High-Temperature Aqueous Solutions

The chemistry of hot water solutions has established a new and rapidly developing frontier in science.

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Many scientists are still somewhat surprised to learn that there is any interest at all in water solutions at temperatures very far removed from room temperature. I suppose this simply reflects the fact that these solutions have been used *ad nauseam* to train generations of students in the principles of chemical equilibrium, thermodynamics, and irreversible processes, without much consideration being given to the fascinating and useful properties of the solvent itself. The purpose of this article is to point out that the chemistry of aqueous solutions takes on a new dimension as the temperature range is extended. The field appears to hold great promise, both theoretical and utilitarian. Unfortunately, the low normal boiling point of water has apparently proved a barrier to exploration, particularly of the more fundamental aspects of the subject. For this reason, much of the pioneering work has been done by geochemists (*1*) and engineers, who needed answers to many practical problems. With the exception of the early work of A. A. Noyes on conductance (*2*), studies of the physical chemical properties of aqueous solutions had been largely confined to temperatures below 100°C (*3*).

The turning point came right after World War II when it became known that German scientists had succeeded (*4*) in growing synthetic α-quartz crystals, at economically practical rates, under hydrothermal conditions—that is, at high temperatures and pressures, with aqueous solutions as a medium. The ill-fated homogeneous nuclear reactor project in the United States, which was started about 1948, provided a sudden and widespread interest in the thermodynamic properties of aqueous species, particularly of actinide and fission-product elements in high-temperature solutions.

The reactor project itself has fallen by the wayside (at least for the present), but it left a valuable legacy of know-how and information concerning solutions at high temperatures. Equally important, it stimulated the interest of a number of chemists who are still engaged in many aspects of such research.

More recently the increased emphasis on purification of saline water has reinforced the demand for fundamental work in this field. Without doubt, these practical projects have contributed substantially to breaking down the old 100°C barrier. At present, spectrophotometric data, activity coefficients, and data on conductance, heat capacity, homogeneous and heterogeneous equilibria, and aqueous densities at temperatures all the way to the critical point are available. Conductance measurements have been extended by Quist, Marshall, and Jolley to temperatures of 800°C and pressures of 4000 bars in steam (*5*).

For the purposes of this discussion, the various temperature regions are defined as follows: low temperatures, 0°–60°C; moderate, 60°–100°C; high, 100°–374°C (374°C is the critical point). The temperature region approximately 10°C to either side of 374°C is called the critical region. The region above 374°C has usually been called the supercritical region; it is necessary, of course, to define the density of the system at temperatures above 374°C (and also below this temperature, if the pressure is different from the saturated vapor pressure of water).

Theoretical Interest

Because, at temperatures between 25° and 375°C, the dielectric constant of water falls from 78.3 to 9.2 (*6*), water is sometimes considered a poor ionizing solvent at high temperatures. This is an erroneous conclusion because the theoretical term which always enters into calculations of ion pairing and change of solute properties with concentration is the product DT of the dielectric constant D and the absolute temperature T, raised to some appropriate power. One qualitative measure of the ionizing power of a solvent can be inferred from a form of A_γ, the Debye-Hückel limiting slope for activity coefficients, which I define by the equation

$$\log \gamma_{\pm} = \frac{-A\gamma\,|Z_+\,Z_-|\,I^{\frac{1}{2}}}{1 + I^{\frac{1}{2}}}$$

where $\gamma_{\pm}$ is the mean activity coefficient, I is the ionic strength, and Z represents the charges of the solute ions.

Highly ionizing solvents, such as N-methyl formamide, have low values of A_γ, and the thermodynamic properties of solutes, such as activity coefficients and heats of dilution, change only slowly with concentration (*7*). On the other hand, dioxane has a very high value of A_γ, and it is very difficult to obtain, except at extremely low concentrations, any information on ions which are not paired in such solutions. Figure 1 summarizes the situation for a number of solvents, including water, over a wide range of temperatures. Although in such a qualitative diagram it is not possible to place any clear-cut borderline between dissociating solvents and associating solvents, dimethyl sulfoxide is usually considered to be on such a borderline. Therefore it is not completely arbitrary to consider most aqueous solutions to be dissociating and ionizing, at least at temperatures up to the critical point. Some justification for this placing of the borderline can be found from the data of Franck (*8*), from which the extent of dissociation of 0.001M potassium chloride at 340°C can be estimated as > 99 percent.

