the line $P_1$-$p_4$ parallel to *e*-*B*. The phase composition is then given along the ine $\overline{AB}$-*B* as $(\overline{AB}\text{-}p_3)/(\overline{AB}\text{-}B)$ of *B*, $(p_4\text{-}B)/(\overline{AB}\text{-}B)$ of *AB*, and $(p_3\text{-}p_4)/(\overline{AB}\text{-}B)$ of liquid *e*.

As $P_1$ lies within the compatibility triangle formed by $\overline{AB}$, *C*, and *B*, crystallization is completed at *e*, which point represents the equilibrium between the three named phases. At point *e*, at minimum heat content, that is, when the last trace of liquid has crystallized, the proportions of $\overline{AB}$, *C*, and *B* may be found by the appropriate construction of triangle $p_5$-$P_1$-$p_6$ similar to triangle $\overline{AB}$-*C*-*B*. The phase composition is then given as $(\overline{AB}\text{-}p_5)/(\overline{AB}\text{-}B)$ of *B*, $(p_6\text{-}B)/(\overline{AB}\text{-}B)$ of $\overline{AB}$, and $(p_5\text{-}p_6)/(\overline{AB}\text{-}B)$ of *C*.

The increase in amount of *B* during crystallization along the path from *a* to *e* can be seen both qualitatively and quantitatively by comparing the lengths of the segments $\overline{AB}$-$p_1$, $\overline{AB}$-$p_3$, and $\overline{AB}$-$p_5$. By a similar comparison of the segments $p_2$-*B*, $p_4$-*B*, and $p_6$-*B* the changes in amount of solid $\overline{AB}$ can be followed. The segments $p_3$-$p_5$, $p_5$-$p_6$, and $p_6$-$p_4$ represent the amounts of solids *B*, *C*, and $\overline{AB}$, respectively, formed from the eutectic liquid *e* during the change from maximum to minimum heat content at constant temperature.

The phase composition at the various selected points along the path of crystallization is given in the table associated with Fig. XIX.

The course of crystallization of the melt $P_2$, Fig. XX will next be considered. From $P_2$ to $b_1$, solid *A* crystallizes, and *A*, $P_2$, and $b_1$ are colinear. Along the path $b_1$ to $b_2$, compound $\overline{AB}$ crystallizes, and the two solid

phases $A$ and $\overline{AB}$ are in equilibrium with liquid of varying composition as represented along the line $b_1$-$b_2$. Determination of the amounts of the three phases present at any point along the crystallization path is similar to that for the melt $P_1$. At point $b_2$ the side $b_2$-$\overline{AB}$ of the triangle $A$-$b_2$-$\overline{AB}$ is coincident with the side $P_2$-$\overline{AB}$ of the similar triangle $l_1$-$P_2$-$\overline{AB}$. Thus, along the path $b_1$ to $b_2$, solid $A$ has been completely resorbed, as the segment of line representing the amount of $A$ has been reduced to zero. It is evident that crystallization along the $A$, $\overline{AB}$, boundary cannot proceed beyond $b_2$ (toward $r_1$), for then $P_2$ would lie outside the triangle formed by the equilibrium phases $A$, $\overline{AB}$, and liquid, and no positive combination of these phases could give the composition $P_2$. At $b_2$, therefore, the crystallization path cuts across the $\overline{AB}$ field as $\overline{AB}$ continues to crystallize, and $\overline{AB}$, $P_2$, $b_2$, and $b_3$ are colinear. At $b_3$ solid $C$ starts to crystallize and the melt proceeds along the path $b_3$ to $e$. At any point along the path, $b_4$, e.g., $C$, $\overline{AB}$, and liquid of composition $b_4$ are in equilibrium. If the triangle $l_2$-$P_2$-$l_3$ be constructed similar to triangle $\overline{AB}$-$b_4$-$C$, then $(\overline{AB}\text{-}l_2)/(\overline{AB}\text{-}C)$ = fraction of $C$, $(l_3\text{-}C)/(\overline{AB}\text{-}C)$ = fraction of $\overline{AB}$, and $(l_2\text{-}l_3)/(\overline{AB}\text{-}C)$ = fraction of liquid. As $P_2$ lies within the crystallization triangle $\overline{AB}$-$B$-$C$, crystallization will be completed at $e$, as for melt $P_1$ (Fig. XIX), and the proportion of phases present at maximum and minimum heat content can be determined as has been illustrated. The table associated with Fig. XX gives the phase composition at the various points considered.

(*e*) *Summary of Alternate Method*

This alternate method for determining phase composition can be summarized as follows: The composition of three phases (usually but not necessarily, two solids and a liquid) in equilibrium at any point along the crystallization path are connected together with straight lines to form a triangle. If the composition of the original melt does not fall within this triangle, an inconsistency exists for it is not now possible to describe the original melt in terms of positive quantities of the separated phases. Using the composition of the original melt for one vertex and any convenient side of the phase triangle for a base, another triangle is constructed similar geometrically to the phase triangle. The side of the phase triangle selected as a base will then be divided into three segments proportional to the amounts of the three phases.

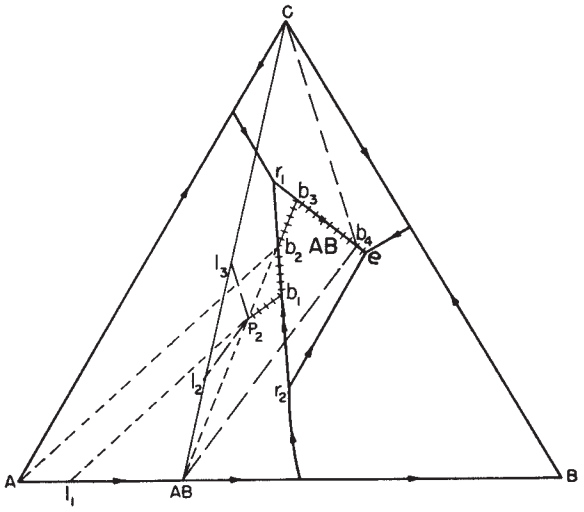
## (B) Ternary Systems with Solid Solutions

In ternary systems it is necessary to locate boundary curves, isotherms, and the compositions of the phases crystallizing in order to determine the course of crystallization within the system. In systems without solid solutions where the phases are invariable in composition, the crystallization curve within the primary phase field of a compound follows the extension of the straight line connecting the composition of the mixture and the primary phase until the line intersects a boundary curve. In ternary systems containing solid solutions, however, the crystallization curve within the primary phase field of the solid solution is no longer a straight line because the composition of the primary phase continually changes as crystallization proceeds. In determining the crystallization curve in a ternary system containing solid solution, it is necessary to know the position of the boundary curves, the isotherms, and the tie lines[12(c)] for numerous points on the isotherms.[14]

(*a*) *The Solid Solution Diagram*

A simple case of solid solution in ternary systems as discussed by Bowen is shown in Figs. XXI($A$) and ($B$). In the binary system $A$-$B$ of Fig. XXI($A$), the tie lines, 1′-5′ and similar ones parallel to the base, give the composition of the solid phase in equilibrium with the liquid phase at the corresponding temperature. The line 5-4-6 (Fig. XXI($B$)) is the isotherm for the temperature $T_1$, and line 5′-4′-6′ is the isotherm for the temperature $T_2$.

[14] The tie lines have been referred to by some writers, particularly Schreinemakers,[8] as solid-phase indicating lines because they indicate the composition of the solid phase in equilibrium with a definite liquid phase. The tie lines must be determined experimentally; they cannot be constructed. In special cases where the extremities of the tie lines or solid-phase indicating lines are on the boundary lines of the three-phase system, they are designated as three-phase boundaries




| POINT | PHASE COMPOSITION, WT. FRACTION | | | | |
|---|---|---|---|---|---|
| | A | B | C | AB | LIQ. |
| $b_1$ | $\frac{P_2-b_1}{A-b_1}$ | | | | $\frac{A-P_2}{A-b_1}$ |
| $b_2$ | | | | $\frac{A-l_1}{A-AB}$ | $\frac{l_1-AB}{A-AB}$ |
| $b_2$ Alternate | | | | $\frac{P_2-b_2}{AB-b_2}$ | $\frac{AB-P_2}{AB-b_2}$ |
| $b_3$ | | | | $\frac{P_2-b_3}{AB-b_3}$ | $\frac{AB-P_2}{AB-b_3}$ |
| $b_4$ | | | $\frac{AB-l_2}{AB-C}$ | $\frac{l_3-C}{AB-C}$ | $\frac{l_2-l_3}{AB-C}$ |

FIG. XX.—Composition of phase assemblages for a crystallization path showing resorption of (A) in a system having a binary compound with a ternary field but without a binary field.

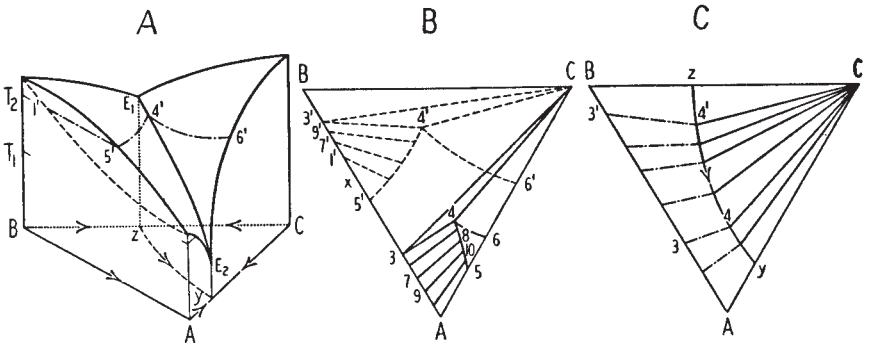



FIG. XXI.—(*A*) Melting surface of a three-component system in which one of the binary systems, *A*–*B*, has solid solutions present. In the ternary system these binary solid solutions exist as the primary phase to boundary $E_1$–$E_2$.

Modified from N. L. Bowen, *Am. J. Sci.*, 4th Ser., **38**, 221 (1914).

(*B*) Sections produced by planes passed parallel to base triangle at the temperatures, $T_1$ (solid lines) and $T_2$ (dotted lines), and tie lines at these temperatures.

(*C*) Series of three-phase boundaries (tie lines) at temperatures from $E_1$ to $E_2$; solid-solution tie lines are broken and single-crystal, *C*, tie lines are solid; tie lines 3-4-*C* and 3′-4′-*C* taken from Fig. XXIB.

The phases present at $T_1$ (Fig. XXI(*B*)) are as follows:

(1) Area 5-4-6, all liquid.

(2) Area *A*-5-4-3, liquid plus solid solution; composition of liquids on line 4-5 and solid solutions on line 3-*A*.

