Enthalpies of Solution and of Formation of Several Terbium Oxides

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The enthalpies of formation of $TbO_{1.510}$, $TbO_{1.709}$, $TbO_{1.817}$, and $TbO_{1.975}$ have been determined to be $\Delta H^\circ_{f\,298.15^\circ\,K.} = -223.1 \pm 0.9$, -227.6 ± 0.9, -230.0 ± 0.9, and -232.0 ± 0.7 kcal. per mole, respectively. By extrapolation the enthalpies of formation of $TbO_{1.500}$ and $TbO_{2.000}$ are found to be $\Delta H_{f\,298.15^\circ\,K.} = -222.9 \pm 0.9$ and -232.2 ± 0.7 kcal. per mole, respectively. These values were obtained by measuring the enthalpies of solution of terbium metal and terbium carbonate in 1.00*M* HCl and of terbium carbonate and the various oxides in 6.00*M* HNO_3 and combining the results with the enthalpy of formation of water.

THE ENTHALPIES of formation of several terbium oxides have been reported by Stubblefield *et al.* (*8*), based upon their own measurements of the enthalpies of solution of the oxides in 6.00*M* HNO_3 containing a small amount of Na_2SiF_6 as a solution aid, and an estimated value for the enthalpy of solution of terbium metal obtained by interpolation between the values for gadolinium and erbium measured by Spedding and Flynn (*7*). This paper reports the results of experiments in which the enthalpies of solution of terbium metal and several terbium oxides were measured.

PROCEDURE

The enthalpy of solution of terbium metal was measured in 1.00*M* HCl solution containing 0.0025*M* Na_2SiF_6 and the enthalpies of solution of the terbium oxides were measured in 6.00*M* HNO_3 also 0.0025*M* in Na_2SiF_6. The Na_2SiF_6 was added to increase the rate of solution of the oxides. The terbium metal was not dissolved in HNO_3 for fear of reducing some of the HNO_3, and the oxides were not dissolved in HCl for fear of oxidizing some of the HCl. In order to compare the results in the two solvents it was desirable to measure the enthalpy of solution of some compound in both solvents. Terbium sesquioxide, Tb_2O_3, would be the logical compound to use. However, all the preparations of Tb_2O_3 tried were too slowly soluble for accurate enthalpy measurements in the calorimeter. So terbium carbonate was used for this comparison. The reaction scheme is represented by the following equations:

$$2\,Tb(c) + 210\,HCl\cdot 11{,}400\,H_2O \rightarrow 2\,TbCl_3\cdot 204\,HCl\cdot 11{,}400\,H_2O + 3\,H_2(g) \qquad (1)$$

$$Tb_2(CO_3)_3\cdot 2.3\,H_2O + 210\,HCl\cdot 11{,}400\,H_2O \rightarrow 2\,TbCl_3\cdot 204\,HCl\cdot 11{,}405.3\,H_2O + 3\,CO_2(g) \qquad (2)$$

$$5.3\,H_2O(l) + 2\,TbCl_3\cdot 204\,HCl\cdot 11{,}400\,H_2O \rightarrow 2\,TbCl_3\cdot 204\,HCl\cdot 11{,}405.3\,H_2O \qquad (3)$$

$$Tb_2(CO_3)_3\cdot 2.3\,H_2O + 1260\,HNO_3\cdot 9356\,H_2O \rightarrow 2\,Tb(NO_3)_3\cdot 1254\,HNO_3\cdot 9361.3\,H_2O + 3\,CO_2(g) \qquad (4)$$

$$2\,TbO_{1.500+x} + 1260\,HNO_3\cdot 9356\,H_2O \rightarrow 2\,Tb(NO_3)_3\cdot 1254\,HNO_3\cdot 9359\,H_2O + x\,O_2(g) \qquad (5)$$

$$2.3\,H_2O(l) + 2\,Tb(NO_3)_3\cdot 1254\,HNO_3\cdot 9359\,H_2O \rightarrow 2\,Tb(NO_3)_3\cdot 1254\,HNO_3\cdot 9361.3\,H_2O \qquad (6)$$

$$3\,H_2(g) + \tfrac{3}{2}\,O_2(g) \rightarrow 3\,H_2O(l) \qquad (7)$$

$$2\,Tb(c) + (\tfrac{3}{2} + x)\,O_2(g) \rightarrow 2\,TbO_{1.500+x}(c) \qquad (8)$$

$$\Delta H_8 = \Delta H_1 - \Delta H_2 + \Delta H_3 + \Delta H_4 - \Delta H_5 - \Delta H_6 + \Delta H_7$$

$$\Delta H_f(TbO_{1.500+x}) = \tfrac{1}{2}\,\Delta H_8$$

EXPERIMENTAL

Enthalpies of solution at 25° C. were measured in a calorimeter which has been described (*4*). Briefly, the calorimeter is an isothermal solution calorimeter whose environmental temperature may be kept constant at any setting between 23° and 33° C. to within 0.001° 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° to within 0.0001°. 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 the electronic decade counter whose time base is derived from a 100-kc. crystal-controlled oscillator, accurate and stable to 0.01%.

