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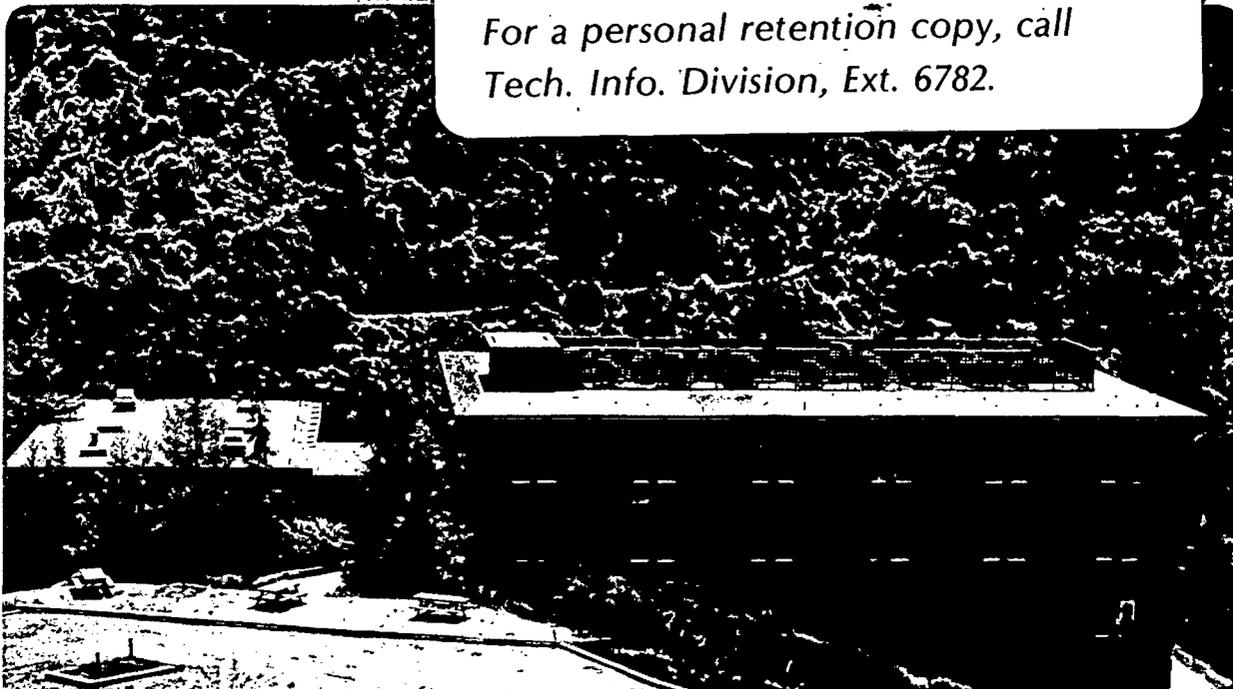
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CALCULATION OF DEW POINTS IN TAR-CONTAINING GAS STREAMS

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**Solubilities of Heavy Fossil Fuels in Compressed Gases.
Calculation of Dew Points in Tar-Containing Gas Streams**

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ABSTRACT

A molecular-thermodynamic model is used to establish a correlation for solubilities of heavy fossil fuels in dense gases (such as those from a coal gasifier) in the region ambient to 100 bar and 600 K. This model is then applied to calculate dew points in tar-containing gas streams.

The heavy fuel is fractionated in a spinning-band column at high reflux; each fraction is considered to be a pseudo-component. Each fraction is characterized by one vapor-pressure datum (obtained during fractionation), elemental analysis, and proton-NMR spectra (to determine aromaticity). Liquid-phase properties are obtained from the SWAP equation for vapor pressure and from a density correlation. Vapor-phase properties are obtained using the virial equation of state with virial coefficients from Kaul's correlation.

Experimental solubility measurements have been made for two Lurgi coal-tar fractions in dry and moist methane. Calculated and experimental solubilities agree well.

The correlation is used to establish a design-oriented computer program for calculating isobaric condensation as a function of temperature as required for design of a continuous-flow heat exchanger.

Introduction

The high cost of energy has stimulated new process technologies toward more efficient utilization of energy resources; therefore, there has been growing interest in upgrading coal, heavy petroleum fractions, tar sands, shale oil, etc.

Design of "downstream units" for emerging processes requires quantitative information for equilibrium properties of heavy fossil fuels at elevated temperatures and pressures. This work is concerned with the solubility of a heavy, fossil-fuel mixture in a compressed gas. This solubility is of interest in process design: e.g. for petroleum-reservoir pressurization with light gases, toward removal of high-molecular-weight hydrocarbons remaining after primary recovery; for design of coal-liquefaction reactors; for design of coal-gasification process steps (condensation and quenching) where product gas streams often contain high-boiling coal tars; and for design of heavy-fossil-fuel/light-gas separation operations. Solubilities may be of particular interest for calculating dew points as required in heat-exchanger design.

Fossil-fuel mixtures typically contain very many components. The wide range of properties and the analytical problem to identify these components makes phase-equilibrium predictions difficult. A common procedure is to separate the mixture into fractions with fewer components and smaller

ranges of properties and to characterize each fraction. Phase-equilibrium predictions and process design are then based on average or effective (pseudocomponent) properties of the characterized fractions.

In this work, we separate a heavy fuel by distillation into narrow-boiling fractions and we characterize each fraction. Characterization data are used with previously established physical-property correlations to determine required parameters in our molecular-thermodynamic model.

Fossil-Fuel Fractionation and Characterization

To obtain narrow-boiling fractions, we use a Perkin-Elmer Model 251 Annular Still, operated at high reflux, as described by Macknick (1979) and Alexander and Prausnitz (1981). Each fraction has a boiling-point range of about 20 K. Figure 1 shows a schematic of this spinning-band column and indicates operating conditions.

During fractionation, the head temperature and pressure are recorded for each fraction at the beginning and end of collection. The average temperature and pressure provide a vapor-pressure datum for the fraction since the liquid fraction is in equilibrium with its vapor as it is collected. Each fraction is weighed. Further, each fraction is analyzed for carbon, hydrogen, nitrogen, and sulfur. Finally, proton NMR spectra are obtained as discussed elsewhere (Alexander and Prausnitz, 1981). The

carbon-to-hydrogen ratio, along with the NMR spectra, determine fractional aromaticity (fraction of carbon atoms which are aromatic), as briefly explained in Appendix A.

Table 1 summarizes characterization results for a Lurgi creosote (coal tar) obtained from Sasol's coal-gasification plant in South Africa. A vapor-pressure datum for Lurgi fraction number 10 is not given because that part of the original sample could not be distilled overhead.

Solidification of compounds (probably anthracene) in the head of the column limited the lowest column pressure to above 50 torr. Since the pot temperature was limited to 300°C to minimize thermal decomposition, the heaviest overhead fraction that could be obtained has a normal boiling point of about 350°C.

Phase Equilibria: Molecular-Thermodynamic Framework

Each fraction is considered to be a pseudocomponent. At equilibrium, for any component i , the fugacity of i in the liquid phase equals that in the vapor phase:

$$f_i^L = f_i^V \quad (1)$$

For the heavy-hydrocarbon mixtures of interest here, the liquid-phase fugacity of component i is given by

$$f_i^L = x_i P_i^s (PC)_i \quad (2)$$

where x_i is the mole fraction of component i in the liquid, P_i^s is the pure-component vapor pressure, and $(PC)_i$ is the

Poynting correction.

The liquid-phase fugacity of a noncondensable (light-gas) component is here given by

$$f_i^L = x_i H_i (PC)_i \quad (3)$$

where H_i is Henry's constant for light gas i , dissolved in the mixture of condensible components.

The vapor-phase fugacity of component i is given by

$$f_i^V = y_i \phi_i P \quad (4)$$

where y_i is the mole fraction of component i in the vapor, ϕ_i is the fugacity coefficient, and P is the total pressure.

