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HIGH-TEMPERATURE STUDY OF PHASE EQUILIBRIA IN THE SYSTEMS CsCl–LnCl$_3$ (*Ln*=Ce, Nd) BY KNUDSEN EFFUSION MASS SPECTROMETRY

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Abstract

The vaporization of samples of different chemical and phase compositions in the systems CsCl–LnCl$_3$ (*Ln*=Ce, Nd) was investigated in the temperature range between 850 and 1050 K by the use of Knudsen effusion mass spectrometry. The gaseous species CsCl, Cs$_2$Cl$_2$, LnCl$_3$, Ln$_2$Cl$_6$ and CsLnCl$_4$ were identified in the vapour and their partial pressures were determined. The thermodynamic activities of CsCl, and LnCl$_3$ and the free enthalpies of formation for the phases Cs$_3$LnCl$_{6(s)}$ were determined at 950 K in the two phase fields {liquid+Cs$_3$LnCl$_{6(s)}$}. The correlations between the condensed phase equilibria and the partial pressures of the vapour components at the phase boundaries are discussed and illustrated with the present experimental data.

Keywords: free enthalpy of formation, Knudsen effusion mass spectrometry, systems CsCl–LnCl$_3$, thermodynamic activities, vaporization

Introduction

Several groups have investigated the thermodynamic properties of the pseudobinary systems alkali metal chloride–lanthanide chloride in the past few years. Among them, the systematic investigations of Seifert *et al.* [1–3] by means of calorimetry, galvanic cells and differential thermal analysis are the most extensive. Unfortunately, because of the experimental difficulties, only limited electrochemical investigations have been performed on the systems CsCl–LnCl$_3$.

Gaune-Escard *et al.* [4] determined the molar enthalpies of the solid–solid and solid–liquid phase transitions for several phases A$_3$LnCl$_{6(s)}$ (*A*=K, Rb, Cs; *Ln*=La, Ce, Pr, Nd) by differential scanning calorimetry. The data agree reasonably with the results reported by Seifert *et al.* (Refs [1–3] and references quoted therein).

We reported previously [5–8] on a vaporization study of the systems ACl–LnCl$_3$ (*A*=Na, Cs; *Ln*=Ce, Nd) by Knudsen effusion mass spectrometry. In

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the present paper, we analyse the results of a vaporization study of the systems $CsCl–LnCl_3$, considering their phase diagrams. The aim of the work was to demonstrate the potential of the method for the determination of the thermodynamic properties of condensed phases in equilibrium with their vapour.

Condensed-phase equilibria and partial pressures of components

A knowledge of the thermochemical properties of the multicomponent systems is necessary for predictions of their chemical stability, reactivity and vaporization behaviour. Among the thermodynamic quantities, the phase equilibria and the thermodynamic activities of the components in the solid and liquid phases are of great importance.

The phase diagrams of the multicomponent systems result from the free enthalpies of all the phases (including the melt) which can be stable at the given temperature and chemical composition. The free enthalpies of the phases result, in turn, from the thermodynamic potentials of the individual components, $\mu(i)$. If the pure component i is considered as a standard state, its thermodynamic potential in the system can be determined from the equilibrium partial pressure of the gaseous species, $p(i)$, as follows:

$$\mu(i) = \mu^{\square}(i) + RT\ln a(i) = \mu^{\square}(i) + RT\ln p(i) - RT\ln p^{\circ}(i) \qquad (1)$$

where $\mu^{\square}(i)$, $a(i)$ and $p^{\circ}(i)$ are the standard thermodynamic potential, the thermodynamic activity in the system and the partial pressure of the pure component i, respectively.

