[CONTRIBUTION FROM THE MCPHERSON CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

The Thermodynamic Properties of Neodymium Hydroxide $Nd(OH)_3$, in Acid, Neutral and Alkaline Solutions at 25°; the Hydrolysis of the Neodymium and Praseodymium Ions, Nd^{3+}, Pr^{3+}

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RECEIVED DECEMBER 9, 1957

The equilibria between neodymium hydroxide and hydrogen ions and hydroxide ions have been studied by measuring the solubility of neodymium hydroxide in dilute hydrochloric and perchloric acids, neutral water and sodium hydroxide solutions. The following equilibrium constants and free energy changes were determined: $Nd(OH)_3(s) + 3H^+(aq) \rightleftarrows Nd^{+3}(aq) + 3H_2O(l)$, $K = 8.7 \times 10^{18}$, $\Delta F^0_{298} = -25.9 \pm 0.3$ kcal.; $Nd(s) + 3/2O_2(g) + 3/2H_2(g) \rightleftarrows Nd(OH)_3(s)$, $\Delta F^0_f = -299.6 \pm 0.3$ kcal.; $Nd(OH)_3(s) \rightleftarrows Nd^{+3}(aq) + 3(OH)^-(aq)$, $K = 8.7 \pm 4.7 \times 10^{-24}$, $\Delta F^0_{298} = 31.5 \pm 0.3$ kcal.; $Nd(s) + 3(OH)^-(aq) \rightleftarrows Nd(OH)_3(s) + 3e^-$, potential in basic solution, $E_b = 2.701 \pm 0.004$ v. The water solubility was found to be 4.8×10^{-5} mole of $Nd(OH)_3$ per 1000 g. of water. The solubility in base initially decreases from the water solubility, passes through a minimum at 0.2 molar NaOH and increases to approximately the water solubility in 1 molar NaOH. In addition, to confirm the conclusions drawn from the solubility data, the hydrolysis of the trivalent ions of neodymium and also praseodymium has been studied. The reactions appear to be slow at 25° and most likely proceed according to the equation $Nd^{3+}(aq) + H_2O \rightleftarrows Nd(OH)^{2+}(aq) + H^+(aq)$, $Pr^{3+}(aq) + H_2O \rightleftarrows Pr(OH)^{2+}(aq) + H^+(aq)$. The pK_a values for these reactions were equal within the experimental error and were determined to be 8.5 ± 0.4.

The purpose of this investigation was to obtain data on the equilibria between crystalline neodymium hydroxide and hydrogen ions and hydroxyl ions in aqueous solution at 25°.

The early qualitative work done on the basicity of the oxides and hydroxides of the rare earth elements is reviewed by Moeller and Kremers.[3]

The neodymium oxide–water system has been investigated by Weiser and Milligan,[4] Fricke,[5] Fricke and Seitz,[6] and Seitz.[7] The compound precipitated at 100° from aqueous solutions of neodymium salts by the addition of hydroxide ion has been identified as a hydrous hydroxide, by examination of dehydration isobars. This has the stoichiometric composition $Nd_2O_3 \cdot 3H_2O$ or $Nd(OH)_3$ and crystallizes in the hexagonal system. No quantitative observations have been made on the material precipitated from solution at 25°; however, it is stated that initially the precipitate contained large amounts of the anion present in solution.[8,9] The solubility of the oxide in water at 29° was measured by Busch[10] from electrometric titrations of the liberated hydroxide ion, assuming that the solubility was $^1/_6$ the molality of the hydroxide ion. No investigation was made of the solid phase at equilibrium, however. The solubility of neodymium sesquioxide was given as 5.75×10^{-6} mole per liter, while that for praseodymium sesquioxide is reported to be much less, 6.1×10^{-7} mole per liter. Moeller and Kremers[11] estimated the solubility of freshly precipitated neodymium hydroxide, from the value of the solubility product, to be 2.7×10^{-6} mole per liter at 25°.

The data on the solubility product of neodymium hydroxide all have been obtained by measuring the pH of a solution of a neodymium salt either at the beginning of precipitation of the hydroxide by added hydroxide ion or at a given ratio of Nd^{+3}:OH^- after the appearance of the solid phase. Moeller and Kremers[11] have given these solubility products for $Nd(OH)_3$: from nitrate solution 3.1×10^{-22}, sulfate solution 2.6×10^{-21}, acetate solution 2.8×10^{-21}, and an "average" solubility product of 1.9×10^{-21}. All of these were for the "freshly precipitated hydroxide" at 25°, but again no investigation was made of the solid phase present. Moeller and Fogel[9] extended this study to perchlorate solutions and found a solubility product of 3.2×10^{-22}.

Latimer[12] has estimated the free energy of formation of solid neodymium hydroxide to be −309.3 kcal./mole. The National Bureau of Standards tables[13] give a value for the free energy of formation of neodymium hydroxide of −309.6 kcal./mole as determined from the work of Endres.[14] Exactly how this value was calculated remains somewhat of a mystery, as Endres' paper gives only ratios of the solubility products of the rare earth hydroxides and no absolute values.

