Topic0250

Apparent Molar Properties: Solutions: Background

A given solution, volume V, is prepared using n_1 moles of solvent (e.g. water) and n_j moles of solute, chemical substance j.

Thus $$V(aq) = n_1 \cdot V_1(aq) + n_j \cdot V_j(aq) \qquad (a)$$

Here $V_1(aq)$ is the partial molar volume of the solvent and $V_j(aq)$ is the partial molar volume of the solute-j [1]. Experiment yields the density of this solution at defined T and p. In order to say something about this solution we would like to comment on the two partial molar volumes, $V_1(aq)$ and $V_2(aq)$. But we have only three known variables; the amounts of solvent and solute and the density. If we change the amount of, say, solute then V(aq) together with the two partial molar volumes change. So we end up with more unknowns than known variables. Hence it would appear that no progress can be made. All is not lost. Equation (a) is rewritten in terms of the molar volume of the solvent, $V_1^*(\lambda)$ which is calculated from the density of the pure solvent and its molar mass. At a given T and p, density $\rho_1^*(\lambda) = M_1 / V_1^*(\lambda)$. We replace $V_j(aq)$ in equation (a) by the apparent molar volume, $\phi(V_j)$; equation (b) .

$$V(aq) = n_1 \cdot V_1^*(\lambda) + n_j \cdot \phi(V_j) \qquad (b)$$

Now we have only one unknown variable. But we anticipate that the apparent molar volume $\phi(V_j)$ depends on the composition of the solution, the solute, T and p.

These comments concerning partial molar volumes establish a pattern which can be carried over to other partial molar properties. The following apparent molar properties of solutes are important; (i) apparent molar enthalpies $\phi(H_j)$, (ii) apparent molar isobaric heat capacities $\phi(C_{pj})$, (iii) apparent molar isothermal compressions $\phi(K_{Tj})$, and (iv) apparent molar isobaric expansions $\phi(E_{pj})$. Apparent molar (defined) isentropic compressions $\phi(K_{Sj};def)$, and apparent molar (defined) isentropic expansions $\phi(E_{Sj};def)$ are also quoted but new complexities emerge.

Lewis and Randall commented [2] that 'apparent molal quantities have little thermodynamic utility', a statement repeated in the second [3] but not in the third edition of this classic monograph.[4] Suffice to say, their utility in the analysis of experimental results has been demonstrated by many authors.

Apparent molar properties of solutes $\phi(E_{pj})$, $\phi(E_{Sj};def)$, $\phi(K_{Tj})$, $\phi(K_{Sj};def)$ and $\phi(C_{pj})$ are calculated using in turn the extensive properties of solutions, isobaric expansions E_p, isentropic expansions E_S, isothermal compressions K_T, isentropic compressions K_S and isobaric heat capacities C_p.

Footnotes

[1] Equation (a) is interesting . We do not have to add the phrase 'at constant temperature and pressure'

[2] G. N. Lewis and M. Randall, Thermodynamics and The Free Energy of Chemical Substances, McGraw-Hill, New York, 1923. [The title on the front cover of the monograph is simply 'Thermodynamics'.]

[3] G. N. Lewis and M. Randall, Thermodynamics, revised by K. S. Pitzer and L. Brewer, McGraw-Hill, New York, 2nd. edn. 1961, p. 108.

[4] K. S. Pitzer, Thermodynamics, McGraw-Hill, New York, 3d. edn., 1995.