

The Atomic Distribution in the Allotropic Forms of Phosphorus at Different Temperatures

C. D. Thomas and Newell S. Gingrich

Citation: *The Journal of Chemical Physics* **6**, 659 (1938); doi: 10.1063/1.1750147

View online: <http://dx.doi.org/10.1063/1.1750147>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/6/11?ver=pdfcov>

Published by the **AIP Publishing**

Articles you may be interested in

[Pressure of phosphorus in equilibrium with solid InP at different temperatures](#)

J. Appl. Phys. **75**, 2406 (1994); 10.1063/1.356980

[Direct transitions among the allotropic forms of boron nitride at high pressures and temperatures](#)

J. Chem. Phys. **63**, 3812 (1975); 10.1063/1.431874

[The Effect of the Rate of Cooling on the Allotropic Transformation Temperatures of Uranium](#)

J. Appl. Phys. **24**, 152 (1953); 10.1063/1.1721230

[A P-V-T Diagram of the Allotropic Forms of Ice](#)

Am. J. Phys. **7**, 187 (1939); 10.1119/1.1991435

[The Atomic Distribution in Red and Black Phosphorus and the Crystal Structure of Black Phosphorus](#)

J. Chem. Phys. **3**, 351 (1935); 10.1063/1.1749671



THE JOURNAL OF CHEMICAL PHYSICS

VOLUME 6

NOVEMBER, 1938

NUMBER 11

The Atomic Distribution in the Allotropic Forms of Phosphorus at Different Temperatures*

C. D. THOMAS† AND NEWELL S. GINGRICH
University of Missouri, Columbia, Missouri

(Received July 25, 1938)

Monochromatic x-ray diffraction patterns of liquid yellow phosphorus, amorphous red phosphorus and amorphous black phosphorus were obtained, using $\text{Mo } K\alpha$ radiation. The effect of temperature upon these patterns was investigated for the first two forms. Analysis of these patterns led to the determination of the atomic distribution curves in each case. The number of nearest neighbors is three for all forms. This is taken as direct proof of the existence of P_4 molecules in liquid yellow phosphorus. Comparisons are made of the atomic distribution curves of each form and at the different temperatures for liquid yellow and amorphous red phosphorus.

INTRODUCTION

X-RAY diffraction methods, together with the theories of Zernike and Prins¹ and of Debye and Menke,² make possible the most quantitative determination of the so-called "structure" of a liquid. Such determinations have been made for liquid elements in the cases of mercury,² gallium,³ sodium⁴ and potassium.⁵ Liquid yellow phosphorus is a convenient element to study, and it is of special interest because phosphorus occurs in several allotropic forms. Furthermore, this method has been of use in certain crystal structure determinations,⁶ and it is possible that work of this sort on liquid yellow

phosphorus will serve to confirm the reported crystal structure⁷ of yellow phosphorus, or to assist in arriving at a more complete determination of it.

Phosphorus exists in at least three allotropic forms, yellow (or white), red and black. Yellow phosphorus melts at 44.1°C , is highly inflammable, and has a density of 1.82 g/cc ; red phosphorus melts at 593°C , is inflammable, and has a density of 2.20 g/cc ; black phosphorus does not burn readily, and has a density of 2.70 g/cc . Red or black phosphorus may be made by subjecting yellow phosphorus to high hydrostatic pressures, and both forms may exist as crystalline or as amorphous material. Red may be formed from yellow through the application of heat alone. The vapor from each form consists of P_4 molecules. In both crystalline and amorphous forms of red and black phosphorus, there are three nearest neighbors about any one atom⁶ in accord with the coordination to be expected

* Presented to the American Physical Society at the Washington meeting, April 30, 1938.

† On leave of absence from the School of Mines and Metallurgy, University of Missouri, Rolla, Missouri.

¹ Zernike and Prins, *Zeits. f. Physik* **41**, 184 (1927).

² Debye and Menke, *Erg. d. Tech. Röntgenkunde*, **II** (1931).

³ Menke, *Physik. Zeits.* **33**, 593 (1932).

⁴ Trimble and Gingrich, *Phys. Rev.* **53**, 278 (1938).

⁵ Thomas and Gingrich, *J. Chem. Phys.* **6**, 411 (1938).

