

ment and lead are wholly identical. We hope and intend to continue the study, and solve the highly interesting questions which it presents.

We are greatly indebted to the Carnegie Institution of Washington for much of the apparatus and material used in this research.

Summary.

In this paper a description is given of parallel experiments determining the equivalent weights of various samples of lead chloride obtained from different sources. It was found that all of the radioactive specimens possess a lower atomic weight than ordinary lead, as determined under identical conditions, the deficiency in one case amounting to as much as 0.75 of a unit.

No simple linear quantitative relationship between the exact amount of radioactivity and the atomic weight was found. The radioactivity of the various samples was compared by means of the quantitative electro-scope.

The ultraviolet spectrum of a typical radioactive sample was compared with that of ordinary lead, with the help of G. P. Baxter, in a quartz spectrograph. No difference was found between the spectra of these specimens, except for a trace of copper too small to affect the result, and a negligible trace of silver known to have been present. The inference seems to be that radioactive lead contains an admixture of some substance different from ordinary lead, and very difficult to separate from it by chemical means. This substance cannot be identified in the ultraviolet spectrum of the material, either because it has the same spectrum as lead, or because it has no spectrum in that part of the field, or because its spectrum is masked or aborted by that of lead.

This amazing outcome is contrary to Harvard experience with several other elements, notably copper, silver, iron, sodium, and chlorine, each of which seems to give a constant atomic weight, no matter what the geographical source may have been. No attempt is made here to discuss the theoretical aspects of the facts presented, but attention is called to their qualitative agreement with the hypothesis of Fajans and of Soddy.

CAMBRIDGE, MASS.

TWO NEW MODIFICATIONS OF PHOSPHORUS.

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Received May 4, 1914.

The two new modifications of phosphorus to be described here were obtained during an investigation of the effect of high pressure on the melting point of ordinary white phosphorus. The two new forms have perfectly distinct characteristics; in this they are different from the questionable modifications of red phosphorus often announced. The first of these modifications is a new form of white phosphorus, which changes

into the ordinary white modification reversibly under the proper conditions. The second is a form obtained irreversibly from white at high pressures and moderate temperatures, which is 15% more dense than Hittorff's "metallic" red phosphorus.

In addition to a description of some of the physical properties of these two new modifications, this paper will contain an account of a few experiments made on a specimen of red phosphorus formed under somewhat unusual conditions of temperature and pressure; and, at the end will be found a consideration of the problem of the mutual relationships of the various modifications, now at least four in number. No attempt has been made to completely solve the problem, as this is now more properly a research for a chemist than a physicist, and since black phosphorus was discovered only incidentally, in the course of other investigations.

White Phosphorus II.

The new modification of white phosphorus was first produced by increasing pressure on ordinary white phosphorus to about 11000 kg./cm.² at 60°. The existence of the new form was shown by a discontinuous change in the volume at this pressure. A number of points on the transition curve of these two modifications were then obtained at temperatures down to 0°, and the corresponding changes of volume, when one modification passes to the other, were measured. These measurements suffice for a computation of the latent heat and the change of internal energy when the one form passes to the other. These data have already been published,¹ and for convenience of reference the results are reproduced here in Table I.

TABLE I.—DATA FOR THE TRANSITION BETWEEN THE TWO FORMS OF WHITE PHOSPHORUS.

Pressure. Kgm./cm. ²	Temperature.	ΔV . Cm. ³ /gm.	Latent heat. Kgm. m./gm.	Change of energy. Kgm. m./gm.
1	-76.9°
6000	— 2.4	0.00851	18.61	18.10
7000	9.6	825	19.43	18.86
8000	21.4	799	20.24	19.61
9000	32.7	772	21.04	20.34
10000	43.7	746	21.82	21.06
11000	54.4	720	22.58	21.77
12000	64.4	694	23.29	22.44

The points found at high pressures indicated by extrapolation that there should be a transition point at atmospheric pressure in the neighborhood of -80° C. This transition point at atmospheric pressure has lately been realized.

The method employed was the usual one of determining a heating curve. This method is well adapted to showing the existence of a transition point, but is not capable of giving a very accurate value of the transition

¹ P. W. Bridgman, *Phys. Rev. N. S.*, 3, 126-141, 153-203 (1914).

temperature, and gives no value for the change of volume. About 100 g. of white phosphorus were melted under water and allowed to solidify in a cylindrical mold, in which a platinum resistance thermometer was held axially. This thermometer had been calibrated between 0° and $+60^{\circ}$, and the negative readings calculated according to Callendar's formula, using 1.50 for the value of δ .¹ The maximum error in the temperature determined in this way cannot be more than 0.1° at -80° . The phosphorus with the thermometer was then transferred to a thin metal cylinder containing pentane, and the whole cooled down in liquid air. After coming to the temperature of liquid air, the metal cylinder with the phosphorus was transferred to a cylindrical Dewar flask, in which it was centrally supported without contact with the walls. The rise of temperature with time was followed with the platinum thermometer. Transition from the low temperature to the high temperature modification was shown

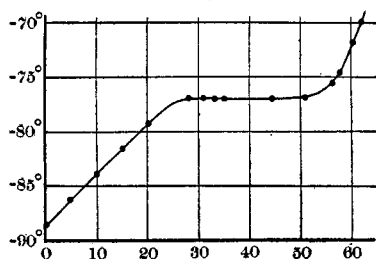


Fig. 1. Heating curve of ordinary white phosphorus, temperature in degrees against time in minutes. The arrest point shows the transition from the low to the high temperature modification.

by an arrest in the regular rise of temperature with time. This is shown in Fig. 1. The heat absorbed during the transformation was sufficient to keep the temperature nearly constant during half an hour. There was a very slight retrogression of temperature during this half hour, which shows that there was some slight superheating before the transition started. The temperature found in this way must, therefore be somewhat higher than the true temperature of transition. Just how much higher, it would be impossible to say, but the approximate constancy of temperature during the transformation makes it probable that the temperature found is not far above the true value. This is also strongly indicated by the smoothness of the curve connecting the point at atmospheric pressure with the points found at the high pressures. The completed phase diagram of these two modifications is shown in Fig. 2.

