[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Kinetics of the Reduction, in Acid Solution, of Hydrogen Peroxide by Iodide Ion

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Introduction

The first successful quantitative investigation in chemical kinetics, completed in 1866 by Harcourt and Esson,[1] proved that the rate of the reaction

$$H_2O_2 + 2H^+ + 3I^- = 2H_2O + I_3^- \tag{1}$$

is proportional to the amounts of peroxide and iodide present, and that it is "accelerated" by the addition of acid. A quarter century later Magnanini,[2] in a remarkable investigation, which we shall subsequently consider in some detail, demonstrated how this "acceleration" is related to the acid added. Noyes,[3] interested chiefly in clarifying the fundamental concept "order of a chemical reaction," was the first to point out that Magnanini's results and those of Scott[3a] followed a differential equation of the form

$$d(I_3^-)/dt = k_1^\circ(H_2O_2)(I^-) + k_1(H_2O_2)(I^-)(H^+) \qquad (2)^4$$

He regarded the "accelerating" action of hydrogen ion as catalytic even though this substance is consumed in the reaction. Other investigators,[5] however, have preferred to interpret Equation 2 in terms of two independent rate-determining steps, which may be formulated

$$H_2O_2 + I^- \xrightarrow{k_1^\circ} H_2O + IO^- \tag{3}$$

$$H_2O_2 + H^+ + I^- \xrightarrow{k_1} H_2O + HIO \tag{4}$$

Reaction 3 is a compensating reaction in the catalytic decomposition of hydrogen peroxide by the iodine–iodide couple, which has been much investigated;[6] Reaction 4, however, seems to have been studied recently only as a means of determining hydrogen peroxide.[7] Consequently, the specific rate of the former reaction ($k_1^\circ = 0.69$ at 25°) is well established, while no very accurate value can be assigned to that of the latter.[8]

Reactions whose rate laws involve hydrogen ion in the manner of Equation 2 are not very common; one of this type is the reduction of

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(1) (a) Harcourt and Esson, *Phil. Trans. Roy. Soc.*, **157**, 117 (1867) (second paper) and (b) Harcourt, *J. Chem. Soc.*, **20**, 460 (1867).

(2) Magnanini, *Gazz. chim. ital.*, **21**, 476 (1891).

(3) (a) Noyes, *Z. physik. Chem.*, **18**, 119 (1895); (b) **19**, 601 (1896).

(4) As in previous communications, ( ) will be used to denote concentrations in moles per liter, and $\longrightarrow$ will be restricted to reactions which may be rate-determining.

(5) Bray, *Z. physik. Chem.*, **54**, 463–97 (1906).

(6) (a) Abel, *ibid.*, **136**, 161 (1928); **96**, 1 (1920). In the latter reference, a comprehensive historical summary of earlier work by Abel and others is given. (b) Liebhafsky, THIS JOURNAL, **54**, 1792 (1932); (c) *ibid.*, **54**, 3499 (1932).

(7) Bray and Livingston, *ibid.*, **50**, 1654–65 (1928).

(8) For these constants at 25°, Bray in 1906 chose the values $k_1^\circ = 0.60$ and $k_1 = 16$; since the first value is too low, the second is probably too high.

iodate by hydrogen peroxide,[9] the study of which suggested a reinvestigation of Reaction 1 in order that accurate values for the heats of activation of Reactions 3 and 4 might be secured for comparison with those of the corresponding rate-determining steps involving iodate ion. Such a reinvestigation may be regarded, also, as contributing to research of a more general type that has long been under way in this Laboratory,[6a,b,9,10] namely, the interaction of hydrogen peroxide and iodine compounds of all valences. Further, Reactions 3 and 4 are simple, and their rates can be measured accurately; consequently, they are well adapted to studies of the kinetic salt effect. And, finally, they possess low apparent heats of activation so that they may be investigated over a considerable range of temperatures for the purpose of determining how these heats vary with the temperature.

