# 70. *The Kinetics of the Reaction between Cobalt*(III) *and Thallium*(I) *in Aqueous Perchloric Acid.*

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Kinetic experiments have shown that the principal reaction path in the reduction of cobalt(III) by thallium(I) in aqueous perchloric acid is independent of the hydrogen-ion concentration under the conditions chosen. The activation energy and temperature-independent factor have been found. The catalysis of this system by sulphate ions has been studied briefly.

IN solution in dilute aqueous perchloric acid, cobalt(III) is reduced by thallium(I), 2Co(III) + Tl(I) ⟶ 2Co(II) + Tl(III), and the kinetics of this reaction can be followed conveniently by titration of cobalt(III) in samples taken at appropriate times. Thallium(III) reacts slowly with many reducing agents, so the estimation of cobalt(III) in reaction solutions is comparatively simple. The concentration conditions for kinetic experiments must be chosen carefully since cobalt(III) decomposes in solution with the formation of cobalt(II) and oxygen.[1] Under conditions similar to those in our experiments, this reaction is of between first and second order in cobalt(III),[2] while in the presence of thallium(I) our preliminary experiments showed that the rate of disappearance of cobalt(III) was of first order in both species. By use of the lowest initial concentrations of cobalt(III) compatible with sufficiently accurate analysis for our purposes, and relatively high thallium(I) concentrations, the rate of the decomposition can be reduced to less than 10% of the total rate of disappearance of cobalt(III) in most experiments, but the study of the cobalt(III)–thallium(I) reaction is thus restricted to experiments in which thallium(I) is in considerable excess. Initial concentrations were $0{\cdot}74$—$3{\cdot}1 \times 10^{-3}$M-cobalt(III) and $9{\cdot}7$—$65{\cdot}0 \times 10^{-3}$M-thallium(I).

The influence of the products upon the rate of reaction was investigated. Thallium(III), in concentration 15 times greater than that formed by the reaction, caused a slight increase in rate. This effect was not studied further but may have been due to the presence of thallium(I) as impurity in a thallium(III) stock solution. Cobalt(II), in relatively high concentration, caused a decrease in rate as shown in Fig. 1, in which concentrations of cobalt(III) are plotted against time for two experiments at 25°. In this respect the reaction resembles the oxidation of iron(II) by thallium(III), in which iron(III) exerts a retarding effect.[3] From this qualitative evidence we conclude that the reaction mechanism can be represented by

$$\mathrm{Co(III)} + \mathrm{Tl(I)} \longrightarrow \mathrm{Co(II)} + \mathrm{Tl(II)} \quad \ldots \ldots \quad (1)$$

$$\mathrm{Co(II)} + \mathrm{Tl(II)} \longrightarrow \mathrm{Co(III)} + \mathrm{Tl(I)} \quad \ldots \ldots \quad (-1)$$

$$\mathrm{Co(III)} + \mathrm{Tl(II)} \longrightarrow \mathrm{Co(II)} + \mathrm{Tl(III)} \quad \ldots \ldots \quad (2)$$

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[1] Bawn and White, *J.*, 1951, 331.

[2] Baxendale and Wells, unpublished work.

[3] Ashurst and Higginson, *J.*, 1953, 3044.

the retardation by cobalt(II) occurring through reaction (—1). This conclusion is more tentative than that reached in studying the iron(II)–thallium(III) reaction, where it was possible to evaluate the ratio of the rate constants for the reactions : Fe(III) + Tl(II) $\longrightarrow$ Fe(II) + Tl(III), and Fe(II) + Tl(II) $\longrightarrow$ Fe(III) + Tl(I), which correspond to (—1) and (2) above. In the cobalt(III)–thallium(I) system, however, our results are not sufficiently accurate to enable the ratio of the rate constants of reactions (—1) and (2) to be found.

