

## ARTICLE

Thermodynamic Properties of Vapor Complex  $\text{Na}_2\text{HfCl}_6$ Jun-li Li<sup>a</sup>, Jin Yu<sup>a,b</sup>, Dong-mei Yang<sup>a</sup>, Zhi-chang Wang<sup>a\*</sup>*a.* School of Sciences, Northeastern University, Shenyang 110004, China; *b.* School of Sciences, Shenyang University of Technology, Shenyang 110023, China

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Thermodynamic studies were carried out for the vapor complex of sodium chloride with hafnium tetrachloride at 712-778 K and 0.5-3.1 kPa by using high temperature phase equilibrium-quenching experiments, with closed Pyrex glass ampoules as the reaction containers. The results show that the sole predominant vapor complex is  $\text{Na}_2\text{HfCl}_6$  for the  $\text{HfCl}_4$ -NaCl system under the experimental conditions. The thermodynamic equilibrium constants and other thermodynamic functions of the reaction  $2\text{NaCl}(\text{s}) + \text{HfCl}_4(\text{g}) = \text{Na}_2\text{HfCl}_6(\text{g})$  have been derived from the measurements. The results for the changes in enthalpy and entropy are  $-65.5 \pm 1.5$  kJ/mol and  $-99.6 \pm 2.0$  J/(mol K) in the temperature range.

**Key words:**  $\text{HfCl}_4$ , NaCl,  $\text{Na}_2\text{HfCl}_6$ , Vapor complex, Phase equilibrium-quenching experiment

## I. INTRODUCTION

Vapor complexes formed from dissimilar metal halides were first discovered about fifty years ago by Fischer and Grothe in the  $\text{AlCl}_3$ -NaCl and  $\text{AlCl}_3$ -KCl binary systems [1,2]. Since then, metal halide vapor complexes have shown their numerous applications in high temperature processes of catalysis, chemical synthesis, extraction and separation, lamps and lasers. To understand the nature of such high temperature processes, it is necessary to research the compositions and thermodynamic properties of these vapor complexes [3-12].

The vapor complexes of the IIIB, IVB and VB group elements, on which the lanthanide contraction has important effects have attracted much attention. There have been more experimental and theoretical studies on the structure, properties and applications of the IIIB group (rare earths) element halide vapor complexes [6,12-19] and references therein). Previously, we [8-11,20-23] have determined the compositions and thermodynamic properties of the vapor complexes in the  $\text{AlCl}_3$ -LnCl<sub>3</sub> and  $\text{AlBr}_3$ -LnBr<sub>3</sub> systems from Ln=Sc to Ln=Lu of the IIIB group and in the  $\text{NbCl}_5$ -NaCl and  $\text{NbCl}_5$ -KCl binary systems at about 580-680 K by high temperature phase equilibrium-quenching experiments; and the results of the  $\text{AlCl}_3$ -LnCl<sub>3</sub> systems have been used in theoretical analysis of the mutual separation characteristics of rare earths using chemical vapor transport by several groups [7,24-39].

The lanthanide contraction makes zirconium and hafnium closely similar in their chemical properties so that they often occur together in ore minerals and are very difficult to separate by normal methods. However,

they are different in some high technology applications. For example, the cross section for the capture of thermal neutrons for hafnium is 105 barn/atom, which is approximately 600 times greater than zirconium that is 0.18 barn/atom. In looking for new separation processes, the complexation reactions of the IVB group element chlorides with alkali metal chlorides have carefully been investigated by Flengas' group [40-49]. The compositions of the complexes in the solid and liquid states have been determined to be  $\text{A}_2\text{MCl}_6$ , where M=Ti, Zr and Hf and A=Li, Na, K, Rb and Cs, and their thermodynamic properties have also been determined [40-49]. However, the same information is lacking for complexes in the gaseous state.

In this work, we extended the phase equilibrium-quenching measurements to the  $\text{HfCl}_4$ -NaCl and  $\text{HfCl}_4$ -KCl systems to determine the compositions and thermodynamic properties of their vapor complexes. Unfortunately, however, the K-containing vapor complexes were very unstable and its yield was too low to be quantitatively determined by this method, which makes us unable to report the thermodynamic data only for the vapor complexes in the  $\text{HfCl}_4$ -KCl system.

