6. *Kinetic Studies of the Oxidation of Metal Ions by Cobalt(III) in Solution in Aqueous Perchloric Acid.*

By D. R. Rosseinsky and W. C. E. Higginson.

The kinetics of the oxidation of (a) mercury(I), (b) vanadium(IV), and (c) vanadium(III) by cobalt(III) in aqueous perchloric acid have been studied over a range of temperature. The form of the rate equation in both (a) and (b) is

$$d[Co^{III}]/dt = -(k + k'/[H^+])[Co^{III}][reductant]$$

Activation energies and entropies corresponding to k and k' have been found. System (c) is more complex owing to the concurrent oxidation of vanadium(IV), a product of the initial reaction. Allowance being made for this second stage, the rate equation for the first stage is

$$d[V^{III}]/dt = -k''[Co^{III}][V^{III}]$$

k'' varies as an inverse function of $[H^+]$, but the form of this function is uncertain.

IN previous investigations of the kinetics of reduction of cobalt(III) by metal ions in aqueous perchlorate solutions, cerium(III)[1] and thallium(I)[2] have been used as the reducing agents. Here we describe kinetic experiments on the systems cobalt(III)–mercury(I), cobalt(III)–vanadium(IV) and cobalt(III)–vanadium(III) in perchlorate solutions of ionic strength 3·0. All these reactions were followed spectrophotometrically.

Cobalt(III)–Mercury(I).—The overall reaction is $2Co^{III} + Hg^I_2 \longrightarrow 2Co^{II} + 2Hg^{II}$ where Hg^I_2 represents Hg_2^{2+}, together with any ion-pairs in which Hg_2^{2+} is present. This reaction proceeds to completion as shown by estimating the concentration of mercury(I) at the end of several experiments in which either equivalent concentrations of the two reactants were used, or mercury(I) was in excess. If cobalt(III) is in large excess, the reaction is not stoicheiometric owing to the slow oxidation of water by cobalt(III). The reaction was found to be of first order in each of the reactants, plots of log $([Co^{III}]/[Hg^I_2])$ against time being linear for at least 80% of reaction (Fig. 1 *A*). The velocity constant k_a, defined by $2d[Hg^I_2]/dt = d[Co^{III}]/dt = -2k_a[Co^{III}][Hg^I_2]$, was obtained from such plots; if $[Co^{III}]_0$ and $[Hg^I_2]_0$ represent initial concentrations, then the gradient is $\{[Co^{III}]_0 - 2[Hg^I_2]_0\}k_a/2\cdot303$. Experiments, summarised in Table 1, showed that the presence of a

TABLE 1.

ClO$_4^-$	Concns. (M) H$^+$	Na$^+$	Other cations	k_a (1. mole^{-1} min.$^{-1}$)
3·0	2·00	0·96	—	12·4 (19·9°)
2·67	2·00	—	0·314M-Hg^{2+}	12·7
2·52	2·00	—	0·160M-La^{3+}	12·9
3·0	0·75	2·23	—	28·9
2·26	0·75	—	0·745M-Co^{2+}	30·0
2·52	0·75	0·79	0·473M-Hg^{2+}	30·6
2·24	0·75	—	0·743M-Mg^{2+}	31·0
1·89	0·75	—	0·373M-La^{3+}	29·4

Temp. = 20·0°. Initial concns. (1—2) $\times$ 10^{-3}M-Hg$^I_2$, and (5—6) $\times$ 10^{-3}M-Co^{III} when $[H^+]$ = 2·0M; (1—2) $\times$ 10^{-3}M-Co^{III} when $[H^+]$ = 0·75M.

large excess of either of the products, cobalt(II) or mercury(II), has little effect on the rate of reaction. The corresponding logarithmic rate plots were linear. Other experiments in this Table showed that at a given concentration of hydrogen ions the rate is affected little by varying the concentration of perchlorate ions. In contrast, the rate of oxidation of mercury(I) by thallium(III) decreases as the concentration of perchlorate ions is increased.[3]

[1] Sutcliffe and Weber, *Trans. Faraday Soc.*, 1956, **52**, 1225.
[2] Ashurst and Higginson, *J.*, 1956, 343.
[3] Armstrong and Halpern, *Canad. J. Chem.*, 1957, **35**, 1020.

