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The Enthalpy of Formation of Terbium Trifluoride by Fluorine Bomb Calorimetry

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Abstract

The energy of formation of terbium trifluoride has been measured by a direct fluorination of terbium metal with fluorine gas in a bomb calorimeter, giving a value of $-(1698 \pm 14)$ KJ mol⁻¹. From this value, the standard enthalpy of formation of TbF₃ (c) is deduced as $-(1701 \pm 14)$ kJ mol⁻¹, and the standard Gibbs energy of formation of TbF₃ (c) is calculated to be $-(1623 \pm 14)$ kJ mol⁻¹, using estimates for the entropy. These values should be considered as being tentative.

1. Introduction

The present study was performed to determine the enthalpy of formation ΔH_f° of terbium trifluoride by fluorine bomb calorimetry. Several values of ΔH_f° for terbium trifluoride reported previously are estimates from the enthalpy of solution of trifluoride, the equilibrium constant of the reaction of terbium chloride with aluminum trifluoride, the enthalpy of solution of terbium metal in a concentrated mixture of hydrofluoric and hydrochloric acids and the solid-electrolyte galvanic-cell e. m. f. However, these values are in serious disagreement. The fluorine bomb calorimetry developed by Hubbard's group¹⁾ in the Argonne National Laboratory, U. S. A., is considered as the best method to determine the ΔH_f° value.

2. Materials

2-1 Terbium metal sample

The terbium metal samples were supplied from Research Chemicals Co., U. S. A., in the form of chips. The chemical and spectrochemical analysis of the impurities in the samples was done by the Shin-etsu Chemical Co. Ltd., Japan. The values of the impurity analysis are given in Table 1. Carbon and oxygen were determined by coulometry, hydrogen by gas chromatography, nitrogen by the Kjeldahl method,

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Table 1. Impurities in the terbium specimen given as mass fraction w .

Element	$10^6 w$	Element	$10^6 w$	Element	$10^6 w$
C	350	Cr	13	Sm	10
H	10	Cu	5	Eu	5
O	2,810	Mn	6	Gd	50
N	30	Ni	32	Y	45
F	10	Al	160	Dy	17
S	100	Zn	5	Er	78
Fe	40	Pb	15	Tm	10
Cd	5	Ta	500	Yb	5
Ca	1,030	La	30		
Mg	5	Nd	100		

fluorine by absorptiometric method, sulfur by neutralization-titration method, and the metallic impurities by the atomic absorption method or emission spectroanalysis. The precisions of the impurity analysis were as follows (as $10^2 \delta w/w$ where w is mass fraction): C, ± 5 ; O, ± 2 ; H, ± 10 ; N, ± 10 ; S, ± 10 ; rare earths, ± 10 ; the others, ± 5 . Because oxygen was the most significant impurity, the following experiment was carried out. When a considerable amount of the terbium sample was dissolved in 3 mol dm^{-3} HCl, some amount of undissolved material precipitated, and its X-ray diffraction pattern was found to definitely fit those of TbOF, Tb_2O_3 and Ta_2C , on reference to JCPDS. Regarding the states of combination of the impurities, assumptions were made as follows. Tantalum was assumed to be present in the sample as Ta_2C . The other metallic impurities and S were presumed to be dissolved in their elemental states without significant thermal effects. Carbon being not combined with tantalum, hydrogen and fluorine were assumed to be present in the samples as TbC_2 , TbH_2 , TbN and TbOF, respectively. As for oxygen, if all the oxygen is considered to be present in Tb_2O_3 and TbOF, 21.35 mg of the precipitation product per 10^3 mg of the terbium metal sample may be expected, but actually only 8.97 mg was precipitated. One possible explanation for the difference is the presence of Tb_4O_7 , which is very soluble to HCl. Table 2 shows the states of combination and the abundance of the non-metallic elements on the basis of the foregoing assumptions.

