

altogether. If we make the substitution  $\lambda' = \lambda + \lambda_0$  in Eq. (3), we obtain a new determinantal equation, the solutions of which are each greater by  $\lambda_0$  than the corresponding ones of the original equation. In addition, we note that each  $a_{ii}$  has been increased by an amount  $I_i \lambda_0$ . In principle then, we can always eliminate the necessity for "negative" springs by making  $\lambda_0$  sufficiently large. If the secular equation being solved has one or more zero roots (translation or rotation), the machine will also display modes of motion of zero frequency with the result that it has no stable equilibrium position. This difficulty may be overcome by the use of the substitution just described, which increases all the frequencies. It might also be mentioned here that the usual transformations which leave the value of a determinant unchanged or multiply it by a number, such as multiplying a given row and a given column by a number or adding rows and columns, may often be applied to Eq. (3) to give a determinant which is more convenient to set up on the machine.

The normal frequencies of this machine range from one to ten cycles per second, so that it is a simple matter to observe the amplitudes and phase relationships of the motions of the various units when the machine is in resonance, and thus to obtain the normal mode of vibration corresponding to each frequency.

#### ACCURACY

The five unit instrument at present in use has been tested in a number of ways. The quantitative results, except in especially unfavorable circumstances, have been within about one percent of the calculated values. One series of tests was made in which the symmetrical motions of formaldehyde were studied and these showed that even in such simple applications the labor using the mechanical method was less than that required to solve the problem analytically.

## Phosphorus at High Temperatures and Pressures

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(Received September 20, 1937)

A detailed study of the transformations of the element phosphorus has been carried out at high hydrostatic pressures and at elevated temperatures. This has resulted in the discovery of a new modification of phosphorus, which is noncrystalline in structure and black in color. Its properties have been investigated to a certain extent. Some new calorimetric data are described which shed light on the question of the relative thermodynamic stabilities of this and the other forms of phosphorus.

#### INTRODUCTION

BLACK phosphorus is formed from white phosphorus by an *irreversible* transition at a pressure of approximately 12,000 atmospheres, and at a temperature of about 200°C. The manner in which this transition progresses with time is most unusual, and it has been studied somewhat in detail by Bridgman.<sup>1 2</sup> He found the rate of transformation to be not at all regular; it possessed neither uniform acceleration nor exponential characteristics. On the contrary, the process starts out quite slowly, and acceleration is almost imperceptible for about ten or fifteen minutes. At this time there is extremely rapid acceleration, and the transition from white to black phosphorus goes to completion with almost explosive characteristics. During this last part of the reaction more than 90 percent of the total volume change takes place. This fact could be taken as evidence supporting the interpretation of the first slow stage of the reaction as one in which nuclei of the new crystal type are being formed preparatory for the final rapid crystal growth. If this were the case, white phosphorus intermixed with finely powdered black phosphorus would probably transform completely into black phosphorus without the usual preliminary period. However, experiments by Bridgman<sup>3</sup> along these lines have shown this not to be the case. Hence, doubt was cast upon the "nuclei formation" hypothesis, and the whole problem invited further consideration.

New experiments by this author soon pointed to the possible existence of an entirely different type of "black phosphorus" which was responsible for the aforementioned "slow stage" of the transformation. Identification of the new form was carried out first by picnometric and x-ray diffraction methods, and later by measurements of its heat of reaction with bromine. This heat of reaction was sufficiently different from that of the usual type of black phosphorus to establish definitely the identity of a new form.

The question of the relative stabilities of these two forms then naturally arose, and along with it the still unsettled question as to the relative stabilities of red and black phosphorus. Further calorimetric experiments were carried out for information which might settle these points. This data supplemented by other known data on vapor pressure and specific heats served to confirm Bridgman's original hypothesis that black phosphorus was the most stable form of phosphorus at room temperature and atmospheric pressure. And in turn, the new type of black phosphorus from all lines of available evidence appears *less* stable than the original type of black phosphorus.

#### EVIDENCE FOR A NEW FORM OF BLACK PHOSPHORUS

First of all, a series of experiments at high pressures was undertaken in an effort to gain some information concerning the nature of the process which is responsible for the almost stationary period of about twelve minutes which invariably had preceded the final rapid change into black phosphorus. It is emphasized that during this part of the transformation there is a

\* This work done while author was a National Research Fellow.

<sup>1</sup> P. W. Bridgman, *J. Am. Chem. Soc.* **36**, 1344 (1914).

