Enthalpies of Formation of Alkali-metal Hexachloro-zirconates and -hafnates

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Enthalpies of reaction have been determined by solution calorimetry for the process (i) where M′ = Na, K, or Cs

$$2\,\mathrm{M'Cl(c)} + \mathrm{MCl_4(c)} \longrightarrow \mathrm{M'_2[MCl_6](c)} \tag{i}$$

and M = Zr or Hf. Heats of formation for the complexes, $\Delta H_f^{\ominus}$(298 K), have been calculated using mean values of $\Delta H_f^{\ominus}$ for MCl_4 taken from the literature. The reaction is marginally more favourable when M = Hf but both $ZrCl_4$ and $HfCl_4$ are somewhat better acceptors of chloride ion than is $NbCl_4$ and both are markedly better acceptors than $SnCl_4$.

We have previously reported the heats of formation of some alkali-metal hexahalogenoniobates and potassium hexachlorotantalate.[1] It was therefore of interest to extend the investigation to similar compounds formed by neighbouring elements in the second and third transition periods. Most of the various analogues are isostructural with lattice constants which differ very little from one to another. Thermochemical comparisons may therefore be made without having to consider differences in structure. Zirconium(IV) and hafnium(IV) are interesting because of their almost unique chemical similarity in spite of the difference in principal quantum number of the outer electrons. If their compounds were highly ionic this would not be surprising, but as their ions bear a high formal charge considerable covalency must be present.

Decomposition pressures of alkali-metal chlorozirconates have been measured by a static method [2] and by a novel flow technique.[3] A redetermination of decomposition pressures [4] was in poor agreement with the former methods. In all three studies, measurements were carried out above the $M'Cl$–$M'_2[ZrCl_6]$ eutectic temperature and decomposition led to liquid solutions saturated with $M'_2[ZrCl_6]$. Under these conditions the Van't Hoff relation does not precisely give the enthalpy of decomposition of the salt into its components but gives instead a quantity which is too large by an amount equal to twice the partial molar heat of mixing of M′Cl.[4]

For these reasons we felt that a calorimetric determination of the heats of formation of some alkali-metal hexachloro-zirconates and -hafnates would be desirable. This provided data to compare with those obtained by Welsh *et al.* for similar complexes of tin(IV) and lead(IV).[5]

RESULTS AND DISCUSSION

Enthalpies of complexing for $M'_2[ZrCl_6]$ and $M'_2[HfCl_6]$, *i.e.* enthalpies of reaction (1), were determined by

$$2\,\mathrm{M'Cl(c)} + \mathrm{MCl_4(c)} \longrightarrow \mathrm{M'_2[MCl_6](c)} \tag{1}$$

measuring the heats of solution of each of the compounds in equation (1). We assumed that $M'_2[MCl_6]$ dissolved in hydrochloric acid solution to give the same species as were formed when MCl_4 and M′Cl were dissolved separately. At any rate the complex salt may be crystallized from a solution of the components in concentrated acid.[6] The calorimeter liquid was 4.02M-HCl.† The acid was used to minimize hydrolysis of the dissolved compounds. Extensive hydrolysis would have been accompanied by a considerable evolution of heat and the calculation of enthalpies of complex formation would have entailed taking the difference between large numbers. Initially attempts were made to use 6M-HCl but the zirconium and hafnium compounds gave sparingly soluble residues in this medium.

Partial reactions (2)—(6) were used to calculate heats of complexing. Braces denote solution components.

$$2\,\mathrm{KCl(c)} + \{\mathrm{H_2ZrCl_6} + 373\,\mathrm{HCl}\} \xrightarrow{\Delta H_1} \{2\,\mathrm{KCl} + \mathrm{H_2ZrCl_6} + 373\,\mathrm{HCl}\} \tag{2}$$

$$\mathrm{ZrCl_4(c)} + \{2\,\mathrm{KCl} + 375\} \xrightarrow{\Delta H_2} \{2\,\mathrm{KCl} + \mathrm{H_2ZrCl_6} + 373\,\mathrm{HCl}\} \tag{3}$$

