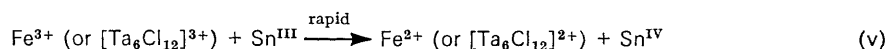
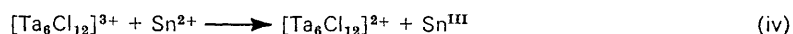
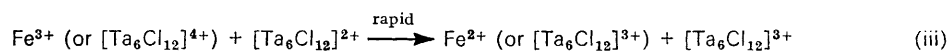
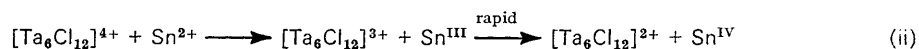


Catalysis by Dodeca- μ -chloro-*octahedro*-hexatantalum(3+) Ion of the Oxidation of Tin(II) by Iron(III) in Aqueous Solution

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Rate constants have been obtained for the reaction $\text{Fe}^{3+} + [\text{Ta}_6\text{Cl}_{12}]^{3+} \longrightarrow \text{Fe}^{2+} + [\text{Ta}_6\text{Cl}_{12}]^{4+}$ and its reverse, and for the reduction of $[\text{Ta}_6\text{Cl}_{12}]^{3+}$ and of $[\text{Ta}_6\text{Cl}_{12}]^{4+}$ by Sn^{2+} . The results make possible an interpretation of the catalysis of the reaction $2\text{Fe}^{3+} + \text{Sn}^{2+} \longrightarrow 2\text{Fe}^{2+} + \text{Sn}^{\text{IV}}$ by $[\text{Ta}_6\text{Cl}_{12}]^{3+}$ in aqueous solutions at 25 °C, $[\text{H}^+] = 0.50 \text{ mol dm}^{-3}$, $[\text{Cl}^-] \approx 0.04 \text{ mol dm}^{-3}$, and $I = 1.1 \text{ mol dm}^{-3}$ ($\text{Na}[\text{ClO}_4]$). The dominant path of catalysis at low iron(II) concentrations is as in (i)–(iii). At higher iron(II) concentrations there is a proportionately greater contribution from other reactions, including (iv) and (v).



THE reaction $2\text{Fe}^{3+} + \text{Sn}^{2+} \longrightarrow 2\text{Fe}^{2+} + \text{Sn}^{\text{IV}}$ occurs very slowly with perchlorate as the sole anion,¹ but is more rapid in the presence of chloride ions.² It is probable³ that the major route involves the reactions $\text{Fe}^{3+} + \text{Sn}^{2+} \rightleftharpoons \text{Fe}^{2+} + \text{Sn}^{\text{III}}$ and $\text{Fe}^{3+} + \text{Sn}^{\text{III}} \longrightarrow \text{Fe}^{2+} + \text{Sn}^{\text{IV}}$. This system is an example of a non-complementary redox reaction,⁴ in which the preferred change in oxidation state of an oxidant does not match that for the reductant with which it is reacting. The work reported in the present paper is part of a general investigation of the activity of water-soluble cluster ions as catalysts for various types of reaction. It was thought that several factors might be favourable to strong catalytic activity. These include the ease of conversion of $[\text{Ta}_6\text{Cl}_{12}]^{3+}$ into higher and lower charged states, the relations between the reduction potentials involving these states and the reduction potentials of the iron(III) + iron(II) and tin(IV) + tin(II) couples, and the

possibility of a complementary reaction involving a two-equivalent change between $[\text{Ta}_6\text{Cl}_{12}]^{4+}$ and tin(II).

Under our conditions of reaction, the dominant forms of the several metal ions are Fe^{3+} , Fe^{2+} , and Sn^{2+} , and hence we use these symbols in equations, although the species $[\text{FeCl}]^{2+}$ and $[\text{SnCl}]^+$ are also present in substantial proportions. The forms of tin(III) and tin(IV) are uncertain, and hence we use Sn^{III} and Sn^{IV} . The formulae adopted for the cluster ions are those of the basic skeleton of metal atoms and bridging chlorine atoms.

RESULTS

Preliminary Experiments.—The addition of $[\text{Ta}_6\text{Cl}_{12}]^{2+}$ (to give a final concentration of *ca.* $10^{-4} \text{ mol dm}^{-3}$) to mixtures of Fe^{3+} and an excess of Sn^{2+} in dilute perchloric acid increased their rate of reaction greatly. In these and subsequent experiments, the progress of the reaction was

¹ M. H. Gorin, *J. Amer. Chem. Soc.*, 1936, **58**, 1787.

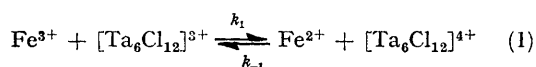
² F. R. Duke and R. C. Pinkerton, *J. Amer. Chem. Soc.*, 1951, **73**, 3045.

³ E. A. M. Wetton and W. C. E. Higginson, *J. Chem. Soc.*, 1965, 5890.

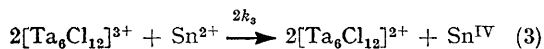
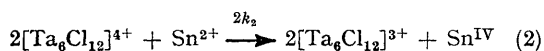
⁴ J. Halpern, *Quart. Rev.*, 1961, **15**, 207.

followed by spectrophotometric estimation of Fe^{III} in samples diluted with ammonium thiocyanate solution. The preliminary experiments showed that at 25.0 °C convenient rates for the catalysed reaction were obtained with *ca.* 0.04 mol dm⁻³ chloride and 0.50 mol dm⁻³ hydrogen ion. Both the catalysed and the uncatalysed reactions were accelerated by increasing the chloride concentration.

