Chemistry. — *The Exact Measurement of the Specific Heats of Metals at High Temperatures.* **XXIII.** *The Calorimetrical, Electrical and Thermoelectrical Behaviour of Ductile Titanium.* **II.** By F. M. JAEGER, E. ROSENBOHM and R. FONTEYNE.

(Communicated at the meeting of March 28, 1936).

§ 1. In our previous paper we have drawn attention to the fact that, besides the true allotropic change of *titanium* at about 882°—900° C. into a cubic β-form, a series of minor "transition"-points were found by the calorimetrical measurements, although *no* allotropic changes could be stated at those temperatures by means of *X*-ray analysis. In the present paper we have in the first place, made a series of tentatives to corroborate the existence of these minor transition-points by means of *differential heat-capacity-curves*, obtained by the aid of the experimental device previously described [1]) and to control their presence further by the measurement of the *electrical resistance* of the metal in its dependence on the temperature, according to the twin galvanometer-method also previously dealt with [2]).

§ 2. *The Minor Transition-points of Titanium as revealed by differential Heat-capacity-curves.* As to the way of determining the *differential* curves according to the method mentioned above, we can refer to our previous publication [1]) on this subject.

The experiments made with *titanium*, — *copper* being used as a standard of comparison, — now completely corroborated the results obtained in the calorimetrical measurements in so far, as about *the same* discontinuities at only slightly different temperatures as in those experiments were also found in the curves recorded in this case, — the localization of these points being somewhat dependent on the way of heating and cooling and on a number of hysteresis-effects manifesting themselves on several occasions. More especially reproducible breaks in the curves at 250°—270°, 297°—300°, at about 508°, at about 631° and at 882° C. etc. were observed, which, however, showed a tendency to become gradually somewhat less pronounced when the heatings and coolings were very often repeated with the same sample, — with the exception of the break at 882° C., which corresponds to the transition: α-$Ti \rightleftarrows \beta$-$Ti$. The latter fact, as we shall see, was also stated in the measurements of the electrical resistance, the results of which are, for the rest, in very close agreement with those mentioned. In Fig. 1 four successive parts of the curve observed are reproduced, from which the localization of the different minor discontinuities can be verified.

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1) E. ROSENBOHM and F. M. JAEGER, Proc. Royal Acad. Amsterdam, **39**, 366 (1936).
2) Idem, Proc. Royal Acad. Amsterdam, **39**, 374 (1936).

By comparison with *nickel*, the order of magnitude of these discontinuities proves to be about the same as that at the transitionpoint of α- ⇄ β-*nickel.*

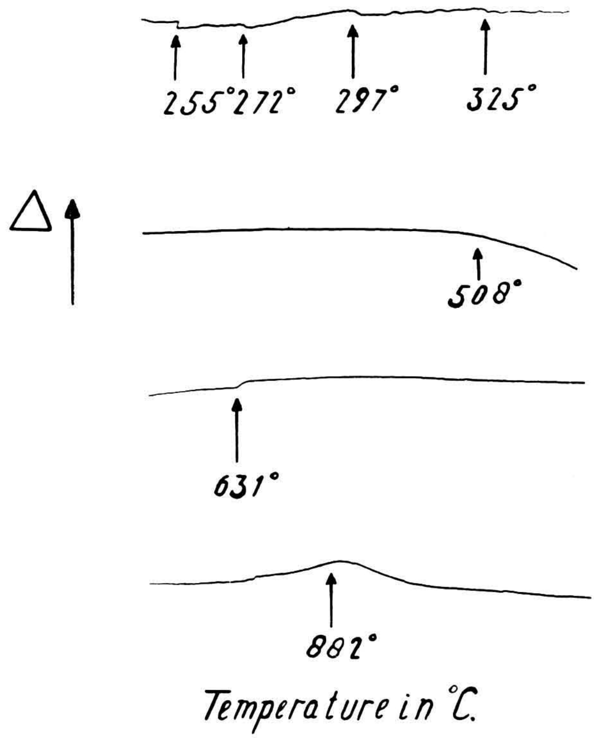

Fig. 1. *Breaks in the Differential curves at Different Temperatures.*

§ 2. *Measurements of the Resistance of Titanium at different Temperatures.* As to the technique of these determinations we refer to our previous communication about this subject.

