75. *Reactions of the Cobaltic Ion. Part I. The Reaction of the Cobaltic Ion with Water.*

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Aqueous solutions containing the cobaltic ion rapidly decompose, the cobalt reverting to the cobaltous state and oxygen being evolved. Results of some kinetic studies on this reaction are presented. The rate of the reaction depends in a complex manner on the hydrogen-ion concentration and its dependence on the cobaltic-ion concentration may be described by a rate equation of the form

$$-\mathrm{d}[\mathrm{Co}^{+++}]/\mathrm{d}t = A[\mathrm{Co}^{+++}] + B[\mathrm{Co}^{+++}]^2$$

in which A and B are constants whose values depend on the temperature, ionic strength, and hydrogen-ion concentration.

It is concluded that the rate-determining step is an electron transfer between cobaltic and hydroxyl ions producing the free hydroxyl radical, but that the simplicity of this process is obscured by hydrolysis of, and complex formation involving, the cobaltic ion.

The cobaltic ion, Co^{+++}, is stable only in the form of complex salts of which a large number are known; the only simple cobaltic salts which have so far been isolated are the fluoride, chloride, sulphate, and acetate which are all solids. On storage these salts all revert gradually to the cobaltous state.

The sulphate, which is the most readily available of the cobaltic salts, was first obtained by Marshall (*J.*, 1891, **59**, 760) by the anodic oxidation of the cobaltous salt in aqueous sulphuric acid solution. This method was further investigated by Oberer (Dissertation, " Beitrage zur Kenntniss der Kobaltisulphate," Basle, 1903) and by Swann and Xanthalsos (*J. Amer. Chem. Soc.*, 1931, **53**, 400); the latter authors devising a convenient method for its preparation.

Cobaltic sulphate is extremely reactive and will oxidise a wide variety of organic and inorganic compounds. The reaction with water follows the overall course given by the equation :

$$2\mathrm{Co}_2(\mathrm{SO}_4)_3 + 2\mathrm{H}_2\mathrm{O} = 4\mathrm{CoSO}_4 + 2\mathrm{H}_2\mathrm{SO}_4 + \mathrm{O}_2$$

and is almost instantaneous with pure water at room temperature but is markedly retarded by hydrogen ions. The first kinetic studies of the reaction were those of Oberer (*loc. cit.*) who stated that the reaction was of first order with respect to the cobaltic-ion concentration. He proposed the following mechanism :

$$(1)\quad Co^{+++} + OH^- \longrightarrow Co^{++} + OH\cdot$$

$$(2)\quad 2OH\cdot \longrightarrow H_2O_2$$

$$(3)\quad H_2O_2 \longrightarrow H_2O + O_2$$

or

$$(4)\quad 2OH\cdot \longrightarrow H_2O + O_2$$

reaction (1) being assumed to be the slow rate-controlling step.

The work of Noyes and Deahl (*J. Amer. Chem. Soc.*, 1937, **59**, 1337) on electrolytically prepared solutions of cobaltic nitrate failed to substantiate these findings. These authors state that in the presence of 1—4N-nitric acid the reaction was kinetically complex, being of approximately second order with respect to the cobaltic ion at the start and nearly first order at the end of the reaction. They suggested that there were two simultaneous reactions, one of first and the other of second order with respect to the cobaltic-ion concentration, but were unable to offer any reaction scheme from which the observed kinetics could be derived except to suggest the occurrence of the " percobaltic," Co^{++++}, ion. However, in view of the instability of the trebly-charged ion and the large energy change to be expected for the removal of the fourth electron, this latter event appears to be extremely unlikely. In Noyes and Deahl's experiments the reactions were followed by changes in the cobaltous–cobaltic electrode potential. In all but one of their experiments silver nitrate was added as a potential mediator and was found to increase markedly the velocity of the reaction. For this reason the value of their work must be very limited.

The discrepancy between Oberer's results and those of Noyes and Deahl led to a re-examination of those of Oberer. This revealed that his results were also of a complex nature, the kinetic order with respect to the cobaltic ion varying from first to fifth according to the experimental conditions. As the principal reaction appeared to be (*a*) a simple electron-transfer reaction between ions with a rate slow enough to measure, and (*b*) a suitable method of generating free hydroxyl radicals * unaccompanied by any other products, a detailed investigation of the kinetics were carried out. Two methods were used to follow the course of the reaction. In the first the concentration of the cobaltic ion was determined directly by a volumetric method based on the reaction with ferrous salts, whilst in the second method the rate of evolution of oxygen was measured.

