The Kinetics of the Reaction between Ferric and Stannous Perchlorates in Acid Solution
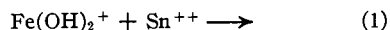
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The present investigation was undertaken to study the reduction of ferric salts by stannous salts in solutions in which it is reasonably certain no complex ions exist; perchlorates were therefore used. Sufficient perchloric acid was added to suppress the formation of colloidal ferric hydroxide.

The kinetics of the comparatively rapid reaction between ferric and stannous chlorides has been much investigated.[1] A rather complete discussion of these researches and new experimental material has been given by the author in a thesis.[2] It is sufficient to state here that the rate-determining step is not a third order reaction involving two ferric and one stannous ions, as is generally supposed, but a second order reaction between unpolymerized chloride complexes of ferric iron and stannous tin. Timofeew[1c] first proved that the reaction is second order and the author[2] and Robertson and Law[1d] independently demonstrated the influence of chloride ion.

It was expected that the reaction rate would be very much smaller with perchlorates than with chlorides, since the repulsive forces between the highly charged and positive ferric and stannous ions are very great and those between the lower valent or neutral chloride complexes (as $FeCl_3$ and $SnCl^+$ or $SnCl_3^-$) are small or negligible. Actually the rate was found to be smaller by a factor of 10^5 to 10^6 under comparable conditions. Moreover, no evidence was found that ferric ion itself reacts directly with stannous ion in a range of temperature from 55 to 70° and of hydrogen-ion concentrations from 0.02 to 1 M.

The rate-determining step for the reduction of the ferric salt was concluded to be

$$Fe(OH)_2^+ + Sn^{++} \longrightarrow \qquad (1)$$

The actual kinetics are complicated by the fact that the reactions involved in the hydrolysis equilibrium, $H_2O + FeOH^{++} \rightleftharpoons Fe(OH)_2^+ + H^+$, are often not rapid compared to reaction 1; and by the fact that in most of the solutions an appreciable proportion of the ferric iron was present in the form of hydrolysis products. It was found that the presence of colloidal ferric hydroxide increased the rate; this complication was avoided by the addition of perchloric acid in amounts sufficient to suppress its formation.

Materials.—A solution of *ferrous perchlorate* was prepared by the addition of equivalent amounts of a barium perchlorate solution to a ferrous sulfate solution; the mixture was held at a temperature of 100° for several hours in the absence of air in order to coagulate the precipitate of barium sulfate. The clear resulting solution was pipetted off after cooling.

A solution of *stannous perchlorate*, free from excess acid, was prepared by a method formerly employed by Noyes and Toabe.[3]

Experimental Method.—The reaction was started in all experiments by adding a small volume of a concentrated solution of stannous perchlorate to a solution containing the other reactants. The progress of the reaction was followed by the method used by all previous investigators: stannous ion was rapidly destroyed by quenching the sample with mercuric chloride solution, and the extent to which the reaction had progressed was determined by an analysis for the ferrous ion produced.

The reaction mixture, exclusive of stannous perchlorate, contained ferric perchlorate and perchloric acid. It was made up by adding the desired amounts of ferrous perchlorate and perchloric acid solution and an excess of hydrogen peroxide to the desired volume of water in a volumetric flask. The reaction mixture was then transferred to the apparatus employed and allowed to remain at the temperature of the run for a period of at least one day in order to ensure complete decomposition of the excess hydrogen peroxide and attainment of equilibrium.

The apparatus shown in Fig. 1 was employed to enable the withdrawal of samples in the complete absence of air and to eliminate the loss of water by evaporation.

The concentration of ferrous ion in the sample was determined by titration with 0.01 N potassium dichromate, using diphenylamine[4] as the indicator.

Experimental Results.—If $Fe(OH)_2^+$ is at equilibrium with ferric and hydrogen ions, the rate law corresponding to equation 1 is

$$d(Fe^{++})/dt = 2k_3K_1K_2(Fe^{+++})(Sn^{++})/(H^+)^2 \quad (2)$$

where

$$K_1 = (Fe(OH)^{++})(H^+)/(Fe^{+++}) \quad (3)$$

and

$$K_2 = (Fe(OH)_2^+)(H^+)/(Fe(OH)^{++}) \quad (4)$$

and k_3 is the specific rate of reaction 1.

(1) (a) Kahlenberg, THIS JOURNAL, 16, 314 (1894); (b) Noyes, Z. physik. Chem., 16, 546 (1895); (c) Timofeew, Muchen and Gurewitch, ibid., 115, 161 (1925); (d) Robertson and Law, Trans. Faraday Soc., 31, 899 (1935).

(2) Gorin, Ph.D. Thesis, Sept., 1933, University of California Library.

(3) Noyes and Toabe, THIS JOURNAL, 39, 1539 (1917).

(4) Benedetti-Pichler, Z. anal. Chem., 73, 200 (1928).

At the moment of starting, the system must be at equilibrium and therefore the initial rate will be given by equation 2. It was found that the experiments fell into two groups: (1) in those with *ferric perchlorate in excess* the results can be accurately extrapolated to obtain the initial rate; (2) in those with *stannous perchlorate in excess* the rate drops off so quickly from the initial value that no accurate extrapolation can be made.
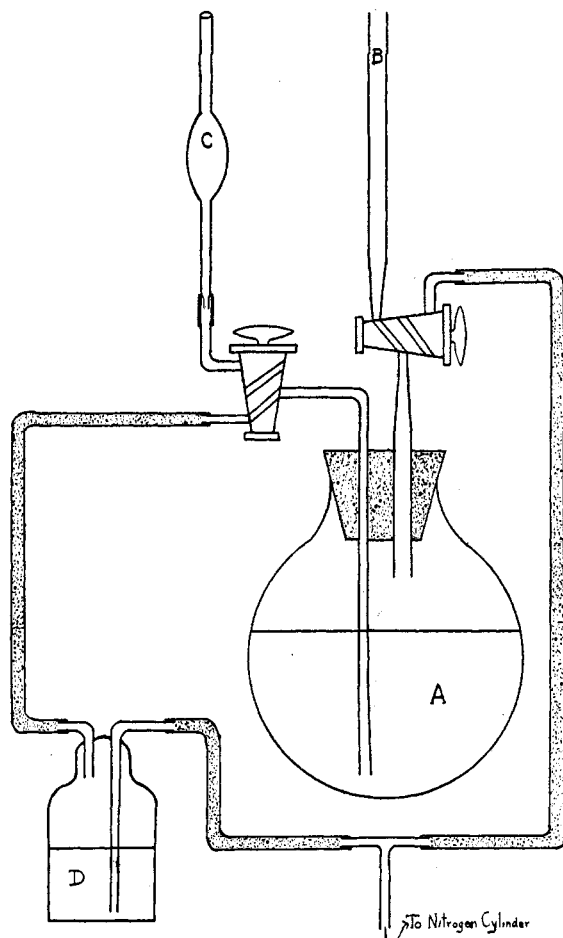

Fig. 1.—Apparatus for rate measurements at 70°: A, reaction vessel in thermostat; B, condenser; C, sampling pipet; D, pressure regulator containing mercury.

