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Correction

Correction: Ocádiz Flores et al. Thermodynamic Description of the ACl-$ThCl_4$ (A = Li, Na, K) Systems. *Thermo* 2021, *1*, 122–133

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Corrected excess Gibbs energies of the liquid solutions in the ACl-$ThCl_4$ (A = Li, Na, K), as well as revised standard enthalpies of formation and standard entropies of the intermediate phases occurring in the binary systems, are presented. The phase diagrams are reproduced to a similar level of accuracy as in the original publication, and the trends in thermodynamic stability of the liquid solutions are maintained. That is, the main conclusions of the paper are not affected. The original publication has also been updated.

Text Correction

The optimized Gibbs energies for the second-nearest neighbor (SNN) exchange reactions of the liquid solutions were incorrectly reported to be polynomial expansions in terms of pair fraction expansions in Equations (7)–(9) of the original publication [1]. Rather, they were polynomial expansions in terms of coordination-equivalent fractions Y_A, Y_{Th} (A = Li, Na, K). Given $Z^A_{AB/Cl}$ and $Z^B_{AB/Cl}$, the SNN coordination numbers of ions A and B in a binary chloride melt, their equivalent pair fractions are defined as [36]:

$$Y_A = Z^A_{AB/Cl} \cdot n_A / (Z^A_{AB/Cl} \cdot n_A + Z^B_{AB/Cl} \cdot n_B) \quad (1)$$

$$Y_B = 1 - Y_A \quad (2)$$

where n_i corresponds to the number of moles of species i. To be consistent with the notation just introduced, the aforementioned Equations (7)–(9) in [1] should have been written as:

$$\Delta g_{LiTh/Cl} = -8000 - 4000 \cdot Y_{Li} - 2700 \cdot Y_{Th} \text{ J} \cdot \text{ mol}^{-1} \quad (3)$$

$$\Delta g_{NaTh/Cl} = -27,700 - 10,000 \cdot Y^2_{Na} - 20,000 \cdot Y_{Th} \text{ J} \cdot \text{ mol}^{-1} \quad (4)$$

$$\Delta g_{KTh/Cl} = -28,000 - 16,000 \cdot Y^2_{K} - 25,000 \cdot Y_{Th} \text{ J} \cdot \text{ mol}^{-1} \quad (5)$$

However, in order to be compatible with existing molten salt databases for nuclear applications, the excess Gibbs energies of the liquid solutions should better be expressed as polynomial expansions in the composition term χ:

$$\chi_{AB/Cl} = \frac{X_{AA}}{X_{AA} + X_{AB} + X_{BB}} \quad (6)$$

where X_{AA}, X_{BB} and X_{AB} represent cation–cation pair mole fractions. Note that in the case of binary solutions with a common anion, $\chi_{AB/Cl} = X_{AA}$, and $\chi_{BA/Cl} = X_{BB}$. Equations (7)–(9) were found to reproduce the ACl-$ThCl_4$ (A = Li, Na, K) phase diagrams with comparable accuracy to that obtained with Equations (3)–(5).

$$\Delta g_{LiTh/Cl} = -8000 - 3600 \cdot \chi_{LiTh/Cl} - 7300 \cdot \chi_{ThLi/Cl} \text{ J} \cdot \text{ mol}^{-1} \quad (7)$$

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$$\Delta g_{NaTh/Cl} = -27,700 - 7500 \cdot \chi_{NaTh/Cl} - 14,000 \cdot \chi_{ThNa/Cl} \text{ J} \cdot \text{ mol}^{-1} \quad (8)$$

$$\Delta g_{KTh/Cl} = -40,000 - 10,000 \cdot \chi_{ThK/Cl} \text{ J} \cdot \text{ mol}^{-1} \quad (9)$$

Related to the changes in the thermodynamic model, two amendments to the original text were necessary, related to the mixing entropy of (K,Th)Cl_x solution (see Figure 4 in [1]). In Section 3.2, the sentence '(K,Th)Cl_x displays such a strong SRO that the entropy of mixing is negative at its minimum near $X(ThCl_4) = 0.4\ldots$' has been replaced with '(K,Th)Cl_x displays such strong SRO that the entropy of mixing approaches zero at its minimum near $X(ThCl_4) = 0.4$'. In Section 4, the sentence '(K,Th)Cl_x even displays negative entropy of mixing where the enthalpy of mixing is greatest in magnitude' has been replaced with '(K,Th)Cl_x even displays an entropy of mixing close to zero where the enthalpy of mixing is greatest in magnitude'.

