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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 II. Mercury and Antimonium. General Methods”. By Dr. J. J. VAN LAAR. (Communicated by Prof. H. A. LORENTZ).

(Communicated in the meeting of March 25, 1916).

I. In our foregoing paper ¹⁾ we have found that the values of b and \sqrt{a} at the critical temperature can be built up *additively* from a few constant, *fundamental values* for the different elements. (See the tables on p. 1223 and p. 1229 of the cited paper). The elements H, C, N, and O presented in this, as far as the values of b are concerned, two different fundamental values (H even three), of which the second may be considered as a *contraction* — about in the ratio of $\frac{1}{2}\sqrt{2} \cdot 1$ — of the fundamental value. [For H the third value is to the first as $(1 - \frac{1}{2}\sqrt{2}) : 1$]. The way in which these multiple values must be used in the *reconstruction* of the values of b and \sqrt{a} of the different chemical combinations has been sufficiently set forth in the first paper (henceforth to be indicated by I). (See the different tables and the summary on p. 1234). With regard to the values of \sqrt{a} we should pay attention to the fact that for compounds as CH_4 , CCl_4 , CH_3Cl , CHCl_3 , C_2H_6 , etc., and also for NH_3 and PH_3 , GeCl_4 and SnCl_4 , the *central* atoms do *not* take part in the attraction; so that in the reconstruction the values of \sqrt{a} for C, N, P, Ge, Sn must all be put = 0. But for doubly bound C half the value $C = 1,55$ is found, and for the triply bound C the full value 3,1. (see further again the tables, and also p. 1220—1221 and 1235; also with regard to the two values for H).

Below we reproduce the two principal tables ²⁾.

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

¹⁾ These Proc. of Jan. 29, 1916.

²⁾ In the table for \sqrt{a} on p. 1229 $\text{Ne} = 6,3 \times 10^{-2}$ [= $\sqrt{39,6 \times 10^{-2}}$] has been written instead of $\text{Ne} = 2,0 \times 10^{-2}$ [= $\sqrt{3,96 \times 10^{-4}}$]. Correct further on p. 1224: H_2 found = 97⁵ instead of 97; on p. 1229: H_2 found = 1,96 instead of 1,95; on p. 1237 read: neutralized in ordinary circumstances; “closed”, as M. expresses himself — would be free and “open”.

In every *vertical* column the increase is therefore 55 units, while in every *horizontal* row the decrease amounts to 15 units. The values for Si, As, and Te, which we have placed between parentheses, could not be verified as yet by known compounds, the critical data of them being imperfectly known.

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

If we add to this $Hg = 11,0$, as we shall immediately find, it may be said that in the different horizontal principal series of the periodic system the values of \sqrt{a} are very nearly constant, the ratio in round numbers being (taking $He = 1$)

$$1 : 3 : 5 \cdot 7 \cdot 9 : 11.$$

We add that the values of b in the column of the halogens are in exactly the same ratio as the values 1 . 2 . 3 . 4 (taking $Cl = 110$).

II. Before proceeding to the calculation of some new fundamental values — in which some methods will be discussed for the calculation of the values of a and b for substances where T_k and p_k are unknown, and besides of the unknown values of T_k and p_k themselves — we will make a few general remarks.

In the first place we draw attention to this, that when the above tables are used to calculate the critical temperature and pressure for *elements*, the critical data of which are unknown as yet, the *molecular state* of these elements at T_k must be taken into account.

Thus at the critical temperature mercury has long become Hg_2 . Only at lower temperatures the mercuryvapour is $= Hg_1$ on account of the great volume, as is known. But at higher temperatures, where the vapourvolume gets smaller and smaller, the association to Hg_2 increases more and more, and is almost complete at T_k . For mercury, namely, just as for some other associating substances the increase of volume of the vapour triumphs on the *decrease* of temperature, and therefore the association does not increase, but *decreases*. The same thing is probably the case for water, but for this substance the association at T_k (of the vapour namely) is still slight,

1*

while for mercury it is complete. To this case belong those substances, for which the heat of dissociation q of the double molecules (i.e. the absorbed heat in dissociation) is comparatively small or $= 0$ (at any rate $< fT_k$; hence for ordinary substances $< 7 T_k$, when q is expressed in gr. cal.). Acetic acid belongs to the other category of substances, for which the association in the vapour decreases on increase of temperature, till a minimum is reached in the neighbourhood of T_k . At still higher temperature the association in the vapour increases again. Here (below the temperature of inversion) the temperature-change therefore prevails over the volume-change. To this belong those substances, for which the heat of dissociation of the double molecules is comparatively large ($> 7 T_k$).

Accordingly mercury — and we shall also see this confirmed on other grounds — is *bimolecular* at T_k .

Now $RT_k = \frac{8}{27} \lambda \frac{a_k}{b_k}$, $p_k = \frac{1}{27} \lambda \frac{a_k}{b_k^2}$, in which λ for substances with high critical temperature has the limiting value $27/28$ ¹⁾, so that with $R = 1:273,1$ we have:

$$T_k = 78,03 \frac{a_k}{b_k} \quad ; \quad p_k = \frac{1}{28} \frac{a_k}{b_k^2}$$

If now $(\sqrt{a_k})_1 = 11,0 \times 10^{-2}$; $(b_k)_1 = 150 \times 10^{-5}$ for Hg_1 , as we shall find presently, then we get for Hg_n :

$$T_k = 78,03 n \frac{121}{150} \times 10^1 \quad ; \quad p_k = \frac{1}{28} \frac{121}{225} \times 10^4$$

because for Hg_n $\sqrt{a_k} = n(\sqrt{a_k})_1$, and also b_k will be $= n(b_k)_1$ (possible contraction for b_k excluded).

Hence we find:

$$T_k = n \cdot 630^\circ \text{ (abs.)} \quad ; \quad p_k = 192 \text{ atm.}$$

And as the critical temperature of mercury (see § 3) is lying with great probability in the neighbourhood of 1260° (absolute)²⁾, and

1) For λ we have namely found the expression $\lambda = \frac{27}{8\gamma-1} \left(\frac{\gamma}{\gamma+1} \right)^2$, in which

γ (the reduced coefficient of direction of the straight line between D_k and D_0 in a D, T -diagram, i. e. of the ideal "straight diameter") verges to 1. (Cf. These Proc. of March 26, 1914, p. 88, formula (18)).

2) Not in all the tables Celsius degrees are distinguished from absolute temperatures with sufficient care in records of temperatures. Thus e.g. in the "*Tables annuelles*" (which contain many errors also in other respects), I find continually amidst records of temperatures in Celsius degrees, values which are meant in absolute temperature, *without this being stated*. For the critical temperature of mercury I found the value $\pm 1270^\circ$ C., given somewhere in those tables. The value is correct, but the addition: degrees Celsius is faulty. For then T_k would be about 1540° absolute, whereas in reality $T_k = 1260^\circ$ absolute.

p_k being about 200 atm., we find [besides total absence of any contraction of the b -value in the dissociation of Hg_2 , i. e. $(b_k)_2 = 2 \times (b_k)_1$] a value for n which differs but very little from 2.

For *Antimonium*, where $(\sqrt{a_k})_1 = 8,9 \times 10^{-2}$ and $(b_k)_1 = 250 \times 10^{-5}$, we should find on the supposition of Sb_1 at T_k :

$$(T_k)_1 = 78 \times \frac{79,2}{250} \times 10^1 = 247^\circ \text{ (abs.)}$$

It is found that the critical temperature of Sb is at least $\hat{=} 2900^\circ$ (abs.), so that at this temperature Sb would be associated to about $\text{Sb}_{1,2}$.

