sequence during the fast addition of concentrated ferrocyanide than in the case of slow addition of the dilute reducing agent.

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LOS ALAMOS, NEW MEXICO

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE STATE UNIVERSITY OF IOWA]

Praseodymium Oxides. III. The Heats of Formation of Several Oxides[1]

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Several stable oxides were prepared, including four of non-stoichiometric composition, and their heat of solution measured in an adiabatic microcalorimeter. The molal heats of reaction at 25° in 6.00 *M* HNO_3 of $PrO_{1.500}$ (A form), $PrO_{1.703}$, $PrO_{1.717}$, $PrO_{1.804}$ and $PrO_{1.833}$ were found to be −53.5 ± 0.1, −47.9 ± 0.1, −47.4 ± 0.4, −44.9 ± 0.1 and −43.8 ± 0.1 kcal., respectively. These values when combined with other data yielded the corresponding molal heats of formation for PrO_x of −217.9 ± 0.8, −223.5 ± 0.8, −224.0 ± 0.9, −226.5 ± 0.8 and −227.6 ± 0.8 kcal. mole^{-1}.

Ferguson, Guth and Eyring[2] have made a phase study of the praseodymium oxide system. This study was extended by Guth, Holden, Baenziger and Eyring[3] to include X-ray and differential thermal analyses. These studies revealed several stable oxides of non-stoichiometric composition intermediate to $PrO_{1.50}$ and $PrO_{2.00}$. The most interesting of these compounds have the empirical formulas $PrO_{1.703}$, $PrO_{1.717}$, $PrO_{1.804}$ and $PrO_{1.833}$.

It was desired to know the heat of formation and the integral heats of oxidation of these interesting non-stoichiometric oxide phases but the thermochemical data which would permit such calculations were not available.

Existing thermochemical data supplemented with the measured heats of reaction of these oxides with nitric acid solutions make possible the desired calculations. The heat of transition of $PrO_{1.50}$ from the hexagonal to the body centered cubic lattice is also calculable from the heat of reaction measurements.

The data were obtained using the adiabatic microcalorimeter described in a previous paper.[4]

Experimental Methods

Preparation and Properties of the Oxides.—The starting material for the preparation of all the samples was Pr_6O_{11} (99.9+ % pure) obtained from the Ames Laboratories, Ames, Iowa. The oxygen used was obtained from the thermal decomposition of $KMnO_4$ as previously described.[2] The atomic weight of praseodymium used was 140.92, and the defined calorie was assumed equal to 4.1840 absolute joules.

The conditions for preparation of the oxides and a full description of the apparatus used are given by Ferguson, Guth and Eyring.[2] Each oxide was quenched[3] after equilibrium was established at the predetermined pressure and temperature in order to freeze the oxide at a specific composition. The exact composition was determined by weight change. All the praseodymium oxides dissolve in nitric acid to produce the trivalent praseodymium ion in solution.

In general, the oxides prepared at low temperatures dissolved more readily than those prepared at higher temperatures, probably because of different particle size and degree of ordering in the crystal.

The composition of the calorimeter samples together with their color and lattice properties are tabulated in Table I.

TABLE I

PHYSICAL PROPERTIES OF THE CALORIMETER SAMPLES

Oxide	Color	Lattice	Lattice constants (Å.)
$PrO_{1.500}$	Yellow-green	Hexagonal	3.859 ± 0.003; 6.008 ± 0.003
$PrO_{1.703}$	Brown	Body centered cubic	11.055 ± 0.005
$PrO_{1.717}$	Brown	Rhombohedral	11.02; 89°40′[a]
$PrO_{1.804}$	Brown	Face centered cubic	5.482 ± 0.003
$PrO_{1.833}$	Black	Face centered cubic	5.468 ± 0.002

[a] Cell dimensions not determined by analytical extrapolation method.

Results

Heats of Reaction.—The enthalpy change upon reaction of the various oxides of praseodymium with oxygen saturated 6.00 *M* HNO_3 were determined in the microcalorimeter and are tabulated in Table II. It was apparent that a small concentration of Na_2SiF_6 did not significantly affect the heat of reaction of the oxides with 6.00 *M* HNO_3 as shown by the results obtained for $PrO_{1.703}$, Table II. The absence of a heat effect above experimental error upon addition of the complexing agent is probably due to a cancellation of terms.

