

Chemistry. — *The Exact Measurement of the Specific Heats of Metals at High Temperatures. XXVI. The Specific Heats and the Electrical Resistance of Cerium.* By F. M. JAEGER, J. A. BOTTEMA and E. ROSENBOHM.

(Communicated at the meeting of September 26, 1936).

§ 1. In 1934 JAEGER and ROSENBOHM ¹⁾ in a paper from this laboratory already drew attention to the fact that between 310° and 550° C. no reproducible values for the mean specific heats of *cerium* could be obtained: the inner state of this metal evidently is a very complex one, depending as well on previous heatings, as on the time during which the heated samples are subsequently preserved at room-temperature. It was, moreover, found that each value of \bar{c}_p observed at a definite temperature t , increased after each renewed heating; but that subsequently it proved to decrease at the same temperature, if the sample for some days had been preserved at 15° C. As a probable explanation of these facts it was suggested, that at least one transition-point would be present between 360° and 370° C.; the corresponding transformation evidently takes place so very slowly, that, on cooling, only an incomplete change occurs backwards into the modification which is stable at lower temperatures. In this respect an observation of HULL ²⁾ may be of interest, who by means of X-ray-analysis stated the "simultaneous" presence at ordinary temperatures of a cubic and of a hexagonal structure.

The existence of at least two different modifications of *cerium* has since been confirmed by the study of several X-ray-spectrograms ³⁾. The usually occurring, hexagonal, closest-packed form has the parameters: $a_0 = 3,65$ A.U., $c_0 = 5,91$ A.U. and a density of 6,775; the other, cubic face-centred form has the cell-dimension: $a_0 = 5,143$ A.U. and a density of 6,792. From TROMBE's measurements of the changes of the magnetic susceptibility at low temperatures the existence of still another modification, stable below -174° C., seems to be almost certain: the hysteresis-phenomena there observed evidently have the same character as in the case of the transition of *cobaltum* observed between 400°—500° C. ⁴⁾

Whilst the former measurements ¹⁾ were made with separate smaller

¹⁾ F. M. JAEGER and E. ROSENBOHM, Proc. Royal Acad. Amsterdam, **37**, 489 (1934).

²⁾ A. W. HULL, Phys. Rev., **18**, 88 (1921).

³⁾ L. F. AUDRIETH, Metallwirtsch., **14**, 3 (1935); J. C. MC LENNAN and R. W. MC KAY, Trans. R. Soc. Canada, S. III, **24**, 33 (1930); J. C. MC LENNAN and R. J. MONKMAN, ibidem, **23**, 255 (1929); L. L. QUILL, Zeits. anorg. Chem. **208**, 273 (1932); E. ZINTL and S. NEUMAYR, Zeits. Electrochem., **39**, 84 (1933); F. TROMBE, Compt. rend. Paris, **198**, 1592 (1934).

⁴⁾ Conf. M. C. NEUBURGER, Die Allotropie der chem. Elemente, Stuttgart, 20 (1936).

lumps of the metal, so that only a relatively small weight of it could be included within the crucible, — this time we had at our disposal a massive block of *cerium* (98 % *Ce*; 1 % *Fe* and traces of *Si*, *C*, *Al* and *Mg*). This lump, after having been turned-off on the lathe and having been brought into the exact shape of the platinum vacuum-crucible in which it had to be enclosed, finally weighed 22,2098 grammes, whilst the weight of the platinum itself was 28,0393 grammes. As well in the calorimetric measurements as in the study of the differential heat-capacity-curves after SALADIN-LE CHATELIER's method the existence was revealed of two transition-points at 362° C. and at about 503° C. respectively. Moreover, a suspicion arose that there might exist still another transition-point at a temperature above 530° C. Below its meltingpoint (635° C.), *cerium*, therefore, at least shows *three*, but more probably even *four* different crystalline forms.

