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HYDROLYTIC EQUILIBRIA OF METALLIC IONS—I*

THE HYDROLYSIS OF Co(II) ION IN $NaClO_4$ SOLUTION

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Abstract—The first acidic ionization constant of Co(II) as cobaltous perchlorate has been determined by a potentiometric titration in a sodium perchlorate medium of constant ionic strength at temperatures ranging from 15 to 40°C and at different concentrations of Co(II) from 2·5 to 25 × 10^{-3}, M and total ionic strength from 0·327 to 0·867.

The assembled information indicates the hydrolysis reaction of this ion is a mononuclear reaction where the complex $CoOH^+$ is formed with $\Delta G^\circ_{298} = 13{\cdot}4 \pm 0{\cdot}2$ kcal/mole and $\Delta H^\circ_{298} = 8{\cdot}2 \pm 2{\cdot}0$ kcal/mole.

The second acidic ionization constant is higher than the first. This shows that a disproportionation reaction of $CoOH^+$ ions is thermodymanically favoured and has to be considered in the ionic equilibria of aqueous Co(II) ions.

Résumé—La constante de la première ionisation acidique de l'ion Co(II) sous la forme de perchlorate de cobalt a été determiné par titration potentiometrique en solution aqueouse de perchlorate de sodium, celles-ci constituent le milieu à force ionique constante.

Les données experimentales ont été obtenues a temperature entre 15 et 40°C. La concentration de l'ion Co(II) était comprise entre 2,5 et 25 × 10^{-3} M, et la force ionique des solutions entre 0,327 et 0,867.

La reaction d'hydrolyse de l'ion Co(II) est une reaction mononuclear où apparait le complex $CoOH^+$. Les données thérmodynamique obtenues sont: $\Delta G^\circ_{298} = 13{,}4 \pm 0{,}2$ kcal/mole et $\Delta H^\circ_{298} = 8{,}2 \pm 2{,}0$ kcal/mole.

La seconde constante de ionisation acidique est plus large que la premiere. Cela montre qu'une reaction de disproportionation des ions $CoOH^+$ est thermodynamiquement possible au meme temps que cette reaction doit être considerée en traitant les équilibres ioniques des ions Co(II) aqueux.

Zusammenfassung—Die erste Ionisationskonstante von Kobalt (II)—Perchlorat wurde durch electrometrische Titration in Lösungen konstanter Ionenstärke bestimmt. Die Temperatur war 15–40°, die Co(II)-Konzentration 2,5 bis 25 mMol /L und die gesamte Ionenstärke 0,327 bis 0,867. Aus den Ergebnissen geht hervor, dass die Hydrolyse-Reaktion des Co(II)-ions mono-nuklear ist, wobei der Komplex $CoOH^+$ entsteht.

$$\Delta G^\circ_{298} = 13{,}4 \pm 0{,}2 \text{ Kcal/Mol und } \Delta H^\circ_{298-8,2\pm 2,0} \text{ Kcal/Mol.}$$

Die zweite Ionisationskonstante ist grösser als die erste. Dies zeigt, dass eine Disproportionierung des $CoOH^+$-ions thermodynamisch möglich ist und bei Gleichgewichten, an denen Co(II)-Ionen in wässeriger Lösung beteiligt sind, zu berücksichtigen ist.

INTRODUCTION

The hydrolysis reaction of Co(II) ion has been investigated by several authors at one given temperature, they obtained figures for the equilibrium constant of that reaction covering the range of 10^{-8} to 10^{-12}. [1,2,3,4] The smallest figure was obtained by Gayer and Woontner[3], measuring the pH of solutions containing cobaltous chloride. The largest was obtained by Chaberek, Courtney and Martell[4] by potentiometric titration of cobaltous chloride in the presence of a large excess of chloride ion. The same wide dispersion of results is also found for the hydrolysis reaction of other ions. Therefore

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there is a need of further experimental information to achieve more reliable figures for their equilibrium constants.

In the course of a systematic research of the hydrolysis of metallic ions we have determined the equilibrium constant for the hydrolysis reaction of cobaltous ion at different temperatures and experimental conditions, applying an approach where chloride ions and other complex-forming ions, except hydroxyl, were carefully avoided as described later.

