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

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

§ 1. Two modifications of *lanthanum*, corresponding to those of *cerium* are known with certainty [1]): a hexagonal form with: $a_0 = 3{,}754$ A.U., $c_0 = 6.063$ A.U. and with a density of 6,188; moreover a cubic, face-centred modification with the parameter: $a_0 = 5{,}296$ A.U. and a density of 6,165. According to TROMBE [2]), the magnetic measurements seem to indicate the existence of still another modification, stable below —163° C. The indication of the α-, β-, γ-modifications adopted here is quite analogous to that used in the case of *cerium*.

By means of SALADIN-LE CHATELIER's method for the determination of heat-capacity-curves, — which, as has been said, gives a rather good insight into the true dependence of the specific heat on the temperature, — sharp and reproducible discontinuities were observed at 548° C., 665° C. and 709° C. These points prove to be *in*dependent of the preliminary heatings and they constantly also appear on the cooling-curves, but in the latter case shifted towards lower temperatures over about 20° C. For the rest, they appear to be independent of the rate of cooling (Fig. 1).

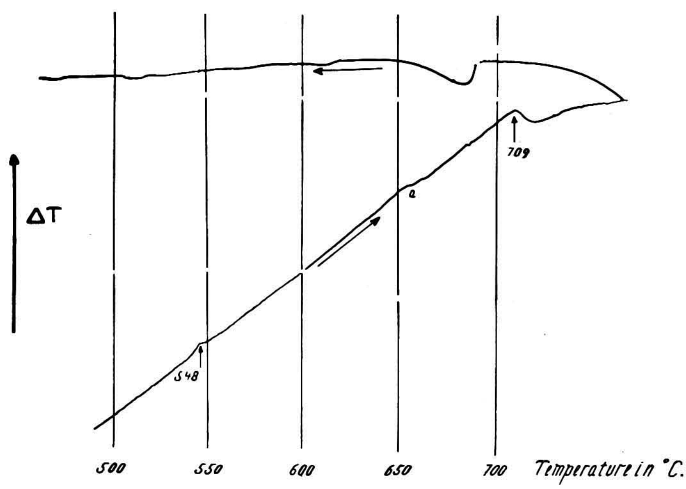

Fig. 1. *Differential Heat-Capacity Curves of Lanthanum with respect to Copper.*

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1) A. ROSSI, Rend. R. Acad. Lincei, **15**, 298 (1932); L. L. QUILL, Zeits. f. anorg. Chem., **208**, 274 (1932).

2) F. TROMBE, Compt. rend. Paris, **198**, 1592 (1934).

It must be remarked that, for instance after passing the transitionpoint at 548° C., the rate of increase of $\bar{c}_p$ with the temperature evidently remains practically *the same* as before — just as we previously stated this fact in the case of Au_7Sb_2 [1]) at 355° C. and as also was observed in the case of *cobaltum* [2]) at 400° C. and in other cases.

§ 2. The supplementary measurements of the change of the electrical resistance of *lanthanum* with the temperature yielded the following results (Table I and Fig. 2):

TABLE I.

The Electrical Resistance of Lanthanum between 250° and 750° C.

Temperature t:	Resistance (in Ohms) on heating:	Resistance (in Ohms) on cooling:	Temperature t:	Resistance (in Ohms) on heating:	Resistance (in Ohms) on cooling:
250° C.	0.01635	—	550°	0.01916	0.01822
300	0.01692	—	560	0.01923 Max.	0.01820
350	0.01753	0.01612	566	0.01913 Min.	0.01819
400	0.01788	0.01661	600	0.01923	0.01801
420	—	0.01681	650	0.02080	0.02049
421	0.01795 Max.	—	675	0.02156	0.02129
436	0.01773 Min.	—	700	0.02186	0.02159
450	0.01794	0.01744	725	0.02203	0.02184
500	0.01859	0.01806	750	0.02227	—
525	0.01885	0.01822			

At 20° C. the resistance of the wire was 0.01360 Ohms. From these data and the figure 2 it becomes clear, that in general, the same discontinuities as in § 1 are manifested, but that, moreover, there also is a discontinuity observed in the vicinity of 420° C., manifesting itself as a conspicuous maximum.

