Thermodynamic modeling progress of uranium chloride and uranium oxide systems

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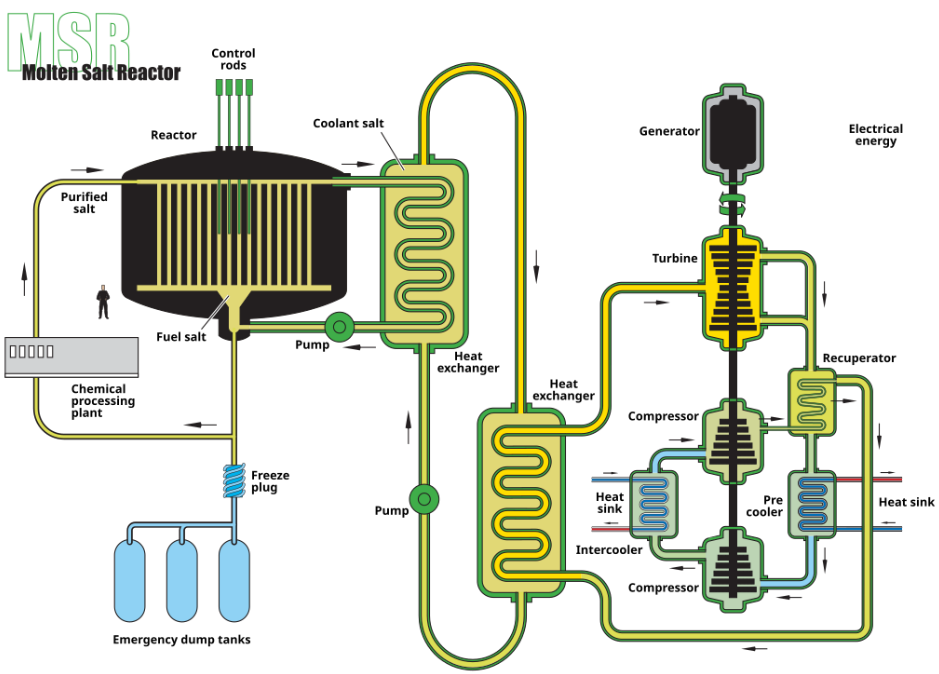
What is the molten salt reactor (MSR)?

Schematic Diagram of MSR



(Salt type: fluoride, chloride)

Key Features

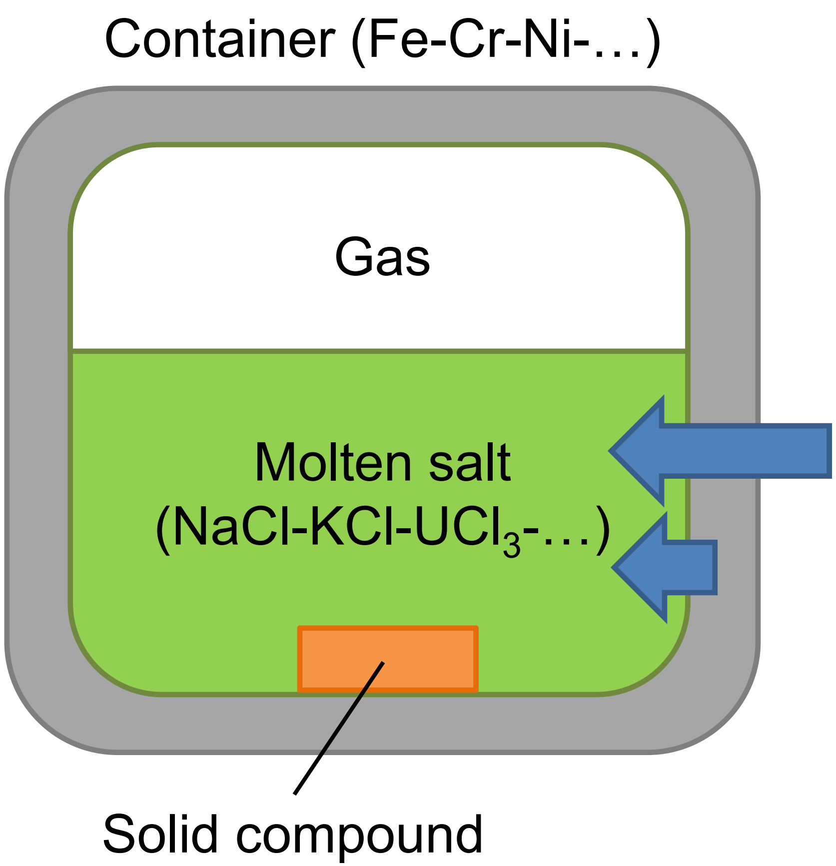
- Liquid molten salt fuel system
- Operation at ambient pressure
- Online chemical processing

Advantages

- Enhanced inherent safety
- Simplify nuclear power plant design
- High sustainability and adoptability

Figure source: https://www.gen-4.org/

Oxygen ingress in MSR



Oxygen ingress source

- Minor leakage through cover gas or off-gas boundaries
- Exposure during salt synthesis, handling, transfer, and storage

Consequences of ingress

- Change in uranium valence distribution ($U^{3+} \rightarrow U^{4+}$, U^{6+})
- Oxide precipitation and phase instability
- Gas phase formation and volatile species under severe oxidation

Thermodynamic modeling is required to predict these off-normal behaviors.