Ferric Ion in Excess at 70°.—In Fig. 2, the quantity, log $(a - x)/(2b - x)$, is plotted against time for the first few experimental points in 6 runs, nos. 1–6. The initial slope, as estimated for each run, is shown by the solid straight lines in Fig. 2. If a, b and c are the initial concentrations of ferric perchlorate, stannous perchlorate and perchloric acid, respectively, x, the concentration of ferrous ion produced at the time, t, and

S the slope of the lines drawn in Fig. 2, it follows that

$$(dx/dt)_{initial} = 2.303S(2b)a/(a - 2b)$$

and that

$$2k_3K_1K_2 = \frac{4.606aS[c + (FeOH^{++})_i + 2(Fe(OH)_2^+)_i]^2}{(a - 2b)[a - (FeOH^{++})_i - (Fe(OH)_2^+)_i]}$$

(5)

The values of K_1 and K_2 are not well known. Bray and Hershey[5] corrected several equilibria involving ferric ion for hydrolysis by considering the first step only. Although they assumed the second step in the hydrolysis to be negligible, their method is a satisfactory empirical one for correcting ferric ion but not hydrogen-ion concentration. It will be shown later that essentially the same results for ferric ion could have been obtained by including the second step and using a smaller value for K_1. The values given in Table I for K_1 and K_1K_2 were calculated from the values, 0.0250 and 35.2 × 10^{-4}, respectively, at zero ionic strength by assuming the activity function given by Bray and Hershey.[5] K_1K_2 was obtained from the kinetic data to be described later and K_1 was assumed to have one-quarter of the value obtained by extrapolating the results of Bray and Hershey[5] to 70°.

The values of $2k_3K_1K_2$ calculated from initial rates are given in Table I.

TABLE I

EVIDENCE FOR EQUATION 2 BASED ON INITIAL RATES MEASURED AT 70° WITH FERRIC PERCHLORATE IN EXCESS

Run	$\mu^{1/2}$	γ	a	$2b$	c	S
1	0.64	0.745	0.0544	0.00358	0.1015	0.0318
2	.64	.745	.0544	.00972	.1015	.0246
3	.49	.758	.0272	.00458	.0869	.0186
4	.49	.758	.0272	.01104	.0869	.0119
5	.43	.767	.0137	.00452	.0991	.00600
6	.28	.804	.00656	.00443	.0400	.00680

Run	$K_1 = \frac{0.025}{(\gamma)^4}$	$\frac{K_1K_2}{\times 10^4} = \frac{35.2}{(\gamma)^6}$	$(FeOH^{++})_i$	$(Fe(OH)_2^+)_i$	$(Fe^{+++})_i$	$(H^+)_i$	$2k_3K_1K_2$
1	0.0078	6.0	0.00345	0.00240	0.0485	0.1099	0.0388
2	.0078	6.0	.00345	.00240	.0485	.1097	.0341
3	.0083	6.9	.00210	.00189	.0232	.0927	.0383
4	.0083	6.9	.00210	.00189	.0232	.0927	.0346
5	.0088	7.2	.00102	.00082	.0119	.1017	.0358
6	.0104	9.7	.00090	.00183	.00383	.0446	.0500

It is seen from Table I that equation 2 represents the initial rate of the reaction quite well over an 8-fold variation in ferric ion, a 3-fold variation in stannous ion and 6-fold variation in the square of hydrogen ion. For the expected and observed

(5) Bray and Hershey, THIS JOURNAL, **56**, 1889 (1934).

variation of the specific rate, $2k_3K_1K_2$, with ionic strength, see Fig. 7.

In Fig. 3, runs 1–6 are plotted for the entire course of the reaction. Since the main reaction at 70° is

$$3H_2O + 2Fe^{+++} + Sn^{++} \longrightarrow H_2SnO_3 + 2H^+ + 2Fe^{++} \tag{6}$$
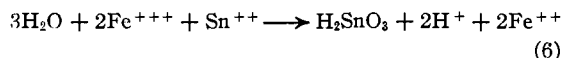
hydrogen ion is produced during the reaction. Therefore the quantity $(c + 2x)/c \log (a - x)/(2b - x)$ is plotted against t rather than the quantity $\log (a - x)/(2b - x)$. The dotted lines in Fig. 3 are the lines that would result if equation 2 were followed over the entire course of the reaction. It is seen that in runs 1 and 3 the dotted line is followed within the experimental error over the entire extent of the reaction. In the other runs the curves slowly deviate from the dotted line and then go through an inflection point and appear to again approach a line whose slope is equal to the slope of the dotted line. The deviation on the positive side of the dotted line at the beginning of the runs is probably due to the fact that the first product is $Sn(OH)_2^{++}$ rather than stannic acid and therefore the calculated hydrogen-ion concentrations in this region are too high; as the run proceeds, $Sn(OH)_2^{++}$ hydrolyzes to stannic acid and toward the end of the reaction the calculated hydrogen-ion concentrations are correct.

The appearance of the inflection points in Fig. 3 confirms the theory that the concentration of $Fe(OH)_2^+$ falls below its equilibrium value and then as stannous ion decreases in concentration $Fe(OH)_2^+$ again begins to build up toward equilibrium.

Stannous Ion in Excess at 70°.—In these experiments the rate drops off very quickly from the initial value demanded by equation 2. The results for the entire course of the reaction are plotted in Fig. 4 in the same way as those in Fig. 2; the dotted line represents the initial rate demanded by equation 2. It is seen that the curves very rapidly deviate from the dotted line and appear to approach a straight line. This would correspond to the differential equation

$$\frac{d(Fe^{++})}{dt} = \psi\ (\Sigma Fe^{iii})(Sn^{++}) = \frac{\psi}{2}\ (a - x)(2b - x) \tag{7}$$

in the region of the straight line. The quantity, ψ, is of course only a constant within each run and is itself a function of stannous and hydrogen-ion concentrations.

