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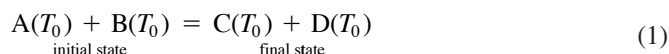
Thermochemistry

EXPERIMENTS

6. Heats of Combustion
7. Strain Energy of the Cyclopropane Ring
8. Heats of Ionic Reaction

PRINCIPLES OF CALORIMETRY

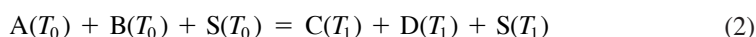
We are concerned here with the problem of determining experimentally the enthalpy change ΔH or the energy change ΔE accompanying a given isothermal change in state of a system, normally one in which a chemical reaction occurs. We can write the reaction schematically in the form



If n is the number of moles of the limiting reagent, the molar quantities for the reaction are $\Delta \tilde{H} = \Delta H/n$ and $\Delta \tilde{E} = \Delta E/n$.

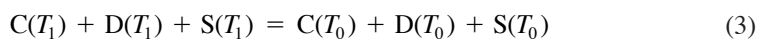
In practice we do not actually carry out the change in state isothermally; this is not necessary because ΔH and ΔE are independent of the path. In calorimetry we usually find it convenient to use a path composed of two steps:

Step I. A change in state is carried out *adiabatically* in the calorimeter vessel to yield the desired products but in general at another temperature:



where S represents those parts of the system (e.g., inside wall of the calorimeter vessel, stirrer, thermometer, solvent) that are always at the same temperature as the reactants or products because of the experimental arrangement; these parts, plus the reactants or products, constitute the system under discussion.

Step II. The products of step I are brought to the initial temperature T_0 by adding heat to (or taking it from) the system:



As we shall see, it is often unnecessary to carry out this step in actuality, since the associated change in energy or enthalpy can be calculated from the known temperature difference.

By adding Eqs. (2) and (3), we obtain Eq. (1) and verify that these two steps describe a complete path connecting the desired initial and final states. Accordingly, ΔH or ΔE for the change in state (1) is the sum of the values of this quantity pertaining to the two steps:

$$\Delta H = \Delta H_{\text{I}} + \Delta H_{\text{II}} \quad (4a)$$

$$\Delta E = \Delta E_{\text{I}} + \Delta E_{\text{II}} \quad (4b)$$

The particular convenience of the path described is that the heat q for step I is zero, while the heat q for step II can be either measured or calculated. It can be measured directly by carrying out step II (or its inverse) through the addition to the system of a measurable quantity of heat or electrical energy, or it can be calculated from the temperature change ($T_1 - T_0$) resulting from adiabatic step I if the heat capacity of the product system is known. For step I,

$$\Delta H_{\text{I}} = q_p = 0 \quad \text{constant pressure} \quad (5a)$$

$$\Delta E_{\text{I}} = q_v = 0 \quad \text{constant volume} \quad (5b)$$

Thus, if *both* steps are carried out at constant pressure,

$$\Delta H = \Delta H_{\text{II}} \quad (6a)$$

and if *both* are carried out at constant volume,

$$\Delta E = \Delta E_{\text{II}} \quad (6b)$$

Whether the process is carried out at constant pressure or at constant volume is a matter of convenience. In nearly all cases it is most convenient to carry it out at constant pressure; the experiment on heats of ionic reaction is an example. An exception to the general rule is the determination of a heat of combustion, which is conveniently carried out at constant volume in a "bomb calorimeter." However, we can easily calculate ΔH from ΔE as determined from a constant-volume process (or ΔE from ΔH as determined from a constant-pressure process) by use of the equation

$$\Delta H = \Delta E + \Delta(pV) \quad (7)$$

When all reactants and products are condensed phases, the $\Delta(pV)$ term is negligible in comparison with ΔH or ΔE , and the distinction between these two quantities is unimportant. When gases are involved, as in the case of combustion, the $\Delta(pV)$ term is likely to be significant in magnitude, though still small in comparison with ΔH or ΔE . Since it is small, we can employ the perfect-gas law and rewrite Eq. (7) in the form

$$\Delta H = \Delta E + RT\Delta n_{\text{gas}} \quad (8)$$

where Δn_{gas} is the *increase* in the number of moles of gas in the system.

