Thermodynamics of chemical interactions in aqueous solutions at elevated temperatures and pressures

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Abstract - Chemical reactions at elevated temperatures (100-350°C) and pressures (15-20 MPa) are important in many commercial, biological, and geochemical environments. There is a need to quantitate these reactions by measuring their equilibrium constants ($\underline{K}$). Corresponding $\Delta\underline{H}$, $\Delta\underline{S}$, and $\Delta\underline{C}p$ values are useful to identify and understand the driving forces of the reactions and the associated solute-solute interactions. Flow calorimetry affords a reliable and rapid means to determine these thermodynamic quantities at specific temperature-pressure coordinates. The ability to regenerate the experimental heat $\underline{vs}$. moles of reactants curves provides evidence for the reliability of the calculated $\underline{K}$ and $\Delta\underline{H}$ values and of the associated activity coefficient calculations. Availability of these measured thermodynamic quantities makes possible the evaluation of extrapolative techniques for estimating $\underline{K}$ values at elevated temperatures.

INTRODUCTION

Chemical reactions in aqueous solutions at elevated temperatures and pressures are of interest in a large and growing number of areas including geochemistry (ref. 1), electricity generating plants (ref. 2), marine chemistry (ref. 3), and industrial chemistry (ref. 4). The driving force in these cases is the need to identify and understand the chemical reactions occurring in the particular systems of interest. A major step in this process is the assignment of equilibrium constants($\underline{K}$) to specific reactions. Without this quantification of the systems, knowledge of the reactions remains qualitative and accurate predictions of chemical behavior are not possible. The need for accurate $\underline{K}$ values at elevated temperatures and pressures becomes even more apparent when one recognizes that under these conditions the behavior of chemical species toward the solvent and toward each other differs markedly from that at 25°C and 0.1 MPa. Furthermore, the divergence increases as temperature increases. Little is known about the effects of pressure on $\underline{K}$, but available $\underline{K}$ data indicate that these are smaller than temperature effects (ref. 5).

The importance of $\underline{K}$ and related $\Delta\underline{H}$, $\Delta\underline{S}$, and $\Delta\underline{C}p$ values in increasing our understanding of chemical reactions at 25°C is well known (ref. 6, 7). As these quantities become available for reactions at elevated temperatures and pressures, our understanding of this chemistry will likewise be given a quantitative foundation. Log $\underline{K}$ values for solute-solute interactions define the extent of a given reaction. Corresponding $\Delta\underline{H}$ and $\Delta\underline{S}$ values provide information concerning the reaction driving force(s). These thermodynamic quantities together with corresponding $\Delta\underline{C}p$ values provide definitive information concerning the chemical reactions studied and the interactions of the solute species with the solvent. This information provides a foundation for formulating and testing models and theories for the behavior of chemical species at elevated temperatures and pressures. Due to the difference in behavior of many chemical species and of water at high temperature from that at 25°C, models and theories based on 25°C data are often inaccurate to an unknown degree when applied to reactions at higher temperatures and pressures. The structure and properties of water change markedly as temperature and pressure increase (ref. 8). These changes result in unexpected changes in $\underline{K}$, $\Delta\underline{H}$, and $\Delta\underline{S}$ values. Differences between activities and concentrations of chemical species increase in an accelerated fashion as temperature increases (ref. 9). Thus, the requirement for accurate activity coefficient values becomes increasingly important in the interpretation of experimental data. Availability of $\underline{K}$ values makes possible the testing of methods which have been devised for the extrapolation of these values from temperatures where they can be measured accurately to high temperatures.

Despite the importance of the above-mentioned thermodynamic quantities in understanding high temperature chemical equilibria, reliable thermodynamic values determined at specific temperature-pressure coordinates are available for relatively few systems. There are several reasons for the lack of these data. First, controlled experimentation at elevated temperatures and pressures is difficult and requires special equipment design. Second, the ion association in the reacting solutes becomes more prevalent as temperature increases.

Ion association is less important at 25°C and is often assumed to be negligible. This assumption can result in large, often undetected, errors in $\underline{K}$ values determined at high temperatures. Third, for species with charges greater than unity, reliable ways to correct activities to concentrations are not well developed (ref. 10). Significant errors in activity coefficient values can result by assuming that procedures used at 25°C can be used at elevated temperatures and pressures.