This effect has been ascribed to the formation of $Hg_2ClO_4^+$. In Table 1 the total concentration of perchlorate is shown; the free concentration is probably lower in the presence of lanthanum ions. [Unpublished experiments by us on the dependence of the rate of oxidation of thallium(I) by cobalt(III) upon the concentration of perchlorate ions in the presence and in the absence of lanthanum(III) suggest that it is mainly in the form $LaClO_4^{2+}$ at high concentrations of perchlorate.] The effects of temperature and the concentration

TABLE 2.

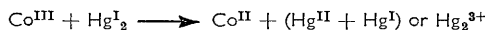| [H+] (M)	Initial concns. (M × 10³) CoIII	HgI₂	k_a (l. mole⁻¹ min.⁻¹)	[H+] (M)	Initial concns. (M × 10³) CoIII	HgI₂	k_a (l. mole⁻¹ min.⁻¹)
	At 5·0°				At 15·1°		
3·00	4·55	9·38	0·755	3·00	2·5	1·25	3·98
3·00	6·9	25·0	0·745	3·00	12·5	3·13	4·13
3·00	6·9	31·3	0·750	3·00	2·45	3·03	4·02
3·00	6·9	75·0	0·735	3·00	2·5	1·21	3·92
3·00	6·85	93·5	0·724	3·00	2·5	3·13	3·98
2·00	6·4	27·65	0·93	3·00	2·5	2·34	3·86
1·50	5·7	46·1	1·13	3·00	2·5	2·34	3·94
1·38	2·1	27·65	1·27	2·90	4·85	12·5	4·12
				2·50	4·85	10·0	4·47 [a]
	At 10·0°			2·00	2·9	6·25	5·24
2·80	4·95	46·1	1·89	1·50	2·9	6·25	6·32
2·20	4·95	46·1	2·29				
1·90	2·95	46·1	2·33		At 19·9°		
1·40	2·95	27·7	2·96	2·95	5·2	3·75	8·5
				2·50	5·15	2·21	10·4
				2·00	5·1	1·48	12·4
				1·50	3·4	1·48	14·4
				0·75	1·85	2·46	31·0
				0·75	3·4	1·23	28·3

Ionic strength = 3·00 ± 0·02. [a] Plot shown in Fig. 1*A*.

of hydrogen ions were investigated (Table 2). At a fixed temperature these results can be represented by $k_a = k_1 + k_2/[H^+]$. Arrhenius plots for k_1 and k_2 enable these constants to be expressed as
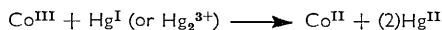
$$k_1 = \text{antilog } (17\cdot1 \pm 1\cdot2) \times \exp\{-(22{,}100 \pm 1600)/\mathbf{R}T\} \text{ l. mole}^{-1} \text{ min.}^{-1}$$

$$k_2 = \text{antilog } (23\cdot0 \pm 0\cdot9) \times \exp\{-(29{,}200 \pm 1200)/\mathbf{R}T\} \text{ min.}^{-1}$$

