

The disagreement of calculated and experimental limiting slopes for the heat contents of this salt is very pronounced. In some respects the results are similar to those given by the bivalent sulfates.<sup>3d</sup> Below 0.0005 *m* for calcium, magnesium and cadmium sulfates, the slopes of the  $\partial(\Phi L_2)/\partial m^{1/2}$  vs.  $m^{1/2}$  curves showed a definite tendency to decrease toward the theoretical values. Slight evidence for a similar behavior by lanthanum sulfate is observable in a plot of the short chords. It would be desirable to extend these measurements to lower concentrations to verify this point, but this does not seem feasible with

the apparatus and technique available at present.

### Summary

Heats of dilution at 25° have been reported for lanthanum chloride between 0.00006 and 0.1 *m* and for lanthanum sulfate between 0.00002 and 0.025 *m*. Relative partial molal heat contents have been computed for the concentration intervals studied.

The results in dilute solutions fail to reveal an approach to the Debye-Hückel theory even at the lowest measured concentrations.

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## Polymorphism of Phosphoric Oxide\*

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Phosphoric oxide, or phosphorus pentoxide, is a component of several phase systems that have great significance in the chemistry of fertilizer manufacture, and accurate knowledge of its behavior in the pure condition is a prerequisite to a complete understanding of complex systems of more immediate practical importance. Thus far the polymorphous nature of phosphoric oxide has been deduced largely from vapor pressure measurements.<sup>2,3,4</sup> These data show that this compound exists in at least two crystalline modifications that melt to different liquids. The low-temperature or volatile form, the one with which the chemist is familiar, was found to change at 260° or above into a high-temperature modification having a negligible vapor pressure below about 400°. Recent crystal structure investigations showed that the low-temperature polymorph belongs to the rhombohedral division of the hexagonal system<sup>5</sup> and that a high-temperature form obtained by heating hexagonal crystals belongs

to the orthorhombic system.<sup>6</sup> These later will be referred to as the H and O forms, respectively. Published vapor pressure data for the H form are for the most part in very good agreement, but results obtained by different workers on high-temperature preparations differ considerably. Existence of a third crystalline form was suggested,<sup>2</sup> but in the absence of adequate microscopic examination of the materials no definite conclusions could be drawn.

The authors approached the problem with a view toward (1) the preparation and identification of the different modifications, (2) the measurement of their optical constants, (3) a study of the phase transformations by the quenching method, and (4) the use of the new findings as a guide to an interpretation of the vapor pressure data.

### Experimental Method

**Materials.**—The starting material was the H form obtained as an exceptionally good reagent grade of phosphorus pentoxide. Sampling was done in a dry chamber of the conventional type, dried with phosphorus pentoxide and provided with long rubber gloves for manipulations. On opening a fresh bottle of the reagent the leathery surface layer of partially hydrated oxide was removed, thus exposing the dry material below. The sample was then taken in successive small quantities, so that any small residual lumps from the surface layer could be recognized and discarded.

High-temperature crystalline modifications were prepared by heating P<sub>2</sub>O<sub>5</sub> in closed glass tubes. In order to

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(2) J. M. A. Hoefflake and F. E. C. Scheffer, *Rec. trav. chim.*, **45**, 191-200 (1926).

(3) (a) A. Smits and H. W. Deinum, *Proc. Acad. Sci. Amsterdam*, **33**, 514-25 (1930); *Z. physik. Chem.*, **A149**, 337-363 (1930); (b) A. Smits, J. A. A. Ketelaar and J. L. Meijering, *Z. physik. Chem.*, **B41**, 87-97 (1938); (c) A. Smits, E. P. S. Parvé, P. G. Meerman and H. C. J. de Decker, *Z. physik. Chem.*, **B46**, 43-61 (1940); (d) A. Smits and A. J. Rutgers, *J. Chem. Soc.*, **125**, 2573-2579 (1924).

(4) J. C. Southard and R. A. Nelson, *Times Journal*, **59**, 911-916 (1937).

(5) H. C. J. de Decker and C. H. MacGillavry, *Rec. trav. chim.*, **60**, 153-176 (1941).

(6) H. C. J. de Decker, *ibid.*, **60**, 413-427 (1941)

avoid contamination from the glass, 4 to 6 g. of free-flowing H crystals was packed into a platinum crucible, which was tightly covered with a piece of platinum foil and then inserted into a dried glass tube which was sealed off without exposure of the contents. By heating the sealed sample at 400° for two hours the hexagonal crystals were completely converted into a chalky aggregate of the O form, whereas heating it at 450° for twenty-four hours gave a horny aggregate of rather large crystals of the stable crystalline modification, thought to be tetragonal and for convenience designated by T in the following discussion. Analyses of preparations of the three varieties of crystals showed them to contain more than 99.87% P<sub>2</sub>O<sub>5</sub>. Although in larger scale preparations the platinum crucible was dispensed with, only slight etching of the glass occurred when the temperature was kept below about 450°.

