size of the heat-effect involved could pretty accurately be determined from the measured height of the vertical deflection observed and was found to be: 0.3 calories per gramme of the alloy. Now from the calorimetrical data for Q_0 for the γ-modification previously determined, when extrapolated to temperatures between 370° and 400° C., it can be deduced that a *constant* difference of exactly 0.39 calories is found, when these values of Q_0 for the γ-modification are diminished by those of the β-modification at the same temperatures. Evidently this constant difference is the heat of transition of the change: β- $\rightleftarrows$ γ-modification and by this fact, indeed, it becomes highly probable that our suggestion, that practically *the same* temperature-coefficient of c_p may be attributed to the γ- as well as to the β-modification, is right.

At the other transition-point of 404° C., however, this certainly is *not* so; moreover, the latter transition: β- $\rightleftarrows$ α-modification occurs *much more slowly*, nor does the heating-curve exactly return to its previous height after the transition-point has once been surpassed. Because of the tardiness of this transition, even on cooling slowly, a strong hysteresis-effect is always observed, which is clearly expressed in the shape and situation of the cooling-curve with respect to that of the heating-curve; whilst on the other hand the change β- $\rightarrow$ γ-form, also on cooling, always proves to occur at practically the same temperature of 355° C. as before on heating.

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Chemistry. — *Measurement of the Electrical Resistance of Metals as Function of the Temperature by means of a Twin Galvanometer with Photographic Recording.* By E. ROSENBOHM and F. M. JAEGER.

(Communicated at the meeting of February 29, 1936).

§ 1. On dealing with the method of the determination of the differential-curves after the method of SALADIN—LE CHATELIER [1]), we already had an opportunity to make some general remarks concerning the possible applications of this method also for other purposes. As in the measurement of the *electrical resistance* in its function of the temperature, the same apparatus after some modifications proved to be equally suited to this special purpose, we here now will go into further details with respect to the necessary conditions to be fulfilled in these experiments, if trustworthy results in the measurement of the temperature-coefficient of the electrical resistance of metal-wires really shall be obtained.

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1) E. ROSENBOHM and F. M. JAEGER, Proc. Royal Acad. Amsterdam, **38**, (1936).

The measurement of the temperature-coefficient mentioned seemed highly promising to us in connection with those of the specific heats of such metals in so far as, from a theoretical point of view, it might be expected that occurring abnormalities in the c_p-t-curve at definite temperatures would show their replica at about the same temperatures in the curve representing the electrical resistance in its dependence on the temperature and vice-versa. Thus the real occurrence of such slow or sudden changes in the metals studied might in this way be rigorously checked by the comparison of the two independent series of data obtained. As it is of more importance for this control to make *comparative* experiments of this kind rather than to collect the exact *absolute* values of the properties thus studied, we have for our purpose again made use of the equipment previously described, but modified in the following way.

§ 2. For the measurements of the change of the electrical resistance of metal-wires in a high vacuum at various temperatures a WHEATSTONE-bridge (O. WOLFF) was used. However, instead of using it as a *zero*-instrument, the deflections of a galvanometer placed in the bridge-circuit and recorded on the photographic plate were measured and utilized for the intended purpose.