Error in Tables

Using the correct Equations (7)–(9), the Gibbs energy terms of the intermediate phases needed some adjustment also, namely the standard enthalpies of formation and, in the case of K_2ThCl_6, also the standard entropy. The re-assessed values are given in Table 2, with all other values for completeness.

The invariant equilibria as calculated with the corrected model are listed in Table 4. The corrected Tables appears below:

Table 2. Thermodynamic data for intermediate compounds used in this work for the phase diagram assessment: $\Delta_f H^o_m(298\ K)/(kJ\cdot mol^{-1})$, $S^o_m(298\ K)/(J\cdot K^{-1}\cdot mol^{-1})$, and heat capacity coefficients $C_{p,m}(T/K)/(J\cdot K^{-1}\cdot mol^{-1})$, where $C_{p,m}(T/K) = a + b\cdot T + c\cdot T^2 + d\cdot T^{-2} + e\cdot T^3$. Optimised data are shown in **bold**.

Compound	$\Delta_f H^o_m(298\ K)/(kJ\cdot mol^{-1})$	$S^o_m(298\ K)/(J\cdot K^{-1}\cdot mol^{-1})$	$C_{p,m}(T/K)/(J\cdot K^{-1}\cdot mol^{-1}) = a + b\cdot T + c\cdot T^2 + d\cdot T^{-2}$				Range	Reference
			a	b	c	d		
LiCl(cr)	−408.266	59.3	44.70478	0.01792765	1.863482×10^{-6}	−194,457.7	298–883	[27]
			73.30619	−0.009430108		33,070.5	883–2000	[27]
LiCl(l)	−388.4342	81.76	44.70478	0.01792765	1.863482×10^{-6}	−194,457.7	298–883	[27]
			73.30619	−0.009430108		33,070.5	883–2000	[27]
NaCl(cr)	−411.260	72.15	47.72158	0.0057	1.21466×10^{-5}	−882.996	298–1074	[28]
NaCl(l)	−390.853	83.302	68.0				298–2500	[28,29]
KCl(cr)	−436.6841	82.555	50.47661	0.005924377	7.496682×10^{-6}	−144,173.9	298–700	[27]
			143.5698	−0.1680399	9.965702×10^{-5}	−8,217,836	700–1044	[27]
			73.59656			−8,217,836	1044–2000	[27]
KCl(l)	−410.4002	107.7311	50.47661	0.005924377	7.496682×10^{-6}	−144,173.9	298–700	[27]
			143.5698	−0.1680399	9.965702×10^{-5}	−8,217,836	700–1044	[27]
			73.59656				1044–2000	[27]
α-$ThCl_4$(cr)	**−1191.3012**	**176.135**	120.293	0.0232672		−615,050	298–1042	this work, [35]
β-$ThCl_4$(cr)	−1186.300	183.499	120.293	0.0232672		−615,050	298–1042	[5,34]
$ThCl_4$(l)	−1149.740	197.626	167.4				298–1500	[5,34]
Li_4ThCl_8(cr)	**−2834.966**	**413.34**	299.11212	0.0949778	7.453928×10^{-6}	−1,392,880.8	298–883	this work
			413.51776	−0.014453232		−482,768	883–1042	
			437.1957	−0.037720432		132,282	1042–2000	
Na_2ThCl_6(cr)	**−2051.540**	**328.0**	215.73616	0.0346672	2.42932×10^{-5}	−616,815.992	298–1042	this work
			239.41	0.0114	2.42932×10^{-5}	−1765.992	1042–1074	
$KThCl_5$(cr)	**−1685.000**	**258.69**	170.76961	0.029191577	7.496682×10^{-6}	−759,223.9	298–700	this work
			263.8628	−0.1447727	9.965702×10^{-5}	−8,832,886	700–1042	
			287.5408	−0.1680399	9.965702×10^{-5}	−8,217,836	1042–1044	
			217.568				1044–2000	
K_2ThCl_6(cr)	**−2139.850**	**380.5**	221.24622	0.035115954	1.4993364×10^{-5}	−903,397.8	298–700	this work
			407.4326	−0.3128126	1.9931404×10^{-4}	−17,050,722	700–1042	
			431.1106	−0.3360798	1.9931404×10^{-4}	−16,435,672	1042–1044	
			291.16408				1042–2000	

Table 4. Invariant equilibrium data in the ACl-$ThCl_4$ systems.