On the other hand the effect at 660° C. seems to be connected with the transition at 709°—715° C.; the traject of 660°—715° C. evidently has the character of a transition-traject.

The form of the curve of Fig. 2 at the transition-points reminds of that

[1]) E. ROSENBOHM and F. M. JAEGER, Proc. Royal Acad. Amsterdam, **39**, 373 (1936).

[2]) U. DEHLINGER, *Gitteraufbau metallischer Systeme* in G. MASING's *Handbuch der Metallphysik*, p. 134 (1933).

observed in the case of *titanium*[1]) and of *zirconium*[2]); but in contrast to the phenomena observed in the case of *titanium*, this time the curve is really reproducible.

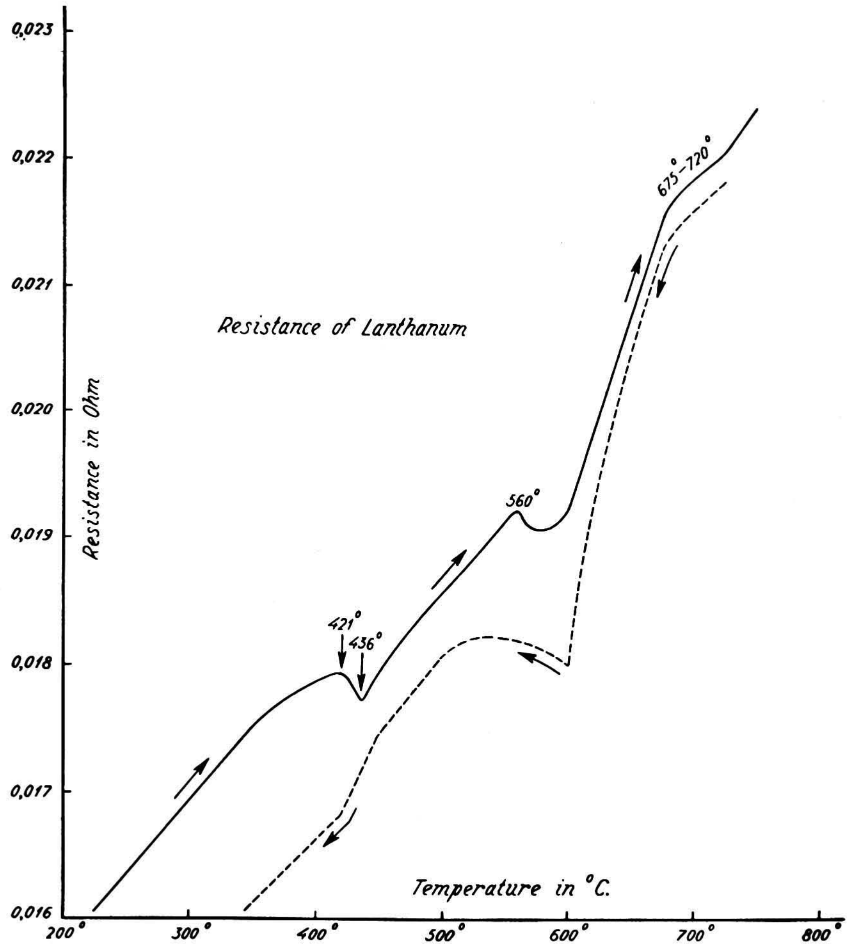

Fig. 2. *The Electrical Resistance of Lanthanum in its Dependence on the Temperature.*

Finally it is worth while to remark here that a preliminary heating at 700° C. causes the shape of the resistance-temperature-curve to be thoroughly altered; this fact proves, that above 709°—715° C. a complete change of the inner structure sets in.

