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

The Equilibria of Nickel Hydroxide, $Ni(OH)_2$, in Solutions of Hydrochloric Acid and Sodium Hydroxide at 25°

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The purpose of this investigation was to obtain data on the equilibria of nickel hydroxide in dilute solutions of sodium hydroxide and hydrochloric acid. Such data make possible (1) the determination of the character of the ions in dilute solutions, (2) the evaluation of the free energy of formation of these ions, (3) the evaluation of the solubility and the solubility product of nickel hydroxide, and (4) the amphoteric nature of the hydroxide.

Previous work on nickel hydroxide is at variance as to the magnitude of the water solubility and the solubility product. Almkvist[1] reported the solubility of nickel hydroxide to be 1×10^{-4} mole at 20°. Britton[2] calculated the solubility product to be 2.07×10^{-17} at 25°; while Wijs[3] reported a value of 1.6×10^{-14}.

No work is reported which can be used to show the complete record of the behavior of nickel hydroxide in acid and basic solutions; data for that record are presented in this paper.

Procedure

The general procedure is similar to that in a previous paper by Garrett and Heiks.[4]

Water.—Triply distilled water was used. It was boiled to free it from carbon dioxide and oxygen then it was 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.

Nickel Nitrate Solutions.—Mallinckrodt C. P. reagent was used to prepare the hydroxide and to prepare the standards for the colorimetric determination of nickel.

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

Other Reagents.—Nickel ammonium sulfate was used to prepare a second set of colorimetric and polarographic standards. A 1% alcoholic solution of dimethylglyoxime was prepared as specified by Sandell.[5]

Nickel Hydroxide.—The nickel hydroxide was prepared is an atmosphere of nitrogen. A hot solution containing 1 g. of nickel nitrate hexahydrate per liter of water was precipitated with an equal volume of 0.02 molar solution of sodium hydroxide. Ten two-liter washings of distilled water sufficed to give pure nickel hydroxide as evidenced by the total absence of sodium from a flame test.

Equilibration.—Two 180-ml. samples 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. Both values were found to check 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 Nickel.—The nickel analysis of the equilibrated samples was made with a Lumetron spectrophotometer using dimethylglyoxime to produce the colored complex; the method is described by Sandell.[5] The analyses were reproducible to ±2%.

The data are collected in Tables I and II and are shown graphically in Figs. 1, 2, and 3. Figure 1 shows the change of solubility of nickel hy-

TABLE I

SOLUBILITY OF $Ni(OH)_2$ IN SOLUTIONS OF NaOH AT 25°

Moles of NaOH/1000 grams H_2O	Moles of $Ni(OH)_2$/1000 grams H_2O	$K_3 = \frac{m_{HNiO_2^-} \times \gamma_{HNiO_2^-}}{m_{OH^-} \times \gamma_{OH^-}}$
[a]1.60×10^{-3}	1×10^{-7}	
1.00×10^{-2}	4×10^{-7}	
1.00×10^{-1}	2×10^{-6}	3×10^{-5}
1.00	6×10^{-6}	9×10^{-6}
8.00	7×10^{-6}	Ionic strength too high to calculate K_2 accurately
10.00	4×10^{-6}	
15.00	5×10^{-6}	
	Av.	6×10^{-5}

[a] By radioactive tracer.

TABLE II

SOLUBILITY OF $Ni(OH)_2$ IN SOLUTIONS OF HCL AT 25°

Moles of HCl/1000 grams H_2O (initial concn.)	a_{H^+} in 1000 g. H_2O from *p*H values at equilibrium	Moles of $Ni(OH)_2$/1000 g. H_2O	$K_6 = \frac{m_{Ni^{++}} \times \gamma_{Ni^{++}}}{m^2_{H^+} \times \gamma^2_{H^+}}$
0.0000	....	0.00010[a]	....
.0025	1.35×10^{-7}	.0013	$6.4 \times 10^{+10}$
.0056	1.68×10^{-7}	.0029	8.6
.0100	2.24×10^{-7}	.0053	8.1
.0160	3.09×10^{-7}	.0083	6.5
.0236	3.72×10^{-7}	.0120	6.3
.0308	4.27×10^{-7}	.0160	6.1
.0447	5.13×10^{-7}	.0230	5.8
.0523	5.37×10^{-7}	.0271	5.9
.0811	6.61×10^{-7}	.0413	5.6
.1001	7.08×10^{-7}	.0511	5.8
		Av.	$6.5 \times 10^{+10}$