⁶ Hultgren, Gingrich and Warren, *J. Chem. Phys.* **3**, 351 (1935).

⁷ Natta and Passerini, *Nature* **125**, 707 (1930).

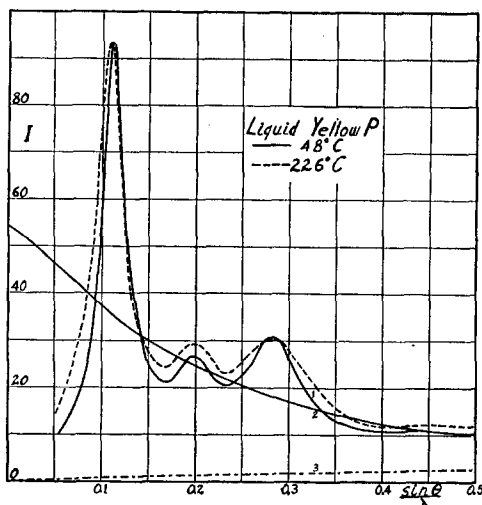


FIG. 1. Curve 1, corrected experimental intensity curve for liquid yellow phosphorus at 48°C; curve 2, independent unmodified scattering; curve 3, incoherent scattering; dashed curve, corrected experimental intensity curve for liquid yellow phosphorus at 226°C.

from covalent bonding of phosphorus. No x-ray diffraction work on liquid yellow phosphorus has been reported, and the reported work on crystalline yellow phosphorus is meager.

In the present work liquid yellow phosphorus was studied at several temperatures. One diffraction pattern was obtained at a temperature considerably above the temperature at which transition to red phosphorus takes place. This pattern showed it was practically identical to that previously obtained except that there was a peak more intense than all the others, at an angle so small as to be completely missed in the previous work.⁶ Investigation showed that the most intense peak in the black pattern had also been missed. Complete determinations of the atomic distribution curves were made in these two cases, on the basis of the new patterns.

EXPERIMENTAL

Mo $K\alpha$ x-rays monochromated by reflection from a rocksalt crystal were diffracted by a cylindrical sample, centralized in a cylindrical camera of 8.85 cm radius. Features of the camera included provision for heating the sample, cooling the film, measuring the temperature next to the sample, and adequate protection of the film against stray radiation. In all cases but one, the sample was contained in a thin-walled Pyrex glass

capillary. In the one case (black phosphorus)⁸ the sample was extruded from a capillary so that no container material was in the x-ray beam. Liquid yellow phosphorus was distilled over into the capillary, and it appeared perfectly clear and colorless. In one case, the sample remained liquid at a temperature of more than 50°C below the melting point. An exposure was made using this sample, but sometime during the exposure, it solidified, and a conglomerate picture was ob-

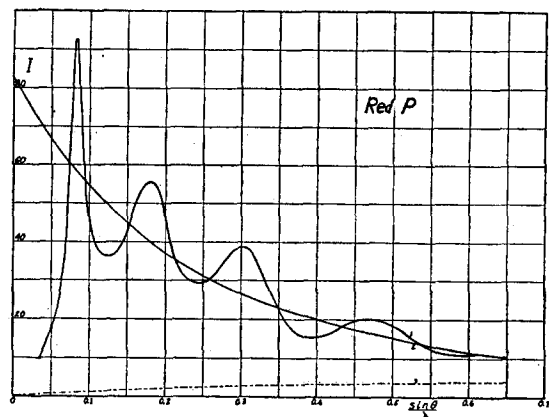


FIG. 2. Curve 1, corrected experimental intensity curve for amorphous red phosphorus at 50°C; curve 2, independent unmodified scattering; curve 3, incoherent scattering.

tained. Normally, the sample was heated to the desired temperature, and an exposure of 40 hours was made. At 48°C, the phosphorus remained clear except for a very slight tinge of orange at the point where x-rays passed through the sample. At 226°C, the sample emerged from the exposure with a brilliant red color, with a slightly deeper red at the point where the x-rays penetrated. However, the pattern was wholly characteristic of yellow phosphorus, with no indication whatsoever of the red pattern. Temperatures intermediate between 48°C and 226°C produced intermediate effects. At a temperature of 271°C, the patterns of red and of yellow phosphorus were superimposed in roughly equal intensities. The sample was then heated to 350°C for seven hours and cooled to 50°C for an exposure. This produced the characteristic red amorphous pattern. Another exposure, with red phosphorus at

⁸ We are indebted to Professor P. W. Bridgman of Harvard University for supplying us with a sample of amorphous black phosphorus.

