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-equilibria [1]) respectively of some of the possible *oxides* with Ti and O_2 or to both phenomena simultaneously.

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> *Physical Chemistry of the University.*

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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.

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

§ 1. In continuation of our investigations [1]) 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 centrically 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

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

crucible intentionally made to emerge somewhat from it, can clearly be seen to the right, whilst to the left the collapsed covers, some diaphragms and the protecting capillaries are shown. The junction of the second *Pt—PtRh*-thermoelement used for the temperature-indication originally was
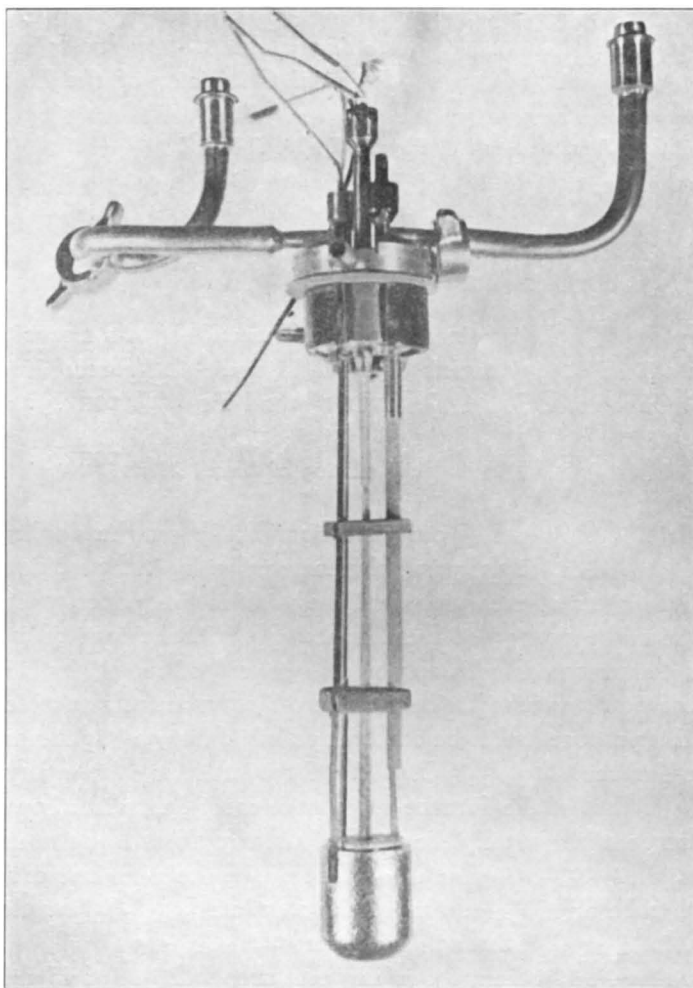

Fig. 1. Dismantled Vacuum-Tube for the Determination of the Thermoelectrical Force Ti—Au at different Temperatures.

brought into contact with the wall of the copper mantle, but later-on freely placed next to the other junction; its temperature was read by means of a suitable and accurate pyrometer. All six wires were carefully isolated and the different wires led to the junctions in the ice-box, the connections of which were linked to the galvanometers; those of the thermocouple to be investigated being connected with the vertically, those of the *Pt—PtRh*-thermocouple with the horizontally recording galvanometer.

§ 2. *Calibration of the Photographic Plate.* Because the sensitivity of the vertically recording galvanometer was great enough to indicate a
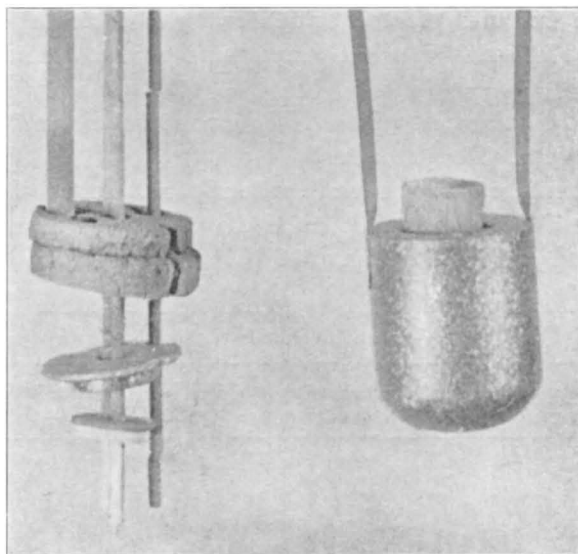

