Thermodynamic assessment of the corrosion products between molten salts and reactor structural materials

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DE LA RECHERCHE À L'INDUSTRIE

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CONTEXT: CHEMICAL EVOLUTION OF MOLTEN SALT REACTOR FUEL

❖ Molten salt mixture = a solvent for the fuel elements (U, Pu, Th) as well as the coolant for primary heat exchanger units

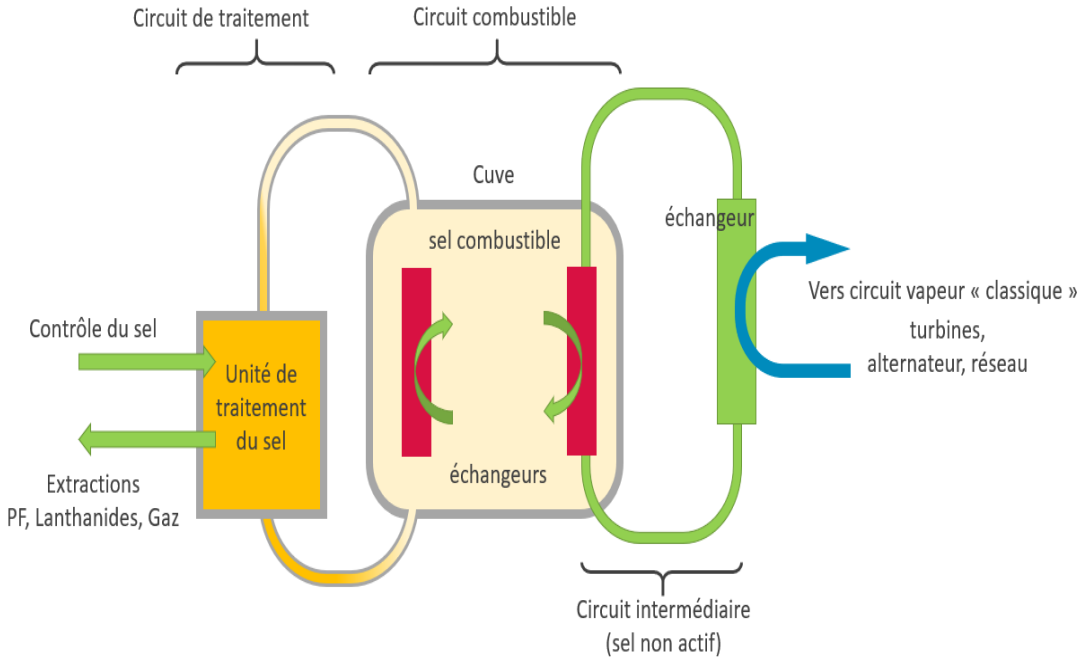
1. Circulation of the salt mixture in the **reactor core** and **intermediate heat exchanger units**

2. Regular circulation of salt through the **chemical treatment unit**

Formation of radioactive fission products as a result of the fission reaction

Addition of fresh fuel material in the salt and a « clean up » of fission products

Evolution of Molten Salt Fuel composition



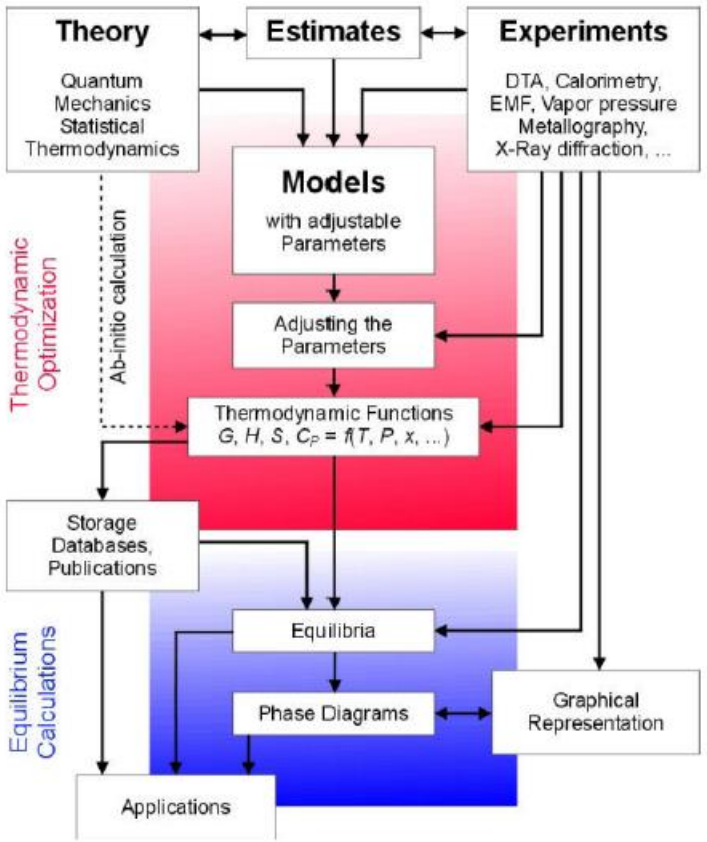
What we need?

