5.12 Solubilities of Solids and Liquids in Compressed Gases

We consider equilibrium between a gas and a solid.

The solubility of the gas in the solid is negligible, and thus all nonideal behavior is attributed to the vapor phase.

1: light component only in gas phase   2: heavy component in both phases

For component 2

$$f_2^{\triangle} = f_2^V \tag{5-121}$$

The solid phase is pure substance, its fugacity is

$$f_2^{\triangle} = P_2^s \varphi_2^s \exp\left(\int_{P_2^s}^{P} \frac{v_2^{\triangle}}{RT} dP \right) \tag{5-122}$$

Recalling the definition

$$\varphi_2 \equiv \frac{f_2^V}{y_2 P} \tag{5-123}$$

substituting into (5-121)

$$\boxed{y_2 = \frac{P_2^s}{P} E} \tag{5-124}$$

$$E \equiv \frac{\varphi_2^s}{\varphi_2} \exp\left(\int_{P_2^s}^{P} \frac{v_2^{\triangle}}{RT} dP \right) \tag{5-125}$$

E is enhancement factor which is a measure of the extent that pressure enhances the solubility of the solid in the gas. As $P \rightarrow P_2^s ,\ E \rightarrow 1$

E is a measure of solvent power as it is the ratio of the observed solubility to the ideal-case solubility.

E has three correction terms:

Nonideality of the pure saturated vapor: φ_2^s ~ close to unity

Effect of pressure on the fugacity of the solid: the Poynting correction ~ 2 or 3

The vapor-phase fugacity: φ_2 the most important

CF_4 / CCl_4 (solid)

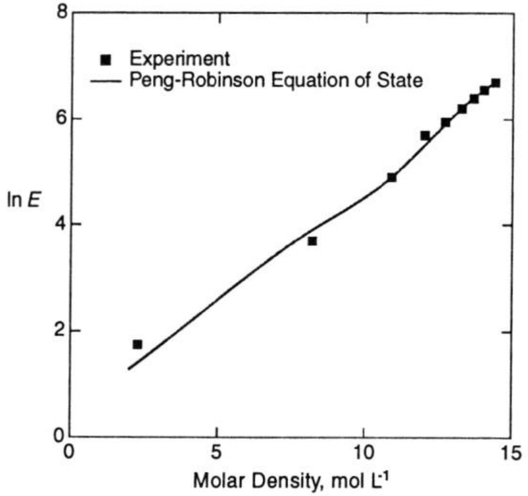

Figure 5-37 Enhancement factors for solid CCl_4 in supercritical CF_4 at 249 K.

At high solvent densities (or pressures), very large deviation from nonideality

Air/ CO$_2$ (solid)

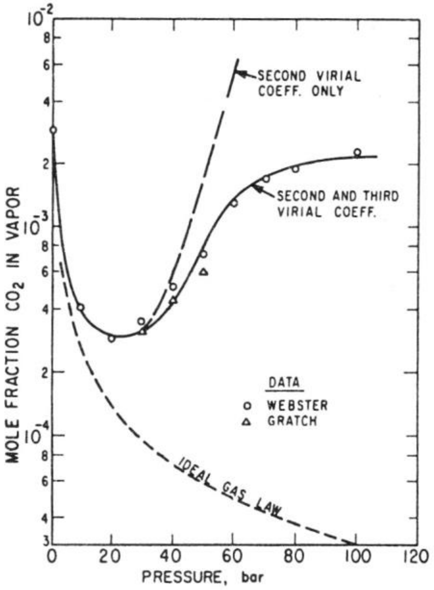

Figure 5-38 Solubility of solid carbon dioxide in air at 143 K.

The dash line is with $\varphi_2 = 1$ and with the Poynting correction.

The long dashed and solid lines are with virial coefficients.

Ethylene / Naphthalene (solid)

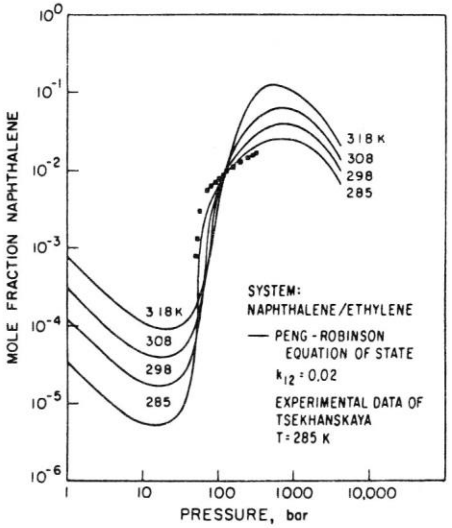

Figure 5-39 Solubility minima and maxima for naphthalene in compressed ethylene.

Virial equation of state is not applicable to high pressures (high densities), and the Peng-Robinson equation of state was used.

Peng-Robinson equation of state

$$P = \frac{RT}{\underline{V} - b} - \frac{a(T)}{\underline{V}(\underline{V} + b) + b(\underline{V} - b)}$$

$$a(T) = 0.45724 \frac{R^2 T_c^2}{P_c}\, \alpha(T) \qquad b = 0.07780 \frac{RT_c}{P_c}$$

$$\alpha(T) = \left[1 + \kappa\left(1 - \sqrt{\frac{T}{T_c}}\right)\right]^2 \qquad \kappa = 0.37464 + 1.54226\omega - 0.26992\omega^2$$

$$\ln\frac{f}{P} = (Z - 1) - \ln\left(Z - \frac{bP}{RT}\right) - \frac{a}{2\sqrt{2}bRT}\ln\left[\frac{Z + \left(1 + \sqrt{2}\right)bP/RT}{Z + \left(1 - \sqrt{2}\right)bP/RT}\right]$$

Solubility of liquid in a compressed gas

Somewhat more difficult because a gas is soluble in a liquid.