What is CALPHAD?

CALculation of **PHA**se **D**iagram (CALPHAD): A thermodynamic modeling technique based on thermodynamic data

CALPHAD Method

Thermodynamic database development

- Thermodynamic models
- Optimized parameters

+

Phase equilibria calculation

- Unary systems
- Binary systems
- Ternary systems
- Multicomponent systems

↓

Gibbs energy minimization

↓

Gibbs energy, activity, thermodynamic equilibrium state, …

Gibbs energy description

Pure compounds

$$G_T^o = H_T^o - TS_T^o$$

$$H_T^o = \Delta H_{298}^o + \int_{298}^{T} Cp\,dT \qquad S_T^o = S_{298}^o + \int_{298}^{T} \frac{Cp}{T}\,dT$$

Solutions

For example, random mixing solution (ideal, regular, sub-regular solutions)

$$G^L = X_A G_A^{o,L} + X_B G_B^{o,L} + RT(X_A \ln X_A + X_B \ln X_B) + G^{ex}$$

$$G^{ex} = \sum q_{AB}^{mn} X_A^m X_B^n$$

To get high predictive ability, thermodynamic model should reflect the structure of solutions (phases)

Thermodynamic database development

Thermodynamic database for (Na^+, K^+, U^{3+}, U^{4+}, U^{6+}, …) // (Cl^-, O^{2-}) system

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Critical Evaluation/Optimization

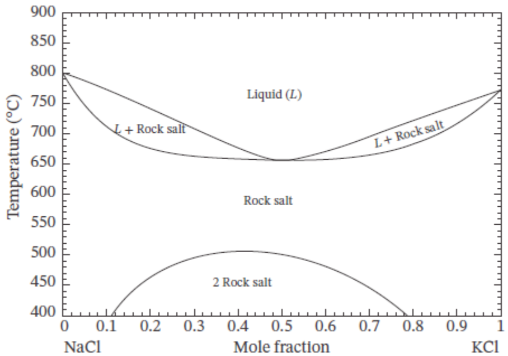
- Phase diagram data
- Thermodynamic data
- Crystal structural data

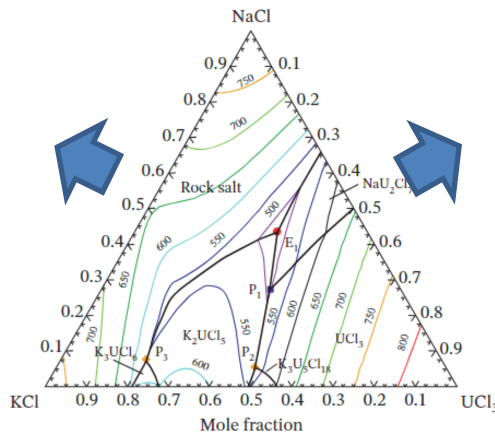
→

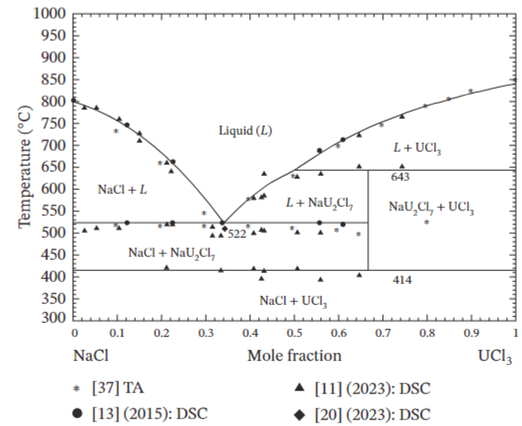
- Thermodynamic database
- Applications in molten salt reactors

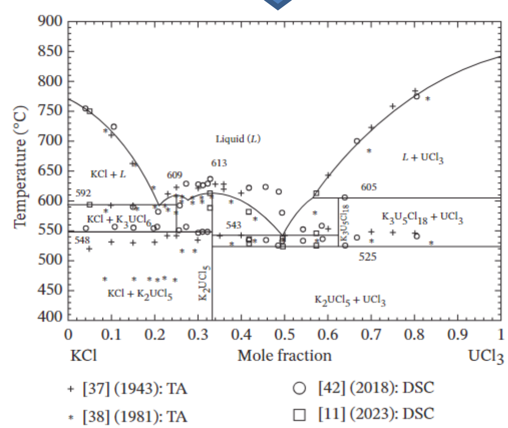
Base chloride fuel salt system: NaCl-KCl-UCl_3

(Na, K, U(3+), U(4+), U(6+)) // (Cl, O) system









Kim et al. (2026). International Journal of Energy Research, 1832897, https://doi.org/10.1155/er/1832897

