

Chemistry. — *The Exact Measurement of the Specific Heats of Metals at High Temperatures: XVII. Calorimetrical Retardation-phenomena in the Case of Cerium and Chromium.* By F. M. JAEGER and E. ROSENBOHM.

(Communicated at the meeting of September 29, 1934).

§ 1. In a number of papers from this laboratory¹⁾ it has recently been demonstrated that *no* definite values of the mean specific heats \bar{c}_p at a certain temperature could be determined in some cases of metals manifesting the phenomenon of allotropism, because more or less strong retardation-phenomena of their heat-development presented themselves and, moreover, it proved to be impossible to obtain the said metals at each temperature in an unambiguously defined internal condition. Such experiences were more particularly met within the case of *beryllium* and of *zirconium*; it makes the impression that in such cases we have to deal, to a certain degree, with so-called "one-phasetransitions" and with the presence of "intermediate phases", in the sense attributed to these expressions by DEHLINGER²⁾ and other modern investigators. These allotropic changes are in striking contrast to such as studied by us, for instance in the case of tetramorphous *ruthenium*³⁾, etc., where sharp and rapid transitions occur, not accompanied by any appreciable retardations.

Two new examples of transitions of the first kind were recently discovered in the case of the metals *cerium* and *chromium*; some of the results obtained by studying these metals are published in the following paper.

§ 2. *Cerium.* A pure sample of the massive metal obtained from MERCK, which besides some oxide only contained some traces of iron, was enclosed within an evacuated platinum crucible, of the usual type: the weight of *cerium* being 13.6814 g., that of the crucible 28.6595 g. According to MUTHMANN and WEISS⁴⁾, the metal melts at 623° C., according to HIRSCH⁵⁾ at 635° C.

¹⁾ F. M. JAEGER and E. ROSENBOHM, *Proceed. R. Acad. Sc. Amsterdam*, **37**, (1934), 67; see also the literature there indicated; *Recueil d. Trav. d. Chim. d. Pays-Bas*, **53**, (1934), 451, 917.

²⁾ U. DEHLINGER, *Metallwirtschaft*, **12**, (1933), 48, 207, and the literature referred to in *Rec.* **53**, (1934), 930.

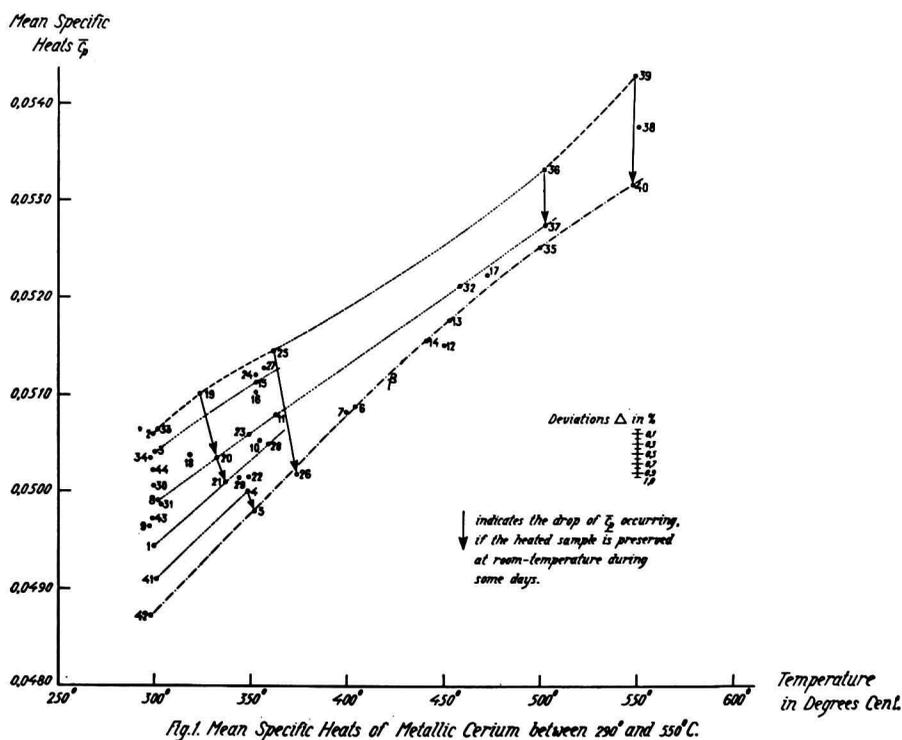
³⁾ F. M. JAEGER and E. ROSENBOHM, *Rec. d. Trav. d. Chim. d. Pays-Bas*, **51**, (1932), 32—36.

