We hope to collect further information by subsequent series of experiments (which have already been commenced) in which in the first place attention will be paid to the basicity of the amines.

The last communication of TASSILLY (Bull. Soc. Chim. January 1920) led us to the publication of these first results.

Lab. for Organic Chemistry of the
Technical High School.

Delft, February 1920.

Physics. — *"On the Critical Quantities of Mercury in Connection with the Increase of the Molecular Attraction on Dissociation of the Double Molecules."* I. By Dr. J. J. VAN LAAR. (Communicated by Prof. H. A. LORENTZ).

(Communicated at the meeting of May 29, 1920).

1. Already twice I published [1]) discussions of the critical quantities of mercury. Starting from the fundamental value $b_c = 150.10^{-5}$ holding for 1 gr. atom Hg (calculated from the densities of the *solid* halogen compounds) and the value $\sqrt{a_c} = 11.10^{-2}$ derived from it (in connection with the critical temperatures of the said compounds), I calculated for mercury, assuming — what is confirmed in different ways — that this substance is quite or almost quite *bi-molecular* at T_c (cf. among others loc. cit. p. 9):

$$T_c = 1260° \text{ abs. } (= 987° \text{ C.}); \quad p_c = 192 \text{ atm.}$$

From determinations of the vapour pressure the pressure corresponding to $T = 1260°$ abs. was calculated < 204 atm. (loc. cit. p. 14). When T_c and p are both assumed to be unknown, the same vapour-pressure observations, on assumption of $\sqrt{a_c} = 2 \times 11.10^{-2}$, yield for T_c the value $1242°$ abs., p_c becoming $= 187$ atm. (loc. cit. p. 15).

In the second of the cited papers I made use of COLARDEAU and RIVIÈRE's later vapour pressure observations (1900), which go up to 880°. With $b_c = 149.10^{-5}$, $\sqrt{a_c} = 10,74.10^{-2}$ (for 1 Gr. atom.; likewise determined from these observations), I now calculated (loc. cit. p. 144):

$$T_c = 1172° \text{ abs. } (= 899° \text{ C.}); \quad p_c = 180 \text{ atm.,}$$

while for D_c about 3,3 was found. Through a simple calculation I got at the same time the *certainty* that mercury is practically quite bi-molecular at T_c (cf. loc. cit. p. 139—140).

The same value $b_c = 149.10^{-5}$ follows also from the limiting density 14,46 at the absolute zero, when 1,2 is assumed for the (reduced) coefficient of direction of the "theoretical" straight diameter. [I determined before $b_c = 120.10^{-5}$ per Gr. atom. for mercury itself, starting from $D_c = 3,77$, calculated by GULDBERG (l. c. p. 8)].

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[1]) Cf. among others These Proc. **19**, p. 6 (1916); **20**, p. 138 (1917). Also Zeitschr. für anorg. Chemie **104**, p. 84 and 126 (1918).

18

2. It appeared, however, more and more that the critical temperature of mercury lies much higher than 900° or 1000° C.

TRAUBE and TEICHNER found no critical phenomena at 1000° C. and HAPPEL [1]) calculated $T'_c = 1370°$ abs. (= 1097° C.), $p_c = 456$ atm, from different observations. This would, therefore, be only 100° higher than my first estimation. W. C. MENZIES [2]) came to 1275° C. (675 atm.), while it became clear from KÖNIGSBERGER's experiments [3]) that the long sought critical temperature must lie above 1400° C. (1000 atm.). At ± 1200° C. the meniscus becomes flat; only the liquid is luminous. Below 1400° C. there are seen small glowing drops, which rise from the liquid and fall back into it, or dissolve in the not-luminous vapour. At 1400° C. the emission of light of the liquid rapidly diminishes, and the critical temperature seems to be near.

Then followed Miss J. BENDER's experiments [4]) giving determinations of density of liquid and vapour up to 1400° C. At 1400° C. the vapour was still *quite transparent*; "the distance of the mercury atoms, therefore, is still so great that the electron cannot yet detach itself from the atom, and can, therefore, not yet take charge of the conduction of the electricity." At 1500° C. (one observation) [5]) there was still liquid mercury present.

When the observed densities are represented in a T,v-diagram, we arrive through graphical interpolation at $T_c = 1400°$ C. about, or slightly higher, hence about 1700° abs. (1427° C.), whilst p_c must be at the least 1100 atm. For the critical density about 4,15 is found. (GULDBERG calculated 3,8).

3. It is the question if this high critical temperature of ± 1700° abs. can be theoretically justified. For this purpose it is required, as we shall see, to modify the values of b_c and $\sqrt{a_c}$ for 1 Gr. atom of mercury somewhat. Instead of $10^5 b_c = 150$ the lower value of about 120 must be assumed for it, while instead of $10^2 \sqrt{a_c} = 11$ it is necessary to assume 10 (hence $10^4 a_c = 100$ instead of 121).

