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**Physics.** — “*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 Periodical System*”. By Dr. J. J. VAN LAAR. (Communicated by Prof. H. A. LORENTZ).

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### 1. Introduction.

The *additive* qualities of the quantity  $b$  of the equation of state have already been pointed out by Prof. v. D. WAALS<sup>1</sup>), particularly as far as the elements C, O, H and Cl are concerned. I have extended this research over many other elements, in which remarkable regularities have come to light with regard to the *fundamental* values of  $b$  for the different elements in connection with the *periodic system*.

In reference to the values of  $a$  VAN DER WAALS mentions nine Papers by MATHEWS<sup>2</sup>), adding that this writer had come to “very remarkable” relations with respect to these values. “Remarkable” MATHEWS’ assertions decidedly are — but in an entirely different sense, I am sorry to say, from that probably meant by VAN DER WAALS. From the critique which I have ventured to give in the following paper on MATHEWS’ treatises, it will be clear to the readers that MATHEWS’ views and the rule at which he thinks he has arrived, lack every sound foundation.

On the other hand I have found that also the values of  $\sqrt{a}$  are *perfectly additive*, and that here too we meet with striking regularities with regard to the periodic system.

But there is more. In this I have found that in all cases, in which the central atom — e.g. C in  $\text{CH}_4$ ,  $\text{CCl}_4$ ,  $\text{CHCl}_3$ ,  $\text{C}_2\text{H}_6$  etc. etc., Ge and Sn in  $\text{GeCl}_4$  and  $\text{SnCl}_4$ , N and P in  $\text{NH}_3$  and  $\text{PH}_3$  — is entirely surrounded on all sides by other atoms or atom groups, the attraction of this central atom to the outside on other molecules *entirely vanishes*. That namely the lines of force of the attracting (cohesive)

<sup>1</sup>) These Proc. of Febr. 28 1914, p. 880. See also *ibid.* March 28 1914, p. 1076 and my treatise These Proc. XVII p. 598. This additivity itself was already long known, however. Cf. among other things GUYE Dissertation, Paris 1892). Afterwards BATSCHINSKI (*Zeitschrift für physik. Chemie* **82**, p. 87 (1913)) found at  $T_c$ , reduced to our unities, H = 67, O = 139, C = 114, all  $\times 10^{-5}$ . These values are, however — particularly those for H and O — quite erroneous (see our table in § 3).

<sup>2</sup>) Journ. of Phys. Chem. 1913.

action are *totally absorbed* by those surrounding atoms, and do not exert any force whatever outside the molecule.

This is, indeed, in perfect harmony with what was found lately by EINSTEIN<sup>1)</sup> with regard to the influence of the *molecules* on each other as far as their sphere of action is concerned (this would namely not extend any further than to the *surrounding* molecules). But now the same thing is found with regard to the *atoms* in the molecule. Only the *peripheral* atoms take part in the cohesive attraction, the *central* ones — for so far as they are *entirely* shut off by the surrounding atoms — are *perfectly inactive*. If, however, these central atoms are *partly* free, as e.g. with the *doubly* and *triply* bound C-atoms, either half the action or the full action immediately shows itself again. This is certainly one of the most remarkable results to which our researches have led us.

In what follows I shall confine myself to what is indispensable as a support of my contention, reserving the fuller discussion of this subject for another occasion.<sup>2)</sup>

## 2. The calculation of the values of $a$ and $b$ .

As  $a$  and  $b$  are in general functions of  $v$  and  $T$  ( $a$  is probably independent of  $v$ ), it is desirable to calculate these quantities for *corresponding* states, and for this the *critical* state is first of all to be taken into account. Also when we pay attention to the fact that the variability of  $b$  with the volume is different for every substance, and that therefore something special continues to adhere even to the critical state, this circumstance can yet be eliminated by the introduction of a new parameter. As I have lately demonstrated<sup>3)</sup>, in the first place we may take for this the quantity  $\gamma$ , i.e. the coefficient of direction of the straight joining line between the densities  $D_c$  and  $D_0$  in a  $D, T$ -diagram, which quantity is at the same time  $= \frac{1}{2} (b_k : b_0)$ . We can then express all the quantities in  $\gamma$ , which henceforth represents the only independent parameter; thus the idea of correspondence will also have obtained a wider meaning.

Thus e.g. the quantity  $s = RT_k : p_k v_k$  is always  $= 8\gamma : (\gamma + 1)$ , and the quantity  $r = v_k : b_k$  will always be  $= (\gamma + 1) : \gamma$ . For  $f' = RT_k : p_k (v_k - b_k) = 1 + (a_k : p_k v_k^2)$  we find  $8\gamma$ . ( $f'$  is the critical coefficient of pressure for the case that  $a$  and  $b$  may be taken independent of  $T$  at  $T_k$ ). Further  $rs = 8$ ,  $f' (r-1) = 8$ ,  $(f' - 1) r^2 =$

<sup>1)</sup> Bemerkung zur dem Gesetz von Eötvös. Ann. d. Ph. (4) 34, 165 (1911).

<sup>2)</sup> In the Journ. de Chimie physique of Prof. GUYE at Genève.

<sup>3)</sup> These Proc. of March 26, April 23, May 29 and Sept. 26, 1914, resp. p. 808, 924, 1047 and 451.

$= 27 : \lambda, (\gamma' - 1) : s^2 = 27 : 64\lambda$ . Compare moreover the table on p. 819 of the first of the cited articles, and that on p. 1052 of the third paper.

For the quantities  $T_k$  and  $p_k$  we find then perfectly accurately:

$$RT_k = \frac{8}{27} \lambda \frac{a_k}{b_k} \quad ; \quad p_k = \frac{1}{27} \lambda \frac{a_k}{b_k^2},$$

at least for normal substances which are not associated at  $T_k$ . In this (see loc. cit.) the factor  $\lambda$  is given by  $\lambda = \frac{27}{8\gamma - 1} \left( \frac{\gamma}{\gamma + 1} \right)^2$ . For substances with a particularly high critical temperature  $\gamma$  has the limiting value 1 and  $\lambda$  becomes  $= \frac{27}{28} = 0,964$ . For "ordinary" substances  $\gamma = 0,9$  and  $\lambda$  becomes  $= 0,977$ ; for argon, where  $\gamma = 0,75$ ,  $\lambda$  becomes  $= 0,992$ ; for  $H_2$  with  $\gamma = 0,6$ ,  $\lambda = 0,999$ ; while for He, where  $\gamma = 0,55$ ,  $\lambda$  will be  $= 0,999$ . For ideal substances, where  $b$  is constant,  $\gamma$  approaches 0,5 and  $\lambda$  approaches 1.