325°C, showed so little difference in the diffraction pattern, from that taken at 50°C, that no further analysis was made. The slight difference that did occur was much less than that in the case of liquid yellow phosphorus taken over a smaller temperature range. Powdered black phosphorus was extruded from a capillary, and no effect of temperature was investigated.

Photographic densities in the various films were obtained by means of a microphotometer. The intensity of x-rays (proportional to the photographic densities here used) is shown in Figs. 1–3 as a function of $\sin \theta/\lambda$, where θ is half the total angle of scattering and $\lambda = 0.710\text{\AA}$. Fig. 1 shows the intensity curve for liquid yellow phosphorus at 48°C and at 226°C; Fig. 2 shows the intensity curve for amorphous red phosphorus; Fig. 3 shows the intensity curve for amorphous black phosphorus. Certain corrections have been made in these curves. The nature of the corrections will be given in the next section. Table I lists the values of $\sin \theta/\lambda$ for the intensity maxima in the various patterns.

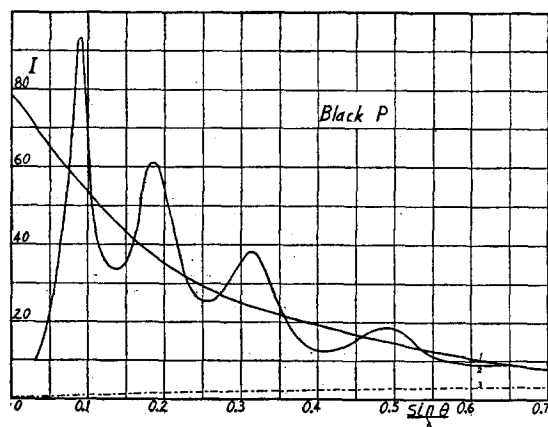


FIG. 3. Curve 1, corrected experimental intensity curve for amorphous black phosphorus at 20°C; curve 2, independent unmodified scattering; curve 3, incoherent scattering.

APPLICATION OF THE FOURIER METHOD

The theory behind this method is outlined elsewhere,⁹ and it leads to the equation

$$4\pi r^2 \rho(r) = 4\pi r^2 \rho_0 + \frac{2r}{\pi} \int_0^\infty si(s) \sin rs ds. \quad (1)$$

⁹ Warren, J. App. Phys. 8, 645 (1937).

In this equation, r is the distance in angstroms from any arbitrary atom, $\rho(r)$ is the actual density of atoms in atoms per cubic angstrom, ρ_0 is the average density of the material in atoms per cubic angstrom, and $s = (4\pi \sin \theta)/\lambda$. The function $i(s)$ contains the experimentally determined intensity (with corrections). It is defined as $i(s) = ((I/N) - f^2)/f^2$ where I/N is the intensity of coherent scattered radiation per atom from a sample having no absorption, and with corrections for the polarization of the x-ray beam; f is the structure factor of the atom.

The experimentally determined intensity is corrected for absorption in the sample, reducing the intensity curve to what it would be if there were no absorption. This is facilitated through the use of a graph¹⁰ for this purpose. Correction for polarization due both to reflection from the crystal and from the sample reduces the intensity curve to the values it would have if there were no polarization of the x-rays at reflection. This correction is described elsewhere.¹¹ Correction is also made for the incoherent radiation. The ratio of coherent to incoherent radiation may be calculated¹² at any scattering angle. By assuming that at large angles, where no further interferences appear, the total radiation is the sum of the independent coherent and the incoherent radiation, the intensity curves may be placed on an absolute basis. The incoherent radiation at any angle may then be drawn in, and subtracted from the intensity curve. In addition to these corrections, it is sometimes necessary to correct for the x-rays scattered by the glass capillary. Capillaries for phosphorus could be made large enough in diameter and thin enough so that this correction was wholly negligible.

