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Phase Equilibrium Data and Methods Implication of Present State on Heavy Petroleum Fractions and Coal Processing

Part. I*.- Review of Some Methods for Predicting Vapor Liquid Equilibrium.

(Recibido el 13 de Abril, 1978)

RESUMEN

La necesidad de producir combustibles líquidos y productos químicos a partir de fracciones y residuos pesados y altamente aromáticos del petróleo y de carbón plantea la pregunta de si los datos y correlaciones termodinámicos existentes son aplicables y qué nuevos datos deben ser medidos.

La evaluación de las correlaciones existentes en cuanto a su aplicabilidad a las condiciones de procesamiento de fluidos del carbón y aceite pesado se presenta en una serie de cuatro artículos. Tales evaluaciones son consideradas importantes en la planificación de la medición de nuevos datos e investigación.

En este primer artículo de la serie, los métodos basados en el enfoque clásico de utilizar presión de vapor, y coeficiente de fugacidad son discutidos.

SUMMARY

The need to produce liquid fuel and chemical fuel stochks from heavy and highly aromatic petroleum fractions, residues, and coal poses the questions whether the existing thermodynamic data correlations are applicable and what new data should be measured.

Evaluations of existing correlations as to their applicability to the conditions of processing coal fluids and heavy oil are presented in a series of four articles. Such evaluations are considered important in planning the measurement of new data and further research.

In the first article of the series, the methods based on the classical approach, utilizing vapor pressure and fugacity coefficient, are discussed.

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* Las partes II, III y IV de este artículo aparecerán en los próximos números de la revista.

I. INTRODUCTION

Phase equilibrium data are vital in separation and treatment of liquid fuels. The experience of more than 100 years of processing crude oil and gas should aid in working with heavier crude oils and coal-derived liquids. However, review of features of the processes for producing fluid (gas and liquid) products from coal such as liquefaction, example given in Figure I, and gasification, example given in Figure 2, would suggest that compositions and types of chemicals that are found in heavy oils are different from those of the oils that have been processed heretofore.

Correlations that are based on data and understanding of the behavior of pure chemicals and mixtures have been developed for utilizing petroleum inspection data for designing separations. Thus, based on available correlations, (laboratory) true boiling point distillation (TBP) curves of the gasoline cuts (curves 1 and 2) in Figure 3 with additional density data can be considered as sufficient information for predicting separation, blending and product specifications, etc. However, the same correlations would yield erroneous results if applied to the carbolic oil, which is a liquid derivative from coal coking.

The distillation curve for the carbolic oil is shown as Curve 3 in Figure 3. Its composition is roughly represented by the heart cut components comprising the creosote oil described in Table 1. Review of Table 1 immediately suggests that the creosote and carbolic oils that are typical coal liquid products are grossly different from their pure hydrocarbon petroleum equivalent products. Therefore, there is danger of serious design errors if petroleum engineering correlations are used without taking account of these major differences.

Nevertheless, classical thermodynamics provides all the necessary relationships to describe the equilibria and distributions encountered. If kinetics and heat and mass transfer are excluded, the phase equilibria and other properties can be developed. There is no need to measure all properties at all conditions. Obtaining sufficient data to permit modelling will allow calculation of other data poinsts.

Parts I and II of this series describes the correlations that have been developed for predicting phase behavior and other properties of mixtures of petroleum fractions and discusses the limitations of these methods. Part III will cover the methods developed by the petroleum industry for obtaining the data points to be inserted in these correlations.

II. GENERAL CONSIDERATIONS

Review of the bases of all (VLE) vapor-liquid equilibrium correlations indicates three approaches that can not be brought together at all conditions. These are the Gibbs concept of chemical potential equality, the Lewis concept of fugacity (I-46) as applied to Raoult's Law, and the Van der Waals equation of state approach. Empirical correlations that have been developed during the past century either relied on one, or attempted to combine virtues of more than one (I-57, I-60, I-36, I-75, I-11, I-38, I-71, I-72, I-13, I-15, I-27, I-72).

In a multi-phase system thermodynamic equilibrium exists when all phases are at the same temperature and pressure, possess the same total free energy and for each component (I-75).

$$\hat{f}_{iV} = \hat{f}_{iL} \tag{1}$$

where $\hat{f}_{iV}$ and $\hat{f}_{iL}$ are the fugacity of component i of the mixture in the vapor phase and the liquid phase, respectively.

III. THE CLASSICAL APPROACH

Expanding Equation 1 in either phase, one can develop the fugacity of i independently from the properties of the compound and system conditions. Here, the Lewis and Randall approach (I-45) departs from the rigorous Gibbs and the Van der Waals (equation of state) approaches, which states that the fugacity of the compound in either phase depends on the concentrations and properties of the other compounds.

In the present paper, Raoult's and Henry's law and the concept of activity coefficients for the components in the liquid phase will be used. The compound's fugacity, in the vapor phase, $\hat{f}_{iV}$ at system temperature and pressure is calculated from

$$\hat{f}_{iV} = \hat{\emptyset}_{iV} Y_i P \tag{2}$$

where $\hat{\emptyset}_{iV}$ is the fugacity coefficient for component i in the mixture, Y_i is its mole fraction and P is the total pressure. Until 1938, the value of $\hat{\emptyset}_i$ i was calculated as if compound i existed alone at system conditions. Several generalized charts were developed (I-47) where the Lewis simplification was worked backwards to provide values at hpothetical conditions to expand the range of applicability beyond valid conditions for the compound. In may cases, the assumptions were sufficient as long as the designers applied them consistently.

The fugacity of the compound in the liquid phase is usually calculated from Gibbs concept of the standard state and the activity coefficient. In practice, some of

Raoult's simplifications are carried over and the vapor pressure of the compound at the temperature is taken as the standard state. The rigorous equation is

$$f_{iL} = \gamma_i x_i f^o_{iL} \qquad (3)$$

where f^o_i is the fugacity in the standard state and γ_i is the activity coefficient of the compound in the liquid phase. If the calculations of f^o_{iL} involve the use of the vapor pressure, P^o_i, one should be careful in setting the variables of the Poynting correction, description of which follows.