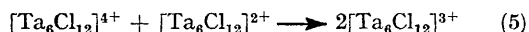
In further experiments, repeated spectrophotometric scans of part of a given reaction mixture were made in the range 600–850 nm where light absorption is due almost entirely to $[\text{Ta}_6\text{Cl}_{12}]$ species, while samples were taken from the remainder of the reaction mixture for iron(III) estimation. The spectra⁵ of the species $[\text{Ta}_6\text{Cl}_{12}]^{n+}$ ($n = 2-4$) are distinct in the range scanned, and showed that, on adding an excess of Sn^{2+} to a mixture of Fe^{3+} and $[\text{Ta}_6\text{Cl}_{12}]^{2+}$, the cluster was initially mainly in the 3+ form, but contained a small proportion (*ca.* 10%) of the 4+ ion. By the time (typically 10 min) half the Fe^{3+} had been reduced, the proportion of the 4+ cluster ion had fallen to <2%, and no further change in spectrum of the catalyst was observed as long as Fe^{3+} remained. When all the Fe^{3+} had been reduced (typically 130 min), slow but substantial changes in the spectrum occurred, consistent with the reduction of $[\text{Ta}_6\text{Cl}_{12}]^{3+}$ to $[\text{Ta}_6\text{Cl}_{12}]^{2+}$. This reduction required typically *ca.* 700 min for completion. The study of Espenson and McCarley,⁶ conducted under somewhat different conditions, showed that equilibrium (1) is attained relatively rapidly, compared with the rate of disappearance of Fe^{3+} observed in



our experiments, and that the value of $K_1 = k_1/k_{-1}$ is substantially less than unity. We therefore surmised that the catalysis of the $\text{Fe}^{3+} + \text{Sn}^{2+}$ reaction might involve (1), and that reactions (2) and (3) might be important. If



reaction (3) occurs, then (4) or (5) would be required; both these reactions have been studied previously⁵ and are likely



to proceed rapidly under our conditions. Following these conclusions we studied the relevant redox reactions of the cluster ions with Fe^{3+} , Fe^{2+} , and Sn^{2+} in order to see if their rates would provide a quantitative explanation for the kinetic behaviour of the $\text{Fe}^{3+} + \text{Sn}^{2+}$ reaction catalysed by $[\text{Ta}_6\text{Cl}_{12}]^{3+}$. Tin(IV) does not appear to undergo redox reactions with the cluster ions.

Rate Constants for Reaction (1).—The reactions in equation (1) have been studied previously and were shown to be first-order in the concentration of each reactant.⁵ Our experiments were made by stopped-flow spectrophotometry and yielded velocity constants valid for the conditions of the catalysis experiments. At 25.0 °C, 0.50 mol dm⁻³ H^+ , and ionic strength $I = 1.1$ mol dm⁻³ ($\text{Na}[\text{ClO}_4]$), we found $k_1 = 25.0 \pm 0.2$ and $k_{-1} = 720 \pm 20$ ($K_1 = 0.035 \pm 0.003$), for 0.030 mol dm⁻³ Cl^- , and $k_1 = 28.5 \pm 0.1$ dm³ mol⁻¹ s⁻¹ and $k_{-1} = 830 \pm 20$ dm³ mol⁻¹ s⁻¹ ($K_1 = 0.034 \pm 0.002$), for

⁵ J. H. Espenson and R. E. McCarley, *J. Amer. Chem. Soc.*, 1966, **88**, 1063.

0.040 mol dm⁻³ Cl^- . Initial concentrations were: for k_1 , 5.19×10^{-2} mol dm⁻³ Fe^{3+} , 8.1×10^{-5} mol dm⁻³ $[\text{Ta}_6\text{Cl}_{12}]^{3+}$; for k_{-1} , 5.19×10^{-3} mol dm⁻³ Fe^{2+} , 8.1×10^{-5} mol dm⁻³ $[\text{Ta}_6\text{Cl}_{12}]^{4+}$. In the measurement of k_1 , *ca.* 95% of the $[\text{Ta}_6\text{Cl}_{12}]^{3+}$ was converted into $[\text{Ta}_6\text{Cl}_{12}]^{4+}$. The values of K_1 were calculated from k_1 and k_{-1} ; similar values were obtained from spectrophotometric measurements of the position of equilibrium in equation (1), but these values were less precise.

Rate Constants for Reactions (2) and (3).—These reactions were studied by conventional spectrophotometry. The product of reaction (2), $[\text{Ta}_6\text{Cl}_{12}]^{3+}$, would be expected even if the reaction proceeds by a two-equivalent change giving $[\text{Ta}_6\text{Cl}_{12}]^{2+}$ as the immediate product, since reaction (5) is very rapid.⁵ With 4×10^{-5} – 1.2×10^{-4} mol dm⁻³ $[\text{Ta}_6\text{Cl}_{12}]^{4+}$ and 3.1×10^{-4} – 2.3×10^{-3} mol dm⁻³ Sn^{2+} , reaction (2) gave linear plots of $\log(D_\infty - D_t)$ against t over at least three half-lives, where D_∞ and D_t are the absorbance of the reaction mixture at the end of the reaction and at time t , respectively. The negative gradients of such plots were proportional to $[\text{Sn}^{2+}]$, and we conclude that the rate equation is (6). At 25.0 °C, 0.50 mol dm⁻³ H^+ , and $I =$

$$-d[\text{Ta}_6\text{Cl}_{12}^{4+}]/dt = 2k_2[\text{Ta}_6\text{Cl}_{12}^{4+}][\text{Sn}^{2+}] \quad (6)$$

1.1 mol dm⁻³ ($\text{Na}[\text{ClO}_4]$), $k_2 = 11.65 \pm 0.21$, 18.7 ± 0.6 , and 33.4 ± 1.3 dm³ mol⁻¹ s⁻¹ at 0.030, 0.040, and 0.130 mol dm⁻³ Cl^- , respectively.

