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

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1. After the group of the noble gases, the halogens, the elements of the oxygen and nitrogen groups, and those of the carbon group, we will, for practical reasons, first treat the group of the alkali metals, and not until after this can we treat the intermediate Beryllium and Borium groups, and the remaining minor groups with some certainty.

The task undertaken by us to compute with some certainty the values of the critical quantities, and those of b_k and $\sqrt{a_k}$, with the required accuracy, gets more and more difficult. For the alkali metals e.g. *compounds* of which the boiling point or the critical temperature are known, are entirely wanting, and thus we are deprived of a valuable test. *Nothing* is known beforehand that could be used in any way as a foundation; everything must be calculated anew, estimated, weighed, and considered. For an element as recalcitrant as e.g. Carbon or Silicium, the critical temperature of which is quite inaccessible, we know at least the value of b_k from *compounds*, from which — in connection with other data — the values of a_k , T_k and p_k can be calculated with almost mathematical certainty.

This is not the case for the alkali metals. Here nothing is known beforehand concerning b_k , and in most cases we shall therefore have to be satisfied with defining limits between which the required values of b_k and $\sqrt{a_k}$ must lie. Fortunately these limits are comparatively narrow, particularly when the course of the vapour tension curve is sufficiently known, so that the values calculated by us can yet lay claim to a satisfactory degree of accuracy.

It will appear that for the alkali metals we are very near the truth with respect to the critical temperature, when we multiply the absolute temperature of the melting point by $5\frac{1}{3}$, and that of the boiling point by 1,7. Thus we have the following survey.

33

Proceedings Royal Acad. Amsterdam. Vol. XX.

	<i>Li</i>	<i>Na</i>	<i>K</i>	<i>Rb</i>	<i>Cs</i>
$T_{tr} =$	452,1	370,6	335,6	311,6	301,3
$T_s =$	—	1156,0	1035,3	971,1	943,1
$T_{tr} \times 5^{1/3} =$	2411	1977	1790	1652	1607
$T_s \times 1,7 =$	—	1965	1750	1651	1603
$T_{tr} \times 4^{2/3} =$	—	1729	1566	1452	1406
$T_s \times 1,5 =$	—	1734	1554	1457	1415

And now we shall see in what follows that — at least for *Na*, *K*, *Rb* and *Cs* — the real values of T_k lie between those obtained with the factors $5^{1/3}$ and 1,7, and those obtained with the factors $4^{2/3}$ and 1,5. Generally nearer to the first group. Besides we know already from former considerations that the factor by which the absolute boiling point temperature must be multiplied to obtain the absolute critical temperature, lies in the neighbourhood of 1,7. This factor can also be smaller, but it seldom becomes smaller than 1,5. For Lithium, there is reason to suppose that T_k lies probably *higher* than would follow from $T_{tr} \times 5^{1/3}$. The factor is there with pretty great certainty = 5,6.

It is certainly rather remarkable that the ratio $T_s : T_{tr}$ is so constant for the alkali metals, viz. about $3^{1/3}$.

2. Lithium. The melting point lies at $1790^\circ \text{C.} = 452,1^\circ \text{ abs.}$ According to the above we may expect the critical temperature between $452,1 \times 5^{1/3} = 2411^\circ$ and $452,1 \times 5 = 2713^\circ \text{ abs.}$ We shall perform the subjoined calculations for both values of T_k , rounded off to 2410° and 2700° .

The value of γ follows from our formula $2\gamma = 1 + 0,038 \sqrt{T_k}$. It gives with $\sqrt{T_k} = 49,09$ to $51,96$ the values 2,865 and 2,975, i.e. $\gamma = 1,43$ to $1,49$. This is accordingly the (reduced) coefficient of direction of the straight diameter between D_k and D_0 .

From formula $\lambda = \frac{27}{8\gamma - 1} \left(\frac{\gamma}{\gamma + 1} \right)^2$, with $\frac{\gamma}{\gamma + 1} = 0,589$ or $0,598$, hence $\left(\frac{\gamma}{\gamma + 1} \right)^2 = 0,347$ or $0,358$, and with $8\gamma - 1 = 10,46$ or $10,90$ we further find the values $\lambda = 0,895$ or $0,886$ for the factor λ in $RT_k = \frac{8}{27} \lambda \frac{a_k}{b_k}$ and $p_k = \frac{1}{27} \lambda \frac{a_k}{b_k^2}$. This renders $\varphi = \frac{8}{27} \lambda : R$ with

$R = 1 : 273,1$ resp. $= 72,44$ to $71,67$ (the value $\frac{8}{27} : R$ is $= 80,915$).