$$\{2\,\mathrm{KCl} + \mathrm{H_2ZrCl_6} + 373\,\mathrm{HCl}\} \xrightarrow{\Delta H_3} \mathrm{K_2[ZrCl_6](c)} + \{375\,\mathrm{HCl}\} \tag{4}$$

$$\{2\,\mathrm{KCl} + \mathrm{H_2ZrCl_6} + 748\,\mathrm{HCl}\} \xrightarrow{\Delta H_4} \{2\,\mathrm{KCl} + 375\,\mathrm{HCl}\} + \{\mathrm{H_2ZrCl_6} + 373\,\mathrm{HCl}\} \tag{5}$$

$$\{2\,\mathrm{KCl} + \mathrm{H_2ZrCl_6} + 373\,\mathrm{HCl}\} + \{375\,\mathrm{HCl}\} \xrightarrow{\Delta H_5} \{2\,\mathrm{KCl} + \mathrm{H_2ZrCl_6} + 748\,\mathrm{HCl}\} \tag{6}$$

Summing these reactions gives equation (1). The sum of the partial heats, ΣH_i, is the enthalpy of complexing, ΔH_c. The quantities shown were chosen to illustrate the typical case of dissolving $ZrCl_4$ (0.5 g) in 4.02N-acid (200 cm^3). The heats of mixing of solutions, ΔH_4 and ΔH_5, were assumed to be negligible with respect to ΔH_c because, as is shown below, the solutes are close to being

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† 1M = 1 mol dm^{-3}.

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at infinite dilution. Moreover, ΔH_4 and ΔH_5 would be always very nearly equal and of opposite sign.

Molar heats of solution for the alkali-metal chlorides are given in Table 1. They appear to be independent of the final concentration, therefore the solutes were close to infinite dilution. A stoicheiometric quantity of $ZrCl_4$ was dissolved in the calorimeter liquid before each run. Addition of $ZrCl_4$ had no discernible effect on the heats of solution of the alkali-metal chlorides. We assumed that this would have been true also if $HfCl_4$ had been added.

TABLE 1

Heats of solution of alkali-metal chlorides in 4.02M-HCl

Compound	Weight/g	$\frac{1}{2}\Delta H_1$/kJ mol^{-1}	Mean/kJ mol^{-1}
NaCl	0.5898	7.78	
	0.6567	8.37	
	0.5400	8.37	
	0.9096	8.16	8.17 ± 0.20
KCl	0.8197	18.28	
	0.5779	18.49	
	0.6457	18.49	
	0.6823	18.41	
	0.5055	18.28	18.39 ± 0.10
CsCl	1.0336	13.93	
	1.0404	13.51	
	0.9066	13.47	
	1.3338	13.89	13.70 ± 0.20

Heats of solution of the tetrahalides are given in Table 2. Equivalent amounts of alkali chloride were added to the calorimeter liquid in most runs but there was no evidence that such additions had any influence on the results. There was a small difference between the values obtained for the first preparation of $ZrCl_4$ and the others and between the two preparations of $HfCl_4$. Slight hydrolysis during handling could account for this. It might be argued that the highest value should correspond to the least hydrolysed preparation. We nevertheless took the mean of all values for calculating the resulting heat, ΣH_i.

TABLE 2

Heats of solution, ΔH_2, of tetrachlorides in 4.02M-HCl

Compound	Weight/ g	Alkali-metal chloride added	ΔH_2/ kJ mol^{-1}	Mean/ kJ mol^{-1}
$ZrCl_4$,	0.5048	None	−248	
preparation (1)	0.4291	None	−247	
	0.3104	None	−248	
	0.5605	KCl	−248	
preparation (2)	0.7170	KCl	−245	
	0.5005	KCl	−246	
preparation (3)	0.4165	CsCl	−246	−247 ± 1
$HfCl_4$,	0.7969	KCl	−261	
preparation (1)	0.5324	KCl	−261	
preparation (2)	0.6113	KCl	−267	
	0.5385	KCl	−265	
	0.5047	NaCl	−265	−264 ± 3

Data for the complex salts are given in Table 3. There was some discrepancy between mean values obtained for different preparations of the same compound. Again varying degrees of hydrolysis during handling could be responsible for this. We found, moreover, that preparations made by a single fusion or sintering of the component compounds gave large and non-reproducible heats of solution. Evidently the synthesis reactions were incomplete. A double heating with regrinding between led to good reproducibility. Further grinding and heating was considered inadvisable as each additional operation in the glove-box increased the risk of hydrolysis.

