Ionization Constants of Water Pollutants

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Ionization constants up to 150 °C are presented for the major pollutants of petroleum refinery wastewater streams: ammonia, hydrogen sulfide, phenols, chlorides, cyanides and thiocyanates, and alkyl mercaptans. New experimental data are obtained at 25–150 °C, by means of the spectrophotometric method, for hydrogen sulfide (first ionization constant), phenol, hydrogen cyanide, and ethyl mercaptan. The value of the second ionization constant of hydrogen sulfide is determined from pH measurements. A four-term equation is used to express the temperature dependence of the ionization constants and the ionic product of water.

Pollutants must be removed from the petroleum refinery wastewater streams because of their undesirable effects—high oxygen demand, toxicity, or an objectionable taste and odor. The major pollutants other than oil in such streams are the following electrolytes: ammonia, hydrogen sulfide, phenols (C_6–C_8, represented in this work by the C_6), chlorides, cyanides and thiocyanates, and alkyl mercaptans (C_1–C_3, represented in this work by the C_2).

Thermodynamic data on the aqueous solutions of the water contaminants are needed to trace the phase distribution of these species through the entire process sequence and to design separation equipment (such as sour water strippers) for their removal. Of these thermodynamic data (ionization constants, Henry's constants, and activity coefficients), only the ionization constants are considered here.

An extensive treatment of water pollution from refineries is given by Beychok (*3*). Although the wastewater ("sour" water) phase generally forms and is separated from the hydrocarbon liquid phase at cooling water temperatures (30–40 °C), the maximum temperature of interest has been set at 150 °C; this temperature can be reached in sour water strippers.

A literature search and critical examination of the data indicated that inadequate information existed, especially above room temperature, for the ionization constants of hydrogen sulfide, phenol, hydrogen cyanide, and ethyl mercaptan. The missing information is provided by the experimental measurements reported in this paper. They cover the temperature range 25–150 °C and are made by means of the spectrophotometric method. (See refs. *10* and *13* for information on this and other experimental methods.) The temperature dependence of the ionization constants is expressed with a four-term equation, and values for the coefficients of this equation are presented for the ionic product of water and the ionization constants of the ammonium ion, hydrogen sulfide, phenols, hydrogen cyanide, and alkyl mercaptans.

Ionization Constants; Definitions

The ionization (or dissociation) constant of an acid HA is given by

$$K_a = \frac{(a_{H^+})(a_{A^-})}{(a_{HA})} \tag{1}$$

where a_i is the activity of species i (ionic or molecular) in solution and is defined by:

$$a_i = \gamma_i m_i \tag{2}$$

γ_i is the activity coefficient (dimensionless), and m_i the molality (g-mol/kg solvent) of component i. It follows that a_i, as well as K_a, has the dimensions of molality. [This convention is common when dealing with electrolyte solutions; see ref. *13*, pages 26–27. It implies that the standard state electrochemical potential contains the concealed term $RT \ln$ (g-mol/kg). Some chemists would prefer to say that the standard state is a hypothetical ideal 1 molal solution.]

The experimentally determinable constant is K_m:

$$K_m = \frac{(m_{H^+})(m_{A^-})}{(m_{HA})} \tag{3}$$

To obtain K_a, the activity coefficient ratio

$$\frac{(\gamma_{H^+})(\gamma_{A^-})}{(\gamma_{HA})} = \frac{(\gamma_{+-})^2}{(\gamma_{HA})} \tag{4}$$

must be determined. In very dilute solutions, say $m_i < 0.01$, γ_{+-} can be calculated with the Debye-Hueckel equation (*13*) and γ_{HA}, the activity coefficient of the undissociated electrolyte, can be set equal to unity. Therefore, measurements on such solutions can give high-precision K_a data.

While the value of K_a measures the strength of the acid, the activity of H^+ is directly related to the acidity, or the pH, of the solution:

$$pH = -\log_{10} a_{H^+} \tag{5}$$

The pH of refinery wastewater streams ranges between 6 and 10.