Let us now calculate the value of b_k . From $b_k : b_0 = 2\gamma$ follows with $b_0 = v_0 = 1 : D_0$:

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

when b_k is calculated in "normal" units, and per Gr. atomic weight. We must, therefore, know D_0 . From the relation for the ideal straight diameter (while namely the vapour density can be neglected) $D = D_0 - 2\gamma D_k \frac{T}{T_k}$ follows with $D_k = \frac{D_0}{2(1+\gamma)}$:

$$D = D_0 \left(1 - \frac{\gamma}{1+\gamma} \frac{T}{T_k} \right).$$

Unfortunately, however, the liquid density for Lithium is unknown. But $D = 0,5935$ holds for solid Lithium at 15°C . For liquid Lithium D is therefore slightly smaller than this value, perhaps 2% smaller. Thus we have:

$$\left. \begin{aligned} < 0,5935 = D_0 \left(1 - 0,589 \times \frac{288}{2410} \right) = 0,930 D_0 \\ \text{or} = D_0 \left(1 - 0,598 \times \frac{288}{2700} \right) = 0,936 D_0 \end{aligned} \right\}$$

so that D_0 becomes $< 0,638$ or $< 0,634$ (according as $T_k = 2410^\circ$ or 2700° abs.) Hence

$$\left. \begin{aligned} b_k > \frac{2,865 \times 6,94}{0,638 \times 22412} = \frac{19,88}{14310} = 139 \cdot 10^{-5} \\ \text{or } b_k > \frac{2,975 \times 6,94}{0,634 \times 22412} = \frac{20,64}{14210} = 145 \cdot 10^{-5} \end{aligned} \right\}$$

The value of b_k can therefore be at most 2% greater, i.e. from 142 to $148 \cdot 10^{-5}$. Now $b_k = 55$ for F , $= 70$ for O , $= 85$ for N , $= 100 \cdot 10^{-5}$ for C .; we might, therefore, expect for B the value 115 , for Be 130 , and for Li the value $145 \cdot 10^{-5}$. If this last value is correct, T_k would have to lie between 2400° and 2700° for Lithium, e. g. it would be about 2550° .

Now the value a_k follows from

$$a_k = \frac{T_k \times b_k}{\varphi},$$

in which $\varphi = \frac{8}{27} \frac{\lambda}{R}$ (see above). This gives:

$$\left. \begin{aligned} \alpha_k &> \frac{2410 \times 13,9 \cdot 10^{-4}}{72,44} = \frac{33500}{72,44} 10^{-4} = 462,5 \cdot 10^{-4} \\ \text{or } \alpha_k &> \frac{2700 \times 14,5 \cdot 10^{-4}}{71,67} = \frac{39150}{71,67} 10^{-4} = 546,3 \cdot 10^{-4} \end{aligned} \right\}$$

from which we find:

$$\sqrt{\alpha_k} > 21,5 \text{ or } > 23,4 \cdot 10^{-2} \text{ (e.g. } \sqrt{\alpha_k} = 21,7 \text{ à } 23,6 \cdot 10^{-2}\text{)}.$$

For p_k immediately follows from (as $8 : R = 8 \times 273,1 = 2185$)

$$p_k = \frac{T_k}{2185 \times b_k}$$

the value

$$\left. \begin{aligned} p_k &= \frac{2410}{2185 \times 142 \cdot 10^{-5}} = \frac{2410}{3,103} = 777 \text{ atm.} \\ \text{or } p_k &= \frac{2700}{2185 \times 148 \cdot 10^{-5}} = \frac{2700}{3,234} = 835 \text{ ,,} \end{aligned} \right\}$$

from which $\log^{10} p_k = 2,890$ to $2,922$ follows, which we should want, when a series of vapour pressures above the melting point were known of Lithium. But of this exceptional element literally nothing more is known than the melting point and the density at 15° C . Not even the boiling point or the density at the melting point. Still less the coefficient of expansion in solid and liquid state.

3. Sodium. Here we tread on firmer ground. The melting point lies at $97,5^\circ \text{ C} = 370,6$ abs. The boiling point lies at $882,9^\circ \text{ C} = 1156^\circ$ abs. according to HEYCOCK and LAMPLUGH (1912). (RUFF and JOHANNSEN gave $877,5^\circ \text{ C}$ in 1905). Hence the critical temperature lies in the neighbourhood of $370,6 \times 5^{1/2} = 1977$, resp. $1156 \times 1,7 = 1965$, mean 1970° abs.; or, as lowest limit, in that of $370,6 \times 4^{1/2} = 1729$, resp. $1156 \times 1,5 = 1734$, mean 1730° abs. We carry out the calculations again at these two temperatures.

With $\sqrt{T_k} =$ from 44,38 to 41,59, we find from our formula (see for Lithium) $2\gamma =$ from 2,686 to 2,580, yielding $\gamma = 1,34$ to 1,29. For $\gamma : (1 + \gamma)$ we find further 0,573 to 0,563, hence for $\gamma^2 : (1 + \gamma)^2$ the values from 0,329 to 0,317, so that the factor λ becomes from 0,910 to 0,919, and φ from 73,67 to 74,38.

VICENTINI and OMODEI (1888) found 0,9287 (liquid) for the density at the melting point $97,6$, so that D_0 can be calculated from

$$\left. \begin{aligned} 0,9287 &= D_0 \left(1 - 0,573 \times \frac{370,7}{1970} \right) = 0,892 D_0 \\ \text{or} &= D_0 \left(1 - 0,563 \times \frac{370,7}{1730} \right) = 0,879 D_0 \end{aligned} \right\}$$

yielding $D_0 = 1,041$ to $1,056$.

