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Phase Behavior of the System He–N_2 at High Pressures[1]

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Recent investigation at our institute revealed that the solid–fluid–fluid three-phase line of the system helium–nitrogen shows two quadruple points in the pressure range up to 10 GPa. Since each quadruple point is connected with four three-phase lines, the phase diagram is very complicated. We have detected the phase transitions representing solid–solid–fluid equilibria. Moreover, two lines of constant composition have been determined as a function of temperature and pressure. These results are discussed together with the implications for the phase diagram of both He–N_2 and pure nitrogen.

KEY WORDS: binary mixtures; diamond anvil cell; helium; high pressure; nitrogen; phase equilibria.

1. INTRODUCTION

The development of diamond anvil cell techniques in the last decade has extended the static experimental pressure range enormously [1]. It has enabled the study of (simple) molecular substances at high densities, and in combination with shock-wave experiments, the intermolecular potential at short distances can be probed. By comparing experimental results with calculations based mainly on perturbation theories, quantitative information can be obtained about the intermolecular potential, which is one of the most important properties of a substance.

It is well known that the phase behavior of binary mixtures depends strongly on the interaction of unlike molecules. Thus studying the phase

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behavior of mixtures provides information on the unlike potential. Knowledge of the phase behavior of mixtures is important not only from a theoretical point of view but also for many practical reasons.

A diamond anvil cell with a corresponding loading system has been developed in our laboratory in order to study the phase behavior and, more specifically, to determine the phase transition lines of binary mixtures up to pressures of 10 GPa and over a large temperature range [2]. Extensive studies have already been performed on the systems Ne–Xe and He–H_2 [3–6].

Recently, van den Bergh and Schouten [7] measured the critical line and solid–fluid–fluid (sff) three-phase line of the system He–N_2 in order to investigate whether fluid–fluid equilibria persist to high pressures. They observed two cusps on the sff three-phase line. These cusps are quadruple points which they attributed to phase transitions in the N_2-rich solid phase. If this is the case, then there should also be two pairs of three-phase lines of the type solid–solid–fluid (ssf) which intersect at the quadruple point. The ssf three-phase lines which move to high temperatures should be related to triple points on the melting line of N_2. In the phase diagram of N_2, however, only one triple point has been observed along the melting curve so far, by Zinn et al. [8]. In a second paper, van den Bergh and Schouten [9] argued that the lower quadruple point may be connected to a triple point along the N_2 melting line which was not noticed by Zinn et al. The upper quadruple point should then be connected to the N_2 triple point at 578 K and 9.9 GPa.

However, the possibility that the lower quadruple point is related to the triple point at 9.9 GPa was not excluded. In that case, the upper quadruple point is related to another triple point along the melting line, outside the experimental pressure range (18 GPa) of Zinn et al. [8].

Thus, the first goal is to observe the solid–solid–fluid (ssf) three-phase lines that meet at the quadruple point. The second target is to establish the solid–fluid equilibria in the system He–N_2.

2. EXPERIMENTAL

The diamond anvil system which has been used in this experiment is described in detail in another paper [2]. The usual ruby technique is used to determine the pressure *in situ*. The pressure coefficient is taken as 0.366 $\mathrm{nm \cdot GPa^{-1}}$. The temperature dependence of the ruby lines was measured by ourselves, since it appeared that our ruby did not obey the dependence given by Shchanov and Subbotin [10]. The ruby is illuminated with an argon laser at beam intensities of less than 10 mW. The gases are of research-grade quality with a purity better than 99.999 %.

The sample space is loaded by pressurizing the anvil cell in a high-pressure vessel with a homogeneous gaseous mixture of a known composition. The mixture is previously prepared in a gas compressor with an accuracy in the composition of about 0.1 mol%. The anvil cell is closed at a pressure of a few tenths of a GPa and placed in the main frame for further pressurizing the sample.

The temperature is measured with a calibrated platinum resistance thermometer. Besides, we corrected for gradients within the cell, yielding a total uncertainity of less than 0.5 K.

Two experimental runs were made, the first with a composition of 31.1 mol% helium in a Be–Cu gasket and the second with a composition of 11.0 mol% in a stainless steel 301 gasket.

3. RESULTS

3.1. Two-Phase Equilibria

The solid–fluid equilibria are observed by visual observation of the sample. Since the method has been described extensively in an earlier paper [4], we give only an outline.

