Fluid Phase Equilibria

Phase Boundaries of Liquid-Gas Fluids and Liquid-Liquid Mixtures: A Unified Description

Sergey V. KAZAKOV* and Natalia I. CHERNOVA

Faculty of Physics, Lomonosov State University, 119899 Moscow, Russia

Key Words: coexistence curve, vapor-liquid equilibria, liquid-liquid equilibria, critical state, asymmetry, pure fluid, mixture, thermodynamic theory of regular mixing, scaling.

* To whom correspondence should be addressed.

ABSTRACT

In this paper we propose a way of uniform consideration of the coexistence curves as for pure fluids and for binary mixtures in the same compositional coordinates. The concept of the method starts from the idea that each molecular system tends to the formation of local liquid structures. Going to the composition of the structures, a phase-separation diagram takes "a compositional" symmetry. A modified thermodynamic equations based on the regular mixing model gives surprisingly good agreement with experimental data, taken from literature, even for the systems with complex topology phase diagram. According to the approach the generalized scaling for the systems with multi-critical points can be naturally derived. We carry out unified comparison of concentration and energy parameters in the frame of the regular mixing model and of the scaling laws both for pure fluids and for binary mixtures of different origin.

INTRODUCTION

One of the interesting features of the coexistence curves (CCs) for the pure fluids and binary liquid mixtures is the asymmetry of their shapes. The modern phase transition theory [1,2] attributes pure liquids, their mixtures, magnetics and 3D - Ising model to the same class of universality. The deduction of a global equation of state for all representatives of the same universality class is one of the topical area in current research [3-7]. The problems of analytical representation of the CC are nowadays recognized to be of identical to all phase-separating systems: (i) non-classical properties behavior near the critical point (CP) and, as a sequence, there is no universally valid expression described the shape of the CC in the wide range of the thermodynamic parameters; (ii) some systems exhibit a variety of liquid-liquid equilibrium phase diagrams, including the cases with several critical points [8]; (iii) compositional asymmetry of the CC shows itself as a deviation of critical mole fraction from 0.5 and as anomalous properties of the rectilinear diameter of the CC [9-14].

A comparison between shape of the pure fluid liquid-gas CC and binary mixtures liquid-liquid CC is made difficult by the fact that (i) composition parameters are chosen variously for different systems in accordance with experimental conveniences, applied measuring technique features, and/or sample preparing method; (ii) the asymmetry of CC is observed in real systems, whereas existed theories and models are initially symmetric relatively to CP.

In previous papers [15,16] we have propose a procedure of transition to the composition parameters, in which a CC has symmetric view.

Up to now there are no attempts to represent a liquid-gas CC in symmetric view with advantage. In our opinion this is due to the fact that each pure substance has its own density scale relatively to CP, whereas concentration scale of mixtures is restricted by the interval from 0 to 1. Moreover, a CC for pure fluid used to be represented as a "density-temperature" diagram or a "refractive index-temperature" diagram. The relationship between the refraction index and the density is the object of many experimental

and theoretical investigations [17,18]. The possibility of deducing concentration and density from the data of refractive index measurements is the goal of such studies.

In this paper we analyze the shape of the liquid-gas CC of one-component systems and show that different composition coordinates lead to distinguished critical concentration parameters. Introduction of some normalized composition coordinates, to have analogy with mole fractions in binary mixtures, makes it possible to symmetrize the CC and to get identical energy parameters both for "ρ-T" and for "n-T" phase diagrams. We also demonstrate that parameters of the symmetrized liquid-gas and liquid-liquid CC can be compared in the unified concentration and energy scales. The energy parameters of a pure fluid liquid-gas CC and a binary mixture liquid-liquid CC are calculated on the frame of both the new thermodynamic model of regular mixing and the generalized scaling approach.

LIQUID-GAS COEXISTENCE CURVES: CHOICE OF COMPOSITION PARAMETERS AND SYMMETRIZATION

According to the modern theories and models [19-23] of phase equilibrium, the asymmetry of the CC cannot be taken into account by none of the way besides introducing density fluctuations, which would be interpreted [15,16] as an ability of system to form energetically preferred and dynamically stable molecular units, assumed the fundamental symmetry of mutual exchange between coexisting macroscopically different components.

For completeness, we will only briefly review the basic points of our approach to symmetrization of CC [15,16]. It is important that components of solution are asymmetric relatively to the composition of molecular aggregates: one component (A) is "a solvent" which forms matrix represented by multimer molecule [mA], and another component (B), associating with molecules of A component, yields the stoichoimetric compound [nA kB] dissolved in the matrix. Formation of the indicated structure units can be represented by the quazichemical equation

$$xA + (1-x)B \Leftrightarrow x_s[mA] + (1-x_s)[nA \cdot kB]. \qquad (1)$$

Here x is the mole fraction (mol.fr.) of component A, x_s is the normalized mol.fr. of aggregates [mA]. The mole ratios of initial components X = x/(1-x) transform to the mole ratios of symmetric coordinates by the following way

$$X_s = \frac{x_s}{1 - x_s} = \frac{X - X_o}{S} . \qquad (2)$$

Parameter X_o characterizes some relative composition of component A, limiting the region at which isotropic solution of dispersed aggregates [nA kB] exists.

$$S = X_c - X_o = \frac{m}{k}, X_o = \frac{x_o}{1 - x_o} = \frac{n}{k}, X_c = \frac{x_c}{1 - x_c} = \frac{m + n}{k}, \qquad (3)$$

where x_o is the limiting concentration of forming freely dispersed aggregates, x_c is the critical concentration. Evidently, $x_{sc} = 0.5$ and $X_{sc} = 1$ for symmetric system. The parameters S and X_o are calculated independently by the least-mean-square fitting, using the properties of symmetric CC [15,16].

$$\begin{aligned} x_s^{/} + x_s^{//} &= 2x_{sc} = 1, \\ X_s^{/} X_s^{//} &= X_{sc}^2 = 1, \end{aligned} \qquad (4)$$

where the prime and the double prime refer to the left and right branches of the CC, respectively.