It can also be shown that some of the irreversible properties of solutes (such as diffusion and conductance) behave as expected in water at temperatures up to the critical point. When a solution is heated the ions share in the increased thermal agitation of the solvent, and mobilities increase. The viscosity of water, of course, decreases very rapidly (from 89×10^{-4} to $4 \times$

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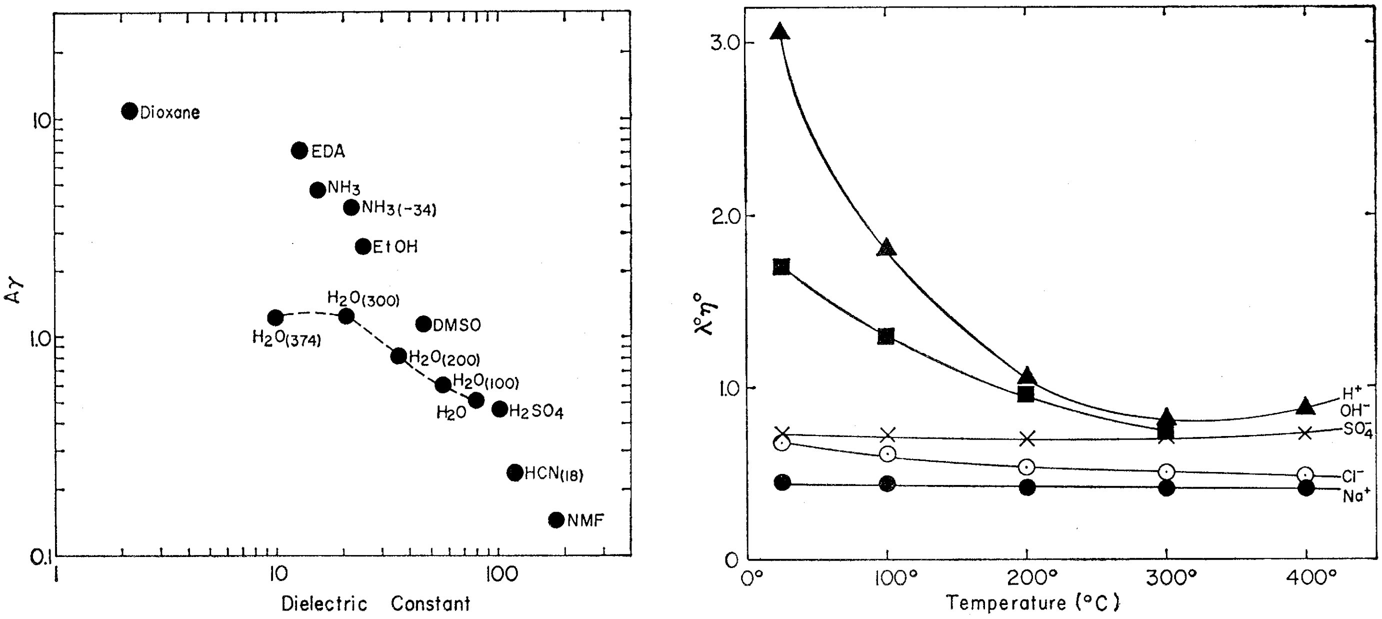

Figs. 1 and 2. Fig. 1 (left). Classification diagram for various solvents. A_γ is the theoretical limiting slope for activity coefficients (see text). *EDA*, Ethylenediamine; *EtOH*, ethyl alcohol; *DMSO*, dimethyl sulfoxide; *NMF*, *N*-methyl formamide; all other symbols are chemical formulas and refer to the solvent at 25°C unless a different temperature is shown in parentheses. [Data for density and for dielectric constant, from Robinson and Stokes (*35*); data for liquid ammonia, from Hunt *et al.* (*36*).] Fig. 2 (right). The Walden product, $\lambda^\circ\eta^\circ$, as a function of temperature. [Values of the limiting ionic conductances, λ°, from Quist and Marshall (*37*); viscosity data (η°), from Franck (*38*).]

10^{-4} poise) at temperatures between 25° and 374°C, but many ionic conductances apparently increase at just about the same rate. A more quantitative comparison of these phenomena is given in Fig. 2, where the product of the limiting ionic conductances, λ°, for some selected ions and the viscosity, η°, of water (this product, $\lambda^\circ\eta^\circ$, is sometimes called the Walden product) is plotted as a function of temperature. Except for H^+ and OH^- (which have special conductance mechanisms), water seems to act as a "normal" solvent over much of the liquid temperature range.

It is not necessary to dwell on the obvious limitations and pitfalls inherent in use of the Walden product for analysis of conductance data. However, Fig. 2 suggests that the primary hydration of simple aqueous ions is fairly constant over a wide range of temperatures. Further, the data also imply that the special conductance mechanisms for H^+ and OH^- fail at higher temperatures. Because this specially enhanced conduction depends strongly upon the hydrogen-bonded structure of the solvent, the number of hydrogen bonds per water molecule *at any instant* must be decreasing rapidly with increasing temperature. A similar conclusion can be reached from the change of dielectric constant with temperature.