In addition to finding the transition temperature at atmospheric pressure, two attempts were made to determine the crystalline form of the new modification. The appearance of this new form in bulk is much like that of ordinary white phosphorus, it may possibly be a trifle yellower, and there are likely to be cracks formed because of the volume contraction of about 2% when the transition occurs. In the first attempt to get the crystalline form, a tube containing white phosphorus was pumped to a low vacuum and the lower part immersed in a flask with liquid air, while the upper part, containing the phosphorus, was exposed to the tempera-

¹ See Kaye and Laby's tables, p. 46.

ture of the room for 24 hours. It was hoped that the phosphorus would distil from the warm end and condense at the cold end in the characteristic crystalline form of the low temperature modification. The experi-

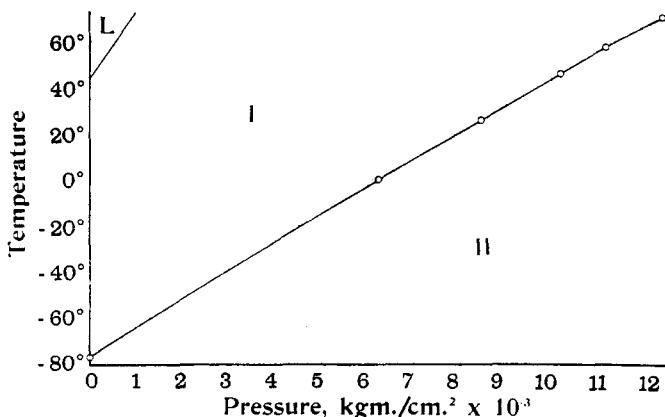


Fig. 2. Shows the relation between temperature and pressure on the transition curve between the two modifications of white phosphorus. A short length of the melting curve is shown in the upper left-hand corner.

ment failed because most of the phosphorus condensed in the cooler parts of the tube above the part exposed to the liquid air. Only an excessively attenuated mist condensed in the lower part of the tube. With the microscope, it was possible to pick out a few needle-like forms, probably the low temperature crystals of phosphorus, but no more exact information as to the crystalline form could be obtained. It should, perhaps, be mentioned that the crystals were examined at the temperature of the room, so that all that one could expect to see would be crystals of ordinary phosphorus with the outer crystalline form of the low temperature form.

The second attempt to obtain the crystalline form was somewhat more successful. A solution of white phosphorus in carbon disulphide was allowed to crystallize at the temperature of a mixture of carbon dioxide snow and gasoline. The phosphorus separates out as a slush composed of fine crystals. Microscopic examination showed that the usual crystalline habit is in needles, about five times as long as broad, with pointed ends of about 60° . It was not possible to specify further the shape of the needles. Scattered among the needles, however, there were occasional plate-like forms of unmistakable hexagonal shape; several nearly perfect hexagons were found. The great probability is, therefore, that this new modification belongs to the hexagonal system. The crystalline form of the usual modification is regular.

A word may be said as to a bearing of this on A. Smit's "New Theory of Allotropy."¹ He found that ordinary liquid white phosphorus behaved

¹ A. Smits and H. L. de Leeuw, *Z. phys. Chem.*, **77**, 367-379 (1911).

in a way that seemed to suggest that it contained two kinds of molecules; he assumed that the second kind of molecule was the molecule of red phosphorus. Quite a part from the legitimacy of his experiments, of which there seems to be some doubt, the hypothesis of the presence of red phosphorus molecules in appreciable quantity in white phosphorus at low temperatures is a surprising one, in view of the inappreciable reaction velocity from white to red. The existence of this new modification of white phosphorus shows that, if the experiments do legitimately point to the existence of another kind of molecule, it is the molecule of this new modification, rather than the molecule of red phosphorus.

Black Phosphorus.

Black phosphorus was discovered during an attempt to force ordinary white phosphorus to change into red phosphorus by the application of high hydrostatic pressure, at a temperature below that at which the transformation runs with appreciable velocity at atmospheric pressure. The phosphorus used was the purest commercial stick phosphorus from Eimer and Amend. This had shown itself perfectly free from dissolved impurities, although it probably contains such impurities as carbon or water mechanically suspended. The phosphorus was melted under water into a steel shell about 15 cm. long and 1.5 cm. in diameter, the water was removed as far as possible, after the phosphorus had solidified, by mechanical shaking, and the shell with the phosphorus was placed immediately under kerosene in a high pressure cylinder. Pressure up to about 6000 kg. per sq. cm. was applied at room temperature to the phosphorus through the medium of the kerosene; the cylinder was raised to 200° in an oil bath controlled by a thermostat, and the pressure was then raised to from 12,000 to 13,000 kg. The transition from white to black phosphorus occurs, under these conditions, in from 5 to 30 minutes. The pressure drops at first very slowly, then more rapidly until apparently a critical point is reached somewhere between 11,000 and 12,000, at which it drops suddenly to about 4,000 kg. Pressure may then be increased again (with the form of apparatus used this secondary increase could not be carried beyond 11,000 kg.) with no further drop of pressure. On cooling the lower cylinder and relieving pressure, the white phosphorus is found transformed into a black substance of very much smaller volume than the original white phosphorus. Proof will be given presently that this is a modification of phosphorus, not a compound. This experiment has been repeated successfully every time that it has been tried, now five times in all. About 50 g. of black phosphorus may be formed at a time.