Both acids and bases contribute to the pH of the solution. In the case of a base B, it has become common practice (*12*) to use the ionization constant of the conjugate acid BH^+:

$$K_a = \frac{(a_{H^+})(a_B)}{(a_{BH^+})} \tag{6}$$

The equilibrium constant for the hydrolysis of B to form BH^+ and OH^- is denoted by K_b, which is equal to the ratio K_w/K_a. K_a is given by Equation 6 and K_w, the ionic product of water, by:

$$K_w = (a_{H^+})(a_{OH^-}) \tag{7}$$

(It is implied that the activity of water is equal to unity.)

Up to now, attention has been focused on monobasic acids; these are acids that release a single proton H^+ and hence have a single ionization constant. With polybasic acids, however, there is a series of ionizations: $H_N A \rightarrow H_{N-1} A^- \rightarrow \ldots \rightarrow A^{-N}$. Therefore, an N-basic acid has N ionization constants, indicated by $K_1, \ldots, K_N$. As an example, the two ionization constants of hydrogen sulfide are given by

$$K_1 = \frac{(a_{H^+})(a_{HS^-})}{(a_{H_2S})}$$

and

$$K_2 = \frac{(a_{H^+})(a_{S^{2-}})}{(a_{HS^-})}$$

Experimental Procedure and Results

A spectrophotometric method previously described by Ang (1), Irving et al. (8), and others, based on the UV absorption of the anion of the acid or an indicator, was used to measure the ionization constants of phenol, hydrogen sulfide, hydrogen cyanide, and ethyl mercaptan. K_a was actually determined from measurements of the equilibrium constant for the hydrolysis of A^-, and the literature values for K_w (7):

$$K_a = \frac{K_w(m_{A^-})}{(m_{HA})(m_{OH^-})} \cdot \frac{\gamma_{A^-}}{\gamma_{HA}\gamma_{OH^-}}$$

Since in the present study $m_i < 0.01$, $\gamma_{HA} \cong 1.00$ and $\gamma_{A^-} \cong \gamma_{OH^-}$; that is, the activity coefficient factor can be set equal to unity.

The solutions were sealed into fused-silica cells with path lengths of 2 cm and capacities of approximately 5 cm³. Each cell had a 5-cm³ expansion chamber that was filled with argon to provide space for expansion of the solution at the higher temperatures. The cell containing the solution under study was housed in a thermostated aluminum block that was placed in a Cary Model 14M spectrophotometer. Four cartridge heaters (CIR 2032) of 100 W each were used to heat the block, which was held at constant temperature with a YSI Model 2161 electronic temperature controller. During each run, the temperature was maintained to within ±0.5 °C (over the range of 25–150 °C).

All solutions were prepared daily (and used immediately) from distilled, deionized water that had a conductivity of no more than 0.1 μmho. Pure phenol was obtained by distilling under vacuum a Mallinckrodt 80% phenol–20% water mix-

ture and collecting a constant-boiling middle fraction. Baker-analyzed reagent grade sodium sulfide (Na₂S·9H₂O), Mallinckrodt analytical reagent grade sodium cyanide, and K and K Laboratories ethyl mercaptan were very pure and were used without further purification to prepare the solutions used in the study. Pure 2,4-dichlorophenol (mp = 43 °C), used as an indicator for HCN and H₂S (K_1), was obtained by recrystallization from hexane. Concentrations of the solutions on which spectrophotometric measurements were made were all confirmed by titration by standard analytical chemical procedures. All solutions were prepared under an argon atmosphere.

The final results are given in Table I. Each value is the average of at least three measurements. The uncertainty in the reported values is generally less than 0.05 pK_a units (or less than 10% in K_a). The only exceptions are for HCN (±0.11 pK_a units at 25 °C) and ethyl mercaptan (±0.10 pK_a units at 125 and 150 °C).

