INL/CON-22-69557-Revision-0

Development of a Thermodynamic Database for Corrosion in Chloride MSRs

October 2022

Jacob Allen Yingling, Johnathon Ard, Juliano , Mina , Amir , Theodore

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Extension of MSTDB to Provide a High-Quality, Validated Thermochemical Database for Predicting/Simulating Corrosion in Molten Salt Reactor Systems - Grant number DE-NE0008985

Development of a Thermodynamic Database for Corrosion in Chloride MSRs

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October 11, 2022

UNIVERSITY OF South Carolina

General Atomics
SmartState Center
for

INL/CON-22-69557

Overview

- Molten Salt Thermal Properties Database -Thermochemical (MSTDB-TC), a free resource for molten salt thermodynamic properties
- Well-specified CALPHAD modeling
- Thermodynamic assessment of NaCl-KCl-$MgCl_2$ with UCl_3-UCl_4 and $CrCl_2$
- Temperature and composition dependent formation of $CrCl_2$

Chloride corrosion systems of MSTDB-TC version 2.0

	KCl	$MgCl_2$	UCl_3	UCl_4	$CrCl_2$	$FeCl_2$	$NiCl_2$
NaCl	✓	✓	●	●	●	✓	✓
KCl	--	✓	●	●	●	✓	✓
$MgCl_2$	--	--	□	□	□	✓	✓
UCl_3	--	--	--	□	□	□	□
NaCl-KCl	--	--	□	□	□	✓	✓
NaCl-$MgCl_2$	✓	--	□	□	□	✓	●
KCl-$MgCl_2$	--	--	□	□	□	□	✓

● New
□ Updated
□ Unavailable

Producing well-specified thermodynamic assessments

- Gibbs energy descriptions can be underdefined

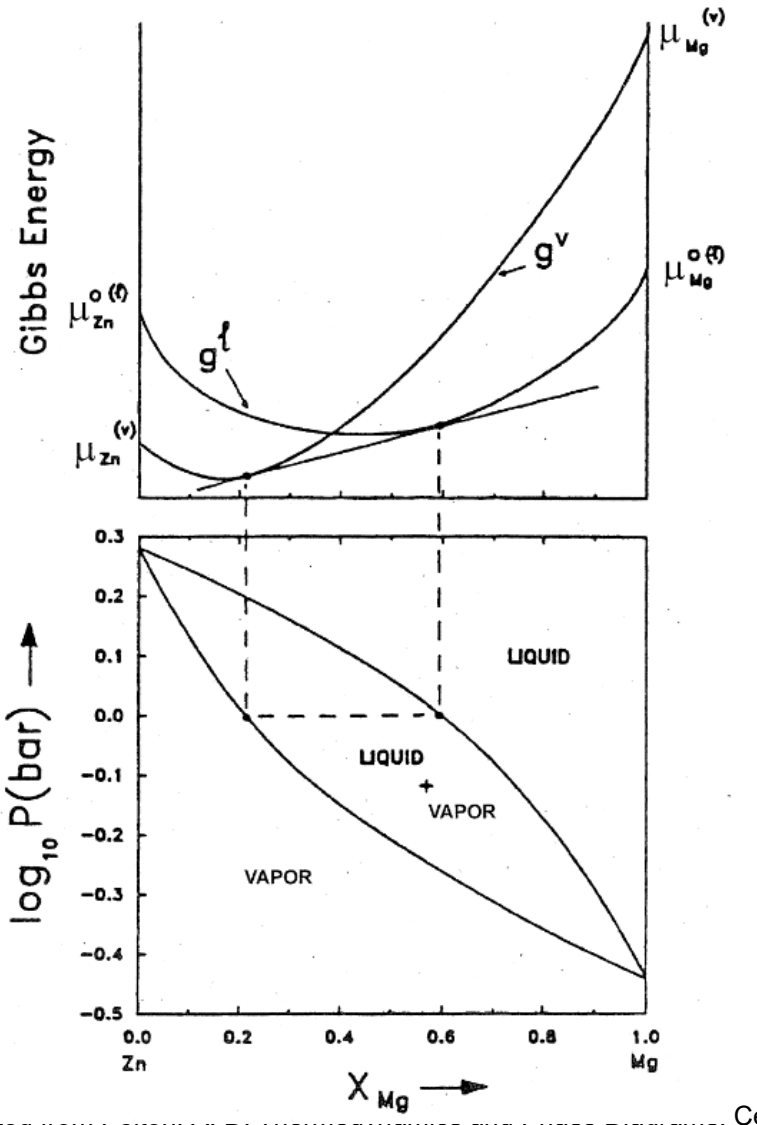
  Phase equilibria

- The modified quasi-chemical model in quadruplet approximation (MQMQA) describes ionic species ordering

