that one mole of Arquad and two moles of 8-quinolinol are required per mole of vanadium (cf. ref. 2).

We found that solubility and entrainment losses of 8-quinolinol to the uranium barren carbonate solution could be held to negligible amounts (0.02%) by adjusting the pH to 9.7 and scrubbing once with MIBK.

Several possible reagents for separating uranium from the organic phase were tested, including solutions of mineral acids, organic acids, acids plus uranyl precipitants, H_2S, Na_2S, $(NH_4)_2CO_3$ and $NaHCO_3$.

The use of strong acids has the complication that 8-quinolinol as well as uranium is removed from the organic phase. The most efficient extracting agent appears to be sodium bicarbonate solutions. While sodium bicarbonate does not take out the organic phase completely in a single stage, complete removal could be achieved on a countercurrent basis. On such a basis, the aqueous phase could be loaded to approximately 30 g./1. U_3O_8 (see Fig. 1). Recovery from the bicarbonate solution could then be made by usual methods.

SAN FRANCISCO, CALIFORNIA

Kinetics of the Formation of the Ferric Thiocyanate Complex

BY JOHN F. BELOW, JR., ROBERT E. CONNICK AND CLAUDE P. COPPEL

An apparatus for rapidly mixing two solutions has been developed and applied to a study of the kinetics of the reaction: $Fe^{+++} + SCN^- = Fe(SCN)^{++}$ in aqueous solution. The forward rate law has been determined to be $d(FeSCN^{+2})/dt = k_1(Fe^{+++})(SCN^-) + [k_2(Fe^{+++})(SCN^-)]/(H^+)$. At 25° and an ionic strength of 0.40 the values of k_1 and k_2 are 127 ± 10 M^{-1} sec.$^{-1}$ and 20.2 ± 2 sec.$^{-1}$, respectively. From the variation of the rate with temperature the following values were found: $\Delta H_1^{\ddagger} = 13.0 \pm 1.4$ kcal./mole, $\Delta S_1^{\ddagger} = -5 \pm 5$ e.u., $\Delta H_2^{\ddagger} = 20.2 \pm 1.4$ kcal./mole and $\Delta S_2^{\ddagger} = 15 \pm 5$ e.u. The entropies of activation are compared with those for analogous reaction rates and with some equilibrium entropies of complexing. The mechanisms are discussed.

Introduction

The red complexes formed between ferric and thiocyanate ions have been studied by numerous workers.[1-10] The principal species in aqueous solution at low thiocyanate concentrations is $FeSCN^{++}$ with some formation of $Fe(SCN)_2^+$. The complexes appear to form instantly upon mixing. Chance,[11] using his rapid mixing device, studied the reaction between dilute ferric alum and NH_4SCN and determined the reaction to be first order in SCN^-. Assuming the reaction to be first order in ferric ion, he found a second-order rate constant of 1.7×10^4 M^{-1} sec.$^{-1}$ at room temperature at an ionic strength of approximately 0.01. Bjerrum and Poulson[12] measured the reaction in methanol at temperatures of -75 and $-100°$. Extrapolating their data, and assuming the reaction to be first order in ferric and thiocyanate ions, one can calculate a rate constant of 10^5 M^{-1} sec.$^{-1}$ at 25°.

The present study was undertaken to obtain more detailed information on this reaction and to test the operation of a newly designed rapid mixing device.

In the experimental measurement of rapid reactions in solution, mixing is a problem because of the relatively high viscosity and low diffusion rates in liquids. Hartridge and Roughton[13] developed a flow mixer with spectrophotometric detection which gave essentially complete mixing in 0.4 msecond. Chance[11,14] improved their apparatus, still using a short optical path length, i.e., 0.8 mm. A review of recent modifications of the short path length devices and some others not discussed here may be found in reference 15. For reactions of higher than first order the half-life may be increased by using lower concentrations. Spectrophotometric detection then requires longer path lengths. Such devices with light-path lengths of 0.5 and 10 cm. have been used by Stern and DuBois[16] and Awtrey and Connick,[17] respectively.

Significant decrease in the mixing time of the mixers with short light-path length did not seem likely. Since we wished to study fast second-order reactions primarily, attention was directed toward the development of a mixer with a long path length but with more rapid mixing than had been achieved previously. After experimenting with a number of designs[18] the device shown in Fig. 1 was developed. It consists essentially of a chamber 5.9 cm. long, with flat glass or quartz windows on the ends. A movable baffle divides the interior into two equal regions which initially contain the reactants. A coil spring mechanism serves to raise

(1) H. E. Bent and C. L. French, THIS JOURNAL, **63**, 568 (1941).
(2) S. M. Edmonds and N. Birnbaum, ibid., **63**, 1471 (1941).
(3) R. K. Gould and W. C. Vosburgh, ibid., **64**, 1630 (1942).
(4) A. K. Babko, Compt. rend. acad. sci. U. R. S. S., **52**, 37 (1946).
(5) A. K. Babko, J. Gen. Chem. U. S. S. R., **16**, 1549 (1946).
(6) H. S. Frank and R. L. Oswalt, THIS JOURNAL, **69**, 1321 (1947).
(7) K. K. Chatterji, Sci. and Culture, **15**, 201 (1949).
(8) R. H. Betts and F. S. Dainton, THIS JOURNAL, **75**, 5721 (1953).
(9) M. W. Lister and D. E. Rivington, Can. J. Chem., **33**, 1572 (1955).
(10) G. S. Laurence, Trans. Faraday Soc., **52**, 236 (1956).
(11) B. Chance, J. Franklin Inst., **229**, 737 (1940).
(12) J. Bjerrum and R. Poulson, Nature, **169**, 463 (1952).