§ 2. The quantities of heat Q delivered between 300° and 530° C. by 1 gramme of *cerium* were determined with the usual care. The data obtained are collected in the Table I; the reduction of Q to Q_0 was made by adopting the value: $\bar{c}_p = 0,0468$ between 20° C. and 0° C., obtained by extrapolation; the latter, however is somewhat hasardous in this case, because of the uncertainty as to the true shape of the curve, as a consequence of the unknown heat-effect of the transition occurring at 362° C.

The following explanatory remarks about these data still have to be made: as long as the temperature of heating remains below 500° C. (Exp. 1—10), the time necessary for attaining the maximum temperature of the calorimeter-block is only 5½ to 6 minutes, but the values obtained between 320°—380° C. are *not* reproducible. They depend on the special way of preliminary heating of the samples. On heating, the mean specific heat of the substance at the same temperature t increases after each heating; but it again decreases, when the sample has for some days been preserved at room-temperature, *without* it being possible ever to reproduce the same maximum or minimum value of \bar{c}_p at a given temperature. The inner state of the metal evidently depends too strongly on the special rate of heating and cooling and on the duration of the preliminary heating at each constant temperature of t^0 .

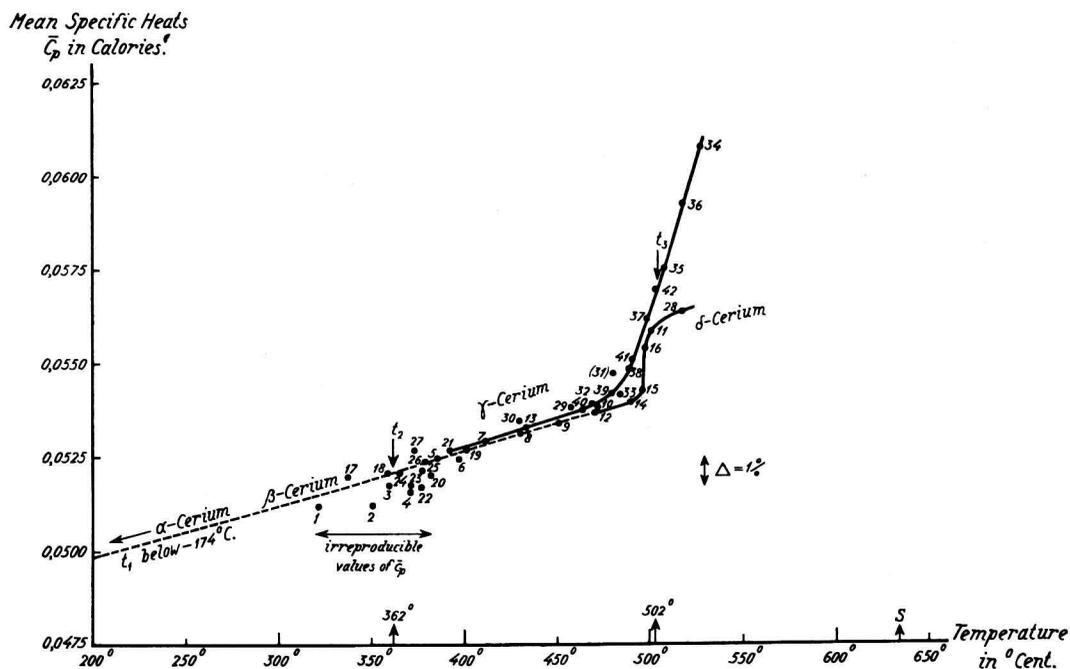
If, however, the sample is kept at a temperature of 500° C. for some hours, the time required for attaining the maximum calorimeter-temperature proves suddenly to have augmented to 15 or 20 minutes; when the experiments are now repeated at the same temperatures below 500° as before (Exp. 11—16, 17—27), *the same* values of \bar{c}_p as formerly are actually obtained, notwithstanding the fact that the amount of heat now is only completely given-off after this much longer time of 15—20 minutes. Evidently the inner state of the metal has, by the heating at 500° C., undergone an appreciable change; so that now a conspicuous retardation