During one of the repetitions of the experiment the effect of inoculating the white phosphorus with a piece of black phosphorus was tried, with the idea that under these conditions it might not be necessary to raise the temperature or pressure so high. It was, nevertheless, necessary to raise

the temperature to 200° and the pressure to 11,750 kg. When pressure and temperature had reached these values, the formation of the black from the inoculated white phosphorus took place in about 5 minutes, a somewhat shorter time than usual. It would appear then, that inoculation may have some effect on hastening the reaction, but the effect is in any event slight, and it may have been due entirely to accidental causes quite apart from the inoculation, judging from the irregularity of the other trials. An attempt to form black phosphorus from white at 175° and nearly 13,000 kg. was without success. Also an attempt to produce black phosphorus from commercial powdered red phosphorus, which had been inoculated with a small piece of black phosphorus was without result in 40 minutes at 12,900 kg. and 200° . Another attempt to produce black phosphorus from the massive red phosphorus, to be described later, was also unsuccessful after 30 minutes at 12,900 kg. and 200° .

The transformation from white to black phosphorus is not quite complete. There is a slight quantity of ordinary red phosphorus formed at the steel walls of the shell or at the surface of contact with the kerosene (never any red phosphorus in the interior of the mass), and throughout the mass of the black phosphorus there may be a few isolated patches in which exceedingly minute traces of white phosphorus remain untransformed. These traces of white phosphorus will catch fire spontaneously on contact with the air, or by friction with the hack saw with which the stick of black phosphorus was cut up for examination. This white phosphorus burns for only a few moments and then goes out, without igniting the mass of black phosphorus.

The black phosphorus presents two distinct characteristic fractures; in some places the fracture is coarsely granular like sugar, apparently crystalline, but the grains under a low power microscope show no semblance of crystalline form, and in other places where the flow under pressure was great, the fracture is fibrous with a metallic lustre, very much like graphite in appearance. In spite of the high pressure of formation, the mass of the black phosphorus is permeated with pores, some of which may be several millimeters in diameter. These pores may at first be filled with kerosene. The presence of these pores doubtless accounts for the slight apparent increase in weight of the specimen after the transformation. In the endeavor to show that the new substance was really a new modification of phosphorus, and not a chemical compound with kerosene or iron, the total weight of two samples was measured before and after the transformation. After formation, the samples were dried by mechanically shaking the kerosene from the surface. The gain of weight of each of the samples was about 2%; too small a gain to be accounted for by the formation of a chemical compound, and sufficiently explained by the

presence of kerosene in the pores. The presence of such occluded kerosene was evident to the sense of smell.

In order to make the proof still stronger that the substance formed was really a new modification of phosphorus and not a compound, C. T. Hawkins very kindly made an analysis of two samples at the Chemical Laboratory of Harvard University under the direction of G. P. Baxter. These samples had been broken into pieces about the size of a pea and soaked in carbon bisulphide to dissolve the white phosphorus, but had not otherwise been purified, as by exhausting in vacuum, for example. The sense of smell showed some kerosene still present. The results of the analysis are as follows:

Wt. of black phosphorus.	Wt. of $Mg_2P_2O_7$.	Per cent. phosphorus.
0.1622	0.5669	97.5
0.1754	0.6182	98.3

The first sample was treated by dissolving in concentrated nitric acid and the second in fuming nitric acid. Preliminary attempts to dissolve the phosphorus in dilute nitric acid showed that under these conditions a large part of the phosphorus was lost as volatile matter during dissolution. The amount of carbon present in the sample was 0.4% or more. No attempt was made to analyze the other 1.5% of impurity, which, in all probability, was water or kerosene. A measurement, to be given later, of the magnetic properties, shows no trace of iron. The fact that the total impurity is less than 2%, and that at least some of this impurity is accounted for, makes it absolutely certain that we have here another modification of phosphorus and not a chemical compound.

The most striking difference between the new black phosphorus and previously known modifications is its high density. The density of ordinary solid white phosphorus is 1.83, and that of red phosphorus may vary according to the method of preparation from 2.05 to a maximum of 2.34 for Hittorf's "metallic" crystallized red phosphorus. Nine determinations of the density of different specimens of black phosphorus were made; several of these were determinations of fairly large pieces by weighing under water, and several were determinations by the suspension method, using a mixture of bromoform and carbon tetrachloride. The density of the large pieces varied widely because of the effect of pores; the minimum density found by weighing in water was 2.47 and the maximum was 2.654. The suspension method, of course, gives more accurate results. The specimens measured by this method had been ground in a glass mortar and purified by soaking in several changes of carbon disulphide for several days, exhausted in vacuum at 100°, boiled in four or five changes of distilled water for eight hours, and exhausted in vacuum at 140° for several hours. Furthermore, the air was exhausted from the pores while the phosphorus was in the suspending liquid. Two different

specimens prepared by this method gave absolutely concordant results for the density, 2.691 at room temperature. The minimum density found by the suspension method for larger pieces less carefully purified was 2.66. We accordingly accept the value 2.691 as the true density of black phosphorus, a value 15% higher than that of the most dense variety of red phosphorus. The conclusion is inescapable that this is a new modification of phosphorus, quite distinct from red phosphorus and, because of its higher density, presumably a more stable form.

Black phosphorus does not catch fire spontaneously, can be ignited with difficulty with a match, and may be heated to perhaps 400° in the air without spontaneous ignition. Unlike commercial red phosphorus, it cannot be ignited by striking with a hammer on an anvil. It is almost, if not entirely, stable in the air. It was discovered in the summer time; pieces of the unpurified phosphorus which had remained for several months freely exposed to the air of the room were observed to collect a thin film of moisture, probably phosphoric acid, as red phosphorus is known to do. But several purified specimens, left for six months exposed to the air of the room during the cold half of the year, have collected no moisture whatever. It may be that the difference was due to the difference in atmospheric conditions at different times of the year, but more likely the effect was due to impurity, and pure black phosphorus is absolutely stable in air. A few simple tests seemed to show that it is much like red phosphorus in chemical properties; it is attacked by cold nitric acid, is not acted on appreciably by sulfuric acid, and is not dissolved by carbon disulfide.

