[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE OHIO STATE UNIVERSITY]

The Solubility of Cobalt Hydroxide, $Co(OH)_2$, in Solutions of Hydrochloric Acid and Sodium Hydroxide at 25°

BY KARL H. GAYER[1] AND A. B. GARRETT

The purpose of this investigation was to secure further information as to the character of the ions of cobalt hydroxide from measurements of its solubility in dilute solutions of sodium hydroxide and hydrochloric acid. In the interpretation of the results obtained, cobalt hydroxide is considered to be amphoteric in nature. From this point of view, its solubility in the presence of added sodium hydroxide is due mainly to the extent to which the weak acid H_2CoO_2 is neutralized by the strong base. On the other hand, its solubility in the presence of the added hydrochloric acid is due mainly to neutralization of the base $Co(OH)_2$ by the strong acid. In order to interpret the results in this latter case, it was necessary to determine the activity of the hydrogen ion in the saturated solutions by means of a glass electrode. The solubility measurements indicate that cobalt hydroxide is much stronger as a base than it is as an acid.

Earlier work on cobalt hydroxide and cobalt chloride is of interest to report here. Britton[2] calculated the solubility product to be 1.06×10^{-18} at 25°. Denham[2] determined the degree of hydrolysis of cobalt chloride at 25° in 0.062 and 0.031 molal solution; he obtained 0.11 and 0.17% hydrolysis, respectively.

No work is reported which shows the complete record of the behavior of cobalt hydroxide in acid and basic solutions; data for that record are presented in this paper.

Procedure

The general procedure is similar to that described by Garrett and Heiks.[3]

Water.—Triple distilled water was used. It was boiled to free it from any carbon dioxide and oxygen, then stored under nitrogen.

Sodium Hydroxide Solutions.—Baker and Adamson Reagent sodium hydroxide pellets were dissolved in freshly boiled distilled water; barium hydroxide was added in slight excess to precipitate all the carbonate. The solutions were standardized against potassium acid phthalate using phenolphthalein indicator.

Cobalt Chloride Solutions.—Mallinckrodt C. P. reagent cobalt chloride was used to prepare the hydroxide and to prepare the standards for the colorimetric determination of cobalt.

Hydrochloric Acid Solutions.—Standard acid solutions for analysis and for the solubility measurements were prepared from C. P. reagent hydrochloric acid; they were standardized gravimetrically.

Nitroso R Salt Solutions.—Coleman and Bell Company reagent nitroso R salt was used to prepare the 0.1% solution.

Cobalt Hydroxide.—Cobalt hydroxide was precipitated from a hot solution of cobalt chloride hexahydrate (50 g. per liter of water) with an equal volume of 0.5 molar solution of sodium hydroxide in an atmosphere of nitrogen. Fifteen two-liter washings with distilled water sufficed to give pure cobalt hydroxide as evidenced by a flame test indicating the total absence of sodium.

Equilibration.—Two 180-ml. samples of cobalt hydroxide, water and acid or base for equilibration, contained in 200-ml. round bottom flasks, were always prepared at each concentration of alkali or acid. One sample was agitated in a thermostat at 35° for a period of five to seven days, then transferred to the thermostat at 25 ± 0.02° for an additional period of seven days. The mates were placed directly in the 25° thermostat for five to seven days. By this means, equilibrium was approached from supersaturation and undersaturation; the solubility values of each such a pair of samples were found to agree with each other within experimental limits.

Sedimentation.—After the completion of the agitation period, the flasks were clamped in an upright position in the 25° thermostat, and allowed to sediment for seven days.

Filtration.—The flasks were opened and the contents removed (under an atmosphere of nitrogen) to a covered sintered glass funnel and from this into a glass-stoppered bottle.

Measurement of Hydrogen Ion Concentration.—The *p*H values of the equilibrated samples were obtained by using a Beckman portable a. c., glass electrode. The meter was calibrated with potassium acid phthalate-sodium hydroxide buffer at *p*H 4, with disodium phosphate-monopotassium phosphate buffer at *p*H 7 and with boric acid–sodium hydroxide buffer at *p*H 10.

Analysis of Cobalt.—The cobalt analysis of the equilibrated samples was made with a Lumetron spectrophotometer using nitroso R salt to produce the colored complex.[4] The analyses were reproducible to ±2%.

