



Thermodynamic evaluation and optimization of the (NaCl + KCl + MgCl₂ + CaCl₂ + ZnCl₂) system

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ABSTRACT

A complete critical evaluation of all available phase diagram and thermodynamic data has been performed for all condensed phases and relevant gaseous species of the (NaCl + KCl + MgCl₂ + CaCl₂ + ZnCl₂) system, and optimized model parameters have been found. The (NaCl + KCl + MgCl₂ + CaCl₂) subsystem has been critically evaluated in a previous article. The model parameters obtained for the binary and ternary subsystems can be used to predict thermodynamic properties and phase equilibria for the multi-component system. The Modified Quasichemical Model for short-range ordering was used for the molten salt phase.

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1. Introduction

ZnCl₂-containing molten salts are of great industrial interest. For instance, a new method to produce solar grade silicon metal from reduction of silicon tetrachloride by liquid zinc metal was proposed recently [1,2]. The production of solar grade Si according to the reaction $\text{SiCl}_4(\text{g}) + 2\text{Zn}(\text{l}) \rightarrow \text{Si}_{(\text{solar grade})} + 2\text{ZnCl}_2(\text{l})$ and the production of Zn by electrolysis of ZnCl₂ according to the reaction $\text{ZnCl}_2(\text{l}) \rightarrow \text{Zn}(\text{l}) + \text{Cl}_2(\text{g})$ take place in a common, combined reactor and electrolysis cell using a ZnCl₂-containing molten salt as electrolyte. The ZnCl₂ produced during the reduction of SiCl₄ dissolves in the molten salt and can regenerate the Zn metal through electrolysis. The chlorine evolved during the electrolysis of ZnCl₂ can be used to produce SiCl₄ according to the reaction $\text{Si}_{(\text{metallurgical grade})} + 2\text{Cl}_2(\text{g}) \rightarrow \text{SiCl}_4(\text{g})$. The system (NaCl + KCl + MgCl₂ + CaCl₂ + ZnCl₂), which could be used as an electrolyte in the process described previously, is considered in the present article. All available thermodynamic and phase equilibrium data for this system were critically evaluated to obtain optimized parameters of models for all condensed phases and relevant gaseous species. The optimization of the (NaCl + KCl + MgCl₂ + CaCl₂) subsystem has been presented in a previous article [3].

The liquid solution was modelled using the Modified Quasichemical Model [4,5] which takes into account short-range order-

ing between nearest-neighbours on a lattice or sublattice. This model has been used successfully to model systems such as (LiCl + NaCl + KCl + RbCl + CsCl + MgCl₂ + CaCl₂ + SrCl₂ + BaCl₂) [3,6,7] and (NaCl + KCl + MgCl₂ + CaCl₂ + MnCl₂ + FeCl₂ + CoCl₂ + NiCl₂) [8,9]. Short-range ordering is treated by considering the relative numbers of second-nearest-neighbour cation–cation pairs of nearest-neighbour pairs (A–B) for species mixing on one lattice. The parameters of the model are the Gibbs free energy changes $\Delta g_{\text{AB/Cl}}$ for the following pair exchange reactions:

$$(\text{A–Cl–A})_{\text{pair}} + (\text{B–Cl–B})_{\text{pair}} = 2(\text{A–Cl–B})_{\text{pair}} \quad \Delta g_{\text{AB/Cl}}, \quad (1)$$

where A and B are two different cations. As $\Delta g_{\text{AB/Cl}}$ becomes progressively more negative, reaction (1) is shifted to the right, (A–Cl–B) pairs predominate, and the solution becomes progressively more ordered. In [4,5], the model was developed in terms of nearest-neighbour pairs (A–B) for species mixing on one lattice. In the present case, since the anionic sublattice is occupied only by Cl[−] ions, the model can be used directly to treat cation–cation pairs on the cationic sublattice. The parameter $\Delta g_{\text{AB/Cl}}$ is the parameter Δg_{AB} (or Δg_{mm}) of [4] (or [5]). When $\Delta g_{\text{AB/Cl}}$ is small, the degree of short-range ordering is small, and the solution approximates a random (Bragg–Williams) mixture of cations on the cationic sublattice. This is the case for the (NaCl + KCl) and (MgCl₂ + CaCl₂) binary systems. On the other hand, molten (alkali chloride + MCl₂) solutions where M is a divalent cation such as Mg²⁺, Ca²⁺, Mn²⁺, Fe²⁺, Co²⁺, Ni²⁺ or Zn²⁺ are well known for exhibiting extensive short-range ordering. The existence of short-range ordering in these solutions has previously been modelled by introducing MCl₄^{2−} complex