The slow reduction of $[\text{Ta}_6\text{Cl}_{12}]^{3+}$ by Sn^{2+} was studied at 4×10^{-5} – 1.2×10^{-4} mol dm⁻³ $[\text{Ta}_6\text{Cl}_{12}]^{3+}$ and 2.33×10^{-3} – 2.44×10^{-2} mol dm⁻³ Sn^{2+} . Plots of $\log(D_\infty - D_t)$ against t showed initial curvature, the magnitude of the negative gradient decreasing with increase in t until *ca.* 30% completion of reaction; beyond this point the plots were linear for at least two half-lives. The gradients of the linear portions were proportional to $[\text{Sn}^{2+}]$, corresponding to the rate equation (7). At 25.0 °C, 0.50 mol dm⁻³ H^+ , and

$$-d[\text{Ta}_6\text{Cl}_{12}^{3+}]/dt = 2k_3[\text{Ta}_6\text{Cl}_{12}^{3+}][\text{Sn}^{2+}] \quad (7)$$

$I = 1.1$ mol dm⁻³ ($\text{Na}[\text{ClO}_4]$), the rate of reaction was unaffected by changes in $[\text{Cl}^-]$ from 0.030 to 0.130 mol dm⁻³, and we found $k_3 = (6.3 \pm 1.0) \times 10^{-3}$ dm³ mol⁻¹ s⁻¹. Similar experiments in the presence of Fe^{2+} or Sn^{IV} gave similar values of k_3 . However, experiments on the rate of this reaction were also made by using solutions in which the $[\text{Ta}_6\text{Cl}_{12}]^{3+}$ -catalysed reaction between an excess of Sn^{2+} and Fe^{3+} had previously occurred. In this system the relatively slow reduction of the cluster ion to $[\text{Ta}_6\text{Cl}_{12}]^{2+}$ by the excess of Sn^{2+} followed the main reaction. Values of $k_3 = \text{ca. } 16 \times 10^{-3}$ dm³ mol⁻¹ s⁻¹ were obtained in this way.

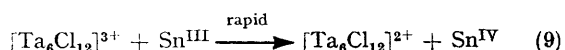
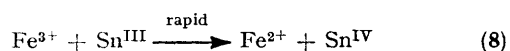
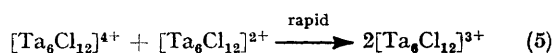
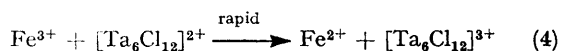
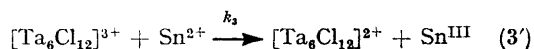
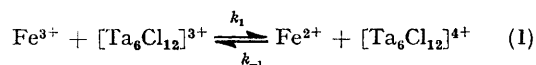
The initial curvature of the rate plots can be ascribed to a second reaction path involving formation of $[\text{Ta}_6\text{Cl}_{12}]^{4+}$ by the reverse of reaction (5), followed by reaction (2). As the overall reaction proceeds, the concentration of $[\text{Ta}_6\text{Cl}_{12}]^{4+}$ becomes kinetically insignificant before the bulk of the $[\text{Ta}_6\text{Cl}_{12}]^{3+}$ has been reduced, so that the direct path (3) occurs alone in the latter stages of the reaction. This conclusion is based on a quantitative comparison of the rate constants k_2 and k_3 , and takes into account the equilibrium constant for reaction (5) which is 5.7×10^4 under similar conditions⁶ to those of our experiments.

Catalysis by $[\text{Ta}_6\text{Cl}_{12}]^{3+}$ of the Oxidation of Sn^{2+} by Fe^{3+} .—The interpretation of the catalysis experiments has been attempted by assuming a probable mechanism in the light

⁶ N. E. Cooke, T. Kuwana, and J. H. Espenson, *Inorg. Chem.*, 1971, **10**, 1081.

of the preliminary experiments. It is then possible, with the aid of the rate constants obtained above, to calculate iron(III) concentrations at various times in catalysis experiments and to compare these with experimental values. Also, under certain concentration conditions, apparent rate constants can be extracted from the experimental results and compared with various appropriate combinations of the rate constants for separate steps.

The mechanism adopted is chosen from reactions (1)—



(5) and (8) and (9). Equations (2) and (3) refer to overall reactions involving more than one step, whereas (2') and (3') are the rate-determining first steps of these reactions; their rates are described by omitting the factors of two shown in the corresponding rate equations for the overall reactions, (6) and (7), respectively. This implies that reverse reactions corresponding to (2') and (3') are unimportant; there was no evidence for such reverse reactions in our studies of the overall reactions. The justification for regarding the first step of reaction (2) as the one-equivalent redox change (2'), rather than a two-equivalent change giving $[\text{Ta}_6\text{Cl}_{12}]^{2+}$ and Sn^{IV} directly, will be discussed later. Equations (4) and (5) are alternative routes for the oxidation of $[\text{Ta}_6\text{Cl}_{12}]^{2+}$ formed by the reduction of higher charged forms of the cluster ion. Taking into account the relative concentrations of Fe^{3+} and $[\text{Ta}_6\text{Cl}_{12}]^{4+}$ during a catalysis experiment, it is not clear which will predominate; although both reactions have been studied,⁵ a lower limit only has been obtained for reaction (5). Similarly, reactions (8) and (9) are alternatives, but their relative importance is unknown.

The rate equations corresponding to the four mechanisms which are obtained by choosing different combinations of the two sets of alternative reactions were all derived by making the stationary-state approximations $d[\text{Sn}^{\text{III}}]/dt = 0$, $d[\text{Ta}_6\text{Cl}_{12}^{2+}]/dt = 0$, and $d[\text{Ta}_6\text{Cl}_{12}^{4+}]/dt = 0$. The first two approximations are entirely justified, but our preliminary experiments showed that low concentrations of $[\text{Ta}_6\text{Cl}_{12}]^{4+}$ were present under the conditions of the catalysis. However, these concentrations did not exceed 2% of the initial concentration of Fe^{3+} . For the combinations (4) + (8), (4) + (9), and (5) + (8), the rate equations are identical, and are shown in equation (10) with the omission of the

