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Authors

Dohrn, R.

Kunstler, W.

Prausnitz, John M.

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Correlation of High-Pressure Phase Equilibria in the Retrograde Region with Three Common Equations of State

Ralf Dohrn^{*)}, Wolfgang Knstler^{**)} and John M. Prausnitz

Chemical Engineering Department, University of California, Berkeley, CA 94720, USA
and Materials and Chemical Sciences Division, Lawrence Berkeley Laboratory,
1 Cyclotron Road, Berkeley, CA 94720, USA

Abstract

Phase equilibria in the retrograde regions were calculated for the methane - n-decane binary system and for a realistic natural-gas system (methane - Kensol-16). Calculations were performed using three equations of state: Peng-Robinson, Redlich-Kwong-Soave and Perturbed-Hard-Chain; calculations were compared to experiment. Liquid drop-out curves and pressure-temperature diagrams were calculated between 301 and 369 K and pressures to 90 MPa. The binary system was represented best by the Peng-Robinson EOS. For the natural-gas system, the Perturbed-Hard-Chain equation yielded the best results, although all equations of state showed appreciable deviations. Good results could only be obtained when binary coefficients were fitted to the experimental retrograde data.

Keywords: retrograde region, phase equilibria, equation of state, natural gas

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^{*)} Present Address: Arbeitsbereich Verfahrenstechnik II, Technische Universitt Hamburg-Harburg, Eißendorfer Str. 38, D-2100 Hamburg 90, West Germany

^{**)} Present Address: Schwimmbadstr. 37, 6919 Bammental, West Germany

1. Introduction

In gas-condensate systems at reservoir, process or transport conditions, retrograde condensation is often observed: at a fixed temperature, a pressure reduction causes a homogeneous gas mixture to separate into a vapor and a liquid phase. Quantitative description of retrograde behavior is required for rational process design in petroleum and natural-gas engineering.

Retrograde condensation was known in the 19th century (e.g. Kuenen, 1893 and Duhem, 1896) but a quantitative description is difficult because it requires a reliable equation of state (Redlich and Kister, 1962). Although experimental high-pressure K-factor data are available for many binary systems, multicomponent phase-equilibrium and density data are scarce.

For a variety of typical engineering applications, high-pressure phase equilibria of hydrocarbon mixtures can be calculated with sufficient precision using well-known equations of state. However, unreliable calculated results are often obtained in the retrograde dew-point region, that is, at temperatures higher than the critical temperature but below the critical condensation temperature of the mixture. Calculated phase equilibria in the retrograde region are particularly sensitive to the calculated critical temperature. If the calculated critical temperature is inaccurate, calculated gas-condensate equilibria can be qualitatively wrong by predicting a bubble point instead of a dew point (Chou and Prausnitz, 1988 and Robinson, 1989). Close to the dew-point locus, the liquid drop-out (volume percent of liquid condensed) falls dramatically with rising pressure. Even when the calculated critical temperature is accurate, correct description of the liquid drop-out is difficult because it is sensitive to details in the equation of state, especially to the binary parameter(s) in that equation.

This work compares calculated and observed liquid drop-out curves for a binary and a multicomponent system. Calculations were performed with three equations of state. Calculated results from two of the most commonly used equations (Peng-Robinson, 1976 and Redlich-Kwong-Soave, 1972) are compared with those from a recent (cubic) version of the Perturbed-Hard-Chain equation (Sako, Wu and Prausnitz, 1989).

2. Experimental Data

Experimental data were used for two different mixtures: a well-defined binary mixture and a complex mixture, containing many components. The binary system contains 97 mol% methane and 3 mol% n-decane. Experimental densities and compositions of the coexisting phases were taken from Reamer (Reamer et al., 1942).

The multicomponent mixture contains 94.365 mol% methane and 5.635 mol% Kensol-16. The latter is a heavy oil fraction with a boiling-point range from 570 to 582 K. Phase compositions and densities of the mixture were measured by Rzasa (Rzasa, 1947). Table 1 gives some properties of the Kensol-16 mixture. The data were smoothed by the experimentalist. Rzasa reports an accuracy of 1.5 % for the dew-point pressure, with maximum deviations reaching 4.2 %.