- Comprehensive knowledge of the corrosion products and the molten salt behavior to predict evolution of the material behavior;
- To understand the effect of changing composition, pressure and temperature conditions for a better evaluation of the reactor performance

✓ Use of CALPHAD method for modeling the thermodynamic properties and phase diagrams for the systems

- **Molten salt systems:** lack of detailed databases on the thermodynamic and physical properties over the required range of temperature (T), pressure (p) and composition (y) for performance assessment.

- **CAL**culation of **PHA**se **D**iagrams: mathematical models (thermodynamic databases) with adjustable parameters for evaluating Molar Gibbs energies $G_M^\theta\ [\mathrm{Jmol}^{-1}]$ of a phase θ as functions of the state variables: *temperature* $T\ [K]$, *pressure* $p\ [Nm^{-2}]$ *and composition* $\left(y_i^\theta\right)_{i\epsilon S}$



1. Identification of all phases present in the system
2. Choice of thermodynamic model for describing Gibbs free energy of each phase :-

$$G_M^\theta : \mathrm{T, p}, y_i^\theta \rightarrow G_M^\theta$$

$$G_M^\theta = a_0 + a_1 T + a_2 T ln T + a_3 T^2 + a_4 T^{-1} + a_5 T^3 \ldots$$

Where: $a_0, a_1 \ldots$ are adjustable model parameters

3. Data from experimental measurements: fitting of model parameters (coefficients) based on the collected data
4. Final function of G(T, p, y) → Thermodynamic database

- Utilization of thermodynamic databases:-
  i. Equilibrium thermodynamic description : minimization of the total Gibbs energy (G), achieved through a Gibbs Energy minimizer code;
  ii. Generation of phase diagrams for systems by assessing the Gibbs energy functions for all the phases present;
  iii. Calculation of 'local-equilibrium' thermodynamic properties for a phase: use of appropriate thermodynamic relations; for example: $\boldsymbol{G = H - TS}$

Possible thermodynamic quantities that can be dervied:

Enthalpy $H = G + TS$; *Entropy:* $-S = \left(\frac{\partial G}{\partial T}\right)_{P,y}$; *Specific heat capacity:* $C_p = -T\left(\frac{\partial^2 G}{\partial T^2}\right)_{P,y}$

- **Tools:**

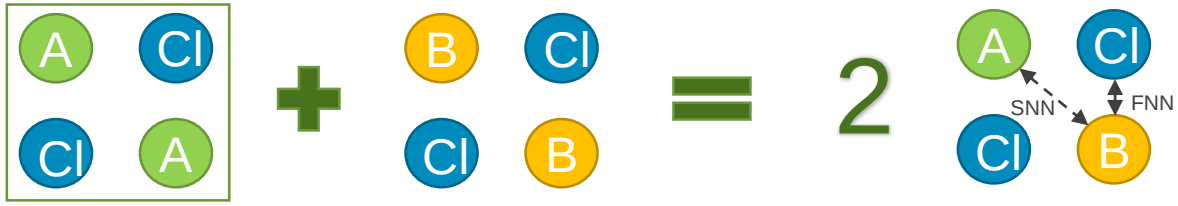
i. FACTSAGE
ii. Thermochimica
iii. Open Calphad

❖ Modified quasi-chemical model for Liquid systems:-

- Distribution of cations (A, B) and anions (Cl) on two sublattices;
- Considering First-Nearest neighbour (FNN) and Second-Nearest Neighbor (SNN) interactions in the quadruplet;

Gibbs energy for the system: $$G = n_A G_A^0 + n_B G_B^0 - T\Delta S^{cfg} + \Delta g_{AB/XX}$$

