Experimental studies in high temperature aqueous chemistry at Oak Ridge National Laboratory

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Abstract: Experimental research is conducted and models are developed in a long-standing program at Oak Ridge on the aqueous chemistry at high temperatures of broad classes of electrolytes emphasizing thermodynamics of reaction equilibria and excess thermodynamic properties of electrolytes. Our experimental methods, their capabilities, data analysis, and results will be summarized. The relevance of the work to problems in power plants, natural and industrial processes as well as basic solution chemistry and geochemistry are given. Progress in potentiometry, electrical conductivity, flow calorimetry, and isopiestic research will be described. The future in this field demands greater precision in measurements and significant gains in our understanding of the solvation phenomena especially in the vicinity and beyond the critical point for water. The communities who do research on scattering, spectroscopy, and computer simulations can help guide these efforts through studies at exteme conditions.

INTRODUCTION

Aqueous chemistry is of great importance in many natural and technological applications involving high temperatures, e.g., natural processes such as those geochemical processes of ore deposition, geothermal reservoir behavior, and transport from hydrothermal oceanic vents. It is also of great importance to industrial and technological applications such as steam generation in power plants, disposal of nuclear and hazardous wastes, and in supercritical water oxidation of hazardous organic wastes. Water as a solvent has challenged scientists from the beginning because of its molecular and solvation properties that lead to large non-idealities for its solutions of most solutes. As a result much experimental data are required to accurately describe the chemistry of even the simplest solutes especially due to the wide range of temperature and pressure over which the liquid phase exists (critical point: 374°C, 221 bar).

A large database on the physical chemistry of water and its solutions has been generated at Oak Ridge National Laboratory since the 1960's using a broad array of unique equipment yielding in excess of four-hundred publications. This work has had substantial impact on many industrial processes as well as the sciences of basic solution chemistry, thermodynamics, and geochemistry. The principal support for this work has been from the Divisions of Chemical Sciences and Geosciences of the Office of Basic Energy Science of DOE but in certain specialized areas support has come from the Division of Geothermal Technology and the Office of Technology Development of DOE, the Electric Power Research Institute, and from the Knolls Atomic Power Laboratory.

The authors wish to recognize at the outset the pioneering accomplishments of W. L. Marshall and C.F. Baes, Jr. in this field at ORNL and to acknowledge that much of what has followed was built on the foundation they laid.

EXPERIMENTAL METHODS

In this experimental program at ORNL, research is conducted to high temperatures and pressures using several classical physical chemical methods of solution chemistry: potentiometry, electrical conductivity, flow calorimetry, isopiestic measurements, flow densimetry, and volatility measurements. The range of conditions accessible to these methods are listed in Table 1. The first two of these emphasize chemical reaction equilibria and the next three, the excess thermodynamic properties of electrolytes. All involve unique equipment developed at ORNL over a period of thirty years. In the remainder of this paper several of these techniques will be described briefly along with some examples of their results and listings of systems studied to this point. It will not be possible to be comprehensive on the published work but we will give some general and a few selected specific references.

TABLE 1. Experimental Apparatus and the Range of Conditions Applicable

	(P/bar)	(t/°C)	(Reference)
Electrochemical Cells	satn.	25 - 300	(1,2)
(H_2 concentration cells)			
Electrical Conductivity	1 - 4000	25 - 800	(3,4)
	1 - 3000	25 - 650	(5)
Flow Calorimeter	1 - 400	25 - 400	(6,7)
Isopiestic Apparatus	satn.	110 - 250	(8,9)
Flow Densimeter	1 - 1000	25 - 500	(10)
Volatility Apparatus	satn.	25 - 350	(11,12)

Potentiometry

The use of hydrogen electrodes in a concentration cell configuration for the study of reactions involving hydrogen ions at high temperatures was invented at Oak Ridge in 1969 (1). These cells represent essentially a high temperature "pH meter" usable in many different ways limited mostly by the ingenuity of the experimenter. These cells have since been used in a large number of studies of reactions such as acid-base ionization, metal ion hydrolysis, metal complexation, precipitation, and most recently adsorption reactions on solids at temperatures to 300°C. This work has been described recently in several recent reviews (13,14,15).

