will take place also when we bring these tissues into such a large quantity of liquid i, that the composition of this liquid will practically change only a little.

We may imagine also that the wall of a space partly loses its elasticity through some influence or other; then this wall will put a smaller pressure on the liquid at the same volume; we may imagine also that at the same time the change in the permeability of the membrane discussed above, occurs as well. A closer consideration of these cases is left to the reader.

(To be continued).

Leiden, Lab. of Inorg. Chemistry.

Chemistry. — *The Exact Measurement of Specific Heats at Higher Temperatures. XI. On the Variability of the Specific Heats of Fused and Solidified Silver under different Circumstances.* By F. M. JAEGER, E. ROSENBOHM and W. A. VEENSTRA.

(Communicated at the meeting of March 25, 1933).

§ 1. In the course of our previous work on the specific heats of stabilized and preliminarily worked metals, some unexplained pecularities in the behaviour of fused and solidified *silver*[1] were observed, which made it desirable again to study this metal at higher temperatures more in detail. On repeating our measurements of the mean specific heats $\bar{c}_p$ with a lump of silver B fused and solidified in air[2]), but being afterwards preserved at room-temperature during five or six months, — the remarkable fact was stated that all values of $\bar{c}_p$, measured by means of the same instrument as formerly used, proved to be *appreciably diminished*. The deviations from the values previously found were in all cases much greater than could be accounted for by the possible experimental errors (see curve B' in Fig. 1). Originally we thought that the stabilized lump of silver, by its long preservation at room-temperature had, in some way or other, returned to a less stable condition, — such as, for instance, was met with in the case of cold-plated and laminated silver (curve P in Fig. 1). Soon,

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[1]) F. M. JAEGER, E. ROSENBOHM and J. A. BOTTEMA, Proceed. R. Acad. Sciences Amsterdam, **35**, (1932), 768; Recueil d. Trav. d. Chim. Pays-Bas, **52**, (1933), 74; conf. Note [13]) at the bottom of page 77, loco cit., on the more rapid increase of $\bar{c}_p$ above 600° – 700° C.

[2]) On page 74, loco cit., it was erroneously mentioned, that the lump of silver used was fused and solidified "in a vacuum": really it occurred *in air*.

however, it became clear to us, that here the situation was quite another one, as may be concluded from the following series of experiments.

Two lumps of silver, fused and solidified *in air*, yielded values of $\bar{c}_p$, which, — within the limits of experimental error, — proved to be identical with those formerly observed in the case of the original mass (conf. curve C in Fig. 1). But if these lumps were remelted and solidified *in a perfect vacuum*, the values of $\bar{c}_p$ at each temperature now proved, — also within the limits of experimental error, — to be *the same* as those obtained in the case of the lump of silver B′, which had been preserved during six months (conf. the curve C′ in Fig. 1). On the other hand, if this last mentioned lump of silver was, in its turn, heated *in air* at 940° C. for 5 or 10 hours, it again yielded values of $\bar{c}_p$, which were the higher, the longer its heating in air was continued (see curves *aa*′ and *bb*′ in Fig. 1). The limits of experimental error in all these experiments never surpassed 0.1—0.2 % of
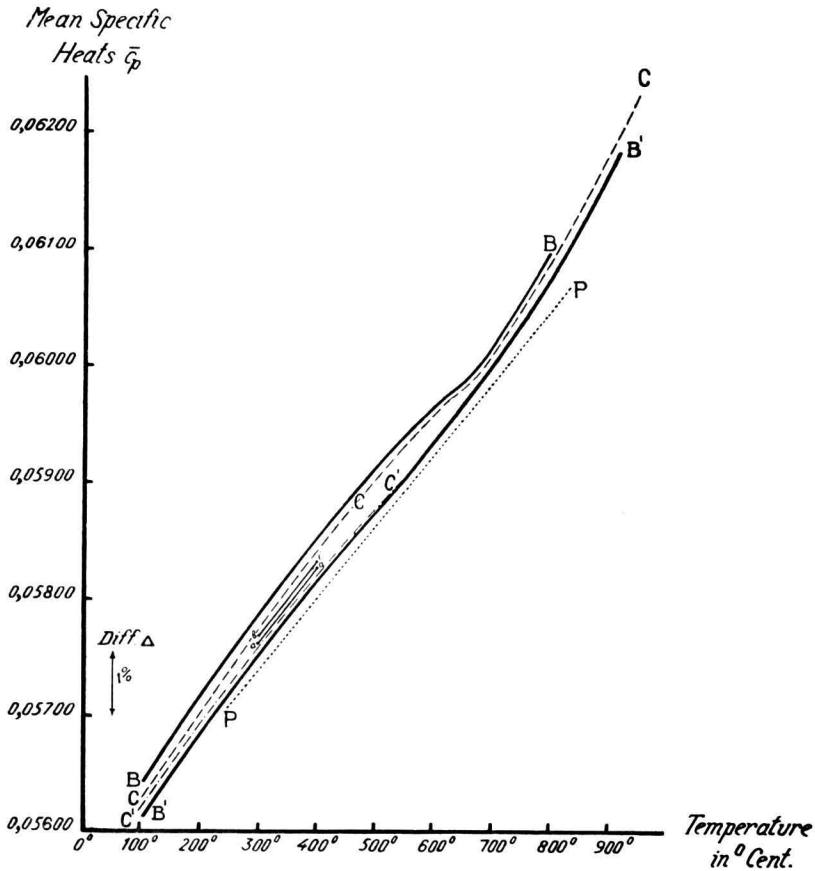
Silver: *B* Original Lump, fused and solidified in Air; *B*′ The same Lump, preserved 5 or 6 Months; *C* Lump of Silver recently fused and solidified in Air; *C*′ The same, fused and solidified in a Vacuum; *aa*′ and *bb*′, both *B*′, after heating at 940° C. in Air during 5, resp. 10 hours; *P* cold-plated and laminated Silver.

