Physics. — "*On the Fundamental Values of the Quantities b and Va for Different Elements, in Connection with the Periodic System. V. The Elements of the Carbon and Titanium Groups.*" By Dr. J. J. VAN LAAR. (Communicated by Prof. H. A. LORENTZ).

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A. The Carbon Group.

1. For the calculation of the critical data and the values of a and b following from them the elements of this group offer very few data indeed. Even the situation of the melting point is still insufficiently known for carbon ; of other elements the accurate knowledge of the boiling point is wanting. Yet it is exactly this group — though we have often to be satisfied with a rough estimation — that gives a fine confirmation of the fact set forth by me in the preceding papers that the values of Va for elements, which (at least for high temperatures) occur as *separate atoms* and not as molecules (either partially dissociated or not), will suddenly become *very much higher* than the normal (rest) values for compounds.

We already found a first example for *Antimonium* and *Bismuth*, where Va_k (per gramme atom) present instead of the normal rest values 9, resp. $11 \cdot 10^{-2}$ the greatly increased values $\underline{32,5}$ and $\underline{36 \cdot 10^{-2}}$. The value of Va_k was only *partially* increased for other elements, as Arsenic, Selenium and Tellurium, owing to the fact that these elements are only partially dissociated to separate atoms at the critical temperature.

For the carbon group we find values for Va_k which lie between 32 and $40 \cdot 10^{-2}$, so that *all* these elements appear in the form of *separate* atoms, as the rest values for Va_k, which would hold for compounds, lie much lower, viz. between 3 and $11 \cdot 10^{-2}$.

2. **Carbon.** The melting point lies very high, viz. at $\underline{4200°}$ absolute. Probably this is only the sublimation point at 1 atm. pressure. According to LUMMER's interesting experiments, described in a paper published by VIEWEG : "*Verflüssigung der Kohle*" [1]), the carbon

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[1]) Sammlung VIEWEG, Heft 9/10. 1914.

melts namely at the ordinary pressure (see inter alia p. 64—65) exactly at 4200° C. abs. (According to accurate spectrometrical determinations). Though the contents of the said treatise is pretty confused and incoherent from a physico-chemical point of view, and very little indeed can be concluded from what is stated for other pressures, yet this one fact — viz. $T_s = 4200$ — seems pretty firmly established. But then the critical temperature lies certainly not below 6000 à 7000° abs., and $\sqrt{a_k}$ must be at least $= 32 \cdot 10^{-2}$, when $b_k = 100 \cdot 10^{-5}$, as we found before (in I). For the formula

$$RT_k = \frac{8}{27} \lambda \frac{a_k}{b_k},$$

in which (see earlier papers) the factor λ at a temperature of 6470° (see below), where $\gamma = 2,11$, has the value 0,781, so that with $R = 1 : 273,09$ we get:

$$T_k = 80,915 \times 0,781 \frac{a_k}{b_k} = 63,19 \frac{a_k}{b_k},$$

then gives :

$$T_k = 63,19 \times \frac{1024 \cdot 10^{-4}}{10 \cdot 10^{-4}} = 6470° \text{ abs.}$$

We remind of the fact that the factor λ is $= \frac{27}{8\gamma-1}\left(\frac{\gamma}{\gamma+1}\right)^2$, in which γ represents the reduced coefficient of direction of the imaginary straight diameter between D_k and $D_\bullet$ in a D,T-diagram [1]).

It is now the question whether the value of γ is confirmed to some extent by another way. We derived before that $b_k : b_0 = 2\gamma$ (see "New Relations" I). As b_k is expressed in so-called "normal" units, the value of b_k must still be multiplied by 22412, and this product divided by the atomic weight A, to obtain b_k in cm³. per gramme. And as $b_0 = v_0 = 1 : D_0$, we get :

$$2\gamma = \frac{b_k \times 22412 \times D_0}{A},$$

so that D_0 can be calculated from

$$D_0 = \frac{2\gamma \times A}{b_k \times 22412},$$

in which (cf. also "New Relations" III) 2γ can be calculated in approximation from the formula

$$2\gamma = 1 + 0,04 \sqrt{T_k}.$$

We, therefore, calculate the value $1 + 0,04 \times 80,4 = 4,22$ for

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[1]) See for all this my series of papers : "A New Relation, etc." in These Proc. of March 26, April 23, May 29 and Sept. 26 1914; resp p. 808, 924, 1047 and 451; especially I.

