



Thermodynamic Evaluation of Phase Equilibria in the GdCl₃-MgCl₂ Binary System†

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Experimental data for the GdCl₃-MgCl₂ binary system were subjected to a critical thermodynamic evaluation using the CALPHAD approach. The modified quasi-chemical model were defined in order to describe the Gibbs energies of the liquid phases and the model parameters were optimized from the experimental phase diagram data. The phase diagram and enthalpies of mixing of the GdCl₃-MgCl₂ system were calculated. Good agreement between the present calculations and the experimental data were obtained.

Key Words: Phase equilibria, CALPHAD technique, GdCl₃-MgCl₂.

INTRODUCTION

Knowledge of the basic physicochemical properties of lanthanide halides and their mixtures with alkali or alkali-earth halides can provide useful information for molten salt mixture design and applications and molten salt technology. As one of the systematic studies on the measurement and calculation of phase diagrams involving rare earth chlorides¹, the present work was undertaken to evaluate the phase diagram and thermodynamic data of the GdCl₃-MgCl₂ system.

EXPERIMENTAL

The phase diagram of the GdCl₃-MgCl₂ system was measured by Enninga *et al.*². Their measurements included differential thermal analysis (DTA) and differential scanning calorimetry (DSC). Their DTA apparatus was constructed in their laboratory and data were taken from heating curves with heating rates of 10 °C min⁻¹ while using silicon as a nontransforming reference material. The X-ray powder diffraction patterns of the solidified melts indicated only the primary phases. The melting points of the specimens obtained were 881 K for GdCl₃ and 980 K for MgCl₂. The GdCl₃-MgCl₂ system has a simple eutectic at 813 K and a composition containing 36 mol % MgCl₂.

The molar enthalpies of mixing $\Delta_{\text{mix}}H_m$ of the GdCl₃-MgCl₂ liquid binary system were taken from the works of Enninga *et al.*². The molar enthalpies of mixing were measured at 1173 K over the whole composition range under argon atmosphere. The apparatus was calibrated with gold. Though the error in these first measurements is high, probably in the

range + 5 to -15 %, the reproducibility was better. Precise measurements of the GdCl₃-MgCl₂ system are difficult, due to the small heat effects, but are in progress. In this system the plots of enthalpies of mixing versus composition were "arc -shaped" curves. The interaction parameter λ ,

$$\lambda = \frac{\Delta_{\text{mix}}H}{x_{\text{MgCl}_2}}(1 - x_{\text{MgCl}_2})$$
, for the GdCl₃-MgCl₂ system is close to linear.

Model: In order to orient the reader, a brief introduction of the modified quasi-chemical model is presented in the following section. Detailed description of the model can be found in the earlier publications^{3,4}. According to the model, the Gibbs energy of A-B binary system is represented by eqn. 1:

$$G = (n_A g_A^0 + n_B g_B^0) + RT(n_A \ln X_A + n_B \ln X_B) + RT \left(n_{AA} \ln \frac{X_{AA}}{Y_A^2} + n_{BB} \ln \frac{X_{BB}}{Y_B^2} + n_{AB} \ln \frac{X_{AB}}{2Y_A Y_B} \right) + \frac{n_{AB}}{2} \Delta g_{AB} \quad (1)$$

where n_i : moles of i ; g_i^0 : molar Gibbs energy of pure i ; n_{ij} : number of moles of the i - j pair; X_i : mole fraction of i ; X_{ij} : mole fraction of the i - j pair; Y_i : equivalent fraction of i ; Δg_{AB} : molar energy of A-B pairs.

RESULTS AND DISCUSSION

All collected data including phase diagram data and the descriptions of pure components that are already available are

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used together to optimize the thermodynamic properties and phase diagrams. According to the thermodynamic data optimized above, the $\text{GdCl}_3\text{-MgCl}_2$ phase diagram was calculated by using the simple computer program. The assessed phase diagram is shown in Fig. 1. The solid lines in figure represent the calculated data and the spots represent the experimental data. The numbers in the parentheses are the experimental critical points. For the $\text{GdCl}_3\text{-MgCl}_2$ system (Fig. 1), the melting points of pure GdCl_3 and MgCl_2 in our data base were 875 and 987 K, respectively. And the calculated eutectic point is at 813.7 K with the composition of 64.3 mol % GdCl_3 . In general, the calculated phase diagram and the experimental data are agreement very well.