The Experimental Method

Results Obtained at 25°.—An examination of Equation 1 will reveal that tri-iodide ion is formed as the reaction proceeds; the simplest experimental conditions obtain when no appreciable change in the concentration of iodide ion results from such complex ion formation. One way of realizing these conditions is by using an amount of hydrogen peroxide so small that no great change in (I^-) has resulted when reaction is complete; if (H^+) and (I^-) are comparable, then (H^+) also will be (nearly) constant during the experiment. Under these conditions the rate law, Equation 2, will assume the simple form

$$d(I_3^-)/dt = -d(H_2O_2)/dt = k'(H_2O_2) = [k_1^\circ(I^-) + k_1(H^+)(I^-)](H_2O_2) \qquad (5)$$

So long as the experimental method employed shows k' to be unchanged during the course of an experiment, average values of (H^+) and (I^-) may be used to calculate k_1° and k_1. All experiments that were carried out by the method described below (the "analytical method") meet this test.

In such experiments all the reaction mixture (c. p. sodium iodide and perchloric acid were used) except the peroxide, contained in a glass-stoppered flask, was placed in a thermostat at the desired temperature and shielded from direct light. After temperature equilibrium had been reached, a measured volume of hydrogen peroxide solution from a reservoir in the bath was added to start the reaction, zero time being taken when the addition was half complete. From time to time 25-cc. samples were withdrawn with a pipet and permitted to flow into 125 cc. of water at 0°, in order to retard Reaction 1 by cooling and dilution. The time of sampling

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(9) Liebhafsky, This Journal, **53**, 896 (1931). No completed investigations are available, but the preliminary results obtained in this Laboratory by Liebhafsky indicate definitely that the rate laws for the reduction of hydrogen peroxide by bromide and by chloride ions have the form of Equation 2; the approximate values at 25° of the specific rates for the steps analogous to Reaction 3 are 2×10^{-7} (chloride) and 2.3×10^{-5} (bromide).

(10) (a) Bray and Liebhafsky, This Journal, **53**, 38 (1931); (b) Bray and Caulkins, *ibid.*, **53**, 44 (1931); (c) Liebhafsky, *ibid.*, **53**, 2074 (1931); (d) Bray, *Chem. Rev.*, **10**, 172 (1932).

was recorded as the time when the pipet was half emptied. So soon as was convenient,[11] these samples were titrated with a 0.004 *N* thiosulfate solution. The increase in the thiosulfate titer of the samples served to measure the rate of Reaction 1.

The evaluation of k', which is independent of concentration units, is easily accomplished. If a represents the thiosulfate titer of a sample when reaction is complete, and x represents this quantity at time t, then

$$d(x)/dt = k'(a - x) \qquad (5a)$$

for a is proportional to the initial (H_2O_2), and $(a - x)$ to (H_2O_2) at time t. Values of log $(a - x)$ for experiments done by this method were plotted as ordinates against the time (*cf.* Fig. 1 and Table I); the slopes of the resulting straight lines, when multiplied by 2.303, gave the values of k' for these experiments.

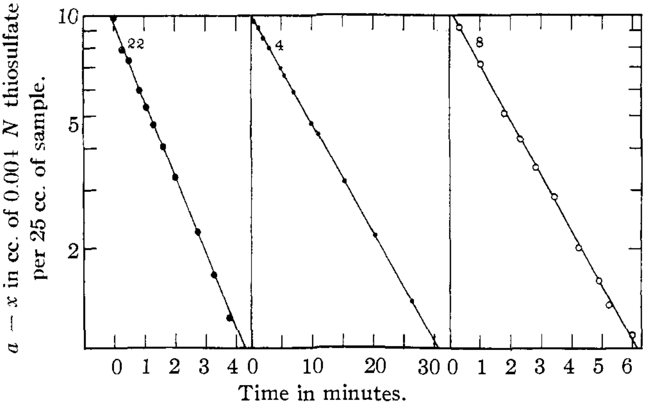

Fig. 1.—Detailed experimental results at 25°. The plot is on *semi-logarithmic* paper. The composition of each reaction mixture is given in Table I (*cf.* footnote b).

To obtain k_1^0 and k_1, values of k' obtained from experiments at various concentrations of iodide and of hydrogen ion are necessary. If Equation 5 is valid, experiments at constant (H^+), but at different (I^-), should yield

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[11] A sample was usually titrated within one minute after its withdrawal; in exceptional cases, when successive samples were taken rapidly, titration was postponed longer—but never for more than ten minutes. During the interval between the time of a sample and the time of its titration, the samples were kept in the dark at 0°.

