[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

Reaction Rates and Heats by the Temperature Rise in a Stirred Flow Reactor[1]

BY MYRON J. RAND AND LOUIS P. HAMMETT[*]

We report herewith on the development of apparatus and methods for the measurement of reaction rate through the determination of the temperature rise in a stirred flow reactor and also on the application of the same method to the measurement of reaction heats in systems whose rates of reaction are such that the usual methods of calorimetry are difficult. Reaction rates have been estimated from temperature rise in a nonflowing system[2] but the determination is complicated by the change in specific rate as the temperature changes. With the stirred flow reactor technique, however, all reaction occurs at a single temperature, that of the reactor. The reaction used in this development was the saponification of ethyl α-hydroxyisobutyrate, but the technique can be applied to any moderately fast reaction of considerable reaction heat.

Principle of the Method

In addition to those of the previous article,[3] the following symbols are used. The time unit is the minute, the volume unit the liter.

ΔT	Observed steady state temperature rise, °C.
ΔT^*	Corrected state temperature rise, °C.
c_0	$\sqrt{a_0b_0}$
C	Average heat capacity of cell contents over range ΔT, cal./deg.-liter
ΔH	Heat evolved per mole of ester reacted, cal./mole
h_1	Heat of stirring, cal./min.
h_2	Heat of mixing at a given flow rate, cal./liter
h_3	Heat loss from cell due to radiation conduction, etc., cal./min.
H_0	Heat content of reactants at thermostat temperature, cal./liter

It is assumed that the heat evolved by the reaction is strictly proportional to the extent of reaction, *i. e.*, to $a_0 - a$, that the heat capacity of the system is unchanged by the reaction, and that the heat losses from the reactor by radiation and conduction at any fixed flow rate are proportional to the temperature difference between the reactor and its surroundings. These assumptions are valid to a satisfactory precision, provided the solutions are dilute and the temperature difference small. On this basis a heat balance for the reactor in the steady state may be set up

$$H_0u + h_1 + h_2u + \Delta H(a_0 - a) = (H_0 + C\Delta T)u + h_3 \quad (1)$$

By virtue of the definition

$$\Delta T^* = \Delta T - h_1/(Cu) - h_2/C + h_3/(Cu) \quad (2)$$

and the equation for a second order reaction in the steady state of the stirred flow reactor

$$(u/V)(a_0 - a) = ka(b_0 - a_0 + a) \quad (3)$$

This can be reduced to

$$\Delta T^* = (\Delta H/2C)(a_0 + b_0 + u/kV - \sqrt{(a_0 + b_0 + u/kV)^2 - 4a_0b_0}) \quad (4)$$

No practical method has been found to obtain the quantities $\Delta H/C$ and k by the application of this equation to a series of experimental data. Fortunately the special case in which a_0 and b_0 differ by not more than a few per cent. is easily achieved experimentally and is more amenable to treatment. The following development is based on a suggestion by Dr. Ernest M. Grunwald. In this case we may replace Eq. 3 by

$$(u/V)(a_0 - a) = k(c_0 - a_0 + a)^2 \quad (5)$$

with an error in k amounting to 0.005% when a_0 and b_0 differ by 3%. From eq. 1, 2 and 5

$$\sqrt{u\Delta T^*/c_0} = \sqrt{V\Delta H/C}\sqrt{k}\,(1 - C\Delta T^*/\Delta Hc_0) \quad (6)$$

Now let $k = \bar{k} + (\mathrm{d}k/\mathrm{d}T)\delta T$ where $\bar{k}$ is the k at the average of the steady state temperatures of a series of experiments at varying flow rate, and δT is the difference between the steady state temperature and this average.

$$\sqrt{k} = \sqrt{\bar{k}},\sqrt{1 + (\mathrm{d}\ln k/\mathrm{d}T)\delta T} = \sqrt{\bar{k}}\{1 + (1/2)(\mathrm{d}\ln k/\mathrm{d}T)\delta T + \cdots\} \quad (7)$$

Substituting (7) in (6)

$$\frac{\sqrt{u\Delta T^*/c_0}}{1 + \frac{1}{2}\frac{\mathrm{d}\ln k}{\mathrm{d}T}\delta T} = \sqrt{\frac{V\Delta H\bar{k}}{C}}\left(1 - \frac{C\Delta T^*}{\Delta Hc_0}\right) \quad (8)$$

The denominator on the left-hand side represents the correction factor for the variation of k with temperature; in these experiments it seldom differs from unity by more than 0.3% and may be neglected to a good first approximation if no estimate for d ln k/dT is available. If the left-hand side of (8) is plotted *vs.* $\Delta T^*/c_0$, a straight line will result whose slope is $-\sqrt{V\bar{k}C/\Delta H}$ and whose intercept at $\Delta T^*/c_0 = 0$ is $\sqrt{V\Delta H\bar{k}/C}$. The product of the slope and intercept is $-V\bar{k}$ and $\bar{k}$ is known.

