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Iron(II) + Iron(III) Isotope Exchange in Presence of Sulfate Ions

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The iron(II) + iron(III) isotope exchange rate has been measured in $NaClO_4$–$HClO_4$–Na_2SO_4 media as a function of sulfate concentration and pH at 25°. The results are consistent with the hypothesis that exchange in the presence of sulfate can occur by the reactions: $Fe^{+2} + {}^*FeSO_4{}^+ \rightarrow FeSO_4{}^+ + {}^*Fe^{+2}$; $Fe^{+2} + {}^*Fe(SO_4)_2{}^- \rightarrow Fe(SO_4)_2{}^- + {}^*Fe^{+2}$; $FeSO_4 + {}^*FeOH^{+2} \rightarrow FeOH^{+2} + {}^*FeSO_4$. These reactions are in addition to the reactions which can occur in the absence of sulfate. The rate constants for these three reactions have the values of 693, 1.94×10^4, and 1.3×10^6 l./mole sec., respectively, at an ionic strength of 0.250 *M*. The first rate constant is dependent on ionic strength whereas the second is independent of ionic strength over the range employed. The third rate constant was not sufficiently accurately determined to tell its dependence on ionic strength.

The catalysis of the Fe(II) + Fe(III) isotope exchange in aqueous solutions by various anions has been rather extensively studied[1] in a quantitative manner. However, the list of quantitative studies does not include the sulfate ion. Qualitative observations were made by Lieser and Schroeder,[2] who found that the isotope exchange was complete in 1 min. at Fe(II) and Fe(III) concentrations approximately equal to 10^{-4} *M* in 1 *M* sulfuric acid. These authors proposed that the rapid electron transfer process occurred by a H-atom transfer mechanism in reactions such as (1) and (2).

$$Fe(H_2O)_6{}^{+2} + {}^*Fe(H_2O)_5SO_4{}^+ \longrightarrow Fe(H_2O)_5OH^{+2} + {}^*Fe(H_2O)_5HSO_4{}^+ \quad (1)$$

$$Fe(H_2O)_5HSO_4{}^+ + {}^*Fe(H_2O)_5SO_4{}^+ \longrightarrow Fe(H_2O)_5SO_4{}^+ + {}^*Fe(H_2O)_5HSO_4{}^+ \quad (2)$$

The reactions maintaining equilibrium between Fe^{+2}, Fe^{+3}, H^+, $HSO_4{}^-$, $SO_4{}^{-2}$, and the complex ions presumably were not rate determining.

If one does not wish to postulate H-atom transfer in particular for reaction 1 then it may be written as in eq. 3, which is similar in form to the reactions postulated for the single anion catalyzed path when the anion is Cl^-, Br^-, $C_2O_4{}^{-2}$, $N_3{}^-$, NCS^-, and F^-. Since the

$$Fe^{+2} + {}^*FeSO_4{}^+ \xrightarrow{k_1} FeSO_4{}^+ + {}^*Fe^{+2} \quad (3)$$

products indicated in reaction 3 are in equilibrium with those indicated for reaction 1 it is immaterial which set of products is chosen. Indeed it is not known that the reaction proceeds by H-atom transfer and since the reaction conceivably may proceed through a $SO_4{}^{-2}$-bridged transition state it will be written as in eq. 3.

By analogy with the mechanisms postulated for the above named anions one also might expect electron transfer by reaction 4. The reactions given in eq. 2 and 4 have activated complexes which differ by the presence of a proton in the activated complex of eq. 2.

$$Fe^{+2} + {}^*Fe(SO_4)_2{}^- \xrightarrow{k_2} Fe(SO_4)_2{}^- + {}^*Fe^{+2} \quad (4)$$

Hence it was decided to study the $SO_4{}^{-2}$ catalysis to see whether activated complexes corresponding to reactions 2, 3, and 4 were formed.

In order to distinguish (2) and (4), if both were present, rather accurate determinations of the observed rate constant and of concentrations of the species present in the solution were necessary. To obtain the latter it was necessary to determine the dissociation constant, K_a, of $HSO_4{}^-$ in the media used. Existing values of K_a did not give good agreement with the values determined by us. Hence the results of K_a determinations also are reported here.

Experimental

Chemicals.—The ^{59}Fe isotope was obtained from Oak Ridge National Laboratory as an iron(III) solution in HCl. The ^{59}Fe was separated from metallic impurities by an extraction method.[3] The resulting aqueous Fe(III) was freed of Cl^- by several cycles of evaporation to dryness with concentrated HNO_3 and a few drops of 30% H_2O_2. The very small precipitate of ferric oxide was dissolved by $HClO_4$. The final solution, containing radioactive iron(III), and designated $^*Fe^{+3}$, in perchloric acid was standardized by spectrophotometrically determining the concentration of tris-(α,α'-dipyridyl)-iron(II) after reduction of Fe^{+3} with hydroxylamine and complexing with α,α'-dipyridyl.[4]

The sodium perchlorate used to maintain constant ionic strength was obtained by mixing sodium carbonate and perchloric acid and crystallizing from this solution. Some commercial sources of sodium perchlorate contained an oxidizing impurity which oxidized Fe(II) to Fe(III). The other chemicals used were reagent grade.

