

SOLUTIONS OF ELECTROLYTES¹

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It has become customary for authors of "Solutions of Electrolytes" to stress the subjects in which they are especially interested. This year the subjects receiving special attention are the degrees of dissociation of strong electrolytes, the thermodynamics and structures of solutions of strong electrolytes, and the properties of solutions of mixtures of electrolytes. Some other topics in which conspicuous progress has been made during recent months are also discussed in considerable detail.

STRUCTURE AND PROPERTIES OF WATER

Frank & Quist (1) extended Pauling's model for liquid water and successfully calculated the P - V - T properties of water. The model represents water as having an ice-like framework, or structure with numerous holes, in which many of the water molecules exist in unbonded states.

Experiments with cold neutrons are in accord with the view that liquid water behaves in many respects as a solid. Singwi & Sjölander (2) calculated the differential scattering cross section for very slow neutrons in liquid water. They assumed the Debye temperature, θ , to be 135°C. Their results led Joshi (3) to calculate θ by a method often used for the evaluation of θ of solids. The result, 155°K, agrees well with the θ employed in the neutron study.

Ginell (4) deduced from the Tait equation that an increase of temperature (pressure constant) causes a decrease in the association of water and an increase in the volume of holes in the liquid and in the number of particles. As pressure is increased (temperature constant) the volume of holes decreases, the degree of association decreases, and the number of particles increases.

Wada (5) used a simple model for water to calculate many physical properties. He pictured a mixture of water in two states, one having an ice-like structure and the other a closely packed structure. The equilibrium between the two states he treated as a function of temperature and by "trial and error" estimated the mole fraction of water in the "icy" state to be 0.2 at 100°C. That estimate was the one basic assumption underlying his interesting calculations.

The fast proton transfers accounting for the anomalous mobilities of the

¹ The literature available to us on the first of December 1961 has been reviewed.

hydrogen and hydroxyl ion in water were measured by Meiboom using nuclear magnetic resonance (6). To account for the NMR spectrum attributable to protons in hydroxyl ions and in hydronium ions, Musher (7) proposed a model locating the ionic charges of the hydroxyl and hydronium ions on the oxygen atom, i.e., OH^- is treated as a complex of a hydrogen atom with an O^- ion, H_3O^+ as a complex of three H atoms with an O^+ ion, and the water molecule as a complex of two H atoms with an O^0 atom. The proton resonance shifts occurring when alkali halides are dissolved in water were measured by Fabricand & Goldberg (8). For dilute solutions of various solutes the shift is proportional to the concentration; for a given concentration the shifts are proportional to the ionic crystal radii. NMR has been used by Hindman (9) to determine "effective" hydration numbers.

Busing & Hornig (10) and Schultz & Hornig (11) studied the effects of halide ions and hydroxide ions on the shapes and intensities of spectral lines resulting from the stretching and bending vibrations of water. Walrafen (12) extended this study to the low-frequency region of the spectrum of water and re-examined the high-frequency region. These authors found that halide anions rather than cations produce significant changes in the intensities of certain lines. The larger, and hence the more polarizable, anions produce the larger effects. Hydrogen bonds are broken by the electrolyte, and weaker bonds (to halide ions) are formed. The 175 cm^{-1} band, related to intermolecular structure, is not affected so much by F^- , OH^- , NO_3^- or SO_4^{2-} , presumably because these anions are bonded to water in the same manner as water is bonded to itself. The variations of the intensities of certain Raman lines with concentration suggest that anions possess small average hydration numbers (as cations do) which remain constant to high concentrations.

Skarre & Tereshkevich (13) concluded from oxygen exchange studies in nitrates of the Group II metals that the hydration number of the cation determines the effect of the cation on the anion.

The dielectric constant of water was determined by Owen, Miller, Milner & Cogan (14) at 100 bar intervals between 1 and 1000 bars and at 5°C intervals between 0° and 70°C . Both the pressure dependence and the temperature dependence of the dielectric constant agree with the results of Lees (15) but there are significant differences from the values reported by Malmberg & Maryott (16).

From a comparison of the infrared spectra of water and of aqueous solutions of acids and alkali hydroxides, Ackermann (17) concluded that hydronium ions and hydroxide ions have the same effect on the water structure. This supports a previous suggestion (18) that the hydroxide ion is hydrated, possibly by a larger number of water molecules than the hydrogen ion.

TRANSPORT PROCESSES

The present status of conductance theory has been nicely summarized by Stokes (19). A large number of experiments have been designed specifically to test existing theory, particularly the extended Fuoss-Onsager theory

(20, 21). Stokes redetermined the conductance of hydrochloric acid up to 1 *N* and found that whereas the Fuoss-Onsager equation fits the data only up to about 0.004 *N*, the equation of Pitts (22) holds up to 0.02 *N*. Precise conductance measurements for the perchlorates of eight univalent ions and potassium iodide dissolved in dimethylformamide are in excellent accord with the Fuoss-Onsager equation [Prue & Sherrington (23)]. These authors also discussed ion solvation in a number of solvents. The Fuoss-Onsager theory has been shown to be successful for electrolytes of high-charge type in water [Atkinson *et al.* (24); Hallada & Atkinson (25); Yokoi & Atkinson (26)], and electrolytes dissolved in dioxane-water mixtures, which cover the range of dielectric constant 78.54 to 12.74. [Lind & Fuoss (27, 28)]

Conductance studies of salts of several cyanocarbon acids were undertaken by Lind & Fuoss (29) to determine the effect of size and dielectric constant on ion association. These salts act as highly-dissociated electrolytes in water and acetonitrile but show considerable association in ethylene dichloride. The estimation of dissociation constants of electrolytes from conductivity measurements has been reviewed by Wirth (30) and a new function proposed. An attempt to obtain association constants from high field conductances has been made by Patterson & Freitag (31). Solutions of uranyl nitrate and perchlorate exhibit a negative Wien effect at 25°C and 65°C which is thought to be due to complex formation. [Bailey *et al.* (32)].

