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**Physics.** — “On the Heat of Dissociation of Di-atomic Gases in Connection with the Increased Valency-Attractions  $\sqrt{A}$  of the Free Atoms”. By Dr. J. J. VAN LAAR. (Communicated by Prof. H. A. LORENTZ).

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*Introduction.*

1. In a series of Treatises in these Proceedings<sup>1)</sup> on the additivity of the values of  $b$  and  $\sqrt{a}$  of the equation of state, and on the fundamental values of these quantities for different elements in connection with the periodic system, I determined the following values of  $b \cdot 10^5$  and  $\sqrt{a} \cdot 10^2$ , expressed in so-called “normal” units.

The values of  $b_k \cdot 10^5$  (per Gr. atom), determined up to now, are found collected in Table I.

TABLE I. (Values of  $b_k \cdot 10^5$ ).

H = 59 (34; 14)						He = 105
Li = 145		C = 100 (75)	N = 85 (60)	O = 70 (50)	F = 55	Ne = 76
Na = 270		Si = 155	P = 144	S = 125	Cl = 110 à 115	Ar = 144
K = 480		Ti = 180				
Cu = 110		Ge = 210	As = 195	Se = 180	Br = 165	Kr = 177
Rb = 580		Zr = 235				
Ag = 150		Sn = 265	Sb = 250	Te = 235	I = 220	X = 228
Cs = 710		Ce = 290				
Au = 150	Hg = 150	Pb = 320 à 375	Bi = 305			Nt = 277
		Th = 400				

It will be remembered that these fundamental values present a great regularity. Starting from the carbon group the decrease in every

<sup>1)</sup> These Proceed. 18, 1220 and 1235; 19, 2, 287 and 295 (1916); 20, 138, 492 and 505 (1917). Cf. also Journ. de Chim. Phys. 14, 3 (1916), and Zeitschr. f. anorg. u. allg. Chem. 104, 56—156 (1918).

horizontal row of the periodic system towards the right is 15 *units*, in every vertical row the increase downward 55 *units*. The elements of the valence-less Helium group evidently fit in with the elements of the preceding Halogen group in a natural way.

In this Helium group the values of  $b_k$  are directly calculated from those of  $T_k$  and  $p_k$ ; also the value 59 for H from that of H, <sup>1)</sup>. The other values have been calculated from the *compounds* of the different elements (for Cl the value 115 seems to be more satisfactory than 110). From  $T_k$  and  $p_k$  we can directly calculate for N, P, O, Cl from N<sub>2</sub>, P<sub>4</sub>, O<sub>2</sub> and Cl<sub>2</sub>:  $b = 86, 135, 71$  and  $113$  to  $125$  (according as for Cl<sub>2</sub> the data of DEWAR or the more recent ones of PELLATON are used).

All the values of  $b$  can now be built up *additively* by the aid of these fundamental values for the most divergent compounds. In this also the "condensed" values 34 and 14 are valid for H; for C, N, and O the condensed values 75, resp. 60 and 50. The rules holding for this are found in the two cited principal papers of 1916 in These Proceedings and in the Journ. de Ch. Ph.

No exceptions have been found to this additive law, those that still existed for a few organic substances (e.g. the *amines*) have now all disappeared, owing to the later determinations of  $T_k$  and  $p_k$  by BERTHOUD <sup>2)</sup> at Neuchâtel, undertaken expressly in connection with these deviations. The critical pressures determined earlier by VINCENT and CHAPPUIS appeared to be all faulty to a high degree <sup>3)</sup>. It is to be foreseen that this will also be the case with other earlier determinations.

We will also state that the values of  $b$  for H, Li, Na, K, Rb and Cs are to each other in the ratio  $1/2 : 1 1/4 : 2 1/8 : 4 : 5 : 6$ .

The values of  $b$  found are *entirely independent* of the state in which the atom is: whether as *free* atom e.g. in metallic tin, or as part of a molecule as in SnCl<sub>4</sub>. It will presently appear that this is *not* the case with the fundamental values of  $\sqrt{a}$ .

2. For the values of  $10^2 \sqrt{a_k}$  per Gr. atom, again expressed in "normal" units, were found up to now the values recorded in table

<sup>1)</sup> Of course the latest data were used for this; for H<sub>2</sub> and Ne the values found very recently by K. ONNES, CROMMELIN and CATH.