That at such a high temperature as 1700° abs. the values of a

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[1]) Ann. der Ph. (4) **13** (1904), p. 340 and 620.

[2]) Am. Chem. Soc. **35** (1913), p. 1065.

[3]) Chem. Zg. **36** (1912), p. 1321. Cf. also ROTINJANZ and SUCHODSKI, Ann. Inst. Pol. P. le Grand **23** (1915), p. 668.

[4]) Physik. Zeitschr. **16** (1915), p. 246; **19** (1918) p. 410.

[5]) Neither KÖNIGSBERGER, nor Miss BENDER state clearly in what way their observations of the temperature have been made. This remains in my opinion the weak point.

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and b will be *smaller* than those which have been determined at the critical temperatures of the mercury-halogenides (which temperatures lie in the neighbourhood of 1000° abs.) is, indeed, to be expected. For it is known that b and a decrease with increasing temperature.

But there is still something else required. If such a high critical temperature and pressure is to be reached, the double molecules must be dissociated at T_c to a slight amount. As at this dissociation the value of a is greatly increased ($10° \sqrt{a_c}$ becomes 40 per Gram-atom of the isolated atoms as against 10 in the double molecules), the calculation (which we shall give in the second part of this paper) shows that, even in case of a slight degree of this dissociation, in the formula a pretty large factor will appear for T_c on account of the large value of da/dx, which will increase the value of T_c by about 30 %, and can consequently raise the value of p_c to *more than four times* the amount of the original value (Cf. also § 8).

Hence it is not because in consequence of this slight degree of dissociation x the value of a_c itself is appreciably increased, and consequently T_c and p_c (which are both proportional to a_c) are likewise increased in the same degree (for this the increase of a_c at so slight a degree of dissociation is much too small) — but because in consequence of this dissociation, *in connection with the very high value of* da/dx, the formula which expresses T_c in a_c obtains a *factor* that is a function of x and da/dx, and through which T_c is increased by the said amount of e.g. 30 %, even though the dissociation of the double molecules is only slight. And *in consequence* of this factor in T_c the formula for

$$p_c = \frac{RT_c}{v_c - b_c} - \frac{a_c}{b_c}$$

will undergo such a modification that p_c is not increased by 30 %, but by more than 300 %.

Thus the extraordinary circumstances connected with the critical temperature and pressure of mercury have induced me to extend my former theory concerning the critical quantities on association [1]) for the special very important case that a is considerably increased

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[1]) Arch. Teyler (2) **11**, 3e Partie (1908), p. 1—96; These Proc. **17** (1914), p. 598 We remind the reader that *the mere fact of the dissociation at* T_c (hence $\triangle b$ and $\triangle a = 0$) causes the values of T_c and p_c to increase considerably. Thus we found for $x = 1/3$ already an increase of 10,6% for T_c; for $x = 1/2$ of 11,5 %, and for $x = 2/3$ of 9,9 % (for $x = 0$ and $x = 1$ the factor is of course $= 1$), i.e. for ideal substances. For "ordinary" substances and for the cases that in the association e.g. $\triangle b$ is not $= 0$, these amounts are considerably increased. And as regards p_c, these

in consequence of the dissociation of the double molecules. According to my recent investigations, this case is met with everywhere where the dissociation (as for Hg_2) leads to *free atoms*, for which the increased attractions of valency are so enormously much greater than for the compounds [1]).

4. Vapour Pressures and Values of the Vapour Densities D_2.

We shall start with the treatment of the experimental material known at present. To supplement this, it is however necessary approximately to know the values of D_2 (the density of the saturate vapour). But for this purpose first the values of the vapour pressures must be known in approximation.

When the critical temperature is assumed $= 1427°$ C. $= 1700°$ abs., and $p_c = 1100$ atm., then follows from the known formula

$$ log \frac{p_c}{p} = f\left(\frac{T}{T'} - 1\right) $$

at $100°$, $200°$, $300°$, $500°$, $700°$ and $880°$ C., where p resp. $= 0,28$ mm., $17,2$ mm., 246 mm., 8 atm., 50 atm. and 162 atm. [2]):

$$ f_{10} = 1,82 \quad 1,81 \quad 1,80 \quad 1,78 \quad 1,80 \quad 1,75. $$

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increases become resp. 47,7, 54,3 and 47,6 % for ideal substances with the same values of x. Hence already on an average 50 % between $x = 1/3$ and $x = 2/3$, which amount is still *considerably increased* for ordinary substances, and for the case that $\angle b$ is not $= 0$.

But when besides $\triangle a$ is so enormously large as in mercury e.g. (formerly we always supposed $\triangle a = 0$, because we had only to do with substances that do not appear as isolated atoms with the so greatly increased attractions of valency), T_c and especially p_c is increased in a still *much greater degree*, even though the value of x be only slight.