A few large crystals (0.5 mm.) of the H form for careful optical measurements were obtained from material that had been sublimed *in vacuo* by Southard and Nelson.<sup>4</sup> Orthorhombic crystals large enough for optical examination were unexpectedly obtained by deposition from the vapor phase. A tube of the H form preheated at 400° for two hours, was heated in a temperature gradient for six days with the crystal mass at 460 to 480° and the upper end of the tube near 375°. After the first day crystals appeared at the cooler end of the tube and by the second day these had grown to a size of 2 to 3 mm. on an edge. This material proved to be the O form with about 5% of glass while the hard porous material in the hotter end of the tube was the T form. The crystals of the O form studied by de Decker<sup>6</sup> and thought by him to be the stable modification were obtained in a similar manner.

**Furnace Procedure.**—Thermal studies were made by quenching small charges in air after heating them at a given temperature for the desired time. The charges were examined with a petrographic microscope and by X-ray powder diffraction methods.

Electrically heated ovens were used for temperatures below 200° and temperatures were measured with calibrated mercurial thermometers. An automatically controlled electrically heated muffle furnace was used for higher temperatures which were measured by means of a protected chromel-alumel couple that had been calibrated in place against a standard platinum to platinum-rhodium (10% Rh) thermocouple. Recorded temperatures are probably accurate to ±3°.

In preparing the furnace charges 2 to 5 mg. of sample was loaded while in the dry box into a small envelope of 0.01-mm. platinum foil, which was closed by folding over the two edges of the open side three times. The loaded envelope was placed in a second platinum envelope and closed in the same way. The platinum-encased charge was inserted in a small glass tube, a few grains of phosphoric oxide were added to supply vapor outside of the envelope, and the tube was tightly stoppered and sealed off promptly upon removal from the dry chamber. It is estimated that the total pressure within the capsule at a furnace temperature of 600° was 2.5 to 3 atmospheres. A photograph of a typical furnace capsule is reproduced in Fig. 1.

The melting point of the H form was determined on

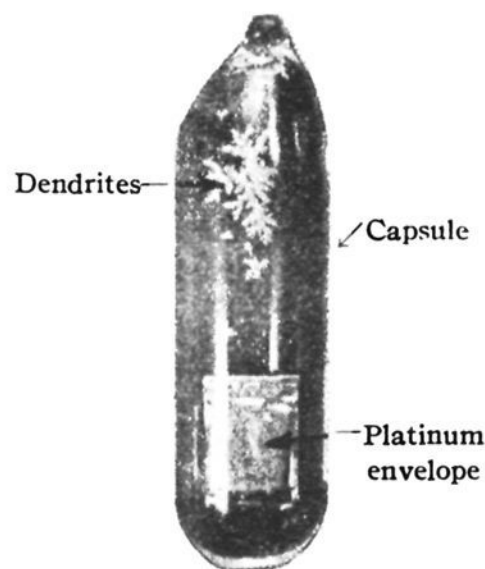


Fig. 1.—Photograph of a furnace charge of phosphoric oxide.

charges sealed in thin-walled capillaries (0.5 × 60 mm.) of lead glass having a refractive index (1.64) greater than that of any of the phosphoric oxide phases. These charges were heated in a bath of fused potassium nitrate.

Great care was exercised in all manipulations to prevent contamination of the charge with moisture and organic substances, such as towel lint, perspiration, etc. To this end all vessels were rinsed with distilled water and dried without wiping; platinum crucibles and envelopes were ignited and thereafter not touched with bare hands; glass tubes were also ignited before use; and prior to transfer of material the dry chamber was allowed to stand until thoroughly dry as indicated by only slight hydration of fresh drier (phosphorus pentoxide) after standing overnight. Reserve materials were placed in glass weighing dishes with ground-on covers and kept over P<sub>2</sub>O<sub>5</sub> in small containers.

**Optical Examination.**—The polymorphic forms of phosphoric oxide are entirely stable in contact with kerosene, mineral oil and monochloronaphthalene, and all optical examinations were therefore made in these liquids or in mixtures of them. Material for microscopic examination was loaded into thin-walled glass capillary tubes open at both ends, and the tube sealed with a dry soft wax was stored over P<sub>2</sub>O<sub>5</sub> in a small desiccator. Before examination the wax was removed from one end of the sample tube, which was immediately touched to the immersion liquid to allow it to flow into the sample. The other end of the tube was then opened so that the wetted sample could be pushed out with a glass rod. The portion used for the slide could thus be taken from the center of the sample tube without direct exposure to the atmosphere.

Rapid microscopic identification of phosphoric oxide crystals is afforded by observations in a liquid having an index of refraction of 1.600, thus: grains matching for one vibration direction are tetragonal (T), those with lower indices that show strong birefringence are orthorhombic (O), whereas those with lower indices that show exceptionally weak birefringence are hexagonal (H).

