*Citation:*

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group is split off by boiling with phenol or acetic acid. The 3.4-dimethyl derivative also reacts readily with nitrous acid in sulphuric acid solution; the compound formed is still under investigation.

Finally, I have allowed nitrous acid to act on the dark red 3.6-dinitrodiethylaniline (m. p. 76°) when a beautiful pale yellow nitroso compound (m. p. 69°) is formed, which on being boiled for a moment with acetic acid, yields on dilution with water beautiful red needles of the 3.6-dinitromonoethylaniline (m. p. 120°) previously described by me, so that in this case also one of the ethyl groups has been eliminated. The 3.6-dinitrodimethyl compound behaves in quite an analogous manner, just like p. nitrodiethylaniline.

These experiments are being continued with other tertiary nitrated amines.

Utrecht. *University Org. Chem. Lab.*

## **Chemistry.** — "*Confirmations of the new theory of the phenomenon of allotropy.*" I. By Prof. A. Smits and Dr. H. L. de Leeuw. (Communicated by Prof. van der Waals).

(Communicated in the meeting of December 24, 1910).

As was set forth before[1]) the above-mentioned theory leads us to expect that for every substance which presents the phenomenon of *heterogeneous* allotropy, so *monotropy* or *enantiotropy*, the phenomenon of *homogeneous* allotropy will also occur, because the two phenomena are in the closest connection.

So in virtue of this theory we can expect for the monotropic and enantiotropic substances that every vapour, liquid, or solid phase in stable condition consists of an internal equilibrium between different kinds of molecules. A consequence of this is then that when we make the temperature vary so rapidly that the internal equilibrium cannot keep pace with the temperature, the more complex nature of the substance will appear, which will, among others, manifest itself in a boiling or melting range of temperature, in which the final boiling point, resp. final melting point will lie higher or lower than the unary stable boiling point, resp. melting point, dependent on the type of the pseudo-system and of the direction of the line which indicates the internal equilibrium in the vapour, resp. liquid phase.

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[1]) These Proc. March 1910 p. 763.

As was shown in the preceding communication[1]) on this subject, this has really already been observed in the melting-point determination of the rhombic sulphur.

The first substance that was closely examined by us in this direction was the *white phosphorus.*

Theory has already drawn attention to the fact that not only the *violet,* but also the *white* phosphorus is built up of different kinds of molecules, so that the possibility existed, that the complexity of this metastable modification could be demonstrated.

Experiment has corroborated this supposition, and that so convincingly that as yet no substance is known, by means of which the validity of the theory can be demonstrated in so simple and clear a way as by means of the *white phosphorus.*

Before this result was obtained, however, a great difficulty had to be surmounted, which consisted in the preparation of pure phosphorus.

It appeared, namely, that none of the known methods yielded a product that melted in a unary way also when the supply of heat took place very slowly, i.e. a substance was always obtained which presented a range of melting temperatures.

The melting-heat of white phosphorus being so small (5 cal.), an exceedingly slight quantity of a second substance can already cause an appreciable range of melting temperatures, and it was therefore to be foreseen that the preparation of a product melting at one and the same temperature might present peculiar difficulties.

As it appeared that the last contaminations must chiefly consist in the oxides of phosphorus, which cannot be sufficiently separated from the phosphorus by the usual methods of purification (treatment with potassium dichromate and sulphuric acid, distillation with steam, etc.) an apparatus was constructed (fig. 1), in which the phosphorus was distilled in vacuo, and then subjected to a repeated partial crystallisation, after which it was transferred, thus purified, to a melting point determination vessel.

The latter is represented in fig. 1 by *A*. A resistance thermometer is sealed to it; this vessel is connected with three bulbs *B*, *C*, and *D*, the last of which (capacity 500 cm.) at first filled with water, was afterwards filled for three quarters with pieces of commercial so-called pure white phosphorus.

After this phosphorus had been melted under water, and had then solidified again, the water was poured off, leaving only a thin layer, and then the tube *d* was sealed.

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[1]) l. c.

Then the tube *c* was connected with the *Gaede-pump* through two U-shaped tubes placed one behind the other.