## II. EXPERIMENTS

The chemicals used in this study were of 98% purity for anhydrous  $\text{HfCl}_4$  and of 99.99% purity for NaCl and KCl, all from Aldrich Chemical Co. The anhydrous  $\text{HfCl}_4$  was further purified by repeated sublimations under vacuum. NaCl and KCl were further crystallized using doubly-distilled water and then dried under vacuum over  $\text{P}_2\text{O}_5$ . The experiments were carried out in closed ampoules made from Pyrex glass with a special shape as shown in Fig.1. Volumes of the ampoules were determined to be 50-60 mL.

The quenching experiments employed in this study were similar to those described [8-11]. An excess of

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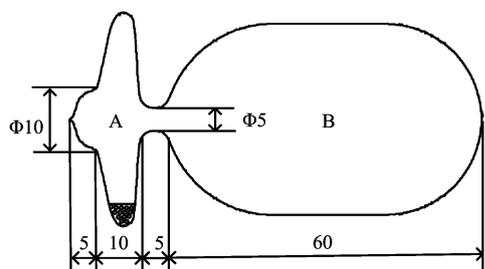
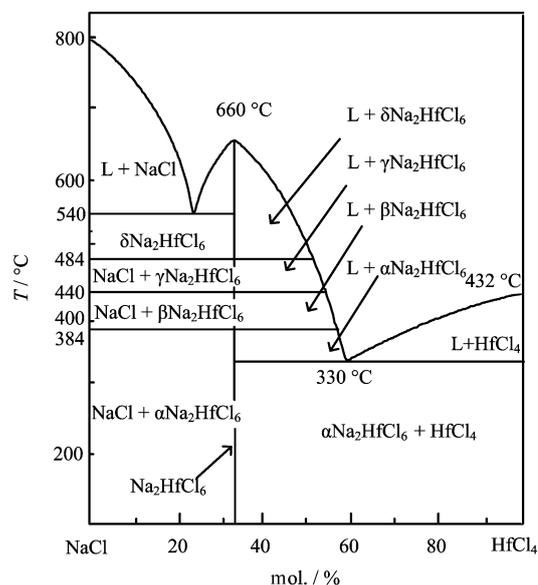


FIG. 1 The ampoule (distance in mm).

NaCl or KCl, and less HfCl<sub>4</sub> were placed in the deep ditch of the ampoule (part A in Fig.1) under argon atmosphere and the ampoule was then sealed under vacuum. Four ampoules were placed in a graphite container and then placed in a furnace, where the four isothermal samples with different initial amounts of anhydrous HfCl<sub>4</sub> and NaCl or HfCl<sub>4</sub> and KCl resulted in a set of isothermal complexation data at different pressures. The temperature was kept constant within  $\pm 0.5$  K measured with a Pt-PtRh<sub>10</sub> thermocouple so as to ensure the four samples were at the same temperature during each run. Our preliminary experiments showed that the maximum temperature difference was always smaller than 1.0 K within the graphite container due to its good heating conduction.

Preliminary experiments showed that the glass ampoule broke easily when quenching from an equilibrium pressure higher than 0.25 MPa at high temperature. The literature [50] showed that the normal sublimation temperature is 589 K and the melting point is 705 K for HfCl<sub>4</sub>. Moreover, the phase diagram of the HfCl<sub>4</sub>-NaCl system [51] (Fig.2) shows that the solid-liquid phases might exist in the HfCl<sub>4</sub>-NaCl system at  $T \geq 813$  K in the concentration range  $n_{\text{NaCl}}/n_{\text{HfCl}_4} > 2.0$  or at  $T \geq 603$  K in the concentration range  $n_{\text{NaCl}}/n_{\text{HfCl}_4} < 2.0$ , where activities of HfCl<sub>4</sub> and NaCl are unknown. Therefore in this study, formal experiments were carried out at pressures lower than 0.25 MPa and at temperatures lower than 800 K but higher than 710 K for the HfCl<sub>4</sub>-NaCl system in the concentration range  $n_{\text{NaCl}}/n_{\text{HfCl}_4} > 2.0$  to ensure the complete evaporation of HfCl<sub>4</sub> and the existence of pure solid NaCl in the deep ditch of the ampoule.