Fig. 2. The Bottom-end of the Vacuum-tube with Porcelain Crucible, Covers and Diaphragms.

thermoelectrical force of some Microvolts by a deviation already covering the whole 13 cm of the height of the photographic plate, while the thermoelectrical forces to be measured in an interval of 200° proved to be about a thousand times greater, — the sensitivity of the first galvanometer had to be sufficiently diminished by inserting a suitable external resistance of the order of 1000 to 1500 Ohms. For the necessary preservation of the aperiodicity of the instrument, a suitable shunt was used.

The calibration-marks for the vertical coordination-axis on the photographic plate now were applied in the following way:

An auxiliary current i, which over a known resistance of r Ohms had a definite voltage of e Millivolts, was applied to the galvanometer plus its external resistance. If the total resistance of the instrument, i.e. the sum of the really active galvanometer-resistance plus the external resistance inserted, is w, — then the potential difference e between the two galvanometer-junctions will be: $e = i \cdot \dfrac{r \cdot w}{r + w}$. During the measurements, the resistance R_t of the thermocouple to be investigated, — which resistance is dependent on the temperature of observation, — plays the role of the resistance r in the said formula. As the external resistance applied is very great (about 1000 Ohms), R_t need not be known with a greater accuracy than about 0,1 Ohm. Therefore, if E be the real electromotive force of the thermocouple to be measured, R_t its resistance at each temperature of $t°$,

then the true potential difference E' of the thermocouple is calculated from:

$E' = E \cdot \dfrac{w}{w + R_t}$, so that evidently the correction to be applied is only very small [1]). The exactness of the determination of E is dependent on the choice of the abscissae, i.e. of the temperature-interval considered.

§ 3. *The Measurement of the Thermoelectrical Force of Iron against Copper at Different Temperatures.*

For these measurements we used a wire of purest electrolytically prepared *iron*; the wire had a length of 90 cm, a diameter of 0,3 mm and a specific resistance: $10^4 \cdot \varrho$ of 0,0984 Ohm at 20° C.

1st Series of Measurements.			
Temperature t in °C.:	Thermoelectrical Force $Fe-Cu$ in Microvolts:	Temperature t in °C.:	Thermoelectrical Force $Fe-Cu$ in Microvolts:
200°	+1656	720°	—1259
250	+1815	730	—1336
300	+1869	740	—1424
350	+1795	750	—1485
400	+1583	760	—1548
450	+1295	800	—1797
500	+ 870	850	—2086
520	+ 673	890	—2322
530	+ 578	900	—2378
540	+ 454	904	—2400
550	+ 361	908	—2448
600	— 119	910	—2493
650	— 619	950	—3104
710	—1182		

In the beginning the thermoelectrical force is *positive* and it approximately increases in a linear way with the temperature, till a rounded maximum at about 300° C. is reached; then a slight discontinuity at 540° C. follows and at 586° C. it becomes *zero*. At still higher temperatures it becomes *negative*: the transition $\alpha\text{-}Fe \rightleftarrows \beta\text{-}Fe$ is indicated by an indistinct discontinuity at 740° C. (A_2); but the transition: $\beta\text{-}Fe \rightleftarrows \gamma\text{-}Fe$, where a real change of

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[1]) In the case of the thermocouple: $Fe-Cu$, at 700° C. we found: $w = 840$ Ohms, $R = 3,6$ Ohms; so that at 700° C. $E = E' \times 1,0043$. At 900° C. $E = E' \times 1,0053$; etc.

the structure takes place, manifests itself by a *very sharp* discontinuity at 906° C. (A_3).

