to 13000 kg. per cm³. When red phosphorus was started from, this black phosphorus did not form, however, under the same circumstances of temperature and pressure. Undoubtedly this difference is owing to the circumstance that the chemical transformation required to obtain the black phosphorus makes its appearance more easily in the strongly metastable liquid than in the much less strongly metastable *intermediate state*, the red phosphorus. At higher temperature also red phosphorus, and also the violet modification, will have to become black.

Whether this· black modification is really a new modification is still to be decided.

After BRIDGMAN's publication had come under our notice, we asked him to supply us with a small quantity of his black phosphorus in order to investigate this state further by means of vapour pressure determinations etc. Mr. BRIDGMAN has very kindly complied with this request, and we gladly avail ourselves of this opportunity to render him our best thanks for his kindness.

Amsterdam, 24th Dec. 1914.   *Anorg. Chem. Laboratory*
                                                                    of the University.

Chemistry. — *"Further particulars concerning the system phosphorus."*
      By Prof. A. SMITS and S. C. BOKHORST. (Communicated by
      Prof. J. D. VAN DER WAALS).

(Communicated in the meeting of December 30, 1914).

1. *The vapour tension formula for the violet phosphorus.*

When calculating the values for $T \ln P$ from the observed vapour tensions of the solid violet phosphorus (see preceding communication), we find what follows.

When just as we have done for . liquid violet phosphorus, we represent $T \ln P$ graphically as function of T, we come to the result that as Fig. 1 shows the values for $T \ln P$ obtained for the preparations 4 and 1 with the exception of the two lowest points, are without any doubt situated practically on a straight line.

That this is not the case with the two lowest points, is of course to be ascribed to an inaccuracy in the experiment. This inaccuracy may be owing to this that during the heating of the phosphorus in the glass spring, when the latter was being evacuated with the GAEDE pump, a small quantity of white phosphorus was condensed from the vapour on the wall of the glass spring, which of course

TABLE I.
Preparation 2.

t	T	P	TlnP
290°	563°	0.05 atm.	— 1686.6
308.5	581.5	0.09 „	— 1400 2
328	601	0.15 „	— 1140.2
346	619	0.25 „	— 858.1
365	638	0.39 „	— 600 7
384.5	657.5	0.60 „	— 335.8
410	683	1.02 „	+ 13 5
429	702	1.54 „	+ 303.1
444.5	717.5	2.16 „	+ 552.5
456	729	2.82 „	+ 755.7

TABLE II.
Preparation 3.

t	T	P	TlnP
308.5°	581.5°	0.08 atm.	— 1468.7
346	619	0.17 „	— 1096.8
375.5	648.5	0.40 „	— 594.2
394 5	667.5	0.65 „	— 287.5
418	691	1.12 „	+ 78 3
448.5	721.5	2.23 „	+ 578.6
457.5	730.5	2.89 „	+ 775.2
461.5	734.5	3.17 „	+ 847.4
474.5	747.5	4.19 „	+ 1070.9

TABLE III.
Preparation 4.

t	T	P	TlnP
308.5°	581.5°	0.07 atm.	— 1543.1
346	619	0.13 „	— 1263.1
379.5	652.5	0.35 „	— 685.13
408 5	681.5	0.79 „	— 160.67
433.5	706.5	1.49 „	+ 281.79
450.5	723.5	2.30 „	+ 587.64
463.5	736.5	3.18 „	+ 852.20
472.5	745.5	3.88 „	+ 1011.0
486 5	759.5	5.46 „	+ 1289.5

TABLE IV.

