

# The Enthalpy of Formation of Dysprosium Trifluoride by Fluorine Bomb Calorimetry

By

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(Received September 21, 1979)

## Abstract

The energy of formation of dysprosium trifluoride has been measured by direct fluorination of dysprosium metal with fluorine gas in a bomb calorimeter, giving a value of  $-(1674 \pm 8)$  kJ mol<sup>-1</sup>. From this value, the standard enthalpy of formation of DyF<sub>3</sub> (c) is deduced as  $-(1678 \pm 8)$  kJ mol<sup>-1</sup>, and the standard Gibbs energy of formation of DyF<sub>3</sub> (c) is calculated to be  $-(1600 \pm 9)$  kJ mol<sup>-1</sup>, using estimates for the entropy.

## 1. Introduction

The enthalpy of formation  $\Delta H_f^\circ$  of a lanthanoid fluoride is one of the important quantities necessary for the study of its thermochemical properties. The present study is part of a series to obtain thermochemical quantities for lanthanoid fluorides, and was performed to determine  $\Delta H_f^\circ$  of dysprosium trifluoride by fluorine bomb calorimetry. Several values of  $\Delta H_f^\circ$  for dysprosium trifluoride have been reported previously, but these values are estimates from the enthalpy of solution of trifluoride, the stability constant of subfluoride, the equilibrium constant of the reaction of dysprosium chloride with aluminum trifluoride, and the enthalpy of reaction of dysprosium metal with a mixture of hydrofluoric and hydrochloric acids. These estimates are in serious disagreement. Fluorine bomb calorimetry, which was developed by Hubbard's group<sup>1)</sup> in the Argonne National Laboratory, U. S. A. is believed to be the best method to determine the  $\Delta H_f^\circ$  value.

## 2. Materials

### 2-1 Dysprosium metal sample

The dysprosium metal samples used in the present study were supplied from

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

Element	$10^6 w$	Element	$10^6 w$	Element	$10^6 w$
C	180	Fe	40	Mg	70
O	2000	Cu	10	Y	90
H	10	Mn	20	Eu	50
N	80	Ni	10	Gd	1170
F	10	Cd	5	Tb	960
Al	100	Pb	40	Er	50
Si	100	Zn	20	Tm	50
Cr	10	Ca	120	Yb	10

Research Chemicals, a Division of the NUCOR Corporation of America, Phoenix, Arizona, U. S. A. in the form of chips. The chemical and spectrochemical analysis of the impurities in the samples was performed by the Shin-etsu Chemical Co. Ltd., Takefu Factory, Fukui, Japan. Carbon and oxygen were determined by coulometry, hydrogen by gas chromatography, nitrogen by the Kjeldahl method, fluorine by the absorptiometric method, and metallic impurities by the atomic absorption method or emission spectroanalysis. The values of the impurity analysis are given in Table 1. The precisions of the impurity analysis were as follows (as  $10^2 \delta w/w$  where  $w$  is mass fraction): C,  $\pm 5$ ; O,  $\pm 2$ ; H,  $\pm 10$ ; N,  $\pm 10$ ; rare earths,  $\pm 10$ ; the others,  $\pm 5$ . The states of combination of the impurities were presumed as follows. Carbon, oxygen, hydrogen, nitrogen, and fluorine were presumed to be present in the sample as  $\text{DyC}_2$ ,  $\text{Dy}_2\text{O}_3$ ,  $\text{DyH}_2$ ,  $\text{DyN}$ , and  $\text{DyOF}$ , respectively. On the basis of the foregoing assumptions, then, the calculated content of elemental Dy in the sample was 98.51 moles per cent.

In order to further ascertain the presumption that virtually all the oxygen and fluorine were contained as the compounds,  $\text{Dy}_2\text{O}_3$  and  $\text{DyOF}$ , the following precipitation experiment was carried out. A known amount of the dysprosium metal sample was dissolved in  $3 \text{ mol dm}^{-3}$  HCl, and 19.8 mg of precipitation product per  $10^3$  mg of dysprosium metal sample was obtained. This amount corresponds somewhat closely to the 15.5 mg of the insoluble  $\text{Dy}_2\text{O}_3$  and  $\text{DyOF}$  precipitate, which was calculated from the above-mentioned presumption and the results of the oxygen and fluorine analysis. The well-defined X-ray diffraction pattern was not obtained. The results of this X-ray analysis, however, seemed to correspond somewhat to the crystal structures<sup>2)</sup> of a mixture of  $\text{Dy}_2\text{O}_3$  of a cubic structure and  $\text{DyOF}$  of a rhombohedral structure.

## 2-2 Fluorine gas

The fluorine gas used in the combustion experiments was purchased from Air Products and Chemicals, Inc., Allentown, Pennsylvania, U. S. A. In Table 2 are given the typical values of the analysis of fluorine gas provided by the commercial supplier.

Table 2. Typical analysis of fluorine gas.

F <sub>2</sub>	>99%	SF <sub>6</sub>	0.1 %
O <sub>2</sub>	0.35%	HF	0.2 %
N <sub>2</sub>	0.2 %	CO <sub>2</sub>	0.05%
CF <sub>4</sub>	0.08%	H <sub>2</sub> O	<0.0001%

This fluorine gas was used without distillation, but prior to use in combustion experiments, it was purified by passing it through a chemical trap filled with sodium fluoride at about 373 K to remove possible hydrogen fluoride contamination.

### 2-3 Auxiliary materials

The dysprosium trifluoride used as a sample support during combustion experiments was supplied in the form of powder from the Shin-etsu Chemical Co., Ltd., Takefu Factory. Impurities less than 0.01 mass per cent were contained in this dysprosium trifluoride. The impurities were thought to be dysprosium oxide. The sample support material was prefluorinated by subjecting it to fluorine gas at about 673 K in order to convert the impurity oxide to trifluoride.

High nickel fuse wire, 0.1 mm in diameter, used for ignition was obtained from Shimadzu Seisaku-sho, Ltd., Kyoto, Japan. No impurity analysis was made on the fuse wire because only about 5 mg was ignited in each run.

## 3. Experimental apparatus

### 3-1 Calorimetric system

The calorimetric system employed in this work was of the Dickinson type, a schematic diagram of which is shown in Fig. 1. The calorimetric system, as shown in Fig.

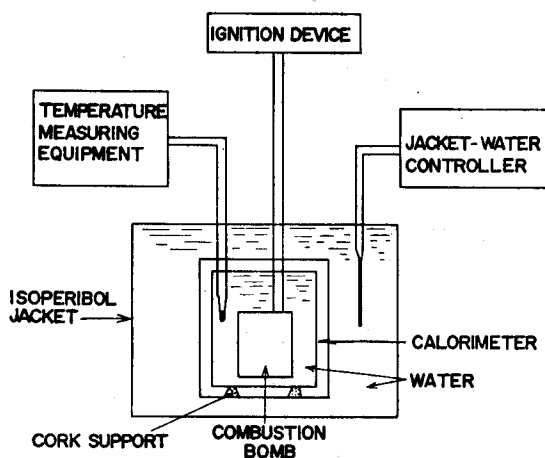


Fig. 1. The calorimetric system.

1, consisted of the combustion bomb, the calorimeter, the isoperibol jacket, the temperature measuring equipment, the jacket-water controller and the ignition device.

The isoperibol jacket is constructed of metal and is 33 cm in width, 40 cm in length, and 40 cm in height. The jacket-water is controlled to  $\pm 0.01$  K at an arbitrary temperature somewhat higher than that of the calorimeter-water by using a platinum resistance thermometer and an automatic temperature controller. The jacket inner cylinder made of brass is 17 cm in diameter, 28 cm in height, and is water-tight by covering it with a brass top lid. The calorimeter is a cylinder made of brass and is 14 cm in diameter and 25 cm in height. It contains calorimeter-water, the volume of which is exactly 2350.0 cm<sup>3</sup> at 283 K in each combustion experiment. A stirrer, a guide tube for circulating water, a heater, a lead for ignition, and a thermistor are installed in it. The calorimeter stands on cork supports which prevent it from coming in direct contact with the bottom of the jacket inner cylinder. An air space of 12 to 14 mm is left between the calorimeter and the jacket inner cylinder in order to restrain the heat transfer between the calorimeter and the jacket-water.