From the fully corrected intensity curve, the function $i(s)$ was determined. The values of the

TABLE I. Peak positions in terms of $\sin \theta/\lambda$.

	FIRST PEAK	SECOND PEAK	THIRD PEAK	FOURTH PEAK
Liquid yellow 48°C	0.111	0.198	~0.28	none
Liquid yellow 226°C	0.108	0.194	~0.28	none
Amorphous red 50°C	0.083	0.180	0.302	~0.47
Amorphous black 20°C	0.090	0.185	0.314	~0.49

¹⁰ Blake, Rev. Mod. Phys. 5, 169 (1933).

¹¹ Katzoff, J. Chem. Phys. 2, 841 (1934).

¹² Compton and Allison, *X-Rays in Theory and Experiment* (D. Van Nostrand, 1935), p. 781.

integral of Eq. (1) for various values of r were obtained graphically. The quantity $4\pi r^2 \rho(r)$ was then obtained, and it was plotted as a function of r . These atomic distribution curves are shown in Figs. 4-7. Fig. 4 shows this curve for liquid yellow phosphorus at 48°C; Fig. 5 shows this curve for liquid yellow phosphorus at 226°C; Fig. 6 shows this curve for amorphous red phosphorus at 50°C; Fig. 7 shows this curve for amorphous black phosphorus at 20°C. Table II lists the positions of the peaks in the atomic distribution curves for the various cases.

DISCUSSION OF RESULTS

The diffraction pattern of yellow phosphorus (Fig. 1) shows a strong first peak, a weak second peak and a fairly strong third peak. In all other liquid elements so far studied, the intensity of the peaks decreases progressively. Several exposures were taken at each temperature, and the relative intensities of the peaks remained the same in the duplicate pictures taken at a given temperature. Thus, the experimental reality of this anomalous progression of intensities seems to be well established.

The effect of x-rays upon yellow phosphorus was noted qualitatively. At 48°C, several 40-hour exposures using Mo $K\alpha$ radiation produced faint orange coloring in the part of the sample which was irradiated. Exposure to Cu $K\alpha$ radiation for 40 hours produced considerably more coloring of the sample. Whether exposed to x-rays or not, and otherwise exposed only to relatively weak artificial illumination, the perfectly clear liquid samples very slowly acquired a turbid appearance. Successive melting and freezing hastened the appearance of this slightly yellow turbid condition.

A few attempts were made to obtain a diffraction pattern of crystalline yellow phosphorus. The material was melted, and suddenly cooled in some cases, and in other cases, it was cooled slowly. When solidified by cooling slowly, the yellow phosphorus solidified suddenly, producing an audible click. In none of the cases was a satisfactory pattern obtained. One of the patterns showed three distinct lines grouped in the region where the main liquid peak appeared, but generally, only radial asterism lines appeared.

The effect of temperature upon the yellow phosphorus samples was quite marked. A clear

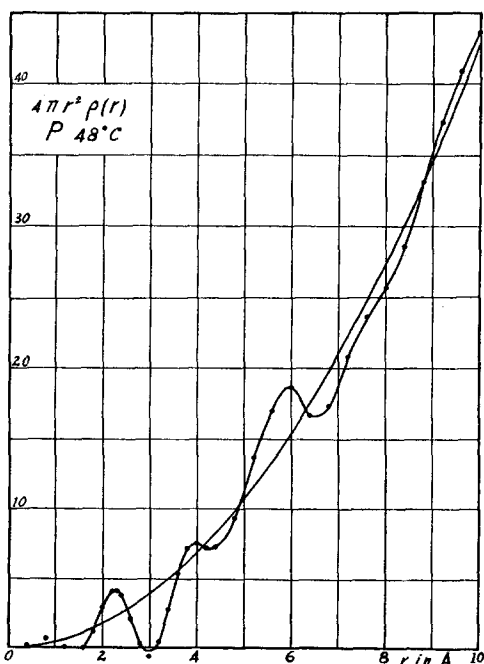


FIG. 4. The radial density distribution of atoms about any one atom in liquid yellow phosphorus at 48°C.