§ 4.   For a better insight into the prevailing relations, the part of the curve between 700° C. and 950° C. was studied by measurements on heating and on cooling, in combination with those of the electrical resistance of *iron* (Fig. 3); the curve for the electromotive force thus obtained is represented in Fig. 4.

In Fig. 3 *two* curves are represented which at increasing temperatures approach each other ever more closely: the numbers of the table are the *intermediate* values of the two, all values being corrected in the usual way. The following remarks may elucidate the meaning of the two different curves represented.
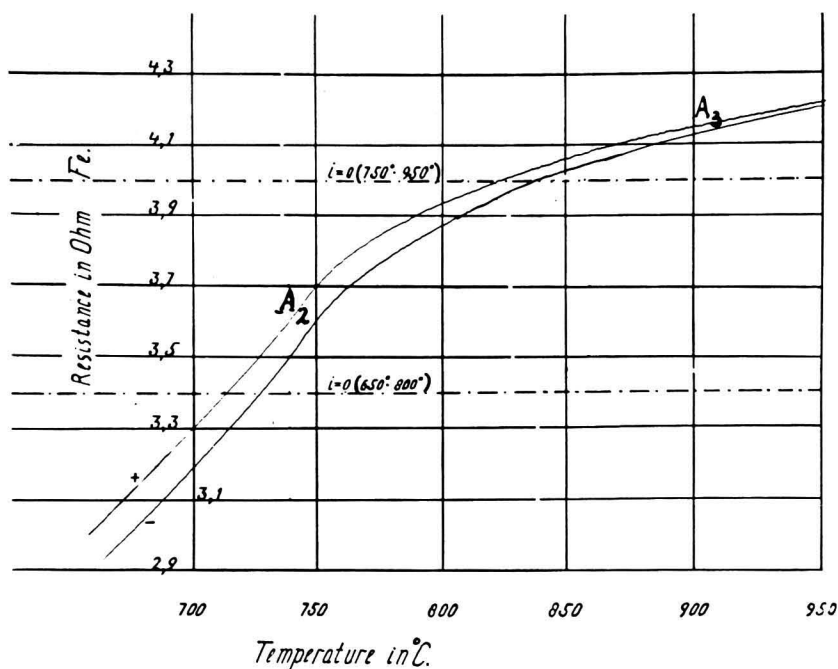

Fig. 3.   *Electrical Resistance of Iron.*

On measuring the resistance of the *iron*-wire on heating, a systematic shift of the zeropoint of the recording galvanometer was observed, if the auxiliary current in the WHEATSTONE-bridge was switched off. For the purpose of eliminating a possible induction by the direct furnace-current on the *iron*-wire, the latter now was wound in a bifilar way; but even in this case, the shift of the zero-point proved still to be present. Moreover, this shift even remained present, when the heating current was completely switched off. The other possibility: the presence of a thermoelectrical force as the cause of this effect, had also to be rejected, as the magnitude of the shift observed proved to be independent of the rate of heating and also independent of the

fact whether the connections *Fe—Cu* were situated on the same level of the tube or on levels differing more than 3 cm from each other. The shift
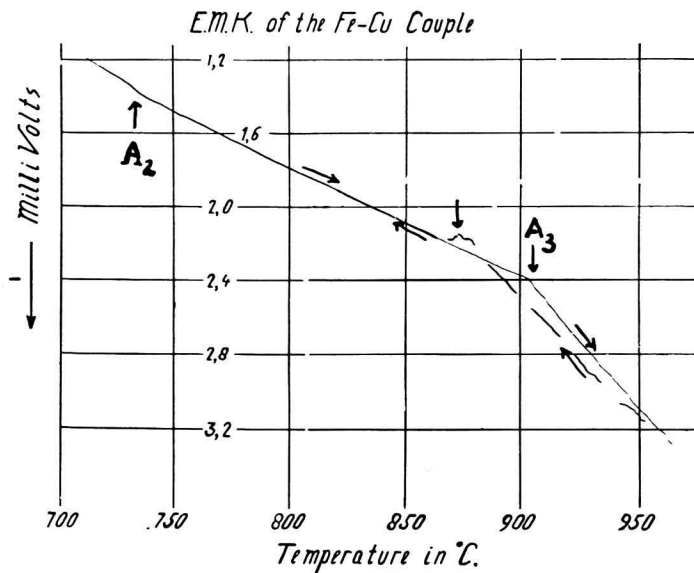

