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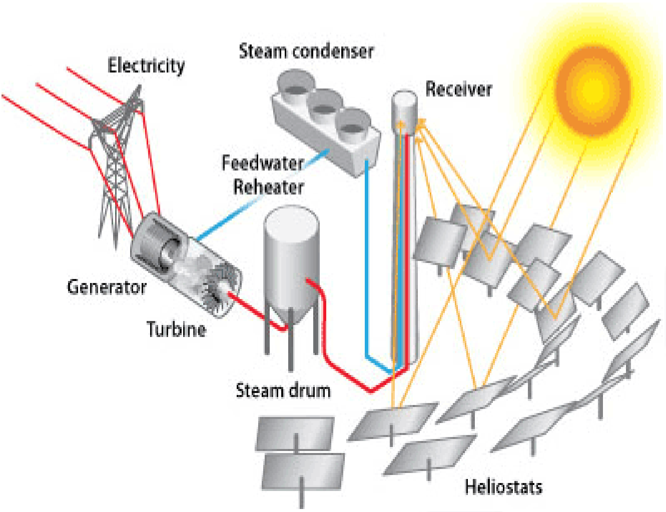

Thermophysical Properties of Gen3 Molten Chloride Salts: Experimental Challenges Unique for High Temperature Liquids

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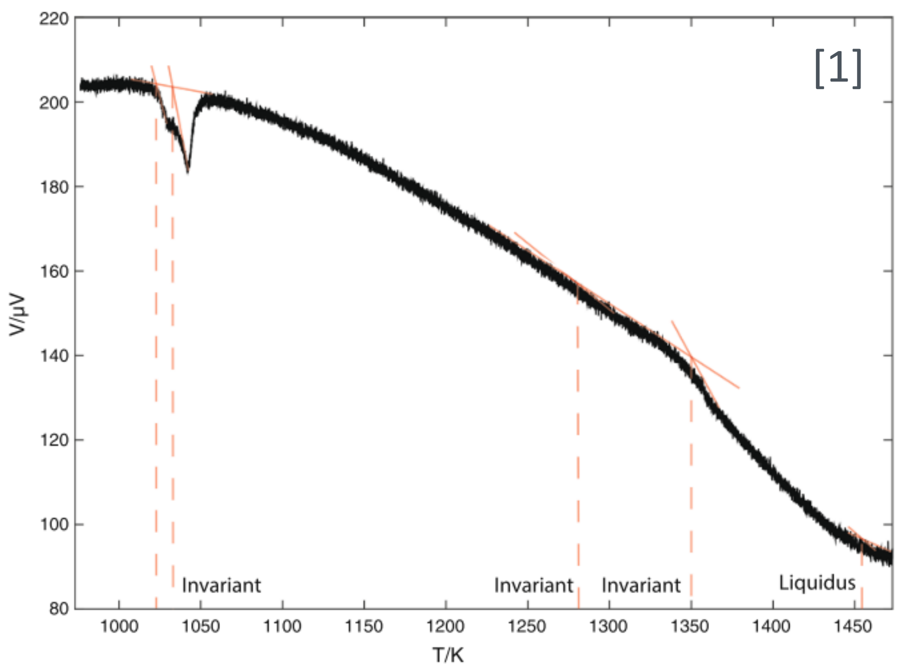
Thermophysical Properties of Gen3 Molten Chlorides

- Melting point
- Liquid-state heat capacity
- Vapor pressure

Melting Point Measurement with DSC

- Main challenge – The ternary salt is NOT expected to have a simple solid-to-liquid phase transition
  - Most likely, melting starts with a first-order phase transition (i.e., discontinuity in the first derivative of G) where a latent heat is involved
    - Easier to detect the eutectic or solidus with a DSC
  - Next, melting may complete with a higher-order phase transition (i.e., discontinuity in higher derivatives of G)
    - Much harder to detect the liquidus with a DSC

