

*Citation:*

J.J. van Laar, On the Fundamental Values of the Quantities B and Va for Different Elements, in Connection with the Periodic System IV. The Elements of the Halogen- Oxygen- and Nitrogen Groups, in:  
KNAW, Proceedings, 19 I, 1917, Amsterdam, 1917, pp. 295-320

That for the Helium group, where the molecules also consist of only one atom, only the ordinary rest attraction asserts itself, and not the so much greater valence-attractions, is owing to this that the noble gases mentioned are *valenceless*.

Clarens, May 1916.

**Physics.** — “On the Fundamental Values of the Quantities  $b$  and  $\sqrt{a}$  for Different Elements, in Connection with the Periodic System. IV. The Elements of the Halogen- Oxygen- and Nitrogen Groups.” By Dr. J. J. VAN LAAR. (Communicated by Prof. H. A. LORENTZ.)

(Communicated in the meeting of June 24, 1916).

### I. The Halogen Group.

After the treatment of the valenceless eighth group of the periodic system, i.e. of the group of the noble gases (to which we have added the hydrogen for convenience, sake)<sup>1)</sup>, we shall now discuss the seventh group, that of the Halogens. We remind the reader that our chief aim is now to determine the values of  $\sqrt{a_k}$  of the *elements themselves*, independent of the values calculated before in I and II<sup>2)</sup> from their *compounds*.

**a. Fluor.** The critical temperature is unknown; I find somewhere stated  $-170^\circ \text{C.} = 103^\circ \text{abs.}$ , but this cannot possibly be true, as the boiling point temperature lies already at  $-187^\circ \text{C.} = 86^\circ \text{abs.}$  according to MOISSAN and DEWAR (1903). Now for the Halogens the ratio  $T_k : T_b$  (Cf. the table in II on p. 18) is resp. 1,72 for  $\text{I}_2$ , 1,73 for  $\text{Br}_2$ , and 1,75 for  $\text{Cl}_2$ . If, therefore, for  $\text{F}_2$  we also assume 1,75 for it,  $T_k$  would become  $= 151^\circ \text{abs.}$  To this corresponds  $2\gamma = 1 + 0,038\sqrt{151} = 1,467$ , hence  $\gamma = 0,733$ . If, therefore, the triple point temperature lies at  $-223^\circ \text{C.} = 50^\circ \text{abs.}$  (MOISSAN and DEWAR, 1903)<sup>3)</sup>, then  $m_1 = 50 : 151 = 0,331$ , and the factor  $f_1 = b_k : v_1$  becomes:

$$f_1 = 1,467 \left[ 1 - \frac{0,733}{1,733} \times 0,331 \right] = 1,467(1 - 0,140) = 1,262.$$

Hence to find  $b_k = 55 \cdot 10^{-5}$  for 1 Gr. atom Fluor, the atomic volume at the triple point must be  $= (55 : 1,262) 10^{-5} = 43,6 \cdot 10^{-5}$ . Now for  $-200^\circ \text{C.}$  MOISSAN and DEWAR (1897) found  $D = 1,14$ ,

<sup>1)</sup> See III, These Proc. p. 287.

<sup>2)</sup> These Proc. of Jan. 29 and March 25, 1916; p. 1228 and 2.

<sup>3)</sup> In the “Chemisch Jaarboekje” for 1915–1916, I find  $-233^\circ \text{C.}$  given.

giving  $v = 74,4 \cdot 10^{-5}$ ; this volume will probably be somewhat smaller at the triple point, which lies lower; not smaller, however, than about  $63 \cdot 10^{-5}$ , as is easy to calculate.

From all this it may be inferred that at present there is not much chance of reconciling the few data for Fluor.

If  $f_1 = 1,262$  is correct, then

$$f_1 \mu_1 = 1,262 \times 3,020 = 3,81$$

would follow, with  $\mu_1 = 151 : 50 = 3,020$ .

**b. Chlorine.** With  $D = 1,717$ ,  $D' = 0$  at  $-100^\circ \text{C}$ . (PELLATON. Thèse 1915, p. 31) we calculate from

$$2\gamma = \frac{(d + d') - 2}{1 - m} = \frac{T_k(D + D') - 2D_k}{D_k(T_k - T)}$$

for  $2\gamma$  the value

$$2\gamma = \frac{417,1}{0,573} \cdot \frac{1,716 - 1,146}{417,1 - 173,1} = 1,700^1).$$

The values of  $T_k$  and  $D_k$ , and also the others, have been borrowed from PELLATON.

From the formula  $2\gamma = 1 + 0,038 \sqrt{417,1}$  the somewhat greater value 1,776 would have been calculated for  $2\gamma$ .

Now the triple point lies at  $-101,5^\circ \text{C} = 171,06$  abs. (JOHNSON and Mc. INTOSH, 1909); hence from  $(D_1 - D) : D_k = 2\gamma(m - m_1)$  we find:

$$D_1 = 1,717 + 0,573 \times 1,700(0,4150 - 0,114) = 1,721,$$

from which follows  $A : D_1 = 20,61$ ,  $v_1 = 91,96 \cdot 10^{-5}$ .

We find further for the factor  $f_1$ :

$$f_1 = 1,700 \left[ 1 - \frac{0,85}{1,85} \times 0,411 \right] = 1,7(1 - 0,189) = 1,379.$$

From this is calculated  $b_k = 91,96 \cdot 10^{-5} \times 1,379 = 126,8 \cdot 10^{-5}$ , while from  $T_k$  and  $p_k$  (values of PELLATON) 125,5 is directly calculated (for 1 atom Cl).

From  $\gamma = 0,85$  would follow  $v = v_k : b_k = (\gamma + 1) : \gamma = 2,176$ . As  $D_k = 0,573$ , we have  $v_k = 35,46 : 0,573 : 22412 = 276,1 \cdot 10^{-5}$  for 1 atom. Hence  $b_k$  would be  $= (276,1 \cdot 2,176) 10^{-5} = 126,9 \cdot 10^{-5}$ , quite identical to the value found just now by the aid of  $\gamma$  from the so distant value of  $D_1$  at the triple point.

As  $\mu_1 = T_k : T_v = 2,436$ , we get:

$$f_1 \mu_1 = 1,379 \times 2,436 = 3,36.$$

<sup>1)</sup> Between  $0^\circ \text{C}$ . and  $T_k$  with  $D = 1,4678$ ,  $D' = 0,0128$  we should have found the slightly lower value 1,692.

c. **Bromine.** As for want of data  $\gamma$  cannot be directly calculated, we shall determine the approximated value from our formula. From  $T_k = 575,3$  (NADEJDINE, 1885) follows  $2\gamma = 1,912$ ,  $\gamma = 0,956$ . Hence we find for  $f_1$ :

$$f_1 = 1,912 \left[ 1 - \frac{0,956}{1,956} \times 0,462 \right] = 1,912 (1 - 0,226) = 1,480.$$

From  $T_b = -7^\circ,3$  C. =  $265^\circ,8$  abs. (v. D. PLAATS, 1886; the latter found for the boiling point  $63^\circ,05$  C., while RAMSAY and YOUNG later found for it  $58^\circ,7$  C.) follows namely  $m_1 = 0,462$ .

As the density at  $0^\circ$  C. is found =  $3,187$  (v. D. PLAATS), it will be at the triple point:

$$D_1 = 3,187 + 1,06 \times 1,912 (0,4747 - 0,4620) = 3,213.$$

In this the calculated value  $1,06$  has been taken for  $D_k$ <sup>1)</sup>. (NADEJDINE found  $1,18$ ).

As  $v_1 = 111,0 \cdot 10^{-5}$ , we find further from  $f_1$   $b_k = 111,0 \cdot 10^{-5} \times 1,480 = 164,3 \cdot 10^{-5}$ , while  $165 \cdot 10^{-5}$  has been found from compounds.

As  $\mu_1 = 575,3 : 265,8 = 2,164$ , we get:

$$f_1 \mu_1 = 1,480 \times 2,164 = 3,20.$$

d. **Iodine.** Here too we must determine  $\gamma$  from our approximate formula. With  $T_k = 785^\circ,1$  abs. we then find  $2\gamma = 2,065$ ,  $\gamma = 1,032$ .

The density at  $0^\circ$  C. is according to GAY LUSSAC  $4,948$ . But this value cannot possibly be correct, as DEWAR found the *smaller* value  $4,894$  at  $-188^\circ$ .

If in approximation we assume continuity in the thermal expansion of the solid and liquid state — i.e. if we assume that the expansivity of solid iodine (about which I have not been able to find any values recorded) is the same as that of liquid iodine at low temperatures, where the vapour density can be neglected, so that the straight diameter can be thought prolonged unchanged as far as in the solid phase — then  $D_1$  at the triple point  $113^\circ,7$  C. =  $386^\circ,8$  abs. (LADENBURG, 1902; he found for the boiling point  $183^\circ,05$  C.) can be approximately determined from

<sup>1)</sup> This value can be calculated in two ways. First of all from  $v_k = r b_k = b_k \times (\gamma + 1) : \gamma$ . This gives with  $b_k = 165 \cdot 10^{-5}$ ,  $\gamma = 0,956$  for  $v_k$  the value  $165 \times 2,046 \times 10^{-5} = 337,6 \cdot 10^{-5}$ . Hence  $D_k$  becomes =  $79,92 : 337,6 : 0,22412 = 1,056$ .

Then from the formula  $\frac{1}{2} D : D_k = 1 + \gamma(1 - m)$ , when the vapour density  $D'$  can be neglected. With  $D = 3,187$  at  $0^\circ$  C. ( $m = 0,475$ ) this gives the value  $1,5935 : 1,502 = 1,061$  for  $D_k$ .

$$D_1 = 4,894 + 1,275 \times 2,065 (0,1083 - 0,4927) = 3,882,$$

because at  $-188^\circ \text{C.} = 85^\circ \text{abs.}$  the value of  $m$  is  $= 0,1083, m_1 = 0,4927$  being calculated. For  $D_k$  we have assumed the value  $1,275^1$  ( $1,34$  is given somewhere as "calculated"). For  $v_1$  we therefore find  $v_1 = 145,9 \cdot 10^{-5}$ .

For the factor  $f_1$  we calculate further:

$$f_1 = 2,065 \left[ 1 - \frac{1,032}{2,032} \times 0,493 \right] = 2,065 (1 - 0,250) = 1,548.$$

Because of this  $b_k$  becomes  $= 145,9 \cdot 10^{-5} \times 1,548 = 225,9 \cdot 10^{-5}$ ,  $220 \cdot 10^{-5}$  being found from the compounds. The value for  $D_1$  calculated only by approximation is therefore, probably, slightly too low.

At last we calculate for the product  $f_1 \mu_1$ :

$$f_1 \mu_1 = 1,548 \times 2,030 = 3,14$$

These products are therefore not constant for the Halogen group either. From  $3,8$  (?) with  $\text{F}_2$   $f_1 \mu_1$  steadily decreases to  $3,4$  with  $\text{Cl}_2$ ,  $3,2$  for  $\text{Br}_2$ , and  $3,14$  for  $\text{I}_2$ . Yet (leaving  $\text{F}_2$  out of consideration) the decrease is not very great, so that we may possibly assume a middle value of  $3,2$ .

In the following table the fundamental values of the group have again been combined. The values of  $v_1$  and  $b_k$  always refer to 1 atom.

