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REVIEW ARTICLE

Recent advances in the study of high-pressure binary systems

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Abstract. Until recently the research on binary systems at high pressures was mainly focused on the phase behaviour of the fluid phases. In the last few years the interest has shifted towards other properties of the mixtures and towards the coexisting solid phases. Several exciting new discoveries have been made. In this article the recent developments in the field will be described.

1. Introduction

Several excellent review articles and books on the behaviour of mixtures at high pressures have already appeared [1–5]. This article will describe some recent developments in the field. The pressure range under consideration will generally be restricted to pressures above 1 GPa.

In [5] the emphasis was on the demixing in the fluid phase but since then many other aspects of mixtures have also been studied in a diamond anvil cell (DAC). In this respect we should mention the detection of the existence of new solid phases in simple systems, the investigations of high-pressure clathrate hydrates, the study of unlike interactions and critical fluctuations by spectroscopic methods, and the experiments on mixed solids. The results of these investigations promise interesting new fields of research.

The high experimental pressures imply that the research has mainly been carried out with the use of DAC. A DAC consists of two opposed diamond anvils with a metal gasket (of thickness of the order of 0.2 mm) between the diamond faces (of diameter 0.5 mm). A small hole (about 0.1 mm) in the gasket serves as the sample space. A chip of ruby is introduced into the sample space and the shift of the fluorescence lines is measured to determine the pressure. The DAC can be used to determine a variety of properties of matter at high pressures since diamonds are transparent for electromagnetic radiation in a large wavelength interval [6]. For mixtures the most important techniques are x-ray diffraction, Raman spectroscopy, microscopy, Brillouin spectroscopy, and p - T scans.

Raman spectroscopy is one of the most powerful tools for studying simple molecular systems at high density [7]. The vibrational frequency of a molecule changes when its surroundings are changed. Therefore, the formation of other phases by phase separation, changes in bond length as a function of pressure and temperature, the formation of new structures, etc can be easily detected. The shift of the frequency and the profile of the spectrum give information about the microscopic behaviour of the system. Of course, x-ray spectroscopy is used to determine the structure and the lattice parameters.

With the help of microscopy the phase boundaries can be determined very accurately if, apart from solid phases, one or two fluid phases are involved. If only solid phases are present it is often much more complicated. In mixtures three-phase lines play almost

the same role as two-phase lines in pure substances. Generally the molar volume changes discontinuously if a three-phase line is crossed. Such a change can be easily detected by measuring the pressure as a function of temperature at (nearly) constant volume (a p - T scan), also in the case of solid phases. It should be noted that microscopy and p - T scans are also effective if the system is not Raman active. Finally, Brillouin scattering can be used to determine thermodynamic properties at very high densities.

We start in section 2 with a description of the latest results concerning phase equilibria, in particular between fluid phases. In the analysis of the phase diagrams some of the solid-fluid equilibria will also be mentioned. However, the character of the solid phases is discussed in section 3, where it is shown that a variety of solid phases may be in equilibrium with one or two fluid phases. In some cases the stability criteria are discussed. In section 4 calculations using perturbation theory, density functional theory, computer simulations, etc are discussed. Section 5 gives the results on inclusion compounds with emphasis on new phases in clathrate hydrates and the latest results on fullerenes. Section 6 treats the information obtained from spectroscopic measurements. Moreover, some measurements on the thermodynamic properties in the homogeneous fluid phase will be presented since they are used in the calculations. Finally, in section 7 an outlook will be given for future developments.

2. Phase equilibria

In this section new experimental results on high-pressure phase equilibria are described with emphasis on the equilibrium between fluid phases. In many cases the fluid phases are in equilibrium with a solid phase, but the character of the solid phase will be discussed in section 3, if any information is available. During the last five years supplementary data have been obtained on helium-hydrogen and more substantial information on helium-nitrogen while the high-pressure phase diagrams of the following new systems have been experimentally investigated: helium-neon, hydrogen-neon, nitrogen-methane, nitrogen-carbon dioxide, nitrogen-oxygen, and nitrogen-water. The results obtained so far will be extensively discussed below.

2.1. Helium-hydrogen

A few years ago there were some discrepancies [5] between the phase diagrams of helium-hydrogen measured by two different groups [8,9]. Recently the phase diagram at room temperature has been redetermined [9]. Both the position of the fluid-fluid-solid triple-point and the slope of the fluid branch of the solid-fluid equilibrium are now in agreement. The meaning of an interesting cusp on the helium rich branch (90 mol% He) of the fluid-fluid equilibrium should be investigated by performing measurements at other temperatures. It seems unlikely that this cusp would evolve at high temperatures to a closed fluid-fluid domain as suggested in [9] since it will be difficult to construct a thermodynamically acceptable critical line in agreement with this hypothesis.