2γ, so that γ has the high value 2,11. [For "ordinary" substances with critical temperature of about 400° to 625° absolute (125ᶜ to 350° C.) we find for this the value 0,9 à 1]. For all other elements of the carbon group we shall find values for 2γ, lying between 4 and 3.

Hence we find:

$$D_0 = \frac{4,22 \times 12}{100 . 10^{-5} \times 22412} = \frac{50,6}{22,4} = \underline{2,26}. \text{ (calculated)}$$

For *graphite* (at high temperatures all carbon forms are converted to graphite, and this is therefore the only stable form at T_k) $D = 2,10$ to 2,25 at ordinary temperatures, according to different statements. Thus among others MOISSAN gives from 2,10 to 2,25, MEYER from 2,14 to 2,25; LE CHATELIER has found 2,255 for artificial Acheson-graphite. The value for the limiting density D_0, *calculated.* by us is therefore in excellent harmony with the experimental value at the ordinary temperature, which will be only very little lower.

The value of p_k is now found from

$$p_k = \frac{1}{27} \lambda \frac{a_k}{b_k^2},$$

in which $\lambda = 0{,}781$ (see above). Hence with $\sqrt{a_k} = 32 . 10^{-2}$, $b_k = 10 . 10^{-4}$:

$$p_k = 0{,}0289 \times \frac{1024 . 10^{-4}}{100 \ 10^{-8}} = \underline{2970 \text{ atm.}}$$

From the formula

$$log^{10} \frac{p_k}{p_s} = f_s{}^{10} \left(\frac{T_k}{T_s} - 1 \right)$$

follows at $T_s = 4200°$ (T_s is properly speaking the boiling point, but probably represents the sublimation. point at 1 atm. here) and $p_s = 1$:

$$3{,}473 = f_s{}^{10} \left(\frac{6470}{4200} - 1 \right),$$

from which follows $f_s{}^{10} = 3{,}473 : 0{,}540 = 6{,}43$, i.e. $f_s = 6{,}43 \times$ $\times 2{,}303 = \underline{14{,}8}$. This value is very well possible, as according to one of our formulae (see "New Relations" I) $\underline{f_k = 8\gamma}$, when a and b at T_k are independent of T, so that f_k would be $= \underline{16{,}9}$. And f_s is always somewhat smaller than f_k.

If T_k is really $= 6470°$ abs., $T_k : T_s$ would be $= \underline{1{,}54}$ for carbon.

3. Silicium. If we assume here $\sqrt{a_k} = \mathbf{34} . 10^{-2}$, we get with, $\lambda = 0{,}816$ ($2\gamma = 3{,}81$, see below) and $b_k = \underline{155} . 10^{-5} = 15{,}5 . 10^{-4}$;

$$T_k = \frac{66,03 \times 1156}{15,5} = 4920° \text{ abs.}$$

The melting point, lying at 1426° C. = 1699° abs. (98,9%, Si) according to Doerinckel (1906), $T_k : T_{tr}$ would be = 2,90.

If we repeat the above check-calculation (§ 2), it follows (2γ becoming = 1 + 0,04 × 70,2 = 3 81) that

$$D_0 = \frac{3,81 \times 28,3}{155 . 10^{-5} \times 22412} = \frac{107,8}{34,74} = 3,10. \text{ (calculated)}$$

This value seems somewhat too high, as at the ordinary temperature for Si values have been found in the neighbourhood of 2,50 (Wöhler gives 2,49; in Rudorf's book on the periodic system we find 2,48; etc.), but these earlier values may be too low.