Sample sizes ranged from 0.3 gram for the metal and oxides to 0.9 gram for the carbonate. The oxides were ground in a mortar to pass through a 400-mesh screen before weighing in the glass sample bulb. About 420 ml. of solvent was weighed before a run to within 10 mg. and made 2.5×10^{-3} *M* in Na_2SiF_6 as a solution aid. The constituents in every solution run were weighed to give a resulting terbium ion molarity of 3.924×10^{-3}. All weights were corrected to vacuum.

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, which varies from a few hundredths of 1% for Tb metal where the temperature rise is large and the rate of dissolution high, to something of the order of 1% for $TbO_{1.510}$ which

Table I. Enthalpies of Solution of Tb, Tb Carbonate, and Tb Oxides

Solvents. 420 ml. of 1.00*M* HCl–0.0025*M* Na_2SiF_6 or 420 ml. of 6.00*M* HNO_3–0.0025*M* Na_2SiF_6

Solute and Solvent	Mass of Solute, G.	Energy Equiv., Cal./Arb. Unit	Temp. Rise, Arbitrary Unit	Energy from Solute, Cal./G.	Dev., Cal./G.
Tb in HCl	0.26210	17.786	15.420	1050.8	2.6
	0.26262	17.851	15.439	1054.0	5.8
	0.26152	17.790	15.262	1042.7	5.5
	0.26200	17.900	15.228	1044.6	3.6
	0.26172	17.825	15.337	1049.0	0.8
				1048.2	3.7
		2 × standard deviation of mean			4.1
$Tb_2(CO_3)_3 \cdot 2.3\ H_2O$ in HCl	0.88600	17.536	2.326	48.71	1.08
	0.88308	17.593	2.393	50.20	0.41
	0.88600	17.482	2.394	49.83	0.04
	0.88590	17.502	2.401	50.01	0.22
	0.88610	17.730	2.375	50.20	0.41
				49.79	0.43
		2 × standard deviation of mean			0.54
$Tb_2(CO_3)_3 \cdot 2.3\ H_2O$ in HNO_3	0.88645	17.189	2.379	48.71	0.93
	0.88545	16.941	2.335	47.22	0.56
	0.88623	16.924	2.402	48.53	0.75
	0.88571	16.909	2.352	47.60	0.18
	0.88566	16.714	2.343	46.85	0.93
				47.78	0.67
		2 × standard deviation of mean			0.76
$TbO_{1.510}$ in HNO_3	0.30150	16.831	4.597	256.7	1.6
	0.30175	16.864	4.494	251.3	3.8
	0.30100	16.862	4.623	258.9	3.8
	0.30105	16.885	4.490	251.3	3.8
	0.30158	17.160	4.519	257.3	2.2
				255.1	3.0
		2 × standard deviation of mean			3.2
$TbO_{1.709}$ in HNO_3	0.30694	17.238	4.008	225.0	1.5
	0.30630	17.220	4.014	225.5	1.0
	0.30637	17.385	4.050	229.8	3.3
	0.30617	17.301	4.062	229.8	3.3
	0.30640	17.403	3.896	222.3	4.2
				226.5	2.7
		2 × standard deviation of mean			2.9
$TbO_{1.817}$ in HNO_3	0.30960	16.851	3.780	214.4	2.3
	0.31014	16.802	3.858	209.0	3.1
	0.31024	17.037	3.899	213.8	1.7
	0.30974	17.000	3.774	206.4	5.7
	0.30998	17.250	3.881	215.4	3.3
	0.31046	17.152	3.850	213.4	1.3
				212.1	2.9
		2 × standard deviation of mean			2.9
$TbO_{1.975}$ in HNO_3	0.31373	16.801	3.693	197.9	0.6
	0.31417	16.886	3.670	197.4	1.1
	0.31404	16.790	3.744	200.0	1.5
	0.31414	16.838	3.705	198.4	0.1
	0.31403	16.940	3.683	198.9	0.4
				198.5	0.7
		2 × standard deviation of mean			0.9

gives a small temperature rise and takes about 1½ hours to dissolve.

MATERIALS

Terbium Metal. The metal was received through the courtesy of F. H. Spedding, Ames Laboratory, Ames, Iowa, and was analyzed by ultraviolet spectroscopy and chemically. The oxygen, hydrogen, carbon, and nitrogen were assumed to be present as Tb_2O_3, TbH_2, TbC_2, and TbN, respectively. The composition calculated from the analysis, expressed as weight per cent, was: Tb, 98.403; Tb_2O_3, 0.175; TbH_2, 0.878; TbC_2, 0.495; and TbN, 0.049. No metallic impurities were detected except Si and Fe in trace amounts.

Before weighing, the metal was cut into small pieces to increase the rate of dissolution.