Originally we used a *titanium*-wire, the diameter of which as well as its length being varied in the successive experiments; its resistance at 20° C. for $\delta = 0{,}31$ mm and $l = 358$ mm e.g. proved to be 2,993 Ω, while that of the connections outside the vacuum tube was 0,021 Ω and inside it 0,0014 Ω. The following values of the resistances observed are all corrected, except for the very small change in resistance of the connections within the furnace as a consequence of their variation with its temperature. The arrows in the tables indicate: ↓ on augmenting, ↑ on decreasing the temperature of the wire; *t* is the temperature of the wire in degrees Centigrade.

First and second Series of Experiments.

Under *a* the resistances observed are given (in Ohms) at the first heating till 360° C.; under *b* the same, after the wire having been cooled to 200° C. and then the heating being immediately repeated; under *c* the results, when the wire, after being cooled to roomtemperature, had remained so during 24 hours and then was again heated up to 430° C.; finally under *d* the values obtained on cooling the wire immediately after the last heating. The irreversibility of the values observed is clearly demonstrated, as those under *d* are all *smaller* than sub *c*:

t:	*a*: ↓	*b*: ↓	*c*: ↓	*d*: ↓
250°	—	—	—	6.139
260	6.213	—	6.214	6.233
270	6.353	6.354	6.362	6.324
275	6.426	6.425	6.425	—
280	6.482	6.480	6.479	6.417
285	6.543	6.533	6.533	—
290	6.598	6.580	6.581	6.510
295	6.646	—	—	—
300	6.692	6.678	6.678	6.602
310	6.782	6.772	6.770	6.691
320	6.866	6.867	6.860	6.779
330	6.963	6.956	6.946	6.864
340	7.030	7.044	7.038	6.952
350	7.109	7.133	7.119	7.035
360	7.190	7.220	7.203	7.120
370	—	—	7.275	7.200
380	—	—	7.356	7.280
390	—	—	7.431	7.365
400	—	—	7.515	7.450

Third Series of Experiments.

Sub. *a*: resistances observed on heating the previous wire, sub *b*: the values observed on cooling immediately afterwards; interval: 300°—500° C. and vice-versa.

t:	*a*: ↓	*b*: ↑	*t*:	*a*: ↓	*b*: ↑
300°	6.723	6.667	410°	7.621	7.544
310	6.814	6.759	420	7.690	7.616
320	6.902	6.842	430	7.758	7.688
330	6.990	6.924	440	7.824	7.758
340	7.076	7.007	450	7.893	7.828
350	7.160	7.086	460	7.962	7.900
360	7.244	7.167	470	8.031	7.969
370	7.321	7.244	480	8.103	8.042
380	7.400	7.320	490	8.176	8.118
390	7.476	7.396	500	8.245	8.190
400	7.548	7.471			

Also in this case the irreversibility is evident: on cooling all values again prove to be *smaller* than before at the same temperatures and the differences are more appreciable than in the previous series.

4th Series of Experiments. (Heatings as above : 450°—600° and vice-versa).					
t:	a: ↓	b: ↑	t:	a: ↓	b: ↑
450°	7.994	—	510°	8.392	7.975
460	8.060	—	515	—	8.012
470	8.128	—	520	8.457	8.055
480	8.193	—	525	—	8.098
490	8.259	—	530	8.522	8.137
500	8.324	—	540	8.586	8.199

The differences on heating and cooling still lie *in the same direction* as in the preceding cases, but now they are more appreciable than previously. Also the *initial* values (450°—500°) are noticeably greater than sub *a* as well as sub *b* of the 3rd series.

5th Series of Experiments. (Heating and Cooling as before; range 650°—805° C. and vice-versa).					
t:	a: ↓	b: ↑	t:	a: ↓	b: ↑
650°	8.926	9.302	750°	9.367	9.671
660	8.970	9.343	760	9.433	9.701
670	9.014	9.386	762.5	—	9.689
680	9.054	9.426	765	9.463	9.692
690	9.093	9.452	770	9.496	9.702
700	9.130	9.505	780	9.570	9.726
710	9.177	9.540	790	9.646	9.752
720	9.212	9.569	800	9.731	9.776
730	9.260	9.598	805	9.780	9.785
740	9.314	9.632			

The irreversibility in this interval is still more strongly expressed; but it is most remarkable that the values on cooling now are appreciably *greater* than those observed on heating the wire: the algebraïc sign of the differences now proves to be *reversed*.