The temperature of a mixture with a certain bulk composition is decreased from the homogeneous region of the phase diagram until part of the mixture solidifies. The temperature is then increased until the solid phase vanishes. At this point, pressure and temperature are measured. This yields one point on the fluid branch of the coexistence surface of the solid–fluid equilibrium.

We observed that on lowering the pressure, the composition sometimes changed from the known composition on loading. Probably some of the sample escapes. In the case of an inhomogeneous mixture, the fluid phase will get away more easily. Since a constant composition is essential for the measurements of the two-phase lines, we always performed these measurements at increasing pressures. For the determination of three-phase lines a constant composition is not needed.

Two lines of constant composition have been determined in the fluid–solid range for mixtures with 11.0 and 31.1 mol% helium, respectively. The results are presented in Fig. 1 toghether with the three-phase line as determined by van den Bergh and Schouten [7]. These investigators determined cusps at 3.3 GPa and 192 K and a 5.8 GPa and 236 K. They observed that, along all three parts of this line, two of the coexisting phases are fluid phases. In the following discussion we denote the third phase, the solid, by S_1 below the lowest cusp, S_2 between the two cusps, and S_3 above the highest cusp. F_1 is the nitrogen-rich fluid phase and F_2 is the helium-rich fluid phase.

Figure 1 shows that both two-phase lines also exhibit a cusp. This cusp marks the point where the two-phase line crosses the three-phase line $S_1+S_2+F_1$. The cusp for the mixture with 31.1 mol% helium is not so pronounced due to a lack of experimental points at lower pressures. The coordinates of the phase transition points are given in Table I. Also, two points calculated from the work of Streett et al. [11, 12] at low pressure are included in the table. These points have been taken at the intersection of the two-phase lines with the three-phase lines. Figure 1 shows that the pressure along the two-phase lines rises continously with increasing temperature.

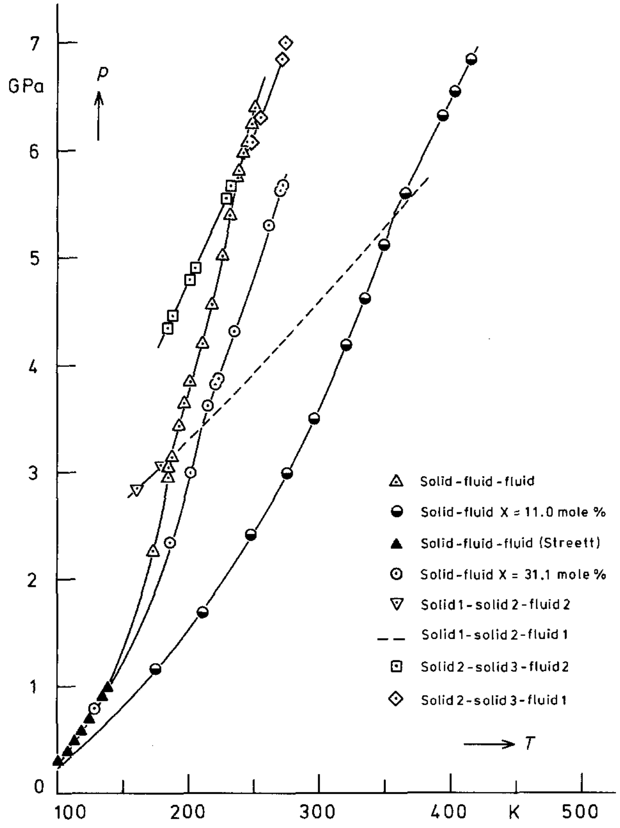

Fig. 1. p–T diagram of the system He–N_2 showing the two-phase lines for $x = 11.0$ and $x = 31.1$ mol% helium, as well as the solid–fluid–fluid and solid–solid–fluid three-phase lines.

