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What is Different in Mixtures? From Critical Point to High Pressures[1]

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It is well known that the properties of mixtures may be very different from those of the pure constituent components, due to the unlike forces. Even for mixtures composed of simple molecules, this behavior can be rather complicated at high pressures, where the system may exhibit gas–gas equilibrium, a critical double point and density inversions. A few mixtures such as He–H_2 and He–N_2 are discussed. It is demonstrated that Raman spectroscopy is an important tool not only for obtaining knowledge about the dynamical behavior of mixtures but also for determining phase equilibria at high pressures. The frequency shift, the linewidth, and the line shape provide information about the solubility, the state of aggregation, and other conditions of the system. Recently, a new type of compound has been found, the so-called van der Waals compound. The results obtained in simple mixtures, such as Ne–N_2 and Xe–N_2, are compared with the results of molecular dynamics (MD) simulations of hard sphere mixtures. It is pointed out that energy, and not a geometrical effect (or entropy), is the driving force for compound formation.

KEY WORDS: compounds; critical double point; fluid–fluid demixing; high pressure; mixed solids; mixtures; Raman spectroscopy; van der Waals compound.

1. INTRODUCTION

The contributions of the van der Waals laboratory in the field of mixtures under high pressure are presented in this paper. This is a very broad field of research, and only a limited number of topics are discussed.

It is well known that the thermodynamic quantities of even binary mixtures composed of simple spherical molecules cannot be obtained by

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simply adding the values for the pure components, weighted by the mole fractions. A subtle balance between the Gibbs free energies of the various phases governs phase equilibria. This already poses a problem in pure substances at relatively low pressures, but the calculation of fluid–fluid, fluid–solid, and solid–solid phase equilibria in mixtures at high pressures is extremely difficult. On the other hand, the sensitivity for the details of the unlike intermolecular potential leads to very rich and very interesting phase diagrams.

Our interest in mixtures is clearly in line with the work by van der Waals. In the early sixties the pressure range was limited to 0.3 GPa at the institute and the research was concentrated on the investigation of the phase behavior of mixtures, composed of simple molecules, in particular, on liquid–gas and so-called gas–gas equilibria. A very interesting aspect was the temperature minimum in the critical line and, related to it, the existence of a critical double point. To find out what happens with the critical line at higher pressures—the occurrence of a second critical double point, the intersection with the solidification surface, or a monotonic continuation towards higher pressures and temperatures—equipment was built for pressures up to 1.5 GPa. Only a few systems were investigated with this equipment. Meanwhile, Streett [1] published the results of his investigations for various mixtures up to about 9 GPa. It became clear very soon that a much larger experimental pressure range was needed. Fortunately, at that time, the diamond anvil technique was developed rapidly due to the invention of the ruby pressure scale. Generally, it was used for pure substances but we developed a method to load the diamond anvil cell at high pressures with mixtures of known composition. Since then, a large number of binary mixtures have been investigated using microscopy, Raman spectroscopy, and p–T scans.

The dynamical behavior in mixtures may differ considerably from that in pure substances. Good insight in the dynamical aspects can be obtained from a combination of experiments and computer simulations. During the last decade many experimental investigations were stimulated by the results obtained from simulations and, *vice versa*.

The following subjects are discussed: (i) phase equilibria including one or more fluid phases, (ii) the application of Raman spectroscopy in studying high-pressure mixtures, (iii) critical behavior, and (iv) mixed solids and compounds.

2. PHASE EQUILIBRIA INCLUDING ONE OR MORE FLUID PHASES

In mixtures of highly similar components—i.e., a small difference in the intermolecular interactions of the pure substances—the critical line moves directly from the critical point of the first to that of the second component (1 in Fig. 1). If the difference in interactions is larger, the line will show a pronounced pressure maximum, and for very large dissimilarity, the shape changes dramatically. The low temperature part disappears under the solidification surface, while the high temperature part may show a temperature minimum at the critical double point and extend beyond the critical temperature of the least volatile component (2 in Fig. 1). In some cases the critical pressure increases monotonically as a function of temperature (3 in Fig. 1). Near the double point the character of the critical behavior is different from that of the normal critical point. Moreover, the phase behavior is rather complex as discussed in Section 4. Possible extensions of the critical line at very high pressures are shown schematically in Fig. 1. As already suggested by van der Waals, the possibility of the existence of another inflection point on the critical line, and thus a second critical double point (or even a third one at a pressure maximum), is an intriguing question (extension c in Fig. 1). This second point implies a temperature beyond which the fluid state will be homogeneous at all pressures while the third point means that above this pressure, the fluid is homogeneous at all temperatures, apart from the formation of solid phases.