System	Equilibrium	Invariant Reaction	This Study (calc.)		Tanii et al. [21]		Vokhmyakov et al. [20]		Oyamada [19]	
			X($ThCl_4$)	T / K	X($ThCl_4$)	T / K	X($ThCl_4$)	T / K	X($ThCl_4$)	T / K
LiCl-$ThCl_4$	Congruent Melting	LiCl = L	1	883	1	881			1	910
	Peritectic	Li_4ThCl_8 = LiCl + L	0.2	723	0.2	725	0.2	723	-	-
	Eutectic	Li_4ThCl_8 + β-$ThCl_4$ = L	0.343	695	-	690	0.38	681	0.35	703
	α-β transition	α-$ThCl_4$ = β-$ThCl_4$	1	679						
	Congruent Melting	β-$ThCl_4$ = L	1	1042	1	1041			1	1070
NaCl-$ThCl_4$	Congruent melting	NaCl = L	0	1074	0	1074			0	1097
	Eutectic	NaCl + Na_2ThCl_6 = L	0.251	657	-	639	0.255	633	0.26	667
	Congruent Melting	Na_2ThCl_6 = L	1/3	703	1/3	708	1/3	708	1/3	729
	Eutectic	Na_2ThCl_6 + α-$ThCl_4$ = L	0.457	654	-	637	0.45	648	0.49	686
KCl-$ThCl_4$	Congruent melting	KCl = L	0	1044	0	1043			0	1070
	Eutectic	KCl + K_2ThCl_6 = L	0.206	894	-	895	0.25	903	0.15	917
	Congruent melting	K_2ThCl_6 = L	1/3	977	1/3	988	1/3	978	0.25 [a]	997
	Eutectic	K_2ThCl_6 + $KThCl_5$ = L	0.467	697	-	705	0.42	668	0.43	681
	Congruent melting	$KThCl_5$ = L	0.5	702			0.5	703	0.5	741
	Eutectic	$KThCl_5$ + β-$ThCl_4$ = L	0.536	699			0.54	693	0.56	706

[a] Interpreted by the author to be the congruent melting of K_3ThCl_7.

Error in Figures

The phase diagrams as calculated with this corrected model are shown in Figures 1–3. These figures replace Figures 1–3 of the original publication, while the mixing properties of the liquid solutions are shown in Figures 4a,b and 5, in place of Figures 4a,b and 5 of the original publication [1]. The latter properties display the same trends (discussed in [1]) as those appearing when polynomials in coordination-equivalent sites were used.

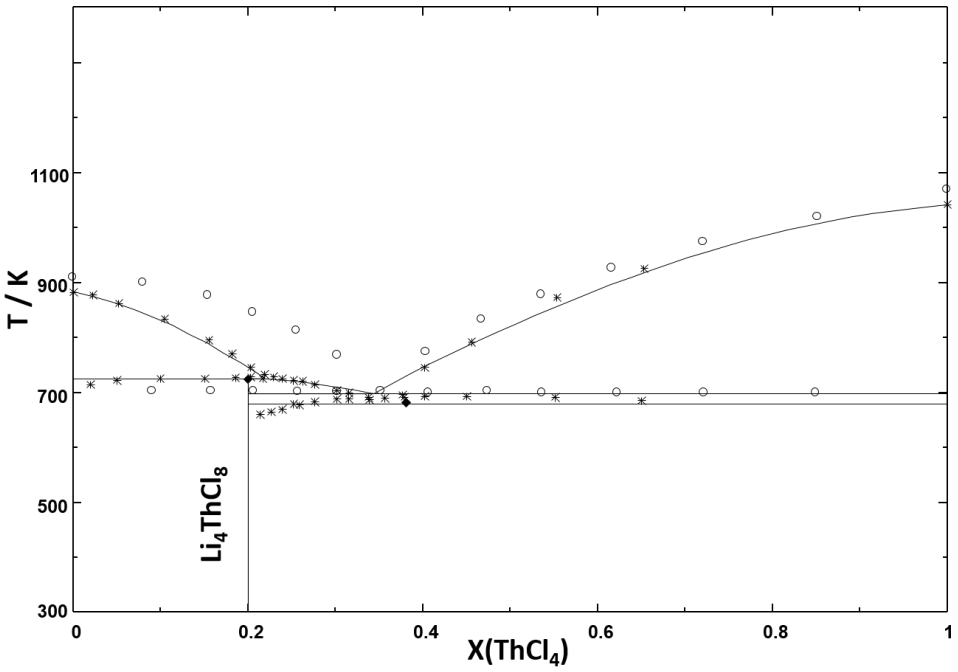


Figure 1. The LiCl-$ThCl_4$ phase diagram as re-calculated in this work. Symbols: phase diagram data reported by Tanii [21] (⁎), Oyamada [19] (○) and Vokhmyakov et al. [20] (⬥).