The metal-wire within the high-vacuum-tube was inserted in one of the side-branches of the WHEATSTONE-bridge, whilst the vertically recording galvanometer was placed in the diagonal shunt, i.e. in the bridge-circuit properly speaking. When the measuring device is initially compensated for a definite resistance, then the change of resistance of the metal-wire during its heating will produce certain deflections of the galvanometer, — for instance vertically upwards for an increase, downwards for a diminution of the wire-resistance; these deflections can at every moment be recorded on the photographic plate. If this change of resistance now should be measured for an interval, — let us say of 500°, — then the WHEATSTONE-bridge was initially compensated for a mean temperature of about 250°, in such a way that the beam of light for this special temperature made its impression exactly in the *midst* of the photographic plate, the current in the galvanometer now being *zero*: the instrument now will be over-compensated for lower and under-compensated for higher temperatures. For the purpose of deducing the special resistance of the heated wire at each moment from the deflections recorded on the photographic plate, the latter must preliminarily be provided with a series of calibration-marks by substituting the wire investigated by a variable, but accurately known auxiliary resistance of about the same magnitude. If, for instance, the resistance of the wire to be expected, for a deflection of the horizontally recording galvanometer corresponding to that resistance, were 1.5 Ohm in the middle of the plate, — then the WHEATSTONE-bridge was compensated for 1.5 Ohm at the very start of the experiment, so that the current in the bridge-circuit then was zero, when the substituted variable resistance also was taken = 1.5 Ohm; the vertically recording galvanometer, therefore, now showed *no* deflection. This point was fixed on the photographic plate by the short exposure (10 sec.) of the latter to a fine, point-shaped luminous source, the plate thus receiving an indication-mark for a current = zero and a resistance of 1.500 Ohm. When the whole measuring device now is kept constant, whilst only the variable resistance is systematically changed, the corresponding calibration-marks on the photographic plate could in just the same way be imprinted upon it for resistances of 1.4 Ohm, 1.3 Ohm, etc. and of 1.6 Ohm, 1.7 Ohm, etc. In this way the vertical co-ordinates of the curve were directly expressed in Ohms and the intermediate values, — after the subsequent development of the plate, — were finally found by calculation and graphical interpolation: the latter yielded sufficiently accurate results, as in most cases it proved to be an almost *linear* one to both sides from the fixed zero-point. The sensitivity of the recording galvanometer must, — by inserting suitable external resistances, — be regulated, of course, in such a way that within the whole interval of temperatures considered the vertical deflections never reach the extreme borders of the photographic plate: in the case of very irregularly and unexpectedly varying wire-resistances, — as e.g. with *titanium*, — this regulation is by no means an easy job, so that in the beginning many tentatives must be made before failures are completely avoided.

The method most advantageously furnishes data about the *variation* of the resistance with the temperature, rather than such for the absolute size of the latter; by changing the sensitivity of the recording galvanometer as well as the intensity of the current in the bridge, this variation of the resistance can, within wide limits, be made *in*dependent of the absolute magnitude of the resistance itself. If a photographic plate of 13 × 18 cm is used, an exactness of 0.1 % of the variation mentioned can readily be attained. When the length of the plate available for the ordinates is 12 cm and, for instance, the change of the resistance within the temperature-interval studied is 1 Ohm, — then a variation of 0.001 Ohm corresponds to 0.12 mm or about the real breadth of the curve itself. By means of suitable filters placed before the luminous source, curves of very sharp and thin tracks can be obtained: we commonly used a yellow and red filter combined.

In WHEATSTONE's bridge two different ways of connection are possible, as the places of the galvanometer and the electromotive force can be interchanged. The one method has the advantage of enabling the observer to use a very weak current, — which may be advisable in cases where the metal-wire is very thin and thus a heating of it by the current must be feared; the other involves the use of currents of all intensities and guarantees a higher independency for the observer from occasionally occurring thermoelectrical forces. For this reason we have always preferred the latter way of connecting; the final elimination of such thermoelectrical forces will be dealt with more in detail further on.

In such complicated and capricious cases as in that of *titanium*, where several disturbing factors and retardation-phenomena play a role, the high degree of accuracy of the method can, of course, not nearly be attained. The method proved, however, most satisfactorily to meet with our requirements even in the complicated case mentioned. Its great advantage is that the curve desired need not to be built up from the determinations of singular points but is immediately recorded as an uninterrupted, *continuous* one, so that even small irregularities presenting themselves in it can never be overlooked.

§ 3. In the case of some metals difficulties are often met with concerning the way of producing the necessary contacts. Therefore, this was done in the following way, which proved to be applicable in almost all cases.

The supplying wires were of copper and had a diameter of 3 mm; at their ends they were hammered out over a length of about 2 cm and so flattened to about 1 mm thickness. At about 1 cm from the lower end they were perforated, the hole which was provided for having a boring somewhat less than the diameter of the *metal*-wire to be studied; this flattened end was subsequently bent in *U*-shaped fashion and the *metal*-wire pulled through the hole, upwards in the case of the one and downwards in that of the other copper-wire. Then both ends were tightly compressed, so that the *metal*-wire to be investigated was deeply impressed into the preliminarily heated and thus very soft copper terminals.

