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THERMODYNAMICS OF DILUTE SOLUTIONS

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Abstract - Twenty-nine papers in the dilute solutions section of the IUPAC Conference on Chemical Thermodynamics are summarized and discussed in relation to other investigations, with references to appropriate publications. Opinions are expressed concerning various approaches to thermodynamics of dilute solutions, along with further opinions concerning desirable directions for further research in this area.

INTRODUCTION

In the nineteenth century much of what we now call the physical chemistry or thermodynamics of dilute solutions was concerned with the electrical conductivities of solutions of strong and weak electrolytes and with the colligative properties of various solutions. Later, from about 1900 through about 1940, there was a considerable focus on the kinds of thermodynamic measurements and calculations (activity coefficients, etc.) that were substantially initiated by G. N. Lewis and subsequently taught by Lewis and Randall (1). It was in the middle of this forty year period that Debye and Hückel(2) developed their theory of the activity coefficients and other properties of strong electrolytes in dilute solutions. Following this development, which was of great importance in our field, considerable efforts were made to extend the Debye-Hückel theory of the limiting law for strong electrolytes to higher concentrations and to make various measurements related to the Debye-Hückel theory.

It is gratifying to be able to report that the "classical" areas of research mentioned in the paragraph above are still alive and attracting the attentions of capable researchers, as illustrated by several papers in this section of our Conference.

Solution calorimetry is an old experimental method for investigating the thermodynamics of dilute solutions. Again, it is gratifying to be able to report that this old area of research is still the scene of substantial advances in experimental methods and in uses of results of such measurements; several papers in this section of the Conference are devoted to such subjects.

I will later be referring more specifically to a number of papers presented at this Conference that deal with the subjects mentioned in the preceding paragraphs, and will also be referring to papers published elsewhere that deal with these and other problems in the general area of dilute solutions.

The twenty-nine papers included in this section of the IUPAC Conference on Chemical Thermodynamics are a reasonably accurate reflection of present activity in the general area of investigations of thermodynamic properties of dilute solutions. It is, however, worth noting that certain kinds of investigations of dilute solutions are not represented at all in this collection of presentations. Some of these omissions are a consequence of having "only" twenty-nine papers in this section, while other omissions simply reflect the fact that certain kinds of investigations of thermodynamics of dilute solutions are not attracting much contemporary attention. It is my opinion that some of these omissions are in areas where further work is needed and therefore represent a combination of scientific obligation and scientific opportunity for individual researchers. Later I will be mentioning some kinds of investigations that I think need more attention.

Before going on with a discussion of the papers included in this section of our Conference, I want to make two related educational points. First, many of us who work in the general area of chemical thermodynamics have not done as well as we might at educating other chemists (also other scientists and engineers) about the contributions that chemical thermodynamics can make to their fields. Second, and more specifically, I suggest that we have not done very well at informing other scientists about the need for information about dilute solutions in relation to problems in other areas. To illustrate these points I cite the example (hypothetical, but realistic) of an analytical, inorganic, or organic chemist concerned with chemical equilibria in reasonably concentrated solutions of an electrolyte. It is obvious to us, but not always to these other chemists, that activities (rather than only concentrations) should be considered. Further, it is known by most thermodynamicists, but sometimes forgotten, that most methods for obtaining activities and related activity coefficients of solutes in such concentrated solutions require knowledge of dilute solutions. For example, evaluation of the needed activity or activity coefficient of solute from the vapor pressure of the solvent requires an integration of the Gibbs-Duhem equation, which involves knowlege of activities at lower concentrations into the very dilute solution range. Similarly, various electrochemical methods of obtaining useful knowledge about properties of concentrated solutions require related knowledge (standard potentials, etc.) of dilute solutions.

ACTIVITY COEFFICIENTS AND RELATED PROPERTIES

The Debye-Hückel theory is probably most often used in the form of an equation that gives the mean activity coefficient of the ions in solution as a function of the concentration of the electrolyte. Because some of us are often more interested in various other properties of strong electrolyte solutions, it is then more useful to begin with the Debye-Hückel theory in the form of an equation that expresses the Gibbs energy of dilution as a function of concentration. Differentiation of this equation with respect to temperature or pressure and combination with formulas of classical solution thermodynamics leads to useful equations for the concentration dependence of such properties as apparent and partial molar enthalpies, heat capacities, and volumes. Procedures for these calculations and some illustrations of uses of the results have been provided by Pitzer and Brewer (3).