(13) H. Hartridge and F. J. W. Roughton, Proc. Roy. Soc. (London), **104**, 376 (1923).
(14) B. Chance, J. Franklin Inst., **229**, 455, 613 (1940); Rev. Sci. Instr., **13**, 158 (1942).
(15) Disc. Faraday Soc., No. 17 (1954).
(16) K. G. Stern and D. DuBois, J. Biol. Chem., **116**, 575 (1936).
(17) A. D. Awtrey and R. E. Connick, THIS JOURNAL, **73**, 1341 (1951).
(18) J. F. Below, Thesis, University of California, June, 1955; unclassified University of California Radiation Laboratory Report UCRL-3011.
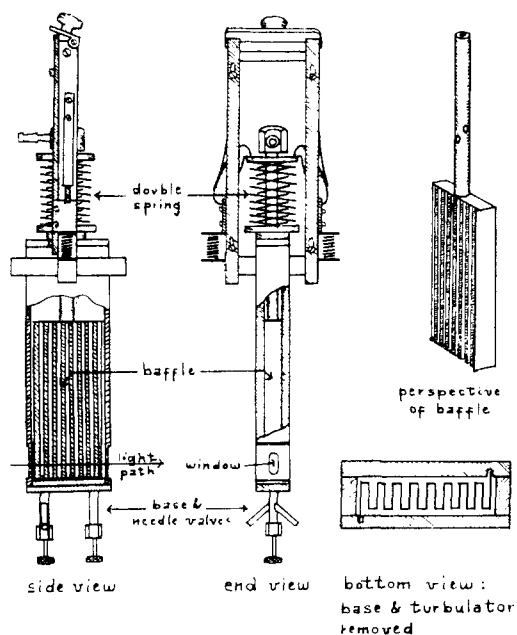
Fig. 1.—The fast mixing device.

the baffle rapidly out of the lower area and turbulence produced in its wake mixes the reactants. As will be discussed later, the mixing time was measured by studying a very rapid reaction. Although comparison is difficult because of different methods of testing, it would appear that for second-order reactions the present device has about the same, or a somewhat poorer, limit of performance than that of Caldin and Trowse.[19]

Experimental

Mixer and Recording System.—The details of construction of the mixing device are shown in Fig. 1. Except for the windows, all parts in contact with liquid were made of stainless steel. The metal walls were screwed together and the outside seams were soft soldered. All outside seams were painted with Glyptal varnish and the interior was coated with "Harrisite,"[20] a phenolic resin which exhibits extreme chemical inertness to all common reagents and is remarkably tough and tenacious. The removable base plate was sealed with either a neoprene or cork gasket and possessed two needle valves through which reactants could be admitted.

Two types of movable baffles were used in this work. The first, shown in Fig. 1, was constructed from a stainless steel rectangular bar into which were drilled a series of slots from both sides. The baffle was connected at the top to a hollow circular tube which transmitted the spring force and at the bottom to a flat perforated base plate. The base plate seated against the chamber base and hence acted to prevent the reactants from mixing before firing and, due to the perforations, provided an exit and turbulence when the baffle was raised. Along each end of the baffle was silver soldered a flat plate which projected $1/8''$ on one side and rode in a narrow groove milled in the mixing compartment. The effect was to divide the mixer into two regions of liquid separated by the baffle, which had 17 separators, giving 18 laminae of liquid. This baffle was later replaced in order to eliminate pre-mixing caused by leakage of the reactants around the $1/8''$ projections before the run was initiated.

The second baffle consisted of a stainless steel rectangular box connected as before to a circular tube and a perforated base plate. The box was of such dimensions that the volume within the baffle was equal to that which surrounded it. It served to separate the reactants, one within the box and one occupying the space between the box and the chamber walls. In this way reactants could only pre-mix

(19) E. F. Caldin and F. W. Trowse, ref. 15, p. 133.
(20) Harrisite and Chemical Company, Manitowoc, Wisconsin.

by leaking under the base plate, and this was prevented by placing a neoprene gasket underneath the baffle and applying a small external pressure to the baffle until the reaction was started.

The top of the chamber included a mechanical device for cocking and releasing the coiled springs which actuated the baffle. The hollow tube on the baffle projected through the top of the chamber and supplied a means for producing a vacuum within the chamber.

It was difficult to thermostat the mixing device. Therefore the temperature of each experiment was measured immediately after a run. For experiments near room temperature a sample was removed from the mixer through one of the needle valves, and the temperature quickly measured. At higher and lower temperatures it was found necessary to measure the temperature directly inside the mixer. This was done by inserting a Western Electric 14B thermistor into the mixing chamber. The resistance was measured with a Leeds and Northrup Wheatstone bridge which enabled temperature to be measured to $\pm 0.02°$. The thermistor has been found to be stable and reproducible to this accuracy after at least one year's usage.

The mixer was filled by drawing the reactants contained in glass bulbs through the needle valves in the base. Since the presence of any dissolved gas in the liquids caused severe bubble formation on firing, the liquids were previously outgassed, either by sharply rapping the storage bulbs containing them or by shaking the bulbs on a mechanical shaker while submitting them to a vacuum of approximately 3 cm. For filling, the mixing chamber also was evacuated. It was found unnecessary to maintain the vacuum while firing, since the baffle did not rise far enough to churn air into the solution in the light path. Evaporation of the reactants under the vacuum was found to be trivial for aqueous solutions with the technique used. The chamber was filled to contain either 45 or 30 ml. of each reactant with 25 to 55 ml. of free space above the solutions.

Monochromatic light was obtained from the optical system of a Beckman DU spectrophotometer. The photo-tube compartment was replaced by a specially built compartment housing an RCA-1P28 photomultiplier tube and resistor network, whose power was supplied by an 1800 volt d.c. power supply, designed and built by the University of California Radiation Laboratory. A 330 KΩ protective resistance was included in series. The output was fed to the vertical input of an RCA-WO56A oscilloscope. Mounted in front of the cathode ray tube was a view camera with a four-inch f4.5 lens and a reducing back for $2^1/4'' \times 3^1/4''$ sheet film.

The Beckman spectrophotometer and the photomultiplier compartment sat on separate tables about 6 inches apart. Between these tables the mixing apparatus, stiffly bolted between large lead blocks, rested on a tall, narrow table 5 inches wide and filled with sand for added stability. This narrow table rested on the floor and was coupled to the other two tables only through sponge rubber pads which helped to hold it erect. This minimized the effect on the optical components of the shock of firing the mixer.

Procedure.—To make a kinetic run, the mixer was filled with the reactants and placed in position. The oscilloscope sweep frequency was adjusted with a known frequency to give two or three sweeps per half-life of the substance whose absorbency was being measured. In the present work, the sweep frequency varied between 6 and 60 cycles per second. The lens of the camera, set at maximum aperture, was uncapped and the coiled mixer springs released. After a second or two the lens was recapped. Super Panchro Press Type B film was used. The washed and dried negative was measured with a ruler or low power microscope to obtain a concentration vs. time curve. A typical negative is reproduced in Fig. 2.

