Enthalpy of Formation of Nd_2O_3-Hexagonal

GEORGE C. FITZGIBBON, DANIEL PAVONE, and CHARLES E. HOLLEY, Jr.
University of California, Los Alamos Scientific Laboratory, Los Alamos, N. M. 87544

The enthalpy of solution of Nd_2O_3-hexagonal in 2.00M HCl and 4.36 molal HCl has been measured and found to be −103.73 ± 0.15 and −104.76 ± 0.31 kcal. per mole, respectively. The latter value is combined with the literature values for the enthalpy of solution of Nd metal in 4.36 molal HCl and the enthalpy of formation of water to give a value for the enthalpy of formation of Nd_2O_3-hexagonal as obtained by solution calorimetry. This value is then combined with the literature value for the same quantity as obtained by oxygen bomb calorimetry to give the weighted average $\Delta H^\circ_{f\,298^\circ\,K.}$ = −432.11 ± 0.22 kcal. per mole for the enthalpy of formation of Nd_2O_3-hexagonal.

TO CHECK the value for the enthalpy of formation of Nd_2O_3-hexagonal as obtained from the combustion of Nd metal in oxygen, experiments were performed to determine the enthalpies of solution of Nd metal and Nd_2O_3-hexagonal in 2.00*M* HCl. The results of these experiments were not entirely satisfactory because of the large uncertainty interval introduced by the lack of precision in correcting for impurities in the Nd metal sample. Meanwhile, Stuve (*8*) reported results on the enthalpy of solution of high-purity Nd metal in 4.36 molal HCl which were in good agreement with our uncertain results and which embodied a much smaller uncertainty interval. Additional measurements of the enthalpy of solution of Nd_2O_3-hexagonal in 4.36 molal HCl were therefore made. These results were then combined with Stuve's (*8*) value for the enthalpy of solution of Nd metal to give a value for the enthalpy of formation of Nd_2O_3-hexagonal.

EXPERIMENTAL

The enthalpy of solution measurements were made in a calorimeter which has been described (*2*). Briefly, it is an isothermal solution calorimeter whose environmental temperature may be kept constant at any setting between 23° and 33° C. to within 0.001° C. in an 800-liter thermostatically controlled bath. The vacuum-jacketed, silver-bodied, platinum-lined calorimeter reaction vessel has a volume of ~450 cc., a thermal leak modulus of 0.005 per minute, and a heat capacity including solvent of ~420 cal. per degree.

Within the reaction chamber are a heater, a thermistor, a borosilicate glass rod to which is attached a platinum stirrer, and a glass sample bulb. The heater consists of a 15.24-cm. length of 0.64-cm. o.d. platinum tubing, the lower end gold-soldered, the upper end sealed to glass tubing which extends through the calorimeter lid and carries the heater leads. The platinum tubing contains 23 ohms of bifilarly wound, helically coiled, silk-covered Manganin wire with leads to measure the voltage drop located at the solution level. A Fenwal 2300-ohm thermistor is used as the sensing element to measure temperature differences up to 1.6° C. to within 0.0001° C. A Brown recorder was modified to an automatic-changing, multiscale, self-balancing Wheatstone bridge, whose arm position is an indication of the resistance of the thermistor.

The energy equivalent is determined by passing a current from a precision voltage-regulated supply through the calorimeter heater and a 0.1-ohm standard resistor in series and measuring the voltage drops using a Rubicon Type B potentiometer and a Rubicon reflecting galvanometer. The input time is read directly from an electronic decade counter whose time base is derived from a 100-kc. crystal-controlled oscillator, accurate and stable to 0.01%.

In these experiments the solute is weighed to 10^{-5} gram and the solvent to 10^{-2} gram. The electrical energy is measured to a few hundredths of 1%. Temperatures are measured to about 3×10^{-3} arbitrary unit (about 10^{-4} ° C.). The limit on the absolute accuracy is thus the accuracy of measurement of the temperature rise, about 0.03% for a 0.3° C. rise. In actual experiments this precision is not realized because of other factors, the most important of which is probably sample variability.