2.2. Helium-nitrogen

The helium-nitrogen system has been extensively studied from 100 to about 450 K and pressures up to 12.5 GPa [9-13]. The first indications of a complicated phase diagram were given by two cusps in the three-phase fluid-fluid-solid line, representing quadruple points [10]. These quadruple points do not match with corresponding triple points in the phase diagram of nitrogen. It turned out that the ϵ - δ phase transition line of nitrogen was

considerably shifted towards higher temperatures and lower pressures due to the admixture of helium. Measurements (with mixtures containing up to 11 mol% helium) at about 7 GPa and 170 K showed that under these circumstances considerable amounts of helium could be dissolved in ϵ -nitrogen [11]. The conclusions have been confirmed by Raman spectroscopic measurements [12]. Later x-ray diffraction, visual observation, and Raman spectroscopy revealed [13] that at room temperature and about 9 GPa a stoichiometric, solid van der Waals compound was formed with composition $\text{He}(\text{N}_2)_{11}$. This unusual solid will be discussed in section 3. The p - x diagram at room temperature is given in figure 1.

The system exhibits fluid-fluid equilibria up to at least 10 GPa. The critical composition is about 80 mol% helium and is nearly independent of pressure from 2 to 10 GPa. The triple-point composition (fluid-fluid-solid) slightly shifts as a function of pressure towards higher helium concentrations, narrowing the fluid-fluid region. A complete survey of the phase behaviour of helium-nitrogen is given in [14].

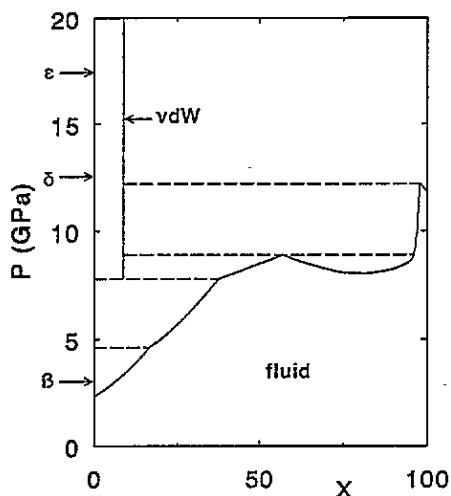


Figure 1. The p - x diagram of helium-nitrogen at 295 K [13, 14]. x is mole per cent helium. The van der Waals compound is indicated by vdW, while β , δ , and ϵ are solid nitrogen polymorphs.

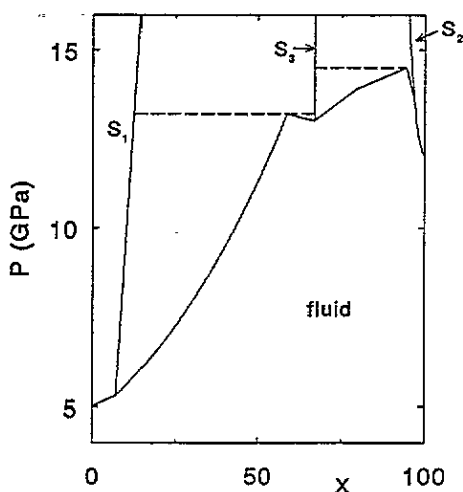


Figure 2. The p - x diagram of helium-neon at 296 K [15]. x is mole per cent helium. S_3 is the $\text{Ne}(\text{He})_2$ compound.

2.3. Helium-neon

The p - x diagram of this system, consisting of simple spherical molecules, has been determined at room temperature and pressures up to 15 GPa [15]. The p - x diagram is given in figure 2. Apart from a small region around 13 GPa the components are completely miscible in the fluid phase. At high helium concentrations helium-neon shows the usual eutectic point. A second eutectic point appears at a mole fraction of about 0.5. It is to be expected that such a point is related to fluid-fluid equilibrium but in this case only solid-fluid equilibrium was observed. The most interesting aspect of this apparently simple system is the existence of a homogeneous solid mixture at a helium mole fraction of $\frac{2}{3}$. The properties and importance of this solid phase will be discussed later.

2.4. Hydrogen–neon

This system has been investigated at room temperature up to about 7.5 GPa [16]. The experimental results are presented in figure 3. In the fluid phase, which extends up to about 5 GPa nearly independent of composition, the components are miscible in all proportions except for a small region at about 25 mol% neon. The behaviour of the solid phases seem to be rather complicated although the experimental information is limited. It needs further investigation before conclusions can be drawn about the mutual solubility in the solid phases.