At the other intercept, where $u = 0$

$$\sqrt{\frac{V\Delta H\bar{k}}{C}} = \sqrt{\frac{VC\bar{k}}{\Delta H}}\frac{\Delta T^*}{c_0} \quad (9)$$

and

$$\Delta H/C = \Delta T^*/c_0$$

so that the intercept on the abscissa axis is $\Delta H/C$.

Experimental

The Temperature Correction Terms.—h_2/C was determined empirically by assuming that it

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[2] Westheimer and Kharasch, THIS JOURNAL, **68**, 1871 (1946).

[3] Saldick and Hammett, *ibid.*, **72**, 283 (1950).

was the sum of the two heats of dilution of the reactants. The heat accompanying the dilution of each reactant with inert material approximating the steady state mixture was observed, and since all the reactants in this research were in dilute aqueous solution, it is believed that the sum is a good approximation; at any rate, the effect is very small, between 0.002 and 0.005°.

The heat of stirring was found to vary slightly from run to run, probably due to varying frictional effects where the stirrer passed through the cell top. A separate h_1/Cu correction was determined for each run by observing the temperature rise when only one reactant was flowing, and correcting the result for the different flow rate. That is, in each run, without disturbing the apparatus, two experiments were done

$$\Delta T_1 = (\Delta H/c)(a_0 - a) + h_1/(Cu_1) + h_2/C - h_3/(Cu)_1 \quad (10)$$

$$\Delta T_2 = k_1/(Cu_2) - h_3'/(Cu_2) \quad (11)$$

If h_3' is known, h_1/Cu_2 is known from (11), and $h_1/Cu_1 = (h_1/Cu_2)(u_2/u_1)$. This assumption that the temperature rise due to stirring is inversely proportional to the flow rate was checked by experiment.

The reaction cell was calibrated for the heat leak factor h_3 by studying the neutralization of sodium hydroxide by hydrochloric acid. For this reaction the $a_0 - a$ of (10) is replaced by the a_0 for the acid, since the base was kept in slight excess to avoid error from carbonate; and the mixing term h_2/C is not included. The assumption that C is the same for the stirring blank is good to 0.5%, and, since the stirring heat is small, introduces no error into the values for the correction terms. With these modifications (10) combined with (11) leads to

$$C(u_1\Delta T_1 - u_2\Delta T_2) - \Delta H u_1 a_0 = -h_3 + h'_3 \quad (12)$$

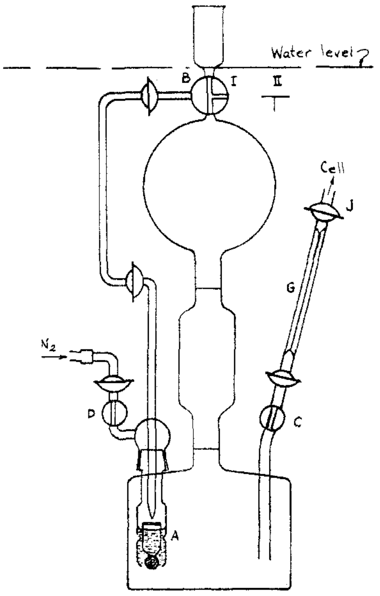

Fig. 1.—Constant flow pipet.

To solve (12), the first assumption to make is $h_3'/\Delta T_2 = h_3/\Delta T_1$ at the two different flow rates, so that

$$h_3'/\Delta T_1 = (h_3'/\Delta T_2)(\Delta T_2/\Delta T_1) = (h_3/\Delta T_1)(\Delta T_2/\Delta T_1) \quad (13)$$

Denoting this first approximation by I, (12) becomes

$$\frac{I_{\mathrm{h}_3}}{\Delta T_1} = \frac{\Delta H u_1 a_0 - C(u_1\Delta T_1 - u_2\Delta T_2)}{\Delta T_1 - \Delta T_2} \quad (14)$$

$h_3/\Delta T_1$ was calculated by (14) for the neutralization experiments and found to change with flow rate, necessitating a second approximation which changed the result by 2%. No further approximations were needed. Comparing (12) and (14)

$$\frac{h_3}{\Delta T_1} = \frac{I_{\mathrm{h}_3}}{\Delta T_1}\,\frac{\Delta T_1 - \Delta T_2}{\Delta T_1} + \frac{h_3'}{\Delta T_1} \quad (15)$$

The last term is small and is obtained with sufficient accuracy from (13).

Materials and Apparatus.—Selection and purification of materials, standardization of solutions for titration, methods of analysis and calibration of equipment met customary standards for precision work. A large thermostat bath with good stirring, a large mercury thermoregulator, and a small (250-watt) heater maintained the temperature of 25.00° with fluctuations of ±0.001°.

The Flow Control.—One of the constant-flow pipets used to regulate and measure the flow of reagents into the reaction cell is diagrammed in Fig. 1. This device, which has not been described in the literature, operates on the principle of the Cartesian manostat, and achieves constant liquid flow into the cell by applying constant liquid pressure through a capillary. At the same time, the flow is accurately measured by displacement by timing the liquid level between the two graduations on the pipet section.

