LXX.—The Allotropic Modifications of Phosphorus.

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It is generally believed that there are at least three distinct allotropic modifications of phosphorus, namely, the transparent, red, and metallic varieties. The transparent variety may be converted into the red most conveniently by the action of heat; this change takes place with tolerable rapidity, at a temperature of from 240° to 250° , but still more readily at a higher temperature or if traces of certain impurities, such as iodine, are present. The same change may be effected by the action of sunlight at ordinary temperatures. Pedler (Trans., 1890, 57, 599) has shown that amorphous phosphorus is formed by the action of tropical sunlight, even on a solution of ordinary phosphorus in carbon bisulphide, and that when obtained in this way it is a yellow powder changing gradually to red. Amorphous phosphorus is also sometimes formed at the ordinary temperature in certain chemical reactions; it may be obtained, for instance, by the action of oxalic acid on phosphorus trichloride as a yellow powder, which, on exposure to the air for some time, becomes red. Metallic phosphorus, the supposed third variety, was first obtained by Hittorf (Pogg. Ann., 1865, 126, 193), who heated lead and phosphorus in a sealed tube at a temperature approaching a red heat for 10 hours, and afterwards removed the lead with nitric acid of specific gravity 1.1. Pedler believes that this third variety is only red phosphorus, but he has left unanswered certain very strong evidence derived from the vapour tension and supporting the view that there are three varieties. Brereton Baker (Phil. Trans., 1888, 179, 571) has shown that vapour is emitted from red phosphorus at a temperature approaching that of boiling mercury, and that below this temperature the phosphorus is unaltered; this was done by introducing one end of an exhausted tube containing red phosphorus into the vapour of boiling mercury, a small quantity of ordinary phosphorus condensing at the cool end of the tube. Pedler has noticed the same fact. The temperature at which metallic phosphorus begins to be converted into vapour is also that of boiling mercury, so that in this particular the two varieties resemble one another.

Evidence adduced from Appearance.—Pedler has examined commercial red phosphorus, the yellow variety obtained by the action of light on a solution in carbon bisulphide, and metallic phosphorus under the microscope, and from the facts that they all consist of transparent particles of varying size, that the colour which they present to the naked eye depends on the size of the particles, and that the action of all the varieties on polarised light is the same, he concludes that red and metallic phosphorus are identical, a conclusion which is supported by the following experiments.

Preparation of Metallic Phosphorus.—This substance is formed by dissolving phosphorus in lead at a high temperature, and, according to Hittorf (loc. cit.), separates in microscopic rhombohedra in the lead on cooling. Pedler states that it may be formed more easily by projecting amorphous phosphorus into lead at a somewhat high temperature. Both methods are open to the objection that the amorphous phosphorus may only have mixed with the lead, and this may account for the similarity of properties observed by Pedler in red and metallic phosphorus. In order to obviate the objection, an experi-

ment was arranged in such a manner that the lead only came into contact with the vapour of phosphorus. If a substance and its vapour are soluble in a common solvent, both are equally soluble, so that if metallic phosphorus is formed by Hittorf's method, it must also be formed when the vapour alone comes into contact with the lead. A hard glass tube was drawn out as in the diagram. The compartment Acontained pure lead, and a plug of glass wool was rammed tightly down against the constriction C. Amorphous phosphorus was introduced into the compartment B, and the tube, after being exhausted and sealed, was placed in an iron tube and heated to dull redness in an inclined position. After cooling, the lead was removed by nitric acid of specific gravity 1·1, and a black powder remained behind; this, when examined on a slide under the microscope, was found to consist of black, opaque masses, which, if lightly pressed against the slide,



separate into exceedingly minute, regular, transparent particles, all of approximately the same size, and so small that it is impossible to assert with confidence what their exact shape is; they have, however, two pairs of parallel edges, and are probably cubes or rhombohedra.

