Critical Curves and Phase Equilibria of Binary Methanol-Systems for High Pressures and Temperatures

M. Neichel* and E. U. Franck

Institut für Physikalische Chemie, Universität Karlsruhe, Kaiserstraße 12, D-76128 Karlsruhe, Germany

Dedicated to Prof. Dr. E. Wicke on the occasion of his 80th birthday

The critical curves of binary systems of methanol combined with CH_4, N_2, H_2, CO and CO_2 have been determined experimentally up to 100 MPa and higher by Brunner. In the present work a rational equation of state of the perturbation type with a repulsion and an attraction term has been applied to reproduce these critical curves up to high pressures. A square well potential for intermolecular interaction is used. With pairwise combination rules for these potentials three adjustable parameters are needed. Values for these parameters, obtained from the fitting of the critical curves are used to calculate isotherms of the two-phase high pressure equilibrium surfaces for the four systems of methanol combined with CH_4, N_2, H_2, and CO. Three of these have not yet been investigated experimentally. It is suggested to use this procedure for predictions of the extent of three-dimensional two-phase regions in temperature-pressure-composition spaces.

I. Introduction

Thermophysical properties of binary fluid systems at supercritical and nearcritical conditions receive increased interest [1]. Industrial applications of supercritical solvents are developed. Supercritical aqueous fluids are of importance in geochemistry [2] and are proposed for toxic waste disposal [3]. Binary systems have a critical curve between the two critical points in the three-dimensional pressure-temperature-composition space [4]. Of particular interest are nonpolar-polar mixtures, which often have an interrupted critical curve. Its upper branch begins at the critical point of the higher boiling partner, it proceeds to higher pressures and temperatures and ends at an often unaccessible "upper critical endpoint". A number of critical curves with the related phase equilibrium data have been determined experimentally up to pressures of 200 MPa for systems of water combined with rare gases, with atmospheric gases and with alkanes. These critical curves could also be calculated with a special "rational" equation of state.

The critical temperature of methanol is considerably lower than that of water ($T_c(CH_2OH) = 240\,°C$, $T_c(H_2O) = 374\,°C$). Accordingly, supercritical methanolic phases can exist at much lower temperatures

than supercritical aqueous systems. Brunner [5] has measured critical curves for several binary methanol systems up to about 140 MPa. Except for methanol-methane, however, no determinations of the limits of the two-phase regions at subcritical conditions are available. It was the purpose of the present work to create such data by calculation with the equation of state mentioned above. This equation has a repulsion and an attraction term and only three adjustable parameters related to the molecular models. If one succeeds to describe the critical curves with reasonable parameters, these parameters can be applied to calculate the three-dimensional phase equilibrium surfaces. In the case of CH_3OH-CH_4 such surfaces have been measured and the acceptable agreement with the calculations justifies the application of the procedure to other binary methanolic systems.

II. Calculation Procedure

In order to determine phase equilibria and critical phenomena of the binary systems, the stability criteria formulated with the Helmholtz energy A have to be observed:

$$\left(\frac{\partial^2 A}{\partial V^2}\right)_{T,x} > 0, \quad \left(\frac{\partial^2 A}{\partial T^2}\right) < 0,$$
$$\left(\frac{\partial^2 A}{\partial V^2}\right)_{T,x}\left(\frac{\partial^2 A}{\partial x^2}\right)_{T,v} - \left(\frac{\partial^2 A}{\partial V \partial x}\right)_T > 0. \tag{1}$$

* Present address: Institut für Technische Chemie, Forschungszentrum Karlsruhe, P.O. Box 3640, D-76021 Karlsruhe, Germany.

Reprint requests to Prof. Dr. E. U. Franck.