Measurement of $HSO_4{}^-$ Dissociation Constant.—The concentration dissociation constant of bisulfate ion, K_a, was determined by an indicator method employing differential spectrophotometry at various pH values and ionic strengths. The indicator employed was cresol red at a concentration of approximately 2.5×10^{-4} *M*. The wave length used for absorbance measurements was 520 mμ, where the acid form has a maximum and the basic form only a small absorption. The absorbance measurements were made with a Beckman DU spectrophotometer having an insulated and thermostated cell compartment.

Measurement of Isotope Exchange Rate.—A known volume of standard ferrous perchlorate in a solution of perchloric acid, sodium perchlorate, and sodium sulfate was deaerated for ap-

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[1] (a) J. Silverman and R. W. Dodson, *J. Phys. Chem.*, **56**, 846 (1952); (b) J. Hudis and A. C. Wahl, *J. Am. Chem. Soc.*, **75**, 4153 (1953); (c) G. S. Lawrence, *Trans. Faraday Soc.*, **53**, 1326 (1957); (d) D. Bunn, F. S. Dainton, and S. Duckworth, *ibid.*, **55**, 1267 (1959); *ibid.*, **57**, 1131 (1961); (e) R. A. Horne, *J. Phys. Chem.*, **64**, 1512 (1960).

[2] K. H. Lieser and H. Schroeder, *J. Inorg. Nucl. Chem.*, **14**, 98 (1960).

[3] R. W. Dodson, G. J. Forney, and E. H. Swift, *J. Am. Chem. Soc.*, **58**, 2573 (1936).

[4] F. D. Snell and C. T. Snell, "Colorimetric Methods of Analysis," Vol. II, D. Van Nostrand Co., New York, N. Y., 1949, p. 316.

proximately 50 min. by passage of purified, water-saturated, nitrogen gas in a constant temperature bath. To start the reaction a known volume of thermostated, deaerated $*Fe^{+3}$ solution, containing the same concentrations of perchloric acid, sodium perchlorate, and sodium sulfate as in the iron(II) solution, was added by means of a thermostated pipet. Stirring was accomplished by a vigorous flow of nitrogen.

At a time t a sample of reaction mixture was withdrawn by a thermostated pipet and delivered in 1 sec. into a stirred solution of 1.2 M sodium acetate containing α,α'-dipyridyl and 0.04 M Al^{+3} in a 10.00-ml. volumetric flask. Ammonia was added to precipitate Fe^{+3} and Al^{+3} and the solution was brought to volume with distilled water and filtered. A 5.00-ml. portion of each filtrate obtained during a rate experiment was placed in a test tube and the radioactivity determined with a Model DS-5 Nuclear-Chicago scintillation counter and a Model 186 Nuclear-Chicago scaler. The test tubes used were especially selected for uniformity so that all test tubes gave the same count for a standard sample within the statistical counting error. The activities of all Fe(II) samples collected in a given exchange experiment were counted within a short time of one another so as to minimize the effect of a background change.

A plot of log $(\chi_\infty - \chi)$ *vs.* time, where χ is the radioactivity in counts/min. of the 5.00-ml. portion of filtrate obtained from the sample taken at time t and χ_∞ is the same quantity for the "infinite time" sample taken after approximately ten half-times of the reaction had elapsed, yielded a straight line. The rate of exchange, R, could be obtained from the slope of the line.

Results

Determination of K_a.—The H^+ concentration in each "unknown" solution of Na_2SO_4, $NaClO_4$, $HClO_4$, and cresol red at a given ionic strength, μ, was determined by comparing the absorbance, A, at 520 mμ with the absorbance of a set of standards containing methyl red at the same concentration but with different ratios of $HClO_4/NaClO_4$ at the same ionic strength. The total concentrations of $HClO_4$ and Na_2SO_4 added to each unknown were known accurately so that the equilibrium concentrations of HSO_4^- and SO_4^{-2} in each unknown could be calculated from eq. 5 and 6

$$[HSO_4^-] = [HClO_4]_0 - [H^+] \qquad (5)$$

$$[SO_4^{-2}] = [Na_2SO_4]_0 - [HSO_4^-] \qquad (6)$$

where the 0 subscripts mean the total concentration of that species added to the unknown. The value of K_a was obtained by substitution into eq. 7.

$$K_a = [H^+][SO_4^{-2}]/[HSO_4^-] \qquad (7)$$

The results obtained in the determination of H^+ concentration in a typical unknown with $[HClO_4]_0 = 0.0200\ M$, $[Na_2SO_4]_0 = 0.0450\ M$, and $[NaClO_4] = 0.1150\ M$ at $\mu = 0.250$ are shown in Table I. When a smooth curve is drawn through the points for the reference solutions it is found that $[H^+] = 0.0100\ M$ in the unknown. Hence from eq. 5, 6, and 7 it is readily calculated that $K_a = 0.0350$ mole/l. Similarly, K_a was obtained for various pH values at various ionic strengths. The results are listed in Table II.

