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Thermal Properties of Molten Salts: Crucial Data for the Development of MSRs

Prof. Juliano Schorne-Pinto

10 September 2026

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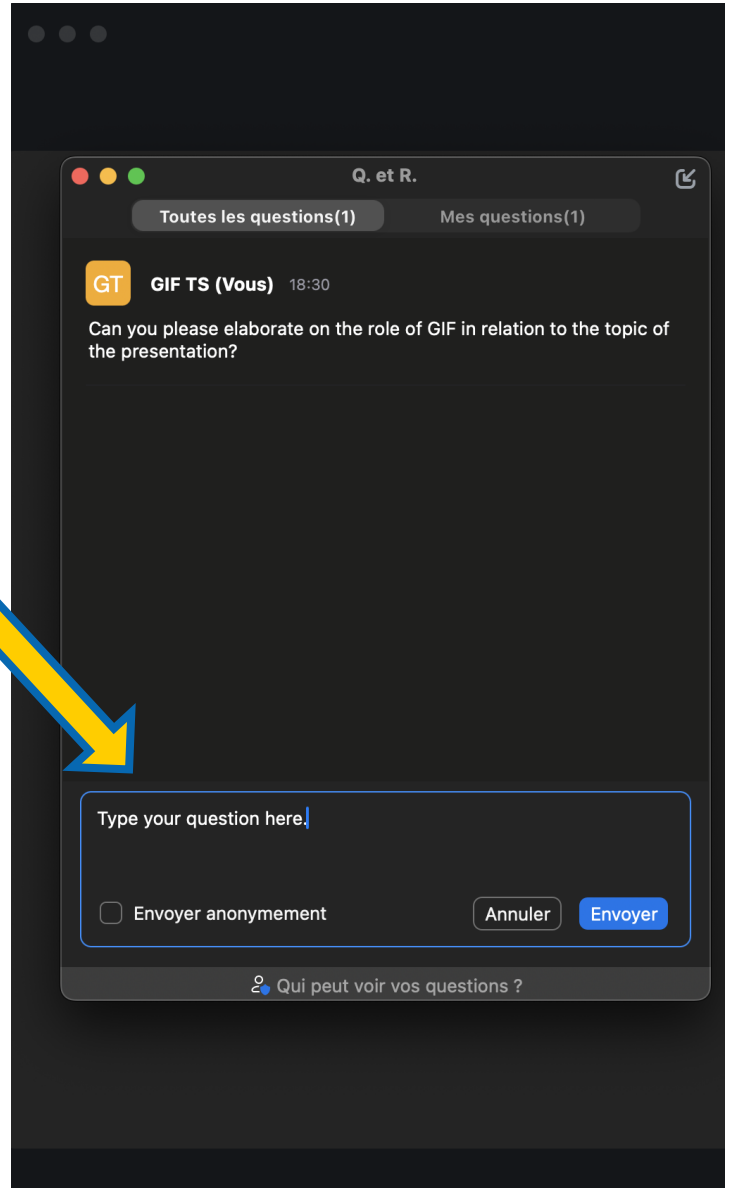

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Thermal Properties of Molten Salts: Crucial Data for the Development of MSRs

Prof. Juliano Schorne-Pinto

10 September 2026

UNIVERSITY OF SOUTH CAROLINA

Meet the Presenter

Dr. Juliano Schorne-Pinto is an Assistant Professor in the Nuclear Engineering Program at the University of South Carolina. His research centers on high-temperature chemistry and thermodynamics, with particular emphasis on actinides, molten salts, and nuclear materials. His expertise covers synthesis, characterization, and thermodynamic modeling (CALPHAD method), as well as thermal analysis techniques for determining phase equilibria, heat capacity, enthalpy increment, and heats of transition and mixing in radioactive and non-radioactive systems.

His work provides reliable experimental data and thermodynamic models for the design, operation, and licensing of molten salt reactors, notably through his role as co-developer of the Molten Salt Database – Thermochemical (MSD-TC), supported by the DOE Molten Salt Reactor Program.

He has authored over 35 peer-reviewed publications. He received his PhD from the National Polytechnic Institute of Toulouse, France, in 2020, his MS from Polytech Montpellier, France, and his BS from the Federal University of Rio Grande do Sul, Brazil.

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One Fluid, Three Roles: Fuel, Coolant and Process Medium

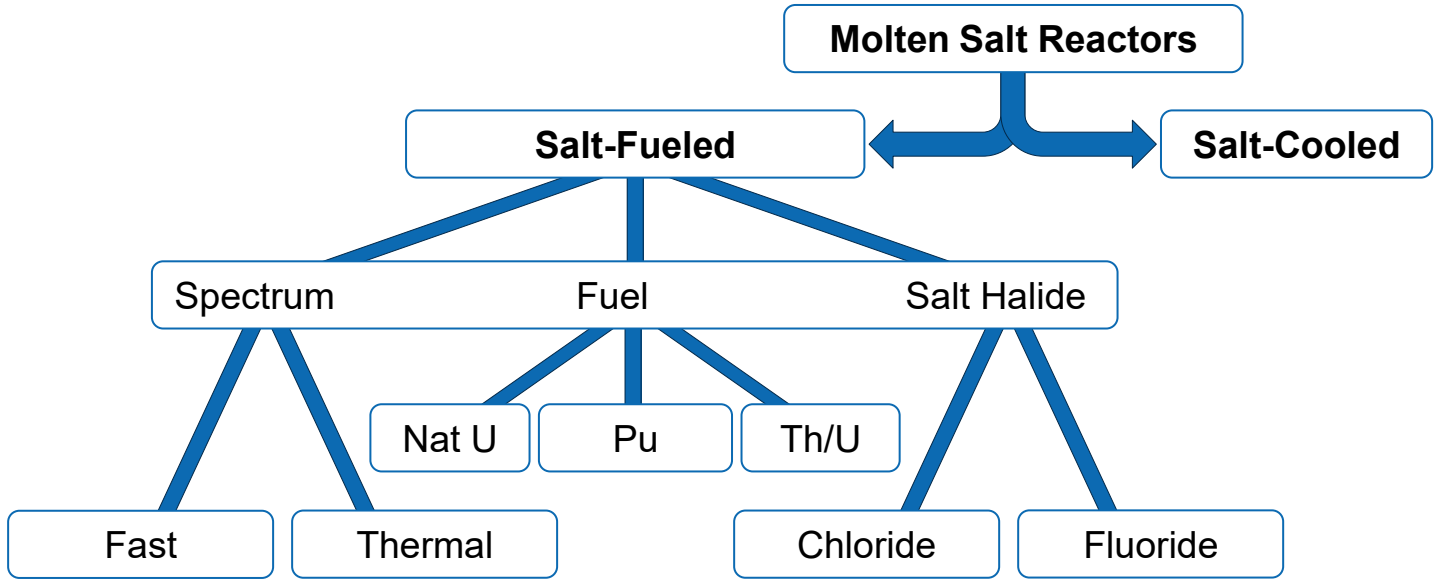
Why salts?

- High solubility of U, Pu and Th
- Excellent heat transfer fluid
- High boiling point
- Compatible with structural materials

Potential areas of interest:

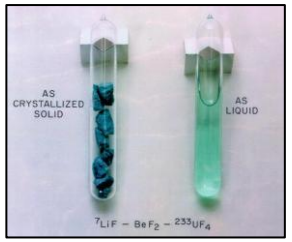
- Pyroprocessing
- Waste Recycling
- **Molten Salt Reactors**

*Salt-Fueled and Salt-Cooled: The MSR Design Space**



Crystallized NaCl-UCl_3 fuel salt (INL)

Solid and molten FLiBe-UF_4 (ORNL)



Today's webinar will be focused on the thermochemical properties

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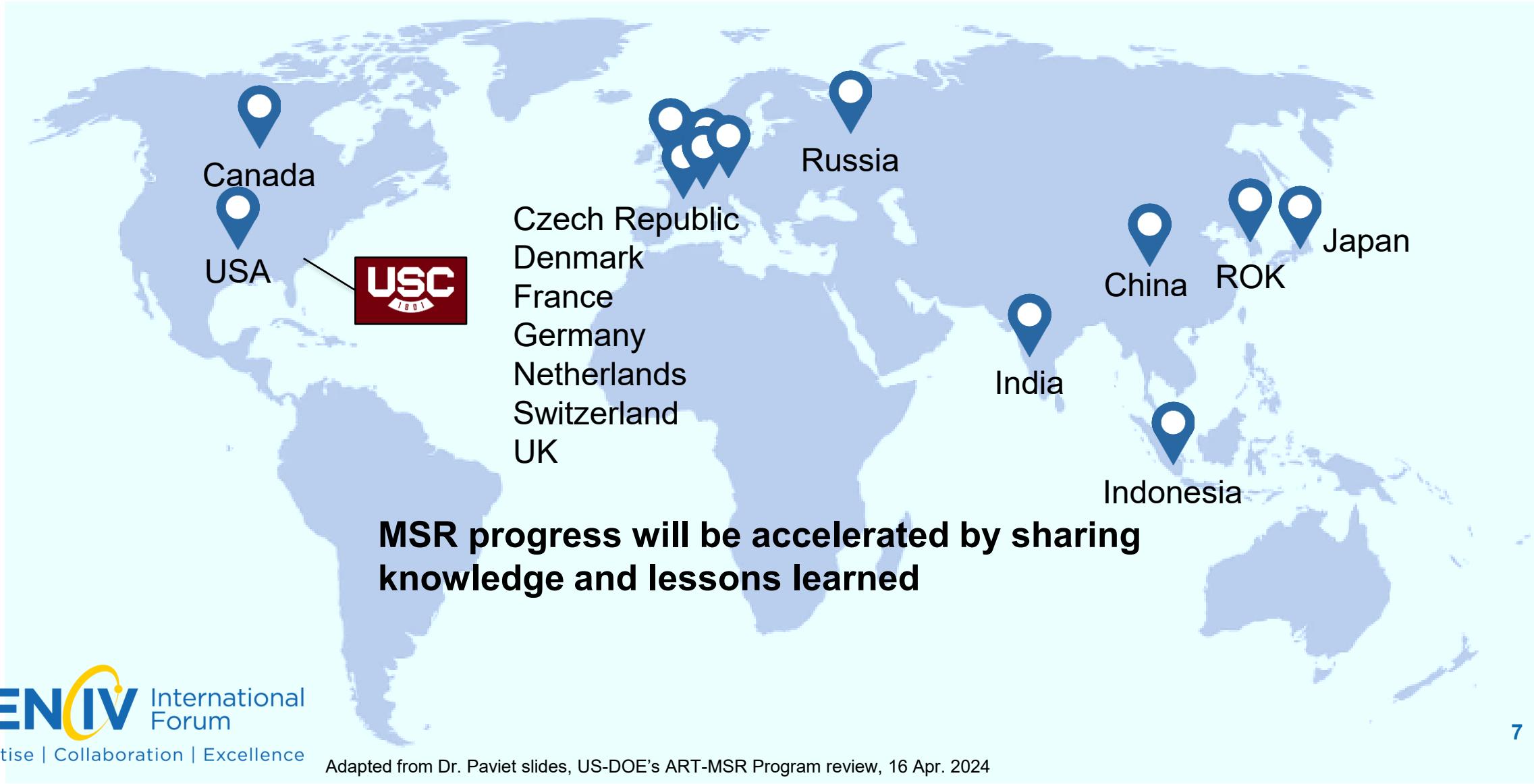
**Adapted from Dr. Paviet slides, US-DOE's ART-MSR Program*

Images: INL, crystallized NaCl-UCl_3 fuel salt, "How molten salt could be the lifeblood of tomorrow's nuclear energy" (19 June 2023); ORNL, solid and molten FLiBe containing UF_4 (public domain).

MSR Research is Global



Adapted from Dr. Paviet slides, US-DOE's ART-MSR Program review, 16 Apr. 2024

Molten Salt Chemistry is Complex

During operation, fission products, corrosion products, and contaminants partition among the salt, gas phase, and system surfaces

In the molten salt:

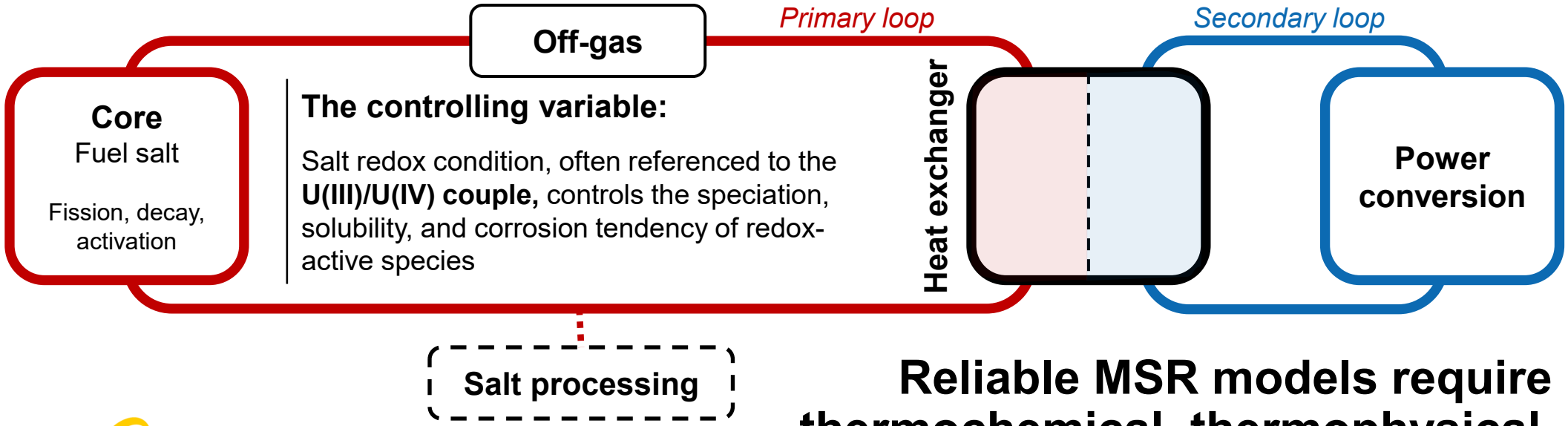
Soluble fission products build up: **Cs, Sr, I, Zr, Ln, actinides**
Raise liquidus, change halide potential

In the gas:

Noble gases Xe, Kr, and He are removed by gas stripping. Ingress of O_2 and H_2O increases the oxidizing potential

On the surfaces

Noble-metal fission products (**Ru, Rh, Pd, Tc, Mo, Ag**) can deposit on metallic surfaces.
Corrosion products: **Cr, Fe, and Ni**



Reliable MSR models require <u>thermochemical</u>, thermophysical, and transport-property data

