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Thermodynamic properties of zirconium chlorides

I. The standard molar enthalpy of formation, the low-temperature heat capacity, the standard molar entropy, and the standard molar Gibbs energy of formation of zirconium trichloride

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The enthalpies of the reactions of $ZrCl_4(cr)$ and of $ZrCl_4(cr)$ with 3 mol·dm⁻³ HCl solution were measured in a 0.1 dm³ reaction vessel of the isoperibol calorimeter LKB-8700. The enthalpy change of the resulting reaction:

 $ZrCl_3(cr) + HCl(sln, 17.06H_2O) = ZrCl_4(cr) + 0.5H_2(g),$

was found to be $\Delta_r H^{\circ}_{m}(298.15 \text{ K}) = -(62.6 \pm 2.7) \text{ kJ} \cdot \text{mol}^{-1}$ which leads to $\Delta_r H^{\circ}_{m}(\text{ZrCl}_3, \text{ cr}, 298.15 \text{ K}) = -(753.9 \pm 3.0) \text{ kJ} \cdot \text{mol}^{-1}$. Heat-capacity measurements between 7 and 312 K were performed on a pure sample of $\text{ZrCl}_3(\text{cr})$. The following standard molar thermodynamic quantities are reported at $T^{\circ} = 298.15 \text{ K}$: the heat capacity: $C^{\circ}_{p.m}(T^{\circ}) = (92.871 \pm 0.089) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$; the entropy: $S^{\circ}_{m}(T^{\circ}) = (137.50 \pm 0.28) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$; the entrapy increment: $\{H^{\circ}_{m}(T^{\circ}) - H^{\circ}_{m}(0)\} = (19239 \pm 29) \text{ J} \cdot \text{mol}^{-1}$; and the Gibbs energy of formation: $\Delta_r G^{\circ}_{m}(T^{\circ}) = -(685.0 \pm 1.5) \text{ kJ} \cdot \text{mol}^{-1}$.

1. Introduction

Literature values of the enthalpy of formation of $ZrCl_3(cr)$ have large discrepancies and are based on unreliable measurements.⁽¹⁻³⁾ There is no publication about heatcapacity measurements on zirconium trichloride. In the present work the enthalpy of formation of $ZrCl_3(cr)$ was determined by calorimetric measurements of solution of $ZrCl_3(cr)$ in 3 mol \cdot dm⁻³ HCl at 298.15 K.

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2. Experimental

ZrCl₄ was synthesized by heating zirconium shavings in a flow of dry chlorine at 650 to 690 K and then purified by sublimation in a flow of dry hydrogen. ZrCl₃ was synthesized by reduction of liquid ZrCl₄ with Zr at 773 K and a pressure of 5 MPa.⁽⁴⁾ For the final purification from ZrCl₄ the sample of ZrCl₃ was heated under the reduced pressure of 1 Pa at 473 K. Table 1 shows the results of chemical analyses. The samples of ZrCl₃ and ZrCl₄ were analysed for amount of Zr by mass in form of ZrO₂ and for chlorine by potentiometric titration with AgNO₃. The analysis of ZrCl₄ and ZrCl₃ by emission spectroscopy did not show Hf, Ti, Ta, Hb, (mass fractions < 1×10^{-6}) and gave mass fractions of Cu, Fe, and Si about 1×10^{-5} . The solution of 3.055 mol dm^{-3} HCl was prepared from a "pro analysi" commercial sample additionally purified by distillation and doubly distilled water.

The measurements of enthalpy change were carried out in the 0.1 dm³ reaction vessel of an isoperibol calorimeter LKB-8700. The design of the calorimeter, control measurements with standard substances, and the calculation method have been described elsewhere.⁽⁵⁻⁶⁾ The samples of zirconium chlorides were ground in a jasper mortar and loaded into ampoules in a box filled with dry argon. The ampoules were sealed without contact of the samples with air. The masses of the samples were calculated by taking into account the effect of buoyancy, including the effect of having argon (instead of air) in the ampoules. The ampoules were weighed on a microbalance "Mettler M5SA" to $\pm 1 \mu g$. The masses of samples are judged to be accurate to 0.01 per cent.

