

**Chemistry.** — *The Exact Measurement of the Specific Heat of Metals at High Temperatures. XXXI. The Mean Specific Heat of Cobaltum in Connection with the Granular Size of its Crystalline Structure.*  
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§ 1. The contents of this paper can be considered as a sequel to our previous publication recently issued on the properties of metallic *cobaltum* <sup>1)</sup>). Moreover, we wish to draw attention in it to some phenomena of more general interest, because they prove to allow of a clearer insight with respect to the influence which the special coarseness of the crystalline structure of metals seemingly has on their physical properties, — more especially on the numerical values of their mean specific heats. The latter fact has previously been emphasized by us in the course of the same kind of measurements made with other metals in this laboratory <sup>2)</sup>); and the present results evidently corroborate our earlier conclusions in a particularly striking way.

In the paper referred to, we made use of two samples of *cobaltum*: one massive sample of very pure cobaltum, consisting of *large* crystallites and furnished by Dr. DE BOER of the PHILIPS' WORKS in Eindhoven and in this paper designated as *cobaltum-A*; and a second specimen from the *Union minière du Haut Katanga* in Brussels, — here indicated as *cobaltum-B*, — which was electrolytically deposited and which proved to be composed of *extremely small* crystallites, which were hardly perceptible in a microscopical enlargement of 600—800 times. The two samples were very hard, sample *B* being the hardest of the two. Whilst *cobaltum-A*, when brought into dilute hydrochloric acid in excess and heated on the waterbath, proved to dissolve *readily* within a few days, an equal weight of *cobaltum-B* treated in the same way did not or only *extremely slowly* dissolve even after several weeks, — notwithstanding the fact, that it contained somewhat more, — although very little, — cobaltous oxide and about 1 % less of metallic cobaltum than the other sample. Only after preliminary heating of *cobaltum-B* at about 1000° C. during a long time,

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<sup>1)</sup> F. M. JAEGER, E. ROSENBOHM and A. J. ZUITHOFF. Rec. d. trav. d. chim. d. Pays-Bas, **59**, 831, (1940).

<sup>2)</sup> F. M. JAEGER and E. ROSENBOHM, *ibid.*, **53**, 456 a. f. (beryllium), (1934); F. M. JAEGER and W. A. VEENSTRA, *ibid.*, **53**, 924, 925 a. f., (*zirconium-B* and *-C*), (1934); T. J. POPPEMA and F. M. JAEGER, *ibid.*, **38**, 824, (1935). Conf. also: F. M. JAEGER, E. ROSENBOHM and J. A. BOTTEMA, Rec. d. trav. d. Chim. d. Pays-Bas, **52**, 61, (1933).

the solubility proved to have increased to that of the other sample and on microscopical examination it now appeared to have obtained a rather coarser texture, composed of readily discernable grains.

This strange behaviour induced us to compare its mean specific heat  $\bar{c}_p$ , — starting at low temperatures, — with that of *cobaltum-A*. The results of these investigations are communicated in the following sections.

§ 2. The measurements of  $\bar{c}_p$  were made in the usual way, the metal being enclosed in a vacuum platinum crucible of the ordinary type. Starting at 588° C., the results of these determinations at increasing temperatures are recorded sub 1—9 in the Table I.

Evidently the whole curve thus determined is situated *beneath* the curve for sample-A: the  $\bar{c}_p$ -values at the same temperature are at 588° C. about 2 %, at 738° C., about 1,8 % and between 797° C. and 1181° C. about 0,6 % (mean values) *lower* than in the case of sample-A. The transition-point (1125° C.), however, has remained *unchanged*; and, as the two curves have about the same course, also the *true* specific heats  $C_p$  of the two samples are practically identical. After this heating at 1182° C. the values of  $\bar{c}_p$  were once more determined, now starting at 649° C., until 1296° C. was reached. This time all values of  $\bar{c}_p$ , up to 1000° C., were seen *practically to co-incide* with those of the curve for sample-A; but at temperatures surpassing 1000° C. the curve takes a course *intermediate* between that for A and the curve for B obtained by measurements 1—9;

