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Thermodynamics of lanthanide elements IV. Molar enthalpies of formation of $Y^{3+}(aq)$, $YCI_{3}(cr)$, $YBr_{3}(cr)$, and $YI_{3}(cr)$

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Enthalpies of solution of high-purity yttrium metal and of yttrium trichloride, tribromide, and triiodide in hydrochloric acid of various molalities lead to the following standard molar enthalpies of formation $\Delta_f H_m^{\circ}/(kJ \cdot mol^{-1})$ at T = 298.15 K and for $p^{\circ} = 101.325$ kPa: $Y^{3+}(aq)$, $-(736.5 \pm 2.6)$; YCl₃(cr), $-(1018.4 \pm 2.6)$; YBr₃(cr), $-(858.1 \pm 2.0)$; YI₃(cr), $-(640.9 \pm 2.7)$. These results are discussed and compared with previous experimental or assessed values.

1. Introduction

This paper continues our investigation of the thermodynamic properties of the lanthanide and related elements, and of their simple compounds,⁽¹⁻³⁾ which was initiated with the purpose of reducing uncertainties associated with earlier experimental determinations and of obtaining missing values. As pointed out by Morss⁽⁴⁾ more than ten years ago, the standard molar enthalpy of formation of $Y^{3+}(aq)$ could at best be assessed with an uncertainty of 2 per cent, namely $-(715\pm15) \text{ kJ} \cdot \text{mol}^{-1}$, a situation worse than that prevailing then for all (except promethium) lanthanide trivalent ions. Taking into account more recent determinations on $\text{Er}^{3+}(aq)$,⁽²⁾ Tb³⁺(aq), Ho³⁺(aq), and Yb³⁺(aq),⁽³⁾ the enthalpies of formation of all (except promethium) lanthanide trivalent ions can now be considered as being established to ± 0.4 per cent in the worst case. The outstanding status of the molar enthalpy of formation of the lanthanide-related ion Y³⁺(aq) and of the corresponding salt YCl₃(cr) was the first reason for this study.

On the other hand, we wanted also to establish on more solid ground the value for the molar enthalpy of formation of $YBr_3(cr)$ for which only estimates exist, and

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WANG XIANG-YUN ET AL.

that of $YI_3(cr)$ for which the only experimental evidence is the early result of Bommer and Hohmann.⁽⁵⁾ Indeed, these authors also reported experimental results on the enthalpies of formation of several lanthanide chlorides and iodides but their results were shown to be scattered by up to $40 \text{ kJ} \cdot \text{mol}^{-1}$ when compared with recently assessed values.⁽⁶⁾

2. Experimental

High-purity yttrium metal obtained from the Ames Laboratory of U.S.D.O.E. (Iowa State University) was used. The results of the analysis of the sample furnished by the supplier are listed in table 1 together with indications of the techniques used. A batch of Y₂O₃ from Aldrich Chemical Company (Milwaukee, Wis., U.S.A.), with purity listed as 99.999 mass per cent was used for the synthesis of the trichloride and of the tribromide. A batch from the same supplier with a purity >99.99 mass per cent was employed to obtain the iodide samples. The halide samples were obtained following well described techniques,(7-15) in triplicate for the chloride and the iodide, and in duplicate for the bromide, each time using a few grams of oxide. For the chloride preparation, the oxide (2 g) was dissolved in 10 cm^3 of $6 \text{ mol} \cdot \text{dm}^{-3}$ HCl. To this solution an appropriate quantity $\{n(NH_4Cl)/n(Y_2O_3) \approx 15\}$ of solid NH₄Cl was added. After the addition of 10 cm³ of concentrated HCl, the solution was carefully heated to near dryness. After cooling, the (yttrium trichloride + ammonium chloride) solid was ground and transferred to a quartz tube with a side arm. After evacuation to about 10 Pa, the tube was heated to 373 K for 15 to 18 h, then the temperature was raised to 673 K to sublime the NH₄Cl under a dynamic vacuum. After driving away with a flame trace amounts of NH₄Cl from the side arm, a pressure of about 0.1 Pa was reached. The temperature was then brought to