### 3-2 Combustion bomb

The combustion bomb used for the present work is analogous in most of the essential features to the bomb described previously by Hubbard's group<sup>11</sup>. Fig. 2 is a schematic diagram of the combustion bomb used in this work. The bomb, made of stainless steel, consists of three parts, namely a cylindrical body to contain the substance to be burned and the fluorine gas for combustion, a cap to close the body, and a sealing nut to hold the cap tightly on the body. The body is 8 cm in diameter,

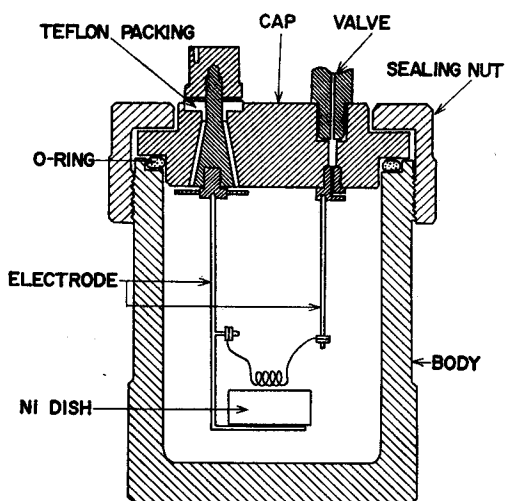


Fig. 2. Schematic diagram of the combustion bomb used in this work.

10 cm in depth, 0.8 cm in wall thickness and has an internal volume of 502.5 cm<sup>3</sup>. The body and the cap are sealed with an O-ring of fluorinated synthetic rubber. The bomb was tested against a hydraulic pressure of  $3 \times 10^4$  kPa, and is guaranteed to  $2 \times 10^4$  kPa in ordinary use. A valve is screwed on to the cap with polytetrafluoroethylene (Teflon) packing. Two electrodes, made of nickel, pass through the cap of the bomb. One is in direct contact with the cap and the other is electrically insulated from the cap with a cone type Teflon packing. The packing is prevented from burning initiated by the combustion spark of the metal sample. To the lower end of the latter electrode is attached a nickel dish which served as a sample support.

Before the combustion experiments, the bomb and its auxiliary contents were fully prefluorinated with fluorine gas.

### 3-3 Fluorine gas supplying system

The system of supplying the bomb with fluorine gas, as illustrated in Fig. 3, consists of a fluorine tank enclosed in an iron box, a Bourdon tube gauge, valves, chemical traps, vacuum gauges, and a vacuum system. The pipe-line was made of monel

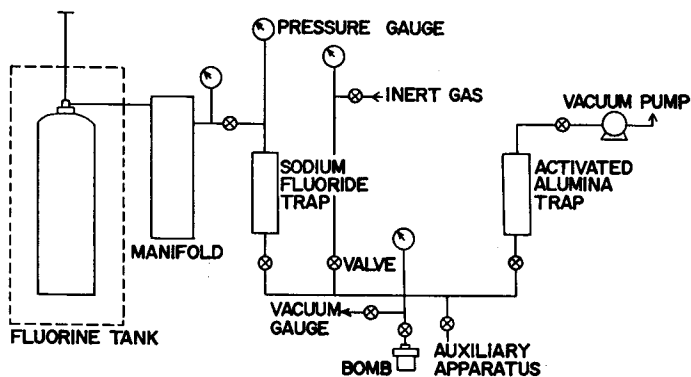


Fig. 3. Schematic diagram of the fluorine gas supplying system.

or copper, and for gasket materials, aluminum or copper was used. The pressure of fluorine gas was restricted to 400 kPa at the highest, by taking account of the allowable stress of some parts of the system such as valves. A sodium fluoride trap at about 373 K is placed in the line to remove possible hydrogen fluoride contamination because of using commercial fluorine without distillation in the combustion experiments. Fluorine gas is discharged through an activated alumina trap at about 373 K by the vacuum pump. A test for any leakage of fluorine gas was made by using starch iodide paper, which turns blue even when exposed to a very small amount of fluorine gas.

## 3-4 Temperature measuring equipment

*Thermistor*

A thermistor employed for the measurement of calorimeter-water temperature was purchased from the Takara Industry Co. Ltd., Japan, and sealed in a glass tube, 2 mm in diameter and 70 mm in length. Since a thermistor has a large electric resistance and the temperature-dependence of resistance is also large, it can detect a slight change of temperature with nearly negligible error due to any change of lead resistance or contact resistance of a circuit. However, in using a thermistor, the self-heating effect due to Joulean heat generation must be taken into account.

Equation (3-1) is well known for the change of electric resistance of a thermistor with temperature.

$$R=R_0 \exp\left\{B\left(\frac{1}{T}-\frac{1}{T_0}\right)\right\} \quad (3-1)$$

where  $R$  and  $R_0$  are the resistances in  $k\Omega$  of a thermistor at the temperature in K of  $T$  and  $T_0$ , respectively, and  $B$  is a thermistor constant.

The thermistor used in this work was calibrated using a standard mercury thermometer under conditions similar to those of the actual measurement. About one hundred calibrations were made between 296 K and 301 K, and the result is expressed with a least square method by

$$R=10.3272 \exp\left\{3431.278\left(\frac{1}{T}-\frac{1}{298.15}\right)\right\} \quad (3-2)$$

as shown in Fig. 4.

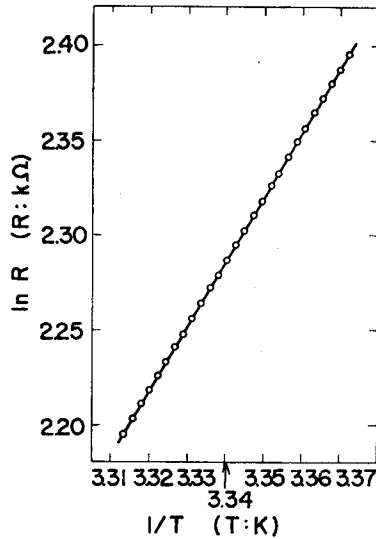


Fig. 4. The change of electric resistance with temperature of the thermistor.

A thermistor, by its self-heating due to Joulean heat generation, keeps thermal equilibrium at a temperature somewhat higher than that of the surroundings. Hence, in order to know the temperature of the surroundings, that is calorimeter-water temperature, corrections must be made by the following relation.

$$W = k(T - T_s) \tag{3-3}$$

where  $W$  is Joulean heat evolved in the thermistor,  $T$  and  $T_s$  are temperatures of the thermistor and its surroundings, respectively, and  $k$  is a heat emission factor. Since the value of  $k$  depends on conditions of water flow around the thermistor, it was determined under conditions similar to the actual measurement. In Fig. 5 is shown the circuit for measuring the voltage-current property of a thermistor. From both voltage-current and temperature-resistance properties the value of  $k$  was determined to be  $5.18 \times 10^{-3}$  Watt  $K^{-1}$  as shown in Table 3. The change of  $(T - T_s)$  value due to that of the resistance of a thermistor was less than  $10^{-4}$  K within the range of temperature change found in the combustion experiments.

As shown in Fig. 6, this thermistor is used as one arm of the Wheatstone bridge, and the other three arms of the bridge are one standard resistance  $R_1$  of 10 k $\Omega$  and two standard resistances  $R_2$  and  $R_3$  of 1 k $\Omega$ . A dry battery  $E$  of about 1.55 V is at-

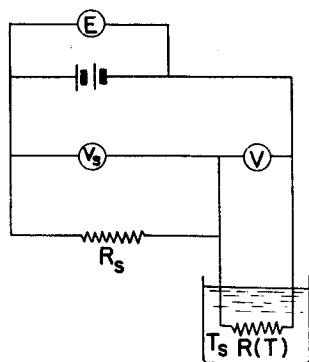


Fig. 5. Circuit for measuring the voltage-current property of the thermistor.

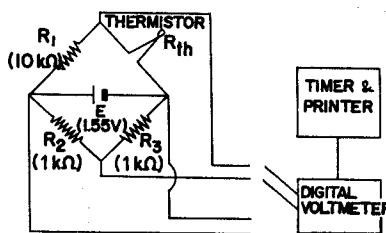


Fig. 6. Wheatstone bridge.