The Data

The data are collected in Tables I and II and are given graphically in Figs. 1, 2 and 3. Figure 1 shows the change of solubility of cobalt hydroxide in sodium hydroxide solutions. Figure 2 shows the change of solubility of cobalt hydroxide in hydrochloric acid solutions (extrapolated to *p*H 7). Figure 3 shows the change of cobalt hydroxide solubility near *p*H 7. Because of the very low

TABLE I

SOLUBILITY OF COBALT HYDROXIDE IN SODIUM HYDROXIDE SOLUTION AT 25°

Moles NaOH/1000 g., H_2O	Moles $Co(OH)_2$/1000 g. H_2O	$K_3 = m_{HCoO_2^-}\gamma_{HCoO_2^-}/m_{OH^-}\gamma_{OH^-}$
0.01	5×10^{-7}	1.0×10^{-5}
.05	8×10^{-7}	0.8×10^{-5}
.24	1.8×10^{-7}	0.6×10^{-5}
.55	3.7×10^{-6}	0.6×10^{-5}
.89	9.2×10^{-6}	1.0×10^{-5}
4.95	5.8×10^{-4}	Ionic strength too high to calc. K_3
9.70	5.1×10^{-3}	
	Av.	8×10^{-6}

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[1] Wayne University, Detroit, Michigan.

[2] (a) Britton, *J. Chem. Soc.*, **127**, 2110 (1925); (b) Denham, *Z. anorg. Chem.*, **57**, 378 (1908).

[3] Garrett and Heiks, THIS JOURNAL, **63**, 562 (1941).

[4] Sandell, "Colorimetric Determination of Traces of Metals," Interscience Publishers, New York, N. Y., 1945, p. 200.

TABLE II

SOLUBILITY OF $Co(OH)_2$ IN SOLUTIONS OF HCl AT 25°

Moles HCl/1000 g. H_2O (initial concentration)	Moles $Co(OH)_2$/1000 g. H_2O	a_{H^+}/1000 g. H_2O from pH at equilibrium	$K_6 = m_{Co^{++}}\gamma_{Co^{++}}/m^2_{H^+}\gamma^2_{H^+}$
0.000	1.3×10^{-5} (extd.)	5.1×10^{-9}	
.003	1.5×10^{-3}	2.69×10^{-8}	1.8×10^{12}
.005	2.6×10^{-3}	3.02×10^{-8}	2.4
.01	4.8×10^{-3}	4.68×10^{-8}	1.7
.03	1.55×10^{-2}	7.41×10^{-8}	2.0
.05	2.4×10^{-2}	8.32×10^{-8}	2.2
.074	3.85×10^{-2}	9.55×10^{-8}	2.5
.100	5.2×10^{-2}	1.05×10^{-7}	2.7
.130	6.8×10^{-2}	1.07×10^{-7}	3.4
.160	8.0×10^{-2}	1.15×10^{-7}	3.3
.170	8.7×10^{-2}	1.17×10^{-7}	3.4
		Av.	2.5×10^{12}

solubility of cobalt hydroxide in water and basic solutions, the inflection of the curve in Fig. 3 is drawn by interpolation and shows the most probable change.

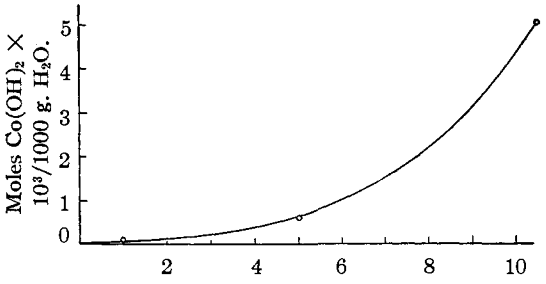

Fig. 1.—Solubility of cobalt hydroxide in sodium hydroxide solutions.

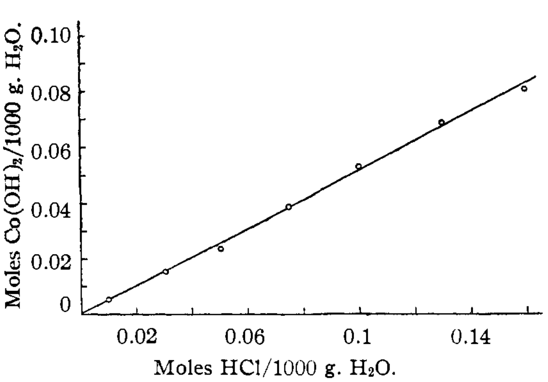

Fig. 2.—Solubility of cobalt hydroxide in hydrochloric acid solution.

Quantitative evidence for the basic character of cobalt hydroxide is obtained from the values of the acidic and basic ionization constants.