Conductance measurements in aqueous solutions at high temperatures provide a new dimension to the theory of salt-solute interactions. With the proper selection of salt and temperature, the entire range from pure solvent to pure molten salt can be studied. For example, Duke and Simmons have investigated the system $NaNO_3$-H_2O over the whole concentration range at 300°C (*9*). Because the melting points of most salts fall sharply when small amounts of water are added, one would expect to find that a number of different salt solutions are amenable to such studies.

The more or less normal properties of water at high temperatures suggest many areas of exploration, both practical and theoretical, which are at present largely untouched. For example, besides having the expected thermal kinetic effect, hot water can stabilize ionic intermediates and activated complexes and may thus provide paths for chemical reactions too slow to occur in pure materials. Electrochemical fuel cells are only one example of the desirable thermal effect of water on the kinetics of electrode reactions at moderate temperatures in ionic media.

Practical Considerations

The main difficulty in working with water solutions at high temperatures is, of course, the solvent pressure; in the supercritical region, one must contend with both high pressures and high temperatures. There are really two aspects to the problem: mechanical difficulties and the chemical corrosive properties of water itself. The vapor pressure of pure water at 200°C is about 8 bars, and with rising temperature it increases rather rapidly up to 221.3 bars at the critical temperature, 374.2°C. In studies of solubility and synthesis, particularly with concentrated solutions where the pressure is depressed, good results have been obtained through use of sealed glass or silica tubes (*4, 10*). A practical limit of 6 to 10 bars is usually indicated for this type of enclosure. A number of stainless steels (*4*) make satisfactory containers except for halide solutions; "Udimet" (nickel) alloys have been used successfully to temperatures of 800°C and at very high pressures (*11*). In our laboratories at Purdue, titanium of high purity (tensile strength, 6900 bars) has been found useful in studies of dilute corrosive solutions at high temperatures. Another standard technique involves fitting stainless steel bombs or autoclaves with platinum or gold liners, but the liners tend to weld to the bombs at high pressure. Electroplating of liners is difficult at best, and repeated thermal cycles are likely to lead to flaking and penetration.

Figure 3 is a photograph of a titanium heat-of-solution calorimeter (*12*) designed for precise thermal measurements on a variety of salt solutions to 300°C. Also, a remarkable instrument has been constructed (*13*) from a Cary spectrophotometer; it is capable of making quantitative measurements of solution spectra at high temperatures (250°C) and moderate pressures (70 bars).

Fortunately, from the standpoint of theoretical interpretation, data on the viscosity, dielectric constant, PVT and density of water are largely available (*11*), and the ionization constant is available from room temperature into the supercritical region (*11, 14*).

Hydrothermal Synthesis

Much of the hydrothermal synthesis of inorganic compounds that is now being done involves the use of aqueous solutions as mass transfer media in producing crystals. Slightly soluble mineral crystals (nutrient) are placed in contact with an appropriate solution at some high temperature. Seed crystals, at a somewhat lower temperature, are then placed in contact (through a baffle) with the same solution. Different temperature gradients and different solutions are used, depending upon the particular synthesis involved. A wide variety of crystalline materials, such as α-quartz, ferrites, corundum, sapphires, and garnets, have resulted (*4, 15*). The advantages of such a method are that phases can be prepared which are not stable at their melting points; crystals more free of strain than those grown from melts are frequently obtained, and this freedom from strain is of utmost importance in determining their electrical properties. Further, substances can sometimes be prepared at higher temperatures which are actually unstable at lower temperatures and cannot be produced except by hydrothermal synthesis.

In some cases water participates directly in the synthesis, and a number of interesting hydrates and mixed compounds not observable at lower temperatures result (*10*). It should be noted that many substances which might be expected to hydrolyze extensively do survive hydrothermal conditions intact (for example, $CuSO_4$, $NiSO_4$, ZnS, and $AlPO_4$). This is not because hydrolysis ceases to be an important process at higher temperatures but because, in general, H_2O and OH^- maintain about the same relative strength as bases, with respect to other ions, that they have at room temperature. Further, the entropy change, $\Delta S°$, for hydrolytic polymerization becomes even more unfavorable at high temperatures, and highly discriminates against many such processes (*16*) in the relationship

$$\ln K°_{eq} = \frac{-\Delta H°}{RT} + \frac{\Delta S°}{R},$$

where $\Delta H°$ refers to the heat of the polymerization reaction.