(3) Area 6-4-*C*, liquid and solid *C*; composition of liquid on 4-6.

(4) Area 3-4-*C*, liquid 4, solid solution 3, and solid *C*.

(5) Area 3-*C*-*B*, solid *C* and solid solution; compositions of solid solutions on line 3-*B*.

The phases present at $T_2$ (Fig. XXI(*B*)) are as follows:

(1) Area *A*-5′-4′-6′, all liquid.

(2) Area 5′-4′-3′, liquid plus solid solution; compositions of liquids on line 4′-5′, compositions of solid solutions on line 3′-5′.

(3) Area 6′-4′-*C*, liquid and solid *C*; compositions of liquids on line 4′-6′.

(4) Area 3′-4′-*C*, liquid 4′, solid solutions 3′, and solid *C*.

(5) Area 3′-*C*-*B*, solid *C* and solid solution; compositions of solid solutions on line 3′-*B*.

Point 4 represents the composition of liquid in equilibrium at temperature $T_1$ with two solid phases, namely, solid solution 3 and solid *C*. Point 4′ represents the composition of the liquid in equilibrium at temperature $T_2$ with the two solid phases, *C* and solid solution 3′. Both 4 and 4′ lie on the boundary, $E_1$-$E_2$, of Fig. XXI(*A*). The extremities of lines 3-4 and 3′-4′ lie on boundaries (lines $E_2$-$E_1$ and *A*-*B*) of the ternary system. These tie lines are two of the infinite number of possible three-phase boundaries, some of which are shown in Fig. XXI(*C*). Line 7-8 is the simple type of tie line showing the composition of solid solution 7 in equilibrium with liquid 8 at temperature $T_1$.

Melts represented by a composition in area *z*-*y*-*C* on crystallizing follow a radial line from *C* with phase *C* separating until boundary *z*-*y* is reached at which point of intersection a solid solution begins to separate; the composition of the solid solution is represented by the other extremity of the three-phase boundary at that temperature. For example, a melt whose composition lies on the line *C*-4 will reach the boundary curve at 4 and the composition of the first solid solution to appear is given at point 3. As the temperature drops the liquid changes in composition along *y*-*z* toward *y* while at the same time the solid solution is changing along *B*-*A* toward *A* and the solid *C* remains unchanged in composition. All solutions do not reach *y* before complete solidification takes place, as the original composition of the melt determines the final solidification temperature.

(*b*) *Mechanics of Crystallization*

(i) *No compounds present:* To aid discussion of crystallization paths in ternary systems with solid solutions, a hypothetical diagram is given in Fig. XXII. This diagram is the two-dimensional drawing of Fig. XXI(*A*) on which the following are shown: (1) isotherms, $T_1$, $T_2$, $T_3$, etc. (not related to designations in Fig. XXI), (2) representative tie lines for each of the isotherms in the solid-solution area *B*-$E_1$-$E_2$-*A*, and (3) representative crystallization paths (*d*-*e*, *a*-*k*-3, *k*-*m*, and *f*-4). It is to be emphasized again that in solid solution systems, the crystallization paths are curved lines. The compositions of the solid phase and the liquid existing in equilibrium with it for any respective temperature are joined by a tie line. For example, the solid in equilibrium with the liquid 1 on the isotherm $T_5$ is shown at 1′ and the solid in equilibrium with a liquid of composition 2 on isotherm $T_4$ is shown at 2′.

As an example of crystallization, the composition *a* on isotherm $T_5$ is selected. The crystallization curve for this point is *a*-*k*-3. Upon cooling this melt, the first solid appears at temperature $T_5$ and is represented at the other extremity of the tie line passing through point *a* at temperature $T_5$. This tie line is shown as a dot-dash line and the composition of the solid solution is *a*′. As the temperature is lowered the trace of the compositions of the liquid phase follows the crystallization curve from *a* to 3 and thence the boundary line from 3 to *c*.

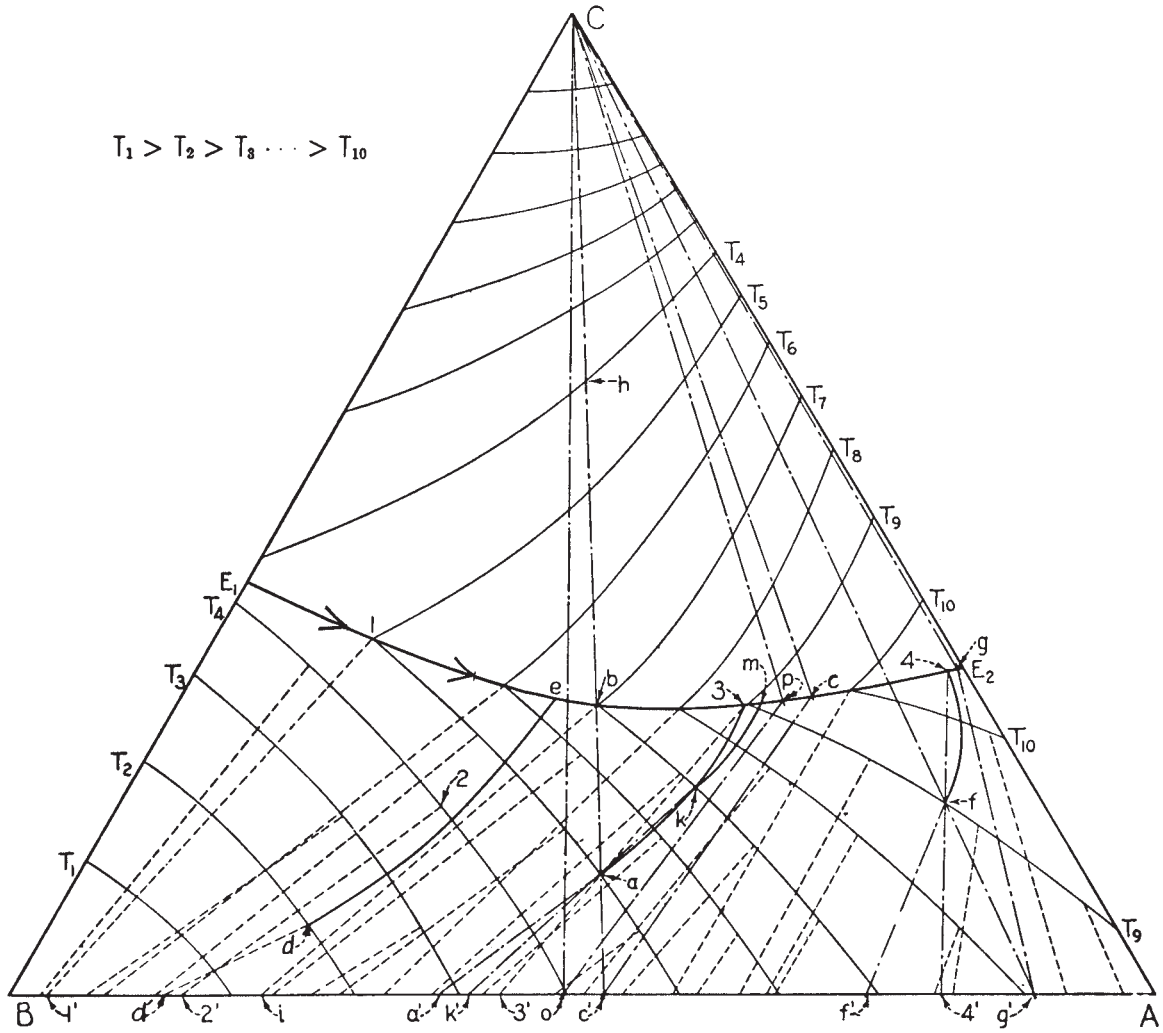



FIG. XXII.—Course of crystallization in a ternary system where one of the binary systems is a complete solid solution series.

The compositions of the solid solutions in equilibrium with the liquids during crystallization from *a* to 3 are represented by the series of tie lines connecting points on the crystallization curve with the corresponding solid solutions; all of these tie lines pass through *a*, for example, *a*-*a'*, *k*-*a*-*k'*, and 3-*a*-3'. But, during cooling from 3 to *c*, the tie lines do not pass through *a;* instead they pass to the right of *a*.[15]

The crystallization will end when the temperature of tie line *c*-*c'* has been reached; this tie line being the one which passes through the point where the extension of line *C*-*a* intersects the boundary line, *A*-*B;* that is, line *C*-*a*-*c'* connects the compositions of the two final solid phases. The line *c*-*c'* is the tie line (three-phase boundary line) for temperature *c* and the triangle *c'*-*c*-*C* is of the same type as 3-4-*C* in Fig. XXI(*B*).

During the cooling period from 3 to *c*, crystalline *C* and solid solution are precipitated together, the solid solution changing in composition from 3' to *c'*, and the liquid from 3 to *c*. The final products of crystallization are, therefore, crystalline *C* and the solid solution of composition *c'*, with the ratio of *C* to solid solution being given by the lever reaction *c'*-*a*/*C*-*a*.

The above example shows that in solid solution systems the end point of the crystallization is not determined by a eutectic but stops at a point determined by the join passing through the composition of the original melt.

[15] In any system, the summation of the phases present equals the composition of the mass being studied. During cooling of composition *a* from *a* to 3, the sum of the liquid plus the solid solution always must equal *a;* hence, the line (i.e., tie line) connecting the compositions of the two coexisting phases must pass through *a*. During cooling from 3 to *c*, a third phase (solid *C*) is present, therefore, the complete composition is expressed by a triangle rather than a straight line. For example, at temperature *p* which is between 3 and *c*, the two solid phases, *C* and solid solution *o*, and liquid *p* coexist; hence, the composition *a* is represented by corners of the triangle *C*-*o*-*p*, and the tie line *o*-*p* does not pass through *a*.

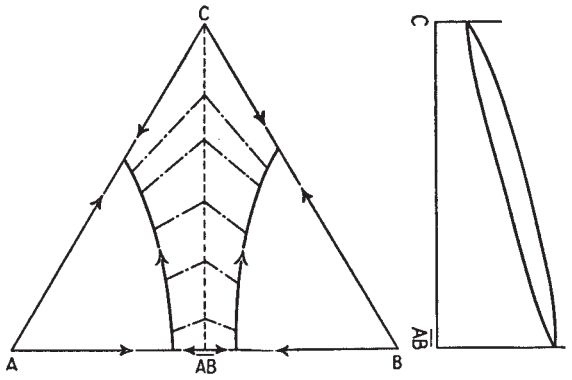



FIG. XXIII.—Ternary system containing a binary compound stable at its melting point which forms a complete series of solid solutions with the third component.
N. L. Bowen, *Am. J. Sci.*, 4th Ser., **38**, 223 (1914).