### Quenching Experiments

Results of critical experiments in the temperature range 70 to 600° are given in Table I. The H

form was observed to melt at  $422 \pm 6^\circ$  (items 11 to 13) in comparison with  $423^\circ$  found by Smits, *et al.*,<sup>2c</sup> from vapor pressure measurements. The liquid polymerizes rapidly and solidifies to a glass containing crystals of the O form. In these ex-

TABLE I  
CRITICAL QUENCHES

Item	Temp., °C.	Time <sup>a</sup>	Final condition of charge <sup>b</sup>
Charge initially hexagonal form (H)			
1	70	46 d	H
2	70	76 d	H, vr O
3	120	30 d	H, vr O
4	120	60 d	H, rO
5	180	30 d	H, rO
6	180	60 d	O
7	354	12 m	H
8	354	60 m	H, rO
9	378	20 m	O, mH
10	378	60 m	O, rG
11	416	20 m	O, rH
12	428	5 m	H, rG, vrO
13	428	10 m	O, aG
14	428	20 m	G, mO
15	450	20 m	O, rG
16	450	48 h	T, rG
17	515	142 h	T, rG
18	560	24 h	O, T, mG
Charge initially orthorhombic form (O) plus rare glass (rG)			
19	70	46 d	O, vrT
20	120	30 d	T, rG, rO
21	120	60 d	T, rG, rO
22	180	30 d	T
23	550	22 h	O, rG, vrT
24	558	22 h	O, aG
25	565	18 h	G, O
26	565	45 h	G, O
27	565	90 h	G, vrT
28	565	165 h	G, rT
29	570	19 h	G
Charge initially tetragonal (?) form (T)			
30	70	76 d	T
31	120	60 d	T
32	550	22 h	T
33	558	22 h	T, mG
34	565	18 h	T, mG
35	565	90 h	T, mG
36	565	165 h	T, rG
37	570	19 h	T, rG
38	575	26 h	T, vrG
39	585	28 h	G, corroded T
40	600	135 h	G, vrT
41	600	135 h	G

<sup>a</sup> Days, hours and minutes are indicated by d, h and m, respectively. <sup>b</sup> The following abbreviations are used: H, hexagonal crystals; O, orthorhombic crystals; T, tetragonal crystals; G, glass; vr, very rare about 1%; r, rare about 5%; m, minor about 15%; a, abundant 25% or more.

periments the liquid was not directly observed, but Smits, *et al.*,<sup>3c</sup> found that under their optimum conditions the interval between complete melting and subsequent solidification of a very small sample was about ten seconds. At temperatures below its melting point the H form changed directly into the O form. This change took place very slowly at  $70^\circ$ , but was complete in one hour at  $378^\circ$  (item 10).

The melting point of the O form lies between  $550$  and  $570^\circ$  (Items 23 to 29). Slow rates of melting, presence of some glass initially in the charge, and the tendency toward the formation of the T form make the results at the intermediate temperatures appear indefinite. Under such circumstances appearance of abundant glass may be taken as the criterion of melting, and accordingly the indicated melting point is  $558 \pm 6^\circ$ . Triple point temperatures found from vapor pressure measurements on unidentified high-temperature preparations of phosphoric oxide range from  $563$  to  $580^\circ$ . The O form is metastable with respect to the T form from the melting point down as low as  $70^\circ$ . Indeed, at the lower temperatures this inversion occurred much more readily than did the change,  $H \rightarrow O$  (Items 1 and 19).

The T form melts very slowly at  $580 \pm 5^\circ$  (Items 39 to 41) to a liquid so viscous that it does not readily assume the shape of the container. This is in agreement with the triple point temperature found by Smits and Deinum<sup>2a</sup> for their high-temperature preparation. Marked superheating of the T form is indicated by items 39 and 40.

Briefly, the results of quenching experiments thus far considered establish the existence of three crystalline modifications of phosphoric oxide, their respective melting points under a pressure of 2.5 to 3 atmospheres in addition to the vapor pressure and their relative stabilities over the range  $70^\circ$  to the melting point of the stable modification. In the investigated temperature range the H form to which the phosphorus pentoxide of commerce belongs, is metastable with respect to the O form which is in turn metastable with respect to the T form. These findings make possible clarification of the published vapor pressure and thermal data for phosphoric oxide.

#### Pressure-Temperature Relations

Published vapor pressure measurements are plotted in Fig. 2. Results obtained on the H

form by Hoeflake and Scheffer, Southard and Nelson and Smits, Parvé, Meerman and de Decker fall along a straight line  $ABT_1$ , which for compact representation has been cut at B. The first vapor pressure measurements were by Smits and Rutgers, who made two series of determinations, with widely differing results, on materials that had been sublimed at different rates. Of these the series with the lower pressure values is shown in the figure. In view of the good agreement of the later results by Smits, Parvé, *et al.*, with those obtained by other workers the results of Smits and Rutgers were disregarded in the location of line  $ABT_1$ .

None of the investigators identified the form of phosphorus pentoxide used. Since Smits and Deinum carried out measurements only after the pressure was "absolutely constant," it is probable that they had the T form. These results fall close to the curve  $ET_3$ . On the other hand, Smits and Rutgers, Hoeflake and Scheffer, and Southard and Nelson probably measured the vapor pressure of the O form (curve  $ET_2$ ). In all cases the starting material was the H form, which was converted to a high-temperature form by heating it in the vapor pressure apparatus at about 400° for three to five hours.