Fig. 1. Mean Specific Heats of Silver in Different Circumstances.

TABLE I.

Quantities of Heat developed Q_0 and Mean Specific Heats $\bar{c}_p$ between $t°$ and $0°$ C. for Silver under Different Conditions.

| Temperature t in °C.: | Original Lump of Silver B: | | The same Lump B', after having been preserved at room-temperature during several months: | | Lump of Silver C melted and solidified in Air: | | The same Lump C' after being remelted and solidified in a Vacuum: | | The Lump of Silver B' after being heated at 940° C. in Air. | | | | Cold plated and laminated Silver P heated in Vacuum: | |
| | | | | | | | | | During 5 hours: | | During 10 hours: | | | |
	Q_0 in Calor. pro Gr.:	$\bar{c}_p$	Q_0 in Calor. pro Gr.:	$\bar{c}_p$:	Q_0 in Calor pro Gr.:	$\bar{c}_p$	Q_0 in Calor. pro Gr.:	$\bar{c}_p$:	Q_0 in Calor. pro Gr.:	$\bar{c}_p$:	Q_0 in Calor. pro Gr.:	$\bar{c}_p$:	Q_0 in Calor. pro Gr.:	$\bar{c}_p$:
99.659	—	—	—	—	5.612	0.05628	—	—	—	—	—	—	—	—
99.766	—	—	—	—	—	—	5.608	0.05621	—	—	—	—	—	—
99.934	—	—	—	—	5.625	0.05631	—	—	—	—	—	—	—	—
100.045	—	—	—	—	—	—	5.628	0.05626	—	—	—	—	—	—
100.41	—	—	5.634	0.05611	—	—	—	—	—	—	—	—	—	—
100.54	—	—	5.643	0.05613	—	—	—	—	—	—	—	—	—	—
100.87	5.690	0.05641	—	—	—	—	—	—	—	—	—	—	—	—
248.1	14.255	0.05744	—	—	—	—	—	—	—	—	—	—	—	—
295.9	17.115	0.05782	—	—	—	—	—	—	—	—	—	—	—	—
299.40	—	—	—	—	17.294	0.05776	—	—	—	—	—	—	—	—
299.83	—	—	—	—	—	—	—	—	—	—	17.292	0.05767	—	—
299.86	—	—	—	—	—	—	—	—	17.279	0.05762	—	—	—	—
299.98	—	—	—	—	—	—	17.256	0.05751	—	—	—	—	—	—
300.0	—	—	17.264	0.05755	—	—	—	—	—	—	—	—	17.1724	0.05724
300.27	—	—	17.285	0.05756	—	—	—	—	—	—	—	—	—	—
396.86	—	—	—	—	23.182	0.05841	—	—	—	—	—	—	—	—
397.2	23.254	0.05853	—	—	—	—	—	—	—	—	—	—	—	—
397.26	—	—	—	—	—	—	—	—	—	—	23.178	0.05834	—	—
397.3	—	—	23.095	0.05813	—	—	—	—	—	—	—	—	—	—
397.44	—	—	—	—	—	—	23.144	0.05816	—	—	—	—	—	—
397.48	—	—	—	—	23.205	0.05838	—	—	—	—	—	—	—	—
397.64	—	—	—	—	—	—	—	—	23.182	0.05830	—	—	—	—
398.6	—	—	23.178	0.05815	—	—	—	—	—	—	—	—	—	—
420.44	—	—	—	—	—	—	—	—	—	—	—	—	24.496	0.05826
516.5	—	—	—	—	—	—	30.395	0.05885	—	—	—	—	—	—
516.6	—	—	30.438	0.05892	—	—	—	—	—	—	—	—	—	—
628.7	—	—	37.545	0.05972	—	—	—	—	—	—	—	—	37.360	0.05942
629.1	—	—	—	—	—	—	37.571	0.05972	—	—	—	—	—	—
629.15	—	—	—	—	37.606	0.05977	—	—	—	—	—	—	—	—
631.4	—	—	—	—	—	—	—	—	—	—	—	—	37.397	0.05923
634.95	—	—	—	—	—	—	—	—	—	—	—	—	37.802	0.05953
640.0	38.306	0.05984	—	—	—	—	—	—	—	—	—	—	—	—
701.9	—	—	42.271	0.06022	—	—	—	—	—	—	—	—	—	—
749.2	—	—	45.396	0.06059	—	—	—	—	—	—	—	—	—	—
800.7	—	—	—	—	—	—	—	—	—	—	—	—	48.527	0.06060
800.97	—	—	—	—	48.865	0.06101	—	—	—	—	—	—	—	—
801.1	—	—	48.791	0.06090	—	—	—	—	—	—	—	—	—	—
801.2	—	—	—	—	—	—	—	—	—	—	—	—	48.476	0.06050
804.4	49.096	0.06103	—	—	—	—	—	—	—	—	—	—	—	—
849.9	—	—	52.052	0.06124	—	—	—	—	—	—	—	—	—	—
850.87	—	—	—	—	52.254	0.06141	—	—	—	—	—	—	—	—
894.83	—	—	—	—	55.309	0.06181	—	—	—	—	—	—	—	—
895.3	—	—	55.298	0.06176	—	—	—	—	—	—	—	—	—	—
940.3	—	—	—	—	58.553	0.06227	—	—	—	—	—	—	—	—