We must now concern ourselves with procedures for determining ΔH or ΔE for step II. We might envisage step II being carried out by adding heat to the system or taking heat away from the system and measuring q for this process.† Usually, however, it is much easier to measure work than heat. In particular, electrical work done on the system by a heating coil (often referred to as *Joule heating*) can be used conveniently to carry out

†This could be done by placing the system in thermal contact with a heat reservoir (such as a large water bath) of known heat capacity until the desired change has been effected and calculating q from the measured change in the temperature of the reservoir.

either step II or its inverse, whichever is endothermic. Since the work is dissipated *inside* the system, the work is positive:

$$w_{\text{el}} = \int V_h dQ = \int V_h I dt \quad (9a)$$

where V_h is the voltage drop across the heater, Q is the electric charge, and I is the electric current. For precise work, one should measure both V_h and I during the heating period. In many instances, however, it is possible to assume that the resistance of the heating coil R_h is constant and make only measurements of I by determining the potential drop V_s across a standard resistance R_s in series with the heating coil. In such a case, one can write

$$w_{\text{el}} = \int I^2 R_h dt = \frac{R_h}{R_s^2} \int V_s^2 dt \quad (9b)$$

Note that the electrical work given by Eq. (9) is in joules when resistance is in ohms, potential (voltage) is in volts, and time is in seconds. If the electrical heating is done adiabatically,

$$\Delta H_{\text{II}} = w_{\text{el}} \quad \text{constant pressure} \quad (10a)$$

$$\Delta E_{\text{II}} = w_{\text{el}} \quad \text{constant volume} \quad (10b)$$

Our discussion so far has been limited to determining ΔH_{II} or ΔE_{II} by directly carrying out step II (or its inverse). However, it is often not necessary to carry out this step in actuality. If we know or can determine the heat capacity of the system, the temperature change ($T_1 - T_0$) resulting from step I provides all the additional information we need:

$$\Delta H_{\text{II}} = \int_{T_1}^{T_0} C_p (C + D + S) dT \quad (11a)$$

$$\Delta E_{\text{II}} = \int_{T_1}^{T_0} C_v (C + D + S) dT \quad (11b)$$

The heat capacities ordinarily vary only slightly over the small temperature ranges involved: accordingly we can simplify Eqs. (11) and combine them with Eqs. (6) to obtain the familiar expressions

$$\Delta H = -C_p (C + D + S) (T_1 - T_0) \quad (12a)$$

$$\Delta E = -C_v (C + D + S) (T_1 - T_0) \quad (12b)$$

where C_p and C_v are average values over the temperature range.

The heat capacity must be determined if it is not known. A direct method, which depends on the assumption of the constancy of heat capacities over a small range of temperature, is to measure the adiabatic temperature rise ($T'_2 - T'_1$) produced by the dissipation of a measured quantity of electrical energy. We then obtain

$$\left. \begin{array}{l} C_p \\ C_v \end{array} \right\} = \frac{w_{\text{el}}}{T'_2 - T'_1} \quad (13a)$$

$$(13b)$$

at constant pressure or at constant volume, respectively. This method is exemplified in the experiment on heats of ionic reaction.

An indirect method of determining the heat capacity is to carry out another reaction altogether, for which the heat of reaction is known, in the same calorimeter under the same conditions. This method depends on the fact that in most calorimetric measurements on

chemical reactions the heat-capacity contributions of the actual product species (C and D) are very small, and often negligible, in comparison with the contribution due to the parts of the system denoted by the symbol S. In a bomb-calorimeter experiment the reactants or products amount to a gram or two, while the rest of the system is the thermal equivalent of about 2.5 kg of water. In calorimetry involving dilute aqueous solutions, the heat capacities of such solutions can in a first approximation be taken equal to that of equivalent weights or volumes of water. Thus we may write, in place of Eqs. (12a) and (12b),

$$\left. \begin{aligned} \Delta H \\ \Delta E \end{aligned} \right\} = -C(S)(T_1 - T_0) \quad \begin{aligned} (14a) \\ (14b) \end{aligned}$$

for constant-pressure and constant-volume processes, respectively. In Eqs. (14a) and (14b) we have omitted any subscript from the heat capacity as being largely meaningless, since only solids and liquids, with volumes essentially independent of pressure, are involved. The value of $C(S)$ can be calculated from the heat of the known reaction and the adiabatic temperature change ($T_2' - T_1'$) produced by it, as follows:

$$C(S) = \begin{cases} \frac{-\Delta H_{\text{known}}}{T_2' - T_1'} & \text{constant pressure} \\ \frac{-\Delta E_{\text{known}}}{T_2' - T_1'} & \text{constant volume} \end{cases} \quad \begin{aligned} (15a) \\ (15b) \end{aligned}$$