Table 2. States of combination for the non-metallic elements

Element	state	$10^6 w$	Element	state	$10^6 w$
F	TbOF	102	O	TbOF	102
H	TbH_2	805		Tb_2O_3	8,350
N	TbN	371		Tb_4O_7	11,387
C	TbC_2	2,541	S	S	100
	Ta_2C	517	Purity(Tb) = 97.42 wt %		

2-2 Fluorine gas and auxiliary materials

The fluorine, of a purity greater than 99 moles per cent, was purchased from Air Products and Chemicals, Inc., U. S. A. It was used without distillation. However, prior to its use in combustion experiments, it was purified by passing it through a chemical trap filled with NaF at about 373 K so as to remove any possible hydrogen fluoride contamination.

The terbium fluoride, used as a sample support during combustion, was supplied by the Shin-etsu Chemical Co. Ltd., in the form of TbF₃ powder having a 99.3 % purity. This sample-support material was pre-fluorinated by subjecting it to fluorine gas at about 673 K in order to convert all the impurities to trifluorides.

The high purity nickel fuse wire of 0.1 mm in diameter, used for ignition, was obtained from Shimadzu Seisaku-sho, Ltd., Japan. About 5 mg of fuse wire was ignited in each combustion run.

3. Experimental apparatus and procedure

The fluorine gas supplying system and the calorimetric system, which was composed of the combustion bomb, the calorimeter, the isoperibol jacket, and the temperature-measuring device, were analogous to those described in detail earlier²⁾. The experimental procedure involving thermal corrections was also almost the same as that described already²⁾.

The energy equivalent of the calorimetric system was determined in the standard manner by combustion of the reference benzoic acid in oxygen gas under the prescribed conditions³⁾. A series of five combustions yielded a mean value of the energy equivalent of (13543 ± 5) J K⁻¹, where the indicated error is the standard deviation of the mean for the set of five combustions.

The samples, weighed to 10⁻⁹ kg with a micro-balance were burnt in 200 to 300 kPa of fluorine gas, on a bed of sample-support terbium trifluoride powder distributed over a thin nickel dish. No attack on the nickel dish by combustion was detected.

Preliminary observations showed no detectable change in mass nor in the appearance of the terbium metal when it was exposed to ambient air for several hours. However, it showed a very slight increase in mass and a change in the appearance after an exposure to about 300 kPa of fluorine gas for several hours at room temperature. The increase in mass had almost ceased after a 15 h exposure. Hence, all samples were handled in air, but were pre-fluorinated with 200 kPa of fluorine gas for 15 h before the combustion experiments. The amount of pre-fluorination was determined from the gain in mass of the metal sample by subjecting it to fluorine gas. It was assumed that only the elemental terbium in the sample was fluorinated in the pre-fluorination, and that the pre-fluorination product was only TbF₃. Moreover, the

pre-fluorination of the sample was presumed to end after a 15 h exposure to fluorine gas, and any correction for the additional exposure of the sample to fluorine gas prior to ignition was neglected. Moisture was not picked up by the pre-fluorinated sample on a short time exposure to room atmosphere. The bomb and its auxiliary contents were also adequately pre-fluorinated with fluorine gas before the combustion experiments.

About 80 to 95 per cent of the introduced sample was burnt with fluorine gas. The crystal structure of the combustion product was determined by an X-ray diffraction analysis.

The amount of unreacted metal residue was determined by dissolving the combustion products in 3 mol dm⁻³ HCl and measuring the amount of H₂ evolved with a MacLeod gauge. The hydrogen-evolution system was calibrated by dissolving a known amount of the metal sample and measuring the amount of H₂ evolved. From the six calibration experiments, 98.64±0.14 per cent was obtained as the mean recovery of H₂ gas, and this value was used as a calibration factor of the system.

4. Experimental results

The reaction product was identified as TbF₃(c), having an orthorhombic structure, on reference to JCPDS File No. 9-416. TbF₄(c) was not found in the product by an X-ray diffraction analysis, though it is known to be stable at room temperature.

