Partial Molar Quantities at Infinite Dilution in Dissociating Solvents.

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Gibbs's discussion of chemical potentials at infinite dilution is applied directly to dissociating solvents, for which the result $(\partial\mu_1/\partial m_2)_0 = 0$, discussed by Dunning and Dunning (*J.*, 1952, 2993), follows immediately (m_2 refers to a dissociation product). An alternative demonstration of this theorem, making direct reference to dissociation equilibria, and yet avoiding the limitations of Dunning and Dunning's methods, is also described. The formula $(\partial\overline{X}_1/\partial m_2)_0 = 0$ applies generally to the other common partial molar quantities, and the curvature of the rate of change of any of these quantities at the composition of the pure solvent is given by the expression $m_1(\partial^2\overline{X}_1/\partial m_2{}^2)_0 = -(\partial\overline{X}_2/\partial m_2)_0$.

IN a paper on the thermodynamics of dissociating solvents (*J.*, 1952, 2993), Dunning and Dunning discuss the effects of complex forms of dissociation upon the proof that $(\partial\mu_1/\partial m_2)_{T, P, m_1} = 0$ when $m_2 = 0$ (the suffixes 1 and 2 referring respectively to the solvent and to a solute which is a product of the dissociation of the solvent). This part of their paper invites comment for two reasons. First, it may give the misleading impression that specific reference to involved equations referring to complex equilibria is necessary to establish the general validity of the result that $(\partial\mu_1/\partial m_2) = 0$ when $m_2 = 0$. Secondly, one of their methods of obtaining this result (*loc. cit.*, p. 2995) seems to be open to criticism, since to make the assertion at any stage of the proof that $(\partial\mu_2/\partial m_2)$ is not infinite when $m_2 = 0$ is, by the Gibbs–Duhem equation (1) equivalent to asserting that

$$m_1(\partial\mu_1/\partial m_2) + m_2(\partial\mu_2/\partial m_2) = 0 \quad \cdots \cdots \quad (1)$$

$(\partial\mu_1/\partial m_2)_0 = 0$ which is what is to be proved. It would seem therefore that either such an assertion should be avoided or, if it is regarded as self-evident, a direct appeal should be made to (1) to establish that $(\partial\mu_1/\partial m_2)_0 = 0$ before proceeding to the useful discussion of the second derivative to examine the extent of the curvature of the function of μ_1 with m_2.

Gibbs's Method.—Such a simple result as that required seems, however, to demand a much more direct proof, and it is curious that Gibbs's relevant discussion should have been ignored by later writers. Gibbs ("Collected Works," Vol. I, Longmans Green, New York, 1928, p. 111) first establishes that for stability with regard to continuous changes μ_i must be an increasing function of m_i, and then shows that $(\partial\mu_1/\partial m_2)$ must be zero when $m_2 = 0$ " if m_2 is capable of negative as well as positive values " (*op. cit.*, p. 135). This argument is quite general and independent of any chemical reactions in the solution; and the example

discussed by Gibbs, namely the addition of water to a salt hydrate (*op. cit.*, p. 136), could equally well have involved the hydrate of dinitrogen pentoxide Once this argument is accepted, the more complicated discussions by later writers seem only to verify the internal consistency of the equations used to characterize the chemical equilibria involved.

An Alternative Demonstration making Direct Mention of Chemical Equilibria.—The alternative argument which follows is free from the restriction of Dunning and Dunning's first method (*loc. cit.* p. 2994) since it is not limited to slightly dissociated solvents.

Let S be a dissociating solvent for which the dissociation equilibrium can be represented by the chemical equation

$$i\text{A} + j\text{B} + k\text{C} \ldots \ldots \ldots \rightleftharpoons \text{S} \qquad \qquad (2)$$
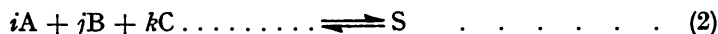
where i, j, k refer to the numbers of molecules of A, B, C, . . . formed by the dissociation of one molecule of S : they may be simple fractions when necessary (*e.g.*, $\frac{1}{2}\text{H}_2\text{O} + \frac{1}{2}\text{N}_2\text{O}_5 \rightleftharpoons$ HNO_3).   The products A, B, C, . . . may themselves dissociate further to any extent (even completely) since the argument is only concerned with the partial molar free energy of the substance A, etc., as it exists in the solction.   The condition of chemical equilibrium gives :

$$i\text{d}\mu_\text{A} + j\text{d}\mu_\text{B} + k\text{d}\mu_\text{C} \ldots \ldots = \text{d}\mu_\text{S} \qquad \qquad (3)$$