TABLE B<sub>1</sub>.

| $N$              | $A$       | $A/N$ | $D_1$ | $A/D_1$ | $10^5 v_1 = \text{id.} : 0,22412$ | $\gamma$ | $\gamma'$ | $m_1$ | $f_1$ | $10^5 b_k$ calculated | $10^5 b_k$ found |
|------------------|-----------|-------|-------|---------|-----------------------------------|----------|-----------|-------|-------|-----------------------|------------------|
| 9 $\text{F}_2$   | 19,0      | 2,11  | —     | —       | —                                 | —        | 0,733     | 0,331 | 1,262 | —                     | (55)             |
| 17 $\text{Cl}_2$ | 35,46     | 2,09  | 1,721 | 20,61   | 91,96                             | 0,850    | 0,888     | 0,411 | 1,379 | 127                   | 125,5 (115)      |
| 35 $\text{Br}_2$ | 79,92     | 2,28  | 3,213 | 24,87   | 111,0                             | —        | 0,956     | 0,462 | 1,480 | 164                   | (165)            |
| 53 $\text{I}_2$  | 126,92    | 2,39  | 3,882 | 32,69   | 145,9                             | —        | 1,032     | 0,493 | 1,548 | 226                   | (220)            |
| 85 —             | $\pm 216$ | 2,54  | —     | —       | —                                 | —        | —         | —     | —     | —                     | —                |

The values of  $b_k$  "found" placed between brackets could not be determined directly from  $T_k$  and  $\mu$ , as  $p_k$  is unknown; they are the values which were formerly calculated from the compounds

<sup>1</sup>) With  $b_k = 220 \cdot 10^{-5}$ ,  $\gamma = 1,032$  we really find  $v_k = 220 \times 1,969 \times 10^{-5}$ , hence  $D_k = 126,92 : (220 \times 1,969 \times 0,22412) = 1,307$ . With  $D = 4,894$  at  $-188^\circ \text{C.}$  ( $m = 0,083$ ) the value  $2,447 : 1,920 = 1,275$  is found for  $D_k$ . We have preferred this latter value.

(see I). The value 125,5 for  $10^5 b_k$  for chlorine has been calculated from PELLATON's critical data, 113 following from those of DEWAR.

When  $p_k$  is unknown the values of  $\sqrt{a_k}$  for 1 atom can be calculated from the formula  $RT_k = \frac{27}{2} \lambda \cdot n_k \cdot (a_{k_1} : b_{k_1})$ , in which  $n_k$  represents the number of atoms in the molecule at  $T_k$ . For if to distinguish between  $a_k$  and  $b_k$  (which now refer to the whole molecule), we denote the values referring to 1 atom by  $a_{k_1}$  and  $b_{k_1}$ , evidently  $a_k = n_k^2 \cdot a_{k_1}$  and  $b_k = n_k \cdot b_{k_1}$ . If in the formula mentioned the factor  $\lambda$  is in the neighbourhood of  $\frac{27}{28}$  for substances with comparatively high critical temperature (when namely  $\gamma = 1$ ), then, as we already saw before, this formula reduces to  $T_k = 78,03 n_k \cdot (a_{k_1} : b_{k_1})$ . But as soon as  $\gamma$  differs considerably from unity, it is better to use the general formula, in which  $\lambda = \frac{27}{8\gamma-1} \left( \frac{\gamma}{\gamma+1} \right)^2$ .

Thus we calculate for  $a_{k_1}$  the value  $5,47 \cdot 10^{-4}$ , hence  $\sqrt{a_{k_1}} = 2,34 \cdot 10^{-2}$ , for  $F_2$  with  $n_k = 2$ ,  $T_k = 151^\circ$  abs.,  $b_{k_1} = 55 \cdot 10^{-5}$ . This value is considerably lower than that found for compounds, namely about  $2,9 \cdot 10^{-2}$ .

For  $Cl_2$  we calculate directly the value  $\sqrt{a_{k_1}} = 5,75 \cdot 10^{-2}$  from  $T_k$  and  $p_k$ , when we use the critical data of PELLATON, but  $5,43 \cdot 10^{-2}$  with those of DEWAR. In compounds on an average  $5,4 \cdot 10^{-2}$  was found.

For  $Br_2$  and  $I$  we find in the same way for  $a_{k_1}$  resp. the values  $60,4 \cdot 10^{-4}$  and  $111,2 \cdot 10^{-4}$ , when namely  $n_k = 2$  is taken. This would give  $\sqrt{a_{k_1}} = 7,77 \cdot 10^{-2}$ , resp.  $10,55 \cdot 10^{-2}$ . But these values are *much greater* than the normal values 7, resp. 9 found for compounds, so that from this we can draw the conclusion that in connection with what we shall find later concerning the so much greater attraction for the *isolated* atoms, which for the present we may put at about  $30 \cdot 10^{-2}$  — the two elements  $Br_2$  and  $I_2$  at the critical temperature have already been dissociated for a small part into atoms  $Br_1$  and  $I_1$ ), where therefore the *full* attraction of these atoms begins to make itself felt. But on account of this  $n_k$  will no longer be  $= 2$ , hence we should reconsider our calculation of  $\sqrt{a_{k_1}}$ .

If we namely assume that the above formula for  $RT_k$  continues to hold by approximation, when instead of with a *simple* substance we have to do with a *mixture* of two substances (e.g.  $I_2$  and  $I$ ),<sup>2)</sup>

<sup>1)</sup> As far as  $I_2$  is concerned, this dissociation at  $512^\circ$  C. cannot astonish us, as it is known that the dissociation  $I_2 \rightarrow 2 I_1$  is already *complete* at about  $1500^\circ$  C.

<sup>2)</sup> In reality (cf. *Arch. Teyler* 1808 and *These Proc.* of May 30 1914, p 601)  $T_k$  will not depend linearly on the degree of association  $n_k$ , but it can deviate from it  $6\frac{1}{2}\%$  as a maximum (for  $x = \frac{2}{3}$ ). If, however,  $x$  is slight, e.g. 0,1, the deviation is so insignificant that it may be neglected.

then with  $n_k = 2 : (1 + x)$ , in which  $n_k$  now represents the so-called degree of association of the atoms Br and I, and  $x$  the degree of dissociation of the molecules  $\text{Br}_2$ , resp.  $\text{I}_2$ , we get:

$$a_{k_1} = \frac{RT_k \cdot b_{k_1}}{s/27 \lambda} : \frac{2}{1+x} \text{ instead of } a'_{k_1} = \frac{RT_k \cdot b_{k_1}}{s/27 \lambda} : 2,$$

so that evidently we have still to multiply the values found above of  $\sqrt{a_{k_1}}$  by  $\sqrt{1+x}$ .

If now the attractions  $\sqrt{a_{k_1}}$  for the atoms differ for the cases that they are either united in a molecule to e.g.  $\text{I}_2$ , or occur freely as  $\text{I}_1$ , evidently:

$$\sqrt{a_{k_1}} = (1-x) \sqrt{(a_{k_1})_2} + x \sqrt{(a_{k_1})_1},$$

so that at last we have for the calculation of the degree of dissociation  $x$ :

$$\sqrt{a'_{k_1}} \cdot \sqrt{1+x} = (1-x) \sqrt{(a_{k_1})_2} + x \sqrt{(a_{k_1})_1},$$

in which  $\sqrt{a'_{k_1}}$  denotes the value calculated above with  $n_k = 2$ . If now for  $(a_{k_1})_1$  we assume the preliminary value  $30 \cdot 10^{-2}$  (see above), we have for  $\text{Br}_2$ :

$$7.8 \sqrt{1+x} = 6.9(1-x) + 30x,$$

as before  $\sqrt{(a_{k_1})_2} = 6.9 \cdot 10^{-2}$  was found for the compounds (see 1). For  $x$  we then find about  $1/21 = 0.048$ , so that  $\sqrt{1+x}$  would become  $= 1.024$ .

For the real value of  $\sqrt{a_{k_1}}$  we thus find  $7.77 \cdot 10^{-2} \times 1.024 = 7.96 \cdot 10^{-2}$ , for which we may therefore write  $8.0 \cdot 10^{-2}$ .

In the same way we shall find for  $\text{I}_2$ , with  $\sqrt{(a_{k_1})_2} = 8.8 \cdot 10^{-2}$ :

$$10.5 \sqrt{1+x} = 8.8(1-x) + 30x,$$

from which  $x = 0.104$ ,  $\sqrt{1+x} = 1.051$  follows, so that the real value of  $\sqrt{a_{k_1}}$  for  $\text{I}_2$  becomes  $= 10.55 \cdot 10^{-2} \times 1.051 = 11.06 \cdot 10^{-2} = 11.1 \cdot 10^{-2}$ .

The values found are joined with some supplementary values in the following table.

TABLE B<sub>2</sub>.

|               | $T_{tr}$ | $T_s$ | $T_k$ | $p_k$ | $D_k$  | $\frac{T_k}{T_s}$ | $\nu_1 = \frac{T_k}{T_{tr}}$ | $f_1 \nu_1$ | $10^2 \sqrt{a_k}$<br>calculated | $10^2 \sqrt{a_k}$<br>in comp. | Diss.<br>degr. $x$ |
|---------------|----------|-------|-------|-------|--------|-------------------|------------------------------|-------------|---------------------------------|-------------------------------|--------------------|
| $\text{F}_2$  | 50       | 86    | (151) | —     | —      | (1,75)            | (3,02)                       | (3,81)      | (2,34)                          | 2,9?                          | —                  |
| $\text{Cl}_2$ | 171,6    | 238,6 | 417,1 | 76,1  | 0,573  | 1,75              | 2,44                         | 3,36        | 5,75                            | 5,4                           | —                  |
| $\text{Br}_2$ | 265,8    | 331,8 | 575,3 | —     | (1,06) | 1,73              | 2,16                         | 3,20        | 8,0                             | 6,9                           | 0,05               |
| $\text{I}_2$  | 386,8    | 456,1 | 785,1 | —     | (1,29) | 1,72              | 2,03                         | 3,14        | 11,0                            | 8,8                           | 0,10               |

In consequence of the *provisional* assumption that the attraction of the isolated atoms amounts here to about  $30 \cdot 10^{-2}$  (which is not quite certain, as no experiments have as yet taken place with atomic Br and I), the values of  $\sqrt{a_k}$  and  $x$  calculated for Br<sub>2</sub> and I<sub>2</sub>, are accurate only in approximation.

## II. The oxygen group.

**a. Oxygen.** For  $\gamma$  0,813 has been experimentally found (MATHIAS and KAMERLINGH ONNES)<sup>1)</sup>. From this follows for the density at the triple point  $54^{\circ},7$  abs. (K. O. and CROMMELIN), where  $m_1 = 0,3546$ :

$$D_1 = 1,2747 + 0,4299 \times 1,626 (0,4065 - 0,3546) = 1,311.$$

At  $62^{\circ},7$  the density  $D$  ( $m = 0,4065$ ) is namely  $= 1,2746$ ,  $D'$  being  $= 0,0001$  (M. and K. O.). Further  $D_k = 0,4299$  (Ibid),  $T_k = 154^{\circ},25$  abs. (K. O., DORSMAN and HOLST, 1915, who also determined  $\rho_k$ ; while K. O. and BRAAK determined  $T_s$ ).

We find for the factor  $f_1'$ :

$$f_1 = 1,626 \left[ 1 - \frac{0,813}{1,818} \times 0,3546 \right] = 1,626 (1 - 0,259) = 1,367.$$

Hence  $b_k = 74,4 \cdot 10^{-5}$  follows from  $v_1 = 54,45 \cdot 10^{-5}$ , whereas  $71 \cdot 10^{-5}$  has been found directly from  $T_k$  and  $\rho_k$ .