Before each experiment the calorimetric solution (solution 1: $3.055HCl + 52.123H_2O$) was saturated with a flow of hydrogen during 20 min. The hydrogen was prepared by reaction of HCl with Zn. It was bubbled through H_2O , through some portion of solution 1, and then slowly through the calorimetric solution in the reaction vessel. The times of the calorimetric experiments involving reaction (1) and (2) were from 20 to 40 min.

The low-temperature heat-capacity measurements were carried out in a vacuum adiabatic-shield calorimeter.⁽⁷⁾ The calorimeter was made from nickel and had an internal volume of 0.01 dm³ and mass of 31.8 g. The mass of the sample of $ZrCl_3$ was 7.0986 g. Temperatures were measured with a capsule-type platinum resistance thermometer. The heat capacity of the empty calorimeter was measured from 6.1 to 336 K at 99 points and an equation derived from these measurements was used for the calculations. Control measurements were made with pure benzoic acid and gave agreement with literature values.⁽⁸⁾

Substance	10	$r^{2}w(Zr)$	10 ² w(Cl)		
	calc.	obs.	calc.	obs.	
ZrCl ₄	39.11	39.0±0.1	60.89	60.8 ± 0.1	
ZrCl ₃	46.13	46.1 ± 0.1	53.87	53.8 ± 0.1	

TABLE 1. Mass fractions w resulting from chemical analysis of zirconium chlorides

3. Results

Results of the measurements of the enthalpies of the reactions of $ZrCl_3(cr)$ and $ZrCl_4(cr)$ with 3.055 mol·dm⁻³ HCl are given in table 2. Compositions of the final solutions (sln 2) in reactions (1) and (2) differed only in the content of HCl (0.003 to 0.007 mol·dm³). The uncertainties quoted for the enthalpies of reactions (1) and (2) are the 95 per cent confidence intervals.

Combination of reactions (1) and (2) gives:

$$ZrCl_{3}(cr) + HCl(sln, 17.06H_{2}O) = ZrCl_{4}(cr) + 0.5H_{2}(g),$$
(3)
$$\Delta_{r}H_{m}^{\circ}(3) = \Delta_{r}H_{m}^{\circ}(1) - \Delta_{r}H_{m}^{\circ}(2)$$
$$= \{(-319.2 \pm 2.6) - (-256.58 \pm 0.88)\} \text{ kJ} \cdot \text{mol}^{-1}$$
$$= -(62.6 \pm 2.7) \text{ kJ} \cdot \text{mol}^{-1}.$$

The following enthalpies of formation are known:

$$\Delta_{\rm f} H^{\circ}_{\rm m}({\rm ZrCl_4, \ cr, \ 298.15 \ K}) = -(979.8 \pm 1.2) \ \rm kJ \cdot mol^{-1},^{(9)}$$

$$\Delta_{\rm f} H^{\circ}_{\rm m}({\rm HCl, \ sln, \ 17.06H_2O}) = -(163.27 \pm 0.09) \ \rm kJ \cdot mol^{-1}.^{(10)}$$

These values were used to calculate:

$$\Delta_{\rm f} H^{\circ}_{\rm m}({\rm ZrCl}_3, \, {\rm cr}, \, 298.15 \, {\rm K}) \\ = \{(-979.8 \pm 1.2) - (-163.27 \pm 0.09) - (-62.6 \pm 2.7)\} \, {\rm kJ} \cdot {\rm mol}^{-1} \\ = -(753.9 \pm 3.0) \, {\rm kJ} \cdot {\rm mol}^{-1}.$$

Results of measurements of the low-temperature heat-capacity at 97 temperatures from 7.01 to 312 K are given in table 3. The temperature increment ΔT for each experiment was approximately 1 K for $\langle T \rangle < 20$ K and 4 K for $\langle T \rangle > 20$ K. No

