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**LIQUID-LIQUID EQUILIBRIUM. COMPUTATION OF LIQUID-LIQUID EQUILIBRIUM IN TERMS OF AN EQUATION OF STATE**

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An algorithm for calculating the boiling point pressure at a chosen temperature and composition was used for computing liquid-liquid equilibrium. A lot of attention is paid to the determination of the first approximation which is specified in terms of the conditions of thermodynamic stability. The conditions of thermodynamic stability make as well possible to localize the lower and upper critical end points (LCEP and UCEP). The Redlich-Kwong-Soave equation of state was applied in calculations, and it was found out that this equation with zero interaction parameters predicts well the lower and upper critical end temperatures in the systems methane-n-hexane, ethane-n-eicosane and ethane-n-docosane.

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The computation of liquid-liquid equilibrium (LLE) stems mostly from the relations which thermodynamically describe the given system in terms of the Gibbs energy, as *e.g.*, the Redlich-Kister, NRTL, UNIQUAC, or modified Wilson equations<sup>1-3</sup>. An advantage of this procedure is a simple application both in correlating the data and in predicting in chemical-engineering practice. On the other hand this method is rather complicated when describing systems in a wider temperature and pressure range. Insuperable difficulties arise in the vicinity of the critical point of some of components where the effect of pressure plays a significant role.

Equations of state have recently been in common use for describing vapour-liquid equilibrium and begun more strongly compete with the classical description by means of activity coefficients. When correlating vapour-liquid equilibrium under higher pressures especially in mixtures of nonpolar substances, this method is quite usual<sup>4</sup>. Lately, equations of state have begun to be used even for the description of liquid-liquid equilibrium<sup>5-10</sup>. A disadvantage of describing the systems in terms of equations of state is a more complicated calculation of compositions of equilibrium phases and, in case of LLE, in addition, a more difficult determination of the first approximation which is necessary for numerical calculation of equilibrium.

It is shown in this work that, when calculating the composition of coexisting phases in case of LLE, it is possible to apply the previously proposed algorithm<sup>11</sup> for calculating the boiling point pressure in terms of which it is also possible to determine very accurately the first approximation. It is as well shown that by means of this

algorithm one can accurately localize in binary systems the lower and upper critical end point temperatures in which the number of phases changes.

When calculating LLE in multicomponent systems, we can proceed in a similar way to that proposed for calculating LLE on the basis of relations for activity coefficients. Then as a basis of calculation serve the values obtained for the heterogeneous binary system, and by an appropriate rearrangement of set of equations (3), it is possible to obtain the optimum first approximation for calculating LLE in an  $N$ -component system. The details may be found in cited work.

### Brief Description of Algorithm

To calculate vapour-liquid equilibrium, an algorithm was developed<sup>11</sup> for solving the set of equations which follows from the equilibrium conditions in  $N$ -component system

$$\begin{aligned} P(T, d^L, x_1, x_2, \dots, x_{N-1}) &= P(T, d^g, y_1, y_2, \dots, y_{N-1}), \\ f_i(T, d^L, x_1, x_2, \dots, x_{N-1}) &= f_i(T, d^g, y_1, y_2, \dots, y_{N-1}), \\ i &= 1, 2, \dots, N. \end{aligned} \quad (1)$$

In these equations,  $T$ ,  $P$ ,  $d^L$ ,  $d^g$  denotes the temperature, pressure, and densities of equilibrium phases, respectively,  $f_i$  the fugacity of component  $i$ ,  $x_1, x_2, \dots, x_{N-1}$  the composition of the liquid phase and  $y_1, y_2, \dots, y_{N-1}$  the composition of the gas phase.

If the temperature and composition of the liquid phase are given, the solution of set of equations (1) is referred to as the boiling point pressure calculation; when the values of temperature and composition of the vapour phase are given, on the contrary, as the dew point pressure calculation. It is evident that both the problems can be solved by a single program, and the type of calculation is chosen only by the choice of the respective first approximation.

