

Chemistry. — *The Exact Measurement of the Specific Heats of solid Substances at High Temperatures: VI. Metals in Stabilized and Non-stabilized Condition: Platinum and Silver.* By F. M. JAEGER, E. ROSENBOHM and J. A. BOTTEMA.

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§ 1. In the course of our measurements of the specific heats of pure metals at high temperatures, we already had an opportunity to draw attention to the remarkable fact that many of those metals, as, for instance, *osmium*, *iridium*, *silver*, *gold*, etc., — even if no allotropic changes occur in them, — often yield too low and, moreover, irreproducible values of their mean specific heats, as long as they have not yet been subjected to a particular, preliminary thermal treatment¹⁾. A prolonged heating at temperatures in the vicinity of the meltingpoint or somewhat lower, followed by a slow cooling, appears, — thus, for instance, with *osmium* and *iridium*, — to bring them in most cases into a stable condition, in which, within the limits of experimental error (0.1—0.2 %), definite values of \bar{c}_p at each temperature can be determined. If the metal has once been brought into this stable condition, it remains so in successive experiments, yielding values of \bar{c}_p , which now prove to be perfectly reproducible within the limits of error mentioned.

In the present paper we wish to communicate some of the results hitherto obtained in the systematical study of these phenomena. Their importance for the whole technique of specific heat measurements will be clear: many of the numerous discrepancies in the values of \bar{c}_p for the same metal, as are met with in the literature, certainly must, for a good deal, be attributed to the fact that these numbers are not only obtained without taking the necessary painstaking precautions during the measurements themselves, but also with metals in a still *unstabilized* and, therefore, *indefinite* inner condition. As small errors in the determination of the integral function: $Q_0 = F(t)$ can already imply rather considerable divergences in the differential function: $c_p = \frac{\partial Q}{\partial t} = F'(t)$, it must be clear that a sufficient inambiguity about the true dependence of c_p on t , can possibly only be ascertained, if the calorimetric method used is able to furnish data of the very highest precision and reliability. In this laboratory two calorimeters of the most recent type of development, provided with all the improvements necessary to render them into the desired condition²⁾, are now used for the

¹⁾ F. M. JAEGER and E. ROSENBOHM, these *Proceed.*, **34**, (1931), 809; conf. also the Note at the bottom of the page.

²⁾ F. M. JAEGER, E. ROSENBOHM and J. A. BOTTEMA, these *Proceed.*, **35**, (1932).

measurements of the mean specific heats by two different and independently working observers, whose results at each moment can be compared and mutually controlled.

The observations here described were made with *platinum* and *silver*, both these metals being of the purest quality.

§ 2. *Platinum*. Because the values of \bar{c}_p obtained in this laboratory¹⁾ for purest *platinum* happened to agree within about 0.15 % with those obtained by WHITE²⁾ by means of his liquid-calorimeter, — in the first place comparisons of these values by means of two different calorimeters of the type described were made between 400° and 1600° C.

A vacuum-crucible of the shape mentioned before³⁾ was filled with *platinum*-spheres of pea-size, obtained by suddenly quenching droplets of molten *platinum* of HERAEUS' purest quality (for resistance-thermometers) in a vacuum. The total weight of the *platinum* used was 75.598 grammes, of which 30.1 grammes represented the weight of the crucible itself, made of the metal hammered at 800°—900° C. and having been previously heated to the meltingpoint only at its upper rim, during the process of electrical soldering its cover, while the remaining part of the crucible was kept at a low temperature.

The values of the mean specific heats thus obtained (see Table I and the dotted lines *B'* in Fig. 1) proved to be *considerably lower*, — about 1.5 to 2 %, — than the values obtained before. Moreover, on starting the experi-