For p_k we find with $\lambda = 0,816$ (see above):

$$p_k = \frac{0,0302 \times 1156 . 10^{-4}}{240,25 . 10^{-8}} = 1450 \text{ atm.}$$

If we assume the value 1,6 for the ratio $T_k : T_s$, T_s (the boiling point) would be about 3080° abs. V. Wartenberg's value 1902), viz. > 1205° C. (the melting point n.b. lying as high as 1426° C.), is therefore rather euphemistic.

The value $f_s^{10} = 3,161 : 0,6 = 5,27$, hence $f_s = 12,1$, would correspond with $T_s = 3100°$. For f_k may be expected $f_k = 8\gamma = 15,2$.

4. Germanium. With $\sqrt{a_k} = 36 . 10^{-2}$ we find ($\lambda = 0,835$, as 2γ is = 3,58), b_k being = 210 . 10 [5]:

$$T_k = \frac{67,56 \times 1296}{21,0} = 4170° \text{ abs.}$$

According to Biltz (1911) the melting point lies at 958° C. = 1231° abs., hence $T_k : T_{tr}$ would here be = 3,39.

For 2γ is found $2\gamma = 1 + 0,04 \times 64,6 = 3,58$, so that we calculate:

$$D_0 = \frac{3,58 \times 72,5}{210 . 10 \times 22412} = \frac{259.6}{47,07} = 5,52. \text{ (calculated)}$$

Winkler found 5,47 for 20° C., so that the agreement is again striking.

We further calculate for p_k:

$$p_k = \frac{0,0309 \times 1296 . 10^{-4}}{441 . 10^{-8}} = 910 \text{ atm.}$$

With $T_k : T_s = 1,6$ we should find about 2600° abs. for T_s. Rudorf gives $T_s > 1300°$ C. Remark as above for Silicium.

For f_s^{10} we calculate $2,959 : 0,6 = 4,93$, hence $f_s = 11,4$, while f_k would be = 14 3.

5. Tin. When we put $\sqrt{a_k}$ again 2 units higher, viz. $\sqrt{a_k} = 38.10^{-2}$, we calculate with $b_k = 265.10^{-5}$, $2\gamma = 3{,}44$ (see below), $\lambda = 0{,}847$:

$$T_k = \frac{68{,}54 \times 1444}{26{,}5} = 3730 \text{ abs.}$$

At the time (1887) GULDBERG calculated the too low value $3000°$ abs. from various data.

For 2γ we find $1 + 0{,}04 \times 61{,}1 = 3{,}44$, and thus we have:

$$D_0 = \frac{3{,}44 \times 118{,}7}{265.10^{-5} \times 22412} = \frac{408{,}3}{59{,}4} = 6{,}87. \text{ (calculated)}$$

At $-163°{,}4$ COHEN and OLIE (Zeitschr. f. ph. Ch. **71**, 400; 1909) found for white tin $7{,}35$ and for grey tin $5{,}77$. The value calculated by us lies near that of white (tetragonal) tin, which is stable at higher temperature. TRECHMANN (1880) found the value $6{,}5$ to $6{,}6$ for the density of the rhombic tin, which is stable above $161°$. Our value $6{,}9$ lies, therefore, between that of tetragonal $(7{,}3)$ and rhombic tin $(6{,}6)$[1].

And now the vapour pressure determinations, made by GREENWOOD in 1911 (Z.f. ph. Ch. **76**, 484). Let us, however, first calculate the probable value of the critical pressure.

For this we find:

$$p_k = \frac{0{,}0314 \times 1444.10^{-4}}{702{,}25.10^{-8}} = 650 \text{ atm.}$$

As GREENWOOD found $2270° \text{ C.} = 2543°$ abs. for the boiling point, the ratio would be $T_k : T_s = 1{,}47$, which is too low in my opinion, so that either the temperature is still higher than $3700°$, or — what in connection with what will appear for lead, is by no means improbable — the boiling temperature determined by GREENWOOD has been given too high (or the vapour pressure at that temperature too low). If $2543°$ were correct, a value about equal to $2543 \times 1{,}6 = 4100°$ abs. might be expected for T_k, in consequence of which also $\sqrt{a_k}$ would have to be raised to about 40.10^{-2} instead of 38.10^{-2}.