Method		10 ⁶ w								
Spark-source	Li	< 0.05	Mn	< 0.006	Мо	< 0.5	w	83	Pr	8.2
mass	Be	< 0.0004	Fe	19	Ru	<1	Re	< 0.6	Nd	< 0.7
spectrometry	В	< 0.01	Co	< 0.07	Rh	< 0.2	Os	<1.3	Sm	0.5
	Na	< 0.01	Ni	7.3	Pd	< 0.3	Ir	<0.4	Eu	< 0.2
	Mg	< 0.2	Cu	7.1	Ag	< 0.05	Pt	< 0.4	Gd	27
	Aľ	1.8	Zn	< 0.05	Cď	< 0.06	Au	< 0.1	Tb	0.70
	Si	6.3	Ga	< 0.02	In	< 0.06	Hg	0.68	Dy	< 0.7
	Р	< 0.07	Ge	< 0.06	Sn	< 0.09	TĨ	< 0.09	Ho	< 0.4
	S	< 0.1	As	< 0.02	Sb	< 0.01	Pb	0.70	Er	< 0.9
	Cl	0.8	Se	< 0.09	Te	< 0.06	Bi	< 0.07	Tm	< 0.4
	K	< 0.3	Br	< 0.04	I	< 0.03	Th	<1	Yb	< 0.6
	Ca	< 0.09	Rb	< 0.05	Cs	< 0.006	U	< 0.5	Lu	<0.6
	Ti	< 0.2	Sr	< 0.5	Ba	< 0.1	Sc	< 0.5		
	v	0.23	Zr	< 0.7	Hf	<2	La	14		
	Cr	0.44	Nb	<3	Та	30	Cr	5		
Vacuum fusion	Н	23	Ν	9	0	19				
Combustion	С	43								
Absorptiometry	F	<3	Fe	17	О	19				

TABLE 1. Mass fractions w of impurities in the yttrium metal (I.S.U. batch 012584C)

1223 K to sublime the YCl₃. Dry and oxygen-free argon (99.996 mass per cent, grade N-46 from Air Liquide, Liège, Belgium) was then admitted to the quartz tube to obtain a pressure of about 10 Pa. The YCl₃ sublimate was melted by means of a flame and collected in the side arm of the tube. The side arm was then sealed. Any subsequent handling of the product (and of the other halides) was made in an argon-filled glovebox with a H₂O(g) mass fraction below 1×10^{-5} as measured with an ALNOR (Casella, London) dew-point meter. YBr₃(cr) was prepared using the same procedure as for YCl₂, with, of course, hydrobromic acid and ammonium bromide as reagents. Yttrium triiodide was obtained by following an analogous acid and method. using concentrated hydroiodic ammonium iodide $\{n(NH_4I)/n(Y_2O_3) \approx 8\}$. The crude product obtained after sublimation of NH₄I and known to contain YOI was purified by sublimation at 1223 K under a pressure lower than 1×10^{-2} Pa. The melting temperature of YI₃ being relatively high, (1270 ± 10) K,⁽¹⁶⁾ the sample was used as sublimed.

The halides were characterized by X-ray powder diffraction (generator: Philips PW1010; Ni-filtered Cu radiation "fine focus" tube; 57.3 mm diameter Philips Debye-Scherrer type camera using Straumanis film mounting). The films showed no extraneous lines, and the patterns were in perfect agreement with those calculated for the known structures *i.e.* monoclinic AlCl₃ type, space group $C2/mC_{2h}^2$ for YCl₃; rhombohedral FeCl₃ type, space group $R3-C_{3i}^2$, for YBr₃ and YI₃. The lattice obtained were $a_0 = (0.697 \pm 0.005)$ nm, $b_0 = (1.189 \pm 0.003)$ nm, dimensions $c_0 = (0.644 \pm 0.002) \text{ nm}, \ \beta = (1.951 \pm 0.009) \text{ for } \text{YCl}_3; \ a_0 = (0.7098 \pm 0.0003) \text{ nm},$ for YBr₃; $a_0 = (0.7491 \pm 0.0006)$ nm, $c_0 = (2.087)$ $c_0 = (1.9169 \pm 0.0008) \text{ nm}$ ± 0.002) nm for YI₃, using the lattice-parameter refinement programme L.C.R. 2.⁽¹⁷⁾ The dimensions were identical within their uncertainty limits (1σ) with the values found in the literature⁽¹⁸⁻²⁰⁾ for the trichloride and triiodide. For the tribromide, Brown et al.⁽¹⁹⁾ reported $a_0 = (0.7072 \pm 0.0003)$ nm, $c_0 = (1.915 \pm 0.001)$ nm. In each YCl₃ and YBr₃ preparation, the halide was determined by potentiometric titration with AgNO₃. For YCl₃ {calculated: 54.47 mass per cent of Cl; found: 54.71 (preparation I), 54.51 (preparation II), 54.54 (preparation III) mass per cent of Cl}; for YBr₃ {calculated: 72.95 mass per cent of Br; found: 72.92 (preparation I), 72.49 (preparation II) mass per cent of Br}. As smaller amounts of pure YI₃ were obtained, we decided to determine yttrium in the calorimetric solutions by complexometry using ethylenediamine-tetraacetic acid with xylenol orange as indicator and zinc solution as standard. Thus, for YI₃ {calculated: 18.93 mass per cent of Y; found: 18.96 (preparation I), 18.84 (preparation II), 18.91 (preparation III) mass per cent of Y}.