EXPERIMENTAL

The experimental technique is based on the theory of the constant ionic medium, as developed by Bjerrum and his school and later applied to hydrolytic equilibrium reactions by Sillén *et al.* Recently this author has reviewed his work[5,6] on this type of process.

When this method is applied to a particular system its total ionic strength does not vary significantly in the course of the experiment; then it is possible to employ concentrations instead of activities without introducing a significant error in the calculations. To keep the ionic strength as constant as possible a large excess of another, inert, electrolyte is present in the system. In the present case sodium perchlorate solution (0·250 to 0·750 M) has been used as the ionic medium, with the cobaltous ion concentration in the range from 0·002 to 0·025 M present as cobaltous perchlorate.

The hydrogen-ion concentration due to the hydrolysis reaction and to the perchloric acid initially present in a known amount was measured by potentiometric titration in a suitable cell, employing standard sodium hydroxide solution. To maintain the cobaltous-ion concentration as constant as possible during the titration, equal volumes of the alkaline and cobaltous solutions were added simultaneously during each run.

With the data assembled from the titrations the equilibrium constant K_a' of the reaction in the range of temperature between 15 and 40°C has been calculated.

Chemicals and solutions

(*a*) *Cobaltous perchlorate solution.* In general, most of the difficulties encountered in metal-ion hydrolysis reactions are concerned with the preparation of the electrolytic solutions. Several authors have obtained their results with crystallization of the salt and its further purification. Although this is common technique, unknown amounts of free acid might be left in the crystallized salt which would interfere with the acidity due to the hydrolysis reaction, causing serious errors in the results. This may account for some of the differences in the values recorded in the literature for the ionic acidic ionization constants of metallic ions.

The method for the preparation of the solution we use tends to avoid these shortcomings by yielding an ionic solution of very high quality and well established concentrations where any further purification is not required.

A solution containing 30·0 g per cent of A.R. hydrated cobaltous sulphate was purified by electrolysis employing platinum electrodes at a low current density and intermittent electrolysis with stirring, to remove traces of heavy metals. The purified solution was then electrolyzed with the same electrodes (previously cleaned), at a current density of 6–8 A/dm^2, to obtain a known amount of metallic cobalt. The deposit, after being washed, dried and weighed, was dissolved in a known amount of standard perchloric acid solution, calculated so as to leave a small excess of acid in the final solution. The dissolution was carried out by heating the metal and the acid in an all-glass reflux apparatus on a boiling water bath. The cobaltous perchlorate concentration of the final solution was checked by analysing its cobaltous ion content by the usual electrolytic method. The figure obtained for the cobaltous-ion content was always the same as that derived from the electrolytic cell. The final concentrations of the solutions were adjusted using concentrated sodium perchlorate solutions. Since the only acidity left in the system is that remaining from the initial perchloric acid employed in the preparation of the solution, it can be calculated from the difference between the initial amount of acid and the cobaltous-ion concentration.

(b) *Sodium perchlorate* was prepared by neutralizing sodium hydroxide (Merck A.R.) with a slight excess of perchloric acid and adjusting finally to neutrality with a very dilute alkaline solution. Its concentration was determined by two independent methods; by gravimetry as potassium perchlorate, and by dry residue, heating up the sample up to 120°C in an oven until it was dry and finally during 15 minutes up to 350°C. The solution gave negative tests for chloride and sulphate ions.

(c) *Perchloric acid* 1 N and 0·1 N solutions were prepared from the concentrated acid (Merck or Riedel de Haën A.R.) and standardized against borax, as usual.

(d) *Sodium hydroxide.* Diluted solutions were prepared from a 50% stock solution and standardized with potassium acid phthalate.

(e) *Solutions employed in the potentiometric titration.* All the solutions were prepared with triple distilled water, freed from air and carbon dioxide, obtained in an all-glass still. Those three solutions were stored in Pyrex flasks provided with standard tapered heads with bubbling and outlet tubes allowing passage of purified nitrogen.

