

Thermodynamic Assessment of PrCl₃-CaCl₂ and NdCl₃-CaCl₂ Systems

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By using the CALPHAD technique, an assessment of the binary PrCl₃-CaCl₂ and NdCl₃-CaCl₂ systems have been carried out. From measured phase equilibrium data and experimental integral properties, the PrCl₃-CaCl₂ and NdCl₃-CaCl₂ phase diagrams were optimized and calculated. A set of thermodynamic functions has been optimized based on an interactive computer-assisted analysis. The calculated results by present method agree well with the experimental data.

Keywords binary system, CALPHAD approach, enthalpy of mixing, phase equilibria, thermodynamic assessment

1. Introduction

Molten salt electrolysis has been widely used for the production of rare earth metals and their alloys. Phase diagrams are the most important data for fused electrolytes. The phase diagrams of rare-earth metal halides in combination with alkali or alkali-earth metal halide systems are of prime importance when considering those salt systems for possible use in this reprocessing application; specifically, the temperature and liquid composition at the eutectic reaction need to be known. Following our previous work,^[1-3] an extension to the PrCl₃-CaCl₂ and NdCl₃-CaCl₂ systems are carried out here.

The phase diagram of the PrCl₃-CaCl₂ system was measured by different research groups^[4-6] with a differential thermal analysis (DTA) method. All measured results indicate a eutectic-type system. The earlier results were reported by Hattori et al.,^[4] and the measured eutectic point was at 880 K with a composition of 42 mol.% PrCl₃. Trifonov et al.^[5] remeasured the system, their eutectic point was 41 mol.% PrCl₃ at 888 K. Later Zheng et al.^[6] again with DTA examined the system. 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 Al₂O₃ as a nontransforming reference material. The measured results of Zheng et al. agreed well with Trifonov et al. Sharma and Rogers^[7] calculated the PrCl₃-CaCl₂ system by the Clausius-Clapeyron equation with Temkin's model and literature^[4] data, the calculated eutectic point was 44.5 mol.% PrCl₃ at 888 K.

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The phase diagram of the NdCl₃-CaCl₂ system was only measured by Sharma and Rogers.^[7] Their measurements included DTA and differential scanning calorimetry (DSC). The x-ray powder diffraction patterns of the solidified melts indicated only the primary phases. The NdCl₃-CaCl₂ system has a simple eutectic at 873 ± 2 K and a composition containing 41 ± 1 mol.% NdCl₃.

The molar enthalpies of mixing $\Delta_{\text{mix}}H_m$ of the PrCl₃-CaCl₂ and NdCl₃-CaCl₂ liquid binary systems were taken from the works of Gaune-Escard et al.^[8] The molar enthalpies of mixing were measured at 1073 K over the whole composition range under argon at atmospheric pressure. Their apparatus was a Calvet-type high-temperature micro-calorimeter and mixing of the two liquid components was obtained by the break-off ampoule technique. In both systems the plots of enthalpies of mixing versus composition were "S-shaped" curves. The enthalpy of mixing values are positive for NdCl₃- and PrCl₃-rich compositions, and negative for other compositions. These values are very small (from about -200 to about 180 J mol⁻¹). In the PrCl₃-CaCl₂ and NdCl₃-CaCl₂ liquid binary systems, $\Delta_{\text{mix}}H_m \approx 0$ at $x_{\text{PrCl}_3} \approx 0.6$ and at $x_{\text{NdCl}_3} \approx 0.4$, respectively.

2. Model

In order to orient the reader, a brief introduction of the modified quasi-chemical model is presented in the following section. A detailed description of the model can be found in earlier publications.^[9-14] According to the model, the Gibbs energy of A-B binary system is represented by Eq. 1:

$$G = (n_{\text{A}}g_{\text{A}}^{\circ} + n_{\text{B}}g_{\text{B}}^{\circ}) + RT(n_{\text{A}} \ln X_{\text{A}} + n_{\text{B}} \ln X_{\text{B}}) + RT \left(n_{\text{AA}} \ln \frac{X_{\text{AA}}}{Y_{\text{A}}^2} + n_{\text{BB}} \ln \frac{X_{\text{BB}}}{Y_{\text{B}}^2} + n_{\text{AB}} \ln \frac{X_{\text{AB}}}{2Y_{\text{A}}Y_{\text{B}}} \right) + \frac{n_{\text{AB}}}{2} \Delta g_{\text{AB}} \quad (\text{Eq 1})$$

where n_i is the moles of i , g_i° is the molar Gibbs energy of pure i , n_{ij} is the number of moles of the i - j pair, X_i is the mole fraction of i , X_{ij} is the mole fraction of the i - j pair, Y_i is

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the equivalent fraction of i , Δg_{AB} is the molar energy of A-B pairs.