If the value $3730°$, calculated by us, is correct, the ratio $T_k : T_{tr}$

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[1] When we take the density of *liquid* tin at the melting point, viz. $6{,}99$ (VICENTINI and OMODEI, 1888), as standard, we might certainly expect D_0 to be > 7. But then it is overlooked that the solid rhombic modification, which has the density $7{,}2$ at the melting point $(232°)$, has the so much *smaller* density $6{,}5$ à $6{,}6$ at the ordinary temperature. Abnormal changes of density are, therefore, also to be expected in the *liquid* phase at decreasing temperature, if this phase could be realized below the melting point.

becomes $= 3730 : 505 = 7,4$, which is very high; with $T_k = 4100°$ or still higher this ratio would even become 8 or 9.

Greenwood's vapour pressure determinations gave the following result.

$T =$	2243	2373	2543 abs.
$p =$	0,133	0,345	1 atm.

From the well-known formula $log \dfrac{p_k}{p} = f\left(\dfrac{T_k}{T} - 1\right)$ or $log\, p =$

$= (f + log\, p_k) - \dfrac{f T_k}{T}$ we find :

$$f + log\, p_k = \frac{T_2\, log\, p_2 - T_1\, log\, p_1}{T_2 - T_1},$$

every time from two successive observations (between which f is supposed constant), after which fT_k can further be calculated from $fT_k = T(f + log\, p_k) - T log\, p$. Thus we find from

$log^{10} p =$	0,12385(—1)	0,53782(—1)	0
$T log^{10} p =$	277,8—2243	1276—2373	0

resp. $f^{10} + log^{10} p_k = 6,681$ and $6,453$; $f^{10} T_k = 16950$ and 16410. (Greenwood calculates for this the too low values $29 : 4,571 = 6,344$ and $73900 : 4,571 = 16167$).

Hence f^{10} becomes resp. $= 3,868$ and $3,640$ with $p_k = 650$ atm., $log^{10} p_k = 2,813$, from which 4380, resp. 4510, mean $4450°$ would follow for T_k. And a modification, even a considerable one, in the assumed value of p_k has little influence on this.

The value of f_s^{10} lies here, therefore, in the neighbourhood of $3,75$, i.e. f_s in that of $8,6$. This value seems too low to us, as $2\gamma = 3,44$ already corresponds with the critical temperature $T_k = 3730°$, so that f_k then would be $= 13,8$. And 2γ would be $= 3,7$ with $4500°$, i.e. $f_k = 14,8$. Everything points therefore to the fact that the boiling point determined by Greenwood is too high, or rather that the vapour pressures determined by him, have been given too low.

If we retain the value $T_k = 3730°$, calculated by us, the real boiling point temperature T_s would be $= 2330°$ abs. with $T_k : T_s = 1,6$, instead of $2543°$ abs. as Greenwood gives, and the value f_s^{10} would then be $= 4,69$, i. e. $f_s = 10,8$.

6. Lead. If we assume here $\sqrt{a_k} = 40 . 10^{-5}$, and $b_k = 320. 10^{-5}$ again 55 units higher than tin, though this cannot be ascertained in default of *compounds*, the critical temperature and pressure of which are known), we get with $2\gamma = 3,35, \lambda = 0,855$:

$$T_k = \frac{69,16 \times 1600}{32,0} = \underline{3460°} \text{ abs.}$$

The value of 2γ is then $= 1 + 0\,04 \times 58,8 = \underline{3,35}$, and we find for D_0:

$$D_0 = \frac{3,35 \times 207,2}{320 \cdot 10^{-5} \times 22412} = \frac{694,2}{71,72} = \underline{9,68}. \text{ (calculated)}$$

D has been found $= \underline{11,4}$ at the ordinary temperature, so that 9,7 would be about 15 °/$_0$ too low — unless lead, like tin, is converted to a less dense modification at lower temperature. COHEN and HELDERMAN's researches (cf. among other things Z. f. ph. Chem. **74**, 202 (1910) and **89**, 733 (1915)) suggest already the existence of even more than two allotropic forms.