When combining Equations 2 and 3, the equality must be at the same pressure, and the integration of the free energy difference, the "Poynting effect" (Equation 4) must be done correctly.

$$\Delta \hat{G}_i = \int_{P^0_i}^{P} \overline{V}_i \, dP \qquad (4)$$

The choice of either P^o_i or P as the standard state dictates the path of integration and also whether V_i, the partial molal volume, or V_i the pure compound's molal volume in the liquid phase, is used in Equation 4.

At equilibrium, the classical Lewis approach leads to

$$\hat{\phi}_{iV} Y_i P = \gamma_i x_i f^o_{iL} \qquad (5)$$

If simplifying assumptions are made, f^o_{iL} is calculated from vapor pressure and the correction of Equation 4. Thus Equation 5 becomes

$$\hat{\phi}_{iV} Y_i P = \gamma_i x_i P^o \phi^o_i \quad \exp \int_{P^o_i}^{P} \frac{\overline{V}_{iL}}{RT} dP \qquad (6)$$

The above equation is extensively used in the chemical industry, where the simplifying assumptions governing the transitions from Equation 5 do not cause serious errors. Born in mind is the idea that compound i has a real vapor pressure at system temperature, i.e., it is not a supercritical gas or solid.

The empirical approach named after Henry is:

$$P\, Y_i = \hat{P}_i = H_i x_i \qquad (7)$$

Substituting Equation 7 into Equation 5 and 6

$$H_i = f^0_{iL} y \dashrightarrow y_i P^0_i \phi^0_{iL} \exp \int_{P^0_i}^{P} \frac{\overline{V}_i}{RT} dP \qquad (8)$$

Prausnitz has introduced terms that are widely used in describing the application of Equations 6 and 7 to compounds at supercritical conditions. In 1960, he introduced the "hypothetical standard state fugacity", f^o_i, as a function of reduced properties and the third parameter, ω, the "acentric factor". Later he introduced the term "asymmetrical correlation", where H_i of Equations 7 and 8 replaces f^0_{iL} for supercritical compounds, while Equation 6 is used for the compounds that are liquids with real vapor pressures at the system temperature.

The Chao and Seader Correlation (I-15) and that of Grayson and Streed (I-27) are further developments of the Smith and Watson (I-67) hypothesis that the term

$$\nu^o_i = f^o_{iL} / P \qquad (9)$$

follows the theorem of corresponding states. These correlations will be further discussed.

It can be shown that, if ideal gas behavior is assumed for the vapors at all conditions and if the liquid is incompressible, Equation 5 degenerates into Raoult's Law with the activity coefficients. Based on these assumptions, van Laar (I-35) and Margules (I-49), and later Hildebrand (I-33), Scatchard and others (I-34, I-56, I-1, I-12, I-64, I-78) addressed themselves to the nonideality in the liquid phase expressed in terms of activity coefficients. The reader may note that although the activity coefficient γ can be derived as the partial molal derivative of the excess Gibbs free energy,

$$RT \ln \gamma_i = \overline{G}^E_i = \left(\frac{\partial G^E}{\partial n_i}\right)_{n_2} \qquad (10)$$

the simple equation used by van Laar and others

$$P\, Y_i = P^o_i \gamma_i x_i \qquad (11)$$

cannot always be rigorously derived with Equation 4 from the total Gibbs free energy.

Of the widely used methods for predicting VLE, the method of Chueh and Prausnitz is based on Equations 8 and 9, and the Chao-Seader and Grayson-Streed methods are based on Equation 9. The variations are in the correlations for the standard state f^o or H_i and the methods by which the activity coefficient, γ_i, is generated. In all three methods, the Redlich-Kwong equation of state (I-62) is used for predicting the $\hat{\phi}_{iV}$, of Equation 2, though Chueh and Prausnitz used a more refined form (I-16).

For mixtures under low pressures, and for systems where all compounds are subcritical, Equation 6 is used directly with $\hat{\phi}_{iV}$ calculated by an equation of state or a generalized chart as is ϕ^o_i. The molar volume V_i is often used as $\bar{V}_i$.

Data on the solubility of supercritical compounds, e.g. H_2, N_2, CH_4, H_2S, in solvents are sometimes expressed by Henry's Law constants H_i, although with so many variables affecting it, H_i is not a constant. At some conditions the variations cancel each other and a semblance of constancy results.

Because of the relative insensitivity of the ratio $K_i = y_i/x_i$ to variations in composition, it is generally adopted for use in flash and distillation calculations. Hence, Equation 5 is usually presented as a function of Equation 9.

$$K_i = \frac{Y_i}{x_i} = \frac{f_{iL}\,\gamma_i}{\hat{\phi}_{iv}\,P} = \frac{v^o_i\,y_i}{\hat{\phi}_{iv}} \qquad (12)$$

IV. THE CHAO-SEADER AND GRAYSON-STREED CORRELATIONS

As a form of the classical Equation 5, Chao and Seader (E-3) presented a generalized approach for predicting K values

$$K_i = \frac{v^o_i\,\gamma_i}{\phi_{iV}} \qquad (13)$$

They proposed calculating $\hat{\phi}_{iV}$ for each component in the vapor phase by the equation of Redlich and Kwong (I-62); the activity coefficient γ_i was assumed for that correlation to be exactly calculated by the Hildebrand Regular Solution Theory (I-34)

where

$$\ln \gamma_i = \frac{V_i\,(\delta - \bar{\delta})^2}{RT} \qquad (14)$$

δ_i being the solubility parameter (I-34) and the average δ for the mixture,

$$\bar{\delta} = \sum \Phi_i\,\delta_i \qquad (15)$$

and

$$\phi_i = V_i\,x_i / V_m \qquad (16)$$

(Note that Φ_i is not the fugacity coefficient).

Assuming the validity of the prediction of γ_i and ϕ_{iV} (the fugacity coefficient), Chao and Seader used many thousands of experimental K values to develop an expression for $\ln \nu^o_i$ as a function of the reduced properties T_{Ri} and P_{Ri} of component i with the Pitzer (I-57) acentric factor ω_i as the third parameter.

$$\ln v^o_i = f^{(o)}\,(T_{Ri}\;P_{Ri}) + w_i\,f^{(1)}\,(T_{Ri},\,P_{Ri}) \qquad (17)$$

In their publication, Chao and Seader (I-15) presented the functions $\nu^{(o)}$ and $\nu^{(1)}$ of Equation 17. They also presented a table of V_i and δ_i for many light hydrocarbons and hydrogen for use with their correlation. Later, Chao and Erbar (1964) and Cavett (I-14) expanded the tables to include constants for H_2S and CO_2, and showed how the correlation could be used for petroleum fractions, using standard petroleum measurements. The method has become the workhorse of the petroleum industry design routines.