The solubility of a heavy component in a gas is determined primarily by that component's vapor pressure. Macknick and Prausnitz (1978) tested predictions of several vapor-pressure correlations for five representative heavy hydrocarbons; they found that the SWAP correlation (Smith et al., 1976) is likely to give the best results for typical heavy, fossil-fuel mixtures where the molecular structures of the heavy-hydrocarbon components are not well known. The SWAP correlation requires only a single vapor-pressure datum and an estimate of the heavy hydrocarbon's fractional aromaticity. Edwards et al. (1981) extended the SWAP vapor-pressure correlation to include the effects of heteroatoms nitrogen and sulfur. Appendix B summarizes the procedure for applying Edwards' extension of SWAP to heavy, fossil-fuel fractions.

For poorly defined mixtures, such as fossil-fuel fractions, there is little basis for prediction of the effect of liquid-phase nonidealities (activity coefficients) on fugacity. However, liquid-phase nonidealities are probably at least partially taken into account through the "effective" pseudocomponent vapor-pressure datum which is used to characterize fractions and to predict "effective" vapor pressures of pseudocomponents.

An estimate of each fraction's molar liquid volume V_L , is needed to calculate the Poynting correction $(PC)_i$, in Equation (2),

$$(PC)_i = \exp \left[\frac{V_i^L (P - P_i^s)}{RT} \right] \quad (5)$$

To estimate V_i^L , we use a correlation that requires only a normal boiling point and fractional aromaticity, as discussed in Appendix B.

To calculate mole fractions from weight fraction, we require the molecular weight for each fraction. Molecular weights are estimated as shown in Appendix B.

For water, the liquid-phase fugacity is given by

$$f_w^L = x_w \gamma_w P_w^s \phi_w^{sat} (PC)_w \quad (6)$$

For our purposes here, we assume water condenses as a pure liquid and we neglect the solubility of light gases in liquid water; thus mole fraction x_w , and activity coefficient γ_w , are set equal to unity. P_w^s , $(PC)_w$ and the

saturated-water-vapor fugacity coefficient ϕ_w^s , are calculated using empirical relations based on literature data for water. These are given in Appendix B.

Vapor-phase solubilities are not sensitive to Henry's constants when the light gases are only sparingly soluble in the liquid phase. Henry's constants for gases in fractions are estimated as shown in Appendix B.

In a mixture containing m components, vapor-phase fugacity coefficients are calculated using

$$\ln(\phi_i) = 2 \frac{P}{RT} \sum_{j=1}^m (y_j B_{ij} - B) \quad (7)$$

where B_{ij} is the cross second virial coefficient for components i and j , and for the gas-phase mixture:

$$B = \sum_{i=1}^m \sum_{j=1}^m y_i y_j B_{ij}. \quad (8)$$

Virial coefficients are calculated from the square-well potential as discussed in Appendix C.

Experimental

To test the molecular-thermodynamic framework, we have used the total-vaporization technique (Monge and Prausnitz, 1981; Monge 1982) to measure the solubilities of two Lurgi coal-tar fractions in compressed methane mixtures. Figure 2 compares experimental and predicted solubilities at 3.8, 42, and 70 bar. Comparison at the lowest pressure, where vapor-phase nonidealities are small, provides an appropriate

test of vapor-pressure prediction. As shown, agreement is good. Comparison at higher pressures, where gas-phase nonidealities and the Poynting correction are large, is also good.

The measurement for Fraction 1 at 42 bar and 200° C has been repeated for a gas mixture containing 25 mol % water in methane. The effect of water on tar-fraction solubility in the gas was found to be negligible, as correctly predicted by the model.

Molecular-weight predictions were also tested. Table 2 compares predicted molecular weights with those determined from freezing-point depression measurements (Alexander and Prausnitz, 1981) for four Lurgi coal-tar fractions.

Calculation of Solubilities

The proposed molecular-thermodynamic model, coupled with fossil-fuel-characterization data, has been incorporated into a design-oriented computer program. If a sample of the heavy-fossil fuel has been fractionated and characterized, the computer program can: (1) predict the dew-point temperature of a superheated gas mixture containing the vaporized fossil fuel at specified pressure and composition, and (2) predict the change in gas-phase solubility as the temperature falls isobarically.

Dew-Point Calculation. A fossil-fuel-containing gas is at specified pressure and composition. An iterative

procedure is used to search for the temperature at which the gas becomes saturated and the heavy fossil fuel begins to condense. At this temperature, the fugacity of each component in the liquid f_i^L , equals its fugacity in the vapor f_i^V ; the objective function F , equals zero within a specified tolerance:

$$F = \sum_{i=1}^m \left[\frac{f_i^L - f_i^V}{f_i^V} \right]^2 \quad (9)$$

Solubility versus Temperature. At constant pressure, as the temperature falls below the dew-point temperature, the gas-phase solubility of the heavy fossil fuel decreases. This decrease can be calculated assuming either, that the gas is maintained in contact with its condensing liquid or, that the condensing liquid is removed after an incremental decrease in temperature. The first option can be used to generate isobaric, solubility-versus-temperature curves. The second option provides the condensation characteristics of a saturated gas cooled in a continuous-flow heat exchanger. These calculations are useful for the design of heat exchangers for recovery of thermal energy from hot coal-gasifier effluents containing heavy tars, assuming, as we do here, that very heavy tars have been previously removed.

Newton's method is used to determine iteratively the solubility of the fossil fuel in gas after an incremental

drop in the gas temperature. Flash calculations begin by determining if water condenses at the new temperature, i.e. by asking

$$f_w^L > f_w^V ? \quad (10)$$

If the answer is yes, water does not condense. In that event, we iterate on the vapor-to-feed ratio α , using the objective function S , and its derivative with respect to α , S' , as given by Rachford and Rice (King, 1971) for a two-phase system,

$$S = \sum_{i=1}^m (y_i - x_i), \quad (11)$$

$$S' = \sum_{i=1}^m -z_i \left[\frac{(K_i - 1)}{\Phi} \right]^2, \quad (12)$$

where

$$x_i = z_i / \Phi \quad (13)$$

$$\Phi = \alpha(K_i - 1) + 1 \quad (14)$$

$$y_i = K_i x_i. \quad (15)$$

Here, z_i is the mole fraction of component i in the feed and K_i is the equilibrium K factor ($K_i = y_i / x_i$). S and S' , evaluated at α_{old} (old estimate for α), are used to obtain a new estimate for α ,

$$\alpha_{new} = \alpha_{old} - S/S'. \quad (16)$$

The iterative procedure is repeated until α_{new} is found where S equals zero within a specified tolerance.

However, if

$$f_w^V > f_w^L, \quad (17)$$

water condenses. In that event, we use an objective function derived from material balances for a three-phase system, where one phase is pure (liquid water). The derivation of the three-phase objective function is given in Appendix D.

At a given temperature, the gas-phase solubility of the fossil fuel is given by the sum of the converged gas-phase mole fractions for all fossil-fuel fractions.

For isobaric condensation-versus-temperature calculations, the total number of moles in the gas phase is adjusted after each incremental temperature decrease because the condensed liquid is removed from consideration (as in a flow heat exchanger). The vapor-to-feed ratio is used in the material balances to calculate the fraction of the vapor condensed as hydrocarbon-rich liquid and water. The calculations are repeated at incrementally lower temperatures (typically 5°C).

Figure 3 shows some solubility-versus-temperature calculations for a typical coal-gasifier effluent containing all but the heaviest parts of the Lurgi coal tar described in Table 1. Figure 3 also shows the initial gas composition (heaviest tars previously removed). Figure 4 shows the results of condensation-versus-temperature calculations for

the same system.

The computer program is available, upon request, from the authors.

Discussion and Conclusion

Vapor-phase nonidealities and Poynting corrections can have a significant effect on the solubility-versus-temperature behavior of light-gas/heavy-fossil-fuel systems, even at moderate pressures. Neglect of the fugacity coefficient and Poynting correction, can cause solubility to be underpredicted by a factor of three. Figure 5 compares corrected (proposed model) and "uncorrected" solubility-versus-temperature curves for a Lurgi coal-tar fraction in methane at 70 bar. In the solubility range 0.01 to 0.001, "uncorrected" predictions lead to errors of about 30°C in the dew-point temperature. Figure 3 shows a similar comparison for the typical coal-gasifier effluent described earlier. In this case, "uncorrected" predictions lead to errors of about 15°C in the dew-point temperature.