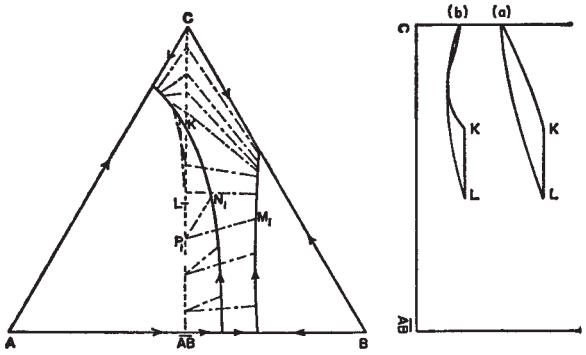



FIG. XXIV.—Ternary system containing a binary compound unstable at its melting point which forms a series of solid solutions with the third component.
N. L. Bowen, *Am. J. Sci.*, 4th Ser., **38**, 225 (1914); see also N. L. Bowen, "The Evolution of Igneous Rocks," Princeton University Press.

A further example is given for the crystallization of composition *f* whose crystallization path is *f*-4-*g*. The first solid to appear upon cooling a melt of this composition is given at *f'*, and the solid at the intersection of the crystallization curve with the boundary line $E_1$-$E_2$ is given at 4'. At the intersection with the boundary line at 4, phase *C* begins to crystallize along with the solid solution and the two coexist from 4 to *g*. The final products of crystallization are solid solution *g'* and *C*.

A melt of composition *h* crystallizes as follows: at temperature $T_4$, crystalline *C* precipitates and continues to do so from *h* to *b;* at *b* solid solution *i* appears and the two solid phases continue together to *c* at which temperature crystallization ceases. The final solid is composed of the two solids, *C* and solid solution *c'* in the proportions *c'-h/C-h*.

Every composition in the solid solution area, *B*-$E_1$-$E_2$-*A*, has a crystallization path different from every other. For example, composition *k* lies on the crystallization path of composition *a*, but its crystallization path is along *k-m* and not *k*-3.

(ii) *Congruent melting binary compound:* Figure XXIII illustrates a case where the compound, $\overline{AB}$, forms a complete series of solid solutions with the component *C*. This case can be considered as two ternary systems of the type represented in Fig. XXI(*A*), namely, systems *C*-$\overline{AB}$-*A* and *C*-$\overline{AB}$-*B*.

(iii) *Incongruent melting binary compound:* In the case where the compound, $\overline{AB}$, is unstable at its melting point (Fig. XXIV) the system cannot be treated in the same manner as the last case. Mixtures along *C-K* behave as true binary mixtures, but from *K* to $\overline{AB}$, the crystallization is ternary. There are two possibilities in this region of the ternary system as are shown in Fig. XXIV at (*a*) and (*b*), that is, there may be a simple solid solution or a solid solution with a minimum. Mixtures in the region *K* to *L* behave on melting as true binary mixtures until the temperature of the isotherm passing through *K* is reached, at which point solid *A* begins to separate from the solid solution. Mixtures between *L* and $\overline{AB}$ melt at temperatures above that of point *K* with the separation of pure *A*. The broken lines in Fig. XXIV are the three-phase boundaries for this type of system. The diopside-forsterite-silica system (Fig. 608) is of the type just described.

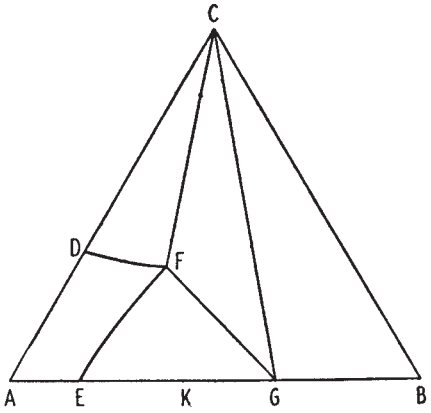



FIG. XXV.—Determination of the position of the three-phase boundary, *F-G*.
Modified from N. L. Bowen, *Am. J. Sci.*, 4th Ser., **40**, 171 (1916).

### (*c*) *Determining Three-Phase Boundaries*

In determining the position of the three-phase boundaries shown on Fig. XXI(*C*), it is necessary to determine the physical properties of the solid solutions present. In Fig. XXV, the lines *D-F* and *F-E* are the isotherms for another system, *A-B-C*, at temperature *T* (similar to lines 4'-5' and 4'-6' of Fig. XXI(*B*)). The phases present in the areas are as follows:

(1) Area *D-F-E-A*, all liquid.

(2) Area *E-F-G*, liquid and solid solution; compositions of liquids on line *E-F*, and composition of solid solutions on line *K-G* (solid solution *G* is in equilibrium with liquid *F* at this temperature).

(3) Area *C-D-F*, liquid plus solid *C;* composition of liquids on line *D-F*.

(4) Area *C-F-G*, liquid *F*, solid solution *G*, and solid *C*.

(5) Area *B-G-C*, solid solution plus solid *C;* composition of solid solutions on line *B-G*.

In order to be able to predict the phases present at any specific temperature, such as *T*, it is necessary to know the position of the line, *F-G*. If the isotherms are known, this line can be fixed by determining only point *G*, the composition of the solid solution at that temperature, because point *F* is already known. This composition may be determined by optical methods provided the optical properties, especially the refractive indices, of the complete series of solid solutions in the binary system are known. X-Ray diffraction methods may be similarly used provided the diffraction constants of the binary solid solutions are known. Lines *C-F* and *C-G* also bound the three-phase field *C-F-G*, and they are merely straight lines radiating from *C*.

A three-phase boundary may also be determined by starting with a mixture of known composition and (1) determining the temperature at which the three-phase area is entered by cooling the melt from a higher temperature to a lower temperature or (2) determining the temperature of beginning of melting by starting with a mixture of solid *C* (Fig. XXV) and a solid solution of known composition lying between *A* and *B*.

## *(4) Multicomponent Systems*

### (A) General

The phase rule, of course, does not limit the number of components that may compose a system, but as the number of components increases, the complexity of the system mounts. Furthermore, for systems of more than three components a simple, convenient graphical representation of equilibrium relations is no longer possible.

The complete phase diagram of a condensed binary system may be represented on a plane surface as the two available dimensions of a plane suffice to permit the plotting of the two independent variables of composition and temperature.

A condensed ternary system is visualized usually as a triangular prism, in which the variables of composition (two independent and one dependent) are represented on an equilateral triangular base, and the independent variable of temperature on an axis vertical to the triangular variable of temperature on an axis vertical to the triangular base (Fig. XII). Three binary systems constitute the boundaries, or outside faces, of the triangular prism. From the binary invariant points (eutectics and peritectics) univariant curves, possessing one degree of freedom, penetrate the interior of the triangular prism. These univariant curves are formed by the intersection of two divariant primary phase surfaces, and along the univariant curves two solid phases are in equilibrium with liquids whose compositions lie on the boundary curves. The junction of three univariant curves forms a ternary invariant point corresponding to the single composition and temperature of a liquid in equilibrium with three solid phases.

In practice, the ternary system is drawn as a plane equilateral triangle, the base of a prism, upon which liquidus temperatures of the primary phase fields are projected as contours (isotherms). In such a representation, the unique liquidus temperature for every composition, a dependent variable, has been chosen as a specialized condition for projection on the composition plane. Fortunately, the physical nature of systems is such that by proper interpretation of the ternary "map," equilibrium relations at any other temperature within the melting range are easily obtainable, provided that solid solutions are not present. If, however, solid solutions exist within the system, the compositions of two coexisting phases must be indicated for every composition and temperature within the solid solution region, namely, that of the liquid solution and that of the coexisting solid solution. For the case of solid solutions, therefore, representation of equilibrium relations on a plane surface may be extremely complicated.

The complete graphical representation of a condensed quaternary system, or one showing the relationships between temperature and all possible mixtures of four components, requires four dimensional space. All possible mixtures of four components, however, may be depicted by a regular tetrahedron, each apex of which represents 100% of one component. The tetrahedron is subdivided into various primary phase volumes, which are separated, in general, by curved surfaces. Each primary phase volume represents the composition of all quaternary liquids that can exist in equilibrium with one particular solid phase. Boundaries between two primary phase volumes are quaternary divariant curved surfaces, in which lie the compositions of all quaternary liquids that can exist in equilibrium with two particular solid phases. The intersections of three divariant curved surfaces, the common boundaries of three intersecting primary phase volumes, form univariant curved lines, on which lie the compositions of quaternary liquids that can exist in equilibrium with three particular solid phases. Finally, quaternary invariant points,[16] each representing the composition of the liquid in equilibrium with four particular solids, are formed by the intersection of four univariant curves, each of which has been formed by three divariant surfaces, each of which, in turn, is the common boundary of two adjoining primary phase volumes. Six curved surfaces intersect at a quaternary invariant point.

Four ternary systems limit the quaternary system, and they are represented by the four equilateral triangles forming the faces of the tetrahedron. The quaternary univariant curves end (or originate) in the ternary invariant points; the quaternary divariant surfaces end (or originate) in the ternary univariant curved lines.

In a condensed ternary system, forming binary and/or ternary compounds, Alkemade lines (joins connecting the composition points of primary phases whose fields are adjacent) divide the equilateral triangle into smaller triangles. The substances indicated at the three vertices of these smaller triangles designate the final products of crystallization at the solidus for all

[16] An invariant point may be a eutectic point, an inversion point, or a reaction point, depending upon the nature of the solid phases and the temperature distribution along the univariant lines which meet at the point.

compositions within the triangular field. If a univariant boundary curve intersects its Alkemade line, it always does so at a maximum temperature on the boundary curve. If the boundary curve does not intersect the Alkemade line, then the maximum on the boundary curve is that end which if prolonged would intersect the Alkemade line.

A condensed quaternary system, similarly, may be divided into smaller tetrahedra by triangular planes connecting the compositions of all primary phases having adjoining liquidus regions. The final products of crystallization at the solidus for all compositions within each tetrahedron are designated by the four phases forming the apices of the tetrahedron. Analogous to the case for ternary systems, the intersection of a quaternary univariant curve with its composition plane always represents a temperature maximum on the univariant curve; or the maximum temperature on the univariant curve is that end which if extended would intersect the appropriate composition plane.

Inasmuch as no independent axis is available for the temperature variable in a condensed quaternary system represented by a compositional tetrahedron, isotherms are depicted as a series of intersecting curved surfaces through the various primary phase volumes. They cannot be represented in a simple manner on a plane diagram. An isothermal section may be represented as a tetrahedron, but mapping difficulties are still inherent in this approach. The above discussion has been based on fixed compositions of the crystallizing phases and excludes solid solution, which further complicates the determination and the mapping of the equilibrium relations.