The ratio of ferric and thiocyanate solutions actually mixed was not constant with the first baffle, so that the initial stoichiometry in the light path was not calculable from initial reactant concentrations and had to be deduced from the analysis of the final mixed solution. After firing, a sample was withdrawn from the bottom and the concentration of $FeSCN^{+2}$ measured spectrophotometrically. The concentration of ferric ion in the sample then was determined by adding excess thiocyanate and observing the spectrum. The thiocyanate concentration of the experiment was calculated both from the $FeSCN^{+2}$ complexing constant and from the ratio of the ferric concentration found in the mixed

sample to that in the original stock solutions. The two values generally agreed within 5%, the value used being a mean value of the two weighted 2 to 1 in favor of the equilibrium value. The species followed spectrophotometrically was Fe(SCN)$^{++}$, using a wave length of 605 mμ.

Mixing Rate.—In order to observe the mixing rate, a reaction was sought which was very rapid and in which a sharp color change occurred. The reaction

$$\left[O_2N\langle\!=\!=\!\rangle O\right]^-_{aq} + H_{aq}^+ \longrightarrow O_2N\langle\!=\!=\!\rangle OH$$
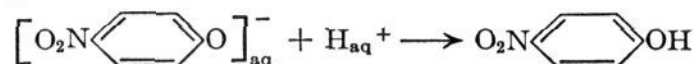
has a strong color change, the phenol absorbing less strongly than the ion at 490 mμ. Bell and Pearson[21] have shown the reaction to be complete in less than one millisecond, using 0.01 M solutions. The mixer was tested with 0.0100 M solutions of p-nitrophenol and sodium hydroxide, using essentially the reverse of the above reaction. The wave length chosen was 490 mμ and the sweep frequency 60 c.p.s. The mixing, using the rectangular box baffle, was in the ratio of 1.00 to 1.22. The average of three runs gave 16 mseconds for 83% reaction and 32 mseconds for 93% reaction. Tests with the slotted baffle indicated mixing times about half as great.

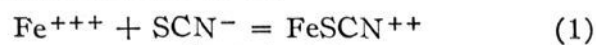**Reagents.**—Distilled water was redistilled from alkaline permanganate. All chemicals were reagent grade.

Solutions of 0.1 M[22] ferric perchlorate were prepared by dissolving spectroscopic grade iron rod in hot nitric acid, centrifuging to remove carbon and then fuming with 60% perchloric acid. The resulting product, on addition of silver nitrate, showed by Tyndall beam about 10^{-5} M chloride ion. The solution gave no "brown ring" test for nitrate ion. Ferric ion concentration was determined either by a Zimmerman–Reinhardt method or a Jones reductor type method. Acidity was measured by the method of Schumb, Sherrill and Sweetser,[23] i.e., a hot titration with sodium hydroxide to the phenolphthalein end-point. Ferrous perchlorate solution was prepared by electrolytic reduction of the ferric perchlorate.
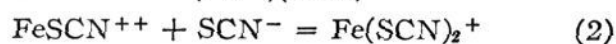
Sodium thiocyanate solutions were prepared from the recrystallized, oven dried salt and analyzed by silver nitrate titration. Reagent grade perchloric acid was standardized either with mercuric oxide or sodium hydroxide with potassium acid phthalate as primary standard. The sodium perchlorate solution used in adjusting the ionic strength was prepared by dissolving sodium carbonate in a slight excess of perchloric acid, heating to expel carbon dioxide and titrating to neutrality with sodium hydroxide. It was standardized by drying at 150° and weighing as NaClO$_4$.

Results and Interpretation

Complexing Constants.—The principal equilibria between ferric and thiocyanate ions in aqueous solution are known to be

$$Fe^{+++} + SCN^- = FeSCN^{++} \qquad (1)$$
$$Q_1 = \frac{(FeSCN^{++})}{(Fe^{+3})(SCN)^-}$$
$$FeSCN^{++} + SCN^- = Fe(SCN)_2^+ \qquad (2)$$
$$Q_2 = \frac{(Fe(SCN)_2^+)}{(FeSCN^{+2})(SCN^-)}$$

where parentheses indicate concentrations in moles per liter and Q is the value of the equilibrium quotient expressed in concentrations.

Table I lists the thermodynamic values obtained by previous workers.

The work reported here was carried out at an ionic strength of 0.40. The first complexing constant was determined at this ionic strength by measuring the concentration of the complex in prepared mixtures of Fe(ClO$_4$)$_3$ and NaSCN.

The optical density of Fe(SCN)$^{++}$ was determined at 460 mμ using the molar extinction coefficient of 5000 ± 50 determined by Betts and Dain-

(21) R. P. Bell and R. G. Pearson, *J. Chem. Soc.*, 3443 (1953).

(22) M designates moles per liter of solution.

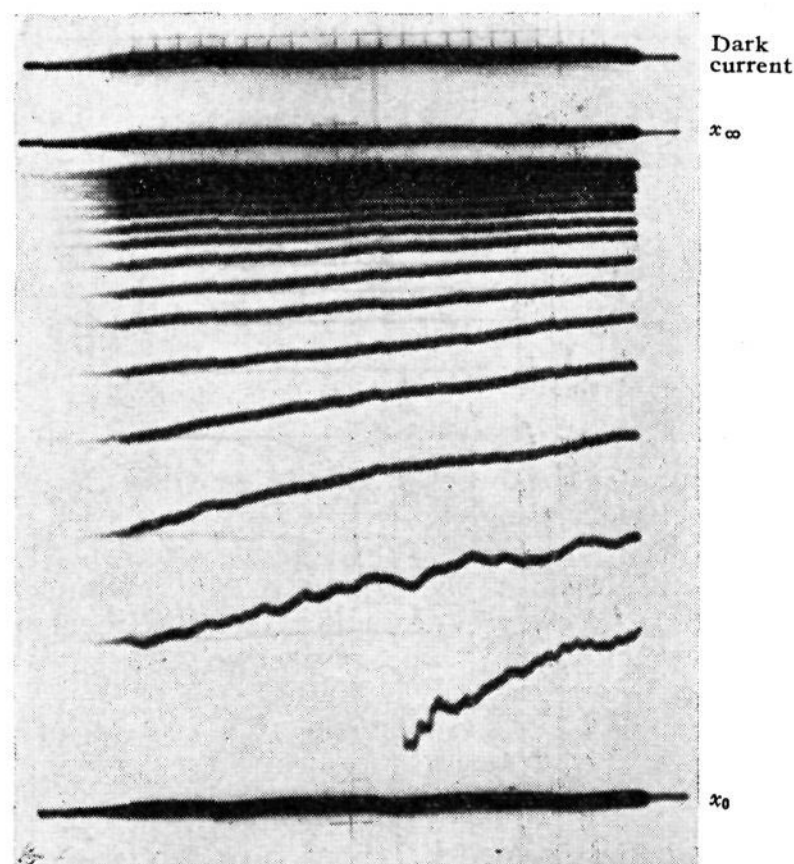(23) W. C. Schumb, M. S. Sherrill and S. B. Sweetser, THIS JOURNAL, **59**, 2360 (1937).