Preparation 1. [1])

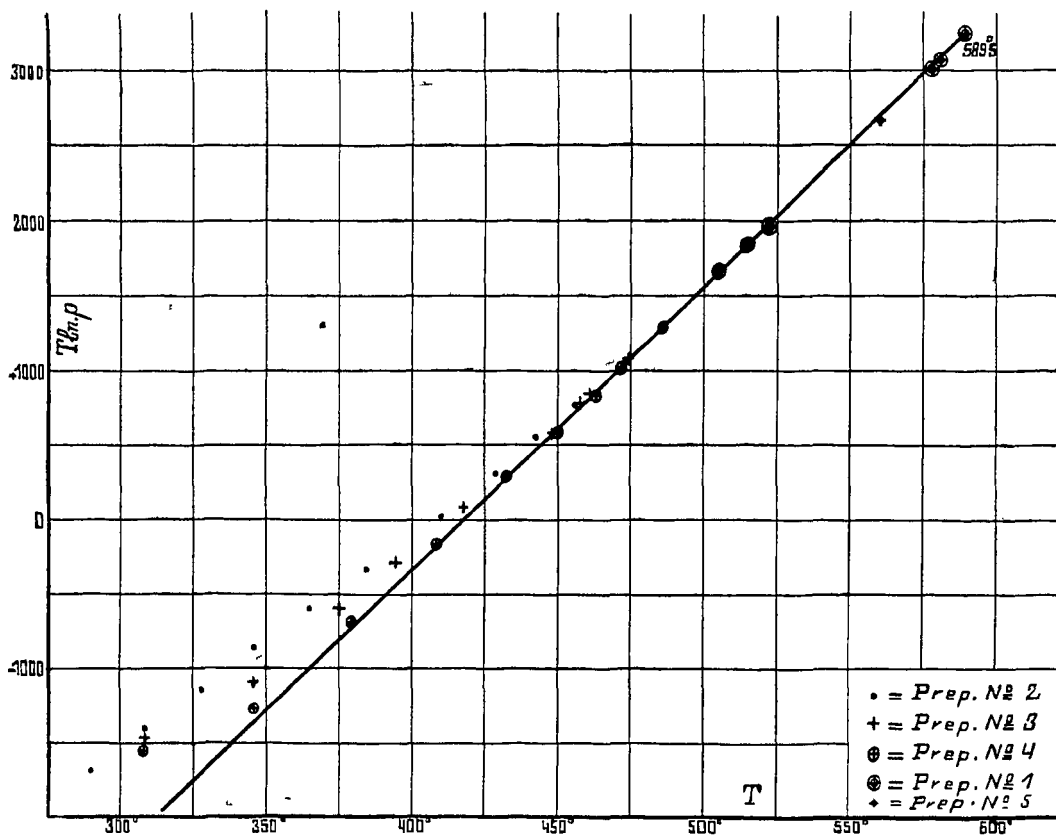| t	T	P	TlnP
505°	778°	8.67 atm.	1680 4
515	788	10.43 „	1847.6
522.5	795.5	11.61 „	1950.4
561	834	24.3 „	2661.3
578	851	34.35 „	3009.6
581	854	36.49 „	3071.8
587 5	869.5	41.77 „	3211.5
588	861	42.10 „	3220.1
589	862	42 5 „	3232.1
589.5	862.5	43.1 „	3246 6

Fig. 1

[1]) Only the most reliable determinations have been used here. The determination at 561° refers to preparation 5.

gives rise to a too high pressure at the lower temperatures, where the establishment of the internal equilibrium takes place so exceedingly slowly.

Besides it is possible, and this is probably the chief reason, that preparation 4 has not yet entirely assumed internal equilibrium at the temperature of preparation, and that therefore the preparation still contained somewhat too much of the volatile pseudo-component.

This somewhat too much caused at those temperatures at which the internal equilibrium sets in most slowly, the greatest error and this will probably be the reason why the deviations are greatest at the lowest temperatures. Considered from this point of view also the much greater discrepancies which the preparations 2 and 3 exhibit at lower temperatures, can be accounted for in a plausible way.