Efforts to extend the Debye-Hückel theory from the original limiting law region of very low concentrations to higher concentrations that are generally of more interest and ultimate importance have traditionally taken what I describe as either of two paths. One approach has been to make mathematical modifications in the Debye-Hückel treatment, with these changes intended to make the result a better approximation to reality for solutions that are more concentrated than consistent with the limiting law. The other general approach has been to modify the original Debye-Hückel physical model in ways that are intended to be more realistic pictures of more or less concentrated solutions and thence make the derived equations more realistic and useful. Naturally, there is overlap of what I have described as two paths. Pitzer (4) has provided a clear review of such theoretical work through 1977 and has subsequently provided another account (5) in a useful book concerned with industrial applications of thermodynamics of aqueous solutions.

The Debye-Hückel theory of the limiting law predicts correctly that the logarithm of the mean activity coefficient and various other thermodynamic properties vary linearly with the square root of electrolyte concentration in very dilute solutions. Various modern extensions (4) of the Debye-Hückel limiting law predict more complicated dependences of thermodynamic properties on concentration at higher concentrations, with all of these reducing to the square root dependence of the limiting law at very low concentrations. Practical problems associated with all of these extensions of the Debye-Hückel limiting law into the experimentally important region of intermediate and high concentrations are that the modern theories are difficult for non-theoreticians to understand and the resulting theoretical equations are sometimes not directly useful for such problems as relating a measured electrochemical potential or enthalpy of solution or heat capacity for a relatively concentrated solution to the desired standard state (infinite dilution) property. It is my opinion that the "Pitzer theories" (4,5) are presently the most useful (in the senses indicated above) of all of the various modern approaches to electrolyte theory.

It has been known for a long time that graphs of various thermodynamic properties of electrolytes against the cube root of concentration are linear over wide ranges of concentrations. These cube root dependences have attracted the attention of theoreticians for more than fifty years, and it is worth pointing out here that such dependences are potentially useful to experimentalists who make measurements outside the concentration realm of simple application of the Debye-Hückel theory. In recent years the lattice theory approach of Bahe (6-9) has yielded theoretical equations with cube root dependences that provide accurate fits of activity coefficients, enthalpies of dilution, and partial molar volumes over impressively wide ranges of concentrations. Singh (10-12) has made use of a similar approach and in this Conference Gomez Estevez is reporting on his application of Bahe's lattice model to heat capacities of electrolyte solutions.

It is readily apparent that the various equations based on Bahe's lattice model provide accurate fits over wide ranges of concentration to various thermodynamic properties of electrolytes, all with a small use of adjustable parameters. These equations therefore have clear value as convenient means of storing and representing a lot of experimental results.

The Bahe lattice model and resulting equations that emphasize cube root dependences on concentration also have potential values as providing means for extrapolating from relatively high concentration to infinite dilution and as an attractively simple representation of physical reality for electrolyte solutions. There are, however, several difficulties with respect to these potential values.

First, and easiest to remedy, the original approach by Bahe (6) does not adequately distinguish between total and partial molar Gibbs energies; doing this correctly leads to a numerical change in his Madelung-like coefficient of the cube root of concentration. Unfortunately, some unpublished calculations (13) show that this change diminishes the quality of fit of theoretical equations to some experimental results.

Another difficulty with Bahe's lattice model and resulting theoretical equations is that the equations do not reduce to the Debye-Hückel limiting law for very dilute solutions. Use of the Bahe equations therefore leads to different infinite dilution properties than are obtained by way of similar use of the Debye-Hückel theory. This latter objection can be circumvented by using the Bahe equations to extrapolate from high concentrations to some selected low concentration, with further extrapolation from this selected low concentration to infinite dilution being done with an appropriate equation based on the Debye-Hückel theory.