TABLE I.
Mean Specific Heats \bar{c}_p of Cerium between 300° and 530° C.

| Sequence-number of the Experiment: | Temperature t° in °C.: | Final temperature t° of the Calorimeter: | Quantity of Heat Q developed by 1 Gr. between t° and t' in Calories: | Quantity of Heat Q_0 given off between t° and 0° by 1 Gr. of the metal in Calories: | Time necessary for reaching the maximum temperature of the Calorimeter (in Minutes): | Mean Specific Heats \bar{c}_p between t° and t' : |
|------------------------------------|-------------------------------|---|---|--|--|--|
| 1 | 322.81 | 20.76 | — | — | 6 | 0.05109 |
| 2 | 351.17 | 20.88 | — | — | 5½ | 0.05116 |
| 3 | 361.03 | 20.95 | — | — | 5½ | 0.05171 |
| 4 | 372.42 | 21.35 | — | — | 5½ | 0.05160 |
| 5 | 384.84 | 21.30 | 19.06 | 20.06 | 5½ | 0.05243 |
| 6 | 396.95 | 21.25 | 19.71 | 20.70 | 6 | 0.05246 |
| 7 | 409.58 | 21.14 | 20.54 | 21.52 | 5½ | 0.05287 |
| 8 | 430.82 | 21.20 | 21.74 | 22.73 | 6 | 0.05307 |
| 9 | 451.39 | 21.24 | 22.94 | 23.94 | 5½ | 0.05333 |
| 10 | 471.63 | 21.29 | 24.18 | 25.18 | 5½ | 0.05370 |
| 11 | 502.10 | 21.37 | 26.77 | 27.77 | 14½ | 0.05586 |
| 12 | 470.70 | 21.00 | 24.10 | 25.08 | 17 | 0.05359 |
| 13 | 432.51 | 21.15 | 21.88 | 22.87 | 17 | 0.05318 |
| 14 | 490.15 | 21.28 | 25.24 | 26.24 | 15 | 0.05382 |
| 15 | 495.90 | 21.00 | 25.71 | 26.69 | 11 | 0.05414 |
| 16 | 498.94 | 22.00 | 26.37 | 27.40 | 8½ | 0.05528 |
| 17 | 338.30 | 20.96 | — | — | 17 | 0.05196 |
| 18 | 357.90 | 20.97 | — | — | 17½ | 0.05198 |
| 19 | 400.94 | 21.06 | 20.00 | 20.99 | 17½ | 0.05264 |
| 20 | 381.56 | 20.98 | — | — | 17½ | 0.05199 |
| 21 | 392.84 | 21.05 | — | — | 18 | 0.05264 |
| 22 | 376.20 | 21.40 | — | — | 17 | 0.05155 |
| 23 | 370.88 | 21.23 | — | — | 17½ | 0.05169 |
| 24 | 364.90 | 21.15 | — | — | 17 | 0.05197 |
| 25 | 379.10 | 20.60 | — | — | 18 | 0.05208 |
| 26 | 378.84 | 20.84 | — | — | 17½ | 0.05227 |
| 27 | 374.00 | 20.92 | — | — | 18 | 0.05265 |
| 28 | 517.40 | 21.23 | 27.90 | 28.89 | 4½ | 0.05623 |
| 29 | 457.47 | 22.08 | — | — | 15 | 0.05375 |
| 30 | 430.00 | 21.60 | — | — | 18 | 0.05351 |
| 31 | 480.55 | 21.87 | — | — | 18 | 0.05467 |
| 32 | 471.18 | 21.87 | — | — | 17½ | 0.05380 |
| 33 | 484.80 | 22.10 | — | — | 8 | 0.05416 |
| 34 | 530.90 | 21.90 | 30.98 | 32.01 | 3½ | 0.06086 |
| 35 | 510.25 | 21.94 | 28.00 | 29.03 | 6 | 0.05733 |
| 36 | 520.04 | 21.54 | 29.49 | 30.50 | 3½ | 0.05915 |
| 37 | 500.35 | 21.45 | 26.81 | 27.81 | 4 | 0.05598 |
| 38 | 490.37 | 21.52 | 25.66 | 26.67 | 7 | 0.05474 |
| 39 | 480.42 | 21.42 | 24.84 | 25.84 | 15 | 0.05412 |
| 40 | 464.80 | 22.30 | 23.78 | 24.82 | 15 | 0.05373 |
| 41 | 492.87 | 22.02 | 25.86 | 26.89 | 4½ | 0.05492 |
| 42 | 505.00 | 21.70 | 27.50 | 28.52 | 5½ | 0.05690 |