The present paper reviews flow calorimetric work done by us which involves the determination at specific temperature-pressure coordinates of log $\underline{K}$ and $\Delta\underline{H}$ values valid from 150 to 320°C. From these values, $\Delta\underline{S}$ and $\Delta\underline{Cp}$ values are calculated. The reaction(s) are identified by the fit of the calculated thermodynamic quantities to the experimental data over a temperature range. The use of activity coefficients in calculating the log $\underline{K}$ values is described. The isocoulombic method for predicting $\underline{K}$ values at high temperatures from $\underline{K}$ values measured at lower temperatures is evaluated and found to be reliable except above 300°C. Systems studied have included protonation of amines (ref. 11), Cl^- (ref. 12), and acetate ion (ref. 12); and the interaction of Na^+ with SO_4^{2-} (ref. 13), HSO_4^- (ref. 13), and acetate ion (ref. 12).

EXPERIMENTAL DIFFICULTIES IN HIGH TEMPERATURE RESEARCH

High temperature calorimetric studies involve contact between metal components of the calorimeter and potentially corrosive solution components. Since corrosion reactions generate heat, this behavior is unacceptable in calorimetric experiments. Materials of construction must be inert to the reagents used. This point will be discussed below. It is important to exclude reactive gases such as oxygen from the solutions since these gases may either react with or be absorbed by the metal tubing in the calorimeter. In the first case, the resulting oxidation produces large amounts of heat making the calorimetric determinations invalid. In the second case, the resulting progressive embrittlement causes the eventual failure of the calorimeter.

Perhaps a major reason that more quantitative work involving solute-solute interactions has not been done is the difficulty of carrying out reactions at specific temperature-pressure coordinates. We have surmounted this difficulty with flow calorimeters designed for use at temperatures to 350°C and pressures to 20 MPa (ref. 14-16). A schematic of the flow calorimeter operation is shown in Fig. 1. The solutions to be studied are placed in separate pushers. ISCO pumps deliver precisely controlled amounts of solution. The two solutions are equilibrated at the temperature of measurement by heat exchange with the exit fluid and the walls of the concentric cylinders for a length of two meters before entering the mixing chamber located on the surface of the innermost cylinder which is operated in an isothermal mode. (The entering and exiting tubes are shown as separate lines in Fig. 1 for clarity.) A passive heat leak located at the bottom of each concentric cylinder removes heat at a constant rate from the innermost cylinder while a heater supplies pulses of energy as required to maintain the innermost cylinder at a constant temperature. Imposition on the system of a chemical reaction with its associated heat change results in an increased or decreased number of heater pulses per second depending on whether the reaction is endothermic or exothermic. Pressure is maintained using a back pressure regulator. The solutions in the calorimeter are maintained at a pressure a little above the vapor pressure of water at the temperature of study. Thus, no vapor space is present during the runs. The control of pressure and temperature to allow study at a single well defined point is essential to obtaining reliable and reproducible data. The temperature is controlled at ±0.05 K at each temperature from 150 to 320 K and the pressure is controlled to ±1% of the total pressure between 0.1 and 20 MPa.

