

**556.** *Kinetic Studies of the Oxidation of Vanadium(III) by Iron(III) in Solution in Aqueous Perchloric Acid.*

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Kinetic studies have shown that in aqueous perchloric acid the oxidation of vanadium(III) by iron(III),  $\text{Fe}^{\text{III}} + \text{V}^{\text{III}} \longrightarrow \text{Fe}^{\text{II}} + \text{V}^{\text{IV}}$ , proceeds by two distinct routes. The first is a single-stage reaction corresponding to the stoichiometric equation. The second involves two steps,  $\text{Fe}^{\text{III}} + \text{V}^{\text{IV}} \rightleftharpoons \text{Fe}^{\text{II}} + \text{V}^{\text{V}}$  followed by  $\text{V}^{\text{V}} + \text{V}^{\text{III}} \longrightarrow 2\text{V}^{\text{IV}}$ . The concentration equilibrium constant for the first step has been found by using an e.m.f. cell; values of the velocity constant of the second step have been obtained by combining these equilibrium measurements with kinetic data for the two-stage route of reaction.

The reaction between vanadium(III) and iron(III) is catalysed by copper(II) according to the scheme,  $\text{Cu}^{\text{II}} + \text{V}^{\text{III}} \longrightarrow \text{Cu}^{\text{I}} + \text{V}^{\text{IV}}$  (rate-determining) followed by  $\text{Fe}^{\text{III}} + \text{Cu}^{\text{I}} \longrightarrow \text{Fe}^{\text{II}} + \text{Cu}^{\text{II}}$  (rapid).

The velocity constants for the oxidation of vanadium(III) by copper(II), iron(III), and vanadium(V) have been found at various temperatures and concentrations of hydrogen ion, and the corresponding activation parameters have been evaluated.

VANADIUM(III) is slowly oxidised by iron(III) in aqueous solutions of perchloric acid,  $\text{Fe}^{\text{III}} + \text{V}^{\text{III}} \longrightarrow \text{Fe}^{\text{II}} + \text{V}^{\text{IV}}$ , and here we report a kinetic investigation of this system by a conventional spectrophotometric method. By combining certain of our kinetic results with values of the concentration equilibrium constant for the reaction,  $\text{Fe}^{\text{III}} + \text{V}^{\text{IV}} \rightleftharpoons \text{Fe}^{\text{II}} + \text{V}^{\text{V}}$ , we have obtained rate constants for the relatively rapid reaction  $\text{V}^{\text{V}} + \text{V}^{\text{III}} \longrightarrow 2\text{V}^{\text{IV}}$ . Finally we describe the catalysis of the reaction between iron(III) and vanadium(III) by copper(II). The main experimental findings have been summarised previously.<sup>1</sup>

Preliminary experiments in the initial absence of the products of the reaction showed it to be of the first order both in iron(III) and vanadium(III), concordant second-order rate constants being obtained for various ratios of the initial concentrations of these reactants. Plots of the reciprocal of the vanadium(III) concentration against time are shown in Fig. 1 for experiments in which the initial concentrations of reactants were almost equal. Plot A is typical for experiments in which neither of the products had been added initially; in such experiments initial concentrations of the product vanadium(IV) were a few per cent of the initial vanadium(III) concentration owing to the presence of small amounts of vanadium(IV) in the stock solutions of vanadium(III). The initial presence of vanadium(IV) in concentrations similar to the reactant concentrations increased the rate considerably during the first part of the reaction and the reaction plots were curved (plots B and C). The amount of the increase in the initial rate of the reaction was roughly proportional to the initial concentration of vanadium(IV). On the other hand, the initial presence of iron(II) caused a small decrease in the rate of reaction and the corresponding plots remained almost linear. The change in the rate of reaction became smaller for successive equal increments in the initial concentration of iron(II) and no further change was observed when this concentration exceeded about thrice that of the reactants. Plot D shows the limiting second-order plot observed under these conditions. These and similar experiments led us to the assumption, subsequently justified by further experiments reported below, that the rate expression is

$$-d[\text{Fe}^{\text{III}}]/dt = -d[\text{V}^{\text{III}}]/dt = k_1[\text{Fe}^{\text{III}}][\text{V}^{\text{III}}] + k'[\text{Fe}^{\text{III}}][\text{V}^{\text{III}}][\text{V}^{\text{IV}}]/[\text{Fe}^{\text{II}}]. \quad (1)$$

<sup>1</sup> Higginson, Rosseinsky, Stead, and Sykes, *Discuss. Faraday Soc.*, 1960, **29**, 49.

When the initial concentrations of iron(III) and vanadium(III) are equal, eqn. (1) can be written in the form

$$d(1/[V^{III}])/dt = k_1 + k'[V^{IV}]/[Fe^{II}]. \quad (2)$$

In agreement with eqn. (2), gradients obtained from plots such as B and C (Fig. 1) of  $1/[V^{III}]$  against time were linearly dependent upon the corresponding values of  $[V^{IV}]/[Fe^{II}]$