Oxides. The oxides were made from 99.9% pure terbium oxide obtained from the Michigan Chemical Co. All the oxides were characterized by determining the active oxygen by the KI-$Na_2S_2O_3$ method of Barthauer and Pearce (*2*), and by x-ray analysis. In general the x-ray patterns agreed with those given by Baenziger *et al.* (*1*). The sample of $TbO_{1.510}$ gave a = 10.7307 ± 0.0005 A. compared to a = 10.7281 ± 0.0005 A. found by them for $TbO_{1.500}$, and the sample of $TbO_{1.817}$ gave lines too diffuse to measure. The uncertainties given on the composition are the arithmetic means of three analyses. Each oxide was ground in a mortar and brushed through a 400-mesh screen before weighing into the sample bulb.

$TbO_{1.510 \pm 0.003}$. The stock oxide was reduced in H_2 at 600° for 72 hours. Color: light brown.

$TbO_{1.709 \pm 0.003}$. The stock oxide was heated in air in a muffle furnace at 850° for 16 hours.

$TbO_{1.817 \pm 0.003}$. The $TbO_{1.510}$ was heated in O_2 at 430° in a thermogravimetric apparatus and quenched with He at the correct weight.

$TbO_{1.975 \pm 0.003}$. The stock oxide was heated with a 9 to 1 mixture of glacial acetic acid and concentrated hydrochloric acid for 3 hours according to the method of Brauer and Pfeiffer (*3*).

Terbium Carbonate. Terbium carbonate was prepared by precipitation from a homogeneous solution of the trichloroacetate by heating under CO_2 pressure according to the method of Head (*5*). It was analyzed by combustion for C and H and ignition to constant weight in oxygen. The formula was approximately $Tb_2(CO_3)_3 \cdot 2.3\ H_2O$ with about 0.14% by weight of $Tb(CCl_3COO)_3$ as an impurity.

RESULTS

The details of the measurements are shown in Table I.

For the terbium metal a correction was necessary for the evaporation of H_2O by the escaping hydrogen. Since the atmospheric pressure at Los Alamos is about 585 mm. of Hg, this correction amounted to −0.47 ± 0.047 kcal. per gram atom. This correction is included in the values given in Table I. The correction for the impurities was estimated to be −1.1 ± 0.2 kcal. per gram atom. The corrected value for the enthalpy of solution of Tb in 1.00*M* HCl is −167.7 ± 0.6 kcal. per gram atom.

The terbium oxide results required a correction for the evaporation of H_2O by the escaping oxygen. This amounted to only about 0.1 kcal. per mole for TbO_2 and $TbO_{1.817}$, and was negligible for $TbO_{1.709}$ and $TbO_{1.510}$.

Table II. Enthalpies of Solution and Formation of Terbium Oxides at 298° K.

Substance	$-\Delta H_{solution}$, Kcal./Mole		$-\Delta H_{formation}$, Kcal./Mole
	This work	Stubblefield	
$TbO_{1.500}$	46.9 ± 0.6[a]	47.1 ± 0.3	222.9 ± 0.9[a]
$TbO_{1.510}$	46.7 ± 0.6		223.1 ± 0.9
$TbO_{1.709}$	42.2 ± 0.5		227.6 ± 0.9
$TbO_{1.71}$		42.2 ± 0.5	
$TbO_{1.817}$	39.8 ± 0.5		230.0 ± 0.9
$TbO_{1.80}$		39.2 ± 0.5	
$TbO_{1.975}$	37.8 ± 0.2		232.0 ± 0.7
$TbO_{2.000}$	37.6 ± 0.2[a]		232.2 ± 0.7[a]

[a] Extrapolations.

Similarly, the terbium carbonate results required a correction for the evaporation of H_2O by the escaping CO_2, which amounted to −1.4 ± 0.14 kcal. per mole. The enthalpy of solution of $Tb_2(CO_3)_3 \cdot 2.3\ H_2O$ in 1*M* HCl is −26.8 ± 0.3 and in 6*M* HNO_3 is −25.7 ± 0.4 kcal. per mole, respectively.

The enthalpies of formation were calculated from the data according to the reaction scheme given earlier. The atomic weight of Tb was taken to be 158.924. ΔH_1, ΔH_2, ΔH_4, and ΔH_5 were measured. ΔH_7 is three times the enthalpy of formation of liquid water, taken (*9*) to be −204.95 kcal. ΔH_6 is assumed to be the same as 2.3 times the partial molar enthalpy of solution of H_2O in 6.00*M* HNO_3 because the concentration of terbium ion is low. Similarly, ΔH_3 is assumed to be 5.3 times the corresponding quantity for 1.00*M* HCl. They were estimated from data of Rossini *et al.* (*6*) to be −0.3 and −0.01 kcal., respectively. The enthalpies of solution and of formation are listed in Table II. The values for $TbO_{1.500}$ and $TbO_{2.000}$ were obtained by extrapolation of a plot of the measured values against composition.

DISCUSSION

The values for the enthalpies of solution of the oxides are in complete agreement with those measured by Stubblefield *et al.* (*8*), also listed in Table II. The enthalpies of formation are about 4 kcal. per mole more negative than reported by them. The main difference is in the value used for the enthalpy of solution of terbium metal. The enthalpy of formation of Tb_2O_3-cubic is thus −445.8 ± 1.8 kcal. per mole, which places it in the neighborhood of dysprosium rather than gadolinium.

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