

**Chemistry.** — *The Exact Measurement of the Specific Heats of Solid Substances at High Temperatures. V. On the Cooling Correction of the Metal Calorimeter in Exact High Temperature Calorimetry.*  
By F. M. JAEGER, E. ROSENBOHM and J. A. BOTTEMA.

(Communicated at the meeting of April 2, 1932.)

§ 1. The use of the metal calorimeter for exact high temperature calorimetry, as developed in recent years, involves the application of a correction for the leakage, occurring during the time necessary for the establishment of complete thermal equilibrium within the instrument. If the electro-motive force of the thermoelements indicating the increase of temperature of the metallic block above that of its environment is  $e_{\tau_1}$  at the moment  $\tau_1$  and  $e_{\tau_2}$  at the moment  $\tau_2$ , the relation between those numbers, on assuming the validity of NEWTON'S law of cooling, has the form :

$$N \ln e_{\tau_1} - N \ln e_{\tau_2} = k \cdot (\tau_2 - \tau_1),$$

or, if ordinary logarithms are used :

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

The factor  $k$  in this equation is called the "leakage modulus"; the knowledge of its exact value is of vital importance for the calculation of the temperature  $X$ , to which the metallic block would have been heated at the moment  $\tau_0$  of introduction of the heated object into the calorimeter, if its total amount of heat were given-off with an infinitely great velocity.

The value of  $k$  is found to be :

$$k = \frac{2,3026 \cdot ({}^{10}\log e_{\tau_1} - {}^{10}\log e_{\tau_2})}{(\tau_2 - \tau_1)}.$$

If  $e_{\tau}$  is expressed in Mikrovolts and  $\tau$  in minutes,  $k$  is expressed in Mikrovolts pro minute.

As for the extrapolation of  $e_{\tau}$  to the moment  $\tau_0$ , — the cooling correction to be applied is:  $0,4343 \cdot k \cdot (\tau_2 - \tau_0)$ , — it is desirable to make this correction as small as possible; moreover, the extrapolation mentioned is the less uncertain, the more the interval of time  $(\tau_2 - \tau_0)$ , necessary for the establishment of complete heat-equilibrium within the instrument, is reduced.

From this it appears advantageous to diminish the value of  $k$  as much as possible by constructive means. However, by reducing  $k$  to an extraordinary small value, the minimum interval of time necessary for the establishment of thermal equilibrium may, on the other hand, be too much increased; so that one loses in accuracy on one side, what is gained on

the other. As the metal calorimeter does not allow an acceleration of the establishment of its heat-equilibrium by stirring, — as is the case in using a calorimeter-liquid, — a compromise must be found in such a way, that the product:  $k \cdot (\tau_2 - \tau_0)$  finally obtains the most desirable order of magnitude.

For this reason we have made a systematical study of the size and behaviour of the leakage-modulus  $k$  in its dependence on the special circumstances and on the particular construction of the apparatus.

§ 2. In the original calorimeter, used in our first measurements, the metallic block was suspended in a large DEWAR-flask, which, in its turn, was placed within a somewhat wider metallic cylinder in such a way, that a layer of air of about 1 cm. thickness remained between the outer wall of the DEWAR-vessel and the metallic cylinder, the latter being in direct contact with the water of the surrounding thermostat. The metallic block itself was on the exterior covered by a thin sheet of felt, so as to separate the inner wall of the DEWAR-vessel from the block and to protect the glass vessel from breaking. In this instrument the factor  $k' = 0,4343 \cdot k$  had a value of about: 0.0008. After removing the felt and replacing it by a metallic contact with the inner glass wall, consisting of piled-up strips of metal foil in the form of a flat, elastic layer, the curious fact was observed, that the new value of  $k'$  ( $= 0.0005$ ) proved much to be *diminished*<sup>1)</sup>. This remarkable fact, — which is rather contrary to the behaviour which could be expected, — was, independent of us, also observed by MAGNUS and HOLTZMANN<sup>2)</sup>, who lowered the value of  $k'$  in this way from 0.0013 to 0.00065.

From this follows, that it is evidently possible arbitrarily to vary the leakage-modulus by the special construction of the apparatus. Momentaneously the contact between the inner glass wall and the metallic block is, in our much improved, recent construction of the calorimeter, obtained by filling up the space between the block and the inner glass wall with grained graphite. In the case of this new instrument the value of  $k'$  was reduced in this way to about a third part of its original value and lowered from 0.00061 to the extraordinarily small value of 0.00023. However, a closer examination taught us, that this value *did not remain constant*, but that the leakage-modulus regularly and slowly decreased with an increasing lapse of time, as may be seen from the following data: (see next page).

In this case a difference of temperature of 1° C. was equivalent to 2430 M.V., while the temperature of the surrounding water-jacket was kept constant at 19°,9865 C. From this it becomes evident that the leakage-modulus  $k$  of the instrument in this form is *not* a really constant, but a *variable* value, slowly decreasing with the increasing lapse of time. It must,

<sup>1)</sup> Conf.: F. M. JAEGER and E. ROSENBOHM, these Proceed., 33, (1930), 458.