We used the pseudocomponent method to describe the heavy oil fraction Kensol-16. Two normal alkanes, n-octadecane and n-eicosane, were selected as pseudocomponents to represent the paraffinic components of the mixture. The aromatic influence is represented by 1-pentylnaphthalene and the naphthenic influence by bicyclohexane. The residue of 2 volume percent in the Kensol-16 mixture is represented by n-tetracosane. The composition of the pseudocomponent system was determined by fitting density, molecular weight and boiling point, with the help of a density correlation (4-5.1) and a correlation for vapor pressures of pure

components published by the American Petroleum Institute (API, 1984). To calculate the normal boiling point, Raoult's law was used. Table 1 compares the properties of the Kensol-16 mixture with those of the pseudocomponent mixture and gives the composition of the methane - Kensol-16 system.

3. Calculation of Vapor-Liquid Equilibria and Densities

For engineering applications in the retrograde region, it is useful to calculate the liquid drop-out, i.e. the volume of the condensed liquid phase divided by the total volume, at a fixed temperature and pressure. To calculate liquid drop-outs, the compositions and densities of the coexisting phases have to be determined. The equilibrium conditions are:

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

$$P^L = P^V \quad (2)$$

$$f_i^L = f_i^V \quad (\text{all } i) \quad (3)$$

where T is the temperature, P the pressure and f_i the fugacity of component i ; superscript L designates the liquid phase, and superscript V designates the vapor phase. The fugacity of component i is related to mole fraction ξ_i through the fugacity coefficient ϕ_i

$$f_i = \xi_i \phi_i P \quad (4)$$

Following Topliss (Topliss, 1985), the fugacity coefficient is found from

$$\ln \phi_i = \frac{\partial}{\partial n_i} \left(\int_0^P \frac{Z-1}{\rho} d\rho \right)_{\rho, T, n_{k \neq i}} - \ln(Z) + Z - 1 \quad (5)$$

where compressibility factor $Z=Pv/RT$ and density $\rho=1/v$.

For convenience, the derivative in Equation (5) can be rewritten as summarized in Appendix A. From Equation (3), the K-factor can be calculated:

$$K_i = \frac{y_i}{x_i} = \frac{\phi_i^L}{\phi_i^V} \quad (i = 1, N) \quad (6)$$

where x is the mole fraction in the liquid phase, y is the mole fraction in the vapor phase and N is the total number of components.

We consider an isothermal flash calculation, where F moles of feed separate into L moles of liquid and V moles of vapor. Mole fraction z refers to the feed. With the material balance

$$z_i = x_i \frac{L}{F} + y_i \left(1 - \frac{L}{F}\right) \quad (i = 1, N) \quad (7)$$

and constraints on composition for equilibrium phases

$$\sum_i^N x_i = \sum_i^N y_i = 1 \quad (i = 1, N), \quad (8)$$

a useful objective function λ is

$$\lambda(L/F) = \sum_i^N \frac{\frac{z_i}{K_i}}{1 + L/F \left(\frac{1}{K_i} - 1\right)} = 0 \quad (9)$$

Equations (6) and (9) are solved iteratively. The fractional liquid drop-out χ can be calculated from saturated vapor and liquid densities, ρ^V and ρ^L :

$$\chi = \frac{\frac{L}{F}}{\frac{L}{F} + \left(1 - \frac{L}{F}\right) \rho^L / \rho^V} \quad (10)$$

Since L/F is determined in Equation (9) by varying the K -factor, the liquid drop-out χ is influenced by the ability of an equation of state to calculate reliable K -factors and saturated densities.

The Perturbed-Hard-Chain (PHC) equation is applicable to small and long-chain molecules; it takes density-dependent rotations and vibrations of the molecules into account by the use of an additional parameter c (for methane, $c=1$). We use here a recent simple version of the PHC equation (Sako et al., 1989) which reduces to a form similar to the Redlich-Kwong-Soave equation of state when $c=1$. Pure-component parameters for the PHC equation and some physical constants are shown in Table B1 in Appendix B. Table 2 shows the three equations of state used in our study.

To calculate parameters a_M , b_M and c_M for mixtures, conventional mixing rules were used:

$$a_M = \sum_i^N \sum_j^N \xi_i \xi_j a_{ij} \quad a_{ij} = \sqrt{a_{ii} a_{jj}} (1 - k_{ij}) \quad (11)$$

$$b_M = \sum_i^N \xi_i b_i \quad (12)$$

$$c_M = \sum_i^N \xi_i c_i \quad (13)$$

where k_{ij} is a binary interaction parameter.