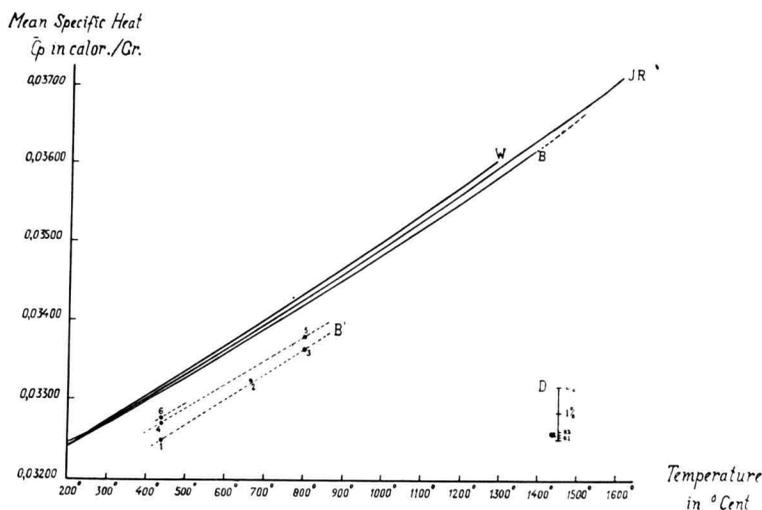


Fig. 1. Mean Specific Heats of Platinum in various Conditions.

1) F. M. JAEGER and E. ROSENBOHM, *Receuil d. Trav. d. Chim. d. Pays-Bas*, **47**, (1928), 534.

2) W. P. WHITE, *Phys. Review*, (2), **12**, (1918), 436.

3) F. M. JAEGER and E. ROSENBOHM, *Receuil d. Trav. d. Chim. d. Pays-Bas*, **51**, (1932), 2.

TABLE I.
Mean Specific Heats \bar{c}_p of Platinum in Different Conditions.

Temperature in ° C.:	Platinum (molten and sud- denly quenched): (B')	The same Metal (after heating at 1600° C. and slowly cooling): (B)	Platinum (hammered and plated at 800°–900° C.):	Normal Platinum JAEGER and ROSENBOHM: (JR)	WHITE: (W)
404.5	—	—	0.03301	0.03298	0.03304
407.8	—	0.03305	—	0.03299	0.03305
418.2	0.03270	—	—	0.03301	0.03307
419.0	0.03244	—	—	0.03301	0.03308
419.7	0.03264	—	—	0.03302	0.03309
429.3	0.03241	—	—	0.03306	0.03312
443.5	—	—	0.03308	0.03310	0.03317
629.3	—	0.03362	—	0.03369	0.03377
630.2	0.03309	—	—	0.03370	0.03378
631.3	—	—	0.03365	0.03371	0.03379
733.0	—	—	0.03406	0.03402	0.03404
799.9	0.03375	—	—	0.03421	0.03430
801.6	0.03360	—	—	0.03422	0.03431
801.9	—	0.03414	—	0.03423	0.03431
803.0	—	0.03423	—	0.03424	0.03432
1061.1	—	—	0.03505	0.03504	0.03512
1062.7	—	0.03505	—	0.03504	0.03513
1064.4	—	0.03507	—	0.03505	0.03514
1066.2	—	—	0.03518	0.03507	0.03516
1200.3	—	0.03538	—	0.03552	0.03563
1391.3	—	0.03604	—	0.03616	0.03619

ments at low temperatures, these values appeared to be quite *irreproducible*, gradually increasing after each successive heating. If the crucible and its contents was, however, at once heated at 1600° C. for several hours and then slowly cooled, the values of \bar{c}_p now proved to be identical within 0.15 % with those obtained by JAEGER and ROSENBOHM (curve B in Fig. 1).

These numbers remained constant in all later experiments.

The question, therefore, arises: are these discrepancies caused by the

contents of the crucible or by the hammered *platinum* of the crucible itself?

Experiments made with the empty crucible did not yield reliable results, as a consequence of the uncontrolable loss of heat of the shapeless and thin sheet of *platinum* during its introduction into the calorimeter and of the retarded heat-interchange with the calorimeter-block. Therefore, a vacuum-crucible was completely filled with the same hammered material, cut into small pieces, its total weight being 61.9075 grammes. The values of \bar{c}_p measured (Table I) proved to be *practically identical* with those obtained by JAEGER and ROSENBOHM. From this result it must be concluded that the lower values of \bar{c}_p of the curves B' , which deviate about 2 % from the normal ones, are characteristic of the *platinum*-spheres, i.e. of the metal in the quenched condition. If the quenched *platinum* be heated at 1600° C. for five hours and then slowly cooled, its internal structure evidently returns to the normal, stable condition; then the values of c_p re-assume their normal magnitude. In this connection we once more wish to emphasize, that the phenomenon just described has nothing at all to do with any occurring allotropic change: no such transformation does occur in the metal. Attention must also be drawn to the fact that, in this special case, the hammering of the metal at 800°—900° C. has evidently *no* appreciable effect on the values of \bar{c}_p of normal *platinum*.