[a] Extrapolated value.

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[1] Almkvist, *Z. anorg. Chem.*, **103**, 240 (1918).

[2] Britton, *J. Chem. Soc.*, **127**, 2110 (1925).

[3] Wijs, *Rev. trav. chim.*, **44**, 663 (1925).

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

[5] Sandell, "Colorimetric Determination of Traces of Metals," Interscience Publishers, New York. N. Y., 1945, p. 339.

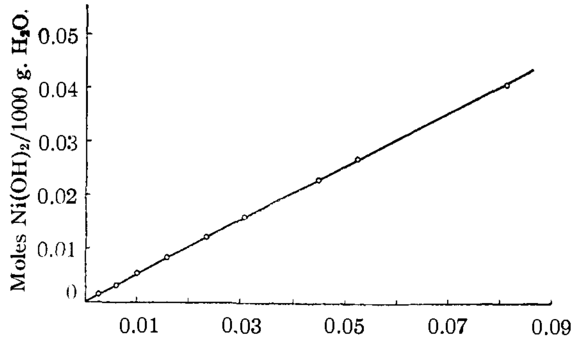

Fig. 1.—Solubility of nickel hydroxide in hydrochloric acid solutions.

droxide in hydrochloric acid solutions and Fig. 2 shows the change of solubility of nickel hydroxide in dilute hydrochloric acid solutions with the extrapolation to pH 7. Figure 3 shows the change of nickel hydroxide solubility near pH 7. Due to the extremely low solubility of nickel hydroxide in water and basic solutions, the inflection of the curve in Fig. 3 is drawn by interpolation and shows the most probable change.

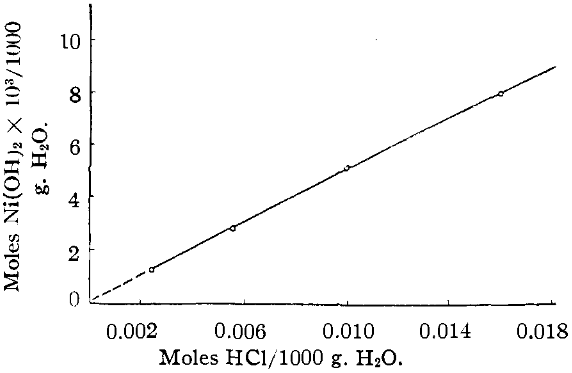

Fig. 2.—Solubility of nickel hydroxide in hydrochloric acid solution.

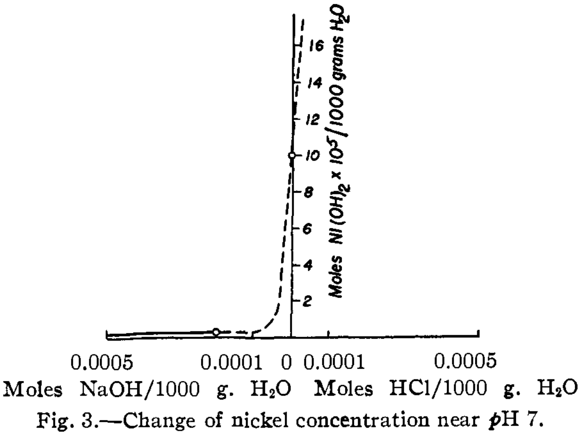

Fig. 3.—Change of nickel concentration near pH 7.

