

Thermochemistry and lattice energetics of hexahalogenozirconates

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Abstract

A critical review is presented of the enthalpies of the thermal dissociation (ΔH_d) and formation (ΔH_f) available in the literature, as well as the crystal lattice energies (E_c) for inorganic and organic hexahalogenozirconates $M_2^{I}(or M^{II})ZrX_6$, where M^I and M^{II} denote monovalent and divalent cations respectively, and X denotes a halogen. The enthalpies of formation of the salts were determined from known ΔH_d values and the enthalpies of formation of the decomposition products of hexahalogenozirconates, taken from the literature. The combination of the values of the enthalpies of formation of hexahalogenozirconates thus evaluated, and those of the literature, with the literature values of the enthalpy of formation of cations and the theoretically determined enthalpies of formation of ZrX_6^{2-} (or the electrostatic lattice energies of the salts) has afforded lattice energies of the salts (or enthalpies of formation of gaseous ZrX_6^{2-}). Values of ΔH_f were also assessed, taking theoretically determined electrostatic lattice energies of the salts and enthalpies of formation of ZrX_6^{2-} , and literature or theoretically determined values of the enthalpy of formation of gaseous cations. Finally, the lattice energetics was examined following the Kapustinskii–Yatsimirskii approach which enabled an independent set of crystal lattice energies and thermochemical radii for ZrX_6^{2-} and complex cations to be obtained. The various thermochemical quantities correlate with each other reasonably well, thus increasing their reliability.

INTRODUCTION

Hexahalogenozirconates are one of the simplest derivatives of zirconium, an element of great interest owing to its scientific and applicative importance [1–4]. Of particular interest are octahedral ZrX_6^{2-} ions which, due to their high symmetry, have long been of interest [1–8]. Compounds containing these species have often been taken as models in studies of the structure and behaviour of complex salt-like derivatives. Despite the extensive interest in hexahalogenozirconates, only scattered, fragmentary information regarding their thermochemistry is available. The aim of this work is, therefore, to summarize the available information on the thermochemistry of hexa-

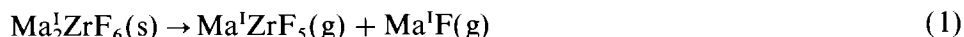
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halogenozirconates, to subject the data to critical review and, finally, to evaluate new characteristics on the basis of current knowledge of the problem.

THERMOCHEMISTRY OF HEXAHALOGENOZIRCONATES

Thermodynamics of the thermal decomposition

At elevated temperatures, hexahalogenozirconates undergo decomposition into smaller fragments, accompanied by volatilization of all or some of the products. Table 1 summarizes the available information on the dissociation, without considering the mechanism of the process. It is, however, known from the literature that the decomposition of some hexahalogenozirconates in the absence of oxygen proceeds in two stages [9–17], e.g. in the case of alkali metal (Ma) hexafluorozirconates



and



Inorganic hexachloro- and hexaiodozirconates, however, decompose in one step, which is reflected schematically in Table 1. The thermal decomposition of hexachlorozirconates of nitrogen aromatic bases, carried out in contact with the atmosphere, results in the release of gaseous bases and HCl, and in the instantaneous oxidation of the remaining ZrCl_4 to ZrO_2 [7].

All the enthalpies of decomposition listed in Table 1 are derived from direct or indirect vapour pressure measurements. In their determination, it was assumed that equilibrium was achieved under experimental conditions, which justified the application of the van't Hoff equation and enabled evaluation of the $\Delta H_{\text{d},T}^\ominus$ values. The data obtained initially were relevant to the temperature range in which the pressure was measured (in Table 1, only mean temperatures are listed (T)). To adjust them to standard conditions ($\Delta H_{\text{d},298}^\ominus$), we modified the $\Delta H_{\text{d},T}^\ominus$ values by adding the heats of solid-state phase transitions and melting, in the case of organic hexahalogenozirconates, and for all the systems examined, by subtracting the heat capacity term (estimated by considering changes in the possibilities of the storage of energy in translational and rotational degrees of freedom of only the gaseous reactants upon transfer from T to 298 K and assuming their perfect behaviour) [7].