Extension to higher uranium chlorides

(Na, K, U(3+), U(4+), U(6+)) // (Cl, O) system

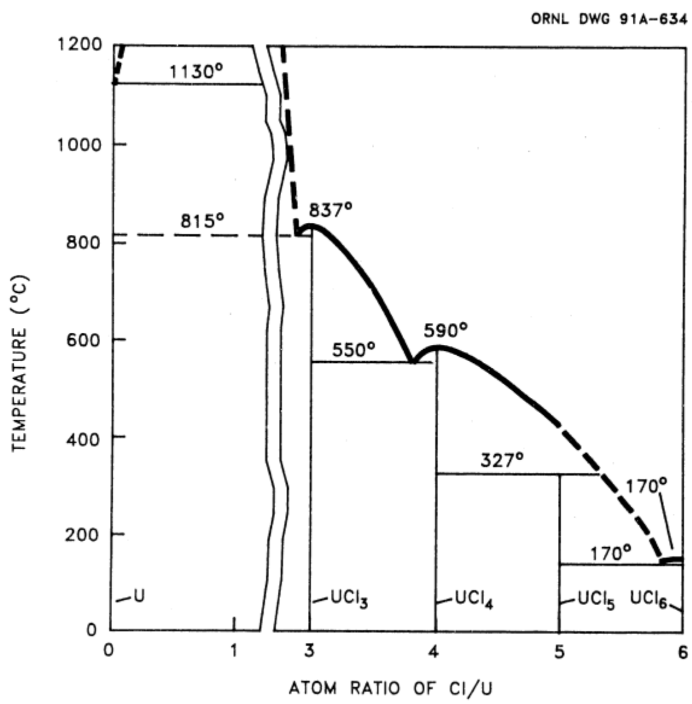
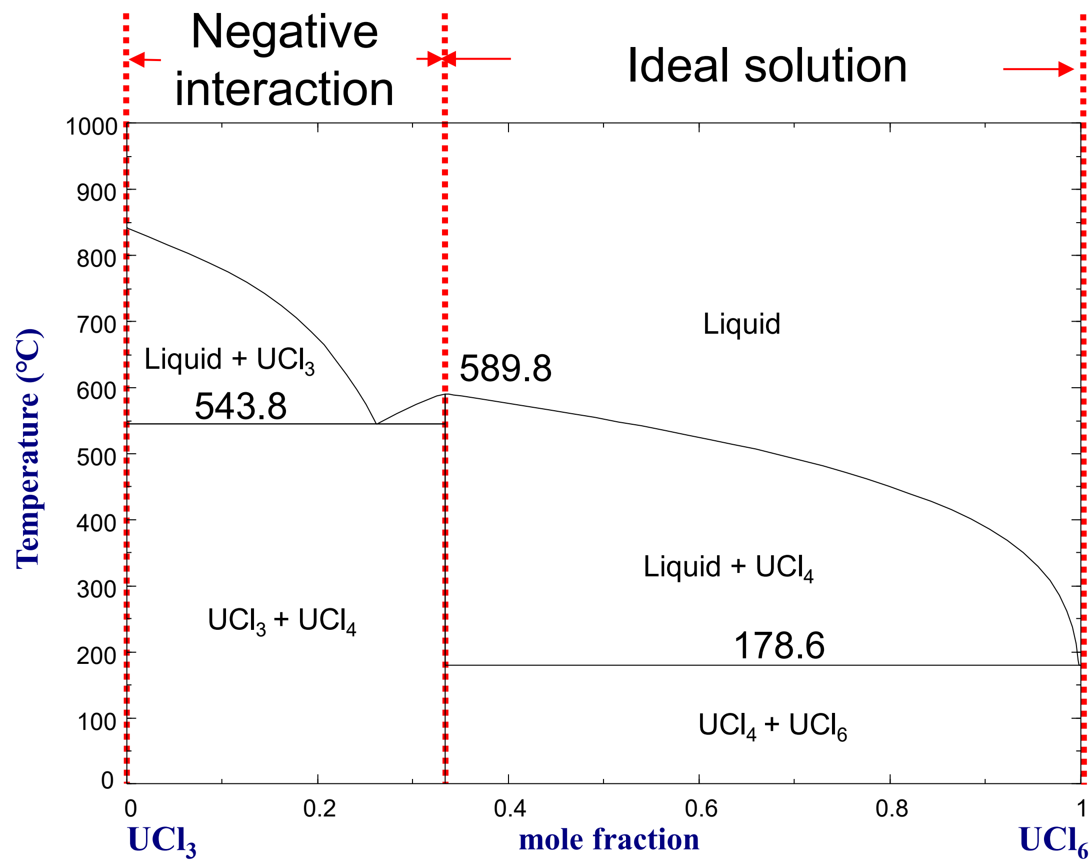


Fig. 3. Phase diagrams for the compounds of uranium and chlorine.[7]

