Thermodynamic Properties of KCl–$CeCl_3$ Binary System

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ABSTRACT

The relative partial free energies of $CeCl_3$ and KCl within KCl-$CeCl_3$ binary molten salts were derived through reassessment of the experimental data reported in the literature.

Keywords: KCl–$CeCl_3$; Thermodynamic calculation; Phase diagram

1. INTRODUCTION

During a course of studies for better understanding of pyrometallurgical treatment of spent nuclear fuel, it became necessary to establish appropriate oxygen and chlorine potentials to recover cerium as CeO_2 from $CeCl_3$-containing molten salts. With respect to this, attention should be focused on phase stability of CeO_2. Dotted line in **Figure 1** indicates phase boundaries between $\{CeCl_3\}$ and $<CeO_2>$ at 1073 K, corresponding to equilibrium equation;

$$<CeO_2> + (3/2)\,Cl_2 = \{CeCl_3\} + O_2 \qquad (1)$$

Thermodynamic data used to draw this diagram were taken from Kubaschewski et al./1/. This figure implies that cerium would be separated as solid CeO_2 from chloride melts. Keeping this in mind, {KCl–$CeCl_3$} molten salts of X_{CeCl_3} = 0.03 were brought into equilibrium with gas streams of controlled P_{O_2} and P_{Cl_2} at 1073 K /2/. With P_{O_2} and P_{Cl_2} expressed by solid circles of Figure 1, $<CeO_2>$ precipitated from molten {KCl-$CeCl_3$} salts of X_{CeCl_3} = 0.03, while no precipitation was observed at open circles, even though they lie in the stability field of CeO_2. This is not surprising because the phase boundaries given by broken line of Figure 1 are for unit activities. The $CeCl_3$ activities in molten {KCl-$CeCl_3$} salts of X_{CeCl_3} = 0.03 should be much lower than unity. In order to draw exact phase boundary line between $<CeO_2>$ and {KCl-$CeCl_3$} with $X_{CeCl_3} < 1$, knowledge of the $CeCl_3$ activities is essential.

To the best of the authors' knowledge, however, such thermodynamic data are not available in the literature, while phase diagram of the system KCl-$CeCl_3$ was reported by Sun and Morozov /3/, as shown in **Figure 2**. In their experiments, twenty mixtures of KCl and $CeCl_3$ were first melted in quartz vessels, and then cooled. First, second and third temperature halts were observed, depending upon compositions. These are expressed by open and solid circles, and open triangles, respectively. Based upon such cooling-curve measurements, Sun and Morozov gave dotted lines of Figure 2.

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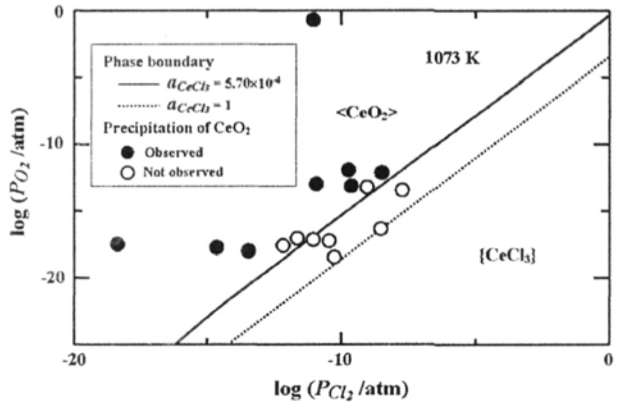

Fig. 1: Phase boundary line between solid CeO$_2$ and KCl–CeCl$_3$ molten salt at 1073 K.