Earlier versions of this calorimeter were constructed of stainless steel or Hasteloy-C tubing and pumped organic fluids in heat of mixing studies (ref. 14,15). The use of reactive solutes capable of corroding the metal components required certain modifications. Corrosion was a problem in three locations. First, in the pumps from which the solutions were metered into the calorimeter reaction vessel, second, in the tubing and reaction vessel, and, third, at the tubing connection points. In the first case, the possibility of corrosion was eliminated using teflon pushers (ref. 17) similar to those used at Oak Ridge (ref. 18). The pumps (Fig. 1) were filled with water which was metered into a stainless steel cylindrical tube (0.6 meters long and 5 cm in diameter). Within the cylinder was a teflon tube filled with the solution to be studied. The entering water displaced the solution which entered the calorimeter tubing. Second, the tubing and reaction vessel were found to corrode rapidly in contact with several inorganic salts and acids when they were constructed of stainless steel. Hasteloy-C, a nickel-containing alloy was much more corrosion resistant (ref. 15). However, several solutions such as acid chlorides still caused appreciable corrosion. Tantalum was found to be resistant to the inorganic acids and salts studied and has been used in our studies (ref. 12, 13, 16). However, tantalum has several disadvantages. It reacts with solutions of high pH and it becomes brittle after extended use. In the latter case, replacement was necessary after about one year because the tubing could not be manipulated or repaired without breaking. In the third case, corrosion was minimized by using titanium valves and connections in the lines.
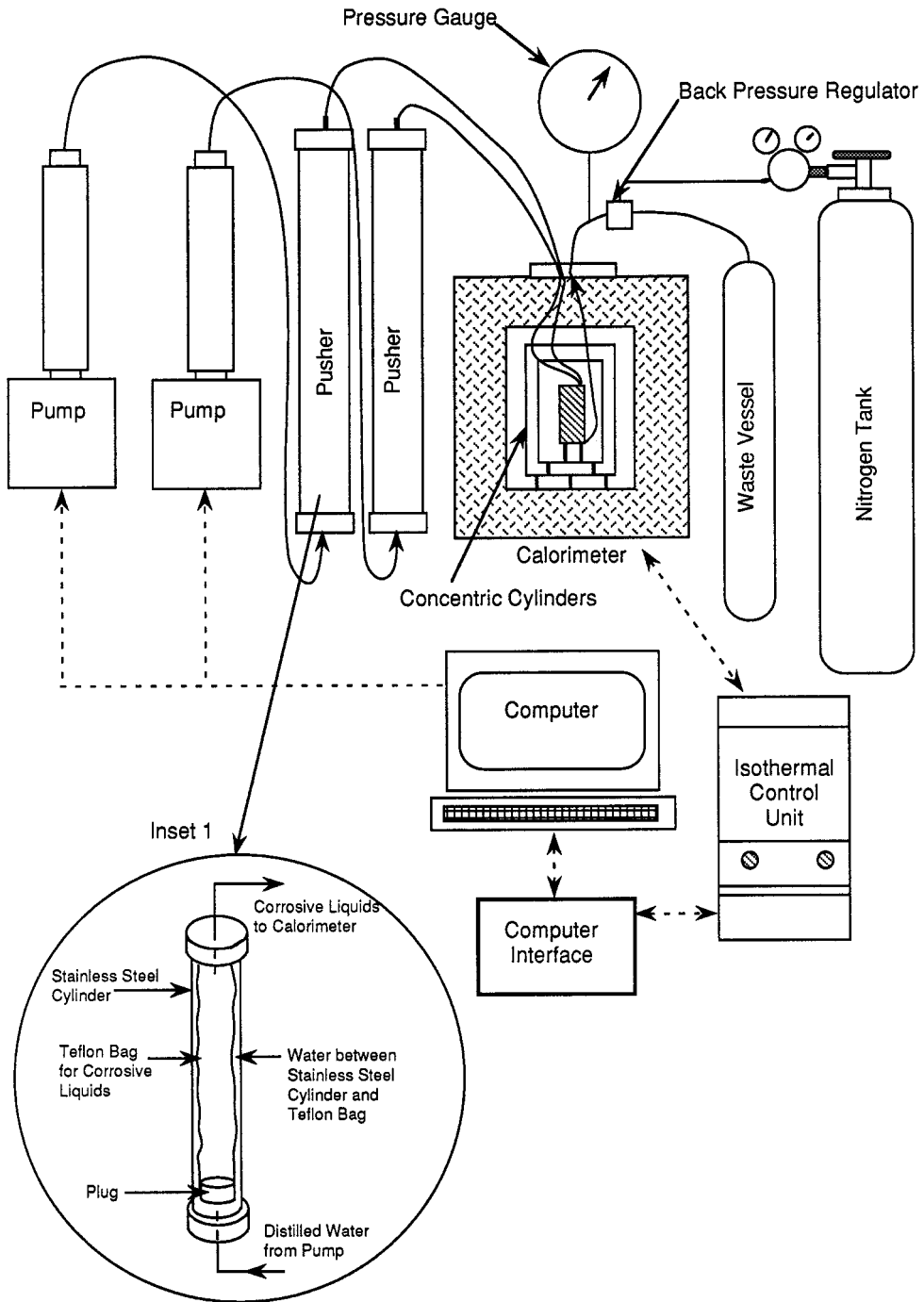
Fig. 1. Schematic of flow calorimeter operation. Solid lines represent fluid flow and dashed lines represent electrical connections.

