[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF WASHINGTON UNIVERSITY]

The Kinetics of the Exchange Reactions between Iron(II) Ion and the Fluoride Complexes of Iron(III)

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The rate of the iron(II)–iron(III) exchange at 0.5 ionic strength has been measured as a function of fluoride ion concentration. The data are interpreted in terms of exchange reactions between Fe^{++} and the species FeF^{++}, FeF_2^+, and FeF_3, the second-order rate constants at 0° in units of M^{-1} sec.$^{-1}$ being 9.7, 2.5, and ~0.5, respectively. The activation energies in units of kcal./mole for the first and second paths are 9.1 and 9.5, respectively. At relatively high fluoride ion concentrations, where iron(III) exists as negatively charged fluoride complexes the second-order rate constant for the exchange is ~1 f^{-1} sec.$^{-1}$ at 0°. Values for the following equilibrium quotients were obtained from the kinetic data at $\mu = 0.5$ and 0°: $(FeF^{++})(H^+)/(Fe^{+++})(HF) = 171$, $(FeF_2^+)(H^+)/(FeF^{++})(HF) = 13.5$, $(FeF_3)(H^+)/(FeF_2^+)(HF) = \sim 1.8$.

Anionic complexing agents have been observed generally to catalyze isotopic exchange reactions between simple cations. For example, in perchloric acid solutions hydroxide,[2,3] chloride,[2,4] and nitrate[3] ions catalyze the thallium(I)–thallium(III) exchange, hydroxide[5] and fluoride[6] ions catalyze the cerium(III)–cerium(IV) exchange, chloride ion catalyzes the europium(II)–europium(III) exchange,[7] and hydroxide and chloride ions catalyze the iron(II)–iron(III) exchange.[8]

The demonstration by Dodson[9] that the iron(II)–iron(III) exchange rate was measurable by use of the dipyridyl method of separation opened the way for the study described in this paper of the effect of fluoride ion on the rate of the iron(II)–iron(III) exchange. This study was chosen because Dodgen and Rollefson[10] had demonstrated that increasing amounts of first FeF^{++} and then FeF_2^+ and FeF_3 are formed as very small fluoride ion concentrations are increased. They determined the values of the formation constants of these complexes at 25° and ionic strength 0.5. They cite evidence against the formation of iron(II)–fluoride complexes under conditions that the above-mentioned iron(III) complexes form. Thus it seemed possible that by varying the concentration of fluoride ion one could measure the rates of the exchange reactions between Fe^{++} and the species FeF^{++}, FeF_2^+ and FeF_3.

Since the values of the formation constants of the iron(III)–fluoride complexes are large,[10] the complexes can be formed at very low concentrations of fluoride ion. Thus the exchange reactions between Fe^{++} and the various iron(III)–fluoride complexes can be studied under essentially the same conditions, not only of ionic strength but of actual concentrations of the principal ions in solution, so uncertainties about the validity of replacing one ion by another at constant ionic strength are minimized.

Experimental

Iron Tracer.—Three-year Fe^{55} produced by the *n*,γ reaction was obtained from the Oak Ridge National Laboratory on allocation from the U. S. Atomic Energy Commission. It was purified by two iron(III) hydroxide precipitations from ammonium hydroxide solution and two extractions of iron(III) chloride into isopropyl ether from 8 *f* hydrochloric acid. The final back-extracted aqueous iron(III) chloride solution was fumed with perchloric acid until all traces of chloride were gone. The iron(III) perchlorate solution in concentrated perchloric acid was then diluted to give an iron(III) perchlorate solution in *ca.* 1 *f* perchloric acid. The iron(III) concentration was determined spectrophotometrically by the procedure of Moss and Mellon.[11] The specific activity of the radioactive iron solution used was *ca.* 10^6 counts/min./mg. of iron.

Measurement of Radioactivity.—Samples were mounted for counting by electrolytic deposition of iron on copper from an ammonium oxalate solution. The electrolytic cell used was similar to that described by Vosburgh, Flexner and Cowie[12] except the top of the cell was machined from lucite instead of brass. It was found that with no stirring other than that afforded by the evolution of hydrogen and oxygen, an electrolysis time of 12 hours at 150 milliamperes was sufficient to give a quantitative deposition of iron from solution. Because of the small amount of iron (*ca.* 0.01 mg.) in the aliquot to be electroplated, 0.2 mg. of iron carrier was added to each cell to aid in the deposition. The total thickness of an iron deposit was less than 0.1 mg./cm.^{2}.

All radioactive measurements were made on a flow-type proportional counter using a 90% argon–10% methane gas mixture. The counter, a side window type with a two mil stainless steel wire anode, operated at slightly above atmospheric pressure. Pulses from the counter were fed through a four-stage amplifier into the discriminator circuit of a scaler which employed the standard Higginbotham circuit. The window was cellophane coated on the inside with "aquadag." All samples were counted long enough to reduce the statistical counting error to *ca.* 0.5% standard deviation.

Chemicals.—G. F. Smith "Reagent Grade" iron(II) perchlorate was recrystallized twice from water and dissolved in 1 *f* perchloric acid. Spectrophotometric analyses for iron(II) and total iron showed the presence of 5 to 10% iron(III). The free acid concentration was determined by the addition of excess standard alkali to an aliquot of the iron(II) perchlorate solution, heating to coagulate the precipitated iron(III) hydroxide, and back titrating with standard acid to a phenolphthalein end-point. The iron(II) perchlorate solutions were about 0.02 *f* in iron(II) and 1.0 *f* in perchloric acid and were stored at 0° to minimize oxidation.

Iron(III) perchlorate solutions were prepared from recrystallized iron(II) perchlorate by fuming with perchloric acid and diluting to *ca.* 1 *f* perchloric acid. The concentration of iron(III) was determined spectrophotometrically, and the free acid concentration was determined as described above.