Hittorf states that metallic phosphorus may also be formed by heating amorphous phosphorus at the temperature of boiling phosphorus pentasulphide and condensing the vapour at the temperature of boiling sulphur. I performed a similar experiment. An exhausted tube containing red phosphorus was placed in the vapour of boiling phosphorus pentasulphide. With any liquid of high boiling point, the vapour at the bottom of the vessel is always at a higher temperature than that at the top, unless special precautions are taken, and so in my experiment, after several hours heating, amorphous phosphorus was deposited at the top of the tube in a yellowish-red layer. The tube was opened under carbon bisulphide to dissolve the ordinary phosphorus, and the layer of red phosphorus on the glass, when examined under the microscope, was found to consist of crystals of the same size and shape as those formed by crystallisation from lead.

Red phosphorus obtained by the action of sunlight, after purification from ordinary phosphorus by carbon bisulphide, and the yellow variety obtained by the action of phosphorus trichloride on oxalic acid, were also examined under the microscope, and were found to consist of similar microscopic particles. The yellow colour of the variety obtained from phosphorus trichloride and oxalic acid is due to the more complete separation of the crystals; these, after exposure to moist air, stick together, and the yellow colour changes to red. In the cases which I have examined, the darker colour of some specimens of red phosphorus was always due to the aggregation of the microscopic rhombohedra, and not to the varying sizes of the crystals.

Commercial red phosphorus consists of irregular masses of varying sizes. When treated with caustic soda or carbon bisulphide, or heated in a vacuum, no alteration in appearance is noticeable. If, however, it is boiled with caustic soda and then with hydrochloric acid, a fine powder rises to the surface of the acid, and, when examined under the microscope, presents the same appearance as the variety known as metallic phosphorus.

The crystalline form of metallic and of red phosphorus is therefore the same. The crystals of red phosphorus, however obtained, are very uniform in size; commercial red phosphorus consists of these microscopic crystals so firmly cemented together by the action of moist air that they form brittle blocks with a metallic lustre, the crystals being probably held together by an oxide or acid of phosphorus. Ordinary phosphorus is not present, as vapour is not given off in a vacuum until a temperature of 358° is reached.

Evidence for the Existence of Two Distinct Varieties of Red Phosphorus.

Hittorf (*loc. cit.*) has shown that, when amorphous phosphorus is heated for 8 hours in a sealed tube at the temperature of boiling sulphur, the vapour tension at first rises and then falls, and that during the operation the specific gravity of the phosphorus increases. This he explains by assuming that there are two distinct forms of red phosphorus, and that the change from one variety to the other takes place gradually at the temperature of boiling sulphur.

Lemoine (*Compt. rend.*, 1871, 73, 797) examined this point also, and found that when white phosphorus is heated in a closed glass bulb in the vapour of boiling sulphur it is first converted into red, and then

the vapour tension falls very gradually until it arrives at the limit of 3.6 grams of vapour per litre. When red phosphorus is heated in a closed vessel under similar circumstances, the vapour tension gradually rises, the rate of increase depending on the amount of amorphous phosphorus present at the beginning ; if the amount originally present is more than 16 grams per litre, the vapour tension at first rises and then falls, whilst with 30 grams per litre it rises as high as 4.7 grams, and finally falls to the limit, or 3.7 grams per litre. Lemoine attributes the temporary rise in tension to an alteration of the surface similar to the polarisation of electrodes. The facts, however, admit of an explanation identical with that given by Hittorf-namely, that the phosphorus is very gradually converted into another form, the vapour tension of which is lower. Under these circumstances, the excess of vapour formed by the evaporation of the less stable form would be gradually condensed to the new variety, after the change in the solid had taken place.

The facts therefore at first sight appear to support the view that there are two distinct forms of red phosphorus.