TABLE I

DETERMINATION OF $[H^+]$ IN A SOLUTION CONTAINING 0.0200 M $HClO_4$, 0.0450 M Na_2SO_4, 0.1150 M $NaClO_4$; μ = 0.250; 25.0 ± 0.1°

Solution[a]	A	$[H^+]$, M
A	0.000[b]	0.00850
B	.063	.00950
C	.113	.0105
D	.148	.0115
Unknown	.089	.0100

[a] Solutions A, B, C, and D are reference solutions.

TABLE II

DETERMINATION OF K_a AT VARIOUS μ, 25.0 ± 0.1°

μ	$[HClO_4]$, M	$[NaClO_4]$, M	$[Na_2SO_4]$, M	$K_a \cdot 10^2$, mole/l.
1.53	0.1022	1.42	0.0041	7.23
1.53	.1040	1.41	.0082	7.45
1.53	.1089	1.39	.0163	7.38
1.53	.1138	1.37	.0244	7.33
1.53	.1187	1.35	.0327	7.40
				Av. = (7.36 ± 0.08)
0.750	.0399	0.528	.0740	5.89
.750	.0801	.468	.0940	5.67
.750	.0801	.468	.0940	5.76
.750	.120	.408	.120	5.54
.750	.120	.408	.120	5.74
.750	.160	.348	.134	5.37
.750	.160	.348	.134	5.56
				Av. = (5.64 ± 0.17)
.250	.0200	.115	.0450	3.50
.250	.0200	.115	.0450	3.92
.250	.0360	.0910	.0530	3.65
.250	.0500	.0700	.0600	3.50
.250	.0700	.0400	.0700	3.84
.255	.1000	0	.0850	3.29
				Av. = (3.62 ± 0.24)
.100	.0150	.0395	.0185	2.80
.100	.0225	.0295	.0211	2.24
.100	.0300	.0195	.0235	2.70
.100	.0446	0	.0284	2.55
				Av. = (2.57 ± 0.24)

The best value of the dissociation constant at infinite dilution appears to be 1.02×10^{-2} mole/l. given by Kerker[5] in his re-evaluation of literature values. With this value of K_a for infinite dilution a least squares treatment of our data gave eq. 8, representing the variation of the concentration equilibrium constant with ionic strength for the $NaClO_4$–$HClO_4$–Na_2SO_4 media used at 25.0°.

$$\log K_a = -1.991 + \frac{2.04\sqrt{\mu}}{1 + 1.70\sqrt{\mu}} + 0.0314\mu \qquad (8)$$

Dependence of Exchange Rate on Iron Concentrations.—The observed rate constant, defined by eq. 9, was found to be independent of the total concentrations of Fe(II) and Fe(III) as shown in Table III. In eq. 9 R is the rate of exchange. Values of k_{obs} were calculated from eq. 10. The half-time of the exchange, $t_{1/2}$,

$$R = k_{obs}[Fe(II)][Fe(III)] \qquad (9)$$

$$k_{obs} = 0.693/\{[Fe(II)] + [Fe(III)]\}t_{1/2} \qquad (10)$$

for a given set of conditions was determined from a plot of log $(\chi_\infty - \chi)$ *vs.* time such as is shown in Fig. 1. A small zero-time exchange could not be eliminated but the precision obtained was very good, as can be seen from Fig. 1.

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(5) M. Kerker, *J. Am. Chem. Soc.*, **79**, 3664 (1957).

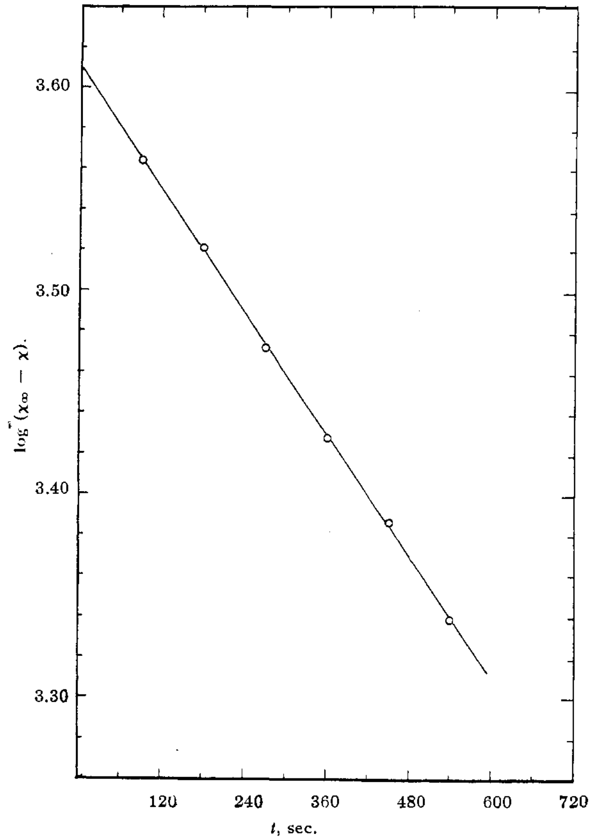

Fig. 1.—Plot of $\log (\chi_\infty - \chi_0)$ *vs.* time: $[\mathrm{Fe(II)}] = 0.506 \times 10^{-6}\ M$, $[\mathrm{Fe(III)}] = 1.10 \times 10^{-6}\ M$, $[\mathrm{SO_4}^{-2}] = 4.00 \times 10^{-3}\ M$, $[\mathrm{H}^+] = 0.125\ M$, $\mu = 0.250$, 25.0°.