The proposed molecular-thermodynamic model predicts solubilities which are in good agreement with measured solubilities at pressures to 70 bar and 275°C. The average error is 4.5% for 16 solubility data. On the basis of these results, it is likely that the proposed model provides useful predictions for process design.

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Appendix A. Fractional Aromaticities from Proton-NMR Spectra and Carbon-to-Hydrogen Ratio

In hydrocarbons, the relative concentrations of aromatic and paraffinic hydrogen atoms are readily determined from proton-NMR spectra where four types of hydrogen atoms yield distinct chemical shifts relative to the absorption for hydrogens of a reference substance, hexamethyldisiloxane, HMDS (Alexander and Prausnitz, 1981). Hydrogen atoms which are attached to aromatic carbon atoms H_{aro} , shift in the range 6.0 - 9.0 δ relative to HMDS. Hydrogen atoms attached to carbons alpha to aromatic carbons H_{α} , shift in the range 1.7 - 4.0 δ relative to HMDS. Hydrogen atoms attached to nonterminal, nonalpha, aliphatic carbons H_{β} , shift in the range 0.9 - 1.7 δ relative to HMDS. Finally, hydrogens attached to terminal, nonalpha, aliphatic carbons H_{γ} , shift in the range 0.5 - 0.9 δ relative to HMDS.

Fractional aromaticity F_A , can be determined from proton-NMR measurements as follows:

$$\begin{aligned}
 F_A &= \frac{C_{\text{aro}}}{C_{\text{tot}}} = 1 - \frac{H_{\text{tot}}}{C_{\text{tot}}} \left[\frac{C_{\alpha} + C_{\beta} + C_{\gamma}}{H_{\text{tot}}} \right] \\
 &= 1 - (H/C)_{\text{tot}} \left[(C/H)_{\alpha} \frac{H_{\alpha}}{H_{\text{tot}}} + (C/H)_{\beta} \frac{H_{\beta}}{H_{\text{tot}}} + (C/H)_{\gamma} \frac{H_{\gamma}}{H_{\text{tot}}} \right] \quad (\text{A1}) \\
 &= 1 - (H/C)_{\text{tot}} \left[(C/H)_{\alpha} I_{\alpha} + (C/H)_{\beta} I_{\beta} + (C/H)_{\gamma} I_{\gamma} \right] / I_{\text{tot}}
 \end{aligned}$$

where H_c is the concentration of hydrogen atoms which are bonded to carbon atoms of type c and C_c is the concentration of carbon atoms of type c. I_c is the integral of the

proton-NMR spectra within the limits of type c. The subscript tot, refers to the sum ($\alpha + \beta + \gamma$). If one assumes: no alkyl bridges, no naphthenic rings, no branching except at alpha carbons, and no heteroatoms, then

$$(C/H)_{\alpha} = 1/3$$

$$(C/H)_{\beta} = 1/2$$

$$(C/H)_{\gamma} = 4/9$$

and

$$F_A = 1 - (H/C) \left[\frac{\frac{I_{\alpha}}{3} + \frac{I_{\beta}}{2} + \frac{4}{9}I_{\gamma}}{I_{\alpha} + I_{\text{aro}} + I_{\beta} + I_{\gamma}} \right] \quad (A2)$$

with the qualifier:

If $I_{\alpha} = 0$, and $I_{\text{aro}} = 0$; then $F_A = 0$.

Figure A1 shows sample spectra for a Lurgi coal-tar fraction. The spectra are for a solution of coal-tar fraction in totally deuterated pyridine. The solvent must be periodically tested for purity as trace non-deuterated pyridine forms by reaction with atmospheric water. (Non-deuterated pyridine adds to the H_{α} shift.)

Appendix B. Liquid-Phase Properties

To estimate an effective or average property (molecular weight, molar liquid volume, Henry's constants for solutes, and square-well parameters) of a heavy fraction, we use its fractional aromaticity to interpolate between the appropriate property of a pure alkane and that of a pure aromatic, both having the same normal boiling point as that of the heavy fraction. Literature data have been used to correlate, with normal boiling point, the needed properties of pure alkanes and aromatics. We use Edwards' et al. (1981) extension of SWAP (Smith et al., 1976) to estimate the normal boiling point of a fraction.

Vapor Pressures of Heavy Fractions. To apply Edwards' extension of SWAP, we need the normal boiling point, T_{760} of the homomorph of the heavy fraction. The homomorph is defined as the compound obtained by replacing heteroatoms (nitrogen and sulfur) with equivalent carbon atoms. For example, the homomorph of quinoline is naphthalene. The original SWAP correlation is used to estimate T_{760} of a heavy fraction's homomorph. To estimate the fractional aromaticity of the homomorph F_A^{homo} (required to use SWAP correlation), we assume that all nitrogen and sulfur atoms in the heavy fraction are bound in fused rings, displacing aromatic carbons, as nitrogen does in quinoline,

$$F_A^{\text{homo}} = F_A \left[\frac{\text{no. of C atoms}}{\text{no. of C + S + N atoms}} \right] + F_N + F_S, \quad (\text{B1})$$

where F_N and F_S are determined from elemental analysis,

$$F_N = \frac{\text{no. of N atoms}}{\text{no. of N + S + C atoms}} \quad (\text{B2})$$

$$F_S = \frac{\text{no. of S atoms}}{\text{no. of N + S + C atoms}} \quad (\text{B3})$$

and F_A is the fractional aromaticity determined from elemental analysis and proton-NMR spectra.

Molecular Weights of Heavy Fractions. To estimate MW, the molecular weight of a heavy fraction, we interpolate between the molecular weight of the alkane and that of the aromatic, both having the same T_{760} as that of the heavy fraction:

$$\text{MW} = (1 - F_A)(\text{MW})_{\text{alkane}} + F_A(\text{MW})_{\text{aromatic}} \quad (\text{B4})$$

where

$$(\text{MW})_{\text{alkane}} = -385.01 + 2.637T_{760} - 0.005019T_{760}^2 + 4.0234 \times 10^{-6}T_{760}^3 \quad (\text{B5})$$

and

$$(\text{MW})_{\text{aromatic}} = -68.28 + 0.4062T_{760} \quad (\text{B6})$$

Equations B5 and B6 were obtained from molecular-weight and T_{760} data for the normal alkanes, C_5 to C_{40} , and for fused-ring aromatics, benzene, naphthalene, anthracene, and chrysene (Macknick, 1979).

Molar Liquid Volumes of Heavy Fractions. To estimate molar volume as a function of temperature, we estimate the fraction's volumetric coefficient of expansion θ ,

$$\theta = \frac{1}{V^L} \left[\frac{\partial V^L}{\partial T} \right]_P \quad (B7)$$

Assuming that θ is constant,

$$\theta = \ln \left[\frac{V^L(T_{760})}{V^L(T=300)} \right] (T_{760} - 300)^{-1} \quad (B8)$$

We obtain $V^L(T=300)$ from the molecular weight and from the specific gravity (Nokay, 1959). To obtain $V^L(T_{760})$, we interpolate between corresponding values for the alkane and aromatic.

$$V^L(T_{760}) = (1 - F_A) V_{alk}^L(T_{760}) + F_A V_{aro}^L(T_{760}) \quad (B9)$$

where

$$V_{alk}^L(T_{760}) = 27.65 NC - 34.2 \quad (B10)$$

$$V_{aro}^L(T_{760}) = 83.86 NR - 5.48 \quad (B11)$$

$$NC = \exp \left[-0.128814 + 5.581 \times 10^{-3} T_{760} - 9.40 \times 10^{-7} T_{760}^2 \right] + 1 \quad (B12)$$

$$NR = -1.9256 + 8.124 \times 10^{-3} T_{760} \quad (B13)$$

NC and NR are, respectively, the number of aliphatic carbons and the number of fused rings in the alkane and aromatic, with normal boiling point, T_{760} . Equations B10 through B13 were obtained from predicted (Hankinson and Thomson, 1979) molar volumes at T_{760} for normal alkanes, (C_4 to C_{40}), and for fused-ring aromatics, benzene, naphthalene, anthracene, and chrysene.

