PREDICTION OF SOME THERMODYNAMIC PROPERTIES OF PETROLEUM RELATED HYDROCARBONS AND SELECTED NON-HYDROCARBONS

By

EDWARD WENDELL WEST

Bachelor of Science

University of Wisconsin

Madison, Wisconsin

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Thesis Approved:

John H Erbar
Thesis Adviser

John B West

Robert H Robinson Jr.

D D Durham
Dean of the Graduate College

PREFACE

This study was concerned with comparison of various prediction methods in their ability to represent accurately thermodynamic data. Vapor pressures of pure components were predicted by the Chao-Seader, Lee-Edmister, and Soave methods. Entropy departures predicted by the Chao-Seader and Lee-Edmister methods were compared to literature values for pure components as well as mixtures.

Vapor-liquid equilibrium calculations were performed for selected binary mixtures as well as multicomponent systems. The methods used in this phase of the study were the Chao-Seader, Lee-Edmister, Robinson-Chao, Starling and Han Benedict-Webb-Rubin, and Soave.

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CHAPTER I

INTRODUCTION

Thermodynamic properties such as vapor pressure, enthalpy, entropy, and fugacity all are related to pressure, temperature, volume, and composition. Accurate prediction of these thermodynamic properties by methods using equations of state is desirable for industrial application as well as research work. Several of these methods have been successful in predicting experimental data over a practical range of conditions. Among these methods are the Chao-Seader (7), Lee-Edmister (15), Robinson-Chao (20), Starling and Han Benedict-Webb-Rubin (BWR) (23, 24), and Soave (22).

There were three main objectives of this study. The first of these objectives was to test the abilities of the prediction methods, Chao-Seader, Lee-Edmister, and Soave on experimental pure component vapor pressure data. Second, the Chao-Seader and Lee-Edmister methods were applied to literature pure component and mixture entropy departure data. The final and chief objective was to apply all methods to binary and multicomponent hydrocarbon and non-hydrocarbon mixture equilibrium data.

Two calculational procedures for comparing K-values, "with flash" and "without flash," were employed in predicting vapor-liquid equilibria of binary and multicomponent mixtures. The "without flash" calculation procedure involves using the experimentally determined phase compositions in the appropriate equations to predict the partial fugacity coefficients. These partial fugacity coefficients are then combined in the appropriate form to predict K-values. This procedure does not assure that the partial component fugacities in the two phases are equal. A further restriction of this method is that it does not represent a realistic comparison, since in most cases of industrial interest, the composition of the phases are unknown. The "with flash" calculations make use of a standard method of predicting the composition of the co-existing equilibrium phases starting with no knowledge of their composition. In this procedure, the partial fugacities of the components in each phase will be equal when the trial and error calculations are completed. This procedure is typical of the industrial use of thermodynamic prediction methods.

The latter procedure is probably a more exacting test of thermodynamic prediction methods. For K-value predictions, the "without flash" method depends on the experimental phase compositions; the "with flash" method must estimate its own phase compositions. If, then, there is an error in the predicted phase composition, this error should be magnified by its subsequent use in the prediction procedure.

CHAPTER II

BACKGROUND

Many vapor-liquid equilibrium prediction methods have been developed. From the availability of Oklahoma State University computer programs and literature data, five recent methods were chosen for this study. These methods, Chao-Seader (7), Lee-Edmister (15), Robinson-Chao (20), Starling and Han BWR (23, 24), and Soave (22), can be applied over wide temperature-pressure ranges and are capable of predicting the thermodynamic properties of a variety of compounds. Other methods were not considered due to temperature-pressure limitations; general lack of applicability to the hydrocarbon systems of interest; convenience of use, etc.

The thermodynamic properties most frequently used in the following methods are defined below for a given component "k" in a mixture:

1. Vapor fugacity coefficient, ϕ_k, is a ratio of partial fugacity to the system pressure and phase mole fraction:

$$\phi_k = \frac{\tilde{f}_k}{P y_k}$$

   This term may be applied to either the vapor phase or liquid phase or both depending on the particular method.

2. Liquid fugacity coefficient, ν_k^o, is the ratio of fugacity of the pure liquid component to pressure at system conditions:

$$\nu_k^o = \frac{f_k^{oL}}{P}$$

3. Liquid activity coefficient, γ_k, is the ratio of liquid fugacity to the pure liquid component fugacity and liquid mole fraction:

$$\gamma_k = \frac{f_k^L}{f_k^{oL} x_k}$$

The following discussion gives a brief survey of the methods used in this study. Many specific constants (those appearing as successive coefficients in an equation) are required for application of these methods. The reader is referred to the original articles for a more detailed discussion of these terms and tabulation of the constants required in a particular procedure.

Chao-Seader Method

The Chao-Seader method (7) employs three terms, ϕ, ν, and γ. Three equations describe these quantities respectively: (a) a two-parameter basic Redlich-Kwong (RK) equation of state, (b) a Curl and Pitzer three-parameter corresponding states equation, and (c) a two-constant Hildebrand model.

The basic Redlich-Kwong equation of state is given in terms of compressibility factor:

$$Z = \frac{V}{V - b} - \frac{a}{RT^{1.5}(V + b)} \tag{2-1}$$

where

$$a = \sum_{i=1}^{n} \sum_{j=1}^{n} y_i y_j a_{ij} \tag{2-2}$$

$$b = \sum_{j=1}^{n} y_j b_j \tag{2-3}$$

Equation (2-1) is a cubic equation; it can be solved analytically. The maximum root, Z, is picked to determine the vapor mixture volume:

$$V = \frac{ZRT}{P} \tag{2-4}$$

The vapor fugacity coefficient can be computed by the following expression:

$$\ell n\ \phi_k = -\ell n \left\{ \frac{P}{RT} (V - b) \right\} + \frac{\left(2 \sum_{i=1}^{n} y_i b_{i_k} - b\right)}{(V - b)}$$

$$- \frac{2 \sum_{i=1}^{n} y_i a_{i_k} \ell n\left(\frac{V+b}{V}\right)}{RT^{1.5} b} - \frac{a \left(2 \sum y_i b_{i_k} - b\right)}{RT^{1.5}\ b}$$

$$\left\{ \frac{1}{V+b} - \frac{1}{b} \ell n\left(\frac{V+b}{V}\right) \right\} \tag{2-5}$$

Liquid phase fugacity coefficients are calculated from the equation:

$$\log \nu_k^o = \log \nu_k^{(0)} + \omega_k \log \nu_k^{(1)} \tag{2-6}$$

where the quantity $\nu_k^{(0)}$ is given by:

$$\log \nu_k^{(0)} = A_0 + A_1/T_{r_k} + A_2 T_{r_k} + A_3 T_{r_k}^2 + A_4 T_{r_k}^3$$
$$+ (A_5 + A_6 T_{r_k} + A_7 T_{r_k}^2) P_{r_k} + (A_8 + A_9 T_{r_k}) P_{r_k}^2 - \log P_{r_k} \tag{2-7}$$

and where the quantity $\nu_k^{(1)}$ is given by:

$$\log \nu_k^{(1)} = b_1 + b_2 T_{r_k} + b_3/T_{r_k} + b_4 T_{r_k}^2 + b_5 (P_{r_k} - 0.6) \qquad (2\text{-}8)$$

The liquid solution activity coefficient is calculated from the following model (the Hildebrand regular solution model):

$$\ell n\, \gamma_k = \frac{V_k(\delta_k - \bar{\delta})^2}{RT} \qquad (2\text{-}9)$$

where

$$\bar{\delta} = \frac{\sum_{k=1}^{n} x_k V_k \delta_k}{\sum_{k=1}^{n} x_k V_k} \qquad (2\text{-}10)$$

Chao and Seader (7) determined the limits of the correlation to be:

1. For hydrocarbons (except methane):
    a. Reduced temperature range is 0.5 to 1.3 (based on pure component reduced temperature).
    b. Maximum system pressure is 2000 psia.
2. For light gases, methane and hydrogen:
    a. Temperature range is from -100°F to 500°F.
    b. Maximum system pressure is 8000 psia.

Lee-Edmister Method

The Lee-Edmister method (15) employs three empirical relationships for ϕ, ν, and γ. These three relationships are respectively: (a) a three-parameter equation of state, (b) a single function of reduced temperature and pressure, and acentric factor, ω, and (c) an empirical correlation of binary interaction coefficients and solubility parameters.

The three-constant equation of state in terms of compressibility factor is:

$$Z = 1 + \frac{b}{V - b} - \frac{a}{RT(V - b)} + \frac{bc}{RT(V - b)(V + b)} \qquad (2\text{-}11)$$

and

$$V = \frac{ZRT}{P} ,$$

molar mixture volume.

Equation (2-11) is solved analytically in the same manner as in the Chao-Seader method. Vapor phase fugacity coefficients are calculated by the equation:

$$\ell n\ \phi_k = \frac{1}{bRT} \{(2A_k' - aB_k' - bRT)\ \ell n(1 - \frac{b}{v}) + (\frac{cB_k'}{2} - C_k')\ \ell n(1 - \frac{b^2}{V^2})\}$$

$$+ B_k'(Z - 1) - \ell n\ Z \qquad (2\text{-}12)$$

where:

$$a = \sum_{i=1}^{n} \sum_{j=1}^{n} y_i y_j \alpha_{ij} (a_i a_j)^{\frac{1}{2}} \qquad (2\text{-}13)$$

$$b = \sum_{i=1}^{n} y_i b_i \qquad (2\text{-}14)$$

$$c = \sum_{i=1}^{n} \sum_{j=1}^{n} y_i y_j \beta_{ij} (c_i c_j)^{\frac{1}{2}} \qquad (2\text{-}15)$$

where

$$\beta_{ij} = \left[\frac{(T_{c_i} + T_{c_j})}{2(T_{c_i} T_{c_i})^{\frac{1}{2}}} \right]^{m_1} \qquad (2\text{-}16)$$

and

$$\alpha_{ij} = \beta_{ij}^{\ m_2} \qquad (2\text{-}17)$$

$$A_k' = a_k^{\frac{1}{2}} \sum_{j=1}^{n} y_j \alpha_{kj} a_j^{\frac{1}{2}} \qquad (2\text{-}18)$$

$$B'_k = \frac{b_k}{b} \qquad (2\text{-}19)$$

$$C'_k = c_k^{\frac{1}{2}} \sum_{j=1}^{n} y_j \beta_{kj} c_j^{\frac{1}{2}} \qquad (2\text{-}20)$$

The terms, a_i, b_i, and c_i, are all functions of T_r, P_r, and acentric factors.