<sup>2</sup> P. W. Bridgman, *J. Am. Chem. Soc.* **38**, 609 (1916).

<sup>3</sup> P. W. Bridgman, *The Physics of High Pressures* (G. Bell and Sons, Ltd., London, 1931), p. 384.

small but unmistakable change in volume. This itself could be used roughly as an indicator of the progress of the reaction, and an attempt could be made to interrupt the same at any desired time before its completion.

The white phosphorus was placed under pressure in a small cylinder provided with a heating coil and thermocouple. To avoid contact between the active white phosphorus and the steel cylinder wall, the former was enclosed in a thin lead capsule. After the pressure was adjusted to a desired value, the temperature was raised. The reaction would now begin, and when it had progressed any desired amount, the pressure was suddenly reduced to about half its highest value, in an effort to check further progress. A complete reduction in pressure was avoided since it would allow any untransformed white phosphorus to pass over into a liquid phase, whence, at the existing temperature, it would immediately be changed into red phosphorus. The reduction to half-pressure would, at least, suffice to keep the phosphorus always in the solid state, and hence eliminate this hazard. And it was reasonable to expect that a partial reduction in pressure of this nature would be sufficient to stop further progress of the transition immediately. The temperature could then be reduced to that of the room, the remaining pressure released, and the sample removed for inspection.

Six runs of this type were made. The pressure in each was about 13,000 atmospheres, and the temperature approximately 205°C. The samples were identical as to source of material, size, shape, etc. The only difference in the individual procedures was in the elapsed time allowed from the attainment of reaction conditions to the first reduction in pressure. This time was varied for the individual samples in steps of about two minutes each, so as to space them evenly over the fifteen minute period. After cooling, the samples were removed from the press and washed with CS<sub>2</sub>, which served to dissolve out any untransformed white phosphorus. Upon examination each sample was found to contain a carbon-like powder residue. The amount of this bore a direct correlation to the length of time the reaction had been allowed to progress. A visual inspection suggested that this residue was not the usual crystalline black phosphorus, which is quite

similar to graphite in appearance, whereas this substance was definitely more "sooty" or carbon-like. A density determination (flotation method) gave the value 2.25 which is quite far from that of Bridgman's black phosphorus which has a density of 2.69.

As a further test for the identity of this lower density black phosphorus, x-ray diffraction pictures were used. A number of these were taken employing the usual Debye-Scherrer type of powder camera and a copper target x-ray tube. Under these conditions, Bridgman's black phosphorus gives sharp lines belonging to an orthorhombic type of crystal structure.<sup>4</sup> However, under no circumstance whatsoever, would the new black phosphorus give diffraction lines. This would clearly indicate that either the new form is an amorphous material, or that it is microcrystalline in structure.

In case the latter proved to be the correct interpretation, it would still be impossible to say whether or not the microcrystals were, except for size, identical with Bridgman's black phosphorus. If they were, there should be only at most a very small difference in the heat content of the two forms. Values for the difference in the thermodynamic total heats could be obtained by means of a calorimetric measurement of the heats of reaction of these forms of phosphorus in some reaction which would lead to the same end product for each. Measurements of this nature were taken and are completely described in a later part of this paper. What is important at this point is the fact that a difference of over 14 kilojoules per gram-atom was found between the heat contents of the two forms. The experimental error could not account for more than 5 percent of this difference.

These measurements, then, seem to give conclusive evidence for a new form of black phosphorus, which is noncrystalline, at least as far as x-ray patterns go, and which is definitely not the same polymorphic form ordinarily called black phosphorus.

#### TIME-PRESSURE-TEMPERATURE RELATIONS

The existence of this new form of phosphorus complicated the problem as a whole. Accordingly

<sup>4</sup> R. Hultgren, N. S. Gingrich, B. E. Warren, J. Chem. Phys. 3, 992 (1935).