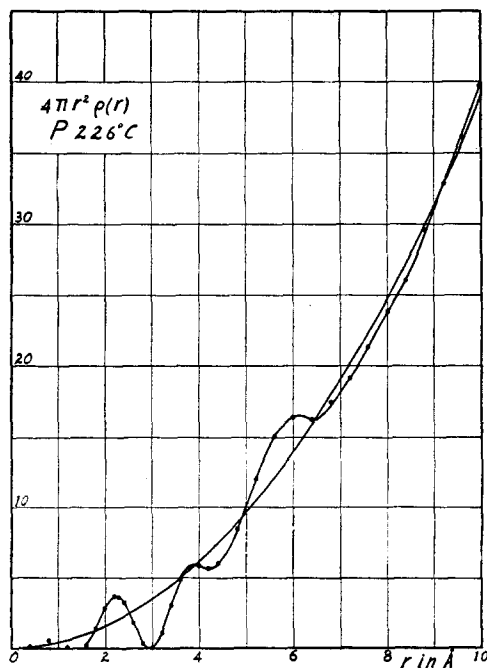


FIG. 5. The radial density distribution of atoms about any one atom in liquid yellow phosphorus at 226°C.

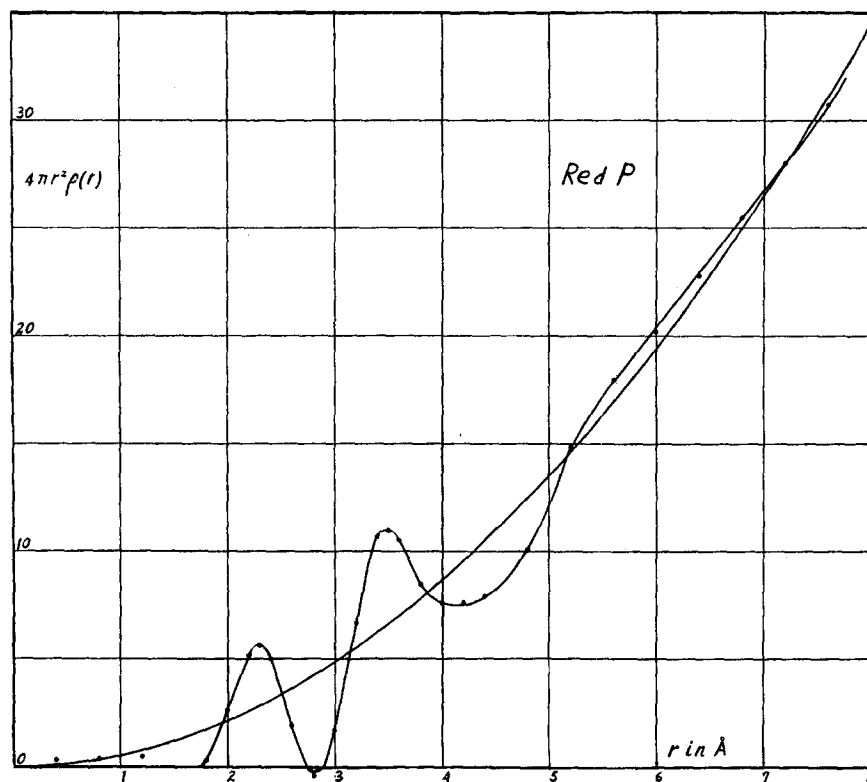


FIG. 6. The radial density distribution of atoms about any one atom in amorphous red phosphorus at 50°C.

sample exposed for 40 hours to a temperature of 226°C was changed to an opaque, deep red liquid. The region where x-rays penetrated was slightly deeper red in color. When these capillaries were broken open at room temperature, the red colored phosphorus burned much the same as yellow phosphorus.

The diffraction pattern of yellow phosphorus at 226°C (Fig. 1) shows typical temperature modification, but no great change over that at 48°C in spite of the fact that the liquid was deep red. The relative intensity of the background radiation was increased, i.e., for given main peak intensities at 48°C and 226°C, the background in the 226°C case was higher.

The pattern obtained at 271°C showed two distinct patterns superimposed in roughly equal intensities. This may mean that the transition from yellow to red phosphorus took place slowly during the exposure, or that it took place suddenly, half-way through the exposure. The former interpretation is in better accord with other

observations¹³ on the transition of phosphorus from yellow to red.

