Thermodynamic Quantities for the Ionization Reactions of Buffers

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This review contains selected values of thermodynamic quantities for the aqueous ionization reactions of 64 buffers, many of which are used in biological research. Since the aim is to be able to predict values of the ionization constant at temperatures not too far from ambient, the thermodynamic quantities which are tabulated are the pK, standard molar Gibbs energy $\Delta_r G^\circ$, standard molar enthalpy $\Delta_r H^\circ$, and standard molar heat capacity change $\Delta_r C_p^\circ$ for each of the ionization reactions at the temperature $T = 298.15\,\mathrm{K}$ and the pressure $p = 0.1\,\mathrm{MPa}$. The standard state is the hypothetical ideal solution of unit molality. The chemical name(s) and CAS registry number, structure, empirical formula, and molecular weight are given for each buffer considered herein. The selection of the values of the thermodynamic quantities for each buffer is discussed.

Key words: buffers; enthalpy; equilibrium constant; evaluated data; Gibbs free energy; heat capacity; ionization; pK; thermodynamic properties.

Contents

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Nomenclature

Symbol	Name	Unit
a	activity	dimensionless
A_m	Debye–Hückel constant	$kg^{1/2}\,mol^{-1/2}$
B	parameter in Debye–Hückel equation	$kg^{1/2}\,mol^{-1/2}$
c	concentration	$mol\,dm^{-3}$ or M[a]
$\Delta_r C_p^\circ$	standard molar heat capacity of reaction at constant pressure	$J\,K^{-1}\,mol^{-1}$
C_i^{ex}	excess heat capacity of species i	$J\,mol^{-1}\,K^{-1}$
$\Delta_r G°$	standard molar Gibbs energy of reaction	$kJ\,mol^{-1}$
$\Delta_r H°$	standard molar enthalpy of reaction	$kJ\,mol^{-1}$
H_i^{ex}	excess enthalpy of species i	$kJ\,mol^{-1}$
I	ionic strength, molality or concentration basis	$mol\,kg^{-1}$ or M[a]
I_c	ionic strength, concentration basis	$mol\,dm^{-3}$
I_m	ionic strength, molality basis	$mol\,kg^{-1}$
K	equilibrium constant[b]	dimensionless
m	molality	$mol\,kg^{-1}$
p	pressure	Pa
pK	$-\lg K$[b]	dimensionless
R	gas constant (8.31451 $J\,K^{-1}\,mol^{-1}$)	$J\,K^{-1}\,mol^{-1}$
T	temperature	K
T_r	reference temperature (usually 298.15 K)	K
z	charge number	dimensionless
γ	activity coefficient[b]	dimensionless
Γ	ratio of activity coefficients	dimensionless
ρ	density	$kg\,dm^{-3}$

[a]The symbol M has been used as an abbreviation for mol dm^{-3}.
[b]When needed, a subscipt c or m has been added to these quantities to designate, respectively, a concentration, or molality basis.

1. Introduction

Thermodynamic data on the ionization reactions of acids and bases are needed to predict the extent of these reactions and the position of equilibrium for processes in which these reactions occur. Acid-base chemistry is a particularly large area of chemical research and extensive tabulations[1,2] of thermodynamic data (primarily pKs) currently exist for a very large number of acids and bases. Of the many thousands of acid and base reactions which have been studied, the ionization reactions of those substances that are used as buffers in aqueous solutions assumes a particular significance in that a knowledge of these ionization constants plays an important role in the establishment and use of the pH scale.[3] Also, in order to maintain the pH at a constant value, biochemical reactions are generally studied in buffered solutions. Thus, one needs the values for the pertinent ionization constants to properly analyze the results of any equilibrium measurements which have been performed. Additionally, calorimetric measurements on biochemical reactions require a knowledge of the molar enthalpy changes for the ionization reactions. Corrections for the enthalpy of buffer protonation can be quite significant in the treatment of calorimetric data for biochemical reactions.[4]

The aim of this study is to survey the available literature that leads to values of the equilibrium constants, standard molar enthalpies, and standard molar heat-capacity changes for the ionization reactions of a variety of commonly used buffers at the temperature $T = 298.15$ K. This is the data that is needed to predict the value of the ionization constant over the temperature range that is generally encountered in the vast majority of biochemical studies. The selection of buffers was done by first constructing a list of those buffers identified in previous reviews[5–10] to have been used in thermodynamic studies on enzyme-catalyzed reactions. To this list we have added the commonly used buffers of the type suggested by Good *et al.*[11–13] as well as several other buffers that have often been used in much of general chemistry.

2. Thermodynamic Background

Of primary interest to this review is the (thermodynamic) equilibrium constant

$$K_{a,m}=a\{\mathrm{H^+(aq)}\}\cdot a\{\mathrm{A^-(aq)}\}/a\{\mathrm{HA(aq)}\} \quad (1)$$

for the ionization reaction

$$\mathrm{HA(aq)}=\mathrm{H^+(aq)}+\mathrm{A^-(aq)}. \quad (2)$$

The above equilibrium constant has been defined in terms of activity and has been denoted as such by affixing a subscript a to the equilibrium constant. It is also necessary to specify the standard state. In this review the principal standard state used for the solute is the hypothetical ideal solution at the standard molality ($m^\circ=1\ \mathrm{mol\,kg^{-1}}$). The standard state for the solvent is the pure solvent. This choice of a molality standard state has been indicated by attaching a subscript m to the equilibrium constant. Eq. (1) can also be written in terms of the molalities and activity coefficients (molality basis) γ_m of the solute species:

$$K_{a,m}=(m\{\mathrm{H^+(aq)}\}\cdot m\{\mathrm{A^-(aq)}\}/[m\{\mathrm{HA(aq)}\}\cdot m^\circ])\cdot(\gamma_m\{\mathrm{H^+(aq)}\}\cdot\gamma_m\{\mathrm{A^-(aq)}\}/\gamma_m\{\mathrm{HA(aq)}\}). \quad (3)$$

The standard molality m° has been used in Eq. (3) to keep the equilibrium constant dimensionless. An alternative way of writing Eq. (3) is

$$K_{a,m}=K_m\cdot\Gamma_m, \quad (4)$$

where

$$K_m=m\{\mathrm{H^+(aq)}\}\cdot m\{\mathrm{A^-(aq)}\}/[m\{\mathrm{HA(aq)}\}\cdot m^\circ], \quad (5)$$

and

$$\Gamma_m=\gamma_m\{\mathrm{H^+(aq)}\}\cdot\gamma_m\{\mathrm{A^-(aq)}\}/\gamma_m\{\mathrm{HA(aq)}\}. \quad (6)$$

Here K_m is the equilibrium constant (molality basis) that pertains to an actual real solution as distinct from the equilibrium constant (activity basis) that relates to a hypothetical standard state that is approached by real solutions as the sum of the molalities of all solute species approaches zero.

One can also formulate equilibrium constants in terms of concentrations c:

$$K_{a,c}=K_c\cdot\Gamma_c, \quad (7)$$

where

$$K_c=c\{\mathrm{H^+(aq)}\}\cdot c\{\mathrm{A^-(aq)}\}/[c\{\mathrm{HA(aq)}\}\cdot c^\circ], \quad (8)$$

and

$$\Gamma_c=\gamma_c\{\mathrm{H^+(aq)}\}\cdot\gamma_c\{\mathrm{A^-(aq)}\}/\gamma_c\{\mathrm{HA(aq)}\}. \quad (9)$$

Here, c° is the standard concentration ($1\ \mathrm{mol\,dm^{-3}}$) and γ_c is the activity coefficient on a concentration basis. The density of the pure solvent ρ is needed to calculate values of $K_{a,m}$ from $K_{a,c}$ and vice versa:

$$K_{a,c}=\rho\cdot K_{a,m}. \quad (10)$$

On a logarithmic scale the difference between $K_{a,c}$ and $K_{a,m}$ in water at $T=298.15\,\mathrm{K}$ is very small ($\mathrm{p}K_{a,c}=\mathrm{p}K_{a,m}+0.001\,27$) and can be neglected except for the most accurate work. While values of the standard molar enthalpy of reaction Δ_rH° are identical for different standard states, values of Δ_rH° are often determined by use of the van't Hoff equation

$$\Delta_rH^\circ=RT^2(\partial\ln K/\partial T)_p. \quad (11)$$

Equation (11) is exact for equilibrium constants that have been determined by using a molality standard state. However, if Eq. (11) is used with values of $K_{a,c}$, one has introduced an additional term $RT^2(\partial\ln\rho/\partial T)_p=0.187\ \mathrm{kJ\,mol^{-1}}$ at $T=298.15\,\mathrm{K}$ for studies done with water as the solvent. We have applied this correction term to the values of Δ_rH° only when it was very clear that the measured equilibrium constants were based on the concentration scale. Since, in such cases, Δ_rH° is calculated as a derivative of equilibrium constants measured at several temperatures, temperature dependent errors in the values of K_c are amplified. Thus, in the vast majority of cases, this correction term is significantly less than the overall uncertainty in the value of Δ_rH°.

In this paper, we have used the equation of Clarke and Glew[14] to represent the temperature dependence of equilibrium constants:

$$R\ln K=-\Delta_rG^\circ/T_r+\Delta_rH^\circ(1/T_r-1/T)+\Delta_rC_p^\circ\{(T_r/T)-1+\ln(T/T_r)\}+(T_r/2)(\partial\Delta_rC_p^\circ/\partial T)_p\{(T/T_r)-(T_r/T)-2\ln(T/T_r)\}. \quad (12)$$

Here, T_r is a reference temperature (typically 298.15 K) and R is the gas constant ($8.31451\ \mathrm{J\,K^{-1}\,mol^{-1}}$);[15] Δ_rG°, Δ_rH°, and $\Delta_rC_p^\circ$ are, respectively, the standard molar Gibbs energy, enthalpy, and heat-capacity changes for a reaction occurring at the selected reference temperature T_r. A significant advantage to using Eq. (12) is that the parameters that predict the temperature dependence of the equilibrium constant are the standard thermodynamic quantities that can be obtained from additional types of measurements—calorimetry being the most important. Additional terms that involve higher order derivatives of $(\partial\Delta_rC_p^\circ/\partial T)_p$ can be added to the right-hand side of Eq. (12). However, the values of these higher order derivatives are not known for most ionization reactions. In fact, since the quantity $(\partial\Delta_rC_p^\circ/\partial T)_p$ involves the third derivative of $\ln K$ versus T data, it is exceedingly difficult to obtain an accurate value of $(\partial\Delta_rC_p^\circ/\partial T)_p$ from measurements involving the temperature dependence of ionization constants. Errors in $(\partial\Delta_rC_p^\circ/\partial T)_p$ can also be substantive when this quantity is obtained from the temperature dependence of Δ_rH°. Thus, the direct measurement of heat capacities is the favored method for obtaining information on the temperature dependence of Δ_rH° and $\Delta_rC_p^\circ$.

Many values of the ionization constants are reported under conditions of ionic strength and solution composition where the values of the activity coefficients are not known. Yet, it is useful to make some attempt to adjust these pK values to $I=0$ for purposes of comparison with other results. In the

absence of experimental values for these activity coefficients, we have used the extended Debye–Hückel equation

$$\ln \gamma_i = -A_m z_i^2 I^{1/2}/(1+BI^{1/2}) \quad (13)$$

to estimate the needed values of the activity coefficients and then the ratio Γ_m in Eq. (4). Here A_m is the Debye–Hückel constant,[16] z_i is the charge number of the species, and B is an empirical constant (sometimes referred to as an "ion size" parameter) which we have taken to equal 1.6 $kg^{1/2}\,mol^{-1/2}$. This value has been selected following prior usage of this value in the treatment of biochemical reactions[17,18] and earlier usage by Vasil'ev[19] and Vanderzee and Dawson.[20] Based upon the activity coefficient model, Eq. (13), the Debye–Hückel expressions for the excess enthalpy H_i^{ex} and heat capacity C_i^{ex} of species i are

$$H_i^{ex} = RT^2(\partial A_m/\partial T)_p z_i^2 I^{1/2}/(1+BI^{1/2}). \quad (14)$$

$$C_i^{ex} = RT^2(\partial^2 A_m/\partial T^2)_p z_i^2 I^{1/2}/(1+BI^{1/2}) + 2RT(\partial A_m/\partial T)_p z_i^2 I^{1/2}/(1+BI^{1/2}). \quad (15)$$

Analogously, we have used these expressions to adjust values of enthalpy and heat-capacity changes determined at finite ionic strengths to $I=0$. The parameter B has also been maintained at the same constant value of 1.6 $kg^{1/2}\,mol^{-1/2}$. It should be noted that for charge symmetric reactions (e.g., the deprotonation reaction of amines), the model used in this paper predicts corrections of zero for the adjustment of pK, $\Delta_r H°$, and $\Delta_r C_p^\circ$ values to $I=0$. In the light of existing data (e.g., the study of Cox *et al.*[21] on the ionization reactions of alkyl ammonium ions) it is clear that the above equations are approximations. Thus, additional terms can and have been added to Eqs. (13)–(15) or to similar type equations.[22,23] These terms serve to extend the model to higher molalities and ionic strengths by accounting for specific interactions. However, due to a general lack of the needed interaction parameters for the systems and actual solutions of interest, we have used Eqs. (13)–(15) and the assumed value of the parameter B. Thus, in our evaluations, we have relied, insofar as possible, on the results of experiments where the data have been more rigorously adjusted to the standard state. However, such results do not exist for several buffers and in these situations, it is estimated that the use of the above equations could cause errors in the standard value of the pK of about ± 0.05 to ± 0.10. Also, if the results are adjusted from high ionic strengths ($I > 0.1\,mol\,dm^{-3}$) to $I=0$, the errors could be substantially larger.

A significant fraction of the buffers considered herein undergo multiple ionizations. In such cases, it is also possible to consider the various microscopic ionization constants that can arise. The determination of values for these microscopic ionization constants requires an experimental method [e.g., nuclear magnetic resonance (NMR)] that can distinguish the pertinent species. In this paper, we have limited the scope to the macroscopic ionization constants that are determined by using the usual methods. All thermodynamic quantities given herein pertain to the macroscopic ionization reactions.

3. Presentation of Data

Tables 7.1–7.68 contain the following information on each of the buffers considered in this review: (1) the chemical name(s) and CAS registry number; (2) the structure, empirical formula, and molecular weight; (3) the selected values of thermodynamic quantities (pK, $\Delta_r G°$, $\Delta_r H°$, and $\Delta_r C_p^\circ$) for the ionization reaction(s) at $T=298.15$ K and for the molality standard state (see Sec. 2). The remainder of each table gives the basis for the selected values, namely a summary of values of thermodynamic quantities (pK, $\Delta_r H°$, and $\Delta_r C_p^\circ$) from the literature; and finally values of pK, $\Delta_r H°$, and $\Delta_r C_p^\circ$ that have been adjusted from the reported conditions to $T=298.15$ K and to the standard state, which has been denoted as "$I=0$." In constructing these tables, we have generally recalculated the values of $\Delta_r H°$ and $\Delta_r C_p^\circ$ from the pK values which have been determined at several temperatures. This has been done by using the model given in Eq. (12). Values of $\Delta_r H°$ and $\Delta_r C_p^\circ$ are given only when they were statistically significant. In no case did we select values for $(\partial \Delta_r C_p^\circ/\partial T)_p$, although such values are generally noted. Since the molality standard state is the preferred one in this paper, all selected values for pK and for $\Delta_r G°$ are on this basis. For simplicity of expression, we have used "pK" rather than the more exact notation "pK_m" in these tables.

We have attempted to make our survey of the literature essentially complete for most of the buffers considered herein. One exception is the omission of a substantial fraction of studies from the very early literature where the results were often very approximate. Also, for 17 of the buffers, the extent of the literature is sufficiently large that practical considerations mitigated against the desire for completeness. This has been noted in the comments section for each of these 17 buffers. Nevertheless, in each such case we attempted to include all studies that involved any of the following features: the use of an electrochemical cell without a liquid junction; results that had been extrapolated to $I=0$; calorimetric measurements, and pKs that had been measured at several temperatures. Additionally, the existing evaluations for three substances (carbonate, sulfate, and sulfite) appeared to be sufficiently thorough as to make it doubtful that an additional evaluation would provide any real improvement in the values of the selected thermodynamic quantities.

Except for the calculation of values of $\Delta_r H°$ and $\Delta_r C_p^\circ$ from values of ionization constants reported at several temperatures we have, for the most part, not recalculated the values of the thermodynamic quantities reported in the various studies cited herein. However, in some cases we have extrapolated reported pK and $\Delta_r H°$ values to $I=0$, recalculated calorimetric results by using evaluated ("best") values[24] for $\Delta_r H°$ and $\Delta_r C_p^\circ$ for the ionization of water, and, when necessary, converted values of basicity constants to ionization constants. Such recalculations have, as a rule, been noted in the tables. In almost all of the studies performed by means of potentiometric titrations, only the summary results are reported and a recalculation of the data is not possible. However, in the studies based on electrochemi-

cal cells (both with and without liquid junctions) and conductivity measurements, the primary experimental data (the composition of solutions and measured values of electromotive forces or conductivities) are given in essentially all of the publications that report such results. Similarly many, but not all, of the calorimetric studies also give information on the composition of solutions along with the measured enthalpies. Thus, in such cases, it is possible to perform a recalculation of the results by using various models and by applying any corrections deemed necessary. While such recalculations could prove to be useful in providing more accurate values of thermodynamic quantities for several ionization reactions, it would very significantly extend the scope of this review. Thus, in such cases, we have generally relied upon the treatment(s) done by the various investigators of their primary data in order to obtain their reported results. In any case, by indicating the methods used under ''Method(s) and comments'' the interested reader can easily determine which publications would most likely contain data that could be reanalyzed.

Section 8 contains a summary of the selected values of pK, $\Delta_r H°$, and $\Delta_r C_p^\circ$ for the various buffers considered in this review. It is seen that there are no data available for four of the ''Good'' buffers—namely CABS, HEPBS, MOBS, and TABS. CABS is similar in structure to CHES and CAPS in that all three substances are sulfonic acids that differ only in the number of methylene groups separating the sulfonate group from the remaining portion of the molecule. More specifically, CHES, CAPS, and CABS have, respectively, two, three, and four methylene groups. Identical situations also exist for the three sets of buffers (HEPES, HEPPS, and HEPBS), (MES, MOPS, and MOBS), and (TES, TAPS, and TABS). Thus, carefully performed measurements on the four buffers CABS, HEPBS, MOBS, and TABS would not only provide important data on these biological buffers, but could also be used to determine the effect of the methylene increment on thermodynamic quantities for the ionization reactions of these substances. Examination of the tables in this review shows that there are many cases where new and careful measurements could provide useful data that are either missing or that could resolve discrepancies in existing results.

4. Evaluation of Data

The selection of the final set of values for the desired thermodynamic quantities involved a *subjective* evaluation as to which methods lead to the most accurate values and also which studies appeared to be the most reliable. In this regard, we have generally given the highest weight to those studies that used an electrochemical cell without a liquid junction. These very important studies provide the basis for many of the selected values given herein. Also given a high weight are carefully performed conductivity measurements and electrochemical cells with liquid junctions where corrections for the junction potential have been applied and the results have been extrapolated to $I=0$. Finally, there is a very large body of literature that is based on the use of a glass electrode and already established buffers to determine pK values under a specified set of conditions. This latter method, while generally not as accurate but considerably easier to use than the aforementioned methods, has been widely used to build a very substantial and important body of information on both proton and metal ion binding to ligands. Also, in some studies it is not clear whether the workers have reported an equilibrium constant of the type defined in Eq. (5) or whether their results report a ''mixed'' or ''practical constant,'' i.e., the quantity $a\{H^+(aq)\}\cdot m\{A^-(aq)\}/m\{HA(aq)\}$. We have converted such mixed constants to equilibrium constants only when it was clear that it was a mixed constant that had been reported. An excellent treatise dealing with the measurement of ionization constants has been written by King.[25]

Carefully performed calorimetric measurements often provide the most definitive values for $\Delta_r H°$ and $\Delta_r C_p^\circ$. In this regard, it is particularly interesting to examine the agreement, or lack thereof, between the calorimetrically determined values for these quantities and the values calculated from equilibrium constants that have been measured at several temperatures.

The final evaluation also involved a *subjective* judgment as to the accuracy of the selected values of the thermodynamic quantities. Thus, a letter code has been assigned to each of the quantities determined for the ionization reactions. This code denotes our estimate of the approximate uncertainty in the value of the quantity. The codes for the pK values are: A, ± 0.003; B, ± 0.03; C, ± 0.1; and D, ± 0.3. The codes for the $\Delta H°$ values are: A, ± 0.2 kJ mol^{-1}; B, ± 0.5 kJ mol^{-1}; C, ± 2.0 kJ mol^{-1}; and D, ± 5.0 kJ mol^{-1}. The codes for the $\Delta_r C_p^\circ$ values are: A, ± 10 J K^{-1} mol^{-1}; B, ± 20 J K^{-1} mol^{-1}; C, ± 40 J K^{-1} mol^{-1}; and D, ± 80 J K^{-1} mol^{-1}. In some cases we are either unable to provide an assessment of the uncertainty or we feel that it may be larger than the limits for type ''D'' measurements; here we have used the letter ''U.'' Thus, in the case of a reaction where the values of pK, $\Delta_r H°$, and $\Delta_r C_p^\circ$ are, respectively, judged to be uncertain by ± 0.003, ± 0.5 kJ mol^{-1}, and ± 60 J K^{-1} mol^{-1}, the evaluation code would be ''ABD.'' If for this same reaction, the value of $\Delta_r C_p^\circ$ had not been determined, the evaluation code would be ''AB.'' It is important to recognize that a major part of the uncertainty in the final values arises due to possible errors in the extrapolation to $I=0$.

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7. Tables of Thermodynamic Quantities for Ionization Reactions

TABLE 7.1. ACES

Other names	*N*-(acetamido)-2-aminoethanesulfonic acid; *N*-(2-acetamido)-2-aminoethanesulfonic acid; *N*-(carbamoylmethyl)taurine; 2-[(2-amino-2-oxoethyl)amino]ethanesulfonic acid; 2-[(2-amino-2-oxoethyl)amino]ethanesulfonic acid; 2-(carbamoylmethylamino)-aminoethane sulfonic acid; CAS No. 7365-82-4
Empirical formula	$C_4H_{10}N_2O_4S$
Molecular weight	182.20

Ionization Reaction

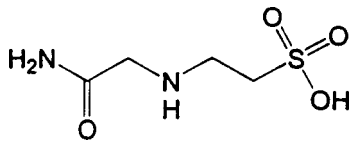
$$HL^{\pm} = H^+ + L^-, \text{ where } HL = C_4H_{10}N_2O_4S$$

Selected values at $T=298.15$ K and $I=0$:

$$pK = 6.847,\ \Delta_r G°/(\text{kJ mol}^{-1}) = 39.083,\ \Delta_r H°/(\text{kJ mol}^{-1}) = 30.43, \text{ and } \Delta_r C_p^\circ/(\text{J K}^{-1}\,\text{mol}^{-1}) = -49$$

Evaluation: AAA

Structure:



Values from literature

p*K*	$\Delta_r H°/(\text{kJ mol}^{-1})$	*T*/K	*I*	Method(s) and comments	Reference
7.32		273.15	≈0.1 M	Potentiometric titration—glass electrode.	66GOO/WIN
6.90		293.15	≈0.01 M		
6.88		293.15	≈0.1 M		
6.88		293.15	≈0.2 M		
6.56		310.15	≈0.1 M		
6.65	30.1	298.15	≈0.01 M	Potentiometric titration—glass electrode; and calorimetry. Dilute solutions (0.005–0.01 M) were titrated with 0.1 M NaOH or 0.1 M HCl.	76MCG/JOR
6.81		298.15	0.1 M	Potentiometric titration—glass electrode.	80POP/STE
6.75		298.15	≈0.012 M	Potentiometric titration of sample (0.01–0.014 M) with 0.1 M HCl or 0.1 M NaOH.	87KIT/ITO
6.84		298.15	0.00505 M	Based on measurements of ionic mobilities.	87POS/DEM
6.62		298.15	0.16 M	Coulometric titration.	92GLA/HUL
6.35		310.15	0.16 M		
6.9		298.15	0.10 M		
6.56		310.15	0.10 M		
6.56		310.15	≈0.1 M		
7.2375		278.15	0	Electrochemical cell—no liquid junction. The value of $\Delta_r H°$ given here was calculated from p*K*s measured at several temperatures. Note that the values of $\Delta_r H°$ given in Table 5 of Roy *et al.* [97ROY/BIC] contain some typographical errors [2001ROY]. The value $\Delta_r C_p^\circ/(\text{J K}^{-1}\,\text{mol}^{-1}) = -62$ was also calculated from the temperature dependency of their [97ROY/BIC] reported p*K*s.	97ROY/BIC
7.1343		283.15	0		
7.0341		288.15	0		
6.9385		293.15	0		
6.8475	30.43	298.15	0		
6.7599		303.15	0		
6.6758		308.15	0		
6.6420		310.15	0		
6.5953		313.15	0		
6.5180		318.15	0		
6.4441		323.15	0		
6.3749		328.15	0		
6.75	31.41	298.15	0.1 M	Electrochemical cell with liquid junction; calorimetry. Fukada and Takahashi [98FUK/TAK] also obtained $\Delta_r C_p^\circ/(\text{J K}^{-1}\,\text{mol}^{-1}) = -27$ at $I = 0.1$ M from the temperature dependence of $\Delta_r H°$ over the range 278.15–323.15 K.	98FUK/TAK

Values adjusted to $T=298.15$ K and $I=0$

pK	$\Delta_r H°/(\text{kJ mol}^{-1})$	$\Delta_r C_p^\circ/(\text{J K}^{-1}\text{ mol}^{-1})$	Reference
6.99			66GOO/WIN
6.9			72GOO/IZA
6.74	30.0		76MCG/JOR
7.02			80POP/STE
6.85			87KIT/ITO
6.91			87POS/DEM
6.94			92GLA/HUL
6.847	30.43	−62	97ROY/BIC
6.96	30.8	−35	98FUK/TAK

Comments: The most definitive results leading to the pK values are those of Roy *et al.* [97ROY/BIC] who used an electrochemical cell with no liquid junction. We have adopted the respective averages of the reported $\Delta_r H°$ and $\Delta_r C_p^\circ$ values.

TABLE 7.2. Acetate

Other names	acetic acid; athylic acid; glacial acetic acid; vinegar; methanecarboxylic acid; ethanoic acid; CAS No. 64-19-7
Empirical formula	$C_2H_4O_2$
Molecular weight	60.052

Ionization Reaction

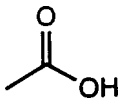
$$CH_3COOH = H^+ + CH_3COO^-$$

Selected values at $T=298.15$ K and $I=0$:

p$K=4.756$, $\Delta_r G°/(\text{kJ mol}^{-1}) = 27.147$, $\Delta_r H°/(\text{kJ mol}^{-1}) = -0.41$, and $\Delta_r C_p^\circ/(\text{J K}^{-1}\text{ mol}^{-1}) = -142$

Evaluation: AAA

Structure:



Values from literature

pK	$\Delta_r H°/(\text{kJ mol}^{-1})$	T/K	I	Method(s) and comments	Reference
	−0.80	298.15	0	The value of $\Delta_r H°$ given here is based on the calorimetric measurements by Richards and Mair [29RIC/MAI] of the enthalpy of neutralization of acetic acid by NaOH. We have used their [29RIC/MAI] value $\Delta_r H°/(\text{kJ mol}^{-1}) = -57.07$ at $T=293.15$ K and $I=0$ together with $\Delta_r H°$ for the ionization of water at this temperature [75OLO/HEP] to obtain $\Delta_r H°/(\text{kJ mol}^{-1}) = -0.09$ for the ionization of acetic acid at $T=293.15$ K. Use of the value $\Delta_r C_p^\circ/(\text{J K}^{-1}\text{ mol}^{-1}) = -142$ leads to the value $\Delta_r H°/(\text{kJ mol}^{-1}) = -0.80$ for the ionization of acetic acid at $T=298.15$ K.	29RIC/MAI
4.756		298.15	0	Conductivity.	32MAC/SHE
4.781		273.15	0	Electrochemical cell—no liquid junction. The value of $\Delta_r H°$ given here was calculated from pKs measured at several temperatures. The value $\Delta_r C_p^\circ/(\text{J K}^{-1}\text{ mol}^{-1}) = -173$ was also calculated from the temperature dependency of their [33HAR/EHL] reported pKs. Inclusion of the term $d\Delta_r C_p^\circ/dT$ in these calculations did not substantively change the value of either $\Delta_r H°$ or $\Delta_r C_p^\circ$. The value of $\Delta_r H°$ given here differs from the value −0.41 kJ mol^{-1} given by Harned and Owen [39HAR/OWE] in their recalculation of the data of Harned and Ehlers [33HAR/EHL]. Interestingly, Harned and Owen [39HAR/OWE] also calculated $\Delta_r C_p^\circ/(\text{J K}^{-1}\text{ mol}^{-1}) = -173$ in complete agreement with the value that we calculate from their data.	33HAR/EHL
4.770		278.15	0		
4.762		283.15	0		
4.758		288.15	0		
4.756		293.15	0		
4.756	−0.63	298.15	0		
4.757		303.15	0		
4.762		308.15	0		
4.769		313.15	0		
4.777		318.15	0		
4.787		323.15	0		
4.799		328.15	0		
4.812		333.15	0		
	−0.29		0	Calorimetry.	58CAN/PAP
	3.02	298.15	3.0 M	Calorimetry.	61SCH/MAR
	0.75	298.15	0.2 M	Calorimetry.	62WAD

Values from literature—Continued

pK	$\Delta_r H°/(\mathrm{kJ\,mol^{-1}})$	T/K	I	Method(s) and comments	Reference
4.763		298.15	0	Conductivity.	63ELL
4.799		323.15	0		
4.957		373.15	0		
5.204		423.15	0		
5.509		473.15	0		
5.757		498.15	0		
	0.38	298.15	0.1 M	Calorimetry.	64NEL
	−0.38	298.15	0	Calorimetry.	66AVE
	−0.08	298.15	0	Calorimetry.	67CHR/IZA
	0.38	298.15	0	Calorimetry. The value given here is based on our extrapolation to $I=0$ of the unpublished results of Hansson that are given by Gerding [67GER]. The value of $\Delta_r H°$ was found to be highly dependent on ionic strength and on the medium in which the ionization reaction was carried out.	67GER
	3.36	273.15	0	Calorimetry. From the temperature dependence of $\Delta_r H°$, one obtains the value $\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}}) = -147$ for the ionization of acetic acid at $T=298.15$ K.	70LEU/GRU
	2.75	278.15	0		
	1.15	288.15	0		
	−0.57	298.15	0		
	−1.80	308.15	0		
	−2.81	318.15	0		
	−3.77	328.15	0		
	1.17	298.15	0.1 M	Calorimetry.	72SIM/IVI
	−0.4	298.15	≈0.005 M	Calorimetry.	74MOR/FAU
				The value $\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}}) = -143$ at $T=298.15$ K was obtained from direct heat capacity measurements on acetic acid solutions. Values of $\Delta_r C_p^\circ$ at $T=283.15$ K and $T=313.15$ K are also reported.	81ALL/WOO
	3.19	273.65	0	Calorimetry. From the temperature dependence of $\Delta_r H°$, one obtains the value $\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}}) = -143$ for the ionization of acetic acid at $T=298.15$ K.	84OLO
	−0.41	298.15	0		
	−3.86	323.15	0		
	−11.02	373.15	0		
				The value $\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}}) = -143$ at $T=298.15$ K was obtained from direct heat capacity measurements on acetic acid solutions.	84RIE/JOL
4.74	0.0	298.15	0	Potentiometric titration—glass electrode. The value of $\Delta_r H°$ given here was calculated from pKs measured at three temperatures.	85DAN/DER
4.780		273.15	0	Electrochemical cell with liquid junction. The pK values given here are based on Mesmer *et al.*'s ''Model I'' (see their Table V). The value of $\Delta_r H°$ given here was calculated from pKs measured at several temperatures. The value $\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}}) = -139$ at $T=298.15$ K was also calculated from the temperature dependency of their [89MES/PAT] reported pKs.	89MES/PAT
4.757	−0.51	298.15	0		
4.786		323.15	0		
4.848		348.15	0		
4.937		373.15	0		
5.047		398.15	0		
5.180		423.15	0		
5.334		448.15	0		
5.515		473.15	0		
5.727		498.15	0		
5.978		523.15	0		
6.282		548.15	0		
6.664		573.15	0		
	0.316	293.15	0	Calorimetry. From the temperature dependence of $\Delta_r H°$, one obtains the value $\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}}) = -142$ for the ionization of acetic acid at $T=298.15$ K.	91HU/YEN
	−0.436	298.15	0		
	−1.104	303.15	0		
	−1.779	308.15	0		
	−2.468	313.15	0		
	−4.156	318.15	0		
	−0.414	298.15	0	Calorimetry.	94LEI/ZON
4.62	0.49	298.15	0.1 M	Electrochemical cell with liquid junction; calorimetry. Fukada and Takahashi [98FUK/TAK] also obtained $\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}}) = -128$ at $I=0.1$ M from the temperature dependence of $\Delta_r H°$ over the range 278.15–323.15 K.	98FUK/TAK
				The value $\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}}) = -138$ at $T=298.15$ K and $I=0$ was obtained from direct heat capacity measurements on acetic acid solutions. Values of $\Delta_r C_p^\circ$ from $T=278.15$ to $T=393.15$ K are also reported. The pressure was 0.35 MPa.	99BAL/FOR

Values adjusted to $T=298.15$ K and $I=0$

pK	$\Delta_r H°/(\mathrm{kJ\,mol^{-1}})$	$\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}})$	Reference
	−0.80		29RIC/MAI
4.756			32MAC/SHE
4.756	−0.63	−173	33HAR/EHL
	−0.29		58CAN/PAP
	—		61SCH/MAR
	≈−0.02		62WAD
4.763			63ELL
	−0.24		64NEL
	−0.38		66AVE
	−0.08		67CHR/IZA
	0.38		67GER
	−0.57	−147	70LEU/GRU
	−0.90		72SIM/IVI
	−0.59		74MOR/FAU
		−143	81ALL/WOO
	−0.41	−143	84OLO
		−143	84RIE/JOL
4.74	0.0		85DAN/DER
4.757	−0.51	−139	89MES/PAT
	−0.44	−142	91HU/YEN
	−0.41		94LEI/ZON
4.82	−0.13	−136	98FUK/TAK
		−138	99BAL/FOR

Comments: The very carefully done measurements of Harned and Ehlers [33HAR/EHL] still remain the definitive set of results for the pK of acetic acid at $I=0$. These results are in excellent agreement with the pK value determined at $T=298.15$ K by MacInnes and Shedlovsky [32MAC/SHE] using conductivity and with more recent electrochemical measurements [89MES/PAT]. We judge the calorimetric results of Olofsson [84OLO] to be the most reliable for $\Delta_r H°$. Her [84OLO] result at $T=298.15$ K is essentially equal to the average value $\langle \Delta_r H° \rangle/(\mathrm{kJ\,mol^{-1}}) = -0.40$ which is obtained from consideration of all of the above studies with the exception of the results of Gerding [67GER] and of Schlyter and Martin [61SCH/MAR] which we did not attempt to adjust to $I=0$. There are several studies [70LEU/GRU, 81ALL/WOO, 84OLO, 84RIE/JOL, 89MES/PAT, 91HU/YEN, 98FUK/TAK, 99BAL/FOR] that are in excellent agreement with the selected value $\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}}) = -142$ for this ionization reaction. Additional studies, performed under a variety of conditions, are cited by Martell *et al.* [2001MAR/SMI] and by Pettit and Powell [2000PET/POW].

TABLE 7.3. ADA

Other names	*N*-(2-acetamido)-2-iminodiacetic acid; *N*-(2-acetamido)iminodiethanoic acid; *N*-(carboxymethyl)iminodiacetic acid; *N*-acetamidoiminodiacetic acid; *N*-(2-amino-2-oxoethyl)-*N*-(carboxymethyl)glycine; nitrilotriacetic acid monoamide; [(carbamoylmethyl)imino]diacetic acid; *N*-(carbamylmethylimino)acetic acid; CAS No. 26239-55-4
Empirical formula	$C_6H_{10}N_2O_5$
Molecular weight	190.15

Ionization Reactions

$$H_3L^+ = H^+ + H_2L^\pm \quad (1)$$
$$H_2L^\pm = H^+ + HL^- \quad (2)$$
$$HL^- = H^+ + L^{2-} \quad (3)$$

where $H_2L = C_6H_{10}N_2O_5$

Selected values at $T = 298.15$ K and $I = 0$:

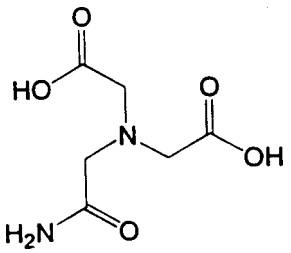
pK = 1.59 and $\Delta_r G°/(\text{kJ mol}^{-1}) = 9.08$ for reaction (1)

pK = 2.48, $\Delta_r G°/(\text{kJ mol}^{-1}) = 14.16$, and $\Delta_r H°/(\text{kJ mol}^{-1}) = 16.7$ for reaction (2)

pK = 6.844, $\Delta_r G°/(\text{kJ mol}^{-1}) = 39.066$, $\Delta_r H°/(\text{kJ mol}^{-1}) = 12.23$, and $\Delta_r C_p^\circ/(\text{J K}^{-1}\,\text{mol}^{-1}) = -144$ for reaction (3)

Evaluation: reaction (1), C; reaction (2), CC; reaction (3), ABB

Structure:



Values from literature

pK	$\Delta_r H°/(\text{kJ mol}^{-1})$	T/K	I	Method(s) and comments	Reference
			Reaction (1): $H_3L^+ = H_2L^\pm + H^+$		
1.59		298.15	0.10 M	Potentiometric titration—glass electrode.	79NAK
			Reaction (2): $H_2L^\pm = HL^- + H^+$		
2.3		293.15	0.1 M	Potentiometric titration—glass electrode.	55SCH/AND
2.31		298.15	0.10 M	Potentiometric titration—glass electrode.	79NAK
2.27		288.15	0.1 M	Potentiometric titration—glass electrode. The value of $\Delta_r H°$ given here was calculated from pKs measured at several temperatures.	80BEN/BAL
2.18		293.15	0.1 M		
2.13	17.3	298.15	0.1 M		
2.09		303.15	0.1 M		
2.06		308.15	0.1 M		
2.35		298.15	0.10 M	Potentiometric titration—glass electrode.	96SHO/KHA
			Reaction (3): $HL^- = H^+ + L^{2-}$		
6.60		293.15	0.1 M	Potentiometric titration—glass electrode.	55SCH/AND
6.85		273.15	≈0.1 M	Potentiometric titration—glass electrode.	66GOO/WIN
6.78		293.15	≈0.01 M		
6.62		293.15	≈0.1 M		
6.60		293.15	≈0.15 M		
6.45		310.15	≈0.1 M		
6.75	11.5	298.15	≈0.01 M	Potentiometric titration—glass electrode; and calorimetry. Dilute solutions (0.005–0.01 M) were titrated with 0.1 M NaOH or 0.1 M HCl.	76MCG/JOR
6.67		298.15	0.10 M	Potentiometric titration—glass electrode.	79NAK
6.77		288.15	0.1 M	Potentiometric titration—glass electrode. The value of $\Delta_r H°$ given here was calculated from pKs measured at several temperatures.	80BEN/BAL
6.71		293.15	0.1 M		
6.66	14.3	298.15	0.1 M		
6.63		303.15	0.1 M		
6.60		308.15	0.1 M		

Values from literature—Continued

pK	$\Delta_r H°/(\mathrm{kJ\ mol^{-1}})$	T/K	I	Method(s) and comments	Reference
7.011		278.15	0	Electrochemical cell—no liquid junction. The value of $\Delta_r H°$ given here was calculated from pKs measured at several temperatures. The value $\Delta_r C_p^\circ/(\mathrm{J\ K^{-1}\ mol^{-1}}) = -144$ was also calculated from the temperature dependency of their [97ROY/GIB] reported pKs.	81ROY/GIB
6.968		283.15	0		
6.924		288.15	0		
6.884		293.15	0		
6.844	12.23	298.15	0		
6.796		303.15	0		
6.780		308.15	0		
6.763		310.15	0		
6.749		313.15	0		
6.723		318.15	0		
6.704		323.15	0		
6.678		328.15	0		
6.52		298.15	0.10 M	Potentiometric titration—glass electrode.	96AHM/ELR
6.81		298.15	0.10 M	Potentiometric titration—glass electrode.	96SHO/KHA

Values adjusted to T=298.15 K and I=0

pK	$\Delta_r H°/(\mathrm{kJ\ mol^{-1}})$	$\Delta_r C_p^\circ/(\mathrm{J\ K^{-1}\ mol^{-1}})$	Reference
	Reaction (1): $H_3L^+ = H_2L^\pm + H^+$		
1.59			79NAK
	Reaction (2): $H_2L^\pm = HL^- + H^+$		
2.51			55SCH/AND
2.52			79NAK
2.34	16.7		80BEN/BAL
2.56			96SHO/KHA
	Reaction (3): $HL^- = H^+ + L^{2-}$		
7.03			55SCH/AND
6.99			66GOO/WIN
6.93	11.0		76MCG/JOR
7.10			79NAK
7.09	13.1		80BEN/BAL
6.844	12.23	−144	81ROY/GIB
7.03			96AHM/ELR
7.23			96SHO/KHA

Comments: The average of the pK values has been adopted for reaction (2). For reaction (3), the results of Roy *et al.* [81ROY/GIB], which are based on an electrochemical cell without liquid junction, have been judged to be the most accurate.

TABLE 7.4. 2-Amino-2-methyl-1,3-propanediol

Other names	AMPD; AMP; ammediol; BIS; 2-amino-2-methylpropane-1:3-diol; 2-ammonium-2-methyl-1,3-propanediol; 1,1-(dihydroxymethyl)ethylamine; CAS No. 115-69-5
Empirical formula	$C_4H_{11}NO_2$
Molecular weight	105.14

Ionization reaction

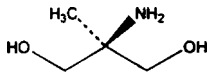
$$HL^+ = H^+ + L, \text{ where } L = C_4H_{11}NO_2$$

Selected values at $T=298.15$ K and $I=0$:

$$pK = 8.801,\ \Delta_r G°/(\text{kJ mol}^{-1}) = 50.237,\ \Delta_r H°/(\text{kJ mol}^{-1}) = 49.85, \text{ and } \Delta_r C_p^\circ/(\text{J K}^{-1}\,\text{mol}^{-1}) = -44$$

Evaluation: AAA

Structure:



Values from literature

pK	$\Delta_r H°/(\text{kJ mol}^{-1})$	T/K	I	Method(s) and comments	Reference
8.76		298.15	0	Potentiometric titration—glass electrode.	47GLA/SCH
8.79		298.15	0	Potentiometric titration—glass electrode.	59DAT/GRZ
9.6116		273.15	0	Electrochemical cell—no liquid junction. The value of $\Delta_r H°$ given here was calculated from pKs measured at several temperatures. The value $\Delta_r C_p^\circ/(\text{J K}^{-1}\,\text{mol}^{-1}) = -44$ was also calculated from the temperature dependency of their [62HET/BAT] reported pKs.	62HET/BAT
9.4328		278.15	0		
9.2658		283.15	0		
9.1049		288.15	0		
8.9508		293.15	0		
8.8013	49.85	298.15	0		
8.6588		303.15	0		
8.5193		308.15	0		
8.3854		313.15	0		
8.2569		318.15	0		
8.1322		323.15	0		
	49.91	298.15	0.07 M	Calorimetry.	68OJE/WAD
9.599		273.15	0	Electrochemical cell with liquid junction. The value of $\Delta_r H°$ given here was calculated from pKs measured at several temperatures. The value $\Delta_r C_p^\circ/(\text{J K}^{-1}\,\text{mol}^{-1}) = -46$ was also calculated from the temperature dependency of their [68TIM/EVE] reported pKs.	68TIM/EVE
9.257		283.15	0		
8.941		293.15	0		
8.792	49.75	298.15	0		
8.649		303.15	0		
8.377		313.15	0		
8.125		323.15	0		
7.891		333.15	0		
8.96		298.15	≈0.5 M	Potentiometric titration—glass electrode.	71HAL/SIM
8.78		298.15	≈0.012 M	Potentiometric titration of sample (0.01–0.014 M) with 0.1 M HCl or 0.1 M NaOH.	87KIT/ITO
8.93		298.15	0.1 M	Potentiometric titration—glass electrode.	90BUN/STE
8.78		298.15	0.5 M	Potentiometric titration—glass electrode; spectrophotometry.	97CAN/CAR

Values adjusted to $T=298.15$ K and $I=0$

pK	$\Delta_r H°$(kJ mol^{-1})	$\Delta_r C_p^\circ$/(J K^{-1} mol^{-1})	Reference
8.76			47GLA/SCH
8.79			59DAT/GRZ
8.801	49.85	−44	62HET/BAT
	49.91		68OJE/WAD
8.792	49.75	−46	68TIM/EVE
8.96			71HAL/SIM
8.78			87KIT/ITO
8.93			90BUN/STE
8.78			97CAN/CAR

Comments: The values from Hetzer and Bates [62HET/BAT], who used an electrochemical cell without liquid junction, are preferred. There is excellent agreement with the calorimetric result of Öjelund and Wadsö [68OJE/WAD] and with the value of $\Delta_r H°$ calculated from the electrochemical results of Timimi and Everett [68TIM/EVE].

TABLE 7.5. 2-Amino-2-methyl-1-propanol

Other names	AMP; 2-aminoisobutanol; isobutanolamine; β-aminoisobutyl alcohol; 2-hydroxy-1,1-dimethylethylamine; 2-amino-2-methylpropan-1-ol; CAS No. 124-68-5
Empirical formula	$C_4H_{11}NO$
Molecular weight	89.137

Ionization Reaction

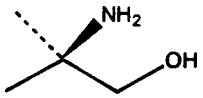
$$HL^+ = H^+ + L, \text{ where } L = C_4H_{11}NO$$

Selected values at $T=298.15$ K and $I=0$:

$$pK = 9.694,\ \Delta_r G°/(\text{kJ mol}^{-1}) = 55.334,\ \Delta_r H°/(\text{kJ mol}^{-1}) = 54.05, \text{ and } \Delta_r C_p^\circ/(\text{J K}^{-1}\text{ mol}^{-1}) \approx -21$$

Evaluation: AAC

Structure:



Values from literature

pK	$\Delta_r H°$/(kJ mol^{-1})	T/K	I	Method(s) and comments	Reference
	54.10	298.15	0.07 M	Calorimetry.	68OJE/WAD
10.562		273.15	0	Electrochemical cell with liquid junction. The value of $\Delta_r H°$ given here was calculated from pKs measured at several temperatures. The value $\Delta_r C_p^\circ/(\text{J K}^{-1}\text{ mol}^{-1}) \approx -21$ was also calculated from the temperature dependency of their [68TIM/EVE] reported pKs.	68TIM/EVE
10.194		283.15	0		
9.853		293.15	0		
9.694	53.99	298.15	0		
9.535		303.15	0		
9.240		313.15	0		
8.963		323.15	0		
8.705		333.15	0		
9.86		298.15	≈0.5 M	Potentiometric titration—glass electrode.	71HAL/SIM
9.694		298.15	0	Potentiometric titration—glass electrode. Values of pKs were obtained from $I=0.0096-2.019$ M and extrapolated to $I=0$. $NaClO_4$ was used as the supporting electrolyte.	75NAS/LIN
9.87		298.15	0.1 M	Potentiometric titration—glass electrode.	90BUN/STE
9.61		298.15	0.5 M	Potentiometric titration—glass electrode.	97CAN/CAR

Values adjusted to T=298.15 K and I=0

pK	$\Delta_r H°/(\mathrm{kJ\ mol^{-1}})$	$\Delta_r C_p^\circ/(\mathrm{J\ K^{-1}\ mol^{-1}})$	Reference
	54.10		68OJE/WAD
9.694	53.99	≈−21	68TIM/EVE
9.86			71HAL/SIM
9.694			75NAS/LIN
9.87			90BUN/STE
9.61			97CAN/CAR

Comments: The pK values reported by Timimi and Everett [68TIM/EVE] and by Näsänen and Lindell [75NAS/LIN] are in excellent agreement. There is also a very good agreement of the calorimetric result of Öjelund and Wadsö with the value of $\Delta_r H°$ calculated from the temperature dependence of the pKs from Näsänen and Lindell [75NAS/LIN]. The value of $\Delta_r C_p^\circ$ is judged to be approximate. Lewis and Wetton [88LEW/WET] report values of pK over the temperature range 373.15–573.15 K.

TABLE 7.6. 3-Amino-1-propanesulfonic acid

Other names	$GABA_A$ agonist; homotaurine; CAS No. 3687-18-1
Empirical formula	$C_3H_9NO_3S$
Molecular weight	139.17

Ionization Reaction

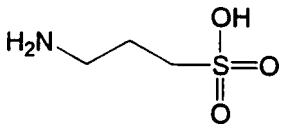
$$HL = H^+ + L^-,\ \text{where } HL = C_3H_9NO_3S$$

Selected values at T=298.15 K and I=0:

$$pK = 10.2 \text{ and } \Delta_r G°/(\mathrm{kJ\ mol^{-1}}) = 58.2$$

Evaluation: D

Structure:



Values from literature

pK	T/K	I	Comments	Reference
9.89	298.15	0.5 M	Adjustment of this result leads to pK≈10.2 at I=0.	72VAN/THI

Comments: There is little information available on the ionization of 3-amino-1-propanesulfonic acid.

TABLE 7.7. Ammonia

Other names	ammonium; CAS No. 7664-41-7
Empirical formula	NH_3
Molecular weight	17.031

Ionization Reaction

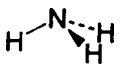
$$NH_4^+ = H^+ + NH_3$$

Selected values at T=298.15 K and I=0:

$$pK = 9.245,\ \Delta_r G°/(\mathrm{kJ\ mol^{-1}}) = 52.771,\ \Delta_r H°/(\mathrm{kJ\ mol^{-1}}) = 51.95,\ \Delta_r C_p^\circ/(\mathrm{J\ K^{-1}\ mol^{-1}}) = 8$$

Evaluation: AAA

Structure:



Values from literature

pK	$\Delta_r H°/(\mathrm{kJ\,mol^{-1}})$	T/K	I	Method(s) and comments	Reference	
	52.5	298.15		Calorimetry. Vanderzee and King [72VAN/KIN] later applied dilution corrections to Pitzer's [37PIT] result and obtained $\Delta_r H° = 3.35\ \mathrm{kJ\,mol^{-1}}$ for the reaction ($NH_3+H_2O=NH_4^+ + OH^-$). This value when combined with $\Delta_r H°$ for the ionization of $H_2O(1)$ [75OLO/HEP] leads to $\Delta_r H° = 52.5$ for the reaction ($NH_4^+ = H^+ + NH_3$). Pitzer's [37PIT] original, uncorrected result led to $\Delta_r H°/(\mathrm{kJ\,mol^{-1}}) = 52.2\ \mathrm{kJ\,mol^{-1}}$.	37PIT	
9.867		278.15	0	Electrochemical cell with liquid junction. The value of $\Delta_r H°$ given here was calculated from pKs measured at several temperatures. The value $\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}}) \approx 3$ was also calculated from the temperature dependency of their [38EVE/WYN] reported pKs. Everett and Landsman [54EVE/LAN] later stated that these results were in error due to the presence of carbonate in the hydroxide solutions used to prepare the buffer.	38EVE/WYN	
9.529		288.15	0			
9.215	51.7	298.15	0			
8.923		308.15	0			
8.645		318.15	0			
10.0813		273.15	0	Electrochemical cell—no liquid junction. The value of $\Delta_r H°$ given here was calculated from pKs measured at several temperatures. The value $\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}}) \approx -5$ was also calculated from the temperature dependency of their [49BAT/PIN2] reported pKs.	49BAT/PIN2	
9.9040		278.15	0			
9.7306		283.15	0			
9.5641		288.15	0			
9.4002		293.15	0			
9.2449	52.24	298.15	0			
9.0926		303.15	0			
8.9466		308.15	0			
8.8047		313.15	0			
8.6700		318.15	0			
8.5387		323.15	0			
10.081		273.15	0	Electrochemical cell—no liquid junction. This study used a somewhat different methodology than that used by Bates and Pinching [49BAT/PIN2] in their earlier work. The value of $\Delta_r H°$ given here was calculated from pKs measured at several temperatures. The value $\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}}) \approx -5$ was also calculated from the temperature dependency of their [50BAT/PIN] reported pKs	50BAT/PIN	
9.904		278.15	0			
9.730		283.15	0			
9.564		288.15	0			
9.401		293.15	0			
9.246	52.19	298.15	0			
9.093		303.15	0			
8.947		308.15	0			
8.805		313.15	0			
8.671		318.15	0			
8.540		323.15	0			
9.5537		288.15	0	Electrochemical cell with liquid junction. The pK values given here, and which pertain to a molality standard state, were calculated from the pK values given by Everett and Landsman [54EVE/LAN] and which pertained to the molarity scale. The value of $\Delta_r H°$ given here was calculated from the pKs measured at several temperatures. The value $\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}}) \approx -24$ was also calculated from the temperature dependency of their [54EVE/LAN] reported pKs.	54EVE/LAN	
9.2378	51.9	298.15	0			
8.9425		308.15	0			
8.6683		318.15	0			
	52.59	298.15	0		Calorimetry.	61TYS/MCC
9.29	52.01	298.15	0.1 M	Potentiometric titration—glass electrode; calorimetry.	65PAO/STE	
	52.15	298.15	0	Calorimetry. Values of $\Delta_r H°$ were determined for the temperature range $291.15 \leqslant T/\mathrm{K} \leqslant 313.15$. Results were obtained at several ionic strengths and extrapolated to $I=0$. The value $\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}}) = 7$ at $T=298.15$ was calculated from the temperature dependence of the $\Delta_r H°$ values. In performing this calculation values of $\Delta_r H°$ for the ionization of water were taken from Olofsson and Hepler	68VAS/KOC	
	52.34	298.15	0	Calorimetry.	69CHR/IZA	
	50.12	?	?	Calorimetry.	71MAR/BER	
	51.99	298.15	0	Calorimetry. Vanderzee *et al.* [72VAN/KIN] report $\Delta_r H° = 3.828\ \mathrm{kJ\,mol^{-1}}$ for the reaction ($NH_3+H_2O=NH_4^+ + OH^-$) at $T=298.15$ K and $I=0$. This value when combined with $\Delta_r H°$ for the ionization of $H_2O(1)$ [75OLO/HEP] leads to $\Delta_r H° = 51.99\ \mathrm{kJ\,mol^{-1}}$ for the reaction ($NH_4^+ = H^+ + NH_3$).	72VAN/KIN	
	51.92	298.15	0	Calorimetry. Values of $\Delta_r H°$ were determined for the temperature range $278.15 \leqslant T/\mathrm{K} \leqslant 418.15$. The value $\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}}) = 11$ at $T=298.15$ was calculated from the temperature dependence of the $\Delta_r H°$ values.	75OLO	
				The result $\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}}) = 7$ at $T=298.15$ K was obtained by direct heat capacity measurements.	81ALL/WOO	

Values adjusted to T=298.15 K and I=0

pK	$\Delta_r H°$/(kJ mol^{-1})	$\Delta_r C_p^\circ$/(J K^{-1} mol^{-1})	Reference
	52.5		37PIT
9.215	51.7	≈3	38EVE/WYN
9.245	52.24	≈−5	49BAT/PIN2
9.246	52.19	≈−5	50BAT/PIN
9.238	51.9	≈−24	54EVE/LAN
	52.59		61TYS/MCC
9.29	52.01		65PAO/STE
	52.15	7	68VAS/KOC
	52.34		69CHR/IZA
	50.12		71MAR/BER
	51.99		72VAN/KIN
	51.92	11	75OLO
		7	81ALL/WOO

Comments: We adopt pK=9.246 based on the careful work of Bates and Pinching [49BAT/PIN2, 50BAT/PIN]. For $\Delta_r H°$ we prefer the very accurate studies of Vanderzee *et al.* [72VAN/KIN] and of Olofsson [75OLO] which can be considered to be in agreement with the values of $\Delta_r H°$ calculated from the temperature dependency of the pK values and with most of the other calorimetric results. We adopt the average of the calorimetrically determined values of $\Delta_r C_p^\circ$. Additional studies, performed under a variety of conditions, are cited by Martell *et al.* [2001MAR/SMI] and by Pettit and Powell [2000PET/POW].