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anions [10–12]. For example, a fully-ordered liquid solution of the composition K_2ZnCl_4 would be treated as consisting of K^+ and $ZnCl_4^{2-}$ ions. The present model does not explicitly introduce complex anions. Instead, the ordering is described as a preponderance of K–Cl–Zn second-nearest-neighbours, with the ratio of the second-nearest-neighbour coordination numbers of Zn^{2+} and K^+ equal to 2.0. Hence, in a fully-ordered solution of the composition K_2ZnCl_4 , every Zn^{2+} ion is surrounded only by K^+ ions in its second coordination shell, just as in the complex ion model. Depending on how negative $\Delta g_{KZn/Cl}$ is, some (K–Cl–K) and (Zn–Cl–Zn) pairs can be present in the liquid at the K_2ZnCl_4 composition. The complex ion models [10–12] cannot evaluate this without introducing new complex anions or without postulating two types of Zn ions (Zn^{2+} and $ZnCl_4^{2-}$).

The present article, which describes the addition of $ZnCl_2$ to the previously developed [3] thermodynamic database for the (NaCl + KCl + $MgCl_2$ + $CaCl_2$) system, confirms that the Modified Quasichemical Model can satisfactorily be used to predict the properties of multicomponent molten salt solutions solely from the subsystem model parameters even when appreciable short-range ordering is present.

2. Thermodynamic data for the pure compounds

All thermodynamic data ($H_{298.15K}^\circ$, $S_{298.15K}^\circ$ and C_p) for the condensed pure compounds of the (NaCl + KCl + $MgCl_2$ + $CaCl_2$) subsystem have been given previously [3]. All thermodynamic data for the condensed pure compounds of the (NaCl + KCl + $MgCl_2$ + $CaCl_2$ + $ZnCl_2$) system not already present in the (NaCl + KCl + $MgCl_2$ + $CaCl_2$) subsystem were optimized in the present study and are given in table 1. The $ZnCl_2$, Zn_2Cl_4 , $NaZnCl_3$, and $KZnCl_3$ gaseous species are also included in table 1.

There are large discrepancies in the reported properties of fusion of pure $ZnCl_2$. The thermodynamic properties selected in this work for $ZnCl_2$ (solid, liquid, gas) are described in detail below. The C_p expressions chosen for the solid, liquid, and gas phases were directly taken from the literature. Therefore, only the $H_{298.15K}^\circ$ and $S_{298.15K}^\circ$ values for the three phases were adjusted with the following constraints:

- respect as closely as possible the error limits reported in the literature for the $H_{298.15K}^\circ$ and $S_{298.15K}^\circ$ values for the solid and gas phases;
- reproduce the selected values of the temperature of fusion and enthalpy of fusion (these choices are discussed below);

- reproduce the experimental vapour pressure of pure liquid $ZnCl_2$ as a function of temperature along with the reported boiling point.

Finally, only our selected $S_{298.15K}^\circ$ values for the solid and gas phases are somewhat outside the reported error limits. The thermodynamic properties selected in this work for $ZnCl_2$ (solid, liquid, gas) are believed to correspond to a good compromise.

2.1. Pure solid $ZnCl_2$

Our optimized $H_{298.15K}^\circ$ value of $-415,649 \text{ J} \cdot \text{mol}^{-1}$ agrees with the value of $-(415,100 \pm 800) \text{ J} \cdot \text{mol}^{-1}$ recommended by Kubaschewski *et al.* [13]. Our optimized $S_{298.15K}^\circ$ value of $106.6 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ is lower than the value of $(111.5 \pm 0.4) \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ recommended by the same authors. Finally, the C_p expression chosen for $ZnCl_2(s)$ over the temperature range 298.15 K to 591 K is from Barin [15].