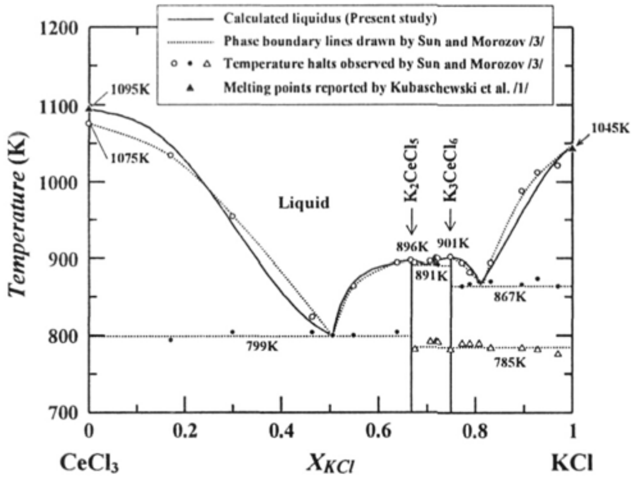

Fig. 2: The measured and calculated liquidus lines for KCl–CeCl$_3$ binary system.

The present study is aimed at deriving the relative partial molar free energies of CeCl$_3$ and KCl through reassessment of the experimental data by Sun and Morozov. Toward this objective, the formula to describe the activities of KCl referred to pure liquid KCl, $a_{KCl}{}^{(L)}$ with best fitting was

$$
\begin{aligned}
&RT \ln a_{KCl}{}^{(L)}\\
&= RT \ln X + a(1-X)^6 + b(1-X)^5 + c(1-X)^4\\
&+ d(1-X)^3 + e(1-X)^2
\end{aligned}
\qquad (2)
$$

where $X = X_{KCl}$ and a, b, c, d and e are constants. Through Gibbs–Duhem integration, it follows

$$
\begin{aligned}
&RT \ln a_{CeCl_3}{}^{(L)}\\
&= RT \ln(1-X) + aX^6\\
&- [(24/5)a + b]X^5 + [9a + (15/4)b + c]X^4\\
&- [8a + 5b + (8/3)c + d]X^3\\
&+ [3a + (5/2)b + 2c + (3/2)d + e]X^2
\end{aligned}
\qquad (3)
$$

where $a_{CeCl_3}{}^{(L)}$ is the CeCl$_3$ activity referred to pure liquid CeCl$_3$.

The activities of KCl and CeCl$_3$ referred to pure solid KCl and CeCl$_3$, $a_{KCl}{}^{(S)}$ and $a_{CeCl_3}{}^{(S)}$, are given by

$$
\begin{aligned}
&RT \ln a_{KCl}{}^{(S)}\\
&= RT \ln X + a(1-X)^6 + b(1-X)^5\\
&+ c(1-X)^4 + d(1-X)^3 + e(1-X)^2\\
&+ \Delta G^{\circ}{}_f(KCl)
\end{aligned}
\qquad (4)
$$

$$
\begin{aligned}
&RT \ln a_{CeCl_3}{}^{(S)}\\
&= RT \ln(1-X) + aX^6 - [(24/5)a + b]X^5\\
&+ [9a + (15/4)b + c]X^4\\
&- [8a + 5b + (8/3)c + d]X^3\\
&+ [3a + (5/2)b + 2c + (3/2)d + e]X^2\\
&+ \Delta G^{\circ}{}_f(CeCl_3)
\end{aligned}
\qquad (5)
$$

where $\Delta G^{\circ}{}_f(KCl)$ and $\Delta G^{\circ}{}_f(CeCl_3)$ represent Gibbs energy changes for the fusions of KCl and CeCl$_3$, respectively.

2. THERMODYNAMIC DATA USED FOR CALCULATION

Thermodynamic data used for calculations are listed in Tables 1(a), (b) and (c).

2.1 Heat capacities and heats of fusion of KCl and CeCl$_3$

For pure KCl and CeCl$_3$, values for *Cp*, heats of fusion, and the melting temperatures were taken from Kubaschewski et al./1/. It is noted as shown in Figure 2, melting point of CeCl$_3$ reported by Kubaschewski et al., 1095 K, are 20 K greater than that by Sun and Morozov.