A rough study of K_2, the second ionization constant of H₂S, was made by titrating 0.28 molar Na₂S with 0.1 normal HCl and measuring the pH in the range 10–13. (An identical titration curve was obtained when dilute NaOH was used in place of Na₂S.) The pH at the first equivalence point was 10.5 (at 25 °C). Since at that point pH = $\sqrt{(pK_1)(pK_2)}$, and pK_1 is known, pK_2 can be determined. The results are discussed in the next section.

Temperature Dependence of Ionization Constants

The variation of the ionization constants with temperature can be described most satisfactorily with the following equation:

$$-\log_{10} K_a = pK_a = A/T + B \log_{10} T + CT + D \qquad (8)$$

Equation 8 implies that ΔC_p°, the standard heat capacity change of the ionization reaction, is a linear function of temperature. The exceptionally accurate data for K_w (7), however, suggest that ΔC_p° has a maximum; hence, a quadratic function would be needed to describe its temperature dependence. Nevertheless, a T^2 term in Equation 8 was of little value in fitting K_a data.

Equation 8, with the coefficients in Table II, summarizes our recommendations for the temperature dependence of the ionization constants of the electrolytes under consideration. This is also shown in Figures 1–4 and is briefly considered below.

Water. Fisher and Barnes (7) measured the ionic product of water (K_w) in the temperature range 100–350 °C and then fitted their own data and those of Noyes et al. (after recalculating the 306 °C value), Harned and Robinson, and Ackermann. Only the data up to 225 °C were used in the regression with Equation 8.

Ammonium ion. The ionization constant of the ammonium ion was calculated using K_w and the smoothed data re-

Table I. Experimental Ionization Constants (pK_a)
pK_a = $-\log_{10} K_a$; K_a in g-mol/kg

t, °C	H₂S (K_1)	C₆H₅OH	HCN	C₂H₅SH	2,4-Di-chloro-phenol[a]
25	7.045	9.960	9.21	10.61	7.891
50	6.744	9.602	8.59	10.215	7.636
75	6.549	9.385	8.18	10.04	7.466
100	6.467	9.256	7.89	9.84	7.383
125	6.467	9.207	7.74	9.696	7.358
150	6.496	9.172	7.64	9.55	7.351
Av uncertainty in pK_a	0.019	0.039	0.08	0.07	...[b]

[a] Used as indicator for measurements on H₂S (K_1) and HCN. [b] The three measurements per temperature were in very good agreement.

Table II. Ionization Constants of Weak Acids
$-\log_{10} K_a$ = pK_a = $A/T + B \log_{10} T + CT + D$; K_w in (g-mol/kg)², K_a in g-mol/kg, and T in kelvins

	A	B	C	D	t range, °C (no. points)	SD[a] of pK_a
Water (K_w)	5839.50	22.4773	...	-61.2062	0–225 (15)	0.0062
Ammonium ion	4390.82	23.9744	-0.0160935	-60.0072	0–225 (12)	0.0045
Hydrogen sulfide (K_1)[b]	5643.83	33.5471	...	-94.9363	0–150 (21)	0.0513
Phenol[c]	5068.19	27.7262	...	-75.6249	25–150 (12)	0.0211
Hydrogen cyanide	4319.29	...	0.0215317	-11.6908	10–150 (15)	0.0286
Ethyl mercaptan[d]	2896.14	12.1231	...	-29.1135	25–150 (7)	0.0334

[a] Standard deviation = $\sqrt{\dfrac{(\text{residuals})^2}{\text{no. points} - \text{no. coefficients}}}$. [b] $K_2 \cong 0.018 \times K_w$. [c] o-Cresol: $D = -75.315$; 2,6-xylenol: $D = -75.015$. [d] Methyl mercaptan: $D = -29.36$; n-propyl mercaptan: $D = -28.86$.

ported by Fisher and Barnes (7) for the ionization constant of ammonium hydroxide ($K_{NH_4^+} = K_w/K_{NH_4OH}$). Fisher and Barnes fitted the data of Noyes et al. (which had to be recalculated), Bates and Pinching, Wright et al., and Quist and Marshall. The coefficients in Table II were obtained by fitting the data up to 225 °C.

