Electron Transfer between Ferrous and Ferric Ions in Perchloric Acid Solutions

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Two brief notes have appeared recently on the subject of electron transfer between ferrous and ferric ions in 3 M perchloric acid solutions. The first of these, by Van Alten and Rice,[1] described a physical technique by which these ions were partially separated by diffusion through a sintered glass membrane. A separation factor ($S = R_0/R$) of the order of 0.5 was found, where R_0 was defined as the concentration ratio of ferric to ferrous initially, and R the corresponding value for the diffusate. This indicated that the ferric ion diffuses more rapidly than the ferrous ion in 3 M perchloric acid. They observed a half-time of 18.5 $\pm$ 2.5 days for the exchange. Subsequently, Linnenbom and Wahl[2] reported results for supposedly identical experiments, in which they found that the exchange was complete within the one to two hour diffusion time. In their experiments ferrous ion appeared to diffuse more rapidly than ferric ion. A third investigation by Dr. H. Keirstead of Brown University is now extant. Keirstead repeated Rice's work, and found that the exchange was apparently even slower than Rice found it to be.[3] He reports for three experiments S values ranging from 2.80 to 3.98. The most reliable value for the half-life of the exchange was 166 $\pm$ 12 days.

The present work was begun in the interval between the publication of the first two of the above papers. Two series of experiments are described, both of which made use of the separation technique of Rice.[1] The main object in the second series was to reduce the possibility of contamination by foreign anions, e.g., chloride and sulfate. Since somewhat different procedures were used in preparation of reagents for the two series, it will be convenient to describe these aspects separately. In view of the disagreement in the published results, a more complete statement of experimental details is desirable in this paper than was given in the earlier work.

Experimental

Preparation of Reagents, Series I.—Tracer Fe[59] was prepared by neutron irradiation of 99.8% iron wire in the NRX pile at Chalk River. It was purified by two treatments with diisopropyl ether, as described by Nachtrieb and Fryxell.[4] The final active ferric chloride solution obtained as an end-product from this process was precipitated with ammonia, the precipitate washed four times with distilled water, and then redissolved in 3 M perchloric acid. Two further precipitations from perchloric acid were made, the final precipitate of ferric hydroxide being washed thoroughly to remove ammonium perchlorate. The final solution was fumed down to remove any last traces of organic solvent or chloride ion and then readjusted to 3 M perchloric acid. The iron in this solution had initially a specific activity of 80,000 c./min./mg. The specific activity had decreased to 34,000 c./min./mg. of ferric iron for the last experiment in this series.

Inactive ferric perchlorate was made from a ferric chloride solution by precipitation with ammonia, followed by successive washings of the precipitate with water and re-solution in perchloric acid until no chloride ion could be detected. Ferrous perchlorate was made from this solution by electrolytic reduction at a bright platinum electrode in a two-compartment glass cell. A sufficiently low current density was used so that no visible amounts of hydrogen were evolved at the cathode. The anolyte was 3 M perchloric acid. The concentrations of sulfate ion and chloride ion in the resulting ferrous perchlorate solution, and in the active ferric perchlorate solution, were below the limits of detection (10^{-6} and 5×10^{-5} M, respectively).

Preparation of Reagents, Series II.—The water used in all phases of the preparation and analyses of materials in Series II was prepared from ordinary distilled water by redistillation from dilute alkaline permanganate in a well-seasoned all-glass still. The first 20% of each distillate was rejected. The ammonium thiocyanate used in Series II was recrystallized twice from this water and dried in vacuo. Fe[59] was prepared as before, except that the isopropyl ether was washed three times with alkaline permanganate, water and then dried over calcium chloride. The fraction boiling between 67.8–67.9° at 745.5 mm. (uncor.) was used. To minimize contamination by chloride ion, the final precipitation and re-solution of active ferric hydroxide was made in fresh glassware. The iron in this solution had a specific activity of approximately 380,000 c./min./mg., about twelve times higher than the weakest activity used in Series I.

Ferric chloride used for preparation of inactive ferrous perchlorate was purified initially by two extractions into isopropyl ether. The final precipitation of ferric hydroxide was again made in fresh glassware. Ferrous perchlorate was then prepared from this material as described for Series I.

All glassware, including the diffusion cell, used in Series II was cleaned in chromic acid, followed by a prolonged rinsing in ordinary distilled water. All items were then steamed out, and given a final thorough rinse in redistilled water.

