CAPSTONE PROJECT

Thermochemical modelling of LiF-CsF-ThF mixtures for MSFR application

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Framework & scope of the work

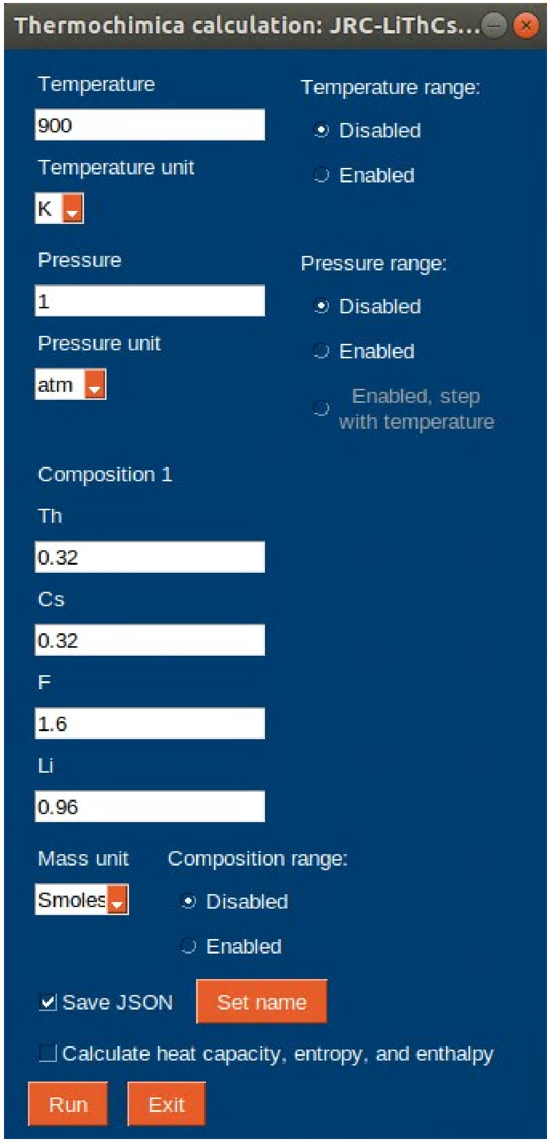
This project is centred on the **use of the equilibrium thermodynamics software library Thermochimica,** available on GitHub, with the JRC molten salt database. Thermochimica determines a unique combination of phases and their compositions at thermochemical equilibrium.

<u>Molten Salt Fast Reactor (MSFR) application:</u>
→ study the **behaviour of fluoride salts** considered as fuel for the MSFR interacting with **fission products** (e.g., Cs).

- Reference salt for the MSR: binary eutectic mixture LiF,-ThF_4 with UF_4 or PuF_3 as fissile and UF_3 for redox control.

- Fission products formed during irradiation accumulate in the fuel mixture and influence its properties (e.g., melting behaviour, solubility limit, vapor pressure).

The considered system (Li, Cs, Th//F) contains cations (Li^+, Cs^+, Th^{4+}) and the anion F^-.



Task #1: Effects of F hyper/hypo-stoichiometry

System composition
0.6 moles LiF
0.2 moles CsF
0.2 moles ThF

(1.6 total moles F)

at 900 K and 1 atm.

Thermochimica output

System properties		
Temperature (K)	900	
Pressure (atm)	1	
System component	Mass (mol)	Chemical potential (J/mol)
Th	0.32	-59597.63
Cs	0.32	-103312.9
F	1.6	-575096.3
Li	0.96	-92638.69
Integral Gibbs energy (J)	-1061220	
Entropy (J/K)	198.909	
Enthalpy (J)	-882200	
Heat capacity (J/K)	452.314	
Functional norm (/)	1.65888E-06	
# of stable pure condensed phases	*2*	
# of stable solution phases	*2*	

1.539 mol of salt solution

1.6 moles of F

0.851 moles of solid (53.19 %) — LiF, CsF, ThF_4, $ThCs_3F_7$

0.749 moles of solution (46.81%) — LiF, CsF, ThF_4

Task #1: Effects of F hyper/hypo-stoichiometry

System composition
0.6 moles LiF
0.2 moles CsF
0.2 moles ThF

(1.65 total moles F = + 3.125 %)

at 900 K and 1 atm.