Hydrogen sulfide. Loy and Himmelblau (11) have examined the available information for K_1 (the first ionization constant of H_2S) and measured its value at 0, 25, and 50 °C. Their data and those of Wright and Maass (14) in the range 0–60 °C were selected for this analysis, even though there is substantial disagreement—especially at 50 °C. Ellis and
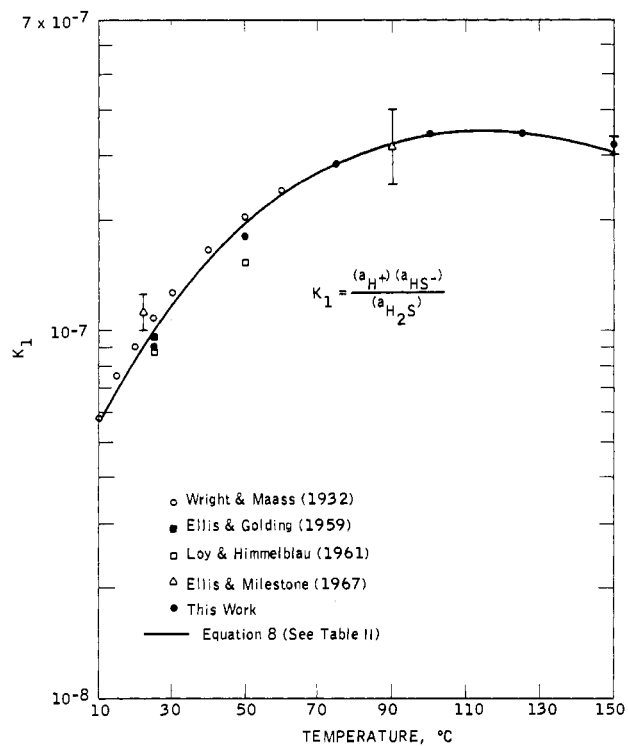

$$K_1 = \frac{(a_{H^+})\,(a_{HS^-})}{(a_{H_2S})}$$

o Wright & Maass (1932)
■ Ellis & Golding (1959)
□ Loy & Himmelblau (1961)
△ Ellis & Milestone (1967)
● This Work
—— Equation 8 (See Table II)

Figure 1. First ionization constant of hydrogen sulfide

$$K_{HCN} = \frac{(a_{H^+})(a_{CH^-})}{(a_{HCN})}$$

□ Ang (1959)
△ Izatt et al (1962)
● This Work
—— Equation 8 (See Table II)
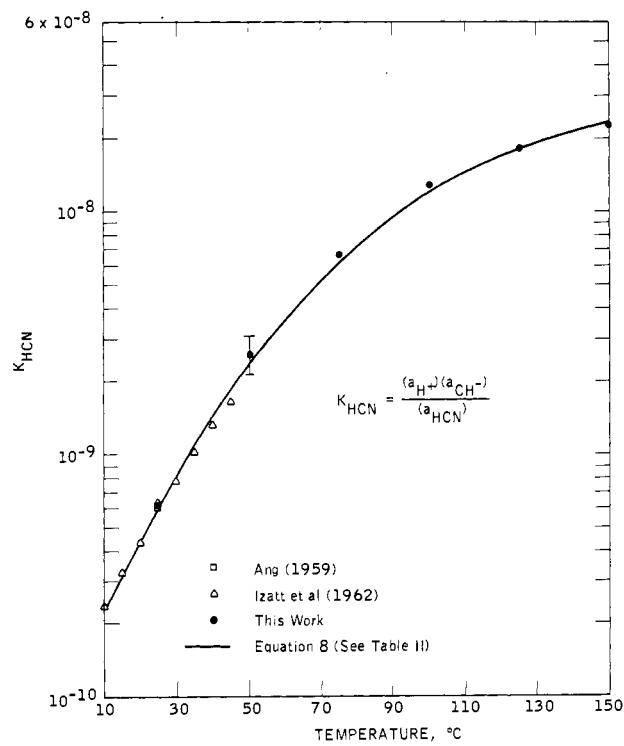
Figure 3. Ionization constant of hydrogen cyanide