The neodymium oxide was obtained from the Michigan Chemical Co. as 99.99% pure material. Spectroscopic analysis showed the presence of about 0.005% each of Ca and Mg. No other cation impurities were detected. The oxide was heated in an Alundum crucible in an induction furnace under vacuum to 1250° C. to remove any H_2O and CO_2. X-ray examination of the material after ignition showed it to be the hexagonal form. The material was stored in an inert atmosphere glove box (dew point < −50° C.) until used.

For an experiment approximately 0.46 gram of this Nd_2O_3 was weighed into a thin-walled borosilicate glass sample bulb. About 420 ml. of HCl solution, weighed to within 10 mg., was used as the solvent. The HCl solutions were prepared from reagent grade acid and standardized by titration with standardized KOH using phenolphthalein as the indicator. The average initial temperature of the runs was 24.8° C.

RESULTS

The details of the measurements are shown in Table I. These average values, 308.34 ± 0.44 and 311.41 ± 0.89 cal. per gram, must be corrected for the Ca and Mg impurities, assumed to be present as CaO and MgO, respectively. The corrected values are 308.28 ± 0.44 and 311.33 ± 0.89 cal. per gram in 2.00*M* and 4.36 molal HCl, respectively. The enthalpy of solution of Nd_2O_3-hexagonal in 2.00*M* HCl is thus ΔH°_{soln} = −103.73 ± 0.15 kcal. per mole and in 4.36 molal HCl, ΔH°_{soln} = −104.76 ± 0.31 kcal. per mole (atomic weight of Nd taken as 144.24). Apparently, the only value in the literature available for comparison is that of Matignon (*5*), who found −105.5 kcal. per mole in 0.5*M* HCl.

Enthalpy of Formation of Nd_2O_3-Hexagonal. The enthalpy of formation of Nd_2O_3-hexagonal has been determined by oxygen bomb combustion calorimetry on the metal to be $\Delta H^\circ_{f\,298^\circ\,K.}$ = −432.15 ± 0.24 kcal. per mole (*3*). From the enthalpies of solution of the metal and oxide, a value of the enthalpy of formation can be derived on the basis of the following equations:

$$2\,Nd(c) + 6\,HCl\ (4.36\ molal) \rightarrow 2\,NdCl_3\ (in\ 4.36\ molal\ HCl) + 3\,H_2(g) \qquad (1)$$

Table I. Enthalpy of Solution of Nd_2O_3-Hexagonal in HCl at 298° K.

Mass of Nd_2O_3, G.	Mass of Solvent, G.	Energy Equiv., Cal./Arb. Units	ΔT, Arb. Units	Energy from Solution, Cal./G.	Dev., Cal./G.
		Solvent, 2.00*M* HCl Av. temp. rise, 0.34° C.			
0.4597	400.16	15.984	8.886	308.96	0.60
0.4610	401.33	15.953	8.912	308.37	0.01
0.4605	400.84	15.919	8.911	308.07	0.29
0.4595	399.95	15.904	8.921	308.79	0.43
0.4602	400.57	15.927	8.883	307.45	0.91
0.4597	400.16	15.900	8.917	308.40	0.04
			Av.	308.34	0.38
	2 × standard deviation of mean				0.44
		Solvent, 4.36 molal HCl Av. temp. rise, 0.36° C.			
0.4672	448.01	16.339	8.909	311.57	0.16
0.4667	447.53	16.401	8.845	310.84	0.57
0.4671	447.91	16.245	8.914	310.01	1.40
0.4671	447.91	16.350	8.920	312.23	0.82
0.4666	447.43	16.133	9.035	312.39	0.98
			Av.	311.41	0.79
	2 × standard deviation of mean				0.89

