c = critical property
M = mixture property
r = reduced property
r1, r2 = reference fluid
1, 2, i, j = component 1, 2, i, j

(L) = simple fluid
(r), (r1), (r2) = reference fluid
(0) = simple fluid

Introduction
Fluid fuels and chemical feedstocks derived from coal are becoming increasingly attractive as a substitute for oil. Supercritical gas extraction of coal is promising in many liquefaction techniques12).

Received June 5, 1981. Correspondence concerning this article should be addressed to H. Masuoka.
nized as far back as in 1879 by Hanay and Hogarth.\(^6\) Fank\(^3\) reports the pronounced solvent power of supercritical water. Weale\(^21\) has presented an excellent discussion of solubility of solids in compressed gases. Hagenbach\(^5\) demonstrated enhanced solvent properties of supercritical polar gases. Paul and Wise\(^15\) have shown from theoretical considerations that the volatility enhancement is greatest when the temperature at which the extraction is carried out is near the critical temperature of the extracting gas. Gangoli and Thodos\(^4\) have given an extensive technical review of supercritical gas extraction.

The ethylene-naphthalene system has been extensively studied by Diepen and Scheffer\(^2\) at five temperature levels from 12 to 60°C and at various pressures in the range of 40-270 atm. Tsekhanskaya et al.\(^18\) also studied extensively the influence of pressure levels on the extractive property of supercritical ethylene and carbon dioxide acting on naphthalene. These observations are limited to higher pressures, down to 40 atm.

At moderate pressures a virial equation of state is used to calculate the solubility\(^9\). At higher pressures, however, the utility of the equation is limited by lack of knowledge about higher-order virial coefficients.

Vetere\(^20\) has recently presented a predictive method for calculating the solubility of solids in supercritical gases. He reported that good agreement was obtained between experimental and calculated data for the ethylene-naphthalene system. He treated the supercritical gas mixture as a hypothetical liquid mixture in phase equilibrium determinations. However, it was pointed out by the authors\(^14\) that his paper contains some errors and that his predictive method leads to erroneous results.

Thus, at present, thermodynamically predictive methods for the solubility of heavy compounds in supercritical solvents are limited in application due to lack of understanding of the behavior of both the dense-fluid state and highly asymmetric mixtures of substances.

The purpose of this work is to obtain experimental data for the solubility of solid naphthalene in ethylene in the lower pressure range and to propose a new predictive method for calculating the solubility of solids in supercritical gases.

1. Thermodynamics of Solid-Vapor Equilibria

The solubility of a nonvolatile solute in a supercritical gas is determined from standard thermodynamics\(^8\). Solid-vapor equilibria considered in this study are those for which the solid phase is assumed to be pure solute (component 1) and the vapor phase is a saturated solution of the solute in the solvent (component 2). For such a system, the equation of equilibriums for the solute is given by

\[
\begin{align*}
\frac{f_1}{V^g_1} &= \varphi_1^e f_1^* \\
\varphi_1 &= \varphi_1^e P y_1
\end{align*}
\]

where \(f_1^*\) is the fugacity of pure solid, \(y_1\) is the mole fraction of the solute in the solution, and \(\varphi_1^e\) is the fugacity coefficient of the solute in the vapor mixtures. Arranging Eqs. (1) and (2), solid solubility is expressed as

\[
y_1 = (f_1^*/f_1^e)(\varphi_1^e/\varphi_1^e)
\]

where \(f_1^*\) is the fugacity of pure subcooled liquid and \(\varphi_1^e\) is the fugacity coefficient of the pure subcooled liquid solute. The fugacity ratio of component 1, \(f_1^*/f_1^e\), can be evaluated by the relation

\[
\ln f_1^* = \frac{\Delta S_f}{R} \left(1 - \frac{T_i}{T}ight) + \frac{\Delta C_p}{R} \left(\frac{T}{T} - 1\right)
\]

where \(T_i\) and \(P_i\) are the triple-point temperature and pressure, respectively, \(\Delta S_f\) is the molar entropy of fusion of the solute, and \(\Delta C_p\) and \(\Delta V\) are the differences between the liquid and solid molar heat capacities and molar volumes, respectively.

The fugacity coefficients of the pure solute in subcooled liquid and those of the solute in vapor mixtures were calculated from the generalized equation of state of Lee and Kesler\(^11\) together with the pseudocritical method\(^8\),\(^13\), as described in the following section.