For *carbon* with $(\sqrt{a_k})_1 = 3,1 \times 10^{-2}$, $(b_k)_1 = 100 \times 10^{-5}$ we should have found:

$$(T_k)_1 = 78 \times \frac{9,61}{100} \times 10^1 = 75^\circ \text{ (abs.)}$$

whereas the critical temperature of C is certainly lying above 6000° abs., so that for T_k carbon would at least have to be $= C_{80}$.

And the same thing holds with respect to silicium and all the metals ¹⁾.

In the second place we draw attention to this, that substances like CCl_4 , SnCl_4 etc., where the attraction of the C- or the Sn-atom is cancelled, will consequently have a *relatively low* critical temperature. That is to say that these and similar substances (CH_4 , NH_3 , PH_3) would be *much less volatile* at the ordinary temperature, when the said circumstance were not present.

Thus $\sqrt{a_k} = 0 + 4 \times 5,4 = 21,6$ for CCl_4 , whereas, if the attraction of C could make itself felt, $\sqrt{a_k}$ would be $= 24,7$ ($\times 10^{-2}$). That is to say: now a is only 467, whereas it would be 610 in case of attraction of C. Hence in the latter case we should have found for T_k the value 556,2 (the real value of T_k), multiplied by $610 : 467$, so that we should have found $726^\circ,5$ absolute $= 453^\circ \text{ C.}$ instead of 283° C. The difference (170°) is very large.

For SnCl_4 , with $\sqrt{a_k} = 9$ for Sn, the value of $\sqrt{a_k}$ would have been found 30,6 instead of 21,6, i. e. that of a_k 936 instead of 467, which would have brought T_k to 1189° abs. $= 916^\circ \text{ C.}$ instead of 319° C. , as it is now. Hence a difference of 600° .

If for NH_3 the attraction of the central C-atom could have made itself felt, then $\sqrt{a_k}$ would have been $= 2,9 + 3 \times 3,2 = 12,5$ instead of 9,6, so that then T_k would have come from 406,0 to

¹⁾ In a following paper we shall however, mention — besides such a formidable association at T_k — another unexpected circumstance, which can account for the high critical temperature for metals and some metalloids.

$406 \times (156 : 92) = 688^\circ \text{ abs.} = 415^\circ \text{ C.}$, whereas now the critical temperature of ammonia only amounts to 133° C.

And as last example CH_4 . Here *with* the attraction of C $\sqrt{a_k}$ would be $= 3,1 + 4 \times 1,6 = 9,5$ instead of $6,4$, so that T'_k would then have become $= 190,2 \times (90 : 41) = 418^\circ \text{ abs.} = + 145^\circ \text{ C.}$, instead of $- 83^\circ \text{ C.}$, as it really is.

All these substances therefore owe their relative volatility, resp. low critical temperature, to the circumstance that the central atoms cannot make their attractive action felt towards the outside, in consequence of the absorbing action of the surrounding atoms. Substances with double or multiple bindings (C_2H_4 , C_2H_2), where the attractive action can operate again fully or partially (see I), will, therefore, at once be relatively less volatile than those of the category considered just now.

III. The critical values of mercury.

a) Calculation of b_k from the densities of the solid halogen compounds.

According to the property of the straight diameter $\frac{1}{2}(d_1 + d_2) = 1 + \gamma(1-m)$, hence at low temperatures, where the (reduced) density of the vapour d_2 can be neglected:

$$d_1 = \frac{v_k}{v_1} = 2[(1 + \gamma) - \gamma m].$$

As now $v_k = r b_k = \frac{1+\gamma}{\gamma} b_k$, we have:

$$b_k = v_1 \times \frac{2\gamma[(1 + \gamma) - \gamma m]}{1 + \gamma} = v_1 \times 2\gamma \left[1 - \frac{\gamma}{1 + \gamma} m \right] \quad (1)$$

This formula enables us to calculate the value of b_k from v_1 (the molecular volume of the *liquid*), when γ (coefficient of direction of the straight diameter) and m (the reduced temperature) are known. And as at *low* temperatures the volume of the solid phase will not differ much from that of the liquid phase, the above formula may be used by *approximation* also for the calculation of b_k from the molecular volume of the solid phase.

Thus for Argon, where $\gamma = 0,75$, $b_k = v_1 \times 1,5(1 - \frac{3}{4}m)$. For $84^\circ(\text{abs.})$, i. e. at the triple point, the density is $= 1,413$, hence $v_1 = 39,88 : 1,413 = 28,2$. The value of m is $84^\circ : 151^\circ = 0,55$, so that $b_k = 28 \times 1,15 = 32,4$; i. e. expressed in the normal volume v_0 , $32,4 : 22412 = 144 \times 10^{-5}$, which is perfectly identical with the value of b_k calculated directly from T'_k and p_k in Treatise I.

The factor, therefore, by which v_1 is to be multiplied to get b_k , is $= 1,15$.

For solid *Oxygen* the density at 21° is $= 1,4256$, hence $v_1 = 32 : 1,426 = 22,4$. The factor by which we must multiply, has the value $1,5$ with $m = 21^\circ : 126^\circ = 1/6$ and $\gamma = 0,8$, so that b_k becomes $33,6$; i. e. expressed in v_0 , $33,6 : 22412 = 150 \times 10^{-5}$. Determined directly in I from T_k and p_k 142×10^{-5} was found, so that the value of b_k calculated from the solid phase (34° below the triple point) turns out only 5 or 6% too high.

The factor by which v_1 must be multiplied to get b_k , is therefore very variable, and depends in a high degree on γ and m . For *metals* and *salts*, where T_k lies between 1000° and 3000° abs., γ is generally in the neighbourhood of 1, and then we become:

$$b_k \approx v_1 (2 - m), \dots \dots \dots (1a),$$

in which m varies from $1/3$ to $1/10$, when v_1 is determined at the ordinary temperature ($\pm 300^\circ$ abs.). The factor, therefore, varies from 1,7 to 1,9. (The sign of inequality refers to the fact that v_1 of the solid phase is generally smaller than the value of v_1 , which would hold at the same temperature with regard to the liquid phase).

Now at T_k for HgCl_2 , HgBr_2 and Hgl_2 , ROTINJANZ (Z. f. ph. Ch. **87**, p. 253) has found resp. the values 976° , 1011° and 1072° absolute. We may therefore put $m = 0,28$ or $0,26$, which makes the factor $2 - m = 1,72$ or $1,74$. From

$$b_k = \frac{1,7}{22412} \times \frac{M}{D_1}$$

follows therefore:

For HgCl_2 :

$$b_k = \frac{1,72}{22412} \times \frac{271,52}{5,424} = 0,00384,$$

hence $\text{Hg} = 384 - 230 = 154 \times 10^{-5}$.

For HgBr_2 :

$$b_k = \frac{1,73}{22412} \times \frac{360,44}{5,738} = 0,00484,$$

which gives $\text{Hg} = 484 - 330 = 154 \times 10^{-5}$.

For Hgl_2 (yellow):

$$b_k = \frac{1,74}{22412} \times \frac{454,44}{6,060} = 0,00582,$$

giving $\text{Hg} = 582 - 440 = 142 \times 10^{-5}$.