§ 3. For the measurements of the mean specific heats of *lanthanum* a massive lump (98 % *La*; 1 % *Fe*; traces of *C*, *Si*, *Al* and *Mg*) was used weighing 18,7912 grammes; it was enclosed within a platinum vacuum crucible of 27,5209 grammes. At the temperatures higher than

[1]) E. ROSENBOHM and F. M. JAEGER, Proc. Royal Acad. Amsterdam, **39**, 467 (1936).
[2]) J. H. DE BOER and J. D. FAST, Recueil d. Trav. d. Chim. d. Pays-Bas, **55**, 459 (1936).

650° C. the metal had to be separated from the walls of the crucible by means of a thin mica-sheet, so as to prevent any reaction between the two metals at temperatures above 700° C. The weight of the mica was so small, that it safely could be taken into account as platinum. The data obtained between 350° and 725° C. are collected in Table II; for the reduction of Q to Q_0, the value of $\bar{c}_p$ between 20° and 0° C. : 0,04725 obtained by extrapolation was used. With respect to this extrapolation, however, the same remark as in the case of *cerium* must here be made.

These data are graphically represented in Figure 3.

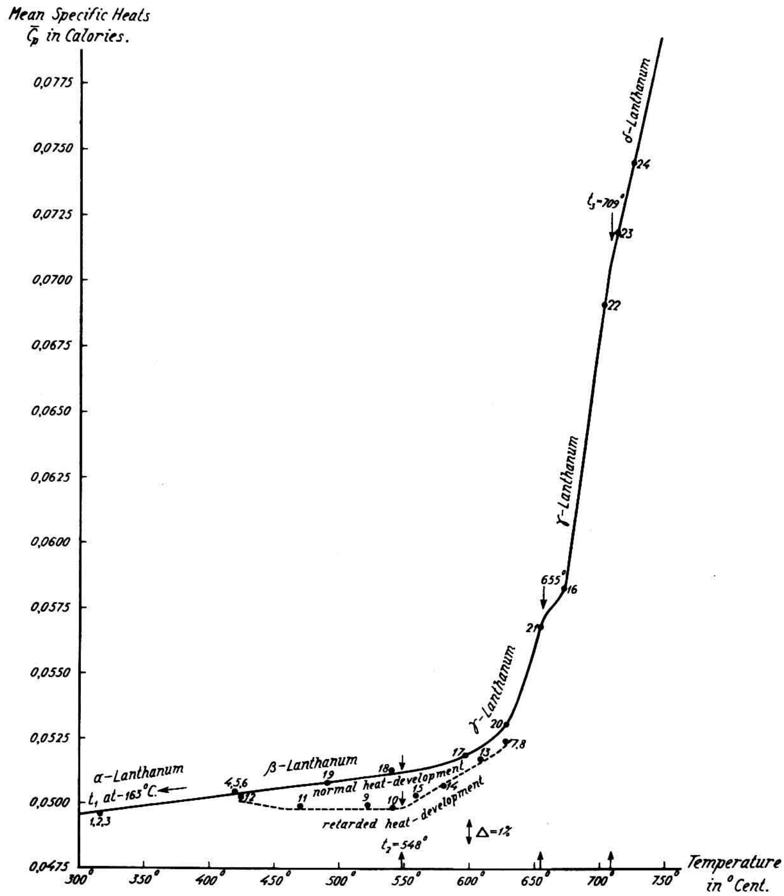

Fig. 3. *Mean Specific Heats of Lanthanum between 300° and 750° C.*

In connection with these measurements attention must be drawn to the following facts:

In the experiments 1—6 the heat-development proved to be quite normal (5—6 minutes). After heating the sample at 628° C. (Exp. 7 and 8), however, it proved to have got retarded. On subsequent repeating of the measurements at temperatures inferior to 628° C., this retardation (17—20 minutes) still proved to be present, whilst the curve obtained (Exp.