Constant-pressure nitrogen is supplied to the pipet through stopcock D. The gas pressure is regulated by the height of a dibutyl phthalate column, since gas is kept bubbling out slowly at the bottom of the column during a run. A ballast bottle smooths out the slight irregularities due to the bubbling, and a 35-foot coil of $^5/_{16}$ inch copper tubing in the thermostat brings the gas to within 0.001° of bath temperature with even the highest flows.

The successful operation of the pipet depends entirely upon the excellence of the seal which the float A makes against the nozzle. The float top must be covered with soft, very smooth rubber, and the nozzle carefully ground and fire-polished. A thin film of D-C 550 silicone liquid on the rubber aids the sealing but does not cause appreciable sticking; neither does it evaporate nor deteriorate the rubber. The float chamber has four small projections to keep the float free of the walls. When the pipet is operating properly, the motion of the float as it regulates is just barely visible.

The pipet is filled from the stock bottle by gravity through C, with D closed and B turned to position I. After filling, B and C are closed. In operation, the gas pressure is applied first, then D opened. C is opened to start the flow, and finally B is carefully turned to position II. Liquid rises in the float chamber until the float seals the nozzle and regulation starts. Performance of the pipet may be checked by watching the liquid level in the float chamber—as long as this level does not change, the flow passing through C and capillary G to the cell must remain constant, barring capillary plugging.

The total pipet volume is about 850 cc. The dimensions are such that steady state is reached before the liquid level reaches the first graduation. Thus the individual liquid flows are measured accurately while the reactor contents are at steady state and while the readings for ΔT are being taken. It is important that the flow rates be known exactly, since a_0 and b_0 are calculated from the concentration of the solution in the pipet multiplied by the ratio of the flow to the total flow through the cell. The time for the liquid level to pass between the graduations was measured with an electric stopclock to 0.1 sec.; this time varied from seven to twenty-seven minutes.

The total flow and the reactant concentrations in the cell can be controlled by the flow from each pipet. The separate flows, in turn, can be controlled either by the height of the butyl phthalate column or by the capillary diameter. Several interchangeable capillaries with ball joints were used at different times between the pipets and cell.

The pipet performance is illustrated by the following typical experiment. Ten timed samples of from 25 to 35 cc. were collected and weighed while the liquid level in the pipet dropped from near the top of the upper bulb to well down into the lower chamber. The flow rates computed from these samples ranged from 0.1290 to 0.1293×10^{-3} whereas the rate computed from the time required for the level to drop from the upper to the lower graduation and the measured volume included between the graduations was 0.1290×10^{-3}.

When the liquid level has fallen in the lower chamber to about the level of the nozzle, the float will no longer regulate, but constant flow can still be obtained by closing B. Now the gas maintains the pressure by bubbling out the bottom of the float chamber; the driving head has been changed by an amount equivalent to the height of the liquid in the float chamber when in normal operation. The change is about 3%, and the new flow rate can be calculated easily to 1%, which is adequate for the stirring blank runs. The main run was finished when the liquid level had passed the lower graduation, and the stirring heat was determined afterwards with the pipet operating in this fashion, which will be called "float off."

Apparatus for Temperature Measurement.—The observed temperature difference ΔT between the reactant solutions in the pipets—*i. e.*, the thermostat—and the steady state temperature of the cell was measured with thermistors.[4,5] Thermistor is the name given by the Bell Telephone–Western Electric Companies to a semiconducting resistance thermometer of high (ten times that of platinum) negative temperature coefficient of resistance. The thermistors used were designated as Type 14-A by the manufacturer, and had a resistance of about 75,000 ohms at 25°, with a temperature coefficient of −4.8% per degree. Thermistors were aged for a month at 105° before use.

A thermistor and its mounting is diagrammed in Fig. 2. The glyptal cement where the leads emerge from the glass of the thermistor discourages moisture film adsorption between them in humid weather, a necessary precaution with such high resistance elements.

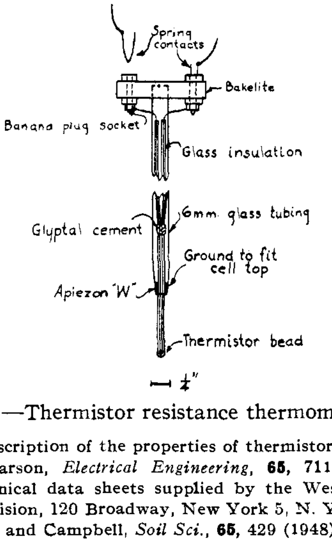

Fig. 2.—Thermistor resistance thermometer.

Figure 3 shows the Wheatstone bridge circuit used for the measurement of ΔT. Thermistor T_1 is in the reaction cell and T_2, which has a much longer glass tubing mounting, is in a test-tube containing water which is immersed well down into the bath, not far from the reactant reservoirs. R_2 was usually set at 5000.0 ohms and R_1 varied to follow T_1. R was set to make the driving potential 1.08 v. and was never disturbed. With this potential the current flowing in the thermistor arms of the bridge was 7.2 microamps, and the power dissipated in each thermistor was 4.3 microwatts. Since the thermistors have a dissipation constant of about six milliwatts/°C. in water, heating of the thermistors is less than 0.001°. A change in R_1 of 0.1 ohm corresponds to 0.0004°, and produces a galvanometer deflection of 0.7 mm. at one meter scale distance; this change is easily detectable. The galvanometer used had a sensitivity of 0.0002 μa/mm. at one meter, a coil resistance of 510 ohms, an external critical damping resistance of 9000 ohms, and was used slightly underdamped. The Wheatstone bridge was constructed entirely of shielded copper wire, and no trouble from stray thermal e. m. f.'s or alternating current fields was experienced.

