

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

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

§ 1. By a suitable modification of the twin galvanometer method we finally were able to study the thermoelectrical force of ductile *titanium* with respect to pure *gold*; for the details of this method we here refer to the following paper by E. ROSENBOHM and F. M. JAEGER. In this paper we only communicate the results of these measurements and some of the conclusions to which the study of *titanium* in its calorimetric, electrical and thermoelectrical aspects finally led us.

For the measurement of the thermoelectrical force of *titanium* in combination with another metal as a function of the temperature, it first had to be decided *what* second metal had here to be chosen. *Platinum* was rejected for this purpose, because of its tendency to combine with *titanium*; finally our choice was fixed on *gold*. The latter metal, like platinum, does not show any transition-point at temperatures upwards to its melting-point (1063° C.). Moreover, a soldering of the junction of the two metals had to be avoided and so in *gold* we exactly found the metal which lent itself best to the technical execution of a solderless connection with *titanium*. This connection was made in the following way: a *gold*-wire with a diameter of about 0,4 mm was at its end molten into a sphere of about 3 mm thickness, which then was provided with a hole of 0,3 mm diameter, through which one end of the *titanium*-wire was drawn. This combination then was laid on a support provided with a slight depression and covered with a stamp, in which the form of the sphere and both wires were cut out. By carefully hammering, the two metals now were compressed so as to form a combination, which proved to be so tight, that it was impossible again to disconnect it; even at 1000° C., this junction remained in a perfect condition, so that, even after several repeated experiments, no flaw whatsoever could be detected.

The wires of the thermocouple: *Ti—Au* and equally those of a thermocouple: *Pt—PtRh* were over a length of about 10 cm covered with narrow protecting capillaries and centrically fixed within a small porcelain crucible provided with a doubly perforated cover of porcelain; care must be taken, of course, that the two thermocouples could neither make contact with each other, nor with the crucible walls. The crucible in its turn then was surrounded by the thick copper block already mentioned in the case of the

determinations of the electrical resistance and fixed within the high-vacuum tube in about the same way as previously described.

§ 2. The results obtained in this way are collected in the following tables and are graphically represented by the reproduction in Fig. 1. As before, ↓ means: on heating; ↑ on cooling. In the series of experiments I and II the resistance of the first galvanometer + its external resistance was 1040 Ohm, the mean resistance of the thermocouple studied 5,4 Ohm at 360° C.; the range of heating was from 50° to 620° C., with a speed of about 3° pro minute. A *positive* value of *E* means, that at the hot junction the current is directed from the *gold*-wire towards the *titanium*-wire.

Series I and II.			
Temperature in °C.:	I <i>E</i> in Micro-V.:	II <i>E</i> in Micro-V.:	IIb <i>E</i> in Micro-V.:
50°	+310	+260	—
100	+540	+590	—
150	+720	+740	—
200	+790	+810 (M)	—
250	+800 (M)	+800	—
300	+770	+760	+900
350	+660	+640	+850
400	+480	+450	+730
450	+240	+220	+530
—	(break at 478°)	(break at 478°)	(break at 466°)
489	0	0	
500	—	—410	+160
522	—	—	0
600	—	—770	—520

The degree of reproducibility of the values of *E*, also after the wire had been heated to 620° C., may be judged from these numbers: at the second heating the maximum is somewhat shifted to the left.

If, however, the temperature once has risen *above* the transition-point, e.g. after heating to about 1000° C., — the values of *E* prove, even at lower temperatures, to have appreciably changed: at 50° C. *E* = + 510 M. V.; at 100° C.: + 1060 M. V.; at 150° C.: + 1480 M. V.; at 200° C.: + 1690 M.V.; etc.