It can be noted, reviewing the data in Table 1, that values from refs. 18, 19 and 25 are much lower than those from other sources. Moreover, the values of ΔH_{d} for some of the compounds are very scattered, which is seen in particular in the case of Na_2ZrCl_6 . It is thus difficult to evaluate the

reliability of these characteristics. We shall try to do this after using them to determine other thermochemical characteristics.

Enthalpy of formation

Values of this important characteristic were evaluated in two ways.

Firstly, following the thermochemical cycle [7], the enthalpy of formation of monovalent alkali metal (Ma^I) hexahalogenozirconates is expressed by the relationship

$$\Delta H_{f,298}^{\circ}[\text{Ma}_2^I\text{ZrX}_6(\text{s})] = 2H_{f,298}^{\circ}[\text{Ma}^I\text{X}(\text{g or s})] + \Delta H_{f,298}^{\circ}[\text{ZrX}_4(\text{g})] - \Delta H_{d,298}^{\circ} \quad (3)$$

In the case of salts containing nitrogen bases (B), the enthalpies of formation are obtained from the equation

$$\Delta H_{f,298}^{\circ}[(\text{BH})_2\text{ZrX}_6(\text{s})] = 2 \Delta H_{f,298}^{\circ}[\text{HX}(\text{g})] + 2 \Delta H_{f,298}^{\circ}[\text{B}(\text{g})] + \Delta H_{f,298}^{\circ}[\text{ZrX}_4(\text{g or s})] - \Delta H_{d,298}^{\circ} \quad (4)$$

where $\Delta H_{f,298}^{\circ}$ denotes the standard enthalpy of formation of the species indicated in square brackets, and g or s indicates gaseous or solid (crystalline) state of the system, respectively. Determination of the enthalpies of formation by eqns. (3) or (4) requires knowledge of the $\Delta H_{d,298}^{\circ}$ values. This method, therefore, was applied only in the case of compounds for which the thermal decomposition process was examined quantitatively, i.e. those listed in Table 1. Other necessary data were as follows: the enthalpies of formation of crystalline alkali metal halides were taken from refs. 2, 28, 29, and of gaseous alkali metal fluorides from either ref. 29 (CsF) or obtained by adding heats of sublimation (in the case of RbF, KF and NaF from ref. 2, and LiF from ref. 9) to the former values; the enthalpies of formation of zirconium tetrahalides were also taken from the literature and modified, if necessary, by adding heats of sublimation (all in kJ mol^{-1}): $\Delta H_{f,298}^{\circ}[\text{ZrF}_4(\text{s})] = -1912$ [2, 29] and $\Delta H_{f,298}^{\circ}[\text{ZrF}_4(\text{g})] = -1674$ (adding heat of sublimation from ref. 1); $\Delta H_{f,298}^{\circ}[\text{ZrCl}_4(\text{g})] = -870$ [6]; $\Delta H_{f,298}^{\circ}[\text{ZrI}_4(\text{s})] = -482$ [29]; and $\Delta H_{f,298}^{\circ}[\text{ZrI}_4(\text{g})] = -380$ (adding heat of sublimation from ref. 27). Finally, the enthalpies of formation of gaseous nitrogen organic bases were taken from ref. 7, and for HF, HCl and NH_3 were taken (in kJ mol^{-1}) as -271.2 , -92.3 and -46.1 [28, 29], respectively. The determined and literature values of the enthalpies of formation of crystalline hexahalogenozirconates are compiled in Table 2 under column A.

Secondly, the enthalpies of formation of solid hexahalogenozirconates are related to their lattice energies (E_c) through the equation [7].

$$\Delta H_{f,298}^{\circ}[\text{M}_2^I(\text{or M}^{II})\text{ZrX}_6(\text{s})] = 2(\text{or } 1)\Delta H_{f,298}^{\circ}[\text{M}^{I+}(\text{or M}^{II2+})(\text{g})] + \Delta H_{f,298}^{\circ}[\text{ZrX}_6^{2-}(\text{g})] - E_c^{\circ}[\text{M}_2^I(\text{or M}^{II})\text{ZrX}_6(\text{s})] - 3(\text{or } 2)RT \quad (5)$$