Yellow phosphorus heated at 350°C for seven hours, and cooled to 50°C for an exposure gave a diffraction pattern identical to that previously observed⁶ except that a peak stronger than all others was found at a smaller angle than was included in the previous work. Because of this, a complete redetermination of the atomic distribution was made. In addition, a pattern was obtained for red amorphous phosphorus at 325°C. Although there was a definite and typical difference, the difference was considered too small to make an analysis of this worth while.

The atomic distribution curve for yellow phosphorus at 48°C is shown in Fig. 4. The first peak is discrete, it has its maximum at 2.25Å, and it covers an area of slightly over 2.9 units. This indicates that there are three permanent nearest

¹³ Mellor, *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Vol. VIII (Longmans, Green and Co., 1928), p. 745.

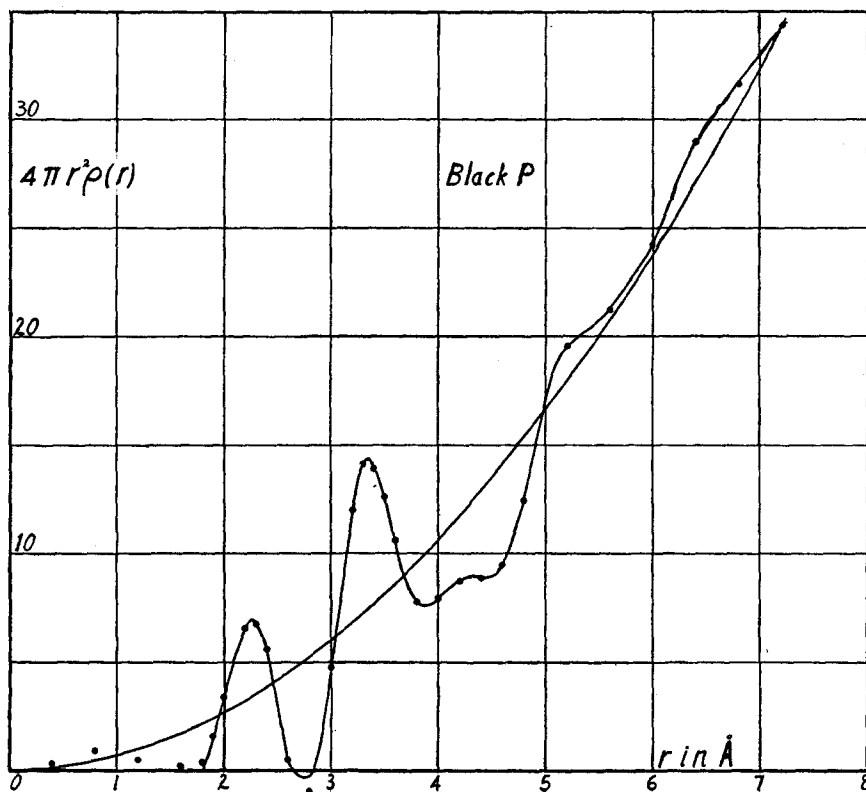


FIG. 7. The radial density distribution of atoms about any one atom in amorphous black phosphorus at 20°C.

neighbors at a distance of 2.25Å from a given atom. The first peak for other liquid elements does not extend to the axis on the large " r " side of the maximum, and this is interpreted as being due to a constant interchange of nearest neighbors. Discrete neighbors have heretofore been characteristic of solids. This arrangement of three permanent nearest neighbors is in accord with the assignment of P_4 molecules in the yellow phosphorus liquid. From the symmetrical shape of the first peak, it may be inferred that all P atoms are equivalent, or very nearly so. This equivalence gives the P_4 molecule in liquid yellow phosphorus the same or very nearly the same tetrahedral symmetry that was found for P_4 vapor by electron diffraction.¹⁴ The interatomic distance 2.25Å in the present work compares favorably with that of 2.21Å for P_4 vapor. The small peak at 3.9Å is interpreted as being due to the closest distance of approach of P atoms not

in the same P_4 molecule. This interpretation appears reasonable in the light of what is known concerning crystalline orthorhombic sulphur.¹⁵ For this, the ratio of the distance between nearest neighbors within a molecule to that between sulphur atoms not in the same molecule is 2.12/3.3. In the present case, this ratio is 2.25/3.9. The area under the peak at 3.9Å cannot be determined with much certainty, but it represents roughly 6 or 8 atoms. The large peak at 5.9Å is interpreted as representing the average number of next nearest neighbors of P atoms not in the same P_4 molecule. The area under a reconstructed, isolated, symmetrical peak with its maximum at 5.9Å is roughly 32, indicating that on the average, there are about 32 atoms at this distance.