The differential equation

$$\frac{d(Fe^{++})}{dt} = \frac{2k_3K_1K_2(Fe^{+++})(Sn^{++})}{(H^+)^2\ [1 + x(Sn^{++})]} \tag{8}$$

will be applied to the results, where x of course is a constant. From equations 7, 8, 3 and 4 we obtain the result

$$x = \frac{[(2k_3K_1K_2/\psi) - (H^+)[(H^+) + K_1] - K_1K_2]}{(H^+)[(H^+) + K_1](Sn^{++})} \tag{9}$$

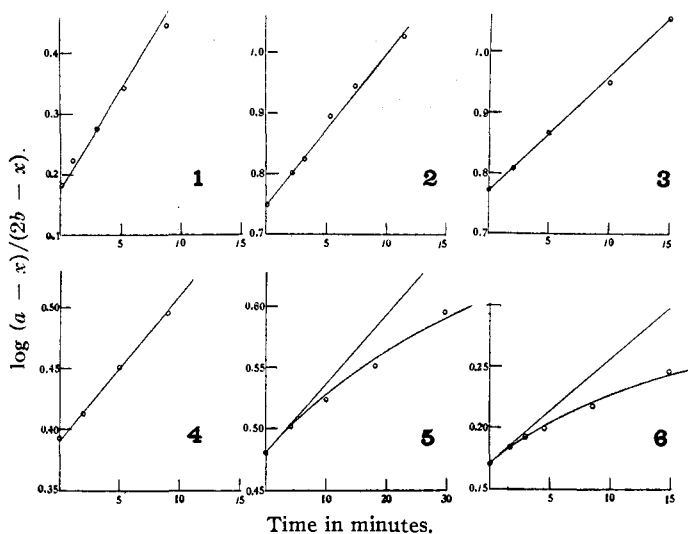The value of $2k_3K_1K_2$ is taken from the graph in

Fig. 2.—Determination of initial rates at 70° in Expts. 1–6: $a - x$ $b - x/2$ are the concentrations in moles per liter of ferric perchlorate and stannous perchlorate at time t.

Fig. 7; ψ is calculated from the slopes of the lines in Fig. 4, $\psi = 4.6S/(2b - a)$; x is calculated for the two points, indicated in each run by the symbols ① and ②. The calculations are presented in Table II.

It is demonstrated in Table II that equation 8 represents the rate quite well for these experiments, which cover a 10-fold variation in (Sn^{++}) and a 20-fold variation in $(H^+)^2$. The variation of x with ionic strength will be discussed later.

Experimental Results at 55°.—In Fig. 5 the rate measurements at 55° are plotted. In runs 17, 18 and 19 no perchloric acid was added to the reaction mixture and therefore the initial rates could not be used, since small amounts of colloidal ferric hydroxide were present. For this reason the last half of these runs only is presented. In runs 13 and 14 the initial rates were estimated

TABLE II
CALCULATION OF χ AT 70°

Run	$\mu^{1/2}$	S	ψ	$2b - a$	K_1 $\times 10^4$	K_1K_2 $\times 10^4$	$2k_3K_1K_2$
9	0.66	0.00125	0.218	0.0261	78	6.0	0.0376
7	.46	.00262	1.00	.0120	84	7.2	.0386
10	.27	.0109	6.28	.00798	110	10.0	.0436
11	.28	.00635	7.00	.00417	108	9.5	.0432
12	.28	.0161	5.22	.01822	108	9.5	.0432

Run	$(Sn^{++})_1$	$(Sn^{++})_2$	$(H^+)_1{}^a$	$(H^+)_2{}^a$	$(\chi)_1$	$(\chi)_2$	$(\bar{\chi})$
9	0.0230	0.0191	0.1944	0.2094	149	151	150
7	.0102	.0066	.1131	.1233	173	200	187
10	.0053	.0046	.0457	.0480	242	239	241
11	.0033	.00252	.0492	.0575	235	250	242
12	.0103	.0096	.0430	.0450	210	199	204

^{a} Corrected for hydrolysis, $(H^+) = c + 2x + (Fe(OH)^{++}) + 2(Fe(OH)_2{}^{++})$.

and $2k_3K_1K_2$ calculated by means of equation 2. Equation 2 was also applied to run 17 since (Sn^{++}) is very small. The results are presented in
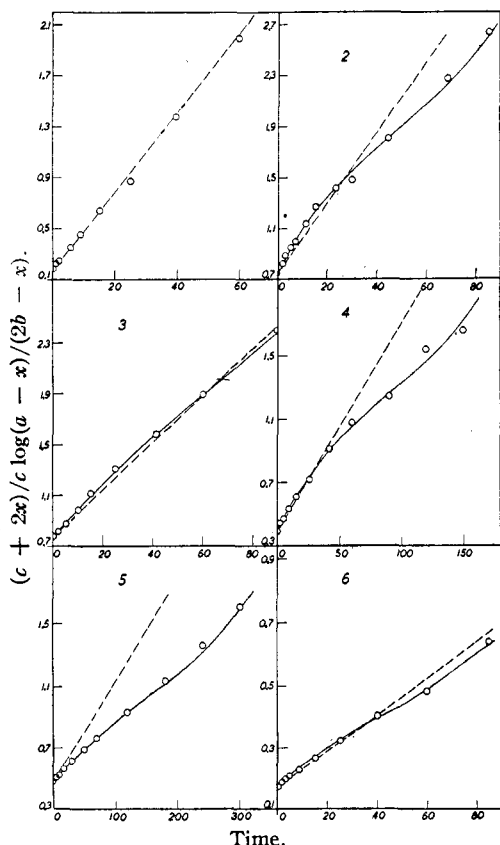

Fig. 3.—Rate measurements in Expts. 1–6, with ferric perchlorate in excess at 70°.

Table III. The values of K_1 and K_1K_2 at 55° were estimated from the temperature coefficients given later.

The runs presented in Table III cover a 1500-fold variation in $(H^+)^2$, a 14-fold variation in

TABLE III
DETERMINATION OF $2k_3K_1K_2$ AT 55°

Run	$\mu^{1/2}$	$\psi \times 10^3$	a	$2b$	c	K_1
14	1.13	1.74	0.0690	0.0292	1.000	0.0039
13	0.54	117.0	.0287	.0287	0.100	.0042
17	0.45	1630.0	.00630	.0051	.0261	.0046

Run	K_1K_2 $\times 10^4$	$(FeOH^{++})_i$	$\begin{array}{c}(Fe(OH)_2{}^+)_i\\\times 10^{-6}\end{array}$	$(Fe^{+++})_i$	$(H^+)_i$	$2k_3K_1K_2$
14	1.05	0.00026	7	0.0687	1.000	0.000175
13	1.20	.00112	340	.0272	0.102	.000129
17	1.31	.00070	700	.0049	.0282	.000168

