Erstens würde die jetzt durch die Zahl 0.496 als äusserst gering gekennzeichnete Schiefe etwas grösser, $\frac{M-m}{P}$ also kleiner, herauskommen, wenn man mit den ungestörten Maxima, welche ja gewöhnlich den gestörten vorangehen, gerechnet hätte.

Zweitens muss ich auf die früher (*Astr. Nachr.* **176**.179) gegebene Beschreibung der Lichtkurve zurückkommen, und jetzt Herrn GRAFF beistimmen, der a.a.O. das Minimum als scharf, das Maximum als flach bezeichnete. Allerdings ist der Unterschied klein (s. *Figur 2*): das Minimum dauert nach meinen Beobachtungen 77^d, das Maximum 86^d; die Dauer wird durch die Epochen der mittleren Helligkeit $\frac{1}{2}(M+m)$ bestimmt.

Die Streuung in der Nähe von 40^d erreicht die Werte:

	m	M	
im aufsteigenden Aste :	$0^m.363$	$0^m.372$	$0^m.366$
im absteigenden Aste :	0 .316	0 .366	0 .341
Mittel:	0 .340	0 .369	

Die Streuung ist wieder grösser beim Maximum, und grösser im aufsteigenden Aste. Das Verhältnis der Streuungen 0.366 und 0.341 ist 1.07, das Verhältnis der durchschnittlichen Geschwindigkeiten des Lichtwechsels bei Auf- und Abstieg ist 1.01.

Utrecht, April 1935.

Chemistry. — *The Exact Measurement of the Specific Heats of Solid Substances at Higher Temperatures:* XVIII. *On the Use of Dewar Vacuum Vessels in the Metal block Calorimeter for the Control of the Cooling-rate.* By F. M. JAEGER, R. FONTEYNE and E. ROSENBOHM.

(Communicated at the meeting of April 27, 1935).

§ 1. The use of DEWAR vacuum vessels as an enclosure of the central metal block in high-precision calorimetric work presents many difficulties, as has already been emphasized by several investigators in this field. The principal inconveniences of the DEWAR vessel in this connection are caused by the complicated way in which it gives off its stored heat to the surrounding isothermal water-shield and by the extreme slowness of its establishing the necessary thermal equilibrium. Some investigators[1]),

[1]) W. A. ROTH, Zeits. f. Electrochem., 38, 94, 95, (1932); W. P. WHITE, private communication.

therefore, rejected its use in the calorimeter altogether, taking it for granted that the larger cooling-rate of the instrument then caused by the elimination of the protecting enclosure is, on the other hand, sufficiently compensated by the simultaneously obtained diminution of the time-interval in which the normal cooling-rate of the calorimeter is re-established. This may be true, if one has to deal with objects behaving normally and giving off their heat with a sufficiently great velocity, but it does no longer hold in cases, in which very *slowly* occurring transformations or *strong retardative* effects in the objects investigated are involved, of the kind which during the latter years were in ever increasing number discovered by us [1]) with several metals, such as *beryllium*, *zirconium*, *chromium*, *cerium*, etc. Here the presence of the DEWAR vessel is certainly preferable, because it allows an accurate regulation of the rate of cooling of the instrument and its systematic control at every moment. Moreover, a systematic study made in this laboratory [2]) concerning the apparent non-validity of NEWTON's cooling-law and of the variability of the cooling-modulus with the time elapsed convinced us that, in a calorimetrical equipment of such high perfection as the instruments now in use really represent, the apparent capriciousness of the cooling-phenomena can be accounted for and can be thoroughly held under severe control, if only the changes of k (or k') are continuously checked during sufficiently long intervals of time. Since we have recently continued our investigations of the particular behaviour of such DEWAR vessels in the calorimeter, having simultaneously applied some important and highly effective improvements to the special way in which they are used, we are now able here to communicate some of the most interesting results already obtained.

§ 2. We will illustrate the influence which slow transformations in the objects studied have upon the apparent values of k, as calculated from the formula:

$$k = \frac{\log e_1 - \log e_2}{\tau_2 - \tau_1}$$

by means of some examples taken from our recent experiences.

If a substance like *platinum*, — which shows a quite normal behaviour at all temperatures, because no inner transformation manifests itself in it, — after being heated at a temperature t (here: 629° C.) is dropped into the calorimeter, the temperature-maximum of the metal block is usually reached after 3—5 minutes. However, a thermal equilibrium is then not yet established within the instrument: if the cooling-curve, after the maximum temperature is passed, is recorded over its whole extension, we

[1]) F. M. JAEGER and E. ROSENBOHM, Recueil d. Trav. d. Chim. d. Pays-Bas, **53**, 451, (1934); F. M. JAEGER and W. A. VEENSTRA, ibid., **53**, 91, (1934).