An attempt has been made by Brummer & Hills (33, 34) to describe Λ_i^0 by means of transition state theory rather than empirical adjustment of the Walden rule. Experimental values of the limiting conductance and values obtained from a modified form of Walden's rule were compared by Berns & Fuoss (35) and found to agree within about 1 per cent.

Relationships between size of solvent molecules, size of solute ions, and conductance were studied by French & Tomlinson (36); those between conductivity of water and its viscosity by Kalyakin (37); and those between conductivity and temperature of aqueous solutions by Gorbachev & Kondrat'ev (38).

The importance of thorough mixing to avoid errors in conductance measurements due to the Soret effect was pointed out by Stokes (39). Errors due to the "shaking effect" were discussed by Prue & Sherrington (23). Improvements in the design of conductivity cells [Mysels (40)] and apparatus for conductivity measurements at high temperatures [Kondrat'ev & Gorbachev (41)] were described.

Conductance results have been reported for CuCl_2 and Na_2SO_4 at high concentrations (42), for iron group chlorides dissolved in methanol (43), tin chlorides (44), borohydride ion (45), cyanocarbon salts for which the charge on the anion is highly delocalized (46), salts dissolved in ethanolamine (47) and for some organic solutes dissolved in HF (48). The HF solutions exhibit surprisingly high conductance.

The effect of dielectric relaxation on ionic motion has been treated theoretically by Boyd (49). A method has been proposed by Pearson &

Munson (50) for the determination of ionic mobilities from measurement of the resistance change during voltage pulses through a cell containing two electrolytes separated by a boundary.

Transport numbers have been reported for HCl up to 14.4 m (51) and for LiCl and LiI in solvents of dielectric constant 10.0 and 5.75 (52). Transference numbers of LiCl (53), KCl (54), and NaCl (55) in water and water-ethanol solvents have been measured in the presence of an inert reference substance to study solvation phenomena. A comparison of transference number, equivalent conductance, and dissociation constant of some 2-1 electrolytes was made by Goldenberg & Amis (56).

RELATIVELY STRONG ELECTROLYTES

It has been known for about two decades that the transference number of zinc ion in dilute aqueous zinc bromide solution falls slowly until the molality nears unity, passes through a point of inflection, and then drops rapidly as the concentration is further increased [Parton & Mitchell (57)]. It continues to decrease, passing through zero a little before the molality reaches 3 mole kg^{-1} of H_2O , and then drops to a large negative value (-0.56) as the molality reaches 10 mole kg^{-1} . The cation transference number of ZnCl_2 solutions [Harris & Parton (58)] and of ZnI_2 solutions [Stokes & Levien (59)] behaves similarly. On the other hand, the cation transference number of $\text{Zn}(\text{ClO}_4)_2$ [Stokes & Levien (60)], CaCl_2 and many other salts of the 1-2 and 2-1 charge types do not exhibit similar complexities. If the explanation of these highly variable transference numbers is a chemical one, it seems that zinc in zinc halide solutions must exist in at least two molecular species other than the simple doubly charged (hydrated) cation.

Yellin & Plane (61) have now applied the modern techniques of high-resolution photoelectric Raman spectroscopy to the development of an explanation for the behavior of aqueous zinc bromide solutions. They measured the intensities of Raman lines as they varied both the concentration of the cation and the ratio of the concentrations of the anion to that of the cation. They were able to demonstrate effectively that there are at least three complex species containing zinc and recognized the possibility that a fourth might exist. A reasonable interpretation of their data indicates the presence of the molecular species, ZnBr^+ , ZnBr_2 , and $\text{Zn}(\text{Br})_4^{2-}$. They proceeded also to determine approximate values of the respective equilibrium constants.

A similar investigation of aqueous solutions of CdBr_2 led clearly to the conclusion that at least two cadmium-bearing species (other than Cd^{++}) exist. Because the stability of the CdBr_4^{2-} is so great, however, it overshadows the manifestations of the other species.

The hydrogen ion concentration in acid solutions was evaluated by Högfeldt (62), using the Hammett acidity function. Tentative values for the degree of dissociation of HCl and HBr, and pK values for HF, CH_2ClCOOH , and CHCl_2COOH were estimated.

Bjerrum's equation (63), although satisfactorily describing the variation of equilibrium constants with dielectric constant, was found to be unsatis-

factory for the prediction of the temperature dependence of K in media of low dielectric constant [Ryzhkov & Sukhotin (64)]. A theory relating the dielectric constant of solutions to concentration fluctuations was proposed [Shakhparonov (65)].

Effects of environment on the extinction coefficient of an ion or other molecular species were studied by Hope, Otter & Prue (66). When corrections are not made for these effects, errors in the estimation of dissociation constants result. These may be especially troublesome for large dissociation constants.

A study of the effect of temperature on the ultraviolet spectra of solvated anions led Maruyama *et al.* (67) to the conclusion that the shift of the spectrum to longer wavelengths with increasing temperature is a result of the increase of ionic radii of the cavity.

New evidence for the existence of the trihydrated hydronium ion, $\text{H}_3\text{O}(\text{H}_2\text{O})_3^+$, was obtained from solvent extraction studies of strong acids [Tuck & Diamond (68)]

Kido & Fernelius (69) inferred that the solvation of the proton and hydroxide ion in dioxane-water mixtures, varying from 0 to 75 volume per cent dioxane, is essentially identical with the solvation of these ions in pure water, since heats of neutralization show only a 2.4 per cent variation.

