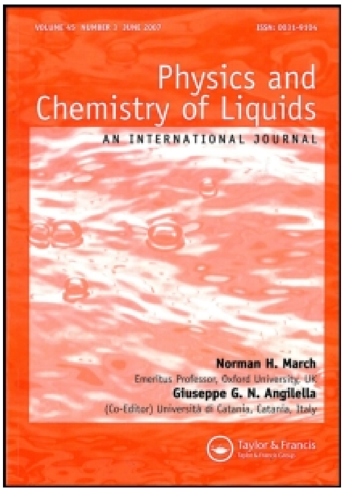

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Thermodynamics and Osmosis: A Comment on the Papers of Hammel

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Thermodynamics and Osmosis: A Comment on the Papers of Hammel

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In recent volumes of this Journal, Hammel[1–3] has put forward new thermodynamic arguments in defence of the old solvent tension theory of osmosis. However, as I shall try to demonstrate, Hammel's radical contention is incorrect and the rest of his arguments goes by default.

When a solution of solute B in solvent A is in osmotic equilibrium with the pure solvent, at constant temperature, we have

$$\mu_A^*(T, p) = \mu_A(T, p + \pi, x_A), \tag{1}$$

where π is designated the osmotic pressure of the given solution and the other symbols have the usual meaning. In short, Hammel tried to show that equality (1) is extensible to other partial molar properties of the solvent, namely, to $\bar{V}_A(T, p)$ and to $\bar{S}_A(T, p)$, the partial molar volume and the partial molar entropy, respectively.

For the sake of argumentation, Hammel's crucial reasoning is quoted in full (Ref. 1, footnote 3, except for differences in notation): "*Consider that the pressure applied to pure solvent is p and that the chemical potentials of the solution solvent and pure solvent are equalized by a pressure p + π′ applied to the solution, so that at T*

$$\mu_A(T, p + \pi', x_A) = \mu_A^*(T, p). \tag{i}$$

Next, consider that the pressure applied to the same solution is p and that a pressure p − π is applied to the pure solvent to equate the chemical potentials of the solution solvent and pure solvent, so that at T

$$\mu_A(T, p, x_A) = \mu_A^*(T, p - \pi). \tag{ii}$$

It might perhaps be thought, at first sight, that $\pi' = \pi$ only if the solution were ideal. Suppose that a pressure π' is added to both pressures in Eq. (ii), so that

$$\mu_A(T, p + \pi', x_A) = \mu_A^*(T, p - \pi + \pi'). \tag{iii}$$

Then according to Eq. (i), $\pi' - \pi$ must equal zero, that is $\pi' = \pi$ for every solution. The osmotic pressure of the solvent in any solution is always π, the difference in pressures applied to the solution and pure solvent for which the chemical potentials of solution solvent and pure solvent are equal".

Notwithstanding this, it can be readily proved that, in general, $\pi \neq \pi'$. For the osmotic pressure is a function of T, p *and* x_A. Thus, at constant T, if the composition of the solution is unaltered, the osmotic pressure of the solutions in instances (i) and (ii) should be different, because there is a change in pressure: $p + \pi' \neq p$. Hammel has overlooked that, if '*a pressure π' is added to both pressures in Eq. (ii)*', we have either a change in composition in the case of solution and pure solvent being separated by a membrane permeable to the solvent, leading to

$$\mu_A(T, p + \pi', x'_A) = \mu_A^*(T, p - \pi + \pi'),$$

or, otherwise,

$$\mu_A(T, p + \pi', x_A) \neq \mu_A^*(T, p - \pi + \pi'),$$

but never equality (iii).

As a consequence,

$$\int_p^{p+\pi} \bar{V}_A(T, p', x_A)\, dp' \neq \int_{p-\pi}^{p} V_A^*\, dp'$$

and Eq. (5) in both Refs. 1 and 2 are also false. According to Hammel,[1,2] $\bar{V}_A(T, p + \pi, x_A)$ should be equal to $V_A^*(T, p)$. It can be easily shown that this is not true, even for ideal solutions. For, in this case, $\bar{V}_A(T, p + \pi, x_A)$ must be equal to $V_A^*(T, p + \pi)$. Obviously, only for an incompressible solvent would $V_A^*(T, p + \pi)$ equal $V_A^*(T, p)$.

Lastly, and for the same reason, the '*exact relationship between compressibility of solution and compressibilities of its pure constituents*' obtained by Hammel,[3] is a null relation, that is, it is only valid for incompressible constituents and solution. The correct relationship has been derived by March;[4] it contains additional terms which make allowance for the pressure dependence of the osmotic pressure at constant temperature and composition.

Apart from these criticisms, I feel sympathetic with some of Hammel's views. In particular, a complete treatment of the thermodynamics of solutions in osmotic equilibrium is still lacking, even not forgetting the works of Friedman[5] and of Kodýtek.[6] I hope to contribute to it in the near future with the help of a new kind of partial molar properties, those specified for constant temperature and solvent chemical potential. They are based on a generalizaton[7] of the concept of a partial molar property and are defined by

$$\bar{X}_{\mathbf{B}}(T, \mu_{\mathbf{A}}) = (\partial X/\partial n_{\mathbf{B}})_{T,\mu_{\mathbf{A}},n''},$$

where X is any extensive thermodynamic property of the phase, and n' indicates that all n are held constant apart from $n_{\mathbf{B}}$. They comply with the condition

$$X = \sum_{\mathbf{B}} n_{\mathbf{B}} \bar{X}_{\mathbf{B}}(T, \mu_{\mathbf{A}}),$$

the summation running over all the components, A included.

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