

**460.** *A Thermal Method for measuring the Rates of Moderately Fast Reactions.*

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A simple thermal method is described for measuring the rates of reactions with half-times from 2 sec. to 2 min., using 5- or 10-c.c. liquid samples. Although small cooling corrections have to be made, the method is effectively adiabatic and requires successive temperature (*i.e.*, galvanometer) readings at short times intervals. Complications due to a time-lag in the response of the galvanometer are easily eliminated.

THERMOCOUPLES give a rapid and accurate indication of the progress of an exothermic (or endothermic) reaction and their uses are well known in flow techniques for fast reactions<sup>1</sup>

<sup>1</sup> Roughton, "Techniques of Organic Chemistry," Vol. VIII, ed. Friess and Weissberger, Interscience, New York, 1953, p. 712.

and in the thermal-maximum method for reactions with half-times from 0.2 sec. to 3 min.<sup>2,3</sup> They do not, however, appear to have been exploited in the more straightforward way of following the whole course of a reaction under adiabatic conditions, to give data which can be dealt with as for ordinary slow techniques such as dilatometry. This paper describes a simple method for doing this for reactions in solution with rates in roughly the same half-time range as that covered by the thermal-maximum method. Since the method involves taking galvanometer readings at regular intervals, the minimum practicable interval (2 sec.) sets the lower limit to the reaction half-times which can be studied in this way. The upper half-time limit depends upon the rate of heat loss from the cell, and this can be reduced by increasing the size of the solution sample. The present apparatus was designed initially for concentrated salt solutions, however, and the sample volume was restricted to 5 or 10 c.c., for which the workable upper limit was about 2 min.

The apparatus can be calibrated to measure the heat of reaction at the same time as the rate, and since initial heat-of-mixing effects show up immediately, they can be both measured and eliminated from the kinetic calculations.

It is not claimed that there is any special novelty in the method, but the apparatus is relatively cheap and simple to construct and a useful range of rate constants is covered.

#### EXPERIMENTAL

*Apparatus.*—An ordinary platinum crucible (15–20 c.c.) served as the reaction cell, and this was mounted in a polystyrene-foam insulating-jacket inside a beaker, which was itself suspended in a thermostat (a 4-l. Dewar vessel). The top of the cell was stoppered by a closely fitting bung from which were suspended a small heater (~1 ohm), a motor-driven stirrer (562 r.p.m.), a guide-tube for an adding device, and a single-junction copper-constantan thermocouple (sheathed in very thin glass<sup>3</sup>), the reference junction of which was immersed in the thermostat. All glass parts in contact with the cell liquid were made of as thin glass as practicable to minimise errors due to their slow heating. (For this reason a platinum crucible in a polystyrene-foam jacket was preferred to a small Dewar vessel.) The adding device for the second reactant was a simple syringe made of a fine glass tube with a rubber cap: weighed quantities of solution as small as 0.01 g. could be added rapidly in this way.

It was convenient to assemble the apparatus in the equipment designed by Bell and Clunie<sup>2</sup> for the thermal-maximum method. This enabled the cell to be dismantled easily without altering the alignment of its fragile upper parts with its base, simply by lowering the base of the cell with the thermostat. The thermocouple e.m.f., corresponding to the temperature difference between the cell and the thermostat, was amplified photoelectrically<sup>3,4</sup> (so that the total temperature change could be kept down to 0.2° or less) and read off on a glass scale. When a reaction was about to be carried out and a 10-c.c. sample of the first reactant was ready in the cell, this temperature difference was brought to zero and held there by adjusting the current through the heater, which thus exactly balanced the residual heat losses from the cell at the bath temperature. This heater current was kept fixed during a reaction, so that the additional heat losses at the slightly higher temperatures prevailing during the experiment caused a very slow return to the bath-temperature at the end of a reaction, thus necessitating a small correction to the later points.

The beginning of a reaction and the subsequent galvanometer readings were timed by a calibrated metronome. (It was convenient to use ticks on only one side of the instrument.)

*Treatment of Results.*—Since the rate of cooling is very small, no significant error is introduced by making simple corrections to the readings on the assumption that cooling begins when the galvanometer deflection reaches half its maximum value. (For many reactions this amounts to adding no more than 0.1–0.3 cm. to the later scale readings.) The corrected readings are then treated in the ordinary way, the temperature difference,  $T$ , between the cell and the thermostat being proportional to the concentration of the reaction products. ( $T$  is conveniently expressed as a scale reading in cm. units.)