The solubilities of many salts decrease (often rapidly) as temperature increases (ref. 9). The solubilities of some salts, such as Na_2SO_4, decrease markedly above 320°C. This solubility decrease results, in part, from the decrease in the water dielectric constant and the change in water structure. At temperatures approaching the water critical point (374°C), water becomes an excellent solvent for gases and non-polar organic compounds and a progressively poorer solvent for inorganic salts. One has a major problem when a salt crystallizes in the 0.8 mm inner diameter tubing.

A problem encountered at high temperature which does not have a counterpart at 25°C is that nearly all aqueous solution species are associated. At first, this seems opposite to what is expected. Our knowledge of 25°C chemistry suggests that increasing the temperature should lead to an increasing degree of dissociation. As will be illustrated in a later section, the increase in $\underline{K}$ values can be attributed to favorable $\Delta\underline{S}$ values which offset unfavorable $\Delta\underline{H}$ values by increasing amounts as temperature increases. Many incorrect $\underline{K}$ values have resulted from the failure of investigators to take into account these ion pairs. In many cases, the associated species do not exist in measurable amounts at 25°C. Examples include HCl and HNO_3. The technique described here provides a rigorous method for identifying the reactions which must be considered to account for the heat generated in solute-solute interaction.
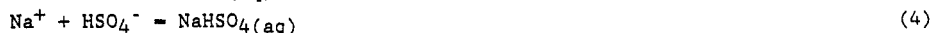

COLLECTION OF CALORIMETRIC DATA

An important initial step in determining the log $\underline{K}$ and $\Delta\underline{H}$ values for reactions in high temperature aqueous solutions is to choose the reactants with care. This requirement stems from the fact that, in almost all cases, more than one reaction occurs in the calorimeter. Nearly all cations and anions associate with one another at high temperatures. Therefore, $\Delta\underline{H}$ and log $\underline{K}$ values must be found for more than one reaction making the mathematical scheme as well as the experimental procedure more complex. An example of this is the formation of $HCl_{(aq)}$ (ref. 12), Equation (1).

$$H^+ + Cl^- = HCl_{(aq)} \tag{1}$$

$HCl_{(aq)}$ is essentially 100% dissociated at 25°C, it is somewhat associated at temperatures above 250°C and the extent of association increases with temperature above 250°C. At elevated temperatures, calculations used to calculate $\underline{K}$ and $\Delta\underline{H}$ for an acid/base reaction using HCl as one of the reactants must include these values for Equation (1).

Five examples of reactants involving Equation (1) which could be used are: (H_2SO_4 + NaCl), (HCl + Na_2SO_4), (NaCl + $NaHSO_4$), (NaCl + $HC_2H_3O_2$), and (HCl + $NaC_2H_3O_2$). Other reactants could be used by choosing new cations or anions. No matter which reactant set is chosen, it is probable that more reactions will take place than the reaction of interest. If any of the first three sets were used, the following reactions would need to be considered in addition to reaction (1).

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

$$H^+ + HSO_4^- = H_2SO_{4(aq)} \tag{3}$$

$$Na^+ + HSO_4^- = NaHSO_{4(aq)} \tag{4}$$

$$Na^+ + SO_4^{2-} = NaSO_4^- \tag{5}$$

$$Na^+ + NaSO_4^- = Na_2SO_{4(aq)} \tag{6}$$

A similar set of reactions must be considered no matter which reactants are used. Selection of the reactants requires that one consider all of the likely reactions which could take place. Log $\underline{K}$ and $\Delta\underline{H}$ values for these reactions either must be known or be calculated as part of the computation process. Whenever possible, it is important to select reactants where log $\underline{K}$ and $\Delta\underline{H}$ values are known for as many of the interactions as possible. As more thermodynamic data become available, this task becomes easier. In addition, successful use of a given log $\underline{K}$ value in a series of different reaction schemes lends confidence that this log $\underline{K}$ value is valid for the particular reaction.

Once the set of reagents is chosen, consideration should be given to the conditions of the calorimetric runs. The reaction runs should be made at a minimum of two concentrations (three or four is better). At each concentration, dilution runs should be made for each reactant stream (*i.e.*, the reactants should be mixed with water in the calorimeter). The reaction and dilution runs should be repeated at a minimum of three temperatures. It is desirable to use two sets of reactants, such as (HCl + Na_2SO_4) and (NaCl + $NaHSO_4$) in these determinations in order to provide a check on the accuracy of the calculated $\underline{K}$ values.

