235. *The Cryoscopic Constants of Dissociating Solvents (with Special Reference to Nitric and Sulphuric Acids).*

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By making allowance for the heat of dissociation, it is shown that the cryoscopic constants (k_f) of dissociating solvents are expected to vary when the extent of dissociation is altered by added solutes. A method is outlined for investigating simple dissociation equilibria by means of variations in k_f and applied, partially, to Dunning and Nutt's nitric acid data, yielding a heat of dissociation ~10 kcal. Sulphuric acid, a more associated solvent, exhibits a variation of k_f from 5·5 in 0·11M-SO_3 to 6·9 in 0·23M-H_2O, as shown by the use of the non-electrolytes 2 : 4 : 6-trinitrotoluene and nitromethane. This result is not in accordance with the simple treatment and leads to some further discussion on partial molar heat contents in these systems. Empirical k_f values based upon Gillespie, Hughes, and Ingold's data are suggested for the determination of the extent of dissociation of solutes in sulphuric acid.

(1) *General Considerations.*

ALTHOUGH solvents of appreciable dissociation have often been used in cryoscopic investigations, there is one aspect of their theoretical treatment which appears to have escaped attention, namely, that, in cases in which the extent of dissociation can be altered by added solutes, the cryoscopic " constant " will be expected to vary with the extent of such alteration. A familiar example is afforded by the solvent sulphuric acid, in which cryoscopic measurements are usually conducted in the presence of a little water which serves to suppress the dissociation of the solvent. In this case it is not permissible to deduce a cryoscopic constant from thermal data relating to the pure solvent, as Hammett has done (*J. Amer. Chem. Soc.*, 1933, **55**, 1900; 1937, **59**, 1708), or to abstract a single value from experimental data, as Gillespie, Hughes, and Ingold have recently done (*J.*, 1950, 2473—2551), unless it can be shown by special experiments that dissociation heat effects are negligibly small. It is the object of the present paper to draw attention to this point and to attempt some measure of reinterpretation of the data for sulphuric and nitric acids, both of which are believed to have variable cryoscopic constants.

The quantitative argument which follows assumes that changes in the partial molar heat content of the solvent can be explained in terms of species which themselves have constant partial molar heat contents (see, however, Section 3). The heat term, ΔH_f, in the conventional cryoscopic constant, $\boldsymbol{R}T^2/m_1\Delta H_f$, is the heat which is absorbed when 1 mole of the solvent passes from the solid phase into the liquid. If dissociation is suppressed, this heat will simply correspond to the production of undissociated solvent in the liquid phase; but if each mole further dissociates to the fractional extent x, a further amount of heat of magnitude $x\Delta H_d$ will have to be absorbed, ΔH_d being the molar heat of dissociation. (It is assumed that the solid phase is not affected in any way by dissociation changes within the liquid.) The cryoscopic constant (represented hereafter by k_f) therefore becomes $\boldsymbol{R}T^2/m_1(\Delta H'_f + x\Delta H_d)$, where $\Delta H'_f$ represents the heat of fusion of the solvent when its dissociation is completely suppressed, m_1 is the solvent molality, $\boldsymbol{R}$ the gas constant, and T the hypothetical melting point of the solvent dissociated to the extent x. If x_0 represents the degree of dissociation of the pure solvent, the normal latent heat of fusion can be written as $\Delta H'_f + x_0\Delta H_d$. Now the dissociation of a solvent commonly increases with temperature, so ΔH_d will normally be positive; whence $\boldsymbol{R}T'^2/m_1\Delta H'_f > \boldsymbol{R}T_0^2/m_1(\Delta H'_f + x_0\Delta H_d)$, *i.e.*, k_f will increase with suppression of dissociation. (T' represents the hypothetical melting point of the completely undissociated solvent.)

