Chemistry. — *"On Black Phosphorus"*. II. By Prof. A. SMITS, G. MEYER, and R. TH BECK. (Communicated by Prof. S. HOOGEWERFF).

(Communicated in the meeting of June 30, 1917).

As was already communicated before, our researches carried out with BRIDGMAN's black phosphorus have corroborated the supposition that this new form of phosphorus is always metastable under the vapour pressure.

That this is the case at the triple point temperature of the black phosphorus, is beyond doubt, for it appeared that the black phosphorus melts ± 2° lower than the violet phosphorus, hence at ± 587.5°. The vapour tension determinations, however, gave results which, though this did not seem probable, pointed to the possibility that below ± 560° the black phosphorus, and above that temperature the violet phosphorus would possess the smallest vapour tension, or in other words that there exists a transition point between black and violet P at 560°. This conclusion seemed, however, by no means necessary, as the results could also be explained by a too slow establishment of the internal equilibrium at temperatures under ± 560°.

To ascertain whether the black phosphorus under 568° is really stable, the following experiments were made. Equal quantities of violet and black P were heated with 1 % Iodine in a tube of glass that melts with difficulty in vacuum 13 *days* in succession in a bath of KNO_3—$NaNO_3$ at ± 480°.

Then the tube was quickly taken out of the bath, the contents extracted with CS_2 etc. and then the specific weight is determined according to the suspension method. It then appeared that almost everything had been changed into a substance with a specific weight **2.3**, some particles still possessing the spec. weight **2.7**. Accordingly it already follows from this that 560° is no transition temperature, for at 480° the black P was still converted into the violet phosphorus and was therefore metastable [1]).

In the following experiment the proportion between black and

[1]) Without contact with violet P we have not been able to convert the black P into violet P. Even after 4 hours' heating of black P with 1 % I at 580° not the slightest change had occurred.

violet phosphorus was chosen differently, viz. 0.9 black P and 0.1 violet P, and 1 % I was again added to this mixture. The result was that after 16 *days'* heating at 450° practically everything had obtained a specific weight of 2.4, from which therefore in agreement with the result of the preceding experiment, it follows that the violet P is metastable at 450° under the vapour pressure.

It was now the question whether this could also still be demonstrated at lower temperature.

Two tubes were taken of glass that does not melt easily; one filled with $^4/_5$ violet P + $^1/_5$ black P, and the other with $^1/_5$ violet + $^4/_5$ black P. Again 1 % I was added to both mixtures. After being pumped empty and fused off, the tubes were heated for $3^1/_2$ *months* at 380° When then the contents of the two tubes was examined, it appeared that the mass, which at first consisted for $^4/_5$ of violet P and for $^1/_5$ of black P, had been *quite* converted to the violet modification, whereas the mixture that at first consisted for $^1/_5$ of violet, and for $^4/_5$ of black P, had not appreciably changed.

To what it is owing that when the black phosphorus was greatly in the minority, it was entirely converted to violet phosphorus, whereas in the other case nothing could be perceived of a conversion, cannot yet be stated with certainty; the one positive result, however proves already that also at 380° the black modification is the metastable one under the vapour pressure, and this makes the view, set forth in the preceding communication [1]), greatly gain in probability.

Amsterdam, April 10, 1917. *Anorg. Chem. Laboratory of the University.*

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[1]) Proc. **18**, 992 (1915).