Then b_k becomes:

$$\left. \begin{aligned} b_k &= \frac{2,686 \times 23,0}{1,041 \times 22412} = \frac{61,78}{23330} = 265 \cdot 10^{-5} \\ \text{or } b_k &= \frac{2,580 \times 23,0}{1,056 \times 22412} = \frac{59,34}{23670} = 251 \cdot 10^{-5} \end{aligned} \right\}$$

We find for a_k :

$$\left. \begin{aligned} a_k &= \frac{1970 \times 26,5 \cdot 10^{-4}}{73,67} = \frac{52210}{73,67} 10^{-4} = 708,7 \cdot 10^{-4} \\ \text{or } a_k &= \frac{1730 \times 25,1 \cdot 10^{-4}}{74,38} = \frac{43420}{74,31} 10^{-4} = 583,8 \cdot 10^{-4} \end{aligned} \right\}$$

so that we have $\sqrt{a_k} = 26,6$ to $24,2 \cdot 10^{-2}$.

We calculate for the critical pressure:

$$\left. \begin{aligned} p_k &= \frac{1970}{2185 \times 265 \cdot 10^{-5}} = \frac{1970}{5,790} = 340 \text{ atm.} \\ \text{or } p_k &= \frac{1730}{2185 \times 251 \cdot 10^{-5}} = \frac{1730}{5,484} = 315,5 \text{ " } \end{aligned} \right\}$$

which renders $\log^{10} p_k =$ from 2,532 to 2,499.

The found values of γ , viz. 1,34 to 1,29, may be tested, however little, by the experimentally found value of the *coefficient of expansion* α in *liquid* state. In order to reduce α to γ we can derive the following relation. From

$$\alpha = \frac{1}{v_1} \frac{v_2 - v_1}{t_2 - t_1}$$

follows immediately:

$$\alpha = D_1 \frac{\frac{1}{D_2} - \frac{1}{D_1}}{t_2 - t_1} = \frac{1}{D_2} \frac{D_1 - D_2}{t_2 - t_1},$$

so that the quantity γ' in $D_1 - D_2 = \gamma' (t_2 - t_1)$ is found from

$$\gamma' = \alpha \times D_2, \text{ or } \alpha \text{ from } \alpha = \frac{\gamma'}{D_2}.$$

Now (reduced) $d_1 - d_2 = 2 \gamma (m_2 - m_1)$, when the vapour densities can be neglected, hence as $d = D : D_k$ and $m = T : T_k$, also $D_1 - D_2 = 2 \gamma \frac{D_k}{T_k} (T_2 - T_1)$, so that we have:

$$\gamma' = 2\gamma \frac{D_k}{T_k},$$

and

$$\alpha = 2\gamma \frac{D_k}{D_s} \frac{1}{T_k}$$

But $D_s = D_s \left(1 - \frac{\gamma}{1 + \gamma} \frac{T_2}{T_k}\right)$, and $D_k = \frac{D_0}{2(1 + \gamma)}$, so that

$$\alpha = \frac{\frac{\gamma}{1 + \gamma} \frac{1}{T_k}}{1 - \frac{\gamma}{1 + \gamma} \frac{T_2}{T_k}} = \frac{\frac{\gamma}{1 + \gamma}}{T_k - \frac{\gamma}{1 + \gamma} T_2}$$

T_2 is therefore always the higher of the temperatures, between which the experimentally determined expansibility holds. When we now apply this to Sodium, where $278 \cdot 10^{-6}$ has been found for α between 101° and 168° C. (HAGEN), we calculate ($T_2 = 168 + 273 = 441$)

$$\alpha = \frac{0,573}{1970 - 0,573 \times 441} = \frac{0,573}{1717} = 334 \cdot 10^{-6}$$

$$\text{or } \alpha = \frac{0,563}{1730 - 0,563 \times 441} = \frac{0,563}{1482} = 380 \cdot 10^{-6}$$

As the coefficient of expansion near the melting point will probably be still somewhat too small (we need only think of water, mercury, etc.), the found value 278 is probably to be raised to 334. If we have to make a choice, the *higher* of the two assumed critical temperatures, viz. 1970° , seems in any case to be nearest the truth.

If we assume that the determined coefficient of expansion really holds for the mean temperature ($101 + 168$): $2 = 134,5^\circ$ C. = 408° abs., we should have calculated the values from 330 to $375 \cdot 10^{-6}$, which are only slightly lower.

Also from VANSTONE'S density determinations we can determine the value of γ' , hence also of α . VANSTONE found namely at 110° , 184° and 237° C. resp. the values $D = 0,9265$, $0,9058$ and $0,8891$, yielding $\gamma' = 280 \cdot 10^{-6}$ between the two first, and $\gamma = 315 \cdot 10^{-6}$ between the two last. Or $295 \cdot 10^{-6}$ between the first and the third. If we assume this last value to hold at the mean temperature $173,5$, at which $D =$ about $0,909$, then

$$\alpha = \frac{295 \cdot 10^{-6}}{0,91} = 325 \cdot 10^{-6} \text{ follows from } \alpha = \gamma' : D \text{ (see above),}$$

hence very near the above calculated value 330.