The results of the combustion experiments for terbium are summarized in Table 3. The symbols used therein have the following significance: (1), the mass of sample

Table 3. Results of terbium combustion experiments.

Experiments No.	1	2	3	4
(1) $m(\text{sample introduced})/10^{-3} \text{ kg}$	0.751097	0.601090	0.633509	0.654185
(2) $m(\text{Tb prefluorinated})/10^{-3} \text{ kg}$	0.011948	0.000318	0.000217	0.000282
(3) $m(\text{sample unburnt})/10^{-3} \text{ kg}$	0.147925	0.074575	0.031882	0.030433
(4) $m(\text{sample burnt})/10^{-3} \text{ kg}$	0.591334	0.526287	0.601504	0.623569
(5) $\Delta\theta_e/\text{K}$	0.4602	0.4181	0.4718	0.4963
(6) $\varepsilon(\text{calor})(-\Delta\theta_e)/\text{J}$	-6232.4	-5662.2	-6389.6	-6721.8
(7) $\Delta U(\text{contents})/\text{J}$	-24.3	-23.1	-27.1	-28.0
(8) $\Delta U(\text{ignition})/\text{J}$	4.8	8.3	7.7	5.6
(9) $\Delta U(\text{fuse})/\text{J}$	43.7	67.8	50.4	78.2
(10) $\Delta U_o^*/M(\text{sample})/\text{kJ kg}^{-1}$	-10498.6	-10658.1	-10571.2	-10689.3
(11) $\langle \Delta U_o^*/M(\text{sample}) \rangle = -(10604 \pm 43) \text{ kJ kg}^{-1} \text{ }^a$				
(12) Impurity correction = $-(198 \pm 9) \text{ kJ kg}^{-1} \text{ }^a$				
(13) $\Delta U_o^*/M(\text{Dy}) = -(10682 \pm 90) \text{ kJ kg}^{-1} \text{ }^b$				

^a Standard deviation of the mean. ^b Uncertainty interval.

introduced; (2), the mass of terbium metal reacted with fluorine gas in pre-fluorination; (3), the mass of sample unburnt; (4), the mass of sample burnt; (5), the true temperature rise caused by the reaction; (6), the energy absorbed by the calorimeter-exclusive of its contents; (7), the energy absorbed by the contents of the bomb; (8), the electrical energy input for the ignition of the nickel fuse; (9), the energy from the combustion of the nickel fuse; (10), the energy change per unit mass of the sample burnt; (11), the mean specific energy of combustion of the sample; (12), the net correction for the impurities in the sample; and (13), the energy change per unit mass of the metal element for the reaction:



with the reactants and product in their respective standard states at 298.15 K.

In Table 4 are given the auxiliary values used for the calculation of various numerical quantities. The contents of the bomb were terbium metal, 0.1034 kg of nickel and varying masses of terbium trifluoride powder bed of 0.0153, 0.0194, 0.0232, 0.0210 kg for the four experiments listed in Table 3. The calculation of the impurity correction was carried out on the basis of the assumption that C, H, O, N and S formed CF₄, HF, O₂, N₂ and SF₆ respectively, and that the metallic impurities formed their most stable fluorides. The uncertainty involved in the impurity correction was estimated from the uncertainty of the impurity analysis. The net correction of the bomb gas to the standard state has been omitted, because the values calculated in the usual manner²⁸⁾ were less than 0.1 J in magnitude for all combustion experiments.

In accordance with equation (1) and the foregoing considerations and assumptions,

Table 4. Numerical values used in the calculation (at 298.15 K).