The first of these tubes was placed in a vessel with solid carbonic acid and alcohol to condense all the water-vapour, the second being immerged in a vessel with liquid air to solidify the last traces of phosphorus so that a high vacuum could be obtained.

Now first of all the apparatus was exhausted, and the flask *D* was carefully heated with the flame to distill off the water.

When nothing of the water was to be detected any more we continued the boiling in vacuo for another half hour to be sure that also the water dissolved in the phosphorus was entirely removed.

After the connection of the apparatus with the pump had been broken by sealing it at *b*, three fourths of the phosphorus was distilled over into *B*, in which a liquid was obtained, which at first opalized somewhat, but became perfectly clear and colourless afterwards.

Though this phosphorus appeared to be as pure or purer than the purest product obtained by other methods, it was not yet pure enough for our purpose, as experiment showed that this phosphorus could not be made to melt sharply at one temperature by any means whatever.

To reach a still higher degree of purity the phosphorus in *B* was almost entirely melted, and then made to crystallize again by slow cooling; when three quarters of the mass had solidified, the remaining liquid was conveyed to *C* by tilting of the apparatus, and solidified there by strong local cooling of the supercooled liquid (by means of solid carbonic acid and alcohol).

This manipulation was repeated a great many times, in which the mass remaining in *B* did not only get continually a higher melting-point, but also became coarser and more perfectly crystalline.

When through this repeated partial crystallisation and removal of the liquid four fifths of the quantity originally present in *B* was conveyed into *C*, we filled the vessel *A* with the phosphorus which had remained in *B* by melting it in *B*, and by then making it flow into *A* by tilting the apparatus.

By then sealing off at *a* we broke the connection of the melting-point-vessel with the other part of the apparatus, and the experiment could begin.

The perfectly colourless coarsely crystalline phosphorus obtained in this way now appeared te be so pure, that on immersion of the melting point-vessel in a thermostat the temperature of which varied slowly, a melting-range was found smaller than 0.02°, so that we may say that we have determined the unary melting-temperature of the white phosphorus, for which we found 44,0°. Here we must remark however that only the differences of temperature are exact to one hundredth of a degree; the absolute values of the temperature may perhaps need a small correction, as we used as a standard of temperature a thermostat which had the temperature of 44° according to a controlled normal thermometer.

When it had thus been proved that the phosphorus obtained by us has the property of melting resp. solidifying in a unary way, it was examined in how far the complexity of the phosphorus betrayed itself when we worked rapidly.

As the result can be most clearly demonstrated by curves of cooling resp. of heating, we shall successively discuss figs. 2, 3, 4, and 5, which will give us a highly interesting insight into the inner nature of the white phosphorus.[1]

Fig. 2 refers to the following experiment: the meltingpoint vessel with white phosphorus was kept in a thermostat of 40° for a day, and then suddenly transferred to a bath of 50°, after which the temperature was read every 10 seconds by means of the galvanometer in a WHEATSTONE bridge. Now it follows from the curve in fig. 2, which indicates the temperature as a function of the time, that the melting set in at **43,92°**, and was completed at **43,96°**.

The small range of melting temperatures of 0,04° shows that the substance behaved in an almost unary way, but not perfectly so, which is owing to this that the internal equilibrium had set in at 4° under the unary melting-point.

In another experiment another course was taken. The meltingpoint-vessel was kept for some time in a bath of ± 46°, and then taken from the bath to make the cooling take place under exposure to the air.

As the phosphorus is very easily supercooled, the crystallisation had to be started by grafting. For this purpose the capillary point *e* of the meltingpoint-vessel was for a moment brought in contact with solid carbonic acid and alcohol, when the temperature of the

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[1] In Fig. 2 the curve begins to rise more slowly at 42°, because melting occurs already in the outer layers of the phosphorus, which are warmer than the layer in contact with the thermometer. If this was not the case, we should have got the dotted line and melting would not have appeared before 43.92.

At *c* the curve begins to rise more rapidly because the heterogeneous equilibrium no longer sets in rapidly enough — in consequence of the small quantity of solid substance present — that the heat applied to the solid substance is consumed entirely in melting it. If this had been the case, the course would have been also here as the dotted line indicates and the melting would have been completed at 43°.96.

phosphorus had fallen below 44°, in consequence of which immediately solid phosphorus formed in the capillary, which started the crystallisation of the large mass, during which the temperature rose in consequence of the heat of solidification.