The most probable formulation of the mechanism of this reaction is

$$Co^{III} + Hg^I_2 \longrightarrow Co^{II} + (Hg^{II} + Hg^I) \text{ or } Hg_2^{3+}$$

followed by

$$Co^{III} + Hg^I \text{ (or } Hg_2^{3+}) \longrightarrow Co^{II} + (2)Hg^{II}$$

the second step being much more rapid than the first. Our experiments do not enable us to decide which of the two possible intermediates, Hg^I or Hg_2^{3+}, is formed. In the oxidation of mercury(I) by thallium(III), the reaction proceeds by oxidation of mercury atoms, present in equilibrium with mercury(II) and mercury(I), and the direct oxidation of mercury(I) is unimportant.[3] We can exclude the corresponding reaction route, the oxidation of mercury atoms by cobalt(III), since the rate of reaction does not show an inverse dependence on the concentration of mercury(II). By use of 10^{15} min.$^{-1}$ as the normal frequency factor, the entropy of activation of the bimolecular reaction (velocity constant k_1) between Co^{3+} and Hg_2^{2+} is found to be $9\cdot0 \pm 6$ cal. deg.$^{-1}$ mole^{-1}. The transition state corresponding to the reaction path of velocity constant k_2 presumably contains Co^{3+}, Hg_2^{2+}, and OH^-. The apparent entropy of activation of this reaction path is 37 ± 4 cal. deg.$^{-1}$ mole^{-1}.

Cobalt(III)–*Vanadium*(IV).—The reaction is $Co^{III} + V^{IV} \longrightarrow Co^{II} + V^V$ and in various experiments with vanadium(IV) present in excess, the final concentration of vanadium(V)

was found equal to the initial concentration of cobalt(III). Linear plots of log ([Co^{III}]/[V^{IV}]) against time were obtained for at least 80% of reaction (*e.g.*, Fig. 1B), showing a first-order dependence upon each of the reactants. From such plots values of $k_b = -(d[Co^{III}]/dt)/[Co^{III}][V^{IV}]$ were obtained in the usual way for a second-order reaction.

The effects of high initial concentrations of the products of reaction were investigated. Vanadium(V) (0·024M) had little effect on the rate of reaction. Cobalt(II) (*ca.* 0·1M) increased the rate of formation of vanadium(V), and chloride ions were found in the reaction mixture. Experiments showed that although solutions of vanadium(IV) in perchloric acid are fairly stable, reduction of this acid and oxidation of vanadium(IV) occur in the presence
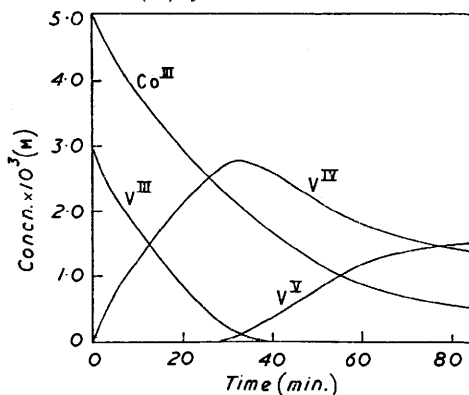
FIG. 1. *Typical kinetic plots.*

FIG. 2. *Dependence of concentrations of reactants and products upon time in the cobalt(III)–vanadium(III) system.*
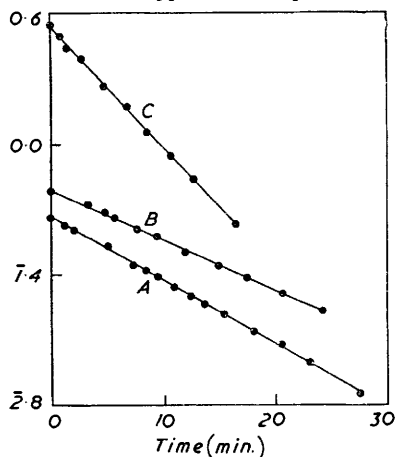
A log {[Co^{III}]/[HgI$_2$]} against *t* (min.) (Table 2).
B log {[Co^{III}]/[V^{IV}]} against *t* (min.) (Table 3).
C log {[Co^{III}]/($k_c k_b^{-1}$[V^{III}] + [V^{IV}])} against *t* (min.) (Table 4).

Initial concentrations of reagents are shown in the Tables indicated.