Hence it follows from our investigation about the vapour tension of the solid violet phosphorus that just as for the liquid violet phosphorus $T \ln P$ represented as function of T, yields a straight line, from which it therefore appears that the quantity Q in the equation:

$$\frac{d \ln p}{dT} = \frac{Q}{RT} \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (1)$$

may be considered as a constant, so that we get through integration:

$$\ln p = -\frac{Q}{RT} + C \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (2)$$

or

$$T \ln p = -\frac{Q}{R} + CT \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (3)$$

As we have also done for the liquid violet phosphorus, we can again find the constant C graphically also here, as it is equal to the tangent of the angle α, which the line $T \ln P$ as function of T forms with the temperature axis, for:

$$C = \frac{T_2 \ln p_2 - T_1 \ln p_1}{T_2 - T_1} = tg\alpha.$$

We have $T_1 \ln P_1 = -1400$ for $T_1 = 343,5° + 273°$; $T_2 \ln P_2 = 3246,6$ for $T_2 = 589,5° + 273°$, from which follows $C = 18,889$, a value which is about twice the value of the constant for the *liquid* violet phosphorus.

When with this value for C we now calculate the quantity $\frac{Q}{R}$ for different temperatures, making use of the tables II and IV, we get what follows:

Temperature	$\dfrac{Q}{R}$
308°.5	12527
346	12958
. . . . . .	. . . . .
379.5	13010
408.5	13034
433.5	13065
450.5	13079
463.5	13060
472.5	13071
486.4	13057
505	13006
515	13037
522.5	13076
(561)	(13092)
578	13065
581	13060
587.5	13043
588	13044
589	13051
589.5	13046

Mean 13050

When we now disregard the two first values, because as the graphical representation shows, they certainly refer to determinations which contain a much greater error than the others, and if we also exclude the determination at 561°, because certainly no internal equilibrium had set in here yet, we get as mean value 13050.

Now that C and $\dfrac{Q}{R}$ are known, we can calculate the pressures for the temperatures at which the preparations 1 and 4 have been investigated. Doing this, we get what follows:

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Temperature	Observed pressure	Calculated pressure
308.5°	0.07 atm.	0.03 atm.
346	0.13 ,	0.11 „
. . .	. . . .	. . . .
379.5	0.35 „	0.33 „
408.5	0.79 „	0.77 „
433.5	1.49 „	1.52 „
450.5	2.30 „	2.34 „
463.5	3.18 „	3.22 „
472.5	3.88 „	3.99 „
486.5	5.46 „	5.51 „
505	8.67 „	8.29 „
515	10.43 „	10.26 „
522.5	11.61 „	11.98 „
561	(24.2)	25.5 „
578	34.35 „	34.95 „
581	36.49 „	36.90 „
587.5	41.77 „	41.38 „
588	42.10 „	41.77 „
589	42.6 „	42.5 „
589.5	43.1 „	42.9 „

2. *Heat of sublimation, heat of evaporation and heat of melting of the violet phosphorus in connection with the theory of allotropy.*

From the foregoing calculations exceedingly remarkable conclusions may be drawn.

From the value for $\frac{Q}{R} = 13050$ follows for the mol. heat of sublimation the extraordinarily high value 25.839 K. Cal., while we have found 9.962 K. Cal. for the mol. heat of evaporation of liquid violet phosphorus, so that 15.877 K. Cal. follows from these two quantities for the mol. heat of melting.

According to the theory of allotropy evaporation and melting is accompanied with a chemical reaction between the pseudo components of the substance, and the more the coexisting phases differ in con-

centration, the greater will be the chemical transformation of one phase into another. It follows from this that the sublimation heat, the evaporation heat of the liquid and the melting heat will consist for a greater part of a chemical heat as the coexisting phases differ more in concentration. The quantities of heat found above are of importance in this respect, because they confirm this view in the most convincing way.

According to the theory of allotropy the difference in concentration between the solid violet phosphorus and the vapour is greatest, and that between the liquid phosphorus and the vapour smallest. This tallies perfectly with the colour of the phases; the vapour phase is always colourless, just as the liquid phase.