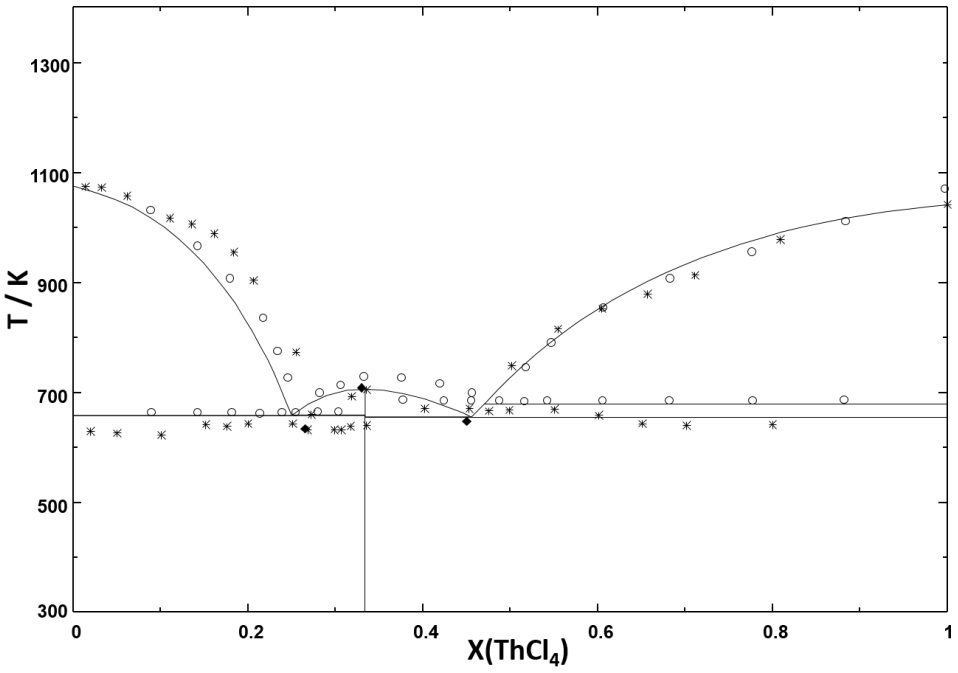


Figure 2. The NaCl-$ThCl_4$ phase diagram as re-calculated in this work. Symbols: phase diagram data reported by Tanii [21] (⁎), Oyamada [19] (○) and Vokhmyakov et al. [20] (⬥).