In my opinion only the surface of the field of hydrothermal synthesis, in which water is used as a *reactant* rather than a *medium*, has been touched. While a number of organic syntheses of commercial value (for example, synthesis of phenol from chlorobenzene, of polyhydric alcohols from chlorinated pentanes, and of alcohols from olefins) are known, the corresponding inorganic area is largely untouched. One would expect that rather significant advances could be made in this direction in the future. Since many substances are appreciably soluble in water at temperatures above the critical temperature, there must be specific interactions and hydration. There is further evidence of hydration even above the critical temperature from other sources (see *11*) (Fig. 2).

Chemical Thermodynamics

The great power and flexibility of chemical thermodynamics in providing one framework on which to build aqueous solution chemistry at room temperature has provided great incentive to extend such methods to higher temperatures. It seems certain that, until a reasonable number of thermodynamic data are available, solution chemistry at high temperatures will not develop efficiently or as rapidly as would otherwise be the case.

Data on solubility have been collected by geochemists (*17*) for substances of geologic interest (mainly for the less soluble substances, such as carbonates, silicates, hydroxides, sulfates, and sulfides). Such data, obtained under proper conditions, can provide approximate values for the temperature dependences of $\Delta H°$ and $\Delta S°$, which are not constant over the extended temperature intervals under discussion. For more soluble species, one must also estimate activity coefficients. Various empirical methods of obtaining such coefficients have been suggested and tried (*14, 18, 19*), and the work of Lietzke and Stoughton (*18*) and of Marshall *et al.* (*19*) indicates that useful information on activities can be obtained by the solubility method. Data now available suggest that the concept of ionic strength is equally applicable at high temperatures.

Some equilibrium constants for complex ionic species at high temperatures have also become available from conductance measurements and solubility data, but in general this area is still largely unexplored. At present it is not possible to predict with any degree of certainty the composition of some complex ion (for example, $PtCl_6^{--}$) in various salt solutions even up to 200°C. It is fairly clear, however, that complexes will exist, particularly those which are formed from equilibria having favorable entropy changes at room temperature. However, the total num-

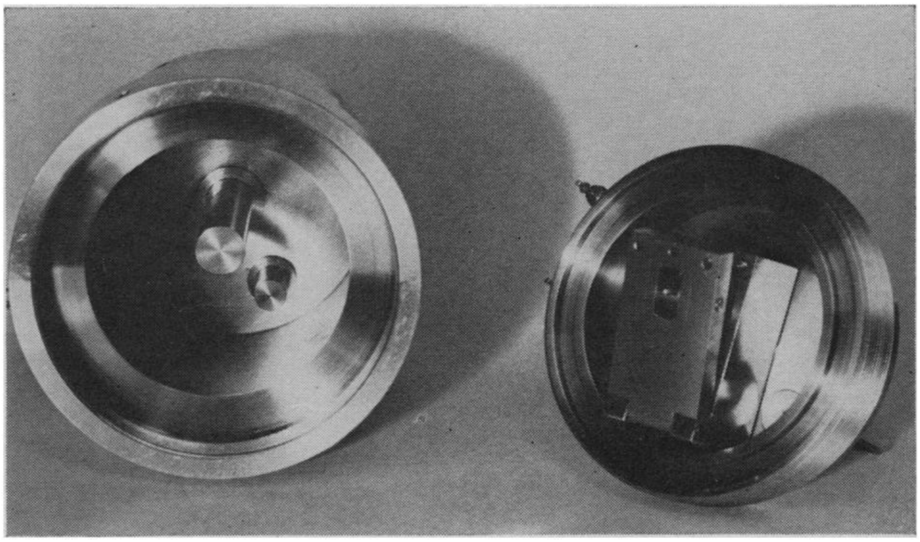

Fig. 3. Photograph of an all-titanium heat-of-solution calorimeter, showing bomb body (at left) and cap. The cap is fitted with a pressure-operated enclosure for introducing substances into solution. Stirring is accomplished by cyclic rotation about the axis of the partially filled calorimeter through a 45-degree angle.

ber of complexes may be somewhat less at high temperatures than at low temperatures, where thermodynamically unstable states can frequently be obtained because of their slow rates of decomposition.

A few electrochemical cells have been investigated at temperatures up to 250°C (*20*) in studies that have provided some valuable thermochemical data, particularly on activity coefficients. Interest in practical fuel cells has stimulated measurements on a wide variety of electrodes in various media at high temperatures (*21*), but as yet, very few useful thermodynamic data have resulted from such work.

Slow Progress

From the foregoing discussion it seems clear that thermochemical data will become available, in increasing abundance, for various unrelated systems. However, when one remembers how many generations of scientists it took to advance our knowledge of solution thermodynamics to its present state at just one temperature, 25°C, it is obvious that some more rapid method of obtaining such information is required.

