Thermochemical properties of zirconium halides: a review

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Abstract

Physico-chemical experiments are reviewed and the thermodynamic properties of solid and gaseous zirconium halides of the general formula ZrX_n (X = F, Cl, Br, I; $n = 1$–4) are evaluated and, where necessary, estimated by analogy with other metal halide systems. Thermodynamic key values at 298.15 K and heat capacity equations are tabulated up to 1500 K for the solid phase and 3000 K for the gas phase. © 1997 Elsevier Science B.V.

Keywords: Enthalpy of formation; Heat capacity; Molecular parameters; Thermodynamic properties; Zirconium halides

1. Introduction

The most recent and complete evaluation of the thermodynamics of zirconium halides was performed by the JANAF team more than 25 years ago [1]. Since then, a number of new physico-chemical experiments have been reported which can be used to update and extend the knowledge of the thermodynamic properties of zirconium halides, which is of interest in several scientific fields such as chemical vapour deposition, nuclear engineering and metal refining. For example, zirconium tetrachloride and tetrabromide are used in the preparation of chemical vapour deposited zirconium carbide layers of TRISO-coated fuel particles for High-Temperature Gas-cooled Reactors (HTGR) [2,3]. Using the appropriate thermodynamic data, equilibrium calculations can be used to optimize process conditions, such as temperature and partial pressure of the reactants [4].

Zircaloy (zirconium with minor alloying additives such as tin) is used as a cladding for fuel rods in water-cooled nuclear reactors because of its low thermal neutron cross section, excellent high-temperature strength, and resistance to corrosion in water. However, the fuel cladding sometimes fails by cracking. A possible explanation for this failure is the stress-corrosion cracking caused by fission products such as iodine [5,6]. The mechanism of this stress-corrosion cracking presumably involves reactions between zirconium and iodine. For this reason, the understanding of the formation of condensed and vapour phases in the Zr–I system is important. Another important feature associated with a zirconium fuel cladding is the necessity of a low hafnium content, because hafnium has a high thermal-neutron cross section. Since the elements zirconium and hafnium have similar chemical properties, the zirconium minerals always contain a small amount of hafnium. For the improvement of chemical processes to separate zirconium from hafnium, such as fractional distillation [7] and the use of fused salt mixtures [8], fuller thermodynamic know-

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ledge of the halides, and especially the chlorides, is required.

2. Experimental

Thermodynamic calculations were performed using a set of computer programs, developed at ECN [9,10]. Auxiliary thermodynamic data needed for the calculations were taken from the following works, in order of importance: CODATA [11], Thermodynamic Properties of Individual Substances [12,13], and the NBS tables [14].

3. The solid zirconium halides

Several compounds exist in the Zr–X systems, which can be described by the general formula ZrX_n ($n = 1, 2, 3, 4$), except for the Zr–F system, since ZrF has never been identified. The tetrahalides are stoichiometric compounds. While zirconium monochloride and monobromide are considered to be line

compounds, the monoiodide, and di- and trihalides possess homogeneity regions.

The thermodynamic properties of the solid zirconium halides, deduced in the following sections, are listed in Table 1.

3.1. Crystal structure and phase transitions

β-ZrF$_4$ has a monoclinic structure at room temperature [16]. In addition, a tetragonal (α-ZrF$_4$) [17] and an unidentified γ-modification have been reported, which transform irreversibly to the monoclinic form at temperatures above 673 K [18–20]. The melting point of ZrF$_4$ was found at 1191 K by Sense et al. [21], at (1201 ± 2) K by Grande et al. [22], and at (1205 ± 2) K by McDonald et al. [23]. The latter value, obtained by drop calorimetry, has been considered the most accurate.

ZrCl$_4$ has a monoclinic structure at room temperature [24,25] which probably transforms to a cubic structure at 538 K [26–28]. The enthalpy change at this phase transition must be very small since no thermal effect was observed in the drop calorimetric

Table 1
Thermodynamic constants for solid zirconium halides from 298.15 to 1500 K

Compound	S^o_m (298.15 K) $J K^{-1} mol^{-1}$	$\Delta_f H^o_m$ (298.15 K) $kJ mol^{-1}$	$C^o_{p,m}(T)/J K^{-1} mol^{-1}$ [a]			T_{fus} K	$\Delta_{fus}H^o_m$ $kJ mol^{-1}$
			a	$b \times 10^3$	$c \times 10^{-5}$		
ZrF(s)	55.6 ± 5.0	−478 ± 50	47.00	11.69	4.53		
ZrF$_2$(s)	71.9 ± 5.0	−962 ± 50	69.89	14.63	8.35		
ZrF$_3$(s)	88.3 ± 5.0	−1433 ± 50	92.75	17.56	12.18		
ZrF$_4$(s)	104.70 ± 0.21	−1911.3 ± 1.0	115.613	20.5000	16.0051	1205±2	64.26 ± 0.42
ZrF$_4$(l)			123.6				
ZrCl(s)	60.94 ± 0.50	−300 ± 10	45.64	12.12	1.81		
ZrCl$_2$(s)	99.2 ± 1.0	−531 ± 5	68.64	15.72	3.01		
ZrCl$_3$(s)	137.50 ± 0.50	−759.4 ± 3.4	91.63	19.30	4.20		
ZrCl$_4$(s)	182.05 ± 0.50	−981.0 ± 2.0	119.19	23.614	5.627	710 ± 1	33 ± 5
ZrCl$_4$(l)			140				
ZrBr(s)	72 ± 5	−212 ± 10	48.45	11.51	1.55		
ZrBr$_2$(s)	120 ± 4	−389 ± 15	72.73	14.27	2.41		
ZrBr$_3$(s)	169 ± 3	−592 ± 15	97.02	17.02	3.26		
ZrBr$_4$(s)	224.4 ± 2.0	−761.2 ± 5.0	121.30	19.78	4.117	723 ± 1	
ZrI(s)	78 ± 5	−152 ± 15	48.98	10.55	1.18		
ZrI$_2$(s)	133 ± 4	−286 ± 10	73.79	12.35	1.65		
ZrI$_3$(s)	188 ± 3	−402 ± 10	98.61	14.15	2.13		
ZrI$_4$(s)	250.2 ± 1.0	−489.1 ± 4.0	123.42	15.95	2.607	772 ± 1	
α-Zr(s) [b]	39.18 ± 0.25	0	24.162	8.7558	0.6994		

[a] $C^o_{p,m}(T)/J K mol^{-1} = a + b(T/K) - c(T/K)^{-2}$.
[b] Reference [15].

study by Coughlin and King [29]. Therefore, $ZrCl_4$ is thermodynamically treated as a single phase. The melting point of $ZrCl_4$ has been reported as (710 ± 1) K [30–36].