3. Thermodynamic Optimization

All thermodynamic data of pure components come from the FACTBASE^[15] and USERBASE, and the latest published thermodynamic data are stored in the USERBASE.

The Gibbs energies of fusion are given by:

$$\Delta G_{\text{fus}}^{\circ} = A + BT + CT^2 + DT \ln T + E/T \text{ J mol}^{-1} \quad (\text{Eq 2})$$

Table 1 shows coefficients for the Gibbs energies of pure compounds for the various components from which the coefficients in Eq. 2 can be derived.

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 by using a simple computer program.

For calculation of the phase diagrams, an initial determination of the Z_{ij} is needed. On the basis of past experience with mixed salt systems, values for the coordination number were set at $Z_{\text{PrPr}} = Z_{\text{NdNd}} = Z_{\text{CaCa}} = 6$, where the selection was based on experimental input.^[16] In the authors studies of rare-earth (RE) chloride-metal chloride systems of the type $\text{RECl}_3\text{-MCl}_n$ ($n = 1$ or 2) system, a tendency to form an intermediate phase of the type $\text{RECl}_3\text{-3MCl}_n$ [$\text{REM}_3\text{Cl}_3(1+n)$] has been found. On the basis of this information with Ca-RE pair ratio occurring at 3:1, the values of $Z_{\text{PrPr}} = Z_{\text{NdNd}} = Z_{\text{CaCa}} = 6$ and $Z_{\text{CaPr}} = Z_{\text{CaNd}} = 2$, and $Z_{\text{PrCa}} = Z_{\text{NdCa}} = 6$ were selected for all alkaline earth elements through the calculations.

The molar energy of A-B pairs Δg_{AB} is a function of mole fractions of i - j pairs and can be expressed as follows.

$$\Delta g_{AB} = \sum_j X_{AB} X_n^j (C_1 + C_2 T) \quad (\text{Eq 3})$$

where n can be AA and BB, as well as C_1 and C_2 correspond to excess enthalpy of mixing and excess entropy, respectively. In these systems $j = 0, 1$. All the coefficients for the $\text{PrCl}_3\text{-CaCl}_2$ and $\text{NdCl}_3\text{-CaCl}_2$ binary systems shown in Table 2.

4. Results and Discussion

According to the thermodynamic data optimized above, the $\text{PrCl}_3\text{-CaCl}_2$ and $\text{NdCl}_3\text{-CaCl}_2$ phase diagrams were

Table 1 Thermodynamic properties of pure compounds

Compound	T_{fus}, K	$A \times 10^{-3}$	B	$C \times 10^3$	D	$E \times 10^{-5}$
CaCl ₂	1045	2.51	209.52	10.73	-28.33	0
PrCl ₃	1059	2.69	281.61	23.85	-47.70	0
NdCl ₃	1032	10.47	433.05	30.55	-68.41	0

calculated by using the THERMOVALC computer program. The assessed phase diagrams are shown in Fig. 1-2. The solid lines in the figures represent the calculated data, and the spots represent the experimental data. The numbers are the calculated critical points. In the $\text{PrCl}_3\text{-CaCl}_2$ phase diagrams (Fig. 1), the calculated eutectic point is at 888 K with the composition of 41.3 mol.% PrCl_3 . For the $\text{NdCl}_3\text{-CaCl}_2$ system (Fig. 2), the calculated eutectic point is at 873.7 K, 41.5 mol.% NdCl_3 . It can be seen that the calculated phase boundaries and invariant points agree well with the experimental data.