The amount of iodine formed in a sample while it awaited titration was obtained as follows. Before the beginning of a run a blank, having the volume and composition that would result from diluting a sample of the reaction mixture before iodine formation had begun, was prepared and kept in the dark at 0°. When the experiment was over this blank was titrated with thiosulfate. If C represents the amount of iodine formed during this time (t minutes), then C/t represents the rate of its formation (C is so small that (H^+) and (I^-) and (H_2O_2) in the sample may be regarded constant). If Δt minutes have elapsed between the time of dilution and the time of titration in a sample of reaction mixture, the iodine formed in this interval is equivalent to $(\Delta t/t) \times ((a - x)/a) \times C = d$; the second factor corrects for the difference in the peroxide concentrations of the blank and of the actual sample (*cf.* Equation 5a above). This amount of iodine, d, which must be subtracted from the iodine equivalent to the thiosulfate titer of a sample, was always small; it seldom exceeded 0.5% of the latter, and was usually very much less.

k' values that lie on a straight line intersecting the origin when these are plotted as ordinates against (I^-); from the slope of this line, which is equal to $k_I^\circ + k_1(H^+)$, the specific rates are easily calculated. Curve I, Fig. 2, gives the results of a series of such experiments; its slope has the value 1.128. If, on the other hand, (I^-) is kept constant for a series of experiments, and (H^+) is varied, Equation 5 demands that the resulting k' (or $k'/(I^-)$) values yield a straight line intersecting the ordinate axis when they are plotted against (H^+) as abscissa. If $k'/(I^-)$ values are thus plotted, the intercept on the ordinate axis should give directly the value of k_I°; the slope, that of k_1. Curve II, Fig. 2, represents the results of two such series of measurements: its intercept yields $k_I^\circ = 0.69$, in perfect agreement with the recent measurements of

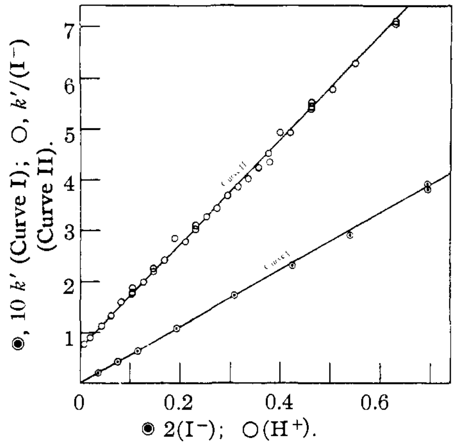

Fig. 2.—Summary of rate measurements at 25° in perchloric acid–sodium iodide solutions.

TABLE I

EXPERIMENTAL RESULTS AT 25°. INITIALLY (H_2O_2) IS APPROXIMATELY $8(10^{-4})$ MOLES/LITER. AVERAGE VALUES FOR (H^+) AND (I^-) ARE GIVEN

Data for Curve I, Fig. 2 $(H^+) = 0.0413$; (I^-) variable		Data for Curve II, Fig. 2 $(I^-) = 0.0572$; (H^+) variable				Data for Curve II, Fig. 2 $(I^-) = 0.0614$; (H^+) variable	
$(I^-) \times 10^2$	$k' \times 10^2$	$(H^+) \times 10^2$	$k'/(I^-)$	$(H^+) \times 10^2$	$k'/(I^-)$	$(H^+) \times 10^2$	$k'/(I^-)$
1.86	2.1	0.762	0.770	37.7	4.51	10.4	1.81
3.78	4.2	2.03	.893	42.0	4.92	10.4	1.76
5.71	6.4	4.20	1.120	46.2	5.38	10.4	1.78
9.58	10.8	6.23[b]	1.320	46.2	5.44	14.6	2.18
15.40	17.3	8.34	1.608	46.2	5.52	14.6	2.25
21.20	23.0	12.55	1.98	50.4	5.78	18.8	2.84
27.00	29.0	16.76	2.41	55.0	6.28	23.0	3.03
34.71[b]	38.0	20.97	2.78	63.1	7.10	23.0	3.10
34.71	39.2	25.18	3.27	63.1	7.05	27.3	3.43
$k_I^\circ = 0.69$;		29.38	3.68	84.1[b]	9.20[c]	31.5	3.86
	$k_1 = 10.6$	33.60	4.01	$k_I^\circ = 0.69$;		35.7	4.23
		37.8	4.33		$k_1 = 10.4$	39.9	4.92
						$k_I^\circ = 0.69$;	$k_1 = 10.4$

[a] Initial (final) values of (H^+) and (I^-) may be obtained by adding (subtracting) $8(10^{-4})$ moles/liter to (from) the average concentrations.