Figure 1 is a schematic drawing of the cell that shows the two Teflon compartments with a porous plug joining them to complete the electrical circuit. The small inner compartment generally contains the reference solution (R), usually a strong acid or base, and the large compartment contains the test solution in which a titration can be performed. The cell representation is given below for the study of the ionization of a weak acid, HA,

$$H_2Pt/m_{HCl},m_{NaCl}//m_{HA},m_{NaA},m_{NaCl}/Pt,H_2 \qquad (1)$$
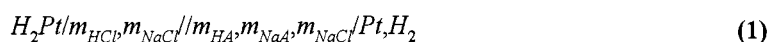
Here the molality of NaCl, present as a supporting, non-complexing electrolyte, is high compared to the other solutes, e.g., $m_{NaCl}/m_{HCl} \sim m_{NaCl}/m_{NaA} \sim 100$ and consequently, the activity coefficients of the minor components can be assumed to be equal in the two compartments. In this way the liquid junction potential is minimized and is calculable by the Henderson equation. [1] The cell potential is given by

$$\Delta E = RT/F \cdot \ln ([H^+]_R/[H^+]) + E_{LJ} \qquad (2)$$

Figure 2 shows the ionization constants for fourteen acids and bases from 25° to 300°C measured with this cell (13) to which a number of organic acids and bases could be added now. These data are one of the most accurately known sets and have formed the basis for the "isocoulombic" approach for extrapolation of temperature dependences (16-18). For this purpose reactions are written in the form of cations only, or anions only, or with the same charges on both sides.
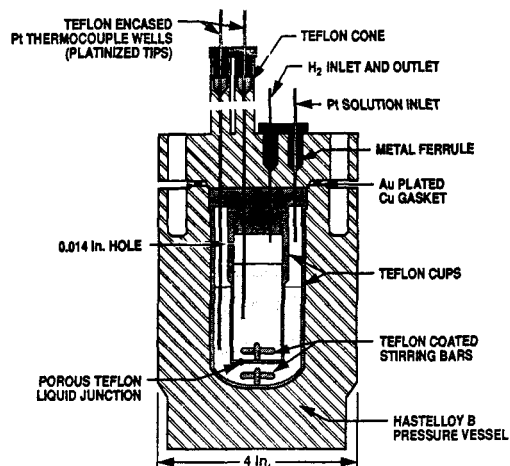
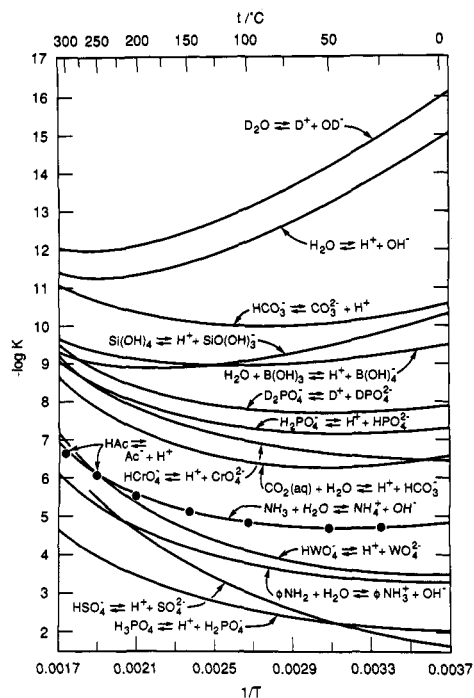Fig.1 Schematic of the ORNL hydrogen electrode concentration cell (Mesmer et al. (1)).

Fig. 2. Ionization constants of some acid-base equilibria determined with the EMF cell at ORNL (13).

Other uses of the cell are well summarized by Mesmer et al. (13), Wesolowski et al. (14), and Palmer et al.(15). An important recent innovation is the large volume version, with facility for handling solids, that has been used for the study of the solubility of boehmite to 250°C (19). Another is the use of the concentration cell in studies of the adsorption of hydrogen ions onto TiO_2 (20) to 250°C, a first, that shows the increased adsorption with temperature as well as the temperature dependence of the zero-point-charge.

Electrical Conductivity

More than any other method, electrical conductivity measurements have provided the basis for our awareness of the strong tendency for ion association to occur for all electrolytes in the supercritical region. Much of the data on electrolytes was generated with the apparatus built originally at ORNL in the early 1960's by W. L. Marshall, E. U. Franck and others (3,4). This apparatus was used extensively by Marshall and his collaborators (21) and since 1990 by Patience Ho and Donald Palmer (5,22) with modifications.