Table 3. Heat emission coefficient,  $k$

$I$ [mA]	$E$ [V]	$R$ [k $\Omega$ ]	$T$ [K]	$T_s$ [K]	$T - T_s$ [K]	$E \times I$ [mW]	$k$ [WK $^{-1}$ ]
0.4580	4.207	9.186	301.12	300.75	0.37	1.9268	$5.21 \times 10^{-3}$
0.6186	5.619	9.083	301.42	300.75	0.67	3.4759	$5.19 \times 10^{-3}$
0.9562	8.406	8.791	302.28	300.75	1.53	8.0378	$5.25 \times 10^{-3}$
0.7831	7.005	8.945	301.82	300.76	1.06	5.4856	$5.18 \times 10^{-3}$
0.7894	7.005	8.874	302.03	300.95	1.08	5.530	$5.12 \times 10^{-3}$
Mean							$5.18 \times 10^{-3}$

tached. The voltage difference  $V$  was measured with a digital voltmeter having a sensitivity of  $1 \mu V$ . The resistance  $R$  of the thermistor can be calculated from the equation

$$R = R_1 \left\{ 1 + \frac{(2-\alpha)E + 2\alpha V}{(\alpha-1)E - \alpha V} \right\} \quad (3-4)$$

where  $\alpha = (R_2 + R_3)/R_3 \approx 2$ . The bridge sensitivity was about  $15 \text{ mV K}^{-1}$  at an excitation potential of about  $1.5 \text{ V}$ .

### 3-5 Hydrogen evolution system

A hydrogen evolution system was employed in order to determine the amount of an unburned metal sample after each combustion experiment. The system was made of Pyrex glass and consisted of a reaction vessel, a cold trap, a Toepler pump, a MacLeod vacuum gauge, and a vacuum system.

Hydrogen gas evolved by dissolving a combustion product in  $3 \text{ mol dm}^{-3} \text{ HCl}$  passed through the cold trap and was transferred to the pressure measuring part by the Toepler pump. The pressure of hydrogen gas was measured with the MacLeod vacuum gauge as shown in Fig. 7. Mercury is pushed up by introducing air through the cock  $K$  and stops at the zero point of an open capillary  $C_b$ . On the other hand, mercury stopping up the cut-off, compresses the gas in the compression bulb  $A$  and stops at  $h \text{ mm}$  below the top of the closed capillary  $C_a$ . Then, by Boyle's law,  $PV_a = hv_a(h+P)$  or

$$P = \frac{h^2 v_a}{V_a - h v_a} = \frac{h^2 \delta}{1 - h \delta} \quad (3-5)$$

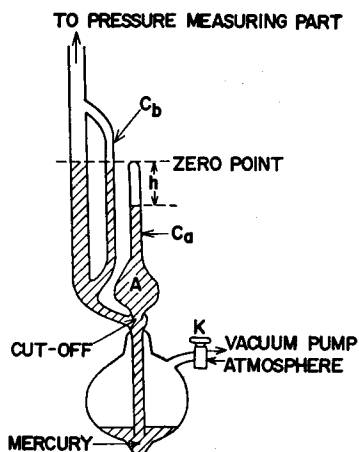


Fig. 7. The MacLeod vacuum gauge.



where  $P$  is the pressure in mmHg before compression of the gas in the bulb A, namely that of the measuring part,  $V_a$  the volume of the bulb A including that of the capillary  $C_a$ ,  $v_a$  the volume of the capillary  $C_a$  per 1 mm length, and  $\delta = v_a/V_a = 1.0493 \times 10^{-4} \text{ mm}^{-1}$ . The number of moles  $n$  of the hydrogen gas evolved can be calculated from the following equation.

$$n = \frac{V}{RT}(P - P_0) = \frac{V\delta}{RT} \left\{ \frac{h^2}{(1-h\delta)} - \frac{h_0^2}{(1-h_0\delta)} \right\} \quad (3-6)$$

where  $V$  is the volume of the pressure measuring part including  $V_a$ ,  $T$  the temperature when the pressure is measured,  $R$  the gas constant, and the suffix "0" refers to the initial state.

Actually, all of the hydrogen gas evolved could not be completely transferred to the pressure measuring part of the system. Therefore, it was necessary to determine the recovery efficiency of the gas. The recovery efficiency was obtained as follows. A known amount of the metal sample was dissolved in  $3 \text{ mol dm}^{-3}$  HCl, and the number of moles  $n$  of the evolved gas was determined from the equation (3-6). Then, the recovery efficiency  $r$  was  $r = n/n_0$ , where  $n_0$  is the number of moles of the gas calculated theoretically from the metal sample. In Table 4 are given the results of the calibration experiment of the system for the dysprosium sample.

Table 4. Results of the calibration experiment of the  $\text{H}_2$  evolution system for dysprosium sample.

$m(\text{Dy sample})/\text{mg}$	25.143	30.971	21.510	40.356
$h_0/\text{mm}$	(i) 12.6 (ii) 13.2	(i) 12.9 (ii) 10.7 (iii) 10.0	10.5	11.7
$h/\text{mm}$	(i) 71.5 (ii) 68.4	(i) 63.7 (ii) 62.2 (iii) 64.5	91.0	122.9
$T/\text{K}$	(i) 295.4 (ii) 295.8	(i) 296.3 (ii) 296.3 (iii) 296.1	296.0	284.0
$n \times 10^4/\text{mol}$	2.2484	2.7749	1.9440	3.7240
$n_0 \times 10^4/\text{mol}$	2.2884	2.8188	1.9577	3.6730
$r (= n/n_0)$	0.9825	0.9844	0.9930	1.0139
Mean $r = 0.9935 \pm 0.0072$				

### 3-6 Auxiliary apparatus

#### Ignition device

Combustion was initiated by passing an electric current through a nickel fuse wire. Electrical energy supplied for the ignition was determined with an electric-current integrating device similar to that used by Pilcher and Sutton<sup>3)</sup>. The ignition circuit is shown in Fig. 8. The voltages across the condenser by the initial charging and that after discharging for ignition were measured by a voltmeter. The energy required for the ignition,  $\Delta U$  (ignition) is given by

$$\Delta U (\text{ignition}) = \frac{1}{2} C (V_i^2 - V_f^2) \quad (3-7)$$

where  $C$  is a capacity of the condenser,  $V_i$  and  $V_f$  are the initial and final voltages across the condenser, respectively.

#### Glass combustion bomb

Preliminary combustions were necessary in order to observe the ignition and burning characteristics of the dysprosium metal sample. For this purpose, a glass bomb similar to that reported by Nuttal *et al.*<sup>4)</sup> was constructed in which trial combustions could be observed virtually. Fig. 9 shows this glass bomb. The bomb body consists of a wall which is a standard commercial Pyrex glass pipe spacer, 7 cm in outer diameter, 6 cm in inner diameter, and 8 cm in height. It is held between stainless steel end plates cushioned by Teflon gaskets.

For safety reasons, the combustions were carried out with fluorine gas of less than 200 kPa pressure, and the bomb was located in a sealed box with glass windows.

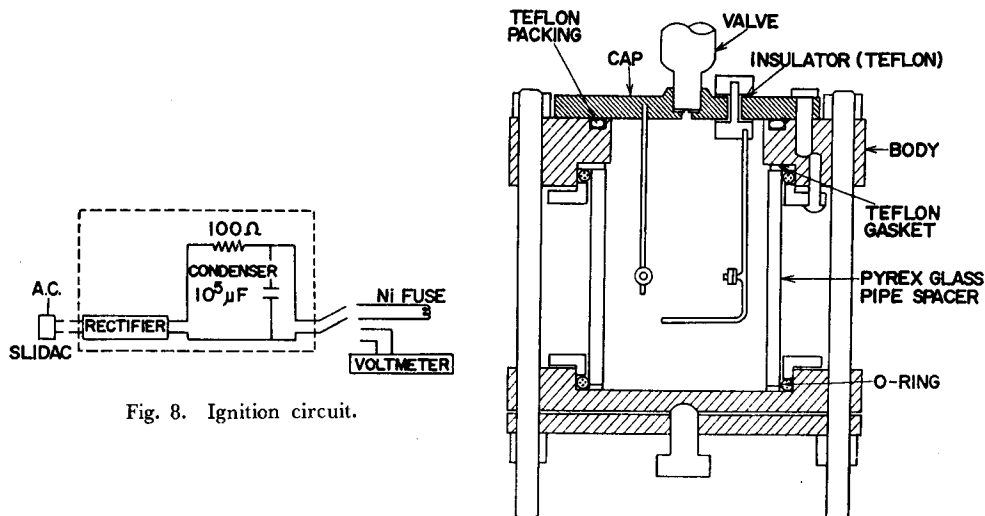


Fig. 8. Ignition circuit.