The other curves represent data for liquids.  $FG$  is drawn through the results obtained by Smits and Deinum on the stable liquid produced by melting the T form. Southard and Nelson's five points in the vicinity of the triple points,  $T_2$  and  $T_3$ , fall almost exactly on this line, and the results for their "transient phase," an intermediate phase obtained in certain instances by the inversion of the H form in the neighborhood of 400°, fall very close to the metastable segment of this curve. The straight line  $F'G'$  is determined by Hoeflake and Scheffer's data for their vitreous phase, which was obtained by heating the H form near 500°. The fact that one set of Southard and Nelson's measurements (not shown in Fig. 2) on a transient phase lies on  $F'G'$  lends emphasis to the view that Hoeflake and Scheffer's vitreous phase was an intermediate glass and not identical with the supercooled liquid studied by Smits and Deinum.

Pressure-temperature relationships are shown in Figs. 3 and 4. There are three monotropic systems whose triple points  $T_1$  (Fig. 3),  $T_2$  or  $T_2'$  (Fig. 4) and  $T_3$ , correspond to the melting points of the three known monotropic crystalline forms of phos-

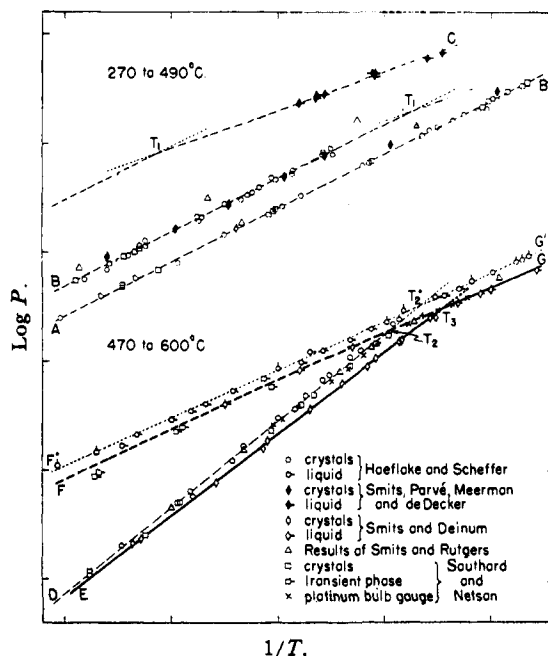


Fig. 2.—Vapor pressure data for phosphoric oxide. (The plot for the H form is folded back at B and  $T_1$ .)

phoric oxide, hexagonal, orthorhombic and tetragonal(?), respectively. The vapor pressure of the H form becomes appreciable just above 200° and reaches atmospheric pressure at 359°. The composite results (Fig. 2) indicate that the triple point lies at 420° and 360 cm. in comparison with 423° and 380 cm. found by Smits, Parvé, *et al.*, on the basis of their data alone. From vapor pressure data extant in 1933 Frandsen<sup>7</sup> deduced a value of  $358 \pm 7^\circ$  for the atmospheric sublimation temperature, and since that time the works of Southard and Nelson and Smits, Parvé, *et al.*, have supplied two other results, 358.9 and 357°, respectively.

Vapor pressure data place the triple point of the stable modification at 580° ( $T_3$ ) and 55.5 cm., in agreement with Smits and Deinum. Similarly, the triple point of the O form is found to lie at  $T_2$ , corresponding to 562° and 43.7 cm., whereas Smits and Rutgers found their high-temperature form to begin melting at 563° and 44.8 cm. Higher values were found by Southard and Nelson (565.6° and 45.6 cm.) and by Hoeflake and Scheffer (569° and 46 cm.). Since Southard and Nelson used a dynamic method in this temperature range, their pressure measurements below the liquidus with increasing temperature were almost certainly low since sufficient time could not be

(7) M. Frandsen, *Bur. Standards J. Research*, 10, 35-58 (1933).

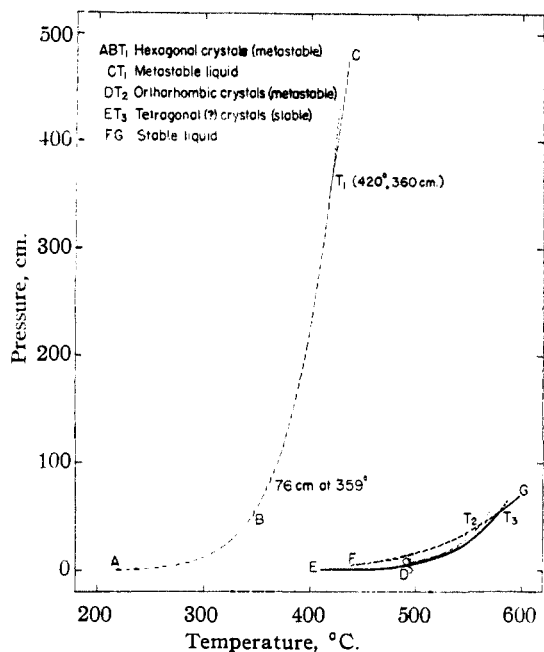


Fig. 3.—Pressure-temperature diagram for phosphoric oxide (200 to 600°).