Experiments devised to clear up this point lead to the conclusion that the temporary rise of vapour tension is not due to a change of state, but to the presence of compounds of phosphorus, which decompose at the temperature of boiling sulphur giving, amongst other products, phosphorus vapour. In all the experiments, bulbs of about 30 c.c. capacity were employed, and about 1 gram of red phosphorus was introduced into them. The bulb communicated by a capillary tube with a drying tube containing phosphorus pentoxide, and then with the Sprengel pump; the phosphorus and bulb may thus be dried in a vacuum at any required temperature. When dry, the bulb is closed, and suspended by means of a platinum wire in sulphur vapour, the bath consisting of a porcelain tube, similar to the water tube of Victor Meyer's vapour density apparatus, the part above the bulb being jacketed with asbestos as recommended by Callendar (Phil. Trans., 1891, 182, 119). After removal of the bulb from the bath, the vapour of phosphorus condenses in perfectly colourless drops quite free from the red modification. The bulb, when cold, is opened under carbon bisulphide, the solution filtered from amorphous phosphorus, and the carbon bisulphide distilled off in the presence of aqua regia. A small quantity of trichloromethylsulphonic chloride is formed during this operation. No phosphorus could be detected in the distillate of carbon bisulphide, although, by several blank experiments, it was shown that phosphorus, when dissolved in carbon bisulphide, may be very accurately estimated by evaporating almost to dryness with aqua regia, and precipitating the phosphoric acid, first with ammonium molybdate, and then twice with magnesia mixture, with the ordinary

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precautions. When the bulb is first exhausted, a gas smelling like phosphoretted hydrogen, is evolved, and can only be completely expelled by heating for half an hour at the temperature of sulphur vapour in a vacuum. Commercial red phosphorus therefore is not pure, but contains some compound which, by the action of heat and reduced pressure, decomposes with the formation of phosphoretted hydrogen. It is probably this compound which binds the microscopic crystals so firmly together.

Three series of experiments on the vapour tension were performed. In the first, commercial red phosphorus, which had been exposed to the air, was used. In the second, phosphorus which had been purified



by boiling with caustic soda was employed, the caustic soda being removed by washing successively with hydrochloric acid and water, the phosphorus was then rapidly dried on a porous plate and afterwards in a vacuum over sulphuric acid. In the third, the phosphorus, purified and dried in this way, was heated for half an hour in a vacuum at the temperature of boiling sulphur until gas ceased to be evolved. The results are recorded in the following table in grams of vapour per litre, the duration of the experiment being given in hours :---

	1 hour.	2 hours.	3 hours.	4 hours.	16 hours.
Red phosphorus which had been ex- posed to the air Purified and dried red phosphorus Phosphorus in which the impurity	3.65 3.58	4:68 4:24	4.71	4·70 4·21	3.68
had been decomposed by heating	3.62	3.94	3.91		

On comparing the results obtained after heating for 2 hours, it will be seen that the highest vapour tension is obtained with the impure substance; the rise in vapour tension is therefore due to the formation of phosphorus vapour by the gradual decomposition of some compound, which may be partially removed by boiling with caustic soda. When this compound has been partially decomposed by heating for half an hour in a vacuum, the vapour tension is 3.94 grams per litre, and thus approaches the limit of 3.7 grams per litre. Thorpe and Tutton have shown (Trans., 1890, 57, 545) that P_4O_6 decomposes into P_2O_4 and phosphorus at the boiling point of sulphur, and it is possible that other compounds of phosphorus may also decompose with the formation of phosphorus.

We are therefore compelled to conclude that there is only one variety of red phosphorus; firstly, from identity of appearance, and, secondly, because the higher vapour tension observed in some cases, and supposed to furnish evidence for the existence of two forms, is due to the presence of impurities.

Hittorf has shown that phosphorus vapour has the same density whether it is obtained by the evaporation of ordinary or of red phosphorus. It is important to establish this point, since no explanation of the mutual changes which occur can be given until it is settled; the density of the vapour has therefore been determined in both cases.