From a consideration of the phase rule in addition to the thermodynamic equilibrium conditions in the gaseous phase, one can predict the regularities in the partial pressures as functions of temperature and/or the chemical composition, providing that the phase diagram of the multicomponent system is known. On the other hand, the regularities in the partial pressures as determined for the different compositions and temperatures of the system yield the information concerning the phase equilibria if the phase diagram is unknown. It has been shown [9] that the difference in the thermodynamic potentials of two components is especially useful in such a case, due to its more significant changes at the phase transitions in comparison with the changes in the thermodynamic potentials of the individual components. This difference can be related to the partial pressures of two components i and j as follows:

$$\mu(i) - \mu(j) = RT\ln[p(i)/p(j)] + C \qquad (2)$$

where C is a constant involving the standard thermodynamic potentials and the pressures of the pure components. Therefore, determination of the partial pressures is a useful tool for investigations of the phase equilibria of the condensed phases in the multicomponent systems. Knudsen effusion mass spectrometry [10–12] is nowadays the most powerful and established method for the determination of partial pressures.

A knowledge of the thermodynamic activities of the components in equilibrium with the condensed phase of stoichiometry A_nB_m at temperature T permits determination of the free enthalpy of formation of the phase from the pure substances A and B:

$$\Delta_f G^o(T) = RT\ln[a(A)^n a(B)^m] \tag{3}$$

The phase diagram of the system A–B can be calculated if the free enthalpies of all the phases occurring in the system are known in addition to the thermodynamic properties of the pure components A and B. If the phase diagram A–B is known, the consistency of the thermodynamic data obtained for the system can be checked and the thermodynamics of the system can be optimized by computer modelling (e.g. Ref. [13]).

Vaporization study

The mass spectrometric investigations were carried out with a substantially modified [14] Knudsen cell – mass spectrometer system MI 1201 supplied by Sumy (Ukraine). The vapour species were ionized with electrons of energy 60 eV. Knudsen cells made of silica and tantalum with knife-edged effusion orifices 0.45 and 0.65 mm in diameter were employed in the measurements. Temperature was measured with a platinum – platinum +10% rhodium thermocouple calibrated in situ at the melting point of silver.

Samples CsCl–$LnCl_3$ with compositions x(CsCl)=0.10–0.80 were investigated in the study. The details of the sample preparation are given in Refs [5, 6]. The samples were placed in the Knudsen cells and heated in the mass spectrometer at 750 K for 3 h. The temperature was then increased until the intensity of Cs^+, the most intense ion signal in the mass spectrum, was detected. The stability of the ion intensities with time was treated as evidence of the attainment of equilibrium between the gaseous and condensed phases inside the cell. The temperature was then raised or lowered stepwise by 10–30 K and the mass spectra were scanned after the temperature in the Knudsen cell had stabilized. The initial compositions correspond to different two-condensed-phase fields on phase diagrams [15, 16] in the temperature range of investigations, as shown by the points with arrows in Figs 1a, b.

Mass spectra and partial pressures of the gaseous species

The ion intensities observed on vaporizing the samples in the systems CsCl–$LnCl_3$, and their assignment to the gaseous vapour species from which the

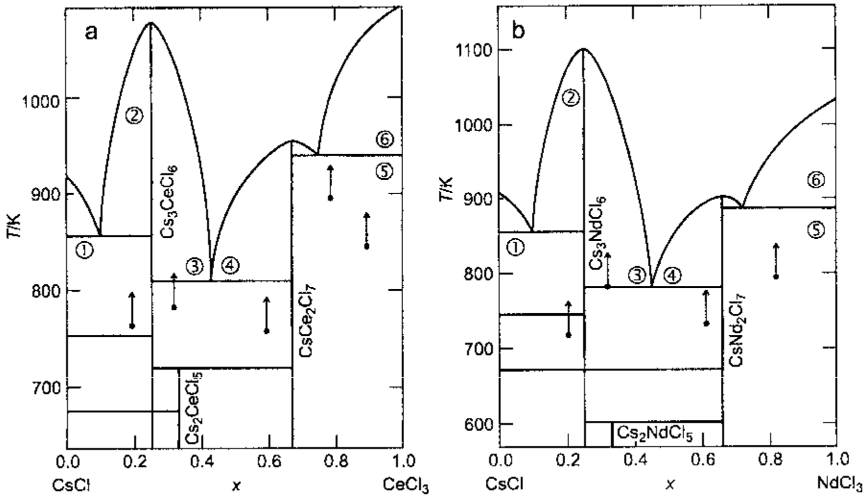

Fig. 1 Phase diagrams of CsCl–CeCl$_3$ [15] (a), and CsCl–NdCl$_3$ (b). The points with arrows show the initial mole fractions and temperatures of measurements

ions originate by electron impact, are shown in Tables 1 and 2. The methods used for this assignment are discussed in Refs [5, 6]. In addition, small intensities of the ions Ln$^+$, LnCl$^+$ and LnCl$_3^+$ (probably from both LnCl$_{3(g)}$ and CsLnCl$_{4(g)}$) and trace intensities of Ln$_2$Cl$_5^+$ (from Ln$_2$Cl$_{6(g)}$) were detected in the mass spectra.