TABLE 7.8. AMPSO

Other names	3-[(1,1-dimethyl-2-hydroxyethyl)amino]-2-hydroxypropanesulfonic acid; 2-hydroxy-3-[(2-hydroxy-1,1-dimethylethyl)amino]-1-propanesulfonic acid; CAS No. 68399-79-1
Empirical formula	$C_7H_{17}NO_5S$
Molecular weight	227.28

Ionization reaction

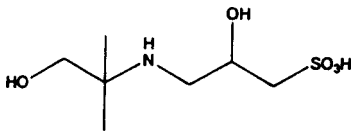
$$HL^{\pm} = H^+ + HL^-, \text{ where } HL = C_7H_{17}NO_5S$$

Selected values at T=298.15 K and I=0:

pK=9.138, $\Delta_r G°$/(kJ mol^{-1})=52.160, $\Delta_r H°$/(kJ mol^{-1})=43.19, and $\Delta_r C_p^\circ$/(J K^{-1} mol^{-1})=−61

Evaluation: AAB

Structure:



Values from literature

pK	$\Delta_r H°$/(kJ mol^{-1})	T/K	I	Method(s) and comments	Reference
9.686		278.15	0	Electrochemical cell—no liquid junction. The value of $\Delta_r H°$ given here was calculated from pKs measured at several temperatures. The value $\Delta_r C_p^\circ$/(J K^{-1}mol^{-1})=−61 was also calculated from the temperature dependency of Roy *et al.*'s [97ROY/CAR] reported pKs.	97ROY/CAR
9.544		283.15	0		
9.409		288.15	0		
9.271		293.15	0		
9.138	43.19	298.15	0		
9.010		303.15	0		
8.893		308.15	0		
8.845		310.15	0		
8.778		313.15	0		
8.674		318.15	0		
8.560		323.15	0		
8.463		328.15	0		
9.11		298.15	0.1 M	Potentiometric titration—glass electrode.	98AZA/ORA

Values adjusted to $T=298.15$ K and $I=0$

pK	$\Delta_r H°/(\text{kJ mol}^{-1})$	$\Delta_r C_p°/(\text{J K}^{-1}\text{mol}^{-1})$	Reference
9.138	43.19	−61	97ROY/CAR
9.32			98AZA/ORA

Comments: The results of Roy *et al.* [97ROY/CAR] which used an electrochemical cell without liquid junction are judged to be the most reliable.

TABLE 7.9. Arsenate

Other names	arsenic acid; orthoarsenic acid; CAS No. 7778-39-4
Empirical formula	AsH_3O_4
Molecular weight	141.94

Ionization Reactions

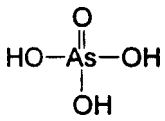
$$H_3AsO_4 = H^+ + H_2AsO_4^-$$
$$H_2AsO_4^- = H^+ + HAsO_4^{2-}$$
$$HAsO_4^{2-} = H^+ + AsO_4^{3-}$$

Selected values at $T=298.15$ K and $I=0$:

p$K=2.31$, $\Delta_r G°/(\text{kJ mol}^{-1}) = 13.19$, and $\Delta_r H°/(\text{kJ mol}^{-1}) = -7.8$
p$K=7.05$, $\Delta_r G°/(\text{kJ mol}^{-1}) = 40.24$, and $\Delta_r H°/(\text{kJ mol}^{-1}) = 1.7$
p$K=11.9$, $\Delta_r G°/(\text{kJ mol}^{-1}) = 67.93$, and $\Delta_r H°/(\text{kJ mol}^{-1}) = 15.9$

Evaluation: reaction (1): CC; reaction (2): CC; reaction (3): CC

Structure:



Values from literature

pK	$\Delta_t H°$/(kJ mol^{-1})	T/K	I	Method(s) and comments	Reference
			Reaction (1): $H_3AsO_4 = H^+ + H_2AsO_4^-$		
2.30		298.15	?	Conductivity.	07LUT
2.36		298.15	0	Conductivity.	13WAS/STR
2.25		291.15	?	Potentiometric titration—glass electrode.	34BRI/JAC
2.094		273.15	0	Electrochemical cell. The value of $\Delta_t H°$ given here was calculated from pKs measured at several temperatures.	53AGA/AGA
2.114		278.15	0		
2.138		283.15	0		
2.163		288.15	0		
2.194		293.15	0		
2.223	2.2	298.15	0		
2.265		303.15	0		
2.296		308.15	0		
2.332		313.15	0		
2.383		318.15	0		
2.420		323.15	0		
2.65		293.15	?	Glass electrode.	59CHU
2.49		283.15	0	Potentiometric titration—glass electrode. The approximate value of $\Delta_t H°$ given here was calculated from pKs measured at several temperatures.	59FLI/MIS
2.19	≈−3	298.15	0		
1.95		308.15	0		
2.15		323.15	0		
2.301		298.15	0	Glass electrode.	64SAL/SCH
	−7.07	298.15	≈0.2 M	Calorimetry.	64SEL/SUN
2.32		298.15	3.0 M	Potentiometric titration—glass electrode; spectrophotometry. The reported value is approximate.	70SEC/IND
2.26		298.15	0.1 M		76TOS
2.128		298.15	1.0 M	Potentiometric titration—glass electrode.	88KHO/ROB
			Reaction(2): $H_2AsO_4^- = H^+ + HAsO_4^{2-}$		
4.40		298.15	?	Conductivity.	20BLA
6.80		298.15	?	Kinetic data.	27SKR/ZAH
7.08		298.15	?	Glass electrode.	28HUG
6.77		291.15	?	Potentiometric titration—glass electrode.	34BRI/JAC
7.054		273.15	0	Electrochemical cell. The value of $\Delta_t H°$ given here was calculated from pKs measured at several temperatures.	53AGA/AGA
7.032		278.15	0		
7.015		283.15	0		
6.999		288.15	0		
6.990		293.15	0		
6.980	−0.15	298.15	0		
6.974		303.15	0		
6.973		308.15	0		
6.973		313.15	0		
6.973		318.15	0		
6.980		323.15	0		
6.39		298.15	1.0 M	Glass electrode.	58MAD
5.89		293.15	?	Glass electrode.	59CHU
7.05		283.15	0	Potentiometric titration—glass electrode. The approximate value of $\Delta_t H°$ given here was calculated from pKs measured at several temperatures.	59FLI/MIS
6.94	−0.7	298.15	0		
6.90		308.15	0		
6.79		323.15	0		
	3.22	298.15	≈0.2 M	Calorimetry.	64SEL/SUN
6.10		277.95	1.0 M	Potentiometric titration—glass electrode.	71BEE/LIN
5.75		295.15	0.1 M	Potentiometric titration—glass electrode.	73BEE/LAW
6.76		298.15	0.1 M		76TOS
7.09		298.15	0	Potentiometric titration—glass electrode.	76WAU
6.47		298.15	1.0 M	Glass electrode.	86GRE/TRA
			Reaction(3): $HAsO_4^{2-} = H^+ + AsO_4^{3-}$		
9.21		298.15	?	Conductivity.	20BLA
11.53		291.15	?	Potentiometric titration—glass electrode.	34BRI/JAC
11.34		283.15	0	Potentiometric titration—glass electrode. The approximate value of $\Delta_t H°$ given here was calculated from pKs measured at several temperatures.	59FLI/MIS
11.48	0.9	298.15	0		
11.66		308.15	0		
11.91		323.15	0		
11.52		293.15	?	Glass electrode.	59CHU
	18.20		≈0.2 M	Calorimetry.	64SEL/SUN
11.29		298.15	0.1 M		76TOS

Values adjusted to $T=298.15$ K and $I=0$

pK	$\Delta_r H°/(\text{kJ mol}^{-1})$	Reference
	Reaction (1): $H_3AsO_4=H^+ + H_2AsO_4^-$	
≈2.5		07LUT
2.36		13WAS/STR
≈2.5		34BRI/JAC
2.22	2.2	53AGA/AGA
≈2.9		59CHU
2.19	≈−3	59FLI/MIS
2.30		64SAL/SCH
	−7.8	64SEL/SUN
≈2.8		70SEC/IND
2.47		76TOS
≈2.5		88KHO/ROB
	Reaction(2): $H_2AsO_4^- = H^+ + HAsO_4^{2-}$	
≈4.8		20BLA
≈7.2		27SKR/ZAH
≈7.5		28HUG
≈7.2		34BRI/JAC
6.98	−0.15	53AGA/AGA
≈7.2		58MAD
≈6.3		59CHU
6.94	−0.7	59FLI/MIS
	1.7	64SEL/SUN
≈6.8		71BEE/LIN
6.17		73BEE/LAW
7.19		76TOS
7.09		76WAU
≈7.3		86GRE/TRA
	Reaction(3): $HAsO_4^{2-} = H^+ + AsO_4^{3-}$	
≈9.9		20BLA
≈12.1		34BRI/JAC
11.48	0.9	59FLI/MIS
≈12.1		59CHU
	15.9	64SEL/SUN
11.9		76TOS

Comments: We have adopted the calorimetric results of Sellers *et al.* [64SEL/SUN] for all three reactions. The extrapolation to $I=0$ is the major uncertainty in the values of $\Delta_r H°$. For the first and third reactions, there are serious discrepancies between the values of $\Delta_r H°$ calculated from the pKs determined at several temperatures and the calorimetric values. The pK value for reaction (1) is based on an average of five sets of results [13WAS/STR, 53AGA/AGA, 59FLI/MIS, 64SAL/SCH, 76TOS] where the extrapolation to $I=0$ has either been done or is not too uncertain. For reaction (2), the pK is based on an average of what appear to be the most reliable results [53AGA/AGA, 59FLI/MIS, 76TOS, 76WAU]. For reaction (3), we have adopted a pK value based on an average of all of the results with the exception of that of Blanc [20BLA] which is discordant. A definitive study of these ionization reactions is needed.

TABLE 7.10. Barbital

Other names	barbitone; 5,5-diethylbarbituric acid; veronal; diethylmalonylurea; barbitone; BAN; 5,5-diethyl-2,4,6(1H,3H,5H)-pyrimidinetrione; 5,5′-diethylbarbituric acid; 5,5-diethylperhydro-1,3-diazine-2,4,6-trione; CAS No. 57-44-3
Empirical formula	$C_8H_{12}N_2O_3$
Molecular weight	184.19

Ionization Reactions

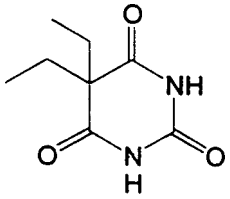
$$H_2L = H^+ + HL^- \quad (1)$$
$$HL^- = H^+ + L^{2-} \quad (2)$$
where $H_2L = C_8H_{12}N_2O_3$

Selected values at $T = 298.15$ K and $I = 0$:

p$K = 7.980$, $\Delta_r G°/(\text{kJ mol}^{-1}) = 45.550$, $\Delta_r H°/(\text{kJ mol}^{-1}) = 24.27$, and $\Delta_r C_p^\circ/(\text{J K}^{-1}\,\text{mol}^{-1}) = -135$ for reaction (1)
p$K = 12.8$ and $\Delta_r G°/(\text{kJ mol}^{-1}) = 73.06$ for reaction (2)

Evaluation: reaction (1), AAA; reaction (2), C

Structure:



Values from literature

pK	$\Delta_r H°$/(kJ mol^{-1})	T/K	I	Method(s) and comments	Reference
			Reaction (1): $H_2L=H^+ + HL^-$		
7.43		298.15	0.016 M	Conductivity.	06WOO
≈7.8		298.15	0.07 M	Approximate value obtained from reported potentiometric titration data [40KRA].	30MIC
≈7.9		291.15	0.04 M	Potentiometric titration.	31BRI/ROB
7.89		298.15	?	Electrochemical cell with liquid junction.	37BUS
7.91		298.15	0	Electrochemical cell with liquid junction.	40KRA
8.3971		273.15	0	Electrochemical cell—no liquid junction. The pK values given here were those obtained by using Ag,AgI electrodes. Values of pK very close ($\Delta pK \leqslant 0.0010$) to these were obtained by use of Ag,AgCl electrodes. The value of $\Delta_r H°$ given here was calculated from pKs measured at several temperatures. The value $\Delta_r C_p^\circ$/(J K^{-1} mol^{-1}) $=-135$ was also calculated from the temperature dependency of their [52MAN/SCH] reported pKs.	52MAN/SCH
8.3040		278.15	0		
8.2171		283.15	0		
8.1367		288.15	0		
8.0592		293.15	0		
7.9798	24.25	298.15	0		
7.9092		303.15	0		
7.8471		308.15	0		
7.8226		310.15	0		
7.7858		313.15	0		
7.7290		318.15	0		
7.6776		323.15	0		
7.6264		328.15	0		
7.5762		333.15	0		
7.971		298.15	0	Spectrophotometry.	56BIG
8.00		298.15	0	Potentiometric titration—glass electrode; Spectrophotometry.	59NAS/HEI
	24.31	298.15	0	Calorimetry.	65MIL/AHL
8.169		288.15	0	Spectrophotometry. The value of $\Delta_r H°$ given here was calculated from pKs measured at several temperatures. The value $\Delta_r C_p^\circ$/(J K^{-1} mol^{-1}) $=-134$ was also calculated from the temperature dependency of their [69BRI/SAW] reported pKs.	69BRI/SAW
8.093		293.15	0		
8.019	24.24	298.15	0		
7.950		303.15	0		
7.878		308.15	0		
7.806		313.15	0		
7.738		318.15	0		
7.675		323.15	0		
7.98		298.15	0	Potentiometric titration—glass electrode.	80MCK
7.55		310.15	0.15 M	Potentiometry. The ''practical'' pK value of Cowden *et al.* [82COW/JAC] was adjusted to obtain the pK value given here.	82COW/JAC
7.97		298.15	≈0.012 M	Potentiometric titration of sample (0.01–0.014 M) with 0.1 M HCl or 0.1 M NaOH.	87KIT/ITO
			Reaction(2): $HL^- = H^+ + L^{2-}$		
12.31		311.15	0.1 M	Spectrophotometry; glass electrode.	55BUT/RUT
12.8		298.15	0	Potentiometric titration—glass electrode; Spectrophotometry.	59NAS/HEI

Values adjusted to $T=298.15$ K and $I=0$

pK	$\Delta_r H°/(\mathrm{kJ\,mol^{-1}})$	$\Delta_r C_p°/(\mathrm{J\,K^{-1}\,mol^{-1}})$	Reference
	Reaction (1): $H_2L=H^+ + HL^-$		
≈7.5			06WOO
≈8.0			30MIC
7.95			31BRI/ROB
≈8.1			37BUS
7.91			40KRA
7.980	24.25	−135	52MAN/SCH
7.97			56BIG
8.00			59NAS/HEI
	24.31		65MIL/AHL
8.019	24.24	−134	69BRI/SAW
7.98			80MCK
7.96			82COW/JAC
8.07			87KIT/ITO
	Reaction (2): $HL^- = H^+ + L^{2-}$		
≈12.7			55BUT/RUT
12.8			59NAS/HEI

Comments: The pK values determined by Manov *et al.* [52MAN/SCH] are judged to be the most reliable and their [52MAN/SCH] value of pK_1 at $T=298.15$ K has been selected. Several other studies [30MIC, 31BRI/ROB, 56BIG, 59NAS/HEI, 69BRI/SAW, 80MCK] are also in good agreement with the results of Manov *et al.* [52MAN/SCH]. We adopt the average value $\Delta_r H°/(\mathrm{kJ\,mol^{-1}})=24.27$ for reaction (1).

TABLE 7.11. BES

Other names	*N*,*N*-bis[2-hydroxyethyl]-2-aminoethanesulfonic acid; CAS No. 10191-18-1
Empirical formula	$C_6H_{15}NO_5S$
Molecular weight	213.25

Ionization reaction

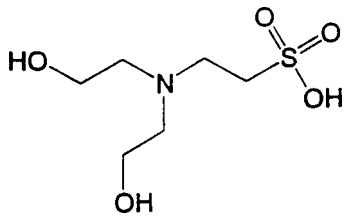
$$HL^{\pm} = H^+ + L^-, \text{ where } HL = C_6H_{15}NO_5S$$

Selected values at $T=298.15$ K and $I=0$:

$$pK=7.187,\ \Delta_r G°/(\mathrm{kJ\,mol^{-1}})=41.024,\ \Delta_r H°/(\mathrm{kJ\,mol^{-1}})=24.25,\ \text{and}\ \Delta_r C_p°/(\mathrm{J\,K^{-1}\,mol^{-1}})=-2$$

Evaluation: AAA

Structure:



Values from literature

pK	$\Delta_r H°/(\mathrm{kJ\,mol^{-1}})$	T/K	I	Method(s) and comments	Reference
7.5		273.15	0.1 M	Potentiometric titration—glass electrode.	66GOO/WIN
7.20		293.15	0.01 M		
7.17		293.15	0.1 M		
7.18		293.15	0.2 M		
6.90		310.15	0.1 M		
6.92	23.1	298.15	≈0.01 M	Potentiometric titration—glass electrode; and calorimetry. Dilute solutions (0.005–0.01 M) were titrated with 0.1 M NaOH or 0.1 M HCl.	76MCG/JOR

Values from literature—Continued

pK	$\Delta_r H°/(\mathrm{kJ\,mol^{-1}})$	T/K	I	Method(s) and comments	Reference
7.492		278.15	0	Electrochemical cell—no liquid junction. The value of $\Delta_r H°$ given here was calculated from pKs measured at several temperatures. The value $\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}}) = -4$ was also calculated from the temperature dependency of their [76VEG/BAT] reported pKs.	76VEG/BAT
7.416		283.15	0		
7.333		288.15	0		
7.257		293.15	0		
7.187	24.39	298.15	0		
7.115		303.15	0		
7.049		308.15	0		
6.982		313.15	0		
6.915		318.15	0		
6.856		323.15	0		
7.494		278.15	0	Electrochemical cell—no liquid junction. The value of $\Delta_r H°$ given here was calculated from pKs measured at several temperatures. The value $\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}}) = -4$ was also calculated from the temperature dependency of their [77ROY/GIB] reported pKs.	77ROY/GIB
7.410		283.15	0		
7.331		288.15	0		
7.256		293.15	0		
7.187	24.18	298.15	0		
7.118		303.15	0		
7.050		308.15	0		
7.023		310.15	0		
6.985		313.15	0		
6.920		318.15	0		
6.858		323.15	0		
6.800		328.15	0		
7.16		298.15	≈0.012 M	Potentiometric titration of sample (0.01–0.014 M) with 0.1 M HCl or 0.1 M NaOH.	87KIT/ITO
7.16		298.15	0.00602 M	Based on measurement of ionic mobilities.	87POS/DEM
	25.67	288.15	≈0.16 M	Calorimetry. $\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}}) = 4$ was also calculated from the temperature dependency of their [93ROI/BAC] reported pKs.	93ROI/BAC
	25.78	298.15	≈0.16 M		
	25.76	310.15	≈0.16 M		
	24.41	298.15	≈0.01 M		
	25.39	298.15	≈0.11 M		
	25.72	298.15	≈0.16 M		
	23.9	298.15	0		
7.06	25.17	298.15	0.1 M	Electrochemical cell with liquid junction; calorimetry. Fukada and Takahashi [98FUK/TAK] also obtained $\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}}) = 2$ at $I = 0.1$ M from the temperature dependence of $\Delta_r H°$ over the range 278.15–323.15 K.	98FUK/TAK

Values adjusted to T=298.15 K and I=0

pK	$\Delta_r H°/(\mathrm{kJ\ mol^{-1}})$	$\Delta_r C_p^\circ/(\mathrm{J\ K^{-1}\ mol^{-1}})$	Reference
7.30			66GOO/WIN
	22.8		76MCG/JOR
7.187	24.40	1	76VEG/BAT
7.187	24.18	−5	77ROY/GIB
7.26			87KIT/ITO
7.23			87POS/DEM
	23.9	4	93ROI/BAC
7.27	24.5	−6	98FUK/TAK

Comments: The pKs obtained by Vega and Bates [76VEG/BAT] and by Roy *et al.* [77ROY/GIB] are in excellent agreement. For $\Delta_r H°$ and $\Delta_r C_p^\circ$, we adopt the respective averages of the values obtained from four studies [76VEG/BAT, 77ROY/GIB, 93ROI/BAC, 98FUK/TAK]: $\langle \Delta_r H° \rangle/(\mathrm{kJ\ mol^{-1}}) = 24.25$ and $\langle \Delta_r C_p^\circ \rangle/(\mathrm{J\ K^{-1}\ mol^{-1}}) = -2$.

TABLE 7.12. Bicine

Other names	N,N-bis(2-hydroxyethyl)glycine; [bis(2-hydroxyethyl)amino]acetic acid; diethylolglycine; N,N-di-(2-hydroxyethyl)glycine; DHEG; N,N'-dihydroxyethylglycine; Versene; CAS No. 150-25-4
Empirical formula	$C_6H_{13}NO_4$
Molecular weight	163.17

Ionization reactions

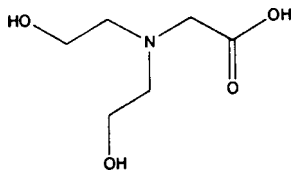
$$H_2L^+ = H^+ + HL^\pm \quad (1)$$
$$HL^\pm = H^+ + L^- \quad (2)$$
where $HL = C_6H_{13}NO_4$

Selected values at T=298.15 K and I=0:

pK=2.0 and $\Delta_r G°/(\mathrm{kJ\ mol^{-1}}) = 11.4$ for reaction (1)
pK=8.334, $\Delta_r G°/(\mathrm{kJ\ mol^{-1}}) = 47.571$, $\Delta_r H°/(\mathrm{kJ\ mol^{-1}}) = 26.34$, and $\Delta_r C_p^\circ/(\mathrm{J\ K^{-1}\ mol^{-1}}) = 0$ for reaction (2)

Evaluation: reaction (1), DD; reaction (2), AAA

Structure:



Values from literature

pK	$\Delta_r H°/(\mathrm{kJ\ mol^{-1}})$	T/K	I	Method(s) and comments	Reference
				Reaction (1): $H_2L^+ = H^+ + HL^\pm$	
2.50		298.15	0.5 M	Potentiometric titration—glass electrode.	55TOR/KOL
1.99		293.15	0.1 M	Potentiometric titration—glass electrode.	64JOK/MAJ
1.68		293.15	0.1 M	Spectrophotometry.	67KAR/SPR
2.48		303.15	0.1 M	Potentiometric titration—glass electrode.	84GHO
1.658		298.15	0.10 M	Potentiometric titration—glass electrode.	84MOT/MAR
2.230	≈9.4	298.15	0	Electrochemical cell—no liquid junction. The value of $\Delta_r H°$ given	89ELH/SAD
2.204		303.15	0	here was calculated from the pK values of El—Harakany *et al.*	
2.190		308.15	0	[89ELH/SAD] by using the Clarke and Glew equation with $\Delta_r C_p^\circ$ set	
2.165		313.15	0	to zero. This value does not agree with the value given by El—	
2.120		318.15	0	Harakany *et al.* [89ELH/SAD] in their paper.	
1.70		298.15	0.1 M	Potentiometric titration—glass electrode.	91DUM/MAR
1.78		298.15	0.10 M	Potentiometric titration—glass electrode.	91KRI/NAK
1.95		298.15	0.5 M	Potentiometric titration-glass electrode.	92COR/SON
				Reaction(2): $HL^\pm = H^+ + L^-$	
8.08		303.15	0.1 M	Potentiometric titration—glass electrode.	53CHA/COU
8.11		298.15	0.5 M	Potentiometric titration—glass electrode.	55TOR/KOL

Values from literature—Continued

pK	$\Delta_r H°/(\mathrm{kJ\,mol^{-1}})$	T/K	I	Method(s) and comments	Reference
8.7536		273.15	0	Electrochemical cell—no liquid junction. The value of $\Delta_r H°$ given here was calculated from pKs measured at several temperatures. The value $\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}}) = 5$ was also calculated from the temperature dependency of their [64DAT/GRZ] reported pKs.	64DAT/GRZ
8.6637		278.15	0		
8.5769		283.15	0		
8.4930		288.15	0		
8.4119		293.15	0		
8.3335	26.27	298.15	0		
8.2576		303.15	0		
8.1840		308.15	0		
8.1552		310.15	0		
8.1127		313.15	0		
8.0436		318.15	0		
7.9766		323.15	0		
7.9115		328.15	0		
8.41		293.15	0.1 M	Potentiometric titration—glass electrode.	64JOK/MAJ
8.7		273.15	0.1 M	Potentiometric titration—glass electrode.	66GOO/WIN
8.4		293.15	0.01 M		
8.35		293.15	0.1 M		
8.3		293.15	0.2 M		
8.2		310.15	0.1 M		
8.14		293.15	0.1 M	Spectrophotometry.	67KAR/SPR
8.29		293.15	0.02 M	Potentiometric titration—glass electrode; spectrophotometry.	68KOS/ROM
8.31	26.2	298.15	≈0.01 M	Potentiometric titration—glass electrode; and calorimetry. Dilute solutions (0.005–0.01 M) were titrated with 0.1 M NaOH or 0.1 M HCl.	76MCG/JOR
8.39		298.15	0.1 M	Potentiometric titration—glass electrode.	83NAK/KRI
8.00		303.15	0.1 M	Potentiometric titration—glass electrode.	84GHO
8.093		298.15	0.10 M	Potentiometric titration—glass electrode.	84MOT/MAR
8.34		298.15	1.0 M	Potentiometric titration—glass electrode.	86AND
8.30		298.15	≈0.012 M	Potentiometric titration of sample (0.01–0.014 M) with 0.1 M HCl or 0.1 M NaOH.	87KIT/ITO
8.14		298.15	0.1 M	Potentiometric titration—glass electrode.	91DUM/MAR
8.39		298.15	0.10 M	Potentiometric titration—glass electrode.	91KRI/NAK
8.22		298.15	0.2 M	Potentiometric titration—glass electrode.	92COR/SON
8.22	27.05	298.15	0.1 M	Electrochemical cell with liquid junction; calorimetry. Fukada and Takahashi [98FUK/TAK] also obtained $\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}}) = 2$ at $I = 0.1$ M from the temperature dependence of $\Delta_r H°$ over the range 278.15–323.15 K.	98FUK/TAK

Values adjusted to $T = 298.15$ K and $I = 0$

pK	$\Delta_r H°/(\mathrm{kJ\,mol^{-1}})$	$\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}})$	Reference
	Reaction (1): $H_2L^+ = H^+ + HL^\pm$		
2.50			55TOR/KOL
1.96			64JOK/MAJ
1.65			67KAR/SPR
2.51			84GHO
1.66			84MOT/MAR
2.23	9.4		89ELH/SAD
1.70			91DUM/MAR
1.78			91KRI/NAK
1.95			92COR/SON
	Reaction(2): $HL^\pm = H^+ + L^-$		
8.37			53CHA/COU
8.45			55TOR/KOL
8.334	26.27	5	64DAT/GRZ
8.54			64JOK/MAJ
8.49			66GOO/WIN
8.27			67KAR/SPR
8.33			68KOS/ROM
8.40			76MCG/JOR
8.60			83NAK/KRI
8.29			84GHO
8.31			84MOT/MAR

Values adjusted to $T=298.15$ K and $I=0$—Continued

pK	$\Delta_r H°/(\mathrm{kJ\,mol^{-1}})$	$\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}})$	Reference
8.73			86AND
8.39			87KIT/ITO
8.35			91DUM/MAR
8.60			91KRI/NAK
8.49			92COR/SON
8.43	26.4	−6	98FUK/TAK

Comments: The results for reaction (1) are very scattered and we have adopted the rounded average of the pK values. For reaction (2), the results of Datta *et al.* [64DAT/GRZ], which were obtained by using an electrochemical cell with no liquid junction, are judged to be the most reliable for the pK value. We have adopted the respective averages of the reported $\Delta_r H°$ and $\Delta_r C_p^\circ$ values for reaction (2).

TABLE 7.13. Bis-tris

Other names	bis(2-hydroxyethyl)iminotris(hydroxymethyl)methane; 2-[bis(2-hydroxyethyl)amino]-2-(hydroxymethyl)-1,3-propanediol; 2,2-bis(hydroxymethyl)-2,2′,2″-nitrilotriethanol; bis(2-hydroxyethylamino)tris(hydroxymethyl)methane; CAS No. 6976-37-0
Empirical formula	$C_8H_{19}NO_5$
Molecular weight	209.24

Ionization reaction

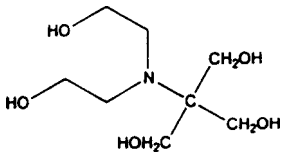
$$H_3L^+ = H^+ + H_2L^\pm, \text{ where } H_2L = C_8H_{19}NO_5$$

Selected values at $T=298.15$ K and $I=0$:

$$pK = 6.484,\ \Delta_r G°/(\mathrm{kJ\,mol^{-1}}) = 37.011,\ \Delta_r H°/(\mathrm{kJ\,mol^{-1}}) = 28.4,\text{ and } \Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}}) = 27$$

Evaluation: AAA

Structure:



Values from literature

pK	$\Delta_r H°/(\mathrm{kJ\,mol^{-1}})$	T/K	I	Method(s) and comments	Reference
6.46		298.15	0	Potentiometric titration—glass electrode. Lewis [66LEW] stated that the results have been corrected for ionic strength—presumably to $I=0$.	66LEW
6.9314		273.15	0	Electrochemical cell—no liquid junction. The value of $\Delta_r H°$ given here was calculated from pKs measured at several temperatures. The value $\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}}) = 24$ was also calculated from the temperature dependency of their [70PAA/BAT] reported pKs.	70PAA/BAT
6.8344		278.15	0		
6.7429		283.15	0		
6.6536		288.15	0		
6.5665		293.15	0		
6.4835	28.24	298.15	0		
6.4013		303.15	0		
6.3212		308.15	0		
6.2441		313.15	0		
6.1690		318.15	0		
6.0959		323.15	0		
6.41	29.2	298.15	≈0.01 M	Potentiometric titration—glass electrode; and calorimetry. Dilute solutions (0.005–0.01 M) were titrated with 0.1 M NaOH or 0.1 M HCl.	76MCG/JOR
6.41		298.15	0	Potentiometric titration—glass electrode. Values of pKs were extrapolated to $I=0$.	80SCH/ABE
6.74		298.15	1.0 M	Potentiometric titration—glass electrode.	82SIG/SCH
6.50		298.15	0.012 M	Potentiometric titration of sample (0.01–0.014 M) with 0.1 M HCl or 0.1 M NaOH.	87KIT/ITO
6.481	28.5	298.15	0	Electrochemical cell—with a liquid junction. The value $\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}}) = 22$ was also calculated from the temperature dependency of their [89WES/PAL] reported pKs.	89WES/PAL

Values from literature—Continued

pK	$\Delta_r H°/(\text{kJ mol}^{-1})$	T/K	I	Method(s) and comments	Reference
	28.4	318.15	?	Calorimetry. We calculate the value $\Delta_r C_p^\circ/(\text{J K}^{-1}\,\text{mol}^{-1}) \approx 36$ from the temperature dependency of their [92SMI/ZAN] reported values of $\Delta_r H°$.	92SMI/ZAN
	29.3	343.15	?		

Values adjusted to T=298.15 K and I=0

pK	$\Delta_r H°/(\text{kJ mol}^{-1})$	$\Delta_r C_p^\circ/(\text{J K}^{-1}\,\text{mol}^{-1})$	Reference
6.46			66LEW
6.484	28.24	24	70PAA/BAT
6.41	29.2		76MCG/JOR
6.41			80SCH/ABE
6.74			82SIG/SCH
6.50			87KIT/ITO
6.481	28.5	22	89WES/PAL
	27.7	36	92SMI/ZAN

Comments: We adopt the pK determined by Paabo and Bates [70PAA/BAT] who used an electrochemical cell with no liquid junction. There is a very good agreement with the results of Wesolowski and Palmer [89WES/PAL]. The selected values of $\Delta_r H°$ and $\Delta_r C_p^\circ$ are based on the respective averages of the values determined for these quantities.

TABLE 7.14. Bis-tris propane

Other names	1,3-bis[tris(hydroxymethyl)methylamino]propane; BTP; 2,2′-(1,3-propanediyldiimino)bis[2-(hydroxymethyl)-1,3-propanediol]; 2,2′-(trimethylenediimino)bis[2-(hydroxymethyl)-1,3-propanediol]; CAS No. 64431-96-5
Empirical formula	$C_{11}H_{26}N_2O_6$
Molecular weight	282.34

Ionization reactions

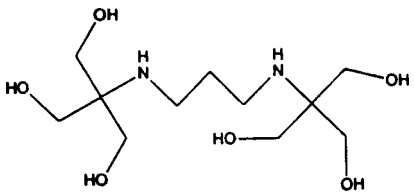
$$H_2L^{2+} = H^+ + HL^+ \quad (1)$$
$$HL^+ = H^+ + L^\pm \quad (2)$$
where $L = C_{11}H_{26}N_2O_6$

Selected values at T=298.15 K and I=0:

pK=6.65 and $\Delta_r G°/(\text{kJ mol}^{-1}) = 37.96$ for reaction (1)
pK=9.10 and $\Delta_r G°/(\text{kJ mol}^{-1}) = 51.94$ for reaction (2)

Evaluation: reaction (1), D; reaction (2), D

Structure



Values from literature

pK	T/K	I	Methods and comments	Reference
			Reaction (1): $H_2L^{2+} = H^+ + HL^+$	
6.75	298.15	0.012 M	Potentiometric titration of sample (0.01–0.014 M) with 0.1 M HCl or 0.1 M NaOH.	87KIT/ITO
			Reaction (2): $HL^+ = H^+ + L$	
9.10	298.15	0.012 M	Potentiometric titration of sample (0.01–0.014 M) with 0.1 M HCl or 0.1 M NaOH.	87KIT/ITO

Values adjusted to T=298.15 K and I=0

pK	Reference
Reaction (1): $H_2L^{2+}=H^+ + HL^+$	
6.65	87KIT/ITO
Reaction (2): $HL^+=H^+ + L$	
9.10	87KIT/ITO

Comments: The literature on Bis-tris propane is sparse. Additional measurements are needed.

TABLE 7.15. Borate

Other names	boric acid; CAS No. 10043-35-3
Empirical formula	H_3BO_3
Molecular weight	61.833

Ionization Reaction

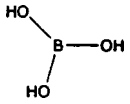
$$H_3BO_3 = H^+ + H_2BO_3^-$$

Selected values at T=298.15 K and I=0:

$$pK=9.237,\ \Delta_r G°/(\text{kJ mol}^{-1})=52.725,\ \Delta_r H°/(\text{kJ mol}^{-1})=13.8,\ \text{and}\ \Delta_r C_p^\circ/(\text{J K}^{-1}\,\text{mol}^{-1})\approx -240$$

Evaluation: ABD

Structure:



Values from literature

pK	$\Delta_r H°/(\text{kJ mol}^{-1})$	T/K	I	Method(s) and comments	Reference
9.380		283.15	0	Electrochemical cell—no liquid junction. The value of $\Delta_r H°$ given here was calculated from pKs measured at several temperatures. The value $\Delta_r C_p^\circ/(\text{J K}^{-1}\,\text{mol}^{-1})=-200$ was also calculated from the temperature dependency of their [34OWE2] reported pKs.	34OWE2
9.327		288.15	0		
9.280		293.15	0		
9.236	14.0	298.15	0		
9.197		303.15	0		
9.132		313.15	0		
9.080		323.15	0		
9.440		278.15	0	Electrochemical cell—no liquid junction. The value of $\Delta_r H°$ given here was calculated from pKs measured at several temperatures. The value $\Delta_r C_p^\circ/(\text{J K}^{-1}\,\text{mol}^{-1})=-307$ was also calculated from the temperature dependency of their [35OWE] reported pKs.	35OWE
9.380		283.15	0		
9.326		288.15	0		
9.279		293.15	0		
9.237	13.2	298.15	0		
9.198		303.15	0		
9.164		308.15	0		
9.132		313.15	0		
9.440		278.15	0	Electrochemical cell—no liquid junction. The value of $\Delta_r H°$ given here was calculated from pKs measured at several temperatures. The value $\Delta_r C_p^\circ/(\text{J K}^{-1}\,\text{mol}^{-1})=-301$ was also calculated from the temperature dependency of their [43OWE/KIN] reported pKs.	43OWE/KIN
9.3800		283.15	0		
9.3265		288.15	0		
9.2795		293.15	0		
9.2365	13.4	298.15	0		
9.1975		303.15	0		
9.164		308.15	0		
9.1320		313.15	0		
9.080		323.15	0		
9.5078		273.15	0	Electrochemical cell—no liquid junction. The value of $\Delta_r H°$ given here was calculated from pKs measured at several temperatures. The value $\Delta_r C_p^\circ/(\text{J K}^{-1}\,\text{mol}^{-1})=-200$ was also calculated from the temperature dependency of their [44MAN/DEL] reported pKs. Manov *et al.* [44MAN/DEL] also summarize earlier results from the literature.	44MAN/DEL
9.4374		278.15	0		
9.3785		283.15	0		
9.3255		288.15	0		
9.2780		293.15	0		
9.2340	14.2	298.15	0		
9.1947		303.15	0		
9.1605		308.15	0		
9.1282		313.15	0		

Values from literature—Continued

pK	$\Delta_r H°$/(kJ mol^{-1})	T/K	I	Method(s) and comments	Reference
9.1013		318.15	0		
9.0766		323.15	0		
9.0537		328.15	0		
9.0310		333.15	0		
	14.3	293.15	?	Calorimetry. The value given here was calculated from the experimental results of Harries *et al.* [68HAR] together with the value of $\Delta_r H°$ for the ionization of water at $T=298.15$ K calculated from Eq. (9) of Olofsson and Hepler [75OLO/HEP]. Harries [68HAR] did not specify the ionic strength.	68HAR
9.242	13.5	298.15	0	Electrochemical cell with liquid junction. Mesmer and Baes [72MES/BAE] obtained pK values for the reaction $\{B(OH)_3+OH^-=B(OH)_4\}$ at temperatures over the range $323 \leqslant T/K \leqslant 563$. The values given here were calculated from the equation given by Mesmer and Baes [72MES/BAE] in their abstract and by using thermodynamic data from Olofsson and Hepler [75OLO/HEP] [see their Eq. (9b)] for the ionization of water. Mesmer and Baes [72MES/BAE] also give data leading to $\Delta_r C_p^\circ/(J\,K^{-1}\,mol^{-1}) \approx -197$ at $T=298.15$ K.	72MES/BAE
9.088		323.15	0		
8.998		348.15	0		
8.952		373.15	0		
8.938		398.15	0		
8.950		423.15	0		
8.983		448.15	0		
9.041		473.15	0		
9.135		498.15	0		
9.291		523.15	0		
9.550		548.15	0		
9.970		573.15	0		
	16.3	298.15	2.0 M	Calorimetry	73BAR/RED

Values adjusted to $T=298.15$ K and $I=0$

pK	$\Delta_r H°$/(kJ mol^{-1})	$\Delta_r C_p^\circ$/(J K^{-1} mol^{-1})	Reference
9.236	14.0	−200	34OWE2
9.237	13.2	−307	35OWE
9.237	13.4	−301	43OWE/KIN
9.234	14.2	−200	44MAN/DEL
	≈14.3		68HAR
9.242	13.5	−197	72MES/BAE
	≈16.3		73BAR/RED

Comments: We have selected the value pK=9.237 based on the results of Owen *et al.* [34OWE2, 35OWE, 43OWE/KIN]. The differences between this selected value and the results of Manov *et al.* [44MAN/DEL] and of Mesmer and Baes [72MES/BAE], while small, are slightly larger than one would like to see for this fundamental system. We adopt $\Delta_r H°/(kJ\,mol^{-1})=13.8$ based on the work of the above studies excepting the discordant value from Barres *et al.* [73BAR/RED]. The difficulties inherent in obtaining an accurate value of $\Delta_r C_p^\circ$ from the second derivative of pK values determined as a function of temperature are apparent from the above results. We have adopted the value $\Delta_r C_p^\circ/(J\,K^{-1}\,mol^{-1}) \approx -240$. While the apparent molar heat capacity of H_3BO_3 has been determined [95HNE/MAJ], the ion $H_2BO_3^-$ has not been the subject of a similar study. Carefully done calorimetric measurements as a function of temperature would also be useful in firmly establishing the value of $\Delta_r H°$ and of $\Delta_r C_p^\circ$. Additional studies, performed under a variety of conditions, are cited by Martell *et al.* [2001MAR/SMI] and by Pettit and Powell [2000PET/POW].

TABLE 7.16. CABS

Other names	4-(cyclohexylamino)-1-butanesulfonic acid; CAS No. 161308-34-5
Empirical formula	$C_{10}H_{21}NO_3S$
Molecular weight	235.34

Ionization Reaction

$$HL^{\pm}=H^+ + L^-, \text{ where } HL=C_{10}H_{21}NO_3S$$

There do not appear to be any thermodynamic data in the literature for the ionization of CABS.

Structure:

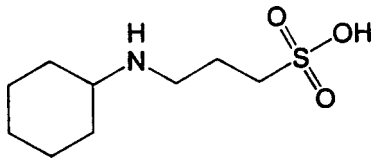


TABLE 7.17. Cacodylate

Other names	cacodylic acid; dimethylarsinic acid; CAS No. 75-60-5
Empirical formula	$C_2H_7AsO_2$
Molecular weight	138.00

Ionization reactions

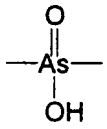
$$H_2L^+ = H^+ + HL \quad (1)$$
$$HL = H^+ + L^- \quad (2)$$
where $HL = C_2H_6AsO_2$

Selected values at T=298.15 K and I=0:

pK=1.78, $\Delta_r G°/(\text{kJ mol}^{-1}) = 10.16$, and $\Delta_r H°/(\text{kJ mol}^{-1}) = -3.5$ for reaction (1)
pK=6.28, $\Delta_r G°/(\text{kJ mol}^{-1}) = 35.85$, $\Delta_r H°/(\text{kJ mol}^{-1}) = -3.0$, and $\Delta_r C_p^\circ/(\text{J K}^{-1}\,\text{mol}^{-1}) = -86$ for reaction (2)

Evaluation: reaction (1), CBB; reaction (2), BBB

Structure:



Values from literature

pK	$\Delta_r H°/(\text{kJ mol}^{-1})$	T/K	I	Methods and comments	Reference
				Reaction (1): $H_2L^+ = H^+ + HL$	
1.78	−3.51	298.15	0	Potentiometric titration—glass electrode; calorimetry. Results were extrapolated to $I = 0$.	76LEW/HAN
				Reaction (2): $HL = H^+ + L^-$	
6.19		298.15	?	Conductivity.	04JOH
6.13		298.15		Kinetic method.	10HOL
6.22		303.15	0	Electrochemical cell with liquid junction—hydrogen and calomel electrodes. The pK values have been extrapolated to $I = 0$.	28MOR
6.17		293.15	0	Kinetic data.	29BRO/WYN
6.273		298.15	0	Colorimetry and electrometric. Values of pK were extrapolated to $I = 0$.	49KIL
6.14	−2.64	298.15	0	Potentiometric titration—glass electrode; calorimetry. We have extrapolated the results to $I = 0$.	76LEW/HAN
6.288		298.15	0	Potentiometric titration—glass electrode.	76WAU
6.06		298.15	1.0 M	Potentiometric titration—glass electrode.	82TAK/YAG
6.24		293.15	0	Mass spectrometry.	83CAP
6.17		298.15	0.012 M	Potentiometric titration of sample (0.01–0.014 M) with 0.1 M HCl or 0.1 M NaOH.	87KIT/ITO
6.015		298.15	0.60 M	Potentiometric titration—glass electrode; NMR.	97KOB/SUG
6.14	−1.96	298.15	0.1 M	Electrochemical cell with liquid junction; calorimetry. Fukada and Takahashi [98FUK/TAK] also obtained $\Delta_r C_p^\circ/(\text{J K}^{-1}\,\text{mol}^{-1}) = -78$ at $I = 0.1$ M from the temperature dependence of $\Delta_r H°$ over the range 278.15–323.15 K.	98FUK/TAK

Values adjusted to $T=298.15$ K and $I=0$

pK	$\Delta_r H°/(\text{kJ mol}^{-1})$	$\Delta_r C_p°/(\text{J K}^{-1}\text{ mol}^{-1})$	Reference
	Reaction (1): $H_2L^+=H^++HL$		
1.78	−3.51		76LEW/HAN
	Reaction (2): $HL=H^++L^-$		
≈6.3			04JOH
≈6.3			10HOL
6.31			28MOR
6.18			29BRO/WYN
6.273			49KIL
6.14	−3.3		76LEW/HAN
6.288			76WAU
≈6.45			82TAK/YAG
6.25			83CAP
6.27			87KIT/ITO
≈6.4			97KOB/SUG
6.35	−2.6	−86	98FUK/TAK

Comments: The selected pK value for reaction (2) encompasses the results of what we believe to be the most reliable of the studies [49KIL, 76WAU]. There is a reasonable agreement of this selected pK value with the other results. We adopt $\Delta_r H°/(\text{kJ mol}^{-1})=-3.0$, the rounded average of the calorimetric results for reaction (2).

TABLE 7.18. CAPS

Other names	3-(cyclohexylamino)-1-propanesulfonic acid; CAS No. 1135-40-6
Empirical formula	$C_9H_{19}NO_3S$
Molecular weight	221.32

Ionization reaction

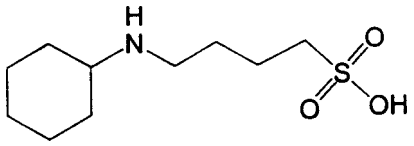
$$HL^{\pm}=H^++L^-, \text{ where } HL=C_9H_{19}NO_3S$$

Selected values at $T=298.15$ K and $I=0$:

$$pK=10.499,\ \Delta_r G°/(\text{kJ mol}^{-1})=59.929,\ \Delta_r H°/(\text{kJ mol}^{-1})=48.1,\text{ and } \Delta_r C_p°/(\text{J K}^{-1}\text{ mol}^{-1})=57$$

Evaluation: AAC

Structure:



Values from literature

pK	$\Delta_r H°/(\text{kJ mol}^{-1})$	T/K	I	Method(s) and comments	Reference
10.35	48.5	298.15	≈0.01 M	Potentiometric titration—glass electrode; and calorimetry. Dilute solutions (0.005–0.01 M) were titrated with 0.1 M NaOH or 0.1 M HCl.	76MCG/JOR
10.60		298.15	?	Potentiometric titration of sample (0.01–0.014 M) with 0.1 M HCl or 0.1 M NaOH.	87KIT/ITO
10.39		298.15	0.10 M	Potentiometric titration—glass electrode.	97ORA/AZA
11.094		278.15	0	Electrochemical cell—no liquid junction. The pK value at $T=278.15$ K in the published paper [97ROY/MOO] contains a typographical error. The value given here is correct [2001ROY]. The value of $\Delta_r H°$ given here was calculated from pKs measured at several temperatures. The value $\Delta_r C_p°/(\text{J K}^{-1}\text{ mol}^{-1})=93$ was also calculated from the temperature dependency of Roy *et al.*'s [97ROY/MOO] reported pKs.	97ROY/MOO
10.940		283.15	0		
10.790		288.15	0		
10.643		293.15	0		
10.499	48.22	298.15	0		
10.359		303.15	0		
10.223		308.15	0		
10.168		310.15	0		
10.087		313.15	0		
9.958		318.15	0		
9.831		323.15	0		

Values from literature—Continued

pK	$\Delta_r H°/(\mathrm{kJ\,mol^{-1}})$	T/K	I	Method(s) and comments	Reference
9.705		328.15	0		
10.39	48.54	298.15	0.1 M	Electrochemical cell with liquid junction; calorimetry. Fukada and Takahashi [98FUK/TAK] also obtained $\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}}) = 29$ at $I = 0.1$ M from the temperature dependence of $\Delta_r H°$ over the range 278.15–323.15 K.	98FUK/TAK

Values adjusted to T=298.15 K and I=0

pK	$\Delta_r H°/(\mathrm{kJ\,mol^{-1}})$	$\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}})$	Reference
10.44	48.2		76MCG/JOR
10.7			87KIT/ITO
10.60			97ORA/AZA
10.499	48.22	93	97ROY/MOO
10.60	47.9	21	98FUK/TAK

Comments: The results of Roy *et al.* [97ROY/MOO] are judged to be the most reliable. There is satisfactory agreement with the calorimetric results of McGlothlin and Jordan [76MCG/JOR] and of Fukada and Takahashi [98FUK/TAK]. However, the values for $\Delta_r C_p^\circ$ are not in agreement. We have adopted the respective averages of the reported $\Delta_r H°$ and $\Delta_r C_p^\circ$ values.

TABLE 7.19. CAPSO

Other names	3-(cyclohexylamino)-2-hydroxyl-1-propanesulfonic acid; 3-(cyclohexylamino)-1-propanesulfonic acid; CAS No. 73463-39-5
Empirical formula	$C_9H_{19}NO_4S$
Molecular weight	237.32

Ionization reaction

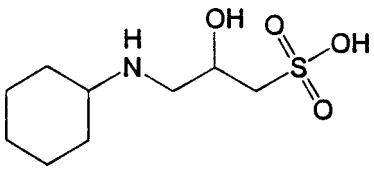
$$HL^{\pm} = H^+ + L^-, \text{ where } HL = C_9H_{19}NO_4S$$

Selected values at T=298.15 K and I=0:

$$pK = 9.825,\ \Delta_r G°/(\mathrm{kJ\,mol^{-1}}) = 56.082,\ \Delta_r H°/(\mathrm{kJ\,mol^{-1}}) = 46.67,\ \text{and}\ \Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}}) = 21$$

Evaluation: AAB

Structure:



Values from literature

pK	$\Delta_r H°/(\mathrm{kJ\,mol^{-1}})$	T/K	I	Method(s) and comments	Reference
9.65		298.15	0.10 M	Electrochemical cell—no liquid junction.	97ORA/AZA
10.4098		278.15	0	Electrochemical cell—no liquid junction. The pK values at T = 293.15 K and T = 298.15 K in the published paper [97ROY/MOO] contain typographical errors. The values given here are correct [2001ROY]. The value of $\Delta_r H°$ given here was calculated from pKs measured at several temperatures. The value $\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}})$ = 21 was also calculated from the temperature dependency of their [97ROY/MOO] reported pKs.	97ROY/MOO
10.2562		283.15	0		
10.1083		288.15	0		
9.964		293.15	0		
9.825	46.67	298.15	0		
9.6903		303.15	0		
9.5592		308.15	0		
9.5080		310.15	0		
9.4309		313.15	0		
9.3083		318.15	0		
9.1882		323.15	0		
9.0736		328.15	0		

Values adjusted to $T=298.15$ K and $I=0$

pK	$\Delta_r H°/(\text{kJ mol}^{-1})$	$\Delta_r C_p°/(\text{J K}^{-1}\text{ mol}^{-1})$	Reference
9.86			97ORA/AZA
9.825	46.67	21	97ROY/MOO

Comments: The results of Roy *et al.* [97ROY/MOO] are based on an electrochemical cell without liquid junction and are judged to be the most reliable.

TABLE 7.20. Carbonate

Other names	carbon dioxide; carbonic acid; bicarbonate; CAS No. 124-38-9 (Note: CAS No. of carbonic acid is 463-79-6)
Empirical formula	CO_2
Molecular weight	44.01

Ionization reactions

$$H_2CO_3 = H^+ + HCO_3^- \quad (1)$$
$$HCO_3^- = H^+ + CO_3^{2-} \quad (2)$$

Selected values at $T=298.15$ K and $I=0$:

p$K=6.351$, $\Delta_r G°/(\text{kJ mol}^{-1})=36.252$, $\Delta_r H°/(\text{kJ mol}^{-1})=9.15$, and $\Delta_r C_p°/(\text{J K}^{-1}\text{ mol}^{-1})=-371$ for reaction (1)
p$K=10.329$, $\Delta_r G°/(\text{kJ mol}^{-1})=58.958$, $\Delta_r H°/(\text{kJ mol}^{-1})=14.70$, and $\Delta_r C_p°/(\text{J K}^{-1}\text{ mol}^{-1})=-249$ for reaction (2)

The values for pK, $\Delta_r G°$, and $\Delta_r H°$ for this ionization reaction are based on the study and review of Berg and Vanderzee [78BER/VAN]. The "CODATA Key Values for Thermodynamics" [89COX/WAG] relies heavily on their [78BER/VAN] results in the calculation of formation properties for the above species. Peiper and Pitzer [82PEI/PIT], in their review, selected the values p$K_1=6.355$ and p$K_2=10.337$. The differences between these and the Berg and Vanderzee [78BER/VAN] values is probably within the experimental uncertainty in the pK values. The values for $\Delta_r C_p°$ are calculated from the standard molar heat capacities of CO_2(aq), HCO_3^-(aq), and CO_3^{2-}(aq) reported by Larson *et al.* [82LAR/ZEE] and by Barbero *et al.* [83BAR/HEP]. Alberty [95ALB, 97ALB] has discussed the thermodynamic treatment of carbon dioxide solutions both in terms of the species present and in terms of total carbon dioxide as a reactant. Many additional studies, performed under a variety of conditions, are cited by Martell *et al.* [2001MAR/SMI] and by Pettit and Powell [2000PET/POW].

Evaluation: reaction (1), AAA; reaction (2), BAA

Structure:

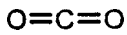


TABLE 7.21. CHES

Other names	2-(cyclohexylamino)ethanesulfonic acid; *N*-cyclohexyltaurine; 2-(*N*-cyclohexylamino)ethanesulfonic acid; CAS No. 103-47-9
Empirical formula	$C_8H_{17}NO_3S$
Molecular weight	207.29

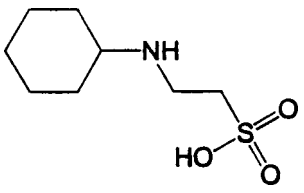
Ionization reaction

$$HL^{\pm} = H^+ + L^-, \text{ where } HL = C_8H_{17}NO_3S$$

Selected values at $T=298.15$ K and $I=0$:

p$K=9.394$, $\Delta_r G°/(\text{kJ mol}^{-1})=53.621$, $\Delta_r H°/(\text{kJ mol}^{-1})=39.55$, and $\Delta_r C_p°/(\text{J K}^{-1}\text{ mol}^{-1})=9$

Evaluation: AAB
Structure:



Values from literature

pK	$\Delta_r H°/(\mathrm{kJ\,mol^{-1}})$	T/K	I	Method(s) and comments	Reference
9.38		298.15	≈0.012 M	Potentiometric titration of sample (0.01–0.014 M) with 0.1 M HCl or 0.1 M NaOH.	87KIT/ITO
9.8897		278.15	0	Electrochemical cell—no liquid junction. Note that the value of $\Delta_r S°$ at $T=298.15$ K given in Table 5 of Roy *et al.* [97ROY/BIC] contains a typographical error [2001ROY]. The value of $\Delta_r H°$ given here was calculated from pKs measured at several temperatures. The value $\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}})=9$ was also calculated from the temperature dependency of the reported [97ROY/BIC] pKs.	97ROY/BIC
9.7597		283.15	0		
9.6342		288.15	0		
9.5132		293.15	0		
9.3944	39.55	298.15	0		
9.2790		303.15	0		
9.1687		308.15	0		
9.1236		310.15	0		
9.0603		313.15	0		
8.9562		318.15	0		
8.8551		323.15	0		
8.7596		328.15	0		

Values adjusted to $T=298.15$ K and $I=0$

pK	$\Delta_r H°/(\mathrm{kJ\,mol^{-1}})$	$\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}})$	Reference
9.48			87KIT/ITO
9.394	39.55	9	97ROY/BIC

Comments: The results of Roy *et al.* [97ROY/BIC] have been selected as the most definitive.

