

§ 7. Die ϱ^3 , welche eine vorgegebene Ebene φ berühren, bilden eine Fläche Φ .

In der Kongruenz der ϱ^3 durch vier Punkte (A_1, A_2, A_3, U_1) welche eine Gerade b zweimal treffen, gibt es 8 Kurven, welche eine Gerade (c_2) schneiden und eine Ebene (φ) berühren. Hieraus erhellt, dass die Bildkurve des Systems Φ einen *achtfachen Punkt* in U_1 (also auch in U_2) besitzt, wonach sie eine $\varphi^{16}(U_1^8U_2^8)$ ist.

Im Bündel (β^3) gibt es vier Kurven, die φ berühren; denn die Gerade $a\varphi$ wird durch (β^3) in einer kubischen Involution geschnitten, wo es bekanntlich vier Gruppen mit einem Doppelpunkt gibt. Demnach hat φ^{16} in S_0 einen *vierfachen Punkt*.

Im Bündel (α_1^2) finden sich 2 Kurven, welche φ berühren; also ist S_1 *Doppelpunkt* von φ^{16} .

Die Bildkurve des Systems Φ entspricht daher dem Symbol $\varphi^{16}(U_1^8U_2^8S_0^4S_1^2S_2^2S_3^2)$.

Mit einer Bildkurve $\lambda^8(U_1^4U_2^4S_0S_1S_2S_3)$ hat sie $16 \times 8 - 2 \times 8 \times 4 - 4 - 3 \times 2$, also 54 Punkte R gemein. Die ϱ^3 , welche eine vorgegebene Ebene berühren, bilden daher eine *Fläche vierundfünfzigsten Grades*.

Chemistry. — *The Exact Measurement of the Specific Heats of Solid Substances at Higher Temperatures: XVI. The Specific Heats of metallic Thorium and of Thoriumdioxide between 20° and 1400 °C.* By F. M. JAEGER and W. A. VEENSTRA.

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§ 1. In this paper we wish to publish the results of the exact measurement of the specific heats of metallic *thorium* and of *thoriumdioxide* at a series of temperatures ranging from 300° to 1400° C.

Thorium crystallizes in the cubic system: its face-centred cell has: $a_0 = 5.04$ A.U.; its specific gravity is: 11.96 at 0° C. and the melting-point lies above 1700° C. For the determination of the specific heats of metallic *thorium*, we had at our disposal a rod A of the pure metal, which most kindly was furnished us by the *Westinghouse Lamp Company* in *Bloomfield N. J.* On analysis it proved to contain 93.94% *Th*, traces of iron, bismuthum, lead, calcium and phosphorus and, moreover, 6.04% *ThO*₂. A second preparation B consisted of *thorium* in powderform from E. MERCK; this specimen contained 26.8% *ThO*₂. With the purpose of applying the necessary corrections for this content of dioxide, also the specific heats of *ThO*₂ within the same range of temperatures were determined. The metal, as well as the dioxide, were included in evacuated platinum crucibles of the usual type; because the platinum proved to

be attacked at about 1400° C. by the metal enclosed, the measurements were not continued above that temperature and stopped at about 1200° C. The behaviour of the metal was, in the beginning, not quite normal, although no retardation phenomena to such a degree as stated in the cases of beryllium, zirconium, cerium, chromium, etc., were observed. After stabilisation of the metal at 1200° C., finally we were able to determine data for \bar{c}_p which were pretty accurate, — at least in the case of the massive rod A.

§ 2. The measurements with this specimen were started at 400° C.: as the maximum temperature of the calorimeter, however, proved no sooner to be reached than after 25 minutes, while the normal cooling-rate of the instrument was only re-established after 2 hours, — the

TABLE I.
Mean specific Heats \bar{c}_p of Thorium between 400° and 1200° C.

Temperature t in °C.:	Final temperature t' of the Calorimeter:	\bar{c}_p between t° and t'° C.:	Corrected specific heat \bar{c}_p for the oxide-free metal:	Corrected values of \bar{c}_p calculated from the formula:
397.6	21.10	0.03651	} 0.03496	0.03496
397.53	21.02	0.03658		
499.95	21.32	0.03722	} 0.03556	0.03537
500.05	21.27	0.03721		
628.72	21.30	0.03756	} 0.03584	0.03584
629.13	21.55	0.03756		
700.03	21.42	0.03795	0.03623	0.03617
801.23	21.39	0.03844	} 0.03666	0.03666
801.26	21.31	0.03833		
1065.5	21.7	0.04023	} 0.03853	0.03842
1062.7	21.9	0.04033		
1062.6	21.7	0.04015		
1062.5	21.5	0.04002		
1201.1	21.7	0.04121	} 0.03959	0.03959
1201.1	21.8	0.04124		