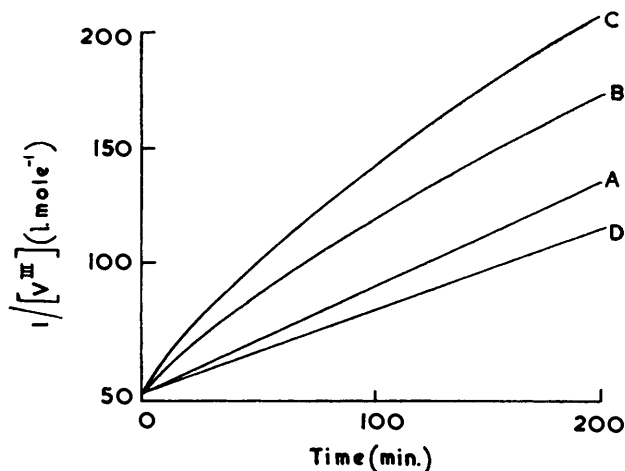
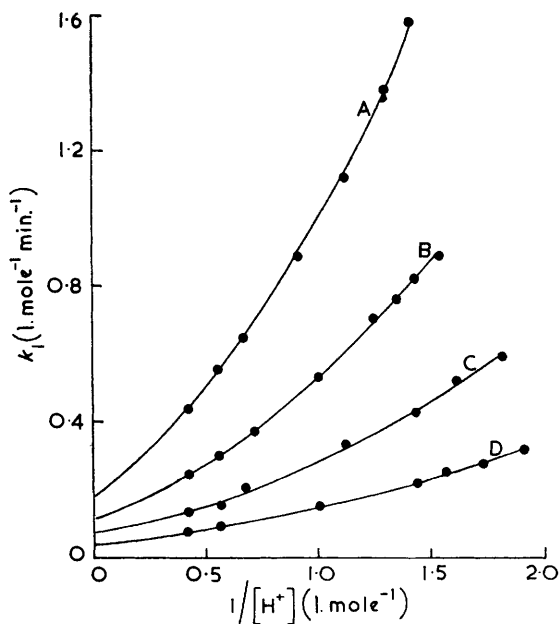


FIG. 1. Effect of initial presence of products upon the rate of the iron(III)-vanadium(III) reaction.

Initial concns.:  $Fe^{III} = 0.0226M$ ;  $V^{III} = 0.022M$ ;  $Fe^{II} = ca. 10^{-4}M$  (A,B,C);  $0.07-0.12M$  (D);  $V^{IV} = ca. 10^{-3}M$  (A,D),  $0.057M$  (B),  $0.094M$  (C);  $H^+ = 1.00M$ ; ionic strength  $3.0M$ ; temp.  $20.0^\circ$ .

FIG. 2. Dependence of  $k_1$  upon hydrogen-ion concentration and temperature.

A,  $30.0^\circ$ . B,  $25.0^\circ$ . C,  $20.0^\circ$ . D,  $15.0^\circ$ .  
Initial concns.:  $Fe^{III} \approx 0.040M$ ;  $V^{III} \approx 0.023M$ ;  $Fe^{II} = 0.056-0.093M$  ( $30.0^\circ$ ),  $0.056M$  ( $25.0^\circ$ ),  $0.048M$  ( $20.0^\circ$ ),  $0.046-0.129M$  ( $15.0^\circ$ );  $V^{IV} < 2 \times 10^{-4}M$ ; ionic strength  $3.0M$ . Experimental error in values of  $k_1$  is  $\pm 3-4\%$ .



within the rather large errors introduced in finding these gradients. The value of  $k'$  was about one-quarter of that of  $k_1$ . According to eqn. (1), if iron(II) is present initially in sufficiently high concentration, the term in  $k'$  is negligible over most of the reaction, in accord with the observation that the decrease in the reaction rate reached a limit as the concentration of iron(II) was increased in successive experiments. When neither iron(II)

nor vanadium(IV) was added initially, the concentrations of these two products were equal throughout the reaction, and under these conditions eqn. (1) simplifies to

$$-d[\text{V}^{\text{III}}]/dt = (k_1 + k')[\text{Fe}^{\text{III}}][\text{V}^{\text{III}}]. \quad (3)$$

Thus, although the products influence the rate of reaction, the observation that simple second-order reaction plots were obtained in the initial absence of the products can be understood.

*The Direct Reaction between Iron(III) and Vanadium(III).*—These preliminary observations suggested that the products are formed by two distinct routes, one of which can be eliminated by the use of a sufficiently high initial concentration of iron(II). We believe that the other route, corresponding to the term in  $k_1$  in eqn. (1), involves a single-stage oxidation-reduction,  $\text{Fe}^{\text{III}} + \text{V}^{\text{III}} \longrightarrow \text{Fe}^{\text{II}} + \text{V}^{\text{IV}}$ . A series of kinetic experiments was performed in which the temperature and hydrogen-ion concentration were varied, the initial concentration of iron(II) being sufficient to suppress the contribution of the term in  $k'$  over at least the first half of the reaction. Particularly at higher temperatures and lower hydrogen-ion concentrations, certain of the second-order rate plots showed curvature in the final stages of the reaction, corresponding to an apparent increase in  $k_1$ . We ascribe this to a small contribution from the term in  $k'$  as vanadium(IV) accumulates. Experiments in which the initial concentration of iron(II) was varied showed that concordant values of  $k_1$  could be obtained from the initial, linear portions of these plots. We summarise the results of this series of experiments in Fig. 2,  $k_1$  being obtained from gradients of plots of  $\log_{10} ([\text{Fe}^{\text{III}}]/[\text{V}^{\text{III}}])$  against time for the first 30–50% of the reaction. The curves in Fig. 2 are consistent with the equation

$$k_1 = b + c/[\text{H}^+] + d/[\text{H}^+]^2, \quad (4)$$

in which  $b$ ,  $c$ , and  $d$  are constant at a given temperature. Equations containing three terms for the hydrogen-ion dependence of the velocity constants of electron-transfer reactions are uncommon, and we have considered the possibility that either  $b$  or  $d$  is a spurious constant arising from changes in the activity coefficients of the reactants and transition complexes when sodium ions are replaced by hydrogen ions at constant ionic strength. If this type of effect operates we should expect to observe changes in  $k_1$  if sodium ions are replaced by other singly charged ions at constant ionic strength and hydrogen-ion concentration. Several experiments at 1.00M-hydrogen ion were performed in which sodium perchlorate was progressively replaced by an equivalent concentration of lithium perchlorate up to a concentration of *ca.* 1.4M while the concentrations of other constituents of the reaction mixture were maintained constant. Within the experimental variation of  $\pm 3\%$  the values of  $k_1$  obtained in these experiments were identical, and hence we conclude that the three constants in eqn. (4) indicate the occurrence of three parallel reactions, for which the corresponding transition complexes differ in the number of bound protons present, in the direct formation of iron(II) and vanadium(IV) from iron(III) and vanadium(III). Eqn. (4) can be written in the form

