AIP | The Journal of Chemical Physics

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Citation: The Journal of Chemical Physics **15**, 560 (1947); doi: 10.1063/1.1746593
View online: http://dx.doi.org/10.1063/1.1746593
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/15/8?ver=pdfcov
Published by the AIP Publishing

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 15, NUMBER 8 AUGUST, 1947

On a Method of Correcting for Incomplete Thermal Isolation in Measurements of Small Heat Capacities

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(Received April 7, 1947)

The treatment originally given by Keesom and Kok is simplified in such a manner as to make it applicable to heat-capacity measurements in which the temperature of the system is known only before and after heating.

IN the usual determination of heat capacities in an isothermal calorimeter, the temperature drift of the calorimeter is established in the periods before and after heating and the drifts extrapolated linearly to the mid-time of the heating period. However, at temperatures below 20°K, where the heat capacity of the shield and calorimeter with contents drop to a very small value, this procedure is not generally applicable. Keesom and Kok[2a, b] have treated this problem and derived expressions for the corrected or true mid-time of the heat capacity, i.e., the time to which the fore and after drifts should be extrapolated.

The method and conclusions of Keesom and Kok can be summarized as follows:

ASSUMPTIONS MADE

(1) heat capacity of block (shield) and calorimeter constant during the period considered;
(2) the temperature (T) of block and calorimeter are uniform;
(3) heat exchange is proportional to temperature difference (i.e., Newton's Law is applicable);
(4) the heat production during the heating period is constant;
(5) the temperature of the surrounding bath is some regular function of time.

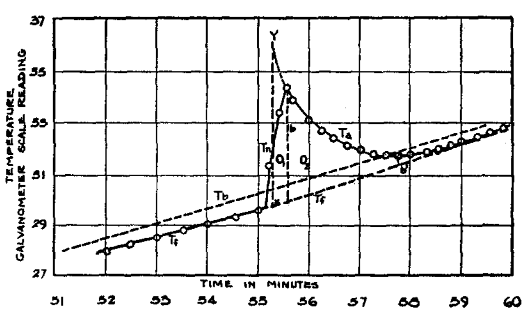

FIG. 1. Time-temperature curve.

MEANING OF SYMBOLS

T_h = real temperature during heating period;
T_f = temperature of block (shield);
T_a = real temperature in the after period;
k = heat exchange between calorimeter and shield in cal. per degree temperature difference per second;
l = heat production during heating period in cal. per second;
c = true heat capacity of system studied;
t = time (variable);
t_1 = end of heating period.

Figure 1 reproduces one of the figures given by Keesom and Kok and shows the time temperature curve during one of their measurements.

From these definitions and Fig. 1, the following equations are deduced by Keesom and Kok:

$$T_h - T_f = \frac{l}{k}\left[1 - \exp\left(-\frac{k}{c}t\right)\right], \tag{1}$$

$$T_a - T_f = b \exp\left[-\frac{k}{c}(t-t_1)\right], \tag{2}$$

$$b = \frac{l}{k}\left[1 - \exp\left(-\frac{k}{c}t_1\right)\right], \tag{3}$$

$$kO_1 = k\int_0^{t_1}(T_h - T_f)dt = lt_1 - bc, \tag{4}$$

$$kO_2 = k\int_{t_1}^{\infty}(T_a - T_f)dt = bc, \tag{5}$$

$$kO = k(O_1 + O_2) = lt_1. \tag{6}$$

If the heat exchange is (relatively) small, the curves in Fig. 1 can be extrapolated by means of

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[1] Phillips Petroleum Fellow, 1945–47.
[2a] Keesom and Kok, Comm. Phys. Lab., University of Leyden, No. 219c (1932).
[2b] Keesom and Kok, Proc. Acad. Amsterdam **35**, 294 (1932).

their tangents at $t=t_1$ to a time t^* which corresponds to half the time of heating in the usual correction (when the fore and after drifts are constant), and then

$$t^*=t_1-O_1/b. \tag{7}$$

The use of these equations as given by Keesom and Kok depends on a knowledge of the temperature of the calorimeter at all times. However, in the cases frequently encountered, where the same electrical circuits are used for the temperature measurements on the resistance thermometer and for the current and potential measurements of the heat input, these data are not available. For such cases the following procedure was developed several years ago and used in this laboratory.

Starting with Eqs. (4) and (7), we obtain by simple transformations

$$t^*=\frac{t_1}{2}+\left[\frac{t_1}{2}-\left(\frac{O_1}{b}\right)\right] \tag{7'}$$

$$\frac{O_1}{b}=\frac{lt_1}{kb}-\frac{c}{k}, \tag{4'}$$

and substituting from (3)

$$\frac{O_1}{b}=\frac{t_1}{1-\exp[-(k/c)t_1]}-c/k$$

$$=-c/k\left[\frac{-(k/c)t_1}{1-\exp[-(k/c)t_1]}\right]-c/k. \tag{8}$$

Let

$$Z=-(k/c)t_1,$$

then

$$-\frac{-(k/c)t_1}{1-\exp[-(k/c)t_1]}=-\frac{Z}{1-\exp Z}$$

$$=+\frac{Z}{\exp Z-1}. \tag{9}$$

Upon expanding we get

$$\frac{Z}{\exp Z-1}=1-\frac{Z}{2}+\frac{1}{6}\frac{Z^2}{2!}-\frac{1}{30}\frac{Z^4}{4!}+\frac{1}{42}\frac{Z^6}{6!}-\frac{1}{30}\frac{Z^8}{8!}+\frac{5}{66}\frac{Z^{10}}{10!}, \tag{10}$$

where the numbers 2, 6, 30, 42, etc. are the Bernouilli numbers. This converges for $|Z|<2\pi$. Thus

$$\frac{-(k/c)t_1}{1-\exp[-(k/c)t_1]}=1+\left(\frac{k}{c}\right)\frac{t_1}{2}+\frac{1}{2!6}\left(\frac{k}{c}t_1\right)^2-\frac{1}{4!30}\left(\frac{k}{c}t_1\right)^4. \tag{11}$$

Therefore

$$\frac{O_1}{b}=\frac{t_1}{2}+\frac{1}{2!6}\left(\frac{k}{c}\right)t_1^2-\frac{1}{4!30}\left(\frac{k}{c}\right)t_1^4, \tag{12}$$

and combining with (7), we get

$$t^*=t_1-\frac{t_1}{2}-\frac{1}{2!6}\frac{k}{c}t_1^2+\frac{1}{4!30}\left(\frac{k}{c}\right)^3t_1^4. \tag{13}$$

Since $c\gg k$ and t_1 is usually 4 (or less), we neglect all terms after the third and get

$$t^*=(t_1/2)-(k/c)(t_1^2/12), \tag{14}$$

wherein t_1 is the actual time of heating, and t^* is the "true" or "corrected" mid-time of the heating period, as discussed above.

APPENDIX

An example.

Measurement made on Butene-1, in isothermal calorimeter C[3]

Foredrift: +0.0281°/min.,
Afterdrift: +0.0075°/min.,
Total time = 5 min.; Uncorrected temperature rise = 1.698°,
$(k/c)=0.055$ min.$^{-1}$, $t^*=5/2-(0.055)(25/12)=2.385$.

This produces a difference in ΔT of 0.0024°, or 0.14 percent in the uncorrected, net heat capacity of the system. This amounts to about 0.3 percent of the heat-capacity value calculated for the sample.

[3] Aston *et al.*, J. Am. Chem. Soc. **68**, 52 (1946).