the values measured; all data obtained are collected in the following table I and graphically represented in Fig. 1.

§ 2. From the experience gathered in this way, it must be concluded, that the variability of the values of $\bar{c}_p$ is immediately connected with a *content of oxygen of the melted and solidified metal.*

The true values of $\bar{c}_p$ for really *oxygen-free,* stabilized silver are the *smaller* ones, represented by the curves B' and C' in Fig. 1, while the *higher* ones (curves B, C and aa' and bb' in Fig. 1) correspond to a mass of the metal which contains a greater or smaller quantity of oxygen, absorbed during the process of fusion in air and evidently partially retained during its solidification, or absorbed by the solid metal heated at 940° C.

TABLE II. Mean specific Heats $\bar{c}_p$ of stabilized, oxygenfree Silver between 0° and 900° C.				
Temperature in 0° C.:	Quantity of Heat Q_0 in Cal. developed by 1 Gr. silver between $t°$ and 0° C.:	Mean specific Heat $\bar{c}_p$ between $t°$ and 0° C.:	$\bar{c}_p$ calculated from Formula I:	$\bar{c}_p$ calculated from Formula II:
100.48	5.639	0.05612	—	—
300.14	17.275	0.05755	0.05752	0.05770
397.4	23.120	0.05818	—	—
516.55	30.416	0.05888	0.05898	0.05893
628.9	37.558	0.05972	—	—
701.9	42.271	0.06022	0.06019	—
749.2	45.396	0.06059	0.06050	0.06054
801.1	48.791	0.06090	0.06083	—
849.9	52.052	0.06124	0.06114	0.06129
895.3	55.298	0.06176	0.06142	—
(940.3)	(58.553)	(0.06227)	—	(0.06238)

The absorption of oxygen by the metal evidently causes an increase of $\bar{c}_p$ at each temperature, which is the more considerable, the greater the quantity is of oxygen absorbed by the solid metal. The most accurate values of $\bar{c}_p$ for *oxygen-free,* stabilized silver between 0° C. and 900° C. are collected in table II. Without any doubt the more rapid increase of the $\bar{c}_p$-*t-curve* above 700° C. and its particular $\sim$-shape, are also connected

with the more accelerated absorption of oxygen by or its diffusion through the heated metal at higher temperatures: all investigations hitherto made [1]) seem to confirm the fact, that *no* allotropic changes of the metal, — at least at higher temperatures, — occur.