[1]) These Proc. **18—21**; especially **21** (1918), p. 644. Cf. also Z. f. anorg. Ch. **104**, 56—156 (1918) and J. d. Ch. Ph. **16** (1918), p. 411.

[2]) $p_c = 1150$ atm. instead of 1100 atm. would give 1,83 for the first value of f, 1,80 for the last, which would render the almost constant course of this quantity still slightly better. The more p_c is assumed to be below 1100 atm., the greater the unjustifiable decrease of the f-values on rise of the temperature. The value of 1100 atm. is therefore to be regarded as a minimum, and p_c will sooner be found somewhat greater than this amount than smaller. We remind that the course of the values of f is a strict criterion for the determination of the critical pressure. For in the neighbourhood of the critical temperature these values always increase on rise of temperature; for ordinary substances there is a minimum at about $T = 3/4 T_c$; for substances as He, H_2, etc., where a continually decreases instead of increasing at falling temperature, f will also continue to decrease from T_c to lower temperatures, without passing through a minimum. (Cf. also Recueil des Tr. Ch., N⁰. 3 and 5 of 1920).

With $f_{10} = 1,8$ ($f = 4,14$)[1]) and $p_c = 1100$ atm. the following values are further calculated for the temperatures above $880°$ C.

$$ 900° \quad 1000° \quad 1100° \quad 1200° \quad 1300° \quad 1400° \quad 1427° \text{ C.} $$
$$ p = 171 \quad 274 \quad 410 \quad 581 \quad 787 \quad 1029 \quad 1100 \text{ atm.} $$

We can now easily calculate the values of D'_2 from the subjoined values of the vapour pressures, on the supposition that the vapour is and remains monatomic, and besides continues to follow the laws of the ideal gases.

t	p	D_2' (calc.) (ideal)	D_2 (found)	$\dfrac{D_2 \text{ (found)}}{D_2' \text{ (ideal)}}$
100° C.	0,28 mm.	0,0000	—	—
200°	17,2 "	0,0001	—	—
250°	74,1 "	0,0005	—	—
300°	246 "	0,0014	—	—
350°	670 "	0,0034	—	—
400°	2,06 atm.	0,0076	—	—
500°	8,0 "	0,0253	—	—
600°	22,3 "	0,0624	—	—
700°	50 "	0,126	—	—
800°	102 "	0,232	—	—
900°	171 "	0,356	—	—
1000°	274 "	0,526	0,55	1,05
1100°	410 "	0,730	0,80	1,10
1200°	581 "	0,964	1,15	1,19
1300°	787 "	1,222	1,65	1,35
1400°	1029 "	1,503	2,60	1,73
$T_c = 1427°$	$1100 = p_c$	1,581	$(4,15) = D_c$	2,62

The "found" values of D_2 have been graphically interpolated from the following values of D_2, determined by Miss BENDER.

$$ 1050° \quad 1210° \quad 1230° \quad 1295° \quad 1330° \quad 1380° \text{ C.} $$
$$ D_2 = 0,70 \quad 1,15 \quad 1,35 \quad 1,65 \quad 1,90 \quad 2,50 $$

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[1]) It appears from this value of f that — at least at temperatures below 1000° C. — mercury behaves almost as an ideal substance (for them $f_c = 4$, and $f < 4$ below T_c).

The "calculated" values of D_2 have been determined from $v_2 = RT : p$ for 1 Gr. atom, hence $v_2 = \dfrac{RT}{p \times M} \times 22415 \text{ cm}^3$ for 1 Gr., when p is given in atm. and $R = 1 : 273.1$. Hence we have:

$$D'_2 = \frac{p}{T} \times \frac{200,64}{22415 : 273,1} = \frac{p}{T} \times \frac{200,64}{82,08} = \frac{p}{T} \times 2,444.$$

It appears from the value at 1000° that at this temperature the vapour is still mon-atomic, and the deviation from the law of BOYLE is still very slight. The deviation increases more and more, and close to the critical temperature the vapour will be almost bi-molecular like the liquid. As D (calc.) : D (found) is about 2,6 at T_c, the deviation from the law of MARIOTTE would be there about $2,6 : 2 = 1,3$. In an ideal substance $s = 2,67$; in an ordinary substance $s = 3,8$ to 4. We see therefore, that the normal value of s is very considerably decreased in consequence of the greatly increased value of p_c through the small dissociation of the double molecules at T_c. Also the values of v_c and T_c are modified by this, but not in the same degree as p_c. The result is accordingly that, whereas p_c is more than four times greater than the normal value in case of non-dissociation of the double molecules, s will be about 3 times smaller than the normal value 3,8 to 4, i.e. 1,3.

We shall discuss this more at length in § 8.