- Exchange reactions between the SNN pairs (A-Cl-A) and (B-Cl-B) :-



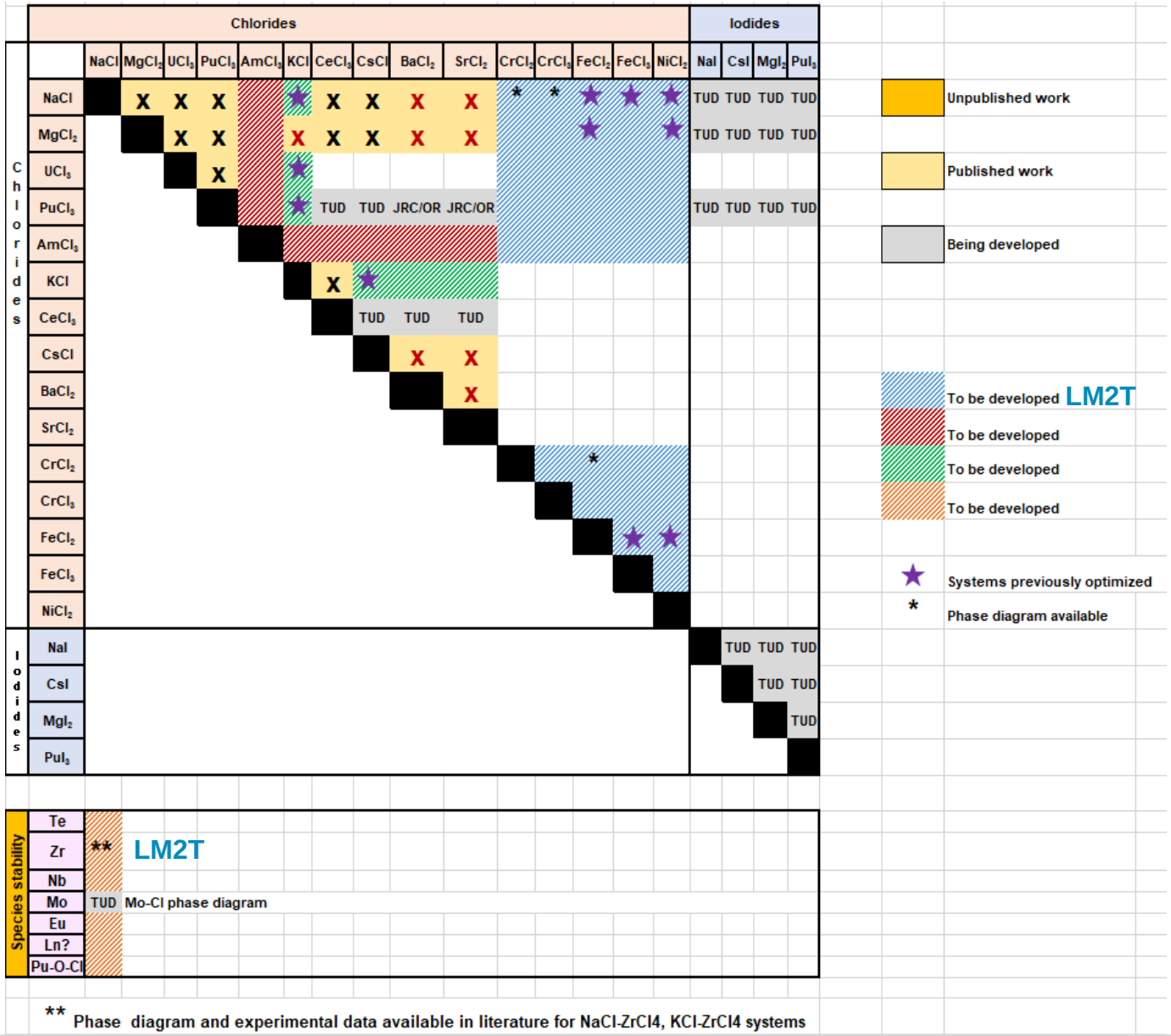
Basic unit: quadruplet

$$(\mathbf{A-Cl-A}) + (\mathbf{B-Cl-B}) = \mathbf{2}\,(\mathbf{A-Cl-B}) \quad \Delta g_{\mathbf{AB/ClCl}}^{\mathbf{exchange}}$$ *(excess Gibbs free energy associated with the SNN exchange of pairs)*

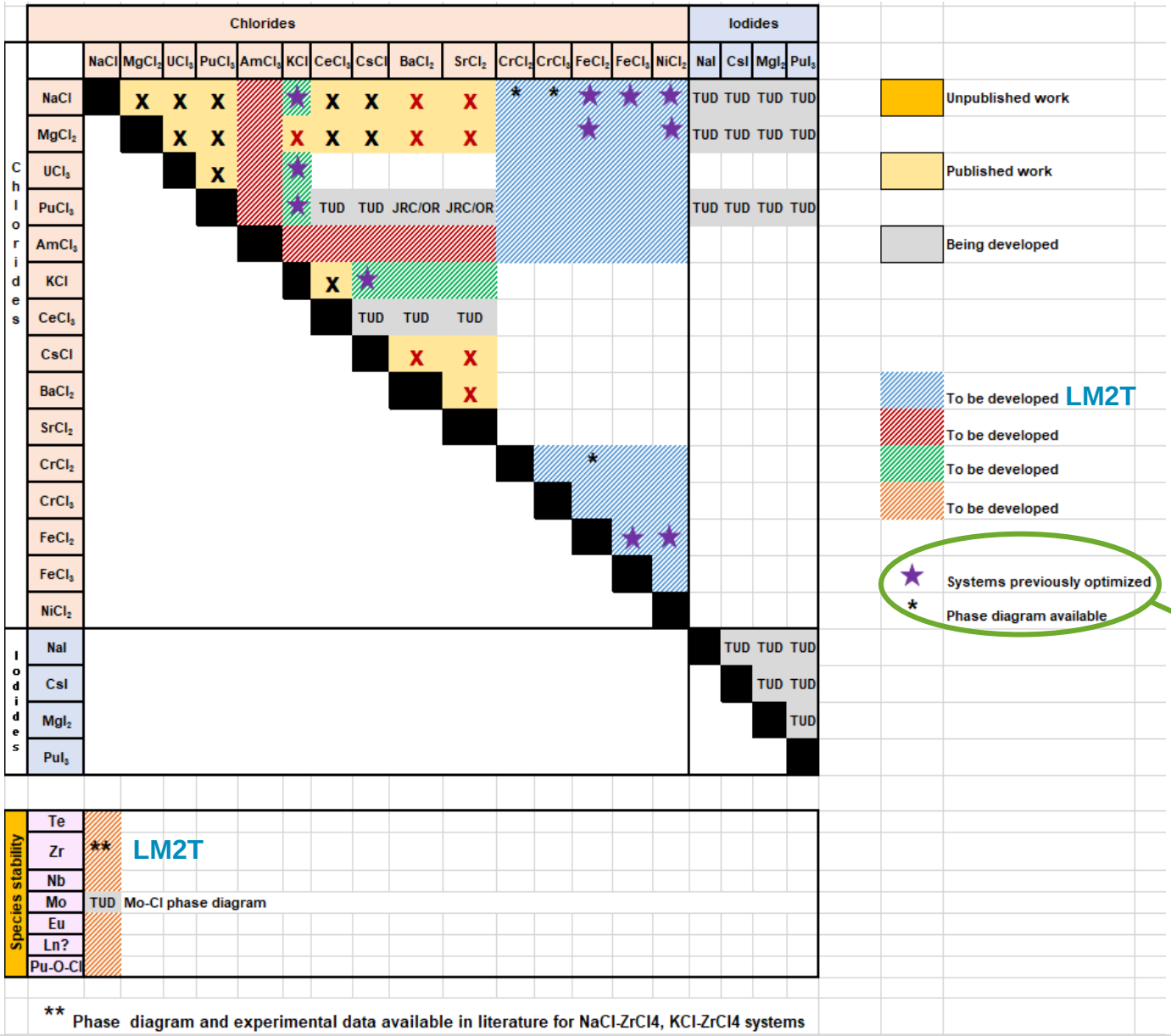
- $\Delta g_{AB/ClCl}^{exchange}$: *model parameter, to be optimized based on the experimental data*
- $\Delta g_{AB/ClCl}^{exchange} < 0$: reaction shifts in right direction to favor the formation of (A-Cl-B) pairs

