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**Physics.** — “*On the Critical Temperature and Pressure of Mercury and Phosphorus.*” By Dr. J. J. VAN LAAR. (Communicated by Prof. H. A. LORENTZ).

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### A. Mercury.

1. In a previous paper<sup>1)</sup> I calculated the value 1260° abs. (987° C.) for the critical temperature of mercury, and 192 atm. for the critical pressure.

We namely calculated as most probable value from the densities of the compounds HgCl<sub>2</sub>, HgBr<sub>2</sub> and HgI<sub>2</sub> (loc. cit. p. 7—8) for  $\bar{b}_k$  for mercury per Gr. atom the value  $150 \cdot 10^{-5}$ , and further for  $\sqrt{a_k}$  from the values of  $T_k$ , found by ROTINJANZ (Z. f. ph. Ch. **87**, p. 153) for these compounds, the mean value (likewise per Gr. atom)  $11,0 \cdot 10^{-2}$ . (loc. cit. p. 8). With these values of  $\sqrt{a_k}$  and  $\bar{b}_k$  we further calculate from the formulae

$$RT_k = \frac{8}{27} \lambda \frac{a_k}{\bar{b}_k} \times n \quad ; \quad p_k = \frac{1}{27} \lambda \frac{a_k}{\bar{b}_k^2},$$

with  $R = 1 : 273,1$ ,  $\lambda = \frac{27}{28} = 0,964$ ,  $n = 2$ , the values

$$T_k = 1260 \quad ; \quad p_k = 192 \text{ atm.}$$

All this on the supposition that (saturated) mercury vapour at  $T_k$  is bimolecular ( $n = 2$ ); a supposition, to which the course of the vapour tensions between 0° and 500° C. leads us necessarily. (Cf. also loc. cit. p. 12—16).

2. Since then the vapour pressure observations of CAILLETET, COLARDEAU and RIVIÈRE (1900) have become known to me, which go up to 880° C. With

$$\log \frac{p_k}{p} = f \left( \frac{T_k}{T} - 1 \right), \quad \text{or} \quad f + \log p_k = \log p + \frac{fT_k}{T}$$

we calculate for  $fT_k$  the values 3004, 2979, 3233, 3107 (mean 3080) from the values 8,0, 22,3, 50, 102, 162 atm. at resp. 500°, 600°, 700°, 800°, and 880° C.; always from a corresponding couple of

<sup>1)</sup> On the Fundamental Values of the Quantities  $\bar{b}$  and  $\sqrt{a}$  etc. II. These Proc. of March 25, 1916, p. 4 and 9.

values of  $T$  and  $p$ . ( $f$  between two observations supposed to be constant). And for  $f + \log p_k$  the values 4,789, 4,760, 5,022, 4,905; evidently the value 4,880 for  $f + \log p_k$  corresponds with the mean value 3080 found just now for  $fT_k$ .

The correction quantity  $\lambda$  is represented (compare also loc. cit. p. 4) by the expression  $\lambda = \frac{27}{8\gamma-1} \left( \frac{\gamma}{\gamma+1} \right)^2$ . And as  $\gamma$ , the coefficient of direction of the straight connecting line between  $D_k$  and  $D_0$ , is given by the approximative formula  $2\gamma = 1 + 0,04\sqrt{T_k}$ , we find, with about  $\sqrt{T_k} = 34,5$ , for  $2\gamma$  the value 2,38 (which at the same time indicates the ratio  $b_k : b_0$ ), i. e. 1,19 for  $\gamma$ . Therefore  $\lambda$  becomes = 0,936, i. e. somewhat smaller than we assumed formerly (0,964, see above).