For Hg in compounds we can therefore assume about:

$$b_k = 150 \times 10^{-5}.$$

For mercury itself we find from the density of liquid mercury at 0°C :

$$b_k = \frac{1,78}{222412} \times \frac{200,6}{13,6} = 117 \times 10^{-5}$$

GULDBERG calculated the critical density = 3,77. From this would therefore follow:

$$v_k = \frac{200,6}{3,77 \times 22412} = 238 \times 10^{-5}$$

If $b_k = \frac{1}{2} v_k$ is assumed (to $\gamma = 1$ corresponds $r = 2$), he finds 119×10^{-5} . The value calculated from mercury itself, viz. about 120×10^{-5} , is therefore apparently lower than the value calculated from the compounds, viz. 150×10^{-5} — a phenomenon that can be explained by the different molecular states at T_k and at lower temperature.

β) Calculation of $\sqrt{a_k}$ from the values of T_k and b_k of the halogen compounds.

From $T_k = 78,03$ $a_k \cdot b_k$ (See § 2) follows immediately:

$$a_k = \frac{T_k}{78,03} \times b_k, \dots \dots \dots (2)$$

from which we can calculate a_k , as soon as besides T_k the value of b_k (e.g. according to the method of α) is known. For the mercury halogen compounds we now have successively:

For HgCl_2 :

$$a_k = \frac{976}{78,03} \times 384 \times 10^{-5} = 480 \times 10^{-4}; \sqrt{a_k} = 21,9 \times 10^{-2},$$

hence $\sqrt{a_k}$ for Hg = $21,9 - 2 \times 5,4 = 11,1 \times 10^{-2}$.

For HgBr_2 :

$$a_k = \frac{1011}{78,03} \times 484 \times 10^{-5} = 627 \times 10^{-4}; \sqrt{a_k} = 25,0,$$

from which Hg = $25,0 - 2 \times 6,9 = 11,2 \times 10^{-2}$.

For HgI_2 :

$$a_k = \frac{1072}{78,03} \times 582 \times 10^{-5} = 800 \times 10^{-4}; \sqrt{a_k} = 28,3,$$

hence Hg = $28,3 - 2 \times 8,8 = 10,7 \times 10^{-2}$.

For $\sqrt{a_k}$ for mercury in compounds we are therefore justified in assuming as mean value:

$$\sqrt{a_k} = 11,0 \times 10^{-2}$$

The found value agrees perfectly with the expected value in the 5th principal series. In the 4th principal series an average of 9 was namely found for Iodine and Xenon — so that in view of the value 7 in the 3rd series — 11 could now be expected.

We can now also calculate the critical temperature and pressure of Hg, and find (see § 2):

$$T_k = 2 \times 630^\circ = 1260^\circ \text{ (abs.)}; p_k = 192 \text{ atm.},$$

as mercury is quite bimolecular at T_k .

Also the missing critical pressures of the mercury halogenides, investigated by ROTINJANZ, can now be calculated.

The following value follows namely for $p_k = \frac{1}{28} \frac{a_k}{b_k^2}$.

For HgCl_2 :

$$p_k = \frac{1 (21.9)^2 \cdot 10^{-10}}{28 (384)^2 \cdot 10^{-10}} = \frac{1 (219)^2}{28 (384)^2} = \frac{(57,03)^2}{28} = 116 \text{ atm.}$$

For HgBr_2 :

$$p_k = \frac{1 \left(\frac{250}{484}\right)^2}{28} = \frac{(51,65)^2}{28} = 95 \text{ atm.}$$

And for HgI_2 :

$$p_k = \frac{1 \left(\frac{283}{5,82}\right)^2}{28} = \frac{(48,63)^2}{28} = 84 \text{ atm.}$$

As the triple point temperature for mercury = $-38,84 + 273,09 = 234,25$ abs., and the boiling point temperature = $356,7 + 273,1 = 629,8$ abs., the ratios of these temperatures to the critical temperatures are resp.:

$$\frac{T_k}{T_t} = 5,4; \quad \frac{T_k}{T_s} = 2,0.$$

The first value is still higher than the highest found value, viz. 5,2 for Helium. Generally a value is found in the neighbourhood of 2¹), so that in the liquid state Hg has probably another molecular weight than at T_k .²⁾

As to the second value, this too is considerably higher than the mean value for a great many normal substances, viz. 1,60. This

¹⁾ It is certainly remarkable that the ratio $T_k : T_{tr}$ lies either in the neighbourhood of $1\frac{1}{3}$ (e.g. CO_2), or in that of 2 (for many substances), or in that of $2\frac{2}{3}$ (for several substances), or in that of $3\frac{1}{3}$ (for a smaller number of substances), or at last in that of 4 (e.g. for iso-pentane). These values differ every time $\frac{2}{3}$ of a unit. 4 would be followed by $4\frac{2}{3}$ and $5\frac{1}{3}$ (for helium and mercury). We shall come back to this.

[Fritz thought that this ratio would be either 1,2 or 1,8 or 2,7, but this is evidently not quite correct, as one can see oneself, when one determines the quotient $T_k \cdot T_{tr}$ for a great number of substances. See the Table further on].

²⁾ Though it is less explicable then, that at lower temperature and smaller volume (two factors tending in the same direction) there would be less association present than at higher temperature.

too points to increasing association in the vapour of Hg_1 to Hg_2 , when the temperature gets higher.

In agreement with the abnormally high value of $T_k : T_s$, viz. 2,0 instead of 1,6, the value of f_s in VAN DER WAALS' vapour pressure formula

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

will be comparatively low. For with $p_s = 1$ (atm.), $T_k : T_s = \varphi$ we have:

$$f_s = \frac{\log^{10} p_k}{\varphi - 1},$$

which (as $\log p_k$ has little influence as a rule) leads to a too low value of f_s , when φ is too large. We really find for mercury with $\varphi = 2$ for f_s the value $f_s = \log^{10} p_s = \log^{10} 192 = 2,28$, the mean value for many normal substances being $= 2,90 (= 6,7$ with NEPER'S log.).

γ). The course of the vapour-tension factor f for mercury.

Though for some associated substances, as acetic acid, methyl alcohol, etc. the value of f_s (hence also that of f_k) is found *greater* than for normal substances (mean 3,35 or with Nep. log. 7,7), the opposite behaviour can also be expected. For as the vapour-pressure curve for substances, which are almost entirely bi-molecular at the critical temperature, but gradually become mono-molecular on decrease of temperature (as is the case with mercury vapour), will evidently lie *above* the normal value for Hg_2 (the critical pressures of Hg_1 and Hg_2 are namely equal, whereas T_k for Hg_1 will be double T_k for Hg_2), the vapour pressure will be comparatively large, hence *f too small* at a temperature (referring to T_k of Hg_2) below $(T_k)_2$. For associating substances as acetic acid, however, where the association decreases at higher temperature, the vapour-pressure curve on the other hand — if namely at T_k the association has disappeared for the greater part — will lie *below* that for $(Ac)_1$. In consequence at a certain value of $T : (T_k)_1$ below $(T_k)_1$ the vapour pressure becomes relatively too small, hence *f too large*.

All this refers to the said extreme cases. In intermediate cases — when the substance at T_k is only partly associated, so that T must be referred to a temperature *between* T_{k_1} and T_{k_2} — the value of f , in reference to the normal value at that reduced temperature m , will entirely depend on the value of m , and it is impossible to say beforehand whether in a definite case the value of f will be smaller or greater than the normal value of f .

Besides, the value of f can be modified, when in the dissociation of the double molecules increase or diminution of volume takes place, or when the heat of dissociation differs from 0. This is e.g. very apparent in the formula, which I derived before for f_k in the most general case ¹⁾.