The liquid phase fugacity coefficient of a pure component, "k", in a mixture is calculated by the equation:

$$\begin{aligned} \ell n\ \nu_k = {} & A_{1k} + A_{2k}T_{rk}^{-1} + A_{3k}\,\ell n\ T_{rk} + A_{4k}T_{rk} + A_{5k}\,T_{rk}^2 + A_{6k}T_{rk}^7 \\ & + (A_{7k} + A_{8k}T_{rk}^{-1} + A_9\ \ell n\ T_{rk} + A_{10}T_{rk}^2 + A_{11k}T_{rk}^7)P_{rk} \\ & + A_{12k}T_{rk}^3P_{rk}^2 + \omega_k\{(1 - T_{rk})(A_{13k} + A_{14k}T_{rk}^{-1} + A_{15k}T_{rk}) \\ & + A_{16k}P_{rk}T_{rk}^{-1} + A_{17k}T_{rk}P_{rk}^2\} - \ell n\ P_{rk} \qquad (2\text{-}21) \end{aligned}$$

The liquid activity coefficient is calculated by the model:

$$\ell n\ \gamma_k = \frac{V_k}{RT}\{\sum_{j=1}^{n} B_{kj}\Phi_j - \frac{1}{2}\sum_{j=1}^{n}\sum_{m=1}^{n} B_{jm}\Phi_j\Phi_m\} \qquad (2\text{-}22)$$

where

$$B_{kj} = (\delta_k - \delta_j)^2 + 2\ell_{kj}\delta_k\delta_j \qquad (2\text{-}23)$$

and ℓ is the binary interaction coefficient defined by Eckert and Prauznitz (9):

$$\begin{aligned} \ell_{kj} = {} & \frac{(\delta_k - \delta_j)^2}{2\delta_k\ \delta_j}\{q_1 - 1 + q_2(T_{rk}T_{rj})^{\frac{1}{2}} + q_3[\frac{2(T_{rk}T_{rj})^{\frac{1}{2}}}{T_{rk}+T_{rj}}] \\ & + q_4T_{rk}T_{rj}\} - q_5\{\frac{V_k+V_j}{2(K_kV_j)^{\frac{1}{2}}} - 1\} \qquad (2\text{-}24) \end{aligned}$$

The factors Φ_j, Φ_m are volume fractions of the respective species "j" and "m" in the mixture such that

$$\Phi_k = \frac{x_k V_k}{\sum_{j=1}^{n} x_j V_j} \tag{2-25}$$

Limits of application of the Lee-Edmister method have been estimated to be:

1. Temperature limits are from -250°F to 500°F.
2. Maximum system pressure is 4000 psia.

These temperature and pressure limits are not well defined at this time.

Robinson-Chao Method

The Robinson-Chao method (20) like the Chao-Seader and the Lee-Edmister methods uses three separate expressions for ϕ, ν, and γ. These quantities are respectively predicted from: (a) a modified form of the basic Redlich-Kwong equation, (b) the three-parameter Pitzer and Curl corresponding states equation, and (c) a liquid solution equation modeled after the Scatchard-Hildebrand form.

Robinson and Chao (20) use the same vapor phase equation of state and volume expressions as in the Chao-Seader method. Mixture parameters are given by Robinson and Chao as follows:

$$a = \sum_{j=1}^{n} \sum_{k=1}^{n} y_j y_k a_{jk} \tag{2-26}$$

$$b = \sum_{k=1}^{n} y_k b_k \tag{2-27}$$

However, they use the modified Redlich-Kwong equation constants developed by Chueh and Prausnitz (8):

$$a_{jk} = \frac{(\Omega_{aj} + \Omega_{ak})R^2T_{cjk}^{2.5}}{2P_{cjk}} \tag{2-28}$$

$$b_k = \frac{\Omega_{bk}RT_{ck}}{P_{ck}} \tag{2-29}$$

$$a_{kk} = \frac{\Omega_{ak}R^2T_{ck}^{2.5}}{P_{ck}} \tag{2-30}$$

where:

$$P_{cjk} = \frac{Z_{cjk}RT_{cjk}}{V_{cjk}} \tag{2-31}$$

$$V_{cjk} = \frac{1}{2}(V_{cjj}^{1/3} + V_{ckk}^{1/3}) \tag{2-32}$$

$$Z_{cjk} = 0.291 - 0.04(\omega_j + \omega_k) \tag{2-33}$$

$$T_{cjk} = (T_{cj}T_{ck})^{\frac{1}{2}}(1 - K_{jk}) \tag{2-34}$$

The changes made by Chueh and Prausnitz are in the values Ω_a, Ω_b, and K_{jk}. These constant values in the RK equation are replaced by tabulated values for a variety of pure components and binary pairs. The vapor phase fugacity coefficient is calculated in a similar manner as in the Chao-Seader method.

The liquid phase fugacity coefficient is calculated by the same basic equation (2-6) given in the Chao-Seader section. The form of correlating equations and the constants for the $\nu^{(0)}$ and $\nu^{(1)}$ expressions have been revised.

The liquid activity coefficient is calculated from the following equation:

$$\ln \gamma_k = \left(\frac{V_k}{RT}\right)\left(a_k - 2\sum_{j=1}^{n} \Phi_j a_{kj} + \sum_{k=1}^{n}\sum_{j=1}^{n} \Phi_k \Phi_j a_{kj}\right)$$

$$+ \ln\left(\frac{V_k}{V_m}\right) + 1 - \left(\frac{V_k}{V_m}\right) \qquad (2\text{-}35)$$

where the molar mixture volume V_m is given by:

$$V_m = \sum_{j=1}^{n} x_j V_j \qquad (2\text{-}36)$$

and Φ_j is the volume fraction:

$$\Phi_j = \frac{x_j V_j}{V_m} \qquad (2\text{-}37)$$

The cohesive energy density term, a, is given by:

$$a_k = \delta_k^2 \qquad (2\text{-}38)$$

and

$$a_{kj} = (1 - \ell_{kj})\delta_k \delta_j \qquad (2\text{-}39)$$

where ℓ_{kj} is a binary interaction parameter Robinson and Chao (20) correlated for several hydrocarbon and non-hydrocarbon binary pairs.

The correlation limits were estimated by Robinson and Chao (20) to be:

1. Temperature range is from -116°F to 160°F.
2. Maximum system pressure is 3000 psia.

Starling and Han BWR Method

The original BWR equation of state is an eight-parameter equation (3, 4) and is over 30 years old. It has been developed chiefly for accurately describing pure component and mixture phase behavior in the range $T_r > 0.6$ and $\rho_r < 1.8$. For light hydrocarbon systems, the BWR predicts vapor-liquid equilibrium data with remarkable accuracy. In this study, a modified form of the BWR equation by Starling and Han (23) is used. This modified equation uses binary interaction parameters in a manner similar to Chueh and Prausnitz and eleven constants instead of eight employed in the original equation. In addition, these eleven constants have been generalized. They may be predicted from specific equations as functions of critical temperature, critical pressure, and the acentric factor of the component. The binary interaction parameters have not been generalized.

The Starling and Han BWR equation of state in terms of compressibility factor is given by:

$$\begin{aligned} Z = {} & 1 + \frac{1}{RTV}\left(B_oRT - A_o - \frac{C_o}{T^2} + \frac{D_o}{T^3} - \frac{E_o}{T^4}\right) \\ & + \frac{1}{RTV^2}\left(bRT - a - \frac{d}{T}\right) + \frac{\alpha}{RTV^5}\left(a + \frac{d}{T}\right) \\ & + \frac{c}{RT^3V}\left(1 + \frac{\gamma}{V^2}\right)\exp\left(\frac{-\gamma}{V^2}\right) \end{aligned} \tag{2-40}$$

where:

$$B_o = \sum_{i=1}^{n} x_i B_{o_i} \tag{2-41}$$

$$A_o = \sum_{i=1}^{n}\sum_{j=1}^{n} x_i x_j A_{o_i}^{\frac{1}{2}} A_{o_j}^{\frac{1}{2}} (1 - K_{ij}) \tag{2-42}$$

$$C_o = \sum_{i=1}^{n}\sum_{j=1}^{n} x_i x_j C_{o_i}^{\frac{1}{2}} C_{o_j}^{\frac{1}{2}} (1 - K_{ij})^3 \tag{2-43}$$

$$\gamma = \left(\sum_{i=1}^{n} x_i \gamma_i\right)^2 \tag{2-44}$$

$$b = \left(\sum_{i=1}^{n} x_i b_i^{1/3}\right)^3 \tag{2-45}$$

$$a = \left(\sum_{i=1}^{n} x_i a_i^{1/3}\right)^3 \tag{2-46}$$

$$\alpha = \left(\sum_{i=1}^{n} x_i \alpha_i^{1/3}\right)^3 \tag{2-47}$$

$$c = \left(\sum_{i=1}^{n} x_i c_i^{1/3}\right)^3 \tag{2-48}$$

$$D_o = \sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j D_{o_i}^{\frac{1}{2}} D_{o_j}^{\frac{1}{2}} (1 - K_{ij})^4 \tag{2-49}$$

$$d = \left(\sum_{i=1}^{n} x_i d_i^{1/3}\right)^3 \tag{2-50}$$

$$E_o = \sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j E_{o_i}^{\frac{1}{2}} E_{o_j}^{\frac{1}{2}} (1 - K_{ij})^5 \tag{2-51}$$

Analytical solution of the above equation for Z is impossible. An iterative technique is required to determine the roots of the equation. Maximum and minimum roots are found to calculate the vapor and liquid mixture volumes, respectively. From these volumes the vapor and liquid fugacity coefficients can be found from the following equation (24):

$$\begin{aligned}
\ell n\ \phi_k = {} & \frac{1}{V}(B_0 + B_{0k}) + \frac{2}{RTV}\sum_{j=1}^{n}\{x_j - (A_0A_{0k})^{\frac{1}{2}}(1 - K_{kj}) \\
& - \frac{(C_0C_{0k})^{\frac{1}{2}}}{T^2}(1 - K_{kj})^3 + \frac{(D_0D_{0k})^{\frac{1}{2}}}{T^3}(1 - K_{kj})^4 \\
& - \frac{(E_0E_{0k})^{\frac{1}{2}}}{T^4}(1 - K_{kj})^5\} + \frac{1}{2RTV^2}\{3(b^2b_k)^{1/3} \\
& RT - 3(a^2a_k)^{1/3} - \frac{3(d^2d_k)^{1/3}}{T}\} + \frac{\alpha}{5RTV^5}\{3(a^2a_k)^{1/3} \\
& + \frac{3(d^2d_k)^{1/3}}{T}\} + \frac{3}{5RTV^5}(a + \frac{d}{T})(\alpha^2\alpha_k)^{1/3} \\
& + \frac{3(c^2c_k)^{1/3}}{RT^3V^2}\{\frac{1 - \exp(\frac{-\gamma}{V^2})}{(\frac{\gamma}{V^2})} - \frac{\exp(\frac{-\gamma}{V^2})}{2}\} \\
& - \frac{2c}{\gamma RT^3}(\frac{\gamma_k}{\gamma})^{\frac{1}{2}}\{1 - \exp(\frac{-\gamma}{V^2})(1 + \frac{\gamma}{V^2} + \frac{\gamma^2}{2V^4})\} \qquad (2\text{-}52)
\end{aligned}$$

Starling and Han (23) applied their modified BWR equation of state over these ranges of conditions:

1. Temperatures are from -283°F to 460°F.
2. Pressures are from 14.7 psia to 5000 psia.

Soave Method

Equilibrium ratios and other thermodynamic properties can be predicted by a method applying a single modified form of the basic RK equation of state. This modification was developed recently by Soave (22). Soave replaces the second term, $a/T^{0.5}$, by a temperature dependent function a(T). In this study, binary interaction parameters were determined for nitrogen-paraffin hydrocarbon systems, carbon dioxide-paraffin hydrocarbon systems, hydrogen sulfide-paraffin hydrocarbon systems, and the binary systems nitrogen-carbon dioxide, nitrogen-hydrogen sulfide, carbon dioxide-hydrogen sulfide.