The heats of the complexing reactions are given in Table 4 together with heats of formation $\Delta H_f^{\ominus}$ (298 K).

TABLE 3

Heats of solution, $-\Delta H_3$, of alkali-metal hexachlorometallates in 4.02M-HCl

Compound	Weight/g	$-\Delta H_3$/kJ mol^{-1}	Mean/kJ mol^{-1}
$Na_2[ZrCl_6]$	0.5002	−200	
	0.4051	−197	
	0.5017	−199	
	0.4062	−197	
	0.5220	−200	−199 ± 2
$K_2[ZrCl_6]$	0.3155	−130	
	0.2099	−133	
	0.2518	−131	
	0.2314	−129	−131 ± 2
$Cs_2[ZrCl_6]$	0.7937	−75	
	0.5194	−75	
	0.7123	−74	
	0.5976	−74	−74.5 ± 0.5
$Na_2[HfCl_6]$	0.6080	−203	
	0.7577	−200	
	0.7323	−201	
	0.5575	−203	−202 ± 1
$K_2[HfCl_6]$	0.3705	−130	
	0.6630	−131	
	0.7842	−130	
	0.5898	−132	−131 ± 1

TABLE 4

Heats of complexing and standard heats of formation of alkali-metal hexachloro-zirconates and -hafnates

Compound	ΔH_c/kJ mol^{-1}	$\Delta H_f^{\ominus}$/kJ mol^{-1}
$Na_2[ZrCl_6]$	−32 ± 2	−1 835 ± 4
$K_2[ZrCl_6]$	−79 ± 2	−1 932 ± 4
$Cs_2[ZrCl_6]$	−145 ± 2	−1 992 ± 4
$Na_2[HfCl_6]$	−46 ± 3	−1 857 ± 12
$K_2[HfCl_6]$	−96 ± 3	−1 957 ± 12

The heats of formation of the alkali-metal chlorides were taken from Rossini's compilation.[7] For $\Delta H_f^{\ominus}$ of $ZrCl_4$, we used the mean of the two more recent literature values,[8,9] *viz.* -981 ± 1 kJ mol^{-1}. In the case of $HfCl_4$, we used the mean of three literature values,[8-11] *viz.* -990 ± 10 kJ mol^{-1}. As expected, there was not a large difference in the ΔH_c values for analogous compounds of the two metals. The hafnium compounds are slightly more stable.

In order to compare chloride-ion affinities of the tetrahalides, it is best to convert all reacting compounds to gases. This has the advantage of eliminating the effect of crystal forces but it introduces the energy of

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reorganizing the sp^3 hybridization of the gaseous MCl_4 molecules to sp^3d^2 hybrids in the complex ions. This permits us to compare $ZrCl_4$ with $SnCl_4$. From the work of Welsh *et al.*[5] we can write equation (7). This may be

$$SnCl_4(g) + 2\,Cl^-(g) \longrightarrow [SnCl_6]^{2-}(g);\quad \Delta H = -1\,547\text{ kJ} + U(K_2[SnCl_6]) \quad (7)$$

compared with our data obtained for $K_2[ZrCl_6]$ in equation (8). The calculation of the gas-phase enthalpy

$$ZrCl_4(g) + 2\,Cl^-(g) \longrightarrow [ZrCl_6]^{2-}(g);\quad \Delta H = -1\,597 \pm 5\text{ kJ} + U(K_2[ZrCl_6]) \quad (8)$$

utilized the value 707 kJ mol^{-1} as the lattice energy of KCl and 103 ± 1 kJ mol^{-1} as the enthalpy of sublimation of $ZrCl_4$.[12] The lattice energy of $K_2[ZrCl_6]$ cannot be calculated with great accuracy because knowledge of the electron distribution in the salt is lacking. However, the two salts are isomorphous with lattice constants of 9.98 ($K_2[SnCl_6]$) [13] and 10.08 Å ($K_2[ZrCl_6]$).[14] Assuming that the electron distribution is the same in both, the simplified method of calculating lattice energies proposed by Yatsimirski [15] may be used to estimate the difference $U(K_2[SnCl_6]) - U(K_2[ZrCl_6])$. Using this procedure we found the difference to be only *ca.* 15 kJ mol^{-1}. Thus, in the gaseous state, $ZrCl_4$ is the better acceptor of chloride ion.