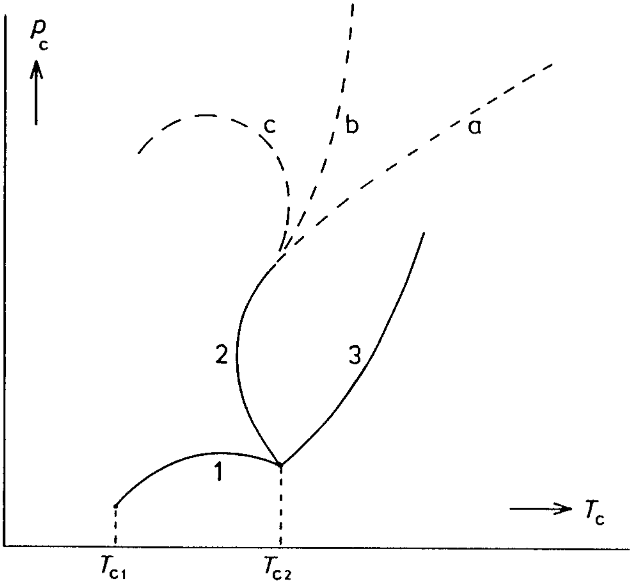

Fig. 1. Some experimentally observed fluid–fluid critical lines (full lines) of binary systems (schematically). Dashed lines are possible extensions.

Several systems have been investigated. In many cases the critical line is terminated by the intersection with the solid–fluid–fluid three-phase line as in helium-argon (1.1 GPa) [1] and neon-xenon (1.5 GPa) [2]. However, in helium hydrogen [3] the solid fluid–fluid three-phase line and the critical line still diverge at 350 K and 7.5 GPa (Fig. 2). Helium nitrogen has been investigated up to 10 GPa and 350 K. Most probably the critical line will disappear under the crystallization surface above 13 GPa and 375 K. In both systems there is no indication of the occurrence of a maximum in the critical temperature and, thus, for a second critical double point. Calculations for helium–hydrogen up to the megabar region showed the same tendency (extension b in Fig. 1) [4]. Nitrogen–water has been investigated up to 800 K [5]. The critical line and three-phase line diverge strongly but the increase in the critical pressure as a function of temperature is very small and the experimental temperatures needed to obtain high pressures are too high.

High-pressure phase equilibria have been calculated using statistical mechanical perturbation theory, in combination with the modified van der

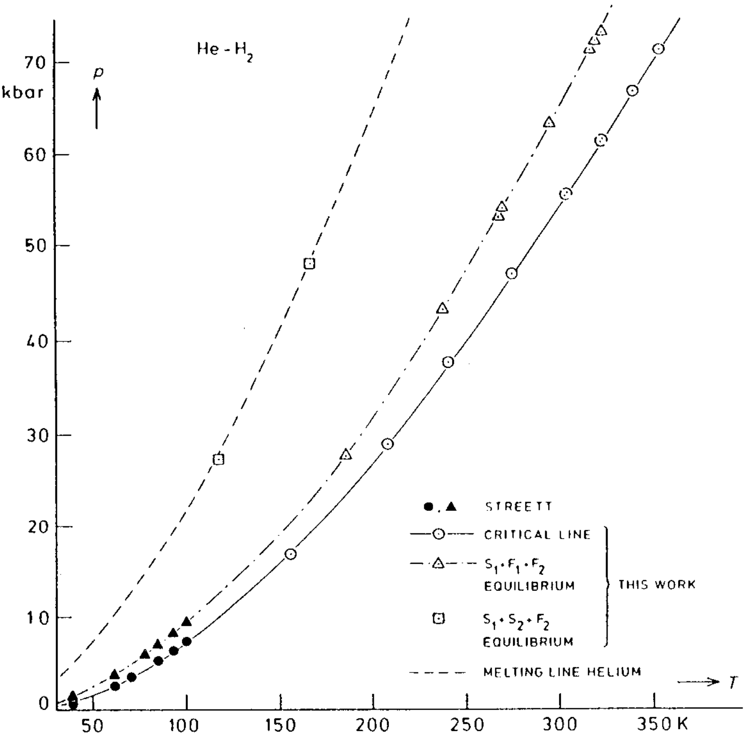

Fig. 2. Experimental p–T diagram of He–H$_2$.

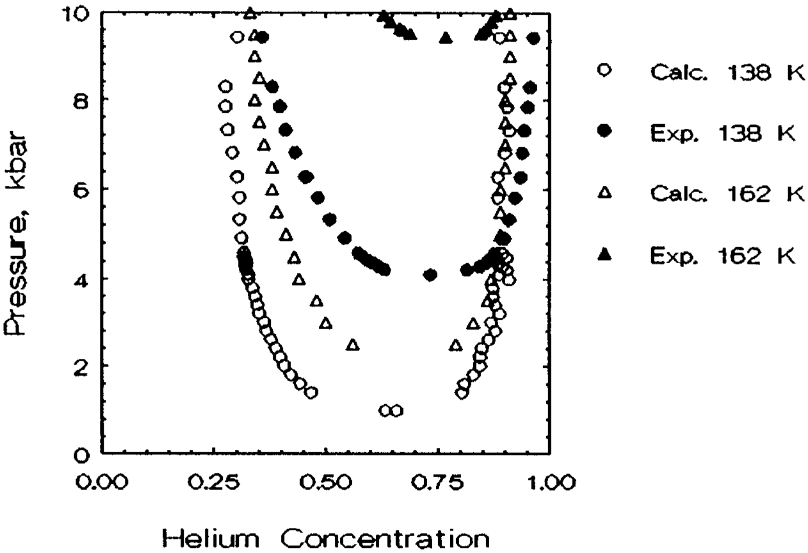

Fig. 3. Comparison between calculated and experimental demixing curves of He–N_2 [7].