HYDROLYSIS OF IONS

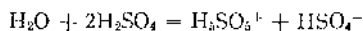
Conventional methods used in the investigation of hydrolysis of metal ions may succeed in revealing the number of OH^- units withdrawn from a solution by each metal ion without affording information concerning the molecular weight of the species formed or the magnitude of the charge carried by each molecular unit of the new species. The "critical coagulation concentration" characteristic of certain colloid materials such as AgBr or AgI solution varies very rapidly with the charge on the ion which, when adsorbed by the sol, causes it to precipitate. Systematic time-turbidity measurements can be used to determine the "critical coagulation concentration" and, hence, the charge on the molecules of the species produced by hydrolysis [Matijević, Mathai, Ottewill, & Kerker (70)]. A study of the hydrolysis of Al^{3+} in aqueous solution of pH 4.5 to 7 indicated that the ionic charge is $+4$. Since it has been shown that the hydrolysis product contained 2.5 OH^- per Al^{3+} , the charge of $+4$ could be accounted for only by the formula $\text{Al}_8(\text{OH})_{20}^{4+}$ (70). The result is surprising! It is so important that it should be tested by any means possible. Similar work with thorium nitrate solutions indicate that the species produced by hydrolysis is merely $\text{Th}(\text{OH})^{3+}$ (71).

If the method develops as its proponents hope, it can be improved by the development of new sols which will permit work with solutions of higher cation concentration.

It is to be hoped that a technique involving isotope exchange or electron transfer (72) may be capable, in at least a few representative cases, of confirming the method.

AQUEOUS SOLUTIONS OF SULFURIC ACID

Intensities of Raman lines from very concentrated aqueous sulfuric acid solutions indicate the existence of a new species—probably H_5SO_6^+ , (i.e., $\text{H}_3\text{O}^+\cdot\text{H}_2\text{SO}_4$ or $\text{H}_2\text{O}\cdot\text{H}_3\text{SO}_4^+$) [Young & Walrafen (73)]. The principal equilibrium in this concentration range appears to be:



The solvation of the H_3O^+ ion by an H_2SO_4 molecule is in general agreement with the views of Wyatt (74).

Vibrational frequency assignments for H_2SO_4 , HSO_4^- and SO_4^{2-} were made by Walrafen & Dodd (75) from new infrared absorption measurements. Several standard thermodynamic quantities were estimated (75, 76, 77).

The acidity and proton activity in sulfuric acid-water mixtures were determined from measurements of the electromotive force of cells (78). Transference numbers of sulfuric acid and other heteropoly acids have been measured by the moving boundary method [Kerker *et al.* (79)].

The distribution of sulfuric acid between water and 1,2-dichloroethane has been studied by Hayes & Pepper (80). They calculated the heats of transfer of the acid from water to the organic solvent, observing that the heats parallel the relative partial molal enthalpies of sulfuric acid in water as they should if molecular H_2SO_4 is the principal species in $\text{CH}_2\text{Cl}-\text{CH}_2\text{Cl}$, i.e., if the heat of dilution of the acid in the organic solvent is small.

Recent investigations of the HSO_4^- in aqueous solution are discussed below. See Tables I and II.

ANHYDROUS SULFURIC ACID

In anhydrous liquid acid, the principal equilibrium is believed to be [Gillespie & Robinson (81); Giguère & Savoie (82)]



The heat of the autoprotolysis has been remeasured by Dacre & Wyatt (83) and compared with previous estimates.

A portion of the conductance of anhydrous sulfuric acid at 25°C has been ascribed by Wyatt (84) to a special conductance mechanism, involving asymmetrical dissociation in an electric field.

OLEUMS

The constitution of oleums was investigated by Cerfontain (85) using optical extinction of ultraviolet light. Though it was not at first apparent, the results are in good agreement with Raman measurements (86). The spectra were interpreted as indicating the presence of the species $\text{H}_2\text{S}_2\text{O}_7$, H_2SO_4 , SO_3 , and possibly HS_2O_7^- but not higher polyacids. Their observations do not mean, of course, that there might not be significant concentrations of polyacids or polyanions, especially in oleums free of B_2O_3 inhibitor

(87). The spectra of the various polyacids, and likewise those of the poly-anions, may differ less than the natural width of the spectral lines. Indeed, Dacre & Wyatt (88) have argued for the existence of $\text{HS}_3\text{O}_{10}^-$ anion instead of the HS_2O_7^- anion. The infrared studies of Giguère & Savoie (82) do not resolve this problem. Clearly, further investigation is necessary, although much progress has been made.

A portion of the SO_3 molecules present in concentrated oleum solutions exist as polymeric species, probably the cyclic trimer [Gillespie & Robinson (89)]. The heat of fusion of disulfuric acid [Dacre & Wyatt (90)] and the vapor pressure and viscosity of liquid sulfur trioxide [Hyne & Tiley (91)] have been reported.

No evidence for the higher polyacids was reported. The lack of evidence for the polyacids must not be taken as definitive proof that they do not exist in small concentrations. They may exist in significant but small concentrations if the properties of the new bonds formed are so much like the old that the associated Raman vibrations differ only slightly from those observed for other species.

Studies involving the use of H_2SO_4 and oleums as solvents are too numerous to discuss in detail. They include investigations of kinetics (92, 93, 94), nitric acid-sulfuric acid mixtures (95, 96, 97), corrosion (98, 99), extraction (100, 101), and various solutions (102 to 106).

PHOSPHORIC ACID

The third dissociation constant of orthophosphoric acid was obtained by an optical extinction-indicator method [Vanderzee & Quist (107)]. The heat of solution over the range 0 to 89.13 per cent H_3PO_4 was also remeasured by Egan, Jr. & Luff (108).

Apparent acidity functions (H_0) of polyphosphoric acid were redetermined [Downing & Pearson (109)].