TABLE 4
Enthalpies of the thermal dissociation (ΔH_d°) of hexahalogenozirconates

Compound ^a	→ Reaction ^b	$\Delta H_{d,T}^\circ /$ (kJ mol ⁻¹)	T/K	Ref.	$\Delta H_{d,298}^\circ /$ (kJ mol ⁻¹)
Li ₂ ZrF ₆ (s)	→ 2LiF(g) + ZrF ₄ (g)	465	1115	9, 10	391
Na ₂ ZrF ₆ (s)	→ 2NaF(g) + ZrF ₄ (g)	469	1144	10, 11	392
K ₂ ZrF ₆ (s)	→ 2KF(g) + ZrF ₄ (g)	465	1140	10, 12, 13	388
Rb ₂ ZrF ₆ (s)	→ 2RbF(s) + ZrF ₄ (g)	451	1088	10, 14	379
Cs ₂ ZrF ₆ (s)	→ 2CsF(g) + ZrF ₄ (g)	428	1000	10, 15	364
(NH ₄) ₂ ZrF ₆ (s)	→ 2NH ₃ (g) + 2HF(g) + ZrF ₄ (s)	361	657	16	323
		364	632	17	322
Li ₂ ZrCl ₆ (s)	→ 2LiCl(s) + ZrCl ₄ (g)	33	701	18	20
Na ₂ ZrCl ₆ (s)	→ 2NaCl(s) + ZrCl ₄ (g)	32	747	18, 19	17
		108	804	1, 20–22	91
		113	959	23	91
		152	816	24	135
K ₂ ZrCl ₆ (s)	→ 2KCl(s) + ZrCl ₄ (g)	19	781	18, 25	3
		217	993	1, 20–22	194