[b] In Fig. 1, $(I^-) = 0.3471$ is No. 8; $(H^+) = 0.0623$ and 0.841 are Nos. 4 and 22, respectively.

[c] This value of $k'/(I^-)$ coincides exactly with Curve II, but it could not be plotted in Fig. 2 because of the restricted scale.

Liebhafsky;[6b] its slope, 10.4, gives the value of k_1; both values are for 25°. Using $k_1^\circ = 0.69$ and $(\mathrm{H}^+) = 0.0413$, the acid concentration corresponding to the k' values for Curve I, $k_1 = 10.6$, is obtained from the slope of this curve. The agreement of these independently obtained values of k_1 is satisfactory. We may thus consider Equation 5 to be established definitely over a concentration range sufficiently large.

Reëxamination of Magnanini's Data.—The desirability of comparing Magnanini's results with ours led us to reëxamine his data.[12] It was then observed that Magnanini's rate constants decreased during each run, and that this decrease became pronounced earlier in experiments in which the absolute rates were higher; *e. g.*, in experiments at high (H^+). In Table II are given the data for the experiments with the lowest (in which only hydriodic acid was used to furnish H^+) and the highest (H^+) in his series of measurements with hydrochloric acid. Values of $\Sigma(\mathrm{I}_2)$, the sum of (I_2) and (I_3^-), are those given by Magnanini; and the concentrations of I_3^- were computed with the aid of the equilibrium constant $(\mathrm{I}^-)(\mathrm{I}_2)/(\mathrm{I}_3^-) = 0.00140$ at 25°.[13] The "corrected" values of $k'/(\mathrm{I}^-)$ resulted from Magnanini's when the latter were multiplied by $[(\mathrm{I}^-) + {}^1/_2(\mathrm{I}_3^-)]/(\mathrm{I}^-)$.[14] Although this correction is only approximate, the constancy of the "corrected" values is sufficiently good to leave no doubt that failure to consider the diminution in (I^-) resulting from I_3^- formation caused Magnanini's rate constants to decrease as the reaction proceeded.

In Fig. 3 Magnanini's results with the strong acids are plotted, the values of $k'/(\mathrm{I}^-)$ used corresponding to measurements over the first time interval at each concentration of acid; correction for I_3^- formation has been made.[14] The slope of the line is 11.0, a value of k_1 in excellent agreement with ours. Had no correction for I_3^- been made, and Magnanini's results plotted as he gives them, this agreement would not have been altered, since this correction is very small during the initial time intervals; a plot of his

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[12] The results of Scott[3a] cannot yield an accurate measure of k_1, since (H^+) in his experiments varied only from 0.005 to 0.020; under these conditions Reaction 4 contributes less than 25% to the absolute rate.

[13] Jones and Kaplan, THIS JOURNAL, **50**, 1485 (1928).

[14] Magnanini obtained $C(100\ C = k'/(\mathrm{I}^-)$; the factor 100 is necessary because of a difference in concentration units) from the integrated form

$$C = \frac{1}{t}\,\frac{1}{2a - 2x} - \frac{1}{2a}$$

of the second order rate law for the special case $2a = b$ (we have used only those of his experiments in which this restriction holds). Here a and x have the meanings of Equation 5a and b represents the initial (HI), also the initial (I^-). x further represents $\Sigma(\mathrm{I}_2)$ at time t; $\Sigma(\mathrm{I}_2) = (\mathrm{I}_2) + (\mathrm{I}_3^-)$. Now, this evaluation of C implicitly assumes that $(\mathrm{I}^-) = (b - 2x)$ as the reaction proceeds; and, since $(b - 2x)$ really represents $(\mathrm{I}^-) + (\mathrm{I}_3^-)$, values of C will be too small when (I_3^-) is appreciable. At time t the rate calculated by use of C (or of $k'/(\mathrm{I}^-)$) must be multiplied by $[(\mathrm{I}^-) + (\mathrm{I}_3^-)]/(\mathrm{I}^-)$ if the actual rate is to be obtained; at $t = 0$, however, (I_3^-) is negligible and this multiplicative factor is $(\mathrm{I}^-)/(\mathrm{I}^-)$, or unity. The mean of these two factors, or $[(\mathrm{I}^-) + {}^1/_2(\mathrm{I}_3^-)]/(\mathrm{I}^-)$ may thus be used as an average correction for C, if this rate constant has been calculated for the interval $t = 0$ to $t = t$; multiplication of C by this average factor will give approximately the value that would have been obtained had the correction for I_3^- formation been included in the differential equation for the rate; the evaluation of C from this exact expression for the rate would naturally be very laborious.

