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

Kinetic and Equilibrium Measurements of the Reaction $2Fe^{+++} + 2I^- = 2Fe^{++} + I_2$

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The reaction

$$2Fe^{+++} + 2I^- = 2Fe^{++} + I_2 \qquad (1)$$

furnishes an example in which the rates of both the forward and reverse reactions may be measured conveniently, and in which the kinetic results may be checked by comparison between values of the equilibrium quotient

$$K = (Fe^{++})^2(I_2)/(Fe^{+++})^2(I^-)^2 \qquad (2)$$

based on measurements of rate, electromotive force and equilibrium concentrations. Wagner[1] in 1924 suggested the complete rate law

$$\frac{d(Fe^{++})}{dt} = \frac{k_1(Fe^{+++})(I^-)^2}{1 + (Fe^{++})/(Fe^{+++})\epsilon_4} - \frac{k_4(Fe^{++})(I_2)}{1 + (Fe^{+++})\epsilon_4/(Fe^{++})} \qquad (3)$$

which corresponds to a single path with two rate determining steps. Application of the condition that $d(Fe^{++})/dt$ is equal to zero at equlibrium leads to the relation $K = k_1\epsilon_4/k_4$. A check of equation 3 is thus furnished by the calculation of K from experimental values of k_1, k_4 and ϵ_4, provided all measurements are made at the same temperature and the same ionic strength.

Wagner's evidence for the rate law of the forward reaction

$$\frac{d(Fe^{++})}{dt} = \frac{k_1(Fe^{+++})(I^-)^2}{1 + (Fe^{++})/(Fe^{+++})\epsilon_4} \qquad (3a)$$

comprised the early work of Schukarew[2] showing that the initial rate depends on the third order reaction $Fe^{+++} + 2I^- \longrightarrow$, the retarding effect of ferrous ion, and the identity of this rate law with that demonstrated by Wagner himself for the analogous reaction between ferricyanide ion and iodide ion. He gives one pair of values of k_1 and ϵ_4 at 15° and a single ionic strength. As evidence that the first step of the reverse reaction is $Fe^{++} + I_2 \longrightarrow$, Wagner refers to the results of Banerji and Dhar.[3a] However, we were not able to calculate values of k_4 in conventional units from the published data.[3] Additional experimental work was therefore necessary before the above mentioned test could be applied to equation 3.

Our measurements were made at 25° in dilute acid solutions having an ionic strength of 0.09, and are in agreement with a rate law of the form

$$\frac{d(Fe^{++})}{dt} = \frac{k_1(Fe^{+++})(I^-)^2}{1 + (Fe^{++})/(Fe^{+++})[\epsilon_4 + \epsilon_6(I^-)]} - \frac{k_4(Fe^{++})(I_2) + k_6(Fe^{++})(I_3^-)}{1 + (Fe^{+++})[\epsilon_4 + \epsilon_6(I^-)]/(Fe^{++})}\ \mathrm{I}$$
$$+ \frac{k_1'(Fe^{+++})(I^-)}{1 + (Fe^{++})(H^+)/(Fe^{+++})\epsilon'} - \frac{k_4'(Fe^{++})(I_2)/(H^+)(I^-)}{1 + (Fe^{+++})\epsilon'/(Fe^{++})(H^+)}\ \mathrm{II} \qquad (4)$$

The two parts, I and II, correspond to two paths, each with two rate determining steps. If the terms containing ϵ_6 and k_6 are omitted, I is the rate law suggested by Wagner. II is dominant only at low concentrations of iodide ion. Setting $d(Fe^{++})/dt$ equal to zero in equation 4 gives the relations

$$k_1\epsilon_4/k_4 = K_{I_3^-}k_1\epsilon_6/k_6 = k_1'\epsilon'/k_4' = K \qquad (5)$$

where $K_{I_3^-}$ is the equilibrium quotient of the reaction $I_3^- = I_2 + I^-$.

Equation 4 was constructed by combining into one rate law the results of rate measurements on both sides of equilibrium. The two positive terms of the rate law were derived from an analysis of the data for the forward reaction between ferric ion and iodide ion, and the sum of the numerators of the negative terms was in agreement with the data for the reverse reaction between ferrous ion and iodine. The denominators of the negative terms were included in the rate law to make it consistent with the equilibrium law, 2. They did not exceed unity by an amount significant in comparison with the experimental errors. Equations 5 were checked by comparison with the results of equilibrium determinations.

The specific rates and equilibrium quotients of ferric reactions vary rapidly with changing ionic strength. According to the Debye–Hückel theory, the relationship between any equilibrium quotient, K, the ionic strength, μ, and the charge of each ion, z, may be expressed in the form

$$\log_{10}(K/K^0) = -(\Delta z^2)f(\gamma)$$

where $f(\gamma)$ is a function of the activity coefficients of the ions, and at 25° approaches the limit $-0.5\ \mu^{1/2}$ as $\mu^{1/2}$ approaches zero.

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(1) Wagner, *Z. physik. Chem.*, **113**, 269 (1924).

(2) Schukarew, *ibid.*, **38**, 353 (1901).

(3) (a) Banerji and Dhar, *Z. anorg. Chem.*, **134**, 172 (1924); (b) Bhattacharya and Dhar, *J. Ind. Chem. Soc.*, **6**, 455 (1929); *Z. anorg. allgem. Chem.*, **196**, 28 (1931).

Randall[4] has shown that, when Δz^2 is not zero, the $-(1/\Delta z^2) \log K/K^0$ curve in a $\mu^{1/2}$ diagram may be represented by the $\log \gamma$ curve for some one of the strong electrolytes. Bray and Hershey[5a] adopted this method of plotting in their study of certain equilibria involving ferric ion, and their values of $f(\gamma)$ have been used in this investigation. Thus at $\mu = 0.09, f(\gamma) = -0.097$; in reaction 1, $\Delta z^2 = -12$, $\log (K/K^0) = -12 (0.097)$, and $K/K^0 = 0.0685$.

In applying these ideas to the specific rates in equation 4 the value $\Delta z^2 = -12$ must be distributed among the specific rates in each part of the rate law. The following values are based upon the Brönsted rule and equation 5.

	k_1	ϵ_4	k_4	ϵ_6	k_6	k_1'	ϵ'	k_4'
Δz^2	-10	-2	0	-6	-4	-6	-4	$+2$

In each case $f(\gamma)$ was assumed to be -0.097 at $\mu = 0.09$.

Allowance was made for the formation of the complex ferric iodide ion, FeI^{++}, by comparing two sets of calculations, the first based on the complete ionization of ferric iodide, the second on the assumption that, at $\mu = 0.09$, $K_{FeI^{++}} = (FeI^{++})/(Fe^{+++})(I^-) = 20$.

$$Fe^{+++} + I^- = FeI^{++} \quad \Delta z^2 = -6 \tag{6}$$

The corresponding value of $K_{FeI^{++}}$ at $\mu = 0$ is 75.

Corrections for the hydrolysis of ferric ion were based on the results of Bray and Hershey.[5a]

$$Fe^{+++} + H_2O = FeOH^{++} + H^+ \quad \Delta z^2 = -4 \tag{7}$$

$K^0_{FeOH^{++}} = 60(10^{-4})$. At $\mu = 0.09$, $K_{FeOH^{++}} = 24.6(10^{-4})$. The hydrolysis ranged from 10 to 30% and was controlled by the addition of nitric acid. We believe that the hydrolysis corrections are at least approximately correct since the values of the hydrolysis quotients[5a] were determined from a study of equilibria involving ferric ion. The calculation of ferric ion concentrations is the reverse step, and may be accepted as an empirical method even if the values of $K_{FeOH^{++}}$ are incorrect.[5b]

The concentrations of triiodide ion were calculated by means of the equilibrium constant $K_{I_3^-} = (I_2)(I^-)/(I_3^-) = 0.00141$[6]

$$I_3^- = I_2 + I^- \quad \Delta z^2 = 0 \tag{8}$$

Similarly, in one group of experiments in which bromide ion was present, the concentrations of I_2Br^- were calculated by means of the constant $K_{I_2Br^-} = 0.08$.[7]

The standard potentials used in calculating the equilibrium constant of reaction 1 were

$$Fe^{+++} + E^- = Fe^{++} \quad \Delta z^2 = -5 \quad E^0 = 0.772^{5a} \tag{9}$$

and

$${}^1/_2 I_2 + E^- = I^- \quad \Delta z^2 = 1 \quad E^0 = 0.534 \tag{10}$$

To determine the latter value, the correction recommended by Randall and Young[8] was applied to the value, 0.5357, chosen by Lewis and Randall.[9]