In view of the well-known propensity of the cobaltic ion for complex formation it was decided to check that the measurements on cobaltic sulphate solutions were not those of the rate of decomposition of some specific complex ion. To this end measurements were also carried out on solutions of cobaltic perchlorate.

EXPERIMENTAL.

Materials.—All reagents used were of " AnalaR " grade and no further purification was attempted.

Cobaltic Salts.—Cobaltic sulphate was prepared by Swann and Xanthakos's electrolytic method (*loc. cit.*), the solid being filtered off from the anode liquor on a coarse sintered-glass funnel, sucked free from mother liquor, dried on a porous plate, transferred to a dry bottle, and stored in a desiccator in the dark. Material prepared and stored in this manner was found to be stable for several weeks.

Attempts to obtain the perchlorate by electrolytic oxidation of cobaltous perchlorate in perchloric acid solutions were unsuccessful. Solutions of cobaltic perchlorate were therefore prepared from solutions of the sulphate in perchloric acid by double decomposition with barium perchlorate.

pH Determinations.—The pH of the reaction mixtures containing cobaltic sulphate in sulphuric acid–sodium sulphate solutions were determined by using the glass electrode and a Cambridge pH meter. The pH of the perchlorate solutions was calculated from the known quantity of perchloric acid added to the reaction mixture.

Determination of Cobaltic-ion Concentration.—Cobaltic-ion concentrations were determined by the volumetric method used by Noyes and Deahl (*loc. cit.*). In this the cobaltic salt solution was added to an excess of well-acidified ferrous ammonium sulphate, whereupon the reaction

$$Fe^{++} + Co^{+++} \longrightarrow Fe^{+++} + Co^{++}$$

occurred instantaneously. The excess of ferrous ion was then determined by back titration with standard permanganate solution. Owing to the pink colour of the cobaltous ion a potentiometric method of detecting the end point was necessary; for this purpose Garman and Droz's titrimeter (*Ind. Eng. Chem. Anal.*, 1939, **11**, 398) was used.

Kinetic Measurements.—As the reaction was one involving ions it was necessary that it should be carried out at constant ionic strength. To avoid changes in ionic strength due to conversion of cobaltic

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* The decomposition of water by the cobaltic ion readily initiates vinyl polymerisation and this may be ascribed to the formation of hydroxyl radicals.

into cobaltous ion during the reaction it was therefore necessary that the total ionic strength should be large in comparison with that due to the cobalt salt alone. Further, as hydrogen ion is generated during the reaction and as this ion has a retarding effect on the rate, it was also essential that the initial total acid concentration should be large compared with that produced by the reaction.

To fulfil these requirements measurements were made on solutions which were not greater than 10^{-2}M. with respect to the cobaltic ion, had an ionic strength not less than 0·3, and a pH in the region 0—1·2. In order to vary the hydrogen-ion concentration at constant ionic strengths, use was made of sulphuric acid–sodium sulphate in the experiments on the sulphate and perchloric acid–sodium perchlorate in the experiments on the perchlorate.

Kinetic measurements were made in the usual manner by removing aliquots from the reaction mixture at suitable intervals and determining the cobaltic-ion concentration by the volumetric method described above. The reaction vessel was immersed in a thermostat the temperature of which was maintained constant to within ±0·05°. In the case of the runs at 0° however the reaction vessel was immersed in melting ice in a large Dewar vessel. In these cases the temperature was constant over the longer periods involved only to about ±0·2°.

In the second method of determining the rate of the reaction, its progress was followed by measurement of the amount of oxygen evolved as a function of time. The reaction vessel was immersed in a large thermostat and vigorously agitated by means of an electrically driven shaking mechanism. The amount of oxygen evolved was determined by measuring the increase of pressure in the system by means of a manometer attached directly to it by pressure tubing. The manometer was 50 cm. long and used water as manometric fluid, the scale was graduated in mm. and readings could normally be made to at least 1 mm. in each limb. The capacity of the reaction vessel was approximately 80 ml.; a baffle sealed to the reaction vessel prevented the contents from being forced up into the manometer connection by the vigorous agitation employed. A 1·5-l. vessel, immersed in a thermostat, served effectively as a constant-pressure source for the second limb of the manometer. and obviated any effects of change in barometric pressure during a run.