As we shall soon see, this is by no means generally the case.

The values obtained by MAGNUS¹⁾ are, at 600° C. already about 1 %, at 850° C. about 1.5 % lower than those of WHITE and ours; probably they correspond to one of the curves B' in Fig. 1 and then refer to an unstabilized material.

The curve B in Fig. 1 only differs slightly from our previously determined one; between 0° and 1400° C. it corresponds to the equation:

$$Q'_0 = 0,031678 \cdot t + 0,315287 \cdot 10^{-5} \cdot t^2 - 0,541626 \cdot 10^{-10} t^3;$$

so that the true specific heat c_p between these limits of temperature can be calculated from:

$$c_p = 0,031678 + 0,630574 \cdot 10^{-5} \cdot t - 0,1624878 \cdot 10^{-9} \cdot t^2.$$

Although the agreement between these four series of measurements, — including WHITE's results, — is a very satisfactory one, yet the divergences of the calculated *differential* values \bar{c}_p are *appreciably greater* than those of the *mean* specific heats \bar{c}_p . This fact, as seen from the data in Table II and the curves of Fig. 2, once more illustrates, that even if the values of \bar{c}_p agree within 0.1 or 0.2 %, the slope of the corresponding c_p - t -curves can still differ by 1 % or more; properly speaking, the method must yield results accurate within 0.01 %, instead of within 0.1 %, if the \bar{c}_p - t -curve

¹⁾ A. MAGNUS, Ann. d. Physik, **48**, (1915), 998

Temperature in °C.:	c_p JAEGER, ROSENBOHM; WHITE		c_p (stabilized at 1600° C.):	c_p (hammered at 800°—900° C.):
200°	0.03295	0.03303	0.03293	0.03291
300	0.03349	0.03367	0.03355	0.03358
400	0.03413	0.03431	0.03417	0.03435
500	0.03476	0.03496	0.03479	0.03487
600	0.03541	0.03560	0.03540	0.03548
700	0.03605	0.03624	0.03601	0.03608
800	0.03661	0.03689	0.03662	0.03666
900	0.03736	0.03753	0.03722	0.03721
1000	0.03802	0.03818	0.03782	0.03775
1100	0.03869	0.03882	0.03842	0.03827
1200	0.03936	0.03947	0.03901	—
1300	0.04004	0.04011	0.03960	—
1400	0.04072	(0.04076)	0.04019	—
1500	0.04140	(0.04141)	—	—
1600	0.04209	(0.04206)	—	—
(1700)	(0.04279)	(0.04270)	—	—

would really present a perfectly true image of the dependence of c_p upon t . At the moment this is quite impossible, — were it only because of the fact, that the furnace-temperatures cannot be fixed with necessary accuracy. The values of c_p in Table II according to WHITE's measurements are calculated by means of the formula :

$$c_p = 0,031753 + 0,63964 \cdot 10^{-5} \cdot t + 0,27 \cdot 10^{-10} \cdot t^2,$$

which is valid between 0° and 1300° C. Even by extrapolation up to 1700° C., however, the values calculated prove to be almost identical with those found by us.

The curve for *hammered platinum*, as deduced from the values of \bar{c}_p at 404°·5 C., at 733° C. and at 1061°·1 C., corresponds to the equation :

$$Q'_0 = 0,031509 \cdot t + 0,359551 \cdot 10^{-5} \cdot t^2 - 0,315573 \cdot 10^{-9} \cdot t^3.$$

Between 0° and 1100° C. the true specific heat c_p of hammered *platinum*, therefore, can be found from the formula :

$$c_p = 0,031509 + 0,719102 \cdot 10^{-5} \cdot t - 0,94672 \cdot 10^{-9} \cdot t^2.$$