By using heat capacity data for KCl and CeCl$_3$, given in Table 1(a), Gibbs energy changes for the fusions of KCl and CeCl$_3$, $\Delta G^{\circ}{}_f(KCl)$ and $\Delta G^{\circ}{}_f(CeCl_3)$, respectively, could be calculated as

$$\Delta G^\circ f(KCl)\ /\mathrm{J{\cdot}mol^{-1}} = 4.77\times10^{3} + 2.15\times10^{2}\,T + 1.27\times10^{-2}\,T^{2} + 1.82\times10^{5}\,T^{-1} - 3.36\times10\,T\ln T \quad (6)$$

$$\Delta G^\circ f(CeCl_3)\ /\mathrm{J{\cdot}mol^{-1}} = 1.04\times10^{4} + 3.17\times10^{2}\,T + 6.80\times10^{-3}\,T^{2} - 2.51\times10^{5}\,T^{-1} - 4.77\times10\,T\ln T \quad (7)$$

Table 1(a) Thermodynamic data used for calculations:
Heat capacities Cp, heats of fusion ΔHf and melting points Tm of KCl and $CeCl_3$.

Substance	Cp /J·K^{-1}·mol^{-1} = $a + b\times10^{-3}\,T + c\times10^{5}\,T^{-2}$			ΔHf/J·mol^{-1}	Tm /K	Ref.
	a	b	c			
<KCl>	40.02	25.47	3.64	-	-	/1/
{KCl}	73.60	-	-	26,300	1045	/1/
<$CeCl_3$>	97.49	13.60	-5.02	-	-	/1/
{$CeCl_3$}	145.18	-	-	54,000	1095	/1/

Table 1 (b) Eutectic temperatures and compositions X_{KCl} for KCl–$CeCl_3$ binary system.

Eutectic reaction	*Eutectic temperature /K*	X_{KCl} *in liquid phase*	Ref.
Liquid ↔ $CeCl_3$ + K_2CeCl_5	799	0.507	/3/
Liquid ↔ K_2CeCl_5 + K_3CeCl_6	891	0.698	/3/
Liquid ↔ K_3CeCl_6 + KCl	867	0.810	/3/

Table 1(c) Congruent melting temperatures.

Compound	*Congruent melting temperature /K*	Ref.
K_2CeCl_5	896	/3/
K_3CeCl_6	901	/3/

2.2 Eutectic temperatures and compositions

For the following eutectic reactions, the temperatures and the compositions of the liquid phases the values reported by Sun and Morozov /3/ were accepted.

Eutectic reaction{1}	Liquid ↔ <$CeCl_3$> + K_2CeCl_5>	T=799K X=0.507
Eutectic reaction{2}	Liquid ↔ <K_2CeCl_5> + <K_3CeCl_6>	T=891K X=0.698
Eutectic reaction {3}	Liquid ↔ <K_3CeCl_6> + <KCl>	T=867K X=0.810

2.3 Melting points and formation free energies of K_2CeCl_5 and K_3CeCl_6

For the melting points of K_2CeCl_5 and K_3CeCl_6, values reported by Sun and Morozov, *i.e.* 896 K and 901 K, respectively, were accepted /3/, while the Gibbs free energy changes for the formations of K_2CeCl_5 and K_3CeCl_6 are not available in the literature, hence assumed to be expressed as the linear functions of temperature;

$$2\,\langle KCl\rangle + \langle CeCl_3\rangle = \langle K_2CeCl_5\rangle \quad (8)$$

$$\Delta G^\circ\langle K_2CeCl_5\rangle = A + B\,T \qquad (A, B = \text{constant}) \quad (9)$$

$$3\,\langle KCl\rangle + \langle CeCl_3\rangle = \langle K_3CeCl_6\rangle \quad (10)$$

$$\Delta G^\circ\langle K_3CeCl_6\rangle = C + D\,T \qquad (C, D = \text{constant}) \quad (11)$$

3. OPTIMIZATION PROCEDURE AND DISCUSSION

At the melting points of K_2CeCl_5, 896 K, molten {KCl-$CeCl_3$} salt of X = 0.667 is to be in equilibrium with <K_2CeCl_5>. Hence we have

$$\Delta G^\circ\langle K_2CeCl_5\rangle = 2\,RT\ln a_{KCl}{}^{(S)} + RT\ln a_{CeCl_3}{}^{(S)} \qquad \Big|\ T=896\mathrm{K},\ X=0.667 \quad (12)$$