A comparison with data [1] for $K_2[NbCl_6]$ is also interesting. The unit cell of this salt is likewise very comparable with a length of 9.97 Å.[16] Process (9) shows

$$NbCl_4(g) + 2\,Cl^-(g) \longrightarrow [NbCl_6]^{2-}(g);\quad \Delta H = -1\,571\text{ kJ} + U(K_2[NbCl_6]) \quad (9)$$

that gaseous $NbCl_4$ is a slightly poorer chloride-ion acceptor than $ZrCl_4(g)$. As before, by means of the Yatsimirski equation for lattice energies, we obtained $U(K_2[NbCl_6]) - U(K_2[ZrCl_6]) = 15$ kJ mol^{-1}. The decrease in acceptor power in going from $ZrCl_4$ to $NbCl_4$ may be the result of a decrease in $p_\pi \rightarrow d_\pi$ dative bonding. The $t_{2g}{}^1$ configuration of Nb^{IV} presumably gives the ion less tendency to accept *p*-electron donation from the chlorine atoms into the set of t_{2g} orbitals. As the effective nuclear charge of M^{4+} ions increases toward the right in a Period, the σ bonding should become stronger because the effective nuclear charge increases. Apparently, the loss of π bonding in passing from Zr to Nb exceeds in importance any increase in σ bonding. This suggests that the π bonding in $[ZrCl_6]^{2-}$ is very important. A similar effect was found in an earlier study [17] of the enthalpies of adduct formation. It was found that $MoCl_4$ formed more stable adducts with pyridine and tetrahydrofuran than did $ZrCl_4$. This illustrates the difference in σ-bond strength. When a thioether was used to form adducts with these tetrachlorides, $MoCl_4$ was only marginally a better acceptor. A π contribution is probably more important in the Zr–S bond and is not as strong for neutral as for negative ligands.

The enthalpy of reaction (10) differs little from that of

$$HfCl_4(g) + 2\,Cl^-(g) \longrightarrow [HfCl_6]^{2-}(g);\quad \Delta H = -1\,611 \pm 14\text{ kJ} + U(K_2[HfCl_6]) \quad (10)$$

(8). This value was obtained from the calorimetric data for $K_2[HfCl_6]$. If the electron distributions in $K_2[ZrCl_6]$ and $K_2[HfCl_6]$ are assumed to be the same, $U(K_2[HfCl_6]) - U(K_2[ZrCl_6]) = 3$ kJ mol^{-1}. In the calculation we used $a = 10.06$ Å for the lattice constant [18] of $K_2[HfCl_6]$ and the mean of two literature values [12,19] for the enthalpy of sublimation of $HfCl_4$, *viz.* 101 ± 2 kJ mol^{-1}. The uncertainty in this and other quantities make precise comparison of the gaseous zirconium and hafnium complexes impossible at this time but it is evident that they are equally stable to within *ca.* ±10 kJ mol^{-1}.

Comparison with Previous Work.—Zvara and Tarasov [3] measured decomposition pressures of $K_2[ZrCl_6]$ and $K_2[HfCl_6]$ at 710—800 K. The process of decomposition of the zirconium complex is represented by equation (11). At equilibrium, the potassium chloride

$$K_2[ZrCl_6](c) \longrightarrow 2\,KCl\text{ (dissolved)} + ZrCl_4(g) \quad (11)$$

