Chemistry. — *On the Exact Determination of the Specific Heat of Solid Substances between 0° and 1625° C. I. Method and Apparatus.* By Prof. Dr. F. M. JAEGER and Dr. E. ROSENBOHM.

(Communicated at the meeting of September 24, 1927).

§ **1.** In connection with the development of the modern theories concerning the specific heat of solid substances, during the last decennia the attention of numerous investigators has again been drawn more particularly to this physical quantity, which, since the classic investigations of DULONG and PETIT and the establishment of the empirical rule named after them, has become of so much interest also to chemists.

In connection with a series of investigations made in this laboratory with the purpose of developing a number of methods of measurement of several physical constants, allowing the exact and reproducible determination of these constants also at high temperatures, — we have during the last years developed i.a. a method for the accurate measurement of the specific heats of solid substances under constant pressure. This method, which has been tested now by us in the case of several substances, has appeared to enable us to determine the specific heats mentioned with a degree of accuracy, which under favourable circumstances, even at very high temperatures may attain about 0.001 of the determined value.

We intend to test experimentally the validity of the modern theories in this way up to these high temperatures in a number of cases, and especially to study the variation of the so-called "atomic heat" of the solid elements with the temperature, also under these extreme conditions. In the following we give the description of the apparatus used and of the method of experimenting followed by us.

§ **2.** The principle of the metal-calorimeter was made use of here, after the manner originally proposed by NERNST, KOREF and LINDEMANN [1]) and as applied more in particular also to measurements at temperatures up to 900° C. by MAGNUS [2]). During the construction of the apparatus, the experiences of many investigators, more in particular of WHITE, were borne in mind. Besides, all improvements necessary for our purpose were made, so that the instrument and the method followed have now reached a very high degree of perfection.

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[1]) Compare: Sitz. Ber. d. preus. Akad. d. Wiss. Berlin, (1910), 247; Ann. der Physik, **36**, 49, (1911).

[2]) A. MAGNUS, Phys. Zeits., **14**, 5, (1913); Ann. der Physik, (4) **70**, 303, (1923); A. MAGNUS and A. HODLER, Ann. der Physik, (4), **80**, 808, (1926).

In Fig. 1 the arrangement of the calorimeter used by us has been represented diagrammatically [1]). A double-walled prismatic vessel *O*, made

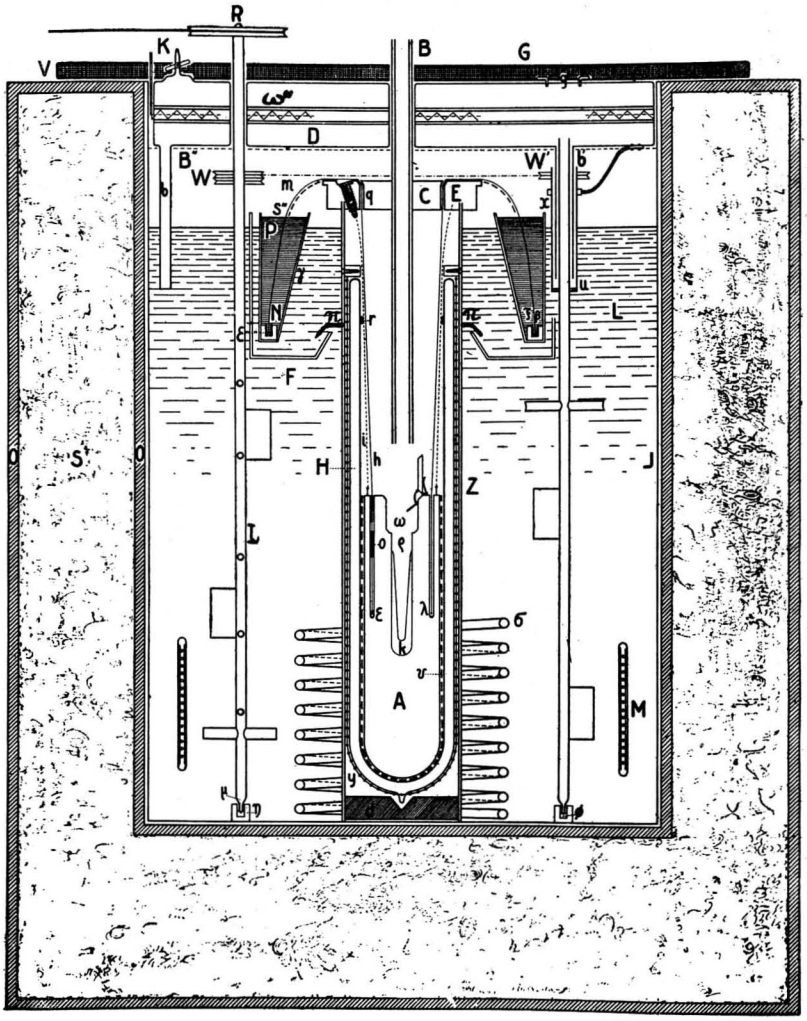

Fig. 1.

of thick wood, the outside measurements of which are 95 × 95 × 100 cm., the inside measurements 65 × 65 × 81 cm., whose interspace is completely filled out with slag wool *S*, forms, together wich a water-reservoir of great capacity placed in it, the insulation of the calorimeter from the surrounding. The water-reservoir is provided with a water-bearing cover and covered with a layer *V* of felt several cms. thick. The surrounding space is, moreover, maintained as much as possible at a constant temperature. In this vessel a zinc vessel *J* has been placed which impinges on its walls and