$$K_{C_6H_5OH} = \frac{(a_{H^+})\,(a_{C_6H_5O^-})}{(a_{C_6H_5OH})}$$

■ Binns (1959)
▲ Kortüm et al (1961)
▽ Chen & Laidler (1962): Excluded From Data Reduction With Eq. 8
● This Work
—— Equation 8 (See Table II)
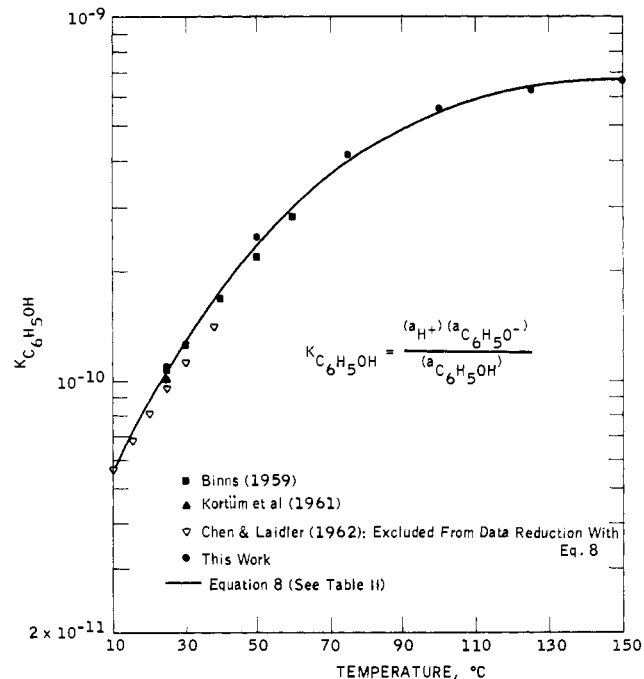
Figure 2. Ionization constant of phenol

$$K_{C_2H_5SH} = \frac{(a_{H^+})\,(a_{C_2H_5S^-})}{(a_{C_2H_5SH})}$$

△ Irving et al (1964)
o This Work
—— Equation 8 (See Table II)
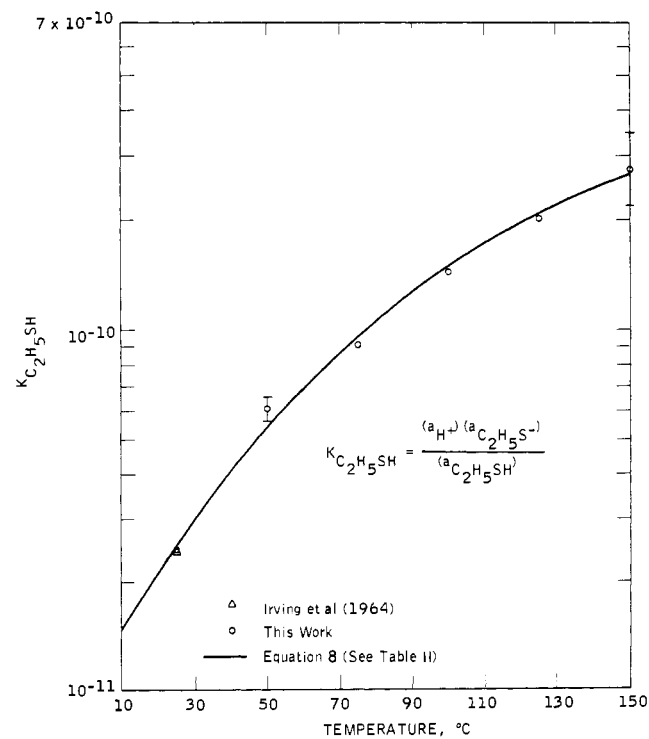
Figure 4. Ionization constant of ethyl mercaptan