TABLE II

DETAILED RESULTS OF TWO EXPERIMENTS BY MAGNANINI

(a) "No acid added" (Ref. 2, p. 479)

Initially, $(H^+) = (I^-) = 2(H_2O_2) = 0.0111$; temperature, 25°

Time in minutes	5	15	30	60	120
$\Sigma(I_2) \times 10^4$	2.40	6.40	11.10	17.85	25.35
$(I_3^-) \times 10^4$	2.00	5.00	8.2	11.8	13.5
Magnanini $k'/(I^-)$	0.82	0.78	0.75	0.71	0.63
Corrected $k'/(I^-)$	.83	.80	.79	.77	.71[a]

[a] The remaining decrease in the "corrected" values is due principally to the decrease in (H^+) resulting from the progress of Reaction 1; this causes a decrease in the rate of Reaction 4, for which Magnanini made no allowance in his calculations. The corrected values for the "50 HCl" experiment are much more nearly constant.

(b) "50 HCl" (Ref. 2, p. 482)

Initially, $(I^-) = 2(H_2O_2) = 0.0111$; $(H^+) = 0.567$; temperature, 25°

Time in minutes	3	5	8	10	12	14
$\Sigma(I_2) \times 10^4$	1.01	1.47	1.97	2.25	2.47	2.64
$(I_3^-) \times 10^4$	7.5	10.0	12.0	13.0	13.6	13.8
Magnanini $k'/(I^-)$	6.66	6.44	6.19	6.12	5.98	5.84
Corrected $k'/(I^-)$	7.03	6.90	6.76	6.80	6.75	6.70

uncorrected constants yielded $k_1 = 10.6$, in perfect agreement with the results from Fig. 2.

With hydrochloric and nitric acids Magnanini obtained identical results over the entire concentration range he studied; but with sulfuric acid he found that the effectiveness of the acid in "accelerating" Reaction 1 decreased with the stoichiometric concentration thereof, as the solid circles in Fig. 3 show. This decrease is due principally to an increase in the concentration of the weak acid, HSO_4^-, at the higher concentrations of sulfuric acid; for this reason the ratio $(H^+)/\Sigma(H^+)$ becomes smaller as (H_2SO_4) increases. If kinetic salt effects are absent, rate measurements may, under proper conditions, yield the dissociation constant of HSO_4^-, a circumstance which has already been turned to use in this Laboratory.

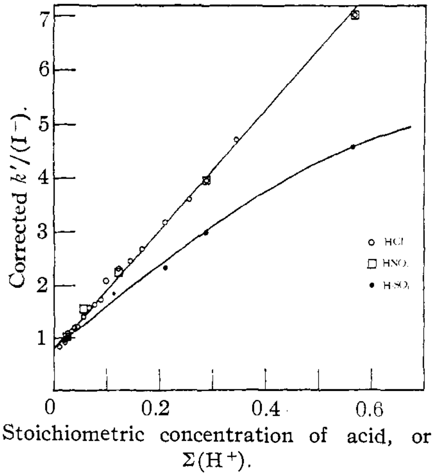

Fig. 3.—Summary of Magnanini's rate measurements in hydriodic acid solutions with hydrochloric, nitric or sulfuric acid added.

Magnanini also employed weaker acids, such as acetic and oxalic, for additional rate measurements. The results of these we have not recalculated because of the great difference in (H^+) and $\Sigma(H^+)$, which renders these acids almost ineffective in "accelerating" Reaction 1. It is worthy of special mention that Magnanini, over forty years ago, appreciated the cause of this ineffectiveness.

We cannot dismiss Figs. 2 and 3 from consideration without calling attention to the absence of appreciable kinetic salt effect for Reaction 4; did such an effect exist in the ionic strength range investigated, the excellent agreement of the various k_1 values could not have been secured.