We find for the critical pressure:

$$p_k = \frac{0,0317 \times 1600 \cdot 10^{-4}}{1024 \cdot 10^{-8}} = \underline{490} \text{ atm.}$$

For the boiling point GREENWOOD (1911) found 1525° C. $= 1798°$ abs.; v. WARTENBERG (1908) found 1580° C. $= 1853°$ abs. The two values do not differ much. If we assume the mean value $T_s = \underline{1825°}$ abs. as correct, $T_k : T_s$ becomes $= \underline{1,90}$, which is very high, and f_s^{10} becomes $= 2,69 : 0,9 = 2,99$, i. e. $f_s = \underline{6,9}$, whereas $f_k = 8\gamma = \underline{13,4}$ is expected. The value of f_s would, therefore, be much too low. And as $T_{tr} = 327°,3$ C. $= 600°,4$ abs., $T_k : T_{tr}$ would become $\underline{5,76}$. Possibly the critical temperature has been assumed somewhat too high. From GREENWOOD's vapour pressure determinations a temperature would follow for T_k somewhat below 3000°. But then b_k must not be assumed to be $= 320 \cdot 10^{-5}$, but e. g. again 55 units higher, hence $b_k = \underline{375 \cdot 10^{-5}}$. In virtue of the Cerium-Tantalium period, inserted after the tin, this may not be improbable. With $2\gamma = \underline{3,19}$, $\lambda = 0,868$ we should then have obtained for T_k the value $70,23 \times 1600 : 37,5 = \underline{3000°}$ abs., in perfect agreement with GREENWOOD's experiments. But a still lower value would then be calculated for D_0, viz. $660,9 : 84,05 = \underline{7,86}$. The value of p_k would be $= 0,0321 \times 1600 \cdot 10^{-4} : 1406,25 \cdot 10^{-8} = \underline{370}$ atm., and the two ratios $T_k : T_s$ and $T_k : T_{tr}$ would be found resp. $= \underline{1,64}$ and $\underline{5}$.

GREENWOOD's determinations now gave what follows.

$T = 1588$	1683	1798	2143	2373 abs.
$p = 0,138$	0,350	1,0	6,3	11,7 atm.
$log^{10} p = 0,13988(-1)$	0,54407(-1)	0	0,79934	1,06819
$T log^{10} p = 222,1-1588$	915,7-1683	0	1713	2535

A similar calculation as that for tin yields between each successive couple of observations:

$$f^{10} + log^{10} p_k = \quad 6{,}301 \quad 6{,}672 \quad | \quad 4{,}965 \quad 3{,}573$$