Phase-equilibrium calculations were performed with a flash program developed at the Technische Universität Hamburg-Harburg (Dohrn and Brunner, 1989). A density-finding routine, developed at the University of California, Berkeley, was integrated into the main program (Topliss, 1985). Critical properties of mixtures were calculated with a subroutine, written by Heidemann (Heidemann and Khalil, 1980).

4. Results

4.1 Binary System

For the binary system methane - n-decane, phase compositions, saturated densities and liquid drop-outs were calculated at temperatures between 310.93 and 377.59 K. For each temperature, the binary interaction parameter k_{12} was fitted only to phase compositions (not to densities) using the following objective function:

$$\Delta\xi = \sqrt{\frac{1}{2r} \left(\sum_{j=1}^r (x_j^{\text{exp}} - x_j^{\text{calc}})^2 + \sum_{i=1}^r (y_i^{\text{exp}} - y_i^{\text{calc}})^2 \right)} \quad (14)$$

The total composition range of the dew-point curve and the boiling-point curve was used for the fitting process, except for the critical region; pressures $> 0.9 P_{\text{cM}}$ were excluded.

Figure 1 shows experimental and calculated liquid drop-outs at 344.26 K. The interaction parameters of the different equations of state are nearly the same. The chain-dotted curve indicates the influence of the binary interaction parameter on the results from the Peng-Robinson equation. When k_{12} is raised by 30 % (compared to the optimum value, dashed curve), the falling part of the liquid-drop-out curve is shifted to higher pressures, while the rising part of the curve remains nearly unchanged.

For the rising part of the liquid-drop-out curve, the PHC equation gives the best results. The Peng-Robinson equation is second best, while the RKS equation shows the largest deviations. The falling part of the curve (after the maximum) is best represented by the Peng-Robinson equation. Although the PHC equation yields good

densities, the calculated upper dew-point curve is too high because of deviations in phase composition.

4.2 Multicomponent System

Liquid drop-out curves were calculated for the methane - Kensol-16 mixture between 301 and 369 K. The entire pressure range from atmospheric pressure to the upper dew point (90 MPa) was included. Binary interaction parameters were fitted for each equation of state to the liquid drop-out curves. Some simplifying assumptions were made: all alkanes were assigned identical interaction parameters with the other components and some interaction parameters were set to zero. This simplification leads to a reduction of 15 binary parameters to 5 (Appendix D).

The literature gives interaction parameters for only some of the binary subsystems (e.g. Legret et al., 1984). We correlated these interaction parameters and used them for the multicomponent system, obtaining only fair results. The description of the multicomponent experimental data was significantly better when fitted binary interaction parameters were used.

The k_{ij} s were assumed to vary linearly with temperature. Since Rzasas's experimental data cover a temperature range of less than 70 K, a more complicated dependence was not justified. During the initial fitting process, the Peng-Robinson equation yielded subcritical behavior for a medium temperature, but supercritical behavior for both higher and lower temperatures contrary to experiment. Therefore, the coefficients of the temperature dependence were readjusted. Appendix D gives details on the temperature dependence for all k_{ij} . Table D6 demonstrates the influence of the binary interaction parameters on the shape of the liquid drop-out curve.

Figures 2 and 3 show the liquid drop-out as a function of pressure for two temperatures. To facilitate comparisons, the experimental points and the curves from all equations of state are plotted on one diagram. At low and medium pressures the Perturbed-Hard-Chain equation shows the best results. But, as in the binary system, the PHC equation overpredicts the upper dew point. The Peng-Robinson equation and the Redlich-Kwong-Soave equation describe the liquid drop-out curves with comparable accuracy. The Peng-Robinson EOS is better at lower and medium temperatures, while the RKS equation is better at high temperatures.

Figures 4 to 6 show pressure-temperature diagrams for the methane - Kensol-16 mixture. Each figure compares the experimental data of Rzasa with calculations from one of the equations of state. The symbols represent different experimental liquid drop-outs, while the lines were calculated with a constant liquid drop-out, according to the numbers indicated.

Results from the Perturbed-Hard-Chain equation are shown in Figure 4. At low and medium pressures, the deviations between experiment and calculation are small. The slope of the drop-out curves is much better represented by the PHC equation than by the other equations of state (Fig. 4 - 6). The high-pressure region is not well described by any of the equations, since in this region, close to the maximum of the curve, small variations in the liquid drop-out can drastically change the calculated pressure.