[2]) F. M. JAEGER, E. ROSENBOHM and J. BOTTEMA, Recueil d. Trav. d. Chim. d. Pays-Bas, **52**, 61, (1933); these Proceed., **35**, 347 (1932).

can at regular intervals of time calculate the factor k at each moment, as deduced from the formula mentioned, based upon the supposed validity of NEWTON's law. These apparent values of k then prove to be situated on a curve of the shape represented by 1 in figure 1, in which $60 \times k$ (for 1 hour) is plotted against the time elapsed in minutes. The apparent values of k are too great and they prove to *decrease* very rapidly and in the beginning very steeply, then ever more slowly; finally the curve,

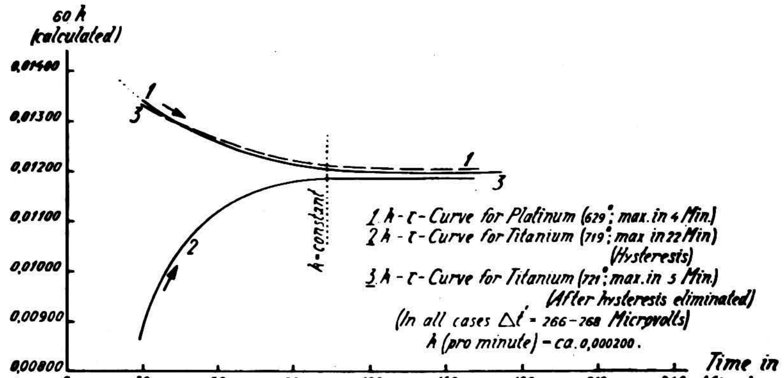

Fig. 1. The Change of the calculated Values of k with the Time elapsed in the Case of normally and of abnormally behaving Metals.

after a certain moment τ, practically becomes parallel to the axis of the abscissae. At this moment τ the thermal equilibrium within the instrument may be considered to be re-established.

If, however, instead of *platinum*, a substance like *titanium* is used ($t = 719°$ C.), in which a rather slow, but not even very strongly retarded transformation sets in some time after its introduction into the calorimeter (the time for reaching the maximum temperature is 22 minutes), the shape of the k-τ-curve thus calculated presents quite another aspect (curve 2 in Fig. 1), the apparent values of k now *increasing* with the time. Now, in a way to be described in a later publication, we can in this case beforehand eliminate the hysteresis mentioned (the maximum temperature then is reached in 5 minutes): now the shape of the k-τ-curve ($t = 721°$ C.) is changed into that represented by curve 3 in Fig. 1, which is completely analogous to that observed in the case of *platinum*. These examples are chosen in such a way, that the increase $\Delta t'$ of the final temperature of the calorimeter block was in all three cases practically the same: only 266—268 microvolts. The shape of curve 2 clearly proves that the values of k are far too small: this is a consequence of the fact that the gradual development of heat accompanying the inner change of the quenched metal is continuously retarded, but for a long time supplies a supplementary quantity of heat to the metal block, — a time which coïncides and forms a part of the time necessary for reaching the moment τ.

The value of k appears to be too small, owing to the fact that the flow of heat to the surrounding water-mantle is, during a certain time, counterbalanced by a continuous supply of heat from the interior.

The advantage of the use of the DEWAR vessel now is this, that by a rational regulation of the flow of heat to the exterior, — and thus by the regulation of the interval of time to elapse before τ is reached, — there is no danger to overlook the occasional occurrence of such retardation-effects within the metals studied: the increase of the time necessary for re-establishing the normal course of the calorimeter, on the other hand, forms no serious drawback, if only the values of k and their variation with the time elapsed are continuously and thoroughly controlled.

Experience, moreover, has convincingly taught us that it is always possible to state such occurring phenomena of hysteresis exactly by means of the abnormal shape of the calculated k-τ-curve plotted in the way described; a complementary control by other experimental devices has in all such cases corroborated our initial suspicion concerning the occurrence of such slow transformations within the heated metals studied. As a constant value of k is often only reached after several hours, it must be evident that a rigorous control of k during the whole course of an experiment is strictly necessary; and exactly this possibility is created by the regulating function of the DEWAR vessel with respect to the rate of flow of the heat to the instrument and from it to the surrounding isothermal water-jacket.