<sup>2)</sup> Journ. de Chim. Phys. 15, 3 (1917).

<sup>3)</sup> Thus  $p_k$  appeared to be = 55,5 for NH<sub>2</sub>.C<sub>2</sub>H<sub>5</sub>, whereas V. and Ch. found 66; for NH(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub> the value 36.6 was found, against 40 by V. and Ch.; etc. Also for C<sub>3</sub>H<sub>7</sub>Cl BERTHOUD found 45,2, whereas V. and Ch. found 49. Errors therefore from 10 to 20%!

II; the values printed in bold type refer to the *increased* values of the *free atoms*, the others to those which are found in *compounds*: hence the *rest-values*.

TABLE II. (Values of  $\sqrt{a_k} \cdot 10^2$ ).

H = 1,1 (3,2; 1,6)						He = 0,8
Li = ? 23		C = 3,1 32	N = 2,9	O = 2,7	F = 2,9	Ne = 2,1
Na = ? 27		Si = ? 34	P = 6,4	S = 6,3	Cl = 5,4	Ar = 5,2
K = ? 33		Ti = ? 35				
		Ge = ? 36	As = 7	Se = 7	Br = 6,9	Kr = 6,9
Rb = ? 35		Zr = ? 37				
		Sr = ? 38	Sb = 8,9 33	Te = 9,8	I = 8,8	X = 9,1
Cs = ? 38		Ce = ? 39				
	Hg = 10,7	Pb = ? 40	Bi = 11 36			Nt = 11,5
		Th = ? 41				

Not from the fundamental values of  $a$  can the values of  $a$  of all possible compounds be built up additively — but those of  $\sqrt{a}$  from the fundamental values of  $\sqrt{a}$  given in the above table. Here too no important deviations were found; those for the amines have again disappeared for the greater part through the later determinations of BERTHOUD (loc. cit.).

The values of  $\sqrt{a_k}$  for the noble gases (calculated directly from those of  $T_k$  and  $p_k$ ) fit in again perfectly with the values holding for every horizontal row. It may be said of them that (starting from the carbon group) the values of  $\sqrt{a_k}$  in *compounds* are *about the same* for every horizontal row of the periodic system, and can be represented in approximation by the whole numbers 1. 3. 5. 7. 9. 11 from the 0. to the 5. row (inclusive).

The values of  $\sqrt{a_k}$  calculated for N, P, O, and Cl directly from  $N_2$ ,  $P_4$ ,  $O_2$ , and  $Cl_2$  are resp. 2,6, 6,4, 2,6 and 5,4 to 5,8 (DEWAR or PELLATON).

For H in compounds only the values 3,2 and chiefly 1,6 hold. The value 1,1 calculated directly from  $T_k$  and  $p_k$  of  $H_2$  is only found for  $H_2$  itself.

3. However — what is self-evidently *not* found for  $b$  — it should be taken into account that for the fundamental values of  $\sqrt{a}$  the indicated attractions can be entirely or partly *destroyed* by an interception of the rays of attraction. Thus the value of  $\sqrt{a}$  of a central atom surrounded on all sides by atoms or atom groups — as e. g. C in  $CH_4$ ,  $C_2H_6$  etc., Si in  $SiCl_4$ , Sn and Ge in  $SnCl_4$  and  $GeCl_4$ , N and P in  $NH_3$  and  $PH_3$  — is found  $= 0$  everywhere, so that these enclosed atoms do not exert *any attractive action towards the outside*<sup>1)</sup>.

But as soon as the C-atom gets *partly free* again, by *double bindings* e.g. as in  $C_2H_4$  (only imagine the position of the C-atom stereo-chemical), the value of  $\sqrt{a_k}$  rises immediately from 0 to 1,55, hence half the fundamental value 3,1. And when the C-atom gets *entirely free*, for *triple bindings* e.g. as in  $C_2H_2$ , the full value 3,1 is accordingly at once found.

This rule holds everywhere. An interesting example is the *isomylene*. Here there are three singly bound and two doubly bound C-atoms. Hence the value  $3 \times 0 + 2 \times 1,55 + 10 \times 1,6 = 19,1$  is calculated for  $\sqrt{a_k}$ . From  $T_k$  and  $p_k$  19,2 was found. Indeed, an exceedingly remarkable confirmation of the rule.