SOLUTIONS CONTAINING TWO OR MORE ELECTROLYTES

The discovery of the ionic strength principle (110) and its theoretical justification (111) was followed by rapid advances in the understanding of equilibria in solutions of electrolytes. So great was the need for such a guiding rule that the advances occurred in spite of the fact that the principle was intended to be used only for very dilute solutions—often more dilute than those in which equilibria, e.g., dissociation, or the formation of complex ions or ion pairs, were to be investigated. Unfortunately, progress was seriously hampered by the fact that the principle often proved to be inadequate even when very dilute solutions were used. The early discovery of systematic linear deviations from the principle, described by Harned's rule (112), suggested that systematic studies of the effects of an electrolyte upon the partial molal properties of a second electrolyte be fully investigated. A dilute solution of H_2SO_4 may be regarded as a mixture of an electrolyte of the 1-1 charge type with another of the 1-2 charge type. Since one of the

principal objectives of the study of electrolytes is the understanding of ionic equilibria, the investigation of the dependence of the properties of an electrolyte upon the nature and concentration of a second solute is one of the most important problems confronting the student of electrolytic solutions.

In 1953, McKay & Perring (113) formulated equations for the calculation of the activity coefficients of each of two solutes from the vapor pressure of the solvent. Robinson (114) made new isopiestic measurements of aqueous solutions containing NaCl and KCl. He deliberately arranged conditions for the efficient application of the equation of McKay & Perring. Deviations of the activity coefficient of KCl from the ionic strength principle obeyed Harned's rule closely. The logarithm of the activity coefficient of NaCl was not quite a linear function of the KCl concentration. Similarly, Makarov & Stupin (115) studied ternary solutions of KI and RbI. The Harned rule and the Akerlöf-Thomas (116) rule were obeyed satisfactorily. Scatchard (117) studied aqueous ternary solutions containing HCl, LiCl, NaCl, KCl, and CsCl and reviewed the calculation of activity coefficients of electrolytes in aqueous binary solutions. The isopiestic method was also used by Stakhanova & Vasilev (118) to study certain ternary and quaternary mixtures of chlorides of the alkali metals. Vapor-liquid equilibria of HCl, H_2SO_4 , H_2O , and of HCl, CaCl_2 , H_2O solutions were studied by Moriyama & Sakayori (119). The calculation of heats of solution in saturated ternary solutions was investigated by Iyengar (120). Benz & Leary (121) used an E.M.F. method to investigate the thermodynamic properties of solutions of plutonium chloride and NaCl.

Platek & Marinsky (122) used ion exchange to study mixtures of LiCl and other alkali metal chlorides. Solutions of hippuric acid and NaCl were studied by Larese & Canady (123), using solubility determinations. E.M.F. methods were used by Schonhorn & Gregor (124) to study mixtures of alkali-metal chlorides and alkaline earth halides. Ift, Voet & Vinograd (125) studied mixtures containing alkali metal halides in the ultracentrifuge.

Electrical conductivity of ternary aqueous solutions of NaCl, HCl, H_2O was studied by Berecz & Andras (126). Conductivity, viscosity, and volume of the ternary system, Na^+ , Cl^- , SO_4^{2-} , H_2O were investigated by Usanovich & Aksel'rod (127). Density and viscosity of LiCl, HCl, H_2O were studied by Berecz & Horanyi (128).

Rush & Scatchard (129) made an extensive study of molal volumes and of refractive index increments of solutions containing electrolytes of two different charge types, BaCl_2 and HCl. They proposed a general equation for the calculation of the excess thermodynamic functions of mixtures of electrolytes of dissimilar charge types.

DISSOCIATION CONSTANTS VERSUS METHODS

In any extensive table of the values that have been reported for some equilibrium constant there are differences which appear to be random and which seem to be consequences of the limited precision of the measurements

and their mathematical or theoretical treatment. It is possible, however, that the limited precision is concealing the fact that the relations between one or more properties and the dissociation constant have not been understood or have been naïvely interpreted. Errors of this type affected values reported for many dissociation constants prior to 1923—for example, those evaluated from conductance measurements. It is possible, however, that there is another source of difference. Two properties of a solution may actually be related to different aspects of dissociation. There may be pairs of ions which are correctly to be regarded as associated insofar as some of their manifestations are concerned and as dissociated in their role in other phenomena. The fraction of the ions to be considered as associated may actually be different when the method of measurement is changed. Whether the distant future will bring sufficient understanding of molecular statistics to permit the calculation of one correct value from another is irrelevant if it can be satisfactorily demonstrated in the near future that two properties, e.g., conductance and free energy, actually lead to different results.

The significance of differences between estimates of degrees of dissociation and similar differences between estimates of dissociation constants which result from the use of a variety of methods of measurement and of interpretation, was discussed by Pitzer and Brewer (130) and by Scatchard (131). Referring to the Raman spectral method, Pitzer and Brewer wrote, "It should be realized, however, that . . . other experimental phenomena might give different values of the degree of dissociation . . ." Scatchard remarked " . . . each experimental method, or each method of handling experimental data, involves its own definition and so, perhaps, its own value of the equilibrium constant."

We must be prepared to find that values of the constants vary with the experimental method used; we must determine how much they vary by examination of the results. Harned & Owen (132) have described the beginning of such a study of the dissociation constants of weak electrolytes. They compared conductance measurements and electromotive force data from cells without liquid junctions for six weak acids in aqueous solution. For five of the six, the pairs of constants agreed within satisfactory limits—presumably within the limits of precision of the methods (about 1.5 per cent or less). For formic acid, a difference of 3 per cent indicates either that the methods are fundamentally different in meaning or that the precision of at least one set of measurements is somewhat poorer than was expected. Since discrepancies found in earlier comparisons (133, 134) of values of the dissociation constant of acetic acid were eventually eliminated by improved precision of measurement, it seems likely that the discrepancies in the data for formic acid will also be resolved by additional advances in technique. The procedures already employed were very highly developed, however. The outcome is by no means certain.