We see from this that the correction factor  $\lambda$  deviates about 2,3 % from unity for ordinary substances, so that in the second of the relations:

$$b_k = \frac{1}{8} \frac{RT_k}{p_k} \quad ; \quad a_k = \frac{27}{64\lambda} \frac{(RT_k)^2}{p_k}$$

the value of  $a_k$  must then be augmented by this amount; and by a smaller amount when the critical temperature, as for argon,  $O_2$ ,  $N_2$ ,  $H_2$ , etc., is particularly low. We have always taken this factor into account.

When the substances at  $T_k$  are still associated, the above simple formulae must be replaced by much more intricate ones.<sup>1)</sup> For the few abnormal substances, however, which occur in the following tables, we have calculated the values of  $a_k$  and  $b_k$  on the supposition that these substances are normal at  $T_k$  and then added that the accurate values are *smaller*. (Always in reference to a *single* molecular quantity.)

For  $R$  we have put the value  $0,0036618 = 1 : 273,09$ , so that the values  $a_k$  and  $b_k$  are expressed in the ordinary "normal" unities, i.e.  $b$  in the normal volume  $v_0 = 22412 \text{ cm}^3$  (the volume of 1 gr. mol. of substance at 1 atm. and  $0^\circ \text{C}$ . in the AVOGADRO staté), and  $a$  in atm., when 1 gr. mol. has the volume  $v_0$ .

Want of room obliges me to omit the extensive table of 74 substances, in which  $T_k$ ,  $p_k$ ,  $b_k$ ,  $a_k$ ,  $\sqrt{a_k}$ , and  $\lambda$  have been given; therefore the values of  $T_k$  and  $p_k$  have been added in the following partial tables for  $b_k$ . These values have been taken from the best

<sup>1)</sup> Cf. Arch. FEYLER 1908 and also These Proc. of Nov. 7, 1914, p. 598.

and newest sources (tables of ABRAHAM and SACERDOTE, Tables Annuelles, values given by K. ONNES and his collaborators, determinations of CARDOSO and others).

### 3. The additive qualities of $b$ in connection with the periodic system.

The values of  $b_k$  found can now be composed additively from the following *fundamental values* for  $b_k \times 10^5$ .

H = 48,5 (34;14)	C = 100 (75)	N = 85 (60)	O = 70 (50)	F = 55	He < 105 ? Ne = 71 ?
	(Si = 155)	P = 140	S = 125	Cl = 115	Ar = 144
	Ge = 210	(As = 195)	Se = 180	Br = 165	Kr = 177
	Sn = 265	(Sb = 250)	(Te = 235)	I = 220	X = 228

The regularity is very striking. In every *vertical* column the increase is 55 units, whereas in every *horizontal* row the decrease amounts to 15 units. (Only Cl = 115 fits in better than 110). Hydrogen seems to belong to the first series, the noble gases evidently always prolonging the horizontal rows. (The value for He still continues to be very uncertain; nor is Ne quite certain).

It must be further observed that C presents *two* different values. In the *anorganic* compounds and in the *aliphatic organic* compounds C is always = 100, but in the *aromatic* compounds, i.e. in the cyclically built compounds, the smaller value 75 should be taken for 75. (75 is somewhat greater than  $100 \times \frac{1}{2} \sqrt{2} = 71$ ).

The same thing is found for N. Only for  $N_2$  itself do we find the fundamental value 85; for *all other* compounds of N on the other hand the condensed value 69 ( $= 85 \times \frac{1}{2} \sqrt{2}$ ).

As for O, here the fundamental value 70 holds *everywhere*; only for  $CO_2$  and for *one* of the two oxygen atoms of the organic acid group  $CO.OH$  (or of the group  $CO.OX$  of the compound esters), viz. that which just as both atoms in  $CO_2$  is bound to C through a *double binding*, the diminished value 50 ( $= 70 \times \frac{1}{2} \sqrt{2}$ ) is found.

For H *three* values are found. The fundamental value 48,5 only for  $H_2$  and HCl. In the *anorganic* compounds  $NH_3$  (and also in the radicals  $NH_2$  and  $NH$ ),  $PH_3$ ,  $H_2O$ ,  $H_2S$ ,  $H_2Se$  H is everywhere = 34 ( $= 48,5 \times \frac{1}{2} \sqrt{2}$ ), whereas in the *organic* compounds, where H is directly bound to C — both in the aliphatic and in the aromatic series — the doubly condensed value  $H = 14$  [ $= 48,5 \times (1 - \frac{1}{2} \sqrt{2})$ ] is found.

Now the different tables for the reconstruction of the  $b$ -values may follow.

*a. Elements.*

	Found	$T_k$	$p_k$		$T_k$	$p_k$	
$H_2 = 2 \times 48,5 = 97$	$97 (\times 10^{-5})$	31,95	15,0	He	5,20	$> 2,26$	0,9999
$N_2 = 2 \times 85 = 170$	172	126,0	33,5	Ne	$\pm 45$	29	0,9976
$O_2 = 2 \times 70 = 140$	142	154,25	49,7	Ar	150,65	48,0	0,992
$P_4 = 4 \times 140 = 560$	535	968	82,8	Kr	210,5	54,3	0,989
$Cl_2 = 2 \times 115 = 230$	226	414,1	83,9	X	289,7	$58,2?$	0,988

*b. Anorganic Compounds.*

	Found	$T_k$	$p_k$
$(CN)_2 = 2 \times (100 + 60) = 320$	$307 (\times 10^{-5})$	401,4	59,75
$CO = 100 + 70 = 170$	172	133,4	35,5
$CO_2 = 100 + 2 \times 50 = 200$	191	304,1	72,9
$CS_2 = 100 + 2 \times 125 = 350$	343	546,1	72,9
$Ge Cl_4 = 210 + 4 \times 115 = 670$	663	550,0	38,0
$Sn Cl_4 = 265 + 4 \times 115 = 725$	733	591,8	36,95
$NH_3 = 60 + 3 \times 34 = 162$	165	406,0	112,3
$N_2O = 2 \times 60 + 70 = 190$	198	309,6	71,65
$NO = 60 + 70 = 130$	114 (127)	177,1	71,2 (64)
$*NO_2 = 60 + 2 \times 70 = 200$	$\approx 197$	431,3	100
$PH_3 = 140 + 3 \times 34 = 242$	233	325,9	64,0
$*H_2O = 2 \times 34 + 70 = 138$	$\approx 141$	638,1	200,5
$H_2S = 2 \times 34 + 125 = 193$	192	373,5	89,05
$SO_2 = 125 + 2 \times 70 = 265$	254	430,2	77,65
$H_2Se = 2 \times 34 + 180 = 248$	206?	410,1	91,0
$HCl = 48,5 + 115 = 163,5$	173	324,5	86,0

Only  $H_2Se$  deviates considerably, but it is very well possible that the critical pressure (91 atm) has been found too high. With regard to  $NO$  it is known that the critical data of this substance necessarily

require revision. Indeed, with OLSZEWSKI's second value, viz.  $p_k = 64$  instead of the first value used by us (which gives better agreement in other respects), we should have found  $b_k = 127$ , in good agreement with the calculated value<sup>1)</sup>.