The compressibility factor form of the equation of state is essentially the same as the RK in the Chao-Seader section. The mixing rules of the Soave modified RK equation are the same as the Chao-Seader rules with one variation in the "a" constant calculation. This revision is:

$$a = \left[0.42747 \sum_{i=1}^{n} x_i \alpha_i^{0.5} \frac{T_{c\,i}}{P^{0.5}} \right]^2 \qquad (2\text{-}53)$$

where α_i's are functions of T_r and ω:

$$\alpha_i = [1 + m_i(1 - T_{r_i}^{0.5})]^2 \qquad (2\text{-}54)$$

and

$$m_i = a_0 + a_1\omega_i + a_2\omega_i^2 \qquad (2\text{-}55)$$

The minimum and maximum roots are determined analytically by a cubic equation solution procedure. These maximum and minimum roots are used to determine vapor and liquid mixture volumes, respectively, by:

$$V = \frac{ZRT}{P}$$

Liquid and vapor phase fugacity coefficients are calculated by this single equation:

$$\ln \phi_k = \frac{b_k}{b}(Z - 1) - \ln(Z - B) - \frac{A}{B} \left(\frac{2a_k^{0.5}}{a^{0.5}} - \frac{b_k}{b}\right) \ln\left(1 + \frac{B}{Z}\right) \quad (2\text{-}56)$$

where

$$A = 0.42747 \frac{P}{T^2} \left(\sum_{k=1}^{n} y_k \frac{T_{c_k} \alpha_k^{0.5}}{P_{c_k}^{0.5}} \right)^2 \quad (2\text{-}57)$$

and

$$B = 0.08664 \frac{P}{T} \sum_{k=1}^{n} y_k \frac{T_{c_k}}{P_{c_k}} \quad (2\text{-}58)$$

This modified RK equation has been applied over the following range of conditions:

1. Temperatures were from -270°F to 500°F.
2. Upper pressure limit was 5000 psia.

Thermodynamic Property Data

A standard set of K-value systems and conditions was established in this study. The temperature and pressure ranges were respectively, from -260°F to 500°F and from 14.7 psia to 4000 psia. This set of systems was chosen to evaluate the capabilities of the Chao-Seader, Lee-Edmister, Robinson-Chao, Starling and Han BWR, and Soave methods. Some of these methods were extrapolated beyond their range of correlation to calculate vapor-liquid equilibrium data covering this P-T range. Thus large errors should be expected.

Vapor-liquid equilibrium data used in this study were taken from Chevron Research Corporation (11) and Yarborough (25). Entropy departure data were taken from API 44 (2) and Bhirud and Powers (5). Vapor pressure data were selected from several sources: API 44 (2), Carruth (6), proprietary (11), and Sage and Lacey (21).

Role of Partial Properties in Thermodynamic Property Predictions

In vapor-liquid equilibrium systems, the composition of each component is described by a K-value. This K-value is the numerical ratio of vapor to liquid mole fractions. K-value calculations depend on the number of models (empirical equations for liquid and vapor fugacities), number of components in the system, and the number of phases present (in this case, two phases, liquid and vapor). When compared to vapor pressure and entropy departure calculations in this study, K-value computations are more difficult to handle. The reason is that fugacity coefficients are a result of partial properties as shown by this integral:

$$\ell n\ \phi_k = \frac{1}{RT}\int_0^P \{\tilde{V}_k - \frac{RT}{P}\}\ dP \qquad (2\text{-}59)$$

where

$$\tilde{V}_k = \left(\frac{\partial V}{\partial n_k}\right)_{T,P,n_j \neq n_k} = \text{partial molar volume of } k\ .$$

This partial molar volume term serves as the basis for deriving partial fugacities.

For pure components equation (2-59) reduces to a total integral (non-partial molar form):

$$\ell n\left(\frac{f}{P}\right) = \frac{1}{RT}\int_0^P \{V - \frac{RT}{P}\}\ dP \qquad (2\text{-}60)$$

The results of this integral are used for calculating pure component entropy departures and vapor pressures in the standard bubble point procedure. A more convenient form of equation (2-59) for determining K-values of a mixture is a volume-explicit integral:

$$\ell n\ \phi_k = \frac{1}{RT}\int_{\infty}^{V}\{\frac{RT}{V} - (\frac{\partial P}{\partial n_k})_{T,V,n_j \neq n_k}\}\ dV - \ell n\ Z \qquad (2\text{-}61)$$

where Z is the total mixture compressibility factor. Similar equations for partial enthalpy and entropy departures can be developed using the appropriate thermodynamic relationships. All composition dependent parameters (i.e., mixing rules) are differentiated (in the basic equations of state discussed) when the partial derivative of the pressure is taken with respect to component composition ($\frac{\partial P}{\partial n_k}$ term of equation (2-61)). As a result composition has a great effect on partial molar properties and subsequent K-value predictions. Similar problems are encountered when attempting to predict partial enthalpy or entropy departures. However, when predicting bulk phase properties such as total molar enthalpy or entropy departures, these effects tend to be eliminated through internal compensation of the equations of state. Even though entropy mixture calculations include partial fugacities for each component, these partial quantities are additive and contribute to a total value for entropy departure.

CHAPTER III

COMPARISON OF PREDICTED VAPOR PRESSURES AND ENTROPY DEPARTURES BY USING THE CHAO-SEADER, LEE-EDMISTER, AND SOAVE METHODS

Vapor Pressure

Vapor pressures predicted by the Chao-Seader, Lee-Edmister, and Soave methods were compared with pure component literature data (2, 6, 11, 21). The range of the test was from the normal boiling point and 14.7 psia to approximately the critical point. These values were computed using the standard bubble point temperature calculation. Table I gives a comparison summary of the results for the paraffins methane through n-decane. The Lee-Edmister predictions were within 3.00% of the experimental data; the Soave method gave results that agreed within 2.00% of the experimental data. The Chao-Seader method proved to be the least accurate--over 18.00% in the case of methane. This overall average error was due to consistently large deviations (11.00% to 35.00%) from -259.0°F to -157.1°F. However, this large error should be expected since the Chao-Seader method was being extrapolated beyond its original correlation limits. Overall, the Soave method consistently gives the best prediction of pure component vapor pressures. This quality of agreement for the Soave method should be expected since the

TABLE I

DEVIATIONS OF CALCULATED VAPOR PRESSURES FROM EXPERIMENTAL DATA (2, 6, 11, 21)

Hydrocarbon	Number of Points	Min. Temp. °F	Abs. Ave. Deviation %		
			C&S	L&E	SRK
Methane	21	-259.0	18.47	2.16	1.71
Ethane	25	-127.5	3.59	2.81	1.04
Propane	12	-43.7	1.90	1.81	1.13
I-Butane	35	10.6	3.36	3.33	1.11
N-Butane	19	31.1	2.59	2.59	1.38
I-Pentane	27	81.8	1.85	2.28	1.10
N-Pentane	25	96.9	1.92	1.90	1.27
N-Hexane	21	155.7	3.74	0.60	1.55
N-Heptane	30	209.2	3.41	2.45	1.38
N-Octane	22	258.2	4.29	1.94	1.67
N-Nonane	9	303.4	4.71	2.94	0.46
N-Decane	3	345.4	5.64	2.91	0.36
Overall	249		4.42	2.31	1.28

acentric factors used in the correlation (equation 2-55) are adjusted to match the vapor pressure at the normal boiling point.

Pure Component Entropy Departures

Two methods, the Chao-Seader and Lee-Edmister, were used to predict isothermal entropy departure values of pure components. These data are in API 44 (2). Table II gives vapor phase deviation comparisons of these two methods for methane through n-pentane. This pressure range covered in this part of the study was from 100.0 psia to 3000.0 psia. For this range of paraffins the Lee-Edmister method is more accurate with deviations averaging less than 1.00%. The Chao-Seader gave an absolute average error of 2.83%.

Mixture Entropy Departures

The predictive ability of the Chao-Seader and Lee-Edmister methods was tested on isothermal entropy difference data of a 5% propane-95% methane system (5). These literature entropy departure values were derived from volumetric data and isothermal enthalpy differences determined from calorimetric data. Table III shows liquid and vapor phase deviations over the temperature range from -250°F to 300°F and pressure range from 250 psia to 2000 psia. A total of 178 data points were tested in this part of the study. Table III unlike Tables I and II presents the predictions on a point-by-point basis due to the presence of both liquid and vapor phases. Large deviations appeared near the critical region in the temperature range from -60°F to -40°F for both methods. The Lee-Edmister method again gives consistently better results. The average deviation is within 2.00% or 0.0099 Btu/lb-°R.

TABLE II

DEVIATIONS OF CALCULATED ENTROPY DEPARTURES FROM DATA (2)

Hydrocarbon	Number of Points	Temp. Range, °F		Abs. Ave. Deviation %	
		Min.	Max.	C&S	L&E
Methane	49	-99.7	440.3	0.23	0.18
Ethane	50	260.3	500.3	0.24	0.19
Propane	50	210.3	470.3	2.44	0.60
I-Butane	51	80.3	500.3	3.25	0.64
N-Butane	50	270.3	500.3	4.51	0.75
I-Pentane	50	300.3	500.3	4.04	0.89
N-Pentane	50	290.3	480.3	5.05	0.93
Overall	350			2.83	0.60

TABLE III

DEVIATIONS OF CALCULATED ENTROPY DEPARTURES FROM DATA (5) FOR 5% PROPANE IN METHANE MIXTURE

Temperature °F	Pressure Psia	Abs. Ave. Deviation, % C&S	L&E	Phase
-250.0	250.0	-4.32	-0.28	Liquid
-250.0	400.0	-4.00	-0.20	Liquid
-250.0	500.0	-3.77	-0.12	Liquid
-250.0	650.0	-3.59	-0.18	Liquid
-250.0	800.0	-3.49	-0.31	Liquid
-250.0	1000.0	-3.08	-0.22	Liquid
-250.0	1500.0	-2.41	-0.33	Liquid
-250.0	2000.0	-1.69	-0.38	Liquid
-240.0	250.0	-3.36	-0.28	Liquid
-240.0	400.0	-3.09	-0.23	Liquid
-240.0	500.0	-2.91	-0.19	Liquid
-240.0	650.0	-2.75	-0.25	Liquid
-240.0	800.0	-2.61	-0.33	Liquid
-240.0	1000.0	-2.29	-0.29	Liquid
-240.0	1500.0	-1.68	-0.40	Liquid
-240.0	2000.0	-1.02	-0.47	Liquid
-220.0	250.0	-1.46	-0.15	Liquid
-220.0	400.0	-1.37	-0.24	Liquid
-220.0	500.0	-1.35	-0.32	Liquid
-220.0	650.0	-1.16	-0.29	Liquid
-220.0	800.0	-0.96	-0.24	Liquid
-220.0	1000.0	-0.85	-0.38	Liquid
-220.0	1500.0	-0.39	-0.47	Liquid

TABLE III (CONTINUED)

Temperature °F	Pressure Psia	Abs. Ave. Deviation, %		Phase
		C&S	L&E	
-220.0	2000.0	0.12	-0.54	Liquid
-200.0	250.0	0.51	0.02	Liquid
-200.0	400.0	0.26	-0.31	Liquid
-200.0	500.0	0.22	-0.40	Liquid
-200.0	650.0	0.43	-0.27	Liquid
-200.0	800.0	0.71	-0.08	Liquid
-200.0	1000.0	0.51	-0.40	Liquid
-200.0	1500.0	0.79	-0.43	Liquid
-200.0	2000.0	1.15	-0.41	Liquid
-180.0	250.0	2.65	0.03	Liquid
-180.0	400.0	2.03	-0.52	Liquid
-180.0	500.0	1.89	-0.64	Liquid
-180.0	650.0	2.01	-0.49	Liquid
-180.0	800.0	2.37	-0.10	Liquid
-180.0	1000.0	1.86	-0.56	Liquid
-180.0	1500.0	1.90	-0.46	Liquid
-180.0	2000.0	2.11	-0.25	Liquid
-160.0	400.0	4.15	-1.11	Liquid
-160.0	500.0	3.79	-1.31	Liquid
-160.0	650.0	3.56	-1.31	Liquid
-160.01	800.0	4.04	-0.66	Liquid
-160.0	1000.0	3.31	-1.09	Liquid
-160.0	1500.0	3.04	-0.77	Liquid
-160.0	2000.0	2.99	-0.30	Liquid