TABLE 7.22. Citrate

Other names	citric acid; 2-hydroxy-1,2,3-propanetricarboxylic acid; β-hydroxytricarballylic acid; 2-hydroxytricarballylic acid; hydroxy-1,2,3-propanetricarboxylic acid; hydroxytricarballylic acid; 2-hydroxypropane-1,2,3-tricarboxylic acid; CAS No. 77-92-9
Empirical formula	$C_6H_8O_7$
Molecular weight	192.13

Ionization reactions

$$H_3L=H^+ + H_2L^- \quad (1)$$
$$H_2L^-=H^+ + HL^{2-} \quad (2)$$
$$HL^{2-}=H^+ + L^{3-} \quad (3)$$

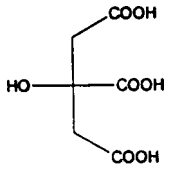
where $H_3L=C_6H_8O_7$

Selected values at $T=298.15$ K and $I=0$:

pK=3.128, $\Delta_r G°/(\mathrm{kJ\,mol^{-1}})=17.855$, $\Delta_r H°/(\mathrm{kJ\,mol^{-1}})=4.07$, and $\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}})=-131$ for reaction (1)
pK=4.761, $\Delta_r G°/(\mathrm{kJ\,mol^{-1}})=27.176$, $\Delta_r H°/(\mathrm{kJ\,mol^{-1}})=2.23$, and $\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}})=-178$ for reaction (2)
pK=6.396, $\Delta_r G°/(\mathrm{kJ\,mol^{-1}})=36.509$, $\Delta_r H°/(\mathrm{kJ\,mol^{-1}})=-3.38$, and $\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}})=-254$ for reaction (3)

Evaluation: reaction (1), AAB; reaction (2), AAB; reaction (3), AAB

Structure:



Values from literature

pK	$\Delta_r H°$/(kJ mol^{-1})	T/K	I	Method(s) and comments	Reference
				Reaction (1): $H_3L=H_2L^-+H^+$	
3.07		291.15	0	Electrochemical cell.	28KOL/BOS
3.08		298.15	0	Potentiometric titration.	28SIM
3.086		291.15	0	Electrochemical cell with liquid junction. The pK values given here, and which pertain to a molality standard state, were calculated from the pK values given by Bjerum and Unmack [29BJE/UNM] and which pertained to the molarity scale. The value of $\Delta_r H°$ given here was calculated from pKs measured at three temperatures.	29BJE/UNM
3.056	4.1	298.15	0		
3.039		310.15	0		
3.200		278.15	0	Electrochemical cell—no liquid junction. The value of $\Delta_r H°$ given here was calculated from pKs measured at several temperatures. The value $\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}}) = -131$ was also calculated from the temperature dependency of their [49BAT/PIN] reported pKs.	49BAT/PIN
3.176		283.15	0		
3.160		288.15	0		
3.142		293.15	0		
3.128	4.17	298.15	0		
3.116		303.15	0		
3.109		308.15	0		
3.099		313.15	0		
3.097		318.15	0		
3.095		323.15	0		
3.08		298.15	0	Potentiometric titration.	51HEI
3.124	3.97	298.15	0	Potentiometric titration—glass electrode; calorimetry.	80ARE/CAL
3.098		310.15	0		
3.132		298.15	0	Potentiometric titration—glass electrode.	90DAN/DER
3.191		283.15	0	Potentiometric titration—glass electrode. The value of $\Delta_r H°$ given here was calculated from pKs measured at several temperatures. The value $\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}}) \approx -178$ was also calculated from the temperature dependency of their [90DER/DES] reported pKs.	90DER/DES
3.145		293.15	0		
3.128	5.40	298.15	0		
3.114		303.15	0		
3.094		313.15	0		
3.084		323.15	0		
3.232		273.15	0	Electrochemical cell with liquid junction. The value of $\Delta_r H°$ given here was calculated from pKs measured at several temperatures. The value $\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}}) = -162$ was also calculated from the temperature dependency of their [97BEN/PAL] reported pKs.	97BEN/PAL
3.127	4.06	298.15	0		
3.095		323.15	0		
3.103		348.15	0		
3.135		373.15	0		
3.186		398.15	0		
3.255		423.15	0		
3.456		473.15	0		
				Reaction (2): $H_2L=HL^{2-}+H^+$	
4.75		291.15	0	Electrochemical cell.	28KOL/BOS
4.74		298.15	0	Potentiometric titration.	28SIM
4.768		291.15	0	Electrochemical cell with liquid junction. The pK values given here, and which pertain to a molality standard state, were calculated from the pK values given by Bjerum and Unmack [29BJE/UNM] and which pertained to the molarity scale. The value of $\Delta_r H°$ given here was calculated from pKs measured at three temperatures.	29BJE/UNM
4.758	2.2	298.15	0		
4.744		310.15	0		
4.837		273.15	0	Electrochemical cell—no liquid junction. The value of $\Delta_r H°$ given here was calculated from pKs measured at several temperatures. The value $\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}}) = -178$ was also calculated from the temperature dependency of their [49BAT/PIN] reported pKs.	49BAT/PIN
4.813		278.15	0		
4.797		283.15	0		
4.782		288.15	0		
4.769		293.15	0		
4.761	2.45	298.15	0		
4.755		303.15	0		
4.751		308.15	0		
4.750		313.15	0		
4.754		318.15	0		
4.757		323.15	0		
4.66		298.15	0	Potentiometric titration.	51HEI
4.769	2.01	298.15	0	Potentiometric titration—glass electrode; calorimetry.	80ARE/CAL
4.758		310.15	0		
4.751		298.15	0	Potentiometric titration—glass electrode.	90DAN/DER
4.823		283.15	0	Potentiometric titration—glass electrode. The value of $\Delta_r H°$ given here was calculated from pKs measured at several temperatures. The value $\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}}) \approx -150$ was also calculated from the temperature dependency of their [90DER/DES] reported pKs.	90DER/DES
4.789		293.15	0		
4.777	3.85	298.15	0		
4.766		303.15	0		
4.754		313.15	0		
4.749		323.15	0		

Values from literature—Continued

pK	$\Delta_r H°/(\mathrm{kJ\,mol^{-1}})$	T/K	I	Method(s) and comments	Reference
4.841		273.15	0	Electrochemical cell with liquid junction. The value of $\Delta_r H°$ given	97BEN/PAL
4.759	2.19	298.15	0	here was calculated from pKs measured at several temperatures. The	
4.758		323.15	0	value $\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}}) = -192$ was also calculated from the	
4.801		348.15	0	temperature dependency of their [97BEN/PAL] reported pKs.	
4.871		373.15	0		
4.962		398.15	0		
5.072		423.15	0		
5.357		473.15	0		
				Reaction (3): $HL^- = L^{3-} + H^+$	
6.41		291.15	0	Electrochemical cell.	28KOL/BOS
6.26		298.15	0	Potentiometric titration.	28SIM
6.397		291.15	0	Electrochemical cell with liquid junction. The pK values given here,	29BJE/UNM
6.399	−2.5	298.15	0	and which pertain to a molality standard state, were calculated from	
6.421		310.15	0	the pK values given by Bjerum and Unmack [29BJE/UNM] and which pertained to the molarity scale. The value of $\Delta_r H°$ given here was calculated from pKs measured at three temperatures.	
6.393		273.15	0	Electrochemical cell—no liquid junction. The value of $\Delta_r H°$ given	49BAT/PIN
6.386		278.15	0	here was calculated from pKs measured at several temperatures. The	
6.383		283.15	0	value $\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}}) = -254$ was also calculated from the	
6.384		288.15	0	temperature dependency of their [49BAT/PIN] reported pKs.	
6.388		293.15	0		
6.396	−3.40	298.15	0		
6.406		303.15	0		
6.423		308.15	0		
6.439		313.15	0		
6.462		318.15	0		
6.484		323.15	0		
6.38		298.15	0	Potentiometric titration.	51HEI
6.419	−3.35	298.15	0	Potentiometric titration—glass electrode; calorimetry.	80ARE/CAL
6.445		310.15	0		
6.418		298.15	0	Potentiometric titration—glass electrode.	90DAN/DER
6.411		283.15	0	Potentiometric titration—glass electrode. The value of $\Delta_r H°$ given	90DER/DES
6.408		293.15	0	here was calculated from pKs measured at several temperatures. The	
6.411	−1.75	298.15	0	value $\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}}) \approx -225$ was also calculated from the	
6.418		303.15	0	temperature dependency of their [90DER/DES] reported pKs.	
6.440		313.15	0		
6.472		323.15	0		
6.394		273.15	0	Electrochemical cell with liquid junction. The value of $\Delta_r H°$ given	97BEN/PAL
6.397	−3.58	298.15	0	here was calculated from pKs measured at several temperatures. The	
6.481		323.15	0	value $\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}}) = -231$ was also calculated from the	
6.607		348.15	0	temperature dependency of their [97BEN/PAL] reported pKs.	
6.759		373.15	0		
6.931		398.15	0		
7.120		423.15	0		
7.556		473.15	0		

Values adjusted to $T = 298.15$ K and $I = 0$

pK	$\Delta_r H°/(\mathrm{kJ\,mol^{-1}})$	$\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}})$	Reference
		Reaction (1): $H_3L = H_2L^- + H^+$	
3.05			28KOL/BOS
3.08			28SIM
3.056	4.1		29BJE/UNM
3.128	4.17	−131	49BAT/PIN
3.08			51HEI
3.12	3.97		80ARE/CAL
3.132			90DAN/DER
3.128	5.40	−178	90DER/DES
3.127	4.06	−162	97BEN/PAL
		Reaction (2): $H_2L = HL^{2-} + H^+$	
4.74			28KOL/BOS
4.74			28SIM
4.758	2.2		29BJE/UNM

Values adjusted to $T=298.15$ K and $I=0$—Continued

pK	$\Delta_r H°/(\text{kJ mol}^{-1})$	$\Delta_r C_p^\circ/(\text{J K}^{-1}\text{ mol}^{-1})$	Reference
4.761	2.45	−178	49BAT/PIN
4.66			51HEI
4.77	2.01		80ARE/CAL
4.751			90DAN/DER
4.777	3.85	−150	90DER/DES
4.759	2.19	−192	97BEN/PAL
	Reaction (3): $HL^- = L^{3-} + H^+$		
6.42			28KOL/BOS
6.26			28SIM
6.399	−2.5		29BJE/UNM
6.396	−3.40	−254	49BAT/PIN
6.38			51HEI
6.42	−3.35		80ARE/CAL
6.418			90DAN/DER
6.412	−1.75	−225	90DER/DES
6.397	−3.58	−231	97BEN/PAL

Comments: The careful investigation of Bates and Pinching [49BAT/PIN] was performed using an electrochemical cell without liquid junction and is judged to be the most carefully done study. It is in agreement with most of the other studies where pK values were adjusted to $I=0$. The values of $\Delta_r H°$ determined in the calorimetric study of Arena *et al.* [80ARE/CAL] are in good agreement with the results obtained from the temperature dependance of the pK values determined by Bates and Pinching [49BAT/PIN]. We have adopted the average of the $\Delta_r H°$ values from these two studies [49BAT/PIN, 80ARE/CAL]. Direct heat capacity measurements would be useful. Many additional studies, performed under a variety of conditions, are cited by Martell *et al.* [2001MAR/SMI] and by Pettit and Powell [2000PET/POW].

TABLE 7.23. L-Cysteine

Other names	(*S*)-(−)-cysteine; L-*β*-mercaptoalanine; Cys; C; cysteine; 2-amino-3-mercaptopropanoic acid; CySH; (+)-2-amino-3-mercaptopropionic acid; L-(+)-cysteine; 3-mercapto-L-alanine; thioserine; (*R*)-2-amino-3-mercaptopropanoic acid; (*R*)-2-amino-3-mercaptopropanoic acid; Half-cystine; CAS No. 52-90-4
Empirical formula	$C_3H_7NO_2S$
Molecular weight	121.16

Ionization reactions

$$H_3L^+ = H^+ + H_2L \quad (1)$$
$$H_2L = H^+ + HL^- \quad (2)$$
$$HL^- = H^+ + L^{2-} \quad (3)$$

where $H_2L = C_3H_7NO_2S$

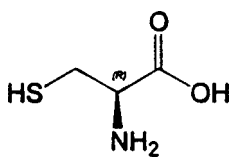
Selected values at $T=298.15$ K and $I=0$:

p$K=1.71$, $\Delta_r G°/(\text{kJ mol}^{-1}) = 9.76$, and $\Delta_r H°/(\text{kJ mol}^{-1}) \approx -0.6$ for reaction (1)

p$K=8.36$, $\Delta_r G°/(\text{kJ mol}^{-1}) = 47.72$, $\Delta_r H°/(\text{kJ mol}^{-1}) = 36.1$, and $\Delta_r C_p^\circ/(\text{J K}^{-1}\text{ mol}^{-1}) \approx -66$ for reaction (2)
p$K=10.75$, $\Delta_r G°/(\text{kJ mol}^{-1}) = 61.36$, $\Delta_r H°/(\text{kJ mol}^{-1}) = 34.1$, and $\Delta_r C_p^\circ/(\text{J K}^{-1}\text{ mol}^{-1}) \approx -204$ for reaction (3)

Evaluation: reaction (1), CD; reaction (2), BBD; reaction (3), BBD

Structure:



Values from literature

pK	$\Delta_r H°$/(kJ mol^{-1})	T/K	I	Method(s) and comments	Reference
			Reaction (1): $H_3L^+ = H_2L + H^+$		
1.71		298.15	0	Potentiometric titration—glass electrode.	37BOR/ELL
2.44	0.3	298.15	3.0 M	Potentiometric titration—glass electrode; calorimetry. The first set of pK and $\Delta_r H°$ values is based on calorimetry; the second set is based on the potentiometric titration data. The same values are also given in a subsequent publication [76COR/WIL].	72GRA/WIL
2.4	−1.4	298.15	3.0 M		
			Reaction (2): $H_2L = HL^- + H^+$		
8.33		298.15	0	Potentiometric titration—glass electrode.	37BOR/ELL
8.53		293.15	≈0.01 M	Potentiometric titration—glass electrode.	53PER
8.39	36.1	298.15	0	Potentiometric titration—glass electrode; calorimetry.	64WRA/IZA
8.15	28.9	303.15	0.1 M	Potentiometric titration—glass electrode.	66WAL/STR
8.84		278.15	0	Potentiometric titration—glass electrode. The value of $\Delta_r H°$ given here was calculated from pKs measured at several temperatures. The value $\Delta_r C_p^\circ$/(J K^{-1} mol^{-1}) ≈ −66 was also calculated from the temperature dependency of their [69COA/MAR] reported pKs.	69COA/MAR
8.58		288.15	0		
8.37	35.3	298.15	0		
8.17		308.15	0		
7.98		318.15	0		
7.85		328.15	0		
7.69		338.15	0		
7.52		348.15	0		
7.38		358.15	0		
7.28		368.15	0		
	32.3	?	?	Calorimetry.	71MAR/BER
8.78	38.8	298.15	3.0 M	Potentiometric titration; calorimetry. The same values were also given in a subsequent publication [76COR/WIL].	72GRA/WIL
			Reaction (3): $HL^- = L^{2-} + H^+$		
10.78		298.15	0	Potentiometric titration—glass electrode.	37BOR/ELL
10.53		293.15	≈0.01 M	Potentiometric titration—glass electrode.	53PER
10.76	34.1	298.15	0	Potentiometric titration—glass electrode; calorimetry.	64WRA/IZA
10.47	22.6	303.15	0.1 M	Potentiometric titration—glass electrode.	66WAL/STR
11.20		278.15	0	Potentiometric titration—glass electrode. The value of $\Delta_r H°$ given here was calculated from pKs measured at several temperatures. The value $\Delta_r C_p^\circ$/(J K^{-1} mol^{-1}) = −204 was also calculated from the temperature dependency of their [69COA/MAR] reported pKs.	69COA/MAR
10.89		288.15	0		
10.70	34.9	298.15	0		
10.50		308.15	0		
10.34		318.15	0		
10.23		328.15	0		
10.08		338.15	0		
9.93		348.15	0		
9.85		358.15	0		
9.76		368.15	0		
	35.9	?	?	Calorimetry.	71MAR/BER
10.71	40.4	298.15	3.0 M	Potentiometric; calorimetry. The same values were also given in a subsequent publication [76COR/WIL].	72GRA/WIL

Values adjusted to T=298.15 K and I=0

pK	$\Delta_r H°$/(kJ mol^{-1})	$\Delta_r C_p^\circ$/(J K^{-1} mol^{-1})	Reference
	Reaction (1): $H_3L^+ = H_2L + H^+$		
1.71			37BOR/ELL
≈2.4	≈−0.6		72GRA/WIL
	Reaction (2): $H_2L = HL^- + H^+$		
8.33			37BOR/ELL
8.51			53PER
8.39	36.1		64WRA/IZA
8.47	28.6		66WAL/STR
8.37	35.3	≈−66	69COA/MAR
	≈32.3		71MAR/BER
	≈37.4		72GRA/WIL

Values adjusted to $T=298.15$ K and $I=0$—Continued

pK	$\Delta_r H°/(\text{kJ mol}^{-1})$	$\Delta_r C_p^\circ/(\text{J K}^{-1}\text{ mol}^{-1})$	Reference
	Reaction (3): $HL^- = L^{2-} + H^+$		
10.78			37BOR/ELL
10.60			53PER
10.76	34.1		64WRA/IZA
11.00	22.3		66WAL/STR
10.70	34.9	≈−204	69COA/MAR
	≈35.9		71MAR/BER
	≈37.7		72GRA/WIL

Comments: For reaction (1), we adopt pK≈1.71 based on the result of Borsook *et al.* [37BOR/ELL]; for reactions (2) and (3), we adopt the respective averages of the results of the investigations of Borsook *et al.* [37BOR/ELL], Wrathall *et al.* [64WRA/IZA], and Coates *et al.* [69COA/MAR]. We prefer the values of $\Delta_r H°$ for reactions (2) and (3) that are based on the calorimetric results of Wrathall *et al.* [64WRA/IZA]. These values are probably in agreement with the values of $\Delta_r H°$ obtained from the temperature dependence of the pKs reported by Coates *et al.* [69COA/MAR]. Coates *et al.* [69COA/MAR] have pointed out how problems with the L-cysteine purity and hence its concentration can lead to errors of ≈0.04 in the pK values. Also, L-cysteine is light sensitive. Considering these problems, the agreement in the pK values appears reasonable. The selected values are very close to the values recommended by Berthon [95BER], excepting that Berthon does not give a value for $\Delta_r H°$ for reaction (1). Many additional studies, performed under a variety of conditions, are cited by Berthon [95BER], Martell *et al.* [2001MAR/SMI], and by Pettit and Powell [2000PET/POW].

TABLE 7.24. Diethanolamine

Other names	2,2′-iminobisethanol; bis(2-hydroxyethyl)amine; 2,2′-iminodiethanol; 2,2′-dihydroxydiethylamine ; 2,2′-dihydroxydiethylamine; diolamine; CAS No. 111-42-2
Empirical formula	$C_4H_{11}NO_2$
Molecular weight	105.14

Ionization reaction

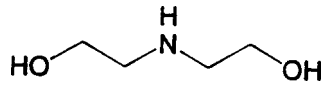
$$HL^+ = H^+ + L, \text{ where } L = C_4H_{11}NO_2$$

Selected values at $T=298.15$ K and $I=0$:

$$pK = 8.883,\ \Delta_r G°/(\text{kJ mol}^{-1}) = 50.705,\ \Delta_r H°/(\text{kJ mol}^{-1}) = 42.08,\ \text{and}\ \Delta_r C_p^\circ/(\text{J K}^{-1}\text{ mol}^{-1}) = 36$$

Evaluation: AAA

Structure:



Values from literature

pK	$\Delta_r H°/(\text{kJ mol}^{-1})$	T/K	I	Method(s) and comments	Reference
8.88		298.15	?	Electrochemical cell with a liquid junction.	32HAL/SPR
9.00		298.15	0.4	Unpublished results of Bjerrum and Refn.	50BJE
9.00		298.15	0.50 M	Potentiometric titration—glass electrode.	56BJE/REF
8.96	30.9	298.15	0	Glass electrode. The values of pK and $\Delta_r H°$ given here were calculated from Chremos and Zimmerman's [59CHR/ZIM] equation (45).	59CHR/ZIM
9.550		273.15	0	Electrochemical cell—no liquid junction. The value of $\Delta_r H°$ given here was calculated from pKs measured at several temperatures. The value $\Delta_r C_p^\circ/(\text{J K}^{-1}\text{ mol}^{-1}) = 51$ was also calculated from the temperature dependency of the reported [62BOW/ROB] pKs.	62BOW/ROB
9.404		278.15	0		
9.268		283.15	0		
9.133		288.15	0		
9.005		293.15	0		
8.883	42.40	298.15	0		
8.759		303.15	0		
8.632		308.15	0		
8.518		313.15	0		
8.406		318.15	0		
8.297		323.15	0		

Values from literature—Continued

pK	$\Delta_r H°$/(kJ mol^{-1})	T/K	I	Method(s) and comments	Reference
8.955		303.15	0.5 M	Polarography.	62FIS/HAL
9.12		298.15	?	Potentiometric titration—glass electrode.	65DOU
9.09		298.15	0.43 M	Potentiometric titration—glass electrode.	66SKL/KAR
8.95		303.15	0.5 M	Polarography.	67FIS/HAL
	44.89	?	?	Calorimetry.	67POP/ROM
8.90		293.15	?	Potentiometric titration—glass electrode.	68DAV/PAT
8.88	41.88	298.15	0	Calorimetry.	69CHR/IZA
8.93		303.15	3.0 M	Polarography; glass electrode.	71SRI/SUB
9.15		298.15	0.5 M	Potentiometric titration—glass electrode.	72VAN/EEC
9.27		293	1.00 M	Potentiometric titration—glass electrode.	81BLA/BOS
9.02		303	1.00 M		
8.78		313	1.00 M		
8.54		323	1.00 M		
8.93		298.15	0.50 M	Potentiometric titration—glass electrode; Spectrophotometry.	83DJU/BJE
9.07		298.15	1.0 M	Potentiometric titration—glass electrode.	86CAS/TAU
8.87		298.15	0.1 M	Coulometric titration.	87GLA/SKR
	41.93	298.15	0	Calorimetry.	87KIM/DOB
8.88		298.15	0	Potentiometric titration—glass electrode; calorimetry. The value $\Delta_r C_p^\circ$/(J K^{-1} mol^{-1}) = 36 was calculated from the temperature dependency of the reported [89OSC/WU] enthalpies. The calorimetric measurements were carried out over the temperature range 299.9–422.1 K.	89OSC/WU
	42.1	299.9	0		
9.072		298.15	0.60 M	Potentiometric titration—glass electrode.	91CRA/EHD

Values adjusted to T=298.15 K and I=0

pK	$\Delta_r H°$/(kJ mol^{-1})	$\Delta_r C_p^\circ$/(J K^{-1} mol^{-1})	Reference
8.88			32HAL/SPR
9.00			50BJE
9.00			56BJE/REF
8.96	30.9		59CHR/ZIM
8.883	42.40	51	62BOW/ROB
9.08			62FIS/HAL
9.12			65DOU
9.09			66SKL/KAR
8.95			67FIS/HAL
	44.89		67POP/ROM
8.77			68DAV/PAT
8.88	41.88		69CHR/IZA
≈9.0			71SRI/SUB
9.15			72VAN/EEC
9.13			81BLA/BOS
9.07			83DJU/BJE
9.08			86CAS/TAU
	41.93		87KIM/DOB
8.88	42.1	36	89OSC/WU
9.07			91CRA/EHD

Comments: The pK values determined by Bower *et al.* [62BOW/ROB] are judged to be the most reliable. Also, their [62BOW/ROB] result at T = 298.15 K is in excellent agreement with the results of two other very careful studies [69CHR/IZA, 89OSC/WU]. An average value $\Delta_r H°$/(kJ mol^{-1}) = 42.08 of what we judge to be the most careful studies [62BOW/ROB, 69CHR/IZA, 87KIM/DOB, 89OSC/WU] has been adopted. The value $\Delta_r C_p^\circ$/(J K^{-1} mol^{-1}) = 36 based on the calorimetric results of Oscarson *et al.* [89OSC/WU] is judged to be the most accurate. Approximate values for the subsequent ionization (pK≈15.7) of diethanolamine in extremely alkaline solution have also been reported [55SCH, 62DOU/PAR].

TABLE 7.25. Diglycolate

Other names	2,2′-oxydiacetic acid; diglycolic acid; 2,2′-oxybisacetic acid; diglycollic acid; 3-oxapentanedioic acid; 2,2′-oxydiethanoic acid; CAS No. 110-99-6
Empirical formula	$C_4H_6O_5$
Molecular weight	134.09

Ionization reactions

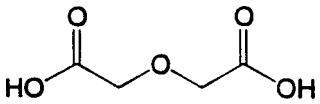
$$H_2L = H^+ + HL^- \quad (1)$$
$$HL^- = H^+ + L^{2-} \quad (2)$$
where $H_2L = C_4H_6O_5$

Selected values at $T = 298.15$ K and $I = 0$:

pK=3.05, $\Delta_r G°/(\text{kJ mol}^{-1}) = 17.41$, $\Delta_r H°/(\text{kJ mol}^{-1}) = -0.1$, and $\Delta_r C_p^\circ/(\text{J K}^{-1}\,\text{mol}^{-1}) \approx -142$ for reaction (1)
pK=4.37, $\Delta_r G°/(\text{kJ mol}^{-1}) = 24.94$, $\Delta_r H°/(\text{kJ mol}^{-1}) = -7.2$, and $\Delta_r C_p^\circ/(\text{J K}^{-1}\,\text{mol}^{-1}) \approx -138$ for reaction (2)

Evaluation: reaction (1), BCD; reaction (2), BCD

Structure:



Values from literature

pK	$\Delta_r H°/(\text{kJ mol}^{-1})$	T/K	I	Method(s) and comments	Reference
				Reaction (1): $H_2L = H^+ + HL^-$	
2.90		303.15	0.1 M	Glass electrode; spectrophotometry.	57TIC/BEN
2.77		298.15	0.1 M	Glass electrode.	60YAS/YAM
3.06		293.15	0.1 M	Potentiometric titration—glass electrode.	61CAM/OST
2.80		293.15	1.0 M	Potentiometric titration—quinhydrone electrode.	63GRE/TOB
2.69	1.6	298.15	1.0 M	Potentiometric titration; calorimetry.	69GRE/HAN
2.91		298.15	2.0 M	Glass electrode; Spectrophotometry.	72APL/NOI
2.83		278.15	1.0 M	Potentiometric titration—quinhydrone electrode. The value of $\Delta_r H°$	72GRE/OTS
2.83		293.15	1.0 M	is calculated from the temperature dependence of the pKs.	
	≈0.66	298.15	1.0 M		
2.81		303.15	1.0 M		
2.81		323.15	1.0 M		
2.85		338.15	1.0 M		
	4.13	278.15	1.0 M	Calorimetry. The value $\Delta_r C_p^\circ/(\text{J K}^{-1}\,\text{mol}^{-1}) = -142$ is calculated	72GRE/OTS2
	1.76	293.15	1.0 M	from the temperature dependence of the $\Delta_r H°$ values.	
	0.11	308.15	1.0 M		
	−2.40	323.15	1.0 M		
2.80		298.15	0.5 M	Potentiometric titration—glass electrode.	72NAP
2.82		293.15	1.0 M	Potentiometric titration—glass electrode.	73CAS/DIB
2.73		298.15	0.1 M	Potentiometric titration—glass electrode.	74MIY/SHI
2.78		298.15	0.1 M	Potentiometric titration—glass electrode.	75FIE/COB
2.83		298.15	0.1 M	Potentiometric titration—glass electrode.	78ARE/MUS
2.81		298.15	0.1 M	Potentiometric titration—glass electrode.	79HOG/NIL
2.67		298.15	0.1 M	Potentiometric titration—glass electrode.	79SIN/DUB
2.88		308.15	0.1 M		
2.96		318.15	0.1 M		
3.05	−0.84	298.15	0	Potentiometric titration—glass electrode; calorimetry.	80CAL/RIZ
2.80		298.15	0.5 M	Potentiometric titration—glass electrode.	81NAP/PAO
2.73		298.15	0	Potentiometric titration—glass electrode.	83DUB/BEW
2.82		298.15	0.1 M	Potentiometric titration—glass electrode.	84MOT/MAR2
3.06		298.15	0	Potentiometric titration—glass electrode.	85CAP/DER
2.97	≈4	298.15	0	Potentiometric titration—glass electrode.	85DAN/DER
3.07		283.15	0	Potentiometric titration—glass electrode. The value of $\Delta_r H°$ given	90DER/DES
3.05		293.15	0	here was calculated from pKs measured at several temperatures. The	
3.05	1.2	298.15	0	value $\Delta_r C_p^\circ/(\text{J K}^{-1}\,\text{mol}^{-1}) \approx -182$ was also calculated from the	
3.04		303.15	0	temperature dependency of their [90DER/DES] reported pKs.	
3.05		313.15	0		
3.06		323.15	0		

Values from literature—Continued

pK	$\Delta_r H°/(\mathrm{kJ\,mol^{-1}})$	T/K	I	Method(s) and comments	Reference
			Reaction (2): $HL^- = H^+ + L^{2-}$		
4.03		303.15	0.1 M	Glass electrode; spectrophotometry.	57TIC/BEN
3.92		298.15	0.1 M	Glass electrode.	60YAS/YAM
4.11		293.15	0.1 M	Potentiometric titration—glass electrode.	61CAM/OST
3.74		293.15	1.0 M	Potentiometric titration—quinhydrone electrode.	63GRE/TOB
3.76	0.4	298.15	1.0 M	Potentiometric; calorimetry.	69GRE/HAN
3.97		298.15	2.0 M	Glass electrode; Spectrophotometry.	72APL/NOI
3.73		278.15	1.0 M	Potentiometric titration—quinhydrone electrode. The value of $\Delta_r H°$ is calculated from the temperature dependence of the pKs.	72GRE/OTS
3.75		293.15	1.0 M		
	−3.8	298.15	1.0 M		
3.78		303.15	1.0 M		
3.83		323.15	1.0 M		
3.89		338.15	1.0 M		
	−0.60	278.15	1.0 M	Calorimetry. The value $\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}}) = -138$ is calculated from the temperature dependence of the $\Delta_r H°$ values.	72GRE/OTS2
	−2.69	293.15	1.0 M		
	−4.56	308.15	1.0 M		
	−6.87	323.15	1.0 M		
3.76		298.15	0.5 M	Potentiometric titration—glass electrode.	72NAP
3.75		293.15	1.0 M	Potentiometric titration—glass electrode.	73CAS/DIB
3.92		298.15	0.1 M	Potentiometric titration—glass electrode.	74MIY/SHI
3.95		298.15	0.1 M	Potentiometric titration—glass electrode.	75FIE/COB
3.89		298.15	0.1 M	Potentiometric titration—glass electrode.	78ARE/MUS
3.94		298.15	0.1 M	Potentiometric titration—glass electrode.	79HOG/NIL
4.00		298.15	0.1 M	Potentiometric titration—glass electrode.	79SIN/DUB
4.12		308.15	0.1 M		
4.26		318.15	0.1 M		
4.37	−7.8	298.15	0	Potentiometric titration—glass electrode; calorimetry.	80CAL/RIZ
3.76		298.15	0.5 M	Potentiometric titration—glass electrode.	81NAP/PAO
4.15		298.15	0	Potentiometric titration—glass electrode.	83DUB/BEW
3.94		298.15	0.1 M	Potentiometric titration—glass electrode.	84MOT/MAR2
4.37		298.15	0	Potentiometric titration—glass electrode; calorimetry.	85CAP/DER
4.36	≈−11	298.15	0	Potentiometric titration—glass electrode.	85DAN/DER
4.283		283.15	0	Potentiometric titration—glass electrode. The value of $\Delta_r H°$ given here was calculated from pKs measured at several temperatures. The value $\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}}) \approx -97$ was also calculated from the temperature dependency of the reported pKs of De Robertis *et al.* [90DER/DES].	90DER/DES
4.335		293.15	0		
4.362	−9.3	298.15	0		
4.390		303.15	0		
4.446		313.15	0		
4.504		323.15	0		

Values adjusted to T=298.15 K and I=0

pK	$\Delta_r H°/(\mathrm{kJ\,mol^{-1}})$	$\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}})$	Reference
	Reaction (1): $H_2L = H^+ + HL^-$		
3.11			57TIC/BEN
2.98			60YAS/YAM
3.27			61CAM/OST
3.19			63GRE/TOB
3.08	0.5		69GRE/HAN
3.35			72APL/NOI
3.22	−1.2		72GRE/OTS
	0.0	−142	72GRE/OTS2
3.14			72NAP
3.21			73CAS/DIB
2.94			74MIY/SHI
2.99			75FIE/COB
3.04			78ARE/MUS
3.02			79HOG/NIL
2.88			79SIN/DUB

Values adjusted to $T=298.15$ K and $I=0$—Continued

pK	$\Delta_r H°/(\mathrm{kJ\ mol^{-1}})$	$\Delta_r C_p^\circ/(\mathrm{J\ K^{-1}\ mol^{-1}})$	Reference
3.05	−0.84		80CAL/RIZ
3.14			81NAP/PAO
2.73			83DUB/BEW
3.03			84MOT/MAR2
3.06			85CAP/DER
2.97	≈4		85DAN/DER
3.05	1.2	≈−182	90DER/DES
	Reaction (2): $HL^- = H^+ + L^{2-}$		
4.45			57TIC/BEN
4.35			60YAS/YAM
4.55			61CAM/OST
4.54			63GRE/TOB
4.55	−1.9		69GRE/HAN
4.86			72APL/NOI
4.55	−6.1		72GRE/OTS
	−5.5	−138	72GRE/OTS2
4.44			72NAP
4.55			73CAS/DIB
4.35			74MIY/SHI
4.38			75FIE/COB
4.32			78ARE/MUS
4.37			79HOG/NIL
4.43			79SIN/DUB
4.37	−7.8		80CAL/RIZ
4.44			81NAP/PAO
4.15			83DUB/BEW
4.37			84MOT/MAR2
4.37			85CAP/DER
4.36	≈−11		85DAN/DER
4.36	−9.3	≈−97	90DER/DES

Comments: We adopt the values $pK_1 = 3.05$ and $pK_2 = 4.37$ based on the results of three careful studies [80CAL/RIZ, 85CAP/DER, 90DER/DES] where the pKs were adjusted to $I = 0$. The average of all studies leads to $pK_1 = 3.07$ and $pK_2 = 4.43$. For reaction (1), we adopt the average of all of the $\Delta_r H°$ values excepting the approximate result of Daniele *et al.* [85DAN/DER]. For reaction (2), we adopt the average of all of the $\Delta_r H°$ values excepting the approximate result of Daniele *et al.* [85DAN/DER] and the somewhat discordant result of Grenthe and Hansson [69GRE/HAN]. The values of $\Delta_r C_p^\circ$ are based on the results of Grenthe and Ots [72GRE/OTS2].

TABLE 7.26. 3,3-Dimethylglutarate

Other names	3,3-dimethylglutaric acid; β,β-dimethylglutaric acid; 3,3-dimethylpentanedioic acid; 2,2-dimethylpropane-1,3-dicarboxylic acid; CAS No. 4839-46-7
Empirical formula	$C_7H_{12}O_4$
Molecular weight	160.17

Ionization reactions

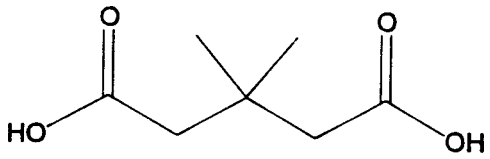
$$H_2L = H^+ + HL^- \quad (1)$$
$$HL^- = H^+ + L^{2-} \quad (2)$$
where $H_2L = C_7H_{12}O_4$

Selected values at T=298.15 K and I=0:

pK=3.70 and $\Delta_r G°/(\text{kJ mol}^{-1})$=21.12 for reaction (1)
pK=6.34 and $\Delta_r G°/(\text{kJ mol}^{-1})$=36.19 for reaction (2)

Evaluation: reaction (1), B; reaction (2), B

Structure:



Values from literature

pK	T/K	I	Method(s) and comments	Reference
			Reaction (1): $H_2L = H^+ + HL^-$	
3.70	298.15	0	Potentiometric.	31GAN/ING
3.70	298.15	0	Electrochemical cell—no liquid junction.	36JON/SOP
4.89	323.15	0		
4.03	347.15	0		
3.75	298.15	≈0.012 M	titration of 0.01–0.014 M sample with 0.1 M HCl or NaOH	87KIT/ITO
			Reaction (2): $HL^- = H^+ + L^{2-}$	
6.29	298.15	0	Potentiometric.	31GAN/ING
6.34	298.15	0	Electrochemical cell—no liquid junction.	36JON/SOP
6.49	323.15	0		
6.60	347.15	0		
6.35	298.15	≈0.012 M	titration of 0.01–0.014 M sample with 0.1 M HCl or NaOH	87KIT/ITO

Values adjusted to T=298.15 K and I=0

pK	Reference
Reaction (1): $H_2L = H^+ + HL^-$	
3.70	31GAN/ING
3.70	36JON/SOP
3.85	87KIT/ITO
Reaction (2): $HL^- = H^+ + L^{2-}$	
6.29	31GAN/ING
6.34	36JON/SOP
6.54	87KIT/ITO

Comments: The results of Jones and Soper [36JON/SOP] are judged to be the most reliable. They are in reasonable accord with the results of the other two studies in the literature.

TABLE 7.27. DIPSO

Other names	3-[*N*,*N*-bis(2-hydroxyethyl)amino]-2-hydroxypropanesulfonic acid; 3-[bis(2-hydroxyethyl)amino]-2-hydroxy-1-propanesulfonic acid; 2,3-[*N*-bis(hydroxyethyl)amino]-2-hydroxypropanesulfonic acid; CAS No. 68399-80-4
Empirical formula	$C_7H_{17}NO_6S$
Molecular weight	243.28

Ionization reaction

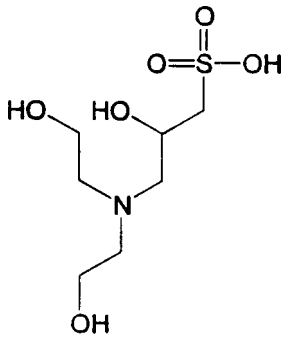
$$HL^{\pm} = H^+ + L^-, \text{ where } HL = C_7H_{17}NO_6S$$

Selected values at $T=298.15$ K and $I=0$:

$$pK = 7.576,\ \Delta_r G°/(\text{kJ mol}^{-1}) = 43.244,\ \Delta_r H°/(\text{kJ mol}^{-1}) = 30.18,\ \text{and}\ \Delta_r C_p^\circ/(\text{J K}^{-1}\,\text{mol}^{-1}) = 42$$

Evaluation: AAB

Structure:



Values from literature

p*K*	$\Delta_r H°/(\text{kJ mol}^{-1})$	*T*/K	I	Method(s) and comments	Reference
7.6		293.15	?	Few details are given.	80FER/BRA
7.57		298.15	≈0.012 M	Potentiometric titration of sample (0.01–0.014 M) with 0.1 M HCl or 0.1 M NaOH.	87KIT/ITO
7.951		278.15	0	Electrochemical cell—no liquid junction. The value of $\Delta_r H°$ given here was calculated from p*K*s measured at several temperatures. The value $\Delta_r C_p^\circ/(\text{J K}^{-1}\,\text{mol}^{-1}) = 42$ was also calculated from the temperature dependency of their [97ROY/CAR] reported p*K*s.	97ROY/CAR
7.854		283.15	0		
7.758		288.15	0		
7.664		293.15	0		
7.576	30.18	298.15	0		
7.489		303.15	0		
7.403		308.15	0		
7.368		310.15	0		
7.324		313.15	0		
7.240		318.15	0		
7.158		323.15	0		
7.083		328.15	0		
7.54		298.15	0.1 M	Potentiometric titration—glass electrode.	98AZA/DEG

Values adjusted to $T=298.15$ K and $I=0$

p*K*	$\Delta_r H°/(\text{kJ mol}^{-1})$	$\Delta_r C_p^\circ/(\text{J K}^{-1}\,\text{mol}^{-1})$	Reference
≈7.6			80FER/BRA
7.67			87KIT/ITO
7.576	30.18	42	97ROY/CAR
7.75			98AZA/DEG

Comments: The results of Roy *et al.* [97ROY/CAR], which are based on an electrochemical cell without liquid junction, are judged to be the most accurate.

TABLE 7.28. Ethanolamine

Other names	2-aminoethanol; 2-hydroxyethylamine; monoethanolamine; monoethanolammonium; colamine; 2,2′-aminoethanol; β-aminoethanol; MEA; colamine; glycinol; β-hydroxyethylamine; 2-ethanolamine; 2-hydroxyethanamine; 2-amino-1-ethanol; 1-amino-2-hydroxyethane; hydroxyethylamine; CAS No. 141-43-5
Empirical formula	C_2H_7NO
Molecular weight	61.083

Ionization reaction

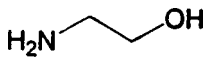
$$HL^+ = H^+ + L, \text{ where } L = C_2H_7NO$$

Selected values at $T=298.15$ K and $I=0$:

$$pK = 9.498,\ \Delta_r G°/(\text{kJ mol}^{-1}) = 54.215,\ \Delta_r H°/(\text{kJ mol}^{-1}) = 50.52, \text{ and } \Delta_r C_p^\circ/(\text{J K}^{-1}\text{mol}^{-1}) = 26$$

Evaluation: AAB

Structure:



Values from literature

pK	$\Delta_r H°/(\text{kJ mol}^{-1})$	T/K	I	Method(s) and comments	Reference
9.470		298.15	0	Potentiometric titration: hydrogen and calomel electrodes.	28SIM
9.504		298.15	0	Conductivity.	40SIV/REI
9.45		298.15	0	Glass electrode.	47GLA/SCH
9.74		298.15	0.5 M	Glass electrode.	48BRU/VER
9.51		308.15	0.5 M		
	50.06	283.15	0.054 M	Calorimetry. The value $\Delta_r C_p^\circ/(\text{J K}^{-1}\text{mol}^{-1}) = 26$ was calculated from the temperature dependence of the measured enthalpies.	49LEV/MCE
	50.42	293.15	0.054 M		
	50.58	303.15	0.054 M		
10.3064		273.15	0	Electrochemical cell—no liquid junction. The value of $\Delta_r H°$ given here was calculated from pKs measured at several temperatures. The value $\Delta_r C_p^\circ/(\text{J K}^{-1}\text{mol}^{-1}) \approx -6$ was also calculated from the temperature dependency of their [51BAT/PIN] reported pKs.	51BAT/PIN
10.1341		278.15	0		
9.9654		283.15	0		
9.8037		288.15	0		
9.6467		293.15	0		
9.4980	50.54	298.15	0		
9.3485		303.15	0		
9.2082		308.15	0		
9.0702		313.15	0		
8.9401		318.15	0		
8.8130		323.15	0		
9.60		298.15	0.5 M	Potentiometric titration—glass electrode.	56BJE/REF
9.71		298.15	0.1 M	Glass electrode.	56ORO/CLA
9.57		293.15	0		58ALN/SME
9.51		298.15	0.015 M	Potentiometric titration—glass electrode.	59DAT/GRZ
9.54		298.15	0.15 M	Potentiometric titration—glass electrode.	59FOL/OST
9.97		283.15	?	Glass electrode. The pK values are not accurate enough to allow for a meaningful calculation of $\Delta_r H°$.	59LOT/BLO
9.66		293.15	?		
9.36		303.15	?		
9.11		313.15	?		
9.45	50.63	298.15	0	Calorimetry.	61TYS/MCC
9.50		298.15	0.1 M	Potentiometric titration—glass electrode.	62COC/WAL
10.1362		278.15	0	Electrochemical cell—no liquid junction. The value of $\Delta_r H°$ given here was calculated from pKs measured at several temperatures. The value $\Delta_r C_p^\circ/(\text{J K}^{-1}\text{mol}^{-1}) \approx 43$ was also calculated from the temperature dependency of their [62DAT/GRZ] reported pKs.	62DAT/GRZ
9.8062		288.15	0		
9.4994	50.89	298.15	0		
9.2117		308.15	0		
8.9336		318.15	0		
9.55		303.15	0.5 M	Polarography.	62FIS/HAL
9.74		298.15	?	Potentiometric titration—glass electrode.	65DOU
9.62		298.15	0.43 M	Potentiometric titration—glass electrode.	66SKL/KAR
9.54		303.15	0.5 M	Glass electrode.	67FIS/HAL
	34.3	298.15	0.015 M	Calorimetry.	67POP/ROM
9.56		293.15	0	Potentiometric titration—electrochemical cell.	68ALN/LAN
9.48		298.15	?	Conductimetric titration.	68DAV/PAT
	50.50	298.15	0.07 M	Calorimetry.	68OJE/WAD
9.47		298.15	1.0 M	Polarography.	68VER/BEN

Values from literature—Continued

pK	$\Delta_r H°/(\mathrm{kJ\ mol^{-1}})$	T/K	I	Method(s) and comments	Reference
	50.38	298.15	0	Calorimetry.	69CHR/IZA
	48.28	298.15	0	Calorimetry.	70EAT
9.40		303.15	2.0 M		71SRI/SUB
9.72		298.15	0.5 M	Potentiometric titration—glass electrode.	72VAN/EEC
9.498		298.15	0	Potentiometric titration—glass electrode. Values of pK are given as a function of ionic strength (0.002 M≤I≤2.019 M).	73NAS/KOS
9.52		298.15	0.1 M	Glass electrode.	80JAM/HUN
9.451		298.15	0.1 M	Potentiometric titration—glass electrode.	81HAN
9.62		298.15	0.1 M	Potentiometric titration—glass electrode.	81LIM
9.77		298.15	1.0 M	Potentiometric titration—glass electrode.	81NAK/MAK
9.54		298.15	0.5 M	Glass electrode; spectrophotometry.	83DJU/BJE
9.55		298	0.1 M		86ANT/ARC
9.38		305.5	0.1 M		
9.24		313	0.1 M		
9.67		298.15	1.0 M	Glass electrode.	86CAS/TAU
9.66		298.15	1.0 M	Electron spin resonance; glass electrode.	86TAU/CAS
9.26		298.15	0.1 M	Coulometric titration.	87GLA/SKR
9.51	50.55	298.15	0	Potentiometric titration—glass electrode; calorimetry.	87KIM/DOB
9.64		298.15	0.1 M	Potentiometric titration—glass electrode.	90BUN/STE
10.414		278.15	1.0 M	Potentiometric titration—glass electrode. The approximate value of $\Delta_r H°$ given here was calculated from pKs measured at several temperatures.	91MAR
10.208		288.15	1.0 M		
9.785	≈55.0	298.15	1.0 M		
9.493		308.15	1.0 M		

Values adjusted to T=298.15 K and I=0

pK	$\Delta_r H°/(\mathrm{kJ\ mol^{-1}})$	$\Delta_r C_p^\circ/(\mathrm{J\ K^{-1}\ mol^{-1}})$	Reference
9.470			28SIM
9.504			40SIV/REI
9.45			47GLA/SCH
9.74			48BRU/VER
	50.50	26	49LEV/MCE
9.498	50.54	≈−6	51BAT/PIN
9.60			56BJE/REF
9.71			56ORO/CLA
9.57			58ALN/SME
9.51			59DAT/GRZ
9.54			59FOL/OST
9.51			59LOT/BLO
9.45			61TYS/MCC
9.50			62COC/WAL
9.499	50.89	≈43	62DAT/GRZ
9.55			62FIS/HAL
9.74			65DOU
9.62			66SKL/KAR
9.54			67FIS/HAL
	34.3		67POP/ROM
9.56			68ALN/LAN
9.48			68DAV/PAT
	50.50		68OJE/WAD
9.47			68VER/BEN
	50.38		69CHR/IZA
	48.28		70EAT
9.40			71SRI/SUB
9.72			72VAN/EEC
9.498			73NAS/KOS
9.52			80JAM/HUN
9.451			81HAN
9.62			81LIM
9.77			81NAK/MAK
9.54			83DJU/BJE
9.55			86ANT/ARC

Values adjusted to T=298.15 K and I=0—Continued

pK	$\Delta_r H°$/(kJ mol^{-1})	$\Delta_r C_p^\circ$/(J K^{-1} mol^{-1})	Reference
9.67			86CAS/TAU
9.66			86TAU/CAS
9.26			87GLA/SKR
9.51	50.55		87KIM/DOB
9.64			90BUN/STE
9.785	≈55.0		91MAR

Comments: There is excellent agreement between the carefully done measurements of Bates and Pinching [51BAT/PIN] and of Datta and Grzybowski [62DAT/GRZ]. Both studies utilized electrochemical cells without liquid junctions. Also, the calorimetric results of Levi *et al.* [49LEV/MCE] and Kim *et al.* [87KIM/DOB] are in excellent agreement with the values of $\Delta_r H°$ calculated from the temperature dependence of the pKs of Bates and Pinching [51BAT/PIN] and of Datta and Grzybowski [62DAT/GRZ]. We prefer the value of $\Delta_r C_p^\circ$ obtained from the calorimetric results of Levi *et al.* [49LEV/MCE].

TABLE 7.29. *N*-Ethylmorpholine

TABLE 7.29.

Other names	4-ethylmorpholine; CAS No. 100-74-3
Empirical formula	$C_6H_{13}NO$
Molecular weight	115.17

Ionization reaction

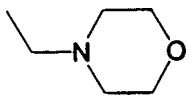
$$HL^+ = H^+ + L, \text{ where } L = C_6H_{13}NO$$

Selected values at T=298.15 K and I=0:

pK=7.77, $\Delta_r G°$/(kJ mol^{-1})=44.35, and $\Delta_r H°$/(kJ mol^{-1})=27.4

Evaluation: CC

Structure:



Values from literature

pK	$\Delta_r H°$/(kJ mol^{-1})	T/K	I	Method(s) and comments	Reference
7.77	27.4	298.15	0.5 M	Electrochemical cell with a liquid junction.	75BLA/ENE
7.70		298.15	≈0.012 M	Potentiometric titration of sample (0.01–0.014 M) with 0.1 M HCl or 0.1 M NaOH.	87KIT/ITO

Values adjusted to T=298.15 K and I=0

pK	$\Delta_r H°$/(kJ mol^{-1})	Reference
7.77	27.4	75BLA/ENE
7.70		87KIT/ITO

Comments: The results of Blais *et al.* [75BLA/ENE] appear to be the most reliable results to date. Additional and careful measurements would be useful.

TABLE 7.30. Glycerol 2-phosphate

Other names	β-glycerophosphate; 2-glycerophosphate; glycerol 2-monophosphate; glycerylphosphoric acid; CAS No. 17181-54-3
Empirical formula	$C_3H_9O_6P$
Molecular weight	172.07

Ionization reaction

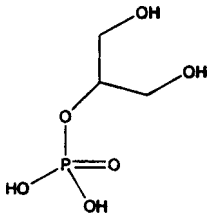
$$H_2L = H^+ + HL^- \quad (1)$$
$$HL^- = H^+ + L^{2-} \quad (2)$$
where $H_2L = C_3H_9NO_6P$

Selected values at $T = 298.15$ K and $I = 0$:

pK = 1.329, $\Delta_r G°/(\text{kJ mol}^{-1}) = 7.586$, $\Delta_r H°/(\text{kJ mol}^{-1}) = -12.2$, and $\Delta_r C_p°/(\text{J K}^{-1}\,\text{mol}^{-1}) = -330$ for reaction (1)
pK = 6.650, $\Delta_r G°/(\text{kJ mol}^{-1}) = 37.958$, $\Delta_r H°/(\text{kJ mol}^{-1}) = -1.85$, and $\Delta_r C_p°/(\text{J K}^{-1}\,\text{mol}^{-1}) = -212$ for reaction (2)

Evaluation: reaction (1), ABB; reaction (2), AAA

Structure:



Values from literature

pK	$\Delta_r H°/(\text{kJ mol}^{-1})$	T/K	I	Method(s) and comments	Reference
				Reaction (1): $H_2L = H^+ + HL^-$	
1.40		293.15	≈0.05 M	Electrometric titration—hydrogen electrode.	26MEY/SUR
1.36		291.15	≈0.06 M	Potentiometric titration—glass electrode.	30MOR
1.37		298.15	≈0.06 M	Electrometric titration—hydrogen electrode. The temperature was ambient and is assumed to be ≈298.15 K.	34KIE
1.221		278.15	0	Electrochemical cell—no liquid junction. The value of $\Delta_r H°$ given here was calculated from pKs measured at several temperatures. The value $\Delta_r C_p°/(\text{J K}^{-1}\,\text{mol}^{-1}) = -330$ was also calculated from the temperature dependency of the reported [54ASH/CRO] pKs.	54ASH/CRO
1.252		283.15	0		
1.272		288.15	0		
1.296		293.15	0		
1.329	−12.18	298.15	0		
1.373		303.15	0		
1.416		308.15	0		
1.460		313.15	0		
1.509		318.15	0		
1.549		323.15	0		
				Reaction (2): $HL^- = H^+ + L^{2-}$	
6.33		293.15	≈0.07 M	Electrometric titration—hydrogen electrode.	26MEY/SUR
6.67	0	303.15	0	Electrochemical cell with liquid junction—hydrogen and calomel electrodes. The results have been extrapolated to $I = 0$.	28MOR
6.32		291.15	≈0.09 M	Potentiometric titration—glass electrode.	30MOR
6.34		298.15	≈0.09 M	Electrometric titration—hydrogen electrode. The temperature was ambient and is assumed to be ≈298.15 K.	34KIE
6.34		302.65	≈0.02 M	Potentiometric titration—hydrogen and calomel electrodes. Titrations were performed at $T = 295.15$ K and at $T = 310.15$ K. Since only a mean value of the pK is reported, we have assigned a mean temperature of 302.65 K. The same result was again reported by Delory and King [43DEL/KIN].	39KIN/DEL
6.657		278.15	0	Electrochemical cell—no liquid junction. The value of $\Delta_r H°$ given here was calculated from pKs measured at several temperatures. The value $\Delta_r C_p°/(\text{J K}^{-1}\,\text{mol}^{-1}) = -228$ was also calculated from the temperature dependency of the reported [54ASH/CRO] pKs.	54ASH/CRO
6.650		283.15	0		
6.646		288.15	0		
6.647		293.15	0		
6.650	−1.74	298.15	0		
6.655		303.15	0		
6.667		308.15	0		
6.678		313.15	0		

Values from literature—Continued

pK	$\Delta_r H°/(\mathrm{kJ\,mol^{-1}})$	T/K	I	Method(s) and comments	Reference
6.694		318.15	0		
6.711		323.15	0		
6.26	−0.72	298.15	0.1 M	Electrochemical cell with liquid junction; calorimetry. Fukada and Takahashi [98FUK/TAK] also obtained $\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}}) = -179$ and $(\partial \Delta_r C_p^\circ/\partial T)_p/(\mathrm{J\,K^{-2}\,mol^{-1}}) = 0.8$ at $I = 0.1$ M from the temperature dependence of $\Delta_r H°$ over the range 278.15–323.15 K.	98FUK/TAK

Values adjusted to T=298.15 K and I=0

pK	$\Delta_r H°/(\mathrm{kJ\,mol^{-1}})$	$\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}})$	Reference
	Reaction (1): $H_2L = H^+ + HL^-$		
1.60			26MEY/SUR
1.59			30MOR
1.55			34KIE
1.329	−12.18	−330	54ASH/CRO
	Reaction (2): $HL^- = H^+ + L^{2-}$		
6.67			26MEY/SUR
6.66			28MOR
6.73			30MOR
6.75			34KIE
6.57			39KIN/DEL
6.650	−1.74	−228	54ASH/CRO
6.69	−1.96	−195	98FUK/TAK

Comments: The pK values reported by Ashby *et al.* [54ASH/CRO] are based on an electrochemical cell with no liquid junction and are judged to be the most reliable values. For reaction (2), the values of $\Delta_r H°$ and of $\Delta_r C_p^\circ$ determined by Ashby *et al.* [54ASH/CRO] and by Fukada and Takahashi [98FUK/TAK] are in satisfactory agreement and we have adopted the respective average values for these quantities.

