

573. *The Thermodynamics of Dissociating Solvents.*

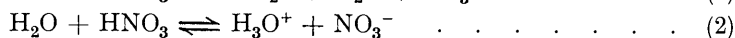
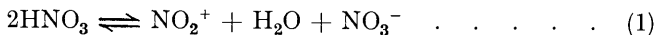
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The thermodynamic properties of solvents which dissociate are examined. It is shown that if a certain species is present in a conventionally pure solvent as a result of dissociation, then no matter how complicated the equilibria may be which involve that species, $(\partial\mu_s/\partial m)_0$ of the solvent is zero. Other consequences of the dissociation are discussed.

It is well known that if the two components of a binary system form a chemical compound in both the liquid and the solid state, then the melting point–composition curve shows a maximum at the stoichiometric point of the compound and that this maximum is more or less rounded, the greater or smaller the degree of dissociation of the compound. Theoretical consideration (H. A. Lorentz in Stortenbeker, *Z. physikal. Chem.*, 1892, **10**, 183; Lewis, *ibid.*, 1908, **61**, 129; Van Laar, *ibid.*, 1909, **66**, 197) has been confined to the discussion of one simple equilibrium between the two components. Recent interest in this topic (Dunning and Nutt, *Trans. Faraday Soc.*, 1951, **47**, 15; Gillespie, *J.*, 1950, 2493; Gillespie, Hughes, and Ingold, *J.*, 1950, 2552) presents the converse problem. A solvent is suspected

of dissociation. The dissociation products are not in the first instance known and they may be interrelated by any number of equilibria. Without a detailed knowledge of the products and the equilibria involved, the former methods of proof are inapplicable. A proof is offered which depends only on the fact that if a certain species is present in the conventionally pure solvent, then $(\partial\mu/\partial m)_0$ of that species is not infinite. This appears in the second part of the paper. In the first part, at the suggestion of Professor E. A. Guggenheim, the approaches of Lewis and of Van Laar are extended to more complicated systems and not only is the proof more satisfactory, but it can be readily extended to any dissociating solvent, provided the products and equilibria are known. It is limited to slightly dissociated solvents.

1. In the first procedure, it is convenient to consider, as an example, the following equilibria in nitric acid :



Quantities referring to the species NO_2^+ , H_2O , NO_3^- , and H_3O^+ will be designated by the subscripts n^+ , h , n^- , and h^+ . In the same way, n_s is the number of moles of the species HNO_3 which are present and is distinct from n_o , the number of moles of conventional nitric acid originally present. Suppose now that n_w moles of water are added to the n_o moles of nitric acid, the following relations apply during the additions ;

$$n_s + 2n_h + 3n_{h^+} = n_o + 2n_w \quad (\text{Hydrogen-atom balance}) \quad \dots \quad (3)$$

$$n_s + n_{n^+} + n_{n^-} = n_o \quad (\text{Nitrogen-atom balance}) \quad \dots \quad (4)$$

$$n_{n^+} - n_{n^-} + n_{h^+} = 0 \quad (\text{Charge balance}) \quad \dots \quad (5)$$

$$2d\mu_s = d\mu_{n^+} + d\mu_h + d\mu_{n^-} \quad (\text{Equilibrium 1}) \quad \dots \quad (6)$$

$$d\mu_h + d\mu_s = d\mu_{h^+} + d\mu_{n^-} \quad (\text{Equilibrium 2}) \quad \dots \quad (7)$$

$$n_s d\mu_s + n_{n^+} d\mu_{n^+} + n_{n^-} d\mu_{n^-} + n_h d\mu_h + n_{h^+} d\mu_{h^+} = 0 \quad (\text{Gibbs-Duhem}) \quad \dots \quad (8)$$

By putting $m_{n^+} = n_{n^+}/n_s$ and $d\mu_{n^+} = RT \log m_{n^+}$, etc., we obtain from (8),

$$d\mu_s + RT(dm_{n^+} + dm_h + dm_{n^-} + dm_{h^+}) = 0 \quad \dots \quad (9)$$

from (6),

$$d\mu_s - \frac{RT}{2} \left(\frac{dm_{n^+}}{m_{n^+}} + \frac{dm_h}{m_h} + \frac{dm_{n^-}}{m_{n^-}} \right) = 0 \quad \dots \quad (10)$$

and from (7),

$$d\mu_s - RT \left(\frac{-dm_h}{m_h} + \frac{dm_{n^-}}{m_{n^-}} + \frac{dm_{h^+}}{m_{h^+}} \right) = 0 \quad \dots \quad (11)$$