$\text{Cs}_2\text{ZrCl}_6(\text{s})$	$\rightarrow 2\text{CsCl}(\text{s}) + \text{ZrCl}_4(\text{g})$	12	744	18	-3
$(\text{NH}_4)_2\text{ZrCl}_6(\text{s})$	$\rightarrow 2\text{NH}_3(\text{g}) + 2\text{HCl}(\text{g}) + \text{ZrCl}_4(\text{g})$	217	1023	1, 20–22	193
$(\text{PyH})_2\text{ZrCl}_6(\text{s})$	$\rightarrow 2\text{Py}(\text{g}) + 2\text{HCl}(\text{g}) + \text{ZrCl}_4(\text{g})$	533	700	26	496
$(2\text{-MePyH})_2\text{ZrCl}_6(\text{s})$	$\rightarrow 2(2\text{-MePy})(\text{g}) + 2\text{HCl}(\text{g}) + \text{ZrCl}_4(\text{g})$		479	7	354
$(3\text{-MePyH})_2\text{ZrCl}_6(\text{s})$	$\rightarrow 2(3\text{-MePy})(\text{g}) + 2\text{HCl}(\text{g}) + \text{ZrCl}_4(\text{g})$		446	7	346
$(4\text{-MePyH})_2\text{ZrCl}_6(\text{s})$	$\rightarrow 2(4\text{-MePy})(\text{g}) + 2\text{HCl}(\text{g}) + \text{ZrCl}_4(\text{g})$		519	7	300
$(2,4\text{-diMePyH})_2\text{ZrCl}_6(\text{s})$	$\rightarrow 2(2,4\text{-diMePy})(\text{g}) + 2\text{HCl}(\text{g}) + \text{ZrCl}_4(\text{g})$		458	7	366
$(2,6\text{-diMePyH})_2\text{ZrCl}_6(\text{s})$	$\rightarrow 2(2,6\text{-diMePy})(\text{g}) + 2\text{HCl}(\text{g}) + \text{ZrCl}_4(\text{g})$		471	7	407
$(3,4\text{-diMePyH})_2\text{ZrCl}_6(\text{s})$	$\rightarrow 2(3,4\text{-diMePy})(\text{g}) + 2\text{HCl}(\text{g}) + \text{ZrCl}_4(\text{g})$		512	7	331
$(3,5\text{-diMePyH})_2\text{ZrCl}_6(\text{s})$	$\rightarrow 2(3,5\text{-diMePy})(\text{g}) + 2\text{HCl}(\text{g}) + \text{ZrCl}_4(\text{g})$		504	7	343
$(2,4,6\text{-triMePyH})_2\text{ZrCl}_6(\text{s})$	$\rightarrow 2(2,4,6\text{-triMePy})(\text{g}) + 2\text{HCl}(\text{g}) + \text{ZrCl}_4(\text{g})$		458	7	349
$(\text{QuH})_2\text{ZrCl}_6(\text{s})$	$\rightarrow 2\text{Qu}(\text{g}) + 2\text{HCl}(\text{g}) + \text{ZrCl}_4(\text{g})$		487	7	378
$(2\text{-MeQuH})_2\text{ZrCl}_6(\text{s})$	$\rightarrow 2(2\text{-MeQu})(\text{g}) + 2\text{HCl}(\text{g}) + \text{ZrCl}_4(\text{g})$		470	7	375
$(\text{iso-QuH})_2\text{ZrCl}_6(\text{s})$	$\rightarrow 2(\text{iso-Qu})(\text{g}) + 2\text{HCl}(\text{g}) + \text{ZrCl}_4(\text{g})$		517	7	385
$(\text{AcH})_2\text{ZrCl}_6(\text{s})$	$\rightarrow 2\text{AcH}(\text{g}) + 2\text{HCl}(\text{g}) + \text{ZrCl}_4(\text{g})$		474	7	394
$\text{Li}_2\text{ZrI}_6(\text{s})$	$\rightarrow 2\text{Li}(\text{s}) + \text{ZrI}_4(\text{g})$	136	518	7	367
$\text{Na}_2\text{ZrI}_6(\text{s})$	$\rightarrow 2\text{Na}(\text{s}) + \text{ZrI}_4(\text{g})$	99	686	27	123
$\text{K}_2\text{ZrI}_6(\text{s})$	$\rightarrow 2\text{K}(\text{s}) + \text{ZrI}_4(\text{g})$	126	670	27	87
$\text{Rb}_2\text{ZrI}_6(\text{s})$	$\rightarrow 2\text{Rb}(\text{s}) + \text{ZrI}_4(\text{g})$	149	806	27	109
$\text{Cs}_2\text{ZrI}_6(\text{s})$	$\rightarrow 2\text{Cs}(\text{s}) + \text{ZrI}_4(\text{g})$	150	857	27	130
			907	27	129

^a Py, pyridine; Qu, quinoline; iso-Qu, isoquinoline; Acr, acridine; and Me, methyl (CH_3). ^b g or s denote gaseous or solid state, respectively.

TABLE 2
Thermodynamic data for the hexahalogenozirconates and their cations^a

Compound	Cation		Hexahalogenozirconate							
	r_C	r_C^b/nm	$\Delta H_{f,298}^\circ /$ (kJ mol ⁻¹)	$\Delta H_{f,298}^\circ /$ (kJ mol ⁻¹)	A ^d	B ^e	C ^f	D ^g	E ^h	F ⁱ
Li ₂ ZrF ₆		0.068	680	-2784	-3589	2439	1634			1925
Na ₂ ZrF ₆		0.097	609	-2795	-3587	2105	1503			1797
K ₂ ZrF ₆		0.133	514	-2851	-3711	2229	1369			1660
Rb ₂ ZrF ₆		0.149	490	-2838	-3566	2036	1308			1605
Cs ₂ ZrF ₆		0.167	458	-2756	-3491	1897	1162			1549
(H ₃ O) ₂ ZrF ₆			599 [30]		-3359	2046				
(NH ₄) ₂ ZrF ₆		0.137 [31, 32]	630	-2870	-3271	1959 ⁺	1620			1646
				-2869	-3255	2005	1619			
				-2910 [17]	-3189	1939 ⁺	1660			
(CN ₃ H ₆) ₂ ZrF ₆			633*	-2919 [2, 16]	-2968	1724	1669			
					-2767	1523 ⁺				
CuZrF ₆		0.091	3055		-2597	3144				2429
					-2803	3350				
					-3096	3643				
MgZrF ₆		0.075	2349		-3311	3152				2523
CaZrF ₆		0.106	1926		-3391	2809				2347
BaZrF ₆		0.142	1661		-3494	2647				2172
ZnZrF ₆		0.077	2783		-2848	3123				2511
PbZrF ₆		0.127	2374		-2886	2752				2241
CrZrF ₆		0.084	2654		-2876	3022				2469