Density of the Vapour of White Phosphorus.*

The molecular weight found by Mitscherlich (Annalen, 1834, 12, 137) at 515° was 131.6, and by Deville and Troost (Compt. rend., 1863, 56, 891) at 1040° was 129.3. From these results, it was thought probable that a further condensation of the molecule might take place at a lower temperature. The variation from the theoretical value for P_4 at the temperatures of boiling sulphur and mercury is, however, not more than we should expect in an imperfect gas.

The vapour bath, A, consisted of a porcelain tube with a slit ab in the side through which the tube attached to the bulb B can be inserted; during the experiment, the neck of the bath is surrounded with asbestos. C contains well-dried red phosphorus; F is a drying tube containing phosphorus pentoxide. The pressure may be read off on the manometer, G; e and d lead respectively to the Sprengel pump, and to a gasholder containing nitrogen, free from carbon dioxide, and standing over sulphuric acid. The nitrogen enters d through a fine capillary tube, which enables the supply to be better regulated.

^{*} The molecular weights calculated from the vapour density are here given in stead of the vapour density compared with air.

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Before beginning an experiment, the whole apparatus is dried by first exhausting, then allowing dry nitrogen to enter and exhausting again. The phosphorus in C is then distilled into E, and when a sufficient supply has condensed, C is removed by the blowpipe. The bulb B is next heated in the sulphur vapour, the heat radiating from the burner and the bath being sufficient to keep the phosphorus in the tube melted during the experiment. The pressure



within the whole apparatus is gradually increased by allowing nitrogen to enter. The phosphorus in E is thus driven along the tube C to the entrance of the bath, where it evaporates.

When the pressure has risen sufficiently high, the tap H is closed, and the tube c, leading to the bulb, is sealed with the blow-pipe near to the entrance of the bath. The bulb B is then opened under boiled distilled water; it is always found to contain a small bubble of gas, which collects in the drawn out end of the bulb f, and may be con-

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veniently measured by making a file mark on the glass, a correction for this bubble of gas being made in the calculation. The amount of phosphorus in the bulb is determined by converting it into phosphoric acid with aqua regia, and estimating it as magnesium pyrophosphate after previous precipitation with ammonium molybdate. The advantage of this method of finding the vapour density is that no non-volatile phosphorus compounds can be introduced into the bulb, since it is the vapour only which enters, one of the chief sources of error in Dumas' determinations being the introduction of impurities.

A similar bulb of the same glass, after exhaustion, is dried by filling several times with dry nitrogen, free from carbon dioxide, while at the temperature of the bath; it is sealed when filled with nitrogen at a known pressure, the nitrogen which it contains being afterwards measured by opening under mercury. The temperature of the bath calculated from this experiment is 444.8° , 0.000008613 being taken as the coefficient of expansion of glass. From these experiments, data sufficient for calculating the density are obtained. Five determinations of the density were made, and the molecular weights calculated from them are :

127.1, 126.9, 126.7, 127.0, 126.9; mean, 126.9.

The density was also found at the boiling point of mercury, and the molecular weight calculated from it is 126.5.

Density of the Vapour of Red Phosphorus.

In these experiments, the entrance to the bulb was a very fine capillary tube, the bulb itself containing amorphous phosphorus. Since the rate at which the vapour is formed is very slow, at least one gram of red phosphorus must remain in the bulb at the end of the experiment, or a large volume of nitrogen will diffuse through the capillary. The pressure during the experiment was a little below that of the atmosphere. It is impossible to remove the bulb from the vapour-bath immediately after closing it, and during the short time it remains there the tension rises slightly, making the results too high. The amount of ordinary phosphorus remaining in the bulb was estimated, as already described, by dissolving in carbon bisulphide. The numbers obtained from five experiments were :

130.81, 131.83, 130.3, 130.7, 131.23; mean 130.97.