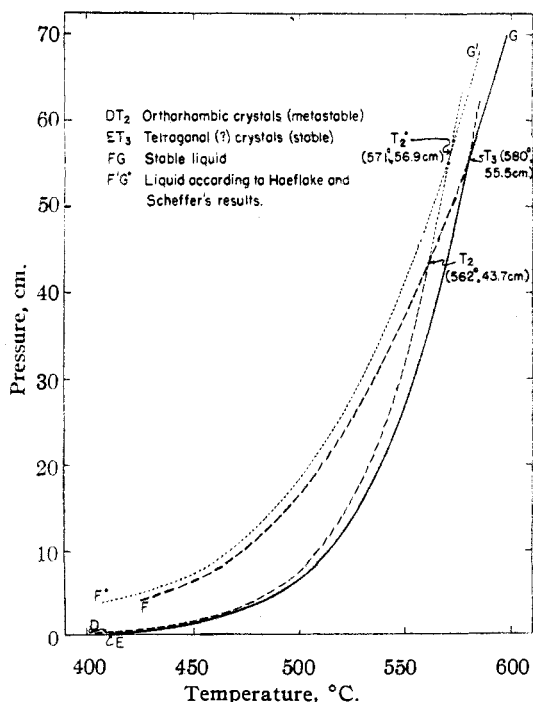


Fig. 4.—Pressure-temperature diagram for phosphoric oxide (400 to 600°).

given for the establishment of equilibrium pressures.

Heats of vaporization in calories per mole of  $P_4O_{10}$  derived from vapor pressure data for the several forms of phosphoric oxide as interpreted in

this paper are: H form, 22,700 cal.; O form, 36,400 cal.; T form 33,900 cal.; metastable liquid from H form 16,200 cal.; liquid according to data of Hoeflake and Scheffer, 20,300 cal.; stable liquid, 18,700 cal. These values are subject to the usual error of this type of determination which for quantities of this magnitude is of the order of 1000 cal. The heat of vaporization of the metastable O form is significantly greater than that of the T form. Since the T form is still the stable one at 70° (Table I) there must be considerable relative curvature of curves  $ET_3$  and  $DT_2$  (Fig. 2) below 400° to prevent their crossing.

Frandsen's value of  $17,600 \pm 2600$  cal. for the heat of vaporization of the H form, obtained from calorimetric data, is probably low because of the presence of the O form in samples prepared at elevated temperatures since such samples were heated for "at least three hours" before introduction into the calorimeter.

#### Optical Properties and Densities of the Phases

**Hexagonal Form.**—The H form occurs largely as tiny plates which appear to be easily deformed under slight pressure in the immersion media. The outline of the crystals is distinctly hexagonal (Fig. 5), and is presumably made up of a prism and the basal pinacoid. Some grains were noted which appeared to be trigonal in character. Polysynthetic twinning is common and may in part be due to the apparent deformability. The crystals are uniaxial positive with  $\omega = 1.469$ ,  $\epsilon = 1.471$  and  $\epsilon - \omega = 0.002$  for sodium light. The accuracy is  $\pm 0.002$ .

**Orthorhombic Form.**—This phase consists of platy aggregates (Fig. 5). Two cleavages were observed, a good one parallel to the optic plane and a poor cleavage normal thereto. Optically these crystals are strongly birefringent (0.044) and biaxial negative with  $2V$  equal to about  $65^\circ$ . The indices of refraction for sodium light are  $\alpha = 1.545$ ,  $\beta = 1.578$ ,  $\gamma = 1.589$ , all values being  $\pm 0.002$ .

**Tetragonal (?) Form.**—This polymorph generally develops in a lath-shaped habit with excellent prismatic cleavage, but in some charges needles were not at all uncommon. There is also some tendency toward the formation of coarse laths arranged in a hemispherical aggregate. Crystals are well terminated and occasionally twinned in simple relations. The laths exhibit parallel extinction and have positive elongation.



Determination of the optical character of this phase proved very difficult, but such off centered figures as were obtained indicated that the crystals are uniaxial and positive. Indices of refraction for sodium light are  $\omega = 1.599$ ,  $\epsilon = 1.624$  with  $\epsilon - \omega = 0.025$ , all  $\pm 0.002$ . The crystal habit is illustrated in Fig. 5.

**Glasses.**—Indices of refraction of the glasses formed by melting of different crystalline modifications varied between 1.500 and 1.518 for Na D light. There was some indication that the index was in part determined by the differences in polymerization of the molecules in the glass, which was determined by the initial crystalline form and the time of heating. Lowest values, namely, 1.500, were obtained in portions of glass made by heating the H form at  $480^\circ$  for ten minutes. Significantly higher values, namely, 1.506–1.511 were obtained by heating glass from the H form at  $540$  or  $580^\circ$  for three to seven minutes. Indices of refraction between 1.516 and 1.518 were obtained for glasses from all forms upon heating for two days or longer.