TABLE III (CONTINUED)

Temperature °F	Pressure Psia	Abs. Ave. Deviation, % C&S	L&E	Phase
-140.0	500.0	6.06	0.38	Liquid
-140.0	650.0	5.52	0.10	Liquid
-140.0	800.0	5.94	0.72	Liquid
-140.0	1000.0	5.02	0.12	Liquid
-140.0	1500.0	4.29	0.06	Liquid
-140.0	2000.0	3.94	0.24	Liquid
-120.0	650.0	9.58	1.44	Liquid
-120.0	800.0	8.41	0.68	Liquid
-120.0	1000.0	7.27	0.01	Liquid
-120.0	1500.0	5.81	-0.45	Liquid
-120.0	2000.0	4.99	-0.45	Liquid
-100.0	800.0	13.78	3.35	Liquid
-100.0	1000.0	10.74	1.12	Liquid
-100.0	1500.0	7.77	-0.40	Liquid
-100.0	2000.0	6.22	-0.83	Liquid
-80.0	1000.0	18.84	6.45	Liquid
-80.0	1100.0	15.45	3.74	Liquid
-80.0	1200.0	13.65	2.43	Liquid
-80.0	1500.0	10.50	0.45	Liquid
-80.0	2000.0	7.73	-0.79	Liquid
-60.0	1100.0	26.50	11.75	Liquid
-60.0	1200.0	21.85	8.04	Liquid
-60.0	1500.0	14.46	2.53	Liquid
-60.0	1700.0	11.95	0.93	Liquid

TABLE III (CONTINUED)

Temperature °F	Pressure Psia	Abs. Ave. Deviation, % C&S	L&E	Phase
-60.0	2000.0	9.64	-0.29	Vapor
-40.0	250.0	-2.40	-1.73	Vapor
-40.0	400.0	-0.79	0.10	Vapor
-40.0	500.0	-2.00	-0.99	Vapor
-40.0	1000.0	43.18	24.00	Liquid
-40.0	1100.0	36.39	18.65	Liquid
-40.0	1200.0	30.94	14.39	Liquid
-40.0	1500.0	19.74	5.86	Liquid
-40.0	1700.0	15.57	2.94	Liquid
-40.0	2000.0	11.92	0.71	Vapor
-20.0	250.0	-2.94	-2.41	Vapor
-20.0	400.0	-1.88	-1.19	Vapor
-20.0	500.0	-2.36	-1.61	Vapor
-20.0	650.0	-2.19	-1.32	Vapor
-20.0	800.0	-5.38	-4.48	Vapor
-20.0	1000.0	6.77	7.89	Vapor
-20.0	1500.0	-2.45	-0.97	Vapor
-20.0	1700.0	-2.61	-0.97	Vapor
-20.0	2000.0	-2.62	-0.98	Vapor
0.0	250.0	-3.18	-2.77	Vapor
0.0	400.0	-2.02	-1.50	Vapor
0.0	500.0	-2.32	-1.75	Vapor
0.0	650.0	-2.35	-1.68	Vapor
0.0	800.0	-2.56	-1.84	Vapor

TABLE III (CONTINUED)

Temperature °F	Pressure Psia	Abs. Ave. Deviation, % C&S	L&E	Phase
0.0	1000.0	-4.85	-4.06	Vapor
0.0	1500.0	-2.11	-0.92	Vapor
0.0	1700.0	-2.36	-0.92	Vapor
0.0	2000.0	-2.50	-0.78	Vapor
20.0	250.0	-3.20	-2.90	Vapor
20.0	400.0	-1.92	-1.51	Vapor
20.0	500.0	-1.43	-0.96	Vapor
20.0	650.0	-2.33	-1.80	Vapor
20.0	800.0	-2.43	-1.86	Vapor
20.0	1000.0	-1.82	-1.18	Vapor
20.0	1500.0	-1.77	-0.83	Vapor
20.0	1700.0	-2.07	-0.93	Vapor
20.0	2000.0	-2.25	-0.78	Vapor
40.0	250.0	-3.10	-2.86	Vapor
40.0	400.0	-1.85	-1.55	Vapor
40.0	500.0	-2.23	-1.87	Vapor
40.0	650.0	-2.21	-1.80	Vapor
40.0	800.0	-2.16	-1.72	Vapor
40.0	1000.0	-1.74	-1.23	Vapor
40.0	1500.0	-1.68	-0.93	Vapor
40.0	1700.0	-1.88	-0.97	Vapor
40.0	2000.0	-2.08	-0.86	Vapor
60.0	250.0	-2.94	-2.73	Vapor
60.0	400.0	-1.89	-1.63	Vapor

TABLE III (CONTINUED)

Temperature °F	Pressure Psia	Abs. Ave. Deviation, % C&S	L&E	Phase
60.0	500.0	-2.17	-1.89	Vapor
60.0	650.0	-2.06	-1.73	Vapor
60.0	1000.0	-1.72	-1.31	Vapor
60.0	1500.0	-1.66	-1.07	Vapor
60.0	1700.0	-1.77	-1.06	Vapor
60.0	2000.0	-1.90	-0.93	Vapor
80.0	250.0	-2.60	-2.44	Vapor
80.0	400.0	-1.97	-1.79	Vapor
80.0	500.0	-2.02	-1.81	Vapor
80.0	650.0	-1.88	-1.64	Vapor
80.0	800.0	-1.74	-1.46	Vapor
80.0	1000.0	-1.63	-1.30	Vapor
80.0	1500.0	-1.61	-1.12	Vapor
80.0	1700.0	-1.68	-1.09	Vapor
80.0	2000.0	-1.75	-0.96	Vapor
100.0	500.0	-2.05	-1.86	Vapor
100.0	1000.0	-1.68	-1.43	Vapor
100.0	1500.0	-1.63	-1.22	Vapor
100.0	2000.0	-1.72	-1.06	Vapor
120.0	500.0	-2.02	-1.87	Vapor
120.0	1000.0	-1.69	-1.48	Vapor
120.0	1500.0	-1.58	-1.25	Vapor
120.0	2000.0	-1.64	-1.10	Vapor
140.0	500.0	-2.00	-1.90	Vapor

TABLE III (CONTINUED)

Temperature °F	Pressure Psia	Abs. Ave. Deviation, % C&S	L&E	Phase
140.0	1000.0	-1.69	-1.51	Vapor
140.0	1500.0	-1.56	-1.28	Vapor
140.0	2000.0	-1.60	-1.15	Vapor
160.0	500.0	-1.98	-1.89	Vapor
160.0	1000.0	-1.64	-1.50	Vapor
160.0	1500.0	-1.52	-1.29	Vapor
160.0	2000.0	-1.55	-1.17	Vapor
180.0	500.0	-1.99	-1.91	Vapor
180.0	1000.0	-1.66	-1.55	Vapor
180.0	1500.0	-1.54	-1.35	Vapor
180.0	2000.0	-1.55	-1.20	Vapor
200.0	500.0	-1.99	-1.92	Vapor
200.0	1000.0	-1.67	-1.57	Vapor
200.0	1500.0	-1.55	-1.37	Vapor
200.0	2000.0	-1.51	-1.23	Vapor
220.0	500.0	-4.05	-4.01	Vapor
220.0	1000.0	-1.64	-1.56	Vapor
220.0	1500.0	-1.53	-1.38	Vapor
220.0	2000.0	-1.45	-1.18	Vapor
240.0	500.0	-1.91	-1.86	Vapor
240.0	1000.0	-1.62	-1.54	Vapor
240.0	1500.0	-1.50	-1.35	Vapor
240.0	2000.0	-1.39	-1.17	Vapor
260.0	500.0	-1.88	-1.86	Vapor

TABLE III (CONTINUED)

Temperature °F	Pressure Psia	Abs. Ave. Deviation, % C&S	L&E	Phase
260.0	1000.0	-1.61	-1.53	Vapor
260.0	1500.0	-1.49	-1.36	Vapor
260.0	2000.0	-1.35	-1.13	Vapor
280.0	500.0	-1.94	-1.91	Vapor
280.0	1000.0	-1.63	-1.57	Vapor
280.0	1500.0	-1.51	-1.40	Vapor
280.0	2000.0	-1.34	-1.15	Vapor
300.0	500.0	-2.03	-2.01	Vapor
300.0	1000.0	-1.74	-1.70	Vapor
300.0	1500.0	-1.60	-1.49	Vapor
300.0	2000.0	-1.40	-1.21	Vapor
Maximum		43.18	24.00	
Average		4.04	1.65	

The BWR method was not evaluated since Starling and Han (23) report an average deviation of 0.0055 Btu/lb-°R for about the same mixture conditions.

CHAPTER IV

VAPOR-LIQUID EQUILIBRIUM DATA COMPARISONS

Vapor-liquid equilibrium calculations are important in the design of distillation columns, absorber-strippers, and flash tanks. Good estimates of vapor-liquid equilibrium data for multi-component systems are needed for reliable equipment sizing. The Chao-Seader, Lee-Edmister, Robinson-Chao, Starling and Han BWR, and Soave methods are applied in this study to approximately 100 typical industrial gas-liquid mixtures. The binary systems methane-propane, methane-n-heptane, methane-n-decane, carbon dioxide-propylene, methane-hydrogen sulfide, and nitrogen-ethane are selected as examples to show specific effects. Similar effects can be noted for the remaining systems. Deviations in the predicted K-values for these systems are shown in Tables IV through IX.