⁴⁾ W. MUTHMANN and L. WEISS, *Ann. der Chem.*, **331**, (1904), 1.

⁵⁾ A. HIRSCH, *Trans. Amer. Electr. chem. Soc.*, **20**, (1911), 57; *J. Ind. Eng. Chem.*, **3**, (1911), 880; **4**, (1912), 65.

From the data available in the literature it follows that the limiting value of $3R$ calories for the atomic heat is already considerably surpassed at rather low temperatures. According to an X-ray analysis by HULL¹⁾, the metal is *dimorphous*: a hexagonal, close-packed modification, with: $a_0 = 3.65$ A.U.; $c_0 = 5.91$ A.U. being present at room temperature, besides a cubic, face-centred one, with: $a_0 = 5.12$ A.U. and a specific gravity of: 6.897; the observed value of d_{40} at 25° C. was: 6.92. SCHUMACHER and LUCAS²⁾ only observed the cubic modification.

The measurements of \bar{c}_p were made with the usual precautions, the working condition of the calorimeter and the right indication of the thermocouples being controlled by means of alternately inserted determinations of the mean specific heats of pure, stabilized *platinum* in vacuo. Already in the very beginning of the measurements it became clear that the values of \bar{c}_p were, even at temperatures so low as 300° C., by no means constant and not reproducible. The results obtained in a large number of experiments between 296° and 551° C. are collected in the following table and graphically reproduced in Fig. 1.



The time τ , elapsing between the moment of dropping the crucible into the calorimeter and that necessary for reaching the maximum temperature

1) A. W. HULL, Phys. Rev., 18, (1921), 88—90.

E. E. SCHUMACHER and F. F. LUCAS, J. Amer. Chem. Soc., 46, (1924), 1167.

TABLE I.

Measurements of the Mean Specific Heats \bar{c}_p of Cerium at Different Temperatures between 300° and 550° C.				
Number of the Experiment:	Temperature t of Observ.:	Final temperature t' of the Calorimeter:	\bar{c}_p observed:	Remarks:
1	297.29	20.44	0.04948	Time $\tau = 4$ Min.
2	299.05	20.75	0.05061	id.
3	297.18	21.12	0.05045	id.
4	346.43	20.98	0.05006	id.
5	350.94	21.23	0.04984	Here the time τ suddenly changes to 9—10 minutes and remains so in all further experiments
6	403.05	20.76	0.05090	id.
7	399.89	21.30	0.05087	id.
8	301.54	20.77	0.04992	id.
9	293.72	20.56	0.04968	id.
10	353.35	20.94	0.05057	id.
11	361.00	21.42	0.05081	id.
12	448.54	21.49	0.05155	id.
13	451.02	21.04	0.05179	id.
14	440.20	21.07	0.05159	id.
15	350.93	21.55	0.05117	id.
16	350.74	21.55	0.05107	In the subsequent heatings a surpassing of the temperature t is carefully avoided in all further experiments
17	473.00	21.16	0.05228	id.
18	317.89	21.35	0.05035	id.
19	323.29	21.63	0.05105	id.
20	329.70	20.99	0.05042	
			(After a pause of 3 days at 15° C.)	id.
21	335.30	21.42	0.05018	id.
22	345.74	21.53	0.05019	id.
23	346.66	21.02	0.05062	Rapidly heated to 375°—380° C. then cooled to t° in $\frac{1}{2}$ hour
24	351.09	21.52	0.05123	id.
25	361.09	21.85	0.05149	
			(After a pause of 3 days at 15° C.)	id.
26	371.91	21.30	0.05022	id.
27	353.74	20.85	0.05128	Heated to 370° C., then rapidly cooled to t° C.

