



## Thermodynamic Optimization and Calculation of LaCl<sub>3</sub>-MgCl<sub>2</sub> System†

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Published online: 10 March 2014;

AJC-14856

The thermodynamic properties and phase diagram of the LaCl<sub>3</sub>-MgCl<sub>2</sub> system were analyzed by means of the CALPHAD method in this work. Thermodynamic models were defined in order to describe the Gibbs energies of the individual phases and the model parameters were optimized from the experimental thermodynamic and phase diagram data. Based on measured phase equilibrium data and experimental thermo-chemical properties of the binary system, the phase diagram and the enthalpy of mixing of LaCl<sub>3</sub>-MgCl<sub>2</sub> liquid were calculated. The present description of binary LaCl<sub>3</sub>-MgCl<sub>2</sub> system showed the good agreement with the corresponding experimental data.

**Keywords:** Thermodynamic optimization and calculation, Phase equilibria, CALPHAD technique, LaCl<sub>3</sub>-MgCl<sub>2</sub>.

### INTRODUCTION

Lanthanide halide-alkali or alkali-earth metal halide systems play a significant role in everyday life and in many industrial applications. They are extracted and processed into metals, magnetic alloys, oxides and other forms. Extraction and processing of lanthanides are largely based on molten salt technologies. 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 chlorides<sup>1-5</sup>, the present work was undertaken to evaluate the phase diagram and thermodynamic data of the LaCl<sub>3</sub>-MgCl<sub>2</sub> system.

### EXPERIMENTAL

To the LaCl<sub>3</sub>-MgCl<sub>2</sub> system, the phase diagram was studied by Vogel and Schneider<sup>6</sup> and Enninga *et al.*<sup>7</sup>. All the measured results are of the eutectic-type. In Vogel and Schneider's work<sup>6</sup>, the measured eutectic point is at 949 K with the composition of 75 mol % MgCl<sub>2</sub>. Later Enninga *et al.*<sup>7</sup> remeasured the system, the eutectic point is 75 mol % MgCl<sub>2</sub> at 946 K. Their DTA apparatus was constructed in their laboratory and data were taken from heating curves with heating rates of 10 °C min<sup>-1</sup> while using silicon as a nontransforming reference material. The molar enthalpies of mixing  $\Delta_{\text{mix}}H_m$  of the LaCl<sub>3</sub>-

MgCl<sub>2</sub> liquid binary systems were taken from the works of Enninga *et al.*<sup>7</sup>. The molar enthalpies of mixing were measured at 1173 K over the whole composition range under argon at atmospheric pressure. The apparatus was calibrated with gold. In the LaCl<sub>3</sub>-MgCl<sub>2</sub> system, the plots of enthalpies of mixing versus composition were "arc-shaped" curves. The interaction parameter  $\lambda = \Delta_{\text{mix}}H/x_{\text{MgCl}_2}(1-x_{\text{MgCl}_2})$ , for the LaCl<sub>3</sub>-MgCl<sub>2</sub> system is close to linear.

**Thermodynamic model:** In order to optimize the phase diagram with short-range ordering a modification of the quasi-chemical theory of Guggenheim was made by Pelton and Blander<sup>8-10</sup>. Instead of the real components in the system, first-nearest-neighbor pairs are used in the new approach. For example, A and B are the real components in an A-B binary system then three first-nearest-neighbor pairs AA, BB and AB are considered.

$$(A-A)_{\text{pair}} + (B-B)_{\text{pair}} = 2(A-B)_{\text{pair}} \quad (1)$$

The Gibbs energy of "reaction" (1),  $\Delta g_{AB}$ , is the nonconfigurational Gibbs energy change for the formation of 2 moles of (A-B) pairs and it is composition and temperature dependent. And the Gibbs energy of the A-B system is given by eqn. 2:

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

†Presented at The 7th International Conference on Multi-functional Materials and Applications, held on 22-24 November 2013, Anhui University of Science & Technology, Huainan, Anhui Province, P.R. China

$$+ \frac{n_{AB}}{2} \Delta g_{AB} \quad (2)$$

where  $n_i$ : moles of  $i$ ;  $n_{ij}$ : number of moles of  $i$ - $j$  pair;  $X_i$ : mole fraction of  $i$ ;  $X_{ij}$ : mole fraction of  $i$ - $j$  pair;  $Y_i$ : equivalent fraction of  $i$ .