Now the product  $f_1 \mu_1$  becomes:

$$f_1 \mu_1 = 1,367 \times 2,820 = 3,85.$$

**b. Sulphur.** In 1888 VICENTINI and OMODEI found the value 1,8114 for the density at the melting point of the metastable rhombic sulphur ( $112^{\circ},8$  C.). The melting point of monoclinic sulphur lying at  $119^{\circ},25$  (just as the preceding value given by KRUYT, Thesis for the Doctorate 1908; or at  $118^{\circ},95$  given by WIGAND, 1911), we can by approximation determine the density of monoclinic sulphur at the melting point by the aid of the cubic coefficient of expansion of liquid sulphur (0,000458 between  $126^{\circ}$  and  $167^{\circ}$  C. according to KOPP). We then find 1,8063.

For the coefficient of direction of the straight diameter we calculate from  $T_k = \pm 700^{\circ}$  C.  $= 973^{\circ}$  abs. the approximate value  $2\gamma = 2,185$ ,  $\gamma = 1,093$ .

This gives for the factor  $f_1$  ( $m_1 = 0,403$ ):

$$f_1 = 2,185 \left[ 1 - \frac{1,093}{2,093} \times 0,403 \right] = 2,185 (1 - 0,210) = 1,725.$$

As  $v_1 = 79,24 \cdot 10^{-5}$ ,  $b_k$  becomes  $= 136,7 \cdot 10^{-5}$ ,  $125 \cdot 10^{-5}$  having

<sup>1)</sup> With  $T_k = 154^{\circ},25$  the formula for  $2\gamma$  would have yielded the value 1,4720, from which  $\gamma = 0,736$  would follow, i.e. much smaller than M. and K. O. found.

been found from compounds. Hence the value used for  $\gamma$  is possibly somewhat too great.

As  $\mu_1 = 973 \cdot 392 = 2,482$ , we get

$$f_1 \mu_1 = 1,725 \times 2,482 = 4,28$$

With regard to the value of  $\sqrt{a_k}$  it may be stated that this value can only be calculated with any certainty from  $T_k$ , when the molecular state is known there. Now we only know (see PRELNER and SCHUPP, Z. f. ph. Ch. 68, p. 129) that sulphur vapour consists of molecules  $S_8$ ,  $S_6$ ,  $S_2$ , and  $S_1$  at different temperatures; between  $500^\circ$  and  $800^\circ$  C. chiefly of  $S_6$  and  $S_2$ -molecules [At lower temperatures more and more  $S_8$ -molecules occur, and only at very high temperatures — according to v. WARTENBERG (Z. f. ph. Ch. 77, p. 66) not before about  $2000^\circ$  C. — atoms  $S_1$ ]. From the formula for  $T_k$  follows with  $b_{k_1} = 125 \cdot 10^{-5}$

$$a_{k_1} = 973 \times 125 \cdot 10^{-5} : 780 n_k = 158,0 \cdot 10^{-4} : n_k,$$

because  $\theta$  (the correction factor for  $\lambda$ , about which we spoke above,

and which is evidently  $= \frac{28}{8\gamma - 1} \left( \frac{\gamma}{\gamma + 1} \right)^2$ ) is  $= 0,9866$ . As now  $6,3 \cdot 10^{-2}$

has been found for  $\sqrt{a_{k_1}}$  from compounds, and  $a_{k_1}$  therefore becomes  $= 39,7 \cdot 10^{-4}$ ,  $n_k$  would become  $= 3,98$  — which therefore practically means that sulphur at the critical temperature would on an average consist almost entirely of molecules  $S_4$ .<sup>1)</sup> If however  $\sqrt{a_{k_1}}$  should be  $= 5 \cdot 10^{-2}$ ,  $n_k$  would become  $= 6,32$ , and chiefly  $S_6$ -molecules would be present.

In order to find out something about the attraction of sulphur in compounds, we have examined also  $S_2Cl_2$ ,  $SOCl_2$ , and  $SO_2Cl_2$ . We find successively:

|             | $T_k$  | $10^5 b_k$                          | $10^4 a_k$ | $10^2 \sqrt{a_k}$ |                         |
|-------------|--------|-------------------------------------|------------|-------------------|-------------------------|
| $S_2 Cl_2$  | 664,4? | $2 \times 125 + 2 \times 115 = 480$ | 408,7      | 20,2              | S = $4,7 \cdot 10^{-2}$ |
| $SO Cl_2$   | 569,9  | $125 + 70 + 230 = 425$              | 310,4      | 17,6              | " 4,1 "                 |
| $SO_2 Cl_2$ | 549,7  | $125 + 140 + 230 = 495$             | 348,7      | 18,7              | " 2,5 "                 |

If for Cl we take the value  $5,4 \cdot 10^{-2}$  and for O the value  $2,7 \cdot 10^{-2}$ , we find for S the above given values, which are all smaller than the fundamental value 6,3 found for  $H_2S$  and  $SO_2$ . In the two first compounds the attraction is, however, not far from the normal fundamental value 5, it being about half this value for the last compound.

<sup>1)</sup> I.e. such a mixture of  $S_6$  and  $S_2$  molecules that on an average  $n_k$  is  $= 4$ .

c. **Selenium.** As  $T_k = 973^{\circ},1$  abs. and  $T^* = 717^{\circ},6$  abs. for sulphur [444<sup>o</sup>,5b C. was namely found for  $T_s$  by WAIDNER and BURGESS (1910), HOLBORN and HENNING (1911), DAY and SOSMAN (1912)], the ratio  $T_k : T_s$  is = 1,36 (it was = 1,71 for O<sub>2</sub>). If in approximation we assume for selenium for  $T_k : T_s$  the same value as for sulphur, we find the value 1310° abs. for  $T_k$  from  $T_s = 688^{\circ}$  C. = = 961° abs. [PREUNER and BROCKMÖLLER, Z. f. ph. Ch. 81, p. 146 (1912). Already in 1902 BERTHELOT gave 690° C.]. From this the value 2,375 would follow for  $2\gamma$ , hence  $\gamma = 1,19$ . Hence

$$f_1 = 2,375 \left[ 1 - \frac{1,19}{2,19} \times 0,377 \right] = 2,375 (1 - 0,205) = 1,889.$$

For the density of grey Selenium 4,8 or 4,5 was found by SAUNDERS (1900)<sup>1)</sup> Further SPRING found for the (linear) coefficient of expansion between 0° and 100° the value 0,00006604. From this we calculate for the density at the melting point 220°,2 C. = = 493°,3 abs. (BERGER, 1914)  $D_1 = 4,61$  or 4,32, giving  $v_1 = 76,7$  or  $81,8 \cdot 10^{-5}$ . From this follows therefore with the just found value of  $f_1$  for  $b_k$  the value 145 or 155  $10^{-5}$ , while  $180 \cdot 10^{-5}$  is expected.<sup>2)</sup> (RUDORF's value for  $D_1$  would have given  $b_k = 163 \cdot 10^{-5}$ ).

If  $T_k = 1310^{\circ}$  abs.<sup>3)</sup>, then  $\mu_1 = 2,655$ , and hence

$$f_1 \mu_1 = 1,889 \times 2,655 = 5,02.$$

For the attraction of Selenium itself, we find at last with  $b_k = 180 \cdot 10^{-5}$ :

$$a_{k_1} = 1310 \times 180 \cdot 10^{-5} : 78 \theta n_k = 311,7 \cdot 10^{-4} : n_k,$$

as  $\theta = 0,9694$ . As the normal value of  $\sqrt{a_{k_1}}$  is = 7,1  $\cdot 10^{-2}$  for Se, and therefore  $a_{k_1} = 50,4 \cdot 10^{-4}$ , the value 6,18 would follow from this for  $n_k$ , so that at the critical temperature Selenium would on an average be =  $\pm$  Se<sub>6</sub>. But according PREUNER and BROCKMÖLLER's researches (p. 139 loc. cit.) the dissociation of Se<sub>6</sub> molecules into Se<sub>2</sub>-molecules would already be complete at 850° C., so that at  $T_k =$  about 1040° C. the molecular formula cannot possibly be Se<sub>6</sub>. Even if we take 160 or 170 atm. for the critical pressure, the degree of dissociation would be about = 1 at this temperature. If we assume therefore  $n_k = 2 : (1+x)$ , we find  $a_{k_1} = 155,9 \cdot 10^{-4} \times (1+x)$ , or  $\sqrt{a_{k_1}} = 12,49 \cdot 10^{-2} \times \sqrt{(1+x)}$ .

1) In his well-known book on the periodic system (1904) RUDORF gives for the density the still lower value 4,26.

2) From H<sub>2</sub>Se (see I) Se = 138  $\cdot 10^{-5}$  is indeed calculated, but this value is evidently much too low.

3) From the vapour-pressure determinations of PREUNER and BROCKMÖLLER (loc. cit. p. 146) between 390° and 710° C. we can hardly conclude with any accuracy to the values of  $T_k$  and  $p_k$ , on account of the great variability of the molecular condition between these two temperatures.

But as 12,5 is much greater than the normal value 7,1 for compounds, decomposition of the  $\text{Se}_2$ -molecules into simple Se, atoms with greater attraction must necessarily have set in at  $T_k$  already. If  $x$  is the degree of dissociation of the  $\text{Se}_2$ -molecules,  $n_k$  will be  $= 2 : (1+x)$ , and 12,5 must still be multiplied by  $\sqrt{1+x}$ . On the assumption that also for Selenium the attraction of the atoms is about  $30 \cdot 10^{-2}$ , we have therefore for the determination of  $x$ .

$$12,5 \sqrt{1+x} = 7,1 (1-x) + 30 x,$$

from which  $x=0,315$  follows, so that  $\sqrt{a_{k_1}} = 12,49 \cdot 10^{-2} \times 1,147 = 14,3 \cdot 10^{-2}$ , as  $\sqrt{1+x} = 1,147$ .

In contradiction with v. WARTENBERG's statement [Z. f. anorg. Ch. 56, p. 320 (1907)], according to whom a perceptible decomposition into Se, atoms would not set in before  $2000^\circ \text{C}$ ., we find already a very pronounced dissociation at a little above  $1000^\circ \text{C}$ .

Accordingly the above found value of  $a_k$  leaves us the alternative  $n_k = 6,2$  or  $n_k = 2 : 1,315 = 1,5$ . According to what has been said the latter value is the more probable one.

**d. Tellurium.** In 1880 ST. CLAIRE DEVILLE found for the boiling point  $1390^\circ \text{C} = 1663^\circ \text{abs}$ . Hence with the factor 1,36 (see for Selenium)  $T_k$  would become  $= 2260^\circ$ . For  $2\gamma$  we calculate from this in approximation by means of our formula the value  $2\gamma = 2,807$ , hence  $\gamma = 1,403$ . Hence

$$f_1 = 2,807 \left[ 1 - \frac{1,403}{2,403} \times 0,321 \right] = 2,807 (1 - 0,1875) = 2,281.$$

The value of  $m_1$  has been calculated from the melting-point temperature determined by JAEGER (1909), viz.  $452^\circ,5 \text{C} = 725^\circ,6 \text{abs}$ .

KAHLBAUM (1902) gives 6,235 for the density at the ordinary temperature<sup>1</sup>). SPRING found 0,00003687 for the (linear) coefficient of expansion between  $0^\circ$  and  $100^\circ$ , which — extrapolated to  $450^\circ \text{C}$ . — would render the density at the melting-point about 5,94. From this we calculate  $v_1 = 95,7 \cdot 10^{-5}$ . With  $f_1 = 2,28$  the value  $218 \cdot 10^{-5}$  is then found from this for  $b_k$ , whereas  $235 \cdot 10^{-5}$  was expected. Possibly the value of  $D_1$  is taken too high, or that for  $f_1$  and  $\gamma$  (through  $T_k$ ) too low, just as for Selenium.