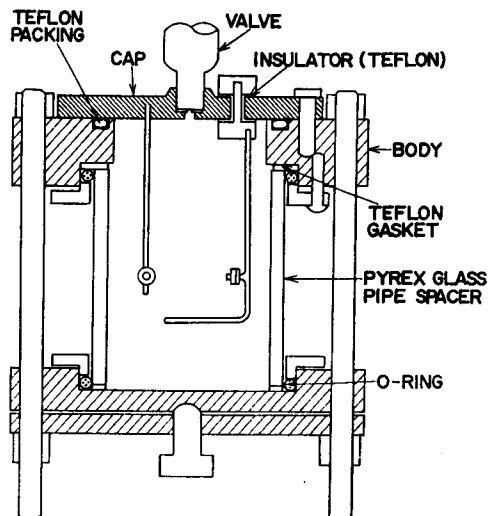


Fig. 9 The glass bomb.

#### 4. Thermal corrections and experimental procedures

##### 4-1 Corrected temperature rise

In a combustion experiment using the isoperibol jacket calorimeter, the relation between the calorimeter-water temperature,  $\theta$ , and time,  $t$ , is illustrated by the curve in Fig. 10. After the calorimeter placed in the isoperibol jacket attains a steady state

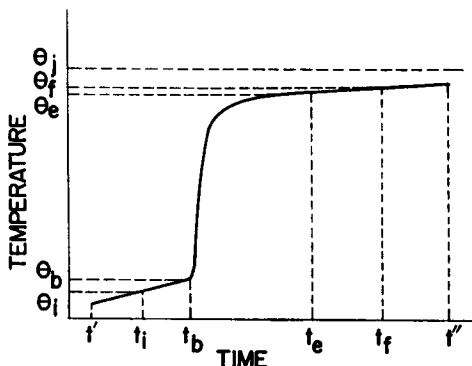


Fig. 10 Time-temperature curve for the isoperibol jacket calorimeter.

the measurement of the temperature begins at the time  $t'$ . At the time  $t_b$  the combustion reaction occurs by the ignition of the fuse and a rapid increase of temperature is observed. After the time  $t_e$ , the calorimeter again attains a steady state and the measurement ends at the time  $t''$ . The parts of the curve between  $t'$  and  $t_b$ ,  $t_b$  and  $t_e$ , and  $t_e$  and  $t''$  represent the time-temperature relations in the initial, main, and final periods, respectively.

The observed temperature rise,  $(\theta_e - \theta_b)$ , of the calorimeter must be corrected for the heat exchanged between the calorimeter and its surroundings, and for the heat generated by stirring the water in the calorimeter in order to obtain the true temperature rise resulting from the reaction which takes place in the bomb. This correction,  $\Delta\theta$ , is calculated from the observations of time and temperature on the basis of Newton's law of cooling:

$$\frac{d\theta}{dt} = u + k(\theta_j - \theta) \quad (4-1)$$

where  $k$  is the "cooling constant" of the calorimeter, and  $u$  represents the rate of temperature change of the calorimeter due to the heat of stirring. Assuming  $u$  to be constant, the resulting expression for  $\Delta\theta$  is as follows.

$$\begin{aligned} \Delta\theta &= -g_f(t_e - t_b) - k \int_{t_b}^{t_e} (\theta_j - \theta) dt \\ &= -[g_f + k(\theta_j - \theta_m)](t_e - t_b) \end{aligned} \quad (4-2)$$

where  $\theta_m$  represents the average temperature of the calorimeter in the main period and  $g_f$  the value of  $d\theta/dt$  at the mean temperature  $\theta_f$  of the final period. The value of  $k$  is calculated from the following equation.

$$k = \frac{g_i - g_f}{\theta_f - \theta_i} \quad (4-3)$$

where  $g_i$  represents the value of  $d\theta/dt$  at the mean temperature  $\theta_i$  of the initial period.

The value of  $\theta_m$  is obtained by the numerical integration according to the Regnault-Pfaundler method because there is no simple analytical expression for the timetemperature relation in the main period. When  $n$  temperatures,  $\theta_r$ , are measured at equal time intervals (= 10 seconds in this work) during the main period, the value of  $\theta_m$  is expressed as follows.

$$\theta_m = \left\{ \sum_{r=2}^{n-1} \theta_r + \frac{\theta_b + \theta_e}{2} \right\} \frac{1}{n-1} \quad (4-4)$$

In accordance with the above discussion, the corrected temperature rise,  $\Delta\theta_{corr}$ , is given by the equation

$$\Delta\theta_{corr} = \theta_e - \theta_b + \Delta\theta. \quad (4-5)$$

#### 4-2 Thermodynamic standard states

The value for the enthalpy of formation is obtained from the corrected temperature rise caused by the reaction and the energy equivalent of the calorimeter. Since this quantity is referred to an arbitrary thermodynamic state, it is necessary to correct the quantity to the standard state at 298.15 K. The thermodynamic process of formation of dysprosium trifluoride is illustrated by the schematic diagram as in Fig. 11.

(i) The dysprosium metal is placed in the bomb and compressed from a pressure of 1 atm<sup>†</sup> to a pressure of  $P^i(\text{F}_2)$ .

$$\Delta U^i(\text{Dy}) \Big|_1^{P^i(\text{F}_2)} = n_R(\text{Dy}) \left( \frac{\partial U}{\partial P} \right)_T(\text{Dy}) [P^i(\text{F}_2) - 1] \quad (4-6)$$

The change of internal energy in this step was usually negligible.

(ii) The  $n_R(\text{F}_2)$  moles of reacting  $\text{F}_2$  gas in the ideal gas state at 298.15 K are mixed with  $n^i(\text{F}_2) - n_R(\text{F}_2)$  moles of excess  $\text{F}_2$  gas initially in the ideal gas state at 298.15 K and 1 atm. This step does not involve any change in internal energy.

(iii) The  $n^i(\text{F}_2)$  moles of mixed  $\text{F}_2$  gas is compressed into the remaining space of the bomb to the pressure  $P^i(\text{F}_2)$ .

$$\Delta U^i(\text{F}_2) \Big|_1^{P^i(\text{F}_2)} = n^i(\text{F}_2) \left( \frac{\partial U}{\partial P} \right)_T(\text{F}_2) [P^i(\text{F}_2) - 1] \quad (4-7)$$

<sup>†</sup> 1 atm = 101.325 kPa ; 1 cal<sub>th</sub> = 4.184 J.

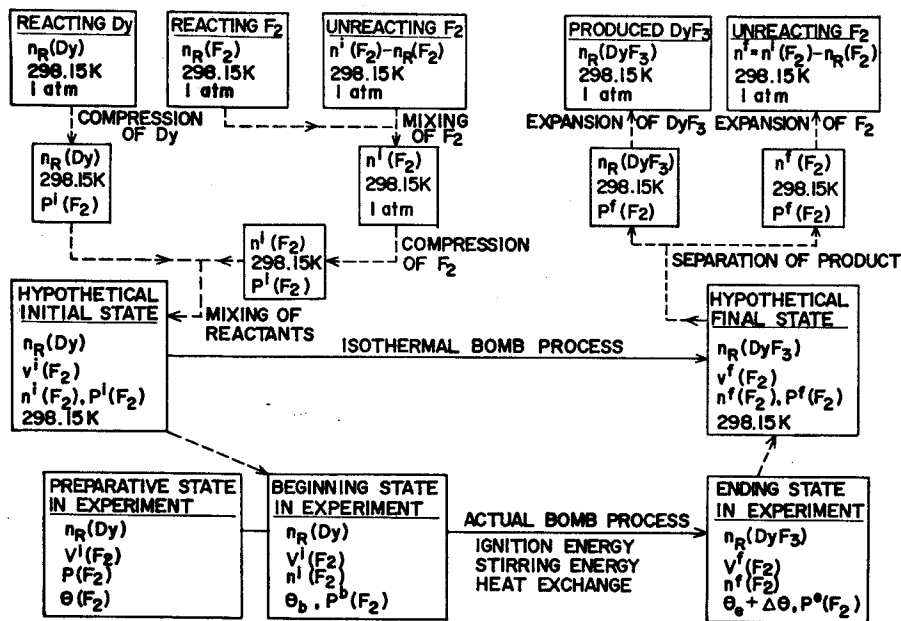


Fig. 11. Schematic diagram of the thermodynamic process of formation of  $\text{DyF}_3(\text{c})$ .

where, because the value for  $(\partial U/\partial P)_T(\text{F}_2)$  is unavailable, it was used as  $-1.780 \text{ cal}_h \text{ mol}^{-1} \text{ atm}^{-1}$  at 298.15 K which was obtained using the relation,

$$\left(\frac{\partial U}{\partial P}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_P - P\left(\frac{\partial V}{\partial P}\right)_T, \quad (4-8)$$

the equation of state, and the intermolecular force constants.