- With well-defined endmembers depends only on and the cation-cation coordination numbers (

- In a simple eutectic, and satisfied by and

Connection between phase equilibria, chemical potential (), and

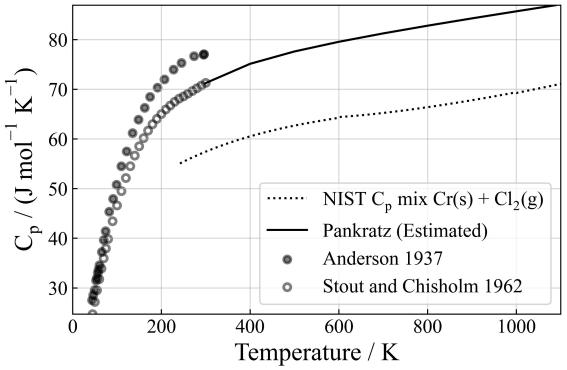


Adapted from Pelton, A.D. Thermodynamics and Phase Diagrams, Centre de Recherche en Calcul Thermodynamique: Montréal, Canada, 2011.

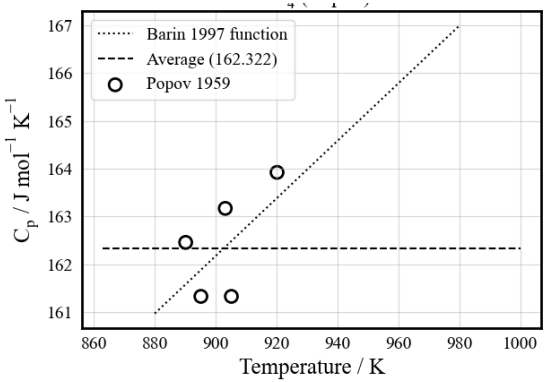
Endmember characterization

- , , and from primary sources.

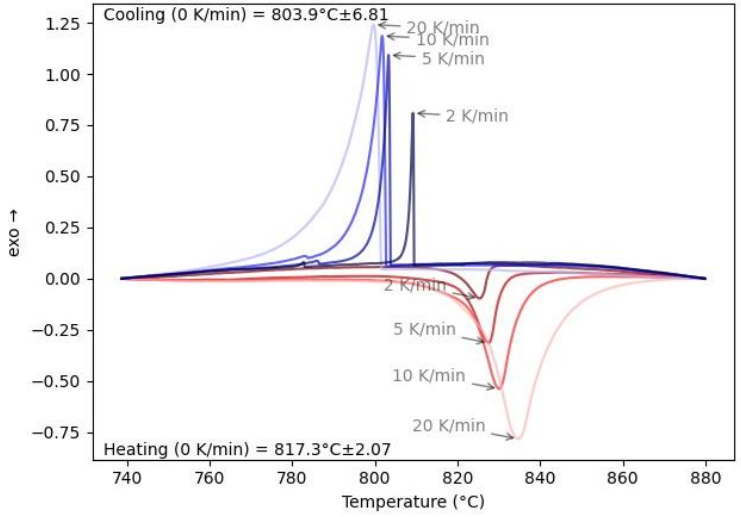
$CrCl_2$

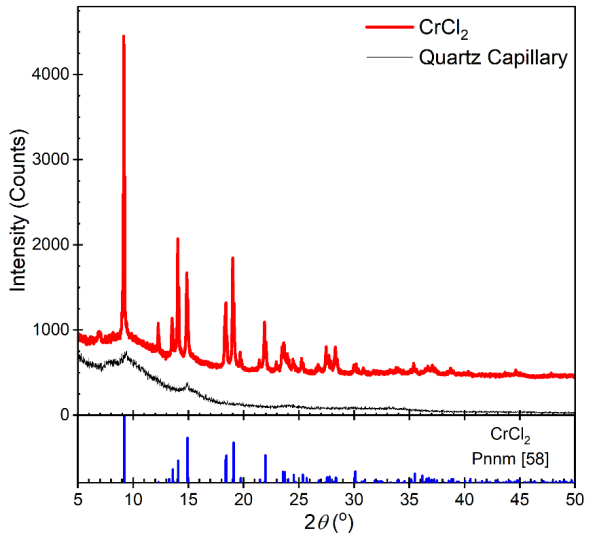


UCl_4



- Purity benchmarking of obtained salts.