A five component condensed system illustrates the increasing difficulties involved in studying multicomponent systems composed of more than four components, because for such cases the independent variables of composition can no longer be represented on a single model. Ten basic binary systems form the simplest boundary systems. These ten binary systems, in groups of three, form the boundaries for ten different ternary systems, which, in turn, in groups of four, form the boundaries for the five quaternary systems. Finally, the five quaternary systems define a region in five-dimensional space in which lie the primary phase regions and invariant points. Five-dimensional space can neither be portrayed or even visualized, and it becomes necessary to resort to mathematical concepts.[17]

Figure XXVI shows in tabular form the interrelations of sub-regions both within a given system and between boundary systems and is designed to clarify some of the relations already discussed, as well as to indicate those in more complicated systems. The figure gives (numbers in the squares) the number of solid phases in equilibrium with liquid for regions having different numbers of degrees of freedom, in 2, 3, 4, 5, or $n$ component systems. The number of solid phases is derived simply from the phase rule formula, $P = C + 1 - F$, bearing in mind that the number of solid phases is $P$-1, inasmuch as a liquid phase has been specified as being present in all cases. The sub-regions designated as $O$ solid phases are, of course, regions corresponding to the presence of liquid alone.

In the geometrical representation of degrees of freedom, an invariant condition, zero degrees of freedom, is always represented by a point, whether it be located in a 2, 3, 4, or $n$ dimensional system. A univariant condition, one degree of freedom, is always depicted by a curve, which may, also, lie in a system having any number of dimensions. Similarly, a divariant condition, with two degrees of freedom, may be represented on a surface; and a trivariant condition, with three degrees of freedom, within a volume. Variance of greater than three degrees of freedom cannot be represented physically on a single model.

The number in parentheses at the base and to the left of each vertical arrow in Fig. XXVI indicates the number of regions designated below the arrow that intersect to form the region of next lower variance, indicated above the arrow. For example, in a quinary system the intersection of two, nonrepresentable, four-dimensional primary-phase regions forms a trivariant region wherein lie compositions for which two particular solid phases are in equilibrium with quinary liquids. Three of these trivariant regions intersect in a divariant surface in which three particular solid phases are in equilibrium with quinary liquids. Four divariant surfaces intersect in a univariant boundary curve, along which four solid phases are in equilibrium with quinary liquids. Finally, five univariant curves meet in an invariant point, corresponding to the composition and temperature of liquid in equilibrium with five solid phases.

Figure XXVI also shows the relations between regions in a system and its boundary systems, as indicated by the diagonal arrows. Thus, a curve in a quaternary system may end (or originate) in a ternary invariant point of the boundary system; a volume in a quinary system may end (or originate) in quaternary divariant surfaces, which, in turn, may end (or originate) in univariant curves of ternary boundary systems, etc. It should be noted at this point, however, that regions do not necessarily originate or terminate in boundary systems. As an example, a quaternary univariant curve may connect two quaternary invariant points, in which case, also, the three intersecting divariant surfaces (and volumes) do not contact boundary systems along the univariant curve in question.

From inspection in Fig. XXVI of the numbers (in parentheses) beside each vertical arrow, indicating the relation between two different subregions within a system, it may be observed that the values are prescribed by the mathematical law of combination. Each value is the number of sets of $s_2$ solid phases (in the region below the arrow) that can be formed from $s_1$ solid phases (in the region above the arrow). The

[17] See Mathematical Treatment in Selected Bibliography.

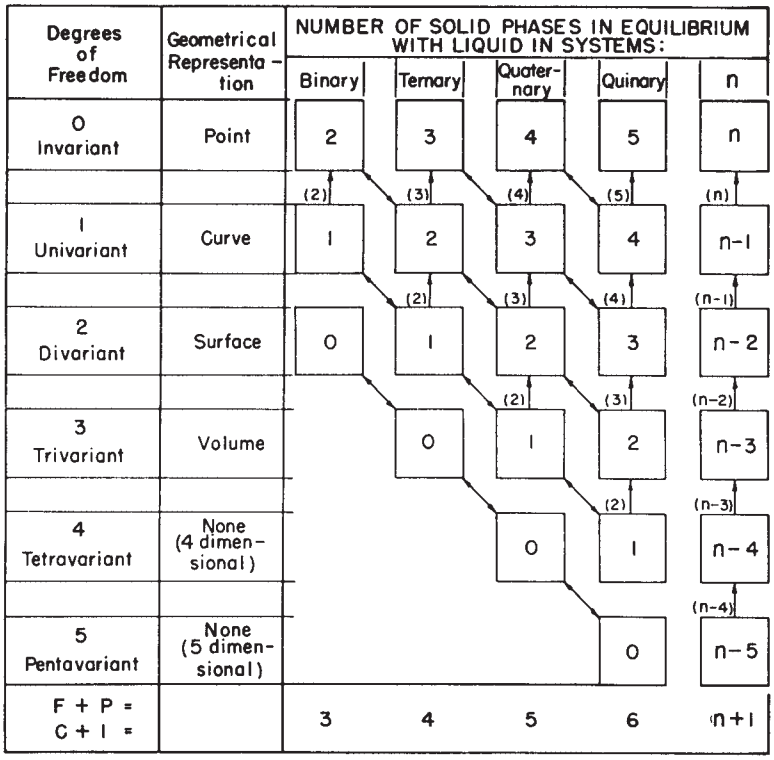



FIG. XXVI.—The interrelationships of sub-regions of multicomponent condensed systems.

The number of regions of $F_2$ degrees of freedom that can be common to a region of lesser degrees of freedom, $F_1$, is given by the mathematical law of combination:

$$C_{s_1,s_2} = \frac{s_1!}{s_2!(s_1 - s_2)!},$$

where $Cs_1,s_2$ is the number of sets of $s_2$ solid phases that can be selected from $s_1$ solid phases, where $s_2$ and $s_1$ are the number of solid phases, respectively, for the two regions.

general formula, which can be found in most algebra texts, is given as:

$$C_{s1,\,s2} = s_1\,!/s_2!(s_1 - s_2)! \qquad (1)$$

where $C_{s1,s2}$ is the number of sets or combinations of $s_2$ objects that can be chosen from $s_1$ objects. As an illustration, suppose the problem is to calculate for a quinary system the number of intersecting divariant surfaces (regions corresponding to equilibrium between three solids and a liquid) that form a univariant curve (regions corresponding to equilibrium between four solids and a liquid). Substituting in equation (1):

$$C_{s1,\,s2} = C_{4,\,3} = \frac{4!}{3!(4-3)!} = 4$$

The four combinations of three solids chosen from four solids, designated *A*, *B*, *C*, *D* are *ABC*, *ABD*, *ACD*, *BCD*.

The combination formula can be further applied to obtain additional information not given in the figure. For example, in a quinary system how many trivariant regions participate in forming a univariant curve? It cannot be reasoned that because three trivariant regions intersect to form a surface, and four surfaces to form a univariant curve that, therefore, 4 × 3 or 12 regions meet at a univariant line, for trivariant regions may be common to more than one of the surfaces involved. Mathematically, the problem is to calculate the number of pairs of solid phases that can be chosen from four. Substituting in equation (1):

$$C_{4,\,2} = \frac{4!}{2!\,(4-2)!} = 6$$

Half of the trivariant regions must be common to two surfaces.

Considering the complexity of even the simplest possible types of multicomponent systems, it is not surprising that the complete equilibrium relations for even a single quaternary system have never been established. Nevertheless, portions of multicomponent systems, especially those of geological and industrial importance, are being studied, and an ever increasing body of data is being accumulated in the literature. It suffices for the purposes of this Compilation to indicate some of the

more common methods which are used to represent graphically such data. The methods, in general, depend on the judicious choice of specializing conditions and restrictions, employing the principles already set forth for binary and ternary systems.

## (B) Graphic Representation

### (a) *Joins*

One approach to the study of multicomponent systems is to determine the phase relations of pertinent joins within the system. The selected joins, either binary, ternary, quaternary, etc., may be found to be true subsystems or most likely pseudo-subsystems.

In the five-component system $K_2O$–CaO–MgO–$Al_2O_3$–$SiO_2$, Bowen and Schairer have found the important join $K_2O \cdot Al_2O_3 \cdot 4SiO_2$ (Leucite)-$CaO \cdot MgO \cdot 2SiO_2$ (Diopside) (Fig. 974) to be a binary subsystem. All phases appearing in the system can be expressed in terms of the end-members, and the course of crystallization of any liquid can be traced to completion. In the system $Na_2O$–CaO–MgO–$Al_2O_3$–$SiO_2$, however, Bowen has shown that the equally important join $CaO \cdot MgO \cdot 2SiO_2$ (Diopside)-$Na_2O \cdot Al_2O_3 \cdot 2SiO_2$ (Nephelite) (Fig. 978) is pseudo-binary. All of the phases appearing in the system cannot be expressed in terms of the end-members; and all areas representing more than two phases in equilibrium are non-binary. Courses of crystallization can be partially traced for the binary portions of the liquidus curve, but invariant points, showing final products of crystallization, lie outside the plane of the figure.

Similarly, in the quaternary system CaO–MgO–$Al_2O_3$–$SiO_2$ the join $MgO \cdot Al_2O_3$–$2CaO \cdot SiO_2$–$2CaO \cdot Al_2O_3 \cdot SiO_2$ (Fig. 919) is a ternary system. Within the same quaternary system, the join $CaO \cdot MgO \cdot 2SiO_2$–$2MgO \cdot SiO_2$–$CaO \cdot Al_2O_3 \cdot 2SiO_2$ (Fig. 909) is not a ternary system because of the appearance of spinel ($MgO \cdot Al_2O_3$), whose composition lies outside the join. Courses of crystallization which do not enter the spinel field can be traced.

Equilibrium relations in a single ternary join of a quaternary system can only provide limited information about the quaternary system. The study of several selected joins, of course, gives additional information. Such a procedure was used by Greene and Bogue in studying four composition planes (joins) in the system $Na_2O$–CaO–$Al_2O_3$–$SiO_2$ (Figs. 828 and 829). If, however, the significant portions of a system be divided by joins into lesser tetrahedra, and the equilibrium relations for the four ternary joins forming each tetrahedron be determined, then considerable information about the quaternary relations may be derived. The principle of this method is illustrated in Fig. 894 which shows relations in the quaternary join $2MgO \cdot SiO_2$ (Forsterite)–$CaO \cdot MgO \cdot 2SiO_2$ (Diopside)–$CaO \cdot Al_2O_3 \cdot 2SiO_2$ (Anorthite)–$SiO_2$ (Silica), part of the quaternary system CaO–MgO–$Al_2O_3$–$SiO_2$. Univariant curves, along which three crystalline phases and liquid are in equilibrium, intersect the ternary joins at points. Such points may be of two general types: ternary invariant points, either eutectic or peritectic, if ternary relations obtain; or "piercing points," according to the nomenclature of J. F. Schairer,[18] if ternary relations do not apply. The sketch in Fig. 894 is conveniently simple from the standpoint that no quaternary invariant points are present. The univariant curves all originate and end in the points in the faces of the tetrahedron (see lower part of figure and explanation).

