dilute solution. The values of $(\overline{C}_p - \overline{C}_{p0})$ calculated in this manner are in all probability only approximate. It is doubted whether the accuracy of the experimental data warrants the rigorous treatment necessary for this calculation.

Summary

1. Using cells of the type Ba (2-phase amalgam) | $BaCl_2$ (m) | Hg_2Cl_2 | Hg, e. m. f. measurements have been made at 0, 15, 25, 35 and 45°.

2. A modification of the method of Jones and Dole for the calculation of the constants of the Hückel equation, by the method of least squares, has been developed and applied to the data obtained.

3. Calculations have been made of the activity coefficients, relative partial molal heat contents and heat capacities of barium chloride in aqueous solution.

WEST LAFAYETTE, INDIANA RECEIVED MAY 7, 1934

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

The Kinetics of the Reduction of Hydrogen Peroxide by the Halides

BY ALI MOHAMMAD AND HERMAN A. LIEBHAFSKY

Introduction

A recent investigation[1] of the reaction

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

has shown, in agreement with older results, that its rate law has the form

$$-d(H_2O_2)/dt = k_1^0(H_2O_2)\ (X^-) + k_1(H_2O_2)(X^-)(H^+) \qquad (2)^2$$

and this confirms the conclusion that Reaction 1 involves two rate-determining steps of the types

$$H_2O_2 + X^- \xrightarrow{k_1^0} H_2O + XO^- \qquad (3)$$

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

proceeding simultaneously and independently. k_1^0 and k_1 may be measured over a rather large temperature range if suitable experimental conditions are chosen; the equations

$$-d \log k_1^0/d(1/T) = 2943, \text{ and } k_1^0 = 4.91(10^9)\ e^{-13,400/RT} \text{ from 0 to } 50° \qquad (5a)$$

$$-d \log k_1/d(1/T) = 2271, \text{ and } k_1 = 4.58(10^8)\ e^{-10,450/RT} \text{ from 0 to } 40° \qquad (5b)$$

adequately summarize the accurate experimental results obtained with iodide as reducing agent.[1]

Compounds of the halogens often show strikingly analogous kinetic behavior, and it is thus not surprising that the rate laws for the reduction of hydrogen peroxide by bromide and by chloride should each be formally identical with Equation 2. For these halides, however, the specific rates of the steps not involving hydrogen ion (*cf.* Reaction 3) are very much smaller[3] than 0.69, the value at 25° of k_1^0 for the iodide reaction. Certain difficulties attending the study of these reactions become more marked as the specific rates decrease, and render highly accurate measurements difficult in the case of bromide and impossible in the case of chloride. Nevertheless, we have made measurements involving these halides over a range of temperatures in order that the results might be tabulated with those of Equations 5 to reveal any significant regularities. A complete absence of such regularities where reactions so closely related as these are concerned would indicate that a general theoretical treatment of ionic reactions in solution can scarcely hope for success—in any event, data such as ours are necessary to test whatever theoretical treatment is proposed.

The rates at which bromide and chloride reduce hydrogen peroxide were measured by following the rates at which oxygen was evolved from reaction mixtures in which the steady state had been reached. C. P. sodium salts and perchloric acid, together with concentrated hydrogen peroxide (Merck's "Superoxol"), were employed as reagents. The apparatus and its manipulation have been described previously.[4] The rate at which a halogen-halide couple decomposes hydrogen peroxide governs the rate at which oxygen is evolved, and is twice the rate at which hydrogen peroxide is reduced at the steady state.[5] The rate of this reduction we shall write

$$-d(H_2O_2)/dt = k'(H_2O_2) \qquad (6)$$

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(1) Liebhafsky and Mohammad, THIS JOURNAL, **55**, 3977 (1933).

(2) As in previous communications, ( ) will be used to denote concentrations in moles per liter, $\longrightarrow$ will be restricted to reactions that may be rate-determining, and unit time will be the minute. X will be employed as a general symbol for I, Br or Cl.

(3) Liebhafsky has found 2.3 (10^{-5}) (bromide) and $2(10^{-7})$ (chloride) to be provisional values of k_1^0 at 25° for these halides (see Ref. 1, footnote 9).

(4) Liebhafsky, THIS JOURNAL, **54**, 1792 (1932).

