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Potentiometric Studies at ORNL with Hydrogen Electrode Concentration Cells

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ABSTRACT

A description of hydrogen electrode concentration cells developed in the late sixties and currently in use at Oak Ridge is given. The method of measurement, data interpretation, and published results are reviewed for studies of acid-base ionization, metal ion hydrolysis, and metal complexation reactions using principally such cells in titration or flow modes.

INTRODUCTION

Measurement of the hydrogen ion concentration or activity is important for the description of many chemical equilibria in aqueous chemistry because of the central involvement of H^+ ions in reactions promoted by the amphoteric character of the water itself. Electrochemical measurements have been the most accurate and commonly used method for such measurements because of the availability principally of glass and hydrogen electrodes. It has been known for a long time that use of glass electrodes is limited to 0-150°C but Lietzke and his coworkers (cited in ref. 1) demonstrated the excellent performance of hydrogen electrodes at temperatures to at least 200°C. Lietzke and his coworkers studied a series of $HX-MX_n$ electrolyte mixtures in cells with hydrogen electrodes combined with silver-silver chloride reference electrodes. In the combination with in situ $Ag/AgCl$ electrodes the highest precision was limited to about 200°C because of complications from the reduction of $AgCl$. The absence of suitably stable reference electrodes for and to 300°C (Lietzke, 1973) led us to develop hydrogen electrode concentration cells for studies of equilibria of interest in reactor and steam generator systems to about 300°C during the late 1960's and seventies. [2] The first such cell (Mesmer et al., 1970) was described in 1970 for measurements of the ion-product of water in 1 m KCl to 295°C. [3] Soon thereafter (Sweeton, et al., 1971) a flow-cell without a vapor phase was reported and later used for a number of important volatile buffer systems.[4] During the intervening two dozen years over twenty scientists have participated in potentiometric studies at Oak Ridge and much of that work will be summarized in this paper. The very high precision and ease of operation make these cells appropriate for much the same applications in solution chemistry to 300°C as glass electrodes have been at near ambient conditions.

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HYDROGEN ELECTRODE CONCENTRATION CELLS

Experimental Apparatus and Procedures

Because of space limitations here we will devote this description solely to the titration cell shown in Figure 1(a), but the same general principles apply to the flow-cell with the exception of a high impedance channel in that cell to isolate the metal vessel from the electrochemical cell solution. The pressure vessel was machined of Haselloy B, chosen for its resistance to corrosion especially stress-cracking in the presence of chloride and to hydrogen embrittlement. Two concentric internal compartments are machined from Teflon with volumes of about 125 ml and 30 ml, respectively. The smaller or inner compartment contains a reference solution with the acidity or basicity fixed by a known amount of a strong acid or strong base. A small hole near the top of the inner cup assures H_2 pressure equalization while limiting the vapor transfer. Electrical contact is made through a small porous plug of Teflon compressed in a hole in the bottom of the reference compartment. The leak-rate is adjusted by compressing the plug to give a flow-rate less than 1 mg/(cm of H_2O head) per hour at ambient conditions. Titrations are conducted by injection of a titrant from a calibrated pressure generator fabricated from Zircoloy-2. The titrant is transmitted through Peek or platinum lines and valves for experiments in which composition variation is advantageous.

Cell Potentials and Data Analysis

Electrochemical cells with glass and hydrogen electrodes for sensing hydrogen ions in aqueous solutions are generally used with reference electrodes near ambient conditions. If, as is the custom however, the reference electrode is separated from the test solution by a bridge solution (i.e., liquid junction is present) then the nature of the reference solution makes no difference. Also, these cells have similar limitations as concentration cells. Hydrogen electrode concentration cells have been the workhorse for studies at high temperatures principally at Oak Ridge for nearly twenty-five years because of the excellent response and stability of hydrogen electrodes.

The cell representation for a hydrogen electrode concentration cell is given below for the study of the ionization of a weak acid, HA,

Here the molality of NaCl, present as a supporting, non-complexing electrolyte, is high compared to the other solutes, e.g., $m_{NaCl}/m_{HCl} \sim m_{NaCl}/m_{NaA} \sim 100$ and consequently, the activity coefficient of the minor components can be assumed to be equal in the two compartments, while the liquid junction potential is minimized and is calculable by the Henderson equation. [1,5] The cell potential is given by

$$\Delta E = RT/F \cdot \ln ([H^+]_r / [H^*]) + E_{LJ} \quad (1)$$

The γ_{H^+} in the two compartments are equal, the bracketed terms represent molalities, and E_{LJ} represents the liquid junction potential estimated using limiting conductances for the ions. For the special case of small differences in ion concentrations for the two solutions the logarithm term of the Henderson equation is linearized and there is a term in the sum for each ion present and the liquid junction potential is