In a pressure-temperature diagram, the distance between two liquid drop-out curves becomes smaller when the temperature approaches the critical temperature of the mixture. All liquid drop-out curves intersect at the mixture critical point. In a retrograde region, the upper half (with respect to pressure) of the liquid-drop-out

curves converge, when the temperature is reduced. Calculated drop-out curves should show the same behavior.

As indicated in Figure 5, the Peng-Robinson equation shows larger deviations at low pressures but describes the upper dew-point region well. Unfortunately, the drop-out curves do not converge to the critical point, indicating that the linear temperature dependence of the binary interaction parameters is not adequate. Figure 6 indicates that the Redlich-Kwong-Soave equation yields increasing deviations at low and medium pressures and a fair description at high pressures. Deviations decrease with rising temperature.

At the May 1989 meeting of thermodynamicists in Banff, Canada, Robinson reported unexpected behavior when he measured phase equilibria in the retrograde region for a gas-condensate system with heavy components; he found that the liquid drop-out curve does not fall steeply as it approaches the upper dew point. Instead, after going through a point of inflection, it curves to higher pressures (Robinson, 1989). For a particular set of binary interaction parameters, similar behavior was calculated with the RKS equation, as shown in Figure 7.

In addition to the original RKS equation, a volume translation for this equation of state, proposed by Chou and Prausnitz (Chou and Prausnitz, 1989), was used to correlate drop-out curves for the methane - Kensol-16 system. The unknown true critical volumes of the mixture, which are important input data for the volume translation, were estimated using an empirical method (Appendix C). Overall, this volume-translation method did not bring significant improvements over the original Redlich-Kwong-Soave equation.

5. Conclusions

Phase equilibria in the retrograde region of gas-condensate systems can be fitted reasonably well with equations of state. For the binary system methane - n-decane, the Peng-Robinson equation gave the best description of the experimental data. For the multicomponent system methane - Kensol-16, liquid drop-out curves can be calculated with small deviations, provided that binary interaction parameters k_{ij} are fitted to experimental multicomponent data. At low and medium pressures, the Perturbed-Hard-Chain equation showed the best results. In the retrograde dew-point region, the fitting performance of all equations was only partly satisfactory. Predictions using binary data only were not successful.

The results of this study show once again that currently available knowledge is not sufficient for calculating multicomponent phase equilibria in the retrograde region unless multicomponent data in that region are used to determine adjustable binary constants. To attain that knowledge, it will be necessary, first, to obtain reliable high-pressure experimental data for well-characterized multicomponent systems and second, to establish a better equation of state applicable to multicomponent mixtures at retrograde conditions. Efforts toward that end will require extensive, dedicated research and generous funding.

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Nomenclature

Symbol	Dimension	
a	$\text{J m}^3/\text{mol}^2$	equation of state parameter
A	-	dimensionless molar residual Helmholtz energy
A^r	J	residual molar Helmholtz energy
b	m^3/mol	equation of state parameter
c	-	equation of state parameter
D_0	-	constant in PHC equation of state
f	bar	fugacity
k_{ij}	-	binary mixture interaction parameter
K_i	-	equilibrium ratio (K factor) of component i
l	-	number of experimental points
m	-	constant in RKS and PR equation of state
N	-	number of components
n	mol	number of moles
P	bar	pressure
r	-	number of experimental points
R	$\text{J}/(\text{mol K})$	gas constant, 0.0831439 bar-l/mol-K
T	K	temperature
T_R	-	dimensionless temperature
U	-	total number of EOS parameters, Equation (A5)

v	m^3/mol	molar volume
v_{cM}	m^3/mol	true critical molar volume, e.g. Equation (C1)
V	m^3	volume
x_i	-	molefraction of component i in the liquid phase
y_i	-	molefraction of component i in the vapor phase
z_i	-	molefraction of component i in the feed
Z	-	compressibility factor

Greek letters

symbol	dimension	
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α	-	equation of state constant (Table 2)
β_u	-	EOS parameter, Equation (A5)
$\Delta\xi$	mol %	standard deviation of mole fraction
ϕ	-	fugacity coefficient
χ	-	liquid drop-out, Equation (10)
ϑ	$^{\circ}\text{C}$	temperature
λ	-	objective function, Equation (9)
μ	J/mol	chemical potential
Θ	m^3/mol	defined by Equation (A1)
ρ	mol/m^3	molar density
ξ_i	-	molefraction in either the liquid or the vapor phase