TABLE 7.31. Glycine

Other names	Gly; aminoacetic acid; glycocoll; 2-aminoethanoic acid; CAS No. 56-40-6
Empirical formula	$C_2H_5NO_2$
Molecular weight	75.067

Ionization reactions

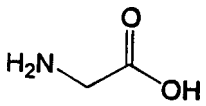
$$H_2L^+ = H^+ + HL^\pm \quad (1)$$
$$HL^\pm = H^+ + L^- \quad (2)$$
where $HL = C_2H_5NO_2$

Selected values at T=298.15 K and I=0:

pK=2.351, $\Delta_r G°/(\mathrm{kJ\,mol^{-1}}) = 13.420$, $\Delta_r H°/(\mathrm{kJ\,mol^{-1}}) = 4.00$, and $\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}}) = -139$ for reaction (1)
pK=9.780, $\Delta_r G°/(\mathrm{kJ\,mol^{-1}}) = 55.825$, $\Delta_r H°/(\mathrm{kJ\,mol^{-1}}) = 44.2$, and $\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}}) = -57$ for reaction (2)

Evaluation: reaction (1), AAA; reaction (2), AAB

Structure:



Values from literature

pK	$\Delta_r H°/(\mathrm{kJ\,mol^{-1}})$	T/K	I	Method(s) and comments	Reference
				Reaction (1): $H_2L^+ = HL^\pm + H^+$	
2.405		283.15	0	Electrochemical cell—no liquid junction. The value of $\Delta_r H°$ given here was calculated from pKs measured at several temperatures. The value $\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}}) = -142$ was also calculated from the temperature dependency of Owen's [34OWE] reported pKs.	34OWE
2.384		288.15	0		
2.366		293.15	0		
2.350	4.81	298.15	0		
2.338		303.15	0		
2.327		308.15	0		
2.318		313.15	0		
2.313		318.15	0		
	3.89	298.15	0	Calorimetry.	41STU
2.4176		278.15	0	Electrochemical cell—no liquid junction. The value of $\Delta_r H°$ given here was calculated from pKs measured at several temperatures. The value $\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}}) = -136$ was also calculated from the temperature dependency of King's [45KIN] reported pKs.	45KIN
2.3980		283.15	0		
2.3795		288.15	0		
2.3640		293.15	0		
2.3508	3.98	298.15	0		
2.3404		303.15	0		
2.3318		308.15	0		
2.3252		313.15	0		
2.3212		318.15	0		
2.3194		323.15	0		
2.3194		328.15	0		
2.3971		283.15	0	Electrochemical cell—no liquid junction. The value of $\Delta_r H°$ given here was calculated from pKs measured at several temperatures. The value $\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}}) = -147$ was also calculated from the temperature dependency of King's [51KIN] reported pKs.	51KIN
2.3800		288.15	0		
2.3640		293.15	0		
2.3503	3.97	298.15	0		
2.3394		303.15	0		
2.3312		308.15	0		
2.3266		313.15	0		
2.3242		318.15	0		
2.3200		323.15	0		
2.355		298.15	0	Electrochemical cell—no liquid junction.	55EVA/MON
2.34	5.98	298.15	0	Calorimetry.	64IZA/CHR
2.41		283.15	0	Glass electrode. The approximate value of $\Delta_r H°$ given here was calculated from pKs measured at several temperatures.	66AND/GRE
2.39	≈4.5	298.15	0		
2.33		313.15	0		
	4.06	298.15	0	Calorimetry.	66PAR/CHR
	4.10	298.15	0	Calorimetry.	67CHR/IZA
	5.90	283.15	0	Calorimetry. The value $\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}}) = -131$ was calculated from the temperature dependency of the $\Delta_r H°$ values.	68CHR/OSC
	4.10	298.15	0		
	1.97	313.15	0		
2.39	4.60	298.15	0.1 M	Potentiometric titration—glass electrode; calorimetry.	71LIM/NAN
2.36	4.39	298.15	0.2 M	Potentiometric titration—glass electrode; calorimetry.	73GER/SOV
	9.0	298.15	3.0 M	Calorimetry.	76COR/WIL
2.36	4.4	298.15	0.2 M	Potentiometric titration—glass electrode; calorimetry.	76SOV/GER
2.33	≈9.6	298.15	0.2 M	Potentiometric titration—glass electrode. The approximate value of $\Delta_r H°$ given here was calculated from pKs measured at three temperatures.	79MOH/BAN
	4.27	298.15	0	Calorimetry.	79VAS/KOC
2.46	4.27	298.15	1.0 M	Calorimetry.	83BIS/RIZ
2.33	3.0	298.15	0	Potentiometric titration—glass electrode. The approximate value of $\Delta_r H°$ given here was calculated from pKs measured at three temperatures.	85DAN/DER
2.68	5.5	298.15	3.0 M	Calorimetry.	86ISH/PIT
2.36		298.15	0	Potentiometric titration—glass electrode. Values of pK were determined as a function of ionic strength ($0.10 \leqslant I/\mathrm{M} \leqslant 1.04$) in solutions containing $NaClO_4$, KCl, and KBr. Results were extrapolated to $I = 0$ using various activity coefficient models. The pK value given here is based on the Guggenheim and Scatchard models and uses the $NaClO_4$ results.	98ALO/BAR

Values from literature—Continued

pK	$\Delta_r H°/(\mathrm{kJ\,mol^{-1}})$	T/K	I	Method(s) and comments	Reference
				Reaction (2): $HL^{\pm}=L^{-}+H^{+}$	
10.204		283.15	0	Electrochemical cell—no liquid junction. We have used pKs for the ionization of water [75OLO/HEP] to calculate the pK values given here from the pK_B values given in Owen's [34OWE] Table II. The value of $\Delta_r H°$ given here was calculated from pKs measured at several temperatures. The value $\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}}) = -130$ was also calculated from the temperature dependency of Owen's [34OWE] reported pKs.	34OWE
10.055		288.15	0		
9.914		293.15	0		
9.780	44.56	298.15	0		
9.653		303.15	0		
9.532		308.15	0		
9.415		313.15	0		
9.303		318.15	0		
	44.22	298.15	0	Calorimetry. The value given here was calculated from the measured value of $\Delta_r H°$ for the reaction ($HL^{\pm}+OH^{-}=L^{-}+H_2O$) and by using the value of $\Delta_r H°$ for the ionization of water [75OLO/HEP].	41STU
10.1928		283.15	0	Electrochemical cell—no liquid junction. The value of $\Delta_r H°$ given here was calculated from pKs measured at several temperatures. The value $\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}}) = -84$ was also calculated from the temperature dependency of King's [51KIN] reported pKs.	51KIN
10.0493		288.15	0		
9.9103		293.15	0		
9.7796	44.18	298.15	0		
9.6517		303.15	0		
9.5300		308.15	0		
9.4124		313.15	0		
9.2988		318.15	0		
9.1887		3232.15	0		
9.773		298.15	0	Electrochemical cell—no liquid junction.	55EVA/MON
10.25		273.50	0.09 M	Potentiometric titration—glass electrode. The approximate value of $\Delta_r H°$ given here was calculated from pKs measured at three temperatures.	57MUR/MAR
	≈43.5	298.15	0.09 M		
9.44		303.15	0.09 M		
9.00		321.95	0.09 M		
10.3404		278.15	0	Electrochemical cell—no liquid junction. The value of $\Delta_r H°$ given here was calculated from pKs measured at several temperatures. The value $\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}}) = -46$ was also calculated from the temperature dependency of their [58DAT/GRZ] reported pKs.	58DAT/GRZ
10.0478		288.15	0		
9.7775	44.21	298.15	0		
9.5277		308.15	0		
9.2956		318.15	0		
9.73	44.35	298.15	0	Calorimetry.	64IZA/CHR
10.20	48.41	283.15	0	Glass electrode; calorimetry. The value $\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}}) = -188$ was calculated from the temperature dependency of the $\Delta_r H°$ values.	66AND/GRE
9.77	45.02	298.15	0		
9.46	42.76	313.15	0		
	44.2	298.15	0	Calorimetry.	66PAR/CHR
9.59	44.7	298.15	0.01 M	Calorimetry.	68CHR/WRA
	44.1	298.15	0	Calorimetry. The value given here was calculated from the measured value of $\Delta_r H°$ for the reaction ($HL^{\pm}+OH^{-}=L^{-}+H_2O$) and by using $\Delta_r H°$ for the ionization of water [75OLO/HEP].	71HAN/LEW
9.56	42.7	298.15	0.1 M	Potentiometric titration—glass electrode; calorimetry.	71LIM/NAN
	41.9	?	?	Calorimetry.	71MAR/BER
9.56	42.7	298.15	0.1 M	Calorimetry.	72I/NAN
9.84		288.15	0.1 M	Potentiometric titration—glass electrode. The approximate value of $\Delta_r H°$ given here was calculated from pKs measured at four temperatures.	72ISR/VOL
9.55	≈44.4	298.15	0.1 M		
8.92		323.15	0.1 M		
8.56		343.15	0.1 M		
	45.40	283.15	0	Calorimetry. The value $\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}}) = -66$ at $\langle T \rangle = 298.15$ K was calculated from the temperature dependency of the $\Delta_r H°$ values.	72IZA/JOH
	44.14	298.15	0		
	43.43	313.15	0		
9.55	46.52	298.15	0.2 M	Potentiometric titration—glass electrode; calorimetry.	73GER/SOV
10.231		278.15	0.1 M	Electrochemical cell with liquid junction. The approximate value of $\Delta_r H°$ given here was calculated from pKs measured at three temperatures.	73REI/DRE
9.655	≈46.4	298.15	0.1 M		
9.135		318.15	0.1 M		
	51.2	298.15	3.0 M	Calorimetry.	76COR/WIL
9.55	44.3	298.15	0.2 M	Potentiometric titration—glass electrode; calorimetry.	76SOV/GER
	46.4	298.15	1.0 M	Calorimetry. The value given here was calculated from the measured value of $\Delta_r H°$ for the reaction ($HL^{\pm}+OH^{-}=L^{-}+H_2O$) and by using the value of $\Delta_r H°$ for the ionization of water [75OLO/HEP] adjusted to $I = 1.0$ M.	79ENE/BER

Values from literature—Continued

pK	$\Delta_r H°/(\mathrm{kJ\ mol^{-1}})$	T/K	I	Method(s) and comments	Reference
9.60	≈44.4	298.15	0.2 M	Potentiometric titration—glass electrode. The approximate value of $\Delta_r H°$ given here was calculated from pKs measured at three temperatures.	79MOH/BAN
	45.40	298.15	0	Calorimetry. The value given here was calculated from the measured value of $\Delta_r H°$ for the reaction ($HL^{\pm}+OH^{-}=L^{-}+H_2O$) and by using the value of $\Delta_r H°$ for the ionization of water [75OLO/HEP].	79VAS/KOC
9.63	44.35	298.15	1.0 M	Calorimetry.	83BIS/RIZ
9.75	≈41.0	298.15	0	Potentiometric titration—glass electrode. The approximate value of $\Delta_r H°$ given here was calculated from pKs measured at three temperatures.	85DAN/DER
9.94	57.9	298.15	3.0 M	Calorimetry.	86ISH/PIT
9.96		288.15	0.1 M	Potentiometric titration—glass electrode. The approximate value of $\Delta_r H°$ given here was calculated from pKs measured at several temperatures.	90BUN/STE
9.68	≈45.8	298.15	0.1 M		
9.41		308.15	0.1 M		
9.18		318.15	0.1 M		
	43.95	298.15	0	Calorimetry. These results pertain to the pressure range 0.43≤p/MPa≤12.5.	92IZA/OSC
9.20	43.07	323.15	0	However, the authors [91IZA/OSC] state that the effect of pressure on the enthalpies is small. The value $\Delta_r C_p^{\circ}/(\mathrm{J\ K^{-1}\ mol^{-1}}) = -32$ at $\langle T\rangle = 323.15$ K was calculated from the temperature dependency of the $\Delta_r H°$ values.	
8.70	42.37	348.15	0		
8.71	40.6	348.15	0	Calorimetry. The value $\Delta_r C_p^{\circ}/(\mathrm{J\ K^{-1}\ mol^{-1}}) = -76$ at $\langle T\rangle = 373.15$ K was calculated from the temperature dependency of the $\Delta_r H°$ values.	95GIL/OSC
7.98	36.8	348.15	0		
9.78		298.15	0	Potentiometric titration—glass electrode. Values of pK were determined as a function of ionic strength (0.10≤I/M≤1.04) in solutions containing $NaClO_4$, KCl, and KBr. Results were extrapolated to $I=0$ using various activity coefficient models. The pK value given here is based on the Guggenheim and Scatchard models and uses the $NaClO_4$ results.	98ALO/BAR

Values adjusted to $T=298.15$ K and $I=0$

pK	$\Delta_r H°/(\mathrm{kJ\,mol^{-1}})$	$\Delta_r C_p^\circ(\mathrm{J\,K^{-1}\,mol^{-1}})$	Reference
	Reaction (1): $H_2L^+ = HL^\pm + H^+$		
2.350	4.81	−142	34OWE
	3.89		41STU
2.351	3.98	−136	45KIN
2.351	3.97	−147	51KIN
2.355			55EVA/MON
2.34	5.98		64IZA/CHR
2.39	≈4.5		66AND/GRE
	4.06		66PAR/CHR
	4.10		67CHR/IZA
	4.10	−131	68CHR/OSC
2.39	4.60		71LIM/NAN
2.36	4.39		73GER/SOV
	≈9		76COR/WIL
	4.4		76SOV/GER
	≈10		79MOH/BAN
	4.27		79VAS/KOC
	4.3		83BIS/RIZ
2.33	3.0		85DAN/DER
	≈5.5		86ISH/PIT
2.36			98ALO/BAR
	Reaction (2): $HL^\pm = L^- + H^+$		
9.780	44.56	−130	34OWE
	44.22		41STU
9.780	44.18	−84	51KIN
9.773			55EVA/MON
9.78	≈43		57MUR/MAR
9.778	44.21	−46	58DAT/GRZ
9.73	44.35		64IZA/CHR
9.77	45.02	−188	66AND/GRE
	44.2		66PAR/CHR
9.68	44.4		68CHR/WRA
	44.1		71HAN/LEW
9.77	42.1		71LIM/NAN
	≈42		71MAR/BER
9.77	42.1		72I/NAN
9.76	≈43.8		72ISR/VOL
	44.14	−66	72IZA/JOH
9.82	45.7		73GER/SOV
9.87	45.8		73REI/DRE
	≈50		76COR/WIL
9.82	43.5		76SOV/GER
	≈45.3		79ENE/BER
9.87	43.6		79MOH/BAN
	45.4		79VAS/KOC
	≈43.2		83BIS/RIZ
9.75	≈41.0		85DAN/DER
	≈57		86ISH/PIT
9.89	45.2		90BUN/STE
	43.95	−32	92IZA/OSC
	44.4	≈−76	95GIL/OSC
9.78			98ALO/BAR

Comments: The exceptionally carefully done studies of King [45KIN, 51KIN] provide the most accurate pK values for the ionization reactions of glycine. For pK_1, there is excellent agreement with the result of Owen [34OWE] and also probably agreement with the result of Evans and Monk [55EVA/MON]. For pK_2, there is an excellent agreement with the pKs reported by Owen [34OWE] and by Datta and Grzybowski [58DAT/GRZ]. For reaction (1), a value $\Delta_r H°/(\mathrm{kJ\,mol^{-1}}) = 4.00$ gives a good representation of what appear to be the results of the most careful investigations [41STU, 45KIN, 51KIN, 66PAR/CHR, 67CHR/IZA, 68CHR/OSC]. For reaction (2), the most reliable of the $\Delta_r H°$ values center around 44.2 kJ mol^{-1} and this value has been selected. For both reactions (1) and (2), there is agreement between values of $\Delta_r H°$ determined from calorimetry and from pK values measured at several temperatures. We adopt the average value, $\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}}) = -139$, based on the results of all of the studies leading to this quantity for reaction (1). For reaction (2), we adopt $\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}}) = -57$ based on the results of four investigations [51KIN, 58DAT/GRZ, 72IZA/JOH, 92IZA/OSC]. Kiss *et al.* [91KIS/SOV] recommended values for the pKs for the ionization reactions of glycine that are essentially the same as our selected values. However, their [91KIS/SOV] selected $\Delta_r H°$ values differ by 0.4 kJ mol^{-1} from the $\Delta_r H°$ values that we have selected. Additional studies, performed under a variety of conditions, are cited by Martell *et al.* [2001MAR/SMI], by Pettit and Powell [2000PET/POW], and by Kiss *et al.* [91KIS/SOV].

TABLE 7.32. Glycine amide

Other names	2-amino acetamide; glycinamide; 2-aminoethanoic acid amide; CAS No. of the hydrochloride is 598-41-4
Empirical formula	$C_2H_6N_2O$
Molecular weight	74.082

Ionization reaction

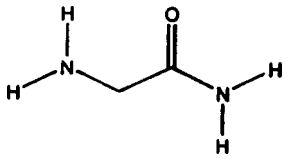
$$HL^+ = H^+ + L, \text{ where } L = C_2H_6N_2O$$

Selected values at $T=298.15$ K and $I=0$:

$$pK = 8.04,\ \Delta_r G°/(\text{kJ mol}^{-1}) = 45.89, \text{ and } \Delta_r H°/(\text{kJ mol}^{-1}) = 42.9$$

Evaluation: CC

Structure:



Values from literature

pK	$\Delta_r H°/(\text{kJ mol}^{-1})$	T/K	I	Method(s) and comments	Reference
7.99		298.15	?	Potentiometric titration—glass electrode. Glycine amide (0.01 M) was titrated with 0.1 M HCl or 0.1 M NaOH.	56DAT/RAB
8.06		298.15	≈0.20 M	Potentiometric titration—glass electrode.	57LI/DOO
8.06		298.15	0.15 M	Potentiometric titration—glass electrode.	58LI/CHE
8.8		273.15	0.1 M	Potentiometric titration—glass electrode.	66GOO/WIN
8.15		293.15	0.01 M		
8.2		293.15	0.1 M		
8.25		293.15	0.2 M		
7.7		310.15	0.1 M		
8.19		298.15	1.0 M	Potentiometric titration—glass electrode.	67REG
8.04		298.15	0.1 M	Potentiometric titration—glass electrode.	68SIG
7.96		298.15	0.1 M	Potentiometric titration—glass electrode.	71YAM/MIY
8.03	41.0	298.15	0.1 M	Potentiometric titration—glass electrode; calorimetry.	72BRU/BUR
7.95		298.15	0.10 M	Potentiometric titration—glass electrode.	75DOR/BIL
7.73	44.8	298.15	≈0.01 M	Potentiometric titration—glass electrode; and calorimetry. Dilute solutions (0.005–0.01 M) were titrated with 0.1 M NaOH or 0.1 M HCl.	76MCG/JOR
7.89		310.15	0.15 M	Potentiometric titration—glass electrode.	80NAI/SAN
8.208		298.15	1.0 M	Potentiometric titration—glass electrode.	81NAK/MAK
8.07		298.15	0.1 M	Potentiometric titration—glass electrode.	90BUN/STE
7.99		298.15	0.2 M	Potentiometric titration—glass electrode; polarography.	90KOZ/URB
8.040		298.15	0.1 M	Potentiometric titration—glass electrode.	93SUG/SHI

Values adjusted to $T=298.15$ K and $I=0$

pK	$\Delta_r H°/(\text{kJ mol}^{-1})$	Reference
7.99		56DAT/RAB
8.06		57LI/DOO
8.06		58LI/CHE
8.06		66GOO/WIN
8.19		67REG
8.04		68SIG
7.96		71YAM/MIY
8.03	41.0	72BRU/BUR
7.95		75DOR/BIL
7.73	44.8	76MCG/JOR
8.18		80NAI/SAN
8.21		81NAK/MAK
8.07		90BUN/STE
7.99		90KOZ/URB
8.04		93SUG/SHI

Comments: We have adopted the respective averages of the above pK and $\Delta_r H°$ values.

TABLE 7.33. Glycylglycine

Other names	*N*-glycylglycine; diglycine; α-glycylglycine; glycine dipeptide; CAS No. 556-50-3
Empirical formula	$C_4H_8N_2O_3$
Molecular weight	132.12

Ionization reactions

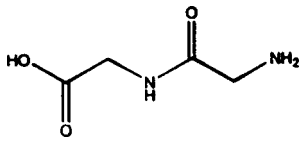
$$H_2L^+ = H^+ + HL^\pm \quad (1)$$
$$HL^\pm = H^+ + L^- \quad (2)$$
where $HL = C_4H_8N_2O_3$

Selected values at $T=298.15$ K and $I=0$:

pK=3.140, $\Delta_r G°/(\text{kJ mol}^{-1})=17.923$, $\Delta_r H°/(\text{kJ mol}^{-1})=0.11$, and $\Delta_r C_p°/(\text{J K}^{-1}\text{ mol}^{-1})=-128$ for reaction (1)
pK=8.265, $\Delta_r G°/(\text{kJ mol}^{-1})=47.177$, $\Delta_r H°/(\text{kJ mol}^{-1})=43.4$, and $\Delta_r C_p°/(\text{J K}^{-1}\text{ mol}^{-1})=-16$ for reaction (2)

Evaluation: reaction (1), AAB; reaction (2), AAB

Structure:



Values from literature

pK	$\Delta_r H°/(\text{kJ mol}^{-1})$	T/K	I	Method(s) and comments	Reference
				Reaction (1): $H_2L^+ = HL^\pm + H^+$	
3.201		274.15	0	Electrochemical cell—no liquid junction. The value of $\Delta_r H°$ given here was calculated from pKs measured at several temperatures. The value $\Delta_r C_p°/(\text{J K}^{-1}\text{ mol}^{-1})\approx -136$ was also calculated from the temperature dependency of their [42SMI/SMI] reported pKs.	42SMI/SMI
3.166		285.65	0		
3.148	1.6	298.15	0		
3.148		310.65	0		
3.148		323.15	0		
3.1574		278.15	0	Electrochemical cell—no liquid junction. The value of $\Delta_r H°$ given here was calculated from pKs measured at several temperatures. The value $\Delta_r C_p°/(\text{J K}^{-1}\text{ mol}^{-1})=-128$ was also calculated from the temperature dependency of King's [57KIN] reported pKs.	57KIN
3.1495		283.15	0		
3.1444		288.15	0		
3.1409		293.15	0		
3.1397	0.11	298.15	0		
3.1410		303.15	0		
3.1420		308.15	0		
3.1459		313.15	0		
3.1519		318.15	0		
3.1599		323.15	0		
3.21		283.15	0.06 M	Potentiometric titration—glass electrode. The same results were also reported later by Vaissermann [66VAI]. The value of $\Delta_r H°$ given here was calculated from pKs measured at several temperatures.	66VAI/QUI
3.20	1.2	298.15	0.06 M		
3.20		303.15	0.06 M		
3.19		308.15	0.06 M		
3.19		313.15	0.06 M		
3.23	1.5	293.15	?	Potentiometric titration—glass electrode; calorimetry.	74MAR/MAR
3.51	5.6	298.15	3.0 M	Potentiometric titration—glass electrode; calorimetry.	76COR/WIL
3.17	1.7	298.15	0.2 M	Potentiometric titration—glass electrode; calorimetry.	77GER/NAG
	0.21	298.15	0	Calorimetry.	91ROD/FAN
				Reaction (2): $HL^\pm = L^- + H^+$	
8.944		274.15	0	Electrochemical cell—no liquid junction. The value of $\Delta_r H°$ given here was calculated from pKs measured at several temperatures. The value $\Delta_r C_p°/(\text{J K}^{-1}\text{ mol}^{-1})\approx -78$ was also calculated from the temperature dependency of their [42SMI/SMI] reported pKs.	42SMI/SMI
8.594		285.65	0		
8.252	44.1	298.15	0		
7.948		310.65	0		
7.668		323.15	0		
8.21		295.15	0	Potentiometric titration—glass electrode.	52PER
8.71		273.50	0.09 M	Potentiometric titration—glass electrode. The approximate value of $\Delta_r H°$ given here was calculated from pKs measured at three temperatures.	57MUR/MAR
	≈46.9	298.15	0.09 M		
8.01		303.15	0.09 M		
7.50		312.95	0.09 M		

Values from literature—Continued

pK	$\Delta_r H°/(\mathrm{kJ\,mol^{-1}})$	T/K	I	Method(s) and comments	Reference
8.64		283.15	0.06 M	Potentiometric titration—glass electrode. The same results were also reported later by Vaissermann [66VAI]. The value of $\Delta_r H°$ given here was calculated from pKs measured at several temperatures.	66VAI/QUI
8.22	42.5	298.15	0.06 M		
8.11		303.15	0.06 M		
7.97		308.15	0.06 M		
7.86		313.15	0.06 M		
8.085	44.35	298.15	0.1 M	Potentiometric titration—glass electrode; calorimetry.	68BRU/LIM
	44.1	298.05	0.1M	Calorimetry.	72TIP/SKI
8.38	43.3	293.15	?	Potentiometric titration—glass electrode; calorimetry.	74MAR/MAR
8.813		278.15	0	Electrochemical cell—no liquid junction. The value of $\Delta_r H°$ given here was calculated from pKs measured at several temperatures. The value $\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}}) = -16$ was also calculated from the temperature dependency of King's [75KIN] reported pKs.	75KIN
8.668		283.15	0		
8.529		288.15	0		
8.394		293.15	0		
8.265	43.38	298.15	0		
8.140		303.15	0		
8.018		308.15	0		
7.901		313.15	0		
7.788		318.15	0		
7.680		323.15	0		
8.56	48.7	298.15	3.0 M	Potentiometric titration—glass electrode; calorimetry.	76COR/WIL
8.21	43.7	298.15	≈0.01 M	Potentiometric titration—glass electrode; and calorimetry.	76MCG/JOR
8.20	45.4	298.15	0.2 M	Potentiometric titration—glass electrode; calorimetry.	77GER/NAG
	42.9	298.15	0	Calorimetry.	91ROD/FAN

Values adjusted to T=298.15 K and I=0

pK	$\Delta_r H°$/(kJ mol^{-1})	$\Delta_r C_p^\circ$/(J K^{-1} mol^{-1})	Reference
	Reaction (1): $H_2L^+ = HL^\pm + H^+$		
3.148	1.6	≈−136	42SMI/SMI
3.140	0.11	−128	57KIN
	≈1.2		66VAI/QUI
	≈0.9		74MAR/MAR
	≈5.6		76COR/WIL
	1.7		77GER/NAG
	0.2		91ROD/FAN
	Reaction (2): $HL^\pm = L^- + H^+$		
8.252	44.1	≈−78	42SMI/SMI
8.21			52PER
	46.3		57MUR/MAR
	42.0		66VAI/QUI
	43.7		68BRU/LIM
	43.4		72TIP/SKI
	≈43.6		74MAR/MAR
8.265	43.4	−16	75KIN
	≈47.3		76COR/WIL
	43.4		76MCG/JOR
	44.6		77GER/NAG
	42.9		91ROD/FAN

Comments: The very carefully done measurements of King [57KIN, 75KIN] provide the most reliable set of results for this system. For reaction (1) there is agreement of King's results [57KIN] with the calorimetric result of Rodante and Fantauzzi [91ROD/FAN] and a possible agreement with the pK value determined by Smith and Smith [42SMI/SMI] at T = 298.15 K. For reaction (2), there is excellent agreement of King's [75KIN] value of $\Delta_r H°$ with three sets of calorimetric results [72TIP/SKI, 74MAR/MAR, 76MCG/JOR]. Additional studies, performed under a variety of conditions, are cited by Martell *et al.* [2001MAR/SMI] and by Pettit and Powell [2000PET/POW].

TABLE 7.34. Glycylglycylglycine

Other names	triglycine; gly-gly-gly; diglycylglycine; CAS No. 556-33-2
Empirical formula	$C_6H_{11}N_3O_4$
Molecular weight	189.17

Ionization reactions

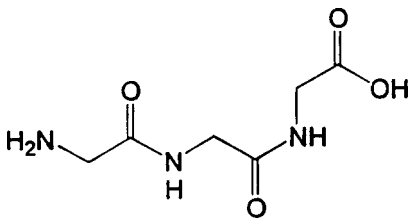
$$H_2L^+ = HL^\pm + H^+ \quad (1)$$
$$HL^\pm = H^+ + L^- \quad (2)$$
where $HL = C_6H_{11}N_3O_4$

Selected values at T=298.15 K and I=0:

pK=3.224, $\Delta_r G°$/(kJ mol^{-1})=18.403, and $\Delta_r H°$/(kJ mol^{-1})=0.84 for reaction (1)
pK=8.090, $\Delta_r G°$/(kJ mol^{-1})=46.178, and $\Delta_r H°$/(kJ mol^{-1})=41.7 for reaction (2)

Evaluation: reaction (1), AC; reaction (2), AC

Structure:



Values from literature

pK	$\Delta_r H°$/(kJ mol^{-1})	T/K	I	Method(s) and comments	Reference
			Reaction (1): $H_2L^+ = HL + H^+$		
3.19		293.15	≈0.1 M	Potentiometric titration—glass electrode.	41GLA/HAM
3.24		293.15	0	Potentiometric titration—glass electrode; spectrophotometry.	55DOB/KER
3.224		298.15	0	Electrochemical cell—no liquid junction.	55EVA/MON
3.30		298.15	0.1 M	Glass electrode.	61JAM/WIL
3.38		298.75	0.1 M	Glass electrode; spectrophotometry.	63KIM/MAR
3.30		298.15	0.16 M	Glass electrode; spectrophotometry.	63KOL/ROT
3.27		298.05	0.1 M	Glass electrode; spectrophotometry.	66KIM/MAR
3.18	0.84	298.15	0.1 M	Electrochemical cell, glass electrode; calorimetry.	68BRU/LIM
3.71		298.15	3.0 M	Potentiometric titration—glass electrode.	68OST/SJO
3.35		298.15	1.0 M	Potentiometric titration—glass electrode.	69OST
3.12		298.15	0.1 M	Potentiometric titration—glass electrode.	71HAU/BIL
3.30		298.15	0.8 M	Glass electrode; NMR.	72RAB/LIB
3.28		298.15	0.1 M	Potentiometric titration—glass electrode.	72SIG/GRI
3.34		298.15	0.1 M	Glass electrode.	73FEI/MOC
3.26		298.15	0.1 M	Potentiometric titration—glass electrode.	73YAM/NAK
3.21		298.15	0.1 M	Potentiometric titration—glass electrode.	75BRO/PET
3.63		298.15	3.0 M	Potentiometric titration—glass electrode.	75COR/MAK
3.11		310.15	0.15 M		
3.25		298.15	0.1 M	Potentiometric titration—glass electrode.	75KAN/MAR
3.63	4.0	298.15	3.0 M	Potentiometric titration—glass electrode; calorimetry.	76COR/WIL
	≈19	298.15	1.0 M	Potentiometric titration—glass electrode. The value of $\Delta_r H°$ given	90PAN/PAT
3.20		303.15	1.0 M	here is very approximate.	
3.10		313.15	1.0 M		
3.00		323.15	1.0 M		
3.14		298.15	0.1 M	Potentiometric titration—glass electrode.	92LU/PET
3.26		298.15	1.0 M	Potentiometric titration—glass electrode.	93COS/LUZ
3.32		298.15	0.1 M	Potentiometric titration—glass electrode.	99AGO/JAN
			Reaction (2): $HL = L^- + H^+$		
8.11		293.15	≈0.1 M	Potentiometric titration—glass electrode.	41GLA/HAM
7.91		298.15	0	Potentiometric titration—glass electrode.	54PER
8.20		293.15	0	Potentiometric titration—glass electrode; spectrophotometry.	55DOB/KER
8.090		298.15	0	Electrochemical cell—no liquid junction.	55EVA/MON
8.09		298.15	0.15 M	Glass electrode.	57LI/DOO
8.57		273.5	0.09 M	Potentiometric titration—glass electrode.	57MUR/MAR
7.74	≈38	303.15	0.09 M		
7.51		321.95	0.09 M		
8.02		298.15	0.1 M	Potentiometric titration—glass electrode.	58LI/CHE
8.01		298.15	0.16 M	Glass electrode; spectrophotometry.	60MAR/CHA
8.02		298.15	0.1 M	Glass electrode.	61JAM/WIL
7.97		298.75	0.1 M	Glass electrode; spectrophotometry.	63KIM/MAR
7.96		298.15	0.16 M	Glass electrode; spectrophotometry.	63KOL/ROT
7.90		298.05	0.1 M	Glass electrode; spectrophotometry.	66KIM/MAR
7.87	42.3	298.15	0.1 M	Electrochemical cell, glass electrode; calorimetry.	68BRU/LIM
8.55		298.15	3.0 M	Potentiometric titration—glass electrode.	68OST/SJO
8.06		298.15	1.0 M	Potentiometric titration—glass electrode.	69OST
7.88		298.15	0.1 M	Potentiometric titration—glass electrode.	71HAU/BIL
8.16		298.15	1.0 M	Glass electrode; spectrophotometry.	71MAR/MOS
8.10		298.15	0.8 M	Glass electrode; NMR.	72RAB/LIB
7.96		298.15	0.1 M	Potentiometric titration—glass electrode.	72SIG/GRI
8.02		298.15	0.1 M	Glass electrode.	73FEI/MOC
7.93		298.15	0.1 M	Potentiometric titration—glass electrode.	73YAM/NAK
7.94		298.15	0.1 M	Potentiometric titration—glass electrode.	75BRO/PET
8.60		298.15	3.0 M	Potentiometric titration—glass electrode.	75COR/MAK
7.59		310.15	0.15 M		
7.88		298.15	0.1 M	Potentiometric titration—glass electrode.	75KAN/MAR
8.60	49.5	298.15	3.0 M	Potentiometric titration—glass electrode; calorimetry.	76COR/WIL
	≈19	298.15	1.0 M	Potentiometric titration—glass electrode. The value of $\Delta_r H°$ given	90PAN/PAT
7.90		303.15	1.0 M	here is very approximate.	
7.80		313.15	1.0 M		
7.70		323.15	1.0 M		
7.93		298.15	0.1 M	Potentiometric titration—glass electrode.	92LU/PET
8.01		298.15	1.0 M	Potentiometric titration—glass electrode.	93COS/LUZ
7.93		298.15	0.1 M	Potentiometric titration—glass electrode.	99AGO/JAN

Values adjusted to $T=298.15$ K and $I=0$

pK	$\Delta_r H°/(\mathrm{kJ\ mol^{-1}})$	Reference
	Reaction (1): $H_2L^+=HL+H^+$	
3.19		41GLA/HAM
3.24		55DOB/KER
3.224		55EVA/MON
3.30		61JAM/WIL
3.38		63KIM/MAR
3.30		63KOL/ROT
3.27		66KIM/MAR
3.18	0.84	68BRU/LIM
≈3.7		68OST/SJO
3.35		69OST
3.12		71HAU/BIL
3.30		72RAB/LIB
3.28		72SIG/GRI
3.34		73FEI/MOC
3.26		73YAM/NAK
3.21		75BRO/PET
≈3.6	4.0	75COR/MAK
3.25		75KAN/MAR
≈3.6	≈19	76COR/WIL
3.20		90PAN/PAT
3.14		92LU/PET
3.26		93COS/LUZ
3.32		99AGO/JAN
	Reaction (2): $HL=L^-+H^+$	
8.20		41GLA/HAM
7.79		54PER
8.08		55DOB/KER
8.090		55EVA/MON
8.33		57LI/DOO
8.04	≈37	57MUR/MUR
8.04		58LI/CHE
8.26		60MAR/CHA
8.23		61JAM/WIL
8.20		63KIM/MAR
8.21		63KOL/ROT
8.11		66KIM/MAR
8.08	41.7	68BRU/LIM
9.02		68OST/SJO
8.45		69OST
8.09		71HAU/BIL
8.55		71MAR/MOS
8.48		72RAB/LIB
8.17		72SIG/GRI
8.11		73FEI/MOC
8.14		73YAM/NAK
8.15		75BRO/PET
9.07		75COR/MAK
8.09		75KAN/MAR
9.07	≈48	76COR/WIL
8.42	≈18	90PAN/PAT
8.14		92LU/PET
8.40		93COS/LUZ
8.14		99AGO/JAN

Comments: For the pK values, we prefer the results of Evans and Monk [55EVA/MON] who used an electrochemical cell without liquid junction. We judge the calorimetric results of Brunetti *et al.* [68BRU/LIM] to be the most reliable.

TABLE 7.35. HEPBS

Other names	*N*-(2-hydroxyethyl)piperazine-*N*′-4-butanesulfonic acid; CAS No. 161308-36-7
Empirical formula	$C_{10}H_{22}N_2O_4S$
Molecular weight	266.36

Ionization reaction

$$HL^{\pm} = H^+ + L^-, \text{ where } HL = C_{10}H_{22}N_2O_4S$$

There do not appear to be any thermodynamic data in the literature for the ionization of HEPBS.

Structure:

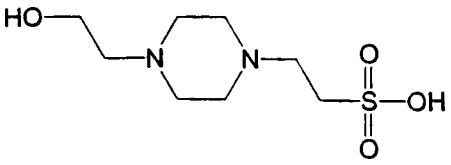


TABLE 7.36. HEPES

Other names	*N*-(2-hydroxyethyl)piperazine-*N*′-2-ethanesulfonic acid; 4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid; CAS No. 7365-45-9
Empirical formula	$C_8H_{18}N_2O_4S$
Molecular weight	238.31

Ionization reactions

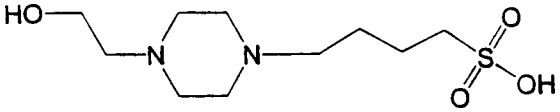
$$H_2L^+ = H^+ + HL^{\pm} \quad (1)$$
$$HL^{\pm} = H^+ + L^- \quad (2)$$
where $HL = C_8H_{18}N_2O_4S$

Selected values at T=298.15 K and I=0:

$pK \approx 3.0$ and $\Delta_r G°/(\text{kJ mol}^{-1}) \approx 17.1$ for reaction (1)
$pK = 7.564$, $\Delta_r G°/(\text{kJ mol}^{-1}) = 43.176$, $\Delta_r H°/(\text{kJ mol}^{-1}) = 20.4$, and $\Delta_r C_p^{\circ}/(\text{J K}^{-1}\,\text{mol}^{-1}) = 47$ for reaction (2)

Evaluation: reaction (1), U; reaction (2), ABB

Structure:



Values from literature

pK	$\Delta_r H°/(\text{kJ mol}^{-1})$	T/K	I	Method(s) and comments	Reference
				Reaction (1): $H_2L = H^+ + HL^{\pm}$	
≈3.0		298.15	?	Approximate pK value obtained by titrating 0.05 M Na^+HEPES^- with 1 M HCl.	87KIT/ITO
				Reaction (2): $HL^{\pm} = H^+ + L^-$	
7.85		273.15	0.1 M	Potentiometric titration—glass electrode.	66GOO/WIN
7.55		293.15	0.01 M		
7.55		293.15	0.1 M		
7.55		293.15	0.2 M		
7.31		310.15	0.1 M		
	20.96	298.15	≈0.1 M	Calorimetry.	71BER/STU
	19.7	278.15	?	Calorimetry.	71HIN/SHI
7.24	16.4	298.15	≈0.01 M	Potentiometric titration—glass electrode; and calorimetry. Dilute solutions (0.005–0.01 M) were titrated with 0.1 M NaOH or 0.1 M HCl.	76MCG/JOR

Values from literature—Continued

pK	$\Delta_r H°/(\mathrm{kJ\ mol^{-1}})$	T/K	I	Method(s) and comments	Reference
7.818		278.15		Electrochemical cell—no liquid junction. The value $\Delta_r C_p^\circ/(\mathrm{J\ K^{-1}\ mol^{-1}}) = 46$ was also calculated from the temperature dependency of their [76VEG/BAT] pKs.	76VEG/BAT
7.751		283.15			
7.690		288.15			
7.629		293.15			
7.565	20.38	298.15			
7.508		303.15			
7.450		308.15			
7.393		313.15			
7.337		318.15			
7.283		323.15			
7.50		298.15	0.012 M	Potentiometric titration of sample (0.01–0.014 M) with 0.1 M HCl or 0.1 M NaOH.	87KIT/ITO
7.51		298.15	0.00545 M	Chromatography, based on ionic mobilities.	87POS/DEM
7.878		273.15	0	Electrochemical cell—no liquid junction. The value $\Delta_r C_p^\circ/(\mathrm{J\ K^{-1}\ mol^{-1}}) = 26$ was also calculated from the temperature dependency of their [89FEN/KOC] pKs.	89FEN/KOC
7.747		283.15	0		
7.683		288.15	0		
7.622		293.15	0		
7.562	20.04	298.15	0		
7.427		310.15	0		
7.285		323.15	0		
	21.08	288.15	0.014 M	Calorimetry. The value $\Delta_r C_p^\circ/(\mathrm{J\ K^{-1}\ mol^{-1}}) = 66$ was calculated from the temperature dependency of the measured values of $\Delta_r H°$.	93ROI/BAC
	21.68	298.15	0.11 M		
	22.52	310.15	0.16 M		
	20.7	298.15	0		
7.45	21.01	298.15	0.1 M	Electrochemical cell with liquid junction; calorimetry. Fukada and Takahashi [98FUK/TAK] also obtained $\Delta_r C_p^\circ/(\mathrm{J\ K^{-1}\ mol^{-1}}) = 49$ at $I = 0.1$ M from the temperature dependence of $\Delta_r H°$ over the range 278.15–323.15 K.	98FUK/TAK

Values adjusted to $T = 298.15$ K and $I = 0$

pK	$\Delta_r H°/(\mathrm{kJ\ mol^{-1}})$	$\Delta_r C_p^\circ/(\mathrm{J\ K^{-1}\ mol^{-1}})$	Reference
	Reaction (1): $H_2L = H^+ + HL^\pm$		
≈3.0			87KIT/ITO
	Reaction (2): $HL^\pm = H^+ + L^-$		
7.69			66GOO/WIN
	20.3		71BER/STU
	20.7		71HIN/SHI
7.33	16.1		76MCG/JOR
7.565	20.38	48	76VEG/BAT
7.60			87KIT/ITO
7.58			87POS/DEM
7.562	20.06	31	89FEN/KOC
	20.7	66	93ROI/BAC
7.66	20.4	41	98FUK/TAK

Comments: For reaction (2), we adopt the average of the pK values from Vega and Bates [76VEG/BAT] and from Feng *et al.* [89FEN/KOC]. The values $\langle \Delta_r H° \rangle/(\mathrm{kJ\ mol^{-1}}) = 20.4$ and $\langle \Delta_r C_p^\circ \rangle/(\mathrm{J\ K^{-1}\ mol^{-1}}) = 47$ are the averages of the results of several careful studies [71BER/STU, 71HIN/SHI, 76VEG/BAT, 89FEN/KOC, 93ROI/BAC, 98FUK/TAK].

TABLE 7.37. HEPPS

Other names	EPPS; *N*-[2-hydroxyethyl]piperazine-*N′*-[3-propanesulfonic acid]; CAS No. 16052-06-5
Empirical formula	$C_9H_{20}N_2O_4S$
Molecular weight	252.33

Ionization reaction

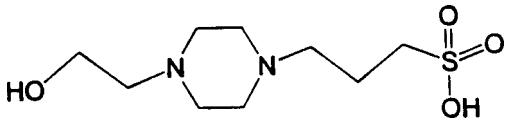
$$HL^{\pm} = H^+ + L^-, \text{ where } HL = C_6H_{20}N_2O_4S$$

Selected values at $T=298.15$ K and $I=0$:

$pK=7.957$, $\Delta_r G°/(\text{kJ mol}^{-1}) = 45.419$, $\Delta_r H°/(\text{kJ mol}^{-1}) = 21.3$, and $\Delta_r C_p^\circ/(\text{J K}^{-1}\,\text{mol}^{-1}) = 48$

Evaluation: AAA

Structure:



Values from literature

p*K*	$\Delta_r H°/(\text{kJ mol}^{-1})$	*T*/K	I	Method(s) and comments	Reference
8.1		?	?	Few details are given.	72GOO/IZA
7.82	17.9	298.15	≈0.01 M	Potentiometric titration—glass electrode; and calorimetry. Dilute solutions (0.005–0.01 M) were titrated with 0.1 M NaOH or 0.1 M HCl.	76MCG/JOR
7.94		298.15	≈0.012 M	Potentiometric titration of sample (0.01–0.014 M) with 0.1 M HCl or 0.1 M NaOH.	87KIT/ITO
	21.66	288.15	~0.15 M	Calorimetry. The value $\Delta_r C_p^\circ/(\text{J K}^{-1}\,\text{mol}^{-1}) = 79$ was calculated from the temperature dependency of their [93ROI/BAC] reported $\Delta_r H°$ values.	93ROI/BAC
	22.45	298.15	~0.15 M		
	23.40	310.15	~0.15 M		
			~0.15 M		
8.217		278.15	0	Electrochemical cell—no liquid junction. The value of $\Delta_r H°$ given here was calculated from p*K*s measured at several temperatures. The value $\Delta_r C_p^\circ/(\text{J K}^{-1}\,\text{mol}^{-1}) = 47$ was also calculated from the temperature dependency of their [97ROY/MOO3] reported p*K*s.	97ROY/MOO3
8.150		283.15	0		
8.085		288.15	0		
8.021		293.15	0		
7.957	21.20	298.15	0		
7.894		303.15	0		
7.835		308.15	0		
7.810		310.15	0		
7.776		313.15	0		
7.719		318.15	0		
7.661		323.15	0		
7.607		328.15	0		
7.87	21.55	298.15	0.1 M	Electrochemical cell with liquid junction; calorimetry. Fukada and Takahashi [98FUK/TAK] also obtained $\Delta_r C_p^\circ/(\text{J K}^{-1}\,\text{mol}^{-1}) = 56$ at $I = 0.1$ M from the temperature dependence of $\Delta_r H°$ over the range 278.15–323.15 K.	98FUK/TAK

Values adjusted to $T=298.15$ K and $I=0$

p*K*	$\Delta_r H°/(\text{kJ mol}^{-1})$	$\Delta_r C_p^\circ/(\text{J K}^{-1}\,\text{mol}^{-1})$	Reference
≈8.1			72GOO/IZA
7.91	17.6		76MCG/JOR
8.04			87KIT/ITO
	21.7		93ROI/BAC
7.957	21.20	47	97ROT/MOO3
8.08	20.9	48	98FUK/TAK

Comments: The results of Roy *et al.* [97ROY/MOO3] which are based on an electrochemical cell without liquid junction are judged to be the most accurate for the p*K* value. With the exception of the result of McGlothlin and Jordan [76MCG/JOR], we have adopted the respective averages of the reported $\Delta_r H°$ and $\Delta_r C_p^\circ$ values.

TABLE 7.38. HEPPSO

Other names	*N*-[2-hydroxyethyl]piperazine-*N*′-[2-hydroxypropanesulfonic acid]; CAS No. 68399-78-0
Empirical formula	$C_9H_{20}N_2O_5S$
Molecular weight	268.33

Ionization reaction

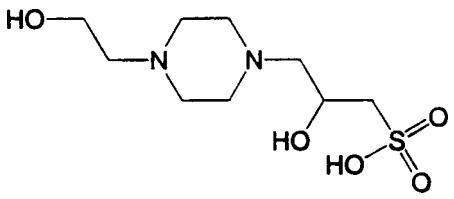
$$HL^{\pm} = H^+ + L^-, \text{ where } HL = C_9H_{20}N_2O_5S$$

Selected values at $T=298.15$ K and $I=0$:

$$pK = 8.042,\ \Delta_r G°/(\text{kJ mol}^{-1}) = 45.904,\ \Delta_r H°/(\text{kJ mol}^{-1}) = 23.70,\ \text{and}\ \Delta_r C_p^\circ/(\text{J K}^{-1}\,\text{mol}^{-1}) = 47$$

Evaluation: AAB

Structure:



Values from literature

p*K*	$\Delta_r H°/(\text{kJ mol}^{-1})$	*T*/K	I	Method(s) and comments	Reference
7.9		293.15	?		80FER/BRA
7.90		298.15	≈0.012 M	Potentiometric titration of sample (0.01–0.014 M) with 0.1 M HCl or 0.1 M NaOH.	87KIT/ITO
7.99		298.15	0.00520 M	Chromatography, based on ionic mobilities.	87POS/DEM
8.333		278.15	0	Electrochemical cell—no liquid junction. The value $\Delta_r C_p^\circ/(\text{J K}^{-1}\,\text{mol}^{-1}) = 47$ was also calculated from the temperature dependency of their [98ROY/CRA] p*K*s.	98ROY/CRA
8.184		288.15	0		
8.042	23.70	298.15	0		
7.973		303.15	0		
7.876		310.15	0		
7.775		318.15	0		
7.651		328.15	0		
7.79		298.15	0.1 M	Potentiometric titration—glass electrode.	98AZA/ORA

Values adjusted to $T=298.15$ K and $I=0$

p*K*	$\Delta_r H°/(\text{kJ mol}^{-1})$	$\Delta_r C_p^\circ/(\text{J K}^{-1}\,\text{mol}^{-1})$	Reference
≈8.0			80FER/BRA
8.00			87KIT/ITO
8.06			87POS/DEM
8.042	23.72	50	98ROY/CRA
8.00			98AZA/ORA

Comments: The results of Roy *et al.* [97ROY/CRA], which are based on an electrochemical cell with no liquid junction, are preferred. The remaining p*K* values are not too far from the selected value.