Apparatus

The potentiometric titration cell consists of a glass and a calomel electrode. Both were held in the Lucite cover of a 400-ml Pyrex beaker. The calomel electrode was filled with a 4 M sodium chloride solution and was placed into a special glass tube which ended in a hook shaped capillary tube,[7] to let the liquid junction of the cell be established. The special tube was filled up with the supporting solution. This device prevented any diffusion of chloride ions from the reference electrode into the solution. The whole cell was placed in a thermostat and the temperature adjusted to ±0·05°C.

A Leeds and Northrup type 7663-Al potentiometer was used for the emf. measurements. L. and N. type 1199 and Beckman type 41263 tested glass electrodes have been employed.

The nitrogen purifier was similar to that described by Weissberger[8] and consisted of an oven with a pyrex tube filled with copper turnings operating at 450°C, and a set of traps with alkaline pyrogallate, concentrated sulphuric acid, ascarite and finally one filled with the supporting solution to saturate the gas at the vapour pressure of water in this solution, in order to prevent any evaporation from the cell. Nitrogen was bubbled through the cell for ½ hr before readings were taken.

Procedure

The cell employed can be represented as

$$\begin{matrix}\text{glass}\\ \text{electrode}\end{matrix}\ \Big|\ \text{H}^+,\ \text{NaClO}_4(\text{M}),\ \text{Co(ClO}_4)_2\ \Big\|\ \text{NaClO}_4(\text{M})\ \Big|\ \text{NaCl}(4\text{M})\ \Big|\ \begin{matrix}\text{calomel}\\ \text{electrode}\end{matrix}\ ,$$

and its e.m.f. is given by Nernst equation

$$E_g = E_g^\circ - \frac{2{\cdot}303RT}{F}\log h - E_j = E' - \frac{2{\cdot}303RT}{F}\log h\,,$$

where E_g° is defined as the standard potential of the cell in mV, E_j is the potential of the liquid junction, h is the hydrogen-ion concentration in mmole/l and the other symbols having their usual meanings. E' is the sum of E_j and E_g°; it was determined in each run. E_j and hence E' are functions of the hydrogen-ion concentration.[7,9] E' varies also from one experiment to another due to fluctuations in the potential of the glass electrode, but this does not affect the results at all.

Each experiment comprised two parts. In the first the E' value was determined by putting into the cell 50·00 ml of the acid solution and titrating it potentiometrically with the alkaline solution. The equivalence point was determined graphically by plotting $\Delta V/\Delta E$ vs. volume of alkaline solution added. In this way the hydrogen-ion concentration of that solution is found and E' can be calculated.

This procedure was repeated, but with the addition of only enough alkaline solution to reach the equivalence point. If the total volume of solution in the cell was less than 75·00 ml then supporting sodium perchlorate solution was added up to that volume. Then the second part of the titration was done.

Now 75·00 ml of cobaltous-ion solution was mixed with the solution in the cell and titrated with the alkaline solution by adding it simultaneously with an equal volume of cobaltous ion solution in order to keep the metal ion concentration practically unchanged. The titration was continued until the precipitation of cobaltous hydroxide became evident. When this point is reached the cobaltous-ion concentration changes very rapidly and the e.m.f. of the cell becomes erratic because of the colloidal nature of cobaltous hydroxide and its adsorption effect on hydroxyl ions.

Experiments were done in the range of concentration from 0·002 M to 0·025 M and of temperatures from 15 to 40°C. Some typical results are reported in Tables 1–8. The symbolism employed in them is:

C, cobaltous-ion concentration in mmole/l.

H, hydrogen-ion concentration calculated assuming no hydrolysis of cobaltous ion from the analysis of the solution, in mmmole/l.

TABLE 1

EXPERIMENT 55 15°C
ALKALINE SOLUTION: NaOH: 10·48 mM; $NaClO_4$: 250 mM.
COBALTOUS ION SOLUTION: Co: 10·66 mM; H^+: 0·467 mM; ClO_4^-: 250 mM.
E' FROM PREVIOUS ACID-BASE TITRATION: −282 mV.