(Fe^{+++}) and a 6-fold variation in (Sn^{++}), with only a small variation in $2k_3K_1K_2$.
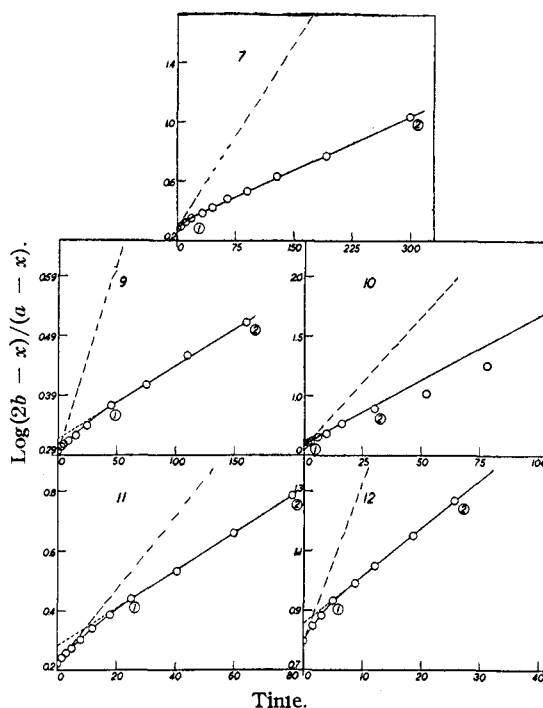

Fig. 4.—Rate measurements with stannous perchlorate in Expts. 7–12 at 70°.

Equation 8 was applied to the latter part of the reaction in the same way as at 70°. The calculations are presented in Table IV; $(\overline{H}^+)$ is the average value of (H^+) in the region through which the points in Fig. 5 fall on a straight line and
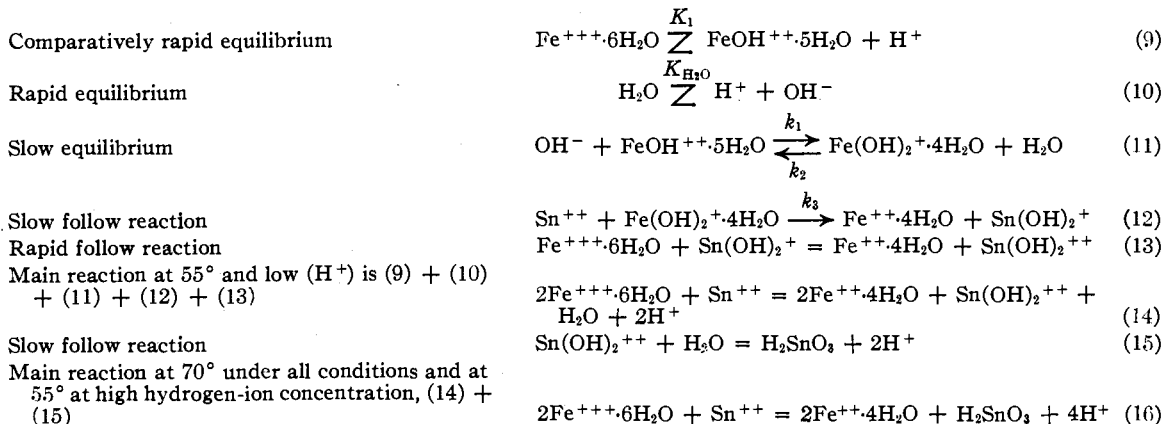
TABLE IV
DETERMINATION OF χ AT 55°

Run	$\mu^{1/2}$	K_1	K_1K_2 $\times 10^4$	$2k_3K_1K_2$	$(\overline{H}^+)$	$(\overline{Sn}^{++})$	ψ	χ
18^a	1.13	0.0039	1.05	0.00180	0.0270	0.0184	0.952	59
14	1.13	.0039	1.05	.00180	1.01	.0121	.00104	61
13	0.54	.0041	1.20	.00150	0.125	.0090	.0504	77
19^a	0.50	.0041	1.21	.00150	.0258	.0194	.735	93

^{a} Runs 18 and 19 are identical except that the reaction mixture in run 18 contained, in addition to 0.0332 M $Fe(ClO_4)_3$ and 0.0323 M $Sn(ClO_4)_2$, 1 M NH_4ClO_4.

$(\overline{\text{Sn}^{++}})$ is defined similarly. The value of $2k_3K_1K_2$ used is taken from Fig. 7. In runs 18 and 19, (H^+) was small and no precipitation of H_2SnO_3 was observed. It was found that one rather than two hydrogen ions were formed per ferric ion produced in these two runs.

Table IV demonstrates that the experimental results at 55° are in good agreement with equation 8 over a 1400-fold change in $(\text{H}^+)^2$.

Interpretation of Results.—The following scheme for the mechanism of the reaction satisfies the experimental results.

Comparatively rapid equilibrium

$$\text{Fe}^{+++}\cdot 6H_2O \overset{K_1}{\rightleftarrows} \text{FeOH}^{++}\cdot 5H_2O + H^+ \tag{9}$$

Rapid equilibrium

$$H_2O \overset{K_{H_2O}}{\rightleftarrows} H^+ + OH^- \tag{10}$$

Slow equilibrium

$$OH^- + \text{FeOH}^{++}\cdot 5H_2O \underset{k_2}{\overset{k_1}{\rightleftarrows}} \text{Fe(OH)}_2^+\cdot 4H_2O + H_2O \tag{11}$$

Slow follow reaction

$$\text{Sn}^{++} + \text{Fe(OH)}_2^+\cdot 4H_2O \overset{k_3}{\longrightarrow} \text{Fe}^{++}\cdot 4H_2O + \text{Sn(OH)}_2^+ \tag{12}$$

Rapid follow reaction

$$\text{Fe}^{+++}\cdot 6H_2O + \text{Sn(OH)}_2^+ = \text{Fe}^{++}\cdot 4H_2O + \text{Sn(OH)}_2^{++} \tag{13}$$

Main reaction at 55° and low (H^+) is (9) + (10) + (11) + (12) + (13)

$$2\text{Fe}^{+++}\cdot 6H_2O + \text{Sn}^{++} = 2\text{Fe}^{++}\cdot 4H_2O + \text{Sn(OH)}_2^{++} + H_2O + 2H^+ \tag{14}$$

Slow follow reaction

$$\text{Sn(OH)}_2^{++} + H_2O = H_2SnO_3 + 2H^+ \tag{15}$$

Main reaction at 70° under all conditions and at 55° at high hydrogen-ion concentration, (14) + (15)

$$2\text{Fe}^{+++}\cdot 6H_2O + \text{Sn}^{++} = 2\text{Fe}^{++}\cdot 4H_2O + H_2SnO_3 + 4H^+ \tag{16}$$