Variations in the quantity of the dissociation product A only being considered :

$$i(\partial\mu_\text{A}/\partial m_\text{A}) + j(\partial\mu_\text{B}/\partial m_\text{A}) + k(\partial\mu_\text{C}/\partial m_\text{A}) \ldots = (\partial\mu_\text{S}/\partial m_\text{A}) \qquad (4)$$

We note that the equations (3) and (4) will in fact hold even if the solvent is completely dissociated since the removal of 1 mole of S from the solution would involve the same operation as the removal of i moles A + j moles B + etc.

The solution may also be regarded in terms of the dissociation products as thermo-dynamic components; the Gibbs–Duhem equation will then apply in the following form :

$$m_\text{A}(\partial\mu_\text{A}/\partial m_\text{A}) + m_\text{B}(\partial\mu_\text{B}/\partial m_\text{A}) + m_\text{C}(\partial\mu_\text{C}/\partial m_\text{A}) + \ldots = 0 \qquad (5)$$

Now as the composition of the pure solvent is approached, the ratio $m_\text{A} : m_\text{B} : m_\text{C} \ldots$ will approach the ratio $i : j : k \ldots$ and at the exact composition of S, the left-hand sides of equations (4) and (5) will become identical (apart from an unimportant arbitrary multiplier) whatever the values of the individual differential coefficients.   Hence it follows that the right-hand side of (4), namely $(\partial\mu_\text{S}/\partial m_\text{A})$, must be identical with the right-hand side of (5), *i.e.* zero.   The same obviously applies also to $(\partial\mu_\text{S}/\partial m_\text{B})$, etc.   This demonstration will hold for a dissociating solvent which is a compound of any number of components and is dissociated to any extent.

Ionic species of dissociation products present no special difficulty in either of the above methods when the electroneutrality condition is obeyed (Guggenheim, " Modern Thermo-dynamics," Methuen, London, 1933, p. 133; or " Thermodynamics, 2nd Ed., North-Holland Publishing Co., Amsterdam, 1950, pp. 296, 330).   Thus on the addition of potassium nitrate to nitric acid, for example, the nitrate ion, being capable of positive and negative increments (subject to the condition of electroneutrality), will have no effect initially on the chemical potential of the solvent; whilst the potassium ion, being capable of only positive increments, will produce an initial effect similar to that of a foreign non-electrolyte.

Curvature of the Solvent Potential–Composition Function at Infinite Dilution.—It is possible to express the curvature of function of the solvent chemical potential and other partial molar quantities with composition in a simple, yet exact, form in the neighbourhood of the pure solvent composition.

Further differentiation of equations (4) and (5) with respect to m_A, and elimination of the terms $(\partial^2\mu_i/\partial m_i{}^2)$ after multiplication of the derivative of (4) by $\alpha = m_\text{A}/i = m_\text{B}/j$, etc., yields, when $m_\text{A} : m_\text{B} : m_\text{C} \ldots = i : j : k \ldots$:

$$\alpha(\partial^2\mu_\text{S}/\partial m_\text{A}{}^2) = -(\partial\mu_\text{A}/\partial m_\text{A}) \qquad \qquad (6)$$

By changing the notation and regarding the solvent as component 1 and the solute (a dissociation product of 1) as component 2, we may differentiate equation (1) and obtain :

$$m_1(\partial^2\mu_1/\partial m_2{}^2) = -(\partial\mu_2/\partial m_2) - m_2(\partial^2\mu_2/\partial m_2{}^2) \quad \ldots \ldots \quad (7)$$

Equation (7), unlike equation (6) which refers only to the composition of the pure solvent, is quite general and exact. Comparison with equation (6), however, shows that, when $m_2 = 0$, $(\partial^2\mu_2/\partial m_2{}^2)$ cannot be infinite (which could clearly have been deduced in other ways) ; so that at $m_2 = 0$ (represented by suffix 0) :

$$m_1(\partial^2\mu_1/\partial m_2{}^2)_0 = -(\partial\mu_2/\partial m_2)_0 \quad \ldots \ldots \ldots \quad (8)$$

