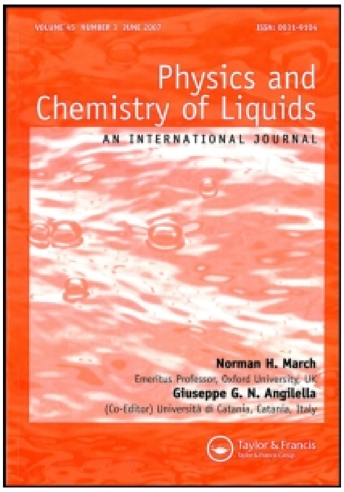

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Gas-Gas Equilibrium of Mixtures of Noble Gases at High Pressures from a Perturbation Theory

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GAS-GAS EQUILIBRIUM OF MIXTURES OF NOBLE GASES AT HIGH PRESSURES FROM A PERTURBATION THEORY

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An accurate version of thermodynamical perturbation theory is used to predict gas-gas immiscibility in a mixture of noble gases at high pressures. Critical temperatures and molar fractions are calculated for several densities and a region where dp_c/dT_c is positive, is found. This region goes beyond the critical point of pure Xe showing gas-gas immiscibility. The possibility of this prediction requires an adequate rule to obtain crossed interaction parameters. In fact, Lorentz-Berthellot rule is unable to predict the phenomenon while a new rule proposed by Kohler gives a semiquantitative agreement. A critical exponent is also calculated. Computed value is very close to experimental exponent. A second plait-point not found experimentally is also predicted.

KEYWORDS: Immiscibility, critical exponent.

I INTRODUCTION

The study of equilibrium of binary mixtures at high pressures is a subject which has been receiving increasing interest during the last few years[1-3]. This interest comes from their practical applications in Chemical Engineering as well as its theoretical relevance. In particular, the so-called gas-gas immiscibility namely the phase separation above the critical point of the less volatile component of a mixture, has been described for a great number of systems since the pioneer work of Krichevski[4]. Krichevski's experiments confirmed the theoretical predictions of Kammerlingh-Ones and Keesom[5] formulated at the beginning of our century. Lately, classification of different types of binary mixtures[1-2] has allowed to distinguish several kinds of gas-gas immiscibility and particularly that which appears in binary mixtures of noble gases of very different molecular weight, experimentally studied by Trappeniers

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et al.[6–7] These mixtures belong to the class III in the Scott-van Konynenburg scheme.[2] This kind of mixtures, due to their molecular simplicity could be object both either of theoretical studies or of simulations in a systematic way. However, the achievement of these studies always encounters important practical difficulties. On the first place, correlation lengths between particles increase when the mixture approaches a critical point and, therefore, the boxes of very short length used in simulations are inadequate near the critical lines. Even so, there are valuable simulations of mixtures of noble gases at high pressures[8–9] but these results must be carefully considered in the vicinity of phase separation. On the other hand, some other difficulties appear from a theoretical point of view. The task of calculating gas-gas phase equilibrium in binary mixtures from standard integral equations as Percus-Yevick equation[10] or the more recent RHNC equation[11] seems to be too far of any reasonable availability of computational time in the most advanced computers. Furthermore, there is the problem of crossed interaction since for molecules of so different sizes and well depths as neon and xenon, or neon and krypton, crossed parameters may be very far from the Lorentz-Berthellot combination classical rules. As we shall show below, the problem of combination rules becomes crucial and we shall be able to overcome it with help of a recent proposal of Kohler *et al.*[12] This treatment has already shown to be valid for relatively simple fluids at low pressures using either a van der Waals one-fluid (vdWlf)[12] theory or a perturbation theory[13]. vdWlf theory gives for a lot of cases results of similar quality than those arising from perturbation theory. The advantage of vdWlf theory is its major simplicity and less computational time. Unfortunately, vdWlf theory is inapplicable in the case of mixtures of noble gases of very different sizes. This size difference is not so critical for perturbation theories. Moreover, because of gas-gas equilibrium occurs at densities comparable to those of liquid-liquid equilibrium, the main failure of perturbation theories which is their inability to predict the low density branch in the gas-liquid equilibrium using only the first order perturbation term, is avoided. So, the main purpose of this paper is to examine whether a very accurate version of perturbation theories for mixtures proposed by Fischer and Lago[14] could predict, at least in a semiquantitative way, the gas-gas equilibrium for a system without multipolar interactions like neon-xenon. As we shall show, this is the case when Kohler combination rule is used for the crossed interaction. Thus, Section II is devoted to a brief exposure of the thermodynamical as well as statistical basis of our work and presents an introduction to combination rules. Since perturbation theories yield directly Helmholtz free energy, A, the most of our computations has been made on the thermodynamical surface (A, v, x) where Rowlinson's thermodynamical formulation is available[15] and not on the (G, p, x) surface more adequate to experimental work. In this way, we have been able to avoid in a large scale the errors coming from numerical derivation which could darken the results of our work. Section III displays our numerical results, making a special emphasis on the different curves which define phase equilibria and computing, moreover, the critical exponent of the variation of instability molar fraction with the temperature around a critical point. The paper closes with some remarks about the future of perturbation theory concerning gas-gas equilibrium what constitutes section IV.