Waals one-fluid theory, and self-consistent integral equations. For high pressures Ross variational theory [6]—a semiempirical type of perturbation theory—together with the exp-6 potential is generally assumed to be the best choice. However, although the thermodynamic properties are described quite well, the agreement between calculated and experimental fluid–fluid demixing is poor for systems such as He–Ar and He–N_2 (Fig. 3). At 140 and 160 K, phase separation starts in He–N_2 at about 0.1 and 0.2 GPa [7], respectively, while according to the experiments, the mixture is homogeneous up to 0.4 and 0.9 GPa, respectively (Fig. 2). On the other hand, good agreement has been obtained for He–H_2 [4] and He–Ne [7].

Several factors may attribute to the disagreement: (i) the limitations of the one-fluid model for large differences in size and well depth, (ii) the effect of concentration fluctuations and of the temperature range on the perturbation expression, and (iii) the influence of the molecular shape and the many-body interactions on the effective potential. Extensive molecular dynamics simulations have been carried out for He–N_2 to investigate the influence of the various effects [7]. It turned out, in contrast to current ideas, not only that the size ratio is important but also that the one-fluid model is not applicable when the well-depth ratio of the two pure substances is larger than about three. In variational theory the free energy is obtained by a temperature expansion around the Lennard–Jones system as a reference system and by neglecting higher-order terms (e.g., energy fluctuations). To improve perturbation theory, a mixture (e.g., a Lennard–Jones mixture, as has been done for vapor–liquid equilibria at low pressure [8]) should be taken as the reference system and fluctuation terms should be included to account for the critical concentration fluctuations.

Calculations have also been performed using integral equation theory [7] but with disappointing results. At 250 K demixing in He–N_2 already occurs at 0.5 GPa, while experimentally it happens at 4.5 GPa. In this theory the one-fluid approximation is not used directly, but the unlike potential parameters have been determined from thermodynamic data using a combination of one-fluid and perturbation theory. Possibly the parameters obtained in this way are not accurate enough to predict phase equilibria because it is well known that demixing is very sensitive to the unlike interaction.

It is interesting to note that the critical line and coexistence curves of N_2–H_2O have been calculated with an equation of state of the van der Waals type. The agreement with the experimental critical line is very good, while the correspondence of calculated and experimental coexistence curves is reasonable [9].

Many other interesting phenomena can be observed in fluid mixtures at high pressures. For example, one of the well-known features in binary mixtures, with one of the components having a low molecular weight, is the occurrence of the barotropic effect: the density inversion between the gas-like and the liquid-like phase. Density inversion between the liquid and the solid phase of a mixture has not been observed previously (if the pure solids are denser than the pure liquids, as in He and H_2). However, He–H_2 mixtures with about 10% helium do show such a density inversion over the whole experimental pressure range (2 to 7 GPa) [10]. Therefore, in mixtures with the appropriate composition, the density inversion is complete: the solid floats on top of the liquid, which, in turn, floats on top of the gas phase!

Another interesting example is provided by methane-nitrogen. At high pressures (1 to 4 GPa) mixtures of about 75% nitrogen exhibit fluid–fluid demixing in a small temperature region near the melting temperature of nitrogen [9]. This is unexpected since the generally accepted criterion for the occurrence of this type of equilibrium is a large relative difference in the intermolecular forces of the two components, much larger than in the case of nitrogen and methane. At low pressures this system shows the usual critical line from the critical point of nitrogen to that of methane. The vapor–liquid curves, measured at temperatures below the critical curve (down to 100 K and 1 bar) do not show the onset of a liquid–liquid coexistence region, and thus, this fluid–fluid critical line is probably not a continuation of the liquid–liquid critical line. Moreover, the molecular diameters of nitrogen and methane are nearly equal. Therefore, one would expect the critical composition to be about 50% N_2 and not 75% N_2.

Another aspect is the possibility of measuring the critical line in the metastable region, thus above the critical end point. It is quite normal that an *existing* phase or phase equilibrium can be maintained in the metastable region. In the case of neon-xenon the critical end point is at 1.5 GPa. If a homogeneous fluid mixture of about critical composition is cooled at 1.8 GPa, the stable solid–fluid equilibrium does not appear but the metastable fluid–fluid equilibrium does. At increasing temperature the metastable critical point can be determined [2]. This point shows up and disappears at will on decreasing or increasing the temperature. If the temperature is decreased too much, the stable solid–fluid equilibrium is obtained. On demixing one can observe large fluctuations in the system. With such disturbances one would expect the stable equilibrium to appear. Similar behavior has been observed in helium–nitrogen, where, on cooling a homogeneous fluid mixture, a metastable solid could be formed or where, on heating, a metastable extension of the melting line was observed [11]. This can be very useful in determining the coordinates of a triple or quadruple point.

3. HIGH-PRESSURE RAMAN SPECTROSCOPY

Raman spectroscopy is a very useful tool in studying fluid and solid mixtures at high pressures. Phase transitions can be detected, and information about the dynamics of the transition can be obtained from the spectra. Both the peak position and the linewidth reveal information about the microscopic behavior of the molecules, orientational as well as translational. In mixtures, Raman spectroscopy can be used as a tool for determining the concentration or the concentration fluctuations. A comparison of experimental data with results of molecular dynamics simulations gives substantial insight into the effects of the surrounding medium on the spectra.

