preted, in the flowing case, as the Euler total time derivative which follows the fluid. It is easy to show that this equation is not restricted to reactors operating with negligible pressure drop, since the density may be considered to depend explicitly on both the composition and the pressure, each of which depend explicitly on the time of contact.

These considerations are in agreement with the expressions which were obtained by Benton[1] with a less general argument for the special cases of first- and second-order reactions at constant pressure, and they confirm the form of rate law that was employed, without supporting argument, by Hulbert.[2]

The hydrodynamic rate law, equations (3) and (8), may be written in various forms for special cases. For example, if the system has attained the steady state, it is sometimes convenient to employ position as independent variable instead of time of contact by means of the substitution (*cf.* equation (2)) $d/dt = \mathbf{u}\cdot\nabla$.

If the reactor cannot be considered to be isothermal, the solution of the hydrodynamic problem must include consideration of the equation for energy transport, and the rate constant becomes a function of temperature, which may be considered to depend explicitly upon the time of contact (or upon position).

At low velocities of flow, diffusion may be of sufficient importance to require consideration of equation (1) instead of its approximate form, equation (3).

It has been assumed that the reaction is homogeneous. A more elaborate analysis is required if surface reactions or diffusion to a surface are rate controlling.[1,10,11]

Summary

1. A reaction-rate law, which is not restricted to either constant pressure or constant volume, is obtained for homogeneous, isothermal reactions in ideal systems.

2. It is shown that this expression is applicable to flowing systems with negligible diffusion if the time derivative is interpreted as the Euler total time derivative which follows the fluid.

3. Mention is made of the modifications required for the consideration of systems which are non-isothermal or in which diffusion currents are not negligible.

(10) Benton, *Ind. Eng. Chem.*, **19**, 494 (1927).

(11) Hulburt, *ibid.*, **37**, 1063 (1945).

PITTSBURGH, PENNA. RECEIVED DECEMBER 18, 1946

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Stability and Light Absorption of the Complex Ion $FeSCN^{++}$

BY HENRY S. FRANK AND ROBERT L. OSWALT

Introduction

Møller[1] was apparently the first to publish evidence that when Fe^{+++} and SCN^- are mixed at high dilution the principal colored substance formed is $FeSCN^{++}$, but this conclusion was also reached independently by Bent and French,[2] Edmonds and Birnbaum[3] and by at least one other group[4] as well. In each case an estimate was made of the value of K_1 for the reaction

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

but these results are not equally susceptible of straight-forward interpretation. Rabinowitch and Stockmayer[5] have shown that several complexes of Fe^{+++} and Cl^- exist, and have found K for

$$Fe^{+++} + Cl^- = FeCl^{++} \qquad (2)$$

to have a value close to 4.2 in perchlorate solutions at an ionic strength of 1.0. They have also shown that when (Cl^-) is greater than a few hundredths molal higher chloride complexes cannot be neglected. The fact, therefore, that Møller and Bent and French worked in chloride solutions and either took no account of ferric chloride complexes or treated them in ways incompatible with Rabinowitch and Stockmayer's figures makes it impossible to use their values of K_1 without further discussion (see below).

The Edmonds and Birnbaum value of K_1, on the other hand, should be usable as it stands, for they worked in perchlorate solutions, with perchloric acid at about 1.0 M to repress hydrolysis and keep the ionic strength constant at unity and there seems to be no evidence either for the formation of complexes between Fe^{+++} and ClO_4^- or for weakness of thiocyanic acid.[6] Their value of $1/K_1$ for room temperature is 0.0079 ± 0.0006. They do not report the wave length or range of wave lengths used in their experiments, and give

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(1) Max Møller, "Studies on Aqueous Solutions of Iron Thiocyanates," Copenhagen, Dana Bogtrykkeri, 1937.

(2) H. E. Bent and C. L. French, THIS JOURNAL, **63**, 568 (1941).

(3) S. M. Edmonds and N. Birnbaum, *ibid.*, **63**, 1471 (1941).

(4) Reuben E. Wood and Miss Tsao Hang-Sang worked on this problem with one of us (H. S. F.) at Lingnan University in 1935 and 1936. The former made measurements with a Duboscq colorimeter which established the 1-1 composition of the first complex. Miss Tsao subsequently constructed a photometer using balanced photronic cells and studied the equilibrium in sulfate solutions using 2.0 M sulfuric acid to repress hydrolysis and provide sensibly constant ionic strength. She obtained a value for K_1 of 100 ± 10.