The abnormal  $H_2O$  does not seem to be considerably associated at the critical temperature. (Abnormal substances are indicated in the tables by an asterisk). From SCHEFFER's researches we know already that  $NO_2$  at  $T_k$  is hardly associated to  $N_2O_4$ .

c. Carbon-hydrogens.

			Found	$T_k$	$p_k$
$CH_4$	$= 100 + 4 \times 14$	$= 156$	191 (156) ( $\times 10^{-5}$ )	190,2	45,6 (53)
$C_2H_6$	$= 200 + 6 \times 14$	$= 284$	286	305,2	48,9
$C_3H_8$	$= 300 + 8 \times 14$	$= 412$	377	370,6	45,0
n- $C_4H_{10}$	$= 400 + 10 \times 14$	$= 540$	525	$\pm 424$	$\pm 37$
$\left\{ \begin{array}{l} \text{n-}C_5H_{12} \\ \text{i-}C_5H_{12} \end{array} \right.$	$= 500 + 12 \times 14$	$= 668$	652	470,3	33,0
	$= 500 + 12 \times 14$	$= 668$	641	460,9	32,9
n- $C_6H_{14}$	$= 600 + 14 \times 14$	$= 796$	785	507,9	29,6
n- $C_7H_{16}$	$= 700 + 16 \times 14$	$= 924$	919	539,9	26,9
n- $C_8H_{18}$	$= 800 + 18 \times 14$	$= 1052$	1059	569,3	24,6
$C_2H_2$	$= 200 + 2 \times 14$	$= 228$	229	308,6	61,65
$C_2H_4$	$= 200 + 4 \times 14$	$= 256$	255	282,6	50,65
i- $C_5H_{10}$	$= 500 + 10 \times 14$	$= 640$	627	464,7	33,9
$C_6H_6$	$= 6 \times (75 + 14)$	$= 534$	537	561,6	47,9
$C_7H_8$	$= 534 + (100 + 2 \times 14)$	$= 662$	653	593,7	41,6
o- $C_8H_{10}$	$= 662 + 128$	$= 790$	789	636,1	36,9
Cyclohexaan	$= 6 \times (75 + 2 \times 14)$	$= 618$	636	553,1	39,8
$C_{10}H_8$	$= 10 CH - 28$	$= 862$	866	741,3	39,2

The value 191 found for methane is probably too high in consequence of the too low value of  $p_k$ . For this we have, namely,

<sup>1)</sup> Prof. GUYE is so kind as to inform me that in 1910 ADWENTOWSKI found  $T_k = 180,2$ , almost identical with 177,1 assumed by us, but  $p_k = 64,6$  atm. This is really the value, which gives the expected value for  $b_k$ .

For  $Cl_2$  PELLATON (Dissertation, Neuchatel 1915) found  $T_k = 417,1$ ,  $p_k = 76,1$ . These values would yield  $b_k = 251 \times 10^{-5}$ ,  $\sqrt{a_k} = 11,5 \times 10^{-2}$ .

assumed CARDOSO's value, which is 45,6 atm., whereas DEWAR found 50, and OLSZEWSKY and v. WROBLEWSKI on an average 56 atm. With  $p_k = 53$  156 would have been found for  $b_c$  instead of 191, in perfect harmony with the calculated value.

In all *cyclical* compounds  $C = 75$ , i.e. in the *core*. But of course  $C$  again = 100 in the substitution groups  $CH_3$  (in toluene and xylene e. g.). For H we find everywhere 14.

The fact that the values which have been found for  $b_k$  for n-pentane and iso-pentane from YOUNG's data differ as much as 11 units, suggests that the *constitutive* influences should not be *entirely* neglected, even though they do not make their influence felt much, compared with the so much stronger additive influences.

d. Other organic compounds.

			Found	$T_c$	$p_c$
$CH_3F$	$= 100 + 42 + 55$	$= 197$	235 ? ( $\times 10^{-5}$ )	318,0	62,0
$CH_3Cl$	$= 100 + 42 + 115$	$= 257$	260	414,6	73,0
$CHCl_3$	$= 100 + 14 + 345$	$= 459$	456	536,0	53,8
$CCl_4$	$= 100 + 0 + 460$	$= 560$	566	556,2	45,0
$C_2H_5Cl$	$= 200 + 70 + 115$	$= 385$	386	455,6	54
$C_2H_4Cl_2$	$= 200 + 56 + 230$	$= 486$	484	562,4	53
$C_3H_7Cl$	$= 300 + 98 + 115$	$= 513$	462 ?	494,1	49,0
$(C_2H_5)_2O$	$= 400 + 140 + 70$	$= 610$	600	466,9	35,6
$(CH_3, C_2H_5)O$	$= 300 + 112 + 70$	$= 482$	436 ?	441,5	46,3
* $CO(CH_3)_2$	$= 300 + 84 + 70$	$= 454$	$\overline{=}$ 444	505,9	52,5
H. $COOCH_3$	$= 200 + 56 + (70 + 50)$	$= 376$	376	487,1	59,25
$CH_3 \cdot COOCH_3$	$= 300 + 84 + 120$	$= 504$	501	506,8	46,3
$CH_3 \cdot COOC_2H_5$	$= 400 + 112 + 120$	$= 632$	630	523,2	38,0
$CH_3 \cdot COOC_3H_7$	$= 500 + 140 + 120$	$= 760$	758	549,3	33,2
$C_6H_5F$	$= 520 + 55$	$= 575$	574	559,6	44,6
$C_6H_5Cl$	$= 520 + 115$	$= 648$	648	632,3	44,6
$C_6H_5Br$	$= 520 + 165$	$= 685$	687	(670,1)	(44,6)
$C_6H_5I$	$= 520 + 220$	$= 740$	740	(721,1)	(44,6)
$C_4H_4S$	$= 400 + 56 + 125$	$= 581$	567	590,4	47,7

The abnormal acetone seems already to be normal at  $T_k$ .

For  $CH_3F$ ,  $C_3H_7Cl$  and  $(CH_3, C_2H_5)O$  we have had to be satisfied



with old determinations of  $T_k$  and  $p_k$ ; hence the critical pressures may be inaccurate. As we have already observed above, for the compound esters one O in COOX (of OX) = 70, the other (of CO) = 50. In the group  $C_6H_5$ , C = 75 as in benzene, whereas we find C = 100 in thiophene. This is rather strange, as in cyclohexane (Hexamethylene), also a cyclical compound, C is very decidedly = 75, just as in  $C_6H_6$ . But it is very well possible that the reduction of the value from 100 to 75 only takes place in the cyclical binding of *six* C-atoms and not of *four*.

e. Some alcohols and amines.