When black phosphorus is heated in a closed glass tube it vaporizes and condenses in the colder parts of the tube to red and white phosphorus. The appearance under these conditions is exactly the same as when red phosphorus is similarly treated. It would seem, therefore, that the vapors of black and red phosphorus are, at least in large part, identical. The vaporization from black phosphorus is slow, as it is also from red phosphorus. If distillation from the hot to the cold parts of the tube is pushed to completion by heating for several hours, the black phosphorus leaves behind it a very fine, feathery, black residue, which is unaltered by further heating the glass to redness. This residue is in all probability the slight impurity of carbon disclosed by the above analysis.

Professor Palache, of the University Museum, was kind enough to determine the mechanical hardness of black phosphorus and to make a microscopic examination for the crystalline form. The hardness is about 2. Under the microscope none of the ground fragments show any semblance of external crystalline form. The fragments are opaque, except the most minute, which are translucent of an olive-brown color. These very minute fragments between crossed nicols show extinction and illumination with slight changes of color in perpendicular directions,

Black phosphorus is, therefore, unmistakably crystalline, and the crystal system is not regular; the fragments are too minute to permit any further specification of the system. That the crystalline structure should be very minute is what one would expect from the rapidity of formation and the great distortion during formation under high pressure; in fact it is rather surprising that there should be any crystalline structure on a scale large enough for microscopic detection.

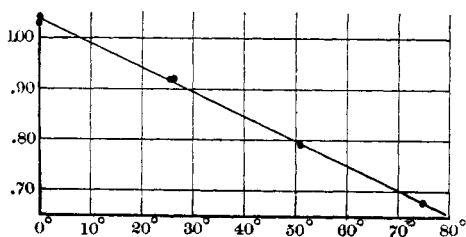
The specific heat of black phosphorus was determined by the method of mixtures, using about 40 g. of the ground and purified substance. Several preliminary determinations gave results near those finally obtained, but the proportions of the apparatus were not good. Two final determinations with improved apparatus gave 0.1716 and 0.1685, mean 0.170 g. cal. per g., as the average specific heat at constant pressure over the range from 30° to 100°. One of the reasons for making the specific heat determination was that it might give an idea as to the relative stability of black and red phosphorus. Analogy with other substances would lead us to expect that the more stable form would have the lower specific heat. The specific heat of red phosphorus between 15° and 98° has been found to be 0.170 by Regnault, and Wigand has found 0.183 for the range 0° to 51°, and 0.212 from 0° to 134°. The agreement between these values for red phosphorus is not good, due in part to the different sources of the material, but there can be little doubt that the correct value is above 0.170. It is unfortunate that Hittorf's "metallic" red phosphorus cannot be obtained in sufficient quantities for a determination of its specific heat, because this is apparently the only variety of red phosphorus with definite properties. The evidence afforded by the specific heats is not very valuable, therefore, but such as it is would indicate that black phosphorus is a form of greater stability (greater entropy content) than red phosphorus.

Black phosphorus is a fairly good conductor of electricity, in distinction from white and red phosphorus, which in the pure state seem to be nearly perfect insulators. It is usually stated in tables that white phosphorus is a perfect insulator, but that red phosphorus has some conducting power. This is on the authority of Faraday. The conductivity of red phosphorus found by Faraday must have been due to some slight impurity, however, because very recently Stock and Stamm¹ have found that the most carefully purified Hittorf's red phosphorus is a perfect insulator, and is therefore not at all entitled to its usual appellation of "metallic." The specimen of black phosphorus whose conductivity was measured here was selected from all the available pieces for its great apparent compactness. It was prepared by turning in a lathe, leaving for the final test a cylindrical piece about 1.52 cm. in diameter and 2.69 cm. long. The

¹ A. Stock and E. Stamm, *Ber.*, 36, 3497-3513 (1913).

electrodes were attached by copper plating terminals on the plane ends and soldering copper wires to the copper plating. It is possible in this way to make somewhat better contact than by using a contact with mercury, even when the surfaces are freshly scraped under mercury. The temperature coefficient of resistance was found between 0° and 75° in an oil bath with thermostat regulation. There may be some slight error introduced by imperfect contact at the copper plating; the plating is not firmly adherent as to a metal surface, but may be pulled off with the fingers. However, this error can be only slight, as is shown by the nearly perfect return of the resistance to its zero reading after raising the temperature to 75° . The character of the conduction is entirely metallic; there is not the slightest polarization effect on closing or opening the circuit. Measurements of the resistance were made on a Carey Foster bridge, using a current through the phosphorus not greater than 0.2 amp. The value found for the specific resistance is 0.711 ohms per cm. cube at 0° . The temperature coefficient

of resistance has a large negative value, and between 0° and 75° the relation between temperature and resistance is nearly linear. Fig. 3 shows the relation between temperature and resistance over this range. It is evident that presently, at some higher temperature, the curve must depart from linearity. The temperature coefficient of resistance at 0°



is -0.00465 ; this is an unusually high value, higher than for any substance usually listed. It is about 10 times higher than for carbon, and makes it practically certain that the small amount of carbon known to be present cannot be taking a large share in the conduction. It should be remarked that in respect to the sign of the temperature coefficient black phosphorus is not like the metals. The specimen of black phosphorus whose resistance was measured contained, like all large pieces, a number of fine pores, as is shown by the low value of its density, 2.562. About 5% of the total volume must have been occupied by pores, therefore. Precisely what effect these pores would have on the value of the specific resistance is uncertain, because the shape of the pores makes a difference, but in any event the specific resistance of pure black phosphorus must be somewhat lower than that given above.

