The percentage of water remaining unfrozen corresponds to the empirical formula $Fe_2O_3.4.25H_2O$.

In view of the results obtained above, which show quite definitely that considerable amounts of water can be frozen from colloidal precipitates after all water in its usual free condition has been removed, it is necessary to correct the conclusions which were drawn by one of us[1] (Foote) regarding the condition of water in hydrogels. A method was developed in the work referred to which showed the point where free water was just removed, and the water remaining was considered to be in solid solution. It is evident, however, that after free water is removed, it will be followed by capillary water, with its lower vapor pressure corresponding to lower freezing point, so that the method is one for determining the amount of combined and capillary water in a hydrogel instead of water in solid solution. For this purpose, the method probably gives more reliable data than any other. The results of the two methods are, however, not strictly comparable, the main reason being that the dilatometer method includes part of the capillary water in the free water, as previously explained, so that the "apparent capillary water" found is less than the capillary water which really exists.

We are indebted to Prof. W. G. Mixter of this laboratory for suggesting the use of lampblack and water in our work.

Work on the freezing of colloids is being continued in this laboratory.

NEW HAVEN, CONN.

[CONTRIBUTION FROM THE JEFFERSON PHYSICAL LABORATORY OF HARVARD UNIVERSITY.]

FURTHER NOTE ON BLACK PHOSPHORUS.

BY P. W. BRIDGMAN.

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In a previous number of THIS JOURNAL[2] I have described a new black modification of phosphorus. It was produced by heating white phosphorus to 200° under a pressure of 12000 kg. or more; attempts to form it by other methods failed. Professor A. Smits, of Amsterdam, who had made such exhaustive studies of the relations between white and red phosphorus, has interested himself in the subject and has made measurements of the vapor pressure of black phosphorus. He has suggested in correspondence that it would be of interest to find the effect of high pressures on red phosphorus in the presence of iodine as a catalyzer. The purpose of this note is to describe this experiment and several others dealing with the same subject—the possibility of changing red to black phosphorus.

"Red" phosphorus is known not to be a definite substance, but varies

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[1] THIS JOURNAL, 30, 1388 (1908); 31, 1020 (1909).

[2] *Ibid.*, 36, 1344 (1914).

greatly in appearance and density according to the method of preparation. The varieties close to the upper limits of density are violet in appearance, and are called by Smits "violet" phosphorus. At a definite temperature there is a definite constitution at which violet phosphorus is in internal equilibrium; in this sense violet phosphorus is a definite substance. In the following experiments, two varieties of red phosphorus are to be distinguished; a bright brick red variety formed by heating white phosphorus to a red heat at a pressure of 500 kg. in an atmosphere of nitrogen, and a sample of violet phosphorus, probably much the same as the violet phosphorus of Smits.

The violet phosphorus was made by heating white phosphorus under pressure in the presence of sodium. I discovered quite by accident that metallic sodium is a very efficient catalyzer of the transition from white to violet. The white phosphorus, with a trace of sodium, was subjected to a pressure of 4000 kg. at room temperature, and then heated at constant volume to 200°. The rise of pressure during the rise of temperature was abnormally low, only 500 kg. At 200°, pressure was raised to 12500 kg. for 20 minutes and then to 130000 kg. for 45 minutes. The expected transition to black phosphorus did not occur. The apparatus was then cooled while under pressure, and pressure released at room temperature. The white phosphorus was found entirely transformed to violet. A small piece of the bright red phosphorus which had been placed originally at the bottom of the mass of white phosphorus was quite unaltered in appearance. There can be no question, as shown by the change of pressure, that the change from white to violet took place during the heating at some temperature below 200°. An interesting point not settled by the experiment is as to whether the change to violet takes place above or below the melting point of white phosphorus; at 4000 kg. the melting temperature is about 150°. The density of this violet phosphorus determined by the suspension method was 2.348. This is quite normal. In view of the method of formation, including cooling under high pressure, it is very probable that the violet phosphorus obtained in this way is in a condition corresponding to internal equilibrium at 200° and 12000 kg. The normal value for the density shows that the internal equilibrium conditions at this pressure and temperature cannot be much different from the equilibrium conditions at atmospheric pressure.

A piece of the violet phosphorus formed in this way, together with a piece of the bright red variety, were then subjected to pressure and temperature in the presence of iodine; this is the experiment suggested by Professor Smits. Pressure was raised to 8000 at 20°, temperature raised to 200° at constant volume, and then pressure raised to 12500 for $5^1/_2$ hours. The cylinder was then cooled and the pressure released. No black phosphorus had been formed. There was no change whatever of the violet in appearance, but the bright red variety was changed to the same violet as the other. Evidently then, the violet modification is the stable form as compared with the red at 200° between 8000 and 12000 kg.