$$(k_1 - b)[\text{H}^+] = c + d/[\text{H}^+], \quad (5)$$

and plots of the left-hand side of eqn. (5) against  $1/[\text{H}^+]$  should be linear. The constants can therefore be evaluated by choosing a value of  $b$  such that the resulting plot is linear,  $c$  and  $d$  being obtained from the intercept on the ordinate axis and the gradient, respectively. In practice, only about a five-fold variation in  $[\text{H}^+]$  was made at a given temperature and linear plots of eqn. (5) were obtained for a small range of values of  $b$  with similar ranges of possible values for  $c$  and  $d$ . For example, at 25.0° we found  $b = 0.08_5 - 0.13_5$  l. mole<sup>-1</sup> min.<sup>-1</sup>,  $c = 0.28 - 0.20$  min.<sup>-1</sup>,  $d = 0.15 - 0.21$  mole l.<sup>-1</sup> min.<sup>-1</sup>. (A high extreme value of  $c$  corresponds to low extreme values of  $b$  and  $d$ .) The curves shown in Fig. 2 were obtained by calculating values of  $k_1$  at various hydrogen-ion concentrations from the

mean values of  $b$ ,  $c$ , and  $d$ . Similar curves calculated by using the extreme values fitted the experimental values within the reproducibility of individual experiments ( $\pm 3$ – $4\%$ ). From Arrhenius plots for  $b$ ,  $c$ , and  $d$  we found

$$b = \text{antilog}_{10} (11.8 \pm 2.9) \exp \{-(17.3 \pm 4.1)10^3/RT\} \text{ (l. mole}^{-1} \text{ min.}^{-1}\text{)}$$

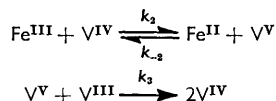
$$c = \text{antilog}_{10} (16.4 \pm 3.9) \exp \{-(23.2 \pm 5.4)10^3/RT\} \text{ (min.}^{-1}\text{)}$$

$$d = \text{antilog}_{10} (17.1 \pm 2.0) \exp \{-(24.5 \pm 2.8)10^3/RT\} \text{ (mole l.}^{-1} \text{ min.}^{-1}\text{)}$$

In further experiments, conducted subsequently by J. B. Stead, values of  $k_1$  differing from those reported here by up to  $10\%$  were obtained when the initial concentration of vanadium(III) was varied by a factor of two, although  $k_1$  appeared insensitive to changes in the initial concentration of iron(III). We do not know the cause of this variation. The corresponding changes in  $b$ ,  $c$ , and  $d$  are larger and so the values of these constants calculated from the mean temperature-independent factors and activation energies given in the above expressions hold only under the experimental conditions quoted in Fig. 2.

We identify  $b$  as the rate constant for the bimolecular oxidation–reduction between  $\text{Fe}^{3+}$  and  $\text{V}^{3+}$ . However, our experiments give no information about the incorporation of perchlorate ions in the transition complex, although it is probable that, in  $3.0\text{M}$ -perchlorate, unhydrolysed iron(III) and vanadium(III) are largely in outer-sphere association with these anions. The rate constants  $c$  and  $d$  correspond to the formation of transition complexes which can formally be represented as containing  $\text{Fe}^{3+}$ ,  $\text{V}^{3+}$ , and, respectively, one or two  $\text{OH}^-$  ions; again there is uncertainty about the contribution of perchlorate ions. Frequently the rate constant for an oxidation–reduction path involving an inverse dependence upon the hydrogen-ion concentration is regarded as the product of the rate constant for a bimolecular reaction between an unhydrolysed cation and a partly hydrolysed cation, and the corresponding hydrolysis constant. The unhydrolysed cation is usually chosen as the cation of lower hydrolysis constant. The validity of this type of interpretation seems doubtful to us and in the case of the rate constant  $c$  such an attempt to identify the reacting species fails since the first hydrolysis constants of  $\text{Fe}^{3+}$  and  $\text{V}^{3+}$  are very similar in magnitude.

*Catalysis of the Reaction between Iron(III) and Vanadium(III) by Vanadium(IV).*—We believe that the second term in eqn. (1) corresponds to a two-stage process,



The magnitude of the equilibrium constant  $K_2 = k_2/k_{-2}$  is such (see below) that in our experiments the concentration of vanadium(V) was less than  $0.1\%$  of the reactant concentrations. By making the stationary-state assumption  $d[\text{V}^{\text{V}}]/dt = 0$ , and taking into account the direct reaction between iron(III) and vanadium(III) we obtain

$$\frac{-d[\text{V}^{\text{III}}]}{dt} = k_1[\text{Fe}^{\text{III}}][\text{V}^{\text{III}}] + \frac{k_2k_3[\text{Fe}^{\text{III}}][\text{V}^{\text{III}}][\text{V}^{\text{IV}}]}{k_{-2}[\text{Fe}^{\text{II}}] + k_3[\text{V}^{\text{III}}]} \quad (6)$$

Eqn. (6) is of similar form to eqn. (1) and would be identical with it if  $k_{-2}[\text{Fe}^{\text{II}}]$  greatly exceeds  $k_3[\text{V}^{\text{III}}]$ , in which case  $k' = k_2k_3/k_{-2} = k_3K_2$ . Eqn. (6) can be written