Measurements in the fluid mixture proved to be important for understanding the spectral behavior of pure substances as will be demonstrated using the data of nitrogen and nitrogen in helium. The result is essential to extract information from the spectra about the phase diagram, the compound formation, and the microscopic behavior of the system. In nitrogen the experimental vibrational frequency first decreases as a function of pressure and, via a minimum at 0.14 GPa (Fig. 4), then increases. Above 1 GPa the red shift turns into a blue shift. Sometimes, this behavior is loosely explained as follows: at low pressures the attractive forces between the molecules are dominant, leading to a larger bond length and thus to a lower frequency, while at higher pressure the repulsive forces are the most important. Such an explanation is misleading as will be shown. Schweizer and Chandler [12] calculated the density dependence of the frequency shift by modeling the nitrogen molecule as a hard dumbbell in surroundings of

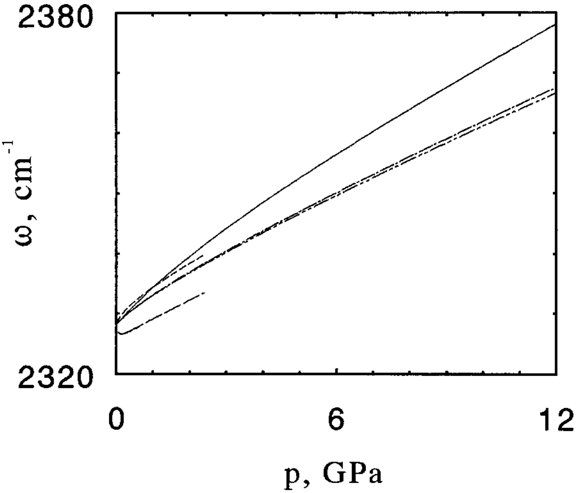

Fig. 4. Raman shift of N_2 diluted in He. Solid line: experiment. Long-dashed line: experiment, pure N_2. Dashed double dotted line: hard-fluid result. Dashed dotted line: hard-fluid without second order effect (not discussed). Dashed line: hard-fluid result for pure N_2.

hard spheres ("hard-fluid" model). An attractive term, linear in density, was added to take into account the bond-length dependence of the interaction. This method was modified by Ben-Amotz and co-workers [13] and resulted in a good agreement for nitrogen but not for other systems. Ben-Amotz made the important statement that "the constant (adjustable parameter) depends on the differential attractive solvation energy of the solute in the ground state and excited vibrational states."

The reason for this discrepancy is most easily demonstrated by the frequency behavior of a dilute mixture of nitrogen in helium. In Fig. 4 the experimental results are presented for this mixture at room temperature and up to 12 GPa. Also shown are the hard-fluid (HF) calculations for the system. The most important feature is that, in contrast with pure nitrogen, in the mixture the frequencies calculated with the HF model are clearly below the experimental values. Therefore, it is impossible to get agreement with experiment by adding the attractive correction, which is always negative, to the HF values.

Computer simulations provide the opportunity to investigate the relative importance of the various contributions to the frequency shift and to study the sensitivity of the results for variations in the intermolecular potential. Simulations carried out with the full potential (thus both repulsive and attractive parts) always result in a blue shift of the frequency with respect to the isolated molecule. In general, it turns out that the details of the intermolecular potential hardly influence the bond-length independent contribution to the frequency shift. In recent simulations [14] the problem is solved by determining the change in potential energy, at vibrational excitation of the molecule, from the difference in frequency (the energy gap) between the simulated and the experimental data of the shift. The correction is called the dispersion correction, and a full discussion of the simulations is given by Michels and Schouten [15].

The details of the vibrational spectrum, e.g., the linewidth, provide information about the dynamical behavior of the system. The linewidth has been determined experimentally for a number of pure substances and mixtures. As a function of pressure it exhibits the same behavior as the frequency. Previously, various investigators have tried to calculate the linewidth by analytical methods and computer simulations but with limited success. Introduction of the above-mentioned dispersion correction results in good agreement between experimental and simulated linewidths [14].

Although the information obtained by Raman spectroscopy on the microscopic behavior of the system is of fundamental importance, we restrict the discussion to the application of the technique to the exploration of the phase diagram.

Raman spectroscopy can be used for the detection of phase transitions. In many cases it is advisable to perform measurements along isobars. First, the Raman frequency is only a weak function of temperature. Moreover, at high densities the pressure is a measure for the *average* forces on the molecules, while by a change in orientation the *axial* components of these forces will change. The shift of the Raman frequency due to the surrounding medium is caused mainly by axial components of the intermolecular forces. Therefore, measuring data along isobars is a suitable method to study the frequency change due to a change in orientation, because the average forces hardly change. In this way even a second-order transition has been detected in δ nitrogen and in the solid argon–nitrogen mixture [16]. Note that in the last system one obtains, from the intensity of the lines, also information on the position of the argon atoms on the lattice.