5. The values of D_1 and $D_1 + D_2$.

We now proceed to the values of D_1, i.e. those of the liquid densities. At the same temperatures (to which three more temperatures below 100° C. have been added) the following values are found. The "found" values of $D_1 + D_2$ (see table following page) have been obtained by addition of the above found values of D_2 to those of D_1.

The "found" liquid densities D_1 above 350° C. are graphically interpolated from the following values determined by Miss BENDER.

500° 600° 800° 900° 1000° 1100° 1130° 1200° 1270° 1320° C.
$D_1 = 12,5$ 12,15 11,6 11,15 10,55 10,0 9,40 8,85 8,25 7,8

As regards the "calculated" values of $D_1 + D_2$, they were calculated from 0° to 350° from

$$D_1 + D_2 = 13,5956 - 0,0024507\, t + 0,0_6 2089\, t^2, \quad . \quad . \quad . \quad (a)$$

in which the coefficients of t and t^2 were calculated from the observations at 150° and 300° C. The calculated and the found

t	D_1 (found)	D_2 (found)	$D_1 + D_2$ (found)	$D_1 + D_2$ (calc.)
(trip.) — 38°,85 C.	13,6902	—	13,6902	13,6911
0°	13,5956	—	13,5956	13,5956
50°	13,4733	—	13,4733	13,4736
100°	13,3524	—	13,3524	13,3526
150°	13,2327	—	13,2327	13,2327
200°	13,1139	(0,0001)	13,1140	13,1138
250°	12,9957	(0,0005)	12,9962	12,9960
300°	12,8778	(0,0014)	12,8792	12,8792
350°	12,7640	(0,0034)	12,7674	12,7635
400°	12,65	(0,008)	12,66	12,66
500°	12,425	(0,025)	12,45	12,45
600°	12,18	(0,06)	12,24	12,24
700°	11,90	(0,13)	12,03	12,03
800°	11,60	(0,23)	11,83	11,80
900°	11,15	(0,36)	11,51	11,48
1000°	10,55	0,55	11,10	11,12
1100°	9,90	0,80	10,70	10,69
1200°	9,00	1,15	10,15	10,15
1300°	7,80	1,65	9,45	9,46
1400°	6,00	2,60	8,60	8,58
1427°	$(4,15) = D_c$	$(4,15) = D_c$	(8,30)	8,30

values are in good concordance with each other; at 350° a small deviation begins to appear. At — 38°,85 the deviation is still exceedingly slight. The fictitious value D_0 at the absolute zero ($t = -273°,1$ is found $= 14,2804 = 14,28$ (if the mercury were still liquid then).

For temperatures above 350° C. another term must be added to the above formula. As this formula yields somewhat too small values from 400° to about 835°, and on the other hand to an ever increasing degree too large values above 835°, the term

$$16,4 . 10^{-6} \left(\frac{t}{100}\right)^4 \left[8,35 - \frac{t}{100}\right]^{2/3} . \quad . \quad . \quad . \quad (b)$$

has been added to (a) from 400°. [1] The calculation teaches that the deviations from the found values are least, when the exponent of the first factor (viz. $t:100$) amounts to 4, and that of the second factor to $^2/_3$. Every modification in one of the exponents immediately gives not only greater, but *much* greater deviations. [2] Here follows a survey of the values of the two parts (a) and (b), from 400° C.

	(a)		(b)		
400° C.	12,6486	+	0,0112	= 12,6598 =	12,66
500°	12,4225	+	0,0230	= 12,4455 =	12,45
600°	12,2004	+	0,0376	= 12,2380 =	12,24
700°	11,9825	+	0,0490	= 12,0305 =	12,03
800°	11,7687	+	0,0334	= 11,8021 =	11,80
900°	11,5592	−	0,0807	= 11,4785 =	11,48
1000°	11,3538	−	0,2290	= 11,1248 =	11,12
1100°	11,1526	−	0,4598	= 10,6928 =	10,69
1200°	10,9557	−	0,8063	= 10,1494 =	10,15
1300°	10,7627	−	1,3050	= 9,4577 =	9,46
1400°	10,5740	−	1,9985	= 8,5755 =	8,58
1427°	10,5238	−	2,2254	= 8,2984 =	8,30

The first table shows clearly that the thus calculated values are in perfect concordance with the found values. As we have calculated the coefficient $16,4.10^{-6}$ of the correction term (b) exclusively from observations up to 1300° (inclusive), the agreement at 1400° C. is the more valuable. We may, therefore, safely assume the calculated value $8,30:2 = 4,15$ to be accurate for the critical density.

6. The Value of $D_1 - D_2$ near T_c and that of γ at different Temperatures.

We have another means to control the approximate correctness of the values of D_1 and D_2, e.g. above 900°, and of that of the

[1] Below 400° the correction term (b) is no longer valid. For 300° it would yield + 0,0041; for 200° + 0,0009 and for 100° + 0,00006, which values are too great.