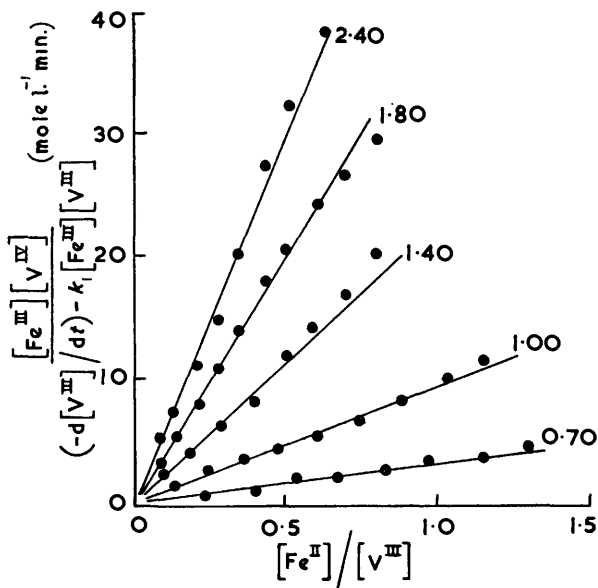
$$\frac{[\text{Fe}^{\text{III}}][\text{V}^{\text{IV}}]}{(-d[\text{V}^{\text{III}}]/dt) - k_1[\text{Fe}^{\text{III}}][\text{V}^{\text{III}}]} = \frac{k_{-2}[\text{Fe}^{\text{II}}]}{k_2k_3[\text{V}^{\text{III}}]} + \frac{1}{k_2} \quad (7)$$

[the term  $1/k_2$  is omitted in the corresponding form of eqn. (1)]. We used eqn. (7) in our original interpretation of a series of experiments at high initial concentrations of vanadium(IV). Values of  $-d[\text{V}^{\text{III}}]/dt$  could be obtained from plots of reactant or product concentrations against time, but we plotted  $[\text{Fe}^{\text{II}}]^2$  against time since this plot showed

only a gentle curvature and was particularly suitable for taking gradients. Values of  $-d[V^{III}]/dt$  were obtained from the relation: gradient =  $d[Fe^{II}]^2/dt = 2[Fe^{II}]d[Fe^{II}]/dt = 2[Fe^{II}](-d[V^{III}]/dt)$ . Since  $k_1$  was known, the left-hand side of eqn. (7) could be evaluated and plotted against corresponding values of  $[Fe^{II}]/[V^{III}]$ . Fig. 3 shows typical plots, obtained at 25.0°; the limits of error in the quantity plotted as ordinate are estimated as  $\pm 8\%$  of its value. Within this error, largely introduced in obtaining  $-d[V^{III}]/dt$ , these plots pass through the origin, so that  $k_2$  could not be found. We conclude that  $k_2[Fe^{II}]$  greatly exceeds  $k_3[V^{III}]$ , except possibly in the very early stages of the reaction, and hence that eqn. (6) can be replaced by eqn. (1). As an alternative to this procedure for finding  $k'$ , which is the reciprocal of the gradient of such plots, we can therefore use the

FIG. 3. Typical plots for evaluating  $k'$  by using eqn. (7).

Hydrogen-ion concentrations (M) are shown in the Figure; other initial concentrations are given in Table I. Temp. 25.0°. Errors are discussed in the text.



integrated form of eqn. (1). If the initial concentrations of iron(III), vanadium(III), vanadium(IV), and iron(II) are respectively  $p$ ,  $q$ ,  $r$ , and zero, we obtain on integration

$$A \log_e (p - x) + B \log_e (q - x) + C \log_e (r + sx) = k't + \text{Constant}, \quad (8)$$

where  $x$  is the concentration of iron(II) at time  $t$ ,

$$s = (k' + k_1)/k', \quad A = -p/(q - p)(r + ps), \\ B = q/(q - p)(r + qs), \quad C = -r/(r + ps)(r + qs).$$

For the case when  $p = q$  we obtain

$$D/(p - x) + E \log_e \{(r + sx)/(p - x)\} = k't + \text{Constant}, \quad (9)$$

where

$$D = p/(r + ps), \quad E = -r/(r + ps)^2.$$

In order to evaluate  $k'$  from gradients of plots of the left-hand side of eqn. (8) or (9) against time, it was necessary to assume an approximate value of  $s$ . This value was obtained for each experiment from  $k_1$ , which was already known under similar conditions, and the value of  $k'$  obtained by the earlier procedure described above. The new value of  $k'$  obtained from the plot of eqn. (8) or (9) was then used to evaluate a better value of  $s$ , and a second plot was made. The values of  $k'$  obtained from plots of eqn. (8) or (9) are not very sensitive to small variations in  $s$  and for many experiments the values of  $k'$

obtained from the first and the second plots were in close agreement. For other experiments satisfactory agreement between the values of  $k'$  assumed and found was only obtained for a third plot. In all cases these plots were linear.

The second method of finding  $k'$  is preferable to the first since errors introduced in finding gradients of curved plots are eliminated. In Table 1 we summarise values of  $k'$  found by the second method; these supersede the values used in our previous paper<sup>1</sup> which were obtained by the first method only. However, even the preferred values are subject to considerable errors. Small errors in the determination of the components of stock reagent solutions led to a corresponding error in the optical density at zero time which was calculated for each experiment. The reactant and product concentrations at

TABLE 1.

[H <sup>+</sup> ] (M)	10 <sup>2</sup> $k'$ (l. mole <sup>-1</sup> min. <sup>-1</sup> )	10 <sup>-4</sup> $k_3$	[H <sup>+</sup> ] (M)	10 <sup>2</sup> $k'$ (l. mole <sup>-1</sup> min. <sup>-1</sup> )	10 <sup>-4</sup> $k_3$	[H <sup>+</sup> ] (M)	10 <sup>2</sup> $k'$ (l. mole <sup>-1</sup> min. <sup>-1</sup> )	10 <sup>-4</sup> $k_3$	[H <sup>+</sup> ] (M)	10 <sup>2</sup> $k'$ (l. mole <sup>-1</sup> min. <sup>-1</sup> )	10 <sup>-4</sup> $k_3$
At 15·0° (pK <sub>2</sub> ' = 5·56 <sub>5</sub> )			At 20·0° (pK <sub>2</sub> ' = 5·33 <sub>0</sub> )			At 25·0° (pK <sub>2</sub> ' = 5·09 <sub>5</sub> )			At 30·0° (pK <sub>2</sub> ' = 4·87 <sub>0</sub> )		
0·70	3·5	0·62 <sub>5</sub>	0·60	15·5	1·19	0·70	31	1·89	1·00	29·6	2·20
1·00	1·36	0·50 <sub>0</sub>	0·85	6·5	1·06	0·85	17·5	1·57	1·40	13·2	1·92
1·00	1·41	0·52 <sub>0</sub>	1·40	1·95	0·82	1·00	12·0	1·49	1·80	7·2	1·73
1·30	0·76	0·47 <sub>5</sub>	1·80	1·15	0·80	1·00	12·5	1·56	2·00	5·9	1·74
1·80	0·38	0·45 <sub>0</sub>	2·37	0·56	0·67	1·40	5·8	1·42	2·37	4·3	1·78
2·37	0·190	0·39 <sub>5</sub>				1·80	3·1	1·25			
						2·10	2·07	1·14			
						2·40	1·60	1·15			