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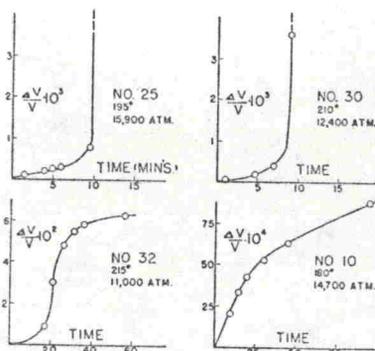


FIG. 1. Progress of transitions. These curves show the extent of the transition ( $\Delta v/v$ ) versus time. The upper curves are typical for transitions leading to black crystalline phosphorus, the lower for transitions leading to noncrystalline black.

some new experiments were tried in an effort to isolate transitions which would involve only one type of black phosphorus. The method used was perfectly straightforward. White phosphorus was subjected to a wide variation of temperatures and pressures in a rather extended series of experiments. In each case the progress of the reaction was plotted against time: i.e., in Fig. 1,  $\Delta v/v$  vs. time. As a further check on what the transition actually involved, the phosphorus was examined in each case for structure and density, immediately after removal from the apparatus. A direct correlation between these properties and the rate of reaction curve was soon made evident. It will be noticed that in this same figure the upper curves are pretty much alike in having a steep vertical section which indicates a final rapid conclusion to the transition. The lower curves are different; they slope off toward the horizontal after a considerable lapse of time, indicating a slow exponential termination of the reaction.

The correlation referred to then is that the lower type of curve leads invariably to the formation of black noncrystalline phosphorus alone. On the other hand, the upper type of curve consistently leads to the crystalline form. Hence it could be said that a complete isolation of the reaction of the white phosphorus to noncrystalline black is possible if temperature and pressure are correct. Whether or not the transition could be made to go from white phosphorus directly into crystalline black was still uncertain, since

there was no way of knowing if the formation of noncrystalline black was a necessary part of this reaction. Aside from this point there was still the question of a new P-T diagram which would include noncrystalline phosphorus. Accordingly, the P-T region was systematically covered by a series of some forty odd experiments. These were designed to give pertinent information both for a revised diagram and for settling the question of a possible complete isolation of the black crystalline reaction.

In this series of runs, certain pressures were chosen (from 11,000 to 16,000 atmos.), and the effect of a variation in temperature at each was noted. In order to get accurate timing of the transition speed, the experimental procedure was somewhat modified from that previously described. The difficulty, of course, had been that the temperature rise is, of necessity, slow, and consequently the transition will start before the maximum temperature for that run is attained. To raise the temperature first and then apply pressure is completely disastrous, since this procedure will first melt the white phosphorus and consequently will allow it to pass over into red phosphorus. To circumvent both of these failings, a pressure of about 7000 atmos. was first applied, and then the temperature was raised to its final value. Under these conditions the phosphorus remains in the solid state as white phosphorus. Any time after this, the final pressure may be quickly applied (in a few seconds time), and the progress of the transition observed from that point on. Using this procedure one has an accurate knowledge of what happens from the instant that experimental conditions are attained, and the issue is not confused by the transition starting at some unknown time.

In Fig. 2 the results of some representative experiments are plotted. These curves show the time for the "complete" reaction plotted against temperature. It is emphasized that time here is recorded from the instant attainment of final pressure to the observation of the "collapse in volume" which is indicative of the completion of the transition into black crystalline phosphorus. Most noteworthy of the features of these curves is that apparently for every pressure at which the transition can be made to take place it can be made to do so instantaneously providing the

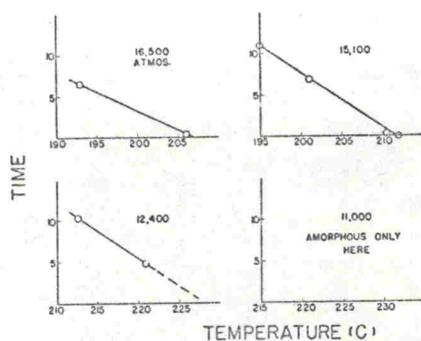


FIG. 2. Reaction times. Time for transitions to black crystalline phosphorus against temperature for several different pressures. At sufficiently high temperatures, the curves always cross the origin of the time axis.

temperature is sufficiently high. A second important feature is that in these experiments it was found that, if there was no collapse in volume in a time of about ten or fifteen minutes, the transition would not result in the formation of black crystalline phosphorus at all, but would continue as a simple reaction into black noncrystalline phosphorus.

On the basis of these observations the data could be plotted on a P-T diagram as has been done in Fig. 3. Here three regions are apparent. Points lying in region (3) indicate that at the corresponding temperature and pressure, there is an instantaneous reaction. In region (2) the transition is accompanied by a preliminary period. While, finally, in region (1), only the transition to black noncrystalline phosphorus is possible.