The method of analysis for chloride ion in the final solutions depended on the light-scattering power of silver chloride suspensions. Silver nitrate was added to solutions of ferrous and ferric perchlorates in 3 M perchloric acid, containing known amounts of sodium chloride. The intensity of light scattered from these solutions was measured using a Beckman fluorescence accessory set. These results were compared to our final solutions, similarly treated. The method is not precise at low concentrations of chloride; nevertheless we were able, by numerous trials, to fix an upper limit of 5×10^{-6} M for the concentration of chloride ion in the Series II solutions. This value corresponds to the lower limit of sensitivity of the method. The upper limit for the concentration of sulfate ion remained at approximately 10^{-6} M.

The Diffusion Cell.—The diffusion cell was made from a Pyrex 30 mm., medium porosity, sintered glass disc. A stopcock was sealed on about 4.5 cm. above the disc. The membrane was filled with wax, ground flat on its outer surface, and then thoroughly cleaned with carbon tetrachloride followed by treatment with dichromate cleaning mixture. The cell was mounted on a stand, and adjusted

(1) Van Alten and Rice. This Journal. **70**, 883 (1948).

(2) Linnenbom and Wahl. ibid., **71**, 2589 (1949).

(3) We are indebted to Dr. Keirstead for sending us the results of his work prior to publication. and for his courtesy in allowing us to refer to it here: J. Chem. Phys., **18**, 856 (1950).

(4) Nachtrieb and Fryxell. This Journal. **70**, 3553 (1948).

so that the lower surface of the diaphragm was horizontal. Such a treatment is recommended[5] to reduce streaming from the cell.

Separation Procedure.—Desired volumes of solutions of active ferric perchlorate and inactive ferrous perchlorate were mixed and drawn into the cell by moderate suction. The outside of the cell was rinsed thoroughly in 0.44 or 3 M perchloric acid, depending on the concentration of acid inside the cell, and the cell was then immersed in a beaker containing 12–13 ml. of the same acid. The solution and cell were maintained at 25.0°. The liquid levels inside and outside the cells were approximately the same. After 20–30 minutes, the first diffusate was in general discarded, and replaced by a second portion of acid. After a further 0.5–1.0 hour, this diffusate was removed, and portions taken for determination of ferrous and ferric content, and for measurement of Fe^{59} activity (see below). In certain experiments, up to three such diffusates were collected in this manner.

Analytical Methods.—Analysis for ferric iron was made by the thiocyanate method. To an aliquot of the stock or diffusate was added sufficient 0.5 M ammonium thiocyanate to make the final solution (generally 10.00 or 25.00 ml.) 0.0100 M in thiocyanate ion. The sample was then diluted to the required volume with 0.44 or 3 M perchloric acid. The transmission of this solution was then determined vs. perchloric acid with a model DU Beckman spectrophotometer, using matched Corex cells of 1-cm. light path. A wave length of 470 mμ and a slit-width of 0.02 mm. was used. All solutions and the Beckman cell-compartment were maintained at 25.0 ± 0.1°. The optical measurements were taken at a fixed time (9.0 minutes) after development of the color to eliminate errors due to fading.

Total iron was determined by the same method, after oxidation of ferrous perchlorate with bromine. Excess bromine was removed by volatilization. The small amount of bromide ion formed in solution had no effect on the analysis. The concentration of ferrous iron was then calculated by difference. Oxidation of ferrous ion by air was found to be negligible in the time taken for any experiment.

The method was standardized with ferric perchlorate solution made from 99.8% iron wire. Beer's law was shown to apply over the entire range of concentration of ferric ion used in this work.

Corrections were made for iron in the reagents. The best reagent-grade perchloric acid available to us contained 0.3–0.6 part per million ferric iron.

The precision of the method depended on the absolute value of the transmission of the solutions. Wherever possible, a sufficient amount of iron was taken to give a transmission in the region 40–60%. Under these conditions, the precision of the method was ±0.4%. Some samples of diffusate gave (unavoidably) higher readings, up to 55 or 86% on occasion. The precision of the method was then not worse than ±1.5%. These deviations correspond to an error of ±0.2 unit on the transmission scale.

