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Prediction of the Dew Point Locus in Methane-Light Hydrocarbon Binary Systems in the Neighborhood of the Methane Critical Point

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Chen et al. (1972) have developed an elution technique for the determination of the dew point concentration of binary mixtures in the 98 to 100 mole % range. The experimental results of Chen et al. (1973) exhibit a phenomena which could not be observed with less accurate methods. The dew point isotherm is multiple valued in the region (~5°C) about the critical temperature T_c of the more volatile component. Isotherms at temperatures slightly above T_c are quadruple valued, as observed in methane-*n*-pentane (Chen et al., 1973); and at T_c and slightly lower temperatures the isotherms are triple valued or S shaped, as observed in methane-*n*-butane (Chen et al., 1973). This phenomena has been termed *double retrograde vaporization* by Carnahan et al. (1972).

The present study evaluates the ability of the Benedict-Webb-Rubin (BWR) (1951) equation of state for the computation of these phenomena.

COMPUTATION

The BWR equation was used in an iterative fashion to calculate fugacities, various derivatives, and K-values as required. The ordinary BWR combining rules with the modification proposed by Stotler and Benedict (1953) were used:

$$A_0 = y_1^2 A_{01} + 2\, y_1\, y_2\, m \sqrt{A_{01} A_{02}} + y_2^2 A_{02} \qquad (1)$$

which introduces a binary interaction parameter m.

The points A, B, C, D on Figure 1 have certain mathematical restrictions which may be used for computational purposes:

$$(\partial P/\partial y_1)_T = \infty \quad \text{or} \quad (\partial y_1/\partial P)_T = 0 \qquad (2)$$

We restrict ourselves to these points and apply an analysis similar to that of Redlich and Kister (1962). At equilibrium conditions for component 1:

$$\ln k_1\, x_1\, \gamma_1 + \int_0^P (\overline{V}_{1L}/RT)\, dP = \ln y_1\, \phi_1\, P \qquad (3)$$

where the partial molal volume term is required since the activity coefficient is defined at low pressure. Differentiating Equation (3) at constant temperature gives

$$\begin{aligned}(d \ln x_1/dP)_T + (d \ln \gamma_1/dx_1)_T\, (dx_1/dP)_T + \overline{V}_{1L}/RT \\ = (d \ln y_1/dP)_T + (d \ln \phi_1/dy_1)_T\, (dy_1/dP)_T + \overline{V}_{1G}/RT\end{aligned} \qquad (4)$$

We multiply Equation (4) by x_1; perform similar operations for component 2; add; and simplify using

$$\sum_i x_i\, (d \ln \gamma_i/dx_i)\, (dx_i/dP) = 0 \qquad (5)$$

to obtain

$$\begin{aligned}(dy_1/dP)\, [x_2/y_2 - x_1/y_1 - x_1\, (d \ln \phi_1/dy_1) \\ - x_2\, (d \ln \phi_2/dy_1)] = [x_1\, (\overline{V}_{1G} - \overline{V}_{1L}) \\ + x_2\, (\overline{V}_{2G} - \overline{V}_{2L})]/RT\end{aligned} \qquad (6)$$

From Equation (2) the left-hand side of Equation (6) is zero, or

$$x_1\, (\overline{V}_{1G} - \overline{V}_{1L}) + x_2\, (\overline{V}_{2G} - \overline{V}_{2L}) = 0 \qquad (7)$$