1: gaseous solvent 2: heavy solute

For component 2

$$f_2^L = f_2^V = \varphi_2 y_2 P \qquad (5\text{-}126)$$

As the gas is only sparingly soluble, the solubility of component 1 is described by Henry's law with pressure correction.

$$f_1^L = H_{1,2} x_1 \exp\left(\int_{P_2^s}^{P} \frac{\overline{v}_1^\infty}{RT} dP\right) \qquad (5\text{-}127)$$

where $H_{1,2}$ is Henry's constant, $\overline{v}_1^\infty$ is the partial molar volume at infinite dilution, and x_1 is the solubility of gas 1 in liquid.

From the Gibbs-Duhem equation, it can be shown that

$$f_2^L = (1 - x_1) P_2^s \varphi_2^s \exp\left(\int_{P_2^s}^{P} \frac{v_2^L}{RT} dP\right) \qquad (5\text{-}128)$$

Substituting (5-126)

$$\boxed{y_2 = \frac{(1 - x_1) P_2^s \varphi_2^s \exp\left(\int_{P_2^s}^{P} \frac{v_2^L}{RT} dP\right)}{\varphi_2 P}} \qquad (5\text{-}129)$$

$$x_1 = \frac{y_1 \varphi_1 P}{H_{1,2} \exp\left(\int_{P_2^s}^{P} \frac{\overline{v}_1^\infty}{RT} dP\right)} \qquad (5\text{-}130)$$

requiring a trial-and-error calculation

Nitrogen / Decane (liquid)

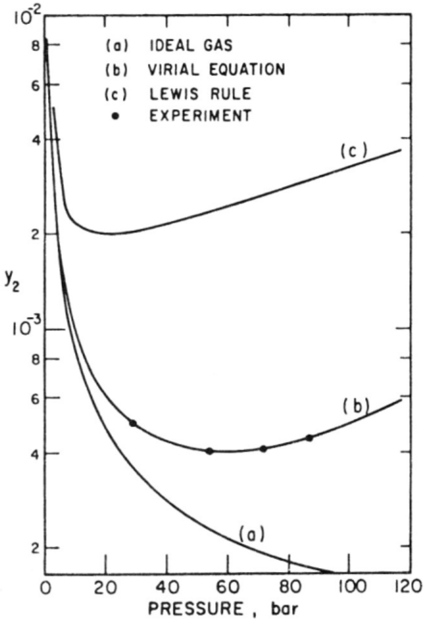

Figure 5-41 Vapor-phase solubility of decane in nitrogen at 50°C.

(c) Lewis fugacity rule for decane.

B_{12} was back-calculated from experimental data.

Calculation based on the ideal-gas assumption is not seriously in error as nitrogen is weakly attractive at low pressures.

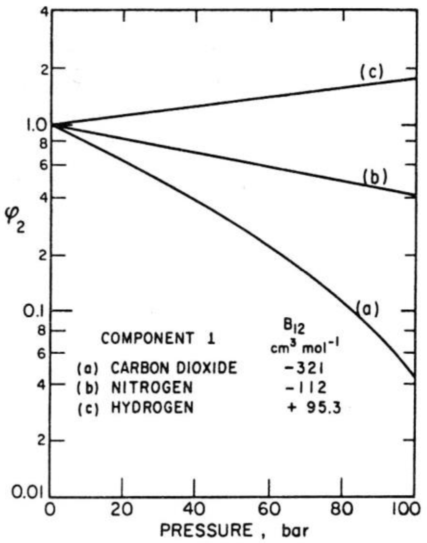

Figure 5-42 Fugacity coefficients of decane in hydrogen, nitrogen, and carbon dioxide at 75°C.

The vapor-phase fugacity is strongly dependent on the nature of the gaseous component.

At 100 bar, decane is about 10 times more soluble in carbon dioxide than in nitrogen.

A rough measure of attractive forces of a gaseous solvent is its critical temperature.

CO_2 (T_c =304 K) is a better solvent than nitrogen (T_c = 126 K)

Gas / Methanol

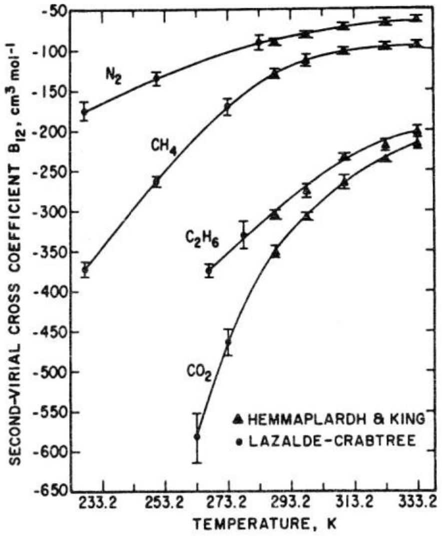

Figure 5-43 Second-virial cross coefficients for binary mixtures containing methanol.

Attractive forces between methanol and nitrogen are weak compared to those between methanol and carbon dioxide.