P. A. Haas (1992)

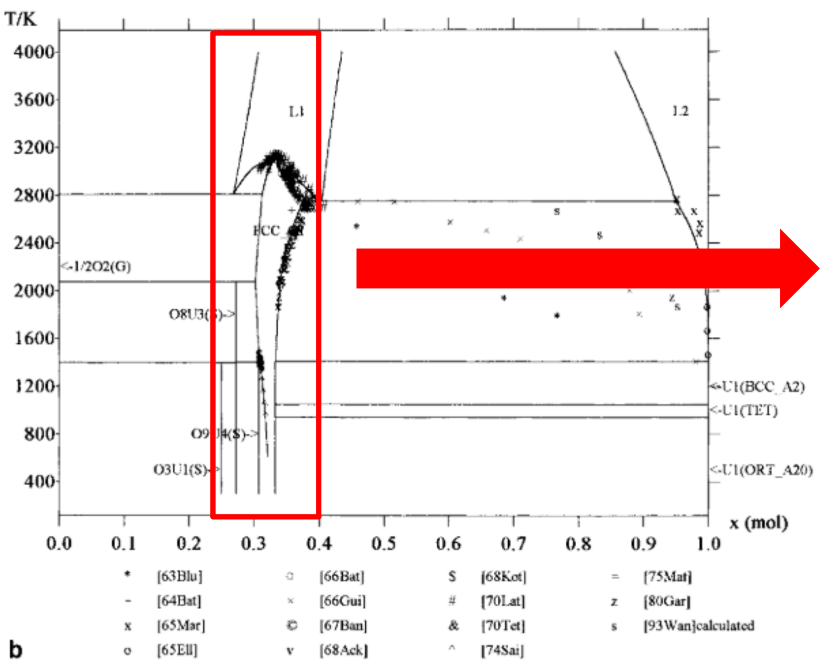


P. A. Haas (1992), ORNL/TM-11955.

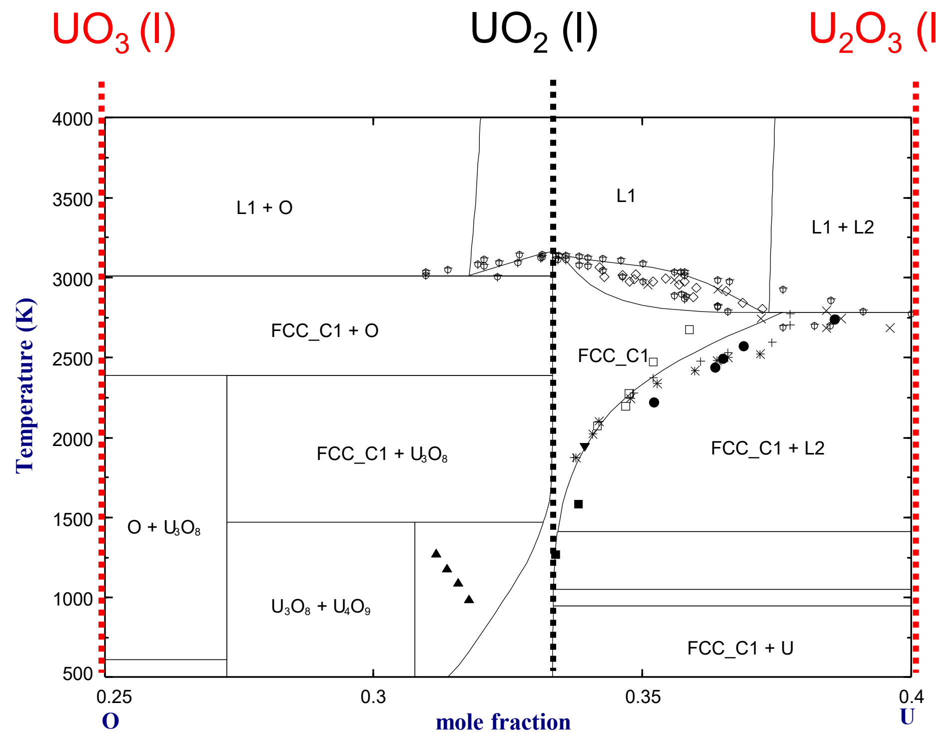
David Brown (1979), Gmelin Handbuch der Anorganischen Chemie, Vol. C9.

Uranium oxide subsystem for oxygen ingress

(Na, K, U(3+), U(4+), U(6+)) // (Cl, O) system



Chevalier and Fischer (1998)

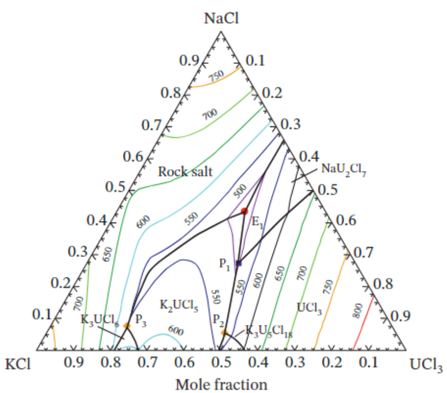


- Black: Assessed in our group
- Red: No data available

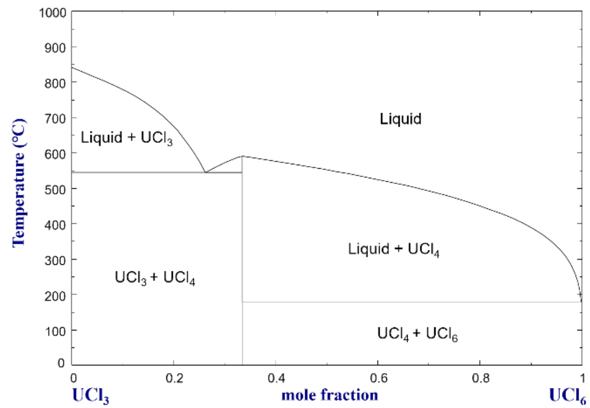
U_2O_3, UO_3 liquid phases were estimated with the Gibbs energy of liquid solution