Initial concns.: 4·99 × 10^{-3}M-Co^{III}; 2·93 × 10^{-3}M-V^{III}; 3 × 10^{-5}M-V^{IV}; 2·96M-H$^+$; ionic strength 3·0; temp. 5·0°.

of high concentrations of cobalt(II). In 0·75M-perchloric acid at ionic strength 3·0 the half-life of 0·0053M-vanadium(IV) was 36 min. at 20° in the presence of 0·54M-cobalt(II). In the cobalt(III)–vanadium(IV) reaction solutions, with little cobalt(II) initially present,

TABLE 3.

[H$^+$] (M)	Initial concns. (M × 10^3) Co^{III}	V^{IV}	k_b (l. mole^{-1} min.$^{-1}$)	[H$^+$] (M)	Initial concns. (M × 10^3) Co^{III}	V^{IV}	k_b (l. mole^{-1} min.$^{-1}$)
	At −2·1°				At 15·0°		
2·93	4·79	20·6	4·6	2·95	2·75	8·90	35·9
2·00	4·78	17·15	6·0	2·50	2·74	8·90	37·8
1·00	4·77	13·7	12·8	2·00	2·72	5·34	45·0
0·50	2·38	10·3	21·6	1·50	2·71	3·56	52·2
	At 5·0°				At 20·0°		
2·94	6·49	10·7	9·6	2·94	2·50	7·00	57·1
2·00	6·42	10·7	12·2 ^{a}	2·70	2·75	5·34	61·5
1·50	3·20	8·90	15·4	2·20	2·75	3·56	71·2
0·75	3·19	5·34	28·0	1·80	1·38	1·78	84·0
0·75	3·14	5·34	25·2 ^{b}				
0·75	3·16	5·34	26·2 ^{c}				
	At 10·0°						
2·92	3·18	8·90	17·3				
2·50	3·18	7·12	19·1				
2·00	3·17	5·34	21·7				
1·50	3·16	3·56	24·6				

^{a} Plot shown in Fig. 1B. ^{b} Initial [V^V] = 0·024M. ^{c} Ionic strength made 3·0 by addition of La(ClO$_4$)$_3$; final concn. of La(ClO$_4$)$_3$ = 0·37M.

C

tests for chloride ions showed that none was formed. Together with the observation that the cobalt(III)–vanadium(IV) reaction is stoicheiometric under these conditions, this shows that the low concentrations of cobalt(II) formed are insufficient to cause appreciable loss of vanadium(IV) by catalysing its oxidation by perchloric acid. At a fixed temperature the results summarised in Table 3 can be expressed in the form $k_b = k_3 + k_4/[H^+]$. Arrhenius plots for k_3 and k_4 enable these constants to be expressed as

$$k_3 = \text{antilog} \ (17.7 \pm 2.0) \times \exp \ \{-(21{,}800 \pm 2700)/\boldsymbol{R}T\} \ \text{l. mole}^{-1} \ \text{min.}^{-1}$$
$$k_4 = \text{antilog} \ (13.8 \pm 1.3) \times \exp \ \{-(15{,}900 \pm 1300)/\boldsymbol{R}T\} \ \text{min.}^{-1}$$

Although the formation of intermediates of abnormal oxidation state is improbable in this reaction, unlike the oxidation of thallium(I) or mercury(I), the stable oxidised and reduced forms of vanadium involved in this reaction differ in their degree of hydrolysis. It is not clear from our experiments whether VO^{2+} is oxidised to VO^{3+} which subsequently undergoes rapid hydrolysis to VO_2^+, or whether in the transition complex some degree of hydrolysis has already occurred. The reaction path corresponding to k_3 does not incorporate hydroxyl ions in the transition complex, but this does not rule out the possibility of a spread of charge within the complex and its associated water molecules so that there is incipient formation of solvated protons. From the pre-exponential terms in k_3 and k_4 we calculate entropies of activation of 12 ± 9 and -5 ± 6 cal. deg.$^{-1}$ mole^{-1} respectively.