The samples were weighed with an Ainsworth FDJ, Optical lever, microbalance (sensitivity: 2.5 micrograms per division). The enthalpy change was not corrected for the vaporization of water into the liberated oxygen because this correction (about 0.04 kilocalorie per mole for $PrO_{1.833}$) is small compared to the experimental error.

The reaction which occurred in the calorimeter may be represented by equation 1

$$PrO_x(c) + yHNO_3 \cdot zH_2O = Pr(NO_3)_3 \cdot (y-3)HNO_3 \cdot (z + 3/2)H_2O + {}^1/_2(x - 3/2)O_2(g) \qquad (1)$$

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[1] These data were reported at the 126th meeting of the American Chemical Society at New York City in September, 1954, and were included in a dissertation submitted by C. T. Stubblefield to the Graduate College of the State University of Iowa in partial fulfillment of the requirements for the Ph.D. degree. The work was supported by the Atomic Energy Commission through the Research Contracts Division.

[2] R. Ferguson, E. Daniel Guth and L. Eyring, THIS JOURNAL, **76**, 3890 (1954).

[3] E. Daniel Guth, J. R. Holden, N. C. Baenziger and L. Eyring, *ibid.*, **76**, 5239 (1954).

[4] G. Machlan, C. T. Stubblefield and L. Eyring, *ibid.*, **77**, 2975 (1955).

Heats of Formation.—The heats of formation of the oxides correspond to equation 2

$$Pr(c) + 0.5xO_2(g) = PrO_x(c) \qquad (2)$$

when the reactants and the products are in their standard states.

The heat of solution of the sesquioxide is given approximately by equation 3

$$PrO_{1.500}(c) + 6.00\ M\ HNO_3 = Pr(NO_3)_3 \cdot 6.00\ M\ HNO_3 \qquad (3)$$

Subtraction of (1) from (3) gives (4), which is the equation for the oxidation of the sesquioxide to a higher oxide

$$PrO_{1.500}(c) + 0.5(x - 1.5)\ O_2(g) = PrO_x(c) \qquad (4)$$

It follows that if the heat of formation of the sesquioxide is known, the heat of formation of PrO_x is

$$\Delta Hf°_{298}\ (PrO_x(c)) = \Delta H_{ox} + \Delta Hf°_{298}\ (PrO_{1.5}(c))$$

TABLE II

HEAT OF REACTION OF PrO_x WITH 6.00 M HNO_3 AT 25°

Oxide	Time (min.)	Wt. (mg.) (*vacuo*)	ΔH (kcal./mol.) reaction
$PrO_{1.500}$	30	22.865	−53.6
	25	17.596	−53.4
	30	20.603	−53.4
	35	25.741	−53.7
		Av.	−53.5 ± 0.1
$PrO_{1.703}$	150	11.387	−48.1[a]
	130	8.904	−47.7[a]
	90	13.198	−48.0
		Av.	−47.9 ± 0.2
$PrO_{1.717}$	45	10.665	−47.5
	45	13.441	−47.9
	35	9.024	−47.0
	35	8.658	−47.8
	40	11.673	−46.8
		Av.	−47.4 ± 0.4
$PrO_{1.804}$	50	10.282	−45.0
	60	11.499	−44.8
	45	8.935	−45.0
		Av.	−44.9 ± 0.1
$PrO_{1.833}$	55	13.068	−43.7
	50	11.036	−43.7
	50	10.959	−43.9
		Av.	−43.8 ± 0.1

[a] Acid solution was 0.01 M in Na_2SiF_6.

The heat of formation of the sesquioxide is represented by the equation 5

$$Pr(c) + 0.75O_2(g) = PrO_{1.5}(c) \qquad (5)$$

Also it is given by a combination of the following seven reactions

$$PrO_{1.500}(c) + YHNO_3 \cdot ZH_2O = Pr(NO_3)_3 \cdot (Y - 3)HNO_3 \cdot (Z + 1.50)H_2O \qquad (a)$$

$$1.50\ H_2(g) + 0.75O_2(g) = 1.50\ H_2O(l) \qquad (b)$$

$$Pr(c) + 3HNO_3 \cdot \infty H_2O = Pr(NO_3)_3 \cdot \infty H_2O + 1.50\ H_2(g) \qquad (c)$$

$$Pr(NO_3)_3 \cdot (Z + 1.50)H_2O + \infty H_2O(l) = Pr(NO_3)_3 \cdot \infty H_2O \qquad (d)$$

