

Thermal Determination of the Kinetics of the Iron(III)–Tin(II) Redox Reaction in Chloride Solution

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From a temperature against time curve measured when a chemical reaction occurs in a batch reactor immersed in a constant temperature environment, it is possible to calculate both the rate constant and the enthalpy of a single reaction. This technique has been applied to the iron(III)–tin(II) redox reaction in chloride solution, studied over a twenty-fold variation in non-complexed chloride concentration and over a 50 K temperature range. Over this range of conditions the pseudo-second order rate constant for the reaction varied by a thousand-fold. Heats of reaction were also calculated.

The experimental results obtained at 298 K agree with those of Duke and Pinkerton and support the finding that the rate-determining step involves chloro-complexes of the stannous and ferric ions. However, results at different temperatures indicate that rate-determining electron transfer occurs *in* precursor complexes of the tin(II), iron(III) and chloride ions rather than *between* iron(III) and tin(II) chloride complexes as suggested by Duke and Pinkerton. There is a common precursor complex for a given number of chloride ions. Furthermore, the enthalpies of activation of the electron transfer reaction in the precursor complexes are all the same and the different rate constants for electron transfer in each precursor complex is determined by the charge on the precursor complex.

The temperature against time history of a chemical reaction in a temperature-controlled environment contains a great deal of information about the nature of the reaction. Various methods have been developed to extract the kinetic and thermodynamic parameters of the reaction from temperature-time curves. Experimental techniques commonly used are flow reactors,¹⁻⁴ adiabatic calorimeters,⁵⁻⁸ differential thermal analysis,^{9, 10} and Peltier cooling.¹¹ All these approaches involve either complicated experimental apparatus or the evaluation of the kinetic parameters from a limited number of data points on the (temperature, time) curve. Simple experimentation at the expense of fairly complex data analysis has been achieved by Becker and Maelicke,¹² using an analogue computer, and by Williams and Glasser,¹³ using a digital computer. Scott, Williams and Glasser¹⁴ have recently developed an experimentally and computationally simple but accurate technique for obtaining kinetic and thermodynamic parameters from temperature against time curves.

In this work the techniques developed by Williams and Glasser and Scott, Williams and Glasser have been extended to the study of the electron transfer reaction between ferric and stannous ions in chloride ion solution. The iron(III)–tin(II) redox reaction has been studied by many investigators.¹⁵⁻²² Duke and Pinkerton have argued that their and previous kinetic results may be interpreted in terms of the rate of electron transfer between the various iron(III) and tin(II) chloride complexes, which exist in chloride ion solution. This gives rise to a rate expression which is a polynomial in the free chloride ion concentration. A study, by the same investigators of the rate of reaction in bromide and iodide solutions, appeared to indicate

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that electron transfer between tin(II) and iron(III) halide complexes was the rate-determining step of the reaction.

THEORETICAL

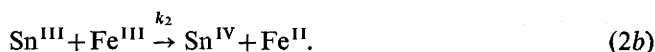
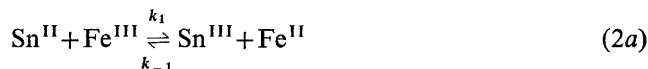
One can describe a reaction occurring in a stirred vessel, contained in an isothermal environment, by

$$H \frac{dx}{dt} - U_A(T - T_S) = MC_p \frac{dT}{dt} \quad (1)$$

where T is the temperature (K) of reactor contents; t the time (min); H the heat of reaction related to extent ($\text{cal mol}^{-1} \text{dm}^3$); x the extent of reaction (mol dm^{-3}); MC_p the heat capacity of reactor plus contents (cal K^{-1}); T_S the steady state temperature (K) of reactor (not equal to the temperature of the environment because of the heat generated by the stirrer); U_A the heat transfer coefficient for heat transfer between reactor and surroundings ($\text{cal min}^{-1} \text{K}^{-1}$).