Between 0° and about 800° C. the values of $\bar{c}_p$ in table II for pure, *oxygen-free* silver can, in function of the temperature, very well be expressed by the formula:

$$\bar{c}_p = 0,055401 + 0,7207 \cdot 10^{-5} \cdot t - 0,54053 \cdot 10^{-9} \cdot t^2 \quad . \quad . \quad \text{(I)},$$

and the corresponding *true* specific heats, therefore, by:

$$c_p = 0,055401 + 0,14414 \cdot 10^{-4} \cdot t - 0,16216 \cdot 10^{-8} \cdot t^2.$$

This formula can be applied between 0° and about 800° C.: the deviations of the values observed and calculated are all situated within the limits of experimental error. The atomic heats C_p can, therefore, be calculated, — within the same limits of the temperature, — by means of the formula:

$$C_p = 5,9767 + 0,1555 \cdot 10^{-2} \cdot t - 0,17494 \cdot 10^{-6} \cdot t^2.$$

Some values of C_p thus calculated are the following:

Temperature in °C. :	Atomic Heat C_p :
0°	5.977
100	6.130
200	6.281
300	6.427
400	6.571
500	6.710
600	6.847
700	6.979
800	(7.109)

This curve I for C_p is represented in Fig. 2; it may be considered as the *normal* curve for the atomic heats in their dependance on the temperature.

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[1]) J. F. L. HAUSMANN, Abh. Kön. Ges. Wiss. Göttingen, (1850), 4; V. KOHLSCHÜTTER and E. EYDMANN, Ann. d. Chem., **390**, (1912), 340; **398**, (1913), 14; G. W. A. KAHLBAUM, K. ROTH and P. SIEDLER, Zeits. f. anorg. Chem., 29, (1902), 177; W. HAIDINGER, Jahrb. Geol. R. Anst. Wien, 1, (1850), 150; L. VEGARD a.o., conf. *Strukturbericht*, Erg. Bnd. Zeits. f. Kryst. (1931), 36—38, 748. The existence of a rhombic modification in electrolytically precipitated silver: G. ABLARD, Compt. rend. Paris, **187**, (1928), 223, is very dubious.

Just as formerly stated, this curve is *concave* towards the temperature-axis; the values of C_p are right within about $\pm$ 0.5 %. If, however, the abnormally steep change of $\bar{c}_p$ at higher temperatures shall also be taken into account, $\bar{c}_p$ can only be expressed pretty accurately by means of a formula with more than three constants, — for instance, by:

$$\bar{c}_p = 0{,}05355 + 0{,}37946 \cdot 10^{-4} \cdot t - 0{,}15285 \cdot 10^{-6} \cdot t^2 + 0{,}3278 \cdot 10^{-9} \cdot t^3 - \left.\right\} \text{(II)}.$$
$$- 0{,}32422 \cdot 10^{-12} \cdot t^4 + 0{,}1214 \cdot 10^{-15} \cdot t^5 \left.\right\}$$

The true specific heat c_p is, therefore, expressed by:

$$c_p = 0{,}5355 + 0{,}75892 \cdot 10^{-4} \cdot t - 0{,}45855 \cdot 10^{-6} \cdot t^2 + 0{,}13112 \cdot 10^{-8} \cdot t^3 -$$
$$- 0{,}16211 \cdot 10^{-11} \cdot t^4 + 0{,}7284 \cdot 10^{-15} \cdot t^5,$$

and the atomic heat C_p by:

$$C_p = 5{,}7770 + 0{,}81873 \cdot 10^{-2} \cdot t - 0{,}49469 \cdot 10^{-4} \cdot t^2 + 0{,}14145 \cdot 10^{-6} \cdot t^3 -$$
$$- 0{,}17488 \cdot 10^{-9} \cdot t^4 + 0{,}7857 \cdot 10^{-13} \cdot t^5.$$

A series of values of c_p and C_p thus calculated are the following:

Temperature t in °C.	True specific Heats c_p :	Atomic Heats C_p :
350°	0.05966	6.436
400	0.06041	6.517
500	0.06220	6.710
600	0.06377	6.879
700	0.06491	7.003
800	0.06678	7.204
900	0.07276	7.849
950	0.07916	8.540

From the graph (Fig. 2) it becomes clear that, within the limits of experimental error, there is only above 780° C. a more considerable deviation between the two curves I and II: indeed, taking into account the exactness reached in the measurement of $\bar{c}_p$, the uncertainty in c_p is still about 0.5 %, so that both curves I and II may be considered as practically coinciding up to about 800° C. Curve I evidently represents the true values of C_p in function of the temperature between 0° and 800° C.; its shape is the same as that previously found for stabilized silver.