The density found in this way is almost 3 per cent. higher than that found with white phosphorus, but the difference is easily accounted for by the evaporation which takes place after closing. In fact, if the

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experiment is conducted at a lower pressure, the molecular weight is found to be much higher, since the evaporation, during the short interval which elapses between closing and removing from the vapourbath, takes place more rapidly. The numbers, however, are sufficiently near to those obtained with ordinary phosphorus to justify the conclusion that the vapours of red and ordinary phosphorus are identical. This conclusion might also be reached by consideration of the fact that the vapour of red phosphorus condenses to ordinary phosphorus whenever the temperature is below that at which white phosphorus changes to red, and even at a temperature above it, although, in the latter case, red phosphorus is gradually deposited on the surface of the glass, whereas, if the vapours of the two varieties were different, red phosphorus would be expected whenever the evaporation was from red phosphorus.

Variation of Vapour Tension of both varieties of Phosphorus with Change of Temperature, and deductions therefrom.

The vapour pressures supported by both varieties of phosphorus have been found by Troost and Hautefeuille (*Compt. rend.*, 1873, 76, 219) for a considerable range of temperature, and are shown in curves (Fig. 4). It will be noticed that the two curves approach one another, so that at a higher temperature it may be expected that they will meet. At the temperature and pressure of the point of intersection, both varieties ought to exist together—that is, the red ought to melt, forming the ordinary modification. This anticipation has been realised experimentally by heating red phosphorus in sealed capillary tubes of hard glass, as, at a temperature near to the fusing point of potassium iodide, red phosphorus melts to a colourless liquid exactly similar in appearance to ordinary phosphorus, although the temperature is far above that at which the colourless variety changes readily to the red.*

Not a single instance has yet been recorded of red phosphorus changing *directly* into white below its melting point, although the converse change may be effected by the action of light, heat, or pressure; indeed, the only way to change red phosphorus into white is, indirectly, through its vapour. The facts therefore lead to the conclusion that at the ordinary temperature, and below the melting point, red phosphorus is stable, whilst the white modification is unstable, being liable to change into it.

The correctness of this conclusion may be demonstrated. Let a_1T

*Hittorf (loc. cit.) states that amorphous phosphorus cannot be melted when heated to redness in a sealed tube. An ordinary sealed tube will not stand the pressure.

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(Fig. 5) be the equilibrium curve for ordinary phosphorus and phosphorus vapour on the pressure temperature diagram, and a_2T the corresponding curve for red phosphorus and vapour. Since all three states exist at T, the white phosphorus | red phosphorus curve must pass through this point. Experimental determination of the latter curve would no doubt prove exceedingly difficult, but its relative position with respect



to the curves a_1T and a_2T may easily be found. Let v_1 , v_2 , v_3 be the volumes of unit mass of red phosphorus, white phosphorus, and the common vapour respectively. Then v_1 , v_2 , and v_3 are in ascending order of magnitude. Let $\left(\frac{dp}{dT}\right)_1$, $\left(\frac{dp}{dT}\right)_2$, and $\left(\frac{dp}{dT}\right)_3$ be the slopes of the curves a_1T , a_2T , and a_3T respectively, at the triple point T. Then at the triple point,

$$(v_1 - v_2) \left[\left(\frac{dp}{dT} \right)_3 - \left(\frac{dp}{dT} \right)_2 \right] = (v_3 - v_2) \left[\left(\frac{dp}{dT} \right)_1 - \left(\frac{dp}{dT} \right)_2 \right].$$

Since v_1 , v_2 , and v_3 are in ascending order of magnitude, $v_1 - v_3$,

* Le Potentiel Thermodynamique et ses application .-- M. Duhem.

and $v_3 - v_2$ must have opposite signs, consequently $\left(\frac{dp}{dT}\right)_3 \quad \left(\frac{dp}{dT}\right)_2$ and $\left(\frac{dp}{dT}\right)_1 - \left(\frac{dp}{dT}\right)_2$ must have opposite signs, and therefore $\left(\frac{dp}{dT}\right)_2$ must lie between $\left(\frac{dp}{dT}\right)_1$ and $\left(\frac{dp}{dT}\right)_3$, consequently the curve must be situated as in the figure, with Ta_2 between Ta_1 and Ta_3 .