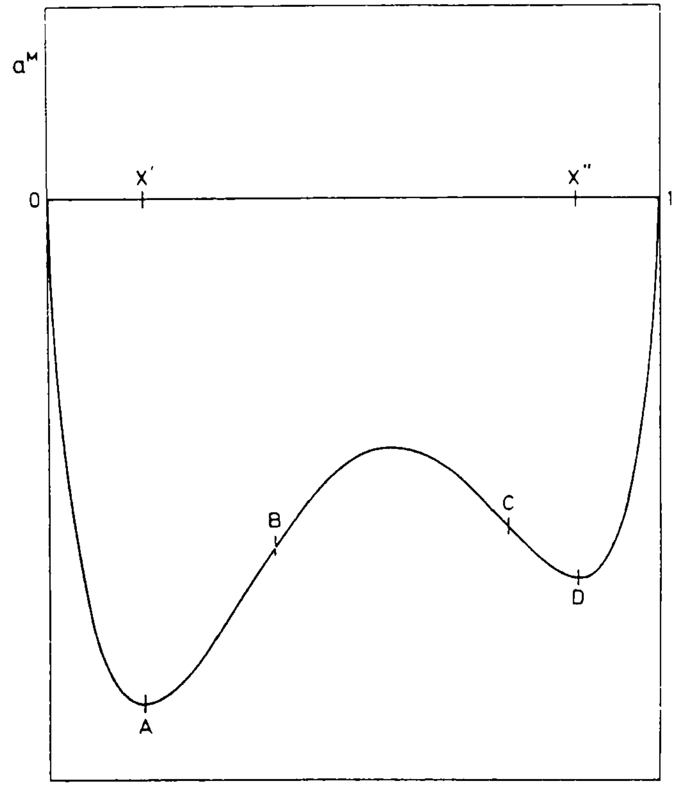

Figure 1 Variation of molar Helmholtz energy of a mixture with molar fraction below a critical temperature.

IIA THERMODYNAMICS OF A MIXTURE OF GASES

As we have indicated above and due to the fact that we shall apply a perturbation theory where the quantity directly obtained is the Hemholtz free energy, A, we shall discuss the behaviour of the system on an isochore section of the (a, v, x) surface at constant temperature, T. Small letters design, as usual, molar quantities.

Stability of a binary mixture, whose components are denoted by subscripts 1 and 2, by composition fluctuations requires:

$$(\partial^2 a^M/\partial^2 x^2)_{T,v}(\partial^2 a^M/\partial v^2)_{x,T} - (\partial^2 a^M/\partial x \partial v)^2_{v,x,T} > 0 \tag{1}$$

where a^M is the mixing Helmholtz energy defined as:

$$a^M = a - (x_1 a_1 + x_2 a_2) \tag{2}$$

Thus, the states of the system corresponding to the part of the curve in the Figure 1 between B and C will be instable because any fluctuation in the composition leads to a decrease in a^M and, therefore, to a spontaneous decomposition of the system in two phases. Points A and D correspond to two phases of composition x' and x'', *which are* *not in thermodynamical equilibrium* because they correspond to different pressures. We call those quantities, instability molar fractions (IMF). However, quite obviously:

$$(\partial a^M/\partial x)^A_{v,T} = (\partial a^M/\partial x)^D_{v,T} \tag{3}$$

Furthermore, we have the thermodynamical identity[2,15]:

$$(\partial a^M/\partial x)_{v,T} = (\partial g^M/\partial x)_{p,T} \tag{4}$$

where p is the pressure of the system with molar volume v, molar fraction x and temperature T. In principle, the pressure of the minima could be obtained and a complete phase diagram for each composition be drawn solving the equations:

$$p' = p'' \tag{5}$$

$$\mu_1' = \mu_1'' \tag{6}$$

$$\mu_2' = \mu_2'' \tag{7}$$

Unfortunately, this goal is also too ambitious for a stringent perturbation theory and we should resign to obtain the critical line. In fact, if our system in the Figure 1 is heated, keeping equal the volume of the two phases adjusting conveniently the pressure, the system reaches a critical state at the temperature T_c where intensive properties in both phases are the same. For coexisting phases near a critical point the following relation is found:

$$\ln|x' - x''| = \beta \ln|T - T_c| + C \tag{8}$$

Theoretical classical treatment of binary mixtures[15] leads to a value for critical exponent $\beta = 1/2$ while a value of $\beta = 0.35 \pm 0.02$ has been experimentally obtained[7]. This treatment is based on the expansion of chemical potential around a critical point, supposed μ is an analytical function. Following Hansen and McDonald[16] we can expand the molar Helmholtz free energy, a, taking as independent variables T and x on surfaces where ρ = constant. We obtain retaining only the first non vanishing terms:

$$\Delta a = a - a_c = \alpha_{10}\Delta T + \alpha_{11}\Delta T \Delta x + \alpha_{03}(\Delta x)^3 \tag{9}$$

where the subscript c refers to the critical line $\Delta T = T - T_c$, $\Delta x = x - x_c$, and the coefficients α_{ij} are given by:

$$\alpha_{ij} = (\partial^{i+j} a/\partial T^i \partial x^j)_c \tag{10}$$

We can immediately write from Eq. (9):

$$\alpha_{03}(\Delta x)^2 = \frac{\Delta a}{\Delta x} - \alpha_{10}\frac{\Delta T}{\Delta x} - \alpha_{11}\Delta T \tag{11}$$