TABLE 7.39. L-Histidine

Other names	(*S*)-(−)-histidine; glyoxaline-5-alanine; His; H; histidine; α-amino-4-imidazole propionic acid; L-(−)-histidine; 2-amino-3-(1H-imidazol-4-yl)-propanoic acid; L-2-amino-3-(4-imidazolyl)propionic acid; (*S*)-α-amino-1H-imidazole-4-propionic acid; 4-(2-amino-2-carboxyethyl)imidazole; L-2-amino-3-(4-imidazolyl)propanoic acid; 2-amino-3-(4′-imidazolyl)propanoic acid; CAS No. 71-00-1
Empirical formula	$C_6H_9N_3O_2$
Molecular weight	155.16

Ionization reactions

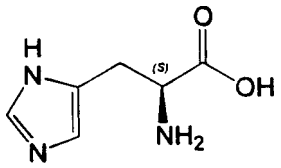
$$H_3L^{2+} = H^+ + H_2L^+ \quad (1)$$
$$H_2L^+ = H^+ + HL \quad (2)$$
$$HL = H^+ + L^- \quad (3)$$
where $HL = C_6H_9N_3O_2$

Selected values at $T = 298.15$ K and $I = 0$:

p$K = 1.5_4$, $\Delta_r G°/(\text{kJ mol}^{-1}) = 8.8$, and $\Delta_r H°/(\text{kJ mol}^{-1}) = 3.6$ for reaction (1)
p$K = 6.07$, $\Delta_r G°/(\text{kJ mol}^{-1}) = 34.65$, $\Delta_r H°/(\text{kJ mol}^{-1}) = 29.5$, and $\Delta_r C_p°/(\text{J K}^{-1}\,\text{mol}^{-1}) = 176$ for reaction (2)
p$K = 9.34$, $\Delta_r G°/(\text{kJ mol}^{-1}) = 53.31$, $\Delta_r H°/(\text{kJ mol}^{-1}) = 43.8$, and $\Delta_r C_p°/(\text{J K}^{-1}\,\text{mol}^{-1}) = -233$ for reaction (3)

Evaluation: reaction (1), DBA; reaction (2), BCA; reaction (3), CBA

Structure:



Values from literature

p*K*	$\Delta_r H°/(\text{kJ mol}^{-1})$	*T*/K	*I*	Method(s) and comments	Reference
			Reaction (1): $H_3L^{2+} = H_2L^+ + H^+$		
1.78		296.15	0	Potentiometric titration. Birch and Harris [30BIR/HAR] summarize results from the earlier literature.	30BIR/HAR
1.82		298.15	0	Potentiometric titration.	30SCH/KIR
1.82		293.15	0.01 M	Potentiometric titration—glass electrode.	52ALB
1.82		298.15	0.01 M	Potentiometric titration—glass electrode.	59LEB/RAB
1.77		298.15	0.2 M	Potentiometric titration—glass electrode.	63CHA/COT
1.98		273.15	0.25 M	Potentiometric titration—glass electrode. The value of $\Delta_r H°$ given here was calculated from p*K*s measured at four temperatures.	65AND/ZEB
1.79		288.15	0.25 M		
1.96	1.2	298.15	0.25 M		
1.85		313.15	0.25 M		
	≈5.0	298.15	0.1 M	Calorimetry.	69THO/SKI
2.02	3.0	298.15	0.16 M	Potentiometric titration—glass electrode; calorimetry.	70MEY/BAU
2.282	1.05	298.15	3.0 M	Potentiometric titration—glass electrode; calorimetry.	70WIL
2.00	−1.05	310.15	3.0 M	Potentiometric titration—glass electrode; calorimetry. The value $\Delta_r C_p°/(\text{J K}^{-1}\,\text{mol}^{-1}) = -176$ was obtained by measuring $\Delta_r H°$ at several temperatures.	71JON/WIL
2.22		294.15	0.01 M	Potentiometric titration—glass electrode.	74YOK/AIB
1.58		298.15	0.1 M	Potentiometric titration—glass electrode.	77BRO/PET
1.38		298.15	≈0.005 M	Potentiometric titration—glass electrode.	80JOZ/MUL
1.78	3.0	298.15	0.1 M	Potentiometric titration—glass electrode; calorimetry.	84ARE/CAL
1.45	≈−1	298.15	0	Potentiometric titration—glass electrode. The approximate value of $\Delta_r H°$ given here was calculated from p*K*s measured at three temperatures.	85DAN/DER
1.58	−5	298.15	0	Potentiometric titration—glass electrode. The value of $\Delta_r H°$ given here was calculated from p*K*s measured at three temperatures.	91DER/DES
1.68		298.15	0.1 M	Potentiometric titration—glass electrode.	92URB/KOZ
1.77		298.15	0.1 M	Potentiometric titration—glass electrode.	93GOC/VAH
			Reaction (2): $H_2L^+ = HL + H^+$		
5.97		296.15	0	Potentiometric titration. Birch and Harris [30BIR/HAR] summarize results from the earlier literature.	30BIR/HAR

Values from literature—Continued

pK	$\Delta_r H°/(\mathrm{kJ\,mol^{-1}})$	T/K	I	Method(s) and comments	Reference
6.04		298.15	0	Potentiometric titration.	30SCH/KIR
6.08		293.15	0.01 M	Potentiometric titration—glass electrode.	52ALB
6.14		293.15	0	Potentiometric titration—glass electrode. The DL-form of histidine was used.	53PER
6.17		298.15	≈0.20 M	Glass electrode; ion exchange.	57LI/DOO
6.00		298.15	0.01 M	Potentiometric titration—glass electrode.	59LEB/RAB
6.08		300.15	0.15 M	Electrochemical-glass electrode.	60BRO/DAV
6.16		298.15	0.1 M	Potentiometric titration—glass electrode.	61JAM/WIL
6.08		298.15	0.2 M	Potentiometric titration—glass electrode.	63CHA/COT
6.65		273.15	0.1 M	Polarography. The approximate value of $\Delta_r H°$ given here was	64AND/ROM
6.08	≈36.5	298.15	0.1 M	calculated from pKs measured at three temperatures	
5.66		318.15	0.1 M		
6.62		273.15	0.25 M	Potentiometric titration—glass electrode. The value of $\Delta_r H°$ given	65AND/ZEB
6.24		288.15	0.25 M	here was calculated from pKs measured at four temperatures.	
6.12	29.8	298.15	0.25 M		
5.88		313.15	0.25 M		
	29.9	298.15	0	Calorimetry.	69CHR/IZA
	30.5	298.15	0.1 M	Calorimetry.	69THO/SKI
6.17	29.3	298.15	0.16 M	Potentiometric titration—glass electrode; calorimetry.	70MEY/BAU
6.970	36.6	298.15	3.0 M	Potentiometric titration—glass electrode; calorimetry.	70WIL
	28.74	298.15	0.1 M	Calorimetry.	71BAR/PET
6.02	≈31.0	298.15	0.1 M	Potentiometric titration—glass electrode. The approximate value of	71HAY/MOR
5.80		310.15	0.1 M	$\Delta_r H°$ given here was calculated from pKs measured at three	
5.60		323.15	0.1 M	temperatures.	
6.68	29.1	310.15	3.0 M	Potentiometric titration—glass electrode; calorimetry. The value $\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}}) = -628$ was obtained by measuring $\Delta_r H°$ at several temperatures.	71JON/WIL
	30.9	?	?	Calorimetry.	71MAR/BER
6.17		294.15	0.01 M	Potentiometric titration—glass electrode.	74YOK/AIB
6.052		298.15	0.1 M	Potentiometric titration—glass electrode.	77BRO/PET
6.12		288.15	0	Potentiometric titration—glass electrode. The approximate value of	78VAS/ZAI
5.97	≈22.1	298.15	0	$\Delta_r H°$ given here was calculated from pKs measured at three	
5.86		308.15	0	temperatures.	
6.20		298.15	≈0.005 M	Potentiometric titration—glass electrode.	80JOZ/MUL
6.03	29.1	298.15	0.1 M	Potentiometric titration—glass electrode; calorimetry.	84ARE/CAL
5.97	27	298.15	0	Potentiometric titration—glass electrode. The approximate value of $\Delta_r H°$ given here was calculated from pKs measured at three temperatures.	85DAN/DER
6.24		283.15	0	Potentiometric titration—glass electrode. We have extrapolated the	85DAN/RIG2
5.95	≈28.9	298.15	0	pK values reported by Daniele *et al.* [85DAN/RIG2] to $I = 0$. The	
5.73		313.15	0	approximate value of $\Delta_r H°$ given here was calculated from pKs measured at three temperatures.	
5.99	32	298.15	0	Potentiometric titration—glass electrode. The value of $\Delta_r H°$ given here was calculated from pKs measured at three temperatures.	91DER/DES
6.06		298.15	0.1 M	Potentiometric titration—glass electrode.	92URB/KOZ
	≈55.3	298.15	0.1 M	Potentiometric titration—glass electrode; spectrophotometry. The approximate value of $\Delta_r H°$ given here was calculated from pKs measured at three temperatures.	91PAN/PAT
6.15		303.15	0.1 M		
5.85		313.15	0.1 M		
5.56		323.15	0.1 M		
6.14		298.15	0.1 M	Potentiometric titration—glass electrode.	93GOC/VAH
				Jardine *et al.* [2001JAR/CAL] determined the value $\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}}) = 176$ at $T = 298.15$ K by performing direct heat-capacity measurements on L-histidine solutions. Values of $\Delta_r C_p^\circ$ are presented for the temperature range $278.15 \leqslant T/\mathrm{K} \leqslant 393.15$. The pressure was 0.35 MPa.	2001JAR/CAL

Reaction (3): $HL = L^- + H^+$

8.97		296.15	0	Potentiometric titration. Birch and Harris [30BIR/HAR] summarize results from the earlier literature.	30BIR/HAR
9.12		298.15	0	Potentiometric titration.	30SCH/KIR
9.20		293.15	0.01 M	Potentiometric titration—glass electrode.	52ALB
9.40		293.15	0	Potentiometric titration—glass electrode. The DL-form of histidine was used in this study.	53PER

Values from literature—Continued

pK	$\Delta_r H°/(\mathrm{kJ\,mol^{-1}})$	T/K	I	Method(s) and comments	Reference
9.20		298.15	≈0.20 M	Glass electrode; ion exchange.	57LI/DOO
9.16		298.15	0.01 M	Potentiometric titration—glass electrode.	59LEB/RAB
9.12		300.15	0.15 M	Electrochemical-glass electrode.	60BRO/DAV
9.05		298.15	0.1 M	Potentiometric titration—glass electrode.	61JAM/WIL
9.17		298.15	0.2 M	Potentiometric titration—glass electrode.	63CHA/COT
9.97		273.15	0.1 M	Polarography.	64AND/ROM
9.18		298.15	0.1 M		
8.63		318.15	0.1 M		
9.81		273.15	0.25 M	Potentiometric titration—glass electrode. The value of $\Delta_r H°$ given here was calculated from pKs measured at four temperatures.	65AND/ZEB
9.46		288.15	0.25 M		
9.17	39.4	298.15	0.25 M		
8.86		313.15	0.25 M		
9.40		?	?	Potentiometric titration—glass electrode.	65HAR/STE
	43.6	298.15	0	Calorimetry.	69CHR/IZA
	46.0	298.15	0.1 M	Calorimetry.	69THO/SKI
9.21	43.6	298.15	0.16 M	Potentiometric titration—glass electrode; calorimetry.	70MEY/BAU
9.63	40.4	298.15	3.0 M	Potentiometric titration—glass electrode; calorimetry.	70WIL
	44.14	298.15	0.1 M	Calorimetry.	71BAR/PET
9.31	≈42.8	298.15	0.1 M	Potentiometric titration—glass electrode. The approximate value of $\Delta_r H°$ given here was calculated from pKs measured at three temperatures.	71HAY/MOR
9.025		310.15	0.1 M		
8.73		323.15	0.1 M		
9.37	34.6	310.15	3.0 M	Potentiometric titration—glass electrode; calorimetry. The value $\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}}) = -481$ was obtained by measuring $\Delta_r H°$ at several temperatures.	71JON/WIL
	44.7	?	?	Calorimetry.	71MAR/BER
9.28		294.15	0.01 M	Potentiometric titration—glass electrode.	74YOK/AIB
9.128		298.15	0.1 M	Potentiometric titration—glass electrode.	77BRO/PET
9.59		288.15	0	Potentiometric titration—glass electrode. The approximate value of $\Delta_r H°$ given here was calculated from pKs measured at three temperatures.	78VAS/ZAI
9.28	≈42.6	298.15	0		
9.09		308.15	0		
9.18		298.15	≈0.005 M	Potentiometric titration—glass electrode.	80JOZ/MUL
9.09	44.1	298.15	0.1 M	Potentiometric titration—glass electrode; calorimetry.	84ARE/CAL
9.27	42	298.15	0	Potentiometric titration—glass electrode. The approximate value of $\Delta_r H°$ given here was calculated from pKs measured at three temperatures.	85DAN/DER
9.52		283.15	0	Potentiometric titration—glass electrode. We have extrapolated the pK values reported by Daniele *et al.* [85DAN/RIG2] to $I = 0$. The approximate value of $\Delta_r H°$ given here was calculated from pKs measured at three temperatures.	85DAN/RIG2
9.07	≈48.1	298.15	0		
8.67		313.15	0		
9.30	46	298.15	0	Potentiometric titration—glass electrode. The value of $\Delta_r H°$ given here was calculated from pKs measured at four temperatures.	91DER/DES
	≈46.9	298.15	0.1 M	Potentiometric titration—glass electrode; spectrophotometry. The approximate value of $\Delta_r H°$ given here was calculated from pKs measured at three temperatures.	91PAN/PAT
9.05		303.15	0.1 M		
8.80		313.15	0.1 M		
8.55		323.15	0.1 M		
9.13		298.15	0.1 M	Potentiometric titration—glass electrode.	92URB/KOZ
9.24		298.15	0.1 M	Potentiometric titration—glass electrode.	93GOC/VAH
				Jardine *et al.* [2001JAR/CAL] determined the value $\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}}) = -233$ at $T = 298.15$ K by performing direct heat-capacity measurements on L-histidine solutions. Values of $\Delta_r C_p^\circ$ are presented for the temperature range $278.15 \leqslant T/\mathrm{K} \leqslant 393.15$. The pressure was 0.35 MPa.	2001JAR/CAL

Values adjusted to $T=298.15$ K and $I=0$

pK	$\Delta_r H°/(\mathrm{kJ\ mol^{-1}})$	$\Delta_r C_p^\circ/(\mathrm{J\ K^{-1}\ mol^{-1}})$	Reference
	Reaction (1): $H_3L^{2+}=H_2L^{+}+H^{+}$		
1.77			30BIR/HAR
1.82			30SCH/KIR
1.72			52ALB
1.73			59LEB/RAB
1.50			63CHA/COT
1.68	2.0		65AND/ZEB
	≈5.6		69THO/SKI
1.77	3.7		70MEY/BAU
≈1.81	2.4		70WIL
≈1.54	≈2.7	≈−176	71JON/WIL
2.12			74YOK/AIB
1.37			77BRO/PET
1.32			80JOZ/MUL
1.57	3.6		84ARE/CAL
1.45	≈−1		85DAN/DER
1.58	−5		91DER/DES
1.47			92URB/KOZ
1.56			93GOC/VAH
	Reaction (2): $H_2L^{+}=HL+H^{+}$		
6.07			30BIR/HAR
6.04			30SCH/KIR
5.99			52ALB
6.05			53PER
6.17			57LI/DOO
6.00			59LEB/RAB
6.11			60BRO/DAV
6.16			61JAM/WIL
6.08			63CHA/COT
6.08	≈36.5		64AND/ROM
6.12	29.8		65AND/ZEB
	29.9		69CHR/IZA
	30.5		69THO/SKI
6.17	29.3		70MEY/BAU
≈7.0	≈36.6		70WIL
	28.7		71BAR/PET
6.02	≈31.0		71HAY/MOR
≈6.9	≈37	≈−628	71JON/WIL
	≈31		71MAR/BER
6.10			74YOK/AIB
6.05			77BRO/PET
5.97	≈22		78VAS/ZAI
6.20			80JOZ/MUL
6.03	29.1		84ARE/CAL
5.97	27		85DAN/DER
5.95	≈29		85DAN/RIG2
5.99	32		91DER/DES
6.24	≈55		91PAN/PAT
6.06			92URB/KOZ
6.14			93GOC/VAH
		176	2001JAR/CAL
	Reaction (3): $HL=L^{-}+H^{+}$		
9.34			30BIR/HAR
9.12			30SCH/KIR
9.16			52ALB
9.27			53PER
9.47			57LI/DOO
9.25			59LEB/RAB
9.42			60BRO/DAV
9.26			61JAM/WIL
9.44			63CHA/COT
9.39			64AND/ROM
9.45	38.6		65AND/ZEB
≈9.4			65HAR/STE

Values adjusted to $T=298.15$ K and $I=0$—Continued

pK	$\Delta_r H°/(\text{kJ mol}^{-1})$	$\Delta_r C_p°/(\text{J K}^{-1}\text{ mol}^{-1})$	Reference
	43.6		69CHR/IZA
	45.4		69THO/SKI
9.46	42.9		70MEY/BAU
≈10.1	≈39		70WIL
	43.5		71BAR/PET
9.52	42.2		71HAY/MOR
≈10.1	≈39	≈−481	71JON/WIL
	≈45		71MAR/BER
9.26			74YOK/AIB
9.34			77BRO/PET
9.28	≈42.6		78VAS/ZAI
9.24			80JOZ/MUL
9.30	43.5		84ARE/CAL
9.27	42		85DAN/DER
9.07	≈48.1		85DAN/RIG2
9.30	46		91DER/DES
9.40	≈46		91PAN/PAT
9.34			92URB/KOZ
9.45			93GOC/VAH
		−233	2001JAR/CAL

Comments: The following selected values for the enthalpies of reaction are based on the averages of what we consider to be the most reliable of the calorimetric results: $\Delta_r H°/(\text{kJ mol}^{-1})=3.6$ for reaction (1) [70MEY/BAU, 84ARE/CAL], $\Delta_r H°/(\text{kJ mol}^{-1})=29.5$ for reaction (2) [69CHR/IZA, 69THO/SKI, 70MEY/BAU, 71BAR/PET, 84ARE/CAL], and $\Delta_r H°/(\text{kJ mol}^{-1})=43.8$ for reaction (3) [69CHR/IZA, 69THO/SKI, 70MEY/BAU, 71BAR/PET, 84ARE/CAL]. We adopt $pK_1=1.5_4$ based on the average of all of the results for reaction (1) excepting the very early results [30BIR/HAR, 30SCH/KIR, 52ALB], the values based on adjustment from results obtained at a very high ionic strength [70WIL, 71JON/WIL], and the discordant result of Yokoyama *et al.* [74YOK/AIB]. We adopt $pK_2=6.07$ based on the average of all of the results for reaction (2) excepting the values based on an adjustment from a very high ionic strength [70WIL, 71JON/WIL]. Finally, we adopt $pK_3=9.34$, dropping only the results based on measurements made at a high ionic strength [70WIL, 71JON/WIL] and the very early results [30BIR/HAR, 30SCH/KIR, 52ALB]. The value of pK_1 is the most uncertain of these values. The selected values of $\Delta_r C_p°$ for reactions (2) and (3) are based on the recent measurements of Jardine *et al.* [2001JAR/CAL].

In his review, Pettit [84PET] gives the following selected values that are pertinent to the ionic strength range 0.1 M≤I≤0.2 M: $pK_1=1.72\pm0.09$, $pK_2=6.05\pm0.03$, and $pK_3=9.11\pm0.02$. Adjustment of these pK values to $I=0$ gives: $pK_1=1.48$, $pK_2=6.05$, and $pK_3=9.35$. Considering the uncertainties, particularly in the value of pK_1, we consider these values to be in satisfactory agreement with our selected values. Additional studies, performed under a variety of conditions, are cited by Martell *et al.* [2001MAR/SMI], by Pettit and Powell [2000PET/POW], and by Pettit [84PET].

A carefully done study using an electrochemical cell without liquid junction could serve to better establish the pK values for these reactions.

TABLE 7.40. Hydrazine

Other names	CAS No. 302-01-2
Empirical formula	H_4N_2
Molecular weight	32.045

Ionization reactions

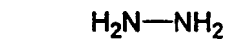
$$H_2L^{2+}=H^+ + HL^+ \quad (1)$$
$$HL^+=H^+ + L \quad (2)$$
where $L=H_4N_2$

Selected values at $T=298.15$ K and $I=0$:

p$K=-0.99$, $\Delta_r G°/(\text{kJ mol}^{-1})=-5.65$, and $\Delta_r H°/(\text{kJ mol}^{-1})=38.1$ for reaction (1)
p$K=8.02$, $\Delta_r G°/(\text{kJ mol}^{-1})=45.78$, and $\Delta_r H°/(\text{kJ mol}^{-1})=41.7$ for reaction (2)

Evaluation: reaction (1), CC; reaction (2), BB

Structure:



Values from literature

pK	$\Delta_r H°$/(kJ mol^{-1})	T/K	I	Method(s) and comments	Reference
			Reaction (1): $H_2L^{2+}=H^+ + HL^+$		
−0.88		293.15	0	Electrochemical measurements.	36SCH
3.85		303.15	1.0 M	Potentiometric titration—glass electrode.	67BAN/SIN
−0.67	37.2	298.15	0.42 M	Potentiometric titration—glass electrode; calorimetry.	69CHR/IZA
			Reaction (2): $HL^+=H^+ + L$		
8.23		≈293.15	≈0.10 M	Solubility.	29GIL
8.10		293.15	0	Electrochemical measurements.	36SCH
8.24		288.15	0	Electrochemical cell with liquid junction.	36WAR/SPU
7.99	≈36	298.15	0		
7.82		308.15	0		
7.95		298.15	?	Electrochemical cell with liquid junction.	41YUI
8.03		293.15	≈0.5 M	Glass electrode.	52SCH/ZOB
8.07		303.15	?	Potentiometric titration—glass electrode.	58HIN
7.87		303.15	1.0 M	Potentiometric titration—glass electrode.	67BAN/SIN
8.260		288.15	0	Potentiometric titration—glass electrode.	67SAL/LUM
8.139		293.15	0		
7.965	≈44	298.15	0		
7.750		308.15	0		
8.07		298.15	0.1 M	Potentiometric titration—glass electrode.	68ERL/FLI
	41.7	298.15	0	Calorimetry.	69CHR/IZA
8.04		298.15	0.5 M	Electrochemical cell with liquid junction.	70ASC/BRI
8.01		303.15	~0.1 M	Potentiometric titration—glass electrode.	70BIS/GOL
7.97		298.15	0.05–3.0 M	Potentiometric titration—glass electrode.	73KOM/NAU
7.99		?	0.05–2.7 M	Potentiometric titration—glass electrode.	74KOM/NAU

Values adjusted to $T=298.15$ K and $I=0$

pK	$\Delta_r H°$/(kJ mol^{-1})	Reference
	Reaction (1): $H_2L^{2+}=H^+ + HL^+$	
−0.99		36SCH
≈3.5		67BAN/SIN
−0.99	38.1	69CHR/IZA
	Reaction (2): $HL^+=H^+ + L$	
8.11		29GIL
7.98		36SCH
7.99	≈36	36WAR/SPU
7.95		41YUI
7.91		52SCH/ZOB
8.19		58HIN
7.99		67BAN/SIN
7.965	≈44	67SAL/LUM
8.07		68ERL/FLI
	41.7	69CHR/IZA
8.04		70ASC/BRI
8.13		70BIS/GOL
7.97		73KOM/NAU
7.99		74KOM/NAU

Comments: For reaction (1), we adopt the results from Schwarzenbach and from Christensen *et al.* [69CHR/IZA]. For reaction (2), we adopt the average value of the pKs reported in the literature. Christensen *et al.*'s [69CHR/IZA] calorimetric value for $\Delta_r H°$ for reaction (2) is preferred to the values of $\Delta_r H°$ obtained from the temperature dependency of the pK values.

TABLE 7.41. Imidazole

Other names	glyoxaline; 1H-imidazole; 1,3-diazole; 1,3-diaza-2,4-cyclopentadiene; *N*,*N*′-vinylene-formamidine; iminazole; IMD; *N*,*N*′-1,2-ethenediyl-methanimidamid; CAS No. 288-32-4
Empirical formula	$C_3H_4N_2$
Molecular weight	68.077

Ionization reaction

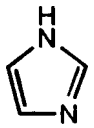
$$HL^+ = H^+ + L, \text{ where } L = C_3H_4N_2$$

Selected values at T=298.15 K and I=0:

$$pK = 6.993,\ \Delta_r G°/(\text{kJ mol}^{-1}) = 39.916,\ \Delta_r H°/(\text{kJ mol}^{-1}) = 36.64, \text{ and } \Delta_r C_p^\circ/(\text{J K}^{-1}\,\text{mol}^{-1}) = -9$$

Evaluation: AAA

Structure:



Values from literature

pK	$\Delta_r H°/(\text{kJ mol}^{-1})$	T/K	I	Method(s) and comments	Reference
6.95		298.15	0	Electrochemical cell with liquid junction.	38KIR/NEU
7.31		288.15	0.15 M	Potentiometric titration—glass electrode. The approximate value of $\Delta_r H°$ given here was calculated from pKs measured at three temperatures.	53TAN/WAG
7.12	≈32.3	298.15	0.15 M		
6.93		308.15	0.15 M		
7.50		277.65	0.16 M	Potentiometric titration—glass electrode.	54EDS/FEL
7.11		296.15	0.16 M		
7.09		298.15	0.135 M	Potentiometric titration—glass electrode.	55MIC/AND
	32.2	298.15	?	The value of $\Delta_r H°$ given here is a correction of the value of $\Delta_r H°$ reported previously by Gurd and Wilcox [56GUR/WIL].	57NOZ/GUR
7.12		300.15	0.15 M	Glass electrode.	60BRO/DAV
	36.78	298.15	0.2 M	Calorimetry.	62WAD
7.12		298.15	0.2 M	Potentiometric titration—glass electrode.	63CHA/COT
7.580		273.15	0	Electrochemical cell—no liquid junction. The value of $\Delta_r H°$ given here was calculated from pKs measured at several temperatures. The value $\Delta_r C_p^\circ/(\text{J K}^{-1}\,\text{mol}^{-1}) = 1$ was also calculated from the temperature dependency of their [66DAT/GRZ] reported pKs.	66DAT/GRZ
7.455		278.15	0		
7.333		283.15	0		
7.216		288.15	0		
7.102		293.15	0		
6.993	36.65	298.15	0		
6.887		303.15	0		
6.785		308.15	0		
6.685		313.15	0		
6.589		318.15	0		
6.496		323.15	0		
7.06	37.8	298.15	0.3 M	Potentiometric titration—glass electrode; calorimetry.	67HOL/WIL
6.986	36.7	298.15	0.011 M	Calorimetry.	68CHR/WRA
7.206		288.15	0	Potentiometric titration—glass electrode. The value of $\Delta_r H°$ given here was calculated from pKs measured at four temperatures.	69LUM/VIR
7.095		293.15	0		
6.979	37.3	298.15	0		
6.768		308.15	0		
7.33		298.15	1.0 M	Potentiometric titration—glass electrode.	69NAK/NAK
	36.44	298.15	0	Calorimetry.	70WOO/WIL
	35.7	?	?	Calorimetry.	71MAR/BER
7.00	36.81	298.15	0	Calorimetry.	72EAT/IZA
7.16	36.1	293.15	?	Calorimetry.	74MAR/MAR
7.02	33.27	298.15	0.15 M	Potentiometric; calorimetry.	76EIL/WES
7.46		283.15	0.15 M	Potentiometric titration. The value of $\Delta_r H°$ given here was calculated from pKs measured at several temperatures.	76PAI/JUL
7.37		288.15	0.15 M		
7.25		293.15	0.15 M		
7.14	36.1	298.15	0.15 M		
7.03		303.15	0.15 M		
6.94		308.15	0.15 M		
6.83		313.15	0.15 M		

Values from literature—Continued

pK	$\Delta_r H°$/(kJ mol^{-1})	T/K	I	Method(s) and comments	Reference
7.22	38.0	298.15	0.5 M	Potentiometric titration—glass electrode; calorimetry.	77BLA/ENE
7.10		293.15	0.1 M	Potentiometric titration—glass electrode.	77EVA/RAB
7.20	38.1	298.15	0.5 M	Potentiometric titration—glass electrode; calorimetry.	78MAR/HAN
	36.53	298.15	≈0.1 M	Calorimetry. We calculate $\Delta_r C_p^\circ$/(J K^{-1} mol^{-1})≈−11.	79BRE
	36.36	313.15	≈0.1 M		
7.18		298.15	0.5 M	Potentiometric titration—glass electrode.	85BAR/GAB
	36.8	298.15	0.1 M	Calorimetry.	85BEN/BOU
7.18		298.15	0.5 M	Potentiometric titration—glass electrode.	86BAR/GAB
7.246		283.15	0.1 M	Potentiometric titration—glass electrode. The value of $\Delta_r H°$ given here was calculated from pKs measured at four temperatures.	86VAS/MAC
7.319		288.15	0.1 M		
7.002	33.5	298.15	0.1 M		
6.723		313.15	0.1 M		
7.075	35.9	298.15	0.16 M	Potentiometric titration—glass electrode; spectrophotometry. The result given here is for $NaClO_4$ solutions.	88AND/BER
7.14		298.15	0.5 M	Potentiometric titration—glass electrode.	89BAR/LEN
6.963		298.15	0	Potentiometric titration—glass electrode.	89DAN/DER
7.02		298.15	0.1 M	Potentiometric titration—glass electrode.	89IMA/OCH
	≈47.0	298.15	0.1 M	Potentiometric titration—glass electrode; spectrophotometry. The	91PAN/PAT
7.10		303.15	0.1 M	approximate value of $\Delta_r H°$ given here was calculated from pKs	
6.80		313.15	0.1 M	measured at three temperatures.	
6.60		323.15	0.1 M		
7.09	36.59	298.15	0.1 M	Electrochemical cell with liquid junction; calorimetry. Fukada and Takahashi [98FUK/TAK] also obtained $\Delta_r C_p^\circ$/(J K^{-1} mol^{-1})=−16 at I=0.1 M from the temperature dependence of measured values of $\Delta_r H°$ over the range 278.15–323.15 K.	98FUK/TAK

Values adjusted to $T=298.15$ K and $I=0$

pK	$\Delta_r H°/(\mathrm{kJ\,mol^{-1}})$	$\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}})$	Reference
6.95			38KIR/NEU
7.12	≈32.3		53TAN/WAG
7.07			54EDS/FEL
7.09			55MIC/AND
	32.2		57NOZ/GUR
7.16			60BRO/DAV
	36.78		62WAD
7.12			63CHA/COT
6.993	36.65	1	66DAT/GRZ
7.06	37.8		67HOL/WIL
6.99	36.7		68CHR/WRA
6.98	37.3		69LUM/VIR
≈7.33			69NAK/NAK
	36.4		70WOO/WIL
	≈36		71MAR/BER
7.00	36.82		72EAT/IZA
7.05	36.7		74MAR/MAR
7.02	33.27		76EIL/WES
7.14	36.1		76PAI/JUL
7.22	38.0		77BLA/ENE
6.99			77EVA/RAB
7.20	38.1		78MAR/HAN
	36.53	≈−11	79BRE
7.18			85BAR/GAB
	36.8		85BEN/BOU
7.18			86BAR/GAB
7.00	33.5		86VAS/MAC
7.08	35.9		88AND/BER
7.14			89BAR/LEN
6.963			89DAN/DER
7.02			89IMA/OCH
7.21	≈47		89IMA/OCH
7.09	36.6	−16	98FUK/TAK

Comments: The results of Datta and Grzybowski [66DAT/GRZ], which were obtained by using an electrochemical cell with no liquid junction, provide the most reliable values for the pKs for imidazole. The value of $\Delta_r H°$ calculated from the temperature dependency of Datta and Grzybowski's [66DAT/GRZ] pKs is in excellent agreement with several calorimetric results [62WAD, 68CHR/WRA, 70WOO/WIL, 72EAT/IZA, 74MAR/MAR, 79BRE, 85BEN/BOU, 98FUK/TAK]. We adopt the average of the $\Delta_r H°$ values obtained from these several studies [62WAD, 68CHR/WRA, 70WOO/WIL, 72EAT/IZA, 74MAR/MAR, 79BRE, 85BEN/BOU, 98FUK/TAK]. We select the value $\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}})=-9$ based on the average of the results from three studies [66DAT/GRZ, 79BRE, 98FUK/TAK]. Approximate values {pK≈14.5 and $\Delta_r H°/(\mathrm{kJ\,mol^{-1}})\approx 75$} for the subsequent ionization of imidazole in extremely alkaline solution have also been reported [56WAL/ISE, 64GEO/HAN, 86VAS/MAC].

Additional studies, performed under a variety of conditions, are cited by Martell *et al.* [2001MAR/SMI], by Pettit and Powell [2000PET/POW], and by Sjöberg [97SJO]. The latter review [97SJO] gives recommended values for the ionization of imidazole up to $I=3.0$ M.

TABLE 7.42. Maleate

Other names	maleic acid; *cis*-butenedioic acid; 2-butenedioic acid; malenic acid; 2-butenedioic acid (*Z*)-; (*Z*)-butenedioic acid; *cis*-1,2-ethylenedicarboxylic acid; (*Z*)-1,2-ethylenedicarboxylic acid; maleinic acid; (*Z*)-2-butenedioic acid; cis-2-butenedioic acid; *cis*-ethylene-1,2-dicarboxylic acid; (*Z*)-but-2-ene-1,4-dioic acid; *cis*-maleic acid; (2*Z*)-2-butenedioic acid; Toxilic acid; CAS No. 110-16-7
Empirical formula	$C_4H_4O_4$
Molecular weight	116.07

Ionization reactions

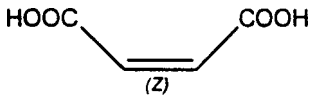
$$H_2L = H^+ + HL^- \quad (1)$$
$$HL^- = H^+ + L^{2-} \quad (2)$$
where $H_2L = C_4H_4O_4$

Selected values at $T=298.15$ K and $I=0$:

pK=1.92, $\Delta_r G°/(\text{kJ mol}^{-1}) = 10.96$, $\Delta_r H°/(\text{kJ mol}^{-1}) = 1.1$, and $\Delta_r C_p^\circ/(\text{J K}^{-1}\,\text{mol}^{-1}) \approx -21$ for reaction (1)
pK=6.27, $\Delta_r G°/(\text{kJ mol}^{-1}) = 35.79$, $\Delta_r H°/(\text{kJ mol}^{-1}) = -3.6$, and $\Delta_r C_p^\circ/(\text{J K}^{-1}\,\text{mol}^{-1}) \approx -31$ for reaction (2)

Evaluation: reaction (1), CBD; reaction (2), BBD

Structure:



Values from literature

pK	$\Delta_r H°/(\text{kJ mol}^{-1})$	T/K	I	Method(s) and comments	Reference
				Reaction (1): $H_2L = HL^- + H^+$	
2.04		291.15	?	Potentiometric titration—glass, antimony, and tungsten electrodes.	32BRI/ROB
1.92		298.15	0	Conductivity; potentiometric titration—quinhydrone electrode. The conductivity result is judged to be more reliable than the value obtained from the potentiometric titration.	36GER/VOG2
1.905		291.15	0	Electrochemical cell with liquid junction.	39ADE
≈2.34		298.15	0	Conductivity.	40TOP/DAV
1.910		298.15	0	Electrochemical cell—no liquid junction.	60DAH/LON
1.98		298.15	0	Glass electrode.	60GLA/LON
1.92		298.15	0.15 M	Potentiometric titration—glass electrode.	62DEB/KAI
	0.33	298.15	0	Calorimetry.	67CHR/IZA
1.98		298.15	0.2 M	Glass electrode.	67NOZ/MIS
1.65		298.15	1.0 M	Potentiometric titration—glass electrode.	67RAJ/MAR
1.77		298.15	0.1 M	Potentiometric titration—glass electrode.	70ROU/FEU
1.66		293.15	1.0 M	Electrochemical cell with liquid junction.	72TOM/MAG
1.60	−0.63	298.15	1.0 M	Potentiometric titration—glass electrode; calorimetry.	73DEL/MAL
2.038		298.15	0	Conductivity and electrochemical cell with no liquid junction.	74LOW/SMI
1.65		298.15	1.0 M	Potentiometric titration—glass electrode.	75OLI/SVA
1.70		298.15	0.1 M	Potentiometric titration—glass electrode.	76BON/MUS
1.91	1.9	298.15	0	Potentiometric titration—glass electrode; calorimetry.	78ARE/CAL
1.961		298.15	0	Electrochemical cell-glass electrode. The pK value given here is the average of the results obtained by Monk and Amira's [78MON/AMI] methods A to D.	78MON/AMI
1.962		288.15	0	Electrochemical cell—no liquid junction. The value of $\Delta_r H°$ given here was calculated from pKs measured at several temperatures. The value $\Delta_r C_p^\circ/(\text{J K}^{-1}\,\text{mol}^{-1}) \approx -21$ was also calculated from the temperature dependency of their [80DAS/DAS] reported pKs.	80DAS/DAS
1.945		293.15	0		
1.932	5.44	298.15	0		
1.909		303.15	0		
1.898		308.15	0		
1.887		313.15	0		
1.870		318.15	0		
1.77		298.15	0.15 M	Potentiometric titration—glass electrode.	83DAN/DER
1.92		310.15	0.01 M	Potentiometric titration—glass electrode.	83DAN/RIG
1.84		298.15	0.1 M	Potentiometric titration—glass electrode.	84ITO/IKE
1.80		298.15	0.1 M	Potentiometric titration—glass electrode.	84VEN/SWA
1.62		298.15	2.0 M	Potentiometric titration—glass electrode.	85ABD/MON
1.71		298.15	1.0 M	Coulometric titration.	85BIL/SJO

Values from literature—Continued

pK	$\Delta_r H°$/(kJ mol^{-1})	T/K	I	Method(s) and comments	Reference
1.88	2.0	298.15	0	Potentiometric titration—glass electrode. The value of $\Delta_r H°$ given here was calculated from pKs measured at several temperatures.	85DAN/DER
1.77		310.15	0.15 M	Potentiometric titration—glass electrode.	88BAL/CHR
1.94		283.15	0	Potentiometric titration—glass electrode.	90DER/DES
1.93		293.15	0		
1.93	0.0	298.15	0		
1.93		303.15	0		
1.94		313.15	0		
			Reaction (2): $HL^- = L^{2-} + H^+$		
≈6.15		291.15	?	Potentiometric titration—glass, antimony, and tungsten electrodes.	32BRI/ROB
6.23		298.15	0	Potentiometric titration—quinhydrone electrode.	36GER/VOG2
6.269		291.15	0	Electrochemical cell with liquid junction.	39ADE
6.332		298.15	0	Electrochemical cell—no liquid junction.	60DAH/LON
6.28		298.15	0	Glass electrode.	60GLA/LON
5.79		298.15	0.1 M	Potentiometric titration—glass electrode.	60YAS/YAM
5.91		298.15	0.15 M	Potentiometric titration—glass electrode.	62DEB/KAI
	−3.5	298.15	0	Calorimetry.	67CHR/IZA
5.81		298.15	0.2 M	Glass electrode.	67NOZ/MIS
5.61		298.15	1.0 M	Potentiometric titration—glass electrode.	67RAJ/MAR
5.85		298.15	0.1 M	Potentiometric titration—glass electrode.	70ROU/FEU
5.63		293.15	1.0 M	Electrochemical cell with liquid junction.	72TOM/MAG
5.62	−0.75	298.15	1.0 M	Potentiometric titration—glass electrode; calorimetry.	73DEL/MAL
5.63		298.15	1.0 M	Potentiometric titration—glass electrode.	75OLI/SVA
5.85		298.15	0.1 M	Potentiometric titration—glass electrode.	76BON/MUS
6.28	−2.34	298.15		Potentiometric titration—glass electrode; calorimetry. The pK and $\Delta_r H°$ values pertain, respectively, to $I = 0$ and $I = 0.1$ M.	78ARE/CAL
6.117		288.15	0	Electrochemical cell—no liquid junction. The value of $\Delta_r H°$ given here was calculated from pKs measured at several temperatures. The value $\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}}) \approx -31$ was also calculated from the temperature dependency of their [80DAS/DAS] reported pKs.	80DAS/DAS
6.128		293.15	0		
6.139	−3.72	298.15	0		
6.151		303.15	0		
6.160		308.15	0		
6.171		313.15	0		
6.184		318.15	0		
6.242		298.15	0	Electrochemical cell—glass electrode.	80MON/AMI
5.99		298.15	0.15 M	Potentiometric titration—glass electrode.	83DAN/DER
6.17		310.15	0.01 M	Potentiometric titration—glass electrode.	83DAN/RIG
5.83		298.15	0.1 M	Potentiometric titration—glass electrode.	84ITO/IKE
5.85		298.15	0.1 M	Potentiometric titration—glass electrode.	84VEN/SWA
5.62		298.15	2.0 M	Potentiometric titration—glass electrode.	85ABD/MON
5.58		298.15	1.0 M	Coulometric titration.	85BIL/SJO
6.33	−4.0	298.15	0	Potentiometric titration—glass electrode. The value of $\Delta_r H°$ given here was calculated from pKs measured at several temperatures.	85DAN/DER
6.18		298.15	≈0.012 M	Potentiometric titration—glass electrode.	87KIT/ITO
5.82		310.15	0.15 M	Potentiometric titration—glass electrode.	88BAL/CHR
6.306		283.15	0	Potentiometric titration—glass electrode.	90DER/DES
6.311		293.15	0		
6.318	−2.9	298.15	0		
6.329		303.15	0		
6.357		313.15	0		

Values adjusted to $T=298.15$ K and $I=0$

pK	$\Delta_r H°/(\mathrm{kJ\ mol^{-1}})$	$\Delta_r C_p^\circ/(\mathrm{J\ K^{-1}\ mol^{-1}})$	Reference
	Reaction (1): $H_2L=HL^-+H^+$		
≈2.2			32BRI/ROB
1.92			36GER/VOG2
1.90			39ADE
≈2.3			40TOP/DAV
1.910			60DAH/LON
1.98			60GLA/LON
2.16			62DEB/KAI
	0.33		67CHR/IZA
2.25			67NOZ/MIS
2.04			67RAJ/MAR
1.98			70ROU/FEU
2.05			72TOM/MAG
1.99	≈−1.8		73DEL/MAL
2.04			74LOW/SMI
2.04			75OLI/SVA
1.91			76BON/MUS
1.91	1.9		78ARE/CAL
1.96			78MON/AMI
1.932	5.44	≈−21	80DAS/DAS
2.01			83DAN/DER
2.01			83DAN/RIG
2.05			84ITO/IKE
2.01			84VEN/SWA
			85ABD/MON
2.10			85BIL/SJO
1.88	2.0		85DAN/DER
2.02			88BAL/CHR
1.93	0.0		90DER/DES
	Reaction (2): $HL^-=L^{2-}+H^+$		
6.59			32BRI/ROB
6.23			36GER/VOG2
6.28			39ADE
6.332			60DAH/LON
6.28			60GLA/LON
6.22			60YAS/YAM
6.40			62DEB/KAI
	−3.5		67CHR/IZA
6.34			67NOZ/MIS
6.40			67RAJ/MAR
6.28			70ROU/FEU
6.42			72TOM/MAG
6.41	≈−2.9		73DEL/MAL
6.42			75OLI/SVA
6.28			76BON/MUS
6.28	−3.6		78ARE/CAL
6.139	−3.72	≈−31	80DAS/DAS
6.242			80MON/AMI
6.23			83DAN/DER
6.33			83DAN/RIG
6.26			84ITO/IKE
6.28			84VEN/SWA
			85ABD/MON
6.37			85BIL/SJO
6.33	−4.0		85DAN/DER
6.37			87KIT/ITO
6.30			88BAL/CHR
6.32	−2.9		90DER/DES

Comments: We adopt pK=1.92 for reaction (1) and pK=6.27 for reaction (2) based on the results of several studies [36GER/VOG2, 39ADE, 60DAH/LON, 78ARE/CAL, 78MON/AMI, 80DAS/DAS, 80MON/AMI, 85DAN/DER, 90DER/DES] where the results were extrapolated to $I=0$. The uncertainty in these selected pK values is ≈0.05 and an additional, *very* careful study would be useful. The values of $\Delta_r H°$ obtained by Christensen *et al.* [67CHR/IZA] and by Arena *et al.* [78ARE/CAL] using calorimetry are judged to be the most reliable of the enthalpy values. For reaction (1), there is an approximate agreement with the values of $\Delta_r H°$ calculated from the temperature dependency of the pKs determined by Daniele *et al.* [85DAN/DER] and by De Robertis *et al.* [90DER/DES]. However, there is a large difference with the result of Das *et al.* [80DAS/DAS]. For reaction (2), there is a satisfactory agreement of the calorimetric results with most of the other results leading to $\Delta_r H°$ [80DAS/DAS, 85DAN/DER, 90DER/DES]. The values of $\Delta_r C_p^\circ$ are very approximate.

TABLE 7.43. 2-Mercaptoethanol

Other names	2-hydroxyethylmercaptan; β-mercaptoethanol; ethylene thioglycol; 2-hydroxy-1-ethanethiol; thioethylene glycol; thioglycol; monothioethylene glycol; CAS No. 60-24-2
Empirical formula	C_2H_6OS
Molecular weight	78.13

Ionization reaction

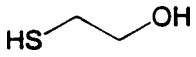
$$HL = H^+ + L^-, \text{ where } HL = C_2H_6OS$$

Selected values at $T = 298.15$ K and $I = 0$:

$$pK = 9.7_5, \ \Delta_r G°/(\text{kJ mol}^{-1}) = 55.7, \text{ and } \Delta_r H°/(\text{kJ mol}^{-1}) = 26.2$$

Evaluation: CB

Structure:



Values from literature

pK	$\Delta_r H°/(\text{kJ mol}^{-1})$	T/K	I	Method(s) and comments	Reference
9.5		298.15	0.15 M		54COL/LAZ
9.48		298.15	0.1 M		58SCH/GUB
9.77		?	?		61ARM/MER
9.44		298.15	0	Potentiometric titration—glass electrode.	62ANT/TEV
9.72	26.0	298.15	0.015 M	Spectrophotometry and calorimetry.	64IRV/NEL
9.52	27.2	293.15	0.10 M		65SCH/SCH
9.45		293.15	0.1 M	Electrochemical cell with liquid junction.	70AND/MAL
9.49		298.15	0.5 M	Potentiometric titration—glass electrode.	71DEB/VAN
9.61		298.15	1.0 M	Spectrophotometry.	71JEN/SAL
9.48		293.15	0.1 M	Potentiometric titration—glass electrode.	71TUN/SCH
9.49		298.15	0.5 M	Potentiometric titration—glass electrode.	72DEB/VAN
9.55		?	?		72SCH/GAU
9.49	25.7	298.15	0.5 M	Calorimetry	74DEB/HER
9.74	26.1	293.15	?	Potentiometric titration—glass electrode; calorimetry.	74MAR/MAR
9.62		298.15	0.3 M	NMR.	81BAC/RAB
9.412		298.15	0.15 M		82JAC/HAN
9.583		298.15	0.1 M	Potentiometric titration—glass electrode.	83ARN/CAN
9.5		298.15	0.1 M	Glass electrode; kinetic method.	84JOH/WIL
9.64		298.15	0.3 M	Potentiometric titration—glass electrode.	87HYN/ODO

Values adjusted to $T = 298.15$ K and $I = 0$

pK	$\Delta_r H°/(\text{kJ mol}^{-1})$	Reference
9.74		54COL/LAZ
9.69		58SCH/GUB
≈9.8		61ARM/MER
9.44		62ANT/TEV
9.82	25.7	64IRV/NEL
9.66	26.6	65SCH/SCH
9.58		70AND/MAL
9.83		71DEB/VAN
10.00		71JEN/SAL
9.61		71TUN/SCH
9.83		72DEB/VAN
9.76		72SCH/GAU
9.83		74DEB/HER
≈9.9	≈26	74MAR/MAR
9.92		81BAC/RAB
9.66		82JAC/HAN
9.80		83ARN/CAN
9.71		84JOH/WIL
9.94		87HYN/ODO

Comments: With the exception of two approximate results [61ARM/MER, 74MAR/MAR], we adopt the average of the above values, $\langle pK \rangle = 9.7_5$. The value $\Delta_r H°/(\text{kJ mol}^{-1}) = 26.2$ based on the average of the results of Schwarzenbach and Schellenberg [65SCH/SCH] and Irving *et al.* [64IRV/NEL] has been adopted.

TABLE 7.44. MES

Other names	2-[*N*-morpholino]ethanesulfonic acid; 4-morpholineethanesulfonic acid; morpholine-*N*-ethylenesulfonic acid; CAS No. 4432-31-9
Empirical formula	$C_6H_{13}NO_4S$
Molecular weight	195.24

Ionization reaction

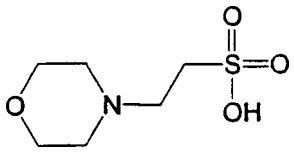
$$HL^{\pm} = H^+ + L^-, \text{ where } HL = C_6H_{13}NO_4S$$

Selected values at T=298.15 K and I=0:

$$pK = 6.270,\ \Delta_r G°/(\text{kJ mol}^{-1}) = 35.789,\ \Delta_r H°/(\text{kJ mol}^{-1}) = 14.8, \text{ and } \Delta_r C_p^\circ/(\text{J K}^{-1}\,\text{mol}^{-1}) = 5$$

Evaluation: AAA

Structure:



Values from literature

pK	$\Delta_r H°/(\text{kJ mol}^{-1})$	T/K	I	Method(s) and comments	Reference
6.18		273.15	0.01 M	Potentiometric titration—glass electrode.	66GOO/WIN
6.38		273.15	0.1 M		
6.17		273.15	0.2 M		
6.15		293.15	0.1 M		
5.98		310.15	0.1 M		
6.08	12.7	298.15	≈0.012 M	Potentiometric titration—glass electrode; and calorimetry. Dilute solutions (0.005–0.01 M) were titrated with 0.1 M NaOH or 0.1 M HCl.	76MCG/JOR
6.453		278.15	0	Electrochemical cell—no liquid junction. The value of $\Delta_r H°$ given here was calculated from pKs measured at several temperatures. The value $\Delta_r C_p^\circ/(\text{J K}^{-1}\,\text{mol}^{-1}) = 4$ was also calculated from the temperature dependency of their [76VEG/BAT] reported pKs.	76VEG/BAT
6.405		283.15	0		
6.359		288.15	0		
6.313		293.15	0		
6.270	14.6	298.15	0		
6.227		303.15	0		
6.187		308.15	0		
6.146		313.15	0		
6.108		318.15	0		
6.071		323.15	0		
6.10		298.15	≈0.012 M	Potentiometric titration of sample (0.01–0.014 M) with 0.1 M HCl or 0.1 M NaOH.	87KIT/ITO
6.13		298.15	0.0050 M	Chromatography, based on ionic mobilities.	87POS/DEM
6.02		298.15	0.16 M	Coulometric titration.	92GLA/HUL
5.96		310.15	0.16 M		
	15.0	298.15	0	Calorimetry	96TEW/SCH
6.453		278.15	0	Electrochemical cell—no liquid junction. The value of $\Delta_r H°$ given here was calculated from pKs measured at several temperatures. The value $\Delta_r C_p^\circ/(\text{J K}^{-1}\,\text{mol}^{-1}) = 4$ was also calculated from the temperature dependency of their [97ROY/MOO2] reported pKs.	97ROY/MOO2
6.405		283.15	0		
6.358		288.15	0		
6.313		293.15	0		
6.269	14.686	298.15	0		
6.227		303.15	0		
6.186		308.15	0		
6.168		310.15	0		
6.145		313.15	0		
6.106		318.15	0		
6.069		323.15	0		
6.034		328.15	0		
6.07	15.53	298.15	0.1 M	Electrochemical cell with liquid junction; calorimetry. Fukada and Takahashi [98FUK/TAK] also obtained $\Delta_r C_p^\circ/(\text{J K}^{-1}\,\text{mol}^{-1}) = 16$ at I = 0.1 M from the temperature dependence of $\Delta_r H°$ over the range 278.15–323.15 K.	98FUK/TAK

Values adjusted to $T=298.15$ K and $I=0$

pK	$\Delta_r H°/(\text{kJ mol}^{-1})$	$\Delta_r C_p^\circ/(\text{J K}^{-1}\text{ mol}^{-1})$	Reference
6.24			66GOO/WIN
6.17	12.4		76MCG/JOR
6.270	14.62	5	76VEG/BAT
6.20			87KIT/ITO
6.19			87POS/DEM
6.29			92GLA/HUL
	15.0		96TEW/SCH
6.269	14.68	3	97ROY/MOO2
6.28	14.9	8	98FUK/TAK

Comments: The pK values obtained by Vega and Bates [76VEG/BAT] and by Roy *et al.* [97ROY/MOO3] are in excellent agreement. The average of the $\Delta_r H°$ values from four studies has been adopted [76VEG/BAT, 97ROY/MOO3, 96TEW/SCH, 98FUK/TAK] has been adopted. The value $\Delta_r C_p^\circ/(\text{J K}^{-1}\text{ mol}^{-1})=5$ is based on the average of three studies [76VEG/BAT, 97ROY/MOO2, 98FUK/TAK].

TABLE 7.45. Methylamine

Other names	CAS No. 74-89-5
Empirical formula	CH_5N
Molecular weight	31.057

Ionization reaction

$$HL^+ = H^+ + L, \text{ where } L = CH_5N$$

Selected values at $T=298.15$ K and $I=0$:

$$pK = 10.645,\ \Delta_r G°/(\text{kJ mol}^{-1}) = 60.762,\ \Delta_r H°/(\text{kJ mol}^{-1}) = 55.34, \text{ and } \Delta_r C_p^\circ/(\text{J K}^{-1}\text{ mol}^{-1}) = 33$$

Evaluation: AAA

Structure:

Values from literature

pK	$\Delta_r H°/(\mathrm{kJ\,mol^{-1}})$	T/K	I	Method(s) and comments	Reference
10.70		298.15	0	Conductivity.	1894BRE
10.645		298.15	0	Electrochemical cell—no liquid junction.	28HAR/ROB
10.80		291.15	?	Potentiometric titration—glass electrode.	35BRI/WIL
10.81		291.15	≈0.02 M	Potentiometric titration—glass electrode.	36BRI/WIL
11.496		273.15	0	Electrochemical cell with liquid junction. The values of $\Delta_r H°$ given here was calculated from the pKs measured at several temperatures. The value $\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}}) = 32$ was also calculated from the temperature dependency of the pKs.	41EVE/WYN
11.130		283.15	0		
10.787		293.15	0		
	54.80	298.15	0		
10.466		303.15	0		
10.161		313.15	0		
9.876		323.15	0		
10.72		298.15	0.5 M	Glass electrode. This result was also given by Bjerrum [50BJE].	50BJE/LAM
10.74		296.15	0.20 M	Electrochemical cell—glass electrode.	56CHA/GAM
	56.5	298.15	0	Calorimetry.	64WAN/BAU
10.59	55.44	298.15	0	Potentiometric titration—glass electrode; calorimetry.	66PAR/CHR
	55.61	298.15	0	Calorimetry.	69CHR/IZA
10.67		298.15	0	Potentiometric titration—glass electrode.	71HAN/TEM
10.98	51.9	293.15	?	Potentiometric titration—glass electrode; calorimetry.	74MAR/MAR
10.81		298.15	≈0.5 M	NMR.	74RAB/OZU
	54.28	273.15	0	The value $\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}}) = 33$ was calculated from the temperature dependence of the $\Delta_r H°$ values.	77BER/OLO
	55.34	298.15	0		
	55.96	323.15	0		
	56.86	348.15	0		
	57.36	373.15	0		
	58.63	398.15	0		
10.64		298.15	0.1 M	Potentiometric titration—glass electrode.	80HAN
11.671		278.15	1.0 M	Potentiometric titration—glass electrode. The value of $\Delta_r H°$ was calculated from the temperature dependence of the pKs.	91MAR
11.294		288.15	1.0 M		
10.941	57.4	298.15	1.0 M		
10.618		308.15	1.0 M		
10.51		298.15	0.1 M	Potentiometric titration—glass electrode.	92SHO

Values adjusted to $T = 298.15$ K and $I = 0$

pK	$\Delta_r H°/(\mathrm{kJ\,mol^{-1}})$	$\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}})$	Reference
10.70			1894BRE
10.645			28HAR/ROB
10.80			35BRI/WIL
10.81			36BRI/WIL
10.62	54.80	32	41EVE/WYN
10.72			50BJE/LAM
10.74			56CHA/GAM
	56.5		64WAN/BAU
10.59	56.4		66PAR/CHR
	55.6		69CHR/IZA
10.67			71HAN/TEM
10.98	51.9		74MAR/MAR
10.81			74RAB/OZU
	55.34	33	77BER/OLO
10.64			80HAN
10.94	57.4		91MAR
10.51			92SHO

Comments: We adopt pK=10.645 based upon the very careful measurements of Harned and Robinson [28HAR/ROB] who used an electrochemical cell without liquid junction. This pK value is reasonably close to several other careful studies shown above. The values of $\Delta_r H°$ and $\Delta_r C_p^\circ$ determined by Bergström and Olofsson [77BER/OLO] using calorimetry are judged to be the most reliable.

TABLE 7.46. 2-Methylimidazole

Other names	2-methyl-1*H*-imidazole; 2-methylglyoxaline; 2-methyl-1,3-diazole; CAS No. 693-98-1
Empirical formula	$C_4H_6N_2$
Molecular weight	82.104

Ionization reaction

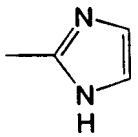
$$HL^+ = H^+ + L, \text{ where } L = C_4H_6N_2$$

Selected values at $T = 298.15$ K and $I = 0$:

$$pK = 8.0_1, \ \Delta_r G°/(\text{kJ mol}^{-1}) = 45.7, \text{ and } \Delta_r H°/(\text{kJ mol}^{-1}) = 36.8$$

Evaluation: CD

Structure:



Values from literature

p*K*	$\Delta_r H°/(\text{kJ mol}^{-1})$	*T*/K	I	Method(s) and comments	Reference
7.86		298.15	0	Electrochemical cell with liquid junction.	38KIR/NEU
8.13		298.15	1.0 M	Potentiometric titration—glass electrode.	69NAK/NAK
	38.7	?	?	Calorimetry	71MAR/BER
8.05		298.15	0.5 M	Spectrophotometry.	74LEN/KUL
7.88	38.8	298.15	0.1 M	Spectrophotometry and calorimetry.	76EIL/WES
8.41		283.15	0.15 M	Potentiometric titration—glass electrode. The value of $\Delta_r H°$ given here was calculated from p*K*s measured at several temperatures.	76PAI/JUL
8.29		288.15	0.15 M		
8.16		293.15	0.15 M		
8.02	41.8	298.15	0.15 M		
7.90		303.15	0.15 M		
7.79		308.15	0.15 M		
7.68		313.15	0.15 M		
8.10		293.15	0.20 M		77GUN/ZUB
8.05		298.15	0.5 M	Potentiometric titration—glass electrode.	85BAR/GAB
	32.9	298.15	0.1 M	Calorimetry.	85BEN/BOU
8.05		298.15	0.5 M	Potentiometric titration—glass electrode.	86BAR/GAB
8.18	40.7	298.15	0.1 M	Spectrophotometry and calorimetry.	88CAT/CLA
8.03		298.15	0.5 M	Potentiometric titration—glass electrode.	89BAR/LEN
7.91		298.15	0.1 M	Potentiometric titration—glass electrode.	89IMA/OCH
	≈28.0	298.15	0.1 M	Potentiometric titration—glass electrode; spectrophotometry. The approximate value of $\Delta_r H°$ given here was calculated from p*K*s measured at three temperatures.	91PAN/PAT
7.90		303.15	0.1 M		
7.80		313.15	0.1 M		
7.60		323.15	0.1 M		

Values adjusted to T=298.15 K and I=0

pK	$\Delta_r H°/(\mathrm{kJ\ mol^{-1}})$	Reference
7.86		38KIR/NEU
8.13		69NAK/NAK
	≈38.7	71MAR/BER
8.05		74LEN/KUL
7.88	38.76	76EIL/WES
8.02	41.9	76PAI/JUL
7.96		77GUN/ZUB
8.05		85BAR/GAB
	32.9	85BEN/BOU
8.05		86BAR/GAB
8.18	40.7	88CAT/CLA
8.03		89BAR/LEN
7.91		89IMA/OCH
8.03	≈28	91PAN/PAT

Comments: We adopt the average of the above pK values. The values for $\Delta_r H°$ are less consistent than is desirable. Nevertheless, we have adopted the average value $\langle \Delta_r H° \rangle/(\mathrm{kJ\ mol^{-1}}) = 36.8$.

TABLE 7.47. MOBS

Other names	4-[*N*-morpholino]butanesulfonic acid; CAS No. 115724-21-5
Empirical formula	$C_8H_{17}NO_4S$
Molecular weight	209.29

Ionization reaction

$$HL^{\pm} = H^+ + L^-, \text{ where } HL = C_8H_{17}NO_4S$$

There do not appear to be any thermodynamic data in the literature for the ionization of MOBS.