In general, the Raman frequency in simple molecular systems shifts as a function of concentration due mainly to a change in dispersion correction. This provides a way to estimate the composition and to detect a phase separation in a homogeneous fluid mixture, even if one of the coexisting phases is not Raman active. In principle, the same holds for the mixed solid, although complications may occur, as in the δ phase of nitrogen. At a solid–solid phase transition a discontinuity in the frequency usually occurs and sometimes the number of lines changes. The shift also gives an indication for the appearance of a compound because the frequency

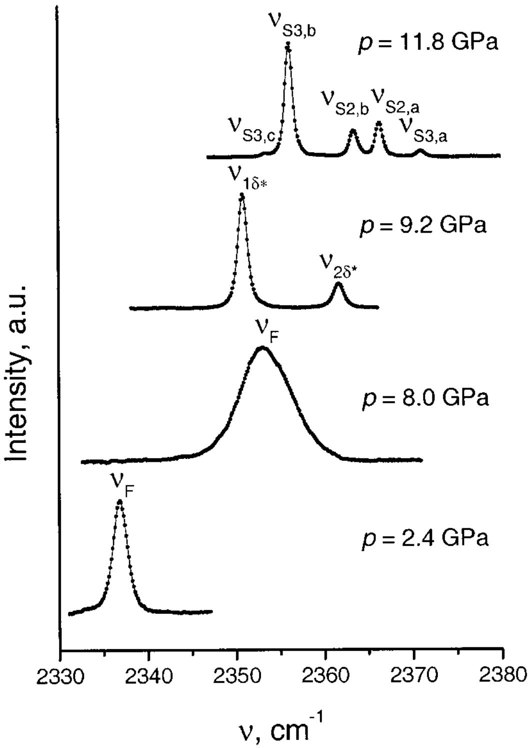

Fig. 5. Raman spectra of N_2 in Ne–N_2 at 296 K. The mole fraction of N_2 is 0.35 [16].

is influenced by the structure (Fig. 5). Some illustrative examples have been presented in Ref. 17. Finally, if a smaller molecule is dissolved in the lattice of a larger molecule, the axial force exerted on the small molecule is lower than in its own lattice at the same pressure. This results in an additional decrease in the Raman frequency.

The linewidth also provides information on the system. In fluids the lines are broad and the width is strongly dependent upon pressure, while in solids the linewidth is small and less pressure dependent. Due to the effect of concentration fluctuations, in fluids the linewidth shows a pronounced maximum when the volume fractions of the two components are equal. In critical mixtures this maximum is even higher; in this case there is an appreciable temperature effect on the linewidth. A comparable situation is encountered in disordered mixed solids. It is clear that in these cases the concentration gradients will last a very long time, which result in a slower modulation time and thus a broader line.

4. CRITICAL PHENOMENA

In some systems the critical line starts at the critical temperature of the least volatile component with a negative slope but moves, via a temperature minimum, toward higher temperature at higher pressures. This temperature minimum is a so-called critical double point where the character of the critical behavior is different from that in the normal critical point. Near the critical double point the phase behavior is rather complex: a very small temperature variation changes the shape of the isotherms dramatically. For example, in neon–krypton at 164.69 K (−108.46°C, Fig. 6) an isothermal coexistence curve consists of a liquid and a gas branch, well separated from each other. At 164.73 K (−108.42°C) the isotherm forms a closed gas–liquid equilibrium curve at lower pressures with a critical point at the maximum pressure and a high-pressure gas-gas equilibrium curve with a critical point at the pressure minimum [18]. According to Griffiths and Wheeler [19], an anomalous critical behavior occurs because the critical line is asymptotic parallel to one of the field axes (the p-axis). Relevant

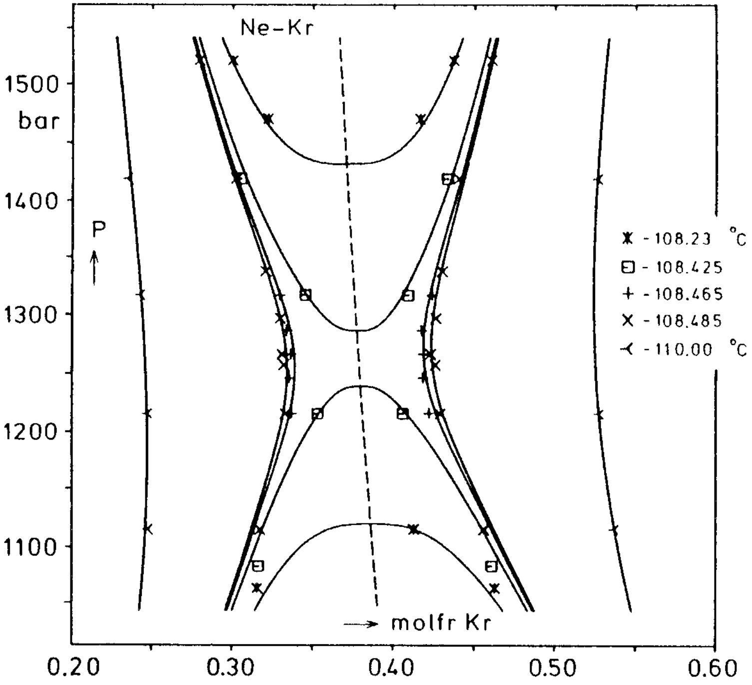

Fig. 6. Experimental p–x diagram of neon–krypton in the vicinity of the critical double point [17].