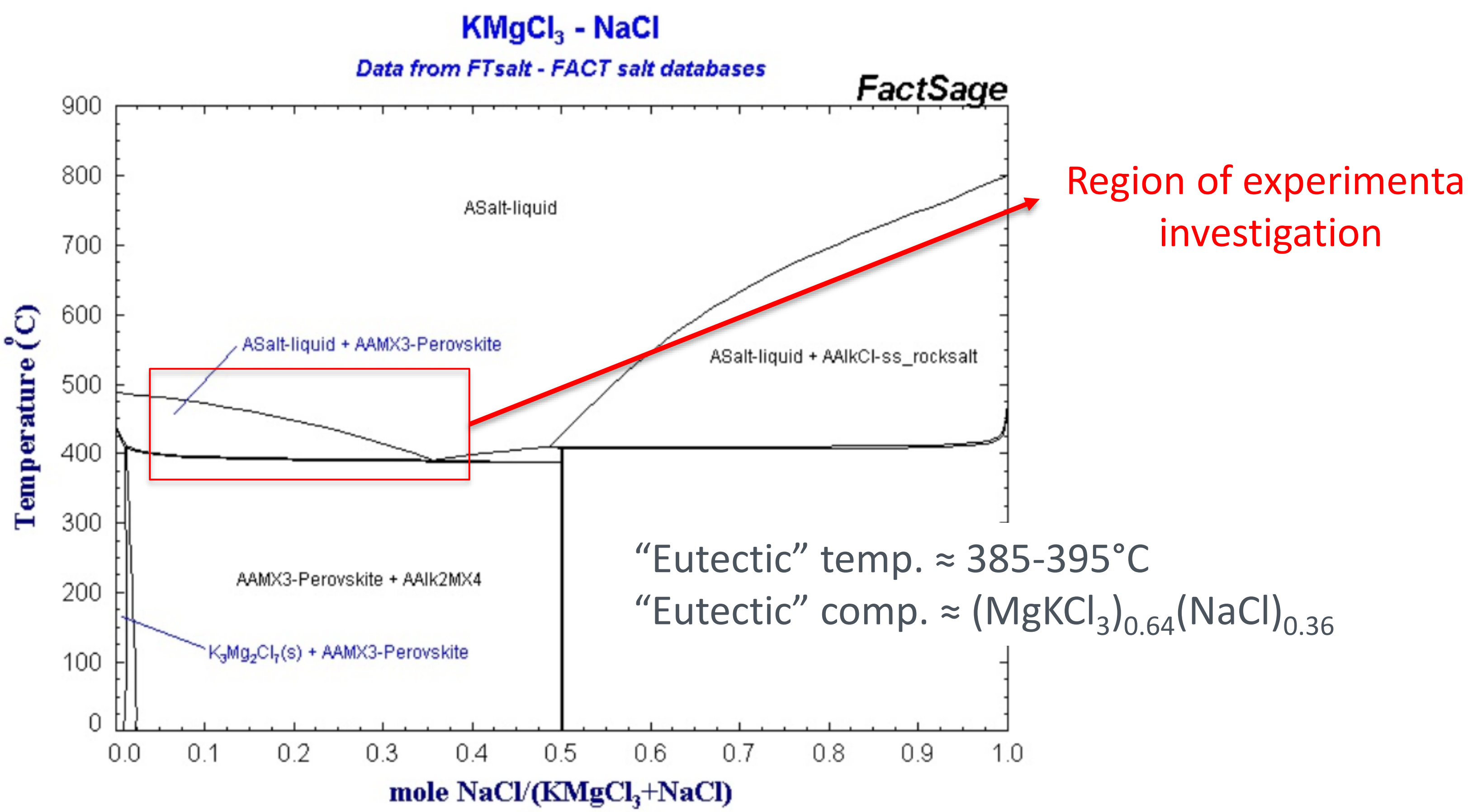


DTA scan of 80BaS/20Cu_2S (mol%) [2]

[1] C. Stinn, K. Nose, T. Okabe, and A. Allanore, "Experimentally Determined Phase Diagram for the Barium Sulfide-Copper(I) Sulfide System Above 873 K (600 °C)," *Metall. Mater. Trans. B Process Metall. Mater. Process. Sci.*, vol. 48, no. 6, pp. 2922–2929, 2017