As the value of \bar{c}_p at 10° C. can hardly be deduced from the \bar{c}_p - t -curve with a sufficient degree of accuracy, the slight corrections of Q_0 between t' and 0° C. have not been applied.

crucible was heated at 1200° C. for some hours and then slowly cooled: now the maximum temperature was reached after 16—17 minutes, above 800° C. after 10—13 minutes and the calorimeter proved to have re-assumed its normal cooling-rate within the ordinary interval of time. Although the interval of 10—13 minutes is still rather appreciable in comparison with that observed with most metals, the values of \bar{c}_p thus measured are, however, sufficiently accurate. The results obtained are collected in the following table I.

These latter (corrected) values of \bar{c}_p between 400° and 1200° C. can, with sufficient accuracy, be represented by the formula:

$$\bar{c}_p = 0,03437 + 0,99078 \cdot 10^{-6} \cdot t + 0,14384 \cdot 10^{-8} \cdot t^2 + 0,113014 \cdot 10^{-11} \cdot t^3.$$

The true specific heats, therefore, by:

$$c_p = 0,03437 + 0,198156 \cdot 10^{-5} \cdot t + 0,43152 \cdot 10^{-8} \cdot t^2 + 0,452056 \cdot 10^{-11} \cdot t^3,$$

and the atomic heats C_p by:

$$C_p = 7,97816 + 0,45997 \cdot 10^{-3} \cdot t + 0,10014 \cdot 10^{-5} \cdot t^2 + 0,10493 \cdot 10^{-8} \cdot t^3.$$

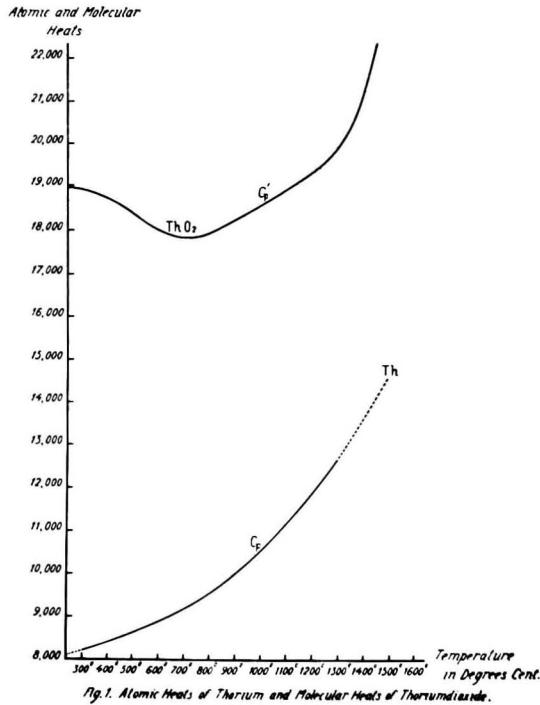
Some of the values of C_p thus calculated, are collected in Table II and graphically represented in Fig. 1; most remarkable are the very

Temperature t in °C.	Specific Heats c_p	Atomic Heats C_p
300°	0.03547	8.235
400	0.03618	8.390
500	0.03700	8.590
600	0.03809	8.841
700	0.03942	9.151
800	0.04103	9.524
900	0.04294	9.968
1000	0.04518	10.489
1100	0.04779	11.092
1200	0.05077	11.785

high values: 8,235 at 300° C.; 10,489 at 1000° C.; and, extrapolated, 14,463 at 1500° C., as would follow from the formula, if the increase of C_p with the temperature might supposed to continue in the same way up to 1500° C.

As no data concerning the compressibility and the coefficient of thermal

expansion of *thorium* are available in the literature, no calculation of c_v and C_v could be made.



§ 3. The values of \bar{c}_p obtained in the case of *thorium* in powderform (B) were the following (Table Ia). As this preparation contained 26.8%₀

Temperature t in °C.:	Final temperature t' of the Calorimeter:	Time elapsed till temperature-maximum of the Calorimeter:	Mean Specific Heat \bar{c}_p observed:	Mean Specific Heat \bar{c}_p after Correction:
397.20	21.20	5 minutes	0.04977	0.04546
500.03	21.28	5.5 ..	0.05124	0.04682
629.30	21.31	5.5 ..	0.05346	0.04940
800.68	21.56	4.5 ..	0.05859	0.05609
500.00	21.28	5 ..	0.05111	0.04669
1062.30	21.70	6.5 ..	0.05256	0.04756
629.43	21.15	7.5 ..	0.04750	0.04123

Prolongated heating at higher temperatures obviously causes the values of \bar{c}_p to decrease, as is illustrated by the determinations repeated at 500° and at 629°.4 C. This fact seems to indicate, that also in the case of thorium not only recrystallisation occurs, but that the metal really has a complex character.