This formulation shows that the percentage change in k_f could easily be ten times as great as the percentage dissociation; for molar heats of fusion are of the order of 1 kcal., and heats of dissociation of the order of 10 kcal. would not be considered unreasonable (cf. 14 kcal. for water). Thus a pure solvent dissociating only to the extent of 1% could have its cryoscopic constant altered by as much as 10% within the relatively small change of composition required to suppress its dissociation. It also appears that an addition compound AB should have a minimum k_f at the maximum freezing point, and that an increasing excess of either A or B should lead to an increasing k_f, reaching the same maximum on both sides of the composition AB when dissociation has been completely suppressed.

This could be made the basis for an investigation of the dissociation equilibria for such compounds, since the use of a non-electrolyte as an indicator of k_f in solutions of various compositions would give ΔH_d and ΔG_d directly from the same set of cryoscopic data. Even if there is ambiguity about the form of dissociation, such an investigation could help in choosing between alternative forms if used in conjunction with calorimetric data.

(2) *Nitric Acid.*

A complete quantitative analysis in the case of nitric acid is hampered by the fact that there is considerable disagreement between the most recent sets of data for the solutes N_2O_5 and H_2O (Gillespie, Hughes, and Ingold, *J.*, 1950, 2552; Dunning and Nutt, *Trans. Faraday Soc.*, 1951, **47**, 15). Both groups of authors are, however, in agreement in finding larger slopes in the freezing point–molality curves for suppressing solutes than those calculated from Forsythe and Giauque's thermal data (*J. Amer. Chem. Soc.*, 1942, **64**, 48). Gillespie *et al.* have sought to explain this by assuming solvation, using, unfortunately, a formula which is not valid for such high concentrations (especially after allowance for extensive solvation); but a heat of dissociation effect must at once be suspected.

In order to deal with the large concentrations of suppressing solutes and dissociation products involved, it is most convenient in this case to use the mole-fraction type of formula (always assuming of course that Raoult's law is approximated to sufficiently closely), *viz.*:

$$T = T' + (2{\cdot}303\boldsymbol{R}T'^2/\Delta H'_f)(1 - 0{\cdot}00230)\log_{10} N_1$$

Here T is the freezing point of the solution, T' that of the undissociated solvent: $0{\cdot}0023\theta$ contains the usual correction term for variation of ΔH_f with temperature and has been evaluated here with sufficient accuracy from the properties of the pure solvent. The mole-fraction of the solvent is given by the formula

$$N_1 = m_1/(m_1 + \nu_2 m_2)$$

where m_1 and m_2 are the molalities of solvent and solute respectively, and ν_2 represents the number of particles given per solute molecule. [This is not to be confused with the stoicheiometrical mole-fraction, $m_1/(m_1 + m_2)$, used by Dunning and Nutt.]

When Dunning and Nutt's data for ammonium and potassium nitrate were plotted upon this basis (with $\nu_2 = 2$), it was found that they lay upon a common curve, of which the last four points (*i.e.*, for most concentrated solutions) defined a straight line of slope 110 ($= 2{\cdot}303\ \boldsymbol{R}T'^2/\Delta H'_f$), giving $\Delta H'_f = 2250$ cal., and intercept 1·25° above the freezing point of the pure solvent. The abscissa of the point on this straight line at the freezing point of the pure solvent was $-0{\cdot}0113$, indicating a mole-fraction of undissociated molecules in the pure solvent of 0·974; and hence $x_0 \sim 0{\cdot}026/\nu_1$ [strictly, this has to be multiplied by $1 + (\nu_1 - 1)x_0$], where ν_1 represents the number of particles given per dissociating solvent molecule. (This method of obtaining x_0 appears to be new. It makes direct use of the condition that the chemical potential of the solvent has the same value in all solutions in equilibrium with the solid at the same temperature, but requires also the additional assumption that the potential of the undissociated species depends only upon its own mol.-fraction, which will not be valid if interionic attraction effects are important.) If it is now assumed that a simple heat of dissociation effect is being dealt with here, we have for the latent heat of the pure solvent (2503 cal. per mole; Forsythe and Giauque, *loc. cit.*) :

