$$- \frac{\nu}{1-\nu} + f\left(\left(\frac{1-\nu}{6}\right)^{1/2} \alpha\lambda\right)$$

$$- (1 - x^{o}_{H_2}) \exp\left\{\frac{\alpha^2}{6} (\lambda^2 - 1) + \frac{\lambda^3 \alpha^2 \pi x^{c}_{V*}}{3} \left(\frac{1}{\lambda} - 1\right)\right\}. \tag{14}$$

The case of $\nu = 1$ requires special treatment, because when $\alpha > \alpha_{crit}$ and $\pi > 1$ all volatiles released in the core deposit before reaching the reaction interface. The boundary layer analysis then breaks down as stable volatiles and inerts diffuse in from the sheath to fill the core. Otherwise the analysis parallels that above and determines the position of the reactive interface through

$$1 = \frac{\alpha^2}{6} (2\lambda^3 - 3\lambda^2 + 1)$$

$$+ (1 - x^{o}_{H_2}) \exp\left\{- \frac{\alpha^2}{6} (2\lambda^3 - 3\lambda^2 + 1)\right\}. \tag{15}$$

In both cases the rapid $I$-$H_2$ diffusion increases the penetration of hydrogen and thereby reduces $\lambda$, the size of the core.

## INSTANTANEOUS YIELD

For rapid devolatilization the deposition within the core reduces the instantaneous yield

$$\eta = 3N_V|_{r=1} = 1 - \pi x^{c}_{V*} \lambda^3 \tag{16}$$

with $x^{c}_{V*}$ from (8) and $\lambda$ from (14) or (15). Typical numerical results for $\eta$ as a function of $\pi$, $\alpha^2$, and $x^{o}_{H_2}$ are plotted in Figure 1. As indicated above the results differ most from those for equal diffusivities when $\nu \rightarrow 1$ and $x^{o}_{H_2} \rightarrow 0$ and least when $\nu \rightarrow 0$ or $x^{o}_{H_2} \rightarrow 1$.

The most important conclusion rests on the qualitatively similar trends. The quantitative differences are significant, but may not be detectable experimentally unless the effective diffusivities within the coal particle are measured independently. If they must be deduced from hydropyrolysis data, the two models may be indistinguishable.

## NOTATION

$c$ = constant defined after Eq. 13
$D_{ij}$, $D^{e}_{ij}$ = binary diffusivities in gas and within particle, respectively
$f$ = function defined after Eq. 13
$N_i$ = flux of $i^{th}$ species
$p$ = pressure
$r$ = radial position
$R$ = dummy variable
$R_i$ = rate of reaction producing $i^{th}$ species
$x_i$ = mole fraction of $i^{th}$ species
$x^{o}_{H_2}$ = mole fraction of $H_2$ in bulk gas
$y$ = position measured inward from reaction interface
$\alpha^2$ = dimensionless particle size (Russel et al., 1979)
$\gamma_1$, $\gamma_2$ = ratios of binary diffusivities within particle defined after Eq. 4
$\lambda$ = dimensionless position of reaction interface
$\eta$ = dimensionless yield (Russel et al., 1979)
$\pi$ = dimensionless pressure (Russel et al., 1979)
$\Pi$ = 3.1415 . . .
$\nu$ = fraction of volatiles which are reactive

### Subscripts

$I$ = inerts
$H_2$ = hydrogen
$V$, $V*$ = unreactive and reactive volatiles, respectively.

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# Solubility Extrema in Solid-Fluid Equilibria

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**Experimental data and theory both support the contention that there is a maximum solubility in solid-fluid equilibria. An example system, naphthalene-ethylene, at temperatures between the upper and lower critical end points and at pressures from 1 to 1000 bar is considered. There is also a solubility minimum in this system.**