Mallinckrodt "A. R." sodium fluoride and Baker and Adamson ammonium fluoride were the sources of fluoride

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[1] (a) This paper is a portion of the dissertation presented by Jerome Hudis in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the Graduate School of Washington University, June, 1952; (b) Monsanto Fellow, 1951 and 1952.

[2] G. Harbottle and R. W. Dodson, THIS JOURNAL, **73**, 2442 (1951).

[3] R. J. Prestwood and A. C. Wahl, *ibid.*, **71**, 3137 (1949).

[4] L. Eimer and R. W. Dodson, Brookhaven Quarterly Report, BNL-93 (S-8), p. 67 (1950).

[5] J. W. Gryder and R. W. Dodson, THIS JOURNAL, **73**, 2890 (1951).

[6] H. C. Hornig and W. F. Libby, *J. Phys. Chem.*, **56**, 869 (1952).

[7] D. J. Meier and C. S. Garner, *ibid.*, **56**, 853 (1952).

[8] J. Silverman and R. W. Dodson, *ibid.*, **56**, 846 (1952).

[9] R. W. Dodson, THIS JOURNAL, **72**, 3315 (1950).

[10] H. W. Dodgen and G. K. Rollefson, *ibid.*, **71**, 2600 (1949).

[11] M. L. Moss and M. G. Mellon, *Ind. Eng. Chem., Anal. Ed.*, **14**, 862 (1942).

[12] G. J. Vosburgh, L. B. Flexner and D. B. Cowie, *J. Biol. Chem.*, **175**, 391 (1948).

ion. Aqueous solutions 0.01 *f* and 0.1 *f* in each salt were prepared and stored in polyethylene bottles. Both salts were analyzed gravimetrically by the precipitation of lead chlorofluoride according to the method of Hillebrand and Lundell.[13] The sodium fluoride and ammonium fluoride were found to contain 99.5 and 98%, respectively, of the theoretical fluorine.

G. F. Smith anhydrous sodium perchlorate was dried at 150° for two hours and kept over phosphorus pentoxide.

Mallinckrodt perchloric acid ("A. R.," 70–72%) was used directly. The acid was analyzed by titration with standard alkali.

The exchange solutions gave no qualitative tests for chloride or sulfate ion. Since Dodson and Silverman[8,9] have shown that trace amounts of chloride or sulfate ion have no effect on the exchange rate, no further tests were performed.

Iron Analyses.—Iron was determined spectrophotometrically as tris-(2,2′-dipyridyl)-iron(II) ion in one-centimeter corex cells at 5220 Å. on a Beckman Model DU quartz spectrophotometer. Total iron was determined by the procedure of Moss and Mellon,[11] iron(II) was determined by the procedure of Schulek and Floderer,[14] and iron(III) was obtained by difference. The procedures were standardized against solutions prepared from iron wire of 99.9% purity.

The optical cells were subject to etching by the hydrofluoric acid present in the exchange solutions, so periodic checks of the cells were made. No noticeable etching occurred until ammonium fluoride was substituted for sodium fluoride for experiments at high fluoride concentrations (see below). After the experiments with ammonium fluoride were completed, the cell windows were noticeably etched, and blank corrections amounting to five to ten per cent. of the measured optical density had to be applied. The kinetic data were analyzed quantitatively only in the low fluoride region where etching was not noticeable.

Separation of Reactants.—The separation procedure used was essentially that of Dodson.[9] The exchange reaction was quenched by the rapid addition of a solution of 2,2′-dipyridyl followed by sodium acetate to bring the *p*H to 5. The iron(III) was then precipitated with ammonium hydroxide and filtered. Preliminary work, in which the specific activity of the iron(III) fraction was followed, failed to yield results which were reproducible to better than 5%. In subsequent work it was found that: (1) the exchange reaction between iron (II)-dipyridyl complex and iron (III) in acetate solution at *p*H 5 was slow (half-time > 20 hours at room temperature and 0.01 *f* reactants); (2) precipitation and filtration of tagged iron(III) hydroxide in the presence of iron(II)-dipyridyl complex left less than 1% of the activity in the filtrate containing the iron(II)-dipyridyl complex; (3) iron(III) hydroxide precipitated in the presence of tagged iron(II)-dipyridyl complex carried 2–10% of the iron(II) complex. On the basis of these results it was decided to follow the specific activity of the iron(II) fraction.

Procedure.—Appropriate volumes of tagged iron(III) perchlorate, perchloric acid, and sodium fluoride solutions were added to the pear-shaped 125-ml. exchange vessel that had been coated with beeswax. Solid sodium perchlorate was added in sufficient quantity to bring the ionic strength of the final solution to 0.5.

All solutions used in the exchange run were placed in a large refrigerated constant temperature bath whose maximum temperature variation was ±0.05°. The exchange solutions were prepared at room temperature, and no correction was made for the small change in the concentration that occurred when the solutions were cooled from room temperature to 0.0°.

The exchange was started by the rapid addition of iron(II) perchlorate to the exchange vessel. The exchange solution was further agitated by the removal and reinjection of an aliquot. It was assumed that solution volumes were additive and that dissolved solids did not change the original volume of the solutions. Approximately 5-ml. aliquots of the exchange solutions were removed from the reaction vessel at timed intervals and delivered into 25-ml. erlenmeyer flasks containing 10 ml. of a 0.1% solution of 2,2′-dipyridyl. Five milliliters of 0.1 *f* sodium acetate solution was then added quickly to bring the *p*H to 5 and quench the reaction. The exchange vessel and the bottles of iron(II) perchlorate and sodium acetate were equipped with automatic pipets (Alfred Bicknell Associates), with which aliquots of solutions could be transferred rapidly and mixed by rapid injection. "Celite" filter aid and ammonium hydroxide were added in the order mentioned to the quenched exchange samples, and the iron(III) hydroxide was filtered. The filtrate was treated with 3% hydrogen peroxide to destroy the organic material, and the resulting iron(III) hydroxide was centrifuged, washed and dissolved in dilute sulfuric acid. Six samples were taken in each experiment spread evenly over two half-times.