The apparatus was calibrated, to enable pressure readings to be converted into ml. of oxygen, by connecting it through a tap to a gas burette, forcing in known volumes of gas, and noting the pressure difference produced on the manometer.

In a run, 40 ml. of the appropriate sodium sulphate–sulphuric acid–water mixture were placed in the reaction vessel and allowed to reach a steady temperature in the thermostat. At the same time 3—5 ml. of 2N-sulphuric acid, in a test-tube in the thermostat, were allowed to come to temperature equilibrium. Approximately 0·2 g. of cobaltic sulphate was weighed and added to the acid in the test-tube; the mixture was agitated until all the solid had dissolved, and 2 ml. of the solution were then added to the contents of the reaction vessel, *via* a side-arm. The stopper was immediately replaced in the side-arm, the shaker started, and the taps connecting the burette and pressure-balancing vessel to the atmosphere simultaneously closed. The moment of closure of these two taps was taken as zero time. Readings of the manometer were then made at suitable intervals.

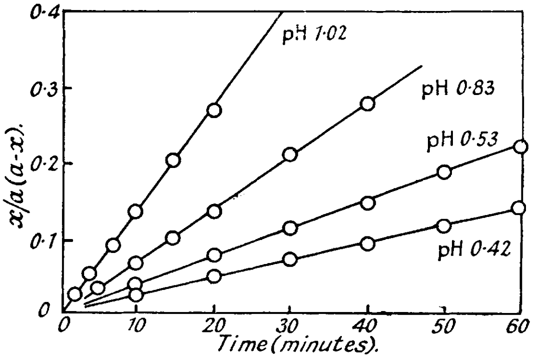
Some effect of rate of agitation of the reaction vessel on the rate of liberation of oxygen was to be expected, for except in a very slow reaction an increase in the gas–liquid interfacial area, such as is caused by shaking, must of necessity entail an increase in the rate of transfer of gas which would continue until the gas–liquid interfacial area was no longer a controlling factor in the rate of transfer of gas from one phase to the other. It was found under constant reaction conditions that the reaction velocity increased with rate of shaking and that in order to obtain results which were independent of it a shaking speed of over 350 cycles/minute was essential. All were therefore carried out at 500 cycles/minute.

RESULTS.

Titration Method.—The results of the kinetic experiments on both sulphate and perchlorate, using the titration method and an initial cobaltic-ion concentration of $\sim 10^{-2}$N., were found in all cases to agree best with a kinetic expression which was of second order with respect to the cobaltic ion. This is illustrated in Figs. 1 and 2 in which are presented two typical groups of second-order plots for a series of

FIG. 1.

Decomposition of cobaltic sulphate at 25·2° *showing second-order plots* (μ = 0·32).



runs with cobaltic sulphate at 25° and perchlorate at 20° and various pHs. In both cases it will be seen that straight lines are obtained and that the slopes, *i.e.* the second-order constants, are inversely dependent on some function of the hydrogen-ion concentration. (At lower concentrations a decrease in order was observed and this is discussed in the next section.)

It is therefore possible to write as a rate equation for the disappearance of the cobaltic ion :

$$-d[Co^{+++}]/dt = k[Co^{+++}]^2/[H^+]^x$$

Thus if the velocity constant at some fixed value of $[H^+]$ is measured the observed constant k_0 is

$$k_0 = k/[H^+]^x$$

and

$$\log_{10}k_0 = \log_{10}k + x\text{pH}$$

Therefore a plot of $\log_{10}k_0$ against pH should be linear and will permit the determination from its slope of the value of x, the order of the reaction with respect to hydrogen ion.

Fig. 2.

Decomposition of cobaltic perchlorate at 20·0°, *showing second-order plots* (μ = 1·0).