The same thing holds for benzene and naphthalene. But for the singly bound C-atoms in the *substitution groups* the old value 0 is again valid. Thus for Toluene  $= C_6H_5.CH_3$  the value of  $\sqrt{a_k}$  is  $= 6 \times 1,55 + 1 \times 0 + 8 \times 1,6 = 22,1$ , while 22,2 is found; for O-Xylene  $= C_6H_4(CH_3)_2$  we calculate  $6 \times 1,55 + 2 \times 0 + 10 \times 1,6 = 25,3$ , quite identical with the value 25,3 found from  $T_k$  and  $p_k$ . We might add numerous others to these examples, but we refer for this to the earlier principal papers.

We have now reached the *main question*: what happens when the atoms no longer occur in compounds, as N in  $N_2$ , Cl in  $Cl_2$ , etc. — but can occur *entirely free*, as for the *metals*, or for the *free atoms* Cl, Br and I in  $Cl_2$ ,  $Br_2$ ,  $I_2$ , which get decomposed at

<sup>1)</sup> Accordingly in consequence of this (see the table) we were not able to give the values of  $\sqrt{a_k}$  for Si, Ti, Ge and Sn in compounds, though compounds of them are known, of which  $T_k$  and  $p_k$  have been determined. But it is exactly in *these* compounds ( $SiCl_4$ ,  $GeCl_4$  etc.) that the attraction of the central atom Si, Ti, Ge, Sn is eliminated.

high temperatures, or for H, N and O in the gases  $H_2$ ,  $N_2$ ,  $O_2$ , which also dissociate at very high temperatures?

Then — and this is perhaps the most remarkable of our results, which is fully confirmed by what follows presently with respect to the heats of dissociation — the values of  $\sqrt{a}$  rise at once to the greatly increased values from **30** to **40** (instead of from 1 to 11). These increased values are therefore the real *valency-attractions*, whereas the values found in compounds represent only the so-called *rest-values*: what still remains for action outside, after the chief valencies are saturate, and have therefore become inactive towards the outside.

That for the elements of the helium group only the ordinary rest values are found in spite of their atomistic behaviour is of course owing to this that these elements are *valence-less*.

For arsenic only a partially increased value was found, pointing to a dissociation of  $As_4$  at  $T_k$  to an amount of 20%, whereas phosphorus appeared to be still perfectly normal =  $P_4$  at  $T_k$ . For Se and Te we found amounts of dissociation (always at  $T_k$ ) of 30% resp. 80%. In the halogen group only a very slight degree of dissociation (5 and 10%) was observed for  $Br_2$  and  $I_2$ . As the atoms occur more and more as *free atoms*, the *metal character* asserts itself more and more in a group:  $As \rightarrow Sb \rightarrow Bi$ ,  $Se \rightarrow Te$ ; etc.

Besides the rise from 0 to 1.55 and 3.1 for *carbon* — according as the C-atom is entirely or only partially shadowed by surrounding atoms or atom groups, to which it is *bound* — another rise of  $\sqrt{a}$  takes place, up to 32, the *ten-fold value*, when the C-atom has also got released from these bindings, and can occur *quite independent* as *atomistic carbon*. Hence the enormously high value of the critical temperature, viz. 6500 abs., which would only have amounted to 120° abs. in the case of  $C_2$ , as is easy to calculate. The carbon would have become comparable with  $N_2$ ,  $O_2$ , etc., whereas it is now on a line with a metal that is exceedingly difficult to melt.

For *Tellurium* the peculiarity is still found that the normal rest-attraction 9, which is among others found for  $TeCl_4$  <sup>1)</sup>, has already

<sup>1)</sup> That for  $TeCl_4$  the central Te atom does not exert an intercepting influence like C in  $CCl_4$ , Ge in  $GeCl_4$ , etc. is owing to the configuration of the molecule. While for  $CCl_4$  the four chlorine atoms are regularly situated in the *space* round the C-atom (in the direction of the four angular points of a tetrahedron), it should be supposed that for  $TeCl_4$  the Cl atoms lie in one plane round the central Te-atom. Nor do we find a complete intercepting influence for  $PCl_3$  and  $POCl_3$ ,  $AsH_3$  and  $AsCl_3$ ,  $SbH_3$  and  $SbCl_3$ , which for these substances is probably owing to the comparatively greater extension of the central atom. For  $SbCl_3$  we find even again the full rest value 9 (Cf. the cited papers in these Proceedings).

risen to 13 for  $\text{TeCl}_4$ , — where two valencies have been liberated. For entirely free metallic Te  $\sqrt{A}$  will rise still further, namely to about 30.