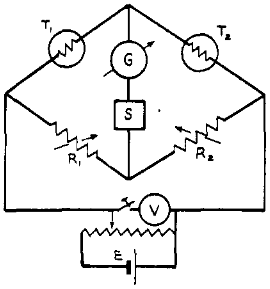

Fig. 3.—Balanced bridge circuit used for measuring small temperature differences: T_1, T_2, Western Electric Co. 14-A thermistors; R_1, R_2, 10,000-ohm. 5-dial resistance boxes, Leeds & Northrup No. 4720; G, Leeds & Northrup HS type galvanometer, No. 2285; R, 120-ohm rheostat; E, Willard DH-5-1 Low Discharge 2-volt storage cell; S, galvanometer control: resistances, tap key and toggle switch; V, voltmeter.

To calibrate the thermistors, T_2 was left in the thermostat in its usual position (clamped to the frame which holds the apparatus) and T_1 was put into a large Dewar filled with water, along with an efficient stirrer and a Beckmann thermometer which had been recently certified by the Bureau of Standards. Temperature in the Dewar was varied over the range 24.5–26.0° by adding a little hot or cold water. This temperature range was covered several times with temperatures both rising and falling. The calibration experiments were done over a period of three weeks, and one or both thermistors were often removed from the apparatus and put away between runs. In all, 132 calibration points were taken.

Thermistors are known to obey approximately the relation $\log R = K/T + \text{const.}$, where R is the resistance and T the absolute temperature. Over the small temperature range used here, the equation seemed to be obeyed exactly, since large scale plots of $\log R_1$ *vs.* $1/T$ gave good straight lines. The slopes of these lines were determined in eight separate calibration experiments, five with a rising and three with a falling temperature, and with from thirteen to eighteen points to an experiment. The resulting values of K ranged from 1834.2 to 1837.4 with an average of 1836.2 and average deviation of ±0.7. The average for the experiments with falling temperature was 1836.0. A recalibration five months later gave 1836.6.

In reading temperature rises, the reading of R_1 was taken with both thermistors in the bath, and then later with T_1 in the cell at the steady state condition. ΔT was calculated by the formula

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[4] For a description of the properties of thermistors, see Becker, Green and Pearson, *Electrical Engineering*, **65**, 711 (1946), and numerous technical data sheets supplied by the Western Electric Co., Radio Division, 120 Broadway, New York 5, N. Y.

[5] Richards and Campbell, *Soil Sci.*, **65**, 429 (1948).

$$\Delta T = \frac{TT' \log R'/R}{K}$$

The Reaction Cell.—The reaction cell assembly is shown in Fig. 4. The cell has a silvered vacuum jacket and an evacuated glass top which is ground to fit. Reactants flow from the pipets through the capillaries and enter the cell through 1-mm. orifices at the end of the inlet tubes. The steady state mixture leaves the cell around the stirrer at F and passes to the overflow chimney; it is not collected or investigated further in any way. The clearance at F, about half a millimeter, is small enough to define the cell volume quite accurately and yet offers little resistance to the flow. In addition to this outlet, the cell top carries a small port whose walls are ground to receive the cell thermistor T_1. W is the water level in the thermostat.

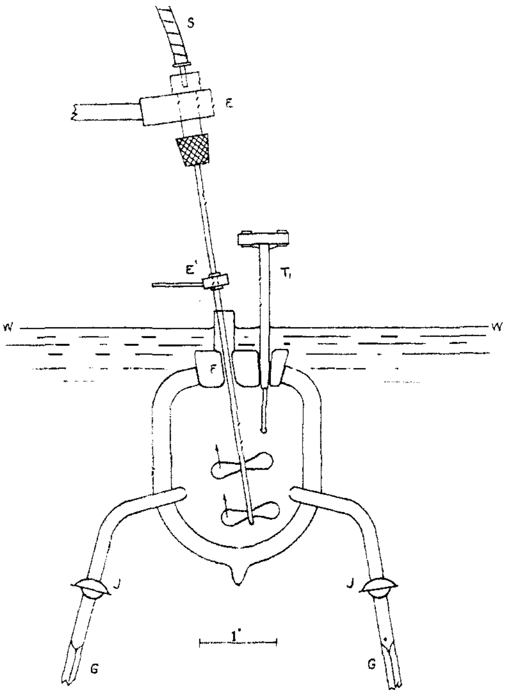

Fig. 4.—Reaction cell assembly.