❖ Utilisation of CALPHAD models in MSR multiphysics codes:-

- Phase diagrams: *to understand and predict material composition (in terms of phases present: solid, liquid and gas) and the amount of species present in the complex multicomponent systems that evolve in the salt during operation*
- Material performance: *changes in temperature and material composition are useful to understand driving forces and stablitiy of phases and species during thermochemical processes (eg: corrosion)*



- **Collaborative project: JRC (Karlsruhe), CEA, ORANO, TU Delft :** Database development for **chloride** and **iodide** systems
  - Fuel system with $PuCl_3$ ($AmCl_3$): JRC + ORANO
  - Fission product systems: TU Delft + ORANO + CEA
  - Corrosion systems: CEA + TU Delft
- **Fuel choice:** $NaCl - MgCl_2 - PuCl_3 - AmCl_3$



❖ What we need?

➢ Experimental data for $NaCl - MgCl_2 - AmCl_3$

i. Influence of Am on redox and corrosion chemistry

ii. Interaction of fuel with chlorides of corrosion elements Fe(II, III), Cr(II, III) and Ni

➢ Thermodynamic models on the interaction of molten salt with fission products and structural material

i. $ZrCl_4$ vapours

ii. Nb, Te, Mo, etc

❖ **What we have:** Existence of experimental data (and phase diagrams) and thermodynamic models in literature for many systems (marked ★)

What's missing: Thermodynamic models for interactions of molten salt with the corrosion element Cr (II,III)

❖ $NaCl - CrCl_2$ system

- no thermodynamic model exists at present;
- phase diagram available in literature [1]

- Single intermediate solid compound found $Na_3CrCl_5(s)$ that melts incongruently at $T = 458°C\ (731.15\ K)$
- Eutectic formation at 46.3 mole % of $CrCl_2$ that melts at $T = 437°C\ (710{,}15\ K)$
- Experimental melting point of pure $CrCl_2$ reported at $T = 820°C\ (1088\ K)$

- Thermodynamic data:

i. pure compounds: obtained from Factsage Database (FactPS) and [2];

ii. Intermediate solid: obtained from the FactSage Mixer tool.