Therefore, these results indicate that the symmetrization have to be controlled by two concentration parameters x_c and x_o. On the example of a pseudobinary microemulsion system Water/Aerosol OT/n-decane we have shown [24,25] that this parameters correspond to the definite characteristic points on the phase diagram.

To apply the approach to the liquid-gas CC of one-component system it is necessary to transit to normalized composition parameters analogous to mole fractions in binary mixtures. In our point of view the transition is possible if we assume the existence of a limiting density, ρ_o. Moving along the saturation line, the density of system cannot exceed this value of ρ_o. Normalizing the density of system on the limiting density , we formally find "a concentration" parameter $x = \rho/\rho_o$. If an experimental liquid-gas equilibrium boundary is represented by the temperature dependence of the refractive index, than we are able to associate measured refractive index n with the density ρ,

using in the first approximation the Lorentz-Lorenz relationship

$$L = \frac{n^2 - 1}{n^2 + 2} = \frac{4}{3}\pi\alpha\rho ,$$

where α is the electron polarizability. In the case we take $L_o = (n_o^2-1)/(n_o^2+2)$ as a value proportional to the limiting density. Hereby, the consequent concentration parameter equals to $x = L/L_o$, where n_o is the limiting refractive index of liquid, connected with ρ_o.

At present there are no experimental data on direct measurement of parameter ρ_o which is individual for every substance and would be a characteristic of the liquid-gas phase equilibrium. The approach described gives a possibility of independent calculation of the parameter ρ_o from the experimental data on the liquid-gas CC. It will allow us to associate ρ_o with microscopic parameters of the substance and to understand its physical meanings.

In fig.1a and b the CCs of CO_2 cannot be compared quantitatively because they are represented in different “composition” parameters. Here the critical and limiting composition characteristics of the system are schematically specified. The transition to the "quasimole" fractions, x, is represented in fig.1c. The CCs obtained from the density data and from the refractive indices data are shifted relatively to each other. The displacement observed cannot be explained only due to experimental errors. It will be most likely caused by a nonlinear variation of the polarizability α alone the saturation line.

But even if we use this coordinates, the liquid-gas CC appears to be asymmetric. The deviation of the critical mole fractions x_c from 0.5 indicates that in pure fluids density fluctuations lead to the asymmetry of composition exchange between coexisting phases. These notions are in agreement with well known concept of associated liquids [26], according to which the molecules of the same substance can simultaneously be contained in two thermodynamically different states A and A'. A solvent matrix structurally can be written down as a multimer molecule [mA] and dissolved within this matrix molecular aggregates described by the formula [kA']. Molecules A and A' cannot give rise to mixed structures [nA·kA'], that is why X_o always equals to zero for a pure liquid, and from (1)-(3) we have

$$X_s = X / X_c , \quad (5)$$

where $X_c = m/k$, $x_c = \rho_c/\rho_o$, ρ_c is the density of fluid in the liquid-gas CP.

We used the properties of symmetrized CC (4) to determine the composition parameters ρ_c and ρ_o (or n_c and n_o) from experimental data on the liquid-gas equilibrium diagrams, taken from literature (see Table 1). We applied these data to compare the shape and parameters of the CCs obtained by different methods in various composition coordinates g (order parameter).

In fig.1d and e the symmerized CCs of CO_2 are demonstrated. We notice that there are no rectilinear diameter anomaly. Concentration parameters which symmetrize the CC of binary mixtures of different origin, are represented in [16].

Thus only after symmetrization (independent determination of concentration parameters) it becomes possible to compare the CC shape in uniform coordinates "x_s-T" and to carry out a theoretical analysis of the equilibrium boundaries (calculation of energy parameters).

THEORETICAL ANALYSIS OF SYMMETRIZED COEXISTENCE CURVES

General equations of extended theory of regular mixing

The concepts of symmetric regular solution theory [27] can be applied to the symmetrized CC. In a wake of J.B.Thompson [28], we are here using the term regular solution in a more general sense to denote any solution conforming to a simple equation of state. According to the regular mixing theory the excess thermodynamic functions are proportional to the $x_i x_j$, i.e. to the probability of finding a couple of i-j type in some fixed position. Equations of binodal and spinodal are obtained as a result of calculation the first and second derivatives of free energy of mixing on concentration, respectively, and setting them equal to zero:

$$\text{(binodal)} \quad X_s = \exp\left(\frac{X_s - 1}{X_s + 1} \cdot \frac{W_G}{RT}\right), \quad (6)$$

$$\text{(spinodal)} \quad X_s = 2 x_s^2 \frac{W_G}{RT}, \quad (7)$$

where $W_G = W_H - T W_S$ is the general interaction energy parameter expressed in units of

free energy, R is the gas constant. Critical temperature is found from the extremum conditions, coincided for both curves (6) and (7). We have shown [25,29] that for any number of critical points the parameter W_G can be expressed in universal form

$$W_G = 2RT^* + W_s(T^* - T). \quad (8)$$

$T^* = f(T, T_{ci})$ is the so called current critical temperature, which is the function of the absolute temperature T and critical temperatures T_{ci}. For example, in the case of one critical point: $T^* = T_c$; if the system has two critical points: $T^* = \frac{T_u T_l + T^2}{T_u + T_l}$; for the case of three critical points: $T^* = \frac{T_{c1}T_{c2}T_{c3} + T_{c2}(T_{c1} + T_{c2} + T_{c3}) - T^3}{T_{c1}T_{c2} + T_{c1}T_{c3} + T_{c2}T_{c3}}$.