Eutectic Temp. and Composition – Thermodynamic Calculation

- Educated guess by FactSage thermodynamic calculation

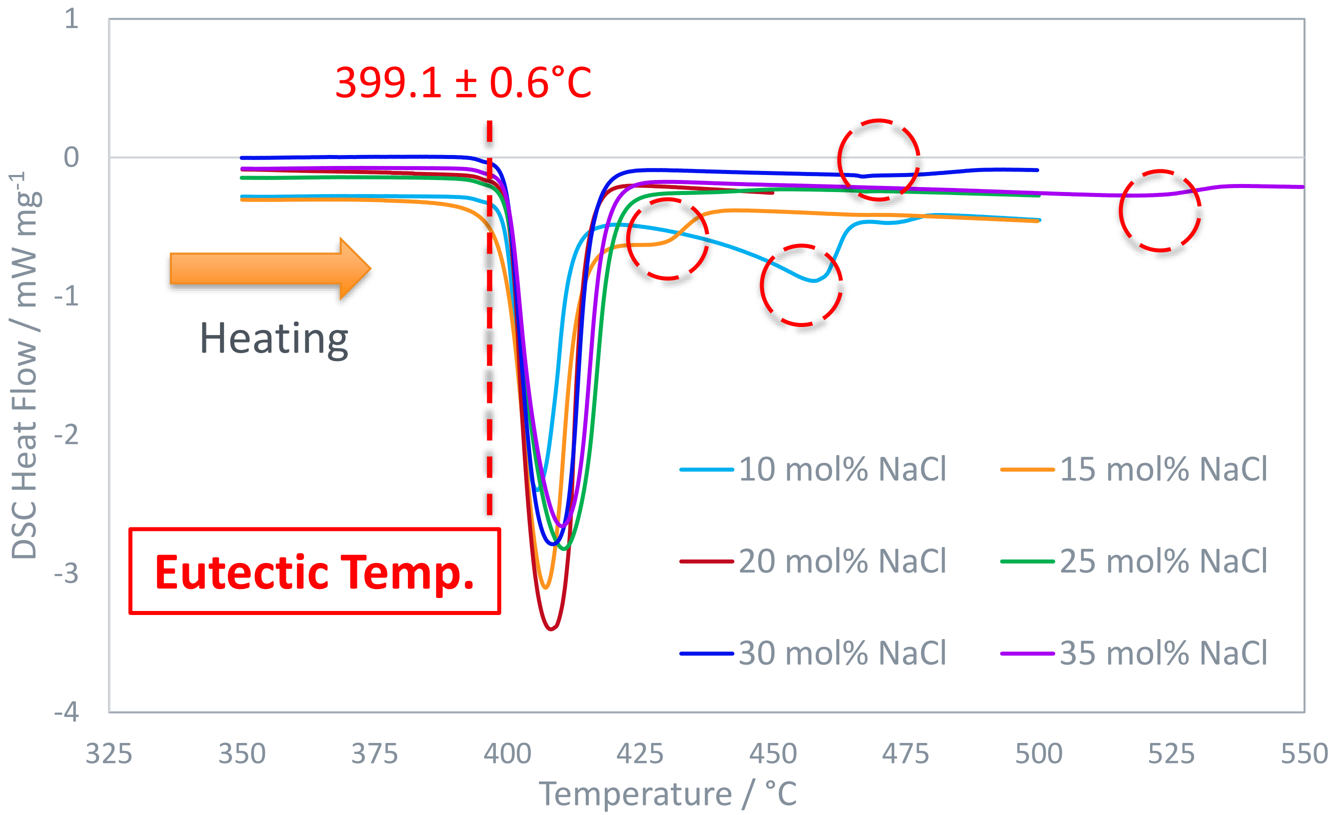


"Eutectic" temp. ≈ 385-395°C

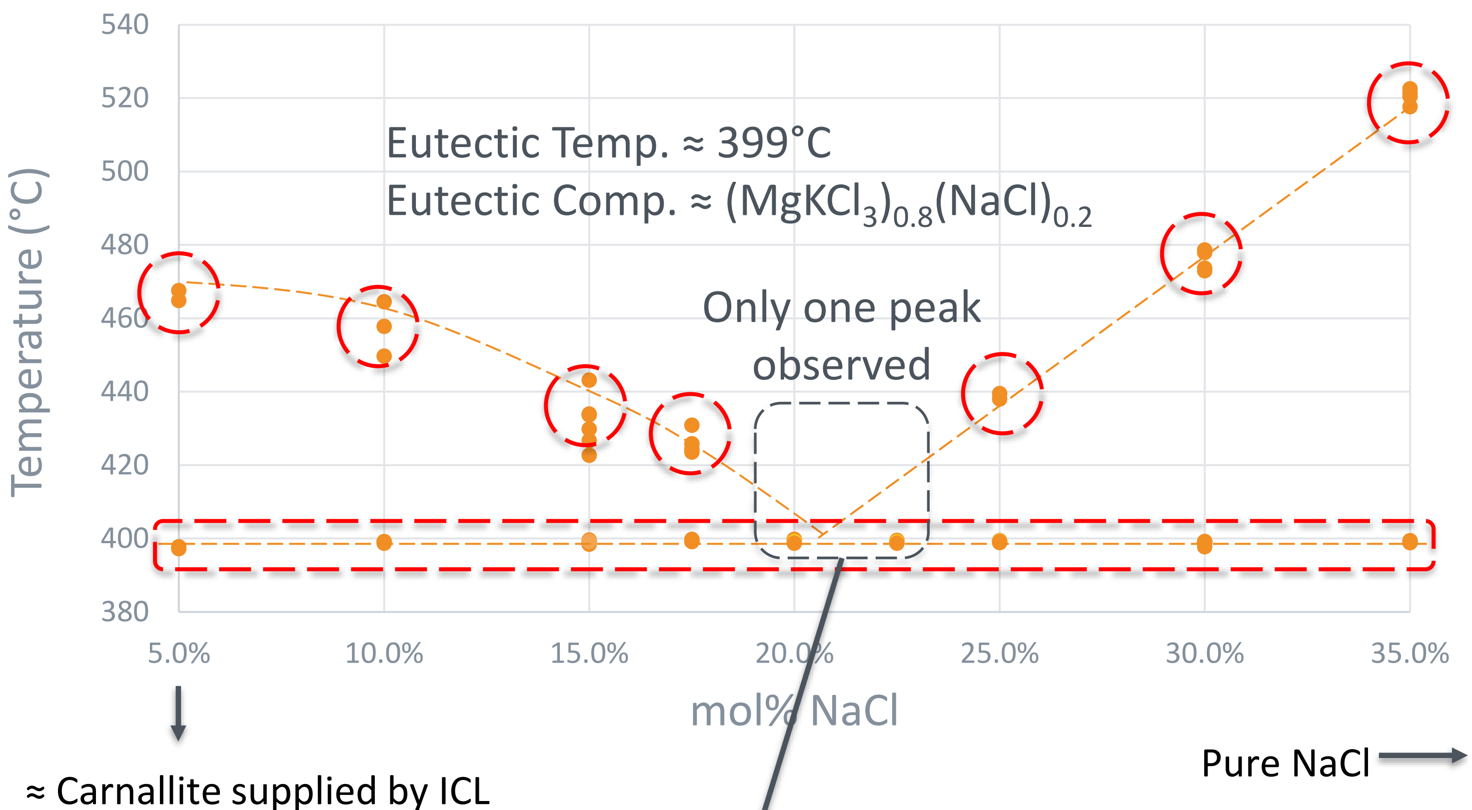
"Eutectic" comp. ≈ $(MgKCl_3)_{0.64}(NaCl)_{0.36}$