Under conditions where $U_A(T - T_S)$ is of the same order of magnitude as Hdx/dt , Williams and Glasser¹³ have shown that a non-linear regression analysis on the differential eqn (1) can be used in order to obtain the kinetic and thermodynamic parameters of the reaction. When $U_A(T - T_S) \ll Hdx/dt$, Scott, Williams and Glasser¹⁴ have shown that the adiabatic (temperature, time) curve of the reaction is easily obtained from the real (temperature, time) curve, allowing the kinetic parameters to be obtained from the equivalent of classical (concentration, time) plots.

Duke and Pinkerton have shown that the iron(III)-tin(II) redox reaction in chloride ion solution is first order in the ferric and stannous ion concentrations, respectively. Wetton and Higginson²³ have shown that the iron(III)-tin(II) redox reaction occurs in two steps, namely



Eqn (2a) is the rate-determining step. Under the conditions employed here and by Duke and Pinkerton, only the forward reaction in eqn (2a) is kinetically significant. Using Duke and Pinkerton's notation we have

$$dx/dt = k'(a-x)(2b-x) \quad (3)$$

where a is the initial iron(III) concentration (mol dm^{-3}); b the initial stannous concentration (mol dm^{-3}); x the iron(III) ion concentration (mol dm^{-3}), at any time; k' the second order rate constant ($\text{dm}^3 \text{mol}^{-1} \text{min}^{-1}$).

It can be shown that k' is a negligible function of temperature over the temperature range ($\leq 0.1 \text{ K}$) of each experiment. This result enables us to obtain an analytical solution to eqn (1). Depending on the value of $U_A(T - T_S)$ relative to Hdx/dt we can obtain the parameters H and k' from the reaction (temperature, time) curve, either by non-linear regression or by simple graphical plots. Details of the analyses of (temperature, time) data, standard deviations and typical U_A values are given in ref. (13) and (14).

EXPERIMENTAL

APPARATUS AND METHOD

The reactions studied were carried out either in a 200 cm³ round-bottomed polythene flask (large heat transfer coefficient) or in a 500 cm³ thermos flask (small heat transfer coefficient). Experimental details are given in ref. (13) and (14).

REAGENTS

All reagents were AnalaR grade. A stock of iron(III) perchlorate was prepared by dissolving iron wire in an excess of HClO_4 and oxidising the iron(II) to iron(III) with H_2O_2 . Excess H_2O_2 was decomposed by heating. Iron(III) was determined iodometrically. SnCl_2 solutions were prepared before each run and standardised against KIO_3 . Chloride ion was determined by titration with AgNO_3 .

All runs were carried out in 2 mol dm^{-3} acid at an ionic strength of 2 mol dm^{-3} (the reactant ions made a negligible contribution to the total ionic strength). HCl was used to adjust the chloride concentration and HClO_4 the ionic strength. The conditions of ionic strength and acidity used in this work were the same as those used by Duke and Pinkerton.

RESULTS

Kinetic studies at various non-complexed chloride ion concentrations and at various temperatures are recorded in table 1.

The range of non-complexed chloride ion concentrations at which runs were carried out varies from 0.05 to 1.0 mol dm^{-3} . Rates have been measured at each free chloride ion concentration for approximately a 45 K temperature range. The