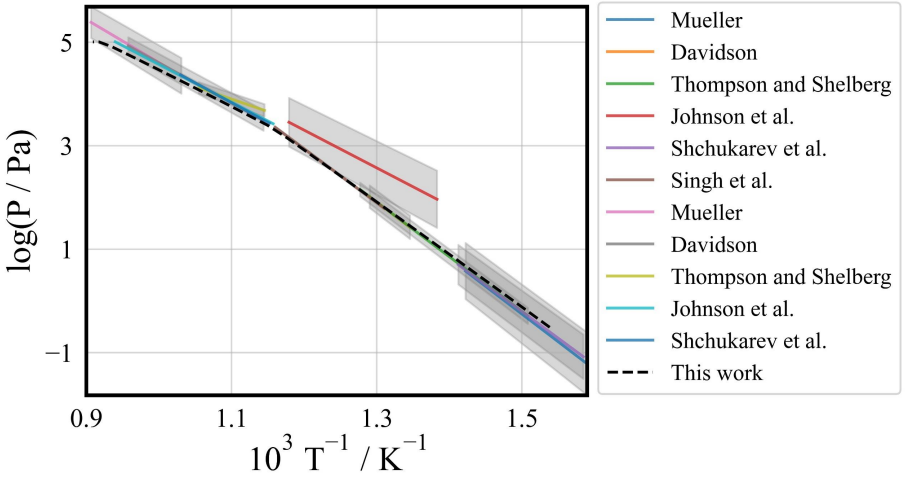




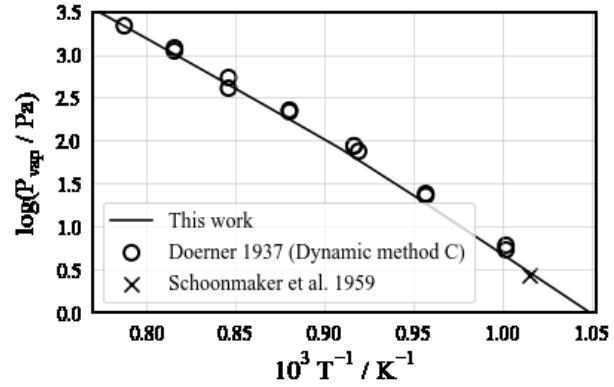
- Comparison of calculated values against experimental

