Molten Salt Reactor PROGRAM

General Atomics Center
Molinaroli College of Engineering and Computing
UNIVERSITY OF SOUTH CAROLINA

# Generation of Molten Salt Thermochemical Properties and Database Development


Ted Besmann

Juliano Schorne-Pinto, Jorge Paz Soldan Palma, Clara Dixon, Ronnie Booth, Jack Wilson, Aiswarya Padinhare Manissery, Zachary Gardiner

*Nuclear Engineering Program*

*University of South Carolina*


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# Accomplishments

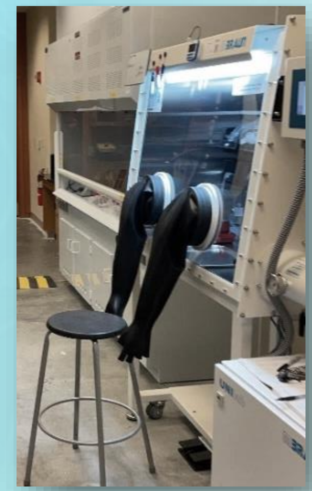
- **FY24 M3 Milestone**
  - *Complete the assessment of $CeF_3$-$UF_4$: $LaF_3$-$UF_4$; $BaCl_2$-$UCl_3$; $SrCl_2$-$UCl_3$; $LaCl_3$-$UCl_3$; $CeCl_3$-$UCl_3$; $ZrCl_4$-, NaCl, KCl, $MgCl_2$, $UCl_3$; NaCl-$LaCl_3$; $MgCl_2$-$LaCl_3$ systems and their inclusion in MSTDB-TC as documented in a letter report and accompanying database*. 9/30/2024
- **MSTDB-TC Versions 3.0, 3.1, and very recent 4.0 released with expanded documentation**
- **Papers**
  - *Thermodynamic Assessment of the Li, Na, K, Cs | F, I Eight-Component Reciprocal System*, Clara M. Dixon, Mina Aziziha, Juliano Schorne-Pinto, and Theodore M. Besmann –J. Chem. Thermo. Accepted with minor revision
  - *Density Measurements of Molten LiF−$BeF_2$ and LiF−$BeF_2$−$LaF_3$ Salt Mixtures by Neutron Radiography,* Jisue Moon, Joanna McFarlane, Hunter B. Andrews, Kevin R. Robb, Molly Ross, Dino Sulejmanovic, Yuxuan Zhang, Erik Stringfellow, Can Agca, Juliano Schorne-Pinto, Theodore M. Besmann, ACS Omega, 9 (25) 2024 27204–27213
  - *Thermodynamic modeling of CsF with LiF-NaF-KF for molten fluoride-fueled reactors*, Clara M. Dixon, Juliano Schorne-Pinto, Mina Aziziha, Jacob A. Yingling, Ronald E. Booth, Theodore M. Besmann, Journal of Molecular Liquids, 406 (2024) 125056
  - *Thermal Property Modeling and Assessment of the Physical Properties of FLiNaK,* Schorne-Pinto, Juliano; Aziziha, Mina; Tisdale, Hunter; Mofrad, Amir; Birri, Anthony; Christian, Matthew; Ard, Johnathan ; Booth, Ronald; Yingling, Jacob; Palma, Jorge; Dixon, Clara; zur Loye, Hans-Conrad; Besmann, Theodore, ACS Applied Energy Materials, 2024, 7, 9, 4016–4029
- **Conference Presentations:** ACS: 4; MS&T: 3; TMS: 3
- ***Workshop on Measurement and Analysis of Thermochemical and Thermophysical Properties of Molten Salts:*** Organized by Ted Besmann and Tony Birri, Virtual, July 16-17, 2024 – Averaged almost 100 participants

# Collaborations

- Toni Karlsson (INL): $NaCl\text{-}PuCl_3\text{-}UCl_3$ and $NaCl\text{-}PuCl_3$ phase equilibria and thermal functions
- Jacob Yingling (INL): U-Cl heat capacity studies
- Marisa Monreal and Hannah Patenaude (LANL): $NaCl\text{-}MgCl_2\text{-}UCl_3$ Phase equilibria
- Joanna McFarlane and Katie Johnson (ORNL): $LiF\text{-}BeF_2$ phase equilibria
- David Andersson (LANL) and Chao Jiang (INL): First principles calculations
- Tony Birri (ORNL): Workshops and database management
- Markus Piro (McMaster Univ.): Automated QA determination
- Stephen Raimen (Univ. Michigan): Measurement of oxygen in salts
- Brian Powell (Clemson Univ.): Solution calorimetry for $NaCl\text{-}MgCl_2$ intermediate phases

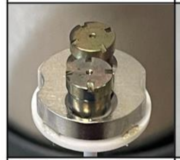
# Major Issue of Salt Purity Has Been a Focus: Determination and Purification

**Salts**

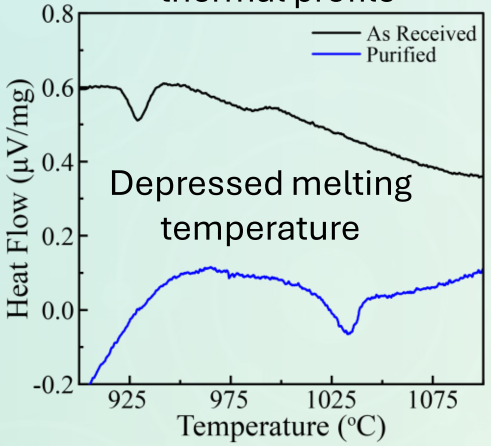


**Argon glovebox#1**, $H_2O$ < 3 ppm, $O_2$ < 0.1 ppm
> 50 salts (chlorides, fluorides and iodides)

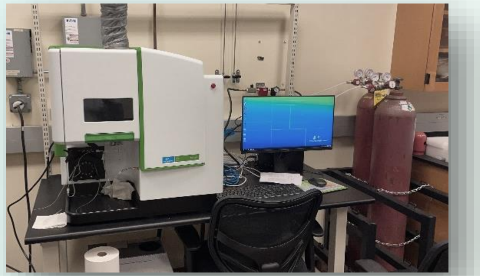

**Purity by DSC**

| | 100 µl SS w Ni liner | 27µl SS w Ni liner |
|---|---|---|
| |  |  |
| **Source** | Netzsch + UOIT & USC | Netzsch + UOIT & USC |
| **Mass** | ~1480 mg | ~ 875 mg |
| **Max. sample mass** | 10-50 mg | 10-20 mg |

Effect of oxygen on DSC thermal profile




**Chemical analysis**



**ICP-OES**


**O and H analyzer**
The gaseous combustion products are measured by infrared and thermal conductivity cells

**Purification**
**Drying**

Vitreous Carbon, 0.9ml

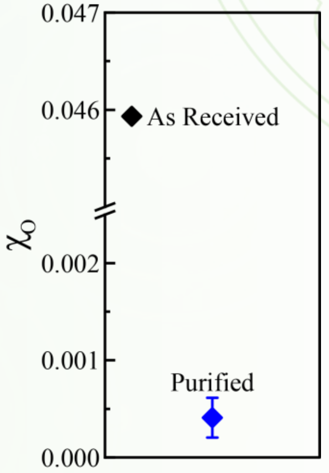
Quartz, 5ml

Quartz tube

**Muffle/Tube furnace (RT-1200°C)** installed in **Glovebox#2**, $H_2O$ < 0.1 ppm, $O_2$ < 0.1 ppm

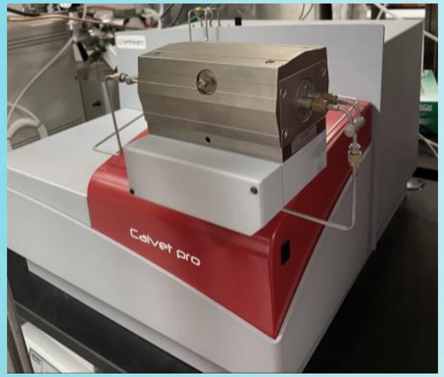
Inert gas (Ar, Ar + 4%$H_2$) or vacuum (35 mbar)

**Very low oxygen product**



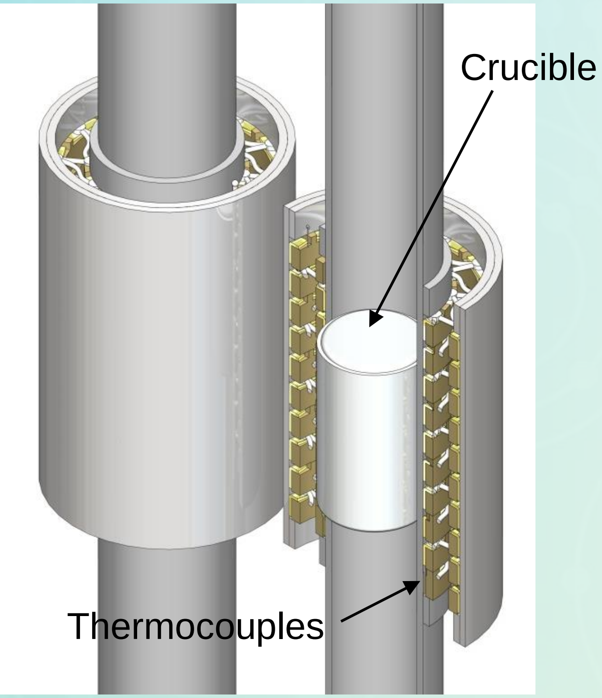
# New Capability Allows Generation of Highly Accurate Heat Capacity Values

**Calvet Pro - Setaram**

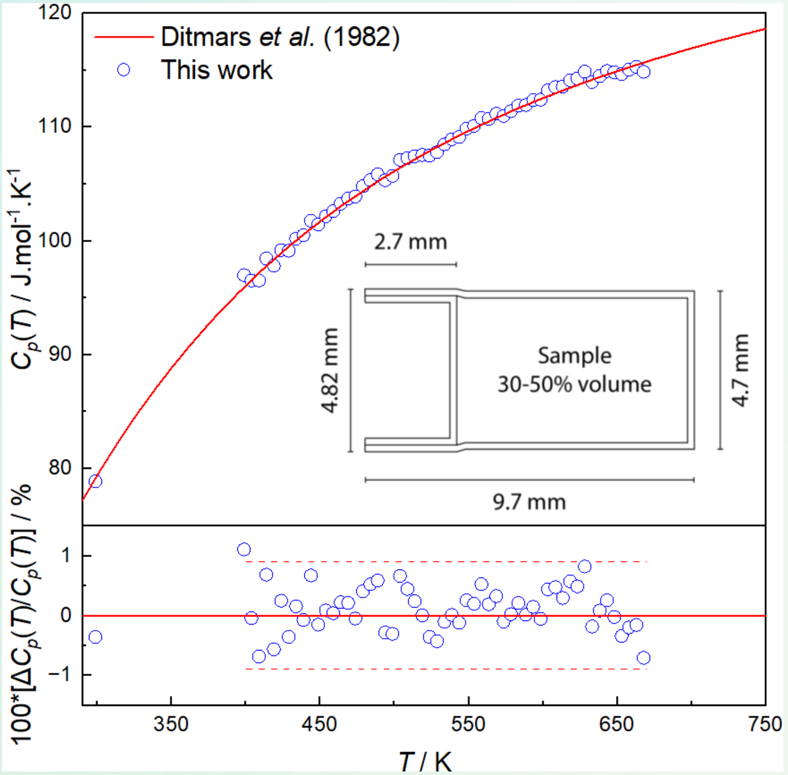



- Tian-Calvet Heat-Flow Microcalorimeter equipped with two 3D thermopiles now allows for superior heat capacity determination
- Developed salt encapsulation to improve sample/crucible weight ratio

