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Enthalpy of Formation of Gadolinium Sesquichloride, Gd_2Cl_3*

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The discovery of the remarkable Gd_2Cl_3 [1, 2] has been followed by syntheses of several other sesquihalides, e.g. see refs. 3 and 4. Such compounds are now recognized to contain clusters with chains of edge-sharing metal octahedra [5, 6]. Synthetic research has led to other early transition-metal halides with extended metal–metal bonds and to clusters with interstitial H, C, or N atoms [7–9]. These studies have led to correlations of their properties and to theoretical treatments of their electronic structure [10].

This paper reports the direct determination of the enthalpy of formation of the first-discovered lanthanide condensed cluster halide.

Experimental

A sample of Gd_2Cl_3 was made available from syntheses that had been carried out by slow reactions of $GdCl_3$ on Gd metal in sealed Ta ampoules [3]. It was handled in nitrogen-filled dry boxes. DTA scans showed no indication of the $GdCl_3$–Gd_2Cl_3 eutectic. Microchemical analyses were carried out on three samples by acid–base titration to determine Gd oxidation number [11] and by potentiometric titration for Cl^-; calc. for Gd 74.7 mass%, found 74.0 (as $Gd^{1.5+}$); calc. for Cl 25.3 mass%, found 24.9. Modified Guinier X-ray powder photographs confirmed only the presence of Gd_2Cl_3.

Samples of each preparation were weighed into glass ampoules and reacted with dilute HCl(aq) in multiple-batch isoperibol solution calorimeters [12]. The enthalpies of reaction are shown in Table I. The acid concentration was chosen to match that used for enthalpy of solution of Gd metal [13] in order to close the thermochemical cycle.

TABLE I. Enthalpy of Solution of Gd_2Cl_3 in 140 cm^3 of 0.25 mol dm^{-3} HCl(aq) at 298.15 K

Mass (mg)	q^a (J)	ΔH (kJ mol^{-1})
20.39	40.05	−826.0
16.10	31.99	−835.0
12.11	23.61	−820.5

[a] Corrected for evaporation of water into N_2 in ampoule and into H_2 evolved.

Results and Conclusions

The thermochemical cycle leading to $\Delta_f H°(Gd_2Cl_3, s, 298\ K)$ is shown in Table II. Using the enthalpy of formation of $GdCl_3$, −1007.6 ± 2.0 kJ mol^{-1} [14, 15], we calculate the important enthalpy of the symproportionation reaction

$$Gd(s) + GdCl_3(s) = Gd_2Cl_3(s) \qquad (1)$$

to be -30 ± 15 kJ mol^{-1}, a small but significant exothermic effect.

TABLE II. Thermochemical Cycle for $\Delta_f H°(Gd_2Cl_3,s)$ at 298.15 K [(soln) = 0.25 mol dm^{-3} HCl(aq)]

$Gd_2Cl_3(s) + 3HCl(soln)$	$= 2GdCl_3(soln) + \frac{3}{2}H_2(g)$	$\Delta H_1 = -827 \pm 15$ kJ[a]
$2Gd(s) + 6HCl(soln)$	$= 2GdCl_3(soln) + 3H_2(g)$	$\Delta H_2 = 2(-683.6 \pm 2.4$ kJ)[b]
$\frac{3}{2}H_2(g) + \frac{3}{2}Cl_2(g)$	$= 3HCl(soln)$	$\Delta H_3 = 3(-166.0 \pm 0.1$ kJ)[c]
$\Delta_f H°(Gd_2Cl_3, s, 298.15\ K)$	$= -\Delta H_1 + \Delta H_2 + \Delta H_3$	
	$= -1038 \pm 15$ kJ mol^{-1}	

[a] This work. [b] Ref. 13. [c] Ref. 14.

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The structure of Gd_2Cl_3 has been discussed in terms of Gd–Gd and Gd–Cl bonding [2, 3, 10]. Magnetic [16] and UPS [17] measurements have characterized the Gd as a $4f^7$ ion and the Gd–Cl bond distances are similar to those in $GdCl_3$. It is clear from the small $\Delta H(1)$ that the sum of the bonding interactions in Gd_2Cl_3 are very similar to those of the Gd–Gd bonds in the metal and the Gd–Cl bonds in the trichloride.

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