A more complicated example is shown in Fig. 873, for the quaternary join $FeO$–$CaO \cdot SiO_2$–$2CaO \cdot SiO_2$–$2CaO \cdot Al_2O_3 \cdot SiO_2$ in the quaternary system CaO–FeO–$Al_2O_3$–$SiO_2$. The data of primary interest regarding quaternary equilibrium relations are the compositions and temperatures at the invariant points. These can be estimated from the compositions and temperatures of the invariant points and "piercing points" on the faces of the tetrahedron and from the direction of temperature drop along the quaternary univariant curves originating from these points. The maximum temperature on a univariant curve, as discussed earlier, is at its intersection (or a projected intersection) with the appropriate composition triangle. Therefore, with one exception the temperature decreases along a univariant curve as it proceeds from a ternary invariant point in the face of a join to a quaternary invariant point. In the one exception, however, the temperature may rise if within the tetrahedron solid solutions exist between one or more substances not present at the ternary invariant point and the three solid phases present along the univariant curve. The temperature may rise or fall along a univariant curve penetrating the interior of a tetrahedron from a piercing point. A piercing point by definition is not an invariant point and can only lie in a join other than the one defined by the compositions of the three solid phases in equilibrium with liquids represented by the univariant line. The diagram in the lower part of Fig. 873 indicates schematically, after the method of Schairer,[18] the relationships between univariant curves and invariant points existing in the system. It should be emphasized that the diagram does not depict spatial relations of the univariant curves within the tetrahedron and that the lengths of the univariant curves (shown as straight lines) are arbitrary and without significance. Additional accuracy in locating the compositions and temperatures of the invariant points may be secured by the study of selected quaternary mixtures.

### (b) *Sections*

Another general approach which has been used in the study of multicomponent systems is the section method. Sections may be isothermal, in which case temperature is constant, or they may be planes through a system at constant percentages of one or more of the components.

(i) *Isothermal:* The phase relations at four different temperatures in a quaternary section $Na_2O \cdot SiO_2$–$CaO \cdot SiO_2$–$Na_2O \cdot Al_2O_3 \cdot 2SiO_2$–$CaO \cdot Al_2O_3 \cdot 2SiO_2$ of the

[18] J. F. Schairer, "The System CaO–FeO–$Al_2O_3$–$SiO_2$: I, Results of Quenching Experiments on Five Joins," *J. Am. Ceram. Soc.*, **25**, 241–73 (1942).

system $Na_2O$–CaO–$Al_2O_3$–$SiO_2$ (Fig. 840) were determined by Joseph Spivak. This method is especially convenient when studying complicated solid solution regions where tie lines between solid solutions and liquid solutions are to be indicated, as shown, for example, in Fig. 684. The method of isothermal sections is most useful for showing sub-liquidus relations in refractory oxide systems whose liquidus temperatures can not be determined with available equipment. For example, Fig. 581 shows the 1750°C isotherm for the system BeO–$CeO_2$–$ZrO_2$. Sub-solidus compatibility tetrahedra have been determined in the system CaO–MgO–$SnO_2$–$TiO_2$ (Figs. 939 and 940). In other words, for a given composition in this system, it is possible to state the final products of crystallization, although crystallization paths cannot be followed.

(ii) *Compositional Restraint.* A quaternary system can be represented by a series of ternary diagrams in which one of the composition variables is held at a constant but different value in each diagram. Thus, Lea and Parker (Figs. 943–947) determined equilibria relations in the system CaO–$5CaO{\cdot}3Al_2O_3$–$2CaO{\cdot}SiO_2$–$4CaO{\cdot}Al_2O_3{\cdot}Fe_2O_3$, of particular interest in cement technology, by studying planes through the base (CaO–$5CaO{\cdot}3Al_2O_3$–$2CaO{\cdot}SiO_2$) of the tetrahedron at 0, 2, 5, 10, and 20 percent $Fe_2O_3$, or 0, 6.1, 15.2, 30.4, and 60.8 percent, respectively, of $4CaO{\cdot}Al_2O_3{\cdot}Fe_2O_3$. Figure 943 is a perspective diagram of the system showing primary phase volumes and temperatures of some of the invariant points, derived from the data on the study of the sections together with the phase diagrams of the faces of the tetrahedron (Fig. 944).

A five component system could be studied by a similar technique, although it would be a long and tedious process. Three chosen components would form the apices of a series of ternary diagrams in a two dimensional array. The percentage of a fourth component would vary in the horizontal series, while the percentage of the fifth component would be held constant. In each vertical series the fourth component would remain constant while the fifth increased from row to row.

A five component system might be represented, also, as a series of tetrahedra in which the percentage of the fifth component varied systematically in the diagrams. It should be noted that each tetrahedron would correspond to a constant percentage of the fifth component and that the position of a point within a given tetrahedron would give only the ratio of percentages of the first four components. A primary phase region in any particular tetrahedron would identify the one phase which crystallized first from a liquid whose composition lay within the boundaries of that region.

(c) *Other Specializing Conditions*

In a study of the quaternary system CaO–MgO–$2CaO{\cdot}SiO_2$–$5CaO{\cdot}3Al_2O_3$ (Fig. 891), McMurdie and Insley determined the divariant surface representing the compositions of all liquids that can exist in equilibrium with MgO and one other solid phase (the lower level of the primary phase volume of MgO). By making the MgO component a dependent variable by considering only the MgO content of the limiting surface, it becomes possible to project this surface, as contours of constant MgO content, onto the ternary base of the tetrahedron (Fig. 892); and the representation is greatly enhanced.

An interesting restricting condition was applied by Swayze in a study of a portion of the quinary system CaO–MgO–$Al_2O_3$–$Fe_2O_3$–$SiO_2$, namely, the system CaO–$5CaO{\cdot}3Al_2O_3$–$2CaO{\cdot}Fe_2O_3$–$2CaO{\cdot}SiO_2$ modified by 5% MgO (Fig. 991). This figure requires careful interpretation. The addition of 5% MgO served to saturate the liquids at or near complete melting; to quote Swayze: ". . . , a small amount of periclase has been observed in the MgO-saturated glasses formed by complete or nearly complete melting of the compositions studied." Periclase, therefore, is the primary phase for the whole tetrahedron of compositions. The volumes labeled in the figure are the secondary phases, and the temperature values refer, not to liquidus temperatures, but to temperatures at which the secondary phases start to crystallize. The convenient and essential restricting condition in this case is not the 5% MgO content, per se, but that only the boundaries between the MgO primary phase region and the secondary crystallizing phases be considered. The 5% MgO designated in the figure as "Edge 95% tetrahedron" is of little significance, except to indicate the estimated maximum solubility of MgO in the compositions studied. Any higher percentage of MgO in the mixtures would give the same diagram.

In the graphic representation of multicomponent systems, no one method can be considered superior to another. To a large extent a chosen method will depend upon such factors as the exact region to be studied, the type of information sought, and the detail desired, as well as upon the actual data obtained. Any scheme of representation is acceptable which shows the data with the greatest clarity. It is of utmost importance, however, that the specializing or restricting conditions adopted be explicitly and carefully stated, both in the text and in the legends of the figures. As more and more phase diagrams of binary and ternary systems are made available, an increasing emphasis will be placed on the study of quaternary, quinary, and higher systems. It seems reasonable to suppose that mathematical expression of the relationships among many variables must accordingly assume greater importance in the future as an indispensable complement to the graphical representation of these complex relationships.

## IV. EXPERIMENTAL METHODS FOR HIGH-TEMPERATURE HETEROGENOUS EQUILIBRIUM

Several methods of phase equilibrium determination are possible. All[19] have their definite fields of usefulness and several methods may be needed in different parts of the same system.

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[19] Deformation of Seger or similar ceramic cones is not a method by which phase equilibrium can be determined. The temperature at which a cone deforms depends on a number of factors: amount and viscosity of liquid formed, and rigidity and strength of the cone at the particular temperature, etc.

Methods of determination may be divided into two general classes: the static and the dynamic. Static methods are those in which the temperature of the sample is held constant until equilibrium is attained. The fractionation method and the quenching method are two examples. The dynamic methods are those in which phase changes causing heat effects are indicated by an arrest in temperature change within the sample during uniform heating or cooling.

In systems where equilibrium is reached quickly, such as systems of metallic components, the dynamic methods are the most satisfactory. In systems where equilibrium is sluggish, because of high viscosity in the liquids or of low "crystallization potential" of the solids, the dynamic methods are unusable and it is necessary to resort to the static methods.

The most useful of the static methods is the quenching method since it permits the use of small samples. This procedure was developed for use in the silicate systems at the Geophysical Laboratory and the apparatus is described in several publications.[20] A small sample of homogeneous character having a known composition within the system under consideration is enclosed in a suitable container (usually an envelope of platinum foil or other chemically inert, high-melting metal) and heated at the desired temperature until equilibrium is established. The sample is then rapidly quenched from that temperature by dropping it instantaneously into a liquid at low temperature and the equilibrium conditions prevailing at the high temperature are "frozen." In other words, solid phases present at the high temperature are retained, perhaps metastably, at ordinary temperatures; phases which are liquids at high temperatures exist as glasses at low temperatures. Phases are identified by microscopic means or by crystal diffraction methods. The quenching method is applicable only to systems where changes are sufficiently sluggish to prevent transitions during quenching. The method has the great advantage that phases solid at the equilibrium temperature may be identified at room temperatures by their physical and optical properties.

If it is found that the sample contains more than one crystalline phase, a sample of the same composition is heated to a higher temperature, quenched and examined. If this quenched charge contains only one crystalline phase, which in this case is called the primary phase for that part of the system, the process is repeated until a temperature is found at which the primary phase disappears and leaves only liquid (glass at room temperature). This temperature and composition locate a point on the melting curve of the system investigated. Another static method of determining equilibrium diagrams is by fractionation in which the phases are separated mechanically at the equilibrium temperature and individually analyzed. In ternary systems containing solid solutions, Bowen[21] has shown how the results obtained under conditions of perfect fractionation, where the solids already crystallized have no opportunity of reacting with the liquid, can be used to determine the phase relations under conditions of perfect equilibrium. While the fractionation method is very useful in phase studies in aqueous systems or systems at ordinary temperatures, it presents great difficulties in nonaqueous systems at high temperatures where liquids are often of high viscosity and where it is difficult to prevent the erosion of filtering agencies such as screens.