What consequences this behaviour of molecules and atoms with regard to the attraction exercised by them can have for the properties of many substances (volatility, surface tension, etc.), has been set forth at length by me elsewhere.<sup>1)</sup>

#### 4. The heat of dissociation of di-atomic gases.

After these introductory remarks we may now proceed to the real subject of this Paper, viz. the calculation of the *heats of dissociation*  $Q$  from the values of the increased valency attractions  $\sqrt{A}$ , which were mentioned above, and which are recorded in table II (the values printed in bold type under the elements), for so far as they are now known.

Let us take hydrogen as an example. For the internal energy of the not dissociated gas  $\text{H}_2$ , we may write:

$$E_{\text{H}_2} = (E_0 - Q_0) - \frac{a}{v} + c_{\text{H}_2} T, \quad . . . . . (a)$$

in which  $E_0$  represents the so-called *constant of Energy* of the *unbound* H-atoms, hence  $E_0 - Q_0$  that of the *bound*  $\text{H}_2$ -atoms in  $\text{H}_2$ . Hence  $Q_0$  is the absorbed (internal) heat of dissociation (in units of energy e.g.) in the dissociation  $\text{H}_2 \rightarrow 2\text{H}$ , at  $T = 0$  — i.e. the chemical energy (at  $T = 0$ ), which is liberated in the formation of 1 Gr. mol.  $\text{H}_2$  from the separate H-atoms).

For the dissociated  $\text{H} + \text{H}$  we have evidently:

$$2E_{\text{H}} = E_0 - \frac{4A}{v} + 2c_{\text{H}} T. \quad . . . . . (b)$$

While, namely, for  $\text{H}_2$  the quantity  $a$  represented the ordinary rest attraction (per Gr. mol.) between the *molecules*,  $A$  now represents the increased attraction of valency between the separate, now free *atoms* per Gr. atom, hence  $4A$  per Gr. mol. = 2 Gr. atoms.

In the *ideal gasstate*, where  $v$  is very great, we shall simply have:

$$E_{\text{H}_2} = (E_0 - Q_0) + c_{\text{H}_2} T \quad ; \quad 2E_{\text{H}} = E_0 + 2c_{\text{H}} T,$$

and as these two quantities of energy will just differ the *total* (internal) heat of dissociation  $Q$ , we have then:

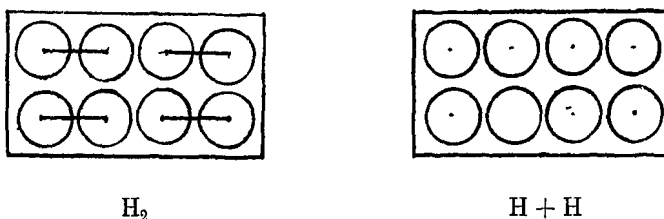
$$Q = 2E_{\text{H}} - E_{\text{H}_2} = Q_0 + (2c_{\text{H}} - c_{\text{H}_2}) T, \quad . . . . . (c)$$

the well-known expression for  $Q$  in the function of  $T$ , when  $c_{\text{H}}$  represents the limiting value of the specific heat at constant (large)

<sup>1)</sup> Cf. Chemisch Weekblad, Sept. 14, 1918, No. 37 (p. 1124—1137).

volume of 1 Gr. atom H, and  $c_{H_2}$  the same quantity for  $H_2$ . As  $c_{H_2}$  is = 5, and  $c_H = 3$  (in Gr. cal.),  $Q = Q_0 + T$  may be written in the case of  $H_2 \rightarrow 2H$  for  $Q$ .

When, however, the volume becomes smaller and smaller, and the quantities  $\frac{a}{v}$  and  $\frac{A}{v}$  larger and larger, at last a (fictitious) volume will arise, in which the difference of the two energies has become = 0, in consequence of the fact that with respect to the internal energy it will then have become quite indifferent whether the atoms are separately present in that small space, or combined to molecules — i.e. when also the energies of translation do not differ, hence at  $T = 0$ .