General Equilibria.—In general the possible equilibria of cobalt hydroxide in neutral, acidic and alkaline solutions may be represented by equations (1) to (8).

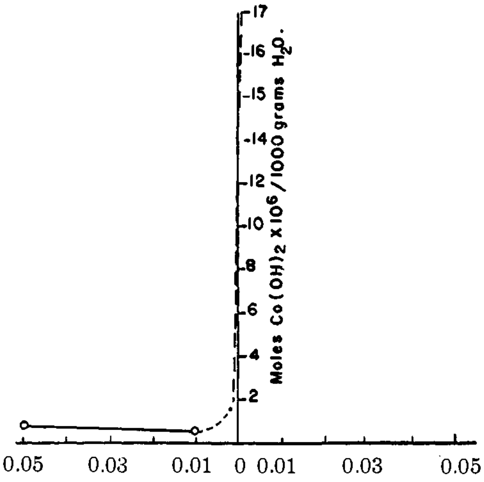

Fig. 3.—Change of cobalt concentration near pH 7.

$$Co(OH)_2(s) \rightleftharpoons Co^{++} + 2OH^- \quad (1)$$

$$Co(OH)_2(s) \rightleftharpoons CoOH^+ + OH^- \quad (2)$$

$$Co(OH)_2(s) + OH^- \rightleftharpoons HCoO_2^- + H_2O \text{ or } Co(OH)_3^- \quad (3)$$

$$Co(OH)_2(s) + 2OH^- \rightleftharpoons CoO_2^{=} + 2H_2O \quad (4)$$

$$Co(OH)_2(s) + H^+ \rightleftharpoons CoOH^+ + H_2O \quad (5)$$

$$Co(OH)_2(s) + 2H^+ \rightleftharpoons Co^{++} + 2H_2O \quad (6)$$

$$Co(OH)_2(s) \rightleftharpoons HCoO_2^- + H^+ \quad (7)$$

$$Co(OH)_2(s) \rightleftharpoons Co(OH)_2 \quad (8)$$

Equilibria in Basic Solutions.—The constancy of the values of K_3 in Table I indicate that the two main reactions which determine the solubility of cobalt hydroxide in the presence of sodium hydroxide are represented by Equations (3) and (8). Using the data over the range of 0.01 to 0.89 molar sodium hydroxide, and subtracting the concentration of undissociated cobalt hydroxide (0.4×10^{-6} mole), due to Equation 8, found by extrapolating (large scale) the solubility of $Co(OH)_2$ to $m_{NaOH} = 0$, K_3 for the following reaction was calculated

$$Co(OH)_2(s) + OH^- \rightleftharpoons HCoO_2^- + H_2O \quad (3)$$

$$K_3 = \frac{m_{HCoO_2^-}\ \gamma_{HCoO_2^-}}{m_{OH^-}\gamma_{OH^-}} = 8 \times 10^{-6} \pm 2 \times 10^{-6}$$

$$\Delta F^0 = 7000$$

In this calculation it is assumed the $\gamma_{HCoO_2^-}/\gamma_{OH^-} = 1$ over the range of concentration studied. Using the value of K_3 and the ionization constant, K_w, for water, the acid dissociation constant K_7 for the following reaction was calculated

$$Co(OH)_2(s) \rightleftharpoons HCoO_2^- + H^+ \quad (7)$$

$$K_7 = K_3K_w = 8 \times 10^{-20} \pm 2 \times 10^{-20}$$

$$\Delta F^0 = 26{,}000$$

The evaluation of the ionization constant for the equilibrium

$$Co(OH)_2(aq) \rightleftharpoons H^+ + HCoO_2^- \quad (9)$$

is obtained from the ratio $K_7/K_8 = K_9 = 2 \times 10^{-13}$.

Equilibria in Acid Solutions.—The data of columns 1 and 2 of Table II indicate that equations (6) and (8) can account for the chemical change involved; if any $CoOH^+$ ions are present, they must be in small amounts. The value of K_6 was obtained by the use of a_{H^+} measured by the glass electrode

$$Co(OH)_2(s) + 2H^+ \rightleftarrows Co^{++} + 2H_2O \qquad (6)$$

$$K_6 = \frac{m_{Co^{++}}\gamma_{Co^{++}}}{m^2_{H^+}\gamma^2_{H^+}} = 2.5 \times 10^{12}$$

$$\Delta F^0 = -17{,}000 \text{ cal.}$$

the value of $m_{Co^{++}}$ = total solubility − undissociated cobalt hydroxide; and the values of $\gamma_{Co^{++}}$ were obtained from a table of activity coefficients for divalent ions compiled by Harned and Owen.[5] Further evidence that the reaction indicated by equation (5) has little or no effect on the value of K_6 is the near constancy of K_6 over the concentration range of $m_{HCl} = 0$ to 0.17. The error in K_6 is in the order of $\pm 1 \times 10^{+12}$.