[2] We point out that the exponent $^2/_3$ is assumed not to influence the sign of $8,35 - t/_{100}$, so that this remains negative for $t > 835°$.

assumed critical temperature (1427° C.), viz. in the empirical law that below T_c (not *immediately* below T_c, however, where $D - D_2 \because \sqrt{1-m}$), the equation

$$D_1 - D_2 = C \sqrt[3]{1-m}$$

holds in approximation, so that $(D_1-D_2)^3$ is proportional to $1-m$, i.e. to $T_c - T$ $(m = T : T_c)$. Now we get the following table

	1000°	1100°	1200°	1300°	1400°
$D_1 - D_2 =$	10,0	9,1	7,85	6,15	(3,40)
$(D_1-D_2)^3 =$	1000	754	484	233	(39)

so that the four first values of $(D_1-D_2)^3$ are roughly to each other as $4:3:2:1$, which would give the value 1400° C. for T_c.

The corresponding values of $(D_1-D_2)^2$ are to each other as $100:83:62:38$ (: 11,6), i.e. as $5:4:3:2$ about, which would point to $T_c = 1500°$ C. And as (except close to T_c) the $\sqrt[3]{}$-law is sooner fulfilled than the $\sqrt[2]{}$-law, T_c will lie nearer to 1400° than to 1500° — in concordance, therefore, with our assumption (1427°). A critical temperature higher than 1500°, as would follow from a few values recorded by Miss BENDER, is in my opinion in conflict with her own observations concerning D_1 and D_2. When the two last values of $(D_1-D_2)^2$, viz. 38 and 11,6 are taken as criterion of the $\sqrt[2]{}$-law, holding theoretically near T_c, then the value of about 1440° C. would follow from this for T_c.

Let us now examine the (reduced) coefficient of direction of the so-called straight diameter. For the total course between the absolute zero and the critical temperature evidently $2(1-\gamma) = 14,28 : 4,15 = 3,44$ is found, hence $1 + \gamma = 1,72$, $\gamma = 0,72$. But this amount can only be assigned to the last piece between 1000° C. and T_c, where — in consequence of the increasing association in the vapour-phase — the straight diameter after its almost linear course between — 40° and + 1000° C. suddenly begins to show an appreciable curvature towards the side of the large volumes.

As regards the said part below 1000° (where the vapour phase is still absolutely without influence), we find there e.g. between 0° and 300° C. :

$$2\gamma = \frac{13,5956 - 12,8792}{300} \times \frac{1700}{4,15} = 0,9782,$$

hence $\gamma = 0,489 = 0,49$.

And between 0° and 1000° C.:

$$2\gamma = \frac{13,5956 - 11,1248}{1000} \times \frac{1700}{4,15} = 1,012,$$

hence $\gamma = 0,506 = 0,51$, almost equal to the value between 0° and 300° C. The value $\gamma = 0,5$ is that which is due to "ideal" substances with a and b invariable (chiefly b no function of v). We saw above that below 1000° C. also the value of f (viz. 4,1) points to the quasi-ideal behaviour of mercury at those comparatively lower temperatures.

7. General Formulae for v_c, T_c, p_c and s.

When v_c is the critical volume (expressed in normal units) of 1 Gr. atom, then

$$D_c = \frac{200,64}{22415\, v_c},$$

hence with $D_c = 4,15$:

$$v_c = rb_c = \frac{200,64}{22415 \times 4,15} = 0,002157 \quad . \quad . \quad . \quad (1)$$

Accordingly the value of b_c with given D_c will only depend on r. If e.g. $r = 2$, then b_c would be $= 108.10^{-5}$, but if r should be $= 1,8$, b_c would become $= 120.10^{-5}$.

For T_c holds the relation $RT_c = \frac{8}{27}\frac{a'_c}{b'_c} \times \theta$, hence

$$RT_c = \frac{8}{27} n \frac{a_c}{b_c} \times \theta, \quad . \quad . \quad . \quad . \quad . \quad (2)$$

in which a_c and b_c refer to 1 Gr. atom (200,6 Gr. mercury), so that in reality $a'_c = n^2 a_c$ and $b'_c = nb_c$, when $n = 2 : (1 + x)$ represents the factor of association [1].

In normal cases $(n = 1$ or $2)$ θ is a factor somewhat smaller than unity, which we before represented by λ. (If e.g. $r = 2$, we find for λ the value $^{27}/_{28}$, whilst for ideal substances $(r = 3)$ λ becomes $= 1$).