TABLE 2. Enthalpies of reaction of $ZrCl_3(cr)$ and $ZrCl_4(cr)$ with 3.055 mol dm^{-3} HCl at 298.15 K: *n* is the amount of substance, ΔH is the measured enthalpy of the reaction, $\Delta_{vap}H$ is the correction for the enthalpy of vaporization of water in hydrogen evolved in reaction (1), and $\Delta_r H_m^\circ$ is the standard molar enthalpy of reaction. Values of ΔH include a correction: (0.044 to 0.046) J, for enthalpy of vaporization of the calorimetric solution into air in each ampoule⁽⁵⁾

$\frac{10^9n}{\text{mol}}$	$\frac{10^{3}\Delta H}{J}$	$\frac{10^3 \Delta_{\rm vap} H}{\rm J}$	$\frac{\Delta_{\rm r} H_{\rm m}^{\circ}}{\rm kJ\cdot mol^{-1}}$	$\frac{10^9n}{\text{mol}}$	$\frac{10^{3}\Delta H}{\mathrm{J}}$	$\frac{10^{3}\Delta_{\rm vap}H}{\rm J}$	$\frac{\Delta_{\rm r} H_{\rm m}^{\circ}}{\rm kJ\cdot mol^{-1}}$				
Reaction (1): $ZrCl_3(cr) + HCl(sln 1) = (sln 2) + 0.5H_2(g)$											
281005	90604	177	-323.06	466120	148866	293	-320.00				
375428	120577	236	-321.80	654823	206685	412	-316.26				
449231	143308	283	-319.64	692327	217854	435	-315.30				
453558	144162	285	-318.48			mean:	-319.2 ± 2.6				
Reaction (2): $\operatorname{ZrCl}_4(\operatorname{cr}) + \operatorname{HCl}(\operatorname{sln} 1) = (\operatorname{sln} 2)$											
451165	116124		-257.39	604185	154658		255.98				
510818	130397		-255.27	714041	183569		-257.09				
556212	143119	—	-257.31			mean:	-256.58 ± 0.88				
574874	147408		-256.42								

$\langle T \rangle$	C_{p.m}	$\langle T \rangle$	$C_{p,\mathbf{m}}^{\circ}$	$\langle T \rangle$	$C_{p,m}^{\circ}$	$\langle T \rangle$	$C_{p,m}^{\circ}$
K	$J \cdot K^{-1} \cdot mol^{-1}$	К	$J \cdot K^{-1} \cdot mol^{-1}$	KJ	$V K^{-1} mol^{-1}$	K	$J \cdot K^{-1} \cdot mol^{-1}$
7.01	0.800	58.22	36.116	133.73	72.124	214.05	86.895
7.91	1.041	61.16	38,127	136.73	72.796	218 11	87 291
9.75	1.638	63.57	39.683	139.69	73.648	222.14	87 569
10.79	2.087	69.52	43.272	142.60	74.429	225.43	87 765
12.10	2.864	72.04	44.787	145.47	75.235	228.88	88 447
13.44	3.588	74.42	46.182	148.76	75.865	232.29	88.619
14.68	4.456	76.70	47.515	152.23	76.642	235.66	88 872
15.86	5.167	79.14	48.882	155.77	77.461	239.01	89.215
17.00	6.079	81.65	50.139	159.68	78.302	243.25	89.563
18.12	6.850	85.28	52.084	163.22	79.205	248.17	90.011
19.22	7.663	88.34	53.766	166.70	80.070	263.05	91.034
20.32	8.487	89.09	54.194	170.15	80.533	267.79	90.953
24.73	11.896	92.05	55,625	173.55	81.281	272.46	91.486
26.12	13.023	94.91	56,944	175.33	81.486	277.09	91 776
27.75	14.369	97.48	58.156	176.92	81.926	281.88	97 374
32.78	18.169	100.16	59,411	178.75	82.035	286.62	92.316
34.74	19.703	103.48	60.862	180.26	82.520	291.51	92.435
36.53	21.061	107.25	62.468	181.14	82.571	297.65	93 185
40.89	24.225	110.88	63.969	185.91	83.001	301.34	92.865
42.92	25.672	114.40	65.324	190.05	83.692	304.94	93.264
44.92	27.170	117.83	66.579	194.15	84.514	308.56	93.372
49.71	30.616	121.15	67.724	198.21	84.656	312.15	93.778
51.54	31.693	124.39	69.024	202.23	85.487		
53.39	32.994	127.57	69.980	206.20	85.996		
55.40	34.203	130.68	71.043	210.14	86.492		