Henry's Constant and Poynting Correction for Light Gases. A rough approximation for Henry's constant H_{ij} , for light gas i , in pseudocomponent j , is calculated from

$$\log_{10}[H_{ij}(\text{atm.})] = A_i + B_i \frac{T}{T_{760}} + C_i F_A . \quad (\text{B14})$$

Table B1 gives constants A_i , B_i , and C_i for nine light gases. These approximate correlations, necessary to account for the relatively small effect of the solubility of light gases in the heavy liquids on vapor-phase solubility, are based on the data of Cukor (1972), Chappelow (1974), and Tremper and Prausnitz (1976). Henry's constant H_i , for a light gas in the heavy-fraction mixture is calculated using the mixing rule,

$$\log_{10}(H_i) = \frac{\sum_{j=1}^n (x_j \log_{10} H_{ij})}{\sum_{j=1}^n x_j} \quad (\text{B15})$$

where n is the number of pseudocomponents.

The Poynting correction in Equation (3) is given by,

$$(\text{PC})_i = \exp \left[\frac{\bar{V}_{ij}^{\infty} (P - P_j^s)}{RT} \right] . \quad (\text{B16})$$

The partial molar volume \bar{V}_{ij}^{∞} , of gas i , at infinite dilution in pseudocomponent j , is estimated by the method of Lyckman et al. (1965). Gas-phase solubility results are not sensitive to inaccuracies in Equations B14, B15, and B16.

Fugacity of Liquid Water. Vapor pressure of water is calculated using expressions given in the NEL Steam Tables (1964). Molar liquid volume is calculated using the COSTALD correlation (Hankinson and Thomson, 1979). Saturated-vapor fugacity coefficient ϕ_w^s , is calculated using the empirical relation

$$\phi_w^s(\text{bar}) = 1.0204 + 5.722 \times 10^{-4}T - 1.761 \times 10^{-6}T^2, \quad (\text{B17})$$

for T greater than 420 K. For T less than 420 K, ϕ_w^s is set equal to unity.

Appendix C. Virial Coefficients

Virial coefficients are based on a square-well potential (Hirschfelder et al., 1954) as described by Kaul and Prausnitz (1978). The well width is fixed at 0.2 nm.

$$\frac{B_{ij}}{b_{oij}} = 1 - (g_{ij}^3 - 1) \left[\exp\left(\frac{\epsilon_{ij}}{kT}\right) - 1 \right] \quad (C1)$$

where

$$b_{oij} = \frac{2\pi N}{3} \sigma_{ij}^3$$

$$g_{ij} = \frac{\sigma_{ij} + 0.2}{\sigma_{ij}} \quad (\sigma \text{ in nm}) \quad (C2)$$

$$\sigma_{ij} = \frac{1}{2}(\sigma_i + \sigma_j)$$

where k is Boltzmann's constant, N is Avogadro's number, and σ_{ij} and ϵ_{ij} are size and energy parameters for molecular pair ij .

Light Gases. For light-gas molecules and their mixtures, σ_{ij} and ϵ_{ij} have been obtained from reduction of second virial-coefficient data. Tables C1 and C2 give parameters for nine light gases.

Water and Water/Light-Gas Pairs. The energy parameter for water has been split into a nonpolar contribution ϵ_w^0 , and a polar contribution ϵ_w^1 ,

$$\epsilon_w = \epsilon_w^0 + \frac{\epsilon_w^1}{T} \quad (C3)$$

Reduction of pure-water second virial-coefficient data does not yield unique values of the three adjustable parameters

σ , ϵ^0 and ϵ^1 . However, reasonable values can be chosen such that σ_w is physically sensible and such that ϵ_w^0/k gives good results for water-nonpolar mixtures (Equation C6). The values chosen here are:

$$\begin{aligned}\sigma_w &= 0.28 \text{ nm}, \\ \epsilon_w^0/k &= 186 \text{ K}, \\ \epsilon_w^1/k &= 1.67 \times 10^5 \text{ K}^2.\end{aligned}\tag{C4}$$

For water/light-gas (j) mixtures, the cross energy parameter is calculated from,

$$\epsilon_{wj} = (\epsilon_w^0 \epsilon_{jj})^{1/2}\tag{C6}$$

The water/carbon dioxide binary (j=carbon dioxide) is given special treatment to account for association. The cross virial coefficient is split into a chemical contribution, B_{wj}^{chem} , and a physical contribution, B_{wj}^{phys} , (Nothnagel et al., 1973),

$$B_{wj} = B_{wj}^{\text{phys}} + B_{wj}^{\text{chem}}\tag{C7}$$

where

$$B_{wj}^{\text{chem}} = -0.5RTK_{wj}\tag{C8}$$

The equilibrium constant of association K_{wj} , has been fit (De Santis et al., 1974) to experimental data,

$$\ln(K_{wj}) = -11.071 + \frac{5953}{T} - 2.746 \times 10^6 T^{-2} + 4.646 \times 10^8 T^{-3}\tag{C9}$$

where K_{wj} is in atmospheres and T is in kelvin. The experimental data of Coan and King (1971) and Equations C7,

C8, and C9 were used to obtain for water/carbon dioxide:

$$\frac{\epsilon_{wj}}{k} = 186.7K . \quad (C10)$$

The size parameter was calculated using

$$\sigma_{wj} = \frac{1}{2}(\sigma_w + \sigma_j) . \quad (C11)$$

Heavy-Fraction/Light-Gas Binaries. Calculation of effective square-well parameters for heavy-fraction/light-gas binaries is based on the correlation of Kaul and Prausnitz (1978). To account for molecular flexibility, Kaul calculated the effective size parameters of heavy hydrocarbons from their mean radius of gyration RG , relative to that of methane,

$$\frac{1}{2} \sigma_i = \frac{1}{2} \sigma_{\text{methane}} + (RG)_i - (RG)_{\text{methane}} . \quad (C12)$$

For methane, $RG = 0.0443$ nm (Moelwyn-Hughes, 1961) and $\sigma/2 = 0.1675$ nm (Sherwood and Prausnitz, 1964). To estimate the effective RG for heavy fractions, we interpolate between values corresponding to a saturated alkane $(RG)_{\text{alkane}}$, and that corresponding to a fused-ring aromatic $(RG)_{\text{aromatic}}$, when both have the same T_{760} as that of the heavy fraction:

$$(RG)_i = (1 - F_A)(RG)_{\text{alkane}} + F_A(RG)_{\text{aromatic}} . \quad (C13)$$

$(RG)_{\text{alkane}}$ has been correlated with NC using the molecular-dynamics results of Bellemans (1973),

$$(RG)_{\text{alkane}} = 0.0637(NC)^{0.6} \left[1 + \frac{0.547}{NC} \right]^{1/2} \quad (\text{nm}) \quad (C14)$$

where

$$NC = \exp [-0.128814 + 5.581 \times 10^{-3} T_{760} - 9.40 \times 10^{-7} T_{760}^2] \quad (C15)$$

(RG)_{aromatic} has been correlated with NR using values calculated from molecular structure data (Bower and Sutton, 1965) for benzene, naphthalene, anthracene, and chrysene:

$$(RG)_{aromatic} = 0.0794 + 0.0398(NR) \quad (nm) \quad (C16)$$

$$NR = -1.9256 + 8.124 \times 10^{-3} T_{760} \quad (C17)$$

Kaul proposed a correlation of s_{ij} with ΔH (Hildebrand enthalpy of vaporization of the heavy hydrocarbon) for calculating s_{ij} for heavy-hydrocarbon/light-gas pairs. ΔH is defined as the enthalpy of vaporization at the temperature where the saturated-vapor volume is 49.5 L/gmol. For heavy fractions, ΔH is obtained from Edwards' SWAP vapor-pressure curve using the Clausius-Clapeyron equation. Table C3 gives correlations for s_{ij} with ΔH for nine light gases.