The cell used predominantly is shown schematically in Figure 3 with its closure seal at the right and the alumina insulated axial electrode. This cell was used to 800°C and 4 kbar but the present adaptation with improved temperature control and measurement capability is limited to 650°C and 3 kbar. The association constants for NaCl(aq) recently obtained with the cell (5) are shown in Fig. 4 as a function of temperature at fixed densities. As is customary for electrolytes the Onsager equation describes the conductances at the low temperatures quite adequately when strong electrolyte behavior is exhibited. As the viscosity decreases, the conductance increases until ion association commences (~300°C). At the temperatures near and greater than the critical point and at the lower densities, the conductance (corrected for the solvent) drops strongly. In this region the association constant can be derived using one of the standard theories (e.g., Shedlovsky or Fuoss and Hsia (5,22,23,24)). All the conductance results thus far in the supercritical range are fit by the model

$$\log K = a + b/T + (c + d/T) \log \rho \qquad (3)$$

or a simple variation thereof. The similarity found for 1-1 electrolytes is striking but the association behavior has been shown to be ΔS dominated with divergences occurring for ΔS, ΔV, and ΔC_p as the appropriate derivatives of equation 3 predict (25).
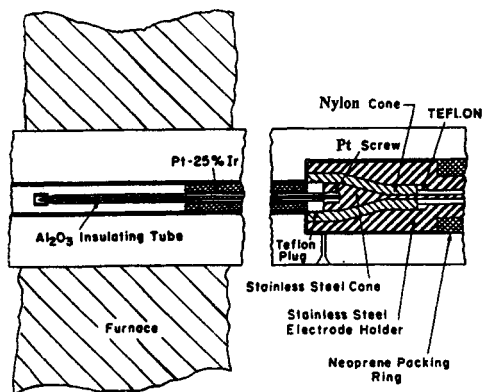
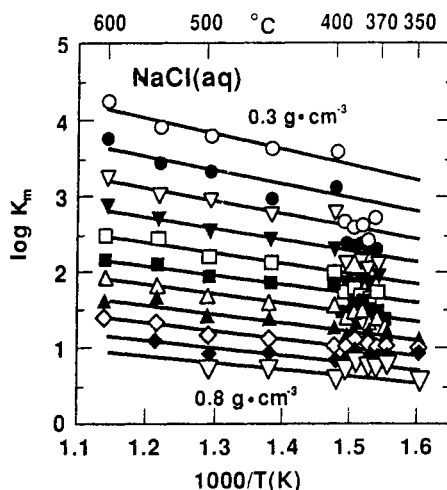Fig. 3. Schematic drawing of the ORNL conductance cell with slight modification from Ref. (21).

Fig. 4. Equilibrium constants derived for NaCl(aq) from conductance results of Ho et al (5) (densities in 0.05 g·cm⁻³ increments).

Earlier work of Quist and Marshall (1) on H_2O (26) and NH_3 (27) along with EMF results reported in Ref. 13 have made these the only two cases for which there are data from ambient to the supercritical range. One of the important discoveries of this and other earlier work was the linearity of the variation of log K vs. log ρ at a constant temperature. This very powerful relationship provides an excellent basis for modeling of pressure dependences of reactions, and it points to a simple proportionality between the ΔV for the reaction and the compressibility coefficient, β, for the solvent at constant temperature.

Early work also shows a linear relationship for the limiting equivalent conductance for the electrolyte vs the solvent density. More recent work of Ho et al. (5) and Zimmerman et al. (23) suggest a deviation at lower densities (<about 0.5 g·cm⁻³) toward lower limiting values than the linear relationship suggests.