<sup>2)</sup> A. MAGNUS and H. HOLTZMANN, Ann. d. Physik, (5), 3, (1929), 591.

Difference of Temperature between the Calorimeter and the Water of the Thermostat (each time after 1 hour more):	Value of $k'$ $= 0,4343 \cdot k$	Difference of Temperature between the Calorimeter and the Water of the Thermostat (each time after 1 hour more):	Value of $k'$ $= 0,4343 \cdot k$
5354 M.V.	0.000238	9181 M.V.	
5180	0.000236	8844	0.000270
5014	0.000233		
4855	0.000233	8523	0.000268
4701	0.000232		
4408	0.000233	8216	0.000265
4268	0.000230		
4134	0.000228	7925	0.000261
3883	0.000226		
3763	0.000225	7641	0.000263
3648	0.000213		
2563	0.000206	7374	0.000258
2491		6868	0.000258

however, be remarked, that, on calculating the cooling correction, the influence of this variability of  $k$  is almost imperceptible: for  $k'$  is itself only a very small number and the time necessary for an experiment does never surpass  $1\frac{1}{2}$  or 2 hours. Moreover, on observing the change of  $k'$  in its dependence on the time elapsed, the real change of  $k'$  can, at each moment, truly be taken into account. It then appears that the final correction to be applied, never influences the final value of  $\bar{c}_p$  obtained, by more than about 0.1 %. So, for instance, we successively found the following values for the mean specific heats of *silver* (133.339 Gr.), on cooling from  $397^{\circ}.2$  C. to  $22^{\circ}.1$  C., when the calculations were made after 2, 3, 4 and 5 hours since the introduction of the object into the calorimeter:

after 2—3 hours: heat developed: 3657.7 cal.;  $\bar{c}_p = 0.05870$ .

after 2—4 hours: heat developed: 3656.2 cal.;  $\bar{c}_p = 0.05868$ .

after 2—5 hours: heat developed: 3655.5 cal.;  $\bar{c}_p = 0.05866$ .

From this example it becomes clear, that a prolongation of the experiments even to 5 hours, makes no more difference in the final result, than 0.07 % of the whole value. But the necessary extrapolation for determining the temperature of the metallic block at the moment  $\tau_0$ , is no longer allowed in this way, as soon as the interval of time ( $\tau_2 - \tau_0$ ) becomes

rather considerable, or if the cooling object in the calorimeter undergoes a change of its condition, which is accompanied by a thermal effect protracted during a somewhat long interval of time, as was, for instance, observed in the case of *beryllium* heated at temperatures surpassing 500° C.

§ 3. The fact that  $k$  is not constant, at first view makes the impression as if NEWTON's law were no longer valid. However, there is no reason to doubt the soundness of the fundamental principle expressed by it: it is much more probable, that there are secondary causes present, influencing the way of cooling of the instrument in such a way, that only in appearance the law mentioned seems no longer to be obeyed. Immediately the suspicion arose, that the DEWAR-vessel might be the principal cause of these phenomena and experience has fully confirmed this supposition.

For this reason the inner metallic cylinder surrounding the vacuum-flask and separating it from the waterbath by a thin layer of air, was now perforated, so that the water was brought into immediate contact with the outer wall of the DEWAR-vessel.

If the DEWAR-vessel was completely removed and the metallic block thus immediately placed in the water, the modulus  $k$  was trebly increased; but at the same time it now proved to remain *practically constant*. After the DEWAR-vessel was once more replaced, but this time brought into immediate contact with the water, the whole problem at once proved to be solved: *for not only the value of  $k$  was now reduced to a suitable magnitude, but, moreover, it proved to become practically constant after a sufficiently short interval of time, as may be seen from the following data:*

Interval of time (in Minutes) after the introduction of the object into the calori- meter :	Value of $k'$ ( $= 0.4343 \cdot k$ ) in M.V. pro Min.:
30— 40	0.001289
35— 45	0.001254
40— 50	0.001220
50— 60	0.001224
60— 70	0.001234
70— 80	0.001218
70— 130	0.001220
130—190	0.001223

It is clear, that after 40 or 50 minutes after the dropping of the heated body into the calorimeter had occurred,  $k'$  had become practically constant, having a magnitude, which is quite suitable to the purpose. Therefore, it

appears to be quite unnecessary, completely to reject the use of the DEWAR-vessel, as occasionally has been proposed by some authors<sup>1)</sup>: its presence offers so many advantages, especially by allowing the regulation of the feasible value of  $k$  and the maintenance of the constant temperature in the apparatus, that the solution of the problem just mentioned, appears much more preferable.

The two conditions to be fulfilled in using the DEWAR-vessel within the calorimeter are, therefore, the following:

1. The space between the metallic block and the inner glass wall must be filled up with a well conducting material, such as grained graphite.
2. The outer wall of the DEWAR-vessel must be brought into immediate and persistent contact with the water in the thermostat-jacket.