Procedure

The experimental procedure and method of preparing reagents followed in this work are similar to that of earlier papers in this series.[15-17]

Neodymium Oxide.—Johnson Matthey and Company "Specpure" Nd_2O_3, containing approximately 0.07% of Pr_2O_3 and less than 0.003% of Sm_2O_3 was used. The oxide was purified by dissolving it in reagent grade perchloric acid, and precipitating the neodymium as $Nd_2(C_2O_4)_3$ with doubly recrystallized oxalic acid, washed free of soluble impurities, dried at room temperature and ignited in platinum at higher than 850° in a stream of oxygen.

Praseodymium Oxide.—Johnson Matthey "Specpure" oxide which contained approximately 0.04% of neodymium oxide was used.

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(1) Taken from the dissertation presented by R. Stuart Tobias to the Graduate School of The Ohio State University in partial fulfillment of the requirements for the degree Doctor of Philosophy, 1956.

(2) Research Division, Photo Products Department, E. I. du Pont de Nemours and Company, Parlin, New Jersey.

(3) T. Moeller and H. E. Kremers, *Chem. Revs.*, **37**, 97 (1945).

(4) H. B. Weiser and W. O. Milligan, *J. Phys. Chem.*, **42**, 673 (1938).

(5) R. Fricke, *Z. Naturforsch.*, **3A**, 62 (1948).

(6) R. Fricke and A. Seitz, *Z. anorg. allgem. Chem.*, **254**, 107 (1947).

(7) A. Seitz, *Z. Naturforsch.*, **1A**, 321 (1946).

(8) H. T. S. Britton, *J. Chem. Soc.*, **127**, 2142 (1925).

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(12) W. Latimer, "The Oxidation States of the Elements and Their Potentials in Aqueous Solutions," Second Ed., Prentice-Hall, Inc., New York, N. Y., 1952, p. 288.

(13) "Selected Values of Chemical Thermodynamic Properties," Circular 500, of the National Bureau of Standards Feb. 1, 1952, Washington, D. C.

(14) G. Endres, *Z. anorg. allgem. Chem.*, **205**, 321 (1932).

(15) A. B. Garrett and R. E. Heiks, THIS JOURNAL, **63**, 562 (1941).

(16) K. Gayer and A. B. Garrett, *ibid.*, **71**, 2973 (1949).

(17) R. A. Gilbert and A. B. Garrett, *ibid.*, **78**, 5501 (1956).

Neodymium and Praseodymium Perchlorate Buffer Solutions.—The neodymium and praseodymium perchlorate solutions were prepared by dissolving weighed amounts of the ignited oxides in standard perchloric acid, titrating the excess acid with standard sodium hydroxide solution and adding additional sodium perchlorate to give a total concentration of perchlorate ion of 3.00 molar.

Sodium Chloride Solutions.—All of the standard sodium chloride solutions were prepared from weighed quantities of C.P. sodium chloride that had been dried in platinum at 600° for three hours.

Sodium Perchlorate Solutions.—The sodium perchlorate solutions were prepared by dissolving weighed amounts of repurified G. Frederick Smith sodium perchlorate in distilled water. The sodium perchlorate was purified by dissolving it in water–ethanol mixtures, filtering and recrystallizing the product as described by Biederman and Sillén.[18] No trace of chloride ion could be detected in the solutions prepared in this manner.

Perchloric Acid Solutions.—All of the perchloric acid solutions were prepared by dilution of Reagent grade, 60% perchloric acid with distilled water. Recrystallized sodium perchlorate was added to give $[ClO_4]^- = 3.00$ *M;* they were analyzed by the method of Oesper.[19]

Solubility Measurements

Preparation of Samples and Equilibration.—Two 150-ml. samples were prepared at each concentration of acid and base and equilibrated by the method described previously.[17–19] In the case of the samples prepared later in the work, equilibration was at 25° only, since it was observed that the samples reaching equilibrium from above saturation tended frequently to give colloidal sols. In the samples where sol formation did not occur, the neodymium concentrations of the 25 and 35° solutions were found to check within the experimental error. To determine whether the reaction had reached completion within the time limit of the experiment, samples were agitated at 25° for 2.5, 7, 14 and 21 days. The values for the total neodymium in solution and the equilibrium hydrogen ion concentration were the same within the experimental error for the last three samples, indicating that the reaction was complete in 7 days.

Sedimentation and Method of Transfer.—These were the same as previous work.[17] Nitrogen gas was used to prevent contact of the solutions with the atmosphere during all of these processes.

Measurement of the Hydrogen Ion Concentration.—The hydrogen ion concentrations of the samples after equilibration were determined with a Beckman model G *p*H meter, using a Beckman general purpose glass electrode and a calomel reference electrode. For the hydrogen ion concentration measurements at equilibrium, the electrodes were standardized at *p*H 7.00 with Beckman *p*H 7 buffer solutions accurate to ±0.02 *p*H unit. For the equilibrium *p*H measurement of the pure water equilibrated samples, standardization was with a boric acid–sodium hydroxide buffer at *p*H 9.00.

For the *p*H measurements of the samples equilibrated with perchloric acid with $[ClO_4^-] = 3.00$ *M*, the calomel cell electrolyte was 4 *M* sodium chloride instead of the usual potassium chloride to avoid precipitation of potassium perchlorate at the liquid–liquid junction.