With  $\mu_1 = 3,115$  we get

$$f_1 \mu_1 = 2,281 \times 3,115 = 7,10.$$

At last the value of  $\sqrt{a_{k_1}}$ . With  $b_k = 235 \cdot 10^{-5}$  we calculate from  $T_k$ :

$$a_{k_1} = 2260 \times 235 \cdot 10^{-5} : 78 \theta n_k = 729,3 \cdot 10^{-4} : n_k,$$

<sup>1</sup>) LENHER and MORGAN (1900) give 6,199; KRÖNER (Diss.) values which vary between 6,27 and 6,10.

as  $\theta = 0,9333$ . With the normal value  $9 \cdot 10^{-2}$  for the attraction for Te about  $n_k = 15$  would have been found, which is of course impossible. If we assume that also here for  $T_k$  the dissociation to  $Te_2$  is complete, and that the  $Te_2$ -molecules are still further dissociated to  $Te_1$ , then  $n_k = 2:(1+x)$ , and  $a_{k_1}$  becomes  $= 364,6 \cdot 10^{-4} \times (1+x)$ , hence  $\sqrt{a_{k_1}} = 19,10 \cdot 10^{-2} \times \sqrt{1+x}$  — hence again much greater than the normal value 9, so that there are really isolated atoms  $Te_1$  present at  $T_k$ .

The value of the degree of dissociation  $x$  is calculated from

$$19,1 \sqrt{1+x} = 9(1-x) + 30x,$$

giving  $x = 0,787$ . Accordingly at the critical temperature Tellurium is already dissociated to separate atoms at least for the greater part. If the atomic attraction should then be greater than  $30 \cdot 10^{-2}$ , e.g.  $35 \cdot 10^{-2}$ ,  $x$  would be somewhat smaller, viz. 0,576. With  $x = 0,79$   $\sqrt{a_{k_1}}$  becomes  $= 19,10 \cdot 10^{-2} \times 1,337 = 25,5 \cdot 10^{-2}$ , as  $\sqrt{1+x} = 1,337$ .

Just as for sulphur we have investigated the value of the molecular attraction of a few more compounds, viz.  $TeCl_4$  and  $TeCl_2$ . We find for this what follows.

|          | $T_k$ | $10^5 b_k$                 | $10^4 a_k$ | $10^2 \sqrt{a_k}$ |                          |
|----------|-------|----------------------------|------------|-------------------|--------------------------|
| $TeCl_4$ | 1099  | $235 + 4 \times 115 = 695$ | 979,2      | 31,3              | Te = $9,7 \cdot 10^{-2}$ |
| $TeCl_2$ | 955   | $235 + 2 \times 115 = 465$ | 569,1      | 23,9              | " 13,1 "                 |

The critical temperatures have been calculated from the known boilingpoint temperatures, viz.  $687^\circ$  and  $597^\circ$  abs. by multiplication by 1,6. For  $TeCl_4$  the normal value  $9 \cdot 10^{-2}$  seems to be found. For  $TeCl_2$ , however, the increased atomic attraction makes itself already felt in consequence of the released valencies.

The different fundamental values have again been joined in the following table.

TABLE C<sub>1</sub>.

| $N$              | $A$       | $A/N$ | $D_1$ | $A/D_1$ | $10^5 v_1 = \text{id.}: 0,22412$ | $\gamma$ | $\gamma'$ | $m_1$ | $f_1$ | $10^5 b_k$ calculated | $10^5 b_k$ found |
|------------------|-----------|-------|-------|---------|----------------------------------|----------|-----------|-------|-------|-----------------------|------------------|
| 8 O <sub>2</sub> | 16,00     | 2,00  | 1,311 | 12,20   | 54,45                            | 0,813    | 0,736     | 0,355 | 1,367 | 74,4                  | 71 (7)           |
| 16 S             | 32,06     | 2,00  | 1,806 | 17,76   | 79,24                            | —        | 1,09      | 0,403 | 1,725 | 137                   | (125)            |
| 34 Se            | 79,2      | 2,33  | 4,3   | 18,3    | 81,8                             | —        | 1,19      | 0,377 | 1,889 | 155                   | (180)            |
| 52 Te            | 127,5     | 2,45  | 5,9   | 21,5    | 95,7                             | —        | 1,40      | 0,321 | 2,281 | 218                   | (235)            |
| 84 Po            | $\pm 215$ | 2,56  | —     | —       | —                                | —        | —         | —     | —     | —                     | —                |

20

Proceedings Royal Acad. Amsterdam. Vol. XIX.

The value of  $b_k$  found for oxygen has been immediately calculated from  $T_k$  and  $p_k$  (see I); the other values (placed between brackets) are those which have been found for the compounds. We have further still:

TABLE C<sub>2</sub>.

|                 | $T_{tr}$ | $T_s$ | $T_k$  | $p_k$ | $D_k$  | $\frac{T_k}{T_s}$ | $\nu_1 = \frac{T_k}{T_{tr}}$ | $f_1 \nu_1$ | $10^2 \sqrt{ak}$<br>calculated                 | $10^2 \sqrt{a_k}$<br>in comp. | Diss.<br>degr. $x$ |
|-----------------|----------|-------|--------|-------|--------|-------------------|------------------------------|-------------|------------------------------------------------|-------------------------------|--------------------|
| O <sub>2</sub>  | 54,7     | 90,10 | 154,25 | 49,71 | 0,4299 | 1,71              | 2,82                         | 3,85        | 2,6                                            | 2,7                           | 0                  |
| S <sub>8</sub>  | 392,0    | 717,6 | 973    | —     | —      | 1,36              | 2,48                         | 4,28        | 6,3 (S <sub>4</sub> )<br>5,1 (S <sub>6</sub> ) | 6,3                           | 0                  |
| Se <sub>2</sub> | 493,3    | 961   | (1310) | —     | —      | (1,36)            | 2,63                         | 4,97        | 14,3                                           | 7,1                           | 0,32               |
| Te <sub>2</sub> | 725,6    | 1663  | (2260) | —     | —      | (1,36)            | 3,11                         | 7,10        | 25,5                                           | 9                             | 0,79               |

The value  $2,6 \cdot 10^{-2}$  for O<sub>2</sub> has been directly calculated from  $T_k$  and  $p_k$  (see I).

As for the values of  $f_1 \nu_1$ , they ascend from about 4 to 7. But in this it is noteworthy that the derivation of the relation  $f_1 \nu_1 = \text{constant}$  from the hypothetical assumption that at the triple point  $(v_1 - b_1) : v_1$  should be constant, is only valid for the case that the molecular state at the triple point and the critical point is the same. This now is certainly not the case for Sulphur, Selenium and Tellurium. In the following paragraph we shall treat this point (for Phosphorus) more at length.

For the first time we meet with an element (Tellurium) in this group which at the critical temperature has already been greatly dissociated to *atoms*, and which accordingly begins to exhibit a metallic character. In the following groups of the periodic system, which we shall discuss now, this phenomenon stands out more and more clearly.

### III. The Nitrogen group.

**a. Nitrogen.** The value of  $\gamma$  is known here from the researches of MATHIAS, K. ONNES and CROMMELIN, who found for this 0,793<sup>1)</sup>. From this we can calculate the density  $D_1$  at the triple point (63°,06 abs. according to KEESOM and K. ONNES; CROMMELIN found 78° abs. for the boiling point). As for 64°,73 abs.  $D = 0,8622$ ,  $D' = 0,0009$  (M., K.O., Cr.), we get with  $\gamma = 0,3110$  (the same authors) and

<sup>1)</sup> We calculate from our approximate formula  $\gamma = 0,713$ , therefore just as for O<sub>2</sub> smaller than the experimentally found value.

$T_k = 125^{\circ},96$  abs. (K.O., DORSMAN and HOLST, who also determined the critical pressure):

$$D_1 = 0,8631 + 0,3110 \times 1,586 (0,5193 - 0,5006) = 0,8697.$$

From this follows  $A : D_1 = 16,11$ , hence  $v_1 = 71,88 \cdot 10^{-5}$ .

For the factor  $f_1 = b_k : v_1$  we find further:

$$f_1 = 1,586 \left[ 1 - \frac{0,793}{1,793} \times 0,5006 \right] = 1,586 (1 - 0,221) = 1,235.$$

We therefore calculate  $88,8 \cdot 10^{-5}$  for  $b_k$ , while  $86 \cdot 10^{-5}$  was found directly from  $T_k$  and  $p_k$ .

Finally we have for the product  $f_1 \mu_1$ :

$$f_1 \mu_1 = 1,235 \times 1,998 = 2,47.$$

**b. Phosphorus.** From the approximate formula the value 2,182 follows for  $2\gamma$  from  $T_k = 968^{\circ}$  abs., so that  $\gamma$  becomes = 1,091. With  $T_u = 44^{\circ},1$  C. = 317,2 abs. for the *yellow* phosphorus (SMITS and DE LEEUW, 1911) we find therefore ( $m_1$  being = 0,3277):

$$f_1 = 2,182 \left[ 1 - \frac{1,091}{2,091} \times 0,3277 \right] = 2,182 (1 - 0,171) = 1,809.$$

All this refers to the *yellow* (white) phosphorus, which according to SMITS c. s. is a metastable continuation of the liquid phosphorus below  $589^{\circ},5$  (the melting point of the red phosphorus). As this latter point lies too high for the calculation (the vapour pressure is there already 43,1 atm.), and the density  $D_1$  is perfectly unknown there, we have chosen the melting point of the yellow phosphorus as starting point.

For the density of the yellow phosphorus 1,82 has been found at  $0^{\circ}$  C. (JOLIBOIS, 1910); hence  $D_1 = 1,79$  will be found at  $44^{\circ}$  with the (linear) coefficient of expansion 0,0001278 (between  $16^{\circ}$  and  $42^{\circ}$  C. according to KOPP). Therefore  $A : D_1$  becomes = 17,34 and  $v_1 = 77,37 \cdot 10^{-5}$ . We find therefore  $140,0 \cdot 10^{-5}$  for  $b_k$ , while the value  $134 \cdot 10^{-5}$  has been found from  $T_k$  and  $p_k$ , and the theoretical value amounts to  $140 \cdot 10^{-5}$ .

The product  $f_1 \mu_1$  becomes for the yellow phosphorus:

$$f_1 \mu_1 = 1,809 \times 3,053 = 5,52.$$

For the *red* phosphorus, where  $\mu_1 = 968,1 : 862,6 = 1,122$  and  $m_1 = 0,8913$ , therefore  $f_1 = 2,182 (1 - 0,465) = 1,167$ ,  $f_1 \mu_1$  becomes:

$$f_1 \mu_1 = 1,167 \times 1,122 = 1,31$$

There exists therefore a great difference in these values for the two phosphorus modifications, which is chiefly caused by the different molecular state at the two triple points. Really a higher degree of polymerisation is assigned to the red phosphorus than to the yellow

phosphorus ( $P_4$ ) — probably considerably higher than  $P_8$  (SCHENK).