The evaporation of the solid phosphorus and the melting of the solid phosphorus will therefore be processes which are accompanied with a strong chemical conversion, whereas this reaction is probably only slight during the evaporation of the liquid.

The found values for the three mentioned quantities of heat confirm this perfectly, and the exceedingly high values for the mol. sublimation heat and the mol. melting heat prove that the heat effect is for the greater part a chemical heat. The sublimation heat of the violet phosphorus is even so great that it is of the order of magnitude of the sublimation heat of NH_4Cl, which amounts to 37.9 K. Cal., and in which the dissociation heat is included.

For the difference of energy between white and violet phosphorus per gram-atom the following has been found:

$$P_{white} \rightarrow P_{violet} + 4.4 \text{ cal. [1]}.$$
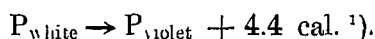
If we now assume for a moment, what certainly is not far from the truth, that this heat effect is entirely a chemical heat, and if we further assume that these two phases differ almost as much from each other in concentration as the violet phosphorus and its vapour, then a chemical heat of about $4 \times 4{,}4$ K. Cal. will be included in the mol. sublimation heat. If we subtract this heat effect from the molecular sublimation heat, we keep for the physical heat $25{,}8 - 17{,}6 = 8.2$ K. Cal.; this is a heat effect that lies already much nearer the sublimation heats of other comparable substances in which a chemical heat is also included, but a much smaller one than for the violet phosphorus. The mol. sublimation heat of SO_3 e.g. amounts to 11,79 K. Cal.[2].

The difference in concentration between violet phosphorus and

[1] GIRAN, Ann. Chim. phys. (7) 30, 203 (1903).

[2] C. R. 90, 1511 (1880).

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the coexisting colourless liquid phase is certainly considerably smaller than that between violet phosphorus and its vapour, which also follows from the molecular heat of melting, for which we found, as was stated above, 15,877 K. Cal. from the mol. sublimation heat and evaporation heat.

3. Size of the phosphorus molecule.

As we published some time ago[1]) we succeeded in determining the vapour tension line of liquid phosphorus between 504° and 634°. On that occasion we showed at the same time that when $T \ln P$ is represented as function of T, a perfectly straight line is formed as a proof that here too the Q from the equation:

$$T \ln P = -\frac{Q}{R} + CT$$

is no appreciable function of the temperature.

Now lately Wahl[2]) determined the critical temperature of liquid violet phosphorus in a quartz tube, and found for it the temperature 695°. As now the line for $T \ln P$ as function of T, appeared to be a straight line from 504° to 634°, it was perfectly justifiable to prolong this line to 695°, hence to read the value of $T \ln P$ at $T = 695° + 273° = 968°$ by extrapolation, and derive from this the value of P, hence of the critical pressure. In this way 4284 was found for $T \ln P$, from which follows $P_k = 83.56$ atm.

Now that we know the critical data for the liquid violet phosphorus it is of importance to inquire what can be derived from these data about the size of the phosphorus molecule.

For this purpose we calculate the b value by the aid of van der Waals' relation:

$$b = \frac{1}{8.273} \cdot \frac{T_k}{P_k} = \frac{1}{8.273} \cdot \frac{268}{83.6}$$

or

$$b = 0,005304.$$

When we now assume the b to be an additive quantity we can find the b of a phosphorus atom e.g. from the b-value of e.g. PH_3, and when we then divide the b value of the phosphorus molecule by this value, we find the number of atoms of phosphorus present in the molecule.

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[1]) These Proc. Vol XVI. p. 1174.
[2]) Meddelanden Fran Finska Kemistsamfundet 1913, 3.