The solubility product of silver iodide

$$AgI = Ag^+ + I^- \quad \Delta z^2 = +2$$
$$K^0_{AgI} = (9.0 \pm 0.5)(10^{-17}) \tag{11}$$

was calculated by combining the standard iodine potential (equation 10) with the results of Jones and Kaplan[6] for the reaction

$$Ag + {}^1/_2I_2(s) = AgI \quad E^0_{298} = 0.6845$$

and the silver electrode potential[5a]

$$Ag^+ + E^- = Ag \quad E^0_{298} = 0.7985$$

The solubility product of silver bromide

$$AgBr = Ag^+ + Br^- \quad K^0_{AgBr} = (5.3 \pm 0.3)(10^{-13}) \tag{12}$$

was determined by combining the silver electrode potential with the silver bromide electrode potential

$$AgBr + E^- = Ag + Br^- \quad E^0_{298} = 0.0723 \pm 0.0002$$

The latter was obtained by plotting in a $\mu^{1/2}$ diagram the results of Lewis and Storch[10] for the reaction $AgBr + {}^1/_2H_2 = Ag + H^+ + Br^-$. This potential is in agreement with the value 0.072 ± 0.001 obtained by combining the measurements of Afanasiev[11] for the reaction $AgCl + Br^- = AgBr + Cl^-$ with the silver chloride potential of Randall and Young.[8]

On account of the great tendency of ferric ion to form addition compounds, the presence of chloride and sulfate ions is to be avoided, but ferric nitrate may be assumed to be completely ionized. The ionic strength was controlled by the addition of potassium nitrate. C. P. chemicals were used without further purification. Ferrous

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(4) (a) Randall and Vietti, THIS JOURNAL, **50**, 1526 (1928); (b) Randall, *J. Chem. Education*, **8**, 1062 (1931).

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

(5) (b) In our previous calculations (Ref. 5a) we assumed that the hydrolysis of $FeOH^{++}$ is negligible in comparison with that of Fe^{+++}. If this assumption is in error our values of $K_{FeOH^{++}}$ are too large. Also, methods which are based on the determination of hydrogen ion concentrations should yield higher values of $K_{FeOH^{++}}$ than we obtained. This may explain the higher results of Brönsted and Volqvartz, *Z. physik. Chem.*, **134**, 127, 133 (1928), which we unwittingly overlooked in 1934. Their value of $K^0_{FeOH^{++}}$ at 15° is nearly the same as ours at 25°.

(6) Jones and Kaplan, THIS JOURNAL, **50**, 1845 (1928).

(7) Jakowkin, *Z. physik. Chem.*, **20**, 31 (1896).

(8) Randall and Young, THIS JOURNAL, **50**, 1003 (1928).

(9) Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., New York City, 1923, p. 430.

(10) Lewis and Storch, THIS JOURNAL, **39**, 2544 (1917).

(11) Afanasiev, *ibid.*, **52**, 3477 (1930).

TABLE I

INITIAL RATES OF THE REACTION BETWEEN FERRIC ION AND IODIDE ION AT 0.09 IONIC STRENGTH AND 25°

								$10^6 d(Fe^{++})/dt$	
Expt.	$Fe(NO_3)_3$	KI	HNO_3	$Fe(NO_3)_2$	(Fe^{+++})	(I^-)	(H^+)	Obsd.	Calcd.
1	0.0112	0.01	0.0188		0.0087	0.0085	0.0198	3850	3330
2	.0056	.01	.0194		.0043	.0092	.0199	1870	1930
3	.0112	.003	.0188		.0096	.0025	.0200	345	333
4	.0124	.01	.0076		.0088	.0085	.0098	3550	3350
5	.0124	.01	.0076		.0088	.0085	.0098	3450	3350
6	.0062	.01	.0088		.00435	.0092	.0099	1825	1950
7	.00124	.01	.0098		.00086	.0098	.0100	485	440
8	.0124	.003	.0076		.0096	.0025	.0099	310	334
9	.0124	.003	.0076		.0096	.0025	.0099	285	334
10	.00124	.003	.0098		.00096	.00295	.0100	43.5	45
11	.0148	.01	.0002		.0088	.0085	.0047	3250	3370
12	.00148	.01	.0045		.00088	.0098	.0050	440	448
13	.0148	.003	.0002		.0096	.0025	.0049	305	334
14	.00148	.003	.0045		.00096	.00295	.0050	41	45
15	.0148	.001	.0002	0.001	.0099	.00084	.0050	13.25	13.4
16	.0148	.0005	.0002	.001	.0099	.00042	.0050	4.07	4.01
17	.0074	.01	.0026	.001	.0044	.0092	.0048	950	931
18	.0062	.01	.0088	.001	.00435	.0092	.0099	950	921
19	.0062	.008	.0088	.001	.0045	.0073	.0099	535	539
20	.0062	.005	.0088	.001	.0046	.0046	.0099	155	177
21	.0062	.003	.0088	.001	.0048	.00275	.0100	46	52
22	.0074	.003	.0026	.001	.0048	.00275	.0050	47	54
23	.0062	.001	.0088	.001	.0049	.00091	.0100	5.0	4.6
24	.0062	.001	.0088	.001	.0049	.00091	.0100	4.8	4.6
25	.0074	.001	.0026	.001	.0049	.00091	.0050	5.05	5.05
26	.0074	.0005	.0026	.001	.0050	.00046	.0050	1.5	1.56
27	.0062	.0005	.0088	.001	.0050	.00046	.0100	1.4	1.29
28	.00248	.01	.0095	.001	.00173	.0097	.0100	225	228
29	.00248	.003	.0095	.001	.00191	.0029	.0100	9.6	11.4
30	.00124	.01	.0098	.001	.00086	.0098	.0100	68	69
31	.00124	.003	.0098	.001	.00096	.00295	.0100	3.25	3.2
32	.00062	.01	.0099	.001	.00043	.0099	.0100	21.5	18.8
33	.00062	.003	.0099	.001	.00048	.0030	.0100	1.0	0.87
34	.0074	.01	.0026	.002	.0044	.0092	.0048	622	610
35	.0074	.003	.0026	.002	.0048	.00275	.0050	31	32
36	.0074	.0005	.0026	.002	.0050	.00046	.0050	0.965	0.99
37	.0062	.0005	.0088	.002	.0050	.00046	.0100	.735	.75
38	.0074	.0005	.0026	.003	.0050	.00046	.0050	.725	.74
39	.0062	.0005	.0088	.003	.0050	.00046	.0100	.51	.53
40	.0074	.01	.0026	.01	.0044	.0092	.0048	150	161
41	.0074	.003	.0026	.01	.0048	.00274	.0050	6.7	7.4
42	.0074	.001	.0026	.01	.0049	.00091	.0050	0.62	0.76
43	.0074	.0005	.0026	.01	.0050	.00046	.0050	.25	.27
44	.0062	.0005	.0088	.01	.0050	.00046	.0100	.18	.175

nitrate solutions were prepared by mixing barium nitrate and ferrous sulfate solutions in equivalent amounts and filtering off the precipitated barium sulfate. Atmospheric oxidation of the ferrous salt was closely watched, and fresh solutions were prepared when the ferric iron content exceeded 3% of the total iron. To diminish the oxygen concentration the solutions and reaction systems were shaken with carbon dioxide. Although the effect of the diffuse daylight of the laboratory on the rates was found to be negligible, the precaution was taken to shield the reaction vessels from light in the rate measurements with iodine and ferrous salts and in the equilibrium determinations. All concentrations were measured in moles per liter, and time intervals in minutes.

Rate Measurements of the Reaction between Ferric Ion and Iodide Ion

Sasaki[12] and Kiss and Bossányi[13] have studied the reaction in low ferrous ion concentration. To

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[12] Sasaki, *Z. anorg. allgem Chem.*, **137**, 181, 291 (1924).

[13] Kiss and Bossányi, *ibid.*, **191**, 289 (1930).

measure the initial rate they added starch and a small known quantity of sodium thiosulfate to the reaction system, and observed the interval of time from the start of the reaction to the appearance of the blue color of starch-iodine. Ferric ion reacts directly with thiosulfate ion, however, and the method is subject to error. Increasing the quantity of the thiosulfate increases the amount lost by direct reaction with ferric ion, but there is then a greater average concentration of ferrous ion and the reaction between ferric ion and iodide ion is retarded. The two effects cancel and the rate appears to be independent of the quantity of thiosulfate used. The specific rate in low ferrous ion concentration was redetermined, therefore, by a more direct method.