A very elaborate comparison has been made of dissociation constants obtained for acetic acid from conductance measurements and from electro-

motive forces of a series of cells without transference. Both series of data were obtained for the purpose. Using the conductance method, MacInnes & Shedlovsky (135) obtained 1.758×10^{-5} mole per kg of water. Harned & Ehlers (136) obtained a figure of 1.754×10^{-5} from their electromotive force measurements. The difference, only 0.23 per cent, is the result of years of elaborate work of the finest precision. The chief value of the extensive work in the two laboratories is that it does demonstrate that a method based upon a transport property and another method based upon a thermodynamic property involve the same "definition of the dissociation constant." At any rate, that is now established for dilute aqueous solutions of acetic acid at 25°C. Of course, other methods also yield dissociation constants which differ from 1.76×10^{-5} mole kg⁻¹ by amounts which, though larger than 0.23 per cent, are readily accounted for by the deliberate use of approximate, but less time-consuming methods. These methods apparently involve essentially the same "definitions of dissociation." Whether they involve exactly the same definition we do not know. Many of us will continue to assume that they do (for weak electrolytes, at least) until theory or experiment leads us to suspect that they do not.

Eigen (137) and Pitzer & Brewer (130) pointed out that there is one method which is more likely than most methods to be associated with a significantly different aspect of dissociation. The method is one which depends upon the determination of the extremely rapid rates of dissociation and association and the fact that the rates are equal in absolute magnitude when equilibrium exists. Using his now-famous relaxation technique, Eigen (138) measured the kinetic rate constants for the dissociation of acetic acid and for the combination of its ions to form the undissociated acid. From the rate constants it follows that the equilibrium constant for acetic acid in aqueous solution is 1.67×10^{-5} mole per kilogram of solvent. For ammonium hydroxide, Eigen obtains 1.8×10^{-5} mole kg⁻¹. The agreement is all that can be expected (138) at present. It will be interesting to watch developments during the coming years as techniques improve. It is already clear that the dissociation constant indicated by the kinetic measurements is, within about 10 per cent, the same as the constant derived from any of the other commonly used methods.

STRONGER ELECTROLYTES

Electrolytes which are much more highly dissociated than acetic acid pose new and separate problems. Fortunately, there are two relatively strong electrolytes which have been studied by a sufficiently large variety of methods. They have also been studied over such wide temperature ranges that heats of dissociation derived from temperature coefficients of the constants may be compared with calorimetric determinations. The dissociation constant of one of these, HSO_4^- , is three orders of magnitude larger than that of acetic acid and the dissociation constant of the other, HNO_3 , is

about six orders of magnitude larger. The investigations of the three electrolytes, therefore, cover a range of six orders of magnitude in K , 250°C in temperature, and a wide variety of methods of measurement. They also permit the study of a single electrolyte through a temperature range wide enough to produce variations in K of over 1000-fold.

To facilitate a discussion of the differences between methods they are here grouped into several classes. Those in the first class depend directly upon the measurement of a thermodynamic property. Every member of the class has been or can be used for a rigorous determination of stoichiometric activity coefficients, i.e., activity coefficients of the type defined and discussed by Lewis & Randall (130). Each of the methods may possess a defect or blemish peculiar to itself. The cryoscopic method, for example, depends upon the condition that essentially pure solvent be in equilibrium with the solution at its freezing temperature. Likewise, electromotive methods depend upon the use of electrode materials which are not sufficiently soluble in the electrolyte solution to affect the escaping tendency of the constituents of the solution in the cell or to introduce errors into the potential difference between the electrodes of the cell which are caused by the junction of two liquids of different composition. Both depend upon the attainment of nearly perfect equilibrium within a time short enough to preclude significant errors due to side reactions of any kind.

Fortunately, it is often possible to select materials or adjust conditions so that serious blemishes do not exist. When the blemishes have been virtually eliminated, the methods may be regarded as "true thermodynamic" methods and all of them in this class must yield consistent values of stoichiometric activity coefficients. The principal reason for the comparison of two or more members of class I is to detect the existence of a blemish or to demonstrate the absence of serious blemishes in the methods. The most useful procedure is usually a direct comparison of the activity coefficients themselves. The fact is that the causes of blemishes are sufficiently well understood to assure that the results from the methods in class I usually agree within the precision of measurement attainable in the laboratory.

The calculation of equilibrium constants from the stoichiometric activity coefficients (or directly from measurements from which the activity coefficients could be explicitly evaluated) involves extrapolations to infinite dilution. Before the advent of the Debye-Hückel theory, extrapolation was a serious source of uncertainty, but today it introduces little uncertainty if precision of measurement, e.g., of the potentiometric measurement of the electromotive force of a cell, can be maintained to sufficiently great dilutions. When sufficiently dilute solutions can be investigated, the parameter in the denominator of the Debye-Hückel approximation may be determined as an empirical constant and the extrapolation made with considerable precision. Under ideal conditions, the denominator term may be ignored entirely; the Debye-Hückel limiting law is then adequate for extrapolation.

Since all of the methods of the first class, when treated with consistent

extrapolation procedures, must yield exactly the same result for any dissociation constant, the basic task is to compare the result of each method in the other classes with the results from the other members of those classes and with the best values from the methods of class I. The best values may be either weighted averages or simply the series of values believed to be the best. To demonstrate the precision attained and the absence of blemishes it is customary to include in the tabulation all of the precise results from methods of class I. There need be no doubt, however, that the meaning of the term "degree of dissociation" is the same for all methods of class I.

Methods of class II are also fundamentally thermodynamic methods, but each involves one or more relationships which are not purely thermodynamic. These relations are, in general, not exact although the errors introduced by them may be negligibly small in particular cases. An example is the determination of the dissociation constant of the HSO_4^- ion from the solubility of silver sulfate in aqueous sulfuric acid solutions. The nature of the method is such that the concentrations of acid and salt can not be maintained in constant ratio. Hence, extrapolation to infinite dilution is not well defined. In practice the faulty ionic strength principle is used as a guide for extrapolation. The method as applied to the HSO_4^- ion seems to be satisfactory for the higher temperatures. At the lower temperatures the precision is not so good. The dissociation constant of the HSO_4^- ion is larger, the enhancement of the solubility of Ag_2SO_4 is correspondingly smaller, and the various errors are proportionally more important. The need for further information, however, depended upon new determinations at the higher temperatures, not at the lower temperatures. This method is discussed further below.