Since μ_2 is an increasing function of m_2, $\partial\mu_2/\partial m_2$ is positive and (8) therefore formally shows μ_1 to be at a maximum. (The identification of equations (6) and (8) rests, of course, on the fact that differential coefficients with respect to changes in the mass of a given substance are independent of the choice of the other components in the system, as explained by Gibbs, *op. cit.*, p. 92—93.) Dunning and Dunning's equation (28) is an approximate, special form of equation (8); and a similar argument to theirs relating the curvature expressed by equation (8) to the degree of dissociation obviously follows. For if the potential depends roughly logarithmically upon the actual quantity of A present, there will obviously be a larger increment in μ_2 per mole of A added when there is a small amount of A in the pure solvent (slightly dissociated) than when there is a large amount (highly dissociated).

Other Partial Molar Quantities.—The condition that $(\partial\mu_1/\partial m_2)_0 = 0$ is clearly independent of the temperature and pressure provided that these remain constant during the differentiation. Therefore

$$\partial/\partial T(\partial\mu_1/\partial m_2)_0 = \partial/\partial m_2(\partial\mu_1/\partial T)_0 = -(\partial\bar{S}_1/\partial m_2)_0 = 0 \quad \ldots \quad (9)$$

and

$$\partial/\partial P(\partial\mu_1/\partial m_2)_0 = -(\partial\bar{V}_1/\partial m_2)_0 = 0 \quad \ldots \ldots \ldots \quad (10)$$

Also, since $\mu_1 = \bar{H}_1 - T\bar{S}_1$:

$$(\partial\bar{H}_1/\partial m_2)_0 = 0 \quad \ldots \ldots \ldots \quad (11)$$

Differentiation of (11) with respect to temperature also gives

$$(\partial\bar{C}p_1/\partial m_2)_0 = 0 \quad \ldots \ldots \ldots \quad (12)$$

Thus, all the common partial molar quantities of a dissociating solvent in mixtures involving only dissociation products are of Lewis and Randall's " first type " (" Thermodynamics, etc.," McGraw Hill, 1923, p. 44).

By similar methods the second differential coefficients can all be shown to follow the same pattern as for the solvent potential (8), *i.e.* :

$$m_1(\partial^2\bar{X}_1/\partial m_2{}^2)_0 = -(\partial\bar{X}_2/\partial m_2)_0 \quad \ldots \ldots \quad (13)$$

where X represents any partial molar quantity. Whether equation (13) represents a maximum or a minimum in $\bar{X}_1$ depends upon the characteristics of the dissociation process. If the solutions can be regarded as ideal when the dissociation has been allowed for, $\bar{H}_1$ will be given approximately by $\bar{H}_1' + x\Delta H_d$, where $\bar{H}_1'$ is the solvent partial molar heat content when the dissociation is completely suppressed, x the fractional extent of dissociation, and ΔH_d the heat of dissociation. (The cryoscopic implications of this formulation have been discussed in an earlier paper; Wyatt, *J.*, 1953, 1175.) Thus whether equation (13) represents a maximum or a minimum in $\bar{H}_1$ depends upon whether the dissociation is endothermic or not; and corresponding arguments apply to the other partial molar quantities, which can be formulated similarly, *e.g.* $\bar{V}_1 = \bar{V}_1' + x\Delta V_d$. The possibility of a point of inflection in $\bar{H}_1$, etc., does not seem to be absolutely excluded, since it is possible to imagine an addition compound's having a heat of dissociation of zero at the composition

of the pure compound, and yet having dissociation products which cause thermal non-ideality of opposite signs on opposite sides of this composition. In general, however, $\bar{H}_1$ would be expected to exhibit a maximum or a minimum, and $\bar{H}_2$ would then have the characteristic S-shaped curve found by Kunzler and Giauque for water in sulphuric acid (*J. Amer. Chem. Soc.*, 1952, **74**, 3472), since it follows from the analogue of equation (1), and the value of $(\partial \bar{H}_2/\partial m_2)_0$, that when m_2 is positive $\bar{H}_1$ and $\bar{H}_2$ will vary in opposite directions, whilst when m_2 is negative $\bar{H}_1$ and $\bar{H}_2$ will vary in the same direction. [The author's former discussion of partial molar heat contents in sulphuric acid (*loc. cit.*, p. 1178) was in error on this point, and the cryoscopic behaviour of non-electrolytes in this solvent therefore seems to demand a less simple explanation than that involving a variable cryoscopic constant; cf. Wyatt, *J.*, 1954, 2647.]

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