ORDINARY AND HEAT FLOW CALORIMETERS: A UNIFIED VIEW

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SUMMARY

A new way of treating isoperibol (constant surroundings temperature) calorimeter data is proposed which applies equally well to ordinary and heat flow calorimetry with advantage in both cases. In the former, heat loss to the surroundings is compensated for; and in the latter account is taken of calorimeter temperature changes.

In the present treatment all relevant contributions are inserted into the enthalpy balance equation of the calorimeter. This results in a differential equation which may be integrated numerically along the path of the experiment; algorithms for data treatment are given. In this way a precise measure is obtained of the enthalpy change, or rate of change, as a function of time whether ordinary or heat flow calorimetry is envisaged. Using the same calorimeter the method was tested with three enthalpy sources: (i) a short (5 min) Joule heat pulse (ii) inversion of sucrose at two rates (first order constant: 2.26 h^{-1}; 0.398 h^{-1}) and (iii) a constant supply of Joule heating at several levels (including zero) over more than 13 h. The enthalpy, as calculated numerically, agrees well with experimental data in all cases.

In the periods before start and after stop of a thermochemical experiment the calculated enthalpy remains at a constant level, so that hundreds of readings may serve to determine the level difference with a corresponding increase in precision; and during the experiment enthalpy measurement may be used for kinetic studies in the case of slow reactions.

INTRODUCTION

To the thermochemist who endeavours to make precise measurements of the temperature jump in his isoperibol calorimeter, heat exchange with the surroundings is an error which must be kept at the lowest level possible, and which limits his realm to that of fast reactions. To his colleague who works with a heat flow calorimeter, on the contrary, heat exchange is the principal quantity of interest, and temperature changes are usually neglected as being transient phenomena. Traditionally, each has focussed on what he considers to be the main effect, treating the other term as an undesirable perturbation. In spite of Tian's work (refs. 1,2) few, and foremost among them Professor McGlashan, (refs. 3,4) have realized that Newton's law of cooling is used implicitly or explicitly in all calorimetry, and that large k calorimetry is perfectly feasible.

The present contribution shows how, based on the enthalpy balance of an isoperibol calorimeter of either type, one may derive from the thermogram of an experiment a function which is proportional to the enthalpy change, or rate of change, of the experiment.

ENTHALPY BALANCE EQUATION

Let the system be an open calorimeter, including the inner vessel and its contents, and let H designate its enthalpy. To get a concise description, substitute the independent variables $\{T,\ p,\ n_B\}$ for the usual set $\{S,\ p,\ n_B\}$ so as to obtain the following total differential

$$dH = C\ dT + V(1 - \alpha T)\ dp + \sum_B H_B\ dn_B \qquad (1)$$

which relates the system enthalpy change to changes in T, p and n_B. C is the system heat capacity at constant pressure (normally designated C_p); at constant pressure the second term vanishes; and the last accounts for changes in amounts of substance. If a chemical reaction r takes place in the calorimeter, shifting the extent by $d\xi$, then the amount of any reacting substance B changes by $dn_B = \nu_B d\xi$ while the amounts of other substances present remain constant. The sum term may then be written as $\Delta_r H\ d\xi$, and equation (1) simplifies to

$$dH = C\ dT + \Delta_r H\ d\xi \qquad (2)$$

At constant pressure dH is related to heat and work by

$$dH = \delta w' + \delta q \qquad (3)$$

where $\delta w'$ includes all work except pV work, and δq all heat transferred to the system. It may be noted in passing that in the ideal open calorimeter both terms are zero so that $dH = 0$: such a calorimeter is isenthalpic. In that case the temperature change closely matches the reaction enthalpy decrease.

In the general case, combination of equations (2) and (3) results in the enthalpy balance equation

$$\Delta_r H\ d\xi + C\ dT = \delta w' + \delta q \qquad (4)$$

where the terms on the RHS are to be specified according to apparatus and conditions.

DIFFERENTIAL EQUATION

The term $\delta w'$ includes two types of work: electric work, supplied in the calibration phase only, at a known power $P = U \cdot I$; and a small but steady contribution of mechanical work from the stirrer and possibly electric work from the temperature sensor. We shall neglect the latter for simplicity; it may be corrected for by a simple shift of the temperature baseline, as shown in ref. 5.