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[1] From 1 single molecule (or atom) $= \frac{1}{2}$ double molecule $\frac{1}{2}(1 - x) + \frac{1}{2}(2x) = \frac{1}{2}(1 + x)$ molecules arise on dissociation of the double molecule. These molecules occupy the molecular volume b_c (leaving contraction out of account; this has been reckoned with in the factor θ), so that every molecule on an average occupies the volume $b'_c = b_c : \frac{1}{2}(1 + x) = b_c \times 2 : (1 + x)$. If the degree of dissociation x of the double molecules $= 0$, then $n = 2 : (1 + x) = 2$, hence $b'_c = 2b_c$ (all the molecules are then double molecules). And when $x = 1$ (all the molecules single), then $n = 1$ and $b'_c = b_c$. And the same thing holds with regard to Va and v.

But in all cases of association $(n > 1 < 2)$ θ will be a function of x, and besides of the contractions Δb and ΔVa, if they exist. As we stated above, this factor can become pretty large, e.g. 1,3. From $p_c = \frac{RT_c}{v'_c - b'_c} - \frac{a'_c}{v'^2_c}$ after substitution of the above-mentioned value of RT_c, and of $v'_c = nv_c$, $b'_c = nb_c$, $a'_c = n^2 a_c$, we find for p_c:

$$p_c = \frac{1}{27}\frac{a_c}{b_c^2}\left[\frac{8\theta}{r-1} - \frac{27}{r^2}\right] = \frac{1}{27}\frac{a_c}{b_c^2} \times \pi, \quad . \quad . \quad . \quad (3)$$

when besides rb_c is substituted for v_c. Then with $r = 2$ the factor π becomes therefore $= \frac{8 \times {}^{27}/_{28}}{1} - \frac{27}{4} = 27 \times \left(\frac{2}{7} - \frac{1}{4}\right) = \frac{27}{28}$, just as θ, the factor of RT_c — i.e. in the normal cases $(n = 1$ and $2)$. And if then $r = 3$, in which $\theta = 1$, then π becomes also $= \frac{8}{2} - \frac{27}{9} = 1$.

But for $n > 1 < 2$ π will again be a function of x, Δb and ΔVa, and in general much greater than θ. If e.g. $\theta = 1,363$ (see § 8), $r = 2$, then π becomes $= 10,91 - 6,75 = 4,16$, so that π is more than three times as great as θ. The critical pressure will then be $4,16 \times \frac{28}{27} = 4,3$ times greater than the normal value for $r = 2$, when there is no association, in which case $\pi = \theta = \lambda = {}^{27}/_{28}$ [1]).

From (1), (2) and (3) the following equation follows now further with $v'_c = nv_c = n \times rb_c$:

$$s' = \frac{RT_c}{p_c v'_c} = \frac{8}{r} \times \frac{\theta}{\pi}, \quad . \quad . \quad . \quad . \quad . \quad (4)$$

in which $s' = s : n$ (where s refers, therefore, to v_c per Gr. atom). Now we do not find $rs' = 8$ as in normal cases — but

$$rs' = 8 \times \frac{\theta}{\pi}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (4a)$$

in which $\theta : \pi$ can be $^1/_3$ in some cases (see above). In consequence of this s' may be reduced from 4 (the normal value for $r = 2$) to $4 : 3 = 1,3$, i.e. to the *third* of this normal value. (See the table in

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[1] We found before that in normal cases $\theta = \pi$. Then $\theta = \frac{8\theta}{r-1} - \frac{27}{r^2}$, from which $\lambda = \theta = \frac{{}^{27}/_{r^2}}{8 : (r-1) - 1}$. When in this $(1 + \gamma) : \gamma$ is substituted for r, in which γ represents the reduced coefficient of direction of the straight line between D_c and $\frac{1}{2} D_0$ in a D,T-diagram, we find back $\lambda = \frac{27}{8\gamma - 1}\left(\frac{\gamma}{\gamma + 1}\right)^2$, the formula derived by me, yielding $\lambda = 1$ for $r = 3$ $(\gamma = 0,5)$ and $\lambda = {}^{27}/_{28}$ for $r = 2$ $(\gamma = 1)$.

§ 4, in which we found for D_c (found) : D_c (MARIOTTE) the value $2,62 : 2 = 1,31$, when n is practically $= 2$ at T_c. The great decrease of s' is, therefore, almost exclusively owing to the exceedingly great increase of p_c with comparatively little changed value of T_c and of v_c. (the latter in consequence of a slight modification in the value of r).