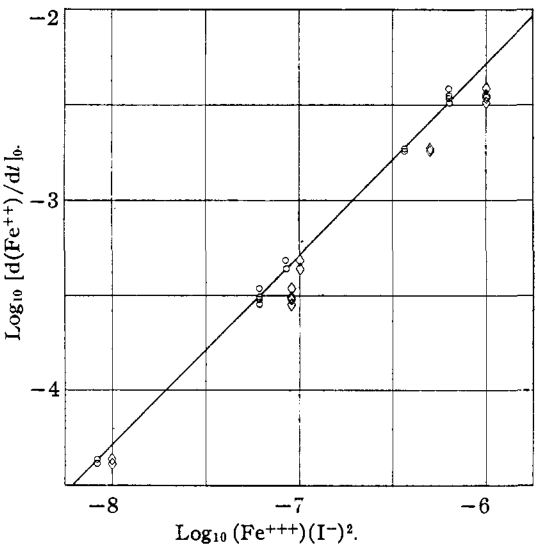

Fig. 1.—Rate measurements in low (Fe^{++}), Expts. 1 to 14: ○, concentrations based on $K_{\mathrm{FeI}^{++}} = (\mathrm{FeI}^{++})/(\mathrm{Fe}^{+++})(\mathrm{I}^-) = 20$; ◇, concentrations based on $K_{\mathrm{FeI}^{++}} = 0$.

Control experiments showed that when iodine is in excess it can be titrated with sodium thiosulfate in the presence of ferric ion without loss of accuracy. Ten-cc. samples of the reaction system were quenched in about 0.075 *M* $\mathrm{FeSO_4}$, and the iodine was titrated without delay. The effectiveness of the quenching was indicated by the slowness with which the blue color reappeared after the starch end-point had been reached.

The results are summarized in Table I. The initial concentrations of ferric nitrate, potassium iodide, nitric acid and ferrous nitrate, composing the reaction systems, are listed in the second, third, fourth and fifth columns. The initial concentrations of ferric ion, iodide ion and hydrogen ion, corrected for the complex ion, FeI^{++}, by means of $K_{\mathrm{FeI}^{++}} = 20$, are listed in the sixth, seventh and eighth columns.

The "observed" initial rates listed in the ninth column were determined from the experimental data by the following method. An approximate rate law was formulated, and values of the rate were calculated at convenient values of (Fe^{++}), the concentration of ferrous ion. For each experiment the reciprocal of the rate, $dt/d(\mathrm{Fe}^{++})$ was plotted against (Fe^{++}). By graphically integrating $[dt/d(\mathrm{Fe}^{++})]d(\mathrm{Fe}^{++})$ from the initial value of (Fe^{++}), time intervals were determined, and compared with those found experimentally. The rate law was modified and the calculations repeated until these two sets of time intervals were brought into agreement. This procedure made certain that the initial rate chosen in each experiment is consistent with the rates during the experiment. The points in Figs. 1 to 4 below correspond to these observed initial rates.

The method of calculating the initial rates listed in the last column is explained at the end of the section.

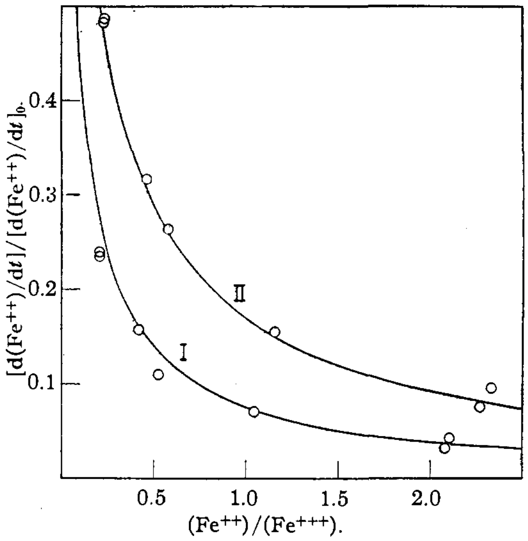

Fig. 2.—The retarding effect of ferrous ion. Curve I, 0.003 *M* KI, Expts; 21, 22, 29, 31, 33, 35 and 41; Curve II, 0.01 *M* KI; Expts. 17, 18, 28, 30, 32, 34 and 40.

The rate is proportional to the concentration product $(\mathrm{Fe}^{+++})(\mathrm{I}^-)^2$ when the concentration of ferrous ion is small and that of iodide ion is not less than about 0.003 molal. This is shown in Fig. 1, where, for the experiments with zero initial ferrous salt, the logarithm of the initial rate is plotted against $\log(\mathrm{Fe}^{+++})(\mathrm{I}^-)^2$. The results obtained without correcting for FeI^{++} are also included in Fig. 1 (but not in Figs. 2, 3 and 4 below). The two values of the specific rate, k_1, determined from the two sets of data are listed at the end of the section.

The retarding effect of ferrous ion is shown in Figs. 2 and 3, where the ratio of the initial rate in each experiment to the rate at zero concentration of ferrous ion, $[d(Fe^{++})/dt]_0$, is plotted against the ratio $(Fe^{++})/(Fe^{+++})$. If equation 3a were the correct rate law, a single curve would be obtained starting at unity on the ordinate axis and approaching zero at high values of $(Fe^{++})/(Fe^{+++})$. The incompleteness of this rate law is therefore shown at once by the existence of two curves in Fig. 2 when the concentration of potassium iodide is varied from 0.01 to 0.003 *M* KI; and in Fig. 3 when, at a much lower iodide concentration, the concentration of hydrogen ion is varied from approximately 0.005 to 0.01 *M* H^+.

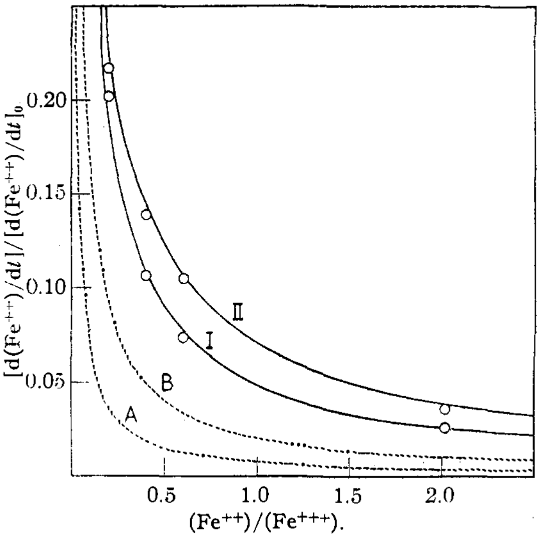

Fig. 3.—The retarding effect of ferrous ion at 0.0005 *M* KI. Curve I, approximately 0.01 *M* H^+; Expts. 27, 37, 39 and 44; Curve II, approximately 0.005 *M* H^+; Expts. 26, 36, 38 and 43.

In Fig. 2, as $(Fe^{++})/(Fe^{+++})$ is increased, the ordinate becomes nearly proportional to (I^-), indicating a rate law of the form

$$\frac{d(Fe^{++})}{dt} = \frac{k_1(Fe^{+++})(I^-)^2}{1 + (Fe^{++})/(Fe^{+++})(I^-)\epsilon_6} \tag{13a}$$

However, when this equation and the data in Fig. 2 are used to calculate the curve for 0.0005 *M* KI, Curve A in Fig. 3 is obtained, and the ratio $[d(Fe^{++})/dt]/[d(Fe^{++})/dt]_0$ is much too small. Some of the discrepancy may be removed by introducing another constant, ϵ_4, in equation 13a

$$\frac{d(Fe^{++})}{dt} = \frac{k_1(Fe^{+++})(I^-)^2}{1 + (Fe^{++})/(Fe^{+++})[\epsilon_4 + \epsilon_6(I^-)]} \tag{13b}$$

which raises Curve A to Curve B. The retarding action of hydrogen ion at low (I^-) and high $(Fe^{++})/(Fe^{+++})$, as shown in Fig. 3, suggests the presence of an additional term in the rate law which is important only at low (I^-), and is therefore of less than the second degree in (I^-)

$$\frac{d(Fe^{++})}{dt} = \frac{k_1'(Fe^{+++})(I^-)}{1 + (Fe^{++})(H^+)/(Fe^{+++})\epsilon'} \tag{13c}$$

The effect of changing (I^-) at constant (Fe^{++}) is shown in Fig. 4. Curves B and B′ are based on equation 13b. At low iodide concentration B is much lower than Curves I and II, and B′ is lower than III; which again shows the need for an added term, such as 13c, in the rate law. Were this added term of the form

$$\frac{d(Fe^{++})}{dt} = \frac{k_1'(Fe^{+++})(I^-)}{(H^+)[1 + (Fe^{++})/(Fe^{+++})\epsilon']}$$

Curve B would have been raised to C, instead of to II, by halving the concentration of hydrogen ion. Were it of the form

$$\frac{d(Fe^{++})}{dt} = \frac{k_1'(Fe^{+++})^2(I^-)}{1 + (H^+)(Fe^{++})/\epsilon'}$$

Curve B′ would have been raised to D, instead of to III, by doubling the concentration of ferric ion.

