

Citation:

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not too hazardous. As we know the permeability of red blood-corpuscles agrees, in many respects, with that of the other body cells. We also know that acids affect the permeability of blood-corpuscles and other body-cells. Then we are not so far removed from the conclusion that, if in vivo this stable permeability of the red blood-corpuscles has been affected, the permeability of the other body-cells might also have been modified.

Conclusions.

On the ground of these facts we might form the following conception. As in vitro the permeability of cells can be changed by an addition of acid, this can be done in vivo by other influences, in the case of some febrile diseases. In the latter case chlorine enters the cells under the same circumstances under which it leaves the cells in the normal individual. The consequence of this may be that with these patients chlorine cannot pass from the tissues into the blood.

The fact that the chlorine-transfer is constant in normal people and in patients with a normal chlorine-excretion, that the chlorine-transfer is constant in an opposite direction, in people with chlorine-retention, suggests the possibility that a modified permeability of the cells will have to be reckoned among the causes of chlorine-retention in febrile diseases.

Groningen, March 1913.

Chemistry. — “*The systems phosphorus and cyane.*” By Prof. A. SMITS. (Communicated by Prof. J. D. VAN DER WAALS).

As was already stated before¹⁾ it has been ascertained that the vapour tension curve of liquid white phosphorus cannot be the metastable prolongation of the vapour tension line of molten red phosphorus. This fact is in perfect harmony with the circumstance that it can be calculated from the determinations of ASTON and RAMSAY²⁾ on the surface tension that the liquid white phosphorus must become critical at $\pm 422^\circ$.

In consequence of the existence of this critical point the particularly interesting case presents itself that the *P, T*-figure for white

¹⁾ These Proc.

²⁾ Journ. Chem. Soc. 65, 173 (1894).

phosphorus lacks any connection with that of the violet and the red modification. Precisely the same holds for cyane and paracyane, and what is most remarkable about it, is that what follows only indirectly from experiment for phosphorus, may be easily realised for the system cyane and vice versa. The critical point of liquid white phosphorus below the melting point of the red modification is not to be realised, but follows from the vapour tension curve and from the surface tension; the critical point of cyane on the other hand is easy to observe, and lies at 126.5 and under a pressure of 58.2 atmospheres.

On the other hand the melting-point under the vapour pressure of the red phosphorus can be determined, though not easily, at 588.5 and 42 atmospheres, whereas the melting-point of paracyane, which represents the stable modification and is therefore comparable to the red phosphorus above 460° , cannot be realised, because paracyane is decomposed before this temperature is reached. It follows from this that the systems phosphorus and cyane supplement each other in the most convenient way. As I suspected this, I charged Mr. TERWEN with the examination of the system cyane hoping to come to a decision in this way as to whether we have to do with internal equilibria for the system cyane, just as for phosphorus.

The first thing required was to have cyane of great purity at our disposal, and it was particularly this part of the investigation that presented difficulties which were difficult to surmount. In the preparation of cyane a part is always decomposed, and in consequence of this the product always contains nitrogen. The removal of this nitrogen presented great difficulties, and only after a long laborious process, in which the solid cyane was subjected to repeated fractionated sublimation did we finally succeed in obtaining cyane of so great purity that the investigation about the complexity of cyane could be undertaken. The result rewarded the pains.

Just as for phosphorus the complexity was examined by the determination of curves of solidification under *perfectly* the same circumstances during the solidification. The difference in the successive experiments consisted only in this that in one case the liquid had been previously slowly cooled down, in the other case rapidly from higher temperature.

As was expected the result was that in case of slow previous cooling a line of solidification with perfectly horizontal intermediate portion was found, and that this was wanting when the cooling took place rapidly. The initial point of solidification could be raised 0.5 in the latter case. So the result was qualitatively the same as

for phosphorus, and shows clearly that pure liquid cyane is built up of different kinds of molecules, which get into equilibrium when the process goes slowly. Though in consequence of its small conductivity of heat solid cyane did not furnish reliable results in the determination of curves of heating, we may accept without any doubt that what holds for the liquid phase, will also hold for the solid phase, though it can only be shown in a less clear way.

It is for the rest clear that it is sufficient for our purpose to show the complexity of one of the phases, so that it does not matter that paracyane is altogether inaccessible to an investigation as to its internal constitution.

We may therefore conclude in virtue of the obtained result that phosphorus and cyane are really quite comparable systems.