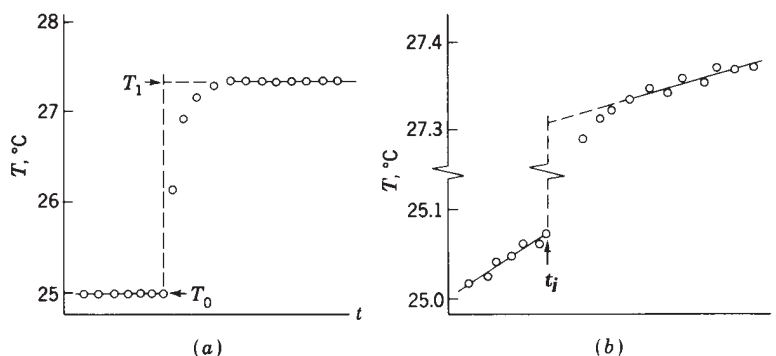
This method is exemplified in the experiment on heats of combustion by bomb calorimetry.

Let us now consider step I, the adiabatic step, and the measurement of the temperature difference ($T_1 - T_0$), which is the fundamental measurement of calorimetry. If this step could be carried out in an *ideal* adiabatic calorimeter, the temperature variation would be like that shown in Fig. 1a. In this case there would be no difficulty in determining the temperature change $\Delta T = T_1 - T_0$, since $(dT/dt) = 0$ before the time of mixing the reactants and after the products achieve thermal equilibrium. The only cause of temperature change here is the chemical reaction. However, it is an unrealistic idealization to assume that step I is truly adiabatic; as no thermal insulation is perfect, some heat will in general leak into or out of the system during the time required for the change in state to occur and for the thermometer to come into equilibrium with the product system.

In addition, we usually have a stirrer present in the calorimeter to aid in the mixing of reactants or to hasten thermal equilibration. The mechanical work done on the system by the stirrer results in the continuous addition of energy to the system at a small, approximately constant rate. During the time required for the change in state and thermal equilibration to occur, the amount of energy introduced can be significant. A typical temperature–time variation is shown in Fig. 1b, where a greatly expanded temperature

FIGURE 1

(a) Plot of temperature T versus time t for an ideal adiabatic calorimeter.
(b) Plot with interrupted temperature axis and greatly expanded temperature scale for a typical calorimeter run. Such a plot is designed to show clearly the temperature variation before and after the time t_i when the reaction is initiated.



scale has been used with an interrupted temperature axis in order to show clearly the pre- and postreaction temperature changes. In this case, a more detailed analysis is needed in order to extract the adiabatic ΔT value from the observed data points.

Consider Fig. 2, which shows a schematic plot of $T(t)$ associated with step I as carried out in a typical calorimeter. This plot is based on the assumptions that the heat leakage through the calorimeter walls is small and the energy input due to the stirrer is moderate. These assumptions are appropriate for the thermochemistry experiments described in this book. The initial temperature T_i is conveniently taken to be the value at time t_i when the reaction is initiated following a period of essentially linear T, t readings that serve to establish the initial (prereaction) drift rate $(dT/dt)_i$. The temperature is followed after reaction for a period long enough to achieve a roughly linear variation and to establish the drift rate $(dT/dt)_f$ at an arbitrary point T_f, t_f .

The analysis of step I will be given for a constant-volume calorimeter run, but analogous results hold at constant pressure. The effect of heat leakage is evaluated using Newton's law of cooling,

$$\frac{dq}{dt} = -k(T - T_s) \quad (16)$$

where T_s is the temperature of the surroundings (air temperature in the laboratory) and k is a thermal rate constant that depends on the thermal conductivity of the calorimeter insulation. The mechanical power input to the system (dw/dt) will be denoted by P , which is assumed to be a constant independent of t . Thus

$$C_v \frac{dT}{dt} = \frac{dE}{dt} = P - k(T - T_s) \quad (17)$$

or

$$\left(\frac{dT}{dt} \right)_{\text{leak+stir}} = \frac{1}{C} [P - k(T - T_s)] \quad (18)$$