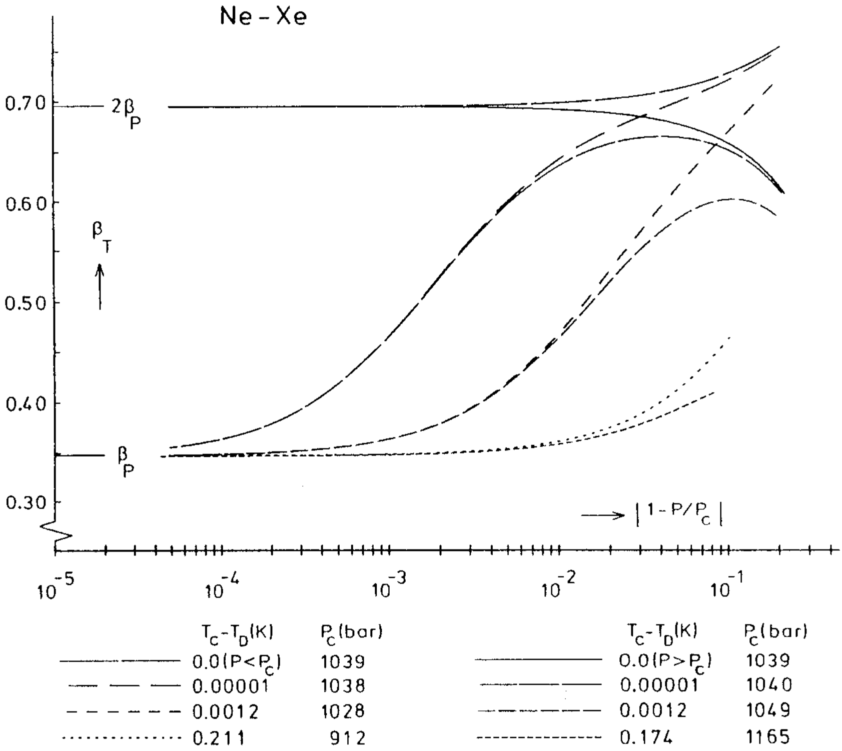

Fig. 7. Critical exponent β_T in Ne–Xe as a function of the distance to the critical point [17].

for the phase diagram is only the critical exponent β_T that should have a value twice that of the normal critical point. An elaborate study of the shape of the coexistence surface near the critical double point has been made for neon–xenon [18]. It turns out that the anomalous critical behavior is hardly relevant for the phase diagram. Deviations in the exponent β_T only occur very close (not more than a few millikelvin) to the double point (Fig. 7).

In pure substances critical phenomena occur at maximum pressures of the order of 100 bar (except water). In liquid mixtures critical behavior is usually studied at atmospheric pressure. The above example shows that, if the interaction potentials of the two components are quite different, this behavior can be studied at much higher pressures. In some cases it is of great advantage to carry out an investigation at very high pressures. Measurements have been performed up to 10 GPa on helium–hydrogen and helium–nitrogen [20] with Raman spectroscopy and microscopy. At room temperature the critical pressures for these systems are 5.5 and 7 GPa and the critical mole fractions of helium are 0.6 and 0.8, respectively. Even in these circumstances critical opalescence due to concentration fluctuations can be easily observed under the microscope. When the critical point is approached from below, the meniscus gradually broadens (with large fluctuations inside the region of the meniscus) and straightens out before it disappears, and when it is approached from above, large fluctuations appear through the sample space.

As far as the Raman line shift is concerned, the critical point appeared to be no special point. The shift is nearly a linear function of the volume fraction over the whole range [20]. This suggests that the average local composition is not different from the bulk composition. On the other hand, the linewidth shows a considerable broadening, in particular, at the critical composition. Line broadening also occurs in mixtures far from the critical point due to noncritical concentration fluctuations but it is assumed that this effect is much smaller. In a paper by Michels and Schouten [15], it is discussed how one can distinguish between critical and noncritical concentration fluctuations by performing MD simulations. It is remarkable that at temperatures more than 100 K above the critical temperature, or at pressures less than half the critical pressure, this broadening is easily observable. This is understandable if one realizes that with Raman spectroscopy the influence of the immediate surroundings on the molecule under consideration is sampled. Therefore, even if the wavelength of the concentration fluctuations is only a few molecular diameters, the effect can be measured.

5. MIXED SOLIDS AND COMPOUNDS

An important conclusion from studies on metallic systems is that solubility at high density, in particular in solid systems, is governed mainly by geometrical effects, as expressed by the well-known Hume–Rothery rule [21]. This empirical rule states that a binary mixed solid is obtained only if the ratio of the diameters of the molecules, α, is larger than 0.85. In recent years, the phase diagram of hard-sphere systems has been accurately calculated by computer simulations as well as by analytical theories, such as density functional theory and cell theory. For completely disordered mixed solids, the Hume–Rothery rule is in fair agreement with the simulations and analytical theories. An interesting aspect, shown by the simulations [22], is that the solubility of large spheres in the solid formed by small spheres is much smaller than *vice versa*. We will investigate whether these geometrical rules are also valid for molecular systems.