Recently, several research papers have addressed the question of the solubility of solid, pure solutes into supercritical fluids (Francis and Paulaitis (1980), Johnston and Eckert (1980), Kurnik et al. (1980), Mackay and Paulaitis (1979), McHugh and Paulaitis (1980), Van Leer and Paulaitis (1980). In some of these, naphthalene-ethylene was one of the systems studied. Experimental solubilities could then be compared to earlier data of Tsekhanskaya et al. (1964) to validate the experimental procedure. In the ethylene-naphthalene system, the temperature range is limited to that between the two critical end points (283.9 and 325.3 K). Experimental pressures ranged up to 400 bar. Various equations of state were employed to estimate the fugacity coefficient of naphthalene in ethylene so as to allow a correlation to be developed between experimental solubilities

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and those calculated from equilibrium thermodynamics. For example, we have found the Peng-Robinson equation of state (1976) to be applicable over our experimental pressure range of 1-350 bar.

It is interesting, however, to extend the computer simulation to even higher pressures. The results of such calculations are shown in Figure 1 for the solubilities of naphthalene in supercritical ethylene for pressures up to 4 kbar and for several temperatures. Experimental data are shown only for the 285 K isotherm to indicate the range covered and the applicability of the Peng-Robinson equation. [The values of the interaction parameter, $k_{ij}$, in this equation were found from regressing the experimental solubility data for four isotherms and averaging the results. Over the temperature range studied, an average interaction parameter correlates isothermal solubility data at most 4% different than when using a temperature-dependent interaction parameter.]

For the naphthalene-ethylene system, the solubility attains a minimum value in the range of 15 to 20 bar and a maximum at several hundred bar. The minimum concentration is of interest to those who wish to purify a gas from a volatile impurity by compression and condensation. (See Hinckley and Reid, 1964.) The maximum concentration of solute is clearly of concern to those who would like to employ supercritical fluids to extract a solute into the fluid phase.

The existence of the concentration maxima for the naphthalene-ethylene system is confirmed by considering the earlier work by Van Welie and Diepen. They also graphed the mole fraction of naphthalene in ethylene as a function of pressure and covered a range up to about 1 kbar. Their smoothed data (as read from an enlargement of their original graphs) are plotted in Figure 2. At temperatures close to the upper critical end point (325.3 K), a maximum in concentration is clearly evident. At lower temperatures, the maximum is less obvious. The dashed curve in Figure 2 represents the results of calculating the concentration maximum from the Peng-Robinson equation of state. The simulation could only be carried out to 322 K; above this temperature, convergence becomes a problem as the second critical end point is approached, and the formation of two fluid phases is predicted. Table 1 compares the theoretical versus experimental maxima.

Concentration maxima have also been noted by Czubryt et al. (1970) for the binary systems stearic acid-$CO_2$ and 1-octadecanol-$CO_2$. In these cases, the experimental data were all measured past the solubility maxima—which for both solutes occurred at a pressure of about 280 bar. An approximate correlation of their data was achieved by a solubility parameter model.

The solubility minimum and maximum with pressure can be related to the partial molal volume of the solute in the supercritical phase. With subscript 1 representing the solute, then with equilibrium between a pure solute and the solute dissolved in the supercritical fluid,

$$d\ln \hat{f}_1^F = d\ln \hat{f}_1^S \tag{1}$$

Expanding Eq. 1 at constant temperature and assuming the pure solute is incompressible,

$$\frac{\bar{V}_1^F}{RT}\,dP + \left(\frac{\partial \ln \hat{f}_1^F}{\partial \ln y_1}\right)_{T,P} d\ln y_1 = \frac{V_1^S}{RT}\,dP \tag{2}$$

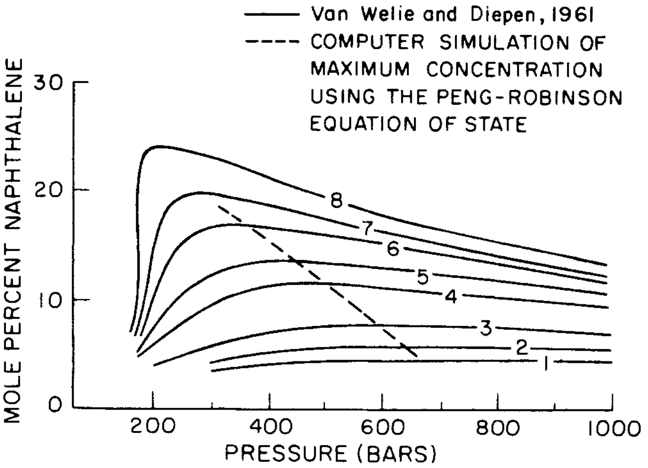
Using the definition of the fugacity coefficient,