Draw the horizontal line b_1 , b_2 , b_3 cutting the curve Ta_1 , Ta_3 , Ta_3 , and let it be supposed that red phosphorus is in such a condition that



FIG. 5.

it is represented by the point P. Since this point is not on the curve a_3T , the phosphorus is in a condition of unstable equilibrium. Moreover, the point P is to the right of the curve a_3T , and therefore any change which takes place must be one accompanied by an absorption of heat*; in other words, it must be a change from red to white phosphorus; but the point P is also to the right of Ta_1 and Ta_2 , and therefore both the red phosphorus and white phosphorus formed from it must be simultaneously changed into vapour. Since the white phosphorus is a liquid, it will be converted into vapour immediately it is formed. As the curve a_3T is almost vertical, P cannot be much below the temperature at the triple point, and therefore red phos-

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phorus can be converted into white only at a temperature (the fusing point of potassium iodide) near to the triple point; and even at this temperature, if the pressure is below that at the triple point, the white phosphorus will evaporate so rapidly that it will be impossible to prove its presence except by showing that there is a sudden increase in the rate of evaporation immediately we pass across the curve a_3T .

An attempt was made to find the point b_3 experimentally, when the line $b_1b_2b_3$ represents atmospheric pressure (that is, the melting point of amorphous phosphorus at atmospheric pressure) by observing the rate at which phosphorus distils; but although the vapour was formed quite slowly as the temperature was rising, the rate of increase in evaporation at this point was so rapid that explosion invariably occurred in the tube, a result to be expected in the case of a solid melting far above the boiling point of the liquid.

For any point P' to the left of a_3T the change is from white to red phosphorus, and, since Ta_3 is almost vertical, we may say that for any temperature not far below the melting point of potassium iodide white can change to red phosphorus, but not vice versa. It is therefore incorrect to assert that red phosphorus is changed into white phosphorus at the boiling point of mercury; to be correct, we should say that red phosphorus is converted into vapour at that temperature.

It has been asserted above that red phosphorus can be converted into white phosphorus only at a temperature approaching the melting point of potassium iodide; this does not mean that red phosphorus cannot be converted into vapour below this temperature and then condensed to the liquid, but that the direct change is impossible.

On referring to the curves (Fig. 5) it will be seen that they are identical with the equilibrium curves for a solid and vapour, liquid and vapour, and solid and liquid below the triple point, and as a liquid is in the superfused condition below the triple point, we must regard melted ordinary phosphorus as superfused red phosphorus. Red phosphorus therefore exhibits the phenomenon of superfusion to a much more remarkable degree than the ordinary variety.

Conclusions.

(1) Metallic phosphorus and red phosphorus are identical. This is proved by their similarity in appearance when viewed under the microscope. The higher vapour tension attributed to some varieties of red phosphorus is due to impurity, which on heating decomposes, forming phosphorus vapour.

(2) The vapours of red and ordinary phosphorus are identical. The vapour density of ordinary phosphorus at the temperature of boiling

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sulphur and mercury has been found to agree closely with the density calculated on the assumption that the molecule consists of four atoms, although the results obtained by Mitscherlich and by Deville and Troost at higher temperatures would scarcely seem to make this probable.

(3) Red phosphorus melts, changing into ordinary phosphorus, under pressure, at the melting point of potassium iodide. This point on the pressure temperature diagram, I propose to call the triple point of red phosphorus. Melted ordinary phosphorus thus becomes superfused red phosphorus, and superfused ordinary phosphorus becomes the superfused liquid of both varieties. As at ordinary temperatures the red modification is stable and the white unstable, phosphorus appears to have in a remarkable degree the property of remaining in an unstable condition.

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