The most obvious approach is to focus attention on some thermodynamic property which can be used to extend, in a rigorous manner, many of the existing lower-temperature data. Fortunately, such functions exist for aqueous species; they are called partial molal heat capacities $\langle C_{p_2} \rangle_{\text{av}}$, or $\langle C_{v_2} \rangle_{\text{av}}$. At lower pressures (at temperatures up to approximately 300°C and in dilute solutions), the constant pressure function, $\langle C_{p_2}{}^\circ \rangle_{\text{av}}$ is most useful. Using 25°C (298°K) as a reference state, one can show that, for the free energy $\Delta F_{(T)}$

$$\Delta F^\circ_{(T)} = \Delta F^\circ_{(298)} - \Delta S^\circ_{(298)}\, \Delta T + \int_{298}^{T} \Delta C_p{}^\circ \; dT - \int_{298}^{T} \Delta C_p{}^\circ \frac{dT}{T} \qquad (1)$$

where (T) refers to the higher temperature and $\Delta T = (T - 298°)$; $C_p{}^\circ$ refers to a standard state heat capacity. An approximate but sufficiently accurate form of this equation which is more useful is:

$$\Delta F^\circ_{(T)} = \Delta F^\circ_{(298)} - \Delta S^\circ_{(298)}\, \Delta T + \langle \Delta C_p \rangle_{\text{av}} \Big]_{298}^{T} \left(\Delta T - T \ln \frac{T}{298}\right) \qquad (2)$$

where $\langle \Delta C_p \rangle_{\text{av}}$ refers to an average heat capacity change over the temperature interval $T - 298$°C.

It is pertinent to recall that heat capacity changes, ΔC_p, are not very large for a wide variety of reactions involving pure substances. Except in a few special cases this situation results from the facts that the internal motions of atoms in molecules do not change grossly in the course of chemical reactions and the translational heat capacities for gases are small. Normal ΔC_p values for such systems are of the order of a few calories per degree per mole. In aqueous (and nonaqueous) systems, solvation results in much larger effects, with values of ΔC_p for ionic systems reaching ± 50 to 100 calories per degree per mole. Over a temperature range of 200° to 300°C, these effects can introduce many hundreds of calories into the free energy function. To further complicate the picture, ΔC_p is itself frequently highly dependent on temperature. Unfortunately, direct determination of heat capacities of electrolytes is one of the most difficult of thermodynamic measurements, and only two laboratories are at present engaged in such measurements (*22, 23*). Until a few years ago, the slow pace of such measurements, in view of the total number of ionic species, was not very encouraging.

Operation Bootstrap: The Correspondence Principle

In 1961 one of my students, C. M. Criss, and I came upon what we now believe to be a widely applicable principle that can sharply reduce the need for extensive thermodynamic data at high temperature. In brief, the observations (*23*) suggested that there was a simple correspondence between the (partial molal) entropies of ions at one temperature and some higher (or lower) reference temperature:

$$\bar{S}^\circ_{(t_2)} = a_{(t_2)} + b_{(t_2)}\, \bar{S}^\circ_{25} \qquad (3)$$

Since the constants $a_{(t_2)}$ and $b_{(t_2)}$ depend only on the temperature and not on the ion, then data on only two ions at some temperature, t_2, would fix the two constants in this equation. In actual fact, one more entropy is needed to fix a standard state at each temperature, and the cations and anions have separate constants. While the temperature dependences of entropies are in themselves interesting, far more interesting is the resulting heat capacity function:

$$\langle C_{p_2}{}^\circ \rangle_{\text{av}} \Big]_{298}^{T_2} = \frac{\bar{S}^\circ_{(T_2)} - \bar{S}^\circ_{298}}{\ln (T_2/298)} \qquad (4)$$

This function is just the one required to fix the heat-capacity term for ions in Eq. 2. Because the entropies for most ions are known or can be estimated (*24*) at one reference temperature, 25°C (298°K), it follows that three solute entropies known at some higher temperature can fix the heat capacities for up to a hundred ions over the temperature interval involved. Such tables and constants have recently been published for ions at temperatures up to 300°C (*23*). I personally believe that this "bootstrap" method, or correspondence principle, can be extended to other thermodynamic variables, some of which are of great importance to an understanding of high-temperature solutions. The reason for this optimism lies in the nature of Eq. 3. This expression is really a type of equation of state, and it eliminates the need to know the fundamental details of what actually determines the property under discussion (in this case, the ionic entropy). Another way of looking at Eq. 3 is to view it as expressing a property under one set of conditions in terms of the same property under a reference set of conditions. It is hard to imagine a simpler way to sidestep our still widespread theoretical ignorance of some of the most fundamental properties of aqueous solutes.