REDUCTION OF CALORIMETRIC DATA

Reduction of the calorimetric data requires a reasonable activity coefficient model. The easiest of these to use is the model substance approach (ref. 2, 12, 13). Its use does not require any adjustment of the parameters in the activity coefficient model, but it does lead to some errors in data reduction, especially for multiply charged ions. If a more complex activity coefficient equation is used, some terms in the equation will become adjustable parameters, making it difficult to separate the effects of log K and ΔH from the effects of changing the parameters in the activity coefficient equations (ref. 2, 18). At our present level of understanding, the model substance approach appears adequate. However, better activity coefficient models are needed to enable us to differentiate between the behavior of individual ions as a function of temperature and concentration. This need is particularly pressing in the case of multivalent ions.

The data reduction should include a computerized optimization procedure which will search for those ΔH and log K values that will minimize the error between the calculated and measured heats. The investigator must choose which set of reactions is expected to be involved in the particular system of interest. This choice requires some intelligent guess work. This guess work is markedly aided by a knowledge of the literature on high temperature chemical reactions. It is best, initially, to guess a small number of the most likely reactions. Once a guess of the important reactions is made, the optimization procedure will find the best values of ΔH and log K for these reactions for a given temperature. The optimization routine must call on a computer program which can calculate the heat changes if the reactions and their log K and ΔH values are given. This computer program uses the log K values and an activity coefficient model to find the concentrations of all of the species in the reactant and product streams for all of the calorimetric data including the heats of dilution. The computer program used by us employs a multivariate Newton method to solve for the species concentrations. In each step, it is assumed that the activity coefficients are constant (i.e., their derivatives with respect to concentration are 0). The activity coefficients are recalculated after each iteration. Once the concentrations of the reactant and product streams are known, the enthalpies of these streams are calculated relative to a reference state using the ΔH values and the activity coefficients. The reference state for water is pure water and that for the solutes is a hypothetical 1 molal solution of dissociated ions at infinite dilution. The heat changes are next found by subtracting the enthalpies of the reactant streams from those of the product streams. The heat changes are then calculated. If the agreement between the measured and calculated heat changes is poor, the next most likely reaction is included in the list of reactions and the process repeated, until the addition of a new reaction does not improve the fit or forces the log K and ΔH values to be unreasonable. Once the best set of reactions with their corresponding ΔH and log K values has been found at one temperature, the process is repeated at the other temperatures. The log K and ΔH values at each temperature calculated by the optimization procedure can then be checked against those obtained using the integrated form of the van't Hoff equation.

$$\left(\frac{\partial \ln K}{\partial T}\right)_P = \frac{\Delta H}{RT^2} \qquad (7)$$

This equation can be integrated numerically by using measured ΔH values or analytically by assuming some functional form for ΔH as a function of temperature. If the log K values obtained by integration of equation (7) from one temperature to another do not agree with the log K values found by the optimization at that temperature, then the process must be repeated with consideration given to including additional or different reactions. An alternative approach is to assume some functional form for ΔH as a function of temperature and have the optimization routine optimize on the data at all temperatures to find the parameters in the assumed function. This latter approach has merit in that it automatically forces the results to fit the van't Hoff equation, but it limits the way in which ΔH changes with temperature. Examples have been reported of the application of these procedures to several systems (ref. 12, 13).

The association of ions at high temperature makes it impractical to use excess electrolyte to maintain a "constant" ionic strength. Thus, it is necessary to calculate activity coefficients for the various species involved. In the reactions at high temperatures, the ionic strength at the end of the reactions is different than it is before the reaction takes place, so the enthalpy departure must be calculated for the reactant and product streams.

At high temperatures, activity coefficients differ markedly from unity, especially for multiply charged ions. For example, the activity coefficient for Ca^{2+} is close to 0.01 at ionic strengths as low as 0.10 (ref. 10). This has two effects on subsequent calculations. First, the equilibrium ratio for ion association changes considerably with concentration and requires considerable iteration in order to find the concentrations of the species in solution even when the K values are known. Second, the dilutional heat effects are very large. At 25°C, dilutional heats typically contribute approximately 1% of the total heat measured. At 250°C, the dilutional heat may contribute the majority of the heat. Careful calculations are required to take into account this effect which includes the enthalpy departure or change in enthalpies for the reactants, the products, and the water due to changes in ionic strength.

