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Electron Affinity of Iron(III) Chloride

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The electron affinity of $FeCl_3$ has been determined by Knudsen cell mass spectrometry [$E_{ea}(FeCl_3) = 4.3 \pm 0.2$ eV]; the electron affinity of iron chloride is higher than that of iron fluoride.

So far, no data have been published concerning the electron affinities (E_{ea}) of inorganic chlorides. Comparison of the oxidation properties of fluorides and chlorides suggested that E_{ea} of fluorides should be somewhat higher than those of chlorides. The purpose of the present work was to obtain the E_{ea} value for the iron trichloride molecule. Iron trifluoride belongs to a class of compounds with high E_{ea} and its electron affinity has been determined previously.[1]

Measurements were carried out using an MI-1201 mass spectrometer equipped with a combined ion source.[2] Experimental details and calculation methods have been reported previously.[2] E_{ea} ($FeCl_3$) was calculated from the enthalpy of addition of a Cl^- anion to an $FeCl_2$ molecule [eqn. (1)].

$$FeCl_2 + Cl^- \rightarrow FeCl_3^- \qquad (1)$$

Since the enthalpy of reaction (2) is known,[3] the electron

$$FeCl_2 + Cl \rightarrow FeCl_3 \qquad (2)$$

affinity of iron(III) chloride may be calculated as the difference equilibrium constants.

$$E_{ea}(FeCl_3) = \Delta H^\circ_0(2) - \Delta H^\circ_0(1) - E_{ea}(Cl).$$

In order to find $\Delta H^\circ_0(1)$ an experimental study of equilibria (3)–(5) has been performed and $K_r(3)$–$K_r(5)$ were determined.

$$FeCl_2 + AlCl_4^- \rightleftharpoons AlCl_3 + FeCl_3^- \qquad (3)$$

$$FeCl_2 + AlFCl_3^- \rightleftharpoons AlFCl_2 + FeCl_3^- \qquad (4)$$

$$FeCl_2 + AlF_2Cl_2^- \rightleftharpoons AlF_2Cl + FeCl_3^- \qquad (5)$$

Table 1 Typical mass spectra of thermal negative ions and of positive ions produced by electron impact for systems I and II; $U_{ion} = 70$ eV

System I[a]

Ion	I^b (%)	Ion	I (%)	Ion	I (%)
Fe^+	4.9	Al^+	2.0	$FeCl_3^-$	97.4
$FeCl^+$	45.1	$AlCl^+$	8.6	$FeCl_4^-$	1.9
$FeCl_2^+$	47.1	$AlCl_2^+$	100.0	$AlCl_4^-$	100.0
KCl^+	3.8	$AlCl_3^+$	34.8		

System II[c]

Ion	I (%)	Ion	I (%)	Ion	I (%)	Ion	I (%)
Fe^+	5.5	AlF^+	31.7	$FeCl_3^-$	8.5	$AlF_2Cl_2^-$	100.0
$FeCl^+$	44.1	$AlFCl^+$	52.4	AlF_4^-	19.9	$AlFCl_3^-$	33.2
$FeCl_2^+$	55.5	AlF_2^+	100.0	AlF_3Cl^-	92.8	$AlCl_4^-$	3.8
$AlCl^+$	3.1	AlF_2Cl^+	42.1				
$AlCl_2^+$	16.0	$AlFCl_2^+$	13.4				

[a] System I: AlOCl–$FeCl_2$–KCl, $T = 1010$ K. [b] I = relative intensity of the ionic current. [c] System II: AlOCl–$FeCl_2$–KCl, $T = 1015$ K.

Table 3 Bond dissociation enthalpies for certain fluoride and chloride anions

Reaction	ΔH°_0/kJ mol^{-1} (ref.)
$AlF_4^- \rightarrow AlF_3 + F^-$	488 ± 10 (8)
$AlCl_4^- \rightarrow AlCl_3 + Cl^-$	321 ± 12 (4)
$LaF_4^- \rightarrow LaF_3 + F^-$	431 ± 10 (9)
$LaCl_4^- \rightarrow LaCl_3 + Cl^-$	287 ± 15 (10)[a]
$FeF_3^- \rightarrow FeF_2 + F^-$	367 ± 15 (1)
$FeCl_3^- \rightarrow FeCl_2 + Cl^-$	296 ± 16 (this work)
$SiF_5^- \rightarrow SiF_4 + F^-$	251 ± 17 (11)
$SiCl_5^- \rightarrow SiCl_4 + Cl^-$	105 ± 8 (11)

[a] ΔH°_{298} is given.