It should be noted, that the difference (T*-T) is referred to the relative distance of system with several critical points from the critical state, and is connected with the general reduced temperature

$$\tau_o = \frac{T^* - T}{T_o} = \tau_1 \tau_2 \cdots \tau_n , \quad (9)$$

where $\frac{1}{T_o} = \frac{2R + W_S}{W_H} = \sum_{i=1}^{n} \frac{1}{T_{ci}}$ and T_o has been named [25] as the enthalpy-entropy compensation temperature and for systems with one critical point coincides with the critical temperature T_c, $\tau_i = (T-T_{ci})/T_{ci}$ is the reduced temperature.

We have studied temperature dependence of W_S/R for the systems taken from literature. It has been shown [25] that near critical point W_S/R increases up to the infinity, and the reduced temperature dependence can be satisfactorily fitted by the power-law function with σ critical exponent

$$W_S / R = B\tau^{-\sigma} . \quad (10)$$

Optimum value of critical exponent σ was found by calculating the dependence of multivariable function

$$\delta F = \sqrt{\frac{\sum_{i=1}^{N} (x_i^{\exp} - x_i^{calc})^2}{N - Z}} \qquad (11)$$

on σ for about 85 systems taken from literature. Here, N is the number of points, Z is the number of fitting parameters. One can see in fig.2 that sharp minimum of the function corresponds to the optimum value of σ = 0.298 which appears to be very close, but somewhat less, to the main critical exponent β of the CC. Since there are strong dependence of fitted critical amplitudes B on critical exponent σ it is not be able to interpret unequivocally the variations of the amplitudes B from system to system. That is why we used the value σ = β = 0.325 in calculation of critical amplitudes B. At this fixed value critical amplitudes for various composition parameters become almost equal to each other for the same liquid (see, Table 2). Calculated critical temperatures are in good agreement with experimental values.

It is followed from here that the regular mixing pattern is ubiquitous and requires reexamination of a large body of experimental data interpretations.

Scaling interpretation of multi-critical point coexistence curve

Considerable recent attention has been focused on binary and pseudobinary liquid mixtures having two CPs [22,23,30,31].The choice of a field variable τ_o on the basis of the isomorphism hypothesis has been justified by Malomuzh and Veytsman [31]. The thermodynamic approach developed yields a simple and a clear sight on the complex topology CC, generalizing the choice of a field variable not only for the double critical point, but for the critical double point, as well as for the CC with any number of the CPs.

To spread the ideas of the scaling theory on the systems with several CPs it is necessary to define a simultaneous crossover from one CP to another, and vice versa. Such a transition can be available by simple replacing the critical temperature T_c on the current critical temperature T*, and the reduced temperature on the generalized reduced

temperature. In this case the symmetric CC with any number of the CPs is described by the simple scaling

$$x_s - 0.5 = \pm B \tau_o^{\beta}, \tag{12}$$

signs "+" and "-" refer to the left and the right branches of the CC. Herein $\tau_o = (T^*-T)/T_o$ is the general reduced temperature, which can be expressed using (12) in the following form

$$\tau_o = \pm\left[\frac{x_s - 0.5}{B}\right]^{1/\beta}. \tag{13}$$

In particular of systems with two CPs an equation of binodal looks like the roots of the quadratic equation

$$T = \frac{T_u + T_l}{2} \pm \sqrt{\frac{(T_u + T_l)^2}{4} - T_u T_l (1 - \tau_o)}. \tag{14}$$

The crossover from one CP to another occurs at the temperature $T_t = \sqrt{T_u T_l}$, at which the square root expression equals to zero. Here signs "+" and "-" refer to $T > T_t$ and $T < T_t$, respectively. Analyzing (14) one can conclude that at $\tau_o \leq 0$ we have the closed-loop CC, and at $\tau_o > 0$ we have two unclosed CCs ($T_u < T_l$).

The optimum value of critical exponent β=0.314 has been obtained on the experimental data for 85 systems of different nature, including systems with two CPs. However, as for the CC with one CP [16] it was found out that there exists a strong dependence of fitted critical amplitude B on the critical exponent β. As a result we would be forced to calculate critical amplitudes at fixed value β= 0.325, which is equal to the Ising model critical exponent. Surprisingly very good description of the entire solubility curve for systems with two CPs is demonstrated in figs 3 and 4.

Uniform description of the phase-separating boundaries for the pure fluids and binary mixtures of different nature

Table 3 gives the results of the least-mean-square fitting of symmetrized CC for the systems of different origin, including alkali-silicate binaries; polymer solution; two mixtures that display the closed-loop CC; one system with two unclosed miscibility gaps; mixtures of polar and nonpolar liquids in various combinations, crystalline solution; gaseous mixture under pressure, pure fluid (under normal conditions gas); liquid alkali metal; and inert gas.

The absolute values of critical amplitudes B obtained on the frame of the regular mixing model range between 0.15R to 21R for the systems studied, characterizing the contribution to the entropy of mixing of changes in the internal degrees of freedom $\Delta S = x_1 x_2 W_S$. In the case of system with the upper CP critical amplitudes $B = W_S/R$ are the largest known for polymer solution and are the smallest known for oxide system. Large negative values of B are characteristic of the closed-loop CC, and large positive values are for systems with two unclosed CCs, when $T_u<T_l$. The most of the typical binary mixtures exhibit critical amplitude B ranged from about 1 to 3.

On the other hand, the absolute value of B ranges between 0.59 and 2.12 in the case of the CC scaling representation.

All studied CCs for the systems of different origin can be depicted by universal scale (fig.5). Comparing the CC of c-C_6H_{12}/polystyrene, which has a large value of B, with the CC of systems with several CPs, one can conclude that the width of an immiscibility gap depends not only on the value of critical amplitude. It is easily noticeable that critical amplitudes for the systems with two CPs (Table 3) differ not very considerably, whereas primary CCs exhibit strong distinctions in the width of the immiscibility gaps. The distinctions may be associated with the asymmetry of the CC caused by formation of different in size and composition local liquid structures.