A cubic structure has been reported for $ZrBr_4$ [37,38]. Krebs, however, stated that $ZrBr_4$ is isostructural with monoclinic $ZrCl_4$ [24,25]. Nuclear quadrupole resonance spectroscopy of $ZrBr_4$ is also consistent with a monoclinic structure [27,39]. $ZrBr_4$ melts at (723 ± 1) K [30–32].

For ZrI_4 as much as three modifications, orthorhombic (α), monoclinic (β), and triclinic (γ), are known [40,41]. Ferrante and McCune [42] interpreted the X-ray diffraction pattern as a cubic structure but this observation was not confirmed by Troyanov [41]. As discussed by this author, the structural differences between the modifications of ZrI_4 are very small, and all three modifications are expected to have similar thermodynamic properties. Since no phase transitions were observed in the enthalpy increment curve [42], ZrI_4 is thermodynamically treated as a single phase. The temperature of fusion of ZrI_4 is (772 ± 1) K [30–32].

Since, for all zirconium tetrahalides, the temperature of sublimation is lower than the temperature of fusion, liquid zirconium tetrahalides are thermodynamically unstable at atmospheric pressure.

The lower zirconium halides have been less well studied. The available information on the crystal structures and phase limits is summarized in Table 2.
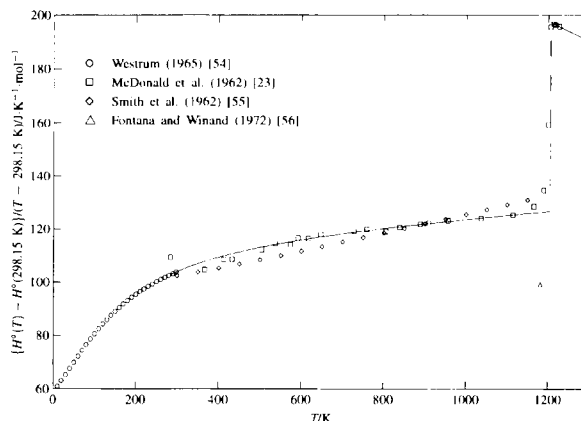

Fig. 1. Reduced enthalpy increments of ZrF_4 (s,1).

3.2. Heat capacity and entropy

The low-temperature heat capacity (from 7 to 305 K) [54] and high-temperature enthalpy increments (from 366 to 1226 K) [23] of ZrF_4 do join smoothly. According to the sample preparation, both measurements were made on β-ZrF_4. The enthalpy of fusion derived from the drop calorimetric study is (64.26 ± 0.42) kJ mol^{-1}. The enthalpy increments reported by Smith et al. [55] and Fontana and Winand [56] have been rejected because their results do not smoothly join the low-temperature data (Fig. 1), probably due to different crystallographic states of the samples, which were not specified.

Table 2
Phase limits and crystal structures of the lower solid zirconium halides

Nominal phase	Composition range	Crystal structure	Ref.
ZrF_2	ZrF_{2-x} [a]	orthorhombic	[43,44]
ZrF_3	unknown	cubic [b]	[45]
$ZrCl$	$ZrCl_{1.00\pm0.01}$	trigonal	[46,47]
$ZrCl_2$	$ZrCl_{1.6\pm0.1}$–$ZrCl_{2.0\pm0.1}$	rhombohedral	[48–50]
$ZrCl_3$	$ZrCl_{2.94\pm0.02}$–$ZrCl_{3.03\pm0.02}$	hexagonal	[51]
$ZrBr$	$ZrBr_{1.00\pm0.01}$	trigonal	[46]
$ZrBr_2$	unknown	rhombohedral	[52]
$ZrBr_3$	$ZrBr_{2.87\pm0.02}$–$ZrBr_{3.23\pm0.02}$	hexagonal	[51]
ZrI	$ZrI_{1.05\pm0.1}$–$ZrI_{1.30\pm0.1}$	unknown	[53]
ZrI_2	$ZrI_{1.9\pm0.1}$–$ZrI_{2.1\pm0.1}$	rhombohedral	[49,50,53]
ZrI_3	$ZrI_{2.83\pm0.05}$–$ZrI_{3.43\pm0.05}$	hexagonal	[51]

[a] According to Basile et al. [44] the ZrF_{2-x}-phase extends to the lower fluorine content $(x > 0)$.
[b] Although not all lines could be indexed, Ehrlich et al. [45] classified ZrF_3 as cubic ReO_3-type.

The heat capacity of ZrF_n ($n = 1, 2, 3$) is estimated to be:

$$\tfrac{1}{4}[nC_{p,m}^{o}(ZrF_4(s)) + (4 - n)C_{p,m}^{o}(Zr(s))]$$

S_m^{o} (298.15 K) is estimated in the same manner.

Two sets of measurements are known for the low-temperature heat capacity of $ZrCl_4$ [57–60]. The reported heat capacities are in concordance up to 80 K, but above this temperature the results deviate and the discrepancy increases to 2.6% at 298.15 K. Since the results reported by other investigators of the Bureau of Mines for Zr(s), $ZrO_2(s)$, and $ZrSiO_4(s)$ agree well with selected thermochemical data [15,61,62], Todd's results [57] have been preferred in the temperature range 51–298.15 K. The value of S^o (51 K) has been taken from the measurements of Prokopenko and co-workers [58–60]. Coughlin and King [29] measured high-temperature enthalpy increments from 335 to 567 K, which smoothly join the low-temperature heat capacity data of Todd. The enthalpy of fusion and heat capacity of liquid $ZrCl_4$ have been estimated from the vapour pressure data by combining the second-law values at 710 K for the enthalpy of vaporization and sublimation, and by optimizing the agreement between second- and third-law enthalpies of vaporization.

Entropy values derived from low-temperature heat capacity measurements have also been reported for $ZrCl_3$ and $ZrCl$ [58,60,63,64]. The entropy of $ZrCl_2$ has been estimated by interpolation of the $ZrCl_n$ series.