The partial pressures $p(i)$ of the species i at temperature T were obtained from the equation

$$p(i) = [kT\,\Sigma\, I(i)]/\sigma(i) \tag{4}$$

where k is the calibration factor and $\sigma(i)$ is the ionization cross-section of species i. $\Sigma I(i)$ is the sum of the ion intensities originating from the ionization and/or fragmentation of species i. The partial pressure evaluation procedure was described previously for the systems CsCl–CeCl$_3$ [5] and CsCl–NdCl$_3$ [6], respectively.

Partial pressures and phase equilibria in the condensed phases

Figures 2a, b present the partial pressures of the gaseous species obtained in the vaporization measurements in Tables 1 and 2 at different temperatures. In these measurements, samples with initial composition x(CsCl)=0.80 were completely evaporated at several temperatures, with simultaneous recording of the mass spectrum of the equilibrium vapour. At the beginning, two solid phases, CsCl$_{(s)}$ and Cs$_3$LnCl$_{6(s)}$, were present in the effusion cell, in equilibrium with the gaseous phase according to the phase diagram (field 1 in Fig. 1). In consequence of the considerably higher volatility of CsCl in comparison with that of $LnCl_3$, the chemical composition of the condensed phase changed continually during the vaporization experiment, towards pure $LnCl_{3(s)}$. The fall in $CsCl_{(g)}$ partial pressure within the phase $Cs_3LnCl_{6(s)}$ indicates the narrow homogeneity range of the ternary compounds and quantifies the difference between the CsCl activity in the phase fields adjacent to the ternary compound. Only the partial pressures of

Table 1 Ion intensities (in arbitrary units) measured upon vaporizing the sample $CsCl–CeCl_3$, and the assignment of the ions to their neutral precursors

T/K	Phase composition [a]	CsCl		$CsCeCl_4$	$CeCl_3$	Cs_2Cl_2
		$I(CsCl^+)$	$I(Cs^+)$	$I(CsCeCl_3^+)$	$I(CeCl_2^+)$	$I(Cs_2Cl^+)$
768	$CsCl_{(s)}+Cs_3CeCl_{6(s)}$ (1)		24.1			1.54
787		2.40	64.9			3.53
807		3.17	132			8.65
826		5.40	229			16.3
845		8.23	412			34.1
862	$Cs_3CeCl_{6(s)}$+liquid (2)	16.2	647			56.7
880		26.0	968			81.9
896		38.3	1390			116
913		55.7	1910			160
930	$Cs_3CeCl_{6(s)}$	54.8	1670			94.4
932		13.4	1420			63.1
933		30.3	1080	0.47		32.1
933		5.31	578	0.47		10.0
933	$Cs_3CeCl_{6(s)}$+liquid (3)	6.86	323	0.94	1.28	2.73
933		7.54	313	0.94	1.28	2.73
916		4.37	185	0.70		1.37
881		1.29	61.2			0.46
932		6.60	314	0.70	1.14	3.07
950		12.3	511	1.64	2.56	5.92
967		19.5	819	2.82	4.70	9.90
983		33.9	1250	3.29	6.98	18.0
1000		57.4	1810	5.87	12.0	31.4
1016	liquid	60.8	2140	18.1	89.7	23.6

[a] See Fig. 1a

Table 2 Ion intensities (in arbitrary units) measured upon vaporizing the sample CsCl–$NdCl_3$, and the assignment of the ions to their neutral precursors