The existence of this "instantaneous" reaction is new. The fact that it does exist clears up to a certain extent the mystery which previously had been ascribed to the "delayed" transition. However, it would still be impossible to say that the transition to black crystalline phosphorus had not been accompanied by a partial transition to black noncrystalline just as in the former cases. The higher temperature could account for a general acceleration of both reactions so as to make them indistinguishable. Just what part the transition to noncrystalline black played in cases coming in region (2) likewise was not clear. Two suggestions are almost self-evident. The first is that the transition goes from white phosphorus

to black noncrystalline to black crystalline. The second is that the heat of formation given off when black noncrystalline phosphorus is formed at a temperature and pressure at which it alone could be formed, is sufficient to heat up the remaining untransformed white phosphorus to a temperature sufficiently high to enable it to transform into the black crystalline form.

The first suggestion was tested quite simply by preparing a sample of pure black noncrystalline phosphorus, and subjecting it to an elevated temperature and pressure to see if it would transform into the black crystalline form. In this experiment, it was taken to a pressure of 15,000 atmospheres and to a temperature of 300°C without a change of form. This, then, definitely ruled out the suggestion of a two-step reaction: phosphorus does *not* go from white to black noncrystalline, to black crystalline. The question now asked was this: Would the amount of heat generated by a fractional part of the phosphorus going over into the noncrystalline black form be sufficient to raise the temperature of the entire mass any appreciable degree? This could be answered decidedly in the affirmative, with the aid of the heat content differences given in the next section of this paper. For instance, a one-percent conversion into the noncrystalline form would account for a temperature rise of 26° throughout the entire mass, if the conditions were adiabatic.

As a further test along these lines experiments were tried under a number of different conditions in regard to thermal isolation of the phosphorus sample. For this purpose a number of odd shaped lead containers were prepared for the phosphorus.

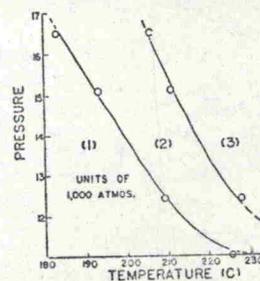


FIG. 3. P-T diagram of phosphorus. Region (3) indicates an "instantaneous" transition to black crystalline phosphorus, region (2) a delayed transition, and region (1) transitions only to noncrystalline phosphorus.

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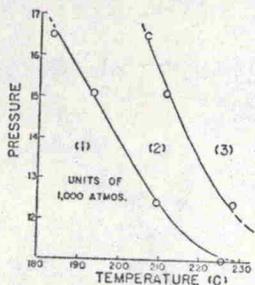


FIG. 3. P-T diagram of phosphorus. Region (3) indicates an "instantaneous" transition to black crystalline phosphorus, region (2) a delayed transition, and region (1) transitions only to noncrystalline phosphorus.

These are shown in Fig. 4. The normal type of container is the simple lead cylinder closed at both ends which is shown mounted in place in the high pressure steel cylinder in the upper part of Fig. 4. The blackened portions in all cases represent the lead, the dotted portions the phosphorus. Container (6) was designed to give the highest degree of thermal isolation since it is lined with soapstone. The general conclusion arrived at from the use of these containers was that the heat conductivity from the phosphorus to the steel wall played a very important part in the transitions. For instance, using containers of the type (1), one would have a condition in which all of the phosphorus was near the metallic outer wall, and hence the thermal isolation would be very poor. And, indeed, it was found with this type of container that at 14,000 atmospheres the transition temperature was 10° higher than with the ordinary simple container. The explanation would apparently be that all of the phosphorus is quite near the outer wall and consequently cannot easily acquire a temperature much higher than it. Consequently heat developed by a partial transition to black noncrystalline phosphorus does not serve to heat the phosphorus to a considerable extent but simply passes off into the steel cylinder. An opposite but smaller effect was found with container number (6), which afforded the highest degree of thermal isolation. It was further revealed in its use that it produced the most perfect specimen of black phosphorus that the author has ever seen. The crystals were large and grew out to the very edge of the container. Usually the phosphorus is pure only in the center of the specimen, and as one examines the edges he finds increasing amounts of the different polymorphic forms (red, etc.) there.