At present we are looking closely at the temperature dependence of the partial molal volumes of ions as a function of temperature. One can hope that generalized expressions of the form

$$\bar{V}_2{}^\circ_{(t_2)} = a_{(t_2)} + b_{(t_2)}\, \bar{V}_2{}^\circ_{(25)} \qquad (5)$$

$$\bar{V}_2{}^\circ_{(P_2)} = x_{(P_2)} + y_{(P_2)}\, \bar{V}_2{}^\circ_{(P_1)} \qquad (6)$$

exist. The need for ionic molal volumes becomes increasingly important in the critical and supercritical temperature regions for water, where constant-volume thermodynamic functions are needed. If a link is ever to be established between the regions on either side of the critical temperature, data on molal volumes are absolutely necessary. Some density data on high-temperature salt solutions (*25*) and on changes in molal volumes (*5*) are beginning to appear, but this area is still sadly neglected.

Real Solutions

In general, theory and most of the data-collection for high-temperature aqueous systems are deliberately confined to the more dilute solutions. This is the logical approach to development of the field, since standard states are usually based on "ideal" or infinitely dilute systems. Yet the time comes when one must deal with concentrated or "real" solutions and, in many cases, with multicomponent systems. Some data have been obtained, from cell measurements, on activity coefficients in concentrated acids at high temperatures (*20*), and some data from isopiestic studies are directly fixing osmotic coefficients for a wide variety of salt solutions at high temperatures (*26*). Methods have been suggested for determining and predicting activity coefficients for both moderately (*14*) and highly (*18, 19*) concentrated solutions. Unfortunately, all these methods require systems of relatively few components.

Theory for mixed electrolytes, even at low temperatures, is still in an early stage, and for that reason the novel approach suggested by Helgeson (*27*) for many-component systems is of great interest. This approach involves estimation of the individual ionic activities, and it can readily be applied to systems with large numbers of components. Recently, Frank (*28*) has also suggested a return to the concept of individual ionic activities, in spite of opposition, over the years, on the part of the thermodynamics purists. Until we have more experimental data on activity coefficients, however, the ultimate importance of these various methods will not be known.

Chemical Kinetics: Faster and Faster?

At first glance, the field of aqueous chemical kinetics would seem to be of rather limited scope at higher temperatures. One would simply expect all reactions to proceed so fast as to eventually become unmeasurable. Because most kinetic studies are directed toward elucidating *mechanisms* of reactions, rather than toward evaluating rate constants per se, the only apparent advantage of studies at high temperatures would be that they would provide information on reactions which, at room temperature, are too slow to be observable. This, in itself, may be quite important. However, there are other and far more imporant reasons for looking at the kinetics of aqueous reactions over extended temperature ranges; these have to do with the nature of the activation energy and its temperature coefficient. Up to the present, all but a few workers in solution kinetics (*29*) have been content to study the first temperature coefficient of the specific rate constant which experimentally fixes the activation energy, $\Delta E^\ddagger$ or $\Delta H^\ddagger$. Under certain simplifying assumptions, absolute rate theory as developed by Eyring and his associates (*30*) can provide estimates of the entropy of activation, $\Delta S^\ddagger$. While attempts have been made from time to time to correlate these entropies with the nature and structure of the activated complex, such attempts have been only partially successful, in contrast to the very good results obtained in calculating and correlating entropies of stable aqueous species (*24*).

There are a number of possible reasons for this situation, and undoubtedly one of them has to do with the inherently poor accuracy of kinetic data vis-à-vis thermodynamic data. However, a much more fundamental reason is our lack of knowledge of the structure of activated complexes in solution. The symmetry and nature of this complex controls the exact relationship between the observed $\Delta H^\ddagger$ (or $\Delta E^\ddagger$) of activation and the calculated $\Delta S^\ddagger$ of activation. Up to now, the exactness of the relationship has been only approximated for solution complexes. Consequently, the problem becomes one of providing more information on the activated complex, whose mean life is too short ($\sim 10^{-13}$ second) to permit direct study. Now, the temperature coefficient of the heat of activation is the heat capacity of activation, $[d(\Delta H^\ddagger)]/dt = \Delta C_p{}^\ddagger$, and fortunately, determination of this latter quantity is not dependent upon detailed knowledge of the activated complex. However, the heat capacity of activation can also be calculated by the principles of statistical thermodynamics, if the partition function is known. This function is in turn directly related to the nature of the activated complex. Consequently, there is some hope that one can work backward from the heat capacities of activation to obtain more information on the activated complex.