Thermochimica output

System properties		
Temperature (K)	900	
Pressure (atm)	1	
System component	Mass (mol)	Chemical potential (J/mol)
Th	0.32	-59597.63
Cs	0.32	-103312.9
F	1.65	-575096.3
Li	0.96	-92638.69
Integral Gibbs energy (J)	-1089970	
Entropy (J/K)	194.955	
Enthalpy (J)	-914514	
Heat capacity (J/K)	288.457	
Functional norm (/)	1.64924E-06	
# of stable pure condensed phases	*2*	
# of stable solution phases	*2*	

0.85187 mol of salt solution (-55.35 %)

1.65 moles of F

1.253 moles of solid (75.92%) — LiF, CsF, ThF_4, $ThCs_3F_7$

0.397 moles of solution (27.08%) — LiF, CsF, ThF_4

Task #1: Effects of F hyper/hypo-stoichiometry

System composition
0.6 moles LiF
0.2 moles CsF
0.2 moles ThF

(1.55 total moles F = - 3.125 %)

at 900 K and 1 atm.

Thermochimica output

System properties		
Temperature (K)	900	
Pressure (atm)	1	
System component	Mass (mol)	Chemical potential (J/mol)
Th	0.32	-59597.63
Cs	0.32	-102163.4
F	1.55	-575091.0
Li	0.96	-92025.97
Integral Gibbs energy (J)	-1032460	
Entropy (J/K)	200.547	
Enthalpy (J)	-851965	
Heat capacity (J/K)	158.366	
Functional norm (/)	2.45319E-06	
# of stable pure condensed phases	*1*	
# of stable solution phases	*2*	

2.0042 mol of salt solution (+ 30.23%)

1.55 moles of F

0.6 moles of solid (38.77 %)

LiF, CsF, ThF_4

0.95 moles of solution (61.23 %)

