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Improved phase diagram of nitrogen up to 85 kbar

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A quasi-isochoric scanning method has been used to study the phase diagram of nitrogen from 150 to 550 K and up to 85 kbar in a diamond anvil cell in order to make a comparison with previous measurements of the binary phase diagram He-N₂. It has been confirmed that there is only one solid-solid-fluid triple point in N₂ up to 85 kbar. However, both the δ - β transition line and the melting line have shifted appreciably towards lower pressures. The present experiment shows that, as a result of this, the triple point is located at 555 ± 5 K and 80 ± 2 kbar, which is 20% lower in pressure than previous data.

I. INTRODUCTION

In order to investigate fluid-fluid demixing at high pressures in simple molecular systems, a study of the binary mixture helium-nitrogen was undertaken in our laboratory. It was found that the fluid-fluid equilibria persist up to at least 100 kbar.¹ The most remarkable feature, however, was the occurrence of two quadruple points along the three-phase line solid-fluid-fluid at 34 and 58 kbar. A quadruple point in a binary mixture is related to a triple point in a pure substance. On the basis of the known phase diagram of nitrogen, only one quadruple point could be expected, since only one solid-solid-fluid triple point was known² with which it could be related. Therefore, van den Bergh and Schouten proposed that there might be a second triple point along the melting line of nitrogen at a lower pressure than the one already known.³ In that case, the upper quadruple point in the mixture would be related to the known triple point of N₂ and the quadruple point at 34 kbar would be connected to the second triple point. Another possibility could be that the lower quadruple point is connected to the known triple point of N₂ and that the quadruple point at 58 kbar is related to a triple point at higher pressure. Therefore it is worthwhile to study the phase diagram of nitrogen, because either it shows a new triple point along the melting line below 100 kbar or by comparing the δ - β line with the three-phase line of the mixture, one can deduce if gaseous helium dissolves in solid nitrogen.

In spite of its simple molecular structure, nitrogen shows a very rich phase diagram (see Fig. 1). At zero pressure and low temperature it exists in a cubic and ordered structure with space group⁴ $Pa\bar{3}$, known as α -N₂. Between 35.6 K and the melting point at 63.1 K it exhibits a hexagonal disordered structure, β -N₂ with space group⁵ $P6_3/mmc$.

Pressurizing α -N₂ to about 4 kbar yields⁶ γ -N₂, which is also an ordered phase with tetragonal space group⁷ $P4_2/mnm$. On further pressurizing, one obtains ϵ -N₂ at about 20 kbar.⁸ This is an ordered rhombohedral phase with space group⁹ $R\bar{3}c$. At still higher pressures of about 200 kbar,⁸ it reveals another phase whose structure is possibly rhombohedral with space group⁹ $R3c$.

At room temperature, fluid nitrogen freezes at 24 kbar¹⁰ into¹¹ β -N₂. At 48 kbar, a transition occurs¹² to δ -N₂, a cubic disordered phase with space group^{13,14} $Pm\bar{3}n$. Pressurizing

of δ -N₂ yields phase transitions at 200, 660, and 1000 kbar to other, yet unidentified, phases.¹⁵ Previous investigators report that the δ - β phase line and the melting line intersect at 578 K and 99 kbar to yield the β - δ -fluid triple point.²

II. EXPERIMENTAL

The diamond anvil cell (DAC) which was used in this experiment has been described in detail in an earlier paper.¹⁶ The usual ruby technique is used to determine the pressure *in situ*. The pressure coefficient is taken as 0.0366 nm/kbar.¹⁷ Heating was accomplished through an electrical coil wound on a "cold" finger projecting from a copper ring surrounding the cell.

The temperature dependence of the ruby lines was not taken from literature data, but has been determined experimentally before and after each run at about ten temperatures. The average of the measurements before and after each run was used. The temperature dependence, which may

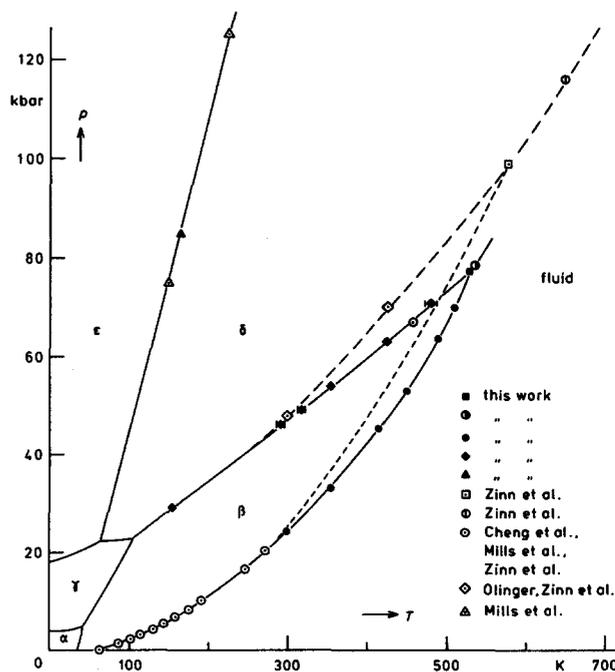


FIG. 1. p - T diagram of nitrogen. \square Triple point Zinn *et al.* \bullet Triple point this work. — Melting curve Eq. (1).

