The causes for the presence of growth rate dispersion have been listed previously (Garside, 1977). The most likely cause is a variation in dislocation density on the surface of various nuclei resulting in different growth rates. This would be true if the growth followed a Burton-Cabrera-Frank surface diffusion mechanism, which was demonstrated for larger sucrose crystals by Valcic (1975). The mechanism of contact nucleation is still in question and further experimentation is necessary.

CONCLUSIONS

1. Sucrose contact nuclei appear to grow at a size independent rate.
2. Both initial size and growth rate distributions are observed for contact nuclei of sucrose.
3. The "constant crystal growth" model should be used to model growth rate dispersion in the sucrose-water system.
4. Curvature in semilogarithmic population density-size plots from continuous sucrose crystallization studies is probably due to growth rate dispersion and not size dependent growth.

ACKNOWLEDGMENTS

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Solubilities Near the Solvent Critical Point

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INTRODUCTION

Solubilities of gases in liquids are needed for the design of reactors and separation equipment. High-temperature data are rarely available and are difficult to measure. Hayduk and Laudie (1973) observed that all gas solubilities in a solvent tend towards a common value as the solvent critical temperature is approached. Beutier and Renon (1978) showed that this is due to the thermodynamic relationship for the solute (2):

$$H_2 = \phi_2 P_{c_1} \tag{1}$$

at the solvent (1) critical point. This is a very useful relationship for the extrapolation of solubilities to high temperatures. Beutier and Renon attempted also to derive an expression for the variation with temperature at the solvent critical point:

$$\frac{d(H_2/\phi_2)}{dT} = -\infty \tag{2}$$

Although the final result is correct, their derivation is questionable as will be shown below. The vapor-liquid equilibrium equation for the solute is:

$$y_2 \phi_2 P = H_2 x_2 \gamma_2^* c_2 \tag{3}$$

where c_2 is the Poynting correction:

$$c_2 = \exp\left[\int_{P_1^0}^{P} \frac{\bar{v}_2}{RT}\, dP\right] \tag{4}$$

Equation 3 can also be written as

$$\frac{y_2}{x_2} P = \frac{H_2}{\phi_2} \gamma_2^* c_2 \tag{5}$$

Similarly for the solvent:

$$\frac{y_1}{x_1} P = \gamma_1 \frac{\phi_1^0}{\phi_1} P_1^0 c_1 \tag{6}$$

where

$$c_1 = \exp\left[\int_{P_1^0}^{P} \frac{\bar{v}_1}{RT}\, dP\right] \tag{7}$$

Beutier and Renon took derivatives of Eqs. 5 and 6 with respect to T and x_2 at constant pressure along an equilibrium curve. The two derivatives were divided, which should give:

$$\frac{\frac{d(H_2/\phi_2)}{dT} + \frac{H_2}{\phi_2}\left(\frac{\partial(\gamma_2^* c_2)}{\partial T}\right)_P}{\frac{dP_1^0}{dT} + P_1^0\left[\frac{\partial(\gamma_1\phi_1^0 c_1/\phi_1)}{\partial T}\right]_P} = \frac{\left[\frac{\partial(y_2/x_2)}{\partial x_2}\right]_P}{\left[\frac{\partial(y_1/x_1)}{\partial x_2}\right]_P} \tag{8}$$

They concluded, therefore, that $d(H_2/\phi_2)/dT = -\infty$, since which goes to $-\sim$ when $x_2 \rightarrow 0$. Unfortunately, their equation did not contain the terms:

$$\frac{H_2}{\phi_2}\left[\frac{\partial(\gamma_2^* c_2)}{\partial T}\right]_P \text{ and } P_1^0\left[\frac{\partial(\gamma_1\phi_1^0 c_1/\phi_1)}{\partial T}\right]_P$$

They concluded, therefore, that $d(H_2/\phi_2)/dT = -\sim$, since $dP_1^0/dT \neq 0$. However, x_2 changes with temperature when derivatives are taken at constant pressure along the equilibrium curve. Derivatives of γ_2^*, γ_1, ϕ_1, c_1, and c_2 with respect to temperature and, therefore, also concentration cannot be neglected. The righthand side of Eq. 8 becomes infinite because the denominator becomes zero:

$$\frac{d(y_1/x_1)}{dx_2} = \frac{y_1}{x_1^2} - \frac{1}{x_1}\left(\frac{dy_1}{dx_1}\right) = \frac{1}{x_1}\left(\frac{y_1}{x_1} - \frac{dy_1}{dx_1}\right) = 0 \tag{9}$$

since $y_1/x_1 = 1$ and $dy_1/dx_1 = 1$ at the solvent critical point. There is no information regarding the terms $[\partial(y_2/x_2)/\partial x_2]_P$, $[\partial(\gamma_2^* c_2)/\partial T]_P$, and $[\partial(\gamma_1\phi_1^0 c_1/\phi_1)/\partial T]_P$. Therefore, one cannot conclude from Eq. 8 whether or not $d(H_2/\phi_2)/dT \rightarrow -\infty$ at the solvent critical point. A different derivation of the effect of temperature on the Henry's law constant follows.