Merck titrated 1.000 mol \cdot dm⁻³ HCl(aq) was used. The 1 × 10⁻³ mol \cdot dm⁻³ HCl solutions were obtained by dilution. The calorimeter was an LKB (Bromma, Sweden) air-jacketed isoperibol instrument (Model 8700-1) with a glass vessel (100 cm³) equipped with a strip-chart recorder. Details of calibration runs, which were repeated at frequent intervals, have been published.⁽²⁾

As indicated above, samples were handled and weighed in a glovebox filled with dry argon. A Cahn (Paramount, California) model GRAM electrobalance was used. Apparent masses in argon were corrected to masses. The weighings were made directly in the LKB calorimetric ampoules (1 cm³) which were subsequently sealed with polypropylene plugs protected by melted beeswax.

3. Results and discussion

Table 2 shows the results for the dissolution of yttrium metal in 1.000 mol \cdot dm⁻³ HCl according to the equation:

$$Y(cr) + (aHCl + bH_2O) = \{YCl_3 + (a-3)HCl + bH_2O\} + (3/2)H_2(g),$$
(1)

with b/a = 54.41 and a = 200 to 300 and of the three yttrium halides (X = Cl, Br, I) in 1.000 mol \cdot dm⁻³ HCl, and 1 \times 10⁻³ mol \cdot dm⁻³ HCl, according to the equation

$$YX_3(cr) + (aHCl + bH_2O) = (YX_3 + aHCl + bH_2O),$$
(2)

TABLE 2. Molar enthalpies of solution of yttrium metal, yttrium trichloride, yttrium tribromide, and yttrium triiodide at T = 298.15 K and $p^{\circ} = 101.325$ kPa

Sample	m(solution)	ΔH ^a	$-\Delta_{\rm sof}H_{\rm m}$	Sampla	m(solution)	ΔH^{a}	$-\Delta_{ m sol}H_{ m m}$	
	mg	1	$kJ \cdot mol^{-1}$	Sample	mg	J	$kJ \cdot mol^{-1}$	
Y	31.94	261.18	729.0 ^{<i>b</i>}	Y۴	31.82	261.94	733.9 ^{<i>b</i>}	
	38.36	314.00	729.8 ^{<i>b</i>}		41.34	340.43	734.1 ^b	
	38.30	315.28	733.9 <i>°</i>		42.00	343.96	730.1 ^b	
	28.06	231.42	735.3 ^b		38.58	317.08	732.7 ^b	
	29.08	239.90	735.4 ^b		46.82	386.28	735.5 ^b	
					Mean: $(733.0 \pm 1.8)^{d}$			
YCl ₃ -I °	65.66	70.244	208.9	YCl ₃ -I ^e	61.10	67.969	217.2	
YCl3-II ^c	81.95	86.033	205.0	YCl ₃ -III ^e	56.38	62.688	217.1	
YCl ₃ -III ^c	37.48	38.982	208.3	-	64.52	71.967	217.8	
5	67.62	71.965	207.8		53.52	59.075	215.5	
	45.91	48.992	208.4		56.90	63.753	218.8	
		Mear	n: $(207.7 \pm 1.9)^d$		Mean: (217.3±1.5			
YBr ₃ -I ^c	64.54	45.702	232.7	YBr ₃ -I ^e	64.72	47.194	239.6	
-	74.14	52.682	233.5	YBr ₃ -II ^e	64.30	47.623	243.4	
YBr ₁ -II ^c	47.45	33.585	232.6	-	84.44	61.967	241.2	
5	44.72	31.816	233.8		76.26	56.316	242.7	
	61.68	43.620	232.4		62.60	46.244	242.8	
		Mear	n: $(233.0 \pm 0.8)^{d}$		66.58	48.924	241.5	
			· - /			Mean: $(241.9 \pm 1.7)^{d}$		
YI ₃ -I°	43.04	23.570	257.2	YI ₃ -I ^e	59.90	33.660	263.9	
5	69.85	38.817	261.0		71.24	40.571	267.5	
	52.14	28.922	260.5		55.17	31.427	267.5	
YI ₃ -II°	15.54	8.602	259.9		68.37	38.548	264.8	
YIJ-III '	38.30	21.176	259.7	YI3-III "	37.54	21.292	266.4	
~	39.68	21.639	256.1	2		Mean	$(266.0 \pm 2.0)^d$	
	44.62	24.307	255.8					
		Mear	n: $(258.6 \pm 2.0)^{d}$					