The high-temperature heat capacity of the lower zirconium chlorides can be estimated using the same relation as for the lower zirconium fluorides. For $ZrCl_3$ and $ZrCl$, it is possible, however, to check this relation using the experimental low-temperature heat capacities, which reveals a small, almost constant, deviation. Introducing this deviation (δ) in the formula for zirconium fluorides results in the following equation for the zirconium chlorides:

$$C_{p,m}^{o}(ZrCl_n(s), T)/J\,K^{-1}mol^{-1}$$
$$= \tfrac{1}{4}[(n - \delta)C_{p,m}^{o}(ZrCl_4(s), T)$$
$$+ (4 - n + \delta)C_{p,m}^{o}(Zr(s), T)]$$

For $ZrCl_3$ and $ZrCl$, the experimental heat capacities, together with the heat capacity of Zr(s) [15], have been used to calculate δ. For $ZrCl_3$, δ slowly increases from

0.10 at 200 K to 0.16 at 300 K. The latter value has been used to estimate the heat capacity above room temperature. For $ZrCl$, δ remains virtually constant in the temperature range 200–300 K, and the value $\delta = 0.096$ has been used to estimate the heat capacity. For $ZrCl_2$, the value $\delta = 0.128$ has been deduced by linear interpolation.

There are no reports in the literature on the heat capacity or enthalpy increments of $ZrBr_n$ compounds. The adopted heat capacity and entropy value for $ZrBr_4$ have been estimated in such a way as to give reasonable trends in comparison with $ZrCl_4$ and ZrI_4 and to be consistent with existing sublimation data. For $ZrBr_3$, $ZrBr_2$, and $ZrBr$, the entropy values have been estimated by comparison with the zirconium chlorides. The high-temperature heat capacity has been estimated in the same way as for the zirconium fluorides.

Low-temperature heat capacity measurements have not been published for ZrI_4. The adopted entropy value for the condensed phase has been derived by third-law treatment of the sublimation data [31,65–68]. High-temperature enthalpy increments have been measured by Ferrante and co-workers [42,68]. The entropy and heat capacity values for ZrI_3, ZrI_2, and ZrI have been estimated in the same way as for the zirconium bromides.

3.3. Enthalpy of formation

The enthalpy of formation of β-ZrF_4, $\Delta_f H_m^{o}$ (298.15 K) $= -(1911.3 \pm 1.0)$ kJ mol^{-1}, has been taken from the fluorine combustion calorimetric measurements by Greenberg [69]. Since ZrF_2 and ZrF_3 are stable compounds at room temperature, the enthalpies of the formation are estimated using the boundary condition $\Delta_r G_o \geq 0$ for the following reactions:

$$ZrF_2(s) = \tfrac{1}{2}ZrF_4(s) + \tfrac{1}{2}Zr(s)$$
$$ZrF_3(s) = \tfrac{3}{4}ZrF_4(s) + \tfrac{1}{4}Zr(s)$$
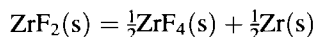
resulting in $\Delta_f G_m^{o}$ ($ZrF_2(s)$, 298.15 K) ≤ -905 kJ mol^{-1} and $\Delta_f G_m^{o}$ ($ZrF_3(s)$, 298.15 K) ≤ -1358 kJ mol^{-1}, or $\Delta_f H_m^{o}$ ($ZrF_2(s)$, 298.15 K) ≤ -956 kJ mol^{-1} and $\Delta_f H_m^{o}$ ($ZrF_3(s)$, 298.15 K) ≤ -1433 kJ mol^{-1}. The value for the enthalpy of formation of ZrF_2 compares very well with the estimate of Brewer (cited in Ref. [1]) and his value of -962 kJ mol^{-1} has

Table 3
The enthalpy of formation of $ZrCl_4(s)$ at 298.15 K

Authors	Method [a]	$\Delta_f H_m^o$ (298.15 K)/kJ mol^{-1}
Beck (1928) [70]	S	−1138
Siemonson and Siemonson (1952) [71]	C	−970.3±2.1
Gross et al. (1957) [72]	C	−982.0±1.7
Gal'chenko et al. (1965) [73]	C	−980.5±8.8
Gal'chenko et al. (1968) [74]	C	−979.8±1.2
Efimov et al. (1986, 1989) [60,75]	S	−981.9±1.9
	selected value:	−981.0±2.0

[a] C = chlorine combustion calorimetry, S = solution calorimetry.

been adopted. Our estimate of -1433 kJ mol^{-1} for ZrF_3 lies in between the values estimated by Brewer and by the JANAF team [1]. Assuming that ZrF is not stable at room temperature, the enthalpy of formation has been estimated using the boundary condition $\Delta_r G_o \leq 0$ for the reaction:

$$ZrF(s) = \tfrac{1}{4}ZrF_4(s) + \tfrac{3}{4}Zr(s)$$
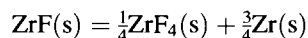
resulting in $\Delta_f G_m^o$ (ZrF(s), 298.15 K) ≥ -453 kJ mol^{-1}, or $\Delta_f H_m^o$ (ZrF(s), 298.15 K) ≥ -478 kJ mol^{-1}. This value has been adopted.

The results of the enthalpy-of-formation measurements for $ZrCl_4$ are summarized in Table 3. Beck [70] obtained a value of -1138 kJ mol^{-1} by measuring the enthalpy of hydrolysis of $ZrCl_4$. This value is presumably too low, because of uncertainties in identification of the hydrolysis products. In the work reported by Siemonsen and Siemonsen [71], where a value of $\Delta_f H_m^o$ (298.15 K) $= -(970.3 \pm 2.1)$ kJ mol^{-1} was obtained, the zirconium samples were incompletely chlorinated; also, the purity of the starting materials was not completely specified. Gross et al. [72] and Gal'chenko et al. [73,74] measured the enthalpy of chlorination of zirconium metal. Their results are in excellent agreement, although the earlier measurements of Gal'chenko et al. [73] have a large uncertainty range as a result of a fairly large impurity correction. Recently, Efimov et al. [60,75] measured the enthalpy of formation of $ZrCl_4$ by solution calorimetry in (1.0 mol dm^{-3} HF + 3.0 mol dm^{-3} HCl)(aq), being in excellent agreement with the chlorination data. For the enthalpy of formation of $ZrCl_4$, we select $\Delta_f H_m^o$ (298.15 K) $= -(981.0 \pm 2.0)$ kJ mol^{-1}, based on the results of Gross et al. [72], Gal'chenko et al. [74], and Efimov et al. [60,75].

Efimov et al. [64,76] also measured the enthalpy of solution of $ZrCl_3(s)$ in 3.0 mol dm^{-3} HCl solution. The molar enthalpy of solution of $ZrCl_3(s)$ depended on the amount of substance. Therefore, the value $-(317.7 \pm 0.3)$ kJ mol^{-1}, derived by a least-squares treatment, instead of the mean value $-(319.2 \pm 2.6)$ kJ mol^{-1}, has been used for the present calculation. Combining the enthalpies of reaction with the selected values for the enthalpy of formation of $ZrCl_4(s)$ and the partial enthalpy of formation of HCl(sln) (the integral value was erroneously used by Efimov et al.), we obtain $\Delta_f H_m^o$ (298.15 K) $= -(759.4 \pm 3.0)$ kJ mol^{-1}.

