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CALCULATION METHOD FOR A CONSTANT-ENVIRONMENT TEMPERATURE CALORIMETER

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ABSTRACT

A method of calculation has been given for the determination of solution and reaction heats in a constant-environment calorimeter.

Calculation of a correction term for the temperature change connected with the heat exchange of the vessel with the surroundings is the focus of this work.

An electrical calibration based on the instantaneous power allows one to neglect the calibration time.

The choice of the K/C coefficient is fundamental for a correct interpretation of the thermogram.

INTRODUCTION

The rapid growth of thermal analysis during the past 30 years has created a number of new techniques (TG, DTG, DTA, DSC) for solid-state investigations [1,2].

In spite of this, the calorimetric solution technique still holds considerable importance in a wide range of applications (chemical, biological reactions, etc.). It is also possible, by using solution and reaction calorimeters, to study solid-state reactions [3,4].

Some commercial calorimeters (Tronac, LKB) can be used for a number of purposes: reaction, solution, titration, flow, batch calorimeters.

The solution calorimeters are generally divided between adiabatic and constant-environment temperature calorimeters.

The difference between them lies in the heat loss shown by the latter.

The heat exchange with the surroundings follows Newton's cooling law

$$Q = K\int (T - T_e)\mathrm{d}t \tag{1}$$

where t denotes time, T the temperature of the outer surface of the calorimeter, T_e the temperature of its thermal environment and K a leakage constant.

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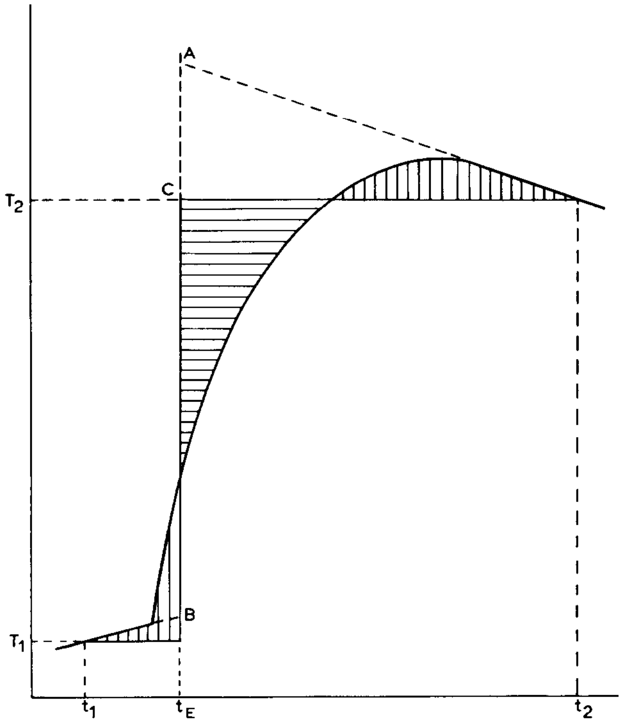

Fig. 1. Correction for the heat leaks and graphical extrapolation for a constant-environment temperature calorimeter by using the Dickinson method.

One of the most useful methods for evaluating the corrected temperature change for this type of calorimeter is the Dickinson method [5–8]. In this method the observed, ΔT_{obs}, temperature change can be corrected by means of the equation

$$(T_2 - T_1)_{\text{corr}} = (T_2 - T_1)_{\text{obs}} + K/C\int_{t_1}^{t_2}(T - T_s)\mathrm{d}t \tag{2}$$

where T_2 and T_1 are the temperatures at times t_2 and t_1 in the latter and former parts of the calorimetric experiment when the temperature is drifting towards the steady-state temperature, T_s. A time, t_E, between t_1 and t_2 is chosen (Fig. 1) so that

$$\int_{t_1}^{t_E}(T - T_1)\mathrm{d}t + \int_{t_E}^{t_2}(T - T_2)\mathrm{d}t = 0 \tag{3}$$

The correction term can also be written as

$$K/C\int_{t_1}^{t_2}(T - T_s)\mathrm{d}t = -(\mathrm{d}T/\mathrm{d}t)_{t_1}(t_E - t_1) + (\mathrm{d}T/\mathrm{d}t)_{t_2}(t_2 - t_E) \tag{4}$$

so that the values of the slope dT/dt at times t_1 and t_2 give the (values of the) correction term. If the former and latter parts of the curve can be replaced by straight lines (Fig. 1) the correction term may be written as $(T_2 - T_1) = T_A - T_B$.