When calculating LLE, we as well stem from the equality of pressures and fugacities of the components in coexisting phases

$$\begin{aligned} P(T, d^{(1)}, x_1^{(1)}, x_2^{(1)}, \dots, x_{N-1}^{(1)}) &= P(T, d^{(2)}, x_1^{(2)}, x_2^{(2)}, \dots, x_{N-1}^{(2)}), \\ f_i(T, d^{(1)}, x_1^{(1)}, x_2^{(1)}, \dots, x_{N-1}^{(1)}) &= f_i(T, d^{(2)}, x_1^{(2)}, x_2^{(2)}, \dots, x_{N-1}^{(2)}), \\ i &= 1, 2, \dots, N. \end{aligned} \quad (2)$$

This set is, with the exception of the denotation of mole fractions of components and phases, identical with set of equations (1). Consequently, if we choose temperature and composition of any phase (e.g.,  $T, x_1^{(1)}, x_2^{(1)}, \dots, x_{N-1}^{(1)}$ ), we can use the program for calculating vapour-liquid equilibrium without any rearrangements.

In the calculation itself, the Newton method is applied, and from set of equations (2) we get after small rearrangement

$$\begin{aligned}
 & (\partial P/\partial d)^{(1)} \Delta d^{(1)} - (\partial P/\partial d)^{(2)} \Delta d^{(2)} - \sum_{j=1}^{N-1} (\partial P/\partial x_j)^{(2)} \Delta x_j^{(2)} = \\
 & = P^{(2)} - P^{(1)} - \sum_{j=1}^{N-1} (\partial P/\partial x_j)^{(1)} \Delta x_j^{(1)} + [(\partial P/\partial T)^{(2)} - (\partial P/\partial T)^{(1)}] \Delta T, \\
 & (\partial f_i/\partial d)^{(1)} \Delta d^{(1)} - (\partial f_i/\partial d)^{(2)} \Delta d^{(2)} - \sum_{j=1}^{N-1} (\partial f_i/\partial x_j)^{(2)} \Delta x_j^{(2)} = \\
 & = f_i^{(2)} - f_i^{(1)} - \sum_{j=1}^{N-1} (\partial f_i/\partial x_j)^{(1)} \Delta x_j^{(1)} + [(\partial f_i/\partial T)^{(2)} - (\partial f_i/\partial T)^{(1)}] \Delta T, \\
 & \qquad \qquad \qquad i = 1, 2, \dots, N. \qquad \qquad \qquad (3)
 \end{aligned}$$

For a specified temperature and composition of some of phases (*i.e.*, *e.g.*,  $\Delta T = 0$ ,  $\Delta x_1^{(1)} = \Delta x_2^{(1)} = \dots = \Delta x_{N-1}^{(1)} = 0$ ), we get a set of  $(N + 1)$  equations for unknowns  $\Delta d^{(1)}$ ,  $\Delta d^{(2)}$ ,  $\Delta x_1^{(2)}$ ,  $\Delta x_2^{(2)}$ , ...,  $\Delta x_{N-1}^{(2)}$ . After determining the coefficients in set of equations (3) and these increments, we obtain the next approximation of values of unknowns:

$$\xi_{i+1} = \xi_i + \Delta \xi, \quad \xi = d^{(1)}, d^{(2)}, x_1^{(2)}, x_2^{(2)}, \dots, x_{N-1}^{(2)}. \quad (4)$$

As soon as the increments, or better the sum of their squares decreases under a chosen value, the calculation for the given temperature and composition of the first phase is finished.

If we wish to carry out the calculation for another temperature  $T_{\text{new}}$  and composition  $x_{j,\text{new}}^{(1)}$ , we can again stem from set of equations (3), the right-hand sides containing in addition the contributions with  $\Delta T$  and  $\Delta x_j^{(1)}$ :

$$\begin{aligned}
 \Delta T & = T_{\text{new}} - T, \\
 \Delta x_j^{(1)} & = x_{j,\text{new}}^{(1)} - x_j^{(1)}, \quad j = 1, 2, \dots, N - 1. \qquad (5)
 \end{aligned}$$

In terms of a new solution of set of equations (3) at a given equilibrium point we obtain  $\Delta d^{(1)}$ ,  $\Delta d^{(2)}$ ,  $\Delta x_j^{(2)}$ ,  $j = 1, 2, \dots, N - 1$  which will be used according to Eqs (4) to estimate the first approximation of densities and composition of the second phase at the temperature  $T_{\text{new}}$  and composition  $x_{j,\text{new}}^{(1)}$ . Further details on calculation and the corresponding relations for calculating the derivatives of pressure and fugacity of a component with respect to independent variables (temperature, density, and composition) for the Redlich-Kwong-Soave equation are given elsewhere<sup>11</sup>.