Table X gives absolute average K-value deviations of a ten-component system (25) for the Chao-Seader, Lee-Edmister, Starling and Han BWR, and Soave methods. Temperatures range from -45°F to 250°F and pressures range from 107 psia to 3741 psia. A total of 211 data points were tested in this system. The computer time required to calculate the vapor-liquid equilibrium data for each method shown is central processing unit time. Table XI gives a total average error summary for the Chao-Seader, Lee-Edmister, Starling and Han BWR, and Soave methods

TABLE IV

DEVIATIONS IN K-VALUE PREDICTIONS FROM EXPERIMENTAL DATA (1, 16, 17) FOR METHANE-PROPANE BINARY SYSTEM

Temp.	Press.	Absolute Average Deviation %				
°F	Psia	C&S	L&E	R&C	S&H BWR	SRK
			Methane			
-200.0	100.0	-3.01	3.90		-2.36	2.04
-150.0	100.0	17.74	-6.63		4.78	3.76
-150.0	200.0	8.15	3.32		-4.77	1.93
-100.0	100.0	16.21	-12.25	1.23	2.53	66.83
-100.0	200.0	20.13	2.69	11.21	7.19	8.49
-100.0	600.0	-14.12	5.30	5.69	-4.88	-1.14
-50.0	100.0	8.38	-16.08	-2.52	-7.15	-5.81
-50.0	200.0	15.07	-0.99	7.94	1.44	4.50
-50.0	400.0	5.42	2.28	5.16	-5.98	0.65
-50.0	800.0	-10.95	7.85	3.39	-7.40	0.31
0.0	100.0	7.60	-8.07	-1.33	-7.12	-1.31
0.0	200.0	9.81	-0.66	3.14	-3.59	3.35
0.0	600.0	-2.99	4.66	-0.72	-9.70	0.96
0.0	1100.0	-24.05	5.09	-7.66	-9.06	-0.51
50.0	400.0	8.41	8.54	4.64	0.04	11.80
50.0	600.0	-3.72	4.11	-4.37	-8.47	5.06
50.0	800.0	-7.89	5.91	-5.49	-7.91	5.39
50.0	1100.0	-25.09	2.39	-15.12	-9.79	1.13
100.0	200.0	-0.47	1.82	-7.02	-5.22	10.24
100.0	400.0	-8.79	-1.48	-13.70	-11.35	6.22
100.0	800.0	-20.41	-1.35	-20.05	-11.10	4.77

TABLE IV (CONTINUED)

Temp. °F	Press. Psia	Absolute Average Deviation %				
		C&S	L&E	R&C	S&H BWR	SRK
100.0	1100.0	-33.58	-3.24	-27.39	-5.31	3.51
160.0	400.0	-26.50	-11.98	-40.92	-11.26	11.33
160.0	600.0	-34.94	-15.82	-48.09	-10.90	8.51
160.0	800.0	-43.39	-18.23	-54.29	-3.41	7.71
Maximum		-43.39	-18.23	-54.29	-11.35	66.83
Average		15.07	6.19	13.23	6.51	7.07
			Propane			
-200.0	100.0	82.35	80.30		83.92	86.47
-150.0	100.0	11.87	26.38		32.97	33.52
-150.0	200.0	42.13	40.80		54.40	54.32
-100.0	100.0	8.90	16.83	21.77	20.62	-1250.71
-100.0	200.0	-2.05	2.82	12.64	12.14	10.63
-100.0	600.0	36.60	0.30	26.23	25.40	25.15
-50.0	100.0	4.81	6.64	6.32	9.59	7.65
-50.0	200.0	-0.03	0.97	2.81	6.76	3.82
-50.0	400.0	2.92	-0.75	6.21	11.75	6.73
-50.0	800.0	9.35	-14.60	4.93	11.87	2.59
0.0	100.0	-0.33	-2.77	-3.44	-0.48	-3.18
0.0	200.0	2.33	0.04	0.61	3.69	0.47
0.0	600.0	3.91	-1.77	4.52	9.42	2.61
0.0	1100.0	18.61	-1.39	13.90	14.30	4.76
50.0	400.0	4.36	0.92	5.73	4.59	0.69
50.0	600.0	4.62	0.47	6.86	6.29	0.91

TABLE IV (CONTINUED)

Temp. °F	Press. Psia	Absolute Average Deviation %				
		C&S	L&E	R&C	S&H BWR	SRK
50.0	800.0	5.21	-0.43	7.77	7.34	0.61
50.0	1100.0	10.75	-0.85	11.37	7.89	0.02
100.0	200.0	2.80	-0.27	6.08	0.45	-1.72
100.0	400.0	2.72	-0.46	5.74	0.83	-1.96
100.0	800.0	4.61	0.05	6.50	2.72	-2.17
100.0	1100.0	8.12	-0.07	8.01	0.22	-4.08
160.0	400.0	1.02	0.97	5.68	-0.07	-0.78
160.0	600.0	3.30	1.98	4.98	0.48	-0.96
160.0	800.0	5.54	2.84	4.52	-0.30	-1.78
Maximum		82.35	80.30	26.23	83.92	-1250.71
Average		11.17	8.23	8.03	13.14	60.33

TABLE V

DEVIATIONS IN K-VALUE PREDICTIONS FROM EXPERIMENTAL DATA (18) FOR METHANE-N-HEPTANE BINARY SYSTEM

Temp. °F	Press. Psia	Absolute Average Deviation %				
		C&S	L&E	R&C	S&H BWR	SRK
			Methane			
40.0	600.0	8.95	-1.55	2.98	0.86	10.60
40.0	1250.0	5.08	4.53	1.75	-12.30	8.94
100.0	200.0	6.69	-8.19	4.42	-2.73	6.97
100.0	800.0	4.53	-2.96	1.90	-12.70	6.38
100.0	1500.0	1.46	1.90	0.58	-21.46	5.48
160.0	200.0	3.52	-5.66	-1.73	-12.71	4.73
160.0	800.0	3.56	-2.01	-2.88	-18.53	5.63
160.0	1500.0	2.16	1.31	-4.10	-23.79	5.41
220.0	200.0	2.09	0.19		-18.88	5.55
220.0	400.0	2.21	0.05		-20.67	5.60
220.0	1000.0	2.25	0.54		-24.78	5.57
280.0	200.0	1.20	6.47		-21.77	8.60
280.0	400.0	0.61	4.40		-24.58	7.53
280.0	1000.0	1.57	2.53		-26.51	7.02
280.0	2250.0	-1.18	3.63		-62.93	3.33
340.0	200.0	-6.01	6.58		-28.06	8.80
340.0	400.0	-6.54	3.17		-30.97	7.14
340.0	1000.0	-2.35	1.22		-26.95	7.66
340.0	1750.0	-1,32	0.44		-27.78	5.62
400.0	200.0	-2.47	15.15		-14.29	22.04
400.0	400.0	-8.43	5.37		-23.31	14.85
400.0	1000.0	-13.00	-6.68		-19.83	6.95

TABLE V (CONTINUED)

Temp. °F	Press. Psia	Absolute Average Deviation %				
		C&S	L&E	R&C	S&H BWR	SRK
400.0	1500.0	-17.52	-11.68		-7.25	2.82
460.0	400.0	-28.93	-8.87		-6.08	18.06
460.0	600.0	-38.48	-22.14		0.82	10.02
460.0	800.0	-43.99	-30.18		1.58	5.34
Maximum		-43.99	-30.18	4.42	-62.93	22.04
Average		8.31	6.05	2.54	18.93	7.95
			N-Heptane			
40.0	600.0	25.24	38.43	58.80	57.92	43.21
40.0	1250.0	15.84	6.50	57.55	62.52	23.77
100.0	200.0	7.90	21.53	27.80	24.43	19.48
100.0	800.0	13.50	21.80	42.31	45.75	24.66
100.0	1500.0	13.75	3.67	45.73	54.50	13.57
160.0	200.0	0.92	7.61	9.76	9.46	4.73
160.0	800.0	-2.21	6.10	20.09	27.10	5.72
160.0	1500.0	1.66	-0.84	28.27	40.10	2.53
220.0	200.0	0.31	2.33		2.98	-0.73
220.0	400.0	5.77	9.70		15.01	7.09
220.0	1000.0	-4.26	2.30		22.31	0.27
280.0	200.0	4.69	4.40		3.78	1.58
280.0	400.0	-3.54	-1.17		2.25	-4.54
280.0	1000.0	-3.40	2.06		15.76	-1.72
280.0	2250.0	13.52	2.42		24.29	-1.46
340.0	200.0	3.00	2.57		0.81	-0.20

TABLE V (CONTINUED)

Temp. °F	Press. Psia	Absolute Average Deviation %				
		C&S	L&E	R&C	S&H BWR	SRK
340.0	400.0	-0.15	0.93		1.80	-2.53
340.0	1000.0	0.76	3.90		11.61	-1.23
340.0	1750.0	6.42	5.29		15.50	-1.99
400.0	200.0	-3.08	-1.69		-4.52	-4.44
400.0	400.0	-2.16	-1.08		-2.44	-4.81
400.0	1000.0	4.75	4.88		5.85	-1.99
400.0	1500.0	13.02	9.26		5.30	-1.06
460.0	400.0	-2.88	-0.98		-4.60	-4.60
460.0	600.0	1.15	1.31		-4.37	-4.54
460.0	800.0	7.50	5.71		-2.25	-2.32
Maximum		25.24	38.43	58.80	62.52	43.21
Average		6.21	6.48	36.29	17.97	7.11

TABLE VI

DEVIATIONS IN K-VALUE PREDICTIONS FROM EXPERIMENTAL DATA (19) FOR METHANE-N-DECANE BINARY SYSTEM

Temp. °F	Press. Psia	Absolute Average Deviation %				
		C&S	L&E	R&C	S&H BWR	SRK
			Methane			
100.0	40.0	-7.99	-6.60	3.40	-0.55	2.83
100.0	1500.0	1.63	5.55	5.25	-21.56	10.88
160.0	40.0	-9.89	-10.41	-0.42	-20.53	-0.60
160.0	600.0	-2.99	-4.49	1.49	-24.78	4.92
160.0	1500.0	1.20	-0.83	1.42	-33.90	7.54
220.0	40.0	-7.24	-5.67		-30.96	1.05
220.0	200.0	-5.32	-5.05		-31.94	2.38
220.0	800.0	-0.35	-3.89		-36.28	5.23
280.0	40.0	-3.07	2.26		-35.46	5.16
280.0	200.0	-2.08	0.97		-37.34	5.28
280.0	1000.0	3.19	-2.13		-42.90	6.35
400.0	400.0	-1.52	3.34		-50.18	7.26
400.0	1000.0	4.13	-1.85		-57.17	6.69
460.0	100.0	-9.43	7.17		-50.44	9.44
460.0	400.0	-9.09	-2.40		-57.75	4.87
460.0	1000.0	0.24	-6.92		-47.46	5.41
Maximum		-9.89	10.41	5.25	-57.75	10.88
Average		4.33	4.35	2.40	-36.20	5.37
			N-Decane			
100.0	40.0	-13.53	24.09	-0.52	19.06	22.62
100.0	1500.0	19.86	-18.64	-18.44	76.69	-0.89

TABLE VI (CONTINUED)

Temp. ^{o}F	Press. Psia	Absolute Average Deviation %				
		C&S	L&E	R&C	S&H BWR	SRK
160.0	40.0	-7.77	9.85	-10.47	7.37	7.41
160.0	600.0	-11.25	3.18	-12.35	38.93	4.39
160.0	1500.0	8.07	-16.25	-27.73	65.45	-10.95
220.0	40.0	-1.76	3.37		1.68	0.49
220.0	200.0	-0.86	6.57		14.49	4.10
220.0	800.0	-8.97	-1.10		37.54	-2.95
280.0	40.0	2.09	0.98		-0.87	-1.99
280.0	200.0	3.65	5.77		11.45	2.80
280.0	1000.0	-12.91	-6.31		33.06	-11.05
400.0	400.0	-1.18	1.81		8.46	-2.49
400.0	1000.0	-1.60	5.35		22.93	-1.54
460.0	100.0	5.82	5.82		2.35	2.98
460.0	400.0	2.13	4.64		7.23	0.19
460.0	1000.0	0.70	6.25		18.80	-1.83
Maximum		19.86	24.09	-27.73	76.69	22.62
Average		6.38	7.50	13.90	22.90	4.92