$$Nd_2O_3(c) + 6\ HCl\ (4.36\ molal) \rightarrow 2\ NdCl_3\ (in\ 4.36\ molal\ HCl) + 3\ H_2O \qquad (2)$$

$$3\ H_2O\ (in\ 4.36\ molal\ HCl) \rightarrow 3\ H_2O(l) \qquad (3)$$

$$3\ H_2(g) + 3/2\ O_2(g) \rightarrow 3\ H_2O(l) \qquad (4)$$

$$2\ Nd(c) + 3/2\ O_2(g) \rightarrow Nd_2O_3(c) \qquad (5)$$

$$\Delta H_5 = \Delta H_1 - \Delta H_2 - \Delta H_3 + \Delta H_4$$

ΔH_1 is taken to be −331.56 ± 0.40 kcal., which is twice the enthalpy of solution of Nd metal in 4.36 molal HCl, −165.78 ± 0.20 kcal. per gram atom as reported by Stuve (*8*). Other values for the enthalpy of solution of Nd metal in aqueous HCl are −162.6 kcal. per gram atom in 0.25*M* HCl reported by Spedding and Miller (*7*) for metal not as well characterized as that used by Stuve and probably not as pure, −171.4 kcal. per gram atom in 0.1*N* HCl reported by Bommer and Hohmann (*1*), whose value for the enthalpy of solution of lanthanum metal is known to be in error (*7*), and −163.9 kcal. per mole reported by Polyachenok and Novikov (*6*), who dissolved Nd(c) in 0.2*N* HCl.

ΔH_2 is taken to be −104.76 ± 0.31 kcal. as discussed earlier. ΔH_3 = 204 cal., three times the negative of the partial molal enthalpy of water in 4.36 molal HCl, which is taken to be −68 cal. per mole from data tabulated by Klotz (*4*). ΔH_4 is three times the enthalpy of formation of liquid water = 3 × (−68.315) = −204.945 kcal. (*9*).

Summing as indicated above, ΔH_5 = −431.95 ± 0.51 kcal. per mole. The weighted average of this value and the value from combustion calorimetry is $\Delta H^\circ_{f\ 298^\circ K}$ (Nd_2O_3-hexagonal) = 432.11 ± 0.22 kcal. per mole.

ACKNOWLEDGMENT

The authors are pleased to acknowledge the assistance of H. D. Cowan and O. R. Simi in the chemical analysis, and F. H. Ellinger in the x-ray examination.

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RECEIVED for review April 15, 1968. Accepted July 15, 1968. Work done under the auspices of the U. S. Atomic Energy Commission.

Viscosities of Binary Aqueous Solutions of NaCl, KCl, Na_2SO_4, and $MgSO_4$ at Concentrations and Temperatures of Interest in Desalination Processes

ALEXANDER KOROSI and B. M. FABUSS[1], Monsanto Research Corp., Boston Laboratory, Everett, Mass. 02149

Experimental viscosity and density measurements are reported on binary salt solutions over the range of ionic strength levels from 0.1 to 3.5 and the temperature range from 25° to 150° C. The estimated precision for the viscosity data is 0.1 to 0.2% and for densities, 0.02%. The data were correlated by using Othmer's rule, yielding an over-all precision of 0.4 to 0.5%. Literature data were reviewed and compared with the correlation.

UNDER a continuing program to establish the property values of aqueous electrolyte solutions encountered in desalination processes, viscosity measurements were made on these solutions over the temperature range from 25° to 150° C. The first part of this investigation, covering the viscosities of the four major sea water components in their binary aqueous solutions, is presented here.

Measured rather than calculated densities were used in converting kinematic viscosities to dynamic viscosities to avoid excessive extrapolations from our previous set of density data (*2*). Determined viscosities were correlated and compared with other sources. At elevated temperatures, though, the comparison was hindered by the lack of relevant literature information.

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[1] Present address: Lowell Technological Institute, Research Foundation, Lowell, Mass.