The Chao-Seader correlation was developed with data on mixtures of light hydrocarbons and hydrogen at temperatures up to 400°F. Grayson and Streed (I-27) expanded its use up to 700°F and above 3000 psia. The resultant Grayson-Streed correlation is of the same form as the Chao-Seader, with different coefficients for the Chao-Seader, with different coefficient for the functions in Equation 17. They also added values for V_i and δ_i for petroleum fractions.

V. CORRELATION AND PREDICTION OF ACTIVITY COEFFICIENT γ_i, VALUES

Per Equation 3, the activity coefficient γ_i is a direct description of the component's partial molal excess Gibbs free energy. By this definition, deviation from ideal mixing is implied. For simplicity, we shall refer to Equations 6 and 11 as a means for calculating γ_i for component i from experimental data, x_i, y_i, P_T and P^o_i or f^o_i which are functions of temperature. The values for all components are interrelated through the Gibbs-Duhem equation.

Of the many available integral forms of the Gibbs-Duhem equation only four are of direct interest to modern designers.

- The Van Laar equation for binary mixtures (I-74) and the Black modification for multicomponent computations (I-12).
- The Wohl (I-81) expansion of the Margules type of equation (I-49) as proposed by Adler et al (I-1).

- Hildebrand-Scatchard (I-34) Regular Solution approach, and the Flory-Huggins formulas for mixtures of large and small molecules (I-23, I-37, I-55, I-73).
- The Wilson (I-79) equation as expanded to multicomponent solutions (I-54) and the NRTL, Renon equation (I-65).

Each of the above procedures predict values of γ utilizings empirical correlation parameters. In practically all cases, the prediction of the multicomponent system is done via some combination of the coefficients for the binary pairs, although some attempts have been made to develop coefficients for ternary interactions (I-1).

Activity coefficients are thoroughly discussed in the literature (I-4, I-12, I-30, I-34, I-56, I-60, I-64, I-75). The correlation parameters for the binary mixture have specific nomenclature that will be used in the present discussion. These are given in Table 2.

Experimental results indicate that no single equation fits all conditions. The van Laar equation for binary mixtures is best for one type of deviation and fails badly on other systems. It cannot be utilized for multicomponent systems. The choice between the Black equation and the form of the Wohl equation proposed by the M. W. Kellogg group (I-1) depends on availability of a data analysis program for establishing the coefficients. This can be also said for the Wilson and the Renon equations.

In several large scale evaluations (I-25, I-35, I-36, I-54), the Wilson equation on the average yielded more reliable results than the van Laar or the Margules type equations. However, that equation cannot be applied to mixtures where separation to two liquid phases is possible. This observation led to development of the Renon equation, where the additional parameter allows flexibility in the shape of the calculated free energy curves, and the Renon equation is preferred.

The following observations should be noted.

- The Black and Renon equations are applicable to both binary and multicomponent mixtures. Although the Renon equation is very hard to use in hand calculations, it is quite suitable to machine computation. Also, the equation has been widely used and the parameter α , when not known, can be approximated.
- Although the Wilson equation has been shown to fit experimental data well, it is less widely applicable, due to limitations mentioned above. Where it fails, the Renon equation, which is equally good, can be used.
- The Renon, Wilson, Black and van Laar equations require correlation equation coefficients to be established from experimental data. However, while a curve fitting solution can yield unique coefficients for a van Laar and Margules equations, the interdependence of the Wilson and Renon energy parameters leads to the possibility of multiple roots, as seen in Figure 4 (I-59). This, however, does not greatly diminish their usefulness.
- For many hydrocarbon systems, the simple Regular Solution approach of Hildebrand (I-34) is adequate. That explains the usefulness of the Chao-Seader and the Grayson-Streed prediction techniques, (see discussion of Equation 12). However, when nonhydrocarbons, especially water and polar compounds, are present the standard procedures for predicting δ_i and V_i would lead to erroneous answers.

EFFECTS OF PRESSURE AND THE LIMITATIONS OF THE CLASSICAL VLE AND THE HIPOTHETICAL STANDARD STATES APROACHES

a. The High Pressure-Critical Region Phenomena.

Since the time of van der Waals, it has been observed that, in any binary and multicomponent system, for every composition there is, al least theoretically, a true critical point. At this point, the vapor is indistinguishable from the liquid, hence VLE separations are impossible. Thermodynamically, the partial derivatives indicating stability for a single component system at the critical point do not apply to the true critical point of a mixture. Therefore, other relations involving fugacity and composition are used (I-66). Furthermore, correlations of the volumetric and other properties of the mixture, with application of the theorem of the corresponding states, do not rely on the true critical temperature and pressure, but on their pseudo equivalents. The pseudo critical temperature and the pseudo critical pressure are also used, directly or indirectly, by combining the correlation parameters, whenever equations of state are applied.

When VLE of a mixture is considered, the high pressure region at temperatures above the critical of the light key component, or the critical azeotrope, is called the critical region. The shaded area in Figure 5 roughly describes such a region in a simple binary system with a dome-shaped critical locus. Isothermal curves of K-values within the critical region tend to converge at the critical point. As illustrated in Figure 3, all the K - values equal unity at the critical pressure, P_{cm}.

Such convergence cannot occur at all temperatures. If prediction of K-values of components in an ideal mixture at low pressures is carried out by the method of Lewis and Randall (I-45) or a simple version of Equation 6 as described by the dotted curve in Figure 6, the critical region may be, paradoxically, defined by its correspondence to the largest deviations between predicted and actual K-values.