where C is C_v for constant-volume reactions and C_p for constant-pressure reactions. The temperature difference $T_f - T_i$ shown in Fig. 2 is given by

$$T_f - T_i = \Delta T + \int_{t_i}^{t_f} \left(\frac{dT}{dt} \right)_{\text{leak+stir}} dt \quad (19)$$

where $\Delta T = T_1 - T_0$ is the change due to an adiabatic chemical reaction and the integral is the net change due to heat leak and stirrer power input. Thus it follows that

$$T_1 - T_0 \equiv \Delta T = (T_f - T_i) - \frac{1}{C} \int_{t_i}^{t_f} \{P - k[T(t) - T_s]\} dt \quad (20)$$

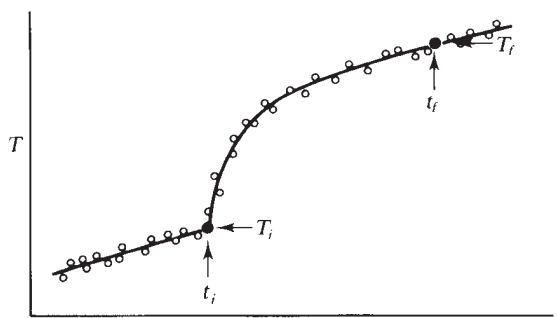


FIGURE 2

Schematic plot of temperature T versus time t observed in a typical calorimeter experiment. The temperature-time points (T_i, t_i) and (T_f, t_f) can be chosen somewhat arbitrarily as long as t_i is prior to or at t_{react} and t_f is a sufficiently long time after t_{react} (see text).

The following are the most important experimental approaches aimed at minimizing the effect of nonadiabatic conditions and the effect of the stirrer; they can be used separately or in combination.

1. The calorimeter may be built in such a way as to minimize heat conduction into or out of the system. A vessel with an evacuated jacket (Dewar flask), often with silvered surfaces to minimize the effect of heat radiation, may be used. This corresponds to making the thermal rate constant k very small.
2. One may interpose between system and surroundings an "adiabatic jacket," reasonably well insulated from both. This jacket is so constructed that its temperature can be adjusted at will from outside, as, for example, by supplying electrical energy to a heating circuit. In use, the temperature of the jacket is continuously adjusted so as to be as close as possible to that of the system, so that no significant quantity of heat will tend to flow between the system and the jacket. This corresponds to making $T - T_s$ very small.
3. The stirring system may be carefully designed to produce the least rate of work consistent with the requirement of thorough and reasonably rapid mixing. This corresponds to making P small.
4. We may assume that the rate of gain or loss of energy by the system resulting from heat leakage and stirrer work is reasonably constant with time at any given temperature. We may therefore assume that the temperature variation as a function of time should be initially and finally almost linear.

One simple possibility would be $k(T - T_s) = 0$ and $P = \text{constant}$, in which case $(dT/dt) = P/C$ has the same value at all $t < t_i$ and $t > t_f$ and Eq. (19) gives

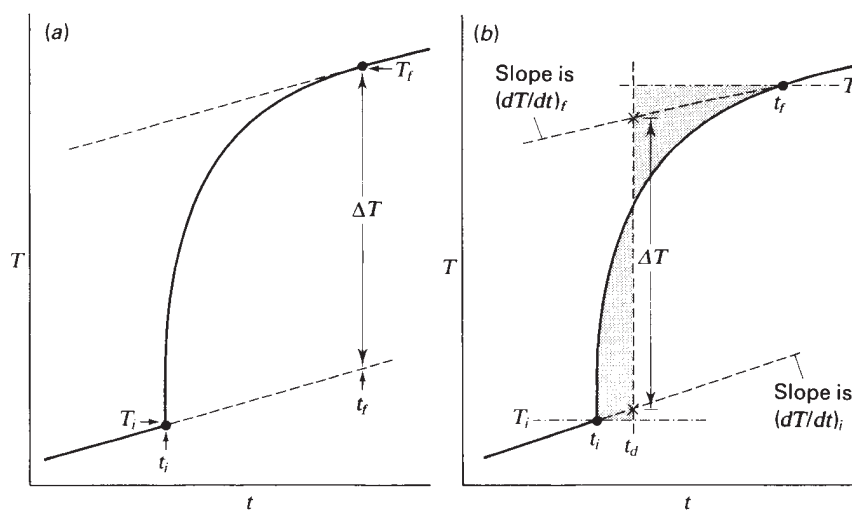
$$\Delta T = T_f - T_i - \frac{dT}{dt}(t_f - t_i) \quad \text{if } k(T - T_s) = 0 \quad (21)$$