The rapid increase of the curve II above about 780° C. is clearly manifested and certainly must be connected with the absorption of oxygen by the heated metal, as *it exactly begins at the temperature, at which,*

according to TROOST [1]), *the diffusion of oxygen through solid silver sets in with an observable velocity.*
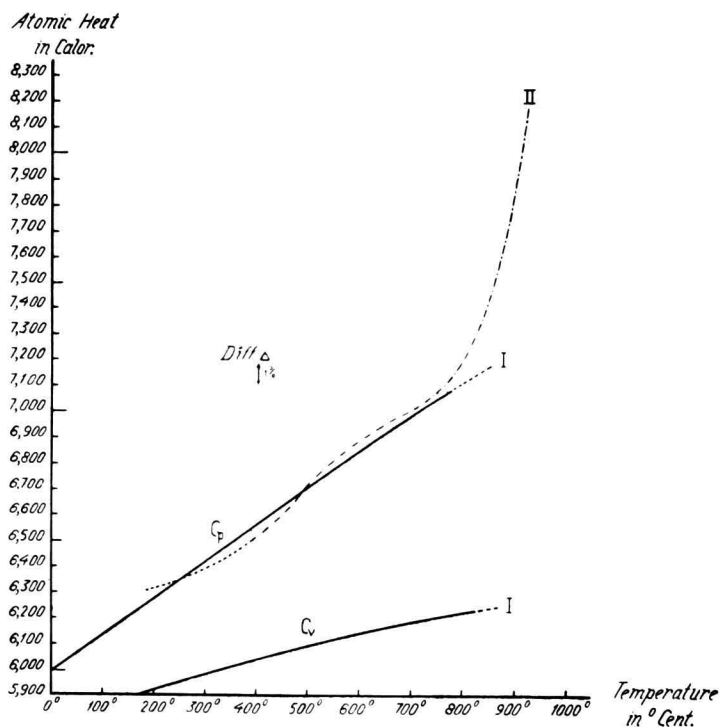

Fig. 2. True Atomic Heats C_p of Oxygenfree Silver.

Above 800° C., therefore, the values of $\bar{c}_p$ determined, evidently have no longer a real significance, as they depend on the accidental way of executing the experiments.

§ 3. The fact that *molten* silver absorbs considerable quantities of oxygen has already been known [2]) since 1819 and also the fact, that, on cooling, the metal gives off the total or the greater part of this oxygen by manifesting the phenomenon of "spitting". As to the question, whether *all* the gas absorbed by the liquid metal is really liberated on cooling and solidifying, there has been much controversy. DUMAS [3]), TROOST [4]) and other investigators stated, that the solidified metal, on heating, still gave off considerable quantities of oxygen; but VAN DER PLAATS [5]), BRAUNER [6])

[1]) L. TROOST, loco cit.

[2]) S. LUCAS, Ann. de Chim. et Phys., (2), **12**, (1819), 402.

[3]) J. B. A. DUMAS, Compt. rend. Paris, **86**, (1878), 65; Ann. d. Chim. et Phys., (5), **14**, (1878), 289.

[4]) L. TROOST, Comp. rend. Paris, **98**, (1884), 1427.

[5]) J. VAN DER PLAATS, Rec. d. Trav. d. Chim. d. Pays-Bas, **5**, (1886), 212.

[6]) B. BRAUNER, Bull. Acad. de Belg., (3), **18**, (1889), 81.

and other investigators [1]) have contested this. HEYCOCK and NEVILLE [2])
found that the meltingpoint of silver in an atmosphere of oxygen is
lowered by 10°—17°; CALLENDAR [3]) demonstrated, that molten and
solidified silver, — after "spitting", — still showed a depression of its
meltingpoint of 6°.4. LE CHATELIER [4]) found, that solid silver already at
300° C. takes up oxygen, if the pressure of the gas be greater than 12
atmospheres. According to MANCHOT [5]), silver is covered with a very
thin film of its oxide, if it be heated in air at 200° C. TROOST [6]) demon-
strated, that at 780° C. oxygen *diffuses* through solid silver, while to other
gases, like CO, N_2, etc. it is impermeable under the same circumstances.
As the concentration of the oxygen absorbed by the molten metal proves to
be proportional to the square root of the oxygen-pressure [7]), the oxygen
in it cannot be present as O_2, but must be present either *in the atomic
state* [2]) or as Ag_2O. Between these two alternatives a final decision cannot
be made (conf. DONNAN and SHAW [8])).