For the value of $\left(\frac{T}{p_{12}} \frac{dp_{12}}{dT}\right)_k = f_k$ we find namely at T_k :

$$f_k = (f_k)_0 \times \varphi \left(1 + \lambda \frac{q'_k}{RT_k}\right),$$

in which $(f_k)_0$ is the value of f_k , when the substance were simple, i.e. β (degree of dissociation of the double molecules) = 0 or 1. The factor φ is a rather complicated function of β (and of the possible change of volume Δb for dissociation of $\frac{1}{2}$ double molecule to one single molecule), while λ is also a function of β and Δb . The quantity q' represents the *internal* heat of dissociation (absorbed) for the said dissociation. When $\Delta b = 0$, the value of φ is always < 1 , both in the neighbourhood of $\beta = 0$ and in that of $\beta = 1$. The latter is apparently in contradiction with what we observed above with regard to substances which behave as acetic acid, where for lower temperatures f is found greater than normal. But then we should forget that in the neighbourhood of T_k the association also of the acetic acid vapour — after having passed through a minimum in the neighbourhood of T_k — again increases with increase of temperature, just as for substances as mercury, water etc.

If $(f_k)_0$ lies in the neighbourhood of 7, the factor φ ($\Delta b = 0$ being assumed) is e.g. = 0,84 for $\beta = 0,1$, and 0,96 for $\beta = 0,9$. We find a minimum, viz. $\varphi = 0,72$, for $\beta = 0,4$. As far as λ is concerned, this coefficient is = 0 for $\beta = 0$ and $\beta = 1$, and reaches a maximum value, e.g. 0,22, for $\beta = 0,5$. For $\beta = 0,1$ λ is = 0,086; also for $\beta = 0,9$ λ is = 0,086. This quantity is namely symmetrical with respect to β .

If, therefore, also $q' = 0$, then in consequence of the factor φ the value of f_k can be as much as 28% smaller than the normal value. The value 7 can therefore decrease to 5 (when viz. for T_k the value of $\beta = 0,4$). For substances where $\beta = 0,1$ at T_k , the value 7 would any way have already been reduced to $7 \times 0,84 = 5,9$. Etc. If therefore we find for T_k a value for f that is *greater* than the normal one — as for acetic acid, methyl alcohol, etc. — then it is certain that q' differs from 0. (the value of Δb has but little influence). This is in perfect concordance with what we remarked

¹⁾ See Archives TEYLER 1908, p. 40—42, and also TheseProc. of Nov. 7, 1914, p. 606.

in § 2. For acetic acid and such substances with a minimum association near T_k the heat of dissociation of the double molecules must be comparatively large, namely $> f T_k$. If $\beta = 0,1$ for T_k , then $\lambda = 0,086 (\Delta b = 0)$. Hence with $q'_k = 7 T_k$ we have $\lambda \times (q'_k : R T_k) = 0,086 \times 3,5 = 0,30$, so that $f_k = (f_k)_0 \times 0,84 \times 1,30 = (f_k)_0 \times 1,09$, hence already $\bar{y} > (f_k)_0$. The value 7 would then already increase to 7,63. For $\beta = 0,2$ we have $\rho = 0,76$, $\lambda = 0,15$, when $\Delta b = 0$; hence when $q'_k = 7 T_k$, the factor of $(f_k)_0$ becomes $= 0,76 \times 1,52 = 1,15$, so that the normal value 7 has then already increased to 8,1.

From what precedes we see sufficiently that at T_k the value of f can be both smaller and greater than the normal one. For mercury, q' being probably very small, f_k will be somewhat too small (if β namely differs from 0), and then at lower temperature f will be continually *smaller* than is normal (see above). As soon as the dissociation to simple molecules is completed, f will of course have become normal again at the corresponding low temperatures. (In this "normal" course of f also the usual minimum in the value of f at about $m = 0,75$ is included, which minimum is generally about 6% lower than f_k).

After this digression, which is also necessary for what follows, we will determine the values of f for mercury at some temperatures below and above the boiling point on the supposition that $T_k = 1260$, $p_k = 192$ atm. We find what follows.

t	p	$\log p_k$	$\log p$	f_{10}	f
0° C.	0,00024 mm.	8,784		2,430	5,59 ⁵
50°	0,014	7,018		2,419	5,57
100°	0,270	5,733		2,409	5,55
150°	2,684	4,735		2,394	5,51
200°	17,015	3,933		2,365	5,45
250°	74,59	3,291		2,337	5,38
300°	246,7	2,772		2,309	5,32
$T_s = 357°$	760,0	2,283		2,283	5,26
400°	1459,6	1,989		2,281	5,25
450°	2996,1	1,688		2,270	5,23
500°	5435,0	1,429		2,273	5,23

It follows from this that at 0° C. Hg-vapour is not yet completely Hg₁, nor completely Hg₂ at 500° C. Yet it seems that between the boiling point (357°) and 500° the greatest deviation occurs between the real vapour curve and that which would hold, when mercury were Hg₂ all-over the temperature range. From this moment the approach to the latter curve will become closer and closer, and f_{10} will gradually increase to a value in the neighbourhood of 3, resp. f to 7.

The vapour pressures used are RAMSAY and YOUNG'S. At 50° the mean value has been taken between that of R. and Y. (0,015) and that of HERTZ (0,013); at 0° C. a value between that of HERTZ (0,00019) and that of v. D. PLAATS (0,00047). For $\log p_k$ has been taken $\log^{10} (192 \times 760) = 5,1641$. Further f_{10} has been calculated from $f_{10} = (5,1641 - \log^{10} p) : (T_1/T - 1)$.

d) Calculation of p_k and T_k from vapour pressure observations.

Reversely, when T_k is known and p_k unknown, we can determine the value of p_k from the vapour pressure course by approximation. For $\log p_k - \log p_1 = f(T_k - T_1) : T_1$ and $\log p_k - \log p_2 = f(T_k - T_2) : T_2$ follows from the vapour pressure formula for two temperatures T_1 and T_2 , so that

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

from which p_k can be determined. If for one of these temperatures, e.g. for T_2 , we take the boiling point T_s , then in atm. $p_2 = 1$, $\log p_2 = 0$, and (if we simply write T for T_1) we get:

$$\frac{\log p_k - \log p}{\log p_k} = \frac{T_s T_k - T}{T T_k - T_s},$$

from which follows:

$$\log p_k = \log p \times \frac{T T_k - T_s}{T_k T - T_s} \dots \dots \dots (3)$$

In this it has of course been supposed that the value of f does not appreciably differ for the two temperatures. The greatest chance to realise this exists, when we remain in the neighbourhood of the minimum of f . This may be illustrated by a few examples. PELLATON has found for *chlorine* (Thèse, Neuchatel, 1915, p. 20) $p = 2766$ mm. at 0° C. At this temperature and at the boiling point — 34°,5 f is near the minimum (somewhat above 0° C.). For T_k was found 144°,0 C., so that we have in atm.:

$$\log p_k = \log 3,6395 \times \frac{273,1}{417,1} \times \frac{178,5}{34,5} = 0,5610 \times 0,6547 \times 5,174 = 1,900,$$

hence $p_k = 79,4$ atm. (PELLATON found 76,1).

With $T_k = 141^\circ,0$ C. according to DEWAR $\log p_k$ would have been $0,5610 \times 0,6595 \times 5,087 = 1,882$, hence $p_k = 76,3$. (DEWAR found 83,9).

As f at $-34^\circ,5$ is somewhat greater than at 0° C., p_k must be $< 79,4$ (resp. 76,3). The value 76,1 found by PELLATON can thus be exact, that of DEWAR is probably too high.

If we calculate the values of a_k and b_k for Cl, found by us in I with the values found by PELLATON for T_k and p_k , viz. 417,1 abs. and 76,1 atm., we find the somewhat higher values $b_k = 251 \times 10^{-5}$, $\sqrt{a_k} = 11,5 \times 10^{-2}$, instead of $b_k = 226 \times 10^{-5}$, $\sqrt{a_k} = 10,9 \times 10^{-2}$; giving for Cl the values resp. 125 and 5,75. (From the compounds we found 115 and 5,4).