The behavior of mixtures within the shaded area of Figure 6, above that corresponding to the minimum in the curve of K-against P for the heavy component, also represents critical region phenomena. In essence, this sudden curving upwards of the K-value curves for the heavy compounds is totally consistent with the rigorous Equation 5. As the pressure is increased, two factors that are dormant at low pressures become significant. These are the fugacity coefficient of the compound in the misture, $\emptyset_i$, and the Poynting effect,

$$\exp \int_{P^0}^{P} \frac{\overline{V}_i}{RT}\, dP$$

The $\emptyset_i$ coefficient decreases with pressure more significantly for high molecular weight hydrocarbons than for light ones. Similarly, the integral of VdP for heavy compounds is positive and spans a wider range due to the low vapor pressure, or P^o_i of the heavy compound. When this efect, compounded with the large partial molar volume $\overline{V}_i$ of the heavy molecule, taken exponentially we have quite an effect. Similar variations, but with opposite sign, affect the K-values of the light compounds. Since all components contribute toward all phenomena, the net effect is that, if the temperature is within the range of the continum of the critical locus, convergence at $K = 1$ can occur for all compounds.

It is clear from the above that a good correlation for the VLE within the critical region should be capable of predicting the convergence at the critical point. For this purpose, expressions of all variables in Equation 5 should be symmetrical in nature, i.e. the expressions on both sides of the equation should contain all needed elements for being identical at three important milestones where $K = 1$. These are the saturated pure compound, any azeotropic mixture, and the critical point, if the latter is possible at the temperature in question.

The Chao-Seader and Grayson-Streed methods (I-15, I-27) fall into the same category as the above, as they depend on generalized predictions of hypothetical standard states. Although generally useful over a wide range of conditions the correlation becomes increasingly inaccurate as the true critical point is approached. The failure of the Chao-Seader method in the critical region is largely due to lack of inter-relationship between the correlations applied to the two phases; the prediction of the fugacity of a component in one phase does not have much in common with the correlation of the behavior of the other phase. Thus, as illustrated in Figures 6 and 7, the K-value predicted by this method may not converge at the critical point.

The method of Chueh and Prausnitz (I-16) like that of Chao and Seader does not lead to convergence. In some cases it may fare better than the former. Chueh and Prausnitz suggested caution when applying their method within the critical region.

b. Methods Based on the Concept of Convergence Pressure.

The empirical methods based on the convergence pressure (I-28, I-29, I-42, I-44, I-53, I-80) are founded on the observation that, in mixtures of light paraffins, K ratios of individual components appear to converge to unity when plotted against pressure at constant temperature. The pressure at which convergence to unity takes place is known as the convergence pressure of the system. In binary systems, convergence corresponds to a true critical point of the mixture. Since, as yet, there is no rigorous method for predicting real or quasi convergence points in multicomponent systems, the convergence pressure method is based on purely empirical procedures. The techniques, both for finding convergence pressures and using these to predict K ratios, have been described by Hadden (I-28), Winn, (I-80) Lenoir and his coworkers (I-42, I-43, I-44), and the GPA (formerly NGSMA) Data Book (I-53). The API Data Book presents the Hadden-Grayson (I-29) modification of Winn's method.

Since the convergence pressure methods have been developed primarily from data for the light paraffinic compounds, they are largely limited to paraffinic and some olefinic systems. Convergence pressure correlations employ assumptions based on domeshaped critical loci, which are characteristic of light paraffin - paraffin hydrocarbon binaries. However, some binaries, particularly those in which carbon dioxide or hydrogen sulphide is a component, possess an S-shaped rather than a domeshaped critical locus (I-67, I-38). Also, the critical locus curves of many systems (I-67) are neither continuous nor domeshaped. Accordingly, application of the convergence pressure methods of systems containing non-hydrocarbon constituents may lead to large errors.

The utilization of any of the convergence pressure methods requires experience, as judgement is needed in selecting the appropriate convergence pressure and in deciding when to abide by many of the arbitrary rules. Nevertheless, the convergence pressure methods offer quick first estimates of K values for hand calculations (I-26, I-29, I-42, I-53). Programming for computer use is quite a task, which, in view of the limited accuracy and field of application, may not be worth undertaking.

Table 1. Gas Chromatographic Analysis of Creosote Oil (I-58)

Compound	Wt %	
Coumarone	0.10	
p-Cymene	0.02	
Indan	0.11	
Phenol	0.12	
O-Cresol	0.05	
Benzonitrile	0.12	
p-Cresol	0.37	
m-Cresol	0.16	
O-Ethylaniline	0.03	
Naphthalene	5.1	Compounds of Carbolic Oil Residue (See Figure 3)
Thianaphthene	0.08	
Quinoline	0.37	
2-Methylnaphthalene	1.3	
Isoquinoline	0.30	
1-Methylnaphthalene	0.38	
4-Indanol	0.55	
2-Methylquinoline	0.47	
Indole	0.21	
Biphenyl	0.49	
1,6-Dimethylnaphthalene	0.39	
2,3-Dimethylnaphthalene	0.19	
Acenaphthene	6.0	
Dibenzofuran	5.7	
Fluorene	10.3	
1-Naphthonitrile	0.18	
3-Methyldiphenylene oxide	1.7	
2-Naphthonitrile	0.14	
9,10-Dihydroanthracene	2.4	
2-Methylfluorene	0.85	
Diphenylene sulfide	0.52	
Phenanthrene	18.6	
Anthracene	4.3	
Acridine	0.19	
3-Methylphenanthrene	0.98	
Carbazole	2.2	
4,5-Methylenephenanthrene	2.5	
2-Methylanthracene	0.24	
9-Methylanthracene	1.2	
2-Methylcarbazole	1.7	
Fluoranthene	5.5	
1,2-Benzodiphenylene oxide	0.46	
Pyrene	2.6	
Unidentified compounds in distillate	3.56	
Total distillate	88.18	

[a] By Allied Chemical Co.