It may pay to pause here to take thought of this conductivity of black phosphorus. Here is a substance which in two modifications possess no electrical conductivity, but in some way, when the atoms are rear-

Fig. 3.—The resistance in ohms of a cylinder of black phosphorus as a function of temperature. Notice that the resistance decreases rapidly with increasing temperature.

ranged more closely together, sets free electrons and becomes a conductor. It would seem to point to some more deep-seated change than a mere rearrangement of atoms; possibly the electrons are squeezed out of the atoms by their great propinquity. Phosphorus is not the only example of this; graphite and carbon are another case in which the volume relations of phosphorus are reversed. But in any event, this is a significant fact for contemplation.

As we might expect from its electrical conductivity, black phosphorus is also a rather good conductor of heat. Observations of the thermal conductivity were of the roughest qualitative nature; when soldering the leads to the copper plated terminals the entire mass of phosphorus rapidly became too hot to hold in the hand, very much more rapidly than would a piece of glass, for example.

The magnetic permeability of black phosphorus was very kindly determined in the laboratory by H. C. Hayes. It is feebly diamagnetic; less diamagnetic than either red or white phosphorus. He found for two specimens the values -0.27 and -0.29×10^{-6} . This diamagnetism makes it evident that any impurity of iron can be present only in excessively minute quantities.

The Relation of the Several Modifications.

The most important problem connected with this new modification is the determination of its relation to the other known modifications of phosphorus. It was hoped that the existence of this new modification might offer some clue to the vexed question as to the true nature of red phosphorus. Some facts of importance have been found, but the exact nature of the relationship has not yet been discovered. In the course of the investigation red phosphorus was prepared in a somewhat unusual way, and was found to have slightly different properties from the usual varieties. The rest of this paper will contain a description of this new red phosphorus and of the experiments to determine the relation of the different modifications to each other.

It seemed reasonable to expect that black phosphorus might be prepared by the application of pressures lower than 12,000 kg. at temperatures considerably higher than 200°. It is surprising that no experiments seem ever to have been made on phosphorus at high temperatures at pressures higher than its own vapor pressure. A long steel cylinder, about $\frac{3}{4}$ inch in inside diameter, was made for the attempt at higher temperatures. The lower end of the cylinder, which was to contain the phosphorus and was to dip unto a bath of molten lead, was closed by a packing device of copper rings, much like the packing recently described.¹ The upper end of the cylinder projected far enough beyond the lead bath so that it could be kept cool with water, and connection was made at this end

¹ P. W. Bridgman, *Proc. Am. Acad.*, 49, 627-643 (1914).

with a Cailletet pump giving 1000 kg. In the first experiment, commercial red phosphorus powder was placed in a trap with a seal of fusible solder containing 50% bismuth in the lower part of the cylinder, and exposed to a dull red heat at 400 kg. for 30 minutes. On cooling and releasing pressure, the red phosphorus was found completely permeating the solder. The appearance was that of a solidified emulsion. Evidently at the high temperature the red phosphorus had dissolved in the solder and separated out on cooling. If any of the crystallized Hittorf's phosphorus was formed, it must have been in very small quantity, although a fairly large yield might be expected under the conditions of high pressure. In a second experiment, in order to avoid the solvent action of the solder at the high temperatures, pressure was transmitted directly to a specimen of red phosphorus by a heavy tempering oil. This was heated and pressure applied as in the first experiment. The white phosphorus changed to red almost immediately, judging by the sudden drop of pressure, but there was no further change. The cylinder was found filled with red phosphorus and the soft charred residue of the tempering oil. In a third attempt, ordinary white phosphorus was placed under water, and heated as before to a dull red, pressure being transmitted by the water. In this run, pressure was kept at 850 kg. for 6 hrs., then raised to 950 kg. for $1\frac{3}{4}$ hrs., and then raised to a maximum, 1000, for 10 or 15 minutes. After this time at the maximum pressure, a slight leak developed owing to the stretching of the steel. The cylinder was immediately removed from the lead bath and plunged into cold water. The white phosphorus was found entirely transformed into a bright brick-red variety, compact, and with no evident trace of white phosphorus. This is what one would expect from the high pressure of formation; during the cooling there was no chance for any of the red phosphorus to vaporize and condense as white. The red phosphorus prepared in this way shows in general a bright red fracture, but when scratched with a knife or a piece of glass shows a gray metallic streak. Furthermore, there are isolated patches throughout the mass where the fracture shows black, as if the transformation to black had begun here. The density of fairly large pieces of the red phosphorus is 2.26, but the density of the smallest heaviest pieces (these heaviest pieces were bright red in color) was found by the suspension method to be 2.387, a value higher than for Hittorf's "metallic" phosphorus (2.34) or even for the "phosphore pyromorphique" of Jolibois¹ (2.37), about which there seems to be some doubt.

This red phosphorus was purified by the same method as the black phosphorus, although no impurity could be detected in it. When heated in a closed tube it vaporizes and condenses to red and white phosphorus

¹ P. Jolibois, *Compt. rend.*, 149, 287-289 (1909); 151, 382-384 (1910).

in the same way as the ordinary commercial red phosphorus. It leaves no residue.

Red phosphorus of the same bright red color may also be prepared by heating commercial red phosphorus under its own vapor pressure to a high temperature (almost a yellow) in a heavy nickel steel bomb. This bright red preparation shows the same gray metallic streak when scratched as that prepared at a higher pressure and lower temperature. It is barely possible that the bright red color of these two preparations is due to a minute impurity of iron, since both of these specimens were directly in contact with the steel walls of the cylinder. Red phosphorus heated under its own vapor pressure in a glass vessel to a lower temperature does not assume this bright red color. However, the iron present must be very minute in quantity, because the bright red phosphorus can be evaporated without sensible residue.