The curve representing the result of this experiment has been drawn in fig. 3. In this fig. *a* denotes the point where the grafting took place. Then the temperature fell to *b*, after which it rose to *c*, then it descended at first very slowly, then all of a sudden very rapidly. The result is that also in this way of working the phosphorus solidifies in an almost unary way, for the interval of solidification amounts only to 0,05°, but in consequence of the comparatively large difference of temperature with the surroundings the unary melting temperature was no more to be reached.

In a third experiment which yielded a very important result, the meltingpoint-vessel was first placed in boiling water for some time, and then suddenly transferred to a bath of 15° to make the cooling take place so rapidly that the internal equilibrium could certainly not keep pace with it. When then grafting took place at about 43°.5 after taking out of the bath, the temperature rose above 44°, from which, therefore, followed that *when the cooling takes place very rapidly the liquid phosphorus is already supercooled above* 44°.

Therefore another time the grafting took place *above* 44°, when the temperature rose to 45°.5, and we succeeded in getting a rise of temperature to 46° with still earlier grafting, which, however, is by no means the highest temperature to which the phosphorus can rise in this way.

The curve of cooling, obtained in one of these experiments, is represented in fig. 4, and it is noteworthy how much this curve, which is the result of a perfectly analogous experiment to that to which fig. 3 relates, apart from the previous history of the phosphorus, differs from the curve in this last figure. The grafting took place above 44° at about 44.°5; at first the temperature descended, then it rose to 45°,05, after which it fell again, at first pretty rapidly, then less rapidly and at last very rapidly again.

The whole line shows the type of a line of solidification of a mixture, the melting-range is here about 1°.8, but can be considerably larger still, which already follows from this that in one experiment a temperature maximum was observed of 46°.

That the phosphorus which has been ill-treated in this way, and at first unites to a *distinctly visible conglomerate* in the solid state tries to reach internal equilibrium pretty rapidly, follows from fig. 5. The curve traced in this figure is, namely, a curve of heating, which

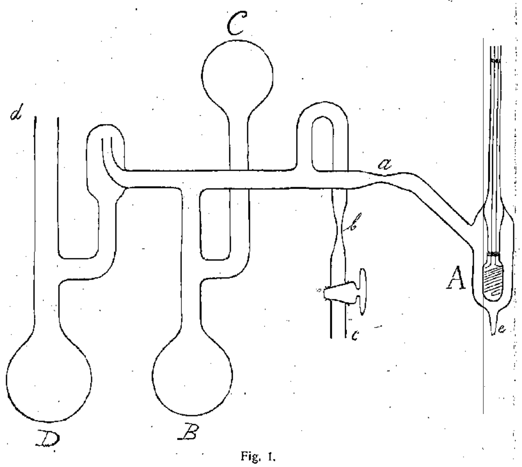

Fig. 1.

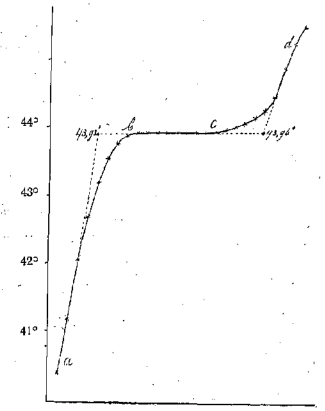

Fig. 2.

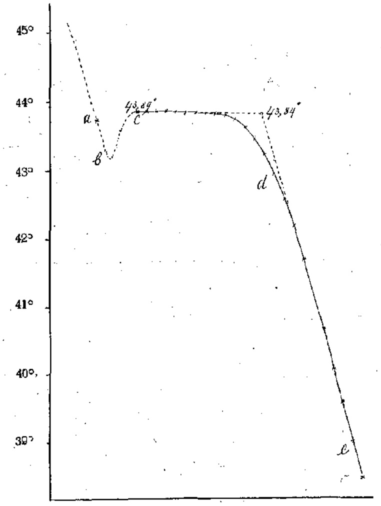

Fig. 3.