Considering that the Newton method is used twice in the solution, *viz.* for the first time for solving the equilibrium conditions itself and for the second time for determining the next approximation of densities and composition of the second

phase, this procedure was denoted as the DAN method (Double Application of the Newton-Raphson Method).

As it has been shown previously<sup>11</sup>, the calculation converges (in case of a good first approximation) regardless of the fact whether the phase whose composition was chosen, is thermodynamically stable or not. However, if the phase whose composition is sought is thermodynamically unstable, then the calculation converges only in isolated cases. The reason is the fact that the determinant of set of equations (3) is proportional to the determinant of thermodynamic stability of the phase whose composition is sought. This determinant changes its sign when passing from the metastable to labile region, and is equal to zero on the spinodal surface. Consequently the contributions in the vicinity of spinodal surface acquire very high values. If we get into the region where the phase whose composition is sought stops being thermodynamically stable, we usually obtain the so-called trivial solution ( $d^{(1)} = d^{(2)}$ ,  $x_j^{(1)} = x_j^{(2)}$ ) or the calculation oscillates.

#### Determination of the First Approximation and the Calculation Itself

The key point in calculating LLE is the determination of the first approximation. For this purpose, the employment of the conditions of thermodynamic stability has appeared to be the most optimum for they answer generally the question of the phase splitting of a system. The conditions of thermodynamic stability of a phase can be expressed in different ways. For the sake of lucidity and for the purpose of expedience, we limit further to binary systems only.

In a binary system under constant temperature and pressure, the separation into two phases necessarily takes place as far as holds<sup>12-14</sup>

$$(1/x_2) (\partial\mu_1/\partial x_1)_{T,P} = (\partial^2 G/\partial x_1^2)_{T,P} = (RT) G11 < 0, \quad (6)$$

where  $\mu_i$  is the chemical potential of the first component and  $G$  the molar Gibbs energy of the respective phase. The course of  $G11$  ( $= [\partial^2(G/RT)/\partial x_1^2]_{T,P}$ ) as a function of  $x_1$  for a homogeneous and heterogeneous system is given in Fig. 1a.

For the independent variables temperature  $T$ , molar volume  $V$  (or molar density  $d = 1/V$ ) and composition, the conditions of thermodynamic stability are usually formulated in terms of the molar Helmholtz energy  $A$  (refs<sup>12-14</sup>). For the labile region then holds

$$D_A = \begin{vmatrix} \partial^2 A/\partial V^2 & \partial^2 A/\partial V\partial x_1 \\ \partial^2 A/\partial V\partial x_1 & \partial^2 A/\partial x_1^2 \end{vmatrix} = (\partial^2 A/\partial V^2) (\partial^2 A/\partial x_1^2) - \\ - (\partial^2 A/\partial V\partial x_1)^2 = d^2 \cdot G11 \cdot (\partial P/\partial d)_{T,x_1} < 0. \quad (7)$$

Derivatives of the Helmholtz energy can be expressed by means of the derivatives

of pressure and fugacities

$$(\partial A/\partial V)_{T,x} = -P = -d^2(\partial A/\partial d)_{T,x}, \quad (8a)$$

and consequently

$$(\partial^2 A/\partial V^2)_{T,x} = -(\partial P/\partial V)_{T,x} = d^2(\partial P/\partial d)_{T,x}, \quad (8b)$$

$$(\partial^2 A/\partial V\partial x_1) = -(\partial P/\partial x_1)_{T,V} = -(\partial P/\partial x_1)_{T,d}. \quad (8c)$$

From the definition of the component fugacity, it is as well possible to obtain

$$(\partial^2 A/\partial x_1^2)_{T,V} = (\partial^2 A/\partial x_1^2)_{T,d} = RT[(\partial \ln f_1/\partial x_1)_{T,d} - (\partial \ln f_2/\partial x_1)_{T,d}]. \quad (8d)$$