" Corrected for ampoule breaking and evaporation of solvent into gas in ampoule

^b Corrected for evaporation of the solvent by the evolved hydrogen. Assuming saturation, the correction amounts to ¹ Corrected for evaporation of the solvent by the solvent in the solvent by the solvent in the solvent of th

with b/a = 54.41 and 55500 for 1.000 and 1×10^{-3} mol·dm⁻³ HCl, respectively, with *a* ranging from approximately 200 to 500, 400 to 700, and 600 to 3000 for the chloride, bromide, and iodide, respectively, in 1.000 mol·dm⁻³ HCl and from approximately 0.3 to 0.4, 0.4 to 0.5, and 0.6 to 1.2 for the same three salts, respectively, in 1×10^{-3} mol·dm⁻³ HCl.

The standard molar enthalpies of formation of the trihalides, relating to the reaction:

$$Y(cr) + (3/2)X_2(g, l, or cr) = YX_3(cr),$$
 (3)

with $X_2 = Cl_2(g)$, $Br_2(l)$, and $I_2(cr)$, respectively, can be calculated by use of equations (1) and (2) above and of

$$(3/2)X_{2}(g, l, or cr) + (3/2)H_{2}(g) + \{YCl_{3} + (a-3)HCl + bH_{2}O\} = (YX_{3} + aHCl + bH_{2}O), \quad (4)$$

which upon combination yield

$$\Delta_{\rm f} H^{\circ}_{\rm m}({\rm YX}_3, {\rm cr}) = \Delta H_3 = \Delta H_1 - \Delta H_2 + \Delta H_4. \tag{5}$$

Here, $\Delta H_4/3$ represents the partial molar enthalpy of formation of hydrochloric, hydrobromic, or hydroiodic acids from the elements in their standard states at 298.15 K and for $p^{\circ} = 101.325 \text{ kPa}$ in 1.000 mol $\cdot \text{dm}^{-3}$ HCl. The values: $\Delta_{\rm f} H_{\rm m}({\rm HCl}, {\rm HCl} + 54.41{\rm H}_2{\rm O}) = -(164.36 \pm 0.04) {\rm kJ} \cdot {\rm mol}^{-1}, \Delta_{\rm f} H_{\rm m}({\rm HBr}, {\rm HCl} +$ $54.41H_2O$ = -(119.37±0.04) kJ·mol⁻¹, and $\Delta_f H_m(HCl + 54.41H_2O)$ = $-(55.50\pm0.04)$ kJ·mol⁻¹ were used. These values were obtained from the standard molar enthalpies of formation of the infinitely dilute acids: $(21, 22) \Delta_{\rm f} H_{\rm m}^{\circ}({\rm HCl, aq}) =$ $-(167.080 \pm 0.088) \text{ kJ} \cdot \text{mol}^{-1}, \Delta_{f} H^{\circ}_{m}(\text{HBr, aq}) = -(121.50 \pm 0.15) \text{ kJ} \cdot \text{mol}^{-1}, \text{ and}$ $\Delta_f H_m^{\circ}(HI, aq) = -(56.90 \pm 0.84) \text{ kJ} \cdot \text{mol}^{-1}$, and the relative apparent molar enthalpies of the HCl, HBr, and HI solutions, respectively.⁽²³⁾ The assumption was made that apparent molar enthalpies of formation of HBr(aq) and HI(aq) are the same in HCl(aq) as in HBr(aq) and HI(aq), respectively, of the same molality, neglecting the influence of $Y^{3+}(aq)$. In combining the terms of equation (5), variations in the low yttrium concentrations ($<5 \times 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$) were also neglected. From the experimental enthalpies of solution (table 2) in 1.000 mol \cdot dm⁻³ HCl, we obtain through equation (5): $\Delta_f H_m^{\circ}(YCl_3, cr) =$ $-(1018.4\pm2.6)$ kJ·mol⁻¹; $\Delta_{\rm f}H^{\circ}_{\rm m}({\rm YBr}_{\rm 3},{\rm cr}) = -(858.1\pm2.0)$ kJ·mol⁻¹, and $\Delta_{\rm f} H_{\rm m}^{\circ}({\rm YI}_3,{\rm cr}) = -(640.9 \pm 2.7) \,{\rm kJ} \cdot {\rm mol}^{-1}.$