Fig. 2.—Negative of experiment 22, Table IV; sweep frequency 20 c.p.s.

ton[8] at an ionic strength of 1.28. A value of Q_1 of 146 ± 5 at 25° and $\mu = 0.40$ was obtained. From Laurence's[10] data and his ionic strength correction equation, we have calculated $Q_1 = 149$ at 25° and $\mu = 0.40$. From Lister and Rivington's[9] data and their ionic strength dependence results, we also have calculated $Q_1 = 144$ at 25° and $\mu = 0.40$.

TABLE I

THERMODYNAMIC DATA FOR FERRIC THIOCYANATE COMPLEXES

Ref.	Method	Temp., °C.	μ^a	Q_1	Q_2	ΔH_1, cal./ mole
Betts and Dainton[8]	Spect.	25.0	1.28	114	20	−1600
Frank and Oswalt[6]	Spect.	Room	0.5	138		
Laurence[10]	E.m.f.	25.0	.5	139	20.5	−1500
Lister and Rivington[9]	Spect.	25.0	.5	146	15.5	− 800

^{a} Ionic strength.

The final values chosen to make our calculations for the kinetic runs were $Q_1 = 146$ (25°, $\mu = 0.40$) and $\Delta H_1 = -1600$ cal./mole. The second complexing constant was not determined at $\mu = 0.40$ because experimental conditions were chosen to make its contribution negligible.

Hydrolysis of Ferric Ion.—It was necessary to correct all data for the hydrolysis of ferric ion. Milburn and Vosburgh[24] found the principal equilibria to be

$$Fe^{+++} + H_2O = FeOH^{++} + H^+ \quad Q_H \qquad (3)$$
$$2Fe(OH)^{++} = Fe_2(OH)_2^{+4} \quad Q_D \qquad (4)$$
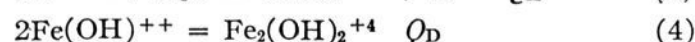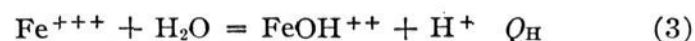
From their data Q_H (25°, $\mu = 0.40$) = 2.05 × 10^{-3} and Q_D (25°, $\mu = 0.40$) = 390. The equilibrium quotients Q_H and Q_D were corrected for temperature

(24) R. M. Milburn and W. C. Vosburgh, *ibid.*, **77**, 1352 (1955).

by using ΔH values of $10.2^{25,26}$ and -8.2^{26} kcal. per mole, respectively, measured for an ionic strength of 1.00.

Rate Law.—As a reasonable working hypothesis the mechanism was assumed to be
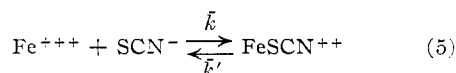
$$Fe^{+++} + SCN^- \underset{k'}{\overset{k}{\rightleftarrows}} FeSCN^{++} \qquad (5)$$

Using the relationship $Q_1 = k/k'$, it follows that

$$\frac{d(FeSCN^{++})}{dt} = k(Fe^{+++})(SCN^-) - \frac{k}{Q_1}(FeSCN^{++}) \qquad (6)$$

Assuming (Fe^{+3}) to be essentially constant during an experiment, expressing (SCN^-) in terms of $(FeSCN^{++})$ and (Fe^{+3}) and defining $(FeSCN^{++})_0$ and $(FeSCN^{++})_\infty$ as the concentrations of complex at the start of the reaction and after attainment of the final equilibrium value, respectively, the above rate may be integrated, yielding

$$-kt = \frac{2.303}{(Fe^{+++}) + 1/Q_1} \log \frac{(FeSCN^{++})_\infty - (FeSCN^{++})}{(FeSCN^{++})_\infty - (FeSCN^{++})_0} \qquad (7)$$

All quantities in eq. 7 except k were determinable experimentally. A plot of $\log \{(FeSCN^{++})_\infty - (FeSCN^{++})\}$ versus time yielded a straight line, thus confirming the assumption of first-order dependence on (SCN^-). The data for a typical experiment (experiment 22 of Table IV) are given in Table II. The displacement on the negative of the trace from the dark current is equal to x. The value of $1.175 \log x_b/x$, where b signifies the blank, is equal to the optical density and therefore pro-

TABLE II

DATA FOR A TYPICAL EXPERIMENT

(Experiment 22 of Table IV and Fig. 2)

Temp. $= 23.38°$; $\mu = 0.40$; $Q_1 = 148$; $(HClO_4) = 0.224$ M; $\Sigma(FeIII) = 7.91 \times 10^{-3}\ M$; final $(FeSCN^{++}) = 6.16 \times 10^{-4}\ M$; $\Sigma(SCN^-)_{calcd.} = 1.20 \times 10^{-3}\ M$; av. $(Fe^{+++})_{calcd.} = 7.51 \times 10^{-3}\ M$.

Time (sec.)[a]	$x\,b$ (mm.)	$\log x - \log x_\infty$
0.0	28.3	0.872
.0'	28.5	.864
.05	23.7	.795
.05'	23.2	.775
.10	18.6	.690
.10'	18.5	.677
.15	15.2	.602
.15'	15.2	.591
.20	12.9	.531
.20'	12.8	.517
.25	11.3	.474
.25'	11.3	.463
.30	10.0	.420
.30'	10.0	.409
.35	8.9	.370
.35'	8.9	.359
.40	8.15	.332
.40'	8.2	.323
∞	3.8	
∞ '	3.9	

[a] The primed entries are for the right side of the negative and the unprimed for the left. [b] x of blank $= 36.7$.