For mercury at 500° C. $p = 5435,0$ mm. = 7,151 atm. Further $T_s = 357^\circ$ C. = 630 abs., $T_k = 1260$ abs. Hence:

$$\log p_k = 0,8544 \times \frac{773}{1260} \times \frac{630}{143} = 0,8544 \times 2,703 = 2,309,$$

giving $p_k = 204$, while we have found 192 by another way.

The value of f being somewhat greater also here at 357° than at 500° , p_k must in any case be < 204 , so that 192 may be correct.

When the case presents itself that both T_k and p_k are unknown, it is yet possible to calculate both values — at least with some approximation. From $\log p_k - \log p = f \left(\frac{T_k}{T} - 1 \right)$ we have then namely:

$$f + \log p_k = \log p + \frac{f T_k}{T}.$$

If we now put $f + \log p_k = y$, $f T_k = x$, then

$$\underline{y = \log p + \frac{x}{T}} \quad \dots \dots \dots (4)$$

so that we can calculate the quantities x and y from two corresponding pairs of values. Then we have, however, only $f + \log p_k$ and $f T_k$ (again on the supposition that the value of f does not appreciably differ for one pair from that of the other pair). To eliminate further the value of f , we may make use of the found property of the quantities \sqrt{a} , that they will namely be about constant in a whole horizontal principal series of the periodic system, e.g. = 9 in the series of I and Sb, = 7 in the series of Br and As, etc.

In the special example of Hg $\sqrt{a_k} = 2 \times 11,0 \times 10^{-2}$ (as mercury is bi-molecular for T_k), so that we have from

$$\frac{(RT_k)^2}{p_k} = \frac{64}{27} \lambda \cdot a_k,$$

with $R = 1 : 273,1$ and $\lambda = 27/28$:

$$\frac{T_k^2}{p_k} = \frac{16}{7} (273,1 \times 2 \times 11,0 \times 10^{-2})^2 = \frac{16}{7} \times (60,08)^2 = 8252.$$

Now $T_k = x : f$, $\log p_k = y - f$, hence

$$\frac{x^2 : f^2}{10^{y-f}} = 8252, \text{ or } x^2 = 8252 f^2 \cdot 10^{y-f},$$

or also

$$2 \log x = \log 8252 + 2 \log f + y - f,$$

yielding

$$f - 2 \log f = y - 2 \log x + 3,9166, \dots \dots \dots (5)$$

from which f (in the case of *mercury*) can be calculated.

If for the calculation we choose the four temperatures beginning with the boiling point, because f changes only little there, we find — seeing that

$$x = \frac{\log p_1 - \log p_2}{1/T_2 - 1/T_1}$$

follows from (4) by subtraction — successively between

$$\begin{array}{l} 356,7^\circ \text{ and } 400^\circ x = \frac{\log 1495,6 - \log 760}{(1:629,8) - (1:673,1)} = 2878 \quad \left| \begin{array}{l} y = 7,451 - 2,881 = 4,570 \\ y = 7,539 - 2,881 = 4,658 \\ y = 7,476 - 2,881 = 4,595 \end{array} \right. \\ 400^\circ \quad ,, \quad 450^\circ x = \frac{\log 2996,1 - \log 1495,6}{(1:673,1) - (1:723,1)} = 2937 \\ 450^\circ \quad ,, \quad 500^\circ x = \frac{\log 5435,0 - \log 2996,1}{(1:723,1) - (1:773,1)} = 2892 \end{array}$$

The value of y must, namely, everywhere be diminished by $\log 760 = 2,881$, because in $\log p$ the pressure p must not be expressed in m.m. but in atm., because also a_k is expressed in atm.

According to (5) the following equations follow from the found values of x and y :

$$\begin{array}{l} f - 2 \log f = 4,570 - 6,918 + 3,917 = 1,569 \quad \left| \begin{array}{l} f = 2,288 \\ f = 2,399 \\ f = 2,322 \end{array} \right. \\ = 4,658 - 6,936 + 3,917 = 1,639 \\ = 4,595 - 6,922 + 3,917 = 1,590 \end{array}$$

From $x = f T_k$ and $y = f + \log p_k$ we find then at once:

$$\left. \begin{array}{l} T_k = 1258 \quad ; \quad 1224 \quad ; \quad 1245 \\ p_k = 191,4 \quad ; \quad 181,6 \quad ; \quad 187,7 \end{array} \right\}$$

giving on an average $T_k = 1242^\circ$ abs.; $p_k = 187$ atm.

Though *both* values, as well T_k as p_k , are supposed to be unknown, yet we find for these quantities (and that for an abnormal substance, for which the state of association continually varies with the temperature) values, which differ only little from the values calculated in the other way. Those that were calculated between 357° and 400° , come very near, indeed, to the latter (viz. 1260° and 192 atm.).

We see from what precedes, that for many substances with as yet unknown p_k or even unknown p_k and T_k these quantities can be calculated with some approximation from a few vapour pressure observations; in the last mentioned case (p_k and T_k unknown) by the aid of the probable value of $\sqrt{a_k}$. But the molecular state in the critical point must then be accurately known.

ε) *Calculation of T_k from the temperature of the boiling point.*

If the foundation of the calculation of the foregoing paragraph is wanting, in consequence of the molecular state at T_k , hence also $\sqrt{a_k}$, being unknown, the equation (4) is still valid. We can, therefore, always determine x and y from two vapour pressure observations, i.e. fT_k and $f + \log p_k$. If the observations are made in the neighbourhood of the boiling point, we can still determine the values of T_k and p_k with some approximation from the approximated value of f at this point (determined from the mean value for a number of analogous substances).

Besides T_k can be determined directly from T_s , when the mean value of the ratio $T_k : T_s$ is used as first approximation.

We will, therefore, in the first place consider the values of f_k and $T_k : T_s$ more closely.

In the following table, besides T_k and p_k , the triplepoint temperature T_t and the boilingpoint temperature T_s of a great number of substances have been given, and also the ratios $T_k : T_t$ and $T_k : T_s$. Further $\log p_k$ and f_s . The ratio $T_k : T_s$ will depend on $\log p_k$ according to the relation ($p_s = 1$ atm.)

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

so that:

$$\frac{T_k}{T_s} = \frac{\log p_k}{f_s} + 1 \dots \dots \dots (6)$$

Now — at least for ordinary substances, where the critical temperatures are not excessively low — the values of f_s (for *normal* substances) will not diverge very much, so that $T_k : T_s$ would have about the same value for all such substances, if $\log p_k$ had the same

value for all. This is, however, not the case; yet the critical pressures do not diverge so much that $\log p_k$ moves within a wide margin: in most cases the values of p_k lie between 40 and 60 atm., hence $\log p_k$ between 1,60 and 1,78. This would cause $T_k : T_s$ (with f_s on an average 2,9) to lie between 1,55 and 1,61. Only in extreme cases will p_k ascend to 100 atm. or descend to 20 atm. Then $\log p_k$ would become resp. = 2 and 1,30, hence $T_k : T_s$ resp. = 1,69 and 1,45, so that then too the values of this last ratio comparatively do not lie far apart. Practically the said ratio can only vary between 1,45 and 1,69 — though $\log p_k$ can lie between 1,3 and 2; in most cases it will vary even between the still narrower limits 1,55 and 1,61. As mean value **1,60** can be given, so that — and strictly speaking this holds only for normal substances, or such associated substances as no longer change in the neighbourhood of T_s , as far as their molecular state is concerned — one can conclude in many cases to the *critical temperature* from the temperature of the *boiling point*. (See following table.)