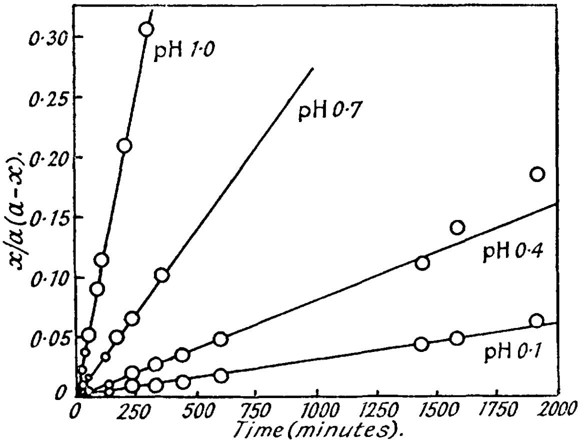


Fig. 3.

Variation of second-order velocity constant with pH. *Cobaltic sulphate* (μ = 0·32).

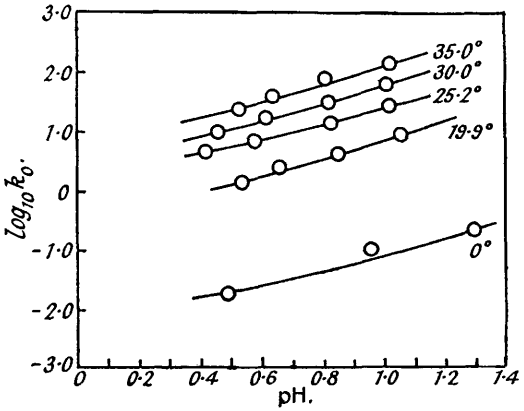


Fig. 4.

Variation of second-order velocity constant with pH. *Cobaltic perchlorate* (μ = 1·0).

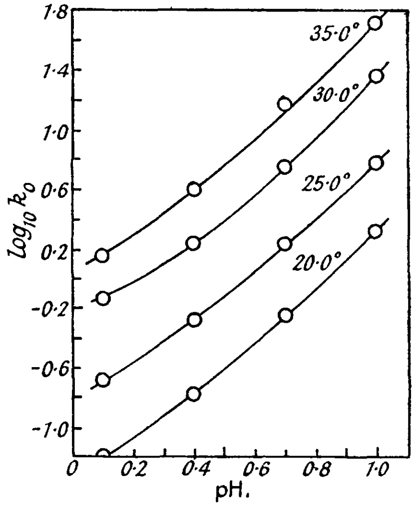
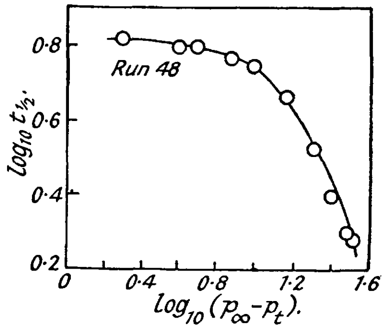


Fig. 5.

Change of order during the course of the reaction.



The results of measurements of k_0 under various conditions of temperature and pH are presented in Figs. 3 and 4 in the form of plots of $\log_{10}k_0$ against pH. It is evident that in both cases the plots are curved, and this must imply that x is dependent on the pH. This change in x with pH is interpreted (see later) in terms of hydrolysis of the cobaltic ion. Before proceeding with the analysis of these results, the corresponding results obtained from the measurement of the rate of oxygen evolution are summarised, since these bring out further interesting features of the kinetics.

Manometric Method.—The manometric experiments were carried out to discover whether there was, between the disappearance of the cobaltic ion and the production of oxygen, any slow step in the reaction sequence which might be rate-controlling for the production of oxygen, and by producing different kinetics give some clue as to the nature of the processes intervening between reactants and end products. These results at an initial concentration of about 2×10^{-3}N. obeyed neither second-order nor first-order form, but were of an intermediate order; furthermore a marked change of order occurred as the reaction proceeded. Fig. 5 shows a typical plot of $\log_{10}t_{\frac{1}{2}}$ against $\log(p_\infty - p_t)$, and in all cases studied the plots were found to be curved, the slope decreasing as the concentration decreased apparently to a limiting value of zero at very low concentration (about 10^{-4}N.).

FIG. 6.