$$-\frac{d[\text{Fe}^{3+}]}{dt} = \frac{2[\text{Ta}_6\text{Cl}_{12}][\text{Sn}^{2+}]\{k_1k_2[\text{Fe}^{3+}] + k_{-1}k_3[\text{Fe}^{2+}] + (2)k_2k_3[\text{Sn}^{2+}]\}}{k_1[\text{Fe}^{3+}] + k_{-1}[\text{Fe}^{2+}] + (2)k_2[\text{Sn}^{2+}]} \quad (10)$$

number 2 shown in parentheses before the terms $k_2k_3[\text{Sn}^{2+}]$

and $k_2[\text{Sn}^{2+}]$. Here $[\text{Ta}_6\text{Cl}_{12}]$ represents the total concentration of cluster ions, the bulk being in the 3+ form. If the correct combination is (5) and (9), the rate equation is (10) including both of the numbers 2 in parentheses. In this rate equation, no allowance is made for the uncatalysed reaction, the rate of which was shown to be negligible by experiments conducted in the absence of the catalyst; as we remark later, this may be an oversimplification. If the initial concentration of Fe^{2+} is comparable with that of Fe^{3+} and that of Sn^{2+} , the greater magnitude of k_{-1} compared with k_1 and k_2 enables the approximate rate equation (11)

$$-d[\text{Fe}^{3+}]/dt = (2k_2'[\text{Ta}_6\text{Cl}_{12}][\text{Sn}^{2+}][\text{Fe}^{3+}]/[\text{Fe}^{2+}] + 2k_3[\text{Ta}_6\text{Cl}_{12}][\text{Sn}^{2+}]) \quad (11)$$

to be advanced, with $k_2' = k_1k_2/k_{-1}$. Here the term in $[\text{Fe}^{3+}]/[\text{Fe}^{2+}]$ describes the catalytic route *via* equations (1), (2'), and (8) or (9), while the term independent of the iron concentrations describes the route *via* (3'), (4) or (5), and (8) or (9). Equation (11) can be integrated to give (12), where

$$\begin{aligned} &\frac{(b+d)}{(b-a)-f(b+d)} \ln[\text{Sn}^{2+}] - \\ &\frac{(a+d)/(1-f)}{(b-a)-f(b+d)} \ln\{(1-f)[\text{Fe}^{3+}] + f(a+d)\} \\ &= k_2'[\text{Ta}_6\text{Cl}_{12}]t + \text{constant} \quad (12) \end{aligned}$$

$a = [\text{Fe}^{3+}]_0$, $b = 2[\text{Sn}^{2+}]_0$, $d = [\text{Fe}^{2+}]_0$, zero subscripts indicating initial concentrations, and $f = k_3/k_2'$. The integration of the full equation (10) with the numbers 2 in parentheses omitted gives equation (13) where a , b , and d

$$A \ln\{(k_1k_2 - k_{-1}k_3)[\text{Fe}^{3+}] + k_2k_3[\text{Sn}^{2+}] + k_{-1}k_3(a+d)\} - B \ln[\text{Sn}^{2+}] = [\text{Ta}_6\text{Cl}_{12}]t + \text{constant} \quad (13)$$

have their previous significance, and A and B are combinations of rate constants and initial concentrations of reactants. A very similar equation to (13), referred to

$$A = \frac{k_1(k_2 - k_3)[\frac{1}{2}k_2(b-a) + k_{-1}(a+d)]}{[k_1k_2(b-a) - k_{-1}k_3(b+d)](k_{-1}k_3 - k_1k_2 - \frac{1}{2}k_2k_3)} \quad (14)$$

$$B = [k_1(b-a) - k_{-1}(b+d)]/[k_1k_2(b-a) - k_{-1}k_3(b+d)] \quad (15)$$

subsequently as the alternative form of (13), is obtained if the form of (10) including the numbers 2 in parentheses is integrated.

If equation (12) applies, it is possible to obtain k_2' by assuming a value of f and plotting the left-hand side against t . This was done for all the experiments in Table 1; these were at sufficiently high values of $[\text{Fe}^{2+}]_0$ for the approximations inherent in equations (11) and (12) to hold. If unduly large or small values of f were chosen, the plots were not linear, the smaller values giving plots which showed an increase in gradient with time, the larger values giving a decrease. Curvature of the plots could be detected for changes in f exceeding 10% of the value finally adopted for a given experiment. The values of k_2' and f shown in Table 1 were obtained in this way. The mean value obtained for k_2' is 0.71 ± 0.04 compared with $0.40 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ calculated from the values of k_1 , k_{-1} , and k_2 found in separate experiments. Values of f are mostly in the region of 0.10, corresponding to an experimental value of $k_3 = ca. 0.07 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, *ca.* 11 times larger than the value observed directly.

The experiments in Table 2 were at low values of $[\text{Fe}^{2+}]_0$,

and hence equation (12) can apply only in the latter stages of the reaction. Trials showed that by choosing an appropriate value of f , linear plots could be obtained for the part of the reaction for which $[\text{Fe}^{2+}] > 2[\text{Fe}^{3+}]$; curvature was always found in the earlier part of the reaction. Approximate values of k_2' could thus be obtained for 16 experiments

appropriate for $0.040 \text{ mol dm}^{-3} \text{ Cl}^-$. The values of k_3 obtained from f varied from experiment to experiment; they were larger than the value observed directly, but were usually somewhat smaller than those appearing in Table 2, which were obtained as described below.