Part of the appeal of the Bahe approach is that the lattice model is attractively simple and leads to relatively uncomplicated equations that are also relatively simple to use for several purposes. It is unnecessary that there be permanent or even long term lattice-like arrangement of the ions in solution for a lattice model to be appropriately realistic and thence useful. It is, however, necessary that the instantaneous locations of most of the ions in such a solution be in accord with a lattice-like arrangement. Consequences of this requirement can be evaluated by way of calculations of concentrations of lattice "defects" by the traditional methods of solid state physics (14), using interionic distances appropriate to the concentration of the ions in the solution under consideration along with the dielectric constant of the solvent, typically water. Such calculations show (13) that the concentrations of defects are too large for a lattice model to be realistic at concentrations of aqueous electrolyte less than one or two molar, which includes a substantial part of the concentration range of empirical application of the Bahe approach.

In spite of my criticisms of the Bahe lattice model and its subsequent applications, it must be admitted that correlations of various thermodynamic properties with the cube root of concentration are empirically well established and deserve theoretical attention.

Another approach to extension of the Debye-Hückel theory has been taken by Chipara, Georgescu, Teodorescu, and Chipara, who have considered two charges located at r_1 and r_2 and the screening effect of ions located between r_1 and

r_2. One result of their analysis is a general expression for the dependence of charge density on r, as reported in this Conference.

Turning now from theoretical considerations to various recent experimental investigations, I first mention the work of Klofutar and Paljk, who report at this Conference the results of their measurements of freezing points of solutions of n-dodecylammonium nitrate in benzene and the derived osmotic and activity coefficients. These workers have also measured enthalpies of dilution and have interpreted their results in terms of solute association. In interesting contrast with this use of the classical freezing point depression method, Oweimreen has made use of the modern gas-liquid chromatographic method for obtaining partition and activity coefficients of alkane solutes in squalane + di-n-nonyl phthalate solutions, with results reported at this Conference. Shcherbina, Shcherbina, and Grushova have also used a chromatographic method for obtaining distribution and activity coefficients for n-hexane in polar solvents, with results used to estimate dissociation constants and related properties, as reported in another presentation in this Conference.

THERMAL AND VOLUMETRIC PROPERTIES

Thermal and volumetric properties of solutions are important because of their relationships to the temperature and pressure dependences of various thermodynamic properties. For example, the van't Hoff equation

$$(\partial \ln K/\partial T)_p = \Delta H^o/RT^2 \tag{1}$$

relates the temperature dependence of the equilibrium constant for a chemical reaction to the standard enthalpy change for that same reaction, while the Kirchhoff equation

$$(\partial \Delta H^o/\partial T)_p = \Delta C_p^o \tag{2}$$

relates the temperature dependence of the enthalpy change for a chemical reaction to the standard change in heat capacity for that same reaction. We also have the equation

$$(\partial \ln K/\partial P)_T = -\Delta V^o/RT \tag{3}$$

that relates the pressure dependence of an equilibrium constant to the standard change in volume for that same reaction. Finally, there is

$$(\partial \Delta V^o/\partial P)_T = -\Delta \kappa^o \tag{4}$$

that relates the pressure dependence of the change in volume to the corresponding change in isothermal compressibility.

One application of equation (1) is to calculate ΔH^o from the first derivative of ln K with respect to temperature. A second differentiation with respect to temperature in combination with equation (2) then leads to ΔC_p^o. Still further differentiations can (at least in principle) lead to information about the temperature dependence of ΔC_p^o. It is also possible to go the other way around in these calculations; use calorimetrically determined values of ΔC_p^o and ΔH^o to calculate the temperature dependence of an equilibrium constant.

As McGlashan (15) has recently written about thermodynamic equations, "They are useful because some quantities are easier to measure than others." I add to McGlashan's important statement the following: the accuracy with which a thermodynamic equation can be used "in one direction" is frequently better than in the other.

Until recently, it was generally easier to measure K and ΔH^o at several temperatures than to make the measurements required to yield ΔC_p^o appropriate to the usual infinite dilution standard state. Now, however, following development of modern flow calorimeters by Picker (16) and others (17,18), it has sometimes become easier to measure the appropriate heat capacities than to measure K and ΔH^o at several temperatures. It is also appropriate to consider here the point made above as a supplement to McGlashan's dictum about ease of measurement; differentiation leads to a "magnification" of uncertainties so that greater accuracy is often obtainable by way of integration of equations such as (1) and (2) than by way of differentiation.