Our ability to calculate reliable activity coefficients at high temperatures is limited as is pointed out in the Reduction of Calorimetric Data section. The model substance approach (ref. 2) has the advantage of being simple, but it lacks the accuracy needed for a precise mathematical description of electrolyte behavior. A more thorough treatment is that used by Holmes et al. (18). However, this treatment has not been applied to mixed electrolytes at high temperatures. A compromise approach has been advocated by Apelblat; et al. (10) in which activity coefficients of the desired species are calculated using that of a model substance (i.e., NaCl or $CaCl_2$) plus one calculated additional species specific term.

The log K and ΔH values can now be checked to see if they fit data taken using different reactants but including some of the same reactions. If the values fit the data in all of the above cases and are in agreement with Equation (7), then the ΔH and log K values obtained are considered to be valid for the proposed reactions.

DISCUSSION

One of the most striking observations in comparing 25°C chemistry to high temperature aqueous solution chemistry is the increasing importance of the entropy change as the driving force for protonation and metal complexation reactions. At 25°C, most reactions are either primarily or partially enthalpy-driven (ref. 19). However, at 300°C all reactions which have been studied by us are entropy-driven (ref. 12, 13). Furthermore, the balance of ΔH and ΔS is such that K increases with increasing temperature. The increased K value results from large $T\Delta S$ increases relative to those of ΔH. Examples of these effects are given in Table 1.

TABLE 1. Log K, ΔH, and ΔS values for the interaction of H^+ and M^{n+} with several ligands.

Reaction	T,C°	P MPa	Log K	ΔH KJ/mol	ΔS J/mol·K	ΔCp J/mol·K	
$H^+ + SO_4^- - HSO_4^-$	25	0.10	1.98	22.60	114	88	(ref. 20)
	150	2.31	3.56	57.36	204	264	
	175	2.24	3.98	64.97	221	349	
	200	2.31	4.41	75.05	243	462	
	250	10.3	5.34	105.03	303	749	
	300	11.0	6.44	150.98	387	1097	
	320	12.8	6.94	174.42	427	1248	
$Na^+ + SO_4^- - NaSO_4^-$	25	0.10	0.65	-2.05	4.6	4	(ref. 21)
	150	2.31	0.95	24.68	77	303	
	175	2.24	1.15	32.80	95	347	
	200	2.31	1.38	42.06	115	394	
	250	10.3	1.93	64.12	160	490	
	300	11.0	2.60	91.09	209	589	
	320	12.8	2.90	103.28	230	630	
$H^+ + Cl^- - HCl(aq)$	275	10.3	0.37	103	195	1222	
	300	10.3	0.87	141	263	1844	
	320	12.8	1.37	184	336	2431	
$H^+ + Ac^- - HAc(aq)$	25	0.1	4.756	0.83	92	155	(ref. 22-24)
(Ac = acetate ion)	275	10.3	6.18	70	245	862	
	300	10.3	6.52	97	293	1320	
	320	12.8	6.86	127	346	1748	

In the absence of a solvent, both ΔH and ΔS would be expected to be negative. In the presence of water both quantities are positive. Both the sign and the changes in magnitude of these quantities can be attributed to solvent effects. These effects are particularly pronounced in aqueous solutions because of the profound changes in water structure as temperature increases. Of particular importance in the present case is the disruption of hydrogen bonding with the resultant increase of the degrees of freedom of the water molecules and the decrease of the bulk dielectric constant. Reference 13 contains a discussion of these solvent-solute effects and how they affect the size and magnitude of ΔH and ΔS values. As the temperature increases, hydrogen bonding in the bulk water phase decreases resulting in a higher energy for the water molecules. In this environment, the energy required to restore water molecules released from interacting solutes to the vibrational, rotational, and translational conditions of the bulk phase increases. The absorption of the required energy from the surroundings is the cause of the large positive ΔH values for the formation reaction. The ΔH value increases as temperature increases since the amount of hydrogen bonding in the bulk water phase decreases rapidly.

