make it possible to draw definite conclusions. The maximum in the absorption curve shifts somewhat to longer wave lengths as (SCN^-) increases, however, and some indication seems to exist that the next higher stable complex may be the 3–1, rather than the 2–1. (That is, that the "extra" color, beyond what is due to $FeSCN^{++}$ increases initially as $(SCN^-)^3$ instead of as $(SCN^-)^2$. A similar possibility in the chloride system is not ruled out by the data reported by Rabinowitch and Stockmayer. Precise experiments, with adequate temperature control, should be able to decide such questions.

Experimental

Ferric perchlorate solution was prepared by precipitating ferric hydroxide from a solution of ferric alum and dissolving in a known excess of perchloric acid. It was standardized by iodimetric titration. The potassium thiocyanate used was analytical reagent; the solution was standardized against silver nitrate. An experiment was performed by measuring out calculated volumes of stock ferric perchlorate and perchloric acid into one flask of potassium thiocyanide and water into a second, the two solutions being mixed immediately before measurement. The time required for measuring T at intervals of 200 from 4000 to 5000 Å. did not exceed about thirty minutes from time of mixing. No evidence of fading was observed in this length of time, and reasons are given above for believing that serious fading did not occur.

The Coleman spectrophotometer was used with a slit width stated to be 50 Å. and a cell thickness of 13.05 mm. in all of the experiments here reported. No check was made on the accuracy of the wave length scale. Distilled water was used in the reference cell, but comparison with ferric perchlorate showed that the latter gave no detectable absorption up to several hundredths molal, throughout the wave length range studied.

Summary

1. The equilibrium of Fe^{+++} and SCN^- in perchloric acid solutions was studied at room temperature. Absorption of light of wave lengths from 4000 to 5000 Å. was measured with the Coleman spectrophotometer.

2. The conclusion of earlier workers was confirmed that the carrier of the color is $FeSCN^{++}$.

For the reaction

$$\mathrm{Fe^{+++} + SCN^- = FeSCN^{++}} \qquad (1)$$

the room temperature value of K_1, at $\mu = 0.50$, corrected for hydrolysis, is 138.0 ± 1.9. The absorption spectrum of $FeSCN^{++}$ has been determined. The maximum absorption occurs at about 4475 Å., where the molal extinction coefficient is 4700 ± 2%. At 4000 Å. the molal extinction coefficient is 3000; at 5000 Å. it is 2900.

3. The effect of ionic strength on K is found to be compatible with current theory. An estimate of K^0 for zero ionic strength, obtained by combining our data with a point reported by Edmonds and Birnbaum and using the Debye–Hückel limiting law, is given by $\log K^0 = 2.95$ ($K^0 = 890$; K 1/L = 0.00122).

4. Møller's measurements in chloride solutions are in marginal agreement with calculations based on our results and those of Rabinowitch and Stockmayer on Fe^{+++}–Cl^- equilibria.

5. At concentrations of SCN^- higher than about 0.003 M higher complexes of the form $Fe(SCN)_n^{3-n}$ become important.

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[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

Application of the Principle of the Concentration Cell to Kinetic Studies. II. The Oxidation of Oxalic Acid by Ceric Sulfate

BY SIDNEY D. ROSS[1] AND C. GARDNER SWAIN[2]

In the first paper of this series[3] we described a concentration cell method for measuring the rate of a chemical reaction. In applying this method to an oxidation–reduction reaction, namely, the oxidation of oxalic acid by ceric ion, an important limitation of the method became apparent. It is the purpose of the present paper to report that limitation.

The apparatus and method used are those reported in our earlier paper.[3] Shiny platinum electrodes were used and all runs were adjusted to the constant ionic strength of 2.0 M by adding the requisite amount of ammonium bisulfate. Both half cells contained equal quantities of sulfuric acid, water, ammonium bisulfate and ceric sulfate when they were placed in a thermostat at 25.0°. At zero time, reaction was initiated by adding a standard solution of oxalic acid to the "reaction cell" and an equal volume of water to the "titration cell." The rate measurement was then carried out by adding measured excesses of a solution of ferrous sulfate to the "titration cell" to reduce the ceric sulfate there and recording the times when the oxidation reaction in the "reaction cell" again brought the galvanometer to the null point.

At balance points the ratio of ceric ion to cerous ion is the same in both the "reaction" and "titration" cells. In the absence of complexing the only way in which the concentration of ceric ion can be lowered is by oxidation of oxalic acid and the null point measurements can therefore be directly related to the oxidation rate. At high sulfuric acid concentrations and low concentrations of both ceric sulfate and oxalic acid complexing is

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[3] Swain and Ross, THIS JOURNAL, 68, 658 (1946).

either completely absent or at least not appreciable. The data for a run satisfying this limiting condition are given below (Table I).