For the difference  $Q' = 2E'_H - E'_{H_2}$  we have in this case.

$$Q' = Q_0 - \frac{4A}{v_1} + \frac{a}{v_1} + (2c_H - c_{H_2})T, \dots \dots \dots (d)$$

in which  $v_1$  represents the above mentioned small volume, which we shall have to define more closely. Now it follows immediately from (d) at  $T = 0$ , in which case  $Q'$  must be = 0, that

$$Q_0 = \frac{4A}{v_1} - \frac{a}{v_1}, \dots \dots \dots (1)$$

and this is the simple relation between the heat of dissociation  $Q_0$  at  $T = 0$  and the two attractions  $A$  and  $a$ , which we have sought.

We must now determine the small volume  $v_1$ . This will evidently be of the order of the limiting volume, which the molecules themselves (see the above figure) occupy in the *natural* state in *unconstrained* condition, i.e. the volume expressed by  $b_g$  — and not e.g. the smaller volume  $b_l$  in the liquid state, where the molecules will be *compressed* in consequence of the smaller space, and which therefore denotes a *constrained*, and no free, no natural condition <sup>1)</sup>. Now  $b_g$  is about =  $b_k$ , so that we may put:

$$v_1 = \gamma b_k,$$

<sup>1)</sup> In this it has also been supposed that  $b_g$  is not =  $4m$ , when  $m$  denotes the *real* volume of the molecules, but simply =  $m$  itself. According to recent views the latter supposition is theoretically at least as well justified as the former  $b_g = 4m$ , which refers specially to collisions of *mathematical spheres*, and not of *real*



in which  $\gamma (> 1)$  will not be far from unity. When we put  $4A = na$ , (1) becomes:

$$Q_0 = \frac{(n-1)a_1}{v_1} = \frac{(n-1)\varepsilon a_k}{\gamma b_k},$$

in which we put  $a_1$ , the attraction in the small volume  $v_1$ ,  $= \varepsilon a_k$ . In this  $\varepsilon (> 1)$  will differ somewhat more from unity than  $\gamma$ , so that  $\varepsilon$  will be  $> \gamma$ . For  $a_k : b_k$  we may now write  $\frac{27}{8\lambda} RT_k$ , in which  $\gamma$  is only little smaller than 1, so that we finally get, when  $\gamma\lambda : \varepsilon = \theta$  is put:

$$Q_0 = (n-1) \frac{27}{8\theta} RT_k, \dots \dots \dots (1a)$$

which enables us to calculate  $Q_0$ , when  $A$  and  $a$ , and in consequence of which also  $n$  and  $T_k$  are known. But as we do not know the values of  $A$  for  $H_2$ ,  $N_2$ ,  $O_2$ , but as we on the other hand *do* know those of  $Q_0$ , in approximation, we shall follow the *reversed* course, and calculate  $n$  from  $Q_0$ . We can then see whether the values of  $\sqrt{A}$  calculated in this way are really of the expected order of magnitude, compared with the already known values of  $\sqrt{A}$  for elements of the periodic system lying near (cf. Table II). We then get:

$$n = 1 + \frac{4}{27} \theta \frac{Q_0}{T_k},$$

hence:

$$4A = a \left( 1 + \frac{4}{27} \theta \frac{Q_0}{T_k} \right),$$

when 2, the value in Gr. cal., is put for  $R$ , which renders it possible to leave also  $Q_0$  expressed in Gr. cal. The value of  $a$  refers to 1 Gr.mol.  $H_2$ . When therefore  $a'$  represents the value of one *gram-atom* (*these* values are recorded in table II), then  $a = 4a'$ , and we get finally:

$$\sqrt{A_k} = \sqrt{a'_k} \times \sqrt{1 + \frac{4}{27} \theta \frac{Q_0}{T_k}}, \dots \dots \dots (2)$$

when we take  $A$  and  $a'$  both at the critical temperature. Accordingly these two quantities now duly refer to 1 Gr.atom. Under the root sign, however,  $Q_0$  refers to 1 Gr.mol. according to the derivation of the formula. As  $\varepsilon$  will always be  $> \gamma\lambda$ ,  $\theta = \gamma\lambda : \varepsilon$  will be *somewhat smaller* than unity, also when we take into account that  $R$  is not

*molecules* (which can differ considerably from the spherical shape, e.g. the elongated molecules of the hydro-carbons). Moreover, when the real size of the molecules is calculated by another method, we also find values that are in concordance with  $b_k$  ( $- b_q$ ), calculated from  $T_k$  and  $p_k$ , and *not* with  $\frac{1}{4} b_k$ . Cf. among others my Article in These Proc. of Oct. 1914 (Vol. 17), especially p 883 and the Note on the same page.

exactly = 2, but somewhat smaller. The values of  $\sqrt{A_k}$  calculated from (2) will, therefore, be sooner *too large* than too small, when we shall take for the present  $\theta = 1$  in what follows.