Cobalt(III)–*Vanadium*(III).—Fig. 2 shows the concentrations of cobalt(III), vanadium(III), vanadium(IV), and vanadium(V) at various times in a solution in which cobalt(III) was present in excess of vanadium(III). Until the concentration of vanadium(III) falls to about one tenth of its original value ($t = ca.$ 28 min.) the overall reaction is simply the oxidation of vanadium(III) to vanadium(IV). At this point vanadium(V) appears, and from $t = ca.$ 37 min., when the concentration of vanadium(III) becomes zero, the reaction follows the course expected of the cobalt(III)–vanadium(IV) system. However, from this and other preliminary experiments we deduced that the rates of the cobalt(III)–vanadium(III) and cobalt(III)–vanadium(IV) reactions are very similar at the same temperature and concentration of hydrogen ions. Since a small concentration of vanadium(IV) was present initially, cobalt(III) is being reduced by vanadium(IV) throughout the reaction, as well as by vanadium(III) during the first half-hour. As the reaction proceeds, oxidation of vanadium(IV) contributes an increasing proportion of the total reduction of cobalt(III), but the product of this oxidation, vanadium(V), does not appear in measurable concentrations until virtually all the vanadium(III) has disappeared, on account of the rapid reaction $V^{III} + V^V \longrightarrow 2V^{IV}$. At 5°, 2.96M-hydrogen ions, and ionic strength 3.0 the second-order velocity constant for this reaction is $ca.$ 5×10^3 l. mole^{-1} min.$^{-1}$.[4] A simple stationary-state calculation shows that in the experiment referred to above, the concentration of vanadium(V) is $ca.$ 5×10^{-5}M when 90% of the vanadium(III) has been oxidised. Provided that vanadium(III) is initially present in excess of cobalt(III), vanadium(V) cannot accumulate in significant concentrations, and similar calculations show that the maximum stationary-state concentration of this ion does not exceed $ca.$ 2×10^{-6}M in any of the experiments summarised in Table 4. Under these conditions, the rate constant of the reaction between vanadium(III) and vanadium(V) does not enter into the rate equation for the system and we have

$$-d[Co^{III}]/dt = k_c[Co^{III}][V^{III}] + k_b[Co^{III}][V^{IV}]$$

On integration we obtain

$$\ln \ \{[Co^{III}]/(k_c k_b^{-1}[V^{III}] + [V^{IV}])\} =$$
$$\{k_c([Co^{III}]_0 - [V^{III}]_0) - k_b([Co^{III}]_0 + [V^{IV}]_0)\}t - \ln \ \{(k_c[V^{III}]_0 + k_b[V^{IV}]_0)/k_b[Co^{III}]_0\}$$

where subscripts zero denote initial concentrations, k_b is the apparent bimolecular rate

[4] Sykes, Thesis, Manchester, 1958.

constant at a given hydrogen-ion concentration, temperature, and ionic strength for the cobalt(III)–vanadium(IV) reaction, and k_c is the corresponding rate constant for the cobalt(III)–vanadium(III) reaction. In plotting the left-hand side of this equation against t it is necessary to assume a value of k_c/k_b, since k_c is unknown. Corresponding values of k_b and k_c proved to be very similar, so we initially assumed their ratio to be 1·00. From the gradient of the plot obtained with this assumption, k_c was found, k_b being known from the experiments described above on the cobalt(III)–vanadium(IV) system. Thus an improved value of k_c/k_b was obtained and the results replotted. By repeating this procedure a few times, a value of k_c can be obtained equal to that used in evaluating the left-hand side of the equation. A typical plot is shown in Fig. 1C.

TABLE 4.