The all-glass stirrer has two sets of propellors as shown, and is held in alignment by the sleeve bearings EE'. The chuck holding the stirrer is driven by the flexible shaft S, a set-screw in the top of the chuck holding the end of the shaft. The stirrer shaft has a mark which is evened with the top of the overflow chimney to assure reproducible position. The stirrer was driven by a synchronous motor through a variable speed reduction device which provided speeds from 450 to 1750 r. p. m. The speeds were calibrated by a stroboscope and were known to ±10 r. p. m. and constant to much better than this.

The volume of the reaction cell was determined by plugging the inlet arms with corks at J so that when the cell was filled, no water leaked into these tubes. With the stirrer and thermistor in place, the cell was weighed empty and filled; the cell volume at 25° was 0.05585 ± 0.00002 liter.

The capillaries were 0.35–0.55 mm. in diameter, length about 10 cm. for all but the highest flow rates. Ball joints on the capillaries were never greased, but were made tight by thin annular rubber gaskets cut with cork borers from surgeons gloves.

Procedure.—The run was usually started by filling the reservoirs with reagent solutions and the cell with dilute sodium chloride solution at about 28°. By the time the flow was started, the cell temperature was about 25.5°, which is roughly steady state temperature, so that thermal steady state was reached more rapidly than if the cell had started empty. In addition, starting with the cell full minimizes the chance of trapping bubbles beneath the cell top.

After about three hours in the thermostat, the bridge potential was applied, and nitrogen admitted to the butyl phthalate columns. When full pressure had been reached fifteen minutes later, stopcocks D were opened, and the flows started by opening C. The stirrer was started, and the nitrogen flows adjusted so that gas bubbles out at the bottom of the butyl phthalate columns once every few seconds. Finally the floats were put into operation by turning B to II.

The temperature in the cell was followed as it approached steady state; it usually stopped rising well before the liquid levels in the pipets had reached the first graduation. During the time period, the steady state temperature was read at least a dozen times; the readings always fell within a range of 0.001°. If the run was acid–base, a drop of phenolphthalein solution was added to the overflow chimney at this time to make sure that alkali was in excess.

After the lower graduation had been passed, the run was stopped by closing C. The stirring was turned off and T_1 removed from the cell and put into a test-tube of water immersed in the thermostat. While T_1 was coming to thermostat temperature, the cell contents were removed by a pipet inserted through the thermistor port. 25° water from the thermostat enters the cell to take the place of the removed steady state mixture. After this process had been repeated several times, the cell was practically at thermostat temperatures.

As soon as a good resistance reading had been obtained with T_1 in the reservoir—*i. e.*, for both thermistors at the same temperature—T_1 was replaced in the cell and the run to determine the stirring heat started. For this only one pipet was used (usually the hydrochloric acid in neutralization runs and the sodium hydroxide in saponification runs) and the pipet was operated in the "float off" condition.

With the stirrer and one pipet operating, the temperature was again followed until steady state had been reached. Afterwards T_1 was put into the test-tube again and the bridge reading at thermostat temperature rechecked. There was usually no significant change in this reading between the two halves of the experiment.

Results

In calculating the results of the neutralization experiments to determine $h_3/\Delta T$, a suitable ΔH and C for the reaction between 0.1 m hydrochloric acid and sodium hydroxide at the steady state temperature must be chosen.[6] The most recent calorimetric value for the ΔH at infinite dilution (heat of ionization of water) as given by Pitzer[7] is ΔH_i^0 = 13,367 cal./mole at 25° with a temperature coefficient of −50 cal./deg. Relative partial molal heat contents for solute and water for sodium hydroxide solutions are given by Harned and Hecker[8] and Sturtevant[9]; for hydrochloric acid solutions by Harned and Ehlers[10]; and for sodium chloride solutions by Robinson.[11] The "best values" calculated from these data for the heats of neutralization are

$$\Delta H = -13{,}485 \text{ cal./mole at } 25.7°, \ m = 0.1 \ (a_0 = 0.05)$$
$$= -13{,}480 \text{ cal./mole at } 25.4°, \ m = 0.07 \ (a_0 = 0.035)$$

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[6] Wherever irreconcilable discrepancies in thermodynamic quantities between the calorimetric and e. m. f. methods appear in the literature, the calorimetric values have been used, since these experiments are primarily calorimetric.

[7] Pitzer, THIS JOURNAL, **59**, 2365 (1937).

[8] Harned and Hecker, *ibid.*, **55**, 4838 (1933).

[9] Sturtevant, *ibid.*, **62**, 2276 (1940).

[10] Harned and Ehlers, *ibid.*, **55**, 2179 (1933).

[11] Robinson, *ibid.*, **54**, 1311 (1932); Gulbransen and Robinson, *ibid.*, **56**, 2637 (1934).