§ 4. If these conditions are fulfilled, the correction:  $0,4343 \cdot k \cdot (\tau_2 - \tau_0)$  proves to be most favourably reduced; its magnitude is then sufficiently small and the thermal equilibrium of the instrument ordinarily reached in so small an interval of time as 40 minutes after the introduction of the heated object into the calorimeter.

It must, however, finally be remarked, that notwithstanding this, a very slight variation of  $k$  in the first 60 minutes constantly manifests itself. This variation always presents itself in an analogous way and, therefore, cannot be wholly accidental, but must in some way still be connected with the reflection of the heat-radiation at the outer wall of the vacuum-vessel. We hoped also to eliminate this slight variation by removing the layer of water immediately adjacent to the outer glass wall, by the application of a stirrer within the inner part of the waterbath. But experience has taught us, that this is *not* the case: the way in which the constancy of  $k$  is reached is not appreciably changed by the action of this new stirrer, as can be deduced from the following numbers:

Time in Minutes elapsed since the introduction of the heated object:	Values of $k'$ on stirring:
45— 55	0.001189
50— 60	0.001184
55— 65	0.001180
60— 70	0.001188
60—120	0.001182

By means of two calorimeters built according to these principles, but still differing in other details of secondary importance, comparative studies now are in progress in this laboratory with the purpose of checking the results.

<sup>1)</sup> Conf. e.g. W. A. ROTH, Zeits. f. Elektrochem., **35**, (1929), 298.

obtained with the same materials under different conditions and by independent observers. The experience hitherto gathered, has already proved the perfect reproducibility of the values obtained under similar conditions and the soundness of the method employed, yielding an exactness of the respective data of 0.1 or 0.2 %.

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

**Chemistry.** — *The Exact Measurement of the Specific Heats of Solid Substances between 0° and 1625° C. VI. On the Law of NEUMANN-JOULE-KOPP-REGNAULT concerning the Molecular Heat of Chemical Compounds in Function of the Atomic Heats.* By F. M. JAEGER and J. A. BOTTEMA.

(Communicated at the meeting of April 2, 1932.)

§ 1. By a series of experimental investigations of NEUMANN<sup>1)</sup> (1831), REGNAULT<sup>2)</sup> (1840), JOULE<sup>3)</sup> (1844), KOPP<sup>4)</sup> (1864), PAPE<sup>5)</sup> (1864) and others, it seemed finally to be proved, that the molecular heat-capacity of a chemical compound can be calculated from the atomic heats of its composing atoms in a simple "additive" way. This law is commonly expressed by saying, that the atoms preserve their individual, normal specific and atomic heats also in their combinations with each other. MEYER<sup>6)</sup> first proved that the law is only an approximate one, calculation and experiment agreeing the better, the more the molecular volume approaches the sum of the atomic volumes, a conclusion contested by VAN AUBEL<sup>7)</sup>. In recent times occasionally doubt has arisen about the validity of the law. By comparison of the specific heats of the pure elements with those of their compounds, SCHIMPF<sup>8)</sup> and SCHÜBEL<sup>9)</sup> tried to demonstrate, that deviations are present in the case of intermetallic compounds. SCHÜBEL, for instance, accepts the rule as an approximate one; he finds positive, as well as negative deviations, in most cases of no more than about 2 %, occasionally of 6 %, and independent of the temperature.

Recently TAMMANN and ROHMANN<sup>10)</sup> have again taken up the subject; they find, by comparison of the data in literature of the quantities of heat

1) F. E. NEUMANN, Pogg. Ann. d. Phys., **23**, (1831), 32.

2) H. V. REGNAULT, Ann. de Chim. et Phys., (2), **73**, (1840), 5; (3), **1**, (1841), 129; (3), **9**, (1843), 322; Pogg. Ann. d. Phys., **51**, (1840), 44, 213; **53**, (1841), 60, 243; **62**, (1844), 50.

3) J. P. JOULE, Phil. Mag., (3), **25**, (1844), 334.

4) H. KOPP, Lieb. Ann. d. Chem., Suppl. **3**, (1864), 1; (1865), 290, 301.

5) C. PAPE, Pogg. Ann. d. Phys., **120**, (1863), 337, 579; **122**, (1864), 408; **123**, (1864), 277.

6) S. MEYER, Wien. Sitzb. **109**, (1901), 405; Drude's Ann. d. Phys., **2**, (1900), 135.

7) E. VAN AUBEL, Journ. de Phys., (3), **10**, (1901), 36.

8) H. SCHIMPF, Zeits. f. phys. Chem., **71**, (1910), 257.

9) P. SCHÜBEL, Zeits. f. anorg. Chem., **87**, (1914), 81, 101, 109.

10) G. TAMMANN und A. ROHMANN, *ibid*, **190**, (1930), 227.