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TABLE 2

PARAMETERS FOR THE FREQUENTLY USED CORRELATIONS OF ACTIVITY COEFFICIENCIES

Equation	Recommended Use	Correlation Parameters and Comments
Van Laar	Binary Mixtures specially mixtures with significant heats of mixing or hygrodichotomy*	A_{12}, A_{21} obtained f—m data or predictions
Black	Multicomponent Systems, wider range of applicability than the Van Laar	A_{ij}, A_{ji}, C_{ij} related to the binary A_{ij} and A_{ji}
Hildebrand	Binary and Multicomponent Mixtures with small deviations, mainly hydrocarbons or members of some groups. Very limited reliability. Judgement in selectivity required.	δ_i, V_i obtained from data or tabulation
Wilson	Multicomponent mixtures. Can not predict hygrodichotomy* and limited by magnitude of heat of mixture.	$(\lambda_{ij}-\lambda_{ii}), (\lambda_{ij}-\lambda_{jj})$ called energy parameters, v_i, v_j; with v_i and v_j selected, the $\Delta\lambda$ values are established from experimental data on binaries.
Flory-Huggins	Binary mixtures with large molecular size differences and no heat of mixing	v_i, v_j, m,n and X. This correlation for polymer solutions requires knowledge of v_i, v_j, m and n. X is obtained from experimental data.
NRTL (Renon)	Binary and Multicomponent mixtures. General purpose if heat of mixing is low.	$\tau_{ij}, \tau_{ji}, \alpha$. All three should be obtained experimentally. However, τ_{ij} and τ_{ji} can be calculated from Wilson's or Van Laar parameters and vice versa if α is assumed.

*Separation into two liquid phases.

TABLE 3

ACCEPTED RESTRICTIONS OF THE CHAO-SEADER (I-11)
CORRELATION FOR VAPOR-LIQUID EQUILIBRIUM

A. ORIGINAL THREE RESTRICTIONS (I-11)

1. For hydrocarbons, a reduced temperature (based on critical of the compound) range from 0.3 to 1.3 limits the range of reliable applicability; methane is an exception.
2. The upper pressure limit is 200 psia, but not exceeding 0.8 of the critical pressure of the system.
3. For methane and hydrogen containing systems:
    - a. The reduced temperature should not exceed 0.93.
    - b. The temperature lies between -100°F and 500°F.
    - c. Pressure up to 8000 psia.
    - d. Concentration of other dissolved gases should be lower than 20 mole % of the liquid.

B. ADDITIONAL RESTRICTIONS PROPOSED BY LENOIR AND KOPPANY (I-44)

4. The methane content in the liquid phase should be below 20 mole %.
5. The upper pressure limit should be set at 1000 psia.

EFFECT OF PRESSURE ON AVERAGE ACCURACY
OF PREDICTION WITH THE CHAO-SEADER METHOD (I-11)
PER LENOIR AND KOPPANY (I-44)

PRESSURE	% DEVIATION
50 psia	6.2
100 psia	3.7
400 psia	7.2
1000 psia	12.4
1500 psia	14.6

6. In predicting K-values for paraffins and olefins, the aromatic content should be less than 50 mole %. Conversely, the paraffinic content should not exceed 50 mole %. This rule eliminates all paraffinic/aromatic systems. But since accurate predictions are required only for purifications, this rule is considered too restricting for normal operations.
7. The temperature should be below 500°F.

C. RESTRICTIONS RECOMMENDED IN PRESENT WORK

8. The temperature range for hydrogen, methane, H_2S, CO and CO_2 systems in aromatics should be below 400°F.
9. Both the Chao-Seader and the Grayson-Streed correlations should be revised to render them capable of predicting the K values of key compounds, H_2, CO, CO_2, H_2S and methane in mixtures with aromatics.
10. The method is highly inaccurate for mixtures containing high concentrations of NH_3 in the liquid.