§ 3. In the first place we once more took up the general question about the best way in which the metal block should be placed within the DEWAR vessel used. As already previously observed, it makes a great difference as to the absolute value of the cooling-modulus, whether the contact of the metal block and the inner wall of the DEWAR vessel is made by means of a substance of higher or of lower thermal conductivity. When the space between the metal block and the vacuum vessel is e.g. filled with molten and then solidified paraffin, the value of k certainly gets smaller; but at the same time it evidently lasts much longer before the thermal equilibrium of the instrument is completely re-established, — as may be seen from the curves 1 (original time-temperature-curve of the calorimeter) and 2 (curve obtained after using the paraffin) in Fig. 2, in which the logarithm of the increase of temperature $\Delta t'$ (in Microvolts) is plotted against the time (in minutes). Once more the result obtained in this case clearly proves the necessity of establishing a highest possible conductive contact between the inner wall of the vessel and the outside of the metal block. For this purpose the inner wall of the DEWAR vessel was covered with a coherent and flawless layer of silver, deposited on it up to the height reached by the metal block. Then the space under the block was filled with copper-filings and similarly into that between the block and the inner glass wall a thin, very ductile sheet of brass was introduced, carefully bent in numerous folds and waves, as designed at L in Fig. 3; the metal block then was carefully and under feeble pressure introduced into the DEWAR vessel, so that a smooth and effective metallic contact was everywhere

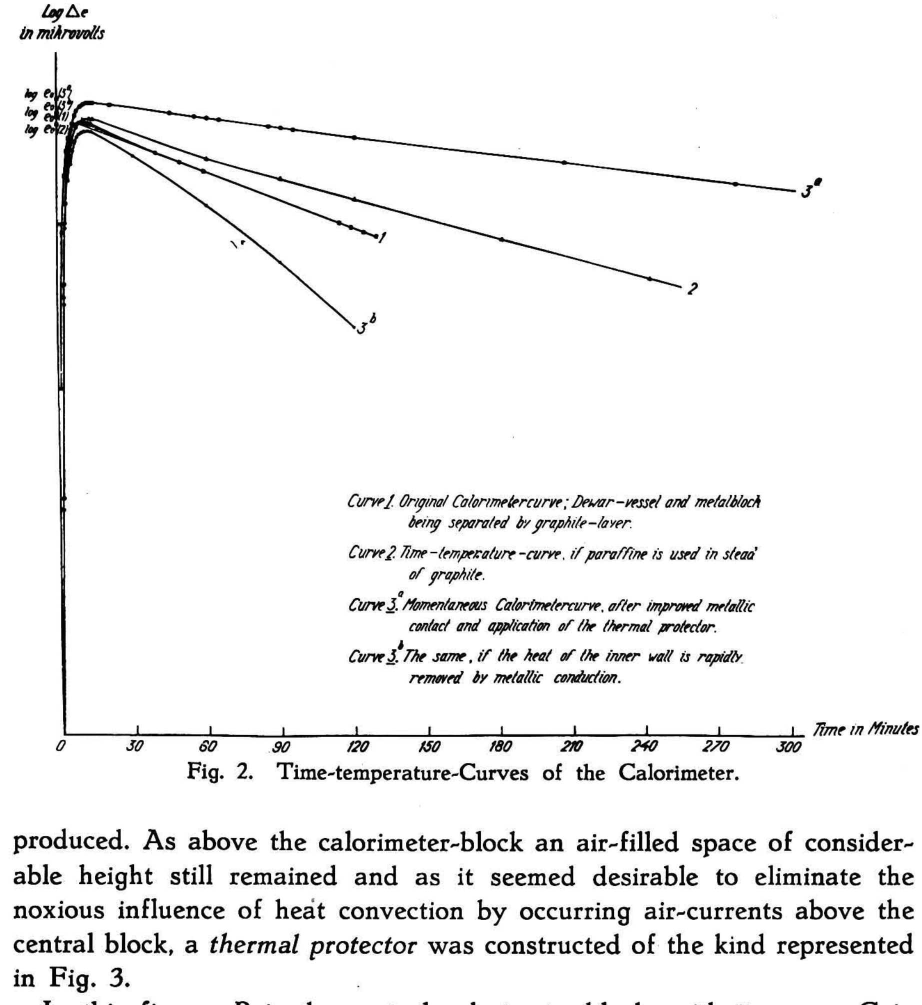

Fig. 2. Time-temperature-Curves of the Calorimeter.

produced. As above the calorimeter-block an air-filled space of considerable height still remained and as it seemed desirable to eliminate the noxious influence of heat convection by occurring air-currents above the central block, a *thermal protector* was constructed of the kind represented in Fig. 3.