In this way a very good contact was guaranteed, which often even at 1000° C. proved to be excellently preserved.

Because of the oxidability of many metals the measurements must be made in a high vacuum. For this purpose a high-vacuum-tube, heated in an electrical furnace, was constructed, which remained gas-tight even at 1400° C. Its construction is in most respects quite similar to that described in our paper on the determination of the differential-curves previously published. It also consists of a gas-tight mantle of PYTHAGORAS-mass, closed at the upper end, — which emerges about 20 cm above the rim of the electrical furnace, — by a double-walled, water-cooled copper-cover, provided with a flange. Through this cover all supplies for the current, the pump-leadings and the thermocouples pass; the space of constant temperature, in which the metal-wire, wound in the shape of a spiral, was freely hanging between the thick copper wires already mentioned, is about 6 cm high and is situated at the bottom end of the vacuum-tube. The about 3 cm long spiral is enclosed within a 2 cm thick mantle of copper or nickel and this space is limited also by an upper and a lower cover of the same metal. As in a high vacuum copper at the highest temperatures (1000°) readily volatilizes, the spiral must be protected against this by screens and walls of PYTHAGORAS-mass: in Fig. 1 to the left the disconnected parts of the copper- and PYTHAGORAS-mantles are shown and to the right

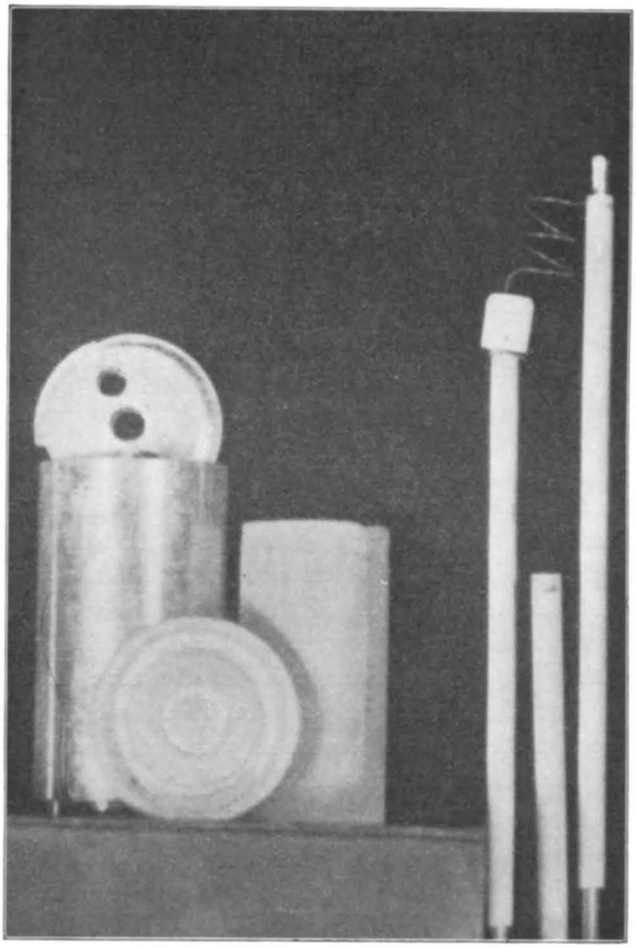
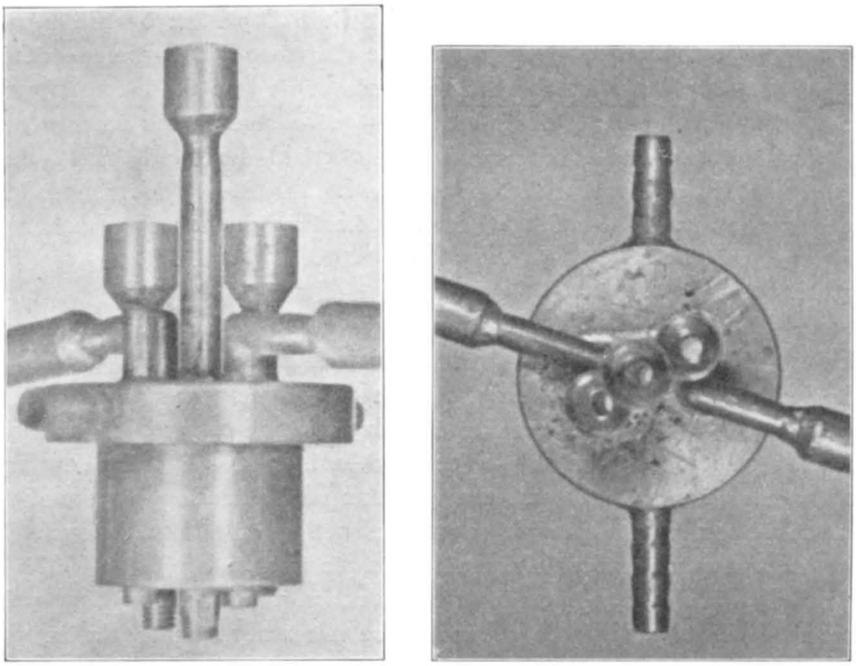