differ for different ruby chips, cannot be conveniently represented here by a simple analytical expression, and will be discussed in a future publication.¹⁸ The ruby was illuminated with an Ar or a HeCd laser at a beam power of about 10 mW to prevent heating. We estimate the error in pressure to be ± 0.3 kbar below room temperature and up to ± 1 kbar at the highest temperatures. The gas used was of research grade quality with a purity better than 99.999%.

The sample space was loaded by mounting the DAC in a high pressure vessel and pressurizing it with nitrogen.¹⁹ The cell was closed at a pressure of a few kilobars and placed in the main frame for further pressurizing the sample. The experiment was performed with a stainless steel 301 gasket in the DAC. The temperature was measured with a calibrated platinum resistance thermometer. Moreover, corrections were made for gradients within the cell, yielding a total uncertainty of less than 0.5 K.

Two experimental methods were applied:

(a) visual observation, in which case a phase transition can generally be detected by a change in color, structure or refractive index,

(b) isochoric scanning,²⁰ where the temperature of the DAC is varied under nearly isochoric conditions and a first-order phase transition manifests itself as a discontinuity in pressure if there is a measurable volume change. In a typical scan, we heated in steps of 1 K and after each step we waited 15 min before measuring the pressure. In order to check if equilibrium conditions were reached, we lowered the temperature while maintaining a two-phase equilibrium and scanned again. We observed then that the results repro-

duced. We were not able to detect any phase transition in nitrogen when using visual observation. This is due to the fact that N_2 forms clear and colorless crystals¹⁵ and that the view through the sample was disturbed by some small pieces of ruby.

The isochoric scanning method worked out very well as can be seen in Fig. 2, which shows very pronounced pressure jumps of about 1 kbar for the δ - β and β -fluid transitions. In fact, we do not observe a discontinuous jump but a sharp increase of the slope of the p - T plot. The p - T plot follows the phase line, because the transition takes place gradually, so that there is a range of temperatures where the two phases coexist. The investigation of the phase lines was hampered by three factors:

(1) At high temperatures, the ruby lines broaden so that above 500 K only one line was resolved by us, which increases the scatter of the data points along a p - T scan. This problem was tackled by taking more points along a scan.

(2) On some occasions the pressure decreased on heating probably due to a rearrangement in the experimental setup. This shortens the trajectory in the p - T plane where two phases coexist and, thus, diminishes the pressure jump. This difficulty was overcome by slightly turning the pressing nut to eliminate the tolerance in the main frame without increasing the pressure.

(3) Sometimes, the sample superheated or supercooled. This is described below in more detail.

III. RESULTS AND DISCUSSION

Some typical examples of p - T plots for the δ - β transition and the melting line are shown in Fig. 2. We have a large number of data points, but for an overview only the mid-points of the p - T scans have been listed in Table I. It is evident from Fig. 1 that the melting line and the δ - β transition line agree with previous data at low temperatures^{10,21,22} but deviate considerably from the previous data above room temperature. We found the δ - β -fluid triple point at 555 ± 5 K and 80 ± 2 kbar, which is considerably lower than the values² of 578 ± 10 K and 99 ± 5 kbar reported previously. Note that if the temperature of the triple point is taken as 560 K, the pressure should be taken as 82 kbar. Similarly, 550 K should correspond to 78 kbar. Our value for the temperature at the ϵ - δ transition at 84 kbar is in reasonable agreement with previous experiments,⁹ but due to the steepness of the ϵ - δ transition line, any possible pressure deviations are not visible.

