No $NH_4F \cdot 4HF$ was detected. However, its existence has not been definitely disproved at $-20°$. A change in slope of the tie line of less than 0.10% would produce an indication of the tetra-HF compound because the line is so close to the 0% H_2O axis. At 0°, however, a change of slope of nearly 5% would be required. Here the possibility of the existence of $NH_4 \cdot 4HF$ seems less. The only solid phase which was less dense than the liquid with which it was in equilibrium was H_2O.

The solid phases exist as the stated compounds over the following HF concentration ranges: at 0°, NH_4F from 0 to 3.7%, $NH_4F \cdot HF$ from 3.5 to 55.5% HF, and $NH_4F \cdot 3HF$ from 55.5 to 70.0% HF. At $-20°$, the solid H_2O phase exists from 13.0 to 14.8% HF, the NH_4F from 13.5 to 57.0%, and the $NH_4F \cdot 3HF$ from 53.7 to 73.0% HF. The reason for the overlap becomes evident on examination of the phase diagrams; at $-20°$ in the HF concentration range 53–58%, the effect of both NH_4F and H_2O on the saturated solution line is more pronounced than that of HF itself.

In general, the solubility of NH_4F in $HF–H_2O$ mixtures is somewhat lower at the lower temperatures. There are marked changes in solubility associated with changes in the solid phase.

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CONTRIBUTION FROM THE RAYTHEON COMPANY,
WALTHAM 54, MASSACHUSETTS

Vitreous Phosphorus

BY RAY C. ELLIS, JR.

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A vitreous allotrope of phosphorus has been prepared by two different methods. This form is compared with the other modifications of phosphorus. The chemistry of vitreous phosphorus has been studied briefly, and the relationship of the various forms of phosphorus is discussed.

Introduction

Phosphorus appears to have more allotropic forms than any other element. Reported are about 12 forms, most of which exist at room temperature and pressure. They have been summarized by Van Wazer.[1]

Experimental

Preparation of Black and Vitreous Phosphorus by Pressure.—Black Phosphorus I was first prepared by Bridgman[2,3] in 1914. Jacobs[4] later showed that the black powder obtained when white phosphorus is transformed by this technique is actually another form, the amorphous black.

Our first method of preparing black phosphorus followed that of Bridgman. As expected, the charge was transformed to an ingot of crystalline black phosphorus I, surrounded by a layer of powdery, amorphous black phosphorus. In two experiments where the initial pressure had been over 7 kilobars and the temperature was above 250° during the high pressure cycle, no usual sudden pressure drop was observed. An examination of the charge from these runs revealed an unexpected vitreous product. This vitreous form in one charge surrounded a core of the crystalline black form and in the other it composed nearly all of the ingot, which was about 1 cm. in diameter by 4 cm. long. The outer layers of the ingots consisted of amorphous black and some red phosphorus. The vitreous material could be separated from the rest of the ingot by breaking or sawing.

Catalytic Preparation of Black and Vitreous Phosphorus.—In 1955 a catalytic method for the preparation of black phosphorus I was reported by Krebs, Weitz, and Worms.[5] Following this method, equal weights of white phosphorus and mercury were sealed in an evacuated tube and heated to 380°. The temperature then was increased to 450° over a period of 4 days. The product is polycrystalline black phosphorus which appears to be the same as the material from the pressure method. It contains up to 30% by weight of mercury, nearly all of which may be removed by heating in a sealed tube with lead or gold.

The catalytic reaction proceeds through a vitreous form, for if the reaction is stopped after reaching a temperature of 380°, the charge is found to be converted entirely to this vitreous form. Tubes opened at various stages show a progressive conversion from the vitreous to the black form. There is always a sharp demarcation between the forms, the black being grainy where cut, broken, or etched, while the vitreous is smooth. The vitreous phosphorus, except for the mercury content, appears to be the same as the vitreous material prepared using high pressure.