Two "infinite-time" samples (specific activity corresponding to complete exchange) were taken in each run. After the six timed samples had been taken, two aliquots of the exchange mixture were delivered directly into centrifuge tubes, treated with ammonium hydroxide and 3% hydrogen peroxide, and from this point on were treated exactly like the timed samples.

Specific activity determinations were made by taking a 5.0-ml. aliquot from the *ca.* 7.5 ml. of iron in dilute sulfuric acid solution and spectrophotometrically determining the amount of iron present. From the same solution a 2.0-ml. aliquot was taken, the iron deposited electrolytically, and the activity measured. The counting rate (counts/min.) divided by the optical density (log I_0/I) gave a number proportional to the specific activity of the sample.

In each experiment aliquots of the exchange mixture were taken and analyses performed to determine the total iron concentration and the iron(II) concentration. Duplicate analyses were run and the results averaged.

At high fluoride concentrations extra precautions had to be taken to prevent rapid oxidation of the iron(II). Oxygen-free nitrogen, prepared by bubbling tank nitrogen through a chromium(II) chloride solution, was used to flush out the iron(II) perchlorate stock solution and the exchange solution before the reaction was started, and was bubbled through the exchange solution during the course of the reaction. Polyethylene tubing was used as the nitrogen delivery tube. The oxidation of iron(II) was noticeable only at fluoride concentrations greater than 10^{-2} *M*.

The use of sodium fluoride as the source of fluoride ion was limited to the range less than 10^{-2} *M* fluoride ion. Above this point it was found that a white flocculent precipitate was formed during the course of the reaction. This precipitate was probably a double salt of sodium fluoride and iron(III) fluoride. Tananaev and Deichman[15] report that the compound $2FeF_3 \cdot 5NaF$ is so slightly soluble in sodium fluoride solutions that it may be used for a quantitative removal of iron(III) from solution. Ammonium fluoride gave no precipitate and therefore was used in all experiments where the fluoride concentration was greater than 10^{-2} *M*. Check experiments were run at low fluoride ion concentrations, and it was found that ammonium fluoride was a suitable substitute for sodium fluoride, yielding the same values for the over-all rate constant at any particular fluoride concentration.

Errors.—Concentrations were known to only ±1% because no correction was made for the ~0.3% volume change that occurred on cooling and because of the assumptions that solution volumes were additive and that dissolved solids induced no volume change.

Specific activity determinations which included analyses and counting were shown from preliminary studies to be reproducible to ±1.5%.

The temperature of the exchange solution fluctuated every time a sample was taken, although the temperature of the bath was constant to ±0.05°. The temperature of the exchange solution was checked during the course of one experiment, and it was found at no time did the temperature rise by more than 0.2°. A 0.2° temperature rise would change the value of the half-time by less than 1.5%.

Although the exchange reactions were rapid (half-times 1 to 10 min.) errors in the rate constants due to inaccuracies in timing the reaction are believed to be no more than a few per cent. This is because aliquots of the exchange mixture were quenched in a very reproducible way so that although the exact time of quenching might be uncertain by five to ten seconds, the time interval between the quenching of any two aliquots was known to one or two seconds. The time

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(13) W. F. Hillebrand and G. E. F. Lundell, "Applied Inorganic Analysis," John Wiley and Sons, Inc., New York, N. Y., 1929.

(14) E. Schulek and I. Floderer, *Ber. ungar. pharm. Ges.*, **15**, 210 (1939); *C. A.*, **33**, 4901 (1939).

(15) I. V. Tananaev and E. N. Deichman, *Zavodskaya Lab.*, **11**, 763 (1945); *C. A.*, **40**, 7038 (1946).

intervals between samples affects the slope of the exchange curves (see, for example, Fig. 1) and therefore the measured rates and rate constants. Error in the absolute time of quenching, or the zero time, merely shifts the exchange curve affecting the apparent zero-time exchange but not the slope.

Duplicate runs performed months apart and with different sets of reagents generally agreed to within two or three per cent., which is consistent with the above estimation of errors.

Results

The exponential exchange law[16] as applied to the iron(II)-iron(III) exchange is

$$Rt = \frac{(\mathrm{Fe^{II}})(\mathrm{Fe^{III}})}{(\mathrm{Fe^{II}}) + (\mathrm{Fe^{III}})} \ln (1 - F) \qquad (1)$$

where R is the constant rate at which iron(II) becomes iron(III) and iron(III) becomes iron(II), and F is the fraction exchange attained at time t, determined in our experiments as the specific activity of the iron(II) fraction at time t divided by the average specific activity of all the iron in the exchange mixture.

$$F = S_t/S \qquad (2)$$

If the exchange is first order in iron(II) and first order in iron(III) as Dodson and Silverman[8,9] found for acid solutions containing perchlorate and chloride ions and as we have found (see below) for acid solutions containing perchlorate and fluoride ions

$$R = {'k'}\,(\mathrm{Fe^{II}})(\mathrm{Fe^{III}}) \qquad (3)$$

where $'k'$ is the specific rate constant at a given temperature, hydrogen ion concentration and fluoride or chloride ion concentration. The half-time, $t_{1/2}$, the time required for the value of $(1 - F)$ to decrease by a factor of two is related to $'k'$ by

$$'k' = \frac{0.693}{t_{1/2}[(\mathrm{Fe^{II}}) + (\mathrm{Fe^{III}})]} \qquad (4)$$

Apparent Zero-time Exchange.—The fact that the semilogarithmic plots of $(1 - F)$ *vs.* t do not pass through one at time zero (apparent zero-time exchange) is due mainly to exchange induced during the quenching procedure (*i.e.*, the formation of the iron(II)-dipyridyl complex), but may in part be due to some uncertainty in the time a reaction was started relative to the times it was quenched. In any case the apparent zero-time exchange, which varied from about 10% at low fluoride ion concentrations to about 1% at high fluoride ion concentrations, was reproducible for a given run (as shown by the points in Fig. 1 falling on straight lines) and therefore did not affect the slope of the exchange curve.