$C_p/\text{J K}^{-1} \text{mol}^{-1}$	Tb, 28.91 ⁴⁾ ; TbF ₃ , 96 ^a ; Ni, 26.1 ⁴⁾ .
$C_p/\text{J K}^{-1} \text{mol}^{-1}$	F ₂ , 23.0 ⁵⁾ .
$\rho/\text{kg m}^{-3}$	Tb, 8.272; TbF ₃ , 5.8; Ni, 8.85.
$\Delta H_f^\circ/\text{kJ mol}^{-1}$	AlF ₃ , -1510.4 ⁶⁾ ; CaF ₂ , -1213 ⁷⁾ ; CdF ₂ , -700.4 ⁸⁾ ; CrF ₂ , -761 ⁷⁾ ; CuF ₂ , -530.5 ⁹⁾ ; FeF ₃ , -983 ⁷⁾ ; MgF ₂ , -1124.2 ⁶⁾ ; MnF ₂ , -795 ⁷⁾ ; NiF ₂ , -658 ¹⁰⁾ ; PbF ₂ , -661 ⁷⁾ ; ZnF ₂ , -764 ¹¹⁾ ; LaF ₃ , -1689 ¹²⁾ ; NdF ₃ , -1660.6 ¹³⁾ ; SmF ₃ , -1669 ¹⁴⁾ ; EuF ₃ , -657.7 ¹⁵⁾ ; GdF ₃ , -1699 ¹⁶⁾ ; YF ₃ , -1718 ¹⁷⁾ ; DyF ₃ , -1678 ²⁾ ; ErF ₃ , -1669 ¹⁸⁾ ; TmF ₃ , -1656 ¹⁹⁾ ; YbF ₃ , -1570 ¹⁸⁾ ; CF ₄ , -933.2 ²⁰⁾ ; HF, -273.30 ²¹⁾ ; SF ₆ , -1221 ²²⁾ ; TaF ₅ , -1903.6 ²³⁾ ; TbOF, -1160 ^a ; Ta ₂ C, -213 ²⁴⁾ ; TbC ₂ , -84 ^a ; TbH ₂ , -205 ^a ; TbN, -299 ²⁵⁾ ; Tb ₂ O ₃ , -1864.4 ²⁶⁾ ; Tb ₄ O ₇ , -3828 ^a .
$S^\circ/\text{J K}^{-1} \text{mol}^{-1}$	Tb, 73 ⁴⁾ ; F ₂ , 203 ²¹⁾ ; CeF ₃ , 115.2 ²⁷⁾ ; TbF ₃ , 117 ^b .
$M/\text{kg mol}^{-1}$	Tb, 0.158924; F, 0.0189984.

^a Estimated.

^b Estimated by the application of Kopp's law.

the derived standard thermal quantities for the formation of $\text{TbF}_3(\text{c})$ at 298.15 K are as follows:

$$\Delta U_f^\circ(\text{TbF}_3, \text{c})/\text{kJ mol}^{-1} = -(1698 \pm 14);$$

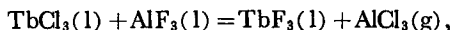
$$\Delta H_f^\circ(\text{TbF}_3, \text{c})/\text{kJ mol}^{-1} = -(1701 \pm 14);$$

$$\Delta G_f^\circ(\text{TbF}_3, \text{c})/\text{kJ mol}^{-1} = -(1623 \pm 14).$$

In deriving the ΔG_f° value, the entropy $S^\circ(\text{TbF}_3, \text{c}, 298.15 \text{ K})$ in Table 4 was estimated on the basis of $S^\circ(\text{CeF}_3, \text{c}, 298.15 \text{ K})$ and Latimer's rule²⁹⁾. The uncertainties assigned to ΔU_f° , ΔH_f° and ΔG_f° were conventionally taken to be twice the combined standard error derived from the scatter of $\Delta U_f^\circ/M$ (sample) values, the calibration results and the impurity correction. In the estimation of ΔG_f° , the uncertainty in ΔS_f° was not included because it was not found in the literature. When it is taken into consideration, the uncertainty in ΔG_f° becomes greater than 14 kJ mol⁻¹.