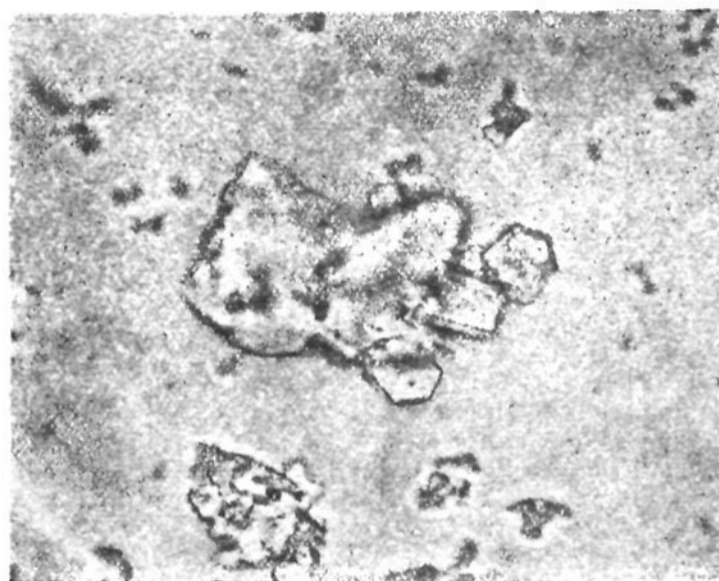
**Densities.**—The densities calculated from structure constants of the H and O forms<sup>5,6</sup> are 2.30 and 2.72. Measured values<sup>8,9</sup> for the density of the H form range from 2.283 to 2.317. Measured values<sup>5,6,9</sup> for the density of the T form are 3.05, 3.00 and 2.737 in comparison with 2.89 calculated from the indices of refraction.

#### Hygroscopic Properties of Crystalline Forms

Statements in the literature<sup>6</sup> would lead one to conclude that the high-temperature forms of phosphoric oxide are less hygroscopic than the usual form, and the authors' experience in handling coarsely crystalline O and T preparations seemed to confirm this view. In order to test this possibility, equal weights of the three modifications, the coarse materials having been ground to a fineness comparable with that of the H form, were exposed in glass weighing dishes to the atmosphere on a moderately damp day, and the gains in weight were determined by periodic weighings. The results (Fig. 6) indicate that the three crystalline varieties absorb atmospheric moisture at the same rate during the first twenty minutes of exposure; thereafter, the H form absorbed at the highest rate. At the end of a period of twenty-

(8) (a) W. Bilz and O. Hülzmann, *Z. anorg. allgem. Chem.*, **207**, 377–384 (1932); (b) K. Boratynski and A. Nowakowski, *Compt. rend.*, **186**, 691 (1933).

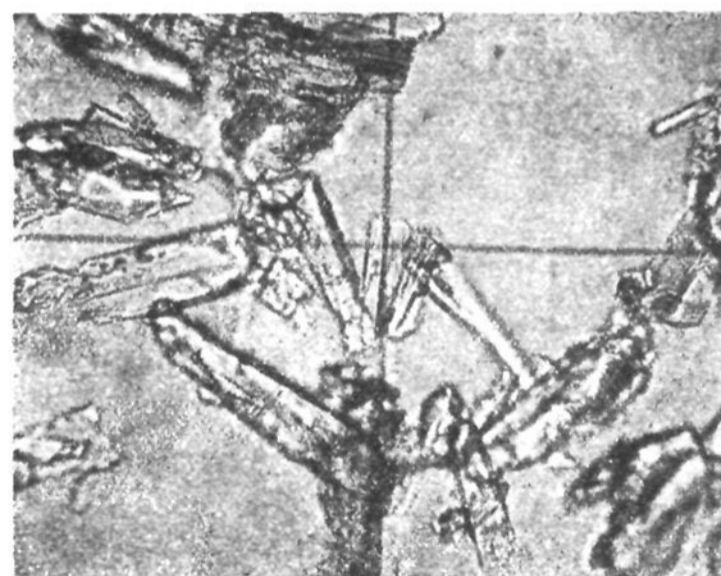
(9) A. N. Campbell and A. J. R. Campbell, *Trans. Faraday Soc.*, **31**, 1567–1574 (1935).



Hexagonal Modification



Orthorhombic Modification  
(Crossed Nicols)



Tetragonal Modification

Fig. 5.—Photomicrographs of the crystalline forms of phosphoric oxide.

four hours the H form had disappeared leaving a clear solution with a few spots of gel adhering to

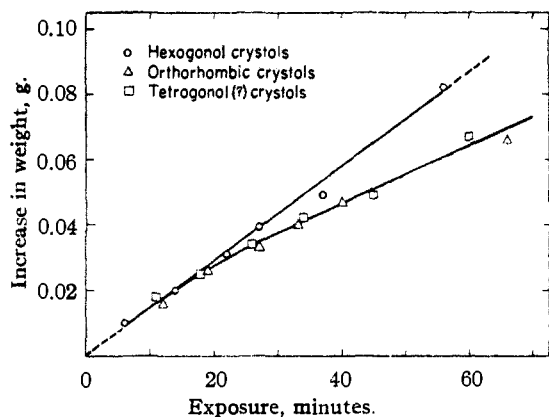


Fig. 6.—Absorption of atmospheric moisture by crystalline phosphoric oxide at room temperature (3-g. samples).

the glass, whereas the tests on the O and T modifications consisted of abundant gritty crystals covered with clear liquid. It is interesting to note in this connection that under the microscope the presence of a little water is manifested by globules of liquid on the H form and by rims on O and T crystals, which prevent optical studies, but are readily distinguished from glass.