The determinant  $D_A$  can be expressed in terms of these relations by the equation

$$D_A = RTd^2(\partial P/\partial d)_{T,x} [(\partial \ln f_1/\partial x_1)_{T,d} - (\partial \ln f_2/\partial x_1)_{T,d}] - (\partial P/\partial x_1)_{T,d}^2. \quad (9)$$

In previous paper<sup>11</sup>, the determinant of thermodynamic stability was defined

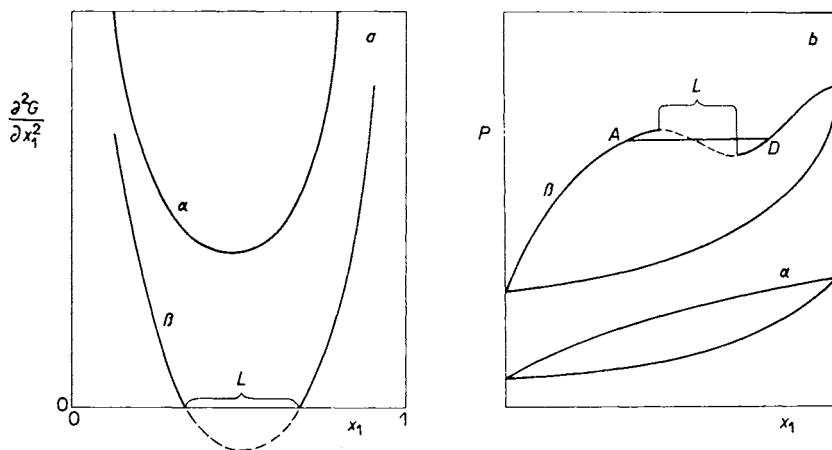


FIG. 1

Course of dependences  $\partial^2(G/RT)/\partial x_1^2 = G11$  and  $P$  on  $x_1$  and  $y_1$  for homogeneous ( $\alpha$ ) and heterogeneous ( $\beta$ ) system (in the liquid phase).  $L$  labile region (in this region a hypothetical course is encountered marked by dashed line)

by the relation

$$D_a = \begin{vmatrix} (\partial P/\partial d)_{T,x} & (\partial P/\partial x_1)_{T,d} \\ (\partial \ln f_1/\partial d)_{T,x} & (\partial \ln f_1/\partial x_1)_{T,d} \end{vmatrix}. \quad (10)$$

It is possible to show that

$$D_a = x_2 D_A/d^2 = x_2 G11(\partial P/\partial d)_{T,x}. \quad (11)$$

An advantage of Eqs (9) and (10) is the fact that only the coefficients needed to solve set of equations (3) appear in them, and so the thermodynamic stability of both phases is easy to verify.

In case of a binary system, the possible splitting into two phases or the existence of a labile region can be determined also from the calculated course of the boiling point curve (or even the dew point curve). From the differential conditions of equilibrium holds<sup>12-14</sup>

$$\begin{aligned} (\partial P/\partial x_1)_{T,\sigma} &= (y_1 - x_1) (\partial \mu_1/\partial x_1)_{T,P} / \{ (1 - x_1) [y_1(\bar{V}_1^g - \bar{V}_1^L) + \\ &+ y_2(\bar{V}_2^g - \bar{V}_2^L)] \} = \end{aligned} \quad (12a)$$

$$= (y_1 - x_1) RT \cdot G11 / [y_1(\bar{V}_1^g - \bar{V}_1^L) + y_2(\bar{V}_2^g - \bar{V}_2^L)], \quad (12b)$$

where the index  $\sigma$  points out that the pressure change with composition along the equilibrium curve (in this case the boiling point curve) is concerned. With regard to the course of  $(\partial \mu_1/\partial x_1)_{T,P} = x_2 RT \cdot G11$  (see Fig. 1a) and considering that the coexisting phases have in equilibrium identical pressure, the dependence of pressure on composition for unstable phase in heterogeneous region has an S-shaped course (outlined in Fig. 1b). In the labile region, if  $y_1 > x_1$  and  $\bar{V}_i^g > \bar{V}_i^L$  ( $i = 1, 2$ ), the pressure diminishes with increasing concentration of component 1. On the basis of Fig. 1b, we can determine very accurately the first approximation of composition (and density) of phases for calculating LLE (they correspond approximately to the points A, D in Fig. 1b).