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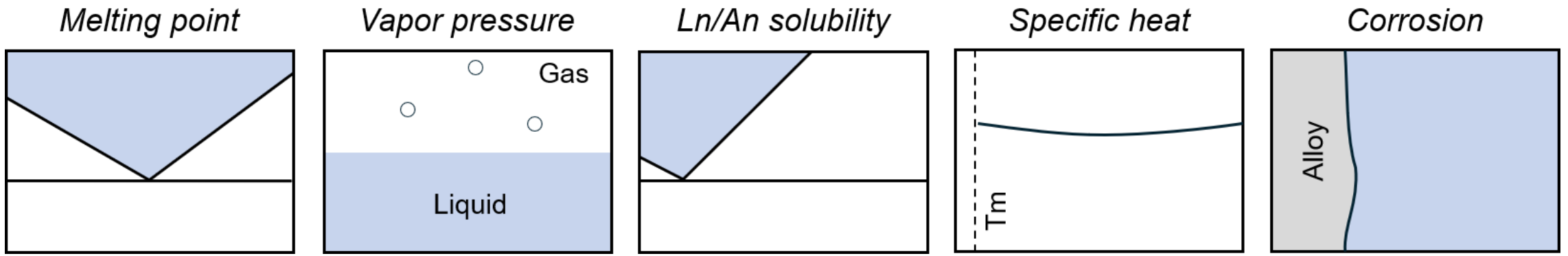
USC Is Supporting MSR Development by Providing the Molten Salt Database – Thermochemical (MSD-TC)

- Salt in a MSR should be near equilibrium due to high temperatures and liquid state
- Thermodynamic values and solution parameters are obtained by fitting models using known thermochemical properties and phase equilibria
- Self-consistent thermodynamic database
- CALPHAD method: minimizing the total Gibbs energy of the system
- Some of the relevant properties that can be calculated:



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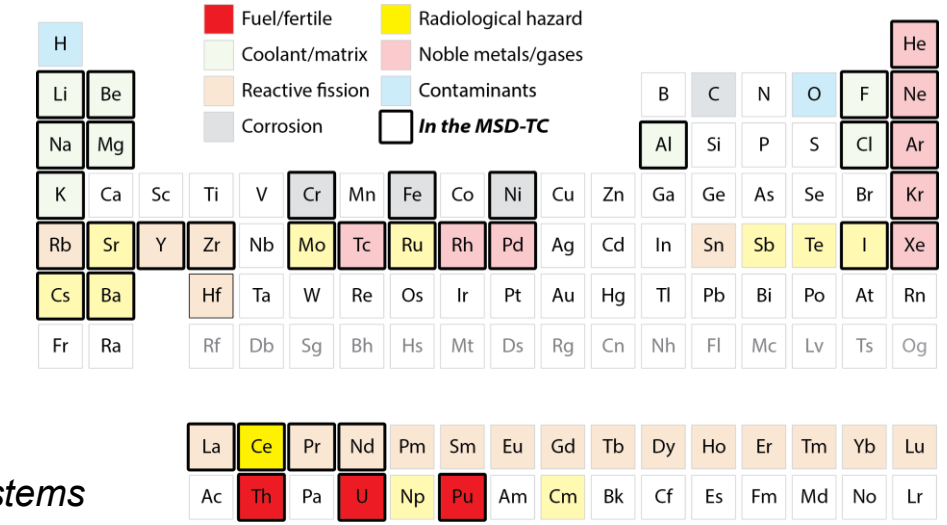
Thermodynamic models allow the accurate calculation of the chemistry of the complex multicomponent systems

MSD-TC Has Now Sufficient Content to Allow Representation of Realistic Systems

Describing major MSR designs:

- **Fuels and coolants** (e.g., FLiBe-U, NaCl-UCl_3)
- **Iodine**-containing systems
- **Cs, Sr, Ba, Y, La, Nd, Ce, and Zr** fission products
- **Fe-Cr-Ni-Mo** alloy phase systems and corrosion-related systems
- **Ru-Rh-Pd-Mo-Tc** noble metal phase systems
- **Kr, Xe, Ne, Ar, He** inert gases (no solubility info)

Elements included in the MSD-TC v.4.1

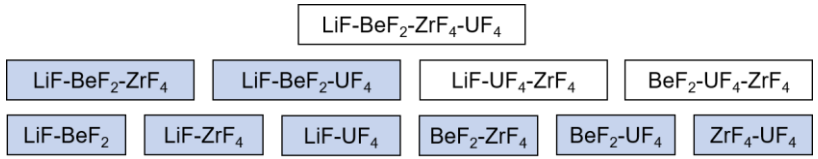


Example of MSRE fuel:

LiF-BeF_2-ZrF_4-UF_4 (65-29.1-5-0.9 mol%)

- Used to benchmark the accuracy of the models
- Excellent agreement was obtained for the extrapolation

MSRE fuel subsystems



Thermophysical properties of the fuel salt

	ORNL reports	MSD-TC ver. 4.1	Difference
Melting point	722 K	717.6 K (93% melted) 743.6 K (100%)	**4.4 K** **21.6 K**
Specific heat (c_P)	2010 J/kg.K	1966 J/kg.K 1681 J/kg.K (NKR*)	**-2.2%** **-16.4%**
Vapor pressure @ 1300 K	0.013 atm (3.95ZrF_4) 0.018 atm (8.13ZrF_4)	0.016 atm	**+23%** **-11%**

*Neumann-Kopp rule

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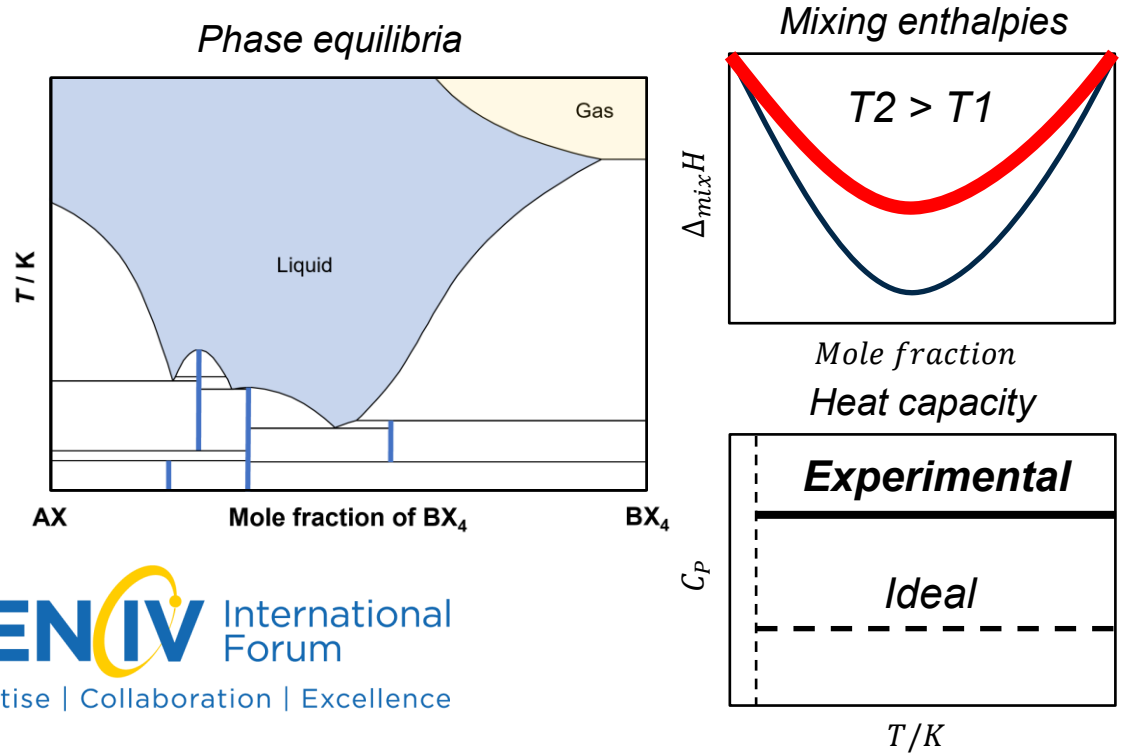
Simulating Molten Salts is Challenging and Requires Accurate Experimental Information

- Local structure evolves with temperature and composition
- These thermostructural changes cause the mixing energy to deviate from ideal (additive) mixing
  - Enthalpy of mixing represents the deviation from ideality at a given temperature
  - Heat capacity captures temperature dependence of the enthalpy of mixing



Predicting this complex behavior requires accurate Gibbs energy functions – These are obtained from

- Exhaustive literature review to critically evaluate experimental data
- **Measurements to fill gaps in knowledge**

$$\Delta G_m^{\circ}(T) = \sum_{i=1}^{n} x_i \Delta G_i^{\circ}(T) + RT \sum_{i=1}^{n} x_i ln(x_i) + \Delta G_m^{xs}(T)$$

Reference | Ideal | Excess

Accurately describing salt mixtures

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Heat Capacity is a Key Property of Molten Salt Fuel and Coolant

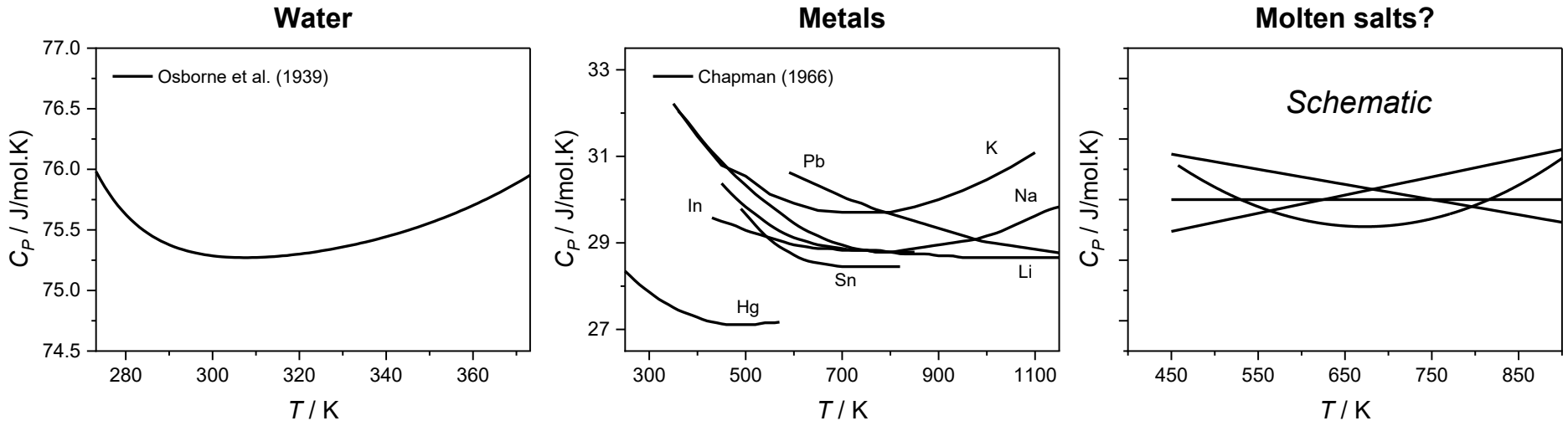
- The heat capacity can be mathematically approximated

$$C_P(T) = \left(\frac{dH}{dT}\right)_P = a_0 + a_1 T + a_2 T^{-2} \ldots$$

Maier-Kelley polynomial

- $C_P(T)$ of molten salts is assumed to be constant (a_0) or linear ($a_0 + a_1 T$), and may not capture the real behavior, biasing the predicted power of the MSR

$C_P(T)$ of various liquids:



Heat capacity of salts, however, may not be adequately known

MSRE: an 11 % Power Revision from One Property

Molten-Salt Reactor Experiment

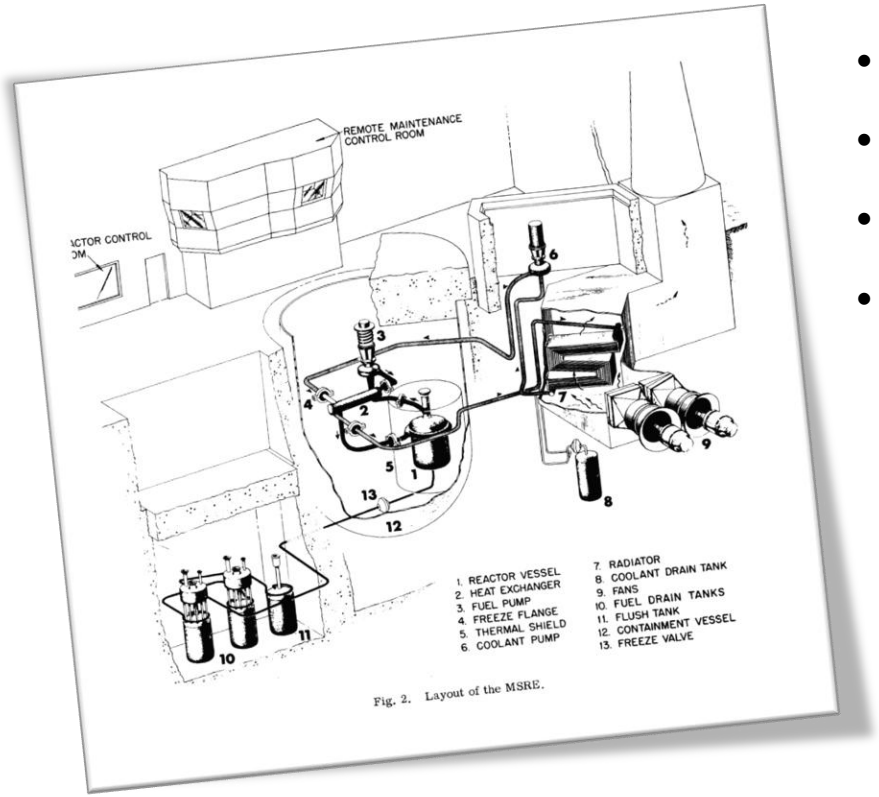
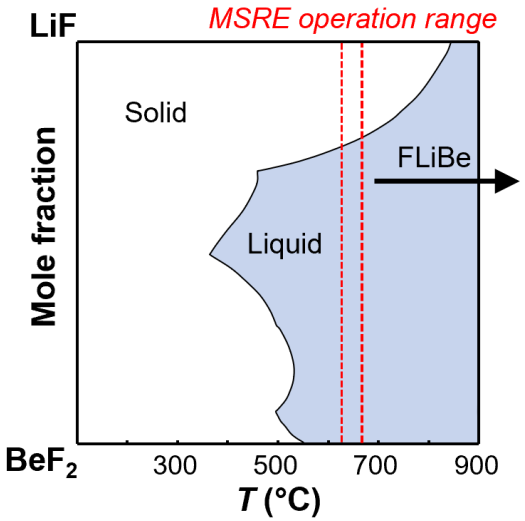
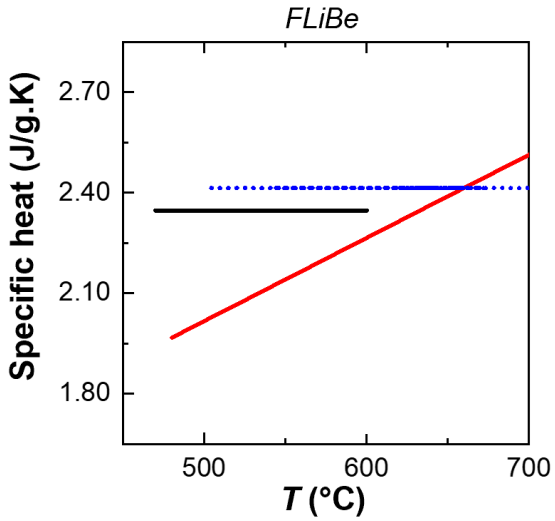


Fig. 2. Layout of the MSRE.