In series III *a. b.* the range of temperatures was 600° to 1020° C. and vice-versa. Here the resistance of the first galvanometer + its external

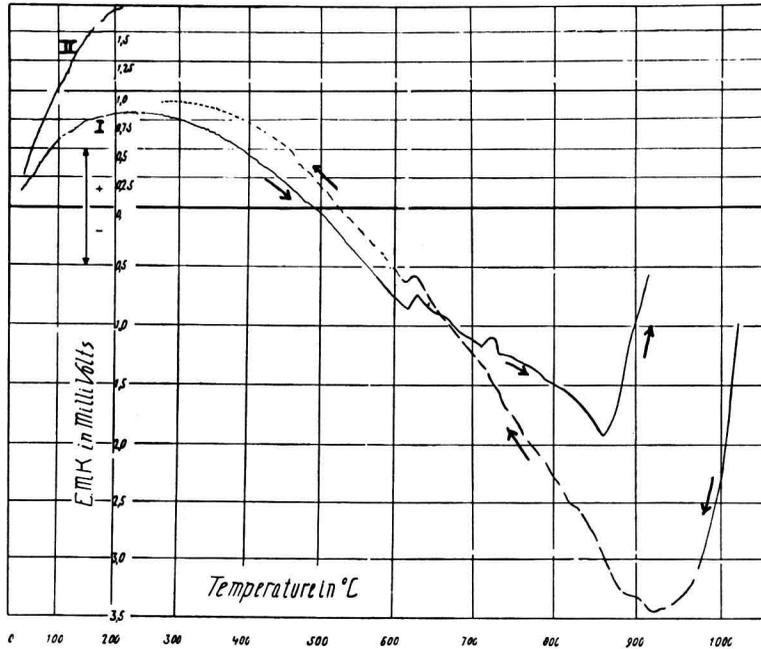


Fig. 1. Dependence of the Thermoelectrical Force Ti-Au on the Temperature.

resistance was 1540 Ohm, the mean resistance of the thermocouple studied: 6,5 Ohm, the mean speed of heating: $3^{\circ},6$ pro minute, whilst that of cooling had about the same value (minimal speed 3° , maximal about $5^{\circ},8$ pro minute).

From these numbers and Fig. 1 and 2 it may be seen that, on heating, the first rounded maximum is reached at about 250° C.; then E decreases with increasing temperature, becomes zero at the temperature of about 490° C. and then has negative values: at 620° C. a slight maximum follows and a second at about 720° C., till at about 860° C. a deep minimum is reached, followed by a very steep rise of the curve, most probably even to positive values of E . Most remarkable, however, is the enormous retardation-effect on cooling from the highest temperature downwards: the cooling-curve has its deeps minimum now at 924° C., so that the transition $\alpha \rightleftharpoons \beta$ -titanium manifests its influence over an interval of 860° — 924° C. Subsequently the negative hysteresis-effect becomes zero at about 670° C. and then gets a positive sign, still showing a slight discontinuity (maximum) at 620° C., but its curve now remains above the heating-curve even at the lower temperatures. In Fig. 1 the part of the curve to the right has been reduced to the same scale as the left part of the figure; in this way the small, insignificant irregularities of the original curve (Fig. 2) are omitted and

Series III.		
Temperature in °C.:	IIIa; <i>E</i> in Micro-V.:	IIIb: <i>E</i> in Micro-V.:
600°	— 760	—
625	— 830	—
630	— 780	—
650	— 880	— 820
670	— 980 (intersect.)	— 980
700	—1130	—1240
716	—1190 (break)	—
724	—1090 (ca) (M')	—
732	—	—1550 (break
750	—1250	—1790
800	—1500	—2320
825	—1630	—
850	—1850	—2820
860	* —1950 (m) ↓	—
870	—1880 ↓	—
900	—1050 β	—3230
910	— 720	
924	—	* —3320 (m) }
950	—	—3270 }
975	—	—2950 }
1000	—	—2200 }
1020	—	— 850 }

smoothed out, with the exception of the two small maxima at 620° and 720° C. In this connection it is of interest to draw attention to the fact that in these thermoelectrical measurements there must be a much smaller dependency of the results on the presence of traces of gases than in the case of those concerning the electrical resistance, because the junction is not altered and the thermo-electrical force thus can hardly vary in any appreciable way. Notwithstanding this, the strong and curious hysteresis-phenomena are preserved, in a direction *opposite* to those observed in the measurements of the electrical resistance, but, for the rest, quite analogous to them.