Table I. Experimental Data for the Fluid Phases in the S_1+F_1 and S_2+F_1 Regions in the Helium–Nitrogen Phase Diagram, with x the Mole Percentage of Helium in the Homogeneous Phase

$x=11.0$				$x=31.1$			
S_1+F_1		S_2+F_1		S_1+F_1		S_2+F_1	
T(K)	p(GPa)	T(K)	p(GPa)	T(K)	p(GPa)	T(K)	p(GPa)
86.7[a]	0.170	363.6	5.56	129.4[a]	0.807	214.6	3.64
175.0	1.15	392.2	6.30	186.4	2.32	219.8	3.81
210.4	1.69	400.8	6.52	201.8	2.98	222.6	3.88
210.5	1.71	401.0	6.51			235.0	4.31
247.2	2.41	413.0	6.81			260.9	5.30
274.8	3.00					268.8	5.62
295.6	3.50					271.5	5.72
319.4	4.15						
333.7	4.60						
347.8	5.10						

[a] Data from Streett and co-workers [11, 12].

Several interesting phenomena have been observed during the measurements. For example, in the case of the 11.0 mol% helium mixture, the appearance of the solid phases was quite different. S_1 started to grow as a tree, the branches making an angle of about 60°. This is in agreement with the known h.c.p. structure in pure N_2 under these conditions. S_2 appeared all over the sample space at the same moment and looked like a very fine network. In the mixture with 31.1 mol% helium, both solids appeared in the form of many small crystals, minimizing the light transmission through the cell. After recrystallization the solids were transparent and colorless.

As usual, at decreasing temperature the transition from a homogeneous mixture to solid–fluid equilibrium was delayed considerably. With 31.1 mol% helium the metastability range was 20 to 40 K for both S_1 and S_2. Since the difference between the two-phase and the three-phase line is less than 40 K for this composition, we often ended up in a different two-phase region than intended.

With the 11.0 mol% helium mixture we observed a peculiar phenomenon at pressures just above the pressure of the cusp point in the two-phase line. On cooling the homogeneous mixture, the metastable solid S_1 appeared instead of the stable solid S_2. A schematic isobaric cross-section is given in Fig. 2. The pressure is taken just above the cusp point on

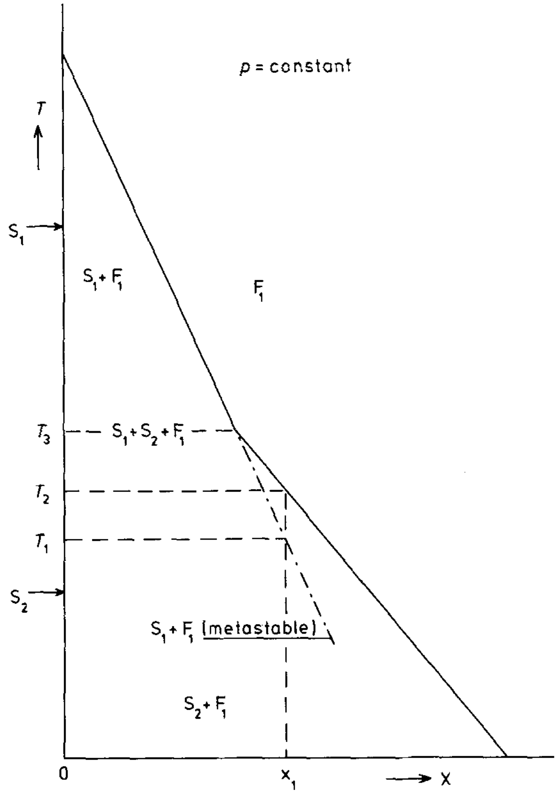

Fig. 2. A schematic isobar of the system He–N_2 in the region of solid–fluid equilibria. The dashed-dotted line indicates the metastable fluid branch of the S_1+F_1 coexistence surface.

the two-phase line for a specific composition x_1. T_3 is the temperatuire of the cusp point at this pressure. Note that with a smaller helium mole fraction, the pressure and temperature of the cusp point are higher. For the sake of simplicity, it is assumed that helium does not dissolve in the solid. The metastable extension of S_1+F_1 is given by the dashed-dotted line. Figure 2 shows that, at composition x_1, the transition from the equilibrium S_2+F_1 to homogeneous F_1 occurs at a higher temperature (T_2 in Fig. 2) than from S_1+F_1 (T_1). However, in order to obtain S_2+F_1 the sample had to be undercooled by about 40 K, compared to about 10 K to obtain S_1+F_1. Using this effect we were also able to measure the metastable extension of S_1+F_1. Figure 3 shows that the metastable S_1+F_1 points lie on a smooth curve with the stable points. The intersection of S_1+F_1 with S_2+F_1 gives a cusp at 356 K and 5.4 GPa.