The entropy of activation is also fixed by the same statistical calculations, but in a somewhat different form. Since $\Delta S^\ddagger$ and $\Delta C_p{}^\ddagger$ can be directly related by ordinary thermodynamics,

$$\left(\frac{\partial \Delta S^\ddagger}{\partial t}\right)_p = \frac{\Delta C_p{}^\ddagger}{T},$$

then an additional check is available in assigning symmetries and internal motions in the activated complex.

One might ask why such evaluations have not been carried out previously. Certainly the necessary theory has been available and understood for over two decades. Some of the reasons are fairly simple. The first great kinetic studies were limited to gas phase systems, where first principles could be used to calculate collision and diffusion rates. As I have pointed out, changes in heat capacity are small for the reactions of pure substances, particularly gases, and the temperature ranges which would have to be covered in order to evaluate $\Delta C_p{}^\ddagger$ have only recently become accessible. For reactions of substances in aqueous solution, changes in heat capacity are much larger; it has been noted (*14*) that values of $\Delta C_p{}^\ddagger$ as great as $+100$ to -100 calories per degree can be expected. However, the normal liquid temperature range of water is only 100°C, and physical-chemical experimentation on pressurized aqueous solutions is, again, a more recent development. Further, many reactions become extremely rapid at high temperatures, and techniques for studying fast kinetic systems are difficult and also new.

There is yet another aspect of the kinetics of solutions at high temperature which could conceivably be of even more fundamental significance than the information on the activated complex which is provided by such studies. For purposes of illustration, let us consider a kinetic system having a well-known mechanism, and focus attention on the rate-determining step, or, more precisely, on the activated complex. According to any existing rate theory, a determination of the specific rate constant for this step over a small temperature range gives an activation energy. About the only assumption involved is the assumption that the latter quantity has all the dimensions and quality characteristic of an energy and must therefore obey the ordinary laws of thermodynamics. The discussion that follows is equally applicable to $\Delta E^\ddagger$ and $\Delta H^\ddagger$ of activation.

For aqueous solutions, where $\Delta C_p{}^\ddagger$ may be large, from a determination of the activation energy at one temperature T_1, one can obtain the value at some other temperature T_2, the two being related as follows:

$$\Delta H^\ddagger{}_{(T_2)} = \Delta H^\ddagger{}_{(T_1)} + \Delta C_P{}^\ddagger\,(T_2 - T_1) \qquad (7)$$

It is now convenient to divide all kinetic reactions into two types, those having positive and those having negative values of $\Delta C_p{}^\ddagger$. The trivial situation of $\Delta C_p{}^\ddagger = 0$ is not of much significance except for the fact that for 50 years $\Delta C_p^\ddagger$ has almost always been assumed to be zero. In actual fact, failure to observe the temperature dependence of $\Delta H^\ddagger$ required by Eq. 7 has largely been due to $(T_2 - T_1)$ having been too small to be observable.

Those reactions having negative and, let us assume for the sake of simplicity, constant values of $\Delta C_p^\ddagger$ are of particular interest. For, as the temperature and ΔT are increased, the normally positive activation energy will decrease until it becomes zero. Above this inversion temperature, the activation energy *must* become negative if there is any meaning at all to the concept of activation energy. It also follows that a negative activation energy requires that the reaction rate *decrease* with increasing temperature above the inversion point, and that a region of retrograde kinetics is reached. Studies under way in our laboratories at Purdue are aimed at investigating this predicted inversion region, but at present there appear to be no data for testing this imporant and possibly overlooked requirement of rate theory. One important question is this: How many reactions have already entered the inversion region at room temperature and gone unrecognized through lack of understanding of this fundamental relationship?

The Supercritical Region

Detailed discussion of gaseous solutions above the critical temperature of water is beyond the scope of this article. At present, research in this area has been limited to measurements of solubility and conductance. The advantage of being able to change the density of the solvent at constant temperature is quite important, as the pioneering work of Franck (*8, 11*) has shown. At presently obtainable densities, most electrolytes are incompletely dissociated at temperatures above 400°C, but the association is not as great as might at first be thought. For example, at density of 0.4 gram per cubic centimeter and at temperature of 700°C, 0.001M potassium chloride is about 50 percent dissociated. Under the same conditions, hydrochloric acid of the same concentration is only 3 percent dissociated, and the percentage for hydrogen fluoride is still lower. By measuring the change of the dissociation constant with density, Franck was able to derive a total hydration number of $\sim$13 for $K^+ + Cl^-$ at temperatures between 400° and 750°C; this is about what one expects for the primary hydration at room temperature. Such data reinforce the statement, made above, that no significant changes in primary hydration take place at high temperatures.