In III we saw that the ratio  $(v_1 - b_1) : v_1$ , is only dependent on the product  $f_1 \mu_1$ . But — we observed it already above — in this it was supposed that the molecular state at  $T_l$  and  $T_h$  is the same. If this is no longer the case, the relation derived there, is slightly modified. If the quantities  $a$ ,  $b$ , and  $v$  refer to atom quantities, then at the triple point the relation

$$\frac{a_1}{v_1^2} (v_1 - b_1) = \frac{1}{n_1} RT_1$$

holds ( $\rho$  being neglected), when  $n_1$  represents the number of atoms in the molecule. But for  $T_k$  the relation

$$RT_k = \frac{2}{7} \frac{a_k}{b_k} \times n_k$$

holds with great approximation ( $a_k$  and  $b_k$  refer again to 1 atom, the factor  $2/7$  holds for comparatively high critical temperatures), because then again the molecular attraction  $= n_k^2 \times a_k$ , and the molecular volume  $= n \times b_k$ . Hence

$$\frac{a_1}{a_k} \times \frac{7 RT_k}{2} \frac{b_k}{n_k} \frac{v_1 - b_1}{v_1^2} = \frac{RT_1}{n_1},$$

or

$$\frac{v_1 - b_1}{v_1} = \frac{2 a_k n_k v_1 T_1}{7 a_1 n_1 b_k T_k}.$$

Now  $T_k : T_1 = \mu_1$ ,  $b_k : v_1 = f_1$ , hence we get :

$$\frac{v_1 - b_1}{v_1} = \frac{2 a_k n_k}{7 a_1 n_1 f_1 \mu_1} = \frac{2}{7} \times \frac{1}{\varphi},$$

so that now not  $f_1 \mu_1$ , but

$$f_1 \mu_1 \times \frac{a_1 n_1}{a_k n_k} = \varphi \dots \dots \dots (1)$$

becomes a measure for the ratio  $(v_1 - b_1) : v_1$  at the triple point.

As for the two phosphorus modifications the atomic attractions  $a_1$  and  $a'_1$  will be the same at the triple point, the values of  $f_1 \mu_1 \times n_1$  will here be decisive for the value of the ratio  $(v_1 - b_1) : v_1$  in the two cases.

Now it is remarkable that 1,31 is about  $1/4$  of 5,52 (in our above calculation the values of  $\gamma$  are put equal for the two modifications, which is certainly not quite true, so that the first value of  $f_1 \mu_1$  will only be accurate by approximation). If therefore we assume the formula  $P_4$  for the yellow phosphorus at the melting-point, then the formula  $P_{16}$  would hold for the red phosphorus at the melting point of this modification.

With regard to the critical temperature we saw above that phosphorus there answers pretty well to formula  $P_4$ . For  $b_k = 535 \cdot 10^{-5}$  was namely found instead of the theoretical value  $4 \times 140 \cdot 10^{-5}$ , from which  $n_k = 3,82$  would follow <sup>1)</sup>.

Accordingly we have for the yellow phosphorus (also  $a_k$  will be  $= a_1$ ):

$$\varphi = f_1 \mu_1 \times \frac{n_1}{n_k} = 5,52 \times \frac{1}{4} = 5,52,$$

whereas the following equation holds for the red phosphorus:

$$\varphi' = f_1' \mu_1' \times \frac{n_1'}{n_k} = 1,31 \times \frac{1}{1} = 5,24.$$

The accurate value of  $\varphi$  lies, therefore, probably in the neighbourhood of  $5^{1/2}$ .

[When we examine the values found for S, Se, and Te in the same light, we shall have to bear in mind with regard to the last elements that on account of the dissociation into isolated atoms the attraction at  $T_k$  will be another than at the triple point.

For *Sulphur* the molecular formula is probably  $S_{6,3}$  at  $T_k$  (see above), that at  $T_t$  being  $S_8$  for both modifications. Hence  $n_1$  will be  $= 8$ ,  $n_k = 6,3$  in (1), so that  $n_1 : n_k$  becomes  $= 1,27$ , and the value of  $\varphi$  will now become  $= 4,28 \times 1,27 = 5,4$ .

For *Selenium*  $n_k = 2 (1 + n_k) = 2 \cdot 1,32 = 1,52$ , but at the triple point  $n_1$  will probably be  $= 6$  <sup>2)</sup>. We find, therefore, 3,96 for the ratio  $n_1 : n_k$ . Further  $\sqrt{a_1} = 7,1 \cdot 10^{-2}$ ,  $\sqrt{a_k} = 14,3 \cdot 10^{-2}$ , hence  $a_1 : a_k = 0,247$ , so that  $f_1 \mu_1$  must finally be multiplied by 0,98. Accordingly the value of  $\varphi$  would become  $= 4,85$  here.

For *Tellurium*  $n_k = 2 \cdot 1,79 = 1,12$ ,  $n_1 = 6$ , hence  $n_1 : n_k = 5,37$ . But  $\sqrt{a_1}$  is about  $9 \cdot 10^{-2}$ ,  $\sqrt{a_k} = 25,5 \cdot 10^{-2}$ , hence  $a_1 : a_k = 0,125$ . We must therefore multiply by 0,669, through which 7,10 passes into 4,75.

Except for  $O_2$ , where  $\varphi = 3,85$  (possibly also oxygen is associated at the triple point, up to e.g.  $n_1 = 2,5$ , which would render  $\varphi = 4,8$ ), we find, therefore, after due correction everywhere a value in the neighbourhood of 5 for the triple point ratio  $(v_1 - b_1) : v_1$ .

<sup>1)</sup> According to PREUNER and BROCKMOLLER (loc. cit.) the dissociation constant (at 1 atm.) of the reaction  $P_4 \rightarrow 2 P_2$  is still slight even at  $800^\circ \text{C}$ , which will, therefore, be the case in a much greater degree at a pressure of 83 atm. At  $800^\circ \text{C}$ .  $c_2^2 : c_4 = 0,00855 : p$  holds for this reaction, i.e.  $c_2^2 : c_4 = 0,0001$  with  $p = 83$ , which gives  $c_2 = 0,01$  when  $c_4$  is near 1. [For the reaction  $P_2 \rightarrow 2 P_1$  we have  $c_1^2 : c_2 = 0,000046 : p$ , so that  $c_1^2 : c_2$  becomes  $= 0,00000055$  for 83 atm., hence  $c_1 = 0,00074$ , referring to  $c_2 = 1$ ].

<sup>2)</sup> In analogy with sulphur also  $\text{Se}_3$ -molecules will probably be present at low temperatures.

Also for a more accurate calculation of the values of  $\varphi$  for Br<sub>2</sub> and I<sub>2</sub> (see § 1)  $n_k$  must be known. For  $n_1$  the normal value 2 can be taken in both cases.<sup>1)</sup>

As  $n_1 : n_k = 2 : (2 : 1,048) = 1,048$ , and  $a_1 : a_k = (7 : 8,0)^2 = 0,766$  for *Bromine*, we must multiply by the factor 0,803, which would render  $\varphi = 3,20 \times 0,8 = 2,6$ .

For *Iodine*, where  $n_1 : n_k = 1,104$ ,  $a_1 : a_k = (9 : 11,1)^2 = 0,657$ , the correction factor becomes 0,725, so that  $\varphi$  becomes  $= 3,14 \times 0,725 = 2,3$ .

In connection with the value 3,4 found for chlorine, the found values are rather small, which would point to this, that the ratios  $a_1 : a_k$  have been taken too great, because the degrees of dissociation have possibly been calculated slightly too high — unless also for Cl<sub>2</sub> the too high value of  $\sqrt{a_k}$  (viz. 5,4 instead of 5) should point to a slight dissociation at  $T_k$ , through which also here  $a_1 : a_k$  becomes  $< 1$ .

In the group of the noble gases the exceptionally high value 5,26 for Helium is certainly striking. This value is, however, lowered, when we assume that  $\sqrt{a_1}$  suddenly becomes very small at so low a temperature as 1° abs. — hence presents an abrupt difference analogous to that of the electrical resistance at extremely low temperatures, as has been found by K. ONNLS].

Of the *compounds* of Phosphorus we have still examined PCl<sub>3</sub> and POCl<sub>3</sub>, chiefly with a view to the fact that before (see I) for PH<sub>3</sub> the attraction of the central P-atom was found = 0.

|                   | $T_k$ | $b_k \cdot 10^5$           | $a_k \cdot 10^4$ | $\sqrt{a_k} \cdot 10^2$ |                         |
|-------------------|-------|----------------------------|------------------|-------------------------|-------------------------|
| PCl <sub>3</sub>  | 558,6 | $140 + 3 \times 115 = 485$ | 347,3            | 18,6                    | $P = 2,4 \cdot 10^{-2}$ |
| POCl <sub>3</sub> | 604,9 | $140 + 70 + 345 = 555$     | 430,2            | 20,7                    | $P = 1,8 \cdot 10^{-2}$ |

When we assume Cl = 5,4, O = 2,7, we find, therefore, for the attraction of P in these compounds about half the theoretical fundamental value 5. [When we diminish Cl to 5,2, then 2,4 becomes 3,0 and 1,8 becomes 2,4. In HCl, namely, Cl has been found = 5,2, in CCl<sub>4</sub> even = 5 (all this  $\times 10^{-2}$ )]. Just as the value found for S was 0,6 unit lower for SOCl<sub>2</sub> than for S<sub>2</sub>Cl<sub>2</sub>, the value of P found for POCl<sub>3</sub> is here too 0,6 lower than for PCl<sub>3</sub> (influence of the inserted oxygen).

<sup>1)</sup> Prof. P. DUTOIT had the kindness to confirm the certainty of this fact for Br<sub>2</sub>, and the high probability for I<sub>2</sub>.

**c. Arsenicum.** The triple point of this substance seems to lie at  $817^{\circ}\text{C}$ . according to GOUBEAU (1914). At least at this temperature Arsenicum has been melted under pressure. The boiling point (sublimation point at 1 atm.) may be calculated from the series of vapour-pressure determinations of PREUNER and BROCKMÖLLER (loc.cit.). The latter namely found the following sublimation pressures at the indicated temperatures

$t = 400^{\circ} 45^{\circ} 470^{\circ} 476^{\circ} 488^{\circ} 500^{\circ} 512^{\circ} 526^{\circ} 557^{\circ} 569^{\circ} 580^{\circ} 600^{\circ}\text{C}$ .  
 $p = 6 \quad 19 \quad 28 \quad 32 \quad 44 \quad 61 \quad 90 \quad 130 \quad 268 \quad 334 \quad 430 \quad 586 \text{ mm.}$

From this we can calculate  $p_k$  and  $T_k$  by approximation (see II); we then find, also in connection with the values of  $a_k$  and  $b_k$  (see further below):

$$p_k = 95000 \text{ mm.} = 125 \text{ atm.}; \quad T_k = 1320^{\circ} \text{ abs.} = 1047^{\circ} \text{ C.}$$

If with these values according to VAN DER WAALS'S vapour pressure formula we calculate the corresponding values of  $F$ , then with  $\log^{10} p_k = 4,978$  from

$$F_{10} = \frac{4,978 - \log^{10} p}{(1320 : T) - 1},$$

where  $p$  must be expressed in mm. and  $T$  in absolute degrees, we find the following values:

$T = 673 \quad 723 \quad 743 \quad 749 \quad 761 \quad 773 \quad 785 \quad 799 \quad 830 \quad 842 \quad 853 \quad 873$   
 $F_{10} = 4,37 \quad 4,48 \quad 4,55 \quad 4,56 \quad 4,54 \quad 4,51 \quad 4,44 \quad 4,39 \quad 4,32 \quad 4,32 \quad 4,28 \quad 4,32$

The mean value is  $F_{10} = 4,42$  ( $F = 10,18$ ); the mean at the four highest temperatures is  $4,31$  ( $F = 9,93$ ). From this latter mean we now calculate easily that the value of  $T_k$ , that corresponds to  $p = 760 \text{ mm.}$ , is  $T_k = 888$ , i.e.  $t_k = 615^{\circ}\text{C}$ . This, therefore, is the temperature where the sublimation pressure amounts to 1 atm. (and not  $450^{\circ}\text{C}$ ., as was given by CONECHY in 1880. The pressure is then only 19 mm. instead of 760 mm.).