Although Ag_2O, once formed, is more or less rapidly decomposed
already at 270°—300° C., all investigations hitherto made seem to indicate,
that the affinity of oxygen for silver at higher temperatures is rather
considerable [9]), but that the oxide formed then is decomposed at lower
temperatures.

The experiments here described now clearly demonstrate, that the
oxygen absorbed by the liquid metal is, on solidification, certainly *not
completely* given off, but is partially occluded in the crystalline mass;
moreover, that on preserving such an oxygen-containing lump at room-
temperature for a long time, the gas is gradually set free by a very slow
process of diffusion and that, reversely, by heating the solid metal in air
at temperatures above about 650° C., oxygen is again absorbed. The
slowness of its progress is readily explained by the extreme slowness of
the diffusion of the gas through the crystalline mass of the metal at these
temperatures. The method of measurement of the specific heats, however,
appears to be sufficiently sensitive for revealing the absorption and the
subsequent escaping of the gas, by the increase or by the diminution
respectively of the values for $\bar{c}_p$ at each temperature.

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[1]) L. MEYER and K. SEUBERT, Ber. d. d. chem. Ges., **18**, (1885), 1098.

[2]) C. F. HEYCOCK and F. H. NEVILLE, Journ. chem. Soc. London. **67**, (1896) 1024.

[3]) H. CALLENDAR, Phil. Mag., (5), **33**, (1892), 220.

[4]) H. LE CHATELIER, Bull. Soc. chim. Paris, (2), **48**, (1887), 342.

[5]) W. MANCHOT, Ber. d. d. chem. Ges., **42**, (1909), 3942.

[6]) E. TROOST, loco cit.

[7]) A. SIEVERTS and J. HAGENACKER, Zeits. f. Phys. Chem., **68**, (1910), 115.

[8]) F. G. DONNAN and T. W. A. SHAW, Journ. Soc. Chem. Ind., **29**, (1910), 987.

[9]) H. ST. CLAIRE DEVILLE and H. DEBRAY, Ann. de Chim. et Phys., (3), **56**, (1859),
385; **80**, (1875), 459; L. TROOST and P. HAUTEFEUILLE, Compt. rend. Paris, **84**, (1877),
946; V. KOHLSCHÜTTER and A. NOLL, Zeitschr. f. Elektrochem., **18**, (1912), 424;
H. VON WARTENBERG, ibid., **19**, (1913), 489.

§ 4. From the data given in the literature concerning the compressibility [1]) and the linear expansion [2]) of silver, the approximate values of C_v can be calculated by means of the usual thermodynamical equation.

From the measurements, the linear expansion of silver between 0° and 875° C., can fairly well be expressed by the formula:

$$l_t = l_0 \ (1 + 0,000018033 \cdot t + 0,000000004833 \cdot t^2).$$

The following values of c_v and C_v thus are found:

Temperature in °C.	c_p :	c_v :	C_p :	C_v :
0°	0.05540	0.05329	5.977	5.748
100	0.05682	0.05415	6.130	5.841
200	0.05822	0.05495	6.281	5.928
300	0.05958	0.05557	6.427	5.995
400	0.06091	0.05610	6.571	6.052
500	0.06220	0.05652	6.710	6.098
600	0.06347	0.05701	6.847	6.150
700	0.06469	0.05743	6.979	6.195
800	0.06590	0.05775	(7.109)	6.230

These values of C_v are also graphically represented in Fig. 2; no indication is manifested of a maximum in this curve, as was found by MAGNUS and HODLER [3]).

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Chemistry of the University.

[1]) P. W. BRIDGMAN, Proceed. Amer. Acad. Arts and Sciences, **58**, (1923), 165. For ϰ . 10⁶ at 30° C. the value: 0.987, at 75° C. the value: 1.004 was used and a linear increase of ϰ with the temperature was assumed.

[2]) L. HOLBORN and A. L. DAY, Ann. der Phys., (4), **2**. (1900), 505; K. SCHEEL, Zeits. Phys., **5**, (1921), 167.

[3]) A. MAGNUS and A. HODLER, Zeits. f. phys. Chem., **110**, (1924), 188.