An alternative expression of solubility is expressed as

\[
y_1 = \left(\frac{P_{sat}}{P}\right) \left(\frac{\varphi_1^{sat}}{\varphi_1^e}\right) \exp \frac{V_s(P - P_{sat})}{RT}
\]

where \(\varphi_1^{sat}\) is the fugacity coefficient for the saturated vapor, and this is essentially unity. This equation, compared to Eq. (3), does not require the subcooled liquid properties but requires vapor pressure data of the solute.

If the virial equation, truncated after the second virial coefficient, is assumed in vapor phase at moderate pressures, one obtains

\[
\ln \varphi_1^e = \frac{2}{V_s} (y_1 B_{11} + y_2 B_{12}) - \ln Z_w
\]

If it is further assumed that \(P \gg P_{sat}\), the enhancement factor, which is a measure of enhanced solubility, may be expressed as

\[
E = \ln \left(\frac{P_{sat}}{P}\right)
\]

This equation is often used in a consistency test of experimental phase equilibrium data.

2. Generalized BWR Equation of Lee-Kesler, and Its Application to Mixtures by the Pseudocritical
Method

In calculating the solubility according to Eq. (3), an equation of state capable of representing the thermodynamic properties of subcooled liquid is required. For this purpose the Lee and Kesler\textsuperscript{11} three-parameter corresponding-states correlation was chosen from considerations similar to those in a previous paper\textsuperscript{13} on the solid solubility in liquid.

The Lee and Kesler equation is an extended and improved version of the Pitzer-Curl tables based on a modified BWR equation of state. The compressibility factor of a real fluid is related to properties of a simple fluid ($\omega=0$) and to those of octane as a reference fluid.

\begin{equation}
Z = Z^{(0)} + \omega Z^{(R)} - Z^{(0)}
\end{equation}

where $\omega^{(0)} = 0.3978$. Other thermodynamic functions (fugacity coefficients and enthalpy departure) have been derived from Eq. (8).

In applying the Lee-Kesler equation to mixtures, we used the pseudocritical method\textsuperscript{8,13}. According to the three-parameter corresponding-states theory, the fugacity coefficient of component $i$ in the mixture can be written as follows:

\begin{equation}
\ln \frac{f_i}{P_i y_i} = \ln \left( \frac{f_m}{P} \right) + \sum_j \frac{n_j}{T} \left( \frac{\partial f_i}{\partial n_j} \right)_{T,P,n_j} \frac{H_m - H_m^*}{RT} - \frac{n_j}{P} \left( \frac{\partial P_i}{\partial n_j} \right)_{T,P,n_j} (Z_m - 1) + \frac{\partial \ln \left( \frac{f_m}{P} \right)}{\partial \omega_m} Z_{m,1} \left( \frac{\partial \ln \left( \frac{f_m}{P} \right)}{\partial \omega_m} \right)_{T',P',n_i}
\end{equation}

For the pseudocritical constants the van der Waals one-fluid model was used.

\begin{align}
V_i &= \sum_j y_i y_j V_{ij} \\
T_i &= \sum_j y_i y_j T_{ij} \\
Z_i &= \sum_j y_i Z_{ij} \\
P_i &= Z_i R T_i V_i \\
\omega_m &= \sum_j y_i \omega_i \\
V_{ij} &= (1 - s_{ij}) V_{ij}^{(2)} + V_{ij}^{(1)} y_i y_j / 8 \\
T_{ij} &= (1 - k_{ij}) (T_i T_j)^{1/2}
\end{align}

where $k_{ij}$ and $s_{ij}$ are parameters determined from binary-phase equilibrium data.

3. Experimental

Various methods for determining the solubility of solid in vapor are noted in the literature. Static methods, which are extensively used in phase equilibrium determinations, may not be suited for systems of very low content of solute in vapor, for several reasons\textsuperscript{11}. One is that adsorption of solute on equilibrium cell or sampling tube can cause serious experimental errors, and it is difficult to minimize this effect. These circumstances are similar to measurement of vapor pressures of high boiling-point substances.

We used a single-pass, continuous-flow (also referred to as gas saturation) method\textsuperscript{8,12,13}. The method is especially suitable for low vapor pressures of solute.

3.1 Apparatus and experimental procedure

The flow apparatus is shown schematically in Fig. 1. The gas from a high-pressure cylinder was passed sequentially through two coils immersed in a constant-temperature bath, which was controlled to within $\pm 0.02^\circ$C. The coils were made of stainless steel pipe (7 mm I.D.). The first coil (1.0 m length) ensured that the gas stream was at the prescribed temperature while passing through the equilibrium coil (0.6 m length) which contained the solute material. Here the solute material was evaporated into a gas stream. A sintered stainless steel filter (2 $\mu$m pore size) was incorporated into the line on the downstream side of the equilibrium coil to eliminate any possible entrainment. After leaving the filter the saturated gas led to a throttle valve. The stream pressure was reduced to approximately atmospheric pressure across the throttle valve, after which the stream flowed through the sampling loop of a gas chromatograph. The throttle valve, sampler (1.37 cc) and tubing outside the bath to the gas chromatograph were heated with a Nichrome-wired heating system and insulated to prevent any condensation of solute. The temperature of the line outside the bath was controlled at 180$\pm$5°C.