Spectrophotometric Analysis of Neodymium.—A Beckman DU spectrophotometer was used to determine neodymium in the acid equilibrated samples. Corex cells were used for these measurements.

The absorption band at 796 mμ was used, since the molar extinction coefficient is greatest at this wave length. A constant slit width of 0.05 mm. was used in all measurements.

High perchlorate concentrations had no effect on the absorption spectra of the hydrated neodymium ion in the range 500 to 900 mμ, nor was any intensification of the absorption bands observed.

Before analysis, the samples were checked for any turbidity that would give high readings for the optical density of the solutions. Samples showing measurable turbidity were discarded. Measurements of the optical density were then taken at 796 mμ on the original samples and also on samples acidified to *p*H 3. The results were the same within the experimental limits indicating that the optical density measurements were related to the total neodymium in solution.

It is quite conceivable that $Nd_2(OH)_2^{4+}$ or some such species might not have its absorption peak at 796 mμ, and analysis on *non*-acidified samples would be related only to $[Nd^{3+}]$ and not to total Nd. The treatment of data assumes total Nd measured.

Activation Analyses for Neodymium.—The solubility of neodymium hydroxide in water and in base was well below the limit of sensitivity of the spectrophotometric analysis. These samples were analyzed by neutron-activation. The samples were transferred in a closed system, by nitrogen pressure, from the equilibration bottles to 250-ml. polyethylene bottles and shipped to the Oak Ridge National Laboratory. Aliquots of the sample material were irradiated for one week in the ORNL Graphite Reactor. A cooling period of about 5.0 days after the reactor discharge was maintained to allow the Na^{24} (15.0 h.) to decay from the sample. After the cooling period, at least 5-ml. duplicate aliquots of each sample were processed by a radiochemical separation using known amounts of inactive yttrium as "carrier" for the neodymium radioactivity. The yttrium carrier was initially precipitated with alkali hydroxide. The hydroxide precipitate was then dissolved, and "scavenging" carriers such as copper, barium, sodium, strontium, etc., were added and removed by additional precipitations. The yttrium was finally precipitated as yttrium oxalate. After filtering onto a tared filtering paper, the precipitate was dried by suction. The chemical yield of the experiment was determined by weighing the oxalate compound as $Y_2(C_2O_4)_3 \cdot 9H_2O$. The radioactivity of the induced Nd^{147} (11.3 d.), produced in the reaction Nd^{146} (n, γ) Nd^{147} was measured by means of γ counting. The radiochemical purity of the separated radioactivity was checked by decay studies and γ spectral analysis by means of a single channel-γ scintillation spectrometer. The comparator samples were Nd_2O_3, and these were processed in the same way as the unknown samples. The results are based upon a comparison of the Nd^{147} radioactivity in both the standards and the test sample.

Analysis of the Solid Phase in the Equilibria.—The solid phases remaining upon the equilibration of the neodymium oxide with hydrochloric acid, perchloric acid, water and sodium hydroxide solutions were all investigated by X-ray diffraction. The oxide samples were dried at 80° in a stream of nitrogen according to the method of Weiser and Milligan.[20] The weight lost after ignition in oxygen at 900° was calculated to be 13.78%. The theoretical weight per cent. of water in $Nd_2O_3 \cdot 3H_2O$ is 13.84%. No traces of chloride ion could be detected in the solid phase remaining after the equilibration with hydrochloric acid.

In order to characterize definitely the solid phases, X-ray powder photographs were taken using copper Kα radiation and sealing the samples in 0.3 mm. capillaries. The calculated spacings agreed well with those given by Roy and McKinstry[21] for $Nd(OH)_3$, or the trihydrate of the oxide.

The anhydrous oxide also was examined and found to be the A type of Nd_2O_3 by comparison of the Bragg angles found with those given by Zachariasen.[22] Vickery[23] states that only oxides capable of forming the A type lattice appear to slake and give true hydroxides.

In the samples equilibrated with 0.1 *M* perchloric acid, no lines other than those of the hydroxide could be detected; however, the diffraction was weak and the lines less sharp than in the case of the other samples. Some material may have been present that was amorphous to X-rays.

The Solubility Data

The solubility data are collected in Tables I and II and shown graphically in Figs. 1 and 2. Figure 1 shows the change in solubility of $Nd(OH)_3$ with the initial hydrochloric acid concentration. Figure 2 shows the relative effect of acid and base on the solubility of $Nd(OH)_3$.

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(20) H. B. Weiser and W. O. Milligan, *J. Phys. Chem.*, **38**, 512 (1934).

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(23) R. C. Vickery, "Chemistry of the Lanthanons," Academic Press, Inc., New York, N. Y., 1953, p. 208.