Before we proceed to a discussion of the pseudo-systems among which the unary systems phosphorus resp. cyane must be classed, it is worth while mentioning what BAKHUIS ROOZEBOOM¹⁾ has stated about the points of agreement between the two said systems.

“Das Cyan unterscheidet sich weiter vom Phosphor darin, dass kein Schmelzpunkt der polymeren Form (Paracyan) bekannt ist. Praktisch ist es unmöglich, einen solchen zu erreichen, weil das Paracyan sich oberhalb 600° stark zersetzt.”

“Es erhebt sich gleichwohl die interessante Frage, ob — falls diese Zersetzung ausgeblieben wäre — ein Schmelzpunkt hätte erreicht werden können.”

Eine Umwandlung des Paracyans in die gewöhnliche Flüssigkeit ist natürlich unmöglich, weil ihr kritischer Punkt bei 124° liegt. Wohl aber wäre eine Umwandlung oberhalb 640°, also unter grösserem Druck als 1 Atm., in eine polymere Flüssigkeit denkbar.”

“In solchen Fällen besteht also kein kontinuierlicher Uebergang zwischen den beiden Flüssigkeiten. Dadurch stehen die verschiedenen festen Phasen eigentlich nicht mehr im Verhältnis der Monotropie zu einander, sondern die polymere Form verhält sich als ein besonderer Körper.” And in a footnote on the same page he writes: “Es ist sogar fraglich, ob nicht auch der Phosphor noch zu dieser Kategorie gehört, denn ein kontinuierlicher Uebergang zwischen dem gewöhnlichen flüssigen Phosphor, und der Schmelze des roten, ist noch nicht konstatiert.”

We see from this that BAKHUIS ROOZEBOOM took a lively interest in the problem in question, and that he indicated already clearly what is peculiar about it.

BAKHUIS ROOZEBOOM pointed out that there is no connection at all

¹⁾ Lehrbuch Heterog. Gleichgewichte, 176.

between the two modifications of the substance cyane, and that therefore strictly speaking it is not correct to speak of monotropy here. Now, however, we come to another conclusion. It is true the lines for the internal equilibrium in the different phases of cyane and paracyane lack any connection, and yet we know that all kinds of phenomena are known which very certainly do point to a connection between cyane and paracyane; thus e.g. the vapour of paracyane yields cyane on cooling, and from the vapour of liquid or solid cyane, paracyane may be obtained when it is heated to a high temperature. So there is, indeed, a connection, but this connection could not be demonstrated formerly, and this was also the case with phosphorus. The theory of allotropy guides us here again. The systems *phosphorus* and *cyane* are, as experiment has shown, pseudo-systems, and for the present it is sufficient to assume that each of these systems is built up of two kinds of molecules. Now it has been pointed out before that the pseudo-system phosphorus may be expected to belong to the type ether-anthraquinone, and the same thing applies to the pseudo-system cyane.

If we first discuss the system phosphorus it is easy to show that the existence of two critical endpoints in the pseudo-system $\alpha P-\beta P$ enables us to explain the peculiar behaviour of phosphorus in an exceedingly simple way. In Fig. 1 in the first place the PT -projection

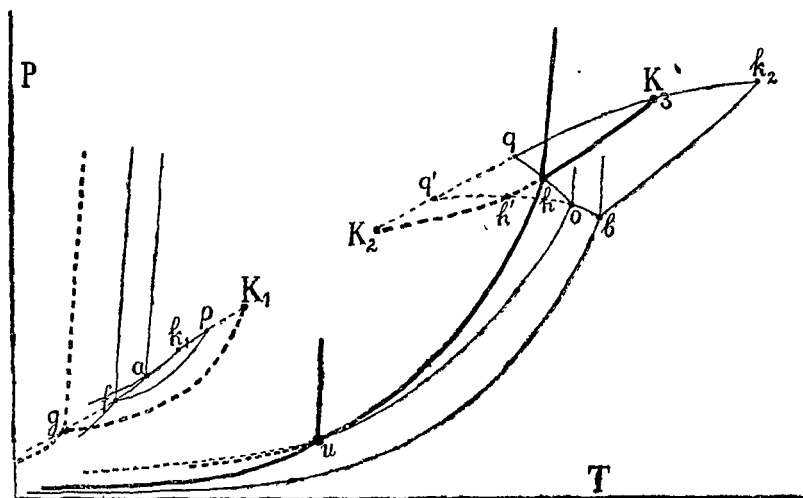


Fig. 1.

of the pseudo-binary system $\alpha P-\beta P$ is indicated. The points p and q denote the critical endpoints and the only thing that makes this P, T -figure somewhat less simple than that of ether-anthraquinone is this that the three-phase line qo , which refers to the equilibrium between red mixed crystals, liquid, and vapour, at o passes into

the three-phase line ob , which holds for the coexistence between violet mixed crystals, liquid, and vapour.