Cobalt(II) occurs as an impurity in the cobalt(III) sulphate used, and in most experiments the initial cobalt(II) concentration was between 25% and 50% of the total cobalt concentration, *i.e.*, of the order $10^{-3}$M-cobalt(II). Variations of this magnitude in the initial cobalt(II) concentration caused no systematic change in the rate of reaction and, since the rate is only halved with 25 × $10^{-3}$M-cobalt(II), we conclude that with *ca.* $10^{-3}$M-cobalt(II) the retarding effect can be neglected. Consequently, the rate of disappearance of cobalt(III) depends only on reaction (1) at low cobalt(II) concentrations, and the rate constant for this reaction, $k_1$, defined by $-d[Co(III)]/dt = 2k_1[Co(III)][Tl(I)]$, can be evaluated. The dependence of $k_1$ upon the hydrogen-ion concentration over the range 0·25—2·50M was investigated at 0°, 7·5°, 15°, and 25°, at ionic strength 2·70. In all these experiments, summarised in Table 1, thallium(I) was in considerable excess,

FIG. 1. *Initial concns.:* (●) 65·0 × $10^{-3}$M-*thallium*(I), 2·50M-*hydrogen-ion, and* 1·12 × $10^{-3}$M-*cobalt*(II) ; (▲) 21·5 × $10^{-3}$M-*cobalt*(II).

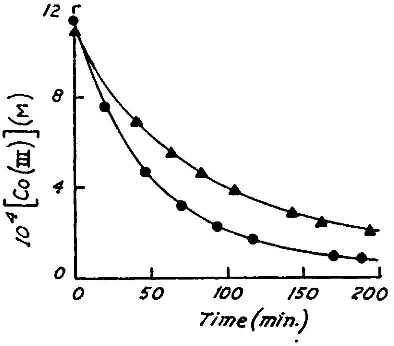


FIG. 2.

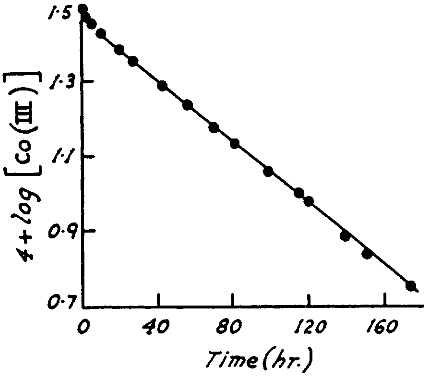


TABLE 1.

| Expt. | 10³ × Initial concns. (M)<br>[H⁺] (M) | Co(III) | Co(II) | Tl(I) | 100$k_1$ (l. mole⁻¹ min.⁻¹) |
|---|---|---|---|---|---|
| | | At 0° | | | |
| 16 | 2·00 | 1·25 | 0·47 | 23·3 | 0·316 |
| 17 | 1·00 | 1·24 | 0·48 | 29·2 | 0·344 |
| 18 | 1·00 | 3·11 | 1·05 | 29·9 | 0·272 |
| 19 | 0·52 | 3·14 | 1·02 | 29·9 | 0·270 |
| 20 | 0·52 | 1·23 | 0·48 | 29·2 | 0·320 |
| 21 | 0·37 | 1·23 | 0·49 | 29·2 | 0·378 |
| 22 | 0·25 | 1·23 | 0·49 | 29·2 | 0·468 |
| | | At 7·5° | | | |
| 23 | 2·00 | 1·26 | 0·46 | 38·9 | 1·07 |
| 24 | 1·00 | 1·25 | 0·47 | 38·9 | 1·05 |
| 25 | 0·52 | 1·25 | 0·47 | 38·9 | 1·10 |
| 26 | 0·30 | 1·24 | 0·47 | 38·9 | 1·14 |
| | | At 25° | | | |
| 14 | 2·00 | 1·19 | 0·53 | 9·7 | 15·4 |
| 15 [b] | 2·00 | 1·19 | 0·53 | 9·7 | 18·2 |
| 40 | 2·00 | 1·13 | 0·59 | 29·2 | 15·7 |
| 41 | 0·70 | 1·08 | 0·64 | 29·2 | 16·0 |
| 42 | 0·37 | 0·99 | 0·73 | 38·9 | 17·0 |
| 43 | 0·25 | 0·99 | 0·73 | 38·9 | 19·0 |
| | | At 15° | | | |
| 27 | 2·50 | 0·91 | 0·61 | 22·4 | 4·47 |
| 12 | 2·00 | 1·93 | 1·51 | 25·2 | 4·34 |
| 13 [a] | 2·00 | 1·94 | 1·49 | 25·2 | 5·02 |
| 28 | 2·00 | 0·96 | 0·56 | 48·2 | 4·54 |
| 29 | 1·50 | 0·98 | 0·54 | 48·2 | 4·61 |
| 30 | 1·00 | 1·00 | 0·52 | 48·2 | 4·74 |
| 31 | 0·70 | 1·45 | 1·45 | 47·7 | 5·39 |
| 32 | 0·50 | 0·98 | 0·53 | 48·4 | 5·21 |
| 33 | 0·50 | 1·08 | 0·74 | 47·7 | 5·16 |
| 34 | 0·50 | 1·08 | 0·74 | 47·7 | 5·21 |
| 35 | 0·37 | 0·84 | 0·77 | 48·2 | 6·10 |
| 36 | 0·25 | 0·83 | 0·69 | 48·2 | 7·08 |
| 37 | 0·25 | 0·92 | 0·83 | 47·7 | 6·74 |
| 38 | 0·10 | 0·74 | 0·87 | 48·2 | 8·46 |
| 39 | 0·10 | 0·95 | 0·80 | 47·7 | 8·19 |