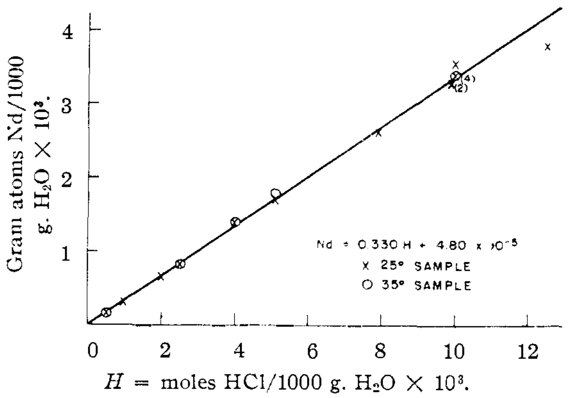

Fig. 1.—Solubility of $Nd(OH)_3$ in dilute hydrochloric acid.

Equilibria with Hydrochloric Acid

Equations (1), (2) and (3) may be written as those most likely to represent the reactions occurring during the dissolution in acid of the samples of neodymium oxide.

$$\text{A-}Nd_2O_3(s) + 3H_2O \longrightarrow Nd_2O_3 \cdot 3H_2O(s) \text{ (or } 2Nd(OH)_3(s)) \quad (1)$$

$$Nd(OH)_3(s) \rightleftarrows Nd(OH)_3(aq) \quad (2)$$

$$qNd(OH)_3(s) + JH^+(aq) \rightleftarrows Nd_q(OH)_p{}^{(3q-p)+}(aq) + JH_2O \quad (3)$$

The generalized reaction 3 is considered, since recent investigations have shown that solutions of scandium, thorium, uranium and the transuranium elements contain significant amounts of polynuclear hydroxyl complexes.

The average charge per neodymium atom in solution, $\bar{n}$, is given by the following equation where H is the initial hydrogen ion concentration of the solution which is reacting with Nd_2O_3, [Nd] the total Nd in soln., h is the equilibrium hydrogen ion concentration after equilibration, and X_{pq} is the equilibrium constant for reactions of type 3. This equation is only valid if no change occurs in the solid phase during the reaction.

$$\bar{n} = \frac{H - h}{[Nd]} = \frac{\sum\limits_{\substack{q=1\\p=0}}^{\infty} J[Nd_q(OH)_p{}^{J+}]}{\sum\limits_{\substack{q=1\\p=0}}^{\infty} q[Nd_q(OH)_p{}^{J+}]} = \frac{\sum\limits_{\substack{q=1\\p=0}}^{\infty} Jh^J X_{pq}}{\sum\limits_{\substack{q=1\\p=0}}^{\infty} qh^J X_{pq}}$$

Since $\bar{n}$ is found to be independent of h and equal to 3, the equilibria for A-Nd_2O_3 and hydrogen ions are given by the equations for the range of concentrations studied.

$$\text{A-}Nd_2O_3(s) + 3H_2O \longrightarrow 2Nd(OH)_3(s) \quad (1)$$

$$Nd(OH)_3(s) + 3H^+(aq) \rightleftarrows Nd^{+3}(aq) + 3H_2O \quad (4)$$

The equilibrium constant for reaction 4 was found to be

$$K_4 = 8.7 \pm 4.7 \times 10^{18} = \frac{a_{Na^{+3}} \cdot a_{Cl^-}{}^3 a_{H_2O}{}^3}{a_{Nd(OH)_3} \cdot a_{H^+}{}^3 a_{Cl^-}{}^3}$$

This corresponds to a standard free energy change of

$$\Delta F^0{}_{298} = -25.9 \pm 0.3 \text{ kcal./mole } Nd(OH)_3$$

The activity coefficients for Nd^{+3} in the neodymium chloride solutions were obtained from the data of Spedding and Porter[24] for the mean coefficient in aqueous solutions of neodymium chloride. According to the Debye–Hückel limiting law, $\gamma Nd^{+3} = (\gamma^{\pm}NdCl_3)^3$, and it was assumed that the activity coefficient for Nd^{+3} in these dilute solutions was accurately given by the cube of the mean activity coefficient. The crystalline neodymium hydroxide was chosen as the standard thermodynamic state, so the activity of the solid hydroxide at 25° is unity.

The activity of water may be considered to be unity in solutions as dilute as these without introducing any appreciable error.

From the value of K_4 and the dissociation constant of water at 25°, the solubility product of the crystalline neodymium hydroxide may be calculated.

$$K_4 \times K^3{}_w = \frac{a_{Nd^{+3}} \times a_{H_2O}{}^3}{a_{Nd(OH)_3} \times a_{H^+}{}^3} \times \frac{a_{H^+}{}^3 \times a_{OH^-}{}^3}{a_{H_2O}{}^3} = K_{sp}$$

$$K_{sp} = 8.7 \pm 4.7 \times 10^{18} \times (10^{-14})^3 = 8.7 \pm 4.7 \times 10^{-24}$$

for the reaction

$$Nd(OH)_3(s) \rightleftarrows Nd^{+3}(aq) + 3(OH)^-(aq) \quad \Delta F^0{}_{298} = 31.5 \pm 0.3 \text{ kcal.}$$

Since $\bar{n} = 3$, and the equilibrium hydrogen ion concentration is very small, the plot of the total neodymium dissolved *vs.* the initial acid concentration is a straight line with slope 0.33. This is shown in Figs. 1 and 2. As was noted in the section on the X-ray diffraction analyses of the solid phase, the solid phase was observed to be $Nd(OH)_3$ in all of the equilibria.