If now  $x$  is the dissociation degree of the  $Hg_2$ -molecules at  $T_k$ , there are on an average  $n = 2 : (1 + x)$  atoms available per molecule (the association degree of  $Hg_1$ ), and we have evidently:

$$\left. \begin{aligned} T_k &= 273 \times \frac{8}{27} \times 0,936 \times \frac{(11(1-x) + 36x)^2 \cdot 10^{-4}}{150 \cdot 10^{-5}} \times \frac{2}{1+x} \\ p_k &= \frac{1}{27} \times 0,936 \times \frac{(11(1-x) + 36x)^2 \cdot 10^{-4}}{(150)^2 \cdot 10^{-10}} \end{aligned} \right\}$$

because the quantity  $\sqrt{a_k}$  is =  $11 \cdot 10^{-2}$  per Gr. molecule for Hg molecules bound to  $Hg_2$ ; much higher on the other hand for the free mercury atoms, viz.  $36 \cdot 10^{-2}$  (cf. IV in These Proc. Vol. XIX, p. 317, where we found for bismuth, which stands in the same horizontal row as mercury, 35,6), so that  $\sqrt{a_k}$  becomes on an average =  $11(1-x) + 36x$  per Gr. atom.

Hence we find:

$$\left. \begin{aligned} T_k &= 10,10 \times \frac{(11(1-x) + 36x)^2}{1+x} \\ \log p_k &= 0,1877 + 2 \log (11(1-x) + 36x) \end{aligned} \right\}$$

with  $fT_k = 3080$ ,  $f + \log p_k = 4,880$  therefore (see above):

$$f = 4,692 - 2 \log (11(1-x) + 36x),$$

so that  $x$  can be found from

$$\frac{10,10 ( )^2}{1+x} = \frac{3080}{4,692 - 2 \log ( )},$$

or from

$$[4,692 - 2 \log (11(1-x) + 36x)] \times (11(1-x) + 36x)^2 : (1+x) = 305.$$

If now  $x = 0$  for  $T_k$ , i. e. everything bimolecular, this becomes with  $10^2 \cdot \sqrt{a_k} = 11$ :

$$316 = 305,$$

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which, considering the uncertainties in the values of  $b_k$  and  $\sqrt{a_k}$  calculated from the halogen compounds, is already very fair agreement. With  $\sqrt{a_k} = 10,8$  we should have found  $306 = 305$ .

With  $x = 0,1$  we should find  $393 = 305$  with  $\sqrt{a_k} = 9,7 + 3,6 = 13,3$ , which therefore does not agree at all. And for still higher values of  $x$  the difference would have become greater and greater.

The *least* dissociation of  $Hg_2$  to  $Hg_1$  for  $T_k$  is accordingly *quite excluded*, so that we must assume that the mercury is *perfectly bimolecular* there. The *liquid* mercury is *à fortiori* bimolecular, the saturated mercury *vapour* on the other hand will be  $Hg_1$  only at *lower* temperatures (where the large volume prevails); at higher temperatures, however, in consequence of the decreasing volume, it will become  $Hg_2$  in ever increasing degree (cf. also loc. cit. p. 3—4).

3. With the somewhat lower value for  $\lambda$ , viz.  $\lambda = 0,936$ , and with  $b_k = 150 \cdot 10^{-5}$ ,  $\sqrt{a_k} = 10,8 \cdot 10^{-2}$  we now find:

$$T_k = 10,10 \times 116,6 = 1178^\circ \text{ abs.} = 905^\circ \text{ C.}$$

It is therefore seen that at  $880^\circ$  CAILLETET c. s. have been *exceedingly near* the critical temperature of mercury, viz.  $\pm 900^\circ$  C.; it lies possibly *scarcely*  $20^\circ$  *higher* than the highest temperature at which they have still carried out a vapour pressure determination ( $880^\circ$  C.).

Would it not be desirable in virtue of this fact to determine the critical temperature of mercury at last experimentally? As it was possible to ROTINJANZ to determine those of the mercury halides, which lie resp. at  $976^\circ$ ,  $1011^\circ$  and  $1072^\circ$  abs., it may also be possible to come to  $\pm 1200^\circ$  abs. (at the melting point of silver, viz.  $960^\circ$  C., we are already far above the critical temperature of mercury).