(25) T. H. Siddall and W. C. Vosburgh, This Journal, **73**, 4270 (1951).

(26) R. M. Milburn, ibid., **79**, 537 (1957).

portional to the $FeSCN^{++}$ concentration. The numerical factor arose from the non-linear characteristics of the oscilloscope. The value of $\log x_b/x_\infty$ is similarly proportional to $(FeSCN^{+2})_\infty$, the final $FeSCN^{+2}$ concentration. Therefore $\log x_b/x_\infty - \log x_b/x$ is proportional to $(FeSCN^{+2})_\infty - (FeSCN^{+2})$ and consequently the slope of a plot of the logarithm of the first quantity yields $-k[(Fe^{+3}) + 1/Q_1]/2.303$. To solve for k the average ferric ion concentration was substituted for (Fe^{+3}).

Table III summarizes the kinetics runs made at room temperature for the purpose of testing the rate law. The third, fourth and fifth columns list the average free ferric ion concentration, the total thiocyanate concentration and the free hydrogen ion concentration, respectively. The first and last quantities were corrected for hydrolysis of the iron. The k values of column 6 have been corrected to $25°$ in column 7. Order with respect to ferric ion and also thiocyanate ion was determined by testing the constancy of the calculated k_1 values when the concentrations of both species were varied: experiments 1, 9, 10, 15 and 17 and experiments 7 and 8. Experiment 9 is perhaps outside of the experimental error relative to 1 and 10, but a calculation made on the assumption of second order gives a far greater discrepancy.

Base-catalyzed Path.—The initial kinetic runs yielded rate constants very much smaller than that of $1.7 \times 10^4\ M^{-1}$ sec.$^{-1}$ reported by Chance.[11] A crude experiment approximating Chance's conditions using ferric alum and no added acid produced a very much faster reaction than found in the experiments of Table III. The simplest explanation was the existence of a base-catalyzed path.

TABLE III

KINETIC DATA AT ROOM TEMPERATURE

($\mu = 0.40$ unless otherwise noted)

Expt.	Temp., °C.	(Fe^{+++}), $M \times 10^3$	$\Sigma(SCN^-)$ $M \times 10^3$	(H^+), M	k M^{-1} sec.$^{-1}$	k_{25} M^{-1} sec.$^{-1}$
1	22.5	7.2	1.19	0.200	180	226
2[a]	23.2	6.8	1.29	.200	209	249
3[b]	24.7	7.0	1.24	.200	235	242
4[c]	25.5	(5.5–7.0)	1.16	.200	250–800[e]	
5	25.5	5.3	1.42	.200	270	257
6	24.4	6.8	1.23	.200	240	255
7	23.9	8.5	1.96	.200	200	221
8	23.6	6.9	0.61	.200	197	225
9	25.7	3.0	1.15	.200	196	185
10	24.3	10.7	1.38	.200	214	234
11[d]	24.0	7.2	1.26	.200	176	193
12	23.7	6.7	1.23	.284	186	211
13	24.0	7.1	1.20	.125	222	245
14	24.0	6.8	1.24	.0404	570	638
15	23.3	6.4	1.24	.0306	660	810
16	23.0	6.0	1.25	.0153	1150	1449
17	23.3	3.8	1.22	.0303	670	822

[a] $(Fe^{++}) = 7.2 \times 10^{-4}\ M$. [b] $(Fe^{++}) = 4.3 \times 10^{-3}\ M$. [c] $(Cl^-) = 5.0 \times 10^{-3}\ M$. [d] $\mu = 1.00$. [e] The uncertainty in Q is allowed for in this estimate.

To test this hypothesis a series of runs was made at varying hydrogen ion concentrations: experiments 12 through 17. In addition, an average of the runs at 0.200 M H^+ was included. This average included experiments 1, 5, 6, 7, 8, 9 and 10.

It was found that a plot of $\bar{k}$ versus $1/(\mathrm{H}^+)$ yielded a straight line (Fig. 3), with a finite intercept at $1/(\mathrm{H}^+) = 0$. This behavior corresponds to the following rate law, where for simplicity only the forward reactions have been shown

$$\frac{d(\mathrm{FeSCN}^{++})}{dt} = k_1(\mathrm{Fe}^{+++})(\mathrm{SCN}^-) + \frac{k_2(\mathrm{Fe}^{+++})(\mathrm{SCN}^-)}{(\mathrm{H}^+)}$$
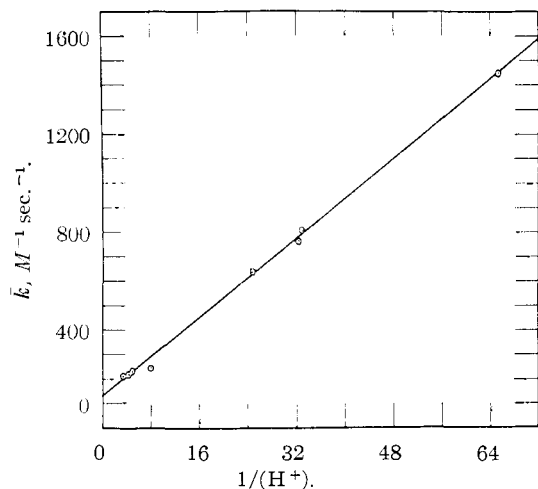
(8)

with $\bar{k} = k_1 + k_2/(\mathrm{H}^+)$.

Fig. 3.—The acid dependence of $\bar{k}$ at 25°, $\mu = 0.40$.

Since ferrous and chloride ions were both present in slight amount as impurities, runs 2, 3 and 4 (Table III) were made to determine their catalytic effect, if any. No significant effect was found for ferrous ion. The chloride run was complicated by the phenomenon, noted by Frank and Oswalt,[6] of intensification of the light absorption by chloride ion, presumably because of the formation of a mixed complex such as $\mathrm{Fe(SCN)Cl}^+$. Consequently (Fe^{+++}) could only be inferred from the other runs. The observed slope calculated from the logarithmic plot versus time was only 10% larger than the mean of the other slopes run under similar conditions. Because of the uncertainty in the ferric ion concentration and Q, an observed rate constant could be calculated only within wide limits. The resultant $\bar{k}$ showed chloride ion catalysis, if any, to be negligible in the other runs.

