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Thermodynamic study and assessment of the fluorine-iron system

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Context and goals

Iron corrosion in fluorinated atmosphere

- FeF₂ and FeF₃ as corrosion products
- improve the Fe-F thermodynamic description
- Fe-F database built using CALPHAD method

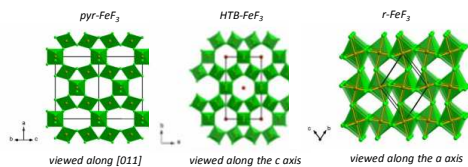
Lithium ion batteries

- FeF₃ as electrode, especially cathode material
- synthesis of nanostructured material => effect on ΔG°_f => nano-CALPHAD

Literature review

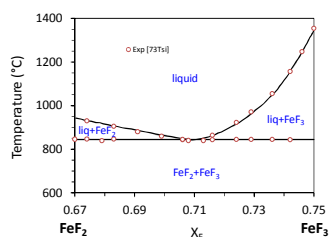
Crystal structure

Compound	Symmetry	Space group	Cell parameters
FeF ₂	tetragonal	P42/mnm	a=4.9696±0.002 Å [58Bau] c=3.1796±0.003 Å
FeF ₃	cubic (pyrochlore)	Fd3m	a=10.325±0.002 Å [86Pap]
	hexagonal (HTB)	Cmcm	a=7.423±0.003 Å [83Leb] b=12.730±0.004 Å c=7.526±0.003 Å
	rhomboedric (ReO ₃)	R-3C	a=5.362±0.001 Å [92Leb] α=57.99±0.01°



Phase diagram

- Only one experimental phase diagram determined by Differential Thermal Analysis between FeF₂ and FeF₃ [73Tsi]



- Discrepancies on the FeF₂ melting temperature (950 °C [73Tsi], 975 °C [89Joh] or 1100 °C [98Cha])
- No FeF₃ fusion: sublimation without melting

Thermodynamic properties

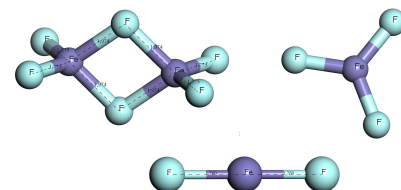
Solid Compounds	$\Delta H^{\circ}_{f,298\text{K}}$ (kJ/mol)	Experimental method	Reference
FeF ₂	-710.12	Mass spectrometry (2 nd law)	[81Sch]
	-715.5±0.5	Mass spectrometry	[81Sch]
	-705.8±41.8	Mass spectrometry (3 rd law)	[28Jel]
FeF ₃	-989.6±2.2	Calometric bomb	[81Joh]
	-1037.6±4.5	F.e.m (3 rd law)	[81Sch]
	-1056	Mass spectrometry (3 rd law)	[28Jel]
	-1043	Mass spectrometry (2 nd law)	[28Jel]
	-993	Mass spectrometry (2 nd law)	[37Dom]
	-990.8±2.1	Calometric bomb	[79Fer]

- Good agreement for $\Delta H^{\circ}_{f,298\text{K}}$ (FeF₂, cr) and $\Delta G^{\circ}_{f,T}$ (FeF₂, cr)
- $\Delta H^{\circ}_{f,298\text{K}}$ (FeF₃, cr) data scattered
- No thermodynamic properties for gaseous molecule Fe₂F₆ and only estimations for FeF₃

First principle calculations

- Calculations on gaseous molecules performed using Density Functional Theory implemented in DMol3 software
- Generalized gradient approximation for exchange and correlation energy (GGA)
- Spin of iron atoms taken into account

Molecules	$\Delta H^{\circ}_{f,298\text{K}}$ (kJ/mol)	Reference
FeF ₂	-387.9 -389.5	This work [98Cha]
FeF ₃	-660.8 -820.9	This work [98Cha]
Fe ₂ F ₆	-1472.5	This work



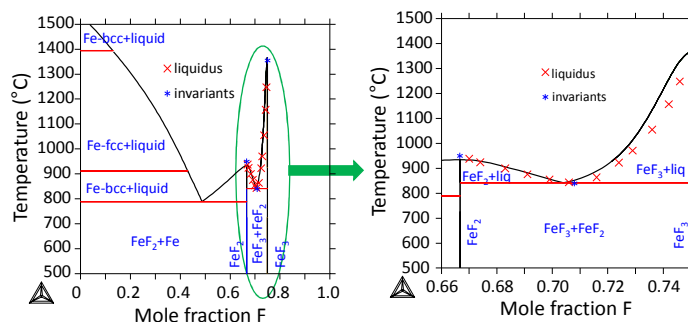
Optimisation (in progress)

Modeling

- At first, selected literature data from [73Tsi] for optimisation
- Liquid associated model : (Fe, FeF₂, FeF₃)
- Hypothetic pure liquid FeF₃ at high pressure
- Interaction parameters : ⁰L(FeF₂, FeF₃)=514668-501xT
¹L(FeF₂, FeF₃)=29253

Results

- $\Delta H^{\circ}_{f,298\text{K}}$ (FeF₂,cr)=-713 kJ/mol
- $\Delta H^{\circ}_{f,298\text{K}}$ (FeF₃,cr)=-990 kJ/mol



Further work

- DTA experiments to check the phase diagram between FeF₂ and FeF₃ and between Fe and FeF₂
- FeF₂ fusion temperature measurement
- Optimisation of the Fe-F system taken into account the new experimental data
- Effect of the nanostructure of FeF₂ and FeF₃ on the phase diagram and thermodynamic properties
- Enlarge the study to Fe-O-F ternary system

Acknowledgment: Financial support of Areva

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