Vapor Pressure

UCl_4



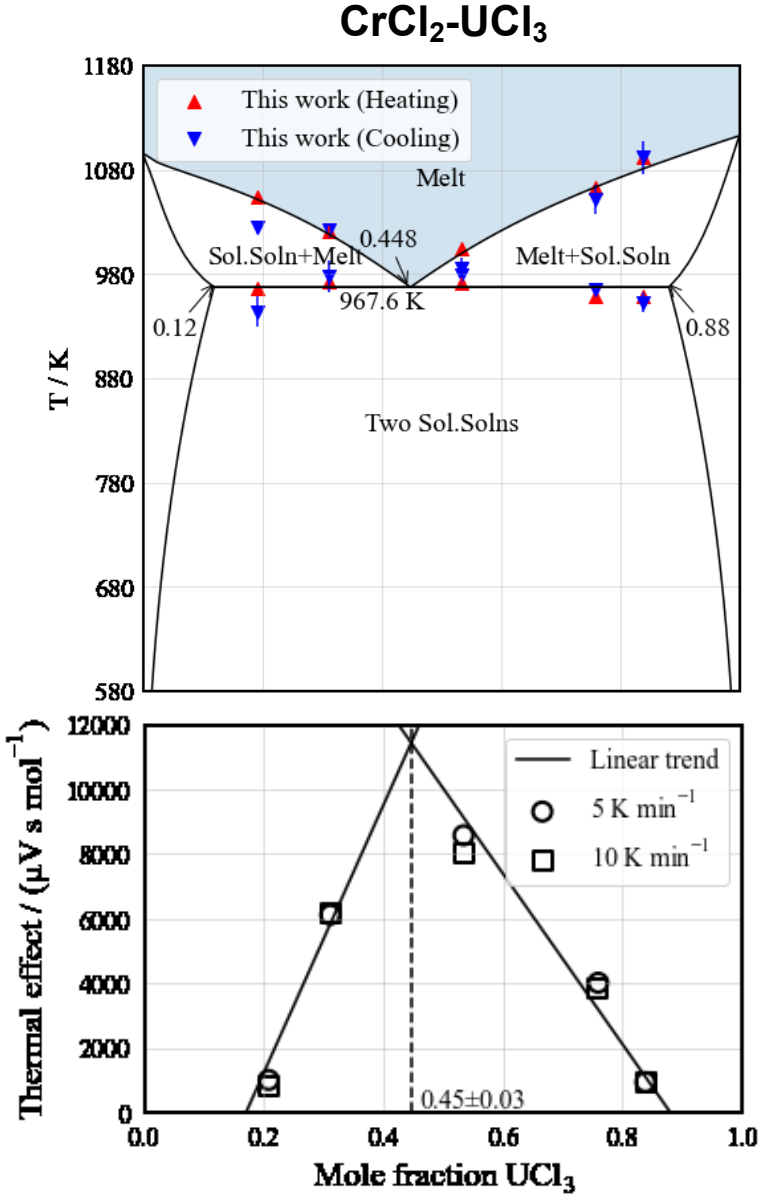
$CrCl_2$



Experiments compliment similar system correlations

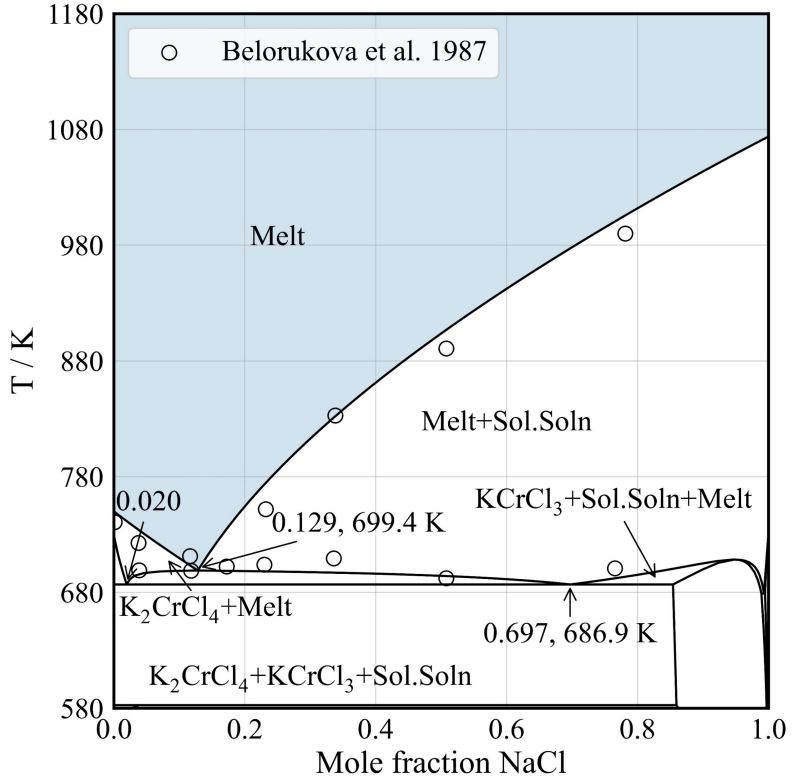
- Cationic potential (trends can predict broad equilibria patterns
- Few DSC measurements needed as confirmation

Cation (A)		# of Compounds
Cs(+)	0.24	2
Rb(+)	0.26	2
K(+)	0.29	2
Na(+)	0.39	1
Li(+)	0.53	1+ Sol. Soln.
Mn(2+)	0.96	Two Sol. Soln.
Fe(2+)	1.03	Two Sol. Soln.
Mg(2+)	1.11	Two Sol. Soln.