In contact with liquid water the H form dissolves with a hissing sound accompanied by spattering, and in the form of a fine powder it reacts with explosive violence. On the other hand, finely-divided O crystals will form a suspension in water that dissolves slowly even at steam-bath temperatures. With a limited amount of water the T form is almost immediately converted into a stiff gel with liberation of much heat, then shortly the gel liquefies to a limpid liquid. The properties of the solutions thus obtained probably depend largely upon the variety of crystal as a consequence of the widely different structural characteristics of the three modifications. Conductivity measurements on metaphosphoric acid solutions prepared by dissolving the H and O forms, respectively, indicated a difference in the state of polymerization of the acid produced.<sup>10</sup>

#### Structural Relationships of Phases

**Crystalline Forms.**—The molecular configuration of the  $P_4O_{10}$  molecule in the vapor phase has been determined from electron diffraction data.<sup>11</sup> The phosphorus atoms are at the corners of a regular tetrahedron and are each bound to three

oxygen atoms (O), opposite the midpoint of adjacent tetrahedron edges, that are shared with three other phosphorus atoms. A fourth neighboring oxygen atom ( $O^-$ ) is symmetrically placed with respect to the other three, thus giving a tetrahedral configuration of oxygen atoms around phosphorus. It is thought that the relatively small P to  $O^-$  distance (1.39 Å.) is due to a polar character of the bond which might be indicated as  $P^+ - O^-$ .<sup>11</sup> According to this concept  $P_4O_{10}$  might better be written  $(P^+ O^-)_4O_6$ .

Molecules of  $P_4O_{10}$  having the same structure as in the vapor are present in the H form of the solid. The rhombohedral unit of structure of the hexagonal crystal<sup>5</sup> contains two  $P_4O_{10}$  molecules with their centers at (000) and  $(\frac{1}{2} \frac{1}{2} \frac{1}{2})$ .

The crystal structure of the orthorhombic modification was determined by de Decker<sup>6</sup> who erroneously considered it to be the stable form. This might best be described as an infinite sheet polymer containing interlocking rings. Phosphorus atoms are again surrounded at tetrahedron corners by four oxygen atoms, three of which are shared with other phosphorus atoms.

A crystal structure analysis has not been made for the T form. Powder diffraction data (Table II) are inadequate for fixing the symmetry which optical properties indicate to be tetragonal. The density of this form indicates that it too is an infinite polymer, either a three dimensional type or a sheet type. A tetragonal symmetry would make a sheet polymer seem improbable. Furthermore, the relatively simple unit of structure indicated by the powder diffraction data and the presence of good cleavage parallel to the apparent  $c$  axis gives considerable weight to the possible presence of a three dimensional polymer.

**Glasses.**—In harmony with modern theories of the structure of glasses<sup>12</sup> and nature of fusion<sup>13</sup> some order inherited from the parent solid probably persists in the liquid. Thus the H form, when it is rapidly heated, probably melts to liquid containing predominant  $P_4O_{10}$  molecules. This liquid ( $T_1C$ , Fig. 3) rapidly polymerizes with accompanying decrease in vapor pressure at a fixed temperature higher than  $T_1$ . In the practical periods of annealing time used it is by no means certain that the structure of the glass is the same

(10) K. Boratynski and A. Nowakowski, *Compt. rend.*, **194**, 89 (1932).

(11) G. C. Hampson and A. J. Stosick, *THIS JOURNAL*, **60**, 1814-1822 (1938).

(12) (a) W. H. Zachariasen, *ibid.*, **54**, 3841 (1932); (b) B. E. Warren, *Z. Krist.*, **86**, 349 (1939); *J. Am. Ceram. Soc.*, **24**, 256-261 (1941); *J. Applied Phys.*, **13**, 602-610 (1942).

(13) J. G. Kirkwood and E. Monroe, *J. Chem. Phys.*, **9**, 514 (1941).

TABLE II  
SPACING MEASUREMENTS AND INTENSITIES FOR POWDER DIFFRACTION PATTERNS OF POLYMORPHIC FORMS OF PHOSPHORIC OXIDE  
(Nickel  $K\alpha$  Radiation)

Hexagonal form			Orthorhombic form			Stable form (probably tetragonal)	
Spacing	Intensity <sup>a</sup>	Indices of reflection <sup>b</sup>	Spacing	Intensity <sup>a</sup>	Indices of reflections <sup>c</sup>	Spacing	Intensity <sup>a</sup>
						5.68	ms
5.44	vs	(10.2)					
5.19	vs	(11.0)					
			4.26	s	(11 $\bar{1}$ )	4.66	ms
			4.05	vw	(400)		
						3.88	ms
3.74	vw	(20.2)				3.695	mw
						3.585	mw
			3.57	vw			
			3.42	w	(31 $\bar{1}$ )		
3.37	w	(12.0)				3.350	m
3.28	mw	(12.1)					
3.165	w	(20.3)					
3.085	m	(12.2)				3.030	s
			2.865	ms	(420)		
			2.62	m	(51 $\bar{1}$ )	2.765	ms
2.59	w	(22.0)					
2.444	w					2.434	m
			2.36	vw			
2.326	w					2.326	vw
2.25	mw					2.238	vw
			2.20	w	(02 $\bar{2}$ )		
						2.146	vw
2.11	vw						
2.07	vw					2.065	vvw
2.00	vvw					1.996	w
1.962	m		1.926	mw			

<sup>a</sup> Abbreviations: vs very strong, s strong, ms medium strong, m medium, mw medium weak, w weak, vw very weak, vvw extremely weak. <sup>b</sup> Reflection planes identified by de Decker and MacGillavry,<sup>5</sup> who determined the structure of the hexagonal form. <sup>c</sup> Reflection planes identified by de Decker,<sup>6</sup> who determined the structure of the orthorhombic form.

as that given by melting of the other crystalline modifications. In some experiments the H form passed into a glass below its triple point. This formation of glass really corresponds to the chemical reaction of  $P_4O_{10}$  polymerization, and does not fix a metastable equilibrium point in that the vapor pressures of the glass and solid differ greatly in the temperature range studied.