However, even such difficulties have been partially overcome by the use of a high-temperature centrifuge developed by Newkirk.[22] With this equipment a charge is centrifuged within the furnace, after having been heated at a desired temperature sufficiently long for equilibrium conditions to prevail. Liquid is separated from solid by forced filtration through a platinum sponge filter contained in the small platinum sample holder. The liquid can then be analyzed chemically by micro methods. Applying this method to a multicomponent system, it is possible to determine the path of crystallization of a particular composition from liquidus to invariant point, without prior knowledge of the location of invariant points or primary phase boundaries.

Heating and cooling curves are the usual dynamic methods of determining phase diagrams. In these, time-temperature determinations for each sample tested are plotted. Every temperature arrest indicates a phase change, that is, the final disappearance or the first appearance of a phase during temperature change. The length of time of the arrest is an indication of the relative amount of the phase changed at that temperature.

A refinement of the time-temperature method called differential thermal analysis (DTA) is more sensitive to phase changes, as measured by the heat effects. In DTA the experimental sample and a standard inert sample, usually $Al_2O_3$ powder, are heated simultaneously according to a prescribed schedule, generally about 10°C. per minute. Thermocouples inserted into both samples are so connected that measurements can be made of both the actual temperature and the differential temperature (in mv.) between the standard and the experimental samples. As long as no phase change occurs, the differential in temperature remains relatively constant, but a temperature arrest or acceleration within the experimental sample, indicating a phase change, is reflected by a sharp change in differential.

Heating and cooling methods are suited to the study of systems which reach equilibrium rapidly and where the heat effect of transitions is large. Even in such systems, however, they have the disadvantage that the phases stable at high temperatures cannot be retained

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[20] (*a*) H. S. Roberts, "Automatic Control of Laboratory Furnaces by Wheatstone Bridge Method," *J. Wash. Acad. Sci.*, 11, 401 (1921).

(*b*) G. W. Morey, "Comparison of Heating Curves and Quenching Methods of Melting-Point Determinations," *ibid.*, 13, 325–29 (1923).

[21] N. L. Bowen, "Certain Singular Points on Crystallization Curves of Solid Solutions," *Proc. Nat. Acad. Sci.*, 27, 301–309 (1941).

[22] See R. H., Bogue, under "Silicate Chemistry" in Selected Bibliography, Part V.

at ordinary temperatures for determination of their physical characteristics.

Another dynamic method, especially useful in studying oxidation and reduction reactions, volatility effects, or hydration and carbonation phenomena, depends on sensitive weight recording measurements during heating and cooling of a specimen. Equipment has been designed which simultaneously records weight changes and differential heat effects as a function of temperature.[23]

Definitive phase equilibria studies in oxide systems involving changes in oxidation state require careful control of partial pressures of the gas phase, in particular oxygen. When considering partial pressures, the condensed statement of the phase rule no longer applies, and the pressure variable introduces another degree of freedom in the system. Considerable progress has been made in the development of techniques for controlling partial pressures at high temperature and in the experimental determination and representation of phase diagrams, as for example, the iron-containing systems.[24]

In studies involving non-quenchable transformations it is necessary to identify phases at temperature. Two methods which have been successfully employed for this purpose are high-temperature X-ray diffractometry[25] and high-temperature microscopy.[26] Additional advantages of these methods, when applicable, are that rapid surveys, with small amounts of sample, can be made over a wide temperature range.

With increasing emphasis on refractory systems, methods are receiving attention for achieving, controlling, and measuring temperatures above 1700°C, about the maximum obtainable with the conventional platinum-rhodium (80%:20%) quench furnace. The strip furnace[27] provides an easy means of attaining high temperatures. It usually consists of a narrow, *V*-shaped, short strip of refractory metal (e.g., Pt-40% Rh, or Ir), which acts both as a sample holder and heating element. For phase studies up to 2400°C., an induction furnace,[28] having an iridium-crucible susceptor, also has been used successfully. Both methods have their limitations, and it cannot be emphasized too strongly that the accuracy of temperature measurements with an optical pyrometer depends in the final analysis on the degree of realization of blackbody conditions.[29]

The diagrams presented refer only to systems which are in equilibrium for the temperatures specified. They give no information as to the velocity of reactions, but they do define the relative amounts of crystalline and liquid phases present at any temperature and composition provided the time has been sufficient for equilibrium to be attained. Most ceramic and related processes are incomplete chemical reactions and the results obtained are dependent upon time as well as temperature. In applying equilibrium diagrams to manufacturing processes, consideration must be given to this difference between the ideal and the practical conditions.

For example, the composition of a porcelain body composed of $X\%$ of flint, $Y\%$ of clay (containing alumina, silica, and water only) and $Z\%$ of potash feldspar can be represented in the system $K_2O$–$Al_2O_3$–$SiO_2$ (Fig. 407) if the batch materials are pure and the body had been fired to a sufficiently high temperature to eliminate water. The composition of the porcelain in terms of the components is as follows:

$$\begin{aligned} SiO_2 &= X + 0.541Y + 0.6472Z \\ Al_2O_3 &= 0.459Y + 0.184Z \\ K_2O &= 0.169Z \end{aligned}$$

It is most improbable, however, that the phases as determined from the equilibrium diagram would be equivalent, quantitatively or qualitatively, to the constituents observed microscopically in the commercially manufactured porcelain of this composition. The high viscosity of the melted feldspar, the low rate of solution of the quartz, and the slow diffusion of the partially mixed and partially melted batch materials would hinder the attainment of equilibrium and of homogeneity so that the constituents would not only differ from the equilibrium phases but the composition (in terms of constituents) would vary widely from place to place in the body.

In the application of equilibrium diagrams to actual processes care must be taken that the actual and ideal are comparable. The presence of an impurity even in small amounts introduces an additional component which in many instances alters the solubility and melting relations so profoundly that no adequate interpretation on the basis of the simpler diagram is possible.

Although the phase diagram gives no information as to rates of reaction, it is often possible to infer from such diagrams what the products of reaction may be under certain conditions of disequilibrium and arrested reaction. The calculations of Lea and Parker[30] and of Dahl[31] on the phases existing in the system, CaO–$Al_2O_3$–$Fe_2O_3$–$SiO_2$, under certain conditions of arrested reaction have enabled the cement chemist to estimate phases present in cement clinkers under plant conditions of partial disequilibrium.

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[23] See F. A. Mauer under "Methods and Techniques, (A) General" of Selected Bibliography.

[24] See A. Muan under "Theory" in Selected Bibliography.

[25] Ernest M. Levin and Floyd A. Mauer, "Improved Sample Holder for X-Ray Diffractometer Furnace," *J. Am. Ceram. Soc.*, **46** [1], 59–60(1963). This paper cites other references on the subejct.

[26] See F. Ordway, also J. H. Welch, under "Methods and Techniques, (A) General" of Selected Bibliography.

[27] H. S. Roberts and G. W. Morey, "Micro Furnace for Temperatures above 1000°C," *Rev. Sci. Inst.*, 1, 576–579 (1930).

[28](a) S. J. Schneider, "Phase Equilibria in Systems Involving the Rare Earth Oxides. Part III. The $Eu_2O_3$–$In_2O_3$ System," *J. Research Natl. Bur. Standards*, **65A** [5], 429–434 (1961).

(b) S. J. Schneider and J. L. Waring, "Phase Equilibrium Relations in the $Sc_2O_3$–$Ga_2O_3$ System," *J. Research Natl. Bur. Standards*, **67A**, [1], 19–25 (1962).

[29] Samuel J. Schneider, "Compilation of the Melting Points of the Metal Oxides," National Bureau of Standards Monograph 68, Oct. 10, 1963. 31 pp.

[30] See section on "Interpretation" in Selected Bibliography, Part V.

[31] See section on "Mathematical Treatment" in Selected Bibliography, Part V.

## V. SELECTED BIBLIOGRAPHY

It is neither the purpose nor intention of the authors to compile a complete set of references for the various topics included in the "Selected Bibliography." Neither is it claimed that all of the most important ones have been listed. Nevertheless, it is hoped that the selection will prove beneficial in introducing the novice to some of the aspects of phase equilibria study which perforce have not been discussed or only partially so in the text.

### *(1) Theory*

**Bowden, S. T.,** "Phase Rule and Phase Reactions," Macmillan and Co., London, 1938.

**Dahl, L. A.,** "Equilibrium in Heterogeneous Systems of Two or More Components," *J. Chem. Education*, **26**, 411 (1949).
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**Findlay, A., Campbell, A. N., and Smith, N. O.,** "The Phase Rule and Its Applications," Ninth Edition, Dover Publications, Inc., New York, 1951. 494 pp. + 236 figs.
A comprehensive introduction to the subject, including chapters on liquid-vapor equilibria, aqueous systems, practical applications, thermodynamic deductions, and experimental determination of binary diagrams.

**"The Collected Works of J. Willard Gibbs,"** Volume I, Thermodynamics, Yale University Press, New Haven, Conn. Reprinted 1957. 434 pp.
This volume includes the well known memoir "On the Equilibrium of Heterogeneous Substances," which forms the theoretical basis for the Phase Rule and the graphical representation of equilibria.

**Marsh, J. S.,** "Principles of Phase Diagrams," First Edition, McGraw-Hill Book Co., New York, 1935. xiv + 193 pp. + 180 figs.

**Masing, G.** (translated by B. A. Rogers), "Ternary Systems," Reinhold Publishing Corporation, New York, 1944. 173 pp. + 166 figs. Available as a paperback from Dover Publications, Inc., New York, N. Y., 1960.
Discussion of the fundamental theory underlying three component systems. Several alloy systems explained in detail.

**Muan, Arnulf,** "Phase Equilibria at High Temperatures in Oxide Systems Involving Changes in Oxidation States," *Am. J. Sci.*, **256**, 171–206 (1958).
This paper discusses theoretical principles of controlling partial pressures of the gas phase and the representation of phase relationships in binary (Fe–O), ternary ($FeO$–$Fe_2O_3$–$SiO_2$) and quaternary ($MgO$–$FeO$–$Fe_2O_3$–$SiO_2$) systems. Four different idealized conditions are considered: (1) constant total composition of condensed phases, (2) constant $O_2$ pressure, (3) constant mixing ratio $pCO_2/pH_2$, and (4) crystallization in contact with metallic iron.

**Ricci, John E.,** "The Phase Rule and Heterogeneous Equilibrium," D. Van Nostrand Co., Inc., New York, 1951. 505 pp.
A systematic study of the meaning and application of the Phase Rule. Good discussion of reciprocal ternary systems and aqueous quaternary and quinary systems. Book is profusely illustrated.