ω - acentric factor (Table 2)

Superscripts

L liquid phase

RKS calculated with the Redlich-Kwong-Soave equation

V vapor phase

Subscripts

M mixture

c critical

i component i

j component j

u number of EOS parameter, Equations (A4) and (A5)

Appendix A. Calculation of the Fugacity Coefficient for the PHC equation

Topliss (Topliss, 1985) suggested a systematic procedure for deriving explicit expressions for the fugacity coefficients from an equation of state (EOS). This procedure divides the overall task into carefully defined, smaller tasks that are more tractable. We define a useful function:

$$\Theta(\rho, T, \xi_1, \xi_2, \dots, \xi_m) = \frac{Z(\rho, T, \xi_1, \xi_2, \dots, \xi_m) - 1}{\rho} \quad (\text{A1})$$

where ρ is the molar density and Z the compressibility factor, calculated by an EOS. The expression for the molar reduced residual Helmholtz energy is given by:

$$\hat{A}(\rho, T, \xi_1, \xi_2, \dots, \xi_m) = \frac{A^r}{RT} = \int_0^\rho \Theta(\rho, T, \xi_1, \xi_2, \dots, \xi_m) d\rho \quad (\text{A2})$$

where A^r is the molar residual Helmholtz energy. The fugacity coefficient ϕ_i can be expressed as:

$$\ln \phi_i = \hat{A} + \left(\frac{\partial \hat{A}}{\partial \xi_i} \right)_{\rho, T, \xi_k \neq i} - \sum_{j=1}^N \xi_j \left(\frac{\partial \hat{A}}{\partial \xi_j} \right)_{\rho, T, \xi_k \neq j} + \rho \Theta - \ln(1 + \rho \Theta) \quad (\text{A3})$$

The differentiation with respect to ξ_i is calculated with all other ξ_k held constant. It is, of course, physically impossible independently to vary the mole fractions of one component while holding all other constant. However, such differentiation provides a useful mathematical tool when used with care. We write the Helmholtz energy as a general function of ρ , T and an arbitrary number of parameters β_u , where each β_u can be a function of ρ , T , and ξ_i :

$$\left(\frac{\partial \hat{A}}{\partial \xi_i}\right)_{\rho, T, \xi_k \neq i} = \sum_{u=1}^U \left(\frac{\partial \hat{A}}{\partial \beta_u}\right)_{\rho, T, \beta_k \neq u} \left(\frac{\partial \beta_u}{\partial \xi_i}\right)_{\rho, T, \xi_k \neq i} \quad (\text{A4})$$

where all ξ_k except ξ_i are held constant. The parameters β_u can be arbitrarily chosen.

For the Perturbed-Hard-Chain equation the following choice is convenient:

$$\beta_1 = \frac{a_M}{RT} \quad \beta_2 = b_M \quad \beta_3 = c_M \quad (\text{A5})$$

where a_M , b_M and c_M are the parameters of the PHC equation for the mixture.

Topliss' Method allows us to change the mixing rules without repeating the entire calculation of the fugacity coefficient. Further, it simplifies the overall calculation process because the integration is made at the beginning of the calculation, not at the end. For the Perturbed-Hard-Chain equation (Sako et al., 1989), the method yields the following expressions:

$$\Theta = \frac{\beta_2 \beta_3}{(1 - \beta_2 \rho)} - \beta_1 \frac{1}{(1 + \beta_2 \rho)} \quad (\text{A6})$$

$$\hat{A} = -\beta_3 \ln(1 - \beta_2 \rho) - \frac{\beta_1}{\beta_2} \ln(1 + \beta_2 \rho) \quad (\text{A7})$$

$$\left(\frac{\partial \hat{A}}{\partial \beta_1}\right)_{\rho, T, \beta_u \neq 1} = -\frac{1}{\beta_2} \ln(1 + \beta_2 \rho) \quad (\text{A8})$$

$$\left(\frac{\partial \hat{A}}{\partial \beta_2}\right)_{\rho, T, \beta_u \neq 2} = \frac{\beta_3 \rho}{(1 - \beta_2 \rho)} - \frac{\beta_1}{\beta_2} \frac{\rho}{(1 + \beta_2 \rho)} + \frac{\beta_1}{\beta_2^2} \ln(1 + \beta_2 \rho) \quad (\text{A9})$$