If we now assume the newer value $325 \cdot 10^{-6}$ to be more accurate than the much older value 278, determined at somewhat lower temperatures, then the value calculated above from γ with $T_k = 1970^\circ$ appears to be much nearer 325 than the too high value 380, calculated with $T_k = 1730^\circ$. T_k lies therefore near 1970° , and (according to the density determinations) sooner somewhat *higher* than somewhat

lower than this temperature; e.g. $T_k = 2000^\circ$ (extrapolated 1997°).

A *second* test is furnished by the *vapour pressure* determinations. We owe the following data to HACKSPILL (1912).

$t =$	350	355	365	390	397	883 C.
$T =$	623	628	638	663	670	1156° abs.
$p =$	0,08	0,12	0,15	0,21	0,26	760 mm.
$\log^{10} p =$	0,903(-2)	0,079(-1)	0,176(-1)	0,322(-1)	0,415(-1)	2,881

According as $T_k = 1970^\circ$ is assumed or 1730° abs., we find $\log^{10} p_k = 2,532$ or $2,499$ (see above), and we have therefore, this being in mm. = 5,413 or 5,380:

$\log^{10} \frac{p_k}{p}$	= 6,509	6,333	6,236	6,090	5,998	2,532
or =	6,477	6,301	6,204	6,058	5,965	2,499
$\frac{T_k}{T} - 1$	= 2,162	2,137	2,088	1,971	1,940	0,7042
or =	1,777	1,755	1,712	1,609	1,582	0,4965
Hence $f^{10} =$	3,02	2,96	2,99	3,09	3,09	3,60 → 4,67
or =	3,64	3,59	3,62	3,76	3,77	5,03 → 4,48

We see, therefore, from this that the vapour pressure factor f is pretty well constant at the lower temperatures 350 to 400° C., but at the boiling point (the values of the last column on the righthand side of the vertical line refer namely to the boiling point) it has considerably increased in both cases: from 3,1 to 3,6, and from 3,8 to 5,0. The latter increment is much too great, the more so as the *limiting value* at T_k , viz. $f_k = 8\gamma = 10,74$ or $10,32$, so $f_k^{10} = 4,67$ to 4,48, would be *smaller* in the latter case than the value at T_s , viz. 5,03, which in view of the great increase of f at higher temperatures is *quite impossible*.

We see from the above how exceedingly *sensitive* the method of the vapour pressures is, especially at higher temperatures. This is owing to this, that then $(T_k : T) - 1$ is exceedingly variable on only a slight variation in the value of T_k . In our example from 0,70 to 0,50 for a decrease from 1970 to 1730. And in consequence of this also the value of f is changed in the same degree (from 3,6 to 5,0).

We can therefore conclude from the vapour pressure determinations for *Na* with great certainty that $T_k = 1730^\circ$ will be out of the question, and that $T_k = 1970^\circ$ will be near the truth.

HEIJCOCK still gave $\frac{dt}{dp} = 0,153$ (p in mm.) at the boiling point temperature $882^\circ,9$ C. Now follows from

$$\log \frac{p_k}{p} = f \left(\frac{T_k}{T} - 1 \right),$$

when f' represents $\frac{df}{dT}$:

$$-\frac{1}{p} \frac{dp}{dT} = -\frac{f T_k}{T^2} + f' \left(\frac{T_k}{T} - 1 \right);$$

hence at the boiling point:

$$f_s = \frac{T_s^2}{T_k} \left[\frac{1}{p_s} \left(\frac{dp}{dT} \right)_s + f' \left(\frac{T_k}{T_s} - 1 \right) \right].$$

This gives with $T_k = 1970^\circ$, $T_s = 1156$:

$$f_s^{10} = \frac{(1156)^2}{1970} \times 0,4343 \left[\frac{1}{0,153 \times 760} + 0,704 f' \right].$$

We can put in approximation $0,51 : 486 = 0,00105$ for f' , so that f_s^{10} would become

$$f_s^{10} = 678 \times 0,4343 (0,00860 + 0,00074) = 295 \times 0,00934 = 2,76.$$

According to the above table, this value is too small, as it would be still smaller than the value of f^{10} at 397° , viz. 3,09. We expect, indeed, a lower value than 3,60, as the latter represents the chord in the curve $y = f(x)$, and 2,76 the tangent — but not a value so much smaller. The value $\frac{dt}{dp} = 0,153$ given by HEIJCOCK is therefore probably too high ¹⁾ — or else the value assumed for f' is too low. Also the value $T_k = 1970$ can have been assumed too low.

4. Potassium. After the above explanations we can be briefer, and simply repeat the same calculations as above.

The melting point lies at $62^\circ,5$ C. = $331^\circ,6$ abs. The boiling point at $762^\circ,2$ C. = $1035^\circ,3$ abs. (HEIJCOCK and L.). RUFF and JOH. give $757^\circ,5$ C. The critical temperature lies, therefore, at $335,6 \times 5^{1/3} = 1790$, $1035,3 \times 1,7 = 1750$, mean 1770° ; or at $335,6 \times 4^{2/3} = 1566$, $1035,3 \times 1,5 = 1554$, mean 1560° abs. These will again appear to be the limiting values.