### 5. Calculation of the values of $\sqrt{A_k}$ from $Q_0$ .

Let us begin with *hydrogen*. ISNARDY (1915) determined  $Q_0 = 95000$  Gr. cal., whereas LANGMUIR (well-known method) gave 132000 Gr. cal. in 1912. But the latter found from 70000 to 80000 Gr. cal. in 1914.

We are therefore not very far from the truth, when for  $H_2$  we put the value of  $Q_0$  at round 90000 Gr.cal. With  $T_k = 33,18$  (K. ONNES, CROMMELIN, CATH, 1917)  $Q_0 : T_k$  becomes therefore = 2700, hence  ${}^{1/27}Q_0 : T_k = 402$ . And as  $\sqrt{a'_k} = 1,1$  (see table II), we get (all the values of  $\sqrt{a'_k}$  and  $\sqrt{A_k}$  are still to be multiplied by  $10^{-2}$ ):

$$\sqrt{A_k} = 1,1 \times \sqrt{403} = 2,08 = \mathbf{22},$$

which is in very good harmony with what we have found for Li (23) and Na (27) (see table II).

For *nitrogen* BRINER<sup>1)</sup> calculates  $Q_0 =$  at least 150000 Gr. cal. from a single value given by LANGMUIR. This value of BRINER's seems too high to me considering the values for  $H_2$  and for  $O_2$ , and in my opinion 130000 Gr. cal. will be nearer the truth. When we calculate  $\sqrt{A_k}$  from the two values of  $Q_0$ , we get  ${}^{1/27}Q_0 : T_k = {}^{1/27} \times \left( \begin{smallmatrix} 150000 \\ 130000 \end{smallmatrix} : 126 \right) = {}^{1/27} \times \left( \begin{smallmatrix} 1190 \\ 1032 \end{smallmatrix} \right) = 176$  to 153. And  $\sqrt{a'_k}$  being = 2,6, we get:

$$\sqrt{A_k} = 2,6 \times \sqrt{\frac{177}{154}} = 34,6 \text{ or } 32,3 = \mathbf{35} \text{ or } \mathbf{32}.$$

As in connection with C = 32 also a value in the neighbourhood of 32 can be expected for N, the result is also here a confirmation of our formula (1) or (1a), the more so when we bear in mind that the result may possibly be slightly too high in consequence of our having put  $\theta = 1$ .

For *Oxygen* SIEGEL<sup>2)</sup> has found  $Q_0 = 160000$  Gr.cal. Hence  ${}^{1/27}Q_0 : T_k$  here becomes =  ${}^{1/27} \times (160000 : 154.25) = {}^{1/27} \times 1040 = 154$ . With  $\sqrt{a'_k} = 2,6$  we find further:

$$\sqrt{A_k} = 2,6 \times \sqrt{155} = 32,4 = \mathbf{32},$$

which is again in excellent agreement.

In the second place we shall examine the *Halogens*.

First of all *Chlorine*. PIER<sup>3)</sup> found the value 113000 Gr.cal. for

<sup>1)</sup> Journal de Chem. Phys. 12, 119 (1914) and 13, 219 and 465 (1915).

<sup>2)</sup> Zeitschr. f. physik. Chem 87, 642 (1914). Cf. also BRINER, l.c.

<sup>3)</sup> Ibid 62, 385 (1908).

$Q_0$ . According to PELLATON the critical temperature is  $144^\circ \text{C} = 417,1$  abs., so that  ${}^{1/27} Q_0 : T_k$  becomes  $= {}^{1/27} \times 271 = 40,2$ . Hence with  $\sqrt{a'_k} = 5,6$  we shall get about (from the critical data of DEWAR would namely follow 5,43, from those of PELLATON 5,75)

$$\sqrt{A_k} = 5,6 \times \sqrt{41,2} = 35,0 = \mathbf{35}.$$

Though this seems somewhat too high to us, as from 32 to 30 may be expected, the order of magnitude is yet again in agreement with what was found for it for  $\sqrt{A}$  with other elements. Possibly  $Q_0$  is somewhat too high, or also  $\sqrt{a'_k} < 5,6$ ; and perhaps in this case — where  $a_k : a_1$  will be further from unity than for  $\text{H}_2$ ,  $\text{N}_2$  and  $\text{O}_2$ , which have so much lower critical temperatures —  $\theta$  will also be so much smaller than 1, that the found value 35 will have to be lowered to  $\pm 32$ .