The large increase in $\Delta \underline{S}$ with increasing temperature reflects the release of water molecules from the interacting solutes into a bulk liquid phase of progressively lower hydrogen bonding. The $\Delta \underline{S}$ effect exceeds the $\Delta \underline{H}$ effect resulting in larger log $\underline{K}$ values. In general, log $\underline{K}$ increases with temperature reflecting the dominant effect of $\Delta \underline{S}$. As temperature increases and the dielectric constant of water decreases, the influence of each ion extends over a larger volume, thus influencing more water molecules.

One approach to estimating the degree of solute-solute interaction has been the extrapolation of log $\underline{K}$ values from 25°C to high temperature regions (ref. 13). This approach has many uncertainties. An assumption inherent in many of these extrapolative procedures is that $\Delta \underline{Cp}$ is constant or zero over the temperature range involved. The data in Table 1 show that this assumption is not valid, at least in some cases. Over the temperature range indicated, $\Delta \underline{Cp}$ is seen to increase in a nonlinear way with temperature. Since the variation of $\Delta \underline{Cp}$ with temperature is unknown due to lack of data in most cases, extrapolative techniques have been devised in which the change in $\Delta \underline{Cp}$ is minimized by simulating situations that do not involve large changes in water structure.

One extrapolative technique involves the formulation of an "isoelectric" or "isocoulombic" reaction, in which the net charges on the left and right sides of the balanced equation are equal. This approach has been treated in detail (ref. 2, 13). Use of isocoulombic reactions represents a great improvement over non-isocoulombic reactions in extrapolation procedures for the estimation of log $\underline{K}$ values for aqueous reactions at temperatures far removed from the temperatures of the source data. However, deviation of our log $\underline{K}$ data from expected isocoulombic behavior becomes important above 300°C. There are at least two possible explanations for this behavior. First, the ions on the two sides of the equation cannot have identical effects on the solvent. Therefore, the changes with temperature of the interactions between these ions and water are not identical. It is not unexpected that these changes accelerate with increasing temperature at high temperatures. Second, the density of the solution changes rapidly with temperature as the critical temperature of water (374°C) is approached. The ΔV value of the isocoulombic reaction is not expected to be zero. The most striking feature of our experimental data is the accelerating increase of $\Delta \underline{H}$ and $\Delta \underline{S}$ with temperature. This feature is most apparent at 320°C, the highest temperature used in our studies.

Future work in the field of high temperature aqueous solutions should include the following items. First, additional reliable thermodynamic data are needed for a variety of reactions. These data should be obtained at the temperature and pressure of interest. Our results show the importance of having log $\underline{K}$, $\Delta \underline{H}$, $\Delta \underline{S}$, and $\Delta \underline{Cp}$ values for the reactions studied. Second, it would be desirable to extend measurements to include the critical temperature of water. Our results at 320°C show rapidly increasing $\Delta \underline{H}$ and $\Delta \underline{S}$ values, deviations from isocoulombic behavior, and increasing log $\underline{K}$ values. These trends are expected to be enhanced as temperature increases. Some of the most interesting changes in water properties occur between about 350 and 420°C (ref. 25). A study of chemical reactions in this region should yield a wealth of chemical information. Third, improved models are needed to describe chemical reactions at high temperatures. An important component of these models is the development of improved activity coefficient equations. More reliable estimations of activity coefficients for multicharged ions are needed. These needs will become increasingly important as reactions at temperatures above 300°C are studied. Fourth, new experimental procedures are needed to determine speciation and driving forces for chemical reactions at specific temperature-pressure coordinates. Two promising procedures are raman spectroscopy (ref. 26) and potentiometry (ref. 27). Several methods now in use are described in two issues of the Journal of Solution Chemistry (ref. 28) and in a recent EPRI report (ref. 29). It would be desirable to devise novel ways to overcome the experimental difficulties and to incorporate the instrumentation which has been so successful in elucidating chemistry at 25°C into high temperature devices. Fifth, reactions other than single phase solute-solute interactions should be investigated at precise temperature-pressure coordinates. Such reactions include solid precipitation and partioning of gases and other neutral species from aqueous to gaseous phases. Finally, reactions in solvents other than water should be investigated. Other solvents differ from water in their properties and their study could provide a rich source of information for development and testing of models for solute-solute and solute-solvent interactions.

Acknowledgements

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