Initial concns.: Fe<sup>III</sup> = 0·0219—0·0240M; V<sup>III</sup> = 0·0228—0·0253M; Fe<sup>II</sup> < 10<sup>-4</sup>M; V<sup>IV</sup> = 0·077—0·119M; ionic strength = 3·0M.

a given time were obtained from the difference between the optical density observed at this time and the calculated initial optical density and so these concentrations were also subject to a small error. For many reactions this would be unimportant, but in this case the dependence of the rate of reaction upon the inverse of the iron(II) concentration leads to a relatively large error in  $k'$ . We find that a change of  $8 \times 10^{-4}$ M (the maximum estimated error) in the initial concentrations of reactants leads to a change of *ca.* 20% in the calculated value of  $k'$ . Since common stock solutions were used for this series of experiments the consequent errors in  $k'$  should be largely systematic and this appeared to be so from the comparison of duplicate experiments, which gave values of  $k'$  agreeing within 5%. By conducting experiments with iron(II) present initially in low concentrations such systematic errors could be reduced, but random errors would be increased since the proportion of reaction occurring by the two-stage route would be reduced. Attempts to find  $k'$  by obtaining ( $k_1 + k'$ ) from experiments with zero initial concentrations of iron(II) and vanadium(IV) [cf. eqn. (3)] and subtracting  $k_1$  were abandoned since  $k'$  was obtained as a small difference between two larger quantities and the consequent random errors were high.

*Determination of the Equilibrium Constant K<sub>2</sub>.*—According to our interpretation,  $k'$  is complex, being the product of  $K_2$ , the concentration equilibrium constant for the reaction  $\text{Fe}^{\text{III}} + \text{V}^{\text{IV}} \rightleftharpoons \text{Fe}^{\text{II}} + \text{V}^{\text{V}}$ , and  $k_3$ , the velocity constant for the reaction  $\text{V}^{\text{V}} + \text{V}^{\text{III}} \rightarrow 2\text{V}^{\text{IV}}$ . To find  $k_3$  we required values of  $K_2$  under conditions comparable with those of the kinetic experiments. Since in strongly acid solutions the dominant forms of vanadium(IV) and vanadium(V) are respectively  $\text{VO}_2^{2+}$  and  $\text{VO}_2^+$ , the equilibrium involving these ions, iron(II) and iron(III), is  $\text{Fe}^{3+} + \text{VO}_2^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{Fe}^{2+} + \text{VO}_2^+ + 2\text{H}^+$ , and hence  $K_2$  varies with the hydrogen-ion concentration. If we define  $K_2' = [\text{Fe}^{2+}][\text{VO}_2^+][\text{H}^+]^2/[\text{Fe}^{3+}][\text{VO}_2^{2+}]$ , then  $K_2 = K_2'/[\text{H}^+]^2$ ; in our earlier report of this work we omitted to make clear the distinction between  $K_2$  and  $K_2'$ . Although values of  $K_2'$  have previously been found in perchlorate media<sup>2</sup> we were unable to use

<sup>2</sup> Kenttämää, *Suomen Kem.*, 1958, B, **31**, 273.

these, since they hold at ionic strengths of 1.0M or less. We obtained  $K_2'$  at ionic strength 3.0M from measurements of the e.m.f. of the cell



the relationship between the e.m.f.  $E$  and  $K_2'$  being

$$E = \frac{2.303RT}{F} \log_{10} \left\{ \frac{[\text{Fe}^{2+}][\text{VO}_2^+][\text{H}^+]^2}{[\text{Fe}^{3+}][\text{VO}^{2+}]} \right\} - \frac{2.303RT}{F} \log_{10} K_2'. \quad (10)$$

The experimental cell contained two separate anode compartments ( $A_1, A_2$ ) and two separate cathode compartments ( $C_1, C_2$ ). For all measurements the concentrations of metal ions were: in  $A_1$ , 0.0239M- $\text{VO}_2^+$ , 0.0398M- $\text{VO}^{2+}$ ; in  $A_2$ , 0.0398M- $\text{VO}_2^+$ , 0.0239M- $\text{VO}^{2+}$ ; in  $C_1$ , 0.0366M- $\text{Fe}^{3+}$ , 0.0237M- $\text{Fe}^{2+}$ ; in  $C_2$ , 0.0248M- $\text{Fe}^{3+}$ , 0.0355M- $\text{Fe}^{2+}$ . Three series of e.m.f. measurements were made; within each series the hydrogen-ion concentration in all four electrode compartments was constant and measurements were made at four temperatures. The ionic strength was made 3.00M in all experiments by addition of sodium perchlorate. At each temperature and hydrogen-ion concentration, the e.m.f. of each combination of anodic and cathodic half-cells was measured, the corresponding values of  $pK_2'$  were found by using eqn. (10), and the mean value was obtained. These mean values, which are subject to an error of  $\pm 0.005$  logarithmic unit, are summarised in Table 2. It can be seen that  $pK_2'$  is not independent of the hydrogen-ion concentration;