With regard to *Bromine* PERMAN and ATKINSON<sup>1)</sup> found for  $Q_0$  the value 57000 Gr.cal. With  $T_k = 302,2^\circ \text{C} = 575,3$  abs. we have  ${}^{1/27} Q_0 : T_k = {}^{1/27} \times 99 = 14,7$ . We calculate with  $\sqrt{a'_k} = 7$ :

$$\sqrt{A_k} = 7 \times \sqrt{15,7} = 27,7 = \mathbf{28},$$

a value that is very plausible.

In conclusion *Iodine*. STARK and BODENSTEIN (1910) found for it  $Q_0 = 35500$  Gr.cal., so that with  $T_k = 512^\circ \text{C} = 785,1$  abs. we find  ${}^{1/27} \times 45,2 = 6,7$  for  ${}^{1/27} Q_0 : T_k$ . With  $\sqrt{a'_k} = 9$  this gives: accordingly:

$$\sqrt{A_k} = 9 \times \sqrt{7,7} = 25,0 = \mathbf{25}.$$

Nor is this value, though somewhat small, at all impossible.

## 6. Conclusion.

It has, indeed, appeared very clearly from the above, that the heats of dissociation  $Q_0$ , on the decomposition of the molecules  $\text{H}_2$ ,  $\text{N}_2$ ,  $\text{O}_2$ ,  $\text{Cl}_2$ , etc. into their atoms, are perfectly accounted for by the increased valence attractions  $\sqrt{A}$  of the separate atoms found by us in earlier papers.

By means of (1) or (1<sup>a</sup>) we are henceforth able to calculate  $Q_0$ , when  $\sqrt{a}$  and  $\sqrt{A}$  are known or reversely to compute  $\sqrt{A}$  according to (2), when  $Q_0$  is known.

In GIBBS-PLANCK's well-known formula for the dissociation of gases<sup>2)</sup>

<sup>1)</sup> Ibid. 33, 215 (1900).

<sup>2)</sup> Of course this formula has *nothing* to do with the so-called theorem of heat of NERNST, as many pupils and followers of this scientist erroneously think (cf. many articles in many periodics). The formula was already given in nuce by GIBBS in 1878, and was later frequently elaborated by PLANCK (1887), v. D. WAALS (1891), myself (1892), DUHEM (1893) and many others for different cases. [Cf.

$$\log K = -\frac{Q_0}{RT} + \Sigma \left[ \nu_1 \left( \frac{c_1}{R} + 1 \right) \right] \log T + (\Sigma \nu_1) \log p + \Sigma (\nu_1 C_1), \quad (3)$$

in which  $K$  represents the constant of dissociation in the relation  $\frac{k_2'^2}{k_1'^2} = K$  (for di-atomic gases, where  $k_2 = \frac{2x}{1+x}$ ,  $k_1 = \frac{1-x}{1+x}$ ,  $\frac{4x^2}{1-x^2}$  will be therefore  $= K$ , when  $x$  represents the so-called degree of dissociation and  $k_1$  etc. the so-called molecular concentrations), we cannot only theoretically get nearer to the constants  $C_1$  etc. (the so-called *chemical constants* of the components), and so also to  $\Sigma (\nu_1 C_1) = C$  — this has been of late done by LORENTZ, PLANCK, SACKUR, TETRODE and others in virtue of considerations of probability in connection with the so-called theorem of heat of NERNST and PLANCK's theory of quanta — but we can also calculate the heats of reaction  $Q_0$  for  $T=0$ . Up to now we had to be satisfied with determining  $Q_0$ , just as  $C = \Sigma (\nu_1 C_1)$ , experimentally from a few values of  $x$ , but now we should be able to calculate the value of  $\log K$  at given temperature and pressure accurately for every gas reaction, as soon as only the values of the chemical constants and of  $\sqrt{A}$  and  $\sqrt{a}$  are accurately known for every element separately.