$$\phi_1^F = \hat{f}_1^F / y_1 P \tag{3}$$

then Eq. 2 can be rearranged to give

$$\left(\frac{\partial \ln y_1}{\partial P}\right)_T = \frac{\left(\dfrac{V_1^S - \bar{V}_1^F}{RT}\right)}{\left[1 + \left(\dfrac{\partial \ln \phi_1}{\partial \ln y_1}\right)_{T,P}\right]} \tag{4}$$

$\phi_1$ may be expressed in terms of $y_1$, $T$, and $P$ with an equation of state (Kurnik et al., 1980). For naphthalene as the solute in ethylene, $(\partial \ln \phi_1 / \partial \ln y_1)_{T,P}$ was never less than $-0.4$ over a pressure range up to the 4 kbar limit studied. Thus the extrema in concentration occur when $V_1^S = \bar{V}_1^F$.



| NUMBER | TEMPERATURE (K) |
|---|---|
| 1 | 303.2 |
| 2 | 308.2 |
| 3 | 313.2 |
| 4 | 318.2 |
| 5 | 321.2 |
| 6 | 323.2 |
| 7 | 324.2 |
| 8 | 325.3 |

**Figure 1. Solubility maxima predictions for naphthalene in ethylene.**

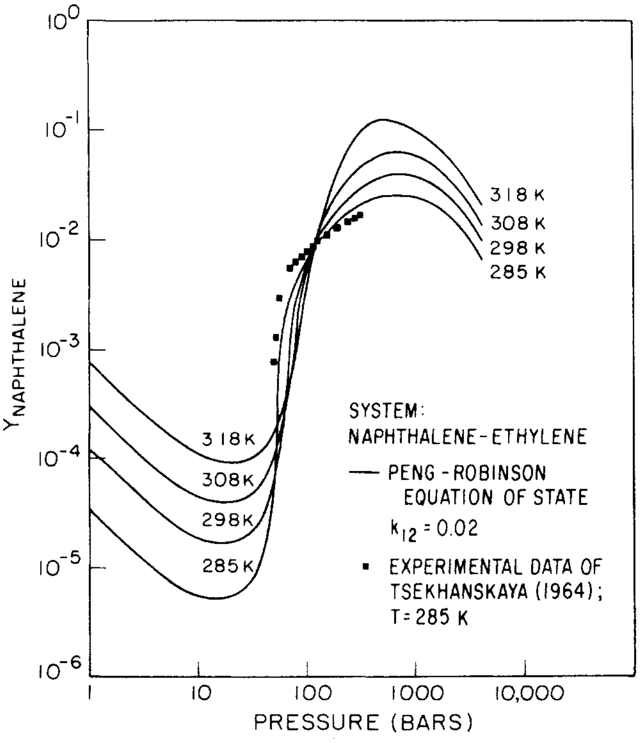


**Figure 2. Experimental data confirming solubility maxima of naphthalene in ethylene.**

Again using the Peng-Robinson equation of state, we have computed $\bar{V}^F$ for naphthalene in ethylene as a function of pressure and temperature. The 318 K isotherm is shown in Figure 3. At low pressures, $\bar{V}^F$ is large and positive; it would approach an ideal gas molar volume as $P \rightarrow 0$. With an increase in pressure, $\bar{V}_1^F$ decreases and becomes equal to $V_1^S$ (111.9 $cm^3$/