Effect on the Reaction System of Changing the Temperature.—The results of experiments showing how the specific rates vary with temperature are given in Table III and plotted in Fig. 4.

TABLE III

VALUES OF SPECIFIC RATES AT DIFFERENT TEMPERATURES

Results of measurements in acid solution, by the "analytical" method. (I^-) = 0.0572 moles/l.; (H^+) variable

T, °C.	0.0	15.0	25.0	40.0
k_1°	0.094	0.35	0.69	2.19
k_1	2.05	5.50	10.4	22.9

Results of measurements[a] in slightly alkaline solution, by the oxygen evolution method

T, °C.	15.4	20.8	25.1	30.0	31.1	35.7	41.3	45.0	49.4
k_1°	0.344	0.528	0.71	0.98	1.19	1.55	2.50	3.14	4.23

[a] These measurements were made at different iodide concentrations, all below 0.1 M.

Most of these data were obtained from Curve II, Fig. 2, and from similar curves at 0, 15 and 40°; the rest (the solid circles) are hitherto unpublished values of k_1°, which Liebhafsky determined by following the rate of oxygen evolution from (initially neutral) solutions containing iodide ion and hydrogen peroxide (*cf.* Ref. 6b). From these combined data we deduce

$$k_1^\circ = 4.91(10^9)e^{-13,400/RT} \quad (6a)$$

$$k_1 = 4.58(10^8)e^{-10,450/RT} \quad (6b)$$

Over the temperature ranges investigated, Equations 6 will give to within 3% (ϵ = 0.0130 for log k_1° and 0.0122 for log k_1)[15] the values of k_1° and k_1; for the average

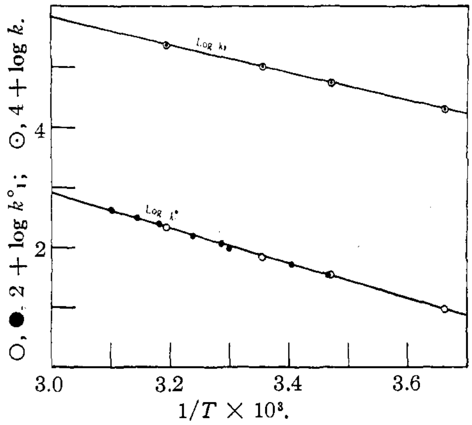

Fig. 4.—Variation of the specific rates with temperature.

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[15] No systematic procedure is uniformly followed in determining the values and the accuracies of the parameters A and Q defined by $k = Ae^{-Q/RT}$. We have employed the following approximate method, which, though not mathematically rigorous, is simple and yields reasonable values for our errors in Q. Values for log k are plotted as ordinates against $1/T$, sufficiently large scales being employed. By successive trials, that line is found for which $\epsilon = \sqrt{\Sigma d^2/(n-2)}$ is a minimum. ϵ is the average error in log k, d is the vertical distance of any point from the line (or curve), n is the number of different temperatures for which observations exist. (In calculating ϵ, n must be diminished by 2 be-

errors in the apparent heats of activation, we have computed $\epsilon_{Q_1^\circ} = 105$ and $\epsilon_{Q_1} = 120$ calories. Obviously, these data extend over a larger temperature range and possess higher accuracy than is usual.

The relationship of the data in Equation 6a to those in 6b is roughly that which obtains also for the similar rate-determining steps involving iodate ion and hydrogen peroxide;[9] a complete discussion of this significant relationship is best postponed until the complete data are available for the analogous pairs of rate-determining steps by which chloride and bromide ions reduce hydrogen peroxide.

One point, however, may be considered briefly. It is well known that, for diverse reasons, the apparent *heat* of activation, Q, defined by

$$\mathrm{d}\ln k/\mathrm{d}\,1/T = -Q/R \tag{7}$$

should normally vary with the temperature. Using the results of investigations in the kinetics of gaseous reactions to guide us,[16] we may write

$$-\frac{Q}{R} = -\frac{E}{R} - \frac{T}{2} + (n-1)T - sT - \frac{1}{R}\sum_{i=1}^{i=m} \Delta H_i \tag{8}$$

In this equation E represents the true *energy* of activation, *i. e.*, the minimum energy that a molecular system can have if the reaction in question is to occur; $-T/2$ is to be included only if the reaction is bimolecular, and because the collision number varies as $T^{1/2}$; $(n-1)T$ represents the effect on Q of the change in energy distribution that accompanies a change in temperature if $2n$ "squared terms" contribute to the activation energy; $-sT$ results if the probability of reaction for a molecular species increases in somewhat the way assumed by Kassel[17] with the amount of energy in

cause 2 values of log k are necessary to fix A and Q. Unless there are special reasons for not doing so, it seems advisable to plot for each temperature only the arithmetic mean of the observations thereat. If d is noticeably larger or smaller at high temperatures than at low, a system of weighting may be introduced.)