From the same formula  $p_{10} = 11720 \text{ mm.} = 15,4 \text{ atm.}$  is found for the pressure which corresponds to the above given triple point  $817^{\circ}\text{C} = 1090^{\circ} \text{ abs.}$

If the found temperatures are correct, we find  $T_k : T_s = 1320 : 888 = 1,49$ , a plausible value. [for  $N_s$  was found 1,61, for  $P$  (red) 1,41]. For  $T_k : T_{10}$  we calculate  $1320 : 1090 = 1,21$  (for red phosphorus 1,12).

The high value found for  $F$  is not very surprising. For as we have found  $F_k = 8\gamma$  in an earlier series of Papers <sup>1)</sup>, and as  $2\gamma = 1 + 0,038 \sqrt{T_k} = 2,38$ , i.e.  $\gamma = 1,19$  is calculated from

<sup>1)</sup> These Proc. of March 26, 1914, p. 808; April 23, p. 924; May 29, p. 1047; Sept. 26, p. 451.

$T_k = 1320$  abs. with our approximate formula,  $F_k$  would be  $= 9,52$ , only slightly divergent, therefore, from the value  $9,93$  found just now for the equilibrium solid-vapour, calculated at  $830^\circ$  à  $870^\circ$  abs.

With  $\gamma = 1,19$  we can now also calculate the factor  $f_1$ . We find: ( $m_1 = 1090 : 1320 = 0,826$ ):

$$f_1 = 2,38 \left[ 1 - \frac{1,19}{2,19} \times 0,826 \right] = 2,38 (1 - 0,449) = 1,312.$$

Now we ought to know the density at the triple point. But the calculation of this from the given density at  $14^\circ$  C. is rather unreliable, as  $817^\circ$  is too far from  $14^\circ$  C., and also the application of the coefficient of expansion determined at  $50^\circ$  C. is certainly not valid. In order to be able to determine the value of  $b_k$  notwithstanding with some approximation from the density at  $14^\circ$  C., we shall calculate  $f$  for this temperature ( $T = 287$ ,  $m = 0,217$ ). We find then:

$$f = 2,38 \left[ 1 - \frac{1,19}{2,19} \times 0,217 \right] = 2,38 (1 - 0,118) = 2,099.$$

As  $v = 71,2 \cdot 10^{-5}$  corresponds to  $D = 4,7$  (amorphous),  $b_k$  would become  $= 150 \cdot 10^{-5}$  instead of  $195 \cdot 10^{-5}$ . Probably, therefore, the assumed value of  $D$  is too high. Only with  $D = 3,62$  we should have found the expected value of  $b_k$ . In this connection we remark that  $D = 3,70$  has been found for the amorphous brown-black Arsenicum (GEUTHER, 1887). Then  $A : D$  would become  $= 20,26$ ,  $v = 90,40 \cdot 10^{-5}$ , hence  $b_k = 190 \cdot 10^{-5}$ , which comes nearer to the theoretical value  $195 \cdot 10^{-5}$ .)

We arrive, therefore, at the right result, if only the density of the "brown-black" modification, which is much slighter than that of the amorphous Arsenicum, is taken as the foundation of the calculation.

We find for the product  $f_1 t_1$ :

1) If for this modification we apply the formula of the straight diameter as first approximation, then

$$D_1 + D_1' = 3,7 - 0,932 \times 2,38 (0,826 - 0,217) = 2,35$$

would follow from  $D_1 + D_1' = (D + D') - D_k \times 2\gamma (m_1 - m)$ , when  $D'$  is neglected at  $14^\circ$  C., and the value  $0,932$  is taken for the calculated value  $D_k$ .

And as generally  $b_k = [A : (D_1 + D_1') : 22412] \times f_1$ ,  $b_k$  becomes  $= 142,3 \cdot 10^{-5} \times 1,312 = 187 \cdot 10^{-5}$  for 1 Gr. atom, also in the neighbourhood of  $195 \cdot 10^{-5}$ .

The value assumed just now for  $D_k$  follows from the relation (These Proc. loc. cit.)  $v_k = r b_k = \frac{1 + \gamma}{\gamma} b_k = \frac{2,19}{1,19} \times 195 \cdot 10^{-5} = 358,8 \cdot 10^{-5}$ . Expressed in ordinary units this is  $358,8 \cdot 10^{-5} \times 22412 = 80,41$ ; for 1 Gr. therefore  $80,41 : 74,96 = 1,073$ . Hence  $D_k = 0,9322$ .

$$f_1 u_1 = 1,312 \times 1,21 = 1,59.$$

The value of  $\varphi$  is obtained from this by multiplication by  $a_1 n_1 : a_k n_k$ . We shall directly find the value  $11,72 \cdot 10^{-2}$  for  $\sqrt{a_k}$ , so that  $a_k$  becomes  $= 137,4 \cdot 10^{-4}$ . Further  $\sqrt{a_1} = 7 \cdot 10^{-2}$ , hence  $a_1 : a_k = 0,357$ . If we again take  $n_1 = 16$ , just as for red phosphorus at the transition liquid-solid,  $n_k = 4 : 1,616 = 2,48$  (see below), then  $n_1 : n_k$  becomes  $= 6,46$ . Hence  $a_1 n_1 : a_k n_k$  would become  $= 2,31$ . But this renders  $\varphi$  no more than  $1,59 \times 2,31 = 3,66$  instead of 5 or higher. Most probably, therefore, the value of  $a_k$  has been taken too high, or the degree of association of liquid Arsenicum at the triple point is still higher than 16.

In connection with this we once more draw attention to what was found for *red* phosphorus, which modification is quite analogous to the *ordinary* arsenicum, whereas the *yellow* phosphorus seems to correspond with the *brown-black* Arsenicum. [density red P 2,20, yellow 1,83: only this latter value gave good results. Ordinary Arsenicum  $D = 4,7$ , brown-black 3,7: again only the latter value gives correct results. Triple point red P is high ( $589^\circ,5$  C.) with a pressure of 43 atm. and near  $T_k$  ( $695^\circ$  C.); triple point ordinary As also very high ( $817^\circ$  C.) with a pressure of 15 atm. and again near  $T_k$  ( $1050^\circ$  C.)]. It was namely found for the red P. by SCHENCK (See inter alia HOLLEMAN, Leerboek I, 2<sup>nd</sup> edition p. 223—224), that the polymerisation state must be considerably higher there than  $P_8$ . Accordingly we may safely assume a degree of association both for red P and for ordinary As of at least 16 at the triple point.

The above used value of  $a_k$  is calculated in the following way. We find the value  $a_k = 340,1 \cdot 10^{-4} : n_k$  (for  $\theta = [28 : (8\gamma - 1)] \times [\gamma : (\gamma + 1)]^2$  is found 0,970), hence,  $\sqrt{a_k} = 18,44 \cdot 10^{-2} : \sqrt{n_k}$  with  $T_k = 1320$ ,  $b_k = 195 \cdot 10^{-5}$  from the formula  $T_k = 78 \theta n_k \times a_k : b_k$ . Now at the critical temperature  $n_k$  is certainly  $< 4^1$ , so that  $\sqrt{a_k}$  will be  $> 9,2 \cdot 10^{-2}$ . And as the normal (theoretical) value for As amounts to  $7 \cdot 10^{-2}$ , there is necessarily already splitting up into isolated atoms  $As_1$  at  $T_k$ , which exhibit a so much greater attraction ( $\sqrt{a_k} =$  about  $30 \cdot 10^{-2}$ ). If we assume that the molecules  $As_4$  split up directly into  $As_1$ , without passing through the transition stage  $As_2^2$ , we may put  $n_k = 4 : (1 + 3x)$ , when  $x$  is the degree, of

<sup>1)</sup> According to PREUNER and BROCKMÖLLER (loc cit.)  $c_2^2 : c_4$  would be  $= 0,066 : p$  at  $1100^\circ$  C. for  $As_4 \rightarrow 2As_2$ , hence at a pressure of 125 atm.  $c_2^2 : c_4 = 0,00053$ , or  $c_2 = 0,023$ , when  $c_4$  is near 1. Further  $c_1^2 : c_2 = 0,013 : 125 = 0,00010$ , i. e.  $c_1 = 0,01$ , referring to  $c_2 = 1$ , would hold for the reaction  $As_2 \rightarrow 2As$  (also at  $1100^\circ$  C.).

<sup>2)</sup> Indeed, if we assumed a slight splitting up into  $As_2$  then, of this almost every-

dissociation, so that for the calculation of  $x$  we shall have:

$$9,22 \sqrt{1+3x} = 7(1-x) + 30x,$$

giving  $x = 0,205$ , hence  $\sqrt{1+3x} = 1,271$ , and  $\sqrt{a_k} = 9,22 \cdot 10^{-2} \times 1,271 = 11,72 \cdot 10^{-2}$ . In this it should be observed that when the attraction of the isolated atoms should be greater instead of  $30 \cdot 10^{-2}$ , the value of  $x$  will be found smaller; also in the case that the normal attraction of As in compounds should be greater than  $7 \cdot 10^{-2}$ .

If really  $\sqrt{a_k}$  is  $= 11,72 \cdot 10^{-2}$ , then follows for the critical pressure:

$$p_k = \frac{1}{28} \frac{a_k}{b_k^3} = \frac{137,4 \cdot 10^{-4} \times 0,970}{28 \times 380,25 \cdot 10^{-8}} = 125,2 \text{ atm},$$

in agreement with the value calculated above from the vapour pressures<sup>1)</sup>.

We may now proceed to give the calculation of a few Arsenicum compounds, viz. of  $\text{AsH}_3$  and  $\text{AsCl}_3$ .

thing would have been converted to  $\text{As}_1$  — in virtue of the comparatively high value of  $x$  (the degree of dissociation  $\text{As}_4 \rightarrow \text{As}_1$ ), viz. 0,2.

1) From the vapour pressures determined at  $557^\circ$  and  $600^\circ$  C we calculate namely easily (see Paper II)  $F_{10} \times T_k = 5727$ ,  $F_{10} + \log^{10} p_k = 9,3270$  (in which  $p_k$  is expressed in mm.). Further follows from this and from the equations

$T_k = 78 \text{ } \epsilon \text{ } n_k \times a_k : b_k$ ,  $p_k = \frac{1}{28} \text{ } \epsilon \text{ } \times a_k : b_k^3$ ,  $\sqrt{a_k} = (7 + 23x) \cdot 10^{-2}$ , in which  $= 0,97$ ,  $b_k = 195 \cdot 10^{-5}$ ,  $n_k = 4 : (1+3x)$  and  $p_k$  in atm., the perfectly accurate values

$$T_k = 1316^\circ \text{ abs.}; p_k = 124,6 \text{ atm.}; F_{10} = 4,351; \sqrt{a_k} = 11,69 \cdot 10^{-2}; \\ x = 0,2041$$

through a calculation of approximation for the five unknown quantities  $T_k$ ,  $p_k$ ,  $F_{10}$ ,  $a_k$  and  $x$ .

For  $p_k$  we found in round numbers 125 atm.; for  $T_k$   $1320^\circ$  abs. If we take  $1316^\circ$ , the somewhat higher values 4,39, 4,51, 4,58, 4,59, 4,57, 4,54, 4,47, 4,42 4,35, 4,35, 4,31, 4,35 are found for the values of  $F_{10}$  corresponding with the different vapour pressures, so that we duly find 4,35 for the 9<sup>th</sup> and 12<sup>th</sup> values in agreement with what precedes.

