Chemistry. — *On the Localization of the Transition-points of Allotropic Metals under varied Circumstances by Means of the Method of* SALADIN—LE CHATELIER. By E. ROSENBOHM and F. M. JAEGER.

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

§ 1. In connection with our investigations, within an interval of 100°—1600° C., on the dependence of the specific heats of metals on the temperature, it gradually proved ever more desirable to check the calorimetrically established localization of the transition-points of the reversible allotropic changes occasionally observed in such metals by means of a quite independent method which, moreover, would enable us to study also some other physical properties of those metals in function of their temperatures.

Such a method, well suited for the purpose, was found by using, in a somewhat modified form, the principle suggested by SALADIN in 1903 and first applied by LE CHATELIER a. o. in metallurgical investigations [1]), because it not only is applicable to the determination of heating-curves in the thermal analysis and to the detection of transformation-temperatures, but, — as later on we will demonstrate, — it is more especially suited for the study of the temperature-coefficient of the electrical resistance of such metals, as well as for that of their thermoelectrical properties. In this paper, however, we only wish to deal with some results obtained during our tentatives to localize the true transition-points just mentioned in the case of allotropic metals or polymorphous alloys, because these results, — more particularly with respect to the influence exerted by small amounts of gases present, — may prove to be of a general interest in all work of this kind.

§ 2. The principle of SALADIN consists in the use of two optically coupled galvanometers in combination with a photographic recording-device.

The two moving coil galvanometers, which in general have different but in rather wide limits adjustable sensitivities, are both steadily mounted upon the same vibrationfree and heavy support. A pencil of light emitted by a luminous source, — for instance by a small incandescent lamp, — first passes a screen provided with a small circular opening and then is reflected by the horizontally swinging mirror of the first, more sensitive

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1) H. LE CHATELIER, Revue Métall., **1**, 134 (1904); conf. H. HARKORT, Metall., **4**, 617 (1907); F. WEVER and K. APEL, Mitt. Kaiser Wilhelm Instit. f. Eisenforschung, **4**, 87 (1922); P. GOERENS, *Einführung in die Metallographie*, Halle, 198 (1932).

galvanometer; it subsequently passes an "inverting double prism", placed between the two galvanometers in such a way that the basal face of the prism is inclined under 45° with respect to the horizontal plane and thus to the surface of the first mirror, so that the originally *horizontal* motion of the reflected ray now is converted into a *vertical* one. This vertically moving luminous ray is subsequently reflected by the equally horizontally swinging mirror of the second galvanometer, the reflecting surface of which is about twice as large as that of the first mirror, so that the deflections of the latter may to their full extent eventually be utilized for the purpose of recording. The ray reflected from this second mirror finally reaches the photographic plate (13 × 18 cm), which is exposed to its action and is mounted in a camera of special construction; a system of lenses is adjusted in such a way, that a sharp, almost point-shaped image of the small circular opening in the diaphragm mentioned, placed closely behind the incandescent lamp, is produced, which, according to the combined horizontal and vertical motions of the pencil of light twice reflected, now will describe its resultant path over the photographic plate. A periodic interruption or weakening of the light-intensity of the ray, regulated by means of a clockwork, allows the indication of the time elapsed at every moment by the broken curve thus produced, simply by counting the number of its hiatus.

If the second, horizontally recording galvanometer during the experiment is compelled to yield deflections which in a regular way increase or decrease with the time elapsed, whilst the first galvanometer is placed within a circuit in which the variable quantity x to be measured is simultaneously inserted, — the path described by the luminous spot will afford the necessary information about all slow or rapid changes occuring in the magnitude of the variable quantity x, in their connection with the values of the horizontal, regularly varying parameter at each arbitrary moment.

§ 3. The second of the two galvanometers in the present experiments now is connected with the thermocouple indicating the furnace-temperature and its sensitivity adjusted so as to allow a complete survey of the special interval of temperatures desired.