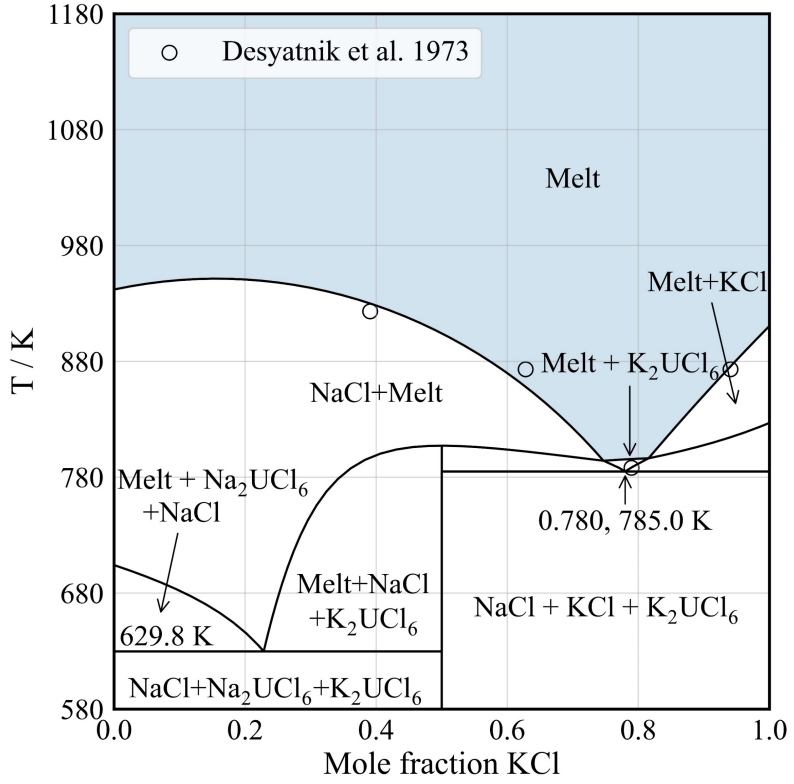


$NaCl\text{-}KCl\text{-}CrCl_2$ and $NaCl\text{-}KCl\text{-}UCl_4$

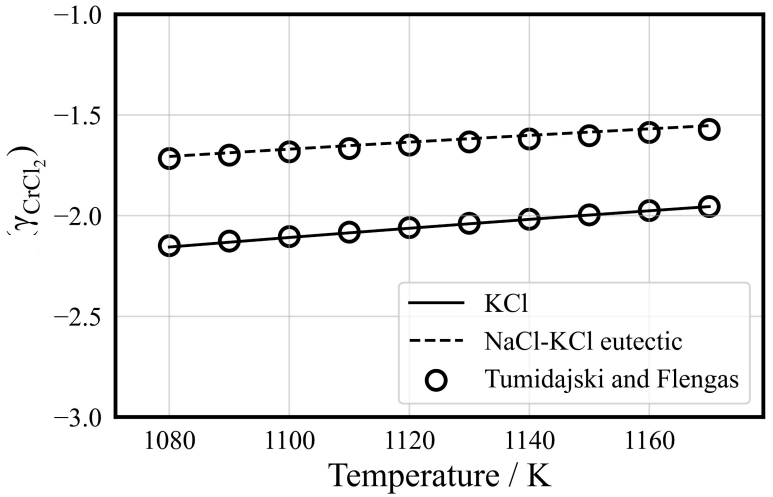
K_2CrCl_4-NaCl



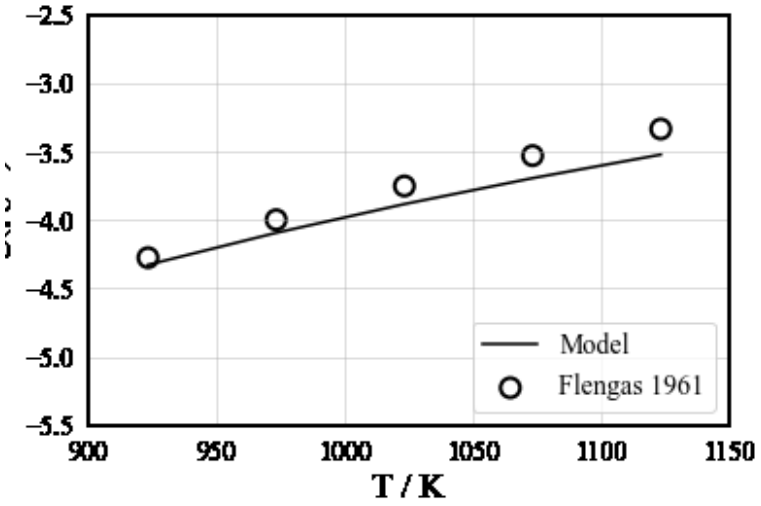
NaCl-KCl Section 20mol% UCl_4



Dilute $CrCl_2$ activity coefficient



Dilute UCl_4 activity coefficient



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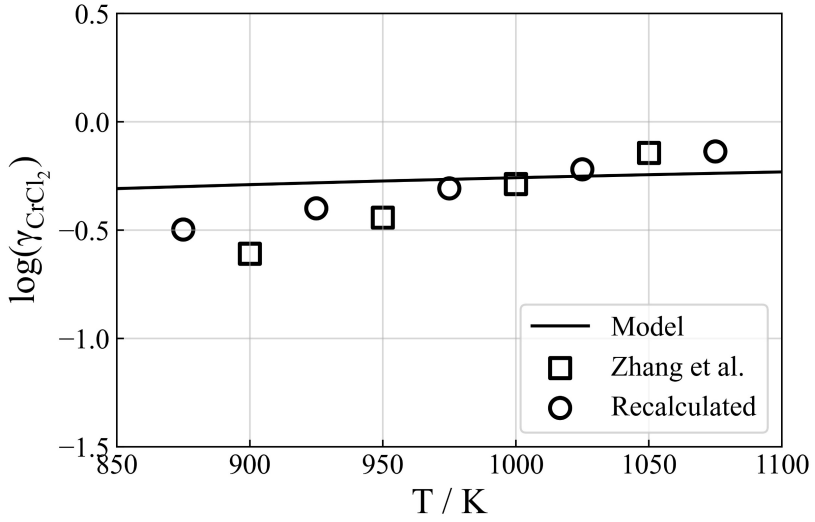