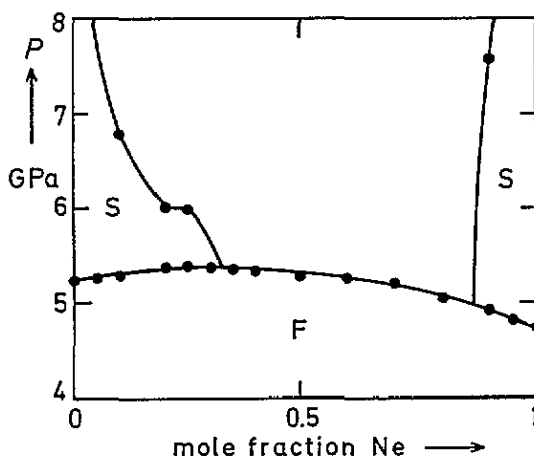


Figure 3. The p - x diagram of neon–hydrogen at 300 K [16].

2.5. Nitrogen–methane

Since the intermolecular potential of the two components is very similar it is considered to be an almost ideal system. However, it turns out [17] that the fluid–solid behaviour at high pressures is rather complicated. Most probably the system has two eutectic points at about 30 and 80 mol% methane and it shows five different solid–fluid equilibria. The (nearly) pure solid substances are separated by a mixed solid in the composition range from 40 to 70 mol% methane. This mixed solid extends over a large temperature range (more than 200 K). A very interesting aspect [18] (see also section 4) is the existence of a fluid–fluid equilibrium for high nitrogen concentrations and close to the melting point of nitrogen.

2.6. Nitrogen–carbon dioxide

The high-pressure phase behaviour of this mixture is of importance for geologists. Rock inclusions often contain these substances and, for the interpretation of the data, knowledge about possible phase separations is crucial. There are two models, only one of which predicts the existence of fluid–fluid equilibrium for an equimolar mixture. Experiments have been performed up to 425 K for mixtures with 50 and 75 mol% nitrogen [19]. Up to 4 GPa the equimolar mixture did not exhibit fluid–fluid demixing. It should be noted that the melting line of this mixture intercepts that of nitrogen at about 25 kbar and 320 K. It should also be noted that in the case of the mixture with 75% nitrogen a region of fluid–fluid equilibrium exists, which extends about 60 K at 1 GPa. The general behaviour seems to be similar to that of nitrogen–methane.

2.7. Nitrogen–oxygen

The room temperature phase diagram of nitrogen–oxygen has been determined up to 12 GPa by Raman spectroscopy [20]. In the fluid phase the two components are completely miscible. Again, the solid phase diagram is rather complicated. It is interesting that only in δ -nitrogen and β -oxygen is the mutual solubility very high.

2.8. Nitrogen–water

Finally we will consider the behaviour of mixtures of nitrogen with a polar component, in particular the shape of the critical line. Two groups have performed a study of the nitrogen–water system [17, 21, 22]. Since the critical temperature of water is rather high (about 650 K) the measurements were performed under difficult experimental conditions and therefore the accuracy is lower. Measurements have been performed for mixtures with 75 mol% water [21] and with 50, 67 and 85 mol% water [17]. It is suggested [17] that e.g. the line of constant composition with 67 mol% water has a peculiar shape. After touching the critical line, as is usual, the slope of the line first decreases and then increases again. The slope of all the isopleths is certainly not as steep as might be expected from literature low-pressure data. As a direct consequence the critical line is rather flat since that slope must be even smaller. At higher pressures the critical mixture contains about 50 mol% water.

3. Solid phases

Of course, the character of the solid phases in equilibrium with fluid phases strongly depends upon the components constituting the system, but, given the system, an important role is played by composition apart from pressure and temperature. Recently, a very interesting development in the study of mixtures took place with the detection of a rather complicated new type of solid in helium–nitrogen [14]. Now it turns out that even in mixtures of simple components various mixed solids may be formed. Another field of research in which considerable progress has been made is that of clathrate hydrates and solubility in water ices. Finally, because of the increasing interest in the behaviour of fullerenes, the first experiments on the inclusion of simple molecules in bucky balls at high pressure and high temperature have been performed.

3.1. Helium–nitrogen

As mentioned before, at about 7 GPa and 170 K considerable amounts of helium can be dissolved in ε -nitrogen [11]. However, a later x-ray investigation at room temperature and 8 GPa revealed the existence of a new type of solid [14]: a weakly bound stoichiometric compound with composition $\text{He}(\text{N}_2)_{11}$ (figure 1). The unit cell is hexagonal and consists of 24 molecules. The structure is different from those of the δ and ε phases that occur in pure nitrogen in the p and T range. Therefore, this phase cannot be formed by continuous admixture of helium in one of the nitrogen phases. Because the interactions take place via weak van der Waals forces it is called a van der Waals compound. As will be shown this result is unexpected, considering the hard-sphere simulations. The stoichiometry as well as the structure of the compound is unusual. Moreover, in contrast with known hard-sphere solids the large species is the major component.