To obtain $\Delta_{\rm f} H^{\circ}_{\rm m}({\rm Y}^{3+},{\rm aq})$ we have made use of our measurements of the enthalpies of solution of the three halides (table 2) in 1×10^{-3} mol \cdot dm⁻³ HCl and corrected these results to infinite dilution using the molar enthalpies of dilution given by Spedding et $al^{(24)}$ for HoCl₃. In the absence of such enthalpies of dilution for YCl₃, HoCl₃ was selected as these two cations have very similar ionic radii {for a coordination number of 6, $r_i(Y^{3+}) = 0.0900$ nm and $r_i(Ho^{3+}) = 0.0901$ nm}.⁽²⁵⁾ For the trichloride dissolution experiments, the individual corrections ranged from -1.33 to -1.47 kJ·mol⁻¹. For the tribromide and the tribidide dissolution experiments. we calculated corrections ranging between -1.13and $-1.29 \text{ kJ} \cdot \text{mol}^{-1}$, and $-0.96 \text{ to } -1.04 \text{ kJ} \cdot \text{mol}^{-1}$, respectively, assuming the same functional dependence of the dilution enthalpies as for the trichloride. The

uncertainty of all these corrections is estimated at $\pm 0.01 \text{ kJ} \cdot \text{mol}^{-1}$. The Debye-Hückel limiting law gave essentially the same values within $\pm 0.01 \text{ kJ} \cdot \text{mol}^{-1}$. Thus, the resulting molar enthalpies of solution of YCl₃, YBr₃, and YI₃ in water at infinite dilution, equation (2), with a = 0 and $b = \infty$, are $-(218.7 \pm 1.5)$, $-(243.1 \pm 1.6)$, and $-(267.0 \pm 2.0) \text{ kJ} \cdot \text{mol}^{-1}$, respectively. With the above reported values for $\Delta_f H^{\circ}_{\text{m}}(\text{YCl}_3, \text{cr})$, $\Delta_f H^{\circ}_{\text{m}}(\text{YBr}_3, \text{cr})$, and $\Delta_f H^{\circ}_{\text{m}}(\text{YI}_3, \text{cr})$, and the standard molar enthalpies of formation of the infinitely dilute HCl, HBr, and HI also given above, equation (5) now yields for infinite dilution, the values $-(735.9 \pm 3.0)$, $-(736.7 \pm 2.6)$, and $-(737.2 \pm 4.2) \text{ kJ} \cdot \text{mol}^{-1}$, respectively, for the standard molar enthalpy of formation of Y³⁺(aq). Given the agreement between these results, we shall accept the weighted average as the preferred value: thus, $\Delta_f H^{\circ}_{\text{m}}(\text{Y}^{3+}, \text{aq}) = -(736.5 \pm 2.6) \text{ kJ} \cdot \text{mol}^{-1}$.

The values for the molar enthalpies of formation of YCl₃(cr) found in the recent literature, $-(996 \pm 10)$,⁽⁴⁾ $-(1000.0 \pm 2.7)$,⁽²⁶⁾ -1000.0,⁽⁶⁾ and -996 kJ·mol⁻¹,⁽²⁷⁾ are based on two thermodynamic cycles involving, on the one hand, the enthalpy of solution of yttrium metal and of yttrium trichloride in 1.43 mol·dm⁻³ HCl by Spedding and Flynn⁽²⁸⁾ and on the other hand, the enthalpy of combustion of yttrium metal to the sesquioxide by Huber *et al.*,⁽²⁹⁾ and the enthalpies of solution of the sesquioxide and the trichloride in 0.5 mol·dm⁻³ HCl by Montgomery and Huber.⁽³⁰⁾ The metal used by Spedding and Flynn⁽²⁸⁾ was probably the best available material 25 years ago. It was reported to be free of other rare-earth and all common elements by spectrographic analysis. No analyses for light elements (H, C, O, N) were performed, however.