V ml	E_g mV	$H \times 10^4$	$h \times 10^4$	$X \times 10^4$	K_a'	pK_{av}'
0·00	−253	2335				
4·00	0	−320	0·116	60	$0{\cdot}70 \times 10^{-10}$	
4·25	+2	−477	0·107	90	$0{\cdot}96 \times 10^{-10}$	
4·50	8	−633	0·084	110	$1{\cdot}00 \times 10^{-10}$	
4·75	10	−788	0·077	148	$1{\cdot}14 \times 10^{-10}$	
						10·03 ±0·13

Table 2

Experiment 60 15°C
Alkaline solution: NaOH: 10·48 mM; $NaClO_4$: 250 mM.
Cobaltous ion solution: Co^{2+}: 2·66 mM; H^+: 0·117 mM; ClO_4^-: 250 mM.
E' from previous acid-base titration: −222 mV.

V ml	E_g mV	$H \times 10^4$	$h \times 10^4$	$X \times 10^4$	K_a'	pK_{av}'
0·00	−125	585				
1·25	+87	−274	0·039	206	$0·80 \times 10^{-10}$	
1·50	93	−443	0·031	333	$0·103 \times 10^{-9}$	
1·75	95	−611	0·028	459	$0·129 \times 10^{-9}$	
2·00	98	−777	0·025	584	$0·146 \times 10^{-9}$	
						9·95
						±0·15

Table 3

Experiment 15 25°C
Alkaline solution: NaOH: 10·35 mM; $NaClO_4$: 750 mM.
Cobaltous ion solution: Co^{2+}: 5·98 mM; H^+: 0·348 mM; ClO_4^-: 750 mM.
E' from previous acid-base titration: −261 mV.

V ml	E_g mV	$H \times 10^4$	$h \times 10^4$	$X \times 10^4$	K_a'	pK_{av}'
0·00	−210	1740				
3·00	+19	−250	0·185	84	$0·155 \times 10^{-9}$	
3·30	38	−441	0·088	148	$0·130 \times 10^{-9}$	
3·50	42	−568	0·076	200	$0·152 \times 10^{-9}$	
3·80	44	−756	0·070	250	$0·175 \times 10^{-9}$	
4·00	45	−880	0·062	294	$0·182 \times 10^{-9}$	
						9·80
						±0·09

Table 4

Experiment 68 25°C
Alkaline solution: NaOH: 10·00 mM; $NaClO_4$: 250 mM.
Cobaltous ion solution: Co^{2+}: 25·00 mM; H^+: 0·120 mM; ClO_4^-: 250 mM.
E' from previous acid-base titration: −243 mV.

V ml	E_g mV	$H \times 10^4$	$h \times 10^4$	$X \times 10^4$	K_a'	pK_{av}'
0·00	−34	600				
1·30	−5	−252	0·64	21·1	$0·135 \times 10^{-9}$	
1·50	7	−380	0·59	31·7	$0·187 \times 10^{-9}$	
1·70	13	−508	0·47	42·4	$0·199 \times 10^{-9}$	
						9·77
						±0·10

Table 5

Experiment 19 25°C
Alkaline solution: NaOH: 10·35 mM; $NaClO_4$: 250 mM.
Cobaltous ion solution: Co^{2+}: 5·98 mM; H^+: 0·348 mM; ClO_4^-: 250 mM.
E' from previous acid-base titration: −257 mV.

V ml	E_g mV	$H \times 10^4$	$h \times 10^4$	$X \times 10^4$	K_a'	pK_{av}'
0·00	−202	1740				
2·80	+10	−122·4	0·307	41·0	$0·126 \times 10^{-9}$	
3·10	35	−314	0·115	105·1	$0·121 \times 10^{-9}$	
3·30	42	−440	0·088	147·2	$0·130 \times 10^{-9}$	
						9·90
						±0·02

Table 6

Experiment 32 35°C
Alkaline solutions: NaOH: 10·35 mM; $NaClO_4$: 250 mM.
Cobaltous ion solution: Co^{2+}: 5·04 mM; H^+: 0·550 mM; ClO_4^-: 250 mM.
E' from previous acid-base titration: −263 mV.