$$\left(\frac{\partial \hat{A}}{\partial \beta_3}\right)_{\rho, T, \beta_u \neq 3} = -\ln(1 - \beta_2 \rho) \quad (\text{A10}) \quad \left(\frac{\partial \beta_1}{\partial x_i}\right)_{\rho, T, x_k \neq i} = \sum_j 2x_j \frac{\sqrt{a_i a_j}}{RT} (1 - k_{ij}) \quad (\text{A11})$$

$$\left(\frac{\partial \beta_2}{\partial x_i}\right)_{\rho, T, x_k \neq i} = b_i \quad (\text{A12}) \quad \left(\frac{\partial \beta_3}{\partial x_i}\right)_{\rho, T, x_k \neq i} = c_i \quad (\text{A13})$$

Appendix B. Physical constants and parameters α_0 and c of the PHC equation (Sako et al., 1989)

Table B1

	M (kg/kmol)	T _c K	P _c bar	v _c m ³ /kmol	ω -	α_0 -	c -
Methane	16.04	190.55	45.95	0.098917	0.008	1.5113	1.00
n-Decane	142.29	617.70	21.2	0.603	0.489	1.7446	2.54
n-Octadecane	254.48	745.26	12.13	1.0009	0.790	1.8316	3.90
n-Eicosane	282.56	767.	11.1	1.1289	0.907	1.8492	4.24
n-Tetracosane	338.64	802.8*	10.24*	1.3372*	1.148*	1.8813	4.92
Bicyclohexane	166.31	731.39	25.64	0.577	0.388	1.6221	2.70
1-Pentyl-naphthalene	198.29	799.41*	22.11*	0.73898*	0.514*	1.6711	3.20

* calculated using correlations of the American Petroleum Institute (API 1984)

M is the molecular weight, T_c the critical temperature, P_c the critical pressure, v_c the critical molar volume, ω the acentric factor; α_0 and c are parameters of the Perturbed-Hard-Chain equation in the form adopted by Sako et al. (1989).

Appendix C. Correlation of the critical molar volume of a multicomponent mixture

The true critical molar volume is needed for the volume translation method, proposed by Chou and Prausnitz (Chou and Prausnitz, 1989). For the binary system methane - n-decane, the Chueh-Prausnitz correlation (Chueh and Prausnitz, 1967) was used.

Since the multicomponent system contains more than 50 mol% methane, the Chueh-Prausnitz correlation is not applicable (API 1984).

Therefore, an empirical correlation was developed to calculate the critical molar volume. It is known that the RKS-EOS usually gives higher molar volumes than those experimentally determined (Peneloux et al., 1982). Therefore, a correction factor was used, which is expressed as a function of the compressibility factors of the pure components, divided by 1/3, which is the value for the critical compressibility, calculated by the RKS EOS for all pure components.

$$v_{cM} = \left(\frac{\sum_i x_i z_i}{1/3} \right) v_{cM}^{RKS} \quad (C1)$$

There are not sufficient experimental data available fully to evaluate Equation (C1). However, Equation (C1) usually provides reasonable critical molar volumes.

Appendix D. Binary Interaction Parameters for the Multicomponent Mixture

The binary interaction parameters for the pseudocomponent mixture were fitted to liquid drop-out curves at temperatures from 300.98 to 369.26 K. To simplify notation, a number was assigned to each of pseudocomponents:

1	methane	2	n-octadecane
3	n-eicosane	4	n-tetracosane
5	bicyclohexane	6	1-pentyl naphthalene

In a 6-component mixture there are a total of 15 interaction pairs. It was assumed, that the interaction between methane and each of the three other n-alkanes are the same: $k_{12} = k_{13} = k_{14}$. From this assumption follows $k_{23} = k_{24} = k_{34}$, $k_{25} = k_{35} = k_{45}$ and $k_{26} = k_{36} = k_{46}$. The interaction parameter for bicyclohexane and 1-pentyl-naphthalene was set to zero ($k_{56} = 0$) since it has only a small influence on the calculation. These simplifications reduced the number of interaction pairs to 5. The following tables give the interaction parameters for the different equations of state.