Fig. 1. *To the left: Copper-mantle and mantle of* PYTHAGORAS-*mass in disconnected Parts. To the right: The Spiral Wire between Copper-wires, covered with Capillaries and one of the Cups.*

the spiral of the wire between its copper leadings, protected by gas-tight capillaries and the ends by cups, so as to avoid a contamination by a deposit of volatilized copper. One of the cups is removed in the figure. Also the wires of the thermocouples had, for the same reason, to be covered by such capillaries. The copper mantle was supported by the copper bottom, which itself was held in position by a ring of nichrome, fixed by bearers connected with the flange at the upper end of the tube. A second ring, higher up in the tube, served as a device for centering and adjusting; between the bearers several diaphragmas of PYTHAGORAS-mass were inserted, so as to guarantee as much as possible the maintainance of a homogeneous distribution of the temperature within the tube. The upper, water-cooled part of the tube consisted of a hollow copper cylinder ending in a flange with a fitting cover (Fig. 2); as it has several perforations for the different inlets, it had to be soldered with a hard solder [1]) and,



2A 2B

Fig. 2. *To the left: The hollow Copper cylinder with its Canals of Copper and Lead and its Flange. To the right: The Cover seen from above.*

moreover, even at a distance of 20 cm above the furnace, it needed intensive cooling by a rapidly streaming flow of cold water. The cylinder bore five tubes, 3 of copper and 2 of lead, — the latter being used for connecting the tube with the high-vacuum pump, whilst of the three copper tubes two oppositely arranged were used for the fixation of the copper wires bearing the wire-spiral to be investigated, whilst the third served for the purpose of a passage of the fourfold bored capillary, in the borings of which the four wires of the two thermocouples were situated. As the cover also has a flange exactly fitting to that of the hollow cylinder, a thin ring of soft rubber at both sides lightly covered with some RAMSAY-fat or better with "Apiezon" (Shell Company), was placed between the two flanges, which then were tightly pressed upon each other by means of three small, screwed claps. As to the passage of the wires of the thermocouples,

[1]) Originally a *soft* solder was used, but soon it became apparent that a hard solder had to be used, notwithstanding the greater technical difficulties of its application, because, — especially with repeated heatings, — the latter yielded longer and gave a better guarantee against leakage.

it still can be remarked, that the capillary with its fourfold borings at its upper end, — there, where it passes through the upper cover, — was over a distance of 1 cm ground off, so that the four wires lay bare; this ground part of the capillary emerged through the tube previously mentioned far enough to reach the upper, funnel-shaped enlargement of the perforation, which then was filled with molten and solidified piceïne or better with "Apiezon"-glue. The hot junctions of the thermocouples were centrically placed about in the midst of the wire-spiral; the one thermocouple was connected with the horizontally recording galvanometer, the other with a sensitive pyrometer, which continuously could be read during the experiment. If the experiments are made with all necessary precautions, the vacuum-tube remains perfectly tight, notwithstanding its rather numerous inlets and outlets.