Containers (4) and (5) provided a thermal gradient along the axis of the sample due to the conical shaped lead center part. They produced nothing new or startling, but simply gave in an axial direction the kind of results which had previously been observed when the gradient was all radial. Several containers of the type (3) were used to see if growth from a central nucleus could be observed. By this one means growth of crystals in a manner whereby a crystal starts somewhere and grows rapidly at the expense of the material in the surrounding regions. The idea

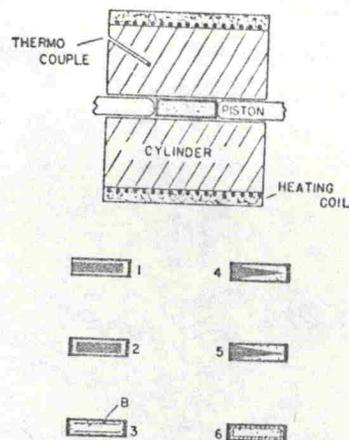


FIG. 4. Types of lead containers. The upper diagram shows the pressure cylinder with a simple type of lead container for the phosphorus. The lower diagrams show various types of containers used to give different degrees of thermal isolation of the phosphorus.

of container (3) then was to impair this type of growth by the imposition of the artificial metallic barrier (B). At the same time the barrier would be sufficiently light so as not to materially effect the thermal conditions within the lead capsule. In no case of this kind was there any observable effect due to this type of barrier. Likewise, all attempts to ascertain a preferred orientation of crystals in these experiments were without success. Hence, it was concluded that the crystalline growth was not much dependent upon "seed crystals," but that the important factor in the whole question was temperature.

The general conclusions of this section are that there is no transition from black noncrystalline phosphorus in the ordinary experiment.<sup>5</sup> The part that black noncrystalline *does* play is to furnish heat when it is formed in quantities sufficient to raise the temperature of all of the phosphorus sufficiently high to enable a transition to black crystalline phosphorus to take place. As a result of this connection between the two forms of black phosphorus it is impossible to give accurately the regions in a P-T plot in which

<sup>5</sup> It has already been mentioned that this transition will not occur at 14,000 atmospheres and 300°C which is undoubtedly a higher temperature than is usually reached during a transition with the outer cylinder at 200°C. In another experiment, employing an internal furnace this transition was made to run at 12,000 atmospheres at temperature of 500°±50°.

the one or the other is formed. There will always be a region like region (2) in Fig. 3. And, finally, the degree of thermal isolation is important in the experiment since the transition temperature is a function of it.

#### RELATIONS OF THE VARIOUS POLYMORPHIC FORMS

This section is concerned with the measurement of the differences in the total heats between the various forms of phosphorus. They were obtained from the heats of reaction of the different kinds of phosphorus with bromine. The purpose of such measurements was twofold. In the first place, the large difference in heat content between the two forms of black phosphorus has already been mentioned as serving as partial evidence favoring the identity of black noncrystalline as a separate polymorphic form. The second purpose of the measurements was for a further attack on the now time-honored problem<sup>6-11</sup> of the relative stabilities of black and red phosphorus. A description of the experimental procedure follows:

A special balanced null method calorimeter was built for the measurement of the heats of reaction for the different samples of phosphorus. It was composed of two identical calorimeters immersed in the same constant temperature bath (constancy of 0.01°). The heat capacities were adjustable by simple addition or removal of water. For these experiments they were made equal to about 1 kg water equivalent. A ten junction copper-constantan thermopile of about 15 ohms resistance ran between the two calorimeters, giving a sensitivity with the galvanometer used of 3900 millimeters per degree. With this sensitivity and heat capacity the calorimeter was accurate to about one-tenth of a calorie in one hundred calories, and its constancy with time sufficiently reliable so as not to impair the above figure for accuracy if the heat was added over a period of as long as two hours. The method of

<sup>6</sup> A. Smits and S. C. Bokhorst, Proc. Amst. Acad. 17, 962 (1915).

<sup>7</sup> A. Smits, G. Meyer and R. Ph. Beck, Proc. Amst. Acad. 18, 992 (1915).

<sup>8</sup> A. Smits and S. C. Bokhorst, Zeits. f. physik. Chemie 91, 3, 249 (1916).

<sup>9</sup> A. Smits, Comptes rendus 26, Nov. (1928).

<sup>10</sup> A. Smits, Comptes rendus 28, Jan. (1929).