(iv) The bomb is placed in the calorimetric system at 298.15 K. By this step the system is brought to the hypothetical initial state of the isothermal bomb process. No change in internal energy is involved in this step.

(v) The temperature of the system is changed from 298.15 K to  $\theta_b$ , and then the system is brought to the beginning state of the actual bomb process. The actual bomb reaction is caused to occur, and the temperature of the system increases from  $\theta_b$  to  $\theta_e + \Delta\theta$ , that is, the system reaches the ending state of the actual bomb process. The temperature of the system is changed from  $\theta_e + \Delta\theta$  to 298.15 K, and this step brings the system to the hypothetical final state of the isothermal bomb process.

The change of internal energy for the isothermal bomb process,  $\Delta U_{\text{IBP}}$ , is the sum of the changes in internal energy for the processes described above.

$$\begin{aligned} \Delta U_{\text{IBP}} = & \varepsilon(\text{calor})(\theta_b - \theta_e - \Delta\theta) + \varepsilon^i(\text{cont})(\theta_b - 298.15) \\ & + \varepsilon^f(\text{cont})(298.15 - \theta_e - \Delta\theta) + \Delta U(\text{ign}) \\ & + \Delta U(\text{fuse}) \end{aligned} \quad (4-9)$$

(vi) The reaction product  $\text{DyF}_3(\text{c})$  and remaining  $n^f(\text{F}_2) = n^i(\text{F}_2) - n_R(\text{F}_2)$  moles of  $\text{F}_2$  gas are removed from the calorimeter at 298.15 K and separated from each other at a pressure of  $P^f(\text{F}_2)$ . There is no change in internal energy.

(vii) The  $n^f(\text{F}_2)$  moles of  $\text{F}_2$  gas are expanded to a pressure of 1 atm.

$$\Delta U^f(\text{F}_2) \Big|_{P^f(\text{F}_2)}^1 = -n^f(\text{F}_2) \left( \frac{\partial U}{\partial P} \right)_T(\text{F}_2) [P^f(\text{F}_2) - 1] \quad (4-10)$$

The produced  $\text{DyF}_3(\text{c})$  is expanded to a pressure of 1 atm.

$$\Delta U^f(\text{DyF}_3) \Big|_{P^f(\text{F}_2)}^1 = n_R(\text{DyF}_3) \left( \frac{\partial U}{\partial P} \right)_T(\text{DyF}_3) [1 - P^f(\text{F}_2)] \quad (4-11)$$

The change of internal energy in this step was negligible.

Though a part of  $\text{Dy}(\text{c})$  remained unreacted in all combustion experiments, the contribution of the unreacted  $\text{Dy}(\text{c})$  to the change of internal energy in steps (vi) and (vii) was negligible.

The idealized combustion reaction corresponds to the net change in the foregoing series of all the steps. Therefore, the change in the internal energy of the idealized combustion reaction,  $n_R \Delta U_c^\circ(\text{sub})$ , is just the sum of the changes in the internal energy in these steps.

$$\begin{aligned} n_R \Delta U_c^\circ(\text{sub}) &= \Delta U_{\text{IBF}} + \Delta U^i(\text{Dy}) \Big|_{P^i(\text{F}_2)}^{P^i(\text{F}_2)} + \Delta U^f(\text{DyF}_3) \Big|_{P^f(\text{F}_2)}^1 \\ &\quad + \Delta U^i(\text{F}_2) \Big|_{P^i(\text{F}_2)}^{P^i(\text{F}_2)} + \Delta U^f(\text{F}_2) \Big|_{P^f(\text{F}_2)}^1 \end{aligned} \quad (4-12)$$

#### *Impurity correction*

The dysprosium metal sample used in this work contained several significant impurities, as shown earlier (in section 2-1). The impurities in a sample should be taken into consideration in the corrections to standard states mentioned above. When the amounts of impurities are small, it is conventional to consider that the impurities are identical with pure metal during most of the corrections to standard states. Denote the mass of the sample—not the pure metal—by  $m_R(\text{sample})$ . Then, the change of internal energy per unit mass of the sample reacted,  $\Delta U_c^\circ/M(\text{sample})$ , is

$$\Delta U_c^\circ/M(\text{sample}) = \frac{n_R \Delta U_c^\circ(\text{sample})}{m_R(\text{sample})} \quad (4-13)$$

where

$$n_R \Delta U_c^\circ(\text{sample}) = n_R \Delta U_c^\circ(\text{sub})$$

The quantity in eqn. (4-13) is corrected for impurities in the sample by using the following quantity as impurity correction per unit mass of the sample.

$$\text{Impurity correction} = \sum_i w_i \Delta U_c^\circ/M(i) \quad (4-14)$$

$$\Delta U_c^{\circ}/M(\text{Dy}) = \frac{\Delta U_c^{\circ}/M(\text{sample}) - \sum_i w_i \Delta U_c^{\circ}/M(i)}{1 - \sum_i w_i} \quad (4-15)$$

where  $w_i$  and  $\Delta U_c^{\circ}/M(i)$  are the mass fraction of, and the change in internal energy for the reaction of impurity  $i$ .

The impurity correction was calculated assuming that carbon, oxygen, nitrogen, and hydrogen formed  $\text{CF}_4$ ,  $\text{O}_2$ ,  $\text{N}_2$ , and  $\text{HF}$ , respectively, and that metallic impurities formed their most stable fluorides.

#### Thermodynamic quantities

Thermal data obtained by bomb calorimetry give the change in internal energy,  $\Delta U$ . In order to derive the change in enthalpy,  $\Delta H$ , the following thermodynamic relation is used.

$$\Delta H = \Delta U + \Delta(PV) \quad (4-16)$$

The value of  $\Delta(PV)$  for a solid phase is usually so small compared to  $\Delta H$  or  $\Delta U$  that it may be neglected, but for a gaseous phase at the ideal state,  $\Delta(PV)$  is given by  $\Delta(PV) = \Delta nRT$ , where  $\Delta n$  is the change in the number of moles of gas as the result of reaction. Therefore, the enthalpy of formation in this work is expressed as follows.

$$\Delta H_f = \Delta U_f + \Delta nRT \quad (4-17)$$

The Gibbs energy of formation,  $\Delta G_f$ , is derived from the relation

$$\Delta G_f = \Delta H_f - T\Delta S_f \quad (4-18)$$

where  $\Delta S_f$  is the entropy of formation. The value of entropy  $S^{\circ}$  for dysprosium trifluoride has not been reported, but it could be derived from the known value of  $S^{\circ}(\text{CeF}_3)^{6)}$  and Latimer's rule<sup>7)</sup>.

$$S^{\circ}(\text{DyF}_3) = S^{\circ}(\text{CeF}_3) + \frac{3}{2}R \ln \frac{M(\text{Dy})}{M(\text{Ce})} \quad (4-19)$$