Considerations similar to those expressed above also apply in connection with the pressure dependence of equilibrium constants and corresponding changes in volume and compressibility. It is easier for many investigators of dilute solutions to make appropriate density measurements leading to partial molar volumes, as reviewed by Millero (19), than to measure equilibrium constants at several pressures. Reasonably accurate and reliable instruments for such measurements are now available commercially (Sodev, Anton Paar, etc.). An accurate, inexpensive, and somewhat tedious dilatometric method (20) has been improved by Bottomley, Glossop, and Staunton (21). It is also of interest to note here that modern sound velocity methods lead to accurate adiabatic compressibilities; calculation of the often more useful isothermal compressibilities from these results requires (22) knowledge of C_p, which is another reason for making such calorimetric measurements.

In this Conference we have a report from Jolicoeur, Alary, Simard, Dumont, and Lemelin on a new flow method, using apparatus designed by Picker, for obtaining thermal expansivities as well as the heat capacities and densities that are commonly derived from such measurements. It is my opinion that specific considerations of thermal expansivities and general considerations of effects of temperature on partial molar volumes show more promise (23, 24) for investigations of "structures" of solutions than is commonly recognized; further measurements and theoretical analyses are recommended.

As part of his substantial program of investigation of volumetric and other properties of aqueous solutions, Høiland has obtained volume changes associated with complex formation between several anions and both α- and β-cyclodextrin by two methods; (i) equilibrium constants determined at several pressures and analyzed according to equation (3), and (ii) density measurements leading to partial molar volumes. Methods of making these measurements and subsequent calculational procedures are reported at this Conference.

At this Conference we also have a report from Burchfield, Noll, and Good on the results of their investigations of volumetric and thermal properties of aqueous systems that may be useful in connection with enhanced recovery of oil. More specifically, they have made density measurements leading to partial molar volumes, measured enthalpies of dilution leading to relative partial molar enthalpies and thence to enthalpies of micellization, and made heat capacity measurements leading to partial molar heat capacities and thence to ΔC_p^o values for micellization. This investigation by Burchfield, Noll, and Good provides several illustrations of kinds of investigations that are needed in future studies of surfactant solutions, which present interesting problems in pure science and are of considerable practical importance in various areas of applied science. Desnoyers, DeLisi, and Perron (25) have provided a useful review of thermodynamic (especially thermal) properties of aqueous micellar systems. There is also a recent discussion (26) of thermodynamics of micelle formation, with particular emphasis on the temperature dependence of the critical micelle concentration.

For many years researchers at Brigham Young University have been devising and carrying out imaginative applications of titration calorimetry, with many of these investigations involving simultaneous evaluation of an equilibrium constant and the corresponding enthalpy of reaction. At this Conference we have a report from Eatough, Lewis, Rehfeld, and Hansen on their calorimetric investigations of binding of surfactants to clays; results have led to evaluation of adsorption isotherms and to enthalpies of adsorption. It is my opinion that similar calorimetric investigations of other processes involving adsorption from solution will also be rewarding.

Saluja is reporting to this Conference on his thermochemical investigations related to problems in safe disposal of radioactive wastes, with particular emphasis on heat capacities of aqueous solutions and the thermodynamics of adsorption of fission products on mineral surfaces. His research program includes application of the Picker calorimeter to determination of heat capacities of solutions and thence partial molar heat capacities of solutes over a range of temperature. In connection with his work on adsorption (ion exchange) on minerals, I point out that a recent calorimetric investigation (27) has led to cation exchange capacities, equilibrium constants, and enthalpies for some exchange reactions on clays; principles involved in these latter determinations are similar to those used by Eatough and colleagues in their investigation summarized in the preceding paragraph.

Jasra and Ahluwalia are reporting to this Conference on their investigations of thermal and volumetric properties of several saccharides in water. They have measured enthalpies of dissolving their saccharides at two temperatures, from which they have calculated ΔC_p^o for the dissolution reaction by way of equation (2). They have also used a Picker flow calorimeter and an Anton Paar densimeter for measuring heat capacities and densities of saccharide solutions. Results are considered in relation to various additivity schemes and also structural considerations. Investigations by Jasra and Ahluwalia in combination with an earlier investigation of various heterocyclic solutes (28) and an impressively wide-ranging investigation by Cabani, Gianni, Mollica, and Lepori (29) are gradually leading to a situation where group contribution schemes will permit usefully accurate estimates of partial molar heat capacities and volumes of aqueous solutions of non-electrolytes.