The atomic distribution curve for yellow phosphorus at 226°C is shown in Fig. 5. The first peak is again discrete, it has its maximum at

¹⁴ Maxwell, Hendricks and Mosley, J. Chem. Phys. 3, 699 (1935).

¹⁵ Warren and Burwell, J. Chem. Phys. 3, 6 (1935).

2.25Å, and it covers an area of slightly over 2.7. This indicates that an atom has three permanent nearest neighbors at a distance of 2.25Å. Whereas in the case of other liquid elements, the position of this first peak changed with temperature, in this case no change can be detected. Thus, the molecule appears to remain as a rigid unit under these conditions. The weak second peak has about the same position as before, but in this case, measurement of its position is made difficult by its diffuse character. The third peak, however, shows a slight shift from 5.9Å at 48°C to 6.1Å at 226°C. This is taken as supporting evidence for the interpretation that the third peak represents in part the average and temporary grouping of molecules about the one in question. If one takes one-third the volume coefficient of expansion¹⁶ for liquid yellow phosphorus and calculates the linear expansion for the experimental temperature change, the 5.9Å peak at 48°C would be expected at 6.08Å at 226°C. This is to be compared with the observed position of about 6.1Å. The area under a reconstructed, isolated, symmetrical peak at 6.1Å is roughly 33.

The atomic distribution curve for red amorphous phosphorus is shown in Fig. 6. The first peak is discrete, it occurs at a distance of 2.29Å and it covers an area of 3 units. The second peak is sharp, but not isolated, and it occurs at 3.48Å. The area to be associated with this peak is roughly 6.7 units. Beyond this distance, the

distribution becomes random almost immediately. The number of nearest neighbors is again 3, due to the covalent bonding of P atoms. In the case of liquid yellow phosphorus, the assignment of P₄ molecules is reasonable because of its low melting point as well as other properties.¹³ However, in amorphous red and amorphous black phosphorus their high melting points indicate that in these cases there are no simple P₄ molecules. It is possible that in the case of red amorphous phosphorus there is a puckered network somewhat similar to that found in crystalline black phosphorus.⁶ If this is true, the number of next nearest neighbors should be 6, and the peak at 3.48Å covers an area of slightly over 6. The bond angle is 99° as compared to 102° in crystalline black P.

The atomic distribution curve for black amorphous phosphorus is shown in Fig. 7. This is very similar to that for red phosphorus, except that the distances to the nearest and to the next nearest neighbors are 2.27Å and 3.34Å, respectively. If one assumes the atoms to be arranged in a puckered network as in crystalline black P, the bond angle is found to be 95.6°.

In the cases of red and black amorphous samples, the introduction of the first and strongest peaks in the intensity curves made relatively minor alterations in the distribution curves. This is an excellent illustration of the fact that the diffraction pattern at large angles is relatively of much greater importance than that at small angles.

It is a pleasure to acknowledge grants in aid of this research made to one of us (N. S. G.) by the Rumford Fund Committee of the American Academy of Sciences, and by the American Association for the Advancement of Science. We are indebted to Professor B. E. Warren and Dr. L. K. Frevel for suggestions regarding the interpretation of the distribution curves.

TABLE II. *Interatomic distances in angstroms.*

	FIRST PEAK	SECOND PEAK	THIRD PEAK
Liquid yellow 48°C	2.25	~3.9	~5.9
Liquid yellow 226°C	2.25	~3.9	~6.1
Amorphous red 50°C	2.29	3.48	—
Amorphous black 20°C	2.27	3.34	—

¹⁶ *International Critical Tables*, Vol. I (McGraw-Hill Book Co., 1926), p. 102.