<sup>11</sup> See reference 1.

using the dual instrument was to always keep the two calorimeter temperatures quite the same by passing an accurately measurable current through a heating coil in the colder of the two until the desired temperature balance was attained. Since the relative heat capacities of the two calorimeters were accurately known, the heat formed by a given reaction could be measured by the current used to balance it in the other. The reaction proper took place in a small glass bulb immersed in the constantly stirred water within the calorimeter, the glass bulb being connected to the exterior by means of small bore tube sealed to it. The procedure was then as follows: The calorimeters were brought to a constant and equal temperature. A weighed amount of phosphorus was then dropped into the glass bulb of one. The bromine solution had previously been poured in. Heating by means of a current was then started in the other and the temperatures maintained equal until the reaction had run to its final completion (about two hours). Due to the long time involved for the reaction, it was fortunate that the balanced type of calorimeter was used. A second experiment was always run in which the reaction took place in the other calorimeter.

The preparation of the phosphorus for the experiment was as follows: The various samples were powdered and screened through a 100 mesh screen, washed out with CS<sub>2</sub>, dried, shaken with CaCO<sub>3</sub> and water, rinsed in water, washed in dilute HNO<sub>3</sub>, again rinsed, and finally dried for several hours at 75°C. It was then accurately weighed out into samples of nearly 100 mg each. A 30 cc volume of the bromine mixture (6 parts CS<sub>2</sub> to one part Br<sub>2</sub>) was used to provide an ample excess of bromine to insure a complete reaction. Now, there is a heat of solution of PBr<sub>5</sub> in C<sub>2</sub>S and Br<sub>2</sub> varying with the concentrations involved. Hence, in each experiment the same amount of phosphorus was used and likewise the same amount of the bromine solution which was mixed in a large quantity to supply the whole series of experiments. In this manner it was ensured that the heat arising from such a source would in all cases be the same, and for the purpose in hand could accurately be canceled out.

The results of the calorimetric determinations are given in Table I; the heats of reaction here

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given include all heats of solution, etc. which add to the total heat under the experimental conditions as outlined above. By subtracting the heat of solution of any one type of phosphorus from that of another we obtain the difference in heat content  $\Delta H$ .

As far as establishing the identity of black noncrystalline phosphorus is concerned these results seem quite conclusive. The difference in heat content between it and black crystalline phosphorus produced from the identical white stock is about 30 kilojoules per gram atom. Since the probable error of an individual measurement is of the order of  $\frac{1}{2}$  kilojoule per gram atom, the above figure appears to be quite significant.

The difference of 7.2 kilojoules per gram atom between the recent black crystalline phosphorus and that of Bridgman produced in 1914 should be explained. The magnitude of the difference is certainly too great to be accounted for by experimental uncertainty. It is, however, reasonably accounted for if one assumes that Bridgman's phosphorus was not uniform in a polymorphic sense, i.e., that it contained several polymorphic forms. In this connection it has already been mentioned that a thermal gradient generally exists in a phosphorus sample during the time that it is undergoing its polymorphic transformation. It has likewise been shown that the hotter (inner) portions will favor a transformation to black crystalline phosphorus, whereas

the outer, cooler portions will probably go to a large extent into noncrystalline phosphorus. This phenomenon was especially pronounced in the experiments in which the gradients were purposely made large. Now, in selecting the samples for the calorimetric work, there was only a limited supply of the 1914 phosphorus, and consequently it was taken pretty much as it came. (Presumably it was not pure black crystalline.) In the case of the recent phosphorus the supply was large and the selection of the samples could be made with considerable care. This undoubtedly could account for the difference observed in the heat content values. The question might be asked, if the presence of the less dense noncrystalline form might not be detected due to the lowering of the density of the whole mass which it produces. Unfortunately it cannot, where the flotation method of density determination must be used, since it will give the density of the more dense (pure) particles only.

The last problem concerns the relative thermodynamic stabilities of the various forms. First consider the case of red and of black crystalline. Bridgman<sup>15</sup> first worked on this employing the method of specific heats, but finding this not

<sup>12</sup> Ogir, Comptes rendus 92, 83 (1881).

<sup>13</sup> H. C. Duss, Thesis 1924, Mallinckrodt Laboratory, Harvard University.

<sup>14</sup> P. W. Bridgman, Phys. Rev. 45, 844 (1934).

<sup>15</sup> See reference 1.

TABLE I. Heats of reaction of different types of phosphorus with bromine.