At this Conference we also have a report from Della Gatta, Rozio, and Venturello concerning their measurements of the enthalpies of solution of various aliphatic aldehydes in n-heptane and in water, with results being interpreted in terms of contributions from the carbonyl group and methylene groups. In the paragraph above, attention was directed to some efforts to correlate and ultimately predict partial molar heat capacities and volumes of aqueous non-electrolytes; here it is noted that Cabani and colleagues (29) were also concerned with Gibbs energies and enthalpies.

It is appropriate here to call attention to two recent papers (30,31) by French and Criss. In the first paper (30) they apply the concept of group additivity to the standard partial molar heat capacities and volumes of polar solutes in methanol and in the second paper (31) they consider more general questions of effects of solvent on heat capacities and volumes of non-electrolyte solutes.

Vlasenko, Zhigunova, Solov'eva, Vorob'ev, and Frolov are reporting to this Conference the results of their calorimetric measurements of enthalpies of mixing of several aqueous electrolytes ($CoSO_4$, $MgCl_2$, $NiSO_4$, LiCl, and CsCl) in various combinations and at several molalities in the range 283 to 313 K. These researchers have made a start toward interpreting their results in terms of hydration of the various ions and related solution "structure" effects. On the experimental side, it will also be interesting to compare the ΔC_p values for mixing obtained by application of equation (2) to these investigators' enthalpies of mixing with results of direct heat capacity measurements.

It is appropriate to end this section of my comments by re-emphasizing the central role of measurements in thermodynamics and calling attention to the work of Benoist and Pithon. These workers are reporting to this Conference on the design (Calvet principle) and use of the Setaram C 80 calorimeter.

AQUEOUS ACIDS AND BASES

Investigations of weak acids and bases in dilute aqueous solutions have attracted the attention of many leading researchers in physical chemistry and chemical thermodynamics over the last century; an incomplete alphabetical list of those who have made important contributions includes Arrhenius, Bates, Bell, Bjerrum, Bronsted, Eigen, Everett, Fuoss, Guggenheim, Gurney, Hammett, Harned, Ives, Kirkwood, MacInnes, Noyes, Ostwald, Pitzer, Robinson, and Shedlovsky. In this Conference we have three excellent papers that deal with this subject.

Roy, Gibbons, Buechter, and Faszholz report the results of their determinations of the second dissociation constants of "BES" (an organic acid that is useful as a buffer) in various water + t-butanol solvent mixtures from

278.15 to 308.15 K. Also, Strong and Blubaugh report the results of their determinations of the ionization constants of several methyl-substituted benzoic acids in aqueous solution over the temperature range 0 to 100°C.

There are several interesting parallels in the investigations described by Roy and by Strong. The first-named group has obtained their equilibrium constants by way of electromotive force measurements on cells without liquid junction, using hydrogen and silver + silver bromide electrodes. The general principles of their method are derived from pioneering studies by Harned and Bates. Strong and Blubaugh have also used a method of considerable historical importance; more specifically, they have used precision measurements of electrical conductances to lead to their equilibrium constants. In this case the experimental procedures used follow those developed by Ives, MacInnes, and Shedlovsky, with subsequent calculations done according to a method developed by Fuoss. Accuracies of results from both groups are sufficient to justify calculations of both ΔH^o and ΔC_p^o for the various reactions investigated. Finally, it should be noted that Professors Roy, Gibbons, and Strong have accomplished the research reported here and also the research reported in an impressive number of earlier papers in collaboration with undergraduate students.

In this section of our Conference we also have a report from Cabani, Matteoli, and Tiné concerning their investigations of the compressibility changes associated with adding $H^+(aq)$ to aqueous organic bases (aliphatic nitrogen compounds). The present results are a useful addition to earlier results from the same group in Pisa, where Cabani and colleagues have been carrying out a comprehensive series of investigations of the thermodynamic properties of organic acids and bases in aqueous solution. Most of their investigations have been concerned with thermal and volumetric properties, making use of methods discussed or cited in the previous section, with results that are useful in connection with equations (1-4).

