Calculation of Temperature Rise in Calorimetry

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The undergraduate student is introduced to calorimetry early in the curriculum. Since the concepts of energy and energy changes play a central role in chemistry, both general chemistry as well as physical chemistry courses deal with thermodynamic concepts like heat capacities and heats of reactions. Consequently, measurements of energy change by calorimetry continue to attract discussion in the pages of *this Journal* (1, 2). There is also a review (3) on recent development in calorimetry.

The concepts of heat capacities and heats of reactions are introduced to the student in some detail in courses of thermodynamics. On the experimental side, introductory work is done without much regard for refinements like heat-loss corrections. In physical chemistry experiments, methods for correcting heat losses are mentioned, but the discussion tends to be brief. A full discussion of this theory is found only in the specialist literature (4, 5). In this article we give a simple but fuller account of the basis for accurately calculating temperature rise in calorimetry, and point out some misconceptions with regard to these calculations.

The Need for Correction to Observed Temperature Rise

In many kinds of calorimetry, changes in state of the system are followed by monitoring changes in temperature. The observed changes of temperature are brought about by factors of direct interest to us, as well as by extraneous factors whose presence we would like to avoid. For example, one might use electrical heating to input an accurately known amount of energy and wish to measure the concomitant change in temperature. Or one might like to measure the temperature change accompanying a known change of composition (chemical reaction). These are examples of factors that are an essential part of our investigation. On the other hand, temperature changes are also brought about by exchange of heat at the system/surroundings interface. Attempts to make the measured temperature uniform by employing stirring will result in an additional temperature change due to the energy of stirring. Because of these extraneous factors, a correction has to be applied to the measured change in temperature in order to obtain the effect of the quantities of interest.

The Basic Equation for Temperature Rise

The basic equation to be used in calculating temperature rise is obtained from the first law of thermodynamics. To apply this equation correctly we need to remind ourselves that our system may consist of more than one part and that the measured temperature is the temperature of only one part of the system. We shall hereafter refer to this part of the system as the calorimeter and contents. This is to distinguish it from other parts of the system like, for example, the bomb in a bomb calorimeter. The calorimeter and contents will in general exchange heat not only with the surroundings but also with other parts of the system.

If H is the enthalpy of the calorimeter and its contents, and these are at constant pressure, we have from energy balance requirements

$$dH/dt = EI + (dH/dt)_1 + w + (dH/dt)_2 \qquad (1)$$

where I is the current flowing through a resistor in contact with the calorimeter and its contents and E is the potential difference across its ends; w is the rate of energy input due to stirring; $(dH/dt)_1$ is the rate of increase of H due to heat exchange at the system/surroundings interface; and $(dH/dt)_2$ is the rate of increase of H due to heat flow from another part of the system, for example, the bomb in a bomb calorimeter.

$(dH/dt)_2$ will in general be a complicated function of time. However, the integral of this term with respect to time will be equal to the change in a thermodynamic function of state. Consequently, a knowledge of the path of the change is not needed to evaluate this term.

$(dH/dt)_1$ will depend on the calorimeter/surroundings interface and not on the nature of the contents of the calorimeter. We will assume that $(dH/dt)_1 = -K(T - T_j)$ where T is the temperature of the calorimeter, T_j is the constant temperature of the surroundings, and K is a constant depending only on the nature of the calorimeter/surroundings interface and not on its contents.

We have now to relate (dH/dt) to (dT/dt). In the general case when a chemical reaction occurs in the calorimeter we may write $dH = C_p dT + h_{rn} d\xi$, where C_p is the heat capacity of the calorimeter and contents, h_{rn} is the enthalpy of the reaction, and ξ denotes the extent of reaction. $h_{rn} d\xi$ denotes the change in enthalpy due to the change in composition brought about by reaction. Combining this with eq 1 we have

$$(dT/dt) = EI/C_p + w/C_p - K(T - T_j)/C_p + f(t) \qquad (2)$$

where

$$f(t) = \frac{1}{C_p}\left\{\frac{dH}{dt_2} - h_{rn}\frac{d\xi}{dt}\right\}$$

is an unknown function of time. However, $\int f(t)dt$ is independent of the path of the reaction and depends only on the initial and final states.