TABLE I (Continued)

Measurements of the Mean Specific Heats \bar{c}_p of Cerium at Different Temperatures between 300° and 550° C.				
Number of the Experiment :	Temperature t of Observ.:	Final temperature t' of the Calorimeter :	\bar{c}_p observed :	Remarks
28	357.58	21.21	0.05053 (After a pause of 3 days at 15° C.)	(Not heated above t°)
29	342.11	21.12	0.05019	—
30	296.87	21.20	0.05009	—
31	302.47	21.31	0.04990	Very slowly heated and kept at t° for 1/2 hour
32	457.22	21.16	0.05217 (After a pause of 3 days at 15° C.)	—
33	301.06	21.48	0.05063	Rapidly heated to t° and kept at t° for 4 hours
34	296.76	21.37	0.05043	Very slowly heated to t° and kept at t° for 1/2 hour
35	499.71	21.62	0.05252	—
36	500.61	21.70	0.05334 (After a pause of 3 days at 15° C.)	—
37	501.49	21.26	0.05277	—
38	550.56	21.82	0.05373	—
39	551.01	21.78	0.05422 (Pause of 2 days at 15° C.)	—
40	547.16	21.80	0.05311	—
41	297.11	21.44	0.04914	Heated to 550° C. for 6 hours on previous day; then slowly cooled to 15° C.
42	293.64	21.29	0.04877	Kept at 15° C. for a day
43	296.92	21.56	0.04972	—
44	295.96	21.72	0.05027	—

The accuracy of these measurements is 0.2—0.3 %.

of the latter, originally was 4 minutes; but after heating the sample to 351° C. it suddenly increased to 9—10 minutes, and this value of τ was preserved in all later experiments, even at temperatures below 350° C. In general, the values of \bar{c}_p at the same temperature t show a tendency to increase, if the metal is previously heated at higher temperatures, and the more so, as the experiment is more frequently repeated. Thus, for instance, in experiment 22, \bar{c}_p at 345° C. is: 0.05019; after rapidly being heated to 375°, this value increases to 0.05062 at 346° C. (N^o. 23) and, when this experiment is repeated twice, \bar{c}_p becomes: 0.05123 at 351° and 0.05149 at

361° C. (N^o. 24 and 25). If, however, *the sample was then preserved at room temperature during three days*, \bar{c}_p proved to have dropped to 0.05022 at 371° 9 C. (N^o. 26). In the same way: $\bar{c}_p = 0.05035$ at 318° C. is augmented to: 0.05105 at 323° 3 C. by heating; but after a pause of 3 days at room temperature, the value of \bar{c}_p proves to have diminished to: 0.05042 at 329° 7 C. and to: 0.05018 at 335° 3 C. (N^o. 18, 19 and 20).

In Fig. 1 several instances of this kind are indicated by an arrow: preserving the samples at 15° C. for 2 and, — as actually was the case in *all* subsequent measurements, — even for only 1 day, causes the value of \bar{c}_p to decrease.

The following general conclusions may evidently be drawn from these results:

1. At ordinary temperatures cerium represents a complex system of (two) different states¹⁾. Its internal condition is changed by variations of the temperature, these changes — as measured by the variation of the specific heats — evidently only partially going back, if the original temperature is re-established.

2. The values of \bar{c}_p determined between about 290° and 400° C. and between 450° and 550° C. are, therefore, neither constant nor completely reproducible at a certain temperature; they are strongly dependent on the preliminary thermal treatment of the metal and its subsequent cooling.

3. In general, preliminary and often repeated heatings at higher temperatures above 360° C. cause the values of \bar{c}_p to increase, the effect being the greater, as these heatings are repeated more frequently.

4. Preserving the heated samples at room temperature for 1, 2, 3, or more days causes the acquired higher values of \bar{c}_p to diminish, the metal obviously slowly going back to its original, stabler condition.