<sup>2</sup> Bell and Clunie, *Proc. Roy. Soc.*, 1952, *A*, **212**, 16.

<sup>3</sup> Bell, Gold, Hilton, and Rand, *Discuss. Faraday Soc.*, 1954, **17**, 151.

<sup>4</sup> Preston, *J. Sci. Instr.*, 1946, **23**, 173.

For first-order reactions, however, a simple and accurate correction is available when using Guggenheim's treatment<sup>5</sup> of the results. As stated above, the purpose of the cell heater is to compensate exactly for heat losses at the thermostat temperature. But when the cell is at a temperature  $T$  above the thermostat temperature heat will be lost at a rate proportional to  $T$ , which is precisely the situation which occurs in the thermal maximum method, where, however, the rate of cooling is very much greater. The same equation<sup>2</sup> may therefore be applied:

$$dT/dt = k_1 T_\infty e^{-k_1 t} - k_2 T \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where  $k_1$  is the first-order rate constant of the reaction,  $T_\infty$  the maximum temperature which would be attained in the absence of cooling,  $k_2$  the cooling constant of the cell, and  $t$  the time (in seconds) after the beginning of the reaction. The solution of (1) can be written as:

$$T_\infty e^{-k_2 t} - (1 - k_2/k_1)T = T_\infty e^{-k_1 t} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

or, in terms of the maximum temperature reading,  $T_m$ , and the time,  $t_m$ , at which this reading occurs,

$$T_m e^{k_2(t_m - t)} - (1 - k_2/k_1)T = T_\infty e^{-k_1 t} \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Since  $k_2 \ll k_1$ , (3) can be written in the approximate form

$$T_m[1 + k_2(t_m - t) + k_2/k_1] - T = (1 + k_2/k_1) T_\infty e^{-k_1 t} \quad . \quad . \quad . \quad . \quad . \quad (4)$$

For sets of readings spaced in time by the interval  $\Delta t$  therefore, the differences in the value of the left-hand side required for Guggenheim's method will be  $T_2 - T_1 + k_2 T_m \Delta t$ , in place of the usual  $T_2 - T_1$ . Thus a constant correction is added to all the reading differences: its magnitude depends upon the rate of cooling and the time interval chosen. Moreover, the rate of cooling at the maximum is  $k_2 T_m$ , so this product can be measured directly with sufficient accuracy at the end of an experiment. (With the apparatus used,  $k_2 T_m \Delta t$  was generally 0.1—0.5 cm., and  $T_m$  10—20 cm.)

Several tests of the method have been made during a study of the catalysed decomposition of hydrogen peroxide by concentrated iodide solutions. With 10-c.c. (or even 5-c.c.) samples of the iodide solutions in the cell and 0.01—0.02 g. of 100-vol. hydrogen peroxide added by the syringe, the reproducibility of the first-order rate constants was often better than  $\pm 3\%$ , except for the shortest half-times, and the values for dilute solutions agreed satisfactorily with those in the literature. Examples are: at 1m-CdI<sub>2</sub>,  $k_1 = 0.0055 \text{ sec.}^{-1} \pm 2\%$ ; at 0.5m-KI,  $0.0133 \text{ sec.}^{-1} \pm 2\%$ ; at 2m-KI,  $0.063_8 \text{ sec.}^{-1} \pm 2\%$  for three additions of hydrogen peroxide to one potassium iodide solution; and  $0.062_2 \text{ sec.}^{-1} \pm 4\%$  for five additions to another; at 7m-KI,  $0.36_8 \text{ sec.}^{-1} \pm 7\%$  for five additions, and  $0.38_1 \text{ sec.}^{-1} \pm 3\%$  for three additions to a different solution. These results all refer to 25° and illustrate the application of the method in determining rate constants in the range 2 sec. to 2 min.