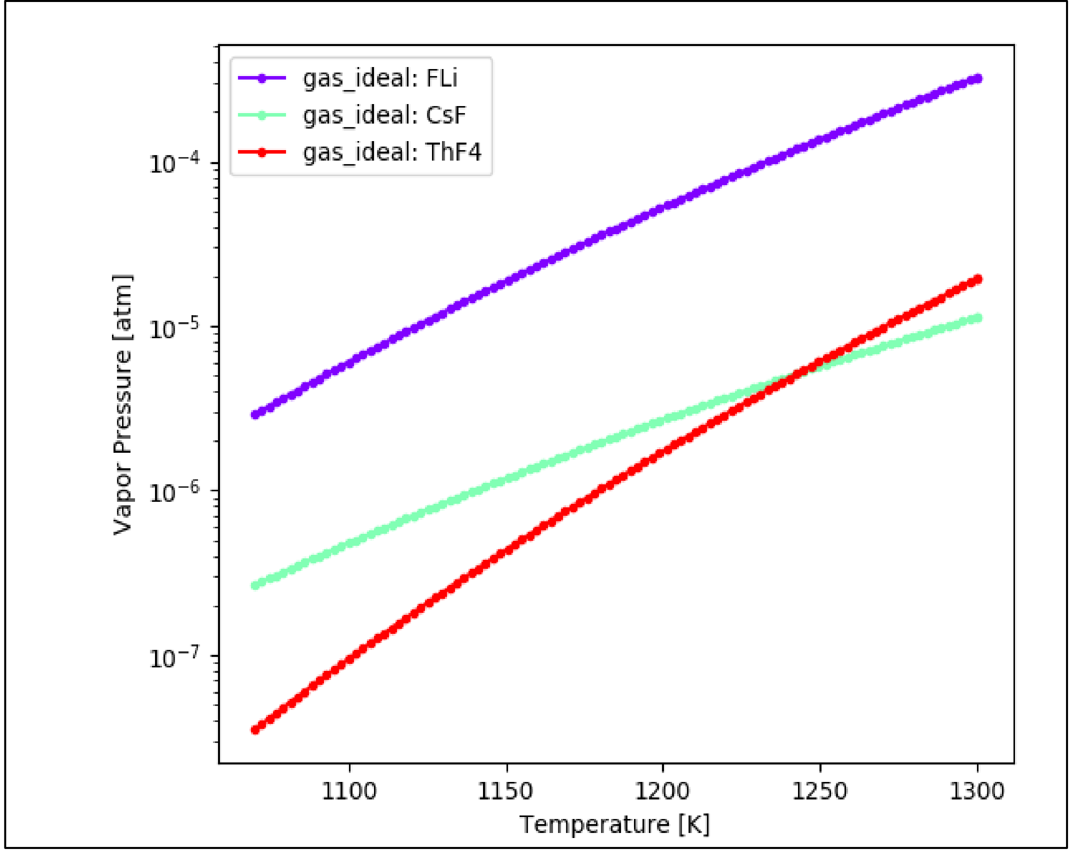
LiF, CsF, ThF_4

Task #2: Vapor pressures

<u>**Consider the mixture:**</u>
75.73 % LiF
23.23 % ThF_4
1.05 % CsF

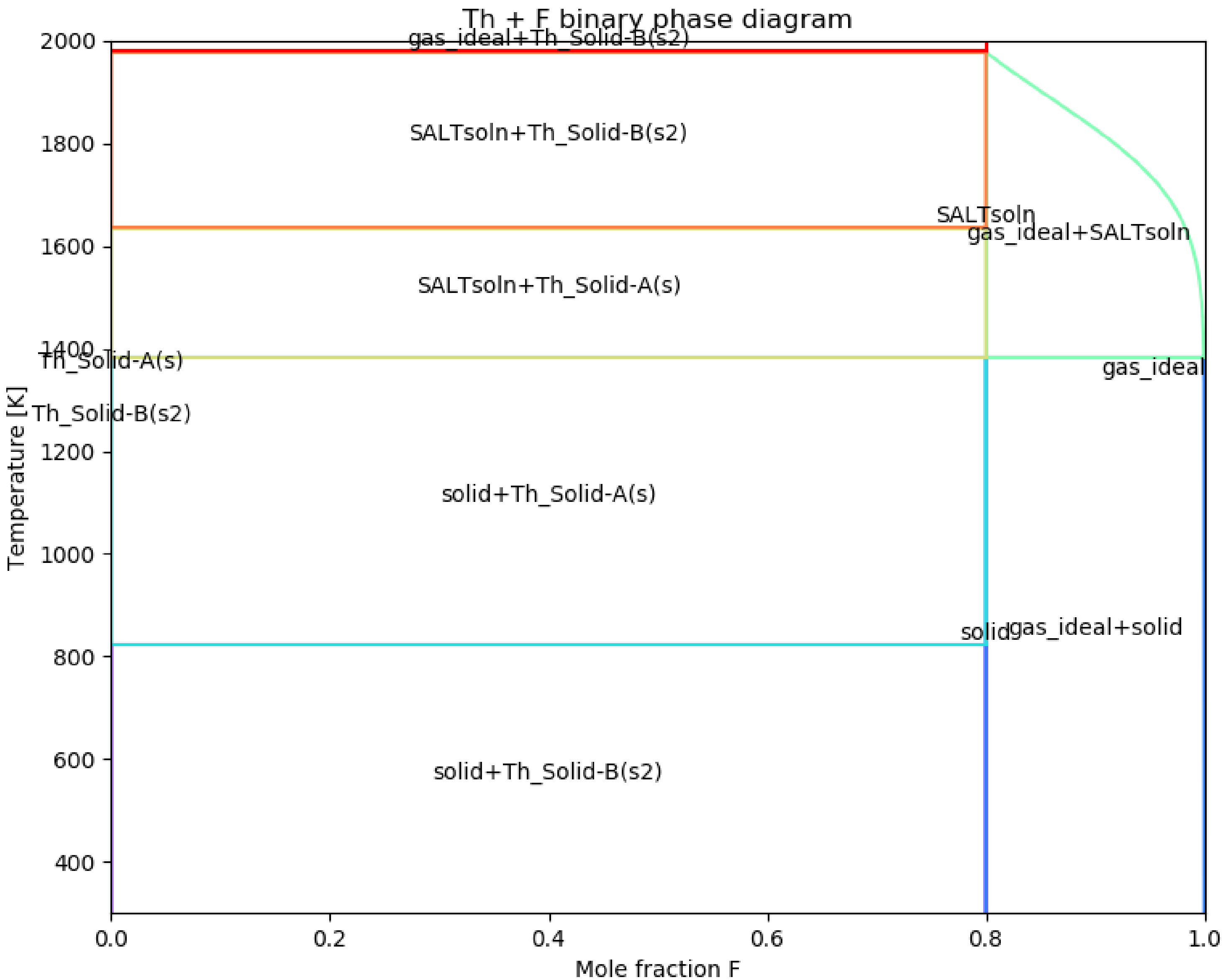
Compare of the vapor pressures of LiF, CsF and ThF_4, over the range 1070 K to 1300 K at 1 atm