The first and the fourth terms constitute the terms of interest to us, while the second and third are the "interference" terms whose presence we have to correct for by the determination of w and K. Thus

$$\int \{EI/C_p + f(t)\}dt = \Delta T - \frac{1}{C_p}\int\{w - K(T - T_j)\}dt \qquad (3)$$

The integral on the right side of the eq 3 constitutes a correction term to the observed change ΔT.

In eq 3 we have assumed that C_p is independent of T. It might seem that this restricts the usefulness of the subsequent treatment. It is possible to give a more rigorous treatment that deals not with ΔT, but with a quantity of greater interest in calorimetry, viz., ΔH. In such a treatment we can deal with a temperature-dependent C_p or, to keep matters simple, the mean heat capacity $\bar{C}_p$ of the calorimeter and contents over the range of the experiment. This mean heat capacity is, by definition, independent of T. The heat capacity C_p of eq 3 may therefore be replaced by the mean heat capacity. Thus the assumption made in eq 3 is not unduly restrictive, and it will be used in the treatment that follows.

We note here that the correction is made possible because the experiment can be divided into

(1) a pre-reaction period from time t_1 to t_i when the electric heating is started and/or a chemical reaction is initiated,

(2) the reaction period t_i to t_f of the experiment (the lower and upper limits of the integrals in eq 3 are t_i and t_f, respectively), and

(3) the post-reaction period from t_f to t_2 when the electrical heating is switched off and the chemical reaction is considered to have gone to completion.

During the pre- and post-reaction periods only the w/C_p and K/C_p terms are operative so that observations of temperature with time during these periods will enable us to calculate w/C_p and K/C_p. More specifically, since C_p is assumed constant we have during the pre- and post-reaction periods

$$dT/dt = w/C_p - K(T - T_j)/C_p \qquad (4)$$

whence

$$\Delta T = \int (w/C_p)\, dt - (K/C_p) \int (T - T_j)\, dt \qquad (5)$$

Since (w/C_p) and (K/C_p) are the only two unknowns it is clear that a minimum of two sets of $T - t$ data will be sufficient to enable us to calculate the unknowns. If we used a calorimeter and contents of known heat capacity we may calculate w and K. The latter values will be valid for other experiments carried out under the same conditions. The values of w and K (or w/C_p and K/C_p) may now be used with eq 1 or eq 2 to evaluate the corrections to the observed ΔT during the reaction period.

The basic method discussed above involves the explicit evaluation of w and K. An alternative method is to evaluate the corrections to ΔT directly from the temperature–time graph. A discussion of this alternative method is conveniently grouped under three cases.

Case 1: Infinitely Fast Reaction, Thermometric Lag

Here we consider the case where the reaction is infinitely fast so that f(t) in eq 2 is a step function. The actual temperature of the system follows eq 4 during the reaction period as well as the post-reaction period. However, because of thermometric lag, eq 4 can be related to experimental observations only during the post-reaction period.

Figure 1 shows a temperature–time graph for this case. The actual (but not recorded) temperature shoots up to a value of T'_f: our problem is to determine this value from the recorded temperatures.

Regarding time t_i as time zero, integration of eq 4 with $T = T'_f$ at $t = 0$ gives

$$T = T'_f - A + Ae^{-(K/C_p)t} \qquad (6)$$

where A is a constant.

The recorded temperatures in the post-reaction period t_f to t_2 will follow eq 4. If the portion BC is sensibly linear (corresponding to small values of $(K/C_p)t$), eq 4 will be approximated by

$$T = T'_f - A(K/C_p)t \qquad (7)$$

and a linear extrapolation to zero time t_i gives AC′ as the actual rise in temperature. The correction to the temperature rise is represented by B′C′. We note that we did not need a knowledge of K or w for this correction.

If BC is not linear, as would happen, for example, when thermal insulation of the calorimeter is not good, we proceed in the following way. From eq 6, for two times t and $t + \delta$, where t is any time and δ is a constant, we have

$$T(t) - T(t + \delta) = Ae^{-(K/C_p)t}[1 - e^{-(K/C_p)\delta}] \qquad (8)$$

whence a graph of $\ln\{T(t) - T(t + \delta)\}$ vs. t will enable us to

calculate (K/C_p) from the slope and then A from the intercept. We can now calculate T'_f from eq 4.