Eutectic Temp. and Composition – DSC Results

- Liquidus at certain composition is easier to detect than at other compositions



Eutectic Temp. and Composition – DSC Results



Final Gen3 salt composition

	$MgCl_2$	KCl	NaCl
Composition	mol.%		
Average	37.51	40.92	21.57
Stdev	1.16	1.54	1.72

Thermophysical Properties of Gen3 Molten Chlorides

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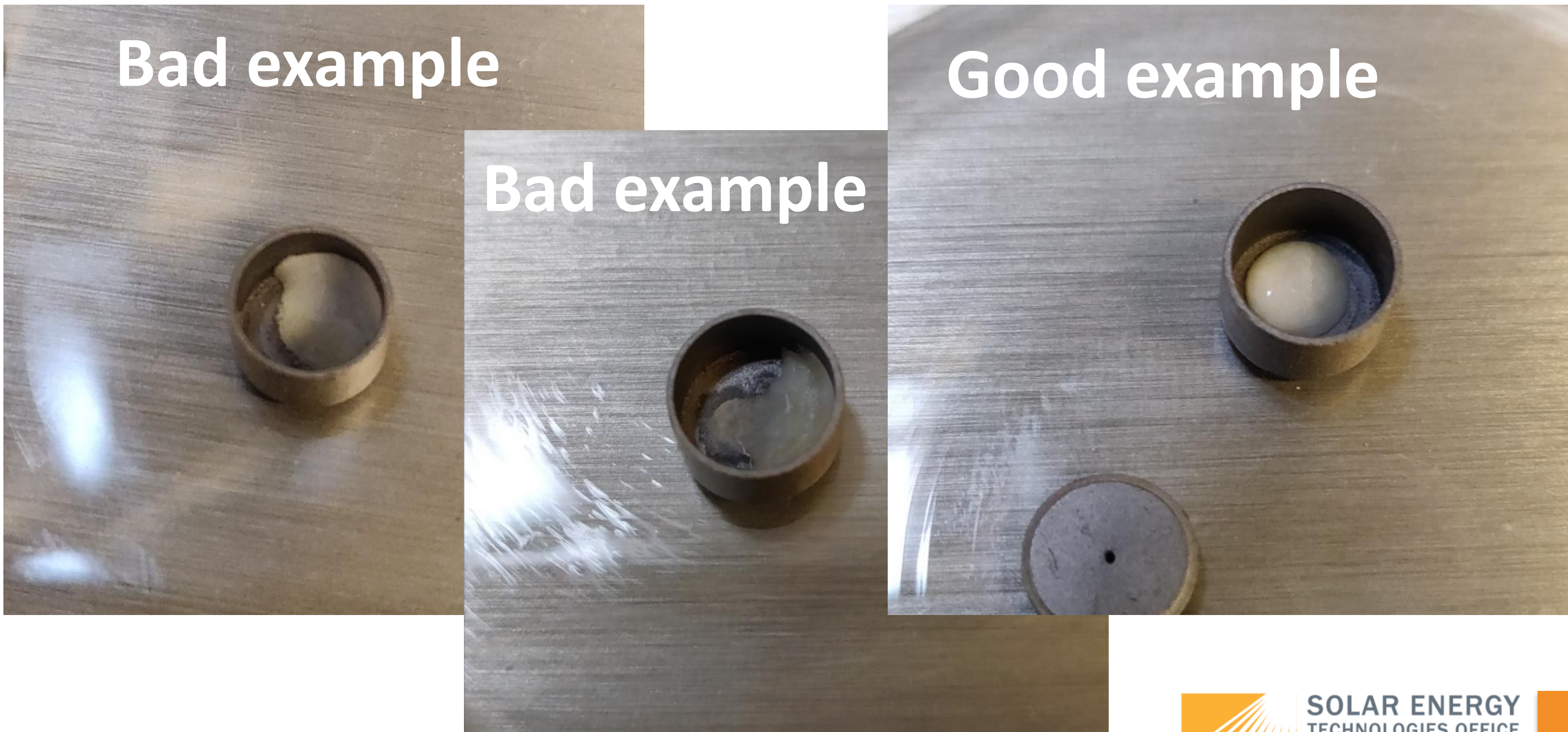
Heat Capacity Measurement with DSC