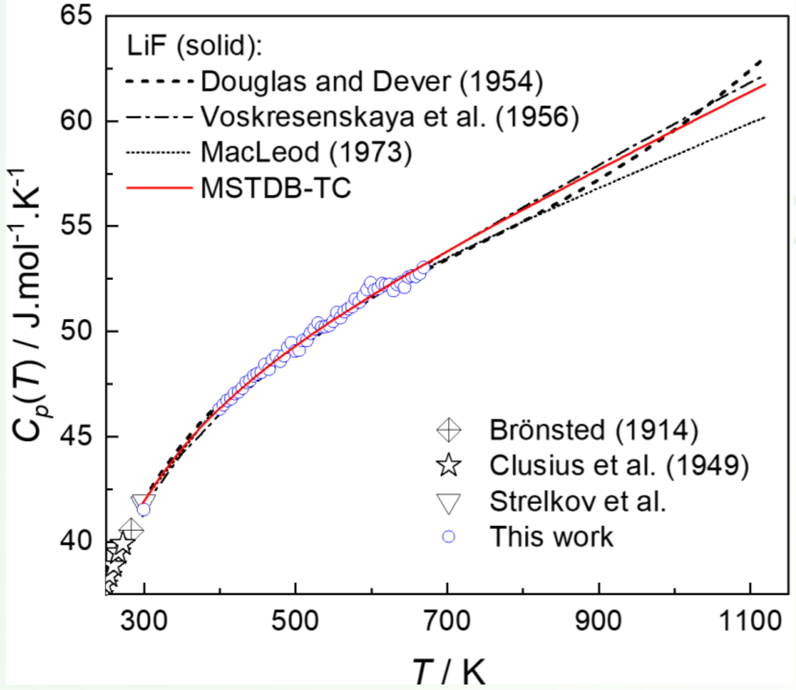
**3D Thermopiles**
**240 thermocouples**




**Accuracy demonstrated with sapphire standard: [U] = ± 0.9%**




**$C_P$ for LiF(cr) in excellent agreement with MSTDB-TC values**

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# Salt Systems Addressed in the Current Period (Some Included in MSTDB-TC Ver. 3.1)

Chlorides

- $ZrCl_4$
- $MgCl_2$-$UCl_3$ (revised)
- NaCl-$MgCl_2$ (revised)
- NaCl-$LaCl_3$
- $MgCl_2$-$LaCl_3$
- $BaCl_2$-$UCl_3$
- $SrCl_2$-$UCl_3$

Fluorides

- $SrF_2$ (revised)
- $SmF_3$
- NaF-$UF_3$
- CsF-$UF_3$
- CsF-$PuF_3$
- LiF-$LaF_3$
- NaF-$LaF_3$
- LiF-$CeF_3$
- NaF-$CeF_3$
- LiF-$PuF_3$
- NaF-$PuF_3$
- $BeF_2$–KF (revised)
- KF–$SrF_2$ (revised)
- LiF–$SrF_2$ (revised)
- NaF–$SrF_2$ (revised)

Reciprocal salts

- Na,K,Cs|Cl,I
- Li, Na, K, Cs | F, I

Pseudo-ternary fluoride*

- LiF-$BeF_2$-$CeF_3$
- LiF-$BeF_2$-CsF
- LiF-$BeF_2$-$LaF_3$
- LiF-$BeF_2$-$NdF_3$
- LiF-$BeF_2$-$PuF_3$
- LiF-$BeF_2$-$UF_3$

*Represented up to the solubility limit of third component due to limited data with LiF-$BeF_2$



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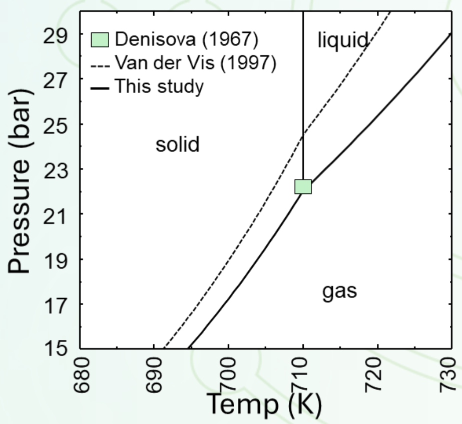
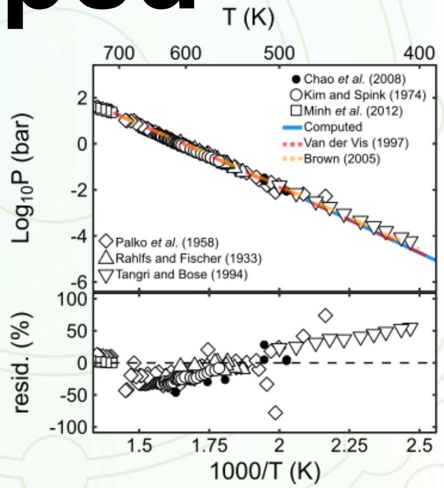
# $ZrCl_4$ and Zr-Fuel Systems Models Developed

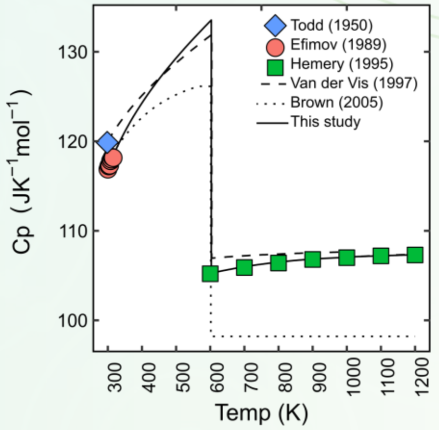
**$ZrCl_4$: Gibbs energy functions for $ZrCl_{4(s,\ l,\ and\ g)}$ fit to phase equilibria, $\Delta_f H°$, $\Delta_{fus} H°$, $\Delta_{sub} H°$, $\Delta_{sub} S°$, Cp, S,**

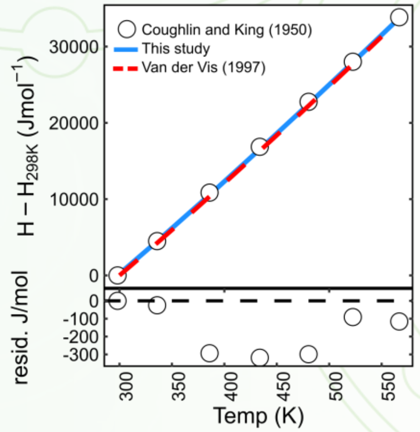
- Better reconciliation of Cp and enthalpy increment data
- Captured triple point
- Better fit the available vapor pressure data

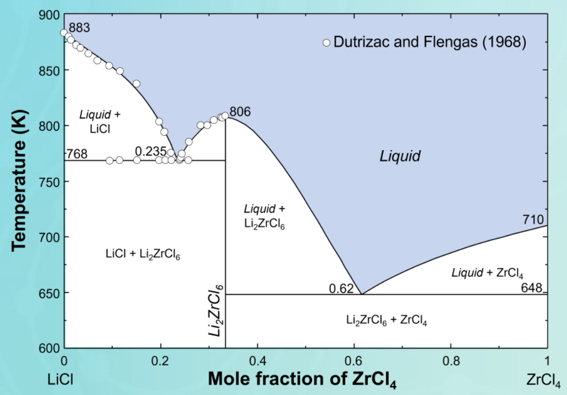
- **Evaluation of pseudo-binary systems of $ZrCl_4$ + alkali chlorides; $KMgCl_3$; and $UCl_3$**

