ELSEVIER

Thermochimica Acta 383 (2002) 31–35

thermochimica acta

www.elsevier.com/locate/tca

Review

Thermodynamic re-optimization of the $DyCl_3$–KCl system

Xianran Xing[a,*], Shuyu Dai[a], Zhenqi Zhu[a], Toshihiro Tanaka[b]

[a]*Department of Physical Chemistry, University of Science and Technology Beijing, Beijing 100083, PR China*
[b]*Department of Materials Science and Processing, Osaka University, 2-1 Yamadaoka, Suita, Osaka 5650871, Japan*

Received 6 May 2001; accepted 29 June 2001

Abstract

The intermediate compounds, K_3DyCl_6, K_2DyCl_5 and KDy_2Cl_7, in the $DyCl_3$–KCl system, are confirmed by X-ray powder diffraction method. With CALPHAD technology the phase diagram of the $DyCl_3$–KCl system is re-optimized and calculated using ChemSage software. A set of thermodynamic functions has been optimized based on an interactive computer-assisted analysis. The calculated phase diagram and optimized thermodynamic parameters are thermodynamically self-consistent.

Keywords: Thermodynamic optimization; Intermediate compound; The $DyCl_3$–KCl system

1. Introduction

The thermodynamic properties and phase diagrams of the $DyCl_3$–MCl systems (M = alkali metals) play an important role to the production of metal dysprosium and useful to the recycle of the spent fuel from fast nuclear reactors.

To the $DyCl_3$–KCl system, the phase diagram was studied by Korshunov and Dorobot [1], Blachnik and Selle [2], Mochinaga et al. [3] and Seifert and Kraemer [4]. Blachnik and Selle [2] determined the part of the phase diagram ($0.5 > x_{KCl} > 0.0$) and found the stoichiometric compound KDy_2Cl_7 existed. The results measured by Mochinaga et al. [3] demonstrate that there exist only two stoichiometries of K_3DyCl_6 and KDy_3Cl_{10}, and agree to the Korshunov's work [1]. But the curve of phase transition at 375 °C in the range of $1.0 > x_{KCl} > 0.4$ could not be elucidated in the phase rule. Seifert et al. [4,5] systematically investigated the phase diagrams of the $DyCl_3$–MCl systems (M = alkali metals) by DTA, XRD and emf measurements. They characterized the phase diagram by three intermediate compounds, K_3DyCl_6, K_2DyCl_5 and KDy_2Cl_7 in the $DyCl_3$–KCl system. On the basis of the phase diagram taken from [3], Hatem and Gaune-Escard [6] assessed the $DyCl_3$–KCl system with surrounded statistical model (SIM) and calculated the Gibbs free energy of formation of two stoichiometries of K_3DyCl_6 and KDy_3Cl_{10}.

The purposes of present work are to identify the intermediate compounds in the $DyCl_3$–KCl system by XRD method, and to self-consistently re-optimize the phase diagram and thermodynamic properties with ChemSage software. The thermodynamic properties of mixed phase in liquid were described in Redlich–Kister equation. The thermodynamic parameters of pure salts $DyCl_3$ and KCl were extracted from SGTE databank [7].

2. Experiments

The hexahydrate $DyCl_3 \cdot 6H_2O$ was made from the starting material Dy_2O_3 (99.9%) dissolved in chlor-

---

[*] Corresponding author.
E-mail address: xing@ustb.edu.cn (X. Xing).

0040-6031/02/$ – see front matter © 2002 Elsevier Science B.V. All rights reserved.
PII: S0040-6031(01)00675-X