The lesson we need to take from the MSRE experience

- Coolant salt FLiBe (66LiF-34BeF_2 mol%)
- Original design used a temperature dependence c_P from 1961
- Operators were surprised when power well-exceeded expectations
- **Because c_P was not well known, new hat balance calculations increased maximum power 11% of its [7.2-MW(th) to 8-MW(th)]**



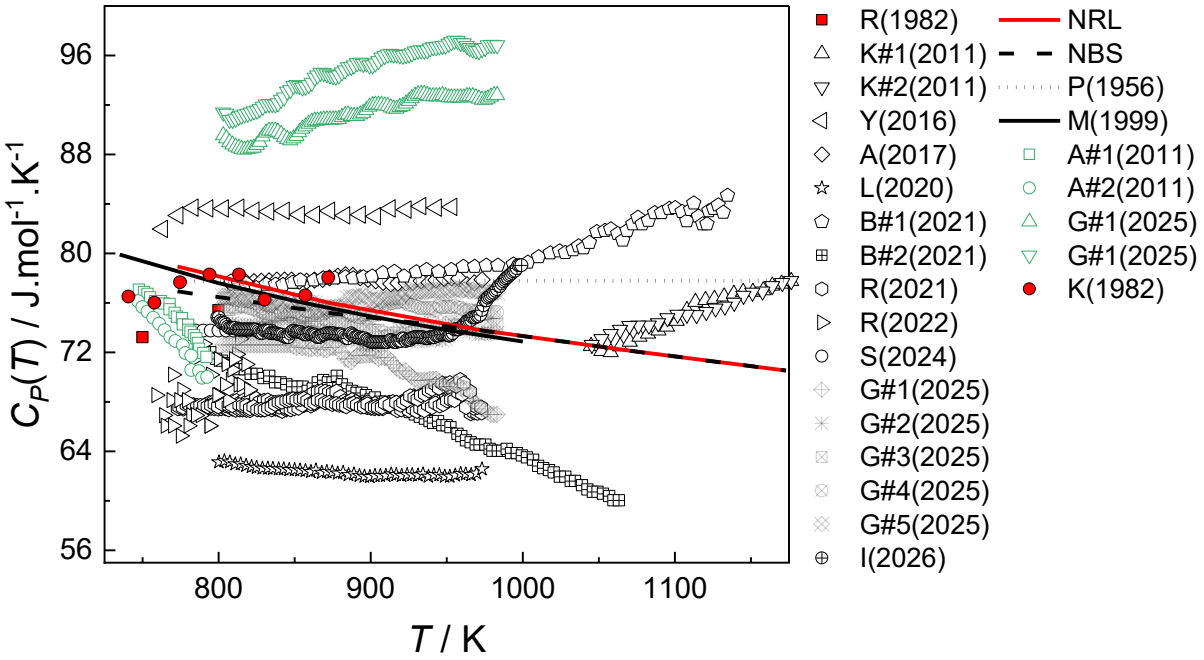


Source	c_P J/g.K	P MWth
B (1961)	2.177	7.2
H (1969)	**2.416**	**8.0**
D (1969)	2.350	7.8

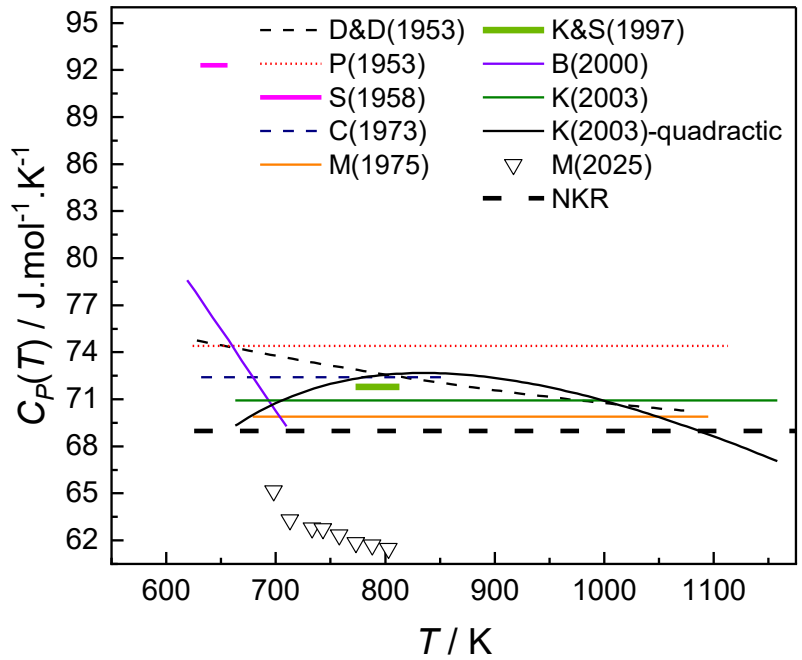
Even Recent Reported Measurements of Largely Studied Eutectics Display a Large Range of C_P Values

In considering values part of FLiNaK and 59LiCl41KCl to refine values for MSD-TC, the lack of consistent values becomes quite this

FLiNaK (46.5LiF-11.%NaF-42KF mol%)



59LiCl-41KCl mixture



Span (max-min) of nearly 61% for FLiNaK and 50% for LiCl-KCl

A Standard Approach Is Needed for Accurate Thermochemical Values

Such a method includes:

- Characterizing samples before and after measurements
- Prioritizing the use of methodologies and instruments with highest sensitivity and resolution
- Demonstrating reproducibility by varying conditions (mass, atmosphere, crucibles) and include all sources of error
- Averaging multiple, consistent measurements

Because the literature spread is too large to use directly:

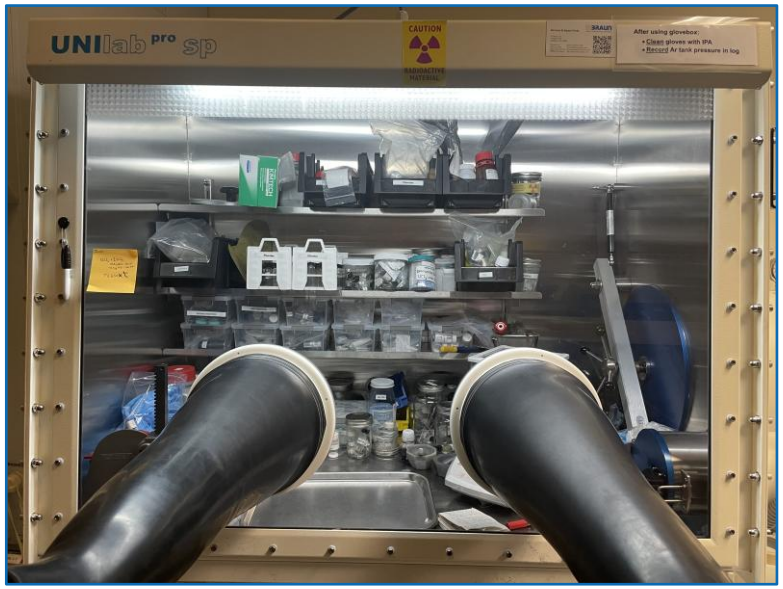
- Averaging all the data would be a mistake – large datasets would dominate results
- Bias toward any single source distorts the recommended value

Path for highly accurate thermochemical data:

1. Assure salt purity
2. Use methods and instruments with the lowest uncertainties
3. Utilize crucibles designed to yield optimal results

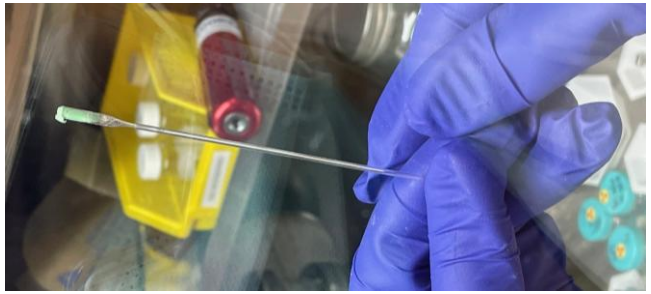
Characterization of Salt Purity is a Requirement: Efforts at USC

Salts ⇨



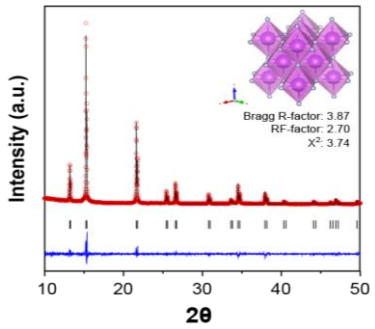
One of two inert atmosphere gloveboxes
H_2O < 3 ppm, O_2 < 0.1 ppm, **> 70 salts**

Bulk purity by XRD



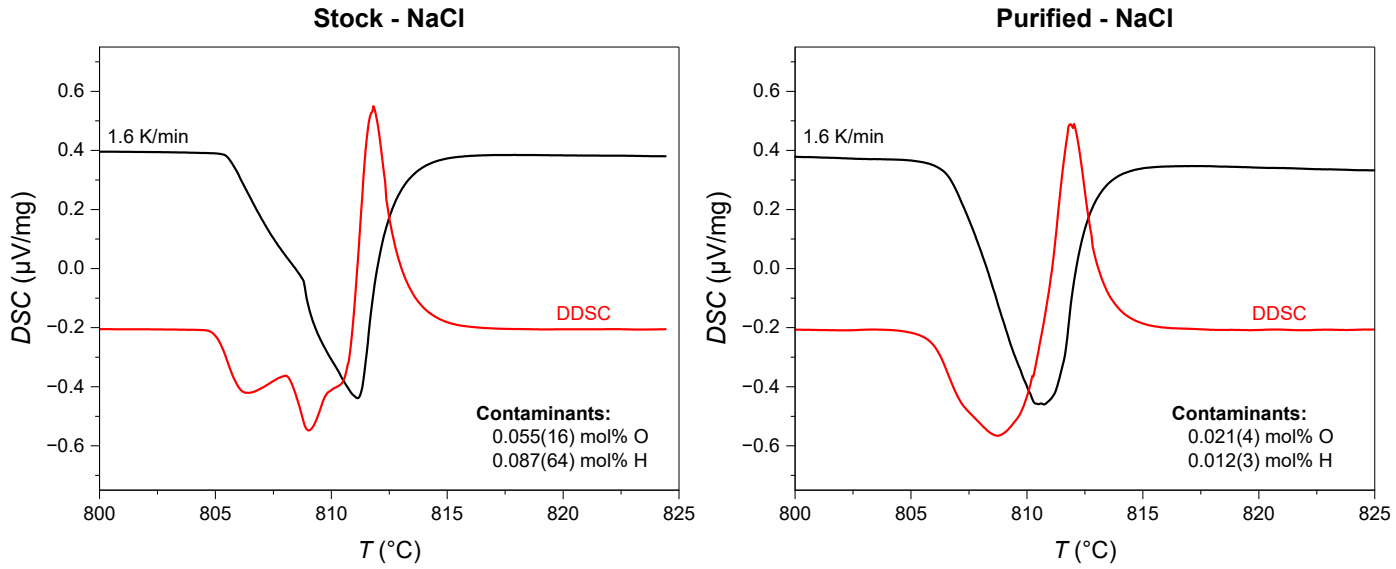
Sample sealed in fused silica capillaries

PXRD in transmission mode
Prof. zur Loye group
RT to 1100 °C



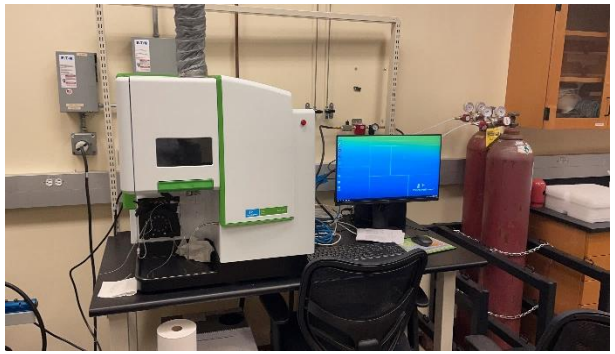
XRD with Rietveld refinement

Thermal analysis by DSC



Chemical analysis

Chemical analysis by ICP-OES

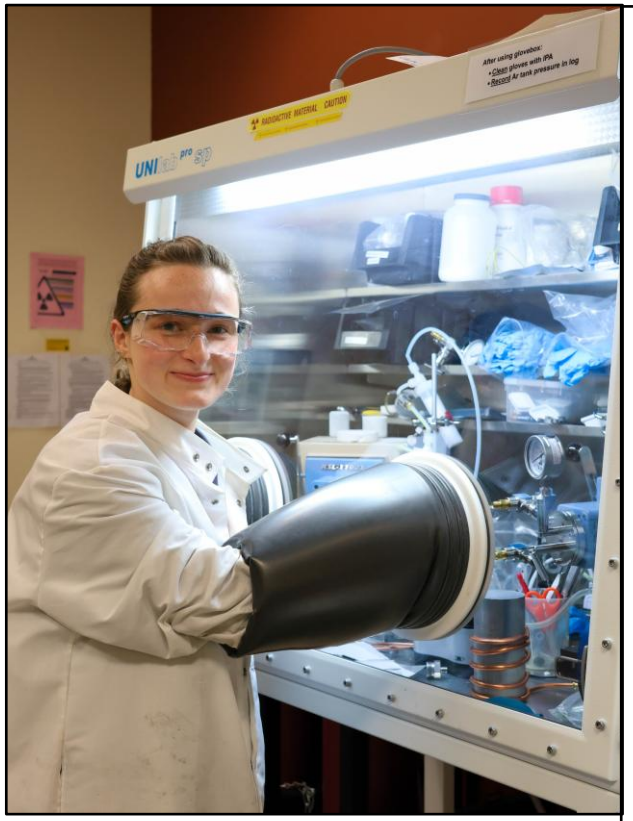


O and H analysis

Inert gas fusion

Purification and Synthesis Often Necessary to Obtain Adequate Material

Salts ⇨



Three in-glovebox furnaces used to synthesize and dry/purify salts

Purification done inside gloveboxes:

