Topic 2925

Variables: Gibbsian and Non-Gibbsian

Experience shows that the thermodynamic state of a closed single phase system can be defined by a minimum set of independent variables where at least one variable is a measure of the 'hotness' of the system; e.g. temperature. The volume of an aqueous solution containing n_1 moles of water and n_j moles of urea is defined by the set of independent variables, T, p, n_1 and n_j.

$$V = V[T, p, n_1, n_j] \qquad (a)$$

Having defined the parameters set out in the brackets [...] the volume of the system, the dependent variable, is uniquely defined. In fact we can replace V in this equation by G, H and S in order to define unique Gibbs energy, enthalpy and entropy respectively.

The set of independent variables in equation (a) is called Gibbsian because the set comprises the intensive variables T and p together with the extensive composition variables [1]. The general form of equation (a) defining the thermodynamic potential function, Gibbs energy G is as follows where ξ is the extensive composition variable.

$$G = G[T, p, \xi] \qquad (b)$$

Other sets of independent variables are used in conjunction of the thermodynamic potential functions, enthalpy H, energy U and Helmholtz energy F.

$$F = F[T, V, \xi] \qquad (c)$$

$$U = U[S, V, \xi] \qquad (d)$$

$$H = H[S, p, \xi] \qquad (e)$$

In equations (c) and (d), V is an extensive variable and in equations (d) and (e) S is an extensive variable. The sets of independent variables in equations (c), (d) and (e) are called non-Gibbsian [1].

Footnote

[1] J. C. R. Reis, M. J. Blandamer, M. I. Davis and G. Douhéret, Phys. Chem. Chem. Phys., 2001, **3**, 1465.