Evaluation of k_1' and k_2' from manometric results. c expressed as $(p_\infty - p_t)$.

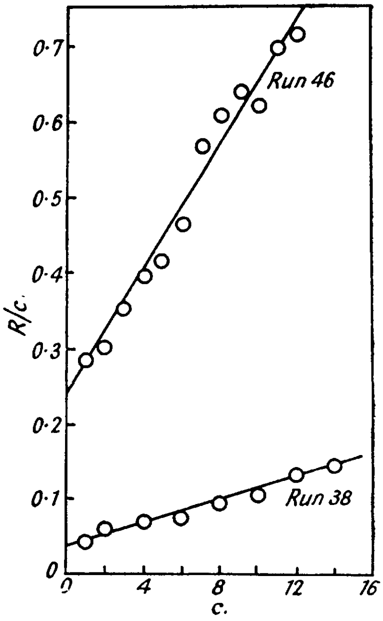


FIG. 7.

Variation of first-order velocity constant with pH. *Cobaltic sulphate : manometric experiments (μ = 0·52).*

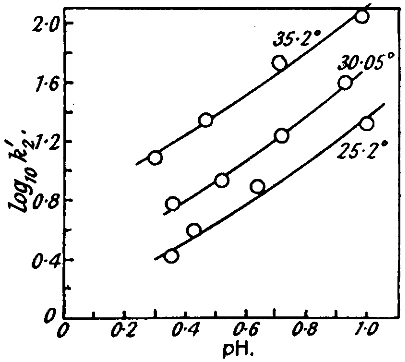


FIG. 8.

Variation of second-order velocity constant with pH. *Cobaltic sulphate : manometric experiments (μ = 0·52)*

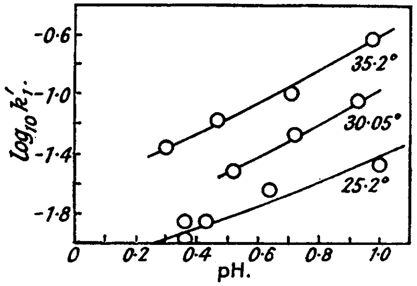
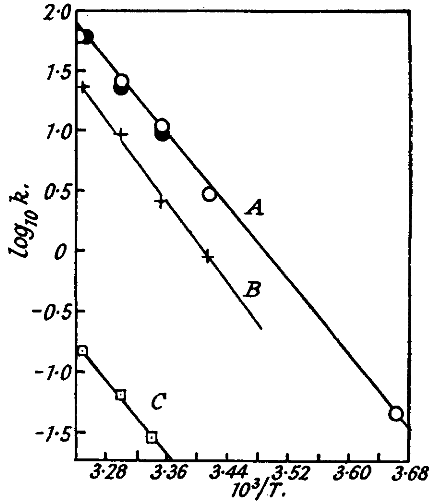


FIG. 9.

Effect of temperature.



○ *Titration experiments.*

□ *and* ● *Manometric experiments.*

A. Cobaltic sulphate, k_2', E = 35·1 kcals.
B. Cobaltic perchlorate, k_2', E = 39·6 kcals.
C. Cobaltic sulphate, k_1', E = 33·6 kcals.

This behaviour is in agreement with that found by Noyes and Deahl (*loc. cit.*) and suggests that there must be two simultaneous reactions occurring, one of second order with respect to the cobaltic ion and the other of first order, the latter occurring at low ion concentrations.

Experiments carried out at low cobaltic-ion concentrations using the titration method confirmed the above viewpoint. As shown in the following table, the results could not be accurately represented by a second-order equation as found at higher concentration, the order now being intermediate between first and second order. The titration method was unsuitable for exploration down to the very low concentration where the reaction becomes essentially of first order.

In view of the agreement of the results of the oxygen evolution with the behaviour found by Noyes and Deahl and of the change of order observed in the titration measurements at low concentrations, it is evident that the rate of oxygen formation is a measure of the rate of reaction of the Co^{+++} ion and not of some intermediate step in the formation of oxygen.

Temp. 25·2° c. $\mu = 0{\cdot}38$. pH $= 1{\cdot}1$.