Flow Microcalorimetry

A liquid and heat-flow microcalorimeter (Fig. 5) was invented at ORNL in 1980 by R. H. Busey (6) to measure enthalpies-of-dilution or enthalpies-of-mixing of fluids to high temperatures. Since then J. M. Simonson and his colleagues have improved the calorimeter system and applied it to a number of electrolyte systems summarized in Table 2. The calorimeter is a Tian-Calvet (SETERAM, Lyon, France) heat flow unit described in Refs. 6 and 7 with a specially wound Pt-Rh heat-exchanger. The detection limit of the flow calorimeter is about 0.01 μV and the sensitivity 3 μV/mW. Solutions are delivered by a twin-sided position displacement pump (Ruska Instrument Corp., Houston, TX) at low flow rates ($\sim 5 \times 10^{-3}$ cm³ · sec⁻¹). The observed enthalpy of dilution, $\Delta_{dil} H_m$, is related to the relative apparent molar enthalpy L_ϕ by

$$\Delta_{dil} H_m = L_\phi(m_f) - L_\phi(m_i). \qquad (4)$$

where m_i and m_f are respectively the initial and final molalities. The dilution enthalpy also yields the activity coefficient γ or osmotic coefficients φ by the appropriate integrations as below

$$\phi - \phi_R = (m^{1/2}/2\nu_R) \int_{T_R}^{T} (\partial L_\phi/\partial m^{1/2}) d(1/T), \qquad (5)$$

$$\ln(\gamma/\gamma_R) = (1/\nu_R) \int_{T_R}^{T} \left\{ L_\phi + 1/2(m^{1/2})(\partial L_\phi/\partial m^{1/2}) \right\} d(1/T).$$ (6)

Quantities listed in Table 2 are dilution, mixing, and reaction enthalpies measured in this program. Key insights into the behavior of aqueous solutions of electrolytes at temperatures near 300°C and beyond can be gained from their dilution enthalpies as a function of temperature and concentration. At temperatures below about 300°C, the slopes of plots of dilution enthalpies as a function of square root final molality typically correspond closely to the theoretical Debye-Hückel limiting law at low concentrations and then depart gradually with increasing concentration (Fig. 6). Such behavior has been successfully described by

TABLE 2. Studies by Heat-and-Liquid Flow Calorimetry (400°C, 400b)

Dilution:

NaCl(aq),* CaCl$_2$(aq),* MgCl$_2$(aq), HCl(aq),* NaOH(aq),* NaHCO$_3$(aq), Na$_2$CO$_3$(aq), H$_2$SO$_4$(aq), (NH$_4$)$_2$ SO$_4$(aq), NH$_4$HSO$_4$(aq).

Mixing:

methanol + H$_2$O,* D$_2$O + H$_2$O,* NaCl(aq) + HCl(aq), NaCl(aq) + NaOH(aq).
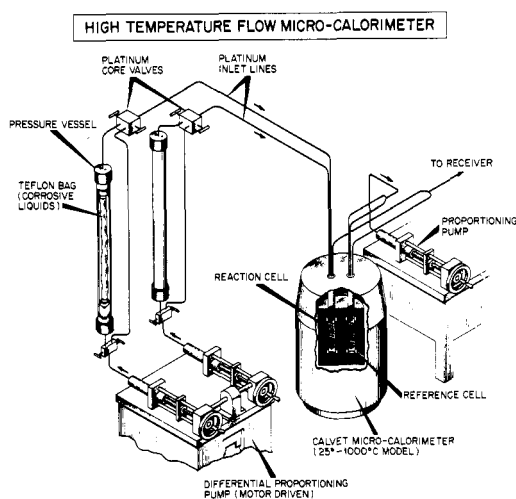
Reaction:

HCl(aq) + NaOH(aq)

* - Published

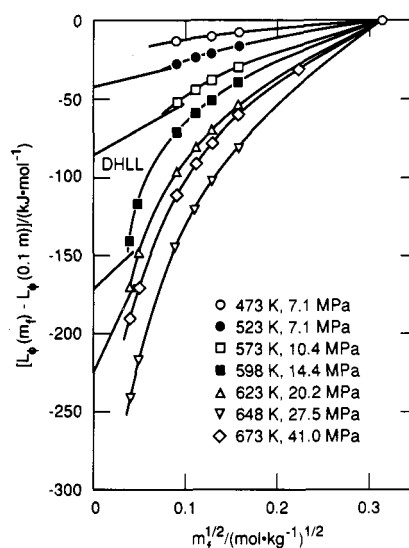Fig. 5. Schematic drawing of the ORNL heat-flow mixing calorimeter (6,7).