In magnified scale (fig.6) the symmetrized CCs for the systems with two CPs show that (a) the closed-loop CC in normalized view are equivalent to the lower CP, and two unclosed CCs correspond to the Upper CP; (b) in the latter case both parts of

the CC with upper CP (3') and lower CP (3") are distinguished, even if they are described by the (6) with the same parameters.

CONCLUSION

We have shown that the liquid-gas CCs of pure fluids can be represented in concentration-binary-mixture-like coordinates assuming the existence of a limiting density of a system. The procedure for symmetrizing the binary mixture CC which have been suggested by us [15,16] is applied to the pure fluids. The concept, which must be introduced to accomplish this, is the assumption that the molecules of a liquid can be simultaneously contained in two different states. This transformation symmetrizes the CCs.

The thermodynamic equations of regular mixing adopted to the critical behavior appear to represent the data of symmetrized CCs well as for pure fluids as for binary liquid mixtures of different nature including the multi-critical phase diagrams. The generalized scaling for the latter systems are naturally derived from the approach.

Generalizing the obtained results we note that the procedure of the CC symmetrizing allows us to separate the calculations of concentration and energy parameters both of the modified regular mixing equations and of the generalized scaling lows, thus providing the most convenient way of quantitative description of the phase-separation boundary by means of four independent parameters (x_c, x_o, T_c, B) and one universal critical exponent σ (or β). Following this approach, a number of systems of different origin were successfully treated.

The results obtained will provide a basis for manifestation of an intrinsic mutual connection between macroscopic parameters of the CC and physico-chemical nature (microscopic characteristics) of the system.

List of symbols

x	mole fraction (mol.fr.) of component A
x_c	critical mol.fr. of component A
x_s	normalized mol.fr. of aggregates [mA]
x_{sc}	critical mol.fr. of aggregates [mA]
x_o	limiting concentration of forming freely dispersed aggregates
$X = x/(1-x)$	mole ratio of initial components
$X_s = x_s/(1-x_s)$	mole ratio of aggregates [mA] and [nA kB]
$X_{sc} = x_{sc}/(1-x_{sc})$	critical mole ratio of aggregates [mA] and [nA kB]
$X_o = x_o/(1-x_o)$	limiting mole ratio
n	refractive index
n_o	limiting refractive index
$W_G = W_H - T\ W_S$	general interaction energy parameter
R	gas constant
T^*	current critical temperature
T_{ci}	critical temperature for system with several critical points
T_u	upper critical temperature
T_l	lower critical temperature
T_o	enthalpy-entropy compensation temperature
B	critical amplitude
α	electron polarizability
β	critical exponent of the CC
ρ	density
ρ_o	limiting density
ρ_c	density of fluid in the liquid-gas critical point
$\tau_i = (T-T_{ci})/T_{ci}$	reduced temperature.
τ_o	general reduced temperature.
σ	critical exponent of W_s/R

REFERENCES

[1] H.E.Stanley, Introduction to Phase Transitions and Critical Phenomena, Oxford University, New York, 1973.
[2] M.A.Anisimov, Critical Phenomena in Liquids and Liquid Crystals, Gordon and Breach, London, 1991.
[3] G.X.Jin, S.Tang, and J.V.Sengers, Phys.Rev. E, 47 (1993) 388-402.
[4] M.A.Anisimov, E.E.Gorodetskii, V.D.Kulikov, and J.V.Sengers, Phys.Rev. E, 51 (1995) 1199-1215.
[5] M.A.Anisimov, S.B.Kiselev, J.V.Sengers, and S.Tang, Physica A, 188 (1992) 487- 525.
[6] J.C.Reinwater, D.G.Friend, Phys.Lett. A, 191 (1994) 431-437.
[7] J.C.Reinwater, D.G.Friend, J.Chem.Phys., 98 (1993) 2298-2307.
[8] A.W.Francis, Liquid-Liquid Equilibrium, Interscience, New York, 1963.
[9] B.Malesinska, Bull.Acad.Polon.Sci., Ser.Sci.Chim., 8 (1960) 53-73.
[10] R.G.Johnston, M.R.Meadows, R.C.Mockler, and W.J.O'Sullivan, Chem.Phys.Lett., 96 (1983) 575-578.
[11] P.Damay and F.Leclercq, J.Chem.Phys., 95 (1991) 590-599.
[12] W.Haller, D.H.Blackburn, and J.H.Simmons, J.Am.Cer.Soc., 57 (1974) 120-126.
[13] D.Minz, CALPHAD, 3 (1979) 259-273.
[14] P.B.Macedo and J.H.Simmons, J.Res.Nat.Bur. of Stand., 78A (1974) 53-59.
[15] S.V.Kazakov and N.I.Chernova, Rus.J.Phys.Chem., 69 (1995) 1010-1014.
[16] S.V.Kazakov and N.I.Chernova, Rus.J.Phys.Chem., 71 (1997) 292-297.
[17] J.M.H.Levelt Sengers, J.Straub, and M.Vicentini-Missoni, J.Chem.Phys., 54 (1974) 5034-5050.
[18] R.Gastand, D.Beysens, and G.Zalczer, J.Chem.Phys., 93 (1990) 3432-3436.
[19] Yu.B.Melnichenko, Zh.Fiz.Khim.(Rus.), 63 (1989) 3153-3165.
[21] J.J.De Pablo and J.M.Prausnitz, AIChE Journal, 34 (1988) 1595-1606.
[22] R.E.Goldstain, J.Chem.Phys., 83 (1985) 1246-1254.
[23] J.S.Walker and F.Ghebremichael, Pure & Appl.Chem., 63 (1991) 1381-1386.
[24] S.V.Kazakov, N.I.Chernova, and E.V.Yablonkaya, Moscow Univ.Phys.Bull., 50 (1995) 47-51.
[25] S.V.Kazakov and N.I.Chernova, Proc. of the Fourth Asian Thermophys. Prop.Conf., D3d6 (1995) 841-845.
[26] I.Prigogine and R.Defay, Chemical Thermodynamics, Longmans Green and Co, London-New York-Toronto, 1954.
[27] E.A.Guggengeim, Thermodynamics, Clarendon, Oxford, 1967.
[28] J.B.Thompson, Jr., in P.H.Abelson (Ed.), Researches in Geochemistry, Vol.2, J.Wiley and Sons, Inc., New York, 1967, pp.340-361.
[29] S.V.Kazakov and N.I.Chernova, in R.M.Pick, G.Thomas, P.S.Salmon (Eds.), #rd Liquid Matter Conf., Univ. of East Anglia, Norwich, 1996, P11-23.
[30] G.Jackson, Molecular Physics, 72 (1991) 1365-1385.
[31] N.P.Malomuzh and B.A.Veytsman, Physics A, 168 (1990) 833-852.