In the limit $\Delta T \to 0$ the first two members of the right side vanish since:

$$\lim_{\Delta T \to 0} \frac{\Delta a}{\Delta x} = (\partial a/\partial x)_c = 0 \tag{12}$$

and:

$$\lim_{\Delta T \to 0} \frac{\Delta T}{\Delta x} = (\partial T/\partial x)_c = \frac{(\partial a/\partial x)_c}{(\partial a/\partial T)_c} = 0 \tag{13}$$

Thus, Eq. (11) reduces to:

$$\Delta x = \pm C(\Delta T)^{1/2} \tag{14}$$

where $C^2 = -\alpha_{11}/\alpha_{03}$

In this case, the critical exponent is also $\beta = \frac{1}{2}$ and critical curve is symmetric respect to $x = x_c$ in the vicinity of critical point. Therefore:

$$x' - x_c = -(x'' - x_c) \tag{15}$$

or:

$$x' + x'' = 2x_c = \text{constant} \tag{16}$$

which is a special case of the law of rectilinear diameters. It must be remarked that molar fraction in formulae (8) and (16) are not necessarily the same because they correspond to coexistence molar fraction in the first case and to IMF in the second one but classical critical exponents have the same numerical value.

At the critical point the Eq. (1) must vanish and the derivative of pressure, corresponding to the second crossed derivative of free energy must also vanish:

$$(\partial p/\partial x)_{CR} = 0 \tag{17}$$

where the subscript CR means that the derivative is taken on the critical line. Now, we approach this derivative by:

$$(\partial p/\partial x)_{v,T} = 0 \tag{18}$$

and the Eq. (1) is reduced to:

$$(\partial^2 a^m/\partial x^2)_{v,T} = 0 \tag{19}$$

on a pseudocritical point. Thus, we shall take as an approximate test of stability of a mixture the equation:

$$(\partial^2 a^m/\partial x^2) > 0 \tag{20}$$

IIB THE FLAVOUR OF STATISTICAL THERMODYNAMICS

We shall use a first order WCA perturbation theory[17] for a binary mixture to obtain their thermodynamical properties. Details of the method and numerical treatment of resulting equations have been given elsewhere[14] and we shall simply outline here the main expressions.

All the pair interactions in the mixture are supposed to be Lennard-Jones interactions. Each actual potential $u_{ij}(r)$ is split in the way:

$$u_{ij} = u_{ij}^0 + u_{ij}^1 \tag{21}$$

where the explicit dependence on r has been supressed for sake of simplicity. Reference and perturbations potentials are defined as:

$$u_{ij}^0 = \begin{cases} u_{ij} + \varepsilon_{ij} & r_{ij} < 2^{1/6}\sigma_{ij} \quad (22a) \\ 0 & r_{ij} > 2^{1/6}\sigma_{ij} \quad (22b) \end{cases}$$

$$u_{ij} = \begin{cases} -\varepsilon_{ij} & r_{ij} < 2^{1/6}\sigma_{ij} \quad (23a) \\ u_{ij} & r_{ij} > 2^{1/6}\sigma_{ij} \quad (23b) \end{cases}$$

respectively.

Taylor's expansion of Helmholtz free energy considered as a functional of pair potential gives:

$$A^* = A_0^* + N\rho/2 \sum_{\alpha,\beta} x_\alpha x_\beta A_{\alpha\beta}^1 \tag{24}$$

where:

$$A_{\alpha\beta}^1 = \int u_{\alpha\beta}^1(r) g_{\alpha\beta}^0(r) dr \tag{25}$$

and the script o means properties of reference system and the star means difference with ideal value. The reference system reduces to a mixture of soft repulsive spheres for a mixture of noble gases as studied here.

Radial distribution functions, g_{ij}^0, for our system are obtained by solving the Percus-Yevick equation with Baxter's formalism. Helmholtz energy of the reference system is obtained through a new series expansion around a system composed by a mixture of hard spheres:

$$\beta A^*/N = \beta A_0^*/N - \rho/2 \sum_{\alpha,\beta} x_\alpha x_\beta B_{\alpha\beta} \tag{26}$$

where B are the "blip" integrals defined as:

$$B_{\alpha\beta} = \int (\exp(-\beta u_{\alpha\beta}^H) - \exp(-\beta u_{\alpha\beta}^0)) y_{\alpha\beta}^0(r) dr \tag{27}$$

Now, superscript H refers to properties of a mixture of hard spheres. y^0 is the background correlation function defined as:

$$y_{\alpha\beta}^0 = g_{\alpha\beta}^0 \exp(\beta u_{\alpha\beta}^0) \tag{28}$$

The choice of hard sphere diameters is not unique and several procedures has been proposed[14,18]. We choose diameters d_{11} and d_{22} which fulfills:

$$B_{11} = 0 \tag{29}$$

$$B_{22} = 0 \tag{30}$$

and we suppose additive the hard sphere diameter to be able to apply an accurate equation of state[19,20] in this case. With all these conditions, we rewrite (24) in final form as:

$$\beta A_H^*/N = \beta A_H^*/N + x_1 x_2 \int (\exp(-\beta u_{12}^H) - \exp(-\beta u_{12}^0)) y_{12}^0(r) dr$$

$$+ \beta\rho/2 \sum_{\alpha,\beta} x_\alpha x_\beta \int u_{\alpha\beta}^1(r) g_{\alpha\beta}^0(r) dr \tag{31}$$

which is already satisfactory for our purposes.