The highly negative value of $\Delta F^0{}_{298}$ for reaction 4, and the absence of measurable concentrations of ionic species containing hydroxyl ion indicate that $Nd(OH)_3$ is a very basic hydroxide. Unfortunately, a lack of thermodynamic data for the hydroxides and aqueous ions of other elements in the +3 oxidation state prevents a quantitative comparison.

The solubility product was found to be smaller by a factor ranging from about 10^1 to 10^2 when compared with most values cited in the literature. This is to be expected since most of these values have been obtained in the presence of sulfate and acetate ions where the neodymium ions are highly complexed. Also the freshly precipitated materials contain appreciable amounts of these anions, and the solid phase therefore varies from experiment to experiment.

There does not appear to be any significant complexing with chloride ion. Moeller and Brantley[25] have shown that there is no change in the absorption spectra of neodymium chloride solutions in the presence of a $Cl^-:Nd^{+3}$ mole ratio as great as 10. Furthermore, the data on the conductivity and transport numbers[26–28] of neodymium chloride, nitrate and perchlorate all follow closely the laws

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(24) F. H. Spedding and P. E. Porter, THIS JOURNAL, **74**, 2781 (1952).

(25) T. Moeller and J. C. Brantley, *Anal. Chem.*, **22**, 433 (1950).

(26) F. H. Spedding, P. E. Porter and J. M. Wright, THIS JOURNAL, **74**, 2055 (1952).

(27) F. H. Spedding, P. E. Porter and J. M. Wright, *ibid.*, **74**, 2278 (1952).

(28) F. H. Spedding and S. Jaffe, *ibid.*, **76**, 882 (1954).

for ideal 3:1 strong electrolytes, indicating the absence of significant complexing.

Finally, concentrations of the rare earth ions were used in all of the so-called equilibrium "constants" given in the literature. This easily can cause the values to be too large by a factor of 10 in these calculations in which the activity of a trivalent ion is involved.

From the standard free energy change determined for reaction 8 together with the free energy of formation of the Nd^{+3}(aq) ion given by Spedding and Miller,[29] and the free energy of formation of liquid water from the National Bureau of Standards tables,[13] the free energy of formation of the crystalline neodymium hydroxide may be calculated. Thus

$$Nd(s) + 3/2H_2(g) + 3/2O_2(g) \rightleftarrows Nd(OH)_3(s) \quad \Delta Ff^0_{298} = -299.6 \pm 0.3 \text{ kcal.}$$

The potential of the neodymium couple in basic solution also may be calculated.

$$Nd(s) + 3(OH)^-(aq) \rightleftarrows Nd(OH)_3(s) + 3e^- \quad \Delta F^0_{298} = -186.9 \pm 0.3 \text{ kcal.}$$

$$E_b = \frac{186.9 \pm 0.3 \text{ kcal.}}{3 \times 23.066 \text{ kcal./v.}} = 2.701 \pm 0.004 \text{ v.}$$

The literature values of the free energy of formation of $Nd(OH)_3$ and the potential in basic solution are all based upon rather inaccurate data. The National Bureau of Standards[13] tables give -309.6 kcal. for the ΔFf^0_{298} neodymium hydroxide with the work of Endres[14] as a reference. As noted earlier this work gives only relative values of rare earth solubility products. Latimer[12] estimates a value of -309.3 kcal./mole for ΔFf^0_{298} of $Nd(OH)_3$ and values of from 2.90 to 2.72 for E_b from lanthanum to lutecium.

Equilibria with Perchloric Acid

An attempt was made to study the equilibria of $Nd(OH)_3$ with perchloric acid to which $NaClO_4$ was added to give $[ClO_4^-] = 3$ M. The values of $\bar{n}$ obtained upon analysis were erratic and approximately 5. This indicates the conversion of the solid phase to a basic salt containing perchlorate ion, and an actual increase in the amount of solid phase present was observed.

To check the measurements made with hydrochloric acid, a small number of samples were prepared using dilute perchloric acid solution. These data also are given in Table I and are similar to those obtained with hydrochloric acid.

Equilibria with Water and with Sodium Hydroxide Solutions

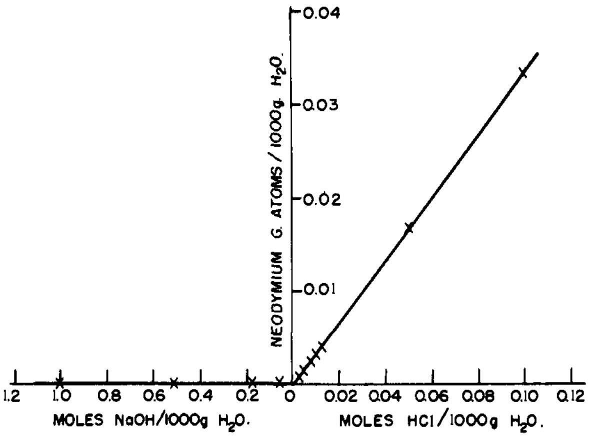

Fig. 2.—Solubility of $Nd(OH)_3$ in sodium hydroxide and hydrochloric acid.