TABLE II.

Mean Specific Heats of Lanthanum between 300° and 725° C.

Sequence number of 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 developed between $t°$ and 0° C. in Calories:	Time necessary for reaching the maximum temperature of the Calorimeter (in Minutes):	Mean Specific Heats $\bar{c}_p$ between $t°$ and $t'°$ C.:	
1	320°.60	21°.14	mean: 14.858	15.849	2	0.04944	0.04964
2	320.08	20.98			2	0.04968	
3	320.66	20.86			2	0.04981	
4	417.06	20.96	mean: 20.112	21.127	5	0.05036	0.05048
5	419.88	21.47			5	0.05065	
6	421.88	21.26			5	0.05043	
7	627.60	21.43	mean: 31.859	32.876	18	0.05255	0.05241
8	629.44	21.53			18	0.05227	
9	521.15	21.48	24.965	25.980	17	0.04996	
10	540.90	21.55	25.900	26.914	19	0.04987	
11	470.10	21.00	22.390	23.390	20	0.04985	
12	424.59	20.74	20.207	21.187	20	0.05003	
13	608.90	21.20	30.449	31.450	20	0.05181	
14	580.54	21.07	28.396	29.391	20	0.05076	
15	559.80	21.27	27.087	28.092	19	0.05030	
16	671.73	21.59	37.864	38.884	3	0.05824	
17	595.70	21.60	29.807	30.827	3	0.05192	
18	541.00	21.33	26.646	27.654	3	0.05127	
19	490.00	21.32	23.799	24.806	4	0.05090	
20	628.50	21.50	32.632	33.648	4	0.05376	
21	655.00	21.50	36.012	37.028	4	0.05685	
22	700.86	21.71	46.880	47.910	— *)	0.06903	
23	711.65	21.99	49.540	50.580	— *)	0.07183	
24	723.68	22.16	52.360	53.410	— *)	0.07464	

*) In the experiments No. 22, 23 and 24 this time was 18, 16 and 10 minutes respectively; these numbers are, however, *not comparable* with the other ones in this column, because in the three latter a mica-sheet had been inserted between the preparation and the wall of the crucible.

9—15) did not coincide with the original one. After heating at 672° C. (Exp. 16), the retardation once more diminished to 3—4 minutes. In the new curve (Exp. 7—15) a discontinuity occurs at 548° C.; on repeating the measurements at lower temperatures (Exp. 17—21), the branch (7—15) could, moreover, *not* be reproduced and the value 12 of this branch shows, that the curve gradually approaches to the other one, — thus perhaps corresponding to the same maximum at 420° C. in it as was observed in the experiments on the electrical resistance. It, therefore, makes the impression, that the values of the curve (7—15), together with their typical retardation in the heat-development, more closely approach to those observed in the experiments by means of the twin-galvanometer-method than to those obtained on rapid cooling. Probably the curve (12—7—15) in a natural way (passing the point 16) joins the curve (22—23—24); so that the whole part of the other curve between 420° and 665° C. seems to be produced by the fact that, because of the "quenching" of the samples, the slow transformations going-on in the metal have no time to proceed to completion. After each of the successive experiments, the final state of the metal at each temperature thus will differ from that which was reached in a previous or is attained in a subsequent experiment. Just as in the case of *cerium* it is, therefore, not feasible, to deduce the true specific heats of *lanthanum* between 420° and 665° C. in the usual way from the values of Q obtained; only the *mean* specific heats can be roughly estimated from the shape of the curves below 665° C., — without even in that case there being a perfect certainty about the true values.