Appendix D. Objective Function for Three-Phase Flash

If vapor, hydrocarbon-rich liquid, and pure liquid are known to exist, we use an objective function derived from material balances for a three-phase system, where one phase is pure, liquid water. The overall material balance, based on one mole of feed is,

$$1 = \alpha + \eta + \mu \quad (D1)$$

where η and μ are the fractions of the feed which condense as hydrocarbon-rich and pure-water phases, and α is the fraction of the feed that does not condense. The component balance for water is

$$z_w = \alpha y_w + \mu \quad (D2)$$

where z_w is the mole fraction of water in the feed. The component balance for component i , other than water is,

$$z_i = y_i \alpha + x_i \eta \quad (D3)$$

Eliminating μ yields,

$$\eta = (1 - z_w) - \alpha(1 - y_w) \quad (D4)$$

Substituting Equation D4 into Equation D3, dividing by x_i , and using the definition of K_i , we obtain

$$x_i = \frac{z_i}{\xi_i} \quad (D5)$$

where

$$\xi_i = \alpha(K_i - 1 + y_w) + 1 - z_w \quad (D6)$$

This expression for x_i and

$$y_i = K_i x_i \quad (D7)$$

are used in the objective-function,

$$S = \sum_{i=1}^m (y_i - x_i) . \quad (D8)$$

The derivative with respect to α is,

$$S' = \sum_{i=1}^m \frac{-z_i (K_i - 1) (K_i - 1 + y_w)}{\zeta_i^2} \quad (D9)$$

where

$$y_w = \frac{f_w^L}{\theta_{wP}} . \quad (D10)$$

Nomenclature

- A_i, B_i, C_i = constants in Equation B14
 B = second virial coefficient of the mixture
 B_{ij} second cross virial coefficient for components i and j
 c = type of carbon atom (aromatic, α , β , or γ)
 C_c = concentration of carbon atoms of type c
 F = objective function (Equation 9)
 F_A = fractional aromaticity
 F_A^{homo} = fractional aromaticity of the homomorph
 (Equation B1)
 F_N = fractional heteroatomicity with respect to nitrogen
 F_S = fractional heteroatomicity with respect to sulfur
 f = fugacity
 H_i = Henry's constant of component i in the liquid mixture
 H_c = concentration of hydrogen atoms of type c
 H_{ij} = Henry's constant of component i in heavy fraction j
 HMDS = hexamethyldisiloxane
 I_c = integral of proton-NMR spectra within the limits of
 type c hydrogen atoms
 k = Boltzmann's constant
 K_i = equilibrium K factor
 K_{12} = equilibrium constant for association of water and
 carbon dioxide
 m = number of components in system
 MW = molecular weight
 MW_{alkane} = molecular weight of normal alkane having same

normal boiling point as heavy fraction (Equation B5)

MW_{aromatic} = molecular weight of aromatic having same
normal boiling point as heavy fraction (Equation B6)

n = number of heavy fractions

N = Avagadro's number

NC = number of aliphatic carbons in alkane having same
normal boiling point as heavy fraction (Equation B12)

NMR = nuclear magnetic resonance

NR = number of fused rings in aromatic having same
normal boiling point as heavy fraction (Equation B13)

P = total pressure

P_i^s = vapor pressure of component i

p_w^s = vapor pressure of water

P_{exp} = average pressure (torr) corresponding to vapor-
pressure datum of heavy fraction

$(PC)_i$ = Poynting correction for component i

RG = radius of gyration of a molecule

R = gas constant

S = objective function (Equation 11 and D7)

S' = derivative of objective function with respect to a
(Equations 12 and D8)

T = absolute temperature

T_{exp} = average temperature (K) corresponding to vapor-
pressure datum of heavy fraction

TR = reduced temperature, T/T_{760}

T_{760} = normal boiling point

v_i^L = molar liquid volume of component i

v_w^L = molar liquid volume of water

$v^L(T=300)$ = molar liquid volume at 300 K

$v^L(T_{760})$ = molar liquid volume at the normal boiling point

\bar{v}_{ij}^∞ = partial molar volume of gas i in heavy liquid j at
infinite dilution

x_i = mole fraction of component i in the liquid

y_i = mole fraction of component i in the vapor

z_i = mole fraction of component i in feed

Greek Letters

α = fraction of feed that is vapor after flash

δ = chemical shift in NMR spectra, dimensionless

γ = activity coefficient

ΔH = Hildebrand enthalpy of vaporization

ϵ_{ij} = energy parameter (square-well potential) for
molecules i and j

ϵ_w = energy parameter of water

ϵ_w^0 = nonpolar contribution to energy parameter of
water

ϵ_w^1 = polar contribution to energy parameter of
water

σ_{ij} = size parameter (square-well potential) for molecules
i and j

σ_w = size parameter for water

η = fraction of feed which condenses as hydrocarbon-rich
phase

μ = fraction of feed which condenses as pure water

ξ_i = defined in Equation D5

ϕ = fugacity coefficient

ϕ^s = saturated-vapor fugacity coefficient

\bar{V} = defined in Equation 13

θ = volumetric coefficient of expansion

Subscripts

aro = aromatic

i = component

w = water

wj = water/(light gas, j)

tot = total

R = reduced

α = carbons alpha to aromatic carbons

β = nonterminal, nonalpha, aliphatic carbons

γ = terminal, nonalpha, aliphatic carbons

Superscripts

chem = chemical

L = liquid

o = nonpolar contribution

phys = physical

s = saturated vapor

V = vapor

l = polar contribution

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Table 1
 Characterization Data for Lurgi Coal Tar

Frac. No.	Weight %	Vapor Pressure Datum			Elemental Analysis, wt%				Aroma- ticity
		T, °C	P, torr	C	H	N	S	Other	
1	0.45	95	57	83.	9.9	0.8	0.5	5.6	0.53
2	1.2	121	53	84.	8.6	1.1	0.2	6.0	0.64
3	1.8	141	50	85.	8.5	0.8	0.3	5.5	0.64
4	1.6	158	51	86.	8.9	1.2	0.4	3.7	0.69
5	4.1	178	52	86.	8.6	1.3	0.5	3.9	0.64
6	17.5	194	52	87.	8.4	1.1	0.3	3.8	0.69
7	20.8	205	52	87.	8.5	1.2	0.5	3.3	0.67
8	10.8	222	51	88.	8.2	1.0	0.4	2.1	0.71
9	15.7	239	50	86.	8.5	1.4	0.3	3.7	0.65
10	26.1	---	--	87.	8.1	1.4	0.3	3.7	0.66

Table 2

Comparison of Predicted and Measured
Molecular Weights for Four
Lurgi Coal-Tar Fractions

<u>Fraction No.</u>	<u>Molecular Weight Predicted</u>	<u>Weight Measured</u>	<u>% Error</u>
6	184	187	1.6
7	192	207	6.8
8	201	209	3.8
9	218	227	4.0

Average 4.0

Table B1

Constants for Approximate[#] Henry's-Constant Correlation
for Light Gases in Heavy Fractions (Pseudocomponents)
(Equation B14)

Light Gas	A	B	C	Reduced- Temp. Range*
Hydrogen	3.55	-0.936	0.524	0.4 < TR < 1.0
Nitrogen	3.21	-0.591	0.567	0.4 < TR < 1.0
Carbon monoxide	2.92	-0.348	0.50	0.4 < TR < 1.0
Methane	1.92 2.40	0.596 0.0	0.531 0.531	0.4 < TR < 0.8 0.8 < TR < 1.0
Ethane	0.28 2.00	2.15 0.0	0.497 0.497	0.4 < TR < 0.8 0.8 < TR < 1.0
Carbon dioxide	1.14 2.23	1.37 0.0	0.270 0.270	0.4 < TR < 0.8 0.8 < TR < 1.0
Hydrogen sulfide	0.27	2.11	0.0	0.4 < TR < 1.0
Propane	-0.66 2.78	2.95 0.0	0.404 0.404	0.4 < TR < 0.8 0.8 < TR < 1.0
Butane	-1.88 2.60	4.27 0.0	0.40 0.40	0.4 < TR < 0.8 0.8 < TR < 1.0

While sufficiently accurate for our work, these approximate correlations may not be sufficiently accurate for other applications.

* $TR = T/T_{760}$ (T_{760} of the fraction)

Data References

1. Chappelow, C. G., and Prausnitz, J. M., AIChEJ., 20,1097 (1974).
2. Cukor, P. M., and Prausnitz, J. M., J. Phys. Chem., 76,598 (1972).
3. Tremper, K. K., and Prausnitz, J. M., J. Chem. Eng. Data, 21,295 (1976).