[a] [Tl(III)] = 0·0157M.
[b] [Tl(III)] = 0·0079M.

and plots of log Co(III) against time were nearly linear. Fig. 2 shows such a plot for Expt. no. 19. As can be seen from this plot, the initial rate of disappearance of cobalt(III) was more rapid than would be observed if first-order kinetics held throughout. This effect was particularly noticeable in experiments at lower hydrogen-ion concentrations, and we think it may be caused by the reaction of dimeric cobalt(III) ions which are probably present under these conditions. Reference to Table 1 shows that at each temperature the variation in rate constant with hydrogen-ion concentration is comparatively small, showing that a reaction path independent of the hydrogen-ion concentration predominates under these conditions. Although there is no accurate measurement of the first acidity constant of the cobalt(III) ion, $K = [CoOH^{2+}][H^+]/[Co^{3+}]$, Baxendale and Wells[2] conclude that $K \leqslant 5 \times 10^{-3}$ mole l.$^{-1}$, and hence in our experiments the extent of hydrolysis is small. We have therefore assumed that the variation of $k_1$ at a given temperature can be represented by $k_1 = k_1' + k_1''K/[H^+]$. Our results are not sufficiently accurate to provide a good test of this assumption, but as shown in Fig. 3, in which $k_1$ is plotted against $1/[H^+]$ for each temperature, a reasonably satisfactory extrapolation to infinite hydrogen-ion concentration is obtained, allowing $k_1'$ to be determined. Values of $100k_1'$ deduced from these plots are 0·25 ± 0·05, 1·04 ± 0·10, 4·1 ± 0·4, and 15·0 ± 1·5 l. mole$^{-1}$ min.$^{-1}$ at 0°, 7·5°, 15°, and 25°. We do not consider that good values of $Kk_1''$ can be obtained from the slopes of these plots. However, a value of $5 \times 10^{-3}$ mole l.$^{-1}$ being assumed for $K$, $k_1''$ is of the order unity (l. mole$^{-1}$ min.$^{-1}$ units) at 15°.

FIG. 3.

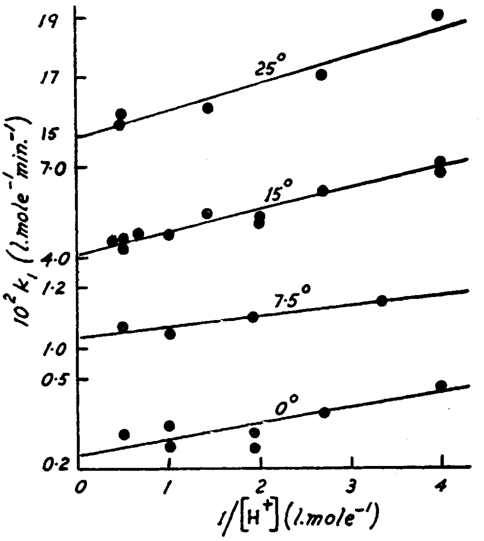
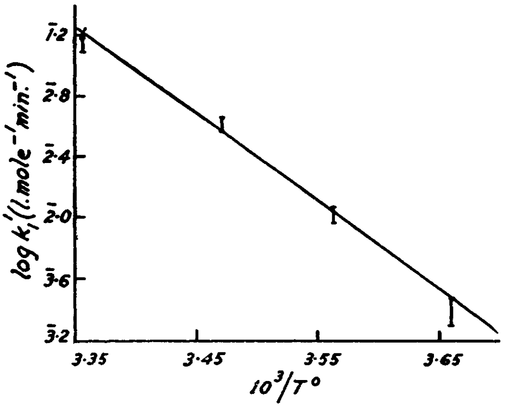


FIG. 4.