§ 3. As to the real significance of the many phenomena observed, in the course of these investigations I—III, we became pretty certain *that at*

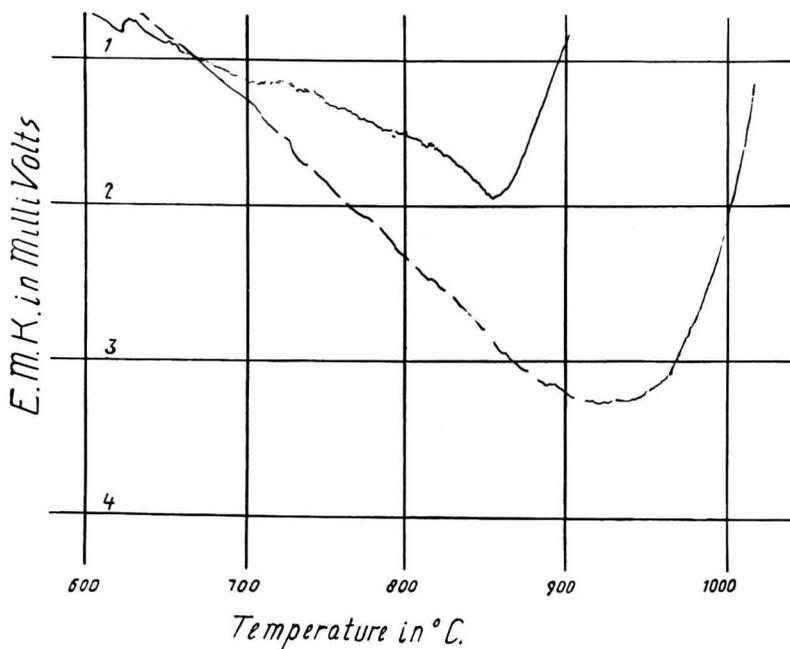


Fig. 2. Thermoelectrical Force of Titanium-Gold.

least there are two different causes of the retardation-phenomena observed, which are superimposed one upon the other. One of them surely is connected with the evident *tardiness of the reversible allotropic change $\alpha \rightleftharpoons \beta$ -titanium* at 882° — 905° C., — in the same way as we already stated these retardation-effects in a number of cases of this kind, more particularly with *beryllium, zirconium, cerium, chromium* etc. It seems pretty sure now that such allotropic changes, — although thermodynamically bound to a distinct “transition-temperature”, which indicates the temperature at which, under the prevailing pressure, the transformation is *completely finished* on heating from lower to higher temperatures, — already start at a temperature often appreciably *lower* than that thermodynamically defined transition-temperature and then only *gradually* proceed to completion. Thus a “transition-interval” precedes the “thermodynamical” equilibrium-point, most probably because of the fact that the different processes involved in the current of events (change of the fundamental grating and the necessary diffusion of the atoms into their new equilibrium-positions) ordinarily occur with very different velocities and thus become temporarily separated events¹⁾, — as recently has been emphasized by

¹⁾ F. M. JAEGER and E. ROSENBOHM, Rec. d. Trav. d. Chim. d. Pays-Bas, **53**, 930 (1934).

several authors¹⁾). Although the different metals showing allotropic changes behave very differently in this respect, — the transition-interval often being reduced to a practically negligible extent, as e.g. in the case of *ruthenium*²⁾, or being extended over a very long range of temperatures, as in the case of *zirconium* and *beryllium*, — this “intermediate phase” in all cases studied showed the general peculiarity: that its specific heats *very steeply increase with the temperature* until just before the thermodynamical transition-point, c_p reaching exceptionally high values and then equally steeply dropping to the value characteristic of the new stable modification.