TEMPERATURE DERIVATIVE OF HENRY'S LAW CONSTANT

Henry's law is best applied at very low concentrations, in the limit of $x_2 \rightarrow 0$, where γ_2^* and c_2 are unity. Then:

$$f_2 = H_2 x_2 \tag{10}$$

Taking the temperature derivative at constant x_2 at equilibrium:

$$\left(\frac{\partial ln f_2}{\partial T}\right)_x = \frac{d ln H_2}{dT} \tag{11}$$

(for simplicity, a derivative with a single subscript, e.g., x, refers to a derivative along an equilibrium curve at constant x). The fugacity is a function of P, T, and x_2:

$$d ln f_2 = \left(\frac{\partial ln f_2}{\partial P}\right)_{Tx} dP + \left(\frac{\partial ln f_2}{\partial T}\right)_{Px} dT + \left(\frac{\partial ln f_2}{\partial x_2}\right)_{PT} dx_2 \tag{12}$$

For points along the critical curve (locus of critical points, denoted by cc):

$$\left(\frac{\partial ln f_2}{\partial T}\right)_{cc} = \left(\frac{\partial ln f_2}{\partial P}\right)_{Tx}\left(\frac{\partial P}{\partial T}\right)_{cc} + \left(\frac{\partial ln f_2}{\partial T}\right)_{Px} \tag{13}$$

since $(\partial ln f_2/\partial x_2)_{PT} = 0$ at all critical points and $(\partial x_2/\partial T)_{cc}$ is finite. The fact that $(\partial x_2/\partial T)_{cc}$ is finite is illustrated by Rozen (1976), who has summarized the results of many studies, particularly those of I. R. Krichevskii and coworkers. Rozen has also listed an equation for points along the critical curve:

$$\left(\frac{\partial \mu_2}{\partial x_2}\right)_{PT} = 0 \tag{14}$$

which leads to:

$$\left(\frac{\partial ln f_2}{\partial x_2}\right)_{PT} = 0 \tag{15}$$

Figure 1 shows equilibrium curves at constant x_2, based on SF_6-CO_2 data of Makarevich and Sokolova as presented by Rozen (1969). The critical curve is the locus of the critical points on the equilibrium curves. The system SF_6-CO_2 was chosen only to illustrate a typical mixture of simple molecules. Rowlinson and Swinton (1982) have discussed critical curves of other types of mixtures, which are less common. In all cases, however, the critical curve cannot intersect an equilibrium curve on a P-T diagram more than once. It is, therefore, tangent to the equilibrium curves:

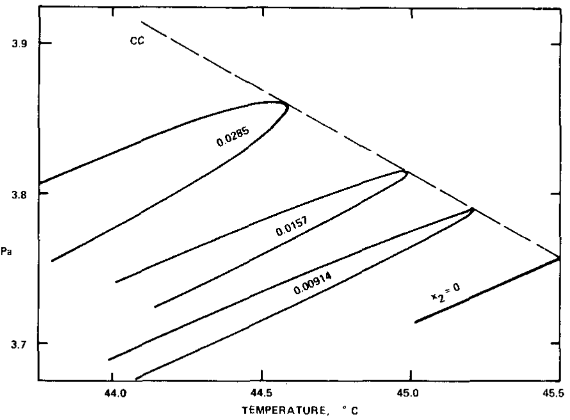

Figure 1. Equilibrium curves at constant $x_2(y_2)$ and critical curve (cc) for $SF_6(1) - CO_2(2)$ mixtures.

$$\left(\frac{\partial P}{\partial T}\right)_x = \left(\frac{\partial P}{\partial T}\right)_{cc} \tag{16}$$

There is a singularity at the solvent critical point. In general, $(\partial P/\partial T)_{cc}$ is negative near $x_2 \rightarrow 0$, whereas for the pure solvent dP_1^0/dT is positive. Here, Eq. 16 should hold, since derivatives along the critical curve and those at constant x_2 are being considered. For equilibrium curves at constant x_2, Eq. 12 becomes:

$$\left(\frac{\partial ln f_2}{\partial T}\right)_x = \left(\frac{\partial ln f_2}{\partial P}\right)_{Tx}\left(\frac{\partial P}{\partial T}\right)_x + \left(\frac{\partial ln f_2}{\partial T}\right)_{Px} \tag{17}$$