Thus $\sqrt{T_k}$ becomes = 42,08 or 39,50, hence $2\gamma = 2,599$ to 2,501, $\gamma = 1,30$ to 1,25. This gives the value from 0,918 to 0,926 for the factor λ , and the value 74,29 to 74,90 for φ . For λ we have used $\gamma : (\gamma + 1) = 0,565$ to 0,556.

¹⁾ Or would 0,153 be a printer's error for 0,135? See Tables Annuelles of 1912, which are full of misprints. Then 860 would become 975, and 0,00934 would become 0,0105, because of which f_s^{10} would become from 2,76 to 3,09. And this value is very well possible and would — like the expansibility — point to a value of T_k which would be slightly higher than 1970, e.g. 2000^o abs.

VICENTINI and OMODEI found $D = 0,8298$ (liquid) at $62^{\circ},1$. From this follows therefore:

$$\left. \begin{aligned} 0,8298 &= D_0 \left[1 - 0,565 \frac{335,2}{1770} \right] = 0,893 D_0 \\ \text{or} &= D_0 \left[1 - 0,556 \frac{335,2}{1560} \right] = 0,881 D_0 \end{aligned} \right\}$$

from which $D_0 = 0,929$ to $0,942$.

From this follows for b_k :

$$\left. \begin{aligned} b_k &= \frac{2,599 \times 39,1}{0,929 \times 22412} = \frac{101,6}{20825} = 488 \cdot 10^{-5} \\ \text{or } b_k &= \frac{2,501 \times 39,1}{0,942 \times 22412} = \frac{97,79}{21120} = 463 \cdot 10^{-5} \end{aligned} \right\}$$

And further for a_k :

$$\left. \begin{aligned} a_k &= \frac{1770 \times 48,8 \cdot 10^{-4}}{74,29} = \frac{86380}{74,29} 10^{-4} = 1163 \cdot 10^{-4} \\ \text{or } a_k &= \frac{1560 \times 46,3 \cdot 10^{-4}}{74,90} = \frac{72230}{74,90} 10^{-4} = 964,4 \cdot 10^{-4} \end{aligned} \right\}$$

yielding $\sqrt{a_k} = 34,1$ à $31,1 \cdot 10^{-2}$.

For p_k we find:

$$\left. \begin{aligned} p_k &= \frac{1770}{2185 \times 488 \cdot 10^{-5}} = \frac{1770}{10,66} = 166 \text{ atm.} \\ \text{or } p_k &= \frac{1560}{2185 \times 463 \cdot 10^{-5}} = \frac{1560}{10,12} = 154 \text{ " } \end{aligned} \right\}$$

in consequence of which $\log^{10} p_k = 2,220$ to $2,188$.

From the formula for the calculation of the coefficient of expansion α from γ , derived above for sodium, we then find:

$$\left. \begin{aligned} \alpha &= \frac{0,565}{1770 - 0,565 \times 363} = \frac{0,565}{1565} = 361 \cdot 10^{-6} \\ \text{or } \alpha &= \frac{0,556}{1560 - 0,556 \times 363} = \frac{0,556}{1358} = 409 \cdot 10^{-6} \end{aligned} \right\}$$

And as $\alpha = 299 \cdot 10^{-6}$ has been experimentally found by HAGEN between 70° and 110° C. (mean temperature 90° C = 363° abs.), it follows from this that the value, calculated from γ with $T = 1770^{\circ}$, is nearer the truth than that value calculated with 1560° . (Just as for sodium the expansibility at 90° C. will probably be lower than the normal value at higher temperatures, so that 299 will be too small. Indeed all HAGEN's values seem to be too small. For Na 278 had to be raised to 325 through the later determinations of VANSTONE).

And now the vapour tensions. HACKSPILL has found:

$t = 264$	316	331	340	350	360	365	762° C.
$T = 537$	589	604	613	623	633	638	1035° abs.
$p = 0,1$	0,75	1,15	1,35	1,75	2,13	2,3	760 mm.
$\log^{10} p = -1$	0,875 (-1)	0,061	0,130	0,243	0,328	0,362	2,881

From the above found values of $\log^{10} p_k$ we find in mm. $\log^{10} p_k = 5,101$ and $5,069$, so that we have:

$\log^{10} \frac{p_k}{p} = 6,101$	5,226	5,040	4,971	4,858	4,773	4,739	2,220
of = 6,069	5,194	5,008	4,938	4,826	4,740	4,707	2,188
$\frac{T_k}{T} - 1 = 2,296$	2,005	1,932	1,887	1,841	1,796	1,774	0,7097
of = 1,905	1,648	1,584	1,544	1,504	1,466	1,445	0,5067
yielding $f^{10} = 2,66$	2,61	2,61	2,63	2,64	2,66	2,67	3,13 → 4,52
of = 3,19	3,15	3,16	3,20	3,21	3,23	3,26	4,32 → 4,34

From the same considerations as for Na it follows also here again very clearly that the upper series of values is better than the lower one, and that therefore $T_k = 1770^\circ$ is preferable to 1560° . The limiting values of f for T_k are viz. $f_k = 8\gamma = 10,40$ to $10,00$, or $f_k^{10} = 4,52$ to $4,34$. Probably the accurate value of T_k lies somewhat below 1770° abs.