This cause undoubtedly also plays a preponderant role in the present case of *titanium*, more particularly in the interval between 600° C. (inflection-point of the C_p — t -curve) and 905° C. But here the phenomena are, moreover, seriously complicated by another circumstance also previously met with, i.e. *the influence of extremely minute traces of absorbed gases*, more particularly of *oxygen* (and perhaps of *nitrogen*). The curious influence of traces of oxygen, more especially upon the temperature-coefficient of c_p of pure metals, has already been emphasized by us³⁾ on several occasions, e.g. with *silver*, *beryllium* and *zirconium*; an influence which appears to make itself felt *in no reasonable proportion to the almost untraceable amounts of the oxygen with respect to that of the metal present*.

From the weight and density of the *titanium* used in the vacuum crucibles and the volume of the latter, it can be calculated that in the calorimetrical experiments one atom of *oxygen*, by complete absorption by the metal, is present on about 300 millions of *titanium*-atoms; consequently it can hardly be assumed that real oxide-films will be produced⁴⁾. It is much more probable that the gas originally is condensed on the surface of the metal and, on heating, gradually penetrates into the metallic mass.

Now *titanium* has a very pronounced tendency to absorb oxygen and nitrogen; this tendency even is so strong that the metal is used in the steel- and in the copper-industry as a *desoxidant* or for the elimination of nitrogen in the former case. Moreover, it combines with oxygen to a whole series of oxides: TiO , Ti_3O_4 , Ti_2O_3 , Ti_3O_5 , TiO_2 , — the latter in 3 modifications, — which in the presence of metallic *titanium* in excess

¹⁾ Cf.: L. GRAF, Z. f. Metallk., **24**, 248 (1932); V. DEHLINGER, *Gitteraufbau Metallischer Systeme*, in *Handbuch der Metallphysik*, **1**, 1, 147—180 (1935); W. L. BRAGG and E. J. WILLIAMS, Proc. Royal Soc. London, A, **145**, 699 (1934); G. SACHS, Z. f. Metallk., **24**, 241 (1932); etc.

²⁾ F. M. JAEGER and E. ROSENBOHM, Rec. d. Trav. de Chim. d. Pays-Bas, **51**, 34 (1932); *ibid*, **53**, 461 (1934).

³⁾ F. M. JAEGER, E. ROSENBOHM and W. A. VEENSTRA, Proc. Royal Acad. Amsterdam, **36**, 291, 293, 297 (1933); F. M. JAEGER and E. ROSENBOHM, Rec. d. Trav. d. Chim. d. Pays-Bas, **53**, 460, 461 (1934); F. M. JAEGER and W. A. VEENSTRA, *ibid*, **924**, 925.

⁴⁾ In the vacuumtubes and in the ROENTGEN-camera, however, where the vacuum is practically the same as the pressure (0,001—0,0001 mm) of the pumps indicates, more oxygen is, of course, accumulated, — especially in experiments of long duration.

possibly seem to be partially reduced and converted in at least some of them at higher temperatures ¹⁾. Moreover ²⁾, of the three or four enantiotropic forms of TiO_2 the *transition-point* of $\alpha \rightleftharpoons \beta$ -*anatase* lies at 642° , that of *anatase* \rightleftharpoons *brookite* at about 840° , that of *brookite* \rightleftharpoons *rutile* between 900° and 1000° C. at a pressure of 1 atmosphere. That a *partial* reduction of TiO_2 by an excess of Ti under the very low *oxygen-pressure* (0,0002 mm) of our pumps at higher temperatures really takes place, is proved by the fact that, although feeble, the *X-ray* spectrum of TiO was observed. In this connection it is worth while once more to remark that, as TiO and TiO_2 thus *certainly* are both observed during the heatings, all other oxides mentioned *can* be supposed to be produced by the combination of these two: $Ti_2O_3 = TiO \cdot TiO_2$; $Ti_3O_4 = 2TiO \cdot TiO_2$; etc. On the other hand, the diagram reproduced in Fig. 6 of the former publication (II) convincingly demonstrates how an introduction of even a trace of air into the vacuum tube during half a minute, — in which experiments now a truly *visible* film of TiO_2 was generated, — really causes analogous retardation-effects to those observed, with breaks of the curve at 640° C. on heating and at 550° C. on cooling. Also the facts mentioned there that, on repeated heatings preceded by continuous pumping during a long time, the peculiar ∞ -shaped part of the resistance-temperature-curve ³⁾ in the vicinity of the transition-point (882° — 906°) seems to shrink to a gradually diminishing range and simultaneously shifts in the direction of higher temperatures, as well as the equally gradually diminishing effects at 300° , 400° , 554° C. etc. in the c_p - t -curve produced in the experiments with SALADIN'S apparatus, as observed in successively repeated readings and also in the measurements of the electrical resistance, when the pumping off of traces of gas has beforehand uninterruptedly been continued, — all point in the same direction: i.e. in that of these discontinuities being intimately connected with the presence of almost imperceptible traces of *oxides* of different properties.