#### 4-3 Energy equivalent of calorimetric system

The energy equivalent of the calorimetric system used was determined by the calibration combustions of reference benzoic acid for calorimetry in oxygen gas under the following conditions<sup>9)</sup>: (1), the combustion reaction is referred to 298.15 K; (2), the calibration sample is burned in a bomb of constant volume in pure oxygen gas at an initial pressure of 30 atm at 298.15 K; (3), the ratio of the weight in  $10^{-3}$  kg,  $m_s$ , of sample burned to the initial volume in  $\text{dm}^3$ ,  $V$  of the bomb is 3; and (4), the ratio of the weight in  $10^{-3}$  kg,  $m_w$ , of water placed in the bomb before combustion to the initial volume in  $\text{dm}^3$ ,  $V$  of the bomb is 3. The heat of combustion of the reference benzoic acid is 26434 J  $\text{kg}^{-1}$ , when burned under the standard conditions spe-

cified above. Since the conditions employed in this work, however, differed by small amounts from the standard conditions, the heat of combustion of the reference benzoic acid was corrected by multiplying the value determined above by the factor  $f$  as shown in

$$f = 1 + 10^{-6} \left[ 20(P - 30) + 42 \left( \frac{m_o}{V} - 3 \right) + 30 \left( \frac{m_w}{V} - 3 \right) - 45(\theta - 298.15) \right], \quad (4-20)$$

where  $\theta$  is the temperature to which the reaction is referred and  $P$  is the initial pressure in atm of the oxygen gas at the temperature  $\theta$ . Then, if the heat of combustion per  $10^{-3}$ kg of benzoic acid at the temperature  $\theta$  is represented as  $\Delta U_B(\theta)$ , the quantity,  $Q(\theta)$ , of heat which would have been evolved by the system if the reactions in the bomb had taken place at the temperature  $\theta$  is given by

$$Q(\theta) = m_s \{ -\Delta U_B(\theta) \} + \Delta U(\text{ign}) + \Delta U(\text{fuse}) + \Delta U(\text{HNO}_3) - \Delta U(\text{carbon}), \quad (4-21)$$

where the first term represents the heat of combustion by the calibration sample and  $\Delta U(\text{ign})$  is the energy supplied for ignition of the fuse,  $\Delta U(\text{fuse})$  the heat of combustion of the fuse,  $\Delta U(\text{HNO}_3)$  the energy of formation of nitric acid produced in the bomb, and  $\Delta U(\text{carbon})$  the heat which would have been produced by the combustion in the bomb of any soot found in the sample dish. Then, the energy equivalent of the initial system is given by

$$\epsilon_i = \frac{Q(\theta_i + \Delta\theta)}{\Delta\theta_{\text{corr}}},$$

and for the energy equivalent of the final system

$$\epsilon_f = \frac{Q(\theta_f)}{\Delta\theta_{\text{corr}}}.$$

The energy equivalent,  $\epsilon_s$ , of the standard calorimetric system is taken as that of the system with a specified mass of water in the calorimeter can and with the empty bomb, or the values,  $\epsilon_{i,s}$  and  $\epsilon_{f,s}$ , of the energy equivalent of the standard initial and final calorimetric systems are given as follows.

$$\epsilon_{i,s} = \epsilon_i - \epsilon_{c,i}$$

$$\epsilon_{f,s} = \epsilon_f - \epsilon_{c,f}$$

where  $\epsilon_{c,i}$  and  $\epsilon_{c,f}$  are obtained from the following equations.

$$\begin{aligned} \epsilon_{c,i} = & C_p(\text{Ni})m(\text{Ni}) + C_p(\text{benzoic acid})m_s + C_p(\text{water})m_w^i \\ & + C_p(\text{fuse})m_{f,u,s}^i + C_v(\text{O}_2)n^i(\text{O}_2) \end{aligned}$$

$$\begin{aligned} \epsilon_{c,f} = & C_p(\text{Ni})m(\text{Ni}) + C_p(\text{water})m_w^f + C_p(\text{fuse})m_{f,u,s}^f \\ & + C_v(\text{O}_2)n^f(\text{O}_2) + C_v(\text{CO}_2)n(\text{CO}_2) + C_p(\text{carbon})m_c \end{aligned}$$



Table 5. Numerical quantities used in the calculation for the calibration experiments at 298.15 K

$C_p / \text{J K}^{-1} \text{kg}^{-1}$	$\text{C}_6\text{H}_5\text{COOH}$ , 9.91 ; Ni, 445.
$C_v / \text{J K}^{-1} \text{mol}^{-1}$	$\text{O}_2$ , 21.2 ; $\text{CO}_2$ , 29.3.
$\rho / \text{kg m}^{-3}$	Ni, $8.85 \times 10^3$ .
$\Delta U_f^\circ / \text{kJ mol}^{-1}$	$\text{NiO}$ , -244 ; $\text{HNO}_3$ , -59.
$\Delta U_c^\circ / \text{kJ kg}^{-1}$	$\text{C}_6\text{H}_5\text{COOH}$ , 26434 ; C, -32800.
$M / \text{kg mol}^{-1}$	$\text{C}_6\text{H}_5\text{COOH}$ , 0.12212.

The numerical values used in the calculation for the calibration experiments are listed in Table 5.

#### 4-4 Preliminary observations

##### *Prefluorination of the sample*

It is well known that dysprosium metal is inert at room temperature. Preliminary observations, in fact, revealed no detectable change in the mass or appearance of the metal samples used in this work when they were exposed to ambient air for several hours. Therefore, all samples were treated in air. On the other hand, the dysprosium metal samples showed a slight increase in mass and a definite change in appearance when they were exposed to about 200 kPa of fluorine gas for about fifteen hours. In order to avoid the error resulting from a reaction of the samples with fluorine gas prior to ignition, all samples were prefluorinated with about 200 kPa of fluorine gas for fifteen hours before the combustion experiments. It was assumed that only elemental dysprosium in the sample reacted in the prefluorination and the reaction product was only dysprosium trifluoride. Moreover, the prefluorination of the samples was presumed to end after a 15 h exposure to fluorine gas, and any correction for the additional exposure of samples to fluorine gas prior to ignition was neglected. Moisture was not adsorbed by the prefluorinated sample on short time exposure to room atmosphere.

##### *Arrangement of sample*

A suitable arrangement of the sample support and electrodes was required in order to react the dysprosium metal sample with fluorine gas as completely as possible. When the reaction occurred, the metal sample melted readily and brought about a side-reaction with the nickel dish. Hence, the arrangement shown in Fig. 12 was adopted in this work, whereby the metal sample was supported on a bed of the powdered dysprosium trifluoride, which was distributed over a thick nickel dish placed on the bottom of the combustion bomb, and a sample chip was inserted into a coiled nickel fuse wire to make ignition certain. By this arrangement, the reacting metal

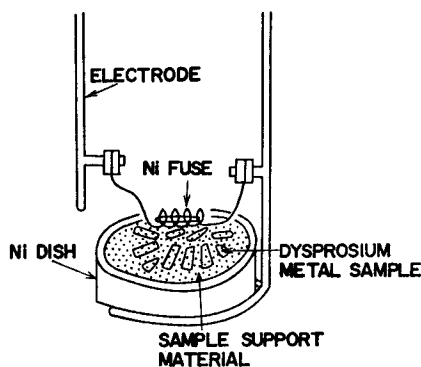


Fig. 12. Arrangement of sample support.

sample was scarcely in contact with the nickel dish, and 80 to 96% of the sample was usually burned.

#### 4-5 Experimental procedures

##### *Preliminary operations*

(i) The dysprosium metal sample, weighed to 0.001 mg with a micro-balance, was prefluorinated with fluorine gas for about fifteen hours and thereafter weighed again.

(ii) The sample was placed on a bed of sample support material distributed over a nickel dish, and a nickel fuse was connected to the electrodes in the bomb.

(iii) The dish with the weighed sample was put in place and the bomb was closed and evacuated fully.

(iv) The bomb was charged with fluorine gas, the pressure of which was measured.

(v) The bomb with ignition leads was put in place in the calorimeter can in the jacket. The calorimeter can was filled with a fixed amount of water, the temperature of which was adjusted to a suitable value beforehand, and was then closed. A thermistor was inserted into the calorimeter through the hole in the lid of the calorimeter and the jacket was closed.

##### *Measurements of calorimeter temperature*

(i) After enough time elapsed to establish a steady rate of temperature change, measurements of temperature in the initial period started and were repeated every 10 seconds.

(ii) At the end of the initial period, combustion was initiated by passing electric current through the fuse wire and the electrical energy required for ignition was

measured. Measurements of temperature in the main period were done every 10 seconds.

(iii) Measurements of temperature in the final period were carried out every 10 seconds after a steady rate of temperature change was again established.

*Determination of amount of unburnt metal residue*

(i) The bomb gas was discharged through the activated alumina trap heated at about 373 K.

(ii) The interior of the bomb was examined for completeness of combustion. The experiment was rejected when a remarkable part of the metal sample remained unburned, or if there was any attack on the nickel dish by combustion. The combustion product was carefully separated from the sample support material and was weighed.