TABLE I

DETERMINATION OF RATE CONSTANT

ΔT	$h_3/(Cu_1)$	$h_1/(Cu_1)$	ΔT^*	b_0	a_0	10^3u_1	$\Delta T^*/c_0$	$\frac{\sqrt{u\Delta T^*}}{c_0}$	Dev. from Fig. 6 line
0.780	0.0280	0.0181	0.787	0.10044	0.09792	13.897	7.936	1.0535	0.0075
.760	.0269	.0137	.770	.09868	.09700	14.015	7.870	1.061	.002
.772	.0273	.0814	.778	.10054	.09725	14.036	7.868	1.0555	− .004
.638	.0083	.0065	.6355	.10008	.09804	28.065	6.416	1.352	.004
.6675	.0107	.0083	.666	.09909	.09922	24.315	6.717	1.286	− .002
.715	.0165	.0096	.7185	.09958	.09889	18.980	7.240	1.1775	− .0065
.8245	.0548	.0095	.867	.09831	.09918	8.700	8.780	0.877	− .001
.3115	.0106	.0132	.307	.04950	.04956	14.457	6.285[a]	1.3725[a]	− .0015
.3285	.0111	.0132	.3245	.05409	.04960	14.511	6.352[a]	1.351[a]	− .0095
.317	.0108	.0143	.3115	.05025	.04965	14.470	6.321[a]	1.3715[a]	.005

[a] For the lower concentrations, both ordinate and abscissa have an additional correction besides that for δT; see text.

The heat capacity C of the steady state is assumed to be that of the sodium chloride solution resulting from the neutralization. The most recent values for the specific heats of dilute sodium chloride solutions are those of Hess and Gramkee.[12] These yield 0.9946 cal.$_{15}$/g. at 25°, $m = 0.05$, and 0.9960 at $m = 0.035$. Combined with densities of 0.9991 and 0.9985, respectively (determined by pycnometer), the values of C are

$$C = 993.7 \text{ cal.}_{15}\text{/deg.-liter at } 25°,\ m = 0.05$$
$$= 994.5 \text{ cal.}_{15}\text{/deg.-liter at } 25°,\ m = 0.035$$

Using the above values of ΔH and C, $h_3/\Delta T_1$ was calculated from (14) and (15). The results are graphed in Fig. 5 as a function of flow rate together with a bar which indicates what uncertainty in $h_3/\Delta T_1$ would give rise to an error of 0.002° in ΔT^* for the saponification runs.

With $h_3/\Delta T_1$ for any flow rate taken from Fig. 5, the heat loss correction h_3/Cu_1 for any observed ΔT_1 can be readily calculated. In (11) h_3' may now be taken from $h_3'/\Delta T_2 = h_3/\Delta T_1$, and h_1/Cu_2 calculated. Now h_1/Cu_1, the stirring heat term, is known, and only the mixing term of (2) remains to be determined before ΔT^* is known.

The dilution heats of sodium hydroxide and of the ester were studied to decide upon the value of the mixing heat term. In one experiment, 0.2 m sodium hydroxide was diluted with 0.2 m ethyl alcohol; the steady state temperature rise was 0.0014°. (For the dilution of 0.2 m sodium hydroxide with water in the proportions used in this run, Sturtevant[13] predicts 0.0014°). Two experiments on the dilution of the ethyl α-hydroxyisobutyrate, 0.2 m, with 0.2 m sodium chloride and with water, gave temperature rises of 0.0064° and 0.0076°, respectively. It was considered that the heat of mixing of 0.2 m ester and sodium hydroxide solutions (the highest concentrations used in this work) if no reaction takes place is 0.008°. Using an approximate k, $a_0 - a$ may be calculated and divided by c_0 to get the degree of conversion, in order to decide what fraction of the reactants contributes only to this mixing heat. The extent of conversion varied between 48 and 67%, with corresponding mixing corrections of about 0.0045 and 0.0025°. These figures are for $c_0 = 0.1$; for the runs at $c_0 = 0.05$, it was assumed that the heat of mixing with linear with $\sqrt{m}$. The degree of conversion for the lower concentration was about 48% and the mixing correction is about 0.002°.

With ΔT^* known, (8) may be tested. From the date of Salmi and Leino,[14] d ln k/dT = 0.064 (activation energy = 11.5 kcal./mole). The inclusion of this term in the ordinate of the plot of (8) changes its values only very slightly, the maximum correction being 0.3%. The results of some experiments at varying flow rate to determine the rate constant are found in Table I.

The runs at the lower concentration were in-

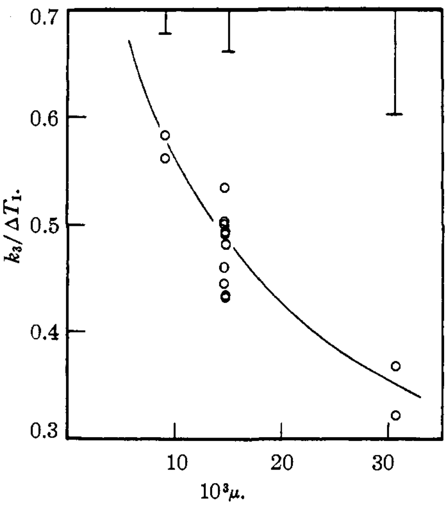

Fig. 5.—Dependence of the heat loss from the cell on flow rate. The experimental points are first approximations calculated by (14); the line is the second (final) approximation from (15). The bars at the top of the figure indicate the uncertainty in the heat loss factor which would give rise to an error of 0.002° in ΔT^* for the saponification runs.