Table D1 Redlich-Kwong-Soave EOS

$$\begin{aligned} k_{12} &= -7.3228 \cdot 10^{-6} \vartheta + 0.0407 \\ k_{15} &= -2.1968 \cdot 10^{-4} \vartheta + 0.0611 \\ k_{16} &= 9.5196 \cdot 10^{-4} \vartheta + 0.1185 \\ k_{25} &= 2.9291 \cdot 10^{-4} \vartheta - 0.0082 \\ k_{26} &= 2.9291 \cdot 10^{-4} \vartheta + 0.0018 \end{aligned}$$

Table D2 Peng-Robinson EOS

$$\begin{aligned} k_{12} &= 1.9365 \cdot 10^{-4} \vartheta + 0.0421 \\ k_{15} &= 0.07 \\ k_{16} &= 6.3278 \cdot 10^{-4} \vartheta + 0.1501 \\ k_{25} &= 1.4646 \cdot 10^{-4} \vartheta + 0.0009 \\ k_{26} &= 5.4222 \cdot 10^{-4} \vartheta + 0.0018 \end{aligned}$$

Table D3 RKS Volume
Translation EOS

$$\begin{aligned} k_{12} &= -7.3228 \cdot 10^{-6} \vartheta + 0.0407 \\ k_{15} &= -2.1968 \cdot 10^{-4} \vartheta + 0.0611 \\ k_{16} &= 9.5196 \cdot 10^{-4} \vartheta + 0.1185 \\ k_{25} &= 2.9291 \cdot 10^{-4} \vartheta - 0.0082 \\ k_{26} &= 3.6614 \cdot 10^{-4} \vartheta - 0.0002 \end{aligned}$$

Table D4 Perturbed-Hard-
Chain EOS

$$\begin{aligned} k_{12} &= -2.9291 \cdot 10^{-4} \vartheta + 0.0182 \\ k_{15} &= -0.02 \\ k_{16} &= 3.3610 \cdot 10^{-4} \vartheta + 0.1501 \\ k_{25} &= 0.00 \\ k_{26} &= -7.7622 \cdot 10^{-4} \vartheta + 0.0596 \end{aligned}$$

where ϑ is the temperature in degrees Celsius. To give an impression of the size of interaction parameters, they are shown in Table D5 for the Peng-Robinson equation of state at four different temperatures.

Table D5 Interaction parameters for the Peng-Robinson equation of state

$10^2 k_{ij}$	Temperature: 300.98 K	320.43 K	339.71 K	369.26 K
1 2	4.75	5.13	5.5	6.07
1 5	7	7	7	7
1 6	16.77	18	19.22	21.09
2 5	0.5	0.78	1.07	1.5
2 6	4.9	5.95	7	8.6

Table D6 summarizes the influence of some interaction parameters on the shape of the liquid drop-out curve for the Peng-Robinson EOS. The arrows indicate the direction of change: $\uparrow$ indicates an increase in the upper dew-point pressure or the maximum of the liquid drop-out curve. One arrow stands for a small change, two arrows for a large change, as illustrated by this example: if the interaction parameter k_{12} (methane - n-alkane) is increased from 0.07 to 0.08, the dew point pressure moves up by 80 bars ($\uparrow\uparrow$) to 820 bars and the maximum of the liquid drop-out curve rises by 0.2 % ($\uparrow$) to 41.2%.

Table D6 Influence of interaction parameters for the Peng-Robinson EOS

Change of k_{ij}		Change of upper dew point pressure	Change of Maximum of liquid drop-out
1 2	$\uparrow$	$\uparrow\uparrow$	$\uparrow$
1 5	$\uparrow$	$\uparrow$	$\uparrow$
1 6	$\uparrow$	$\uparrow\uparrow$	$\downarrow$
2 5	$\uparrow$	$\downarrow$	$\downarrow$
2 6	$\uparrow$	$\downarrow$	$\uparrow\uparrow$

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Table 1. Properties of Kensol-16, the pseudocomponent mixture and the methane - Kensol-16 system

<u>Composition [mol%]</u>	<u>Kensol-16</u>	<u>Pseudocomponent mixture</u>	
paraffinic compounds	66 - 68	n-octadecane	31.84
		n-eicosane	39.36
aromatic hydrocarbons	12 - 14	1-pentyl-naphthalene	12.00
naphthenic hydrocarbons	20	bicyclohexane	15.10
residue	2	n-tetracosane	1.70

	<u>Kensol-16</u>	<u>Pseudocomponent mixture</u>
<u>Molecular weight [kg/kmol]</u>	246.9	246.9
<u>Density 297.6 K, 1.013 bar [kg/m³]</u>	809.8	809.81
<u>Boiling-Point Range [K]</u>	570.4 - 582.6	577.28