Pressure in the coils was read from a calibrated Heise gage (0.5 Kg/cm$^2$ minimum scale, 200 Kg/cm$^2$ full scale). Temperature of the bath was read from a mercury thermometer (0.05$^\circ$C minimum scale).

To assure complete saturation of the gas, the gas
flow rate measured by a soap-film flow meter was varied in the range 10 to 50 ml/min by way of a trial. It was found that any variation of flow rate within a range less than 25 ml/min did not affect the results.

### Table 1: Solubility of solid naphthalene in supercritical ethylene at 35, 50 and 65°C respectively

<table>
<thead>
<tr>
<th>Temperature</th>
<th>35°C</th>
<th>50°C</th>
<th>65°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure [atm]</td>
<td>$y_1$</td>
<td>Pressure [atm]</td>
<td>$y_1$</td>
</tr>
<tr>
<td>8.0</td>
<td>5.44E-5</td>
<td>7.9</td>
<td>1.69E-4</td>
</tr>
<tr>
<td>13.3</td>
<td>4.09E-5</td>
<td>12.7</td>
<td>1.17E-4</td>
</tr>
<tr>
<td>20.0</td>
<td>3.92E-5</td>
<td>19.0</td>
<td>9.55E-5</td>
</tr>
<tr>
<td>30.7</td>
<td>4.27E-5</td>
<td>28.6</td>
<td>1.14E-4</td>
</tr>
<tr>
<td>34.0</td>
<td>5.25E-5</td>
<td>39.1</td>
<td>1.73E-4</td>
</tr>
<tr>
<td>40.0</td>
<td>7.28E-5</td>
<td>47.5</td>
<td>2.17E-4</td>
</tr>
<tr>
<td>48.2</td>
<td>9.84E-5</td>
<td>51.3</td>
<td>2.75E-4</td>
</tr>
<tr>
<td>55.1</td>
<td>1.57E-4</td>
<td>56.9</td>
<td>3.37E-4</td>
</tr>
<tr>
<td>59.1</td>
<td>2.28E-4</td>
<td>61.6</td>
<td>5.04E-4</td>
</tr>
<tr>
<td>62.1</td>
<td>3.72E-4</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The flow rate was held in the range of 10 to 15 ml/min.

### 3.2 Materials

Naphthalene obtained from Wako Pure Chemical Industries was of special-grade purity. Ethylene obtained from Seitetsu Chemical Company had a reported minimum purity of 99.5%. These materials were used without further purification. The column packing was PEG 20 M and the length of the column was 1 m. The thermostat bath containing the column recorded 200°C at all measurements during the test. Nitrogen was the carrier gas.

### 3.3 Gas analysis

To determine solute concentration, measurements were made with a Shimazu gas chromatograph (Model GC-4BPTF) with hydrogen flame ionization detector and a Takeda digital integrator (Model TR-2215A).

### 3.4 Calibration

The flow method (also referred to as the direct injection method) was chosen for calibration of the flame ionization detector.

Helium was chosen as carrier gas because it has very low solubility in naphthalene, and its volumetric properties are accurately known over the temperature range involved.

From Eq. (7) the enhancement factor of naphthalene for the helium-naphthalene system is calculated to be less than 1.003 at 1 atm and over temperature levels of 35 to 65°C. In the calculation the second virial cross-coefficients were estimated by a correlation of Tsonopoulos. Mole fraction of naphthalene in the sampler was calculated as

$$y_1 = E_1 \frac{P_{\text{sat}}}{P}$$

The calibration curve was fitted by a quadratic equation. Arithmetic average deviation of the data from the equation was 3.1%.

### 4. Results and Discussion

Solubility data were obtained at temperature levels of 35, 50 and 65°C and in the pressure range of 8 to...
Eig. 4 Experimental and calculated solubilities of solid naphthalene in ethylene at 65°C

The results are given in Table 1 and Figs. 2 to 4. Data of Tsekhanskaya et al.18 at 35°C and Diepen and Scheffer21 at 50°C are also shown in these figures for comparison. At 35°C there is no apparent discrepancy between our data and those of Tsekhanskaya et al. But at 50°C the data of Diepen and Scheffer appear to be too high at lower pressures compared with our data.