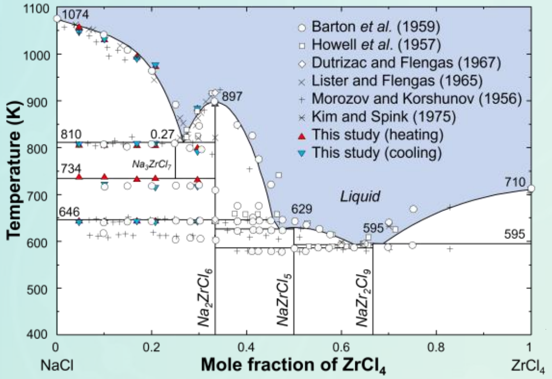


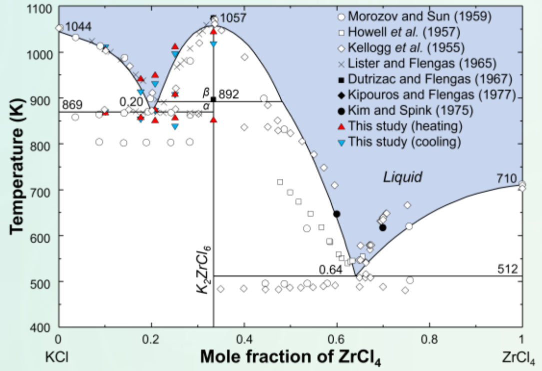



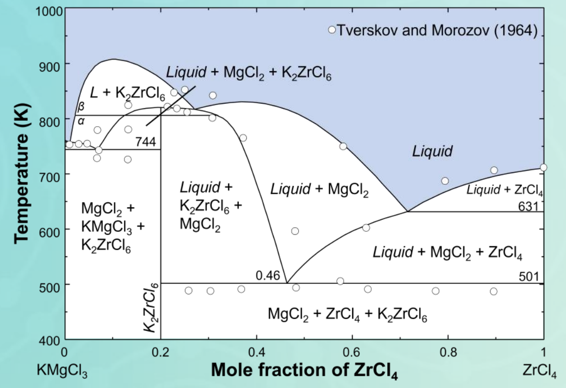



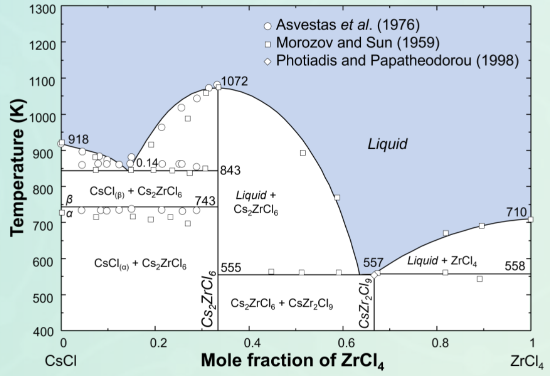



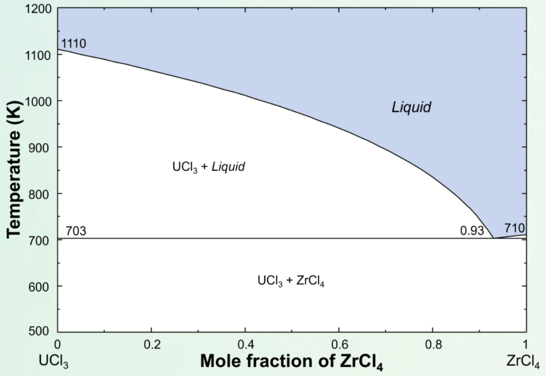

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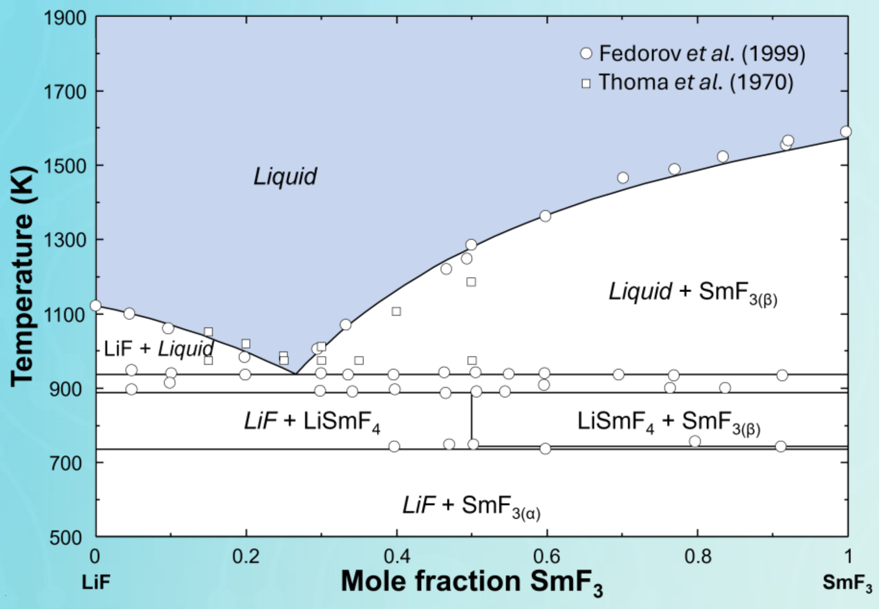
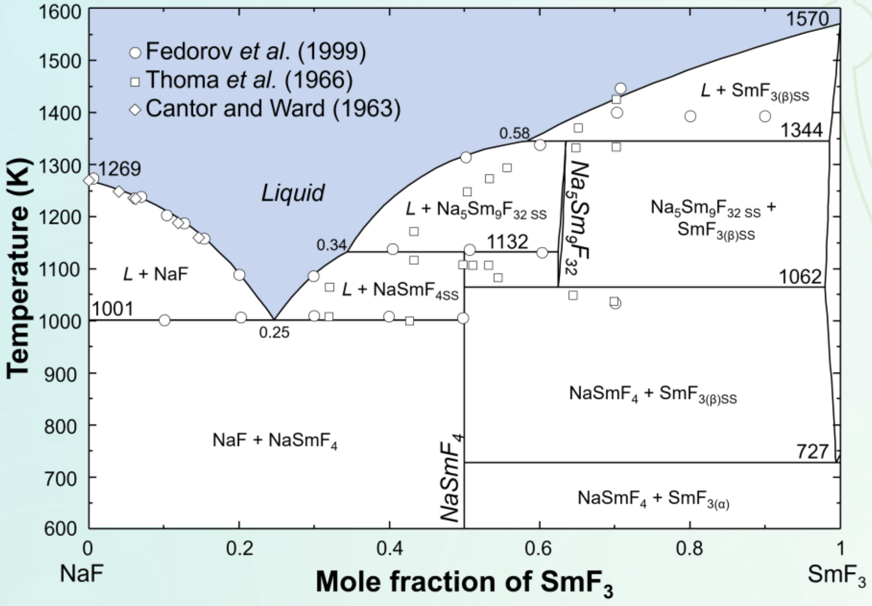
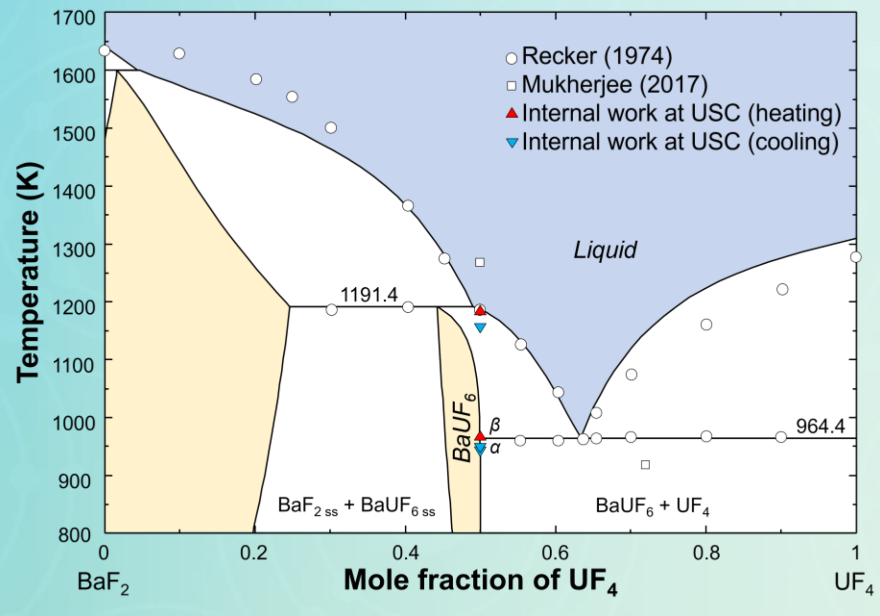
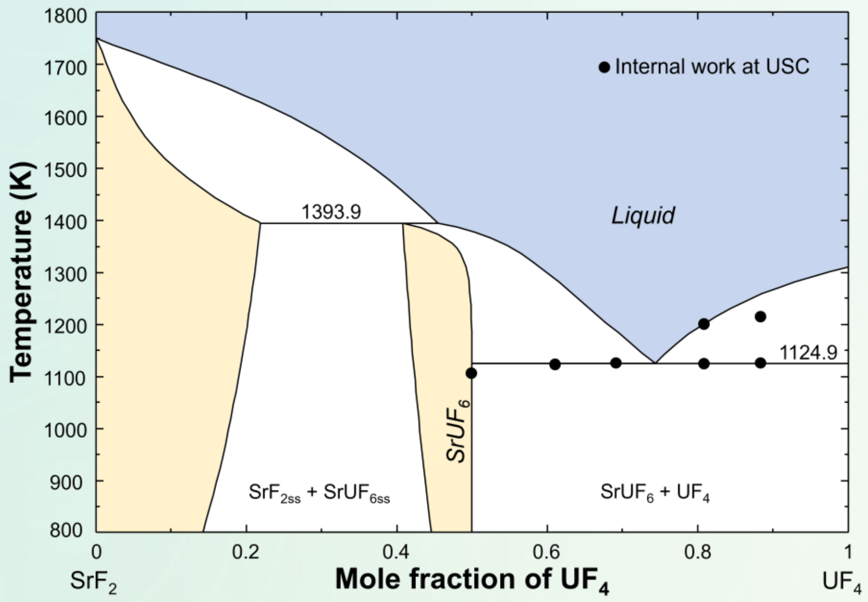
# Computed Phase Diagrams from Derived Models for Newly Added Fluoride Systems



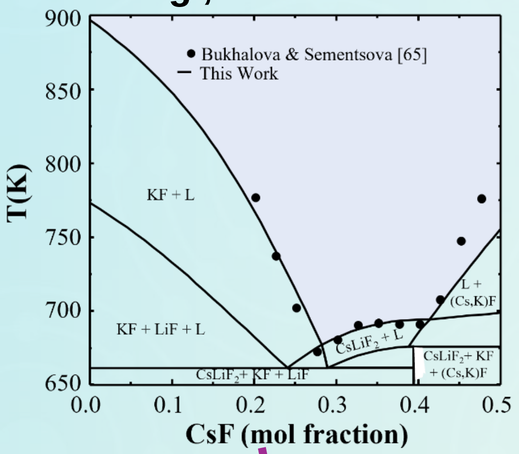




Pseudo-binary systems optimized for fission products:

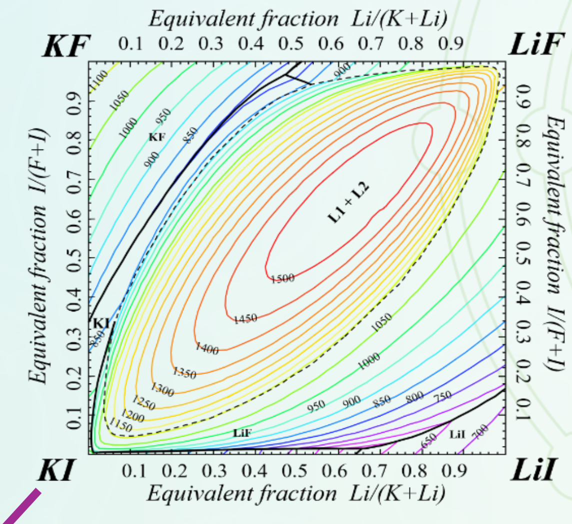
- $BaF_2$
- $SmF_3$
- $SrF_2$

# High Order Models for Reciprocal Salts Require Numerous Subsystem Models

### Additive Psuedo-Ternaries
### e.g., LiF-KF-CsF

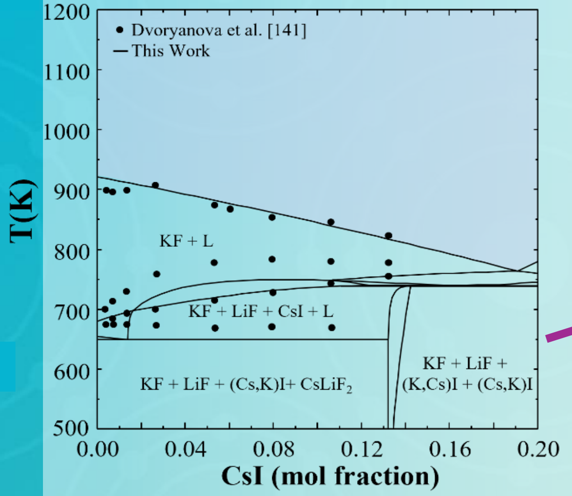


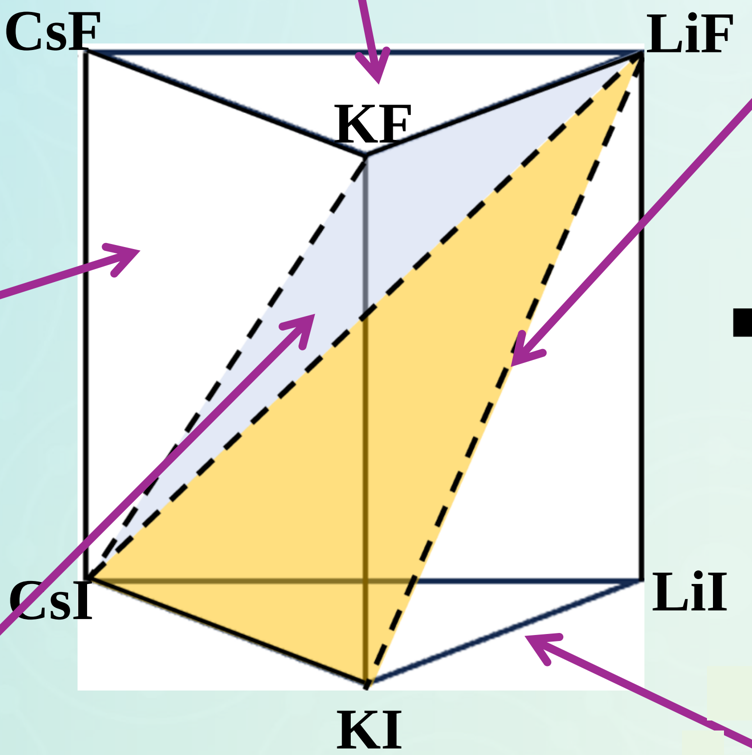

### Reciprocal Ternaries
### e.g., Li, K | F, I

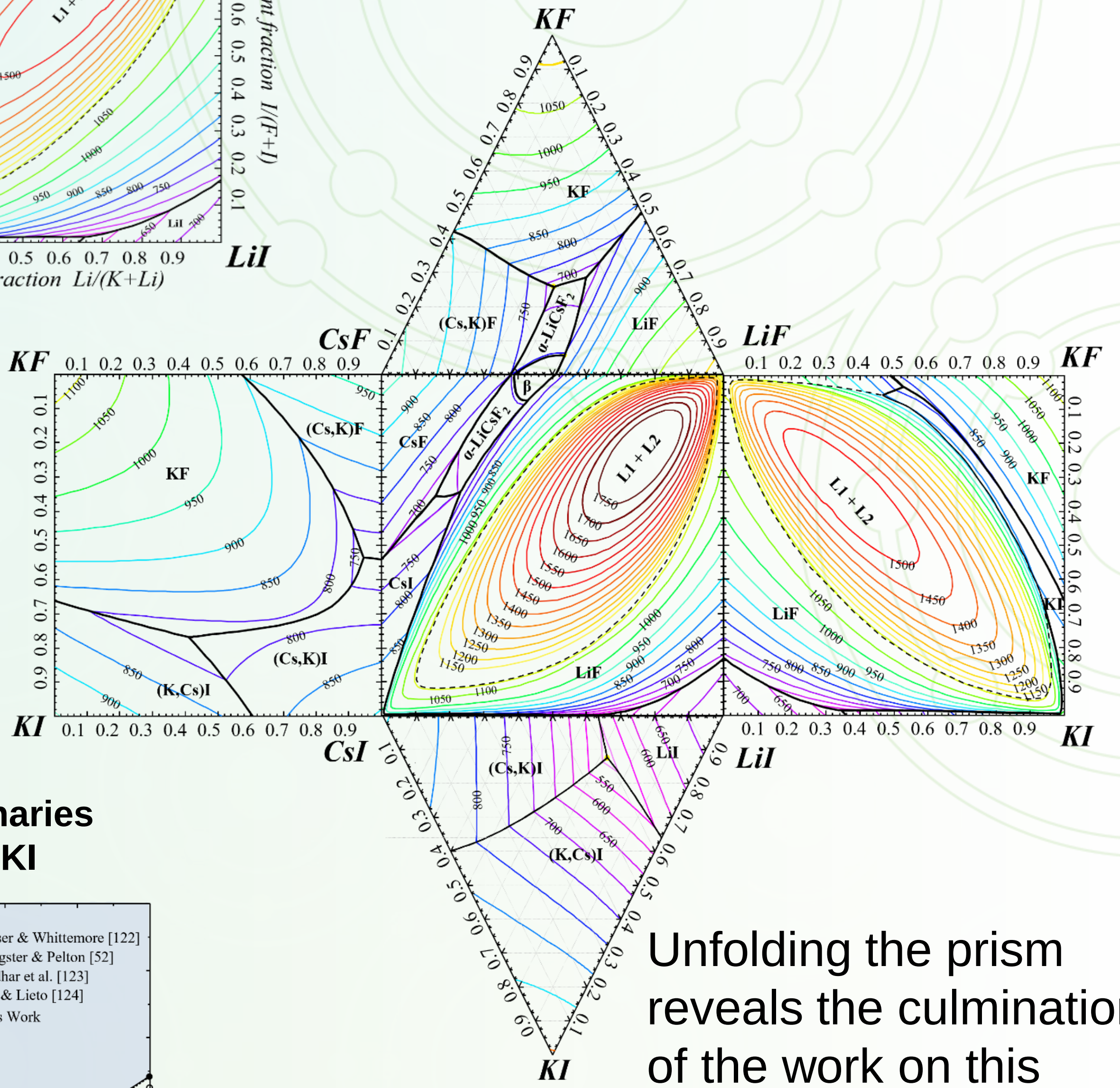



## Example: Li, K, Cs | F, I

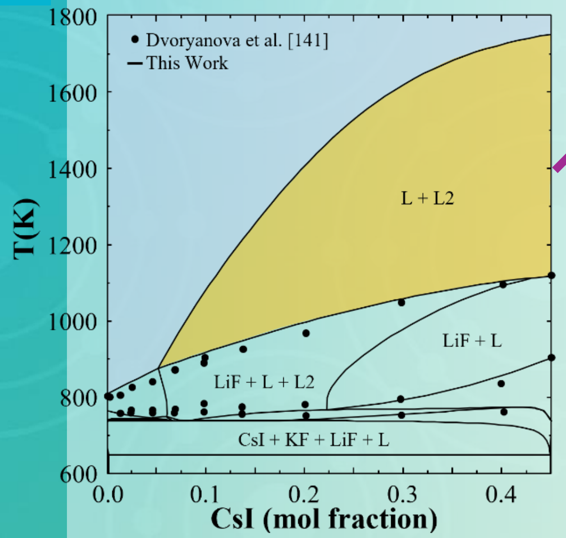
### Reciprocal Quaternary Internal Sections
### LiF-KF-CsF-CsI



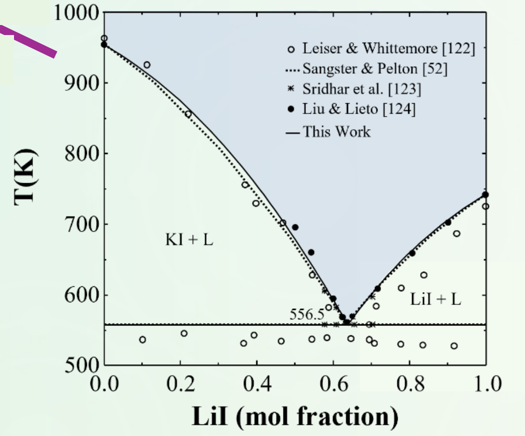




### Reciprocal Quaternary Internal Sections
### LiF-KF-CsI




Representation is validated using reported phase equilibria of quaternary internal sections

### Psuedo-Binaries
### e.g., LiI-KI




Unfolding the prism reveals the culmination of the work on this system

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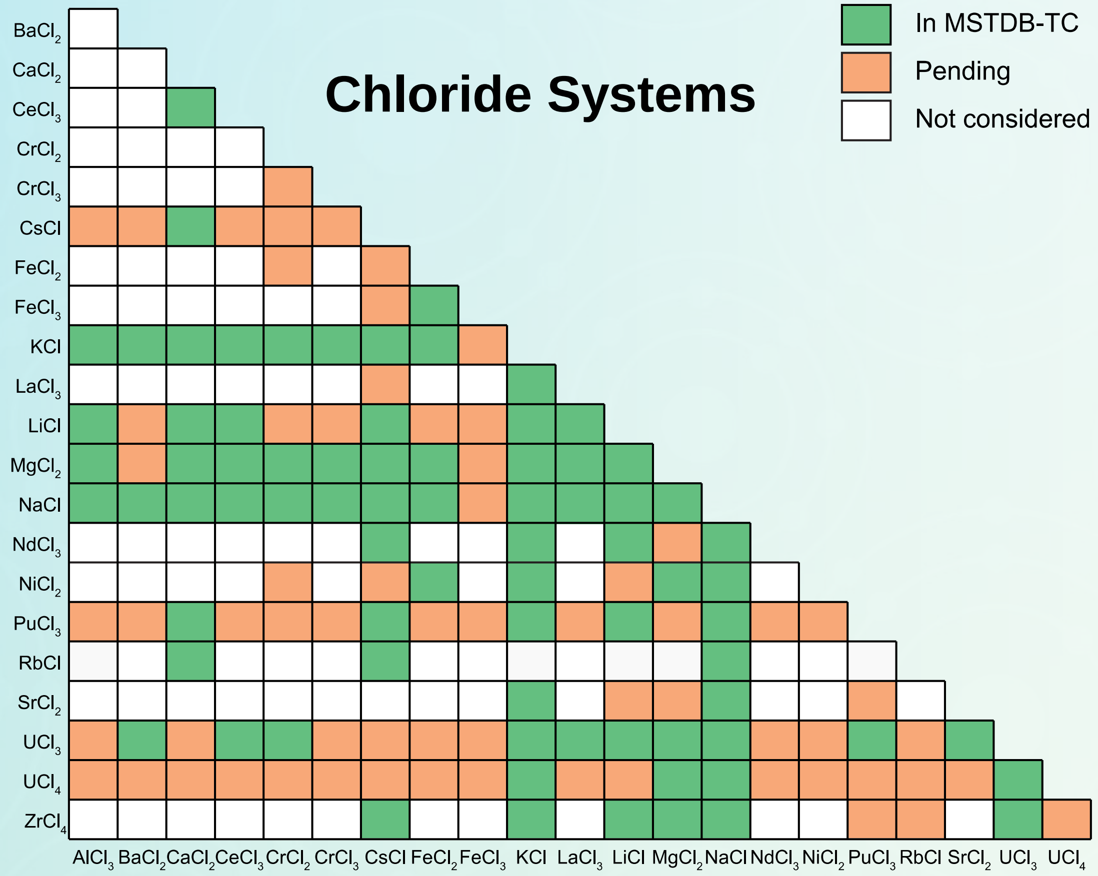
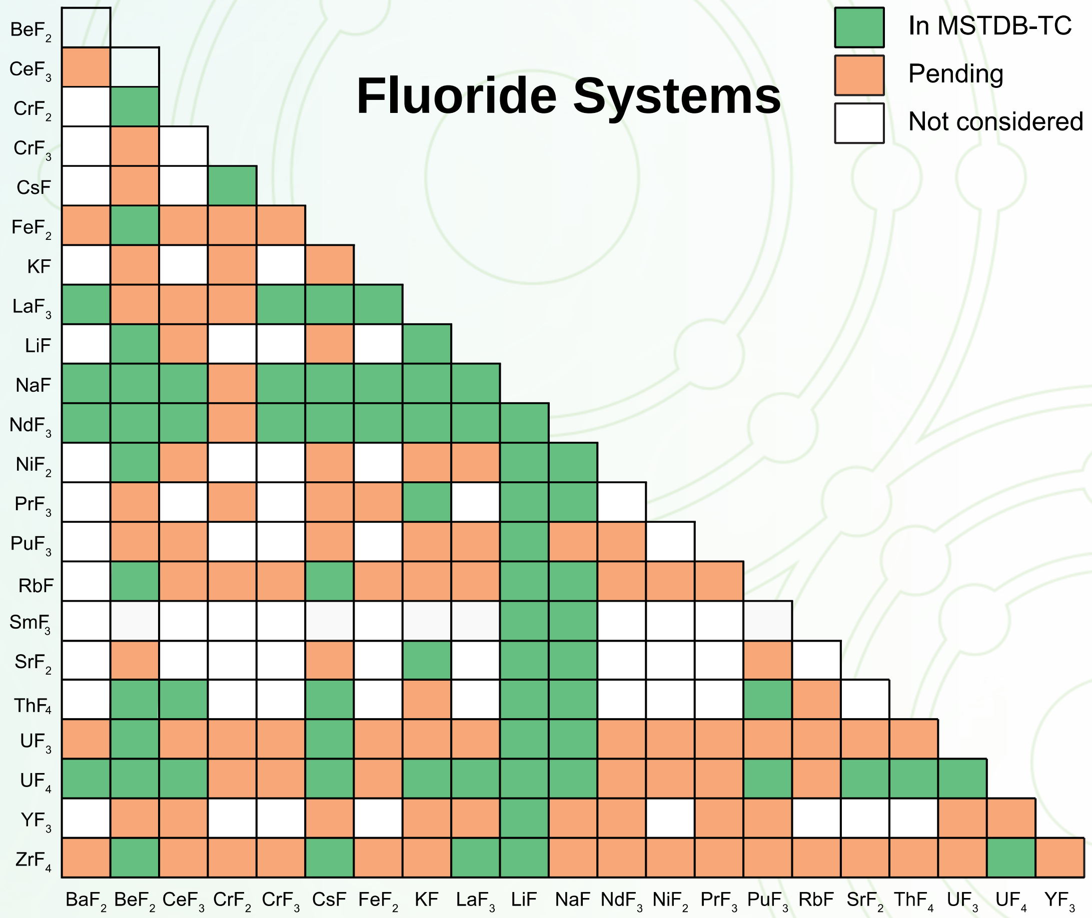
# Pseudo-binary Systems Content Matrices