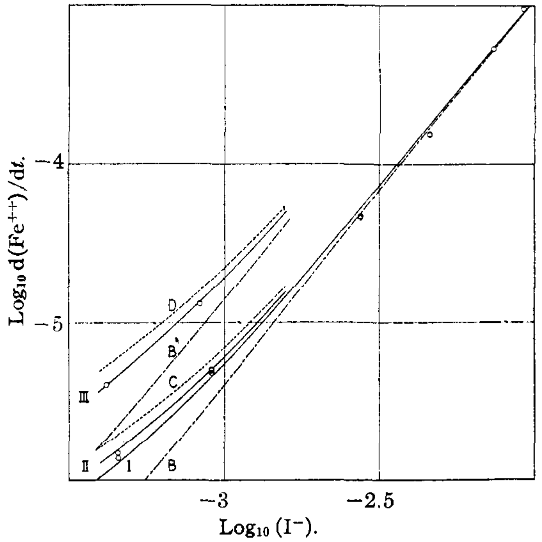

Fig. 4.—Rate measurements at 0.001 *M* Fe^{++}, Expts. 15 to 27: Curve I, 0.0062 *M* $Fe(NO_3)_3$, approximately 0.01 *M* H^+; Curve II, 0.0074 *M* $Fe(NO_3)_3$, approximately 0.005 *M* H^+; Curve III, 0.0148 *M* $Fe(NO_3)_3$, approximately 0.005 *M* H^+.

Our experimental data on the rate of interaction of ferric ion and iodide ion are therefore in agreement with the rate law

$$\frac{d(\mathrm{Fe}^{++})}{dt} = \frac{k_1(\mathrm{Fe}^{+++})(\mathrm{I}^-)^2}{1 + (\mathrm{Fe}^{++})/(\mathrm{Fe}^{+++})[\epsilon_4 + \epsilon_6(\mathrm{I}^-)]} + \frac{k_1'(\mathrm{Fe}^{+++})(\mathrm{I}^-)}{1 + (\mathrm{Fe}^{++})(\mathrm{H}^+)/(\mathrm{Fe}^{+++})\epsilon'} \quad (13)$$

Equation 13 is the sum of 13b and 13c and consists of the positive terms of equation 4. The solid curves in Figs. 1 to 4 and the initial rates in the last column of Table I were calculated by means of equation 13 and the specific rates listed below for $K_{\mathrm{FeI}^{++}} = 20$. When no correction for FeI^{++} was applied, satisfactory agreement between observed and calculated data was also obtained with the same rate law, but with different specific rates.

The values of the specific rates at $\mu = 0.09$ are

	k_1	ϵ_4	ϵ_6	k_1'	ϵ'
$K_{\mathrm{FeI}^{++}} = 20$	5200 ± 500	0.018 ± 0.002	20 ± 1	0.70 ± 0.05	1/(700 ± 50)
$K_{\mathrm{FeI}^{++}} = 0$	3800	.02	17	.55	1/600

Rate Measurements of the Reaction between Ferrous Ion and Iodine

In Homogeneous Solutions at 25°.—Solutions of iodine and ferrous nitrate were mixed and the subsequent changes in the concentration of total iodine, $(\Sigma \mathrm{I}_2)$, were determined by titration against sodium thiosulfate. Since the time required for analysis was negligible in comparison with the time intervals between analyses, no quenching was necessary. The initial concentrations of the substances affecting the rate, corrected for the complex ion, FeI^{++}, are listed in Table II. The ferric iron concentration, $(\Sigma \mathrm{Fe}^{+++})$, was determined iodimetrically. On account of the atmospheric oxidation of some of the ferrous salt, the hydrogen ion concentration is less than that corresponding to the amount of nitric acid added to the reaction system. The iodine solution contained a trace of iodide, which was determined by the permanganate method.[14]

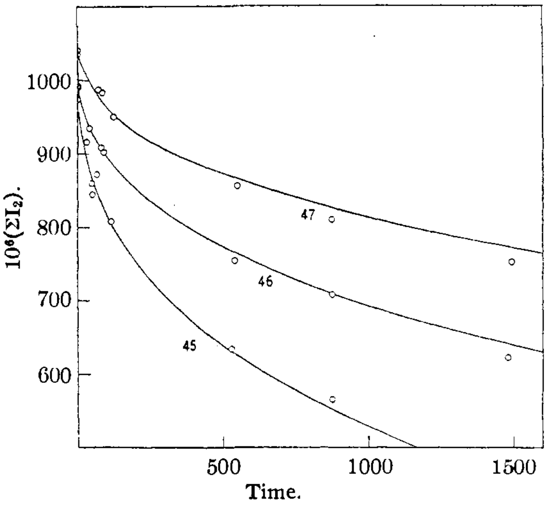

Fig. 5.—The reaction between ferrous ion and iodide ion at 0.005 *M* $\mathrm{HNO_3}$: Expt. 45, 0.025 *M* $\mathrm{Fe(NO_3)_2}$; Expt. 46, 0.01 *M* $\mathrm{Fe(NO_3)_2}$; Expt. 47, 0.005 *M* $\mathrm{Fe(NO_3)_2}$.

TABLE II

INITIAL CONCENTRATIONS

Expt.	(Fe^{++})	10^6 $(\Sigma\mathrm{Fe}^{+++})$	(H^+)	10^6 $(\Sigma \mathrm{I}_2)$	10^6 (I_3^-)	10^6 (I^-)	10^6 (I_2)	μ
45	0.0244	620	0.0046	974	24	36	950	0.09
46	.0098	250	.0048	992	24	36	968	.09
47	.0049	125	.0049	1035	25	35	1010	.09
48	.0244	620	.0046	997	201	356	796	.09
49	.0244	620	.0046	992	335	719	657	.09
50	.0244	620	.0095	930	23	37	907	.09
51	.0244	620	.0195	920	23	37	897	.09
52	.0245	500	.0196	6170	4830	5130	1340	.107

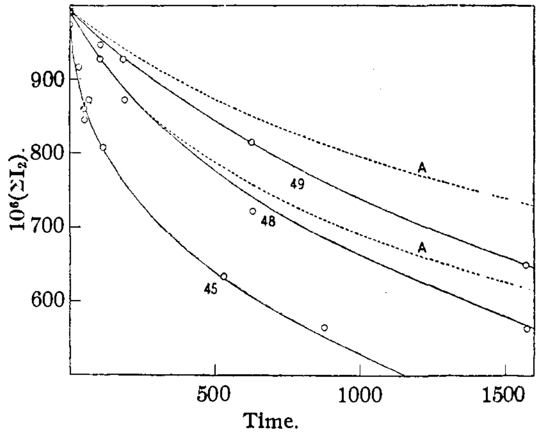

Fig. 6.—The retarding effect of iodide ion at 0.025 *M* $\mathrm{Fe(NO_3)_2}$ and 0.005 *M* $\mathrm{HNO_3}$. Initial concentrations of iodide: Expt. 45, $60(10^{-6})$ *M*; Expt. 48, 0.0005 *M*; Expt. 49, 0.001 *M*.

The experimental results are represented by points in Figs. 5 to 8, where the total iodine concentration is plotted against the time in minutes.

In the analysis of these results, various rate laws were tested by a method similar to that described in the preceding section. The reciprocal of the rate, $-dt/d(\Sigma \mathrm{I}_2)$, was calculated at convenient values of $(\Sigma \mathrm{I}_2)$ by means of the assumed rate law, and plotted against $(\Sigma \mathrm{I}_2)$. The time interval to any selected value of $(\Sigma \mathrm{I}_2)$ was calcu-

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[14] Bray and MacKay, THIS JOURNAL, **32**, 1193 (1910).

lated by graphical integration of $-[dt/d(\Sigma I_2)]\, d(\Sigma I_2)$ from the initial value of (ΣI_2).

In experiments 45 to 51 ferrous nitrate was present in sufficient excess to make the proportionate change in the concentration of ferrous ion during each experiment small in comparison with that of iodine or iodide ion. The results of experiments 45 to 47, which differ only in the concentration of ferrous ion, are given in Fig. 5. At any selected concentration of total iodine the time intervals are inversely proportional to the concentration of ferrous ion. The rate is therefore directly proportional to the concentration of this ion.

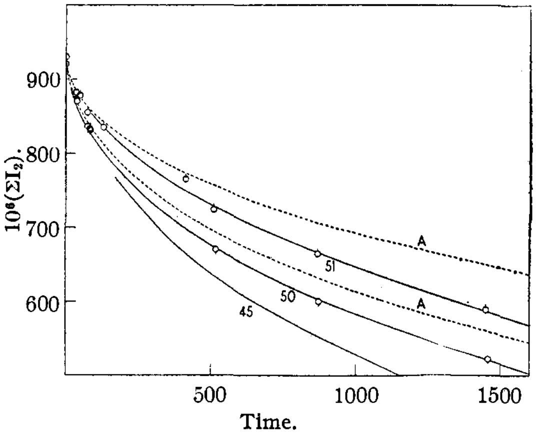

Fig. 7.—The retarding effect of hydrogen ion at 0.025 *M* $Fe(NO_3)_2$: concentrations of HNO_3: Expt. 45, 0.005 *M*; Expt. 50, 0.01 *M*; Expt. 51, 0.02 *M*.