During the calculation itself we proceeded in the following way: First the vapour-liquid equilibrium for a chosen temperature and composition  $x_1, x_1 + \Delta x_1, x_1 + 2\Delta x_1, x_1 + 3\Delta x_1, \dots$  was calculated. In the course of calculation, the fulfilment of the conditions of thermodynamic stability was checked by evaluating the determinant  $D_a$  (Eq. (10)) in both phases. Providing that the labile region was found out, the calculation was repeated with a lower value of  $\Delta x_1$  to obtain a more accurate first approximation which was determined by choosing two points A, D from both sides of the labile region which yielded approximately the same pressure (Fig. 1b).

After determining the first approximation according to the foregoing point, *i.e.* on establishing  $d^{(1)}, d^{(2)}, x_1^{(1)}, x_1^{(2)}$ , the solution of set of equations (3) followed.

Having been solved, it was possible.

- 1) to calculate the entire isotherm for new values  $x_{1,\text{new}}^{(1)} = x_1^{(1)} + \Delta x_1$ ,  $x_1^{(1)} + 2\Delta x_1$ ,  $x_1^{(1)} + 3\Delta x_1$ , etc.,
- 2) to calculate LLE at constant composition for temperatures  $T_{\text{new}} = T + \Delta T$ ,  $T + 2\Delta T$ ,  $T + 3\Delta T$ , etc.,
- 3) to calculate LLE for new values of temperature and composition.

On localizing the lower critical end point (LCEP) we proceeded similarly to that when determining the first approximation for calculation of LLE. The procedure is evident from Fig. 2 representing the system methane-n-hexane. At the temperature  $T_1 = 183$  K, all the chosen compositions on the boiling point curve satisfy the condition of thermodynamic stability and the equilibrium pressure is a monotonous (increasing) function of the liquid phase composition. At the temperature  $T = 183.5$  K in the concentration range  $x_1 = 0.935$  to  $x_1 = 0.95$ , the conditions of thermodynamic stability are not fulfilled, and the calculated equilibrium pressure exhibits an S-shaped course. Consequently the temperature corresponding to LCEP must lie between these temperatures. By halving the increments  $\Delta T$  and  $\Delta x_1$ , the LCEP can be localized

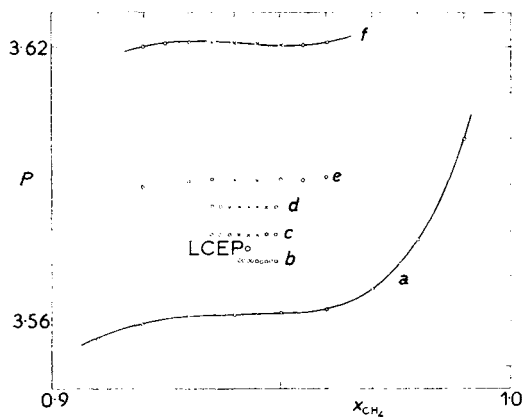


FIG. 2

Dependence of  $P$  (MPa) on  $x_{\text{CH}_4}$  for the system  $\text{CH}_4$ -n-hexane in the vicinity of LCEP at the temperatures:  $a$  183,  $b$  183.1,  $c$  183.15,  $d$  183.2,  $e$  183.25,  $f$  183.5 K

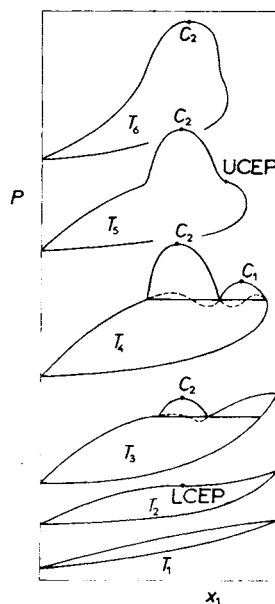


FIG. 3

Schematic course of isotherms in the system  $\text{CH}_4$ -n-hexane

very accurately. At the point corresponding to LCEP, the homogeneous liquid phase, which is in equilibrium with the vapour phase, begins to separate into two liquid phases on increasing temperature. In a similar way it is possible to determine also the position of the upper critical end point (UCEP) which occurs in these systems.