If these latter three-phase lines are prolonged towards lower temperatures, this line must terminate in a metastable critical endpoint q' . From the triple point O two more three-phase lines start, of which OU relates to the equilibrium between violet mixed crystals, red mixed crystals, and vapour. We have now discussed what is peculiar in the P,T -figure of the pseudo-system. If in this figure we now draw the P,T -lines of the unary system, we get what follows. The vapour-tension line of the liquid white phosphorus, which must be considered as a supersaturated solution, lies under the three-phase line fp , and meets the metastable part of the plaitpoint curve at K_1 . If the critical temperature calculated from the surface tension is accepted as correct, this point lies at 422° and 18 atmospheres. At the triple point of the red phosphorus, which was found at $588^\circ,5$ and 42 atmospheres by Mr. BOKHORST ¹⁾, liquid is formed again, and it is now clear that the vapour tension line for liquid phosphorus starting from this point, has nothing to do with the vapour tension line of molten white phosphorus.

Now it is interesting to question how the metastable part of the vapour tension line of liquid red phosphorus prolonged towards lower temperatures will run. In fig. 1 one of the possibilities is drawn. In this it is assumed that the said vapour tension line meets the metastable intermediate part of the plaitpoint curve in K_2 , and will therefore end in a *lower*-critical endpoint. As was stated before unmixing can also occur in the metastable region, and in this case when the plait is closed the point K_2 can occur at much lower temperature and pressure than K_1 , and then the line hK_2 will lie under gK_1 . This line cannot extend far towards low temperature, however, for then there would have to exist two different kinds of liquid white phosphorus, of which nothing has appeared. If the plait was open, the metastable part of the vapour tension line of the liquid red phosphorus would also proceed to lower temperatures under gK_1 , but the objection advanced just now, is then of force, so that the most probable assumption by far is that the said vapour tension line terminates in a metastable lower-critical endpoint K_2 . We shall get perfect certainty when the prolongations of the two vapour tension lines gK_1 and hK_2 intersect. Investigations specially undertaken for this purpose may soon decide this. It must further be noted that the vapour tension line of red phosphorus,

¹⁾ The former determinations were made with an apparatus which appeared to yield inaccurate results at high temperatures.

which starts from h at about 460° must meet the line OU , as the transition point between red and violet phosphorus lies at this temperature. So a triple point occurs again in U , and the only stable unary equilibrium below this point is that between violet phosphorus and vapour.

A similar PT -figure holds for cyane, as Fig. 2 shows. Here it is remarkable that it was not necessary to find the critical point K_1 by calculation as for white phosphorus, but that it could be easily observed. On the other hand, the triple point of the red modification of phosphorus could be determined by experiment; the triple point of paracyane, on the contrary, is not to be realised because the substance decomposes before that time. As we know only one kind of liquid cyane below the temperature of the critical

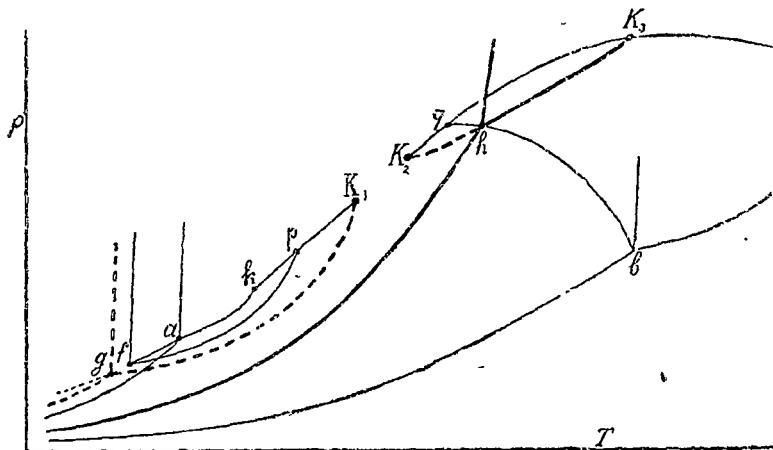


Fig. 2.

point K_1 , it is assumed here too that the metastable prolongation of the vapour tension line of molten paracyane must end in a lower critical endpoint K_2 .