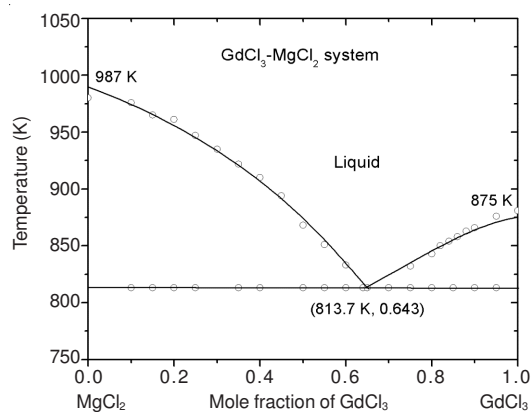


Fig. 1. Phase diagram of the $\text{GdCl}_3\text{-MgCl}_2$ system. Solid lines – calculated; \circ : experimental points form ref.²

Fig. 2 shows the calculated enthalpy of mixing in the $\text{GdCl}_3\text{-MgCl}_2$ system. Clearly, the optimized results show reasonable trends, the enthalpies of mixing is maximum at $x_{\text{GdCl}_3} = 0.5$. Fig. 3 shows the dependence of the interaction

parameter $\lambda = \frac{\Delta_{\text{mix}} H}{x_{\text{GdCl}_3}} (1 - x_{\text{GdCl}_3})$ on the mole fraction of

GdCl_3 . The interaction parameter λ for $\text{GdCl}_3\text{-MgCl}_2$ is close to linear.

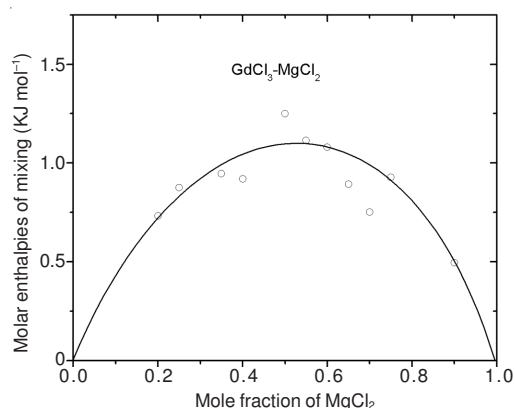


Fig. 2. Molar enthalpy of mixing of the $\text{GdCl}_3\text{-MgCl}_2$ liquid system at 1173 K. Solid lines – calculated; \circ – experimental points form ref.²

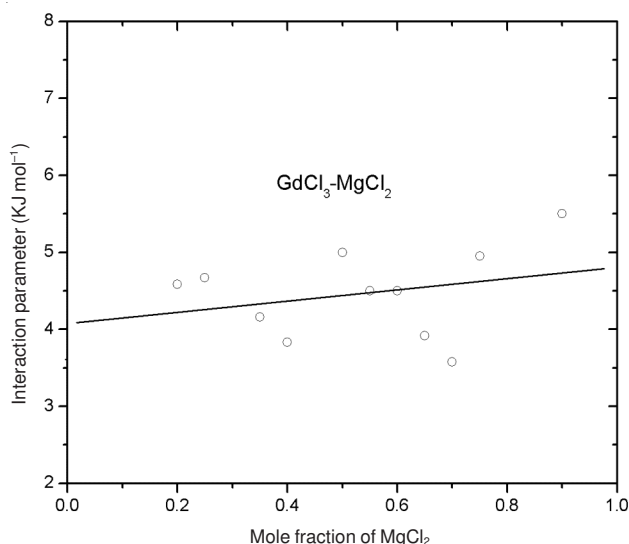


Fig. 3. Interaction parameter I in the $\text{GdCl}_3\text{-MgCl}_2$ liquid system vs. mole fraction of MgCl_2 . Solid lines – calculated; \circ : experimental points form ref.²

Conclusion

Using the CALPHAD method, the phase diagram and thermodynamic data available in the $\text{GdCl}_3\text{-MgCl}_2$ system were critically assessed. The calculated phase boundaries agreed well with the experimental data. The mixing enthalpies, the interaction parameter λ in the liquid melt were calculated. The calculated phase diagram and optimized thermodynamic parameters are thermodynamically self-consistent.

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