The high solubility of nickel hydroxide in acid solutions along with the pH values of these solutions (in the order of pH 7) and the low solubility of nickel hydroxide in basic solutions give qualitative evidence that nickel hydroxide is a strong base. Quantitative evidence for the basic character of nickel hydroxide is given by the values of the acidic and basic ionization constants.

The solubility of nickel hydroxide in sodium hydroxide solution was checked by means of several radioactive tracer experiments using the $^{58}_{27}$Ni isotope (half life of 36 hours). The nickel was prepared by alpha bombardment of iron in The Ohio State University Cyclotron.

The values for the activity coefficients for hydroxyl ions and divalent nickel ions were taken from Harned and Owen.[6]

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

(1) $Ni(OH)_2(s) \rightleftarrows Ni^{++} + 2OH^-$
(2) $Ni(OH)_2(s) \rightleftarrows NiOH^+ + OH^-$
(3) $Ni(OH)_2(s) + OH^- \rightleftarrows HNiO_2^- + H_2O$
(4) $Ni(OH)_2(s) + 2OH^- \rightleftarrows NiO_2^= + 2H_2O$
(5) $Ni(OH)_2(s) + H^+ \rightleftarrows NiOH^+ + H_2O$
(6) $Ni(OH)_2(s) + 2H^+ \rightleftarrows Ni^{++} + 2H_2O$
(7) $Ni(OH)_2(s) \rightleftarrows HNiO_2^- + H^+$
(8) $Ni(OH)_2(s) \rightleftarrows Ni(OH)_2$

The value of K_8 is in the order of 10^{-7} and is too small to affect the values of K_3 and K_6 within the limits of their determinations from these data.

Equilibria in Basic Solutions.—Unfortunately the solubility of nickel hydroxide in alkaline solutions up to 15 molar sodium hydroxide was found to be so slight that only estimates of its solubility could be made by the analytical means available. We can make the very probable assumption that the solubility of nickel hydroxide in alkali is due to the reaction indicated by equation (3).

$$Ni(OH)_2(s) + OH^- \rightleftarrows HNiO_2^- + HOH \quad (3)$$

Values of K_3 calculated over the range of 0.0016 to 0.1 molar sodium hydroxide give an average value of $K_3 = 6 \times 10^{-5} \pm 5 \times 10^{-6}$ with a corresponding $\Delta F°$ of 6000 cal.

Using the value for K_3 and K_w, the ionization constant for water at 25°, the ionization constant K_7

$$Ni(OH)_2(s) \rightleftarrows HNiO_2^- + H^+ \quad (7)$$

for nickel hydroxide was computed

$$K_7 = K_3K_w / a_{H_2O} = 6 \times 10^{-19}$$
$$\Delta F° = 25{,}000 \text{ cal.}$$

Equilibria in Acid Solutions.—The data of columns 1 and 3 of Table II indicate that equation 6 can account for the chemical change involved; if any NiOH$^+$ ions are present, they must

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

be so in small amounts. The value of K_6 was obtained by the use of the a_{H^+} measured by the glass electrode

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

$$K_6 = \frac{m_{Ni^{++}}\gamma_{Ni^{++}}}{m^2_{H^+}\gamma^2_{H^+}} = 6.5 \times 10^{10}$$

$$\Delta F^\circ = -15{,}000 \text{ cal.}$$

the values of $m_{Ni^{++}}$ are given in column 3 of Table II, and the values of $\gamma_{Ni^{++}}$ were obtained from a table of activity coefficients for divalent ions compiled by Harned and Owen.[6] Further evidence that the reaction indicated by equation 5 has little or no effect on the value of K_6 is the constancy of K_6 over the concentration range of $m_{HCl} = 0$ to 0.1. The error in K_6 is in the order of $\pm 0.5 \times 10^{10}$.