Measurement of Fe^{59} Activity.—Four 0.500-ml. samples of each diffusate were evaporated to dryness on 20-mm. watch-glasses with an infrared heat lamp. These watch-glasses were carefully selected for geometrical uniformity. The stock solution in each experiment was diluted suitably with 3 M perchloric acid to give as nearly as possible the same mass-thickness (0.001–0.005 mg./sq. cm.) and counting rate as the diffusate samples. Four 0.500-ml. portions of this diluted stock were prepared for counting. Measurement of Fe^{59} activity was made by β-counting of these samples with an end-on window Geiger counter and associated scaling circuit. The counter had a mica window of mass-thickness 2.8 mg./sq. cm. Sufficient counts were taken in general with each group of four samples to reduce the "reliable" statistical counting error to ±1.0–1.5%. The reproducibility of the sample mounting technique was found to be well within this statistical error. The background count was subtracted from all results.

(5) Northrop and Anson, J. Gen. Physiol., **12**, 543 (1929).

Corrections for radioactive decay of Fe^{59} were made where necessary, using a half-life of 47 days. The measured half-life was found to be 49 ± 2 days, indicating some 4y. Fe^{55}, produced by neutron capture in Fe^{54}. Since the corrections for decay were never more than 2% of the observed counting rate, the contribution of Fe^{55} could therefore be neglected in making such corrections.

Results

The results are summarized in Table I. We find the exchange to be complete in every case within the diffusion time. No significant differences between the results of Series I and Series II were observed. Diffuse daylight has no measurable effect on the rate of exchange. The exchange is apparently equally rapid in 0.44 or 3 M perchloric acid. We find that ferrous ion diffuses more rapidly than ferric ion (see below).

TABLE I

SUMMARIZED DATA FOR FERROUS–FERRIC EXCHANGE
($HClO_4 = 3.0–3.1M$)

R_0 and R are the concentration ratios ferric to ferrous for original solution and diffusate, respectively. $[Fe]_0$ = molarity of total iron in initial solution. $[Fe]_t$ = molarity of total iron in diffusate. S = separation factor = R_0/R.

R_0	R	S	$[Fe]_0 \times 10^2$	$[Fe]_t \times 10^5$	Time, hr.^a	C./min./ml. in diffusate Calcd. for 0% exch.^b	100% exch.^b	Obsd.^c
				Series I				
0.296	0.213	1.39	5.05	22.6	1.5	171	221	216
.214	.172	1.24	6.88	19.7	1.0	115	139	133
.219	.194	1.13	7.63	21.6	0.5	134	147	147
.219	.188	1.16	7.63	23.7	1.0	142	161	161
.217	.189	1.15	7.04	32.6	0.6	146	164	168
.217	.171	1.27	7.04	42.1	1.8	173	212	211
.214	.185	1.16	7.41	31.0	0.7	135	153	152
.214	.174	1.23	7.41	62.5	2.0	258	308	309
.221	.174	1.27	2.72	15.9	1.7	63	77	73
.237	.198	1.20	2.88	16.6	1.8	60	70	67
.237	.194	1.22	2.88	19.1	2.9	68	80	78
.237	.195	1.21	2.88	14.6	4.0	52	61	60
.243	.189	1.28	2.89	17.4	2.8	57	70	67
.243	.196	1.24	2.89	16.9	3.8	57	68	67
.249^d	.211	1.18	2.87	18.6	1.8	62	71	72
.249^d	e	..	2.87	21.7	3.2	...	83	84
.249^d	.197	1.26	2.87	19.0	4.3	60	72	74
.573	.474	1.21	2.32	10.9	1.8	72	82	82
.573	.454	1.26	2.32	16.5	3.2	107	124	123
				Series II				
.273	.221	1.23	2.59	13.6	1.6	553	658	636
.208	.169	1.23	3.45	24.6	1.8	690	820	792
.208	.164	1.27	2.45	28.5	3.3	784	953	930
.283^f	.245	1.15	2.35	13.0	1.6	547	610	624
.283^f	.233	1.21	2.35	22.3	3.0	894	1044	1070
			Completely exchanged solutions					
.259	.206	1.26	5.48	43.3	1.6	318	385	393
.262	.208	1.26	5.52	38.0	1.6	274	331	323
			Inactive solutions					
.257	.211	1.22	6.60	91.3	...	...	..	..
.239	.196	1.22	5.56	92.2	...	...	..	..
.247	.203	1.22	5.49	36.3	...	...	..	..

^a Time to end of diffusion period. ^b Values listed are precise to ±2.5%. ^c Values listed are precise to ±1.5%. ^d In absence of light. ^e Samples for ferric analysis lost. ^f In 0.44 M perchloric acid.