TABLE VII

DEVIATIONS IN K-VALUE PREDICTIONS FROM EXPERIMENTAL DATA (12) FOR CARBON DIOXIDE-PROPYLENE BINARY SYSTEM

Temp. °F	Press. Psia	Absolute Average Deviation %			
		C&S	L&E	S&H BWR	SRK
		Carbon Dioxide			
-22.0	50.0	22.97	30.72	-16.59	14.81
-22.0	100.0	-3.30	8.07	-27.97	-1.94
-22.0	150.0	-19.36	-5.35	-12.65	-1.03
5.0	100.0	1.92	1.11	-27.68	-2.72
5.0	150.0	-2.95	-2.30	-21.41	-1.94
5.0	200.0	-10.44	-8.27	-15.32	-2.08
5.0	250.0	-18.19	-14.51	-7.01	-0.85
32.0	150.0	7.28	3.59	-10.73	6.85
32.0	200.0	0.05	-2.32	-13.19	2.48
32.0	300.0	-11.30	-10.66	-10.87	-1.17
32.0	400.0	-18.28	-14.69	-3.23	-0.28
59.0	200.0	2.99	1.01	-6.65	7.90
59.0	300.0	-5.98	-5.09	-10.21	2.08
59.0	450.0	-14.86	-9.52	-7.60	2.45
59.0	600.0	-18.21	-9.10	-1.58	0.09
86.0	300.0	-8.64	-4.80	-9.19	3.71
86.0	450.0	-12.97	-5.24	-8.72	1.28
86.0	600.0	-16.44	-5.14	-5.57	0.51
122.0	400.0	-14.05	-2.49	-5.09	7.32
122.0	500.0	-18.54	-4.92	-8.33	3.11
122.0	600.0	-17.52	-2.60	-5.75	3.65
140.0	450.0	-21.40	-5.75	-6.81	6.31
140.0	600.0	-22.38	-5.01	-6.77	3.82
Maximum		22.97	30.72	-27.97	14.81
Average		12.61	7.05	10.82	3.41

TABLE VII (CONTINUED)

Temp. °F	Press. Psia	Absolute Average Deviation %			
		C&S	L&E	S&H BWR	SRK
		Propylene			
-22.0	50.0	-3.91	-5.35	-4.09	-6.44
-22.0	100.0	6.43	4.62	2.29	2.70
-22.0	150.0	12.08	10.08	-13.07	-2.23
5.0	100.0	0.60	-2.72	-1.77	-3.71
5.0	150.0	5.92	2.50	1.42	1.11
5.0	200.0	12.43	8.98	1.84	4.74
5.0	250.0	15.51	12.11	-12.56	-1.19
32.0	150.0	0.09	-4.10	-2.98	-5.00
32.0	200.0	2.24	-2.00	-1.60	-2.81
32.0	300.0	10.46	6.27	0.45	2.64
32.0	400.0	16.94	12.93	-13.99	-1.72
59.0	200.0	2.29	-1.87	-0.96	-2.90
59.0	300.0	3.39	-0.84	-0.56	-1.68
59.0	450.0	9.67	5.36	-0.82	-3.26
59.0	600.0	15.35	11.05	-14.97	-3.36
86.0	300.0	3.00	-0.60	-0.09	-1.69
86.0	450.0	4.78	0.99	0.80	-0.10
86.0	600.0	7.01	2.90	-1.19	-0.01
122.0	400.0	2.06	-0.12	-0.52	-1.66
122.0	500.0	3.36	0.89	0.65	-0.55
122.0	600.0	2.71	-0.04	-0.35	-1.43
140.0	450.0	2.32	1.10	0.07	-0.68
140.0	600.0	3.11	1.23	0.51	-0.48
Maximum		16.94	12.93	-14.97	-6.44
Average		6.33	4.29	3.37	2.26

TABLE VIII

DEVIATIONS IN K-VALUE PREDICTIONS FROM EXPERIMENTAL DATA (13, 14) FOR METHANE-HYDROGEN SULFIDE BINARY SYSTEM

Temp. °F	Press. Psia	Absolute Average Deviation %				
		C&S	L&E	R&C	S&H BWR	SRK
			Methane			
-120.0	200.0	75.44	12.07	-42.75	76.16	27.79
-120.0	400.0	66.27	-12.06	-64.13	63.37	9.11
-80.0	200.0	74.26	29.40	3.80	71.45	80.06
-80.0	400.0	56.88	-10.75	-38.45	48.69	2.83
-80.0	600.0	55.30	-9.38	-30.28	44.90	5.02
-40.0	200.0	72.94	42.08	28.26	67.81	44.31
-40.0	400.0	49.12	-3.87	-20.43	37.19	2.13
-40.0	600.0	48.50	-1.70	-13.40	35.39	5.64
0.0	200.0	66.69	43.31	33.22	59.35	42.00
0.0	400.0	39.72	0.16	-12.28	25.25	0.41
0.0	600.0	40.31	3.05	-5.60	25.61	5.24
40.0	600.0	31.22	6.18	-1.43	16.77	5.49
40.0	1200.0	18.21	-4.37	-4.92	4.35	1.64
80.0	800.0	16.91	3.09	-1.70	5.63	5.27
80.0	1200.0	8.11	-4.70	-5.88	-0.75	2.75
120.0	600.0	8.09	6.06	-1.08	3.36	10.06
120.0	800.0	20.22	17.18	12.75	16.28	22.48
120.0	1200.0	6.26	2.11	0.39	5.15	13.45
120.0	1200.0	4.34	7.56	4.53	14.99	26.83
Maximum		75.44	43.31	-64.13	76.16	80.06
Average		39.94	11.53	17.12	32.76	16.45

TABLE VIII (CONTINUED)

Temp. °F	Press. Psia	Absolute Average Deviation %				
		C&S	L&E	R&C	S&H BWR	SRK
		Hydrogen Sulfide				
-120.0	200.0	-17.23	-8.44	27.61	21.70	26.07
-120.0	400.0	21.92	25.91	46.98	42.07	46.85
-80.0	200.0	-21.01	-12.94	12.10	11.50	-85.46
-80.0	400.0	-0.24	6.59	20.42	20.03	22.68
-80.0	600.0	-2.65	5.84	13.31	13.50	16.87
-40.0	200.0	-12.04	-8.84	9.69	12.06	12.66
-40.0	400.0	-8.38	-3.62	5.64	8.55	9.19
-40.0	600.0	-13.89	-5.29	-4.91	-0.85	-0.28
0.0	200.0	-16.95	-19.07	0.79	2.92	2.31
0.0	400.0	-6.14	-5.34	3.71	5.97	5.41
0.0	600.0	-4.89	0.28	0.13	2.99	2.25
40.0	600.0	-1.36	1.20	3.41	2.76	1.46
40.0	1200.0	-0.11	22.58	1.75	-2.88	0.77
80.0	800.0	2.81	10.64	6.53	2.11	0.57
80.0	1200.0	2.76	25.52	6.76	3.03	1.01
120.0	600.0	-0.75	-0.13	4.49	-2.04	-2.94
120.0	800.0	0.94	9.30	3.96	-1.87	-3.03
120.0	1200.0	-0.22	24.75	2.55	-1.94	-3.64
160.0	1200.0	0.20	26.73	1.29	-3.15	-4.04
Maximum		21.92	26.73	46.98	42.07	-85.46
Average		7.08	11.74	9.26	8.52	13.03

TABLE IX

DEVIATIONS IN K-VALUE PREDICTIONS FROM EXPERIMENTAL DATA (10) FOR NITROGEN-ETHANE BINARY SYSTEM

Temp. °F	Press. Psia	Absolute Average Deviation %			
		C&S	L&E	S&H BWR	SRK
		Nitrogen			
-240.0	100.0	14.86	2.23	50.83	-5.02
-240.0	200.0	7.59	-1.40	39.63	-7.33
-200.0	100.0	17.72	6.25	41.05	-4.12
-200.0	200.0	13.12	2.80	34.58	-7.39
-200.0	400.0	6.13	-0.56	22.90	-10.03
-200.0	700.0	-7.87	-5.70	3.10	-13.64
-160.0	100.0	13.97	8.23	27.98	59.93
-160.0	200.0	12.39	7.41	24.73	-7.58
-160.0	500.0	6.76	4.85	14.35	-9.53
-160.0	950.0	-4.14	1.27	-1.72	-11.95
-120.0	100.0	9.77	10.59	16.18	-8.01
-120.0	300.0	9.55	11.38	13.42	-6.27
-120.0	700.0	3.02	8.38	3.10	-8.51
-120.0	1200.0	-9.33	4.62	-10.11	-11.08
-80.0	100.0	8.26	14.57	9.56	-3.68
-80.0	300.0	6.35	13.36	5.64	-4.06
-80.0	700.0	-0.94	9.49	-3.48	-7.07
-80.0	1200.0	-13.21	5.45	-13.66	-9.78
-40.0	200.0	-2.21	8.74	-3.67	-5.25
-40.0	500.0	-3.14	9.10	-5.59	-3.23
-40.0	950.0	-11.52	5.86	-11.76	-4.98

TABLE IX (CONTINUED)

Temp. °F	Press. Psia	Absolute Average Deviation %			
		C&S	L&E	S&H BWR	SRK
-40.0	1200.0	-20.59	2.37	-16.24	-7.46
0.0	300.0	-10.84	2.42	-9.25	0.14
0.0	500.0	-13.12	1.19	-11.02	-0.13
0.0	950.0	-24.37	-3.95	-15.37	-3.09
0.0	1200.0	-34.51	-7.52	-15.81	-4.45
40.0	400.0	-35.58	-20.99	-19.25	1.08
40.0	600.0	-31.09	-16.34	-12.84	5.33
40.0	950.0	-47.45	-25.96	-13.08	0.10
Maximum		-47.45	-25.96	50.83	59.93
Average		13.77	7.69	16.20	7.94
Ethane					
-240.0	100.0	76.31	82.17	83.04	83.61
-240.0	200.0	60.68	66.62	72.48	74.10
-200.0	100.0	40.02	49.95	50.05	51.47
-200.0	200.0	32.49	41.52	45.56	47.29
-200.0	400.0	9.76	16.06	32.49	34.43
-200.0	700.0	-1.72	1.69	36.87	36.09
-160.0	100.0	-2.40	6.87	7.50	-77.20
-160.0	200.0	-1.08	7.40	11.56	11.29
-160.0	500.0	-17.79	-9.73	6.65	5.07
-160.0	950.0	-16.93	-7.90	20.94	16.82
-120.0	100.0	-2.78	0.03	1.36	-0.73
-120.0	300.0	-4.06	-0.25	5.57	3.02

TABLE IX (CONTINUED)

Temp. °F	Press. Psia	Absolute Average Deviation %			
		C&S	L&E	S&H BWR	SRK
-120.0	700.0	-13.72	-7.15	7.18	3.31
-120.0	1200.0	-16.04	-6.04	15.14	9.00
-80.0	100.0	7.28	5.45	6.92	3.94
-80.0	300.0	-0.75	-1.01	3.18	-0.18
-80.0	700.0	-5.10	-1.74	7.02	3.06
-80.0	1200.0	-6.35	0.61	12.84	7.87
-40.0	200.0	5.67	2.08	4.12	0.74
-40.0	500.0	0.95	-0.30	3.70	0.20
-40.0	950.0	-2.42	0.11	6.15	2.30
-40.0	1200.0	-0.09	3.82	9.93	5.93
0.0	300.0	3.71	0.23	1.74	-1.33
0.0	500.0	3.48	0.89	2.73	-0.20
0.0	950.0	3.48	3.47	5.44	2.56
0.0	1200.0	3.68	4.76	5.77	2.78
40.0	400.0	2.44	0.94	1.23	-0.77
40.0	600.0	3.30	1.61	1.45	-0.51
40.0	950.0	5.08	4.06	2.28	0.53
Maximum		76.31	82.17	83.04	83.61
Average		12.01	11.53	16.24	16.77