(5) E. Rabinowitch and W. H. Stockmayer, THIS JOURNAL, **64**, 335 (1942).

(6) A rough test of the latter point was made by adding methyl violet indicator to 10-cc. portions of 1.0 M potassium chloride and 1.0 M potassium thiocyanate and slowly adding 6 N hydrochloric acid to each. For equal additions of acid the colors of the two solutions were practically indistinguishable all the way from clear violet to clear yellow.

no estimate of the extinction coefficient of the complex.

Method and Results

Carrying forward the work referred to in footnote[4] we have studied mixtures of ferric perchlorate and potassium thiocyanate in perchloric acid solutions, using a Coleman absorption spectrophotometer. If a is the stoichiometric concentration of Fe^{+++}, b that of SCN^- and x the actual concentration of $FeSCN^{++}$, then for reaction (1) we have, approximately, for constant ionic strength, ignoring hydrolysis, and so long as no other complexes are formed

$$K_1 = \frac{x}{(a-x)(b-x)} \tag{3}$$

$$x^2 - \left(a + b + \frac{1}{K_1}\right)x + ab = 0 \tag{4}$$

$$x = \frac{ab}{a + b + \frac{1}{K_1}} + \frac{(ab)^2}{\left(a + b + \frac{1}{K_1}\right)^3} + \cdots \tag{5}$$

For all of the experiments we are reporting the second and higher terms on the right-hand side of (5) can be neglected.[6a] Now the optical density of the solution, for the wave length selected, may be defined as $D_\lambda = -(1/l)\log_{10}T_\lambda$ where T_λ is the fraction of the light of this wave length transmitted by a length l cm. of the solution. If Beer's law is obeyed, $D_\lambda = \beta_\lambda c$, which defines β_λ as the molal extinction coefficient, for the specified wave length, of the absorbing species, c being the concentration of the latter in moles per liter. Since we have found by experiment that within the limits of accuracy of our instrument neither ferric perchlorate nor any other of our solutions, in the concentrations employed, absorbed any light in the wave length range studied, we may write

$$D_\lambda = \beta_\lambda x = \frac{B_\lambda ab}{a + b + \frac{1}{K_1}} \tag{6}$$

or

$$\frac{ab}{D_\lambda} = \frac{1}{\beta_\lambda}(a + b) + \frac{1}{\beta_\lambda K_1} \tag{7}$$

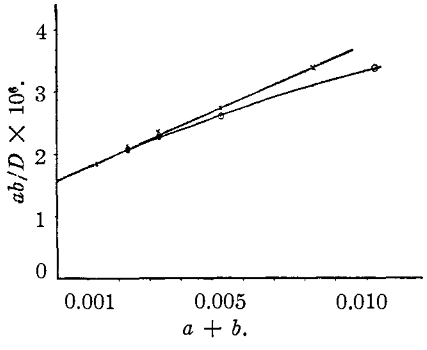

Fig. 1.—Quotient of concentration product by optical density (λ = 4500 Å.) against sum of concentrations of reactants.

Figure 1 shows ab/D_λ plotted against $a + b$ for two typical series of experiments. In the first, represented by crosses, b was kept constant at 0.00030 M and a was varied from 0.001 to 0.008 M; λ = 4500 Å. The fact that these points fall in a straight line as required by (7) confirms the expectation that when (SCN^-) is low and (Fe^{+++}) high the only complex formed is $FeSCN^{++}$. The line is found to have a slope of 0.000218, which yields $\beta = 4580$. The intercept is 1.59×10^{-6}. This is equal to $(\beta K_1)^{-1}$ and gives 0.00728 for $1/K_1$, or 137.4 for K_1. These experiments were performed in solutions 0.500 M in perchloric acid. The ionic strength was therefore sensibly constant at 0.50 and the constant value of (H^+) can be used as discussed below to make a small correction for hydrolysis of Fe^{+++}.

The other set of points in Fig. 1, represented by circles, shows the results of a second series of experiments identical with the first except that here a was constant at 0.0003 M and b varied. For low b the two curves coincide, but as b increases above 0.003 M, ab/D falls below expectation, the discrepancy increasing as b increases. This means that at high (SCN^-) the color is deeper than can be accounted for on the basis of (1). We conclude that this is due to the appearance of one or more higher complexes.