(iii) The combustion product was crushed and was put into the reaction vessel of the H<sub>2</sub> evolution system. After evacuation of the reaction vessel, hydrochloric acid was added into the vessel. The contents in the vessel were stirred all night.

(iv) The amount of unburnt metal residue was determined by measuring the amount of H<sub>2</sub> evolved with a MacLeod gauge.

**5. Experimental results and discussion**

**5-1 Experimental results**

The crystal structure of the reaction product was determined by X-ray diffraction analysis. The reaction product was identified to be dysprosium trifluoride having an orthorhombic structure, on reference to Ref. 2.

The results of the combustion experiments are given in Table 6. The numbered

Table 6. Results of dysprosium combustion experiments.

Experiments no.	1	2	3	4	5	6
(1) $m(\text{sample introduced})/10^{-3}\text{kg}$	0.606558	0.607005	0.598036	0.607146	0.617845	0.611798
(2) $m(\text{Dy prefluorinated})/10^{-3}\text{kg}$	0.000306	0.000606	0.000583	0.000450	0.001843	0.000857
(3) $m(\text{sample unburned})/10^{-3}\text{kg}$	0.025157	0.095700	0.030969	0.026858	0.121471	0.036711
(4) $m(\text{sample burned})/10^{-3}\text{kg}$	0.581095	0.510699	0.566484	0.579838	0.494531	0.573230
(5) $\Delta\theta_c/\text{K}$	0.4338	0.3833	0.4221	0.4314	0.3712	0.4355
(6) $\epsilon(\text{calor})(-\Delta\theta_c)/\text{J}$	-5953.4	-5260.1	-5792.7	-5920.4	-5094.0	-5943.8
(7) $\Delta U(\text{contents})/\text{J}$	-23.8	-21.3	-23.8	-24.7	-31.0	-24.6
(8) $\Delta U(\text{ignition})/\text{J}$	11.4	8.8	8.8	6.8	14.6	9.5
(9) $\Delta U(\text{fuse})/\text{J}$	38.0	40.2	30.2	52.5	59.2	51.4
(10) $\Delta U_c^\circ/M(\text{sample})/\text{kJ kg}^{-1}$	-10201.1	-10245.6	-10198.9	-10150.8	-10214.1	-10305.6

(11)  $\langle \Delta U_c^\circ/M(\text{sample}) \rangle = -(10219.4 \pm 21.3) \text{kJ kg}^{-1}$  <sup>a</sup>

(12) Impurity correction =  $-(142.0 \pm 6.9) \text{kJ kg}^{-1}$  <sup>a</sup>

(13)  $\Delta U_c^\circ/M(\text{Dy}) = -(10301 \pm 45) \text{kJ kg}^{-1}$  <sup>b</sup>

<sup>a</sup> Standard deviation of the mean. <sup>b</sup> Uncertainty interval.

entries in Table 6 are: (1), the mass of the dysprosium sample introduced into the bomb; (2), the mass of the dysprosium metal reacted with fluorine gas in prefluorination; (3), the mass of sample unburned; (4), the mass of sample burned; (5), the corrected 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 burned; (11), the mean specific energy of combustion of the sample; (12), the net correction for the impurities in the sample; (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.

The energy equivalent of the calorimetric system,  $\epsilon(\text{calor})$ , was determined to be  $(13724 \pm 7) \text{ J K}^{-1}$  from a series of nine calibration experiments, where the precision index is the standard deviation of the mean. The contents of the bomb were dysprosium metal, 0.1046 kg of nickel, and varying masses of dysprosium trifluoride powder bed of 0.0193, 0.0184, 0.0218, 0.0273, 0.0202, and 0.0203 kg for the six combustion experiments listed in Table 6. The auxiliary quantities are shown in Table 7.

The net correction of the bomb gas to the standard state has been omitted because the values were less than 0.2 J for all combustion experiments.

The derived standard thermal quantities for the formation of  $\text{DyF}_3(\text{c})$  at 298.15 K according to the reaction (5-1) are as follows.

Table 7. Numerical values used in the calculation ( at 298.15 K)

$C_p/\text{J K}^{-1} \text{ mol}^{-1}$	Dy, 28.2 <sup>9)</sup> ; Ni, 26.1 <sup>9)</sup> ; $\text{DyF}_3$ , 95.0 <sup>a</sup> .
$C_v/\text{J K}^{-1} \text{ mol}^{-1}$	$\text{F}_2$ , 23.0 <sup>10)</sup> .
$\rho/\text{kg m}^{-3}$	Dy, $8.56 \times 10^3$ ; Ni, $8.85 \times 10^3$ .
$\Delta H_f^\circ/\text{kJ mol}^{-1}$	$\text{AlF}_3$ , -1510.4 <sup>13)</sup> ; $\text{CrF}_3$ , -1113 <sup>11)</sup> ; $\text{FeF}_3$ , -983 <sup>11)</sup> ; $\text{CuF}_2$ , -530.5 <sup>14)</sup> ; $\text{MnF}_2$ , -795 <sup>11)</sup> ; $\text{NiF}_2$ , -658 <sup>15)</sup> ; $\text{CdF}_2$ , -700.4 <sup>12)</sup> ; $\text{PbF}_2$ , -661 <sup>11)</sup> ; $\text{ZnF}_2$ , -764 <sup>16)</sup> ; $\text{CaF}_2$ , -1213 <sup>11)</sup> ; $\text{MgF}_2$ , -1124.2 <sup>13)</sup> ; $\text{EuF}_3$ , -1584 <sup>24)</sup> ; $\text{GdF}_3$ , -1699 <sup>19)</sup> ; $\text{TbF}_3$ , -1623.3 <sup>25)</sup> ; $\text{YF}_3$ , -1718 <sup>26)</sup> ; $\text{ErF}_3$ , -1669 <sup>17)</sup> ; $\text{TmF}_3$ , -1569 <sup>18)</sup> ; $\text{YbF}_3$ , -1570 <sup>19)</sup> ; $\text{CF}_4$ , -933.20 <sup>20)</sup> ; $\text{HF}$ , -271 <sup>10)</sup> ; $\text{DyOF}$ , -1155 <sup>b</sup> ; $\text{DyC}_2$ , -46 <sup>27)</sup> ; $\text{Dy}_2\text{O}_3$ , -1863.2 <sup>28)</sup> ; $\text{DyN}$ , -330 <sup>21)</sup> ; $\text{DyH}_2$ , -209 <sup>b</sup> .
$S^\circ/\text{J K}^{-1} \text{ mol}^{-1}$	Dy, 74.89 <sup>9)</sup> ; $\text{F}_2$ , 203 <sup>23)</sup> ; $\text{CeF}_3$ , 115.2 <sup>9)</sup> $\text{DyF}_3$ , 117.1 <sup>b</sup> .
$M/\text{kg mol}^{-1}$	Dy, 0.16251.

<sup>a</sup> Estimated by the application of Kopp's law. <sup>b</sup> Estimated.

$$\Delta U_f^\circ(\text{DyF}_3, \text{c})/\text{kJ mol}^{-1} = -(1674 \pm 8)$$

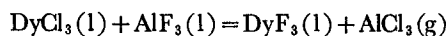
$$\Delta H_f^\circ(\text{DyF}_3, \text{c})/\text{kJ mol}^{-1} = -(1678 \pm 8)$$

$$\Delta G_f^\circ(\text{DyF}_3, \text{c})/\text{kJ mol}^{-1} = -(1600 \pm 9)$$

The uncertainties assigned to these  $\Delta U_f^\circ$  and  $\Delta H_f^\circ$  values were arbitrarily taken to be equal to twice the combined standard error derived from the scatter of  $\Delta U_f^\circ/M(\text{sample})$  values, the calibration results, and the impurity corrections. The uncertainty in  $\Delta G_f^\circ$  includes the estimated additional uncertainty in  $\Delta S_f^\circ$  value.