The only scientist that calculated a fairly plausible value for  $T_k$  for Hg, was HAPPEL (Ann. der Ph. (4) 13, 351 (1904)), who gave  $1370^\circ$  abs., i. e. only  $100^\circ$  higher than was calculated by me in 1916 ( $1260^\circ$  abs.). But the values of KÖNIGSBERGER (1912), viz.  $1270^\circ$  C. ( $1543$  abs.) and of BENDER (1915), viz.  $> 1500^\circ$  C. ( $> 1773^\circ$  abs.) are very certainly too high. As  $f T_k$  not far below  $T_k$  amounts only to  $= 3080$  (this follows with absolute certainty from the vapour pressure observations, see above), the value of the factor  $f$  would at high temperatures be only  $= 2$ , or even  $1,7$ , instead of approaching  $2,8$  (see below), whereas this factor is already about  $2,7$  or  $2,6$  between  $0^\circ$  and  $100^\circ$  C. — still apart from the fact that

then we should find quite improbable values for  $a_k$  and  $b_k$ <sup>1)</sup>.

We calculate for  $p_k$ :

$$\log p_k = 0,1877 + 2,0668 = 2,2545,$$

i. e.

$$p_k = 180 \text{ atm.}$$

In order to get somewhat more certainty concerning the values of  $T_k$  and  $p_k$ , and also of  $\sqrt{a_k}$  and  $b_k$ , we can still make the following calculation.

From  $f T_k = 3080$ ,  $f + \log p_k = 4,880$  follows namely with  $f$  resp. = 2,5, 2,6 and 2,65:

$f = 2,50$	$T_k = 1232$	$\log p_k = 2,380$	$p_k = 240$
2,60	1185	2,280	191
2,65	1162	2,230	170

From  $8n \cdot b_k = R T_k : p_k$  follows then with  $n = 2$ ,  $R = 1$ : 273 for  $b_k$  (per Gr. atom)  $b_k = T_k : 4370 p_k$ , i. e.  $b_k$  resp. = 117, 142 and  $156 \cdot 10^{-5}$ .

With these values for  $b_k$  we get then  $a_k$  resp. = 95,2, 111,3,  $119,6 \cdot 10^{-4}$ , i. e.  $\sqrt{a_k}$  (per Gr. atom) resp. = 9,76, 10,55 and  $10,94 \cdot 10^{-2}$ , from  $T_k = 151,5 a_k : b_k$ .

It appears from this most convincingly that — as  $b_k$  must lie in the neighbourhood of  $150 \cdot 10^{-5}$ ,  $\sqrt{a_k}$  in that of  $11 \cdot 10^{-2}$  — the value 1232 abs. is pretty well excluded for  $T_k$ , and that we have therefore the choice between from 1185 to 1162. Retaining  $b_k = 150 \cdot 10^{-5}$ , we get  $\sqrt{a_k} = 10,77 \cdot 10^{-2}$ , as we assumed above (rounded off 10,8), and further:

$$\underline{T_k = 1172 \text{ abs.} = 899^\circ \text{ C.} \quad ; \quad \underline{p_k = 179 \text{ atm.}}$$

But it is also possible that  $T_k$  becomes somewhat higher, e. g.  $1185^\circ$ , to which corresponds  $p_k = 191$  atm. Then the value of  $\sqrt{a_k}$  would, however, be still lower than that which we calculated from Hg I<sub>2</sub>, viz.  $10,7 \cdot 10^{-2}$  (loc. cit. p. 8), and that of  $b_k$  would become  $= 142 \cdot 10^{-5}$ , i. e. equal to that which was calculated from this same compound. But these were the very lowest values. Those which were calculated from Hg Cl<sub>2</sub> and Hg Br<sub>2</sub>, were both higher (loc. cit. p. 8).