The value of the ionization constant for the equilibrium

$$Co(OH)_2(aq) \rightleftarrows Co^{++} + 2OH^- \qquad (10)$$

is obtained from the ratio $K_{10} = K_1/K_8$ $K_{10} = 6 \times 10^{-10}$.

The Value of the Water Solubility.—The magnitude of the value of the water solubility of cobalt hydroxide seems to be in the order of 1×10^{-5} to 3×10^{-5}. This order of magnitude is obtained by combining the data from Figs. 1 and 2 into Fig. 3. It was found to be impossible to obtain reproducible data on the solubility of cobalt hydroxide in pure water presumably because of the error involved due to (1) adsorbed hydroxyl ions on the cobalt hydroxide and (2) the colloidal nature of highly purified samples of cobalt hydroxide.

The Value of K_1.—From the value of the ion product K_w of water and $K_6 = 2.5 \times 10^{+12}$ obtained from the solubility of cobalt hydroxide in acid, the value of K_1 was calculated for the equation

$$Co(OH)_2(s) \rightleftarrows Co^{++} + 2OH^- \qquad (1)$$

$$K_1 = K_6K_w^2 = m_{Co^{++}}\gamma_{Co^{++}}m^2_{OH^-}\gamma^2_{OH^-}$$

$$K_1 = 2.5 \times 10^{-16}$$

$$\Delta F^0 = 21{,}000 \text{ cal.}$$

This value agrees well with the value estimated by Latimer[6] of $K_1 = 2 \times 10^{-16}$.

Summary

The solubility of cobalt hydroxide has been determined in dilute acid and base at 25 ± 0.02°. The principal reactions occurring in these solutions are shown by equations

$$Co(OH)_2(s) + OH^- \rightleftarrows HCoO_2^- + H_2O \qquad (3)$$

$$Co(OH)_2(s) + 2H^+ \rightleftarrows Co^{++} + 2H_2O \qquad (6)$$

The constants evaluated from the data in this research are

$Co(OH)_2(s) = Co(OH)_2(aq) \quad K_8 = 4 \times 10^{-7}$

$Co(OH)_2(s) = Co^{++} + 2OH^- \quad K_1 = 2.5 \times 10^{-16}$

$Co(OH)_2(aq) = Co^{++} + 2OH^- \quad K_{10} = 6 \times 10^{-10}$

$Co(OH)_2(s) = H^+ + HCoO_2^- \quad K_7 = 8 \times 10^{-20}$

$Co(OH)_2(aq) = H^+ + HCoO_2^- \quad K_9 = 2 \times 10^{-13}$

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[5] Harned and Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corporation, New York, N. Y., 1943, pp. 423, 384.

[6] Latimer, "Oxidation Potentials," Prentice-Hall, New York, N. Y., 1938, p. 199.

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Concerning the Dependence of the Surface Energy and Surface Tension of Spherical Drops and Bubbles on Radius

BY TERRELL L. HILL

For sufficiently large curvatures of gas–liquid interfaces, the surface tension and surface energy presumably no longer have the values associated with plane surfaces. This effect may be of fundamental importance in connection with nucleation of condensation and evaporation, adsorption of gases in highly porous media such as charcoal, etc. In view of the difficulty of direct experimental work in this field, theoretical studies may be especially useful. Tolman[1] has discussed this subject recently from a quasi-thermodynamic point of view. Also, Kirkwood and Buff[2] have given a rigorous treatment of the surface tension of plane surfaces, and indicate that their theory (using a mechanical definition of surface tension rather than a thermodynamic one) is to be extended to curved surfaces. Some years ago Fowler[3] presented an approximate theory of surface tension for plane surfaces based on the thermodynamic definition; the expression for the surface tension and surface energy on this theory

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[1] R. C. Tolman, *J. Chem. Phys.*, **16**, 758 (1948); **17**, 118, 333 (1949).

[2] J. G. Kirkwood and F. P. Buff, *ibid.*, **17**, 338 (1949).

[3] R. H. Fowler, *Proc. Roy. Soc.* (*London*), **A159**, 229 (1937); see also Fowler and Guggenheim, "Statistical Thermodynamics," Cambridge University Press, 1939, pp. 445-451.