In the present investigation the other instrument, the sensitivity of which is also carefully adapted to the temperature-measurements intended, is connected with a *differential-thermocouple*, for the purpose of indicating at each moment the *difference* in temperature of the sample studied and of a standard substance, both simultaneously being heated at the same constant temperature t in the vacuum-tube still to be described. If *no* temperature-difference between the two samples exists, the lightspot on the photographic film will describe a horizontal line parallel to the axis of the furnace-(tube-)-temperatures; but at the least difference in temperature occurring between the two samples, it will deviate from the horizontal line in the one or in the opposite direction. With the necessary precautions, each sudden difference in the specific heats of the two samples thus will immediately be recorded; and if beforehand both galvanometers are carefully calibrated and the scale of the temperatures on the photographic plate is exactly fixed, the temperatures at which the said deviations occur may be sharply localized, as well as the approximate magnitude of the thermal effect observed is roughly estimated. As a standard of comparison, theoretically a metal should be chosen, the specific heats of which, as well as its dependence on the temperature, are not only exactly known, but are as comparable as possible; its mass and that of the sample to be studied must be chosen in such a way, that in the beginning both masses will require about the same heat-quantities for heating them at equal temperatures. In this way the slope of the curve on the film will not appear too steep, — provided that the dependence of the specific heats of both substances on the temperature be at least rather closely comparable.

Attention also must be given to a certain degree of similarity in the state of the surfaces of the two metals, as, especially at intermediate temperatures, the influence of a too different surface-radiation proved to make itself seriously felt.

§ 4. The vacuum-tube used in these experiments is represented in figure 1. It consists of a gas-tight mantle B of PYTHAGORAS-mass, at its upper end closed by a water-cooled gas-tight cover of brass, through which the thermocouple E_3, for measuring the furnace-temperature, as well as the wires of the differential-thermocouple E_1E_2 pass under perfect isolation. Moreover, the inlets and outlets G for occasionally introducing a circulating gas flow, are also conducted through it. Perforated screens are adjusted in such a way as to ascertain the constancy of the temperature throughout the heated tube over the whole extent of the partition in which the objects to be compared are placed; moreover, these heated objects, M_I and Me_0 are, carefully isolated, placed one above the other and surrounded by a vertically divided copper-mantle, so as to improve the equal distribution of the temperature throughout. This mantle too is at its upper end and at its bottom screened off by the diaphragmas S_B and S_0, the shape and perforation of these being indicated on the left in figure 1. The objects to be compared and the wires of the thermocouples, — the latter being enclosed in four crosswise arranged capillaries of PYTHAGORAS-mass, — are besides protected against contamination by copper-vapours at the highest temperatures (900°—1000°) by means of a cylinder of the same material. In the present case the metals studied usually had the shape of spheres of suitable dimensions and their specific heats, in their dependence on the temperature, were beforehand carefully studied.

If no special introduction of a gas is needed, the tube can by means of the tubes G be connected with an oil-pump of high exhausting power, continuously being driven by an electromotor and allowing to maintain an almost constant vacuum (of about 0.001 mm or less) during arbitrarily