Table 1. Symmetrization parameters of liquid-gas coexistence curves

System	g	g_c(exp)	g_c(calc)	g_o	x_c	$X_c = m$
CO_2[a]	ρ, kg/m^3	468.2	464.6	1082.4	0.4272	0.7519
CO_2[b]	n	1.1060	1.1076	1.2458	0.4522	0.8256
NO_2[c]	ρ, kg/m^3	452.	449.	1023.3	0.4388	0.7817
NO_2[b]	n	1.1154	1.11535	1.2628	0.4547	0.8340
Ar[d]	n	1.08587	1.0844	1.2067	0.4194	0.7234
Rb[e]	ρ, kg/m^3	292.	288.	968.	0.2972	0.4228
Cs[e]	ρ, kg/m^3	379.	360.	1300.	0.2769	0.3829
Cs[f]	ρ, kg/m^3	390.	369.2	1302.3	0.2835	0.3956
Hg[g]	ρ, kg/m^3	5800.	5800.	11900.	0.4873	0.9505
Hg[h]	ρ, kg/m^3	5900.	5800.	11600.	0.5000	1.0000

[a] A.Michels, B.Blassie, C.Michels, Proc.Roy.Soc. (London), A902 (1937) 358.
[b] J.M.H.Levelt Sengers, J.Straub, M.Vicentini-Missoni, J.Chem.Phys., 54 (1974) 5034.
[c] D.Cook, Trans.Faraday Soc., 19 (1953) 716.
[d] R.K.Teaque, J.Pings, J.Chem.Phys., 48 (1968) 4973.
[e] S.Jungst, B.Knuth, F.Hensel, Phys.Rev.Lett., 55 (1985) 2160.
[f] N.B.Vargafftic, E.B.Gelman, V.F.Kozhevnikov, and S.P.Naurzakov, Int.J.Thermophys., 11 (1990) 467.
[g] W.Goetzlaff, Ph.D. dissertation, Marburg, 1988.
[h] V.F. Kozhevnikov, S.PO.Naurzakov, and A.P.Senchenkov, J.Moscow Phys.Soc., 1 (1990) 171.

Table 2. Energy parameters of the symmetrized CC of one-component systems

System[a]	Data	T_c(exp)	Regular mixing model			Simple scaling model		
			T_c(calc)	B	σ	T_c(calc)	B	β
CO_2	ρ	304.12	304.41	2.35	0.195	304.13	0.847	0.342
			304.11	1.67	0.325	304.13	0.802	0.325
CO_2	n	304.17	304.14	1.79	0.309	304.13	0.894	0.347
			304.14	1.67	0.325	304.13	0.808	0.325
NO_2	ρ	309.49	309.50	1.80	0.377	309.49	0.863	0.347
			309.49	1.54	0.325	309.49	0.799	0.325
NO_2	n	309.566	309.57	1.76	0.299	309.56	0.866	0.344
			309.57	1.61	0.325	309.56	0.808	0.325
Ar	n	150.704	151.36	2.06	0.026	150.704	0.748	0.332
			150.50	1.24	0.325	150.704	0.736	0.325
Rb	ρ	2017	2017.18	1.34	0.274	2017.16	0.707	0.323
			2017.02	1.20	0.325	2017.16	0.710	0.325
Cs	ρ	1924	1925.0	0.746	0.401	1923.88	0.714	0.322
			1925.6	0.897	0.325	1923.88	0.718	0.325
Cs	ρ	1938	1937.78	1.13	0.325	1936.9	0.669	0.302
						1938.0	0.693	0.325
Hg	ρ	1751	1752.15	0.559	0.326	1751.15	0.749	0.366
			1752.15	0.560	0.325	1751.15	0.664	0.325
Hg	ρ	1783	1783	0.302	0.501	1783.00	0.668	0.344
			1783	0.416	0.325	1783.00	0.642	0.325

[a] For references see Table 1

Table 3. Energy parameters of symmetrized CCs of different nature at fixed values of critical exponents ($\sigma = \beta = 0.325$).

System, A/B	Experiment		Regular mixing model			Simple scaling model		
	T_u	T_l	T_u	T_l	B	T_u	T_l	B
SiO_2/Li_2O[a]	~1275	-	1273.55	-	0.654	1272.53	-	0.664
SiO_2/Na_2O[a]	1110.15	-	1111.15	-	0.146	1111.11	-	0.594
c-C_6H_{12}/Polystyrene[b] (M=200000)	296.99	-	296.985	-	19.5	296.99	-	2.120
1-propoxy-propane-2ol/ H_2O[c]	444.85	307.65	444.94	307.74	-9.7	444.88	307.55	1.080
Glycerol/Guaiacol[d]	356.65	312.65	356.66	312.68	-21.1	356.55	312.95	1.690
C_6H_6/S[e]	431.15	498.15	431.45	496.36	16.8	431.16	496.28	1.360
$C_5H_{12}/C_6H_5NO_2$[f]	304.65	-	304.60	-	1.92	304.65	-	0.841
C_5H_{12}/C_5F_{12}[g]	265.50	-	265.43	-	2.50	265.50	-	0.905
C_7H_{16}/CH_3OH[h]	324.008	-	324.009	-	3.03	324.009	-	1.000
H_2O/C_6H_6O[i]	341.55	-	341.55	-	1.07	341.55	-	0.745
NaCl/KCl[j]	~765.2	-	749.40	-	1.98	757.80	-	0.764
Ne/NH_3[k]	415.93	-	415.93	-	2.30	416.77	-	0.820
CO_2[l]	304.12	-	304.11	-	1.67	304.13	-	0.802
Rb[m]	2017	-	2017.02	-	1.20	2017.16	-	0.710
Ar[n]	150.704	-	150.85	-	1.132	150.86	-	0.736