Class III includes methods which depend upon determinations of properties other than thermodynamic ones. A complete list of the properties probably could not be made but the most commonly used ones seem to be: conductance; reaction kinetics (catalysis by one of the species involved in the equilibrium); kinetics of the opposing reactions involved in the equilibrium itself; spectroscopy (optical extinction, nuclear magnetic resonance, Raman); and optical rotation; etc. It is in this class that we should expect to find a method, if one exists which is associated with a definition of degree of dissociation that differs from the customary one.

There is also a fourth class of methods, or pseudo methods. They are used when the methods of classes I, II, and III are unable to produce answers sufficiently precise to be useful. They sometimes give good answers but they can fail completely, yielding equilibrium constants for the formation of species which do not exist at all. In this group are included concentration cells with transference and other methods which are based upon reasoning in terms of activities of single ionic species (rather than upon products or ratios of ion activities). These cells are useful for very weak electrolytes [cf. Harned & Owen (132) p. 515] but for somewhat stronger electrolytes they may yield erroneous—even negative—constants. When a value obtained

from such a cell differs from a value produced by another method we are not justified in the conclusion that the two procedures imply different definitions of the degree of association. The methods lack precision because of fundamental faults of principle and logic. A comparison of definitions can not be more precise than the methods themselves.

A method, now obsolete, belonging to this class depended upon the supposed equality of the degree of dissociation, α , and the conductance ratio, Λ/Λ_0 . For sufficiently weak electrolytes α differs so little from Λ/Λ_0 that reasonably good results were obtained, e.g., for acetic acid. For moderately strong and stronger electrolytes its failures are notorious.

It has been replaced by a new set of methods which are causing unfortunate confusion. An example is the use of the "Debye-Hückel approximation" with a preselected value of the parameter, a , in the denominator. The value chosen for a —if not quite arbitrary—may have been determined empirically from experimental values of the activity coefficients of a reference electrolyte. The method depends upon the fact or the assumption (or perhaps the declamation) that the degree of dissociation of the reference electrolyte (preferably 100 per cent) is known for the solutions used for the determination of the parameter a . There is also the concomitant requirement that the a parameters associated respectively with the simple ions and with the species produced by association be the same for the subject electrolyte and for the reference electrolyte. Sometimes when the method has been challenged the defense has been offered that [cf. Nancollas (139) p. 410] the results agree with those of a conductance method. The argument is misleading if the values determined for the constants are sensitive to the a used in their determination. The agreement would not be the same if a were allowed to vary from electrolyte to electrolyte or if a different universal value were used for numerous electrolytes of a particular charge type. Moreover, applications of the conductance method have also been faulty when used with solutions of the large concentrations which are required to produce variations in Λ large enough to permit a calculation of an equilibrium constant.

These two methods of class IV (depending on activity coefficients and conductivities, respectively) have been applied to salts of the 2-2 charge type. For CuSO_4 , optical extinction has also been used. The agreement has not been good [Davies, Otter & Prue (140)]. One of the basic difficulties in most of the methods of class IV is that the effects of association are determined only as relatively small differences between measured and calculated quantities. The differences are appreciable only when the concentrations become so large that uncertainties in the calculated quantities become comparable with the differences. Equilibrium constants calculated by these methods are not useful for our purpose because the uncertainties within each method are as great as the differences between methods. As Nancollas has stated in his interesting review (139, p. 410), some writers consider that

TABLE I
DISSOCIATION CONSTANT AT 25°C FOR $\text{HSO}_4^- \rightarrow \text{H}^+ + \text{SO}_4^-$

Method and Author	Date	K_2 mole/kg	Reference
Conductance and transference			
data of Sherrill & Noyes	1926	*	(144)
calculated by Davies, Jones & Monk	1951	0.0102	(145)
calculated by Kerker	1957	†	(146)
Optical extinction (methyl orange)			
Klotz; Singleterry	1940	0.01015 _s	(147, 148)
Electromotive Force of Cells			
data of Hamer**	1951	0.0102	(149)
Davies, Jones & Monk	1951	0.0102	(145)
Nair & Nancollas	1958	0.0106	(150)
Solubility of Ag_2SO_4 in H_2SO_4			
Lietzke, Stoughton & Young	1961	0.0103	(151)
Raman line intensities			
data of Young, Maranville & Smith‡	1959	0.0102	(152)

* Quotient not calculated by Sherrill & Noyes for $m \approx 0$.

† Calculation same as that of Davies, Jones & Monk.

** Calculated by Davies, Jones & Monk.

‡ Calculated for this Table.

TABLE II
HEAT OF DISSOCIATION AT 25°C FOR $\text{HSO}_4^- \rightarrow \text{H}^+ + \text{SO}_4^-$

Method and Author	Date	ΔH° kcal mole ⁻¹	Reference
Conductance			
Noyes <i>et al.</i>	1907	-5.2	(153)
Lietzke, Stoughton & Young*	1961	-5.1	(151)
Optical extinction (methyl orange)			
Singleterry	1940	-5.1 ₉	(148)
Electromotive force of cells			
Davies, Jones & Monk	1951	-5.2 ₀	(145)
Nair & Nancollas	1958	-5.6	(150)
Solubility of Ag_2SO_4 in H_2SO_4			
Lietzke, Stoughton & Young	1961	-4.9	(151)
Calorimetry			
heat of mixing of Na_2SO_4 and HCl			
Pitzer	1937	-5.2	(154)
heat of dilution of aqueous H_2SO_4			
Lange, Monheim & Robinson†	1933	-5.3†	(155)

* Equation 11 of Lietzke, Stoughton & Young (151).

† Calculated by Singleterry (148).

values calculated by these methods are useful as compact summaries of existing experimental information. They reproduce the data even when there is no convincing evidence that association has produced a new species.