HEYCOCK gave 0,135 for $\frac{dt}{dp}$. When we assume $f' = 0,46 : 397 = 0,0016$, the following formula follows for f_s^{10} with $T_k = 1770$ $T_s = 1035$ from the formula derived in § 3:

$$f_s^{10} = \frac{(1035)^2}{1770} \times 0,4343 \left[\frac{1}{0,135 \times 760} + 0,710 \times 0,00116 \right]$$

$$= 606 \times 0,4343 (0,00975 + 0,00082) = 263 \times 0,0106 = 2,78.$$

This value may be correct. It is larger than 2,67 and at the same time smaller than 3,13 (tangent and chord, see for Na). Perhaps T_k lies again somewhat below 1770° abs.

5. Rubidium. $38^\circ,5 + 273,1 = 311^\circ,6$ was found for the absolute melting point temperature. This multiplied by $5\frac{1}{3}$, gives $T_k = 1662^\circ$. RUFF and JOH. (1905) found for the boiling-point 691° C. = $971^\circ,1$ abs. This $\times 1,7$ gives 1651. Let us take the round value 1660. On the other hand $311,6 \times 4\frac{2}{3} = 1452$, and $971,1 \times 1,5 = 1457$, averaged and rounded off 1450.

In consequence of this $\sqrt{T_k}$ becomes = 40,74 to 38,08, hence

$2\gamma = 2,548$ to $2,447$, $\gamma = 1,27$ to $1,22$. We find therefore $0,560$ to $0,550$ for $\gamma : (1 + \gamma)$, hence according to our formula $\lambda = 0,922$ to $0,930$, and $\varphi = 74,60$ to $75,25$. Hence

$$\left. \begin{aligned} b_k &= \frac{2,548 \times 85,45}{1,648 \times 224,2} = \frac{217,7}{36930} = 590 \cdot 10^{-5} \\ \text{or } b_k &= \frac{2,446 \times 85,45}{1,673 \times 224,2} = \frac{209,0}{37500} = 557 \cdot 10^{-5} \end{aligned} \right\}$$

D_0 being $= 1,648$ to $1,673$. For, according to HACKSPILL $D = 1,475$ (liquid) for $38^\circ,5$, hence according to the formula derived by us:

$$\left. \begin{aligned} 1,475 &= D_0 \left(1 - 0,560 \frac{311,6}{1660} \right) = 0,895 D_0 \\ \text{or } &= D_0 \left(1 - 0,550 \frac{311,6}{1450} \right) = 0,882 D_0 \end{aligned} \right\}$$

We find further for a_k :

$$\left. \begin{aligned} a_k &= \frac{1660 \times 59,0 \cdot 10^{-4}}{74,60} = \frac{97940}{74,60} \cdot 10^{-4} = 1313 \cdot 10^{-4} \\ \text{or } a_k &= \frac{1450 \times 55,7 \cdot 10^{-4}}{75,25} = \frac{80770}{75,25} \cdot 10^{-4} = 1073 \cdot 10^{-4} \end{aligned} \right\}$$

giving $\sqrt{a_k} = 36,2$ à $32,8 \cdot 10^{-2}$.

We find for p_k :

$$\left. \begin{aligned} p_k &= \frac{1660}{2185 \times 590 \cdot 10^{-5}} = \frac{1660}{12,89} = 129 \text{ atm.} \\ \text{or } p_k &= \frac{1450}{2185 \times 557 \cdot 10^{-5}} = \frac{1450}{12,17} = 119 \text{ " } \end{aligned} \right\}$$

which causes $\log^{10} p_k = 2,110$ to $2,076$.

From the above values of γ we find for the coefficient of expansion α , resp. with $T_k = 1660$ and 1450 abs.:

$$\left. \begin{aligned} \alpha &= \frac{0,560}{1660 - 0,560 \times 363} = \frac{0,560}{1457} = 384 \cdot 10^{-6} \\ \text{or } \alpha &= \frac{0,550}{1450 - 0,550 \times 363} = \frac{0,550}{1250} = 440 \cdot 10^{-6} \end{aligned} \right\}$$

while HACKSPILL gives $339 \cdot 10^{-6}$ between 40° and 140° C. (mean temperature 90° C. $= 363$ abs.). Here too the first value $38 \cdot 10^{-5}$ is nearer the experimental value 34 (which will have to be raised somewhat, see for potassium and sodium) than the second $44 \cdot 10^{-5}$.