3X

2X

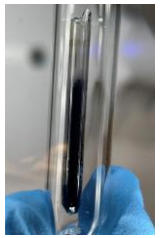
Gas lines in copper
Oxygen Pump Gauge, $2x10^{-22}$ atm O_2

Inert gas (Ar, Ar + 4%H_2) or vacuum (35 mbar)
RT-1100°C

Crucibles adapted for salts:

Quartz 5ml

Vitreous Carbon
0.9ml & 5ml



Flamed quartz

Ni boats
1.5ml

Encapsulating salt samples:

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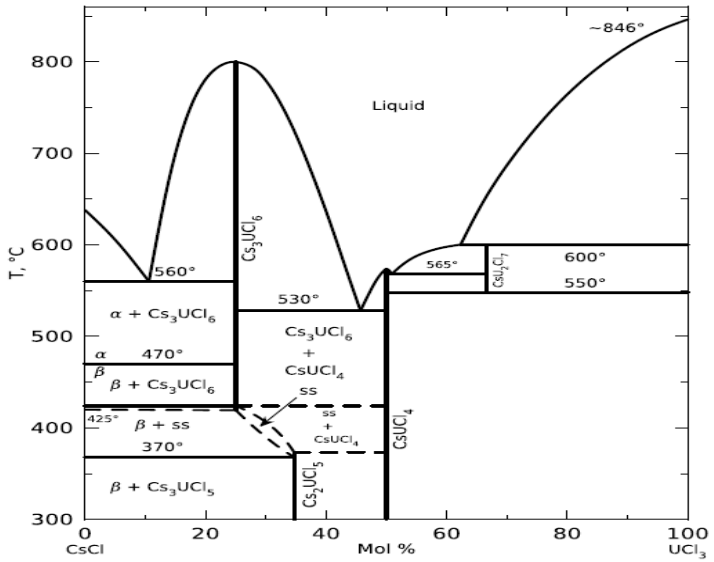
Solid State Reactions Used for Phase Equilibria Studies

- Formation of intermediary phases in salt systems are often poorly understood

Synthesis → Characterization → Thermochemical measurements → Modeling

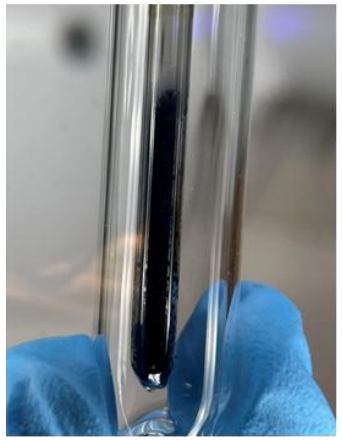
$CsCl$-UCl_3 experimental phase diagram



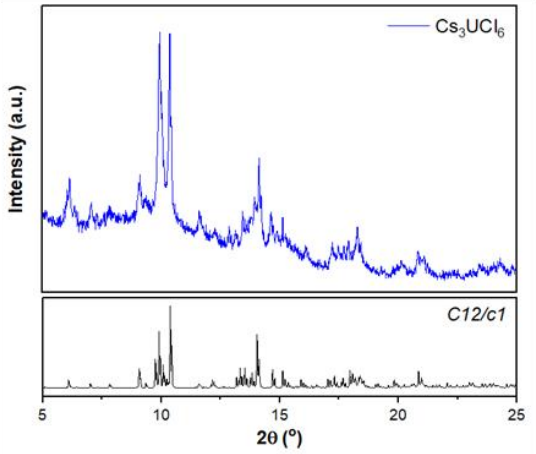
Suglobova et al., Koord. Khim., 7[1] 97 (1981)

Very limited structural and thermodynamic information available

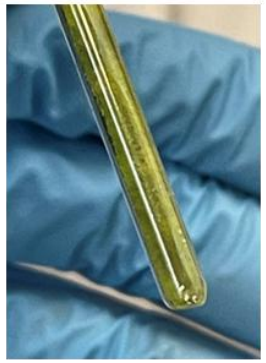
Cs_3UCl_6



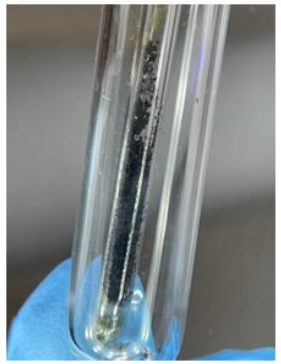
No standard/low precision PXRD pattern



CsU_2Cl_9



CsU_2Cl_7



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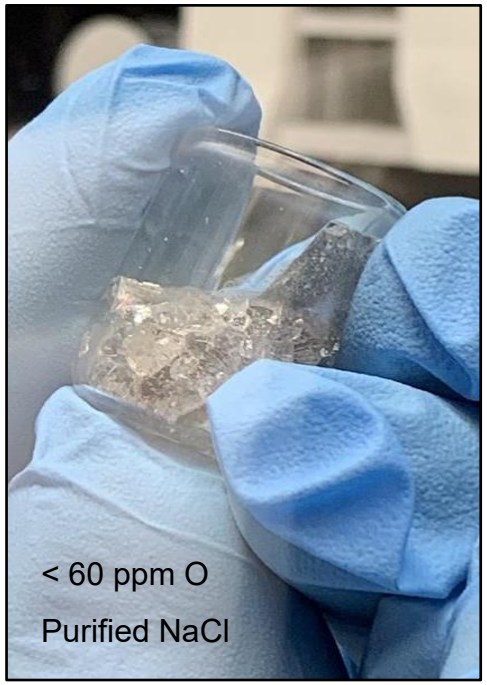
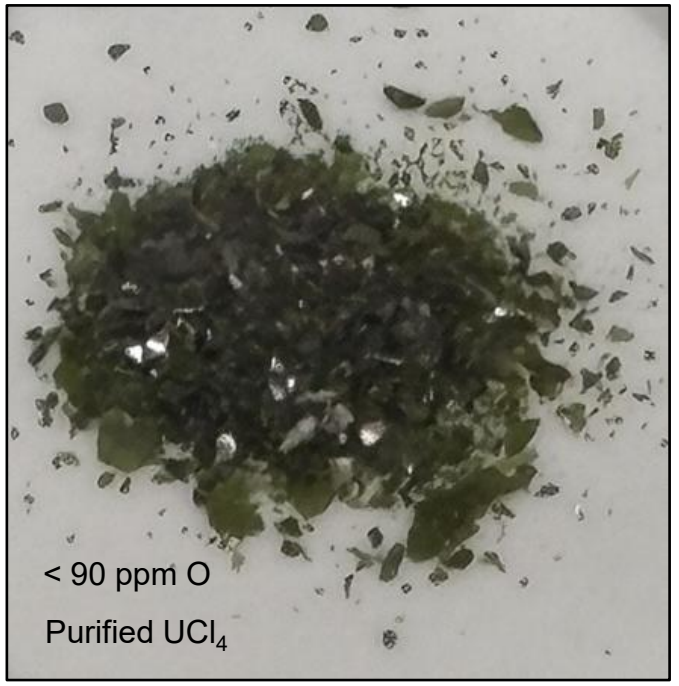
Results suggest that working directly with U, rather than surrogates, will be more representative

Salt Purity: Purification and Synthesis of Salts

- NaCl pre-melted with tantalum scraps to scavenge oxygen
- NH_4HF_2 was used to purify UF_4 down to 70 ppm (initial O was >2,700 ppm)
- Distillation of UCl_4, removing oxides and oxychlorides (initial O was ~ 450 ppm)





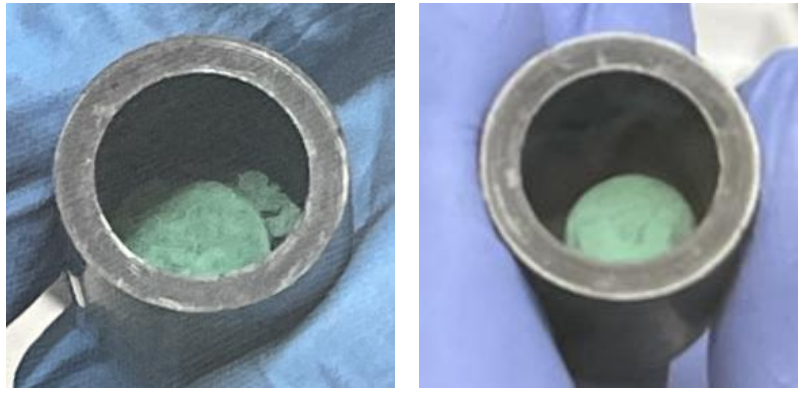
Presence of oxygen can produce additional thermal effects and affect thermochemical properties

The Melting Point of UF_4 Was Inferred for Many Decades

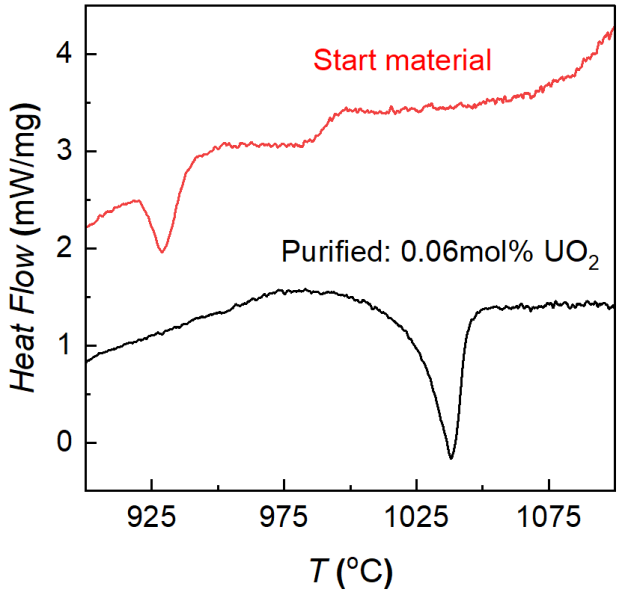
Recommended value: 1308 ± 2 K (literature assessment confirmed by measurement)

- During the Manhattan project: believed to be near 1220 K
- Ryon and Twichell (1947): measured four UF_4-UO_2 mixtures (1.48 to 5.25 mol % UO_2) and extrapolated the reciprocal melting point to zero UO_2, giving 1309.2 K
- Barton *et al.* took a single 0.18 wt% UO_2 sample and applied a cryoscopic oxygen correction to estimate the pure-salt value, 1307.2 K, still a correction, not a measurement

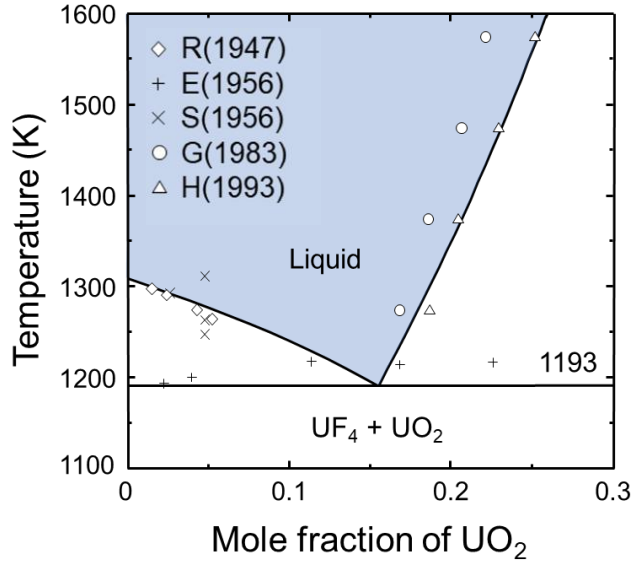
Shades of green can provide insights into the purity



Uranium tetrafluoride shows a eutectic when contaminated



UF_4-UO_2 phase diagram can be used to infer UO_2 content



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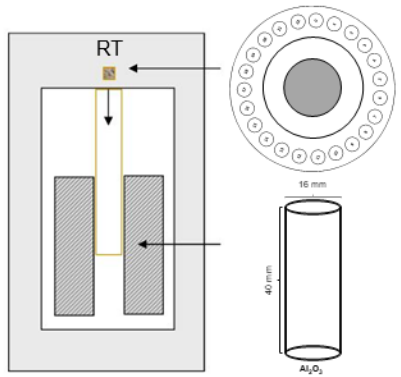
Current Methods Used to Measure C_P of Molten Salts

Drop Calorimetry

- C_P is obtained by differentiating the enthalpy increment (indirect method)
- Uncertainties between 3-10% (with exceptions)
- Historical datasets of the MSRE era

Example of a modern dropping system

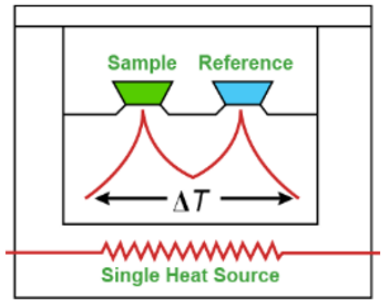


Ice Calorimeter at the Bureau of Mines

Differential Scanning Calorimetry

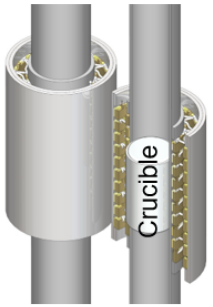
- Dominant method due to its simplicity and largely employed by the community
- Limited by the reproducibility of the thermal contact between crucible and thermocouple
- Uncertainties between 5-30%
- DSCs used at USC:

Heat-flux DSC



Keeps heat-flux constant

Tian-Calvet DSC (high resolution)



Similar to the heat-flux DSC, but with a 3D sensor (240 thermocouples)

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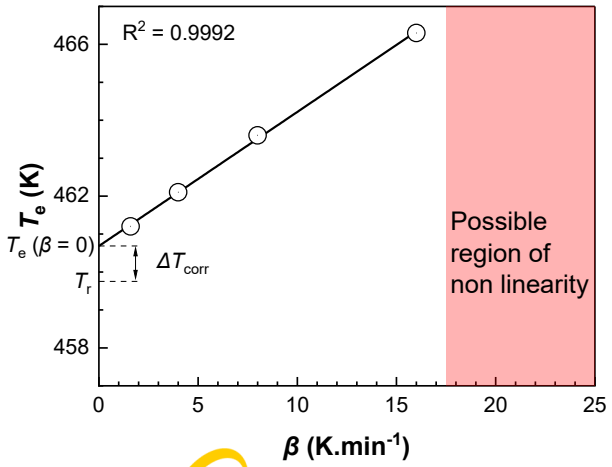
Smith *et al.* (1961) – Construction, Calibration and Operation of Ice Calorimeters; Schorne-Pinto, PhD thesis, INPT, France