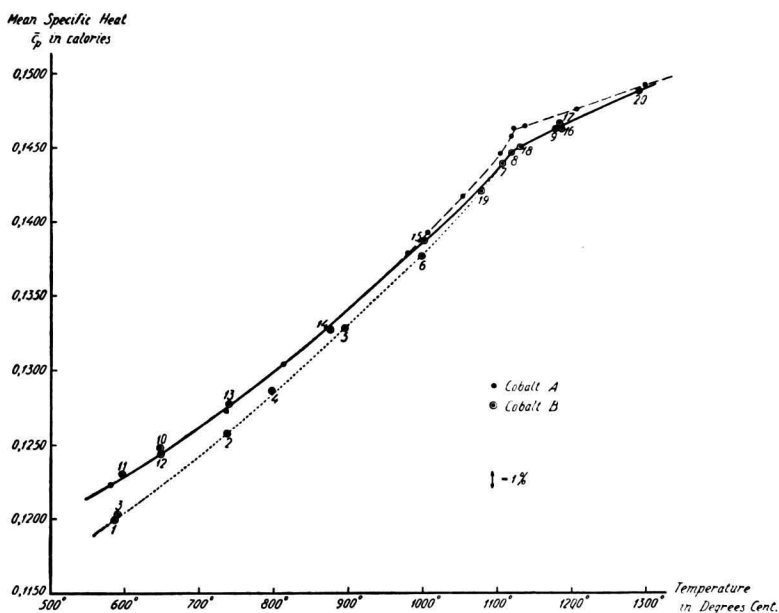


Fig. 1. The mean specific heats of Cobaltum-A and of Cobaltum-B between 580° and 1350° C.

TABLE I. Mean Specific Heats  $\bar{c}_p$  of Cobaltum-B (Katanga) between 100° and 1400° C.

Sequence-number of Measurement:	Temperature $t$ in Cent.:	Final temperature $t'$ of the Calorimeter:	Increase of the temperature of the Calorimeter $\Delta t$ in mikrovolts:	Quantity of Heat Q developed by 1 Gr. between $t^\circ$ and 25° C in cal.:	B Mean Specific Heat $\bar{c}_p$ between $t$ and $t'$ in cal.:	A Mean specific Heat $\bar{c}_p$ of sample-A:	Differences (A-B):	Differences $\Delta$ in percent:
1	587.7	21.45	318.72	67.48 <sup>8</sup>	0.1199	0.1224	+0.0025	Mean: 1.8 <sup>0</sup> / <sub>0</sub>
2	738.2	22.76	419.19	89.65 <sup>6</sup>	0.1257	0.1275	0.0018	
3	589.7	21.66 <sup>7</sup>	320.64	67.97 <sup>2</sup>	0.1204	0.1226	0.0022	
4	797.5	23.04 <sup>5</sup>	462.41	99.30 <sup>0</sup>	0.1285	0.1296	0.0011	Mean: 0.6 <sup>0</sup> / <sub>0</sub>
5	895.1	23.98	534.95	115.57 <sup>4</sup>	0.1328	0.1332	0.0004	
6	1000.1	23.08	618.19	134.13 <sup>4</sup>	0.1376	0.1383	0.0007	
7	1106.4	24.16	709.92	155.69 <sup>3</sup>	0.1440	0.1444	0.0004	Mean: 0.8 <sup>0</sup> / <sub>0</sub>
8	1120.1	23.76	723.99	158.41 <sup>1</sup>	0.1447	0.1458	0.0011	
9	1181.2	25.50	771.12	169.16 <sup>5</sup>	0.1463	0.1472	0.0009	
10	649.1	24.14	363.02	77.77 <sup>2</sup>	0.1246	0.1243	-0.0003	till 1000° C practically 0 <sup>0</sup> / <sub>0</sub>
11	596.3	23.07	329.07	70.24 <sup>4</sup>	0.1230	0.1228	-0.0002	
12	648.8	22.98	362.97	77.59 <sup>6</sup>	0.1244	0.1246	+0.0002	
13	739.9	23.36	425.07	91.16 <sup>8</sup>	0.1277	0.1276	-0.0001	
14	876.8	22.42	523.73	112.96 <sup>0</sup>	0.1327	0.1322	-0.0005	
15	1002.2	24.75	623.07	135.67 <sup>2</sup>	0.1388	0.1386	-0.0002	
16	1184.8	24.08	774.37	169.70 <sup>0</sup>	0.1463	0.1476	+0.0013	
17	1185.4	25.65	775.64	170.27 <sup>0</sup>	0.1467	0.1478	+0.0011	Mean: 0.8 <sup>0</sup> / <sub>0</sub>
18	1130.5	24.96	731.53	160.28 <sup>2</sup>	0.1450	0.1462	+0.0012	0.1 <sup>0</sup> / <sub>0</sub>
19	1079.9	24.42	686.09	149.78 <sup>6</sup>	0.1420	0.1431	+0.0011	
20	1295.9	24.75	861.40	189.11 <sup>1</sup>	0.1488	0.1490	+0.0002	