In this connection it can be remarked that, when once a trace of oxygen has been absorbed by the metal, it is quite impossible ever to withdraw it from the system by any experimental means at our disposal. By comparison with the equilibrium-pressure of the oxygen in the system: incandescent *carbon*, *carbon monoxide*, *carbon dioxide* and *oxygen* at 1000° C., it can easily be calculated that this oxygen-pressure in the equilibrium: *titanium*, *titanium-oxide(s)* and *oxygen*, must certainly be less than 10^{-19} or 10^{-20} atmospheres, i.e. about $3 \cdot 10^{-16}$ or $3 \cdot 10^{-17}$ mm of air. It is clear that the oxygen-pressure in our best vacuum pumps will always be many billions of times greater than these dissociation pressures, so that the possibility of an elimination of once absorbed oxygen is completely excluded.

¹⁾ M. BILLY, Ann. d. Chim. et Phys., 9, 16, 5 (1931).

²⁾ Cf.: P. PASCAL, *Traité de Chimie Générale*, 5, 573, 575 (1932).

³⁾ This curious retardation-effect is of the same kind as that stated by C. ZWICKER (Physica, 6, 361 (1926)) some years ago in the case of pure *zirconium*, — which metal also intensively absorbs oxygen.

If this interpretation is right, then the temperatures at which the discontinuities, stated in the calorimetrical curve, occur, should really correspond either to the polymorphic transition-points of the different modifications of TiO_2 or to the three- and four-phases-equilibria¹⁾ respectively of some of the possible oxides with Ti and O_2 or to both phenomena simultaneously.

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¹⁾ M. BILLY, *Ann. d. Chim. et Phys.*, (9), 16, 5 (1921).

Chemistry. — *The Determination of the Thermoelectrical Force of Metals in a Vacuum by means of the Photographically recording Double Galvanometer.* By E. ROSENBOHM and F. M. JAEGER.

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§ 1. In continuation of our investigations¹⁾ on the applicability of SALADIN—LE CHATELIER's twin galvanometer with photographic recording for different kinds of measurements, we wish in this paper to describe its use for the determination of the thermoelectrical behaviour of metal-wires at varied temperatures with respect to a standard-metal. As also in this case the measurements had to be made in a high vacuum, a suitable furnace-tube for this purpose had to be constructed which, its gas-tight mantle being eliminated, is represented in Fig. 1. Its construction is in many respects analogous to that of the furnace-tubes previously described; however with the difference, that not only the wires of the two thermocouples used in the temperature-measurement, but also those of the thermocouple consisting of the metal to be investigated and of the standard-metal had, under perfect isolation, to be passed through the water-cooled cover.

The wires of these thermocouples were, over a length of 45 cm, covered with narrow, protecting capillaries and the hot junctions centrally fixed within a small porcelain crucible provided with a doubly perforated porcelain cover, which crucible in its turn was surrounded by a cylindrical copper-block to ascertain a homogeneous temperature, just as was described in the case of the measurement of the electrical resistance. Care must, of course, be taken that the two thermocouples could neither make contact with each other, nor with the crucible walls. In Fig. 2, which represents the bottom part of the tube on a larger scale, the copper mantle, with the porcelain

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