Thermochimica output

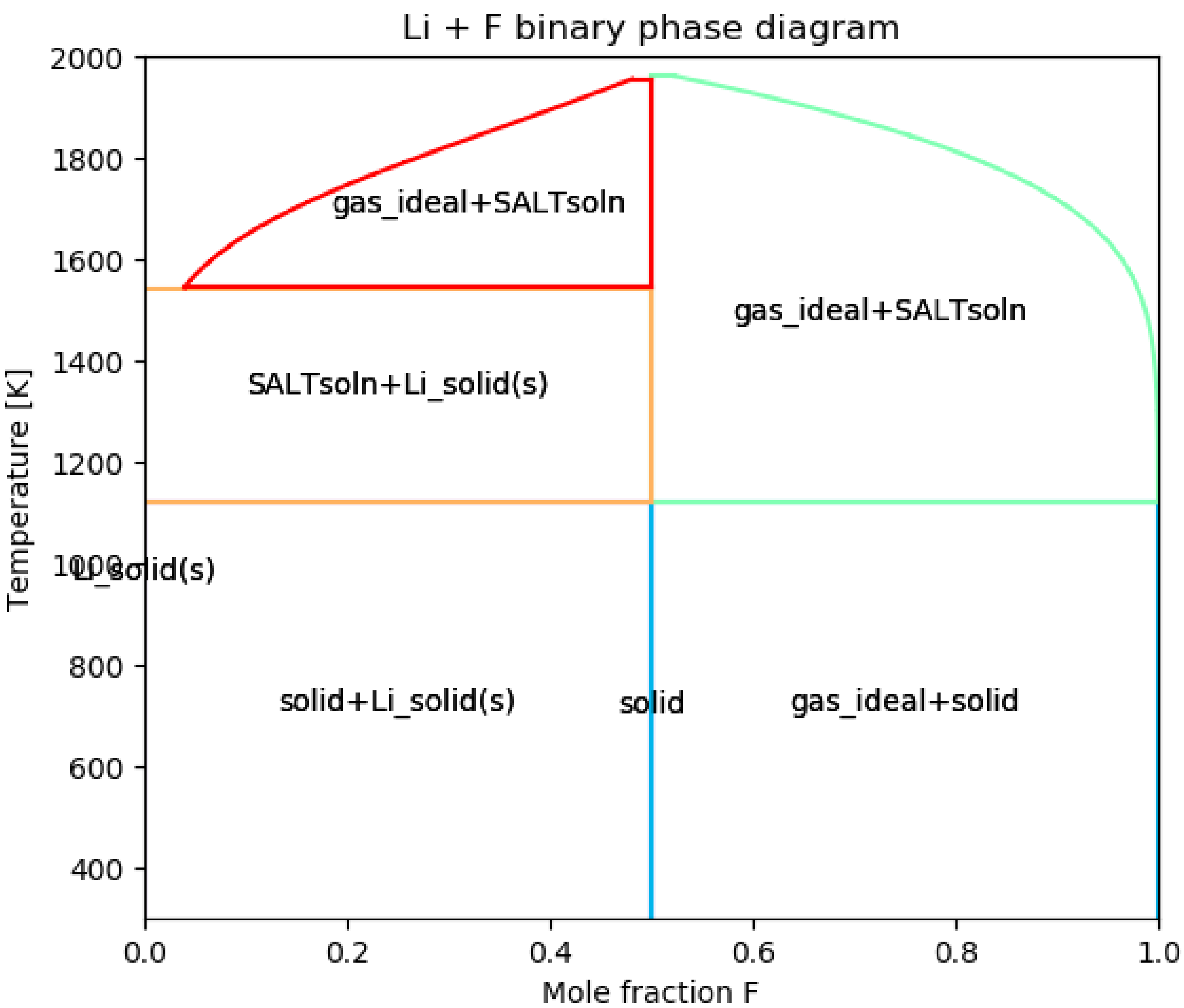


- Low vapor pressures at operative temperature.
- Vaporization behaviour of caesium (volatile fission product) during accidental scenarios.