A mixture of $FeCl_2$ and AlOCl (I) or $FeCl_2$, AlOCl and AlF_3 (II) with a small amount of KCl was introduced into a platinum effusion cell. Molecules $FeCl_2$, $AlCl_3$ (I and II); $AlFCl_2$, AlF_2Cl (II) and ions $FeCl_3^-$, $FeCl_4^-$ (I and II); $AlCl_4^-$ (I); $AlFCl_3$, $AlF_2Cl_2^-$, AlF_3Cl^- (II) were found in the gaseous phase. The ratios of their partial pressures were measured and used to calculate the equilibrium constants. Determination of the partial pressures of the neutral molecules required the interpretation of the mass spectra of the positive ions, obtained by electron impact in system II (Table 1). The mass spectra of individual molecules $FeCl_2$ (obtained in the present study), $AlCl_3$, AlF_2Cl and $AlFCl_2$[4] were used to interpret the mass spectra. In system I there was no superposition of the mass spectra. In order to determine the equilibrium constants, the additive rule and the atomic ionisation cross-sections were used.[5] The equilibrium constants were used for the Third law calculations. The thermodynamic functions for $FeCl_2$, $FeCl_3$, $AlCl_3$ and ions $AlF_nCl_{4-n}^-$ (n = 0–3) necessary for the calculations were taken from refs. 3, 6 and 4 respectively. The thermodynamic functions of the $FeCl_3^-$ ion were calculated from the spectroscopic and molecular constants for the $FeCl_3$ molecule.[7] Only the degeneracy of the major electron state has been changed ($g_0 = 5$ instead of $g_0 = 6$).

Examples of the experimental mass spectra of systems I and II are presented in Table 1. The results of the measurements are presented in Table 2 and a $\Delta H^\circ_0(2)$ value of 304 ± 16 kJ mol^{-1} has been found from the enthalpies of reactions (4)–(6). Bond dissociation enthalpies $\Delta H^\circ_0(AlCl_3 - Cl^-) = 321 \pm 12$, $\Delta H^\circ_0(AlFCl_2 - Cl^-) = 314 \pm 12$, $\Delta H^\circ_0(AlF_2Cl - Cl^-) = 311 \pm 12$ kJ mol^{-1}[4] were used. The electron affinity of $FeCl_3$ was found to be 417 ± 17 kJ mol^{-1} (4.3 ± 0.2 eV).

The obtained results are quite unexpected. From the data of Table 3 it is evident that the bond dissociation enthalpy $\Delta H^\circ_0(FeCl_2 - Cl^-)$ is approximately 100 kJ mol^{-1} higher than could have been anticipated. This leads to an E_{ea} ($FeCl_3$) value

Table 2 Enthalpies of the reactions studied

No.	Reaction	T/K	ΔH°_0/kJ mol^{-1}	Source
3	$AlCl_3 + FeCl_3^- \rightarrow AlCl_4^- + FeCl_2$	998–1010	− 22.0 ± 0.4[a]	This work
4	$AlFCl_2 + FeCl_3^- \rightarrow AlFCl_3^- + FeCl_2$	1005–1039	− 20.9 ± 0.3[a]	This work
5	$AlF_2Cl + FeCl_3^- \rightarrow AlF_2Cl_2^- + FeCl_2$	1005–1039	− 15.5 ± 1.3[a]	This work
1	$FeCl_2 + Cl^- \rightarrow FeCl_3^-$		− 296 ± 16	This work
2	$FeCl_2 + Cl \rightarrow FeCl_3$		− 227 ± 5	Ref. 3
6	$FeCl_2 + e \rightarrow FeCl_3^-$		− 417 ± 17	This work

[a] Reproducibility errors given.

about 1 eV higher than that for FeF_3. In this study the conventional method for ion–molecule equilibria measurements was employed. Accurate equilibrium data have been obtained by this method for many halide and oxide systems.[1,2,8,9]

The agreement between results obtained using different standards (Table 2) confirms the achievement of thermodynamic equilibrium in reactions (3)–(5). Is the correlation between the electron affinities of fluoride and chloride a rule or merely an exclusion from the rule? According to the calculations of the authors of ref. 12 for the hypothetical trihalides of beryllium and magnesium, $E_{ea}(BeCl_3) > E_{ea}(BeF_3)$, and $E_{ea}(MgCl_3) > E_{ea}(MgF_3)$.

The transition metal fluorides (PtF_6, MnF_4, IrF_6 . . .) are strong oxidising agents, capable of oxidising Xe or O_2; the chlorides possess no such properties. However, it should be taken into account that from a thermodynamic point of view (Born–Haber cycle) the oxidising properties are determined not only by the electron affinity of fluoride (or chloride) but also by the lattice energy of the compound formed ($O_2{}^+PtF_6{}^-$ and the like). This lattice energy, in the case of chlorides, should be considerably lower (estimated according to the Kapustinskii equation).

Preliminary results obtained in our laboratory also indicate high electron affinities for $CrCl_3$ and $CrCl_4$.

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