would be dissolved in a melt of $K_2[ZrCl_6]$ at its m.p. The heat of such a reaction is closely related to that of (1) with a reversed sign. The value should differ by the heat of sublimation of $ZrCl_4$, the heat of solution of 2 mol of KCl, and the differences in heat content of the reaction species at 298 K and the high temperature respectively. The heat capacity and heat of fusion of $K_2[ZrCl_6]$ have been measured [20] and the heat contents for KCl and $ZrCl_4$ at various temperatures are given in the JANAF tables.[21] Zvara and Tarasov found the enthalpy of reaction (11) to be 203 kJ. The heat of solution of crystalline KCl in molten $K_2[ZrCl_6]$ is not known but it has been shown [4] to be very close to the heat of fusion of KCl. From these data at 800 K we calculate ΔH_c (298 K) = −77 kJ for the heat of reaction (1). This is in good agreement with the value of −79 ± 2 kJ obtained in this work. Morozov and In-Chzhu [2] obtained 218 kJ for the heat of reaction (11). This leads to poorer agreement with our result, but in view of the uncertainty in the heat of solution of KCl it is not necessarily the less accurate of the two results. Lister and Flengas [4] obtained 352 kJ for the heat of reaction (11). The weight of evidence favours a lower value.

Zvara and Tarasov [3] give 169 kJ mol^{-1} as the heat of

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decomposition of $K_2[HfCl_6]$. As heat-capacity data are lacking it is not possible to make a quantitative comparison with our value for the heat of complexing at 298 K. However, if Zvara and Tarasov's and our value is correct, $K_2[HfCl_6]$ is significantly less stable than $K_2[ZrCl_6]$ at elevated temperature while it is very slightly more stable at room temperature.

EXPERIMENTAL

Materials.—Crystal-bar zirconium and hafnium (99.95%) were supplied by Ventron Alpha Products, Beverly, Massachusetts. Research-grade chlorine (Matheson) was used after passing over P_4O_{10}. The sodium and potassium chlorides were J. T. Baker A.R. grade. Caesium chloride (99.9%) was supplied by K. and K. Laboratories, Hollywood, California.

Preparation of $ZrCl_4$ *and* $HfCl_4$.—The tetrachlorides were obtained by heating the metals in an atmosphere of chlorine. The apparatus used was first flamed and well flushed with chlorine. The initial product of reaction with zirconium was buff coloured. This somewhat impure material was heated with a little zirconium powder for 4 d at 400 °C. The product, when subsequently sublimed in a static atmosphere of nitrogen, was pure white.

Preparation of Complexes.—Our attempts to use the procedure of Lister and Flengas [14] met with only limited success. In order for the reaction to go to completion, a quite thick layer of alkali-metal chloride had to be heated in $ZrCl_4$ vapour. When we attempted to carry out the preparation of $K_2[ZrCl_6]$ on a larger scale a thicker bed of KCl became encrusted on the surface with product, thus preventing reaction at lower levels of the bed. We resorted, therefore, to the following procedure. Alkali-metal chloride (*ca.* 2 g) and a stoicheiometric quantity of zirconium or hafnium tetrachloride were sealed *in vacuo* in a quartz tube and melted in a tube furnace. A tube of 6 mm internal diameter and 1 mm wall thickness was sufficiently strong to withstand the internal pressure in most cases. One sample tube exploded, however. After cooling, the solid mass was ground to powder in a glove-box filled with dry nitrogen and then resealed in an ampoule. This was heated at 450 °C for 20 h after which the product was reground and stored in a sealed ampoule under nitrogen.

X-Ray powder-diffraction patterns showed that the compounds were well crystallized with the $K_2[PtCl_6]$ structure and no lines characteristic of alkali-metal chloride or tetrachloride were visible.

Calorimetric Measurements.—The calorimeter has been described previously.[1] In the present study it contained 4.02M-hydrochloric acid (200 cm^3) and was operated at 25 °C. The sample to be dissolved was contained in a thin-walled glass bulb which was crushed under the acid. Dissolution was complete in 4 min or less. The calorimeter was calibrated electrically before and after each sample run and the mean of the two calibrations was used. The temperature data were treated by the numerical method of Kubaschewski *et al.*[22] in order to correct for heat loss or gain. The accuracy of the calorimeter was checked by measuring the heat of solution of KCl in water (Found: 17.57. Lit.: 17.57 [7] and 17.61 [23] kJ mol^{-1}).

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