<u>Composition [mol%]</u>	<u>methane - Kensol-16 system</u>
methane	94.370
n-octadecane	1.794
n-eicosane	2.218
1-pentyl-naphthalene	0.676
bicyclohexane	0.851
n-tetracosane	0.096

Table 2. Equations of state

Peng-Robinson equation

$$P = \frac{RT}{(v - b)} - \frac{a}{v(v + b) + b(v - b)}$$

$$a = a_c \alpha(T)$$

$$\alpha(T) = \left[1 + m(1 - \sqrt{T_R}) \right]^2$$

$$m = 0.37464 + 1.54226\omega - 0.26992\omega^2$$

$$a_c = 0.45724 \frac{R^2 T_c^2}{P_c}$$

$$b = 0.07780 \frac{RT_c}{P_c}$$

Redlich-Kwong-Soave equation

$$P = \frac{RT}{(v - b)} - \frac{a}{v(v + b)}$$

$$a = a_c \alpha(T)$$

$$\alpha(T) = \left[1 + m(1 - \sqrt{T_R}) \right]^2$$

$$m = 0.480 + 1.574\omega - 0.176\omega^2$$

$$a_c = 0.42747 \frac{R^2 T_c^2}{P_c}$$

$$b = 0.08664 \frac{RT_c}{P_c}$$

Cubic form of the Perturbed-Hard-Chain equation

$$P = \frac{RT(v - b + bc)}{v(v - b)} - \frac{a}{v(v + b)}$$

$$a = a_c \alpha(T)$$

$$\alpha(T) = \frac{\alpha_0(1 - T_R^2) + T_R^2}{1 + T_R^2}$$

$$D_0^3 + (6c - 3)D_0^2 + 3D_0 - 1 = 0$$

$$a_c = \frac{(1 - 2D_0 - 2D_0^2 + 2cD_0 + D_0^2 - cD_0^2)(1 + D_0)^2}{3(1 - D_0)^2(2 + D_0)} \cdot \frac{R^2 T_c^2}{P_c}$$

$$b = \frac{D_0}{3} \cdot \frac{RT_c}{P_c}$$

Captions

Fig. 1: Liquid drop-out χ as a function of pressure for the system methane - n-decane at 344.26 K. • experimental (Reamer et al., 1942); — calculated with the Perturbed-Hard-Chain EOS, $k_{ij} = 0.0435$; - - - - calculated with the Peng-Robinson EOS, $k_{ij} = 0.0402$; — · — · calculated with the Peng-Robinson EOS, $k_{ij} = 0.0523$; calculated with the Redlich-Kwong-Soave EOS, $k_{ij} = 0.0368$.

Fig. 2: Liquid drop-out χ as a function of pressure for the system methane - Kensol-16 at 300.98 K. • experimental (Rzasa, 1947); — calculated with the Perturbed-Hard-Chain EOS; - - - - calculated with the Peng-Robinson EOS; calculated with the Redlich-Kwong-Soave EOS. The temperature functions of the k_{ij} s are given in the Appendix.

Fig. 3: Liquid drop-out χ as a function of pressure for the system methane - Kensol-16 at 369.27 K. See legend of Figure 2.

Fig. 4: Pressure-temperature diagram for the system methane - Kensol-16. All lines are calculated with the Perturbed-Hard-Chain EOS for a constant liquid drop-out, according to the numbers shown. Experimental results from Rzasa (1947).

Fig. 5: Pressure-temperature diagram for the system methane - Kensol-16. All lines are calculated with the Peng-Robinson EOS for a constant liquid drop-out, as in Fig. 4.

Fig. 6: Pressure-temperature diagram for the system methane - Kensol-16. All lines are calculated with the Redlich-Kwong-Soave EOS for a constant liquid drop-out, as in Fig. 4.

Fig. 7: Unusual behavior of the calculated liquid drop-out curve at high pressures for the methane - Kensol-16 system at 369.26 K. Note the curvature (tail) at the right side of the curve. • experimental (Rzasa, 1947); ——— calculated with the Redlich-Kwong-Soave equation; interaction parameters: $k_{12} = k_{13} = k_{14} = 0.02$, $k_{16} = 0.27$, all other $k_{ij} = 0$. See Appendix.

LAWRENCE BERKELEY LABORATORY
TECHNICAL INFORMATION DEPARTMENT
1 CYCLOTRON ROAD
BERKELEY, CALIFORNIA 94720