Experiment 11, at an ionic strength of 1.0, gave a decrease in $\bar{k}$ to 0.84 of the value at $u = 0.40$. Application of the conventional Debye–Hückel expression to the Brönsted salt effect equation would be meaningless at ionic strengths of 0.40 and 1.00, but k_1 may be expected from the assumed mechanism to depend on ionic strength approximately the same as the over-all complexing constant, Q_1. Further, k_2, with an approximately equal contribution to $\bar{k}$ at 0.200 M acid, should probably change in the same direction. The value of Q_1 was determined at $\mu = 1.00$ by the previously described method to be 123, in good agreement with values of 117 and 127 calculated from the work of Laurence[10] and Lister and Rivington,[9] respectively. Therefore Q_1 at $\mu = 1.0$ is approximately 0.84 of its value at $\mu = 0.40$, in close agreement with the change in rate constant.

Temperature Dependence.—In order to determine the enthalpies and entropies of activation, a series of experiments was run covering the temperature range from 13.7 to 31.63° (Table IV). The temperatures as measured by the thermistor are considered to be accurate to 0.05°.

Because of the two term rate law, it was necessary to carry out temperature dependence experiments at two different acidities. From the data in Table IV a plot of log $\bar{k}/T°\mathrm{K}$. versus $1/T°\mathrm{K}$. was made for the two acidities. Since the data showed no signs of specific curvature, the best fitting straight line was drawn through the data. The average deviation from this line was approximately 5%. Values of $\bar{k}$ were taken from this plot at three temperatures corresponding to $1000/T°\mathrm{K}$. = 3.26, 3.40 and 3.54, and from these were calculated values of k_1 and k_2 at these three temperatures. Figure 4 shows a plot of log k_1/T versus
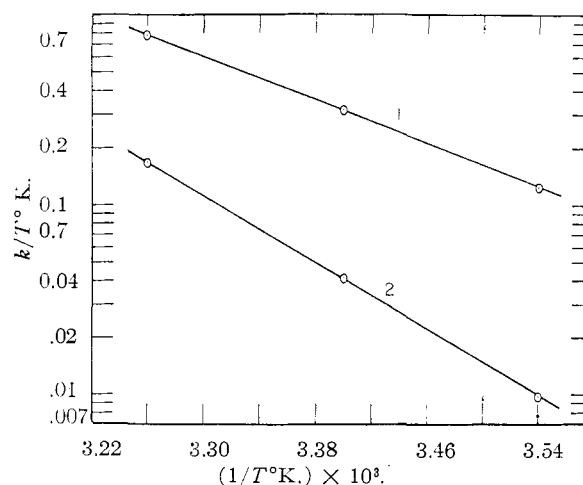

Fig. 4.—The temperature dependence of k_1 (curve 1) and k_2 (curve 2).

$1/T°\mathrm{K}$. and similarly for k_2. From the slopes of these lines, $\Delta H_1{}^{\ddagger} = 13.0 \pm 1.4$ kcal. mole^{-1} and $\Delta H_2{}^{\ddagger} = 20.2 \pm 1.4$ kcal. mole^{-1} were calculated using the Eyring equation. The corresponding entropies of activation at 25° were calculated to be: $\Delta S_1{}^{\ddagger} = -5 \pm 5$ e.u. and $\Delta S_2{}^{\ddagger} = 15 \pm 5$ e.u. The uncertainties were obtained by assuming a possible error of 10% in the rate constants at the high and low temperatures.
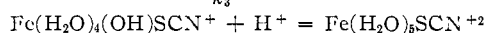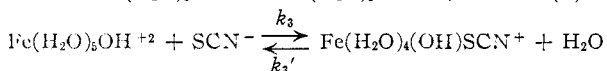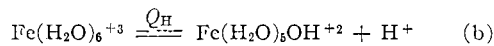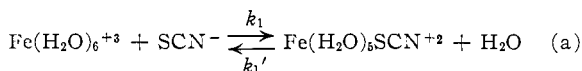
TABLE IV

TEMPERATURE DEPENDENCE DATA

$\mu = 0.40$

Exp.	H$^+$, M	Temp., °C.	(Fe^{+++}), $M \times 10^3$	Σ(SCN$^-$), $M \times 10^3$	$\bar{k}$, M^{-1} sec.$^{-1}$
18	0.224	23.60	7.22	1.22	216
19	.224	17.63	6.55	1.26	109
20	.224	29.51	8.84	1.28	302
21	.224	31.63	8.52	1.09	392
22	.224	23.38	7.50	1.20	188
23	.224	13.73	7.09	1.22	71
24	.0308	24.84	6.59	1.26	733
25	.0308	16.52	6.51	1.29	288
26	.0308	15.73	7.35	1.20	264
27	.0308	26.76	5.14	1.09	1053
28	.0308	30.15	8.21	1.47	1402

The above ΔH values and k_1 at 25° were then used to correct the room temperature values of $\bar{k}$ in Table III to $\bar{k}_{25}°$ values. The final values of k_1 and k_2 at 25° were then taken from Fig. 3 which contains the corrected (H^+) dependence $\bar{k}$ values. They are $k_1 = 127 \pm 10$ M^{-1} sec.$^{-1}$ and $k_2 = 20.2 \pm 2$ sec.$^{-1}$.

Discussion

On the assumption that ferric ion and its complexes are hexacoördinated in aqueous solution, a mechanism consistent with the data can be proposed which consists of the two paths[27]

$$Fe(H_2O)_6^{+3} + SCN^- \underset{k_1'}{\overset{k_1}{\rightleftharpoons}} Fe(H_2O)_5SCN^{+2} + H_2O \quad (a)$$

$$Fe(H_2O)_6^{+3} \overset{Q_H}{=\!=\!=} Fe(H_2O)_5OH^{+2} + H^+ \quad (b)$$

$$Fe(H_2O)_5OH^{+2} + SCN^- \underset{k_3'}{\overset{k_3}{\rightleftharpoons}} Fe(H_2O)_4(OH)SCN^+ + H_2O$$

$$Fe(H_2O)_4(OH)SCN^+ + H^+ = Fe(H_2O)_5SCN^{+2}$$

where $k_3 = k_2/Q_H$.