Effect of Surface Material and Light.—The data in Table I show that the exchange rate is not affected by a change in surface material of the reaction vessel or by the absence of ordinary diffuse light. It is believed, therefore, that the rates measured are those due to thermal exchange reactions, not heterogeneously catalyzed.

TABLE I

EFFECT OF SURFACE MATERIAL AND LIGHT ON EXCHANGE RATE

~2.5 × $10^{-4} f$ $\mathrm{Fe^{II}}$, ~2.5 × $10^{-4} f$ $\mathrm{Fe^{III}}$, 0.4 M $\mathrm{H^+}$, μ adjusted to 0.5 with $\mathrm{NaClO_4}$, 0.0°

(HF), f	Surface material	$'k'$, f^{-1} sec.$^{-1}$
0.00	Pyrex	1.47
.00	Beeswax	1.48
.02	Pyrex	6.40
.02	Beeswax	6.25
.06	Polyethylene	4.20[a]
.06	Beeswax	4.15

[a] Experiment performed in the dark.

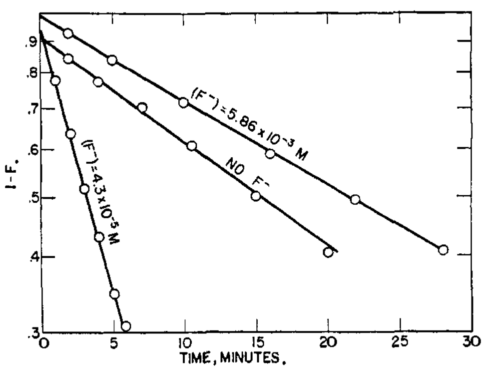

Fig. 1.—Typical exchange curves: 0°, 0.4 M hydrogen ion, ~5 × $10^{-4} f$ total iron, 0.5 ionic strength.

Order of the Reaction.—The first-order dependence of the exchange rate on the iron(II) concentration and on the iron(III) concentration was checked at various fluoride ion concentrations. The data are included in Table II. It was found that equation 3 was valid over the whole range of fluoride ion concentration studied.

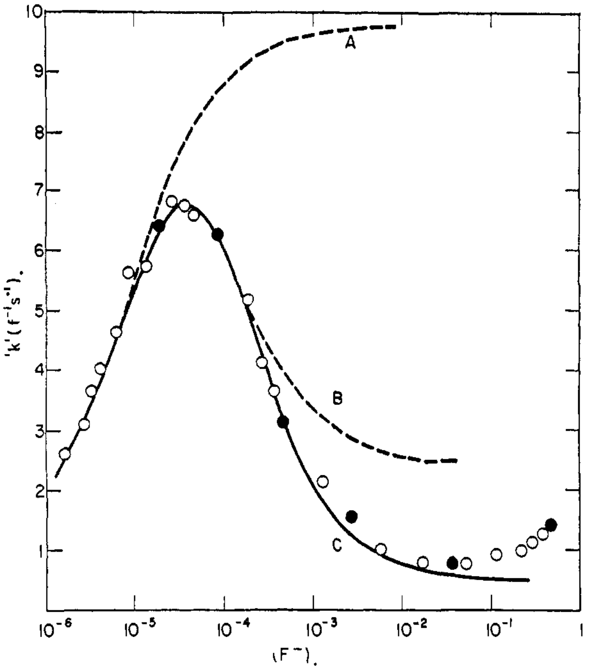

Fig. 2.—Variation of second-order rate constant, $'k,'$ with free fluoride ion concentration at 0.0°, μ = 0.5. Points are experimental. Shaded points denote second-order dependence was checked. Curves are calculated from equation 8 using values of constants given in Table III. Curve A, only paths 0 and 1 considered; curve B, only paths 0, 1 and 2 considered. Curve C, paths 0, 1, 2 and 3 considered.

Fluoride Ion and Temperature Dependence.—There remains the interpretation of the dependence of $'k'$ on the fluoride ion concentration and on the temperature. Dodgen and Rollefson's[10] study at 25° of the dependence of the potential of the iron(II)-iron(III) couple on the fluoride ion concentration can be interpreted on the basis of formation of iron(III) fluoride complexes.

$$\mathrm{Fe^{+++} + F^- = FeF^{++}} \qquad K_1$$

$$\mathrm{FeF^{++} + F^- = FeF_2^+} \qquad K_2$$

$$\mathrm{FeF_2^+ + F^- = FeF_3} \qquad K_3$$

They cite evidence against the formation of iron(II) fluoride complexes at low fluoride ion concentrations.

$$\mathrm{Fe^{++} + F^- = FeF^+} \qquad K < 30$$

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[16] See for example, A. C. Wahl and N. A. Bonner (editors), "Radioactivity Applied to Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1951, Chap. 1 by O. E. Myers and R. J. Prestwood, p. 9.

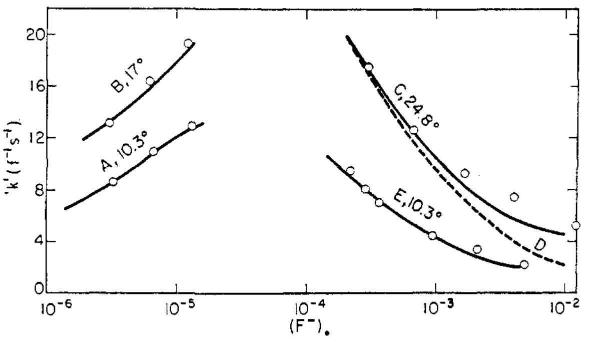

Fig. 3.—Variation of second-order rate constant, '*k*,' with free fluoride ion concentration at $\mu = 0.5$. Points are experimental. Curves are calculated from equation 8 using values of constants given in Table III.