The retarding action of iodide ion is illustrated in Fig. 6, where in three experiments the initial concentration of iodide is varied from a small value in 45 to 0.001 molal in 49. Similarly the retarding action of hydrogen ion is shown in Fig. 7, where the concentration of hydrogen ion is varied from approximately 0.005 molal in 45 to 0.02 molal in 51.

These results indicate a rate law of the form

$$\frac{-d(Fe^{++})}{dt} = \frac{-2d(\Sigma I_2)}{dt} = \frac{k_4'(Fe^{++})(I_2)}{(H^+)(I^-)} \qquad (14a)$$

This rate law is in agreement with the results of experiment 45. However, when it is used to calculate the results of the other experiments in Figs. 6 and 7, the curves labeled A are obtained; and the agreement is not satisfactory. The actual rate is greater than that given by equation 14a and the discrepancy increases rapidly as the product $(H^+)(I^-)$ is increased. The discrepancy may be removed, in these experiments, by including in the rate law an added term, which is independent of $(H^+)(I^-)$

$$-d(Fe^{++})/dt = k_4(Fe^{++})(I_2) \qquad (14b)$$

That there is a third term in the rate law

$$-d(Fe^{++})/dt = k_6(Fe^{++})(I_3^-) \qquad (14c)$$

is indicated by the results of experiment 52, Fig. 8, in which the concentration of triiodide ion was much greater than in the other experiments. Were the rate given by the sum of equations 14a and 14b alone, the measurements would have been represented by Curve B.

Our experimental data on the rate of interaction of ferrous ion and iodine are therefore in agreement with the rate law

$$-d(Fe^{++})/dt = k_4(Fe^{++})(I_2) + k_6(Fe^{++})(I_3^-) + k_4'(Fe^{++})(I_2)/(H^+)(I^-) \qquad (14)$$

Equation 14 is the sum of 14a, 14b and 14c, and consists of the numerators of the negative terms of equation 4. The solid curves in Figs. 5 to 8 were calculated by means of equation 4, the specific rates listed below and the specific rates listed at the end of the preceding section. In evaluating k_6 it is necessary to allow for the rate of reaction between ferric ion and iodide ion, which was relatively large only in experiment 52. The magnitude of this effect is illustrated in Fig. 8 by the difference between Curve C, based on equation 14, and the actual data. The values of the specific rates obtained when the complex ion FeI^{++} was neglected were not changed when the correction was applied.

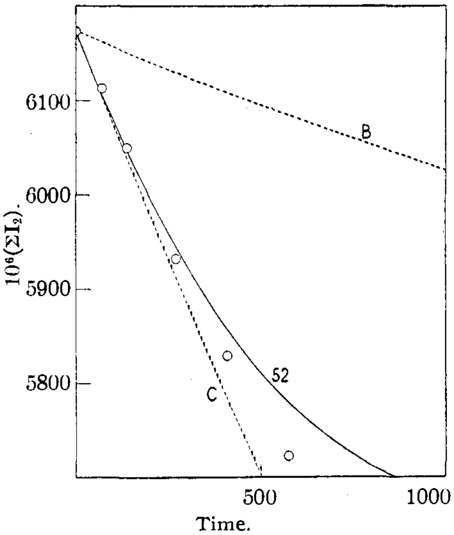

Fig. 8.—The reaction between ferrous ion and triiodide ion at 0.02 *M* HNO_3.

The values of the specific rates at $\mu = 0.09$ are

$$k_4 = 0.009 \pm 0.001$$
$$k_6 = 0.0145 \pm 0.001$$
$$k_4' = (10.0 \pm 0.5)(10^{-8})$$

Rate Measurements in the Presence of Silver Iodide, Silver Bromide and Bromide Ion.—Rate measurements were made also at very low concentrations of iodide ion, maintained by a buffer of silver iodide and silver bromide in a solution containing bromide ion. The ratio $(I^-)/(Br^-)$, which is constant when the system is in equilibrium, is equal to $K_{AgI}/K_{AgBr} = 1.7(10^{-4})$ (*cf.* equations 11 and 12). The ionic strength was 0.055 in these experiments.

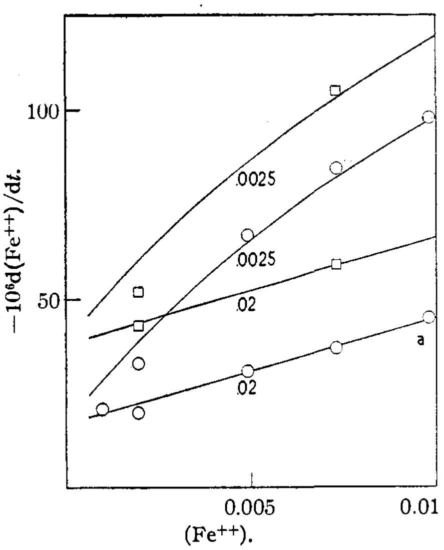

Fig. 9.—Variation of initial rates with the concentration of ferrous ion: ○, 0.005; □, 0.01 mole per liter of AgI and of AgBr; 0.0006 M I_2; 0.01 M Br^-; 0.02 and 0.0025 M H^+; stirring rate, 2000 r. p. m.

An equimolal mixture of the silver halides was precipitated in the reaction vessel before each experiment by adding the calculated amount of a known silver nitrate solution to a solution containing hydrogen ion, potassium ion, iodide ion and bromide ion. After the addition of the ferrous salt solution the reaction was started by adding to the mixture a measured volume of nearly saturated iodine solution (at 25°). The precipitate was kept from settling by vigorously stirring the reaction mixture at a rate of 2000 revolutions per minute, except when otherwise stated. This stirring rate was found to be high enough to bring the reaction rate to within a few per cent. of its maximum value (*cf.* Fig. 11). The results were reproducible when a definite procedure was followed, but they depended on the order in which the reagents were mixed, and are therefore not presented in detail.

The concentration of iodine during the course of the reaction was determined by extraction with carbon tetrachloride and titration with sodium thiosulfate. Since carbon tetrachloride is emulsified by the silver halide precipitate, the latter was first filtered out rapidly on a loosely packed asbestos filter. Some iodine was volatilized in this procedure, and control experiments were made to determine the loss.

(ΣI_2) or $(I_2) + (I_2Br^-)$ could be expressed as a function of the time, t, to within the precision of analysis, by the empirical equation

$$\log [(\Sigma I_2) - \alpha] = -\beta t + \gamma \qquad (15)$$

where α, β and γ were constant during an experiment, but varied from experiment to experiment.

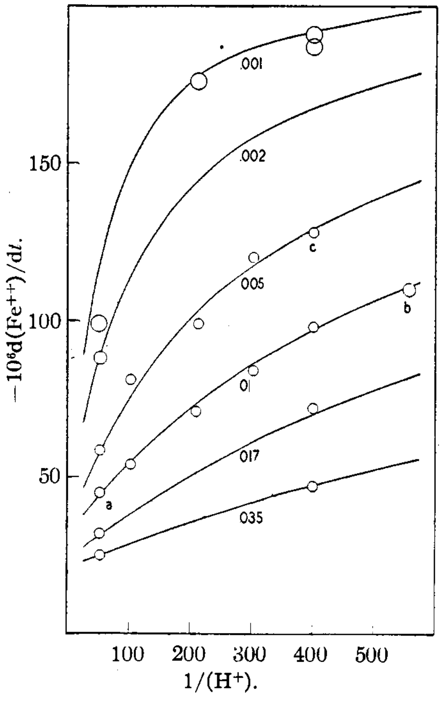

Fig. 10.—Initial rates at various concentrations of hydrogen ion and bromide ion: 0.005 mole per liter of AgI and of AgBr; 0.0006 M I_2; 0.0098 M Fe^{++}; 0.001 to 0.035 M Br^-.

Differentiation of equation 15 gave the rate at any time during the experiment.

$$-d(\Sigma I_2)/dt = -{}^1/_2 d(Fe^{++})/dt = \beta[(\Sigma I_2) - \alpha] \qquad (16)$$

By substituting $t = 0$ in equation 15, the initial value of $(\Sigma I_2) - \alpha$ was calculated, and the initial rate was obtained by substituting this value in equation 16.

The results are presented graphically in Figs. 9, 10 and 11, where the ordinates are the initial rates, reduced to the same iodine concentration, 0.0006 M I_2.