Apparently, the physical information most important for a determination of the relation of red and black phosphorus is a knowledge of the vapor pressures. The best way to measure the vapor pressure would be by use of a quartz membrane, but in the absence of the proper apparatus, two attempts were made with other methods. The first was by a method due to Hittorf,¹ and apparently not used since. The phosphorus under investigation is placed in the sealed short arm of a U-tube, which is closed below by a column of molten metal, as bismuth or lead, which exerts no appreciable vapor pressure at the temperature in question, as would mercury. The free surface of the metal in the long arm of the U is acted on by gas pressure, which may be measured at room temperature with an ordinary mercurial manometer. This original design of Hittorf's was so modified as to give the difference of vapor pressure of the two modifications, by putting red phosphorus in the one arm and black phosphorus in the other arm of the sealed U and observing the difference of level of the columns of melted metal on the two sides. The first measurement at the temperature of the vapor of boiling sulfur showed a greater vapor pressure over the red phosphorus by at least 7 or 8 cm. of mercury. But later attempts with a modified apparatus to get the vapor pressure of the two modifications separately gave values much too high. There must be some chemical action between the phosphorus and the molten solder. Hittorf found the same thing, although his results, using bismuth instead of a solder of tin and lead, were too low rather than too high. In any event, there is apparently no metal melting within the proper range that is without chemical action, and this attractively simple method had to be abandoned.

The method finally used is also one originally due to Hittorf. A small piece of phosphorus is enclosed in an evacuated tube of known volume and

¹ W. Hittorf, *Pogg. Ann.*, 126, 193-228 (1865).

heated to the desired temperature. After heating long enough to make sure that the vapor has reached its maximum pressure, the tube is removed from the bath and allowed to cool quickly at the temperature of the room. The phosphorus vapor condenses on the sides of the tube as white phosphorus, and its amount may be determined either by dissolving it in CS_2 , as did Hittorf, or probably with greater accuracy by determining the loss of weight of the original specimen. The vapor pressure is then computed, assuming that the molecule of phosphorus vapor is 4-atomic. This value of the molecular weight seems to be established beyond doubt for the temperature range used here.¹

Determinations of the vapor pressure of red and black phosphorus were made in this way at the temperatures of boiling mercury and sulfur. It is essential that the temperature of the tube be constant, as is ensured by a vapor bath, or else there will be a continued distillation from the hotter parts to the cooler parts with condensation in the form of red phosphorus, giving too high a computed vapor pressure. The temperature was sufficiently uniform during these experiments, for no condensed red phosphorus was found. Care was taken to avoid any possible distillation during warming to the temperature of the bath by placing the tube suddenly in the vapor after boiling had been going on for some time.

TABLE II.—VAPOR PRESSURE OF PHOSPHORUS IN CM. OF MERCURY.

Temperature. ° C.	P. W. Bridgman.		W. Hittorf.		L. Troorst and P. Hautefeuille.	
	Black phos.	Dense red phos.	Ordinary red.	Crystallized red.	White.	Ordinary red.
357.1°	2.3	5.2
358	3.15
360	243.0	9.1
409	37.1
440	570.0	133.0
443.7°	..	73.2
445.2°	58.5
447	164.0	93.0
487	517.0
494	1370.0	..
503	1660.0	..
510	820.0
511	1990.0	..
530	614.0	413.0
550	2360.0
577	4260.0

The results are shown in Table II, together with those of previous observers. The agreement of the previous results is not good, but in general the conclusion is justified that the vapor pressure of black phosphorus

¹ A. Stock, G. E. Gibson and E. Stamm, *Ber.*, **45**, 3527-3539 (1912).

is less than that of the dense red variety, which in its turn is less than that found by other observers for ordinary red or metallic phosphorus.

The conclusion that would be drawn from the vapor-pressure measurements, therefore, is that black phosphorus is a more stable form than any of the other varieties. But an observation on the remarkable behavior of black and red phosphorus, when heated together, makes it probable that the vaporization of phosphorus is a very complicated process and that conclusions as to relative stability drawn from vapor-pressure observations must be accepted with some reservation. If red and black phosphorus are heated together in a sealed tube, one would expect the red, which has the greater vapor pressure, to distil and condense to the black, which has the smaller vapor pressure, just as water subcooled below zero will vaporize and condense as ice. Three trials of this were made. Once red and black phosphorus were heated together in an exhausted tube to about 380° for 5 days, 9 hours a day, with no increase in the black visible to the eye. For the second trial they were heated together at 445° (sulfur vapor) for 6 hours with no gain of the black phosphorus, but rather a loss of 0.005 g., which is of the order of magnitude that it would lose from its own vaporization in a space of the size used. For the third trial, red and black phosphorus were heated together in an exhausted tube for 20 minutes at a temperature of about 620° , sufficient to start the melting of the red phosphorus, but with no visible increase of the black at the expense of the red. This experiment will be referred to again later. This strange behavior of black and red phosphorus recalls certain observations made by previous experimenters, but which do not seem to have been rated at their full significance. If red phosphorus is heated in a closed space to a given temperature it will give off vapor until a definite pressure is reached, and if it is then heated higher it will give off more vapor until a greater pressure is reached. But if now the vapor is cooled, the pressure does not retrace its original course, but instead lags behind. This observation has been made by Preuner and Brockmüller,¹ and there is also one by Hittorf² which amounts to the same thing. Hittorf found with his U-manometer that a greater pressure was required to produce condensation than could be produced by the spontaneous vaporization of red phosphorus at the same temperature. At 445° he found that, within limits of pressure 1.5 atm. apart, there was neither vaporization from the solid nor condensation from the vapor. Certainly, therefore, the vaporization of red phosphorus cannot be explained by the simple process which we suppose holds for the ordinary vaporization of liquids, which we regard as a kinetic equilibrium between streams of molecules leaving and approaching the surface of separation between the two phases. The recent work of Stock

¹ G. Preuner and I. Brockmüller, *Z. phys. Chem.*, **81**, 129-170 (1913).