TABLE 1

$[\text{Fe}^{3+}] / \text{mol dm}^{-3}$	$[\text{Sn}^{2+}] / \text{mol dm}^{-3}$	free $[\text{Cl}^-] / \text{mol dm}^{-3}$	$k^1 / \text{mol}^{-1} \text{ dm}^3 \text{ min}^{-1}$	$\Delta H / \text{cal mol}^{-1}$	temp./K
0.046 6	0.085 1	0.188	8.37	10 800	298.1
0.044 2	0.085 2	0.183	7.05	11 200	298.0
0.049 2	0.044 4	0.166	5.07	10 500	297.2
0.052 6	0.044 6	0.173	5.66	9 900	297.4
0.043 9	0.066 8	0.170	5.48	10 200	297.8
0.044 6	0.067 5	0.172	5.64	10 400	297.8
0.037 2	0.067 4	0.157	4.32	10 500	297.6
0.037 7	0.055 8	0.150	4.02	10 200	298.1
0.035 6	0.056 0	0.146	3.70	10 100	298.0
0.032 8	0.078 4	0.156	4.92	9 800	298.0
0.029 6	0.078 4	0.150	4.08	9 700	298.0
0.001 38	0.020 9	0.518	86.4	9 800	298.7
0.001 37	0.020 7	0.476	66.0	10 100	298.9
0.000 834	0.009 47	0.993	290.0	10 300 $\frac{1}{2}$	298.1
0.001 22	0.015 0	1.00	5.94	12 200	264.4
0.047 5	0.000 979	0.463	5.5	10 600	276.5
0.047 8	0.000 926	0.944	25.8	10 300	276.1
0.044 7	0.001 94	0.945	24.3	10 400	275.6
0.001 55	0.021 6	0.958	28.8	11 700	276.8
0.410	0.043 7	0.161	2.74	10 600	292.6
0.048 6	0.043 7	0.161	9.81	10 100	302.6
0.049 6	0.043 8	0.161	17.7	9 500	307.9
0.000 712	0.010 0	0.492	300.0	9 000	312.4
0.000 873	0.010 0	0.155	73.0	9,800	323.5
0.044 8	0.001 00	0.057 1	5.5	9 500	321.9
0.054 5	0.001 00	0.054 5	4.98	10 100	321.3
0.000 488	0.010 0	0.061 2	58.5	—	345.1

initial free chloride concentrations were calculated using complexing constants for the tin(II) and iron(III) chloride complexes.²⁴⁻²⁹ We used $K_{1f} = 3.8$; $K_{1f}K_{2f} = 4.94$; $K_{1f}K_{2f}K_{3f} = 0.198$ and $K_{1s} = 11.3$, $K_{1s}K_{2s} = 58.0$, $K_{1s}K_{2s}K_{3s} = 14.0$; $K_{1s}K_{2s}K_{3s}K_{4s} = 14.0$ at 298 K, which are the values used by Duke and Pinkerton.²² This was done to obtain results consistent with their work; these values do not differ significantly from others quoted in the literature.

Values of the complexing constants at temperatures other than 298 K were calculated using

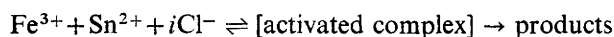
$$\begin{aligned}\Delta H_{1s} &= 2700 \text{ cal mol}^{-1}, \Delta H_{2s} = 300 \text{ cal mol}^{-1}, \\ \Delta H_{3s} &= 1700 \text{ cal mol}^{-1}, \Delta H_{1f} = 3600 \text{ cal mol}^{-1}.\end{aligned}\quad 28, 29$$

We have assumed that these heats of complexing do not vary significantly over the temperature range studied. From table 1 it is evident that rate constants under similar conditions could be determined with a precision of $\pm 5\%$. Also quoted in table 1 are the measured heats of reaction (ΔH) for each run. Apart from three, all of these heats of reaction lie within the estimated experimental error ($\pm 0.9 \text{ kcal mol}^{-1}$) of their mean (mean $\Delta H = 10\,300 \text{ kcal mol}^{-1}$). The rate constant and the heat of reaction were independently evaluated from each (temperature, time) curve.¹⁴

Semi-quantitative complexing experiments in our apparatus indicated that heats of chloride complexing of products and reactants are small and tend to cancel. This is confirmed by the small values of the known heats of complexing given above. The values tabulated are, therefore, approximately the heats of reaction of the electron transfer process.

DISCUSSION

Following Duke and Pinkerton, a plot of the rate constant k' against the concentration of the non-complexed chloride ion concentration indicated (i) a polynomial dependence of the rate on chloride concentration and (ii) that the rate in the absence of chloride is extremely slow, as previously shown by Gorin.¹⁹ Furthermore, under the conditions of high acidity (2 mol dm^{-3}) employed during all kinetic runs, any possible contribution to the rate by hydrolysed ferric or stannous species is negligible.¹⁹ A simplified mechanism of the reaction can therefore be postulated in terms of a series of parallel reactions.



in which $i = 1, 2, 3 \dots$

The rate equation consistent with this mechanism can be written as

$$\text{rate} = \sum_i k_i [\text{Fe}^{3+}][\text{Sn}^{2+}][\text{Cl}^-]^i \quad (4)$$