The term δq covers heat transfer by conduction and convection from the surroundings, of temperature T_e, to the calorimeter. Both T and T_e are supposed uniform in space, and the rate of heat transfer is assumed proportional to their difference $\theta = T - T_e$: $\delta q = -G\theta \ \delta t = -kC\theta \ \delta t$ where k is the familiar cooling rate constant. If furthermore T_e is rigorously constant in time, δT may be replaced by $\delta\theta$. Inserting the values of $\delta w'$ and δq over the time interval δt into (4) and rearranging we get

$$-\Delta_r H \delta \xi \ + \ P \delta t \ = \ C(\delta\theta \ + \ k\theta\delta t) \tag{5}$$

This differential equation which relates increments in time δt, temperature $\delta\theta$, and extent $\delta\xi$ may be modified to suit three purposes:

a) In an ordinary thermochemical experiment (where $P = 0$) integration from t_1 to t_n gives

$$-\Delta_r H(\xi_n \ - \ \xi_1) \ = \ C(\theta_n \ - \ \theta_1) \ + \ kC \int_{t_1}^{t_n} \theta dt \tag{6}$$

where $\xi_n = \xi(t_n)$ etc., provided $-\Delta_r H$ is independent of ξ. This expression differs from the customary equation by the integral which corrects for heat loss to the surroundings. Before reaction the LHS yields a constant value (zero) and after its completion it settles at another constant value; by equation (6) the same applies to the RHS. If the reaction is fast the result is a steplike function of time; if not, the RHS will give information on how the enthalpy changes with time.

b) In heat flow calorimetry (again with $P = 0$), division by δt gives

$$-\Delta_r H \ \dot{\xi} \ = \ C \ (\dot{\theta} \ + \ k\theta) \tag{7}$$

where a dot indicates differentiation with respect to time. In normal practice, heat flow calorimetry presupposes a steady state, i.e. $\dot{\theta} = 0$, but when equation (7) is used this constraint is no longer necessary.

c) In the calibration phase ($d\xi = 0$), integration of equation (5) gives

$$\int_{t_1}^{t_n} P dt \ = \ C(\theta_n \ - \ \theta_1) \ + \ kC \int_{t_1}^{t_n} \theta dt \tag{8}$$

This time both the LHS and $\theta(t)$ are known so that the constants k and C may be determined using the method of least squares.

By their common origin equations (6) and (7) carry the same information (apart from a constant) although they may be used for widely different purposes.

ALGORITHMS

The equations given above readily lend themselves to numerical treatment. Let a set of points $\{t_i, \theta_i\}$ be given, the thermogram of a calorimetric or calibration experiment, with $i = 1, 2, ... , n$ so closely spaced that θ may be considered a linear function of time in each interval. In the ith of the $n - 1$ intervals, let $\delta_i t = t_{i+1} - t_i$, $\delta_i \theta = \theta_{i+1} - \theta_i$, and let the average value $\langle \theta_i \rangle = (\theta_i + \theta_{i+1})/2$.

a) To find the enthalpy change from a thermogram, instead of integrating sum up enthalpy contributions from the time intervals $\delta_1 t, \delta_2 t, ... , \delta_{n-1} t$ according to equation (6). The resulting algorithm is

$$- \Delta_r H \cdot (\xi_n - \xi_1) = C \left\{ \theta_n - \theta_1 + k \sum_{i=1}^{n-1} \langle \theta_i \rangle (t_{i+1} - t_i) \right\} \qquad (9)$$

and applies equally well to ordinary and heat flow calorimetry.

b) To find the enthalpy rate of change from a thermogram, replace time derivatives in equation (7) by difference quotients

$$- \Delta_r H \frac{\delta_i \xi}{\delta_i t} = C \left\{ \frac{\delta_i \theta}{\delta_i t} + k \langle \theta_i \rangle \right\} = C \left\{ \frac{\theta_{i+1} - \theta_i}{t_{i+1} - t_i} + k \langle \theta_i \rangle \right\} \qquad (10)$$

This gives a new value of the enthalpy rate of change for each new measurement. Hence a high resolution in time is obtained, and the reaction rate is tracked closely although with a corresponding loss in precision arising from the difference quotients. The remedy to this is averaging or curve smoothing; or equation (6) may be used instead to find $\Delta_r H \cdot \xi(t)$, followed by differentiation.

c) To find the constants k and C from the thermogram of a calibration experiment, treat equation (8) in a similar way:

$$\sum_{i=1}^{n-1} \langle P_i \rangle (t_{i+1} - t_i) = C \left\{ \theta_n - \theta_1 + k \sum_{i=1}^{n-1} \langle \theta_i \rangle (t_{i+1} - t_i) \right\} \qquad (11)$$

where $\langle P_i \rangle$ is the average value of P in the i'th interval; if P is constant the LHS simplifies to $P(t_n - t_1)$.