Sixth Series of Experiments.

In this series only the values of the resistances observed on heating (sub *a*) are given; those on cooling were, at all temperatures, so much *higher*, that they could not be recorded on the same photographic plate. The differences thus lie in *the same* direction as in the previous case, but they are still very *much greater*. Range: 800° to 940° C. and vice-versa.

t:	a: ↓	b: ↑	t:	a: ↓	b: ↑
800°	10.130	> 12 Ω	877.5	10.340 (min)	> 12 Ω
810	10.176	Much higher than sub *a*, but not measurable on the film.	880	10.343	Much higher than sub *a*, but not measurable on the film.
820	10.225		882.5	10.352	
830	10.277		885	10.368	
840	10.337		887.5	10.374	
850	10.393		890	10.409	
852.5	10.402		895	10.467	
855	10.410		900	10.548	
857.5	10.411 (max)		905	10.644	
860	10.404		910	10.764	
865	10.378		920	11.066	
870	10.353		930	11.408	
873.5	10.343		940	11.805	
875	10.340	↑ > 12 Ω			↑ > 12 Ω

§ 3. All these data are graphically represented in Fig. 2 which gives a true image of the curious hysteresis-phenomena observed. Attention may be drawn to the ∽-shaped part of the curve between 858°—880° C., and the small but evident break at about 915° C., — which temperature practically coïncides with the highest value ever observed for the transition-temperature: α-*Ti* ⇄ β-*Ti*. The point, where the differences between heating and cooling change from positive to negative, corresponds to a temperature in the vicinity of about 640° C.

Of course, the *specific* resistances: $\varrho \,.\, 10^4$ for a wire of 1000 mm length and 1 mm² diameter, can be obtained from all these numbers by multiplying them by 0,2108.

It is worth remarking here that the ∽-shaped part in the neighbourhood of 880° C. proved gradually to get shorter and more compressed, being at the same time a little more shifted in the direction of 900°, when the evacuation of the furnace was continued for a very long time before the heating of the wire was repeated. As, however, the wire after heating at 950° C., — where R was more than 12 Ω, — proves to get completely split up and extremely brittle, it is almost impossible to repeat such measurements more often than once or twice.