$$f^{10} T_k = \quad 11372 \quad 11996 \quad | \quad 8927 \quad 5944$$

From the two last calculated values for $f^{10} + log^{10} p_k$ and $f^{10} T_k$ appears the inaccuracy of Greenwood's vapour pressure determinations, especially at temperatures higher than 2000° abs. (the same therefore as for tin). For as $log^{10} p_k = 2{,}69$ to $2{,}57$, hence on an average about $2{,}63$, it would follow from the last determinations that f^{10} is $= 2{,}34$ to $0{,}94$, which is quite impossible. And if reversely we take the probable value 4 for f^{10}, the much too low values 2200° to 1500° abs. would follow for T_k from the said determinations. Accordingly, both for tin and for lead, we must reject the vapour pressure determinations above 2000 as quite erroneous. It we only take into account those below 2000°, we find with $log^{10} p_k = 2{,}63$ the values $f^{10} = 3{,}67$, resp. $4{,}04$, yielding $T_k = 3100$ to 2970°, mean 3035° abs.; in excellent agreement with the value of T_k computed by us, when $b_k = 375.10^{-5}$ is assumed (viz. 3000°). Very little in agreement, however, with the calculated value of T_k on the assumption of $b_k = 320.10^{-5}$, viz. 3460° abs. It is really difficult to make a choice here; we do not know in how far Greenwood's observations below 2000° are reliable. That, however, v. Wartenberg found an only slightly divergent value for the boiling point, is a reason to assume the middle value 1825° for the boiling point as pretty accurate. But then the critical temperature can probably not be higher than 2900° or 3100°. (According as $T_k : T_s$ is taken 1,6 or 1,7). If we, therefore, retain the value 3000° abs. [1]), which was obtained with $b_k = 375.10^{-5}$, $T_k : T^s$ becomes $= 1{,}64$. As $log^{10} 370 = 2{,}57$, f_s^{10} becomes $= 2{,}57 : 0{,}64 = 4{,}0$, i. e. $f_s = 9{,}2$, while the value 12,8 is expected for $f_k = 4 \times 2\gamma$. (With $log^{10} p_k = 2{,}57$ the value 3,73, resp. 4,10 follows for f_s^{10} from Greenwood's observations, which is in good harmony with the above mentioned value 4,0).

7. Recapitulation. Combining the values of $\sqrt{a_k}, b_k, T_k, p_k$, etc., found above for the elements of the carbon group, in a comprehensive table, we get the following survey. For lead we have given

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[1]) Goldberg (1887) gives also for lead the much too low value $T_k = 2000$ abs. For mercury the same: 1000° abs., which is also too low.

	$\sqrt{a_k}\cdot 10^2$	$b_k\cdot 10^5$	T_k (abs.)	p_k (atm.)	2ι	)	D_0 (calc.)	D_0 (found)	T_s	T_{tr}	$\dfrac{T_k}{T_s}$	$\dfrac{T_k}{T_{tr}}$	f_s	f_k
C	32	100	6470	2970	4,22	0,781	2,26	2,255	4200	—	1,54	—	14,8	16,9
Si	34	155	4920	1450	3,81	0,816	3,10?	2,50	(3080)	1700	(1,6)	2,9	(12,1)	15,2
Ge	36	210	4170	910	3,58	0,835	5,52	5,47	(2600)	1230	(1,6)	3,4	(11,4)	14,3
Sn	38	265	3730	650	3,44	0,847	6,87	6,6 à 7,3	(2330)	505	(1,6)	7,4	(10,8)	13,8
			4450? (from Gr.)						2543? (Gr.)					
Pb	40	(320)	3460 ?	490	3,35	0,855	9,68 ?	11,4	1825	600	1,90 ?	5,8	6,9 ?	13,4
		375	3000 (from Gr.)	370	3,19	0,868	7,86 ?				1,64	5,0	9,2	12,8

both the values corresponding with $b_k = 320.10^{-5}$ and those corresponding with $b_k = 375.10^{-5}$.

B. The Minor-group Titanium, Zircon, Cerium, Thorium.

8. Titanium. Let us in conclusion briefly discuss the minor-

group of Titanium. Here data are still more greatly wanting, as we have not even an idea of the probable values of b_k through compounds of which the critical temperature has been determined. We can, therefore, only assume them in approximation between those of the elements of the principal group. Thus we might put:

	Ti	Zr	Ce	Th
$b_k . 10^5 =$	182,5	237,5	292,5	402,5
$\sqrt{a_k} . 10^2 =$	35	37	39	41

With respect to Titanium we find with $2\gamma = 3,68$, $\lambda = 0,827$:

$$T_k = \frac{66,92 \times 1225}{18,25} = 4490° \text{ abs.}$$

In consequence of this $2\gamma = 1 + 0,04 \times 67,0$ becomes $= 3,68$. We then calculate for D_0:

$$D_0 = \frac{3,68 \times 48,1}{182,5 . 10^{-5} \times 22412} = \frac{177,0}{40,90} = 4,33. \text{ (calculated)}$$

At ordinary temperatures WEISZ and KAISER (1910) found 3,99 (amorph, 85,65 %, i.e. 3,2 % O_2 + 11,15 % iron) and 5,17 (molten 97,4%). MOISSAN (1895) and MEIJER (1899) found 4,87 (molten 2%C). At last HUNTER found the value 4,50 (100%) in 1910. The real value will, therefore, no doubt lie in every case between 4 and 5, so that the value calculated by us is again in fairly good agreement.