In the most general case the concentration of Fe(OH)_2^+ is not negligible and therefore it is not possible to postulate a steady state between reactions 11 and 12. Therefore the following pair of differential equations results

$$d(\text{Fe(OH)}_2^+)/dt = k_1(\text{FeOH}^{++})(OH^-) - (\text{Fe(OH)}_2^+)[k_2 + k_3(\text{Sn}^{++})]$$

$$d(\text{Fe}^{++})/dt = 2k_3(\text{Fe(OH)}_2^+)(\text{Sn}^{++})$$

or

$$d(\text{Fe(OH)}_2^+)/dt = k_1K_1K_{H_2O}(\text{Fe}^{+++})/(\text{H}^+)^2 - (\text{Fe(OH)}_2^+)[k_2 + k_3(\text{Sn}^{++})] \tag{17}$$

$$d(\text{Fe}^{++})/dt = 2k_3(\text{Fe(OH)}_2^+)(\text{Sn}^{++}) \tag{18}$$

If, however, Fe(OH)_2^+ is at equilibrium with FeOH^{++} and hydrogen ion, as is the case at the start of the reaction, equations 17 and 18 become equation 2

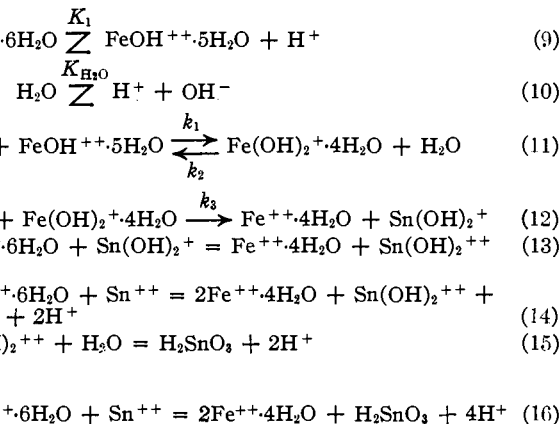$$d(\text{Fe}^{++})/dt = 2k_3K_1K_2(\text{Fe}^{+++})(\text{Sn}^{++})/(\text{H}^+)^2$$

since

$$k_1K_{H_2O}/k_1 = K_2 = (\text{Fe(OH)}_2^+)(\text{H}^+)/(\text{FeOH}^{++}) \tag{19}$$

In the experiments with stannous ion in excess Fe(OH)_2^+ is changing very rapidly while the first 15 or 20% of the reaction occurs. After this initial period, the rate appears to follow the differential equation 8. This indicates that the concentration of Fe(OH)_2^+ must be approaching some kind of "steady state." The ordinary steady state postulate, $d(\text{Fe(OH)}_2^+)/dt = 0$ for two compensating reactions involving an intermediate, would involve appreciable error in some of the experiments, since it is evident that a considerable portion of the ferric salt is present in the form of Fe(OH)_2^+ even at the "steady state stage" of the reaction. It was discovered that another steady state condition could be postulated which involves very much less error. This postulate is that

$$d(\text{Fe}^{++})/-d(\text{Fe(OH)}_2^+) = 0$$

and leads to the equation

$$\frac{-d(\text{Fe(OH)}_2^+)}{dt} = \frac{1}{2}\frac{(\text{Fe(OH)}_2^+)}{(\Sigma\text{Fe}^{iii})}\frac{d(\text{Fe}^{++})}{dt}$$
$$= \frac{1}{2}\,\alpha\,\frac{d(\text{Fe}^{++})}{dt} \tag{20}$$

Applying equation 20 to equations 17 and 18, we obtain

$$(\text{Fe(OH)}_2^+) = \frac{K_1K_2(\text{Fe}^{+++})}{(\text{H}^+)^2[1 + (1 + \alpha)(k_3/k_2)(\text{Sn}^{++})]} \tag{21}$$

and

$$\frac{d(\text{Fe}^{++})}{dt} = \frac{2k_3K_1K_2(\text{Fe}^{+++})(\text{Sn}^{++})}{(\text{H}^+)^2[1 + (1 + \alpha)(k_3/k_2)(\text{Sn}^{++})]} \tag{22}$$

Equation 22 is identical with equation 8 and therefore $\chi = (1 + \alpha)(k_3/k_2)$. Knowing χ we can easily calculate α from equation 21 and therefore k_3/k_2.

$$\alpha = \frac{(\text{Fe(OH)}_2^+)}{(\Sigma\text{Fe}^{iii})} = \frac{K_1K_2}{K_1K_2 + (\text{H}^+)(\text{H}^+ + K_1)[1 + \chi\,\text{Sn}^{++}]} \tag{23}$$

These calculations are given in Table V for the experiments at 70° (see Table II) with stannous in excess.

It is seen that the maximum correction in Table V is about 15%. This is probably smaller than the experimental error (small errors in ψ are greatly magnified in χ). However, it is of inter-

TABLE V

CALCULATION OF k_3/k_2 AT 70°

Run	$(\mu)^{1/2}$	α_1	α_2	x_1	x_2	$\dfrac{(k_3)}{k_2}$	$\dfrac{(k_3)}{1\,k_2\,2}$	$\dfrac{(\overline{k_3})}{k_2}$	$\dfrac{(FeOH^{++})}{(Fe(OH)_2^+)}$
9	0.66	0.0035	0.0035	149	151	149	151	150	10.6
7	.46	.0186	.0187	173	200	170	197	184	3.49
10	.27	.145	.144	242	239	211	208	210	1.03
11	.28	.156	.154	234	250	202	216	209	0.94
12	.28	.115	.115	210	199	188	179	184	1.52

est to consider this analysis and to point out its great accuracy as demonstrated by the constancy of α over the whole "steady state region" of each run.
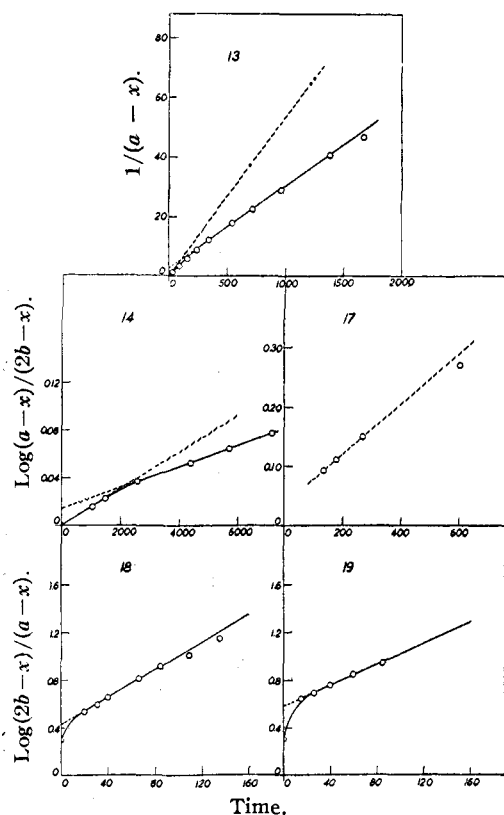
Fig. 5.—Rate measurements at 55°, Expts. 13–19.

