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Note

SOLUBILITY AND THERMODYNAMIC DATA OF NICKEL HYDROXIDE

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Since nickel hydroxide plays an important role in the solubility of hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$, containing nickel as an impurity, the solubility studies of nickel hydroxide at various temperatures ranging from 25 to 40°C at an interval of 5°C has been undertaken and related thermodynamic data calculated. Nickel can be considered to become incorporated into the apatite [1,2] by the ion exchange process

$$Ca_{10}(PO_4)_6(OH)_2 + n\,Ni^{2+} \rightarrow Ca_{10-n}Ni_n(PO_4)_6(OH)_2 + n\,Ca^{2+}$$

In view of the divergent solubility data of nickel hydroxide reported earlier [3—6], as a part of the physico-chemical investigations on hydroxyapatite containing nickel, it is necessary to reinvestigate the solubility product of nickel hydroxide.

EXPERIMENTAL

Nickel hydroxide was precipitated at 37°C in a CO_2-free atmosphere by the dropwise addition of a 0.8 M solution of sodium hydroxide to a 0.4 M nickel nitrate solution for a theoretical yield of 10 g. The mixing of the reagents was completed within about 1 h and the precipitate was left overnight in contact with the mother liquor to improve the crystallinity. The sample was dried at 100°C for 4 h to constant weight. The nickel content of the sample was determined complexometrically using murexide as indicator. The experimental g at.% of nickel was found to be 0.99, approaching the theoretical value of 1.07 for anhydrous nickel hydroxide. The solubility was determined by the method of equilibration used earlier [7,8] at 25, 30, 35 and 40°C.

RESULTS AND DISCUSSION

The solubility of the sample with respect to Ni^{2+} in the solution was found to increase within about 2 h of equilibration and thereafter, it decreased. It attained saturation in about 4 h. The solubility product was then calculated from the experimentally determined nickel content and pH

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TABLE 1

Values of solubility product for nickel hydroxide

Values reported	Our values	
	After 2 h equilibration	After 4 h equilibration
8.7×10^{-19} (ref. 3)	1.301×10^{-12} (25°C)	1.5×10^{-12} (25°C)
1.0×10^{-18} (ref. 4)	2.43×10^{-12} (30°C)	2.03×10^{-12} (30°C)
2.0×10^{-15} (ref. 5)	2.96×10^{-12} (35°C)	1.68×10^{-12} (35°C)
1.006×10^{-11} (ref. 6)	8.586×10^{-12} (40°C)	2.9×10^{-12} (40°C)

of the medium of equilibration using the relationship

$$K_s = 4S^3$$

for the equilibrium

$$\mathrm{Ni(OH)_2(S)} \rightleftharpoons \mathrm{Ni^{2+}(aq)} + 2\ \mathrm{OH^-(aq)}$$

The results are given in Table 1.

The initial increase in the solubility is considered to be consequent upon the formation of a hydrate which corresponded to the composition $Ni(OH)_2 \cdot H_2O$ and the subsequent process is due to the dissolution of this monohydrate. Our thermodynamic data included in Table 2 is for the process of hydration.

The divergent values of the solubility product of nickel hydroxide may be due to the difference in the composition of the samples prepared under different experimental conditions. Such samples were reported to have various compositions, e.g. $4\ Ni(OH)_2 \cdot H_2O$, $Ni(OH)_2 \cdot 1.5\ H_2O$ and $Ni(OH)_2$ [6,9,10]. The difference in the solubility product after about 2 h of equilibration (at the point of highest solubility) and 4 h (after attainment of saturation) was noticeable only at 40° C (see Table 1).

The calculated values of K_s were then fitted to an equation of the form

$$-\log K_s = A + BT + \frac{C}{T} \tag{1}$$

by the method of least squares. The values of the constants A, B and C in eqn. (1) were found to be $A = -449$, $B = 0.62108$ and $C = 82788.305$, respectively. These values were used in eqns. (2)—(5) to evaluate the standard thermodynamic quantities ΔG^0, ΔH^0, ΔS^0 and ΔC_p^0 of the dissolution process

$$\mathrm{Ni(OH)_2(s)} \rightleftharpoons \mathrm{Ni^{2+}(aq)} + 2\ \mathrm{OH^-(aq)}$$

$$\Delta G^0 = 2.3026R(A + BT + CT) \tag{2}$$

$$\Delta H^0 = 2.3026R(A - CT^2) \tag{3}$$

$$\Delta S^0 = 2.3026R(B + 2CT) \tag{4}$$

$$\Delta C_p^0 = 2.3026R(2CT) \tag{5}$$

TABLE 2

Standard thermodynamic quantities of nickel hydroxide in water at different temperatures after 2h equilibration

Temp. (°C)	$\Delta G^0 \times 10^4$ (J mole^{-1})	$\Delta H^0 \times 10^4$ (J mole^{-1})	$\Delta S^0 \times 10^4$ (J mole^{-1} deg^{-1})	$\Delta G_p^0 \times 10^3$ (J deg^{-1})
25	13.890	13.895	−9.48	−9.32
30	14.360	14.336	−9.638	−9.48
35	14.840	14.811	−9.330	−9.63
40	15.320	15.329	−9.790	−9.790

It is observed that ΔG^0 does not change appreciably with temperature, indicating that the dissolution process is less energy consuming. The positive value of ΔG^0 lends support to the view that nickel hydroxide is more soluble by solvation in water. Further, the increase in the positive values of ΔH^0 shows that the dissolution is an endothermic process; the increase of temerature results in increase of solubility of nickel hydroxide. The increase in the negative value of ΔS^0 indicates that the net amount of order created by Ni^{2+} and OH^- ions is more in aqueous media at higher temperatures.

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