The form of equation (13) is unsuitable for deriving values

TABLE 1

Values of k_2' for $[\text{Ta}_6\text{Cl}_{12}]^{3+}$ catalysis of the $\text{Fe}^{3+} + \text{Sn}^{2+}$ reaction obtained by using equation (11). $[\text{H}^+] = 0.50 \text{ mol dm}^{-3}$, $[\text{Cl}^-] = 0.030 \text{ mol dm}^{-3}$, $I = 1.1 \text{ mol dm}^{-3}$ ($\text{Na}[\text{ClO}_4]$), 25.0°C

$10^4[\text{Ta}_6\text{Cl}_{12}]^*$ mol dm^{-3}	$10^3[\text{Fe}^{3+}]_0$ mol dm^{-3}	$10^3[\text{Sn}^{2+}]_0$ mol dm^{-3}	$10^3[\text{Fe}^{2+}]_0$ mol dm^{-3}	k_2' $\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	f
4.18	2.58	2.10	19.6	0.69	0.08
	4.06	2.10	9.78	0.74	0.25
	4.36	2.10	19.6	0.73	0.13
	5.65	2.14	39.1	0.70	0.10
	8.63	2.10	9.78	0.76	0.13
	9.10	2.10	19.6	0.78	0.13
	3.94	4.20	9.78	0.66	0.13
	4.41	4.20	19.6	0.69	0.13
	4.93	6.30	19.6	0.66	0.08
	5.50	6.37	39.1	0.70	0.08
	3.49	2.52	11.3	0.69	0.07
	8.21	2.42	11.6	0.77	0.25
	8.85	2.53	20.3	0.73	0.08
	4.32	4.83	5.05	0.65	0.07
	4.00	4.83	10.8	0.71	0.10
	4.58	4.83	14.6	0.69	0.07
	4.03	5.05	20.1	0.73	0.07

* The stock solutions for the two different catalyst concentrations were separately prepared; the concentration given is that of the total tantalum cluster present, mainly in the form $[\text{Ta}_6\text{Cl}_{12}]^{3+}$.

TABLE 2

Agreement between t_{obs} and t_{calc} for $[\text{Ta}_6\text{Cl}_{12}]^{3+}$ catalysis of the $\text{Fe}^{3+} + \text{Sn}^{2+}$ reaction, obtained by using equation (13). $[\text{H}^+] = 0.50 \text{ mol dm}^{-3}$, $[\text{Cl}^-] = 0.040 \text{ mol dm}^{-3}$, $I = 1.1 \text{ mol dm}^{-3}$ ($\text{Na}[\text{ClO}_4]$), 25.0°C

$10^3[\text{Fe}^{3+}]_0$ mol dm^{-3}	$10^3[\text{Sn}^{2+}]_0$ mol dm^{-3}	$10^3[\text{Fe}^{2+}]_0$ mol dm^{-3}	$10^3[\text{Ta}_6\text{Cl}_{12}]$ mol dm^{-3}	Percentage of reaction ^a	t_1 min	No. of readings	R.s.e. ^b (%)	$60k_3$ $\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$
2.37	2.40	0.10	0.160	95	163	15	11.2	5
4.25	2.37	2.46	0.163	89	439	19	15.0	12
4.75	2.40	0.21	0.160	85	300	16	52.2	14
9.49	2.40	0.21	0.160	88	231	15	18.8	3
4.44	4.75	0.45	0.163	92	112	15	21.6	9
4.53	4.75	2.18	0.163	98	190	16	28.9	10 ^c
4.75	4.81	0.21	0.160	93	164	15	24.3	6
4.74	4.81	0.22	0.160	97	198	17	4.3	5
4.73	4.81	0.23	0.160	96	228	18	4.7	2 ^d
4.75	4.81	0.21	0.160	94	226	18	10.2	1 ^e
4.48	7.21	0.21	0.160	95	108	15	6.1	3
4.67	9.75	0.40	0.169	95	46	13	26.4	12 ^f
4.83	9.75	10.0	0.169	98	114	13	26.1	12 ^f
5.47	9.75	48.4	0.169	97	195	12	43.7	12 ^f
4.67	9.75	0.31	0.179	91	50	14	3.1	6 ^f
4.79	9.75	0.19	0.179	93	50	14	10.7	8
4.76	9.75	0.22	0.179	93	49	13	34.1	8 ^f
4.61	10.65	0.26	0.040	90	133	15	9.5	13
4.61	10.65	0.26	0.080	93	82	13	4.5	12
4.47	10.65	0.40	0.119	94	50	14	3.9	13
4.50	10.65	0.37	0.159	96	39	12	13.2	13

^a Percentage of reaction = $100([\text{Fe}^{3+}]_0 - [\text{Fe}^{3+}]_t)/[\text{Fe}^{3+}]_0$ or $100([\text{Sn}^{2+}]_0 - [\text{Sn}^{2+}]_t)/[\text{Sn}^{2+}]_0$, whichever is the larger, where the zero subscript refers to the initial concentration, subscript t refers to the last concentration measured, and t_1 is the time at which the last concentration measured was obtained. ^b R.s.e. = relative standard error of t_{calc} with reference to t_{obs} at the same reactant concentration, obtained from all measurements of concentration in a given experiment. ^c This experiment is shown in the Figure.

^d $[\text{Sn}^{\text{IV}}] = 1.18 \times 10^{-3} \text{ mol dm}^{-3}$. ^e $[\text{Sn}^{\text{IV}}] = 4.80 \times 10^{-3} \text{ mol dm}^{-3}$. ^f Once-reprecipitated sample of $[\text{Ta}_6\text{Cl}_{12}]\text{Cl}_2$; other experiments used a twice-reprecipitated sample.

in Table 2; in the remaining experiments the scatter of points, *i.e.* measurements of $[\text{Fe}^{3+}]$ at specified times, in the latter part of the reaction was sufficient to prevent the satisfactory application of the criterion of linearity. The mean value of k_2' is 0.99 ± 0.18 , compared with $0.64 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ calculated from values of k_1 , k_{-1} , and k_2

of the four constants it contains from the experimental data. The simple equation (12), applied to the latter stages of experiments in Table 2, in conditions where $[\text{Fe}^{2+}] > 2[\text{Fe}^{3+}]$, showed that, although values of k_2' could be obtained reasonably near to those calculated from k_1 , k_{-1} , and k_2 , the values of k_3 required in catalysis experiments were con-