The molar Helmholtz energy A_m of the fluid mixture in dependence of temperature, molar volume V_m and mole fractions x_i is accessible by integration of a pressure explicit equation of state based on a reference state with chemical potentials μ_i^θ and pressure p^θ. Details were given previously [6]–[11].

$$A_m(T, V_m, x_i) = \sum x_i \mu_i^\theta - RT + RT \sum x_i \ln x_i$$
$$+ RT \ln \left(\frac{RT}{p^\theta V_m} \right) + RT \left[\frac{4 \beta_x}{V_m - \beta_x} + \frac{\beta_x^2}{(V_m - \beta_x)^2} \right]$$
$$+ RT \frac{B_x^2}{C_x} \ln \left(\frac{V_m}{V_m - \frac{C_x}{B_x}} \right). \tag{2}$$

An appropriate equation of state is derived with a perturbation method using a square well molecular interaction potential [7, 8, 12]. It has a repulsion term (Carnahan-Starling-One-Fluid, CSOF) [13] and an attraction term (Square-Well-Pade-Approximant, SWPA). The pressure, with repulsion and attraction terms, is given by

$$p = RT \frac{V_m^3 + V_m^2 \beta_x + V_m \beta_x^2 - \beta_x^3}{V_m (V_m - \beta_x)^3}$$
$$+ RT \frac{B_x}{(V_m^2 - V_m C_x / B_x)}. \tag{3}$$

Molecular volumes:

$$\beta_{ij} = \frac{\pi}{6} \sigma_{ij}^3 N_A,$$
$$\beta_{ii}(T) = \beta_{ii} \left(\frac{T_{ci}}{T} \right)^{3/m}, \tag{4}$$
$$\beta_x = \sum \sum x_i x_j \beta_{ij}.$$

T_{ci} = critical temperature; m = temperature dependence exponent.

Attraction virial terms:

$$B_x = \sum \sum x_i x_j B_{ij},$$
$$C_x = \sum \sum \sum x_i x_j x_k C_{ijk},$$
$$B_{ij} = -4 \beta_{ij} (w_{ij}^3 - 1) \Delta_{ij},$$
$$C_{ijk} = -\frac{1}{3} (I_{33} \Delta_{ij} \Delta_{ik} \Delta_{jk}) \tag{5}$$
$$- \frac{1}{3} (I_{11} \Delta_{ij} + I_{12} \Delta_{ik} + I_{13} \Delta_{jk})$$
$$+ \frac{1}{3} (I_{21} \Delta_{ij} \Delta_{ik} + I_{22} \Delta_{ij} \Delta_{jk} + I_{23} \Delta_{ik} \Delta_{jk}),$$
$$\Delta_{ij} = \exp \left(\frac{\varepsilon_{ij}}{kT} \right) - 1.$$

The auxiliary functions I_{11} to I_{33} are given in [7, 8, 14].

The square well molecular interaction potential has three parameters: the core diameter σ, the relative width of the square well w in units of σ and its depth ε. The combination rules are applied:

$$w = w_{ij} = w_{ii} = w_{jj},$$
$$\varepsilon_{ij} = k_\varepsilon \sqrt{\varepsilon_{ii} \cdot \varepsilon_{jj}}, \tag{6}$$
$$\sigma_{ij} = \frac{k_\sigma}{2} (\sigma_{ii} + \sigma_{jj}).$$

The quantities w, k_ε, and k_σ are adjustable parameters.

The methanol molecules have a rather high dipole moment of 1.70 Debye. The above equation of state does not specifically consider dipole moments. It is expected that the attraction term in (3) takes care of dipole interaction. This expectation appears to be justified because a number of binary polar-nonpolar aqueous systems could be calculated with reasonable success in this way (dipole moment of $H_2O = 1.85$ Debye). The quantities σ_{ii} and ε_{ii} are taken from the critical properties of the two pure compounds. A slight temperature dependence of the hard core diameter σ is introduced with the exponent $3/m$ in (4). For the present purpose always $m = 10$ is used. The mixing coefficients k_ε and k_σ have been adjusted to obtain optimal agreement between experimental and calculated critical curves. The values of these parameters were subsequently used to determine boundary isotherms for the two-phase regions in the temperature-pressure-composition diagrams.