in the heat-development has resulted. The latter also takes place within the interval of 320° — 380° C. mentioned above; but the values of \bar{c}_p still remain just as *irreproducible* within this interval, as they were before (Exp. 17, 18, 20, 22—27). If the metal subsequently be heated above 515° C. (Exp. 28), the time required for the complete delivery of the heat once more proves to get reduced to the original 4—5 minutes; but at temperatures of heating inferior to 500° C., the retardation previously mentioned still appears to be present (Exp. 29—33). On subsequent heating at 530° C. (Exp. 34) the metal still continues to give-off its heat within 5 minutes — just as after a heating at 515° C.; but now \bar{c}_p proves to have got much higher values than after the heating at 515° C. and the \bar{c}_p - t -curve has assumed a quite different shape. This new \bar{c}_p - t -curve (Exp. 34, 36, 42, 37, 41, 39 and 40) seems to meet the curve of Exp. 5—9, so that it almost appears as its natural continuation. The transition-point at about 500° C., moreover, proves to be somewhat shifted towards lower temperatures, whilst the apparent discontinuity at 520° — 530° C. now proves to have completely disappeared. This shift in the transition-temperature at 500° C. towards a lower temperature was also observed in the study of the differential heat-capacity-curves (§ 3).

Figure 1 gives a graphical representation of the facts observed.



§ 3. The differential heat-capacity-curves of cerium, when compared with copper, were determined in a high vacuum, as well on heating as on

cooling after SALADIN—LE CHATELIER's method. The *copper* used had the shape of a sphere of suitable dimension, whilst the mass of *cerium* was brought into the form of a round-edged cube with a volume of about 1 cm³.

In Figure 2 curve 1a represents a heating-curve, 1b a curve obtained on subsequent cooling. Evidently two apparently sharp transformation-points at 362° and 502° C. respectively are observed, of which the latter

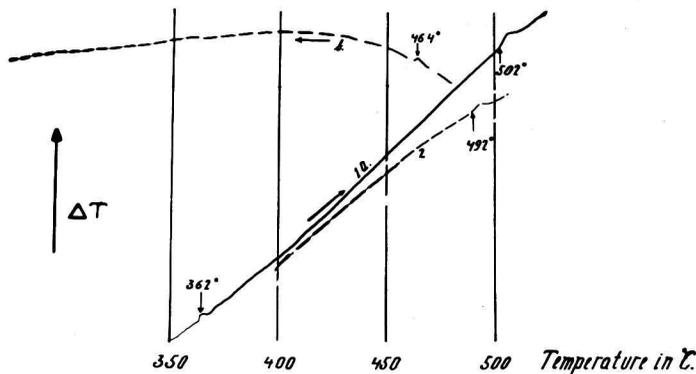


Fig. 2. Differential Heat-capacity-curves of Cerium with respect to Copper on Heating and Cooling.

appears on the cooling-curve to have been shifted towards a lower temperature, as commonly is observed in the case of allotropic metals. In this case it proved impossible to diminish this shift even by very slow cooling; when the sample once has been heated above 502° C., the latter point is shifted to about 492° C., whilst the first transition-point at 362° C. evidently remains reproducible within 1° C. The irreproducibility of the \bar{c}_p -values after heating at temperatures above 502° C. certainly must in some way be connected with the tardiness of the transformation: δ -cerium \rightarrow γ -cerium on cooling¹).