The metal used by Huber *et al.*⁽²⁹⁾ was fully analysed: mass fractions 310×10^{-6} of hydrogen, 420×10^{-6} of carbon, 6900×10^{-6} of oxygen, 88×10^{-6} of nitrogen, 500×10^{-6} of calcium, and 50×10^{-6} of magnesium were reported. The metal thus contained about mass fraction 8500×10^{-6} of impurities and, assuming the formation of the most likely hydrides, carbides, oxides, and so forth, the sample was calculated to contain about 0.95 mass fraction of metallic yttrium. Although corrections for impurities were applied in the evaluation of the enthalpy of combustion of yttrium metal, there is some doubt as to the exact chemical form in which these impurities were present in the sample. On the other hand, the time required to dissolve the sesquioxide in 0.5 mol \cdot dm⁻³ HCl in the experiments of Montgomery and Huber was 1 h in the best cases, which was rather long for an accurate calorimetric operation.

The molar enthalpy of formation of yttrium trichloride reported by Montgomery and Huber,⁽³⁰⁾ based on yttrium oxide, was $-(1000.6\pm2.1)$ kJ·mol⁻¹, while the value obtained by Spedding and Flynn⁽²⁸⁾ and based on the dissolution of the metal, was -973.6 kJ·mol⁻¹. Montgomery and Huber attributed the less negative value of Spedding and Flynn to partial hydration or oxychloride impurities in the yttrium chloride samples. In any case, the scatter found in the recently assessed values for $\Delta_{\rm f} H^{\circ}_{\rm m}({\rm YCl}_3, {\rm cr})$ depends essentially on the weight given to each set of experimental determinations. We believe that the value reported in the present investigation: $\Delta_{\rm f} H^{\circ}_{\rm m}({\rm YCl}_3, {\rm cr}) = -(1018.4\pm2.6)$ kJ·mol⁻¹, with high-purity metal, is more accurate. As discussed above, the molar enthalpy of solution of $YCl_3(cr)$ in water at infinite dilution, equation (2) with a = 0 and $b = \infty$, combined with $\Delta_f H^{\circ}_m(YCl_3, cr)$, is the basis for $\Delta_f H^{\circ}_m(Y^{3+}, aq)$. Extrapolation to m = 0 of acid and infinite dilution of the enthalpies of solution of YCl_3 in 0.50 mol·dm⁻³ HCl by Montgomery and Huber⁽³⁰⁾ and in $1 \times 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$ HCl by Spedding and Flynn⁽³¹⁾ leads to -224.6 and $-203.7 \text{ kJ} \cdot \text{mol}^{-1}$, respectively, while a more recent estimate of $-194.6 \text{ kJ} \cdot \text{mol}^{-1}$ is given by Krestov *et al.*;⁽³²⁾ our value reported above was $-(218.7 \pm 1.5) \text{ kJ} \cdot \text{mol}^{-1}$, in limited agreement with the results of Montgomery and Huber only. These rather divergent values are of course responsible for the large scatter in $\Delta_f H^{\circ}_m(Y^{3+}, aq)$ adopted in the recent literature, namely (-715 ± 15) ,⁽⁴⁾ $-(723.4\pm2.9)$,⁽²⁶⁾ -723.4,⁽⁶⁾ and $-715 \text{ kJ} \cdot \text{mol}^{-1}$.⁽²⁷⁾ It is hoped that our result: $\Delta_f H^{\circ}_m(Y^{3+}, aq) = -(736.5\pm2.5) \text{ kJ} \cdot \text{mol}^{-1}$, based on the three yttrium halides, will clarify the situation.

