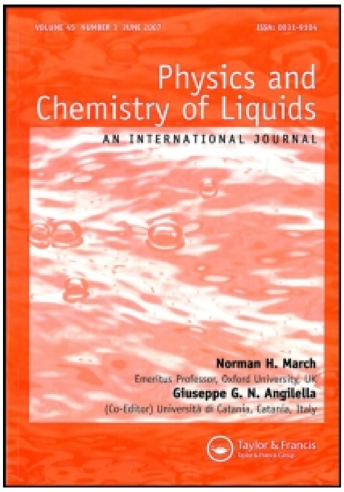

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Effect of Temperature on Henry's Constant in Simple Mixtures

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The molecular theory of dense fluids is progressing rapidly and its extension to mixtures is well underway. The purpose of this note is to call attention to a possibly serious difficulty in comparing experimental Henry's constants with those calculated from theory. The difficulty arises because whereas theorists choose temperature and density as independent variables, experimental equilibrium measurements on mixtures are often made along the saturation line where (at fixed composition) temperature and density are not both independent variables. Unless Henry's constants are defined with care, the effect of temperature on Henry's constants calculated from molecular theory may be qualitatively different from that observed.

Since pure-component vapor pressures increase monotonically with temperature, one might expect that Henry's constant for the solute in a simple liquid mixture would do the same. Experimentally-obtained Henry's constants, however, are conventionally defined and reported at some reference pressure, usually the vapor pressure of the pure solvent. The Henry's constant so defined, however, is not analogous to the vapor pressure of a pure component, and therefore it should not be surprising that experimental Henry's constants for some nonpolar systems have a temperature dependence which is not monotonic but instead rises, goes through a maximum, and then falls as temperature increases.

In recent work⁽¹⁾ we found that in certain respects a formal analogy does exist between Henry's constant and pure-component liquid P-v-T behavior. The pressure in a liquid *at a fixed volume* increases

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monotonically with temperature, and so does Henry's constant for a solute *at fixed solvent volume.*

For a solute 2 in solvent 1, the usual Henry's constant is defined by

$$H_{2,1}^{(P_1^s)} = \lim_{x_2 \to 0} f_2/x_2 \tag{1}$$

where f is the fugacity and the limit is taken at constant temperature. The Henry's constant at fixed solvent volume is related to the experimentally-accessible Henry's constant shown in Eq. (1) by

$$\ln H_{2,1}^{(v_1)} = \ln H_{2,1}^{(P_1^s)} + \int_{P_1^s}^{P(v_1)} \left(\frac{\partial \ln H_{2,1}}{\partial P}\right)_T \mathrm{d}P \tag{2}$$

where $P(v_1)$ is that pressure where the solvent volume at the system temperature is v_1.

Equation (2) can be rewritten

$$\ln H_{2,1}^{(v_1)} = \ln H_{2,1}^{(P_1^s)} + \int_{v_1}^{v_1^s} \frac{\bar{v}_2^\infty}{RT} \frac{\mathrm{d}v_1}{v_1 \beta_1} \tag{3}$$

where v_1^s is the liquid molar volume of solvent 1 at saturation conditions (P_1^s, T) and β_1 is the isothermal compressibility of pure liquid 1. The partial molar volume of solute 2 at infinite dilution is designated by $\bar{v}_2^\infty$. Order-of-magnitude calculations show that even for small differences between v_1^s and v_1, the integral term is positive and is often far from negligible.

To illustrate the effect of the integral term, we considered the system nitrogen–ethane which has been studied experimentally by Ellington *et al.*⁽²⁾ Figure 1 shows that Henry's constant for nitrogen, $H_{2,1}^{(P_1^s)}$, goes through a maximum at about 190 °K. To evaluate $H_{2,1}^{(v_1)}$, we used an equation recently derived by Preston⁽¹⁾

$$\ln \frac{H_{2,1}^{(v_1)} v_1}{RT} = \int_{v_1}^{\infty} \frac{z_2^\infty - 1}{v} \mathrm{d}v + z_2^\infty - 1 \tag{4}$$

The compressibility factor z_2^∞ is given by f, an empirical, corresponding-states equation of state for pure fluids

$$z_2^\infty = f\left(\frac{T}{T_{c_2}^\infty}, \frac{v}{v_{c_2}^\infty}\right) \tag{5}$$

where $T_{c_2}^\infty$ and $v_{c_2}^\infty$ are parameters characterizing the behavior of the solute, component 2, when completely surrounded by solvent,