Two additional attempts to change the bright red phosphorus to black in the presence of sodium were without result; pressure was maintained at 12500 for 3 hours on each of these attempts.

Finally, in the attempt to force red phosphorus to change to black, a piece of red was surrounded by white which was raised to 12500 at 200° until the white was transformed to black, in the regular way. I thought that there was a very slight possibility that if the red were impregnated with white in which the change to black were taking place that the red might, in some way, get carried along by the transition, if the change from red to black is indeed a possible one. This experiment was also without result; the red was found unaltered in the midst of a mass of black. No catalyzer was used for this run; the effect of one would have been to transform the white to violet before reaching the region of formation of black.

During this run I took occasion to determine the precise rate at which white is transformed to black. The results were the same as I have observed qualitatively on every previous occasion; I never happened to make numerical measurements before. After pressure has been raised to something over 12000 at 200° the black phosphorus is never produced instantaneously. There is always a period of preparation extending over from 10 to 30 minutes, during which pressure drops slowly, increasing gradually in speed, until it reaches a critical point at which a cataclysmic transformation of the entire mass to black takes place. In Fig. 1 is plotted the pressure against time before the transition. The total drop of pressure previous to the transition was 400 kg. in 15 minutes; during the transition itself pressure dropped more than 8000 kg. in a few seconds. After the formation of the black with drop of pressure to 4000, pressure was raised again to 11000, the limit of the stroke, with very little or no further drop of pressure. This shows that the change from white to black was practically complete in the first rush.

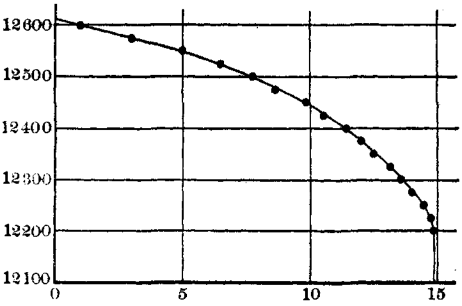

Fig. 1.—Pressure in kg. per cm^2. against time in minutes immediately before the transition from white to black phosphorus. The sudden drop of pressure shown at the extreme right of the figure, which marked the transition, was of 8000 kg. and took place in a few seconds.

The curve of Fig. 1 throws considerable light on the manner of the transition. Direct change from white to black phosphorus does not take place. Some sort of a preliminary change, involving a decrease of volume, must occur before the transition can run. This change takes place at an accelerated pace at 200° and 12000 kg.; it will not take place with practical velocity at much lower pressures or temperatures. When the preliminary change has reached a certain critical stage, at which the change in density necessary to carry white to black is surely not more than 5% accomplished, the entire edifice becomes unstable and topples over into black phosphorus. It is impossible to say just what this preliminary stage consists of. It is most probable, however, that it is some change uniformly distributed throughout the volume. That this preliminary change is necessary is also suggested by an experiment described in the previous paper; white phosphorus inoculated with black does not transform to black much more easily than when not inoculated.

Unless we are going to admit some phenomenon of molecular momentum, which is almost inconceivable, the fact that pressure during the transition drops to 4000 shows that at pressures even as low as this the black modification is stable compared with the white. The great effectiveness of the preliminary preparation is evident; it enables a transition to run at 4000 which will not start without the preparation at 12000. The experiment further shows that red or violet phosphorus cannot be an intermediate product between white and black. If the phosphorus has passed through violet on its way, it would have stopped there, because we have already seen that the transition from violet to black does not run. Probably the reason why the transition from violet to black does not run under the conditions is because the preliminary stage in the transition does not run; in fact, the preliminary process *cannot* run as an affect of pressure, because the density of the modified white phosphorus from which the black forms itself is less than that of the red phosphorus.

These experiments establish, therefore: (1) that black phosphorus is stable compared with white at 200° at pressures above 4000 kg. and probably at lower pressures; (2) that violet phosphorus is stable compared with white at 4000 kg. and somewhat below 200°, which of course is to be expected; and (3) that violet phosphorus is stable compared with red at 200° at least between 8000 and 12000 kg. The experiments were not able to settle the question as to the relative stability of violet and black at high pressures, because the transition from violet to black could not be made to run, even with catalyzers which are effective for the other phosphorus transitions.

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