The high solubility of nickel hydroxide in acid solution and its low solubility in alkaline solution indicate qualitatively that nickel hydroxide is a relatively strong base. Finally, the calculated values of the acid and base constants of nickel hydroxide fully verify the strong basic character.

The Value of the Water Solubility at 25°.—The value of the water solubility of nickel hydroxide, 1.0×10^{-4}, was determined by extrapolating the solubility of nickel hydroxide in dilute acid solution of $m_{HCl} = 0$ (see Figs. 2 and 3). The extrapolation was made graphically (large scale) by the aid of the value of the slope of the line obtained in 0.006 to 0.05 molal acid solutions. This procedure was necessary because the solubility of nickel hydroxide in water is below that which can be determined accurately by any classical chemical method. Furthermore, this is probably a more accurate value than could be obtained by direct measurement, were a satisfactory method of analysis available, because of the error involved in a direct measurement due to (1) any adsorbed hydroxyl ions on the nickel hydroxide and (2) the colloidal nature of highly purified samples of nickel hydroxide. The value of the water solubility is probably good to $\pm 0.5 \times 10^{-4}$.

The Solubility Product Constant.—From the value of the ion product K_w of water and $K_6 = 6.5 \times 10^{+10}$ obtained from the solubility of nickel hydroxide in acid, the solubility product constant K_1 was calculated for the equation

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

$$K_1 = \frac{K_6K^2_w}{a^2_{H_2O}} = m_{Ni^{++}}\gamma_{Ni^{++}}m^2_{OH^-}\gamma^2_{OH^-}$$

$$K_1 = 6.5 \times 10^{-18}$$

$$\Delta F^0 = 23{,}000 \text{ cal.}$$

Summary

The solubility of nickel hydroxide has been determined in dilute acid and base at 25 ± 0.02°. The data show nickel hydroxide to be a relatively strong base. The reactions occurring in basic and acid solution are shown by equations

$$Ni(OH)_2(s) + OH^- \rightleftarrows HNiO_2^- + H_2O \qquad (3)$$

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

The value for the solubility product of nickel hydroxide, is 6.5×10^{-18}. The value for the water solubility of nickel hydroxide is 1.0×10^{-4}. The acid dissociation constant of nickel hydroxide is 6×10^{-19}.

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Measurement of the Capacity of the Electrical Double Layer at a Mercury Electrode

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It has long been known that the slope of the electrocapillary curve of a liquid metal in a salt solution gives the surface charge density of electricity at the interface.[1-5] In a like manner the second derivative of the electrocapillary curve gives the differential capacity,[3,4] a quantity which can also be measured directly with fair precision. It is less well known that from the interfacial tension or from the differential capacity one can obtain a considerable amount of further information about the electrical double layer. For example, it is possible to calculate the charge contributed by each ion separately,[4] the entropy and enthalpy changes associated with the electrochemical process which accompanies an infinitesimal transfer of charge through the cell,[6] and other less easily described properties.[6] In addition there are certain non-thermodynamic properties which are obtained by combining the thermodynamic properties with quantities calculated from the kinetic theory of the electrical double layer.[4] All this has been discussed elsewhere.

It is a matter of great difficulty to make interfacial tension measurements with sufficient precision to serve for these calculations, and we have accordingly attempted to develop apparatus for the precise measurement of the differential capacity of the double layer at a mercury surface. Two models of this apparatus have already been described.[3,7] Considerable changes have now

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(1) Lippmann, *Ann. Physik Chem.* (*Wied. Ann.*), **11**, 316 (1880).

(2) Koenig, *J. Phys. Chem.*, **38**, 111, 339 (1934).

(3) Grahame, THIS JOURNAL, **63**, 1207 (1941).

(4) Grahame, *Chem. Revs.*, **41**, 441 (1947).

(5) Grahame and Whitney, THIS JOURNAL, **64**, 1548 (1942).

(6) Grahame, *J. Chem. Phys.*, **16**, 1117 (1948).

(7) Grahame, THIS JOURNAL, **68**, 301 (1946).