$$2503 = \Delta H'_f + x_0\Delta H_d = 2250 + 0{\cdot}026\Delta H_d/\nu_1$$

whence

$$\Delta H_d \sim 10{,}000\nu_1 \text{ cal.}$$

The most popular choice for the main dissociation scheme seems to be $3HNO_3 = NO_2^+ + NO_3^- + H_2O,HNO_3$, having $\nu_1 = 1$; in this case ΔH_d becomes ~10 kcal. Even without the assumption that H_2O is bound to HNO_3 (Chédin, Fénéant, and Vandoni, *Compt. rend.*, 1948, **226**, 1722), the value of ΔH_d is still only 15 kcal.

A value for ΔH_d of this order of magnitude is clearly reasonable enough to suppose that a dissociation heat effect is an important factor here. The thermal changes ascribed to solvation by Gillespie *et al.* (*loc. cit.*, p. 2556) are also consistent with an endothermic solvent dissociation process : thus part of the reason for the greater heat evolved on the addition of water to pure nitric acid than to a solution of dinitrogen pentoxide must be that solvent dissociation is being suppressed in the former case and increased in the latter. Further, Fig. 3 of Dunning and Nutt's paper (*loc. cit.*, p. 21) shows that " cyclonite " gives a greater freezing-point depression in a solution already containing ammonium nitrate than in the pure acid, which is consistent with the present treatment.

More data are required before this view can be accepted with complete confidence, and in view of the uncertainties in the dissociation scheme, and especially in the magnitude of electrostatic forces, the value of 10 kcal. for ΔH_d can at best only be a rough indication.

(3) *Sulphuric Acid.*

The most recent major contribution to the cryoscopic study of sulphuric acid is contained in a series of papers by Gillespie, Hughes, and Ingold and others (*J.*, 1950, 2473—2551), who give full references to earlier work. These authors have introduced considerable improvements in technique and have provided accurate data for a large number of solutes; but the aspect of their work which is of interest at present is that the whole of their interpretation is based upon a single value for k_f of 5·98 deg. mole^{-1} kg. Two features in the choice of this number immediately attract attention in the light of the argument presented here : (i) it is based principally upon the fact that sulphuryl chloride, treated as an ideal non-electrolyte, gives this same value for k_f *whether small amounts of water are present or not*; (ii) it leads to the rejection of the most accurate data available for the latent heat of fusion of pure sulphuric acid. That (i) is an unreliable criterion without special justification is now immediately obvious, since water suppresses the dissociation of sulphuric acid; and the rejection of accurate calorimetric latent heats shows that there is at least a case for enquiry here.

Further, Gillespie concludes (*loc. cit.*, p. 2547) that nitromethane undergoes ionization on the basis of its behaviour in a solution containing 0·060M-water (Expt. 33), where it gives a molar depression of 6·57. Yet the molar depression found in Expt. 32 (of which, however, full details are not given—see p. 2482) is 6·25, which is not consistent with the same degree of ionization; and, since the molality of water in the second experiment was 0·04, a variation in k_f with the amount of water added is at once suspected. In support of this conclusion, it is observed that 2 : 4 : 6-trinitrotoluene, which had hitherto always been regarded as a non-electrolyte in these systems, gives a molar depression of 6·65 in a solution containing 0·074M-water (p. 2544). Accordingly, an investigation was undertaken in which these two solutes were regarded as ideal non-electrolytes which would serve as indicators of k_f at various compositions. During the course of this work, valuable corroboration has appeared from Brand, Horning, and Thornley (*J.*, 1952, 1374), who have shown by spectrophotometric methods that 2 : 4 : 6-trinitrotoluene is in fact a non-electrolyte in 100% H_2SO_4. These authors noticed the discrepancy between this and the cryoscopic ν-value but suggested tentatively a solvation hypothesis.