TABLE 1. EXPERIMENTAL AND THEORETICAL SOLUBILITY MAXIMA VS. PRESSURE AT THESE MAXIMA

| $T$ (K) | $P^E_{\max}$ (bar) | $P^T_{\max}$ (bar) | % error, $P$ | $y^E_{\max}$ | $y^T_{\max}$ | % error, $y$ |
|---|---|---|---|---|---|---|
| 303 | 612 | 680 | 11.1 | $4.31 \times 10^{-2}$ | $4.83 \times 10^{-2}$ | 12.1 |
| 308 | 590 | 648 | 9.8 | $5.68 \times 10^{-2}$ | $6.06 \times 10^{-2}$ | 6.9 |
| 313 | 576 | 576 | 0.0 | $7.84 \times 10^{-2}$ | $8.43 \times 10^{-2}$ | 7.5 |
| 318 | 477 | 472 | 1.0 | $1.17 \times 10^{-1}$ | $1.19 \times 10^{-1}$ | 1.7 |
| 321 | 398 | 357 | 10.3 | $1.35 \times 10^{-1}$ | $1.60 \times 10^{-1}$ | 18.5 |

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1. Calculations were done using Peng-Robinson Equation of State, $k_{12} = 0.02$.
2. Experimental Data are from Van Welie and Diepen (1961).

mol) at a pressure of about 20 bar. This corresponds to the solubility minimum. $\overline{V}^F_1$ then becomes quite negative. The minimum in $\overline{V}^F_1$ corresponds to the inflection point in the concentration-pressure curve as shown in Figure 1. At high pressures, $\overline{V}^F_1$ increases and eventually becomes equal to $V^S_1$; this then corresponds to the maximum in concentration described earlier.

## CONCLUSION

We have noted the observed solubility minimum and maximum for three solute-supercritical systems. For the naphthalene-ethylene case, the Peng-Robinson equation of state was used to simulate the extrema. Similar attempts to model the stearic acid-$CO_2$ or 1-octadecanol-$CO_2$ systems with this equation of state were not successful and a more accurate high-pressure mixture equation of state would appear to be necessary.

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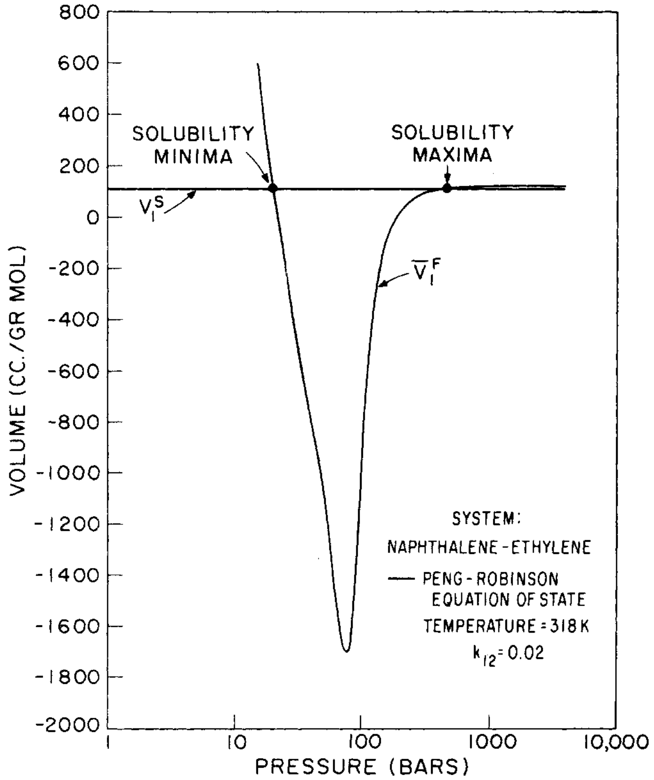

**Figure 3. Partial molar volume of naphthalene in ethylene.**

## NOTATION

$\hat{f}_1$ = fugacity of component 1 in mixture, bar
$P$ = pressure, bar
$R$ = gas constant
$T$ = temperature, K
$V$, $\overline{V}$ = molar volume, partial molar volume, $cm^3$/mol
$y$ = fluid phase mole fraction

### Greek Letters

$\phi_1$ = fugacity coefficient of component 1

### Subscripts

1 = solid component
2 = fluid component

### Superscripts

$E$ = experimental
$F$ = fluid
$S$ = solid
$T$ = theoretical

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