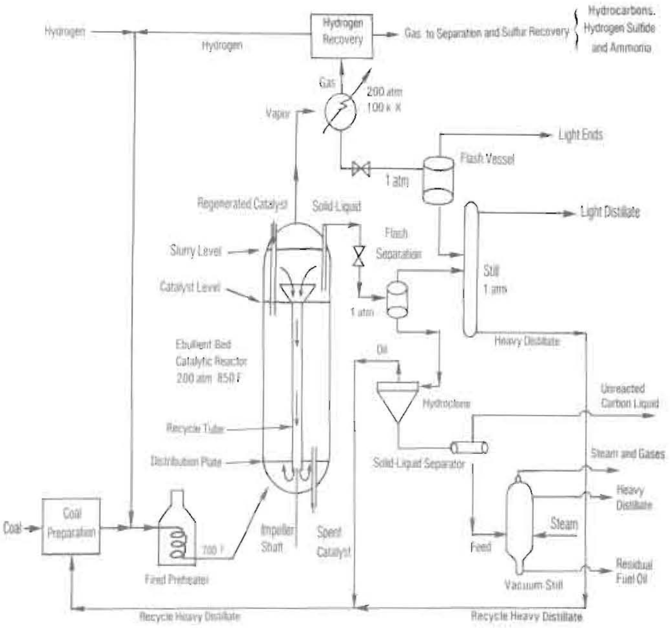


Figure 1 H-Coal Process Schematic

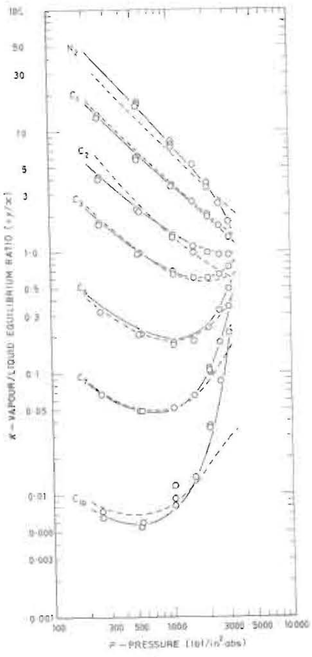
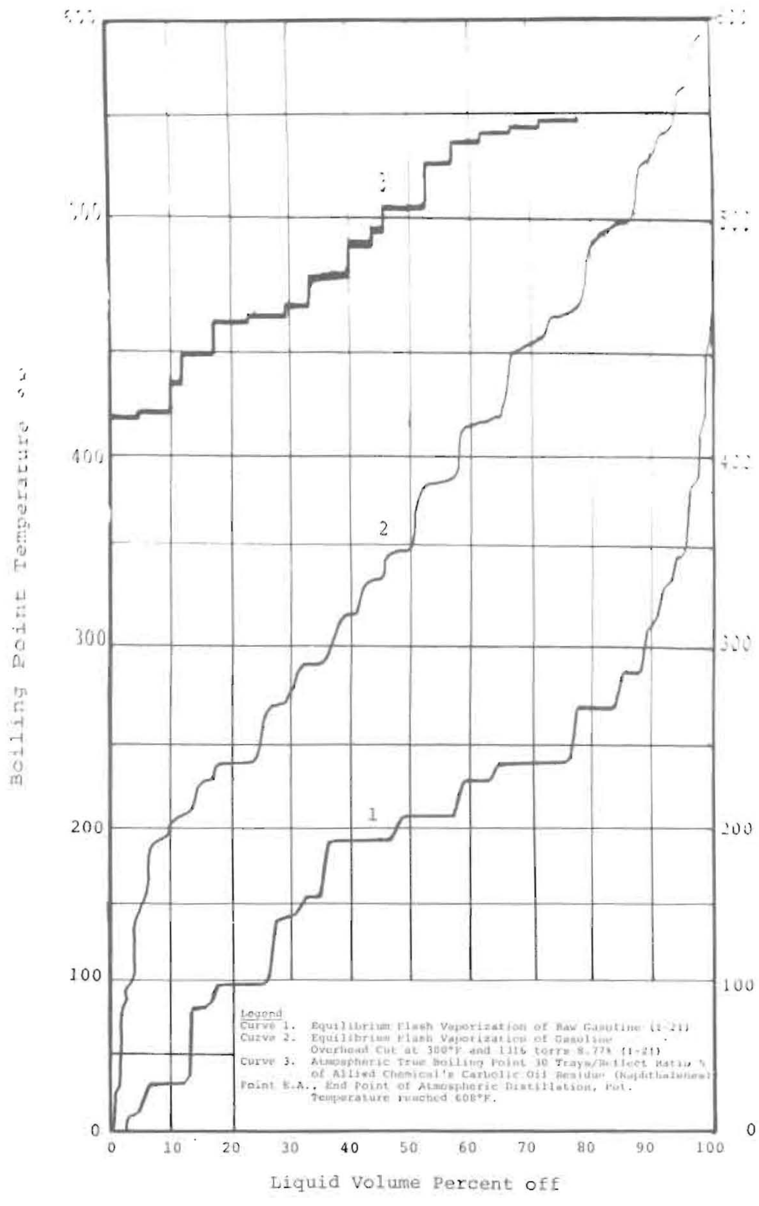
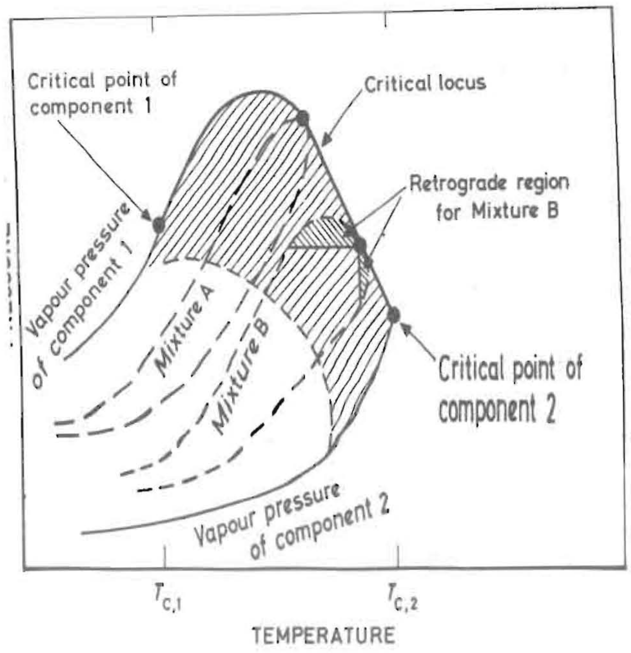
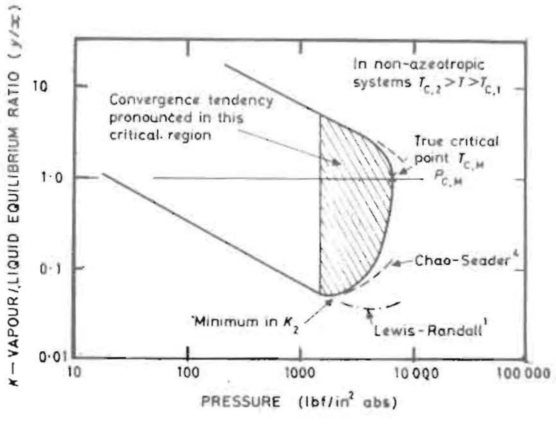


Figure 2 Examples of EFV and TBP Curves







REFERENCES FOR PART I

I-1 Adler, S. B., Friend, L. and Pigford, R. L., AICHE Jour. *12*, 629 (1966).

I-2 American Petroleum Institute. Research Project 60 1968 to 1975.

I-3 American Petroleum Institute - Technical Data Book Petroleum Refining - Chapter V - "Vapor Pressure" Revision Report by Henry, W.P., and Danner, R.P., Report API-4-76, Penn State Univ (October 4, 1976).

I-4 American Petroleum Institute, "Technical Data Book - Petroleum Refining" - Chapter 8, American Petroleum Institute, Washington, D.C., 3rd Edition (March 1977).

I-5 "Annual Book of ASTM Standards, Part 26, Gaseous Fuels; Coal and Coke; Atmospheric Analysis", Amer. Soc. for Testing and Materials, Philadelphia (revision issued annually).

I-6 Baldwin and Daniel, "The Solubility of Gases in Lubricating Oils and Fuels," J. Inst. Petrol. *39*. 105 (1953).

I-7 Beckett, C.W. et al, "Conference on Thermodynamics and National Energy Problems", National Academy of Sciences, Washington, D.C. 424 pages (June 1974).

I-8 Beerbower, A. and Zudkevitch, D., "Predicting the Evaporation Behavior of Lubricants in the Space Environment", a paper presented at the meeting of the Division of Petroleum Chemistry of the ACS, Los Angeles, California (March 31 - April 5, 1963).

I-9 Benedict, M., Webb, G.B. and Rubin, L.C., Jour. Chem. Phys., *10*, 747 (1942).