The mole pair Gibbs energies of A-B pairs, *i.e.*,  $g_{AA}^0, g_{BB}^0$  and  $g_{AB}^0$  are defined according to the following expression.

$$g_{AA}^0 = \frac{2g_A^0}{Z_{AA}}, \quad g_{BB}^0 = \frac{2g_B^0}{Z_{BB}} \quad (3)$$

$$g_{AB}^0 = \Delta g_{AB}^0 + g_{AA}^0 \frac{Z_{AA}}{Z_{AB}} + g_{BB}^0 \frac{Z_{BB}}{Z_{BA}} \\ = \Delta g_{AB}^0 + \left( \frac{2g_A^0}{Z_{AB}} + \frac{2g_B^0}{Z_{BA}} \right) \quad (4)$$

where  $g_i^0$  is molar Gibbs energy of pure  $i$  and  $Z_{ij}$  is coordination number of  $i$ - $j$  pair.  $Z_{ij}$  and  $Z_i$ , the coordination number of  $i$  which can be different and function of pair composition.

$$\frac{1}{Z_A} = \frac{1}{2n_{AA} + n_{AB}} \left( \frac{2n_{AA}}{Z_{AA}} + \frac{n_{AB}}{Z_{AB}} \right) \quad (5)$$

$$\frac{1}{Z_B} = \frac{1}{2n_{BB} + n_{AB}} \left( \frac{2n_{BB}}{Z_{BB}} + \frac{n_{AB}}{Z_{BA}} \right) \quad (6)$$

The molar energy of A-B pair,  $\Delta g_{AB}$ , is a function of mole fractions of  $i$ - $j$  pairs and can be expressed as follows:

$$\Delta g_{AB} = \Delta g_{AB}^0 + \sum g_{AB}^i X_{AA}^i + \sum g_{AB}^j X_{BB}^j \quad (7)$$

$$\text{or} \quad \Delta g_{AB} = \Delta g_{AB}^0 + \sum g_{AB}^{ij} X_{AA}^i X_{BB}^j \quad (8)$$

For eqns. 7 and 8,  $i + j \geq 1$ , in practice we always have either  $i = 0$  or  $j = 0$ .

## RESULTS AND DISCUSSION

All collected data including phase diagram data and the descriptions of pure components that are already available are used together to optimize the thermodynamic properties and phase diagrams. According to the thermodynamic data optimized above, the  $\text{LaCl}_3$ - $\text{MgCl}_2$  phase diagram was calculated by using the THERMOVALC computer program.

The modified quasichemical model was used for the liquid. In this work, let, A =  $\text{LaCl}_3$  and B =  $\text{MgCl}_2$ , the parameters  $Z_{AA}$  and  $Z_{BB}$  were both set equal to 6. On the basis of past experience with mixed salt systems, values for the coordination number were set  $Z_{AB} = 6$  and  $Z_{BA} = 3$ , where the selection was based on experimental input.

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  $\text{LaCl}_3$ - $\text{MgCl}_2$  system (Fig. 1), the melting points of pure  $\text{LaCl}_3$  and  $\text{MgCl}_2$  in our data base were 1131 and 987 K, respectively. And the calculated eutectic point is at 946.3 K with the composition of 25.7 mol %  $\text{LaCl}_3$ . In general, the calculated phase diagram and the experimental data are in good agreement.

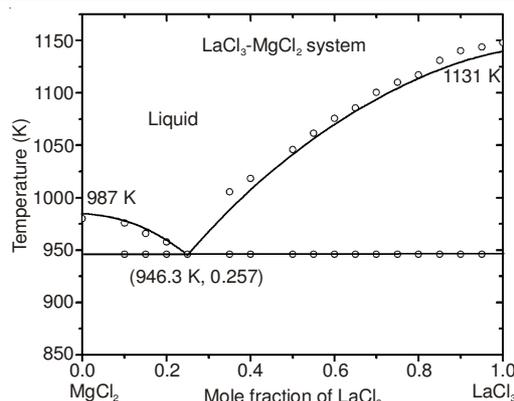


Fig. 1. Phase diagram of the  $\text{LaCl}_3$ - $\text{MgCl}_2$  system. Solid lines — calculated;  $\circ$ : Experimental points from ref.<sup>7</sup>