By combining Eqs. 11, 13, 16 and 17 one obtains:

$$\frac{d ln H_2}{dT} = \left(\frac{\partial ln f_2}{\partial P}\right)_{Tx}\left(\frac{\partial P}{\partial T}\right)_{cc} + \left(\frac{\partial ln f_2}{\partial T}\right)_{Px} \tag{18}$$

As shown, for example, by Prausnitz (1969):

$$\left(\frac{\partial ln f_2}{\partial T}\right)_{Px} = \frac{h_2^0 - \bar{h}_2}{RT^2} \text{ and } \left(\frac{\partial ln f_2}{\partial P}\right)_{Tx} = \frac{\bar{v}_2}{RT} \tag{19}$$

Substitution into Eq. 18 gives:

$$\frac{d ln H_2}{dT} = \frac{\bar{v}_2}{RT}\left(\frac{\partial P}{\partial T}\right)_{cc} + \frac{h_2^0 - \bar{h}_2}{RT^2} \tag{20}$$

As shown by Rozen (1976), Krichevskii (1967) and other workers, both $\bar{v}_2$ and $\bar{h}_2$ go to infinity at the solvent critical point. Equation 20 gives infinity minus infinity, which is undefined. Substitution of:

$$\bar{v}_2 = v + x_1\left(\frac{\partial v}{\partial x_2}\right)_{PT} \tag{21}$$

and a similar equation for $\bar{h}_2$ gives:

$$\frac{d ln H_2}{dT} = \frac{v}{RT}\left(\frac{\partial P}{\partial T}\right)_{cc} + \frac{h_2^0 - h}{RT^2} + \frac{x_1}{RT}\left(\frac{\partial v}{\partial x_2}\right)_{PT}\left(\frac{\partial P}{\partial T}\right)_{cc} - \frac{x_1}{RT^2}\left(\frac{\partial h}{\partial x_2}\right)_{PT} \tag{22}$$

Krichevskii and Lesnevskaya (1979) have derived:

$$\left(\frac{\partial h}{\partial x_2}\right)_{PT} = \left(\frac{\partial u}{\partial x_2}\right)_{vT} + T\left(\frac{\partial P}{\partial T}\right)_{vx}\left(\frac{\partial v}{\partial x_2}\right)_{PT} \tag{23}$$

One obtains from the derivative of P with respect to v, T and x:

$$\left(\frac{\partial P}{\partial T}\right)_{cc} = \left(\frac{\partial P}{\partial v}\right)_{Tx}\left(\frac{\partial v}{\partial T}\right)_{cc} + \left(\frac{\partial P}{\partial T}\right)_{vx} + \left(\frac{\partial P}{\partial x_2}\right)_{vT}\left(\frac{\partial x_2}{\partial T}\right)_{cc} \tag{24}$$

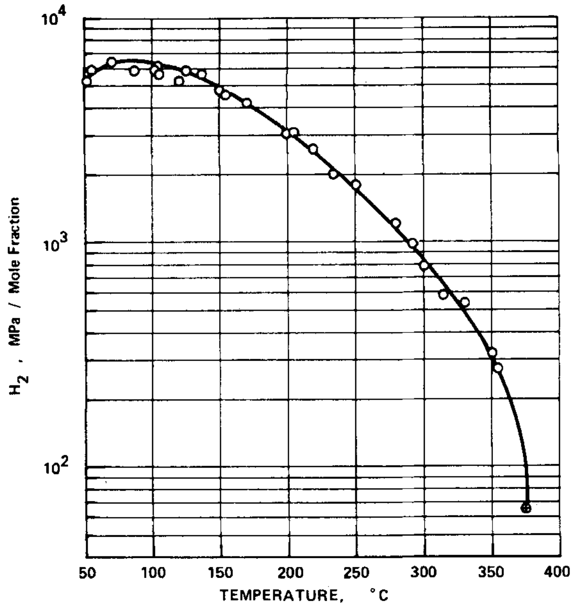

Figure 2. Henry's law constants for CH_4 in H_2O ⊕ Calculated at critical point of H_2O ○ Data of Culberson and McKetta (1951), Davis and McKetta (1960), O'Sullivan and Smith (1970), Price (1979), and Sultanov (1972).