IIC THE CROSSED INTERACTION

In a general way and as we shall show below, thermodynamical properties of a mixture depend strongly on crossed interaction by a potential law similar to the interactions for pure substances with crossed interaction parameters given by:

$$\varepsilon_{12} = \xi(\varepsilon_{11}\varepsilon_{22})^{1/2} \tag{32}$$

$$\sigma_{12} = \eta(\sigma_{11} + \sigma_{22})/2 \tag{33}$$

For $\xi = \eta = 1$, we have the Lorentz-Berthellot combination rule, but experimental and simulation values show that both parameters and expecially ξ differs from 1. A lot of possible combination rules and their influence on the thermodynamical properties have been exhaustively studied by Diaz Peña and Pando[21]. We shall use here one, recently proposed by Kohler *et al.*[12], which does not contain any adjustable parameters what makes it quite satisfactory from a theoretical point of view. This rule is based on the fact that intermolecular dispersion forces could be expressed by London formula[22]:

$$u_{ij}^{\mathrm{disp}}(r) = -\tfrac{3}{4}(\alpha_i\alpha_j)/r^6(2h\nu_i h\nu_j/(h\nu_i + h\nu_j) \tag{34}$$

where h is Plank's constant, ν a characteristic frequency of the molecule and α its polarizability. For the (12-6) potential:

$$u_{ij}(r) = 4\varepsilon_{ij}((\sigma_{ij}/r)^{12} - (\sigma_{ij}/r)^6) \tag{35}$$

the dispersion energy at the minimum is exactly twice the depth of potential well, since this minimum is situated at $2^{1/6}\sigma_{ij}$:

$$\varepsilon_{ij} = \tfrac{3}{16}\alpha_i\alpha_j/\sigma_{ij}^6(2h\nu_i h\nu_j/(h\nu_i + h\nu_j)) \tag{36}$$

Moreover, this rule supposes additive the hard sphere diameters given by BH0 version of Barker-Henderson perturbation theory[23]:

$$d_{ii} = \int_0^\infty (1 - \exp(-\beta u_{ii}^0)) dr \tag{37}$$

namely:

$$d_{12} = (d_{11} + d_{22})/2 \tag{38}$$

Equations (36) to (38) constitute a system from which ε_{12} and σ_{12} can be obtained by successive iterations using interactions parameters and polarizabilities of pure substances.

As we have pointed out this rule is perfectly adequate to our goal not only by the lack of adjustable parameters but also by the definition of molecular diameters based on perturbation theories and, furthermore, by the supposition of additivity of these diameters which is necessary to use the MCSLB equation of state[19,20].

III NUMERICAL RESULTS

Intermolecular parameters for pure Ne and Xe are shown in the two first rows of Table 1. As it has been pointed out above, calculated excess properties depend strongly on combination rules. However, Figure 2 shows that the excess volume of the studied mixture, V^E, goes to 0 when pressure becomes large, using any rule. Pressure has been obtained from the thermodynamical relation:

$$p = N\rho^2(\partial A/\partial \rho)_{N,T} \tag{39}$$

using the derivation formula proposed by Marshall and Jones[24] which is very accurate for the central part of the interval of derivation but it yields some error on the interval extrema. At low pressures the difference between the V^E predicted by both the

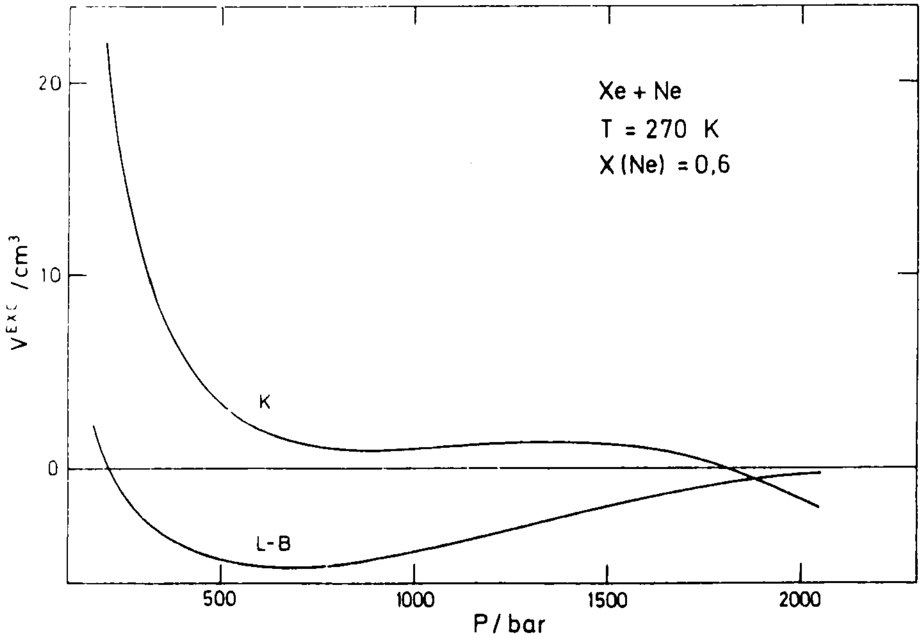

Figure 2 Variation of excess volume with pressure for the combination rules in this work. LB = Lorentz Berthellot rule; K = Kohler rule.