[1]) In the construction of the calorimeter we were assisted in an excellent manner by the nstrumentmaker of the laboratory, Mr. A. VAN DER MEULEN.

measures 65 × 65 ×81 cms. It contains the water surrounding the calorimeter, about 260 Liters, the surface of which rises to about 62 cm. from the bottom. This water-reservoir can be shut by a water-bearing cover *D*, which is supported by iron hoops *B''*. The cover is about 7 cms. high and contains about 29 Liters water, which is forced up from the calorimeter-vessel *J* (see below) and flows back in it by constant circulation. The water is maintained at a constant temperature by means of three heating-spirals *M* of nickelwire, which have been spread out in flat tight soldered brass boxes 0.5 cm. thick ; also with the aid of a spiral tube σ. with circulating cooling water, and of a large thermoregulator *Th*. The arrangement to bring the circulating water into motion, consists of three centrifugal stirrers *l*. These stirrers consist of brass tubes 1.2 cms. wide, are provided with small holes, and are at different heights, supplied with *T*-pieces, the arms of which are about 20 cms. long and out of which the water is hurled with force through the rotation of the stirrers. About 5 cms. above the level of the water the tubes are provided with wooden disks *W* and *W'*, which are interconnected by driving-belts. These driving-belts have been made of spiral-strings of brass-wire and are rotated by being connected with an other disk *R*, which is set in motion by an electromotor. The axes of rotation of the stirrers are provided at the bottom with steel points μ. which rotate in bearings of agate φ; these bearings are fixed in brass cushions η, which are firmly soldered to the bottom of the vessel *J*. Also after a very long use the stirrers thus fitted proved to work perfectly and without any disturbance ; the water does not in any way interfere with the rotation of the shaft-ends in their bearings. The third stirrer *W'* has a construction somewhat different from the other two (for further particulars see below).

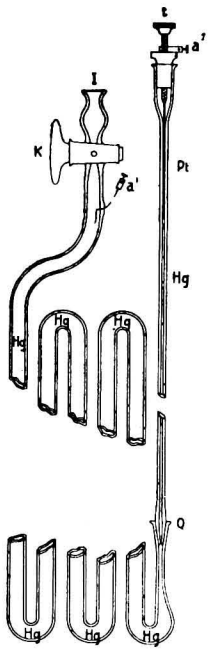

Fig. 2.

For the heating of the water in the reservoir served the above-mentioned heating-spirals *M*, two of which are interconnected. With the help of adjustable resistances, they keep the water just a little below 20° C. The third heating-spiral, however, is connected with a large thermo-regulator *Th.*, which, as is shown in Fig. 2, consists of a glass tube bent four times alternately upward and downward and terminating in a tube narrowed to a capillary ; the regulator is entirely filled with six kilogrammes of purest mercury. To this regulator a number of relays are connected according to the wiring-diagram given in Fig. 3 [1]). It is essential to prevent in the electric thermo-regulator as much as possible the flashing of an induction-spark at the

[1]) Let A_1, A_2 and A_3 represent three accumulators: W_1 to W_8 are adjustable and constant lamp-resistances; R_1, R_2, R_3 are three relays. The current-circuit of A_2 is always closed on relays R_1, with little strength of current only. If e.g. R_1 turns to the right, the

breaking of the contact between platinum-pin and thread of mercury. This was achieved by the system of relays as is shown diagrammatically in

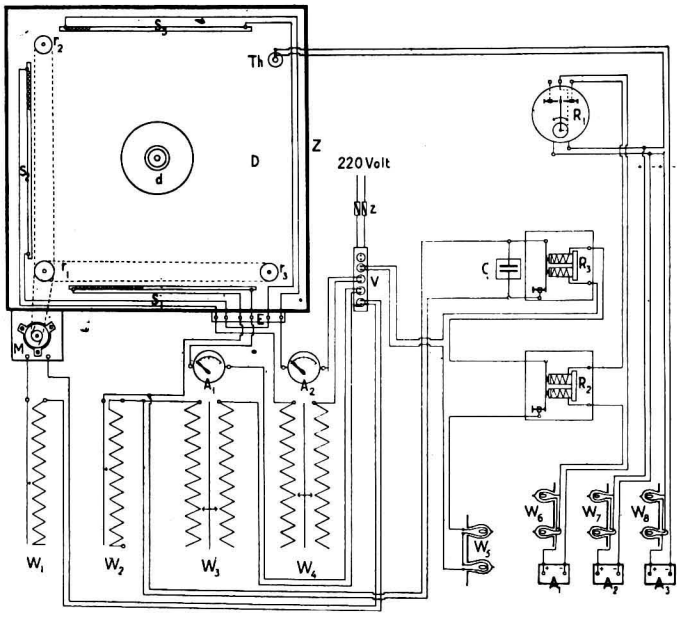

Fig. 3.