III. Results

A) Critical Curves

Figure 1 shows the critical curve for methanol-methane in comparison with experimental curves from Francesconi et al. [15] and from Brunner [5]. The calculated curve describes both experimental data sets reasonably well up to 50 MPa, although it is slightly to low. Above 50 MPa there is a discrepancy between the experimental curves of Brunner and Francesconi et al. With one set of parameters w, k_σ and k_ε, a better fit could be obtained to the Francesconi curve. Of the four systems CH_3OH with CH_4, N_2, H_2 and CO the systems CH_3OH–CH_4 and CH_3CO are the only ones with a critical curve which at pressures of 150 MPa extends to temperatures well below 400 K.
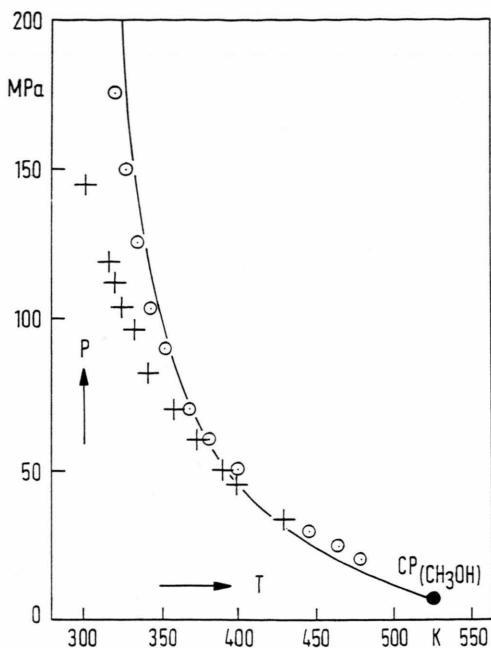
Fig. 1. Critical curve for CH_3OH-CH_4 in the pressure-temperature projection. ——: Calculated with equation of state (3). $w = 2.8$, $k_\sigma = 0.90$; $k_\varepsilon = 0.96$; ooo: Experimental points, Francesconi et al. [15]. + + +: Experimental points, Brunner [5]; CP: Critical point of CH_3OH.
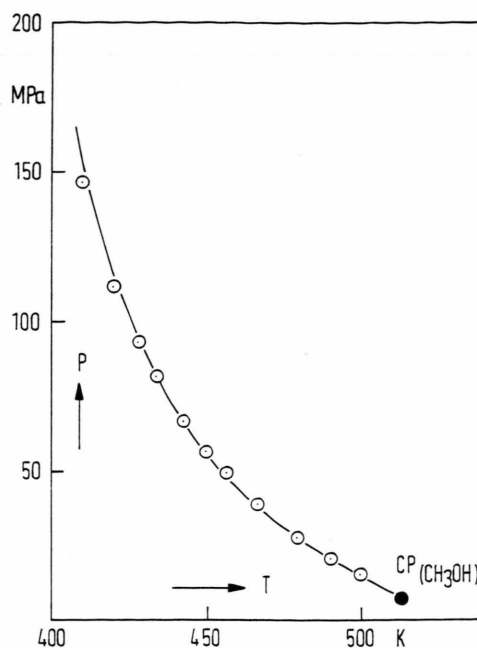

Fig. 2. Critical curve for CH_3OH-N_2 in the pressure-temperature projection. ——: Calculated with equation of state (3). $w = 2.8$; $k_\sigma = 0.95$; $k_\varepsilon = 0.74$. ooo: Experimental points, Brunner [5]. CP: Critical point of CH_3OH.

In Fig. 2 experimental and calculated critical curves for methanol-nitrogen are shown. The agreement is very good. The discrepancies are probably smaller than the experimental uncertainties. Of similar quality is the calculation of the methanol-hydrogen critical curve shown in Figure 3. Measurements extend only up to 100 MPa. The curve is almost linear to this pressure. For methanol-carbon monoxide also no experimental critical values above 100 MPa are available. Figure 4 presents the quality of the reproduction.