For the critical quantities of PH$_3$ Leduc and Sacerdote[1]) found what follows:

$$t_k = 52,8° \text{ and } P_k = 64 \text{ atm.}$$

If the b is calculated from this, we find:

$$b = 0,002330.$$

According to van der Waals' new views "*The volume of the molecules and the volume of the component atoms*"[2]) hydrogen presents the peculiarity that the b of a hydrogen atom in a compound is much smaller than in the hydrogen molecule; it amounts viz. to 0.000362 instead of 0.000825, from which follows that for the 3 hydrogen atoms in PH$_3$, 0,001086 must be taken. We then get:

$$0.002330—0 001086 = 0.001244$$

for the b-value of the phosphorus atom, from which follows:

$$\frac{0,005304}{0,001244} = 4,26$$

for the size of the phosphorus molecule at the critical temperature and pressure of the liquid violet phosphorus.

This result already points to a small association, for on an average the phosphorus molecule is greater than P_4.

4. *Calculation of the factor f of* Van der Waals' *vapour tension formula.*

Finally we have also calculated the value of the factor f from the empirical vapour tension equation of Van der Waals.

$$- \ln \frac{p}{p_k} = f\left(\frac{T_k}{T} - 1\right)$$

When we consider the pressures at two different temperatures, then it follows from this relation that

$$\frac{0,4343 \ (T_1 \ln P_1 - T_2 \ln P_2)}{T_1 - T_2} = f,$$

from which it appears that f is graphically to be derived from the line that represents $T \ln P$ as function of T. Over a range of temperature of 200°, viz. from 500° to 700°, $T \ln P$ increases from 2388 to 4332, so by 1944.

From this follows that:

$$f = \frac{0,4343 \times 1944}{200} = 4,221.$$

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[1]) C.R. **125**, 397 1897).

[2]) These Proc. Vol. XVI. p. 880.

For substances for which the size of the molecules in the vapour and the liquid phase is equal or about equal f is about 3, so that the value 4,221 indicates that for the violet phosphorus the average size of the molecules in the coexisting vapour and liquid phases is different.

A discussion of the vapour tension line of the white phosphorus will be reserved for another paper.

Anorg. Chem. Laboratory of the University.
Amsterdam, Dec. 24, 1914.

Anatomy. — "*On the termination of the efferent nerves in plain muscle-cells, and its bearing on the sympathetic (accessory) innervation of the striated muscle-fibre.* By Prof. J. Boeke.

(Communicated in the meeting of December 30, 1914).

In recent years it has been demonstrated for a large number of different types of striated muscle-fibres of vertebrates, that the motor nerve-endings, which carry the nervous impulses towards the muscular fibres, are hypolemmal in position, i.e. are not lying outside the sarcolemma of the muscle-fibres as maintained by most of the earlier observers, but pass through the sarcolemma, which becomes continuous with the neurilemma, penetrate into the sarcoplasm of the muscle-fibre, which is considerably thickened as the site of formation of the end-organs, and it was further assumed, that here the neurofibrillar expansion of the motor nerve-ending is directly continuous with a reticulum in the sarcoplasm, the so-called "periterminal network" [1].

At the same time it was shown, that beside the common motor nerve-ending there must be distinguished another afferent nerve-ending on the striated muscle-fibres of vertebrates, which may either be found imbedded in the same granular bed of sarcoplasm or "sole" of the motor endorgan of Kühne, or reaching the muscle-fibre independent of this, but always having a hypolemmal position in the muscle-fibre [2]. This "accessory" nerve-ending is always found at the end of a non-medullated nerve-fibre. As it could be shown, that these accessory nerve-endings did not degenerate after the cutting of the efferent muscle-nerve near the place of exit from the central nervous system, before the entering of the sympathetic nerve-fibres

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[1] J. Boeke. Beiträge zur Kenntniss der motorischen Nervenendigungen. I. II. Internat. Monatschr. f. Anatomie und Physiologie Bd. 28. 1911.

[2] J. Boeke. Die doppelte (motorische und sympathetisch) efferente Innervation der quergestreiften Muskelfasern. Anat. Anzeiger. 44. Band. 1913.