Fig. 4. The Thermoelectrical Force of Fe—Cu.

observed also proved to be independent of the substitution of the *iron*-wire by another of the same length. Finally it proved *solely to depend on the temperature of the iron-wire itself*, reaching a maximum value at about 550° C. and then regularly decreasing with increasing temperatures. The algebraïc sign of the effect was *reversed*, when the junctions of the supplying wires in the bridge were *interchanged;* as the latter phenomenon proved to be completely reproducible, the exact values could be determined by consecutively observing *two* curves within *the same* interval of temperatures, but in both cases after having interchanged the said connections in the bridge: the one curve then certainly is *too high*, the other *too low*. In Fig. 3 the two curves are represented: the first part of both relates to an interval of temperature ranging from 670° to 800° C., the second from 750° to 950° C., so that they overlap a range of 50°. The two parts were photographed on two successive days; notwithstanding this, they proved to fit completely together, showing that no change in the shift had occurred. The phenomenon, although quite reproducible, can not yet be explained at this moment.

From the numbers for the resistances in the table it may be deduced that the temperature-coefficient of the resistance rapidly increases in the neighbourhood of A_2, reaches its maximum at about 750° C. and then very rapidly decreases at higher temperatures. The second transition-point A_3, however, is only indicated here by the fact that the temperature-coefficient of the resistance of the *iron*-wire becomes practically *constant* from 900° C. upwards. This result is in fairly good agreement with the

Resistance of Iron between 670° and 950° C. (Length of the wire: 25 cm.)					
Temperature t in °C.:	Resistance in Ohms:	Increments $w_t - w_{t-10}$	Temperature t in °C.:	Resistance in Ohms:	Increments $w_t - w_{t-10}$:
670°	3.012		810°	3.912	0.034
		0.065			0.027
680	3.077		820	3.939	
		0.070			0.026
690	3.147		830	3.965	
		0.074			0.025
700	3.221		840	3.990	
		0.075			0.024
710	3.296		850	4.014	
		0.076			0.023
720	3.372		860	4.037	
		0.081			0.022
730	3.453		870	4.059	
		0.086			0.020
740	3.539		880	4.079	
		0.088			0.018
750	3.627		890	4.097	
		0.075			0.016
760	3.702		900	4.113	
		0.051			0.014
770	3.753		910	4.127	
		0.046			0.015
780	3.799		920	4.142	
		0.041			0.015
790	3.840		930	4.157	
		0.038			0.014
800	3.878		940	4.171	
					0.014
			950	4.185	

data published by Burgess and Kellberg[1]); the small discontinuity at 900° C. indicated by them could, however, not be established by us with absolute certainty.

As to Fig. 4, we can draw attention to the fact that the general course of this curve for the electromotive force: *Fe—Cu* is in fair agreement with that of the curve represented by MELLOR[2]), as deduced from the measurements of BELLOC[3]). In our figure the posterior part of the curve is *double*, because on cooling a most remarkable *hysteresis-effect* presented itself with respect to the transition: *β-Fe* ⇄ *γ-Fe*: on cooling (broken curve) the transformation *γ-Fe* → *β-Fe* evidently is strongly retarded till 865° C., at which temperature the discontinuity there occurring suddenly jumps back to the original heating-curve of the *β*-modification and, on further cooling, this curve is then completely followed in all details. Besides this very remarkable fact of a kind of "undercooling" at a transition-point, manifesting

[1]) G. K. BURGESS and J. N. KELLBERG, Journ. Wash. Acad. **4**, 436 (1914).