- Practical challenge I – Salt creeping
  - Pt crucible was found to cause easier creeping. Graphite crucible was found to have least creeping.

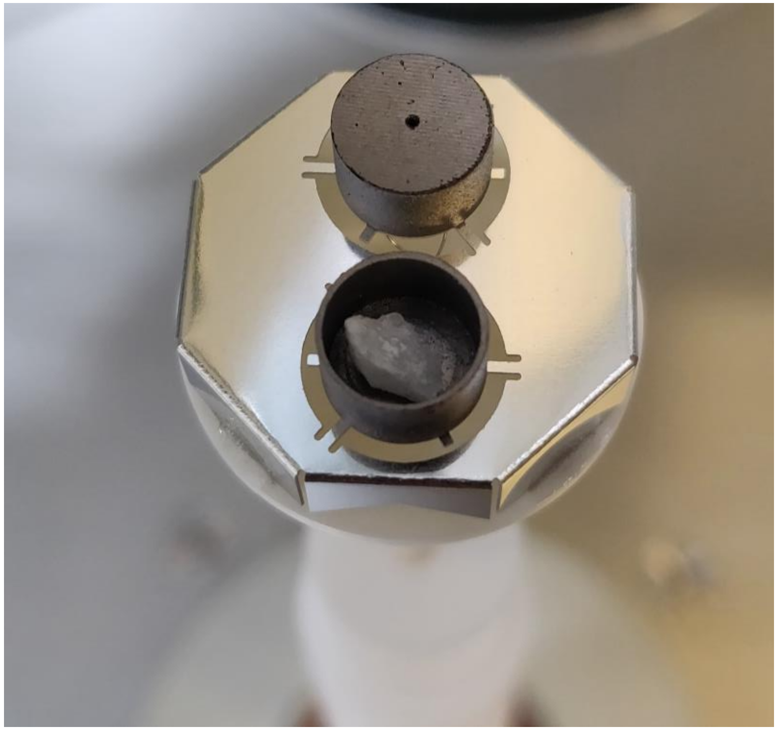


Heat Capacity Measurement with DSC

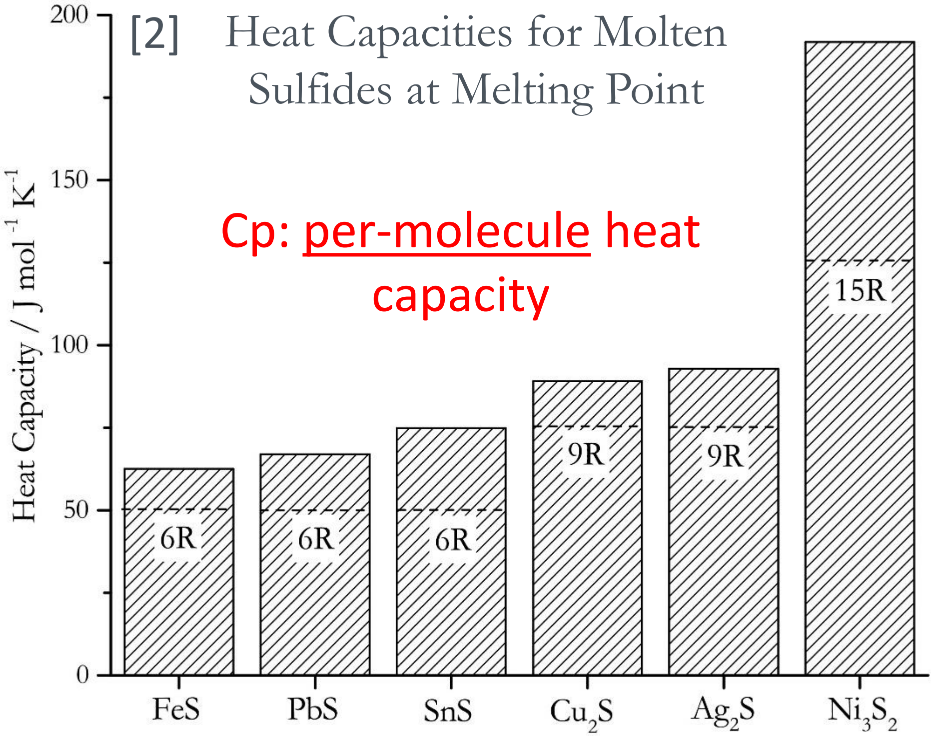
- Practical challenge II – DSC crucible quality
  - Bubbling/delamination of graphite crucible will cause inconsistent heat transfer during measurement. Regular inspection is needed.

Heat Capacity Measurement with DSC

- Practical challenge III – Reproducibility of sample/crucible position
  - Ideally, the reference and sample crucibles need to stay at the exact same position across all runs.