	Found	$T_k$	$p_k$
*CH <sub>3</sub> OH = 142 + (70 + 34) = 246	<300 ( $\times 10^{-5}$ )	513,1	78,5
*C <sub>2</sub> H <sub>5</sub> OH = 270 + 104 = 374	$\bar{\leq}$ 375	516,2	63,0
*C <sub>3</sub> H <sub>7</sub> OH = 398 + 104 = 503	$\bar{\leq}$ 490	536,8	50,2
*CH <sub>3</sub> .COOH = 142 + 254 = 396	<477	594,7	57,1
{ NH <sub>2</sub> CH <sub>3</sub> = 128 + 142 = 270	272	428	72
{ NH <sub>2</sub> C <sub>2</sub> H <sub>5</sub> = 128 + 270 = 398	312 ?	450	66
{ NH <sub>2</sub> C <sub>3</sub> H <sub>7</sub> = 128 + 398 = 526	450 ?	491,1	50
{ NH(CH <sub>3</sub> ) <sub>2</sub> = 94 + 284 = 378	356	436	56
{ NH(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> = 94 + 540 = 634	560 ?	489	40
{ NH(C <sub>3</sub> H <sub>7</sub> ) <sub>2</sub> = 94 + 796 = 890	814 ?	550,1	31
{ N(CH <sub>3</sub> ) <sub>3</sub> = 60 + 426 = 486	484	433,5	41
{ N(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> = 60 + 810 = 870	812 ?	532	30
NH <sub>2</sub> .C <sub>6</sub> H <sub>5</sub> = 128 + 520 = 648	611	698,7	52,35

Ethyl- and propylalcohol seem to be about normal for  $T_k$ , but methylalcohol and acetic acid are still considerably associated. In the group OH O = 70, H = 34, the first O-atom in COOH being = 50.

With amines we are struck with the remarkable phenomenon that always only the lower members agree, the higher ones on the contrary deviate greatly. Thus e.g. NH<sub>2</sub>CH<sub>3</sub> is in good harmony, but NH<sub>2</sub>C<sub>2</sub>H<sub>5</sub> deviates 20 % and NH<sub>2</sub>C<sub>3</sub>H<sub>7</sub> deviates 15 %. It is possible that the determinations of VINCENT and CHAPPIUS, (who have also investigated the divergent C<sub>3</sub>H<sub>7</sub>Cl) are inaccurate, and the critical pressures too high. If e.g. for NH(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub> we substitute  $p_k = 35$  atm. for 40 atm., for N(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>  $p_k = 28$  atm. for 30 atm., and for

$\text{NH}(\text{C}_3\text{H}_7)_2$   $p_k = 28$  atm. for 31 atm., all deviations vanish. And such diminutions of the critical pressures in later, more accurate experiments with purer substances are by no means rare. History even knows more considerable diminutions. Thus e.g. for  $\text{CH}_3\text{Cl}$  the old and the new values are resp. = 73.0 and 65.9 atm.; a difference of almost 11%. In view of such facts it would be rash to attach too much weight to the deviations found for some amines. The more so as the agreement for the many other substances in the foregoing tables is almost perfect, or the deviations do not amount to more than 1 or 2% in the extreme cases.

#### § 4. The additive properties of the values of $\sqrt{a}$ .

As we have seen, the values of  $b$  can be built up additively from a small number of fundamental values — those of the elements —; such an additivity is not found, however, with regard to  $a$ , though it is with regard to  $\sqrt{a}$ .

This is quite natural. For  $a$  is always composed of the product (or the sum of some products) of two values, one of which always refers to the first of two molecules that attract each other, the other to the second molecule.

Thus e.g. when the "attracting mass" of a helium molecule is  $\mu$ , the total cohesion will be  $a = C\mu^2$ , when  $C$  is a certain factor of proportionality, in which also the summation with respect to all the molecules is included. (This summation is the same for all substances, because  $a$  refers to the same volume  $v_0$ , and the molecules lie equally far apart therefore). If the attracting mass of a Cl-atom =  $\mu$ , the cohesion of  $\text{Cl}_2$  will be represented by  $a = C \cdot 4\mu^2$ . Lastly, if  $\mu_1$  is the attracting mass of H,  $\mu_2$  of Cl, the quantity  $a$  for HCl will be represented by  $a = C(\mu_1^2 + 2\mu_1\mu_2 + \mu_2^2) = C(\mu_1 + \mu_2)^2$ .

Accordingly, the cohesion is not supposed "specific" (chemical) — so that e.g. the attraction of an atom H in another molecule being given by  $\mu_1 \times \mu_1 = \mu_1^2$ , the attraction between H and an atom Cl (likewise in another molecule) is determined by  $\mu_1 \times \mu_2$ ; i.e. the attracting mass of H will remain the same, viz.  $\mu_1$ , independent of the fact whether H attracts a second H in another molecule, or whether it attracts an atom Cl.

Hence we assume — and this assumption is perfectly *confirmed* and *justified* by the found additivity of  $\sqrt{a}$  — that the cohesion is of entirely *physical* nature, *only* depending on certain not yet sufficiently known circumstances concerning the number, mass, velocity, path of the different electrons, of which the atoms are built up.

We may add that the above considerations come to this, that the

quantity  $a_{12}$  in  $a = a_1 + 2 a_{12} + a_2$ , in which  $a_1$  and  $a_2$  now refer to the attractions between the homonymous atoms of e.g. two molecules HCl, is always  $= \sqrt{a_1 a_2}$ , so that  $a$  becomes  $= \sqrt{a_1 + \sqrt{a_1 a_2} + \sqrt{a_1 a_2} + a_2}$ , and therefore  $\sqrt{a} = \sqrt{a_1 + \sqrt{a_1 a_2} + \sqrt{a_1 a_2} + a_2}$ .

It is now clear that not the values of  $a$ , but those of  $\sqrt{a}$  must be found to be additive<sup>1)</sup>.

Well, we shall prove in the following tables that the values of  $\sqrt{a}$  can be built up additively from the following fundamental values for  $\sqrt{a_k} \times 10^2$ .

H = 3,2 (1,6)	C = 3,1	N = 2,9	O = 2,7	F = 2,9?	He < 0,8?
	—	P = 6,4	S = 6,3	Cl = 5,4	Ne = 2,0
	—	—	Se = 7,1	Br = 6,9	Ar = 5,2
	—	Sb = 8,9	—	I = 8,8	Kr = 6,9
					X = 9,1

As has already appeared from the table for the fundamental values of  $b$  and is now again confirmed, H belongs genetically to the series C, N, O etc., and does not stand separately somewhere *above* Li in the periodic system. The monatomic noble gases again form the continuation of the different series. The value of Ne seems a little too great that of H too small to us.

a. Elements.