The experimental results can be explained only by assuming two simultaneous reactions, one a homogeneous reaction whose rate is retarded by hydrogen ion and iodide ion (*cf.* equation 14a), and the other a reaction at the surface of the silver halides. As the homogeneous reaction is slow at 0.02 M H^+, the observed rates in the experiments at this concentration, shown in Fig. 9, are due mainly to the heterogeneous reaction. A two-fold increase in the surface, which should double the rate of the heterogeneous reaction, increased the observed rate by the same amount at the two concentrations of hydrogen ion. This result suggests that the rate of the heterogeneous reaction was not altered by an eight-fold change in the concentration of hydrogen ion. A study of all the data supported this result, and led to the additional conclusions that the rate of the heterogeneous reaction was approximately proportional to the concentration of iodine, increased slightly when the concentration of ferrous ion was increased from 0.001 to 0.01 molal, and decreased slightly when the concentration of bromide ion was increased.

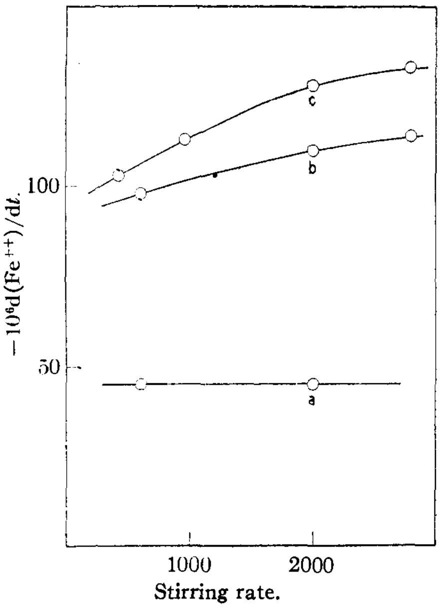

Fig. 11.—Effect of varying the stirring rate in Experiments a, b and c, Fig. 10.

The retarding effects of hydrogen ion and bromide ion (and therefore iodide ion) are illustrated by the data in Fig. 10—and especially by those at low concentrations of hydrogen ion and bromide ion, where the observed rate is due mainly to the homogeneous reaction. When a consistent set of corrections for the heterogeneous reaction were applied to the observed rates, the homogeneous reaction was found to obey rate law 14a at the lowest rates. With increasing values of the quotient $(Fe^{++})/(H^+)(Br^-)$, it approached a value independent of the concentrations of ferrous ion, hydrogen ion and bromide ion. The rates of the homogeneous reaction could therefore be represented by the equation

$$\frac{-d(Fe^{++})}{dt} = \frac{-2d(\Sigma I_2)}{dt} = \frac{k_4'(Fe^{++})(I_2)/(H^+)(I^-)}{1 + \sigma(Fe^{++})/(H^+)(I^-)} \quad (17)$$

The curves in Figs. 9 and 10 represent the sum of the rates calculated by means of this equation and the assumed rates of the heterogeneous reaction. The concentration of iodide ion was assumed to have its equilibrium value, $1.7(10^{-4})$ (Br^-). The corresponding values of σ and k_4' are $28(10^{-8})$ and $8(10^{-8})$ at $\mu = 0.055$.

This value of k_4' corresponds to $8.5(10^{-8})$ at $\mu = 0.09$ and is to be compared with the more accurate value, $10(10^{-8})$, obtained at higher concentrations of iodide ion. The difference could have been eliminated by a small decrease in the corrections for the heterogeneous reaction.

The differential equation, 17, signifies that there are two rate determining steps in series, the first of which is the hydrolysis of iodine. This will become dominant only at high velocities. Thus when the quotient $(Fe^{++})/(H^+)(I^-)$ is increased the equation approaches the limit

$$-d(I_2)/dt = (k_4'/2\sigma)(I_2)$$

$k_4'/2\sigma$ is equal to 0.14, which is of the same order of magnitude as 0.25, the specific rate derived by Abel[15] for the hydrolysis of iodine at 25°. However, this agreement may not be significant, as Liebhafsky[16] has concluded that the specific rate of the iodine hydrolysis has a much higher value. Such a value would require σ to be much smaller than $28(10^{-8})$, and the denominator in 17 would then not be large enough to account for the observed retardations at high reaction rates.

Some or all of the departure of the homogeneous rate from direct proportionality to (Fe^{++}) $(I_2)/(H^+)(Br^-)$ may be explained in another way if the steady state concentration of iodide ion is

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(15) Abel, *Z. physik. Chem.*, **136**, 161 (1928).

(16) Liebhafsky, *ibid.*, **A155**, 289 (1931); THIS JOURNAL, **56**, 2372 (1934). *Cf.* Skrabal, *Z. Elektrochem.*, **42**, 244 (1936).

assumed to have exceeded its equilibrium concentration by an amount which increased rapidly with increasing speed of reaction. This assumption receives some support from the decrease in rate observed when the stirring rate was decreased in experiments b and c, Fig. 11. In order to test this explanation the total reaction rate was assumed to be equal to $\kappa[(I^-) - 1.7(10^{-4})\ (Br^-)]$, where κ is a constant of proportionality. Steady state concentrations of iodide ion were calculated by means of this relation and substituted for (I^-) in equation 14a. Comparison of these rates with the data showed that the homogeneous rate could be represented approximately by equation 14a

$$-2d(\Sigma I_2)/dt = k_4'(Fe^{++})(I_2)/(H^+)(I^-) \quad (14a)$$

if the corrections for the heterogeneous reaction were much larger than before, and if κ and k_4' were equal to 250 and $6(10^{-8})$.

TABLE III

MEASUREMENTS OF THE EQUILIBRIUM $2Fe^{+++} + 2I^- = 2Fe^{++} + I_2$ AT 25°

Expt.	53	54	55
	Initial Concentrations		
KI	0.01916	0.00766	0.0100
$Fe(NO_3)_3$	.01022	.00511	....
HNO_3	.02	.02	.0191
KNO_3	....	.042	....
	Final Concentrations		
$10^6(\Sigma I_2)$	4845 ± 10	2140 ± 7	5360 ± 30
$10^6(\Sigma Fe^{+++})$	598 ± 5	752 ± 7	1530 ± 20
(Fe^{++})	0.00962	0.00436	0.0235
(ΣI^-)	.00950	.00334	.01060
μ	.0715	.087	.108
	Results Based on $K^0_{FeI^{++}} = 75$		
(I^-)	0.00558	0.00205	0.00611
$IO^6(I_2)$	977	873	1010
$10^6(Fe^{+++})$	478	646	1240
K	12,800 ± 600	9500 ± 1000	9700 ± 1000
	Results Based on $K^0_{FeI^{++}} = 0$		
(I^-)	0.00563	0.00206	0.00623
$10^6(I_2)$	970	870	990
$10^6(Fe^{+++})$	530	670	1365
K	10,100 ± 600	8700 ± 1000	7600 ± 1000

In spite of the uncertainties with regard to the magnitude of the corrections for the heterogeneous reaction, the specific rate of the iodine hydrolysis and the amount of supersaturation of iodide ion, the rate measurements at very low concentrations of iodide ion confirm the presence in the rate law of the term represented by equation 14a, and the order of magnitude of the specific rate, $k_4' = 10^{-7}$.

Equilibrium Determinations

After dilute solutions of ferric nitrate and potassium iodide had been allowed to react for nine days, the concentration of iodine was determined by titration with sodium thiosulfate, and the ferric iron concentration was determined iodimetrically. Equilibrium was approached also from the reverse side by allowing ferrous nitrate and iodine to react.

The results are summarized in Table III. The amounts of potassium iodide, ferric nitrate, nitric acid and potassium nitrate composing the reaction systems are listed in the second to fifth rows. The total iodine, (ΣI_2), and the total ferric iron concentration, (ΣFe^{+++}), obtained by analysis at equilibrium, are given in the sixth and seventh rows. In experiments 53 and 54, the total iodide ion concentration, $(\Sigma I^-) = (FeI^{++}) + (I_3^-) + (I^-)$, can be calculated from the data by subtracting either (Fe^{++}) or $2(\Sigma I_2)$ from the concentration of potassium iodide initially added, and the values of (ΣI^-) given in the ninth row of Table III are the averages of these two values. In the remaining rows are given the ionic strengths, and values of the equilibrium quotient, K, calculated with and without correction for the complex ion FeI^{++}.