§ 4. *The Change of the Electrical Resistance of Cerium in connection with the Temperature.* A much clearer insight into the causes of the phenomena described was obtained by the study of the changes of the electrical resistance of *cerium* with increasing and decreasing temperatures in a high vacuum, executed in the way previously indicated²). A thin flat plate was prepared from the bulky mass of the metal and from this plate a *U*-shaped piece was formed with a total length of 50 m.M. and a cross-section of 1 m.M²). The terminals were somewhat broadened and provided with a hole, through which the copperwires of the vacuum

¹) The modification of *cerium* occurring below -174°C . here is considered as α -*cerium*. Then the β -form is the hexagonal, the γ -form the cubic one. About the σ -form stable at still higher temperatures, no further information can at present be given.

²) E. ROSENBOHM and F. M. JAEGER, Proc. Royal Acad. Amsterdam, 39, 374 (1936).

tube were drawn and then thoroughly fixed by clinching. The photographic records of the changes of the electrical resistance of *cerium* at different temperatures thus observed (Fig. 3) proved to allow a much better interpretation of the changes gradually occurring in the metal after repeated heatings than the phenomena met with in the calorimetric measurements just described.

If the metal is heated at temperatures which do not exceed 470° — 500° C.,

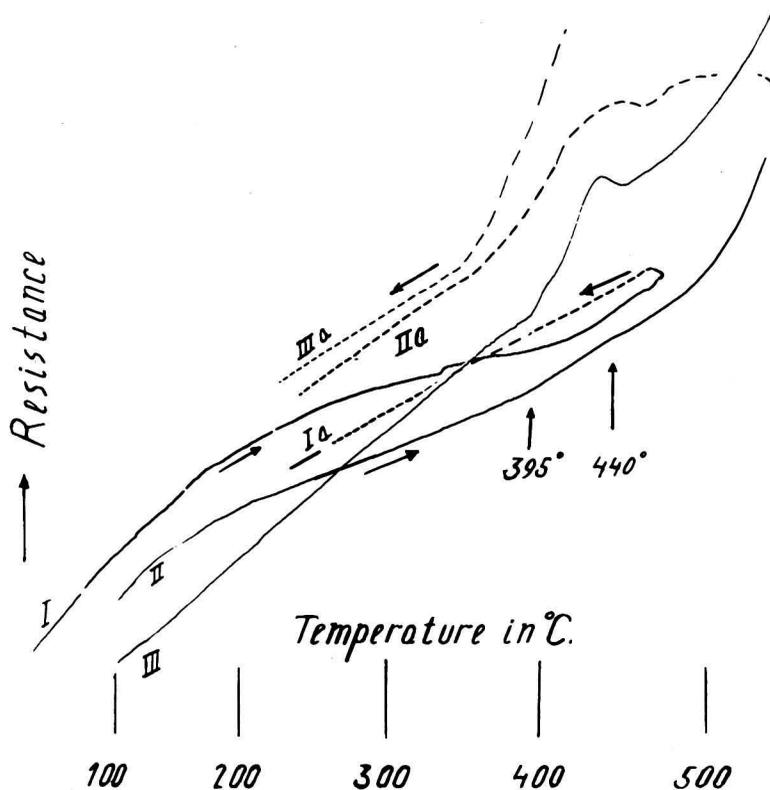


Fig. 3. The Gradual Change of the R - t -Curves of Cerium in successive Heatings and Coolings of the Metal.