T/K	Phase composition [a]	CsCl		$CsNdCl_4$	$NdCl_3$	Cs_2Cl_2
		$I(CsCl^+)$	$I(Cs^+)$	$I(CsNdCl_3^+)$	$I(NdCl_2^+)$	$I(Cs_2Cl^+)$
767	$CsCl_{(s)}+Cs_3NdCl_{6(s)}$ (1)	1.00	91.9			9.91
728			21.0			1.71
746		2.06	44.0			4.55
764		3.86	89.1			8.87
784		10.0	181			22.9
803		19.0	341			47.1
822		38.6	603	0.90		94.4
839		62.6	986	1.36		163
857		111	1550	2.71		290
875	$Cs_3NdCl_{6(s)}$+liquid (2)	170	2290	2.26		437
891		229	3030	1.36		573
909		249	3810	1.36		449
909	$Cs_3NdCl_{6(s)}$	62.1	540	2.26		24.6
909	$Cs_3NdCl_{6(s)}$+liquid (3)	26.0	360	7.23		3.87
909		25.5	337	8.14		3.98
892		15.9	197	3.62		1.93
876		8.66	126			0.68
860		4.29	70.4	1.81		0.46
840		1.46	35.3	0.90		0.34
907		20.8	349	7.23		3.87
926		41.1	592	11.3	4.66	7.40
943		71.1	948	17.6	8.39	14.7
959		115	1430	24.9	13.7	25.6
976		173	2121	35.3	16.2	46.4
992		262	3380	69.2	41.7	71.7
1007	liquid	311	5770	163	159	65.9
958		63.4	1090	42.9	47.6	8.65
923		20.8	402	17.2	15.9	2.39

[a] See Fig. 1b

$CsCl_{(g)}$ and $Cs_2Cl_{2(g)}$ were determined in phase fields 1 and 2, whereas the $CsLnCl_{4(g)}$ pressure was additionally measured in phase field 3.

According to the phase rule, all the partial pressures, and accordingly the mass spectrum, depend only on the temperature in the two-phase field, whereas they do not depend on the chemical composition of the sample. Therefore, the partial pressures of each component determined in the same phase field can be described with the same linear function in the $\ln p(i)=f(1/T)$ diagram (cf. Fig. 2). On the other hand, the partial pressures change continually at the constant tem-

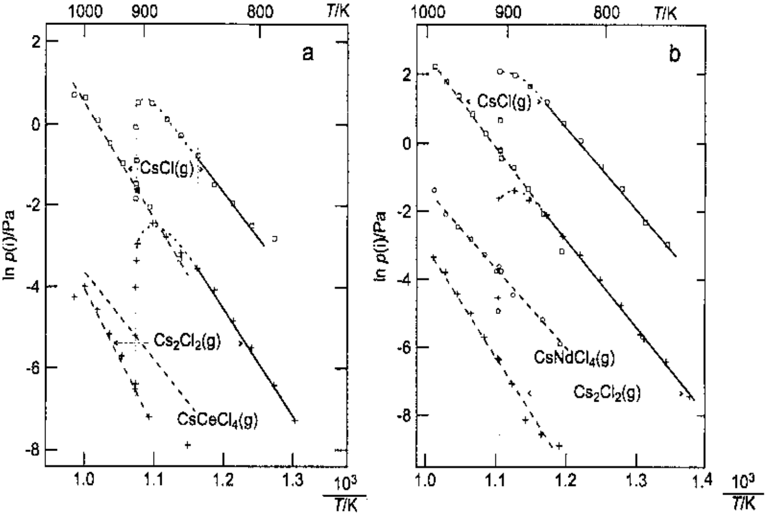

Fig. 2 Partial pressures on vaporizing $CsCl-CeCl_3$ (a) and $CsCl-NdCl_3$ (b) samples with initial composition x(CsCl)=0.80. Full line – phase field 1; dotted line – phase field 2; dashed line – phase field 3 in Fig. 1