When the molecular diameters of the two components differ considerably, stoichiometric compounds can be formed. For hard-sphere systems the entropy or efficient packing stabilizes these compounds. Computer simulations [23], packing considerations, density functional theory, and cell theory on hard-sphere binary systems predict stability of only the compounds AB, AB_2, and AB_{13} (Fig. 8), where the index represents the number of molecules in the (sub-)unit cell, and B is the smaller molecule. The stability ranges as calculated for hard sphere systems by the cell theory of Cottin and Monson [24] are $0.2 \leqslant \alpha \leqslant 0.61$. In recent years several compounds have also been found in molecular systems. Because the interactions between the molecules are of the van der Waals type, these solids are called van der Waals compounds [25]. It is usually assumed that efficient packing of hard spheres drives the formation of these compounds. The stoichiometric composition is dictated mainly by α [26]. In this work we investigate if the formation of van der Waals compounds is indeed determined by these parameters (see also Ref. 27).

Although α might be important, it is reasonable to assume that the factors leading to demixing in the fluid state have influence also on the solubility in the solid state. For example, the shape of the diagrams of mixtures of helium with neon, argon, krypton, and xenon, in particular, the existence and range of fluid–fluid demixing, was explained [28] by the difference in the repulsive part of the potential. However, the attractive part also changes considerably from neon to xenon and it was shown at

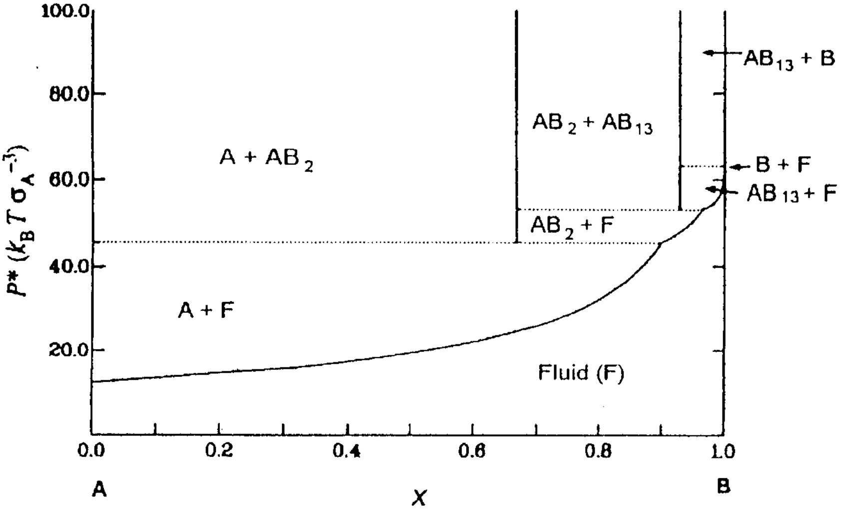

Fig. 8. l_0–x diagram of hard spheres for $\alpha = 0.58$ [22].

the beginning of the last century that, given the size ratio, fluid–fluid equilibrium occurs only for small ratios of the attractive part of the potential.

As far as the disordered mixed solids are concerned, there is at least one aspect, shown by hard-sphere mixtures, which seems to hold also for most of the other systems: the solubility of the large component in the solid of the small component is much less than *vice versa.* This has been observed in He–Ne and, possibly, in He–H_2, He–N_2, and Ne–N_2. However, a closer look at the results reveals differences from hard-sphere systems. The system Xe–N_2 indeed shows mutual solubility (Fig. 9), as expected on the basis of the diameter ratio ($\alpha = 0.89$), but there is a larger solubility of the larger xenon molecules in nitrogen than *vice versa.* There is no solubility of the large nitrogen molecules in solid neon ($\alpha = 0.74$), in agreement with the predictions for hard-sphere systems, but the small neon molecules do dissolve into the β^* and δ^* phases of N_2 (Fig. 10), even though the diameter ratio is much smaller than 0.85. For He–N_2 the difference in diameter is even larger ($\alpha = 0.62$) but helium dissolves into solid nitrogen. This results in a considerable deviation of the Hume–Rothery rule.

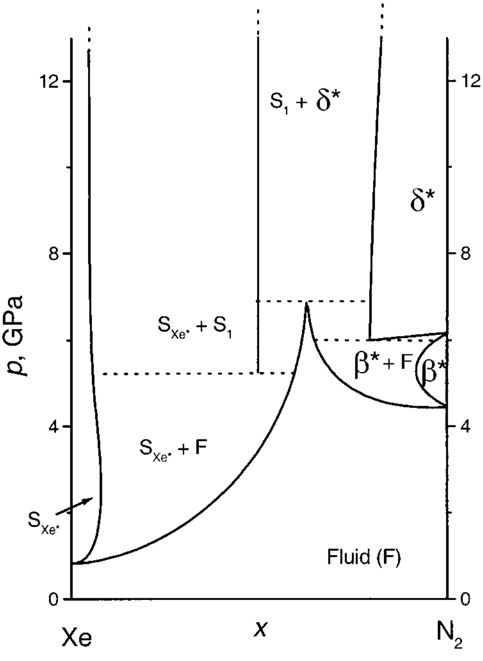

Fig. 9. Proposed phase diagram of Xe–N_2 at 408 K [16].