(5) See, for example, (a) Bray and Livingston, *ibid.*, **45**, 1251 (1923); or (b) Livingston and Bray, *ibid.*, **47**, 2069 (1925); or (c) Abel, *Z. physik. Chem.*, **96**, 1 (1920); or Ref. 4.

a convenient form since (H_2O_2) is the only variable steady-state concentration. In almost all of our experiments, k' was so small that (H_2O_2) did not change greatly even over a long time interval; since small volumes of oxygen could be measured accurately, k' was simply calculated as the quotient of average rate of reduction by average peroxide concentration. (The few experiments in which the reaction went to completion will be pointed out below; k' for these was obtained from the logarithmic plot for a first-order reaction.) From values of k' corresponding to systematically varied experimental conditions k_1^0 and k_1 may be evaluated,[1] as will appear below. For these evaluations, (X^-) may be calculated directly from the amount of halide initially added to the reaction mixture because the concentrations of substances like X_2, X^-_3 or HXO remain negligible even when the steady state is reached.

Experimental Results

Reduction by Bromide.—In Table I are given the results of measurements made on sodium bromide solutions without added acid. Under these conditions, the contribution of Reaction 4 is negligible and, except for the small "stray losses" (to be discussed later), the rate of oxygen evolution is directly proportional to the rate of Reaction 3; consequently, $k'/(Br^-) = k_1^0$.

TABLE I

RESULTS OF RATE MEASUREMENTS IN BROMIDE SOLUTIONS WITHOUT ADDED ACID

Concentrations in moles/liter. Temperature 25°

No.	1	2	3	4	5	6	7
(Br^-)	0.456	0.456	0.833	0.833	1.667	1.692	5.05
(H_2O_2)	1.04	.98	1.03	1.00	0.67	0.68	[a]
$k_1^0 \times 10^5$	2.0	2.1	2.4	2.4	2.4[b]	2.5[b]	310

[a] Run to completion. Rate accurately first order with respect to (H_2O_2) over entire range. Initial (H_2O_2) was 0.03 moles/liter.

[b] This value of k_1^0 obtained when 0.03 *M* $H_2PO_4^-$ was present.

The surprisingly high value $k_1^0 = 310(10^{-5})$ for No. 7 is evidence that a complication, not important at lower bromide concentrations, has entered; it will be convenient to defer discussion of this experiment until later. From the other values we conclude that $k_1^0 = 2.3(10^{-5})$ at 25°, which is the provisional value already given.[3] Now, if the two rate-determining steps, Reactions 3 and 4, really occur with bromide as reducing agent, values of $k'/(Br^-)$ obtained in acid solution at 25° should, when plotted against (H^+) as abscissa, yield a straight line with an ordinate intercept (k_1^0) of $2.3(10^{-5})$ and with a slope (k_1) of approximately $1.4(10^{-2})$.[6] Measurements at other temperatures should yield similar straight lines. The results tabulated below and plotted in Fig. 1 meet these requirements.

TABLE II (See Fig. 1)

RESULTS OF RATE MEASUREMENTS IN PERCHLORIC ACID–SODIUM BROMIDE SOLUTIONS

Throughout (Br^-) = 0.40, and (H_2O_2) = 0.80 mole/liter

Temperature 25.0°

(H^+) × 10^3	4.20	8.38	12.55	16.64	20.75	24.80
$k'/(Br^-) \times 10^4$	0.80	1.41	2.00	2.55	3.14	3.73

$k_1^0 = 2.3(10^{-5})$, $k_1 = 1.40(10^{-2})$

Temperature 32.9°

(H^+) × 10^3	4.20	8.38	12.55	16.64	20.75	24.80
$k'/(Br^-) \times 10^4$	1.68	2.78	3.98	5.38	6.39	7.55

$k_1^0 = 5.0(10^{-5})$, $k_1 = 2.85(10^{-2})$

Temperature 40.6°

(H^+) × 10^3	4.20	8.37	12.50	16.60	20.70	24.70
$k'/(Br^-) \times 10^4$	3.42	5.94	8.95	11.25	13.50	16.00

$k_1^0 = 14.0\ (10^{-5})$, $k_1 = 5.9(10^{-2})$

Temperature 49.6°

(H^+) × 10^3	4.18	8.35	12.45	16.60	20.65	24.60	28.70	32.6
$k/(Br^-) \times 10^4$	7.0	12.5	17.8	22.4	28.3	33.0	38.6	42.8