We see therefore that according to the earlier view not a single connection could be indicated between the different phases of the white phosphorus on one side and the violet and the red phosphorus on the other side; nor could any be given between cyane and paracyane, though some connection *must* exist, because the different forms of the phosphorus resp. cyane can be converted into each other by some means or other.

The theory of allotropy demonstrates this connection in a very simple way, as Figs. 1 and 2 show.

A deeper insight is obtained when the projection of the three-phase regions of the pseudo-binary and that of the two-phase regions of the unary system on the T - X -surface are drawn. These projec-

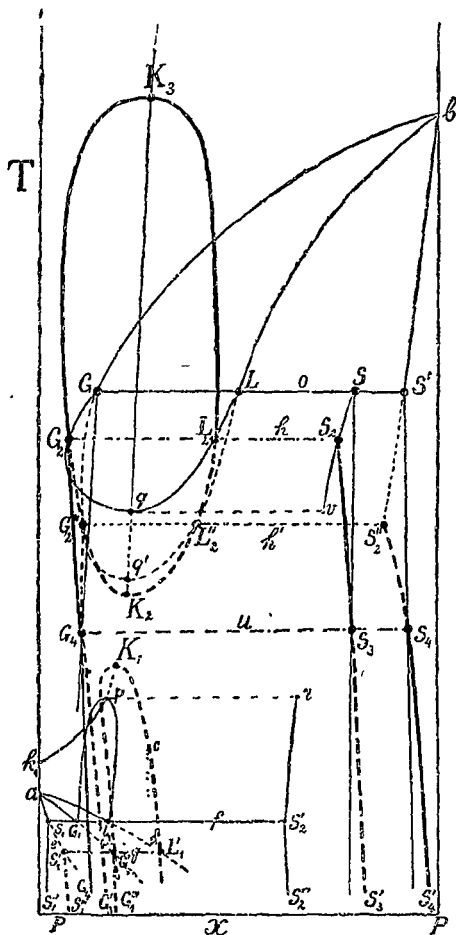


Fig. 3.

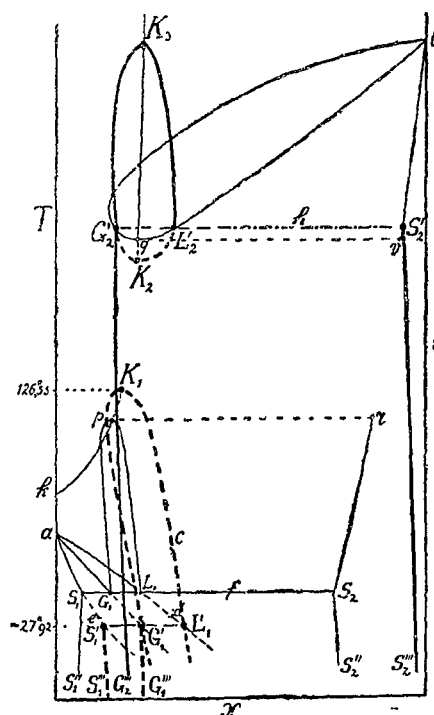


Fig. 4.

tions are given in the figures 3 and 4, and they are easy to understand if we compare what was published before about the system ether-anthraquinone and the system phosphorus.

Anorg. Chem. Laboratory of the University.

Amsterdam, May 30, 1913.

Chemistry. — “*On the pseudo system Methylrhodanide — Methyl-mustard oil.*” By Prof. A. SMITS and H. VIXSEBOXSE. (Communicated by Prof. A. F. HOLLEMAN).

In 1906¹⁾ WALDEN stated the fact that different salts dissolved in methylrhodanide CH_3SCN do not bring about a rise of the boiling point, but a lowering of the boiling point.

It appears from the following table that this phenomenon is brought about by the salts $\text{N}(\text{C}_3\text{H}_7)_4\text{I}$, $\text{N}(\text{C}_2\text{H}_5)_4\text{I}$, CdI_2 , and NH_4CNS .

¹⁾ Zeitschr. f. phys. Chem. 55, 297 (1906).