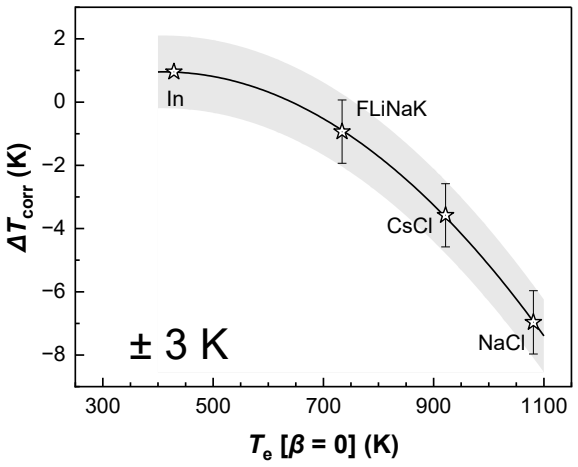
Accurate Calibration of a Calorimeter is Both Critically Important and Challenging

- **Extrapolated to a zero-heating rate to obtain a true melting temperature**
- Use purified salts as calibrants to achieve thermal conductivity effects comparable to those of the samples

Zero-rate calibration



Correction at β = 0 K.min^{-1}



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Our experience:

+	Good compatibility
!	Reacts over time
–	Incompatible

Calibrants:

Metal calibrants – IUPAC — **Crucible/liner material**

Calibrant	T_{fus}/K	Ni	TZM	SiO_2	SS
Gallium	302.915	+	+	+	+
Indium	429.748	+	+	+	+
Tin	505.078	+	+	+	+
Bismuth	544.552	+	+	?	+
Lead	600.612	–	+	+	+
Zinc	692.677	–	+	+	–
Antimony	903.778	–	!	+	–
Aluminum	933.473	–	–	–	–
Silver	1234.93	!	+	+	+
Gold	1337.33	!	!	+	–

Recommended salt calibrants (*evaluated during MSD-TC development)

Calibrant	T_{fus}/K	Ni	TZM	SiO_2	SS
FLiNaK	732.9 ± 1	+	+	–	–
CsCl	918 ± 1	+	+	+	+
NaCl	1074 ± 1	+	+	+	–
NaF	1269 ± 1	+	+	–	–

Significant Effort Over Several Years Was Required to Generate Crucibles That Allow Low Error Limit DSC Measurements

Requirements include

- Hermetic sealing as our DSCs are not in gloveboxes
- Chemically compatibility with the halide salts

Crucibles evaluated and tested as part of our experimental effort to generate phase equilibria

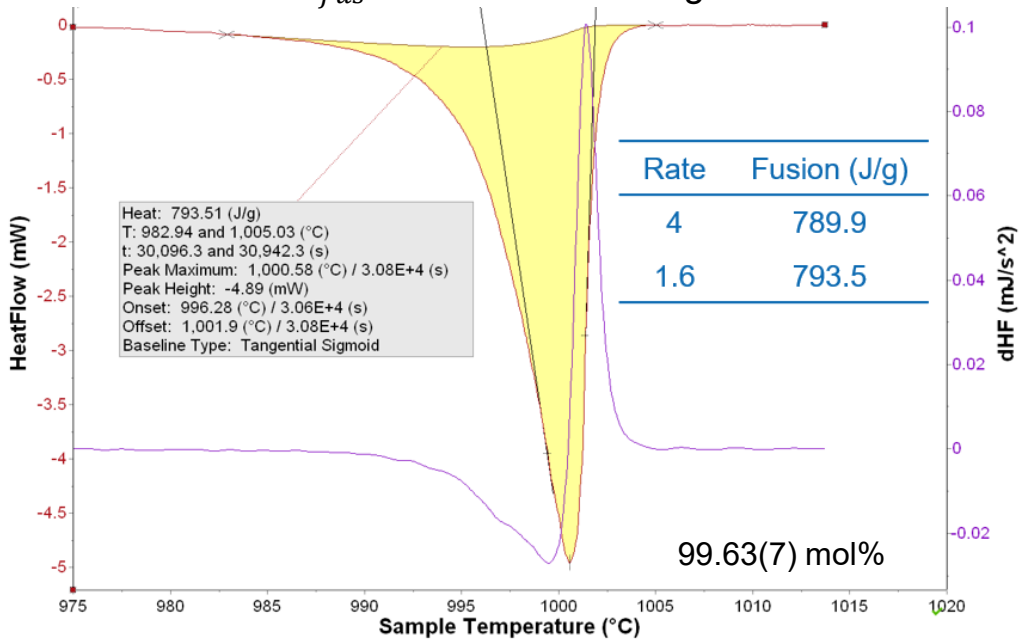
	100 µl SS w Ni	27µl SS w Ni	31.5 µl TZM	200 µl 4N Ni
				
Source	Netzsch + liner	Netzsch + liner	USC	USC
Mass	~1480 mg	~ 875 mg	~2435 mg	510 mg
Max. sample mass	10-50 mg	10-20 mg	30-50 mg	Up to 400 mg
Ratio Wgt_s/Wgt_{cr}	**3.38%**	**2.29%**	**2.05%**	**78.4%**
Leak resistant	Yes	Yes	No	**Better**
Fluorides	Yes	Yes	Yes	Yes
Chlorides	Yes	Yes	Yes	Yes
Melting point	Yes	Yes	No	Yes
Enthalpy of fusion	Yes	Yes	No	Yes
Heat capacity	**Poor**	**Poor**	**Bad**	**Best**
Calorimeter	HF-DSC	HF-DSC	All DSCs	**DSCs & drop**

Melting point can be used as purity check

NaF

Ref.: T_m = 995.9 ± 1 °C,

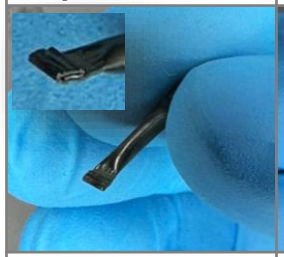
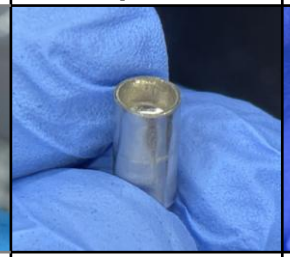
$\Delta_{fus}H$ = 793.3 ± 12.6 J.g^{-1}

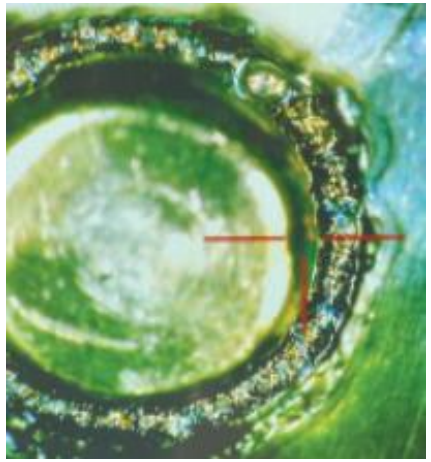


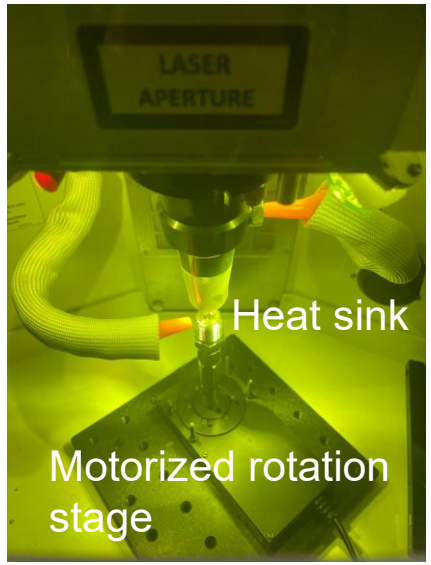
Tailored Crucibles: A Journey to Find Optimal Crucible for C_P

- Highly symmetric and light, to keep the crucible signal small

Crucibles evaluated and tested as part of our experimental effort to generate thermochemical data

	44 µl Ni folded	44 µl Ni welded	100 µl 4N Ni	200 µl 4N Ni
				
Source	USC	USC	USC	USC
Mass	180 mg	110 mg	300 mg	510 mg
Max. sample mass	30-50 mg	30-60 mg	Up to 200 mg	Up to 400 mg
Ratio Wgt_s/Wgt_{cr}	**27.78%**	**54.54%**	**66.7%**	**78.4%**
Leak resistant	No	Yes	**Better**	**Better**
Fluorides	Yes	Yes	Yes	Yes
Chlorides	Yes	Yes	Yes	Yes
Melting point	No	Yes	Yes	Yes
Enthalpy of fusion	No	Yes	Yes	Yes
Heat capacity	**Good**	**Good-Best**	**Best**	**Best**
Calorimeter	Calvet & drop	Calvet & drop	**DSCs & drop**	**DSCs & drop**





Laser welding
Nd:YAG 1064 nm

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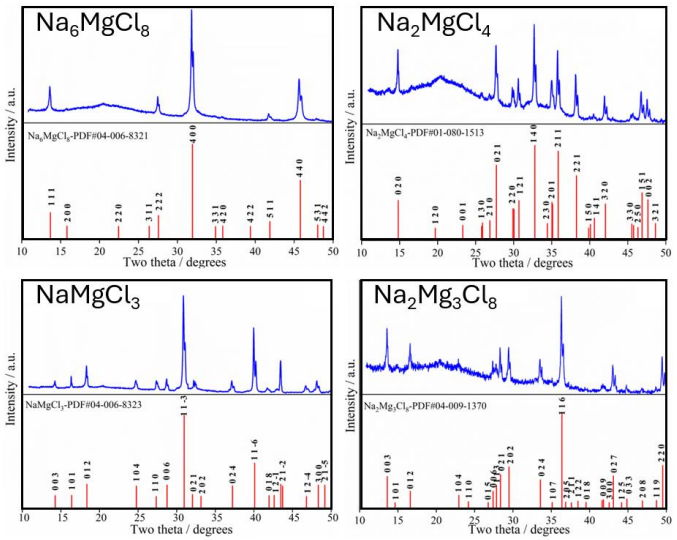
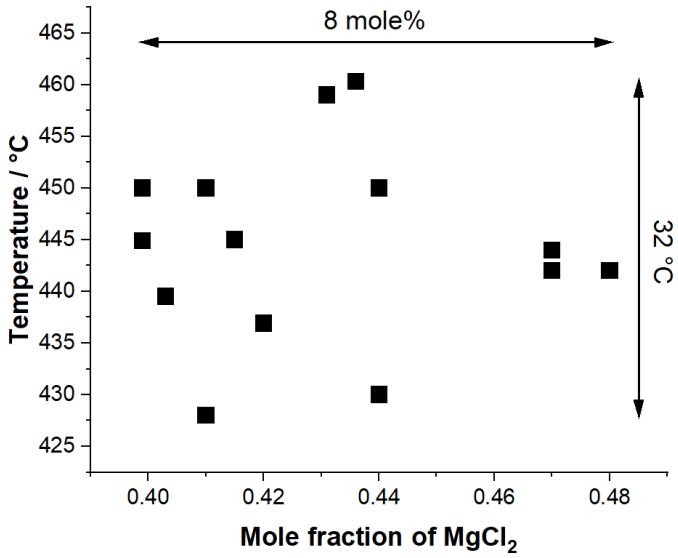
Example of a Challenging Recent Study: Thermodynamics and Phase Equilibria of the NaCl-$MgCl_2$ System

- Confirming the existence of reported intermediate phases by their synthesis as conventional thermal analysis will have issues due to low kinetics
- Establishing their thermal stability and refining the real eutectic and composition

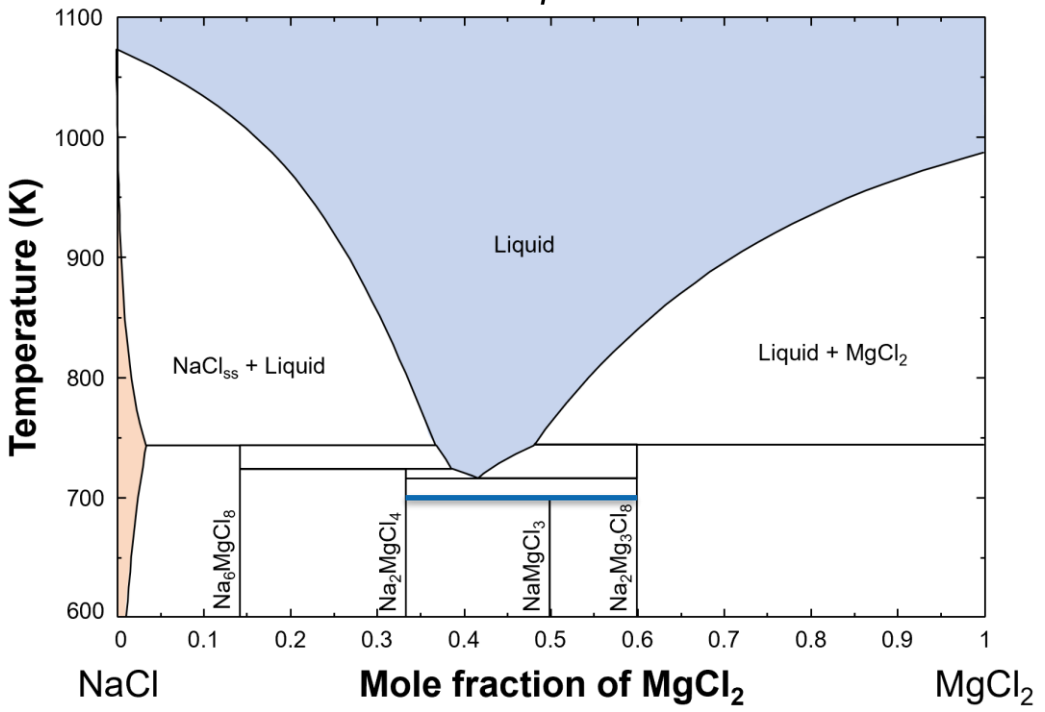
Four intermediate phases confirmed stable



Reported eutectic T & composition



Phase equilibria



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Padinhare Manissery *et al.* (2026) – Elucidating the Thermodynamics and Phase Equilibria of the NaCl-MgCl2 System, Journal of Alloys and Compounds 1080, 190328, https://doi.org/10.1016/j.jallcom.2026.190328