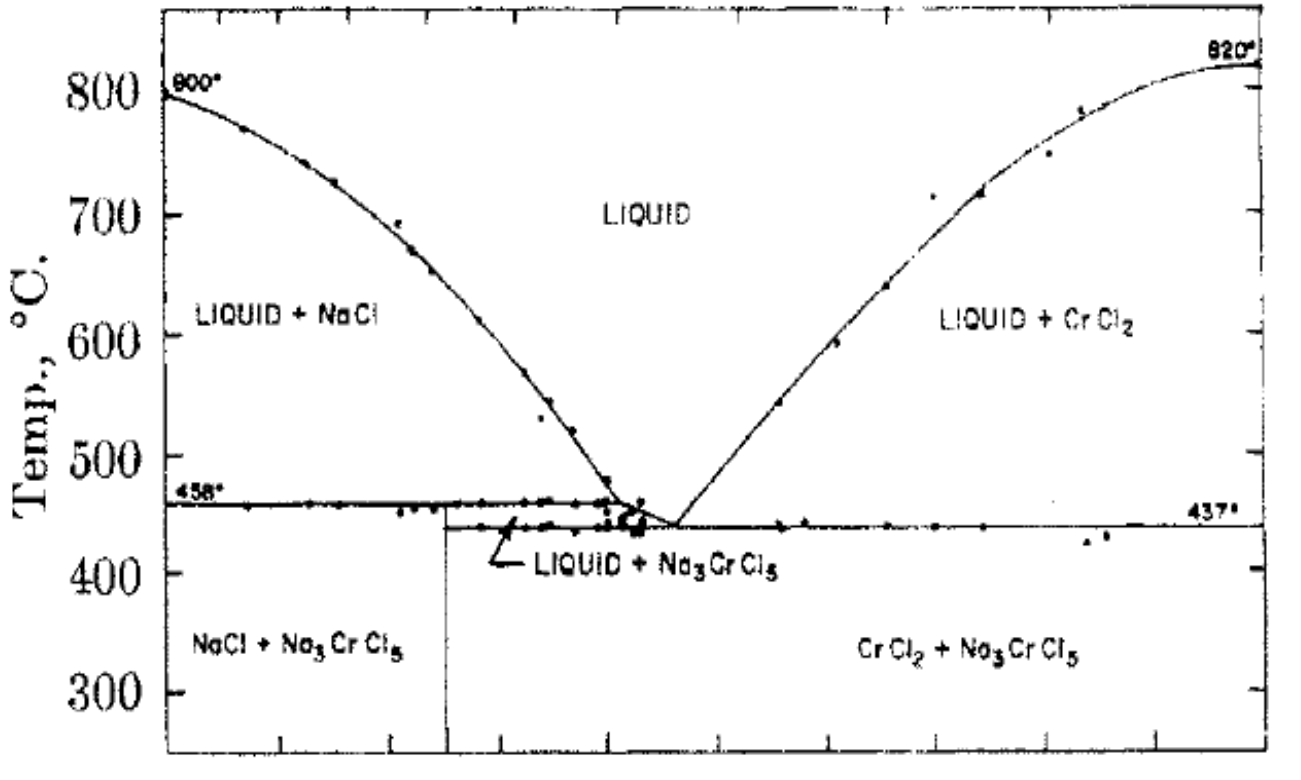


Fig. 2.—$CrCl_2$–NaCl phase diagram.

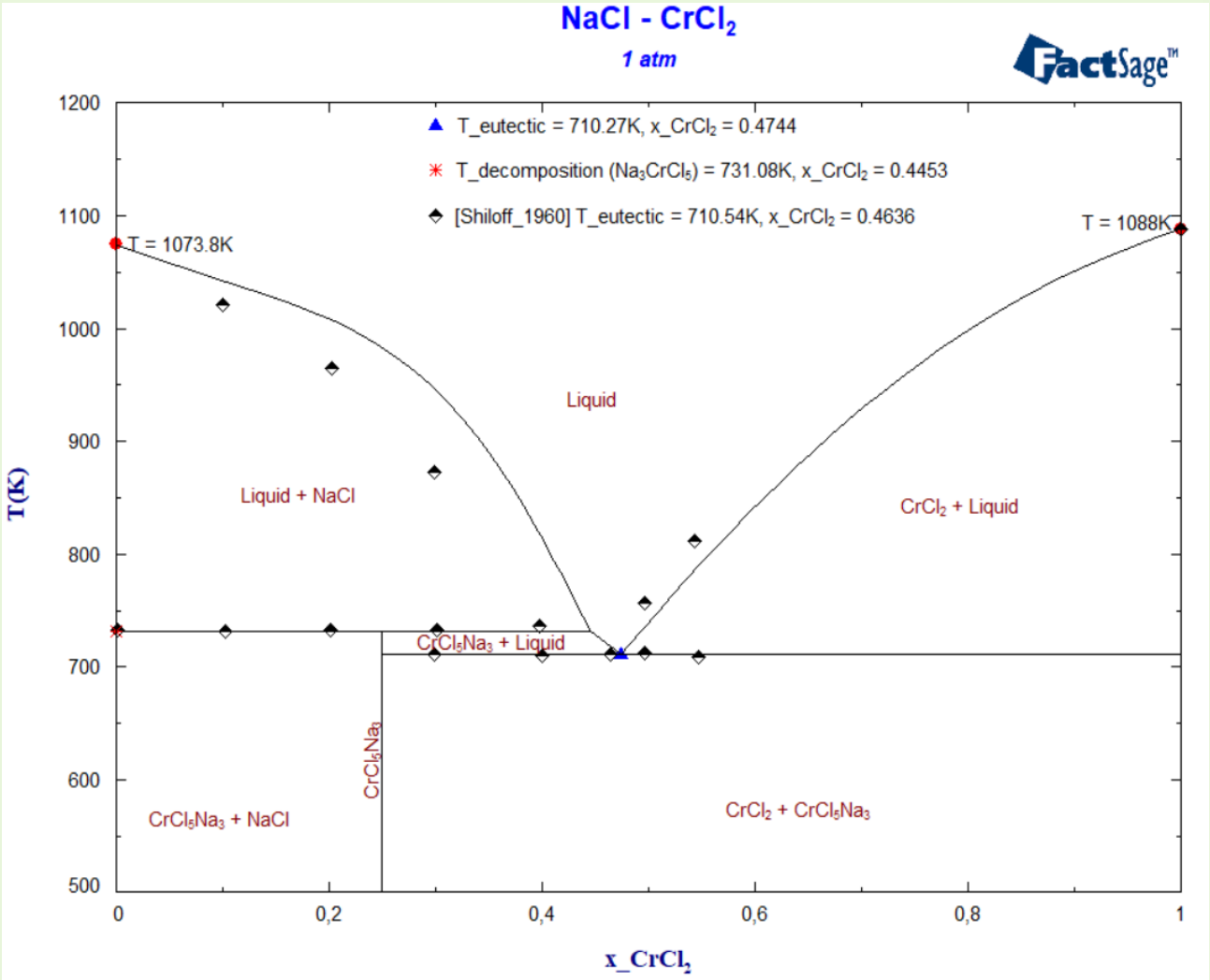
$NaCl - CrCl_2$ system:

- Model for the liquid system: MQM
- Optimization of thermodynamic data for $Na_3CrCl_5(s)$: Enthalpy of formation, Entropy and the Cp functions

Experimental Eutectic	Calculated Eutectic
$T = 710.0\ K$	$T = 710.27\ K$
$x_{CrCl_2} = 0.4630$	$x_{CrCl_2} = 0.4744$

- Need more **thermodynamic** data on the system for the improvement of the thermodynamic model:

i. Thermodynamic data from ab-initio calculations: *(ongoing work on the improvement of the assessment with new estimated data)*
ii. Enthalpy data related to the mixing of $NaCl - CrCl_2$ liquid.
iii. Experimental activities required for confirming the existance of the intermediate solid compound and for obtaining correct thermodynamic data *(planned at TU Delft under the framework of project MIMOSA)*



Calculated phase diagram for $NaCl - CrCl_2$ system

❖ $NaCl - CrCl_3$ system

- no thermodynamic model exists at present;
- phase diagram (partial) available in literature [3]

- Single intermediate solid compound reported $Na_3CrCl_6(s)$:
  i. Undergoes solid state transformation at 590°C (863,15 K);
  ii. melts congruently at $T = 620°C\ (893{,}15\ K)$.
- Observed steep rise in the liquidus of the system for composition $x_{CrCl_3} > 0{,}32$

- Thermodynamic data:

i. pure compounds: obtained from Factsage Database (FactPS) and [2]; ate

ii. Intermediate solid: thermodynamic functions estimated with the help of ab-initio calculations.