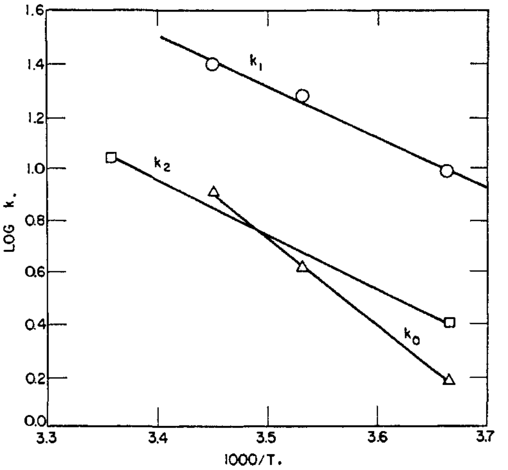

Fig. 4.—Temperature dependences of the rates of the various exchange paths, $\mu = 0.5$.

TABLE II

EXCHANGE RATES

μ adjusted to 0.5 with $NaClO_4$

(NaF), *f*	($HClO_4$), *f*	(Fe^{II}), $f \times 10^4$	(Fe^{III}), $f \times 10^4$	'*k*', f^{-1} sec.$^{-1}$	(F^-)[17], *M*
			0.0°		
....	0.4000	2.22	2.39	1.48^a	....
4×10^{-4}	.4004	2.60	2.30	2.60^a	1.61×10^{-6}
6×10^{-4}	.4006	2.57	2.30	3.10^a	2.45×10^{-6}
8×10^{-4}	.4008	2.54	2.32	3.66	3.27×10^{-6}
1×10^{-3}	.4010	2.30	2.50	4.01	4.07×10^{-6}
1.5×10^{-3}	.4015	1.94	3.02	4.66	6.08×10^{-6}
2×10^{-3}	.402	2.50	2.30	5.60	8.30×10^{-6}
3×10^{-3}	.403	2.55	2.37	5.75	1.25×10^{-5}
4×10^{-3}	.404	2.50	2.28	6.32^a	1.69×10^{-5}
4×10^{-3}	.404	1.28	2.38	6.42	
6×10^{-3}	.406	2.53	2.35	6.80	2.54×10^{-5}
8×10^{-3}	.408	2.52	2.35	6.74^a	$3.42 \times 10^{-}$
1×10^{-2}	.41	2.50	2.39	6.65	$4.30 \times 10^{-}_{5}$
2×10^{-2}	.42	2.50	2.39	6.24^a	8.70×10^{-5}
2×10^{-2}	.42	2.12	1.18	6.27	
2×10^{-2b}	.42	2.16	1.21	6.33	
4×10^{-2}	.44	2.42	2.36	5.18	1.75×10^{-4}
6×10^{-2}	.46	2.51	2.44	4.17^a	2.64×10^{-4}
8×10^{-2}	.48	2.55	2.36	3.62	3.48×10^{-4}
0.10	.50	2.58	2.37	3.11	4.35×10^{-4}
0.10^b	.50	2.19	1.18	2.97	4.35×10^{-4}
.20	.50	2.55	2.37	2.12	1.15×10^{-3}
.30	.50	2.62	2.26	1.49	2.50×10^{-3}
.30	.50	2.42	4.29	1.50	
.30	.50	4.84	2.45	1.52	
$.30^b$	.50	2.22	1.22	1.49	
.40	.50	2.62	2.33	1.08	5.86×10^{-3}
$.40^b$	.50	2.23	1.17	1.08	
$.50^b$	.40	2.12^c	1.23	0.76	.0509
$.50^b$	.30	2.12^c	1.42	0.89	.115
$.50^b$	.20	1.83^c	1.56	0.99^a	.214
$.50^b$	.15	2.06^c	1.35	1.13	.276
$.50^b$	.10	1.89^c	1.49	1.27	.345
$.50^b$	.05	1.85^c	1.60	1.34	.418
$.50^b$	.04	5.30^c	3.37	1.37	.435
$.50^b$	.04	2.08^c	10.00	1.37	
$.50^b$	.02	1.84^c	1.56	1.42	.465
$.60^b$	.02	1.78^c	1.62	1.43^d	.570
$.70^b$	.02	1.60^c	1.80	1.43^d	.670
			10.3°		
....	0.400	2.46	2.39	4.20	....
1×10^{-3}	.401	2.46	2.39	8.66	3.28×10^{-6}
2×10^{-3}	.402	2.52	2.44	10.92	6.49×10^{-6}
4×10^{-3}	.404	2.46	2.44	12.86	1.29×10^{-5}
6×10^{-2}	.46	2.50	2.44	9.54	2.17×10^{-4}
$.50^b$	.50	2.24^c	1.15	0.83	0.0174
$.50^b$	.43	2.12^c	1.21	0.76	0.0376
$.50^b$	.43	2.28^c	8.02	0.72	
$.50^b$	.43	5.52^c	2.91	0.70	
8×10^{-2}	.48	2.42	2.49	8.07	2.90×10^{-4}
0.10	.50	2.51	2.47	6.96	3.62×10^{-4}
.20	.50	2.50	2.46	4.30	9.55×10^{-4}
.30	.50	2.54	2.37	3.36	2.09×10^{-3}
.40	.50	2.49	2.30	2.37	5.0×10^{-3}
			17.0°		
....	0.400	1.75	1.82	8.19	....
1×10^{-3}	.401	1.74	1.76	13.2	3.0×10^{-6}
2×10^{-3}	.402	1.73	1.79	16.4	6.0×10^{-6}
4×10^{-3}	.404	1.78	1.79	19.4	1.19×10^{-5}
			24.8°		
0.10	0.50	2.68^c	2.57	17.6	2.92×10^{-4}
.20	.50	2.68^c	2.45	12.6	7.72×10^{-4}
.30	.50	2.69^c	2.39	9.3	1.70×10^{-3}
.40	.50	2.66^c	2.26	7.5	4.10×10^{-3}
.50	.50	1.85^c	2.85	5.3	1.38×10^{-2}