TABLE III

ORDER OF REACTION WITH RESPECT TO [Fe(II)] AND [Fe(III)]; 25.0 ± 0.1°

$[\mathrm{H}^+]$, M	$[\mathrm{SO_4}^{-2}]\cdot 10^3$, M	$[\mathrm{Fe(II)}]\cdot 10^6$, M	$[\mathrm{Fe(III)}]\cdot 10^6$, M	k_{obs}, l./mole sec.
0.125	6.00	2.21	0.080	626[a]
.125	6.00	1.47	.080	627[a]
.0500	2.00	3.10	.157	516[b]
.0500	2.00	2.33	.157	518[b]
.125	4.00	0.506	1.10	716[b]
.125	4.00	1.24	0.53	733[b]

[a] $\mu = 0.750$. [b] $\mu = 0.250$.

Effect of Sulfate.—The rate of exchange increased with increasing sulfate concentration at a given pH and ionic strength. The concentrations of $\mathrm{SO_4}^{-2}$ and H^+ in a reaction mixture could be carefully controlled by adding the proper amounts of standard $\mathrm{HClO_4}$ and $\mathrm{Na_2SO_4}$ solutions because K_a had been accurately determined for the medium. The iron concentrations were so small that their effect on the $\mathrm{SO_4}^{-2}$ concentration could be neglected. The values obtained for k_{obs} at various $\mathrm{SO_4}^{-2}$ and H^+ concentrations at $\mu = 0.250$ are given in Table IV.

TABLE IV

VARIATION OF k_{obs} WITH $[\mathrm{SO_4}^{-2}]$ AND $[\mathrm{H}^+]$ AT $\mu = 0.250\ M$ AND 25.0°

$[\mathrm{H}^+]$, M	$[\mathrm{SO_4}^{-2}]\cdot 10^3$, M	$[\mathrm{Fe(II)}]\cdot 10^6$, M	$[\mathrm{Fe(III)}]\cdot 10^6$, M	k_{obs}, l./mole sec.
0.125	. . .	31.6	0.400	39.9
.125	2.00	3.10	.550	419
.125	4.00	1.24	.550	733
.125	4.00	0.506	1.10	716
.125	6.00	1.24	0.550	1040
.125	8.00	0.621	.550	1341
.070	. . .	19.0	.200	69.6
.070	2.00	2.33	.550	480
.070	4.00	1.09	.550	812
.070	6.00	0.621	.550	1112
.070	8.00	0.621	.368	1470
.050	. . .	11.4	.200	97.9
.050	2.00	2.02	.550	525
.050	4.00	1.09	.368	887
.050	6.00	0.776	.368	1224
.050	8.00	0.543	.368	1520
.038	. . .	9.50	.550	137
.038	2.00	2.02	.368	584
.038	4.00	1.01	.368	935
.038	6.00	0.506	.550	1264
.038	8.00	0.506	.368	1570

If it is assumed that exchange in the presence of $\mathrm{SO_4}^{-2}$ occurs through reactions 2, 3, 4, 11, 12, and 13, then the rate of exchange R is given by eq. 14. In eq. 14 K_{31}, K_{32}, K_{21}, and K' are the stepwise formation constants for $\mathrm{FeSO_4}^+$, $\mathrm{Fe(SO_4)_2}^-$, $\mathrm{FeSO_4}$, and $\mathrm{FeHSO_4}^+$,

$$\mathrm{Fe}^{+2} + {}^*\mathrm{Fe}^{+3} \xrightarrow{k_0} \mathrm{Fe}^{+3} + {}^*\mathrm{Fe}^{+2} \qquad (11)$$

$$\mathrm{Fe}^{+2} + {}^*\mathrm{FeOH}^{+2} \xrightarrow{k_\mathrm{h}} \mathrm{FeOH}^{+2} + {}^*\mathrm{Fe}^{+2} \qquad (12)$$

$$\mathrm{FeHSO_4}^+ + {}^*\mathrm{FeSO_4}^+ \xrightarrow{k'} \mathrm{FeSO_4}^+ + {}^*\mathrm{FeHSO_4}^+ \qquad (2)$$

$$\mathrm{Fe}^{+2} + {}^*\mathrm{FeSO_4}^+ \xrightarrow{k_1} \mathrm{FeSO_4}^+ + {}^*\mathrm{Fe}^{+2} \qquad (3)$$

$$\mathrm{Fe}^{+2} + {}^*\mathrm{Fe(SO_4)_2}^- \xrightarrow{k_2} \mathrm{Fe(SO_4)_2}^- + {}^*\mathrm{Fe}^{+2} \qquad (4)$$

$$\mathrm{FeSO_4} + {}^*\mathrm{FeOH}^{+2} \xrightarrow{k_{13}} \mathrm{FeOH}^{+2} + {}^*\mathrm{FeSO_4} \qquad (13)$$