No pseudo-ternary liquid interaction parameters needed

NaCl-KCl-$MgCl_2$-$CrCl_2$

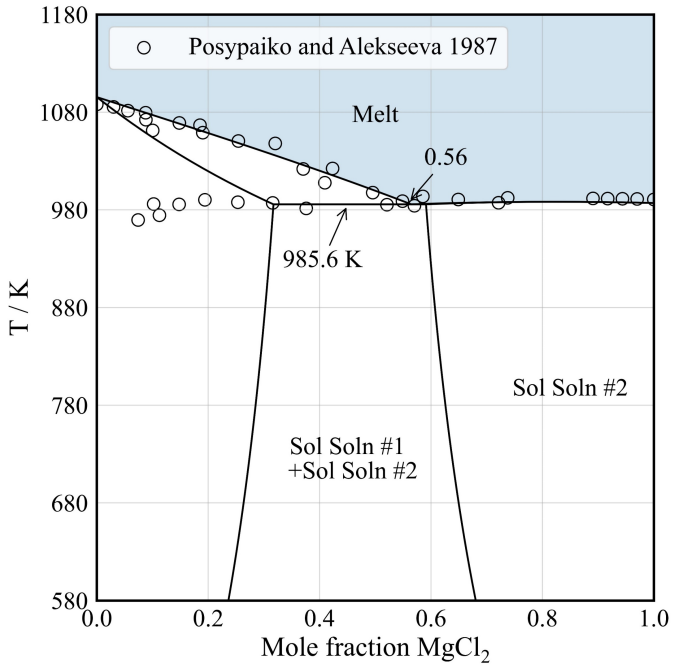
- Sparse data for the $CrCl_2$-$MgCl_2$ system, only a single set of phase equilibria available
- Higher order data may be used to better inform the lower order system assessment

Dilute $CrCl_2$ in MagNaK eutectic



High-order data used in lower order system assessment.