3.2. Helium–neon

The phase diagram of helium–neon has been measured at 296 K and pressures up to 15 GPa [15]. It turned out that a 2:1 mixture of helium and neon formed a homogeneous solid up to at least 25 GPa (figure 2). Mixtures with other compositions resulted in a separation into two solid phases, one of which had a helium mole fraction of $\frac{2}{3}$. X-ray diffraction experiments have been performed on a single crystal of this stoichiometric solid $\text{Ne}(\text{He})_2$. The unit cell is hexagonal with an almost ideal c/a ratio. From the equation of state of helium and neon the number of atoms per unit cell was estimated to be 12. The structure is, therefore, assumed to be similar to that of MgZn_2 Laves phase.

3.3. Hydrogen–argon

Similar to the previous system in a high-pressure hydrogen–argon mixture a stoichiometric solid $\text{Ar}(\text{H}_2)_2$ was found [23]. At 300 K the compound was formed even at 4.3 GPa. As before, the unit cell is hexagonal and contains 12 atoms. A first-order phase transition was detected at 100 K and 175 GPa by measuring the intramolecular hydrogen vibron as a function of pressure. The vibron suddenly disappeared and the sample, which was observed under the microscope, looked more absorbent. Similar experiments on pure hydrogen up to 220 GPa did not show these aspects. It is speculated that these phenomena are related to the metallization of hydrogen.

3.4. Nitrogen–argon

This system is discussed here because of its relation to the study of pressure induced orientational transitions in mixed solids.

Recent investigations [24] of the mixed solid $\text{Ar}_{1-x}(\text{N}_2)_x$ under its own vapour pressure showed that above a certain threshold composition x_0 an orientationally ordered solid (in combination with a new phase transition) was formed on cooling from the orientationally disordered HCP phase while below x_0 the solid transformed to an orientational glass (figure 4). Application of relatively low pressures resulted in a curious behaviour. Cooling down a mixture with $x = 0.82$ under a pressure of 0.14 GPa resulted in a change in the threshold composition, since it entered the orientational glassy state. On the other hand, application of pressure when the sample was already in the $Pa3$ phase (at low p and T) induced a transition to a new phase similar to the γ phase of pure nitrogen. If the temperature was increased under constant pressure the $Pa3$ phase reappeared at 30 K.

Probably these phenomena can be much better investigated in δ -nitrogen under high pressure. Recently, using Raman spectroscopy a second-order transition has been found [25], which is due to an orientational localization of the molecules, analogous to the above mentioned low-pressure orientational ordering in α -nitrogen triggered by argon as spherical diluent. The study of argon in δ -nitrogen is possible in a large p , T , and x range without the disturbing presence of other phases. Moreover, the effect of e.g. composition on the character (e.g. first or second order) and position of the orientational transitions can be studied.

3.5. Colloidal solutions

Although the experiments on these systems are carried out at low pressure the densities are high and the phase behaviour is closely related to that of molecular systems. Of course, we will not provide a complete description of this fast-growing field but only give an indication of the importance of the results for the understanding of simple mixtures at high pressure.

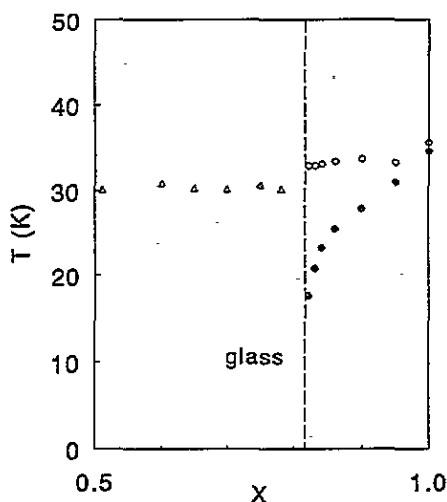


Figure 4. The T - x diagram of $\text{Ar}_{1-x}(\text{N}_2)_x$ under its vapour pressure [24]. x is the mole fraction of nitrogen. Solid circles refer to the transition from disordered HCP to ordered cubic on cooling, the open circles on heating. The triangles mark the transition from disordered HCP to the glass state.

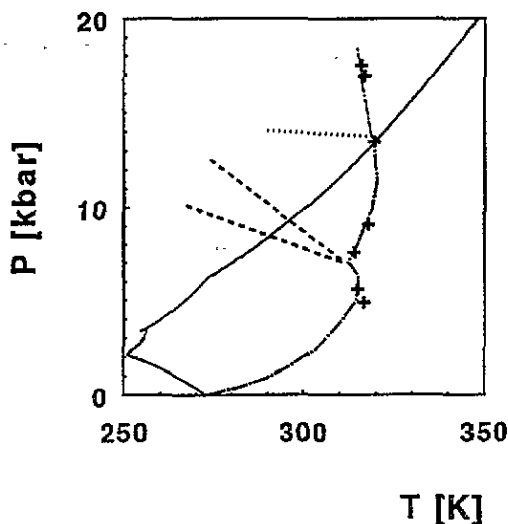


Figure 5. The p - T diagram of water-nitrogen [17, 48]. The solid line is the melting line of water. The dash-dotted line is the three-phase clathrate-ice-fluid line, the dashed lines clathrate, 1-clathrate, 2-fluid, and the dotted line is the upper dissociation limit.