Instead of mechanism (a) which has an activated complex containing iron of coördination number 7, an alternate mechanism for the first path could be[27]

$$Fe(H_2O)_6^{+++} = Fe(H_2O)_5^{+++} + H_2O \quad (c)$$

$$Fe(H_2O)_5^{+++} + SCN^- \overset{k}{\longrightarrow} Fe(H_2O)_5SCN^{++}$$
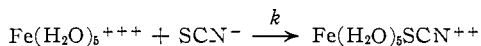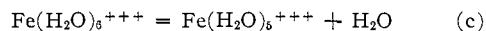
This mechanism requires that the exchange of water molecules in the first coördination sphere with the bulk water molecules be faster than the ferric-thiocyanate rate. The only published work on the water exchange[28] shows that the exchange is complete within 3.5 minutes at room temperature in 1.1 M HClO$_4$—a result which does not preclude mechanism (c). Nuclear magnetic resonance measurements[29] indicate that the water exchange is very much faster than the ferric–thiocyanate reaction and that therefore the mechanism is a possible one. In analogy to (c) a mechanism where water is first eliminated could be written in place of (b).

There appears to be no way at the present time of deciding between these two types of mechanisms for the ferric–thiocyanate reaction. In principle the entropies of activation might be used to distinguish between them. The entropy of activation for the seven coördinated activated complex would be expected to be appreciably more negative than for the six coördinated activated complex of the second mechanism, because an additional water molecule is involved in the former. This difference might be as great as 8 e.u. as discussed below for paths (a) and (c). The observed entropies of activation seem rather negative, which might be taken as evidence for the 7 coördinated activated complex. The uncertainties in the entropies and the estimation of values expected for the two models is so great, however, that no reliance can be placed on such an argument.

For the base-catalyzed path, mechanisms involving hydroxide could be written, but they seem much less plausible, although not impossible, be-

(27) See analogous treatment for Cr(SCN)$^{++}$ by C. Postmus and E. L. King, J. Phys. Chem., 59, 1216 (1955).

(28) J. P. Hunt and H. Taube, J. Chem. Phys., 19, 602 (1951).

(29) R. E. Connick and R. E. Poulson, unpublished work.
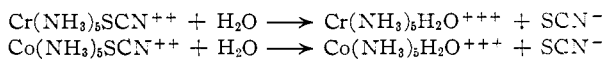
cause of the extremely low concentration of hydroxide ion.

The value of k_3 at 25° and $\mu = 0.40$ is 1.0×10^4 M^{-1} sec.$^{-1}$, compared to $k_1 = 127$ M^{-1} sec.$^{-1}$. The greater rate of the catalyzed path may be due to the weakening of the bonding of the hydrated waters by the negative OH$^-$, thus permitting easier entry of the thiocyanate ion into the coördination sphere. The electrostatic repulsion between the thiocyanate and hydroxide ions would work in the opposite direction. Alternatively, the effect may arise from some interaction of the OH$^-$ with the electronic system of the iron which leads to a more stable activated complex.

The faster rate found by Chance for the reaction between dilute ferric alum and ammonium thiocyanate can be interpreted as arising from extensive base catalysis. Chance used 10^{-3} M ferric alum, which would have a pH of about 3. An apparent rate constant of approximately 1×10^4 as compared with Chance's value of 1.7×10^4 M^{-1} sec.$^{-1}$ would be predicted from the present work.

The rate constant of 10^5 M^{-1} sec.$^{-1}$ in methanol calculated from the data of Bjerrum and Poulson may be explained as arising from the lower dielectric constant of methanol, which would increase the charge attraction between ferric and thiocyanate ions.

In path (a) of the above mechanism, it is observed that the activated complex postulated is somewhat similar in size and charge to the stable end product. Thus a comparison of the entropy of activation with that of the over-all net reaction might be made. Using the value of the complexing constant at $\mu = 0.40$ of 146 and $\Delta H = -1600$ cal./mole previously mentioned, we obtain an entropy for the net reaction of 4.6 e.u. The measured entropy of activation for this path was -5 e.u. Since the activated complex has an additional water coördinated rather than free, as well as one degree of freedom subtracted out, these values may well be consistent. For the analogous comparison based on the (c) mechanism, it would be difficult to account for -5 e.u. of activation, but, allowing the maximum uncertainty, the entropy of activation might be as high as zero entropy unit, which might be consistent with the (c) mechanism.

Adamson and Wilkins have measured the entropies of activation[30] of the reactions

$$Cr(NH_3)_5SCN^{++} + H_2O \longrightarrow Cr(NH_3)_5H_2O^{+++} + SCN^-$$
$$Co(NH_3)_5SCN^{++} + H_2O \longrightarrow Co(NH_3)_5H_2O^{+++} + SCN^-$$

with the entropies at 25° being -9.3 and -9.9 e.u., respectively. These should be comparable to the corresponding entropy of activation of the reaction

$$Fe(H_2O)_5SCN^{++} + H_2O \longrightarrow Fe(H_2O)_6^{+++} + SCN^-$$
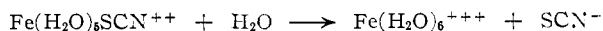
The entropy of activation of this reaction can be calculated from ΔS for the equilibrium and the entropy of activation of the reverse reaction, $\Delta S_1^{\ddagger}$. We obtain a $\Delta S^{\ddagger} = -9.6$ e.u., which is well within the limits of experimental error in making the comparison.

Postmus and King[27] have found for the following

(30) A. W. Adamson and R. G. Wilkins, THIS JOURNAL, 76, 3379 (1954). Recalculated by E. L. King, J. Phys. Chem., 61, 1687 (1957).

reaction a rate law identical to that of equation (8)

$$Cr^{+3} + SCN^- = CrSCN^{+2}$$
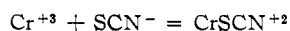
except for an additional term containing $(H^+)^2$ in the denominator. For the entropies of activation corresponding to the k_1 and k_2 terms of equation (8) they report $+0.7$ and $+13$ e.u., respectively, at an ionic strength of 0.08 M and at 25°. These values are within experimental error of those found here.