HACKSPILL gives for the *vapour tensions* of Rubidium:

$t=250$	292	305	330	333	340	346	350	353	356	365	367	698°
$T=523$	565	578	603	606	613	619	623	626	629	638	640	971° at
$p=0,06$	0,98	1,46	2,66	2,95	3,29	3,67	4,0	4,25	4,57	5,51	6,14	760 m
$\log^{10} p=0,778(-2)$	0,991(-1)	0,164	0,425	0,470	0,517	0,565	0,602	0,628	0,660	0,741	0,788	2,881

As $\log^{10} p_k$ in atm. = 2,110 to 2,076, this is in mm. 4,991 to 4,957, and we find then:

$\log^{10} \frac{p_k}{p}$	= 6,213	5,000	4,826	4,566	4,521	4,474	4,426	4,389	4,362	4,331	4,250	4,203	2,110
of =	6,179	4,966	4,792	4,532	4,487	4,440	4,392	4,355	4,328	4,297	4,216	4,169	2,076
$\frac{T_k}{T} - 1$	= 2,174	1,938	1,872	1,753	1,739	1,708	1,682	1,664	1,652	1,639	1,602	1,594	0,7096
of =	1,772	1,566	1,509	1,405	1,392	1,365	1,343	1,327	1,317	1,305	1,273	1,266	0,4933
consequently $f^{10} = (2,86)$	2,58	2,58	2,60	2,60	2,62	2,63	2,64	2,64	2,64	2,64	2,65	2,64	2,97 → 4,
of = (3,49)	3,17	3,18	3,22	3,22	3,25	3,27	3,28	3,29	3,29	3,29	3,31	3,29	4,21 → 4,

Here too the first row of values appears to be nearer the truth than the second. As f is still greatly increasing at T_s , the values past 4,21 cannot possibly remain below the limiting value 4,25 (for T_k). This limiting value is namely $p_k = 8\gamma = 10,19$ to 9,79, i. e. $f_k^{10} = 4,43$ to 4,25. Perhaps T_k lies slightly below 1660° abs.

6. Caesium. At last the last member of the group. Here the triple point is at 28°,25 C. = 301°,3 abs.; the boiling point is at 670° C. (RUFF and JOH.) = 943°,1 abs. So that T_k will lie between $301,3 \times 5\frac{1}{2} = 1607$, $943,1 \times 1,7 = 1603$, mean 1605° abs., and $301,3 \times 4\frac{2}{3} = 1406$, $943,1 \times 1,5 = 1415$, averaged and rounded off 1410° abs.

We find therefore 40,06 to 37,55 for T_k , yielding $2\gamma = 2,522$ to 2,427, $\gamma = 1,26$ to 1,21. The value of $\gamma : (1 + \gamma)$ becomes 0,558 to 0,548, so that λ becomes = 0,924 to 0,931, and $\varphi = 74,77$ to 75,36. And we find for b_k :

$$b_k = \frac{2,522 \times 132,81}{2,061 \times 22412} = \frac{334,9}{46,90} = 725 \cdot 10^{-5}$$

$$\text{or } b_k = \frac{2,427 \times 132,81}{2,090 \times 22412} = \frac{322,3}{46840} = 688 \cdot 10^{-5}$$

because $D_s = 2,061$ to 2,090. For the density at the melting-point 28°,25 HACKSPILL gives namely $D = 1,845$, so that

$$\left. \begin{aligned} 1,845 &= D_0 \left(1 - 0,558 \frac{301,3}{1605} \right) = 0,895 D_0 \\ \text{or} &= D_0 \left(1 - 0,548 \frac{301,3}{1410} \right) = 0,883 D_0 \end{aligned} \right\}$$

And we find for a_k :

$$\left. \begin{aligned} a_k &= \frac{1605 \times 72,5 \cdot 10^{-4}}{74,77} = \frac{116360}{74,77} 10^{-4} = 1556 \cdot 10^{-4} \\ \text{or } a_k &= \frac{1410 \times 68,8 \cdot 10^{-4}}{75,36} = \frac{97010}{75,36} 10^{-4} = 1287 \cdot 10^{-4} \end{aligned} \right\}$$

giving $\sqrt{a_k} = 39,4 \text{ à } 35,9 \cdot 10^{-2}$.

And for p_k we find:

$$\left. \begin{aligned} p_k &= \frac{1605}{2185 \times 725 \cdot 10^{-5}} = \frac{1605}{15,84} = 101 \text{ atm.} \\ \text{or } p_k &= \frac{1410}{2185 \times 688 \cdot 10^{-5}} = \frac{1410}{15,03} = 94 \text{ " } \end{aligned} \right\}$$

giving $\log^{10} p_k = 2,01$ to $1,97$.

The coefficient of expansion may be calculated from

$$\left. \begin{aligned} \alpha &= \frac{0,558}{1605 - 0,558 \times 337} = \frac{0,558}{1417} = 394 \cdot 10^{-6} \\ \text{or } \alpha &= \frac{0,548}{1410 - 0,548 \times 337} = \frac{0,548}{1225} = 447 \cdot 10^{-6} \end{aligned} \right\}$$

The value $39 \cdot 10^{-5}$ was found between 17° and 100° C. (mean $63^\circ,5$ C = 337° abs.) by ECKHARD and GRAEFE (1900). As these experimental values had to be raised a little nearly everywhere in order to get into agreement with the normal expansibility at higher temperatures, given by γ (the older values of HAGEN for Caesium lie still lower, viz. mean $345 \cdot 10^{-6}$), it is possible that the critical temperature of Caesium will lie between 1605° and 1410° abs.

