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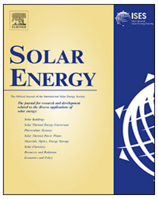

Short note

Thermodynamic modeling of the K-KCl and Mg-$MgCl_2$ binary systems using the CALPHAD method☆

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ABSTRACT

The Calculation of Phase Diagrams (CALPHAD) method uses models that reproduce and predict phase equilibria and thermochemical behavior. To date, the CALPHAD approach has been applied to the KCl-$MgCl_2$ psuedobinary only. The two-sublattice modified quasi chemical (MQM) model, already developed for the KCl-$MgCl_2$ melt and used extensively within the CALPHAD community to represent molten salts, is extended in this work to include excess K and Mg. Phase relations calculated using the MQM is compared to experimentally observed behavior for the K-KCl binary system. Gaps in the experimental data are identified and recommendations are given for better understanding the thermochemistry and phase equilibria.

1. Introduction

The KCl-$MgCl_2$ pseudobinary is the subject of research for use as a heat transfer and/or working fluid in next generation concentrating solar power plants (Liu et al., 2016). Some combination of KCl-$MgCl_2$, perhaps the eutectic composition, is also a candidate base molten salt for inclusion of fissile uranium bearing chlorides as a molten salt reactor fuel or alone as a secondary coolant (Le Brun, 2007). This brief note reports on CALPHAD modeling of KCl and MgCl melts with their respective dissolved metal. The aim is to lay the groundwork for a thermodynamic assessment of the integral K-Mg-Cl ternary as the K-KCl and Mg-$MgCl_2$ binaries are fundamental subsystems that must first be assessed and to define the gaps in the data that should be filled with experimental thermochemical and phase equilibria measurements.

2. Modeling K-KCl and Mg-$MgCl_2$ melts

The modified quasichemical model (MQM) has been used to represent the Gibbs energy of a significant number of molten ionic liquids (Chartrand and Pelton, 2000; Pelton et al., 2000; Chartrand and Pelton, 2001; Chartrand and Pelton, 2001; Pelton and Chartrand, 2001; Pelton et al., 2001). For the MQM, the nearest neighbor (NN) short-range-ordering (SRO) is accounted for with two sublattices, one for cations and one for anions. In extending MQM for the KCl-$MgCl_2$ system (Chartrand and Pelton, 2000) to include K dissolution in the KCl melt, negatively charged vacancies (Va^{1-}), or F-centers, are introduced. To be consistent with the base MQM, the K^{1+} and anion species retain a coordination (Z) of 6. The adjustable parameters well fit the phase equilibria data reported by (Bredig, 1963) without the need for introducing the exchange reaction energy for representing next nearest neighbor (NNN) short-range-ordering. The K and Cl have fixed oxidation states of 1+ and 1− respectively. The sublattice model can therefore be written as $(K^{1+})_1(Cl^{1-}, Va^{1-})_1$. As a result of the preceding, combined with neglecting the NNN SRO, the MQM for the K-KCl system reduces to a regular solution model, here after referred to as RKMP since convention is to represent the excess Gibbs energy (^{xs}G) with a Redlich-Kister-Maggianu Polynomial (RKMP) such as that in Eq. (1). The Z's are equal and constant, thus ^{xs}G for the RKMP is 3 times that that of the MQM (Bale et al., 2002). The Gibbs energy for the K-KCl liquid in RKMP form is given as Eq. (2):

$$^{xs}G = x_K x_{KCl}(60000-0.0372T^2) + x_K x_{KCl}(x_K-x_{KCl})(-24000 + 0.02007T^2) + x_K x_{KCl}(x_K-x_{KCl})^2 1500 \tag{1}$$

$$G^{K-KCL} = x_K G_K + x_{KCl} G_{KCl} + RT(x_K \ln x_K + x_{KCl} \ln x_{KCl}) +^{xs} G \tag{2}$$

where G_i and x_i are the Gibbs energy and mole fraction of species i respectively, R is the ideal gas constant and T is temperature. For extending the MQM for the KCl-$MgCl_2$ melt to model the Mg-$MgCl_2$