[a] Average of two or more runs. [b] NH_4F used in place of NaF. [c] Iron(II) concentration was calculated from amount added because some oxidation occurred during analyses at high fluoride ion concentrations. Rate constant was calculated from total iron concentration, which was determined. [d] $\mu > 0.5$.

We have performed qualitative transference experiments for iron(II) and for iron(III) in 0.5 *f* NH_4F solutions. We found that iron(II) was positively charged and that iron(III) was negatively charged.

In accord with the above, we interpret our exchange data in terms of the exchange of Fe^{++} with Fe^{+++}, $FeOH^{++}$, FeF^{++}, FeF_2^+, FeF_3, . . .

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(17) Fluoride ion concentrations were calculated using the following dissociation constants of HF and HF_2^- calculated from 15, 25 and 35° values of H. H. Broene and T. DeVries, THIS JOURNAL, **69**, 1644 (1947). The values of K_{HF} are corrected to ionic strength 0.5, γ_{HCl} being used.

Temp., °C.	$K_{HF} = \frac{(H^+)(F^-)}{(HF)}$	$K_{HF_2^-} = \frac{(HF)(F^-)}{(HF_2^-)}$
0.0°	1.76×10^{-3}	0.28
10.3°	1.45×10^{-3}	.27
17.0°	1.30×10^{-3}	.26
24.8°	1.17×10^{-3}	.25

TABLE III

SUMMARY OF RATE AND EQUILIBRIUM CONSTANTS

μ adjusted to 0.5 with $NaClO_4$

	0°	10.3°	17°	25°	(kcal./mole)
$k_0(M^{-1}\text{ sec.}^{-1})$	1.50	4.2	8.2	....	$E_{act} = 15.5^b$
$k_1(M^{-1}\text{ sec.}^{-1})$	9.7	19	25	$(40)^a$	$E_{act} = 9.1$
$k_2(M^{-1}\text{ sec.}^{-1})$	2.5	$(5)^a$	..	11	$E_{act} = 9.5$
$k_3(M^{-1}\text{ sec.}^{-1})$	~ 0.5	$(\sim 1)^a$	..	~ 3	....
K_1	9.7×10^4	$(1.2 \times 10^5)^a$	$(1.4 \times 10^5)^a$	1.62×10^{5c}	$\Delta H_1 = 3.3$
K_2	7.8×10^3	$(8.3 \times 10^3)^a$	....	8.9×10^{3c}	$\Delta H_2 = 0.8$
K_3	1×10^3	$(7 \times 10^2)^a$	....	5×10^{2c}	....

[a] ( ) Extrapolated or interpolated value. [b] Empirical value which is a function of the heat of hydrolysis of ferric ion and the activation energies for both mechanisms included in path 0. [c] Calculated from Dodgen and Rollefson's[10] and Broene and DeVries'[17] data.

$$\begin{array}{lll}
Fe^{*+++} + Fe^{++} & \xrightarrow{k} & \multirow{2}{*}{$\left.\begin{array}{l}\\ \\ \end{array}\right\}$ Path 0} \\
Fe^{*}OH^{++} + Fe^{++} & \xrightarrow{k_h} & \\
Fe^{*}F^{++} + Fe^{++} & \xrightarrow{k_1} & \text{Path 1} \\
Fe^{*}F_2^{+} + Fe^{++} & \xrightarrow{k_2} & \text{Path 2} \\
Fe^{*}F_3 + Fe^{++} & \xrightarrow{k_3} & \text{Path 3} \\
\vdots \qquad \vdots & & \vdots
\end{array}$$

$$R = k(Fe^{+++})(Fe^{++}) + k_h\,(FeOH^{++})(Fe^{++}) + k_1(FeF^{++})(Fe^{++}) + k_2(FeF_2^{+})(Fe^{++}) + k_3(FeF_3)(Fe^{++}) + \ldots \quad (5)$$

Since the hydrogen ion concentration was held constant at 0.4 M until the fluoride concentration was so high that the first two terms were unimportant, equation 5 may be rewritten

$$R = k_0(Fe^{+++})(Fe^{++}) + k_1(FeF^{++})(Fe^{++}) + k_2(FeF_2^{+})(Fe^{++}) + k_3(FeF_3)(Fe^{++}) + \ldots \quad (6)$$

where

$$k_0 = k + k_hK_h/(H^+) \quad (7)$$

K_h being the hydrolysis constant. Substitution of (Fe^{+++}), (F^-), and the formation constants for the various iron(III)–fluoride complexes gives

$$R = (Fe^{II})(Fe^{III})\left\{\frac{k_0 + k_1K_1(F^-) + k_2K_1K_2(F^-)^2 + k_3K_1K_2K_3(F^-)^3 + \ldots}{1 + K_1(F^-) + K_1K_2(F^-)^2 + K_1K_2K_3(F^-)^3 + \ldots}\right\} \quad (8)$$

In this expression the quantity in braces is the *'k'* of equation 3 at a certain temperature. It is assumed that all of the iron(II) is in the form of Fe^{++}, and the very small fraction of iron(III) in the form of $FeOH^{++}$ has been ignored.