## 5-2 Discussion

In Table 8 the present value for  $\Delta H_f^\circ(\text{DyF}_3, \text{c})$  was compared with the previous reported values. The value by Brewer *et al.*<sup>11)</sup> was an estimate from the enthalpy of solution of dysprosium trifluoride  $\Delta H_f^\circ(\text{Dy}^{3+}, \text{aq})$  and  $\Delta H_f^\circ(\text{F}^-, \text{aq})$ . This estimate may be revised to  $-1691 \text{ kJ mol}^{-1}$  by using  $-696.5 \text{ kJ mol}^{-1}$  for  $\Delta H_f^\circ(\text{Dy}^{3+}, \text{aq})$  according to Morss<sup>22)</sup> and  $-335.35 \text{ kJ mol}^{-1}$ <sup>13)</sup> for  $\Delta H_f^\circ(\text{F}^-, \text{aq})$  instead of  $-695 \text{ kJ mol}^{-1}$  for  $\Delta H_f^\circ(\text{Dy}^{3+}, \text{aq})$  and  $-327 \text{ kJ mol}^{-1}$  for  $\Delta H_f^\circ(\text{F}^-, \text{aq})$  used in Brewer's estimation. Zmbov and Margrave's<sup>29)</sup> value was derived from the study of the stability of dysprosium subfluoride by the mass spectrometric method at high temperature. From equilibrium studies of the reaction



Polyachenok<sup>18)</sup> derived the value for  $\Delta H_f^\circ(\text{DyF}_3, \text{c})$  by taking  $-975 \text{ kJ mol}^{-1}$  as  $\Delta H_f^\circ(\text{DyCl}_3, \text{c})$ . The value for  $\Delta H_f^\circ(\text{DyF}_3, \text{c})$  can be revised to  $-1614 \text{ kJ mol}^{-1}$  if  $\Delta H_f^\circ(\text{DyCl}_3, \text{c}) = -990.1 \text{ kJ mol}^{-1}$  by Morss<sup>22)</sup> is used. Storozhenko *et al.*<sup>25)</sup> measured the enthalpy of reaction of dysprosium metal with a mixture of hydrofluoric and hydrochloric acids and derived the value for  $\Delta H_f^\circ(\text{DyF}_3, \text{c})$ . The present work is the only fluorine bomb calorimetry and its value is close to the revised value of Brewer *et al.*, but differs from the other reported values.

Table 8. Published values for the standard enthalpy of formation of dysprosium trifluoride,  $\text{DyF}_3$  at 298.15 K.

Investigator	Method	$\Delta H_f^\circ/\text{kJ mol}^{-1}$
Brewer <i>et al.</i> <sup>11)</sup>	Solution calorimetry of trifluoride	$-(1665 \pm 29)$ , $-1691^*$
Zmbov & Margrave <sup>29)</sup>	Stability of subfluoride	$-(1703 \pm 63)$
Polyachenok <sup>18)</sup>	Reaction equilibrium of chloride with aluminum trifluoride	$-(1598 \pm 29)$ , $-1614^*$
Storozhenko <i>et al.</i> <sup>25)</sup>	Solution calorimetry of metal	$-(1640.2 \pm 4.5)$
This work	Fluorine bomb calorimetry	$-(1678 \pm 8)$

\* Revised, see text.

In the calculation for impurity correction, the non-metallic impurities were presumed to be present in the form of specific chemical compounds of dysprosium. From the precipitation experiment of the sample, oxygen and fluorine may be thought to form dysprosium oxide and oxyfluoride. Hence, the value for  $\Delta H_f^\circ(\text{DyF}_3, c)$  will become more positive than the present value by only 2 kJ mol<sup>-1</sup>, even if the non-metallic impurities, except oxygen and fluorine, are assumed to dissolve without significant thermal effects.

### References

- 1) E. Greenberg, J. L. Settle, H. M. Feder and W. N. Hubbard; *J. Phys. Chem.*, **65**, 1168 (1961)
- 2) Joint Committee on Powder Diffraction Standards, File no. (21-314) for Dy<sub>2</sub>O<sub>3</sub>; (19-437) for DyOF; (5-400) for DyF<sub>3</sub>
- 3) G. Pilcher and L. E. Sutton; *Phil. Trans. Roy. Soc., London*, A248, 23 (1955)
- 4) R. L. Nuttal, M. A. Frisch and W. N. Hubbard; *Rev. Sci. Instr.*, **31**, 461 (1960)
- 5) D. White, J. H. Hu and H. L. Johnston; *J. Chem. Phys.*, **21**, 1149 (1953)
- 6) E. F., Jr., Westrum and A. F. Beale; *J. Phys. Chem.*, **65**, 353 (1961)
- 7) K. S. Pitzer and L. Brewer; "Thermodynamics", McGraw-Hill, New York (1962)
- 8) R. S. Jessup; *J. Res. Nat. Bur. Stand.*, **29**, 247 (1942)
- 9) R. Hultgren, P. D. Desai, D. T. Hawkins, M. Gleiser, K. K. Kelley and D. D. Wagman; "Selected Values of the Thermodynamic Properties of the Elements", American Society for Metals Ohio, (1973)
- 10) D. D. Wagman, W. H. Evans, V. B. Parker, I. Halow, S. M. Bailey and R. H. Schumm; *Nat. Bur. Stand. (U. S.) Technical Note* 270-3 (1968)
- 11) L. Brewer, L. A. Bromley, P. W. Gilles and N. L. Lofgren; In "The Chemistry and Metallurgy of Miscellaneous Materials": Thermodynamics, L. L. Quill; editor, *Nat. Nucl. Energy Ser. Div. IV 19B*, McGraw-Hill, New York (1950)
- 12) E. Rudzitis, H. M. Feder and W. N. Hubbard; *J. Phys. Chem.*, **67**, 2388 (1963)
- 13) ICSU-CODATA Task Group, Report on key values for thermodynamics, *J. Chem. Thermodyn.*, **8**, 603 (1976)
- 14) Y.-C. Kim, K. Shingai and J. Oishi; Unpublished work.
- 15) E. Rudzitis, E. H. Van Deventer and W. N. Hubbard; *J. Chem. Eng. Data*, **12**, 133 (1967)
- 16) E. Rudzitis, R. Terry, H. M. Feder and W. N. Hubbard; *J. Phys. Chem.*, **68**, 617 (1964)
- 17) Y.-C. Kim, H. Yano, M. Misumi and J. Oishi; *J. Chem. Thermodyn.*, **11**, 429 (1979)
- 18) O. G. Polyachenok; *Zh. Neorg. Khim.*, **12**, 851 (1967)
- 19) Y.-C. Kim, J. Oishi and S.-H. Kang; *J. Chem. Thermodyn.*, **10**, 975 (1978)
- 20) E. Greenberg and W. N. Hubbard; *J. Phys. Chem.*, **72**, 222 (1968)
- 21) J. Kordis and K. A. Gingerich; *J. Nucl. Mater.*, **66**, 197 (1977)
- 22) L. R. Morss; *Chem. Rev.*, **76**, 827 (1976)
- 23) K. K. Kelley and E. G. King; *Bur. Mines. Bull.*, 584 (1960)
- 24) T. P. Storozhenko, E. I. Khanaev and Yu. A. Afanas'ev; *Russ. J. Phys. Chem.*, **49**, 1241 (1975)
- 25) T. P. Storozhenko, E. I. Khanaev and Yu. A. Afanas'ev; *Russ. J. Phys. Chem.*, **50**, 643 (1976)
- 26) E. Rudzitis, H. M. Feder and W. N. Hubbard; *J. Phys. Chem.*, **69**, 2305 (1965)
- 27) G. Balducci, A. Capalbi, G. De Maria and M. Guido; *J. Chem. Phys.*, **51**, 2871 (1969)
- 28) E. J. Huber, G. C. Fitzgibbon and C. E., Jr., Holley; *J. Chem. Thermodyn.*, **3**, 643 (1971)
- 29) K. F. Zmbov and J. L. Margrave; *J. Phys. Chem.*, **70**, 3379 (1966)

### Note added in proof (April 4, 1980)

Fluorine bomb calorimetric determination of the enthalpy of formation of DyF<sub>3</sub> has recently been reported by Hubbard *et al.* (*J. Chem. Thermodyn.*, **12**, 125 (1980)). Their result for  $\Delta H_f^\circ(\text{DyF}_3, c, 298.15\text{K})$ ,  $-(1692.0 \pm 1.9)$  KJ mol<sup>-1</sup> differs a little from our result and is in excellent agreement with the revised value of the estimate of Brewer *et al.* The discrepancy will be caused by the large amounts of the non-metallic impurities contained in our metal samples.