For each experiment in Table 1 a control was done simultaneously in the absence of thallium(I), the same freshly prepared cobalt(III) perchlorate solution being used, and other conditions being similar. We hoped to use the rate of the cobalt(III) decomposition reaction found in this way to correct the rate of disappearance of cobalt(III) in the presence of thallium(I) to give the true rate of the cobalt(III)–thallium(I) reaction. Under our conditions the cobalt(III) decomposition reaction is poorly reproducible and so we do not feel justified in making this correction. The control experiments show, however, that at hydrogen-ion concentrations of 0·5M or greater at 7·5°, 15°, and 25° the decomposition reaction contributes less than 10% to the total rate. At 0° the corresponding proportion is 15%. The values of $k_1'$ quoted above may be too large by up to these amounts; for our purposes this error is not important. Fig. 4 shows the Arrhenius plot for $k_1'$ (in l. mole$^{-1}$ min.$^{-1}$) from which we find an activation energy of 26·4 ± 2·0 kcal. mole$^{-1}$, and a temperature-independent factor of $10^{(18 \cdot 6 \pm 1 \cdot 5)}$ l. mole$^{-1}$ min.$^{-1}$.

*Catalysis in Sulphate Solutions.*—In the presence of sulphate ions the rate of reduction of cobalt(III) by thallium(I) is increased and this catalysis was investigated briefly in experiments at 15° and ionic strength 2·70, summarised in Table 2. Most of these experiments were done at 2·50M-hydrogen-ion concentration, but in two cases this was *ca.* 1·25M. Our experiments in perchloric acid solutions show that this change in the hydrogen-ion concentration has a negligible effect on the rate of reaction. In the calculation of the sulphate- and bisulphate-ion concentrations, a value of 0·077 mole l.$^{-1}$ was used for the second dissociation constant of sulphuric acid (see p. 349). At the concentrations of sulphate ions present in these experiments it seemed probable that a considerable proportion of the cobalt(III) might be present as a complex cation, $CoSO_4^+$, but we have assumed that higher sulphate complexes are not present in significant concentrations. Accordingly we may write,

TABLE 2.

$[Tl(I)] = 0{\cdot}0482$M. Temp. = 15°.

| | | Initial concns. (M × $10^{-3}$) | | | | |
|---|---|---|---|---|---|---|
| Expt. | $[H^+]$ (M) | Co(III) | Co(II) | $10^3[HSO_4^-]$ (M) | $10^4\,[SO_4^{2-}]$ (M) | $100k_s$ (l. mole$^{-1}$ min.$^{-1}$) |
| 44 | 2·50 | 1·06 | 0·45 | 2·7 | 0·83 | 4·26 |
| 45 | 2·48 | 1·24 | 0·48 | 121 | 37 | 5·34 |
| 46 | 2·49 | 1·26 | 0·46 | 246 | 76 | 8·00 |
| 47 | 2·48 | 1·06 | 0·45 | 272 | 84 | 7·87 |
| 48 | 2·49 | 1·18 | 0·57 | 490 | 152 | 11·1 |
| 49 | 2·49 | 1·08 | 0·43 | 514 | 159 | 10·6 |
| 50 | 2·49 | 1·05 | 0·46 | 757 | 234 | 12·6 |
| 51 | 2·50 | 1·03 | 0·48 | 1006 | 310 | 14·3 |
| 52 | 1·24 | 1·21 | 0·54 | 494 | 307 | 13·7 |
| 53 | 2·49 | 1·06 | 20·4 | 514 | 159 | 10·3 |
| 54 | 1·29 | 1·14 | 0·58 | 993 | 592 | 20·0 |