$k_1^0 = 34.8\ (10^{-5})$, $k_1 = 11.8(10^{-2})$

At 25° the values given in Table II for both k_1^0 and k_1 are in excellent agreement with those from independent measurements (see Table I and Footnote 6); we conclude therefore that the two rate-determining steps, Reactions 3 and 4, do proceed simultaneously and independently with bromide as reducing agent, and that the measurements summarized in Table II will yield reasonably accurate information concerning the effect on k_1^0 and k_1 of changing the temperature.

The Stray Losses.—Ordinarily hydrogen peroxide in aqueous solution decomposes slowly according to the reaction

$$H_2O_2 = H_2O + {}^1/_2O_2 \qquad (7)$$

When the catalytic decomposition effected by an oxidation–reduction couple is being studied, it is usually advisable to choose experimental conditions so that the "stray losses" (Reaction 7) are negligible in comparison with this catalyzed decomposition. If such a choice of conditions is not possible, correction for the stray losses must be made.

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(6) $k_1 = 1.4(10^{-2})$ at 25° is the value given by Bray and Livingston, Ref. 5a, p. 1271, for sulfuric acid solutions above 0.2 *N*. If activity coefficients are introduced into the rate law for the reaction concerned, the value of the specific rate will naturally be different from $1.4(10^{-2})$ (*cf.* Livingston, THIS JOURNAL, **48**, 53 (1926)). In the present investigation, however, we shall not find it necessary to introduce activity coefficients in the interpretation of kinetic measurements.

In our cases the catalyzed decomposition may be written as the sum of the reactions[7]

$$X_2 + H_2O_2 = 2H^+ + 2X^- + O_2 \qquad (8)$$

$$2H^+ + 2X^- + H_2O_2 = X_2 + 2H_2O \qquad (9)$$

The problem involved in the stray loss correction is to decide how much of the observed rate at which the peroxide disappears is due to Reaction 7 and how much to the combination, Reactions 8 and 9. If the stray losses and catalyzed decomposition are completely independent, the rate at which the former proceed, measured in a blank reaction mixture from which the oxidation-reduction couple is absent, may be subtracted from the observed rate to give the rate of the latter. This has been done for all our measurements; *i. e.*, tabulated values of $k'/(X^-)$ are calculated from the difference $k'_{\text{obs.}} - k_s$, k_s being the quotient of the stray loss rate in a perchloric acid–peroxide solution by the peroxide concentration. The values of k_s employed for the different temperatures are

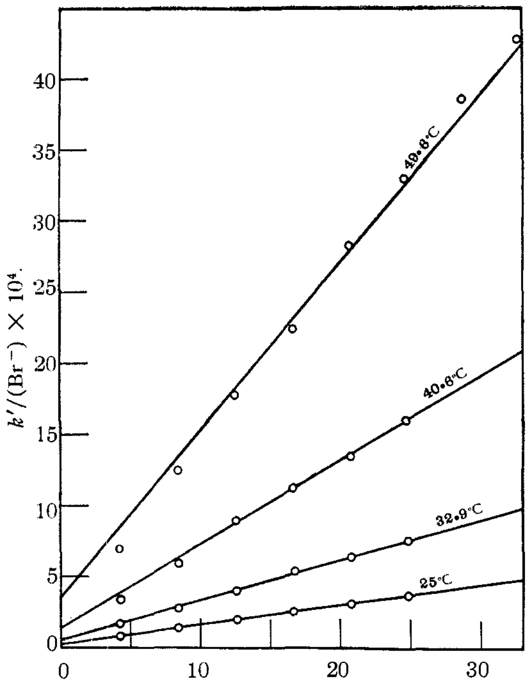

Fig. 1.—(See Table II.) Results of rate measurements in perchloric acid–sodium bromide solutions.