Although the study of thermodynamics of acids and bases in water (and other solvents) is an old subject, the three investigations cited above are consistent with my opinion that this is an important area for still further work. Most of the equilibrium constants for acid-base reactions in aqueous solution that we want to know at about 25°C are either known or can be obtained by methods that are now readily available. On the other hand, we have little or no information about the effects of temperature and pressure on many of these equilibria. Information of these kinds is needed in fields as diverse as boiler water chemistry, ocean water chemistry, and hydrometallurgy. Although water is correctly thought of as the most important single solvent for acid-base systems involving ions, there are good reasons, especially in certain areas of organic chemistry and biochemistry, for wanting thermodynamic data for acid-base equilibria in water + organic solvent systems and in totally non-aqueous systems. In the following paragraphs I cite some recent papers that illustrate some methods that are likely to prove useful in investigations of thermodynamics of acid-base reactions in solutions.

Investigations of acid-base equilibria in aqueous solutions at high temperatures and/or high pressures are experimentally difficult, which is one good reason for obtaining such information indirectly by way of possibly easier calorimetric or volumetric measurements leading to ΔH^o, ΔC_p^o, ΔV^o, and $\Delta \kappa^o$ values to be used in equations (1-4). All the same, direct determinations of such equilibrium constants at high temperatures and/or high pressures are needed. Some good examples of such investigations are the following.

Hamann and colleagues have carried out many excellent investigations on the effects of pressure on acid-base equilibria in solution, as illustrated in a paper by Hamann and Linton (32) in which references to earlier work are given. Bullock and Irving (33,34) have developed and applied a spectrophotometric method for investigating acid-base equilibria in aqueous solutions at high temperatures. This method may prove especially useful for solutes that are too slightly soluble to permit investigation by other methods. Read (35) has illustrated the application of a conductance method in his investigation of ionization of aqueous benzoic acid up to 2000 bar and 250°C.

An example of investigation of temperature and pressure effects by way of calorimetric and volumetric measurements is provided by recent work (36) on the acid dissociation of $HSO_3^-(aq)$ in which values of ΔH^o, ΔC_p^o, and ΔV^o were obtained. I also call attention to a recent paper by Peiper and Pitzer (37) in which they report on their detailed analysis of the thermodynamic properties of various aqueous solutions in the carbonate system; this paper is an excellent example of various thermodynamic calculations, with specific applications to both the first and second ionizations of carbonic acid. Another investigation of interest in this connection concerns calorimetric and densimetric determinations of ΔC_p^o and ΔV^o for acid dissociation of aqueous bicarbonate and bisulfate ions and all three dissociations of aqueous phosphoric acid (38). These latter papers (36-38) have all included consideration of the reaction or equilibrium relaxation contribution to heat capacities, partly following procedures previously reported (39).

It is my opinion that attempts to understand and ultimately to make predictions about acid-base equilibria in solution must go beyond consideration of equilibrium constants or related ΔG^o values referring to one solvent (usually water) at one temperature (usually 298 K) and one pressure (usually 1 atm). This means that it is also necessary to consider other thermodynamic properties, such as ΔH^o, ΔS^o, ΔV^o, and possibly also ΔC_p^o and $\Delta \kappa^o$. Long ago these general considerations in combination with specific consideration of the thermodynamics of acid ionization of aqueous phenol and isomeric nitrophenols (40) led to formulation (41) of explicit expressions for enthalpies and entropies of such reactions as sums of "internal or intrinsic" and "external or environmental" contributions. Subsequent work, has led to application of this approach to theoretical analysis of the Hammett equation, the temperature dependence of solvent effects, isotope effects, and the relationship of acidities in solution to acidities in the gas phase (42-47). It is pleasing to report that the general ideas and methods expounded in these papers (40-47) have been accepted by others and are proving useful in various ways. I call attention to a selected list (48-57) of papers by other investigators who have used, extended, or criticized the ideas and methods (40-47) based on explicit separation of "internal" and "environmental" contributions to thermodynamic properties. It is my opinion that further investigations, both experimental and theoretical, that focus on solvent effects, ΔC_p^o, ΔV^o, and relationships of acidities-basicities in solution to those in the gas phase are likely to prove especially useful.

Much as investigations of dilute solutions can provide information that is useful in other areas of science, so can certain investigations in the gas phase provide information that is useful in considerations of thermodynamics of acid-base reactions in solution. Measurements in the gas phase (no solvent) yield direct information about what I have called "internal or intrinsic" contributions to the various thermodynamic properties associated with acid-base reactions and can therefore be combined with results from measurements on solutions to obtain information about solvent or "environmental" effects. In this connection I cite an excellent review article by Kebarle (58) and a few more recent publications (58-64).