rules is large but it is irrelevant at high pressures. Neither A^E nor G^E go to zero when the pressure increases but to a constant value for density and temperature:

$$G^E = \int V^E dp \tag{40}$$

In the most of cases, we have solved the PY equation for a molar fraction grid of 0.05, keeping constant the total particle density in the mixture, and calculating the excess Helmholtz energy:

$$A^E = A^* - x_{\mathrm{Ne}} A^*_{\mathrm{Ne}} - x_{\mathrm{Xe}} A^*_{\mathrm{Xe}} \tag{41}$$

Reduced critical temperature for a pure substance calculated from WCA theory[25] is $T^* = 1.458$ and the corresponding temperature for Xe is $T_c(\mathrm{Xe}) = 335$ K. Therefore,

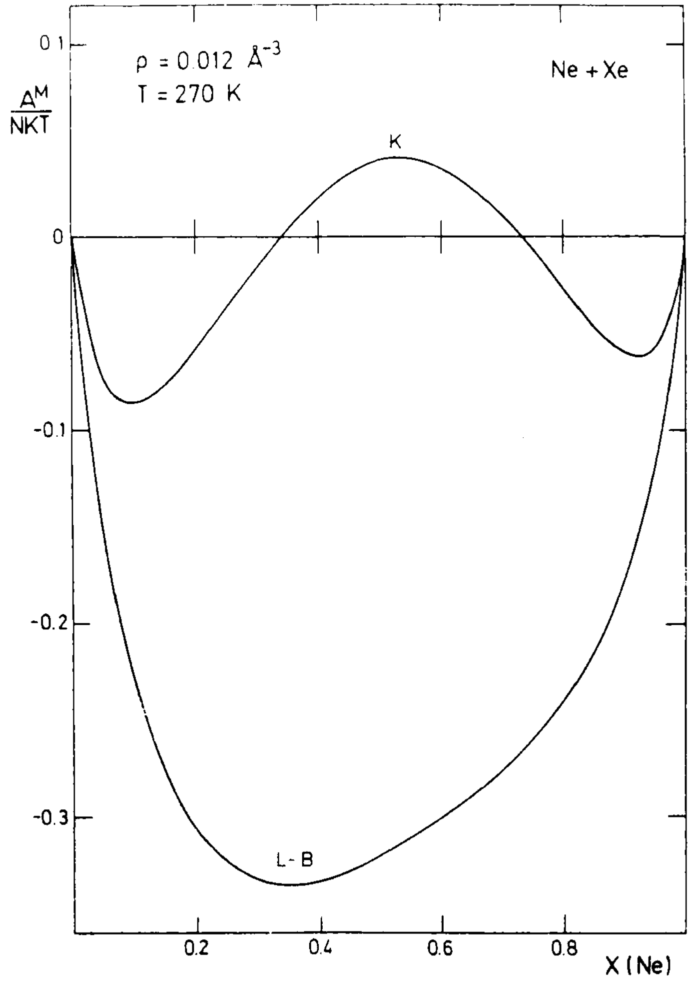

Figure 3 Variation of molar Helmholtz energy with molar fraction at 270 K and $\rho = 1.2 \cdot 10^{-2}$ Å^{-3}. Symbols as in Figure 2.

Table 1 Intermolecular potential parameters (LB = Lorentz-Berthellot rule, K = Kohler's rule).

Interactión	*T/K*	$(\varepsilon/k)/K$	σ/Å
Ne-Ne	—	35.58	2.748
Xe-Xe	—	229.9	3.974
Ne-Xe (LB)	—	90.44	3.361
Ne-Xe (K)	270	27.20	3.593

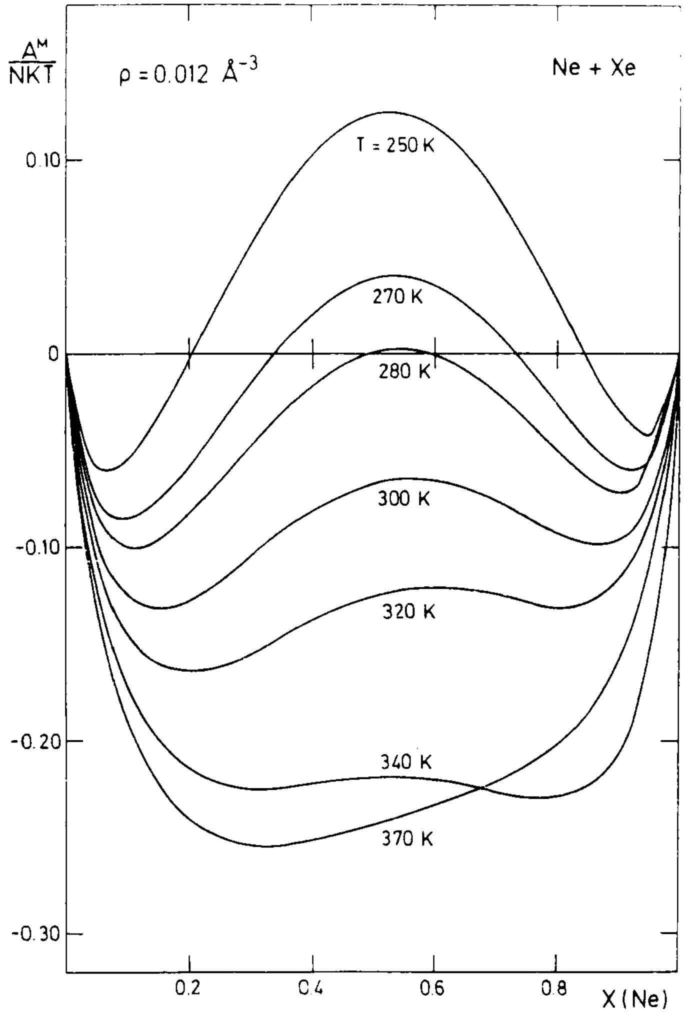

Figure 4 Id. as in Figure 3 but for several temperatures, using only Kohler's rule.