TABLE 2.  
Mean values of  $pK_2'$

[H <sup>+</sup> ] (M)	Temp.			
	15.0°	20.0°	25.0°	30.0°
0.40	5.53 <sub>s</sub>	5.29 <sub>s</sub>	5.05 <sub>s</sub>	4.81 <sub>9</sub>
1.00	5.56 <sub>s</sub>	5.33 <sub>0</sub>	5.09 <sub>s</sub>	4.87 <sub>0</sub>
2.40	5.63 <sub>s</sub>	5.42 <sub>6</sub>	5.18 <sub>s</sub>	4.96 <sub>1</sub>

at each temperature a plot of  $pK_2'$  against the hydrogen-ion concentration is linear. We consider it unlikely that this effect is due to a hydrolysis equilibrium involving one or other of the principal vanadium species, for, although kinetic evidence has been adduced<sup>3</sup> for the protonation of  $\text{VO}_2^+$  in strongly acid solutions, other evidence shows that under our experimental conditions vanadium(v) exists solely as  $\text{VO}_2^+$ ,<sup>4</sup> and vanadium(IV) as  $\text{VO}^{2+}$ .<sup>5</sup> If we assume that this change in  $pK_2'$  is not a spurious effect, it may be due to changes in activity coefficients as hydrogen ions are replaced by sodium ions at constant ionic strength; eqn. (10) holds only on the assumption that activity coefficients are constant at a given temperature. At 25.0° and 1.00M-hydrogen-ion,  $pK_2' = 5.09_5$  compared with the value 4.801 obtained<sup>2</sup> at the same temperature and hydrogen-ion concentration, but at ionic strength 1.06M, and with 4.045 for the negative logarithm of the thermodynamic constant at 25.0°.

*Calculation of Velocity Constants for the Reaction between Vanadium(v) and Vanadium(III).*—Values of  $k_3$  were calculated by using the relation  $k_3 = k'[\text{H}^+]^2/K_2'$ . At each temperature we arbitrarily chose the value of  $K_2'$  found in a solution of hydrogen-ion concentration 1.00M. The values of  $k_3$  so obtained are included in Table 1. We conclude from these values that  $k_3$  can be expressed:  $k_3 = e + f/[\text{H}^+]$  where  $e$  and  $f$  are constant at a given temperature. From the Arrhenius plots for  $e$  and  $f$  we find

$$e = \text{antilog}_{10} (16.1 \pm 1.0) \exp \{-(16.6 \pm 1.4)10^3/RT\} \text{ (l. mole}^{-1} \text{ min.}^{-1}\text{)}$$

$$f = \text{antilog}_{10} (16.6 \pm 1.3) \exp \{-(17.5 \pm 1.9)10^3/RT\} \text{ (min.}^{-1}\text{)}$$

<sup>3</sup> Ramsay, Colichman, and Pack, *J. Amer. Chem. Soc.*, 1946, **68**, 1695; Littler and Waters, *J.*, 1959, 3014.

<sup>4</sup> Rossotti and Rossotti, *Acta Chem. Scand.*, 1956, **10**, 957.

<sup>5</sup> Rossotti and Rossotti, *Acta Chem. Scand.*, 1955, **9**, 1177.

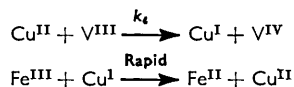
We also calculated values of  $k_3$  by using individual values of  $K_2'$ , each corresponding to the hydrogen-ion concentration employed in the kinetic experiment from which  $k'$  was determined; such values of  $K_2'$  were obtained by interpolation from linear plots of  $pK_2'$  against  $[H^+]$ . Plots of these values of  $k_3$  against  $1/[H^+]$  appeared to be curved at 25.0° and 30.0°, hence our preference for the use of a constant value of  $K_2'$  at each temperature.

If  $K_3$ , the concentration equilibrium constant of the reaction  $V^V + V^{III} \rightleftharpoons 2V^{IV}$ , could be found, it would be possible to calculate  $k_{-3}$ , the velocity constant for the disproportionation  $2V^{IV} \longrightarrow V^V + V^{III}$ , since  $K_3 = k_3/k_{-3}$ . In principle  $K_3$  can be found from e.m.f. measurements by using the cell



We set up this cell, but the potentials were not reproducible. This was traced to the behaviour of the  $VO^{2+}/V^{3+}$  half-cell, although deaerated solutions were used and the half-cell was maintained in an atmosphere of nitrogen. Vanadium(III) is slowly oxidised by perchloric acid solutions,<sup>6</sup> and it is possible that this reaction occurs catalytically at the surface of the platinum electrode, thereby preventing the attainment of a steady e.m.f.

*Catalysis of the Reaction between Iron(III) and Vanadium(III) by Copper(II).*—If copper(II) is present in similar concentration to the reactants, the rate of the reaction between iron(III) and vanadium(III) is greatly increased. Under these conditions plots of  $\log_{10} [V^{III}]$  against time were linear over 80% of the total reaction and their gradients were approximately proportional to the copper(II) concentration. The rate of reaction was hardly affected by changing the initial concentration of iron(III). We believe that the catalysis by copper(II) occurs through the reactions



Since this route of reaction is independent of the routes taken in the absence of copper(II), then, in the initial absence of vanadium(IV) and iron(II), the total rate of reaction should be given by

$$-d[V^{III}]/dt = (k_1 + k')[Fe^{III}][V^{III}] + k_4[Cu^{II}]_0[V^{III}], \quad (11)$$

where  $[Cu^{II}]_0$  represents the initial concentration of copper(II). Although  $k_4$  is much larger than the corresponding value of  $(k_1 + k')$ , the first term on the right-hand side of eqn. (11) was not negligible under the conditions of a series of experiments at various temperatures and hydrogen-ion concentrations (Table 3). Accordingly we adopted the following procedure for evaluating  $k_4$ . On integration, eqn. (11) becomes

$$\log_e [V^{III}] - \log_e \{1 + D[Fe^{III}]\} = -k_4[Cu^{II}]_0\{1 + D([Fe^{III}]_0 - [V^{III}]_0)\}t + \text{Constant}, \quad (12)$$