#### Application of the LLE Calculation to the Mixtures Methane-n-Hexane, Ethane-n-Eicosane and Ethane-n-Docosane

The method proposed was applied to the above-mentioned systems which make great demands on the calculation for the heterogeneous region of corresponding LLE is very small and occurs in the vicinity of critical point of more volatile substance. The used parameters of pure substances are given in Table I.

The behaviour of these systems is schematically plotted in Fig. 3 and is discussed in detail in literature<sup>15-22</sup>. At a temperature lower than LCEP, the isotherm shows a common course corresponding to the homogeneous liquid phase. At a temperature pertaining to LCEP, an inflex with zero slope appears on the boiling point curve, corresponding to the conditions  $G_{11} = 0$ ,  $\partial G_{11}/\partial x_1 = 0$  for the critical point. At a higher temperature (the isotherms  $T_3$ ,  $T_4$ ), the liquid phase already separates to form two phases to which pertains the critical point  $C_2$ . At the temperature  $T_4$ , which is higher than the critical temperature of the more volatile substance, there are two critical points  $C_1$  and  $C_2$  in the system. On increasing temperature, the critical point  $C_1$  is shifted to  $C_2$  as far as at a temperature  $T_5$  the heterogeneous region, to which pertains the critical point  $C_1$ , vanishes. An inflex point with zero slope corresponding to UCEP appears on the isotherm  $T_5$ . If we stem from the temperature  $T_6$  and gradually diminish temperature, it is possible to find up UCEP as a beginning of thermodynamic instability on the dew point curve.

TABLE I  
Used parameters of pure substances<sup>23</sup>

Substance	$T_c$ , K	$P_c$ , MPa	$\omega$
Methane	190.54	4.6030	0.0115
Ethane	305.43	4.8798	0.091
n-Hexane	507.43	3.0112	0.2957
n-Octadecane	745.04	1.2128	0.7895
n-Nonadecane	756.0	1.120	0.8271
n-Eicosane	767.04	1.1165	0.9065
n-Docosane	786.8 <sup>24</sup>	1.093 <sup>24</sup>	0.957 <sup>25</sup>



In Fig. 4, three isotherms are given as calculated in the methane–*n*-hexane system on the basis of the Redlich–Kwong–Soave equation<sup>12</sup>. For a comparison we reproduce as well the data found experimentally by Lin and coworkers<sup>18</sup>. Considering that the zero interaction parameters  $k_{ij}^a = k_{ij}^b = 0$  were used for the calculation, the obtained agreement can be considered as very good. Whereas the isotherm  $T = 193.15$  K is as given by Lin and coworkers<sup>18</sup> still below the temperature of UCEP, according to the equation of state used it is already above UCEP.

Four isotherms are given in Fig. 5 for the system methane–*n*-hexane from the vicinity of UCEP. At the temperature  $T = 192$  K, the heterogeneous region with the critical point  $C_1$  is clearly developed and on intersecting the curve of “dew points” at the points  $A, B$  (composition of the third coexisting phase is not depicted in the figure), the curve delimiting the heterogeneous region goes on through the metastable parts  $\beta'$ . The dew point curve  $d$  which has a typical S-shaped course between the points  $A$  and  $B$ , is quite analogous to the course of the boiling point

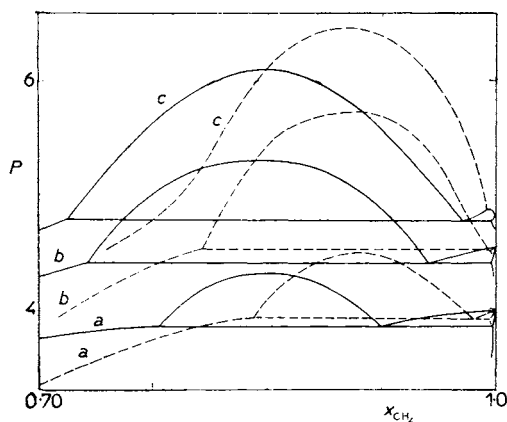


FIG. 4

Comparison of experimental (solid line) and calculated (dashed line) isotherms in the system  $\text{CH}_4$ -*n*-hexane at the temperatures:  $a$  186.23,  $b$  190.5,  $c$  193.15 K; pressure in MPa