CALIBRATION

The parameters k and C must be determined for every new thermochemical experiment since both depend on the filling though their product (the thermal conductance) does not. Here the integrated equation (11) between P and θ is to be preferred since it gives better precision than may be obtained from an equation between derivatives. Two procedures for evaluating k will be described below; when this has been done, C may be calculated.

In perhaps the simplest way to determine k the calorimeter is initially warmer or colder than the surroundings, and no electric power is supplied. A recording is taken of the temperature difference as it decays exponentially towards zero. With $P = 0$ the expression in brackets in equation (11) is identically zero, and since all values of θ and t are known one may plot θ_n versus the sum which is seen to give a straight line of slope $-k$ and intersection θ_1.

A more general, and probably more precise method may be derived from the following considerations. Let electric work, the power of which $P(t)$ is an arbitrary function of time, be transmitted to the calorimeter with $d\xi = 0$. Then, according to equation (5)

$$\delta\theta + k\theta\delta t = C^{-1} P(t)\delta t \tag{12}$$

The general solution to this differential equation is

$$\theta(t)\exp(kt) = \theta(0) + C^{-1} \int_0^t P(t')\exp(kt')dt' \tag{13}$$

which becomes particularly simple in periods of constant P. Thus P may be a positive or negative step function at $t = 0$, or it may change abruptly from one constant value to another a number of times. In any such interval the analytical solution takes the following form

$$\theta(t) = c_1 + c_2 \exp(-kt) \tag{14}$$

Here $c_1 = \theta(\infty)$, $c_2 = \theta(0) - \theta(\infty)$, and k is the cooling rate constant which is vital to subsequent calculations. Given a data set of the form $\{t_i, \theta_i\}$ it is possible to find values for c_1, c_2 and k that will optimize the fit of equation (14) to the observed data, using the method of least squares for the nonlinear case. (refs. 6,7) A small calculator capable of handling matrices (Hewlett–Packard 28 S) was used in these and all subsequent computations which involved typically 20–70 data points, but ready–made programs are available which may be used with personal computers and larger machines, e.g. NLIN by SAS. (ref. 8) This takes care of k.

When k is known, C may be found as follows. With the calorimeter initially at rest (apart from stirring), let calibration work w be supplied at a rate P where $P(t)$ is some function of time in the interval $t_a < t \leq t_b$ and zero outside. The course of events is adequately described by equation (11). Its LHS is zero up to t_a, then rises with time to a new value at t_b, and remains there for the rest of the calibration. The equation tells us that the expression in curly brackets on its RHS must behave in a similar way; its value may be computed for each t_i from the thermogram and k. From the ratio between the steplike increases C is determined. All measurements before t_a

may serve in determining the baseline. and all after t_b can be used in computing the value of the expression after the increase.

In practice both k and C may be determined in one experiment. With the calorimeter initially at rest. θ measurements are taken before, during, and after supply of calibration work. From the decay of θ in the last phase with $P = 0$ (a constant value) k is calculated, and then the RHS bracket expression is evaluated using all data from the thermogram.

EXPERIMENTAL

A primitive open calorimeter shown in Fig. 1 was used to test the method described above. Its surroundings, a cylinder with lid, both made of solid aluminium of thickness nowhere less than 6 mm, was kept at constant temperature to within a few mK by circulating thermostat water around it. The calorimeter proper, a cylindri–
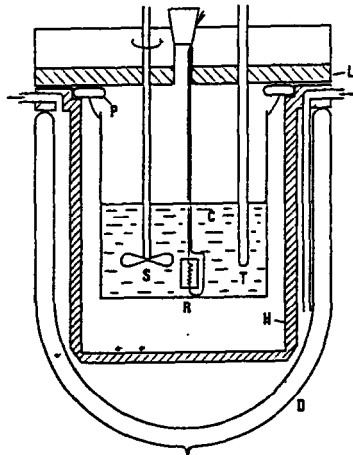