10-ml. samples of reaction mixture were added to 20 ml. of 0·926 N/100-$Fe(NH_4)_2(SO_4)_2$ and back titrated with $KMnO_4$ (20 ml. of $Fe(NH_4)_2(SO_4)_2 \equiv 35{\cdot}82$ ml. of $KMnO_4$). Initial $[Co^{+++}]$ = N/200.

Time (min.).	Titn. (ml. of $KMnO_4$).	$[Co^{+++}]$ as ml. of $KMnO_4$.	$k_{\text{uni.}}$ (min.$^{-1}$).	$k_{bi.}$, min.$^{-1}$ g.-ion^{-1} l.
0	22·51	13·31	—	—
5	30·20	5·62	0·172	39·9
10	32·71	3·11	0·145	47·7
20	34·22	1·60	0·106	53·2
30	34·81	1·01	0·086	59·0
40	35·08	0·74	0·072	61·8

FIG. 10.

Effect of ionic strength on the order of the reaction with respect to cobaltic ion. Oberer's data.

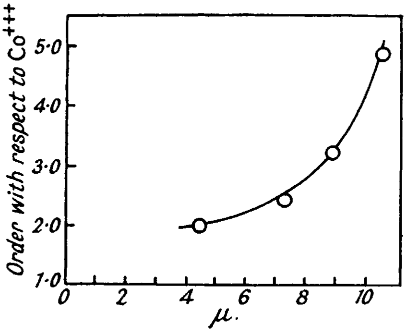
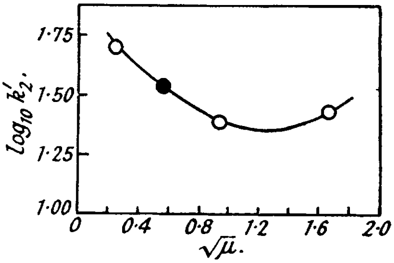


FIG. 11.

Effect of ionic strength on the second-order velocity constant for cobaltic sulphate.



○ *Values from manometric experiments.*
● *Value from titration experiments by extrapolation.*

The rate equation for the reaction at a constant pH may be written :

$$+\mathrm{d}[O_2]/\mathrm{d}t = -\mathrm{d}[Co^{+++}]/\mathrm{d}t = k_1'[Co^{+++}] + k_2'[Co^{+++}]^2$$

from which it is evident that at low concentrations the second-order term will become less and less important and the reaction will appear to be first order, whilst at high concentrations the reverse will be true. The concentration region in which the change over from first-order to second-order kinetics occurs will be marked by an apparently variable order and will depend on the relative magnitudes of k_1' and k_2'.

The correctness of the above equation may be shown by rearranging the expression, *viz.* :

$$\frac{-\mathrm{d}[Co^{+++}]}{\mathrm{d}t}\Big/[Co^{+++}] = k_1' + k_2'[Co^{+++}]$$

and plotting the fraction R/c, where R is the instantaneous rate of the reaction (obtained by measurement of the slope of the c–t curve at a series of points), against the cobaltic-ion concentration (c), which would give a straight line of slope k_2' and intercept k_1'. This process was carried out on all the manometric runs and in each case R/c against c plots were found to be linear. Typical results for two experiments are shown in Fig. 6. Figs. 7 and 8 show the plot of $\log_{10}k_1'$ and $\log_{10}k_2'$ so obtained against pH, and, as previously, a set of curves was obtained. It will be seen that the values obtained for k_2 by this process agree reasonably well (taking into account the different ionic strength) with those obtained directly by the titration method.

Effect of Temperature.—The values of $\log_{10}k$ at a constant pH were read off from the $\log_{10}k$–pH curves, and the activation energy for the overall reaction derived from the $\log_{10}k$ — $1/T$ plot. The data are represented in Fig. 9 and correspond to the rate laws (at pH $= 0{\cdot}8$) : $k_1 = 10^{22\cdot9}e^{-33,600/kT}$ (min.$^{-1}$), $k_2 = 10^{26\cdot5}e^{-35,100/kT}$ (min.$^{-1}$ g.-mol.$^{-1}$ l.) for the sulphate; and $k_2 = 10^{29\cdot3}e^{-39,600/kT}$ (min.$^{-1}$ g.-mol.$^{-1}$ l.) for the perchlorate. As will be shown later the measured constants are composite terms, and the above relationships merely summarise the effect of temperature on the overall reaction under certain fixed conditions.