Equations (3) and (4) give

$$-dm_{n^+} + 2dm_h - dm_{n^-} + 3dm_{h^+} - 2dm_w = 0 \quad \dots \quad (12)$$

and (5) gives

$$dm_{n^+} - dm_{n^-} + dm_{h^+} = 0 \quad \dots \quad (13)$$

The solution of these is

$$d\mu_s/dm_w = -2RT m_{n^-} m_w / (m_{n^+} m_{n^-} + 4m_h m_{n^+} + m_{n^-} m_{h^+} + m_{n^+} m_h + m_{n^-} m_{h^+} + m_h m_{h^+} + 12m_{n^+} m_{n^-} m_{h^+} + 2m_{n^+} m_h m_{h^+} + 6m_{n^+} m_{n^-} m_h + m_{n^-} m_h m_{h^+}) \quad (14)$$

As m_w approaches zero, m_{n^-} etc. all approach their values in the pure dissociated acid. Since these values are all finite and positive at $m_w = 0$, it is clear that

$$d\mu_s/dm_w \longrightarrow 0 \quad \text{as} \quad m_w \longrightarrow 0 \quad \dots \quad (15)$$

By substituting for m_{n^+} and m_{n^-} , it is easily shown that equation (14) reduces to

$$d\mu_s/dm_w = -2RT \quad \dots \quad (16)$$

when excess of water is present. Under these conditions, the change in chemical potential of the solvent with change in the concentration of added solute is that of a solute which dissociates into two ions.

The relationships (15) and (16) may be used to obtain the dependence of the osmotic properties of these solvents and solutes on the amount of solute added. Hence, it is found from (15) that, if a solvent dissociates, then the addition of one of the dissociation products

(water here) does not initially alter the freezing point. From (16) it is clear that at sufficiently high concentrations of this solute, the freezing point curve follows that predicted from van't Hoff's argument for $i = 2$.

2. The same conclusions follow from another argument. In this no explicit calculations are made in which a knowledge of the equilibria present is necessary; the argument is therefore more general, and only the fact that equilibria are present is used.

We shall assume that a solvent (nitric acid) dissociates into certain species (H_2O , NO_2^+ , etc.). If to n_o moles of conventional nitric acid a small amount n_w moles of water is added, then since the Gibbs free energy G of the system is a homogeneous function of the first degree in n_o and n_w , we obtain

$$n_o d\mu_s + n_w d\mu_h = 0 \quad \dots \quad (17)$$

Equation (17) can also be obtained from (8) by using (3), (4), and (5) to eliminate n_{h+} , n_{h-} , and n_h . There results the equation

$$n_s(2d\mu_s - d\mu_{n+} - d\mu_h - d\mu_{n-}) + n_{h+}(-d\mu_{n+} - 3d\mu_h + d\mu_{n-} + 2d\mu_{h+}) + n_o(d\mu_{n+} + d\mu_h + d\mu_{n-}) + 2n_w d\mu_h = 0$$

and comparison of the parenthetical terms with (6) and (7) then gives (17).

Equation (17) is the Gibbs-Duhem equation in a form which would be used were one unaware of the dissociative process, only the suffixes indicate that a dissociation is under consideration. Now

$$\mu_s = \mu_{s_0} + \int_0^{n_w} \frac{\partial \mu_s}{\partial n_w} \cdot dn_w \quad \dots \quad (18)$$

and by using (17)

$$\mu_s = \mu_{s_0} - \int_0^{n_w} \frac{n_w}{n_o} \frac{\partial \mu_h}{\partial n_w} \cdot dn_w \quad \dots \quad (19)$$

By putting

$$\frac{\partial \mu_h}{\partial n_w} = \left(\frac{\partial \mu_h}{\partial n_w} \right)_0 + \left(\frac{\partial^2 \mu_h}{\partial n_w^2} \right)_0 n_w \quad \dots \quad (20)$$

where the subscript 0 designates the values in pure nitric acid when $n_w = 0$, we now have

$$\mu_s = \mu_{s_0} - \int_0^{n_w} \frac{n_w}{n_o} \left\{ \left(\frac{\partial \mu_h}{\partial n_w} \right)_0 + \left(\frac{\partial^2 \mu_h}{\partial n_w^2} \right)_0 n_w \right\} dn_w \quad \dots \quad (21)$$

$$= \mu_{s_0} - \left(\frac{\partial \mu_h}{\partial n_w} \right)_0 \frac{n_w^2}{2n_o} - \left(\frac{\partial^2 \mu_h}{\partial n_w^2} \right)_0 \frac{n_w^3}{3n_o} \quad \dots \quad (22)$$

The Taylor expansion (20) is permissible only when the solvent dissociates and the expanded quantity ($\partial \mu_h / \partial n_w$ in this case) refers to one of the dissociation products; only in this case are the derivatives at $n_w = 0$ finite.