We have taken $\epsilon_Q = 2.3R\epsilon/\Delta(1/T)$ calories, $\Delta(1/T)$ corresponding to the temperature interval over which measurements exist. This method of calculating the error in Q emphasizes the importance of measuring log k over a large temperature range; the method probably gives values of ϵ_Q that become increasingly too large as $\Delta(1/T)$ becomes smaller, n remaining constant.

If Q deviates appreciably from constancy in the temperature range investigated, this method of calculation must be modified; we suggest that it be used to calculate values of Q and ϵ_Q for sections of the temperature range over which the former may be considered constant.

Since ϵ_A is of less importance than ϵ_Q, it need not usually be given; one must always remember, however, that an uncertainty in Q implies a corresponding uncertainty in A.

In work of high precision, the change in the concentrations of reactants due to thermal expansion of the reaction mixture should be considered; the effect of such expansion will be to render the values of rate constants measured at T°, and calculated by using the concentrations of solutions at room temperature, approximately $(m-1)\Delta$ per cent. too low (here Δ is the percentage change in the volume of water between T° and room temperature, and m is the order of the reaction). In none of our work is this correction appreciably over 1%, and we have not applied it; Equations 6, therefore, are based on concentrations of solutions at room temperature, which is convenient.

(16) For an excellent discussion of the heat of activation in gaseous reactions, the reader is referred to Kassel, "Kinetics of Homogeneous Gas Reactions," The Chemical Catalog Co., New York, 1932.

(17) Kassel, *Proc. Nat. Acad. Sci.*, **16**, 358 (1930). As one second order reaction for which Q increases with T as though the probability of reaction varied with the energy of the reacting molecular species approximately in the manner he postulates, Kassel cites the classical decomposition of gaseous hydrogen iodide, so thoroughly and carefully investigated by Bodenstein [*Z. physik. Chem.*, **29**, 295 (1899)]. Bodenstein gave two empirical equations to reproduce Q as a function of T; Kassel modified

excess of E that this system possesses (for systems with energy less than E the reaction probability is zero); and the last term is obtained by summing the heats of reaction for all equilibria involving a substance concerned in the rate-determining step.[18] (If such an equilibrium is not always maintained, its contribution to Q may not always be the ΔH of the corresponding reaction; in this event, its contribution to $\partial Q/\partial T$ will not be merely ΔC_p, the change in heat capacity, but must compensate also any significant change in the nearness to which the equilibrium is appproached at the different temperatures.)

For the temperature coefficient of Q we now have

$$\partial Q/\partial T = R\left(0 + {}^1/_2 - n + 1 + s - \sum_{i=1}^{i=m} \Delta C_{p_i}\right) \qquad (9)$$

if E, n, and s are constant.[19] Equation 9 is to be regarded as tentative, even in form, until accurate experimental material has accumulated in an amount sufficient to render sound judgment possible.

If the errors in Q_1° and Q_1 are not larger than we have calculated, $\partial Q/\partial T$ is not greater than, say, 6 cal./deg. for either **Reaction** 3 or 4. In the interpretation of these results, the possibility that $\partial Q/\partial T$ is very small because some of the terms in Equation 9 are opposed in sign must not be disregarded; to render this possibility less likely, additional measurements are to be made on analogous reactions. We shall conclude this discussion by pointing out that aqueous solutions may prove better adapted to testing Equation 9 than are gases; for what disadvantage the former suffer in offering a more limited temperature range (0 to 100°, under ordinary conditions) may be more than compensated by the opportunities for more accurate rate measurements which they usually give. The interpretation of these measurements, however, will normally be less certain for the solutions because of the enhanced importance of all kinds of intermediates, which is reflected in the last term of Equation 9; that is, the order of a

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the simpler of these by decreasing the coefficient of the log T term from 16 to 13, a change not greater than the uncertainty in the value of this term; the corresponding value of s is $13 + 2 - {}^1/_2 = 14{}^1/_2$.