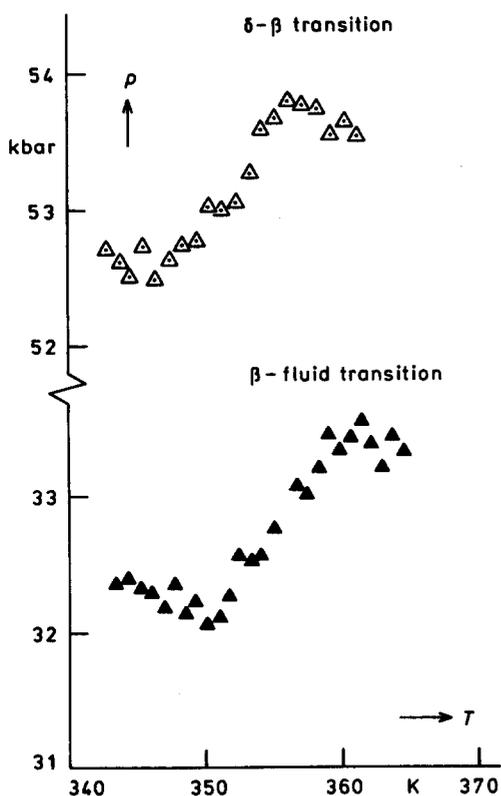


FIG. 2. p - T scans of the δ - β transition and the melting line. The pressure jump of the melting line is about 1/3 that calculated from PVT data for an isochoric transition.

TABLE I. Experimental data for the phase transitions in nitrogen.

β -fluid		δ -fluid (metastable)		δ - β		ϵ - δ	
T (K)	p (kbar)	T (K)	p (kbar)	T (K)	p (kbar)	T (K)	p (kbar)
303.0	24.7	504.8	70.2	166.2	29.2	164.7	84.0
353.4	32.5	513.9	72.3	293 \pm 7	45.7		
412.4	44.7	533.5	76.2	319 \pm 4	49.3		
449.9	53.5			350.3	53.0		
489.3	62.8			423.9	62.7		
511.0	69.0			478 \pm 7	70.1		

The dashed melting line in Fig. 1 represents the tabulated values from Young *et al.*²³ These authors have smoothed the experimental data of Zinn *et al.*² Only one experimental point of Zinn *et al.* (at 450 K and 63 kbar) has been plotted in the interval from 20 to 100 kbar, since this is the only point that has been given numerically. Note the relatively large deviation of this point from the dashed melting line.

Our results for the β -fluid melting line, together with the low pressure results of Cheng *et al.*²¹ and Mills *et al.*,¹⁰ can be fitted to a smooth curve (full line in Fig. 1). A Simon-Glatzel equation yields:

$$P(\text{kbar}) = 0.54910 \cdot 10^{-3} \cdot T(\text{K})^{1.8835} - 1.1 \quad (1)$$

with a standard deviation of ± 0.3 kbar.

The position of the melting line was determined from p - T scans with increasing temperature. At decreasing temperature undercooling of the sample of about 30 to 40 K occurred. This undercooling manifests itself in a p - T scan as a sudden drop in pressure, while on raising the temperature a smooth increase in pressure was always observed as in Fig. 2. The pressure jumps on melting were always 1 kbar or more, so that the transition could be easily detected.

Only two experimental points have been plotted on the dashed δ - β transition line in Fig. 1: one point given by Olinger¹³ and one point reported by Zinn *et al.*² We are unaware of any other tabulated values. The δ - β transition showed both undercooling and overheating. This is shown in Fig. 3. In run 1, the temperature was decreased during the p - T scan and a sudden jump occurred at 419 K. Apparently the whole sample changed from β -N₂ to δ -N₂ at this temperature. On raising the temperature in run 2, the reverse process occurred at 440 K. The third run, performed at increasing

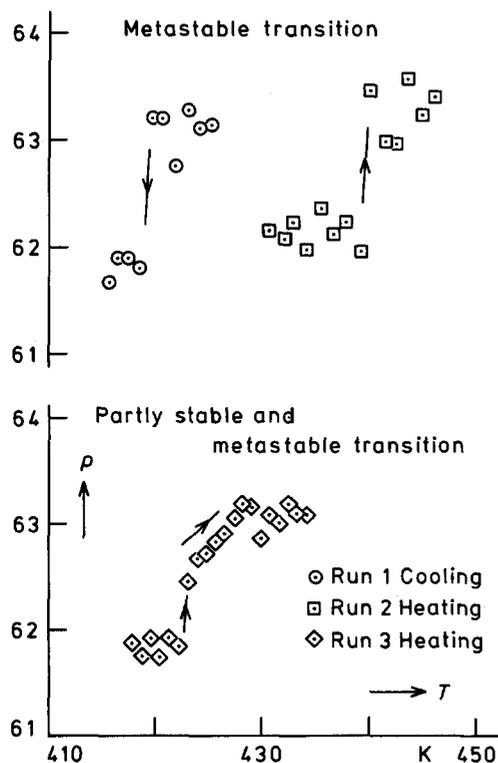


FIG. 3. p - T scans of the δ - β transition near 63 kbar.