Integration of chloride-oxide thermodynamic framework

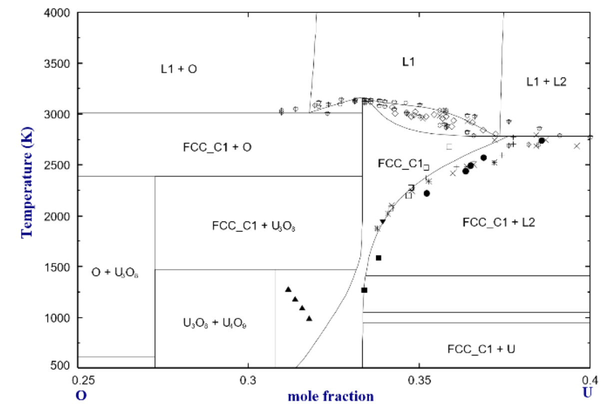
$NaCl-KCl-UCl_3$



UCl_3-UCl_6



$U_2O_3-UO_3$

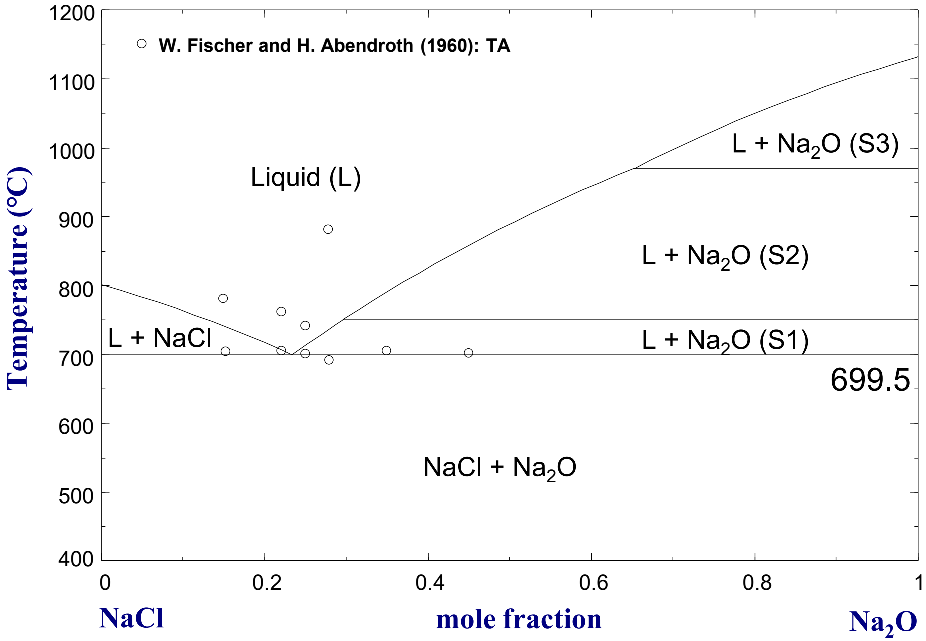


(Na, K, U(3+), U(4+), U(6+)) // (Cl, O) system

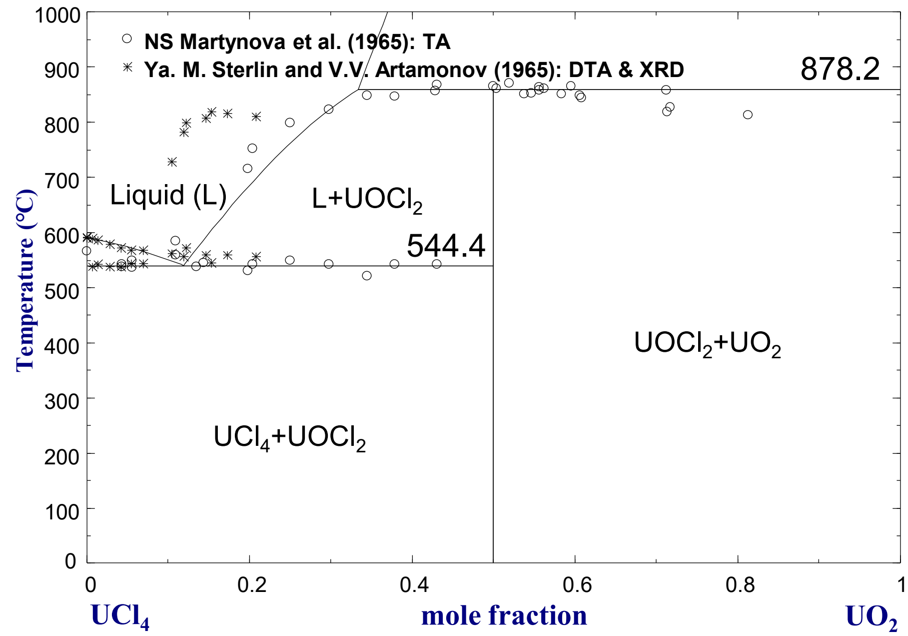
Na_2O — U_2O_3	K_2O — U_2O_3	K_2O — UO_2	
(Na,U(3+))(Cl,O)	(K,U(3+))(Cl,O)	(K,U(4+))(Cl,O)	…
$NaCl$ — UCl_3	KCl — UCl_3	KCl — UCl_4	

Chloride - oxide systems

$NaCl$-Na_2O



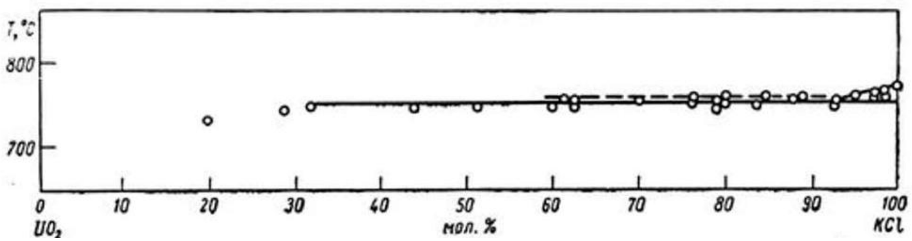
UCl_4-UO_2



Fischer, W. & Abendroth, H. J. (1961). Zeitschrift für anorganische und allgemeine Chemie, 308(1-6), 98-104.