Effect of Ionic Strength.—In this connection some of the results previously given by Oberer are of interest. Oberer carried out a number of experiments at the same temperature but at widely differing ionic strengths; using his experimental data large-scale plots of concentration against time were prepared and the time of 0·9 decomposition was determined at a series of concentrations for each run. It was necessary to use the time of 0·9 decomposition in place of the more usual time of 0·5 decomposition owing to the very small concentration region over which his experiments extended. The plots of $\log_{10}t_{0\cdot9}/\log_{10}c$, for the high cobaltic-ion concentrations ($\sim10^{-1}$N.) and small concentration range covered by each run, were linear. From the slopes of these plots the order of the reaction with respect to the cobaltic ion was determined in each case. The approximate ionic strengths of the reaction mixtures were also calculated and the values of the order of the reaction were then plotted against μ (Fig. 10). From this it is evident that the order of the reaction with respect to the cobaltic ion increases from a limiting value of 2 at low ionic strengths up to as much as 5 at very high ionic strengths. This fact must obviously be taken into account in any attempt to formulate the mechanism of the reaction.

In the present investigation of the effect of ionic strength on the velocity constant several runs were carried out by the titration method at constant pH. The values obtained for the second-order constant in these experiments are plotted as $\log_{10}k_2$ against $\sqrt{\mu}$ in Fig. 11. Also included is a point obtained by extrapolation to pH 1·15 of the $\log_{10}k_2$ — pH curve obtained from the manometric results at 25·2°. The values all fall on a smooth curve the gradient of which at low values of $\sqrt{\mu}$ is negative which is to be expected, from the Brönsted relationship, for a reaction between oppositely-charged ions.

DISCUSSION.

The most important points which have emerged from the experimental work, and which must be explained, are :

(*a*) The $\log_{10}k$ — pH plots are curved.

(*b*) The order of the reaction with respect to the cobaltic-ion concentration is two at high concentrations and tends to unity at low concentrations.

(*c*) The order with respect to cobaltic ion also depends on the ionic strength and increases as μ is increased.

Oberer's suggestion for the mechanism of the reaction

$$\begin{aligned} \mathrm{Co^{+++} + OH^-} &\longrightarrow \mathrm{Co^{++} + OH\cdot} \quad (k_1) \\ \mathrm{2OH\cdot} &\longrightarrow \mathrm{H_2O_2} \\ \mathrm{H_2O_2} &\longrightarrow \mathrm{H_2O + O_2} \end{aligned}$$

gives as a rate equation for the loss of the cobaltic ion :

$$-\mathrm{d}[\mathrm{Co^{+++}}]/\mathrm{d}t = k_1[\mathrm{Co^{+++}}][\mathrm{OH'}]$$

or, in terms of $[\mathrm{H^+}]$: $-\mathrm{d}[\mathrm{Co^{+++}}]/\mathrm{d}t = k_1K_w[\mathrm{Co^{+++}}]/[\mathrm{H^+}]$, where K_w is the ionic product of water, and is clearly inadequate. If it is assumed that in addition to the above reactions the cobaltic ion is capable of being hydrolysed in aqueous solutions then the following additional processes occur :

$$\mathrm{Co^{+++} + H_2O} \rightleftharpoons \mathrm{CoOH^{++} + H^+} \quad (K_1)$$

(This should be more correctly written as

$$\mathrm{Co(H_2O)_6{}^{+++}} \rightleftharpoons \mathrm{\{Co(H_2O)_5(OH)\}^{++} + H^+}$$

but the above form is retained for convenience of representation.)

$$\mathrm{CoOH^{++} + OH^-} \longrightarrow \mathrm{CoOH^+ + OH\cdot} \quad (k_2)$$