The extrapolation is practically carried out using the time for 63% of the ΔT_{obs} [8]. Generally, this method is advantageous in that it allows one to avoid calculation of the integral. In the simpler form there is a graphical procedure which, on the other hand, should not be used for reaction times longer than 5 min.

For the latter, the equations [6,7] of the Regnault–Pfaundler method can be used

$$\Delta T_{corr} = \Delta T_{obs} - [g_i - K/C(T_m - T_i)]\Delta T$$

$$\Delta T_{corr} = \Delta T_{obs} - [g_f - K/C(T_m - T_f)]\Delta T \qquad (5)$$

where g_i and g_f are, respectively, the slopes at initial and final times, K the calorimetric constant, T_m the mean temperature, and T_i and T_f the initial and final temperatures respectively, and C the heat capacity. We think that the use of a microcomputer makes a fast calculation of the integral of the correction term in eqn. (2) possible.

It is the aim of this work to present a calculation method which is more flexible (and personal) and also useful for different calorimeters and reactions types.

METHOD AND CALCULATION

The calorimeter considered here is of the "isothermal-jacket" type. During an experiment with it, there will be some heat exchange between the calorimeter and its isothermal surroundings.

As previously seen [1] the heat exchange with the surroundings follows Newton's cooling law

$$Q = K\int(T - T_e)dt$$

where T is the outer surface of the reaction vessel, T_e is the temperature of the surrounding thermostatic bath (the jacket temperature) and K the calorimeter leakage constant.

Although the heat exchanged is a small proportion of the reaction heat, it must, however, be calculated. The heat exchanged is a function of heating by stirring, of resistance heating across the thermistor, and of heat leaks (heat losses by conduction, radiation, convection and evaporation). The first two heat sources can be eliminated, by substituting the temperature T_e with the constant temperature T_∞, to which the calorimeter vessel will approach after a very long time. During this last, the "jacket temperature" was to be

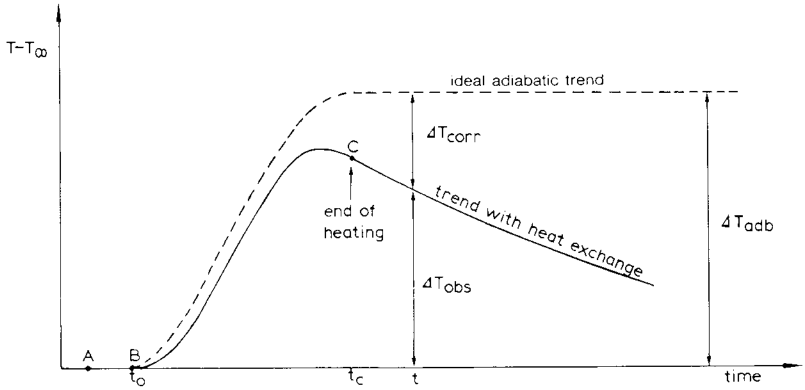

Fig. 2. Temperature–time curves for exothermal real and ideal adiabatic exothermal reactions.

constant and the stirrer and the current supply of the thermistor of the Wheatstone bridge were to be working.

When a chemical reaction or electrical calibration take place in the calorimeter vessel, the temperature of the vessel will be modified and will display a behaviour like that of Fig. 2 (full line) in which A–B is a linear behaviour due to the fact that the calorimetric system has reached thermal equilibrium. The reaction is initiated at B and is complete before point C. B–C is the reaction period. After the time t_c the temperature drifts towards T_∞ with an exponential trend. Let us consider what the temperature change ΔT_{adb} would have been if the calorimeter had behaved as an adiabatic one throughout the reaction (dashed line in Fig. 2).