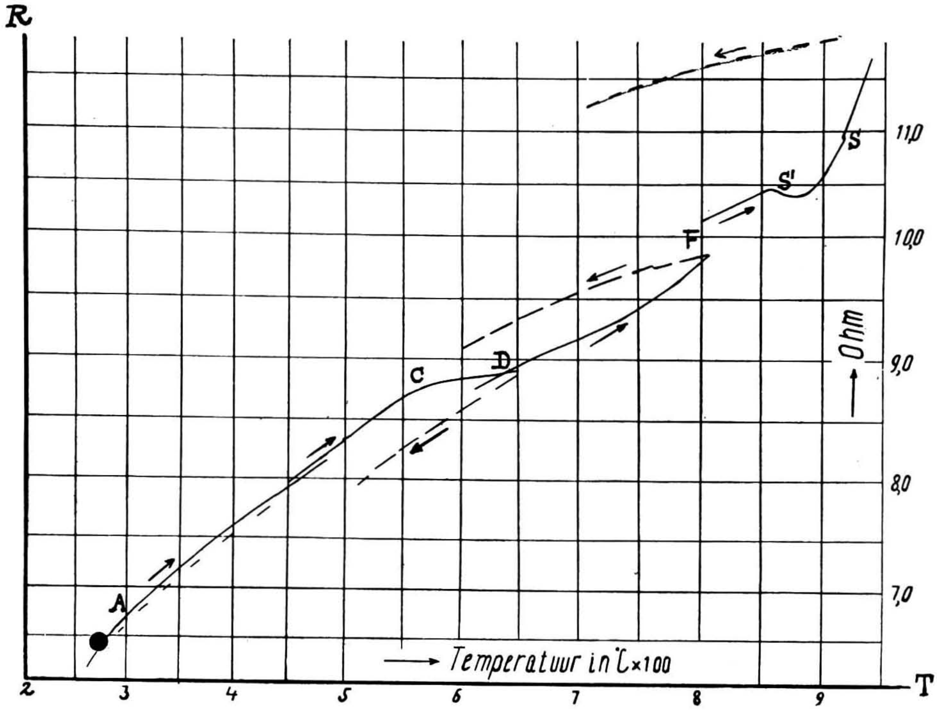

Fig. 2. *Electrical Resistance of Titanium on Heating and Cooling (Hysteresis-Effects). (Intervals: 270°—480°; 450°—660°; 620°—810°; 800°—940° C.).*

We also made the complete experiment in a single run (Fig. 3); of course, now the sensitivity of the galvanometer had to be much lowered, but, although this time the small discontinuities at the indicated temperatures

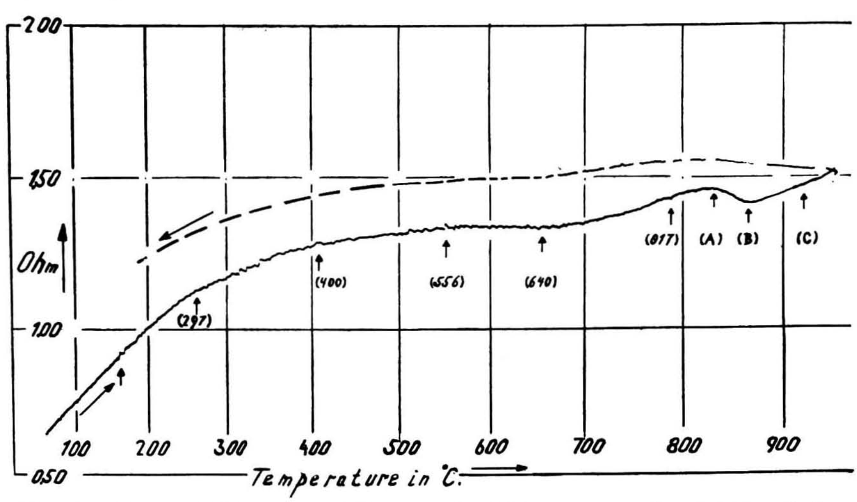

Fig. 3. *Electrical Resistance (Hysteresis) of Titanium in the vicinity of the Transition-point (A—C).*

are less conspicuous, the total aspect of the curve with its inflection-point in the vicinity of 600° C. and its transition-range between 640° and 860° C. clearly demonstrates its character as analogous to that of the atomic heats. The irreversibility on cooling is also clearly demonstrated on this film. Attention may be drawn, moreover, to the sinuous character of the curve, indicating the numerous sudden changes in the shape of the wire at successive moments during its continuous and gradual heating. Only the *reproducible* discontinuities always returning in successively repeated experiments are indicated by arrows.

§ 4. A more detailed insight into the particularities of the course of the hysteresis-phenomena and their relation to the minor "transition"-points was obtained in the following way. First a run was made from 0° to 320° C., i.e. to about 20° *above* the minor transition-temperature at 297°—300° C.: on heating, curve I in Fig. 4 was obtained; on cooling from 320° C. downwards, however, curve I*a* which is situated *much lower* than I, but evidently meets it at about 150° C. Then a heating was made from 0° to 430° C., i.e. to about 30° *above* the minor transition-point at 400° C.: on heating, again curve I was obtained with its characteristic change of direction at 297° C., whilst on cooling the hysteresis-curve I*b* was obtained, equally much lower than I, till at about 215° C. it intersects curve I and subsequently is situated *above it*. If, however, the heating be made from 0° to 475° C. in a *single* run, then first curve I is again followed, but on cooling now curve I*c* is obtained which, just as in Fig. 2 lies *below* I, but at about 270° C. intersects curve I and then runs *above* it, whilst still showing the abrupt