Enthalpy of Fusion of FLiNaK Using a Calvet DSC and Custom Crucibles

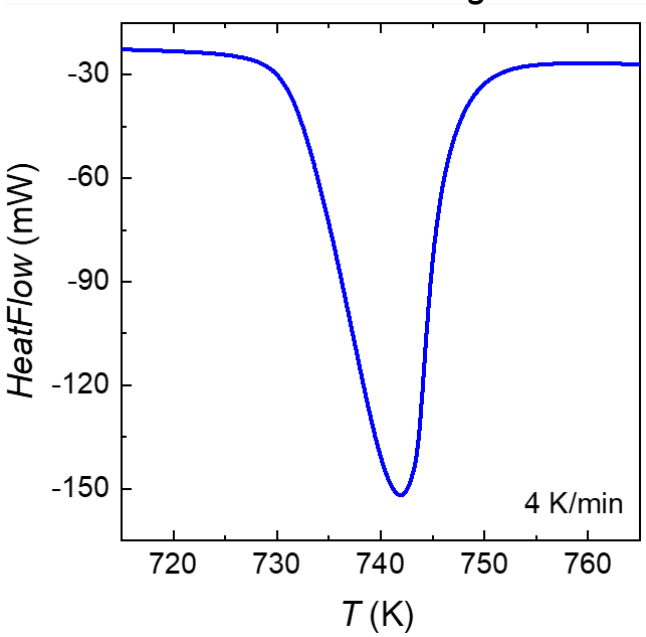
The FLiNaK is commonly used to benchmark thermophysical and thermochemical properties

A pure sample (117 ± 25 ppm O, *N* = 13) was loaded in a Ni crucible to measure its melting point and enthalpy of fusion:

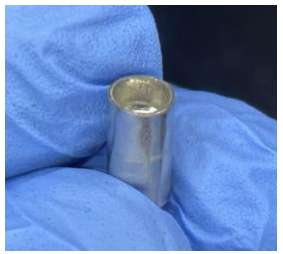
Measured FLiNaK melting point and enthalpy of fusion

Rate	Cycle 2	Cycle 3	Cycle 4	Cycle 5	Average	3.18*SD
K.min^{-1}	K	K	K	K	**K**	**K**
4	731.9	731.8	732.1	732.0	**732.0**	**0.2**
K.min^{-1}	J.mol^{-1}	J.mol^{-1}	J.mol^{-1}	J.mol^{-1}	**J.mol^{-1}**	**J.mol^{-1}**
4	16,565	16,641	16,704	16,633	**16,636**	**90 (0.54%)**

FLiNaK thermogram



Custom crucible



$\Delta_{fus}H$ [J.mol^{-1}]	Error [%]	#	Reference
16,646	2	27	R(1982)
16,318	1	3	Y(2016)
16,483	5	-	P(1956)
17,099	-	-	K(1982)
16,673	3	14	K(2011)
17,610	0.8	3	C(2017)
18,180	3.5	8	S(2024)

Accurate melting points and enthalpy of fusion are generated using custom crucibles

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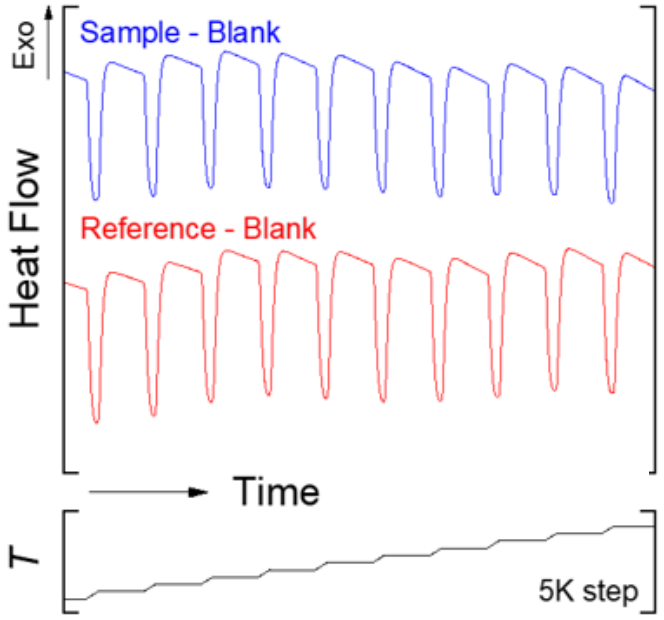
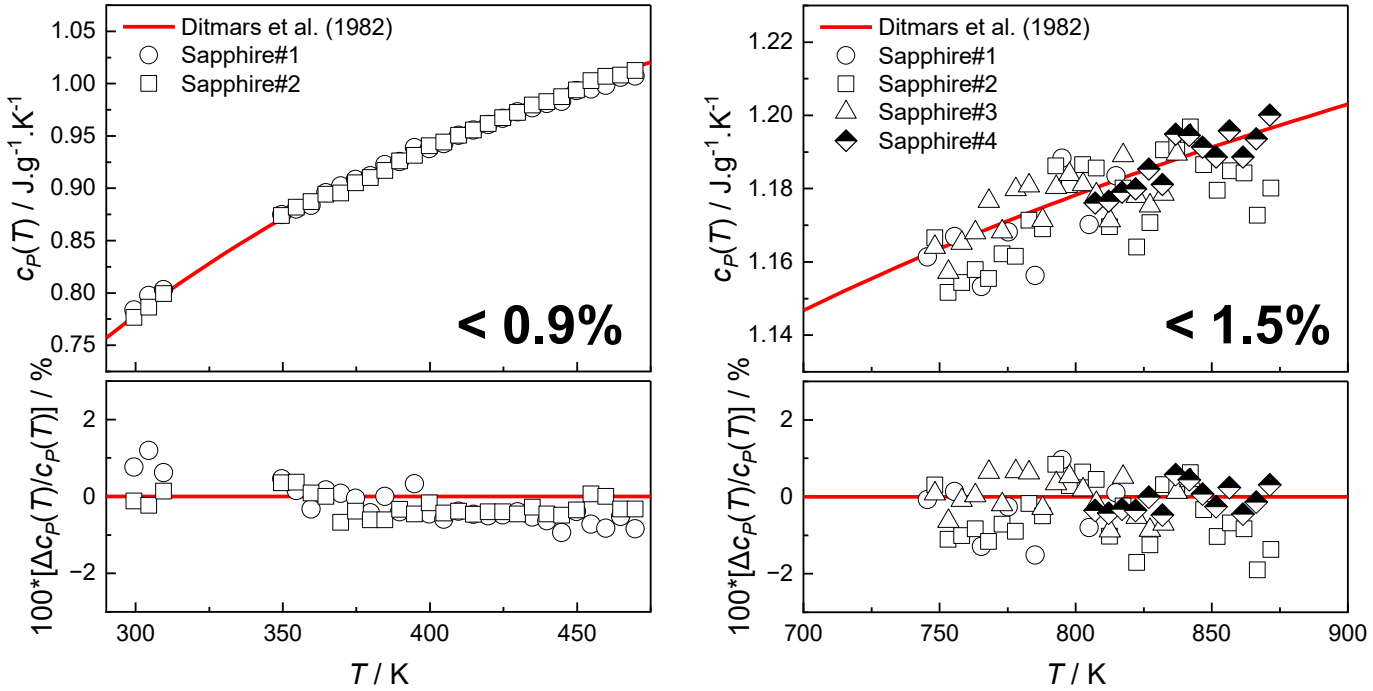
C_P Measurements Using a Calvet DSC for Salts

- Three-step method/Sapphire method (ASTM-E1269 & DIN 51007)
- Small temperature steps (Gaune-Escard & Benigni): steady-state conditions

DSC (small T steps)



Sapphire validation



Instrument choice sets the uncertainty floor
Small temperature steps and a higher sample-to-crucible mass ratio improve accuracy

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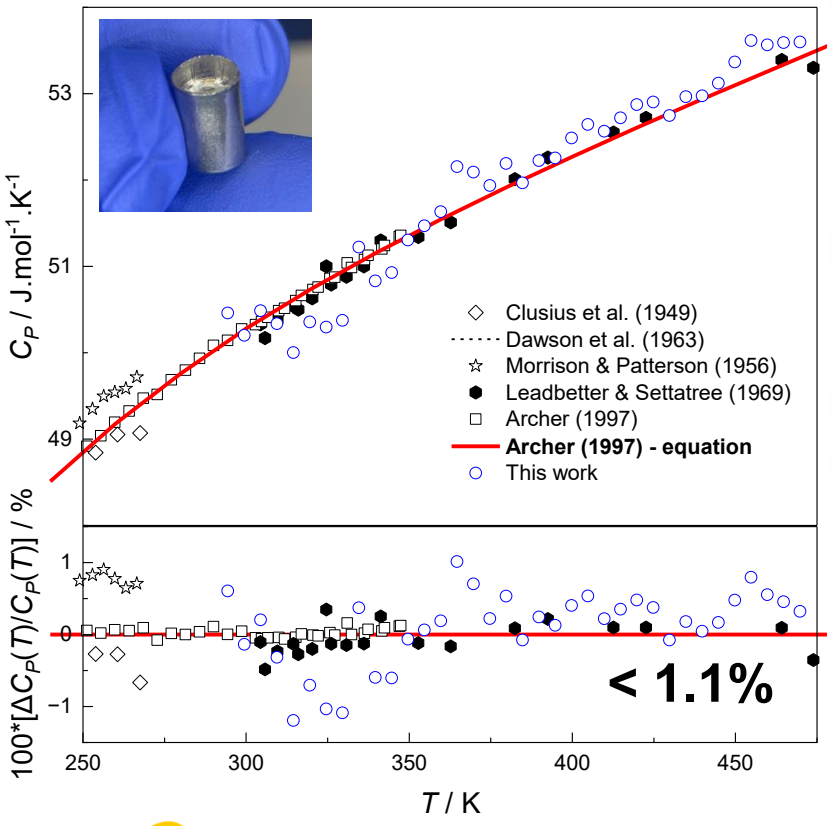
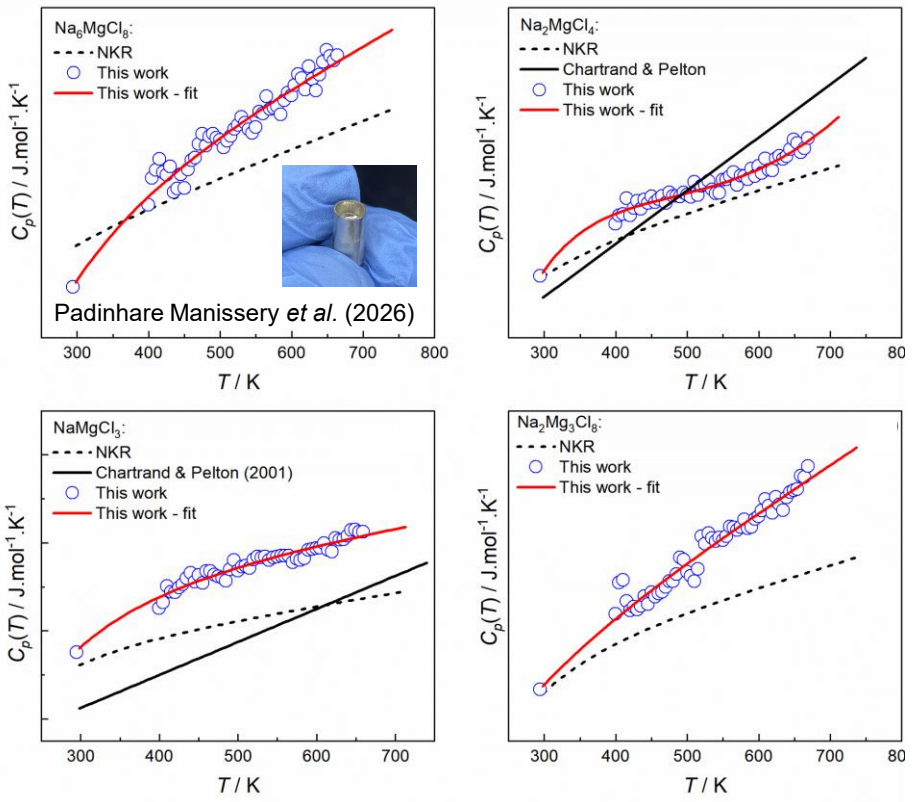
Superior C_P Determination of Solid Salts Is Key For Models

Solid phases are reference for the liquid phase, therefore needing also accurate C_P data

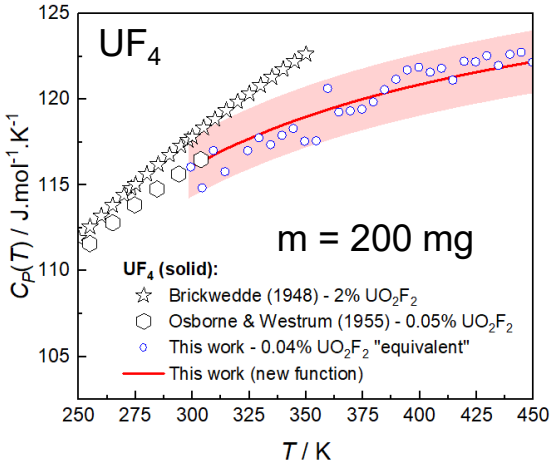
Benchmark using purified NaCl



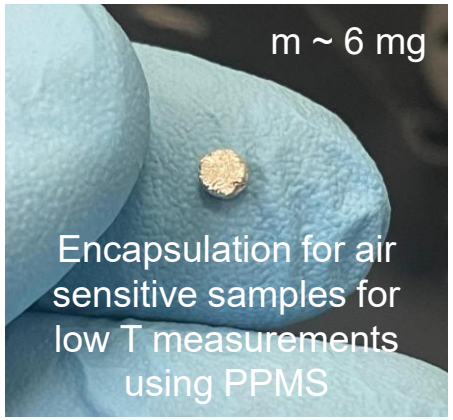
$NaCl-MgCl_2$ intermediaries



Working being extended to actinides



Work completed for UCl_3 & UCl_4 and being analyzed



Limited information exist for actinide salts as they are extremely sensitive to O_2

