

# Nonelectrolyte Solutions: Theory and Applications to Model Systems

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Thermodynamics is one of the foundations of science and represents an essential part of many fields, such as chemistry, physics, chemical engineering, biophysics, earth and environmental science, materials science and biotechnology [1]. This highly formalized scientific discipline is of enormous generality and provides a mathematical framework of equations, and a few inequalities, which yield *exact relations* between macroscopically observable thermodynamic equilibrium properties of matter and *restrict the course* of any natural process. After indicating key concepts associated with the energy-based fundamental property relation [2],

$$d(nU) = Td(nS) - Pd(nV) + \sum_i \mu_i dn_i,$$

when changing over to  $T$ ,  $P$  and  $\{n_i\}$  as *measurable* canonical variables describing  $PVT$ -systems, the differential equations of central interest for *multicomponent nonelectrolyte solutions* are

$$d\left(\frac{nG}{RT}\right) = -\frac{nH}{RT^2}dT + \frac{nV}{RT}dP + \sum_i \frac{\mu_i}{RT}dn_i,$$

and

$$d(nH) = (nC_P)dT + (nV)(1 - \alpha_P T)dP + \sum_i H_i dn_i.$$

Here,  $\mu_i \equiv \left[\partial(nG)/\partial n_i\right]_{T,P,n_{j \neq i}} = G_i$  is the chemical potential/partial molar Gibbs energy, and

$H_i \equiv \left[\partial(nH)/\partial n_i\right]_{T,P,n_{j \neq i}}$  is the partial molar enthalpy associated with component  $i$  (all symbols

have their usual significance). An overview of *molar property changes on mixing*

$$\Delta M(T, P, \{x_i\}) \equiv M(T, P, \{x_i\}) - \sum_i x_i M_i^*(T, P),$$

and of *molar excess properties of mixtures*

$$M^E(T, P, \{x_i\}) \equiv M(T, P, \{x_i\}) - M^{\text{id}}(T, P, \{x_i\})$$

will be presented [2,3], where  $M$  denotes the actual molar value of any extensive thermodynamic property,  $M_i^*$  is the pure-species molar property value of  $i$ , and  $M^{\text{id}}$  is the molar property value calculated for an *ideal* solution (id) at the same  $T$ ,  $P$  and  $\{x_i\}$ . Such an ideal solution is most frequently based on the *Lewis-Randall* (LR) rule or, when the focus is on *dilute* solutions, on *Henry's law*. Selected correlating equations describing the composition dependence of  $M^E = G^E$  (and related properties, such as LR-based activity coefficients) and  $M^E = H^E$  for liquid binaries will be discussed, followed by a few popular models applicable to liquid multicomponent systems [3-5], such as *generalized Kohler* equations [6]. Liquid water is of pivotal importance for the structure, the stability, and the dynamics of proteins and other biomolecules [7], and properties of aqueous solutions, especially of *dilute aqueous solutions*, are of considerable theoretical as well as practical interest. Thus, as final topic, I'll show that by using experimental high-precision data (in conjunction with judiciously determined auxiliary thermophysical properties), previously reported (apparent) differences between *calorimetrically* obtained results on *enthalpy changes on solution* and *heat capacity changes on solution* of nonreactive *gases* in liquid water [4,8] and results obtained via *van't Hoff-type analysis* [3,4] of VLE data, that is, essentially  $VH_2^\infty$  and  $VC_{P,2}^\infty$ , can be reconciled: this supports studies suggesting that differences reported in the literature (larger than experimental uncertainties) presumably result for statistical reasons and *not* from physical causes [9].

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