[a] W.Haller, D.H.Blackburn, and J.H.Simmons, J.Am.Cer.Soc., 57 (1974) 120.
[b] M.Nakata, T.Dobashi, N.Kuwahara, and M.Kaneko, Phys.Rev.A, 18 (1978) 2683.
[c] H.L.Cox, W.L.Nelson, and L.H.Cretcher, J.Am.Chem.Soc., 49 (1927) 1080.
[d] B.McEwan, J.Chem.Soc (London), 123 (1`923) 2284.
[e] H.R.Knuyt, Ann.Chim.Phys., 31 (1908) 486.
[f] S.V.Kazakov and N.I.Chernova, Sov.J.Phys.Chem., 57 (1983) 1275.
[g] J.H.Simmons and R.D.Dunlap, J.Chem.Phys., 18 (1950) 335.
[h] A.G.Aizpiri, J.A.Correa, R.G.Rubio, and M.D.Pena, Phys.Rev.B, 41 (1990) 9003.
[i] V.Rothmund, Z.Physikal.Chem., 28 (1898) 433.
[j] J.B.Thompson, Jr., and D.R.Waldbaum, Geochim. Cosmochim. Acta, 33 (1969) 671.
[k] C.D.Myreat, N.J.Trappeniers, and J.A.Schouten, Physica A, 94 (1978) 559.
[l] A.Michels, B.Blassie, C.Michels, Proc.Roy.Soc. (London), A902 (1937) 358
[m] S.Jungst, B.Knuth, F.Hensel, Phys.Rev.Lett., 55 (1985) 2160.
[n] R.K.Teaque, J.Pings, J.Chem.Phys., 48 (1968) 4973.

Figure captions

Figure 1. Coexistence curve of CO_2: (a) primary data in "temperature-density" coordinates; (b) primary data in "temperature-refractive index" coordinates; (c) primary data in "temperature - quazimole fractions" coordinates (solid line and full points are the density data, dotted line and open points are the refractive index data, lines are calculated using the new regular mixing model with parameters from Table 1), (e) symmetrized coexistence curve (the density data); (d) symmetrized coexistence curve (the refractive index data). Lines are calculated using the new regular mixing model with parameters from Table 2.

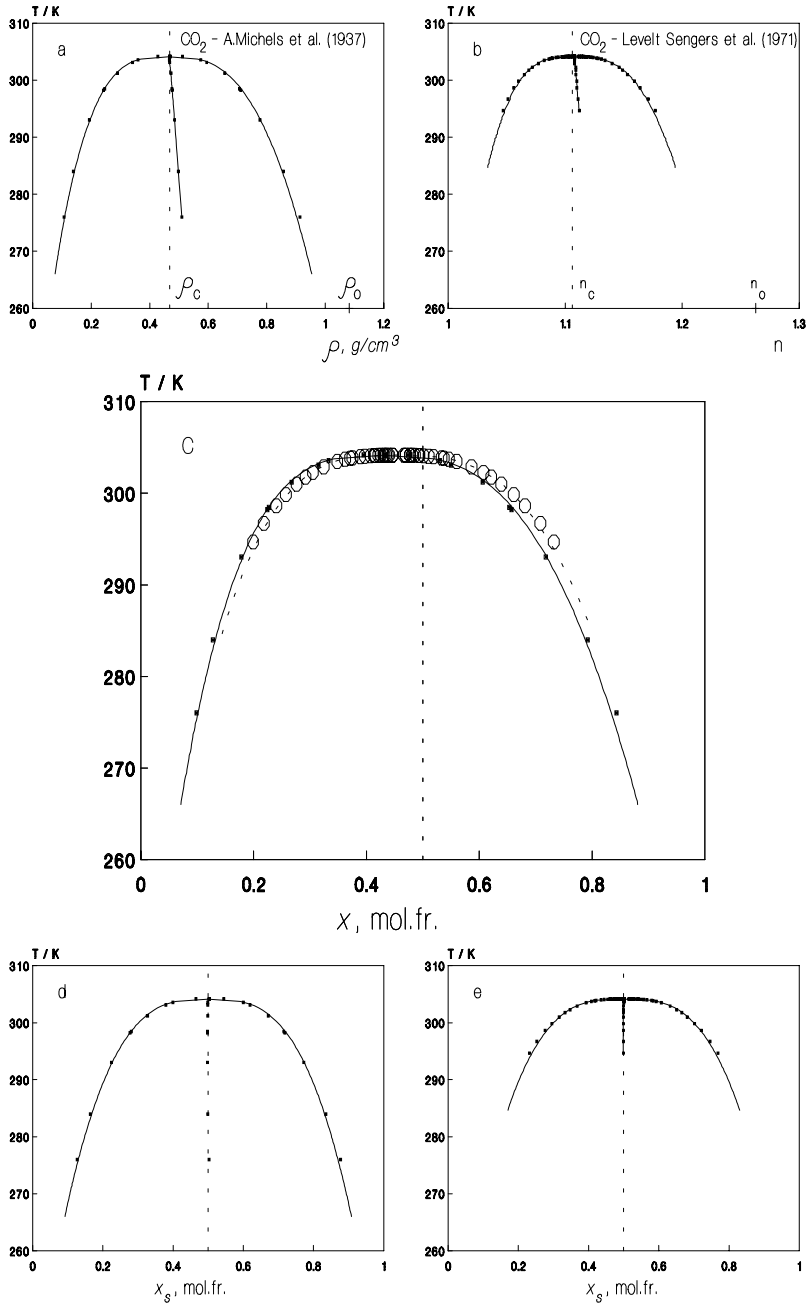
Figure 2. Optimization of the critical exponent σ.