Substitution of Eq. 23 and 24 into Eq. 22 gives:

$$\frac{dlnH_2}{dT}=\frac{v}{RT}\left(\frac{\partial P}{\partial T}\right)_{cc}+\frac{h_2^0-h}{RT^2}-\frac{x_1}{RT^2}\left(\frac{\partial u}{\partial x_2}\right)_{vT}$$
$$+\frac{x_1}{RT}\left(\frac{\partial v}{\partial x_2}\right)_{PT}\left[\left(\frac{\partial P}{\partial x_2}\right)_{vT}\left(\frac{\partial x_2}{\partial T}\right)_{cc}+\left(\frac{\partial P}{\partial v}\right)_{Tx}\left(\frac{\partial v}{\partial T}\right)_{cc}\right] \quad (25)$$

Krichevskii (1967) has derived for the solvent critical point:

$$RT+\frac{x_2}{(\partial P/\partial v)_{Tx}}\left(\frac{\partial P}{\partial x_2}\right)_{vT}^2=0 \quad (26)$$

Since:

$$\left(\frac{\partial v}{\partial x_2}\right)_{PT}=-\frac{(\partial P/\partial x_2)_{vT}}{(\partial P/\partial v)_{Tx}} \quad (27)$$

one obtains:

$$\left(\frac{\partial v}{\partial x_2}\right)_{PT}\left(\frac{\partial P}{\partial v}\right)_{Tx}=-\left(\frac{\partial P}{\partial x_2}\right)_{Tv} \quad (28)$$

and:

$$\left(\frac{\partial v}{\partial x_2}\right)_{PT}\left(\frac{\partial P}{\partial x_2}\right)_{vT}=\frac{RT}{x_2} \quad (29)$$

Substitution of Eqs. 28 and 29 into Eq. 25 gives:

$$\frac{dlnH_2}{dT}=\frac{v}{RT}\left(\frac{\partial P}{\partial T}\right)_{cc}+\frac{h_2^0-h}{RT^2}-\frac{x_1}{RT^2}\left(\frac{\partial u}{\partial x_2}\right)_{vT}$$
$$-\frac{x_1}{RT}\left(\frac{\partial P}{\partial x_2}\right)_{vT}\left(\frac{\partial v}{\partial T}\right)_{cc}+\frac{x_1}{x_2}\left(\frac{\partial x_2}{\partial T}\right)_{cc} \quad (30)$$

Multiplication by x_2 gives:

$$x_2\frac{dlnH_2}{dT}=x_2\left[\frac{v}{RT}\left(\frac{\partial P}{\partial T}\right)_{cc}+\frac{h_2^0-h}{RT^2}\right.$$
$$\left.-\frac{x_1}{RT}\left(\frac{\partial P}{\partial x_2}\right)_{vT}\left(\frac{\partial v}{\partial T}\right)_{cc}\right]$$
$$-\frac{x_1x_2}{RT^2}\left(\frac{\partial u}{\partial x_2}\right)_{vT}+x_1\left(\frac{\partial x_2}{\partial T}\right)_{cc} \quad (31)$$

$(\partial P/\partial T)_{cc}$ is clearly finite. Along the critical curve $(\partial v/\partial T)_{cc}$ is also finite, as has been discussed by Krichevskii, Lesnevskaya, Nikiforova, and Domracheva (1975). Krichevskii and Makarevich (1967) have shown that $(\partial P/\partial x_2)_{vT}$ is also finite. Therefore, all terms with the square brackets are finite. Krichevskii and Lesnevskaya (1979) have shown that $(\partial u/\partial x_2)_{vT}$ becomes infinite, but that $x_2(\partial u/\partial x_2)_{vT}$ is zero or very close to zero when $x_2 \rightarrow 0$. Then

$$\lim_{T=T_{c1}}\left(\frac{dlnH_2}{dT}\right)=\lim_{\substack{x_2=0\\T=T_{c1}}}\left[\frac{1}{x_2}\left(\frac{\partial x_2}{\partial T}\right)_{cc}\right] \quad (32)$$

at the solvent critical point.

The term $(\partial x_2/\partial T)_{cc}$ is finite and negative, since the solute is the more volatile component. Therefore:

$$\lim_{T=T_{c1}}\left(\frac{dlnH_2}{dT}\right)=-\infty \quad (33)$$

The best measurements of gas solubilities over the complete temperature range from room temperature to temperatures not far from the critical point are probably those for CH_4 in H_2O. Figure 2 shows Henry's law constants as a function of temperature and illustrates the infinite slope at the critical point of water.