Figure 3 shows the calculated enthalpy of mixing in the two systems $\text{PrCl}_3\text{-CaCl}_2$ and $\text{NdCl}_3\text{-CaCl}_2$. The figure shows that the rare earth halides repel the other species. The smaller the radius, the larger the repulsion. The ionic radii are Pr 1.013 Å, and Nd 0.995 Å. In the system $\text{NdCl}_3\text{-CaCl}_2$ the zero value of H_m is closer to CaCl_2 than in the system $\text{PrCl}_3\text{-CaCl}_2$: the repulsion of NdCl_3 is stronger than that of PrCl_3 . And the minimum of the enthalpy of mixing is shifted toward the CaCl_2 -rich compositions and appears at $x_{\text{RECl}_3} \approx 0.2-0.4$.

Figure 4 shows the dependence of the interaction parameter $\lambda = \Delta_{\text{mix}} H / x_{\text{CaCl}_2} (1 - x_{\text{CaCl}_2})$ on the mole fraction of CaCl_2 . The interaction parameter λ for $\text{PrCl}_3\text{-CaCl}_2$ and $\text{NdCl}_3\text{-CaCl}_2$ is close to linear, and the values of λ were

Table 2 Calculated coefficients for the $\text{PrCl}_3\text{-CaCl}_2$ and $\text{NdCl}_3\text{-CaCl}_2$ systems

System	$C_1 (j=0)$	$C_1 (j=1)$		$C_2 (j=0)$
		X_{AA}	X_{BB}	
$\text{PrCl}_3\text{-CaCl}_2$	-636.89	630.75	1051.64	1.68
$\text{NdCl}_3\text{-CaCl}_2$	-873.32	951.84	831.45	3.77

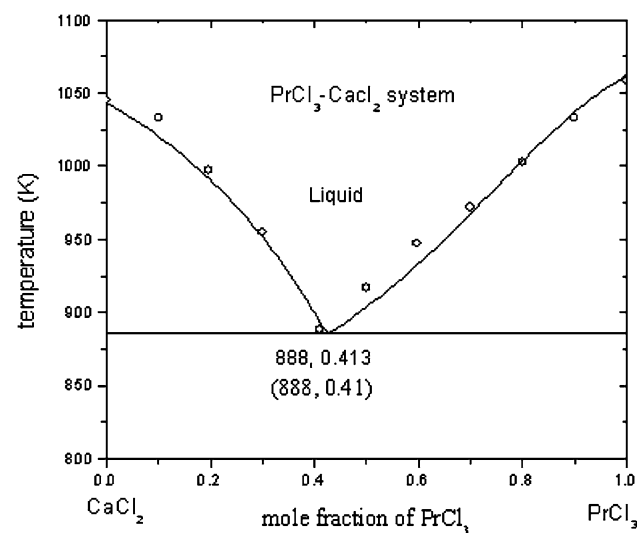


Fig. 1 Phase diagram of the $\text{PrCl}_3\text{-CaCl}_2$ system. Solid lines—calculated; ○—experimental points from Ref 6

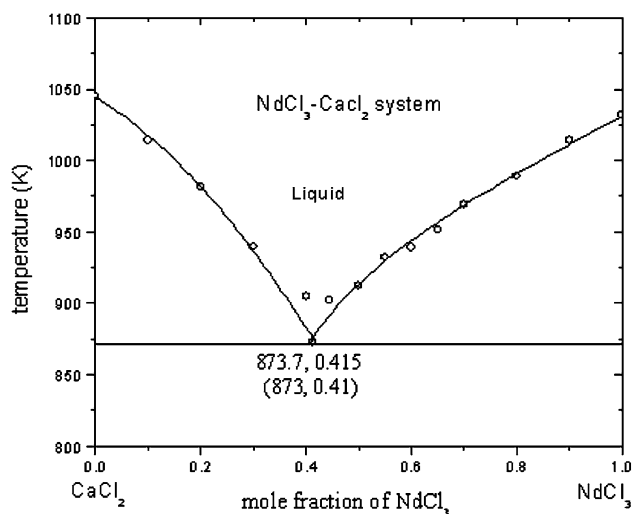


Fig. 2 Phase diagram of the $\text{NdCl}_3\text{-CaCl}_2$ system. Solid lines—calculated; \circ —experimental points from Ref 7