§ 4. The vacuum-tube described was heated in an electrical resistance-furnace of the type always used in this laboratory, the lower end of the tube being placed within the space of constant temperature-gradient of the furnace. In this part the increase of temperature of the furnace, when its temperature is gradually augmented, will also be most regularly distributed. In our experiments the variation of the heating current of the furnace by altering its external resistance was, up to 600° C., completely, or at least as much as possible, avoided; in the interval of 600°—1000° C., where often a slight supplementary regulation of the heating current by inserted external resistances proved to be necessary, the regulation was made with great precaution, in steps of 0.01 Ohm and always within stretches where no irregularities in the curve proved to occur. In the present measurements on nickel, where the temperature-interval did not exceed 400°, no supplementary regulation was needed. As to the cooling-curves, from 1000°—600° C. downwards, simply switching-off the heating circuit usually proved to be sufficiently efficient; the speed of cooling at 1000° C. then was about 6° per minute, slowly diminishing to 3° per minute at 600° C. For cooling from 600° C. downwards a slow current of air, regulated by means of a stopcock, was blown into the furnace from the lower end; in this way the speed of cooling down to 300° C. could be kept fairly constant.

§ 5. *Measurement of the Resistance of a Nickel-wire at different Temperatures between 15° and 430° C.*

As a first example of measurements of this kind we here communicate the results of the application of this method to the study of the allotropic changes of *nickel,* which take place between 350° and 380° C. The measurements were made in a high vacuum as well as in an atmosphere of hydrogen under low pressure, with the purpose of studying the influence which the taking up of traces of such gases may have on the special way of transformation and on the localization of the transition-temperature itself.

The wire used (98 % Ni) had a diameter of 0.4 mm and was wound into the shape of a spiral with a length of 46.3 cm; its specific resistance (for 1000 mm length and a cross section of 1 mm^2) was 0.091 Ohm at 20° C. During the measurements small thermoelectrical effects were

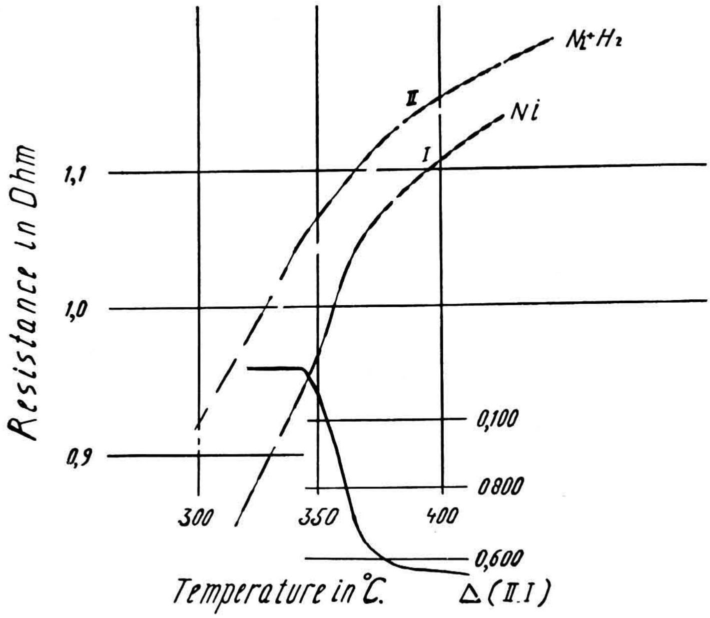


Fig. 3. *The Variation of the Electrical Resistance of Nickel with the Temperature in a Vacuum and in Hydrogen.*

observed, which in the final computations of the results must, of course, be eliminated. For this purpose the shift of the zero-line on the photographic plate was determined by switching off the current in the bridge and intercepting the luminous ray and then localizing the new zero-points on the photographic plate by imprinting the calibration-marks upon it at a series of temperatures below and above the transition-point under these circumstances, by a short exposure (10 sec.) of the plate to the point-shaped spot of light. Within the narrow range of temperatures of only 130°, the thermoelectrical effect is practically independent of the temperature. Several *w-t*-curves were thus determined and, after the necessary corrections for the thermoelectrical effects and the change of resistance of the supplying conductors being duly applied, they proved to co-incide with each other within 0.1 %. As the resistance of the supplying wires leading to the WHEATSTONE-bridge also changes during the experiment, because their temperature will less or more increase, — this variation duly also has to be taken into account, although it is rather small: the total resistance of these connecting parts was 0.023 Ohm, of which 0.002 Ohm correspond to the parts within the heated tube. This correction is not yet considered here; it will be determined separately in the near future.

