Thermodynamic Modelling of the NaCl-$ZnCl_2$-$MgCl_2$ System and Its Subsystems

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Introduction

- **Molten salts have been widely used as thermal energy storage materials for the concentrated solar power (CSP) systems because they have many advantages, such as high heat capacity, low melting point, high thermal stability and low cost. Among the studied molten slats, nitrate mixtures, $NaNO_3$/KNO_3 (Solar salt) and $NaNO_3$/KNO_3/$NaNO_2$ (Hitec salt) attracts the most attention. Compared to nitrate, the multicomponent chlorides, especially $ZnCl_2$-containing eutectic mixtures show higher operating temperatures and low costs which make them more suitable as thermal energy storage materials for CSP.**

- **Phase diagram is a critical index in the screening of the molten salt-based heat storage or transport materials which with higher fusion enthalpies and lower melting points. This work addresses on the thermodynamic model for phase diagram prediction of NaCl-$ZnCl_2$-$MgCl_2$ system and its subsystems**

Methods

- **Pure components**

For the NaCl-$ZnCl_2$-$MgCl_2$ system, Gibbs energies of pure phases were available in literatures and the temperature dependence of the Gibbs energy are described by

$$^{0}G_i^{\varphi} = G_i^{\varphi}(T) - H^{SER} = a + bT + cT\ln(T) + dT^2 + eT^3 + fT^{-1}$$

where 298.15 K is taken as reference state, a, b, c, d, e and f are coefficients. The Gibbs energies of NaCl, $ZnCl_2$ and $MgCl_2$ are listed in Table 1.

Table 1. Thermodynamic data for NaCl, $ZnCl_2$ and $MgCl_2$.

Phase		Temperature(K)	Gibbs energy(J/mol)
NaCl	S	298.15-1074	428494.00+306.56·*T*-56.26·*T*·ln(*T*)
	L	298.15-2000	410185.98+366.41·*T*-67.29·*T*·ln(*T*)
$ZnCl_2$	S	298.15-590	-437761.22+395.39·*T*-75.59·*T*·ln(*T*)
	L	298.15-1000	-425611.20+320.48·*T*-66.02·*T*·ln(*T*)-0.011·T^2
$MgCl_2$	S	298.15-987	-663158.38+380.28·*T*-69.35·*T*·ln(*T*)-0.0085·T^2
	L	298.15-1708	-668025.64+381.35·T-65.52·*T*·ln(*T*)-0.035·T^2

- **Thermodynamic modelling for liquid phase**

Substitutional solution model (SSM) was used to calculate the Gibbs energy, the Gibbs energy expression contains three parts for the liquid phase model, as shown in the following Eqs. (2)-(4).

$$G^{\varphi} = {}^{ref}G^{\varphi} + {}^{id}G^{\varphi} + {}^{ex}G^{\varphi}$$

$${}^{ref}G^{\varphi} = \sum_i x_i\, {}^{0}G_i^{\varphi}$$

$${}^{id}G^{\varphi} = RT\sum_i x_i \ln(x_i)$$

where $^{ref}G^{\varphi}$ is the contribution from pure components of the phase to the Gibbs energy, $^{id}G^{\varphi}$ is the ideal mixing contribution and $^{ex}G^{\varphi}$ is the contribution due to non-ideal interactions between pure components, also known as the Gibbs excess energy of mixing.

The Redlich-Kister form is commonly modelled to represent the excess Gibbs energy of mixing in the CALPHAD method, as written Eq. (5):

$${}^{ex}G^{\varphi} = x_i x_j \sum_v {}^{v}L_{i,j}^{\varphi}(x_i - x_j)$$

Results

- **Thermodynamic model parameters were established based on critical thermodynamic evaluation and optimization for the NaCl-$ZnCl_2$, $ZnCl_2$-$MgCl_2$ and NaCl-$MgCl_2$ binary systems.**