TABLE I

Run 26: 0.00253 M $Ce(SO_4)_2$; 0.00125 M $H_2C_2O_4$; 2.0 M H_2SO_4

Minutes	$FeSO_4$, cc.	Reaction, %
0.31	7.00	42.3
.51	9.00	54.6
.65	10.00	61.2
.86	11.00	66.6
1.01	11.50	69.6
1.15	12.00	72.7
1.36	12.50	75.7
1.58	13.00	78.7
2.19	13.80	83.5
∞	16.50	100

The simplest mechanism for this reaction is a rate-determining reaction between ceric ion and oxalic acid, bioxalate ion, or oxalate ion. When stoichiometric equivalents of ceric sulfate and oxalic acid are used second order kinetics should be obtained. This is, indeed, the case for Run 26. A plot of $z/(1 - z)$ where z is the fraction reacted gives a straight line (Fig. 1), and the average deviation from the mean of the second order rate constant, calculated from all points in this run, is less than 2%.

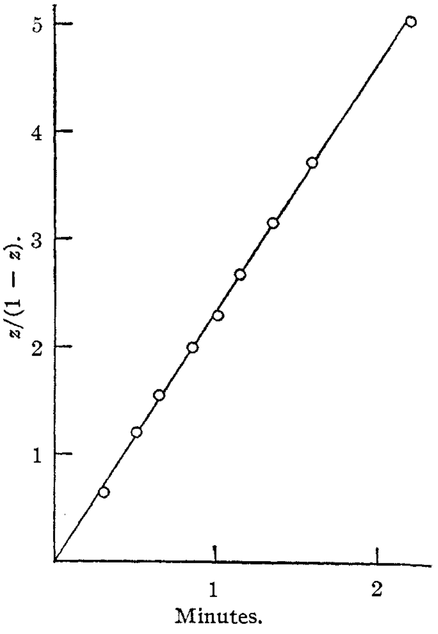

Fig. 1.

In runs where complexing is appreciable, immediately after the oxalate and water are added to the "reaction cell" a potential difference develops caused by a decrease in the effective ceric–cerous ratio as a result of complexing of the ceric ion with oxalate. Accordingly, ferrous ion will be required even before oxidation of the oxalate begins and the null-point measurements cannot be directly related to the oxidation rate since no direct measure of the concentration of oxidant is obtained. In the absence of data on the nature and stability of the ceric oxalate complex we have found it impossible to treat our results quantitatively. Some representative results are presented in the tables below to point up this important limitation of the concentration cell technique. In all of the runs presented the initial ceric–cerous ratio was fifty.

TABLE II

Run 11: 0.01011 M $Ce(SO_4)_2$; 0.004935 M $H_2C_2O_4$; 0.5 M H_2SO_4

Minutes	N = 0.0866 cc. $FeSO_4$	Apparent % reaction
0.11	5.00	43.9
.28	7.00	61.4
.42	8.00	70.2
.68	9.00	78.8
.89	9.50	83.2
1.24	10.00	87.7
1.87	10.50	92.3
∞	11.40	100

Run 13: 0.01011 M $Ce(SO_4)_2$; 0.004935 M $H_2C_2O_4$; 1.0 M H_2SO_4

Minutes	N = 0.0866 cc. $FeSO_4$	Apparent % reaction
0.34	8.00	70.0
.49	9.00	78.8
.68	9.55	83.6
.95	10.00	87.7
1.50	10.50	92.2
∞	11.40	100

Run 15: 0.01011 M $Ce(SO_4)_2$; 0.004935 M $H_2C_2O_4$; 1.9 M H_2SO_4

Minutes	N = 0.0866 cc. $FeSO_4$	Apparent % reaction
0.18	7.00	61.4
.27	8.00	70.2
.41	9.00	78.8
.53	9.50	83.2
.76	10.00	87.7
1.17	10.50	92.3
∞	11.40	100

Run 27: 0.00253 M $Ce(SO_4)_2$; 0.00125 M $H_2C_2O_4$; 1.0 M H_2SO_4

Minutes	N = 0.01506 cc. $FeSO_4$	Apparent % reaction
0.78	13.95	84.0
1.52	14.50	87.3
2.78	15.00	90.4
∞	16.60	100

Summary

The concentration cell technique is applicable to measuring the rate of an oxidation–reduction reaction only when the substance being measured does not form a complex with another product or reactant. The oxidation of oxalic acid by ceric sulfate is bimolecular under conditions where no complexing occurs. In cases involving complexing we have not found it possible to treat the data obtained by use of the concentration cell technique quantitatively.

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