	Found	
$H_2 = 2 \times 1,6 = 3,2$	1,95	0,999
$N_2 = 2 \times 2,9 = 5,8$	5,2	0,992
$O_2 = 2 \times 2,7 = 5,4$	5,2	0,992
$P_4 = 4 \times 6,4 = 25,6$	25,7	0,97
$Cl_2 = 2 \times 5,4 = 10,8$	10,9	0,977

<sup>1)</sup> The relation  $a_{12} = \sqrt{a_1 a_2}$  will evidently have to hold for homogeneous mixtures of two substances. I have always held to this relation of BERTHELOT's in different earlier papers. I am more than ever convinced, that everywhere where  $a_{12} > \sqrt{a_1 a_2}$  has been found, *association* or *molecular compounds* occur. Whenever it is possible to eliminate these disturbing influences by calculation,  $a_{12} = \sqrt{a_1 a_2}$  will always be found back.

<sup>2)</sup> WALDEN and SWINNE (Zeitschr. für physik. Ch. 82, 289 (1913)) cursorily mention the *partial* additivity of the "specific molecular cohesion", i.e. of  $a$  or  $a/v^2$ . They too — like MATHEWS — seek connection between the values of  $a$  and the sum of the effective valencies. On MATHEWS compare the paper following this.

The values found for H<sub>2</sub> and N<sub>2</sub> are too low [? in the last column of the table is the factor in  $a_k = \frac{27}{64} \lambda \frac{(RT_k)^2}{p_k}$ ].

b. Anorganic Compounds.

	Found	
(CN) <sub>2</sub> = 2 × (3,1 + 2,9) = 12	12,5 × 10 <sup>-2</sup>	0,977
CO = 3,1 + 2,7 = 5,8	5,35	0,992
CO <sub>2</sub> = 3,1 + 5,4 = 8,5	8,5	0,988
CS <sub>2</sub> = 3,1 + 12,6 = 15,7	15,4	0,975
GeCl <sub>4</sub> = 0 + 4 × 5,4 = 21,6	21,5	0,975
SnCl <sub>4</sub> = 0 + 4 × 5,4 = 21,6	23,5	0,975
NH <sub>3</sub> = 0 + 9,6 = 9,6	9,2	0,977
N <sub>2</sub> O = 5,8 + 2,7 = 8,5	8,75	0,988
NO = 2,9 + 2,7 = 5,6	5,0	0,992
*NO <sub>2</sub> = 2,9 + 5,4 = 8,3	$\overline{<} 10,4$	0,977
PH <sub>3</sub> = 0 + 9,6 = 9,6	9,8	0,985
*H <sub>2</sub> O = 6,4 + 2,7 = 9,1	$\overline{<} 10,7$	0,97
H <sub>2</sub> S = 3,2 + 6,3 = 9,5	9,5	0,98
SO <sub>2</sub> = 6,3 + 5,4 = 11,7	11,7	0,977
H <sub>2</sub> Se = 3,2 + 7,1 = 10,3	10,3	0,977
HCl = 3,2 + 5,4 = 8,6	8,4	0,985

NO<sub>2</sub> and H<sub>2</sub>O seem to be still a little associated at T<sub>k</sub>. It is further seen that H is everywhere = 3,2, except for H<sub>2</sub>, H<sub>2</sub>S and H<sub>2</sub>Se, where half the value is found, as for *all organic* compounds.

For GeCl<sub>4</sub> and SnCl<sub>4</sub>, and also for NH<sub>3</sub> and PH<sub>3</sub> the attractive action of the elements Ge, Sn, N and P is *entirely eliminated*. In these compounds — and we shall find back the same phenomenon for C in organic compounds — the *central* atom is quite inactive, because it is symmetrically surrounded *on all sides* by atoms H, Cl, etc. (or atom groups), which wholly absorb its attractive action. (shadowing-action).

This is in perfect harmony with what EINSTEIN found already in 1911. Only with us the absorption of the lines of force takes place already *in* the molecule through the surrounding atoms, whereas

EINSTEIN considered the attractive action of the molecules as a *whole*, which was absorbed by the surrounding *molecules*.

A glance at the values of  $\sqrt{a_k}$  for  $\text{CCl}_4$ ,  $\text{GeCl}_4$ , and  $\text{SnCl}_4$  is already sufficient to convince us of the truth of what has been said. They are namely *almost equal*, resp. = 20,0, 21,5, and 23,5, yielding for Cl the mean value 5,4, the *same value* as is also found from other compounds (e.g.  $\text{Cl}_2$  itself).

And the same thing is found for  $\text{NH}_3$  and  $\text{PH}_3$ , where  $\sqrt{a_k}$  is found resp. = 9,2 and 9,8, corresponding with  $\text{H} = 3,2$  as mean value, also again the *same value* as is found for H in  $\text{H}_2\text{O}$  and  $\text{HCl}$ .

c. Carbon hydrogens.

			Found	)
$\text{CH}_4$	$= 0 + 4 \times 1,6$	$= 6,4$	6,7	0,992
$\text{C}_2\text{H}_6$	$= 0 + 6 \times 1,6$	$= 9,6$	10,4	0,988
$\text{C}_3\text{H}_8$	$= 0 + 8 \times 1,6$	$= 12,8$	13,3	0,977
n- $\text{C}_4\text{H}_{10}$	$= 0 + 10 \times 1,6$	$= 16,0$	16,8	0,977
} n- $\text{C}_5\text{H}_{12}$	$= 0 + 12 \times 1,6$	$= 19,2$	19,7	0,977
	i- $\text{C}_5\text{H}_{12}$	$= 0 + 12 \times 1,6$	$= 19,2$	19,3
n- $\text{C}_6\text{H}_{14}$	$= 0 + 14 \times 1,6$	$= 22,4$	22,5	0,977
n- $\text{C}_7\text{H}_{16}$	$= 0 + 16 \times 1,6$	$= 25,6$	25,1	0,975
n- $\text{C}_8\text{H}_{18}$	$= 0 + 18 \times 1,6$	$= 28,8$	27,6	0,975
$\text{C}_2\text{H}_2$	$= 2 \times 3,1 + 2 \times 1,6$	$= 9,4$	9,4	0,988
$\text{C}_3\text{H}_4$	$= 2 \times 1,55 + 4 \times 1,6$	$= 9,5$	9,5	0,988
i- $\text{C}_5\text{H}_{10}$	$= 2 \times 1,55 + 3 \times 0 + 10 \times 1,6$	$= 19,1$	19,2	0,977
$\text{C}_6\text{H}_6$	$= 6 \times 1,55 + 6 \times 1,6$	$= 18,9$	19,5	0,975
$\text{C}_7\text{H}_8$	$= 6 \times 1,55 + 1 \times 0 + 8 \times 1,6$	$= 22,1$	22,2	0,97
o- $\text{C}_8\text{H}_{10}$	$= 6 \times 1,55 + 2 \times 0 + 10 \times 1,6$	$= 25,3$	25,3	0,97
Cyclohexaan	$= 0 + 12 \times 1,6$	$= 19,2$	21,1	0,975
$\text{C}_{10}\text{H}_8$	$= 10 \times 1,55 + 8 \times 1,6$	$= 28,3$	28,6	0,97

We see again at first sight that the values of  $\sqrt{a_k}$  for carbon hydrogens  $\text{C}_n\text{H}_{n+2}$  are simply *proportional* to the number of H-atoms from  $\text{CH}_4$  to  $\text{C}_8\text{H}_{18}$ , and that again  $\text{C} = 0$ , just as Ge and Sn in  $\text{GeCl}_4$  and  $\text{SnCl}_4$ . For in these carbon hydrogens all the

C-atoms are again entirely surrounded by other atoms or atom groups.