The agreement is good, although not quite as good as for nitrogen. The situation for methanol-carbon dioxide is different. Here the critical curve as shown by Brunner [5] is of the uninterrupted type and extends between the two critical points of methanol and carbon dioxide as shown in Figure 5. Such behaviour has been observed previously with combinations of two polar compounds – as with water-ammonia. Here the relatively high quadrupole moment and molecular weight of CO_2 probably account for this phe-

Table 1. Adjustable potential parameters w, k_σ, k_ε see (6), for the five investigated methanolic systems together with critical constants of nonpolar partners. T_c and p_c for methanol: 513 K and 8.10 MPa.

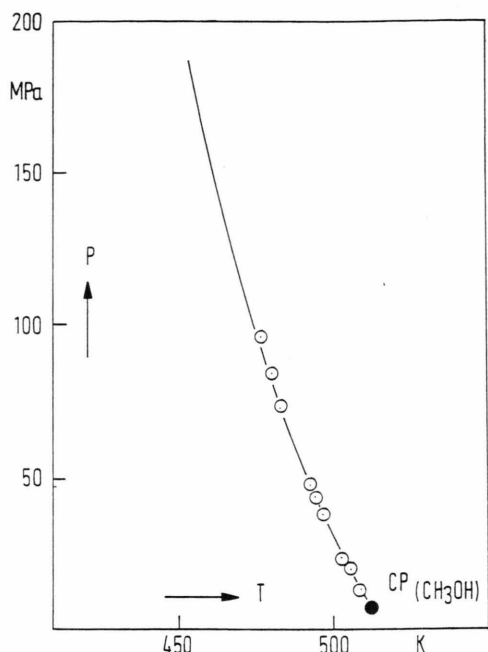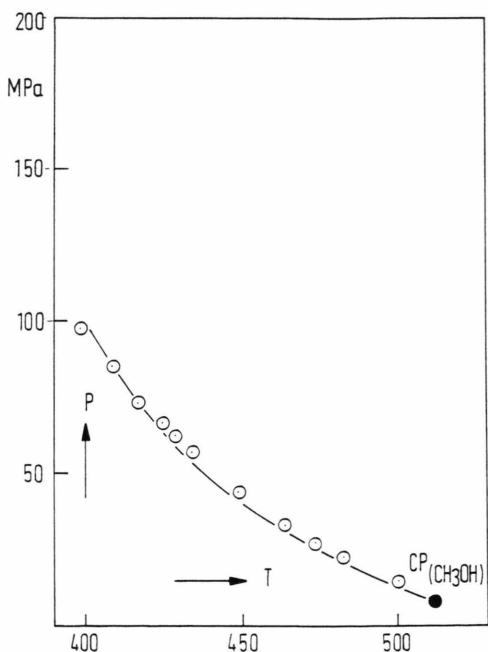|	CH_3OH-CH_4	CH_3OH-N_2	CH_3OH-H_2	CH_3OH-CO	CH_3OH-CO_2
w	2.8	2.8	2.8	2.8	2.6
k_σ	0.90	0.95	1.00	0.93	0.94
k_ε	0.96	0.74	0.88	0.85	1.16
	Critical temperature and critical pressure of nonpolar partners				
T_c/K	190.6	126.2	33.2	132.9	304.2
P_c/MPa	4.60	3.37	1.30	3.50	7.38

Fig. 3. Critical curve for CH_3OH-H_2 in the pressure-temperature projection. ——: Calculated with equation of state (3). $w = 2.8$; $k_\sigma = 1.00$; $k_\varepsilon = 0.88$. ooo: Experimental points, Brunner [5]. CP: Critical point of CH_3OH.
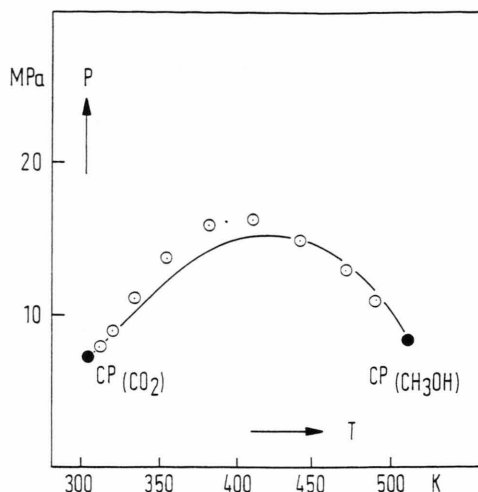