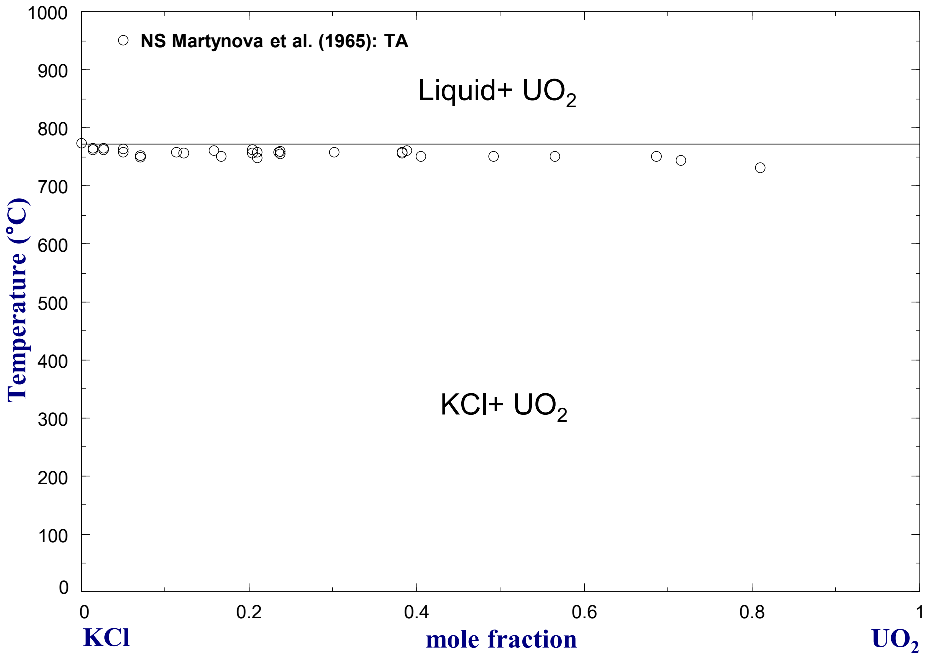
Martynova et al. (1965), Soviet Atomic Energy, 18(6), 777-783.

Sterlin, Y. M., & Artamonov, V. V. (1967). Soviet Atomic Energy, 22(6), 589-593.



Martynova et al. (1965)

UO_2-KCl



No interaction parameter added

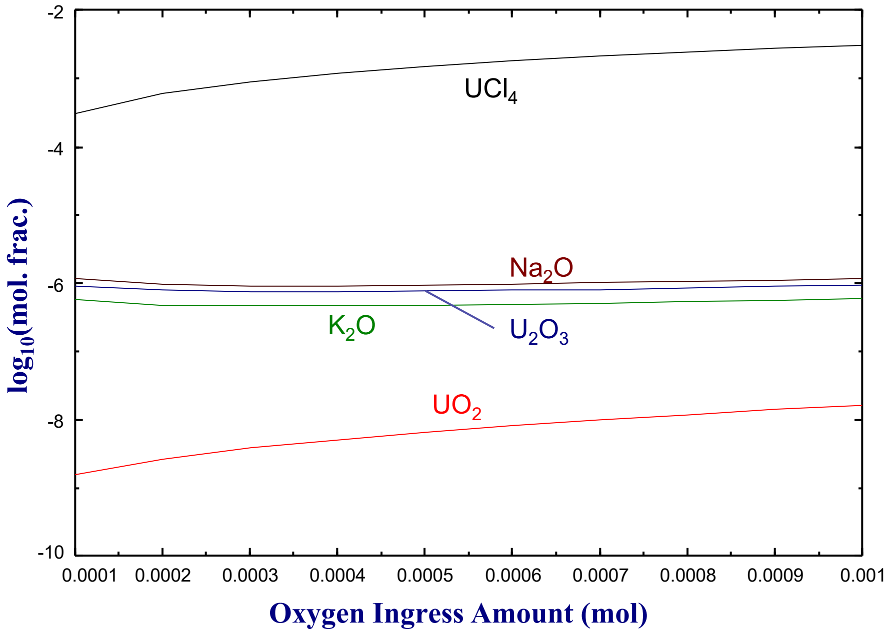
Other reciprocal systems can be reasonably predicted

Martynova et al. (1965), Soviet Atomic Energy, 18(6), 777-783.