$$k_s[\mathrm{Co(III)}] = k_1[\mathrm{Co}^{3+}] + k_A[\mathrm{CoSO_4}^+] + k_B[\mathrm{Co}^{3+}][\mathrm{HSO_4}^-] \quad . \quad . \quad . \quad (3)$$

where $k_s$ is the velocity constant observed in a solution containing given concentrations of sulphate and bisulphate ions, and $[\mathrm{Co(III)}] = [\mathrm{Co}^{3+}] + [\mathrm{CoSO_4}^+]$. $k_1$ has been defined previously, and $k_A$ and $k_B$ are reaction velocity constants for reaction paths involving the formation of transition complexes containing $Co^{3+}$, $SO_4^{2-}$, and $Tl^+$, and $Co^{3+}$, $HSO_4^-$, and $Tl^+$ respectively. Introducing the second dissociation constant of sulphuric acid, $K_2$, and the association constant $K_A = [\mathrm{CoSO_4}^+]/[\mathrm{Co}^{3+}]\,[\mathrm{SO_4}^{2-}]$, we have

$$k_s = k_1/(1 + K_A[\mathrm{SO_4}^{2-}]) + k_AK_A[\mathrm{SO_4}^{2-}]/(1 + K_A[\mathrm{SO_4}^{2-}]) \\ + k_B[\mathrm{H}^+][\mathrm{SO_4}^{2-}]/K_2(1 + K_A[\mathrm{SO_4}^{2-}]) \quad . \quad . \quad (4)$$

whence, by rearranging, we have,

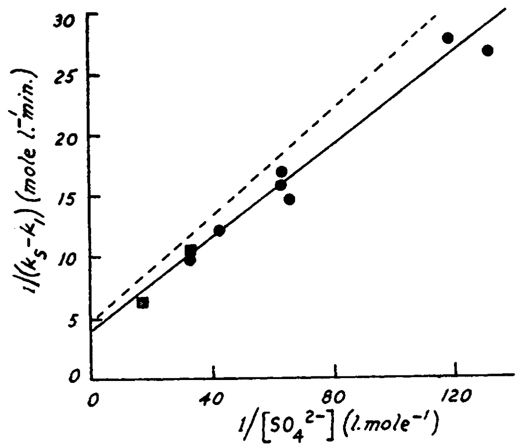
$$1/(k_s - k_1) = (1 + 1/K_A[\mathrm{SO_4}^{2-}])/\{k_A + (k_B[\mathrm{H}^+]/K_AK_2) - k_1\} \quad . \quad . \quad (5)$$

If the catalytic effect of sulphate can be treated in this way, a plot of $1/(k_s - k_1)$ as ordinate against $1/[\mathrm{SO_4}^{2-}]$ should be linear, and enable the reciprocal of the term in the braces in (5) to be evaluated as the intercept on the *y*-axis, and $K_A$ from this intercept and the gradient. Fig. 5 shows this plot based on the results of experiments in Table 2; the value of $k_1$ is taken from Expt. 44 in which the sulphate- and bisulphate-ion concentrations are relatively small. The plot does not include Expt. 45 which lies well off the full line. The error on this point is large and we do not consider that this deviation provides evidence against the validity of equation (5) which appears to be confirmed by the points from the remaining experiments. We find $(k_A + k_B[\mathrm{H}^+]/K_AK_2) = 0{\cdot}29 \pm 0{\cdot}06$ l. mole$^{-1}$ min.$^{-1}$, and $K_A = 22 \pm 7$ l. mole$^{-1}$.

