COMPUTATIONS OF VAPOUR–LIQUID EQUILIBRIUM IN THE CRITICAL REGION*

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The Hlavatý three-constant equation of state without adjustable parameters for the mixture was employed for computations of vapour–liquid equilibrium. This equation of the classical type can describe the continuous transition from a concave shape of the K–P curve to a convex one near the critical temperature and pressure of the more volatile component of the mixture. The computations were tested on methane–ethane and nitrogen–methane systems in the range of K_1 between 1·00 and 1·03.

Presently there are several methods suitable for the thermodynamic description of vapour–liquid equilibrium at increased pressures. These methods which are based on more or less exact principles yield a reliable description of the phase equilibrium with an accuracy which is satisfactory for design of plants working at not too extreme conditions. Nevertheless, continuous improvements in technology lead to the development of separation units working in regimes which are close to boundary (and also critical) conditions. This fact can affect considerably the efficiency of high-pressure distillation columns, especially during production of highly pure substances. The behaviour in the critical region has been described phenomenologically[1] and its practical significance has also been discussed[2]. So far, however, these phenomena have not been described by common thermodynamic methods because of failing of the computations in the critical region.

The correlation of the high-pressure vapour–liquid equilibrium which is based on the Hlavatý equation of state[3] gives results even without any adjustable parameter for the mixture (*i.e.* the vapour–liquid equilibrium is evaluated from properties of pure components only). Temperature-dependent triads of constants are determined so as to represent best the two-phase region which must be considered as especially relevant for any vapour–liquid equilibrium calculation. Constants in each triad correspond unambiguously to saturated liquid and vapour densities and more-

over satisfy the condition of thermodynamic stability. The equation may be written in the form:

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

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

Constants for a mixture may be calculated from the mixing rules

$$a = \sum\sum a_{ij}x_ix_j , \quad b = \sum\sum b_{ij}x_ix_j , \qquad (2), (3)$$

$$c = a\sum x_ic_i/a_i , \quad w = b\sum x_iw_i/b_i , \qquad (4), (5)$$

with the cross-parameters

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

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

where α is an adjustable parameter which is determined from binary data. Eq. (1) with mixing rules (2)–(5) gives the following form for the fugacity coefficient in a two-component mixture*

$$\ln \varphi_i = (3b^3 - 2Vbd_b - 5Vb^2 + 4V^2d_b)/(V - b)^3 - d_a/(RTV) +$$

$$+ [c - d_c + (wd_c + cd_w - 3cw)/V + w(5cw - wd_c - 2cd_w)/(3V^2)]/(RTV) -$$

$$- \ln (PV/RT) , \qquad (6)$$

with

$$d_a = 2(x_1a_1 + x_2a_{12}), \quad d_b = 2(x_1b_1 + x_2b_{12}),$$

$$d_c = ac_1/a_1 + d_ac/a , \quad d_w = bw_1/b_1 + d_bw/b .$$

There are only two independent variables among x, y, P, T, i.e., the remaining two must be determined by a computation procedure. Constants at a given temperature are determined by quadratic interpolation in a set of the triads for pure components. The adjustable parameter in this work is set equal to zero. The resulting curve in the region of high concentrations was found by subsequent changes of the liquid phase composition at constant temperature while the vapour phase composi-

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*   The expression in paper[3] for the fugacity coefficient is in error; it corresponds to other mixing rules.

tion and pressure were being computed. The algorithm is described in a preceding work[3].

The method was applied to methane–ethane and nitrogen–methane systems for which equilibrium data in the close vicinity of the critical pressure of the mixture and critical isotherm of the more volatile component are available. The concave
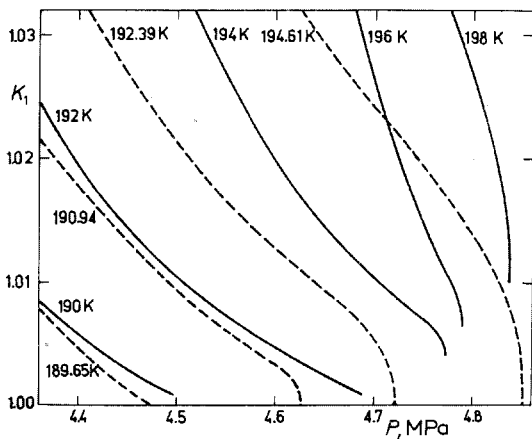

FIG. 1

The $K-P$ Diagram of the Methane–Ethane System in the Vicinity of the Critical Point of Methane (– – – – experiment; ——— calculated)
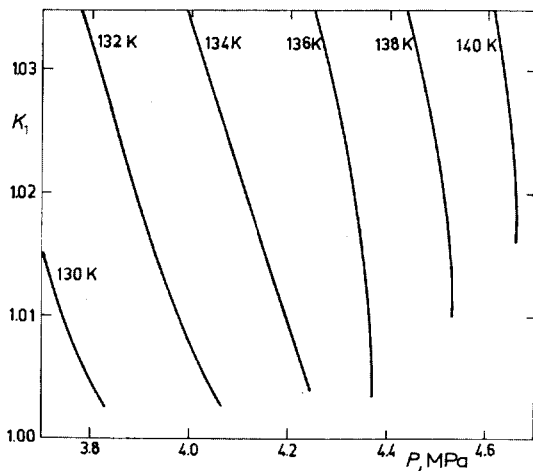

FIG. 2

The $K-P$ Diagram of the Nitrogen–Methane System in the Vicinity of the Critical Point of Nitrogen (calculated curves)

shape of the $K_1 - P$ curve (for subcritical isotherms) changes continuously to a convex one at temperatures above the critical temperature of the more volatile component. It follows from this continuous transition that the transitional curve is S-shaped with an inflection point. This phenomenon was confirmed both experimentally and theoretically[1,4,5] and it is illustrated by a dashed lines on Fig. 1. The isotherm at 190·94 K represents the critical isotherm of methane which is the lower limiting temperature for the convex curve. Below this temperature, all curves are fully concave. (The terms convex and concave should be here understood for the shape of the curve in the close vicinity above $K = 1$). Solid lines correspond to computed results. Even though the computations were performed in a rather narrow range of K_1 — between 1·0 and 1·03 — this interval is sufficiently wide for an illustration of the results. It is also obvious from Fig. 2 that the qualitative description of the change in the shape is very good. From a quantitative point of view, however, the critical pressure of the pure more volatile component, which represents the limit (the point of turnover), is in fact higher than that provided by experiment. This could be improved by using the adjustable parameter α or better PVT data of pure components. The computed lines do not reach the critical points and saturated vapour pressures due to well-known computational difficulties.

Our results thus show that the S-shaped K-P curve experimentally found can be described by means of presented correlation using the equation of state of the classical type.

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