SOLVENTS AND SOLVATION

Such eminent scientists as M. Born, W. M. Latimer, H. S. Frank, and others mentioned elsewhere in this article have long been concerned with efforts to gain knowledge and understanding about the role of solvents in the chemistry of solutions; such considerations of interest to us include hydration enthalpies, thermodynamics of transfer of solutes from one solvent to another, etc. Useful books by Marcus (65) and Conway (66) provide discussions of these and other subjects that are relevant to this section of our Conference.

At this Conference we have a report from Marcus on his considerations of structure-making and -breaking by ions in aqueous solutions. His approach involves considerations of entropies, activation energies associated with rates of exchange of water molecules from the hydration sphere, viscosities, and the ratios of solubilities in $D_2O(liq)$ and $H_2O(liq)$. Consideration of single-ion effects is via the commonly used tetraphenylarsonium/tetraphenylborate assumption.

In another contribution to this Conference, Bloemendal and Somsen have asked the provocative question: "How unique is water as solvent?" They have worked on this interesting and important question by way of calorimetric measurements of enthalpies of dilution of a number of alkyl-substituted amides in N,N-dimethylformamide and have compared their results with those from similar measurements on aqueous solutions. These comparisons have involved considerations of interaction coefficients of the kinds introduced and used by McMillan and Mayer and by Savage and Wood.

Kundu and his colleagues have made many measurements, mostly involving electrochemical cells, that have led to thermodynamic properties of solutes in various pure and mixed solvents. At this Conference we have a related paper by Kundu, Bose, Das, and Datta on their considerations of standard state entropies of transfer of various solutes from various solvents to other solvents, all with a view toward gaining some knowledge of solvation effects and "structures" of solutions.

A group in the Universita di Napoli has been investigating the association of organic dyes in both aqueous and non-aqueous solutions. In this Conference we have a report from Vitagliano, Ortona, Costantino, and Sartorio, who have made spectrophotometric measurements leading to equilibrium constants for the dimerization of acridine orange at several temperatures and thence used equation (1) for calculations of enthalpies of the same reaction. We also have a report from Ortona, Elia, Vitagliano, Barone, and Costantino about their calorimetric measurements of enthalpies of dilution and derived enthalpies of dimerization of acridine in the same solvents. In these two contributions from Naples we have comparisons of calorimetric enthalpies with those derived by way of equation (1) and also some discussion of solvent effects on the dimerization reaction. Some of the methods and principles involved in this research are similar to those also described in this Conference by Burchfield, Noll, and Good and by Klofutar and Paljk.

We also have two papers from Moscow on enthalpies of solution of inorganic salts in mixed solvent systems. Vorob'ev, Monayenkova, and Alekseyev report on their measurements of enthalpies of solution of $MgCl_2$, $CaCl_2$, $SrCl_2$, and $BaCl_2$ in water + dimethylsulfoxide mixtures while Vorob'ev, Kabanov, and Privalova report on their measurements of enthalpies of solution of KI in N-methylformamide + N,N-dimethylformamide + water mixtures. Results of both sets of investigations are discussed in relation to solvent effects.

A common problem in relating the results of thermodynamic measurements on solutions of ions to various theories or models of ion-solvent interaction involves dividing the experimental thermodynamic property of cation plus anion (such as enthalpy of hydration) between cation and anion. Such division is either unnecessary or can be handled arbitrarily (commonly done by way of some specification regarding H^+) for purely thermodynamic calculations; ALL such calculations can be done without any reference to absolute single-ion properties. Because all of the calculations of classical chemical thermodynamics can be done without any reference to single-ion properties, thermodynamics alone does not give us even a clue as to how such divisions should be done. It is therefore necessary to introduce at least one extra-thermodynamic assumption. Although the results of all such divisions are therefore outside the realm of purely classical thermodynamics, it is clear from papers already cited in this section that there are many improvements in our microscopic knowledge of solutions that might accrue from consideration of various single-ion properties.

Among many scientists who have considered the problem referred to in the paragraph above are Khodakovsky and Shapkin, who report to this Conference on their mathematical analysis, which can be regarded as a continuation of an earlier investigation (67) by these same researchers and their colleagues at the Vernadsky Institute of Geochemistry and Analytical Chemistry in Moscow.