Most ionic reactions may be regarded as taking place instantaneously, and the correction used above would be the appropriate one.

Case 2: Infinitely Fast Reaction, Calorimetric Lag

Combustion reactions in a bomb calorimeter fall under this category. Here the combustion reaction takes place instantaneously, but because of the large mass of the calorimeter it takes some time before the "heat evolved" is distributed to the outer calorimeter and its contents. It is the temperature of the latter that we monitor as a function of time. For this case, the EI term in eq 3 would be zero and T is the observed temperature rise during the reaction period $t_i - t_f$. The integral on the right side, between the limits $t = t_i$ and $t = t_f$, constitutes the temperature correction. The important difference between case 1 and case 2 is that eq 4 is valid during the period $t_i - t_f$ in case 1, but is invalid in case 2, since f(t) contributes to dT/dt.

If w, K, and C_p were known for the calorimeter and contents from an independent experiment, there would be no problem in principle in evaluating the required integrals. Most often we do not have this information. We can however evaluate the integral from a knowledge of the $T - t$ graph for the pre- and post-reaction periods.

Figure 2 represents a typical $T - t$ graph for calorimetric lags; t_i is the time when the experiment is started and t_f the time when it ends. How is the time t_f to be chosen? Now, the period $t_f - t_i$ is the reaction period when f(t) makes a contribution to dT/dt; f(t) should make no contribution to dT/dt beyond time t_f. When the temperature is changing rapidly, clearly f(t) is still making a non-zero contribution. It is usual to take the time corresponding to the turning point as the time t_f (see Fig. 2). A choice of t_f beyond the turning point would be acceptable, but an unnecessarily large value of t_f should be avoided since it increases the magnitude of the correction to the observed ΔT.

The correction to ΔT arising from stirring and heat loss is given by the integral on the right-side of eq 3. This cannot be directly evaluated for the reaction period from the corresponding area in the $T - t$ graph because during this period f(t) makes a contribution to dT/dt and hence to the area.
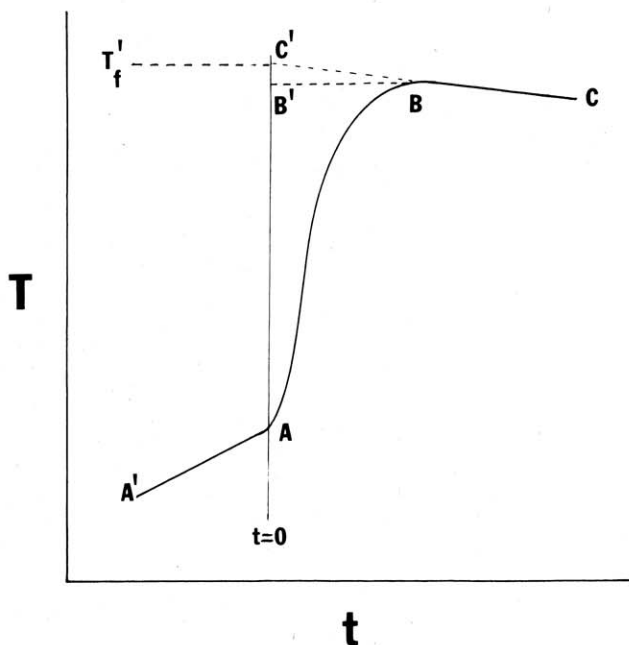
Figure 1. T vs. t for infinitely fast reaction with thermometric lag.

The evaluation may, however, be effected if we combine our knowledge of this area for the reaction period with the characteristics of the $T - t$ graph during the pre- and post-reaction periods, when the contribution of $f(t)$ to dT/dt is zero. To do this we first define a time t_m such that

$$area(ABB'CDEA) = area(ABB'A'A) + area(D'B'CDD')$$

The time t_m may be determined using the above property:

$$\int_{t_i}^{t_f} (T - T_j)dt = \int_{t_i}^{t_m} (T_i - T_j)dt + \int_{t_m}^{t_f} (T_f - T_j)dt \qquad (9)$$

