

Errata: Free Electron Treatment of the Orientation of Substituents in Aromatic Molecules

Sadhan Basu

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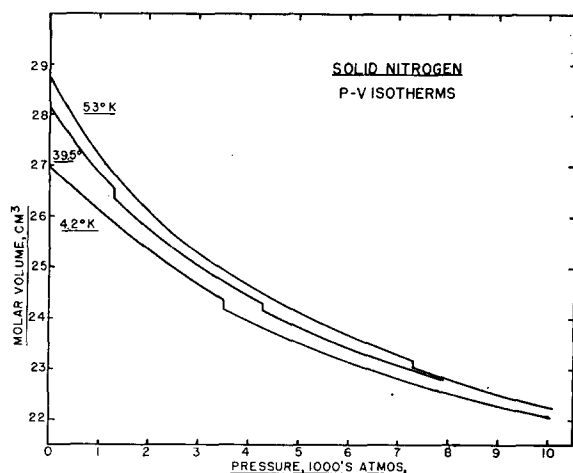


FIG. 1. Typical pressure-volume isotherms as obtained in this work. The transitions shown are, respectively, the $\beta \rightarrow \gamma$ at 53°, the $\beta \rightarrow \alpha$ and $\alpha \rightarrow \gamma$ at 39.5°, and the $\alpha \rightarrow \gamma$ at 4.2°K.

The high-pressure equipment and sample holder used for these measurements is similar to that described by Stewart,³ with a special cryostat⁶ being used to maintain the sample holder at any desired temperature, with fluctuations of less than 0.1°. All temperatures were measured with a copper-constantan thermocouple, calibrated in this laboratory.

Figure 1 shows three of the $P-V$ isotherms which were obtained, plotted in terms of molar volume. The results of seven such isotherms are summarized in Fig. 2 as the proposed phase diagram for solid nitrogen.

The transitions shown in Fig. 1 are quite idealized, and were in practice spread out over two or three hundred atmospheres. The occurrence of the transitions was always quite unambiguous on both the pressure-increasing and pressure-decreasing curves, but the exact pressure was difficult to determine, due both to quite large friction effects (especially below 30°K) and the need for an over pressure of about 500 atmospheres to make the transitions run. The transition pressure was taken as the mean of the pressures needed to initiate the transition in first the

forward direction and then in the reverse direction. The actual volume changes could be measured to about 20%. The large friction at 4.2°K is probably the reason why Stewart failed to observe this transition in his earlier work.³

In Fig. 1, the variation of the volume of solid nitrogen at zero pressure was estimated from incomplete published measurements due to various workers.⁶ The initial compressibilities shown are uncertain since they are the result of an extrapolation.

The volume changes (ΔV) and the entropy changes ($\Delta S = \Delta V dP/dT$) deduced from the ΔV 's and the slopes of the transition lines are given for the triple point (44.5°K, 4650 atmos) in Fig. 2. This point has been chosen, along with the ΔV 's, so that the data are thermodynamically consistent. The observed data for $\Delta V_{\beta\alpha}$ was used to estimate the volume change at zero pressure, and this was used with the known entropy change (1.536 cal/mole-deg)¹ to calculate the initial slope shown. $\Delta V_{\beta\alpha}$ decreases rapidly along this curve (see Fig. 2), as does $\Delta V_{\beta\gamma}$ with increasing pressure, although $\Delta V_{\alpha\gamma}$ is constant within experimental error. In general, the phase existing at the higher pressure has the lower compressibility by about 20%. These results are as yet quite preliminary in nature and it is hoped to continue this work in the near future with an improved setup.

The exact structure of the γ phase cannot be determined easily. Nitrogen crystallizes as a molecular crystal, with the α phase molecules lying on the points of a face centered cubic lattice, and the β phase having a hexagonal structure in which the individual molecules rotate or precess about their center of gravity. Neither structure is close packed, so the effect of pressure probably produces a close-packed structure. Similar results should be obtained for solid CO, which behaves much like solid N₂ at zero pressure.²

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- * Present address: Physics Department, Iowa State College, Ames, Iowa.
¹ W. F. Glauque and J. O. Clayton, J. Am. Chem. Soc. **55**, 4875 (1933).
² For a summary of the x-ray data and other references to them, see L. Vergard, Z. Physik **88**, 240 (1934).
³ J. W. Stewart, Phys. Rev. **97**, 578 (1955).
⁴ C. A. Swenson, Phys. Rev. (to be published).
⁵ C. A. Swenson and R. H. Stahl, Rev. Sci. Instr. **25**, 608-611 (1954).
⁶ For a summary of the density measurements on solid nitrogen see Dokoupil, van Soest, and Swenker, Appl. Sci. Research **3**, 204 (1955).

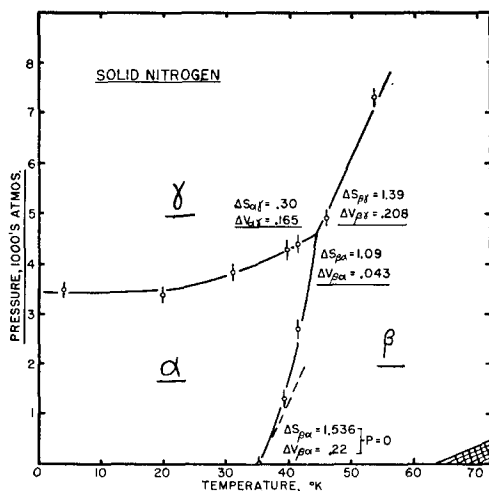


FIG. 2. The proposed phase diagram for solid nitrogen. The shaded area in the lower right is the liquid region. The values of the volume and entropy changes around the triple point and at zero pressure are given in cc/mole and cal/mole-deg, respectively. The coordinates of the triple point are 44.5°K and 4650 atmos.

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SADHAN BASU

Department of Chemistry, University of Calcutta, Calcutta 9, India

IN the calculation of ω values for the model V some mistake has been made. The state $\omega=0$ is absent, and the $\pi/2$ state is not degenerate. Further, if usual assumptions for free electron treatment are introduced, i.e., the box dimension extends half bond beyond the free end, the π -electron energy difference for the various positions comes out as follows:

$$\begin{aligned} \Delta E_{\pi} \\ o &= 0.13 \text{ K} \\ m &= 0.56 \\ p &= 0.20. \end{aligned}$$

This also shows that the substitution will be o,p but with o predominating. However, the slight advantage may be well compensated by the familiar o effect.

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