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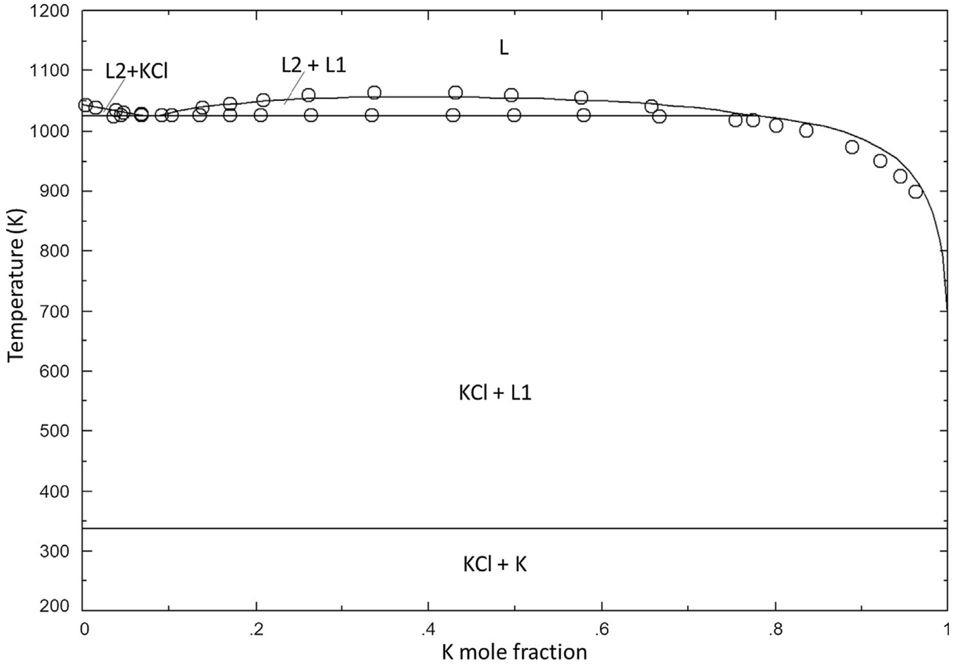

Fig. 1. Computed K-KCl phase diagram using the solution model for the melt developed in this work with the thermodynamic values from the FactSage 7.1 database (Bale et al., 2002) for pure components and stoichiometric compounds. Symbols are experimental points from (Bredig, 1963).

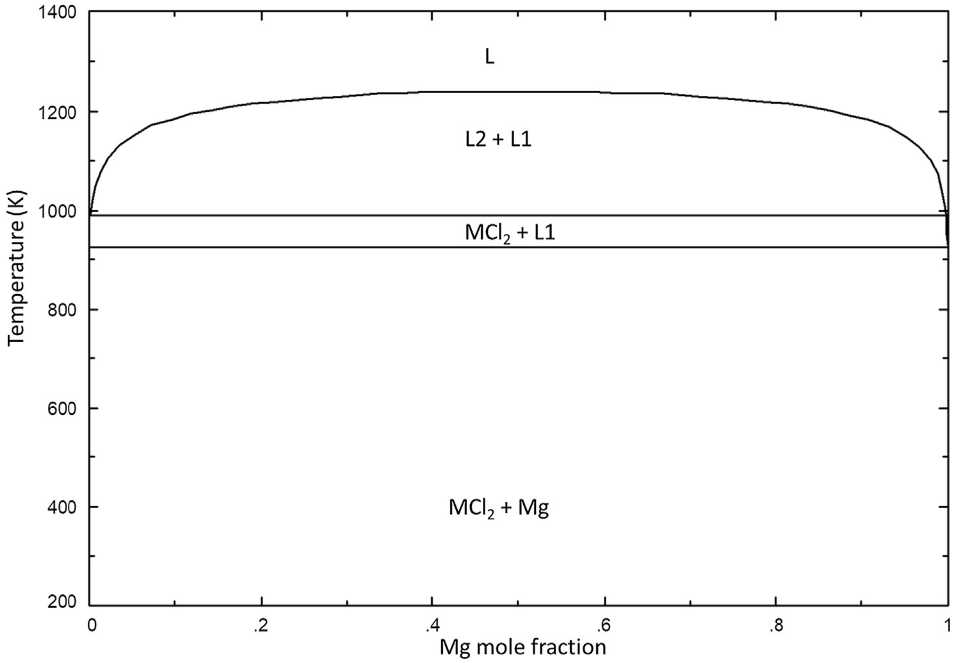

Fig. 2. Computed phase diagram for the Mg-MgCl$_2$ binary using the solution model for the liquid from this work along with the thermodynamic values from the FactSage 7.1 database (Bale et al., 2002) for pure components and stoichiometric compounds.

solution, the 2+ oxidation state for Mg results in an anion sublattice stoichiometry that is not unity but 2. As with K-KCl, next NNN short-range-ordering can and should be neglected due to a paucity of experimental data. The sublattice model is written as $(Mg^{2+})_1(Cl^{1-}, Va^{1-})_2$. The MQM for Mg-MgCl$_2$ simplifies to the compound energy formalism (CEF) (Hillert, 2001) since the ratio of the number of sites on the two sublattices does not vary (Bale et al., 2002). The Gibbs energy for the Mg-MgCl$_2$ melt is defined by Eq. (3). As with the RKMP for K-KCl, the ^{xs}G (the last term in Eq. (3) for the CEF representation is 3 times that of the MQM.

$$G^{Mg-MgCl_2} = x_{Mg}G_{Mg} + x_{MgCl_2}G_{MgCl_2} + 2RT\left(x_{Mg}\ln x_{Mg} + x_{MgCl_2}\ln x_{MgCl_2}\right) + x_{Mg}x_{MgCl_2}(338625-240T) \tag{3}$$

The Gibbs energy functions for pure substances and stoichiometric compounds are taken from the FactSage 7.1 database (Bale et al., 2002).

3. Discussion

The models must be considered preliminary due to the extremely