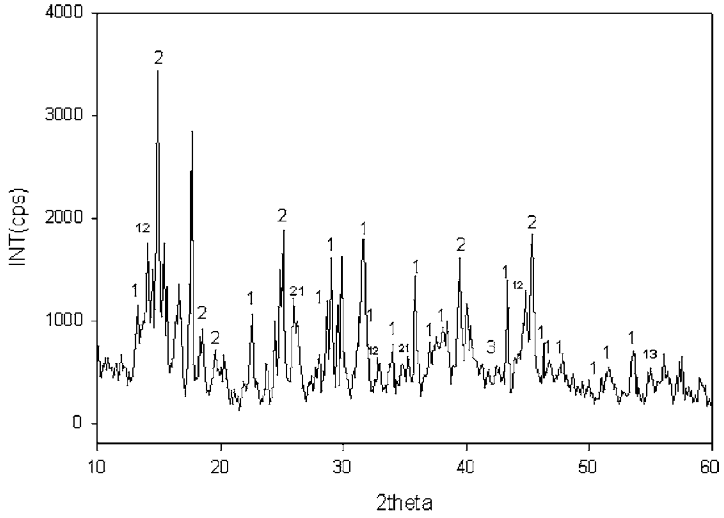

Fig. 1. XRD patterns of the sample at $x_{DyCl_3} = 0.4$ in the $DyCl_3$–KCl system. 1: K_2DyCl_5; 2: KDy_2Cl_7; 3: DyOCl.

hydric acid and recrystallized by vaporizing. The pure $DyCl_3$ was prepared by dehydrating the hexahydrate in an HCl stream. Precautions must be taken into account to avoid the formation of oxychlorides. KCl (AR grade) was dried at 400 °C for 24 h.

The samples (about 2.0 g) were weighed according to the appropriate amounts and fully mixed by melting in vacuum sealed quartz ampoules with a gas flame. The melts were homogenized by shaking and solidified by rapid cooling. The ampoules could be used after annealing for 1 week at 300 °C.

Phase identification and structure characterization were carried out using a Rigaku diffractometer with Cu Kα radiation. For measurements of the lattice parameters of compounds, pure Si powder was added to the samples as an internal standard.

Fig. 1 clearly shows the XRD patterns of the sample at $x_{DyCl_3} = 0.4$. The compounds K_2DyCl_5 and KDy_2Cl_7 were identified and indexed as orthorhombic and monoclinic systems, respectively. However, the weak traces of oxychloride DyOCl also was detected. Our results confirmed the phase diagrams determined by Seifert and Kraemer [4].

3. Optimization

The thermodynamic properties of two pure components $DyCl_3$ and KCl were extracted from SGTE databank provided by the Scientific Group Thermodata [7] (listed in Table 1). The enthalpies of mixing in the melts were taken from the works of Gaune-Escard et al. [8].

Table 1
The thermodynamic data of pure salts $DyCl_3$ and KCl [7]

Compounds	$\Delta H^{\circ}_{f(298)}$ (kJ mol^{-1})	$S^{\circ}_{(298)}$ (J mol^{-1})	$C_p = a + bT + cT^2 + d/T^2$ (Jmol^{-1}K^{-1})				T (K)	$\Delta_{fus}H$ (kJ mol^{-1})
			a	b	$10^4 \times c$	$10^{-5} \times d$		
$DyCl_3$	−995.792	157.737	94.5584	0.01799	0.00000	−1.42256	298–924	25.5200
			144.7660	0.00000	0.00000	0.00000	924–1300	
KCl	−436.684	82.555	50.4776	0.00592	0.00000	−1.44174	298–1044	26.2800
			143.5700	−0.16804	0.99657	−8.21784	1044–1710	

Using the thermochemistry calculation software ChemSage [9], the thermodynamic data in the $DyCl_3$–KCl system was critically assessed and analyzed together with the available phase diagram data. For the modeling of all liquid phases, the Redlich–Kister formula [10] was employed as given in following equation:

$$G^{ex} = x_A x_B \sum_{i=1}^{n} L_i (x_A - x_B)^{i-1}\ (\mathrm{J\,mol^{-1}}) \tag{1}$$

where $L_i = (a_i + b_i T)$. When $n = 2$, the thermodynamic parameters can be optimized as

$$\begin{aligned} L_0 &= -74599.32 - 34.6961T, \\ L_1 &= +73155.05 - 36.6412T \end{aligned} \tag{2}$$

The calculated phase diagram is shown in Fig. 2 and basically agrees to the experimental information [4] except in the melting points of the end $DyCl_3$. The comparisons of relative reactions between [4] and present work were tabulated here (see Table 2). Fig. 3 demonstrates that the calculated enthalpies of mixing in the liquid melts at 1070 K are good in the agreement with the experimental work [8].