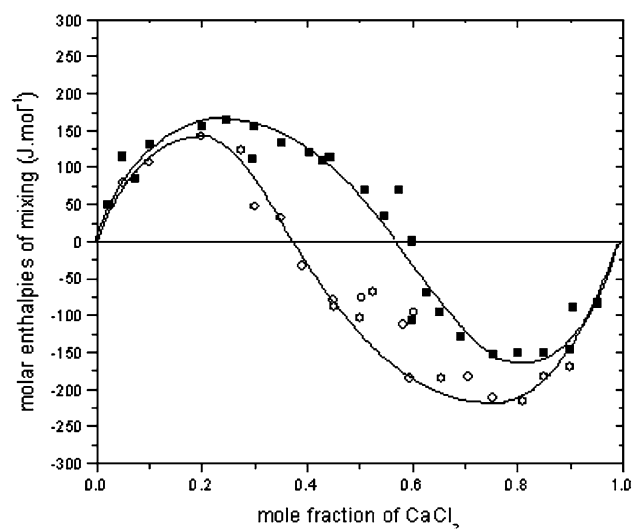


Fig. 3 Molar enthalpy of mixing of the $\text{PrCl}_3\text{-CaCl}_2$ and $\text{NdCl}_3\text{-CaCl}_2$ liquid system at 1073 K. Solid lines—calculated; \circ — $\text{PrCl}_3\text{-CaCl}_2$; \blacksquare — $\text{NdCl}_3\text{-CaCl}_2$; all experimental points from Ref 8

fitted by the method of least squares of polynomials of the form

$$\lambda = A + Bx + Cx^2 + Dx^3,$$

where x is the mole fraction of CaCl_2 . The least squares coefficients and the correlation coefficients (r^2) for the equation of λ are presented in Table 3. The correlation coefficients of the linear regression analysis of the values of λ is again very close to 1.0, in support of a linear relation between the interaction parameter λ and the mole fraction of CaCl_2 .

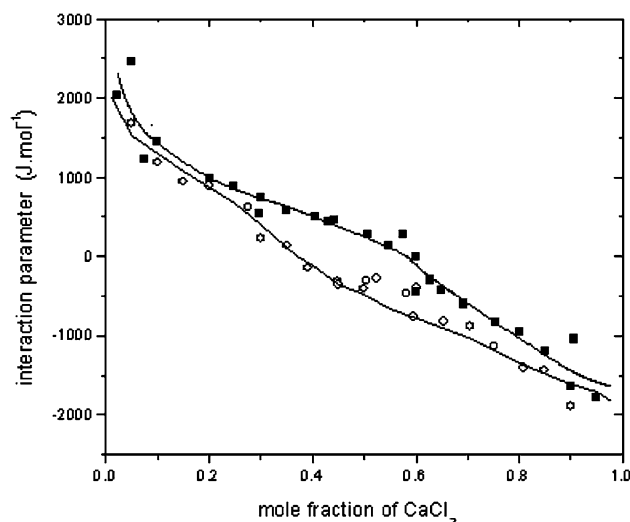


Fig. 4 Interaction parameter λ in the $\text{PrCl}_3\text{-CaCl}_2$ and $\text{NdCl}_3\text{-CaCl}_2$ liquid system vs. mole fraction of CaCl_2 . Solid lines—calculated; \circ — $\text{PrCl}_3\text{-CaCl}_2$; \blacksquare — $\text{NdCl}_3\text{-CaCl}_2$; All experimental points from Ref 8

Table 3 Least squares coefficients and the correlation coefficients (r^2) for the equation of λ for the $\text{PrCl}_3\text{-CaCl}_2$ and $\text{NdCl}_3\text{-CaCl}_2$ systems

System	A	B	C	D	r^2
$\text{PrCl}_3\text{-CaCl}_2$	1978.27	-6555.52	3978.38	-1246.14	0.997
$\text{NdCl}_3\text{-CaCl}_2$	2151.10	-6259.08	6656.53	-4460.19	0.987

5. Conclusions

A thermodynamic assessment of the $\text{PrCl}_3\text{-CaCl}_2$ and $\text{NdCl}_3\text{-CaCl}_2$ systems has been carried out, and the results were obtained as follows: (i) the thermo-chemical properties, i.e., thermodynamic properties of pure compounds, enthalpies of mixing of the liquid phase, and interaction coefficients λ , were calculated by using an interactive computer-assisted analysis. (ii) The calculated phase diagrams and optimized thermodynamic parameters are thermodynamically self-consistent.

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