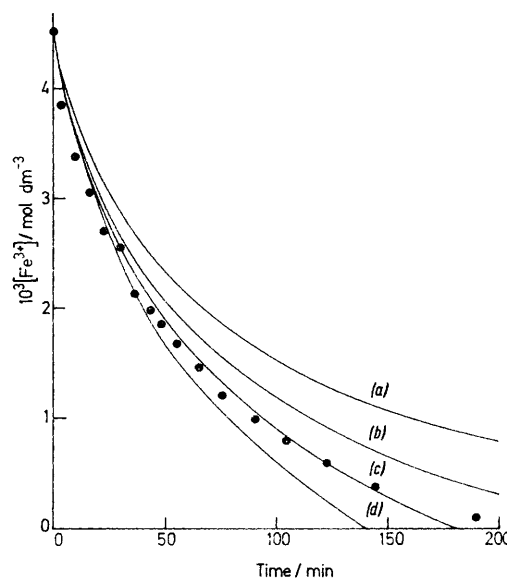
siderably larger than those obtained directly. Accordingly we used the values of k_1 , k_{-1} , and k_2 , found in separate experiments, together with an arbitrary value of k_3 and calculated the time t corresponding to each experimental point in a given catalysis experiment by substituting appropriate values of $[\text{Fe}^{3+}]$ and $[\text{Sn}^{2+}]$ into equation (13). This was done for a range of integral values of k_3 (in $\text{dm}^3 \text{mol}^{-1} \text{min}^{-1}$ units) to obtain the best fit between observed and calculated times. Calculations based on the alternative form of equation (13) gave very similar results, so that the two forms, and hence the mechanistic differences which they imply, cannot be distinguished by experiment. If we define the relative error for a given point as $[100(t_{\text{calc.}} - t_{\text{obs.}})/t_{\text{obs.}}]\%$, the relative standard error obtained by combining the relative errors for all the points in a given experiment is shown in Table 2. The best fit corresponded to the value of k_3 for which the relative standard error was smallest. The relative standard error for all the points in all experiments in Table 2 is 21.1%. When the first point after mixing was excluded for each experiment, the relative standard error for all the remaining points was 11.2%. This first point corresponded to a sample taken between 1 and 3 min after initiating the reaction and is subject to larger relative errors in the recorded time than are subsequent points.

DISCUSSION

The results in Tables 1 and 2 show that the reproducibility in the catalysis experiments is less good than normally achieved in studies of redox reactions between metal ions in aqueous solution. We attribute this in part to the catalyst, solutions of which decompose slowly, although no large systematic trends with ageing were observed. Agreement is moderate between the catalysis experiments and the predictions obtained from the mechanism proposed by using the rate constants for the various contributing reactions. Nevertheless, we consider that the measure of agreement evident from Table 2 is sufficient to validate the mechanism suggested for the catalysis, particularly the major path involving reactions (1), (2), (9), and (4) or (5). The contribution of the subsidiary path, for which the rate-determining step is reaction (3'), is much less well established experimentally, although this route must occur. Values of $60k_3/\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ shown in Table 2 vary from 1 to 13, whereas the measured value is $0.4 \text{ dm}^3 \text{mol}^{-1} \text{s}^{-1}$. Part of this variation is to be expected because the procedure for obtaining the best fit between experimental and calculated points in effect assumes correct values of k_1 , k_{-1} , and k_2 , and makes adjustment by varying k_3 only. The Figure, which shows experimental points and calculated curves for an experiment in which the best fit is not good (relative standard error = 28.9%), makes it clear that for a good fit somewhat different values of k_1 , k_{-1} , and k_2 would have to be chosen. Variations in k_3 cause smaller changes in the early parts of the calculated curves, compared with the later parts. However, although the wide variations in k_3 for best fit lack significance, it is obvious that the average value is considerably higher than the directly measured value; this is also confirmed by the experiments in Table 1. The results in this Table were obtained at relatively high values of $[\text{Fe}^{2+}]_0$, which substantially

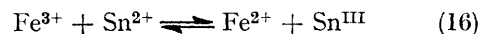
decreases the importance of the major reaction path compared with the results in Table 2. The high value of k_3' observed, relative to the calculated value, appears to indicate the presence of an additional (third) reaction path. The high values for k_3 found when this rate constant was obtained by using solutions in which catalysis by $[\text{Ta}_6\text{Cl}_{12}]^{3+}$ of the reduction of Fe^{3+} by an excess of Sn^{2+} had occurred are of uncertain significance. However, this effect presumably contributes to the unexpectedly rapid occurrence of the catalysis in its latter stages.

In our mechanism we have not taken into account the uncatalysed reaction between Fe^{3+} and Sn^{2+} , because measurements of its half-life under conditions similar to



Plot of $[\text{Fe}^{3+}]$ against time, as observed (individual points) and as calculated for different values of k_3 (full lines). $k_3 = 0.4$ (a), 5 (b), 10 (c), and $15 \text{ dm}^3 \text{mol}^{-1} \text{min}^{-1}$ (d). Reactant concentrations are given in Table 2 (footnote c)

those of the catalysis experiments showed that its rate was negligible. However, if the mechanism of the uncatalysed reaction is (16) followed by (8), a sufficiently labile back reaction for (16) could lead to a much



slower rate for the uncatalysed reaction than would be expected purely on the basis of the forward rate constant for reaction (16). The contribution of this direct reaction between Fe^{3+} and Sn^{2+} in the catalysis experiments could be considerably increased if a more effective means than reaction (8) were available for oxidising Sn^{III} . Such a means could be provided by reaction (9). We consider it likely that this contributes to the high apparent values found for k_3 in the catalysis experiments.