TYPE OF PHOSPHORUS	HEAT OF REACTION (H)	AVERAGE (H)	DIFFERENCE $\Delta H$
(1) Black Crystalline (Recent)	152.2 kilojoules gram-atom	153.2	7.2 kilojoules gram-atom
	154.1 "		
(2) Black Crystalline (Bridgman's 1914)	161.2 "	160.4	16.4 "
	159.7 "		
(3) Commercial Red	177.2 "	176.8	1.1 "
	176.5 "		
(4) Laboratory Red*	177.8 "	177.9	6.6 "
	178.0 "		
(5) Black Noncrystalline	184.0 "	184.5	64.5 "
	185.0 "		
(6) White	See references 12 and 13.	249.0	

\* This phosphorus produced under nitrogen pressure of 6000 atmospheres and at a temperature of 300°C. These conditions maintained for 6 hours.

TABLE II. Vapor pressures of phosphorus.

TEMPERATURE	VAPOR PRESSURE Black	(cm of Hg) Red
357.1°C	2.3	5.2
443.7°C	—	73.2
445.2°C	58.5	—

sufficiently sensitive turned to vapor pressures. On the basis of these measurements he found black phosphorus to be the more stable form since its vapor pressure was the lower. Bridgman's results are given in Table II.

These results are very definite in attributing a lower vapor pressure to black phosphorus at both temperatures, and hence in pronouncing it the more stable form of phosphorus.

The results of Smits<sup>16</sup> and his colleagues are given in Table III.

It will be noticed that below 560° black phosphorus has a lower vapor pressure, and above that red has the lower. Ordinarily we would take this to indicate that black was the stable form below 560° and red above. However, Smits regards this as an extremely unlikely situation, and points to an apparent metastability of black phosphorus below 560° as a solution of the problem. Among other evidence in favor of this he gives the experimental observation that he has made to the effect that the vapor pressure below 560° is not constant for black phosphorus but apparently increases with time, this indicating a disturbed condition of "inner equilibrium" in the solid phase of the black phosphorus. As further evidence in favor of this interpretation Smits cites the fact that he has found the triple-point of black phosphorus to be slightly lower than that of red.

Now, since the temperature ranges covered by the observations of Bridgman and Smits do not overlap, there is no actual conflict in the experimental data. However, their conclusions are in direct contradiction.

Since one can obtain from vapor pressure data of this type, a value for the difference in the heat contents between the two forms of phosphorus, it is possible to compare this vapor pressure data with my calorimetric results. The thermodynamic equation,

<sup>16</sup> See reference 7.

TABLE III. Vapor pressure of phosphorus.

TEMPERATURE	VAPOR PRESSURE (in atmospheres)	
	Black	Red
515°C	8.5 (increasing)	10.5
553°	19.3	21.5
567°	28.6 (constant)	28.5
578°	39.5	35.0

$$\frac{d(\log p)}{d(1/T)} \cdot R = H_v \text{ (Heat of Vaporization)}$$

gives the heat of vaporization from the vapor pressure curve. Now, if one obtains in this manner the heats of vaporization at a certain temperature for the two kinds of phosphorus under discussion, and subtracts one from another, the result will be equal to the difference in heat contents. These, then, may be compared with the values in Table I.

In Fig. 5 the author has plotted the data of Smits and of Bridgman. The points from the data of the latter are connected by dashed lines. The solid lines attempt to connect points given by both. The failure of the curves to continue as straight lines in the region of 560° is a bit distressing, and may have some significance as Smits has indicated. In the lower temperature regions the curves do approximate straight lines. Only in this region can the slopes of the two lines be determined with any accuracy. The change in slope of the lines in the region of 560° is far too

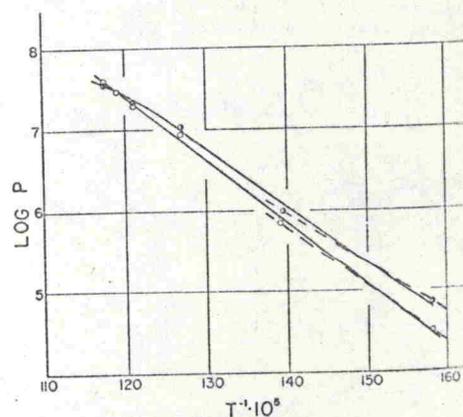


FIG. 5. Vapor-pressure vs. 1/temperature. The lower curve is for black crystalline, the upper for red. Points connected by dashed lines are Bridgman's, the others are Smits'.

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gives the heat of vaporization from the vapor pressure curve. Now, if one obtains in the same manner the heats of vaporization at a certain temperature for the two kinds of phosphorus under discussion, and subtracts one from another, the result will be equal to the difference in heat contents. These, then, may be compared with the values in Table I.