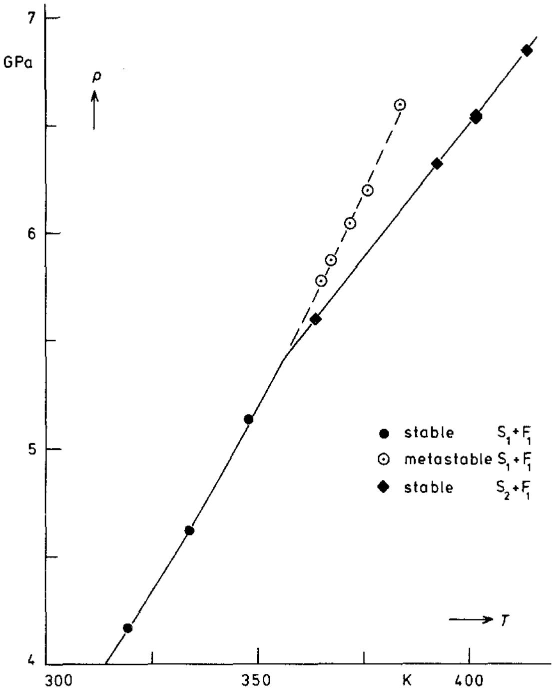

Fig. 3. p–T diagram of the $x = 11.0$ mol% helium two-phase line in the system He–N$_2$. The solid lines indicate the stable S_1+F_1 and S_2+F_1 phase boundaries, while the dashed line represents the metastable S_1+F_1 phase boundary.

3.2. Three-Phase Equilibria

There are a number of different methods for observing three-phase equilibria.

(1) As we have seen before, two-phase lines plotted for constant composition may show cusps. These cusps are points of three-phase lines.

(2) Three-phase equilibria consisting of one solid and two fluid phases can be observed visually, because solids can usually be distinguished from fluids and two fluids can be distinguished if their refractive indices are different. In this way, van den Bergh and Schouten determined the three-phase lines $S_1+F_1+F_2$, $S_2+F_1+F_2$, and $S_3+F_1+F_2$.

(3) We can observe all three-phase lines by using the fact that a sample in a diamond anvil cell is under nearly isochoric conditions. When the

pressure is recorded as a function of temperature, a pressure jump will be observed if the phase transition is accompanied by a volume discontinuity. If this discontinuity is large enough, one can even follow a part of a phase line.

In order to establish equilibrium, the temperature was kept constant for about 10 min before the pressure was measured. The temperature steps were about 1 K.

Table II. Experimental Data for the Three-Phase Equilibria in the System Helium–Nitrogen

$S_1+F_1+F_2$		$S_2+F_1+F_2$		$S_3+F_1+F_2$	
T(K)	p(GPa)	T(K)	p(GPa)	T(K)	p(GPa)
173.4	2.27	190.8	3.30	238.0	5.81
184.1	3.00	191.2	3.30	238.7	5.84
184.3	3.00	192.2	3.35	239.8	5.87
185.6	2.93	192.7	3.35	241.5	5.95
187.5	3.13	196.2	3.53	242.0	5.96
		197.3	3.58	243.4	6.04
		200.8	3.75	244.6	6.11
		210.3	4.21	246.6	6.20
		216.9	4.55	246.8	6.21
		217.0	4.54	247.2	6.24
		217.5	4.57	249.3	6.33
		224.9	5.01	250.3	6.38
		225.8	5.05		
		231.4	5.39		
		237.1	5.74		
		237.2	5.73		
		237.7	5.74		
		237.9	5.78		
		237.9	5.80		

$S_1+S_2+F_1$		$S_1+S_2+F_2$		$S_2+S_3+F_1$		$S_2+S_3+F_2$	
T(K)	p(GPa)	T(K)	p(GPa)	T(K)	p(GPa)	T(K)	p(GPa)
356	5.4	161.4	2.83	247.0	6.04	184.5	4.36
		179.2	3.04	247.5	6.06	188.3	4.45
				248.1	6.09	201.1	4.78
				253.6	6.28	205.3	4.91
				256.5	6.35	229.4	5.55
				270.8	6.83	229.9	5.56
				274.0	6.92	230.9	5.58
						232.6	5.63

The three-phase line $S_1 + S_2 + F_1$ was investigated by method 1, but we have it indicated only with a dashed line in Fig. 1 because the number of data points is too small.

