

Caloric and Volumetric Properties of Dilute Nonelectrolyte Solutions

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Most of this review will focus on *dilute* liquid (L) binary nonelectrolyte solutions, *i. e.* on solutions where one component, called the *solute*, is present in much smaller quantity than the other component, called the *solvent*. When considering only molecular interactions with nearest neighbors, a rough estimate of the dilute region is provided by $x_2 < 0.01$ (where x_2 denotes the solute mole fraction), with the properties in the limit of *infinite dilution* (designated by a superscript ∞) being of particular interest. The importance accorded the measurement, correlation and prediction of high-dilution properties needs little elaboration. For instance, infinite-dilution activity-coefficients are used to characterize solution behavior and provide binary parameters for several popular solution models. In addition to practical aspects, high-dilution properties are also of considerable theoretical interest since the essential absence of solute-solute interactions facilitates the discussion of *solute-solvent* interactions vis-à-vis the dominant background of solvent-solvent interactions. The key quantity here is the Henry fugacity $h_{2,1}(T, P)$, also known as Henry's law constant, which depends on temperature T as well as on pressure P [1]. Its temperature dependence yields information on the partial molar enthalpy change on solution ΔH_2^∞ (with respect to the pure-substance (*) perfect-gas (pg) property), *i.e.*

$$\left(\partial \ln h_{2,1} / \partial T\right)_P = -\Delta H_2^\infty / RT^2 \equiv -\left[H_2^{L\infty}(T, P) - H_2^{pg*}(T)\right] / RT^2,$$

and hence on the partial molar heat capacity change on solution [2]

$$\left(\partial \Delta H_2^\infty / \partial T\right)_P = \Delta C_{P,2}^\infty \equiv \left[C_{P,2}^{L\infty}(T, P) - C_{P,2}^{pg*}(T)\right],$$

while its pressure dependence is given by [3]

$$\left(\partial \ln h_{2,1} / \partial P\right)_T = V_2^{L\infty} / RT.$$

Here, $V_2^{L\infty}$ is the partial molar volume of the solute at infinite dilution in the solvent.

First, I shall concisely present the thermodynamic formalism relevant for the study of dilute solutions, and clarifying issues frequently overlooked. Solubility data reduction and data correlation will be touched upon, and a survey of currently popular estimation techniques for indispensable auxiliary thermophysical properties will be presented. Finally, a few recent experimental results obtained for dilute *aqueous* nonelectrolyte solutions will be discussed.

1. E. Wilhelm, *Low-Pressure Solubility of Gases in Liquids*, in: *Measurement of the Thermodynamic Properties of Multiple Phases: Experimental Thermodynamics, Vol. VII*, R. D. Weir and Th. W. de Loos, eds., pp. 137-176, Elsevier/IUPAC, Amsterdam, 2005.
2. *Heat Capacities: Liquids, Solutions and Vapours*, E. Wilhelm and T. M. Letcher, eds., The Royal Society of Chemistry/IUPAC & IACT, Cambridge, 2010.
3. *Volume Properties: Liquids, Solutions and Vapours*, E. Wilhelm and T. M. Letcher, eds., The Royal Society of Chemistry/IUPAC & IACT, Cambridge, 2015.