Fig. 3 ; by this arrangement the working of the regulator was regulated only by a very small fraction of the heating-current (2 Volt ; 2 milli-Ampère) and each oscillation of temperature above or below 20° C. was compensated almost immediately. The cooling-spiral σ likewise helped to bring about this result. An adjustable current of cold water flows through it very slowly ; the spiral serves to rapidly absorb the excess of heat, in case the temperature of the room comes too near to the temperature of the calorimeter. The expansion of the column of mercury in *Th* appeared to be about 0.5 mm. for 0°.001 C. temperature-difference. In this way it was possible to keep the temperature of the calorimeter-water *L*, — also in the case of prolongated experiments, — constant within 0°.001 C., provided the water-bearing cover *D* is simultaneously made use of. This cover has been made of zinc-plate ; the top is provided with an air-thight tap, which

current of R_2, which comes from A_1, is closed. In this case the current-circuit in which R_3 is inserted, is interrupted, which relay is connected with the municipal current (220 Volt). Owing to this, W_2 is short-circuited, so that the current which runs in the auxiliary-heating-spirals *S*, is now increased. If, however, the temperature of the water rise above 20° C., the thermo-regulator *Th* will cause the circuit of A_3 to be closed. The current in it is stronger now than that of A_2, and of opposed direction. This causes the relay R_1 to turn to the left, thus making currentless the circuit in which R_2 is inserted. Through this, the contacts are now closed for the circuit containing R_3; the resistance W_2 which was short-circuited before, is now switched on again in the circuit of the heating-current, the latter now being diminished; etc. etc.

can be shut hermetically, and with a screw-lock G provided with a glass window g. By means of the thick felt-layer only, small irregularities in the cooling-process of the calorimeter could not be prevented, even if the room-temperature was kept constant. Therefore this cover was provided with a number of nickel heating-spirals w'', surrounded by protecting-tubes, and with a number of partitions, in order to force the circulating water to flow in helical tracks within the cover.

Besides the porcelain tube B, which serves as a feeding-tube for the introduction of objects into the calorimeter and a tube on one of the sides as a passage for the third stirrer, the cover has only at the bottom the passages in which the tubes b and b' are tight soldered. Through these tubes the water in the cover communicates with that in the vessel J; so both tubes reach beneath the surface of the water. The cover is filled by opening K and by connecting it with a suction-pump; then K is shut again and the third stirrer W' is set in motion, by which the water is forced from the cover into the thermostat and then flows again in b. When all precautions are taken, a difference of temperature between the water L and that in the cover can no longer be perceived; so that also in upward direction the insulation of the calorimeter with respect to its surrounding, is complete. The wooden disk W' of the third stirrer is not directly connected to the brass-tube b', but to a much wider tube x, which is shut off at the bottom by a plate provided with little holes. This plate is fastened to the stirrer-shaft, by means of which the space between the cover and the thermostat is closed watertight, without the help of any ground-in connections. At a some space is left between L and the cover, in order to have a passage for the wires of the thermo-elements; etc. When experimenting, a, just as the whole calorimeter, is covered with a layer of felt 4 cms. thick.

§ **3.** In the space of constant temperature described above there is the calorimeter proper. A big DEWAR-vessel H is, by means of a strong net of silk, suspended in a cylinder-shaped vessel Z. This vessel Z is 70 cms. high, has been loaded at the bottom with a thick layer of lead, and is shut off at the top by a ring E of hard wood, saturated with molten paraffine, and by a ditto cover C. The double-walled glass vessel is 42 cms. high and 11.5 cms. wide, and the walls have been silver-plated on both sides [1]). Between the wall Z and the DEWAR-vessel H there remains a thin layer of air; in the vessel and separated from it by a thin layer of felt v, is the calorimeter-body proper, viz. a cylindric block of pure aluminium A, weighing about 6000 grammes, and 27 cms. high, suspended by three strong silk wires, which just as the silk net y are fastened to the wooden

[1]) This beautiful DEWAR-vessel was made at the Physical Laboratory of the Leyden University; for the gracious assistance we wish to express once more our heart-felt thanks to the Directorium of said Institution.

ring E and which are kept together near the margin of H by a wooden ring r The aluminium block A, which has a diameter of 10.1 cms., possesses 38 cylindrical borings, arranged in two concentric circles, each of which is 16 cms. deep and 0.4 cm. wide. These borings serve to fix 36 thermo-elements of copper-constantan, arranged in four series of 9. These series can, at will, be connected parallel or in series. When standardizing these thermo-elements, the other two borings are used to fix two standard-thermo-elements ; or to control by means of two supplementary sets of thermo-elements which are arranged in series, any accidentally occurring, extremely slight fluctuations in the temperature of the calorimeter-water during the measurements. The arrangement of the borings is clearly visible in Fig. 4,

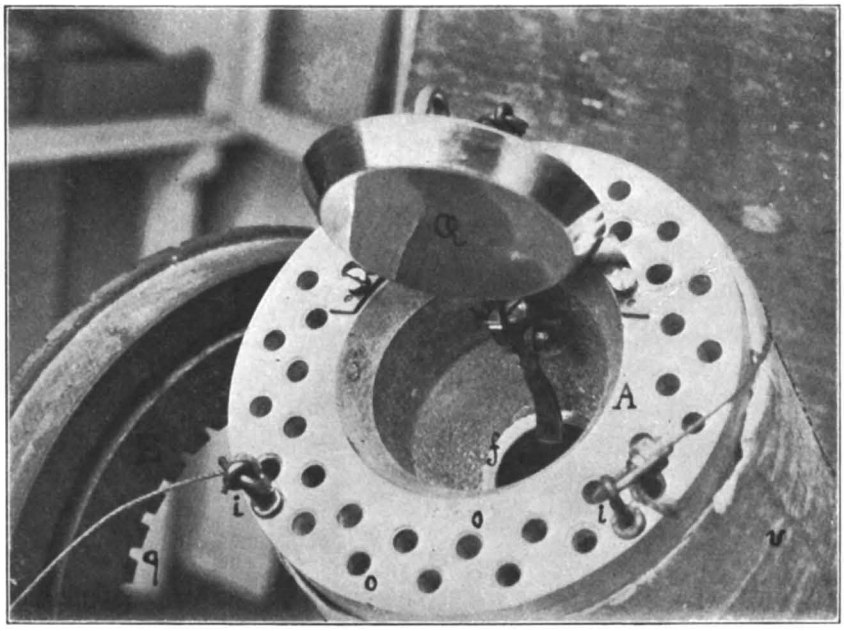

Fig. 4.