At a certain temperature k_0 was determined directly by measurement of the exchange rate in the absence of fluoride ion. At low fluoride ion concentration the data are well fit by the expression

$$'k' = \frac{k_0 + k_1K_1(F^-)}{1 + K_1(F^-)} \quad (9)$$

and values of k_1 and K_1 at 0.0° were obtained. Attempts to fit the data at low fluoride ion concentrations with expressions involving higher powers of (F^-) were unsuccessful, so the initial increase in the rate with increasing fluoride ion concentration is due entirely to the increasing importance of path 1.

Values of K_1 at 10.3 and 17.0° were calculated from the value obtained at 0.0° in our work and the value calculated from Dodgen and Rollefson's[10] data at 25.0° using Broene and DeVries'[17] value for the ionization constant of hydrofluoric acid. Constant values of k_1 at 10.3 and at 17.0° were calculated using the measured values of *'k'* and k_0 and the calculated values of K_1 in equation 9.

Curve A, Fig. 2, and curves A and B, Fig. 3, show the fit of the data at low fluoride ion concentrations by equation 9 with values of k_0, k_1, and K_1 listed in Table III. The temperature dependences of k_0 and k_1 are shown in Fig. 4.

The deviation of curve A, Fig. 2, from the experimental points at higher fluoride ion concentrations indicates that the concentration of rapidly exchanging FeF^{++} is being reduced by the formation of higher-fluoride complexes of iron(III) which exchange more slowly with Fe^{++}. The peak of the experimental curve is well fit when path 2 is considered in addition to paths 0 and 1. Curve B, Fig. 2, shows the fit obtained when the constants at 0.0° in Table III for paths 0, 1, and 2 are used. The breadth of the peak made impossible the fitting of the experimental points on the assumption that FeF_2^+ and/or FeF_3 formed but did not exchange or by consideration of path 3 instead of path 2.

In fitting the valley of the experimental curve it was necessary to consider the formation of fluoride complexes higher than FeF_2^+ which exchange with Fe^{++} more slowly than FeF_2^+. Curve C, Fig. 2, shows the fit obtained when the constants for 0.0° listed in Table III are used.

The slight rise in the experimental points at very high fluoride ion concentrations is attributed to the formation of negatively charged fluoride complexes of iron(III). The rise is too slight to allow resolution.

Use of the extrapolated value of k_1 and the values of the equilibrium constants, calculated from thermodynamic data, listed for 25° in Table III allowed the calculation of values of k_2 and k_3 from the rate measurements made at 25°. Curve D, Fig. 3, shows the fit of the data by use of $k_2 = 11$, $k_3 = 0$, and curve C shows the fit for $k_2 = 11$, $k_3 = 3$.

The temperature dependence of k_2 is shown in Fig. 4. The fit of the rate data at 10.3° and high fluoride ion concentrations using the experimental value of k_1 and the interpolated values of the other constants listed in Table III is shown in curve E, Fig. 3.

Reliability of Constants.—The rate constants for path 0 (k_0) were determined directly and are as reliable as the rate data, which we believe are good to 2 or 3%. Our empirical values of k_0 agree well with those calculated by equation 7 from Silverman and Dodson's[8] values of k, k_h and K_h.

Trial variations of the values of the rate and equilibrium constants revealed limits beyond which the experimental data could not be fit. From such studies we conclude that at 0° the value of k_1 is reliable to 3 or 4%, k_2 is reliable to about 20%, and k_3 is reliable to about a factor of two. The corresponding equilibrium constants at 0° would be about equally reliable except for the uncertainty in the value for the ionization constant of HF. Broene and DeVries'[17] values at 15, 25 and 35°, which we have used in obtaining the 0° value, appear very reliable, and their 25° value corrected to ionic strength 0.5 (1.17×10^{-3}) is in good agreement with values at ionic strength 0.5 reported by Brosset and Gustaver[18] (1.16×10^{-3}, 1.52×10^{-3}) and by Wilson and Taube[19] (1.3×10^{-3}). Whatever uncertainty there is in the value of K_{HF} does not, however, affect the rate constants for the various paths since in the range of fluoride ion concentration where the paths could be resolved, the principal fluoride species was HF, and the principal net reactions for the formation of the ferric fluoride complexes are

$$Fe^{+++} + HF = FeF^{++} + H^+ \qquad K_1'$$
$$FeF^{++} + HF = FeF_2^{+} + H^+ \qquad K_2'$$
$$FeF_2^{+} + HF = FeF_3 + H^+ \qquad K_3'$$

Thus the products $(K)(F^-)$ appearing in equation 8 can be replaced by $(K')(HF)/(H^+)$, (HF) and (H^+) being known

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[18] C. Brosset and B. Gustaver, *Sv. Kem. Tidsk.*, **54**, 155 (1942); *Chem. Zentr.*, **114**, I, 867 (1943).

[19] A. S. Wilson and H. Taube, THIS JOURNAL, **74**, 3509 (1952).

experimental quantities. Fluoride ion concentrations in the HF solutions need not have been calculated at all for the resolution of the exchange paths; calculations were made, however, and the data treated as described in order to inter-compare the kinetic data obtained in hydrofluoric acid and ammonium fluoride solutions.

The values of K_1', K_2' and K_3' obtained from the rate data at $\mu = 0.5$ and 0° are 171, 13.5 and 1.8, respectively. The estimated uncertainties in these values are about 4%, 20%, and a factor of two, respectively.

The activation energy for path 1 is probably reliable to about 0.5 kcal./mole and that for path 2 to about 2 kcal./mole.

Additional confidence in the reliability of the resolved constants is given by the good fit of the experimental data at 10.3° by curve E, Fig. 3, calculated from the interpolated values of the constants.