In this figure, B is the central calorimeter-block, with its cover C in opened condition. Three supports of well-insulating *pertinax* P at the upper end of B bear a ring of pertinax p, in the centre of which a circular hole is spared, which is closed by the pertinax-cover a. This cover is centrally perforated in such a way as to allow the passage of the porcelain tube T, through which the heated sample is introduced from the furnace into the calorimeter, as was previously described in detail. The spaces between the inner wall of the vessel and the ring and between the latter and the cover a are tightly shut off by small layers of felt V; in this way the space above block B over a height of about 5 c.M. is completely shut off, so that no currents of hot air can mount and move upwards and thus no heat will be transported into the remaining layer of air above ap. This device proved to be very happily chosen and the application of this "thermal protector" had a remarkable influence upon the cooling-modulus of the instrument, — as may be seen from Fig. 2, in which the curve 3*a* clearly illustrates the favourable change of the cooling-conditions: the

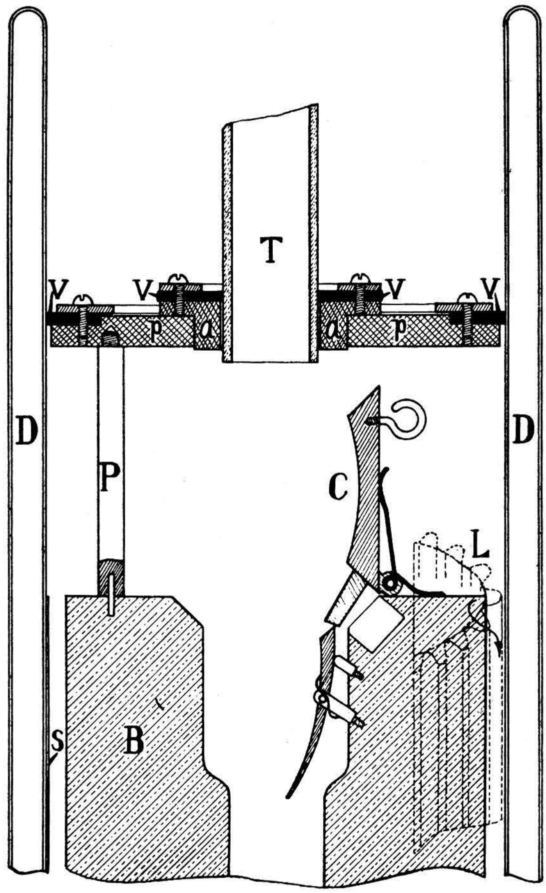

Fig. 3. Thermal Protector above the Calorimeter-block.

value of k now proves to be considerably diminished and the interval of time needed for the re-establishing of the normal course of the calorimeter appears to be appreciably shortened: moreover, the time-temperature curve has assumed an almost ideal shape, so that now correction is no longer necessary for the moment τ_0 of introduction of the object into the calorimeter. [1])

As a proof of the extent to which the values of k in this way have become more constant and reproducible, the dependency of k ($\times$ 90, because the measurements cover $1\frac{1}{2}$ hours) on the logarithm of the temperature-increase $\triangle t'$ of the calorimeter-block is represented in Fig. 4:

[1]) Tentatives made with the purpose of still more improving conditions *by intensively drying* the air above *B* gave *no* better results than before.

the straight line 1 relates to the calorimeter *before* the introduction of the heated sample (i. e. with the *open* cover C), curve 2 to the instrument *after* the sample was introduced; the dotted parallels show the extreme limits between which the values of $\triangle t'$ would vary if they did not exceed

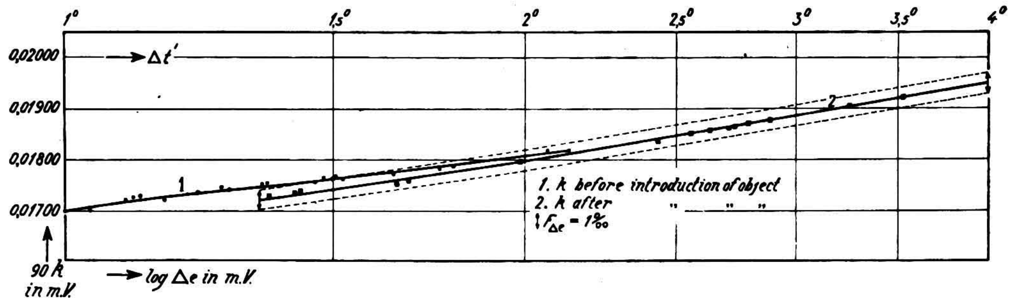

Fig. 4. Observed variations of k with the temperature t' of the Calorimeter-block.