8. Calculation of θ and π, and of a_c and b_c from the given Values of T_c, p_c and v_c.

If $T_c = 1700$ (abs.), $p_c = 1100$ (atm.), and $v_c = 215,7 . 10^{-5}$ according to (1), we find for $s' = s : n$ the value (cf. also the table in § 4; on the supposition, therefore, that n at T_c is not far from 2):

$$s' = \frac{1700 : 273,1}{1100 \times 215,7.10^{-5}} : 2 = 1,312 \quad . \quad . \quad . \quad . \quad (a)$$

From (4^a) follows for θ, the coefficient of RT_c, from

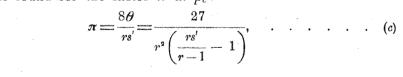$$rs' = \frac{8\theta}{\dfrac{8\theta}{r-1} - \dfrac{27}{r^3}}$$

the value

$$\theta = \frac{27}{8r^2\left(\dfrac{1}{r-1} - \dfrac{1}{rs'}\right)} = \frac{27\,s'}{8r\left(\dfrac{rs'}{r-1} - 1\right)} \quad . \quad . \quad . \quad (b)$$

With $s' = 1,312$ we find from this the following values for different values of r.

$r =$	2	1,9	1,8	1,7	1,6	1,5
$\theta =$	1,363	1,317	1,260	1,191	1,108	1,005

The factor θ becomes, therefore, smaller as r is assumed smaller, which also follows immediately from the formula (b), if only $r < 3,05$, which is of course always the case. It also appears from (b) that θ becomes smaller, if n should be < 2, for then $s' = s : n$ becomes greater.

Then is found for the factor π at p_c:

$$\pi = \frac{8\theta}{rs'} = \frac{27}{r^2\left(\dfrac{rs'}{r-1} - 1\right)}, \quad . \quad . \quad . \quad . \quad (c)$$

yielding

$r =$	2	1,9	1,8	1,7	1,6	1,5
$\pi =$	4,156	4,226	4,268	4,274	4,222	4,087

Hence the factor π increases with decreasing r, as long as r remains $> 1,74$ ($\pi = 4,277$). For smaller values of r π decreases again.

As $\theta = 1,36$ is rather great, $r = v_c : b_c$ will probably lie in the neighbourhood of 1,8 or 1,7 for mercury at the critical temperature [as we shall see from the theoretical concluding part of this paper, this decrease is also a consequence of the degree of dissociation, however small, of the double molecules at T_c, as soon as Δa is great]. Then θ is 1,2 or 1,25 and π in the neighbourhood of its maximum value 4,28.

Let us now examine the values of a_c and b_c, corresponding to the assumed critical data $T_c = 1700°$ abs., $p_c = 1100$ atm., $v_c = 215,7$. $.10^{-5}$) for different values of r.

From $RT_c v_c = \frac{8}{27} n r a_c \times \theta$ follows $a_c = \frac{27}{8} RT_c v_c : n r \theta = \frac{27}{8} \times$ $\times 134,3.10^{-4} : n r \theta$, so that $\overline{10^4 a_c = 226,6 : r\theta}$, when $n = 2$.

With regard to b_c we have simply $b_c = v_c : r$; hence $\overline{10^5 b_c = 215,7 : r}$. This gives the following values of a_c and b_c.

$r =$	2	1,9	1,8	1,7	1,6	1,5
$10^5\, b_c =$	107,9	113,5	119,8	126,9	134,8	143,8
$10^4\, a_c =$	83,13	90,57	99,91	111,9	127,8	150,3
$10^2\, \sqrt{a_c} =$	9,12	9,52	10,00	10,58	11,30	12,26

We see from this that with $r = 1,8$ — in harmony with the slight degree of dissociation corresponding to the increased critical pressure and temperature — the values $10^5 b_c = 120$, $10^4 a_c = 100$ (per Gr.atom) are about corresponding. $\sqrt{a}$ is then somewhat smaller than the value determined from the mercury halogenides at about $1000°$ C., viz. $10 . 10^{-2}$ instead of $11 . 10^{-2}$.

By the aid of these values of a_c and b_c we shall now calculate back the values of T_c and p_c by way of check on *two* suppositions.

In the *first place* that mercury were *not* dissociated at the critical temperature, i.e. consisted merely of double molecules ($x = 0, n = 2$). If we then suppose that $r = 2$, we should get in this case $v_c = rb_c = 2 \times$ $\times 119,8.10^{-5} = 239,6 . 10^{-5}$ (per Gr.-atom). Further $RT_c = \frac{8}{27} \times 2 \times$ $\times \frac{99,91.10^{-4}}{119,8.10^{-5}} \times \frac{27}{28}$, as $\theta = \lambda = 27/28$ corresponds to $r = 2$ (see above); hence $RT_c = 4,766$, $\underline{T_c = 1302°}$ abs. The following equation is then found for p_c:

$$p_c = \frac{1}{27} \times \frac{99,91 \cdot 10^{-4}}{143,5 \cdot 10^{-8}} \times \frac{27}{28} = 248,6 = \underline{249 \text{ atm.}}$$

With the now assumed values of a_c and b_c these would be the values of the critical temperature and pressure of perfectly undissociated Hg_2 at the critical point. They would give for $s' = RT_c : p_c v'_c$ with $v'_c = 2 v_c$ the value $s' = \dfrac{4,766}{248,6 \times 479,2 \cdot 10^{-5}} = \underline{4,00}$, which value properly corresponds to $r = 2$.