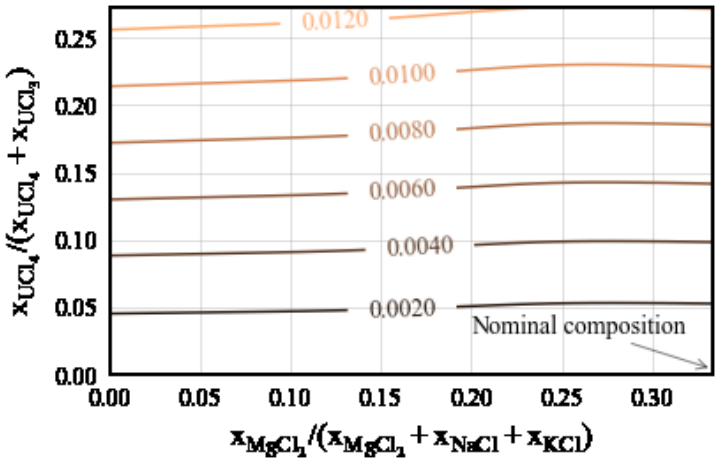
$CrCl_2$-$MgCl_2$



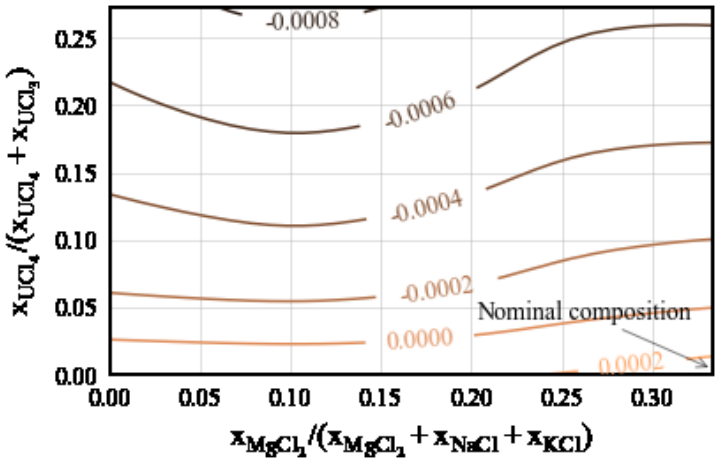
Hastelloy-N Cr corrosion

- Equilibrium $CrCl_2$ formation from Ni-5.7Cr-24.0Mo-4.4mol%Fe alloy
- Nominal salt composition of $10UCl_3$-30NaCl-30KCl-$30MgCl_2$.
- Composition variations have constant total molar content and a 1:1 NaCl:KCl ratio.
- Very small additions of Mg can greatly reduce corrosion product formation.

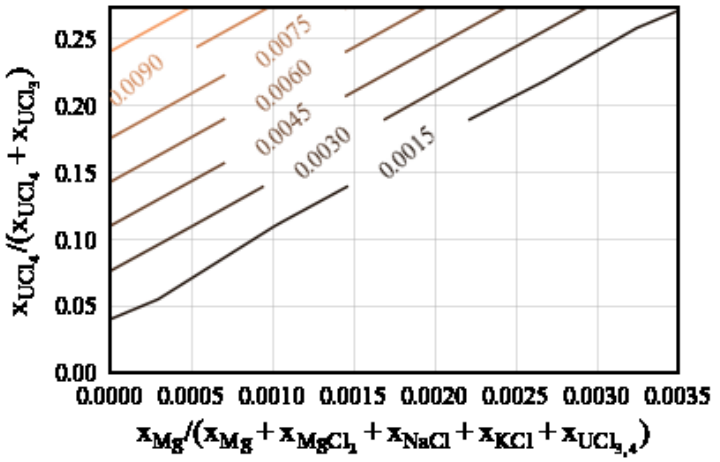
Equilibrium at 1000K



Difference at 1300K



Nominal composition at 1000K with added Mg



Summary and conclusions

- This work added 18 chloride systems (7 pseudo-ternary) to MSTDB-TC
- Correlational approaches, DSC measurements, and constrained equilibria optimizations yield accurate high-order molten salt system assessments
- Chloride corrosion calculations can be performed for
  - $NaCl$-KCl-$MgCl_2$-UCl_3-UCl_4-$CrCl_2$
  - $NaCl$-KCl-$MgCl_2$-($FeCl_2$,$NiCl_2$)
- Driving forces for $CrCl_2$ formation marginally decrease with increasing temperature
- More complete understanding will require phase equilibria of $NaCl$-$MgCl_2$-UCl_3, $NiCl_2$-UCl_3, and $FeCl_2$-UCl_3

Training/Workshop on Molten Salt Thermal Properties Databases
University of South Carolina
November 9, 2022

Thermochemical, MSTDB-TC, and thermophysical, MSTDB-TP

- Details on the development and the current and projected future content
- Use of software for accessing the database content
  - FactSage (commercial) and Thermochemica (open access) for MSTDB-TC
  - Saline (open access) for MSTDTB-TP
  - Examples of coupling to multiphysics codes
- Presenters from U*of*SC, ORNL, Ontario Tech, and others
- Contributed posters on applications

Registration deadline Oct. 28!!!

For registration details and to be added to the mailing list contact: besmann@sc.edu

OAK RIDGE National Laboratory

Organizers:
- ***Ted Besmann, U*of*SC***
- ***Dianne Ezell, ORNL***

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