2.2. Pure liquid $ZnCl_2$

The selected temperature of fusion and enthalpy of fusion are 591 K and $19,565 \text{ J} \cdot \text{mol}^{-1}$, respectively. As emphasized by Perry *et al.* [16], variations in the melting temperature in the range 523 K to 638 K are reported in the literature. These variations are due to the possible presence of impurities, the extent of dehydration, the tendency of liquid $ZnCl_2$ to supercool [16] as well as the relatively high viscosity of pure liquid $ZnCl_2$ (688 mPa · s at $T = 638 \text{ K}$ according to [17]). A temperature of fusion of 591 K was finally selected, in agreement with the recommendations of Kubaschewski *et al.* [13] and Binnewies and Milke [18]. The selected enthalpy of fusion of $19,565 \text{ J} \cdot \text{mol}^{-1}$ is the average of the values of $16,100 \text{ J} \cdot \text{mol}^{-1}$ and $23,030 \text{ J} \cdot \text{mol}^{-1}$ reported by Kubaschewski *et al.* [13] and Belashchenko and Ostrovskii [19]. The enthalpies of fusion of $10,251 \text{ J} \cdot \text{mol}^{-1}$ and $10,300 \text{ J} \cdot \text{mol}^{-1}$ recommended by Barin [15] and Binnewies and Milke [18] must be discarded since they correspond to an unrealistic limiting slope of the $ZnCl_2$ liquidus in the (NaCl + $ZnCl_2$) and (KCl + $ZnCl_2$) phase diagrams as shown in figures 1 and 2. The limiting liquidus slope equation, which assumes no solid solubility, is:

$$\left(\frac{dT}{dx_m^{liquidus}} \right) = \frac{RT_{fusion(m)}^2}{\Delta h_{fusion(m)}^\circ} \quad [at \ x_m = 1], \quad (2)$$

where $\Delta h_{fusion(m)}^\circ$ and $T_{fusion(m)}$ are respectively the enthalpy and temperature of fusion of the pure salt m .

TABLE 1
Thermodynamic properties of compounds optimized in the present study.

| | T Range (K) | $H_{298.15K}^\circ$ (J · mol ⁻¹) ^a | $S_{298.15K}^\circ$ (J · mol ⁻¹ · K ⁻¹) ^b | C_p (J · mol ⁻¹ · K ⁻¹) | |
|---|-------------|---|---|--|---|
| ZnCl ₂ | S | 298.15 to 591 | -415,649.0 | 106.5992 | 62.9410 + 0.0286650(T/K) |
| | L | 298.15 to 1005 | -396,210.7 | 139.3450 | 65.8350 + 0.0231290(T/K) |
| | G | 298.15 to 2000 | -263,200.0 | 280.7000 | 62.3201 - 481,617(T/K) ⁻² |
| Zn ₂ Cl ₄ | G | 298.15 to 2000 | -684,599.5 | 362.1408 | 133.0083 - 963,234(T/K) ⁻² |
| Na ₂ ZnCl ₄ | S | 298.15 to 591 | -1,241,069.2 | 276.9519 | 2C _p (NaCl) + C _p (ZnCl ₂) = 154.8216 + 0.0613002(T/K) |
| | S | 591 to 700 | | | 2C _p (NaCl) + C _p (ZnCl ₂) = 171.7627 + 0.0326352(T/K) |
| NaZnCl ₃ | G | 298.15 to 2000 | -619,393.4 | 386.6464 | 108.0769 - 694,748(T/K) ⁻² + 5,731,636(T/K) ⁻³ |
| | G | 2000 to 6000 | | | 107.9565 - 213,131(T/K) ⁻² + 5,731,636(T/K) ⁻³ |
| K ₂ ZnCl ₄ | S | 298.15 to 591 | -1,302,071.4 | 317.2322 | 2C _p (KCl) + C _p (ZnCl ₂) = 142.9726 + 0.0796010(T/K) + 729,690(T/K) ⁻² |
| | S | 591 to 750 | | | 2C _p (KCl) + C _p (ZnCl ₂) = 159.9136 + 0.0509360(T/K) + 729,690(T/K) ⁻² |
| K ₂ Zn ₄ Cl ₁₃ | S | 298.15 to 550 | -3,945,410.8 | 846.9909 | 5C _p (KCl) + 4C _p (ZnCl ₂) = 451.8429 + 0.2420000(T/K) + 1,824,224(T/K) ⁻² |
| KZn ₂ Cl ₅ | S | 298.15 to 580 | -1,265,792.3 | 348.8516 | C _p (KCl) + 2C _p (ZnCl ₂) = 165.8978 + 0.0827980(T/K) + 364,845(T/K) ⁻² |
| | G | 298.15 to 2000 | -649,591.1 | 426.7767 | 108.0752 - 583,479(T/K) ⁻² |
| KZnCl ₃ | S | 298.15 to 2000 | | | 107.9548 - 101,862(T/K) ⁻² |
| | G | 2000 to 6000 | | | |

^a Enthalpy relative to the enthalpy of the elements in their stable standard states at $T = 298.15 \text{ K}$.

^b Absolute (third law) entropy.

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