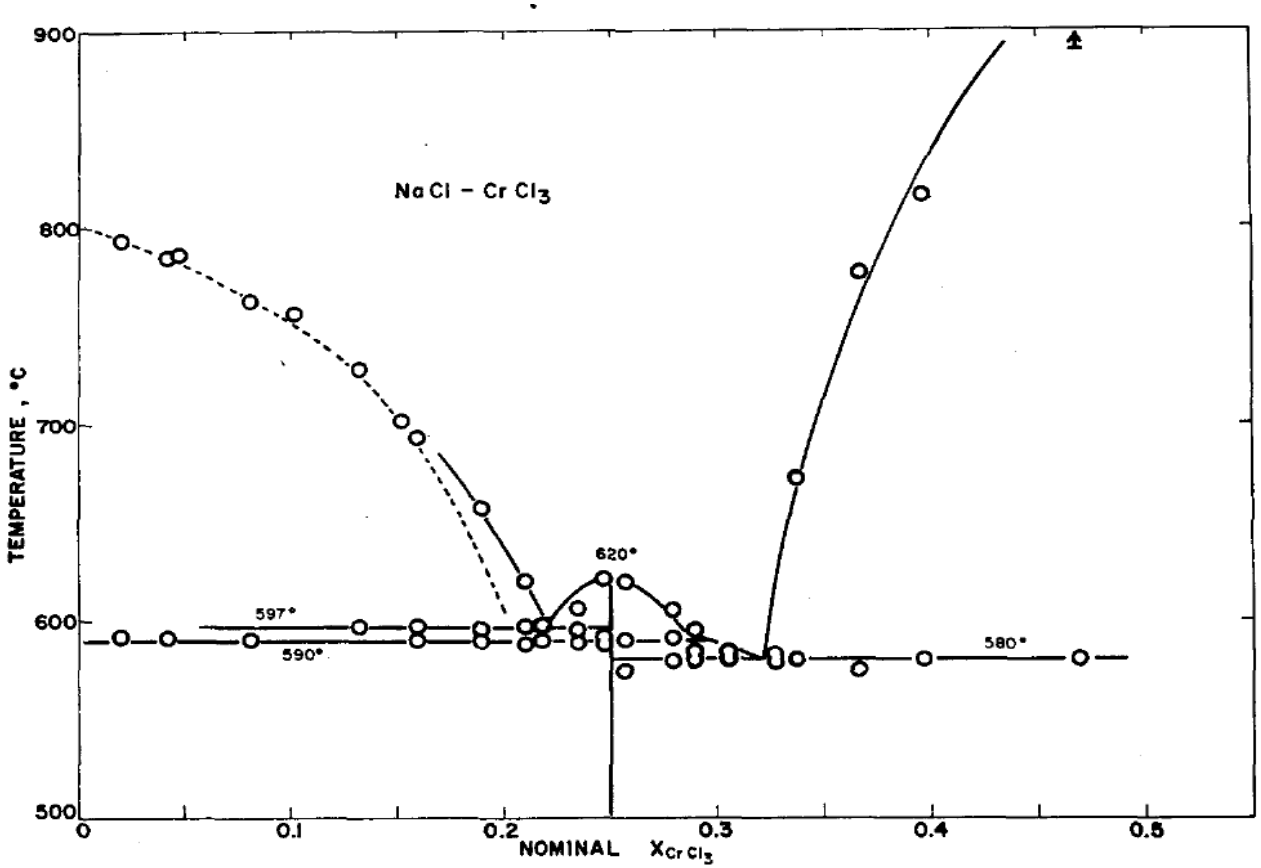


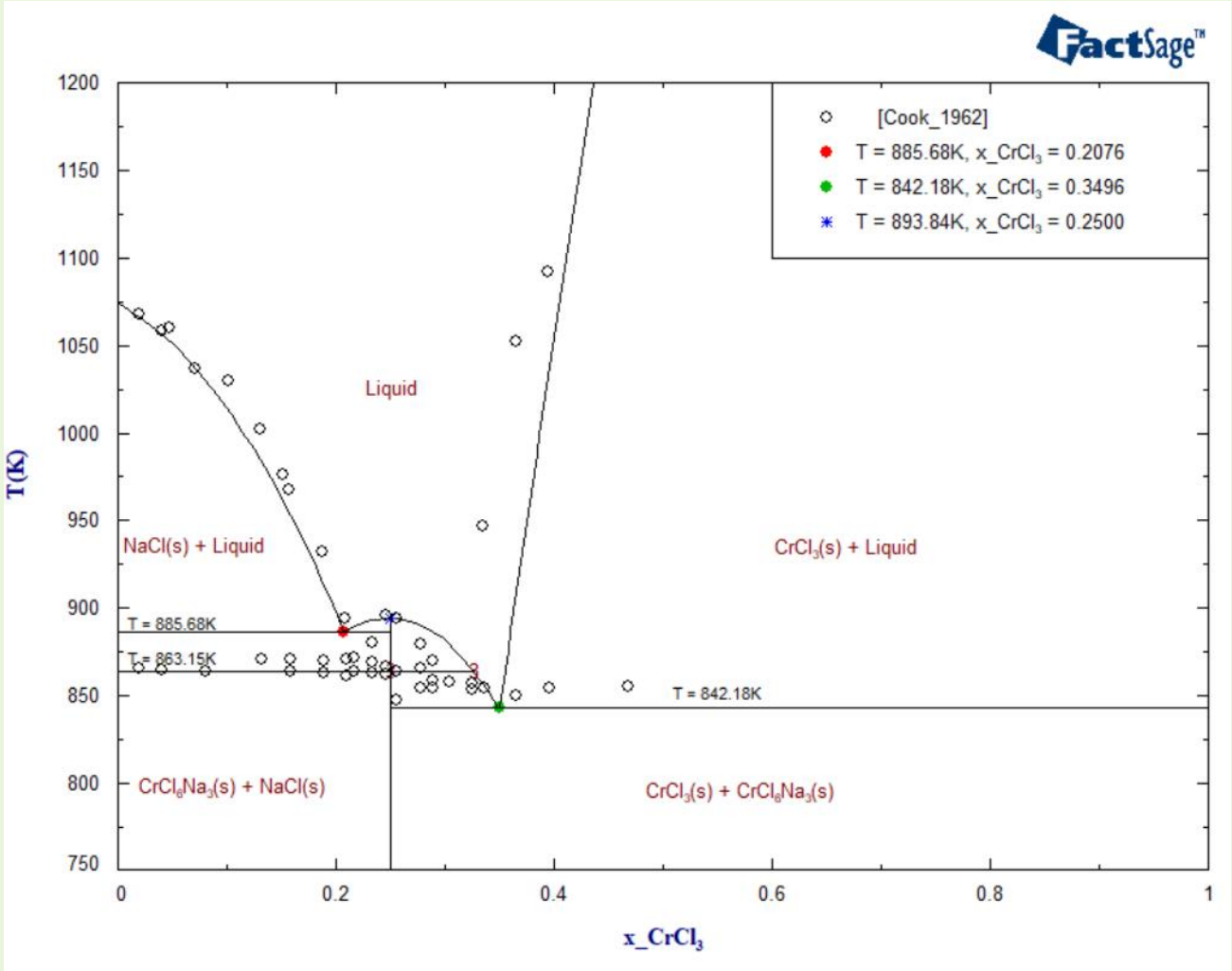
FIG. 1.—Partial solid–liquid phase diagram of the system, NaCl–$CrCl_3$.
– – – – Calculated liquidus if Cr(III) as $CrCl_6^{3-}$.