But for ethylene and iso-amylene, where *double bonds* are found — so that two carbon tetrahedra adjoin along a side instead of by the angular points — *half* the fundamental value is found for C, i.e. 1,55. In each of the compounds  $\text{H}_2\text{C}=\text{CH}_2$  and  $\text{C}_2\text{H}_5 > \text{C}=\text{CH}_2$  there are *two* such tetrahedra, which therefore freely expose part of their surfaces — without shadowing atoms or atom groups — to the attractive (cohesive) action to the outside. For the other atoms of iso-amylene C remains therefore = 0, because *these* remain surrounded on all sides. (single bindings in the angular points of the tetrahedra).

For acetylene there is *triple* binding, i.e. the tetrahedra adjoin each other by an entire side plane, so that now the *whole* central body is exposed to the attractive action to the outside. Accordingly we duly find  $\text{C} = 3,1$  as for the above considered anorganic substances.

For  $\text{C}_6\text{H}_6$  and its homologues we have 6 atoms with a double binding, so that here we have  $6 \times 1,55$ . But in the aliphatic substitution groups  $\text{CH}_3$  with single bindings we find again duly  $\text{C} = 0$ . For naphthaline with 10 double bindings we have also  $10 \times 1,55$ , and for cyclohexane with only single bindings C is again = 0.

From the above table it appears how close the agreement is between the calculated and the found values (for  $\text{C}_2\text{H}_2$ ,  $\text{C}_2\text{H}_4$ , *i*- $\text{C}_6\text{H}_{10}$  among other compounds this agreement is even perfect), only for  $\text{C}_2\text{H}_6$  and cyclohexane a discrepancy exists of 8 à 9 %, probably to be attributed to inaccurately known critical data <sup>1)</sup>.

*Table d*, see following page.

The agreement is again satisfactory. Only  $\text{CH}_3\text{F}$  deviates in a similar way as for  $b_c$ , which may be ascribed to inaccuracy in the critical data.

In acetone the C-atom bound directly to O, just as that of the group  $\text{COOX}$  for the compound esters, is = 3,1 — in accordance with  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{CS}_2$  etc.

<sup>1)</sup> We should be careful not to transfer in our thoughts the deviations in  $\sqrt{a}$  (calculated and found) doubled to  $a$  itself as a standard. An error of 3% in  $\sqrt{a}$  would of course give rise to an error of 6% in  $a$ ; but then we should overlook that  $(RT_k)^2$  occurs in the formula for  $a$ , on the other hand  $RT_k$  in that for  $\sqrt{a}$ , so that an error in  $T_k$  is transferred to  $\sqrt{a}$  *unenlarged*, but doubled to  $a$ . Not the deviations between the values of  $a$  but between those of  $\sqrt{a}$  are therefore to be considered as standard of accuracy. Indeed,  $a$  is always a *product* of two separate factors. And these separate factors must only be taken into account and are comparable with the quantity  $b$ .



holds for H just as in  $H_2O = H \cdot OH$ , and some other organic compounds (see under *c*). The same applies to group OH in  $COOH$ , C again being = 3,1 there.

*e Some alcohols and amines.*

		Found	
* $CH_3OH$	$= 0 + 3 \times 1,6 + (2,7 + 3,2) = 10,7$	< 14,0	0,977
* $C_2H_5OH$	$= 0 + 5 \times 1,6 + 5,9 = 13,9$	$\overline{<} 15,6$	0,977
* $C_3H_7OH$	$= 0 + 7 \times 1,6 + 5,9 = 17,1$	$\overline{<} 18,2$	0,975
* $CH_3 \cdot COOH$	$= 4,8 + (3,1 + 2 \times 2,7 + 3,2) = 16,5$	< 19,0	0,97
$\left\{ \begin{array}{l} NH_2CH_3 \\ NH_2C_2H_5 \\ NH_2C_3H_7 \end{array} \right.$	$= (0 + 2 \times 3,2) + 4,8 = 11,2$	12,1	0,977
	$= 6,4 + 8 = 14,4$	13,3	0,977
	$= 6,4 + 11,2 = 17,6$	16,7	0,977
$\left\{ \begin{array}{l} NH(CH_3)_2 \\ NH(C_2H_5)_2 \\ NH(C_3H_7)_2 \end{array} \right.$	$= 3,2 + 2 \times 4,8 = 12,8$	14,0	0,977
	$= 3,2 + 2 \times 8 = 19,2$	18,6	0,977
	$= 3,2 + 2 \times 11,2 = 25,6$	23,8	0,975
$\left\{ \begin{array}{l} N(CH_3)_3 \\ N(C_2H_5)_3 \end{array} \right.$	$= 0 + 3 \times 4,8 = 14,4$	16,3	0,977
	$= 0 + 3 \times 8 = 24,0$	23,4	0,975
$NH_2 \cdot C_6H_5$	$= 6,4 + 17,3 = 23,7$	23,3	0,97

For the amines the agreement is better than with respect to the values of  $b_k$ ; we should bear in mind that in consequence of  $\sqrt{p_k}$  in the expression  $\sqrt{a_k}$  errors of  $p_k$  are transferred to  $\sqrt{a_k}$  for half the amount, passing to the full amount to  $b_k$ .

S U M M A R Y.

If we summarize what has been discussed above, it may therefore be said that also the values of  $\sqrt{a_k}$  can be built up perfectly *additively* from a few fundamental values. These fundamental values have been given at the head of this paragraph, and roughly it may be said that in the first series of the periodic system (H included)  $\sqrt{a_k}$  is about = **3** ( $\times 10^{-2}$ ); in the second series about **5**; in the third series **7**, and in the fourth series **9**.

After this paper had been written we have seen that in the fourth series Sb = 8,9 quite in agreement with I = 8,8, and X = 9,1.



Further that in the fifth series  $Hg = 11,0$ . Hence we have for the six horizontal principal series of the periodic system resp. the fundamental values (with  $He = 1$  in the series zero)

**1, 3, 5, 7, 9, and 11** ( $\times 10^{-2}$ ),

so that  $\sqrt{a}$  is exactly 2 units greater in every successive horizontal series.