The formation of vitreous phosphorus proceeds exothermically and if the charge is heated rapidly or is large, explosion may result. The vitreous phosphorus forms with the exclusion of the red except for an occasional skin on the charge.

In separate experiments it was confirmed that red phosphorus is not converted to the vitreous or the black using the catalytic method described.

Results and Discussion

Properties of Vitreous Phosphorus.—This form of phosphorus is a dark gray, hard, brittle solid exhibiting conchoidal fracture. X-Ray examination gives no lines or rings and the material therefore is completely amorphous. Its density was found to be 2.26 ± 0.01.

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[1] J. R. Van Wazer, "Phosphorus and Its Compounds," Vol. I, Interscience Publishers, Inc., New York, N. Y., 1958, p. 107.

[2] P. W. Bridgman, *J. Am. Chem. Soc.*, **36**, 1344 (1914).

[3] P. W. Bridgman, *ibid.*, **38**, 609 (1916).

[4] R. B. Jacobs, *J. Chem. Phys.*, **5**, 945 (1937).

[5] H. Krebs, H. Weitz, and K. H. Worms, *Z. anorg. allgem. Chem.*, **280**, 119 (1955).

Although it has a Diamond Pyramid hardness of 60 ± 5, it is not scratched by mild steels. Black phosphorus has a Diamond Pyramid hardness of 31 ± 1, a hardness about equivalent to that of lead. Because of its glass-like nature this new form of phosphorus is termed vitreous.

Vitreous phosphorus is more or less insulating, depending on the surface, having a resistivity of greater than 1000 ohm-cm. at room temperature, increasing into the kilomegohm-cm. region at liquid nitrogen temperatures. Black phosphorus has been found to be a semiconductor[6,7] with a gap width of 0.33 e.v. and a room temperature resistivity of about 1 ohm-cm.

Vitreous phosphorus appears to be stable indefinitely in warm moist air. When struck or sawed, it sparks like flint and may ignite, disintegrating as it burns. Nitric acid slowly attacks vitreous phosphorus, leaving a dull black surface, while bromine in alcohol or water attacks it rapidly and leaves a mirror-like surface. Black phosphorus under these conditions is etched to a rough surface revealing a grainy structure.

Vitreous phosphorus, whether prepared catalytically or by pressure, is converted slowly to the red form upon heating in a sealed tube. Sometimes a distinct maroon hue slowly appears as this conversion progresses. For small samples the conversion of the vitreous to the red is complete in 4 days at 400°.

If a small amount of mercury is added, the vitreous material from either source is transformed into the crystalline black I modification under these same conditions. If vitreous or black phosphorus is heated under vacuum, it sublimes forming white phosphorus on the cooler portions of the tube.

Relationship to Other Modifications.—Hultgren, Gingrich, and Warren[8] mentioned a powder that was prepared using conditions similar to the intermediate stages of the pressure cycle which resulted in vitreous phosphorus. This material differs from the vitreous phosphorus described here because of its red color and its structured X-ray pattern.

Except for the state of subdivision, Jacobs'[4] amorphous black material might be mistaken for vitreous phosphorus were it not that all efforts to convert Jacobs' material to the black crystalline form with mercury have failed.

Careful X-ray examination in this Laboratory of the pressure-derived black powder described by Jacobs gave a few faint lines, whereas the vitreous material using the same procedure gave none.

A comparison of vitreous phosphorus with other known allotropes such as the reds and the white also distinguish it as unique.

Transformation between Modifications.—A summary of the pertinent transformations of vitreous phosphorus with other forms appears in Fig. 1. This figure can be considered to be part of a much larger diagram encompassing all the phases of phosphorus.