In Fig. 5 the author has plotted the data of Smits and of Bridgman. The points from the data of the latter are connected by dashed lines. The solid lines attempt to connect points given by both. The failure of the curves to continue as straight lines in the region of 560° is a bit distressing, and may have some significance as Smits has indicated. In the lower temperature regions the curves do approximate straight lines. Only in this region can the slopes of the two lines be determined with any accuracy. The change in slope of the lines in the region of 560° is far too

rapid for accurate measurement, and a slight experimental error in a vapor pressure measurement would be greatly magnified in a calculation of a heat of vaporization. Consequently the only check with the calorimetric data<sup>18</sup> which would have any meaning is in the neighborhood of 560°C. Here Bridgman's data give a value of 19.1 kilojoules per gram atom as the difference in total heats between black (1914) and red phosphorus. This compares favorably with the value of 17.5 which one obtains from Table I. Apparently, this agreement would tend to support the validity of the vapor pressure data for black phosphorus below 560°. At the same time, it would cast some doubt on Smits' hypothesis of the metastability of black phosphorus in this region. This follows from the fact that Smits has placed emphasis on the fact that the data for black phosphorus below 560°C is not good since constant values cannot be obtained. The tendency, he says, is always toward an increase, and presumably toward a value higher than that of red phosphorus. Were this the case, there would be no agreement with the calorimetric values like

<sup>18</sup> This comparison of calorimetric data at 20°C with vapor pressure data at 350°C is only justified by the fact that there is no measurable difference in the specific heats of black and of red phosphorus.

that indicated above, since the data for the black phosphorus would admittedly be incorrect.

As a consequence, it seems reasonable to conclude, that black phosphorus below 560°C is the stable form of phosphorus.

Now, glancing again at Table I, one is confronted with a progression of this nature: black, red, white. This is the order of the stabilities, the order of the total heats, and the order of the densities. As far as density and total heats are concerned, black amorphous phosphorus belongs between red phosphorus and white phosphorus. One is tempted to argue by analogy and place black amorphous phosphorus there also in order of stability. Of course, there is no thermodynamical justification for so doing. Quite by accident, however, it was discovered that after prolonged heating at about 125°C black amorphous phosphorus could be transformed into a brilliant violet form of phosphorus, this of course, being a form of red phosphorus. Naturally, now one could positively say that at least at 125°C red was more stable than black amorphous, and this would in turn place black crystalline above black amorphous in order of stability.

In conclusion, the author gratefully acknowledges the help he has received on this problem from Professor Bridgman.

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## An Electron Diffraction Study of the Grain Boundaries in Iron

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Grain boundary membranes, left after the dissolution of iron in ammonium persulphate solution, were studied by means of electron diffraction to determine whether crystalline materials are present in the membranes, and if present to identify the crystals. Samples of untreated and heat-treated transformer iron, and heat-treated electrodeposited iron were used. It was found that heat-treated electrodeposited iron left residues which were suitable for study by electron diffraction when supported by Resoglaz backing films. From the electron diffraction patterns obtained, identification was made of the presence of  $\text{Fe}_3\text{C}$  and of  $\alpha\text{FeOOH}$ . It is suggested that the  $\alpha\text{FeOOH}$  did not exist originally in the grain boundaries, but may have been formed by some chemical reaction either between iron and ammonium persulphate, or between some grain boundary constituent such as an iron oxide and the persulphate solution. The method of studying grain boundary materials does not afford a complete analysis, but it is believed that it makes possible important contributions since the presence of crystalline materials in the residues may be detected.

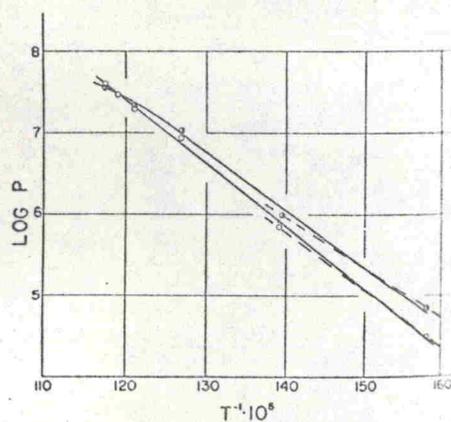


FIG. 5. Vapor-pressure vs.  $1/T$ . The lower curve is for black crystalline, the upper for red. Points connected by dashed lines are Bridgman's, the others are Smits'.