We may still remark that the proportion of the fundamental values of  $b_k$  of the last members in the first four horizontal series (of the halogen group) is exactly as:

1 : 2 · 3 : 4.

a) For the application of the fundamental table for  $\sqrt{a_k}$  we should further bear in mind that the atoms C, Ge, Sn, N, and P *have no part in the attraction*, when (as in  $CH_4$ ,  $CHCl_3$ ,  $CCl_4$ ,  $C_2H_6$  etc.,  $GeCl_4$ ,  $SnCl_4$ ,  $NH_3$ ,  $PH_3$ ) they are surrounded symmetrically on *all* sides by other atoms (or atom groups) which *absorb* the lines of force.

b) Wherever a *carbon atom* exhibits double bindings ( $C_2H_4$ , *i*- $C_5H_{10}$ ,  $C_6H_6$ ,  $C_4H_4S$ ) C must be taken = 1,55, and for *triple* binding ( $C_2H_2$ ) C = 3,1. The same *full* value 3,1 also occurs in CO,  $CO_2$ ,  $CS_2$  etc., just as in the group CO of the ketones, organic acids and compound esters.

c) Finally with regard to hydrogen, the *full* value 3,2 is found for all *anorganic* compounds (except  $H_2S$  and  $H_2Se$ ) and in the group OH of the alcohols and organic acids; whereas *half* the value 1,6 is found for  $H_2S$ ,  $H_2Se$  and for *all organic* compounds, where H is directly bound to C.

**Physics.** — “On the Validity of MATHEWS’ so-called Valency Law.”

By Dr. J. J. VAN LAAR. (Communicated by Prof. H. A. LORENTZ).

(Communicated in the meeting of January 29, 1916).

It now remains to say something about the so-called rule of MATHEWS<sup>1)</sup> that namely  $a$  would be  $= C(M \times v)^{2/3}$ , hence  $\sqrt{a} = \sqrt{C(M \times v)^{1/3}}$ , when  $M$  represents the molecular weight, and  $v$  the total number of effective valencies. Thus e.g. for  $n-C_5H_{12}$   $M = 72$ ,  $v = 5 \times 4 + 12 \times 1 = 32$ , hence  $\sqrt{72 \times 32} = 13,2$ , and  $\sqrt{C} = 19,7 \times 10^{-2} : 13,2 = 1,49 \times 10^{-2}$ . And for  $C_6H_5Cl$   $M = 112,5$ ,  $v = 6 \times 4 + 5 \times 1 + 1 \times 1 = 30$ , hence  $\sqrt{112,5 \times 30} = 15,0$ , and  $\sqrt{C} = 22,8 \times 10^{-2} : 15,0 = 1,52 \times 10^{-2}$ , which is almost equal to  $1,49 \times 10^{-2}$ .

<sup>1)</sup> Journal of Physical Chemistry, 1913 (nine articles).

Unfortunately, however, in about 50 out of 100 substances examined by MATHEWS the rule does not hold good at all; while at least 37 of the 74 substances investigated by us, hence also about half of them, deviate considerably.

MATHEWS determined the values of  $\alpha$  chiefly in two ways, first from the surface tension, reduced to the absolute zero-point, and secondly from the critical data. The two series of values of  $\alpha$  did not differ much, from which M (loc. cit. p. 160) drew the conclusion that  $\alpha$  is almost independent of the temperature. TYRER<sup>1)</sup> came to the same conclusion.

We found, however, by means of an accurate calculation that the two series of values do differ, indeed, and that the values of  $\alpha_0$  are about 16% higher than  $\alpha_k$  (at least when the critical temperature is not too low).

We will not enter here into the details of the calculations (loc. cit. p. 154 et seq.), nor into some theoretical considerations which seem very questionable to us (particularly those in the last Paper, loc. cit. p. 603 et seq.)<sup>2)</sup>, but only mention that M has found  $1,50 \times 10^{-2}$  (loc. cit. p. 183) for  $\sqrt{C}$  as middle value, whereas we find  $1,47 \times 10^{-2}$  as mean value for those substances in our tables for which the rule is more or less valid.

In the numerous cases in which the rule does not hold, M always succeeds in finding means to make his rule hold good. He either pronounces the most normal substances to be *associated* (even still at the critical temperature, where water, ethylalcohol etc. are already almost normal!), or he applies strange corrections to the valencies, and e.g. declares chlorine to be *trivalent* in all the cases in which his rule does not hold good, while this element again falls back to its *monovalent* rôle in the cases in which his rule does apply.<sup>3)</sup>

<sup>1)</sup> Z. f. ph. Chem. 87. p. 195 (1914).

<sup>2)</sup> This will be more fully treated in my book on the Equation of state, which I hope, will be able to be published after the war.

<sup>3)</sup> In the same way M manipulates some numerical factors, e.g. the constant of the formula of EÖTVÖS (resp. RAMSAY and SHIELDS) in order to establish a non-existing identity of the two series of values  $\alpha_0$  and  $\alpha_k$ . For the same purpose also v. D. WAALS' factor  $^{27}/_{64}$  (or corrected by us to  $^{27}/_{64\lambda}$ , in which  $\lambda$  is = 1 for ideal substances, and for ordinary substances about = 0,977) was replaced by

$$[s^2 - (s-2)] : s^2(s-2) = \frac{1}{s-2} - \frac{1}{s^2}, \text{ which is only correct in the limiting case } s = 4$$

(for substances with very high critical temperature), and N.B. does not converge to  $^{27}/_{64}$  for ideal substances ( $s = 8/3$ ), but actually to  $^{87}/_{64}$ ! In the correct expression for  $^{27}/_{64\lambda}$ , viz.  $(f'-1) : s^3$  he namely substitutes for  $f'-1$  the entirely faulty expression  $[s^2 - (s-2)] : (s-2)$ , which for  $s = 8/3$  would not converge to 3, but

We shall now shortly pass in review the different groups of substances, in which the little scrupulous manipulations will be manifest with which M. gets rid of exceedingly troublesome deviations of up to 300%.

*α.* For the *valenceless noble gases* MATHEWS' rule is, of course, not valid at all. For if  $v = 0$ , then  $\sqrt{a} = 0$  would also be  $= 0$ . But this difficulty the author entirely ignores. He simply assumes the formula to be valid, and now simply *calculates* the valencies of He from it etc. Thus he finds for He  $v = 0,04$  à  $0,07$ , for Neon  $v = 0,32$ , for Argon  $v = 1,12$  à  $1,35$ , for  $v = 1,23$ , and finally for Xenon  $v = 1,80$  à  $1,95$  (loc. cit. p. 339).

Hence He  $1/20$ -valent, Ne  $1/3$ -valent, Ar. and Kr.  $1 1/4$ -valent and X very nearly bivalent!

And in order to justify these singular *broken* valencies (among which  $< 1$ ), M assumes that these inactive gases are, indeed, valenceless, but that they yet possess two "extra"-valencies, which are, however only *partially* active. One of these two valencies in extraordinary service would be positive, the other negative, but only for a *part* of the molecules present those valencies — which are neutralized in ordinary circumstances, — would be "closed", as M expresses himself free and "open". And only these "open" valencies are revealed by M's rule. Thus 90% of the valencies are open for X, about 65% for Kr., 60% for Argon, 16% for Ne, and at last about 5%, for He (loc. cit. p. 341).