If, for instance, we endeavour to deduce c_p and C_p only in the restricted interval of temperatures between 300° and 541° C., the following results are obtained:

From the values of Q at 320°, 419° and 541° C., the following dependency of Q on the temperature is deduced:

$$Q = 0{,}04829 \,.\, (t-300) + 0{,}3538 \,.\, 10^{-4} \,.\, (t-300)^2 - 0{,}6106 \,.\, 10^{-7} \,.\, (t-300)^3,$$

from which follows:

$$C_p = 6{,}713 + 0{,}9835 \,.\, 10^{-2} \,.\, (t-300) - 0{,}251 \,.\, 10^{-4} \,.\, (t-300)^2.$$

This leads to a flat maximum of C_p of 7,676 at 497° C.:

t:	C_p:	t:	C_p:
300°	6,713	500°	7,676
400°	7,445	550°	7,604
497°	7,676		

If, however, the value of Q at 490° C. is used in the calculation in stead of the value at 541° C., then Q proves to get expressed by:

$$Q = 0{,}05056 \,.\, (t-300) + 0{,}33625 \,.\, 10^{-4} \,.\, (t-300)^2 - 0{,}11904 \,.\, 10^{-6} \,.\, (t-300)^3,$$

and, therefore, C_p by:

$$C_p = 7{,}028 + 0{,}9348 \,.\, 10^{-2} \,.\, (t-300) - 0{,}4964 \,.\, 10^{-4} \,.\, (t-300)^2.$$

Now the maximum in the curve appears to have been shifted to 394° C.

t:	C_p:	t:	C_p:
300°	7,028	400°	7,466
394°	7,468	500°	6,922

In both cases, therefore, a flat maximum in the C_p-t-curve at some temperature between 394° and 497° C. is observed, as was also stated in the resistance-temperature-curve at about 420° C.; but its location remains uncertain and evidently depends on the specially chosen values of Q used in the calculation. Neither in the heat-capacity-curves, nor in the $\bar{c}_p$-t-curve, such a maximum is, however, manifested, safe perhaps in the lower branch of the latter (Exp. 12).

If, on the contrary, either the values of Q_0 from Table II between 300° and 548° C. (I) or those between 470° and 628° C. (II) are used, we get:

I. $Q_0 = 0{,}049757 \, . \, t - 0{,}53806 . 10^{-5} \, . \, t^2 + 0{,}14595 . 10^{-7} \, . \, t^3.$

$C_p = 6{,}916 - 0{,}14958 . 10^{-2} \, . \, t + 0{,}60861 . 10^{-5} \, . \, t^2.$

II. $Q_0 = 0{,}092804 \, . \, t - 0{,}17211 . 10^{-3} \, . \, t^2 + 0{,}17132 . 10^{-6} \, . \, t^3.$

$C_p = 12{,}899 - 0{,}047847 \, . \, t + 0{,}71441 . 10^{-4} \, . \, t^2.$

Each of these two equations for C_p shows a *minimum*: the first (extrapolated) at 123° C. (6,824 cal.), the second at 335° C.:

I.		II.	
t:	C_p:	t:	C_p:
200°	6,866 (extr.)	200°	6,188
300°	7,015	300°	4,975
400°	7,292	334°,8	4,888
500°	7,690	400°	5,191
548°	7,924	500°	6,836
		600°	9,910

From these few examples it may be clearly seen, that *no reliable* values of c_p or C_p can be deduced in this way; the cause of this was already indicated in our previous paper on *cerium*.

Surely the whole part of the $\bar{c}_p$-t-curve between 600° and 715° C. must, moreover, be considered as being a "transition-traject", — as is also illustrated by the fact already often referred to, that in this interval the apparent values of C_p reach, from the theoretical viewpoint, unaccountably high values: between 672° and 701° C., they are found to be 8—11 calories, between 711° and 750° of 10—12 calories; etc.

Like *cerium*, also *lanthanum* seems at ordinary or rather low temperatures already to show atomic heats which are appreciably superior to $3R$ calories; above 709°—715° C. (Expt. 20, 21, 16, 22—24) a new modification (δ) of the metal, with rather high values of C_p makes, moreover, its appearance.

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