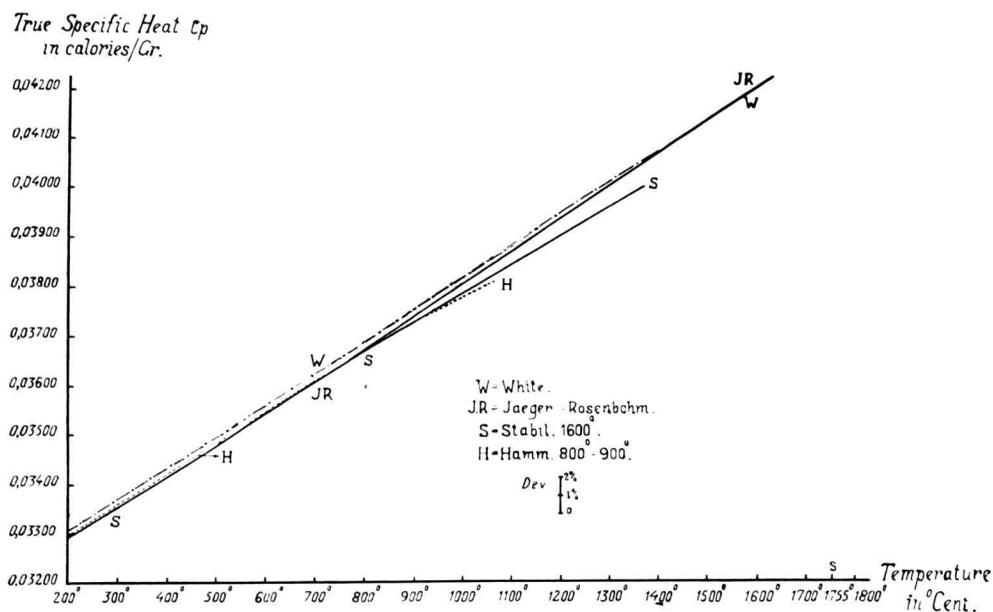


Fig. 2. The True Specific Heats of Platinum in different Conditions.

§ 3. *Silver*. Preliminary experiments had already taught us that *cold-plated silver*¹⁾ yielded considerably *smaller* values for \bar{c}_p than the metal, if preliminarily fused and then slowly cooled. For this reason purest *silver* was melted and cast into the form of a massive crucible-shaped lump, which exactly fitted into the central bore of the calorimeter. A thin tubular hole was spared in it for the introduction of the hot junction of the thermocouple, in the same way as occurs in our usual vacuum-crucibles. A small *silver* hook was fixed at the top, for the purpose of suspending the lump within the electrical furnace; the total weight of *silver* was: 133.339 grammes.

Measurements were made at $100^{\circ}.87$ C., the metal being heated in an airbath by the circulating vapour of conductivity-water, boiling under a known pressure; moreover, such measurements were made between $248^{\circ}.1$ and $804^{\circ}.4$ C. by heating in the electrical furnace.

1) The *silver*, and also the *gold* in the next paper both contained 100% of the metal and were obtained through the kindness of Dr. C. HOITSEMA, from the *State's Mint* at *Utrecht*. Between 20° and 0° C., the mean specific heat \bar{c}_p of this *silver*, was somewhat less than s : 0.0558. Both metals were obtained as cold-plated sheets.

The total amounts of heat Q_0 delivered between t° and 0° C. were found to be :

Temperature t in $^\circ\text{C}.$:	Amount of Heat Q_0 delivered by 1 Gr. silver, in calories :	Amount of Heat Q'_0 in calories, as calculated from the formula :
100.87	5.690	—
248.1	14.255	14.266
295.9	17.115	17.116
397.2	23.254	—
640.0	38.306	38.458
804.4	49.096	—

The value of Q_0 at 640° C. is somewhat (about 0.4 %) too low.

Between 0° and 804° C. these quantities of heat are very satisfactorily expressed by the formula :

$$Q'_0 = 0,055614 \cdot t + 0,0800383 \cdot 10^{-4} \cdot t^2 - 0,15741 \cdot 10^{-8} \cdot t^3.$$

The true specific heat c_p , therefore, can be calculated from the equation :

$$c_p = 0,055614 + 0,1600766 \cdot 10^{-4} \cdot t - 0,47223 \cdot 10^{-8} \cdot t^2$$

and the atomic heat C_p by means of the formula :

$$C_p = 5,9996 + 0,17269 \cdot 10^{-2} \cdot t - 0,50945 \cdot 10^{-6} \cdot t^2. \quad \dots \quad (I)$$

The value of C_p at 0° C. exactly coincides with the value obtained by NERNST in measuring c_p itself at that temperature.

From the values of MAGNUS and HODLER¹⁾, it follows that the atomic heat C_p can be found by means of the equation :

$$C_p = 6,047 + 0,0749 \cdot 10^{-2} \cdot t + 0,712 \cdot 10^{-6} \cdot t^2 \quad \dots \quad (II)$$

The values of C_p , as calculated from I) and II), and those found by SCHÜBEL²⁾, are graphically represented in Fig. 3. Not only are these values in the three cases very strongly deviating, but the real slope of the three curves is even exactly opposite: our curve is *concave* towards the axis of the temperatures, those deduced from MAGNUS' and SCHÜBEL's experiments are *convex*.