representing the aluminium-block seen from the top. In each boring there is a very thin-walled capillary tube o of porcelain at the bottom and fixed in the boring by means of closed ROSE's alloy, so that there exists an immediate metallic contact between the capillary and the aluminium-block. In these capillaries are the wires of the thermo-elements with their junctions in λ, which wires are covered with a layer of a well-isolating varnish and fastened to the bottom by means of shellac. Beforehand they have, over their entire length, been made properly homogeneous by repeated heating and cooling and further treatment according to WHITE [1]). The wires $h'h$ of the thermo-elements, which come from the calorimeter, are also well-

[1]) W. P. WHITE, Phys. Zeits., **8**, 337, (1907).

isolated. On leaving the DEWAR-vessel, they are led through the openings g of the wooden ring E, which are filled inside with a mixture of wax and resin. Giving any kink to the wires should be carefully guarded against. Outside the ring these wires rested originally on pieces of mica, placed on a flat-conical ring s'', which had been made of perforated zinc-plate. Later on, however, it was found that it was even better not to use the ring at all. The second junctions ξ of the thermo-elements are placed in a red-copper ring N below the water-level of the thermostat, this ring having a diameter of about 34 cms. It has been made of rectangular bar-copper of 1.3 cm. by 1.9 cm. These junctions are also placed inside thin-walled porcelain capillaries β, which by means of ROSE's alloy ε, have been sealed in 36 of the 38 borings of the red-copper ring N. When, as has been said above, the two other borings were used to control the temperature of the water, a series of thermo-elements were joined to them, whose other junctions had been placed in a DEWAR-vessel filled with pure ice. The copper ring N lies on the bottom of a hollow conical vessel γ of copper-plate, which has been filled almost to the brim with pure, molten and again solidified paraffine P. In order to maintain a perfectly constant temperature, it proved necessary to surround this jacket γ with a cylinder-shaped copper jacket F of the shape indicated in Fig. 1, and to add to it a screen π. It is better still to place a second copper screen outside the jacket F.

§ **4.** The following remarks must be made about the temperature measurements by means of the thermo-elements. As is always done in this laboratory [1]), all measurements were made with the aid of a potentiometer-installation void of thermo-electric contact-potentials (made by O. WOLFF), this time with five in stead of the usual three decades ; potential differences smaller than those indicated by the smallest decade-unit, were measured by the deflections of a calibrated galvanometer (according to ZERNIKE), which, at a critical resistance of 30 Ohm and a sensibility of 10^{-10} Amp., had a period of only 2 seconds. The working current of the potentiometer was chosen in such a way that each unit of the compensator corresponded to 2000 Mikrovolt ; in the final measurements the deflections of the galvanometer were always measured both to the right and to the left, by means of a switch equally free from all contact-potentials, which allowed to reverse the direction of the current in the compensator at any moment. A very weak current always circulated in the bank, so that no measurements were begun, before there was absolute certainty, that the temperature of the resistance-coils did not undergo any change worth mentioning. Before each measurement, the complete compensation of the instrument was always controlled once more [2]).

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[1]) F. M. JAEGER, *Eine Anleitung zur Ausf. exakter physiko-chem. Messungen* (1913) Groningen, p. 14.

[2]) On moist days it appeared desirable, to blow a slow current of carefully dried air through the box of the potentiometer, in order to eliminate the condensed water-vapour on the coils.

The four couples of wires of the four series of thermo-elements, which had to serve as connections to the potentiometer were, well-isolated, led outside the calorimeter through the opening *a* and fixed side by side in a reservoir filled with solidified paraffine. They were then placed over glass-rods provided with mica-rings and in this way connected with the measuring-apparatus. The same compensator was also used, when measuring the furnace-temperature by means of a platinum-platinum-rhodium-thermo-element. It thus became necessary to put all measuring-instruments on inter- and terrestrial-connected metal-plates, as suggested by WHITE [1]), in order to prevent, when using electric resistance-furnaces, that at high temperatures, any leakage of the furnace-current to the measuring-apparatus could occur.

All temperatures have been reduced to the scale of the nitrogengas-thermometer of *Washington*, as fixed by DAY and SOSMAN. The platinum-platinum-rhodium-thermo-elements used were calibrated by comparison with a standard-element, which was standardized in *Washington*, and by determining a series of characteristic and well known melting-points [2]). For the alternate reading of the thermo-elements in the calorimeter and in the furnace, plug switches free from all contact potentials were constructed. Also for the connection in series or parallel to each other of the four groups of thermo-elements in the calorimeter, plug-contacts were used, which too were practically free from contact-potentials and accessory resistances. Besides, any disturbances of this nature could always be eliminated by the application of the method mentioned above, viz. of reversing the working current in the compensator.