As shown in Fig. 3a, ΔT in this case is just the vertical distance between two parallel $T-t$ lines. Naturally, this distance can be evaluated at any t . A more realistic possibility is that $k(T - T_s)$ is small but not negligible and $P = \text{constant}$. In this case the $T-t$ plot looks like Fig. 3b, where the initial leak + stir drift rate $(dT/dt)_i$ at t_i differs from the final rate $(dT/dt)_f$ at t_f . It can be shown¹ in this case that ΔT is given by

$$\Delta T = (T_f - T_i) - \left(\frac{dT}{dt}\right)_i(t_d - t_i) - \left(\frac{dT}{dt}\right)_f(t_f - t_d) \quad (22)$$

FIGURE 3

Determination of the "adiabatic" temperature change ΔT from experimental $T(t)$ measurements made in nonideal calorimeters: (a) case of no heat leak but a constant stirring power input; (b) case of a small heat leak as well as stirrer energy input. The value of t_d is chosen so that the two shaded regions have equal areas; see text for details.



where t_d is chosen so that the two shaded regions in Fig. 3b are of equal area.

The derivation of Eq. (22) from Eq. (20) requires a bit of sleight-of-hand manipulation. Let us define a new variable $T_c \equiv T_s + (P/k)$, in terms of which Eq. (18) gives

$$\left(\frac{dT}{dt}\right)_i = -\frac{k}{C}(T_i - T_c) \quad \text{and} \quad \left(\frac{dT}{dt}\right)_f = -\frac{k}{C}(T_f - T_c) \quad (23)$$

and Eq. (20) becomes

$$\Delta T = (T_f - T_i) + \frac{k}{C} \int_{t_i}^{t_f} (T - T_c) dt \quad (24)$$

Note that

$$\begin{aligned} \int_{t_i}^{t_f} (T - T_c) dt &= \int_{t_i}^{t_d} (T - T_i) dt + (T_i - T_c)(t_d - t_i) \\ &\quad + \int_{t_d}^{t_f} (T - T_f) dt + (T_f - T_c)(t_f - t_d) \end{aligned} \quad (25)$$

By the definition given above for t_d , the two integrals in Eq. (25) cancel out. Substituting Eq. (25) into Eq. (24) and making use of Eq. (23) leads directly to Eq. (22). It is clear from this derivation that Eq. (22) will be valid even if the T variation prior to t_i and after t_f is not linear. In such a case, one merely uses the tangent to the $T-t$ curves at T_i and T_f .

In summary, one should follow the temperature variation before and after reaction for a period long enough to allow a good evaluation of $(dT/dt)_i$ and $(dT/dt)_f$. Then make a plot like Fig. 3b, choose the point (T_f, t_f) , determine the best value for t_d , and calculate ΔT from Eq. (22). In practice t_f should be chosen as close to t_i as is consistent with a well-characterized final drift rate. Note that t_d will lie much closer to t_i than to t_f for reactions that go to completion quickly. Whenever the time required for a change in state is long, as in the case of determining the heat capacity by electrical heating, the position of t_d will lie near the middle of the range t_i to t_f . As an approximate procedure for handling the analysis of electrical heating plots, one can choose t_i as the time the heater is turned on and t_f as the time it is turned off and choose t_d as the midpoint of this heating period.

In the experiments on heats of combustion, we make use of approaches 2 (optionally), 3, and 4. In the experiment on heats of ionic reaction, we make use of 1, 3, and 4. In all cases the small temperature changes can be measured with adequate precision with a relatively inexpensive mercury thermometer. Alternatively the measurements can be made using a sensitive thermistor (see Chapter XVII), which can be monitored repetitively by a computer. Calibration of the thermistor for improved linearity and accuracy is needed in this case, but this procedure itself can serve as a convenient introduction to interfacing a computer to a measurement device.

REFERENCE

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