Temperature, °C.	25.0	32.9	40.6	49.6
k_s	$3(10^{-7})$	$1(10^{-6})$	$3(10^{-6})$	$1(10^{-5})$

The values at the two highest temperatures are average results of a number of measurements; the others were calculated from these since direct measurement at the lower temperatures gave unreliable results because of the slowness of the stray decomposition. Comparison of k_s with k' at the same temperature will show that, in our experiments with bromide as reducing agent, the former is seldom more than 2% of the latter. (k' may be obtained by multiplying the $k'/(Br^-)$ values in Tables I and II by the bromide concentrations, which are given in the tables.) We have already observed that nearly all the specific rates obtained by use of this method of stray loss correction are concordant, and this provides sufficient justification for its employment.

In the case of Experiment 7, Table I, however, we have a result, $310(10^{-5})$, which is over a hundred times as large as the k_1^0 we have adopted for that temperature. We believe this anomalous increase to indicate that stray loss and catalytic decomposition are no longer independent, but are reinforcing each other so that their combined rate is much greater than the sum of the rates measured for each when it is proceeding alone. As we cannot discuss this anomaly here, we shall mention only that it appears for all three halides, always within a definite range of experimental conditions; and that it is most pronounced when the ionic strength is high, the absolute rate of reaction low and the reaction mixture alkaline. (Thus, addition of acid reduced $k'/(Br^-)$ for No. 7 eightfold while duplicates of Nos. 5 and 6, Table I, but containing no $H_2PO_4^-$, gave value of k_1^0 approximately twice as large as those listed.) With chloride as reducing agent, the anomaly is so pronounced that reliable values of k_1^0 cannot be determined in initially neutral sodium chloride reaction mixtures, and even in slightly acid solution the results are difficultly reproducible. Enough has been said to show that the specific rate of Reactions 3 cannot be determined in neutral or slightly alkaline solutions unless this anomaly is absent; such absence is indicated if k_1^0 as obtained by extrapolating measurements in acid solution (in the manner of Fig. 1) agrees with the value directly measured in initially neutral salt solutions. This kind of agreement has been found for iodide and bromide as reducing agents, but has not been realized for chloride, probably because of the low specific rate characteristic of its Reaction 3.

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(7) The sum of Reactions 8 and 9 is obviously identical with Reaction 7; one difference between these two ways of decomposing the peroxide is that the catalytic decomposition results from the progress of a well-defined oxidation and a well-defined reduction reaction, both of which obey known rate laws and may often be isolated or individual study.

Reduction by Chloride.—The chloride results, corrected for stray losses in the manner just explained, are summarized in Table III and plotted in Fig. 2. The results of three measurements at low acid were particularly divergent and have not been included.

TABLE III (See Fig. 2)

RESULTS OF RATE MEASUREMENTS IN PERCHLORIC ACID-SODIUM CHLORIDE SOLUTIONS

Temperature 25°; (Cl^-) = 3.00 moles/liter (H_2O_2) = 0.80 mole/liter

$(H^+) \times 10^3$	3.82	7.55	11.02	11.35	14.60	18.20	25.30
$k'/(Cl^-) \times 10^7$	2.50	3.90	5.75	5.40	7.31	9.40	12.90

$k_1^0 = 1.1(10^{-7})$, $k_1 = 5.0(10^{-5})$

Temperature 32.9°; (Cl^-) = 3.00 moles/liter; (H_2O_2) = 0.80 mole/liter

$(H^+) \times 10^3$	7.63	7.63	11.43	11.43	15.14	22.50	22.50	26.20	26.20
$k'/(Cl^-) \times 10^7$	13.6	12.8	15.8	14.3	18.5	26.6	28.1	32.3	32.8

$k_1^0 = 2.8(10^{-7})$, $k_1 = 12.4(10^{-5})$

Temperature 40.6°; (Cl^-) = 3.00 moles/liter; (H_2O_2) = 0.80 mole/liter

$(H^+) \times 10^3$	4.19	8.35	12.50	16.55	20.60	24.70	28.75
$k'/(Cl^-) \times 10^7$	39	41	44	49	74	76	91

$k_1^0 = 3.0(10^{-7})$, $k' = 28.8(10^{-5})$

Temperature 49.6°; (Cl^-) = 3.00 moles/liter; (H_2O_2) = 0.80 mole/liter

$(H^+) \times 10^3$	8.40	16.8	25.1	33.4	41.3	49.5	57.5	65.6	73.3
$k'/(Cl^-) \times 10^6$	18.8	15.1	28.4	26.6	33.3	40.6	45.7	47.6	52.6