This scheme yields as a rate equation for the loss of the cobaltic ion :

$$-\mathrm{d}[\mathrm{Co^{+++}}]_T/\mathrm{d}t = k_1[\mathrm{Co^{+++}}][\mathrm{OH^-}] + k_2[\mathrm{CoOH^{++}}][\mathrm{OH^-}] \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$= [\mathrm{Co^{+++}}]\left\{\frac{k_1K_w}{[\mathrm{H^+}]} + \frac{k_2K_1K_w}{[\mathrm{H^+}]^2}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$$= \frac{[\mathrm{Co^{+++}}]_T}{\left\{1 + \dfrac{K_1}{[\mathrm{H^+}]}\right\}}\left[\frac{k_1K_w}{[\mathrm{H^+}]} + \frac{k_2K_1K_w}{[\mathrm{H^+}]^2}\right] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where $[\mathrm{Co^{+++}}]_T$ is the total titratable cobaltic ion in the solution, which is assumed to be $(\mathrm{Co^{+++} + CoOH^{++}})$. The expression (2), which is of the same form as (3), holds if only $\mathrm{Co^{+++}}$ is titratable. These equations are obviously much nearer the truth and are at least adequate to explain the kinetics in very dilute solutions where the reaction is of first order with respect to the cobaltic ion. The observed velocity constant k_0 is

$$k_0 = \left[\frac{k_1K_w}{[H^+]} + \frac{k_2K_1K_w}{[H^+]^2}\right] \Big/ \left[1 + \frac{K_1}{[H^+]}\right]$$

This will give a $\log_{10}k_0$ — pH plot which is curved and the slope of which varies from 1 in the region where hydrolysis is negligible to 2 in the region where it is extensive. The exact region of hydrogen-ion concentration over which the change will occur will depend both on the magnitude of K_1 and on the fraction k_2/k_1.

This scheme does not account for the variable order of the reaction with respect to the cobaltic ion, and the occurrence of second-order reaction at high concentration is not allowed for. The only way of explaining these observations without involving extremely improbable termolecular steps or the production of the " percobaltic ion " suggested by Noyes and Deahl would appear to be the assumption that the cobaltic ion is capable of forming complexes in aqueous solution which contain more than one cobaltic ion. Whether these complexes can be considered to be true complex ions involving ordinary valency linkages or whether they are to be regarded as the ion-association groups first postulated by Bjerrum (*Kgl. Danske Vidensk. Selskab.*, 1926, **7**, No. 9), and involving only a loose physical association, cannot be readily decided. The occurrence of a reaction of fifth order with respect to the cobaltic ion in concentrated salt solutions (*loc. cit.*) would appear to favour the latter, a true complex ion containing five cobaltic ions being a little improbable. It is however possible that both types of linkage occur, for at any rate in the sulphate solutions a structure such as

$$(H_2O)_5Co^{++}\text{-}SO_4\text{-}Co^{++}(H_2O)_5$$

is not impossible, whilst in the perchlorate solutions a structure of the type

$$(H_2O)_5Co^{++}\text{-}O\text{-}\overset{++}{Co}(H_2O)_5$$

similar to those postulated in the case of ceric ions by Sherrill, King, and Spooner (*J. Amer. Chem. Soc.*, 1943, **65**, 170) may arise.

If the existence of dimeric complex ions is assumed and if these can react in the same way as the single cobaltic ion discussed above, then a rate equation may be derived which includes terms in the first and second powers of the cobaltic-ion concentration. Such an equation qualitatively fits all the observed facts but must at the present be regarded as speculative until more information is available regarding the existence of hydrolysis and complex-ion formation in solution. It is hoped to obtain this information by spectroscopic investigations.

Finally, the possible decomposition of the cobaltic ion by direct reaction with water rather than the hydroxyl ion requires discussion. This reaction has been suggested by Weiss (*Naturwiss.*, 1935, **23**, 64) :

$$\begin{aligned} Co^{+++} + H_2O &\longrightarrow Co^{++} + H_2O^+ \\ H_2O^+ &\rightleftharpoons H^+ + OH \\ 2OH &\longrightarrow H_2O + O_2 \end{aligned}$$

This mechanism, as it stands, cannot explain our experimental findings since it would predict that the decomposition of the Co^{+++} would be independent of hydrogen-ion concentration and that only the rate of oxygen production would vary with pH. This objection would be removed if the first reaction were reversible but this would require that the cobaltous ion should also exert an inhibitory effect on the reaction, which has not been observed. We therefore conclude that the direct reaction between water and cobaltic ion plays no part in the thermal reaction.

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