Discussion

The entropies of activation, $\Delta S^{\ddagger}$, for the various paths were calculated from the equation[20]

$$k = \frac{e\mathbf{k}T}{h}\, e^{\Delta S^{\ddagger}/R} e^{-E_{\text{act.}}/RT}$$

These values along with values for the experimental activation energies and rate constants at 0° are summarized in Table IV. The similarity in the magnitudes of the values for the various paths is striking.

TABLE IV

COMPARISON OF VALUES FOR ENERGIES AND ENTROPIES OF ACTIVATION FOR THE VARIOUS PATHS ($\mu = 0.5$)

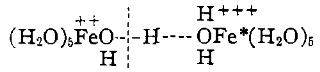
Exchange path	$k_{0°}$, (M^{-1} sec.$^{-1}$)	$E_{\text{act.}}$, (kcal./mole)	$\Delta S^{\ddagger}$, (e.u./mole)
$Fe^{+++} + Fe^{++} \rightarrow$[a]	0.87	9.9	−25
$FeOH^{++} + Fe^{++} \rightarrow$[a]	1010	7.4	−20
$FeF^{++} + Fe^{++} \rightarrow$	9.7	9.1	−21
$FeCl^{++} + Fe^{++} \rightarrow$[a]	9.7	8.8	−24
$FeF_2^{+} + Fe^{++} \rightarrow$	2.5	9.5	−22
$FeCl_2^{+} + Fe^{++} \rightarrow$[a]	~15	...	..
$FeF_3 + Fe^{++} \rightarrow$	~ 0.5	...	..
$FeF_x^{-x+3} + Fe^{++} \rightarrow$	~1	...	..

[a] Silverman and Dodson's[8] values; $\mu = 0.55$.

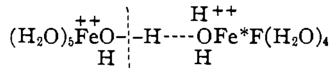
A possible explanation of the fact that there is essentially no change in the entropy of activation as the charge products change from 6 to 4 to 2 may be that the opposing dielectric contributions and ionic interaction contributions to the entropies of activation[21] are of the same magnitude at the experimental ionic strength. This would be reasonable if the distance between the iron nuclei in the transition state were at least 4 Å., corresponding to one or more water molecules or anions between the two iron atoms.

It seems to us difficult to explain the similarity in the rates of the various paths on the basis of a mechanism involving direct electron transfer. Here Franck–Condon type restrictions,[22,23] already probably important in the Fe^{++}–Fe^{+++} reaction due to differences in the hydration atmospheres around the reactants,[22] should become increasingly important as the structures of the reactants become increasingly different due to replacement of water by anions around iron(III). Also, if as postulated by Libby,[22] the catalytic effects of small anions are due to their facilitating the close approach of the exchanging cations so hydration atmospheres are shared thus reducing Franck–Condon restrictions, fluoride ion, due to its small size, should be a much more effective catalyst than chloride ion. This is not observed.

Possibly the Franck–Condon restrictions are so severe for the direct transfer of an electron from hydrated Fe^{++} to hydrated Fe^{+++}, FeF^{++}, etc., that it cannot compete with other exchange mechanisms such as atom transfer, not involving Franck–Condon restrictions. For example, a hydrogen atom from the hydration sphere around Fe^{++} might be transferred to the solvation sphere around Fe^{+++}.

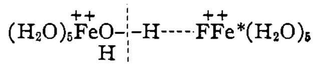


$$(H_2O)_5\overset{++}{Fe}\underset{H}{O}\text{--}\vdots\text{-}H\text{----}\overset{H^{+++}}{\underset{H}{O}}Fe^*(H_2O)_5$$



$$(H_2O)_5\overset{++}{Fe}\underset{H}{O}\text{-}\vdots\text{-}H\text{----}\overset{H^{++}}{\underset{H}{O}}Fe^*F(H_2O)_4$$

or



$$(H_2O)_5\overset{++}{Fe}\underset{H}{O}\text{-}\vdots\text{-}H\text{----}\overset{++}{F}Fe^*(H_2O)_5$$

The resulting new iron(III) and iron*(II) species could then regain equilibrium with the solution through rapid follow reactions.

$$(H_2O)_5FeOH^{++} + HF \longrightarrow (H_2O)_5FeF^{++} + H_2O$$

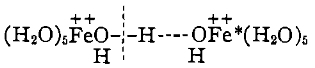
$$H_3OFe^*F(H_2O)_4^{++} + H_2O \longrightarrow Fe^*(H_2O)_6^{++} + HF$$

or

$$HFFe^*(H_2O)_5^{++} + H_2O \longrightarrow Fe^*(H_2O)_6^{++} + HF$$

Such a mechanism would minimize the effect on the rate of complexing anions around iron(III).

The exchange between Fe^{++} and $FeOH^{++}$ would be a special case because a symmetrical transition state could form



$$(H_2O)_5\overset{++}{Fe}\underset{H}{O}\text{-}\vdots\text{-}H\text{----}\underset{H}{O}\overset{++}{Fe^*}(H_2O)_5$$

resulting in a higher probability of hydrogen atom transfer and thus a greater rate of exchange. This has been observed[8] (see Table IV). Dodson[24] also has proposed this hydrogen atom transfer mechanism for this exchange path.

Other plausible mechanisms involving the transfer of fluorine atoms or OH radicals[8] can be postulated. The chief feature of the above mechanism involving the loss of a hydrogen atom by hydrated Fe^{++} is that this step can be common to all the exchange paths and thus account for the similarity in their rates.

We are indebted to Professor Lindsay Helmholz for much helpful discussion.

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[20] S. Glasstone, K. S. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p. 417.

[21] Reference 20, p. 434.

[22] W. F. Libby, *J. Phys. Chem.*, **56**, 863 (1952); Abstracts, Physical and Inorganic Section, 115th Meeting Am. Chem. Soc., San Francisco, Calif., March 27–April 1, 1949.

[23] Reference 16, Chap. 1, p. 27.

[24] R. W. Dodson, discussion following paper referred to in note 8.