5. It is possible that between 360° and 370° C. a real transition temperature exists, although the β -form in that case, — be it as a "metastable" phase, — then would seem to be also partially preserved at temperatures beneath that transition temperature. This conclusion is in agreement with the results of the X-ray examination of the metal at ordinary temperatures.

Tentatives will, therefore, be made for ascertaining the existence of such an inversion temperature by direct thermal analysis; the results will be communicated in a later paper.

§ 3. *Chromium*. Exactly as in the case of *cerium*, the complex character of metallic *chromium* (mpt : > 1700° C.) seems to be highly

¹⁾ In this connection attention may be drawn to a recent investigation on the magnetic properties of cerium, lanthanum and neodymium by F. TROMBE (Compt. rend. Paris, 198, (1934), 1592). In the case of cerium a typical hysteresis-effect was discovered by this author between — 172° C. and — 86° C.; the metal evidently exists in two different states and their mutual transitions occur at different temperatures on cooling and on heating, the change not being accompanied by a distinct heat-effect. This fact probably gives an explanation of the complex character of the metal also at ordinary temperatures, as revealed by the calorimetrical behaviour described here.

probable, although the data available are still somewhat confusing. According to the X-ray measurements of chromium by different authors¹⁾, it seems that two modifications may simultaneously occur in the metal. The most predominant form is cubic, with a body-centred cell and $a_0 = 2.875$ — 2.895 A.U.; $d = 7.07$ — 7.23 . Besides this modification, according to BRADLEY and OLLARD, a hexagonal, closest-packed form, with $a_0 = 2.714$ A.U., $c_0 = 4.41$ A.U. and $a : c = 1 : 1.625$ seems to exist in some preparations. We had at our disposal a sample of a very pure, electrolytically deposited chromium, which subsequently was molten and solidified in a vacuum by the firm of *Heraeus*: 10.0309 g. of this metal were enclosed within an evacuated platinum crucible (30.7007 g.) of the usual construction, and the calorimetric measurements were made with all necessary precautions.

Already at the very start of the experiments the very appreciable duration of the time τ necessary for attaining the maximum temperature (30—56 minutes) immediately seemed to indicate, that also in this case something quite abnormal in the behaviour of the metal must be present: this supposition, moreover, was corroborated by the observation that, even after several hours since the introduction of the heated crucible into the calorimeter, the cooling-modulus of the latter still proved to decrease, instead of attaining a constant value. The latter circumstance compelled us to calculate the total quantity of the heat developed, by also taking into account the values of k after three hours. Only in this way it proved possible to determine the truly total and really constant amount of heat delivered by the metal at each temperature, notwithstanding the curious fact, that each time the way of heat development by the metal, as deduced from the fully determined time-temperature-curves of the calorimeter, proved to vary, according to the special thermal treatment to which the sample had preliminarily been subjected. The latter fact may best be illustrated by means of Figure 2, in which some of those curves are represented for experiments at 400° , 1000° and 1066° respectively. From this figure it is seen that, for instance at 400° C., the original curves, (e.g. I and II) at 400° C., after the sample has been preserved for one or more days at 15° C., are changed into the flatter curve III, which shows a *more distant* temperature-maximum; if, however, this sample subsequently is heated once more at 400° , the calorimeter-curve returns to an appreciably steeper slope (IV at 400° C.) with the temperature-maximum *nearer* to the moment τ_0 of the introduction of the crucible into the calorimeter.

Thus, for instance in experiments No. 23 and 24, the sample was originally heated to 500° , then preserved for 3 days and heated to

¹⁾ A. J. BRADLEY and E. A. OLLARD, *Nature* **117**, 122 (1926); cf. also: A. W. HULL and W. P. DAVEY, *Phys. Rev.*, **14**, 540 (1919); **17**, 571 (1921); W. C. PHEBUS and F. C. BLAKE, *ibid.*, **25**, 107 (1925); R. A. PATTERSON, *ibid.*, **25**, 581 (1925); **26**, 56, (1925); F. SILLERS, *Trans. Am. Electrochem. Soc.*, **52**, 301, (1927); E. A. OLLARD and F. SILLERS, *ibid.*; *Strukturbericht Z. f. Kryst.* (1931), 755.