It has been recognized for some time (*31*) that liquids at temperatures near the critical point develop density gradients under the influence of gravity. This is due to the "flatness" of the pressure-volume isotherm in this region—that is, $(\Delta P/\Delta d)_T$ is small. Because the viscosities near the critical region are always much lower than at lower temperatures, it becomes difficult to establish equilibrium by ordinary means. Corwin (*32*) and his co-workers reported interesting observations on the conductance of aqueous sodium chloride solutions 16 degrees above the critical point. The solution ($d = 0.02$ gram per cubic centimeter) apparently established concentration gradients which could be destroyed by agitation but then reformed. In careful measurements of conductance in water and alcohol solutions (*33*), Copeland, Benson, and their students have also observed gradient effects in the critical region, which are removed by persistent agitation of the solution. Again, these experiments point to the extreme difficulty of achieving mass and thermal equilibrium in solutions at temperatures in the critical region, particularly in solutions of relatively low density. Still, a lot of further careful work is required if understanding of the supercritical region is ever to be tied into the rest of the chemistry of aqueous solutions at high temperatures (*34*).

Summary

I have attempted to set down a broad outline of the field of high-temperature aqueous solutions. It is all too clear that much remains to be done even to fully develop the framework, let alone fill in the unknown areas. Of particular importance, and largely untouched, are the fields of inorganic synthesis, calorimetric measurements, kinetics, mixed electrolyte systems, and the critical region. I have emphasized areas which are of particular interest to me; it is to be hoped that such a bias will not prevent others from becoming convinced that this new frontier of science has great theoretical and practical potentialities.

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NEWS AND COMMENT

Money for Science: The Community Is Beginning to Hurt

There is a tendency among some scientists to equate the refusal of a grant with the persecution of Galileo. Thus, when research, like most wards of the federal treasury, must make a tithe to the Vietnam war, faculty club chatter often seems to suggest that science is going the way of Studebaker. Of course it isn't. In fact, the research community is bigger and richer than ever. But the demands of Vietnam dictate that the country cannot have guns and paté de foie gras. One consequence is that, while the research community is bigger, it is only slightly richer, and the disparity between size and support appears to be squeezing and, in some cases, stranding an indeterminate but possibly significant number of researchers.

Just what effect this is actually having on the condition and progress of American science is difficult to establish. The base line for doleful prognostication is high in the best of times. Furthermore, when it comes to specific cases, disappointed applicants usually prefer not to advertise their lack of success. Nevertheless, there are now innumerable indications of financial strains throughout the scientific community. Through two decades of training and construction programs, the federal government has created a vast population of consumers of research support, all imbued with the spirit of rising expectations. But now, because of the drain of the Vietnam war and the Johnson administration's order of priorities, apparently not enough federal money is being provided to support all their aspirations. And, as a result, some researchers are being left out altogether, while others are beginning to experience the scale of professional living normally associated with the English department.

In general, the impact is said to be greatest among young scientists seeking money for equipment and salary to undertake their first independent investigations. But there is no dearth of long-supported senior researchers who, for the first time in their postdoctoral careers, are finding it hard to get the amounts they desire to underwrite their work.

Since the scientific enterprise in this country is so vast, and the means of supporting it are so diversified among a highly balkanized array of federal programs as well as private and state sources, there is no readily attainable comprehensive assessment of what is happening. But on the basis of inquiries among scientists and administrators from some 20 large and small, public and private, institutions throughout the country, there emerges a picture that looks like this.

At virtually every institution, there is considerable concern about the adequacy of funds for maintaining existing basic research programs or for carrying through with expansion programs now under way. This does not mean, however, that laboratories are being padlocked or that existing or planned programs are tapering off. Rather, it does mean that researchers, department heads, and deans are going through a laborious process of realigning priorities and seeking new sources of support. At one major middle-Atlantic institution, the financial gap caused by the refusal of a grant renewal was partially made up by laying off two technicians, who are reported to have found satisfactory employment elsewhere. The departure of the two adds to the workload of those who remain, but the rejected grantee is still in the laboratory, more or less carrying on with his project.

At a major northeastern institution, some $70,000 was unsuccessfully sought from a federal agency for equipment for a newly arrived physical chemist. The department chairman now expects that the university will provide a good deal of the money out of its own resources and that private foundations will make up the difference. But in terms of long-term planning for the department, the experience has a bearish effect and does not encourage a continuation of the well-established practice of attracting bright young faculty members with the assurance that a federal grant will support their work.

At a small, private medical school, basic research funds are in short supply, but the school recently received a large federal contract for what is supposed to be strictly an applied research project. Nevertheless, the intricacies of bookkeeping and the time-honored