$k_1^0 = 23.4(10^{-7})$, $k_1 = 73.3(10^{-5})$

Temperature 49.6°; (Cl^-) = 1.00 moles/liter; (H_2O_2) = 1.59 moles/liter

$(H^+) \times 10^3$	8.4	16.8	25.0	33.3	41.3	49.4	57.4	65.6	73.1	81.3
$k'/(Cl^-) \times 10^6$	4.8	4.1	11.1	15.6	19.2	23.4	30.6	30.0	36.4	37.9

$k_1^0 = 10.0(10^{-7})$, $k_1 = 45.2(10^{-5})$

Temperature 49.6°; (Cl^-) = 4.70 moles/liter; (H_2O_2) = 0.48 mole/liter

$(H^+) \times 10^3$	8.4	16.8	25.1	33.4	41.3	49.5	57.5	65.6	73.3	81.2
$k'/(Cl^-) \times 10^6$	16.0	22.5	30.1	39.2	47.2	57.3	66.6	74.4	80.1	91.5

$k_1^0 = 27.5(10^{-7})$, $k_1 = 109.5(10^{-5})$

The results in Table III fall into two groups: those at 3 *M* chloride ion, from which the temperature coefficient data are to be deduced; and those at 49.6° and variable chloride concentration, which are to settle the order of the reaction with respect to that substance. As reduction by chloride is much slower than by bromide, the stray loss correction is relatively much more important; under our experimental conditions it varies between, say, 10 and 20% of k'. With the correction so large as this, one could not expect concordant results were the anomaly significant which has been discussed above; and since our results are reasonably concordant, we conclude that it is unimportant here. The measurements at variable (Cl^-) satisfactorily indicate that the rate law involves this concentration to the first power, but show a pronounced salt effect; this increase of specific rate with (Cl^-) was to be anticipated from the work of Livingston and Bray[5b] and that of Budge.[8]

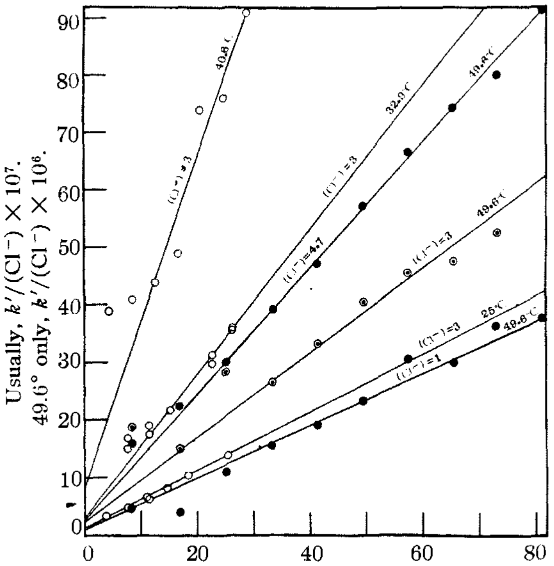

Fig. 2.—(See Table III.) Results of rate measurements in perchloric acid–sodium chloride solutions.

The chloride measurements, unlike those with bromide as reducing agent, are not accurate enough to yield reliable values of both k_1^0 and k_1. Fortunately, however, accurate values of the latter may be calculated from the work of Budge,[8] whose results are in substantial agreement with those of Livingston and Bray.[5b] Such calculations were made for all temperatures and for $(Cl^-) = 3$ *M*; lines with slopes equal to these values of k_1 were drawn through our experimental points and extrapolated in order to establish reliable values of k_1^0, the intercepts. (For the other two chloride concentrations at 49.6° no such guide was employed.) Examination of Fig. 2 will reveal that we have in no instance violated the experimental data by adopting this procedure: indeed, the lines with the calculated slopes fit the points about as well as any others that might have been drawn. There can be no doubt that the reduction of hydrogen peroxide by chloride follows the same type of rate law as its reduction by bromide or iodide, and our values of k_1^0 for the chloride reaction are probably reliable.

Summary of Temperature Data. Conclusions

The temperature data for the three pairs of rate-determining steps involved in the reduction of

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[8] Budge, THIS JOURNAL, 54, 1769 (1932).

hydrogen peroxide by chloride, bromide or iodide are summarized in Table IV and plotted in Fig. 3.