By knowing ΔT_{adb} and the heat capacity of the adiabatic system it is possible to calculate the heat adsorbed or developed during the reaction by using the equation

$$Q = C\Delta T \tag{6}$$

In the real trend with heat exchange between the vessel and the surroundings, the adiabatic value will be given by the following reaction

$$\Delta T_{\mathrm{adb}} = \Delta T_{\mathrm{obs}} + \Delta T_{\mathrm{corr}} \tag{7}$$

where ΔT_{corr} is the correction term which holds in view of the fact that during the reaction the vessel temperature changes by virtue of the heat exchange with the surroundings. Both terms of the right-hand side of eqn. (7) are a function of time. From eqns. (1) and (6) the following can be obtained

$$\Delta T_{\mathrm{corr}} = K/C\int_{t_0}^{t}(T_t - T_\infty)\mathrm{d}t \tag{8}$$

where t_0 is the time at which the reaction is initiated, t any time after the end of the reaction, and T_t is the temperature trend inside the vessel as a function of the time. It is noteworthy that eqn. (8) is only useful if the heat

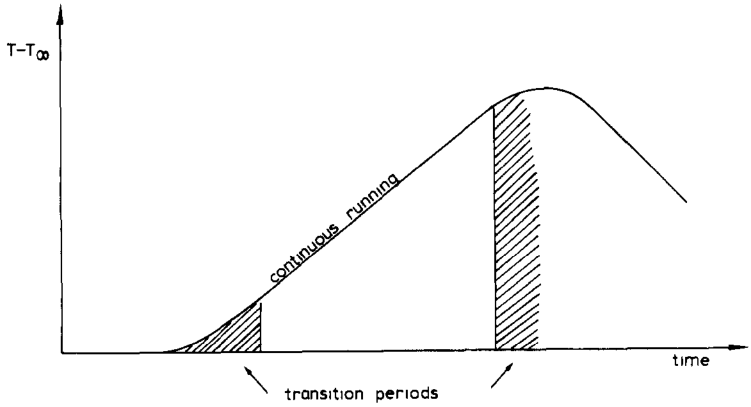

Fig. 3. Transition periods of the heat conduction by virtue of the resistance variation.

capacity displays a small change between the start and the end of the reaction. This only occurs if the system is in thermal equilibrium during the initial and final periods, and there is no heat effect of after-reaction.

The required values for a correct interpretation of the thermogram are those of the constants K and C and of the quantity $T_t - T_\infty$.

CALCULATION OF HEAT CAPACITY

The method usually used for determining the heat capacity is based on the supply of a known amount of energy during the time t across the heater resistance R. From the resulting temperature change, ΔT, and using eqn. (6) it is possible to calculate C. This method has two drawbacks:

(1) the energy supplied in time t cannot be constant because the resistance values are a function of time;

(2) one must wait for the transition periods of the heat conduction to be completed (Fig. 3) before measuring the temperature change, ΔT. This requires longer measuring times which, in turn, oblige one to calculate, by means of the integral, the heat dissipated.

If an infinitesimal range of time, dt, is considered, eqn. (6) becomes

$$dQ = C dT \quad (9)$$

For each (at continuous running) dt infinitesimal time, dQ is equal to the instantaneous power (P) supplied minus the amount, dQ, of heat dissipated at temperature T

$$dQ = P_{\text{calib}} dt - K(T - T_\infty) dt \quad (10)$$

Dividing eqns. (9) and (10) for dt and equalizing one obtains

$$C dT/dt = P_{\text{calib}} - K(T - T_\infty) \quad (11)$$

and again

$$C = \frac{P_{\text{calib}} - K(T - T_\infty)}{\mathrm{d}T/\mathrm{d}t} \tag{12}$$

For calculating C, a measure of the instantaneous power ($= VI$) through the calibration current, I, and the potential drop, V, of the resistance is sufficient. The change in temperature with respect to the equilibrium temperature, T_∞, and the slope of the thermogram are also required.

DETERMINATION OF THE COEFFICIENT K/C

Two ways can be considered which are conceptually equal but different from the computational point of view. In both cases the temperature of the vessel is different from T_∞ and drifts towards the equilibrium temperature. Such a situation occurs after electrical calibration and after completion of the reaction.

The first way of computing K/C may be realized bearing in mind that had the calorimeter been of the adiabatic type, the ΔT_{adb} temperature variation with respect to $T_0(t_0)$ would have been equal to zero (Fig. 4).