V ml	E_g mV	$H \times 10^4$	$h \times 10^4$	$X \times 10^4$	K_a'	pK_{av}'
0·00	−220	2750				
4·50	+12	−179	0·318	71·2	0·226 × 10^{-9}	
5·00	36	−485	0·129	192	0·248 × 10^{-9}	
5·25	41	−636	0·107	252	0·270 × 10^{-9}	
5·50	48	−785	0·082	312	0·256 × 10^{-9}	
						9·61 ±0·04

Table 7

Experiment 26 35°C
Alkaline solution: NaOH: 10·35 mM; $NaClO_4$: 250 mM.
Cobaltous ion solution: Co^{2+}: 5·98 mM; H^+: 0·348 mM; ClO_4^-: 250 mM.
E' from previous acid-base titration: −241 mV.

V ml	E_g mV	$H \times 10^4$	$h \times 10^4$	$X \times 10^4$	K_a'	pK_{av}'
0·00	−188	1740				
3·30	+43	−441	0·227	148	0·336 × 10^{-9}	
3·60	63	−631	0·107	211	0·226 × 10^{-9}	
3·90	65	−818	0·099	274	0·271 × 10^{-9}	
						9·56 ±0·09

Table 8

Experiment 38 40°C
Alkaline solution: NaOH: 10·35 mM; $NaClO_4$: 250 mM.
Cobaltous ion solution: Co^{2+}: 5·040 mM; H^+: 0·550 mM; ClO_4^-: 250 mM.
E' from previous acid-base titration: −265 mV.

V ml	E_g mV	$H \times 10^4$	$h \times 10^4$	$X \times 10^4$	K_a'	pK_{av}'
0·00	−241	2750				
5·00	+34	−484	0·154	192	0·296 × 10^{-9}	
5·25	+41	−635	0·119	252	0·300 × 10^{-9}	
5·50	43	−785	0·111	311	0·345 × 10^{-9}	
						9·50 ±0·04

h, hydrogen-ion concentration known from e.m.f. measurements with the glass electrode, in mmole/l.

X, degree of hydrolysis, equal to $H - h/C$.

$-\log h$, approximate value of the pH of the solution.

K_a and pK_a, usual meanings.

RESULTS AND DISCUSSION

1. *The first acidic ionization constant of cobaltous(II) ion*

As in the case for the hydrolysis equilibrium reaction for other metallic ions, the following reaction has been assumed to determine the equilibrium constant for the first ionization step of the hydrolysis of cobaltous ion

$$Co^{2+}(aq) + H_2O \rightleftharpoons CoOH^+(aq) + H^+(aq). \tag{I}$$

The hydrolysis reaction yields an hydroxo-cobaltous complex ion, which in the simplest case can be represented by the formula in equation (I). The number of hydrogen ions produced is equal to the number of water molecules involved in the reaction. The thermodynamic equilibrium constant K_a° for reaction (I) is

$$K_a^\circ = \frac{a_{\mathrm{CoOH^+}} \times a_{\mathrm{H^+}}}{a_{\mathrm{Co^{2+}}} \times a_{\mathrm{H_2O}}}, \tag{1}$$

where a's are the activities of the reacting species.

The experimental conditions inherent to the potentiometric titration in a constant ionic medium allow equation (1) to be written as a function of concentrations. Then taking the activity of water as unity, we have

$$K_a' = \frac{h \times [\mathrm{CoOH^+}]}{[\mathrm{Co^{2+}}]}, \tag{2}$$

where K_a' is the equilibrium constant in mol/l., h is the hydrogen-ion concentration due to reaction (I) and the terms in square brackets are the concentrations of the other ions. If X is the degree of hydrolysis of the metal ion, and $[\mathrm{CoOH^+}] = X \cdot c$; $[\mathrm{Co^{2+}}] = (1 - X)c$, and it follows from (2) that

$$X = \frac{1}{\dfrac{h}{K_a'} + 1}. \tag{3}$$

Equation (3), which is obviously based on the stoichiometric reaction (I), indicates that the degree of hydrolysis is only a function of hydrogen-ion concentration given in (I). The hydrolytic constant has been calculated from equation (3) by the direct method of calculus, from point to point.