A necessary consequence of the treatment given above for low (SCN^-) is that if measurements are made at several wave lengths for each solution and separate plots corresponding to Fig. 1 are made for different wave lengths, these should give straight lines with different slopes and intercepts, differing in such a way, however, that the quotient of the intercept by the slope is the same in every case. Table I gives the data for such a series of experiments, and Fig. 2 shows typical plots representing them. The points for a given wave length scatter in such a way that a straight line drawn through them by inspection would be somewhat arbitrary. In order, therefore, that there should be no question of our own desires influencing the values chosen for the slopes and intercepts the latter were evaluated by the method of least squares. It will be noted that there is no trend in

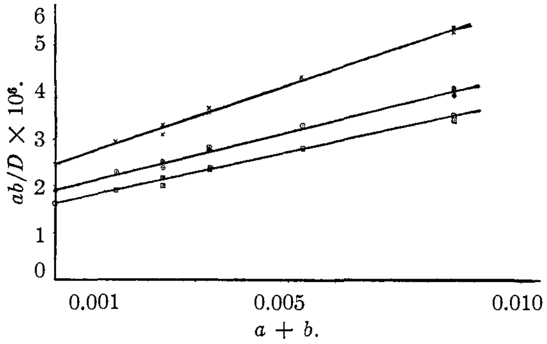

Fig. 2.—Upper curve, λ = 5000 Å., middle curve λ = 4800 Å., lower curve λ = 4600 Å.

[6a] The higher terms of this series do not converge rapidly, so that some care is required to be sure that this approximation is justified in any given case. Here it is accurate within less than 1% which is less than the error arising from other causes.

TABLE I

(Fe^{+++}), a	(SCN$^-$), b	4000 Å. T	4000 Å. D	4000 Å. $ab/D \times 10^6$	4200 Å. T	4200 Å. D	4200 Å. $ab/D \times 10^6$	4400 Å. T	4400 Å. D	4400 Å. $ab/D \times 10^6$	4500 Å. T	4500 Å. D	4500 Å. $ab/D \times 10^6$
0.001	0.0003	0.741	0.0998	3.00	0.655	0.1408	2.13	0.618	0.1601	1.874	0.615	0.1617	1.855
.002	.0003	.556	.1953	3.07	.451	.265	2.264	.401	.304	1.974	.399	.306	1.970
.002	.0003	.581	.1807	3.32	.481	.2435	2.463	.428	.282	2.127	.425	.2845	2.108
.003	.0003	.471	.2505	3.59	.361	.339	2.655	.308	.3915	2.298	.306	.394	2.284
.003	.0003	.478	.245	3.67	.369	.332	2.711	.315	.384	2.343	.313	.386	2.331
.005	.0003	.344	.355	4.225	.241	.474	3.163	.191	.551	2.721	.190	.5529	2.711
.008	.0003	.250	.460	5.22	.153	.624	3.845	.115	.720	3.333	.113	.725	3.310
.008	.0003	.258	.451	5.32	.160	.610	3.933	.120	.705	3.404	.119	.7075	3.392

(Fe^{+++}), a	(SCN$^-$), b	4600 Å. T	4600 Å. D	4600 Å. $ab/D \times 10^6$	4800 Å. T	4800 Å. D	4800 Å. $ab/D \times 10^6$	5000 Å. T	5000 Å. D	5000 Å. $ab/D \times 10^6$
0.001	0.0003	0.624	0.1570	1.91	0.670	0.1332	2.252	0.736	0.1020	2.94
.002	.0003	.407	.299	2.01	.466	.254	2.362	.561	.1922	3.12
.002	.0003	.434	.277	2.17	.491	.237	2.531	.580	.1812	3.31
.003	.0003	.316	.3833	2.35	.375	.326	2.760	.471	.2500	3.59
.003	.0003	.323	.376	2.39	.381	.321	2.804	.477	.247	3.64
.005	.0003	.200	.535	2.805	.252	.458	3.273	.351	.348	4.31
.008	.0003	.120	.703	3.414	.161	.608	3.945	.254	.456	5.26
.008	.0003	.125	.692	3.47	.171	.5875	4.085	.260	.448	5.35

λ	β	$\frac{1}{K_1}$
4000	3003	0.007485
4200	3981	.007225
4400	4642	.007349
4500	4685	.007402
4600	4512	.007276
4800	3914	.007452
5000	2920	.007207
	Average $1/K_1$ =	.007342 ± .000101
5400	1326	
5800	465	
6200	156	
6600	60	
8000	28	

the values found for $1/K_1$, and that the average is 0.007342, the root-mean-square deviation being 0.000102, or 1.39%. This corresponds to K_1 = 136.2 ± 1.9. β is seen to reach a maximum value of about 4700 at a wave length which seems to lie between 4450 and 4500 Å. The absorption spectrum of FeSCN^{++} is plotted in Fig. 3. It should be accurate to about 2%, and has been extended to long wave lengths on the basis of additional measurements not listed in Table I.