If we put

$$\mu_h = {}_o\mu_h + RT \log (f_h n_h / \Sigma n) \quad \dots \quad (23)$$

with f_h an activity coefficient and ${}_o\mu_h$ the chemical potential of water in a solution of unit activity, then

$$\left(\frac{\partial \mu_h}{\partial n_w} \right)_0 = RT \left\{ \left(\frac{1}{n_h} \right)_0 - \left(\frac{1}{\Sigma n} \right)_0 \right\} \left(\frac{\partial n_h}{\partial n_w} \right)_0 + RT \left(\frac{\partial \log f_h}{\partial n_w} \right)_0 \quad \dots \quad (24)$$

It is necessary to comment that an alternative expression to (23) might have been chosen; for example,

$$\mu_h = {}_o\mu_w + RT \log [f_w n_w / (n_o + n_w)] \quad \dots \quad (25)$$

However, since the chemical potential of water is finite in pure nitric acid, this means that f_w must become infinite when n_w , the quantity of added water, becomes zero. This is inconvenient, and it is therefore better to choose (23) in which f_h will approach unity as n_h becomes small; of course f_h will probably still not be unity when $n_w = 0$, unless ${}_o\mu_h$ is chosen suitably. If ${}_o\mu_h$ were so chosen, f_h might then be different from unity in solutions where $n_h < (n_h)_0$, for example, in solutions where the dissociation has been suppressed by addition of dinitrogen pentoxide, but this is not a serious disadvantage. In other words, it is not possible to use an infinitely dilute solution of water in nitric acid as the norm, as is

customary.* We will therefore use (23) as the expression for μ_h and choose $o\mu_h$ so that $f_h = 1$ when $n_w = 0$. With this choice it is to be expected that $(\partial \log f_h / \partial n_w)_0$ will be finite, but in most cases it will be small. Equation (24) can then be replaced by the approximation

$$\left(\frac{\partial \mu_h}{\partial n_w}\right)_0 \doteq RT \left(\frac{1}{n_h} \cdot \frac{\partial n_h}{\partial n_w}\right)_0 \dots \dots \dots (26)$$

By referring now to (22), it is seen that $(\partial \mu_s / \partial n_w)_0$ will be zero. The addition of small traces of water to pure nitric acid will not alter its chemical potential, whilst $(\partial^2 \mu_s / \partial n_w^2)_0$, the curvature, will be given by equation (26); that is

$$(\partial \mu_s / \partial n_w)_0 = 0 \dots \dots \dots (27)$$

and

$$\left(\frac{\partial^2 \mu_s}{\partial n_w^2}\right)_0 \doteq \frac{RT}{n_o} \left(\frac{1}{n_h} \cdot \frac{\partial n_h}{\partial n_w}\right)_0 \dots \dots \dots (28)$$

To assess the significance of (28) the influence of the terms on the right may be examined; if the degree of dissociation is small $(1/n_h)_0$ will be large and $(\partial n_h / \partial n_w)_0$ will be just less than unity. Hence the curvature of the μ_s - n_w function at $n_w = 0$ will be large. On the other hand, if the degree of dissociation is large $(1/n_h)_0$ will be smaller and $(\partial n_h / \partial n_w)_0$ will be much less than unity, and so the curvature will be small.

If now, instead of water, n_p moles of dinitrogen pentoxide had been added to the pure nitric acid, instead of (17) there would be obtained

$$n_o d\mu_s + n_p (d\mu_{n^+} + d\mu_{n^-}) = 0 \dots \dots \dots (29)$$

on the assumption that the pentoxide dissociates into NO_2^+ and NO_3^- ions. Whence,

$$\mu_s = \mu_{s_0} - \left(\frac{\partial[\mu_{n^+} + \mu_{n^-}]}{\partial n_p}\right)_0 \cdot \frac{n_p^2}{2n_o} - \frac{\partial^2(\mu_{n^+} + \mu_{n^-})}{\partial n_p^2} \cdot \frac{n_p^3}{3n_o} \dots \dots \dots (30)$$