5. Discussion

For comparison, the published values for $\Delta H_f^\circ(\text{TbF}_3, \text{c}, 298.15 \text{ K})$ are tabulated in Table 5. Brewer et al.⁷⁾ estimated the value of $\Delta H_f^\circ(\text{TbF}_3, \text{c})$ from the enthalpy of solution of terbium trifluoride, the enthalpy of formation of aqueous trivalent terbium ion, $\Delta H_f^\circ(\text{Tb}^{3+}, \text{aq})$, and of fluoride ion, $\Delta H_f^\circ(\text{F}^-, \text{aq})$. This estimate may be revised to $-1694 \text{ kJ mol}^{-1}$ by using -687 kJ mol^{-1} for $\Delta H_f^\circ(\text{Tb}^{3+}, \text{aq})$ according to Morss³³⁾, and $-335.35 \text{ kJ mol}^{-1}$ ²¹⁾ for $\Delta H_f^\circ(\text{F}^-, \text{aq})$ instead of -703 kJ mol^{-1} for $\Delta H_f^\circ(\text{Tb}^{3+}, \text{aq})$ and -327 kJ mol^{-1} for $\Delta H_f^\circ(\text{F}^-, \text{aq})$ used in Brewer's estimation. From the equilibrium studies of the reaction



Polyachenok³⁰⁾ derived the value for $\Delta H_f^\circ(\text{TbF}_3, \text{c})$ by taking -987 kJ mol^{-1} as $\Delta H_f^\circ(\text{TbCl}_3, \text{c})$. This value for $\Delta H_f^\circ(\text{TbF}_3, \text{c})$ can be revised to $-1631 \text{ kJ mol}^{-1}$, if $\Delta H_f^\circ(\text{TbCl}_3, \text{c}) = -1007 \text{ kJ mol}^{-1}$ by Morss³³⁾ is used. Storozhenko et al.³¹⁾ measured the

Table 5. Published values for the standard enthalpy of formation of terbium trifluoride, TbF_3 , at 298.15 K.

Investigator	Method	$\Delta H_f^\circ/\text{kJ mol}^{-1}$
Brewer et al. ⁷⁾	Solution calorimetry of trifluoride	$-(1674 \pm 29)$, -1694^*
Polyachenok ³⁰⁾	Reaction equilibrium of chloride with aluminum trifluoride	$-(1611 \pm 25)$, -1631^*
Storozhenko ³¹⁾	Solution calorimetry of metal	$-(1623.3 \pm 3.8)$
Kholokhonova ³²⁾	Solid state e. m. f.	$-(1707.9 \pm 5.0)$
This work	Fluorine bomb calorimetry	$-(1701 \pm 14)$

* See text.

enthalpy of solution of terbium metal in a mixture of hydrofluoric and hydrochloric acids and derived the value for ΔH_f° (TbF₃, c). Kholokhonova et al³² obtained the value of ΔH_f° (TbF₃, c) by the study of the solid-state e. m. f. on some metal fluorides including TbF₃. The present work is the only fluorine bomb calorimetry. Its value is close to the revised value of Brewer et al. and also to the value of Kholokhonova et al.

The non-metallic impurities, as described in the earlier section, were presumed to be present in the form of specific chemical compounds of terbium. From the precipitation experiment of the sample, parts of oxygen, carbon and fluorine in the impurities are thought to form terbium sesquioxide, tantalum carbide and terbium oxyfluoride, respectively. Hence, if all the non-metallic impurities except oxygen, carbon and fluorine which are present as compounds, are assumed to dissolve without significant thermal effects, the value for ΔH_f° (TbF₃, c) will become more positive than the present value by 9 kJ mol⁻¹.

The thermochemical values were obtained in this work on the assumption of the unidentified presence of Tb₄O₇ as described earlier. Therefore, these values could not help being considered as being tentative.

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