Discussion

The fact that the positive and negative deviations from the mean value of $1/K_1$ which are found in Table I fall about equally at both ends of the wave length range can be taken as internal evidence that the data are not vitiated by fading. This follows from the fact that the readings were always taken in order beginning at the shorter wave lengths. Had there been a trend toward larger $1/K_1$ for longer wave lengths this would have suggested that SCN$^-$ was being destroyed in significant amounts during the time involved in taking readings. This is seen not to be the case.

Figure 2 shows that the pattern of scattering of the points, consisting principally of failure of "duplicate" experiments to give identical results, is accurately repeated in the plots for different wave lengths. This suggests that the optical measurements are more accurate than the over-all precision of the experiments. This effect could result from errors in pipetting, but we attribute it instead to slight differences in temperature on the different days when the experiments were performed. The spectrophotometer was not adapted to thermostating, and the necessity was not at first apprehended of paying careful attention to the temperature. It is possible to make a rough estimate of the temperature dependence of (1) molal entropies of the ions involved.[7,8] It seems likely that ΔS for (1) is positive by at least 30 E. U. This would correspond to an increase in K_1 of the order of per cent. per degree rise in temperature. Small changes in temperature could therefore account for the observed scattering.

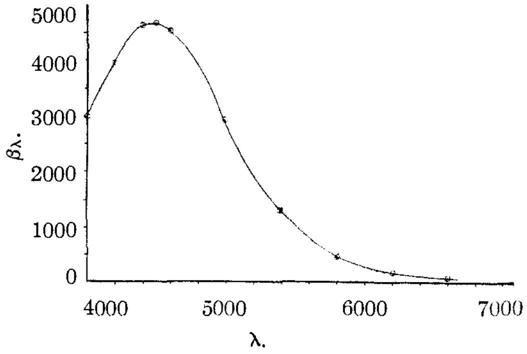

Fig. 3.—Absorption spectrum of FeSCN^{++}. β_λ is the molal extinction coefficient.

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[7] W. M. Latimer, K. S. Pitzer and W. V. Smith, THIS JOURNAL, **60**, 1829 (1938).

[8] *Cf.* discussion given by Rabinowitch and Stockmayer.[5]

Hydrolysis.—The effect on the observed value of K_1 produced by hydrolysis of Fe^{+++} can be investigated by writing

$$Fe^{+++} + H_2O = FeOH^{++} + H^+;\ K = K_h \quad (8)$$

and considering (8) and (1) as coexisting in the same solution. It is not difficult to show that equations (3) to (7) still hold in this case if $K' = K_1(1 + K_h/(H^+))^{-1}$ is substituted for K_1. This is true so long as (H^+) is sensibly constant throughout the series of experiments, as was the case here. The value obtained above is therefore for K' and the corrected value of K_1 can be obtained by multiplying by $(1 + K_h/(H^+))$. Using Bray and Hershey's[9] figure 6×10^{-3} for K_h and $(H^+) = 0.50$, this makes $K_1 = 1.012\,K'$, or 138.0; $1/K_1 = 0.00725$. Because of the small percentage effect of the hydrolysis correction we have not made the second order correction of considering the effect of ionic strength on K_h. In work of great precision this should, of course, be made.

Ionic Strength.—The effect of ionic strength is shown by one set of experiments ($HClO_4$) made constant at 0.116. For these, μ was 0.128, and $1/K_1$ corrected for hydrolysis, was found to be 0.00423, or $K_1 = 236.5$. The value of K_1 obtained by Edmonds and Birnbaum[3] for $\mu = 1.0$ can also be used here. Corrected for hydrolysis, this equals 127.3. These two values, with our corrected one for $\mu = 0.50$, are plotted in Fig. 4 with a solid line drawn so as to make the limiting slope of log K_1 *vs.* $\sqrt{\mu}$ equal to 3.054.[5,9] The three points are seen to be entirely compatible with current theory of the effect of ionic strength on log K_1, and to suggest a value of 2.95 for log K_1 at zero ionic strength, corresponding to a value of 891 for K_1^0 or 0.00122 for $1/K_1^0$.