# Content of Newly Released *MSTDB-TC* Ver. 4.0

## MSTDB Databases Available at

## *mstdb.ornl.gov*




- MSTDB-TC Ver. 4.0 contains
  - 175 pseudo-binary systems
  - 61 pseudo-ternary systems
  - 12 reciprocal systems that include iodine as anion
- Added new models that consider $ZrCl_4$ ,$BaCl_2$, $SrCl_2$, $BaF_2$, $SrF_2$, $LaCl_3$
- NaCl-$MgCl_2$ refined based on new experimental data
- Improved reciprocal system models with iodine

## Higher Order Systems (> Pseudo-ternary)

- Li, Na | F, I
- Li, K | F, I
- Na, K | F, I
- Na, Cs | F, I
- K, Cs | F, I
- Li, Cs | F, I
- Na, K | Cl, I
- Na, Cs | Cl, I
- K, Cs | Cl, I
- Li, K, Cs | F, I
- Li, Na, Cs | F, I
- Na, K, Cs | F, I
- Na, K, Cs | Cl, I
- Li, Na, K, Cs | F, I
- $MgCl_2$-NaCl-CsCl
- $MgCl_2$-NaCl-$UCl_{3,4}$
- $MgCl_2$-KCl-$UCl_{3,4}$

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# Additions/Changes in MSTDB-TC for Ver. 4.0 vs. Ver. 3.1

Newly assessed
<u>pseudo-binary systems</u>

- $NaCl$-$MgCl_2$
- $LiCl$–$ZrCl_4$
- $NaCl$–$ZrCl_4$
- $KCl$–$ZrCl_4$
- $CsCl$–$ZrCl_4$
- $MgCl_2$–$ZrCl_4$
- $UCl_3$–$ZrCl_4$
- $BaF_2$–$UF_4$
- $SrF_2$–$UF_4$
- $LiF$–$SmF_3$
- $NaF$–$SmF_3$

Newly assessed
<u>pseudo-ternary systems</u>

- $KCl$-$MgCl_2$-$ZrCl_4$
- $KCl$-$NaCl$-$ZrCl_4$
- $LiF$-$BeF_2$-$CeF_3$
- $LiF$-$BeF_2$-$CsF$
- $LiF$-$BeF_2$-$LaF_3$
- $LiF$-$BeF_2$-$NdF_3$
- $LiF$-$BeF_2$-$PuF_3$
- $LiF$-$BeF_2$-$UF_3$

<u>Existing models refined</u>

- $SrF_2$
- $BeF_2$–$KF$
- $KF$–$SrF_2$
- $LiF$–$SrF_2$
- $NaF$–$SrF_2$

# Current and Future FY25 Activities

- **FY25 M3 Milestone**
  - Report on the optimization of the thermochemical models for $MgCl_2$-$BaCl_2$, -$SrCl_2$; $BaCl_2$-$BaI_2$; $SrCl_2$-$SrI_2$; and where salts/data are available Sm, Pr, and Gd fluorides with LiF, NaF, KF, and chlorides with NaCl and KCl. The models will be incorporated in MSTDB-TC and database. 9/30/2025
- **Systems undergoing evaluation and modeling**
  - Ba, Sr, and I in $MgCl_2$
  - Sm in LiF, NaF, KF
  - Pr in LiF, NaF, KF
  - Gd in LiF, NaF, KF
  - Sm, in NaCl, KCl
  - Pr in NaCl, KCl
  - Gd in NaCl, KCl
  - NaCl-$MgCl_2$-$UCl_3$
- **2025 Molten Salts Thermal Properties Working Group Virtual Workshop**
  - ***Effect of Oxygen, Hydrogen, and Moisture on Molten Salt Behavior***

    10AM to 3PM EDT, June 3-4, 2025; Registration is not required

    Link will be provided at MSTDB.ornl.gov and in broad email
- **Continued development of GUI for viewing MSTDB-TC data and automated computing of pseudo-binary and –ternary phase diagrams with experimental data**

# Potential Efforts for FY26 and Beyond

- Refining understanding of FLiBe, including behavior of $BeF_2$, e.g., melt temperature
- Measurements and modeling of oxygen thermochemical behavior in base coolant and fuel salts
- Determining thermochemical parameters for hydrogen/tritium behavior in fuel salts, e.g., vapor pressures of hydrogen iodide
- Assessment of the state of tellurium in key salt systems to allow prediction via equilibrium calculations using MSTDB-TC
- Using Henry's law relationships for noble gases to allow including in thermochemical calculations
- Continued expansion of MSTDB-TC with priority additional constituents as identified by users and regulators

# USC General Atomics Center Group


Support for related activities provided by

NEAMS
Nuclear Energy Advanced Modeling and Simulation

NEUP Nuclear Energy University Program
U.S. Department of Energy

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# Thank you

Ted Besmann

besmann@sc.edu

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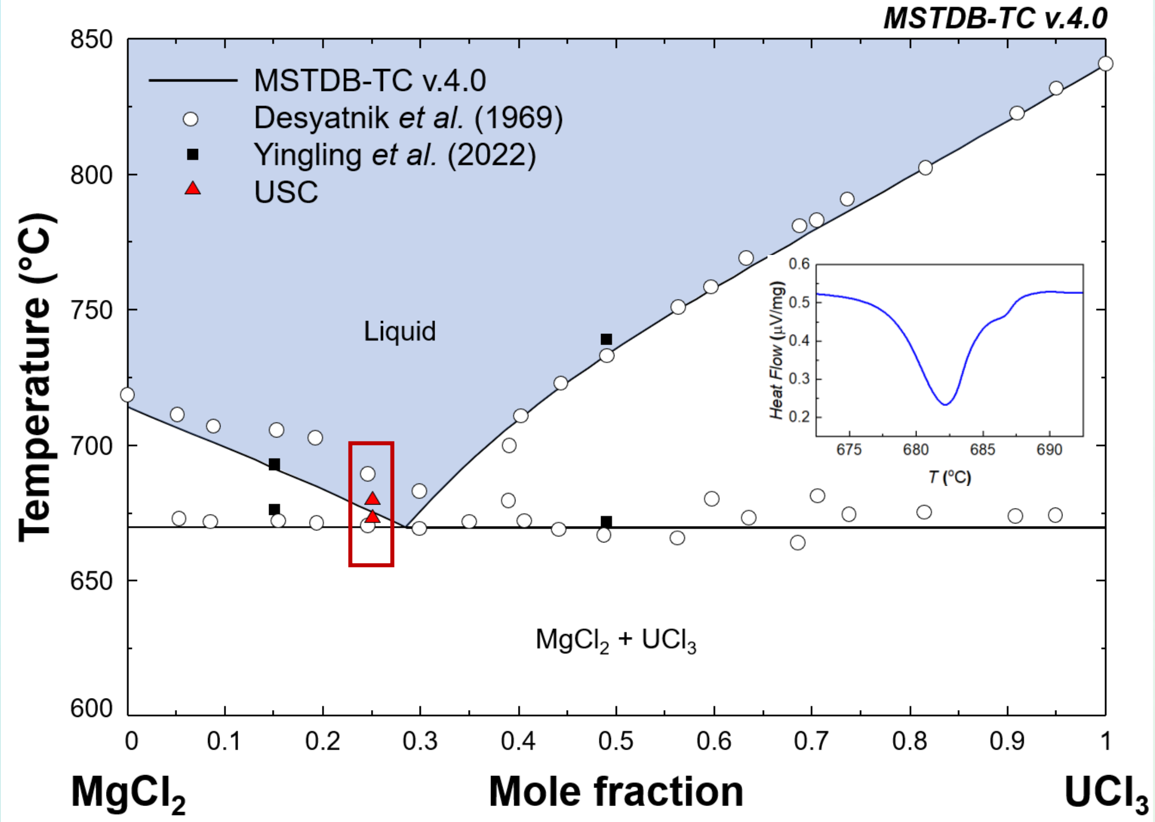
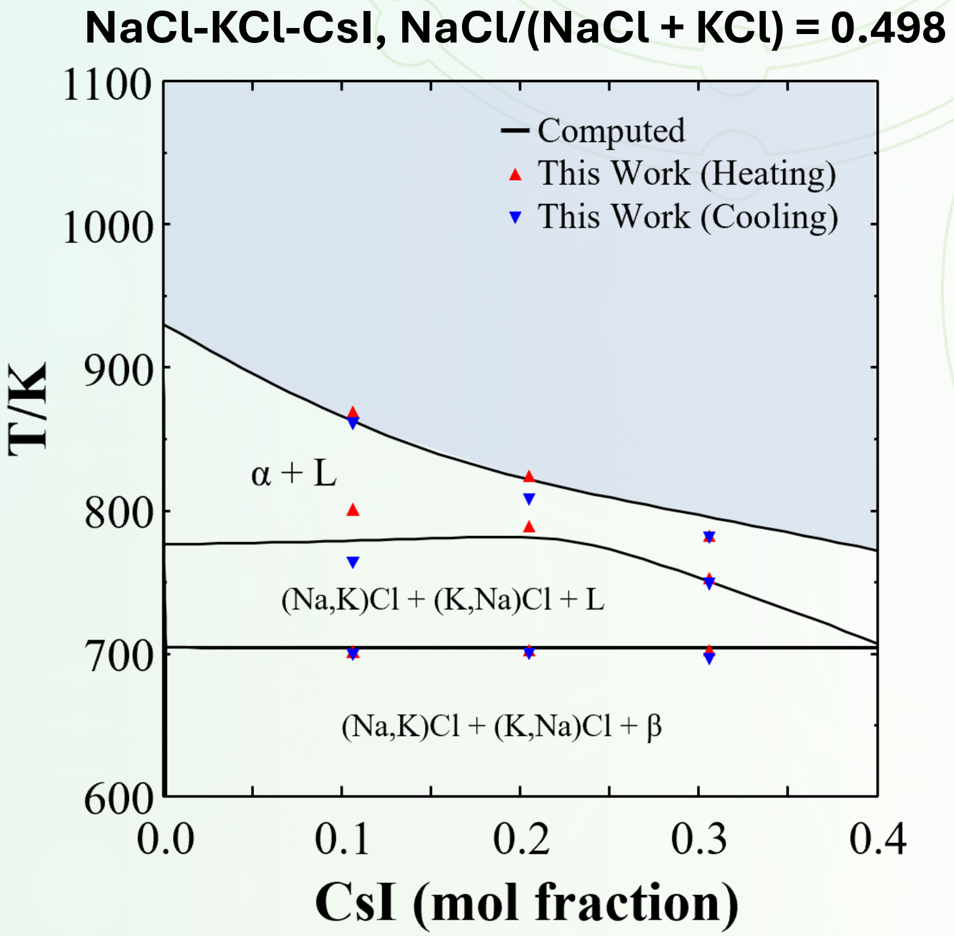
# Additional Slides