MnZrF ₆	0.086	2520	–2986	2998	1519	2458
FeZrF ₆	0.080	2753	–2803	3048	1379	2493
			–2842	3087	1453	
			–2879	3124	1481	
CoZrF ₆	0.078	2842	–2767	3101	1497	
NiZrF ₆	0.074	2931	–2729	3152	1504	
			–2795	3218	1225	1391
(N ₂ H ₆)ZrF ₆	2093*		–3320	2905	1416	
(C ₂ H ₁₀ N ₂)ZrF ₆	1662*		–3154	2739 ⁺	1339 [6, 29]	
(CH ₈ N ₄)ZrF ₆ · 0.5H ₂ O	1910*		–3364	2518	1371 [29]	
			–3041	2195 ⁺	1341 [29]	
			–2889	2169	1348 [6]	
			–2735	2015*	1195 [34]	
Li ₂ ZrCl ₆	0.068	680	–1708		1308 [29]	1353
Na ₂ ZrCl ₆	0.097	609	–1710		1339 [29]	1313
			–1784		1348 [6]	
			–1812 [34]		1195 [34]	
			–1828		1308 [29]	
			–1835 [35]		1339 [29]	
			–1746		1341 [29]	
			–1932 [29, 35]		1348 [6]	
			–1937		1195 [34]	
K ₂ ZrCl ₆	0.133	514	–1842	1321	1110	
			–1833	1264	1282	
			–1743		1306	
			–1915 [6, 36]		1359	
			–1939		1386	
			–1992 [29, 35]		1360	
			–2019 [34]		1327	
			–1997 [34]		1404	
			–1616			
			–1693 [26]			
Rb ₂ ZrCl ₆	0.149	490	–1897	1264	1174 [34]	1302
			–1743		1302	1381
			–1915 [6, 36]			
			–1939			
			–1992 [29, 35]			
			–2019 [34]			
			–1997 [34]			
			–1616			
			–1693 [26]			
Cs ₂ ZrCl ₆	0.167	458	–1897	1264	1110	
			–1743		1282	
			–1915 [6, 36]		1306	
			–1939		1359	
			–1992 [29, 35]		1386	
			–2019 [34]		1360	
			–1997 [34]		1327	
			–1616		1404	
			–1693 [26]			
Fr ₂ ZrCl ₆	0.172 [31]	456 [34]				
(NH ₄) ₂ ZrCl ₆	0.137 [31, 32]	630	–1606	1317	1360	1302
			–1609	1320 ⁺	1327	1381

TABLE 2 (continued)