[H⁺] (M)	CoᴵᴵᴵInitial concns. (M × 10³)	Vᴵᴵᴵ	Vᴵⱽ	k_c (l. mole⁻¹ min.⁻¹)	[H⁺] (M)	CoᴵᴵᴵInitial concns. (M × 10³)	Vᴵᴵᴵ	Vᴵⱽ	k_c (l. mole⁻¹ min.⁻¹)
		At −2·1°					At 5·0°		
2·91	3·15	13·8	0·84	3·4	2·89	3·12	13·1	1·53	8·1
2·00	3·14	13·7	0·89	4·7	2·50	3·12	13·1	1·53	9·3 ᵃ
1·00	3·13	13·3	1·34	8·0	2·00	1·56	6·55	0·76	10·0
0·50	3·13	13·3	1·39	20·5	1·50	1·56	6·55	0·76	12·1
		At 0·0°					At 7·5°		
2·91	3·13	13·2	1·39	4·0	2·95	1·18	5·1	0·21	12·0
2·00	3·13	13·2	1·44	6·1	2·50	1·18	5·1	0·21	13·8
1·50	3·12	13·2	1·49	6·9	2·20	0·59	2·55	0·10	18·0
1·00	3·12	13·1	1·49	11·5	1·80	0·59	2·55	0·10	19·6
		At 2·5°							
2·91	3·14	13·1	1·54	5·6		ᵃ Plot shown in Fig. 1C.			
2·50	3·13	13·1	1·53	6·0					
2·00	3·13	13·1	1·53	7·4					
1·50	3·12	13·1	1·53	9·5					

The proportion of cobalt(III) reduced by vanadium(IV) in the cobalt(III)–vanadium(III) system can be made small by using a large excess of vanadium(III) over cobalt(III) and a low initial concentration of vanadium(IV). In this way more precise values of k_c should be obtained. However, it was convenient to follow the reaction spectrophotometrically at 400 mμ at which wavelength both cobalt(III) ($\varepsilon = 42\cdot5$) and vanadium(III) ($\varepsilon = 8\cdot3$) absorb light. Consequently, too large an excess of vanadium(III) would reduce the relative change in optical density in an experiment and so increase the error in determining the concentrations of reactants. Also, at high concentrations of vanadium(III) the rate of reaction becomes too rapid to be followed satisfactorily by our technique. As a compromise, vanadium(III) was generally used in about four-fold excess of cobalt(III).

Plots of k_c against $1/[\mathrm{H^+}]$ at various temperatures, for the experiments summarised in Table 4, suggest that $k_c = k_4 + k_5/[\mathrm{H^+}] + k_6/[\mathrm{H^+}]^2$, although evidence for a term in k_6 comes only from the curvature of the plot at −2·1°, at which temperature it was possible to cover a wider range of concentrations of hydrogen ions than at the other temperatures. It is evident that we cannot obtain satisfactory values of the constants k_4, k_5, and k_6 from these results. In view of the much lower oxidation–reduction potential of the $\mathrm{V^{3+}/VO^{2+}}$ couple (0·36 v) compared with the $\mathrm{VO^{2+}/VO_2^+}$ couple (1·00 v), it is interesting that the rate of oxidation of vanadium(III) by cobalt(III) is very similar to the corresponding rate of oxidation of vanadium(IV) under similar conditions.

EXPERIMENTAL

Except as described below, solutions of metal perchlorates were prepared from " AnalaR " reagents by precipitating the oxide or hydroxide, followed by solution in aqueous perchloric acid or by double decomposition. Cobalt(III) perchlorate was prepared by electrolytic oxidation