Calculation of K_1K_2.—In the initial part of the experiments with stannous perchlorate in excess the concentration of $Fe(OH)_2^+$ is changing much more rapidly than that of ferric ion and therefore the concentration of ferric ion may be assumed to be constant in this region. If this assumption is made equations 17 and 18 may be integrated, and the following result

$$(y - y_0) = \overline{A}t - \tfrac{1}{2}x -$$
$$2.303(dt/dx)^0A^0(2b) \log (2b)(2b - x) \quad (24)$$

and

$$y = y_0(dx/dt)(dt/dx)^0 (2b)/(2b - x) \quad (25)$$

where $y = (Fe(OH)_2^+)$ and $x = (Fe^{++})$ at time equals t, y_0 is initial value of y

$$A_0 = \frac{k_1K_{H_2O}K_1(Fe^{+++})}{(H^+)^2} = \frac{2k_3K_1K_2}{2(k_3/k_2)}\frac{(Fe^{+++})}{(H^+)^2}$$

at $t = 0$ and $\overline{A} = A^0(a - x)/a$. If x, t and (dx/dt) are known, y_0 may be calculated, since $2k_3K_1K_2$, k_3/k_2 and therefore $(dx/dt)_0$ are known.

In Fig. 6 x is plotted against t for the first three experimental points in two runs, nos. 7 and 9. A smooth curve was drawn from the origin, using the initial slope calculated from equation 2 (or 5) as a guide. Three points were chosen on the smooth curve, and (dx/dt) was determined at each point by estimating the tangent to the curve. The points chosen are marked by the symbol $+$; the experimental point by the symbol 0 and the estimated tangents by the dotted lines.

It is seen that equations 24 and 25 do not involve K_1 and K_2 directly, but of course these constants are involved in calculating the initial rate, $(dx/dt)_0$. However, it is to be noted that the experimental value of $2k_3K_1K_2$ depends upon the choice of K_1 and K_2. Actually, it was found that the value of y_0 from equations 24 and 25 was very slightly dependent upon the choice of K_1 and K_2 and therefore the resulting value of $2k_3K_1K_2$. The calculations presented in Table VI were made using the values of K_1 and K_1K_2 assumed in Table I and of course the resulting value of $2k_3K_1K_2$ from Fig. 7 ($K_1^0 = 0.025$ $K_1^0K_2^0 = 35.2 \times 10^{-4}$).

The constancy of y_0 for the three points in each run in Table VI demonstrates that equations 24 and 25 are good representations of the initial portion of the reaction. Furthermore, the values of y_0 are in good agreement with those calculated and therefore it is demonstrated that the value of K_1K_2 chosen is the experimental value within the experimental error.

Actually of course the value of K_1K_2 assumed in Table I was the experimental value found from equations 24 and 25, but a complete logical presentation of the calculations was avoided in order to save space.

Variation with Ionic Strength and Temperature Coefficients.—By combining the Debye–Hückel theory and the Brönsted theory the following relationships result, as $\mu^{1/2} \longrightarrow 0$

$$\log_{10} K_1 = \log_{10} K_1^0 - 2.0\mu^{1/2} \quad (26a)$$
$$\log_{10} K_1K_2 = \log_{10} K_1^0K_2^0 - 3.0\mu^{1/2} \quad (26b)$$
$$\log_{10} 2k_3K_1K_2 = \log_{10} 2k_3^0K_1^0K_2^0 - 1.0\mu^{1/2} \quad (26c)$$
$$\log_{10} (k_2/k_3) = \log_{10} (k_3^0/k_2^0) + 2.0\mu^{1/2} \quad (26d)$$

<div align="center">

TABLE VI

DETERMINATION OF INITIAL CONCENTRATION OF $Fe(OH)_2^+$ IN TWO RUNS

(a) Calculation of A^0 and $(dx/dt)_0$

</div>

Run	$\mu^{1/2}$	a	$2b$	c	$(FeOH^{++})_i{}^a$	$(Fe(OH)_2{}^+)_i{}^a$	$(Fe^{+++})_i$	$(H^+)_i$	$A^0 \times 10^4$	$\left(\dfrac{dx}{dt}\right)_0 10^4$
9	0.66	0.0268	0.0532	0.177	0.00110	0.00046	0.0252	0.179	0.842	7.84
7	.46	.01265	.02486	.1015	.00083	.00072	.0110	.1037	1.20	4.93

^{a} For K_1, K_1K_2 and $2k_3K_1K_2$ see Table II.

<div align="center">

(b) Presentation of Data

</div>

Run 9

t	x	$\dfrac{dx}{dt} \times 10^4$	$a - x$	$2b - x$	$\bar{A} \times 10^5$	$y - y_0$	y/y^0	y_0
2	0.00069	2.70	0.0261	0.05251	8.33	0.00029	0.33	0.00044
4	.00114	1.72	.0257	.05206	8.25	.00036	.22	.00046
6	.00149	1.60	.0254	.05171	8.20	.00041	.20	.00051

Run 7

5	.00132	1.80	.01133	.02354	11.3	.00043	.40	.00072
10	.00211	1.40	.01054	.02275	11.0	.00049	.31	.00071
20	.00343	1.20	.00922	.02148	10.3	.00055	.29	.00078

However, all of the experimental results are in a region of ionic strength where equations 26 cannot be expected to apply. Instead the method of Randall[6] was used. Applying this method, it follows

$$-\tfrac{1}{4}\log K_1 = -\tfrac{1}{4}\log K_1^0 + f(\gamma) \qquad (27a)$$
$$-\tfrac{1}{6}\log K_1K_2 = -\tfrac{1}{6}\log K_1^0 K_2^0 + f(\gamma) \qquad (27b)$$
$$-\tfrac{1}{2}\log 2k_3K_1K_2 = -\tfrac{1}{2}\log 2k_3^0K_1^0K_2^0 + f(\gamma) \qquad (27c)$$
$$\tfrac{1}{4}\log (k_3/k_2) = \tfrac{1}{4}\log (k_1^0/k_2^0) + f(\gamma) \qquad (27d)$$

where $f(\gamma)$ may be represented by some one of the family of log γ curves for single electrolytes. For K_1 and K_1K_2 the same $f(\gamma)$ was used as that given by Bray and Hershey[6] in Table I, page 1890.

In Fig. 7 the quantities $\tfrac{1}{2}$ log $2k_3K_1K_2$ at 70°, and $\tfrac{1}{2}$ log $2k_3K_1K_2$ + 0.7 at 55°, are plotted against $\mu^{1/2}$. The curve that seemed to fit best is one somewhere between the curve chosen by Bray and Hershey[6] for ferric equilibria and the curve for hydrochloric acid. It can be said that all the points except the one at the lowest ionic strength fit the curve within the experimental error. The 20% deviation of this point from the curve might be attributed to small amounts of colloidal ferric hydroxide.