the data obtained are not completely reproducible, but occasionally may differ about 5 %; notwithstanding this, however, as well the characteristic, elongated S-form of the R - t -curves on heating, as the almost rectilinear shape of the cooling-curves (I and Ia in Fig. 3) appear fairly well to be reproduced in all experiments. The transition-points at 395° and about 440° C. now are either extremely feebly, or occasionally, more distinctly observable. However, once the temperature has been increased above 500° — 540° C., a steep rise of the curve starting at about 500° C., is observed already after the first heating (curve II), whilst the cooling-curve has assumed a quite other form as before: its shape now presents a zig-zag course, with a very steep intermediate branch between 400° and

450° C. If the heatings¹⁾ at 540° C. are several times repeated, the curve *III* begins to manifest an evident subdivision into three rectilinear parts, characterised by very different temperature-gradients of the electrical resistance. At each subsequent heating the middle part of the curve gets a gradually steeper slope: after eight heatings, however, a final state of the metal proves to have been attained, so that in all further experiments a perfectly reproducible *R-t*-curve results, which then is no longer modified.

The corrected values of *R* thus obtained at each temperature are collected in the following table and graphically reproduced in Fig. 4.

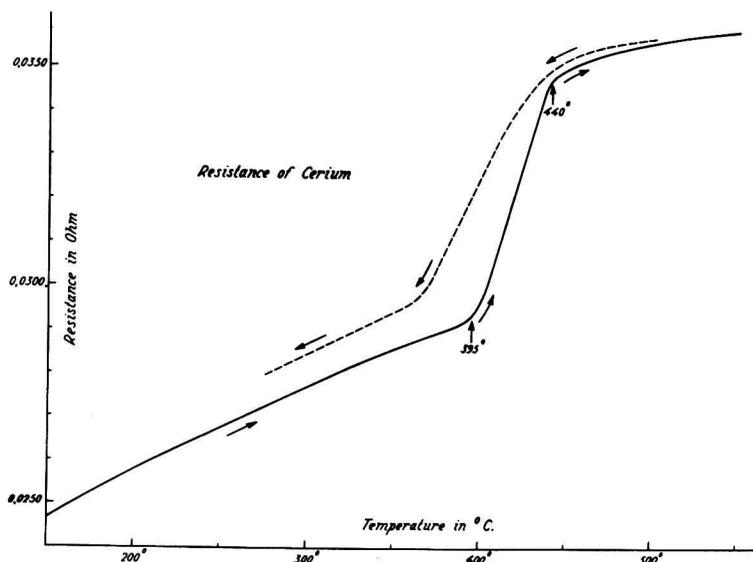


Fig. 4. The final Shape of the *R-t*-Curve of Cerium after often repeated Heatings and Coolings.

The most probable explanation of these facts may be this, that the metal originally has a "mosaic structure" consisting of separate fields of the three β -, γ - and δ -modifications simultaneously present beside each other, each of these modifications having its own field of stability, ranging from lower temperatures up to 393° C. (β -form), from 393° to 440° C. (γ -form) and from 440° upwards (δ -form) respectively. This supposition is corroborated by the *physical inhomogeneity* of the metal, as betrayed by the manifestation of strong thermoelectrical forces during the measurements of the electrical resistance exactly within the temperature-interval between 350° and 440° C. To the latter fact we afterwards will return in detail, in connection with some recent experiences in the case of *neodymium*.

¹⁾ The heatings at 540° C., and the subsequent coolings down to about 150° C. took, in each experiment, about four hours. The curves *I-III* in Fig. 3 are direct photographic records, without any corrections having been applied.