Structure:

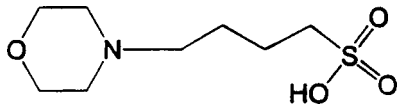


TABLE 7.48. MOPS

Other names	3-(*N*-morpholino)propanesulfonic acid; 4-morpholinepropanesulfonic acid; CAS No. 1132-61-2
Empirical formula	$C_7H_{15}NO_4S$
Molecular weight	209.26

Ionization reaction

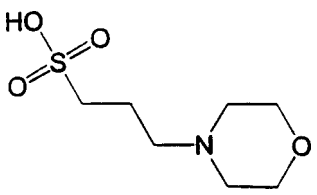
$$HL^{\pm} = H^+ + L^-, \text{ where } HL = C_7H_{15}NO_4S$$

Selected values at T=298.15 K and I=0:

$$pK = 7.184,\ \Delta_r G°/(\mathrm{kJ\ mol^{-1}}) = 41.007,\ \Delta_r H°/(\mathrm{kJ\ mol^{-1}}) = 21.1,\ \text{and}\ \Delta_r C_p^{\circ}/(\mathrm{J\ K^{-1}\ mol^{-1}}) = 25$$

Evaluation: AAA

Structure:



Values from literature

pK	$\Delta_r H°$(kJ mol^{-1})	T/K	I	Method(s) and comments	Reference
7.15		?	?	Few details are given.	72GOO/IZA
6.76	19.0	298.15	≈0.01 M	Potentiometric titration—glass electrode; and calorimetry. Dilute solutions (0.005–0.01 M) were titrated with 0.1 M NaOH or 0.1 M HCl.	76MCG/JOR
7.442		278.15	0	Electrochemical cell—no liquid junction. The value of $\Delta_r H°$ given here was calculated from pKs measured at several temperatures. The value $\Delta_r C_p^\circ$(J K^{-1} mol^{-1}) = 45 was also calculated from the temperature dependency of their [78SAN/BAT] reported pKs.	78SAN/BAT
7.376		283.15	0		
7.310		288.15	0		
7.247		293.15	0		
7.184	20.94	298.15	0		
7.123		303.15	0		
7.064		308.15	0		
7.006		313.15	0		
6.949		318.15	0		
6.893		323.15	0		
7.19		?	0	Mass spectrometric method.	83CAP
7.15		298.15	≈0.012 M	Potentiometric titration of sample (0.01–0.014 M) with 0.1 M HCl or 0.1 M NaOH.	87KIT/ITO
7.16		298.15	0.006 00 M	Based on measurement of ionic mobilities.	87POS/DEM
7.18		298.15	0.1 M	Potentiometric titration—glass electrode.	98AZA/ORA
7.447		278.15	0	Electrochemical cell—no liquid junction. The value of $\Delta_r H°$ given here was calculated from pKs measured at several temperatures. The value $\Delta_r C_p^\circ$/(J K^{-1} mol^{-1}) = 18 was also calculated from the temperature dependency of their [97ROY/MRA] reported pKs.	98ROY/MRA
7.304		288.15	0		
7.183	21.00	298.15	0		
7.121		303.15	0		
7.044		310.15	0		
6.948		318.15	0		
6.892		323.15	0		
6.842		328.15	0		
7.09	21.82	298.15	0.1 M	Electrochemical cell with liquid junction; calorimetry. Fukada and Takahashi [98FUK/TAK] also obtained $\Delta_r C_p^\circ$/(J K^{-1} mol^{-1}) = 39 at I = 0.1 M from the temperature dependence of $\Delta_r H°$ over the range 278.15–323.15 K.	98FUK/TAK

Values adjusted to T=298.15 K and I=0

pK	$\Delta_r H°$/(kJ mol^{-1})	$\Delta_r C_p^\circ$/(J K^{-1} mol^{-1})	Reference
≈7.4			72GOO/IZA
7.24	18.5		76MCG/JOR
7.184	20.94	45	78SAN/BAT
7.19			83CAP
7.25			87KIT/ITO
7.23			87POS/DEM
7.39			98AZA/ORA
7.183	21.00	18	98ROY/MRA
7.30	21.2	31	98FUK/TAK

Comments: The averages of the values determined by Sankar and Bates [78SAN/BAT] and by Roy *et al.* [98ROY/MRA] have been adopted. We have adopted the respective averages of the reported $\Delta_r H°$ and $\Delta_r C_p^\circ$ values from the studies of Roy *et al.* [98ROY/MRA] and of Fukada and Takahashi [98FUK/TAK].

TABLE 7.49. MOPSO

Other names	3-[*N*-morpholino]-2-hydroxypropanesulfonic acid; *β*-hydroxy-4-morpholinepropanesulfonic acid; morpholine-*N*-(2-hydroxypropanesulfonic acid); CAS No. 68399-77-9
Empirical formula	$C_7H_{15}NO_5S$
Molecular weight	225.26

Ionization reactions

$$H_2L^+ = H^+ + HL^\pm \quad (1)$$

$$HL^\pm = H^+ + L^- \quad (2)$$

where $HL = C_7H_{15}NO_5S$

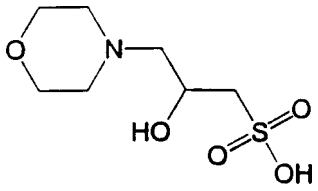
Selected values at $T = 298.15$ K and $I = 0$:

$pK = 0.060$ and $\Delta_r G°/(\text{kJ mol}^{-1}) = 0.34$ for reaction (1)

$pK = 6.90$, $\Delta_r G°/(\text{kJ mol}^{-1}) = 39.39$, $\Delta_r H°/(\text{kJ mol}^{-1}) = 25.0$, and $\Delta_r C_p^\circ/(\text{J K}^{-1}\,\text{mol}^{-1}) \approx 38$ for reaction (2)

Evaluation: reaction (1), A; reaction (2), BCB

Structure:



Values from literature

p*K*	$\Delta_r H°$(kJ mol^{-1})	*T*/K	I	Method(s) and comments	Reference
				Reaction (1): $H_2L^+ = H^+ + HL^\pm$	
0.060		298.15	0	Conductivity.	92WU/KOC
				Reaction (2): $HL^\pm = H^+ + L^-$	
6.95		293.15	?	Few details are given.	80FER/BRA
6.88		298.15	≈0.012 M	Potentiometric titration of sample (0.01–0.014 M) with 0.1 M HCl or 0.1 M NaOH.	87KIT/ITO
6.79		298.15	0.006 20 M	Based on measurements of ionic mobilities.	87POS/DEM
6.79		297.15	0	Cation exchange and conductivity. We have adjusted the reported results to $I = 0$; the adjustment is approximate.	90DAS/NAR
7.231		278.15	0	Electrochemical cell—no liquid junction. The value of $\Delta_r H°$ given here was calculated from p*K*s measured at several temperatures. The value $\Delta_r C_p^\circ/(\text{J K}^{-1}\,\text{mol}^{-1}) = 19$ was also calculated from the temperature dependency of their [93WU/BER] reported p*K*s.	93WU/BER
7.153		283.15	0		
7.076		288.15	0		
7.001		293.15	0		
6.929	24.14	298.15	0		
6.766		310.15	0		
6.599		323.15	0		
7.195		278.15	0	Electrochemical cell—no liquid junction. The p*K* value at $T = 288.15$ K in the published paper [97ROY/MOO3] contains a typographical error. The value given here is correct [2001ROY]. The value of $\Delta_r H°$ given here was calculated from p*K*s measured at several temperatures. The value $\Delta_r C_p^\circ(\text{J K}^{-1}\,\text{mol}^{-1}) = 56$ was also calculated from the temperature dependency of their [97ROY/MOO3] reported p*K*s.	97ROY/MOO3
7.113		283.15	0		
7.033		288.15	0		
6.954		293.15	0		
6.877	25.90	298.15	0		
6.801		303.15	0		
6.728		308.15	0		
6.698		310.15	0		
6.656		313.15	0		
6.585		318.15	0		
6.515		323.15	0		
6.81		298.15	0.1 M		98AZA/DEG

Values adjusted to T=298.15 K and I=0

pK	$\Delta_r H°/(\text{kJ mol}^{-1})$	$\Delta_r C_p^\circ/(\text{J K}^{-1}\,\text{mol}^{-1})$	Reference
	Reaction (1): $H_2L^+ = H^+ + HL^\pm$		
0.060			92WU/KOC
	Reaction (2): $HL^\pm = H^+ + L^-$		
7.09			80FER/BRA
6.98			87KIT/ITO
6.86			87POS/DEM
6.78			90DAS/NAR
6.929	24.14	19	93WU/BER
6.877	25.90	56	97ROY/MOO3
7.03			98AZA/DEG

Comments: The differences in the results of the two apparently careful studies of Wu *et al.* [93WU/BER] and of Roy *et al.* [97ROY/MOO3] are larger than one would expect. In the absence of a resolution of these differences, we have adopted the respective averages of the values reported for the thermodynamic quantities from these two studies.

TABLE 7.50. Oxalate

Other names	ethanedioic acid; oxalic acid; CAS No. 144-62-7
Empirical formula	$C_2H_2O_4$
Molecular weight	90.036

Ionization reactions

$$H_2L = H^+ + HL^- \quad (1)$$
$$HL^- = H^- + L^{2-} \quad (2)$$

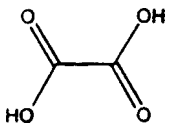
where $H_2L = C_2H_2O_4$

Selected values at T=298.15 K and I=0:

pK=1.27, $\Delta_r G°/(\text{kJ mol}^{-1})$=7.25, $\Delta_r H°/(\text{kJ mol}^{-1})$=−3.9, and $\Delta_r C_p^\circ/(\text{J K}^{-1}\,\text{mol}^{-1})\approx -231$ for reaction (1)
pK=4.266, $\Delta_r G°/(\text{kJ mol}^{-1})$=24.351, $\Delta_r H°/(\text{kJ mol}^{-1})$=−7.00, and $\Delta_r C_p^\circ/(\text{J K}^{-1}\,\text{mol}^{-1})\approx -231$ for reaction (2)

Evaluation: reaction (1), BBC; reaction (2), AAA

Structure:



Values from literature

pK	$\Delta_r H°/(\mathrm{kJ\,mol^{-1}})$	T/K	I	Method(s) and comments	Reference
				Reaction (1): $H_2L=HL^-+H^+$	
1.23		298.15	0	Conductivity.	31GAN/ING
≈1.14		298.15	0.2 M	Electrochemical cell with liquid junction.	38CAN/KIB
1.299		298.15	0	Electrochemical cell—no liquid junction. Kettler *et al.* [98KET/WES] recalculated the original data to obtain the value pK=1.27.	39PAR/GIB
1.340	≈11	298.15	0	Electrochemical cell—no liquid junction. The very approximate value of $\Delta_r H°$ given here was calculated from pKs measured at three temperatures.	39PAR/NIC
1.260		303.15	0		
1.275		308.15	0		
1.27		298.15	0	Conductivity.	41DAR
1.244		273.15	0	Electrochemical cell—no liquid junction. The value of $\Delta_r H°$ given here was calculated from pKs measured at several temperatures. Kettler *et al.* [98KET/WES] recalculated the original data to obtain the value pK=1.48.	61MCA/NAN
1.252		288.15	0		
1.252	−2.0	298.15	0		
1.286		308.15	0		
1.295		318.15	0		
1.270		298.15	0	Conductivity.	62MCD/LON
	−4.27	298.15	0	Calorimetry.	67CHR/IZA
1.47	−3.0	298.15	?	The values given here are based on the results of Maksimova and Yushkevich [66MAK/YUS].	67MAK
1.30	−4.0	298.15	0	Glass electrode. The value of $\Delta_r H°$ given here was calculated from pKs measured at several temperatures. A statistically meaningful value of $\Delta_r C_p^\circ$ could not be calculated.	69KUR/FAR
1.31		303.15	0		
1.32		308.15	0		
1.33		313.15	0		
1.34		318.15	0		
1.36		323.15	0		
1.36		328.15	0		
	−3.14	298.15	0	Calorimetry. Few details are given.	71VAS/KOC
1.05	≈−22	298.15	0	Potentiometric titration—glass electrode. The approximate value of $\Delta_r H°$ given here was calculated from pKs measured at four temperatures.	72NIK/ANT
1.35		323.15	0		
1.54		343.15	0		
1.73		363.15	0		
1.15	−2.93	298.15	2.0 M	Calorimetry. The same results are given in a subsequent publication [75BAR/DUB]. There is also evidence to suggest that the reported sign of $\Delta_r H°$ is in error and we have assumed that the reported value pertains to an exothermic reaction.	73BAR/RED
	−2.71	298.15	1.0 M	Calorimetry.	87LIN/GU
1.252		273.15	0	Electrochemical cell with liquid junction. The value of $\Delta_r H°$ given here was calculated from pKs measured at several temperatures. The value $\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}}) = -168$ was also calculated from the temperature dependency of their [91KET/PAL] reported pKs. These results were later recalculated by Kettler *et al.* [98KET/WES] (see below).	91KET/PAL
1.277	−4.1	298.15	0		
1.358		323.15	0		
1.463		348.15	0		
1.581		373.15	0		
1.709		398.15	0		
1.266		278.15	0	Potentiometric titration—glass electrode. The value of $\Delta_r H°$ given here was calculated from pKs measured at several temperatures. A statistically meaningful value of $\Delta_r C_p^\circ$ could not be calculated.	92DER/DES
1.280		283.15	0		
1.300		288.15	0		
1.306		293.15	0		
1.318	−4.0	298.15	0		
1.326		303.15	0		
1.331		308.15	0		
1.340		313.15	0		
1.346		318.15	0		
1.358		323.15	0		
1.443		273.15	0	Electrochemical cell with liquid junction. This set of results includes new data as well as a recalculation of their earlier results [91KET/PAL]. The value $\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}}) = -231$ was also calculated from the temperature dependency of their [98KET/WES] reported pKs.	98KET/WES
1.401	−0.7	298.15	0		
1.447		323.15	0		
1.540		348.15	0		
1.664		373.15	0		
1.811		398.15	0		
				Reaction (2): $HL^-=L^{2-}+H^+$	
4.19		298.15	0	Conductivity.	31GAN/ING
3.85		298.15	0.2 M	Electrochemical cell with liquid junction.	38CAN/KIB

Values from literature—Continued

pK	$\Delta_r H°/(\mathrm{kJ\,mol^{-1}})$	T/K	I	Method(s) and comments	Reference
4.228		273.15	0	Electrochemical cell—no liquid junction. The results of Harned and Fallon were later recalculated by Pinching and Bates [48PIN/BAT] who obtained pK=4.267 at T=298.15 K and I=0. A more extensive recalculation was done by Ketller *et al.* [98KET/WES] who obtained pK=4.262 at T=298.15 K and I=0. The value of $\Delta_r H°$ given here is based on the recalculated pKs of Kettler *et al.* [98KET/WES]. The value $\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}}) = -241$ was also calculated from the temperature dependency of these recalculated pKs.	39HAR/FAL
4.235		278.15	0		
4.244		283.15	0		
4.255		288.15	0		
4.268		293.15	0		
4.286	−7.06	298.15	0		
4.308		303.15	0		
4.331		308.15	0		
4.356		313.15	0		
4.388		318.15	0		
4.417		323.15	0		
4.300	≈−8.4	298.15	0	Electrochemical cell—no liquid junction. The approximate value of $\Delta_r H°$ given here was calculated from pKs measured at three temperatures. The results of Parton and Gibbons were later recalculated by Pinching and Bates [48PIN/BAT] who obtained pK=4.267 at T=298.15 K and I=0.	39PAR/GIB
4.320		303.15	0		
4.348		308.15	0		
4.276		298.15	0	Conductivity.	41DAR
4.201		273.15	0	Electrochemical cell—no liquid junction. The value of $\Delta_r H°$ given here was calculated from pKs measured at several temperatures. The value $\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}}) = -231$ was also calculated from the temperature dependency of their [48PIN/BAT] reported pKs. Kettler *et al.* [98KET/WES] later recalculated the results of Pinching and Bates. The pK values that they [98KET/WES] obtained were very close to the pK values reported by Pinching and Bates [48PIN/BAT].	48PIN/BAT
4.207		278.15	0		
4.218		283.15	0		
4.231		288.15	0		
4.247		293.15	0		
4.266	−7.00	298.15	0		
4.287		303.15	0		
4.312		308.15	0		
4.338		313.15	0		
4.369		318.15	0		
4.399		323.15	0		
4.30		298.15	0	Glass electrode.	62MCD/LON
	−6.28	298.15	0	Calorimetry.	67CHR/IZA
2.61	−9.7	298.15	?	The values given here are based on the results of Maksimova and Yushkevich [66MAK/YUS].	67MAK
4.26	≈−14	298.15	0	Potentiometric titration—glass electrode. The approximate value of $\Delta_r H°$ given here was calculated from pKs measured at four temperatures.	72NIK/ANT
4.40		323.15	0		
4.54		343.15	0		
4.71		363.15	0		
3.42	−1.17	298.15	2.0 M	Calorimetry. The same results are given in a subsequent publication [75BAR/DUB], except that the sign of $\Delta_r H°$ is different than previously reported. We have assumed that the reaction is exothermic in agreement with the other reported values for $\Delta_r H°$.	73BAR/RED
	−6.49	298.15	0	Calorimetry.	73VAS/SHE
4.34		310.15	0	Potentiometric titration—glass electrode.	81DAN/RIG
4.37		310.15	0	Potentiometric titration—glass electrode. We have adjusted the pKs measured at various ionic strengths ($0.01 \leqslant I/\mathrm{M} \leqslant 0.30$) to I=0.	83DAN/RIG
	−7.80	298.15	1.0 M	Calorimetry.	87LIN/GU
4.261		278.15	0	Potentiometric titration—glass electrode. The value of $\Delta_r H°$ given here was calculated from pKs measured at several temperatures. The value $\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}}) = -273$ was also calculated from the temperature dependency of their [90DER/DES] reported pKs.	90DER/DES
4.279		288.15	0		
4.314	−6.99	298.15	0		
4.361		308.15	0		
4.420		318.15	0		
4.489		328.15	0		
4.224		273.15	0	Electrochemical cell with liquid junction. The value of $\Delta_r H°$ given here was calculated from pKs measured at several temperatures. The value $\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}}) = -261$ was also calculated from the temperature dependency of their [91KET/PAL] reported pKs. These results were later combined with additional data and recalculated—see Kettler *et al.* [98KET/WES] below. The later results [98KET/WES] presumably supercede the earlier results [91KET/PAL].	91KET/PAL
4.275	−6.8	298.15	0		
4.408		323.15	0		
4.586		348.15	0		
4.792		373.15	0		
5.019		398.15	0		
5.264		423.15	0		
5.529		448.15	0		

Values from literature—Continued

pK	$\Delta_r H°/(\mathrm{kJ\,mol^{-1}})$	T/K	I	Method(s) and comments	Reference
4.224		278.15	0	Potentiometric titration—glass electrode. The value of $\Delta_r H°$ given here was calculated from pKs measured at several temperatures. The value $\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}}) = -327$ was also calculated from the temperature dependency of their [92DER/DES] reported pKs.	92DER/DES
4.230		283.15	0		
4.240		288.15	0		
4.254		293.15	0		
4.272	−7.03	298.15	0		
4.294		303.15	0		
4.319		308.15	0		
4.350		313.15	0		
4.384		318.15	0		
4.422		323.15	0		
4.199		273.15	0	Kettler *et al.* [98KET/WES] used an electrochemical cell with liquid junction to obtain additional information to supplement their earlier study [91KET/PAL] on the second ionization of oxalic acid. Additionally, they performed a recalculation of their earlier results [91KET/PAL] and in which they also included the recalculated data of Harned and Fallon [39HAR/FAL] and of Pinching and Bates [48PIN/BAT]. The pK and $\Delta_r H°$ values given here are based on this combined fit. The value $\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}}) = -229$ at $T = 298.15$ K was also obtained from this fit.	98KET/WES
4.264	−7.3	298.15	0		
4.399		323.15	0		
4.574		348.15	0		
4.780		373.15	0		
5.015		398.15	0		
5.280		423.15	0		
5.580		448.15	0		

Values adjusted to $T=298.15$ K and $I=0$

pK	$\Delta_r H°/(\mathrm{kJ\ mol^{-1}})$	$\Delta_r C_p^\circ/(\mathrm{J\ K^{-1}\ mol^{-1}})$	Reference
	Reaction (1): $H_2L=HL^-+H^+$		
1.23			31GAN/ING
≈1.41			38CAN/KIB
1.27[a]			39PAR/GIB
1.34	≈11		39PAR/NIC
1.27			41DAR
1.48[a]	−2.0		61MCA/NAN
1.27			62MCD/LON
	−4.3		67CHR/IZA
≈1.47	≈−3.0		67MAK
1.30	−4.0		69KUR/FAR
	−3.14		71VAS/KOC
1.05	≈−22		72NIK/ANT
≈1.6	≈−4.2		73BAR/RED
	≈−3.8		87LIN/GU
1.40[a]	−0.7[a]	−231[a]	91KET/PAL
1.32	−4.0		92DER/DES
1.40	−0.7	−231	98KET/WES
	Reaction (2): $HL^-=L^{2-}+H^+$		
4.19			31GAN/ING
4.38			38CAN/KIB
4.262[a]	−7.06	−241	39HAR/FAL
4.267[a]	≈−8.4		39PAR/GIB
4.276			41DAR
4.266	−7.00	−231	48PIN/BAT
4.30			62MCD/LON
	−6.28		67CHR/IZA
2.61	−9.7		67MAK
4.26	≈−14		72NIK/ANT
≈4.3	≈−3.7		73BAR/RED
	−6.49		73VAS/SHE
4.28			81DAN/RIG
4.31			83DAN/RIG
	≈−10.0		87LIN/GU
4.314	−6.99	−273	90DER/DES
4.264[a]	−7.3[a]	−229[a]	91KET/PAL
4.272	−7.03	−327	92DER/DES
4.264	−7.3	−229	98KET/WES

[a]Recalculated value (see above).

Comments: For the pK value for reaction (1), we have relied on the conductivity results of Darken [41DAR] and of McDougall and Long [62MCD/LON]. The value obtained from these two studies, p$K=1.27$, is also in agreement with the recalculated [98KET/WES] electrochemical result of Parton and Gibbons [39PAR/GIB]. There are four calorimetric studies [67CHR/IZA, 71VAS/KOC, 73BAR/RED, 87LIN/GU] that lead to $\langle \Delta_r H°/(\mathrm{kJ\cdot mol^{-1}})\rangle = -3.9$ and we have adopted this value. However, a recent careful study by Kettler *et al.* [98KET/WES] has called into question these earlier results. Some additional experiments and analysis are probably needed to fully resolve the discrepencies.

For reaction (2), we adopt the results of the very careful study of Pinching and Bates [48PIN/BAT] which was performed by using an electrochemical cell without a liquid junction. Their results [48PIN/BAT] are in excellent agreement with the results of Harned and Fallon [39HAR/FAL], of Nikolaeva and Antipina [72NIK/ANT] (at $T=298.15$ K), and of Kettler *et al.* [98KET/WES]. There is probably agreement with the results of Darken [41DAR], McDougall and Long [62MCD/LON], Daniele *et al.* [81DAN/RIG, 83DAN/RIG], and of De Robertis *et al.* [92DER/DES]. Many additional studies, performed under a variety of conditions, are cited by Martell *et al.* [2001MAR/SMI] and by Pettit and Powell [2000PET/POW].

TABLE 7.51. Phosphate

Other names	phosphate; phosphoric acid; dihydrogen phosphate; orthophosphate; CAS No. 7664-38-2
Empirical formula	H_3PO_4
Molecular weight	98.00

Ionization reactions

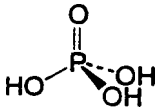
$$H_3PO_4 = H^+ + H_2PO_4^- \quad (1)$$
$$H_2PO_4^- = H^+ + HPO_4^{2-} \quad (2)$$
$$HPO_4^{2-} = H^+ + PO_4^{3-} \quad (3)$$

Selected values at $T=298.15$ K and $I=0$:

pK=2.148, $\Delta_r G°/(\text{kJ mol}^{-1})=12.261$, $\Delta_r H°/(\text{kJ mol}^{-1})=-8.0$, $\Delta_r C_p^\circ/(\text{J K}^{-1}\text{ mol}^{-1})=-141$ for reaction (1)
pK=7.198, $\Delta_r G°/(\text{kJ mol}^{-1})=41.087$, $\Delta_r H°/(\text{kJ mol}^{-1})=3.6$, $\Delta_r C_p^\circ/(\text{J K}^{-1}\text{ mol}^{-1})=-230$ for reaction (2)
pK=12.35, $\Delta_r G°/(\text{kJ mol}^{-1})=70.49$, $\Delta_r H°/(\text{kJ mol}^{-1})=16.0$, $\Delta_r C_p^\circ/(\text{J K}^{-1}\text{ mol}^{-1})=-242$ for reaction (3)

Evaluation: reaction (1), AAA; reaction (2), AAA; reaction (3), BCA

Structure:



Values from literature

pK	$\Delta_r H°/(\text{kJ mol}^{-1})$	T/K	I	Method(s) and comments	Reference
				Reaction (1): $H_3PO_4=H^+ + H_2PO_4^-$	
1.96		291.15	0	Conductivity.	09ABB/BRA
2.120		291.15	0	Electrochemical cell with liquid junction. The approximate value of $\Delta_r H°$ given here was calculated from pKs measured at three temperatures.	29BJE/UNM
2.161	≈−10.2	298.15	0		
2.232		310.15	0		
2.09		291.15	0	This result is a recalculation of the conductivity results of Noyes and Eastman [07NOY/EAS].	31LUG
2.048		276.15	0	Electrochemical cell—no liquid junction. The value of $\Delta_r H°$ given here was calculated from pKs measured at several temperatures. The value $\Delta_r C_p^\circ/(\text{J K}^{-1}\text{ mol}^{-1})=-197$ was also calculated from the temperature dependency of Nim's [34NIM] reported pKs.	34NIM
2.076		285.65	0		
2.124	−7.61	298.15	0		
2.185		310.65	0		
2.260		323.15	0		
1.983		293.15	0	Electrochemical cell.	36SCH/EPP
	−8.16	298.15	0	Calorimetry.	37PIT
2.126		298.15	0	Conductivity.	49MAS/CUL
2.056		273.15	0	Electrochemical cell—no liquid junction. The value of $\Delta_r H°$ given here was calculated from pKs measured at several temperatures. The value $\Delta_r C_p^\circ/(\text{J K}^{-1}\text{ mol}^{-1})=-154$ was also calculated from the temperature dependency of their [51BAT] reported pKs.	51BAT
2.073		278.15	0		
2.088		283.15	0		
2.107		288.15	0		
2.127		293.15	0		
2.148	−7.69	298.15	0		
2.171		303.15	0		
2.196		308.15	0		
2.224		313.15	0		
2.251		318.15	0		
2.277		323.15	0		
2.308		328.15	0		
2.338		333.15	0		
2.12		298.15	0	Potentiometric titration—glass electrode.	54BEU/RIE
2.12		311.15	0	Glass electrode.	58ELL/SHA
≈2.15		298.15	0	Conductivity. Results are also given for pressures to 200 MPa.	61ELL/AND
2.145		298.15	0	Glass electrode.	64SAL/SCH
	−8.66	298.15	0.5 M	Calorimetry.	66IRA/TAU

Values from literature—Continued

pK	$\Delta_r H°$/(kJ mol^{-1})	T/K	I	Method(s) and comments	Reference
2.151	−8.48	298.15	0	Electrochemical cell with liquid junction. Mesmer and Baes report values of lg Q, $\Delta_r H°$, and $\Delta_r C_p^\circ$ for the reaction ($H_3PO_4 + OH^- = H_2PO_4^- + H_2O$) over the temperature range 273.15 ≤ T/K ≤ 573.15. The results of Bates [51BAT] were also used in their data analysis. We have used Olofsson and Hepler's [75OLO/HEP] values of pK, $\Delta_r H°$, and $\Delta_r C_p^\circ$ for the ionization of water together with the results of Mesmer and Baes [74MES/BAE] to calculate the respective values of pK and $\Delta_r H°$ for the ionization reaction of H_3PO_4 given here. The calculated value of $\Delta_r C_p^\circ$ is −190 J K^{-1} mol^{-1}.	74MES/BAE
2.146		298.15	0	Calculated—primarily from data on osmotic coefficients and on buffer solutions.	76PIT/SIL
2.138		298.15	0	Electrochemical cell—glass electrode. The pK value given here is the average of the results obtained using Monk and Amira's [78MON/AMI] methods A, B, C, and D.	78MON/AMI
	−7.95	303.15	0	Calorimetry—based on analysis of enthalpies of dilution.	78MIL/DUE
	−8.6	298.15	0.15 M	Calorimetry.	81VAC/SAB
				Larson *et al.* [82LAR/ZEE] obtained $\Delta_r C_p^\circ$/(J K^{-1} mol^{-1}) = −128 from heat capacity measurements.	82LAR/ZEE
2.148	−11.7	298.15	0	Conductivity. The value of $\Delta_r H°$ given here was calculated from pKs	88REA
2.57		373.15	0	measured at several temperatures. The value $\Delta_r C_p^\circ$/(J K^{-1} mol^{-1})	
2.70		398.15	0	≈44 was also calculated from the temperature dependency of Read's	
2.84		423.15	0	[88REA] reported pKs. Read also reports results up to a pressure of	
3.02		448.15	0	200 MPa.	
3.20		473.15	0		
2.28		297.15	0	Conductivity.	90DAS/NAR
2.147	−7.65	298.15	0	Potentiometric titration—glass electrode. The value of $\Delta_r H°$ given here was calculated from pKs measured at several temperatures. The value $\Delta_r C_p^\circ$/(J K^{-1} mol^{-1}) ≈ −160 was also calculated from the temperature dependency of their [91DAN/DER] reported pKs.	91DAN/DER
				Reaction (2): $H_2PO_4^- = H^+ + HPO_4^{2-}$	
6.710		291.15	0	Conductivity.	09ABB/BRA
6.092		298.15	0	Conductivity.	20BLA
7.16		291.15	0	Electrochemical cell with liquid junction.	27COH
7.227		291.15	0	Electrochemical cell with liquid junction. The approximate value of	29BJE/UNM
7.207	≈5.7	298.15	0	$\Delta_r H°$ given here was calculated from pKs measured at three	
7.165		310.15	0	temperatures.	
7.218		293.15	0	Electrochemical cell—no liquid junction. The value of $\Delta_r H°$ given	33NIM
7.206	3.52	298.15	0	here was calculated from pKs measured at several temperatures. The	
7.197		303.15	0	value $\Delta_r C_p^\circ$/(J K^{-1} mol^{-1}) = −204 was also calculated from the	
7.192		308.15	0	temperature dependency of Nims' [33NIM] reported pKs.	
7.189		313.15	0		
7.189		318.15	0		
7.192		323.15	0		
7.224		298.15	0	Electrochemical cell with liquid junction.	34GUG/SCH
7.207		293.15	0	Electrochemical cell.	36SCH/EPP
	3.35	298.15	0	Calorimetry.	37PIT
7.190		298.15	0	Electrochemical cell—no liquid junction.	38RUL/LAM
7.314		273.15	0	Electrochemical cell—no liquid junction. The value of $\Delta_r H°$ given	43BAT/ACR
7.281		278.15	0	here was calculated from pKs measured at several temperatures. The	
7.254		283.15	0	value $\Delta_r C_p^\circ$/(J K^{-1} mol^{-1}) = −232 was also calculated from the	
7.230		288.15	0	temperature dependency of their [43BAT/ACR] reported pKs. Bates	
7.213		293.15	0	and Acree also summarize results from the earlier literature.	
7.198	4.06	298.15	0		
7.190		303.15	0		
7.185		308.15	0		
7.182		313.15	0		
7.181		318.15	0		
7.184		323.15	0		
7.188		328.15	0		
7.196		333.15	0		

Values from literature—Continued

pK	$\Delta_r H°/(\mathrm{kJ\,mol^{-1}})$	T/K	I	Method(s) and comments	Reference
7.3131		273.15	0	Electrochemical cell—no liquid junction. The value of $\Delta_r H°$ given here was calculated from pKs measured at several temperatures. The value $\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}}) = -237$ was also calculated from the temperature dependency of their [45BAT/ACR] reported pKs.	45BAT/ACR
7.2817		278.15	0		
7.2537		283.15	0		
7.2312		288.15	0		
7.2130		293.15	0		
7.1976	4.02	298.15	0		
7.1891		303.15	0		
7.1850		308.15	0		
7.1809		313.15	0		
7.1809		318.15	0		
7.1831		323.15	0		
7.1970		328.15	0		
7.1944		333.15	0		
7.22		298.15	0	Potentiometric titration—glass electrode.	54BEU/RIE
7.1988	4.14	298.15	0	Electrochemical cell—no liquid junction. The value of $\Delta_r H°$ given here was calculated from pKs measured at several temperatures. The value $\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}}) = -225$ was also calculated from the temperature dependency of their [57END/TEL] reported pKs. Results are also given for (H_2O+methanol).	57END/TEL
7.1891		303.15	0		
7.1814		308.15	0		
7.1777		313.15	0		
7.1776		318.15	0		
7.1796		323.15	0		
7.1859		328.15	0		
7.1918		333.15	0		
7.20		311.15	0	Glass electrode.	58ELL/SHA
7.2797		278.15	0	Electrochemical cell—no liquid junction. The value of $\Delta_r H°$ given here was calculated from pKs measured at several temperatures. The value $\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}}) = -203$ was also calculated from the temperature dependency of Grzybowski's [50GRZ2] reported pKs.	58GRZ2
7.2525		283.15	0		
7.2305		288.15	0		
7.2129		293.15	0		
7.2004	4.16	298.15	0		
7.1902		303.15	0		
7.1828		308.15	0		
7.1783		313.15	0		
7.1758		318.15	0		
7.1764		323.15	0		
	3.1	298.15	0	Calorimetry. We have used Olofsson and Hepler's [75OLO/HEP] value of $\Delta_r H°$ for the ionization of water together with Christensen and Izatt's [62CHR/IZA] results to calculate the value of $\Delta_r H°$ for the ionization reaction given here.	62CHR/IZA
7.18	3.2	298.15	0	Potentiometric titration—glass electrode. The value of $\Delta_r H°$ was calculated from pKs measured as a function of temperature. The same results were also reported later by Phillips *et al.* [65PHI/EIS].	63PHI/GEO
	2.51	298.15	0	Calorimetry.	66IRA/TAU
	3.35	298.15	0	Calorimetry.	67WU/WIT
7.05		298.15	0	Glass electrode.	69SAL/HAK
7.203	3.20	298.15	0	Electrochemical cell with liquid junction. Mesmer and Baes [74MES/BAE] report values of $\lg Q$, $\Delta_r H°$, and $\Delta_r C_p^\circ$ for the reaction ($H_2PO_4^- + OH^- = HPO_4^{2-} + H_2O$) over the temperature range $273.15 \leqslant T/\mathrm{K} \leqslant 573.15$. The results of Bates [51BAT] were included in their data analysis. We have used Olofsson and Hepler's [75OLO/HEP] values of pK, $\Delta_r H°$, and $\Delta_r C_p^\circ$ for the ionization of water together with the results of Mesmer and Baes [74MES/BAE] to calculate the respective values of pK and $\Delta_r H°$ for the ionization reaction of H_3PO_4 given here. The calculated value of $\Delta_r C_p^\circ$ is -256 $\mathrm{J\,K^{-1}\,mol^{-1}}$.	74MES/BAE
	4.70	298.15	0.15 M	Calorimetry.	81VAC/SAB
				Larson *et al.* [82LAR/ZEE] obtained $\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}}) = -220$ from heat-capacity measurements.	82LAR/ZEE
7.22		297.15	0	Conductivity.	90DAS/NAR
7.200	4.11	298.15	0	Potentiometric titration—glass electrode. The value of $\Delta_r H°$ given here was calculated from pKs measured at several temperatures. The value $\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}}) \approx -240$ was also calculated from the temperature dependency of their [91DAN/DER] reported pKs.	91DAN/DER
	4.07	298.15	0	Calorimetry. We calculate $\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}}) = -157$ from the temperature dependence of the $\Delta_r H°$ values.	93VAS/KOC
	2.25	308.15	0		
	0.93	318.15	0		

Values from literature—Continued

pK	$\Delta_r H°/(\mathrm{kJ\,mol^{-1}})$	T/K	I	Method(s) and comments	Reference
6.81	5.12	298.15	0.1 M	Electrochemical cell with liquid junction; calorimetry. Fukada and Takahashi [98FUK/TAK] also obtained $\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}}) = -187$ and $(\partial \Delta_r C_p^\circ/\partial T)_p/(\mathrm{J\,K^{-2}\,mol^{-1}}) = 2.0$ at $I = 0.1$ M from the temperature dependence of $\Delta_r H°$ over the range 278.15–323.15 K.	98FUK/TAK
				Reaction (3): $HPO_4^{2-} = H^+ + PO_4^{3-}$	
12.44		291.15	0	Conductivity.	09ABB/BRA
11.64		298.15	0	Conductivity.	20BLA
12.465		291.15	0	Electrochemical cell with liquid junction. The approximate value of $\Delta_r H°$ given here was calculated from pKs measured at three temperatures.	29BJE/UNM
12.325	≈25.5	298.15	0		
12.180		310.15	0		
	14.6	298.15	0	Calorimetry.	37PIT
12.36		298.15	0	Potentiometric titration—glass electrode.	54BEU/RIE
12.19		311.15	0	Glass electrode.	58ELL/SHA
12.375		298.15	0	Spectrophotometry—indicator method.	61VAN/QUI
12.0	14.6	298.15	0	Potentiometric titration—glass electrode. The value of $\Delta_r H°$ was calculated from pKs measured as a function of temperature. The same results were also reported later [65PHI/EIS].	63PHI/GEO
12.39	18.2	298.15	0	Calorimetry. We have used Olofsson and Hepler's [75OLO/HEP] values of pK and $\Delta_r H°$ for the ionization of water together with the results of Hansen *et al.* [65HAN/CHR] to calculate the respective values of pK and $\Delta_r H°$ for the ionization reaction of HPO_4^{2-} given here.	65HAN/CHR
12.39	18.6	298.15	0	Calorimetry. We have used Olofsson and Hepler's [75OLO/HEP] value of $\Delta_r H°$ for the ionization of water together with Papoff *et al.*'s [65PAP/TOR] results to calculate the value of $\Delta_r H°$ for the ionization reaction of HPO_4^{2-} given here. In a separate study, Papoff and Zambonin [65PAP/ZAM] reported results for higher ionic strengths.	65PAP/TOR
12.39	17.6	298.15	0	Calorimetry. We have used Olofsson and Hepler's [75OLO/HEP] values of pK and $\Delta_r H°$ for the ionization of water together with Christensen and Izatt's [66CHR/IZA] results to calculate the respective values of pK and $\Delta_r H°$ for the ionization reaction of HPO_4^{2-} given here.	66CHR/IZA
	11.3	298.15	0	Calorimetry.	66IRA/TAU
12.15		298.15	0	Glass electrode.	69SAL/HAK
	18.6	298.15	0.15 M	Calorimetry.	81VAC/SAB
				Larson *et al.* [82LAR/ZEE] obtained $\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}}) = -242$ from heat capacity measurements.	82LAR/ZEE
12.21		297.15	0	Conductivity.	90DAS/NAR
12.33	≈27	298.15	0	Potentiometric titration—glass electrode. The value of $\Delta_r H°$ given here was calculated from pKs measured at several temperatures. The value $\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}}) \approx -80$ was also calculated from the temperature dependency of their [91DAN/DER] reported pKs.	91DAN/DER

Values adjusted to $T=298.15$ K and $I=0$

pK	$\Delta_r H°/(\mathrm{kJ\ mol^{-1}})$	$\Delta_r C_p^\circ/(\mathrm{J\ K^{-1}\ mol^{-1}})$	Reference
	Reaction (1): $H_3PO_4=H^+ + H_2PO_4^-$		
1.99			09ABB/BRA
2.16	≈−10		29BJE/UNM
2.12			31LUG
2.124	−7.61	−197	34NIM
2.01			36SCH/EPP
	−8.16		37PIT
2.126			49MAS/CUL
2.148	−7.69	−154	51BAT
2.12			54BEU/RIE
2.06			58ELL/SHA
≈2.15			61ELL/AND
2.145			64SAL/SCH
	−8.66		66IRA/TAU
2.151	−8.48	−190	74MES/BAE
2.146			76PIT/SIL
2.138			78MON/AMI
	−7.31		78MIL/DUE
	−8.6		81VAC/SAB
		−128	82LAR/ZEE
2.148	−11.7		88REA
2.28			90DAS/NAR
2.147	−7.65	≈−160	91DAN/DER
	Reaction (2): $H_2PO_4^- = H^+ + HPO_4^{2-}$		
6.69			09ABB/BRA
6.09			20BLA
7.14			27COH
7.207	≈5.7		29BJE/UNM
7.206	3.52	−204	33NIM
7.224			34GUG/SCH
7.194			36SCH/EPP
	3.35		37PIT
7.190			38RUL/LAM
7.198	4.06	−232	43BAT/ACR
7.198	4.02	−237	45BAT/ACR
7.22			54BEU/RIE
7.199	4.14	−225	57END/TEL
7.22			58ELL/SHA
7.200	4.16	−203	58GRZ2
	3.1		62CHR/IZA
7.18	3.2		63PHI/GEO
	2.5		66IRA/TAU
	3.35		67WU/WIT
7.05			69SAL/HAK
7.203	3.20	−256	74MES/BAE
	4.70		81VAC/SAB
		−220	82LAR/ZEE
7.22			90DAS/NAR
7.20	4.11	≈−240	91DAN/DER
	4.07	−157	93VAS/KOC
7.24	3.9	−203	98FUK/TAK
	Reaction (3): $HPO_4^{2-} = H^+ + PO_4^{3-}$		
12.37			09ABB/BRA
11.64			20BLA
12.325	≈26		29BJE/UNM
	14.6		37PIT
12.36			54BEU/RIE
12.30			58ELL/SHA
12.375			61VAN/QUI
12.0	14.6		63PHI/GEO
12.39	18.2		65HAN/CHR
12.39	18.6		65PAP/TOR
12.39	17.6		66CHR/IZA

Values adjusted to T=298.15 K and I=0—Continued

pK	$\Delta_r H°$/(kJ mol^{-1})	$\Delta_r C_p^\circ$/(J K^{-1} mol^{-1})	Reference
	11.3		66IRA/TAU
12.15			69SAL/HAK
	18.6		81VAC/SAB
		−242	82LAR/ZEE
12.20			90DAS/NAR
12.33	≈27	≈−80	91DAN/DER

Comments: The selected pK values for the first and second ionization are based, respectively, on the very careful measurements of Bates [51BAT] and of Bates and Acree [43BAT/ACR, 45BAT/ACR]. Inspection of the above table shows that there are a substantial number of other careful investigations that yield pK values close to the results of Bates [51BAT] and Bates and Acree [43BAT/ACR, 45BAT/ACR] and that serve to confirm the correctness of these selected values. For the third ionization reaction, a number of studies [09ABB/BRA, 29BJE/UNM, 54BEU/RIE, 58ELL/SHA, 61VAN/QUI, 65HAN/CHR, 65PAP/TOR, 66CHR/IZA, 91DAN/DER] are consistent with the value pK_3=12.35 which we have adopted.

Excepting the values of $\Delta_r H°$ obtained from the results of Bjerrum and Unmack [29BJE/UNM] we have $\langle \Delta_r H° \rangle$/(kJ mol^{-1})=−8.0 for reaction (1). This is very close to the value −8.2 kJ mol^{-1} which is the average of the calorimetric results for this reaction. We have adopted the value $\langle \Delta_r H° \rangle$/(kJ mol^{-1})=−8.0. Similarly, for reaction (2), we have again excluded the approximate value calculated from the results of Bjerrum and Unmack [29BJE/UNM] and obtain $\langle \Delta_r H° \rangle$/(kJ mol^{-1})=3.69. Here, the average of the calorimetric results gives $\Delta_r H°$=3.57 kJ mol^{-1}. Giving some preference to the calorimetric results, we have adopted the value $\Delta_r H°$/(kJ mol^{-1})=3.6 for reaction (2). There is a larger uncertainty in the value of $\Delta_r H°$ for reaction (3) than in the values of $\Delta_r H°$ for reactions (1) and (2). Here we have adopted the average of all of the results excepting the discordant values obtained from two studies [29BJE/UNM, 91DAN/DER]. The selected value, $\Delta_r H°$/(kJ mol^{-1})=16.0, differs by only 0.5 kJ mol^{-1} from the average value obtained from the calorimetric results for this reaction.

For reaction (1) we adopt $\Delta_r C_p^\circ$/(J K^{-1} mol^{-1})=141 based on the results of the studies of Bates [51BAT] and of Larson *et al*. [82LAR/ZEE]. While a realistic uncertainty places both of these studies in agreement with the selected value, there are other careful studies [34NIM, 74MES/BAE, 91DAN/DER] that yield somewhat higher values for $\Delta_r C_p^\circ$ and additional measurements are needed to resolve this matter. We adopt $\Delta_r C_p^\circ$/(J K^{-1} mol^{-1})=−230 based on the average of the results obtained from the studies of Bates and Acree [43BAT/ACR, 45BAT/ACR] and of Larson *et al*. [82LAR/ZEE]. This value is very close to the average (−224 J K^{-1} mol^{-1}) of all of the results for this quantity excepting only that of Vasil'ev *et al*. [93VAS/KOC]. The selected value for $\Delta_r C_p^\circ$ for reaction (3) is based on the result of Larson *et al.* [82LAR/ZEE].

Additional studies, performed under a variety of conditions, are cited by Martell *et al.* [2001MAR/SMI] and by Pettit and Powell [2000PET/POW].

TABLE 7.52. Phthalate

Other names	1,2-benzenedicarboxylic acid; phthalic acid; phthalinic acid; napthalinic acid; benzene-1,2-dicarboxylic acid; CAS No. 88-99-3
Empirical formula	$C_8H_6O_4$
Molecular weight	166.13

Ionization reactions

$$H_2L = H^+ + HL^- \quad (1)$$
$$HL^- = H^+ + L^{2-} \quad (2)$$

where $H_2L = C_8H_6O_4$

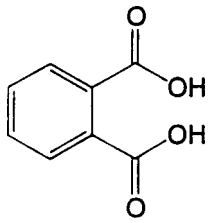
Selected values at T=298.15 K and I=0:

pK=2.950, $\Delta_r G°$/(kJ mol^{-1})=16.838, $\Delta_r H°$/(kJ mol^{-1})=−2.70, and $\Delta_r C_p^\circ$/(J K^{-1} mol^{-1})=−91 for reaction (1)

pK=5.408, $\Delta_r G°$/(kJ mol^{-1})=30.869, $\Delta_r H°$/(kJ mol^{-1})=−2.17, and $\Delta_r C_p^\circ$/(J K^{-1} mol^{-1})=−295 for reaction (2)

Evaluation: reaction (1), AAA; reaction (2), AAA

Structure:



Values from literature

pK	$\Delta_r H°$/(kJ mol^{-1})	T/K	I	Method(s) and comments	Reference
				Reaction (1): $H_2L=HL^-+H^+$	
2.9246		273.15	0	Electrochemical cell—no liquid junction. The value of $\Delta_r H°$ given here was calculated from pKs measured at several temperatures. The value $\Delta_r C_p^\circ$/(J K^{-1} mol^{-1}) = −91 was also calculated from the temperature dependency of their [45HAM/PIN] reported pKs. The previous literature containing pK values for this reaction is summarized.	45HAM/PIN
2.9273		278.15	0		
2.9314		283.15	0		
2.9367		288.15	0		
2.9429		293.15	0		
2.9496	−2.70	298.15	0		
2.9580		303.15	0		
2.9672		308.15	0		
2.9776		313.15	0		
2.9884		318.15	0		
3.0007		323.15	0		
3.0142		328.15	0		
3.0282		333.15	0		
2.76		298.15	0.1 M	Potentiometric titration—glass electrode.	56YAS/SUZ
2.76		298.15	0.1 M	Potentiometric titration—glass electrode.	60YAS/YAM
2.91		298.15	0.15 M	Potentiometric titration—glass electrode.	62DEB/KAI
2.917		288.15	0	Potentiometric titration—glass electrode. The value of $\Delta_r H°$ was calculated from the temperature dependence of the pKs.	75LUM/KAR
2.920		293.15	0		
2.927	−2.7	298.15	0		
2.948		308.15	0		
2.96	−1.2	298.15	0	Potentiometric titration—glass electrode; calorimetry.	78ARE/CAL
2.95		288.15	0.02 M	Spectrophotometry. The value of $\Delta_r H°$ given here was calculated from pKs measured at several temperatures. The value $\Delta_r C_p^\circ$/(J K^{-1} mol^{-1}) ≈ −102 was also calculated from the temperature dependency of their [82ASH/BUL] reported pKs.	82ASH/BUL
2.93	−2.2	298.15	0.02 M		
2.87		305.15	0.02 M		
3.00		323.15	0.02 M		
3.05		348.15	0.02 M		
3.09		373.15	0.02 M		
3.27		398.15	0.02 M		
3.36		423.15	0.02 M		
3.38		435.15	0.02 M		
3.42		448.15	0.02 M		
2.35		310.15	0	Potentiometric titration—glass electrode. We have extrapolated the results of Daniele *et al.* [83DAN/RIG] to $I=0$ to obtain the pK value given here.	83DAN/RIG
2.96	≈−7	298.15	0	Potentiometric titration—glass electrode. The approximate value of $\Delta_r H°$ was calculated from the temperature dependence of the pKs.	85DAN/DER
2.91	≈−2.1	298.15	0	Potentiometric titration—glass electrode. The approximate value of $\Delta_r H°$ was calculated from the temperature dependence of the pKs.	85CAP/DER
2.938		288.15	0	Electrochemical cell—no liquid junction. The value of $\Delta_r H°$ given here was calculated from pKs measured at several temperatures. The value $\Delta_r C_p^\circ$/(J K^{-1} mol^{-1}) ≈ −293 was also calculated from the temperature dependency of Azab's [87AZA] reported pKs. The same pK values at $I=0$ had been reported earlier by Azab *et al.* [86AZA/HAS].	87AZA
2.940		293.15	0		
2.945	−3.0	298.15	0		
2.960		303.15	0		
2.971		308.15	0		
2.83		298.15	0.1 M	Coulometric titration.	87GLA/SKR
2.935		297.15	0	Conductivity.	90DAS/NAR
2.929		278.15	0	Potentiometric titration—glass electrode. The value of $\Delta_r H°$ given here was calculated from pKs measured at several temperatures. The value $\Delta_r C_p^\circ$/(J K^{-1} mol^{-1}) = −124 was also calculated from the temperature dependency of their [90DER/DES] reported pKs.	90DER/DES
2.934		288.15	0		
2.947	−2.7	298.15	0		
2.966		308.15	0		
2.990		318.15	0		
3.019		328.15	0		
				Reaction (2): $HL^-=L^{2-}+H^+$	
5.4323		273.15	0	Electrochemical cell—no liquid junction. The value of $\Delta_r H°$ given here was calculated from pKs measured at several temperatures. The value $\Delta_r C_p^\circ$/(J K^{-1} mol^{-1}) = −297 was also calculated from the temperature dependency of their [45HAM/ACR] reported pKs. The previous literature containing pK values for this reaction is summarized.	45HAM/ACR
5.4180		278.15	0		
5.4096		283.15	0		
5.4052		288.15	0		
5.4048		293.15	0		
5.4083	−2.17	298.15	0		
5.4157		303.15	0		
5.4271		308.15	0		
5.4424		313.15	0		
5.4617		318.15	0		

Values from literature—Continued

pK	$\Delta_r H°/(\mathrm{kJ\,mol^{-1}})$	T/K	I	Method(s) and comments	Reference
5.4849		323.15	0		
5.5122		328.15	0		
5.5413		333.15	0		
4.92		298.15	0.1 M	Potentiometric titration—glass electrode.	56YAS/SUZ
4.92		298.15	0.1 M	Potentiometric titration—glass electrode.	60YAS/YAM
5.13		298.15	0.15 M	Potentiometric titration—glass electrode.	62DEB/KAI
	−0.3	298.15	0.1 M	Calorimetry.	70KUG/CAR
5.348		288.15	0	Potentiometric titration—glass electrode. The value of $\Delta_r H°$ was calculated from the temperature dependence of the pKs.	75LUM/KAR
5.356		293.15	0		
5.358	−2.2	298.15	0		
5.375		308.15	0		
5.35	−0.84	298.15		Potentiometric titration—glass electrode; calorimetry. The values of pK and $\Delta_r H°$ pertain, respectively, to $I=0$ and $I=0.1$ M.	78ARE/CAL
5.13		288.15	0.02 M	Spectrophotometry. The value of $\Delta_r H°$ given here was calculated from pKs measured at several temperatures. The value $\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}}) \approx -182$ was also calculated from the temperature dependency of their [82ASH/BUL] reported pKs.	82ASH/BUL
5.17	−8.9	298.15	0.02 M		
5.14		305.15	0.02 M		
5.28		323.15	0.02 M		
5.46		348.15	0.02 M		
5.75		373.15	0.02 M		
5.90		398.15	0.02 M		
6.13		423.15	0.02 M		
6.25		435.15	0.02 M		
6.35		448.15	0.02 M		
5.25		310.15	0	Potentiometric titration—glass electrode. We have extrapolated the results of Daniele *et al.* [83DAN/RIG] to $I=0$ to obtain the pK value given here.	83DAN/RIG
5.40	≈ -4	298.15	0	Potentiometric titration—glass electrode. The approximate value of $\Delta_r H°$ was calculated from the temperature dependence of the pKs.	85DAN/DER
5.41	≈ -6.7	298.15	0	Potentiometric titration—glass electrode. The approximate value of $\Delta_r H°$ was calculated from the temperature dependence of the pKs.	85CAP/DER
5.406		288.15	0	Electrochemical cell—no liquid junction. The value of $\Delta_r H°$ given here was calculated from pKs measured at several temperatures. The value $\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}}) \approx -234$ was also calculated from the temperature dependency of Azab's [87AZA] reported pKs.	87AZA
5.407		293.15	0		
5.411	−1.9	298.15	0		
5.416		303.15	0		
5.428		308.15	0		
4.96		298.15	0.1 M	Coulometric titration.	87GLA/SKR
5.381		297.15	0	Conductivity.	90DAS/NAR
5.416		278.15	0	Potentiometric titration—glass electrode. The value of $\Delta_r H°$ given here was calculated from pKs measured at several temperatures. The value $\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}}) = -97$ was also calculated from the temperature dependency of their [90DER/DES] reported pKs.	90DER/DES
5.406		288.15	0		
5.410	−4.0	298.15	0		
5.428		308.15	0		
5.457		318.15	0		
5.496		328.15	0		
				Ford *et al.* [2001FOR/CAL] obtained the value $\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}}) = -295$ at $T=298.15$ K and $p=0.35$ MPa from heat capacity measurements on phthalate solutions. Their measurements were carried out over the temperature range $278.15 \leqslant T/\mathrm{K} \leqslant 393.15$.	2001FOR/CAL

Values adjusted to T=298.15 K and I=0

pK	$\Delta_r H°/(\mathrm{kJ\,mol^{-1}})$	$\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}})$	Reference
	Reaction (1): $H_2L=HL^-+H^+$		
2.950	−2.70	−91	45HAM/PIN
2.97			56YAS/SUZ
2.97			60YAS/YAM
3.15			62DEB/KAI
2.927	−2.7		75LUM/KAR
2.96	−1.2		78ARE/CAL
3.05	−2.1	≈−102	82ASH/BUL
2.33			83DAN/RIG
2.96	≈−7		85DAN/DER
2.91	≈−2.1		85CAP/DER
2.945	−3.0	≈−293	87AZA
3.04			87GLA/SKR
2.94			90DAS/NAR
2.947	−2.7	−124	90DER/DES
	Reaction (2): $HL^-=L^{2-}+H^+$		
5.408	−2.17	−297	45HAM/ACR
5.35			56YAS/SUZ
5.35			60YAS/YAM
5.62			62DEB/KAI
	−1.5		70KUG/CAR
5.358	−2.2		75LUM/KAR
5.35	−2.1		78ARE/CAL
5.41	−9.6	≈−182	82ASH/BUL
5.22			83DAN/RIG
5.40	≈−4		85DAN/DER
5.41	≈−6.7		85CAP/DER
5.411	−1.9	≈−234	87AZA
5.39			87GLA/SKR
5.381			90DAS/NAR
5.410	−4.0	≈−97	90DER/DES
		−295	2001FOR/CAL

Comments: The exceptionally careful studies of Hamer *et al.* [45HAM/ACR, 45HAM/PIN] still provide the most reliable set of results for this system. There is satisfactory agreement with more recent determinations of the pK and $\Delta_r H°$ values [75LUM/KAR, 78ARE/CAL, 87AZA, 90DAS/NAR, 90DER/DES]. The recently determined [2001FOR/CAL] value of $\Delta_r C_p^\circ$ for reaction (2) is in excellent agreement with the value of $\Delta_r C_p^\circ$ calculated from the results of Hamer *et al.* [45HAM/ACR, 45HAM/PIN]. Many additional studies, performed under a variety of conditions, are cited by Martell *et al.* [2001MAR/SMI] and by Pettit and Powell [2000PET/POW].