Henry's law constant is not used when the solute is the less volatile component. It is of interest, however, to illustrate what happens when $(\partial x_2/\partial T)_{cc} > 0$ for solute with a critical temperature above that of the solvent. Using f_2/x_2 instead of H_2:

$$\lim_{\substack{T=T_{c1}\\x_2=0}}\left[\frac{\partial ln(f_2/x_2)}{\partial T}\right]_x=+\infty \quad (34)$$

Wichterle and Kobayashi (1972) have made precise measurements of $CH_4(1) - C_2H_6(2)$ vapor-liquid equilibrium data close to the critical point of CH_4. Values of f_2/x_2 at $x_2 = 0$ were calculated from their y_2/x_2 data using the relationship:

$$\frac{f_2}{x_2}=\left(\frac{y_2}{x_2}\right)\phi_2P \quad (35)$$

The equation of state of Peng and Robinson (1976) with its usual mixing rules was used to calculate ϕ_2. Although equations of state are usually weak in the critical region, relative errors in ϕ_2 should not be greater than a few per cent for a simple system such as CH_4-C_2H_6. Values of f_2/x_2 at $x_2 = 0$ are shown as a function of temperature in Figure 3. There is a rather sharp change in slope to +∞ near the critical point of CH_4.

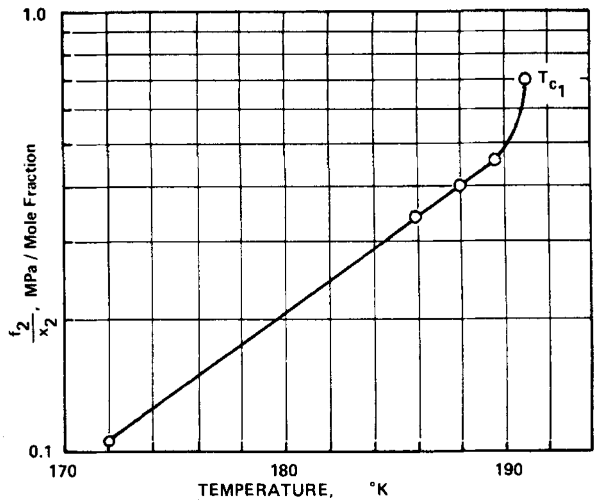

Figure 3. Reciprocal of the solubility of C_2H_6 in CH_4, based on data of Wichterle and Kobayashi (1972).

CONCLUSION

An improved derivation of the effect of temperature on the Henry's law constant at the solvent critical point has been presented. Together with the Beutier and Renon's equation: $H_2 =$

$\phi_2 P_{c_1}$, insight can be gained regarding the extrapolation of solubilities to high temperatures. Although Henry's law does not apply to the less volatile component, the final results: $f_2/x_2 = \phi_2 P_{c_1}$ and Eq. 34 can be applied. Most of the equations, derived in this study, should not be used away from T_{c_1}. Sharp changes in slope near T_{c_1} can alter some of the derivatives drastically.

NOTATION

c = Poynting correction
f = fugacity
h = enthalpy
$\bar{h}$ = partial molar enthalpy
h^0 = molar enthalpy in ideal gas state
H_2 = Henry's law constant of solute
P = pressure
P_1^0 = vapor pressure of pure solvent
P_{c_1} = critical pressure of solvent
R = gas constant
T = absolute temperature
u = molar internal energy
v = molar volume
$\bar{v}$ = partial molar volume
x = mole fraction in the liquid
y = mole fraction in the vapor

Greek Letters

γ = activity coefficient
γ^* = normalized activity coefficient of solute
μ = chemical potential
ϕ = fugacity coefficient (ϕ^0 for pure component)

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Effect of Pore Structure on Particle Ignition During Exothermic Gasification Reactions

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One distinctive feature of a char gasification reaction is the change in pore structure of the solid reactant that occurs continuously as reaction proceeds. Earlier models were proposed by Petersen (1957) and by Hashimoto and Silveston (1973) to study the effect of solid pore structure on gasification kinetics. More recent development of a random pore model (Bhatia and Perlmutter, 1980; Gavalas, 1980) assumed that the reaction rate in the kinetic control regime is proportional to the surface area of the solid and showed that the change of reaction rate with conversion can be characterized by a pore structure parameter ψ in the form:

$$\frac{dX}{d\tau} = \frac{S}{S_o} = (1 - X)\sqrt{1 - \psi \ln (1 - X)} \qquad (1)$$

or in terms of the dimensional time scale as

$$\frac{dX}{dt} = \frac{k_s C_o^n S_o}{1 - \epsilon_o}(1 - X)\sqrt{1 - \psi \ln (1 - X)} \qquad (2)$$

The parameter ψ contains the initial porosity, surface area, and total pore length, all obtainable from the pore volume distribution of the solid reactant before any reaction has taken place (Bhatia and Perlmutter, 1980).