Equation (3) shows also that the degree of hydrolysis of cobaltous ion is independent of its concentration; then, as Hedström[9] and Sillen[8] have proposed, if that value is plotted as a function of log of hydrogen-ion concentration (a term which can be approximately taken as equal to the pH of the solution), results of the experimental runs at different concentrations of cobaltous ion will fit on a curve defined by a constant K_a' which has the average figure found in the calculations. In Fig. 1 experimental data at 25°C is represented; allowing for experimental errors, the agreement is good. Therefore equilibrium reaction (I) gives a satisfactory explanation of the results. As a consequence, we conclude that in the present reaction all the complexes present in appreciable amounts are homonuclear.

It is very likely, as it has been found with other ions, that they are mononuclear complexes. It is however possible that other existing ionic complexes in minor amounts are not detected. The formation of mononuclear complexes occurs preferentially with ligands other than hydroxyl ion, whereas this tends to form polynuclear complexes. Nevertheless the hydrolysis step of the Co(II) aqueous ion is similar to the corresponding reactions of Hg(II)[10] and Fe(II)[9,11] ions, in a constant ionic medium.

2. *Thermodynamic functions related to reaction (I)*

The constant ionic medium technique is convenient to maintain constant the activity coefficients of the ionic species entering reaction (I). However, when other thermodynamic functions of the reaction are to be obtained it is necessary to know the thermodynamic equilibrium constant K_a°, which is usually calculated by extrapolation to zero ionic strength.

The thermodynamic equilibrium constant is independent of the ionic medium while the constants determined through a ratio of concentrations in any ionic medium are not. However when the latter are calculated from experimental data obtained in the presence of a large excess of a known non-complexing supporting electrolyte, the activity coefficients are independent of the concentration of the reacting species, and thus depend only on the nature and concentration of the inert electrolyte. Under these conditions the stoichiometric equilibrium constants are also thermodynamic magnitudes referred to a standard state in which all the activity coefficients are unity at zero concentration of the reacting species in the particular ionic medium. Therefore at 25°C the change of free energy associated to the hydrolysis reaction is

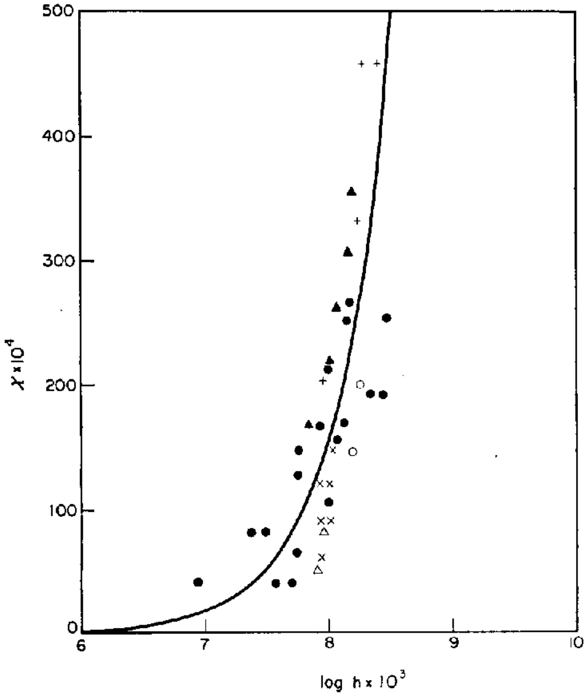

Fig. 1.—Plot of equation (3). $T = 25$°C.
△: Co^{2+}, 10·08 mM; ClO_4^-, 250 mM
+: Co^{2+}, 2·66 mM; ClO_4^-, 250 mM
×: Co^{2+}, 10·66 mM; ClO_4^-, 250 mM
○: Co^{2+}, 5·33 mM; ClO_4^-, 250 mM
●: Co^{2+}, 5·98 mM; ClO_4^-, 250 mM
▲: Co^{2+}, 5·98 mM; ClO_4^-, 750 mM

$$\overline{\Delta G_h}^\circ = -RT \ln K_a' = 13{\cdot}4 \pm 0{\cdot}2 \text{ kcal/mol.}$$

The change of enthalpy can be estimated directly from equation (4) (see later) because its magnitude is included in the second coefficient of that equation,

$$\overline{\Delta H_h}^\circ = 8{\cdot}2 \text{ kcal/mol} \pm 2{\cdot}0 \text{ kcal/mol.}$$

It is obvious that ΔH, and also ΔS, when calculated from ΔG, are in error much larger than the error involved in ΔG. For this reason a calorimetric method is better used to obtain ΔH and ΔS more accurately.