Table C1

Square-Well Parameters for Nine Light Gases
(Well Width = 0.2 nm)

Light Gas	σ , nm	ϵ/k , K
1-Hydrogen	0.245	18.7
2-Nitrogen	0.327	89.1
3-Carbon monoxide	0.325	92.6
4-Methane	0.335	141
5-Ethane	0.403	259
6-Carbon dioxide	0.357	211
7-Hydrogen sulfide	0.387	272
8-Propane	0.465	346
9-Butane	0.514	425

Table C2

Square-Well Parameters for Light-Gas Pairs

Pair#	$\epsilon_{ij}/k, K$	Pair#	$\epsilon_{ij}/k, K$
1-2	43.5	3-7	(127)
1-3	(43.5)	3-8	(178)
1-4	50.3	3-9	(182)
1-5	59.5	4-5	197
1-6	(58.0)	4-6	171
1-7	(55.0)	4-7	154
1-8	79.7	4-8	231
1-9	84.0	4-9	258
2-3	(89.0)	5-6	222
2-4	106	5-7	237
2-5	151	5-8	295
2-6	147	5-9	331
2-7	127	6-7	245
2-8	178	6-8	251
2-9	182	6-9	272
3-4	(106)	7-8	(278)
3-5	(151)	7-9	(310)
3-6	145	8-9	379

#See Table C1

Quantities in parenthesis are estimates.

Table C3

Energy Interaction Parameters for Heavy-Fraction/
Light-Gas Binaries

(ϵ_{ij}/k , K and ΔH_j , Kcal/mole)

Hydrogen Binaries

$$\epsilon_{ij}/k = 146$$

Nitrogen and Carbon monoxide Binaries

$$\epsilon_{ij}/k = 266 - 603 \exp(-0.294\Delta H_j)$$

Methane Binaries

$$\epsilon_{ij}/k = 395 - 915 \exp(-0.224\Delta H_j)$$

Ethane and Hydrogen sulfide Binaries

$$\epsilon_{ij}/k = 477 - 870 \exp(-0.255\Delta H_j)$$

Carbon dioxide Binaries

$$\epsilon_{ij}/k = 437 - 915 \exp(-0.224\Delta H_j)$$

Propane Binaries

$$\epsilon_{ij}/k = 532 - 870 \exp(-0.255\Delta H_j)$$

Butane Binaries

$$\epsilon_{ij}/k = 576 - 870 \exp(-0.255\Delta H_j)$$

Water Binaries

$$\epsilon_{ij}/k = 420 - 915 \exp(-0.224\Delta H_j)$$

List of Figure Captions

Figure 1. Fossil-fuel fractionation via spinning-band column.

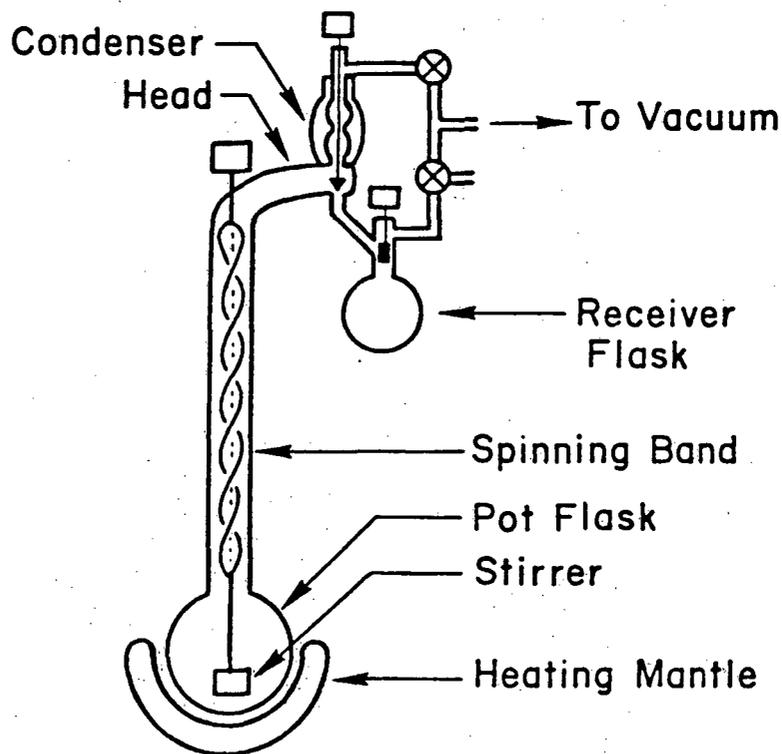
Figure 2. Solubilities of two Lurgi coal-tar fractions in methane: Comparison of predicted and experimental results.

Figure 3. Solubility of coal tar in a typical Lurgi coal-gasifier effluent at 42.7 bar.

Figure 4. Predicted condensation in a continuous-flow heat exchanger for a typical Lurgi coal-gasifier effluent at 42.7 bar.

Figure 5. Solubility of Lurgi-tar Fraction 6 in methane at 70 bar:

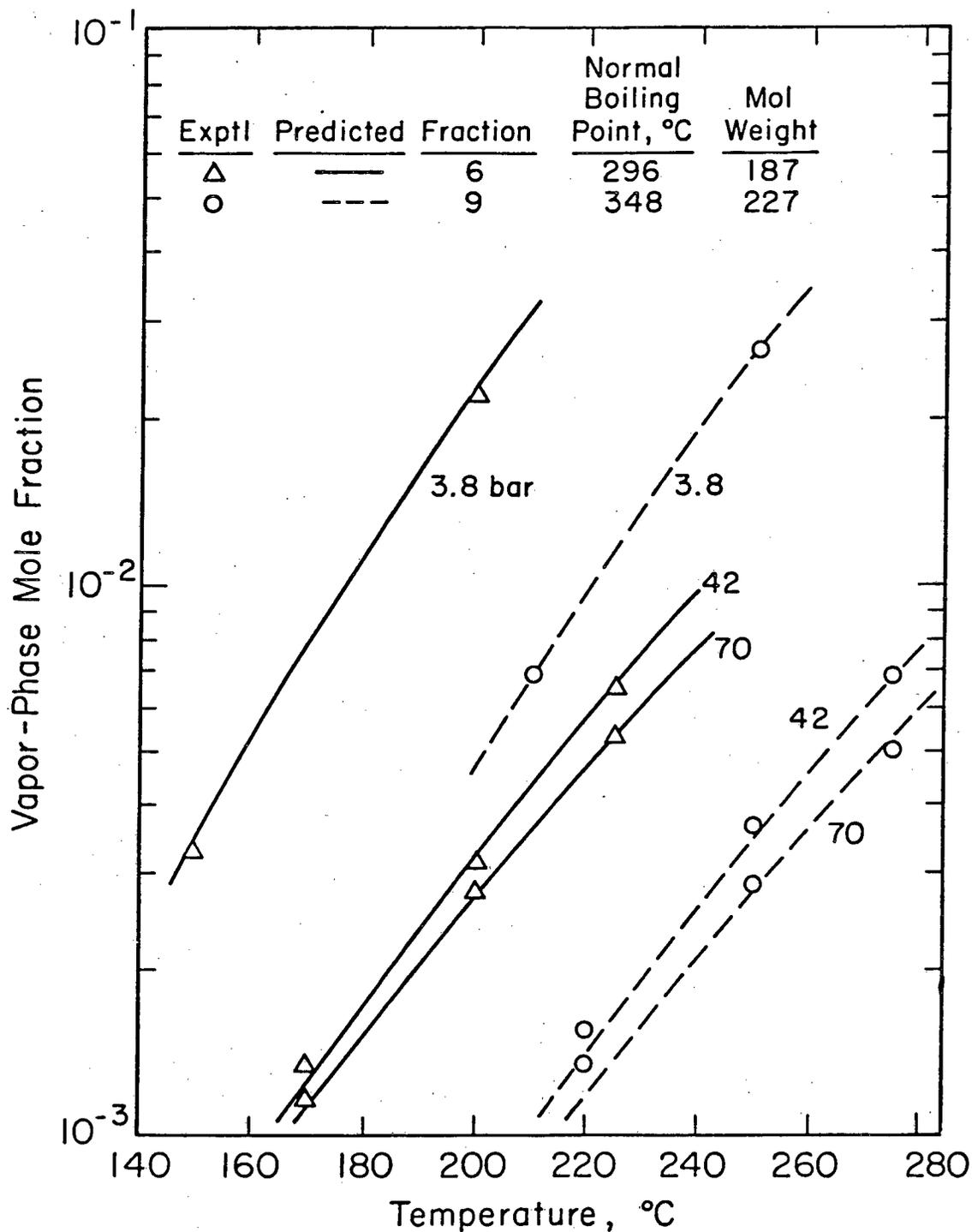
Figure A1. Sample proton-NMR spectra



Still: Perkin-Elmer Model 25I Annular Still
 Spinning Band: 0.91×0.01 m Monel Mesh
 Reflux Ratio: 10:1
 Boilup Rate: $\sim 3 \times 10^{-8}$ m³/s
 Operating Pressure: 0.067 bar absolute
 Maximum Head Temperature: 250°C
 Maximum Pot Temperature: 300°C
 Boiling-Point Range of Fraction: $\sim 20^\circ\text{C}$