For the melting point BURGESS and WALTENBERG (1914) found 1795°, HUNTER (1910) from 1800° to 1850°. If we take the round value 1800° C. $= 2073°$ abs., $T_k : T_{tr}$ becomes $= 2,17$. We have finally for p_k:

$$p_k = \frac{0,0306 \times 1225 . 10^{-4}}{333,06 . 10^{-8}} = 1130 \text{ atm.}$$

9. Zircon. Here we have with $2\gamma = 3,51$, $\lambda = 0,841$:

$$T_k = \frac{68,09 \times 1369}{23,75} = 3920 \text{ abs.}$$

From this follows $2\gamma = 1 + 0,04 \times 62,7 = 3,51$, so that for D_0 we calculate:

$$D_0 = \frac{3,51 \times 90,6}{237,5 . 10^{-5} \times 22412} = \frac{317,6}{52,72} = 6,02 . \text{ (calculated)}$$

This is again in fairly good harmony with the experimentally found value, viz. 5,95 to 6,39 (WEDEKIND and LEWIS, 1910), and 6,40 (WEISZ and NEUMANN, 1910). The former two authors worked resp. with powdery (96,5 %) and molten Zircon (91,3 to 96,5 %);

the two latter with almost pure molten material (99,7 to 100 %). The value calculated by us seems to be slightly too low. Possibly b_k may be assumed too high.

For the boiling point the exceedingly high temperature 2350° (97 %), i. e. 2623° abs., has been found by v. BOLTON (1910), and also by WEDEKIND and LEWIS (1910), so that then $T_k : T_b$ would amount to $= 1.50$ Also from this too low amount it would follow that the critical temperature has been calculated too low in consequence of the value of b_k, which has been assumed too high.

If for $b_k \cdot 10^5$ instead of 237,5 we assume the value 210, which also holds for Germanium, T_k becomes about 4400°, and the ratio $T_k : T_b$ rises from 1,5 to 1,7, the calculated limiting density becoming slightly greater than 7, somewhat too great therefore.

We calculate for p_k :

$$p_k = \frac{0,0312 \times 1369 \cdot 10^{-4}}{564,06 \cdot 10^{-8}} = \underline{760} \text{ atm.}$$

10. Cerium. As $2\gamma = 3,39, \lambda = 0,851$, we calculate:

$$T_k = \frac{68,86 \times 1521}{29,25} = \underline{3580°} \text{ abs.}$$

For 2γ follows from this $2\gamma = 1 + 0,04 \times 59,8 = \underline{3,39}$, so that we get:

$$D_0 = \frac{3,39 \times 140,25}{292,5 \times 22412} = \underline{7,25} \text{ .(calculated)}$$

6,92 (98 %) was found by HIRSCH (1912), and 7,04 by MUTHMANN and WEISZ (1904). The calculated value may possibly be somewhat too high.

As for the melting point 635° (98 %) was found by HIRSCH, and 623° C. by MUTHMANN and WEISZ, we may assume the middle value 629° C. $= 902°$ abs. to be pretty accurate, so that $T_k : T_b$ becomes $= 3,97$.

For p_k we find:

$$p_k = \frac{0,0315 \times 1521 \cdot 10^{-4}}{855,6 \cdot 10^{-8}} = \underline{560 \text{ atm.}}$$

11. Thorium. As 2γ appears to be $= 3,17$, and therefore λ is $= 0,870$, we get:

$$T_k = \frac{70,40 \times 1681}{40,25} = \underline{2940°} \text{ abs.}$$

This makes 2γ really $= 1 + 0,04 \times 54,2 = \underline{3,17}$, and we find for D_0 :

$$D_0 = \frac{3,17 \times 232,15}{402,5 \cdot 10^{-5} \times 2,412} = \frac{735,9}{90,21} = \underline{8,16} \text{ . (calculated)}$$

This value agrees pretty well with the earlier density determinations (1863), which gave 7,7 or 7,8 — but badly with the later ones by NILSON (1882), who found 11,0, and those by v. BOLTON (1908), who even found 12,2. The value of b_k has, therefore, possibly been assumed too high.