Freezing Points of Nitromethane and TNT *Solutions.*—The molar depressions of the freezing point of sulphuric acid produced by the two solutes nitromethane and 2 : 4 : 6-trinitrotoluene have been determined at compositions round about the maximum. The method used was the same as that of Gillespie, Hughes, and Ingold except that a Beckmann thermometer and a mechanical stirrer protected by a mercury-trap were used in place of the more satisfactory devices of these authors. The same super-cooling correction was also applied, although their factor, 0·012, will obviously need reconsideration.

In Tables 1 and 2, m_2 represents the solute molality, θ the depression of the freezing point from that of the solvent containing the amount of SO_3 or H_2O specified; and k_f values (in deg. mole^{-1} kg.) are calculated simply as θ/m_2. In making these measurements, it was found that, even when conditions were kept constant during crystallization, it was still possible to produce capricious errors, particularly on the SO_3 side of the maximum, where amongst a series of readings agreeing to 0·005° an occasional difference of as much as 0·02° was recorded. Such random values were ignored and, in any case, cannot affect the general character of the results quoted above (especially for the higher molalities); but in view of them k_f values are only recorded to one place of decimals and minor corrections (for variation of ΔH_f with temperature and the effect on the solvent mole-fraction of the third component, *i.e.*, SO_3 or H_2O) were not applied.

TABLE 1.
2 : 4 : 6-*Trinitrotoluene as solute.*

$SO_3 = 0·113m$		
m_2	θ	k_f
0·0325	0·176	5·4
0·0941	0·519	5·5
		5·5

$SO_3 = 0·005m$		
m_2	θ	k_f
0·0210	0·124	5·9
0·0327	0·191	5·8
0·0544	0·322	5·9
0·0812	0·481	5·9
		5·9

$H_2O = 0·23m$		
m_2	θ	k_f
0·0190	0·134	7·1
0·0413	0·280	6·8
0·0757	0·526	6·9
0·0940	0·644	6·9
		6·9

TABLE 2.
Nitromethane as solute.

$SO_3 = 0·054m$		
m_2	θ	k_f
0·0351	0·189	5·4
0·0881	0·481	5·5
0·1524	0·889	5·8
0·1954	1·115	5·7
0·2400	1·388	5·8
		5·6

TABLE 3. *Summary of* k_f *values.*

$[SO_3]$, m	k_f	$\bar{L}$ for H_2SO_4 relative to pure H_2SO_4 (calc.)	$[H_2O]$, m	k	$\bar{L}$ for H_2SO_4 relative to pure H_2SO_4 (calc.)
0·113	5·5	300	0·04 *	6·25	−40
0·054	5·6	250	0·06 *	6·57	−160
0·005	5·9	110	0·074 *	6·65	−190
			0·23	6·9	−280

* Gillespie, Hughes, and Ingold's data (*loc. cit.*).

Conclusions concerning Sulphuric Acid.—Table 3 shows that if these nitro-compounds can be regarded as ideal non-electrolytes, the cryoscopic constant must vary continuously through the range of SO_3–H_2O composition studied. Thus in looking for the type of variation described in Section (1), one of a different type has been found, for there is no sign of the minimum expected from the simple treatment. One feature of importance is, however, that there is no reason to doubt that k_f will lie at about 6·1 in the composition of maximum freezing point, as required by the latent heat of fusion (Brønsted, 2550 cal.; Rubin, 2561 cal.; giving k_f 6·15 and 6·12 respectively).