3. *The effect of temperature and ionic concentration*

Fig. 2 shows the average values of the hydrolysis constants at different temperatures. In the range we have studied the equilibrium constant depends on temperature in the form predicted by the van't Hoff equation. The experimental equation calculated by the least square method is

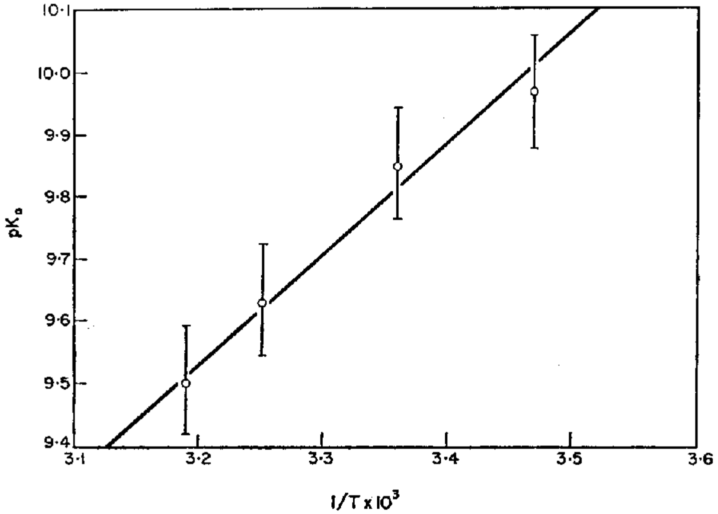

FIG. 2.—pK_a vs. $1/T$.
$T = 15°C$: average from 24 experimental determinations.
$T = 25°C$: average from 45 experimental determinations.
$T = 30°C$: average from 15 experimental determinations.
$T = 35°C$: average from 12 experimental determinations.

$$\log K_a' = 3{\cdot}82 + \frac{1785}{T}, \tag{4}$$

where T is the absolute temperature.

The ionic strength was varied between the available limits, and within them the equilibrium constant did not change appreciably. Nevertheless as variations must occur in the more dilute region, we correct pK_a' to zero ionic strength by using the Debye-Hückel extended equation as suggested by Davies.[12] The figures for p$K'_{a(\mu=0)}$ are some 4 per cent higher than the calculated values from experiment. In the calculation we have employed the pK's directly as obtained, because the correction and extrapolation involve uncertainties.

4. *The second acidic ionization constant of cobaltous ion*

The equilibrium constant K_{a_2} of the reaction

$$\mathrm{CoOH^+(aq) + H_2O \rightleftharpoons Co(OH)_2(}s\mathrm{) + H^+(aq)} \tag{II}$$

can be immediately calculated, since it is related to the solubility product of cobaltous hydroxide ($K_s = 2 \times 10^{-16}$ at 25°C)[13], to the first acidic ionization constant ($K_a' = 1{\cdot}58 \times 10^{-10}$) and to the ionic product of water ($K_w = 1{\cdot}01 \times 10^{-14}$),

$$K_{a_2} = \frac{K_w^2}{K_a' \times K_s},$$

resulting in $K_{a_2} = 3{\cdot}16 \times 10^{-3}$ at 25°C. The free energy change $\Delta G^\circ_{\text{II}}$ related to reaction (II) is 3·4 kcal/mol. On the other hand the equilibrium constant for reaction

$$\text{Co(OH)}_2(J) \rightleftharpoons \text{Co(OH)}_2\text{(aq)} \tag{III}$$

is $K_{\text{III}} = 4 \times 10^{-7}$ at 25°C.[14]