The calibration of the copper-constantan-thermo-elements in series of nine elements, led in the first place to this result, that all elements appeared to be identical and to be fixed in the calorimeter with a complete insulation. For each set of 9 elements, it appeared that the temperature t as a function of the electromotive force E could be expressed by the equation: t (in degrees C) $= 0.00279698\ E - 0.00000000629\ E^2$, when E is expressed in Microvolts. From this it follows, that a potential difference of one Microvolt corresponds between 19 and 23° C., — that is within the limits of the temperature-variations of the calorimeter, which lie between 7000 to 8000 Microvolts in all measurements, — to a change of temperature of 0°.002703 C. for each set of thermo-elements. If all elements are connected in series, the indication of the 36 thermo-elements corresponds consequently to 0°.000676 C. for a potential difference of one Microvolt. Thus it appeared possible to determine temperature-differences of 0°.0001 C. still with absolute certainty.

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[1]) W. P. WHITE, Phys. Rev., (2) **8**, 337, (1907).

[2]) $NaNO_3$ (308°); $NaCl$ (800°); Li_2SiO_3 (1201°); artificial *Diopside* (1391°); artificial *Anorthite*; (1551°); $BaSiO_3$ (1604°) were used. Corrections of thermo-element K: at 308°: + 10 M.V.; at 800°: —13 M.V.; at 1201°: + 6 M.V.; at 1391°: + 23 M.V.; at 1604°: + 56 M.V.

§ **5.** In the centre of the aluminium block A an opening 5 cms. wide was bored which continues with a gradually reduced diameter to a cylindrical boring ϱ of a diameter of about 2.7 cms. At the lower side of it a nicely fitting piece of aluminium k is fixed which firmly impinges on the walls and which has been provided with a steep conical boring. The whole inner-wall of this central channel, and also that of the conical part in its lower end is provided with a lining of purest platinum of 0.35 mm., the turned down and flattened border of which can be clearly distinguished in Fig. 4. This platinum-lining has a weight of about 120 grammes. By applying this conically narrowed part k, a much better contact is brought about between the calorimeter-wall and the introduced heated object, than with the original apparatus in which the object was caught on a platinum sheet, supported by a tungsten-spiral. The time necessary to restore the normal decrease of temperature of the calorimeter since the moment of introducing the heated object into it, could be reduced in this way from several hours to half an hour, while the maximum temperature, e.g. even in the case of platinum heated at 1600° C., appeared now already to be attained in about eight seconds, instead of after several minutes. By constructing a new and better-fitting platinum-lining of the calorimeter-space, it was finally possible to improve the interchange of heat to such a degree, that the total delivery of the heat of the hot object, — in the case that this is a metal [1]), — appeared to be completed *after a few seconds* already; so that it was not even possible to persecute the initial increase of temperature until its maximum by means of the switch gear of the potentiometer.

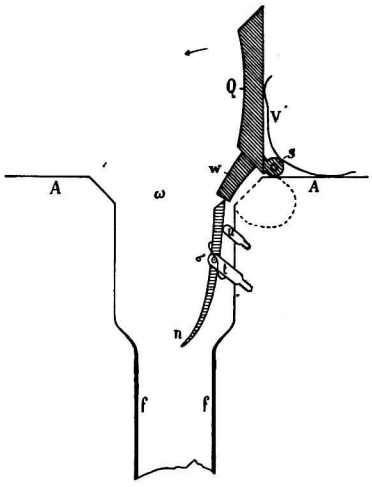

Fig. 5.

The heated object which falls into the openig ω of the metal-block is first caught by an extremely mobile trigger n, which enables the nickel lid Q, — which in its turn is driven, as indicated in Fig. 5, by the strong steel spring V', — to shut off the opening ω in a minimum of time. This mechanism, which works like a "mouse-trap", and the lid Q are clearly visible also in Fig. 4.

Finally it should be stated that the porcelain tube B, which also passes the water-cover D, is firmly fixed in the wooden lid C, by which the cylinder of the calorimeter is closed at the top. This tube B forms the passage for the heated object into the channel of the calorimeter.

§ **6.** For heating the substances to be tested, electrical resistance-

[1]) In the case of such substances as *water, porcelain*, etc. the complete heat-delivery lasts somewhat longer.

furnaces are applied with platinum-coils wound on their inside walls, of the type always used in this laboratory [1]).

In order to prevent as much as possible the heat-radiation from the furnace to the felt-jacket and outwards, the furnaces around and at their-bottom are provided with double-walled, detachable jackets and water-screens, in which a current of cold water is continually flowing (Fig. 6). The construction of these furnaces is indicated in Fig. 6. The furnace has

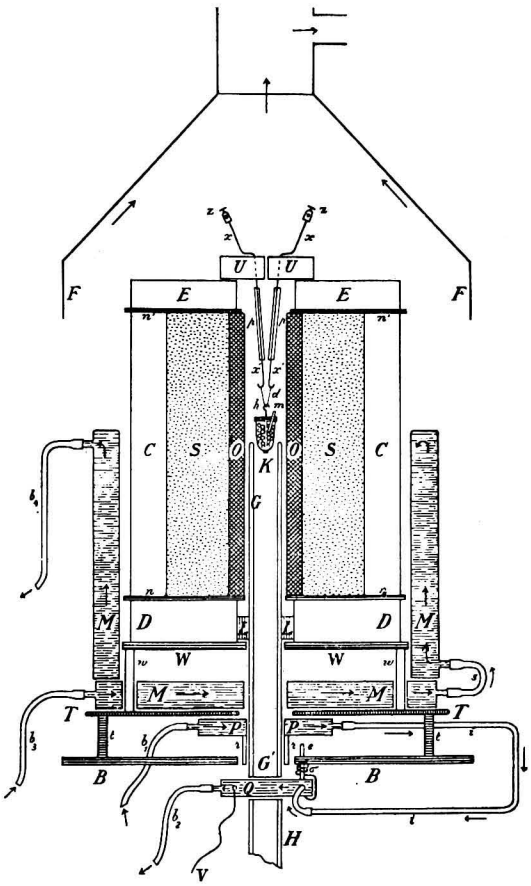

Fig. 6.