Table 3 also contains the values calculable from k_f (*via* ΔH_f) of the partial molar heat content of sulphuric acid relative to the pure solvent. Kunzler and Giauque (*J. Amer. Chem. Soc.*, 1952, **74**, 3472) have already pointed out that all the former heat-content data, including those of Brønsted, are unreliable in this region of composition: although Brønsted's data (*Z. physikal. Chem.*, 1909, **68**, 693) show a variation of only 170 cal. in $\bar{L}_1$ for water from 0·0M to 0·5M, yet these authors quote an 8000 cal. change in $\bar{L}_1$ for a change of only 0·07M-water near 100% H_2SO_4. When the data of Table 3 for the solvent are plotted on a graph, they define an S-shaped curve bearing a striking resemblance to Kunzler and Giauque's Fig. 2 (*loc. cit.*, p. 3475), but with the curvature in the opposite direction, as required theoretically. Giauque has not yet published his calculations for $\bar{L}_2$, but it must be admitted that his variations in $\bar{L}_1$ would lead to smaller changes in $\bar{L}_2$ than those recorded in Table 3. On the other hand, the calorimetric determination of these quantities in this region involves experimental difficulties and Kunzler and Giauque actually mention a source of error (*loc. cit.*, p. 3475). It is also possible that the temperature difference may play a part; for the highly associated, or quasi-crystalline, structure near the freezing point (cf. Ubbelohde, *Quart. Reviews*, 1950, **4**, 361) would be somewhat broken down 15° higher. (This would be reflected in a highly detailed C_p curve; cf. Kunzler and Giauque, *loc. cit.*, p. 3476.) The detailed shape of the solvent $\bar{L}$ curve in the immediate neighbourhood of 100% H_2SO_4 is a matter of considerable importance; for if there were not an additional curvature in this region making $\partial\bar{L}/\partial N_s = 0$ when N_s is zero (where N_s refers to the solute mole-fraction), $\bar{L}$ for the solute would be infinite at that point, and this is not possible since μ (the chemical potential) and $(\partial\mu/\partial T)_p$ are both finite for a dissociation product when $N_s = 0$. There is some indication (on the water side) of such a second curvature, but more extensive data are required before this test can be applied with confidence.

It seems likely that accurate k_f or direct ΔH_f measurements may provide the best means of determining $\bar{L}$ in this region, in which connection it may be significant that Table 3 would demand considerably less water contamination during the ΔH_f determinations by Bronsted's precursors than he himself calculated (*loc. cit.*, p. 712). The highly associated structure of sulphuric acid provides a possible explanation for such large heat changes, the $\bar{L}$ data being in the direction expected for structure-breaking by SO_3 and structure-building by H_2O. The low k_f values recorded for sulphuryl chloride and chlorosulphonic acid by Gillespie, Hughes, and Ingold (*loc. cit.*, p. 2481) might also be due to structure-breaking, as their structural similarity to SO_3 suggests. [Ramsay (*J.*, 1894, **65**, 167; *Z. physikal. Chem.*, 1893, **12**, 433) ascribed to H_2SO_4 an association factor of 32, as against 3·8 for H_2O and 1·7 for HNO_3—at room temperature, however.] But further investigations of $\bar{L}$ and k_f changes for other compounds are required before it can be decided how unusual H_2SO_4 is in this respect, and whether the effect found is merely masking or actually displacing variations of the type described in Section (1) (expected from $x_0 \sim 0{\cdot}002$ to be of the order of a few units % in this case).

The behaviour of the nitro-compounds is not the only evidence for a variable k_f. Despite the interionic-attraction effects expected (Brand, Horning, and Thornley, *loc. cit.*), potassium and ammonium sulphates in the anhydrous acid still give greater molar depressions than would be expected from $k_f = 6{\cdot}1$ after suppression of solvent dissociation (Gillespie *et al.*, *loc. cit.*, pp. 2487, 2488). The actual values of T' and k'_f obtained graphically as for nitric acid in Section (2) (the formula of Gillespie *et al.*, p. 2478, being used without assumptions as to solvation) were

K_2SO_4 : $T' = 10{\cdot}62°$, $k'_f = 6{\cdot}48$
$(NH_4)_2SO_4$: $T' = 10{\cdot}54°$, $k'_f = 6{\cdot}17$