The freezing of binary mixtures of hard spheres is investigated by studying binary mixtures of sterically stabilized particles. An important parameter is the size ratio α of the diameters of the particles. For e.g. $\alpha = 0.61 \pm 0.02$ the experimental results [26] can be summarized as follows (x is the mole fraction of component A, the larger spheres): (i) for $0.66 < x < 1$ and $0 < x < 0.57$ there is complete immiscibility in the solid phases; (ii) for $0.43 < x < 0.58$ an amorphous stoichiometric solid $\text{AB}_{2.5}$ may appear; (iii) for $x \approx 0.028$ the suspension remains amorphous and shows glassy behaviour; and (iv) for $x \approx 0.057$ an ordered stoichiometric solid AB_{13} appears (probably metastable). The behaviour is very sensitive to the value of α as shown by later experiments on mixtures with $\alpha = 0.58$ [27], which gave more conclusive results. The two superlattice phases AB_2 and AB_{13} appeared to be stable and crystalline, each phase being observed at different mole fractions and packing fractions (η). A simple free volume model predicts reasonably well the regions in the α - η plane where the superlattices are stable with respect to phase separation into the pure crystals.

4. Calculations and computer simulations

At high densities the structural behaviour of fluid systems is mainly determined by the repulsive forces. The variational perturbation theory of Ross [28] takes advantage of this situation. In this spirit it is often believed that fluid-solid phase separation at high pressure and the formation of mixed solids is mainly governed by geometrical effects. In this case a hard-sphere mixture would be a good reference system. Hard-sphere mixtures have been studied extensively by means of computer simulations [29, 30] and density functional theory

[31]. The phase behaviour strongly depends on the ratio of the diameters α . The simulations on additive hard-sphere mixtures show that the phase diagram for e.g. $\alpha = 0.58$ is rather complicated. The results are in qualitative agreement with the experimental data on colloidal solutions. However, formation of solid A was not observed experimentally at mole fractions for which it was stable (according to the calculations) with respect to AB_2 . It also turns out that AB_{13} is stable with respect to pure A and B and AB_2 because it has a higher configurational entropy; the free volume is not responsible for the stability!

Calculations have also been performed on the stability of van der Waals compounds at high pressures [15, 32, 33] with the use of the local harmonic approximation and the variational Gaussian approximation [34]. In [32] it is predicted that the helium-xenon system might form a stoichiometric solid phase, $Xe(He)_{13}$. Calculations on $Ne(He)_2$ showed [15] that both the hexagonal and the cubic Laves phases are stable while the A_1B_2 structure is unstable. This is in agreement with expectations since in helium-neon the value of α is 0.8, which fits the Laves phases, while A_1B_2 is expected to occur near $\alpha = 0.6$. A more detailed calculation [33] showed that the volume of the compound is smaller than that of the combination of pure substances. This suggests that the geometrical effects are dominant and that the compound is stabilized by an efficient packing, leading to a maximum in the entropy. However, it turned out that, within the model, the formation of $Ne(He)_2$ is completely driven by the energy.

Fluid-fluid separation has not been found in simulations of hard-sphere mixtures. Although the Percus-Yevick integral equation for hard-sphere mixtures does not predict fluid-fluid demixing, calculations with the Roger-Young integral equation showed evidence for a spinodal instability in the fluid if the size difference is large [35]. Recently [36], fluid-fluid phase separation was found in a hard-core mixture consisting of cubes (with the ratio of the edge lengths equal to three).

Simulations of fluid-fluid equilibria have been performed for a soft-sphere repulsion and the influence of the attractive forces has been determined [37]. Using the α -exp-6 potential, phase separation was found to be in good agreement with experiment for the helium-hydrogen system. Attraction is not necessary for fluid-fluid equilibrium since if only the repulsive part was taken, the demixing shifted to slightly higher pressures. Previously [38], it was shown that fluid-fluid demixing also occurs in additive inverse-12 systems.

The helium-hydrogen phase diagram has been calculated with the use of fluid integral equations and density functional theory of freezing [39]. The fluid-fluid demixing curve obtained from the self-consistent HMSA integral equation is in good agreement with the experimental results. The solid-fluid equilibrium calculated with the use of density functional theory is at best in qualitative agreement. The solid-fluid equilibrium has also been calculated using a cell model [40]. Recently [41] a two-component hard-sphere van der Waals model has been presented to generate a wide spectrum of solid-liquid phase diagrams. In order to obtain quantitative agreement with experiment a soft-sphere reference system should be introduced.