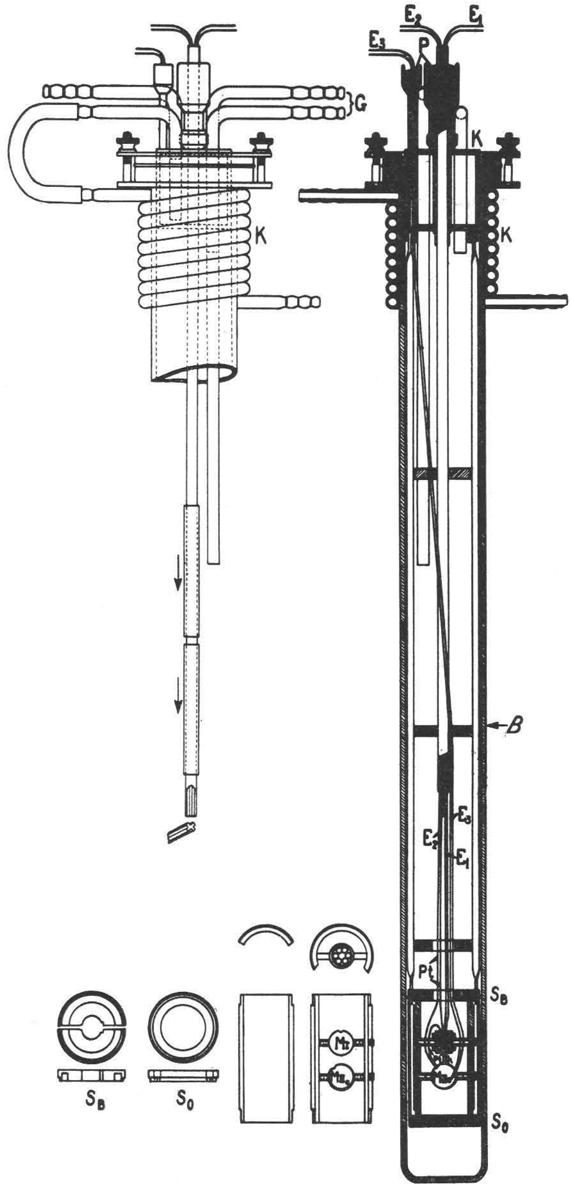

Fig. 1. *Vacuum tube used in the Experiments.*

long intervals of time; the vacuum produced was high enough to prohibit an electrical charge from passing through it. The whole tube is placed within an electrically heated furnace of the type always used in this laboratory, which, under the necessary precautions, allows a very accurate regulation and constancy of the temperature.

More especially the supplementary regulation of the furnace must be avoided in the neighbourhood of the transition-points. For this reason the speed of heating must be chosen in such a way, that at least already a 100° beneath the transition-temperature a further change of the furnace-resistances is no more necessary.

The thermocouples were, of course, beforehand carefully calibrated in the usual way and their indications from time to time controlled and compared. In the course of the experiments, especially with those of long duration, it proved necessary to provide all stopcocks with mercury-fittings and to insert a vacuum-vessel of great capacity between the pump and the vacuum-tube, so as to protect the latter against sudden jumps of pressure.

§ 5. As to the calibration of the galvanometers used, it may be remarked that in our experiments the second horizontally recording galvanometer ordinarily had the lower sensitivity; it was used for the recording of the temperature of the heating-apparatus and of the sample to be investigated enclosed in it. As during the photographic record the motion of the luminous spot, of course, cannot visually be observed and the gradual increase of the temperature of the heated object has yet to be checked at each moment, we for this purpose used a method previously suggested by WEVER and APEL [1]), but somewhat modified for the present occasion. The ends of the thermocouple, therefore, were not only connected with the galvanometer, but simultaneously with a moving coil pyrometer, indicating the temperature in degrees centigrade. As both instruments, however, in this way are used in *parallel* connection, the current produced by the thermocouple will be diminished by them in the ratio of their (unequal) resistances. As long as the external resistance applied to the galvanometer is sufficiently high, the error introduced in this way can readily be neglected; but if more exact measurements are made, — e.g. if the whole length of the photographic plate had to be used for only a short range of temperatures, — the external resistance of the now rather sensitive galvanometer must accordingly be diminished and in that case it is no longer allowed to cancel the said error. Therefore, in the latter case a second thermocouple was used instead of the pyrometer, so that the full sensitivity of the galvanometer now could be utilized: when the maximum sensitivity of the instrument was used, the whole length of 18 cm of the photographic plate proved to correspond to an interval of temperature of about 150° C., in the case that a *Pt-PtRh*-thermocouple is made use oft. The calibration of the galvanometer (internal resistance: 15.4 Ohm) for intervals of 300°, 600° and 1000° C. for the same length of the photographic plate must preliminarily be executed by inserting the suited external resistances; although the deflections of the instrument for these different external resistances were calibrated in the same way as by WEVER and APEL, — here the variable resistances of the circuit continuously needed to be taken into account, when we passed from the calibration-

[1]) F. WEVER and K. APEL, loco cit.

arrangement to the thermocouple itself. This was done by measuring the resistance of the thermocouple plus its supplying joints with an accuracy of 0.1 Ohm from 100° C. upwards at different temperatures between 100° 1000° C.; measured by the aid of a WHEATSTONE-bridge, it proved to increase from 4.2 to 5.6 Ohm. The final conversion of the thermoelectrical force E' of the thermocouple, measured (in Millivolts) into degrees centigrade, was made by measuring E' at 419° (mpt. of *zinc*), at 800° C. (mpt. of *NaCl*) and at 1063° C. (mpt. of *gold*), — these numbers being found in full agreement with the previously determined calibration-scale of both the thermocouples used. Still it must be remarked that on measuring within different intervals of temperature, e.g. from 0°—300°, from 300°—600°, from 600°—900° C., etc. — the zero-point of the galvanometer had, of course, every time to be shifted by a suitable rotation of the top-screw of the instrument [1]).