The water solubility of the crystalline neodymium hydroxide was determined to be 4.8×10^{-5} mole/1000 g. of H_2O, and the equilibrium hydrogen ion concentration was 8×10^{-10} in the two samples measured. The solubility in base describes a minimum at about 0.2 M NaOH and increases to approximately the water solubility in 1 M NaOH. The data are given in Table II.[2] This curve may be formed of two independent parts, one accounting for the initial decrease in solubility where $Nd = k[OH^-]^{-n}$ and the other describing the dissolution at high concentrations of hydroxyl ion where $Nd = k'[OH^-]^m$, with $m = 2$. Since the solubility in base was so slight, no determination could be made of the ionic species present.

Hydrolysis Studies

Experimental Procedure

The general procedure followed is that developed by

TABLE I

PART 1. DATA ON THE EQUILIBRIUM BETWEEN NEODYMIUM HYDROXIDE AND HYDROCHLORIC ACID AT 25°

Initial concn. hydrochloric acid, moles/1000 g. H_2O, H	Equilibrium concn. dissolved neodymium, g. atoms/1000 g. H_2O, [Nd]	$\gamma_{Nd^{+3}}$	Activity Nd^{+3} $\times 10^3$	Activity H^+ $\times 10^8$, h	$\bar{n}$	K_4 $\times 10^{18}$
0.1004	0.0335	0.0778	2.61	7.9	3.00	5.3
.0502	.0167	.129	2.15	7.9	3.01	4.4
.0502	.0167	.129	2.15	6.2	3.01	9.0
.0502	.0167	.129	2.15	6.2	3.01	9.0
.0101	.00337	.309	1.04	5.6	3.00	5.9
.0101	.00337	.309	1.04	4.4	3.00	12
.0100	.00335	.309	1.04	6.3	2.99	4.2
.0100	.00335	.309	1.04	5.8	2.99	5.3
.0099	.00330	.314	1.04	7.9	3.00	2.1
.0099	.00330	.314	1.04	6.0	3.00	4.8
.0099	.00330	.314	1.04	4.8	3.00	9.4
.0099	.00330	.314	1.04	4.2	3.00	14
.0050	.00167	.415	0.693	4.8	2.99	6.2
.0050	.00167	.415	.693	4.5	2.99	7.6
.0049	.00165	.419	.691	5.4		4.4
.0049	.00165	.419	.691	5.1		5.2
.0010	.00033	.988	.33	3.6	..	7.0
.0010	.00033	.988	.33	3.5	..	8.0
.0010	.00033	.988	.33	2.5	..	22
.0010	.00033	.988	.33	2.1	..	36
.0005	.00017	1.00	.17	3.5	..	3.9
.0005	.00017	1.00	.17	3.0	..	6.3

$K_4 = 8.7 \pm 4.7 \times 10^{18}$

PART 2. DATA ON THE EQUILIBRIUM BETWEEN NEODYMIUM HYDROXIDE AND PERCHLORIC ACID AT 25°

0.0998	0.0329			4.9	3.03	
.01051	.00340			6.3	3.09	
.00210	.00070			3.8	3.0	

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[29] F. H. Spedding and C. F. Miller, THIS JOURNAL, **74**, 4195 (1952).

TABLE II

THE SOLUBILITY OF NEODYMIUM HYDROXIDE IN SODIUM HYDROXIDE SOLUTIONS AT 25°

Initial moles of hydroxide ion/1000 g. H_2O	Solubility of $Nd(OH)_3$, moles/1000 g. $H_2O \times 10^5$
0.0607	1.98 ± (0.10)
.1800	0.58 ± (.05)
.1800	0.51 ± (.10)
.5273	1.42 ± (.10)
.5273	0.83 ± (.07)
1.0125	4.30 ± (.80)
1.0125	3.47 ± (.14)

Sillén and co-workers[30-33] for the study of the hydrolysis of multivalent metal ions. All measurements were made in the constant ionic medium 3 M $NaClO_4$.

Electrochemical Cells.—The electrode and titration apparatus used in this work was essentially that described by Forsling, Hietanen and Sillén,[34] and the hydrolysis data were obtained from the e.m.f. values of the cell

Pt (anode)	$HClO_4$ $Me(ClO_4)_3$ quinhydrone $NaClO_4$	3 M $NaClO_4$	4 M NaCl	Hg_2Cl_2	Hg (cathode)

The E^0 for the couple Nd $\rightleftarrows$ $Nd^{+3}(aq) + 3e^-$ is so large that there is no reduction of the $Nd^{+3}(aq)$ in the presence of hydroquinone, and the quinhydrone electrode should therefore be suitable for the measurement of the hydrogen ion activity.

Two gold plated platinum electrodes were used, and these were led through the titration vessel cover in 4 mm. glass tubes. The upper end of each platinum electrode was sealed with wax through a male standard taper plug which was seated in the corresponding female fitting sealed to the upper end of the 4 mm. tubes. In this way, all glass-to-metal seals were eliminated. These have been reported to be the cause of irreproducibility in the e.m.f. values of cells of this type.[35]

The nitrogen used to exclude the atmosphere during the measurements was purified by successive washings in concentrated sodium hydroxide solution, alkaline sodium anthraquinone β-sulfonate solution, concentrated sulfuric acid, aqueous silver nitrate, distilled water, and finally 3 molar sodium perchlorate solution.