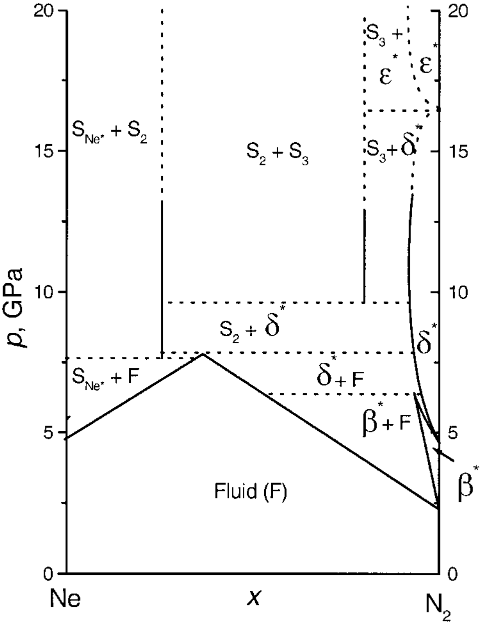

Fig. 10. Proposed phase diagram of Ne–N_2 at 296 K [16].

Obviously the shape of a molecule is of less importance for the properties of the fluid phase than for those of the solid phase, where the orientation behavior plays an important role. In simple diatomic systems such as nitrogen, the shape, in combination with the accompanying quadrupole forces, leads to a complex phase diagram. The molecular sizes of argon and oxygen are almost-equal ($\alpha = 1$). However, the solubility of argon in the various high-pressure phases of nitrogen is quite different from that of oxygen in nitrogen. The explanation could be that the orientational degrees of freedom of N_2 and Ar are quite different, while they are nearly the same for N_2 and O_2. In N_2 the β-region is extended at the cost of the δ-region by adding argon, but at increasing O_2 mole fractions, the β-region shrinks in favor of the δ-region. The directional forces (quadrupole or octupole moment) may be responsible for this difference in behavior. Moreover, the free energy differences between solid phases are very small so that small changes in the Van der Waals, anisotropic, and Coulomb contributions to the interaction may shift the calculated phase transitions substantially.

For α-values smaller than 0.85, van der Waals compounds have been found experimentally with composition $A_{11}B$ (N_2–He, $\alpha = 0.62$), A_2B (CH_4–H_2, $\alpha = 0.72$), AB (CH_4–H_2), A_3B_4 (O_2–H_2, $\alpha = 0.80$), AB_2 (Ne–He,

$\alpha = 0.83$; Ar–H_2, $\alpha = 0.80$; CH_4–H_2), and AB_4 (CH_4–H_2), where B represents the smaller molecule. As mentioned before, hard-sphere systems exhibit only the compounds AB, AB_2, and AB_{13} and only for $\alpha \leqslant 0.61$. Even for Xe–N_2 ($\alpha = 0.89$) a compound has been found recently [17], probably with composition AB or AB_2, while, for N_2-Ne ($\alpha = 0.74$), AB_2, AB_4, or AB_{13} has been suggested and, for another compound, $A_{11}B$ [17]. AB_{13} has not been found in other systems. The above-mentioned experiments clearly show that the occurrence of compounds is not dictated only by the diameter ratio of the molecules and, therefore, that the driving force for the formation of these compounds is not just the entropy.

The compound in He–Ne, although with composition AB_2, is of the $MgZn_2$ type (Laves structure), which does not occur in hard-sphere mixtures. Elaborate calculations [29] have pointed out that in the Laves phase the volume of the compound is smaller than that of the combination of the pure substances, suggesting that the compound is stabilized by efficient packing. However, it also turns out that both the energy and the entropy of the compound are lower than those of the combination of pure substances. Therefore, the formation of this compound is completely driven by the energy. It is interesting to note that the unlike interaction between the particles is less important than the like interaction. In the mixtures H_2–Ar and H_2–CH_4, the AB_2 compounds also have the Laves structure.

The behavior of helium–nitrogen is rather complicated since at room temperature a Van der Waals compound can be formed [25], while at lower temperatures (also) a disordered solution exists [30]. Recent Raman measurements at room temperature up to 40 GPa [31] reveal strong similarities between the spectrum of the compound and that of ε-N_2. The authors suggest a close relationship between the structures of both solids. It is also suggested that the N_2 molecules, which are substituted by helium atoms, originate from the *a* positions in ε-N_2. Therefore, it is possible that the low temperature disordered solution is substitutionally, partially disordered. One would not expect a substitutionally disordered solution of systems with such a small diameter ratio (about 0.62)

Yantsevich *et al.* [32] discussed the limited solubility in cryocrystals. Based on the data for nine binary systems of the maximum solubility in an atomic cryomatrix, they stated that the difference in molecular diameters is not the main parameter for the stability of a solid solution. Their conclusion is that a positive value of the mutual exchange energy is the physical reason for phase separation at low temperatures in binary systems of cryocrystals.

In conclusion, one can say that in all cases the occurrence and the structure of the compounds are in disagreement with hard sphere calculations. The solubility in disordered systems is sometimes in disagreement. As shown, the intermolecular energy plays an important role and the diameter ratio is certainly not the only parameter. The influence of the molecular shape will also be of significant influence.

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