# Example System Evaluations and Modeling

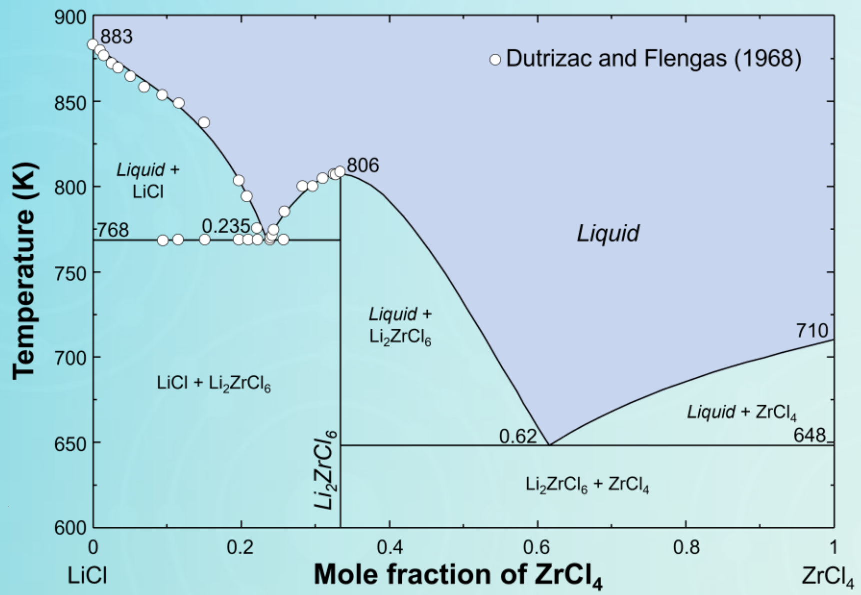
## Additional measurements beyond reported values used to improve $MgCl_2$-$UCl_3$ thermodynamic model

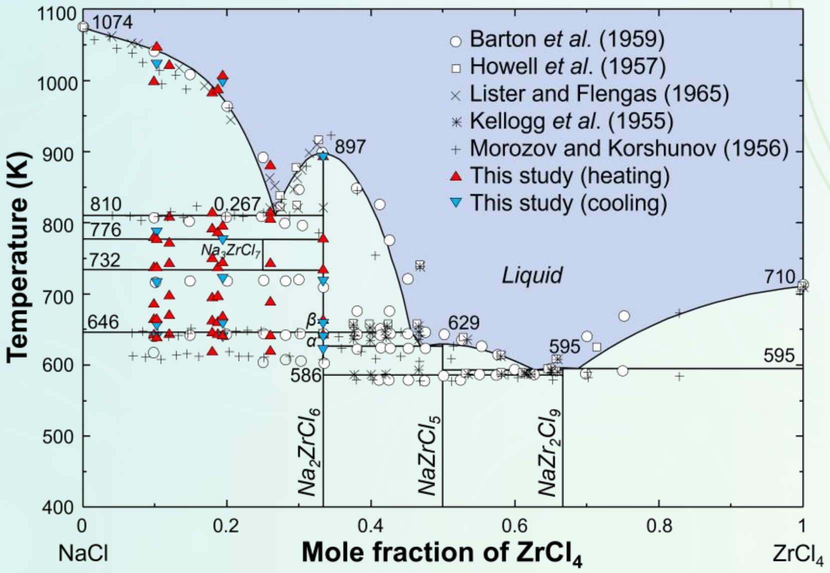


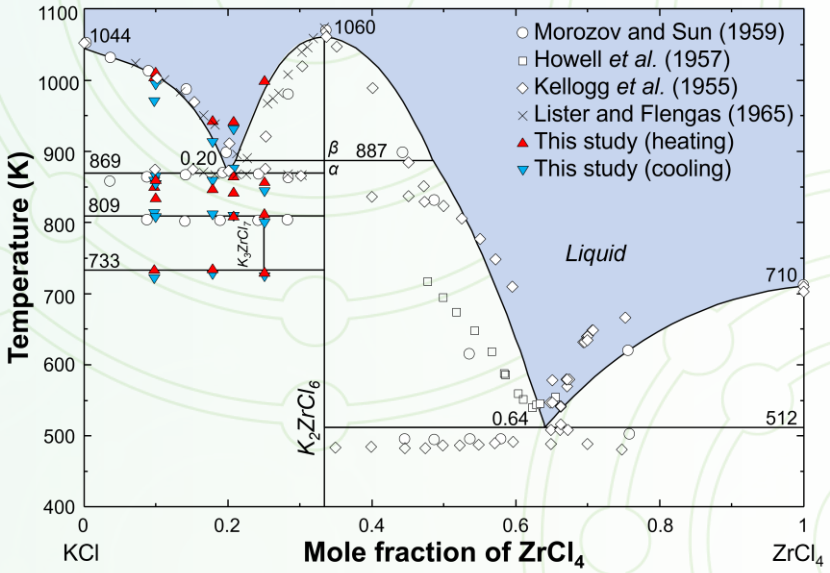

## Na,K,Cs|Cl,I fully modeled and validated using new NaCl-KCl-CsI measurements

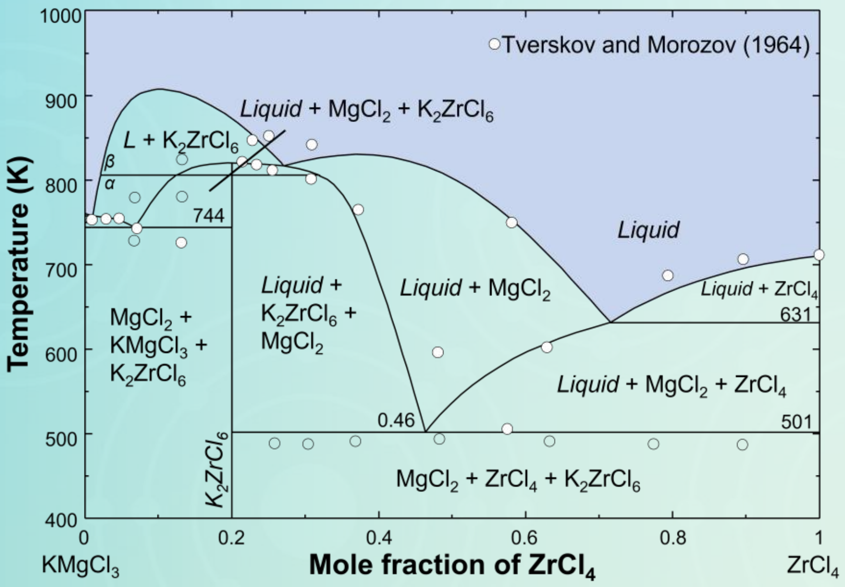


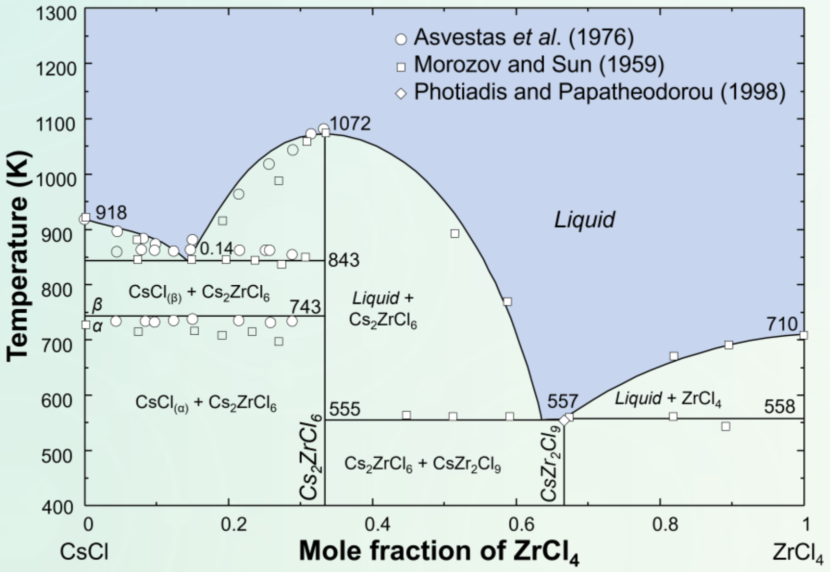
# Computed Phase Diagrams from Derived Models for Zr-Cl-FP Systems