$$E_{LJ} = \sum D_i ([I] - [I]_r) \quad (2)$$

D_i is given by

$$D_i = RT/F \cdot Z_i \lambda_i / |Z_i| \sum |Z_i| \lambda_i [i] \quad (3)$$

where Z_i is the charge on the ion and λ is the limiting conductance. Because of the high mobility of H^+ and OH^- , the terms involving these ions usually make the greatest contribution to E_{LJ} . The magnitude of the calculated liquid junction potential is generally accurate to 15-20% [5] and this contributes little error when E_{LJ} is kept to <1 or 2 mV. The magnitude of the liquid junction potential introduced by replacement of 1% of the Na^+ by H^+ as a function of temperature is shown in Figure 1(b) along with the % error in H^+ concentration represented by ignoring that potential. [1]

The observed ligand number (or average number of ligands per metal ion in solution) is a convenient quantity for examination of titration data in terms of assumed species, and for hydroxide complexes it is given by

$$\bar{n}_o = ([H^+] - [OH^-] - m_H)/m_M \quad (4)$$

where the bracketed terms are actual ion molalities and m_H and m_M are total or stoichiometric molalities of acidity and metal ion present. [5] The numerator presents the missing hydroxide and $\bar{n}$ is equivalent to the average missing hydroxide per metal ion in solution. Typically the metal ion M^{Z+} hydrolyzes according to the equilibria

with the corresponding formation quotients, $Q_{x,y}$, and $\bar{n}_{calc}$ where

$$\bar{n}_{calc} = (\sum y Q_{x,y} [M^{Z+}]^x / [H^+]^y) / m_M \quad (6)$$

and $Q_{x,y}$ is derived by least squares analysis in which the free metal ion concentration is obtained by iteration of material balance equations. Also for a simple ionization of a weak acid

$$\bar{n}_{calc} = Q / ([H^+] + Q). \quad (7)$$

Software has been in routine use at ORNL by which the errors assigned to seventeen observables for solution make-up, temperature, volume of titrant, potential, etc., are propagated to $\bar{n}_o$ for weighting in least-squares analyses.

RESULTS AND DISCUSSION

Acid-Base Equilibria

Figure 2 shows results from EMF studies to 300°C for fifteen ionization reactions with a complete listing in Table 1 for weak acids and bases; this provides the most accurate data-base for any class of reactions in water at high temperatures. [6,7] The new results for organic acids, also listed in Table 1, are consistent with the trends shown in Figure 2 but sometimes results are limited to lower temperatures because of thermal instability. The curvature of the log K vs 1/T plots is similar for all the reactions and when any one reaction is subtracted from the other, much simpler behavior is observed (i.e., the reaction is written in the all-cation or all-anion form (e.g., $NH_3 + H^+ \rightleftharpoons NH_4^+$, or $H_3PO_4 + OH^- \rightleftharpoons H_2PO_4^- + H_2O$). This form is also called "isocoulombic" (Lindsay, 1980) and provides a powerful means for extrapolation or interpretation of equilibrium

and provides a powerful means for extrapolation or interpretation of equilibrium constants. [28] In addition, the potentiometric method provides data on salt effects (and therefore activity coefficients) that is not possible with the conductance approach, for example. The thermodynamics of these reactions have been discussed in some detail. [6,7] The reactions are ΔS driven and the ΔS° , ΔV° , and ΔC_p° have divergences at the critical conditions indicative of involvement of large numbers of solvent molecules (or alternatively electrostriction of an infinitely compressible solvent). Some simplification has been observed when the density is held constant, i.e., $(\partial \log K / \partial \log \rho)_T$ is nearly constant and varies little with temperature. [6,19].

Table 1. Acid/Base Reactions Studied by Hydrogen-Electrode (or Glass Electrode) Potentiometry at ORNL.