² W. Hittorf, *Loc. cit.*

and Stamm¹ brings clearly to light the complicated nature of the vaporization process. Probably vaporization is a combination of a true vaporization in the ordinary sense at the immediate surface with a speedy irreversible process of combination between the molecules in the vapor phase. It is this irreversible process in the vapor that explains why the vapors of red and white phosphorus are nearly, if not quite, identical, although we have every reason to believe that the molecules of solid red and white phosphorus are different.

The failure of black phosphorus to grow at the expense of red points to a similar complicated vaporization process at the surface of black phosphorus. The vapor furnished by the red phosphorus is at a higher pressure than that given off by the black. Failure to grow simply means that the vapor of black phosphorus would not condense on its own surface at the degree of superpressure equal to that given by the vapor of red phosphorus. It would be interesting to see if the reverse condensation of the vapor to black phosphorus could be brought about by any process; it is quite likely that condensation to red would always occur first.

Several experiments were also made to determine the mutual relations of black and red phosphorus in the liquid phase. The experimental difficulties are somewhat greater here than in the previous experiment, because of the high temperature of the melting point, about 610° , and the comparatively high vapor pressure. It is only comparatively recently that glass has been manufactured that will stand the vapor pressure of phosphorus at its triple point, and there is no glass that will stand a much higher temperature. Several attempts were made in the endeavor to avoid this difficulty in one way or another. In the first attempt, black phosphorus was heated to a bright red (perhaps 750°) in water vapor in a steel cylinder at a pressure of 700 kg. The experiment was not regarded as successful because of partial chemical action between the phosphorus and the water vapor. The indications were, however, that the black phosphorus had melted and solidified to red. A second experiment in which pressure was transmitted to the phosphorus by nitrogen compressed to 700 kg. also was not successful, because of distilling of phosphorus to the colder parts of the apparatus and condensing as yellow. It was somewhat of a surprise that the high pressure of the nitrogen did not more effectively prevent condensation. Finally, in order to avoid all chemical action, the phosphorus was placed in exhausted capsules of Jena combustion tubing, which were placed in the steel cylinder and heated in an atmosphere of nitrogen compressed sufficiently to prevent the capsule from exploding under the vapor pressure of the phosphorus within. These experiments were successful, and definitely established several points. In the first place, black phosphorus may be melted at a bright red heat. When cooled,

¹ A. Stock and E. Stamm, *Loc. cit.*

the black phosphorus is found solidified to a glassy mass, of density 2.18, of a chocolate-brown color, identical in appearance with that obtained when red phosphorus is similarly treated. In fact, there is no reason to suppose that the melts of black and red phosphorus are not identical. The minimum pressure of the nitrogen during this run was 150 kg., and it was increased slowly during the heating to a maximum of 400 kg. After the run, the glass capsule was found to have been expanded by the vapor pressure within, in fact, expanded with enough force to stretch a thin steel shell which contained it. The pressure of the vapor must, therefore, be considerably above 150 kg., and is probably in the neighborhood of 300 kg. at a bright red. In a second experiment, red and black phosphorus were placed together in the capsule and heated for about 20 minutes to 620°. The temperature was read with a pyrometer, but there is possibility of error in the exact temperature. The red phosphorus (this was the bright red phosphorus formed as mentioned above at a dull red at 900 kg.) had partially melted and solidified to a chocolate-brown mass. The black phosphorus showed no signs whatever of melting, but had lost its bright metallic luster. There was no trace of condensation of the vapor of the red on the surface of the black. The external pressure in the nitrogen was kept constant for this experiment at 150 kg. The melting point of black phosphorus is therefore probably somewhat higher than that of red. A third experiment was made in the endeavor to heat the phosphorus hot enough to melt the red but not hot enough to melt the black. If the red and the black stand to each other in the relation of unstable and stable solids of the same liquid, then it might be expected that the entire mass of the red would be transformed into black through the liquid. The experiment was unsuccessful, however; both black and red had melted together to the same glassy mass. Evidently, if this experiment is to be successfully performed, the temperature must be capable of more accurate adjustment than was possible with the crude means at hand.

Two experiments made at high pressures may be mentioned also as possibly throwing some light on the problem. The first was an attempt made before the existence of black phosphorus was known. White phosphorus was compressed to 30,000 kg. at room temperature for 15 hours without result. One would almost expect that black phosphorus would have been formed at this high pressure. The second experiment was made unintentionally while determining the freezing curve of ordinary white phosphorus. Successful measurements of the freezing pressure had been made up to 150°, and a run had been begun at 175° with every prospect of success, when the character of the melting changed suddenly from that of a pure liquid to that of a liquid with a dissolved impurity. There was a pronounced rounding of the corners of the curve giving the change of

volume as a function of pressure. The impurity did not increase with time, but stayed constant after it had once formed. This was shown by the fact that the melting curve could be retraced. On examining the phosphorus after the run, it was found of a bright orange color. The effect was in all probability due to the formation of a slight quantity of red phosphorus at the high pressure (5000 kg.) and temperature, which then dissolved in the white phosphorus. It has been many times suggested that the varieties of red phosphorus formed at low temperatures, as Schenck's, for example, are really solutions of one modification in the other, but this is apparently the first direct proof that such a combination of the two varieties really has the properties of a true solution, giving a depressed freezing point. The effect was not found on repeating the experiment, but sharp melting curves were found up to 200° . If the effect were due to dissolved kerosene, it would have been found on repeating the experiment. Probably some small accidental impurity acted as a catalyzer during the first run. It is well known that there are a number of catalyzers for the reaction from white to red phosphorus at low temperatures.