TABLE X

OVERALL K-VALUE DEVIATION COMPARISON OF A TEN-COMPONENT SYSTEM FROM EXPERIMENTAL DATA (25)

Component	Absolute Average Deviation %							
	Without Flash				With Flash			
	C&S	L&E	S&H BWR	SRK	C&S	L&E	S&H BWR	SRK
Methane	5.11	6.54	52.52	4.27	6.68	19.33	75.26	6.11
Ethane	17.61	5.76	13.55	2.94	18.62	9.83	15.93	4.16
Propane	7.73	6.12	10.57	3.04	10.75	15.78	12.42	4.38
N-Pentane	11.71	6.98	22.48	3.73	15.32	45.35	29.30	6.15
N-Heptane	19.80	10.85	37.61	4.40	23.86	107.30	48.62	8.49
N-Decane	46.03	28.10	53.26	17.77	47.96	329.69	76.30	22.08
Toluene	9.15	23.93	26.18	4.52	13.11	217.02	38.93	7.21
Nitrogen	9.11	4806.10	24.46	6.63	11.58	86060.81	36.90	8.15
Carbon Dioxide	20.33	138.54	12.52	7.81	19.68	8127.56	13.98	7.71
Hydrogen Sulfide	11.23	29.55	4.40	4.01	10.03	29.10	4.76	3.90
Computer run time, Minutes:Seconds	0:44	1:04	2:41	1:30	1:19	8:36	25:35	12:21

TABLE XI

OVERALL K-VALUE DEVIATIONS FROM EXPERIMENTAL DATA (11)

Component	No. of Points	Temp. Range		Max. Press. Psia	Absolute Average Deviation %							
					Without Flash				With Flash			
		Min. °F	Max. °F		C&S	L&E	S&H BWR	SRK	C&S	L&E	S&H BWR	SRK
Methane	663	-240.0	460.0	2250.0	14.84	9.56	15.26	9.35	15.67	12.71	18.31	10.94
Ethane	424	-240.0	482.0	1822.0	11.92	7.99	11.22	10.60	12.36	8.33	12.23	9.32
Propane	272	-200.0	400.0	1822.0	8.70	6.54	8.83	14.39	9.15	7.51	10.31	8.75
I-Butane	26	-20.0	218.0	1000.0	6.23	4.07	5.38	4.52	6.93	4.73	7.02	5.09
N-Butane	487	-140.0	460.0	2000.0	11.77	11.22	12.85	13.06	12.78	12.88	14.60	12.52
I-Pentane	38	32.0	338.0	1000.0	3.37	4.35	4.97	3.63	3.35	4.70	6.40	3.85
N-Pentane	199	-20.0	439.0	1965.0	8.93	6.27	9.67	11.61	10.58	8.44	13.27	8.99
N-Hexane	38	77.0	464.0	1822.0	11.40	9.58	15.11	9.94	12.49	12.14	18.46	10.74
N-Heptane	132	40.0	460.0	2250.0	11.34	12.01	17.83	14.17	13.00	14.51	18.49	12.91
N-Octane	35	77.0	302.0	1029.0	36.29	28.05	6.65	26.19	37.78	29.70	6.92	27.75
N-Nonane	5	212.0	302.0	1422.0	35.23	32.47	37.47	35.22	38.01	35.86	41.67	38.65
N-Decane	317	40.0	460.0	2500.0	20.34	17.68	24.98	25.96	21.62	20.20	26.77	25.63
Ethylene	87	-155.0	450.0	1000.0	15.55	11.10	10.76	11.28	15.41	11.21	11.47	12.26
Propylene	62	-22.0	218.0	600.0	5.71	3.91	3.85	3.80	5.75	3.96	3.55	3.74
I-Butene	3	130.0	162.0	300.0	7.51	2.91	4.30	2.89	7.53	2.94	4.30	2.95
Cyclopentane	3	150.0	150.0	800.0	4.85	4.17	3.69	6.08	5.19	4.70	4.33	6.47

TABLE XI (CONTINUED)

Component	No. of Points	Temp. Range		Max. Press. Psia	Absolute Average Deviation %							
					Without Flash				With Flash			
		Min. °F	Max. °F		C&S	L&E	S&H BWR	SRK	C&S	L&E	S&H BWR	SRK
Methylcyclopentane	3	129.8	216.0	14.7	4.44	7.64	8.89	5.31	4.82	7.78	8.91	5.38
Cyclohexane	83	50.0	500.0	1422.0	17.15	16.62	14.41	24.84	19.02	19.58	16.36	17.27
Methylcyclohexane	10	105.8	202.0	800.0	4.55	6.71	9.40	5.86	4.45	6.36	9.62	5.97
Benzene	89	100.0	482.0	3707.0	33.27	28.77	36.32	26.59	37.36	32.89	35.31	28.75
Toluene	44	32.0	464.0	1422.0	40.57	37.33	39.39	64.31	42.81	39.70	40.50	41.06
M-Xylene	4	248.0	320.0	60.4	25.06	25.90	23.37	22.78	25.07	25.71	23.40	22.84
Ethyl Benzene	2	242.1	265.1	14.7	1.12	9.06	2.27	0.34	1.33	8.38	2.47	0.48
Nitrogen	124	-240.0	392.0	3707.0	28.16	93.54	74.76	15.20	30.10	119.92	73.94	16.35
Carbon Monoxide	19	-7.0	150.0	913.8	19.55	218.66	29.25	23.56	21.46	280.63	28.58	28.51
Carbon Dioxide	208	-65.0	500.0	2500.0	19.35	23.66	15.79	13.68	20.12	26.31	19.89	17.37
Hydrogen Sulfide	133	-120.0	340.0	1200.0	8.34	9.70	9.41	9.05	8.78	10.24	10.68	8.17
Total Points	3510											

using Chevron Research Corporation data (11). This data consists of binary and several three-, four-, and five-component systems.

Several groups of K-value deviations are compared. Two separate sections are included in Tables X and XI. One section is without flash convergence procedure and the other includes a flash convergence procedure. K-value results "without flash" represent a simplified evaluation approach. The "with flash" K-value results illustrate typical industrial practice. Tables IV through IX give comparisons on a "without flash" basis. Tables VII and IX do not include the Robinson-Chao method, since no binary liquid phase interaction constants were given for carbon dioxide-propylene and nitrogen-ethane. This method was also not compared in Tables X and XI, since the data of these systems were evaluated for temperatures and pressures beyond the expected Robinson-Chao limits of correlation.

Some of the following systems show considerable error in K-value predictions for the heavy components. This large error may be due in part to experimental difficulties in measuring very small compositions of the heavy components in the vapor phase. For example, in the binary system methane-n-decane, the heavy component, n-decane, exists in very small amounts in the vapor phase (0.001 to 0.003 mole fraction) from 100°F to 160°F. The light component, methane, is nearly all in the vapor phase (0.997 to 0.999 mole fraction). A 0.003 mole fraction measurement error will only cause a 0.3% deviation in the reported methane K-value. However, this same measurement uncertainty will cause at least a 100% deviation in the reported n-decane K-value.

From these tabulated results several observations may be made. In Table IV there are some irregularities in deviations by the Soave method. These are spotted at -100°F, 100 psia; at 50°F, 400 psia; at 100°F, 200 psia; at 160°F, 400 psia for methane and at -100°F, 100 psia for propane. In Table VIII three unusual deviations by the Soave method occur for methane at -120°F, 200 psia; at -80°F, 200 psia; and at -40°F, 200 psia. For this comparison without flash the Soave method has been observed to give occasional poor solutions to liquid phase compressibility factor which leads to poor liquid fugacity values and subsequent large K-value deviations. When running this method through a flash procedure this problem seems to disappear. For points like these the K-value errors were still large, but the errors were smaller than the "without flash" values.

Computation time for flash of the ten-component system (Table X) exceeded 25 minutes in the case of the Starling and Han BWR method. The Chao-Seader method took the least time: 1 minute, 19 seconds. This yields a time ratio of 19 to 1 using the Chao-Seader method as a basis. Similarly the solution time ratios for the Soave RK and Lee-Edmister methods are about 9 to 1 and 7 to 1, respectively. A major portion of the additional time consumed in these other methods is due to many exponential calculations required to develop the constants for each component and iterative calculations associated with the solution of the equation of state. A ratio of about 8 to 1 of Starling and Han BWR to Chao-Seader method run time was determined from Chevron Research Corporation data (11) evaluations. The Soave RK and Lee-Edmister methods gave ratios of about 6 to 1 and 5 to 1, respectively. It appears then that as the number of components in a system increases, the run time ratio increases substantially for the Starling and Han BWR method. The time ratio has been found to increase moderately with component number for the other methods compared to the Chao-Seader.

When using the K-value prediction methods based solely on equations of state--the Starling and Han BWR and the Soave RK methods--additional convergence problems in the flash calculations were encountered. These problems were apparently caused by oscillations in the vapor and liquid phase compositions from one iteration to the next. Once these oscillations started, they would either close to equal compositions for both phases (corresponding to the critical point) or diverge to totally unrealistic compositions in the phases. To eliminate these problems, a damping factor approach was used. In this approach, a weighted average of the calculated phase composition and the previously calculated phase composition were used as the next estimate of the phase composition. Stated mathematically, this is:

$$x_{new} = \beta x_{calculated} + (1 - \beta) x_{old}$$

This procedure eliminated all of the problems with composition oscillation or closure of the two phase compositions to the appropriate values. Typically, values of 0.5 to 0.7 were assigned to β. No significant differences in the required computer time or number of iterations required for a solution were found.

From Table IV the Lee-Edmister, Robinson-Chao, and Starling and Han BWR methods predict good K-values for methane-propane system (agreement of average deviations within 7%). From Tables V and VI the Chao-Seader, Lee-Edmister, and Soave methods predict good K-values for methane-n-heptane and methane-n-decane systems (agreement of average deviations within 3%). Tables VII through IX indicate that the Lee-

Edmister and Soave methods predict equally well the vapor-liquid equilibria for non-hydrocarbon-hydrocarbon systems (agreement of average deviations within 6%). The Lee-Edmister and Soave methods give essentially the same level of error for all of the hydrocarbon systems contained in the Chevron Research data (11). Based on the results presented in Tables X and XI the Soave method appears to be the best prediction method for multi-component vapor-liquid equilibrium data.

Of all methods tested on this variety of vapor-liquid equilibrium data, the Soave method predicts overall the best K-values within the temperature range of -240°F to 500°F and pressures up to 3700 psia. Some preliminary tests have been made on enthalpy departure predictions of pure components and binary mixtures using the Soave method (22). This method compared equally well with proprietary methods for low temperature data (11). The proprietary methods have been specially fitted to this data. Unlike the other recent methods (15, 20, 23), the Soave method requires no interaction parameters for paraffinic, aromatic, and naphthenic systems. Binary interaction parameters are used for nitrogen, carbon dioxide, and hydrogen sulfide in paraffinic, aromatic, and naphthenic systems. These parameters appear to be independent of the hydrocarbon component. This property of the interaction parameters poses a tremendous advantage when considering industrial mixtures that contain C_7^+ or any unidentifiable compounds.