<sup>1)</sup> With regard to the value of  $a$ , I have convinced myself that from the compressibility of mercury at  $0^\circ$ ,  $110^\circ$ , and  $192^\circ$  C. follows about the same value of  $a$  as was calculated from the mercury halides for  $a_1$ . And with regard to  $b_k$ , even on the supposition that Hg<sub>2</sub> for liquid mercury has the stoichiometric properties of mercurio compounds, a value would follow from the densities of Hg<sub>2</sub>Cl<sub>2</sub> and Hg<sub>2</sub>Br<sub>2</sub> for Hg (per Gr. atom) in Hg<sub>2</sub>, which is only little less than was found for Hg in the *mercuri* compounds. (viz. about  $140 \cdot 10^{-5}$  instead of  $150 \cdot 10^{-5}$ ).

4. For the successive values of VAN DER WAALS' vapour pressure factor  $f$  we now find between  $0^\circ$  and  $880^\circ$  C. from the following vapour pressure observations (at lower temperatures mean values)

	$0^\circ$	$100^\circ$	$200^\circ$	$300^\circ$	$400^\circ$	$500^\circ$	$550^\circ$	$600^\circ$	$650^\circ$	$700^\circ$
$p = 24 \cdot 10^{-5}$	0,2775	17,13	246	(mm.)	2,05	8,0	13,8	22,3	34	50
	$750^\circ$	$800^\circ$	$850^\circ$	$880^\circ$ C.						
	72	102	137,5	162 (atm.)						

the following values.

$\log \frac{p_k}{p}$	8,7534	5,6903	3,8998	2,7427	1,9410	1,3497	1,1129
	0,9045	0,7213	0,5538	0,3955	0,2442	0,1145	0,0433
$\frac{T_k}{T} - 1$	3,2930	2,1421	1,4778	1,0454	0,7415	0,5162	0,4241
	0,3425	0,2698	0,2045	0,1457	0,0923	0,0436	0,0165
$f_{10} = 2,66$	2,66	2,66	2,64	2,62	2,62	2,61	2,62
						(min)	
	2,64	2,67	2,71	2,71	2,65	2,63	2,62
$f_e = 6,12$	6,12	6,12	6,08	6,04	6,03	6,02	6,04
	6,08	6,15	6,24	6,25	6,09	6,05	6,04

The value of  $p$  at  $0^\circ$  C. has probably been taken still somewhat too high; we assumed 0,00024 for it (HERTZ gave 0,00019, v. D. PLAATS 0,00047). And especially for the values at the higher temperatures the slightest error in the vapour pressure will make itself greatly felt in the calculated values of  $f$ ; the same thing holds with respect to only an minimum error in the calculated values of  $p_k$  and  $T_k$ . If we assume e. g.  $p_k = 180$  atm. instead of 179 atm.,  $\log p_k$  becomes 24 units in the last decimal greater, which would cause the values of  $f$  at the highest three temperatures to rise immediately to 2,67, 2,68, and 2,77 (with nep. log.: 6,15, 6,17, 6,38). Then  $b_k$  would get the value  $149 \cdot 10^{-5}$  instead of  $150 \cdot 10^{-5}$ , and  $\sqrt{a_k}$  would become 10,74 instead of 10,77. But in any case the course of  $f$  is pretty regular; this quantity decreases from about 2,66 at  $0^\circ$  C. to 2,61 (the minimum value) at  $500^\circ$  C., after which it increases again to 2,7 or 2,8 at the critical temperature. The minimum lies at  $T = 0,66 T_k$ .

The value of  $f$  at the critical temperature might have been expected higher than 6,4 or 6,5 (nep. log.), since  $f_k$  is equal to  $8\gamma$  according to our former considerations, when neither  $a$  nor  $b$  are functions of the temperature. Now  $\gamma$  is about  $= 1,2$ , hence  $8\gamma$  would be  $= 9,6$ . But we should bear in mind that exactly in the case of mercury  $a$  would be a temperature function in a high degree. For only through the predominant influence of the volume does  $Hg_2$  become  $Hg_1$  at higher temperatures, whereas if the temperature influence only could make itself felt,  $Hg_2$  would dissociate to  $Hg_1$ ,

which would cause  $\sqrt{a}$  to rise from about 11 to 36. The value of  $\left(\frac{dn}{dt}\right)_v$  at  $T_k$  will, therefore, be very great positive, and this will lower the value of  $\left(\frac{dp}{dt}\right)_v$  at the critical temperature considerably. Hence the value of  $f_k = \left(\frac{T}{p} \frac{dp}{dt}\right)_k$  will also be considerably lower than the normal value. In our case the expected value is diminished from 9,6 to 6,5.