TABLE IV (See Fig. 3)

SUMMARY OF TEMPERATURE DATA

Halide	d(log k_1^0)/d(1/T)	d(log k_1)/d(1/T)	$A_1^0 \times 10^{-9}$	$A_1 \times 10^{-9}$
Chloride	5150	4530[a]	21.8	79.1[a]
Bromide	4600	3640	66.3	24.2
Iodide	2943	2271	4.91	0.458

Halide	Q_1 (calories)	Q_1 (calories)	$Q_1 - Q_1$ (calories)
Chloride	23,600 ± 570	20,740[a]	2860
Bromide	21,100 ± 450	16,700 ± 180	4400
Iodide	13,400 ± 105	10,450 ± 120	2950

[a] This figure is based on the work of Budge,[8] giving consideration also to that of Livingston and Bray,[5b] whose value for the temperature coefficient of the corresponding reaction he has recalculated.

Within the temperature range investigated, $k_1^0 = A_1^0 e^{-Q_1^0/RT}$ and $k_1 = A_1 e^{-Q_1/RT}$.

For each rate-determining step the Arrhenius constant (A) and the (apparent) heat of activation (Q) are given; the average errors in these heats have been calculated in the manner suggested by Liebhafsky and Mohammad.[1] The corresponding inaccuracies in the A's can be computed only if the value of k at some temperature is fixed; establishing thus the 25° values means that an increase of 1400 calories in Q corresponds approximately to a ten-fold increase in A.[9]

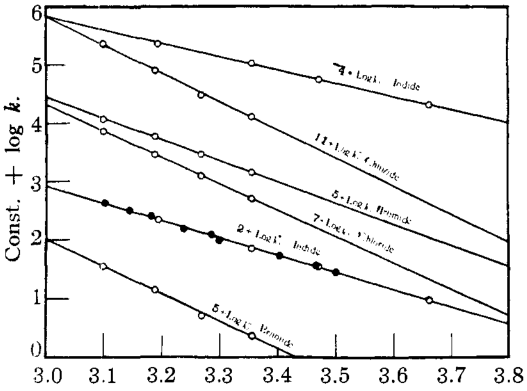

Fig. 3.—Summary of temperature data.

The heats of activation in Table IV show two types of significant regularities. First, these heats become greater for both kinds of rate-determining steps as one passes from iodide through bromide to chloride—in accord with common experience, which considers iodide to be the most, and chloride the least, reactive reducing agent. Second, Q_1^0 for each halide is larger than the corresponding Q_1 by some three or four thousand calories. In a study of the reduction of iodate ion by hydrogen peroxide,[10] a similar difference was found for the heats of activation of two rate-determining steps formally analogous to Equations 3 and 4—but with the difference that HIO_2 and IO_2^-, not HXO and XO^-, were resultants. It was pointed out that the participation of H^+ in the one rate-determining step lowered the heat of activation for the reduction of iodate ion by 4000 calories; and the suggestion was made that this lowering was possible because HIO_2 (and not IO_2^-) was formed in this rate-determining step, that the lowering represented the heat of dissociation of this acid. This suggestion gains plausibility from the differences given in the last column of Table IV, all of which have the sign and magnitude to be expected if they represent the heats of dissociation of the weak acids HXO.

Were A_1^0 for chloride some five-fold (the uncertainty in this quantity is probably not much less than this) larger, there would exist in the Arrhenius constants of Table IV regularities very like those observed in the heats of activation; *i. e.*, the constants would increase as one went from iodide through bromide to chloride, and A_1^0 would throughout be somewhat greater than A_1. Probably more significant, however, than any small differences between them, is the fact that A_1^0 and the corresponding A_1 are identical in order of magnitude, for A_1^0 belongs to a second-, and A_1 to a closely related third-order reaction. (In this connection, *cf.* Ref. 10, p. 908.)