Fig. 5. Critical curve for CH_3OH-CO_2 in the pressure-temperature projection. ——: Calculated with the equation of state (3); $w = 2.6$, $k_\sigma = 0.94$; $k_\varepsilon = 1.16$. ooo: Experimental points, Brunner [5]. $CP(CO_2)$, $CP(CH_3OH)$: Critical points of pure compounds.

nomenon. The procedure is of an iterative character, beginning at the critical point of methanol. Using parameters k_ε similar to those applied for the other small molecules, an uninterrupted connection between the two critical points could not be achieved.

B) Phase Equilibria

Figures 6–9 present calculated pressure-composition, $p - x$, diagrams with isothermal boundary curves of the two phase region. The maxima of these curves are points on the respective critical curve. The two phase region is below these curves. For methanol-methane a comparison with experimental curves of Francesconi et al. [15] is possible. The agreement is not as good as for the critical curves. One has to consider, however, that the experimental determination of composition in these regions is often more difficult than the pressure-temperature determinations. It is assumed that the calculated isotherms of Figs. 6–9 give a useful basis to estimate the regions of homogeneous and two-phase behaviour for practical purposes.
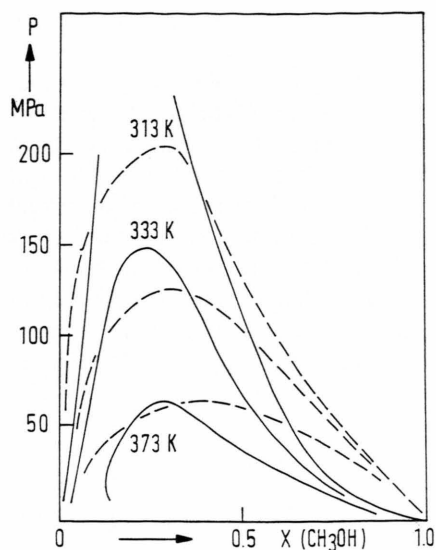

Fig. 4. Critical curve for CH_3OH-CO in the pressure-temperature projection. ——: Calculated with equation of state (3). $w = 2.8$; $k_\sigma = 0.93$; $k_\varepsilon = 0.85$. ooo: Experimental points, Brunner [5]. CP: Critical point of CH_3OH.
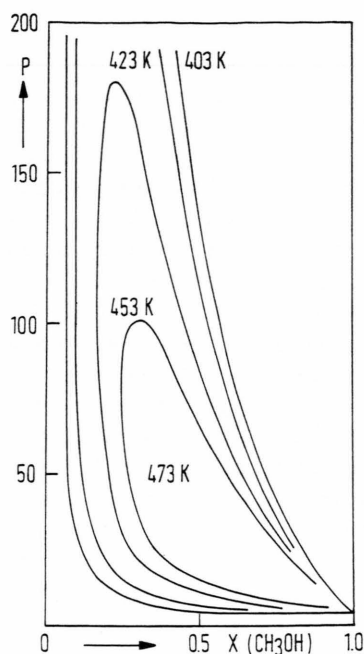
Fig. 6. Isothermal two-phase boundary curves for CH_3OH-CH_4 in the pressure-composition projection. ———: Calculated with the equation of state (3); $w = 2.8$; $k_\sigma = 0.90$; $k_\varepsilon = 0.96$. ---: Experimental curves, Francesconi et al. [15].
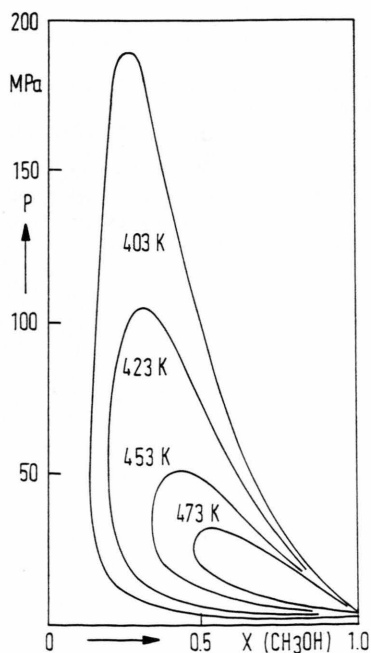