TABLE 3. Experimental heat capacities of $ZrCl_3$ at constant pressure $M(ZrCl_2) = 197.58 \text{ g} \cdot \text{mol}^{-1}$

TABLE 4. Thermodynamic functions of $ZrCl_3(cr)$ to 310 K. $R = 8.3143 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$

T	$C_{p,m}^{\circ}(T)$	$\Delta_0^{\tau} S^\circ_{\mathfrak{m}}(T)$	$\Delta_0^T H_{\mathfrak{m}}^{\circ}(T)$	$\Phi_{\mathfrak{m}}^{\circ}(T,0)$	T	$C^{\circ}_{p.m}(T)$	$\Delta_0^T S^\circ_{\mathfrak{m}}(T)$	$\Delta_0^T H^\circ_{\mathfrak{m}}(T)$	$\boldsymbol{\varphi}_{\boldsymbol{\mathfrak{m}}}^{\circ}(T,0)$
K	R	R	R·K	R	K	R	R	<i>R</i> · K	R
8	0.12362	0.0363	0.2178	0.0091	150	9.1604	9.443	767.2	4.327
9	0.16671	0.0534	0.3629	0.0130	160	9.4303	10.043	860.2	4.667
10	0.21215	0.0732	0.5519	0.0180	170	9.6976	10.623	955.8	5.000
15	0.55546	0.2187	2.403	0.0585	180	9.8980	11.183	1053.8	5.327
20	0.99183	0.4370	6.251	0.1245	190	10.073	11.722	1153.8	5.651
25	1.4592	0.7083	12.38	0.2134	200	10.240	12.243	1255.3	5.967
30	1.9298	1.016	20.84	0.3211	210	10.401	12.747	1358.5	6.277
35	2.3915	1.348	31.66	0.4438	220	10.517	13.234	1463.1	6.583
40	2.8400	1.697	44.74	0.5785	230	10.629	13.704	1568.9	6.882
45	3.2746	2.057	60.03	0.7227	240	10.741	14.159	1675.8	7.176
50	3.6907	2.424	77.46	0.8744	250	10.843	14.599	1783.7	7.464
60	4.4897	3.167	118.4	1.194	260	10.921	15.026	1892.5	7.747
70	5.2400	3.916	167.1	1.530	270	10.987	15.440	2002.1	8.025
80	5.9344	4.663	223.0	1.875	280	11.058	15.840	2112.3	8.297
90	6.5681	5.399	285.5	2.225	290	11.120	16.229	2223.2	8.564
100	7.1353	6.121	354.1	2.579	300	11.182	16.608	2334.7	8.825
110	7.6497	6.826	428.1	2.934	310	11.260	16.976	2446.9	9.082
120	8.1048	7.510	507.0	3.286	273.15	11.009	15.567	2036.7	8.110
130	8.5182	8.176	590.1	3.637	298.15	11.170	16.538	2314.0	8.776
140	8.8700	8.821	677.0	3.985		± 0.011	± 0.034	± 3.5	± 0.013

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anomalies were observed. The experimental heat capacities were smoothed by spline functions.⁽¹¹⁾ Deviations of the experimental values from the smoothed values were not more than 0.4 per cent in the temperature range 20 to 310 K and 1.3 to 2.4 per cent at T < 20 K. The smoothed heat capacities and calculated thermodynamic functions are given at selected temperatures in table 4 for T > 8 K. Thermodynamic functions were computed with help of the coefficients of the cubic spline. Extrapolation to $T \rightarrow 0$ was carried out using Debye T^3 limiting law and yielded $S_m^{\circ}(8 \text{ K}) = 0.3 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ or 0.22 per cent from the standard molar entropy at 298.15 K.