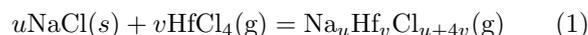
Our preliminary experiments showed that the complexation equilibrium might be achieved within 5 h. Therefore, the formal equilibrium period was chosen to be 6 h for each run. After the equilibrium had been achieved, the graphite container was quickly removed from the furnace and the ampoules were quickly removed from the graphite container, covered with asbestos, and then quenched with ice water. Thus the equilibrium gas phase was rapidly and uniformly condensed all over the ampoules. The mole numbers of Hf<sup>4+</sup> and Na<sup>+</sup> condensed in part B (Fig.1) of the ampoules could then be determined by spectrophotometry

FIG. 2 The phase diagram of the HfCl<sub>4</sub>-NaCl system.

and atomic absorption spectrophotometry, respectively.

### III. RESULTS AND DISCUSSION

At temperatures below 800 K, the equilibrium pressure of pure solid NaCl is negligible. On the other hand, the Na<sup>+</sup> were condensed in part B of the ampoule after quenching. Therefore, the Na<sup>+</sup> condensed in part B of the ampoule may reasonably be assumed to all belong to the vapor complexes Na<sub>u</sub>Hf<sub>v</sub>Cl<sub>u+4v</sub>(g) in the HfCl<sub>4</sub>-NaCl system formed by the reaction



with the equilibrium constant

$$K_{p(uv)} = \frac{p_{c(uv)}/p^\circ}{(p_{\text{HfCl}_4}/p^\circ)^v} \quad (2)$$

which yields

$$\ln \frac{p_{c(uv)}}{p^\circ} = \ln K_{p(uv)} + v \ln \frac{p_{\text{HfCl}_4}}{p^\circ} \quad (3)$$

where  $p^\circ = 0.1$  MPa,  $p_i$  denotes the partial pressure of  $i$ , and  $p_{c(uv)}$  and  $K_{p(uv)}$  denote the vapor complex Na<sub>u</sub>Hf<sub>v</sub>Cl<sub>u+4v</sub> and its equilibrium constant, respectively. The relationships between  $p_i$  and the analysis

TABLE I Quenching experimental results for the vapor complexes Na<sub>2</sub>HfCl<sub>6</sub>

$T/K$	No.	$V/\text{cm}^{-3}$	$p_{\text{Na}_2\text{HfCl}_6}/p^\circ$	$p_{\text{HfCl}_4}/p^\circ$	$p_T/p^\circ$	$v$	$K_p$
712	1	44.80	0.001836	0.004748	0.006584	1.01±0.01	0.3867
	2	42.26	0.001695	0.004472	0.006167		0.3790
	3	42.79	0.001596	0.004128	0.005724		0.3866
	4	44.61	0.001503	0.003927	0.005430		0.3827
728	5	42.50	0.002529	0.008312	0.01084	1.05±0.02	0.3043
	6	44.40	0.002382	0.007907	0.01029		0.3013
	7	43.64	0.002221	0.007227	0.009448		0.3073
	8	41.05	0.002050	0.006874	0.008924		0.2982
753	9	44.00	0.003414	0.01515	0.01856	1.07±0.01	0.2253
	10	41.90	0.003151	0.01441	0.01756		0.2187
	11	41.55	0.003058	0.01384	0.01690		0.2210
	12	42.41	0.002767	0.01252	0.01529		0.2210
778	13	40.89	0.004339	0.02678	0.03112	1.03±0.01	0.1620
	14	42.63	0.003966	0.02448	0.02845		0.1620
	15	40.20	0.003625	0.02282	0.02644		0.1589
	16	41.60	0.003483	0.02149	0.02497		0.1621