We may add that  $T_k$  and  $p_k$  (in atm.) are connected through the equation  $T_k = 5727 : (6,4462 - \log^{10} p_k)$ . Further evidently  $p_k \times (28 b_k^3 : \epsilon) = (7+23x)^2 \cdot 10^{-4}$ ,  $T_k \times (b_k : 78 \text{ } \epsilon) = 4(7+23x)^2 \cdot 10^{-4} (1+3x)$ , so that after elimination of  $T_k$  and  $p_k$  the following equation remains:

$$\frac{4(7+23x)^2 \cdot 10^{-4}}{1+3x} \frac{78 \text{ } \epsilon}{b_k} = 5727 : \left[ 6,4462 - \log^{10} \left\{ (7+23x)^2 \cdot 10^{-4} \frac{\text{ } \epsilon}{28 b_k^3} \right\} \right].$$

or also:

$$\frac{(7+23x)^2}{1+3x} = 369,0 : [6,4866 - \log^{10} (7+23x)^2],$$

from which then  $x = 0,2041$  is calculated. From this  $\log^{10} p_k = 2,0955$ ,  $p_k = 124,6$ . Etc. Etc.

|                   | $T_k$ | $b_k \cdot 10^5$           | $a_k \cdot 10^4$ | $\sqrt{a_k} \cdot 10^2$ |                          |
|-------------------|-------|----------------------------|------------------|-------------------------|--------------------------|
| AsH <sub>3</sub>  | 382   | $195 + 3 \times 34 = 297$  | 145,5            | 12,1                    | As = $2,5 \cdot 10^{-2}$ |
| AsCl <sub>3</sub> | 629   | $195 + 3 \times 115 = 540$ | 435,3            | 20,9                    | As = $4,7 \cdot 10^{-2}$ |

The critical temperature of AsH<sub>3</sub> was calculated from that of the boiling point (218°,3 abs.), multiplied by 1,75 (factor 1,69 for NH<sub>3</sub>, 1,75 for PH<sub>3</sub>). For AsCl<sub>3</sub> 629° abs. has been given as "calculated"; as  $T_s = 403°,3$ , the ratio would here be 1,56 (for PCl<sub>3</sub> it was 1,60). In any case we find *diminished* attraction for the said compounds. For AsCl<sub>3</sub> about 5 instead of 7, for AsH<sub>3</sub> not 0 as for NH<sub>3</sub> and also still for PH<sub>3</sub>, but about half 5, i.e. 2,5 (H assumed = 3,2). [If we take for H half the value 1,6, we should find the value  $7,3 \cdot 10^{-2}$  for As, i.e. about the normal value  $7 \cdot 10^{-2}$ ].

**d. Antimonium.** The melting point is very accurately known, viz. 630°,0 C. according to DAY and SOSMAN (1912). [In 1911 629,8 or 629,2 had been given]. The boiling point lies at 1440° C. according to GREENWOOD (1909). At this temperature the molecular weight of the vapour would already be  $< \text{Sb}_4$  (MENSCHING and V. MEYER), which is confirmed by the calculation of the value of  $\sqrt{a}$  at the critical temperature. With  $T_k : T_s = 1,75$  [for N<sub>2</sub> this ratio was 1,61, for yellow Phosphorus 1,75, for the brown-black Arsenicum unknown; we must namely compare with the said modifications, where just as for Sb the boiling point lies higher than the triple point] we calculate for  $T_k$  the approximated value 2998°, i.e. in round numbers 3000° abs.

Then the value  $1057 \cdot 10^{-4}$ :  $n_k$  follows for  $a_k$  from  $T_k = 78 \theta n_k \times a_k : b_k$  with  $\theta = 0,909$  and  $b_k = 250 \cdot 10^{-5}$ , or for  $\sqrt{a_k}$  the value  $32,51 \cdot 10^{-2} : \sqrt{n_k}$ .

If again we suppose, just as for As<sub>4</sub>, a direct decomposition of Sb<sub>4</sub> into Sb<sub>1</sub>, Sb<sub>2</sub> being skipped, then  $n_k = 4 : (1 + 3x)$ , hence  $\sqrt{a_k} = 16,26 \cdot 10^{-2} \times \sqrt{1 + 3x}$ . The normal theoretical value being = 9, this points to a great dissociation to simple molecules Sb<sub>1</sub>. If for the attraction of them we again assume a value in the neighbourhood of  $30 \cdot 10^{-2}$ , a value  $> 1$  follows for  $x$  from

$$16,3 \sqrt{1 + 3x} = 9(1 - x) + (\pm 30)x,$$

so that  $x = 1$  must be assumed, unless for  $\sqrt{a_{k_1}}$  a value is assumed  $> 32,5 \cdot 10^{-2}$ . The dissociation to Sb<sub>1</sub> is therefore complete, and we

can put  $\sqrt{a_k}$ , at least  $32,5 \cdot 10^{-2}$ . This would probably be also the value of the attraction of the isolated atoms Sn, Te, I, which elements are in the same row of the periodic system with Sb. The "residual attraction", i.e. when the atom valencies are saturate for *compounds*, is for all these elements  $= 9 \cdot 10^{-2}$ , which attraction is also found for the *atoms* of the valenceless Xenon.

Antimonium is the first element in our successive treatment of the different element groups, where the *atom* attraction *fully* manifests itself, and it can, therefore, not only be estimated, but also calculated. In our previous calculations of the degree of dissociation we have, therefore, assumed the preliminary value  $30 \cdot 10^{-2}$  as correct by approximation.

For the quantity  $2\gamma$  we find the value 3,08, hence  $\gamma = 1,54$  from our formula  $2\gamma = 1 + 0,038\sqrt{T_k}$ . At the triple point  $m_1$  is  $= 904,1$  :  $3000 = 0,301$ ,  $\mu_1 = 3,32$ , and  $f_1$  becomes :

$$f_1 = 3,08 \left[ 1 - \frac{1,54}{2,54} \times 0,301 \right] = 3,08 (1 - 0,183) = 2,519,$$

so that  $f_1 \mu_1 = 8,37$ . This must now again be multiplied by  $a_1 n_1$  :  $a_k n_k$ . As  $\sqrt{a_1} = 8,9 \cdot 10^{-2}$ ,  $\sqrt{a_k} = 32,5 \cdot 10^{-2}$ ,  $a_1 : a_k$  becomes  $= 0,0750$ . Further  $n_k = 1$ ,  $n_1$  perhaps  $= 8$  (for Phosphorus and Arsenicum 16 had to be assumed for this), hence  $a_1 n_1 : a_k n_k = 0,6$ . With this  $\mu$  would become  $= 5,02$ .

For the density of Antimonium at  $15^\circ$  C. 6,618 is given (KAHLBAUM, 1902). This gives  $A : D = 18,16$ ,  $v = 81,27 \cdot 10^{-5}$ . The factor by which we must multiply to obtain  $b_k$  — because  $m = 288 : 3000 = 0,096$ , is:

$$f = 3,08 \left[ 1 - \frac{1,54}{2,54} \times 0,096 \right] = 3,08 (1 - 0,0582) = 2,902.$$

We shall, therefore, calculate  $81,27 \cdot 10^{-5} \cdot 2,902 = 235,8 \cdot 10^{-5}$  for  $b_k$ , whereas the 6% higher value  $250 \cdot 10^{-5}$  found for compounds was expected. If the density were 6,2<sup>1)</sup> instead of 6,6, or if the factor  $f$  were slightly higher, in consequence of  $\gamma$  being on an average e.g. 1,63 instead of 1,54 — which is very well possible, as part of the range from  $15^\circ$  to  $3000^\circ$  passes over the solid state (viz.  $15^\circ$  to  $630^\circ$ ) — then for  $b_k$  the expected value would have been found.

Of the Antimonium *compounds* — of these we already treated

<sup>1)</sup> HÉRARD (1889) actually found the value 6,22 for amorphous Sb (98,7 %). But in contradiction to this is the fact that TOEPLER found  $D_1 = 6,41$  at the melting point in 1894, which would have yielded a still lower value for  $b_k$ .

the halogen compounds in II, where for  $\sqrt{a_k}$  the full value  $9 \cdot 10^{-2}$  was found — we shall still examine  $\text{SbH}_3$ .

|                | $T_k$ | $b_k \cdot 10^5$             | $a_k \cdot 10^4$ | $\sqrt{a_k} \cdot 10^2$ |                   |
|----------------|-------|------------------------------|------------------|-------------------------|-------------------|
| $\text{SbH}_3$ | 446   | $250 \div 3 \times 34 = 352$ | 201,3            | 14,2                    | $\text{Sb} = 4,6$ |

The critical temperature of  $\text{SbH}_3$  was calculated from  $T_s = 255^\circ$  abs., which gives  $T_k = 446^\circ$  abs. with  $T_k : T_s = 1,75$  (see for  $\text{AsH}_3$ ). We therefore find for  $\sqrt{a_k}$  about *half* the normal value 9. Noteworthy is the fact that when again we take for  $\text{AsH}_3$  for H not 3,2, but the half value 1,6, we should have found  $\text{Sb} = 9,4 \cdot 10^{-2}$ , i.e. about the normal theoretical value.

e. **Bismuth.** According to ADAMS and JOHNSTON (1912) the melting point lies at  $271^\circ,0 \text{ C.} = 544^\circ,1$  abs. (EGGINK found  $271^\circ,5$  in 1908). The boiling point lies at  $1435^\circ \text{ C.}$ , according to BARUS (1894), whereas GREENWOOD (1910) found the somewhat lower value  $1420^\circ \text{ C.} = 1693^\circ$  abs. With 1,75 as factor  $T_k$  would, therefore, be  $= 2963^\circ$ . If we assume in round numbers  $2960^\circ$ , the value  $1271 \cdot 10^{-4} : n_k$ , follows for  $a_k$  from  $T_k = 78 \theta n_k \times a_k : b_k$  with  $\theta = 0,910$ ,  $b_k = 305 \cdot 10^{-5}$ ; hence  $\sqrt{a_k} = 35,65 \cdot 10^{-2} : \sqrt{n_k}$ .

Just as for Sb, this points to  $n_k = 1$ , so that we find the high value  $35,6 \cdot 10^{-2}$  for the atomic attraction of Bismuth.

For  $2\gamma$  we find the value 3,068, hence  $\gamma = 1,534$ , from our approximate formula. In consequence of this,  $f_1$  becomes with  $n_1 = 544,1 : 2960 = 0,184$ :

$$f_1 = 3,068 \left[ 1 - \frac{1,534}{2,534} \times 0,184 \right] = 3,068 (1 - 0,111) = 2,727,$$

on account of which  $f_1 \mu_1$  assumes the value 14,83 with  $\mu_1 = 5,44$ . Now  $\sqrt{a_1} = 11 \cdot 10^{-2}$ ,  $\sqrt{a_k} = 35,65 \cdot 10^{-2}$ , hence  $a_1 : a_k = 0,0952$ . If further  $n_k = 1$ ,  $n_1 = 4$  (i. e. if at the triple point  $271^\circ \text{ C.}$  the liquid-solid bismuth  $= \text{Bi}_4$ ), then  $a_1 n_1 : a_k n_k = 0,381$ , hence  $\rho = 5,65$ .