It would be of some interest to compare entropies of activated complexes with the entropies of similar stable complexes. We have considered the complexing reactions
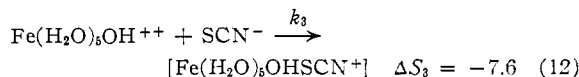
$$Fe^{+++} + F^- = FeF^{++} \quad \Delta S_9 = 30 \text{ e.u.} \quad (9)$$
$$FeF^{++} + F^- = FeF_2^+ \quad \Delta S_{10} = 23 \text{ e.u.} \quad (10)$$
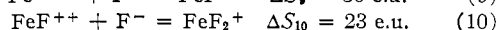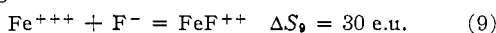
where the ΔS values refer to 25° and $\mu = 0.50$.[31]

The analogous entropies for the thiocyanate rates are

$$Fe(H_2O)_6^{+++} + SCN^- \xrightarrow{k_1}$$
$$[Fe(H_2O)_6SCN^{++}] \quad \Delta S_1 = -5 \quad (11)$$
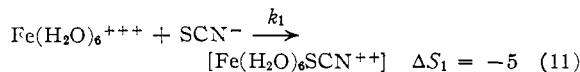
(31) R. E. Connick, L. G. Hepler, Z. Z. Hugus, Jr., J. W. Kury, W. M. Latimer and Maak-Sang Tsao, THIS JOURNAL, 78, 1827 (1956).

$$Fe(H_2O)_5OH^{++} + SCN^- \xrightarrow{k_3}$$
$$[Fe(H_2O)_5OHSCN^+] \quad \Delta S_3 = -7.6 \quad (12)$$

The much more positive entropy changes for fluoride complexing are due to the smaller size of the fluoride ion and consequent greater release of water molecules from its field when the oppositely charged ions combine. The difference, however, between thiocyanate and fluoride should be largely eliminated if we subtract the entropies of reactions 11 and 12 and compare with the difference of reactions 9 and 10. The chief difference now is between the effects of fluoride and hydroxide on the entropies. The values $\Delta S_9 - \Delta S_{10} = 7$ e.u. and $\Delta S_1^{\ddagger} - \Delta S_3^{\ddagger} = 2.6$ e.u. lie within the experimental error of each other.

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The Activity Coefficients of Alkali Metal Nitrates and Perchlorates in Dilute Aqueous Solutions at 25° from Diffusion Coefficients

BY HERBERT S. HARNED AND JOSEPH A. SHROPSHIRE

The diffusion coefficients of lithium and cesium nitrates have been measured at 25° over a concentration range from 0.003 to 0.015 molar. From these data, the activity coefficients of these electrolytes have been computed at low concentrations. Similar calculations have been carried out for lithium and potassium perchlorates and potassium nitrate solutions and the results tabulated.

The method for determining activity coefficients of univalent electrolytes from diffusion coefficients[1] has been employed by us[2] to determine the activity coefficient of sodium nitrate. Measurements of the diffusion coefficients of lithium and cesium nitrates recorded in this contribution and the earlier measurements of the diffusion coefficient of potassium nitrate[3] permit the evaluation of the activity coefficients of these nitrates in dilute solutions at 25° with a high degree of precision. In addition, the activity coefficients of lithium and potassium perchlorates from previously determined diffusion coefficients[4] have been computed and tabulated.

In brief, the method employs the integral

$$\log y_{\pm} = 0.8686 \int_0^c \frac{\mathcal{D}'}{c^{1/2}} dc^{1/2} \quad (1)$$

where the limiting value of $\mathcal{D}'/c^{1/2}$ is fixed and equal to

$$\lim_{c \to 0} \left[\frac{\mathcal{D}'}{c^{1/2}} \right] = -1.1513 \, S_{(f)} \quad (2)$$

$S_{(f)}$ is the theoretical Debye and Hückel slope of the logarithm of the activity coefficient. The quantity

(1) H. S. Harned, Proc. Nat. Acad. Sci., 40, 551 (1954).

(2) H. S. Harned and J. A. Shropshire, THIS JOURNAL, 80, 2618 (1958).

(3) H. S. Harned and R. M. Hudson, ibid., 73, 652 (1951).

(4) H. S. Harned, H. W. Parker and M. Blander, ibid., 77, 2071 (1955).

TABLE I

COMPUTATION OF $\mathcal{D}'/c^{1/2}$ USED FOR DETERMINING THE ACTIVITY COEFFICIENTS OF LITHIUM AND CESIUM NITRATES

c	$A'\sqrt{c}$	$\phi(A'\sqrt{c})$	$(\overline{\mathfrak{M}}'/c) \times 10^{20}$	$(\overline{\mathfrak{M}}''/c) \times 10^{20}$
0.00333	0.0664	1.584	0.077	0.100
.00585	.0880	1.343	.101	.149
.00923	.1105	1.155	.124	.202
.01000	.1150	1.123	.128	.213
.01287	.1305	1.027	.144	.250
.01533	.1424	0.962	.155	.280

$c^{1/2}$	$\mathcal{D}\text{(obsd.)} \times 10^5$	$(\overline{\mathfrak{M}}/c) \times 10^{20}$	$-\mathcal{D}'$	$-\mathcal{D}'/c^{1/2}$
0.0577	1.295	26.998	0.03240	0.5615
.0765	1.287	27.023	.03967	.5186
.0961	1.275	27.053	.04945	.5147
.1000	1.278	27.060	.04766	.4766
.1135	1.273	27.081	.05224	.4603
.1238	1.268	27.100	.05606	.4528

CsNO₃

c	$\mathcal{D}\text{(obsd.)} \times 10^5$	$(\overline{\mathfrak{M}}/c) \times 10^{20}$	$c^{1/2}$	$-\mathcal{D}'/c^{1/2}$
0.00770	1.907	40.0715	0.0877	0.4554
.01378	1.886	40.1533	.1174	.4497
.01412	1.871	40.1577	.1188	.5093

For LiNO₃: $\lambda_+^0 = 38.69$; $\lambda_-^0 = 71.44$; $\Lambda^0 = 110.13$

CsNO₃: $\lambda_+^0 = 77.26$; $\lambda_-^0 = 71.44$; $\Lambda^0 = 148.70$

For both LiNO₃ and CsNO₃: $a = 3.5$ Å.; $D = 78.54$; $10^3\eta = 8.849$