Prokopenko and co-workers [60,77,78] measured the enthalpies of solution of $ZrCl_{1.09\pm0.01}(s)$, Zr(s), HCl(sln), and $H_2O(l)$ in a HCl/HF solution. Combining the enthalpies of reaction with the integral enthalpy of formation of HCl(sln) and correcting the value to the composition 1.0, by assuming that $\Delta_f H_m^o$ (ZrCl$_n$) $= n\Delta_f H_m^o$, the value $-(303.3 \pm 3.4)$ kJ mol^{-1}, has been obtained.

Tsirel'nikov et al. [79] and Makarov et al. [80] measured the vapour pressure of $ZrCl_4$ over solid ZrCl by means of effusion mass spectrometry. A second-law treatment of their data gives for the enthalpy of formation of ZrCl, $\Delta_f H_m^o$ (298.15 K $= -(283.8 \pm 3.1)$ and $-(290.0 \pm 6.8)$ kJ mol^{-1}, respectively. Uchimura and Funaki [81] used a static method to measure the vapour pressure for the same reaction. The enthalpy of formation derived by third-law analysis yields $-(289.6 \pm 6.4)$ kJ mol^{-1}. Troyanov et al. [82] measured the enthalpy change of the same reaction by means of DTA and thermogravimetry. Combining their enthalpy of reaction with the thermodynamic functions of ZrCl(s), Zr(s), and $ZrCl_4(g)$ results in $\Delta_f H_m^o$ (298.15 K) $= -(282.6 \pm 6.3)$ kJ mol^{-1}.

The selected enthalpy of formation of ZrCl(s), $\Delta_f H_m^o$ (298.15 K) = $-(300 \pm 10)$ kJ mol^{-1}, is mainly based on the result of Prokopenko et al., although it is questionable if ZrCl$_{1.09}$ belongs to the ZrCl phase. The uncertainty in the enthalpy of formation has been raised to 10 kJ mol^{-1} to account for the uncertainty in the chemical composition and for the extrapolation method used.

The enthalpy of formation of ZrCl$_2$, $\Delta_f H_m^o$ (298.15 K) = $-(531 \pm 5)$ kJ mol^{-1}, is estimated by interpolation in the ZrCl$_n$ series, which is considered to be more accurate than the values derived from the disproportionation reactions $2ZrCl_3(g) = ZrCl_4(g)+$ $ZrCl_2(s)$ or $3ZrCl_2(s) = ZrCl(s) + Zr(s)$, ranging from -506 to -550 kJ mol^{-1} [81–89].

Turnbull [84] measured the enthalpies of reaction of ZrCl$_4$, ZrBr$_4$, and ZrI$_4$ with both NaOH(sln) and water (zirconium to water molar ratio 1 : 1500) at room temperature, resulting in two independent pathways for both ZrBr$_4$ and ZrI$_4$ to calculate the enthalpies of formation. Combining the enthalpies of reaction with auxiliary data for the aqueous sodium and hydrogen halides results in $\Delta_f H_m^o$ (ZrBr$_4$(s), 298.15 K) = $-(764.5 \pm 3.7)$ and $-(758.0 \pm 2.9)$ kJ mol^{-1}, and $\Delta_f H_m^o$ (ZrI$_4$(s), 298.15 K) = $-(487.7 \pm 4.0)$ and $-(490.5 \pm 3.1)$ kJ mol^{-1}, respectively. The mean values have been adopted.

Troyanov et al. [82] measured the enthalpy of disproportionation of ZrBr(s) by means of thermogravimetry and DTA. For the reaction $4ZrBr(s) = 3Zr(s) + ZrBr_4(g)$, they obtained $\Delta_r H_m^0$ (1100 K) = 136.4 kJ mol^{-1}, which results in $\Delta_f H_m^o$ (298.15 K) = $-(200.9 \pm 8.4)$ kJ mol^{-1}. Marek et al. [90] measured the vapour pressure of ZrBr$_4$(g) over ZrBr(s) using a tensimetric method. A third-law evaluation of their results yields $\Delta_f H_m^o$ (298.15 K) = $-(222.3 \pm 3.9)$ kJ mol^{-1}. The mean value, $-(212 \pm 10)$ kJ mol^{-1}, has been selected here.

Troyanov et al. also measured the enthalpy of disproportionation of ZrBr$_2$(s). For the reaction $3ZrBr_2(s) = 2ZrBr(s) + ZrBr_4(g)$, they obtained $\Delta_r H_m^o$ (900 K) = 81.2 kJ mol^{-1}, which gives the enthalpy of formation of ZrBr$_2$(s), $\Delta_f H_m^o$ (298.15 K) = $-(389 \pm 15)$ kJ mol^{-1}.

For the reaction $2ZrBr_3(s) = ZrBr_2(s) + ZrBr_4(g)$, Troyanov et al. reported $\Delta_r H_m^o$ (870 K) = 136.4 kJ mol^{-1}, resulting in $\Delta_f H_m^o$ (298.15 K) = $-(593\pm 15)$ kJ mol^{-1}. Schläfer and Skoludek [91] measured

the vapour pressure of ZrBr$_4$(g) for the same reaction. Third-law evaluation of their vapour pressure equation results in $\Delta_f H_m^o$ (298.15 K) = $-(591 \pm 14)$ kJ mol^{-1}. The selected value for the enthalpy of formation of ZrBr$_3$(s), based on these two measurements, is $-(592 \pm 15)$ kJ mol^{-1}.

Lamoreux and Cubicciotti [92] calculated activities of Zr(s) and ZrI$_4$(s) at 700 K from vapour pressure measurements in the solid two-phase regions Zr/ZrI, ZrI/ZrI$_2$, ZrI$_2$/ZrI$_3$, and ZrI$_3$/ZrI$_4$, where ZrI$_4$(g) is the dominant gaseous species over all phase regions [53,93,94]. Using the reported activities we have calculated for ZrI, ZrI$_2$, and ZrI$_3$: $\Delta_f H_m^o$ (298.15 K) = -152, -286 and -402 kJ mol^{-1}, respectively.

Mukhametshina et al. [95] used the same vapour pressure data to calculate the Gibbs energies at 600 K by a quasi-ideal solution model (QSM). Although their reported Gibbs energies agree well with those Lamoreux and Cubicciotti, the entropy values differ considerably from our estimates.