$$R = \left\{ \frac{k_0 + \dfrac{k_\mathrm{h}K_\mathrm{h}}{[\mathrm{H}^+]} + \left(k_1K_{31} + \dfrac{k_{13}K_\mathrm{h}K_{21}}{[\mathrm{H}^+]}\right)[\mathrm{SO_4}^{-2}] + \left(k_2K_{31}K_{32} + \dfrac{k'K_{31}K'[\mathrm{H}^+]}{K_\mathrm{a}}\right)[\mathrm{SO_4}^{-2}]^2}{\left(1 + \dfrac{K_\mathrm{h}}{[\mathrm{H}^+]} + K_{31}[\mathrm{SO_4}^{-2}] + K_{31}K_{32}[\mathrm{SO_4}^{-2}]^2\right) \times \left(1 + \dfrac{K'[\mathrm{H}^+][\mathrm{SO_4}^{-2}]}{K_\mathrm{a}}\right)} \right\} \times [\mathrm{Fe(II)}][\mathrm{Fe(III)}] \qquad (14)$$

respectively, and K_h is the acid dissociation constant of Fe^{+3}(aq). Since the inequality $K'[\mathrm{H}^+][\mathrm{SO_4}^{-2}]/K_\mathrm{a} \ll 1$ is valid, the second factor in the denominator of eq. 14 is approximately equal to unity. Hence eq. 14 is readily rearranged to give eq. 15

$$\frac{Dk_{\mathrm{obs}} - Y_0}{[\mathrm{SO_4}^{-2}]} = B + C[\mathrm{SO_4}^{-2}] \qquad (15)$$

in which D is the first factor in the denominator of eq. 14 and Y_0, B, and C are given by eq. 16, 17, and 18. The equilibrium constants K_h,[6] K_{31},[7] and K_{32}[7] are known for the ionic strength and temperature values selected so that the denominator D can be calculated. Also Y_0 is

$$Y_0 = k_0 + k_\mathrm{h}K_\mathrm{h}/[\mathrm{H}^+] \qquad (16)$$

$$B = k_1K_{31} + k_{13}K_\mathrm{h}K_{21}/[\mathrm{H}^+] \qquad (17)$$

$$C = k_2K_{31}K_{32} + k'K_{31}K'[\mathrm{H}^+]/K_\mathrm{a} \qquad (18)$$

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(6) R. M. Milburn and W. C. Vosburgh, *J. Am. Chem. Soc.*, **77**, 1352 (1955).

(7) B. N. Mattoo, *Z. physik. Chem.* (Frankfurt), **19**, 156 (1959).

known from exchange rate measurements in the absence of SO_4^{-2}. Hence the left-hand side of eq. 15 can be plotted *vs.* $[SO_4^{-2}]$. This plot should yield a straight line at constant pH. A straight line was obtained at all pH and μ values selected. Some typical plots are shown in Fig. 2.

Effect of pH.—According to eq. 15 the plot of the left-hand side *vs.* $[SO_4^{-2}]$ should have an intercept, B, which is linearly dependent on $[H^+]^{-1}$ and a slope, C, which is linearly dependent on $[H^+]$. When the plots in Fig. 2 were made, from data for the different H^+ concentrations given in Table IV, it was found that the slopes C were independent of pH and that the intercept, B, was linearly dependent on $[H^+]^{-1}$ as shown in Fig. 3. Hence reaction 2, suggested by Lieser and Schroeder,[2] may be ignored under the conditions employed. The linear dependence of the intercept B on $[H^+]^{-1}$ was the reason why a reaction such as (13) was postulated.

At μ = 0.250 and 25.0° the experimental results are described by eq. 19. When the values $K_h = 2.30 \times 10^{-3}$ mole/l., $K_{31} = 263$ l./mole, $K_{32} = 7.95$ l./mole, and $K_{21} \sim 1.7$ l./mole[8] are substituted into eq. 15 and the corresponding terms of eq. 15 and 19 equated, it is found

$$(Dk_{obs} - Y_0)/[SO_4^{-2}] = 1.82 \times 10^5 + (4.93 \times 10^3/[H^+]) + 4.06 \times 10^7[SO_4^{-2}] \quad (19)$$

that $k_1 = 692$ l./mole sec., $k_2 = 1.94 \times 10^4$ l./mole sec., and $k_{13} \sim 1.3 \times 10^6$ l./mole sec. The value of k_{13} is very uncertain because the value of K_{21} is uncertain. The standard deviations for a single determination for the three numerical coefficients in eq. 19 are 0.03×10^5, 0.14×10^3, and 0.12×10^7, respectively.

At μ = 0.750 and 25.0° the experimental results are described by eq. 20. When the values $K_h = 1.76 \times 10^{-3}$ mole/l., $K_{31} = 162$ l./mole, $K_{31}K_{32} = 575$ l.²/mole², and

$$(Dk_{obs} - Y_0)/[SO_4^{-2}] = 0.95 \times 10^5 + (4.21 \times 10^3)/[H^+] + 1.19 \times 10^7[SO_4^{-2}] \quad (20)$$

$K_{21} \sim 1.7$ l./mole were substituted in eq. 15 and the two equations compared, it was found that $k_1 = 586$ l./mole sec., $k_2 = 2.07 \times 10^4$ l./mole sec., and $k_{13} \sim 1.4 \times 10^6$ l./mole sec.