$$YHNO_3(l) + ZH_2O(l) = YHNO_3 \cdot ZH_2O \qquad (e)$$

$$Pr(NO_3)_3 \cdot (Z + 1.5)H_2O + (Y - 3)HNO_3(l) = Pr(NO_3)_3 \cdot (Y - 3)\ HNO_3 \cdot (Z + 1.5)\ H_2O \qquad (f)$$

$$3HNO_3(l) + \infty H_2O(l) = 3HNO_3 \cdot \infty H_2O \qquad (g)$$

The standard heat of formation at 298°K. for the sesquioxide is

$$\Delta H_f°_{298}(PrO_{1.50}) = -\Delta H_a + \Delta H_b + \Delta H_c - \Delta H_d - \Delta H_e + \Delta H_f + \Delta H_g$$

ΔH_a is the heat of reaction of the sesquioxide in 6.00 M HNO_3 as measured by Eyring, Lohr and Cunningham.[5]

ΔH_b is the heat of formation of liquid water (N.B.S. Circular 500).[6]

ΔH_c is the heat of formation of the aqueous trivalent ion obtained from the data of Spedding and Flynn.[7]

ΔH_d is the heat of infinite dilution of the aqueous praseodymium trinitrate solution which is assumed to be the same as the heat of infinite dilution for the lanthanum trichloride solution of the same concentration. The assumption is probably valid because it is observed from N.B.S. Circular 500[6] that the difference in the heats of solution of two concentrations of a chloride is about the same as the difference for the same concentrations of the corresponding nitrate. This is especially true within the range of low concentrations which are of interest here.

Also, it is known that all the rare earth trichlorides have nearly the same values for their heats of dilution for the same changes in concentration.

ΔH_e to ΔH_g are all the heats of solution of $HNO_3(l)$, the concentration of the praseodymium trinitrate in equation (f) being negligible as compared to that of the acid. Their values are listed in N.B.S. Circular 500.[6]

The values of ΔH_b to ΔH_g are given below.

ΔH_b	−102.48 kcal.	ΔH_e	−3035.31 kcal.
ΔH_c	−167.69	ΔH_f	−3013.37
ΔH_d	− 0.78	ΔH_g	− 23.91

When these heats of the reaction are properly combined with the heat of solution of the oxide in 6.00 M HNO_3, ΔH_a, the heat of formation of the sesquioxide is obtained.

TABLE III

HEAT OF FORMATION OF PrO_x AT 298.16°K.

Oxide	ΔHf (kcal./g. atom of Pr)	ΔHf (kcal./g. atom of O)
$PrO_{1.500}$ (hex)	−217.9 ± 0.8	−145.3 ± 0.5
$PrO_{1.500}$ (cubic)[a]	−218.4 ± .8	−145.6 ± .5
$PrO_{1.703}$	−223.5 ± .8	−131.2 ± .5
$PrO_{1.717}$	−224.0 ± .9	−130.5 ± .5
$PrO_{1.804}$	−226.5 ± .8	−125.6 ± .5
$PrO_{1.833}$	−227.6 ± .8	−124.2 ± .5
$PrO_{2.000}$[a]	−232.9	−116.4

[a] Data from Eyring, Lohr and Cunningham.[5]

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[5] L. Eyring, H. R. Lohr and B. B. Cunningham, THIS JOURNAL, **74**, 1186 (1952).

[6] "Selected Values of Chemical Thermodynamic Properties," Circular of the National Bureau of Standards 500 by Frederick D. Rossini, Donald D. Wagman, W. H. Evans, S. Levine, I. Jaffe, U. S. Gov't. Printing Office, Washington, D. C., 1952.

[7] F. H. Spedding and J. P. Flynn, THIS JOURNAL, **76**, 1474 (1954).

The difference between ΔH_a and the corresponding heat of solution of PrO_x yields the heat of oxidation of $PrO_{1.5}$ to give PrO_x. The sum of the heat of formation of $PrO_{1.5}$ and the heat of oxidation gives the heat of formation of PrO_x. These calculated values are shown in Table III.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, OREGON STATE COLLEGE]

The Nature of Niobium(V) in Hydrochloric Acid Solution[1]

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The nature and dependency of niobium species in solutions of varying hydrogen ion, chloride ion and hydrochloric acid are studied. Only three soluble chloride species appear to exist to any extent in these systems: $Nb(OH)_2Cl_4^-$ in high chloride and high hydrogen ion; $Nb(OH)Cl_3^+$ in extremely high hydrogen ion and low chloride and $Nb(OH)_2Cl_3$ at hydrogen ion and chloride ion in the range of three molar. Decreasing hydrogen ion at high chloride results in colloid formation.