Thus, imposing this condition in eqn. (7) and writing ΔT_{corr} by means of eqn. (8), one can obtain

$$0 = \Delta T_{\text{obs}} + K/C\int_{t_0}^{t}(T_t - T_\infty)\mathrm{d}t \tag{13}$$

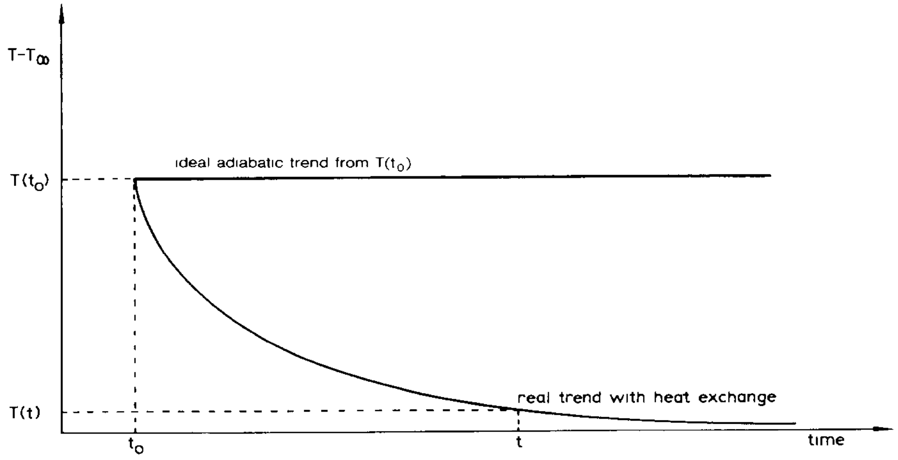

Fig. 4. Temperature–time curves for exothermal real and an ideal adiabatic exothermal reactions.

and again

$$K/C = -\frac{\Delta T_{\mathrm{obs}}}{\int_{t_0}^{t}(T_t - T_\infty)\mathrm{d}t} \tag{14}$$

Thus, this way requires an integral for the K/C determination. In the second way too, the condition $\Delta T_{\mathrm{corr}} = -\Delta T_{\mathrm{obs}}$ is imposed in eqn. (7) with ΔT_{corr} calculated between a generic time, t_0, and an infinite time, t_∞.

$$T_0 - T_\infty = -K/C\int_{t_\infty}^{t_0}(T - T_\infty)\mathrm{d}t \tag{15}$$

Equation (15) provides a differential linear equation which, solved with its initial condition $T_{(t_0)} = T_0$, gives the solution

$$T - T_\infty = (T_0 - T_\infty)\mathrm{e}^{-K/C(t-t_0)} \tag{16}$$

This last shows that the temperature approaches T_∞, as time tends to infinity, with an exponential behaviour dependent on K/C.

In practice, the second method allows a set of points taken during the cooling process to be interpolated with a least-squares analysis. The exponential coefficient will be K/C. From eqn. (16) the K/C term may be obtained

$$K/C = -\ln\frac{(T - T_\infty)/(T_0 - T_\infty)}{(t - t_0)} \tag{17}$$

In eqn. (17), interpolation may be avoided and only two points can be considered. These, however, must be very precise.

Further considerations can be made as regards eqn. (12) in which C is a function of K. This function could be taken away by putting eqns. (12) and (17) in a mathematical system.

We prefer to change this as a function of K/C because this ratio may be calculated independently of the C values.

It is then easily proved that eqn. (12) can be written in the form

$$C = \frac{P_{\mathrm{calib}}}{\mathrm{d}T/\mathrm{d}t + K/C(T - T_\infty)} \tag{18}$$

CONCLUSION

This method is useful for both a constant-environment temperature calorimeter and a quasi-adiabatic calorimeter. Therefore, in this case, the correction term $K/C\int_{t_\infty}^{t}(T - T_\infty)\mathrm{d}t$ approaches zero.

A further advantage of the method resides in the fact that it is possible to choose a posteriori the end-point of the reaction. Such a point is defined as that beyond which the ΔH values become nearly constant, because of the very small contribution of the correction term.

IMPORTANCE OF A PROPER CHOICE OF THE K/C VALUE

The value of the K/C coefficient is decisive for the correct calculation of the correction term.

It is also possible to calculate two values for the K/C coefficient: one for the calibration cooling curve and another for the reaction curve. These values are tightly connected with one another.

In order to obtain an effective term, the two K/C values must be very close. This occurs if the reaction is very fast, so that the stirring speed plays a fundamental role in this respect.

Figure 5 shows how in a "fast" reaction the K/C value is closer to that of the cooling calibration curve because the integral of the correction term lies mostly in the reaction curve.