After this ingenious explanation — we see our way to explain away all discrepancies in the whole of Nature in this way — there is no need of anything further.

*β The other elements.* Where with us only hydrogen departs from the rule with regard to  $\sqrt{a}$ , not a single element is found to conform to his "rule" in MATHEWS. In order to make this rule valid also now, however, he declares the factor  $27/64$  inaccurate by 60% for e.g.  $H_2$  (though it happens to be almost perfectly accurate for  $H_2$ , being  $\lambda = 0,999$ ); further N and O to be *monovalent* in  $N_2$  and  $O_2$ , and chlorine *trivalent* in  $Cl_2$ .

*γ. The anorganic compounds.* In our table all the normal compounds (also CO and NO after correction of  $p_k$  — see  $b_k$  in § 3) are in good agreement. With MATHEWS, however, 12 of the 14 substances of our table do not agree at all. Only  $H_2Se$  and  $SO_2$

to  $9 2/3$ ! For ordinary substances this singular formula gives already errors of 15% for the factor  $27/64$ , and the errors can rise to more than 200% when we approach ideal substances. But his purpose is attained: the values of  $a_k$  now coincide with those of  $u$ , (Cf. the last of the cited papers).

(Se considered as *bivalent*, S as *tetravalent*) concord well. The other substances are "hopelessly aberrant", as M himself remarks with respect to CO. (loc. cit, p. 195).<sup>1)</sup>

To redress this he assumes C and O to be *monovalent* in CO; C and O *bivalent* (mark C bivalent) in CO<sub>2</sub>; S *hexavalent* in CS<sub>2</sub> and H<sub>2</sub>S; N *monovalent* and O *bivalent* in N<sub>2</sub>O; N and O both *monovalent* in NO; N and P *pentavalent* in NH<sub>3</sub> and PH<sub>3</sub>; Cl *trivalent* in SnCl<sub>4</sub> (!), but again *monovalent* in HCl. In GeCl<sub>4</sub> three atoms Cl would be *trivalent*, but the *fourth monovalent*!! (loc. cit. p. 259), though M also pleads for the inaccuracy of the critical data for GeCl<sub>4</sub>.

And to further the good cause CS<sub>2</sub>, NH<sub>3</sub>, PH<sub>3</sub>, H<sub>2</sub>S, HCl are declared to be *associated* at  $T_k$  (loc.cit. p. 190 et seq.).<sup>2)</sup> Then Cl can also be taken *trivalent* in HCl.

I should not have discussed all these things at such length, if VAN DER WAALS had not stated in his paper on the additivity of the *b*-values (cited by us in § 1), that M had found "very remarkable relations" with regard to *a*. I thought it therefore necessary to criticize these papers of M.

*δ. The carbon hydrogen.* Here we find 13 of the 17 substances of our table in accordance with M's rule. But CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub>, C<sub>2</sub>H<sub>4</sub> (important members, indeed, of the series) deviate greatly. For CH<sub>4</sub> MATHEWS again tries to save his cause by declaring the factor  $^{27}/_{64}$  to be faulty (comp. Footnote 3 on p. 1236)<sup>3)</sup>, and as for C<sub>2</sub>H<sub>4</sub>: one C-atom would be *bivalent*, the other *tetravalent*!

The cause why M's rule happens to hold good for the higher members of the series, is this that the values of  $\sqrt{a}$  are simply proportional to the number of H-atoms, and that for compounds, in which also C, N, and O occur by the side of H, the *fundamental values* of these elements *differ little* (resp. 3,1, 2,9, 2,7). But whenever Cl occurs, the fundamental value of which is about double the value, or S etc., the rule does not hold good at all.

*ε. Other organic compounds.* As may therefore be expected CH<sub>3</sub>Cl, CHCl<sub>3</sub>, CCl<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub>, C<sub>4</sub>H<sub>4</sub>S deviate more or less considerably.

1) Instead of  $\sqrt{C} = 1,5 \times 10^{-2}$  we find for  $\sqrt{C} \times 10^2$  resp. 1,4, 0,97, 1,2, 1,8, 1,8, 5,8, 2, 1,24, 0,94, 1,7, 1,85, and 2. Deviations therefore of on an average 45% (for SnCl<sub>4</sub> even 290%).

2) M. also asserts that H<sub>2</sub>O — because it departs more than 70% from his rule — is the most associated (at  $T_k$ ) of all substances known. We found H<sub>2</sub>O at  $T_k$  only slightly associated, just as C<sub>2</sub>H<sub>5</sub>OH etc. *Much less* than CH<sub>3</sub>OH and acetic acid e.g.

3) M even pronounces the conviction that if only the factor  $^{27}/_{64}$  were duly corrected for every substance, *all* the discrepancies would vanish. Indeed.

For this reason Cl is pronounced to be *trivalent*. But in  $C_3H_7Cl$ , where the rule does hold good, Cl is suddenly again *monovalent*. In  $C_4H_4S$  S would be *hexavalent*. Besides: several substances which more or less deviate, are declared to be associated or slightly associated (at  $T_k$ ).

For the compound esters one of the O-atoms in COOX is declared *tetravalent* (except for methyl-isobutyrate and methyl propionate, *where it is unnecessary*), the other O atom *bivalent*.

*φ*. For the *alcohols* and the *acetic acid*  $M$  finds the oxygen in OH tetravalent, the other atom O in COOH is *bivalent*. Compare these assertions with ours in § 4 under *e*). We saw viz. that the cause must not be found in the O-atoms, but that the C in COOH has the normal fundamental value against O in other compounds and that also H and OH have the full value, viz. 3,2, against 1,6 for the other H-atoms (bound to C).

For the *amines*  $NH_2CH_3$  and  $NH_2C_6H_5$  deviate, which accordingly are declared to be *associated* with N *pentavalent*, but for the other amines, which do agree, association is unnecessary, and therefore N may remain *trivalent*.

After these remarks, to which we shall not add anything (in my book to be published later I subject also some very singular theoretical considerations from his latest paper to criticism) the reader himself can form an idea of the value which he will have to attach to this remarkable "rule" of Mathews.

In § 4 we have sufficiently shown, that not only the values of  $b_k$ , but also those of  $\sqrt{a_k}$  can be built up perfectly additively from a few *fundamental values*. With regard to these fundamental values themselves, we found with respect to  $b_k$  exceedingly remarkable regularities in connection with the periodic system, and also the fundamental values of  $\sqrt{a_k}$  — which are almost equal for every horizontal series — certainly open up important perspectives in connection with THOMSON'S and NICHOLSON'S theory about the atomic structure.

But to this we shall revert later on.

Clarens, November 1915.