  - Crucible positioning using automatic sampling arm is preferred over manual positioning.



Liquid Heat Capacity



Cp: per-molecule heat capacity

Heat Capacities for Other Liquids at Melting Point

Liquid Gas	C_p/R	Molten Oxides	C_p/R	Molten Halides	C_p/R
O_2	3.21	CaO	3.77	NaCl	4.16
Cl_2	4.03	Cu_2O	4.10	KBr	4.19
		MgO	4.03	MgI_2	4.02
		FeO	4.01	BaF_2	3.99
		Al_2O_3	4.63	$CaCl_2$	4.22
				KCl	**5.11**
				$MgCl_2$	**3.71**

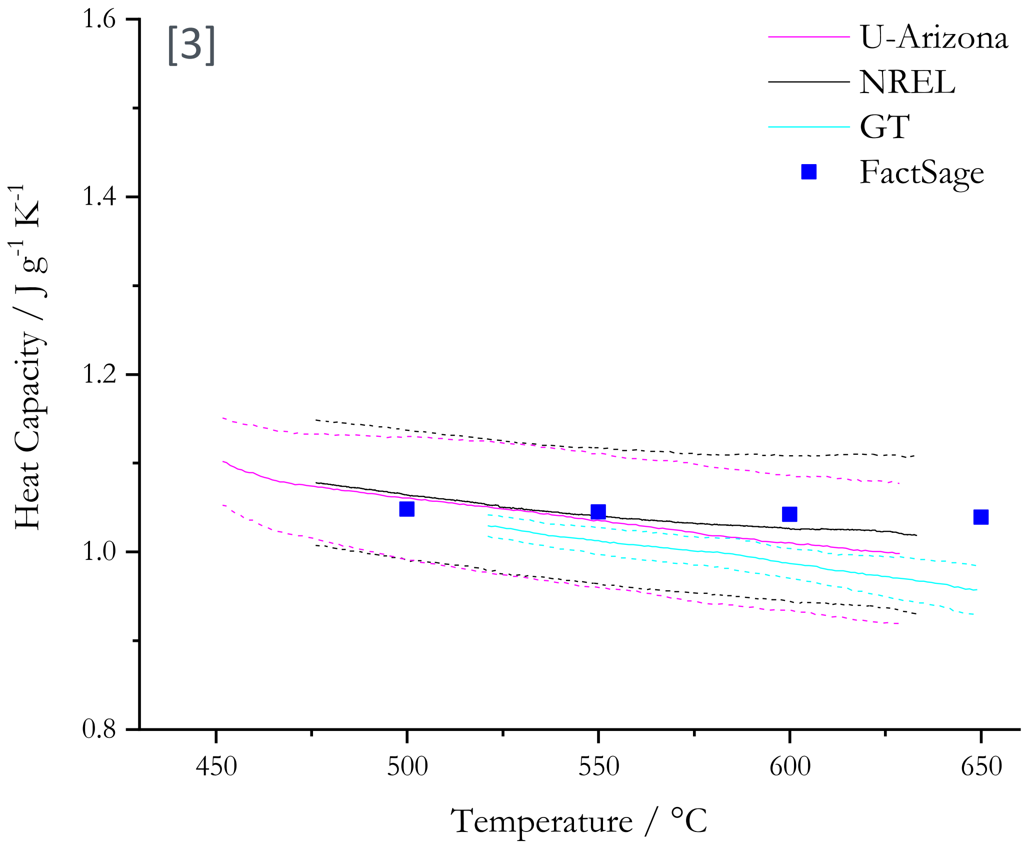
Cp: per-atom heat capacity

All are higher than Dulong-Petit 3R limit on a per-mole-of-atoms basis.