Discussion

Two possible difficulties tend to obscure the interpretation of the results when the exchange

is observed to be complete. These are: (i) homogeneous catalysis caused by trace impurities and (ii) heterogeneous catalysis by the large surface area of the porous disc. The semi-quantitative theory of the effect of ionic charge on the rates of chemical reactions described by Eyring[6] leads one to expect that complexing of ferric ion by chloride ion at concentrations of the latter less than 5×10^{-6} M would have but little effect on the rate of electron transfer. With regard to the second difficulty, we point out that the presence of sintered glass was a feature common to both the present and the earlier work on this subject. In order to reconcile all of the results on this basis alone, it would be necessary to assume that very marked catalysis occurred in two cases, and did not occur in the other two. This appears to be unlikely.

Other aspects of the problem require comment. One striking difference between the present results and Wahl's on one hand, and either Rice's or Keirstead's on the other, is the remarkable variation in the separation factors. For a diffusion-controlled process of this type, it is easy to demonstrate that the separation factor cannot exceed the ratio $D_{Fe^{++}}/D_{Fe^{+++}}$ of the two diffusion coefficients[7]; if streaming occurs from the cell during the separation, or if the outside of the membrane is not rinsed thoroughly after the cell is filled, the value of the separation factor will lie between 1.0 and $D_{Fe^{++}}/D_{Fe^{+++}}$. The value of 0.5 found by Rice[1] indicates that the diffusion coefficient for ferric ion is twice that for ferrous ion. On the other hand, Keirstead[3] reported separation factors between 2.80 and 3.98, indicating that ferrous ion diffuses three to four times faster than ferric ion. The average value of this ratio from the first twenty-five values given in Table I of the present work is 1.22 ± 0.04. Other determinations of S using inactive solutions yielded the same figure (Table I). Wahl's value[2] for this ratio from four experiments is 1.4 ± 0.2, in marginal agreement with our value. We were able to demonstrate that the separation factor was not sensibly affected by the addition of chloride ion to the solution at concentrations up to at least 10^{-4} M. We are unable to offer any explanation for these wide divergences in the published results.

Three steps were taken to check the validity

of the present results. First, we prepared a solution of ferrous and ferric perchlorate known to be completely exchanged with respect to Fe^{59}. This solution was put through the standard diffusion procedure. The results (Table I) show that the exchange, as was to be expected, was complete. Any gross errors in our procedure would in all probability have led to lack of agreement between the calculated and observed values for 100% exchange.

Secondly, other methods are available for determination of the diffusion coefficients of these species, e.g., measurements of diffusion currents at a suitably polarized platinum electrode.[8] Experiments of this kind with ferrous and ferric perchlorate in 3 M perchloric acid gave a value of 1.19 ± 0.05 for the ratio $D_{Fe^{++}}/D_{Fe^{+++}}$.[9] This value agrees within experimental error with the value we report above.

The third step depends on a method, developed by Dr. G. C. Barker of these laboratories, by which exchange reactions of this type may be studied without physical or chemical separation of the two species. The method involves an accurate monitoring of the β-activity of a solution through a very thin gold electrode which forms the base of a glass cell. When this electrode is suitably polarized, concentration gradients of ferrous and ferric ions may be established near the electrode within the range of the β-particles of Fe^{59} in water. Provided that the two species have sufficiently different diffusion coefficients, the relative specific activities of the two valence states may be determined. We have made use of this method, and find that the exchange is fast even in the absence of sintered glass. The details of this technique will form the subject of a separate communication.

Summary

The electron transfer between ferrous and ferric ions in 0.44–3.0 M perchloric acid has been found to be complete within one hour. No diminution of the rate in the absence of light was observed. Ferrous ions diffuse $22 \pm 4\%$ more rapidly than ferric ions in perchloric acid media.

(6) Eyring, Glasstone and Laidler, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p. 435.

(7) Separation factors greater than $D_{Fe^{++}}/D_{Fe^{+++}}$ are possible in the early stages of diffusion if the membrane of the cell is filled initially with perchloric acid instead of with ferrous and ferric perchlorate. However, even in this case after a diffusion time of the order of one hour, the separation factor will approach the ratio $D_{Fe^{++}}/D_{Fe^{+++}}$. Since such a procedure was not used in either the present or earlier work, this point need not be considered further.

(8) Kolthoff and Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1941, p. 21.

(9) We are indebted to Dr. G. C. Barker of these laboratories for his courtesy in making available to us the results of his experiments on this subject.