Fig. 2 shows the calculated enthalpy of mixing in the  $\text{LaCl}_3$ - $\text{MgCl}_2$  system. The open circles indicate the experimental data at different mole fraction of  $\text{MgCl}_2$ . The optimized results show reasonable trends, the enthalpies of mixing is maximum at  $x_{\text{LaCl}_3} = 4$ . Fig. 3 shows the dependence of the interaction parameter  $\lambda = \Delta_{\text{max}}H/x_{\text{LaCl}_3}(1-x_{\text{LaCl}_3})$  on the mole fraction of  $\text{LaCl}_3$ . The interaction parameter  $\Delta$  for  $\text{LaCl}_3$ - $\text{MgCl}_2$  is close to linear.

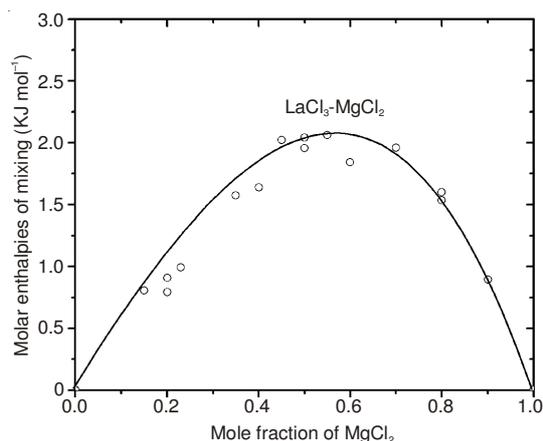


Fig. 2. Molar enthalpy of mixing of the  $\text{LaCl}_3$ - $\text{MgCl}_2$  liquid system at 1173 K. Solid lines — calculated;  $\circ$ : Experimental points from ref.<sup>7</sup>

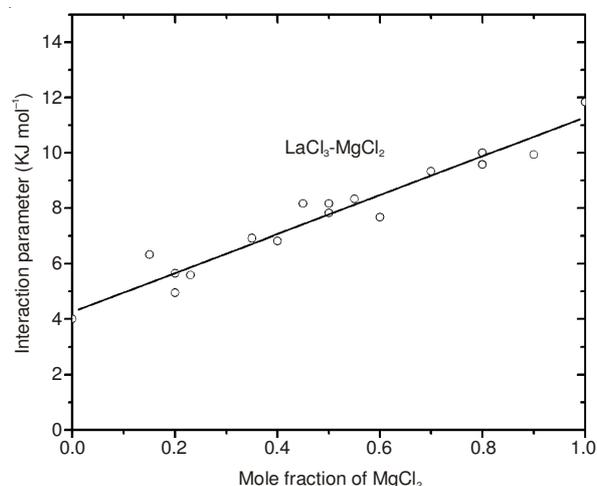


Fig. 3. Interaction parameter  $\lambda$  in the  $\text{LaCl}_3$ - $\text{MgCl}_2$  liquid system vs. mole fraction of  $\text{MgCl}_2$ . Solid lines — calculated;  $\circ$ : Experimental points from ref.<sup>7</sup>

## Conclusions

A thermodynamic assessment of the LaCl<sub>3</sub>-MgCl<sub>2</sub> system has been carried out and the results were obtained following:

(i) The thermo-chemical properties, *i.e.*, thermodynamic properties of pure compounds, enthalpies of mixing of the liquid phase and interaction coefficients  $\lambda$ , were calculated by using an interactive computer-assisted analysis.

(ii) The calculated phase diagrams and optimized thermodynamic parameters are thermodynamically self-consistent.

## ACKNOWLEDGEMENTS

The authors gratefully acknowledge the financial support of the National Science Foundation of China (No. 51102073), Key Laboratory for Advanced Technology in Environmental Protection of Jiangsu Province (AE201361) and the Natural Science Foundation of Anhui Province of China (No. 10040606Q53).

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