¹⁾ A. MAGNUS and A. HODLER, Ann. d. Physik, (4), **80**, (1926), 808; Zeits. f. phys. Chem., **110**, (1924), 188.

²⁾ P. SCHÜBEL, Zeits. f. anorg. C., **87**, (1914), 81.

Temperature t in °C.:	Atomic Heat C_p :		
	MAGNUS-HODLER :	SCHÜBEL :	this Laboratory :
0°	6.047	6.02	6.000
100	6.129	6.08	6.167
200	6.225	6.14	6.324
400	6.460	6.43	6.609
600	6.753	7.07	6.852
800	7.102	—	7.061

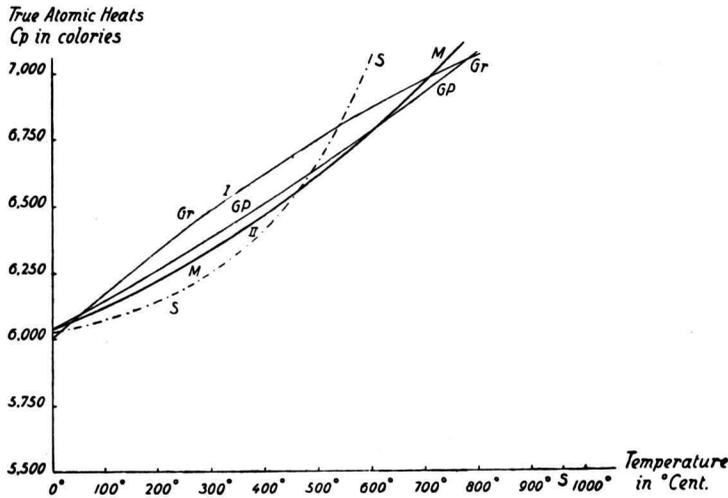


Fig. 3. The Atomic Heats of Silver in various Conditions.

Such discrepancies as these very often occur in literature. They clearly demonstrate how rudimentary our knowledge about the variation of the true specific heat with the temperature still is.

§ 4. Now two vacuum-crucibles were filled with *cold-plated silver*; they contained 23.5861 and 17.8366 grammes of the metal respectively, cut into small pieces. Both crucibles yielded identical results :

Temperature t in °C.:	Total amounts of Heat Q_0 delivered by 1 Gr. silver:
420.4 ₄	24.496
628.7	37.360
631.4	37.397
634.9 ₅	37.802
800.7	48.527
801.2	48.476

The values of Q'_0 are, between 0° and 800° C., very exactly represented by the formula :

$$Q'_0 = 0,055936 \cdot t + 0,528033 \cdot 10^{-5} \cdot t^2 + 0,6055 \cdot 10^{-9} \cdot t^3,$$

and, therefore, the true specific heat c_p of this plated *silver* by :

$$c_p = 0,055936 + 0,105607 \cdot 10^{-4} \cdot t + 0,18165 \cdot 10^{-8} \cdot t^2.$$

The atomic heat C_p can be calculated from :

$$C_p = 6,0343 + 0,11393 \cdot 10^{-2} \cdot t + 0,19596 \cdot 10^{-6} \cdot t^2.$$

If the values of C_p are now calculated for the same temperatures as above, we find :

Temperature t in $^\circ\text{C}.$:	Atomic Heat C_p :
0°	6.034
100	6.150
200	6.270
400	6.521
600	6.788
800	7.072

With the exception of the (extrapolated) value at 0° C. and that at 800° C., where the metal evidently has already almost reached its stabilized condition, all these values (curve GP in Fig. 3) are not only *appreciably smaller* than those for molten and solidified *silver*, but the curve for c_p-t appears, moreover, now to show a *convex shape towards the temperature-axis*, similarly as was the case with MAGNUS' and SCHÜBEL's curves. This example thus demonstrates most convincingly, that the cause of these divergences often met with in the literature, — as far as they must not be ascribed to experimental errors and methodical inaccuracies, — must doubtlessly be explained by the fact, that probably all those measurements were made with *non-stabilized* samples of the metals studied.

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