Table 3 shows rate constants for several of the reactions contributing to the catalysis, together with E^\ominus values⁶ for various related couples. The difference of 0.34 V between the two couples involving cluster species implies

that the equilibrium constant for the electron transfer (2') will be *ca.* 10^6 times greater than that for (3'). This in its turn leads to the conclusion that the ratio of the rate constant of the forward reaction (2') to that of the forward reaction (3') will not exceed 10^6 , but is unlikely to be less than $(10^6)^{1/2} = 10^3$. In fact, the ratio $k_2 : k_3$ is *ca.* $3 \times 10^3 : 1$. Thus, these two rate constants are of a relative magnitude compatible with the suggestion that reaction (2), like (3), involves a rate-determining single electron transfer, *i.e.* reaction (2'). There is no evidence from this ratio that reaction (2) involves a two-equivalent

in the absence of light and its iron(II) content was negligible. Tin(II) chloride stock solution was obtained by dissolving tin(II) chloride dihydrate (*ca.* 5.6 g) in 1.00 mol dm⁻³ hydrochloric acid (50 cm³) and diluting to 250 cm³. The solution was kept under nitrogen and was standardised by titration with potassium iodate in moderately concentrated HCl (Andrews' procedure). After 2 weeks the solution was discarded; during this period the titre fell by *ca.* 2%. Tin(IV) chloride solution was prepared by oxidising tin(II) chloride stock solution with gaseous chlorine, followed by removal of most of the latter by partial evacuation of the containing vessel. A small amount (50% v/v) of tin(II)

TABLE 3

Rate constants and values of E° for individual steps

Reaction	k^a /dm ³ mol ⁻¹ s ⁻¹	E° b/V
$\text{Fe}^{3+} + \text{Sn}^{2+} \rightarrow \text{Fe}^{2+} + \text{Sn}^{\text{III}}$	<i>ca.</i> 3×10^{-4}	0.735 ($\text{Fe}^{3+} - \text{Fe}^{2+}$)
$[\text{Ta}_6\text{Cl}_{12}]^{3+} + \text{Sn}^{2+} \rightarrow [\text{Ta}_6\text{Cl}_{12}]^{2+} + \text{Sn}^{\text{III}}$	6.3×10^{-3}	0.49 ($[\text{Ta}_6\text{Cl}_{12}]^{3+} - [\text{Ta}_6\text{Cl}_{12}]^{2+}$)
$[\text{Ta}_6\text{Cl}_{12}]^{4+} + \text{Sn}^{2+} \rightarrow [\text{Ta}_6\text{Cl}_{12}]^{3+} + \text{Sn}^{\text{III}}$ or $[\text{Ta}_6\text{Cl}_{12}]^{2+} + \text{Sn}^{\text{IV}}$	18.7	0.83 ($[\text{Ta}_6\text{Cl}_{12}]^{4+} - [\text{Ta}_6\text{Cl}_{12}]^{3+}$)
$[\text{Ta}_6\text{Cl}_{12}]^{4+} + \text{Fe}^{2+} \rightarrow [\text{Ta}_6\text{Cl}_{12}]^{3+} + \text{Fe}^{3+}$	830	
$\text{Fe}^{3+} + [\text{Ta}_6\text{Cl}_{12}]^{3+} \rightarrow \text{Fe}^{2+} + [\text{Ta}_6\text{Cl}_{12}]^{4+}$	28.5	

^a This work; $[\text{H}^+] = 0.50$ mol dm⁻³, 0.040 mol dm⁻³ Cl⁻, $I = 1.1$ mol dm⁻³ (Na[ClO₄]), 25.0 °C. Ref. 6, $[\text{H}^+] = 0.10$ mol dm⁻³, $I = 0.1$ mol dm⁻³ (HClO₄), 25.0 °C.

change, avoiding intermediate formation of Sn^{III}. However, since the immediate products of reaction (2') are capable of a further redox reaction, their proximity leads us to suggest that reaction (9) will immediately follow (2'), yielding $[\text{Ta}_6\text{Cl}_{12}]^{2+}$ and Sn^{IV} in an apparent two-equivalent redox change.

Even if we assume that the rate constant for the forward reaction (16) is several times larger than that shown in Table 3, it is clear that the cluster ions are much more labile electron acceptors than Fe³⁺ when the corresponding values of E° are taken into account. This lability of the cluster species in reactions involving single electron transfers has been noted by previous workers,^{5,7} and appears to be the reason for the catalytic activity of this cluster species in the Fe³⁺ + Sn²⁺ system. We have also observed catalysis of this reaction by other polynuclear or cluster species involving iridium, niobium, or tantalum which are similarly capable of undergoing labile electron transfers.

EXPERIMENTAL

Reagents were of AnalaR quality except where stated; stock solutions were made up by weight and were standardised where necessary by appropriate methods. Solutions of iron(II) perchlorate were made by dissolving Johnson, Matthey 'specpure' grade iron sponge (2.8 g) in 2.0 mol dm⁻³ perchloric acid (100 cm³) in absence of air. The solution was kept under nitrogen, standardised by titration against standard cerium(IV) sulphate solution with ferroin as indicator, and was shown to contain less than 1% of iron in the form Fe³⁺. Iron(III) perchlorate stock solution was obtained from the iron(II) stock solution by oxidation with hydrogen peroxide and subsequent dilution to give concentrations of *ca.* 0.2 mol dm⁻³ iron(III) perchlorate and *ca.* 0.2 mol dm⁻³ HClO₄. This solution was kept under nitrogen

chloride solution was then added to scavenge the remaining chlorine.