1000° C. : $\tau = 39$ minutes; then the experiment was repeated after 1 day and once more heating to 1000°. Now τ was only 30 minutes. In the same way, in the experiments 25 and 26, the metal was originally kept at 1060° during 6 hours; then τ proved to be 35 minutes and, on repeating the measurement after 1 day, after heating once more to 1065° C. τ had decreased to 29 minutes. In the experiments 7 and 8 the sample was heated to 671°, then preserved for 3 days, τ being found = 42 minutes, while after 1 day and a renewed heating to 670°, τ proved to have decreased to 30 minutes; etc.

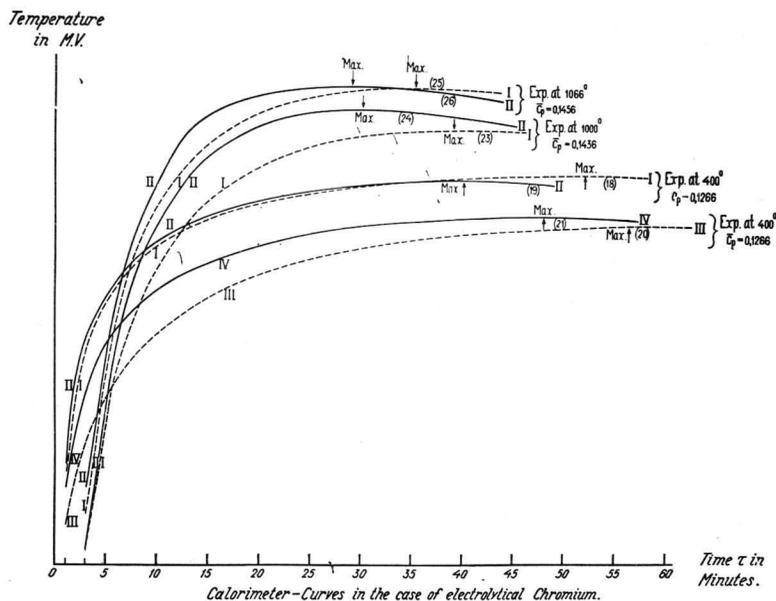


Fig. 2. The Gradual Recurrence of Heated Chromium after preserving for Some Days and Subsequent Heating, as shown by the Heating-Curves of the Calorimeter.

§ 4. These facts clearly prove that the internal state of the metal, on preserving the preliminarily heated sample for some days, is slowly changing and going back to another complex state. As, however, the surfaces enclosed by the curves and the zero-curve prove in all cases to be practically the same at each temperature, the value of \bar{c}_p finally obtained at each temperature remains constant; so that evidently no noticeable heat-effect can accompany the inner changes mentioned. The effect observed, therefore, apparently seems merely to consist in a strongly retarded heat-development by the sample, — the same quantity of heat developed appearing to be distributed over a much longer interval of time. This is exactly the same phenomenon as was previously described by us in the case of *beryllium*¹⁾, where we found, that no appreciable change of the thermal

¹⁾ F. M. JAEGER and E. ROSENBOHM, *Proceed. R. Acad. Sciences Amsterdam*, **35**, 1055, (1932); **37**, 67, (1934); *Rec. d. Trav. d. Chim. d. Pays-Bas*, **53**, 451, (1934).

conductivity of the metal was the cause of this retarded heat-development, — a retardation which, however, caused the cooling-modulus still to decrease after many hours since the introduction of the crucible into the calorimeter. The difference between the two cases is, however, that in the case of beryllium beneath 450° C., no reproducible values of \bar{c}_p could be found on repeated heating, while in the case of chromium this certainly is possible. The phenomenon of this retarded heat-development must, therefore, be intimately connected with and characteristic of the simultaneous presence in the metal of the two "components" or "states", whatsoever their true nature eventually may prove to be.

§ 5. The results of the measurements of \bar{c}_p of chromium in these circumstances are collected in the following table II. With the exception of the value of \bar{c}_p at 400° C., — which seems to correspond to another branch of the \bar{c}_p - t -curve, — the values of \bar{c}_p between 500° and 1066° C. are situated either on a straight line or on a curve, slightly concave with respect to the t -axis.