Several reports on the enthalpy of formation of the lower zirconium halides have not been taken into account in the present assessment for the following reasons:

1. Uncertainties about the phase boundaries and stoichiometry of the compounds taking part in the equilibrium reactions [96–100],
2. Lacking (or insufficient) information on the experimental data [101], or
3. Obscurity of the published work (preliminary or summary report?) [102].

4. The gaseous zirconium halides

4.1. Heat capacity and entropy

The geometric structures and molecular parameters of the zirconium tetrahalides have been investigated extensively in the past. Electron diffraction measurements showed that the tetrahalides are tetrahedral molecules (T_d symmetry) [103–108]. All vibrational frequencies, except ν_1 and ν_3 of ZrF$_4$, were established by infrared and Raman spectroscopy [109–118]. The two missing vibrations of ZrF$_4$ were estimated by Konings and Hildenbrand [117] by an

Table 4
Molecular parameters of gaseous ZrX_n species [a]

Compound	$\nu_i(g_i)$/cm^{-1}				$\omega_e x_e$/cm^{-1}	α_e/cm^{-1}	geometry	σ	r(Zr–X)/nm	$\angle$X–Zr–X	I_{ABC}/kg^3 m^6 [b]
ZrF	680(1)				2.2	0.00124	D_∞	1	0.196		1.0030×10^{-45}
ZrCl	363.5(1)				0.8	0.00036	D_∞	1	0.239		2.4216×10^{-45}
ZrBr	230(1)				0.4	0.00015	D_∞	1	0.253		4.5274×10^{-45}
ZrI	160(1)				0.3	0.00011	D_∞	1	0.273		6.5682×10^{-45}
ZrF_2	623(1)	130(1)	634(1)				C_{2v}	2	0.196	120°	1.7464×10^{-135}
$ZrCl_2$	330(1)	105(2)	400(1)				$D_{\infty h}$	2	0.239	180°	6.7255×10^{-45}
$ZrBr_2$	200(1)	65(2)	290(1)				$D_{\infty h}$	2	0.253	180°	1.6986×10^{-44}
ZrI_2	120(1)	30(2)	210(1)				$D_{\infty h}$	2	0.273	180°	3.1411×10^{-44}
ZrF_3	615(1)	240(1)	170(2)	655(2)			C_{3v}	3	0.1886	105°	8.60975×10^{-135}
$ZrCl_3$	375(1)	115(1)	100(2)	420(2)			D_{3h}	6	0.2319	120°	2.14191×10^{-133}
$ZrBr_3$	230(1)	70(1)	60(2)	315(2)			D_{3h}	6	0.2465	120°	3.53718×10^{-132}
ZrI_3	150(1)	60(1)	55(2)	250(2)			D_{3h}	6	0.2660	120°	2.23753×10^{-131}
ZrF_4	675(1)	156(2)	178.6(3)	668(3)			T_d	12	0.1886	109°28'	2.67949×10^{-134}
$ZrCl_4$	377(1)	98(2)	113(3)	418(3)			T_d	12	0.2319	109°28'	6.01733×10^{-133}
$ZrBr_4$	226(1)	60(2)	72(3)	315(3)			T_d	12	0.2465	109°28'	9.93707×10^{-132}
ZrI_4	158(1)	43(2)	55(3)	254(3)			T_d	12	0.2660	109°28'	6.28593×10^{-131}

[a] Electronic levels $\epsilon_i(g_i)$/cm^{-1}: ZrX_4, 0(1); ZrX_3, 0(2), 1800(2), 4500(2), 12000(2), 30000(2); ZrX_2, 0(3), 7000(6), 17000(6), 22000(15); ZrX, 0(4), 3000(4), 6000(4), 12000(4), 18000(4), 24000(4), 30000(4).
[b] I_A/kg m^2 for linear molecules.

empirical method correlating ν_1 and ν_3, and ν_2 and ν_4 frequencies of other metal tetrahalides.

Little information is known about the molecular parameters of the subhalides. From infrared matrix isolation experiments, Hauge and Margrave [114] deduced the vibrational frequencies and a bend structure for ZrF_2. A linear structure is assumed for the remaining dihalides, as predicted by Drake and Rosenblatt [119]. The only information on the trihalides is the ν_3 frequency of ZrF_3 [114]. A pyramidal structure for ZrF_3 and planar geometries for the remaining trihalides have also been taken from the predictions of Drake and Rosenblatt [119]. The vibrational frequency ω_e and the anharmonicity constant $\omega_e x_e$ of zirconium monochloride were determined from an electronic transition, $^4\Pi-^4\Sigma$, assuming that $^4\Sigma$ is the ground state [120].

The interatomic distances of the subhalides were estimated by comparison with the halides of Si, Ge, Sn, and Pb [121]. The bond length of the trihalides was taken to be identical to that of the tetrahalides. For the mono- and dihalides, an increase in bond length of 0.007 nm was assumed when compared to the corresponding tetrahalides.

All missing frequencies for the subhalides have been estimated from the zirconium tetrahalides and comparison with other compounds such as the titanium, strontium, and calcium halides [122,123]. For

the monohalides, the anharmonicity constant $\omega_e x_e$ and the vibrational–rotational interaction constant α_e have been estimated using the formulas $\omega_e x_e = \omega_e^2/(4D^o + 2\omega_e)$ and $\alpha_e = 6\sqrt{\omega_e x_e B_e^3}/\omega_e - 6B_e^2/\omega_e$ [124].

There is almost no information on the electronic levels of zirconium halides. The available information, only for the monohalides [120,125–129], is insufficient to obtain a complete description. The tetrahalides, which have a closed shell electronic configuration, have a singlet ground state and no low-lying excited states are expected. For the subhalides, the estimates for the zirconium fluorides and chlorides by Chase et al. have been adopted and extended to the other halides [1].

The thermodynamic functions of the zirconium halides in the temperature range 298.15–3000 K have been calculated from the molecular data listed in Table 4, using a harmonic oscillator rigid rotor model. The thermodynamic properties at room temperature and coefficients for the heat capacity equations are given in Tables 5 and Table 6.