Let us consult the vapour tensions. HACKSPILL found:

= 230	244	272	308	315	330	333	350	365	397	670° C.
T = 503	517	545	581	588	603	606	623	638	670	943° abs.
p = 0,2	0,29	0,99	2,58	3,18	4,27	4,45	6,72	9,01	15,88	760 mm.
$\log^{10} p = 0,301(-1)$										2,881
$0,462(-1)$										
$0,996(-1)$										
$0,412$										
$0,502$										
$0,630$										
$0,648$										
$0,827$										
$0,955$										
$1,201$										

We find 4,886 to 4,853 for $\log^{10} p_k$, and further:

$\log_{10} \frac{p_k}{p} =$	5,585	5,424	4,891	4,475	4,384	4,256	4,238	4,059	3,932	3,686	2,006
of =	5,552	5,391	4,857	4,441	4,351	4,223	4,205	4,026	3,898	3,652	1,972
$\frac{T_k}{T} - 1 =$	2,191	2,104	1,945	1,762	1,730	1,662	1,649	1,576	1,516	1,396	0,702
of =	1,803	1,727	1,587	1,427	1,398	1,338	1,327	1,263	1,210	1,104	0,495
hence $f^{10} =$	2,55	2,58	2,51	2,54	2,53	2,56	2,57	2,58	2,59	2,64	2,86 → 4,38
of =	3,08	3,12	3,06	3,11	3,11	3,16	3,17	3,19	3,22	3,31	3,98 → 4,22

It also appears clearly from these values of f , that the real critical temperature will lie between 1605 and 1410. The limiting values of f at T_k are $f_k = 8\gamma = 10,09$ to $9,71$, hence $f_k^{10} = 4,38$ to $4,22$. The value f_s^{10} lies slightly too far from $4,38$; the value $3,98$ lies too near it.

7. Recapitulation of this group. In accordance with the course of the vapour tension factors f we shall assume the critical temperature of sodium to be 2000° abs., i. e. $\frac{1}{3}$ of the difference between 1970° and 1730° higher than the first of these values. Further that of Potassium to be 1710° , i. e. $\frac{2}{3}$ of the difference between 1770° and 1560° abs. lower than 1770° ; that of Rubidium to be $= 1590^\circ$, i. e. $\frac{1}{3}$ of the difference between 1660° and 1450° lower than 1660° ; that of Caesium $= 1510^\circ$, i. e. $\frac{1}{3}$ of the difference between 1605° and 1410° lower than the first value. At last that of Lithium, in virtue of the value of b_k (which we assume $= 145 \cdot 10^{-5}$) halfway between 2410° and 2700° , i. e. $= 2550^\circ$, so that we get the following survey.

	T_{tr}	T_s	T_k	$\frac{T_k}{T_{tr}}$	$\frac{T_k}{T_s}$	γ	b_k $\times 10^5$	$\sqrt{a_k}$ $\times 10^2$	p_k (atm.)	f $Tr.-kp.$	f_k^{10}
Lithium	452	1450?	2550	5,6	1,76?	1,46	145	22,6	806	—	5,1
Sodium	371	1156	2000	5,4	1,73	1,35	266	26,9	343	2,9 3,5	4,7
Potassium	336	1035	1710	5,1	1,65	1,29	481	33,2	163	2,8—3,4	4,5
Rubidium	312	971	1590	5,1	1,64	1,25	579	35,1	126	2,8—3,4	4,4
Caesium	301	943	1510	5,0	1,60	1,24	707	37,7	98	2,8 - 3,4	4,3

These are the most *probable* values following with pretty great certainty from the available data. The inaccuracy will at most amount to 1 or 2 %.

With regard to the values of b_k we will only observe that they

are *about* in the following ratio $1:2:4:5:6$. For $145:1=145$, $266:2=133$, $481:4=120$, $579:5=116$, $707:6=118$.

From the value of T_k and p_k for *Hydrogen*, determined just now by K. ONNES c. s., would follow the value 59.10^{-5} (per Gr. atom) for b_k , i. e. exactly *half* the middle value 118 for K:4, Rb:5 and Cs:6. So that the ratio of the b -values for H to Cs would become $\frac{1}{2}:1\frac{1}{4}:2\frac{1}{8}:4:5:6$.

Possibly the ratio values for Li and Na will later have to be rounded off to 1 and 2 on more accurate knowledge of some data.

And it appears again from the values of $\sqrt{a_k}$, for which rounded off we may write **23, 27, 33, 35, 37,5**, that all these metals occur *atomically* with the very much increased valency attractions. If they were bound to Li_2 , Na_2 , etc., only the "rest-attractions" 3, 5, 7, 9, 11 would have manifested themselves (per Gr. atom). For Li it is possible that undissociated molecules of L_2 are still present at T_k (the abnormally low value 23 would point to this), but it is also possible that this is not the case. All these questions must be left open for the present till the *whole* periodic system shall have been examined.

In a following paper the minor group Cu-Ag-Au will be treated, besides Manganese and the Iron-Platinum group.

Clarens, June 1917.