At μ = 1.53 and 25.0° the sulfate dependence of the exchange rate was studied at pH 1.00 only. The experimental results are described by eq. 21.

$$(Dk_{obs} - Y_0)/[SO_4^{-2}] = 9.37 \times 10^4 + 7.00 \times 10^6[SO_4^{-2}] \quad (21)$$

The standard deviations of the two coefficients are 0.23×10^4 and 0.30×10^6, respectively. Using $K_{31}K_{32} = 347$ l.²/mole² it is found that $k_2 = 2.02 \times 10^4$ l./mole sec. Relatively little information would have been obtained by employing other pH values at this ionic strength because it can be seen from the results at ionic strengths 0.250 and 0.750 that k_1 is somewhat dependent on μ and that k_{13} cannot be obtained sufficiently accurately to determine its change with μ reliably. The values of k_2 show an anomalous lack of dependence on ionic strength over the range studied. All values of k_2 found were within approximately 3% of the average value of 2.01×10^4 l./mole sec.

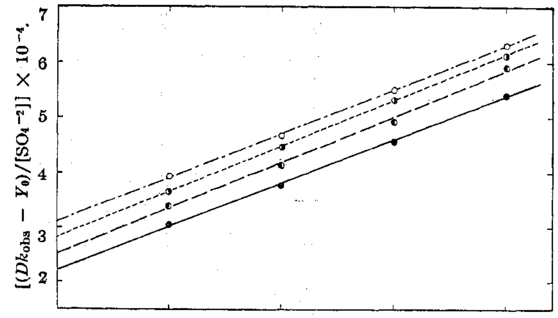

Fig. 2.—Plot of left-hand side of eq. 15 *vs.* $[SO_4^{-2}]$ at different H^+ concentrations: ●, 0.125 M; ◐, 0.0700 M; ◑, 0.0500 M; ○, 0.038 M; μ = 0.250; 25.0°.

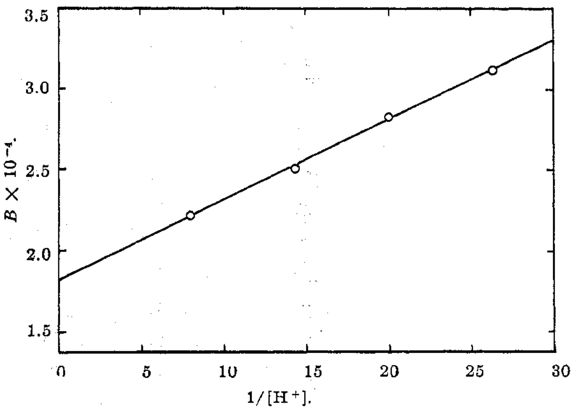

Fig. 3.—Plot of intercept B *vs.* $[H^+]^{-1}$: μ = 0.250, 25.0°.

The values obtained for the rate constants k_1, k_2, and k_{13} are summarized in Table V.

TABLE V

VALUES OF THE SECOND ORDER RATE CONSTANTS k_1, k_2, AND k_{13}; 25.0 ± 0.1°

μ	k_1, l./mole sec.	$k_2 \cdot 10^{-4}$, l./mole sec.	$k_{13} \cdot 10^{-6}$, l./mole sec.
0.250	692	1.94	1.3
0.750	586	2.07	1.4
1.53	...	2.02	...

Discussion

The lack of dependence of k_2 on ionic strength was somewhat unexpected. Apparently the reason for the abnormal behavior of k_2 is that the measured values of K_{32} exhibit abnormal behavior. The coefficient of $[SO_4^{-2}]$ in eq. 15 is given by eq. 22

$$k_2K_{31}K_{32} = k_{2,\infty}K_{31,\infty}K_{32,\infty}\frac{f_{+2}f_{+3}f_{-2}^2}{f_*} \quad (22)$$

where the ∞ subscript refers to zero ionic strength, f_{+2}, f_{+3}, f_{-2}, and f_* are the activity coefficients of Fe^{+2}, Fe^{+3}, SO_4^{-2}, and the activated complex, respectively. This coefficient has a normal dependence upon ionic strength if Debye–Hückel type equations,[9] with an

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(8) J. Beukenkamp and K. D. Herrington, *J. Am. Chem. Soc.*, **82**, 3022 (1960).

(9) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," Second Ed., Butterworth Scientific Publications, London, 1959, p. 229.