Although variational perturbation theory was very successful in describing the fluid-fluid equilibrium in helium-hydrogen [42], it failed in the case of helium-nitrogen [18]. The potential parameters for the unlike interaction were obtained from equation of state and sound velocity data up to 1 GPa. At room temperature the experimentally determined phase separation for the critical composition occurs at a pressure of 7.5 GPa while the calculated pressure is 0.5 GPa. Probably the difference is due to the van der Waals one-fluid approximation, which is used in the calculations, although the ratio of the diameters is about 0.65. It is generally assumed that the one-fluid approximation holds for this ratio of diameters but the above results suggest that the ratio of the well depths is also of importance

[43]. In systems with helium as one of the components this ratio has always an extreme value, except in the cases of hydrogen and neon. Similar calculations have been performed for the nitrogen–methane system [17, 18]. Even in this apparently simple system, good agreement with experimental results was only obtained if temperature dependent potential parameters were used.

The fluid–fluid equilibrium of nitrogen–water, in particular the critical line, has been calculated [44] with the use of an equation of state for aqueous binary systems. The calculated critical line as well as the binodal curve at 700 K is in good agreement with the experimental results [17, 18]. It is amazing that the phase behaviour of the rather complicated water systems can be adequately described by a relatively simple equation of state. Phase separation has also been predicted by Ree [45] at very high temperature and pressure (above 3500 K and 30 GPa) using perturbation theory. These calculations also indicate that the slope of the critical line is very small.

5. Clathrate hydrates and fullerenes

A rather exotic but very interesting type of compound is the so called clathrate hydrates [46]. Clathrate hydrates are a special class of inclusion compound in which the water molecules form a framework of cages. In order for the phase to be stable a minimum number of cages must be occupied by guest molecules. In other types of inclusion compound guest molecules can be included e.g. in channels or between layers. Although in pure water ices no cagelike voids are found, in this article all the water inclusion compounds will be called clathrates. For example, ice II has channels and an analogous structure has been found to 'enclathrate' helium [47] under high pressure.

An investigation of water–nitrogen at elevated pressures [17, 48] provided the answer to a number of questions concerning the stability of clathrate hydrates. It turned out that the clathrate hydrate–liquid–gas three-phase line has a temperature maximum at 321 K and 1.3 GPa (figure 5). Above this temperature no stable nitrogen clathrate hydrate exists. The maximum pressure for the existence of the clathrate is about 1.4 GPa, nearly independent of temperature. Calculations on the thermodynamic stability of clathrate hydrates have been carried out [49], but only for the lower and not for the higher dissociation pressure. Starting from the low-pressure clathrate phase a new phase transition has been found at about 0.84 GPa and room temperature using Raman spectroscopy [48]. The transition line forms a quadruple point with the three-phase line at 0.7 GPa and 317 K. It is interesting to note that the vibrational frequency of the nitrogen guest molecule within the cage is lower than that of the isolated nitrogen molecule. Therefore, there is a considerable attractive interaction between the guest molecule and the cage. It has been predicted [50] that a phase transition to structure I will take place at about 0.1 GPa, but the structure of the new phase at 0.84 GPa is not known. It should be noted that the calculated transition pressure is very sensitive to the size of the cage.

Since even the small helium molecules can form a clathrate hydrate [47] it is to be expected that the same would happen with the interesting hydrogen–water system. Recently [51] several mixtures of water and hydrogen have been investigated in the pressure range from 0.7 to 3.1 GPa. Indeed the formation of two hydrogen clathrate hydrates was observed. In the lower-pressure range the water sublattice is similar to that of ice II and resembles the helium clathrate; at higher pressures a new type of clathrate has been found with a water sublattice similar to that of ice Ic. Almost simultaneously the solubility of helium and hydrogen in ice Ih has been investigated up to 0.3 GPa by another research group [52].

Research in the intermediate range (0.3–0.7 GPa) is now in progress for hydrogen–water [53].

The last few years the interest in the behaviour of fullerenes, in particular C_{60} , is strongly increasing. Although the pure system has interesting properties [54], it is a challenge to modify these properties by the inclusion of small molecules within the C_{60} molecule. If fullerenes are prepared via the standard method noble gas endohedral fullerenes are formed in very small quantities (1 in 800 000). Heating and pressurizing the system might increase the number of fullerenes containing a molecule [55]. If the pressure was increased to 0.27 GPa at 690 K the fraction of occupied C_{60} molecules increased to about 0.1% [56]. In a recent investigation with a DAC a pressure of 5 GPa was reached at 860 K, resulting in a fraction of occupied fullerenes of about 10% [57].