It is evident from equation (5) that, unless $k_B$ is zero, points from experiments at lower hydrogen-ion concentrations should lie on lines of greater intercept and gradient. Thus if $k_B$ has a value of 0·05 l.$^2$ mole$^{-2}$ min.$^{-1}$, the points corresponding to Expts. 52 and 54 (shown as squares in Fig. 5) should lie on the broken line instead of the full line drawn through the remaining points, all of which correspond to experiments at a higher hydrogen-ion concentration. However, the squares lie fairly close to the full line, but are just outside their estimated limits of error from the broken line. We conclude that $k_B$ is not greater than 0·05 l.$^2$ mole$^{-2}$ min.$^{-1}$ and is probably considerably less. From this value of the upper limit for $k_B$ the rate constant observed at 15° would be about four times greater in a 2·70M-bisulphate-ion solution, if it were possible to exclude sulphate ions, than in the 2·70M-perchlorate-ion solutions used in experiments in the absence of other anions. A value of zero for $k_B$ implies that the replacement of perchlorate ions by equal concentrations of bisulphate ions has no effect on the rate of reaction. If $k_B$ is zero, $k_A = 0{\cdot}29 \pm 0{\cdot}06$ l. mole$^{-1}$ min.$^{-1}$, and if $k_B = 0{\cdot}05$ l.$^2$ mole$^{-2}$ min.$^{-1}$, $k_A = 0{\cdot}22 \pm 0{\cdot}06$ l. mole$^{-1}$ min.$^{-1}$. It is clear that the catalysis observed on addition of sulphate ions is largely due to the fairly small concentrations of free sulphate ions, and that there is little increase in rate caused by the much larger concentrations of bisulphate ions inevitably present at the hydrogen-ion concentrations employed in our experiments. In the presence of sulphate ions it is noteworthy that the back-reaction, (—1), is relatively unimportant even at high cobalt(II) concentrations (compare Expts. 49 and 53).

*Discussion.*—In many oxidation–reduction reactions between simple metal ions, kinetic experiments show marked catalysis by negative ions of small radius, the dependence of the reaction rate upon the inverse hydrogen-ion concentration frequently encountered being usually regarded as evidence for catalysis by hydroxyl ions. The probable rôle of such negative ions in reducing the repulsive forces between the metal cations, thus permitting their closer approach in the transition state and facilitating electron-transfer, has been emphasised.[4] In the reaction between cobalt(III) and thallium(I) our experiments show that the principal reaction path is independent of the hydrogen-ion concentration in perchlorate-ion solutions of hydrogen-ion concentration 0·25—2·50M, in contrast to reactions such as Np(IV) + Fe(III) $\longrightarrow$ Np(V) + Fe(II),[5] and V(III) + Fe(III) $\longrightarrow$ V(IV) + Fe(II).[6] In perchloric acid solutions there is evidence only for reaction paths showing dependence on an inverse function of the hydrogen-ion concentration in both these reactions. The charge products of the reacting metal ions, and hence the electrostatic repulsion between them at a given separation, are much greater in these two reactions than in the cobalt(III)–thallium(I) reaction which is seen to be a more favourable case for observing a reaction path which does not involve small anions. Even in this case it is possible that perchlorate ions or, on account of the favourable polarity of their oxygen atoms, water molecules may act as bridging groups and reduce the considerable repulsion energy between the metal ions at distances where the probability of electron-transfer is significant. Unfortunately, our kinetic experiments cannot give any direct information

FIG. 5.



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[4] Zwolinski, Marcus, and Eyring, *Chem. Rev.*, 1955, **55**, 157.
[5] Huizenga and Magnusson, *J. Amer. Chem. Soc.*, 1951, **73**, 3202.
[6] Higginson and Hughes, unpublished work.

regarding the incorporation of water molecules or perchlorate ions in the transition state corresponding to the hydrogen-ion-independent reaction path. However, the entropy of activation of this reaction can be calculated as 22 ± 7 cal. deg.$^{-1}$ mole$^{-1}$ from the temperature-independent factor of $10^{(18\cdot6 \pm 1\cdot5)}$ l. mole$^{-1}$ min.$^{-1}$ by using a value of $6 \times 10^{13}$ l. mole$^{-1}$ min.$^{-1}$ as the normal frequency factor. For a reaction between ions of like charge this large positive entropy of activation seems surprising but, if the transition complex includes one or more perchlorate anions, the loss of charge consequent on its formation should result in a positive entropy change owing to the release of water of solvation. Electron-transfer reactions have been classified according to whether their entropy of activation is positive or negative,[7] and in all the aqueous reactions cited where this entropy is positive the formation of the transition complex is known to involve a net loss of charge. In the reactions between two metal cations this loss of charge occurs through the incorporation of one or more negative ions in the transition complex. That relatively large anions may act as catalysts is shown in the cobalt(III)–thallium(I) reaction by the effect of sulphate ions, and in other reactions nitrate ions have been found effective.[8] Replacement of perchlorate by bisulphate ions has little effect on the rate of reaction, which is in accord with the similarity in size and charge of these two ions. We conclude therefore that there is indirect evidence in favour of the participation of perchlorate ions in the hydrogen-ion-independent cobalt(III)–thallium(I) reaction. In contrast, the entropy of activation is negative in the hydrogen-ion-independent path in the iron(II)–iron(III) electron-exchange reaction, and evidence has been given suggesting that perchlorate ions do not take part.[9]