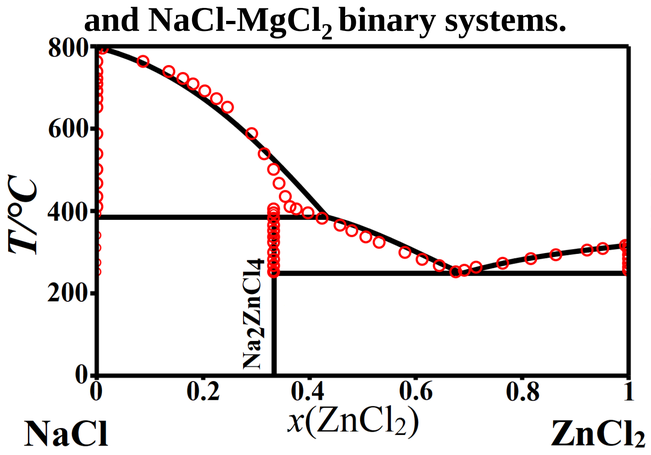

Fig.1. Calculated NaCl-$ZnCl_2$ phase diagram

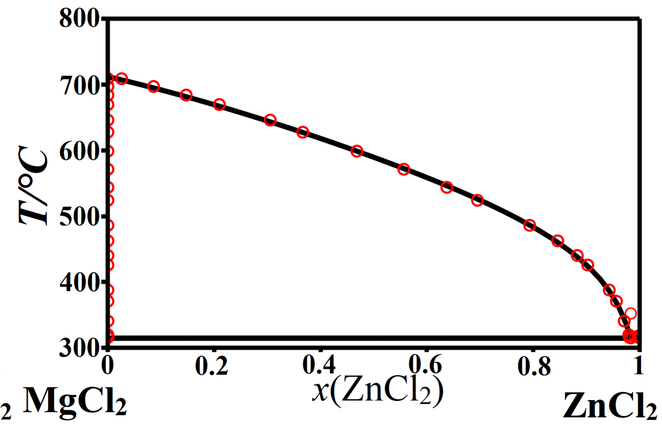

Fig.2. Calculated $ZnCl_2$-$MgCl_2$ phase diagram

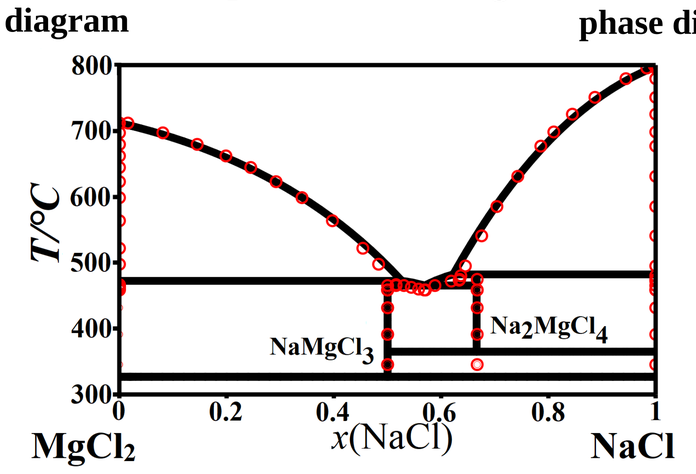

Fig.3. Calculated NaCl-$MgCl_2$ phase diagram

Table 2. Thermodynamic parameters for the NaCl-$ZnCl_2$-$MgCl_2$ subsystems

Subsystems	Phase type	Phase name	Thermodynamic parameters(J/mol)
NaCl-$ZnCl_2$	Solution	Liquid	$^{0}L_{NaCl,ZnCl2}$=-14941.80-19.04·*T*
			$^{1}L_{NaCl,ZnCl2}$=-18385.10+14.32·*T*
	Stoichiometric	Na_2ZnCl_4	$^{0}G_{Na2ZnCl4}$=$^{0}G_{NaCl}$+$^{0}G_{ZnCl2}$+4586.81-13.78·*T*
ZnCl-$MgCl_2$	Solution	Liquid	$^{0}L_{ZnCl2,MgCl2}$=13699.70-17.37·*T*
NaCl-$MgCl_2$	Solution	Liquid	$^{0}L_{NaCl,MgCl2}$=-35605.40+11.86·*T*
			$^{1}L_{NaCl,MgCl2}$=-17920.90+14.17·*T*
	Stoichiometric	$NaMgCl_3$	$^{0}G_{NaMgCl3}$=$^{0}G_{NaCl}$+$^{0}G_{MgCl2}$+7054.27-11.64·*T*
	Stoichiometric	Na_2MgCl_4	$^{0}G_{Na2MgCl4}$=$^{0}G_{NaCl}$+$^{0}G_{MgCl2}$+7707.41-12.50·*T*

- **The database for the phase-equilibria and thermodynamic properties for the NaCl-$ZnCl_2$-$MgCl_2$ ternary system is obtained by performing a serial thermodynamic predictions using the Kohler-Toop extrapolation method.**

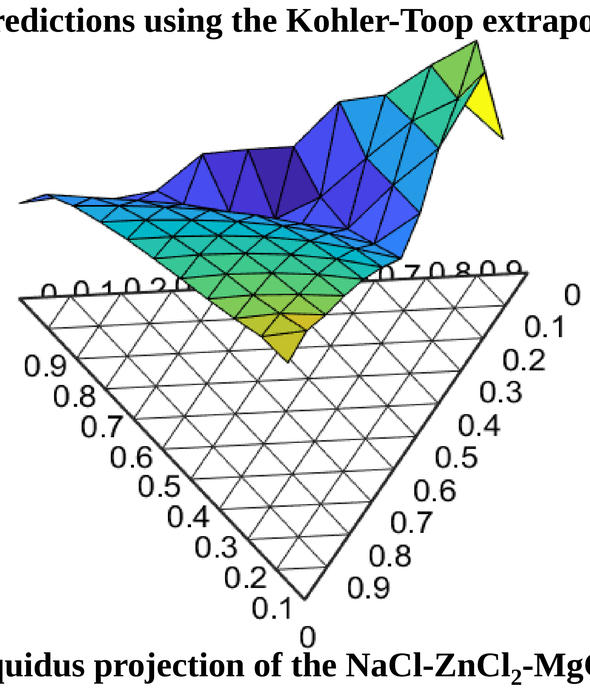

Fig 4. Predicted liquidus projection of the NaCl-$ZnCl_2$-$MgCl_2$ ternary system.

Acknowledge

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Reference

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