The molar enthalpies of solution of $YBr_3(cr)$ and $YI_3(cr)$ in water at infinite reported above from our extrapolation: $-(243.1\pm1.6)$ dilution and (-267.0+2.0) kJ·mol⁻¹, are in limited agreement with the results obtained by Kijowski:⁽³³⁾ -(253.3+3.2) $-(262.1\pm3.6)$ kJ·mol⁻¹, Burgess and and respectively, from dissolution of the two salts in water. Our value for YI₃ is in better agreement with the result (uncorrected to infinite dilution) of Bommer and Hohmann⁽⁵⁾ who reported $-267.8 \text{ kJ} \cdot \text{mol}^{-1}$ for the dissolution of YI₃(cr) in water at molalities approximately 8 times greater than those used in our study.

In a previous publication,⁽³⁾ we have shown that for rhombohedral lanthanide tribromides, a linear dependence was obtained when the relation $\{\Delta_f H^{\circ}_m(MBr_3, cr) - \Delta_f H^{\circ}_m(M^{3+}, aq)\}$ was plotted as a function of the M^{3+} ionic radii. The yttrium bromide does not fit this relation well since from our results we calculate a value of $-(121.6 \pm 3.1) \text{ kJ} \cdot \text{mol}^{-1}$, while a value of $-(134.9 \pm 3.6) \text{ kJ} \cdot \text{mol}^{-1}$ was reported⁽³⁾ for the isomorphous lanthanide tribromide which displays virtually the same lattice dimensions.

Our value for the molar enthalpy of formation of $YI_3(cr)$: $-(640.9 \pm 2.6) kJ \cdot mol^{-1}$, is distinctly more negative than the $-621.8 kJ \cdot mol^{-1}$ assessed⁽⁶⁾ on the basis of the early results of Bommer and Hohmann⁽⁵⁾ (after recalculation using CODATA auxiliary values). The largest part of the difference can be traced to the value adopted for the molar enthalpy of formation of $Y^{3+}(aq)$. Use of our value for $\Delta_f H^{\circ}_m(Y^{3+}, aq)$ in both cases brings the two results for $\Delta_f H^{\circ}_m(YI_3, cr)$ within $6 kJ \cdot mol^{-1}$.

Finally, we make a remark about $\Delta_{\rm f} H^{\circ}_{\rm m}({\rm Y_2O_3}, {\rm cubic})$. For the lanthanides, it has been shown⁽³⁴⁾ that the enthalpies of solution in water at infinite dilution of isomorphous compounds varied smoothly as a function of the molar volume. Using this relation, and taking for ${\rm Y_2O_3}$ a molar volume⁽³⁵⁾ of 44.86 cm³ · mol⁻¹, and also possible differences between ${\rm Y_2O_3}$ and lanthanide sesquioxides of similar molar volumes (analogous to those observed for the tribromides), we suggest a value of $-(400 \pm 10) \, \rm kJ \cdot mol^{-1}$ for the molar enthalpy of solution of ${\rm Y_2O_3}({\rm cr, cubic})$ in water at infinite dilution. Using the molar enthalpy of formation of ${\rm H_2O(l)}$:⁽²¹⁾ $-(285.830 \pm 0.042) \, \rm kJ \cdot mol^{-1}$, and our value for the molar enthalpy of formation of ${\rm Y}^{3+}({\rm aq})$, we obtain the molar enthalpy of formation of ${\rm Y_2O_3}({\rm cr, cubic})$ from the equation:

$$Y_2O_3(cr, cubic) + 6H^+(aq) = 2Y^{3+}(aq) + 3H_2O(l),$$
 (6)

and, thus,

$$\Delta_{\mathbf{f}} H^{\circ}_{\mathbf{m}}(\mathbf{Y}_{2}\mathbf{O}_{3}, \text{cubic}) = 2\Delta_{\mathbf{f}} H^{\circ}_{\mathbf{m}}(\mathbf{Y}^{3+}, \mathbf{aq}) + 3\Delta_{\mathbf{f}} H^{\circ}_{\mathbf{m}}(\mathbf{H}_{2}\mathbf{O}, \mathbf{l}) - \Delta H_{6}.$$
 (7)

We then obtain $\Delta_{\rm f} H^{\circ}_{\rm m}({\rm Y}_2{\rm O}_3,{\rm cubic}) = -(1930\pm11)\,{\rm kJ}\cdot{\rm mol}^{-1}$, while the combustion results of Huber *et al.*⁽²⁹⁾ lead to $-(1905.3\pm2.3)\,{\rm kJ}\cdot{\rm mol}^{-1}$. Additional measurements on Y₂O₃ should, of course, be made to clarify this disagreement.

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1202