As  $T_k$  is now found = 1172° abs. instead of 1260° abs., as I calculated before, the ratios  $T_k : T_s$  and  $T_k : T_n$  will also be somewhat lower. For the former we find 1172 : 630 = 1,86, and for the latter 5,0. So high a value for the ratio  $T_k : T_n$  is only found for He (5,2) and for Bismuth (5,5) of the elements calculated by us up to now. But we shall soon see (in a following paper), that  $T_k : T_n$  is also = over 5 for tin, lead and the alkali metals. A pretty high value of  $T_k : T_s$  (i. e.  $> 1,7$ ) is also found for Argon, Krypton, Xenon, Niton (1,73—1,79), for the Halogenides (1,75 to 1,72), for O<sub>2</sub> (1,71), for P, Sb and Bi (1,75—1,77), but 1,86 was not reached yet. Among the compounds we mention HCl (1,71), HBr (1,78), HI (1,79), H<sub>2</sub>O (1,71), H<sub>2</sub>S and H<sub>2</sub>Se (1,77), PH<sub>3</sub> (1,75), CS<sub>2</sub> (1,71), CH<sub>4</sub> (1,75), H. COH (1,97), while the three mercury halogenides, examined by ROTINJANZ, give 1,69 to 1,71.

5. In conclusion I will still point out that  $b_k = 150 \times 10^{-5}$  does not only ensue from the densities of the mercury halogen compounds (see § 1), but also from the density of mercury itself. For it follows from DEWAR's determinations (1902), who found the value 14,382 for the density at 188° C., and those of MALLETT, who gave 14,193 for the density at -39°, that the limiting density  $D_0$  at about -250° (below this no appreciable volume diminution takes place) will amount to 14,46. 200,6 Gr. of mercury then occupy a space of  $200,6 : 14,46 = 13,87$  ccm., i. e. =  $13,87 : 22412 = 61,9 \cdot 10^{-5}$  in so called normal unities. This is, therefore,  $b_0 = v_0$ . Now according to one of our formulae  $b_k : b_0 = 2\gamma$ , hence  $b_k = 61,9 : 10^{-5} \times 2,4 = 149 \cdot 10^{-5}$ , quite identical to the value which we found above (§ 4) with  $p = 180$  atm. We may, therefore, put the value of  $b_k$  for mercury at  $150 \cdot 10^{-5}$  with great certainty.

The value of  $D_k$  is found from the formula  $D_k = D_0 : 2(1 + \gamma) = 14,46 : 4,4 = 3,3$ .

Recapitulating we probably have for mercury

$T_k = 1172^\circ$  abs. ( $\pm 900^\circ$  C.) ,  $p_k = 180$  atm ,  $d_k = \pm 3,3$   
 $b_k = 149 \cdot 10^{-5}$  ,  $\sqrt{a_k} = 10,74 \cdot 10^{-2}$  ,  $2\gamma = b_k b_0 = 2,4$  ;  $f_k = \pm 6,4$   
 $T_k : T_s = 1,86$  ;  $T_k \cdot T_b = 5,0$ .

These values are pretty certain, the critical temperature lies — taking the vapour pressure observations between  $500^\circ$  and  $880^\circ$  into consideration — almost as much as  $100^\circ$  lower than I had calculated in 1916, and *only*  $20^\circ$  higher than the highest temperature at which CALLETET c.s. have carried out their vapour pressure determinations.