Simple calculation predicts 10.152R (Cp/R = 4.27) or 1.071 J/g K heat capacity for Gen3 chloride composition.

[2] Zhao, Y. (2018). *Engineering Design Criteria for High Temperature Thermoelectric Generators Based on Molten Compounds*. Doctoral Thesis. Massachusetts Institute of Technology.

Heat Capacity Measurement with DSC



Key statistics:

- # of valid measurements: NREL (29), U-Arizona (15), GT (4)
- Overall standard deviation: 7-8% of average value
- Difference between averages of different labs: < 5%
- Difference from FactSage: < 4%

Remaining unknowns – decreasing trend of Cp?

- Instrument contributions?
- The nature of Cp above the 3R limit?

[3] X. Wang, J. Del Rincon, P. Li, Y. Zhao, and J. Vidal, "Thermophysical Properties Experimentally Tested for NaCl-KCl-MgCl2 Eutectic Molten Salt as a Next-Generation High-Temperature Heat Transfer Fluids in Concentrated Solar Power Systems," *J. Sol. Energy Eng.*, vol. 143, no. 4, pp. 1–8, 2021

Thermophysical Properties of Gen3 Molten Chlorides

- Melting point
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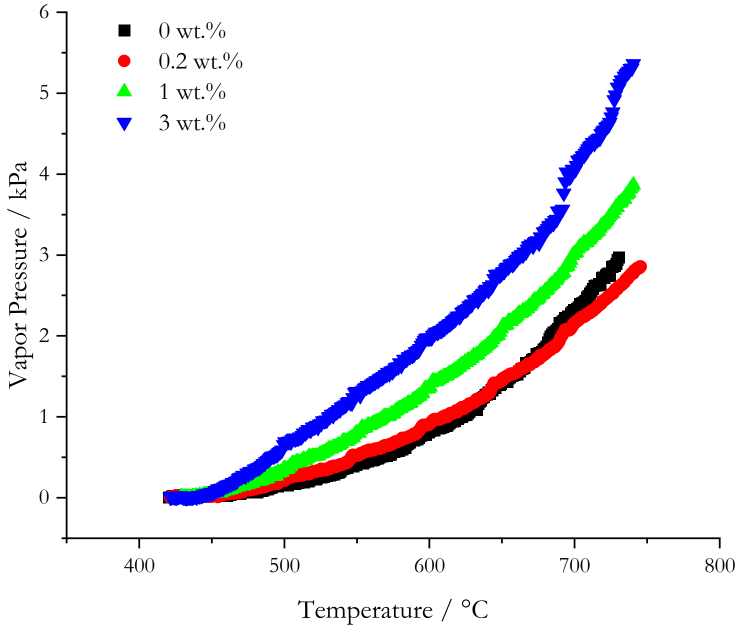
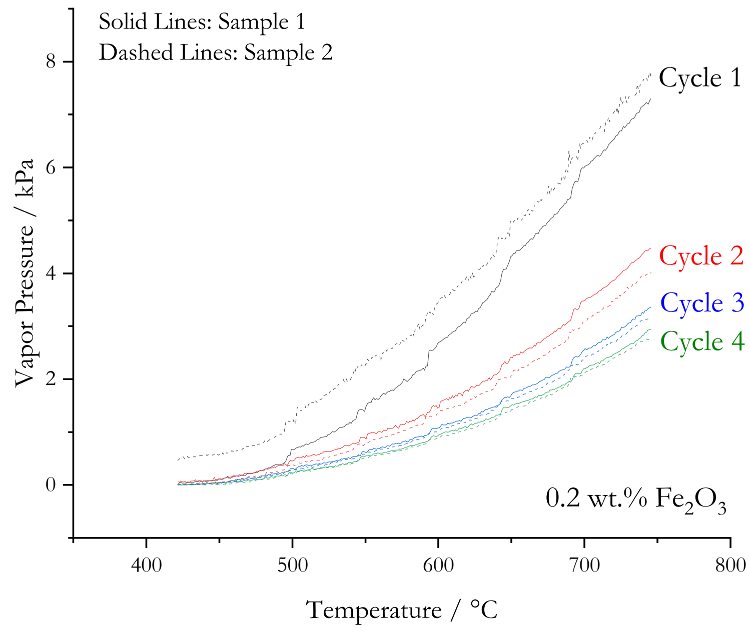
Vapor Pressure Measurements

- Practical challenge – removing effect from contaminations

Effect of Contaminations [4]



Vapor pressure of salts with different levels of Fe_2O_3 addition. The vapor pressure at each Fe_2O_3 addition was measured after at least three vacuum cycles to remove volatile species.