The e.m.f. of the cell, as measured, is given by the equation

$$E = E^0 + E_j + E_j' \frac{-RT}{2F} \ln \frac{a^2_{\mathrm{H}} \times a^2_{\mathrm{Cl^-}} \times a_{\mathrm{Q}} \times a^2_{\mathrm{Hg}}}{a_{\mathrm{Hg_2Cl_2}} \times a_{\mathrm{QH_2}}} \quad (5)$$

where

Q and QH_2 refer to quinone and hydroquinone, respectively
E = measured e.m.f. of cell
E^0 = thermodynamic reversible e.m.f. when the activities of all reactants and products are unity
E_j = junction potential at the interface between the solution in the titration vessel and the 3 M $NaClO_4$ salt bridge electrolyte
E_j' = junction potential at the interface between the 3 M $NaClO_4$ salt bridge electrolyte and the 4 M NaCl calomel half cell electrolyte

Although this separation of the e.m.f. is not thermodynamically valid, it has proved to be of use. The value of E_j' is maintained constant throughout the measurements by the design of the cell.

The magnitude of the potential E_j between the solution being titrated and the salt bridge electrolyte has been the subject of an extensive investigation by Biedermann and Sillén[18] and was found to obey the relation $E_j = 0.0167h$ (v.) where h is the hydrogen ion concentration in moles per liter. Since hydrolysis does not occur until h is about 10^{-5} M, the potential E_j should be negligible in this work. Combining the constant terms in equation 5, assuming that activity coefficients remain constant in the constant ionic medium with $[ClO_4^-] = 3$ M, we obtain the equation

$$E = E_Q' - 59.16 \log h \quad (6)$$

The e.m.f. values are measured in millivolts and h is the equilibrium hydrogen ion concentration.

In practice, the e.m.f. values of two such cells were determined, *i.e.*, each platinum electrode was read against the calomel half cell at every point in the titration to determine whether any poisoning of the electrodes was occurring. If the values of successive readings differed by more than 0.1 mv., the run usually was discontinued. The entire cell and titration vessel were immersed in a water thermostat which was controlled at 25 ± 0.1°.

In addition to the above cells, readings also were made in some of the experiments using a Beckman glass electrode in place of the quinhydrone electrode.

Both types of cells gave the same values, within the experimental error, for the hydrogen ion concentration in the presence of praseodymium and neodymium ions over a wide range of hydrogen ion concentrations. It is thus evident that no complexing reactions occurred involving the rare earth ions and quinone or hydroquinone.

Electrical Circuits.—A Leeds and Northrup K-2 potentiometer was used to measure the potentials of the quinhydrone–calomel cell.

Since the hydrolysis cell had a rather high internal resistance, a Leeds and Northrup type 7673 thermionic amplifier was used to amplify the current produced. A Beckman model G pH meter was used.

Analysis of the Free Acid Concentration of the Rare Earth Buffers.—The free acid concentration is defined as the concentration of hydrogen ion that is bound only to solvent molecules. In addition to the measurement of the pH of the rare earth buffer solutions made with the Beckman G pH meter before the addition of the sodium perchlorate, an accurate determination of the hydrogen ion concentration of these solutions was made using the method of Grau.[36] Essentially this consists of plotting the function $\Delta V_b/\Delta E$ the volume increment of base added divided by the difference in the e.m.f. of the cell before and after the addition of the base, *vs.* the volume of base added, V_b. This plot gives a straight line which intersects the V_b axis at the equivalence point. The data were obtained during the hydrolysis run, so no separate analyses of the solutions were necessary.

The Data

The data for the hydrolysis of the aqua praseodymium and neodymium ions are given in the form $Z(\log h)_B$ where

Z = av. no. of hydroxide groups per metal atom
$Z = \dfrac{h - H}{B}$
h = equilibrium $[H^+]$
H = analytical concn. of hydrogen ion assuming no hydrolysis
B = total metal concentration

The data for neodymium and praseodymium are given in Figs. 3 and 4, respectively.

Discussion of the Data

If the hydrolysis of the neodymium and praseodymium ions occurs according to the Brønsted mechanism

$$M^{+3} + H_2O \rightleftarrows M(OH)^{+2} + H^+$$

and the equilibrium constant for the reaction is K_1, Z is given as a function of $[H^+] = h$ by the equation

$$Z = \frac{1}{1 + [H^+]K_1^{-1}}$$

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[30] L. G. Sillén, *Acta Chem. Scand.*, **8**, 299 (1954).
[31] L. G. Sillén, *ibid.*, **8**, 318 (1954).
[32] S. Hietanen and L. G. Sillén, *ibid.*, **8**, 1607 (1954).
[33] B. O. A. Hedstrom, *ibid.*, **9**, 613 (1955).
[34] W. Forsling, S. Hietanen and L. G. Sillén, *ibid.*, **6**, 901 (1952).
[35] A. B. Garrett, E. Hogge and R. E. Heiks, *Science*, **92**, 18 (1940).
[36] G. Grau, *Acta Chem. Scand.*, **4**, 559 (1950).