That it *seems* at lower temperatures that the critical temperature of mercury lies much higher (as among others KONGSBERGER and BENDER supposed), is owing to this that the expansion of liquid mercury is *abnormally small* at those temperatures ( $0^\circ$ — $300^\circ$  C.). But this is to be attributed to still unknown disturbing circumstances (association e.g.). As little as we may conclude to entirely faulty critical values from the abnormal expansibility of water in the neighbourhood of  $4^\circ$  C. (and still far above it), or of Helium (where likewise a maximum density was observed), may we do so for mercury. We shall come back to this later on.

## B. Phosphorus.

1. From the vapour pressures of liquid phosphorus, found by himself between  $169^\circ$  and  $634^\circ$  (These Proc of Oct. 17, 1914 and Jan. 18, 1915; Z. f. ph. Chem. **88** (1914), **91** (1916)), SMITS extrapolated the value 82,2 atm. for the critical pressure, on the assumption of the value  $695^\circ$  C., found by WAHL for the critical temperature of Phosphorus. It is easy to see that this value is *too low*. If from the vapour pressure formula

$\log \frac{p_k}{p} = f \left( \frac{T_k}{T} - 1 \right)$  with  $T_k = 695 + 273,1 = 968,1$  we, namely, calculate the values of  $f$  at ten different temperatures, we find with  $p_k = 80$ , resp. 90 atm.:

$t =$	169°,0	210°,0	252°,0	298°,6	355°,7	409°,3	504°	550°	593°	634° C
$p =$	0,04	0,20	0,54	1,38	3,88	(7,36)	23,2	33,0	44,2	58,6 atm.
$\log \frac{p_k}{p} =$	3,3010	2,6021	2,1707	1,7632	1,3143	1,0362	0,5376	0,3846	0,2577	0,1352
	3,3522	2,6532	2,2218 <sup>s</sup>	1,8144	1,3654	1,0874	0,5887 <sup>s</sup>	0,4357	0,3088	0,1863
$\frac{T_k}{T} - 1 =$	1,1898	1,0039	0,8437	0,6934	0,5396	0,4187	0,2458	0,1762	0,1178	0,0672
$f =$	2,77	2,59	2,57	2,54	2,44	(2,47)	2,19	2,18	2,19	2,01
	2,82	2,64	2,63	2,62	2,53	(2,60)	2,40 (min)	2,47	2,62	2,77



From this it is evident that the first row of values (which correspond to  $p_k = 80$  atm.) cannot be correct. For then  $f$  would *steadily* decrease from the value 2,77 at  $169^\circ$  up to the critical temperature, where the value would even become  $< 2$ !, whereas it is known that  $f$  always passes through a *minimum* at  $T =$  about 0,7 or 0,8  $T_k$ , after which it *increases* again to  $T_k$ . It is easily seen that also with  $p_k = 82$  atm. the decrease has not been checked up to  $T_k$ , and that not until 90 atm. is reached a suitable and *possible* course for  $f$  is obtained. A further calculation, about which presently more, has even taught me that the correct value of  $p_k$  is still somewhat higher, viz. about 95 atm. — at least when we continue to assume  $T_k = 968,1$ .

That SMITS extrapolated a too low value for  $p_k$ , is owing to this that he used an invalid formula for this extrapolation; a formula namely, which is only valid at temperatures that he far from the critical temperature — and which can therefore not serve to extrapolate up to the critical temperature.