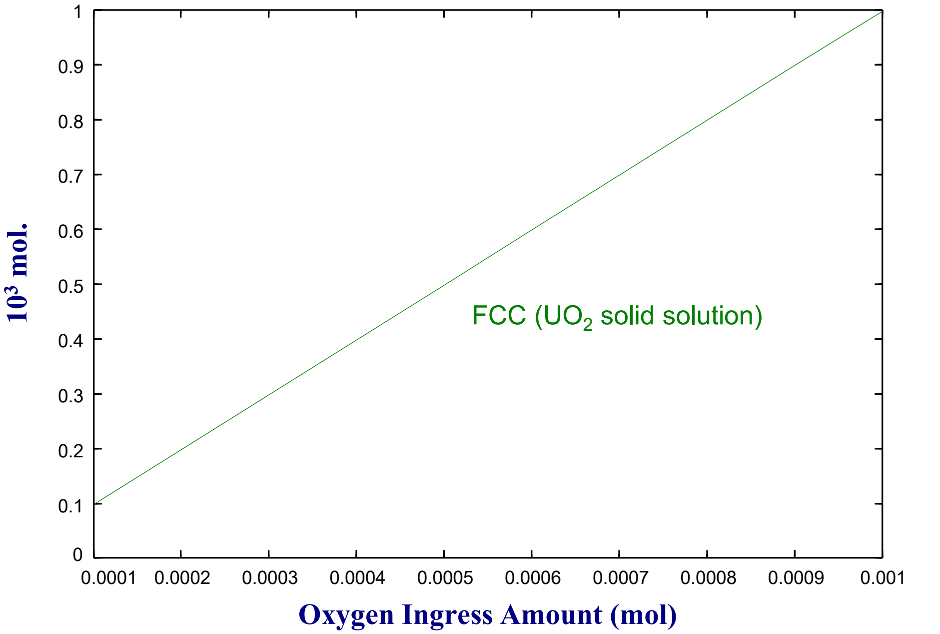
Application 1: trace oxygen ingress condition

- Condition: 1 mol of NaCl-KCl-UCl_3 eutectic salt, 700 °C
- Oxygen input is normalized to 1 mol initial fuel salt

Mole fraction in liquid



Solid amount calculation

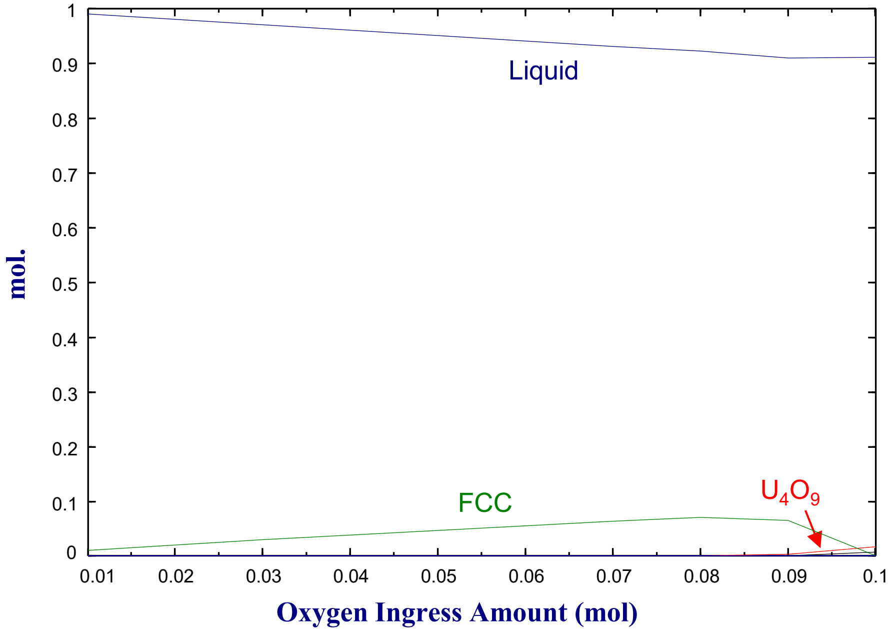


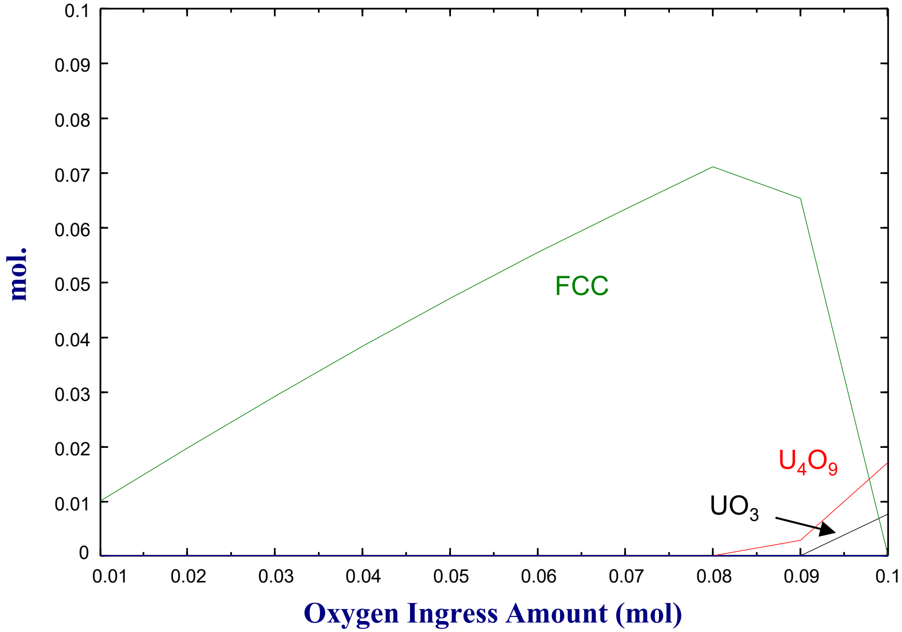
The model can estimate the oxygen threshold for oxide precipitation.