Similarly, for the equilibrium between {KCl–CeCl$_3$} salt of X = 0.750 and <K$_3$CeCl$_6$> at melting point of K$_3$CeCl$_6$, 901 K, we have

$$\begin{array}{l|l} \Delta G^\circ\!<\!K_3CeCl_6\!> & T\text{=901K} \\ = 3\,RT\ln a_{KCl}{}^{(S)} + RT\ln a_{CeCl_3}{}^{(S)} & X\text{=0.750} \end{array} \quad (13)$$

For eutectic reaction {1}, at 799 K, pure solid CeCl$_3$ and K$_2$CeCl$_5$ are to be in equilibrium with molten salt of X = 0.507:

$$\begin{array}{l|l} \Delta G^\circ\!<\!K_2CeCl_5\!> = 2\,RT\ln a_{KCl}{}^{(S)} & T\text{=799K} \\ & X\text{=0.507} \end{array} \quad (14)$$

$$\begin{array}{l|l} RT\ln a_{CeCl_3}{}^{(S)} = 0 & T\text{=799K} \\ & X\text{=0.507} \end{array} \quad (15)$$

In similarly to Eqs. (14) and (15), with eutectic reaction {2}, at 891 K and X = 0.698, we have

$$\begin{array}{l|l} \Delta G^\circ\!<\!K_2CeCl_5\!> & T\text{=891K} \\ = 2\,RT\ln a_{KCl}{}^{(S)} + RT\ln a_{CeCl_3}{}^{(S)} & X\text{=0.698} \end{array} \quad (16)$$

$$\begin{array}{l|l} \Delta G^\circ\!<\!K_3CeCl_6\!> & T\text{=891K} \\ = 3\,RT\ln a_{KCl}{}^{(S)} + RT\ln a_{CeCl_3}{}^{(S)} & X\text{=0.698} \end{array} \quad (17)$$

Similarly for eutectic reaction {3}, it follows with T = 867 K and X = 0.810.

$$\begin{array}{l|l} \Delta G^\circ\!<\!K_3CeCl_6\!> = RT\ln a_{CeCl_3}{}^{(S)} & T\text{=867K} \\ & X\text{=0.810} \end{array} \quad (18)$$

$$\begin{array}{l|l} RT\ln a_{KCl}{}^{(S)} = 0 & T\text{=867K} \\ & X\text{=0.810} \end{array} \quad (19)$$

On the other hand, the liquidus temperatures can be calculated by

For <CeCl$_3$> + liquid;

$$RT\ln a_{CeCl_3}{}^{(S)} = 0 \quad (20)$$

For <K$_2$CeCl$_5$> + liquid;

$$\Delta G^\circ\!<\!K_2CeCl_5\!> = 2\,RT\ln a_{KCl}{}^{(S)} + RT\ln a_{CeCl_3}{}^{(S)} \quad (21)$$

For <K$_3$CeCl$_6$> + liquid;

$$\Delta G^\circ\!<\!K_3CeCl_6\!> = 3\,RT\ln a_{KCl}{}^{(S)} + RT\ln a_{CeCl_3}{}^{(S)} \quad (22)$$

For <KCl> + liquid;

$$RT\ln a_{KCl}{}^{(S)} = 0 \quad (23)$$

Attention is now focused on Eqs. (12) to (19). These eight equations involves nine unknown parameters: *i.e.*, *a*, *b*, *c*, *d*, *e*, *A*, *B*, *C* and *D*. These parameters can be optimized by minimizing the summations of the differences between the liquidus temperatures by Sun and Morozov /3/ and those calculated by Eqs. (20) through (23).The optimized values for *a*, *b*, *c*, *d*, *e*, *A*, *B*, *C* and *D* are listed in **Table 2**. Needless to say, these values are valid for temperatures used for optimization only, *i.e.*, between 799 and 1095 K. The calculated liquidus curves are given by solid lines in Figure 2.