Bodenstein's data are discussed by Hinshelwood [*cf.* Hinshelwood, "Kinetics of Chemical Change in Gaseous Systems," Oxford, 1929, Fig. 1a, p. 42, and pp. 47 and 48)]; but the significant variation of Q with T, given by Bodenstein, has not been mentioned. Calculation of the Q values for the successive pairs of temperatures (*cf.* p. 48) will show that, in spite of irregularities presumably due to slight experimental inaccuracies, Q does decrease with decreasing T.

(18) For convenience we may group the hydration equilibria, the formation and decomposition of Debye-Hückel "clusters," the closely related repulsion process between ions of like sign, and similar reactions, with the better defined equilibria (such as, for example, the hydrolysis equilibrium of iodine in the oxidation of hydrogen peroxide by that substance, *cf.* Ref. 6c) that may influence a rate-determining step.

(19) There seems to be no reason for assuming E to be in any way a function of T; the temperature concept appears meaningless for a molecular system undergoing chemical transformation since such a system is probably effectively isolated at the instant chemical change occurs. Further, it should be mentioned that, in writing Equations 8 and 9, we have tacitly assumed any steric factor concerned in a successful collision, such as the necessity of proper orientation, to be unaffected by a change in temperature. Also, in these equations, we have assumed, as is usually done, that the chance of an energy greater than E in $2n$ "squared terms" is given by

$$[e^{-E/RT}\,(E/RT)^{n-1}]/(n-1)!$$

an approximation sufficiently good so long as E/RT is large.

reaction in solution, coupled with data like those in Equations 6, indicates far less definitely the *intimate mechanism* of a rate-determining step than does the same information in the case of a gaseous reaction—in solutions probably all third-order reactions, and many of the second order as well, involve equilibria, which need not always be established: a third-order reaction might well be unimolecular under one set of limiting conditions, bimolecular under another, and neither alone in the intermediate region. Obviously these complexities render impossible any simple general interpretation of the Arrhenius constant, A,[15] in terms of the collision number Z.

It will be observed that the point of view indicated above differs radically from that just advanced by La Mer.[20]

Summary

1. The rate of the reaction

$$H_2O_2 + 2H^+ + 3I^- = 2H_2O + I_3^- \qquad (1)$$

has for the first time been measured under the simplest experimental conditions, with the result that the law, previously established

$$d(I_3^-)/dt = k_1^\circ(I^-)(H_2O_2) + k_1(H^+)(I^-)(H_2O_2) \qquad (2)$$

has been formally corroborated. Accurate values of k_1 can now be given.

2. The simplest kinetic interpretation of this rate law assumes the rate-determining steps

$$H_2O_2 + I^- \xrightarrow{k_1^\circ} H_2O + IO^- \qquad (3)$$

$$H_2O_2 + H^+ + I^- \xrightarrow{k_1} H_2O + HIO \qquad (4)$$

to proceed simultaneously and independently. At 25°, $k_1^\circ = 0.69$ and $k_1 = 10.5$; these measured values probably do not differ by more than 1% from the true values of these specific rates.

3. An examination of the early work of Magnanini[2] shows it to be in excellent agreement with our results. Certain trends in his rate measurements have been explained.

4. Within the ionic strength range investigated (roughly, from $\mu_c = 0.05$ to 0.5) Reaction 4 is without appreciable kinetic salt effect.

5. We have found

$$k_1^\circ = 4.91(10^9)e^{-13,400/RT} \text{ from 0 to } 50°\text{; and} \qquad (6a)$$

$$k_1 = 4.58(10^8)e^{-10,450/RT} \text{ from 0 to } 40° \qquad (6b)$$

Over the temperature ranges investigated, these equations give to within 3% the values of the specific rates. By use of an approximate method, the details of which are described, we have calculated the average error in Q_1° to be 105, and that in Q_1, 120 calories.

6. A brief discussion of the variation with temperature to be expected for the apparent heats of activation of reactions in aqueous solution has been given.

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[20] La Mer (a) THIS JOURNAL, **55**, 1739 (1933); (b) *J. Chem. Phys.*, **1**, 289 (1933).