Therefore the second acidic ionization constant related to reaction (IV)

$$\text{CoOH}^+\text{(aq)} + \text{H}_2\text{O} \rightleftharpoons \text{Co(OH)}_2\text{(aq)} + \text{H}^+\text{(aq)} \tag{IV}$$

is $1{\cdot}26 \times 10^{-9}$ and $\Delta G^\circ_{\text{IV}} = 12{\cdot}1$ kcal/mol. Comparing the figures for pK_a and pK_{a_2}, the latter is smaller than the former, a fact which is opposite to the expected behaviour of polybasic acids. For these substances the ionization constants are smaller the larger the number of hydrogen ions separated from them, as in the ionization of phosphoric acid, where $K_1 > K_2 > K_3$, the differences between them being of the order of 10^{-5}. This supports the idea that if K_a for the hydrolysis of cobaltous ion is $10^{-9.8}$, K_{a_2} should be of the order of 10^{-15}, because for energetic reasons the separation of a hydrogen ion from a cobaltous(II) aqueous ion is more likely to occur than from a $\text{CoOH}^+_{(\text{aq})}$ ion. Nevertheless K_{a_2} is $1{\cdot}26 \times 10^{-9}$. This fact (similar to what is observed in $\text{Hg(II)}_{(\text{aq})}$ ion) indicates that the following disproportionation reaction is thermodynamically favoured,

$$2\text{CoOH}^+\text{(aq)} \rightleftharpoons \text{Co(OH)}_2(s) + \text{Co}^{2+}\text{(aq)} \tag{V}$$

The equilibrium constant for reaction (V) at 25°C is

$$K_{\text{V}} = \frac{K_{a_2}}{K_a} = \frac{1{\cdot}26 \times 10^{-9}}{0{\cdot}158 \times 10^{-9}} = 7{\cdot}98,$$

and the free energy change $\Delta G^\circ_{\text{V}} = -1{\cdot}2$ kcal/mol.

5. *Comparison of the present value of* pK_a *with previous data*

The data found in the literature for pK_a of Co^{2+} are summarized in Table 9. The figure obtained at 100°C could be explained by means of equation (4). The value calculated with it by extrapolating at that temperature is coincident with the pK_a reported by Kullgren ($\text{p}K^{100°\text{C}}_{a(\text{extrapolated})} = 8{\cdot}60$).

The lower pK_a could also be explained by the procedure employed for preparing.

TABLE 9

T°C	pK_a	Ionic system	Reference
100	8·7	Dil. $\text{Co(NO}_3)_2$ and CoCl_2 solutions	(1)
25	9·3	Dil. CoSO_4 soln.	(2)
25	12·2	$c \to 0$ (CoCl_2 soln.)	(3)
30	8·9	$\mu = 0{\cdot}1$ (KCl)	(4)

the electrolytic solution, since the recrystallization of the salt from acid solutions usually leaves traces of free acid in the salt which later alter the hydrogen-ion concentration. The largest value is not easy to explain, but was obtained with a cobaltous chloride solution, which is not the best choice due to the tendency of chloride ion to form complexes which interfere in the hydrolytic equilibria. But it is interesting to emphasize that the pK_a' given here for 25°C is perfectly coincident with preliminary data obtained in this laboratory with a cobaltous perchlorate solution prepared by dissolving fresh prepared cobaltous hydroxide in dilute perchloric acid solution.[15]

CONCLUSIONS

1. The first acidic ionization constant of Co(II) ion as cobaltous perchlorate has been determined with greater accuracy through an experimental method (more reliable than the previous ones performed by other authors) at a given fixed temperature.
2. Data assembled from experiments at different temperatures, ionic concentrations of cobaltous ion and total ionic strengths show clearly that the first step of the hydrolysis equilibrium reaction is a mononuclear reaction yielding the complex $CoOH^+$.
3. Experimental measurements have been extended from 15 to 40°C and an experimental equation has been obtained for the dependence of the equilibrium constant with temperature.
4. Changes of free energy and enthalpy have been calculated for the reaction at 25°C.
5. The second acidic ionization constant of Co(II) ion comes out with a numerical value higher than the expected one. This fact is an evidence that the disproportionation of $CoOH^+$ is thermodynamically favoured in the ionic equilibria of Co(II) ion in aqueous solution.

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