We also have

$$\begin{aligned}V_G &= y_1\, \overline{V}_{1G} + y_2\, \overline{V}_{2G} \\ V_L &= x_1\, \overline{V}_{1L} + x_2\, \overline{V}_{2L}\end{aligned} \qquad (8)$$

which combine with Equation (7) to give

$$V_G - V_L = (\overline{V}_{1G} - \overline{V}_{2G})\, (y_1 - x_1) \qquad (9)$$

The Gibbs-Duhem relation gives

$$(dV/dy_1)_{P,T} = \overline{V}_{1G} - \overline{V}_{2G} \qquad (10)$$

so that

$$(V_G - V_L) = (dV/dy_1)_{P,T}\, (y_1 - x_1) \qquad (11)$$

Equation (11) holds at the points A, B, C, D and may be used to determine those points. The method of calculation adopted was to evaluate the right-hand side and left-hand side of Equation (11) separately and to determine their intersection. The derivative was evaluated using

$$(dV/dy_1)_{P,T} = -\, (\partial P/\partial y_1)_{V,T}/(\partial P/\partial V_G)_{y_1,T} \qquad (12)$$

RESULTS

Calculations were made on the methane-*n*-butane system with $m = 0$ at 188.0 °K with the BWR coefficients termed *original* in Table 1. The qualitative S shape was obtained, but there was no quantitative agreement.

This lack of quantitative agreement is not surprising, for the vapor phase is almost completely methane very close to its critical condition. Therefore, the BWR coefficients C_0, b, and α for methane were evaluated using the BWR equation applied at the critical conditions for methane and the definitions

$$P_c = P(V_c, T_c), \quad (\partial P/\partial V)_{T_c} = 0, \quad (\partial^2 P/\partial V^2)_{T_c} = 0$$

and the critical constants for methane by Goodwin and Prydz (1972) as $T_c = 190.53$°K, $P_c = 45.356$ atm, and $V_c = 0.0985$ 1/g mole. These calculations gave the values listed as revised in Table 1.

Calculations on the methane-*n*-butane system using the revised coefficients at −119.43°F (189.022°K) gave the S shape but were only in fair agreement with the experimental data.

The calculations with respect to the heavy component occur in the very low reduced temperature range; therefore, the C_0 coefficient for the heavy component was adjusted to the value listed as revised in Table 1 by using the relation $f_L = f_G$ at saturation in the BWR equation and the low temperature vapor pressure data of Carruth and Kobayashi (1973).

An iterative procedure was used with the revised BWR coefficients with Equation (11) to define a best value for the interaction parameter m by fitting calculated results to the experimental data. One example of the calculation is shown in Figure 2. At the intersection points I and II the necessary conditions are met to obtain points B and D of Figure 1. Table 2 gives the values interpolated from the experimental data and those calculated. Excellent agreement was obtained. However, the quadruple valued curve of Figure 1 at temperatures above the critical point of methane could not be calculated.

Subsequent investigations by Hopke and Tomich (1973) on the methane-*n*-pentane system did produce the quadruple valued locus.

It should be noted that qualitative agreement was obtained with the original BWR coefficients. This indicates that the BWR equation of state contains some (if not all) features which are necessary to predict behavior in the critical region. However, to obtain quantitative agreement it was necessary to apply both the necessary conditions (critical and low reduced temperature) for both components and the binary interaction correction. A thorough understanding and theoretical quantification of critical phenomena is desirable.

TABLE 1. BWR COEFFICIENTS

	Original methane	Revised methane	Original *n*-butane	Original *n*-pentane
A_0	1.85500		10.0847	12.1794
B_0	0.0426000		0.124361	0.156751
C_0	22,570.0	25,340.0	992,830.0	212,121.0
a	0.0494000		1.88231	4.07480
b	0.00338004	0.00385941	0.0399983	0.0668120
c	2,545.0		316,400.0	824,170.0
α	0.000124359	0.000105516	0.00110132	0.00181000
γ	0.0060000		0.034000	0.047500

Revised C_0 for *n*-alkanes:
n-Butane: $C_0 = 921{,}206.0$ (189.02°K), 922,761.0 (190.55°K)
n-Pentane: $C_0 = 1{,}960{,}100.0$ (190.55°K), 1,964,220.0 (192.17°K)