[2]) J. W. MELLOR, *Inorg. and Theor. Chemistry*, **13**, 230, fig. 278 (1934).

[3]) G. BELLOC, Bull. Soc. Encour. Nat. Ind., **107**, 492 (1908).

itself in the value of an electromotive force, — a comparison of the Figs. 3 and 4, moreover, teaches us that, whereas in Fig. 3 the transition-point A_2 appears by the change in resistance much more sharply indicated than that at A_3, in Fig. 4 the *reversed* phenomenon manifests itself with respect to the change of the thermoelectrical force at A_2 and A_3. This difference is very remarkable indeed, as the transformation at A_2 is considered not to be accompanied by a sudden change of the structure, but to correspond solely to the sudden change in the magnetic properties of the metal.

§ 5. *The Thermoelectrical Force of Nickel with respect to Copper.* Because between 300° and 400° C. *nickel* shows a transition-point which in many respects is analogous to the point A_2 of *iron*, we also studied the thermoelectrical behaviour of a *nickel-copper*-thermocouple within the said range of temperatures.

Measurements of the Thermoelectrical Force: Ni—Cu between 300° and 400° C.	
Temperature t in °C.:	Electromotive Force in Microvolts:
310°	+7753
320	+7966
330	+8200
340	+8416
342	+8450
343	+8573
350	+8722
360	+8975
370	+9194
380	+9437
390	+9642

The thermoelectrical force is here positive between 300° and 400° C. A small discontinuity (Fig. 5) manifests itself also in this case at about 343° C., but the character of the curve does not change appreciably at higher temperatures. This is in contrast with the behaviour of the resistance-temperature-curve previously obtained with a wire of somewhat less pure *nickel* [1]), where an inflection-point occurs in the neighbourhood of the transition-point and where, after surpassing this point, the resistance drops

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[1]) Proc. Royal Acad. Amsterdam, **39**, 380 (1936).

to less than half its previous value. In the vicinity of their CURIE-points, *nickel* and *iron* evidently behave in a quite analogous manner with respect
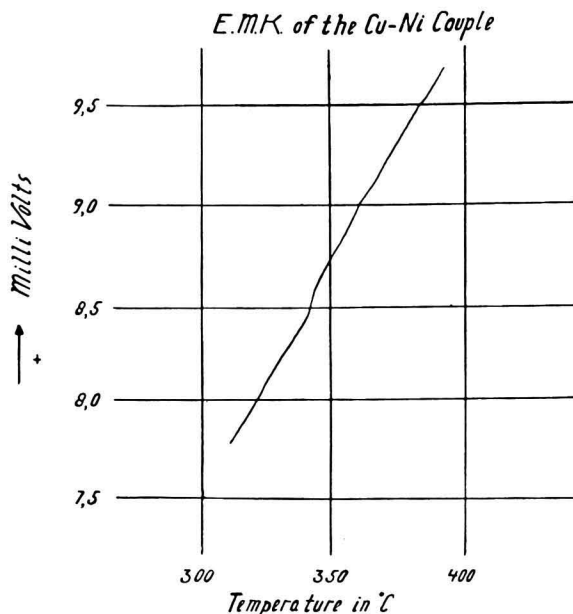

Fig. 5.   *Thermoelectrical Force: Ni—Cu.*

to their electrical resistances, as well as to their thermoelectrical properties towards *copper*.

Groningen, Laboratory for Inorganic and Physical Chemistry of the University.

Physics. — *The most general photographic density-law.* By A. VAN KREVELD and L. S. ORNSTEIN, Utrecht. (Communication of the Dutch Foundation for photographic and cinematographic research).

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

I. *Introduction.*

A photographic density-law is a relation between the intensity I of the light which falls on the photographic plate, the time of exposure t and the effect Z, caused by the exposure. Z may by either the developed density or the number of developed grains or any other measure for the photographic effect.

The following considerations are limited to the most important case