It follows from the equality of areas that

$$area(AA'E) = area(DD'E)$$

whence

$$\int_{t_i}^{t_m} (T - T_i)dt = \int_{t_m}^{t_f} (T_f - T)dt \qquad (10)$$

We now show how the correction to ΔT during the reaction period may be related to the slope $\partial T/\partial t$ of the $T - t$ graph during the pre- and post-reaction periods. With t_m defined thus, it follows that the integral on the right side of eq 3 may be written

$$-\frac{1}{C_p} \int_{t_i}^{t_f} [w - K(T - T_j)dt] = -\frac{1}{C_p} \int_{t_i}^{t_m} [w - K(T_i - T_j)dt]$$

$$-\frac{1}{C_p} \int_{t_m}^{t_f} [w - K(T_f - T_j)dt] \qquad (11)$$

$$= -\int_{t_i}^{t_m} \left(\frac{dT}{dt}\right)_{t_i} dt - \int_{t_m}^{t_f} \left(\frac{dT}{dt}\right)_{t_f} dt \qquad (12)$$

Equation 12 follows from eq 4 since at $t = t_i$ and $t = t_f$ the contributions to dT/dt come only from stirring and heat exchange with the surroundings.

We can now calculate the temperature-rise correction without an explicit knowledge of K or w. If we assume that the variation of T with t is approximately linear before $t = t_i$ and after $t = t_f$, the slopes of the lines before t_i and after t_f represent $(dT/dt)_{t_i}$ and $(dT/dt)_{t_f}$. As shown in Figure 3, the right side of eq 12 becomes $-(-A'E') - (-D'E) = A'E' + D'E$. Thus the corrected temperature rise is represented by E'E.
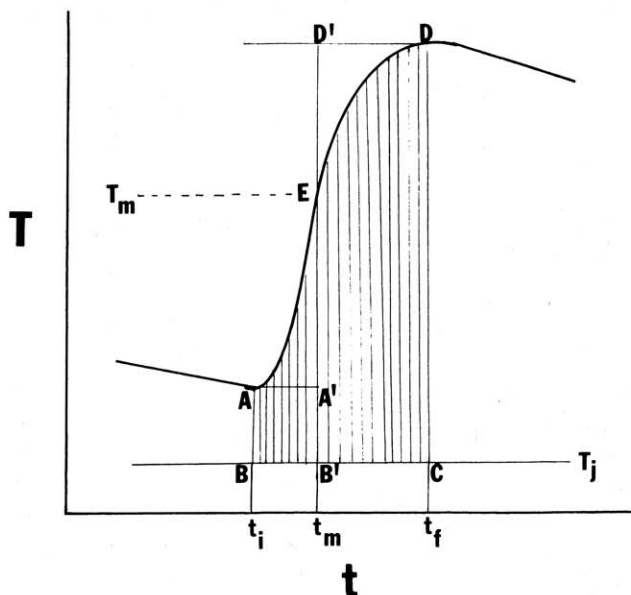
In summary, for this case we do not extrapolate to zero time as we did for case 1. Instead we extrapolate the pre- and post-reaction curves to a time t_m, which is determined by the "equal area" method.

There are two common misconceptions with regard to this method (6). The first is that t_m may be determined by having $area(EMD) = area(AE'M)$. This is not strictly true, and unless the time period $t_i - t_f$ is small the procedure can lead to error. The strict condition is that $area(DD'M) = area-(MAA')$.

The second misconception is that the experiment is equivalent to starting at T' and obtaining an instantaneous rise to T'_f and that consequently ΔH should be calculated for temperature T' or T'_f. This interpretation is erroneous; given the heat capacities of the reactants and products we may validly calculate the enthalpy of reaction at any desired temperature.

Case 3: Slow Reaction, No Thermometric or Calorimetric Lag

If the reaction is slow, but becomes sensibly complete at time t_f, then it is possible to distinguish pre-reaction, reaction, and post-reaction periods, and the method for case 2 can be applied. If, however, the reaction does not go to completion, explicit knowledge of w and K will be needed. Furthermore, the change in extent of reaction must be known before the enthalpy of reaction can be calculated.

The case of electrical heating for the determination of heat capacities will fall into this category, and the equal area method for case 2 is applicable. Very often the temperature rise is linear during the heating period $t_i - t_f$. For this case it is easily shown that $t_m = (t_i + t_f)/2$.