Fig. 1. Sketch of the measuring system. C calorimeter proper with fillng; S stirrer; R resistor encapsulated in ceramics; T temperature transducer. The calorimeter, made from 1 mm copper sheet, is suspended from a plastic ring P reposing on a recess in the aluminium housing H which is lodged in a Dewar vessel D. Thermostat water is circulated through the space between H and D. A lid L equally in aluminium is clamped to the housing and covered by 25 mm of thermal insulation.

cal beaker made from nickel–plated copper sheet 1 mm thick, was in all cases filled with 300 g of aqueus solution. The temperature sensor was a linear transducer (Analog Devices AC2626) with sensitivity 1 μA/K, dissipating about 3 mW and giving a precision of a few mK. The stirrer produced less heat than could be measured with the sensor. The electrical heater was a 103.6–Ω ceramic resistor with teflon coated leads; voltages across this resistor and a suitable series connected resistor were both monitored. The duration of power pulses was measured with a quartz clock trigged by the heat pulse. The diurnal variations of the calorimeter temperature were found to

be of the order of $\pm$ 0.04 K and the hourly changes about one tenth of this. Further details are given in ref. 5.

The contents of the calorimeter were in all cases 250.00 g doubly deionized water plus 50.00 g sucrose. For simplicity the starting condition was chosen to be one of thermal equilibrium as verified by recording the temperature for at least one hour. Reaction was started by adding 10 ml of 0.01 mol·kg^{-1} phosphate buffer, pH = 7.4, containing various small amounts of invertase and thermostatted to T_e for 1 h before use. Thermograms were recorded for periods up to 10 h.

RESULTS

The distinction between ordinary and heat flow calorimetry being essentially one of duration, the method was tested using a fast, an intermediate, and a slow enthalpy change: (i) a Joule heat pulse lasting for about 5 min: (ii) a first order chemical reaction extending over more than 1 h: and (iii) weak Joule heating at several rates (including zero) and lasting for over 10 h.

(i) Fast enthalpy increase. The calorimeter was filled with 250.00 g of water plus 50.00 g of sucrose and left for the temperature to settle at $\theta = 0$. A pulse of power 3.846 W was then applied for 322.1 s and recording continued for 6 h. The thermogram is shown in Fig. 2. A fit of the decaying part gave a k value of
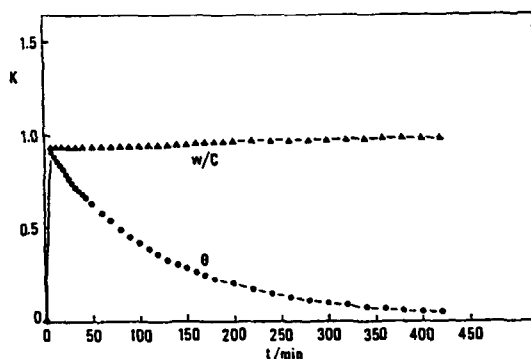

Fig. 2. a) Temperature of the calorimeter T relative to that of the surroundings T_e, $\theta = T - T_e$, as a function of time (lower curve, • − •); b) the function $\int P dt / C = w/C$ as calculated from equation (11) (upper curve, ▲ − ▲). With the calorimeter initially in thermal equilibrium, $\theta = 0$, Joule heating was applied for about 5 min and then stopped.

1.400·10^{-4} s^{-1}. Both the thermogram and the calculated values of the expression in curly brackets of equation (11) are shown in the figure, the latter presenting a sharp rise from 0 K to 0.9317 K, as found by averaging values from the first hour or more after the burst. Hence $C = 1328$ J·K^{-1}.

(ii) Chemical reaction. Next the method was applied to follow the inversion of sucrose which is known to be of order one, and which may conveniently be started and made to proceed at a desired rate by the addition of suitable amounts of
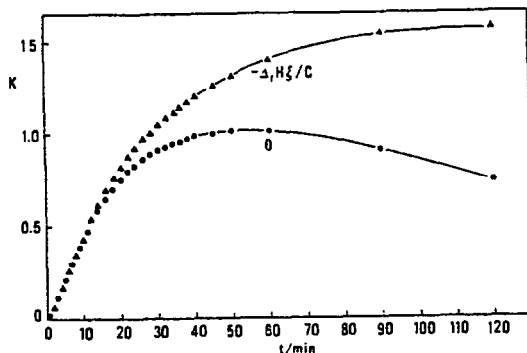
Fig. 3. Plots of $\theta(t)$ (lower curve, • – •) and of $-\Delta H_r \xi/C$ calculated from equation (9) (upper curve, ▲ – ▲) during a chemical reaction started at $t = 0$. θ is seen to decline long before the reaction is over.