been placed on an iron frame W, which rests with three legs w on the iron table T, which in its turn stands with its legs t on the firm foundation-plate B. This last one can be moved on iron rollers over a couple of rails. The water-jackets, which are all interconnected, are indicated by M in Fig. 6. The furnace $U\,E\,C\,D$ which is composed of chamotte-parts and which is kept together by iron rings n and n' and by draw-bars (not indicated), has a core O of hard magnesite with a platinum coil of 1.3 mm. wire-diameter

[1]) F. M. JAEGER, *Anleitung*, etc., Groningen, (1913), p. 37).

wound on its interior wall; the filling s consists of burned magnesia. The MARQUARDT-tube GG' is, at the bottom, surrounded by the water-screen P, and is pressed against the tube by an elastic metal-tube r. A water-screen Q shuts off the tube at the bottom. This screen can be turned on a hinge e provided with a steel spiral string o; it can at the desired moment, — i.e. when the crucible is detached from its suspension-wire in the furnace, — be drawn aside by the pull-rope V, and then, within a very short fraction of a second, immediately be brought in its former position. H is the tube leading into the calorimeter. The cooling by P and Q is so effective, that the outgoing water in b_2 remains *perfectly cold*; and there is no appreciable radiation to the calorimeter possible, even when the furnace is brought at 1625° C. [1]). The chamotte-ring U consists of two parts, which enables the exact centring of the suspended system $xpx'K$ in the furnace at any temperature. The still remaining, but very feeble currents of hot air, rising along the furnace-walls, were rapidly made harmless by letting them out with the help of a big ventilation-flap. In order to prevent an undesired heating of the room by the JOULE's heat of the furnace-current, the furnace-rheostat was also completely surrounded with a jacket of wood, and the heated air in it was, in a similar manner, finally eliminated along a range of pipes. Besides, great care was taken to keep the temperature of the room as much as possible constant at 20° C. day and night, after the central heating of the building had been partly turned off. This was done by means of a gas-oven, which had been provided with a big thermoregulator. The resistance-furnace had been mounted on detachable iron rails over the calorimeter; and from its remote station under the ventilator-flap, it could at the desired moment and with one single grip, be rapidly and perfectly be brought over tube B in the right position and as rapidly be removed to its original position.

In the course of the measurements it appeared however, that the furnace need not be removed, because of the very perfect insulation of the furnace and of the calorimeter; so that it now remains in its place after the necessary precautions have been taken.

The objects were suspended by a thin platinum wire in a platinum vessel (description see below) in the furnace, within its space of constant temperature; this platinum wire was instantaneously melted through by a strong electric current at the moment the object was dropped into the calorimeter. According to the nature of the substances to be investigated, occasionnally it proved necessary to construct, within the platinum-vessel, a lining consisting of a smaller vessel of hard porcelain. With a view to this, both the specific heat of the hard porcelain and that of the platinum had to be determined accurately. When describing the measurements, we shall, when necessary, refer to this arrangement of the experiment.

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[1]) This may be controled by variation of the time of falling of the heated object; usually this time did not exceed 0.05 till 0.1 second.

To determine the water-equivalent of the calorimeter and to standardize the thermocouples, a double-walled copper air-bath was used, which had been well-isolated with asbestos and felt, and in which, by means of electric heating, water-vapour of a temperature given by the momentary atmospheric pressure, was produced. Only after about three quarters of an hour it appeared that the object in it had entirely adopted the temperature of the air-bath, which temperature was determined by means of a thermo-element, which either touches the platinum-vessel or is placed into its centre. Also this heating-apparatus worked most satisfactorily, if the necessary precautions be taken.

§ 7. *Water-equivalent of the calorimeter; way of determining this value and of the coolingconstant k of the instrument.*

After the normal temperature-course of the calorimeter has been determined, and after the heated object has been introduced into the calorimeter at the moment τ_0, the temperature will first rise rapidly; then it will fall again, after which, when all the heat has been given out, the normal cooling-course of the calorimeter is at last re-established. When a calorimeter is used containing a liquid, by means of which a very rapid delivery of the heat and an equal distribution of it is effected by permanent intensive stirring, the temperature X at the moment τ_0, which the calorimeter would have attained at an *infinitely rapid* heat-exchange between the hot object, and the instrument, can, in a well-known manner, be found by a simple graphic extra-polation of the cooling-curve in function of the time. In the metal-calorimeter, in which this stirring is *not* possible, a maximum temperature C will be attained after a short time, which is dependent on the heat-conductivity of the metal, on the place in the metal-block where the thermo-elements have been located, and on other factors. The curve which gives the temperature T as function of the time τ (Fig. 7) can be thought as existing of two parts: the "normal" part DE and the "abnor-