The results in sulphate solutions enable us, subject to the assumptions implicit in equation (3), to find 22 ± 7 l. mole$^{-1}$ for the stability constant of $CoSO_4^+$ at 15° and ionic strength 2·70. This value is of the expected order of magnitude; a list of concentration association constants between other metal ions and sulphate ions at fairly high ionic strengths is given by Whiteker and Davidson.[10]

## EXPERIMENTAL

*Materials.*—Except as described below, reagents used were of "AnalaR" quality. Solid cobalt(III) sulphate was prepared by electrolytic oxidation of cobalt(II) sulphate,[11] and was stored at 0° in a desiccator. The cobalt(III) content was determined by dissolving a weighed amount in 2M-sulphuric acid, adding excess of iron(II) sulphate solution, and back-titrating with cerium(IV) sulphate, ferroin being used as indicator. The accuracy of the end-points, in titrations using ferroin in the presence of the similarly coloured cobalt(II) ion, was checked by potentiometric titration. Total cobalt was estimated by Latimer and Burdett's iodometric method.[12] The acid content was found by dissolving the solid in water whereupon rapid decomposition to cobalt(II) sulphate occurred. Titration with alkali and bromocresol-green as indicator then gave the hydrogen-ion content of the solid, allowance being made for hydrogen ions formed in the decomposition of cobalt(III) before titration, $4Co^{3+} + 2H_2O \longrightarrow 4Co^{2+} + 4H^+ + O_2$. The sulphate-ion content of the solid cobalt(III) sulphate, expressed as equiv. per g., was assumed to be equal to the sum of the cobalt(III), cobalt(II), and hydrogen-ion contents, each being expressed as equiv. per g.

Thallium(I) perchlorate was obtained from pure thallium(I) nitrate by fuming with excess of 60% perchloric acid, and was recrystallised three times from water. A stock solution in water was made up by weight, and its strength checked by titration against standard potassium iodate in hydrochloric acid solution under Andrews's conditions.

Sodium perchlorate solution, used in making the ionic strength in kinetic experiments up to 2·70, was prepared by neutralising 60% perchloric acid with solid sodium hydroxide and filtering. Barium perchlorate solution was prepared similarly by using solid barium hydroxide octahydrate. Cobalt(II) perchlorate solution was prepared by double decomposition between a solution of cobalt(II) sulphate and the barium perchlorate solution.

*Procedure in Kinetic Experiments.*—In kinetic experiments in the absence of sulphate a

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[7] Marcus, Zwolinski, and Eyring, *J. Phys. Chem.*, 1954, **58**, 432.
[8] Prestwood and Wahl, *J. Amer. Chem. Soc.*, 1949, **71**, 3137.
[9] Silverman and Dodson, *J. Phys. Chem.*, 1952, **56**, 846.
[10] Whiteker and Davidson, *J. Amer. Chem. Soc.*, 1953, **75**, 3085.
[11] Swann and Xanthakos, *ibid.*, 1931, **53**, 400.
[12] Latimer and Burdett, *Analyt. Chem.*, 1951, **23**, 1268.

weighed amount of cobalt(III) sulphate was dissolved in perchloric acid, and the sulphate ions removed by adding a slight excess of barium perchlorate solution. The solution was then filtered through No. 4 porosity sintered glass and a measured volume of the filtrate was added to the other constituents of the reaction mixture which had previously been measured into a 500-ml. stoppered flask. The remainder of the cobalt(III) perchlorate solution was used for a control experiment in absence of thallium(I) but at a similar hydrogen-ion concentration and ionic strength. In experiments in the presence of sulphate ions the solid cobalt(III) sulphate was dissolved in perchloric acid, and a measured volume added immediately to the other constituents of the mixture which included sodium sulphate or sulphuric acid. As before, the remainder of the cobalt(III) solution was used for a control experiment in absence of thallium(I).