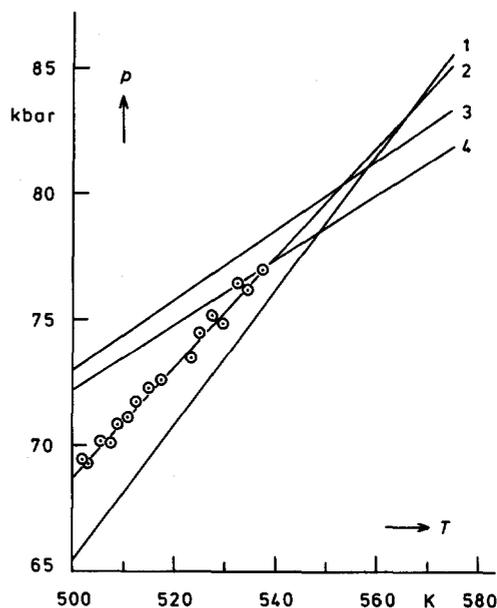


FIG. 4. p - T diagram in the vicinity of the δ - β -fluid triple point. Curve 1 is the β -fluid transition line given by Eq. (1), line 2 is a linear fit through the δ -fluid points, curve 3 is a quadratic fit through the δ - β points and line 4 is a linear fit through the δ - β points. The circles are some of the 70 experimental points determined for the metastable δ -fluid transition.

temperature, shows that the pressure jumps slightly at 423 K, subsequently increases smoothly and then remains nearly constant. We interpret this as follows: at first the sample overheats, then part of it suddenly transforms from the δ phase to the β phase. From then on, the δ phase is in equilibrium with the β phase and the transition proceeds until the δ phase has completely disappeared. On another occasion we observed that the δ - β transition occurred at the same temperature and pressure at decreasing as well as increasing temperature. We conclude from this behavior that the system shows only metastability and no hysteresis as reported previously.²² The data points at which metastability occurred are marked with an error bar in Fig. 1 to show the difference between the heating and the cooling transition temperature. The pressure jump for the δ - β transition remains about 1 kbar over the whole temperature range.

Close to the triple point only one transition was observed on heating instead of the two transitions δ - β and β -fluid. This is most likely to be the metastable δ -fluid transition because, as mentioned before, the δ phase showed overheating with respect to the β phase and because the experimental points do not coincide with an extrapolation of the δ - β or the β -fluid line (see Fig. 4). Moreover the pressure jump on this metastable δ -fluid transition is more than 2 kbar, which is consistent with the sum of the jumps for the δ - β and β -fluid transitions.

The triple point was estimated from extrapolations of the Simon-Glatzel equation and linear and quadratic extrapolations of the δ - β and metastable δ -fluid data, see Fig. 4. It should be noted that, close to a triple point, a melting line does not obey a Simon-Glatzel equation, but deviates to higher pressure.² Therefore 80 kbar was chosen as the most probable value for the triple point pressure. The ϵ - δ points were taken from Mills *et al.*⁹ and this work. A pressure jump of about 0.8 kbar was observed at the ϵ - δ transition.

A possible explanation for the discrepancy with previous data is probably the temperature induced shift in the ruby lines. Our shifts were measured with the same pieces of ruby used in the experiment. Zinn *et al.*² used a value of 0.0068 nm/K, that was probably taken from the literature.²⁴ However, in the literature a number of temperature shifts have been reported,²⁵ which may result in discrepancies of more than 1 kbar per 100 K increase from room temperature.

Another possible reason for the discrepancy may be temperature gradients in the DAC. The temperature difference between the diamonds and the thermometer was measured with a differential thermocouple. One lead was put near the gasket on one of the diamonds and the other next to the thermometer. Care was taken to provide a good thermal contact between the thermocouples and the surrounding parts of the DAC. The maximum difference was -0.4 K at 150 K to $+0.3$ K at 530 K, for which corrections were applied. In the report of Zinn *et al.* an error of up to 10 K below 600 K was suggested. A third possible reason which they do not mention may be laser heating of the ruby. In our experiment, care was taken to avoid this effect.

In a theoretical article by LeSar,²⁶ the error in the pressure measurements of Zinn *et al.*² was estimated to be ± 5 kbar. As mentioned before, in our work the error is probably less than 1 kbar.

The slight discrepancy with the data of Olinger¹³ is caused by his use of the NaF scale instead of the ruby scale.

We do not consider sample impurity to be a possibility, since the data agree at room temperature. Addition of all possible discrepancies results in a total of 13 kbar at 550 K, which is larger than the actual discrepancy of 11 kbar.

IV. CONCLUSION

Accurate measurements of the N₂ phase diagram confirm that, up to 85 kbar, there is only one solid–solid–fluid triple point. The results concerning the position of the δ – β and β –fluid transition lines at high pressures obtained from this work differ considerably from the results obtained by other investigators. In particular, the coordinates of the triple point have shifted from 578 K and 99 kbar to 555 K and 80 kbar. A comparison with the data for the binary mixture He–N₂ will be presented in a separate paper.²⁷

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