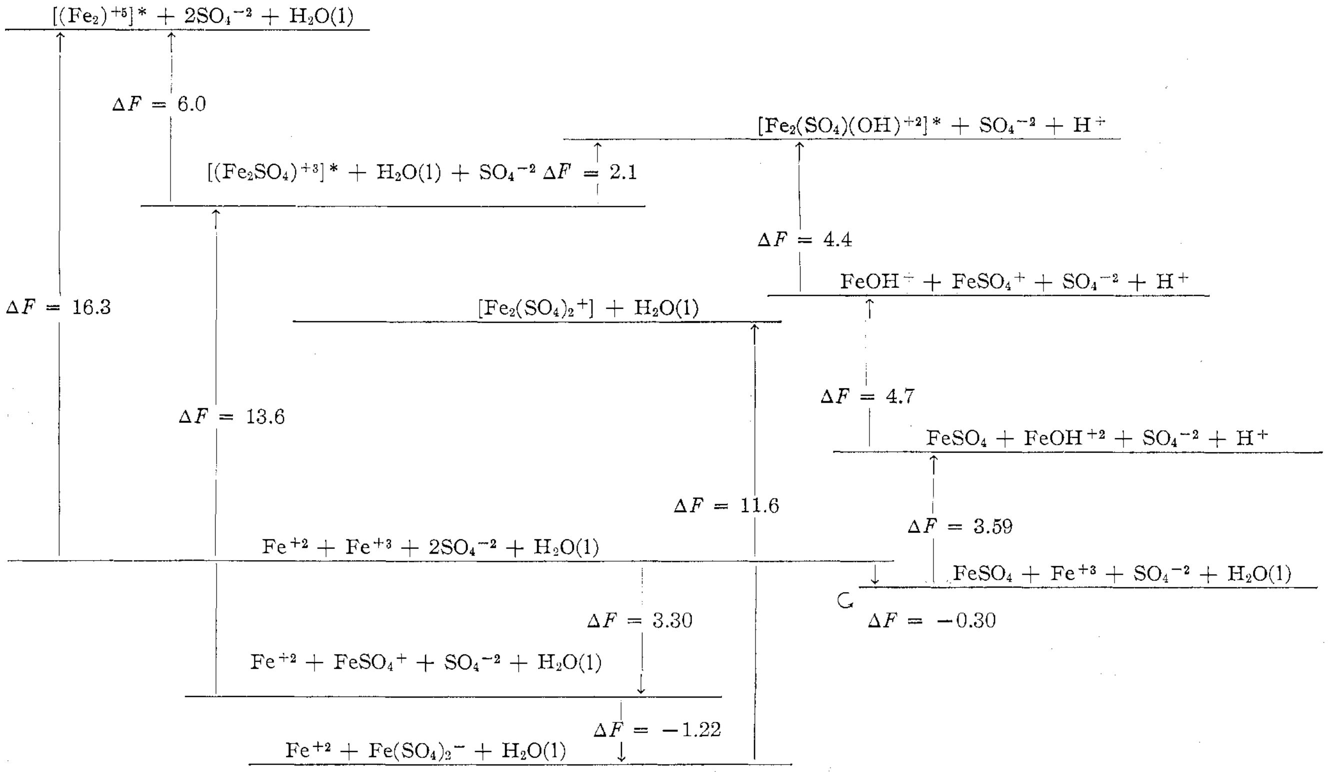

Fig. 4.—Free energy level diagram for the Fe(II) + Fe(III) + SO_4^{-2} system. All free energy differences are in kcal./mole. The zero free energy reference level is the one for separated Fe^{+2}, Fe^{+3}, and SO_4^{-2} ions. All free energy changes are calculated from equilibrium constants and rate constants at 25°.

average $\overline{Ba}$ parameter of 2.7, are assumed for the activity coefficients in eq. 22, as may be verified from its value in eq. 19, 20, and 21. The equilibrium constant K_{31} exhibits normal behavior because its variations with ionic strength also can be fitted with an average $\overline{Ba}$ parameter of 2.7. However, the measured values of K_{32} are anomalous in that an abnormally small value of the $\overline{Ba}$ parameter is needed to fit its variation with ionic strength. This abnormal dependence of K_{32} upon ionic strength is reflected in k_2.

The exchange paths involving SO_4^{-2} ions have rate constants which are considerably larger than those for similar paths involving F^-, Cl^-, Br^-, and NCS^-, and are more nearly comparable to those for paths involving N_3^-[1d] and $C_2O_4^{-2}$.[1e] The rate constant k_1 for SO_4^{-2} is much greater than k_0, as is observed for N_3^- and $C_2O_4^{-2}$ but not for F^-, Cl^-, Br^-, and NCS^-. The rate constant k_2 for SO_4^{-2} is 30-fold (or more) greater than k_1, a fact which has not been observed for the other ions. In the cases of F^-, Cl^-, NCS^-, and $C_2O_4^{-2}$ the rate constants k_1 and k_2 differ by a much smaller factor than this. The exchange path involving two N_3^- ions (if there is one) has not been studied as yet. The data for k_2 in the case of Br^- are somewhat in question. The experimental facts concerning the relative values of k_1 and k_0 mean that the free energy change of reaction 23 in the reaction medium is more negative than the free energy change of reaction 24 for $Z^{-n} = N_3^-$, $C_2O_4^{-2}$, and SO_4^{-2} but that the two free energy changes are nearly equal for $Z^{-n} = F^-$, Cl^-, Br^-, and NCS^-. In eq. 23 X_0^* is the activated complex for reaction 11 and X_1^* is the activated complex with one anion. For $Z^{-n} = N_3^-$, $C_2O_4^{-2}$ the anion stabilizes the activated complex more than it stabilizes the separated reactants. This also may be seen from the free energy level diagram for the SO_4^{-2} complexes in Fig. 4. For $Z^{-n} = F^-$, Cl^-, Br^-, and NCS^- the anion has nearly the same stabilizing influence on the activated complex as on the separated reactants. This can be taken as evidence that the latter group of ions do not play a bridging role in the activated complex and that the reaction Fe^{+2} + $^*FeZ^{+3-n}$ takes place by an outer-sphere mechanism. In the case of an outer-sphere mechanism the free energy change accompanying the substitution of an inner shell H_2O molecule on Fe^{+3} by Z^{-n} is nearly the same in the activated complex as in the separated reactants because a bond of appreciable strength between Fe^{+2} and Z^{-n} does not exist in the activated complex. However, the matter is not quite this simple since possible partial charge transfer in the activated complex will decrease the Fe^{III}–Z^{-n} bond strength as compared to the bond in the separated reactants. This decrease would be partially offset by the "ion-pair" bond between Fe(II) and Z^{-n} in the activated complex since Z^{-n} would be outside of the coördination shell of Fe(II). Because the N_3^- catalyzed exchange goes by the bridged transition state mechanism[1d] it is tempting to postulate the bridged transition state mechanism for $C_2O_4^{-2}$ and SO_4^{-2} also.