Compound	Cation	Hexahalogenozirconate						
		$\Delta H_{f,298}^{\circ}/$ (kJ mol ⁻¹)	$\Delta H_{f,298}^{\circ}/$ (kJ mol ⁻¹)	B ^e	C ^f	D ^g	E ^h	F ⁱ
(NMe ₄) ₂ ZrCl ₆	0.207 [31, 32]	542 [32]		-1643	1178			1232
(NEt ₄) ₂ ZrCl ₆	0.215 [32]	415 [32]		-1639	1174 ⁺			1217
(PyH) ₂ ZrCl ₆	0.255 [7]	749 [7]		-1832	1113 ⁺			1148
(2-MePyH) ₂ ZrCl ₆	0.274 [7]	698 [7]	-1128 [7]			1077	1093 [7]	
(3-MePyH) ₂ ZrCl ₆	0.250 [7]	709 [7]	-1203 [7]			1050	1066 [7]	
(4-MePyH) ₂ ZrCl ₆	0.261 [7]	701 [7]	-1142 [7]			1011	1027 [7]	
(2,4-diMePyH) ₂ ZrCl ₆		649 [7]	-1213 [7]			1066	1082 [7]	
(2,6-diMePyH) ₂ ZrCl ₆		639 [7]	-1334 [7]			1083	1099 [7]	
(3,4-diMePyH) ₂ ZrCl ₆	0.277 [7]	655 [7]	-1269 [7]			998	1014 [7]	
(3,5-diMePyH) ₂ ZrCl ₆	0.258 [7]	663 [7]	-1258 [7]			1019	1035 [7]	
(2,4,6-triMePyH) ₂ ZrCl ₆	0.272 [7]	615 [7]	-1258 [7]			1035	1051 [7]	
(QuH) ₂ ZrCl ₆	0.247 [7]	807 [7]	-1344 [7]			1025	1041 [7]	
(2-MeQuH) ₂ ZrCl ₆	0.263 [7]	744 [7]	-997 [7]			1062	1078 [7]	
(iso-QuH) ₂ ZrCl ₆	0.239 [7]	793 [7]	-1088 [7]			1027	1043 [7]	
(AcrH) ₂ ZrCl ₆	0.274 [7]	861 [7]	-1046 [7]			1083	1099 [7]	
K ₂ ZrBr ₆	0.133	514	-837 [7]			1010	1026 [7]	
CS ₂ ZrBr ₆	0.167	458	-1603 [37]	-1423	1281	1461		1358
Fr ₂ ZrBr ₆	0.172 [31]	456 [34]	-1665 [37]	-1525	1271	1411		1283
Li ₂ ZrI ₆	0.068	680	-1664 [34]	-1949	1473	1406	1090 [34]	1273
Na ₂ ZrI ₆	0.097	609	-1044			1568		1482
			-1132 [27]			1656		1406
			-1043			1425		
			-1030 [27]			1412		
			-1145			1337		
			-1137 [27]			1329		
K ₂ ZrI ₆	0.133	514						1322

Rb ₂ ZrI ₆	0.149	490	-1178 -1161 [27]	1322 1305	1288
Cs ₂ ZrI ₆	0.167	458	-1193 -1178 [27]	1273 1258	1251
Fr ₂ ZrI ₆	0.172 [31]	456 [34]	-1119 [34]	1195	1059 [34] 1242

^a For the names of the compounds, see ref. 8 (Table 1). ^b Values (mean from all cited) were taken from ref. 28; except those for which references are cited (Values from ref. 32 were modified assuming $r_{\text{Cl}^-} = 0.181$ nm [28], whereas those from ref. 7 were extended by those evaluated by the Kapustinskii–Yatsimirskii method (eqn. (7)), using crystal lattice energies of relevant hexachlorozirconates from the thermochemical cycle [7]). ^c Values not marked * were taken from ref. 29; others from the reference cited. Values marked * were determined employing the AM1 method [30] incorporated in the SPARTAN 2.1 program package [33]. ^d Values not marked were evaluated on the basis of eqns. (3) or (4) and the thermal dissociation data summarized in Table 1; others were taken from the references cited. ^e Values determined employing eqn. (5) and using the electrostatic lattice energies given in this table (under column C), enthalpies of formation of gaseous ZrX_6^{2-} ions from ref. 8 (Table 3) and enthalpies of formation of the gaseous cations from this table. ^f Electrostatic lattice energies from ref. 8 (mean values from the two columns given under “MEP fit” in Table VI of ref. 8 values marked + correspond to the location of a +1 charge on the nitrogen (oxygen) atom(s) of the complex cation). ^g Values determined employing eqn. (6) and using enthalpies of formation of gaseous ZrX_6^{2-} from ref. 8 (Table 3) and of cations from this table, as well as enthalpies of formation of the salts listed under column A (this table). ^h Literature values. ⁱ Values evaluated on the basis of the Kapustinskii–Yatsimirskii formula (eqn. (7)), using values of r_{C} from this table and for r_{a} from Table 3 (evaluated in this work).