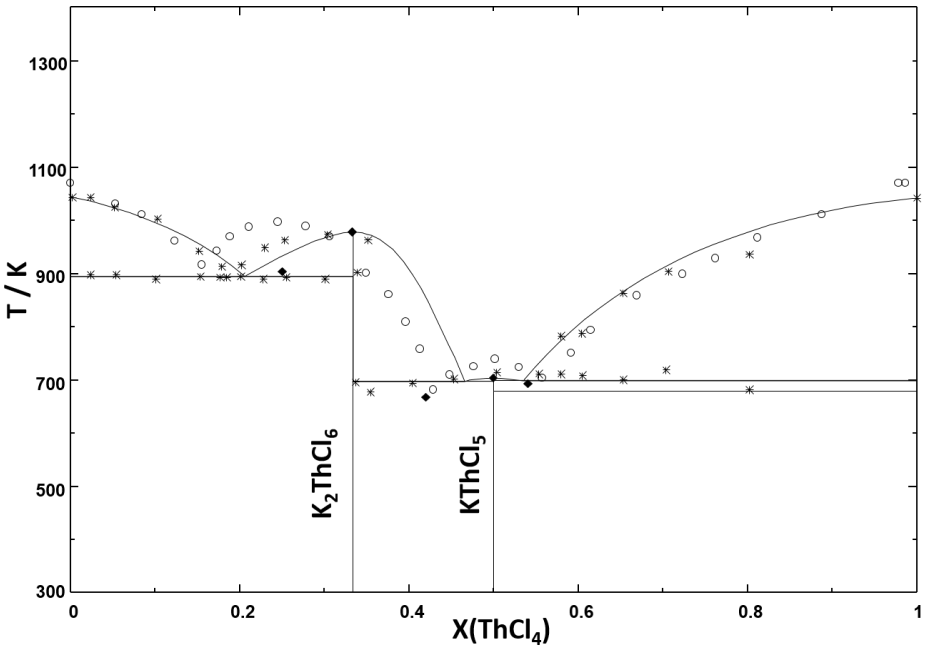
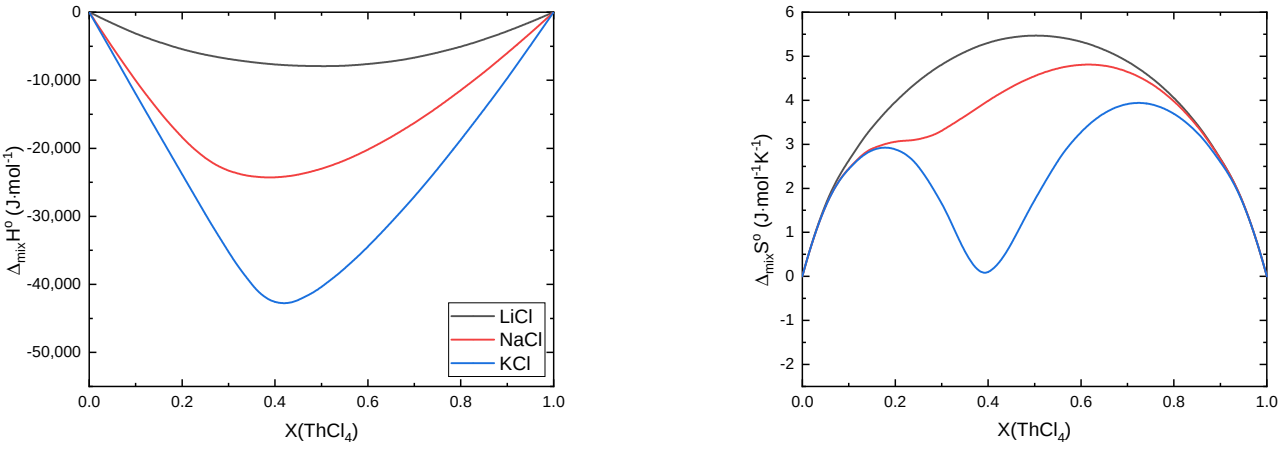


Figure 3. The KCl-$ThCl_4$ phase diagram as re-calculated in this work. Symbols: phase diagram data reported by Tanii [21] (⁎), Oyamada [19] (○) and Vokhmyakov et al. [20] (⬥).



(**a**) (**b**)

Figure 4. (**a**) Enthalpies and (**b**) entropies of mixing of the (A,Th)Cl_x liquid solutions calculated at T = 1100 K.

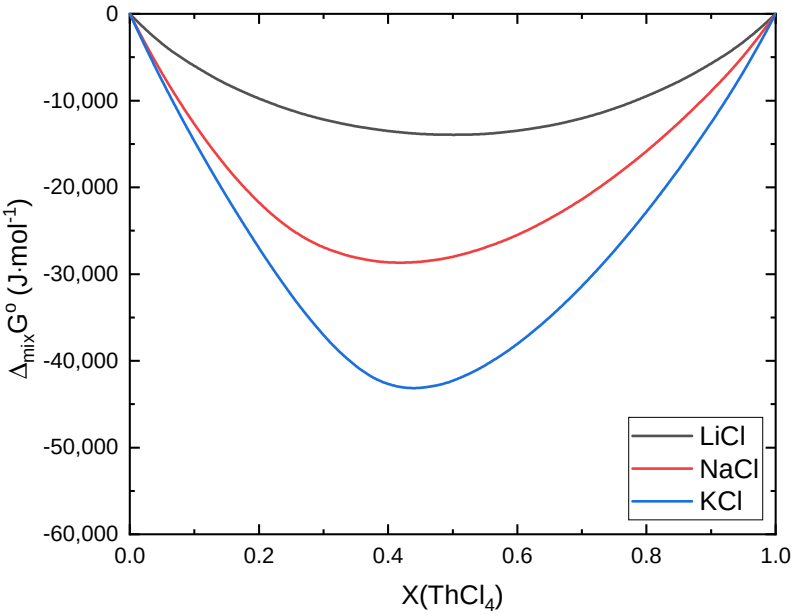


Figure 5. Gibbs energies of mixing of the (A,Th)Cl_x liquid solutions calculated at T = 1100 K.

Reference

1. Ocádiz Flores, J.A.; Rooijakkers, B.A.S.; Konings, R.J.M.; Smith, A.L. Thermodynamic Description of the ACl-$ThCl_4$ (A = Li, Na, K) Systems. *Thermo* **2021**, *1*, 122–133. [CrossRef]