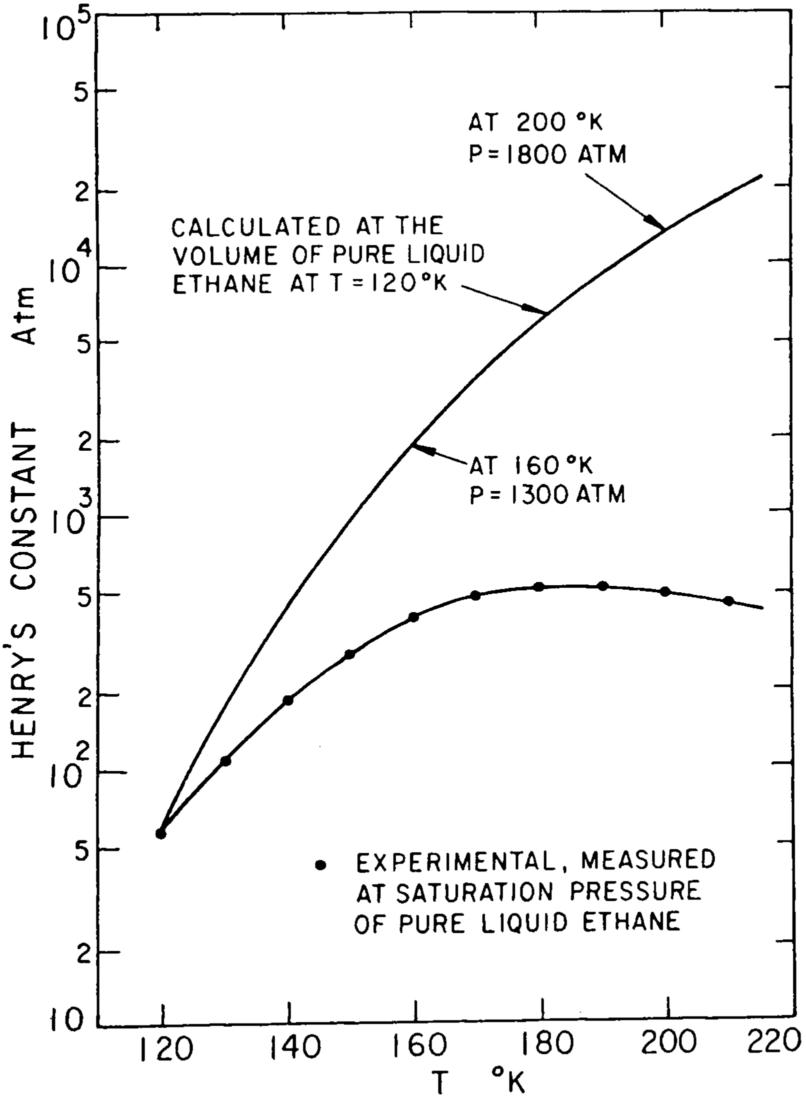

Figure 1. Experimental and calculated constant-volume Henry's constants for nitrogen–ethane

component 1. For f, we used a reduced form of the 16-constant equation of state of Strobridge–Gosman, proposed for argon.(3) In the special case where $v_1 = v_1^s$, Eq. (4) gives us Henry's constant $H_{2,1}^{(P_1^s)}$; using experimental data for that Henry's constant (over the temperature range 120–200 °K), we obtained the characteristic parameters $T_{c_2}^{\infty} = 199$ °K and $v_{c_2}^{\infty} = 152$ cc/gmol. These parameters were then used (with the Strobridge–Gosman equation) to calculate $H_{2,1}^{(v_1)}$ from Eq. (4). For v_1, we chose the liquid molar volume of the solvent (ethane) at 120 °K.

The results, shown in Fig. 1, demonstrate that Henry's constant at constant solvent volume increases monotonically with temperature, while the experimental Henry's constant at the solvent saturation pressure goes through a maximum. The difference between the two plotted curves is the integral term of Eq. (2).

While we should not generalize from this particular example, it is likely that typical nonpolar systems exhibit similar behavior. When comparing experimental Henry's constants with those calculated from a molecular theory of fluids, it is extremely important to define Henry's constant with care, giving particular attention to the effect of pressure (or liquid density) on that constant.

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