TABLE 3

Enthalpies of formation and “thermochemical” radii of ZrX_6^{2-}

Species	$\Delta H_{f,298}^\circ / (\text{kJ mol}^{-1})$			r_A / nm	
	This work	Ref. 8	Others	This work	Others
ZrF_6^{2-}		–2503		0.281	0.273 [31]
$ZrCl_6^{2-}$	–1612	–1542	–1503 [6] –1526 [6, 29] –1549 [6] –1621 [6]	0.373	0.358 [31] 0.376 [7]
$ZrBr_6^{2-}$	–1323	–1163		0.387	
ZrI_6^{2-}	–938	–829		0.403	

where M^I and M^{II} denote mono- and divalent cations, respectively. The evaluation of ΔH_f by this method requires knowledge of E_c . We assumed that values of the latter quantity are well represented by the electrostatic lattice energies which are given in Table 2 under column C (from ref. 8). The combination of these with the enthalpies of formation of the gaseous cations, listed in Table 2, and the ZrX_6^{2-} ions from ref. 8 (Table 3) yields the standard enthalpies of formation of crystalline hexahalogenozirconates which are shown in Table 2 under column B. One can consider the characteristics thus derived as being of solely theoretical origin.

The enthalpies of formation determined by the two above-described, completely independent methods, correspond to each other reasonably well in the case of hexachloro-, hexabromo- and hexaiodozirconates. The exceptions are those values resulting from the use of ΔH_d values taken from refs. 18, 19 and 25 (listed under column A). It may be thought, therefore, that these latter characteristics do not correspond to the decomposition process shown in Table 1. Relatively large discrepancies in the values of ΔH_f of hexafluorozirconates of monovalent cations can also be noted. These may be the consequence of uncertainties in the evaluation of ΔH_d in refs. 9–15, which affect the values given under column A, as well as of difficulties in the determination of electrostatic lattice energies owing to the atypical crystal structure of the salts [8] and the charge distribution in the ZrF_6^{2-} ion, which influence the values shown under column B.

Crystal lattice energy

Four different sets of lattice energies are shown in Table 2. Listed under column C are the electrostatic lattice energies from ref. 8. Values given

under column D were determined according to the equation [7]

$$E_c^\circ [M_2ZrX_6(s)] = 2 \Delta H_{f,298}^\circ [M^{1+}(g)] + \Delta H_{f,298}^\circ [ZrX_6^{2-}(g)] - \Delta H_{f,298}^\circ [M_2ZrX_6(s)] - 3RT \quad (6)$$

using the enthalpies of formation of gaseous cations listed in Table 2 and of ZrX_6^{2-} ions from ref. 8 (Table 3), and the enthalpies of formation of the salts shown under column A (Table 2). Column E gives literature values for the lattice energy. Lastly, lattice energies were determined employing the Kapustinskii–Yatsimirskii method [38, 39]. According to the authors, the crystal lattice energy of ionic compounds can be expressed by the equation

$$E_c/(kJ mol^{-1}) = 120.2 \frac{(\Sigma n)Z_C Z_A}{r_C + r_A} \left[1 - \frac{0.0345}{r_C + r_A} + 0.087(r_C + r_A) \right] \quad (7)$$

where (Σn) is the total number of ions in the simplest stoichiometric unit of the molecule, Z_C and Z_A denote the numerical values of the charges of cation and anion, respectively, and r_C and r_A are the “thermochemical” ionic radii (in nm); r_C values are given in Table 2. “Thermochemical” radii have so far been reported for only ZrF_6^{2-} [31] and $ZrCl_6^{2-}$ [7, 31] (Table 3). The derivation of these values have, however, been based on a very limited number of crystal lattice energy values. Thus, we determined values of r_A for $ZrCl_6^{2-}$, $ZrBr_6^{2-}$ and ZrI_6^{2-} by using eqn. (7), the relevant r_C value, and all crystal lattice energy values given under columns C, D and E (Table 2). The “thermochemical” radius of ZrF_6^{2-} was evaluated from only the lattice energies of the ammonium salt given under column D. Other values of E_c for hexafluorozirconates were not considered owing to their uncertain quality. The mean “thermochemical” radii of ZrX_6^{2-} , shown in Table 3, were obtained by excluding those which did not fit the majority of the data. Such values were subsequently used to determine the lattice energies which are given in Table 2 under column F.