+ 0,5 of — 0,5 pro mille. The observed values of k really proved to oscillate much less than this.

§ 4. A highly interesting result was, moreover, obtained in an experiment, made for the purpose of gaining some insight into the special way in which the stored heat is abducted by the DEWAR vessel. The inner glass wall of the latter above the thermal protector *ap* was covered with a thin and ductile sheet of copper, tightly pressed against the glass walls. Then this coppercylinder was, by means of a strip of soft copper sheet, brought in direct contact with the water of the surrounding thermostat. The most unexpected effect upon the character and the shape of the time-temperature-curve of the calorimeter-block is produced in this way, as is clearly demonstrated by curve 3^b in Fig. 2: not only the value of k is now suddenly and enormously *increased*, but — even after a long time — it does not reach a constant value, the curve evidently falling off at an ever increasing rate. This fact undoubtedly proves that the heat partially "creeps up" along the inner glass wall of the DEWAR vessel.

§ 5. By means of the combined experimental devices described in this paper, it is now fairly well possible to hold all conditions of the experiment completely under vigorous control. Even after a lapse of time extending over several hours the necessary extrapolation of the cooling-curve till the moment τ_0 of the introduction of the heated object into the calorimeter does no longer include any uncertainties and also the slow variation of k with the time elapsed now appears to be a perfectly controlable quantity.

As far as the fixation of the moment is concerned at which k becomes really *constant*, and its dependency on the final temperature t' of the metal block, — the general behaviour in this respect may be seen from Fig. 5. In this figure the decrease of *log* $\triangle t'$ is plotted against the time elapsed τ in minutes. In the various experiments the final temperature of the block was chosen at about 1°,5, 2°, 3°,5 and 4° C. respectively above

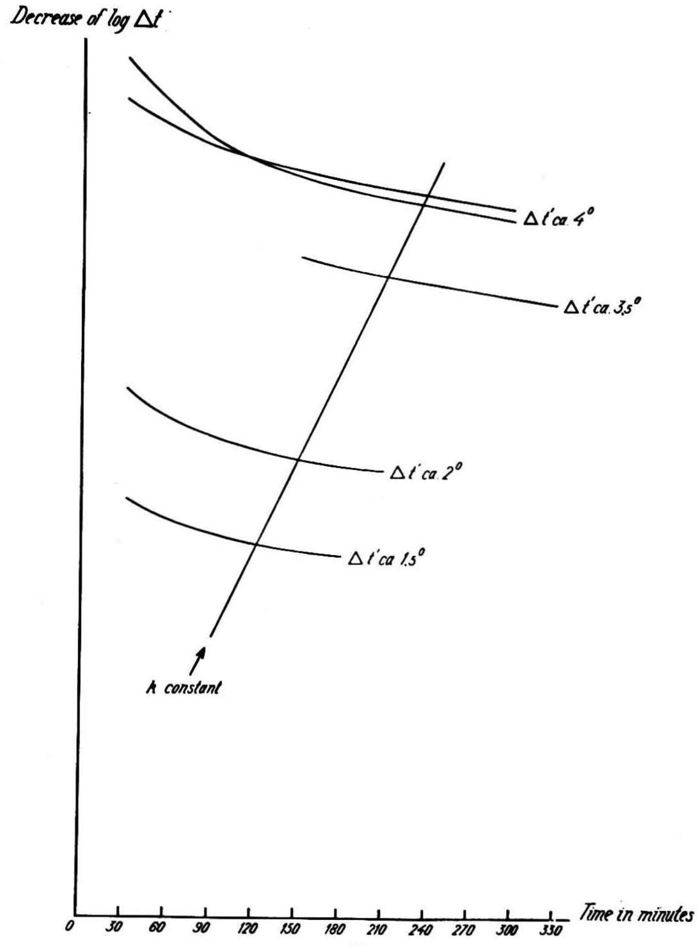

Fig. 5. The Shift of the Moment at which k becomes constant in function of the End-temperature t' of the Block.

that of the surrounding water-jacket. From these measurements it may be concluded, that the time necessary for attaining a constant value of k proves to increase regularly with an increase of the final calorimeter-temperature t'. Of course, in practice this temperature t' rarely rises above circa 3° C.

The results obtained in this series of experiments lead to the conclusion that it is not necessary to condemn the use of DEWAR vessels in high-precision calorimetry, if only the necessary precautions are taken and *a continuous control* of the variations of the cooling-modulus with the time is made during the whole duration of the experiment.

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