§ 6. For the purpose of deducing the true temperatures on the photographic plate from the deflections registered, the plate must preliminarily be calibrated by imprinting calibration-marks upon it for a series of known temperatures or definite temperature-differences respectively. This was done by exposing the plate for a series of known temperatures to the short action (10 seconds) of a point-shaped light-spot, so that afterwards the corresponding calibration-marks got visible when the plate was finally developed.

Of course, the regulation of the sensivities of the galvanometers by inserting varied external resistances in their circuits has to be made in such a way that, during the whole interval of temperatures studied, their deflections never will reach the borders of the photographic plate: this must be ascertained beforehand by a method of trial and error and, especially in the case of very irregularly occurring changes in the differential-curves obtained, in the beginning failures in this respect hardly can be avoided.

§ 7. *The Transition-point of Nickel.* As a first example of the applicability of the method described, the transition-point: *α-nickel* ⇄ *β-nickel* was more especially studied under various circumstances. A sphere of pure *nickel* of about 1 cm diameter was, in these experiments, compared with a suitable sphere of *copper* of about the same heat-capacity. As between 300° and 400° C. the temperature-coefficients of the specific heat c_p of the two metals are pretty accurately the same, it proved possible to make the temperature-difference between the two spheres, up to the transition-point, very small and regular indeed. Thus the first part of the

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[1]) Usually the photographic plate was used for 1000° C. over its whole length, but also intervals of smaller extent occasionally were studied with a corresponding alteration of the sensitivity of the galvanometers. For the purpose of shifting the zero-point of the galvanometer WEVER and APEL made use of an auxiliary current, but we have always avoided to do so.

heating-curve *A* in Fig. 2 is almost horizontal and the transition-point itself, therefore, is revealed as a very sharp discontinuance at 369°—

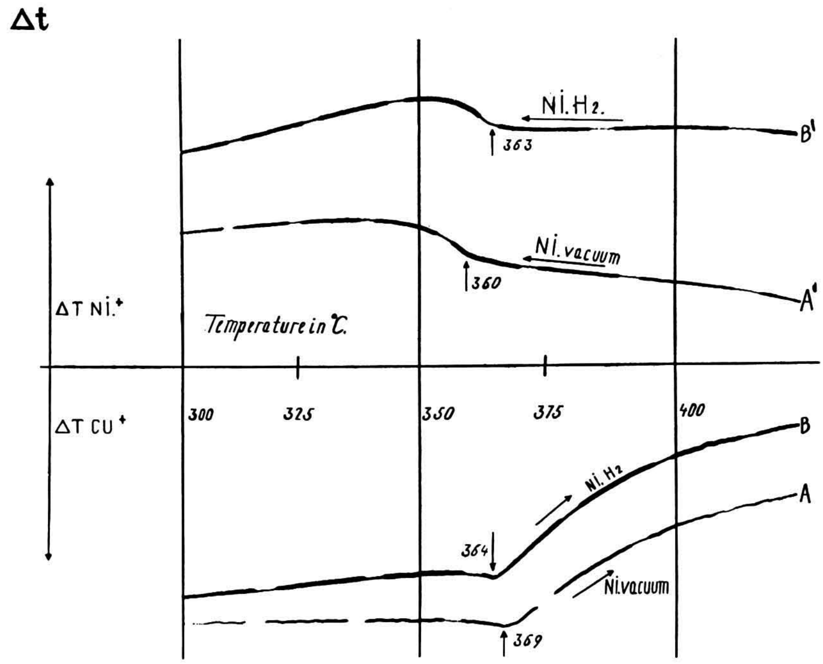

Fig. 2. *Transition-point of Nickel, when heated or cooled in a Vacuum or in an Hydrogen-atmosphere of low Pressure.*