invertase. The graphs of Fig. 3, prepared in the same way as those of Fig. 2, show that while the recorded temperature is seen to fall off towards zero, the calculated function $-\Delta_r H \xi/C$ closely ($\sigma = 13$ mK) follows an exponential approach to a final value of 1.579 K. From these figures $\Delta_r H = -14.35$ kJ·mol^{-1} for the inversion reaction, and its rate constant was found to be $k_1 = 6.27 \cdot 10^{-4}$ s^{-1}.

A slower version of the experiment (with less invertase) gave -14.25 kJ·mol^{-1} and $1.105 \cdot 10^{-4}$ s^{-1} respectively.

(iii) <u>Slow enthalpy change</u>. Again with 300 g of filling as above (except for the invertase) the calorimeter was brought to thermal equilibrium. Constant Joule power was then supplied at the rates: 1) $0 \le t < 220$ min: 200.9 mW;
2) $220 \le t < 350$ min: 162.6 mW; and 3) $350 \le t < 800$ min: 0 mW. Part of the resulting thermogram is seen in Fig. 4. k values were calculated from its first and third sections: $1.357 \cdot 10^{-4}$ s^{-1} (1); and $1.353 \cdot 10^{-4}$ s^{-1} (3). The w/C plot, not shown, was found to consist of three linear sections; instead, its time derivative P/C was
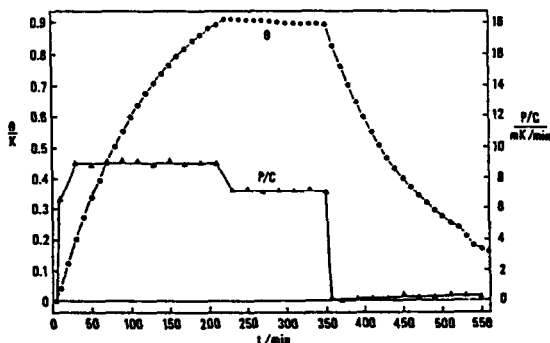

Fig. 4. Plots of $\theta(t)$ (upper curve, • – •) and of P/C (lower levels, ▲ – ▲) as calculated from equation (7). Constant power was applied at three levels: 200.9 mW; 162.6 mW; and 0 mW. Note the sharp transitions between these.

calculated from equation (11) differentiated with respect to time in the same way as (10) was obtained from (9), and leading to the same RHS. The resulting graph clearly reveals the presence of three power input levels: $P/C = 1.503 \cdot 10^{-4} \ \mathrm{K \cdot s^{-1}}$; $1.198 \cdot 10^{-4} \ \mathrm{K \cdot s^{-1}}$; and $0 \ \mathrm{K \cdot s^{-1}}$ respectively, a fact which is effectively camouflaged in the thermogram. Comparing these values to the power levels given above one obtains from the first two cases $C = 1336 \ \mathrm{J \cdot K}$ and $1356 \ \mathrm{J \cdot K}$ respectively.

CONCLUSION

The present method which consists in replacing

$$\theta(t) \qquad \text{by} \qquad \theta(t) + \int_0^t \theta(t')\mathrm{d}t'$$

thereby taking into account both the calorimeter temperature change and its heat exchange with the surroundings, applies to ordinary and heat flow calorimetry. Important advantages result from its use:

  − a correct picture is obtained of the enthalpy change, or rate of change, produced in the calorimeter,

  − values of initial and final temperature may be calculated from measurements over long periods in time before and after an experiment, with considerable increase in precision, see Fig. 2. Without the present method, one would have to extrapolate the $\theta(t)$ backwards using Dickinson's procedure (ref. 9), ·

  − calorimetric studies of kinetic nature of slow reactions are possible, see Fig. 3, and

  − heat flow calorimetry may be extended into the range of relatively fast changes (transients), see Fig. 4.

Finally it should be emphasized that in a test of the method, the results can be no better than permitted by the equipment, and that the quality of the latter leaves much to be desired in the present case. In particular, the stability of the temperature of the surroundings and the sensitivity of the temperature sensor could be improved by one or two orders of magnitude at a reasonable expenditure.

More details may be found in ref. 5.

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