Figure 3. Primary (1) and symmetrized (2) CCs for the system glycerol/quaiacol. Points are the experimental data, represented via mol.fr. of the A component (1) and the aggregates mA (2). Lines are calculated using (6) with parameters from Table 3.

Figure 4. Primary (1) and symmetrized (2) CCs for the system benzene/sulphur. For notations see fig.3.

Figure 5. Reduced shape of the symmetrized systems of different origin (the regular mixing model): (1) SiO_2/Na_2O; (2) Rb; (3) CO_2; (4) C_7H_{16}/CH_3OH; (5) C_6H_6/S; (6) c-C_6H_{12}/polystyrene; (7) 1-propoxypropane-2ol/H_2O.

Figure 6. Relationship between immiscibility gaps of the systems with two CPs in normalized coordinates: (1) 1-propoxypropane-2ol/H_2O; (2) glycerol/guaiacol; (3) C_6H_6/S. ' and " refer to upper and lower CP, respectively.


T / K
a
CO2 - A.Michels et al. (1937)
ρc
ρo
ρ, g/cm3
b
CO2 - Levelt Sengers et al. (1971)
nc
no
n
c
x, mol.fr.
d
xs, mol.fr.
e
xs, mol.fr.

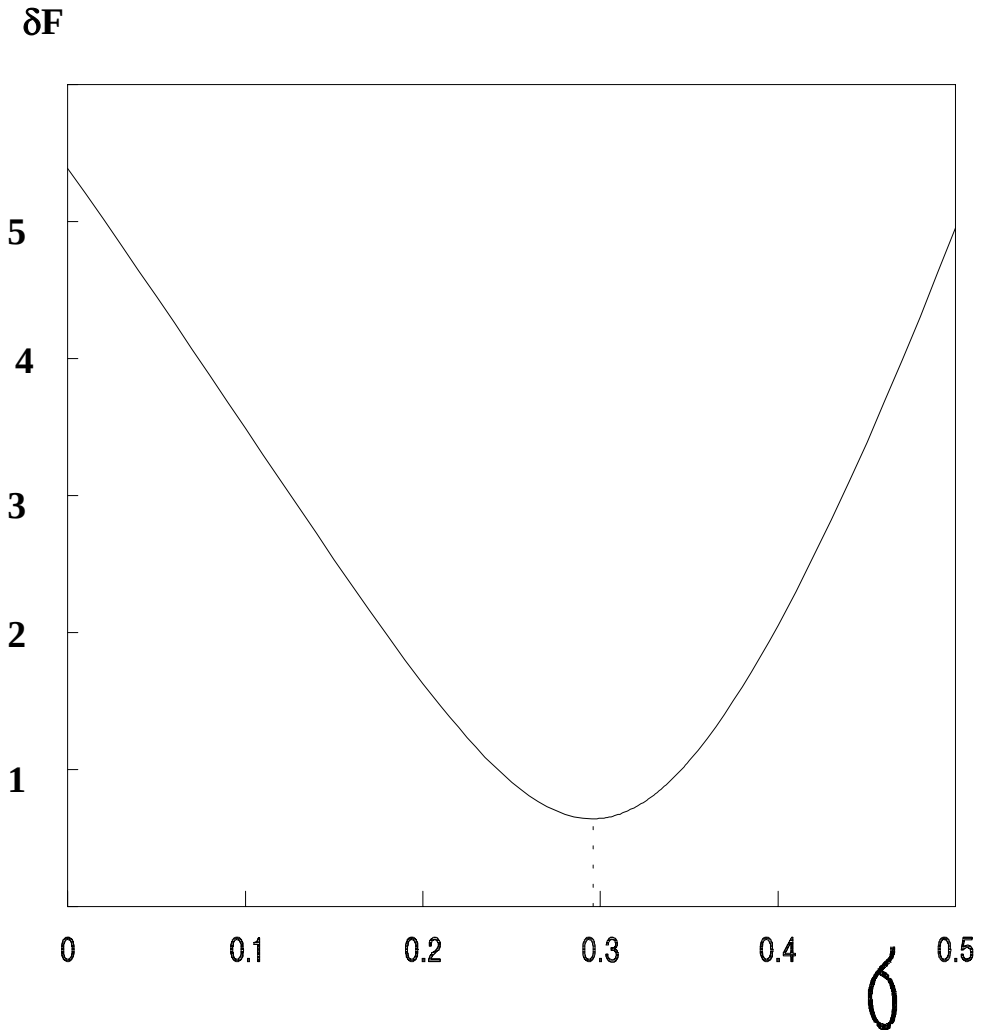


fig.2

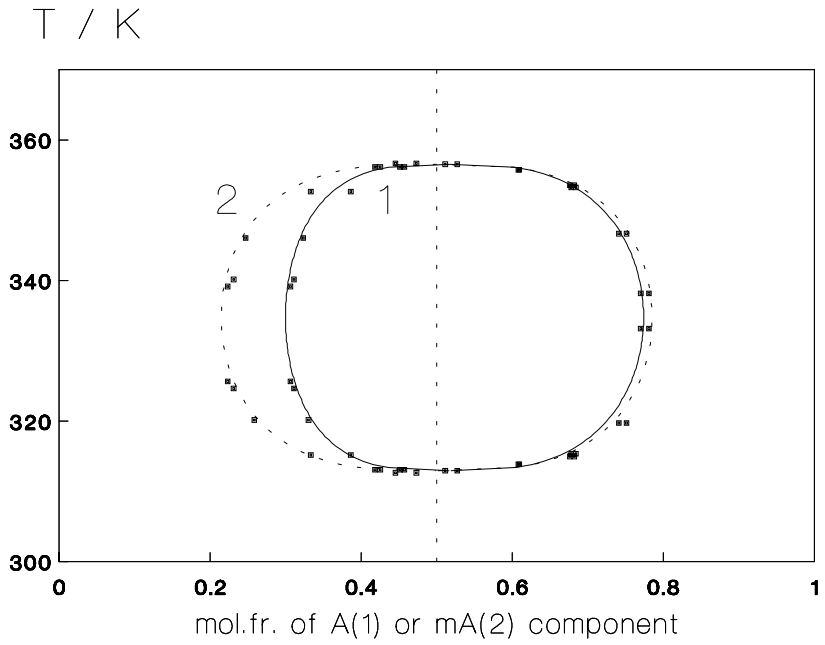


fig.3

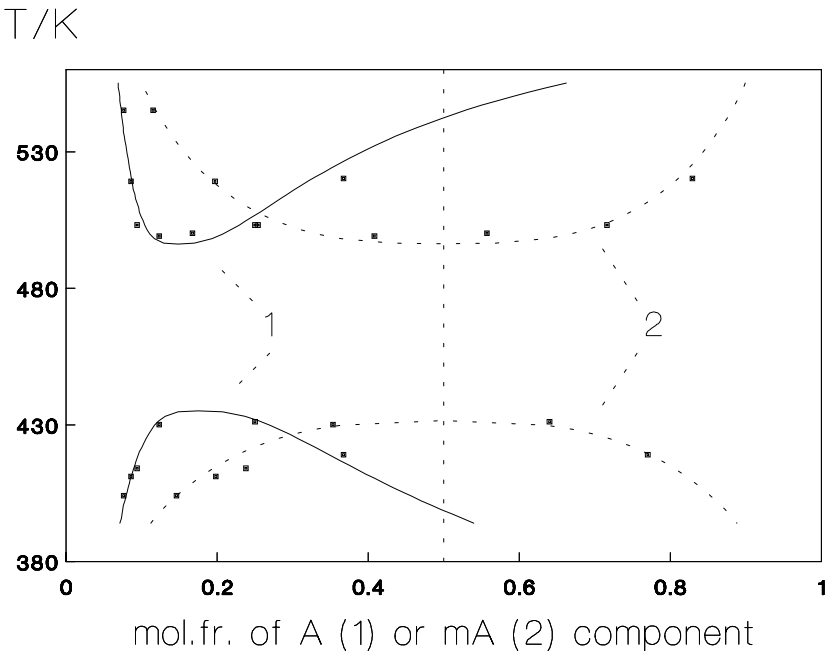


fig.4

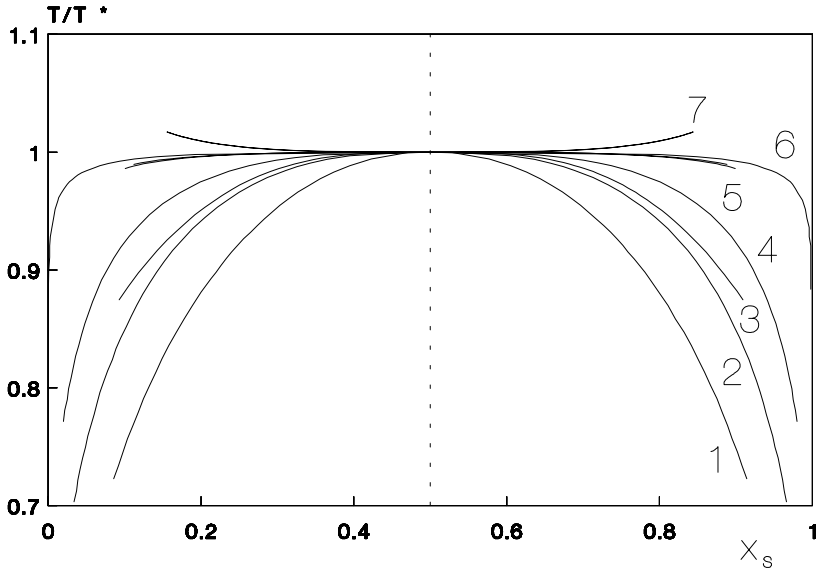


fig.5

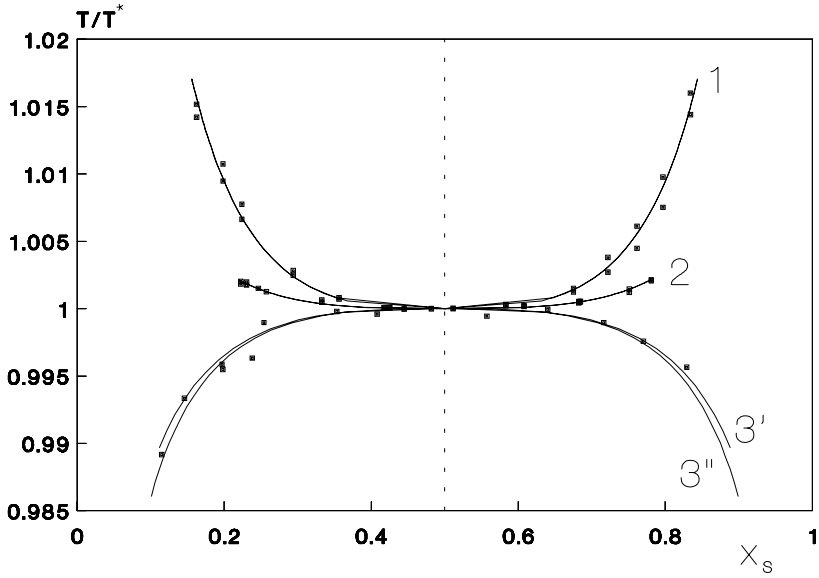


fig.6