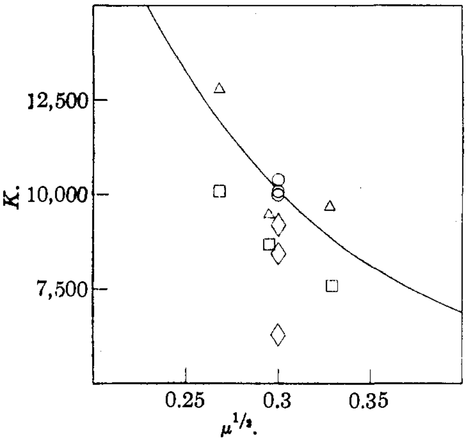

Fig. 12.—$2Fe^{+++} + 2I^- = 2Fe^{++} + I_2$; equilibrium quotients: △, □, from analysis at equilibrium, Table III, assuming $K^0_{FeI^{++}} = 75$ and zero, respectively; ○, ◇, from rate measurements assuming $K^0_{FeI^{++}} = 75$ and zero, respectively; the curve is based on the standard potentials of the ferric–ferrous and iodine–iodide electrodes.

Combination of the standard potentials of the ferric–ferrous and iodine–iodide electrodes, equations 9 and 10, with the solubility of iodine, 0.00132 mole per liter, gives the value of the equilibrium constant, $K^0 = 148{,}000 \pm 2000$ at 25°. This result and the corresponding values of the equilibrium quotients at various ionic strengths, calculated by the method outlined in the introduction, are independent of any assumption regarding the stability of FeI^{++}. At $\mu = 0.09$, $K = 10{,}100$.

The equilibrium quotients at $\mu = 0.09$, calculated from the experimentally determined specific rates by means of equations 5, are

	$K = k_1\epsilon_4/k_4$	$K = K_{\mathrm{I}_3^-}k_1\epsilon_6/k_6$	$K = k_1'\epsilon'/k_4'$
$K_{\mathrm{FeI}^{++}} = 20$	10,400	10,100	10,000
$K_{\mathrm{FeI}^{++}} = 0$	8,450	6,300	9,200

The various values for the equilibrium quotients are compared in Fig. 12. The agreement between the equilibrium quotients calculated from kinetic data, and those determined from measurements of equilibrium concentrations, is fairly close even when no correction for the complex ion FeI^{++} is applied. These "experimental" results are brought into much better agreement with each other, and with the "theoretical" results, represented by the curve in Fig. 12, by correcting for the complex ion, FeI^{++}. This improved agreement may not deserve much weight, since it is the chief basis for the choice of $K_{\mathrm{FeI}^{++}} = 20 \pm 5$ at $\mu = 0.09$ and $K^0_{\mathrm{FeI}^{++}} = 75 \pm 25$. Regardless of the value of $K_{\mathrm{FeI}^{++}}$, however, the results of the various determinations of the equilibrium quotient of reaction 1 confirm the complete rate law, equation 4.

Intermediate Compounds

The rate law expressed by equation 4 signifies that ferric ion may react with either two or one iodide ions in the first rate determining steps of the forward reaction, and that ferrous ion may react with iodine, triiodide ion or hypoiodous acid in the first steps of the reverse reaction. Many reactions are known in which hypoiodous acid is the reactive oxidizing agent in aqueous iodine solutions, and very few in which the iodine itself reacts directly with the reducing agent. This is probably the first example of the direct action of triiodide ion as an oxidizing agent.

To explain part I of the rate law, Wagner[1] advocated intermediate formation of $\mathrm{I_2^-}$, which may be regarded as an addition compound of atomic iodine and iodide ion. Strong supporting evidence is furnished by his more detailed study of the analogous reaction between ferricyanide ion and iodide ion. His theory is a necessary consequence of the assumption that ferrous ion is formed in the rate determining reaction

$$\mathrm{Fe^{+++} + 2I^- \longrightarrow Fe^{++} + I_2^-}$$

since there is then only one unit change in the valence of the iron. The same theory may also be used to explain the kinetic results of Yost and Zabaro[17] for the reaction between trivalent titanium and iodine. The rate determining step is then $\mathrm{TiOH^{++} + I_2 \longrightarrow I_2^- + TiO^{++} + H^+}$. It seems to be impossible in this case for the titanium to increase its valence by more than one unit. The analogous theory for part II of our rate law requires the formation of $\mathrm{IOH^-}$, an addition compound of atomic iodine and hydroxide ion. If this substance exists at all, it is probably in equilibrium with $\mathrm{I_2^-}$

$$\mathrm{IOH^- + I^- + H^+ = I_2^- + H_2O}$$

and therefore is not likely to play a significant role at high concentrations of hydrogen and iodide ions.

The following systems of reactions are in agreement with the rate law:

$$\text{I}$$

$$\mathrm{Fe^{+++} + I^-} \overset{K_2}{Z} \mathrm{FeI^{++}}$$

$$\mathrm{FeI^{++} + I^-} \underset{k_2}{\overset{{}^1/_2k_1/K_2}{\rightleftarrows}} \mathrm{Fe^{++} + I_2^-}$$

$$\left\{\begin{aligned} &\mathrm{I_2^- + Fe^{+++}} \underset{{}^1/_2k_4}{\overset{k_3}{\rightleftarrows}} \mathrm{Fe^{++} + I_2} \\ &\mathrm{I_2^- + FeI^{++}} \underset{{}^1/_2k_6}{\overset{k_5/k_2}{\rightleftarrows}} \mathrm{Fe^{++} + I_3} \end{aligned}\right.$$

$$\text{II}$$

$$\mathrm{Fe^{+++} + I^-} \overset{K_2}{Z} \mathrm{FeI^{++}}$$

$$\mathrm{FeI^{++} + H_2O} \underset{k_2'}{\overset{{}^1/_2k_1'/K_2}{\rightleftarrows}} \mathrm{Fe^{++} + IOH^- + H^+}$$

$$\mathrm{IOH^- + Fe^{+++}} \underset{{}^1/_2k_4'/K_3}{\overset{k_3'}{\rightleftarrows}} \mathrm{Fe^{++} + IOH}$$

$$\mathrm{IOH + I^- + H^+} \overset{1/K_3}{Z} \mathrm{I_2 + H_2O}$$

$$\epsilon_4 = k_3/k_2$$
$$\epsilon_6 = k_5/k_2$$
$$\epsilon' = k_3'/k_2'$$

Each arrow designates a rate determining reaction, and the symbol[18] Z denotes that equilibrium is established relatively rapidly. In deriving the

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(17) Yost and Zabaro, THIS JOURNAL, **48**, 1181 (1926).

(18) Skrabal, *Z. Elektrochem.*, **40**, 235 (1934).

rate law, the concentrations of I_2^- and IOH^- are assumed to be so small that the rate of change of their concentrations may be set equal to zero.

It has usually been assumed that hypohalous acid is reduced to halide in one step, which requires the valence of the element oxidized to increase by two units. For this reason, our preliminary results at low concentrations of iodide and hydrogen ions were cited by Bray and Gorin[19] as one of several items of evidence for the formation of a +4 iron compound as an intermediate.

The following systems of reactions, which involve tetravalent iron compounds as intermediates, are also in agreement with the rate law:

I

$$\mathrm{Fe^{+++} + I^-} \overset{K_2}{\rightleftharpoons} \mathrm{FeI^{++}}$$

$$\mathrm{FeI^{++} + I^-} \underset{k_2}{\overset{{}^1/_2 k_1/K_2}{\rightleftharpoons}} \mathrm{FeI_2^+}$$

$$\mathrm{FeI_2^+ + Fe^{+++}} \overset{K_1}{\rightleftharpoons} \mathrm{Fe^{++} + FeI_2^{++}}$$

$$\left\{\begin{array}{l} \mathrm{FeI_2^{++}} \underset{{}^1/_2 k_4}{\overset{k_3}{\rightleftharpoons}} \mathrm{Fe^{++} + I_2} \\ \mathrm{FeI_2^{++} + I^-} \underset{{}^1/_2 k_6}{\overset{k_5}{\rightleftharpoons}} \mathrm{Fe^{++} + I_3^-} \end{array}\right.$$

II

$$\mathrm{Fe^{+++} + I^-} \overset{K_2}{\rightleftharpoons} \mathrm{FeI^{++}}$$

$$\mathrm{FeI^{++} + H_2O} \underset{k_2'}{\overset{{}^1/_2 k_1'/K_2}{\rightleftharpoons}} \mathrm{FeI(OH)^+ + H^+}$$

$$\mathrm{FeI(OH)^+ + Fe^{+++}} \overset{K_1'}{\rightleftharpoons} \mathrm{Fe^{++} + FeI(OH)^{++}}$$

$$\mathrm{FeI(OH)^{++}} \underset{{}^1/_2 k_4'/K_3}{\overset{k_3'}{\rightleftharpoons}} \mathrm{Fe^{++} + IOH}$$

$$\mathrm{IOH + I^- + H^+} \overset{1/K_3}{\rightleftharpoons} \mathrm{I_2 + H_2O}$$

$$\epsilon_4 = k_3K_1/k_2$$
$$\epsilon_6 = k_5K_1/k_2$$
$$\epsilon' = k_3'K_1'/k_2'$$

An ultimate choice between the two theories will depend upon the results of future investigations of other halogen-halide and other ferric-ferrous reactions. At the present time there is definite supporting evidence for the existence of I_2^- as an intermediate, some less definite evidence for tetravalent iron, and no other evidence for IOH^-. The available evidence thus favors Wagner's theory for part I of the rate law, and the tetravalent iron theory for part II.