The results presented in this chapter and the preceding chapter tend to confirm the earlier comments about the difficulty of predicting the partial molal thermodynamic properties of mixtures. The errors in the predicted K-values are qualitatively larger than the errors observed for the entropy departure and vapor pressure predictions. Similar comments could be made for the enthalpy departure predictions. Lee, Erbar, and Edmister (15) report an absolute average deviation of about 2.0 Btu/lb for enthalpy departure predictions for approximately 1500 data points. This level of error would yield an absolute average error of about 3.0%. This value is close to the errors of 4.0% for vapor pressures and 2.0% for entropy departures. However, the "average error" in the K-value predictions for all components is about 13%-20%. While part of the difference in the level of error is due to inherent experimental measurement errors, not all of the differences in error can be attributed to this problem. This remaining difference simply represents the inability of the prediction methods to completely and accurately describe the partial molal thermodynamic properties of mixtures of relatively complex molecules like the light paraffin molecules. Until this understanding is developed, errors on the level reported here must be accepted.

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

The purpose of this study was to test the ability of the Chao-Seader, Lee-Edmister, Robinson-Chao, Starling and Han BWR, and Soave methods to predict some thermodynamic properties of hydrocarbon and selected non-hydrocarbon systems. The major conclusions are presented along with each of the three main objectives.

The first objective was to test the ability of the Chao-Seader, Lee-Edmister, and Soave methods to predict vapor pressure data. The deviation comparison of calculated and experimental vapor pressures of the paraffins methane through n-decane showed that the Soave method gave the best results.

The second objective was to investigate the predictive ability of the Chao-Seader and Lee-Edmister methods on entropy departure values of pure component data and mixture data. The Lee-Edmister method gave the better estimates of entropy departures for both the pure components, methane through n-pentane, and the 5% propane in 95% methane mixture.

The third and final objective was to investigate the ability of the Chao-Seader, Lee-Edmister, Robinson-Chao, Starling and Han BWR, and Soave methods to predict binary and multicomponent mixture K-values of hydrocarbons and non-hydrocarbons. Binary and ternary mixture K-value data were predicted about equally well by the Lee-Edmister and Soave methods. The Chao-Seader, Lee-Edmister, Starling and Han BWR, and Soave methods were tested on multicomponent mixtures. These mixtures included systems of non-hydrocarbons as well as hydrocarbons. The Soave method gave the best overall predictions of multicomponent vapor-liquid equilibrium data.

Recommendations

Some recommendations for future studies for these prediction methods have arisen from this investigation:

1. Test the Soave prediction method on enthalpy and entropy departure data to determine how it compares to the ability of the Lee-Edmister method.
2. Investigate each prediction method for liquid mole fraction deviations (flash calculation basis only) on a data point-to-data point basis. For each system determine where present interaction parameters can be adjusted so that K-value accuracy can be improved.
3. Improve the ability of the Soave method to better represent experimental liquid volume data. (One or two tests indicate that about 9% error exists.) This objective can probably be achieved by adjusting the "a" constant using the Chueh and Prausnitz approach (8) or through multiproperty curve-fit procedures.

4. Attempt to improve the speed of computation of the Starling and Han BWR and Soave procedures. In this current form, the methods probably consume too much time to be useful in broad scale applications to process simulation systems and tray-by-tray calculations.

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APPENDIX A

METHODS FOR CALCULATING VAPOR PRESSURE, ENTROPY DEPARTURES, AND EQUILIBRIUM RATIOS

Vapor Pressure

The criteria for phase equilibrium in vapor pressure calculations is:

$$T^L = T^V$$

$$P^L = P^V$$

$$\phi^L = \phi^V$$

The bubble point method is used for vapor pressure calculation procedure. These equations must be satisfied for final convergence.

$$y_i = K_i/x_i \tag{A-1}$$

or

$$1 - \sum_{i=1}^{n} K_i x_i = 0.0 \pm \varepsilon \tag{A-2}$$

where $\varepsilon = 0.00005$, the tolerance in the computer program. Outline of the computation procedure is as follows:

Temperature is known.

1. Assume a saturation or bubble point pressure, P_s.
2. Calculate K-values from liquid and vapor fugacity coefficients.
3. Is K = 1?

4. If not, adjust P_s, and repeat steps 1 through 3.
5. If so, solution is correct.

Entropy Departures

The entropy equation used in this study is a derived thermodynamic expression in terms of fugacity, enthalpy difference, and pressure:

$$S - S^o = -R \sum_{i=1}^{n} x_i \ln \phi_i + \frac{H - H^o}{T} - R \ln\left(\frac{P}{P_{ref}}\right) - R \sum_{i=1}^{n} x_i \ln x_i \qquad \text{(A-3)}$$

where $H - H^o$ = enthalpy difference derived from calorimetric data. Liquid or vapor phase entropy departures of pure components or mixtures are calculated by using the Chao-Seader or Lee-Edmister method to first find ϕ_i. Then ϕ_i along with all the other known quantities are directly substituted into equation (A-3).

Equilibrium Ratios

Phase equilibria requirements for calculating K-values are the same as in the determination of vapor pressures. For the Chao-Seader, Lee-Edmister, and Robinson-Chao methods, the K-value is made up of three empirical terms:

$$K_i = \frac{\nu_i^L \gamma_i^L}{\phi_i^V} \qquad \text{(A-4)}$$

For the Starling and Han BWR and Soave methods, the K-value consists of two terms:

$$K_i = \frac{\phi_i^L}{\phi_i^V} \qquad \text{(A-5)}$$

Prediction of K-values of mixtures was accomplished by two independent procedures. The first procedure is without a flash calculation. Vapor-liquid equilibrium data was substituted into the calculation of mixture parameters. Direct computation of K-values was then possible. This is a simplified computational approach. The second procedure is with a flash calculation. Simultaneous solution of material balance and K-value equations for each component in the mixture under study is performed. In the Starling and Han BWR and Soave methods a damping technique is used to estimate new compositions for each iteration:

$$x_{i,new} = \beta x_{i,old} + (1 - \beta) x_{i,calc.} \tag{A-6}$$

$$y_{i,new} = \beta y_{i,old} + (1 - \beta) y_{i,calc.} \tag{A-7}$$

where x_i and y_i = liquid and vapor mole fractions of "ith" component in mixture, and β = damping factor for $0.0 \leq \beta \leq 1.0$. Convergence is reached when calculated K-values agree with the restraints that both liquid and vapor mole fractions sum to unity. This procedure is the industrial approach.

The basic flash calculational procedure for each component in a vapor-liquid mixture is outlined below:

Given: T, P of system.

1. Assume K_i.
2. Calculate x_i, y_i.
3. Calculate mixture parameters.
4. Calculate V^V and V^L (liquid volumes for Starling and Han BWR and Soave methods only).

5. Calculate K_i from the determination of the appropriate coefficients (ϕ_i, ν_i, γ_i in the Chao-Seader, Lee-Edmister, and Robinson-Chao methods and ϕ_i^V and ϕ_i^L in the Starling and Han BWR and Soave methods).
6. Is $K_{i,\text{calculated}}$ equal to $K_{i,\text{assumed}}$?
7. If not, assume a new value of K_i equal to the K_i value just calculated and repeat steps 2 through 6.
8. If so, the calculated results are correct.

APPENDIX B

NOMENCLATURE

Major Symbols

English Letters

a = BWR parameter, equation (2-46), $(\text{liters/gm-mole})^3$ atm

Lee-Edmister parameter, equation (2-13), $(\text{liters/gm-mole})^2$ atm

RK parameter, equation (B-3), $(\text{liters/gm-mole})^2$ atm $(^\circ K)^{0.5}$

A_o = BWR parameter, equation (2-42), $(\text{liters/gm-mole})^2$ atm

b = BWR parameter, equation (2-45), $(\text{liters/gm-mole})^2$

Lee-Edmister parameter, equation (2-14), liters/gm-mole

RK parameter, equation (2-3), $(\text{liters/gm-mole})^2$

B_o = BWR parameter, equation (2-41), liters/gm-mole

c = BWR parameter, equation (2-48), $(\text{liters/gm-mole})^3$ atm $(^\circ K)^2$

Lee-Edmister parameter, equation (2-15), $(\text{liters/gm-mole})^2$ atm

C_o = BWR parameter, equation (2-43), $(\text{liters/gm-mole})^2$ atm $(^\circ K)^2$

d = Starling and Han BWR parameter, equation (2-50), $(\text{liters/gm-mole})^3$ atm $^\circ K$

D_o = Starling and Han BWR parameter, equation (2-49), $(\text{liters/gm-mole})^2$ atm $(^\circ K)^3$

E_o = Starling and Han BWR parameter, equation (2-51), $(\text{liters/gm-mole})^2$ atm $(^\circ K)^4$

f = Fugacity, atm

H = Enthalpy, Btu/lb-mole

K = Robinson-Chao interaction parameter, equation (2-34)

Starling and Han BWR interaction parameter, equation (2-42)

Equilibrium ratio, elsewhere

P = Pressure, atm

R = Gas constant, Btu/lb-mole-^{o}R, equation (A-3)

Gas constant, (liters/gm-mole) atm/^{o}K, elsewhere

S = Entropy, Btu/lb-mole-^{o}R

T = Temperature, ^{o}R, equation (A-3)

Temperature, ^{o}K, elsewhere

V = Volume, liters/gm-mole

x = Liquid mole fraction

y = Vapor mole fraction

Z = Compressibility factor

Greek Letters

α = BWR parameter, equation (2-47), (liters/gm-mole)^{3}

Lee-Edmister coefficient, equation (2-17)

Soave coefficient, equation (2-53)

β = Damping factor, equation (A-6)

Lee-Edmister parameter, equation (2-16)

δ = Solubility parameter, equation (2-9), (atm)$^{0.5}$

γ = Activity coefficient, $f^{L}/F^{oL}x$

BWR parameter, equation (2-44), (liters/gm-mole)^{2}

ε = Tolerance limit

ϕ = Fugacity coefficient, $\tilde{f}/Py$

ν = Fugacity coefficient, f^{L}/P

Σ = Summation

ω = Acentric factor

Ω = Chueh and Prausnitz parameter, equation (2-28)

Φ = Volume fraction

Subscripts

a = Robinson-Chao parameter index, equation (2-28)

b = Robinson-Chao parameter index, equation (2-29)

c = Critical state

i = Component number

j = Component number

k = Component number

m = Mixture property

r = Reduced property

s = Saturated property

Superscripts

L = Liquid state

m_1 = Lee-Edmister constant

m_2 = Lee-Edmister constant

– = Average

' = Prime

∿ = Partial molar property

o = Standard reference state

(o) = Liquid fugacity coefficient reference state

(1) = Liquid fugacity coefficient reference state

V = Vapor state

Abbreviations

calc. = Calculated

ref = Reference state

BWR = Benedict-Webb-Rubin

C&S = Chao and Seader

L&E = Lee and Edmister

R&C = Robinson and Chao

RK = Redlich-Kwong

S&H BWR = Starling and Han Benedict-Webb-Rubin

SRK = Soave Redlich-Kwong

VITA

Edward Wendell West

Candidate for the Degree of

Master of Science

Thesis: PREDICTION OF SOME THERMODYNAMIC PROPERTIES OF PETROLEUM RELATED HYDROCARBONS AND SELECTED NON-HYDROCARBONS

Major Field: Chemical Engineering

Biographical:

Personal Data: Born in Greensboro, North Carolina, April 3, 1945, the son of Mr. and Mrs. Edward B. West.

Education: Attended elementary and junior high school in Racine, Wisconsin; graduated from Washington Park High School, Racine, Wisconsin, in 1963; received the Bachelor of Science degree from University of Wisconsin in January, 1968, with a major in Chemical Engineering; completed requirements for the Master of Science degree in May, 1973.

Professional Experience: Previously employed as a Process Engineer by Continental Oil Company.