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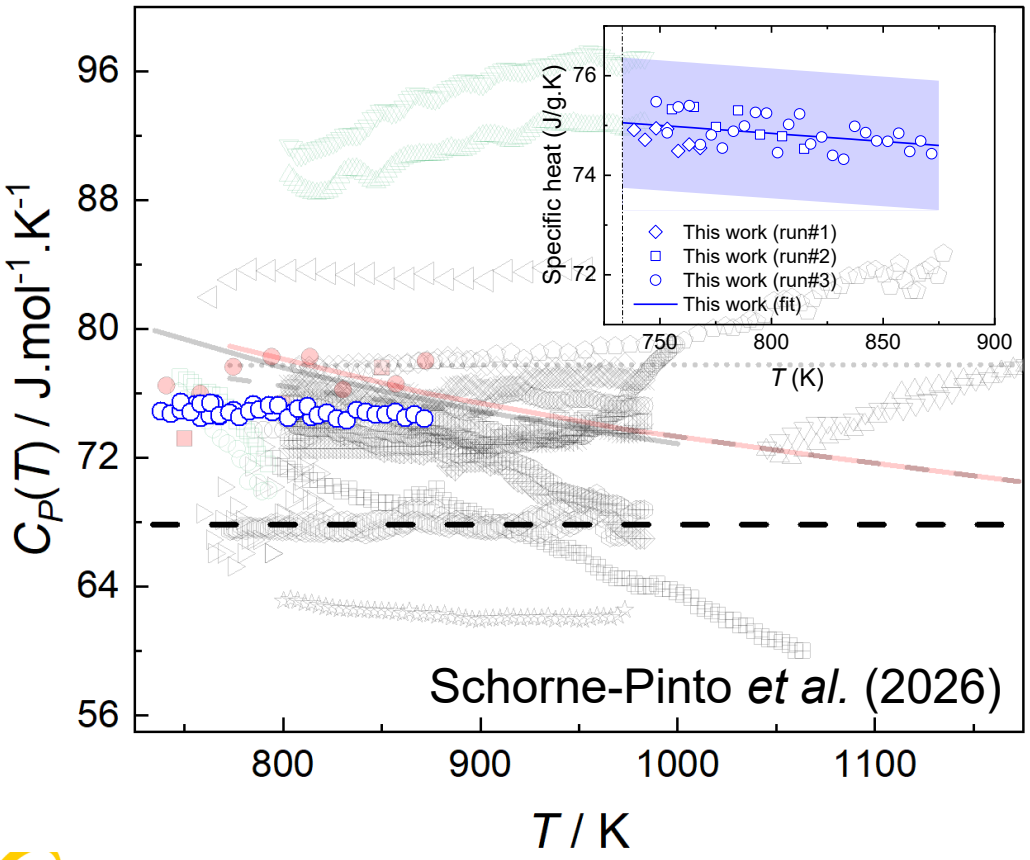
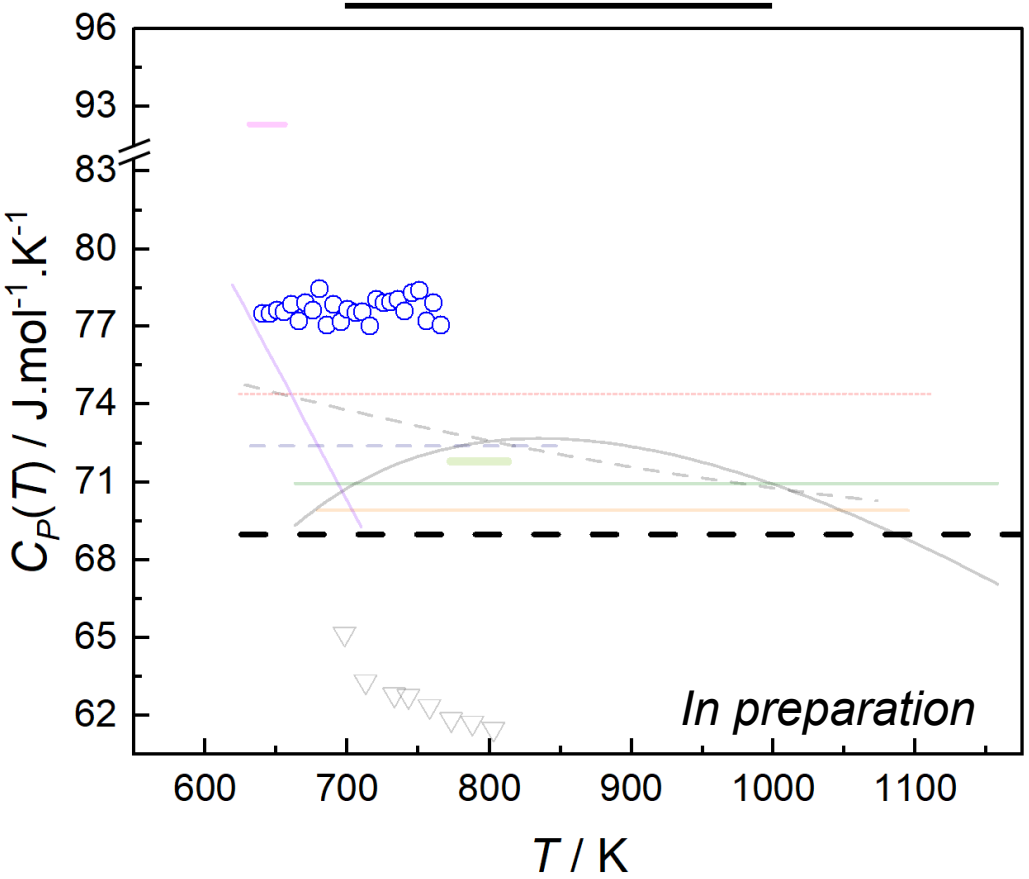
Superior C_P Determination: Example of Molten FLiNaK and LiCl-KCl Eutectics

FLiNaK eutectic



LiCl-KCl eutectic

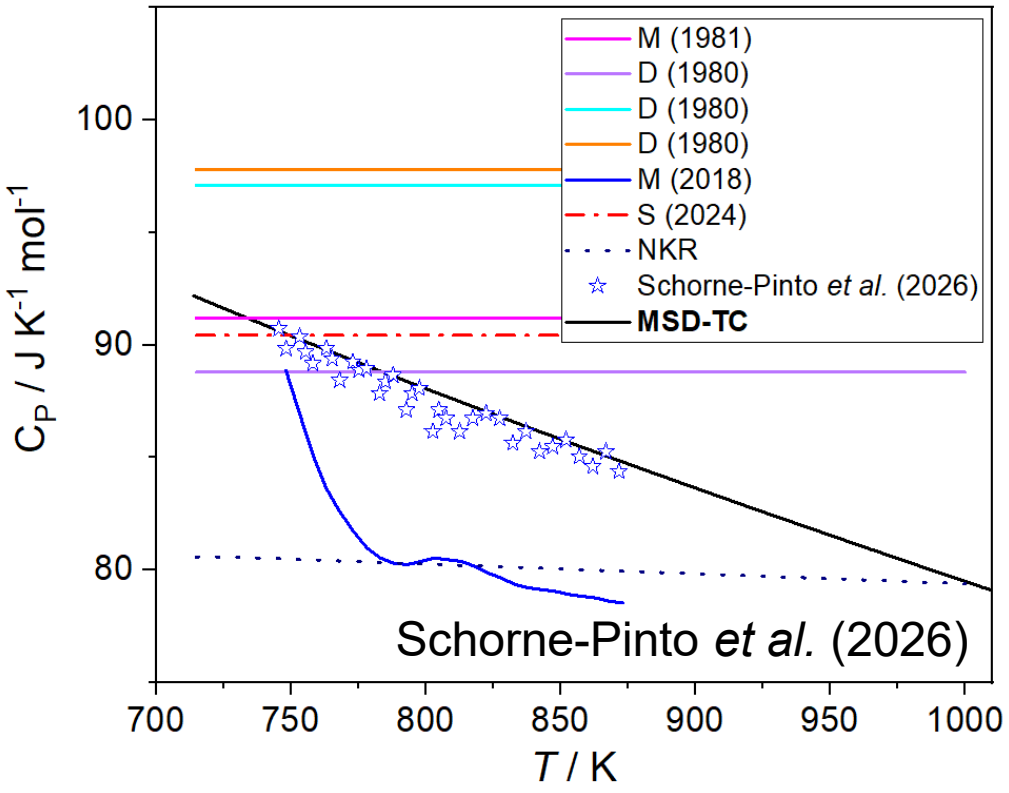


The protocol is highly accurate, and it is being used to generate reference data for MSD-TC/TP

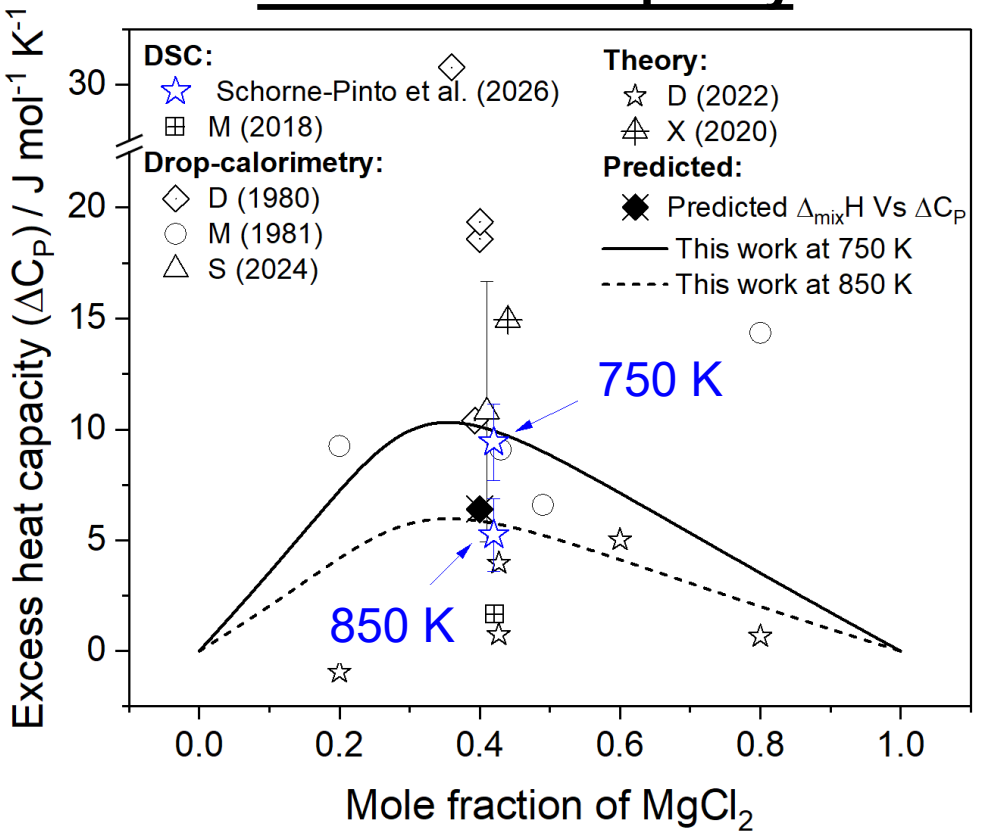
Superior C_P Determination: Example of Molten 58NaCl-42$MgCl_2$

Considered as a potential candidate for coolant and/or fuel matrix for fast spectrum MSR:

Heat capacity



Excess heat capacity



A large temperature dependence was identified that can fundamentally change *T* profile and max power of the MSR

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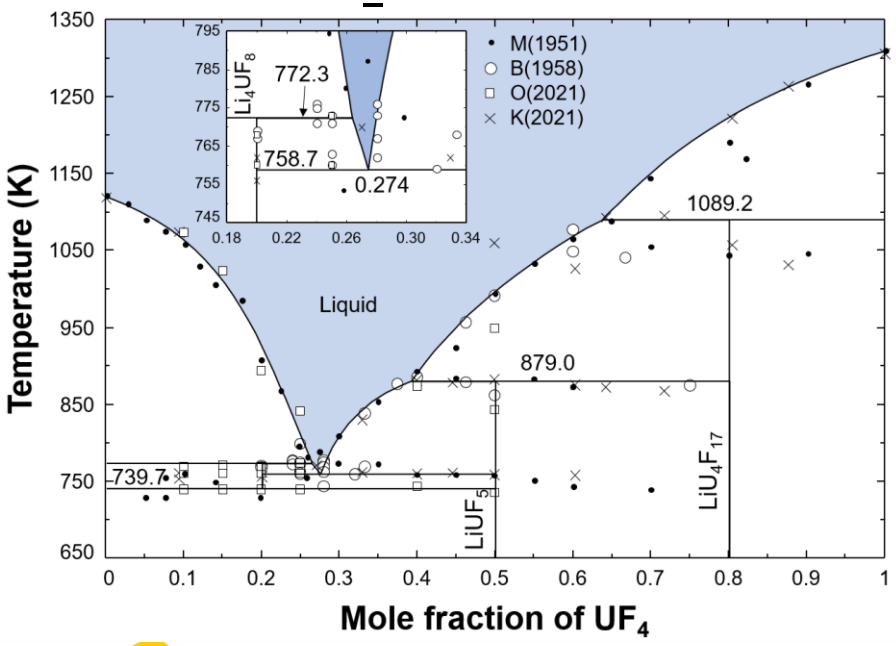
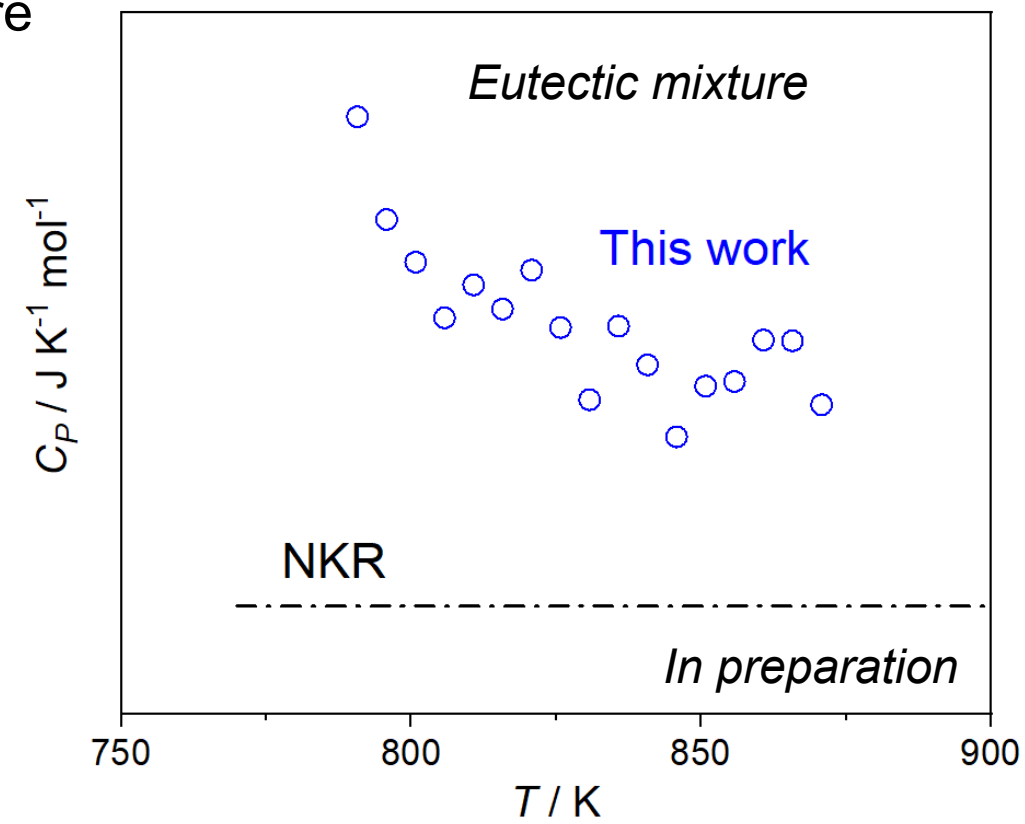
Revealing the Behavior of Molten Actinide Salts: Example of LiF-UF_4 Eutectic Mixture