the transition-point is again *not altered* and about  $1125^{\circ}$  C., the divergence of the higher and lower curves remains 0,8 %, but then gradually approaches the curve for the  $\beta$ -modification of sample-A, so as to *completely* coincide with it at about  $1320^{\circ}$  C. The deviation of the two curves is greatest at the CURIE-point and decreases afterwards up to  $1320^{\circ}$  C., — where it becomes zero. Evidently the heat of transformation still makes itself apparent *above* the CURIE-point.

A special controlling experiment was made, moreover, for the purpose of ascertaining that the values obtained do indeed correspond to *real* equilibria: in experiment 16 the normal time (45 minutes) of heating at a constant temperature was increased to 60 minutes, in 17 to 90 minutes; and in this way it was found that the results of experiments 16, 17 and 9, — all at  $1181^{\circ}$  —  $1185^{\circ}$  C., — were in full accordance with each other.

The data of Table I and those of Table II of our previous paper on cobaltum (loco cit.) are graphically represented in Fig. 1 besides each other.

§ 3. By these experiments it has been clearly established, that the mean specific heats  $\bar{c}_p$  of *cobaltum* are found to be *so much lower, the more its composing crystallites are smaller*: a fact in plain agreement with that previously stated in the case of other metals studied in this laboratory, — where in general it was found, that the values of  $c_p$  observed were *variable with the degree of division* of the materials considered. Thus in the case of *antimony* <sup>1)</sup>  $\bar{c}_p$  of the metal as small granules proved to be about 2 % lower than that of *antimony* in the form of a compact lump; and as well from MAGNUS and HOLTZMANN's experiments with *beryllium* <sup>2)</sup>, as from our investigations <sup>3)</sup> on the same metal, it must be concluded, that  $\bar{c}_p$  depends on the size of the grains constituting the metal. With *zirconium* and *beryllium* <sup>2)</sup> the values of  $\bar{c}_p$  for powdered metals appeared *higher* than those for massive bars; but the fact, that the deviations here considered can occasionally be in the *one*, or, with other instances, in the *opposite* direction, — was also clearly stated during our studies <sup>5)</sup> on the *influence of prealable cold working* of such metals on the values of  $\bar{c}_p$  measured. For in these processes of crushing and drawing, also a change in the *size* of the particles in the metals doubtlessly occurs to a larger or smaller extent. Another most remarkable circumstance is, that the occasionally observed "retardation"-phenomena at, or in the vicinity of, the transition-points in the massive lumps of such metals, are seen strongly to diminish and even totally to disappear, when the same materials are

<sup>1)</sup> T. J. POPPEMA and F. M. JAEGER, loco cit.