Expressing the concentrations of the uncomplexed Fe^{3+} and Sn^{2+} ions in terms of the experimentally measured total iron(III) and tin(II) concentrations, the stability constants of the various known chloro-complexes and the free chloride ion concentration, the following expression can be derived for the rate of reaction.

$$\frac{dx}{dt} = \frac{1}{2} \frac{(a-x)(2b-x)}{F(c)S(c)} [k_1c + k_2c^2 + k_3c^3 + \dots] \quad (5)$$

where c is the free chloride ion concentration and $F(c)$ and $S(c)$ are known polynomials in the free chloride ion concentration.

$$F(c) = 1 + K_{1f}c + K_{1f}K_{2f}c^2 + K_{1f}K_{2f}K_{3f}c^3 + \dots$$

$$S(c) = 1 + K_{1s}c + K_{1s}K_{2s}c^2 + K_{1s}K_{2s}K_{3s}c^3 + \dots$$

where

$$K_{ns} = \frac{[\text{SnCl}_n^{2-n}]}{[\text{SnCl}_{n-1}^{2-n+1}][\text{Cl}^-]}$$

and

$$K_{mf} = \frac{[\text{FeCl}_m^{3-m}]}{[\text{FeCl}_{m-1}^{3-m+1}][\text{Cl}^-]}$$

This form of the rate equation is identical to that used by Duke and Pinkerton who, however, considered that only the terms involving third and higher powers of the chloride ion concentration are kinetically significant and graphically estimated the parameters k_3 , k_4 , k_5 and k_6 at 298 K (table 2).

TABLE 2

	$\frac{k_i}{a} \text{ mol}^{-i-1} \text{ min}^{-1} (\text{dm}^3)^{i+1} \text{ c}^{-b}$	$\frac{\Delta S_i^\ddagger}{\text{cal K mol}^{-1}}$	$\frac{\Delta H_i^\ddagger}{\text{cal mol}^{-1}}$
1			
2			
3	1.2×10^3	$4.5 \pm 0.08 \times 10^3$	34.0
4	7.2×10^4	$5.0 \pm 0.3 \times 10^4$	38.8
5	0	$2.4 \pm 0.3 \times 10^5$	42.1
6	2.7×10^5	$2.4 \pm 0.01 \times 10^5$	42.1
			25 000

^a Duke and Pinkerton's results; ^b present work (our results combined with Duke and Pinkerton's).

TABLE 3.—CROSS-CORRELATION COEFFICIENTS

	k_3	k_4	k_5	k_6
k_3	1	0.88	0.59	0.21
k_4		1	0.85	0.42
k_5			1	0.78
k_6				1

From eqn (3) and (5), the observed second-order rate constant k' can be written in terms of the free chloride ion concentration:

$$k' = \frac{(k_1c + k_2c^2 + k_3c^3 + \dots)}{F(c)S(c)}$$

In this work the set of all available k' values (ours and Duke and Pinkerton's) were used to regress for the parameters k_3 , k_4 , k_5 , k_6 . A weighted sum of squared errors was used in the regression analysis. Each difference was weighted by the experimental k' value. This procedure is based on the assumption that the error in the measurement of a rate constant is approximately proportional to its value and gives equal weight to each measurement. The assumption agrees with our experimental findings. Over the concentration range studied, there is insufficient information to obtain values for k_1 and k_2 and the value of k_6 is probably not very accurate. Values of k_3 , k_4 , k_5 and k_6 are listed in table 2, together with their respective standard deviations. Table 3 contains the correlation coefficient matrix of the k_i values.

Fig. 1 represents a plot of $\log_{10} k'$ against c at 298 K (due to the thousandfold variation in k' over the range of c values, a plot of k' against c is not practicable). The solid line represents the variation of $\log k'$ with c , predicted by eqn (4) using the values of k_3 , k_4 , k_5 , k_6 listed in table 2. Regression on Duke and Pinkerton's data alone gave very similar values for k_3 to k_6 .