Any attempt to correlate Arrhenius constants encounters a fundamental difficulty, which we shall now touch upon. An Arrhenius constant calculated as were those above represents a linear extrapolation (*cf.* Fig. 3) to infinite temperature of measurements usually made within a limited temperature range, often a range so limited that a relatively large variation[11] of Q with T might escape detection even with moderately accurate measurements. Should any such variation occur, the simple extrapolation by which we obtained the A's in Table IV loses significance. It will then be necessary to consider this variation in formulating k as a function of T, and simple equations of the

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[9] To determine what effect a change in Q has on A, k being fixed, we observe that $\Delta(\log k) = \Delta(\log A) - \Delta Q/4.5787\ T$. If T = 298.1° (or 25°), and $\Delta(\log k) = 0$, $\Delta(\log A) = 1$ when $\Delta Q = 4.5787 \times 298.1$.

[10] Liebhafsky, THIS JOURNAL, 53, 896 (1931).

[11] A brief discussion of the variation with temperature to be expected for the apparent heats of activation in aqueous solution is given in Ref. 1.

type $k = Ae^{-Q/RT}$ must yield to others more complex in form, in which the term independent of T may have a value different from that of A by many powers of ten. For this reason no correlation of these A's can be founded securely until it has been proved that Q is in fact independent of T—that the simple Arrhenius equation is valid. Such proof is usually difficult, if not impossible, of attainment, and as a result Arrhenius constants furnish less reliable material for theoretical treatment than do heats of activation. What has just been said obviously applies to any attempted interpretation of A in terms of a collision number, whether the reaction being considered takes place in the gas phase or in solution.

Summary

1. Experimental evidence has been presented for the first time to show that hydrogen peroxide is reduced by bromide or by chloride according to the rate law

$$-d(H_2O_2)/dt = k_1^0(H_2O_2)(X^-) + k_1(H_2O_2)(X^-)(H^+) \quad (2)$$

which is formally identical with that long known to govern its rate of reduction by iodide.

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

$$H_2O_2 + X^- \xrightarrow{k_1^0} H_2O + XO^- \quad (3)$$

$$H_2O_2 + X^- + H^+ \xrightarrow{k_1} H_2O + HXO \quad (4)$$

proceed simultaneously and independently.

3. The effects of k_1^0 and k_1 on temperature variation have been determined; equations of the type $k = Ae^{-R/RT}$ adequately summarize the experimental results. Reasonably accurate values of the parameters A and Q for six closely related reactions (one pair for each halide studied) are now available (Table IV).

4. A partial interpretation of certain regularities which these parameters show has been attempted. The stand has been taken that heats of activation (the Q's) are probably of greater fundamental significance than Arrhenius constants (the A's).

5. Certain difficulties attending the "stray loss" correction have been briefly touched upon.

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

The Activated Adsorption of Water Vapor by Alumina

BY HUGH S. TAYLOR AND AUSTIN J. GOULD

In an earlier communication[1] on the relation between activated adsorption and specific reactions at surfaces it was emphasized that the relative dehydration and dehydrogenation efficiencies of oxide surfaces would be dependent upon the velocities of desorption of water vapor and hydrogen, respectively, from the surface in question. These velocities will in their turn be dependent upon the activation energies of adsorption of the two gases and their respective heats of adsorption. Taylor and Sickman[2] demonstrated by measurements of adsorption of water vapor and hydrogen on zinc oxide, a predominantly dehydrogenation catalyst, that the velocity of desorption of hydrogen from the surface was pronouncedly more rapid than that of water vapor under similar conditions, even though the amount of adsorption of water vapor was greater than that of hydrogen. We have now demonstrated the reverse behavior in the case of a typical dehydration catalyst, precipitated alumina. With such material it has already been shown[1] that hydrogen is only markedly adsorbed in the activated form above 400° with an activation energy of adsorption as great as 27,500 calories, and, as is obvious from the temperature of binding, with a heat of adsorption which must be at least 30,000 calories. We have shown that activated adsorption of water vapor occurs in a much lower temperature range and with much lower heats of adsorption. The experiments also reveal an astonishingly large adsorptive capacity of alumina for water vapor at high temperatures.

Experimental

The apparatus employed was similar to that used by Taylor and Sickman.[2] A small bulb containing water, distilled *in vacuo*, and immersed in an ice-bath, furnished the water vapor. This bulb was connected through a three-way stopcock to a mercury reservoir and to a bulb of 523 cc. capacity which in turn was connected through a

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[1] Taylor, *Z. physik. Chem.*, Bodenstein Festband, 475 (1931).

[2] Taylor and Sickman, THIS JOURNAL, **54**, 602 (1932).