For a "slow" reaction (Fig. 6) the K/C value will be closer to that of the cooling reaction curve. However, in this case it is very hard to read K/C on "pure" cooling. Indeed, for the farthest points, the mathematical errors provided by the correction term are larger than the corresponding heats. Furthermore, after a long time the thermal equilibrium conditions would be changed so that the relation $K/C \int_{t_\infty}^{t}(T-T_\infty)\mathrm{d}t = -\Delta T_{\mathrm{obs}}$ would not be effective. For these reasons in the slow curve, misleading values of K/C could be read. This is also true for the K/C values of the calibration cooling

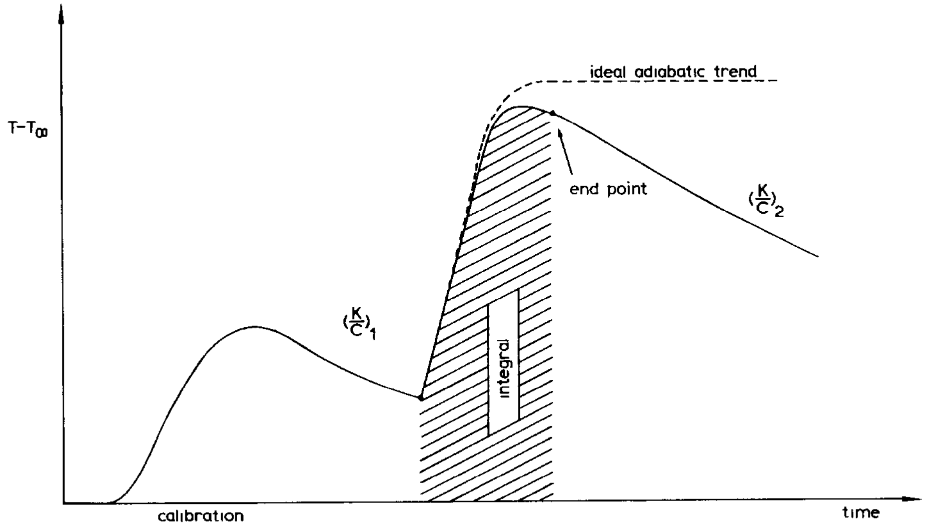

Fig. 5. Temperature–time curve for a fast exothermal reaction.

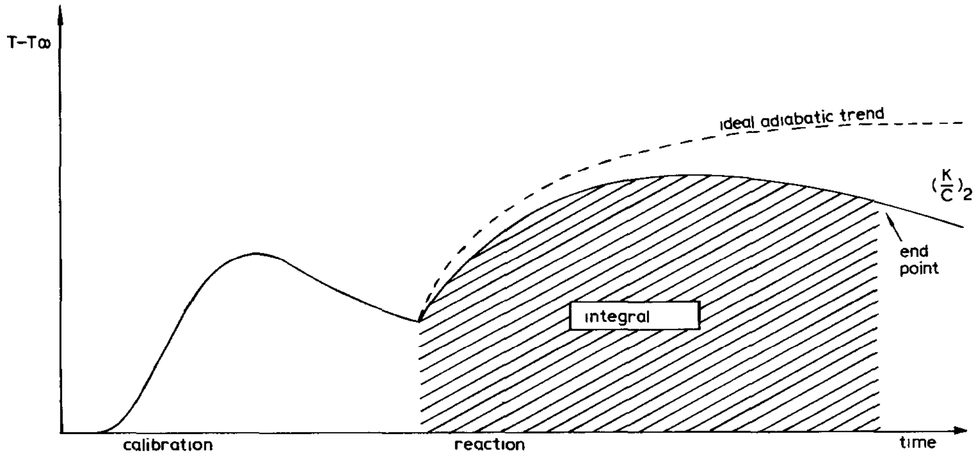

Fig. 6. Temperature–time curve for a slow exothermal reaction.e

curve if the system is not in perfect thermal equilibrium. We think that the two values of K/C must differ by no more than 4–5%. In this case the correlation between C and dT/dt (eqn. 18) hinders large errors.

The data output can be recorded on a strip-chart recorder and subsequently inserted into a program to be run on a microcomputer. This last can be directly interfaced to a voltmeter reading the V values in a programmed sequence. This set-up will be the subject of a further work.

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