Crystal lattice energies of hexahalogenozirconates determined by various methods, as with their enthalpies of formation, generally correspond to each other quite well. Relatively low values of E_c , in the case of hexachlorozirconates, are again noted when they originate from the ΔH_d values taken from refs. 18, 19 and 25. The Ewald method seems to overestimate the lattice energies of hexafluorozirconates (values listed under column C in Table 2) [8]. However, the values listed under column D (Table 2) for alkali metal hexafluorozirconates are most probably underestimated owing to the uncertainties in the determination of ΔH_d values. The crystal lattice energies resulting from the Kapustinskii–Yatsimirskii approach, therefore, seem to be quite reliable because they do not suffer from uncertainties of individual measurements or theoretical calculations.

Features of ZrX_6^{2-}

The species common to all the compounds examined are the octahedral ZrX_6^{2-} ions. The most important thermochemical characteristic of these is the enthalpy of formation. We have recently obtained values of this quantity on a purely theoretical basis using ab initio quantum chemistry methods (Table 3) [8]. Thus determined, the value of $\Delta H_{f,298}^\circ[ZrCl_6^{2-}(g)]$ compares excellently with those available in the literature [6]. Unfortunately, no such data are available for the other ions. Therefore, employing the equation

$$\Delta H_{f,298}^\circ[ZrX_6^{2-}(g)] = E_c^\circ [M_2^I ZrX_6(s)] - 2 \Delta H_{f,298}^\circ[M^{I+}(g)] + \Delta H_{f,298}^\circ[M_2^I ZrX_6(s)] + 3RT \quad (8)$$

we derived enthalpies of formation of $ZrCl_6^{2-}$, $ZrBr_6^{2-}$, and ZrI_6^{2-} taking the electrostatic lattice energies given under column C, the enthalpies of formation shown under column A and the enthalpies of formation of cations given in Table 2. The results are given together with the “thermochemical” radii of anions in Table 3.

Generally speaking, conformity between the values determined here and the theoretical values of ΔH_f is satisfactory considering that both sets of data were obtained completely independently.

CONCLUSIONS

In this paper, existing thermochemical data on the decomposition of hexahalogenozirconates have been compiled and critically reviewed. These characteristics were subsequently combined with others available in the literature, which enabled an evaluation of the enthalpies of formation of the above-mentioned salts. Values for the latter quantity thus determined or existing in the literature compare quite well with those predicted theoretically on the basis of the electrostatic lattice energies and the enthalpies of formation of gaseous ZrX_6^{2-} ions. This proves the theoretical methods can be very useful in determining the thermochemical quantities of solid substances.

The simplest way of predicting theoretically the enthalpies of formation of crystalline ionic compounds requires a knowledge of the enthalpies of formation of the constituent ions and the crystal lattice energies (eqn. (5)). Enthalpies of formation of simple monoatomic ions have been determined very accurately by experiment and are generally available. The enthalpies of formation of complex cations, e.g. protonated organic bases, are also obtainable experimentally [40] and relatively easily theoretically [30, 41, 42]. This cannot, in general, be said about complex ions such as ZrX_6^{2-} . To our knowledge, there is no possibility of the experimental determination of the enthalpies of formation of these species. We have demonstrated, however, in our latest [8] and present paper (Table 3) that these enthalpies can be

reliably predicted by the ab initio quantum chemistry methods. Finally, the determination of the enthalpies of formation of the salts requires a knowledge of the crystal lattice energies. This is not an easy problem to solve. In several of our latest papers, we restricted lattice energy calculations to the electrostatic term, neglecting the dispersive and repulsive interactions [43, 44]. Although the latter two effects combined together do not markedly affect the values of the lattice energy, they should be taken into account in more advanced calculations. This is not, however, an easy task if one intends to approach it on a purely theoretical basis. Nevertheless, the present method seems to be an adequate way of determining the enthalpy of formation of crystalline solid substances.

Examining the data in Table 2, it can be noted that the enthalpies of formation and the crystal lattice energies of hexahalogenozirconates determined in various ways correspond to each other reasonably well. The same is true of the enthalpies of formation of ZrX_6^{2-} ions given in Table 3. This suggests that the experimental and theoretical characteristics are consistent and both can be considered fully reliable.

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