*Effect of the Galvanometer Period.*—Since it was possible to read and record galvanometer deflections at 2- or 3-sec. intervals, it was necessary to show that the significance of the readings is not seriously affected by the period of oscillation of the galvanometer system. The period of the primary galvanometer was 2 sec.; and although this was effectively reduced to 0.85 sec. by the photoelectric amplification system,<sup>4</sup> it was still of the same order of magnitude as the half-times of the fastest reactions studied. The following argument shows that the galvanometer deflections do in fact lag slightly behind the temperature changes in the cell, but that this lag is constant except for a short time during the first second of the reaction. Any effects of this kind can therefore be circumvented when necessary by ignoring the galvanometer reading at zero time.

If the galvanometer system is critically damped, the appropriate differential equation is<sup>6</sup>

$$d^2T/dt^2 + 2b \cdot dT/dt + b^2T = f(t) \quad . \quad . \quad . \quad . \quad . \quad (5)$$

<sup>5</sup> Guggenheim, *Phil. Mag.*, 1926, 2, 538.

<sup>6</sup> Margenau and Murphy, "The Mathematics of Physics and Chemistry," van Nostrand, 2nd edn., 1956, p. 53.

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where  $T$  is the galvanometer deflection at time  $t$  (*i.e.*, the "temperature reading") and  $b$  is the damping constant related to  $\tau$ , the galvanometer period, by the expression  $b = 2\pi/\tau$ . The imposed e.m.f. in the galvanometer circuit, proportional to  $f(t)$ , is produced by the effects of the temperature changes in the cell upon the thermocouple.

The solution <sup>6</sup> is:

$$T = e^{-bt} \left[ \int \phi(t) \cdot dt + c_1 t + c_2 \right] \dots \dots \dots (6)$$

where  $\phi(t) = \int_0^t e^{bt} f(t) \cdot dt$ , and  $c_1$  and  $c_2$  are integration constants.

As an illustration we may consider a first-order reaction, for which

$$f(t) = c_3(1 - e^{-k_1 t}) \dots \dots \dots (7)$$

$c_3$  being a scaling constant and  $k_1$  the first-order rate constant. For the case  $b \neq k_1$  and with the conditions  $t = 0, T = 0, dT/dt = 0$ , and  $t = \infty, T = T_\infty$ , eqn. (7) becomes

$$T = T_\infty [1 - (1 - \alpha)(1 + \alpha + bt)e^{-bt} - \alpha^2 e^{-k_1 t}] \dots \dots \dots (8)$$

in which the quantity  $b/(b - k_1)$  has been written as  $\alpha$ . The implications of (8) become clear when it is rearranged:

$$T_\infty [1 + (\alpha - 1)(1 + \alpha + bt)e^{-bt}] - T = T_\infty \alpha^2 e^{-k_1 t} = T_\infty e^{-k_1(t - t_0)} \dots \dots \dots (9)$$

The left-hand side reduces to  $(T_\infty - T)$  after the initial disturbance in which the exponential term is significant, whilst the first expression on the right-hand side shows that, after this initial disturbance, an ordinary plot of  $\ln(T_\infty - T)$  against  $t$  will give  $-k_1$  correctly as the slope, although the intercept will be  $\ln \alpha^2 T_\infty$  instead of  $\ln T_\infty$ . The second term on the right-hand side shows the alternative interpretation of this latter effect as a time-lag,  $t_0$ , which is related to  $\alpha$  by the expression  $t_0 = (2 \ln \alpha)/k_1$ . For values of  $\alpha$  not greatly different from unity,  $\ln \alpha \sim k_1/b$ ; and hence for practical purposes the time-lag is  $2/b$ , which for a galvanometer period of 1 sec. (*i.e.*,  $b \sim 6 \text{ sec.}^{-1}$ ) amounts to about 0.3 sec. The error in taking the left-hand side of (9) as  $(T_\infty - T)$  is also readily shown to be only 1% of  $T_\infty$  at  $t = 0.5 \text{ sec.}$ , and 0.1% of  $T_\infty$  at  $t = 1 \text{ sec.}$  for  $b = 6 \text{ sec.}^{-1}$ , even when  $k_1 = 0.3 \text{ sec.}^{-1}$ ; *i.e.*, for the fastest reactions which can be studied by this method. For all slower reactions the error in  $(T_\infty - T)$  is negligible, but the time-lag remains at 0.3 sec., although becoming relatively less important as  $k_1$  decreases. In all practical cases, therefore, omission of the initial reading of the galvanometer removes the difficulty completely.

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