It is, of course, possible from these data to calculate a formula for \bar{c}_p in its dependency on t ; but we prefer to postpone this to a later occasion, with respect to the fact that, by means of some technical improvements of the calorimeter, we hope to be able to determine the values of \bar{c}_p with still greater accuracy and at temperatures of 300° and even of 200° C., — so as to make sure, whether perhaps there is a change of direction of the \bar{c}_p - t -curve beneath 400° C. or there is not. From the preliminary calculations it has already become clear, that at 500° C. the value of the atomic heat C_p is considerably greater than $3R$ calories.

Finally in connection with the phenomena described in this paper, attention may be drawn to the results recently obtained by BRIDGMAN¹⁾ in the case of chromium, with respect to the measurement of its compressibility κ at -40° , 30° and 75° C.

The curve for κ in function of the pressure, as well as that for the electric resistance in its dependency on the temperature, prove to have a very complicated shape and clearly corroborate our conclusion that chromium — even at temperatures so low as 0° C. — must correspond to a "complex" system, although no hysteresis was observed with respect to either the one or the other property mentioned. BRIDGMAN²⁾ also hints at the possibility of allotropic changes occurring and their being suppressed by admixed impurities, so that former investigators did not observe the curious phenomena described. It seems that the most obvious internal changes of the metal occur in the temperature-interval between -40° and $+10^{\circ}$ C. However, from the present measurements it is impossible to draw any certain conclusions as to the probable values of κ at higher temperatures.

¹⁾ P. W. BRIDGMAN, *Proceed. Amer. Acad. Arts and Sciences*, 68, 32, (1933).

²⁾ *loco cit.*, p. 36, 37, 38.

TABLE II.

Mean Specific Heats of Chromium between 400° and 1066° C.					
No. of Experiment:	Temperature t :	Final temperature t' of the Calorimeter:	Time τ :	Mean specific Heat \bar{c}_p :	Remarks:
21	399.8	22.0	48 Min.	0.1267	No 20, heated once more to 400°.
20	400.5	21.91	56 ..	0.1264	Preserved for 5 days at 18°.
18	400.6	21.19	52 ..	0.1263	Heated the previous day to 1000°.
19	401.9	21.68	40 ..	0.1264	No 18, once more heated to 400° C.
1	504.5	22.22	30 ..	0.1281	The previous day heated to 400°.
22	501.8	22.38	37 ..	0.1282	—
13	503.2	22.04	43 ..	0.1283	—
14	505.3	22.02	35 ..	0.1283	Heated for 1 hour at 750°; then for 1 hour at 500°.
12	618.3	22.28	35 ..	0.1320	The previous day heated at 620° for 6 hours.
15	629.4	22.33	44 ..	0.1321	—
11	630.1	22.45	32 ..	0.1324	The previous day heated to 656°.
10	656.36	21.68	48 ..	0.1332	After 3 days at 18°.
9	656.9	22.28	31 ..	0.1331	—
7	671.3	21.81	42 ..	0.1336	After 3 days at 18°.
8	672.0	22.82	30 ..	0.1336	No 7 once more heated to 672°.
6	699.3	22.46	26 ..	0.1348	The previous day heated to 400°.
5	796.3	22.85	33 ..	0.1373	—
4	796.7	22.92	36 ..	0.1377	—
16	796.6	22.26	41 ..	0.1372	—
2	800.6	22.34	30 ..	0.1378	(Uncertain).
3	801.0	22.09	36 ..	0.1373	After preserving for 3 days at 18°.
17	1000.3	23.70	24 ..	0.1435	After 3 days at 18°.
23	1000.5	22.56	39 ..	0.1436	After 3 days at 18°.
24	1000.4	22.93	30 ..	0.1435	No 23 once more heated to 1000°.
25	1065.7	22.52	35 ..	0.1457	The previous day heated at 1060° for 6 hours.
26	1065.7	22.53	29 ..	0.1453	No 25 once more heated to 1065°.

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