Extrathermodynamics; Background

Essentially thermodynamics is used to analyse experimental data. In these terms, thermodynamics shows how properties of systems are related and how one can link measured properties with important thermodynamic variables. Nevertheless, there are cases where a pattern seems to emerge from measured variables which is not a consequence of the laws of thermodynamics. Furthermore, it is often discovered that the patterns can actually be accounted for if one or two additional postulates are made. These new postulates are therefore extra-thermodynamic and the analytical method is called extrathermodynamics [1,2]. The analysis has merit in that the new postulates point to patterns which can be developed for other systems.

The essence of the argument can be understood by considering the molar volume of pure ethanol at ambient pressure and 298.2 K. Clearly $V^*(C_2H_5OH; \ell; 298.2 K; 101325 N m^{-2})$ is a properly defined thermodynamic variable. But as chemists we might be tempted to explore an extrathermodynamic postulate in which $V^*(C_2H_5OH; \ell)$ can be subdivided into group contributions. Thus $V^*(C_2H_5OH; \ell) = V(CH_3) + V(CH_2) + V(OH)$ (a)

This equation cannot be justified on thermodynamic grounds. Nevertheless we might examine molar volumes of several (liquid) alcohols at the same T and p and come up with a self-consistent set of group volumes. For example, $[V^*(n-C_3H_7OH; \ell)] = V(CH_3) + 2*V(CH_2) + V(OH)$ (b)

Hence comparison of equations (a) and (b) yields directly $V(CH_2)$, the contribution of methylene groups to the molar volume of (liquid) alcohols at the same T and p. Although such an analysis might be judged naïve, the general approach finds merit in several subject areas; e.g. chemical equilibria and chemical kinetics.

Footnotes