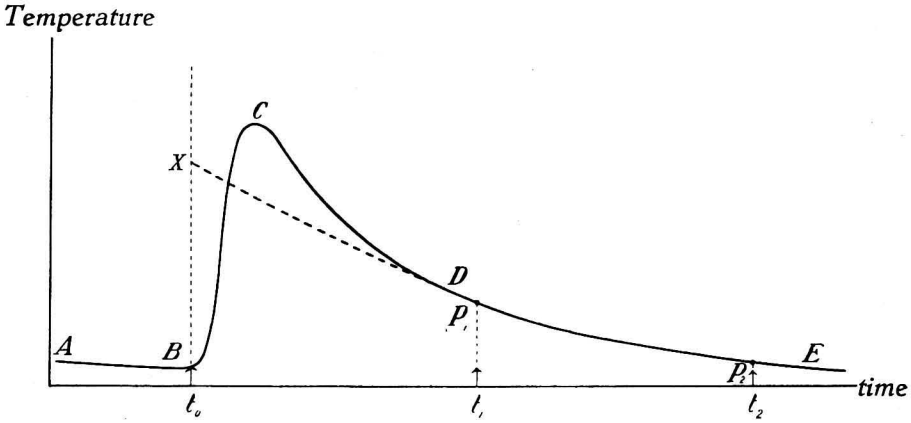

Fig. 7.

mal" part $B\,C\,D$. If the temperature-course of the calorimeter before the introduction of the heated object is represented by $A\,B$, the question is to substitute for this abnormal part the "normal" curve P_1X, which must be considered as the piece of the normal cooling-curve adjoining $D\,E$. In this case X represents the required value of the calorimeter-temperature at the moment τ_0, which would have prevailed in the calorimeter at an infinitely rapid exchange of the heat and at an infinitely rapid indication of the temperature by the thermocouples, as a mere consequence of the heat emitted by the heated object. As the thermo-elements have been fixed about half-way between ω and the outer-wall of the metal-block, the maximal temperature C is always higher here, than the true temperature X.

According to a method of MAGNUS, which is somewhat extended by us, this temperature X can be found by means of the following considerations.

If it be supposed, — which suppositions may be considered as very probable ones, — that :

1st. also during long intervals of time the mean value of the temperature of the water surrounding the calorimeter remains constant ;

2nd. the loss of heat of the calorimeter as a whole is dependent *solely* on the difference in temperature at any moment between the calorimeter and the surrounding water, this loss of heat being always directly proportional to that difference of temperature ;

than, if e is the electromotive force of the thermo-couples and τ the time, we have :

$$-\frac{\partial e}{\partial \tau} = k \,.\, e.$$

If at the time $\tau = 0$, the heated object is introduced into the calorimeter, it follows that :

$$-\int_0^{\tau} \frac{\partial e}{e} = k \,.\, \tau.$$

Therefore :

$$^{10}log\, e_0 - {}^{10}log\, e_\tau = 0{,}4343 \,.\, k \,.\, \tau,$$

e_0 being the electromotive force of the thermo-elements at the time $\tau = 0$.

From this follows :

$$^{10}log\, e_0 = {}^{10}log\, e_\tau + 0{,}4343 \,.\, k \,.\, \tau = {}^{10}log\, e_\tau + k' \,.\, \tau.$$

To find the "cooling-constant" $k' = 0.4343.\ k$ of the calorimeter, we have measured the electromotive forces e_{τ_1} and e_{τ_2} at the moments τ_1 and τ_2, after the cooling-course of the instrument had again become "normal", i.e. in Fig. 7 after the point D has been passed.

From :

$$-\int_{\tau_1}^{\tau_2} \frac{\partial e}{e} = \int_{\tau_1}^{\tau_2} k \,.\, d\tau$$

it follows :

$$k' = 0{,}4343\, k = \frac{{}^{10}log\, e_{\tau_1} - {}^{10}log\, e_{\tau_2}}{(\tau_2 - \tau_1)}.$$

In this way we found in five series of preliminary experiments, which were extended on intervals ranging from 16 to 20 hours, for k' the consecutive values : 0.0006746 ; 0.0006744 ; 0.0006742 ; 0.0006741 ; and 0.0006742 M.V. pro minute. Hence, it is seen that with this arrangement of the apparatus, even during very long intervals of time, k' may indeed be considered as being practically *constant,* having the mean value : 0.0006743 M.V. pro minute. Afterwards, when all necessary improvements of the apparatus were made, in order to eliminate all eventually occurring differences of temperature between the water in the cover and in the vessel J, the value of k' appeared to be somewhat greater, being about 0.000702 M.V. pro minute.

Moreover, the value of k' was redetermined in each measurement by measuring the electromotive forces e_{τ_1} and e_{τ_2} with an interval of 10 minutes since the moment at which the normal course of the calorimeter was re-established.

As an illustration of the way in which for instance the water-equivalent W of the calorimeter was determined, the following data may be mentioned here, which were determined before the final improved platinum-lining of the instrument was applied.

Into a small conical crucible of platinum, accurately fitting in the conical boring k of the calorimeter, a sufficient and exactly known quantity of pure water was introduced. The crucible was closed by means of a platinum cover, tightly soldered to it with silver ; a small platinum tube for filling the crucible, as well a small hooklet were fixed in this cover.

Weight of the platinum : 10.8192 grammes ; *weight of the silver :* 0.0562 grammes ; *weight of the tin :* 0.1408 grammes ; *weight of the water :* 5.9564 grammes.