This must henceforth be the task of physicists: to get to know these values completely. They are essential for the knowledge of the behaviour of the chemical substances reacting on each other. When we are further acquainted with all the values of  $b$  for the different elements, then  $T_k$  and  $p_k$  are known of every simple or compound substance, hence also their further thermal behaviour.

among others my *Lehrbuch der math. Chemie* (BARTH, 1901), p. 1—13, 25—28, and the "Sechs Vorträge" (VIEWEG, 1906), p 64 et seq. These latter appeared originally in the Chem. Weekbl. 1905].

NERNST has only said something about the constant  $\Sigma (\nu_1 C_1) = C$  — which is in connection with the constants of entropy — in reference with his theorem. This enabled him namely to bring the said quantities  $C_1$  (the "chemical constants") in connection with the constants of the equations of the vapour pressure at very low temperature. But all this has of course nothing to do with formula (3) itself, which is quite independent of the theorem of heat. The latter says only something concerning the approach to  $\Theta$  of entropy, specific heat etc. in condensed systems, in connection also with PLANCK's theory of quanta.

When formula (3) ( $p$  constant) is differentiated with respect to  $T$ , we get:

$$\left( \frac{d \log K}{dT} \right)_p = \frac{Q_0}{RT^2} + \frac{\Sigma \{ \nu_1 (c_1/R + 1) \}}{T}.$$

And as  $\left( \frac{d \log K}{dT} \right)_p = \frac{Q}{RT^2}$ ,  $Q_{p=const.} = Q_0 + \Sigma [\nu_1 (c_1 + R)] T$ , hence  $Q_{v=const.} = Q_0 + \Sigma (\nu_1 c_1) T$ , in perfect agreement with (c) of § 4.

As regards the values of  $b$ , and of  $\sqrt{a}$  and  $\sqrt{A}$ , I have already started an examination of them, and I hope I shall be able to continue this work.

Whether after all a substance as  $H_2$  or Na at ordinary temperatures and pressures will occur in the form of *molecules*, e.g.  $H_2$ , or in that of *free atoms*, as Na, depends entirely on the values of  $C$  and  $Q_0$  (hence on  $\sqrt{a}$  and  $\sqrt{A}$ ). The greater  $Q_0$  will be and the smaller  $C$ , the smaller will be the value of  $K$ , hence of  $x$  — the sooner therefore the substance under consideration will occur in the state of molecules, and *not* in that of atoms.

I will still point out that the coefficient of  $\log T$ , viz.  $\Sigma \left[ v_1 \left( \frac{c_1}{R} + 1 \right) \right]$ , is erroneously stereotypically put = 1,75 by NERNST, POLLITZER and many pupils of NERNST. For  $2HI \rightarrow H_2 + I_2$  this coefficient will be  $= -2 \times 7/2 + 1 \times 7/2 + 1 \times 7/2 = 0$  (as is, indeed, sufficiently known), hence not = 1,75. For  $H_2 \rightarrow 2H$  it will be  $= -1 \times 7/2 + 2 \times 5/2 = 1,5$ , which again is not = 1,75! The same thing applies to many other reactions. It will, therefore, be advisable to determine the value of the coefficient under consideration separately for every reaction. The same thing applies to the constant  $C$ . It will not do to assume the chemical constants  $C_1$  all in the neighbourhood of 3; these will, indeed, also no doubt be different according to whether we have to do with a mon-atomic or a di-atomic substance, which theory indeed confirms.

Many values of  $Q_0$  are inaccurate because they have been calculated from experiments by means of a formula with faulty coefficients (1,75 and wrong values of  $C$ ); it will, therefore, deserve recommendation to calculate for a reaction not only the values of  $Q_0$ , but also those of the coefficient in question and of the constant  $C = \Sigma(v_1 C_1)$  from the *experiments themselves*. Only in this way is it possible to obtain accurate experimental values of  $Q_0$ .

Since in the computations of § 5 we could not always reckon with perfectly reliable values of  $Q_0$ , the values found for  $\sqrt{A}$  are of course not *perfectly* accurate. Also in connection with our putting  $\theta = 1$ , which will also not be perfectly true, the agreement between the found values of  $\sqrt{A}$ , and those which we could expect (see table II) in virtue of the values found already (in an entirely independent way) may be considered very remarkable indeed.

*La Tour près de Vevey. August 1918.*