Table 2

Optimized parameters for KCl–CeCl$_3$ binary system.

a (J·mol^{-1})	b (J·mol^{-1})	c (J·mol^{-1})	d (J·mol^{-1})	e (J·mol^{-1})
7.98×10^5	−1.15×10^6	−8.61×10^3	5.07×10^5	−1.68×10^5
A (J·mol^{-1})	B (J·K^{-1}·mol^{-1})	C (J·mol^{-1})	D (J·K^{-1}·mol^{-1})	
7.58×10^4	−9.77×10^1	8.38×10^4	−1.09×10^2	

For the activities of KCl and CeCl$_3$ within {KCl–CeCl$_3$} solutions, eventually we had

$$\begin{aligned} &RT\ln a_{KCl}{}^{(S)}\ /\text{J·mol}^{-1} \\ &= RT\ln X + 7.98\times10^5\,(1-X)^6 \\ &- 1.15\times10^6\,(1-X)^5 - 8.61\times10^3\,(1-X)^4 \\ &+ 5.07\times10^5\,(1-X)^3 - 1.68\times10^5\,(1-X)^2 \\ &+ 4.77\times10^3 + 2.15\times10^2\,T + 1.27\times10^{-2}\,T^2 \\ &+ 1.82\times10^5\,T^{-1} - 3.36\times10\,T\ln T \end{aligned} \quad (24)$$

$$\begin{aligned} &RT\ln a_{KCl}{}^{(L)}\ /\text{J·mol}^{-1} \\ &= RT\ln X + 7.98\times10^5\,(1-X)^6 \\ &- 1.15\times10^6\,(1-X)^5 - 8.61\times10^3\,(1-X)^4 \\ &+ 5.07\times10^5\,(1-X)^3 - 1.68\times10^5\,(1-X)^2 \end{aligned} \quad (25)$$

$$\begin{aligned} &RT\ln a_{CeCl_3}{}^{(S)}\ /\text{J·mol}^{-1} \\ &= RT\ln(1-X) + 7.98\times10^5\,X^6 \\ &- 2.68\times10^6\,X^5 + 2.86\times10^6\,X^4 - 1.12\times10^6\,X^3 \\ &+ 9.43\times10^4\,X^2 + 1.04\times10^4 + 3.17\times10^2\,T \\ &+ 6.80\times10^{-3}\,T^2 - 2.51\times10^5\,T^{-1} - 4.77\times10\,T\ln T \end{aligned} \quad (26)$$

$$\begin{aligned} &RT\ln a_{CeCl_3}{}^{(L)}\ /\text{J·mol}^{-1} \\ &= RT\ln(1-X) + 7.98\times10^5\,X^6 - 2.68\times10^6\,X^5 \\ &+ 2.86\times10^6\,X^4 - 1.12\times10^6\,X^3 + 9.43\times10^4\,X^2 \end{aligned} \quad (27)$$

For {KCl–CeCl$_3$} molten salt of $X_{CeCl_3} = 0.03$ at 1073 K, by using Eq. (27), it follows

$$a_{CeCl_3}^{(l)} = 5.70 \times 10^{-4} \tag{28}$$

This value of 5.70×10^{-4} shows a very much negative deviation from Raoult's law, corresponding to strong affinity between KCl and CeCl$_3$ to form the intermediate compounds K_2CeCl_5 and K_3CeCl_6. Solid line of Figure 1 indicates phase boundary between CeO$_2$ and CeCl$_3$ of 5.70×10^{-4} activity. As shown in Figure 1, open circles now lie within the unstable region of CeO$_2$, being consistent with the experimental observations.

4. CONCLUSIONS

The relative partial molar free energies of CeCl$_3$ and KCl within molten {KCl–CeCl$_3$} salts were derived through reassessment of the experimental data by Sun and Morozov. The calculated phase boundaries between <CeO$_2$> and {KCl–CeCl$_3$} molten salt were consistent with the observations of CeO$_2$ precipitations from molten {KCl–CeCl$_3$} salts.

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