TABLE II.
The (corrected) Dependency of the Electrical Resistance
of Cerium on the Temperature.

| Temperature t in °C.: | Resistance R in Ohm on Heating: | Resistance R in Ohm on Cooling: | Temperature t in °C.: | Resistance R in Ohm on Heating: | Resistance R in Ohm on Cooling: |
|----------------------------|---|---|----------------------------|---|---|
| 150° | 0.0247 | — | 387° | 0.0291 | — |
| 200 | 0.0258 | — | 393 | 0.0293 | — |
| 250 | 0.0268 | — | 397 | 0.0295 | — |
| 275 | 0.0272 | 0.0280 | 400 | 0.0297 | 0.0325 |
| 300 | 0.0277 | 0.0284 | 425 | 0.0329 | 0.0343 |
| 325 | 0.0282 | 0.0290 | 450 | 0.0350 | 0.0354 |
| 350 | 0.0286 | 0.0294 | 475 | 0.0354 | 0.0356 |
| 375 | 0.0289 | 0.0304 | 500 | 0.0356 | 0.0357 |
| | | | 550 | 0.0359 | — |

During the heatings at lower temperatures evidently strong passive resistances occur, which prevent the true establishment of real internal equilibria; they are the cause of the typical irreproducibility of the data, as well in the calorimetrical as in the electrical measurements and of the accompanying hysteresis-phenomena. If, however, the heatings are many times repeated at temperatures above 500° C., these retardative causes prove gradually to get eliminated: so that two sharply defined transition-points at 393° C. and at 440° C. now finally appear, at each of which the temperature-coefficient of the electrical resistance assumes other and considerably different values. Doubtlessly, therefore, *cerium* has a very complex structure, consisting, between the ordinary temperature and the melting-point, of at least three different modifications; although simultaneously co-existent, each of them is truly stable only within a very limited interval of temperatures and is characterised by strongly deviating values of the temperature-coefficient of its electrical resistance. Only after numerous and often repeated heatings, the relative shift in the quantities of these modifications present finally leads to a state of invariable inner condition (Fig. 4).

§ 5. The results obtained with *cerium* by means of the calorimetrical method used by us, clearly demonstrate that it is *not* feasible in this case to use the values of \bar{c}_p observed in the successive intervals of temperature for deducing from them those of the true specific heats in the usual way. For the experimental method applied is, in reality, a method of *quenching*, because the samples studied are always so rapidly cooled, that in cases

as this, — in which *very slow* transformations evidently occur, — serious doubt must arise as to whether the sample after each of the successive experiments really returns to final states which really are directly comparable. On the contrary, — as we shall see in the case of *lanthanum*, — direct proof was given that this is *not* the case. Therefore, in such cases of slowly transforming metals like these rare earth-metals, the SALADIN-LE CHATELIER-method gives a more reliable insight into the way in which the specific heat of those metals depends on the temperature, than does the calorimetrical-method, because in the first case the sample is allowed really to assume the true temperature t at which each measurement is made. It, therefore, must be clear that in such cases as these, a deduction of c_p from the function $Q=f(t)$ by differentiation only can have any significance for some *very narrow* and *carefully selected* intervals of the temperature, after it has been ascertained, that within those intervals *no* appreciable retardation-phenomena nor allotropic changes do manifest themselves.

In the case of *cerium* such an interval is perhaps present between 380° and 480° C. Here the true specific heat c_p can, with a fair degree of accuracy, be represented by:

$$c_p = 0.0523 + 0,31 \cdot 10^{-6} \cdot (t - 380),$$

the atomic heat C_p , therefore, by:

$$C_p = 7,3377 + 0,43493 \cdot 10^{-2} \cdot (t - 380).$$

Thus, for 380° C., C_p becomes: 7,338; for 480° C.: 7.773.

Evidently *cerium* equally seems to belong to those metals, the atomic heats of which, even at moderate temperatures, considerably exceed the value of $3R$ calories. For the rest, not the same degree of certainty can be attributed on the one hand to the results of the calorimetrical experiments in this case, as to those of the electrical ones on the other hand, because the former were executed *before* the final and no longer variable inner state of the metal had completely been attained, as was the case in the latter heatings above 500° C. continued during several subsequent weeks.

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