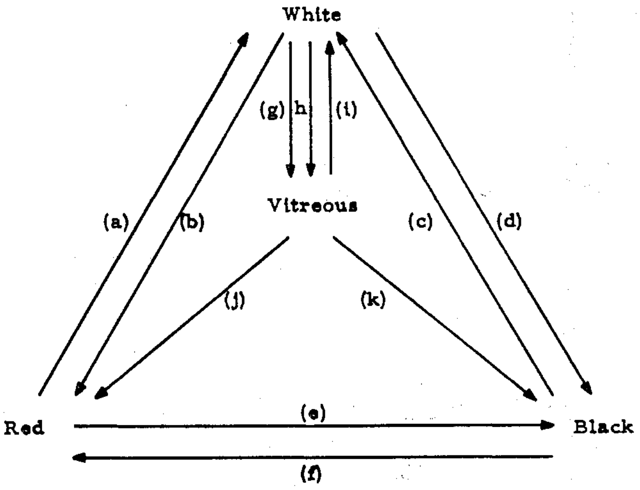

Fig. 1.—Summary of various transformations of phosphorus.

Transformation	Summary of conditions	Ref.
a.	Melt and quench	2
	Sublime under vacuum	
b.	>250°	9, 10
	Accelerated by ultraviolet	1
c.	Melt and quench	2
	Sublime under vacuum	
d.	220°, 12 kilobars	2
e.	25°, 45 kilobars with shear	7
	25°, 80 kilobars	7
f.	>450°, sealed tube, days	2
g.	>250°, 12 kilobars	
h.	380°, mercury	4
i.	Sublime under vacuum	
j.	400°, sealed tube, days	
k.	400°, mercury, sealed tube, days	

It was observed that transformation (k) did not take place under the conditions of (d), whereas it is established that the vitreous form is an intermediate in the catalytic conversion, (h) and (k).

It has been suggested[11] that one bond of the P_4 molecule breaks in the formation (reaction b) of the chain-like structure of red phosphorus. The chain length and terminal groups depend on the method of preparation.[12] The heating of the vitreous material causes a slow rearrangement (reaction j) to chains of red phosphorus.

Three bonds of the P_4 molecule need to be broken[11] to form the puckered, sheet-like[8] molecules of black phosphorus. The heating of the vitreous material with mercury causes a slow rearrangement (reaction k) to black phosphorus. It is suggested that the formation of vitreous phosphorus is the result on the average of somewhat more than one, but less than three, bonds breaking for each P_4 molecule in the formation of a cross-linked, giant molecule. The rearrangement of the vitreous form to the black (reaction k) might

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(6) R. W. Keyes, *Phys. Rev.*, **92**, 580 (1953).

(7) P. W. Bridgman, *Proc. Am. Acad. Arts Sci.*, **70**, 54 (1935).

(8) R. Hultgren, N. S. Gingrich, and B. E. Warren, *J. Chem. Phys.*, **3**, 351 (1935).

(9) W. L. Roth, T. W. DeWitt, and A. J. Smith, *J. Am. Chem. Soc.*, **69**, 2881 (1947).

(10) T. W. DeWitt and S. Skolnik, *ibid.*, **68**, 2305 (1946).

(11) L. Pauling and M. Simonetta, *J. Chem. Phys.*, **20**, 29 (1952).

(12) M. Y. Kraft and V. P. Parini, *Dokl. Akad. Nauk SSSR*, **77**, 57 (1951).

proceed as was suggested by Krebs, Weitz, and Worms[5] for the white.

Summary

A vitreous phosphorus has been prepared from white phosphorus by two totally dissimilar methods. The properties of this form are different from all other known forms of phosphorus.

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Nitrosodifluoramine. II. The Gas Phase Equilibrium

BY FREDERIC A. JOHNSON AND CHARLES B. COLBURN

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The gas phase equilibrium: $2NO + N_2F_4 \rightleftarrows 2NF_2NO \rightleftarrows 2NO + 2NF_2$ has been investigated. The heat of formation of NF_2NO at 295° was found to be +20.4 kcal./mole ± 1.4 kcal. and the N–N bond dissociation energy in $F_2N–NO$ was observed to be 10.1 ± 1.4 kcal.