6. Spectroscopic and thermodynamic properties

Vibrational Raman spectroscopy is one of the most useful tools for studying fluids at high density. Mostly due to anharmonicity of the intramolecular potential the intermolecular forces can cause a change in the frequency of the molecular vibration, but also in the profile of the spectrum. So this technique not only probes the intermolecular forces, but also the fluctuations and dynamics of the system. A wealth of experimental data has been collected for pure substances. In the case of mixtures experimental results for the fluid as well as the solid phase at room temperature and pressures up to 45 GPa have been published for nitrogen–oxygen [58], and hydrogen in argon, helium, neon, or deuterium [9, 59]. The vibrational properties of nitrogen in helium have been investigated in a much larger temperature range [60].

The influence of various simple molecules on the Raman peak position and halfwidth of hydrogen diluted (about 2 mol%) in fluid helium, neon, argon, and deuterium has recently been investigated up to the crystallization surface [59]. The line shape of the vibron mode, which is slightly asymmetrical with a low-frequency tail, results mainly from inhomogeneous broadening. At elevated pressures the shift in the peak position, compared to pure hydrogen at the same pressure, is to higher values of the frequency in the order deuterium, argon, neon, and helium. The calculation of the frequency shift as a function of pressure has been rather successful for pure nitrogen [61] and reasonable for a mixture of ethane and methyl iodide [62]. However, in both cases an adjustable parameter was used for the so called attractive frequency shift. The same model does not explain why the shift is higher for e.g. hydrogen in helium than hydrogen in argon.

In the solid there is also a blue shift but in the order argon, deuterium, and neon. Due to the low solubility, hydrogen in solid helium could not be measured. Figure 6 shows the vibrational frequency of solid hydrogen and that of hydrogen dissolved in solid argon, deuterium, and neon. A very interesting result is that no turnover of the frequency shift as a function of pressure has been observed in the mixtures, in contrast with pure solid hydrogen. It is suggested [59] that in pure hydrogen the turnover is due to a strong negative vibrational coupling between hydrogen molecules caused by charge transfer. In mixtures this coupling is considerably reduced.

In the case of hydrogen in neon equally spaced components could be resolved, the number of components increasing with increasing hydrogen mole fraction. It should be noted that the shape of the lines could be explained with a simple model [59].

Another aspect of mixture behaviour, which can be studied quite well with Raman spectroscopy, is the existence of concentration fluctuations, in particular near the critical

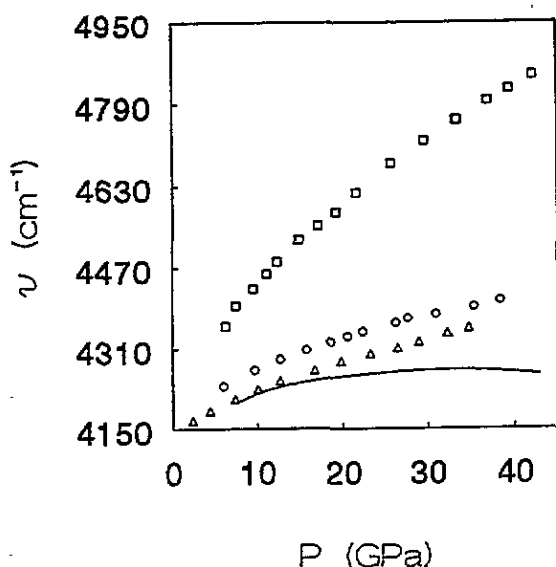


Figure 6. The vibrational frequency of hydrogen in various solid solutions [59]: squares, hydrogen in neon; circles, hydrogen in deuterium; triangles, hydrogen in argon; solid line, pure hydrogen.

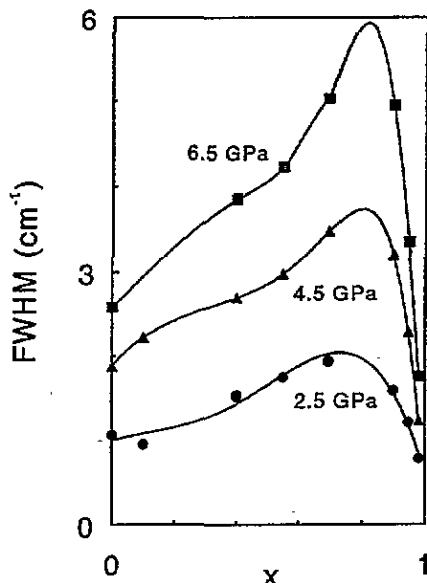


Figure 7. The full width at half maximum of the nitrogen vibrational spectrum in mixtures with helium at room temperature [60]. x is the mole fraction of helium.

point. Since by means of Raman spectroscopy the local environment of the molecule is probed, the amplitude of the critical fluctuations is probed. In pure components the linewidth broadens when the critical point is approached, due to large density fluctuations. One might expect that the same would happen in mixtures due to large concentration fluctuations, but experiment [63] as well as theory [64] showed that there was no critical broadening. The subject was closed. However, recently [60] it has been shown that in the nitrogen–helium mixture at high pressures (about 6 GPa) critical broadening of the nitrogen spectrum does occur (figure 7). The amplitude of the concentration fluctuations has been calculated from the linewidth and the shift of the frequency as a function of composition. Moreover, it was shown that the basic principle used to explain the result had also important consequences for the spectroscopic investigation of critical phenomena in other systems in the same universality class as the Ising system (e.g. polymers, magnets). This principle states that for the determination of the amplitude of the critical fluctuations one needs to determine the peak position of some spectrum as a function of the order parameter together with the profiles of that spectrum close to and far from the critical region.