To check the accuracy of experimental data of this work, a plot of the enhancement factor was tried, as shown in Fig. 5; it must be equal to unity at the vapor pressure for the temperature under consideration. On this basis, the data from the present work appear reasonable.

The solubility of component 1 in component 2 was calculated by two different methods. The first method uses Eqs. (3), (4), (8), (9) and (10). Terms including \( ACP \) in Eq. (4) were neglected, because these terms are much less significant than the others. The second method uses Eqs. (5), (8), (9) and (10). Results obtained by both methods show little difference. The difference ranges from 1% at 65°C to 3% at 35°C. The following discussion is limited to the former method.

The solubility was calculated by a trial-and-error procedure. Temperature and pressure were selected as the independent, known variables; the program calculates the mole fraction in vapor phase. We calculated the solubility by three different approaches; first, assuming \( k_{12} = s_{12} = 0 \); second, using \( k_{12} \) and \( s_{12} \) from the correlation of solid-liquid equilibria of the previous study18; third, using empirical \( k_{12} \) and \( s_{12} \) which best reproduce the experimental solubility data. The results are given in Figs. 2 to 4. They show that the calculations are not too sensitive to values of \( k_{12} \) and \( s_{12} \) in this experimental range. It is interesting to note that the calculations reproduced fairly good results even with \( k_{12} = s_{12} = 0 \). The calculations with \( k_{12} \) and \( s_{12} \) from the correlation of the solid-liquid equilibria did not improve the results very much. This may be due to the difference of phases in which fugacity coefficients were calculated: vapor phase in this work, liquid phase in the solid-liquid equilibria.

Moreover, to test the applicability of our method the calculations were performed at 12 and 25°C, as shown in Fig. 6. Results of calculations at 12°C show that even a small variation of \( k_{12} \) and \( s_{12} \) appreciably affects calculated results. This may be due to the fact that the system temperature of 12°C is very near the critical temperature of ethylene (9.5°C).
Conclusions

Solubility of naphthalene in compressed ethylene was measured at temperature levels of 35, 50 and 65°C and in the pressure range of 8 to 62 atm.

A calculation method was proposed to determine the solubility of a heavy solute in a supercritical solvent. It was shown that the method can correlate well the solubility of solid naphthalene in ethylene in the temperature range between 12 and 65°C and over pressure ranges of 8 to 300 atm. The method uses the Lee-Kesler equation of state together with the pseudocritical method, analogously to the solubility of solids in liquid phase which was reported previously. The correlation requires two adjustable parameters, but even without these parameters the results seem fairly reasonable for the ethylene-naphthalene system.

Acknowledgement

The authors wish to express their thanks to Mr. H. Takeda, Mr. M. Takahashi and Mr. T. Hojyo for their work during the study.

Nomenclature

\( B \) = second virial coefficient \([\text{cc} \cdot \text{mol}^{-1}]\)

\( C_p \) = heat capacity at constant pressure \([\text{cal} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}]\)

\( E \) = enhancement factor \([-\text{]}\)

\( f \) = fugacity \([\text{atm}]\)

\( H \) = molar enthalpy \([\text{cal} \cdot \text{mol}^{-1}]\)

\( k_{ij} \) = interaction parameter \([-\text{]}\)

\( P \) = pressure \([\text{atm}]\)

\( R \) = gas constant, 1.9872 \([\text{cal} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}]\)

\( S \) = molar entropy \([\text{cal} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}]\)

\( s_{ij} \) = interaction parameter \([-\text{]}\)

\( T \) = temperature \([\text{K}]\)

\( V \) = molar volume \([\text{cc} \cdot \text{mol}^{-1}]\)

\( y \) = mole fraction in vapor \([-\text{]}\)

\( Z \) = compressibility factor \([-\text{]}\)

\( \varphi \) = fugacity coefficient \([-\text{]}\)

\( \omega \) = acentric factor \([-\text{]}\)

\(<\text{Superscripts and Subscripts}>\)

\( c \) = critical

\( f \) = fusion

\( l, f, k \) = components in solution

\( l \) = liquid

\( m \) = mixture

\( (R) \) = reference fluid

\( s \) = solid

\( sat \) = saturated

\( t \) = triple point

\( v \) = vapor phase

\( (O) \) = simple fluid

\( o \) = pure

\( 1 \) = solute

\( 2 \) = solvent

\( \ast \) = pseudocritical property of mixture

\( \ast \) = ideal gas

Literature Cited