The low temperature synthesis of nitrosodifluoramine (F_2NNO) and its partial characterization have recently been reported by Colburn and Johnson.[1] These investigators found this substance to possess a blue-purple color in both the liquid and gas phase. The intensity of the color of the material in the gas phase was a function of temperature and pressure. This observation suggested the existence of a gas phase equilibrium

$$2NO + N_2F_4 \rightleftarrows 2NF_2NO \rightleftarrows 2NO + 2NF_2$$

The present investigation is a quantitative study of this equilibrium.

Experimental

Materials.—Nitric oxide (Matheson) was purified by double passage through a trap at −160° (isopentane slush). Nitrogen dioxide was essentially removed by this treatment, and nitrous oxide was reduced to approximately 0.2%.

Tetrafluorohydrazine[2] of high purity was available. The principal impurity in the N_2F_4 was approximately 0.5% N_2O; other impurities were 0.1% NO and 0.1% SiF_4. The purity of the starting materials was determined by mass spectrometric analysis.

Apparatus.—A Beckman DU quartz spectrophotometer was used for the absorbance measurements. The optical cell was a Perkin-Elmer high pressure infrared cell with calcium fluoride windows; the path length was 6.15 ± 0.05 cm. Absorbance readings were taken against air as a standard, since the cell absorbance was relatively small and constant in the region of interest.

Temperature control was achieved by circulation of water through the coils of the Beckman thermospacers. The optical cell fit snugly against the metal faces of the two spacers after removal of the rubber buffer rings from the spacers, and thus gave good thermal contact. The temperature was measured to 0.1° by a two-junction copper–constantan thermocouple read to 0.01 mv. on a Leeds and Northrup potentiometer. The thermocouple junctions were attached to the body of the cell and protected with an asbestos shield.

The remainder of the pressure apparatus consisted of 0.25 in. copper tubing, a vacuum pump, and a 1-l. steel bomb with a pressure gage reading to 2 p.s.i. Materials were charged by condensing the starting materials into the bomb with liquid nitrogen after $P-V$ measurements had been made in a calibrated glass bulb. Expansions and pressure operations were carried out remotely and the optical cell shielded by 3/8 in. Plexiglas sheet (see cautionary note).

The difference in the volatilities of NO and N_2F_4 made it necessary to allow several hours for complete mixing to occur in the gas phase following the volatilization of the condensed reactants. The usual practice was to permit at least 15 hr. mixing time although no detectable change occurred after 2 to 3 hr. The rates of the reactions involved in this equilibrium are not slow since the expected absorbances were established in a very short time when pressures were reduced rapidly by venting.

Results

Stoichiometry.—A series of spectra obtained at 25° by adding various incremental amounts of nitric oxide to a constant concentration of tetrafluorohydrazine is shown in Fig. 1. The absorption peak at 550 mμ is similar to the 570 mμ band assigned[1] to NF_2NO in low temperature solutions. The absorption appears to be due to a single species and is in the approximate position expected from the qualitative observation that the gas possesses a blue color.

The much weaker absorption at approximately 1750 mμ was shown to be characteristic of the nitric oxide used, since it was present when NO was examined in the absence of N_2F_4. It has not been established whether this absorption is an overtone of the N–O stretching vibration or a minor impurity in the NO.

The equilibrium formation of nitrosodifluoramine can be represented by the equation

$$2NO + N_2F_4 \rightleftarrows 2NF_2NO \qquad (1)$$

For this reaction the equilibrium constant expression is

$$K_c = \frac{[NF_2NO]^2}{[NO]^2[N_2F_4]} \qquad (2)$$

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[1] C. B. Colburn and F. A. Johnson, *Inorg. Chem.*, **1**, 715 (1962).

[2] C. B. Colburn and A. Kennedy, *J. Am. Chem. Soc.*, **80**, 5004 (1958).