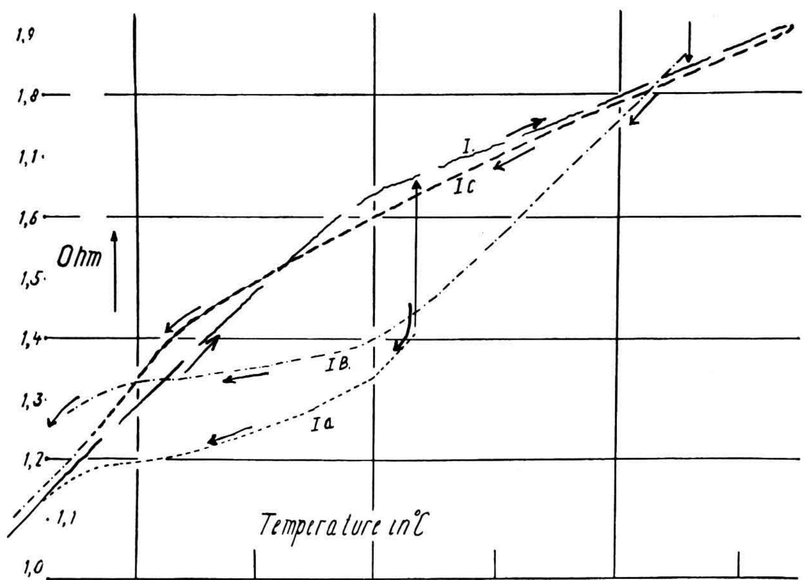

Fig. 4. *Hysteresis-phenomena by Heatings from 0°—320° C., 0°—430° C. and 0°—475° C.*

change of direction characteristic of I (at 297° C.), but shifted (by hysteresis) to about 215° C. From these results it clearly follows *that the influence of the changes occurring at the successive "transition"-points remains always partially preserved* at lower temperatures, being manifested by the particular course of the hysteresis-curve: most probably the inversion of its situation below or above curve I depends on the influence of the changes occurring in the metal at 255°—272° C. previously represented in Fig. 1.

Finally in Fig. 5 the curve for the resistance in its dependence on the temperature between 15° and 1000° C., — as in Fig. 3, — is again represented, this time, however, composed of three different parts and with a greater sensitivity, therefore, of the recording galvanometer. This curve shows somewhat more details than the curve of Fig. 3, — especially the sharper discontinuity in the vicinity of the *α-titanium* ⇄ *β-titanium*-transition-point; — but for the rest, this curve, obtained with a different wire,