at high densities and $T = 270\ K$ we should expect a vapour-liquid phase separation corresponding to experiment. Figure 3 shows that it is really the case when Kohler's combination rule is applied but not for Lorentz-Berthellot rule. For this system and this temperature, crossed interaction parameters given by the two rules are very different as Table 1 shows. Thus, the simple Lorentz-Berthellot rule shows their unadequacy to predict, even qualitatively, gas-gas separation and, hereinafter, we shall only show results obtained from Kohler's rule. Figures 4 to 6 display the behaviour of A^M for different densities. It seems that critical temperature of separation firstly increases when density increases and lastly decreases. IMFs can be calculated from minima in A^M curves and they are displayed on Table 2. These IMF agree well with the Eq. (16) in the neighborhood of the critical point where perturbation results are likely worse.

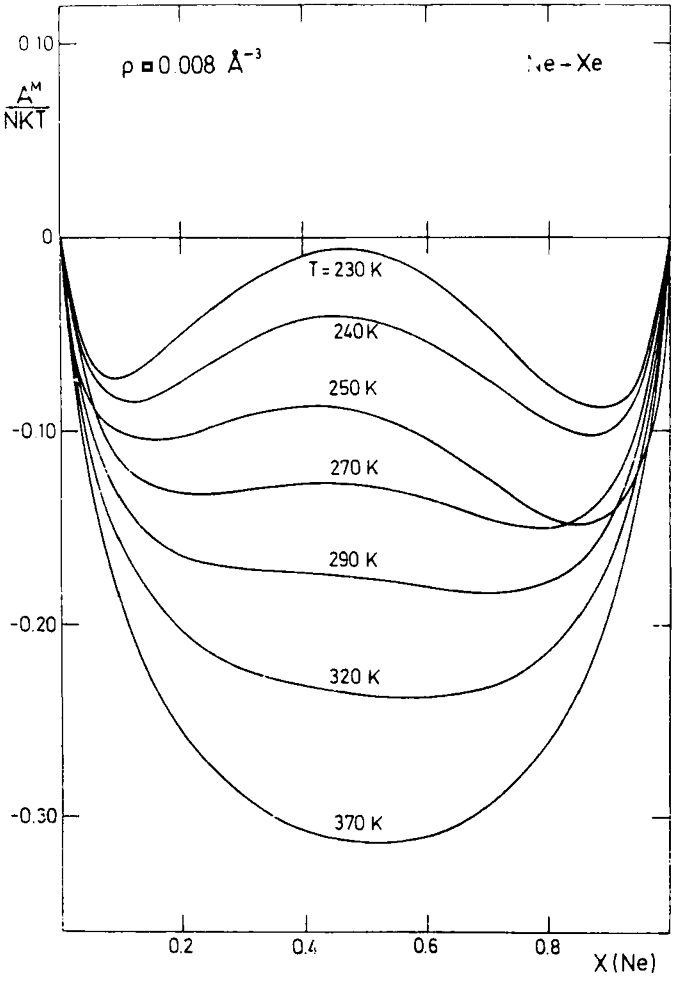

Figure 5 Id. as in Figure 4 but for density $\rho = 8 \cdot 10^{-3}$ Å^{-3}.