In Fig. 8, $-\tfrac{1}{4}$ log k_3/k_2 at 70° and $-\tfrac{1}{4}$ log $k_3/k_2 - 0.087$ at 55°, are plotted against $\mu^{1/2}$. The curve is the same one used in Fig. 7 and is purposely drawn through the points at the higher

(6) See Refs. 5 and 6(a), Randall and Vietti, THIS JOURNAL. **50**, 926 (1928); (b) Randall, J. Chem. Educ., **8**, 1062 (1931); (c) unpublished results.

ionic strengths. The failure of the three points at the lowest ionic strength to reach the curve can be attributed to inaccuracies in the ionic strength functions used, since small errors in K_1K_2, K_1, and especially in $2k_3K_1K_2$, will cause larger errors in k_3/k_2.

Using the extrapolations in Figs. 7 and 8 the following values are obtained for $2k_3^0K_1^0K_2^0$ and k_3^0/k_2^0 at 70 and 55°.

$2k_3^0K_1^0K_2^0$ at 70° is 0.0660 and at 55° is 0.00262,
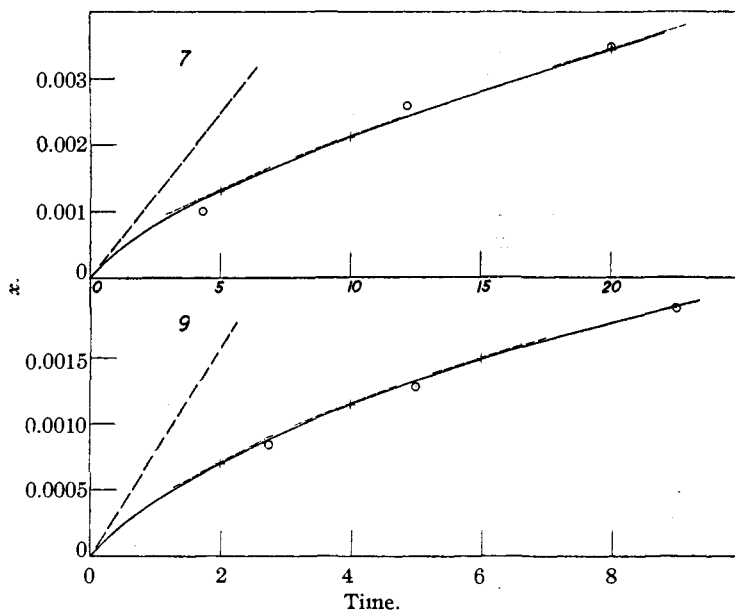

Fig. 6.—Determination of equilibrium concentration of $Fe(OH)_2^+$ in two experiments, nos. 7 and 9.

therefore $\Delta H = 48,600$ calories; k_3^0/k_2^0 at 70° = 58 and at 55° = 25.7, $\Delta H = 12,300$ calories.

The quantities in bold figures in Table VII can

be calculated without knowing ΔH for K_1K_2 and K_1; those in italics depend upon the choice of ΔH for K_1K_2 and K_1, $2 \times 12{,}650$ and $12{,}650$, respectively.
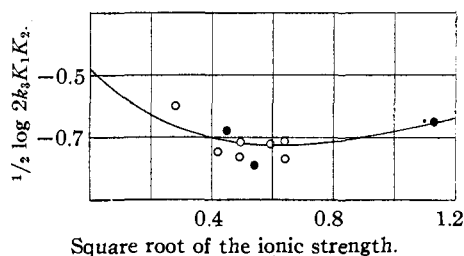

Fig. 7.—Variation of $2k_3K_1K_2$ with ionic strength: O, at $70°$; ●, at $55°$, $^1/_2 \log (2k_3K_1K_2)$ + 0.7.

The values assumed for ΔH_{K_1} and $\Delta H_{K_1K_2}$ depend upon the following: Bray and Hershey[5] would have obtained essentially the same result if they had used a smaller value of K_1 and taken the second step of the hydrolysis into consideration. There are two reasons for this: the first is that the equilibria they were considering did not involve hydrogen ion, and the second that K_1 decreases more rapidly than K_2 with ionic strength. The kinetic value which was obtained at $70°$ for K_1K_2 was extrapolated to $25°$ by using Bray and Hershey's value[5] for ΔH_{K_1}, 12,650, and assuming that $\Delta H_{K_1K_2} = 2\Delta H_{K_1}$. It was found that the value obtained for K_1K_2 at $25°$, 13.0×10^{-6}, taken together with a value for K_1, one-quarter of that used by Bray and Hershey,[5] will give approximately the same results as those obtained by Bray and Hershey.[5]

TABLE VII

TEMPERATURE COEFFICIENTS

	$70°$	$55°$	ΔH
$2k_3K_1K_2$	660×10^{-4}	26.2×10^{-4}	$48{,}600$
k_3/k_2	58	25.7	$12{,}300$
$K_1k_1K_{H_2O}$	568×10^{-6}	50.9×10^{-6}	$36{,}300$
K_{H_2O}	2×10^{-11}	8.12×10^{-12}	$13{,}200$
K_1k_1	284×10^{5}	63×10^{5}	$23{,}100$
K_1K_2	35.2×10^{-4}	6.5×10^{-4}	$(25{,}400)$
k_3	9.4	2.01	$23{,}200$
k_2	0.162	0.0783	$10{,}900$
K_1	(0.025)	0.0106	$(12{,}650)$
k_1	11.4×10^8	5.9×10^8	$10{,}400$

Discussion of Results.—It is considered by the author that the following have been definitely established in perchlorate solutions: (1) the rate determining step for the reduction of the ferric salt is

$$Fe(OH)_2{}^+ \cdot 4H_2O + Sn^{++} \longrightarrow$$
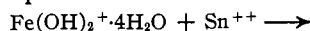
and (2) the mechanism for the reactions involved in the equilibrium

$$FeOH^{++} + H_2O \rightleftharpoons Fe(OH)_2{}^+ + H^+$$
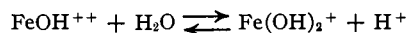
is the one given by equation 11. All alternative formulations to the two above that were tried failed to explain one or more portions of the experimental data.
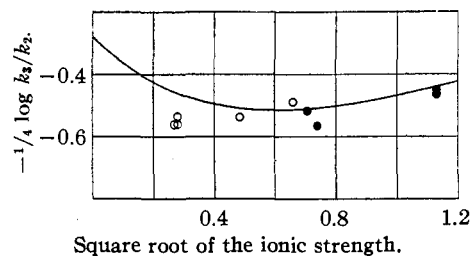

Fig. 8.—Variation of k_3/k_2 with ionic strength at $70°$: O, at $70°$; ●, at $55°$, $-^1/_4 \log (k_3/k_2)$ $- 0.087$.