Thiocyanate–Chloride Mixtures.—The curve of Fig. 4 and the constants obtained by Rabinowitch and Stockmayer[5] for the Fe^{+++}–Cl^- equilibria may be used to calculate values of ($FeSCN^{++}$) in various solutions measured by Møller.[1] The method is to assume that since the concentration of SCN^- is vanishingly small the actual concentration of Fe^{+++} can be calculated from the stoichiometric (Fe^{+++}) and (Cl^-) and the Rabinowitch and Stockmayer constants appropriate to the ionic strength of the solution. (It is found that the third complex has a negligible effect in these solutions if Rabinowitch and Stockmayer's constants are correct, but that it is important to take the second into account.) This "true" value of (Fe^{+++}) is then used with (SCN^-) and a value of K_1 taken from Fig. 4 to get a "true" value of x. When this is multiplied by β_{4700} interpolated from Fig. 3 a value of the optical density is obtained which can be compared with that reported by Møller for the solution. When this is done it is found, as shown in Table II, that Møller's values for D are greater than the calculated ones especially in the more dilute solutions where the calculation should, in principle, be best. One explanation which suggests itself is that the temperature in the Copenhagen laboratory was higher than the Berkeley and Cambridge temperatures. Another could be sought in terms of possible inaccuracy in the lower end of the curve of Fig. 4 and/or a corresponding inaccuracy in the curve given by Rabinowitch and Stockmayer for the chloride system. A third, rather attractive, hypothesis is that advanced by Rabinowitch and Stockmayer to account for the discrepancy between their value for the first chloride constant and that obtained by Bent and French. This is that a mixed complex, $FeCl(SCN)^+$ is formed and that it is more highly colored than $FeSCN^{++}$. The existence of such a complex might account for the present results. The possibility cannot be excluded, however, that the principle of the ionic strength may not be strictly applicable to these mixtures, and that specific influences are at work, which falsify our implied assumptions regarding activity coefficients. Further experiments on such systems should be worth while.

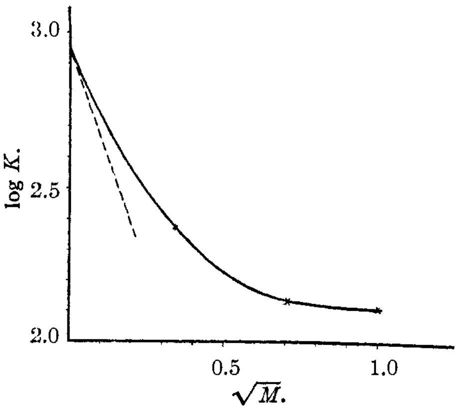

Fig. 4.—Dependence of K_1 on ionic strength in $HClO_4$ solutions.

TABLE II

Møller, ref. 1, p. 47

K_0 is Møller's value for the (fictitious) molal extinction coefficient of potassium thiocyanate in the solution, at $\lambda = 4700$.

Case	HCl, M	$FeCl_3$, M	KSCN, M $\times 10^5$	μ	K_0	$D_{obs.}$	$D_{calcd.}$
1	0.108	0.1076	5.13	0.754	3616	0.185	0.179
2	.106	.0807	5.13	.590	3610	.185	.174
3	.104	.0538	5.13	.427	3420	.175	.167
4	.102	.0269	5.13	.263	3216	.165	.147
5	.102	.0100	5.13	.162	2520	.129	.107

Higher Complexes.—The result found in Fig. 1, that at high SCN^- concentrations higher complexes appear, should be studied further. We performed numerous experiments with this in view, intending to subtract out the effect of the 1–1 complex and study the concentration dependence of the "excess" optical density. We found that the uncertainty in our value of K_1 was too great to

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[9] W. C. Bray and A. V. Hershey, THIS JOURNAL, 56, 1889 (1934).

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

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

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.

RECEIVED SEPTEMBER 3, 1946

[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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[1] Present address: The Sprague Electric Company, North Adams, Mass.

[2] Present address: Massachusetts Institute of Technology, Cambridge, Mass.

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