Samples of the reaction mixture were removed at appropriate intervals of time, added to a small excess of iron(II) sulphate solution, and then titrated against 0·002M-cerium(IV) sulphate solution, with ferroin as indicator. The validity of this method for determining cobalt(III) in these solutions was confirmed by making up solutions of known composition, similar to those obtained during a reaction, and immediately determining cobalt(III) as described above. Attempts to quench the reaction by using cerium(III) instead of iron(II) gave inaccurate results, possibly owing to a slow reaction between cobalt(III) and cerium(III). In the few experiments at high thallium(III) concentrations it was necessary to cool the iron(II) sulphate quenching solution to 0° and perform the back-titration at this temperature to prevent oxidation of the iron(II) by thallium(III). The accuracy of these cobalt(III) concentration determinations was found to be $\pm 0{\cdot}8\%$ for $10^{-3}$M- and $\pm 4\%$ for $10^{-4}$M-cobalt(III) solutions.

It was not possible to conduct experiments in absence of oxygen since this gas is formed by the decomposition of cobalt(III). However, experiments in which pure nitrogen was bubbled through the reaction mixture gave the same results as parallel experiments in which the mixture was open to the air, and therefore we think it unlikely that oxygen has a significant effect on the rate. Other experiments showed that the rate of reaction is not affected by daylight.

*Stoicheiometry of the Cobalt*(III)–*Thallium*(I) *Reaction.*—Several experiments were done to find the amount of thallium(III) formed under the conditions of the kinetic experiments. These quantitative experiments were performed similarly to the kinetic experiments. The control solution was titrated immediately with iron(II) sulphate solution to find the initial cobalt(III) concentration, while the solution containing thallium(I) remained untouched until the completion of reaction. Sodium hydroxide solution was then added with stirring until the pH rose to about 3·5, as found by allowing the thallium(III) oxide precipitate to settle and testing the clear liquor with bromophenol-blue. The precipitation of thallium(III) oxide appeared to be substantially complete at about pH 2. At pH 3·5 cobalt(II) remains in solution,[13] and is not precipitated until about pH 7. The precipitate and solution were stirred for 24 hr. and then filtered through a No. 3 porosity sintered-glass crucible. The precipitate was washed rapidly with very dilute sulphuric acid, and then several times with water, dried *in vacuo* [$Mg(ClO_4)_2$], and weighed. The weight of thallium(III) oxide collected was about 80 mg. in each experiment, and corresponded to between 95% and 99% of the production of thallium(III) calculated from the amount of cobalt(III) present initially. We estimate the error in these figures to be $\pm 5\%$ and conclude that, with the exception of a small loss due to the decomposition of cobalt(III), the cobalt(III)–thallium(I) reaction is quantitative under our conditions.

*Determination of the Second Dissociation Constant of Sulphuric Acid.*—The value of this constant, $K_2 = [H^+][SO_4^{2-}]/[HSO_4^-]$, was required at ionic strength 2·70 and 15°, and was found by an optical method, picric acid being used as indicator. Optical measurements were made with a Unicam model SP500 quartz spectrophotometer; 4-cm. quartz cells were employed. A calibration curve of hydrogen-ion concentration against optical density at 358 mμ was found for $5 \times 10^{-5}$M-picric acid solutions in aqueous perchloric acid–sodium perchlorate mixtures of ionic strength 2·70. The range of hydrogen-ion concentration studied was 0·03—0·12M, and a solution of the latter concentration was used as the optical blank solution. The optical densities of $5 \times 10^{-5}$M-picric acid containing similar, known concentrations (not less than 0·1M) of sodium sulphate and sulphuric acid, and sufficient sodium perchlorate to bring the ionic strength to 2·70, were then determined. The corresponding hydrogen-ion concentrations were found from the calibration curve, enabling the second dissociation constant of sulphuric acid to be calculated. The mean value obtained from five experiments was $0{\cdot}077 \pm 0{\cdot}005$ mole l.$^{-1}$.

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[13] Britton, *Ann. Reports*, 1943, **40**, 45.