I-10 Benedict, M., Webb, G.B., and Rubin, L. C., "An Emprircal Equation for Thermodynamic Properties of Light Hydrocarbons and Their Mixtures -- Constants for Twelve Hydrocarbons," Chem. Eng. Prog., *47*, 419-422 (August 1951).

I-11 Benedict, M., Webb, G. B., and Rubin, L. C., "Fugacities and Vapor Liquid Equilibria", ibid, 449-454 (September 1951).

I-12 Black, C., Ind. Eng. Chem. *50*, 403 (1958); *51*, 211 (1959).

I-13 Cajander, B. C., Hipkin, H. G., and Lenoir, J. M., J. Chem. Eng. Data, *5*, 251 (1960).

I-14 Cavett, R. H., "Physical Data for Distillation Calculations", 27th Mid-Year Meeting of the Division of Refining API, San Francisco (May 15, 1962).

I-15 Chao, K. C. and Seader, J. D., AICHE Jour. 7, 598 (1961).

I-16 Chueh, P.L. and Prausnitz, J.M., Ind. Eng. Chem. *60*, 34 (1968).

I-17 Dooley, J. E., Sturm, G. P. Jr., Woodward, P. W., Vogh, J. W. and Thompson, C. J., "Analyzing Syncrude from Utah Coal, " U. S., ERDA, BERC/RI-75/7 (August 1975).

I-18 Eakin, B. E. and DeVaney, W. E., "Vapor Liquid Equilibrium in Hydrogen-Hydrogen Sulfide in Two Natural Hydrocarbon Fractions", API Project Final Report (May 1974).

I-19 Edmister, W. C., Pollock, D. H., "Phase Relations for Petroleum Fractions", Chem. Eng. Progr. *44*, 905 (1948).

I-20 Edmister, W. C., "Applied Hydrocarbon Thermodynamics Part 14: Integral Technique for Vapor-Liquid Equilibria in Petroleum Distillation Calculations", Petrol. Refiner *38*, (10). 163 (1959); Applied Hydrocarbon Thermodynamics, 147, Gulf Publishing Co., Houston (1961).

I-21 Edmister, W.C., "Applied Hydrocarbons Thermodynamics" Volumes 1 and 2, Gulf Publishing Company, Houston, Texas (1974).

I-22 Erbar, J. H., "Thermodynamic Property Predictions in Process Design", paper presented at the Polish Academy of Sciences Seminar on Vapor Liquid Equilibria, Jablond, Poland (November 3-6, 1975).

I-23 Flory, P. J., Jour. Chem. Phys., 9, 660 (1941).

I-24 Funk, E. S., Chao, F. C., Prausnitz, J. M., "Thermodynamic Properties of Binary Liquid Mixtures, Containing Aromatic and Saturated Hydrocarbons", Proc. API - Div. of Refining, 247 (1970).

I-25 Graboski, M. S. and Daubert, T. E., "Multicomponent Vapor Liquid Equilibrium Calculations", Penn State University Report API-1-76 Technical Data Book Revision of Chapter 8, Report V (April 2, 1976) and Addendum (May 3, 1976).

I-26 Ibid. Reports VI and VII (November 1976 and April 1, 1977).

I-27 Grayson, H. G., and Streed, C. W., "Vapor- Liquid Equilibria for High Temperature, High Pressure Hydrogen Hydrocarbon Systems", 6th World Petroleum Conference, Frankfurt, Germany (June 25, 1963).

I-28 Hadden, S. W., Chem. Eng. Progr. Symp. Ser., *49*, No. 7, 53 (1953).

I-29 Hadden, S. W. and Grayson, H. G., Petro. Ref. *40*, 207 (1961) (Further modifications were made for the API Data Book).

I-30 Hala, E. et al., "Vapor-Liquid Equilibrium", Pergamon Press, 2nd Edition (1967).

I-31 Hala, E., Wichterle, I., Polak, J. and Boublik, T., "Vapor-Liquid Equilibrium Data at Normal Pressures", Pergamon Press, Oxford (1968).

I-32 Henry, W. P., Kabadi, V. N. and Danner, R. P., "Revision of API Data Book Chapter 5 - Vapor Pressure, III", Report No. API-4-77, Penn State University (April 22, 1977).

I-33 Hildebrand, J. H., Jour. Am. Chem. Soc. *51*, 66 (1929).

I-34 Hildebrand, J. H. and Scott, R. L., "Solubility of Nonelectrolytes", Rheinhold Publishing Corp. (1950).

I-35 Holmes, M. J. and Van Winkle, M., "Prediction of Ternary Vapor-Liquid Equilibria from Binary Data", Ind. Eng. Dhem. *62*, 21 (January 1970).

I-36 Hudson, J. W. and Van Windle, M., "Multi-Component Vapor-Liquid Equilibria in Miscible Systems from Binary Parameters", Ind. and Eng. Chem., Proc. Des. and Dev., *9*, 466 (July 1970).

I-37 Huggins, M. L., Jour. Chem. Phys. *9*, 440 (1941), Annals N.Y. Acad. Sci. *43*, 1 (1942).

I-38 Joffe, J. and Zudkevitch, D., Ind. Eng. Chem. Fundamentals, *5*, 455 (1966).

I-39 Kesler, M. G. and Lee, B. I., "On the Development of an Equation of State for Vapor-Liquid Equilibrium Calculations," "Phase Equilibrium and Fluid Properties in the Chemical Industry" edited by Storvick, T. S. and Sandler, S. I., Am. Chem. Soc. Symposium Series 60, page 236, (1977).

I-40 Kurata, F., "Solubility of Heavier Hydrocarbons in Liquid Methane", Gas Processors Associations RR-14, Project 738-A (March 1975).

I-41 Leach, M. J., "An Approach to Multiphase Vapor-Liquid Equilibria", Chemical Engineering, p. 137 (May 23, 1977).

I-42 Lenoir, J. M. and Hipkin, H.G., AICHE Jour. *3*, 318 (1957).

I-43 Lenoir, J. M. and White, G. A., Petr. Ref. *37*, No. 3, 173 (1958).

I-44 Lenoir, J. M. and Koppany, C. R., "Need Equilibrium Ratios? Do it Right", Hydrocarbon Proc., *46*, No. 11, 249 (November 1967).