370° C., when the experiment is made in a high vacuum. On the other hand we did not succeed in localizing the transition-point at the same spot by cooling down the wire under the same circumstances (A'): now it was always situated at a temperature about 6° *lower* than before; on *rapid* cooling even greater deviations proved to occur. If traces of gases, such as oxygen or hydrogen, were present under pressures ranging from 2 to 60 mm instead of a vacuum, a rather appreciable shift of the transition-temperature was observed in all cases, as may be seen from the curves *B* and B' in Fig. 2 obtained under a pressure of 50—60 mm of hydrogen. The transition-point now lies, on heating as well as on cooling, at 363°—364° C. and is in both cases practically identical. Within a pressure-interval of 2—60 mm this shift seems to be independent of the gas-pressure used. The data given in the literature about the localization of the transition-point: $\alpha \rightleftarrows \beta$-*nickel* now are strongly divergent: they show differences as great as 20° C. It seems very likely that these discrepancies for a good deal may be caused by the presence of absorbed gases in the metal used in the various experiments.[1])

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1) However, attention must be drawn to the fact that, according to BREDIG, another (hexagonal) form (α') of *nickel*, would be stable within the interval of 357° to 363° C.; conf. Proc. Royal Acad. Amsterdam, **34**, 818 (1931).

§ 8. *The Transition-points of the polymorphous Alloy: $AuSb_2$.* As a second instance of transitions, this time in a polymorphous compound, the results of the determinations made with the binary compound $AuSb_2$ [1]) are here communicated. Pure *silver* was used as the substance of comparison in this case and the experiments were executed in an atmosphere of hydrogen at low pressures. The two transition-points here were localized at 355° and 404° C. respectively, — in full agreement with the result previously obtained by means of the calorimetrical measurements [1]). The curves represented in Fig. 3 clearly indicate that, on heating, a change evidently occurs at 355° C. different from that at the second transition-point of 404° C.: the first change evidently occurs almost instantaneously and the curve, after its sudden rise, rapidly falls back to almost the same height, as before the change took place. Suspicion might arise, that at this

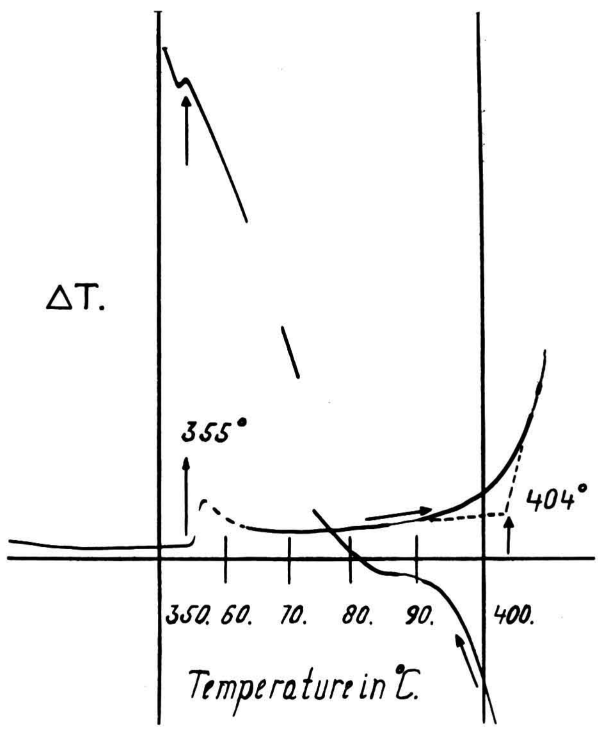

Fig. 3. *Transition-points of $AuSb_2$.*

transition-temperature, where certainly a definite heat-effect occurs, the course of the temperature-coefficient of the specific heat c_p, after passing 355° C., truly remains the regular continuation of that before the change occurred. As the weights of the alloy and the silver used were known and the vertical deflections of the galvanometer were exactly calibrated, the

[1]) F. M. JAEGER and J. A. BOTTEMA, Proc. Royal Acad. Amsterdam, **35**, 916 (1932); Recueil d. Trav. d. Chim. d. Pays-Bas, **52**, 107, 108 (1933). The transition-points were calorimetrically determined to be: 355°.2 C. and 405° C.

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.

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§ 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).