Fig. 6. Enthalpies of dilution of CaCl$_2$(aq) from Simonson et al (20). Right-hand plot is an expanded scale from m = 0.1 mol·kg^{-1}; limiting slopes shown as straight lines in both plots.

models of strong electrolytes that include some empirical parameters to take account of short-range interactions that are poorly understood. Results in this higher temperature, low-concentration range show slopes that considerably exceed those predicted by the theory for hydrochloric acid, calcium chloride (Fig. 6), sodium hydroxide, and, to a lesser extent, sodium chloride. Such behavior cannot be rationalized by strong electrolyte models and suggests that endothermic ion association has begun to occur. That is, as the dielectric constant of water decreases with increasing temperature, these familiar solutes no longer behave as fully dissociated strong electrolytes.

Hydrochloric acid has been used as the test case to develop an extended ion-interaction model that explicitly includes the formation of associated species and their interactions with other solute species. Earlier ORNL conductivity data in the supercritical region were used to assign an association constant and its temperature dependence. The final model leads to very good fits of the data in a temperature range from 25 to 374°C over the concentration range 0.008 to 2 molal; this model is consistent with all other available thermodynamic data.

Isopiestic Measurements

The isopiestic method has been very productive for yielding results on the thermodynamic properties of electrolytes to elevated temperatures at ORNL (Fig. 7). The method involves equilibrating standard reference solutions (usually NaCl (aq)) with other test solutions in a well thermostated chamber with, in this case, an in situ balance for determination of solution compositions at equilibrium (8,9). The facility was refined by H. F. Holmes and applied to the study of 33 single electrolyte solutions and 17 binary electrolytes having a common ion. Table 3 summarizes the systems studied to date (29) and some of the published work is summarized in the text on thermodynamics by K. S. Pitzer (30). The classes studied are principally: alkali metal chlorides, bromides, sulfates, bisulfates, hydroxides, and orthophosphates; alkaline earth chlorides; a few transition metal chlorides and sulfates; sulfuric acid; and phosphoric acid. Mixtures are generally with Na^+, Ca^{2+}, or Cl^-. For 1-1 electrolytes there is an interesting contrast between those showing the "normal" order such as the halides and bisulfates in contrast to the hydroxides which exhibit the reverse order. The normal order is a decrease in activity coefficients with increasing size of the cation at a given temperature. The reverse seen at ambient conditions is preserved at elevated temperatures and has been attributed to "localized hydrolysis" which can be viewed as a solvent separated ion-pair (29).

TABLE 3. Aqueous Electrolytes with Osmotic Coefficients Measured with the
ORNL High-Temperature Isopiestic Facility (29)

NaCl(aq) Standard Solutions, Temperatures to 250°C

Single electrolyte systems

LiCl	LiOH*	LiBr*	$MgCl_2$	H_2SO_4	$LiHSO_4$	H_3PO_4*
KCl	NaOH*	NaBr*	$CaCl_2$	Li_2SO_4	$NaHSO_4$	NaH_2PO_4*
CsCl	KOH*	KBr*	$SrCl_2$	Na_2SO_4	$KHSO_4$	Na_2HPO_4*
	CsOH*	CsBr*	$BaCl_2$	K_2SO_4	$CsHSO_4$	K_2HPO_4*
$CoCl_2$				Cs_2SO_4		
$NiCl_2$	$MgSO_4$	$NiSO_4$				

Common-ion mixed electrolyte systems

{Na,K}Cl	{Ca,Mg}Cl*	Na{Cl,SO_4}*	Na{OH,Al(OH)$_4$}*
{Na,Li}Cl	{Ca,Sr}Cl*	Na{Cl,Br}*	Na{HPO_4, H_2PO_4}*
{Na,Cs}Cl	{Ca,Ba}Cl*	Na{Cl,OH}*	Na{SO_4,HSO_4}*
{K,Mg}Cl*	{Na,Mg}Cl*	{Na,Ca}Cl*	{Cs,Ba}Cl
{K,Ca}Cl*			

*Unpublished. See Ref. (29) for references for publication data.