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(12) Hess and Gramkee, *J. Phys. Chem.*, **44**, 483 (1940); Hess, *ibid.*, **45**, 755 (1941).

(13) Sturtevant, ref. 9 and THIS JOURNAL, **64**, 762 (1942).

(14) Salmi and Leino, *Suomen Kemistilehti*, **17B**, 19 (1940).

cluded to see if the method can distinguish between first and second order kinetics, since changing the concentration is an exacting test of reaction order. If these points are to be plotted with the others, however, an additional correction is necessary—that due to the difference in $\Delta H/C$ between the two concentrations (see eq. 8). Once k is found, $\Delta H/C$ may be determined separately for each run from (4), the general second order expression, as well as from the intercept by (9), which gives the average value. With the average values of $\Delta H/C$ known for the two concentrations, the correction to be applied to ordinate and abscissa to plot the lower concentration runs on the graph of (8) is evident. The results for $\Delta H/C$ are discussed below.

The data of Table I are plotted according to (8) in Fig. 6, and according to the equation

$$\frac{a_0}{\Delta T^*} = \frac{C}{\Delta H} + \frac{C}{kV\Delta H}u$$

which may be shown to be applicable if the reaction followed first order kinetics, in Fig. 7. It is immediately evident that (8) is obeyed well, that the kinetics are second order, and that the technique can distinguish second from first order kinetics without difficulty.

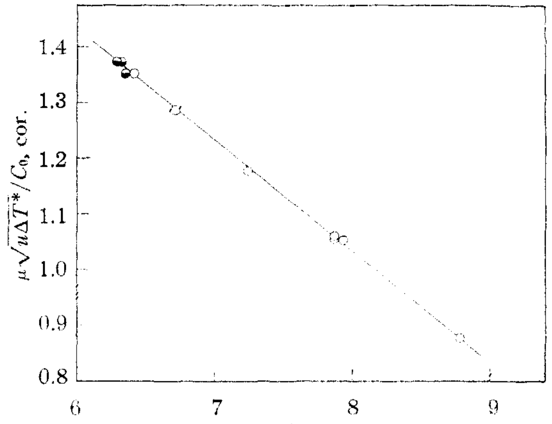

Fig. 6.—Plot according to (8), the second order equation: ○, C_0 = 0.1; ◒, C_0 = 0.05.

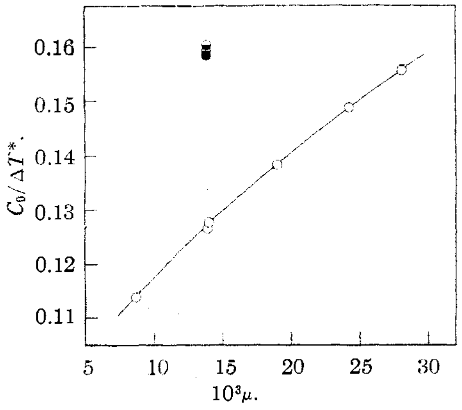

Fig. 7.—Plot according to (16), the first order equation: ○, C_0 = 0.1; ◒, C_0 = 0.05.

By least squares calculation, the slope in Fig. 6 is −0.1987 ± 0.0019 p. e. The intercept at $\Delta T^*/c_0$ = 2.623 ± 0.014 p. e. The product of the two = $-V\bar{k}$ and $\bar{k}$ = 9.33 ± 0.10 liter/mole-min. at 25.73°, the average observed temperature. (In these calculations only the points at c_0 = 0.1 are considered, since any change in the concentrations introduces the complication of the change in $\Delta H/C$.) Using the d ln k/dT of Salmi and Leino, the k at 25.00° is 8.90.

By the method of continuous titration of the output from a stirred flow reactor a value of k at 25.00° for the saponification of this ester of 8.90 ± 1% has been obtained.[3] We have further carried out this reaction by the usual batch technique with the apparatus and procedure specially modified for fast reactions; a thermometer was included to correct for temperature rise as well as possible, and the reaction vessel was stirred continuously with a magnetic stirrer. The result of this determination was k = 9.02 ± about 1.2%.

The intercept on the abscissa axis in Fig. 6, which corresponds to $\Delta H/C$ for c_0 = 0.1, is 13.20. By choosing the proper value of k for the observed steady state temperature a value of $\Delta H/C$ for each run may be obtained from (4). For the runs at c_0 = 0.1 and at a temperature of 25.7° the average value of $\Delta H/C$ obtained in this way is 13.20 with an average deviation of ±0.02; for the runs at c_0 = 0.05 and at a temperature of 25.3° the value is 13.02 with an average deviation of ± 0.03.

It has not been thought worth while in this work to undertake an elaborate analysis of the variation of C and ΔH with extent of reaction, partly because specific heat data for dilute water solutions of organic compounds have not been reported, and partly because no significant trends appear in the results for $\Delta H/C$. The values for ΔH of the reaction will, of course, be limited by the uncertainty in C, but it is believed that C = 995 for c_0 = 0.1 and 997 for c_0 = 0.05 cannot be far in error.[15] The corresponding ΔH's are 13.27 and 13.06 kcal./mole.