TABLE 7.53. Piperazine

Other names	hexahydropyrazine; 1,4-diazacyclohexane; diethylenediamine; CAS No. 110-85-0
Empirical formula	$C_4H_{10}N_2$
Molecular weight	86.136

Ionization reactions

$$H_2L^{2+}=H^++HL^+ \quad (1)$$

$$HL^+=H^++L \quad (2)$$

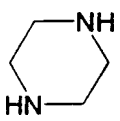
where $L=C_4H_{10}N_2$

Selected values at T=298.15 K and I=0:

pK=5.333, $\Delta_r G°/(\mathrm{kJ\,mol^{-1}})$=30.441, $\Delta_r H°/(\mathrm{kJ\,mol^{-1}})$=31.11, and $\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}})$=86 for reaction (1)
pK=9.731, $\Delta_r G°/(\mathrm{kJ\,mol^{-1}})$=55.545, $\Delta_r H°/(\mathrm{kJ\,mol^{-1}})$=42.89, and $\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}})$=75 for reaction (2)

Evaluation: reaction (1), AAB; reaction (2), AAB

Structure:



Values from literature

pK	$\Delta_r H°$/(kJ mol^{-1})	T/K	I	Method(s) and comments	Reference
			Reaction (1): $H_2L^{2+}=H^+ + HL^+$		
5.32		298.15	0	Potentiometric titration—glass electrode.	49SMI/SMI
5.68		293.15	0.1 M	Potentiometric.	52SCH/MAI
5.51		296.65	0.01 M	Potentiometric titration—glass electrode.	53PIC/COR
5.85		283.15	?	We calculate $\Delta H°$/(kJ mol^{-1})$\approx$26 from the temperature	61PAG/GOL
5.63		293.15	?	dependence of the pK values.	
5.54		303.15	?		
5.37		313.15	?		
5.60	29.8	298.15	0.1 M	Potentiometric titration—glass electrode; calorimetry.	63PAO/CIA
5.816		273.15	0	Electrochemical cell—no liquid junction. The value of $\Delta_r H°$ given	68HET/ROB
5.712		278.15	0	here was calculated from pKs measured at several temperatures. The	
5.614		283.15	0	value $\Delta_r C_p^\circ$/(J K^{-1} mol^{-1})=86 was also calculated from the	
5.518		288.15	0	temperature dependency of their [68HET/ROB] reported pKs.	
5.424		293.15	0		
5.333	31.11	298.15	0		
5.246		303.15	0		
5.153		308.15	0		
5.066		313.15	0		
4.981		318.15	0		
4.896		323.15	0		
6.044	33.6	298.15	1.0 M	Calorimetry.	72CRE/VAN
5.855		293.15	0.1 M	Potentiometric titration. The value $\Delta_r H°$/(kJ mol^{-1})=33.4 was	72ENE/HOU
5.76	31.8	298.15	0.1 M	obtained from the temperature dependence of the pKs. The value	
5.67		303.15	0.1 M	$\Delta_r H°$/(kJ mol^{-1})=28.9 was obtained by using calorimetry and is	
5.58		308.15	0.1 M	judged to be more reliable than the former value.	
5.47		313.15	0.1 M		
	28.9	298.15	0.1 M		
5.81		298.15	0.2 M	Potentiometric titration—glass electrode; spectrophotometry.	89CAS/URE
			Reaction (2): $HL^+=H^+ + L$		
9.70		298.15	0		49SMI/SMI
9.82		293.15	0.1 M	Potentiometric.	52SCH/MAI
9.78		296.65	0.01 M	Potentiometric titration—glass electrode.	53PIC/COR
10.12		283.15	?	We calculate $\Delta H°$/(kJ mol^{-1})=36.2 from the temperature	61PAG/GOL
9.89		293.15	?	dependence of the pK values.	
9.68		303.15	?		
9.48		313.15	?		
9.72	42.55	298.15	0.1 M	Potentiometric titration—glass electrode; calorimetry.	63PAO/CIA
10.407		273.15	0	Electrochemical cell—no liquid junction. The value of $\Delta_r H°$ given	68HET/ROB
10.259		278.15	0	here was calculated from pKs measured at several temperatures. The	
10.126		283.15	0	value $\Delta_r C_p^\circ$/(J K^{-1} mol^{-1})=75 was also calculated from the	
9.996		288.15	0	temperature dependency of their [68HET/ROB] reported pKs.	
9.864		293.15	0		
9.731	42.89	298.15	0		
9.609		303.15	0		
9.485		308.15	0		
9.367		313.15	0		
9.252		318.15	0		
9.142		323.15	0		
10.01	43.5	298.15	1.0 M	Calorimetry.	72CRE/VAN
9.88		293.15	0.1 M	Potentiometric titration. The value $\Delta_r H°$/(kJ mol^{-1})=34.8 was	72ENE/HOU
9.77	34.8	298.15	0.1 M	obtained from the temperature dependence of the pKs. The value	
9.69		303.15	0.1 M	$\Delta_r H°$/(kJ mol^{-1})=43.5 was obtained by using calorimetry and is	
9.58		308.15	0.1 M	judged to be more reliable than the former value.	
9.48		313.15	0.1 M		
	43.5	298.15	0.1 M		
10.20		298.15	?	Potentiometric titration—glass electrode; spectrophotometry.	85FRE/VIV
9.94		298.15	0.2 M	Glass electrode; spectrophotometry. The same result was also	89CAS/URE
				reported later by Castro *et al.* [93CAS/IBA].	

Values adjusted to T=298.15 K and I=0

pK	$\Delta_r H°$/(kJ mol^{-1})	$\Delta_r C_p^\circ$/(J K^{-1} mol^{-1})	Reference
	Reaction (1): $H_2L^{2+}=H^+ + HL^+$		
5.32			49SMI/SMI
5.38			52SCH/MAI
5.39			53PIC/COR
≈5.4	≈27		61PAG/GOL
5.39	30.42		63PAO/CIA
5.333	31.11	86	68HET/ROB
≈5.6	≈35		72CRE/VAN
5.55	29.5		72ENE/HOU
5.42			89CAS/URE
	Reaction (2): $HL^+=H^+ + L$		
9.70			49SMI/SMI
9.69			52SCH/MAI
9.74			53PIC/COR
9.78	≈36		61PAG/GOL
9.72	42.55		63PAO/CIA
9.731	42.89	75	68HET/ROB
≈10.0	≈44		72CRE/VAN
9.77	43.5		72ENE/HOU
10.20			85FRE/VIV
9.94			89CAS/URE

Comments: The results of Hetzer *et al.* [68HET/ROB] are based on an electrochemical cell without liquid junction and are judged to be the most reliable.

TABLE 7.54. PIPES

Other names	piperazine-N,N'-bis(2-ethanesulfonic acid); 1,4-piperazinediethanesulfonic acid; piperazine-1,4-bis(2-ethanesulfonic acid); CAS No. 5625-37-6
Empirical formula	$C_8H_{18}N_2O_6S_2$
Molecular weight	302.37

Ionization reaction

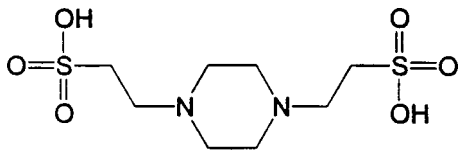
$$HL^{\pm}=H^+ + L^-, \text{ where } HL=C_8H_{18}N_2O_6S_2$$

Selected values at T=298.15 K and I=0:

$$pK=7.141,\ \Delta_r G°/(\text{kJ mol}^{-1})=40.761,\ \Delta_r H°/(\text{kJ mol}^{-1})=11.2,\ \text{and}\ \Delta_r C_p^\circ/(\text{J K}^{-1}\text{ mol}^{-1})=22$$

Evaluation: ABA

Structure:



Values from literature

pK	$\Delta_r H°/(\mathrm{kJ\,mol^{-1}})$	T/K	I	Method(s) and comments	Reference
7.02		273.15	0.1 M		66GOO/WIN
6.96		293.15	0.01 M		
6.82		293.15	0.1 M		
6.82		293.15	0.2 M		
6.70		310.15	0.1 M		
	11.46	298.15	≈0.1 M	Calorimetry.	71BER/STU
	11.30	278.15	?	Calorimetry.	71HIN/SHI
6.79	8.70	298.15	≈0.01 M	Potentiometric titration—glass electrode; and calorimetry. Dilute solutions.	76MCG/JOR
7.277		278.15	0	Electrochemical cell—no liquid junction. The value of $\Delta_r H°$ given here was calculated from pKs measured at several temperatures. The value $\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}}) = 134$ was also calculated from the temperature dependency of their [81ROY/GIB] reported pKs. The pK values given by Roy *et al.* [81ROY/GIB] correct some errors in the calculated pKs made in their previous report [80ROY/GIB].	81ROY/GIB
7.238		283.15	0		
7.207		288.15	0		
7.171		293.15	0		
7.141	11.83	298.15	0		
7.109		303.15	0		
7.073		308.15	0		
7.053		310.15	0		
7.035		313.15	0		
6.997		318.15	0		
6.959		323.15	0		
6.918		328.15	0		
	10.6	298.15	0	The value $\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}}) = 33$ was obtained from the temperature dependence of $\Delta_r H°$.	93ROI/BAC
6.71	11.45	298.15	0.1 M	Electrochemical cell with liquid junction; calorimetry. Fukada and Takahashi [98FUK/TAK] also obtained $\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}}) = 19$ at $I = 0.1$ M from the temperature dependence of $\Delta_r H°$ over the range 278.15–323.15 K.	98FUK/TAK

Values adjusted to T=298.15 K and I=0

pK	$\Delta_r H°/(\mathrm{kJ\,mol^{-1}})$	$\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}})$	Reference
7.02			66GOO/WIN
	10.8		71BER/STU
	12.0		71HIN/SHI
6.88	8.4		76MCG/JOR
7.141	11.83	134	81ROY/GIB
	10.6	33	93ROI/BAC
6.92	10.8	11	98FUK/TAK

Comments: The pK value reported by Roy *et al.* [81ROY/GIB] is based an electrochemical cell without liquid junction and is judged to be the most accurate value for this quantity. An average of the enthalpies, $\langle \Delta_r H°/(\mathrm{kJ\,mol^{-1}}) \rangle = 11.2$, is obtained from five investigations [71BER/STU, 71HIN/SHI, 81ROY/GIB, 93ROI/BAC, 98FUK/TAK] and has been selected. We have adopted the value $\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}}) = 22$ which is the average of the values obtained from the calorimetric measurements of Roig *et al.* [93ROI/BAC] and of Fukada and Takahashi [98FUK/TAK].

TABLE 7.55. POPSO

Other names	piperazine-*N*,*N*′-bis[2-hydroxypropanesulfonic acid]; CAS No. 68189-43-5
Empirical formula	$C_{10}H_{22}N_2O_8S_2$
Molecular weight	362.42

Ionization reaction

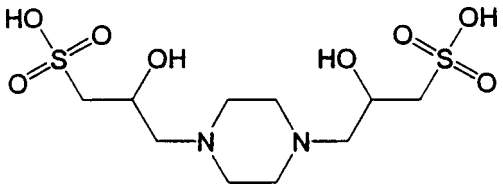
$$HL^{\pm} = H^+ + L^-, \text{ where } HL = C_{10}H_{22}N_2O_8S_2$$

Selected values at $T = 298.15$ K and $I = 0$:

$$pK \approx 8.0 \text{ and } \Delta_r G°/(\text{kJ mol}^{-1}) \approx 45.7$$

Evaluation: U

Structure:



Values from literature

p*K*	*T*/K	I	Method(s) and comments	Reference
7.85	293.15	?	Few details on the determination of the p*K* value are given.	80FER/BRA

Values adjusted to $T = 298.15$ K and $I = 0$

p*K*	$\Delta_r H°/(\text{kJ mol}^{-1})$	Reference
≈8.0		80FER/BRA

Comments: The adjustment to $T = 298.15$ K was done by using an estimated value of $\Delta_r H° = 11$ kJ mol^{-1} based on the value for PIPES. It was assumed that $I \approx 0.1$ M in making the adjustment for ionic strength.

TABLE 7.56. Pyrophosphate

Other names	pyrophosphoric acid; diphosphate; CAS No. 2466-09-3
Empirical formula	$H_4P_2O_7$
Molecular weight	177.98

Ionization reactions

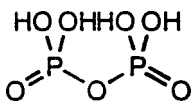
$$H_4P_2O_7 = H^+ + H_3P_2O_7^- \quad (1)$$
$$H_3P_2O_7^- = H^+ + H_2P_2O_7^{2-} \quad (2)$$
$$H_2P_2O_7^{2-} = H^+ + HP_2O_7^{3-} \quad (3)$$
$$HP_2O_7^{3-} = H^+ + P_2O_7^{4-} \quad (4)$$

Selected values at $T = 298.15$ K and $I = 0$

$pK = 0.83$, $\Delta_r G°/(\text{kJ mol}^{-1}) = 4.74$, $\Delta_r H°/(\text{kJ mol}^{-1}) = -9.2$, and $\Delta_r C_p°/(\text{J K}^{-1}\text{ mol}^{-1}) \approx -90$ for reaction (1)
$pK = 2.26$, $\Delta_r G°/(\text{kJ mol}^{-1}) = 12.90$, $\Delta_r H°/(\text{kJ mol}^{-1}) = -5.0$, and $\Delta_r C_p°/(\text{J K}^{-1}\text{ mol}^{-1}) \approx -130$ for reaction (2)
$pK = 6.72$, $\Delta_r G°/(\text{kJ mol}^{-1}) = 38.36$, $\Delta_r H°/(\text{kJ mol}^{-1}) = 0.5$, and $\Delta_r C_p°/(\text{J K}^{-1}\text{ mol}^{-1}) = -136$ for reaction (3)
$pK = 9.46$, $\Delta_r G°/(\text{kJ mol}^{-1}) = 54.00$, $\Delta_r H°/(\text{kJ mol}^{-1}) = 1.4$, and $\Delta_r C_p°/(\text{J K}^{-1}\text{ mol}^{-1}) = -141$ for reaction (4)

Evaluation: reaction (1), CDD; reaction (2), BCD; reaction (3), BBC; reaction (4), DCC

Structure:



Values from literature

pK	$\Delta_r H°/(\mathrm{kJ\,mol^{-1}})$	T/K	I	Method(s) and comments	Reference
			Reaction (1): $H_4P_2O_7 = H^+ + H_3P_2O_7^-$		
0.85		291.15	0	Conductivity.	09ABB/BRA
0.97		338.65	≈0.13 M	Potentiometric titration—glass electrode.	54MCG/CRO
1.0		333.18	0.44	Glass electrode; chemical analysis.	58OST
≈1.7		298.15	1.0 M	Potentiometric titration—glass electrode. This is a very approximate value.	61IRA/CAL
2.5		298.15	0.1 M	Potentiometric titration—glass electrode.	63JOH/WAN
	−12.6	298.15	0	Calorimetry.	66IRA/TAU
0.89	≈−8	298.15	0	Potentiometric titration—glass electrode. We have extrapolated the results of Mitra *et al.* [66MIT/MAL] to $I=0$ and calculated the approximate value of $\Delta_r H°$ that is given here from the temperature dependence of these pKs.	66MIT/MAL
1.10		323.15	0		
1.19		333.15	0		
1.07		338.15	0		
1.03		343.15	0		
0.75		298.15	1.0 M	Electrochemical cell with liquid junction.	68BOT/CIA
1.52		298.15	0.34 M	Amperometric titration.	70GOR/SID
	−6.11	298.15	0	Calorimetry.	70VAS/ALE
0.70		298.15	0	Glass electrode.	73EDW/FAR
1.33		298.15	1.0 M	Spectrophotometry; based on kinetic data.	73PAT/TAY
0.80		298.15	0.5 M	Potentiometric titration—glass electrode.	77THO/TAY
0.6		294.15	0.16 M	Ion exchange.	77WAK/HIS
1.38		298.15	0.5 M	Potentiometric titration—glass electrode.	82DEL/NIC
0.855		298.15	0.15 M	Potentiometric titration—glass electrode.	91DUF/WIL
0.89	−9.0	298.15	0	Potentiometric—few details are given. This study reports summary results of a potentiometric investigation in which pKs were determined as a function of temperature. The authors [94DES/FOT] have extrapolated their measured pKs to obtain values at $I=0$. They also report $\Delta_r H°/(\mathrm{kJ\,mol^{-1}}) = -9.0$ and $\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}}) = -90$ at $T=298.15$ K and $I=0$.	94DES/FOT
			Reaction (2): $H_3P_2O_7^- = H^+ + H_2P_2O_7^{2-}$		
1.96		291.15	0	Conductivity	09ABB/BRA
1.57		293.15	1.0 M	Electrochemical.	32MUU
2.52		293.15	0.1 M	Potentiometric titration.	50SCH/ZUR
2.27		298.15	0	Potentiometric titration—glass electrode.	54BEU/RIE
2.12		338.65	≈0.13 M	Potentiometric titration—glass electrode.	54MCG/CRO
2.64		298.15	0	Potentiometric titration—glass electrode.	57LAM/WAT
2.0		333.18	0.44 M	Glass electrode; chemical analysis.	58OST
1.68		303.15	1.0 M	Potentiometric titration—glass electrode.	58KIN/DAV
2.28		298.15	0	Electrochemical cell—glass electrode.	60NAS
2.5		273.15	0.1 M	Glass electrode. The value of $\Delta_r H°$ was calculated from pKs measured as a function of temperature.	61IRA
2.3		283.15	0.1 M		
2.0	≈11.7	298.15	0.1 M		
1.95		310.15	0.1 M		
1.98		323.15	0.1 M		
2.12		338.15	0.1 M		
1.75		298.15	1.0 M	Potentiometric titration—glass electrode.	61IRA/CAL
2.7		298.15	0.1 M	Potentiometric titration—glass electrode.	63JOH/WAN
	−12.6	298.15	0	Calorimetry.	66IRA/TAU
2.08	≈−19	298.15	0	Potentiometric titration—glass electrode. We have extrapolated the results of Mitra *et al.* [66MIT/MAL] to $I=0$ and calculated the approximate value of $\Delta_r H°$ that is given here from the temperature dependence of these pKs.	66MIT/MAL
2.15		323.15	0		
2.19		333.15	0		
2.10		338.15	0		
2.04		343.15	0		
1.40		298.15	1.0 M	Electrochemical cell with liquid junction.	68BOT/CIA
2.03		298.15	0.34 M	Amperometric titration.	70GOR/SID
	−4.33	298.15	0	Calorimetry.	70VAS/ALE2
2.19		298.15	0	Glass electrode.	73EDW/FAR
1.56		298.15	0.5 M	Potentiometric titration—glass electrode.	77THO/TAY
1.89		298.15	0.5 M	Potentiometric titration—glass electrode.	82DEL/NIC
1.94		298.15	0.1 M	Potentiometric titration—glass electrode; calorimetry.	85DAN/RIG
	−5	308.15	0.25 M		
1.765		298.15	0.15 M	Potentiometric titration—glass electrode.	91DUF/WIL

Values from literature—Continued

pK	$\Delta_r H°/(\mathrm{kJ\,mol^{-1}})$	T/K	I	Method(s) and comments	Reference
2.29	−12.0	298.15	0	Potentiometric—few details are given. This study reports summary results of a potentiometric investigation in which pKs were determined as a function of temperature. The authors [94DES/FOT] have extrapolated their measured pKs to obtain values at $I=0$. They also report $\Delta_r H°/(\mathrm{kJ\,mol^{-1}})=-12.0$ and $\Delta_r C_p°/(\mathrm{J\,K^{-1}\,mol^{-1}})=-130$ at $T=298.15$ K and $I=0$.	94DES/FOT
1.8		298.15	0.1 M	Potentiometric titration—glass electrode.	95JUR/MAR
1.66		298.15	0.2 M	Potentiometric titration—glass electrode.	95BUG/KIS
2.07		298.15	0.1 M	Potentiometric titration—glass electrode.	95LU/MOT
1.67		298.15	0.2 M	Potentiometric titration—glass electrode.	96ATK/KIS
				Reaction (3): $H_2P_2O_7^{2-}=H^+ + HP_2O_7^{3-}$	
6.54		291.15	0	Conductivity	09ABB/BRA
6.679		291.15	0	Electrochemical—hydrogen electrode.	28KOL/BOS2
6.704		303.15	0	Electrochemical cell with liquid junction—hydrogen and calomel electrodes.	28MOR
5.52		293.15	1.0 M	Electrochemical.	32MUU
6.57		298.15	0	Electrochemical cell—glass electrode.	49MON
6.08		293.15	0.1 M	Potentiometric titration.	50SCH/ZUR
6.63		298.15	0	Potentiometric titration—glass electrode.	54BEU/RIE
5.84		338.65	≈0.13 M	Potentiometric titration—glass electrode.	54MCG/CRO
6.76		298.15	0	Potentiometric titration—glass electrode.	57LAM/WAT
5.60		333.18	0.44 M	Glass electrode; chemical analysis.	58OST
6.70		298.15	0	Electrochemical cell—glass electrode.	60NAS
5.68		300.55	0.75 M	Potentiometric titration—glass electrode.	60YAM/DAV
6.17		273.15	0.1 M	Glass electrode. The value of $\Delta_r H°$ was calculated from pKs measured as a function of temperature.	61IRA
6.03		283.15	0.1 M		
6.12	−2.6	298.15	0.1 M		
6.13		310.15	0.1 M		
6.13		323.15	0.1 M		
6.16		338.15	0.1 M		
5.98		298.15	1.0 M	Potentiometric titration—glass electrode.	61IRA/CAL
	−1.25	298.15	0	Calorimetry.	62CHR/IZA
6.0		298.15	0.1 M	Potentiometric titration—glass electrode.	63JOH/WAN
6.23		298.15	0.1 M	Potentiometric titration—glass electrode.	64HAM/MOR
6.54	1.3	298.15	0	Potentiometric titration—glass electrode. The value of $\Delta_r H°$ was calculated from pKs measured as a function of temperature.	65PHI/EIS
	0.42	298.15	0	Calorimetry.	66IRA/TAU
6.38	≈−0.6	298.15	0	Potentiometric titration—glass electrode. We have extrapolated the results of Mitra *et al.* [66MIT/MAL] to $I=0$ and calculated the approximate value of $\Delta_r H°$ that is given here from the temperature dependence of these pKs.	66MIT/MAL
6.57		323.15	0		
6.58		333.15	0		
6.45		338.15	0		
6.31		343.15	0		
5.36		298.15	1.0 M	Electrochemical cell with liquid junction.	68BOT/CIA
6.96		298.15	1.0 M	Potentiometric titration—glass electrode. The result given here is for perchlorate ($c=1.0$ M). A significantly different result (pK=7.45) is obtained for nitrate ($c=1.0$ M).	68COS/FAR
6.12		298.15	0.1 M	Potentiometric titration—glass electrode.	68MCN/HAZ
6.25		298.15	0.34 M	Amperometric titration.	70GOR/SID
6.02		288.15	0.1 M	Potentiometric titration.	72FRE/STU
6.80		298.15	0	Glass electrode.	73EDW/FAR
5.99		278.15	0.1 M	Potentiometric titration—glass electrode. The value of $\Delta_r H°$ was calculated from pKs measured as a function of temperature. Perlmutter-Hayman and Secco [73PER/SEC] also give values of pK as a function of ionic strength at $T=298.15$ K. We have extrapolated these results to obtain the value pK=6.50 at $I=0$.	73PER/SEC
6.06		288.15	0.1 M		
6.06	≈−4.0	298.15	0.1 M		
6.07		308.15	0.1 M		
	0.54	298.15	0	Calorimetry.	73VAS/ALE
5.76		295.15	0.2 M	Electrochemical+kinetic.	75SIL/WEH
	3.43	278.15	0	Calorimetry. The value $\Delta_r C_p°/(\mathrm{J\,K^{-1}\,mol^{-1}})=-136$ was calculated from the temperature dependence of $\Delta_r H°$.	75VAS/ALE
	1.76	283.15	0		
	0.54	298.15	0		
	−0.71	308.15	0		
5.54		298.15	0.5 M	Potentiometric titration—glass electrode.	77THO/TAY
6.02		288.15	0.1 M	Potentiometric titration—glass electrode.	78FRE/STU

Values from literature—Continued

pK	$\Delta_r H°/(\mathrm{kJ\,mol^{-1}})$	T/K	I	Method(s) and comments	Reference
5.79		298.15	0.1 M	Potentiometric titration—glass electrode.	79CRA/MOO
5.97		298.15	0.5 M	Potentiometric titration—glass electrode.	82DEL/NIC
6.18		298.15	0.1 M	Potentiometric titration—glass electrode; calorimetry.	85DAN/RIG
	3	308.15	0.25 M		
5.82		298.15	0.3 M	Potentiometric titration—glass electrode.	87HYN/ODO
6.34		298.15	0.15 M	Potentiometric titration—glass electrode.	88JAC/VOY
5.876		298.15	0.15 M	Potentiometric titration—glass electrode.	91DUF/WIL
6.72	0.0	298.15	0	Potentiometric—few details are given. This study reports summary results of a potentiometric investigation in which pKs were determined as a function of temperature. The authors [94DES/FOT] have extrapolated their measured pKs to obtain values at $I=0$. They also report $\Delta_r H°/(\mathrm{kJ\,mol^{-1}})=0.0$ and $\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}})=-210$ at $T=298.15$ K and $I=0$.	94DES/FOT
5.88		298.15	0.2 M	Potentiometric titration—glass electrode.	95BUG/KIS
5.95		298.15	0.1 M	Potentiometric titration—glass electrode.	95JUR/MAR
6.09		298.15	0.1 M	Potentiometric titration—glass electrode.	95LU/MOT
5.87		298.15	0.2 M	Potentiometric titration—glass electrode.	96ATK/KIS
				Reaction (4): $HP_2O_7^{3-}=H^+ + P_2O_7^{4-}$	
8.44		291.15	0	Conductivity	09ABB/BRA
9.391		291.15	0	Electrochemical—hydrogen electrode.	28KOL/BOS2
9.880		303.15	0	Electrochemical cell with liquid junction—hydrogen and calomel electrodes.	28MOR
9.62		298.15	0	Electrochemical cell—glass electrode.	49MON
8.45		293.15	0.1 M	Potentiometric titration.	50SCH/ZUR
9.24		298.15	0	Potentiometric titration—glass electrode.	54BEU/RIE
8.01		338.65	≈0.13 M	Potentiometric titration—glass electrode.	54MCG/CRO
9.42		298.15	0	Potentiometric titration—glass electrode.	57LAM/WAT
9.40		333.18	0.44 M	Glass electrode; chemical analysis.	58OST
9.53		298.15	0	Electrochemical cell.	59WOL/OVE
9.57		313.15	0		
9.37		298.15	0	Electrochemical cell—glass electrode.	60NAS
8.00		300.55	0.75 M	Potentiometric titration—glass electrode.	60YAM/DAV
9.08		273.15	0.1 M	Glass electrode. The value of $\Delta_r H°$ was calculated from pKs measured as a function of temperature.	61IRA
8.97		283.15	0.1 M		
8.95	≈3.2	298.15	0.1 M		
8.94		310.15	0.1 M		
8.97		323.15	0.1 M		
8.92		338.15	0.1 M		
8.74		298.15	1.0 M	Potentiometric titration—glass electrode.	61IRA/CAL
8.3		298.15	0.1 M	Potentiometric titration—glass electrode.	63JOH/WAN
9.00		298.15	0.1 M	Potentiometric titration—glass electrode.	64HAM/MOR
9.42	11.7	298.15	0	Potentiometric titration—glass electrode. The value of $\Delta_r H°$ was calculated from pKs measured as a function of temperature.	65PHI/EIS
	1.7	298.15	0	Calorimetry.	66IRA/TAU
9.19	≈−8	298.15	0	Potentiometric titration—glass electrode. We have extrapolated the results of Mitra *et al.* [66MIT/MAL] to $I=0$ and calculated the approximate value of $\Delta_r H°$ that is given here from the temperature dependence of these pKs.	66MIT/MAL
9.32		323.15	0		
9.44		333.15	0		
9.40		338.15	0		
9.30		343.15	0		
7.36		298.15	1.0 M	Electrochemical cell with liquid junction.	68BOT/CIA
8.93		298.15	0.1 M	Potentiometric titration—glass electrode.	68MCN/HAZ
8.66		298.15	0.34 M	Amperometric titration.	70GOR/SID
8.36		288.15	0.1 M	Potentiometric titration.	72FRE/STU
9.59		298.15	0	Glass electrode.	73EDW/FAR
8.34		278.15	0.1 M	Potentiometric titration—glass electrode. The value of $\Delta_r H°$ was calculated from pKs measured as a function of temperature. Perlmutter-Hayman and Secco [73PER/SEC] also give values of pK as a function of ionic strength at $T=298.15$ K. We have extrapolated these results to obtain pK=8.93 at $I=0$.	73PER/SEC
8.31		288.15	0.1 M		
8.29	≈1.9	298.15	0.1 M		
8.31		308.15	0.1 M		
	1.63	298.15	0	Calorimetry.	73VAS/ALE
8.04		295.15	0.2 M	Electrochemical+kinetic.	75SIL/WEH

Values from literature—Continued

pK	$\Delta_r H°/(\mathrm{kJ\,mol^{-1}})$	T/K	I	Method(s) and comments	Reference
	4.18	278.15	0	Calorimetry. The value $\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}}) = -141$ was calculated from the temperature dependence of $\Delta_r H°$.	75VAS/ALE
	2.76	288.15	0		
	1.63	298.15	0		
	−0.13	308.15	0		
7.38		298.15	0.5 M	Potentiometric titration—glass electrode.	77THO/TAY
8.36		288.15	0.1 M	Potentiometric titration—glass electrode.	78FRE/STU
8.05		298.15	0.1 M	Potentiometric titration—glass electrode.	79CRA/MOO
8.46		298.15	0.5 M	Potentiometric titration—glass electrode.	82DEL/NIC
8.77		298.15	0.1 M	Potentiometric titration—glass electrode; calorimetry.	85DAN/RIG
	2.0	308.15	0.25 M		
8.22		?	1.0 M	Glass electrode.	86GRE/TRA
8.09		298.15	0.3 M	Potentiometric titration—glass electrode.	87HYN/ODO
8.67		298.15	0.15 M	Potentiometric titration—glass electrode.	88JAC/VOY
8.138		298.15	0.15 M	Potentiometric titration—glass electrode.	91DUF/WIL
9.60	3.0	298.15	0	Potentiometric—few details are given. This study reports summary results of a potentiometric investigation in which pKs were determined as a function of temperature. The authors [94DES/FOT] have extrapolated their measured pKs to obtain values at $I = 0$. They also report $\Delta_r H°/(\mathrm{kJ\,mol^{-1}}) = 3.0$ and $\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}}) = -220$ at $T = 298.15$ K and $I = 0$.	94DES/FOT
8.25		298.15	0.2 M	Potentiometric titration—glass electrode.	95BUG/KIS
8.40		298.15	0.1 M	Potentiometric titration—glass electrode.	95JUR/MAR
8.55		298.15	0.1 M	Potentiometric titration—glass electrode.	95LU/MOT
8.23		298.15	0.2 M	Potentiometric titration—glass electrode.	96ATK/KIS

Values adjusted to $T=298.15$ K and $I=0$

pK	$\Delta_r H°/(\mathrm{kJ\ mol^{-1}})$	$\Delta_r C_p^\circ/(\mathrm{J\ K^{-1}\ mol^{-1}})$	Reference
	Reaction (1): $H_4P_2O_7=H^+ + H_3P_2O_7^-$		
0.89			09ABB/BRA
0.99			54MCG/CRO
1.15			58OST
2.09			61IRA/CAL
2.71			63JOH/WAN
	−12.6		66IRA/TAU
0.89	≈−8		66MIT/MAL
1.14			68BOT/CIA
1.83			70GOR/SID
	−6.1		70VAS/ALE
0.70			73EDW/FAR
1.72			73PAT/TAY
1.14			77THO/TAY
0.87			77WAK/HIS
1.72			82DEL/NIC
1.10			91DUF/WIL
0.89	−9.0	≈−90	94DES/FOT
	Reaction (2): $H_3P_2O_7^- = H^+ + H_2P_2O_7^{2-}$		
1.98			09ABB/BRA
2.36			32MUU
2.96			50SCH/ZUR
2.27			54BEU/RIE
≈2.47			54MCG/CRO
2.64			57LAM/WAT
2.46			58KIN/DAV
≈2.57			58OST
2.28			60NAS
2.43	≈10.5		61IRA
2.54			61IRA/CAL
3.13			63JOH/WAN
	−12.6		66IRA/TAU
2.08	≈−19.0		66MIT/MAL
2.19			68BOT/CIA
2.65			70GOR/SID
	−4.3		70VAS/ALE2
2.19			73EDW/FAR
2.24			77THO/TAY
2.57			82DEL/NIC
2.37	−5.6		85DAN/RIG
2.25			91DUF/WIL
2.29	−12.0	≈−130	94DES/FOT
2.19			95BUG/KIS
2.23			95JUR/MAR
2.50			95LU/MOT
2.20			96ATK/KIS
	Reaction (3): $H_2P_2O_7^{2-} = H^+ + HP_2O_7^{3-}$		
6.53			09ABB/BRA
6.67			28KOL/BOS2
6.70			28MOR
6.69			32MUU
6.57			49MON
6.71			50SCH/ZUR
6.63			54BEU/RIE
6.52			54MCG/CRO
6.76			57LAM/WAT
6.76			58OST
6.70			60NAS
6.80			60YAM/DAV
6.76	≈−4.5		61IRA
≈7.14			61IRA/CAL
	−1.3		62CHR/IZA
6.64			63JOH/WAN

Values adjusted to $T=298.15$ K and $I=0$—Continued

pK	$\Delta_r H°/(\mathrm{kJ\,mol^{-1}})$	$\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}})$	Reference
6.87			64HAM/MOR
6.54	1.3		65PHI/EIS
	0.4		66IRA/TAU
6.38	≈−0.6		66MIT/MAL
6.54			68BOT/CIA
≈8.14			68COS/FAR
6.76			68MCN/HAZ
≈7.17			70GOR/SID
6.64			72FRE/STU
6.80			73EDW/FAR
6.50	−5.9		73PER/SEC
	0.54		73VAS/ALE
	0.54	−136	75VAS/ALE
6.55			75SIL/WEH
6.56			77THO/TAY
6.64			78FRE/STU
6.43			79CRA/MOO
6.99			82DEL/NIC
6.82	2.3		85DAN/RIG
6.71			87HYN/ODO
7.07			88JAC/VOY
6.61			91DUF/WIL
6.72	0.0	≈−210	94DES/FOT
6.68			95BUG/KIS
6.59			95JUR/MAR
6.73			95LU/MOT
6.67			96ATK/KIS
	Reaction (4): $HP_2O_7^{3-}=H^+ + P_2O_7^{4-}$		
8.43			09ABB/BRA
9.38			28KOL/BOS2
9.88			28MOR
9.62			49MON
9.29			50SCH/ZUR
9.24			54BEU/RIE
≈8.95			54MCG/CRO
9.42			57LAM/WAT
≈10.8			58OST
9.53			59WOL/OVE
9.37			60NAS
9.49			60YAM/DAV
9.81	≈0.7		61IRA
	1.7		61IRA/CAL
9.16			63JOH/WAN
9.86			64HAM/MOR
9.42	11.7		65PHI/EIS
	1.7		66IRA/TAU
9.19	≈−8		66MIT/MAL
8.93			68BOT/CIA
9.79			68MCN/HAZ
9.89			70GOR/SID
9.19			72FRE/STU
9.59			73EDW/FAR
9.15	≈−0.6		73PER/SEC
	1.63		73VAS/ALE
9.10			75SIL/WEH
	1.63	−141	75VAS/ALE
≈8.74			77THO/TAY
9.19			78FRE/STU
8.91			79CRA/MOO
9.82			82DEL/NIC
9.63	0.5		85DAN/RIG
≈9.8			86GRE/TRA
9.28			87HYN/ODO
9.65			88JAC/VOY
9.11			91DUF/WIL

Values adjusted to $T=298.15$ K and $I=0$—Continued

pK	$\Delta_r H°/(\text{kJ mol}^{-1})$	$\Delta_r C_p^\circ/(\text{J K}^{-1}\text{ mol}^{-1})$	Reference
9.60	3.0	≈−220	94DES/FOT
9.31			95BUG/KIS
9.26			95JUR/MAR
9.41			95LU/MOT
9.29			96ATK/KIS

Comments: The selected pK values are based on what we judge to be the most reliable of the investigations in which the results have been extrapolated to $I=0$: p$K_1=0.83$ [66MIT/MAL, 73EDW/FAR, 94DES/FOT], p$K_2=2.26$ [54BEU/RIE, 60NAS, 73EDW/FAR, 94DES/FOT], p$K_3=6.72$ [54BEU/RIE, 57LAM/WAT, 60NAS, 73EDW/FAR, 94DES/FOT], and p$K_4=9.46$ [54BEU/RIE, 57LAM/WAT, 59WOL/OVE, 60NAS, 73EDW/FAR, 94DES/FOT]. Interestingly, the average value of pK_3 (all values adjusted to $T=298.15$ K and $I=0$ in the above table) is 6.74 and is very close to our selected value of p$K_3=6.72$. Similarly, the average value of pK_4 (all values adjusted to $T=298.15$ K and $I=0$ in the above table) is 9.40 and is also close to the selected value of p$K_4=9.46$. We have relied upon the calorimetric results in choosing the values of $\Delta_r H°$ given here. Thus, in each case, the selected values of $\Delta_r H°$ are the respective averages of the calorimetric results that have been reported for that reaction. We believe that the calorimetrically determined ($\Delta_r H°$ as a function of temperature) values of $\Delta_r C_p^\circ$ reported by Valil'ev *et al.* [75VAS/ALE] for reactions (3) and (4) are the most reliable values for these two reactions. The values of $\Delta_r C_p^\circ$ for reactions (1) and (2) are judged to be approximate. Because of the large charge numbers on the aqueous species $P_2O_7^{4-}$ and $HP_2O_7^{3-}$, the standard thermodynamic quantities for reaction (4) are particularly dependent on the values of the activity coefficients and are therefore somewhat uncertain. Note: Wu *et al.* [67WU/WIT] measured $\Delta_r H°/(\text{kJ mol}^{-1})=-2.2$ for reaction (5): $2H^+ + P_2O_7^{4-} = H_2P_2O_7^{2-}$. Use of the selected values of $\Delta_r H°$ for reactions (3) and (4) leads to $\Delta_r H°/(\text{kJ mol}^{-1})=-1.9$ for reaction (5). Thus, the result of Wu *et al.* [67WU/WIT] is judged to be in satisfactory agreement with our selected values.

TABLE 7.57. Succinate

Other names	succinic acid; 1,4-butanedioic acid; butanedioic acid; dihydrofumaric acid; 1,2-ethanedicarboxylic acid; ethylenesuccinic acid; CAS No. 110-15-6
Empirical formula	$C_4H_6O_4$
Molecular weight	118.09

Ionization reactions

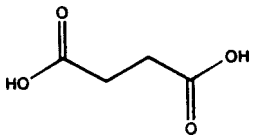
$$H_2L = H^+ + HL^- \quad (1)$$
$$HL^- = H^+ + L^{2-} \quad (2)$$
where $H_2L = C_4H_6O_4$

Selected values at $T=298.15$ K and $I=0$:

p$K=4.207$, $\Delta_r G°/(\text{kJ mol}^{-1})=24.014$, $\Delta_r H°/(\text{kJ mol}^{-1})=3.0$, and $\Delta_r C_p^\circ/(\text{J K}^{-1}\text{ mol}^{-1})=-121$ for reaction (1)
p$K=5.636$, $\Delta_r G°/(\text{kJ mol}^{-1})=32.171$, $\Delta_r H°/(\text{kJ mol}^{-1})=-0.5$, and $\Delta_r C_p^\circ/(\text{J K}^{-1}\text{ mol}^{-1})=-217$ for reaction (2)

Evaluation: reaction (1), AAB; reaction (2), AAA

Structure:



Values from literature

pK	$\Delta_r H°$/(kJ mol^{-1})	T/K	I	Method(s) and comments	Reference
				Reaction (1): $H_2L=HL^-+H^+$	
4.195		298.15	0	Potentiometric titration.	28SIM
4.196		298.15	0	Potentiometric titration—quinhydrone electrode.	36GER/VOG
4.162	≈1.2	298.15	0	Electrochemical cell—no liquid junction. The approximate value of $\Delta_r H°$ given here was calculated from pKs measured at three temperatures.	36JON/SOP
4.135		323.15	0		
4.133		347.15	0		
	2.52	298.15	0	Calorimetry. The value $\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}}) = -131$ is calculated from the temperature dependency of their [48COT/WOL] reported $\Delta_r H°$ values.	48COT/WOL
4.2845		273.15	0	Electrochemical cell—no liquid junction. The value of $\Delta_r H°$ given here was calculated from pKs measured at several temperatures. The value $\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}}) = -133$ was also calculated from the temperature dependency of their [50PIN/BAT2] reported pKs. Pinching and Bates [50PIN/BAT2] also summarize values of pK_1 from the earlier literature.	50PIN/BAT2
4.2631		278.15	0		
4.2449		283.15	0		
4.2316		288.15	0		
4.2176		293.15	0		
4.2066	3.15	298.15	0		
4.1980		303.15	0		
4.1914		308.15	0		
4.1878		313.15	0		
4.1869		318.15	0		
4.1863		323.15	0		
4.21		298.15	0	Potentiometric—glass electrode. Dippy *et al.* [59DIP/HUG] give a summary of pK values from the early literature for the ionization of succinate.	59DIP/HUG
4.00		298.15	0.1 M	Potentiometric titration—glass electrode.	60YAS/YAM
4.05		298.15	0.15 M	Potentiometric titration—glass electrode.	62DEB/KAI
	3.3	298.15	0	Calorimetry.	67CHR/IZA
4.23	3.77	298.15	0	Potentiometric titration—glass electrode; calorimetry.	78ARE/CAL
4.209		298.15	0	Electrochemical cell-glass electrode.	80MON/AMI
4.193		313.15	0		
4.21		310.15	0	Glass electrode. We have adjusted the results of Daniele *et al.* [83DAN/RIG] to $I=0$ to obtain the pK value given here.	83DAN/RIG
4.18		298.15	0	Potentiometric titration—glass electrode.	85CAP/DER
4.21	≈−1.0	298.15	0	Potentiometric titration—glass electrode. The approximate value of $\Delta_r H°$ given here was calculated from pKs measured at three temperatures.	85DAN/DER
4.01		298.15	0.1 M	Coulometric titration.	87GLA/SKR
4.231		288.15	0	Potentiometric titration—glass electrode. The value of $\Delta_r H°$ given here was calculated from pKs measured at four temperatures.	90DER/DES
4.209	2.2	298.15	0		
4.197		308.15	0		
4.194		318.15	0		
4.245		298.15	0	Conductivity. An accurate value for pK_2 could not be obtained due to the difficulty of assigning a reliable value for the limiting conductance of the ion H Succinate.	92APE/BAR
3.93		298.15	0.1 M	Coulometric titration.	92GLA/HUL
4.275		273.15	0	Electrochemical cell—no liquid junction. The value of $\Delta_r H°$ given here was calculated from pKs measured at several temperatures. The value $\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}}) = -98$ was also calculated from the temperature dependency of their [95KET/PAL] reported pKs.	95KET/PAL
4.210	2.9	298.15	0		
4.188		323.15	0		
4.248		373.15	0		
4.420		423.15	0		
4.678		473.15	0		
5.005		523.15	0		
				Reaction (2): $HL^-=L^{2-}+H^+$	
5.570		298.15	0	Potentiometric titration.	28SIM
5.595		298.15	0	Quinhydrone electrode.	36GER/VOG
5.607	≈−4.7	298.15	0	Electrochemical cell—no liquid junction. The approximate value of $\Delta_r H°$ given here was calculated from pKs measured at three temperatures.	36JON/SOP
5.638		323.15	0		
5.726		347.15	0		
	0.18	298.15	0	Calorimetry. The value $\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}}) = -218$ is calculated from the temperature dependency of their [48COT/WOL] reported $\Delta_r H°$ values.	48COT/WOL

Values from literature—Continued

pK	$\Delta_r H°$/(kJ mol^{-1})	T/K	I	Method(s) and comments	Reference
5.6741		273.15	0	Electrochemical cell—no liquid junction. The value of $\Delta_r H°$ given here was calculated from pKs measured at several temperatures. The value $\Delta_r C_p^\circ$/(J K^{-1} mol^{-1}) = −218 was also calculated from the temperature dependency of their [50PIN/BAT] reported pKs. Pinching and Bates [50PIN/BAT] also summarize values of pK_2 from the earlier literature.	50PIN/BAT
5.6608		278.15	0		
5.6490		283.15	0		
5.6425		288.15	0		
5.6390		293.15	0		
5.6358	−0.51	298.15	0		
5.6416		303.15	0		
5.6477		308.15	0		
5.6540		313.15	0		
5.6696		318.15	0		
5.6802		323.15	0		
5.72		298.15	0	Potentiometric—glass electrode. Dippy *et al.* [59DIP/HUG] give a summary of pK values from the early literature for the ionization of succinate.	59DIP/HUG
5.21		298.15	0.1 M	Potentiometric titration—glass electrode.	60YAS/YAM
4.88		298.15	0.15 M	Potentiometric titration—glass electrode.	62DEB/KAI
	0.25	298.15	0	Calorimetry.	67CHR/IZA
5.58	0.71	298.15		Potentiometric titration—glass electrode; calorimetry. The values of pK and $\Delta_r H°$ pertain, respectively, to $I = 0$ and $I = 0.1$ M.	78ARE/CAL
5.647		298.15	0	Electrochemical cell-glass electrode.	80MON/AMI
5.664		313.15	0		
5.58		310.15	0	Glass electrode. We have adjusted the results of Daniele *et al.* [83DAN/RIG] to $I = 0$ to obtain the pK value given here.	83DAN/RIG
5.67		298.15	0	Potentiometric titration—glass electrode.	85CAP/DER
5.64	≈1.0			Potentiometric titration—glass electrode. The approximate value of $\Delta_r H°$ given here was calculated from pKs measured at three temperatures.	85DAN/DER
5.24		298.15	0.1 M	Coulometric titration. The value given here is the average of the results obtained with the single-compartment and two-compartment cells.	87GLA/SKR
5.654		288.15	0	Potentiometric titration—glass electrode. The value of $\Delta_r H°$ given here was calculated from pKs measured at four temperatures.	90DER/DES
5.648	−0.52	298.15	0		
5.652		308.15	0		
5.663		318.15	0		
5.24		298.15	0.1 M	Coulometric titration.	92GLA/HUL
5.674		273.15	0	Electrochemical cell—no liquid junction. The value of $\Delta_r H°$ given here was calculated from pKs measured at several temperatures. The value $\Delta_r C_p^\circ$/(J K^{-1} mol^{-1}) = −215 was also calculated from the temperature dependency of their [95KET/PAL] reported pKs.	95KET/PAL
5.638	−0.5	298.15	0		
5.681		323.15	0		
5.919		373.15	0		
6.278		423.15	0		
6.702		473.15	0		
7.159		523.15	0		

Values adjusted to $T=298.15$ K and $I=0$

pK	$\Delta_r H°/(\mathrm{kJ\,mol^{-1}})$	$\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}})$	Reference
	Reaction (1): $H_2L=HL^-+H^+$		
4.195			28SIM
4.196			36GER/VOG
4.162	≈1.2		36JON/SOP
	2.5	−131	48COT/WOL
4.207	3.2	−133	50PIN/BAT2
4.21			59DIP/HUG
4.21			60YAS/YAM
4.29			62DEB/KAI
	3.3		67CHR/IZA
4.23	3.77		78ARE/CAL
4.21			80MON/AMI
4.23			83DAN/RIG
4.18			85CAP/DER
4.21	≈1.0		85DAN/DER
4.22			87GLA/SKR
4.209	2.2		90DER/DES
4.245			92APE/BAR
4.14			92GLA/HUL
4.210	2.9	−98	95KET/PAL
	Reaction (2): $HL^-=L^{2-}+H^+$		
5.570			28SIM
5.595			36GER/VOG
5.607	≈−4.7		36JON/SOP
	0.18	−218	48COT/WOL
5.636	−0.51	−218	50PIN/BAT
5.72			59DIP/HUG
5.64			60YAS/YAM
5.37			62DEB/KAI
	0.25		67CHR/IZA
5.58	−0.53		78ARE/CAL
5.65			80MON/AMI
5.57			83DAN/RIG
5.67			85CAP/DER
5.64	≈−1.0		85DAN/DER
5.67			87GLA/SKR
5.648	−0.52		90DER/DES
5.67			92GLA/HUL
5.638	−0.5	−215	95KET/PAL

Comments: We adopt the pK values determined by Pinching and Bates [50BIN/BAT] who used an electrochemical cell without liquid junction. There is excellent agreement with several other studies for pK_1 [59DIP/HUG, 60YAS/YAM, 78ARE/CAL, 80MON/AMI, 85DAN/DER, 90DER/DES, 95KET/PAL] and for pK_2 [60YAS/YAM, 80MON/AMI, 85DAN/DER, 95KET/PAL]. We have adopted $\Delta_r H°/(\mathrm{kJ\,mol^{-1}})=3.0$ for reaction (1) and $\Delta_r H°/(\mathrm{kJ\,mol^{-1}})=-0.5$ for reaction (2). These values are based on a consideration of some of the calorimetric results as well as the values of $\Delta_r H°$ obtained from pKs measured at several temperatures. We have adopted the respective averages of the values of $\Delta_r C_p^\circ$. Many additional studies, performed under a variety of conditions, are cited by Martell *et al.* [2001MAR/SMI] and by Pettit and Powell [2000PET/POW].

TABLE 7.58. Sulfate

Other names	sulfuric acid; CAS No. 7664-93-9
Empirical formula	H_2SO_4
Molecular weight	98.079

Ionization reaction

$$HSO_4^- = H^+ + SO_4^{2-}$$

Selected values at $T=298.15$ K and $I=0$:

$$pK=1.987,\ \Delta_r G°/(\text{kJ mol}^{-1})=11.342,\ \Delta_r H°/(\text{kJ mol}^{-1})=-22.4,\ \text{and}\ \Delta_r C_p^\circ/(\text{J K}^{-1}\,\text{mol}^{-1})=-258$$

The above values for pK, $\Delta_r G°$, and $\Delta_r H°$ are based on the "CODATA Key Values for Thermodynamics" [89COX/WAG]. More recent results, obtained by Wu and Feng [95WU/FEN] using conductivity, are pK=1.987 and $\Delta_r H°/(\text{kJ mol}^{-1})=-21.8$ at $T=298.15$ and $I=0$. Thus, the results from this recent very careful study are in excellent agreement with the CODATA values. The values of $\Delta_r C_p^\circ$ was calculated from the standard molar heat capacities of HSO_4^-(aq) and SO_4^{2-}(aq) as selected by Hepler and Hovey [96HEP/HOV]. The review of Clegg *et al.* [94CLE/RAR] also contains a discussion of the selection of values of thermodynamic quantities for this ionization reaction. These investigators [94CLE/RAR] adopted pK=1.979, $\Delta_r H°/(\text{kJ mol}^{-1})=-22.8$, and $\Delta_r C_p^\circ/(\text{J K}^{-1}\,\text{mol}^{-1})=-275$. These results are also in agreement with the values given above. Many additional studies, performed under a variety of conditions, are cited by Martell *et al.* [2001MAR/SMI] and by Pettit and Powell [2000PET/POW].

Evaluation: AAA

Structure:

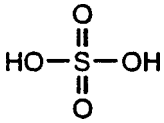


TABLE 7.59. Sulfite

Other names	sulfurous acid; bisulfite; CAS No. 7782-99-2
Empirical formula	H_2SO_3
Molecular weight	82.080

Ionization reactions

$$H_2SO_3 = H^+ + HSO_3^- \quad (1)$$
$$HSO_3^- = H^+ + SO_3^{2-} \quad (2)$$

Selected values at $T=298.15$ K and $I=0$:

Reaction (1): $pK=1.857,\ \Delta_r G°/(\text{kJ mol}^{-1})=10.600,\ \Delta_r H°/(\text{kJ mol}^{-1})=-17.80,\ \text{and}\ \Delta_r C_p^\circ/(\text{J K}^{-1}\,\text{mol}^{-1})=-272$

Reaction (2): $pK=7.172,\ \Delta_r G°/(\text{kJ mol}^{-1})=40.938,\ \Delta_r H°/(\text{kJ mol}^{-1})=-3.65,\ \text{and}\ \Delta_r C_p^\circ/(\text{J K}^{-1}\,\text{mol}^{-1})=-262$

The above values are based on the evaluation of Goldberg and Parker [85GOL/PAR]. Subsequent studies on this system [85MOR/ELA, 91ROY/ZHA] do not affect the outcome of this earlier [85GOL/PAR] evaluation. Goldberg and Parker [85GOL/PAR] have also selected the following values for the reaction ($2\,HSO_3^- = S_2O_5^{2-} + H_2O$) and which are pertinent to $T=298.15$ K and $I=0$: K=0.032, $\Delta_r G°/(\text{kJ mol}^{-1})=8.53$, $\Delta_r H°/(\text{kJ mol}^{-1})=-4.6$, and $\Delta_r C_p^\circ/(\text{J K}^{-1}\,\text{mol}^{-1})\approx -21$.

Evaluation: reaction (1), BBA; reaction (2), BAB

Structure:

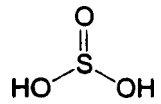


TABLE 7.60. TABS

Other names	*N*-tris(hydroxymethyl)methyl-4-aminobutanesulfonic acid; CAS No. 54960-65-5
Empirical formula	$C_8H_{19}NO_6S$
Molecular weight	257.31

Ionization reaction

$$HL^{\pm} = H^+ + L^-, \text{ where } HL = C_8H_{19}NO_6S$$

There do not appear to be any thermodynamic data in the literature for the ionization of TABS.