In Table I a review of the results obtained is given for the case that the nickel-wire was heated in a high vacuum.

TABLE I.
The Variation of the Electrical Resistance w of a Nickel-wire when heated in a Vacuum at Temperatures between 320° and 430° C.

Temperature t in °C.:	Resistance w obs. in Ohms:	Increments Δ of w for every 10°.	Temperature t in °C.:	Resistance w obs. in Ohms:	Increments Δ of w for every 10°:
320° C.	0.839		375°	1.042	
		0.033			2×0.010=**0.020**
330	0.872		380	1.052	
		0.034			2×0.008=**0.016**
340	0.906		385	1.060	
		0.034			2×0.007=**0.014**
350	0.940		390	1.067	
		2×0.022=**0.044**			**0.014**
355	0.962		400	1.081	
	*	2×0.027=**0.054**			**0.014**
360	0.989		410	1.095	
		2×0.023=**0.046**			**0.015**
365	1.012		420	1.110	
		2×0.016=0.032			**0.014**
370	1.028		430	1.124	
		2×0.014=**0.028**			

From these data it is seen that, before the first transition-point (358° C.) is reached, the increment of w per 10° C. first regularly augments to a maximum value at 358° (= 0.054), but then rapidly decreases till a constant value (0.014) is attained in the neighbourhood of 380° C., which is less than half the value observed before the allotropic changes have occurred (Curve I in Fig. 3).

Between about 350° and 365° C. the curve shows a much steeper interval: perhaps this part of the curve relates to the α- + the α'-modification (hexagonal) observed by BREDIG, which appears to be stable between 357° and 363° C.; conf. these Proceed., **34**, 818 (1931).

Now the same measurements were executed in an atmosphere of *hydrogen* of 60 mm pressure; the results obtained are recorded in Table II.

From these data it can be deduced that *nickel*, after having taken up some hydrogen on heating, has a greater resistance than the metal in vacuo, but that the temperature-coefficient of the resistance remains practically the same as before. From about 345° C. till 375° C. upwards, however, the hydrogen is gradually released: the curve Δ' (II—I) in Fig. 3 clearly shows the course of these differences. In a stretch of transition between 345° and 375° C. there is a steep slope of the curve mentioned, the values of the ordinates rapidly decreasing to less than half the original value; whilst, on further increasing the temperature, the resistance of the still *hydrogenated nickel* slowly and gradually approaches that characteristic

TABLE II.
The Variation of the Electrical Resistance w of a Nickel-wire when heated in Hydrogen ($p = 60$ m.m.) at Temperatures between 300° and 430° C.

Temperature t in °C.:	Resistance w obs. in Ohms:	Increments Δ of w for every 10°:	Temperature t in °C.:	Resistance w obs in Ohms:	Increments Δ of w for every 10°:
300° C.	0.894		370° C.	1.091	
		0.030			2×0.011=**0.022**
310	0.924		375	1.102	
		0.030			2×0.008=**0.016**
320	0.954		380	1.110	
		0.032			2×0.007=**0.014**
330	0.986		385	1.117	
		0.036			2×0.007=**0.014**
340	1.022		390	1.124	
		0.025			**0.012**
350	1.047		400	1.136	
		2×0.012=**0.024**			**0.012**
355	1.059		410	1.148	
		2×0.013=**0.026**			**0 011**
360	1.072		420	1.159	
		2×0.009=**0.018**			**0.011**
365	1.081		430	1.170	
		2×0.010=**0.020**			

of the pure metal. The first steep slope of this part is most probably connected with the insertion of the hexagonal α'-form between the α- and β-modifications.

The Differences Δ' between Curves II and I between 320° and 430° C.

t:	Δ':	t':	Δ':
320°	0.115	375°	0.060
330	0.114	380	0.058
340	0.116	385	0.057
350	0.107	390	0.057
355	0.097	400	0.055
360	0.083	410	0.053
365	0.069	420	0.049
370	0.063	430	0 046

We soon intend to publish more results of this kind: the case here studied may, for the moment, be sufficient to demonstrate the applicability of the method described.

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