It is true that Gillespie *et al.* have used the same data to support $k_f = 5{\cdot}98$, but there are two arguments against this : (*a*) they assumed solvation sufficient to give a constancy in k_f which was far better than anything achieved with sulphuryl chloride; (*b*) they used a fixed value of 10·52° for T' in assessing constancy in the derived k_f values, which is tantamount to investigating the slope of a graph whilst keeping the intercept on the y axis rigidly fixed. This uncertainty in T' weakens the argument advanced by these authors in support of their two forms of dissociation $2H_2SO_4 = H_3SO_4^+ + HSO_4^-$ and $2H_2SO_4 = H_3O^+ + HS_2O_7^-$; for upon the basis of the difference in their values of T' for inorganic sulphates (10·52°) and water (10·62°) they conclude that only the first of these dissociations is suppressed by the addition of bisulphates since the second does not yield HSO_4^-. It is noteworthy that this argument is unsound in any case, as consideration of the connecting equilibrium $H_2SO_4 = H_2O + SO_3$ (or any of its alternative forms, *e.g.*, $2H_2SO_4 = H_3O^+ + HSO_4^- + SO_3$) will show; for any increase in the potential of the water brought about by adding either of its dissociation products must be accompanied by a decrease in the potential of SO_3 ($= \mu_{H_3SO_4^+} + \mu_{HS_2O_7^-}$ in their scheme) : *i.e.*, all forms of dissociation must be suppressed by any of the dissociation products.

This removes an objection to the form of dissociation suggested (for H_2SO_4 as a solute, however) by Stubbs, Williams, and Hinshelwood (*J.*, 1948, 1065), *viz.*, $3H_2SO_4 = HSO_3^+ + H_3O^+ + 2HSO_4^-$, which contains the ionization of SO_3 into HSO_3^+ and HSO_4^-. This form of dissociation would provide a step towards the unification of the theory of oleum solutions, for Brand has already assumed the presence of HSO_3^+ in kinetic studies (*J.*, 1950, 1004) ; it is also obviously analogous to the NO_2^+ dissociation of nitric acid.

Amongst other conclusions from cryoscopic work which now require reconsideration are : the applicability of Raoult's law (in view of the $\bar{L}$ changes), the elimination of interionic-attraction effects by an extremely high dielectric constant, and the incompleteness of the ionization of water.

The Determination of ν-*Values for Solutes.*—When water and hydrogen sulphates are present together as solutes, the disentangling of activity and thermal effects is complicated. The principal use of cryoscopic measurements in sulphuric acid, however, has been in the determination of ν-values (as defined by Gillespie, Hughes, and Ingold), and in this respect the linear relation between molality and freezing point, observed for many compounds in solutions containing a little water, may be utilized in an empirical way despite the probability of its being the fortunate resultant of a number of opposing effects. From the practical point of view, therefore, it is suggested that the following k_f values should be used in this application : they have been derived from a survey of Gillespie's results :

For $\nu \geqslant 2$, $k_f = 6{\cdot}0$, unless water is suspected as a dissociation product, in which case $k_f = 5{\cdot}9$.

For $2 \geqslant \nu \geqslant 1$, $k_f \sim 6{\cdot}6 - (\nu - 1)0{\cdot}6$ (for $m_{H_2O} \sim 0{\cdot}06$, for example). It is stressed that these values are purely empirical and that they should be applied directly to the data, *without any corrections whatsoever* (apart from the practical estimate of the supercooling error) : *i.e.*, $\nu = \theta_{obs.}/k_f m_2$, where $\theta_{obs.}$ is the observed depression from the freezing point of the solvent treated with water. Deviations of 1 or 2% from whole numbers cannot be given any significance since unknown heat effects may be introduced with every new system.

The foregoing discussion shows that in the long controversy over the value of k_f, in which various values ranging from 6 to 7 have been defended, all the authors could have been right for their particular conditions, but were mistaken in regarding it as a constant quantity.

This approach may also have relevance in the study of molten electrolytes, where discrepancies between calorimetric and cryoscopic latent heats are not uncommon.

Acknowledgment is due to Professor C. W. Davies and Dr. M. M. Davies, of Aberystwyth, for valuable comments upon the manuscript, and especially to Dr. A. H. Lamberton, of Sheffield, whose interest in the extent of ionization of urea and urethane in sulphuric acid led the author to examine the cryoscopic method more closely.

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[*Received, November 14th*, 1952.]