The most plausible explanation of the failure of ferric and stannous ions to react directly is that ions of like and multiple charges cannot approach each other closely enough to cause reaction unless their relative kinetic energy is very high. This minimum kinetic energy is estimated to be, at the very least, 15,000 calories. If it is assumed that the ordinary chemical heat of activation for ferric plus stannous is the same as for $Fe(OH)_2{}^+$ plus stannous, then the ratio of the rates at $70°$ will be less than

$$e^{-15{,}000/(343 \times 1.986)} = 3 \times 10^{-10}$$

The products of the rate determining step, equation 1, were assumed in equation 12 to be 2-valent iron and 3-valent tin, rather than 1-valent iron and 4-valent tin. There is no evidence for the existence of univalent iron and Ball[7] and co-workers have recently published evidence for the existence of trivalent tin as an intermediate.

The mechanism of the reactions involved in the hydrolysis of $FeOH^{++}\cdot 5H_2O$ was demonstrated to be

$$FeOH^{++}\cdot 5H_2O + OH^- \underset{k_2}{\overset{k_1}{\rightleftharpoons}} Fe(OH)_2{}^+\cdot 4H_2O + H_2O$$
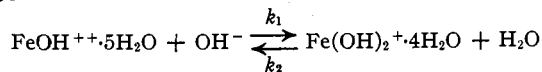
the replacement of water by hydroxide ion and the replacement of hydroxide ion by water. This replacement mechanism is analogous to the theory of Olson[8] for organic substitution reactions. It differs from the one generally assumed for the hydrolysis of hydrated metallic ions

$$FeOH^{++}\cdot 5H_2O \longrightarrow Fe(OH)_x{}^+\cdot 4H_2O + H^+$$
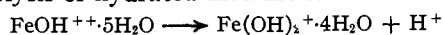
a simple splitting off and addition of a proton.

(7) Ball, Wulfkuehler and Wingard, THIS JOURNAL, **57**, 1729 (1935).
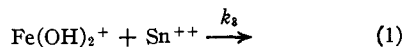
(8) Olson, J. Chem. Phys., **1**, 418 (1933).

In conclusion I wish to express my gratitude to Professor William C. Bray for his advice and suggestions during the progress of the work.
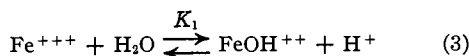
Summary

Rate measurements are presented for the reaction between ferric and stannous perchlorates in solutions containing perchloric acid at 70 and 55°. The rate is much slower than when chloride ion is present.

There is no evidence for a direct reaction between ferric ion and stannous ion. The failure of the two ions to react at an appreciable rate is attributed to the high repulsive forces between these polyvalent, positive ions.
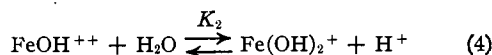
The experimental results are in agreement with the theory that the rate determining step for the reduction of the ferric salt is

$$Fe(OH)_2{}^+ + Sn^{++} \xrightarrow{k_3} \qquad (1)$$

When the hydrolysis equilibria

$$Fe^{+++} + H_2O \underset{}{\overset{K_1}{\rightleftarrows}} FeOH^{++} + H^+ \qquad (3)$$

and

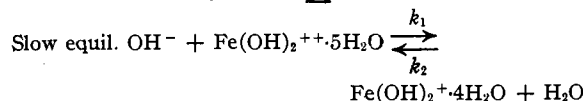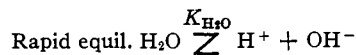$$FeOH^{++} + H_2O \underset{}{\overset{K_2}{\rightleftarrows}} Fe(OH)_2{}^+ + H^+ \qquad (4)$$

are maintained the rate law is

$$d(Fe^{++})/dt = 2k_3K_1K_2(Fe^{+++})(Sn^{++})/(H^+)^2 \qquad (2)$$

This law represents the initial rate in all experiments and applies throughout when the concentration of ferric ion is high compared to that of stannous ion. The specific rate, $2k_3K_1K_2$, is 660 $\times 10^{-4}$ at 70° and 26.2 $\times 10^{-4}$ at 55°.

A study of the deviations from equation 2 led to the conclusions that reaction 4 is not rapid compared to Reaction 1 and that the mechanism of reaction 4 is

$$\text{Rapid equil. } H_2O \overset{K_{H_2O}}{\underset{}{\rightleftarrows}} H^+ + OH^-$$

$$\text{Slow equil. } OH^- + Fe(OH)_2{}^{++}\cdot 5H_2O \underset{k_2}{\overset{k_1}{\rightleftarrows}}$$
$$Fe(OH)_2{}^+\cdot 4H_2O + H_2O$$

The study resulted in the determination of the product, K_1K_2, at 70° and the ratio, k_3/k_2 at 70° and 55°. Combination with the value of the specific rate, $2k_3K_1K_2$, gave the following values at 70°: $K_1K_2 = 35.2 \times 10^{-4}$, $k_3 = 9.4$ and $k_2 = 0.162$.

While neither of the hydrolysis quotients, K_1 nor K_2, has been determined directly, values of each have been chosen which are consistent with the above results and with available data for the hydrolysis of ferric ion. The resulting values of the various equilibrium quotients and specific rates at 70 and 55° are listed in Table VII. Concentrations are expressed in moles per liter and time intervals in minutes.

BERKELEY, CALIF.

The Activation of Specific Bonds in Complex Molecules at Catalytic Surfaces. II. The Carbon–Hydrogen and Carbon–Carbon Bonds in Ethane and Ethane-d

BY KIYOSHI MORIKAWA,[1] W. S. BENEDICT AND HUGH S. TAYLOR

The activation of the carbon–hydrogen and carbon–carbon bonds in ethane at nickel catalyst surfaces can be studied with the aid of deuterium since two reactions may be examined: (a) the exchange reaction which may be generalized as $C_2H_xD_y + D_2 = C_2H_{x-1}D_{y+1} + HD$ in which $x + y = 6$ and y may have any integral values from 0 to 5; and (b) the methane producing reaction $C_2H_6 + H_2 = 2CH_4$. The former reaction involves the C–H bond, the latter the C–C bond. Deuterium permits these reactions to be studied when they are occurring simultaneously on a given catalyst under given conditions of temperature and pressure. During the course of this work, also, investigation was made of the kinetics of methane formation from ethane and hydrogen, the data providing interesting aspects of the mechanism of activation of the ethane at nickel surfaces.

Experimental Details

Materials.—Electrolytic hydrogen and deuterium from the electrolysis of ordinary and heavy water ($d^{25}{}_{25} = 1.1079$) were employed. Ethane was produced catalytically from ethylene and hydrogen over a nickel catalyst at room temperature. It was purified by combustion of the excess hydrogen over copper–copper oxide, followed by fractional distillation to remove nitrogen and methane present.