Fig. 8. Isothermal two-phase boundary curves for CH_3OH-H_2 in the pressure-composition projection. ———: Calculated with the equation of state (3); $w = 2.8$; $k_\sigma = 1.00$; $k_\varepsilon = 0.88$.

Fig. 7. Isothermal two-phase boundary curves for CH_3OH-N_2 in the pressure-composition projection. ———: Calculated with the equation of state (3); $w = 2.8$; $k_\sigma = 0.95$; $k_\varepsilon = 0.74$.
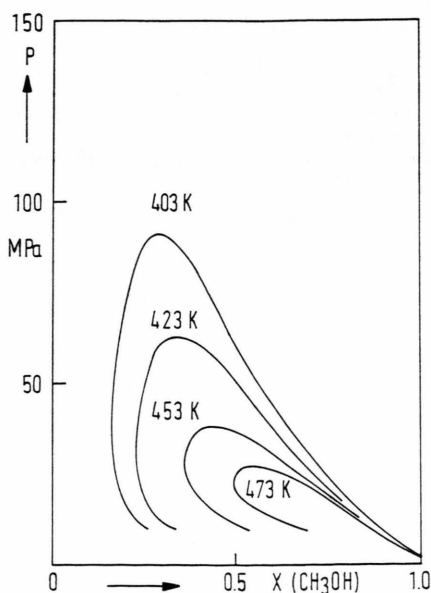

Fig. 9. Isothermal two-phase boundary curves for CH_3OH-CO in the pressure-composition projection. ———: Calculated with the equation of state (3); $w = 2.8$; $k_\sigma = 0.93$; $k_\varepsilon = 0.85$.

IV. Discussion

Table 1 gives a compilation of the parameters used with the equation of state for the five compounds combined with methanol and with the critical constants of the nonpolar partners. The relative width of the square well potential is constant with the exception of carbon dioxide. The k_σ and k_ε values are all close to unity, again with the exception of CO_2. It seems as if the three compounds with particularly low critical temperature need relatively low k_ε-values and k_σ-parameters slightly closer to unity. For approximate predictions of two-phase regions for similar, not yet experimentally investigated systems, parameters in analogy to those of Table 1 might be chosen. It should be emphasized, however, that the rather uncomplicated equation of state (3) should be used only at elevated temperatures, perhaps from a reduced temperature (related to $T_c(CH_3OH)$) of 0.6 and above.

The binary polar-nonpolar systems with water as one component generally have a critical curve which, beginning at $T_c(H_2O)$, passes through a temperature minimum when proceeding to high pressure. None of the interrupted critical curves of the four methanolic systems investigated here exhibits a temperature minimum below pressures of 100 MPa. It is interesting to observe the methanol-hydrogen curve which, from $T_c(CH_3OH)$, extends to lower temperatures at higher pressures. It is of the "second kind" of critical curves, according to common nomenclature. Only CH_3OH-He and CH_3OH-Ne, according to Brunner, have curves of the "first kind" which proceed to higher temperatures and high pressures immediately. In aqueous systems the curves of H_2O-He and H_2O-Ne behave in the same way [10]. The H_2O-H_2-curve, in the p-T-projection however, ascends vertically at constant temperature from $T_c(H_2O)$ and $p_c(H_2O)$ to high pressures. – The calculations on the basis of (3) are able to reproduce the different behaviour in the methanolic and aqueous systems.

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