Structure:

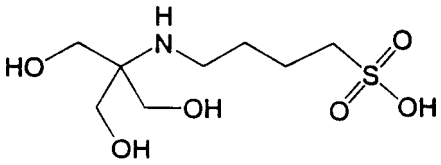


TABLE 7.61. TAPS

Other names	*N*-[tris(hydroxymethyl)methyl-3-amino]propanesulfonic acid; 3-[tris(hydroxymethyl)methylamino]propanesulfonic acid; [2-hydroxy-1,1-bis(hydroxymethyl)ethyl]amino-1-propanesulfonic acid; 3-[[2-hydroxy-1,1-bis(hydroxymethyl)ethyl]amino]-1-propanesulfonic acid; CAS No. 29915-38-6
Empirical formula	$C_7H_{17}NO_6S$
Molecular weight	243.28

Ionization reaction

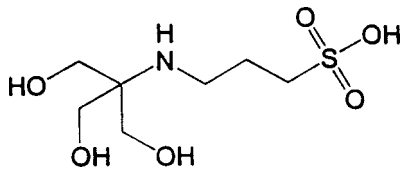
$$HL^{\pm} = H^+ + L^-, \text{ where } HL = C_7H_{17}NO_6S$$

Selected values at $T = 298.15$ K and $I = 0$:

$$pK = 8.44,\ \Delta_r G°/(\text{kJ mol}^{-1}) = 48.18,\ \Delta_r H°/(\text{kJ mol}^{-1}) = 40.4, \text{ and } \Delta_r C_p^{\circ}/(\text{J K}^{-1}\,\text{mol}^{-1}) = 15$$

Evaluation: BBB

Structure:



Values from literature

p*K*	$\Delta_r H°/(\text{kJ mol}^{-1})$	*T*/K	I	Method(s) and comments	Reference
8.55		?	?	Few details are given.	72GOO/IZA
8.34	40.12	298.15	≈0.01 M	Potentiometric titration—glass electrode; and calorimetry. Dilute solutions (0.005–0.01 M) were titrated with 0.1 M NaOH or 0.1 M HCl.	76MCG/JOR
8.42		?		Mass spectrometric method.	83CAP
8.30		298.15	≈0.012 M	Potentiometric titration of sample (0.01–0.014 M) with 0.1 M HCl or 0.1 M NaOH.	87KIT/ITO
8.21		298.15	0.16 M	Coulometric titration.	92GLA/HUL
7.98		310.15	0.16 M		
8.38	41.49	298.15	0.1 M	Electrochemical cell with liquid junction; calorimetry. Fukada and Takahashi [98FUK/TAK] also obtained $\Delta_r C_p^{\circ}/(\text{J K}^{-1}\,\text{mol}^{-1}) = 23$ at $I = 0.1$ M from the temperature dependence of $\Delta_r H°$ over the range 278.15–323.15 K.	98FUK/TAK

Values adjusted to $T=298.15$ K and $I=0$

pK	$\Delta_r H°/(\text{kJ mol}^{-1})$	$\Delta_r C_p^\circ/(\text{J K}^{-1}\text{ mol}^{-1})$	Reference
≈8.6			72GOO/IZA
8.43	39.9		76MCG/JOR
≈8.4			83CAP
8.40			87KIT/ITO
8.48			92GLA/HUL
8.59	40.9	15	98FUK/TAK

Comments: We adopt an average of the pK values from three studies [76MCG/JOR, 87KIT/ITO, 92GLA/HUL]. The value of $\Delta_r H°$ is based on the average result of two calorimetric studies [76MCG/JOR, 98FUK/TAK].

TABLE 7.62. TAPSO

Other names	2-hydroxy-3-[[2-hydroxy-1,1-bis(hydroxymethyl)ethyl]amino]-1-propanesulfonic acid; 3-[*N*-tris(hydroxymethyl)methylamino]-2-hydroxypropanesulfonic acid; CAS No. 68399-81-5
Empirical formula	$C_7H_{17}NO_7S$
Molecular weight	259.28

Ionization reaction

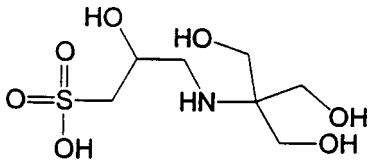
$$HL^{\pm} = H^- + L^-, \text{ where } HL = C_7H_{17}NO_7S$$

Selected values at $T=298.15$ K and $I=0$:

$$pK = 7.635,\ \Delta_r G°/(\text{kJ mol}^{-1}) = 43.58,\ \Delta_r H°/(\text{kJ mol}^{-1}) = 39.09, \text{ and } \Delta_r C_p^\circ/(\text{J K}^{-1}\text{ mol}^{-1}) = -16$$

Evaluation: AAB

Structure:



Values from literature

pK	$\Delta_r H°/(\text{kJ mol}^{-1})$	T/K	I	Method(s) and comments	Reference
7.7		293.15	?		80FER/BRA
7.65		298.15	≈0.012 M	Potentiometric titration of sample (0.01–0.014 M) with 0.1 M HCl or 0.1 M NaOH.	87KIT/ITO
8.1159		278.15	0	Electrochemical cell—no liquid junction. The value of $\Delta_r H°$ given here was calculated from pKs measured at several temperatures. The value $\Delta_r C_p^\circ/(\text{J K}^{-1}\text{ mol}^{-1}) = -16$ was also calculated from the temperature dependency of their [97ROY/ROY] reported pKs.	97ROY/ROY
7.9882		283.15	0		
7.8664		288.15	0		
7.7479		293.15	0		
7.6347	39.09	298.15	0		
7.5244		303.15	0		
7.4188		308.15	0		
7.3757		310.15	0		
7.3148		313.15	0		
7.2159		318.15	0		
7.1193		323.15	0		
7.0291		328.15	0		

Values adjusted to $T=298.15$ K and $I=0$

pK	$\Delta_r H°/(\mathrm{kJ\,mol^{-1}})$	$\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}})$	Reference
≈7.8			80FER/BRA
7.75			87KIT/ITO
7.635	39.09	−16	97ROY/ROY

Comments: We have adopted the results obtained by Roy *et al.* [97ROY/ROY] who used an electrochemical cell without liquid junction.

TABLE 7.63. L(+)Tartaric acid

Other names	L-2,3-dihydroxybutanedioic acid; L-(+)-2,3-dihydroxysuccinic acid; tartaric acid; (+)-(2*R*,3*R*)-tartaric acid; Weinsäure; (*R*,*R*)-tartrate; (2*R*,3*R*)-(+)-tartaric acid; [*R*-(*R**,*R**)]-2,3-dihydroxy-butanedioic acid; 2,3-dihydroxy succinic acid; L-(+)-dihydroxysuccinic acid; (*R*,*R*)-tartaric acid; CAS No. 87-69-4
Empirical formula	$C_4H_6O_6$
Molecular weight	150.09

Ionization reactions

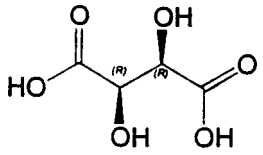
$$H_2L = H^+ + HL^- \quad (1)$$
$$HL^- = H^+ + L^{2-} \quad (2)$$
where $H_2L = C_4H_6O_6$

Selected values at $T=298.15$ K and $I=0$:

pK=3.036, $\Delta_r G°/(\mathrm{kJ\,mol^{-1}})=17.330$, $\Delta_r H°/(\mathrm{kJ\,mol^{-1}})=3.19$, and $\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}})=-147$ for reaction (1)
pK=4.366, $\Delta_r G°/(\mathrm{kJ\,mol^{-1}})=24.921$, $\Delta_r H°/(\mathrm{kJ\,mol^{-1}})=0.93$, and $\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}})=-218$ for reaction (2)

Evaluation: reaction (1), ABA; reaction (2), ABA

Structure:



Values from literature

pK	$\Delta_r H°/(\mathrm{kJ\,mol^{-1}})$	T/K	I	Method(s) and comments	Reference
				Reaction (1): $H_2L=HL^-+H^+$	
2.88		298.15	0.2 M	Electrochemical cell with liquid junction.	38CAN/KIB
≈2.65		298.25	0	Conductivity.	40TOP/DAV
3.118		273.15	0	Electrochemical cell—no liquid junction. The value of $\Delta_r H°$ given here was calculated from pKs measured at several temperatures. The value $\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}})=-175$ was also calculated from the temperature dependency of their [51BAT/CAN] reported pKs.	51BAT/CAN
3.095		278.15	0		
3.075		283.15	0		
3.057		288.15	0		
3.044		293.15	0		
3.036	3.06	298.15	0		
3.025		303.15	0		
3.019		308.15	0		
3.018		313.15	0		
3.020		318.15	0		
3.021		323.15	0		
3.15		298.15	0.133 M	Potentiometric titration—glass electrode. Feldman *et al.* [60FEL/NOR] also report pK=2.99 at $T=298.15$ and $I=0.133$ M for the first ionization of meso-tartaric acid.	60FEL/NOR
2.89		293.15	0	Glass electrode.	65FRE
3.2		293.15	0	Optical rotation.	67FRE
2.83		298.15	0.1 M	Electrochemical cell with liquid junction.	70AND/MAL
3.044		288.15	0	Electrochemical cell with liquid junction. The approximate value of $\Delta_r H°$ given here was calculated from pKs measured at three temperatures.	72DUN/MID
3.063	≈−3.2	298.15	0		
3.082		308.15	0		
3.02		288.15	0	Potentiometric titration—glass electrode. The value of $\Delta_r H°$ given here was calculated from pKs measured at several temperatures.	73KON/KAC
3.00		293.15	0		
2.99	11.5	298.15	0		
2.96		303.15	0		
2.87		308.15	0		

Values from literature—Continued

pK	$\Delta_r H°/(\mathrm{kJ\,mol^{-1}})$	T/K	I	Method(s) and comments	Reference
3.03	3.1	298.15	0	Electrochemical cell with glass electrode. The value of $\Delta_r H°$ given here is based on measurements taken at four different temperatures. The data given here are for the DL form. Results for the meso form are pK=3.17 and $\Delta_r H°/(\mathrm{kJ\,mol^{-1}})=3.4$.	73PUR/TOM
2.83		298.15	0.1 M	Potentiometric titration—glass electrode; calorimetry. Pettit and Swash [78PET/SWA] also report pK=2.95 and $\Delta_r H°/(\mathrm{kJ\,mol^{-1}})=4.3$ for the first ionization of meso-tartaric acid at T=298.15 K and I=0.1 M.	78PET/SWA
3.050	2.76	298.15	0	Potentiometric titration—glass electrode; calorimetry.	80ARE/CAL
3.033		310.15	0		
3.00		310.15	0	Potentiometric titration—glass electrode. We have adjusted the results of Daniele *et al.* [83DAN/RIG] to I=0.	83DAN/RIG
2.794		298.15	0.1 M	Potentiometric titration—glass electrode.	84MOT/MAR
3.03	≈2.0	298.15	0	Potentiometric titration—glass electrode. The approximate value of $\Delta_r H°$ given here was calculated from pKs measured at three temperatures.	85DAN/DER
2.80		298.15	0.1 M	Coulometric titration.	87GLA/SKR
2.73		298.15	0.3 M	Potentiometric titration—glass electrode.	87HYN/ODO
	3.75	298.15	0	Calorimetry.	98VAS/KOC
				Xie and Tremaine [2000XIE/TRE] measured apparent molar heat capacities of L-tartaric acid solutions from which they obtained the value $\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}})=-147$.	2000XIE/TRE
				Reaction (2): $HL^- = L^{2-} + H^+$	
3.94		298.15	0.2 M	Electrochemical cell with liquid junction.	38CAN/KIB
4.426		273.15	0	Electrochemical cell—no liquid junction. The value of $\Delta_r H°$ given here was calculated from pKs measured at several temperatures. The value $\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}})=-218$ was also calculated from the temperature dependency of their [51BAT/CAN] reported pKs.	51BAT/CAN
4.407		278.15	0		
4.391		283.15	0		
4.381		288.15	0		
4.372		293.15	0		
4.366	0.94	298.15	0		
4.365		303.15	0		
4.367		308.15	0		
4.372		313.15	0		
4.380		318.15	0		
4.391		323.15	0		
3.95		298.15	0.133 M	Potentiometric titration—glass electrode. Feldman *et al.* [60FEL/NOR] also report pK=4.44 at T=298.15 and I=0.133 M for the first ionization of meso tartaric acid.	60FEL/NOR
4.52		293.15	0	Glass electrode.	65FRE
4.5		293.15	0	Optical rotation.	67FRE
4.02		298.15	0.1 M	Electrochemical cell with liquid junction.	70AND/MAL
4.374		288.15	0	Electrochemical cell with liquid junction. The approximate value of $\Delta_r H°$ given here was calculated from pKs measured at several temperatures.	72DUN/MID
4.264	≈1.0	298.15	0		
4.365		308.15	0		
4.34		288.15	0	Potentiometric titration—glass electrode. The value of $\Delta_r H°$ given here was calculated from pKs measured at several temperatures.	73KON/KAC
4.23		293.15	0		
4.18	≈3.0	298.15	0		
4.06		303.15	0		
3.98		308.15	0		
4.37	0.84	298.15	0	Electrochemical cell with glass electrode. The value of $\Delta_r H°$ given here is based on measurements taken at four different temperatures. The data given here are for the DL form. Results for the meso form are pK=4.91 and $\Delta_r H°/(\mathrm{kJ\,mol^{-1}})=6.2$.	73PUR/TOM
3.96		298.15	0.1 M	Potentiometric titration—glass electrode; calorimetry. Pettit and Swash [78PET/SWA] report pK=4.46 and $\Delta_r H°/(\mathrm{kJ\,mol^{-1}})=5.7$ for the first ionization of meso-tartaric acid at T=298.15 K and I=0.1 M.	78PET/SWA
4.382	0.67	298.15	0	Potentiometric titration—glass electrode; calorimetry.	80ARE/CAL
4.379		310.15	0		
4.37		310.15	0	Potentiometric titration—glass electrode. We have adjusted the results of Daniele *et al.* [83DAN/RIG] to I=0.	83DAN/RIG
3.93		298.15	0.1 M	Potentiometric titration—glass electrode.	84MOT/MAR

Values from literature—Continued

pK	$\Delta_r H°$/(kJ mol^{-1})	T/K	I	Method(s) and comments	Reference
4.43	≈4.0	298.15	0	Potentiometric titration—glass electrode. The approximate value of $\Delta_r H°$ given here was calculated from pKs measured at three temperatures.	85DAN/DER
4.00		298.15	0.1 M	Coulometric titration.	87GLA/SKR
3.86		298.15	0.3 M	Potentiometric titration—glass electrode.	87HYN/ODO
	1.18	298.15	0	Calorimetry.	98VAS/KOC
				Xie and Tremaine [2000XIE/TRE] measured apparent molar heat capacities of L-tartaric acid solutions from which they obtained the value $\Delta_r C_p°$/(J K^{-1} mol^{-1}) = −218.	2000XIE/TRE

Values adjusted to T=298.15 K and I=0

pK	$\Delta_r H°$/(kJ mol^{-1})	$\Delta_r C_p°$/(J K^{-1} mol^{-1})	Reference
	Reaction (1): $H_2L=HL^-+H^+$		
3.14			38CAN/KIB
≈2.65			40TOP/DAV
3.036	3.06	−175	51BAT/CAN
3.39			60FEL/NOR
2.89			65FRE
3.2			67FRE
3.04			70AND/MAL
3.06	−3.2		72DUN/MID
2.99	≈11		73KON/KAC
3.03	3.1		73PUR/TOM
3.04			78PET/SWA
3.05	2.76		80ARE/CAL
3.02			83DAN/RIG
3.01			84MOT/MAR
3.03	≈2.0		85DAN/DER
3.01			87GLA/SKR
3.03			87HYN/ODO
	3.75		98VAS/KOC
		−147	2000XIE/TRE
	Reaction (2): $HL^-=L^{2-}+H^+$		
4.47			38CAN/KIB
4.366	0.94	−218	51BAT/CAN
4.42			60FEL/NOR
4.52			65FRE
4.5			67FRE
4.45			70AND/MAL
4.264	0.97		72DUN/MID
4.18	3.0		73KON/KAC
4.37	0.84		73PUR/TOM
4.39			78PET/SWA
4.38	0.67		80ARE/CAL
4.39			83DAN/RIG
4.36			84MOT/MAR
4.43	≈4.0		85DAN/DER
4.43			87GLA/SKR
4.46			87HYN/ODO
	1.18		98VAS/KOC
		−218	2000XIE/TRE

Comments: The carefully done study of Bates and Canham [51BAT/CAN] that used an electrochemical cell without liquid junction provides the definitive set of pK values for this system. The averages of the other pK values are 3.04 and 4.40, respectively, and are in agreement with the results of Bates and Canham [51BAT/CAN]. We have adopted the average of the $\Delta_r H°$ values obtained from the carefully done study of Bates and Canham [51BAT/CAN], which is based on pKs at several temperatures, and the calorimetric studies of Arena *et al.* [80ARE/CAL] and of Vasil'ev *et al.* [98VAS/KOC]. The recent heat capacity measurements of Xie and Tremaine provide reliable $\Delta_r C_p°$ values. Many additional studies, performed under a variety of conditions, are cited by Martell *et al.* [2001MAR/SMI] and by Pettit and Powell [2000PET/POW].

TABLE 7.64. TES

Other names	*N*-tris(hydroxymethyl)methyl-2-aminoethanesulfonic acid; 2-([2-hydroxy-1,1-bis(hydroxymethyl)-ethyl]amino)ethanesulfonic acid; *N*-[2-hydroxy-1,1-bis(hydroxymethyl)ethyl]taurine; 2-[tris(hydroxymethyl)methyl]-1-ethanesulfonic acid; CAS No. 7365-44-8
Empirical formula	$C_6H_{15}NO_6S$
Molecular weight	229.25

Ionization reaction

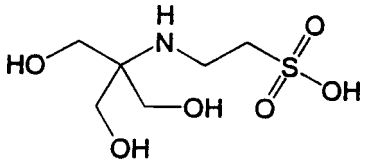
$$HL^{\pm} = H^+ + L^-, \text{ where } HL = C_6H_{15}NO_6S$$

Selected values at $T = 298.15$ K and $I = 0$:

$$pK = 7.550,\ \Delta_r G°/(\text{kJ mol}^{-1}) = 43.096,\ \Delta_r H°/(\text{kJ mol}^{-1}) = 32.13,\ \text{and}\ \Delta_r C_p^\circ/(\text{J K}^{-1}\,\text{mol}^{-1}) = 0$$

Evaluation: AAB

Structure:



Values from literature

p*K*	$\Delta_r H°/(\text{kJ mol}^{-1})$	*T*/K	I	Method(s) and comments	Reference
7.92		273.15	0.1 M	Potentiometric titration—glass electrode.	66GOO/WIN
7.54		293.15	0.01 M		
7.50		293.15	0.1 M		
7.50		293.15	0.2 M		
7.14		310.15	0.1 M		
7.958		278.15	0	Electrochemical cell—no liquid junction. The value of $\Delta_r H°$ given here was calculated from p*K*s measured at several temperatures. The value $\Delta_r C_p^\circ/(\text{J K}^{-1}\,\text{mol}^{-1}) = -19$ was also calculated from the temperature dependency of their [76VEG/BAT] reported p*K*s.	76VEG/BAT
7.848		283.15	0		
7.745		288.15	0		
7.646		293.15	0		
7.550	32.13	298.15	0		
7.457		303.15	0		
7.368		308.15	0		
7.281		313.15	0		
7.198		318.15	0		
7.117		323.15	0		
7.34	29.25	298.15	≈0.01 M	Potentiometric titration—glass electrode; and calorimetry. Dilute solutions (0.005–0.01 M) were titrated with 0.1 M NaOH or 0.1 M HCl.	76MCG/JOR
7.60		298.15	0.1 M	Potentiometric titration—glass electrode.	83NAK/KRI
7.48		293.15	0.05 M	Potentiometric titration—glass electrode.	86VAN/GAS
7.48		298.15	≈0.012 M	Potentiometric titration of sample (0.01–0.014 M) with 0.1 M HCl or 0.1 M NaOH.	87KIT/ITO
7.43		298.15	0.005 66 M	Based on measurement of ionic mobilities.	87POS/DEM
7.30		298.15	0.16 M	Coulometric titration.	92GLA/HUL
7.08		310.15	0.16 M		
7.38		298.15	0.10 M	Potentiometric titration—glass electrode.	94AZA/ELN
7.955		278.15	0	Electrochemical cell—no liquid junction. The p*K* value at $T = 278.15$ K in the published paper [97ROY/MOO2] contains a typographical error. The value given here is correct [2001ROY]. The value of $\Delta_r H°$ given here was calculated from p*K*s measured at several temperatures. The value $\Delta_r C_p^\circ/(\text{J K}^{-1}\,\text{mol}^{-1}) = 16$ was also calculated from the temperature dependency of their [97ROY/MOO2] reported p*K*s.	97ROY/MOO2
7.745		288.15	0		
7.550	32.15	298.15	0		
7.456		303.15	0		
7.336		310.15	0		
7.198		318.15	0		
7.029		328.15	0		
7.42	32.74	298.15	0.1 M	Electrochemical cell with liquid junction; calorimetry. Fukada and Takahashi [98FUK/TAK] also obtained $\Delta_r C_p^\circ/(\text{J K}^{-1}\,\text{mol}^{-1}) = -33$ at $I = 0.1$ M from the temperature dependence of $\Delta_r H°$ over the range 278.15–323.15 K.	98FUK/TAK

Values adjusted to T=298.15 K and I=0

pK	$\Delta_r H°/(\mathrm{kJ\,mol^{-1}})$	$\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}})$	Reference
7.60			66GOO/WIN
7.43	29.0		76MCG/JOR
7.550	32.13	−19	76VEG/BAT
7.81			83NAK/KRI
7.55			86VAN/GAS
7.58			87KIT/ITO
7.50			87POS/DEM
7.48			92GLA/HUL
7.59			94AZA/ELN
7.550	32.15	16	97ROY/MOO2
7.63	32.1	−41	98FUK/TAK

Comments: The pK values obtained from the studies of Vega and Bates [76VEG/BAT] and Roy *et al.* [97ROY/MOO2] are in excellent agreement and the value pK=7.550 is judged to be the best value for this quantity. While the values of $\Delta_r H°$, with the exception of that from McGlothlin and Jordan [76MCG/JOR], are in excellent agreement, the values of $\Delta_r C_p^\circ$ are somewhat discordant. We have adopted the average values $\Delta_r H°/(\mathrm{kJ\,mol^{-1}})=32.13$ and $\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}})=-15$.

TABLE 7.65. Tricine

Other names	*N*-tris(hydroxymethyl)methylglycine; *N*-tris(hydroxymethyl)methaneglycine; [tris[(hydroxymethyl)methyl]amino]acetic acid; *N*-[2-hydroxy-1,1-bis(hydroxymethyl)ethyl]glycine; CAS No. 5704-04-1
Empirical formula	$C_6H_{13}NO_5$
Molecular weight	179.17

Ionization reactions

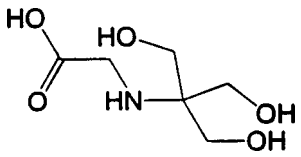
$$H_2L^+ = H^+ + HL^\pm \quad (1)$$
$$HL^\pm = H^+ + L^- \quad (2)$$
where $HL = C_6H_{13}NO_5$

Selected values at T=298.15 K and I=0:

pK=2.023, $\Delta_r G°/(\mathrm{kJ\,mol^{-1}})=11.547$, $\Delta_r H°/(\mathrm{kJ\,mol^{-1}})=5.85$, and $\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}})=-196$ for reaction (1)
pK=8.135, $\Delta_r G°/(\mathrm{kJ\,mol^{-1}})=46.435$, $\Delta_r H°/(\mathrm{kJ\,mol^{-1}})=31.37$, and $\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}})=-53$ for reaction (2)

Evaluation: reaction (1), AAB; reaction (2), AAA

Structure:



Values from literature

pK	$\Delta_r H°/(\mathrm{kJ\,mol^{-1}})$	T/K	I	Method(s) and comments	Reference
			Reaction (1): $H_2L^+ = H^+ + HL^\pm$		
≈2.3		?	?	Potentiometric titration—glass electrode.	66GOO/WIN
2.40		298.15	0.1 M	Potentiometric titration—glass electrode.	72VIE/FRE
2.125		278.15	0	Electrochemical cell—no liquid junction. The value of $\Delta_r H°$ given here was calculated from pKs measured at several temperatures. The value $\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}}) = -192$ was also calculated from the temperature dependency of their [73ROY/ROB] reported pKs.	73ROY/ROB
2.092		283.15	0		
2.064		288.15	0		
2.042		293.15	0		
2.023	5.88	298.15	0		
2.009		303.15	0		
2.000		308.15	0		
1.989		313.15	0		
1.980		318.15	0		
1.976		323.15	0		
2.02		298.15	0.6 M	Potentiometric titration—glass electrode.	91CRA/EHD
			Reaction (2): $HL^\pm = H^+ + L^-$		
8.6		273.15	0.1 M	Potentiometric titration—glass electrode.	66GOO/WIN
8.15		293.15	0.01 M		
8.6		293.15	0.1 M		
8.15		293.15	0.2 M		
7.8		310.15	0.1 M		
7.99		298.15	0.1 M	Potentiometric titration—glass electrode.	72VIE/FRE
8.537		278.15	0	Electrochemical cell—no liquid junction. The value of $\Delta_r H°$ given here was calculated from pKs measured at several temperatures. The value $\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}}) = 50$ was also calculated from the temperature dependency of their [73ROY/ROB] reported pKs.	73ROY/ROB
8.430		283.15	0		
8.326		288.15	0		
8.228		293.15	0		
8.135	31.46	298.15	0		
8.044		303.15	0		
7.957		308.15	0		
7.873		313.15	0		
7.794		318.15	0		
7.717		323.15	0		
8.00	30.50	298.15	≈0.01 M	Potentiometric titration—glass electrode; and calorimetry. Dilute solutions (0.005–0.01 M) were titrated with 0.1 M NaOH or 0.1 M HCl.	76MCG/JOR
8.00		303.15	0.2 M	Polarography.	78KAP/JAI
7.92		298.15	≈0.012 M	Potentiometric titration of sample (0.01–0.014 M) with 0.1 M HCl or 0.1 M NaOH.	87KIT/ITO
7.929		298.15	0.6 M	Potentiometric titration—glass electrode.	91CRA/EHD
8.00	31.97	298.15	0.1 M	Electrochemical cell with liquid junction; calorimetry. Fukada and Takahashi [98FUK/TAK] also obtained $\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}}) = -45$ at $I = 0.1$ M from the temperature dependence of $\Delta_r H°$ over the range 278.15–323.15 K.	98FUK/TAK

Values adjusted to $T=298.15$ K and $I=0$

pK	$\Delta_r H°/(\mathrm{kJ\,mol^{-1}})$	$\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}})$	Reference
	Reaction (1): $H_2L^+=H^++HL^\pm$		
≈2.3			66GOO/WIN
2.40			72VIE/FRE
2.023	5.85	−196	73ROY/ROB
≈2.0			91CRA/EHD
	Reaction (2): $HL^\pm=H^++L^-$		
8.34			66GOO/WIN
8.20			72VIE/FRE
8.135	31.43	−53	73ROY/ROB
8.09	30.2		76MCG/JOR
8.27			78KAP/JAI
8.02			87KIT/ITO
≈8.3			91CRA/EHD
8.21	31.3	−53	98FUK/TAK

Comments: The most reliable results for the pK values are those obtained by Roy *et al.* [73ROY/ROB] who used an electrochemical cell without liquid junction. There is excellent agreement in the values of $\Delta_r H°$ and $\Delta_r C_p^\circ$ reported by Roy *et al.* [73ROY/ROB] and by Fukada and Takahashi [98FUK/TAK]. We have adopted the respective averages of these quantities from these two studies [73ROY/ROB, 98FUK/TAK].

TABLE 7.66. Triethanolamine

Other names	2,2′,2′-nitrilotriethanol; nitrilo-2,2′,2″-triethanol; tris(2-hydroxyethyl)amine; tricolamine; trolamine; TEA; 2,2′,2″-nitrilotrisethanol; 2,2′,2″-nitritotriethanol; 2,2′,2″-trihydroxytriethylamine; tri(2-hydroxyethyl)amine; CAS No. 102-71-6
Empirical formula	$C_6H_{15}NO_3$
Molecular weight	149.19

Ionization reaction

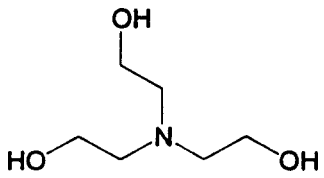
$$HL^+=H^++L, \text{ where } L=C_6H_{15}NO_3$$

Selected values at $T=298.15$ K and $I=0$:

$$pK=7.762,\ \Delta_r G°/(\mathrm{kJ\,mol^{-1}})=44.306,\ \Delta_r H°/(\mathrm{kJ\,mol^{-1}})=33.6,\ \text{and}\ \Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}})=50$$

Evaluation: AAA

Structure:



Values from literature

pK	$\Delta_r H°/(\mathrm{kJ\,mol^{-1}})$	T/K	I	Method(s) and comments	Reference
7.82		295.15	?	Electrochemical cell with liquid junction.	32HAL/SPR
7.77		298.15	?		
7.75		299.15	?		
7.87		293.15	0	Electrochemical cell—no liquid junction.	54BAT/SCH
7.77		298.15	0		
7.68		303.15	0		
7.90		298.15	~0.5 M	Potentiometric titration—glass electrode.	56BJE/REF
8.04		283.15	0	Glass electrode. We calculate $\Delta_r H°/(\mathrm{kJ\,mol^{-1}}) = 29.7$ from the	59WEI/ZIM
7.94		288.15	0	temperature dependence of the pKs.	
7.80		293.15	0		
7.81	29.7	298.15	0		
7.59		308.15	0		
7.52		313.15	0		
7.44		318.15	0		
7.34		323.15	0		
8.2906		273.15	0	Electrochemical cell—no liquid junction. The value of $\Delta_r H°$ given	60BAT/ALL
8.1734		278.15	0	here was calculated from pKs measured at several temperatures. The	
8.0674		283.15	0	value $\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}}) = 51$ was also calculated from the	
7.9632		288.15	0	temperature dependency of their [60BAT/ALL] reported pKs.	
7.8611		293.15	0		
7.7624	33.46	298.15	0		
7.6661		303.15	0		
7.5707		308.15	0		
7.4773		313.15	0		
7.3875		318.15	0		
7.2992		323.15	0		
7.912		303.15	0.5 M	Polarography.	62FIS/HAL
8.08		298.15	?	Potentiometric titration—glass electrode.	65DOU
8.02		298.15	0.43 M	Potentiometric titration—glass electrode.	66SKL/KAR
7.83		303.15	0.5 M	Polarography.	67FIS/HAL
	33.01	?	?	Calorimetry.	67POP/ROM
	34.1	298.15	0	Calorimetry.	69CHR/IZA
7.82		298.15	1.0 M	Potentiometric titration—glass electrode.	70UDO/REI
7.78		303.15	2.0 M	Polarography; glass electrode.	71SRI/SUB
7.89		303.15	1 M	Potentiometric titration—glass electrode.	72BHA/SUB
8.04		298.15	0.5 M	Potentiometric titration—glass electrode.	72VAN/EEC
	35.6	298.15	0	Calorimetry.	79VAS/KOC
8.05		298.15	1.0 M	Potentiometric titration—glass electrode.	82SIG/SCH
8.14		298.15	1.0 M	Potentiometric titration—glass electrode.	86AND
8.00		298.15	1.0 M	Potentiometric.	86CAS/TAU
7.76		298.15	0.1 M	Potentiometric titration—glass electrode.	87GLA/SKR
7.80	33.91	298.15	0	Potentiometric titration—glass electrode; calorimetry.	87KIM/DOB
7.88		298.15	≈0.012 M	Potentiometric titration of sample (0.01–0.014 M) with 0.1 M HCl or 0.1 M NaOH.	87KIT/ITO
7.75		298.15	0	Potentiometric titration—glass electrode. Results were extrapolated to $I = 0$.	92HER/ARM
7.88	33.59	298.15	0.1 M	Electrochemical cell with liquid junction; calorimetry. Fukada and Takahashi [98FUK/TAK] also obtained $\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}}) = 48$ at $I = 0.1$ M from the temperature dependence of $\Delta_r H°$ over the range 278.15–323.15 K.	98FUK/TAK

Values adjusted to T=298.15 K and I=0

pK	$\Delta_r H°/(\mathrm{kJ\ mol^{-1}})$	$\Delta_r C_p^\circ/(\mathrm{J\ K^{-1}\ mol^{-1}})$	Reference
7.77			32HAL/SPR
7.77			54BAT/SCH
7.90			56BJE/REF
7.81	29.7		59WEI/ZIM
7.762	33.46	51	60BAT/ALL
8.01			62FIS/HAL
8.08			65DOU
8.02			66SKL/KAR
8.01			67FIS/HAL
	33.01		67POP/ROM
	34.1		69CHR/IZA
8.04			70UDO/REI
7.88			71SRI/SUB
7.99			72BHA/SUB
8.04			72VAN/EEC
	35.6		79VAS/KOC
8.05			82SIG/SCH
8.14			86AND
8.00			86CAS/TAU
7.76			87GLA/SKR
7.80	33.91		87KIM/DOB
7.88			87KIT/ITO
7.75			92HER/ARM
7.88	33.6	48	98FUK/TAK

Comments: The pK values determined by Bates and Allen [60BAT/ALL] with an electrochemical cell without liquid junction are judged to be the most reliable. We adopt an average value $\Delta_r H°/(\mathrm{kJ\ mol^{-1}}) = 33.6$ based on three of the calorimetric studies [67POP/ROM, 69CHR/IZA, 87KIM/DOB, 98FUK/TAK] as well as the value obtained by Bates and Allen [60BAT/ALL]. The reported [60BAT/ALL, 98FUK/TAK] values of $\Delta_r C_p^\circ$ are in excellent agreement. Approximate values for the subsequent ionization (pK≈14.6) of triethanolamine in extremely alkaline solution have also been reported [55SCH, 62DOU/PAR].

TABLE 7.67. Triethylamine

Other names	N,N-diethylethanamine; triethylammonium; TEA; N,N,N-triethylamine; CAS No. 121-44-8
Empirical formula	$C_6H_{15}N$
Molecular weight	101.19

Ionization reaction

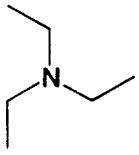
$$HL^+ = H^+ + L, \text{ where } L = C_6H_{15}N$$

Selected values at T=298.15 K and I=0:

$$pK = 10.72,\ \Delta_r G°/(\mathrm{kJ\ mol^{-1}}) = 61.19,\ \Delta_r H°/(\mathrm{kJ\ mol^{-1}}) = 43.13,\ \text{and}\ \Delta_r C_p^\circ/(\mathrm{J\ K^{-1}\ mol^{-1}}) = 151$$

Evaluation: CB

Structure:



Values from literature

pK	$\Delta_r H°/(\mathrm{kJ\,mol^{-1}})$	T/K	I	Method(s) and comments	Reference
10.82		291.15	?	Potentiometric titration—glass electrode.	35BRI/WIL
10.77		298.15	0.4 M	Based on the unpublished results of Bjerrum and Refn.	50BJE
10.78		273.15	0	Electrochemical cell with liquid junction. The value of $\Delta_r H°$ given	55FYF
10.67	26.8	298.15	0	here was calculated from pKs measured at several temperatures.	
10.45		308.15	0		
10.21		318.15	0		
10.75	43.4	298.15	0.1 M	Potentiometric titration—glass electrode; calorimetry. Adjustment of the reported pK value to $I=0$ using the slope pK/I given by Cox *et al.* [68COX/EVE] leads to the value p$K=10.71$ at $I=0$.	65PAO/STE
10.83		303.15	0.5 M	Polarography.	67FIS/HAL
10.75	34.8	?	?	Calorimetry.	67POP/ROM
11.387		273.15	0	Electrochemical cell with liquid junction. The value of $\Delta_r H°$ given	68COX/EVE
11.114		283.15	0	here was calculated from pKs measured at several temperatures. The	
10.848		293.15	0	value $\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}}) \approx 197$ was also calculated from the	
	44.3	298.15	0	temperature dependency of their [68COX/EVE] reported pKs.	
10.589		303.15	0		
10.333		313.15	0		
10.085		323.15	0		
	43.2	298.15	0	Calorimetry.	69CHR/IZA
10.99		298.15	1.0 M	Potentiometric titration—glass electrode.	74VEL/ZIK
	39.04	273.65	0	Calorimetry. The value $\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}}) = 151$ at $T = 298.15$ K	75BER/OLO
	39.52	278.15	0	was also calculated from the temperature dependency of their	
	40.78	285.65	0	[75BER/OLO] reported $\Delta_r H°$ values.	
	43.13	298.15	0		
	46.45	323.15	0		
	48.92	348.15	0		
	51.19	373.15	0		
10.68		298.15	?	Potentiometric titration—glass electrode; spectrophotometry.	85FRE/VIV
10.75		298.15	1.0 M	Potentiometric.	86CAS/TAU
	46.44	298.15	?	Calorimetry.	93SAN/BAY

Values adjusted to $T=298.15$ K and $I=0$

pK	$\Delta_r H°/(\mathrm{kJ\,mol^{-1}})$	$\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}})$	Reference
10.62			35BRI/WIL
10.77			50BJE
10.67	26.8		55FYF
10.71	43.4		65PAO/STE
10.96			67FIS/HAL
≈10.8	≈34.8		67POP/ROM
10.72	44.3	197	68COX/EVE
	43.2		69CHR/IZA
10.99			74VEL/ZIK
	43.13	151	75BER/OLO
10.68			85FRE/VIV
10.75			86CAS/TAU
	46.44		93SAN/BAY

Comments: The study of Cox *et al.* [68COX/EVE] appears to have been done very carefully and we adopt the pK value for triethylamine based on their study. The selected value, p$K=10.72$, is very close to the results obtained from several other studies. However, the very precise calorimetric study of Bergström and Olofsson [75BER/OLO] yields, we believe, the most reliable values for the other two thermodynamic quantities: $\Delta_r H°/(\mathrm{kJ\,mol^{-1}}) = 43.13$ and $\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}}) = 151$.

TABLE 7.68. Tris

Other names	2-amino-2-hydroxymethylpropane-1,3 diol; 2-amino-2-(hydroxymethyl)-1,3-propanediol; tris(hydroxymethyl)aminomethane; 2-amino-2-hydroxymethylpropanediol; THAM; TRIZMA; tromethamine; trometamol; CAS No. 77-86-1
Empirical formula	$C_4H_{11}NO_3$
Molecular weight	121.14

Ionization reactions

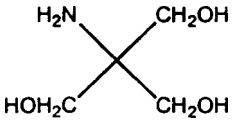
$$HL^+ = H^+ + L, \text{ where } L = C_4H_{11}NO_3$$

Selected values at $T=298.15$ K and $I=0$:

$$pK = 8.072,\ \Delta_r G°/(\text{kJ mol}^{-1}) = 46.075,\ \Delta_r H°/(\text{kJ mol}^{-1}) = 47.45, \text{ and } \Delta_r C_p^\circ/(\text{J K}^{-1}\text{ mol}^{-1}) = -59$$

Evaluation: AAA

Structure:



Values from literature

pK	$\Delta_r H°/(\text{kJ mol}^{-1})$	T/K	I	Method(s) and comments	Reference
8.221		293.15	0	Electrochemical cell—no liquid junction.	49BAT/PIN3
8.076		298.15	0		
7.937		303.15	0		
	45.73	298.15	0.013 M	Calorimetry.	55STU
	48.5	293.15	≈0.6 M	Calorimetry.	56POD/MOR
8.8500		273.15	0	Electrochemical cell—no liquid junction. The value of $\Delta_r H°$ given here was calculated from pKs measured at several temperatures. The value $\Delta_r C_p^\circ/(\text{J K}^{-1}\text{ mol}^{-1}) = -64$ at $T=298.15$ K was also calculated from the temperature dependency of their [61BAT/HET] reported pKs.	61BAT/HET
8.6774		278.15	0		
8.5164		283.15	0		
8.3616		288.15	0		
8.2138		293.15	0		
8.0746	47.58	298.15	0		
7.9344		303.15	0		
7.8031		308.15	0		
7.6772		313.15	0		
7.5543		318.15	0		
7.4365		323.15	0		
	49.75	298.15	≈0.007 M	Calorimetry.	61TYS/MCC
8.8553		273.15	0	Electrochemical cell—no liquid junction. The value of $\Delta_r H°$ given here was calculated from pKs measured at several temperatures. The value $\Delta_r C_p^\circ/(\text{J K}^{-1}\text{ mol}^{-1}) = -73$ was also calculated from the temperature dependency of their [63DAT/GRZ] reported pKs. Datta *et al.* [63DAT/GRZ] allowed for $\Delta_r C_p^\circ$ to be temperature dependent and calculated the value $\Delta_r H°/(\text{kJ mol}^{-1}) = 47.40$ at $T=298.15$ K. The value $\Delta_r C_p^\circ/(\text{J K}^{-1}\text{ mol}^{-1}) = -91$ was also obtained from this [63DAT/GRZ] study.	63DAT/GRZ
8.6792		278.15	0		
8.5158		283.15	0		
8.3602		288.15	0		
8.2124		293.15	0		
8.0686	47.78	298.15	0		
7.9336		303.15	0		
7.8006		308.15	0		
7.6756		313.15	0		
7.5515		318.15	0		
7.4380		323.15	0		
7.3204		328.15	0		
7.2098		333.15	0		
	47.53	298.15	0.10 M	Calorimetry.	64NEL
	47.48	298.15	0.07 M	Calorimetry.	68OJE/WAD
	47.66	298.15	0.010 M	Calorimetry.	68CHR/WRA
	47.50	298.15	≈0.1 M	Calorimetry.	69HIL/OJE
	47.48	298.15	0	Calorimetry.	69WIL/SMI
	49.15	278.15	≈0.015 M	Calorimetry. Grenthe *et al.* [70GRE/OTS] also obtained $\Delta_r C_p^\circ/(\text{J K}^{-1}\text{ mol}^{-1}) = -73$ at $T=298.15$ as well as values for other temperatures over the range $278.15 \leqslant T/\text{K} \leqslant 323.15$.	70GRE/OTS
	47.85	293.15	≈0.015 M		
	47.44	298.15	≈0.015 M		
	46.81	308.15	≈0.015 M		
	46.03	323.15	≈0.015 M		
	47.36	298.15	≈0.01 M	Calorimetry.	71HAN/LEW2
	47.86	278.15	?	Calorimetry.	71HIN/SHI
	47.42	298.15	0	Calorimetry.	72OTS

Values from literature—Continued

p*K*	$\Delta_r H°/(\mathrm{kJ\,mol^{-1}})$	*T*/K	I	Method(s) and comments	Reference
	47.45	293.15	≈0.01 M	Calorimetry.	72SIM/IVI
	47.28	298.15	≈0.01 M	Calorimetry.	76MCG/JOR
	47.39	298.15	?	Calorimetry.	81VAC/SAB
8.670		278.15	0	Electrochemical cell with liquid junction. The p*K* values given here were calculated from Palmer and Wesolowski's [87PAL/WES] Eq. (2). The value of $\Delta_r H°$ given here was calculated by Palmer and Wesolowski [87PAL/WES] from the temperature dependence of the p*K*s. They also give $\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}}) = -67$ at $T = 298.15$ K.	87PAL/WES
8.065	47.50	298.15	0		
7.433		323.15	0		
6.907		348.15	0		
6.461		373.15	0		
6.078		398.15	0		
5.743		423.15	0		
5.448		448.15	0		
5.186		473.15	0		
	47.55	298.15	0	Calorimetry.	93SAN/BAY
				Ford *et al.* [2000FOR/CAL] measured apparent molar heat capacities of Tris(aq) and of Tris·HCl(aq) from $T = 278.15$ K to $T = 393.15$ K and at the pressure $p = 0.35$ MPa. These results were used to calculate values of $\Delta_r C_p^\circ$ over this temperature range. At $T = 298.15$ K, $\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}}) = -59$.	2000FOR/CAL

Values adjusted to $T = 298.15$ K and $I = 0$

p*K*	$\Delta_r H°/(\mathrm{kJ\,mol^{-1}})$	$\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}})$	Reference
8.076			49BAT/PIN3
	45.73		55STU
	48.2		56POD/MOR
8.075	47.58	−64	61BAT/HET
	49.75		61TYS/MCC
8.069	47.78		63DAT/GRZ
	47.53		64NEL
	47.48		68OJE/WAD
	47.66		68CHR/WRA
	47.50		69HIL/OJE
	47.48		69WIL/SMI
	47.44	−73	70GRE/OTS
	47.36		71HAN/LEW2
	46.7		71HIN/SHI
	47.42		72OTS
	47.16		72SIM/IVI
	47.28		76MCG/JOR
	47.39		81VAC/SAB
8.065	47.50	−67	87PAL/WES
	47.55		93SAN/BAY
		−59	2000FOR/CAL

Comments: We adopt the average of the p*K* values obtained by Bates and Hetzer [61BAT/HET] and by Datta *et al.* [63DAT/GRZ]. The most reliable of the $\Delta_r H°$ values center around 47.45 $\mathrm{kJ\,mol^{-1}}$. This $\Delta_r H°$ value is adopted along with the value $\Delta_r C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}}) = -59$ determined by Ford *et al.* [2000FOR/CAL]. Many additional studies, performed under a variety of conditions, are cited by Martell *et al.* [2001MAR/SMI] and by Pettit and Powell [2000PET/POW].

8. Summary of Selected Values of Thermodynamic Quantities for the Ionization Reactions of Buffers in Water at $T=298.15$ K and $p=0.1$ MPa

The standard state is the hypothetical ideal solution of unit molality.

Buffer	Reactions	pK	$\Delta_r H°$ / kJ mol^{-1}	$\Delta_r C_p^\circ$ / (J K^{-1} mol^{-1})
ACES	$HL^{\pm}=H^+ + L^-$, ($HL=C_4H_{10}N_2O_4S$)	6.847	30.43	−49
acetate	$HL=H^+ + L^-$, ($HL=C_2H_4O_2$)	4.756	−0.41	−142
ADA	$H_3L^+=H^+ + H_2L^{\pm}$, ($H_2L=C_6H_{10}N_2O_5$)	1.59		
	$H_2L^{\pm}=H^+ + HL^-$	2.48	16.7	
	$HL^-=H^+ + L^{2-}$	6.844	12.23	−144
2-amino-2-methyl-1,3-propanediol	$HL^+=H^+ + L$, ($L=C_4H_{11}NO_2$)	8.801	49.85	−44
2-amino-2-methyl-1-propanol	$HL^+=H^+ + L$, ($L=C_4H_{11}NO$)	9.694	54.05	≈−21
3-amino-1-propanesulfonic acid	$HL=H^+ + L^-$, ($HL=C_3H_9NO_3S$)	10.2		
ammonia	$NH_4^+=H^+ + NH_3$	9.245	51.95	8
AMPSO	$HL^{\pm}=H^+ + L^-$, ($HL=C_7H_{17}NO_5S$)	9.138	43.19	−61
arsenate	$H_3AsO_4=H^+ + H_2AsO_4^-$	2.31	−7.8	
	$H_2AsO_4^-=H^+ + HAsO_4^{2-}$	7.05	1.7	
	$HAsO_4^{2-}=H^+ + AsO_4^{3-}$	11.9	15.9	
barbital	$H_2L=H^+ + HL^-$, ($H_2L=C_8H_{12}N_2O_3$)	7.980	24.27	−135
	$HL^-=H^+ + L^{2-}$	12.8		
BES	$HL^{\pm}=H^+ + L^-$, ($HL=C_6H_{15}NO_5S$)	7.187	24.25	−2
Bicine	$H_2L^+=H^+ + HL^{\pm}$, ($HL=C_6H_{13}NO_4$)	2.0		
	$HL^{\pm}=H^+ + L^-$	8.334	26.34	0
Bis-tris	$H_3L^+=H^+ + H_2L^{\pm}$, ($H_2L=C_8H_{19}NO_5$)	6.484	28.4	27
Bis-tris propane	$H_2L^{2+}=H^+ + HL^+$, ($L=C_{11}H_{26}N_2O_6$)	6.65		
	$HL^+=H^+ + L$	9.10		
borate	$H_3BO_3=H^+ + H_2BO_3^-$	9.237	13.8	≈−240
CABS	$HL^{\pm}=H^+ + L^-$, ($HL=C_{10}H_{21}NO_3S$)	—		
cacodylate	$H_2L^+=H^+ + HL$, ($HL=C_2H_6AsO_2$)	1.78	−3.5	
	$HL=H^+ + L^-$	6.28	−3.0	−86
CAPS	$HL^{\pm}=H^+ + L^-$, ($HL=C_9H_{19}NO_3S$)	10.499	48.1	57
CAPSO	$HL^{\pm}=H^+ + L^-$, ($HL=C_9H_{19}NO_4S$)	9.825	46.67	21
carbonate	$H_2CO_3=H^+ + HCO_3^-$	6.351	9.15	−371
	$HCO_3^-=H^+ + CO_3^{2-}$	10.329	14.70	−249
CHES	$HL^{\pm}=H^+ + L^-$, ($HL=C_8H_{17}NO_3S$)	9.394	39.55	9
citrate	$H_3L=H^+ + H_2L^-$, ($H_3L=C_6H_8O_7$)	3.128	4.07	−131
	$H_2L^-=H^+ + HL^{2-}$	4.761	2.23	−178
	$HL^{2-}=H^+ + L^{3-}$	6.396	−3.38	−254
L-cysteine	$H_3L^+=H^+ + H_2L$, ($H_2L=C_3H_7NO_2S$)	1.71	≈−0.6	
	$H_2L=H^+ + HL^-$	8.36	36.1	≈−66
	$HL^-=H^+ + L^{2-}$	10.75	34.1	≈−204
diethanolamine	$HL^+=H^+ + L$, ($L=C_4H_{11}NO_2$)	8.883	42.08	36
diglycolate	$H_2L=H^+ + HL^-$, ($H_2L=C_4H_6O_5$)	3.05	−0.1	≈−142
	$HL^-=H^+ + L^{2-}$	4.37	−7.2	≈−138
3,3-dimethylglutarate	$H_2L=H^+ + HL^-$, ($H_2L=C_7H_{12}O_4$)	3.70		
	$HL^-=H^+ + L^{2-}$	6.34		
DIPSO	$HL^{\pm}=H^+ + L^-$, ($HL=C_7H_{17}NO_6S$)	7.576	30.18	42
ethanolamine	$HL^+=H^+ + L$, ($L=C_2H_7NO$)	9.498	50.52	26
N-ethylmorpholine	$HL^+=H^+ + L$, ($L=C_6H_{13}NO$)	7.77	27.4	
glycerol 2-phosphate	$H_2L=H^+ + HL^-$, ($H_2L=C_3H_9NO_6P$)	1.329	−12.2	−330
	$HL^-=H^+ + L^{2-}$	6.650	−1.85	−212
glycine	$H_2L^+=H^+ + HL^{\pm}$, ($HL=C_2H_5NO_2$)	2.351	4.00	−139
	$HL^{\pm}=H^+ + L^-$	9.780	44.2	−57
glycine amide	$HL^+=H^+ + L$, ($L=C_2H_6N_2O$)	8.04	42.9	
glycylglycine	$H_2L^+=H^+ + HL^{\pm}$, ($HL=C_4H_8N_2O_3$)	3.140	0.11	−128
	$HL^{\pm}=H^+ + L^-$	8.265	43.4	−16
glycylglycylglycine	$H_2L^+=H^+ + HL^{\pm}$, ($HL=C_6H_{11}N_3O_4$)	3.224	0.84	
	$HL^{\pm}=H^+ + L^-$	8.090	41.7	
HEPBS	$HL^{\pm}=H^+ + L^-$, ($HL=C_{10}H_{22}N_2O_4S$)	—		
HEPES	$H_2L^+=H^+ + HL^{\pm}$, ($HL=C_8H_{18}N_2O_4S$)	≈3.0		
	$HL^{\pm}=H^+ + L^-$	7.564	20.4	47
HEPPS	$HL^{\pm}=H^+ + L^-$, ($HL=C_6H_{20}N_2O_4S$)	7.957	21.3	48

Section 8—Continued

Buffer	Reactions	pK	$\Delta_r H°$ / kJ mol^{-1}	$\Delta_r C_p^\circ$ / (J K^{-1} mol^{-1})
HEPPSO	$HL^{\pm}=H^+ + L^-$, ($HL=C_9H_{20}N_2O_5S$)	8.042	23.70	47
L-histidine	$H_3L^{2+}=H^+ + H_2L^+$, ($HL=C_6H_9N_3O_2$)	1.5_4	3.6	
	$H_2L^+=H^+ + HL$	6.07	29.5	176
	$HL=H^+ + L^-$	9.34	43.8	−233
hydrazine	$H_2L^{2+}=H^+ + HL^+$, ($L=H_4N_2$)	−0.99	38.1	
	$HL^+=H^+ + L$	8.02	41.7	
imidazole	$HL^+=H^+ + L$, ($L=C_3H_4N_2$)	6.993	36.64	−9
maleate	$H_2L=H^+ + HL^-$, ($H_2L=C_4H_4O_4$)	1.92	1.1	≈−21
	$HL^-=H^+ + L^{2-}$	6.27	−3.6	≈−31
2-mercaptoethanol	$HL=H^+ + L^-$, ($HL=C_2H_6OS$)	9.7_5	26.2	
MES	$HL^{\pm}=H^+ + L^-$, ($HL=C_6H_{13}NO_4S$)	6.270	14.8	5
methylamine	$HL^+=H^+ + L$, ($L=CH_5N$)	10.645	55.34	33
2-methylimidazole	$HL^+=H^+ + L$, ($L=C_4H_6N_2$)	8.0_1	36.8	
MOBS	$HL^{\pm}=H^+ + L^-$, ($HL=C_8H_{17}NO_4S$)	—		
MOPS	$HL^{\pm}=H^+ + L^-$, ($HL=C_7H_{15}NO_4S$)	7.184	21.1	25
MOPSO	$H_2L^+=H^+ + HL^{\pm}$, ($HL=C_7H_{15}NO_5S$)	0.060		
	$HL^{\pm}=H^+ + L^-$	6.90	25.0	≈38
oxalate	$H_2L=H^+ + HL^-$, ($H_2L=C_2H_2O_4$)	1.27	−3.9	≈−231
	$HL^-=H^+ + L^{2-}$	4.266	7.00	−231
phosphate	$H_3PO_4=H^+ + H_2PO_4^-$	2.148	−8.0	−141
	$H_2PO_4^-=H^+ + HPO_4^{2-}$	7.198	3.6	−230
	$HPO_4^{2-}=H^+ + PO_4^{3-}$	12.35	16.0	−242
phthalate	$H_2L=H^+ + HL^-$, ($H_2L=C_8H_6O_4$)	2.950	−2.70	−91
	$HL^-=H^+ + L^{2-}$	5.408	−2.17	−295
piperazine	$H_2L^{2+}=H^+ + HL^+$, ($L=C_4H_{10}N_2$)	5.333	31.11	86
	$HL^+=H^+ + L$	9.731	42.89	75
PIPES	$HL^{\pm}=H^+ + L^-$, ($HL=C_8H_{18}N_2O_6S_2$)	7.141	11.2	22
POPSO	$HL^{\pm}=H^+ + L^-$, ($HL=C_{10}H_{22}N_2O_8S_2$)	≈8.0		
pyrophosphate	$H_4P_2O_7=H^+ + H_3P_2O_7^-$	0.83	−9.2	≈−90
	$H_3P_2O_7^-=H^+ + H_2P_2O_7^{2-}$	2.26	−5.0	≈−130
	$H_2P_2O_7^{2-}=H^+ + HP_2O_7^{3-}$	6.72	0.5	−136
	$HP_2O_7^{3-}=H^+ + P_2O_7^{4-}$	9.46	1.4	−141
succinate	$H_2L=H^+ + HL^-$, ($H_2L=C_4H_6O_4$)	4.207	3.0	−121
	$HL^-=H^+ + L^{2-}$	5.636	−0.5	−217
sulfate	$HSO_4^-=H^+ + SO_4^{2-}$	1.987	−22.4	−258
sulfite	$H_2SO_3=H^+ + HSO_3^-$	1.857	−17.80	−272
	$HSO_3^-=H^+ + SO_3^{2-}$	7.172	−3.65	−262
TABS	$HL^{\pm}=H^+ + L^-$, ($HL=C_8H_{19}NO_6S$)	—		
TAPS	$HL^{\pm}=H^+ + L^-$, ($HL=C_7H_{17}NO_6S$)	8.44	40.4	15
TAPSO	$HL^{\pm}=H^+ + L^-$, ($HL=C_7H_{17}NO_7S$)	7.635	39.09	−16
L(+)tartaric acid	$H_2L=H^+ + HL^-$, ($H_2L=C_4H_6O_6$)	3.036	3.19	−147
	$HL^-=H^+ + L^{2-}$	4.366	0.93	−218
TES	$HL^{\pm}=H^+ + L^-$, ($HL=C_6H_{15}NO_6S$)	7.550	32.13	0
Tricine	$H_2L^+=H^+ + HL^{\pm}$, ($HL=C_6H_{13}NO_5$)	2.023	5.85	−196
	$HL^{\pm}=H^+ + L^-$	8.135	31.37	−53
triethanolamine	$HL^+=H^+ + L$, ($L=C_6H_{15}NO_3$)	7.762	33.6	50
triethylamine	$HL^+=H^+ + L$, ($L=C_6H_{15}N$)	10.72	43.13	151
Tris	$HL^+=H^+ + L$, ($L=C_4H_{11}NO_3$)	8.072	47.45	−59

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