The hydrolysis reactions were found to be slow at 25°, which caused a gradual drift in the hydrogen ion concentration with time. Because of this difficulty the points in Figs. 3 and 4 for different total metal ion concentrations, B, do not lie on the same curve. It was therefore necessary to base the estimate of the hydrolysis constant primarily upon the hydrogen ion concentration at which hydrolysis began. The solid curves in Figs. 3 and 4 were calculated assuming $-\log K_1 = 8.0$ and 8.5, and give Z as a function of $-\log H^+$. By comparison of the experimental data with these curves, it appears that the hydrolysis proceeds by the Brønsted type reactions

$$Nd(H_2O)_n^{+3} + H_2O \rightleftarrows Nd(OH)(H_2O)_{n-1}^{+2} + H_3O^+$$
$$Pr(H_2O)_n^{+3} + H_2O \rightleftarrows Pr(OH)(H_2O)_{n-1}^{+2} + H_3O^+$$

and that the hydrolysis constants for the two reactions are equal to $10^{-8.5}$, within the rather large experimental error. To judge from the spread of the data, the true value probably lies within the limits of $pK_a = 8.5 \pm 0.4$. This corresponds to an equilibrium constant of 3×10^{-9}, and the rare earth ions therefore rank among the weakest of the aquo-acids.

The extremely weak action of Nd^{+3} and Pr^{+3} as aquo-acids is to be expected, since the forces acting between the central ion and the surrounding water molecules must be almost purely electrostatic. The very high basicity and hence the weak bond between the neodymium ion and hydroxide ion has been shown by the results of the solubility measurements.

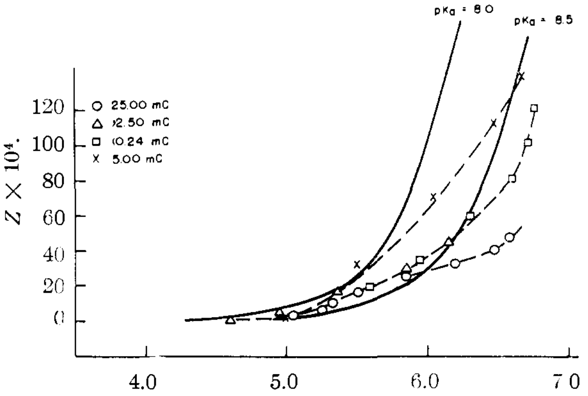

Fig. 3.—Hydrolysis of praseodymium perchlorate.

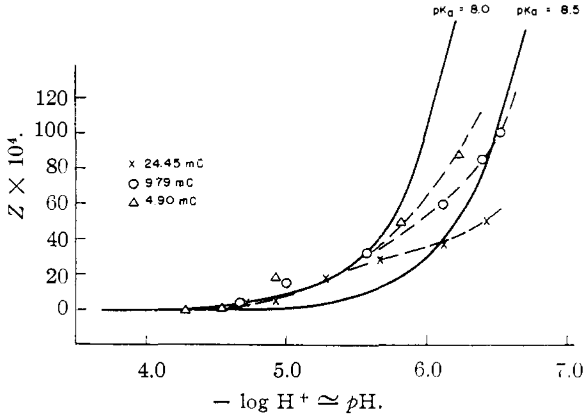

Fig. 4.—Hydrolysis of neodymium perchlorate.

Conclusions

From the large negative value of the standard free energy change for the reaction of neodymium hydroxide with hydrogen ion, it is evident that this hydroxide is a strong base. These data place neodymium hydroxide with the hydroxides of magnesium, calcium, the heavier alkaline earths, and the alkali metals as the strongest of the bases. This indicates that the Nd^{+3}-hydroxide ion bond is weak, being formed by electrostatic attraction alone; this has been verified by the very slight hydrolysis of the trivalent cation. The high coordination number of the neodymium ion with respect to hydroxide ion, 9, gives rise to a high lattice energy for the solid hydroxide, however, and the hydroxide is only slightly soluble in water. By analogy, the heavier of the transuranium elements should form bases about as strong as neodymium hydroxide, although the possibility of a small degree of covalent bonding in the compounds of the transuranium elements[37] will probably cause them to be slightly less basic.

Neodymium hydroxide dissolves in distilled water to give a basic solution with pH 9.1. The very low solubility of the hydroxide prevents the preparation of highly basic solutions even though the hydroxide is a strong base.

Neodymium hydroxide shows a slight tendency to dissolve in concentrated base solutions. No accurate identification of the ionic species present in these solutions could be made.

Acknowledgment.—The authors wish to express their appreciation to Mr. G. W. Leddicotte, of the Oak Ridge National Laboratory, who performed the activation analyses described in this work. Also one of us (R.S.T.) received financial aid from the Visking Corporation and the General Electric Company as recipient of their fellowships in 1954–1955 and 1955–1956, respectively.

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[37] G. T. Seaborg and K. Street, Jr., THIS JOURNAL, **72**, 2790 (1950).