$NaCl - CrCl_3$ system:

- Model for the liquid system: MQM
- Optimization of thermodynamic data for $Na_3CrCl_6(s)$: Enthalpy of formation, Entropy, Cp functions
- Accounting for the solid-state transition of the intermediate solid (enthaply of transition)

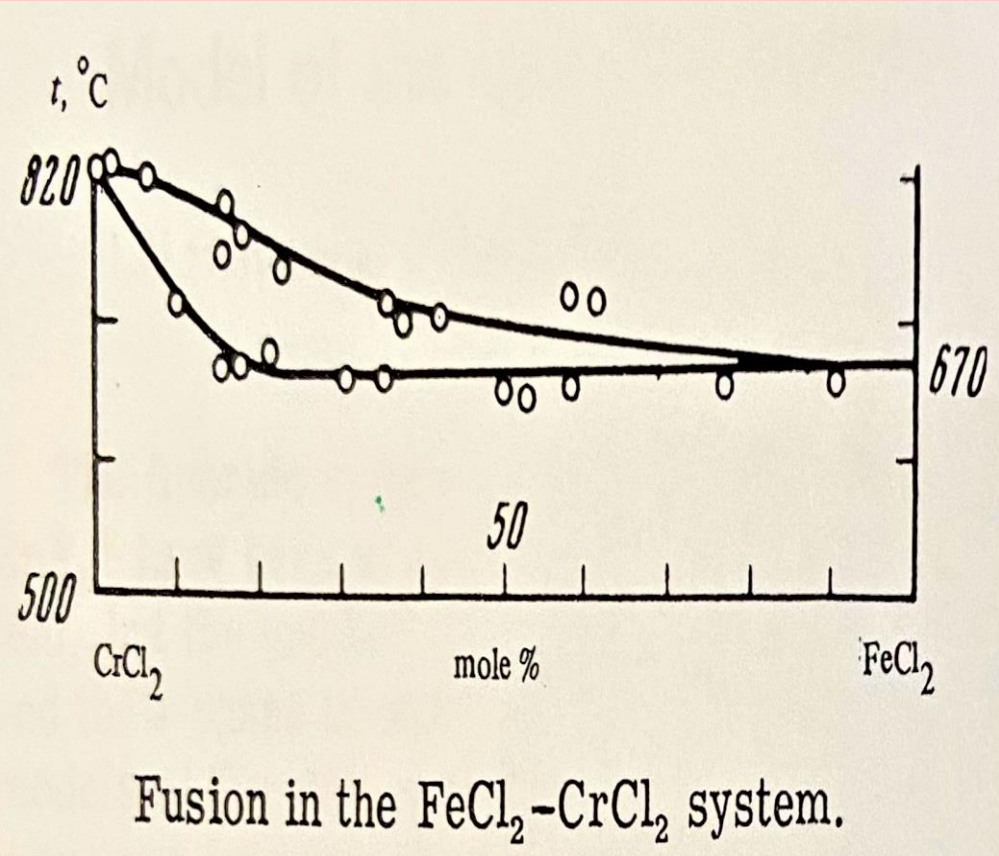
Experimental Eutectic	Calculated Eutectic
$T = 870\ K$ $x_{CrCl_3} \approx 0.225$	$T = 885.68\ K$ $x_{CrCl_3} = 0.2076$
$T = 853\ K$ $x_{CrCl_3} \approx 0.325$	$T = 842.18$ $x_{CrCl_3} = 0.3496$

- Calculated T_{fusion} for $Na_3CrCl_6(s) = 893.84$ K
- Better optimization of the system and experimental thermodynamic data on the system is required for the improvement of the thermodynamic model.



Calculated phase diagram for $NaCl - CrCl_2$ system

Corrosion studies: $FeCl_2 - CrCl_2$ system *[4]*



Fusion in the $FeCl_2$–$CrCl_2$ system.

[4] A.A. Soloshenko and Ya.E. Vil'nyanskii; Russian Journal of Inorganic Chemistry, 14(7), 1969

- No thermodynamic models available for the system $FeCl_2 - CrCl_2$
- Experimentally measured phase diagram available [4].
- System is expected to have the presence of a continuous solid solution (due to similar ionic radii of Fe(+2) and Cr(+2) ions.
- However, the accuracy of the thermodynamic model depends on their ability to confirm the experimental results!

❖ What is missing?

- **Data on Fission products:** *JRC database under constantly updates with the help of collaborative partners; to include certain thermodynamic models on systems including the fission products*
- **Interactions between the fuel (Pu, Am) and corrosion (Fe, Ni, Cr) elements:** *thermodynamic models for depicting the influence of Americium (Am) on the redox and corrosion chemistry are required. The current state of literature review reports a complete absence of experimental thermodynamic data/ phase diagrams for the systems*
  - $AmCl_3 - NaCl/MgCl_2$
  - $AmCl_3 - FeCl_2 - FeCl_3 - NiCl_2 - CrCl_2 - CrCl_3$
  - $PuCl_3 / FeCl_2,\ NiCl_2, CrCl_2, CrCl_3$
  - $PuCl_3 - AmCl_3$
  - $MgCl_2 - FeCl_3$

❑ Ongoing work:

- Thermodynamic assessments for the systems (to be added to the JRC database):
  i. $NaCl - CrCl_2$
  ii. $NaCl - CrCl_3$
  iii. $FeCl_2 - CrCl_2$
  iv. $NaCl - ZrCl_4$

  } *Assessments completed/in progress, to be verified with experimental results*

- Implementation of the complete Modified Quasi-chemical Model in OpenCalphad (OC) (carried out by M. Bo SUNDMAN)
  - Inital tests on the model to be carried out on simple pseudo-binary systems
- Utilization of the database in the CEA code “MOSARELA” to perform thermodynamic calculations for molten salt (ongoing work at CEA IRESNE/DER/SPRC/LE2C).

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Thank you for your attention