This is also evident from the value of $T_k : T_{tr}$. For the melting point WARTENBERG (1910) found, namely, 1700 to 1755° C. (The Thorium contained only 0,15 °/₀ C.). If we assume 1727° C., i. e. 2000° abs., $T_k : T_{tr}$ would become $= \underline{1,47}$, which seems again too low. The same thing, therefore, as for Zircon. If instead of $402,5.10^{-5}$ we assume for b_k the value 375.10^{-5}, which also holds for lead, T_k becomes somewhat higher, and then a value in the neighbourhood of 9,5 follows for D_0, hence still too low.

Finally we find for p_k:

$$p_k = \frac{0,0322 \times 1681 \cdot 10^{-4}}{1620 \cdot 10^{-8}} = \underline{330} \text{ atm.}$$

12. Recapitulation. When we recapitulate what was found here, in a table, we get the following survey.

	$\sqrt{a_k} \cdot 10^2$	$b_k \cdot 10^5$	T_k (abs.)	p_k (atm.)	2γ	$\jmath$	D_0 (calc.)	D_0 (found)	$\dfrac{T_k}{T_{tr}}$
Ti	35	182,5?	4490	1130	3,68	0,827	4,33	4 à 5	2,2
Zr	37	237,5?	3920	760	3,51	0,841	6,02	6 à 6,4	1,5?
Ce	39	292,5?	3580	560	3,39	0,851	7,25	6,9 à 7,0	4,0
Th	41	402,5?	2940	330	3,17	0,870	8,16?	8 à 12	1,5?

12. Conclusion. It follows most convincingly from all that precedes that — in order to determine the elements of the carbon group (and of the Titanium group) — the values of the *molecular attractions* $\sqrt{a_k} \cdot 10^{-2}$ must be taken *very high*, ranging from **32** for carbon to **40** for lead. These values are *very much higher* than the *residual attractions* for the *compounds* of these elements, which range from 3 to 11, as we saw before. (See I to IV). This means, therefore, simply that we have to do here with **free atoms** which exhibit a so much greater attraction than the bound atoms in the molecule.

Thus $\sqrt{a} = 0$ e.g. for carbon, which is surrounded symmetrically on all sides by atoms or atom groups, as in CH_4, CCl_4, C_2H_6 etc. For doubly bound C, as for C_2H_4, C_6H_6, C_4H_4S, we find $\sqrt{a}=1,55.10^{-5}$; whereas for triple bound C, as for C_2H_2 (likewise for CO, CO_2, CS_2, etc.), the *full* residual value $\sqrt{a} = 3,1 . 10^{-5}$ is found (see I). But only for the *free* atoms in the *element* carbon (C_1) we find the so much higher, *ten times* higher value $\sqrt{a} = 32.10^{-2}$.

And the small deviations between theory and experiment which still remain cannot detract from this fact — not for the other elements either. Whether the value 32 will perhaps have to be replaced by 33 in the end, or the value 40 by 41 or 42 — this does not affect the above in the least. And it is noteworthy that also the elements of the minor-group Ti, Zr, Ce, Th., of which so little is known, yet confirm this important fact in the clearest way. Besides we found this already indubiously expressed for *Antimonium* and *Bismuth* (see IV) with $\sqrt{a_k} = 32,5$, resp. $36 . 10^{-2}$.

As far as the values of b_k are concerned, they appear to be the same as those which are also calculated from the compounds (if present) — which might have been expected beforehand.

In my next paper I hope to treat the exceedingly important elements of the group of the *alkali-metals*, besides those of the minor-group Cu, Ag, Au.

Clarens, May 1917.