Table 2
Comparisons of relative reactions in the $DyCl_3$–KCl system

Reaction	Present work		[4]	
	x_{DyCl_3}	T (K)	x_{DyCl_3}	T (K)
$L = DyCl_3(s) + K_3DyCl_6(s)$	0.140	938	0.110	930
$K_3DyCl_6(s) = L + K_2DyCl_5(s)$	0.420	723	0.470	728
$L = K_2DyCl_5(s) + KDy_2Cl_7(s)$	0.450	709	0.480	718
$L = KDy_2Cl_7(s) + KCl\ (s)$	0.855	811	0.785	805

With the optimized thermodynamic properties of the $DyCl_3$–KCl system, the enthalpies of formation, entropies and heat capacities of intermediate compounds K_3DyCl_6, K_2DyCl_5 and KDy_2Cl_7 were estimated and listed in Table 3.

$$DyCl_3(s) + 3KCl(s) = K_3DyCl_6(s) \tag{3}$$

$$DyCl_3(s) + 2KCl(s) = K_2DyCl_5(s) \tag{4}$$

$$2DyCl_3(s) + KCl(s) = KDy_2Cl_7(s) \tag{5}$$

Table 3
Estimated thermodynamic properties of intermediate compounds

Compounds	$-\Delta H^{\circ}_{f(298)}$ (kJ mol^{-1})	$S^{\circ}_{(298)}$ (J mol^{-1})	C_p (J mol^{-1} K^{-1})
K_3DyCl_6	2209.018	669.204	162.703
K_2DyCl_5	1901.700	348.753	234.509
KDy_2Cl_7	2485.493	405.230	255.792

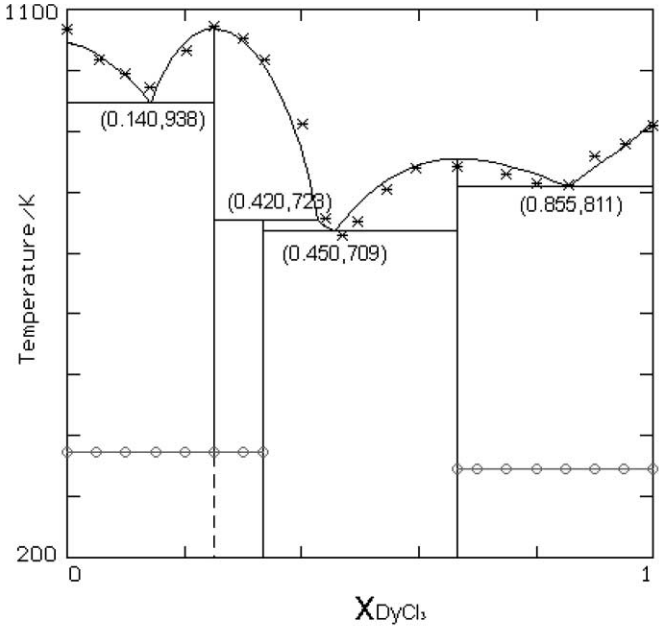

Fig. 2. Calculated phase diagram of the $DyCl_3$–KCl system. (⋇) Experimental data selected from [4].

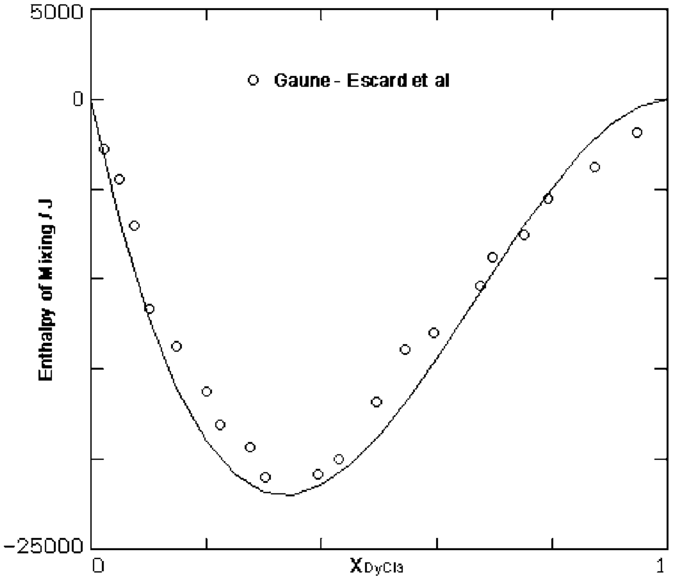

Fig. 3. Enthalpies of mixing in the liquid melts at 1070 K. (○) Experimental data selected from [8].