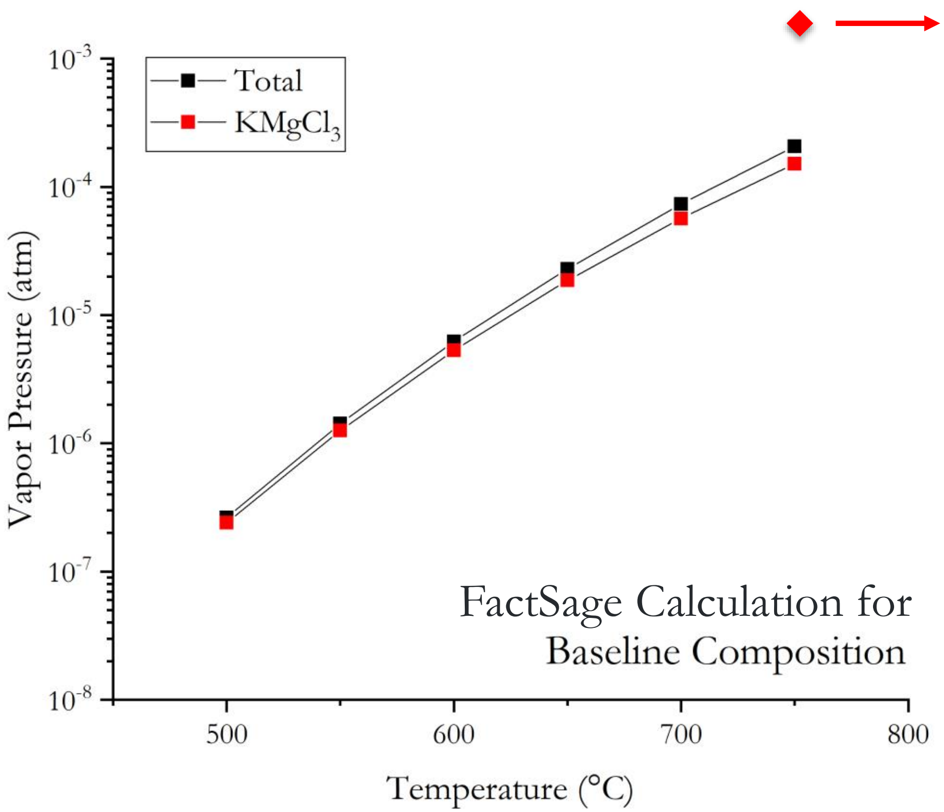


Vapor pressure for purified salt with 0.2 wt.% of Fe_2O_3. Two samples were measured given by the solid and dashed lines. Cycles (1–4) were separated by manual removal of volatile species under vacuum.

[4] Zhao, Youyang. 2020. Molten Chloride Thermophysical Properties, Chemical Optimization, and Purification. Golden, CO: National Renewable Energy Laboratory. NREL/TP-5500-78047.

Vapor Pressure Measurements

- Challenge II – Identifying real gaseous species in the vapor



Experimental result is > 10x higher than thermodynamic calculation. Why??

Vapor Pressure Measurements

- Challenge II – Identifying real gaseous species in the vapor
- We still don’t know what is responsible for the significantly higher vapor pressure.
  - Water vapor? Oxide contaminant?
  - Complicated vapor species? Polymeric gaseous molecules in alkali halide vapor have been reported over 60 years ago (e.g., Na_2Cl_2 dimers [5])
- What technique(s) can be used?
  - FTIR? Is salt vapor transparent to IR like solid salts? Any reference data?
  - Mass spectroscopy? How do salt vapor molecules ionize?
  - Cold trap followed by analysis of the solids? How to ensure rapid quench to avoid possible phase transitions?
    - NREL is currently planning a Molten Chloride Salt Research Tank project led by Dr. Craig Turchi that could potentially provide some insights

[5] J. Berkowitz and W. A. Chupka, “Polymeric gaseous molecules in the vaporization of alkali halides,” *J. Chem. Phys.*, vol. 29, no. 3, pp. 653–657, 1958

Thank you

Contact Information

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