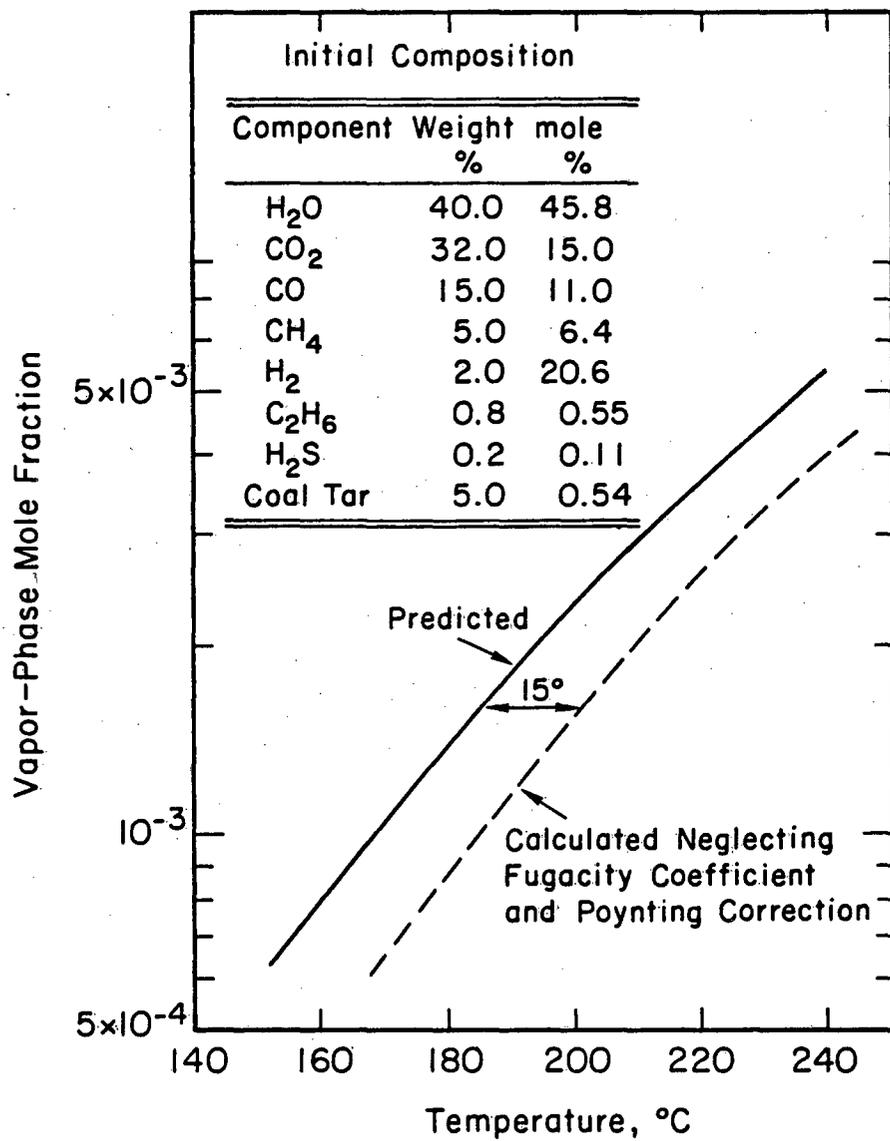
FRACTIONATION VIA SPINNING BAND COLUMN

Figure 1.



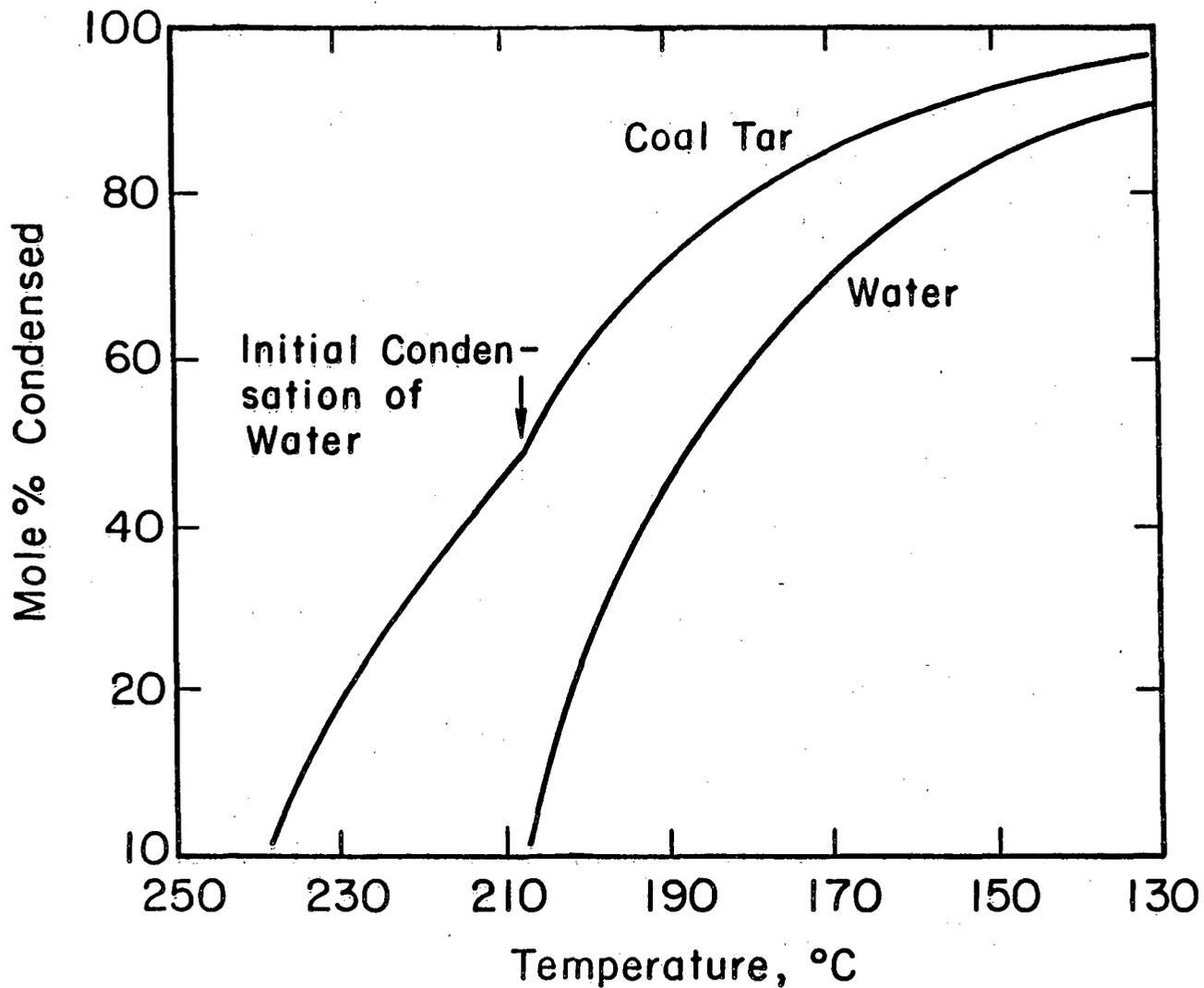
SOLUBILITIES OF TWO LURGI COAL-TAR FRACTIONS IN METHANE: COMPARISON OF PREDICTED AND EXPERIMENTAL RESULTS

Figure 2.