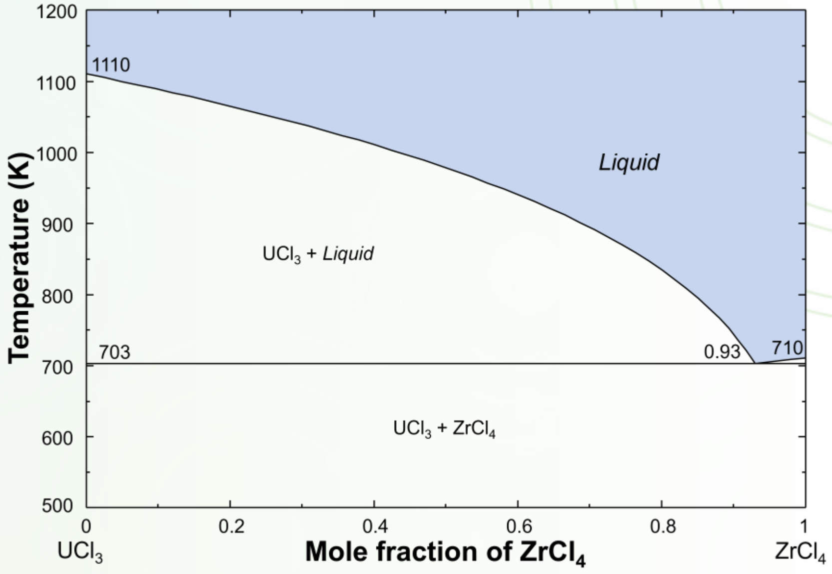


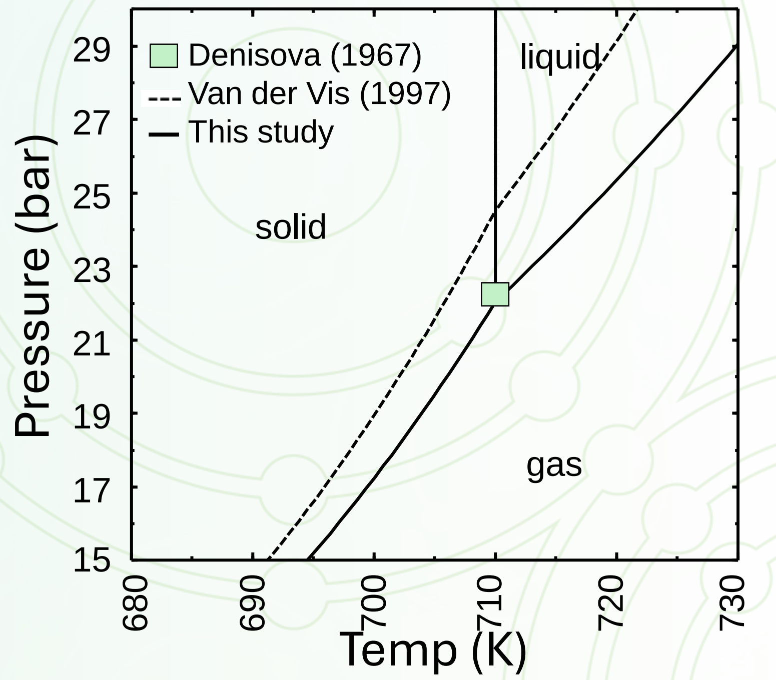



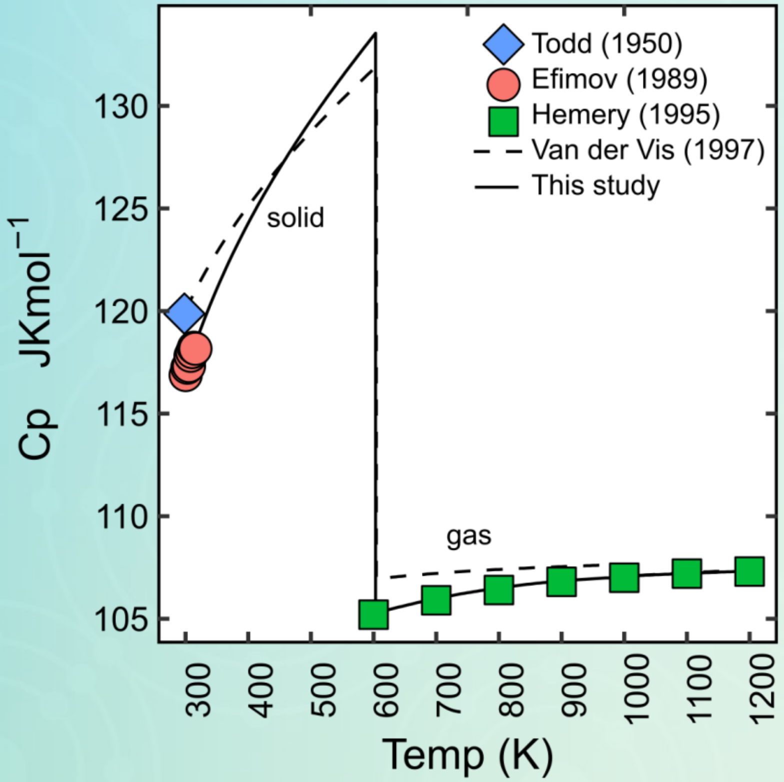
# $ZrCl_4$ Optimized Using Available Thermochemical data

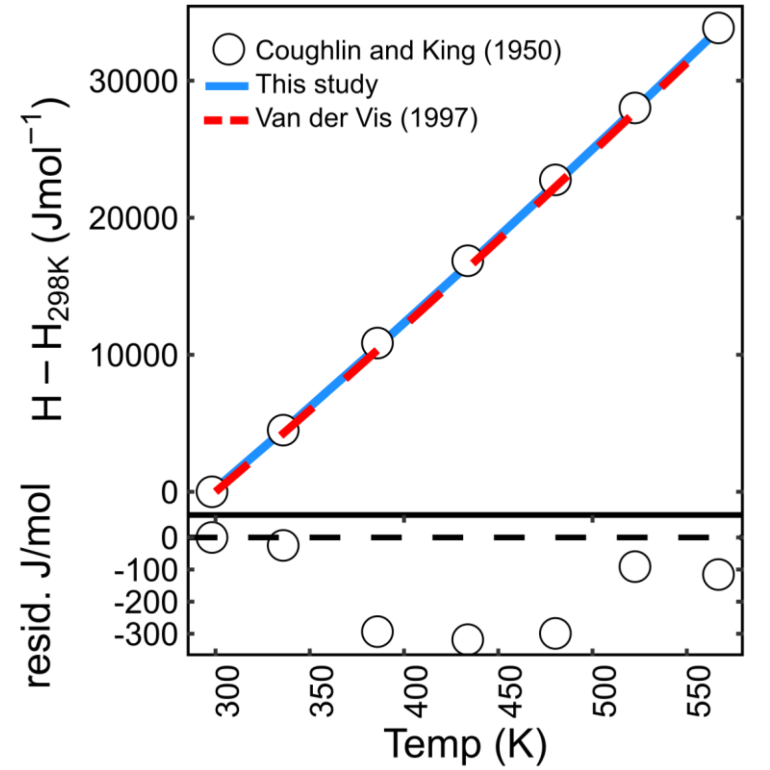
Gibbs energy functions for $ZrCl_{4(s,\,l,\,\text{and } g)}$ fit to phase equilibria, $\Delta_f H°$, $\Delta_{fus} H°$, $\Delta_{sub} H°$, $\Delta_{sub} S°$, Cp, S,

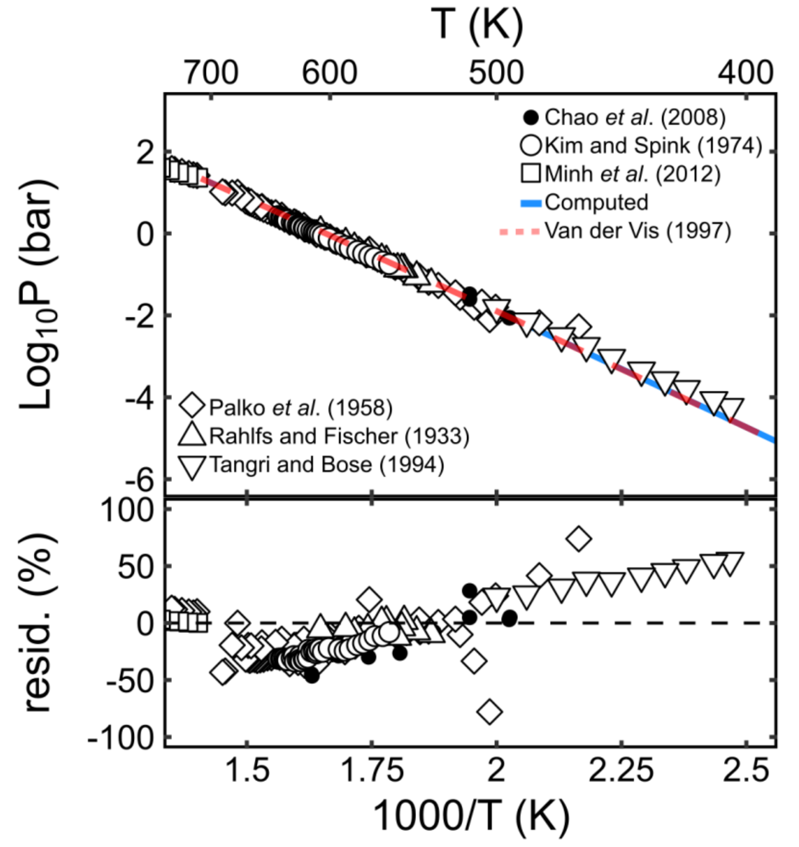
Needed to:

- Better reconcile Cp and enthalpy increment data
- Capture the triple point
- Better fit the available vapor pressures