Finally, in the light of these experiments, some speculation may be allowed as to the probable nature of the phosphorus modifications. The problem of white phosphorus II need not concern us here, for this changes into I by a reversible process, and presents no greater difficulties (which are nevertheless great enough) than any polymorphic transformation. The problem of the nature of red phosphorus has chiefly engaged attention hitherto. The most striking fact is that the density of red phosphorus varies according to the temperature of formation. With the exception of Hittorf's crystallized variety, it is obvious that red phosphorus is not a single well defined substance. This has led Cohen and Olie¹ to suggest that ordinary red phosphorus is a mixture of white and Hittorf's phosphorus in dynamic equilibrium, the equilibrium ratio of the two components changing with temperature. The objection to this is that a dense phosphorus formed at a high temperature does not assume the appropriate lower density when maintained indefinitely at a lower temperature. The explanation suggested by the above experiments is that red phosphorus is a transformation product from white phosphorus to something else, in which the transformation has not run to completion, but is prevented by friction. The distinction between frictional and viscous resistance should be kept in mind; viscous resistance gradually decreases with time, but a true frictional resistance never falls below a certain limiting value. That there should be a true frictional resistance to the reaction from one solid to another is not surprising, and is, moreover, something which has been most strongly suggested by other experiments

¹ E. Cohen and J. Olie, *Z. phys. Chem.*, **71**, 1-27 (1910).

on polymorphic transformations between solids at high pressures. I hope to make this the subject of a special paper.

That there is a frictional resistance is also consistent with the remarkable manner of change of white to red phosphorus. If the change from white to red took place by the growth of a surface of separation with a definite velocity, as during the formation of many crystals, then the hypothesis of an incomplete transition would not be tenable. But apparently the change from white to red does not take place in this manner; it has been carefully observed microscopically a number of times,¹ and nothing of the nature of the growth of a surface of separation has ever been detected. The method of transition seems rather to be by the formation of microscopic or sub-microscopic nuclei, which do not grow appreciably in size, although some sort of change whose nature has not been determined does go on within the nuclei. More complete transition from white to red phosphorus means the existence of a greater number of nuclei, not an increase in size of the individuals. If the mechanism of transition is by the formation of nuclei, which do not grow, it is at least conceivable that there should be a frictional resistance as the space occupied by the nuclei becomes greater and they come to interfere more and more with each other. The effect of increasing temperature is to decrease the frictional resistance to transformation so that the reaction can proceed further.

The existence of a frictional resistance to transformation makes understandable the different densities of red phosphorus formed at different temperatures, it shows why we are not to expect a reverse change of density on cooling to a lower temperature, it explains why the solution of red phosphorus in white at the freezing determination at 5000 kg. and the low temperature of 175° was so dilute and did not grow in strength, and it explains why red phosphorus does not show a sharp melting point as would be expected if it were a single pure substance, but instead melts over an interval like a solution.²

The transformation, of which red phosphorus is a part way product, may well be a combination of two simpler transformations. It seems very reasonable to suppose that the suggestion of Wahl³ is valid; namely, that in ordinary red phosphorus we have a mixture of amorphous glassy red phosphorus with crystalline grains. The crystallization of the glass is prevented by friction, and as the temperature rises, a larger part of the glass crystallizes, so that the density is higher as the temperature of formation is higher. But it is questionable whether all the change of density can be explained in this way; Schenck's red phosphorus has a density of 2.05, whereas a glass formed in an experiment above by rapid cooling

¹ H. Siedentopf, *Ber.*, **43**, 692-694 (1910).

² A. Stock and E. Stamm, *Loc. cit.*

³ W. A. Wahl, *Oef. Fin. Vet. Soc. Förh.*, **54**, No. 9 (1911-1912).

has a density of 2.18. It is very probable that in addition to the effect of Wahl, we must regard the glass itself as in a varying state of transformation.

The problem of the phenomena of vaporization is a complicated one, and one which we do not particularly need to consider in this connection. It has been suggested that we probably have to do here with an irreversible reaction in the vapor phase.

With regard to the relation between black and red phosphorus we can offer only conjectures. It does seem pretty certain, however, that red and black cannot stand in the relation of ordinary monotropic solids. If they did bear this relation, the black must be the more stable form, because of its lower vapor pressure, and in this case we cannot understand the failure of the red to condense as black out of its vapor. The fact that the black apparently melts to the same liquid as the red is puzzling. It may be that the relations here are the same as in the vapor phase; that is, liquid black phosphorus may be unstable, and may transform itself irreversibly to liquid red as rapidly as it is formed.

Summary.

Two new modifications of phosphorus have been found. The first is a new modification of ordinary white phosphorus, possibly hexagonal, with a reversible transition point at atmospheric pressure at about -76.9° . The second modification, black phosphorus, is obtained irreversibly from white phosphorus at 12,000 kg. and 200° . A number of its physical constants have been determined; particularly striking are its high density, 2.691, and fair electrical conductivity. No attempt to transform either white or red to black phosphorus has been successful by any other method except that above. Finally, some conjectural explanations of the relations of the various modifications have been given.

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No. 238.]

THE DISSOCIATION PRESSURES OF AMMONIUM- AND TETRAMETHYLAMMONIUM HALIDES AND OF PHOSPHONIUM IODIDE AND PHOS- PHORUS PENTACHLORIDE.

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Received May 8, 1914.

The dissociation pressures of the chloride, bromide, and iodide of ammonium and of phosphonium iodide have previously been measured. The methods used, and the results obtained are discussed below. The dissociation pressures of the chloride and iodide of tetramethylammonium,