4.2. Enthalpy of formation

The enthalpies of formation of the tetrahalides have been derived from vapour pressure measurements reported in the literature. A second- and third-law

Table 5
Thermodynamic constants of gaseous zirconium halides at 298.15 K ($p^o = 101325\,Pa$)

Compound	S_m^o (298.15 K) J K mol^{-1}	$\Delta_f H_m^o$ (298.15 K) kJ mol^{-1}	$\Delta_0^{298.15} H_m^o$ kJ mol^{-1}
ZrF(g)	243.646	63±15	9002
ZrF$_2$(g)	290.400	−515±15	12459
ZrF$_3$(g)	309.061	−1099±15	15526
ZrF$_4$(g)	322.140	−1671.3±1.4	19244
ZrCl(g)	255.986	283±24	9600
ZrCl$_2$(g)	292.086	−146±15	14304
ZrCl$_3$(g)	341.616	−515±10	18035
ZrCl$_4$(g)	367.602	−871.0±2.3	22561
ZrBr(g)	268.195	366±25	10047
ZrBr$_2$(g)	318.899	−23±25	15506
ZrBr$_3$(g)	379.304	−345±25	19740
ZrBr$_4$(g)	414.537	−644.6±5.4	24943
ZrI(g)	277.184	408.2±6.3	10348
ZrI$_2$(g)	347.212	134.1±8.5	16546
ZrI$_3$(g)	400.730	−128.4±5.0	20630
ZrI$_4$(g)	440.460	−356.2±4.1	26311

Table 6

Heat capacity coefficients of gaseous zirconium halides from 298.15 to 3000 K $C_{p,m}^{\circ}(T)/\mathrm{J\,K^{-1}\,mol^{-1}} = a + b(T/K) + c(T/K)^2 + d(T/K)^3 + e(T/K)^4 + f(T/K)^{-2}$

Compound	T/K	a	$b \times 10^3$	$c \times 10^6$	$d \times 10^9$	$e \times 10^{13}$	$f \times 10^{-5}$
ZrF(g)	298–1000	28.8894	27.6530	−43.7653	39.9608	−134.684	−1.22984
	1000–3000	20.6632	27.3377	−12.6328	2.66570	−2.15834	13.2948
ZrF$_2$(g)	298–1000	39.6553	63.3275	−92.9332	64.6347	−173.102	−2.14464
	1000–3000	76.7090	−32.5117	2.14758	−5.55202	5.18540	−34.8038
ZrF$_3$(g)	298–1700	57.4351	70.4336	−66.0454	28.9168	−49.2405	−4.35247
	1700–3000	90.5197	0.28813	−1.44359	0.46536	−0.46128	−46.8066
ZrF$_4$(g)	298–1000	63.5661	152.209	−225.181	159.310	−440.048	−4.76472
	1000–3000	106.9167	1.43395	−0.74708	0.18405	−0.17563	−23.4627
ZrCl(g)	298–1000	38.5099	−4.80508	4.04519	6.26825	−41.7904	−1.68546
	1000–3000	20.9361	27.0778	−12.4534	2.62061	−2.11439	17.0144
ZrCl$_2$(g)	298–1000	58.7728	12.5115	−18.2501	12.1412	−29.0054	−2.56964
	1000–3000	81.2031	−32.9170	21.6858	−5.60394	5.23537	−28.7405
ZrCl$_3$(g)	298–1200	73.3394	23.6969	−6.88856	−6.94228	36.0055	−3.15027
	1200–3000	84.5380	7.65425	−5.21161	1.36590	−1.29039	−17.3695
ZrCl$_4$(g)	298–1000	97.6615	37.1908	−56.6862	40.9692	−114.933	−5.75231
	1000–3000	107.8842	0.26679	−0.14893	0.03942	−0.04050	−9.70442
ZrBr(g)	298–1000	39.8911	−9.57879	11.2955	1.17196	−27.9636	−1.16748
	1000–3000	20.8924	27.2427	−12.5081	2.63691	−2.13228	18.1662
ZrBr$_2$(g)	298–1000	61.3957	3.26731	−4.31613	2.18559	−1.35430	−1.48186
	1000–3000	81.4275	−33.2447	21.8831	−5.65891	5.29375	−26.9603
ZrBr$_3$(g)	298–1100	79.6126	0.34771	30.0377	−34.4061	114.534	−1.93310
	1100–3000	84.4952	7.69558	−5.22281	1.36534	−1.28619	−13.5056
ZrBr$_4$(g)	298–1000	104.6637	12.3176	−18.8717	13.6798	−38.4287	−3.85789
	1000–3000	107.9370	0.21503	−0.12721	0.03505	−0.03697	−4.95040
ZrI(g)	298–1000	40.1860	−10.5311	13.2597	0.40806	−23.0510	−0.88708
	1000–3000	21.0583	27.2151	−12.3728	2.60109	−2.09609	18.2122
ZrI$_2$(g)	298–1000	62.3957	−0.67891	2.26308	−2.98039	14.2468	−0.80159
	1000–3000	81.3147	−33.0769	21.7809	−5.63013	5.26291	−25.7141
ZrI$_3$(g)	298–1000	83.6526	−17.5208	62.9525	−62.4890	205.615	−1.48181
	1000–3000	84.0796	8.28245	−5.56158	1.45548	−1.37753	−11.10471
ZrI$_4$(g)	298–1000	106.6762	4.99330	−7.49690	5.31689	−14.6042	−2.70046
	1000–3000	108.0882	−0.00873	0.00930	−0.00034	0.00411	−3.26823

treatment of these data is given in Table 7. Within the limits of uncertainty, the enthalpies of formation of zirconium tetrachloride derived from equilibrium measurements involving other species than zirconium tetrachloride, (865 ± 6) kJ mol^{-1} [146], and (863 ± 5) kJ mol^{-1} [147], agree well with the selected value derived from the vapour pressure measurements. The enthalpies of formation of mono-, di-, and tri-fluorides, chlorides, and iodides have been derived by a third-law evaluation of the equilibrium reactions given in Table 8.

Several authors reported mass spectrometric equilibrium studies in the Zr–F system. Murad and Hildenbrand [148] and Potter et al. [149] measured equilibrium constants of the reactions involving ZrF$_4$(g) and Ca(g). From the data of Murad and Hildenbrand, only the reaction leading to enthalpy of formation of ZrF$_3$ has been used. As discussed by Potter et al. [149], the ZrF$_2^+$ ion current (A.P. 12.0 ev) was wrongly associated with ZrF$_2$ instead of ZrF$_3$, making the results of Murad and Hildenbrand unreliable for ZrF$_2$. The reactions reported by Potter et al. have been used to calculate the enthalpies of formation of ZrF$_2$ and ZrF. Equilibrium measurements by Barkovskii et al. [150,151], involving only the Zr–F species, have not been used in the present evaluation, because no experimental data were reported. However, their results for ZrF$_3$, ZrF$_2$, and ZrF, $-(1079 \pm 15)$,