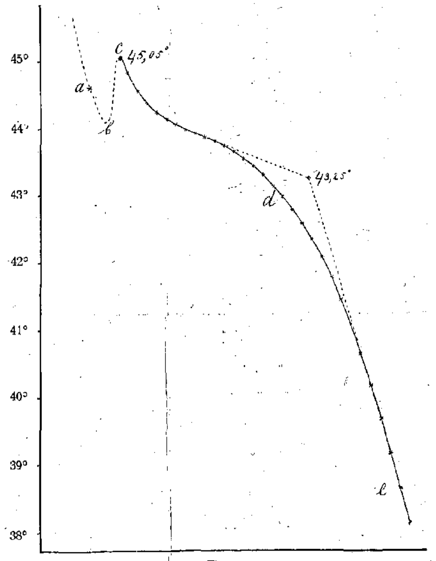

Fig 4

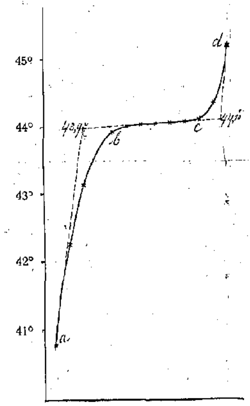

Fig. 5.

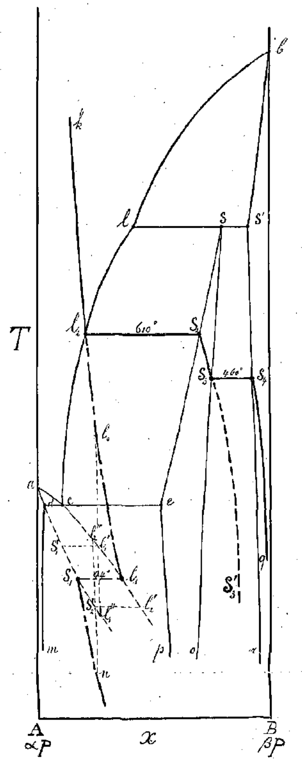

Fig. 6.

shows what has been observed after the solid substance obtained in the previous experiment has been suddenly placed in a bath of 50°. The curve of heating now shows that after some minutes a considerable approach to the state of internal equilibrium has taken place, but it has not been reached as yet, for the melting-range still amounts to 0°.13, and the end-melting point lies above the unary melting-point temperature.

Before proceeding to an interpretation of the observed phenomena, we may point out here that, as CHAPMAN [1]) found that red $P$ melts to a perfectly colourless liquid, it has already been assumed in the preceding communication, that the line for the internal liquid equilibrium runs to the side of $\alpha P$ with rise of temperature [2]). If we do so again here we are obliged, in contradiction to the $T,X$-figure given before, to draw a eutectic point in the pseudo-binary system, as has been indicated in fig. 6, because only in this case the observed phenomena can be explained [3]).

The line $kl_2l_1$ denotes the internal equilibria in the liquids, and $s_1n$ refers to the internal equilibria in the solid white phosphorus, so that $s_1$ and $l_1$ indicate the solid and the liquid phases which are in internal equilibrium, and coexist at the unary melting-point of the white phosphorus.

Now it follows from the course of the mentioned lines of equilibrium, that when the liquid $l_0$ is cooled very rapidly, the crystallisation can already occur at $l_1$. Then in the absence of internal transformations a melting-range $l_1l_1$ would be found, whereas in case of rapid heating of the solid phase $n$ the melting will already begin at $s'_2$, and be completed at $l'_2$, namely in case there are no internal conversions at all. The internal conversions, however, especially when the two phases $S$ and $L$ are in contact, proceed with fairly great rapidity, and this is the reason, that a transgression of the unary melting-point temperature is always much smaller than the lines $l'_1 l'$, and $S'_2 l'_2$ would lead us to expect.

Further the figure shows that the initial solidification resp. the initial melting will appear the sooner according as a higher resp. a lower temperature is started from, and thus we see that the new theory of allotropy, given in our preceding paper, gives a natural explanation of the observed phenomena [4]).

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[1]) Journ. chem. Soc 75, 743 (1899)

[2]) $\alpha P$ is a substance we do not know, but of which we may assume with a high degree of probability, that it is colourless.