The mean value of the ratio $T_k : T_s$ for the 49 *anorganic* substances, for which we could calculate this ratio, amounts to $1 + (327 : 49) = 1,638 = \mathbf{1,64}$.

That for the *organic* substances is somewhat lower; we found for the 58 substances, for which $T_k : T_s$ was calculated: $1 + (3244 : 58) = 1,559 = \mathbf{1,56}$.

The mean of all the 107 substances amounts to $1 + 6371 : 107) = 1,595 = \mathbf{1,60}$.

The ratio $T_k : T_r$ does not exhibit any perceptible regularity; the cause of the great difference, which often exists for closely allied substances with respect to this ratio, has not yet been explained. We need only think of 1,40 for CO_2 , 3,38 for CS_2 .

With regard to the application of the rule $T_k : T_s = 1,60$ for substances as As, Sb, Al, Hg, etc., we should bear in mind that these and suchlike substances can be greatly associated, and that the state of association between the boiling point and the critical point can still vary pretty considerably. Accordingly we shall often find values deviating more or less considerably from the mean value. Thus the ratio $T_k : T_s$ is even 2,00 for mercury.

IV. The critical values of Antimonium.

In the formula (1a) the value of m at the ordinary temperature, referring to the critical temperatures of the compounds SbCl_3 , SbBr_3 , SbI_3 , will be about $\frac{1}{3}$ or $\frac{1}{4}$, so that $b_k \geq 1,67 v_1$ or $1,75 v_1$.

2

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Anorganic Substances.

	T_{tr}	p_{tr}	T_s	T_k	p_k	$\log^{10} p_k$	f_s^{10}	f_s	$\frac{T_k}{T_s}$	$\frac{T_k}{T_{tr}}$
He	± 1		4,20	5,20	$>2,26$	0,354	1,49	3,43	1,24	5,20
Ne	24,42	32,35 cm.	27,17	45?	29	1,462	2,23	5,13	1,66	1,84
Ar	83,79	51,6 "	87,25	150,65	48,0	1,681	2,31	5,32	1,73	1,80
Kr	104,1		121,4	210,5	54,3	1,735	2,36	5,44	1,73	2,02
X	133,1		164,1	289,7	58,2?	1,765	2,31	5,31	1,77	2,18
H ₂	13,9	5,4 "	20,32	31,95	15,0	1,176	2,06	4,73	1,57	2,30
N ₂	63,06	9,0 "	78,0	126,0	33,5	1,525	2,48	5,71	1,61	2,00
O ₂	54,7	0,11 "	90,10	154,3	49,7	1,696	2,38	5,48	1,71	2,82
*P ₄ (viol.)	862,6	43,1 atm.	687(su.)	968	82,8	1,918	2,56	5,90	1,75	1,12
S ₂	392,0		717,6	970?	—	—	—	—	—	—
F ₂	50		86	103?	—	—	—	—	—	—
Cl ₂	171,6		238,6	417,1	76,1	1,881	2,51	5,79	1,75	2,44
Br ₂	265,8		331,8	575,3	—	—	—	—	1,73	2,16
I ₂	386,8	9,1 cm.	456,1	785,1	—	—	—	—	1,72	2,03
*(HF) ₂	180,8		292,6	500?	—	—	—	—	—	—
HCl	161,8		190,2	324,5	81,55	1,911	2,71	6,23	1,71	2,01
HBr	187,1		204,4	364,4	—	—	—	—	1,78	1,95
HI	222,3		237,4	423,8	—	—	—	—	1,79	1,91
*H ₂ O	273,1	0,457 cm.	373,1	638,1	200,5	2,302	3,24	7,47	1,71	2,34
H ₂ S	187,1		211,5	373,5	89,05	1,950	2,55	5,86	1,77	2,00
H ₂ Se	209,1		231,6	410,1	91,0	1,959	2,54	5,85	1,77	1,96
NH ₃	195,4		239,6	406,0	112,3	2,050	2,95	6,80	1,69	2,08
(NH ₂) ₂	274,5		386,6	—	—	—	—	—	—	—
N ₂ O	170,8		183,3	309,6	71,65	1,855	2,69	6,20	1,69	1,81
NO	112,5	14 cm.	122,9	180,2	64,6	1,810	3,88	8,94	1,47	1,60
*NO ₂	263,0		294,7	431,3	100	2,000	4,32	9,94	1,46	1,64
PH ₃	140,6		186,7	325,9	64,0	1,806	2,42	5,58	1,75	2,32
PCl ₃	161,3		349,0	558,6	—	—	—	—	1,60	3,46
POCl ₃	274,3		380,3	604,9	—	—	—	—	1,59	2,21
AsH ₃	159,6		218,3	—	—	—	—	—	—	—
AsCl ₃	255		403,3	629?	—	—	—	—	1,56	2,47

Anorganic Substances (continued).

	T_{tr}	p_{tr}	T_s	T_k	p_k	$\log^{10} p_k$	f_s^{10}	f_s	$\frac{T_k}{T_s}$	$\frac{T_k}{T_{tr}}$
SbH ₃	181,6		255	—	—	—	—	—	—	—
SbCl ₃	346,3		496	797	61?	1,785	2,94	6,77	1,61	2,30
SbBr ₃	363		553	904,5	56?	1,748	2,75	6,33	1,64	2,49
SbI ₃	440		674	1101	55?	1,740	2,74	6,32	1,63	2,50
SO ₂	201,4		263,0	430,2	77,65	1,890	2,97	6,84	1,64	2,14
S ₂ Cl ₂	—		411,2	664,4?	—	—	—	—	1,62	—
SOCl ₂	—		351,9	569,9	—	—	—	—	1,62	—
SO ₂ Cl ₂	—		343,0	549,7	—	—	—	—	1,60	—
TeCl ₂	448		597	—	—	—	—	—	—	—
TeCl ₄	487		687	—	—	—	—	—	—	—
Hg ₂	234,25		629,8	1260?	192?	2,283	2,28	5,25	2,00	5,38
HgCl ₂	560		577,4	976	116?	2,064	2,99	6,88	1,69	1,74
HgBr ₂	517		593,3	1011	95?	1,978	2,81	6,47	1,70	1,96
HgI ₂	514		626,5	1072	84?	1,924	2,71	6,23	1,71	2,09
BCl ₃	—		291,3	—	—	—	—	—	—	—
BBr ₃	—		363,6	—	—	—	—	—	—	—
BI ₃	316		483	—	—	—	—	—	—	—
AlCl ₃	463?	2,5 atm	456 (su.)	629,5	—	—	—	—	1,38	1,36
AlBr ₃	366		533	772	—	—	—	—	1,45	2,11
AlI ₃	398		623	955	—	—	—	—	1,53	2,40
(CN) ₂	238,7		252,5	401,4	59,75	1,776	3,01	6,92	1,59	1,68
HCN	259,7		299,6	—	—	—	—	—	—	—
CO	66,1	10 cm.	83,1	133,4	35,5	1,550	2,56	5,90	1,61	2,02
CO ₂	216,9	5,1 atm.	194 (su.)	304,1	72,93	1,863	3,29	7,57	1,57	1,40
CS ₂	161,5		319,3	546,1	72,9	1,863	2,62	6,04	1,71	3,38
COS	—		—	378,1	—	—	—	—	—	—
SiCl ₄	—		330,7	503,1	37?	1,568	3,01	6,93	1,52	—
SiBr ₄	260		426	656?	—	—	—	—	1,54	2,52
SiI ₄	393,6		563?	—	—	—	—	—	—	—
TiCl ₄	—		409,5	631?	—	—	—	—	1,54	—
GeCl ₄	—		359,1	550,0	38,0	1,580	2,98	6,85	1,53	—
SnCl ₄	240,1		387,2	591,8	36,95	1,568	2,96	6,83	1,53	2,47

Organic Substances.