Milestone (6) measured K_1 at 22 and 90 °C (with an uncertainty of ±0.05 pK units at 22 °C and ±0.1 at 90 °C) and fitted their data and those of Wright and Maass, Loy and Himmelblau, and Ellis and Golding (pK_1 = 7.022 at 25 °C) with the equation

$$pK_1 = 3760/T + 20 \log_{10} T - 55.06$$

This equation has a weak minimum (maximum in K_1) at 160 °C.

The curve in Figure 1 is the best fit of the data (all the mentioned literature results along with the new measurements), as determined with Equation 8 and the coefficients in Table II. Any extrapolation of K_1 should be made algebraically, with Equation 8, rather than graphically; the same holds true for phenol, hydrogen cyanide, and ethyl mercaptan.

A summary of representative values for K_2, the second ionization constant of H_2S, is given in ref. 2. K_2 is less than 10^{-11} below 150 °C; hence, the one-order-of magnitude uncertainty in its value is inconsequential in the pH range of interest (6 ≤ pH ≤ 10). An interesting feature of the K_2 values is their similarity with the K_w values. Indeed, the data suggest that K_w rather than K_2 was measured, for example, by Ellis and Milestone (6).

By means of the pH measurements described above, K_2 was nearly equal to $K_w/55.5$ (= $m_{H^+} m_{OH^-}/m_{H_2O}$). Therefore, S^{2-} is a much stronger base than OH^-, which means that S^{2-} hydrolyzes to form HS^- and the concentration of S^{2-} in dilute aqueous solution will be so slight (especially at pH < 10) that it can be neglected. If K_2 is needed, use 0.018 × K_w.

Phenols. Figure 2 and Equation 8 with the coefficients in Table II give the best fit of the new measurements along with those reported by Binns (4) and Kortüm et al. (10).

The data of Zavitsas (16) were discarded because they are substantially lower than those shown in Figure 3—if the activity coefficient correction is applied; this correction is 0.24–0.26 rather than 0.11 pK units, as used by Zavitsas. Also excluded from the data reduction were the results of Chen and Laidler (5) because their temperature dependence is substantially less steep than that of the new measurements and Binns's values; see Figure 2.

The C_7+ phenols have lower K_a's than phenol; at 25 °C, the pK_a of o-cresol is 10.29 and of 2,6-xylenol, 10.59 (10). Therefore, the coefficient D in Equation 8 must be −75.315 for o-cresol and −75.015 for 2,6-xylenol. All phenols, on the other hand, will have the same A and B as phenol (given in Table II), since members of a homologous series are expected to have approximately the same temperature variation of K_a; this is confirmed by the results of Chen and Laidler (5) for the cresols and the xylenols over the range 5–38 °C.

Hydrogen chloride. Only the inorganic chlorides are of interest in water pollution from refineries, and those ionize completely in aqueous solution. The hydrolysis of Cl^- can be entirely neglected because HCl is a strong acid. At 25 °C its ionization constant is 1.3 × 10^6 (2).

Hydrogen cyanide. The ionization constant of HCN has been measured at 25 °C by Ang (1) and at 10–45 °C by Izatt et al. (9). These and the new data were employed in the regression analysis; the coefficients in Table II were used in preparing Figure 3. (A better fit results by including a T^2 term in Equation 8, but this term was not statistically significant in any other case.)