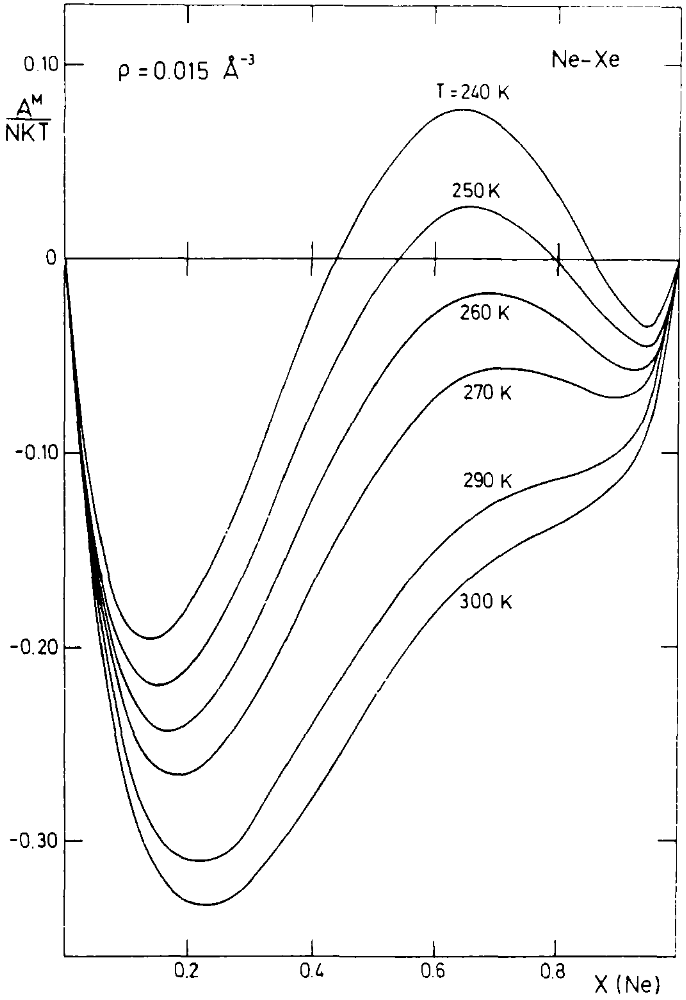

Figure 6 Id. as in Figure 4 but for density $\rho = 1.5 \cdot 10^{-2}$ Å^{-3}.

The difference of IMFs has been fitted to equations of type (8) to obtain the best correlation coefficient and thence T_c and β. As Figure 7 shows an excellent fitting can be reached and instability isochore curves have been recalculated from these values. Figure 8 shows that the calculated curves for two densities agree fairly well with our previous estimations except very near of the critical point. Table 3 shows the critical constants calculated for different densities. Agreement of the critical exponent with experiment[7] ($\beta = 0.35 \pm 0.02$) seems to be excellent at mean densities and to fail completely at higher densities. Although classical exponents are the same for coexistence fraction and IMF, the experimental exponents might not be the same and the agreement could be ony accidental. Moreover, PY equation yields classical

Table 2 Instability molar fractions as obtained from perturbation theory.

$\rho/\text{Å}^{-3}$	T/K	X'	X''	X
0.006	190	0.1320	0.8477	0.488
	210	0.2276	0.7787	0.503
0.007	190	0.0709	0.9108	0.491
	210	0.1094	0.8739	0.492
	230	0.1673	0.8196	0.493
	250	0.3159	0.7479	0.532
0.008	230	0.0994	0.8838	0.492
	240	0.1183	0.8632	0.491
	250	0.1595	0.8484	0.504
	270	0.2205	0.7810	0.501
0.010	270	0.1109	0.8844	0.498
	290	0.1553	0.8406	0.498
	320	0.2557	0.7404	0.498
	335	0.3320	0.6481	0.490
0.012	250	0.072	0.931	0.502
	270	0.102	0.923	0.512
	280	0.117	0.902	0.510
	300	0.158	0.863	0.511
	320	0.203	0.799	0.501
	340	0.317	0.773	0.545
0.013	270	0.1170	0.9262	0.522
	290	0.1538	0.8808	0.517
	310	0.1921	0.8279	0.510
	320	0.2120	0.7280	0.470
0.015	240	0.1421	0.9415	0.542
	250	0.1572	0.9326	0.545
	260	0.1703	0.9233	0.547
	270	0.1856	0.8907	0.538

exponents[26] and the only way to change this conclusion is through the perturbation term which is too unaccurate to give us a definitive conclusion.

As critical temperatures and molar fractions for each density have been obtained, we have made a finer division of densities to determine the pressure according to Eq. (39) obtaining the critical pressures which also appear in Table 3. The phase diagram built from critical pressures and temperatures is qualitatively wrong in several aspects. This diagram shows two double plait-points, one of them at low pressure (low densities) where first order perturbation theories hardly work and whose coordinates are difficult to estimate and a second one at about 370 K, above the experimental as long as the calculated critical point of pure Xe. Therefore, first order perturbation theory truly predicts gas-gas immiscibility but this second double plait-point, which is predicted by the most of theories[27], has not found by Trappeniers *et al.*[28] even at very high pressures.

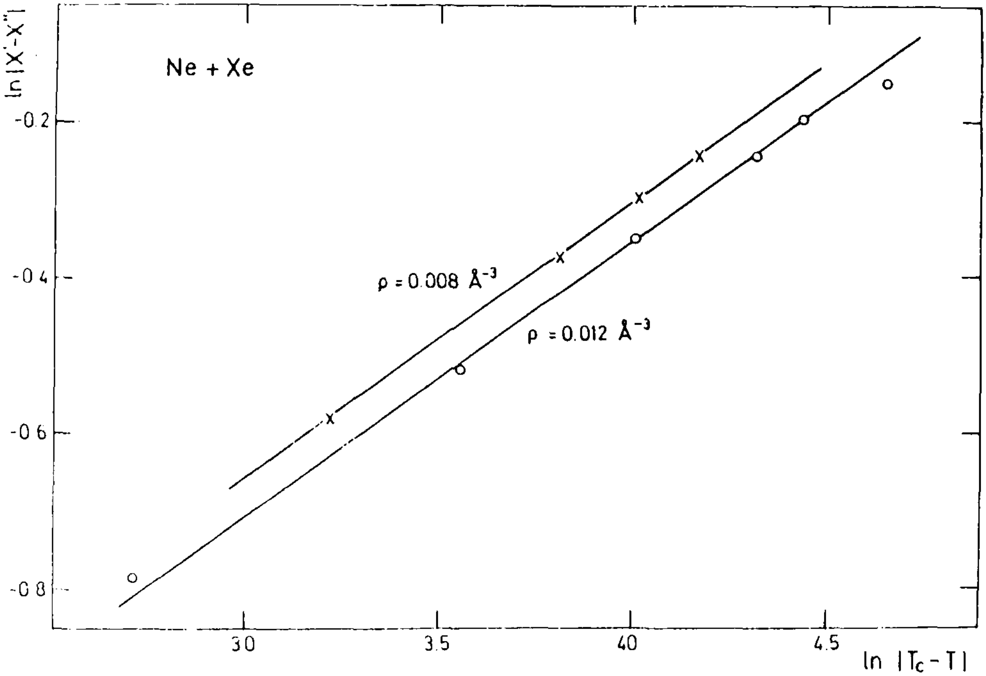

Figure 7 Fitting of differences between instability molar fractions versus differences with critical temperature.

