

Enthalpies of Solution and of Formation of Several Terbium Oxides

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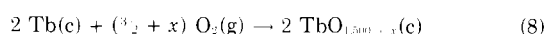
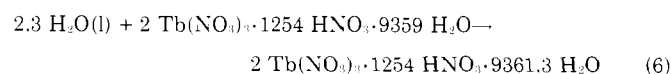
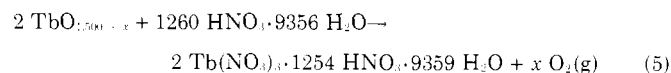
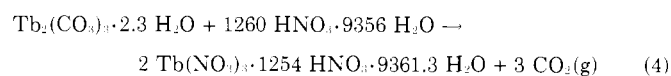
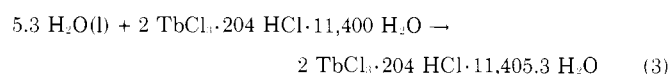
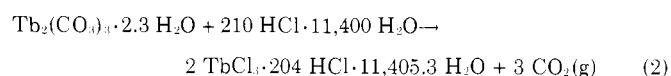
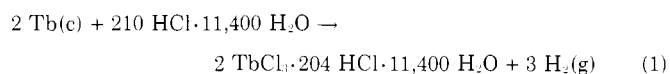
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The enthalpies of formation of $TbO_{1.510}$, $TbO_{1.709}$, $TbO_{1.817}$, and $TbO_{1.975}$ have been determined to be $\Delta H_f^\circ_{298.15\text{ K}} = -223.1 \pm 0.9$, -227.6 ± 0.9 , -230.0 ± 0.9 , and -232.0 ± 0.7 kcal. per mole, respectively. By extrapolation the enthalpies of formation of $TbO_{1.500}$ and $TbO_{2.000}$ are found to be $\Delta H_f^\circ_{298.15\text{ K}} = -222.9 \pm 0.9$ 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 1.00M HCl and of terbium carbonate and the various oxides in 6.00M 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 6.00M 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 1.00M HCl solution containing 0.0025M Na_2SiF_6 and the enthalpies of solution of the terbium oxides were measured in 6.00M HNO_3 also 0.0025M 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:



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

$$\Delta H_f(TbO_{1.500 \dots x}) = \frac{1}{2} \Delta H_s$$

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 $2.5 \times 10^{-3} M$ 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 1.00M HCl-0.0025M Na₂SiF₆ or 420 ml. of 6.00M HNO₃-0.0025M Na₂SiF₆

| 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 ·2.3 H ₂ O 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 ·2.3 H ₂ O 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 _{1.519} 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 |
| | | | 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 chemical-

ly. The oxygen, hydrogen, carbon, and nitrogen were assumed to be present as Tb₂O₃, TbH₂, TbC₂, and TbN, respectively. The composition calculated from the analysis, expressed as weight per cent, was: Tb, 98.403; Tb₂O₃, 0.175; TbH₂, 0.878; TbC₂, 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-Na₂S₂O₃ 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 $a = 10.7307 \pm 0.0005$ A. compared to $a = 10.7281 \pm 0.0005$ 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} ± 0.003. The stock oxide was reduced in H₂ at 600° for 72 hours. Color: light brown.

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

TbO_{1.817} ± 0.003. The TbO_{1.510} was heated in O₂ at 430° in a thermogravimetric apparatus and quenched with He at the correct weight.

TbO_{1.975} ± 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 CO₂ 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 Tb₂(CO₃)₃·2.3 H₂O with about 0.14% by weight of Tb(CCl₃COO)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 H₂O 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 1.00M HCl is -167.7 ± 0.6 kcal. per gram atom.

The terbium oxide results required a correction for the evaporation of H₂O by the escaping oxygen. This amounted

to only about 0.1 kcal. per mole for TbO₂ and TbO_{1.817}, and was negligible for TbO_{1.709} and TbO_{1.510}.

Similarly, the terbium carbonate results required a correction for the evaporation of H₂O by the escaping CO₂, which amounted to -1.4 ± 0.14 kcal. per mole. The enthalpy of solution of Tb₂(CO₃)₃·2.3 H₂O in 1M HCl is -26.8 ± 0.3 and in 6M HNO₃ 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 H₂O in 6.00M HNO₃ because the concentration of terbium ion is low. Similarly, ΔH_3 is assumed to be 5.3 times the corresponding quantity for 1.00M 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 Tb₂O₃-cubic is thus -445.8 ± 1.8 kcal. per mole, which places it in the neighborhood of dysprosium rather than gadolinium.

ACKNOWLEDGMENT

The authors acknowledge the help of of Gordon Wozniak in preparation of TbO_{1.975}, Earl Head, preparation of terbium carbonate, and Finley Ellinger, x-ray analysis.

LITERATURE CITED

- Baenziger, N. C., Eick, H. A., Schuldt, H. S., Eyring, L., *J. Am. Chem. Soc.* **83**, 2219 (1961).
- Barthauer, G. L., Pearce, D. W., *Ind. Eng. Chem., Anal. Ed.* **18**, 479 (1946).
- Brauer, G., Pfeiffer, B., *J. Less Common Metals* **5**, 171 (1963).
- Fitzgibbon, G. C., Pavone, D., Huber, E. J., Jr., Holley, C. E., Jr., "A New Solution Calorimeter," Los Alamos Scientific Laboratory Rept. LA-3031 (1964).
- Head, E. L., Holley, C. E., Jr., "Rare Earth Research," Vol. II, p. 51, Gordon and Breach, New York, 1964.
- Rossini, F. D., Wagman, D. D., Evans, W. H., Levine, S., Jaffe, I., *Natl. Bur. Std. Circ.* **500** (1952).
- Spedding, F. H., Flynn, J. P., *J. Am. Chem. Soc.* **76**, 1474 (1954).
- Stubblefield, C. T., Eick, H., Eyring, L., *Ibid.*, **78**, 3877 (1956).
- Wagman, D. D., Evans, W. H., Halow, I., Parker, V. B., Bailey, S. M., Schumm, R. H., *Natl. Bur. Std. Tech Note* **270-1** (1965).

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

| Substance | $-\Delta H_{\text{solution}}$, Kcal./Mole | | $-\Delta H_{\text{formation}}$, 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 _{1.81} | | 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.

RECEIVED for review April 24, 1967. Accepted July 24, 1967. Work done under the auspices of the U. S. Atomic Energy Commission.