	T_{tr}	p_{tr}	T_s	T_k	p_k	$\log^{10} p_k$	f_s^{10}	f_s	$\frac{T_k}{T_s}$	$\frac{T_k}{T_{tr}}$
CH ₄	89,94	7 cm.	108,4	190,2	53 ?	1,724	2,28	5,25	1,75	2,12
C ₂ H ₆	95,6		189,0	305,2	48,9	1,689	2,75	6,32	1,61	3,19
C ₃ H ₈	—		228,1	370,6	45,0	1,653	2,64	6,09	1,62	—
n-C ₄ H ₁₀	—		274,1	424 ?	37 ?	1,568	2,87	6,60	1,55	—
(n-C ₅ H ₁₂)	142,3		309,2	470,3	33,03	1,519	2,92	6,71	1,52	3,30
i-C ₅ H ₁₂	115,0		301,0	460,9	32,92	1,517	2,86	6,58	1,53	4,01
n-C ₆ H ₁₄	—		342,0	507,9	29,6	1,471	3,03	6,98	1,49	—
n-C ₇ H ₁₆	—		371,5	539,9	26,9	1,430	3,16	7,27	1,45	—
n-C ₈ H ₁₈	—		398,9	569,3	24,6	1,391	3,26	7,50	1,43	—
C ₂ H ₂	192,1	1,25 atm.	190,7(su.)	308,6	61,65	1,790	2,90	6,67	1,62	1,61
C ₂ H ₄	104,1		170,6	282,2	50,65	1,705	2,61	6,00	1,65	2,71
i-C ₅ H ₁₀	—		—	464,7	33,9	1,530	—	—	—	—
C ₆ H ₆	278,5		353,3	561,6	47,89	1,680	2,85	6,56	1,59	2,02
C ₇ H ₈	178,6		383,8	593,7	41,6	1,619	2,96	6,82	1,55	3,32
o-C ₈ H ₁₀	245,1		417,1	636,1	36,9	1,567	2,98	6,87	1,53	2,60
Cyclohexane	—		353,9	553,1	39,8	1,600	2,84	6,54	1,56	—
C ₁₀ H ₈	353,2		491,05	741,3	39,2	1,593	3,13	7,21	1,51	2,10
CH ₃ F	—		—	318,0	62,0	1,792	—	—	—	—
CH ₃ Cl	181,6		249,4	416,3	65,9	1,819	2,71	6,25	1,67	2,29
CH ₂ Cl ₂	—		314,7	518,3	—	—	—	—	1,65	—
CHCl ₃	209,8		334,3	536,0	53,8	1,731	2,87	6,61	1,60	2,55
CCl ₄	250,1		349,8	556,2	44,97	1,653	2,80	6,45	1,59	2,22
C ₂ H ₅ Cl	134,4		286,2	455,6	54	1,732	2,93	6,74	1,59	3,39
C ₂ H ₅ Br	154,1		311,5	509,1	—	—	—	—	1,63	3,30
C ₂ H ₅ I	161,1		345,6	559,1	—	—	—	—	1,62	3,47
C ₂ H ₄ Cl ₂	308,4		356,8	562,4	53	1,724	2,99	6,89	1,58	1,82
C ₂ H ₄ Br ₂	282,7		404,2	583,1	—	—	—	—	1,44	2,06
C ₃ H ₇ Cl	150,3		319,7	494,1	49,0	1,690	3,10	7,14	1,55	3,29
(CH ₃) ₂ O	—		249,4	400,2	53	1,724	2,85	6,56	1,60	—
(C ₂ H ₅) ₂ O	156,9		307,7	466,9	35,60	1,551	3,00	6,90	1,52	2,98
(CH ₃ , C ₂ H ₅)O	—		284,1	441,5	46,3	1,666	3,01	6,92	1,55	—

Organic Substances (continued).

	T_{tr}	p_{tr}	T_s	T_k	p_k	$\log^{10} p_k$	f_s^{10}	f_s	$\frac{T_k}{T_s}$	$\frac{T_k}{T_{tr}}$
*CO(CH ₃) ₂	178,8		329,4	505,9	52,2	1,718	3,21	7,39	1,54	2,83
H.COOCH ₃	—		305,0	487,1	59,25	1,773	2,97	6,84	1,60	—
CH ₃ .COOCH ₃	—		330,2	506,8	46,3	1,666	3,11	7,17	1,53	—
CH ₃ COOC ₂ H ₅	189,7		350,2	523,2	38,0	1,580	3,20	7,36	1,49	2,76
CH ₃ COOC ₃ H ₇	—		374,6	549,3	33,2	1,521	3,26	7,52	1,47	—
C ₆ H ₅ F	232,1		358,3	559,6	44,62	1,650	2,94	6,76	1,56	2,41
C ₆ H ₅ Cl	228,1		405,1	632,3	44,64	1,650	2,94	6,77	1,56	2,77
C ₆ H ₅ Br	242,5		429,2	670,1	44,6	1,649	2,94	6,77	1,56	2,76
C ₆ H ₅ I	241,7		461,6	721,1	44,6	1,649	2,93	6,76	1,56	2,98
C ₄ H ₄ S	—		—	590,4	47,7	1,679	—	—	—	—
*CH ₃ OH	176,0		337,8	513,1	78,5	1,895	3,65	8,41	1,52	2,92
*C ₂ H ₅ OH	143,1		351,4	516,2	62,96	1,799	3,84	8,84	1,47	3,61
*C ₂ H ₅ SH	128,6		309,1	501,1	—	—	—	—	1,62	3,90
*n-C ₃ H ₇ OH	—		370,3	536,8	50,2	1,701	3,78	8,70	1,45	—
*C ₆ H ₅ OH	314,2		454,5	692,3	—	—	—	—	1,52	2,20
*HCOH	—		252,1	496,7	—	—	—	—	1,97	—
*CH ₃ .COH	149,6		293,3	461,1	—	—	—	—	1,57	3,08
*(CH ₃ .COH) ₃	283,6		396,1	559,1	—	—	—	—	1,41	1,97
*H.COOH	281,6		373,7	640?	—	—	—	—	1,71	2,27
*CH ₃ .COOH	289,8		391,6	594,7	57,11	1,757	3,38	7,78	1,52	2,05
*C ₂ H ₅ COOH	253,8		413,4	599,9	—	—	—	—	1,45	2,36
CH ₃ CN	228,2		354,7	547,8	—	—	—	—	1,54	2,40
C ₂ H ₅ CN	—		—	564,3	—	—	—	—	—	—
NH ₂ CH ₃	—		267	428	72	1,857	3,08	7,09	1,60	—
NH ₂ C ₂ H ₅	192,5		289,7	450	66	1,820	3,29	7,58	1,55	2,34
NH ₂ C ₃ H ₇	—		322	491	50	1,699	3,24	7,45	1,52	—
NH(CH ₃) ₂	—		281,6	436	56	1,748	3,18	7,33	1,55	—
NH(C ₂ H ₅) ₂	229,1		330	489	40	1,602	3,32	7,65	1,48	2,13
NH(C ₃ H ₇) ₂	—		—	550	31	1,491	—	—	—	—
N(CH ₃) ₃	—		276	433,5	41	1,613	2,83	6,52	1,57	—
N(C ₂ H ₅) ₃	158,3		362,5	532	30	1,477	3,16	7,27	1,47	3,36
NH ₂ C ₆ H ₅	266,9		457,5	698,7	52,35	1,719	3,26	7,51	1,53	2,62

ROTINJANZ found namely recently (Z. f. ph. Ch. **87**, p. 635) for T_k resp. 797° , $904,05^\circ$ and 1101° absolute.