IV CONCLUDING REMARKS

Results obtained in this work clearly show that a first order perturbation theory using pair potentials not including multipolar interactions is able to predict the gas-gas immiscibility. This conclusion is relevant because the most of theories previously used had a markedly empirical character. It also seems clear that the prediction of this separation depends strongly on the fact that the crossed interaction is described in a proper way. Simple Lorentz-Berthellot rule is totally inadequate in this case.

Calculated phase diagram shows two double plait-points and dp_c/dT_c is positive between them. Experimental results give also a branch with $dp_c/dT_c > 0$. Moreover, theoretical branch goes above the critical point of the Xe giving origin to gas-gas immiscibility. However, the second plait-point which some theories else also predict[27], has not been experimentally found. In fact, although Trappeniers *et al.*[28] have extended their previous measurements to 20 kbar, this second double plait-point has never observed. These authors pointed out that melting curve perhaps meets critical curve below this critical point, but in any case discrepancies between theory and experiment would be extremely large. Possible improvements might get by giving a major role to attractive forces either by the introduction of a second order perturbation term or by a different potential splitting with a less repulsive reference term. This

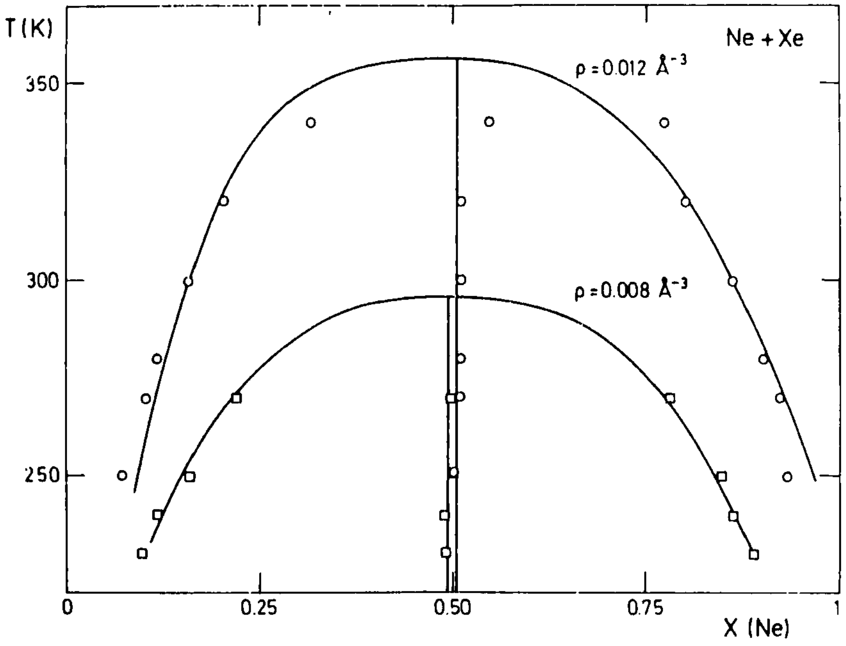

Figure 8 Instability molar fractions versus temperature as calculated from parameters from Figure 7.

second way is simpler and gives better results on a larger range of densities and temperatures at low pressures[23] using perturbation theories. We are currently working in this direction, but our present feeling is that a quantitative prediction of gas-gas separation of phase equilibria at high pressure goes beyond the applicability of usual perturbation theories. Nevertheless, the situation seems not to be so extreme as in the detonation regime where these theories completely fail[29] but perturbation theories should be used very cautiously in this regime of mean temperatures and high densities.

In principle, spinodal line of material instability could also be obtained but due to difficulty of calculating these points in an accurate way, very large computational time

Table 3 Critical constants of the mixtures *Ne* + *Xe*

$\rho/\text{Å}^{-3}$	ρ^*	$\bar{V}_c/(cm.\ mol^{-1})$	T_c/K	$P_c(MPa)$	X_c	β
0.0119	0.164	50.6	335	9.54	0	
0.0060	0.0826	100.4	215 ± 5	14.0	0.488	
0.0070	0.0964	86.0	255 ± 5	16.8	0.492	0.345
0.0080	0.176	75.3	295 ± 5	35.0	0.495	0.345
0.0100	0.219	60.2	340 ± 5	62.7	0.498	0.340
0.0120	0.261	50.2	355 ± 5	95.5	0.507	0.335
0.0130	0.280	46.3	325 ± 5	99.9	0.516	0.185
0.0150	0.314	40.1	280 ± 5	113.1	0.543	0.089

should be required and this seems not to be worth, given the poor agreement with experiment at these pressures.

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