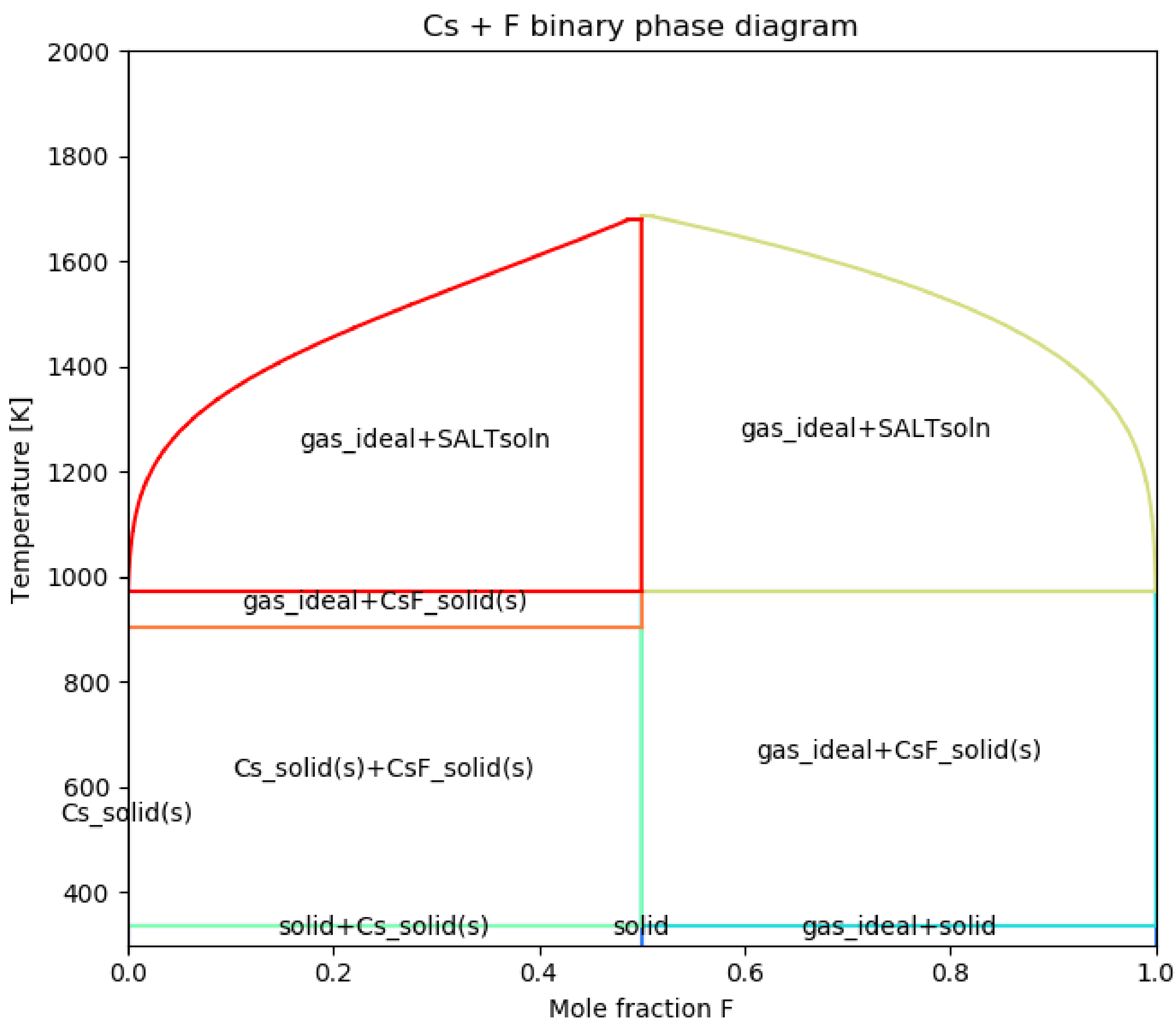
Task #3: Binary Phase Diagrams (Th-F) at 1 atm