The 63% Temperature Rise Method

We have seen that t_m is easily evaluated by using the equal area criterion. Many workers determine t_m by the use of the condition

$$(T_m - T_i)/(T_f - T_i) = 0.63 \qquad (13)$$

where t_m is the temperature at $t = t_m$. This method is popu-

Figure 2. *T* vs. *t* for infinitely fast reaction with calorimetric lag.
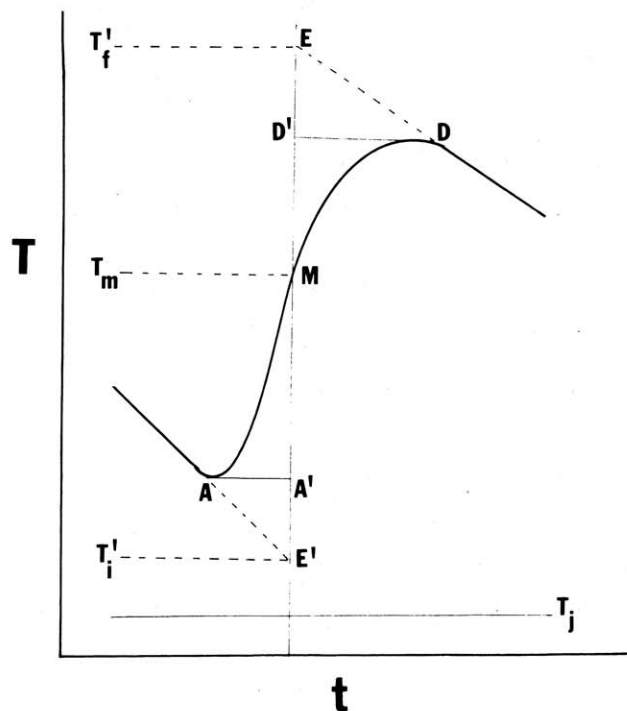

Figure 3. *T* vs. *t* graph showing graphical calculation of temperature rise.

lar because it allows a quicker evaluation of t_m than the equal area method. Its basis is as follows.

If there is no heat loss, it is found that for many reactions the temperature in a reacting system follows approximately an equation of the form

$$T = T_i + A(e^{-kt} - 1) \qquad (14)$$

This exponential variation of temperature is intuitively reasonable for a first-order reaction where the concentrations of reactants and products change exponentially with time. The constant A is negative for exothermic reactions. The final temperature (attained strictly only at time infinity) is $T_i - A$. Even if there are contributions to dT/dt from heat exchange and stirring, eq 14 would still be approximately valid if the reaction makes the dominant contribution. Using eqs 10 and 14 it follows that

$$\int_0^{t_m} A(e^{-kt} - 1)\,dt = -\int_{t_m}^{\infty} Ae^{-kt}\,dt \qquad (15)$$

In eq 15 we have taken t_i to be 0 and t_f to be ∞; the latter identification will clearly lead to a slight error. From eq 15 we have

$$\int_0^{t_m} dt \int_0^{\infty} e^{-kt}\,dt$$

whence

$$t_m = 1/k \qquad (16)$$

Combining eqs 14 and 16 gives us eq 13. Equation 13 can be used to read t_m from the $T - t$ graph. In a large number of combustion experiments Dickinson (5) determined the ratio in eq 13 to be 0.60.

In view of the many approximations in the method using eq 13, it must be used with caution. In many cases its use does not give equal areas, and in such cases the method is clearly invalid. Thus, in two examples (8) this method of getting t_m gives areas whose ratio differs from unity by 20% and 250%. It must be emphasized that no importance attaches to T_m itself; the method is only a way of obtaining the true temperature rise. It would certainly be quite erroneous to state that the enthalpy of reaction has to be calculated at T_m. In reference 7 the heat capacity of the contents is also not correctly determined. Ramette (2) uses the 0.63 method of determining T_m but quite correctly uses an electrical method to determine the heat capacity of the calorimeter and reacted contents.

Conclusion

The accurate determination of the "true" ΔT in calorimetric experiments is important since the percentage error in the calculated enthalpy of reaction cannot be less than the percentage error in ΔT. Two basic methods are available, the extrapolation to zero time and the equal area method. A careful discussion of the theoretical basis of the methods and their underlying assumptions is given so that the reader can avoid an uncritical application of the two methods.

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