The sign of inequality in the above relation refers to the solid state, and as $b_k = 250 \times 10^{-5}$ has already been found by another way (See Treatise I), the factors 1,67 or 1,75 will have to be raised to 1,8 or 1,9. [In what follows we shall have to take this into account, and (for *solid* compounds) we can replace the sign of inequality by the sign of equality by increasing the factor $2-m$ by about 10%].

For the antimonium compounds we then get (see § 3):
SbCl₃:

$$b_k = \frac{1,8}{22412} \times \frac{226,58}{3,06} = 0,00595,$$

hence Sb = 595 - 345 = 250 $\times 10^{-5}$.

SbBr₃:

$$b_k = \frac{1,9}{22412} \times \frac{359,96}{4,15} = 0,00736,$$

giving Sb = 736 - 495 = 241 $\times 10^{-5}$.

SbI₃:

$$b_k = \frac{1,9}{22412} \times \frac{500,96}{4,68} = 0,00908,$$

hence Sb = 908 - 660 = 248 $\times 10^{-5}$.

For the density of SbI₃ that of the monoclinic form has been taken. That of the hexagonal form ($D_1 = 4,85$) would have given too low a value. Now the results are in very good concordance with the value 250×10^{-5} calculated before — a proof that (1) or (1a) is very suitable for the calculation of b_k . In this we can also bring the value of γ to 1,09 instead of augmenting the factor $2-m$ ($\gamma = 1$) by 10% (see above). For substances with critical temperatures of 800 or 1000° abs. the (reduced) coefficient of direction of the straight diameter can, namely, exceed unity. Instead of (1a) we had better take then according to (1):

$$\underline{b_k = v_1 (2,18 - 1,14 m)} \dots \dots \dots (1b)$$

As factor of v_1 with $m = 1/3$ this yields then the value $2,18 - 0,38 = 1,8$, and with $m = 1/4$ the value $2,18 - 0,285 = 1,9$, which factors agree with what was found above.

From formula (2), i. e. $a_k = (T_k : 78,03) \times b_k$, the following values now follow immediately for the three said compounds.

$$\begin{array}{l}
 a_k = \frac{797}{78,03} \times 595 \cdot 10^{-5} = 608 \cdot 10^{-4} \\
 a_k = \frac{904,5}{78,03} \times 736 \cdot 10^{-5} = 863,5 \cdot 10^{-4} \\
 a_k = \frac{1101}{78,03} \times 908 \cdot 10^{-5} = 1286 \cdot 10^{-4}
 \end{array}
 \left|
 \begin{array}{l}
 \sqrt{a_k} = 24,7 \cdot 10^{-2} \\
 29,4 \cdot 10^{-2} \\
 35,9 \cdot 10^{-2},
 \end{array}
 \right.$$

so that we find for Sb itself:

$$\begin{array}{l}
 \sqrt{\sigma_k} = 24,7 - 16,2 = 8,5 \cdot 10^{-2} \\
 29,4 - 20,7 = 8,7 \cdot 10^{-2} \\
 35,9 - 26,4 = 9,5 \cdot 10^{-2},
 \end{array}$$

hence for Sb on an average:

$$\sqrt{a_k} = 8,9 \times 10^{-2},$$

in concordance with the expected value in the 4th horizontal row of the periodic system, which is about 9×10^{-2} ($I = 8,8$, $X = 9,1$; cf. the table in § 1).

We should now find for the critical temperature of Sb—supposing that Sb at T_k possessed the formula Sb_1 :

$$T_k = 78,03 \frac{a_k}{b_k} = 78,03 \times \frac{79,2 \cdot 10^{-4}}{250 \cdot 10^{-5}} = 247^\circ \text{ absolute.}$$

The boiling point of Antimonium being 1440°C or 1713° abs , T_k will not be lower than $1713 \times 1,7 \text{ à } 2$, i. e. $\pm 2900^\circ$, so that at the critical temperature the molecular formula of Antimonium will have to be at least $Sb_{1,2}$ ¹⁾.

The following values now follow from $p_k = \frac{1}{28} \frac{a_k}{b_k^2}$ (see § 2 and § 3, β)) for the critical pressures of $SbCl_3$, $SbBr_3$, and SbI_3 , and also of Sb itself.

$$\begin{array}{l}
 SbCl_3 : p_k = \frac{1}{28} \frac{608 \cdot 10^{-4}}{(595 \cdot 10^{-5})^2} = 61 \text{ atm.} \\
 SbBr_3 : p_k = \frac{1}{28} \frac{863,5 \cdot 10^{-4}}{(745 \cdot 10^{-5})^2} = 56 \text{ ,,} \\
 SbI_3 : p_k = \frac{1}{28} \frac{1286 \cdot 10^{-4}}{(910 \cdot 10^{-5})^2} = 55 \text{ ,,} \\
 Sb : p_k = \frac{1}{28} \frac{79,2 \cdot 10^{-4}}{(250 \cdot 10^{-5})^2} = 45 \text{ ,,}
 \end{array}$$

With these values of p_k and those for $HgCl_2$ etc. the values of f_s for these compounds have been calculated in the large table of § 3; they are in perfect agreement with the values for ordinary

¹⁾ See, however, note 2 of § 2.

normal substances, so that neither the mercury halides, nor those of Sb exhibit any association. The molecular formulae for these latter compounds will, therefore, no doubt be $SbCl_3$, etc., and not Sb_2Cl_6 , etc.

After these somewhat lengthy expositions I can be a good deal shorter in future, now that the Methods for the further calculation have been sufficiently set forth and elucidated by the examples of mercury and also of antimonium.

In the determination of the values of b_k and $\sqrt{a_k}$ for the different metals and the remaining elements of the periodic system we shall, therefore, have to refer continually to this second Paper.

Aluminium, Borium, Arsenicum, Bismuth, Tellurium, Silicium etc. will be treated first.

Clarens, March 1916.

Zoology. — “*On the Setal Pattern of Caterpillars.*” By A. SCHIERBEEK. (Communicated by Prof. J. F. VAN BEMMELEN.)

(Communicated in the meeting of March 25, 1916).

In 1876 WEISMANN proved the ontogeny of the peculiar colour-patterns occurring in many Sphingide-caterpillars to be a further differentiation of the linear ornamentation. From this he concluded that the ocellar and annular markings had also phylogenetically taken origin from longitudinal stripes, and he could back this inference by the fact, that the intermediate stages, which in some genera and species were passed through during their growth, acted as terminal stages in other forms. From that time onwards many investigators have occupied themselves with the study of the external appearance of caterpillars. Independently of each other WILH. MULLER and DYAR called attention to the regular arrangement of the setae in different families; O. HOFMANN, PACKARD, QUAIL, TSOU¹⁾ and others followed them in their track.

J. F. VAN BEMMELEN (1913) pointed out the connections between the colour-pattern of caterpillars, pupae and imagines, which indeed had been remarked by other students, e.g. POULTON, but had not been considered of real importance. VAN BEMMELEN's views therefore introduced a new aspect into the discussions, as he defended the homology of pigmentspots with tubercula and setae. This connection

¹⁾ Tsou's paper only came into my hands, after the writing of the present communication.