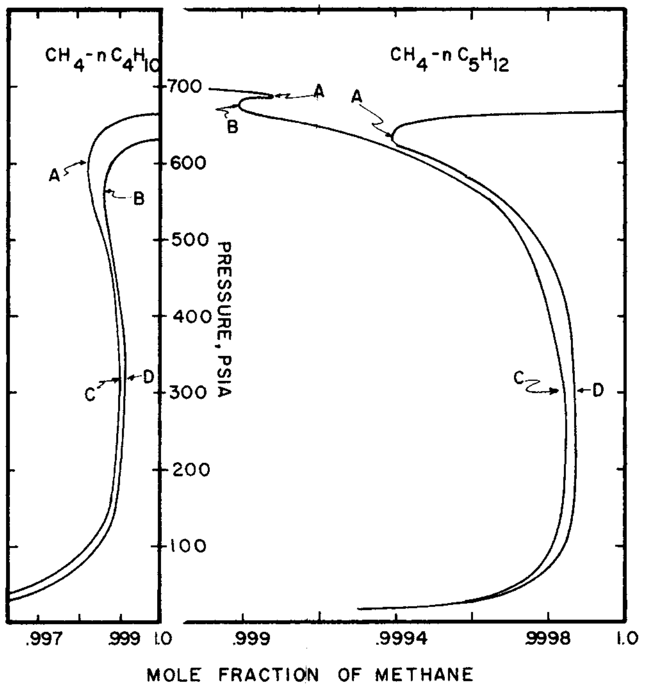

Fig. 1. The double retrograde vaporization phenomena as observed in two systems: methane-*n*-butane and methane-*n*-pentane. Attention is called to the magnitude of the concentration measurements.

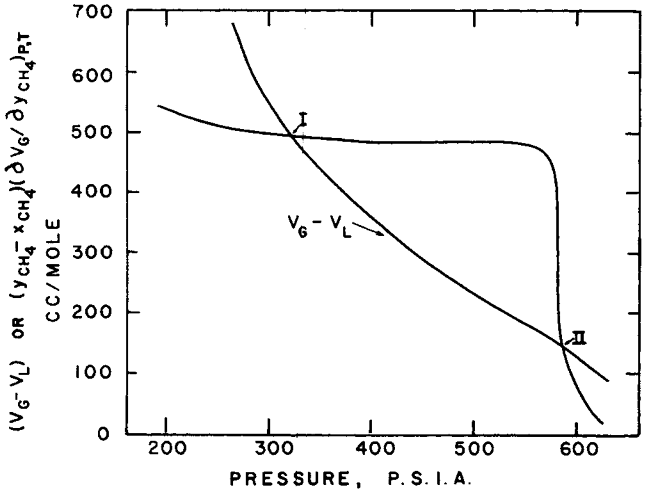

Fig. 2. One example for the solution to Equation (11) at points I and II. The system is methane-n-butane at 189.06°K with the interaction parameter *m* = 0.880 in the BWR calculation.

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NOTATION

A_0 = BWR constant
c = subscript denoting critical condition
γ = activity coefficient
ϕ = fugacity coefficient
L, G = subscript denoting phase as Liquid or Gas
m = BWR interaction parameter

TABLE 2. COMPARISON OF CALCULATIONS WITH EXPERIMENTAL VALUES

Temp., °K			Pressure, lb./sq.in.abs.	y_{CH_4}
Methane-*n*-Butane System ($m = 0.880$)				
189.06	I	Calc.	322	0.99924
		exp.	325	0.99908
	II	calc.	583	0.99856
		exp.	560	0.99860
190.58	I	calc.	326	0.99914
		exp.	320	0.99894
	II	calc.	619	0.99810
		exp.	600	0.99822
Methane-*n*-Pentane System ($m = 0.786$)				
190.58	I	calc.	267	0.99992
		exp.	300	0.99985
	II	calc.	641	0.99889
		exp.	630	0.99924
192.20	I	calc.	271	0.99991
		exp.	300	0.99982

P = pressure
R = gas constant
T = temperature
V = molal volume
x, y = mole fraction in liquid and vapor phase, respectively
1, 2 = subscript denoting component
— = bar superscript denoting partial quantity

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