4. Discussion

Hatem and Gaune-Escard [6] used the phase diagram proposed by Mochinaga et al. [3] and assessed the phase diagram of the $DyCl_3$–KCl system. They selected the thermodynamic data relative to KCl from JANAF thermodynamic tables [11] and relative to $DyCl_3$ from [12]. They pointed out that the results presented by Seifert and Kraemer [4] were probably not correct because of the melting points of two pure salts are much different from others (see Table 4).

Although the melting points of two pure salts are very important to the phase diagram, the difference between the values of melting points of different sources is not enough to change the type of the phase diagram. We think that the intermediate compounds are one of the essential factors to influence the shape of phase diagrams and to determine the type of reaction in the system. Our experimental results found there were three stoichiometric compounds and confirmed the phase diagram proposed by Seifert and Kraemer [4]. The Seifert and Kraemer's work probably is more reliable in such case. However, the comparisons listed in Table 2 show that there still exists considerable difference between present results and those in [4]. From the thermodynamic point of view, the relation between enthalpy of fusion of pure component i, and the limiting slope of liquids (given by the left-hand side of Eq. (6)) can be described by the following formula:

$$\lim_{x_i\to 1}\frac{\mathrm{d}x_i^l}{\mathrm{d}T}=\frac{\Delta_{\mathrm{fus}}H^\circ_{(i)}}{\nu RT^2_{\mathrm{fus}(i)}} \tag{6}$$

where $\nu = 1$, $T_{\mathrm{fus}(i)}$ is the melting point of the pure component. At the $DyCl_3$ end, the tangent from the theoretically calculated limiting slope is in good agreement with the one from the experimental phase diagram. But at the KCl end, unreasonable difference could be found between theoretically calculated results and the phase diagram measured by Seifert and Kraemer [4], probably due to their abnormal value of the melting point ($T_{\mathrm{KCl}} = 1073$ K).

Table 4
The melting points (K) of two pure salts from different sources

Salts	Hatem and Gaune-Escard [6]	Seifert and Kraemer[4]	SGTE [7]
$DyCl_3$	928	919	924
KCl	1044	1073	1044

5. Conclusions

In the present paper, the three intermediate compounds K_3DyCl_6, K_2DyCl_5 and KDy_2Cl_7, in the $DyCl_3$–KCl system have been confirmed by the XRD method. Using the software ChemSage and employing the Ridelich–Kister equation in liquid phases, the phase diagram and thermodynamic data available in the $DyCl_3$–KCl system were critically reassessed. The thermodynamic properties of three stoichiometric compounds K_3DyCl_6, K_2DyCl_5 and KDy_2Cl_7, were estimated. The calculated phase diagram and optimized thermodynamic parameters are thermodynamically self-consistent.

Acknowledgements

The project is financially supported by National Natural Science Foundation of China (No. 29971004). Authors are grateful to Dr. G. Eriksson (GTT Company) for the providing the calculation software, ChemSage.

References

[1] B.G. Korshunov, D.V. Drobot, Z. Neorg. Khim. 10 (1965) 939.
[2] R. Blachnik, D. Selle, Z. Anorg. Allg. Chem. 454 (1979) 90.
[3] J. Mochinaga, H. Ohtani, K. Igarashi, Denki Kagaku Oyobi Kogyo Butsuri Kagaku 49 (1981) 19.
[4] H.J. Seifert, R. Kraemer, Anorg. Z. Allg. Chem. 620 (1994) 1543.
[5] H.J. Seifert, J. Sandrock, J. Uebach, Acta Chem. Scand. 49 (1995) 653.
[6] G. Hatem, M. Gaune-Escard, Thermochim. Acta 293 (1997) 137.
[7] A.T. Dinsdale, SGTE data for pure elements, Calphad 15 (1991) 317.
[8] M. Gaune-Escard, L. Rycerz, A. Bogacz, J. Alloys Compounds 204 (1994) 185.
[9] G. Eriksson, K. Hack, GTT ChemSage Handbook, Ver. 4.0.1, GTT Technologies, Aachen, Germany, (1998).
[10] P.E. Shurai, V.N. Danilin, A.G. Dolesov, et al., Trans. Krasnodar Politekn Inst. 63 (1974) 128 (in Russian).
[11] JANAF Thermodynamic Tables, US Department of Commerce, NBS, NSRDS-NBS 37(1971).
[12] M. Gaune-Escard, L. Rycerz, W. Szczepaniak, A. Bogacz, J. Alloys Compounds 204 (1994) 193.