**Ricci, John E.,** "Guide to the Phase Diagrams of the Fluoride Systems," Oak Ridge National Laboratory Report No. ORNL-2396, Oak Ridge, Tennessee, 1958. 106 pp. Available from the Office of Technical Services, Department of Commerce, Washington, D. C.
Detailed discussion of phase equilibria occurring in several complex ternary salt systems. First sections present general principles and explanations, as an aid in reading, interpreting, and using actual diagrams.

**Tammann, G.,** "Lehrbuch der heterogenen Gleichgewichte," Vieweg, Braunschweig (1924).
Classical textbook on heterogeneous equilibria.

**Vogel, R.,** "Die heterogenen Gleichgewichte," Vol. II: Handbuch der Metallphysik, Leipzig, 1937.

**Wetmore, F. E. W., and LeRoy, D. J.,** "Principles of Phase Equilibria," First Edition, McGraw-Hill Book Company, Inc., New York, 1951. 200 pp.
Lucid explanation of phase equilibria principles, using a combination of the practical and theoretical approaches. Contains a section on thermodynamic considerations. Contrary to convention, arrows on boundary curves in the phase diagrams point in the direction of rising temperatures.

**Wilson, A. J. C.,** "Binary Equilibrium," *J. Inst. Metals* **70**, Part II, 543–560 (1944).
Thermodynamic derivations are given for several rules governing the construction of phase equilibrium diagrams for binary equilibrium.

**Zernike, J.,** "Chemical Phase Theory," Kluwer's Publishing Co., Ltd., Deventer, Netherlands, 1955. 493 pp. (In English).
This book is a critical, comprehensive, and modern treatise on the deduction, the applications, and the limitations of the phase rule.

### *(2) Interpretation*

**Bowen, N. L.,** "Evolution of Igneous Rocks," p. 60, Princeton University Press, Princeton, N. J., 1928. 332 pp.; *Ceram. Abstracts*, **8** [8] 609 (1929).

**Dahl, L. A.,** "Interpretation of Phase Diagrams of Ternary Systems," *J. Physical Chemistry*, **50** [3] March (1946).
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**Foster, Wilfrid R.,** "Contribution to the Interpretation of Phase Diagrams," *J. Am. Ceram. Soc.*, **34**, 151–160 (1951).
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**Foster, Wilfrid R.,** "Solid-State Reactions in Phase Equilibrium Research," I. *Bull. Am. Ceram. Soc.*, **30** [8] 267–270; II. *Ibid.*, [9] 291–296 (1951).
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**Korzhinskiĭ, D. S.,** "Physicochemical Basis of the Analysis of the Paragenesis of Minerals," Translated from Russian by the Consultants Bureau, Inc., New York, 1959. 142 pp.
This book concentrates on the study of the dependence of mineralogical composition on known factors affecting phase equilibrium, namely, pressure, temperature, and composition. Projective geometry is used freely to represent the relationships.

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Contains section on the compound content in quarternary mixes in which equilibrium between solid and liquid is not maintained during cooling.

**Levin, Ernest M., and Block, Stanley,** "Structural Interpretation of Immiscibility in Oxide Systems: I. Analysis and Calculation of Immiscibility. II. Coordination

Principles Applied to Immiscibility. III. Effect of Alkalis and Alumina in Ternary Systems," *J. Am. Ceram. Soc.*, **40** [3] 95–106, [4] 113–118 (1957); **41** [2] 49–54 (1958).

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**Morey, George W.,** "The Interpretation of Phase Equilibrium Diagrams," *The Glass Industry*, **12** [4] 69–80 (1931).

Discusses the interpretation of binary and ternary diagrams as applied to several glass forming systems.

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## *(3) Methods and Techniques*

### (A) General

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**Herzfeld, Charles M.,** Editor-in-Chief, "Temperature, Its Measurement and Control in Science and Industry," Volume 3: Part 1. "Basic Concepts, Standards, and Methods"; Part 2. "Applied Methods and Instruments," Reinhold Publishing Corp., New York, N. Y., 1962. 848 pp., 1094 pp.

These two books comprise the most comprehensive treatise on the subject.

**Hume-Rothery, W., Christian, J. W., and Pearson, W. B.,** "Metallurgical Equilibrium Diagrams," The Institute of Physics, London, 1952.

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**Mauer, Floyd A.,** "An Analytical Balance for Recording Rapid Changes in Weight," *Rev. Sci. Inst.*, **25** [6] 598–602 (1954).

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For additional description see Bogue, "The Chemistry of Portland Cement" (p. 95), under (6) Silicate Chemistry.

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**Welch, J. H.,** "A Simple Microscope Attachment fo Observing High-Temperature Phenomena," *J. Sci. Inst.*, **31**, 458–462 (1954).

This article describes modifications of the hot wire apparatus developed by Ordway.

### (B) Optical Mineralogy

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A collection of the "best" values for selected physical properties of chemical substances that are of interest to ceramists, including data on density, melting point, transition point, boiling point, sublimation point, decomposition temperature, refractive index, crystal form, and color.

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Part III. Determinative Tables, Second Edition, 1929. 204 pp. + 3 charts.

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### (C) Differential Thermal Analysis

**Mackenzie, R. C.,** "Scifax Differential Thermal Analysis Data Index," 1962. Available from Cleaver-Hume Press Ltd., 31 Wright's Lane, Kensington, London, W.8.

The index contains a total of 1630 punched cards, coded according to 29 ranges of the principal and second peaks, respectively. Cards are grouped into Mineral, Inorganic, and Organic sections. Future supplementary sets and occasional replacement cards are planned.

**Smothers, W. J., and Chiang, Yao,** "Differential Thermal Analysis: Theory and Practice," Chemical Publishing Co., Inc., 212 Fifth Ave., New York, N. Y., 1958. 444 pp.

A concise book covering various aspects of differential thermal analysis (DTA), such as origins, equipment, theory, qualitative and quantitative results, and recent developments. About two-thirds of the book is devoted to four appendices: (1) Publications (covering the period 1877–1957). (2) Information on Equipment. (3) Index of Operators of DTA Equipment. (4) Reference List of Materials Studied.

A new edition of this book by the same authors and publisher titled "Handbook of Differential Thermal Analysis" is scheduled for publication in 1964.

## (D) X-ray Powder Diffraction and Crystal Chemistry

**Azároff, Leonid V.,** "Introduction to Solids," McGraw-Hill Book Co., Inc., New York, N. Y., 1960. 460 pp.

Primarily a college text for physical science and engineering students in which crystal chemistry is applied to the structure and properties of various classes of solids, e.g., metals, semiconductors, and insulators.

**Azároff, Leonid V., and Buerger, Martin J.,** "The Powder Method in X-Ray Crystallography," McGraw-Hill Book Co., Inc., New York, N. Y., 1958. 342 pp.

Primarily a textbook on the theory and practice of the x-ray powder method, for the making and interpretation of powder photographs.

**Bunn, C. W.,** "Chemical Crystallography," Second Edition, Oxford, at the Clarendon Press, 1961. 509 pp.

Part I of this book is a guide to the identification of solid substances by means of optical properties and x-ray powder photographs. Part II is concerned with structure determination. The Author uses a practical approach and avoids formal physical or mathematical treatment.

**Donnay, J. D. H., Donnay, Gabrielle, Cox, E. G., Kennard, Olga, and King, Murray Vernon,** "Crystal Data, Determinative Tables," Second Edition, ACA Monograph Number 5, American Crystallographic Association, 1963. 1302 pp. Available from Polycrystal Book Service, G.P.O. Box 620, Brooklyn 1, New York, N. Y., U. S. A.

This monograph contains an estimated 13,000 entries of inorganic compounds, organic compounds, and proteins, systematically arranged in groups according to the six crystal systems. Data given include unit cell dimensions, space point group, Z, crystal structure, and specific gravity.

**Hey, Max H.,** "An Index of Mineral Species and Varieties," Printed by Order of the Trustees of the British Museum, Jarrold and Sons Ltd., Norwich, Great Britain, 1962. 728 pp.

Minerals are listed according to chemical classification and again according to alphabetical order. A pronouncing index of accepted mineral names is included.

**Klug, Harold P., and Alexander, Leroy, E.,** "X-Ray Diffraction Procedures," John Wiley and Sons, Inc., New York, N. Y., 1954. 716 pp.

This book presents in detail the basic techniques, procedures, and applications of the powder method to polycrystalline and amorphous materials. Geiger-counter spectrometric techniques, small-angle scattering methods, and radial-distribution analysis are brought together in a single volume.

**Peiser, H. S., Rooksby, H. P., and Wilson, A. J. C.,** Technical Editors, "X-Ray Diffraction by Polycrystalline Materials," John Wright and Sons Ltd., Bristol, 1955.

Thirty experts make authoritative contributions to the various aspects of crystal analysis through the study of polycrystalline materials. Theory, experimental techniques, and interpretation are covered in detail. An interesting feature of the book is a series of essays at the end, describing application of the polycrystalline method to diverse fields of research.

**Wells, A. F.,** "Structural Inorganic Chemistry," Third Edition, Oxford University Press, Amen House, London, 1962. 1055 pp.

This book is both a textbook and a reference source for crystal chemistry and particular structures.

**Wyckoff, Ralph W. G.,** "Crystal Structures," Second Edition, Vol. 1, John Wiley and Sons, Inc., New York, N. Y., 1963. 467 pp.

This monumental reference work, published in a hard-cover edition, is the first of a series of several volumes. Contents include structures of the elements and of compounds with formula type RX and $RX_2$.

**"Standard X-ray Diffraction Powder Patterns,"** National Bureau of Standards Circular 539, Vols. 1–10 (1953–1960). Continued in National Bureau of Standards Monograph 25, Sections 1–2 (1962–1963). Available from Superintendent of Documents, U. S. Government Printing Office, Washington, D. C. 20234

Standard patterns, suitable for identification of unknown crystalline materials, are presented. High purity materials are used. New data is published continually on groups of 30 to 60 substances.

**"X-Ray Powder Data Card File and Index Book (XR-PDF),"** issued by the American Society for Testing and Materials, X-Ray Department, 1916 Race St., Philadelphia Pa., U. S. A.

Contains X-ray powder data on some 7000 substances; supplements are being added continually.

## (E) Hydrothermal

**Ahrens, L. A., Rankama, Kalervo, and Runcorn, S. K.,** Editors, "Physics and Chemistry of the Earth," McGraw-Hill Book Co., Inc., New York, N. Y., 1956. 317 pp.

A collection of eight articles on geophysics and geochemistry. In the chapter "Investigations Under Hydrothermal Conditions," Rustum Roy and O. F. Tuttle present a brief historical review, a description of equipment, results of studies on mineral synthesis and analysis of phase equilibrium data.