The significance of values determined by these two pseudo methods has been discussed by Robinson & Stokes (141), by Redlich (142), by Davies, Otter & Prue (140), and many others. Guggenheim (143) has initiated a new theoretical approach to the problem. A step toward an eventual answer was taken by Atkinson, Yokoi & Hallada (24). They have begun a search for symmetrical electrolytes of higher charge types which, they hope, can be shown to be unassociated and can be used to establish reference curves for the determination of association constants of other electrolytes. The explicit role of the ionic radius in the new Fuoss-Onsager theory (20, 21) may lead to enough knowledge of ionic radii to permit significant comparisons of the meaning of "degree of dissociation" as determined by different procedures.

THE DISSOCIATION CONSTANT OF HSO_4^-

In Table I are assembled from seven sources values of the second dissociation constant of sulfuric acid. The average deviation from the mean is 1 per cent. This accord is remarkable when contrasted with the lack of agreement which existed in the years just prior to publication of the Debye-Hückel theory (111). Lewis and Randall (110, p. 318) seem not to have been fully convinced that an ionic equilibrium exists in dilute aqueous solutions of sulfuric acid. A. A. Noyes, on the other hand, had studied the equilibrium extensively and he and his co-workers had made definite estimates of the dissociation quotient² and the heat of dissociation at 25°C. The former he was to reduce by about 60 per cent a few years later [Sherrill & Noyes (144)]. The heat of dissociation, however, agrees exactly with the mean of the best of today's determinations [see Table II].

It is unfortunate that it was not possible to include more methods of class I. The applications of those methods to electrolytes as strong as HSO_4^- is difficult. Davies, Jones & Monk (145), however, have calculated a value of the constant for 0°C from available cryoscopic data.

Some of the values in Table I appear to be more precise than is possible at the present time. Difficulties in the measurement of Raman lines mount rapidly as concentration is reduced. The Raman intensities used for the determination of the constant had not been measured for that purpose but to provide information concerning ion concentrations in solutions of finite concentrations. A discrepancy of 5 or even 10 per cent should not have been considered significant. The solubility method was used chiefly to supply information concerning dissociation at temperatures too high for convenient application of the other methods. Near room temperature, the larger dissociation constant of HSO_4^- produces a smaller enhancement of the solubility of Ag_2SO_4 and diminishes the precision of the determination. This condition is evident on a graph showing a curve representing the "least-square" equation and the scatter of the individual points. A deviation of 10

per cent or more from the mean value at 25°C would not have been considered significant.

In Table II are assembled values of the heat of dissociation from various sources. Two are calorimetric determinations. The average deviation from the mean (-5.2 kcal mole $^{-1}$) is 2.3 per cent. Since most of the values are results of the differentiation of empirical equations or depend upon estimates of actual degrees of dissociation in solutions of finite concentration, the precision is excellent; Table II seems to be more dramatic than Table I. Together, they demonstrate that values of ΔG° , ΔH° , and ΔS° are all independent of the method used. So far as can be determined from measurements of the precision now attainable, the meaning of the term "degree of dissociation" is the same for all of the methods available.

The dissociation of nitric acid has also been studied over a wide temperature range (152). The dissociation constant at 25°C is too large for the usual methods of classes I and II, but at higher temperatures the dissociation is so much smaller that conductance may be used for the determination of equilibrium constants. The fact that the constants determined from conductivities at high temperatures and from Raman intensities at lower temperatures merge into a single empirical curve is indirect evidence that the degree of dissociation measured by the two methods has approximately the same meaning. The fact that the heat of dissociation calculated from the equation of that curve is in agreement with a calorimetric determination is further evidence that the various methods refer to the same definition. The comparison is not as clear-cut as for HSO_4^- but is all that could be hoped for at present.

SOLUTIONS AT HIGH TEMPERATURES

Studying the conductivity of HCl in water at high temperatures, Gorbachev & Kondrat'ev (38) extended the work of A. A. Noyes *et al.* (156). They observed that a curve representing the specific conductance of an aqueous KCl solution as a function of temperature possesses both a maximum and an inflection between 25°C and 300°C. The isotherms, logarithm of conductivity versus logarithm of molality, are very nearly linear.

Lietzke, Stoughton and co-workers have been studying the thermodynamics of aqueous solutions at temperatures as high as 250°C. Some of the consequences of that work are discussed in this review in the paragraphs concerning aqueous sulfuric acid.

In one of the symposia of the 1961 meeting of the International Congress of Pure and Applied Chemistry in Montreal (157), E. U. Franck discussed investigations of electrolytes dissolved in water well above the critical temperature [Franck, Dudziak & Coulon (158)]. Pressures as high as 2500 bars and temperatures as high as 750°C are available. The very small ionization constant of HF decreases with rise of temperature and decreases isothermally with decrease in the density of the compressed steam. Solutions of KCl, NaCl, HCl, and NH_3 in water in the supercritical condition have also been

studied. Abstracts of most of the papers presented in the symposium were distributed in a printed book at the meeting.

FUSED SALTS

Great current interest in high-temperature melts was responsible during 1961 for three international symposia. One was organized by two commissions of the International Union of Pure and Applied Chemistry (10th–11th August). About twenty papers were presented at three sessions devoted to "Thermodynamics of Fused Salts, Especially Metal-Fused Salt Systems" (157). "High Temperature Chemistry-Molten Salts" was discussed at a Gordon Research Conference (28th August to 1st September). These were followed by a General Discussion of the Faraday Society in Liverpool at the University (5th to 7th September).

Numerous papers dealing with the structures and properties of fused salts were published during the past year. Not all can be mentioned here, but the following topical synopsis will at least indicate the types of work now being done and the points of view of some of the workers active in this area.

Single Melted Salts.—To test theories of the molten salt state, properties of several salts not mixed with other substances were examined. These include self-diffusion (159), transport numbers in molten CsCl (160), surface tension of fused nitrates and nitrites (161, 162), compressibility (163), vibrational spectra of alkali metal hydroxides (164, 165) and of fused nitrates (166), and electronic spectra of molten alkali metal nitrates (167).