Niobium and tantalum are unique in the very small number of their water-soluble compounds. In order to produce water-soluble compounds of niobium it is necessary to use complexing agents and one of the more important of these is chloride. It has been found that anhydrous niobium pentoxide dissolves in highly concentrated hydrochloric acid to the extent of about four grams of the pentoxide per hundred milliliters.[2]

Spectrophotometric work on niobium(V) solutions in hydrochloric acid of varying concentration has indicated the presence of several species of niobium.[3] The species present in concentrated hydrochloric acid showing an absorption maximum at 281 mμ was used as the basis of a spectrophotometric method for the determination of niobium. Several species have been postulated for niobium in hydrochloric acid but little work has been done to actually prove the existence of any of these in solution.[4-10] In order to place the colorimetric determination on a firm basis and to further study the effect of chloride ion and hydrogen ion variation on the niobium species a study has been made of the nature of the species of niobium present in systems containing hydrogen ion and chloride ion.

The investigation of this system has been carried out primarily by spectrophotometric methods. The complex ion present in concentrated hydrochloric acid has been identified by comparison of the absorption spectrum of this solution to that of a solution of a salt of this ion in an organic solvent. Other species have been characterized by comparison of absorption spectra, ion exchange work and by quantitative study of the effect of independently varying hydrogen ion and chloride ion activity.

Experimental

Spectral Measurements.—All absorbance measurements were made by use of a Beckman Model DU spectrophotometer using matched 1.00-cm. fused silica cells. A hydrogen discharge lamp was used as the source of radiation for all measurements below 340 mμ. All absorbance measurements were made with a reagent blank in the null cell and net absorbances were recorded. Spectral measurements were made at 5 mμ intervals except in the region of peaks at which narrower intervals were used.

Niobium Solutions.—Niobium pentoxide obtained as "Columbium Pentoxide" from A. D. MacKay, 198 Broadway, New York 7, N. Y., was fused with potassium pyrosulfate in the ratio of 1 gram of the pentoxide to 3 grams of the pyrosulfate. The resulting melt was cooled, ground and taken up in 1:1 sulfuric acid. The resulting milky solution was neutralized with concentrated ammonium hydroxide. The hydrous niobium pentoxide was separated and washed by centrifugation, slurried with concentrated hydrochloric acid and placed in an ice-bath. Hydrogen chloride was passed through the solution for from two to three days in an ice-bath to complete the dissolving of the hydrated pentoxide. The solutions thus prepared contained about 20 g. Nb/liter and were used as stock solutions for more dilute solutions.

Compounds for Spectral Comparison.—The compound reported as Cs_2NbOCl_5 by Weinland and Storz[11] was prepared by their method using solutions saturated with hydrogen chloride at temperatures varying from 45 to −20°. Analysis of the compound agreed with that which was reported but was not considered accurate enough to distinguish between Cs_2NbOCl_5 and $Cs_2Nb(OH)_2Cl_5$.

The compound $(C_2H_5)_4NNb(OH)_2Cl_4$ was prepared by mixing 1.0 g. of tetraethylammonium chloride dissolved in a minimum amount of 0° saturated hydrochloric acid with a solution containing 0.5 g. Nb in 25 ml. also in 0° saturated hydrochloric acid. The compound precipitated in the form of fine white crystals which were filtered and washed with 0° saturated hydrochloric acid on a sintered glass filter. The compound was dried over anhydrous magnesium perchlorate and analyzed for niobium, chloride and nitrogen. For niobium the compound was moistened, ignited and weighed as Nb_2O_5. Nitrogen was determined by the micro Dumas method, and chloride was determined by Volhard titration. The rest of the formula of the compound was determined by difference and valence requirements.

Niobium oxychloride ($NbOCl_3$) was prepared by two methods. The first method was the thermal decomposition

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[1] Presented before the Northwest Regional Meeting of the American Chemical Society, Eugene, Oregon, June, 1955. Published with the Approval of the Monographs Publication Committee, Oregon State College, as Research Paper 294, School of Science Department of Chemistry.

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