$$X_0^* + Z^{-n} = X_1^* \tag{23}$$

$$Fe^{+3} + Z^{-n} = FeZ^{+3-n} \tag{24}$$

When a second anion is added to the activated complex as in eq. 25 the free energy change for SO_4^{-2} is more

$$X_1^* + Z^{-n} = X_2^* \qquad (25)$$

negative than is the free energy of reaction 26 since $k_2 > k_1$, whereas the two free energy changes are approximately equal for the other ions where data have been obtained.

$$FeSO_4^+ + SO_4^{-2} = Fe(SO_4)_2^- \qquad (26)$$

A repetition of the argument given in the preceding paragraph suggests that SO_4^{-2} may exert its stabilizing influence in the activated complex, as compared to the reactants, by a bridging role rather than as just an inner-shell ligand in a reactant in an outer-sphere activated complex.

Reaction 13 contains a type of activated complex which, to date, has not been observed in the Fe(II) + Fe(III) exchange catalyzed by the ions already mentioned. A possible reason for this is that the precision obtained is too poor in the case of the other anions. If a SO_4^{-2}-bridged activated complex is formed then several alternatives are possible for the disposal of the OH^- ion. Some of these possibilities are that it may form an additional bridge between Fe(II) and Fe(III) or it may simply replace a water molecule in the inner coördination shell of either Fe(II) or Fe(III). Some evidence as to which possibility is most probable can be obtained from the free energy level diagram in Fig. 4. It is seen that the free energy change in reaction 27 is only slightly less than that in reaction 28 and considerably less than that in reaction 29. Hence it seems

$$X_1^* + H_2O(l) \longrightarrow [Fe_2(SO_4)(OH)^{+2}]^* + H^+ \qquad (27)$$

$$Fe^{+3} + H_2O(l) \longrightarrow FeOH^{+2} + H^+ \qquad (28)$$

$$Fe^{+2} + H_2O(l) \longrightarrow FeOH^+ + H^+ \qquad (29)$$

probable that OH^- ion replaces a water ligand in the first coördination shell of Fe^{+3} in X_1^* and that the Fe(II) coördination shell is not disturbed.

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Studies on Nickel(II) Complexes. IV.[1] Bis-(N-*sec*-alkylsalicylaldimine) Complexes: Conformational Equilibria in Solution

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Evidence is presented that the partial paramagnetism exhibited by bis-(N-*sec*-alkylsalicylaldimine)–Ni(II) complexes in toluene solutions at and above 37° is not a result of molecular association. In inert solvents these complexes have a fundamentally different behavior than their N-methyl, -*n*-alkyl, and -aryl counterparts, whose solution paramagnetism can be accounted for by a model involving molecular association as the sole means of obtaining paramagnetic behavior.[1,6] Evidence is presented in the form of X-ray, molecular weight, spectral, and magnetic data as well as steric considerations to show that a conformational equilibrium exists in solution between planar (diamagnetic) and tetrahedral (paramagnetic) forms.

Introduction

It is now well recognized that an assembly of complexes of bivalent nickel which are four-coördinate on the basis of simplest formulation can achieve partial or complete occupancy of a triplet spin state by one, or a combination of several, basic effects. These are: (1) the presence of an in-plane ligand field whose intrinsic strength, in the absence of any axial interactions, is insufficient to pair spins; (2) the imposition, through the agency of solvent or solute, of an axial component on a given in-plane field so as to reduce the tetragonality of the field and produce a triplet ground state; (3) the presence of tetrahedral or pseudotetrahedral species. No well authenticated examples of (1), *i.e.*, of a rigorously planar triplet complex, are yet known.

Paramagnetic behavior arising from effect (2), especially through solvent–solute interaction, is well established.[2,3] More recently, it has been shown that solute–solute interaction, manifested by molecular association in solutions of inert solvents, has a profound effect on the magnetic behavior in these media. Examples of this effect are found in nickel complexes of β-diketones[4] and certain N-substituted salicylaldimines. Earlier work in this series,[5] as well as that by others,[6] leaves little doubt that the paramagnetic behavior of bis-(N-methyl- and -*n*-alkylsalicylaldimine)–Ni(II) complexes in inert solvents arises solely from an

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