Application 2: excess oxygen ingress condition

- Condition: 1 mol of NaCl-KCl-UCl_3 eutectic salt, 700 °C
- Oxygen input is normalized to 1 mol initial fuel salt

Liquid & Solid amount calculation



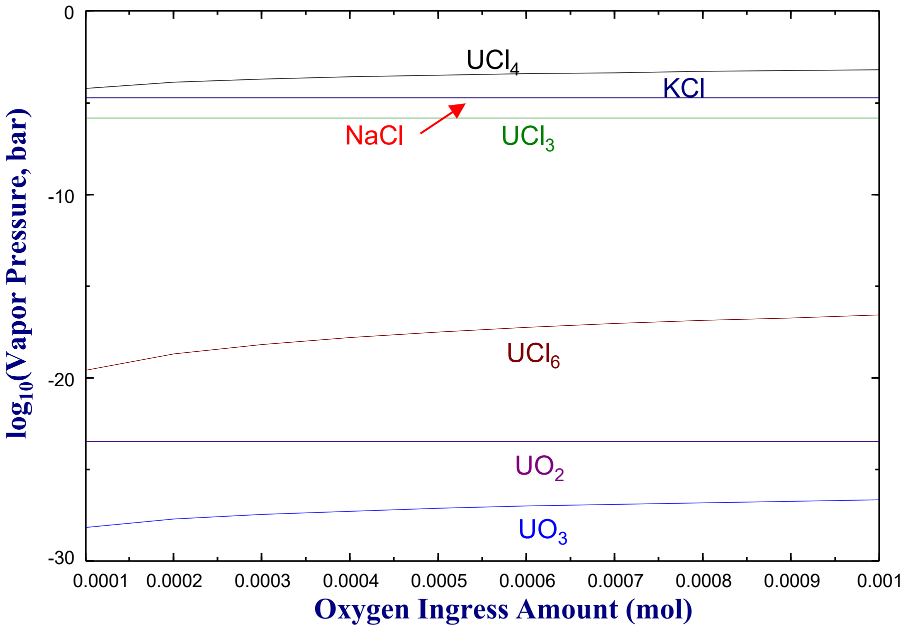


The model predicts phase redistribution under severe oxygen ingress.

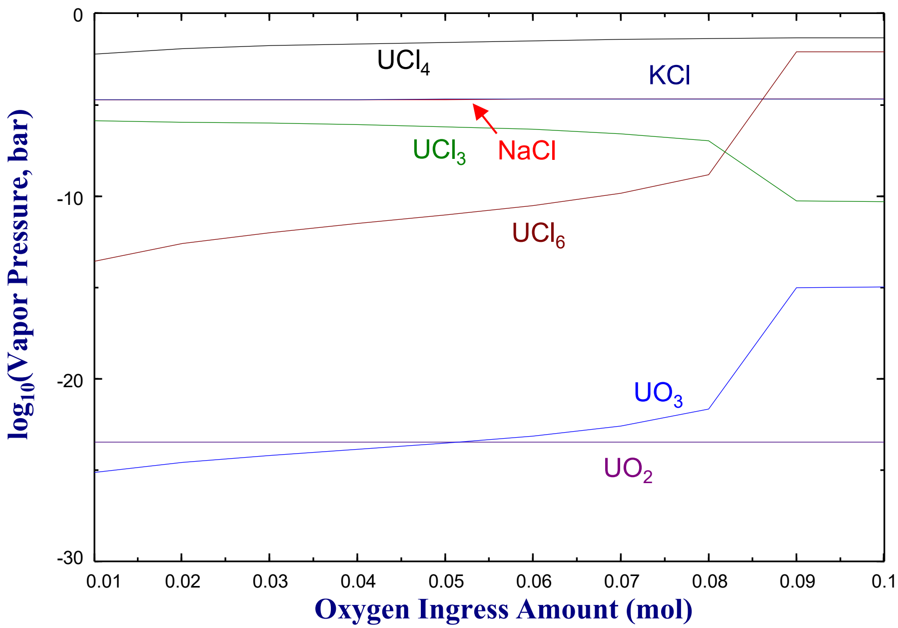
Application 3: vapor pressure response under oxygen ingress

- Condition: 1 mol of NaCl-KCl-UCl_3 eutectic salt, 700 °C

Trace oxygen ingress



Excess oxygen ingress



The model supports preliminary assessment of gas-phase source-term tendency.

Summary

- A thermodynamic database combining uranium chloride and oxide systems was developed for chloride-based MSR applications.
- The U–Cl and U-O system was extended to include higher valence chlorides/oxides (U^{4+}, U^{6+}), ensuring redox consistency under oxidizing conditions.
- The integrated (Na, K, U) // (Cl, O) framework enables prediction of phase stability and redox behavior under oxygen ingress conditions.
- The database was applied to evaluate oxide precipitation, phase redistribution, and vapor pressure response under oxygen ingress scenarios.

Thank you!

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