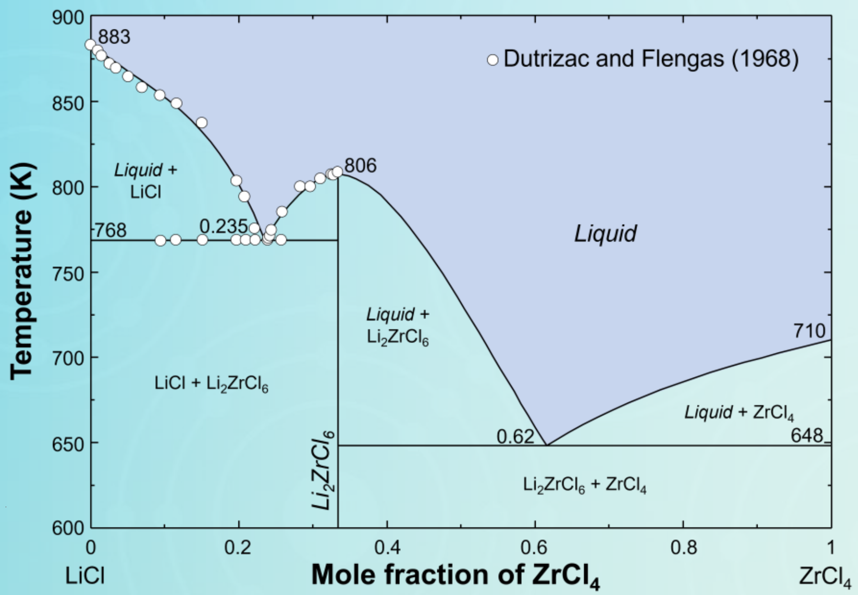


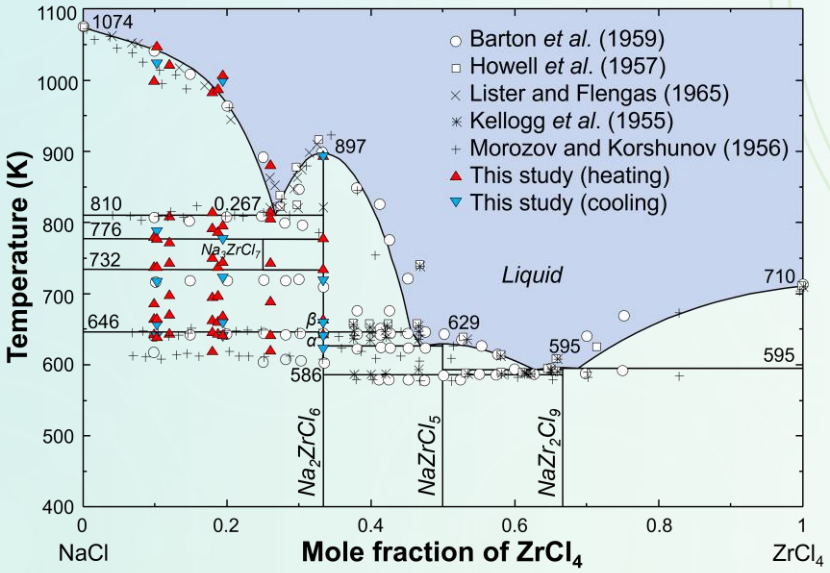



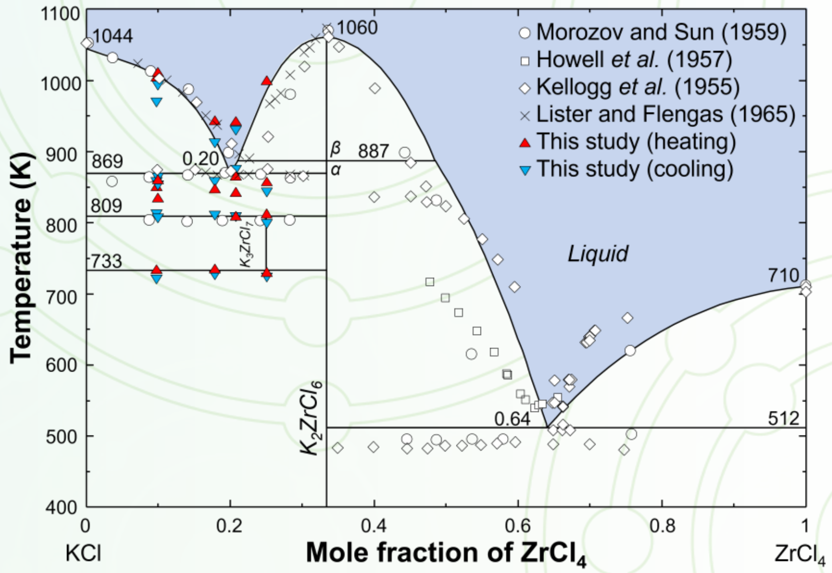



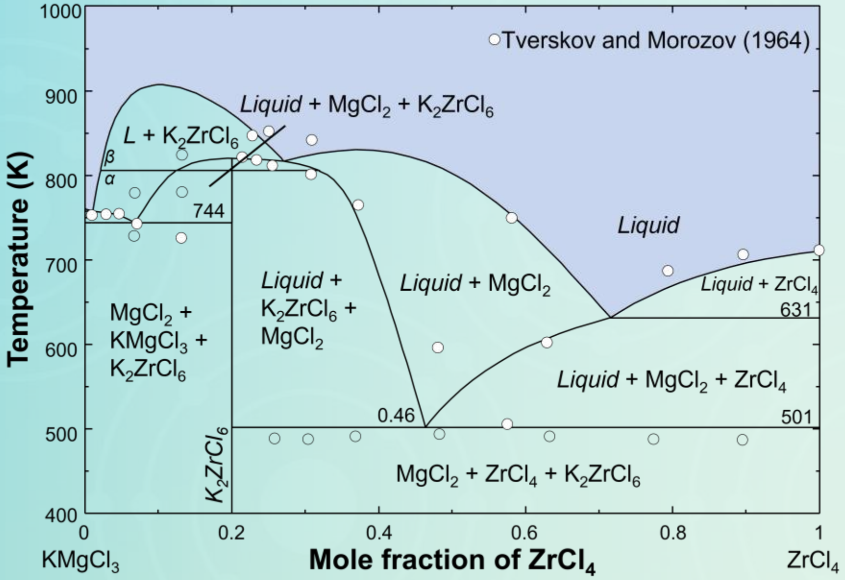



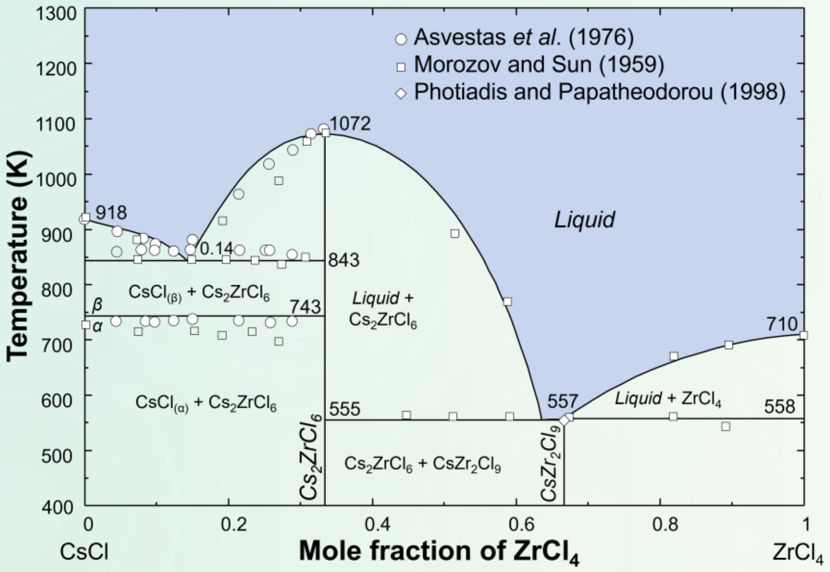
# Computed Phase Diagrams from Derived Models for Zr-Cl-FP Systems

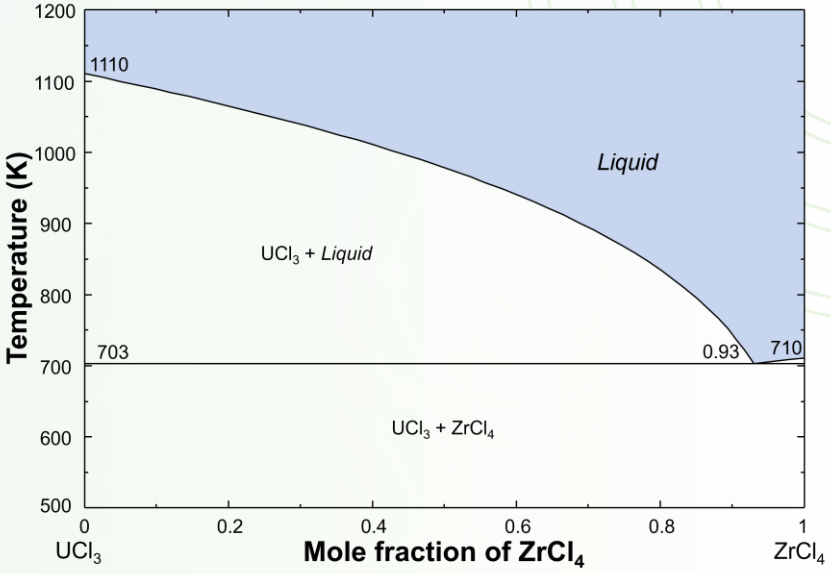


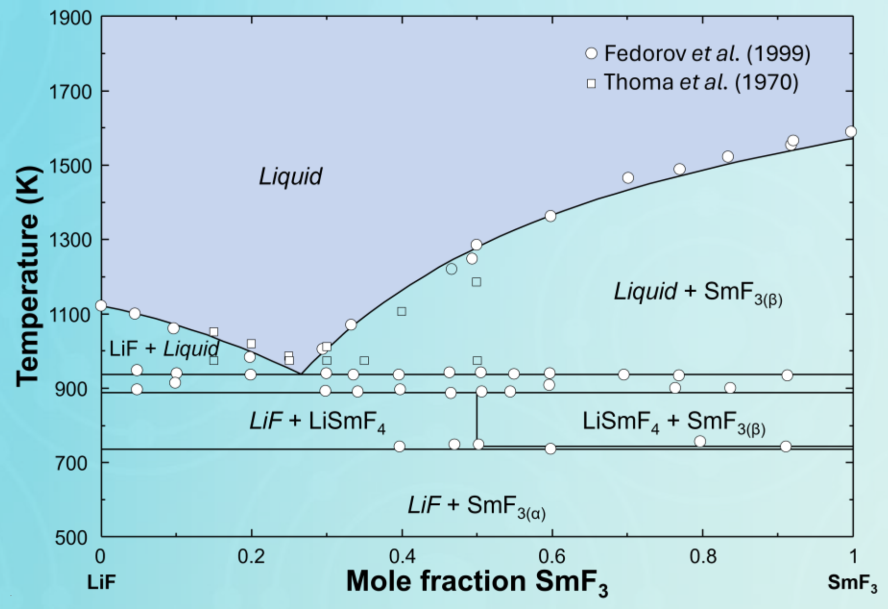



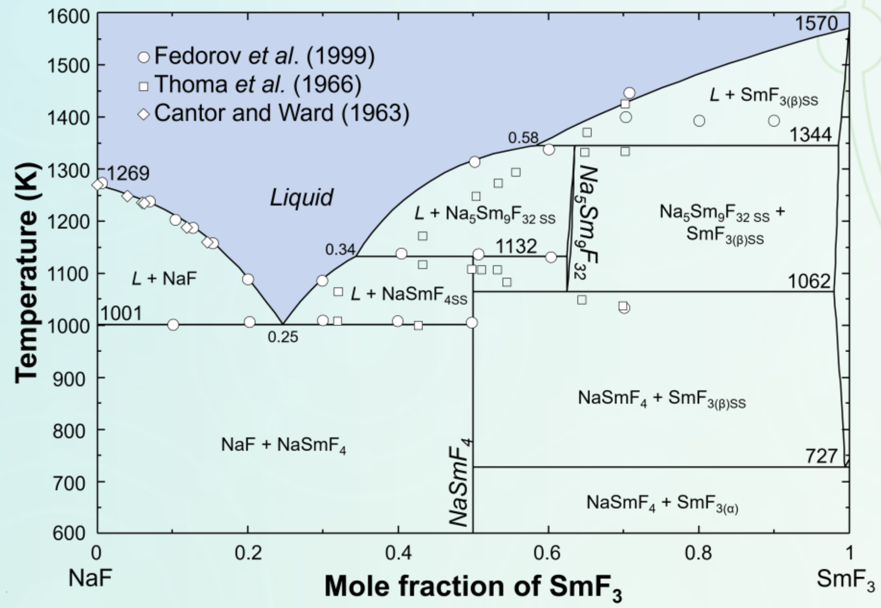



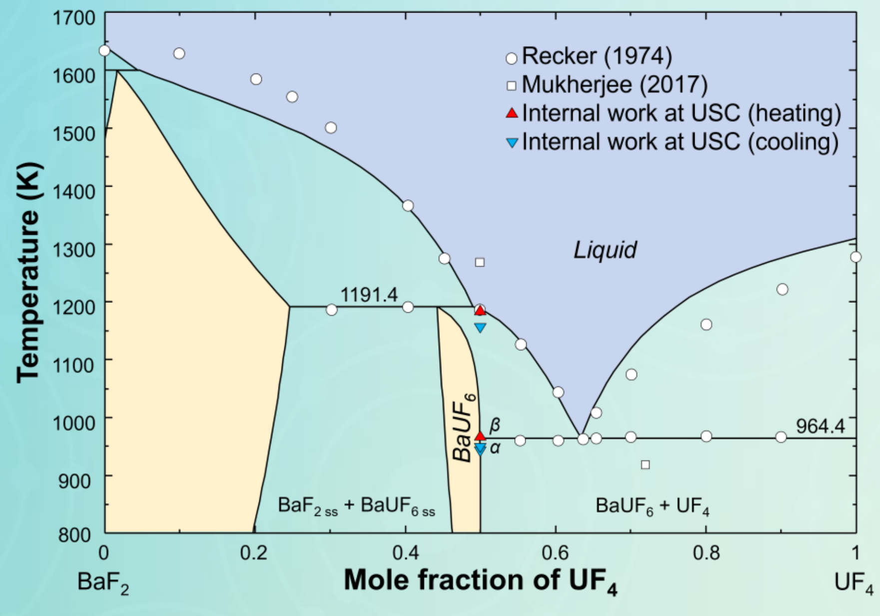

Molten Salt Reactor PROGRAM

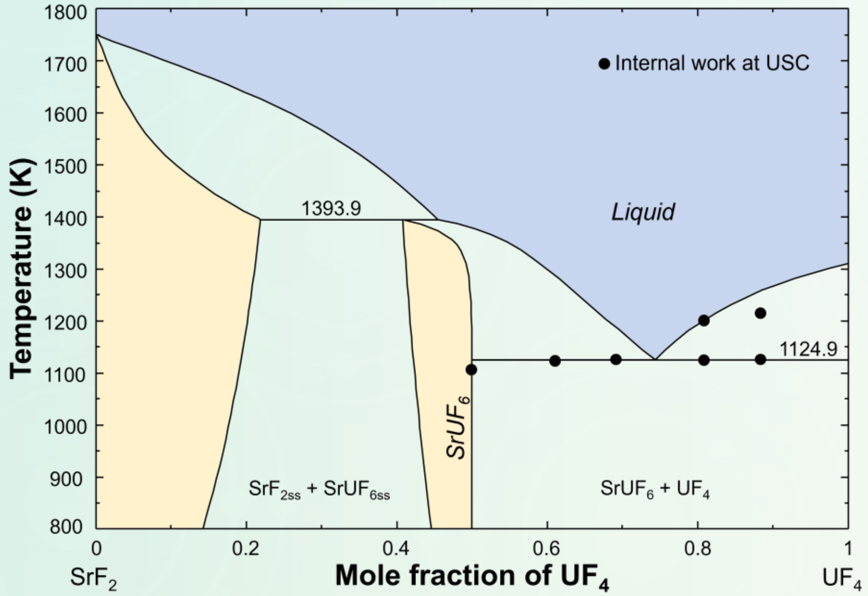
U.S. DEPARTMENT of ENERGY
Office of Nuclear Energy

# Computed Phase Diagrams from Derived Models for Newly Added Fluoride Systems




Pseudo-binary systems optimized for fission products:

- $BaF_2$
- $SmF_3$
- $SrF_2$