

CALCULATION OF THE VAPOUR-LIQUID EQUILIBRIUM IN HIGH PRESSURE REGION*

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The Hlavatý three-parameter equation of state, which is based on the model of rigid spheres and contains an empirical correction term, was employed for a correlation of the vapour-liquid equilibrium in the high pressure region. The constants for pure substances were evaluated. at $T_r < 1$ from the condition of thermodynamic stability and equations for orthobaric densities, at $T_r = 1$ from critical values, conditions of a maximum and the inflection point and at $T_r > 1$ from PVT data in the region relevant for the correlations. From the equation of state with proposed mixing rules, the relation for the fugacity coefficient was derived and the composition of the liquid phase and pressure were calculated from given values of the vapour phase composition and temperature by an iterative procedure. The calculation is based only on the properties of pure components; the correlation does not contain any adjustable parameter for the mixture. The method was tested on five binary systems containing simple hydrocarbons, carbon dioxide and nitrogen.

A calculation of vapour-liquid equilibrium at high pressures which is based on an equation of state constitutes the exact thermodynamic procedure using a suitable equation of state with appropriate mixing rules. For the description of the state behaviour, equations of state of different types have been in use; the two-constant Redlich-Kwong (for its simplicity) and ten-constant Benedict-Webb-Rubin (for its flexibility in a wide range of conditions) equations belong to most successful ones.

Methods for the evaluation of pure component constants differ from case to case; mostly they employ PVT data, densities of saturated phases, vapour pressures *etc.* Because necessary data are often available in excessive amounts, optimization procedures are used. Even though such constants cover a wide range of conditions, they usually do not fulfil all conditions required by the coexistence region which must be considered as especially relevant for calculations of vapour-liquid equilibria. Due to these reasons we should use such an equation of state, the number of parameters of which corresponds exactly to the number of conditions necessary for an unambiguous description of the two-phase region. As the constants are evaluated

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generally at constant temperature, PVT data have been divided into three groups according to the temperature range:

a) Reduced temperatures $T_r < 1$. The isotherm inside the coexistence curve is determined by orthobaric densities and by the condition of thermodynamic stability

$$\int_{V_1}^{V_g} P dV = P(V_g - V_1),$$

where V_1 and V_g are volumes of coexisting liquid and vapour phases. The equation of state is then determined by the three following conditions: 1) validity for the volume of the saturated liquid phase; 2) validity for the volume of the saturated vapour phase; 3) the condition of thermodynamic stability. As simple equations of state contain mostly only two constants, the simultaneous fulfilment of all three conditions is a matter of sheer luck. The exact agreement is made possible only by a three-parameter equation of state, which may be solved for the given temperature and pressure unambiguously. Such set of parameters for different temperatures up to the critical point should then express perfectly the behaviour in the two-phase region. An extrapolation of the isotherm into single-phase regions would not be sufficiently reliable, however, this should not play a decisive role for calculations of phase vapour-liquid equilibria.

b) Reduced temperature $T_r = 1$. An equation of state must satisfy in the critical point the three following independent conditions: 1) validity for critical values; 2) the condition of extreme $dP/dV = 0$; 3) the condition of inflection $d^2P/dV^2 = 0$, which on solving yield again a single triad of constants. For the choice of the type of the equation, a similar consideration holds as in the case of $T_r < 1$.

c) Reduced temperatures $T_r > 1$. The above mentioned unambiguous method cannot be of course applied to supercritical isotherms. Nevertheless, for the calculations they are inevitable because subcritical conditions for a mixture are often supercritical for the light component. Luckily enough, there are often more PVT data for the fluid region than for the two-phase one and so the only remaining thing is to choose the suitable range of pressures. No limitations are imposed on the calculations and common fitting procedures can be used for evaluating the constants.

It follows from the foregoing that the equation of state is determined overall by three conditions. Therefore we used in our work the Hlavatý three-parameter equation of state¹ which is based on the model of rigid spheres and which contains an empirical correction term. This equation is usually written in the following form

$$P = RT \frac{V^3 + V^2b + Vb^2 - b^3}{V(V-b)^3} - \frac{a}{V^2} - \frac{c}{V^4} (V - V_c)^2, \quad (1)$$

where a , b , c are three temperature-dependent constants, P is pressure, T is temperature, V is volume, V_c is critical volume, R is gas constant.

For the fugacity coefficient of component i in the binary mixture obeying Eq. (1) it holds

$$\ln \varphi_i = (3b^3 - 2Vbd_b - 5Vb^2 + 4V^2d_b)/(V - b)^3 - d_a/(RTV) + \\ + [(d_cV_c - cV_c + cd_{vc})/V + V_c(2cV_c - d_cV_c - 2cd_{vc})/3V^2]/ \\ /(RTV) - \ln(PV/RT), \quad (2)$$

where constants of the mixture a , b , c , V_c are evaluated according to the following mixing rules from pure component constants

$$a = a_1x_1^2 + 2a_{12}x_1x_2 + a_2x_2^2, \quad (3)$$

$$b = b_1x_1^2 + 2b_{12}x_1x_2 + b_2x_2^2, \quad (4)$$

$$c = (x_1c_1/a_1 + x_2c_2/a_2) a, \quad (5)$$

$$V_c = (x_1V_{c1}/b_1 + x_2V_{c2}/b_2) b \quad (6)$$

with cross terms

$$a_{12} = (1 - \alpha) \sqrt{(a_1a_2)}, \quad (7)$$

$$b_{12} = [(\sqrt[3]{b_1} + \sqrt[3]{b_2})/2]^3, \quad (8)$$

where α is the possible adjustable parameter of the mixture, which is identically equal to zero in our work, so that $a_{12} = \sqrt{(a_1a_2)}$.