Table 7
The enthalpy of sublimation of ZrX_4 at 298.15 K

Authors	T/K	Method [a]	$\Delta_{sub}H_m$ (298.15 K)/kJ mol^{-1}	
			2nd-law	3rd-law
a. $ZrF_4(s) = ZrF_4(g)$				
Lauter (1948) [b] [130]	913–1178	S	236.2	240.8
Sense et al. (1954) [131]	890–1154	T	253.0±0.4	242.0 ± 0.6
Cantor et al. (1958) [132]	983–1081	S	234.5±2.6	239.9 ± 0.2
Galkin et al. (1963)[133]	710–825	K	217.9±7.3	232.4 ± 1.2
Akishin et al. (1963) [68]	681–913	K	248.2	242.7
Petzel (1964) [134]	951–1177	S	232.2±1.6	241.1 ± 0.3
Sidorov et al. (1965) [135]	769	M		243.1
Konings and Hildenbrand (1994) [c] [117]	696–856	TE	239.2±0.5	240.1 ± 0.1
			selected value:	240.0 ± 1.0
b. $ZrCl_4(s) = ZrCl_4(g)$				
Rahlfs and Fischer (1933) [31]	535–607	S	115.1±1.9	109.7 ± 0.2
Rogers et al. (1949) [d] [136]	510–610	S	113.3	110.3
Palko et al. (1958) [e] [34]	507–627	S	109.1±0.9	110.0 ± 0.1
	551–689	S	108.6±1.7	109.7 ± 0.2
Funika and Uchimura (1965) [137]	513–603	S	105.4±0.9	109.6 ± 0.1
Nisel'son et al. (1965) [35]	707–709	S		109.1 ± 0.1
Denisova et al. (1966) [138]	625–708	S	112.0±1.5	109.4 ± 0.2
Safronov et al. (1968) [139]	376–493	T	110.9±2.7	110.3 ± 0.4
Khodeev and Tsirel'nikov (1973) [140]	373–448	K	113.5±3.2	111.3 ± 0.4
Kim and Spink (1974) [8]	561–642	S	109.0±0.3	110.2
Ray et al. (1978) [141]	383–654	S	53.5	109.2
Tangri and Bose (1994) [142]	405–500	T	102.3±0.6	108.3 ± 0.3
c. $ZrCl_4(l) = ZrCl_4(g)$				
Bromberg (1958) [7]	728–793	S	110.5	108.4
Palko et al. (1958) [34]	714–741	S	109.2±1.6	108.2 ± 0.1
Nisel'son et al. (1965) [35]	711–773	S	115.1±1.2	108.9 ± 0.2
Denisova et al. (1967) [36]	710–775	S	111.0±2.0	108.9 ± 0.8
			selected value:	110.0 ± 1.0
d. $ZrBr_4(s) = ZrBr_4(g)$				
Rahlfs and Fischer (1933) [31]	538–633	S	116.5±1.1	116.4 ± 0.1
Schläfer and Skoludek (1962) [91]	494–620	S	119.3±9.2	115.8
Berdonosov et al. (1965) [143]	489–606	S	120.3±0.6	117.4 ± 0.1
Normanton and Shelton (1970) [144]	400–500	K	109.7±3.6	114.2
			selected value:	116.0 ± 2.0
e. $ZrI_4(s) = ZrI_4(g)$				
Rahlfs and Fischer (1933) [f] [31]	596–606	S	132.3±0.6	133.6 ± 0.1
Sale and Shelton (1965) [65]	425–500	K	124.9±0.2	130.3
Gerlach et al. (1967) [66]	393–453	S	112.3±0.3	129.8
Baev and Shelton (1973) [67]	473–613	S	93.5±0.7	113.7
Cubicciotti et al. (1978) [68]	410–480	TE	133.2±1.7	133.4 ± 0.1
			selected value:	133.4 ± 0.5

[a] S = static, E = effusion, M = mass spectrometry, T = transpiration, TE = torsion–effusion.
[b] Cited by Fischer et al. [145].
[c] This paper replaces older reports by Hildenbrand and Theard (1961) cited in Ref. [1].
[d] Equation obtained from graph.
[e] Points below 507 K rejected.[f] Points below 596 K rejected.

Table 8
Enthalpies of formation of the gaseous zirconium halides at 298.15 K calculated from equilibrium reactions

Species	Reaction	$\Delta_r H_m^o$ (298.15 K) kJ mol^{-1}	$\Delta_f H_m^o$ (298.15 K) kJ mol^{-1}	Ref.
$ZrF_3(g)$	$Ca(g) + ZrF_4(g) = CaF(g) + ZrF_3(g)$	118.1 ± 3.3	-1099 ± 10	[148]
$ZrF_2(g)$	$Ca(g) + ZrF_3(g) = CaF(g) + ZrF_2(g)$	130.3 ± 0.5	-515.0 ± 15	[149]
$ZrF(g)$	$2Ca(g) + ZrF_3(g) = 2CaF(g) + ZrF(g)$	253.8 ± 1.0	63 ± 15	[149]
$ZrCl_3(g)$	$Ca(g) + ZrCl_4(g) = CaCl(g) + ZrCl_3(g)$	64.6 ± 1.9	-524.8 ± 6.9	[149]
	$CaCl(g) + ZrCl_4(g) = CaCl_2(g) + ZrCl_3(g)$	-16.4 ± 3.3	-506.0 ± 8.9	[149]
			selected value: -515 ± 10	
$ZrCl_2(g)$	$ZrCl_2(g) + ZrCl_4(g) = 2ZrCl_3(g)$	-13.0 ± 3.5	-146 ± 15	[149]
$ZrCl(g)$	$ZrCl(g) + ZrCl_3(g) = 2ZrCl_2(g)$	-61.7 ± 2.2	283 ± 24	[149]
$ZrI_3(g)$	$\frac{1}{4}Zr(s) + \frac{3}{4}ZrI_4(g) = ZrI_3(g)$	137.3 ± 0.7	-129.5 ± 3.7	[154]
	$ZrI_4(g) = ZrI_3(g) + I(g)$	335.3 ± 0.3	-127.9 ± 4.2	[154]
			selected value: -128.4 ± 5.0	
$ZrI_2(g)$	$ZrI_4(g) + ZrI_2(g) = 2ZrI_3(g)$	-35.2 ± 2.3	134.1 ± 8.5	[154]
$ZrI(g)$	$ZrI(g) = Zr(g) + I(g)$	297.6 ± 1.7	408.2 ± 6.3	[154]

$-(484 \pm 12)$, and (63 ± 12) kJ mol^{-1}, respectively, are in good agreement with the selected values.

Potter et al. [149] also investigated equilibrium reactions in the Zr–Cl system, and their reported equilibrium constants have been used to calculate the enthalpies of formation of all zirconium sub-halides. Equilibrium measurements in the Zr–Cl system by Farber et al. [152] and Shelest and Safronov [153] have not been taken into account since these studies are not well documented and are subject to several uncertainties.