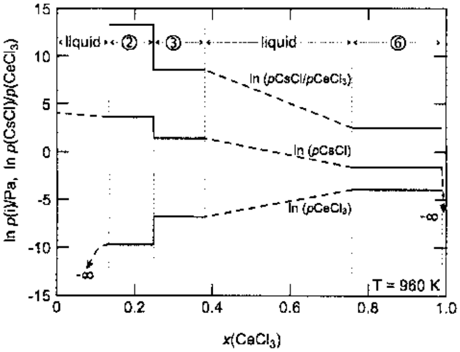

Fig. 3 Equilibrium partial pressures of $CsCl_{(g)}$ and $CeCl_{3(g)}$ in the system $CsCl-CeCl_3$ at 960 K, and the ratio $p(CsCl)/p(CeCl_3)$ as a function of the chemical composition of the samples

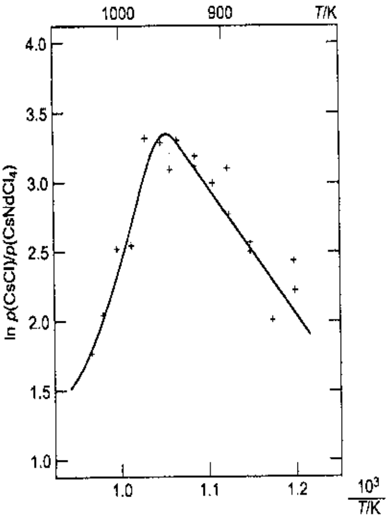

Fig. 4 Temperature dependence of the partial pressure ratio $p(\mathrm{CsCl})/p(\mathrm{CsNdCl_4})$ obtained for the sample CsCl–$NdCl_3$ with $x(\mathrm{CsCl})=0.70$

perature in the measurement stage corresponding to the monophase (Cs_3LnCl_6(s) or liquid) field. In this way, it was possible to ascertain the phase fields crossing during the vaporization measurement as given in Tables 1 and 2. In Fig. 3, we present the partial pressures of CsCl(g) and $CeCl_3$(g) obtained at 960 K in this study throughout the composition range of the system CsCl–$CeCl_3$. The partial pressures were calculated from the thermodynamic activities of the components, obtained in Refs [5, 6]. The partial pressure ratio $p(\mathrm{CsCl})/p(\mathrm{CeCl_3})$ at the same temperature is plotted in Fig. 3 in addition to the individual partial pressures. This ratio reveals more significant changes at the phase boundaries in comparison with the individual partial pressures. Therefore, the analysis of such partial pressure ratios as a function of the system composition at the constant temperature yields accurate data about the phase diagram. Similarly, the temperature dependence of the partial pressure ratio for the constant sample composition demonstrates the characteristic points at the phase boundaries. In Fig. 4, we present the temperature dependence of the partial pressure ratio $p(\mathrm{CsCl})/p(\mathrm{CsNdCl_4})$ obtained for the sample CsCl–$NdCl_3$ with initial composition $x(\mathrm{CsCl})=0.70$. At 940 K, the change in slope of the straight line in the diagram can readily be seen. This temperature corresponds to the liquidus temperature for the sample composition $x(\mathrm{CsCl})=0.6$ (cf. Fig. 1b). This means that the initial sample composition changed from $x(\mathrm{CsCl})=0.7$ to 0.6 during the measurement as a result of incongruent vaporization.

Thermodynamic activities and free enthalpies of formation of $Cs_3LnCl_{6(s)}$

The thermodynamic activities of CsCl in the condensed phases of the systems CsCl–$LnCl_3$ were obtained from the $CsCl_{(g)}$ partial pressures over the pure substance, $p^o(CsCl)$, and over the samples, $p(CsCl)$, according to the equation

$$a(CsCl)=p(CsCl)/p^o(CsCl) \tag{5}$$

The species $CsCl_{(g)}$ and $CsLnCl_{4(g)}$ were identified for all the samples of composition $x(CsCl)<0.75$, whereas the partial pressure of $LnCl_{3(g)}$ could be determined only for the $LnCl_3$-rich samples. The thermodynamic activities of $LnCl_3$ were therefore determined by use of the pressure-independent reaction

$$CsCl_{(g)}+LnCl_{3(s)}=CsLnCl_{4(g)} \tag{6}$$

The following relation resulted for the evaluation of the thermodynamic activities for each composition of the system CsCl–$LnCl_3$ [5]:

$$a(LnCl_3) = p(CsLnCl_4)/[p(CsCl)K^o_p] \tag{7}$$

where K^o_p is the equilibrium constant of the reaction shown in Eq. (6). K^o_p was computed from the partial pressures obtained in phase fields 5 and 6 in Fig. 1, assuming $a(LnCl_3)=1$.