Thiocyanic acid. HSCN is a fairly strong acid (K_a = 0.14 at 25 °C); hence, only the thiocyanate ion (SCN$^-$) will be present in the sour water streams. SCN$^-$ is the product of the reaction of CN$^-$ with polysulfide (or even H_2S).

Alkyl mercaptans. Only the room temperature value of the ethyl mercaptan ionization constant is available in the litera-

ture (8). Thus, the new data are the only source of information above 25 °C. Due to the high volatility and low solubility in water of ethyl mercaptan, which caused substantial difficulties at high temperatures, the spread of the individual results is up to 0.3 pK units. The experimental uncertainty varies between ±0.033 (at 50 °C) and ±0.10 pK units (at 150 °C), as indicated in Figure 4.

The ionization constants of the n-alkyl mercaptans decrease slightly with increasing molecular weight (8, 15), but, as in the case of the phenols, they are assumed to have the same temperature dependence. Hence, the C_1–C_3 mercaptans will have the same values for the coefficients A and B in Equation 8. Approximate values for the coefficient D are −29.36 (methyl mercaptan) and −28.86 (n-propyl mercaptan).

A final comment concerns the pressure dependence of the ionization constants. It is too weak to be of any significance in water pollution abatement work and therefore can be neglected. As an example, the value of the ionic product of water at 25 °C will increase by less than 5% when the pressure is raised by 50 atm. This can be compared with a 10% increase in K_w when the temperature is raised to 26 °C.

Nomenclature

a_i = activity of component i, g-mol/kg
K = ionization constant, g-mol/kg
K_w = ionic product of water, (g-mol/kg)^2
m_i = molality of component i (defined as g-mol of i per kg solvent)
pH = $-\log_{10} a_{H^+}$
pK = $-\log_{10} K$
$t(T)$ = (absolute) temperature; °C (K)
γ_i = activity coefficient of component i

Subscripts

a = property of acid
b = property of base
$1, \ldots, N$ = first, $\ldots$, Nth ionization constant

Literature Cited

(1) Ang, K. P., J. Chem. Soc., **1959**, p 3822.
(2) Barnes, H. L., Helgeson, H. C., Ellis, A. J., "Ionization Constants in Aqueous Solutions", Section 18 of "Handbook of Physical Constants", rev. ed., Geological Society of America, Memoir 97, 1966.
(3) Beychok, M. R., "Aqueous Wastes from Petroleum and Petrochemical Plants", Wiley, London, England, 1967.
(4) Binns, E. H., Trans. Faraday Soc., **55**, 1900 (1959).
(5) Chen, D.T.Y., Laidler, K. J., ibid., **58**, 480 (1962).
(6) Ellis, A. J., Milestone, N. B., Geochim. Cosmochim. Acta, **31**, 615 (1967).
(7) Fisher, J. R., Barnes, H. L., J. Phys. Chem., **76**, 90 (1972).
(8) Irving, R. J., Nelander, L., Wadsoe, I., Acta Chem. Scand., **18**, 769 (1964).
(9) Izatt, R. M., Christensen, J. J., Pack, R. T., Bench, R., Inorg. Chem., **1**, 828 (1962).
(10) Kortüm, G., Vogel, W., Andrussow, K., "Dissociation Constants of Organic Acids in Aqueous Solution", Butterworths, London, England, 1961.
(11) Loy, H. L., Himmelblau, D. M., J. Phys. Chem., **65**, 264 (1961).
(12) Perrin, D. D., "Dissociation Constants of Organic Bases in Aqueous Solution", Butterworths, London, England, 1965.
(13) Robinson, R. A., Stokes, R. H., "Electrolyte Solutions", 2nd ed., Butterworths, London, England, 1959.
(14) Wright, R. H., Maass, O., Can. J. Res., **6**, 588 (1932).
(15) Yabroff, D. L., Ind. Eng. Chem., **32**, 257 (1940).
(16) Zavitsas, A. A., J. Chem. Eng. Data, **12**, 94 (1967).