The equation of state is, of course, also identically satisfied. For $\dfrac{a_c}{v_c^2}$ is calculated $\dfrac{99,91 \cdot 10^{-4}}{574,1 \cdot 10^{-8}} = 1740$ atm., so that $v'_c - b'_c = RT_c :$ $: (p_c + a_c/v_c^2)$ becomes:

$$2 (239,6 - 119,8) 10^{-5} = \frac{4,766}{248,6 + 1740,3},$$

i.e. $\qquad\qquad 239,6 \cdot 10^{-5} = 239,6 \cdot 10^{-5}.$

We may state here that a_c/v_c^2 is also properly $= (f_c - 1) p_c = 7p_c$, because $f_c = 8$ corresponds to $r = 2$.

But all these values are totally changed, when only, in the *second* place, the slightest dissociation of the double molecules exists at T_c, (which we shall further develop theoretically in the second part of this paper).

Let us suppose for convenience that then n remains $= 2$ (x will possibly be 0,01, so that strictly speaking $n = 2 : (1 + x)$ would become 1,98, but in the calculation of θ and π above we have also left $n = 2$), and further that in this case in consequence of the slight dissociation at T_c the value of r would have become 1,8 instead of 2 (this too will be further elucidated in the second part); then v_c becomes $= 1,8 \times 119,8^3 \cdot 10^{-5} = 215,7 \cdot 10^{-5}$. Further with $\theta = 1,260$ and $\pi = 4,268$ (see above) $\overline{RT = 6,228}$, $\overline{T = 1700 \text{ abs.}}$, $\underline{p_c = 1100 \text{ atm.}}$, all of them being the values from which we have started for the calculation of the factors θ and π, and which will give back the value 1,312 for $s' = \dfrac{6,228}{1100 \times 431,4 \cdot 10^{-5}}$.

Accordingly the value of T_c has become $\dfrac{28}{27} \times 1,26 = \underline{1,31}$-times greater, that of p_c $\dfrac{28}{27} \times 4,268 = \underline{4,43}$-times greater, and that of s' $\underline{3,05}$-times smaller.

The equation of state becomes in this case:

$$2 (215,7 - 119,8) 10^{-5} = \frac{6,228}{1100 + 2147}, \text{ or } 192.10^{-5} = 192.10^{-5}.$$

Now a_c/v_c^2 is no longer $= 7 p_c$, but only slightly less than $2p_c$.

In the above discussion we have always supposed n in the neighbourhood of 2. It might, however, be asked, how high e.g. T_c might become, if n was in the neighbourhood of 1. As $\sqrt{a_c}$ would then be $= 40.10^{-2}$ (increased attraction of the isolated atoms) instead of 11 à $10 \cdot 10^{-2}$, we should get (b remaining $= 120 \cdot 10^{-5}$):

$$T_c = 273,1 \times \frac{8}{27} \lambda \frac{1600.10^{-4}}{120.10^{-6}} = 80,92 \lambda \times 133,3 = \text{ about } 10000° \text{ abs.},$$

whereas in reality T_c will certainly not be far from 1700° abs. Total dissociation of Hg_2 into $Hg + Hg$ is, therefore, impossible at the critical point. Only a value of x in the neighbourhood of 0 (n in that of 2) can represent the critical quantities as determined experimentally.

In this first paper we have only specified the experimental data known at present more closely, and drawn from them all the consequences to which these data gave occasion. *If* really $v = 216 \cdot 10^{-5}$, $T_c = 1700°$ abs. and $p_c = 1100$ atm. — and there is no longer any doubt that this will appear to be the case approximately — *then* belong to the values of r mentioned in § 8 the values of θ and π placed under them, viz. the factors for RT_c and p_c in consequence of the small degree of association at T_c in connection with the very great value of $\Delta\sqrt{a}$. And this on the strength of the relations derived in § 7, which are of general validity.

But this is only the foundation of our real task. *To supplement our former theory of the critical quantities on association,* we must now examine *theoretically* what follows, in the case of such great values of $\Delta\sqrt{a}$ on dissociation, from $\dfrac{dp}{dv} = 0$ and $\dfrac{d^2p}{dv^2} = 0$, and derive the relations which are valid for $r = v_c : b$, and also for θ, the factor of T_c — all in function of the degree of dissociation x and of $\Delta\sqrt{a}$. Then the value of π, the factor of p_c, is known at the same time.

And then we shall also be able, on account of the found formulae for r and θ, to define more closely the values of them; which was not yet entirely possible in this paper, because the choice between different values of r had still remained open.

La Tour près Vevey, spring 1920. *To be continued.*