Table 3 gives the thermodynamic activities of both components, obtained at 950 K in different runs for the samples corresponding to phase field 3, $\{Cs_3LnCl_{6(s)}+\text{liquid}\}$. These activities were interpolated from the $\ln a(i)=f(1/T)$ relationships in each run. The free enthalpy of formation for the high-temperature modifications of $Cs_3LnCl_{6(s)}$ according to the reaction

$$3CsCl_{(s)}+LnCl_{3(s)} \rightarrow H\text{–}Cs_3LnCl_{6(s)} \tag{8}$$

was computed from the relation

$$\Delta_f G^o(H\text{–}Cs_3LnCl_{6(s)},T) = RT\ln[a(LnCl_3)a^3(CsCl)] \tag{9}$$

Via adoption of the enthalpies of formation of the compounds $Cs_3LnCl_{6(s)}$ from the constituent chlorides at 298.15 K [15, 16], the entropies of the reactions given in Eq. (8) were calculated. The thermodynamic functions of phase transitions for $CsCl_{(s)}$ [17] and $Cs_3LnCl_{6(s)}$ [4] were additionally used for the calculations. The resulting entropies are presented in Table 3. The mean values obtained in different runs are given in Table 3 as selected values.

Finally, the following relationships were obtained for the formation reactions shown in Eq. (8):

$$\Delta_f G^\circ[\text{H–Cs}_3\text{CeCl}_{6(s)}]\,/\,\text{kJ mol}^{-1} = -27.0-0.0561T,\quad 743\ \text{K}<T<1108\ \text{K} \tag{10}$$

$$\Delta_f G^\circ[\text{H–Cs}_3\text{NdCl}_{6(s)}]\,/\,\text{kJ mol}^{-1} = -40.3-0.0447T,\quad 743\ \text{K}<T<1103\ \text{K} \tag{11}$$

Table 3 Thermodynamic activities in the phase field {liquid+$Cs_3LnCl_{6(s)}$}, free enthalpy and entropy of formation of ternary compounds $Cs_3LnCl_{6(s)}$ from the constituent solid halides

x(CsCl)[a]	a(CsCl)	a($LnCl_3$)	$\Delta_f G^\circ$(950 K)/ kJ mol^{-1}	$\Delta_f S^\circ$(950 K)/ J mol^{-1}K^{-1}
Ln=Ce				
0.80	0.088	0.077	–77.84	53.5
0.80	0.078	0.052	–83.80	59.8
0.70	0.110	0.033	–79.24	55.0
Selected:	0.092±0.016	0.054±0.022	–80.3±3.1	56.1±3.3
Ln=Nd				
0.80	0.068	0.155	–78.60	40.3
0.80	0.080	0.064	–81.54	43.4
0.80	0.043	0.175	–88.55	50.8
0.70	0.051	0.136	–86.18	48.3
0.70	0.079	0.089	–79.11	40.9
Selected:	0.064±0.017	0.124±0.046	–82.8±4.4	44.7±4.6

[a] Initial composition of the sample

Conclusions

The thermodynamic stability of the condensed phases for given temperature and chemical composition results from the thermodynamic functions of these phases. If the phase composition of the system changes, a change also takes place in the thermodynamic properties of the system. The change in the partial thermodynamic quantities at the phase transitions is more significant than the change in the integral functions.

The equilibrium partial pressures of the components as functions of temperature and/or composition therefore yield information relating to the phase equilibria in the condensed phases. We have demonstrated here the potential of Knudsen effusion mass spectrometry for such investigations. The thermodynamic activities in the systems CsCl–$LnCl_3$ and the free enthalpies and entropies of formation of the ternary compounds $Cs_3LnCl_{6(s)}$ resulted from the equilibrium data.

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