In Fig. 8 we compare the activity coefficients (as $\ln \gamma$) of a 2-1 charge type, $CaCl_2(aq)$, and a 1-2 charge type, $Na_2SO_4(aq)$ (29). The activity coefficients in Fig. 8 were calculated from global models for these two electrolytes. Although $CaCl_2$ and Na_2SO_4 have identical long-range electrostatic (Debye-Hückel) contributions to $\ln \gamma$, their total activity coefficients are quite different. This difference is not limited to
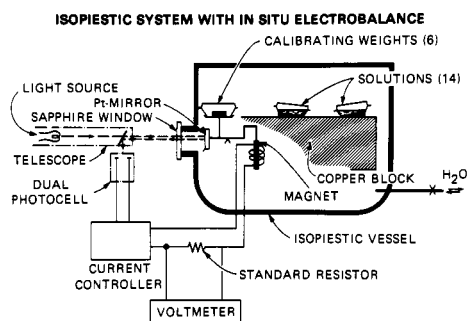

Fig. 7. Schematic drawing of the ORNL isopiestic facility with its in situ electrobalance and its servo-optical control (8,9).
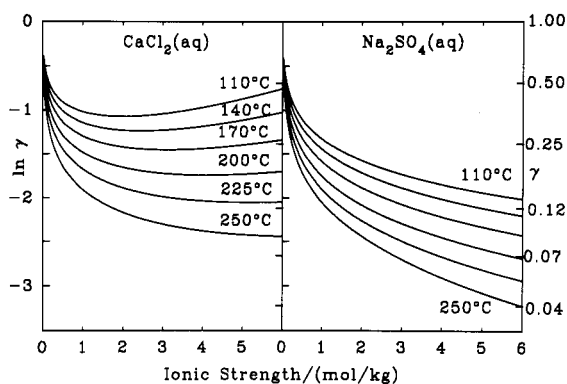

Fig. 8. Activity coefficients (as $\ln \gamma$) for $CaCl_2(aq)$ and $Na_2SO_4(aq)$ as a function of ionic strength and temperature from 100° to 250°C (29).

elevated temperatures as it is quite noticeable at 25°C. There are two plausible explanations for the differing behavior exhibited in the figure - association and hydration. We favor hydration or electrostriction effects as we have demonstrated a positive correlation between the activity coefficients and molar volumes for these two families that is consistent with larger values of the activity coefficient for the more strongly hydrated electrolytes (29). In recent work the apparatus has been used to study water adsorption of solids from The Geysers geothermal formation (31).

Volatility of Electrolytes

The subject of the distribution of aqueous electrolytes between liquid and steam has plagued the power industry for decades because of concern about the transport of corrosive solutes from steam generators through steam turbines. Corrosion and deposition on turbine blades has caused expensive plant down-time as well as catastrophic failures on some occasions. However, the difficulty of obtaining reliable data and models for electrolyte volatility had slowed progress in the area although considerable Russian work was done through the 1960's. Since 1990 we have had an experimental program to address the volatility of a number of inorganic solutes to 350°C for the Electric Power Research Institute.

In a parallel effort for the Division of Geothermal Technology of DOE, we have addressed the origin of high levels of chloride (~100 ppm) in the steam from some of the wells of the geothermal system at The Geysers in northern California. There the high chloride content is of unknown origin and it causes serious corrosion of piping and other plant facilities.

These are inherently tedious experiments because of the low levels in the steam and this research is a very good example of the applicability of basic thermodynamic data in real world situations. Addressing both of the above applications involves the apparatus shown in Fig. 9, devised by Simonson and Palmer (11,12). The research brings together results from earlier basic studies on ionization equilibria and excess

thermodynamic properties for all the relevant components to develop general models in terms of the distribution equilibrium constant K_D,

$$K_D = \frac{m(MX)_v \gamma(MX)_v}{m(M)_l \gamma(M)_l \, m(X)_l \gamma(X)_l} = \frac{m(MX)_v \gamma(MX)_v}{m(M)_l \, m(X)_l \gamma_\pm(MX)^2} \tag{7}$$

where v represents the vapor and *l* the liquid phase. $\gamma_\pm(MX)$ is the stoichiometric mean activity coefficient from isopiestic and calorimetric studies made earlier in this program.