If complete ionization of the dinitrogen pentoxide is assumed, the curvature is given by

$$\left(\frac{\partial[\mu_{n^+} + \mu_{n^-}]}{\partial n_p}\right)_0 = RT \left\{ \frac{n_{n^+} + n_{n^-}}{n_{n^+} n_{n^-}} - \frac{2}{\Sigma n} \right\} \left(\frac{\partial[n_{n^+} + n_{n^-}]}{\partial n_p}\right)_0 + RT \left(\frac{\partial \log f_{n^+} f_{n^-}}{\partial n_p}\right)_0 \quad (31)$$

If only the simple dissociation (1) is considered, $(n_{n^+})_0 = (n_{n^-})_0 = (n_h)_0$; comparison of (31) with (24) then shows that the curvature of the μ_s - n_p function at $n_p = 0$ will be about twice that of the μ_s - n_w curve at $n_w = 0$. The additional equilibrium (2) complicates the issue, but there is another clue to the dissociation of the pentoxide. When the amount of added water or dinitrogen pentoxide greatly exceeds the amounts of the species present in the pure acid, that is, when

$$n_w \gg (n_h)_0 \text{ or } n_p \gg (n_{n^+})_0 \text{ and } (n_{n^-})_0,$$

then

$$n_w \simeq n_h \text{ or } n_p \simeq n_{n^+} \text{ and } n_{n^-}$$

and equations (17) and (29) become

$$n_o \partial \mu_s / \partial n_h + n_h \partial \mu_h / \partial n_h = 0 \dots \dots \dots (32)$$

and

$$2n_o \partial \mu_s / \partial n_{n^-} + n_{n^-} \partial(\mu_{n^+} + \mu_{n^-}) / \partial n_{n^-} = 0 \dots \dots \dots (33)$$

These are the equations of the asymptotes which the μ_s - n_w or μ_s - n_p curves approach as n_s or n_w increases, and they are the conventional relations for non-dissociating and binary dissociating solutes, respectively. By examining the limiting behaviour for relatively large additions of dinitrogen pentoxide, a decision can be made regarding dissociation. Should there be additional equilibria such as



and



the disentangling becomes more difficult. The experimental data would have to be accurate to the third order of differentiability, and deviations due to the non-ideality would become significant.

* The best procedure for detailed calculations would be to refer the chemical potentials of water in the solutions and in the pure acid to the μ_w^0 of the water vapour. This procedure would, however, complicate the present discussion.

Considering now the addition of an inert solute C to the pure nitric acid, it will be clear by analogy with the preceding discussion that a normal behaviour is to be expected, since for an inert solute $\partial\mu_c/\partial n_c$ becomes infinite as n_c approaches zero. Hence in such solutions μ_s will decrease linearly with n_c in the manner usual for dilute solutions.

Let us consider finally the addition of a solute such as potassium nitrate, which dissociates into one ion, K^+ , which is inert, and another, NO_3^- , which takes part in the equilibrium. For this case

$$n_o \partial\mu_s/\partial n_k + n_k \partial(\mu_k + \mu_{n-})/\partial n_k = 0 \quad . \quad . \quad . \quad (36)$$

and it can be shown that

$$\mu_s = \mu_{s_0} - \frac{RT}{n_o} \left(n_k - \frac{n_k^2}{2\Sigma n} + \int_0^{n_k} \frac{\partial \log f_k}{\partial \log n_k} \cdot dn_k \right) - \left(\frac{\partial \mu_{n-}}{\partial n_k} \right)_0 \frac{n_k}{2n_o} - \left(\frac{\partial^2 \mu_{n-}}{\partial n_k^2} \right)_0 \frac{n_k^3}{3n_o} \quad (37)$$

Expression (37) indicates that the limiting slope of the μ_s - n_k curve for a solute such as potassium nitrate is finite, and the tangent at $n_k = 0$ has a slope equal to that of a normal solute. In other words, at the origin the NO_3^- ion is ineffective and only the K^+ ion has influence. Hence, over a limited range of concentration, potassium nitrate would *appear* to be undissociated and only at higher concentrations would it behave as a dissociated electrolyte.

These results show that, however complicated the dissociation of a solvent may be, the addition of one of the dissociation products does not initially alter the chemical potential of the solvent. The curvature at the origin gives some indication of the amount of that species already present as a result of the dissociation. This curvature is enhanced if the added material itself dissociates on addition and all its products take part in the dissociation of the solvent. When the added material dissociates into x and y particles, of which x take part in the dissociation of the solvent and y do not, then the initial slope of the μ_s -concentration curve is $-yRT$.

For higher concentrations of added material, the dissociation of the solvent is suppressed and the rate of change in chemical potential with concentration approaches normal behaviour.

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