As in pure substances, knowledge about the intermolecular forces is indispensable for the interpretation of the behaviour of mixtures. Since at high pressures the repulsive part is most important, experimental determination of the potential by e.g. p - V - T - x or sound velocity measurements should also be performed under these circumstances. Progress has been made although it turns out to be difficult. The sound velocity of equimolar mixtures of helium–nitrogen, helium–methane, and nitrogen–methane has been determined in a range of temperatures up to 1 GPa [65]. Compressibility isotherms of three mixtures of helium–nitrogen have been determined at room temperature and also up to 1 GPa [66]. Considering

the problems in the interpretation of the phase diagrams as discussed in section 4, it would be very useful to have data at even higher pressures. The first results for the sound velocity of an equimolar mixture of helium and hydrogen up to 5 GPa have been obtained, as mentioned in [67] (see also [68]).

7. Outlook

Interesting developments are expected in this rapidly expanding field, in particular in solid mixtures. The addition of a second component might shift the required properties of a pure substance into a more practical region of the p - T space or might create new behaviour. In a short time three new (van der Waals) compounds have been detected in simple mixtures and many others will follow. The time is ripe now for a more extensive study of the behaviour of this type of substance and to exploit their properties. The first step has already been taken in the hydrogen-argon system [23].

The same will happen with inclusion compounds such as clathrate hydrates and fullerenes. It is suggested [69] that, in particular at high pressure, many new clathrate hydrate structures might be stable. These structures might fill up the gap between C_{60} and the structures I and II in clathrate hydrates. The production of endohedral fullerenes is still in the beginning. A combination of high-pressure and high-temperature techniques may be very fruitful.

Since at high pressures the solubility of fluids in solids is generally much higher than that at ambient pressures, these investigations may contribute significantly to our understanding of all types of mutual solubility in the solid phase. However, first it should be investigated whether one deals with ordered mixed solids or disordered mixed solids, whether the molecules of the second component occupy the sites of the lattice of component one or are interstitial, and also whether the solubility is continuous or not. For example, mixtures of helium and nitrogen might show various aspects depending on pressure and temperature. Most probably many stoichiometric compounds can be found in mixtures of simple molecules (nitrogen, carbon dioxide, methane, etc). The interpretation of the results concerning solid mixtures might be provided by an extension of the ideas presented in [40] and [41].

The increasing interest in the orientational behaviour of the molecules in a solid, and in particular the orientational glasses [24], will lead to an increasing interest in high-pressure studies of mixtures. These systems offer the opportunity to manipulate the orientational behaviour by changing the composition or by changing the pressure. In many cases a large pressure range is available [25].

The scientific and industrial interest in complex fluids and polymers is rapidly increasing. Therefore, the number of experimental investigations of the phase diagrams and other properties of mixtures of these systems will also grow appreciably. These studies will be supported by a considerable number of computer simulations.

With respect to the fluid phase of simple mixtures the attention will be concentrated on the determination of the sound velocity and on Raman spectroscopy. The improved methods to determine the sound velocity will be used for a description of the macroscopic behaviour (e.g. phase diagrams). The information obtained from Raman spectroscopy gives more insight into the influence of the environment on the molecule under consideration. In particular the determination of the vibrational spectrum as a function of density and composition leads to a better understanding of fluctuations, correlations, phase behaviour, transport properties, and, maybe, chemical reactions.

As mentioned before, the effective unlike potential parameters are very important for calculating the properties of mixtures. Due to the many-body effects these parameters should be inferred from high-pressure measurements but unfortunately not many data are available. Recently a method has been described to obtain unlike pair interactions from shock wave data [70]. This method has already been applied for carbon dioxide mixtures and nitrogen-water [71], and the programme of shock wave experiments on fluid mixtures is continuing. In the near future the calculation method will be improved. One of the drawbacks is the use of the one-component effective mixture model. Substitution of this model by a more basic mixture model is in progress [71]. It is anticipated that a reliable expression for a non-additive hard-sphere reference mixture is needed. Simulations for an equimolar mixture of non-additive hard spheres with equal diameter have already been performed [72] and investigations of the unequal-diameter, non-symmetric cases are in preparation [71]. The first results on fluid-fluid phase separation in binary mixtures of asymmetric non-additive hard spheres have now been published [73].

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