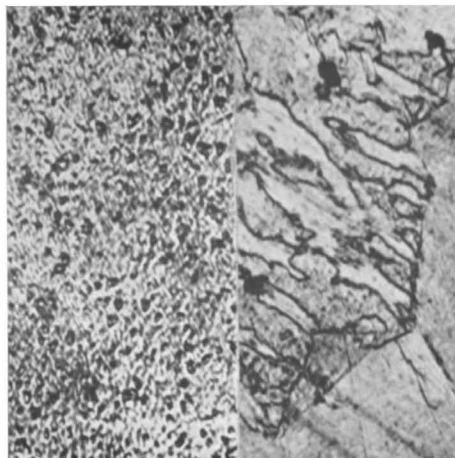
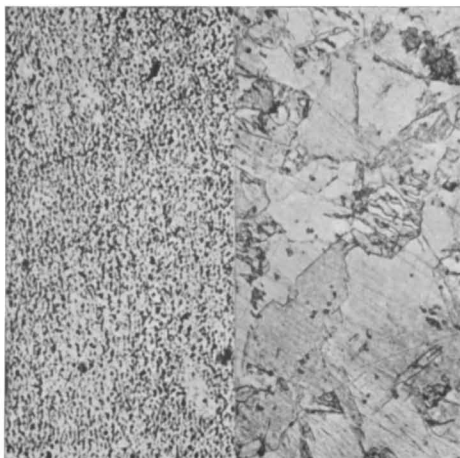
<sup>2)</sup> A. MAGNUS and H. HOLTZMANN, Ann. d. Phys., **3**, 585, (1929).

<sup>3)</sup> F. M. JAEGER and E. ROSENBOHM, Proc. Kon. Akad. v. Wetensch., Amsterdam, **37**, 67, (1934); Recueil, loco cit.

<sup>4)</sup> F. M. JAEGER and W. A. VEENSTRA, loco cit.

<sup>5)</sup> F. M. JAEGER, E. ROSENBOHM and J. A. BOTTEMA, loco cit.; conf. p. 84.

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a.  
*Cobaltum-B*

b.  
*Cobaltum-B*

before heating,  
attacked with aqua  
regia.

after repeated  
heating, attacked  
with aqua regia  
(25%)

The same as in a, but enlargement: 275 times.

Enlargement: 60 times.

Fig. 2. *Microphotographs of Cobaltum-B before and after heating.*



Fig. 3. *Cobaltum-A*

without preliminary heating; etched with 5%  
aqua regia.

Enlargement: 7,5 times.

finely powdered, — the degree of division of the crystallites thus being considerably increased. In the case of *zirconium* it could even be demonstrated, that *sintering* of the powdered material into a coherent mass caused the hysteresis-phenomena once more to return <sup>2)</sup>).

In the case of *cobaltum* doubtlessly the "recrystallisation" of the metal after heating at higher temperatures must be the cause of the fact, that the values of  $\bar{c}_p$  of both *cobaltum-B* and *cobaltum-A* become identical again between 500° and 1000° C. But then the other fact still remains, that about 125° below and till 200° above the CURIE-point, the original deviations persist and that they reach a maximum value at this transition-point itself. It must be evident, that here the influence of the heat of transition at this point must be the cause of the fact, that curve *A* still remains higher situated than curve-*B*. It is this heat of transition corresponding to the transformation at the CURIE-point, which, — making itself already perceptible some 125° below this temperature, — appears to be scattered over a considerable range of temperatures before the CURIE-point is reached, — just as in the case of pure *iron* <sup>6)</sup>. This particular interpretation in the case of the finely-crystallized *cobaltum-B* seems to be justified to a high degree, if it may only be supposed, that the transition-heat at 1125° C. now was appreciably smaller, than in the case of the coarse-crystalline *cobaltum-A*. The situation of the transition-temperature itself, however, is seen not to be altered by this fact.

§ 4. Finally, as a result of the microscopical examinations, we here insert fig. 2, which shows a microphotograph *a* of the original preparation at room-temperature and after heating to 1200° C.; and a micro-photograph *b* of the same samples at an enlargement of 275 times. The increase in size of the crystallites by the gradually achieved recrystallisation is quite evident. The heated sample proved, moreover, now to have become readily soluble in dilute hydrochloric acid. For the purpose of comparison we add (in fig. 3) a microphotograph of *cobaltum-A*, which was not previously heated; here an enlargement was used of only 7—8 times.

<sup>6)</sup> F. M. JAEGER, E. ROSENBOHM and A. J. ZUITHOFF, Rec. d. trav. d. chim. d. Pays-Bas, 57, 1322, (1938).

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