Impure dodecachlorohexatantalum trichloride was prepared by Kuhn and McCarley's method⁸ from tantalum pentachloride (10 g) (Research Organic/Inorganic Chemical Corporation) and aluminium foil (0.5 g) (Hopkin and Williams Ltd.). A portion of the solid material so produced was treated with sufficient water at 50 °C to dissolve soluble material. After cooling, tantalum pentaoxide and other insoluble material was filtered off. An equal volume of concentrated HCl was added, precipitating dodecachlorohexatantalum dichloride which was filtered off, dried in warm air for 30 min, and stored over silica gel. Solutions containing $[\text{Ta}_6\text{Cl}_{12}]^{2+}$ cation (*ca.* 3×10^{-3} mol dm⁻³) were obtained by dissolving the precipitated dichloride in water and making the solution 0.50 mol dm⁻³ in HClO₄. After filtering, the concentration of $[\text{Ta}_6\text{Cl}_{12}]^{2+}$ was determined spectrophotometrically on a diluted sample (ϵ 6 200 dm³ mol⁻¹ cm⁻¹ at 637 nm)⁹ and also potentiometric titration to give $[\text{Ta}_6\text{Cl}_{12}]^{4+}$ with standard cerium(IV) sulphate. The extent of aerial oxidation of such solutions to $[\text{Ta}_6\text{Cl}_{12}]^{3+}$ was *ca.* 2% in 24 h. Solutions of $[\text{Ta}_6\text{Cl}_{12}]^{4+}$ were prepared from $[\text{Ta}_6\text{Cl}_{12}]^{2+}$ solutions by oxidation with gaseous chlorine, the excess of which was removed by passing a stream of air through the solution. Such solutions steadily formed $[\text{Ta}_6\text{Cl}_{12}]^{3+}$ in the absence of chlorine and were therefore used immediately after its removal. Solutions of $[\text{Ta}_6\text{Cl}_{12}]^{3+}$ were obtained by mixing equal volumes of equimolar $[\text{Ta}_6\text{Cl}_{12}]^{2+}$ and $[\text{Ta}_6\text{Cl}_{12}]^{4+}$ solutions, and were stable for several days. The presence and proportion of a cluster ion differing by one unit of charge from the principal constituent of a solution was readily established spectrophotometrically, the spectra of these three cations being dissimilar.⁵

The rate constants for reaction between Fe³⁺ and $[\text{Ta}_6\text{Cl}_{12}]^{3+}$ and its reverse were determined by stopped-flow spectrophotometry using a Durrum model D-110 instrument at 810 nm. The conditions of temperature, ionic strength, and hydrogen-ion and chloride-ion concentrations were the same as those in the catalysis experiments. The smaller

⁷ J. H. Espenson and D. J. Boone, *Inorg. Chem.*, 1968, **7**, 636.

⁸ P. J. Kuhn and R. E. McCarley, *Inorg. Chem.*, 1965, **4**, 1482.

⁹ J. H. Espenson, *Inorg. Chem.*, 1968, **7**, 631.

rate constants for reduction of $[\text{Ta}_6\text{Cl}_{12}]^{4+}$ and $[\text{Ta}_6\text{Cl}_{12}]^{3+}$ by Sn^{2+} under the same conditions as those in the catalysis experiments were obtained by using a Perkin-Elmer model 356 recording spectrophotometer. Reactions took place in a 1 cm optical cell in the temperature-controlled cell compartment of the spectrophotometer. Solutions were degassed before use, and were transferred by Hamilton series 1000 syringes into the optical cell which initially contained argon and was closed by a 'Suba Seal' silicone-rubber stopper. Reduction of $[\text{Ta}_6\text{Cl}_{12}]^{4+}$ to the $3+$ ion was followed at 810 nm, and reduction of the latter to the $2+$ ion at 637 nm. In several instances the solution obtained at the conclusion of the reduction of $[\text{Ta}_6\text{Cl}_{12}]^{4+}$ by an excess of Sn^{2+} was used to obtain the rate constant for reduction of $[\text{Ta}_6\text{Cl}_{12}]^{3+}$ without disturbing the optical cell. Results obtained in this way were very similar to those from a solution of $[\text{Ta}_6\text{Cl}_{12}]^{3+}$ which had been prepared previously by mixing the $2+$ and $4+$ cluster ions.

Kinetic experiments on the catalysis of the reaction between Fe^{3+} and Sn^{2+} were made by mixing appropriate volumes of stock solutions of iron(III) perchlorate, iron(II) perchlorate (if required), sodium perchlorate, dilute HClO_4 , sodium chloride, and $[\text{Ta}_6\text{Cl}_{12}]\text{Cl}_2$, together with water in a small glass vessel. This vessel was equipped with connections *via* taps to a vacuum and an argon supply, and with a small opening for introducing solutions. Hamilton series 1000 syringes were used for measuring out solutions, and the total volume of the mixture was *ca.* 5 cm³. The opening was closed by an unused silicone-rubber stopper, the vessel was degassed by evacuation, and atmospheric pressure was re-established with argon. After placing the vessel in a thermostat, a 0.100 cm³ sample of the mixture was removed

by syringe for determination of the initial concentration of Fe^{3+} , the needle being passed through the stopper. The reaction was initiated by adding the required volume of tin(II) chloride stock solution by syringe, and shaking vigorously. Samples (0.100 cm³) of the reaction mixture were removed at appropriate intervals of time by a syringe, initially filled with argon to compensate for the volume of sample removed. In preliminary experiments a 3.0 cm³ sample of reaction mixture was removed by syringe immediately after initiation of the reaction and was transferred to a 1 cm optical cell fitted with a silicone-rubber stopper and initially filled with argon. The state of the catalyst during an experiment was then monitored by successive scans in the range 600–850 nm on a Unicam model SP 800B spectrophotometer fitted with a temperature-controlled cell compartment. Samples for iron(III) estimation were taken as required from the remaining mixture.

Samples of reaction mixture taken during the course of an experiment were diluted with a standard volume of a solution containing 0.010 mol dm⁻³ ammonium thiocyanate and 0.50 mol dm⁻³ HClO_4 . The concentration of Fe^{III} present was obtained from spectrophotometric measurements at 460 nm on such diluted samples by using a Hilger and Watts Uvispek, model H700.9. The value obtained for the iron(III) concentration in the mixture prior to the addition of Sn^{II} was in agreement with direct spectrophotometric observations that the catalyst, although introduced as $[\text{Ta}_6\text{Cl}_{12}]^{2+}$, is oxidised primarily to $[\text{Ta}_6\text{Cl}_{12}]^{3+}$ by Fe^{3+} .

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