Weak Acid on Base ($K_1, \dots, K_n$) ^a	T(°C)	I (medium)	Reference	
H ₂ O	50-292	1m KCl	Mesmer, et al. (1970)	[3]
	0-300	0-3m KCl	Sweeton, et al. (1974)	[8]
	25-295	0-3m NaCl	Busey, Mesmer (1976)	[9]
	25-250	0-7m NaTr ^b	Palmer, Drummond (1988)	[10]
D ₂ O	50-300	0.2m KCl	Mesmer, Herting (1978)	[11]
H ₃ PO ₄ K_1 , K_2 , K_3 ^c	50-300	0-1m KCl	Mesmer, Baes (1974)	[12]
D ₂ PO ₄ ⁻ (base form)	50-300	0-.2m KCl	Mesmer, Herting (1978)	[11]
NH ₃ (aq) (base form)	50-295	0-3m KCl	Hitch, Mesmer (1976)	[13]
Cyclohexylamine ^c	50-295	0-0.1 KCl	Mesmer, Hitch (1977)	[14]
Morpholine ^c	50-295	0-.1m KCl	Mesmer, Hitch (1977)	[14]
CO ₂ (aq)	50-300	0-5m NaCl	Patterson, et al. (1982)	[15]
HCO ₃ ⁻	50-250	0-5m NaCl	Patterson, et al. (1984)	[16]
Tris ^d	5-200	0-5m NaCl	Palmer, Wesolowski (1987)	[17]
BisTris	5-125	0-5m NaCl	Wesolowski, Palmer (1989)	[18]
CH ₃ COOH	50-300	0-5m NaCl	Mesmer, et al. (1989)	[19]
	25-250	0-5m NaTr ^b	Palmer, Bell (unpublished)	
HSO ₄ ⁻	50-250	0-5m NaCl	Dickson, et al. (1990)	[20]
Oxalic acid (K_1 , K_2)	0-175	0-5m NaCl	Kettler, et al. (1991)	[21]
Malonic acid (K_1 , K_2)	0-100	0-5m NaCl	Kettler, et al. (1992)	[22]
HCOOH (formic acid)	25-200	0-5m NaCl	Bell, et al. (1993)	[23]
C ₆ H ₅ COOH (benzoic acid)	5-250	0-5m NaCl	Kettler, et al. (1994a)	[24]
Succinic acid (K_1 , K_2)	0-250	0-5m NaCl	Kettler, et al. (1994b)	[25]
d-Galacturonic acid	25-100	0-1m NaCl	Narkhede, et al. (1994)	[26]

^a Stepwise dissociation constants. ^bNaTr = sodium trifluoromethanesulfonate. ^c Actual reactions studied were in the "base" form $H_3PO_4 + OH^- \rightleftharpoons H_2PO_4^- + H_2O$ or $NH_3(aq) + H_2O \rightleftharpoons NH_4^+ + OH^-$. ^dtris{hydroxymethyl aminomethane}.

Metal Ion Hydrolysis

Studies of the hydrolysis of metal ions according to the equilibria in Equation (5) at elevated temperatures using concentration cells at ORNL are listed in Table 2. Results for the first hydrolysis reaction of Al³⁺, i.e., (x,y) = (1,1) in dilute solutions by Palmer and Wesolowski are presented in Figure 3 [at I = 0.096 mol•kg⁻¹ at 25° and 75°C. [33] Measurements were made over the range 25 to 125°C at ionic strengths 0.1, 0.3, 1.0, and 5.0 mol•kg⁻¹ with NaCl as the supporting electrolyte. The maximum degree of

Figure 1. (a) Schematic drawing of the ORNL hydrogen electrode concentration cell (modified from ref. 3). (b) Liquid junction contribution to ΔE for cells where 1% of the Na⁺ is replaced by H⁺ in the presence of 1m NaCl; the right ordinate is the error in H⁺ concentration from neglecting E_{LJ} . [1]

Figure 2. (a) Logarithm of the dissociation constants for weak acids and bases to 300°C. [6] (b) Logarithm of the dissociation quotient for $\text{NH}_3(\text{aq})$ to 295°C in KCl media. [13]

hydrolysis observed was ca. 30% at concentrations $<6 \times 10^{-4} \text{ mol} \cdot \text{kg}^{-1}$. The $\log K_{1,1}$ varies from -4.95 ± 0.03 at 25° to -1.36 ± 0.06 at 200°C and is linear in $1/T$.

Table 2. Metal Ion Hydrolysis Reactions Studied by Hydrogen Electrode (or Glass Electrode) Potentiometry at ORNL