The water-equivalent of the whole crucible was, therefore, equal to : $(10.8192 \times 0.032 + 0.0562 \times 0.055 + 0.1408 \times 0.044 + 5.9564) =$ $= 6.3125$ calories [1]) pro degree C. The crucible was suspended in the copper air-bath formely described, by means of a thin wire ; then it was heated by means of water-vapour and, after the temperature had become quite constant, it was suddenly detached by means of a special mechanism and caught in the calorimeter, the temperature being now observed after regular intervals of time.

Reduced barometer-indication : 762.66 mm. (0° C.) ; the boiling point of the water is, therefore, equal to : 100°.096 C. The temperature of the crucible read directly was : 100°.07 + 0°.03 (correction for the projecting mercury-thread) = 100°10 C.

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[1]) Here and in the following we have adopted as unit always the *mean gramme-calorie*; the reduction of this unit to the other usual units is, moreover, in each case easily made.

The temperature of the surrounding water was: 20°.067 C.

(In the following table the electromotive forces of the thermo-couples are indicated by e'; they must be multiplied by 2000, if these values be reduced to Microvolts).

Time:	Electromotive Forces observed: e' (to the right):	e' (to the left):	
P.M. $1^h\ 59^1/_2{}^m$	0.0498	—	Mean value 0.04975.
$2^h\ 0^m$	—	0.0496	
$2^h\ 0^1/_2{}^m$	0.0498	—	
$2^h\ 4^1/_2{}^m$	—	0.0496	
$2^h\ 5^m$	0.0499	—	
$2^h\ 5^1/_2{}^m$	—	0.0496	
$2^h\ 9^1/_2{}^m$	0.0499	—	
$2^h\ 10^m$	—	0.0496	
$2^h\ 10^1/_2{}^m$	0.0499	—	
$2^h\ 11^m$	← The crucible is introduced into the calorimeter		
$2^h\ 15^m$	—	0.2729	
$2^h\ 20^m$	0.3068 (max.)	—	
$2^h\ 25^m$	—	0.3046	
$2^h\ 30^m$	0.3010	—	
$2^h\ 35^m$	—	0.2976	
$2^h\ 39^1/_2{}^m$	0.2952	—	
$2^h\ 40^m$	—	0.2947	
$2^h\ 40^1/_2{}^m$	0.2946	—	
$2^h\ 44^1/_2{}^m$	—	0.2924	Mean value: 0.2923.
$2^h\ 45^m$	0.2923	—	
$2^h\ 45^1/_2{}^m$	—	0.2919	
(After 19 hours):			
A. M. $9^h\ 44^1/_2{}^m$	0.0465	—	Mean value: 0.0463.
$9^h\ 45^m$	—	0.0461	
$9^h\ 45^1/_2{}^m$	0.0465	—	

From the values of e': 0.2923 and 0.0463, the value of k', that of the temperature X at $2^h\ 11^m$, and finally the value W of the water-equivalent, are calculated in the following way:

Calculation of k'. The values of e' mentioned above correspond to the electromotive forces e_{τ_1} and e_{τ_2} of 584.6 M.V. and 92.6 M.V. respectively, $(\tau_2 - \tau_1)$ being here: 1140 minutes. From these data follows: $k' = 0.0007020$ M.V. per minute.

To find e_{τ_0} from $e_{\tau_1} = 584.6$ M.V., it must be remembered that between both moments 34 minutes have elapsed; to find the *increase* of temperature at the moment τ_0, it must be borne in mind, that the temperature of the calorimeter at $2^h\ 11^m$ was 99.5 M.V. above that of the surrounding water (20°.067 C.).

Therefore, we have: $\log e_{\tau_0} = \log 584.6 + 34 . k' = 2.76686 + 0.02387 = 2.79073$; thus $e_{\tau_0} = 617.3$ M.V., this value corresponding to: $617.3 \times 0°.000676$ C. $= 0°.4175$ C. The temperature of the calorimeter at τ_0 was, therefore, equal to: 20°.4845 C.; while the *increase* of the temperature of the instrument was: $(617.3 - 99.5) \times 0°.000676 = 517.8 \times \times 0°.000676 = 0°.3503$ C.

The platinum crucible, consequently, has suffered a decrease of temperature from 100°.096 C. till 20°.4845 C. corresponding to a delivery of heat of: 79.6115×6.3125 calories $= 502.547$ calories. As the *increase* of temperature of the instrument, caused by this heat-emission, was: 0°.3503 C., the water-equivalent W of the calorimeter is, therefore, calculated to be: 502.575 : 0.3503 calories, i.e.: 1435.1 calories.

In a series of experiments of this kind, made with the finally perfectionated instrument, values for the water-equivalent W were determined, which did not differ from each other more than 0.07 %. The improvements applied to the water-cover were made to completely fulfill the condition mentioned above sub 2nd, any oscillations of temperature, even very small ones, now being thoroughly eliminated. After the aluminium-cone k and the new platinum-lining were also applied in the channel of the calorimeter, the renewed measurements of W furnished, in seven series of experiments, consecutively the following data: 1417.2; 1417.9; 1418.7; 1417.0; 1417.9; 1417.8; and 1418.8 calories.

The mean value of these is:

$$W = 1417.9 \pm 0.9 \text{ calories.}$$

The deviations are not greater than ± 0.063 %; which is an accuracy more than sufficient. The number mentioned was, therefore, used by us in all later measurements.

The apparatus here described, which is in use now already for a long time, has given excellent results in all respects. In the next paper we will publish some of these results.

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