where  $D = (k_1 + k')/k_4[Cu^{II}]_0$  and subscripts zero indicate initial concentrations. By assuming an approximately correct value for  $D$ , the left-hand side of eqn. (12) was evaluated and was plotted against the time. A preliminary value of  $k_4$  was then calculated from the gradient. A new value of  $D$  was obtained from this value of  $k_4$ ,  $(k_1 + k')$  being known, and the procedure was repeated until a constant value of  $k_4$  was found. Usually not more than three successive plots of eqn. (12) were necessary for each experiment. In these experiments the initial concentrations of vanadium(IV) were between 2% and 10% of the initial concentrations of vanadium(III) and in consequence we performed an otherwise identical control experiment with copper(II) absent in parallel with each experiment in the presence of copper(II). Linear second-order plots, similar to Fig. 1A, were obtained from the control experiments and in evaluating  $D$  we used the second-order rate constants

<sup>6</sup> King and Garner, *J. Phys. Chem.*, 1954, **58**, 29.



TABLE 3.

[H <sup>+</sup> ] (M)	10 <sup>2</sup> (k <sub>1</sub> + k')' (l. mole <sup>-1</sup> min. <sup>-1</sup> )	k <sub>4</sub>	[H <sup>+</sup> ] (M)	10 <sup>2</sup> (k <sub>1</sub> + k')' (l. mole <sup>-1</sup> min. <sup>-1</sup> )	k <sub>4</sub>
At 25.0°			At 15.0°		
0.70	147	24.3	0.70	32.1	7.5
1.00	70	18.0	1.00	20.0	5.4
1.80	43	11.4	1.80	10.1	3.53 *
2.67	28.1	8.7	2.67	7.5	2.67 †
At 20.0°			At 10.0°		
0.70	76	13.0	0.70	14.4	4.2
1.00	41	9.9	1.00	9.5	3.12
1.80	22.2	6.7	1.80	5.0	1.95
2.65	14.9	4.7	2.65	3.44	1.46

Initial concns.: Fe<sup>III</sup> = 0.0226—0.0232M; V<sup>III</sup> = 0.0210—0.0230M; Cu<sup>II</sup> = 0.0117—0.0176M.

\* Mean of 4 expts. in which V<sup>III</sup> was varied from 0.0114 to 0.0570M and Fe<sup>III</sup> from 0.0169 to 0.0376M.

† Mean of 4 expts. in which Cu<sup>II</sup> was varied from 0.0059 to 0.0293M; ionic strength 3.0M.

found from these plots instead of using the sum of the previously established values of  $k_1$  and  $k'$  at corresponding temperatures and hydrogen-ion concentrations. Strictly, eqn. (12) should be applied only to the results of experiments conducted in the initial absence of vanadium(IV); however, we consider that our use of this equation is justified by the linearity of the plots of the control experiments. The values of  $(k_1 + k)'$ , the second-order rate constants obtained from these control experiments, are recorded in Table 3 and are about 20% larger than corresponding values calculated from  $k_1$  and  $k'$ .

We conclude from plots of  $k_4$  against  $1/[H^+]$  at constant temperature that this constant can be expressed  $k_4 = g + h/[H^+]$ . From Arrhenius plots for  $g$  and  $h$  we find

$$g = \text{antilog}_{10} (16.1 \pm 1.1) \exp \{-(21.3 \pm 1.5)10^3/RT\} \text{ (l. mole}^{-1} \text{ min.}^{-1}\text{)}$$

$$h = \text{antilog}_{10} (15.1 \pm 0.4) \exp \{-(19.0 \pm 0.6)10^3/RT\} \text{ (min.}^{-1}\text{)}$$

We have previously discussed<sup>1</sup> the significance of the values of the entropy of activation corresponding to the bimolecular velocity constants  $b$ ,  $e$ ,  $g$  evaluated in this work. These entropies of activation were calculated from the corresponding pre-exponential terms, as quoted above, in the integrated form of the Arrhenius equation by using  $10^{15}$  l. mole<sup>-1</sup> min.<sup>-1</sup> as the normal frequency factor. Our improved method of evaluating  $k_3$  has not led to a change in the previously quoted value of  $\Delta S^\ddagger = 5$  cal. mole<sup>-1</sup> deg.<sup>-1</sup> corresponding to the velocity constant  $e$ ; the limits of error in this quantity are now reduced to  $\pm 5$  cal. mole<sup>-1</sup> deg.<sup>-1</sup>.

#### EXPERIMENTAL

Ammonium metavanadate in solution in dilute perchloric acid was reduced by sulphur dioxide to vanadium(IV), and the excess of sulphur dioxide was removed by boiling. A solution of ammonium carbonate was then added slowly with stirring until no further precipitate of hydrated vanadium(IV) oxide was formed. The precipitate was separated by centrifugation, washed with water, and dissolved in dilute perchloric acid. Vanadium(IV) was reprecipitated by the same method, washed, and redissolved in a small excess of dilute perchloric acid to give a stock solution of *ca.* 0.3M-vanadium(IV) perchlorate. Sulphate ions were shown to be absent from such stock solutions. Vanadium(III) perchlorate solutions were obtained from vanadium(IV) stock solutions by reduction at a platinum cathode with a current density of 0.06 amp./cm.<sup>2</sup>. Electrolysis was stopped when *ca.* 1% of the original vanadium(IV) remained, as shown spectrophotometrically at 755 m $\mu$ . Stock vanadium(III) solutions were kept under nitrogen at *ca.* 0° in absence of light. Vanadium(V) perchlorate stock solutions were prepared by dissolving vanadium pentoxide in an excess of dilute perchloric acid; the pentoxide was obtained by heating ammonium metavanadate at 500° to constant weight. Iron(II), iron(III), and copper(II) perchlorate solutions were obtained by dissolving the solid perchlorates, supplied by G. F. Smith Chemical Co., in dilute perchloric acid. Identical kinetic

## 2850 *Oxidation of Vanadium(III) by Iron(III) in Solution, etc.*

results were obtained by using, in place of the commercial product, a solution of iron(III) perchlorate prepared by double decomposition between a solution of iron alum in dilute perchloric acid and aqueous barium perchlorate. Sodium perchlorate solutions were prepared by neutralising 60% perchloric acid with solid anhydrous sodium carbonate and filtering the solution after several days; these solutions were used in bringing the ionic strength of kinetic reaction mixtures to  $3.00 \pm 0.03M$ . Lithium and barium perchlorate solutions were obtained by neutralising dilute perchloric acid with lithium hydroxide and barium carbonate, respectively. Except where otherwise stated, all reagents were of "AnalaR" quality.