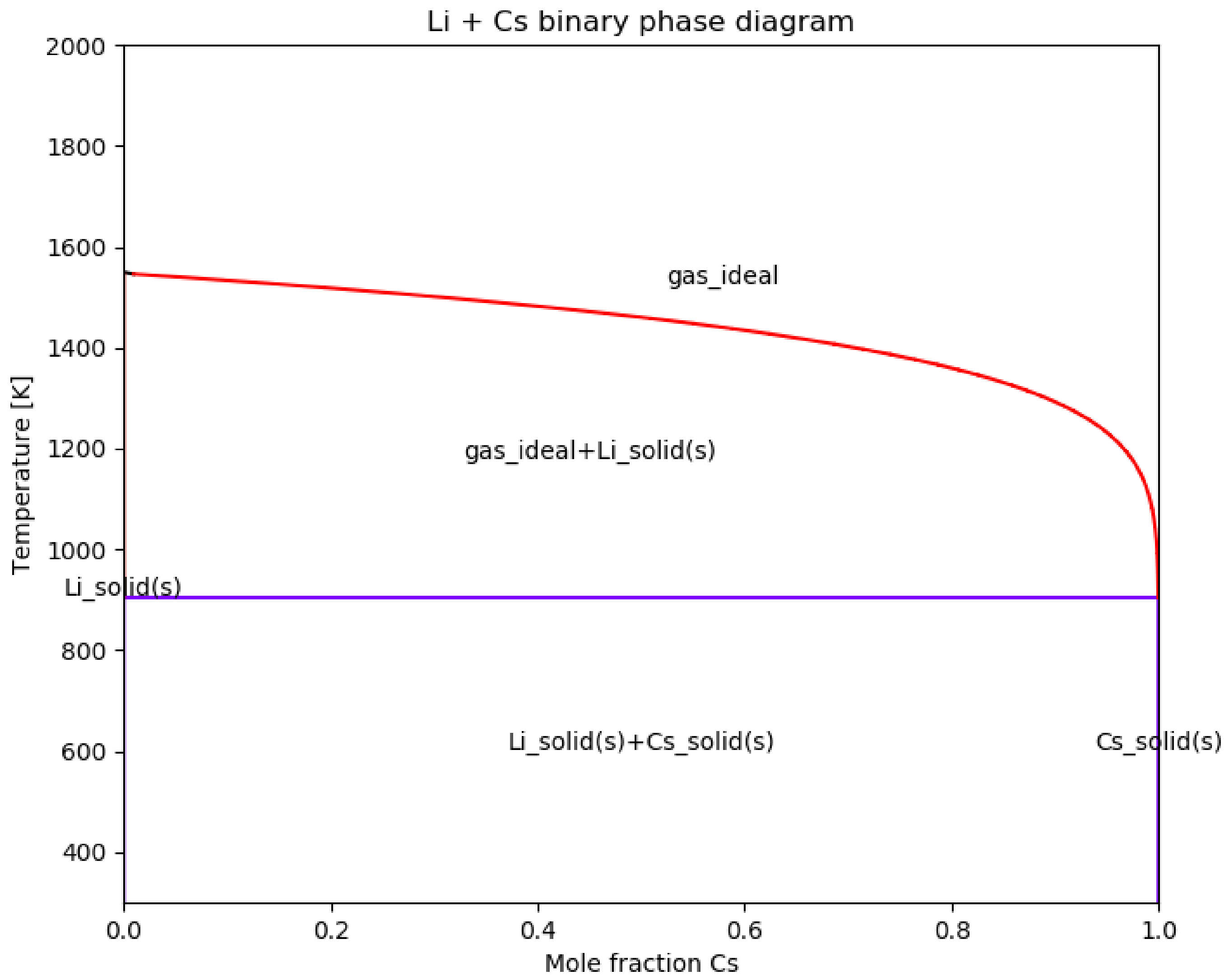
Task #3: Binary Phase Diagrams (Li-F) at 1 atm



Task #3: Binary Phase Diagrams (Cs-F) at 1 atm



Task #3: Binary Phase Diagrams (Li-Cs) at 1 atm



Conclusions

The software Thermochimica can be used to assess the behaviour of fluoride salt of interest for application in the MSFR, interacting with fission products (e.g., Cs).

- Effects of the fluorine hyper/hypo-stoichiometry → chemical control.

- The interaction between fission products and fuel mixture affects the fuel properties (e.g., melting behaviour, solubility limit, vapor pressure) → impact of the fission products on the fuel properties of interest.

- Effect of temperature / pressure variations (e.g., assessment against potential accidental scenarios) on the fuel mixture state → stability phase diagram assessment

Thank you for your kind attention

The software Thermochimica can be used to assess the behaviour of fluoride salt of interest for application in the MSFR, interacting with fission products (e.g., Cs).

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- The interaction between fission products and fuel mixture affects the fuel properties (e.g., melting behaviour, solubility limit, vapor pressure) → impact of the fission products on the fuel properties of interest.
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