**Gilman, J. J.,** Editor, "The Art and Science of Growing Crystals," John Wiley and Sons, Inc., New York, 1963. 493 pp.

Chapter 13, "Hydrothermal Growth," by A. A. Ballman and R. A. Laudise is a concise discussion of the methods and techniques of growing large crystals under controlled conditions, with particular reference to the growth of quartz.

**Morey, George W.,** "Hydrothermal Synthesis," *J. Am. Ceram. Soc.*, **36** [9] 279–285 (1953).

Presents underlying theory, describes apparatus, and gives illustration of the experimental method.

## (F) High Pressure

**Bridgman, P. W.,** "The Physics of High Pressure," G. Bell and Sons, Ltd., London, Reprinted 1952. 445 pp.

This book, by an outstanding investigator, surveys the important work in the field up to the time of publication. Chapters on melting phenomena and polymorphic transitions are of especial interest in phase studies.

**Paul, William, and Warschauer, Douglas M.,** "Solids Under Pressure," McGraw-Hill Book Co., Inc., New York, N. Y., 1963. 478 pp.

This volume contains a collection of thirteen articles dealing with different aspects of research on the physics of crystalline solids at high pressures.

**Wentorf, R. H., Jr.,** Editor, "Modern Very High Pressure Techniques," Butterworth Inc., Washington, D. C., 1962. 233 pp.

The book takes the form of a collection of papers written by experts. Main emphasis is on the design of apparatus for studying the properties of materials at pressures above 20,000 atmospheres.

## (4) Mathematical Treatment

**Dahl, L. A.,** "Analytical Treatment of Multicomponent Systems," *J. Phys. Colloid Chem.*, **52**, 698–729 (1948).

Properties and applications of intrinsic equations in the analytical treatment of multicomponent systems, such as the conversion of compositions from one system of components to another, the classification of compositions, and the estimation of phase proportions at invariant points.

**Dahl, L. A.,** "Parametric Equations in the Treatment of Multicomponent Systems," *J. Phys. Colloid Chem.*, **54**, 547–564 (1950).

Application of parametric equations to phase equilibria problems; especially useful when dealing with a system of a small number of components within a multicomponent system.

**Dahl, L. A.,** "Estimation of Phase Composition of Clinker," *Rock Products*, **41–42** (1938–39).

Paper deals essentially in principles and calculations involved in determining phase composition at temperatures at or above the temperature of liquid formation in the quaternary system $3CaO \cdot SiO_2$–$2CaO \cdot SiO_2$–$3CaO \cdot Al_2O_3$–$4CaO \cdot Al_2O_3 \cdot Fe_2O_3$.

**Morey, George W.,** "Analytical Methods in Phase Rule Problems," *J. Phys. Chem.*, **34** [8] 1745–1750 (1930).

Application of linear equations to phase rule problems, and their solution by determinant notation.

**Ordway, Fred,** "Matrix Algebra for Calculating Multicomponent Mixtures," *J. Portland Cement Assoc. Research and Development Labs*, **2** [1] 28–36 (1960).

**Pepper, Paul M.,** "Coexistence Relations of $n + 1$ Phases in $n$-Component Systems," *J. Appl. Phys.*, **20** [8] 754–60 (1949).

In isothermic-isobaric sections of $n$-component systems representing coexistence relationships of $n + 1$ phases, two coexistence patterns at most are possible. Formulas are derived (using vector methods) for calculating the composition of a "well-chosen sample" from which examination of the phases present clarifies the coexistence relationships of the $n + 1$ phases of known composition. Supplementary formulas are given for the range of coexistence, in the composition space, for any $n$ phases known to coexist.

## (5) Thermodynamic Calculations

**Epstein, Leo F., and Howland, W. H.,** "Binary Mixtures of $UO_2$ and Other Oxides," *J. Am. Ceram. Soc.*, **36** [10] 334–335 (1953).

Phase diagrams of the binary systems containing $UO_2$ and the oxides MgO, $Al_2O_3$, and BeO are constructed using the laws of ideal solutions and an approximation for the entropy of fusion.

**Knapp, W. J.,** "Use of Free Energy Data in the Construction of Phase Diagrams," *J. Am. Ceram. Soc.*, **36** [2] 43–47 (1953).

A review of the use of free energy-composition curves (at constant pressure and temperature and with the assumption of ideal solution behavior) for determining the range of composition over which a phase, or combination of phases, may be stable.

**Kubaschewski, O., and Evans, E. LL.,** "Metallurgical Thermochemistry," Third Edition, Pergamon Press, New York, 1958. 425 pp.

This book serves as both an introduction to the subject and as a work of reference. Emphasis is on practical application of chemical thermodynamics, and extensive tables of thermochemical data are included.

**Morey, George W.,** "The Application of Thermodynamics to Heterogeneous Equilibria," *J. Franklin Institute*, **194** [10] 425–484 (1922).

An exposition of the application of the first two laws of thermodynamics to the equilibrium of heterogeneous substances.

**White, James,** "Phase Relations in Ceramics," pp. 94–161, in "Ceramics: A Symposium," arranged and edited by A. T. Green and Gerald H. Stewart, published by the British Ceramic Society, Stoke-on-Trent (1953). 877 pp.

Elucidation of thermodynamic principles applied specifically to solids and solutions of interest in ceramics.

The general symposium is a survey of the practice, the technology, and the basic science of ceramics and constitutes a valuable contribution to the literature of ceramics.

**Wygant, J. F. and Kingery, W. D.,** "Applications of Thermodynamics in Ceramics":

I. Energy and Heat Content, *Am. Ceram. Soc. Bull.*, **31** [5] 165–168 (1952).

II. Free Energy, Entropy, and Equilibrium, *ibid.*, **31** [6] 213–217 (1952).

III. Stability of Ceramic Materials, *ibid.*, **31** [7] 252–254 (1952).

IV. Crystal Chemistry, Physical Processes and Surface Effects, *ibid.*, **31** [8] 294–297 (1952).

V. Semiempirical Calculations, *ibid.*, **31** [9] 344–347 (1952).

VI. Summary, bibliography, and sources of data, *ibid.* **31** [10] 386–388 (1952).

## (6) Silicate Chemistry

**Bogue, Robert Herman,** "The Chemistry of Portland Cement," Second Edition, Reinhold Publishing Corporation, New York, N. Y., 1955. 793 pp.

This comprehensive treatise is divided into three parts: I. The Chemistry of Clinker Formation; II. The Equilibria of Clinker Components; III. The Chemistry of Cement Utilization. Part II deals with the principles and techniques of high-temperature phase research, as well as with the detailed consideration of specific systems.

**Eitel, Wilhelm,** "Physical Chemistry of the Silicate," 5 volumes, Academic Press, New York, N. Y.

Volume 1, 1963, about 630 pp. Contents (tentative): Silicate Crystal Structures; Clay Mineral Structures; Silicate Dispersoids.

Volume 2, 1963, about 700 pp. Contents (tentative): Properties and Constitution of Silicate Glasses; Industrial Glass and Enamels; Industrial Slags.

Volumes 3–5, in preparation.

**Eitel, Wilhelm,** "Thermochemical Methods in Silicate Investigation," Rutgers University Press, New Brunswick, N. J., 1952. 132 pp.

An exposition of the science of calorimetry applied to silicate investigations. Calorimeters for determining heats of reaction and specific heats are described, along with methods of calculating the thermodynamic properties from the obtained data.

**Eitel, Wilhelm,** "Silicate Melt Equilibria," Rutgers University Press, New Brunswick, N. J., 1951. 159 pp. + 200 figs.

An exposition of phase equilibria principles applied to the understanding of anhydrous silicate systems.

**Frondel, Clifford,** "The System of Mineralogy" of James Dwight Dana and Edward Salisbury Dana, Seventh Edition, Vol. III, Silica Minerals, John Wiley and Sons, Inc., New York, 1962. 334 pp.

This book describes the mineralogy of the polymorphs of silica.

**Greig, J. W.,** "Immiscibility in Silicate Melts," *Am. J. Sci.*, **13**, 1–44, 133–154 (1927).

Classic study on silicate immiscibility.

**Sosman, Robert B.,** "The Properties of Silica," The Chemical Catalog Company, Inc., J. J. Little and Ives Company, New York, 1927. 856 pp.

A comprehensive text on the properties of silica, with a section on industrial applications. A revised edition is in preparation.

## (7) Special Collections of Phase Diagrams

**Osborn, E. F. and Muan, A.,** "Phase Equilibrium Diagrams of Oxide Systems," The American Ceramic Society, 4055 N. High St., Columbus, Ohio.

Ten large-scale ternary phase equilibrium diagrams of fundamental importance are drawn from published data. Each diagram is on a 500 millimeter equilateral triangle, with a scale accurate enough to permit interpolation to within 0.1%.

**Thoma, R. E.,** "Phase Diagrams of Nuclear Reactor Materials," Oak Ridge National Laboratory Report No. ORNL-2548, Oak Ridge, Tennessee, 1959. 205 pp. Available from the Office of Technical Services, Department of Commerce, Washington, D. C.

This compilation presents 145 phase diagrams for possible materials for use in nuclear reactors. Composition and temperature of invariant points, as well as the phase reaction, are listed separately.

## (8) Phase Diagrams in Related Fields

**American Society for Metals,** "Metals Handbook," 1948 edition, 1332 pp., Cleveland 3, Ohio.

Sections on the constitution of binary alloys (pp. 1146 to 1240) and ternary alloys (pp. 1241 to 1268). Each diagram is annotated.

**Hansen, Max,** "Constitution of Binary Alloys," Second Edition, McGraw-Hill Book Co., Inc., New York, N. Y., 1958. 1305 pp. + 684 figs.

This comprehensive volume containing 1334 systems, 717 diagrams, and about 9800 references deals only with binary alloy systems, including the borides, carbides, nitrides, and silicides. All data are critically evaluated and incorporated into composite diagrams. Symmetry and lattice spacings of intermediate phases are given.

**Gschneidner, Karl A., Jr.,** "Rare Earth Alloys," D. Van Nostrand Co., Inc., Princeton, N. J., 1961. 449 pp.

This book is a critical review of the alloy systems of the rare earth, scandium and yttrium metals. A hundred phase diagrams are included which have been constructed from the data of various references. The alloy systems, involving rare earth metals as one or more components, are divided into subgroups of binary, ternary and higher multicomponent systems.

**Schwarzkopf, Paul, and Kieffer, Richard,** "Refractory Hard Metals," Macmillan, New York, 1953. 447 pp. + 92 figs. + 100 tables.

Deals with the preparation, properties, and application to high temperature materials of the so-called hard metals, namely, the refractory and hard carbides, nitrides, borides, and silicides of transition metals. Phase diagrams given where available.