A theory of corresponding states was constructed (168), and the relations between aqueous electrolyte solutions and molten electrolytes were discussed (169).

Mixtures of Fused Salts.—To facilitate concise description and understanding of the thermodynamic properties of a fused salt system, the properties are often compared with those of an "ideal" mixture. The model for the ideal mixture was proposed by Temkin (170). His model and associated terminology were recently discussed by Bloom & Welch (171) and by Grjotheim, Krohn & Toguri (172).

Salt mixtures may be conveniently classified into two groups: (a) those containing common ions, e.g., two alkali metal nitrates, and (b) reciprocal salt pairs. Mixtures in the second group contain two (or more) positive ions plus two (or more) negative ions; e.g., a mixture of NaCl and KNO₃.

A mixture produced by addition to a reciprocal salt system of an electrolyte contributing one or more ions not already present is also regarded as a reciprocal salt system, e.g., CdCl₂, PbSO₄, and Na₂SO₄ (171, 172).

MIXTURES CONTAINING COMMON ANIONS

Investigations of the following types of mixtures containing common anions were reported in recent papers: nitrates, carbonates, chlorides, bromides, and silicates.

Fused Nitrates.—The heats of mixing of alkali metal nitrates (173) and of AgNO_3 with the alkali metal nitrates (174) were measured calorimetrically. Volume changes accompanying mixings were measured (175, 176).

Investigated also were the electrical conductivities (177), the mechanism of conductance (178) in mixtures of nitrates, and, polarographically, the diffusion coefficient of Ag^+ in fused nitrates (179).

Heats of mixing of the alkali metal nitrates are negative. They indicate significant deviations from the Temkin model and appear to be associated with distances between second nearest neighbors and particularly with differences between the radii of the two cations [cf. Blander (180)]. The volume changes for the mixings of NaNO_3 and KNO_3 are small as the Temkin model implies. Indeed they are so small that considerable care was required to determine the algebraic sign of the change. The heats of mixing of AgNO_3 with KNO_3 and of AgNO_3 with RbNO_3 are also negative, but they are positive for the mixing of AgNO_3 with LiNO_3 and with NaNO_3 .

Fused Carbonates.—Surface tension, conductivity, and density were studied (181). The mixtures behave as nearly "ideal" solutions.

Fused Halides.—Investigated (electromotive forces of cells) were the thermodynamic properties of mixtures of CeCl_3 with CaCl_2 (182); KCl with MgCl_2 [vapor pressure] (183); PbBr_2 with KBr [vapor pressure] (184); and CdCl_2 with AgCl [vapor pressure] (171).

Silicate Melts.—Relative mobilities of cations were determined from transference numbers in three-component silicate systems (185).

RECIPROCAL SALT SYSTEMS

The general subject was discussed at length (171, 172) in terms of the Temkin model mentioned above (170). Measurements of the vapor pressures of CdCl_2 and PbCl_2 with argon as the carrier gas (171) were used to determine the thermodynamic properties of several reciprocal salt systems and of the mixture, CdCl_2 , with AgCl . The common-anion system behaves as Temkin's equation predicts, but there are large differences between the predictions of the equation and the experimental properties of the reciprocal systems.

Surface tensions of the reciprocal system KBr-CdCl_2 exhibited large departures from ideal behavior (186). Two prominent minima in the surface tension composition isotherms indicate complex formation. Raman spectra indicate the existence of $\text{CdCl}_4^{=}$ and $\text{CdBr}_4^{=}$.

Other reciprocal salt systems are mentioned below (187, 188).

FUSED SALTS: MISCELLANEOUS TOPICS

Chemical Reactions Within Melts.—Complex ions and other species demonstrated or suspected include AgCl_2^- and AgCl in solutions of AgNO_3 and metal chlorides in fused nitrates (187, 188, 189); CdBr^+ , CdBr_2 , CdBr_3^- , PbBr^+ , and PBr_2 in mixtures of metal bromides and fused nitrates (190);

$\text{CdCl}_4^{=}$ and $\text{CdBr}_4^{=}$ in mixtures of KBr and CdCl_2 (186), CeCl_2^{+} and CeCl_4^{-} in mixtures of CeCl_3 and CaCl_2 (182).

Phase Equilibria.—Phase diagrams of the following systems were studied: $\text{NaPO}_3\text{-Na}_2\text{SO}_4$; $\text{RbPO}_3\text{-Rb}_2\text{SO}_4$ and $\text{RbPO}_3\text{-Na}_2\text{SO}_4$ (191); $\text{ScCl}_3\text{-CsCl}$ (192); LiF-PuF_3 (193); $\text{FeCl}_3\text{-NaCl}$ and $\text{FeCl}_3\text{-KCl}$ (194). The distribution of TlCl between KNO_3 and AgCl and between $\text{K}_2\text{S}_2\text{O}_7$ and AgCl (195) was determined.

Mixtures of Metals and Fused Salts.—Solutions of Na in sodium halides (196) and of Rb in RbCl (197) were investigated. Solutions of Pb in molten PbCl_2 were examined polarographically (198). Solutions of Na in NaI , K in KI , and K in KF were studied by means of conductance (199); solutions of Cd in fused halides, CdX_2 , and in the system $\text{Cd}(\text{AlCl}_4)_2\text{-Cd}_2(\text{AlCl}_4)_2$, were studied by means of phase equilibria and color changes (200); solutions of Bi in BiCl_3 were investigated polarographically (201) and by electromotive force methods (202). Arguments for existence of the species Na_2 , K_2 , Pb_2^{2+} , Cd_2^{2+} , BiCl , and Bi_4Cl_4 were presented.

The conductances of the following solutions of halides in liquid metals were also measured (203): KX in K , RbX in Rb and CsX in Cs .

Gases in Fused Nitrates.—The gases O_2 and N_2 do not dissolve appreciably in molten alkali metal nitrates (Na , K , Cs). Some water does dissolve, apparently in interstices of the nitrate melts (204).

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