For in the well-known relation of CLAPEYRON

$$\frac{dp}{dt} = \frac{\lambda}{T \Delta v}$$

$\Delta v = v_2 - v_1$  can be replaced by  $v_2$  only at *low* temperature, disregarding the liquid volume; and only at *low* temperatures  $v_2 = RT/p$  may be put, on the assumption that the vapour follows the law of BOYLE — so that *only then* this formula becomes:

$$\frac{d \log p}{dt} = \frac{\lambda}{RT^2}$$

in which  $\lambda$  represents the (total) heat of evaporation. In imitation of so many other authors, who are still of opinion that this last formula is of general validity, because VAN 'T HOFF and others always used this *limiting* formula for researches where the above mentioned conditions are *fulfilled*, SMITS assumed that the formula with  $d \log p$  would *continue to be valid up to the critical temperature*, when it was only assumed that  $\lambda$  decreases linearly with the temperature up to  $T_k$ . This now is certainly pretty accurately fulfilled at *lower* temperatures, but near  $T_k$   $\lambda$  suddenly decreases rapidly and becomes  $= 0$  at the critical temperature. On SMITS' assumption of linear decrease, however;  $\lambda$  would retain a large finite value still at  $T_k$ !

But we need not speak about this any longer, because, as we observed, the whole formula, the linear decrease of  $\lambda$  included, holds

only for *lower* temperatures. And this shows at the same time the incorrectness of the extrapolation carried out by SMITS.

At *all* temperatures, however, VAN DER WAALS' vapour pressure holds, which may be written in the form:

$$\log p = (f + \log p_k) - \frac{fT_k}{T}, \quad . . . . . (a)$$

in which  $f$  is still a temperature function. When we compare this expression with the integrated formula  $d \log p = \text{etc.}$ , on the assumption of  $\lambda = \lambda_0 - \varphi RT$ , i. e. with

$$\log p = C - \frac{\lambda_0}{RT} - \varphi \log T = C - \frac{(\lambda_0 : R) + \varphi T \log T}{T}, \quad . (b)$$

it appears that in the formula used by SMITS, which — we repeat it — holds only for relatively low values, the constant  $C$  will be  $= f_0 + \log p_k$ , and that  $\lambda_0 = f_0 RT_k$ . But though the *form* of the last formula shows resemblance with VAN DER WAALS' formula, the numerator of the term with  $1/T$  will be in no connection at all with  $\lambda$  at *higher* temperatures, as  $\lambda$  will approach 0 at  $T_k$ , while the numerator mentioned remains finite, and is virtually  $= fT_k$ , according to VAN DER WAALS' formula.

2. On the assumption of the quadratic relation

$$f = f_k - \alpha \frac{T_k - T}{T_k} + \beta \frac{(T_k - T)^2}{T_k^2}$$

for the portion of the vapour pressure curve between the minimum and the critical temperature, I calculated the values  $\alpha = 11,71$ ,  $\beta = 26,62$ ,  $f_k = 3,77$ ,  $p_k = 95,3$  for the four unknown quantities  $\alpha$ ,  $\beta$ ,  $f_k$ , and  $p_k$  from the four vapour pressure observations at  $504^\circ$ ,  $550^\circ$ ,  $593^\circ$ , and  $634^\circ$ .

However — neither the values  $T_k = 968,1$ ,  $p_k = 95$ , nor even with the somewhat lower pressure 90 atm., can satisfy us. It is namely almost sure that at  $695^\circ$  C., according to the determinations of the density of STOCK, GIBSON and STAMM (1912), the phosphorus vapour is still quite normal, i. e.  $= P_4$ , even at the low pressure of 75 m.m. And this will *à fortiori* be the case at a pressure of 80 à 90 atm. (i. e. at a *total* pressure, internal and external pressure combined, of  $f_k \times 80$  or  $90 = \pm 640$  or  $720$  atm.). The same thing follows also from PREUNER and BROCKMÖLLER's determinations (Z. f. ph. Chem. **81**, p. 159 (1912)).

From the formula  $b_k = RT_k : 8p_k$  the value  $465 \cdot 10^{-5}$  would now follow for  $b_k$  with  $T_k = 968,1$ ,  $p_k = 95,3$ ; and with  $p_k = 90$  the value  $492 \cdot 10^{-5}$ . Both most probably too low, as  $4 \times 140 = 560 \cdot 10^{-5}$  may be expected.

The only way out is that the critical temperature 695° C. determined by WAHL is about 20° or 25° too high, and that 675° or 670° C. is perhaps the correct temperature.