ADAMS and JOHNSTON (1912) found  $D = 9,802$  for the density at  $15^\circ$ , KAHLBAUM (1902) gives 9,791. By an electrolytic way (CLASSEN, 1890) 9,747 was found, and HÉRARD gives 9,483 for amorphous bismuth (contained 0,4 %  $\text{O}_2$ ). At the melting-point VICENTINI and OMODEI (1888) give the value 9,673 for the solid bismuth, 10,004 for the liquid bismuth. (ROBERTS and WRIGHTSON had found the almost identical value 10,039 in 1882).

If we take A. and J.'s value at 15° C. as basis for the calculation,  $A : D$  would become = 21,22,  $v = 94,70 \cdot 10^{-5}$ , so that we find for  $b_k$  with

$$f = 3,068 [1 - 0,6054 \times 0,0973] = 3,068 (1 - 0,0589) = 2,887$$

the value  $b_k = 273,4 \cdot 10^{-5}$ , though the value  $305 \cdot 10^{-5}$ , which is more than 10% higher, was expected. Either the critical temperature, and because of this also  $\gamma$ , has been estimated too low, or the density has been assumed too high. But the latter is not very probable in view of the still greater value at the melting point.

In connection with the values of  $T_k$  and  $p_k$  we still draw attention to a series of vapour pressure determinations of GREENWOOD (1910). If  $\sqrt{a_k}$  is really =  $35,65 \cdot 10^{-2}$ , as we found above, and  $b_k^2 = 305 \cdot 10^{-2}$ ,  $p_k = 444,3$  atm.,  $\log^{10} p_k = 2,6477$  would follow from  $p_k = \frac{1}{28} \theta \times a_k : b_k^2$ .

We find the vapour pressure factor  $F_{10}$  of VAN DER WAALS'S formula  $\log^{10} (p_k - p) = F_{10} (T_k/T - 1)$  therefore from

$$F_{10} = \frac{2,648 - \log p}{(2960 : T) - 1}$$

From:

|                  |              |              |              |              |                   |
|------------------|--------------|--------------|--------------|--------------|-------------------|
| $T = 1473^\circ$ | $1583^\circ$ | $1693^\circ$ | $2013^\circ$ | $2223^\circ$ | $2333^\circ$ abs. |
| $p = 102$        | $257$ mm.    | $1$          | $6,3$        | $11,7$       | $16,5$ atm.       |

would then follow:

$$F_{10} = 3,49 \quad 3,59 \quad 3,54 \quad 3,93 \quad 4,76 \quad 5,32.$$

The rise of the value of  $F$  need not astonish us, when we think that the state of nothing but simple molecules has not been reached from the outset, and that at 1500° abs. molecules  $Bi_2$  (or  $Bi_4$ ) can very well be present. The attraction is then smaller than the final value  $\sqrt{a_k} = 35,6 \cdot 10^{-2}$ , so that also  $T_k$  will be smaller than 2960° abs. And this is accompanied with a decrease of the value of  $F$ . But yet the increase seems somewhat too great to us, because according to the formula  $F_k = 8\gamma$  the value of  $F$  at the critical point will have to be about = 12,3, i.e.  $F_{10} = 5,33$ . And with  $T_k = 2960^\circ$  abs. the value of  $F$  would already be = 5,3 at 2333°, and evidently be still increasing.

If we assume  $T_k = 3000^\circ$  abs., we should find the following values of  $F$ :

$$F_{10} = 3,40 \quad 3,49 \quad 3,44 \quad 3,78 \quad 4,54 \quad 5,02,$$

which increase less rapidly at the highest temperatures, and remain below 5,35.

If  $T_k = 3000^\circ$  abs., also  $a_k$  would become slightly greater, viz. ( $\theta$  is now = 0,909)  $a_k = 1290 \cdot 10^{-4}$ , which would render  $\sqrt{a_k} = 35,92 \cdot 10^{-2}$ . The value  $2\gamma$  would become 3,081 instead of 3,07, on

account of which  $\gamma \cdot (1 + \gamma) = 0,606$ . For  $p_k$  we further find the value 450,1 atm. ( $\log^{10} p_k = 2,6533$ ). By means of this we then find the above values of  $F_{10}$ .

Now  $F = 8\gamma = 12,32$  is expected for the value of  $F$  at  $T_k$ , hence  $F_k = 5,35$  about. This then would be the limiting value, which is reached at the critical temperature.

At  $T_k = 2960^\circ$  abs. the ratio  $T_k : T_s$  was 1,75, at  $3000^\circ$  abs. this ratio will be = 1,77. And for  $T_k : T_u$  we find 5,51. (For  $m_1$  the value 0,181). Etc.

At any rate the critical temperature of Bismuth lies in the neighbourhood of  $3000^\circ$  abs. with an uncertainty of perhaps a few tens of degrees. And the critical pressure in the neighbourhood of 450 atm. with an uncertainty of a few units. From this it is once more seen how great a value the knowledge of some vapour pressures has for the calculation of the critical data — also when as here the condition gradually develops from a mixture of molecules and atoms to nothing but atoms. For Arsenicum the critical temperature could likewise be fixed with a high degree of certainty at somewhat higher than 1300 abs. through the knowledge of the sublimation pressures. There at the temperatures at which the pressures were determined ( $700^\circ$  à  $900^\circ$  abs.), the condition changed still very little, and the value of  $F$  remained beautifully constant.

Let us in conclusion recapitulate all that has been found in the following tabular survey. (p. 320).

At the critical point Nitrogen =  $N_2$ ; Phosphorus =  $P_4$ ; Arsenicum =  $As_4$ , dissociated to  $As_1$  to an amount of 0,2; Sb and Bi are =  $Sb_1$  and  $Bi_1$ , with the increased atomic attractions **33** and **35** about, i. e. 24 units higher than the normal (residual) attractions 7 and 9 (all this  $\times 10^{-2}$ ) in compounds. (For Arsenicum the normal attraction 7 is only partially increased to almost 12).

It is still noteworthy that — where for  $NH_3$  and  $PH_3$  the attraction of the central N- or P-atom is entirely eliminated by the surrounding H-atoms — the attraction of the so much larger As- and Sb-atoms makes itself again partially felt for  $AsH_3$  and  $SbH_3$ . For As 2,5 (normal 7) instead of 0; for Sb 4,6 (normal 9) instead of 0.

Also for  $PCl_3$ ,  $POCl_2$  and  $AsCl_3$  *diminished* attractions are found, while we have seen in II that for  $SbCl_3$  the attraction of Sb is again fully felt.

In conclusion we remark that for the Nitrogen group (Nitrogen itself excepted, unless we assume association at the triple point) the quantity  $\bar{\varphi}$ , by which the ratio  $(v_1 - b_1) : v_1$  at the triple point is determined, seems to lie in the neighbourhood of 5 à 6. In the oxygen group

TABLE D<sub>1</sub>.

| <i>N</i>            | <i>A</i> | <i>A/N</i> | <i>D</i> <sub>1</sub> | <i>A/D</i> <sub>1</sub> | $v_1 \cdot 10^5 = \text{id.} : 0,22412$ | $\gamma$ | $\gamma'$ | <i>m</i> <sub>1</sub> | <i>f</i> <sub>1</sub> | $b_k \cdot 10^5$<br>calculated | $b_k \cdot 10^5$<br>found |
|---------------------|----------|------------|-----------------------|-------------------------|-----------------------------------------|----------|-----------|-----------------------|-----------------------|--------------------------------|---------------------------|
| 7 N <sub>2</sub>    | 14,01    | 2,00       | 0,870                 | 16,11                   | 71,88                                   | 0,793    | 0,713     | 0,501                 | 1,235                 | 89                             | 86 (85)                   |
| 15 P <sup>1)</sup>  | 31,04    | 2,07       | 1,79                  | 17,34                   | 77,37                                   | —        | 1,09      | 0,328                 | 1,809                 | 140                            | 134 (140)                 |
| 33 As <sup>2)</sup> | 74,96    | 2,27       | 3,70 (14°)            | 20,26                   | 90,40                                   | —        | 1,19      | (0,826)               | (1,343)               | 192                            | (195)                     |
| 51 Sb               | 120,2    | 2,36       | 6,62 (15°)            | 18,16                   | 81,27                                   | —        | 1,54      | 0,301                 | 2,519                 | 236                            | (250)                     |
| 83 Bi               | 208,0    | 2,51       | 9,80 (15°)            | 21,22                   | 94,70                                   | —        | 1,54      | 0,181                 | 2,742                 | 275                            | (305)                     |

TABLE D<sub>2</sub>.

|                               | <i>T</i> <sub>tr</sub> | <i>T</i> <sub>s</sub> | <i>T</i> <sub>k</sub> | <i>p</i> <sub>k</sub> | <i>D</i> <sub>k</sub> | $\frac{T_k}{T_s}$ | $\nu_1 = \frac{T_k}{T_{tr}}$ | <i>f</i> <sub>1</sub> <sup>ν<sub>1</sub></sup> | $\varphi$ | $\nu a_k \cdot 10^2$<br>calculated | $\nu a_k \cdot 10^2$<br>in comp. | <i>x</i> |
|-------------------------------|------------------------|-----------------------|-----------------------|-----------------------|-----------------------|-------------------|------------------------------|------------------------------------------------|-----------|------------------------------------|----------------------------------|----------|
| N <sub>2</sub>                | 63,06                  | 78,00                 | 125,96                | 33,49                 | 0,311                 | 1,61              | 2,00                         | 2,47                                           | 2,47      | 2,6                                | 2,9                              | 0        |
| P <sub>4</sub> <sup>1)</sup>  | 317,2                  | 553,6                 | 968                   | 82,8                  | —                     | 1,75              | 3,05                         | 5,52                                           | 5,52      | 6,4                                | 6,4                              | 0        |
| As <sub>4</sub> <sup>2)</sup> | (1090)                 | (889)                 | 1320                  | 125                   | 0,932                 | (1,48)            | (1,21)                       | (1,59)                                         | 3,66?     | 11,7                               | 7                                | 0,2      |
| Sb <sub>4</sub>               | 903,1                  | 1713                  | 3000                  | —                     | —                     | 1,75              | 3,32                         | 8,37                                           | 5,02      | 32,5                               | 8,9                              | 1        |
| Bi <sub>4</sub>               | 544,1                  | 1693                  | 3000                  | 450                   | —                     | 1,77              | 5,51                         | 15,1                                           | 5,67      | 35,9                               | 11                               | 1        |

we found  $\varphi = 4$  à  $5$ ; in the halogen group =  $3$  à  $4$ ; in the group of the noble gases =  $2$  à  $3$ . Here an increase takes unmistakably place in the increase of the number of chief valencies from 0 to 3.

As  $(v_1 - b_1) : v_1 = \frac{8}{27} : \varphi$ , this ratio decreases from about  $\frac{1}{8}$  for the Helium group to  $\frac{1}{20}$  for the Nitrogen group. This is to say that for the first group the free volume at the solidification amounts to about  $\frac{1}{8}$  of the total volume; for the latter group on the other hand only to  $\frac{1}{20}$ .

This, therefore, seems to be the law by which the *solidification* of the elements is governed.

In the following papers only such elements are considered, as are *entirely* dissociated to *atoms* at *T<sub>k</sub>* (as up to now were only Antimony and Bismuth), and for which the *full*, exceedingly high *atomic attraction* manifests itself.

Clarens, June 1916.

<sup>1)</sup> All the experimental values and those derived from them refer to the yellow phosphorus.

<sup>2)</sup> The values of *D*, *A* : *D*, *v* and *b<sub>k</sub>* calculated refer to the *brown-black* modification, which corresponds to the yellow phosphorus; all the other values to the *ordinary* arsenicum, which is analogous with the red (greatly associated) phosphorus.