Figure 10 summarizes K_D values for six solutes (32). Some important conclusions derived for ammonium chloride are (e.g.): (1) the salt distributes mostly as NH_3 and HCl at steam generator conditions but acidic condensate is produced from the steam and (2) in geothermal environments the high levels of chloride must originate from rather acidic brines (pH ≤3) a condition not easily accounted for from hydrolysis reactions or from solids buffering, unless high levels of ammonia are present (11,12).
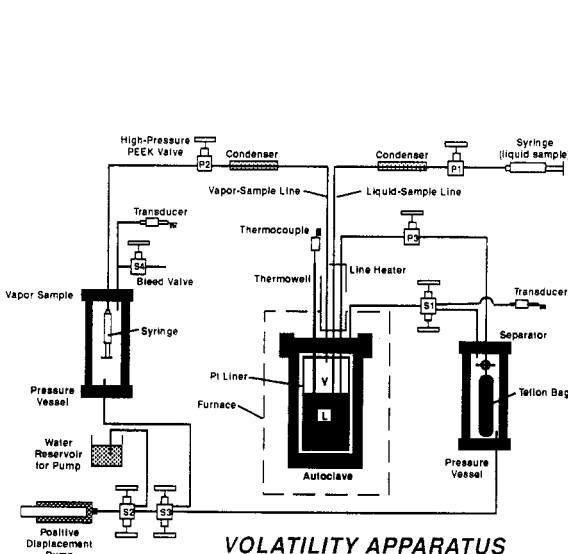
Fig. 9. Apparatus for measurement of the L/V distribution of electrolytes to 350°C (11,12).
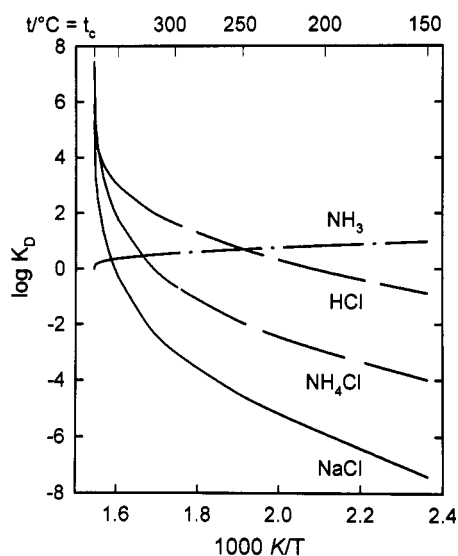
Fig. 10. Distribution coefficients, K_D, for electrolytes measured with the apparatus in Fig. 9 (32).

APPLICATIONS AND NEEDS

The early motivation of our research at ORNL was related to nuclear reactor issues such as the homogeneous reactor experiment (a sulfuric acid medium contained the fissionable uranium as uranyl sulfate), primary circuit coolants, and steam generator chemistry. Later attention was given to desalting, geochemistry, waste isolation, and more recently to chemical processing such as supercritical water oxidation of hazardous wastes. With water as the principal transport fluid in natural systems geochemists have and are applying results from this program toward issues of ore-formation, rock porosity, and permeability, geothermal reservoirs, and even the behavior of oceanic vent fluids. Data and results from this program are found in essentially every computer code being developed for modeling multicomponent aqueous systems at high temperatures of which there are several in prominence.

In the basic physical-chemistry realm, work from this program has led to advances in deriving global models of the thermodynamic properties of electrolytes and predictive models for ionic reactions at high temperatures, especially those involving hydrogen ions. We have contributed to the development of concepts such as isocoulombic reactions (reactions with like ions on both sides) for simplifying temperature dependences and also density models for expressing T-P dependences for reaction thermodynamics.

At this point there is a need for advancement in our knowledge of the chemistry of the elements of the middle of the periodic table, transition elements and heavier elements, where insolubility and stability of oxidation states become major issues. For the pre- and post-transition elements, where the chemistry is simpler and much information now exists, there is need for the emphasis to shift from the measurement of macroscopic properties to microscopic properties to enhance our ability to develop more realistic models. This calls for studies aimed at measurement of distribution functions (g(r)), such as scattering, and the direct observation of energy absorption characteristics of species and their solvation shells by spectroscopy.

Expert molecular-based computer simulations can be expected in time to lead to better capabilities for extrapolation and interpolation of experimental results especially near and beyond the critical point of water where dramatic changes occur and where experiments are more difficult and expensive. Recent molecular dynamics simulation results of Chialvo et al. (33,34) have demonstrated some success in reproducing the association constant for NaCl(aq) at a temperature of $1.05 \times T_c$ and at P_c (critical conditions) in SPC water within experimental error of the results from conductance measurements (5). Future efforts are needed to examine the breadth of this capability in P-T space. These and other efforts are in progress that will, we believe, lead to a synergism of theory and experiment permitting greater progress in understanding the complexity of water's solutions.

ACKNOWLEDGMENT

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