4. Discussion

The enthalpy of formation of ZrCl₃ found in this work, $-(753.9\pm3.0)$ kJ·mol⁻¹, agrees within the limits of the uncertainties with the result of our less accurate earlier measurements,⁽¹⁾ $-(761.5\pm8.4)$ kJ·mol⁻¹. The other values were derived from high-temperature studies of the equilibrium of different reactions with ZrCl₂ and were in the range from -701 to -870 kJ·mol^{-1.(2-3)} As one can see from table 2 the molar enthalpy of reaction (1) depends upon the amount of substance. That was rather unexpected and we did not find any reasonable explanation for it. There is no such dependence for reaction (2). We suppose that both reactions are completely finished during the time of the measurements. Our preliminary special investigations showed that the times of solution of ZrCl₃ and ZrCl₄ were not more than 1 to 2 min. The solution of ZrCl₃ was slightly orange at first because of hydration of the Zr^{3+} ion but after 3 to 4 min the solution became colourless as a result of oxidation of Zr^{3+} to Zr^{4+} . Analysis of the (temperature, time) calorimetric curves definitely showed the ends of the temperature rise for both reactions. The molalities of the final solutions in both reactions were practically the same. The high molality of HCl and the very small molality of zirconium in the final solutions prevented any hydrolysis or polymerization of Zr⁴⁺ ions which did not form any complexes with chloride ions under those conditions and were present as monomeric ions.⁽¹²⁾ The least-squares treatment of the reaction (1) results yielded the equation: $\Delta_r H_m^\circ = -\{328.58 + 19984(n/mol)\} \text{ kJ} \cdot \text{mol}^{-1}$, where n is the amount of substance of ZrCl₃. For $n = 5.685 \times 10^{-4}$ mol, the average amount of substance of ZrCl₄ in reaction (2), this equation gives $\Delta_r H_m^{\circ}(1) = -(317.71 \pm 0.31) \text{ kJ} \cdot \text{mol}^{-1}$. This value differs from the mean value in table 2 by about $1.4 \text{ kJ} \cdot \text{mol}^{-1}$, which is less than the uncertainty of the mean value, $2.6 \text{ kJ} \cdot \text{mol}^{-1}$.

There are no thermodynamic functions for $ZrCl_3(cr)$ except estimated values given in reference books.^(9, 10, 13) The following values are known:⁽⁹⁾

$$S_{\rm m}^{\circ}({\rm Zr, \ cr, \ 298.15 \ K}) = (38.98 \pm 0.30) \ {\rm J} \cdot {\rm K}^{-1} \cdot {\rm mol}^{-1};$$

 $S_{\rm m}^{\circ}({\rm Cl}_2, \ {\rm g}, \ 298.15 \ {\rm K}) = (222.965 \pm 0.010) \ {\rm J} \cdot {\rm K}^{-1} \cdot {\rm mol}^{-1}.$

These values were used to calculate:

 $\Delta_{f} S_{m}^{\circ}(ZrCl_{3}, cr, 298.15 \text{ K})$ $= \{(137.50 \pm 0.28) - (38.98 \pm 0.30) - (3/2)(222.965 \pm 0.010)\} \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ $= -(235.93 \pm 0.41) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1};$

$$\Delta_{f} G_{m}^{\circ}(ZrCl_{3}, cr, 298.15 \text{ K}) = \{(-755.3 \pm 1.5) - 298.15 \times (-235.93 \pm 0.41)/10^{3}\} \text{ kJ} \cdot \text{mol}^{-1} = -(685.0 \pm 1.5) \text{ kJ} \cdot \text{mol}^{-1}.$$

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