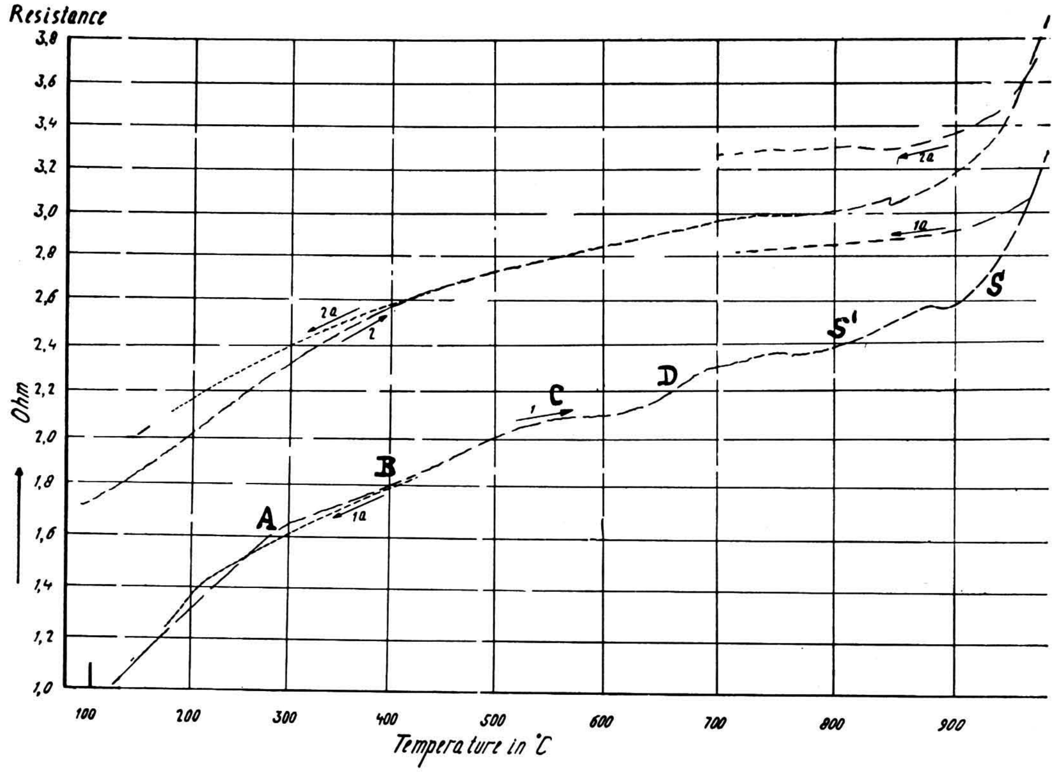

Fig. 5. *Dependence of the Resistance on the Temperature.*

evidently has preserved the same general character as that in the previous experiments. Curve I relates to the first heating: on cooling, the hysteresis-curve Ia lies *under* I and below 250° *above* I; the curves II and IIa relate to the second heating, after once the temperature had risen higher than 950° C.: now the hysteresis-curve is situated *above* the original one. At the same time curve II proves to be shifted considerably upwards with respect to I, thus indicating the persistance of the changes of the wire, caused by the first heating above 950° C.

Fig. 6 shows the influence exerted on the shape of the resistance-temperature-curve, when for about half a minute some air is admitted and then rapidly again withdrawn. The wire now proved to be covered by a very thin, but this time, indeed, a *visible* film of the oxide; the retardation manifested itself, just as in the other cases, but the retardation-curve now is almost parallel to the heating-curve, both showing, however, a sharp discontinuity at about 540° and 640° C. respectively. There can be no

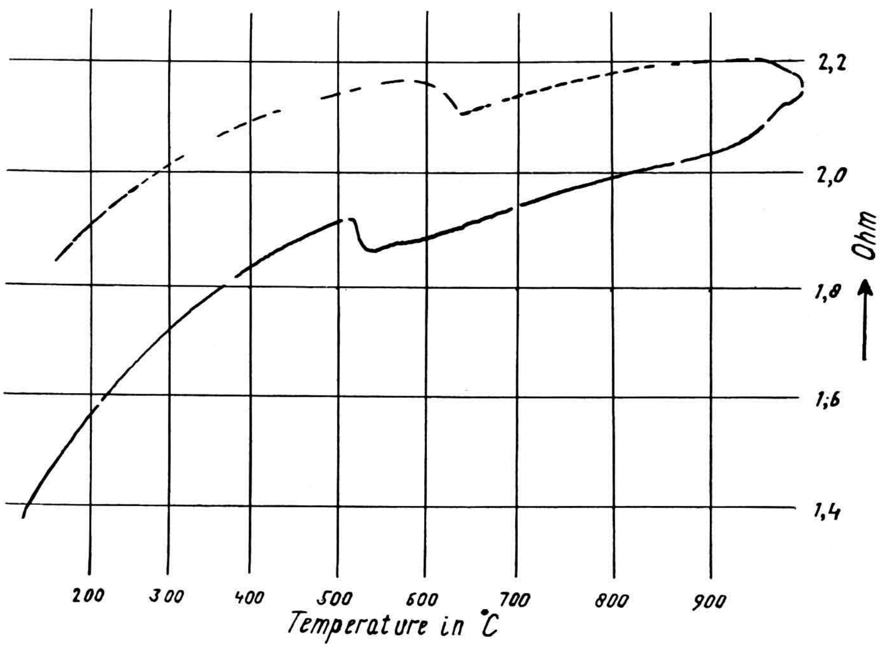

Fig. 6. *The Influence of Traces of Oxygen upon the Electrical Resistance of Titanium.*

doubt about the fact that the presence of oxygen or of *oxides* thoroughly changes the whole aspect of the curve and is, to some extent, responsible for the occurrence of at least some of these minor "transition"-points.

To this factor we will later-on return again more in detail, as the phenomenon clearly demonstrates that at least part of the effects observed are in some way connected with the presence of traces of *oxygen*, either in free or in combined form.

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