The literature on the general subject referred to above is so large that it is impossible to compile any representative short list of leading references. Most of these papers that I do not list are concerned with one or another of three thermodynamic properties: G, H, and S. Partly because of my personal interests and partly because both experimental and theoretical investigations of heat capacities are becoming more numerous, I call specific attention to two recent attempts (68, 69) to establish an ionic scale for aqueous heat capacities.

NON-ELECTROLYTE SOLUTIONS

Gallardo, Urieta, and Gutierrez Losa report to this Conference the results of their measurements of solubilities of 14 non-polar gases in dioxane at temperatures from 285.15 to 303.15 K. These results have led to Gibbs energies, enthalpies, and entropies of solution of each gas in dioxane. Analysis of these results in terms of ideas previously developed by Hildebrand and in terms of scaled particle theory has led to recognition of the unusual properties of CO_2 and to calculation of various pair -potential parameters.

For many years Benson and his colleagues at the National Research Council in Canada have been making very accurate measurements of several thermodynamic properties of many mixtures of organic liquids. At this Conference we have a report from Kimura, Kumaran, and Benson on their recent measurements leading to excess molar volumes and isentropic compressibilities for hexan-1-ol + isomers of n-hexane at 298.15 K. Their volumes were obtained by the dilution dilatometric method, while their compressibilities are from speeds of sound based on the pulse-echo-overlap method. Particularly detailed measurements on solutions with very small mole fractions of hexan-1-ol showed that properties of these dilute solutions can not be predicted in any simple way from knowledge of similar properties at higher concentrations. It will later be interesting to see to what extent the properties of concentrated solutions can be predicted from the properties of dilute solutions.

P.P. Singh is reporting to this Conference on his recent extension of earlier applications (70) of graph theory to analysis and prediction of the thermodynamic properties of liquid mixtures. In the present report he is concerned with prediction of enthalpies and volumes of components of liquid mixtures at very low mole fractions. Agreement between predicted and experimental values is impressive for many of the systems under consideration.

All papers previously cited here have been concerned with <u>liquid</u> solutions, but our "dilute solutions" subject properly includes <u>solid</u> solutions and also gaseous mixtures in which the mole fraction of one component is very small. We have no papers in this section of our Conference that deal with such gaseous mixtures, but we do have a paper from Belaadi, Houriez, Schuffenecker, and Balesdent concerning their investigation of the thermodynamic properties of solid solutions of C_{18} to C_{24} n-paraffins. More specifically, enthalpies of mixing of these solid n-paraffins were evaluated from calorimetrically measured enthalpies of solution in liquid ethylbenzene.

CONCLUDING REMARKS

In these brief concluding remarks I will supplement my earlier comments on kinds of research on dilute solutions that I think are needed or are likely to prove especially interesting.

It is my opinion that investigations of aqueous solutions at temperatures above 100°C will be increasingly valuable in both pure and applied science. I also suggest that increased attention to heat capacities of aqueous solutions at all temperatures will be rewarding, partly because the results of heat capacity measurements at "ordinary" temperatures can be used in calculation of other thermodynamic properties at "high" temperatures.

Recent developments in analytical chemistry now make it possible to carry out needed investigations of solubilities in water of slightly soluble high molecular weight organic substances.

I suggest that there is need for further thermodynamic investigations in the general area of colloid chemistry, and add the specific suggestion that investigations of the thermodynamics of micelle formation, solubilization, and adsorption from solution may be especially rewarding.

In the area of non-electrolyte liquid mixtures I suggest that further investigations of binary systems in which there are relatively strong and specific interactions (chloroform + triethylamine is a commonly studied system) should attract the attentions of thermodynamicists interested in dilute solutions. The "ideal associated solution" model has proven to be a useful basis for representing the properties of such solutions, but it should also be recognized that this model requires further testing. I believe that one of the best approaches to elucidating the limits of reasonable applicability of this model is by way of investigations of the thermal properties of appropriate dilute solutions.

Finally, I should like to close on a note that is partly personal and partly pedagogical. A few years ago I collected a *very long* list of references to papers in which equation (1) was used incorrectly; all of these incorrect uses of equation (1) involved equilibrium constants that were expressed in terms of molarities (or activities with a molar standard state). Correction or elimination of this *very* common error is easy, as recently explained (71).

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