Hydrolysis Products ^a	(x,y) determined	T(°C)	I (medium)	Reference
$(\text{UO}_2)_x(\text{OH})_y^{(2x-y)+}$	(1,1)(2,2)(3,5) (2,2)(3,5)(3,7) (3,8)(3,10)	94.4 25-225	0.5m KCl 0.1m TMATr ^b	Baes, Meyer (1962) [28] Nguyen-Trung, et al (1993) ^c [29]
$\text{Th}_x(\text{OH})_y^{(4x-y)+}$	(1,1)(1,2)(2,2) (4,8)(6,15)	0,95	1.0m NaCl	Baes, et al (1965) [30]
$\text{Be}_x(\text{OH})_y^{(2x-y)+}$	(2,1)(3,3)(5,7)	0-60	1.0m NaCl	Mesmer, Baes (1967) [31]
$\text{Al}_x(\text{OH})_y^{(3x-y)+}$	(2,2)(3,4) (14,34) (1,1)	62-150 25-125	1.0m KCl 0-5m NaCl	Mesmer, Baes (1971) [32] Palmer, Wesolowski (1993) [33]
$\text{B}_x(\text{OH})_y^{(3x-y)-}$	(1,1)(2,1)(3,1) (4,2)	60-290	0-1m KCl	Mesmer, et al (1972) [34]
$\text{Si}_x(\text{OH})_y^{(4x-y)-}$	(1,1)(1,2)(3,1) (4,2)(5,2)(6,3)	60-290	1.0m NaCl	Busey, Mesmer (1971) [27]
$\text{Ca}(\text{OH})^+$	(1,1)	50-250	1.0m KCl	Mesmer (unpubl)
$\text{H}_y(\text{WO}_4)_x^{(y-2x)+}$	(1,1)(1,2)(6,7) (6,10)(12,18)	95-295	0-5m NaCl	Wesolowski, et al (1984) [35]
$\text{H}_y(\text{CrO}_4)_x^{(y-2x)+}$	(1,1)(1,2)(2,2)	25-175	0-5m NaCl	Palmer, et al (1987) [36]
$\text{Mg}(\text{OH})^{2+}$	(1,1)	0-250	0-5m NaCl	Wesolowski, Palmer (1994) [37]

^aHydrolysis in terms of H^+ except for $\text{B}(\text{OH})_3$, $\text{Si}(\text{OH})_4$, and Ca^{2+} which are written in terms of OH^- to form $\text{M}_x(\text{OH})_y^{(xz-y)+}$ species; the unhydrolyzed metal ion is the reactant ion except for $\text{B}(\text{OH})_3$, $\text{Si}(\text{OH})_4$, WO_4^{2-} , and CrO_4^{2-} for which the latter species are the reactants.

^bTMATr = (Tetramethylammonium(trifluoromethanesulfonate)).

^cCoupled with Raman spectroscopy.

Metal Complexation

Studies using concentration cells for measurements of the degree of metal complexation at ORNL are listed in Table 3. Figure 4(a) is an example that demonstrates the power of this EMF approach for studies of complexation by the anion of a weak acid, acetic acid. This study of ferrous acetate complexes was conducted by Palmer and Drummond in sodium trifluoromethanesulfonate as the non-complexing supporting electrolyte. [30] Results are presented in terms of the observed ligand number $\bar{n}_o$, the average number of acetates bound per metal ion in solution. Ligand numbers up to about 1.5 to 2.5 were attained; from the systematic variation of solution composition the equilibrium quotients for reactions involving the species $\text{Fe}(\text{CH}_3\text{CO}_2)_n^{(2-n)+}$ with $(n = 1,2,3)$ were determined and summarized in Table 3. Similar studies have been made for Zn^{2+} and Al^{3+} . [39,40] Ferrous chloride complexes were studied by Palmer and Hyde [41] in the presence of acetate by the competitive ligand approach, and results for the first complex are compared in Figure 4(b) for FeOH^+ , $\text{Fe}(\text{CH}_3\text{CO}_2)^+$

Figure 3. Titration curves showing $\bar{n}_o$ vs pH at (a) 25° and (b) 75° C at $I = 0.096 \text{ mol} \cdot \text{kg}^{-1}$. [33] (Temperatures range 50°-250° C at 50° C intervals with 295° C at the top).

Figure 4. (a) Observed and calculated ligand numbers for $\text{Fe}(\text{Ac})_n^{(2-n)+}$ complexation. [38] (b) Association constants for ferrous complexes of acetate, chloride, and hydroxides. [7]

and FeCl⁺. [7] All show the similar temperature dependencies, the trend expected for charge-neutralization reactions.

Table 3. Metal Complexation Studies Using Potentiometry at ORNL

Reaction $M^{2+} + yX^- \rightleftharpoons MX_y^{(3-y)+}$	T(°C)	I (medium)	Reference
$Fe(CH_3COO)_y^{2-y}; y = 1,2,3$	50-295	0-1m NaTr ^a	Palmer,Drummond (1988) [38]
$Zn(CH_3COO)_y^{2-y}; y = 1,2,3$	50-295	0-1m NaTr ^a	Giordano,Drummond (1991) [39]
$Al(CH_3COO)_y^{3-y}; y = 1,2,3$	25-150	0-1m NaCl	Palmer,Bell (1994) [40]
FeCl ⁺	125-295	1m NaTr ^a	Palmer,Hyde (1993) [41]
$CdCl_y^{2-y}; y = 1,2,3$	25-250	0-5m NaTr ^a	Palmer,et al (unpublished)

^aNaTr = sodium trifluoromethanesulfone

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