ThO_2 , the necessary corrections are applied in the fifth column. All these values prove to be considerably greater (about 27%) than in the case of massive *thorium* (A): this fact is in agreement with what was observed in all such cases, where the mean specific heats of massive metals (*Be, Ce, Zr, Ti*) were compared with those of the pulverized or finely-ground metals at the same temperatures. Also in this case, the time τ necessary for reaching the maximum temperature of the calorimeter is much shorter, than in the case, when the massive metal is investigated. This time increases somewhat after repeated heatings at higher temperatures, in accordance with the fact, that a recrystallisation and a forming of greater granules sets in at increasing temperatures; at 1065° C. the experiments had to be stopped, because the platinum crucible proved to be attacked by the powdered thorium enclosed. The values obtained cannot be considered as sufficiently accurate and have only significance for the purpose of comparison of the influence, which the size of the grains has upon the values of \bar{c}_p observed: the *greater* the grains are, the *lower* the values of \bar{c}_p always prove to be.

§ 4. *Thoriumdioxide*. Pure *thoriumdioxide*: ThO_2 was enclosed in an

Temperature t in °C. :	Final temperature t' of the Calorimeter:	Mean Specific Heats \bar{c}_p :	\bar{c}_p as calculated from the formula:
398.20	21.13	0.06141	0.06141
501.04	21.06	0.06318	0.06332
630.79	21.21	0.06450	0.06444
630.87	21.31	0.06438	
800.93	21.42	0.06533	0.06511
900.17	21.50	0.06556	0.06544
959.57	21.57	0.06566	0.06566
1001.10	21.60	0.06600	0.06583
1062.3	21.70	0.06603	0.06609
1062.3	21.80	0.06614	
1203.7	21.80	0.06675	0.06675
1391.2	21.90	0.06783	0.06783

As the value of \bar{c}_p at 10° C. could, from the \bar{c}_p - t -curve, not be determined with a sufficient accuracy, the slight correction for the interval between 21° and 0° C. has not been applied in this case.

evacuated platinum crucible and its specific heats were determined in the usual way. The data obtained are collected in the following table III the maximum temperature of the calorimeter always was reached within 1.5 to 2 minutes.

The mean specific heats \bar{c}_p , in their dependence on the temperature, can fairly well be expressed by the formula:

$$\bar{c}_p = 0,027316 + 0,183054 \cdot 10^{-3} \cdot t - 0,361497 \cdot 10^{-6} \cdot t^2 + \\ + 0,357245 \cdot 10^{-9} \cdot t^3 - 0,17382 \cdot 10^{-12} \cdot t^4 + 0,33525 \cdot 10^{-16} \cdot t^5.$$

The true specific heats \bar{c}_p , therefore, by:

$$c_p = 0,027316 + 0,366108 \cdot 10^{-3} \cdot t - 0,108449 \cdot 10^{-5} \cdot t^2 + \\ + 0,142898 \cdot 10^{-8} \cdot t^3 - 0,8691 \cdot 10^{-12} \cdot t^4 + 0,20115 \cdot 10^{-15} \cdot t^5$$

and the molecular heats C'_p of the dioxide by:

$$C'_p = 7,2147 + 0,096696 \cdot t - 0,28644 \cdot 10^{-3} \cdot t^2 + \\ + 0,37742 \cdot 10^{-6} \cdot t^3 - 0,22955 \cdot 10^{-9} \cdot t^4 + 0,5313 \cdot 10^{-13} \cdot t^5.$$

It must be remarked, however, that all these formulae may only be applied between 300° and 1400° C.; some of the values of C'_p thus calculated (see below) are graphically represented in Fig. 1.

Temperature:	C'_p :	Temperature:	C'_p :
300°	18.904	1000°	18.470
400	18.749	1100	18.835
500	18.444	1200	19.214
600	18.018	1300	19.695
700	17.818	1400	20.756
800	17.879	1500	22.886
900	18.142	1600	27.295

The curve has a flat minimum at about 720° C. and then rises rapidly with increasing temperatures. The *apparent* atomic heat of 1 atom of oxygen in the compound gradually *decreases* with increasing temperatures from 5.334 at 300° C. to 3.715 at 1200° C.: also¹⁾ in this case, evidently no additivity of the atomic heats of the constituting elements is present after their chemical combination.

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¹⁾ F. M. JAEGER, *Chemisch Weekblad*, 31, (1934), 60.