Concentrations of reagents in stock solutions were determined by established methods as follows. Vanadium(III) was estimated by oxidation to vanadium(IV) with standard potassium iodate; the iodine liberated, plus a small excess of iodate, was then determined by titration against standard sodium thiosulphate in the presence of potassium iodide. Vanadium(IV) stock solutions were standardised by titration against standard potassium permanganate. Vanadium(V) stock solutions were allowed to react with a small excess of standard potassium iodide solution, and the resulting mixture of iodide and iodine was titrated against standard potassium iodate in 4M-hydrochloric acid (Andrews's procedure); the vanadium(IV) produced in the first stage is not affected by the subsequent titration. Iron(II) stock solutions were standardised by titration against standard potassium permanganate. Iron(III) and copper(II) stock solutions were standardised by adding an excess of potassium iodide and titrating the liberated iodine against standard sodium thiosulphate; this method was also used for determining low concentrations of iron(III) present in iron(II) stock solutions. Vanadium(IV), present in vanadium(III) stock solutions, and vanadium(V) in vanadium(IV) solutions were determined spectrophotometrically. The hydrogen-ion concentration of each stock reagent solution was found by determining the total equivalent concentration of cations by ion-exchange on Amberlite IR-120 resin and subtracting the equivalent concentration of the metal cation present. The concentration of hydrogen ions in vanadium(V) stock solutions was determined by this method after reducing vanadium(V) to vanadium(IV) with sulphur dioxide and expelling the excess of this gas by boiling the solution.

Reaction mixtures for kinetic experiments were made under nitrogen and kept in a thermostat-bath. Precautions were taken to avoid ingress of air during the removal of samples for spectrophotometric analysis of reactants or products. A Unicam SP 500 spectrophotometer was used for measurement of optical densities; with the exceptions noted below these measurements were made at  $755 m\mu$  ( $\epsilon_{VO^{3+}} = 17.0$ ,  $\epsilon_{Fe^{3+}} = 0.28$ ,  $\epsilon_{Cu^{2+}} = 11.2$ ). In experiments with copper(II) present it was assumed that the concentration of this reagent did not change during the reaction when calculating the concentrations of reactants from the measured optical densities. The iron(III)-vanadium(III) reaction was shown to be stoichiometric by comparing the final concentration of vanadium(IV) with the initial concentration of iron(III) in experiments in which the latter concentration was less than the initial concentration of vanadium(III). Although aqueous perchlorate ions are slowly reduced to chloride ions by vanadium(III),<sup>6</sup> the extent of this reaction was negligible under our experimental conditions. In the series of experiments for the evaluation of  $k_1$ , the reaction solutions were found to contain not more than  $4 \times 10^{-4}M$ -chloride ion, but the principal source of this chloride was the commercial iron(II) perchlorate. Kinetic experiments performed by J. B. Stead in which the chloride-ion concentration was *ca.*  $10^{-5}M$  gave results identical with otherwise similar experiments employing  $10^{-3}M$ -chloride ion. The iron(II) perchlorate used in these comparative experiments was obtained by electrolytic reduction of iron(III) perchlorate stock solutions and was almost free from chloride. In experiments in which the initial concentration of vanadium(IV) exceeded that of vanadium(III) optical densities were measured at  $398 m\mu$  ( $\epsilon_{Fe^{3+}} \approx 0.3$ ,  $\epsilon_{V^{3+}} \approx 8.4$ ). Owing to the slight hydrolysis of  $Fe^{3+}$  and  $V^{3+}$  the extinction coefficients of iron(III) and vanadium(III) vary with hydrogen-ion concentration and temperature, and values of these extinction coefficients appropriate to the experimental conditions were used in calculating reactant concentrations from optical densities.

The electrical cell consisted of a 600-ml. beaker containing the salt-bridge solution which was of aqueous ammonium nitrate (370 g. l.<sup>-1</sup>). The beaker was closed by a bung drilled to hold five electrode vessels. Four of these were tubes 10 cm. long and 1.5 cm. in diameter and each was terminated at the lower end by a B 10 "Quickfit" socket, the wider end of which was fused to the barrel of the tube. A B10 stopper was placed loosely in each socket. The liquid junction between electrode solution and salt bridge was made in the annular space

between stopper and socket. Each of the four electrode vessels was closed at the top by a bung through which a glass tube was passed holding a bright platinum wire electrode which was wholly immersed in the electrode solution. Two of the electrode vessels ( $A_1, A_2$ ) contained mixtures of vanadium(v) and vanadium(iv) perchlorates in aqueous perchloric acid and the other two ( $C_1, C_2$ ) contained mixtures of iron(III) and iron(II) perchlorates in aqueous perchloric acid. The perchloric acid concentration was the same in all four half-cells for each set of measurements, and in all cases the ionic strength was made 3.00M by the addition of sodium perchlorate. The fifth vessel contained a saturated calomel electrode with a similar annular liquid junction. The electrical cell was immersed in a thermostat-bath and the steady e.m.f. between each of the four combinations of vanadium and iron half-cells was measured on a Cambridge bench-type pH meter. These measurements were made at each of the four temperatures and three hydrogen-ion concentrations quoted above. The e.m.f. between each of the metal-ion electrodes and the calomel electrode was also measured, but these measurements were for purposes unconnected with the subject of this paper.

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