The value of $k_5 = 0$ obtained by Duke and Pinkerton is inconsistent with the proposed mechanism of the reaction, since there is no apparent reason why activated complexes containing five chloride ions in total should not contribute to the reaction rate, when all other combinations involving two to six chloride ions in total do

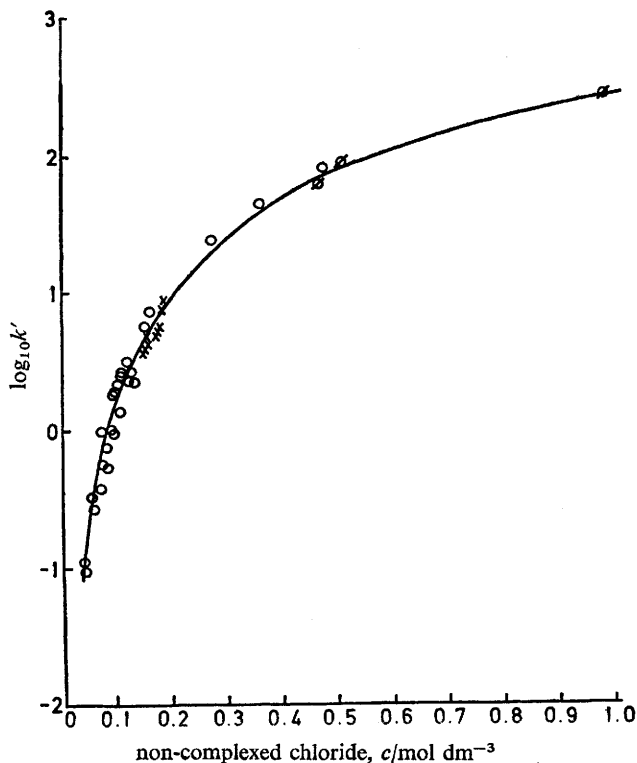


FIG. 1.—Rate constant at 298 K plotted against non-complexed chloride concentration. —, regressed curve; O, Duke and Pinkerton; X ϕ , this work

contribute to the overall rate of reaction. Indeed, the value of k_5 obtained from our regression analysis indicates that activated complexes involving five chloride ions make a major contribution to the reaction rate in the concentration range studied. Inspection of table 2 shows that, with the exception of k_5 , the parameters obtained by Duke and Pinkerton and those obtained in this work, are in reasonable agreement.

Arrhenius plots of the function

$$k'F(c)S(c) = (k_1c + k_2c^2 + k_3c^3 + \dots)$$

against $1/T$ for various free chloride ion concentrations are shown in fig. 2. The lines are (i) both straight and (ii) parallel to a high degree of precision over a range of conditions such that the rate constant varies by some three orders of magnitude. Since it has been shown that the reaction paths associated with k_3 , k_4 , k_5 and k_6 all contribute to a greater or lesser extent to the overall rate, depending on the chloride concentration, it follows that the only reasonable rationalization of the data in fig. 2 is that the constants k_i all have the same temperature dependence, i.e., all these steps have the same enthalpy of activation (ΔH^\ddagger). It may therefore be

concluded that the large variation in rate with free chloride ion concentration must be due to differences in the entropies of activation (ΔS_i^\ddagger) of the various steps.

Using the value of ΔH^\ddagger obtained from the slope of the lines in fig. 2, it is possible to calculate values for ΔS_i^\ddagger from the k_i values in table 2. Examination of these values for ΔS_i^\ddagger (table 2) shows that ΔS_i^\ddagger increases with decreasing positive charge on the activated complex. At first glance, it may appear that the value for ΔS_6^\ddagger does not conform with this trend. ΔS_6^\ddagger , however, refers to an activated complex