of acidified cobalt(II) perchlorate solutions using platinum electrodes, as previously described.[5] The stock solutions, containing 0·1M-cobalt(III) and *ca.* 6M-perchloric acid were kept at $-30°$. The cobalt(II) perchlorate solutions used in this preparation were obtained by dissolving Johnson and Matthey's high-purity cobalt sponge in an excess of aqueous perchloric acid. Owing to the presence of chloride ions, such solutions were unsuitable for use in kinetic experiments. For this purpose, the chloride ions were removed by electrolytic oxidation and the solution was heated to 100° to decompose cobalt(III). Vanadium(V) perchlorate solution was prepared by dissolving vanadium pentoxide in excess of aqueous perchloric acid; the pentoxide was obtained by heating ammonium vanadate at 500° for *ca.* 5 hr. Vanadium(IV) and vanadium(III) perchlorate solutions in excess of aqueous perchloric acid were prepared by electrolytic reduction of vanadium(V) perchlorate solution. The vanadium(III) perchlorate stock solution was kept under nitrogen at 0° to prevent oxidation by oxygen and by perchloric acid;[6] these solutions were tested for chloride ions, which were found to be absent. Mercury(I) perchlorate solution was prepared by shaking acidified mercury(II) perchlorate solution with excess of metallic mercury for 24 hr. All stock solutions were standardised by appropriate methods and the concentrations of other ions likely to be present, *e.g.*, cobalt(II) in cobalt(III) solutions, vanadium(IV) in vanadium(III) solutions, were also found.

Solutions for kinetic experiments were made with thermostatic control. Except where shown otherwise in the Tables, the ionic strength was made $3·00 \pm 0·02$ by the addition of sodium perchlorate solution. In most experiments a part of the solution was rapidly transferred to a 1 or 4 cm. optical cell placed in the cell-compartment (thermostat) of a Unicam SP.500 spectrophotometer. The reactions were then followed by measurements of the optical density of the solutions at appropriate wavelengths. Except in experiments in which a large excess of cobalt(II) was present the cobalt(III)–mercury(I) reaction was followed at 603 mμ ($\varepsilon_{Co^{3+}} = 36·4$), a small correction for cobalt(II) being applied. With excess of cobalt(II) present the wavelength used was 236·5 mμ ($\varepsilon_{Hg_2^{2+}} = 2·78 \times 10^4$), corrections being applied for absorption by mercury(II), cobalt(II), and cobalt(III). In these experiments the reaction solutions were kept in a thermostat and samples were withdrawn at intervals, diluted 100-fold with 2M-perchloric acid, and transferred to an optical cell. Measurements at 236·5 mμ were also made at the conclusion of other experiments to determine whether the reaction was quantitative. The cobalt(III)–vanadium(IV) and cobalt(III)–vanadium(III) reactions were followed at 400 mμ ($\varepsilon_{Co^{3+}} = 42·5$, $\varepsilon_{Co^{2+}} = 0·33$, $\varepsilon_{V^{3+}} = 8·3$, $\varepsilon_{VO^{2+}} = 0$, $\varepsilon_{VO^{2+}} = 12·0$). Stoicheiometry of these reactions was checked by measurements at 755 mμ ($\varepsilon_{VO_2^+} = 17·0$) and by measurements at 401 mμ when reaction was complete. Measurements at 755 mμ were also made in following the oxidation of vanadium(IV) by perchlorate ions in the presence of cobalt(II) as catalyst.

It having been established that these oxidations by cobalt(III) were quantitative under the conditions cited, the concentrations of reactants at various times could be calculated from the corresponding optical densities at the wavelengths stated above. For the reactions of cobalt(III) with mercury(I) and vanadium(IV) the velocity constants k_a and k_b, respectively, were obtained from logarithmic plots of the ratio of the concentrations of reactants against time. We estimate the error of individual values of these constants as $\pm 4\%$. In the cobalt(III)–vanadium(III) system, a more complex logarithmic function of metal-ion concentrations was plotted against time as described earlier in this paper. Values of k_b at $-2·1°$ and 5° which were used in evaluating this function were those obtained in the experiments on the cobalt(III)–vanadium(IV) reaction. Values of k_b at 0°, 2·5° and 7·5° were calculated from the corresponding values of k_3 and k_4, these being obtained by interpolation from the appropriate Arrhenius plots. We estimate the error in individual values of k_c to be *ca.* $\pm 8\%$.

THE UNIVERSITY, MANCHESTER 13.

[5] Hargreaves and Sutcliffe, *Trans. Faraday Soc.,* 1955, **51**, 786.
[6] King and Garner, *J. Phys. Chem.,* 1954, **58**, 29.