The Effect of Stirring Rate.—Several runs were made to see if the stirring speed was critical, and the $\Delta H/C$ for each calculated as a test. These runs, summarized in Table II, all had about the same ΔT; the data at 990 r. p. m. represent the average of three experiments. At the lowest stirring speed, 550 r. p. m., the thermistor was able to detect slight inhomogeneities in the cell.

Evidently adequate stirring is no problem.

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[15] Specific heats of dilute sodium hydroxide solutions are given by Gucker and Schminke, THIS JOURNAL, **55**, 1013 (1933). Their values, combined with the densities determined by pycnometer, give C = 992.8 for 0.2 m, and 994.3 for 0.1 m. It is known that dilute water solutions of organic compounds usually give specific heats differing less from that of pure water than do ionic solutions—see, for example, data on isobutyric acid solutions reported by Davies, *J. Chem. Soc.*, 1166 (1935).

TABLE II

EFFECT OF STIRRING SPEED

Stirring speed, r. p. m.	Stirring heat, h_1/Cu_1, °C.	$\Delta H/C$
550	0.0028	13.22
800	.0077	13.16
990	.0167	13.21
1125	.0182	13.18
1250	.0249	13.17

In most of the runs of this work a stirring speed of about 1000 r. p. m. was used, with occasional higher speeds at fast flow rates or lower speeds in slow runs, since in addition to sufficient stirring, a minimum stirring heat was desirable.

Summary

By the study of the temperature rise in a stirred flow reactor, a method has been developed which yields accurate rate constants and heats of reaction for quite rapid reactions. The rate and heat of saponification of ethyl α-hydroxyisobutyrate in aqueous solution has been determined under conditions for which the reaction half-time was as little as seventy seconds, and the temperature rise as little as 0.3°. The results are in excellent agreement with other precision determinations of this rate. The method distinguishes between first and second order kinetics, and does not depend upon any analytical determination of the product or reactant concentrations.

Heat leak, stirring and mixing corrections which must be applied to the observed steady state temperature rise are discussed and the method for their evaluation given.

Thermistor resistance thermometers have been used in a balanced Wheatstone bridge to measure fractions of a degree to 0.1% or better.

A device has been described which both maintains constant liquid flow and measures the flow by displacement.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, HARVARD UNIVERSITY, AND FROM THE DEPARTMENT OF COLLOID SCIENCE, UNIVERSITY OF CAMBRIDGE, ENGLAND]

The Topochemical Alkaline Hydrolysis of Cellulose Acetates. I. The Kinetics of Alkaline Hydrolysis of Sugar Derivatives

BY BERNARD RABINOVITCH[*,1] AND A. E. ALEXANDER[1a]

Introduction

The reactivity of a swollen cellulose derivative in a chemical exchange depends essentially on its physical condition in the swollen phase, since, other things being equal, this will determine the accessibility of the reaction sites in the polymer chain to the reacting ion or molecule.

Two limiting cases may be considered. In the first, the polymer phase is so highly swollen that the diffusion rate of the reacting ion or molecule to the reaction sites, and of the reaction products away from there, is very much greater than the rate of the chemical exchange.[2] Here, this latter rate is the over-all rate-determining process and gives rise to a "topochemical permutoid reaction" in which the kinetics of homogeneous reactions in solution hold.[3]

In the second case, the polymer phase maintains sufficient of its physical structure in the dry state to slow down the rate of the diffusion process much below that of the chemical reaction. Here, diffusion is the rate-determining step in the over-all reaction, giving rise to "topochemical heterogeneous" conditions, and consequently we must introduce into the kinetic equation a linear diffusion coefficient in order to describe it completely.[4]

When a cellulose acetate is saponified in a topochemical permutoid system, the kinetics of the reaction are complicated by the existence in the polymer molecule of reaction sites of different reactivity, characteristic of primary (6-position) and secondary (2- and 3-positions) ester groups, besides possible steric effects introduced through interference of adjacent acetate groups in the secondary positions. In the topochemical heterogeneous reaction, differences in reactivity in the same chain arise because of the different degrees of swelling attained by the amorphous and the crystalline regions of the cellulose acetate. In fact, we may expect to find, between these two limiting cases, a range of conditions in which a polymer chain, or a part of one, reacts under permutoid conditions at one time during the reaction and heterogeneously at another.

In this paper, we shall concern ourselves with investigating the alkaline hydrolysis, under homogeneous conditions, of sugar esters simpler than, but chemically similar to, cellulose acetate. In this way we may study the difference in reactivity arising solely from the chemical characteristics

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[*] Harvard University Eli Lilly Research Fellow 1948–1949.

[1] Present address: Department of Chemistry, Illinois Institute of Technology, Technology Center, Chicago 16, Illinois.

[1a] Present address: Department of Chemistry, New South Wales University of Technology, Broadway, Sydney, Australia.

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[4] K. Atsuki and M. Ishiwara, *Proc. Imp. Acad., Japan*, **4**, 382 (1928).