[3]) It follows at the same time from this, that we have not to deal with the phenomenon of polymerism for the phosphorus (see preceding communication).

[4]) Rapid heating, from low temperatures, gives only a small change; so the line $ns_1$ has a rather steep course.

We may finally remark here that JOLIBOIS[1]) thinks he has shown with certainty that there are not *two* but *three* solid modifications of the phosphorus, *white, red,* and *pyromorfic* phosphorus, which last we shall call *violet* phosphorus, as is more rational.

As JOLIBOIS remarks it would also follow from his investigation that the violet $P$ is stable under 460°, above it, however, the red modification, which melts to a colourless liquid at 610°.

When we accept these results it is the question how we can account for the behaviour of the phosphorus in the light of the new theory.

We might suppose that if three different solid modifications exist of a substance, these three forms would have to be ascribed to the existence of three different kinds of molecules.

This view has, accordingly, been advanced in the first communication, but if we think of substances with three, four, or more points of transition, this supposition is somewhat improbable, and as it proves on further consideration not to be necessary, we prefer another simpler and more plausible supposition for the present.

Also for the case that a substance occurs in three crystallized modifications, the existence of two kinds of molecules can account for the phenomena, namely, when we assume a second discontinuity in the series of mixed crystals.

This has been done for the phosphorus in fig. 6; we see that the liquids $bl$ coexist with the mixed crystals $bs'$, the liquids $lc$ being in equilibrium with the mixed crystals $se$.

In this figure $s_2$ represents the red phosphorus at the unary melting-point temperature. Below this temperature, which lies at 610° according to JOLIBOIS, the red phosphorus remains stable to 460°, at which the red modification, which is denoted by $s_3$, is converted to the violet $S_4$, which is therefore stable below 460°.

We may further remark that as red $P$ is obtained on a manufacturing scale from yellow $P$ by heating to 280°, the line $l_2l_1$ must be left and the line $s_3s'_3$, reached, which however, is also still metastable, and that then, as JOLIBOIS found, by means of the catalytic agent *Iodium*, the stable state at that temperature, the violet $P$ is obtained, which lies on the line $s_4q$.

The second substance which was examined as to its complexity, was mercury. As only one crystallised state is known of this substance, and as not one of its properties betrays a complex character,

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[1]) Comptes Rendus **149**, 287 (1909).
„ „ **151**, 382 (1910).

it was supposed that this substance would always behave in a unary way. Experiment has fully confirmed this conjecture. Whether mercury was suddenly cooled by water in vacuo from ± 300°, and then by solid carbonic acid and alcohol, or whether it was rapidly heated from 80 , the point of solidification, resp. melting-point always remained the same, and the substance perfectly behaved as a unary one, from which we may therefore draw the conclusion that when the substance is complex the internal transformations must proceed with extraordinarily great rapidity, or what is more probable that mercury really consists of one kind of molecules.

The third substance examined by us, for which in view of its transition points, the same was expected as for the phosphorus, was tin.

Though the investigation made bears as yet still a preliminary character, we may yet communicate that tin of particularly great purity can solidify entirely as a unary substance, but that it betrays its complex character when the experiment is made very rapidly, just as phosphorus does. In a following communication we hope briefly to communicate the result of the final investigation.

*Amsterdam*, December 23rd 1910.

*Anorg. Chem. Lab. of the University.*

**Chemistry.** "*On the determination of threephase pressures in the system hydrogen sulphide + water.*" By Dr. F. E. C. SCHEFFER. (Communicated by Prof. A. F. HOLLEMAN).

1. In the investigation of the systems in which hydrogen sulphide is one of the components, the difficulty presents itself that a chemical action can affect the mercury that shuts off the mixture, when it is not sufficiently purified from admixtures. This action will chiefly be due to the presence of slight quantities of air. By excluding the presence of air (and water), as completely as was possible in the methods used, I succeeded before in determining the situation of the three-phase curves in the system hydrogen sulphide + ammoniac. The methods used in the investigation, had to be adapted to high pressures, as it was my principal aim to determine the points of intersection of the critical line and the three-phase curves, the critical end-points. In this I have at the same time found an opportunity to determine the shape of the spacial figure of the mentioned system at lower temperature; the observations at these low tempe-