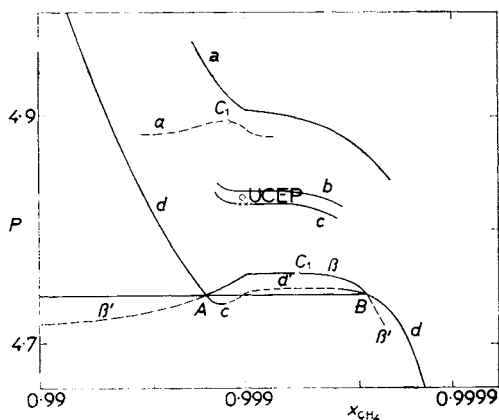


FIG. 5

Course of “dew point curves” in the vicinity of UCEP for the system  $\text{CH}_4$ -*n*-hexane at the temperatures:  $a$  193.15,  $b$  192.60,  $c$  192.55 (shows in a certain range thermodynamic instability),  $d$  192 K (the course in labile region is denoted by  $d'$ ). Curves delimiting heterogeneous region with the critical point  $C_1$ :  $\alpha$  193.15 K (metastable heterogeneous region),  $\beta$  192 K stable heterogeneous region (metastable parts denoted by  $\beta'$ )

curve above LCEP. At the temperature  $T = 193.15$  K which is higher than the predicted temperature of UCEP (Table II), the dew point curve is monotonously decreasing, and the heterogeneous region (metastable curve and with critical point  $C_1$ ) occurs below this curve. The curve  $b$ ,  $c$  correspond to the dew point curves close above ( $b$ ) and below ( $c$ ) the temperature of UCEP. On the isotherm  $T = 192.55$  K, points were still found which exhibit thermodynamic instability.

Very good agreement of both the critical temperatures follows from the comparison of the calculated and experimental data especially on comparing these results with the classical predictions of critical temperature in terms of the relations for activity coefficients<sup>1,3</sup>. But there exists worse agreement in obtained compositions. This shortage may be apparently impute partly to the mixing rules used and mainly to the simplest possible version of describing the  $P$ - $V$ - $T$  behaviour, *viz.* in terms of the cubic equation of state.

The calculated and experimental values of LCEP and UCEP in the systems ethane-icosane and ethane-*n*-docosane are given in Table II. All these values were obtained by means of the Redlich-Kwong-Soave equation with zero interaction parameters  $k_{ij}$ . Calculations were as well carried out for the systems ethane-*n*-C<sub>18</sub> and ethane-*n*-C<sub>19</sub> which as well exhibit limited miscibility in the liquid phase. This limited miscibility, however, was not found out on using the Redlich-Kwong-Soave equation of state with zero interaction parameters.

TABLE II  
Experimental and calculated parameters LCEP and UCEP

System	Point		$T$ , K	$P$ , MPa	$x_1$	Ref.
Methane- <i>n</i> -hexane	LCEP	exp.	182.46	3.4149	0.9286	18
		calc.	183.12	3.5760	0.9429	
	UCEP	exp.	195.91	5.205	0.9976	18
		calc.	192.58	4.826	0.9989	
Ethane- <i>n</i> -C <sub>20</sub>	LCEP	exp.	306.89	4.9535	0.9705	19
		calc.	304.64	4.7732	0.9919	
	UCEP	exp.	309.78	5.2870	0.9974	19
		calc.	306.90	5.0039	0.99975	
Ethane- <i>n</i> -C <sub>22</sub>	LCEP	exp.	300.72	4.388	0.963	20
		calc.	301.805	4.5127	0.9901	
	UCEP	exp.	307.98	5.145	0.9991	20
		calc.	306.31	4.9537	0.99989	

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