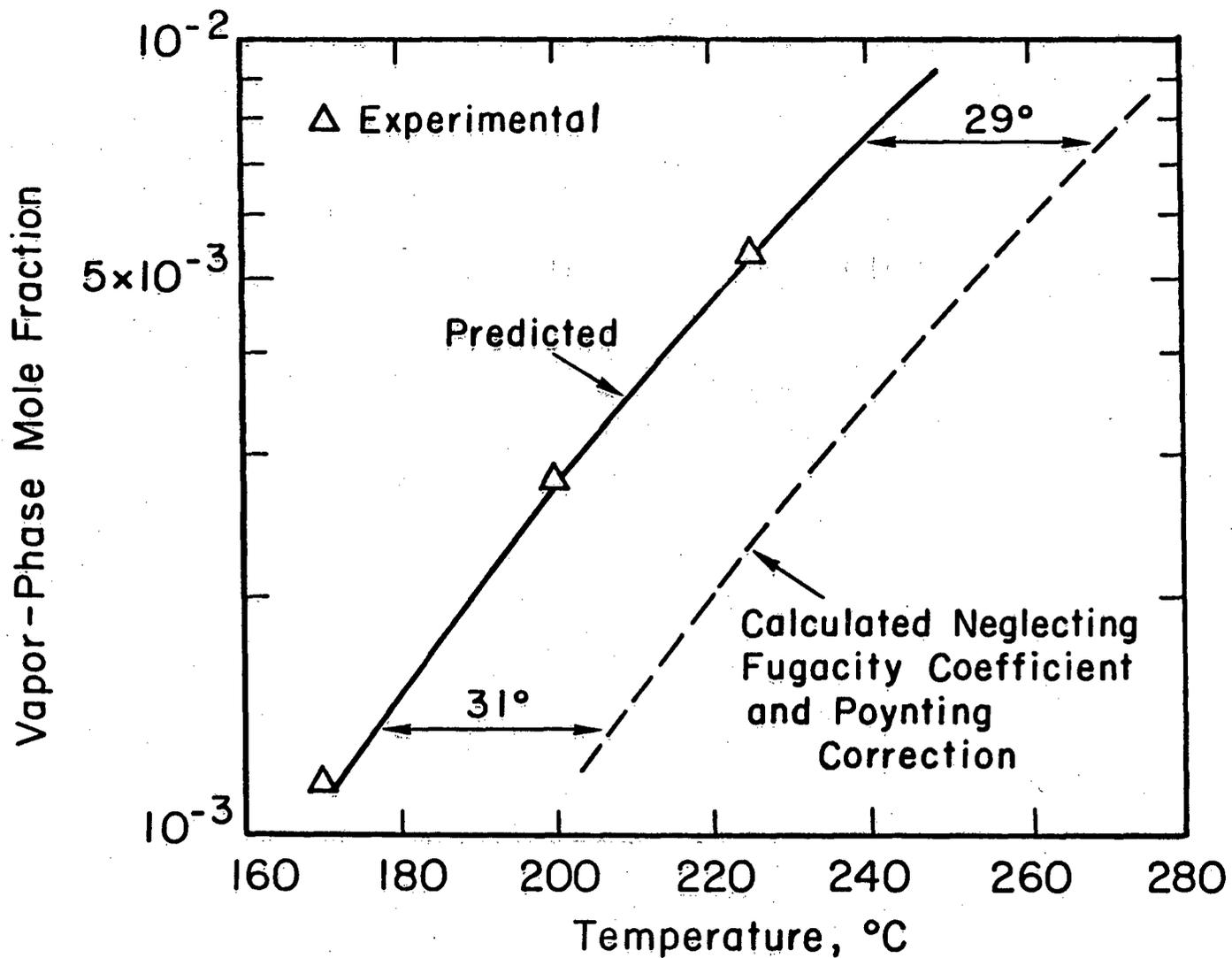
CALCULATED SOLUBILITY FOR A TYPICAL
LURGI COAL-GASIFIER EFFLUENT AT
42.7 BAR

Figure 3.



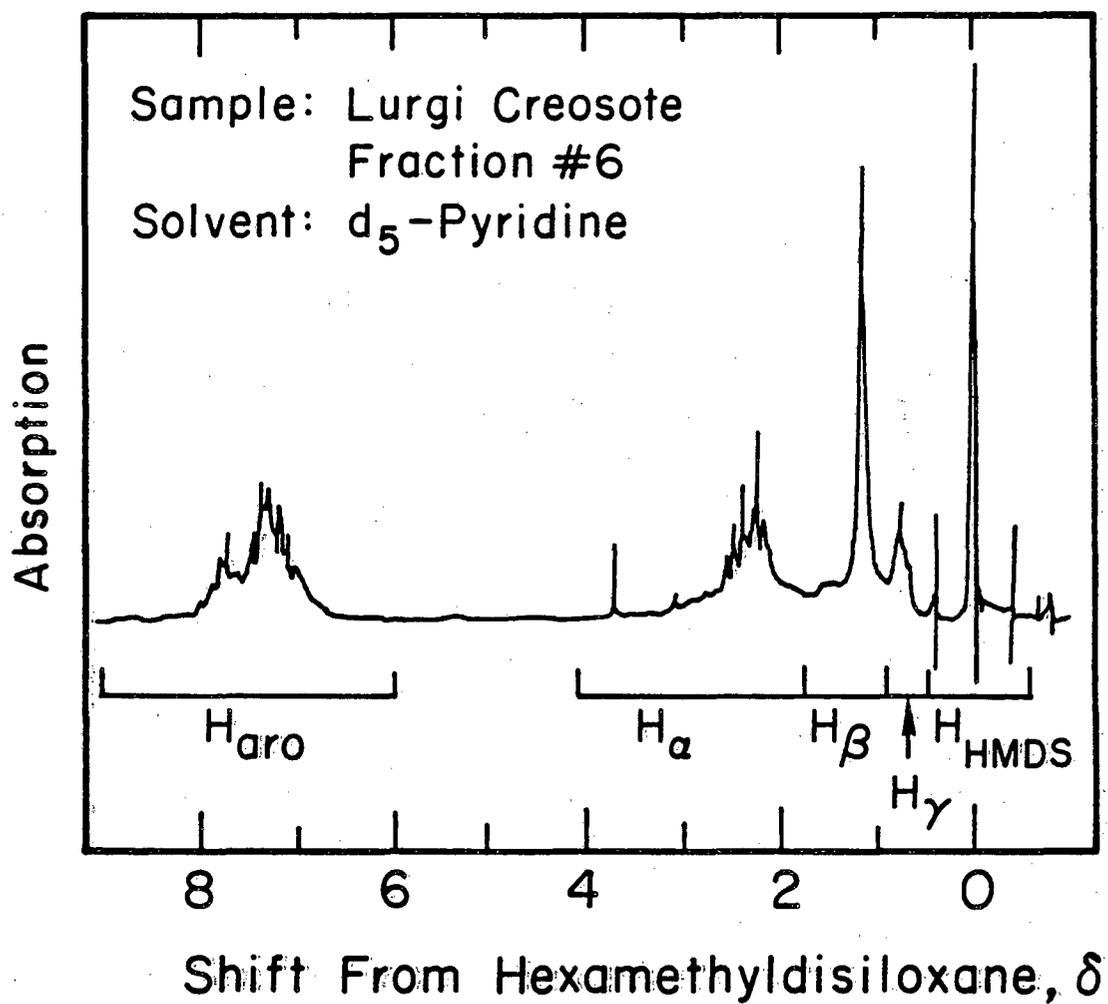
CALCULATED CONDENSATION IN A CONTINUOUS-FLOW HEAT EXCHANGER FOR A TYPICAL LURGI COAL-GASIFIER EFFLUENT AT 42.7 BAR

Figure 4.



SOLUBILITY OF LURGI-TAR FRACTION 6 IN
 METHANE AT 70 BAR: EFFECT OF
 NEGLECTING FUGACITY COEFFICIENT AND
 POYNTING CORRECTION

Figure 5.



SAMPLE PROTON-NMR SPECTRA

Figure A1.

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