I-45 Lewis, G. N. and Randall, M., "Thermodynamics", McGraw Hill, N. Y. (1923).

I-46 Lewis, G. N., J. Am. Chem. Soc., *30*, 668 (1908).

I-47 Lewis, W. K., and Kay, W., Oil and Gas J., *32*, No. 45 (March 29, 1939).

I-48 Lydersen, A. L., Greenkorn, R. A., and Hougen, O. A., "Generalized Thermodynamic Properties of Pure Fluids", Univ. of Wisconsin, Eng. Exp. Sta. Report No. 4, (October 1955).

I-49 Margules, Sitz-beri. Math.-naturw. Kl. Kaiserlichem Akad. Wiss. (Vienna) *104*, 1243 (1895).

I-50 Maxwell, J. B., "Data Book on Hydrocarbons", Van Nostrand Publication, N.Y. (1950).

I-51 Maxwell, J. B. and Bonnell, L. E., "Derivation and Precision of a New Vapor Pressure Correlation for Petroleum Fractions", Ind. Eng. Chem. *49*, 1187 (1957).

I-52 Myers, H. S. and Fenske, M. R., "Measurement and Correlations of Vapor Pressure Data for High Boiling Hydrocarbons", Ind. Eng. Chem. *4 7*, 1652 (1955).

I-53 Natural Gasoline Supply Men's Association, Engineering Data Book, Eighth Edition (1973 y 1976 Revisions).

I-54 Orye, R. V. and Prausnitz, J. M., Ind. Eng. Chem. *57*, 18 (1957).

I-55 Patterson, D., "Free Volume and Polymer Solubility - a Quantitative View", Macromolecules *2*, 672-679, (1969).

I-56 Pierotti, G. J., Deal, C. H. and Derr, E. L., Ind. Eng. Chem. *51*, 95 (1959).

I-57 Pitzer, K. S., Lippman, D. Z., Curl, R. F. Jr., Huggins, C. M. and Petersen, D. M., Jour. Am. Chem. Soc. *77*, 3427 (1955).

I-58 Prather, J. W., Ahangar, A. M., Pilts, W. S., Henley, J. P., Tarrer, A. R. and Guin, J. A., "Solubility of Hydrogen in Creosote Oil at High Temperatures and Pressures", Ind. Eng. Chem. Process Des. Dev. *16*, No. 3, 267 (1977).

I-59 Prausnitz, J. M., "State-of-the-Art Review of Phase Equilibria", presented at a Conference on Phase Equilibria, Asilomar Conference Grounds, Pacific Grove, Calif., (January 16-21, 1977).

I-60 Prausnitz, J. M., "Molecular Thermodynamics of Fluid Phase Equilibrium", Prentice Hall, Englewood Cliffs, N. J. (1968).

I-61 Prigogine, I. "The Molecular Theory of Solutions", North Holland Publishers, Amsterdam (1957).

I-62 Redlich, O. and Kwong, J. N. S., "On the Thermodynamics of Solutions-V-An Equation of State-Fugacities of Gaseous Solutions", Chem. Rev. *44*, 233 (1949).

I-63 Redlich, O., and Kister, A. T., Ind. Eng. Chem., 40, 341, 345 (1958).

I-64 Reid, R. C., Sherwood, T. K. and Prausnitz, J. M., "Properties of Gases and Liquids, 3rd Edition, McGraw Hill, N. Y. (1977).

I-65 Renon, H., and Prausnitz, J. M., AICHE Journal, *14*, 135 (1968).

I-66 Rowlinson, J. S., "Liquids and Liquid Mixtures", Butterworth Publishers, 2nd Edition, London (1969).

I-67 Schneider, G., Chem. Eng. Prog. Symp. Ser., *64*, No. 88, 9 (1968).

I-68 Shen, R. C., "Graphical Correlations of Vapor-Liquid K Values for Hydrogen-Hydrocarbon Systems", Proc. API, *44*, (111), 23 (1964).

I-69 Smith, R. L. and Watson, K. M., "Boiling Points and Critical Properties of Hydrocarbon Mixtures", Ind. Eng. Chem. 29, 19408 (1937), API Tech. Data Book, p. 2-11.

I-70 Smith, K. A., and Watson, K. M., Chem. Eng. Prog., *45*, (1949); Petroleum Processing (December 1949).

I-71 Soave, G., Chem. Eng. Sci. *27*, 1197 (1972).

I-72 Starling, K. E., Hydrocarbon Proc., *50*, 90 (1971).

I-73 Tompa, H., "Polymer Solutions", Chapter 8, Butterworth Publishers, London (1956).

I-74 Van Laar, J. J., Physik, Z. Chem. *72*, 723 (1910), *83*, 599 (1913).

I-75 Van Ness, H. C., "Classical Thermodynamics of Non-Electrolyte Solutions", Macmillan, N. Y. (1964).

I-76 Watson, K. M., Nelson, E. F., "Improved Methods for Approximating Critical and Thermal Properties of Petroleum Fractions", Ind. Eng. Chem. *25*, 880 (1933).

I-77 West, E. W. and Erbar, J. H., "An Evaluation of Four Methods for Predicting the Thermodynamic Properties of Light Hydrocarbon Systems", Proceedings of the 52nd Annual Meeting of the Natural Gas Processors Association, Dallas, Texas (March 26-28, 1973).

I-78 Wilson, G. M., "Thermodynamic Data Needs for Synthetic Gas", A paper presented at the Engineering Foundation Conference, Asilomar, Pacific Grove, California, (January 18, 1977).

I-79 Wilson, G. M., Jour. Am. Chem. Soc. *86*, 127 (1964).

I-80 Winn, F. W., Chem. Eng. Progr. Symp. Ser. 48, No. 2, 121 (1952).

I-81 Wohl, K., Trans. Am. Inst. Chem. Engr. *42*, 215-(1946).

I-82 Yarborough, L. and Vogel, J. L. Chem Engng. Prog. Symp. Ser., 1967, 63, No. 81, p. 1.

I-83 Zudkevitch, D., Joffe, J. and Schroeder G. Chem Engng. Prog. Symp. Ser., 1969, No. 32, p. 141.