When the above given calculation (with  $f = f_k - \alpha$  etc.) is now repeated for different values of  $T_k$ , we find e.g.

$T_k = 695^\circ \text{ C}$	$\alpha = 11,71$	$\beta = 26,62$	$f_k = 3,77$	$p_k = 95,3$	$b_k = 465$
680° "	10,31	25,80	3,48 <sup>5</sup>	83,6	522
670° "	9,40	25,26	3,31	77,1	560

Only the last value of  $T_k$ , viz. 670°, gives a plausible value of  $b_k$  with the corresponding value of  $p_k = 77,1$  atm. But as this value for phosphorus is not *perfectly certain*, it is also possible that an intermediary value, e.g. 675° C., must be assumed. The value of  $p_k$  would then become about 80 atm., and  $b_k$  a little more than  $540 \cdot 10^{-5}$ . With a value 2% lower, i.e. 948,7 abs. instead of 968,1 abs., or 675,6 C., and with  $p_k = 80$  atm. we should find the following values for  $f$  for the same ten temperatures as in § 1.

$\log \frac{p_k}{p}$	3,3010	2,6021	2,1707	1,7632	1,3143	1,0362	0,5376	0,3846	0,2577	0,1352
$\frac{T_k}{T} - 1$	1,1460	0,9638	0,8068	0,6595	0,5088	0,3903	0,2209	0,1527	0,0954	0,0459
$f$	2,88	2,70	2,69	2,67	2,58	2,65	2,43 (min)	2,52	2,70	2,95

The value at 409°,3, still determined by SMITS with difficulty between the two series of observations, is rather divergent, as was to be expected. We find namely 2,65 instead of 2,50 about; but the other values all form actually one single series, so that the liquid white phosphorus can be considered with perfect certainty as the metastable continuation of the liquid red phosphorus below the triple point at 589°,5 — which has been proved irrefutably by SMITS.

We have, therefore, with some probability for the critical data of phosphorus:

$$T_k = \underline{\pm 948,1 \text{ abs.}} = \underline{\pm 675^\circ \text{ C.}}; \quad p_k = \underline{\pm 80 \text{ atm.}}$$

At  $T_k$  the value of  $f$  will then approach 3,4 (with nep. log. it will approach 7,8). For  $b_k$  we find  $542 \cdot 10^{-5}$ , i.e.  $135 \cdot 10^{-5}$ , per

Gr.atom<sup>1)</sup>; and for  $a_k = RT_k \times (27 : 8 \lambda) \times b_k$  the value 0,0665 with  $\lambda = 0,955$  ( $\gamma = 1,09$ ); cf. also IV, These Proc. of June 24, 1916, p. 307), so that  $\sqrt{a_k}$  becomes  $\approx 25,8$ , i.e.  $6,45 \cdot 10^{-2}$  per Gr.atom.

The value 7,8 found for  $f_k$  is somewhat lower than would follow from  $f_k = 8 \gamma$ , viz. 8,7, or 3,8 with ordinary log.

The minimum lies at  $(T_k - T) : T_k = \alpha : 2\beta = 0,193$ , i.e. at  $T = 0,81 T_k$ , or  $183^\circ$  lower than  $T_k$ , hence at  $492^\circ$  C., only slightly below  $504^\circ$  C. And this minimum value of  $f$  will evidently be  $= f_k - (\alpha^2 : 4\beta) = 3,40 - (97,12 : 102,1) = 2,45$ . We found above the slightly lower value 2,43 with the value of 80 atm. for  $p_k$ , which had been taken somewhat too low (80,7 atm. corresponds namely with  $675^\circ,6$ ).

*Fontanivent sur Clarens, March 1917.*

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<sup>1)</sup> From the critical data of  $\text{PH}_3$  would even follow 131 with  $H = 34$  (cf. I, These Proc. of Jan. 29, 1916, p. 1224). But these data are possibly not absolutely accurate either.