Symbol d_k is defined as

$$d_k = dk/dx_i \quad \text{for } k = a, b, c, V_c; i = 1, 2, \quad (9)$$

where x_i is the composition of the phase in mole fraction. It follows from Eqs (3)–(6) and (9) that

$$d_a = 2(x_1a_1 + x_2a_{12}), \quad (10)$$

$$d_b = 2(x_1b_1 + x_2b_{12}), \quad (11)$$

$$d_c = c_1/a_1, \quad (12)$$

$$d_{vc} = V_{c1}/b_1 \quad (13)$$

for $i = 1$. Expressions for $i = 2$ are obtained by interchanging indexes 1 and 2 in Eqs (10)–(13). From the fugacity coefficients in both phases (l, g) and for both components (1, 2), the equilibrium constants may be obtained

$$K_1 = \varphi_1^l/\varphi_1^g, \quad (14)$$

$$K_2 = \varphi_2^l/\varphi_2^g. \quad (15)$$

COMPUTATIONAL PROCEDURE

Firstly, the pure component constants must be evaluated for the temperature range in which the correlation is to be performed. A quadratic interpolation among these constants is then made during actual computation at the required temperature of the system. Because the values of the fugacity coefficients depend on composition and state variables, it is only natural that the composition calculated from Eqs (14) and (15) need not agree with the first approximation. The computation must be consequently performed by an iterative procedure which is based here on initial experimental values of the temperature and composition of the liquid phase (x). For the first approximation of the pressure and composition of the vapour phase (y), experimental values were used. By the trial-and-error method, such values of the pressure and composition of the vapour phase were found in the vicinity of the first approximation, which gave a minimal difference between the initial and computed values of x and y ; these were used in the next iteration. The computation was stopped after reaching an accuracy of 0.0001 in composition and 0.01 atm in pressure.

RESULTS AND DISCUSSION

Sets of the pure component constants were obtained from literature data given in Table I. The actual computations of the vapour–liquid equilibrium were performed with several systems for which mutually comparable experimental data were available:

TABLE I
Sources of Data for Pure Components

Substance	Orthobaric data	Critical data	Supercritical region
Methane	2, 3	2	2
Ethane	4, 5	4	5
Propane	6	6	7
Isobutane	8	8	8
CO ₂ , N ₂	9	9	9

TABLE II
Comparison of Calculated and Experimental Values

System	Number of points	Temperature K	Pressure range atm	Deviation in y mean/max.	Deviation in P mean/max. atm
Methane-ethane	4	172.04	16-23	0.005/0.015	0.39/1.08
	5	192.39	42-47	0.006/0.014	0.37/1.52
	7	233.16	20-58	0.009/0.015	1.45/2.85
Ethane-propane	11	303.15	19-46	0.006/0.014	0.92/1.37
	18	323.15	18-50	0.015/0.039	0.24/0.42
	6	343.17	28-48	0.021/0.055	1.21/3.09
	9	363.16	38-45	0.008/0.026	0.25/0.50
Ethane-isobutane	10	311.26	22-48	0.003/0.020	1.04/1.27
	8	344.48	13-47	0.017/0.024	0.66/1.93
	9	377.43	23-49	0.025/0.052	0.72/1.06
	3	394.04	31-39	0.009/0.016	1.03/1.60
CO ₂ -propane	10	294.25	18-56	0.027/0.056	7.20/9.48
	18	310.95	13-55	0.089/0.104	8.05/11.0
	13	327.55	20-49	0.039/0.063	7.42/12.4
	11	344.25	27-49	0.025/0.041	6.43/11.8
N ₂ -methane	10	155.35	13-44	0.025/0.046	2.23/3.04
	6	172.05	27-44	0.027/0.034	1.70/2.41

methane-ethane^{10,11}, ethane-propane¹², ethane-isobutane¹³, CO₂-propane¹⁴, and nitrogen-methane¹⁵. The isotherms were selected so that the whole two-phase region from subcritical data up to supercritical temperatures of the light y component might be possibly covered.

The results are summarized in Table II, where mean/maximum deviations of calculated and experimental data are given for separate isotherms. It may be seen that the correlation agrees well with experiment in most cases. It must be also taken into account that deviations might result from experimental errors in the data used.

Let us stress again that the entire correlation was performed with parameter $\alpha = 0$, *i.e.* that only pure component data were employed. The accuracy of the correlation can be improved considerably by adjusting the value of this parameter.

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