This system is an important component of proposed multiple fluoride fuel mixtures, yet its properties are not available in the literature

LiF-UF_4 phase diagram





Novel determination of a temperature dependence for the C_P of the LiF-UF_4 eutectic

Summary: Accurate Data for MSR Development

- Reliable MSR design, licensing, and operation depend on accurate thermochemical properties
- Reported values carry large, source-dependent scatter (C_P up to ~61%) and hidden oxygen artifacts
- With ppm-level purity control, Calvet DSC with the small-step method, and custom laser-welded hermetic crucibles, together setting a low uncertainty floor (< 1.5% above 750 K, < 1.1% at room temperature)
- Accurate data was generated for FLiNaK (±1.74%), NaCl-$MgCl_2$ (±1.93%), against 5 to 30% typical. The same protocol is now being applied to actinide fuel salts (e.g., pure UF_4 and LiF-UF_4 eutectic) to expand and improve MSD-TC
- This can directly lower MSR design and licensing risk

MSD Serves as a Resource for Thermochemical and Thermophysical Data

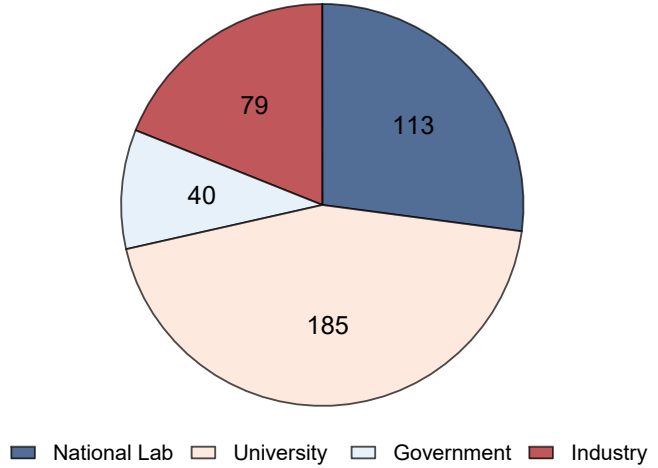
All results are published and integrated into the Molten Salt Database (MSD), the community resource at MSD.ornl.gov

- MSD-TC contains Gibbs energy models (managed by USC)
- MSD-TP contains curated thermophysical properties and relations (managed by ORNL)

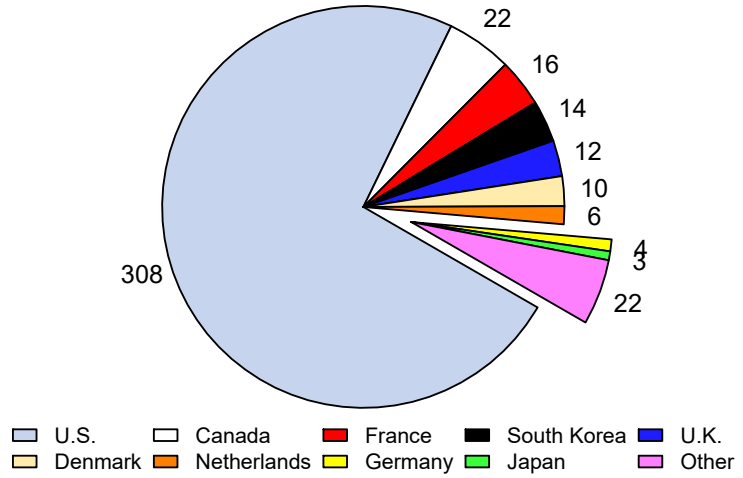
MSR simulation codes use MSD-TC relations for salt chemistry, redox, and speciation

MSD serves almost 500 registered users across institutions and countries

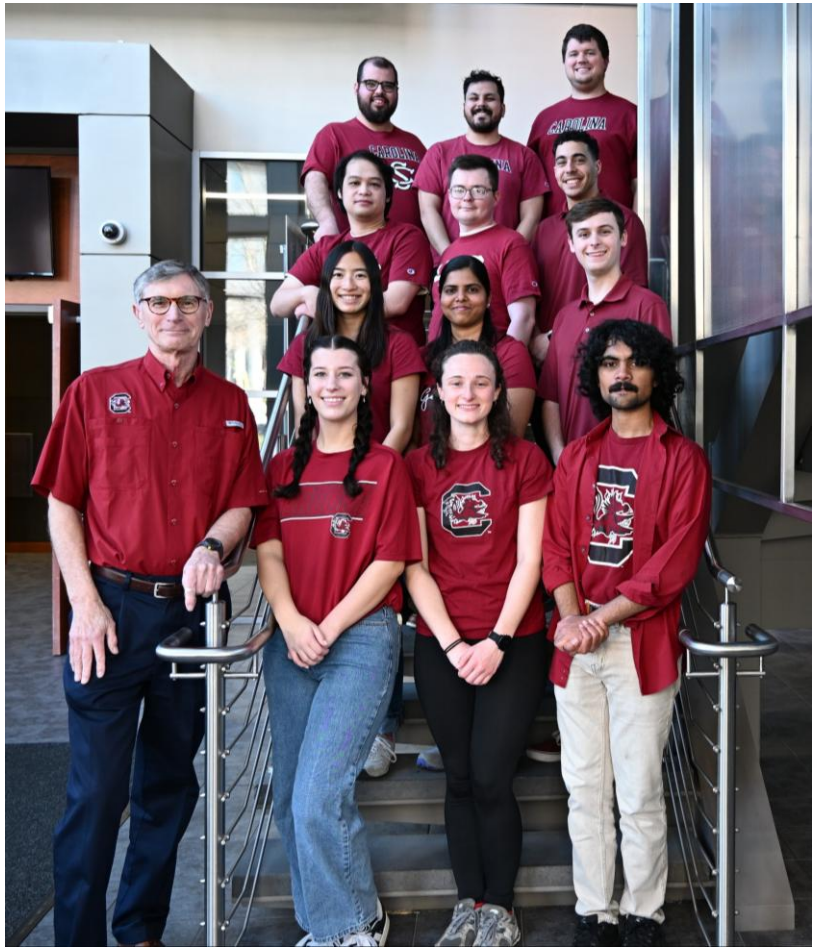
MSD Subscribers by Institution Type



MSD Subscribers by Country



Acknowledgements



General Atomics Center team

ART-MSR Program - funding support

USC startup funding

INL LDRD - laser welding capability development

Collaborators on measurements:

Data management and database

Salt providers:

Upcoming Webinars

Date	Title	Presenter
15 October 2026	A temperature-based approach to estimate decay heat in Sodium-cooled Fast Reactors and validate associated computational tools	Dr. Dorian Da Cunha, CEA, France
12 November 2026	MELCOR: The Evolution of Nuclear Safety Analysis Technology to Enable Nuclear Innovation	Dr. David L. Luxat, and Dr. Matthew S. Christion, SNL, U.S.

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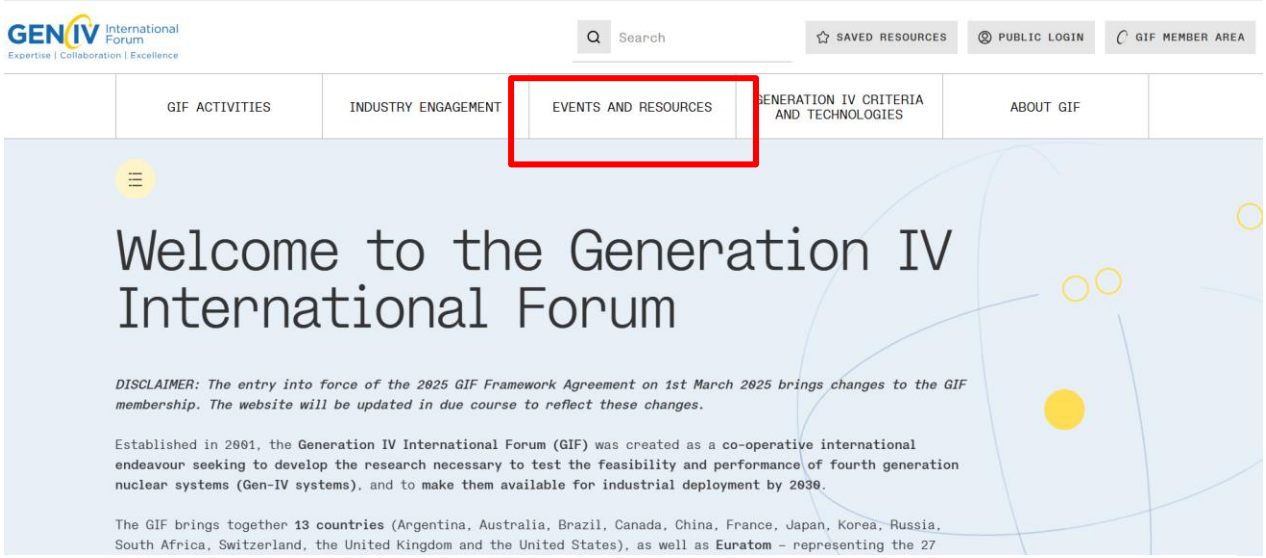
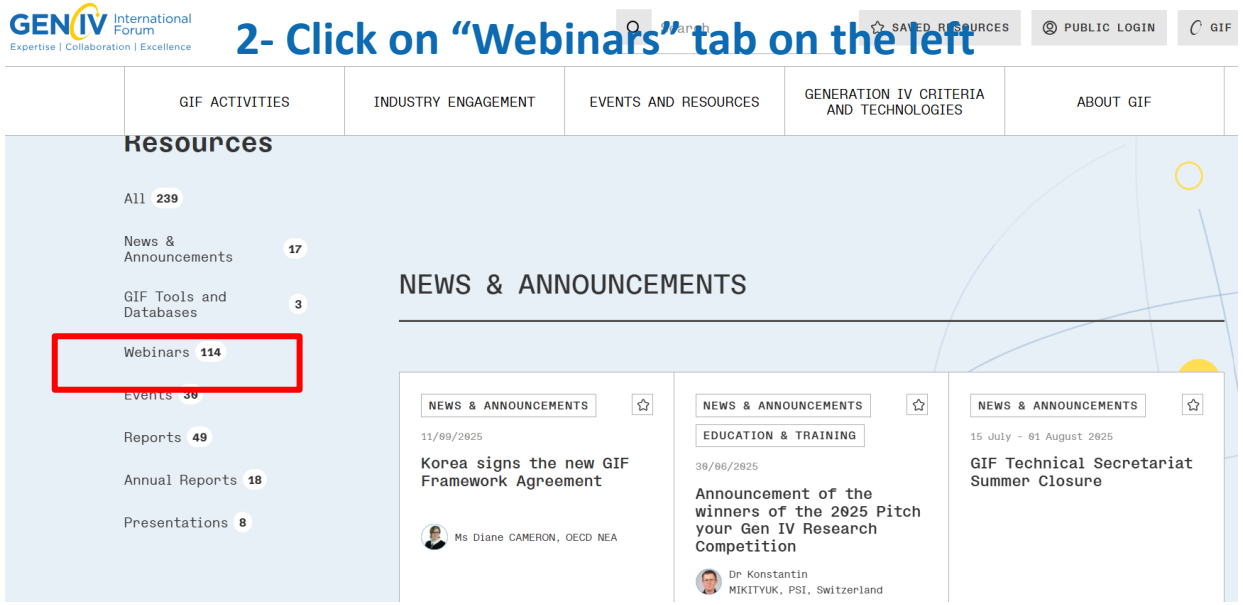


2- Click on “Webinars” tab on the left



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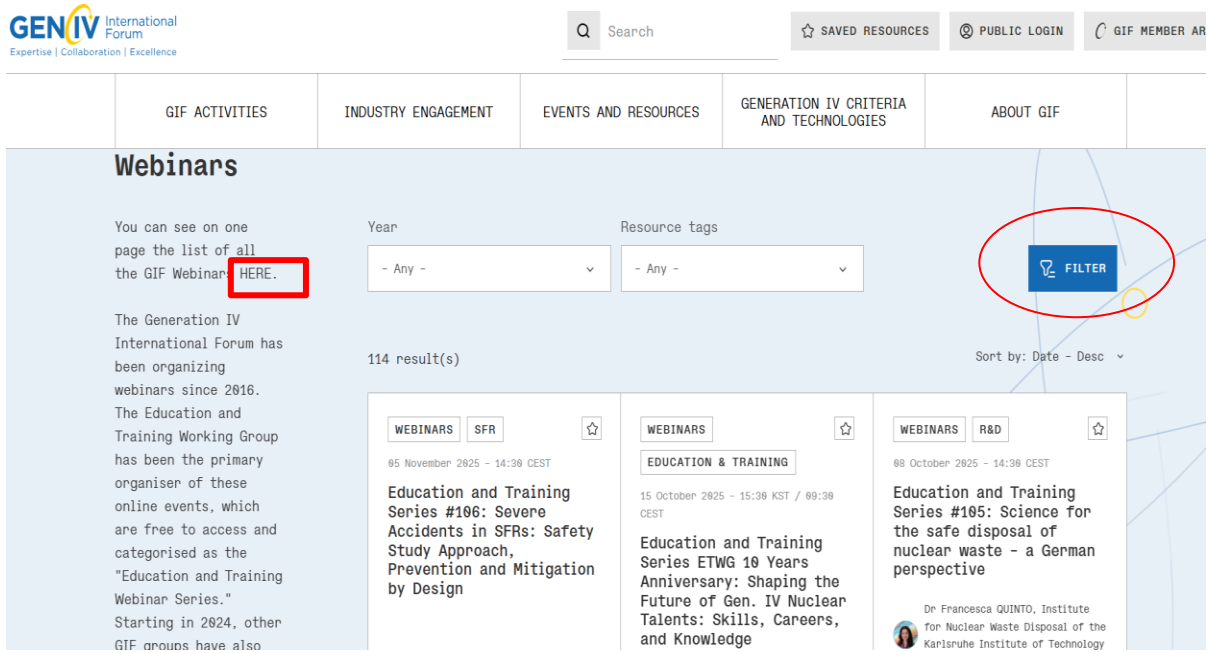

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