Kleinschmidt et al. [154] studied various reaction equilibria of the Zr–I system by high-temperature mass spectrometry. From their data, the enthalpies of formation of the lower gaseous zirconium iodides have been recalculated by the third-law method.

No studies have been made in the Zr–Br system. The selected enthalpies of formation have been estimated from the bond dissociation energies, $D_{298.15\,K}^o$ of the other halides (Table 9). The bond dissociation energies for the monochloride and monoiodide are 56 and 48 kJ mol^{-1} lower than the mean bond dissociation energies of the tetrachloride and tetraiodide, respectively, resulting in an estimated $D_{298.15\,K}^o = 375$ kJ mol^{-1} for zirconium monobromide. The bond dissociation energies for the dibromide, $D_{298.15\,K}^o = 471$ kJ mol^{-1}, and the tribromide, $D_{298.15\,K}^o = 434$ kJ mol^{-1}, have been derived in the same way.

Table 9
Stepwise bond dissociation energy ($D_{298.15\,K}^o$/kJ mol^{-1}) of $ZrX_n(g)$ (X = F, Cl, Br, I) at 298.15 K

n	F	Cl	Br	I
1	616 ± 16	437 ± 25	375 ± 26	298 ± 19
2	656 ± 21	550 ± 28	471 ± 35	381 ± 11
3	663 ± 21	490 ± 18	434 ± 35	369 ± 10
4	652 ± 15	477 ± 10	412 ± 26	334 ± 17

5. Discussion and conclusion

The enthalpy of formation of the solid zirconium halides per number of bonds as a function of the number of halogen atoms is given in Fig. 2. It can be seen that, for the chlorides and iodides, $\Delta_f H_m^o/n$ increases steadily as the number of halogen atoms decreases. The bromides show a somewhat irregular pattern which is most probably due the fact that the values are based on a limited number of experimental disproportionation studies, which are subject to the uncertainty of the phase boundaries of the subbromides.

The enthalpies of formation of the gaseous halides obtained in this study differ considerably from the values given in the JANAF tables [1]; this is especially the case for the lower halides and is due to the fact that more accurate values for the molecular parameters can be derived from measurements and estimations.
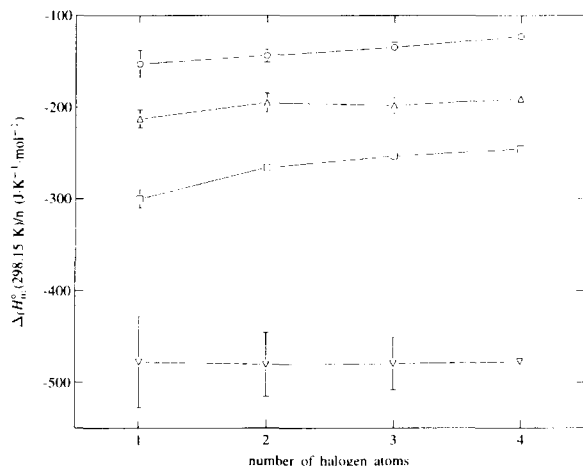
Fig. 2. Enthalpy of formation of $ZrX_n(s)$ per number of halogen atoms (∇=F, $\square$=Cl, $\triangle$=Br, $\bigcirc$=I.
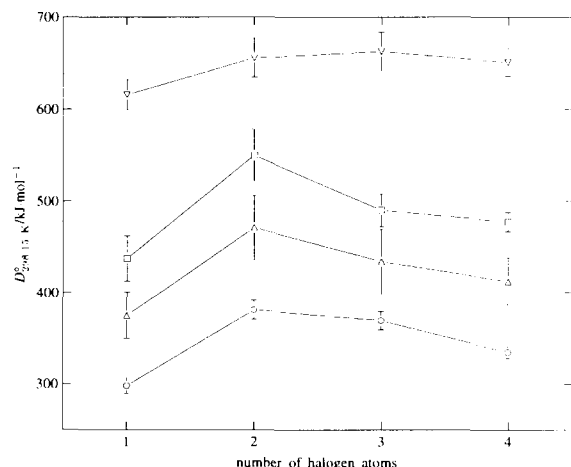

Fig. 3. Stepwise bond dissociation energy of $ZrX_n(g)$ (∇=F , $\square$=Cl, $\triangle$=Br, $\bigcirc$=I.

A graphical comparison of the bond dissociation energies for gaseous zirconium halides is given in Fig. 3. For the iodides and chlorides, the trends observed, $D_1 < D_2 > D_3 > D_4$ and $D_4 > D_1$, are identical. The only difference for the fluorides is the interchange of D_2 and D_3. Judging from the large uncertainties of the bond dissociation energies arising from (1) a limited number of equilibrium studies, and (2) uncertainties in the free energy functions of the lower halides, this interchange could be accidental. At the time of publication, Potter et al. [149] derived

$D_2 > D_3$ for the fluorides, which again indicates the large influence of changing molecular parameters on the free energy functions and hence the enthalpy of formation.

It is also interesting to compare our results with those obtained by ab initio calculations for ZrF, ZrF_2, ZrCl, and $ZrCl_2$ [155,156]. The monohalides compare very well, except for the electronic ground state, $^2\Delta$ according to the calculations and $^4\Sigma$ according to experimental results for zirconium monochloride [120]. The dihalides show more differences. The calculations [156] show ZrF_2 to be linear instead of the generally accepted bent geometry [114]. The calculated bond distance for $ZrCl_2$ is considerably larger than our empirical value. The calculated bonding energies are about 50 kJ mol^{-1} lower, which might be correlated to the differences in the structural parameters.

It is clear that there are still many gaps in the knowledge concerning the thermodynamic properties of zirconium halides. For the condensed phase, zirconium fluoride and chloride have been studied rather well. Low-temperature heat capacity measurements for all zirconium bromides and iodides would be helpful in obtaining a clear view of a possible trend in the entropy values. As for the zirconium chlorides, solution calorimetry is probably the most suitable method for determining the enthalpies of formation of the subbromides and subiodides.

For the gas phase species, several gaps in the knowledge of the structural parameters have to be filled. For the monohalides, all information can be deduced from investigations of the electronic band systems. Matrix isolation studies would be helpful in obtaining the vibrational frequencies and structural information of the di- and trihalides.

The zirconium–bromine system is the only system so far that has not been studied by mass spectrometry. However, additional equilibrium studies in the other systems will also be necessary to minimize the large uncertainties of the enthalpies of formation.

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