Summary

Rate measurements at 25° and at an ionic strength of 0.09 in aqueous solutions containing H^+, Fe^{+++}, Fe^{++}, I^-, I_2, K^+ and NO_3^- were found to be in agreement with the rate law

$$\frac{d(\mathrm{Fe^{++}})}{dt} = \frac{k_1(\mathrm{Fe^{+++}})(\mathrm{I^-})^2}{1 + (\mathrm{Fe^{++}})/(\mathrm{Fe^{+++}})[\epsilon_4 + \epsilon_6(\mathrm{I^-})]} - \frac{k_4(\mathrm{Fe^{++}})(\mathrm{I_2}) + k_6(\mathrm{Fe^{++}})(\mathrm{I_3^-})}{1 + (\mathrm{Fe^{+++}})[\epsilon_4 + \epsilon_6(\mathrm{I^-})]/(\mathrm{Fe^{++}})} \quad \mathrm{I}$$

$$+ \frac{k_1'(\mathrm{Fe^{+++}})(\mathrm{I^-})}{1 + (\mathrm{Fe^{++}})(\mathrm{H^+})/(\mathrm{Fe^{+++}})\epsilon'} - \frac{k_4'(\mathrm{Fe^{++}})(\mathrm{I_2})/(\mathrm{H^+})(\mathrm{I^-})}{1 + (\mathrm{Fe^{+++}})\epsilon'/(\mathrm{Fe^{++}})(\mathrm{H^+})} \quad \mathrm{II}$$

The two parts, I and II, correspond to two paths, each with two rate determining steps. The intermediate compounds involved are either derivatives of zero valent iodine, I_2^- and IOH^-, or derivatives of tetravalent iron, FeI_2^{++} and $FeI(OH)^{++}$. I_2^- and a rate law similar to I were suggested by Wagner in 1924.

Rate measurements of the reaction between ferrous ion and iodine in the presence of silver iodide, silver bromide and bromide ion confirmed the $k_4'(\mathrm{Fe^{++}})(\mathrm{I_2})/(\mathrm{H^+})(\mathrm{I^-})$ term of the rate law. The homogeneous reaction was accompanied by reaction between ferrous ion and iodine at the surface of the silver halides.

The equilibrium quotient was calculated from the specific rates by means of the following relations

$$\frac{(\mathrm{Fe^{++}})^2(\mathrm{I_2})}{(\mathrm{Fe^{+++}})^2(\mathrm{I^-})^2} = K = \frac{\epsilon_4 k_1}{k_4} = \frac{K_{\mathrm{I_3^-}}\epsilon_6 k_1}{k_6} = \frac{\epsilon' k_1'}{k_4'}$$

where $K_{\mathrm{I_3^-}}$ is the equilibrium quotient of the reaction, $I_3^- = I_2 + I^-$.

The quotient, K, was determined in the range $\mu = 0.07$ to 0.11 by analyzing equilibrium solutions. The value at $\mu = 0.09$ was also calculated from the value of K° at $\mu = 0$ based on the standard potentials of the ferric-ferrous and iodine-iodide electrodes.

The several values of K at $\mu = 0.09$ were in fair agreement when ferric iodide was assumed to be completely ionized, and became almost identical when $K_{\mathrm{FeI^{++}}} = (\mathrm{FeI^{++}})/(\mathrm{Fe^{+++}})(\mathrm{I^-})$ was assumed to be 20 ± 5 at $\mu = 0.09$ which corresponds to 75 ± 25 at $\mu = 0$. Corrections for the hydrolysis of ferric ion, and extrapolations to zero ionic strength were made by the method outlined by Bray and Hershey; changing the method of extrapolation would change the results at $\mu = 0$, but would not affect the conclusions at $\mu = 0.09$.

The following values of the specific rates and of the equilibrium quotient were chosen:

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[19] Bray and Gorin, THIS JOURNAL, **54**, 2124 (1932).

	k_1	ϵ_4	ϵ_6	k_4	k_6
At $\mu = 0.09$	5200 ± 500	0.018 ± 0.002	20 ± 1	0.009 ± 0.001	0.0145 ± 0.001
At $\mu = 0$	48,500	0.028	75	0.009	0.035

	k_1'	ϵ'	k_4'	K
At $\mu = 0.09$	0.70 ± 0.05	1/(700 ± 50)	$(10.0 \pm 0.5)(10^{-8})$	10,000 ± 1000
At $\mu = 0$	2.7	1/290	$6.4\ (10^{-8})$	148,000 ± 20,000

Concentrations are expressed in moles per liter and time intervals in minutes.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF DUKE UNIVERSITY]

The Use of Certain Amines for Distinguishing Geometrically Isomeric Aldoximes and their Acyl Derivatives

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A pair of geometrically isomeric aldoximes was originally distinguished by Hantzsch[1] by the reactions of their acetyl derivatives with cold sodium carbonate solution; with this reagent the derivative prepared from the β-aldoxime gave mainly nitrile,[2] whereas the one obtained from the α-isomer was unaffected. In an extensive investigation of this field, Brady and co-workers have found that three acetyl-β-aldoximes,[3] similar to their α-isomers, are unaffected by cold sodium carbonate.[4] These three acetyl-β-aldoximes, however, are readily decomposed by 2 N sodium hydroxide to give nitrile, but, as was shown recently, this reagent decomposes acetyl-β-aldoximes to form oxime in addition to nitrile, the relative yields of these products being dependent upon the temperature of the reaction.[5] The use of sodium hydroxide for distinguishing acyl-aldoximes is further complicated by the fact that certain acetyl-α-aldoximes are decomposed by hot alkali to give some nitrile (or corresponding acid) in addition to oxime;[5] moreover, certain carbethoxy-α-aldoximes, with this reagent, give even more nitrile than oxime.[6]

Obviously, it would be desirable to find a reagent or a combination of reagents which would react with acyl-β-aldoximes to give only nitrile, but which would either not react with the corresponding α-isomers, or form only aldoxime; pyridine, especially when used in connection with n-butylamine, apparently meets these requirements.

In a previous paper[7] it has been shown that the acetyl-β-3,4-methylenedioxybenzaldoxime is readily decomposed by pyridine to form only nitrile, whereas the corresponding α-isomer is stable in pyridine solution even at 100°. These isomers are distinguished, also, by their reactions with n-butylamine;[8] with this reagent the α-isomer dissolves without noticeable rise of temperature to give only the corresponding aldoxime, but the β-isomer reacts vigorously with this amine to form both β-aldoxime[9] and nitrile, the yield of the latter being almost quantitative when n-butylamine[8] is added, in one cubic centimeter portions, to a gram sample of the acetyl-β-aldoxime.

These reactions have now been carried out with a series of representative acetyl-α- and acetyl-β-aldoximes. In Table I are given the yields of

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[1] Hantzsch, *Ber.*, **24**, 21 (1891).

[2] Recently, it has been found that at least certain acetyl-β-aldoximes with sodium carbonate give small amounts of aldoxime in addition to nitrile. See Hauser and Jordan, THIS JOURNAL, **57**, 2450 (1935).

[3] Acetyl-3,4-dimethoxy-5-bromobenzaldoxime, Wentworth and Brady, *J. Chem. Soc.*, **117**, 1045 (1920); acetyl-3,4-dimethoxybenzaldoxime, Brady and Dunn, *ibid.*, **123**, 1800 (1923); acetyl-2-methoxycinnamaldoxime, Brady and Grayson, *ibid.*, **125**, 1419 (1924). See also Brady, *Science Progress*, **29**, 485 (1935).

[4] Whether or not these particular acetyl-β-aldoximes would give nitrile with hot sodium carbonate apparently has not been determined.

[5] Nevertheless, it is possible to distinguish geometrically isomeric acetyl-aldoximes by means of alkali, since, at the same temperature, the β-isomers give much higher yields of nitrile than the corresponding α-isomers; at 30°, the latter generally give only traces of nitrile or corresponding acid. See especially the reference in Note 2.

[6] Hauser, Jordan and O'Connor, THIS JOURNAL, **57**, 2456 (1935).

[7] See Hauser and Jordan, *ibid.*, **58**, 1419 (1936).

[8] Piperidine and diethylamine react in a similar manner; see ref. 7.

[9] It should be pointed out that when the acetyl-β-aldoxime was added in small portions to n-butylamine kept at room temperature or below, mainly β-oxime was obtained, but when the reaction was carried out at the boiling point of the amine (78°), only nitrile could be isolated; see ref. 7.