Results obtained indicate that while some glass forms from the metastable H form below its melting point  $T_1$ , it more commonly passes into the O sheet polymer. This metastable polymer then slowly passes into the more stable T polymer. Both of these processes resemble other polymerization chemical reactions in being relatively slow. The liquid with vapor pressure represented by  $T_3G$  (Fig. 4) is probably the stable liquid

related to the apparently stable crystalline form. It can be supercooled, giving vapor pressures on the curve  $FT_3$ , which crosses the vapor pressure curve,  $DT_2$ , of the metastable O form at  $T_2$ . At this temperature the O modification slowly melts and  $T_2$  can thus be considered a metastable melting point. Above the temperature of  $T_2'$  the O form rapidly melts and it is possible that  $T_2'$  is another metastable triple point, at which the solid melts to a liquid metastable with respect to the one having the vapor pressure  $FG$ . This second liquid would differ structurally from the stable liquid, transformation to which would essentially be a chemical reaction.

A very interesting characteristic of the T form is the ease with which it can be heated above its melting point. It commonly is held that super-



heating of solids has not been observed.<sup>14</sup> However, in the first publication from the Geophysical Laboratory probable superheating of albite and albite-rich plagioclase feldspars was noted and discussed at some length.<sup>15</sup> Furthermore the general failure of heating curve technique for location of melting points in silicate systems is really due to the ease with which many silicates superheat. Members of the staff of the Geophysical Laboratory are fully aware of this possibility. Day and Allen state "... that the crystals (albite) are merely superheated without loss of any of their properties as solids, and that they thus present an analogy to superheated liquids. In the transformation of a solid crystalline substance into another crystal form such superheating has long been known...." They draw particular attention to the extremely viscous melt derived from albite.

Smits and Deinum<sup>3a</sup> also observed superheating of the T form and in fact carried out experiments in which crystals were retained to 700°. In the same place they called attention to possible superheating of the asbestos-like polymer of sulfur trioxide.

An explanation for the superheating of some crystals formed from line (SO<sub>3</sub>), sheet (P<sub>4</sub>O<sub>10</sub>, B<sub>2</sub>O<sub>3</sub>) or space (NaAlSi<sub>3</sub>O<sub>8</sub>) polymers is that melting is really a chemical reaction, involving a possible change in type of polymerization and surely the breaking of covalent chemical bonds. If breaking occurs within a crystal the atoms essentially remain in contact and the bond can form again. On the surface, however, molecular fragments can break off and form an amorphous material. In the case of the T form of phosphoric oxide and albite these amorphous materials are so viscous as barely to flow at temperatures 50° above the melting point. This high viscosity is merely evidence of retention of considerable polymerization in the melt. Superheating would not be expected in the case of the much more common solids, the melting of which does not involve a change in polymerization, for example, com-

(14) See for instance S. Glasstone, "Textbook of Physical Chemistry," D. Van Nostrand Co., New York, N. Y., 1940, p. 452.

(15) A. L. Day and E. T. Allen, "The Isomorphism and Thermal Properties of the Feldspars," Carnegie Institution of Washington Publication No. 31 (1905), p. 45 *et seq.*

pounds such as benzene, ferric oxide, sodium chloride and olivine and elements such as nitrogen and copper.

Another interesting consequence of the different states of polymerization of hexagonal, orthorhombic and tetragonal(?) forms of phosphoric oxide is their strikingly different behaviors toward water. The slow reaction of the O form with water appears to take place first along cleavage cracks with the resultant degradation of the crystal mass into a suspension of very small crystals. These small crystals persist at room temperature for periods greater than an hour. The T form also reacts slowly with water compared with the H form, but rapidly compared with the O form. The gel formed by the T form probably contains fragments in various states of polymerization that are in process of being broken down by water.

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### Summary

The melting points and monotropic relationship of three crystalline forms of phosphoric oxide were determined by the method of quenching. Previous vapor pressure data are discussed and interpreted to establish a pressure-temperature diagram (70 to 600°) for the one-component system.

The system involves three triple points, at which solid, liquid and vapor (P<sub>4</sub>O<sub>10</sub>) coexist in equilibrium, namely: 420° and 360 cm., 562° and 43.7 cm. and 580° and 55.5 cm., corresponding to the hexagonal, orthorhombic and stable polymorphs, respectively, and at least two distinct liquids, one a stable polymer of the other, which are identified with the melting of the stable form and the hexagonal modification, respectively.

Indices of refraction of the polymorphs and glasses were determined. The density and the thermal, hygroscopic and structural properties of the several phases are discussed.

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