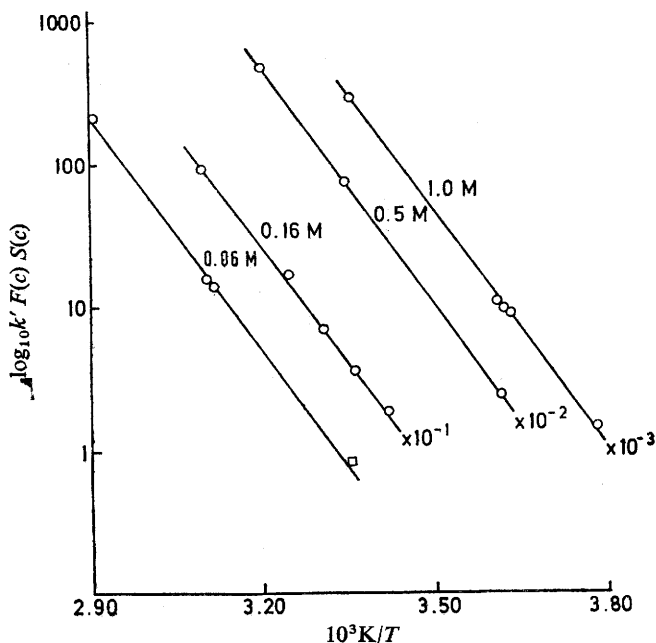
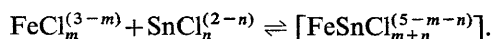


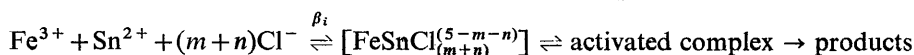
FIG. 2.—Arrhenius plots over a range of non-complexed chloride concentrations. □, interpolated from fig. 1. (M \equiv mol dm $^{-3}$.)

with a net negative charge and there are various reasons, e.g., different solvation effects, why ΔS_6^\ddagger need not necessarily follow the same approximately linear relationship as those ΔS^\ddagger values referring to positively charged activated complexes. These observations support the results of Newton and Rabideau³⁰ and Higginson *et al.*,³¹ who found that a similar linear relationship existed between the charge on the activated complex and its entropy for electron-transfer reactions of the actinide elements and for certain isotopic electron exchange reactions.

While the above mechanism is consistent with the experimental findings, it does not account for the fact that reaction must, as pointed out by Duke and Pinkerton, take place between the various chloro-complexes of iron(III) and tin(II). However, in addition, it is now suggested that reaction occurs through a precursor complex formed from the various chloro-complexes as follows



If it is assumed that the precursor complex is in pseudo-equilibrium with the ions constituting it, then the reaction mechanism can be simply written as



where β_i is a cumulative stability constant. A condition for the validity of this approach is that rate of exchange of chloride ions with the precursor complex must necessarily be faster than the rate of electron transfer. This is undoubtedly true for the highly labile tin(III) ion while the known rate of exchange of chloride with the monchloroiron(III) complex³² suggests that it is probably also true for exchange with the higher complexes of iron(III) and hence also for the precursor complex.³³

Comparison of this reaction mechanism with eqn (4), shows that $k_i = \beta_i k_i^*$ where k_i^* is now the rate constant for electron-transfer within the precursor complex. Since it has been shown that the charge on the activated complex is the major factor determining the entropy of activation, it is, therefore, reasonable to assign ΔS^\ddagger (or the major part of it) to the entropy of formation of the precursor complex. Consideration of the re-organisation required to form the activated complexes from their precursor complexes suggests that this is probably both small and relatively independent of the number of chloride ions in the complex. In addition, it was found that the enthalpies of activation for the various paths are identical. This can only be explained in terms of (i) compensating variations in the temperature dependencies of β_i and k^* or (ii) a predominating temperature dependence of either β_i or k_i^* . However, the enthalpies of formation of the various chloro-complexes of iron(III) and tin(II) are known to be small, i.e., less than 3.6 kcal mol⁻¹ and it can be assumed that the enthalpies of formation of the precursor complexes will be equally small. Under these conditions, the observed constant enthalpy of activation can be assigned to that for electron transfer within the various precursor complexes. Electron (or atom)-transfer *within* a chloride-bridged complex can reasonably be conceived as occurring at a rate which is not strongly dependent on the number of non-bridging chloride ions.

Duke and Pinkerton have shown that the rate of the ferric-stannous redox reaction increases by a factor of $\sim 10^3$ in going from chloride to bromide to iodide ion respectively. Since the strength of the halide bonds to both iron(III) and tin(II) ions exhibit the reverse order, i.e., $I^- < Br^- < Cl^-$, the rate dependence on the nature of the halide ion is interpreted as implying that the rate controlling step of the reaction is the ease of electron transfer within a precursor complex.

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