The three-phase line $S_1 + S_2 + F_2$ was observed by method 3. The transition was hard to observe because of a small pressure jump. Both the $S_2 + S_3 + F1$ and the $S_2 + S_3 + F_2$ equilibria were determined with method 3. The pressure jump is larger at $S_2 + S_3 + F_2$ than at the $S_2 + S_3 + F_1$ curve. The reason is that on $S_2 + S_3 + F_2$ the sample contains relatively more solid than on $S_2 + S_3 + F_1$, because F_1 is richer in nitrogen than F_2. The results are given in Table II and plotted in Fig. 1. One can see that $S_1 + S_2 + F_2$ and $S_1 + S_2 + F_1$ are almost parallel near the lower quadruple point and that both lines have a positive slope in the p–T diagram. It is worthwhile to notice that the δ–β transition line of N_2 [8, 13] lies within a few tenths of a GPa from the $S_1 + S_2 + F_1$ and $S_1 + S_2 + F_2$ lines. Thus it seems plausible that $S_1 + S_2 + F_1$ should be connected to the triple point along the N_2 melting curve at 9.9 GPa and 578 K [8].

We cannot distinguish whether the three-phase lines $S_2 + S_3 + F_1$ and $S_2 + S_3 + F_2$ are parallel at the upper quadruple point or whether they have a slight difference in slope. Considering the present data, it does not seem likely that $S_2 + S_3 + F_1$ is connected to the triple point along the N_2 melting line.

It is important to know whether two of three-phase lines have equal slopes at a quadruple point or not. If two three-phase lines do have equal

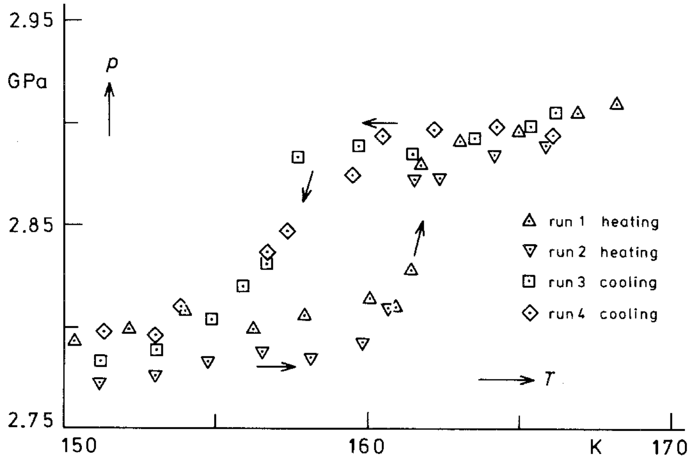

Fig. 4. An isochore in the system He–N_2 showing hysteresis of the $S_2 + S_3 + F_2$ three-phase line.

slopes at a quadruple point and if they also coincide with a phase line in a solid (e.g., the δ–β line in N_2), then there is no gas dissolved in the solid [13]; in our case, no helium is dissolved in solid nitrogen. On the other hand, if the three-phase lines in the mixture and the two-phase line in the pure solid do not coincide and if the three-phase lines exhibit a kink at the quadruple point, then it is easily shown that gas dissolves in the solid. It still remains an open question how much gas will dissolve.

We observed hysteresis on investigating the $S_1 + S_2 + F_2$ three-phase line. The results of four runs, two while heating and two while cooling the sample, are plotted in Fig. 4. It is clearly shown that, when heating, the transition occurs at a temperature which is 4 K higher than when cooling. It is not clear whether this hysteresis is due to the mixture or whether is also occurs in pure nitrogen, since it has not been mentioned in the papers on pure nitrogen [8, 14].

The hysteresis of $S_1 + S_2 + F_2$ has consequences for the position of the quadruple point. It implies that the locus of the quadruple point is at two different p, T points, depending on the direction of approach.

4. CONCLUSIONS

The solid–fluid equilibria of the system He–N_2 have been measured up to 6 GPa. We have succeeded in detecting the four sff three-phase lines near the two quadruple points. Taking the present data into account, we slightly favor the possibility that the lower quadruple point is connected to the triple point along the N_2 melting curve at 9.9 GPa and 578 K [8]. It has been suggested that helium dissolves in solid nitrogen in the region of the highest quadruple point. Further experiments are being carried out to confirm this suggestion.

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