results of Hf<sup>4+</sup> and Na<sup>+</sup> may be given by

$$p_{c(uv)} = n_{c(uv)} \frac{RT}{V} \quad (4)$$

$$p_{\text{HfCl}_4} = n_{\text{HfCl}_4} \frac{RT}{V} \quad (5)$$

$$n_{\text{Hf}^{4+}} = n_{\text{HfCl}_4} + \sum_{u=2}^{u'} \sum_{v=1}^{v'} v n_{c(uv)} \quad (6)$$

$$n_{\text{Na}^+} = \sum_{u=2}^{u'} \sum_{v=1}^{v'} u n_{c(uv)} \quad (7)$$

and the total pressure may be given by

$$p_T = p_{\text{HfCl}_4} + \sum_{u=2}^{u'} \sum_{v=1}^{v'} p_{c(uv)} \quad (8)$$

where  $T$  is the temperature,  $V$  is the volume of part B (Fig.1) of the ampoule, and  $n_i$  is the mole number of the component  $i$ . After calculating the quantities from the analysis results of  $n_{\text{Hf}^{4+}}$  and  $n_{\text{Na}^+}$ , the molar Gibbs energy ( $\Delta_r G^\circ$ ), molar enthalpy ( $\Delta_r H^\circ$ ) and molar entropy ( $\Delta_r S^\circ$ ) of reaction (1) may be determined by

$$\Delta_r G^\circ = -RT \ln K_{p(uv)} = \Delta_r H^\circ - T \Delta_r S^\circ \quad (9)$$

In the literature [42,47,49,51] only the Na<sub>2</sub>HfCl<sub>6</sub> solid and liquid complexes were determined in the HfCl<sub>4</sub>-NaCl system at 712-778 K. Therefore, one may assume the Na<sub>2</sub>HfCl<sub>6</sub> (or Na<sub>2</sub>Hf<sub>v</sub>Cl<sub>4v+2</sub>) to be the sole vapor complex in this study for the same system. In that case,  $K_{p(uv)}$ ,  $n_{c(uv)}$  and  $p_{c(uv)}$  may simply be rewritten as  $K_p$ ,  $n_c$  and  $p_c$ , and Eqs.(6) and (7) may be simplified

to

$$n_{\text{Hf}^{4+}} = n_{\text{HfCl}_4} + v n_c \quad (10)$$

$$n_{\text{Na}^+} = 2n_c \quad (11)$$

The calculation results of Eqs.(3)-(5) and (9)-(11) should lead to straight lines for  $\ln(p_c/p^\circ)$  vs.  $\ln(p_{\text{HfCl}_4}/p^\circ)$  with the slope of  $v$  and for  $R \ln K_p$  vs.  $1/T$  with the slope of  $\Delta_r H^\circ$  for the HfCl<sub>4</sub>-NaCl system.

On the other hand, Schäfer [3] and Papatheodorou [4,6] suggested the  $u=v=1$  type vapor complexes to be the only vapor complexes in many alkali metal chloride-containing binary systems, such as KMgCl<sub>3</sub>, NaSnCl<sub>3</sub>, KLuCl<sub>4</sub> and NaFeCl<sub>4</sub>. According to this, one may also assume the Na<sub>2</sub>HfCl<sub>6</sub> vapor complex to coexist with the NaHfCl<sub>5</sub> vapor complex in the HfCl<sub>4</sub>-NaCl system. In this case, however, the calculation results of Eqs.(3)-(5) and (9)-(11) may result in nonlinear  $\ln(p_c/p^\circ)$ - $\ln(p_{\text{HfCl}_4}/p^\circ)$  and/or  $R \ln K_p$ - $1/T$  relationships in the HfCl<sub>4</sub>-NaCl system, similar to the situations of LaAl<sub>3</sub>Cl<sub>12</sub>-LaAl<sub>4</sub>Cl<sub>15</sub> or CeAl<sub>3</sub>Cl<sub>12</sub>-CeAl<sub>4</sub>Cl<sub>15</sub> coexistence [11] and of DyAl<sub>3</sub>Cl<sub>12</sub>-DyAl<sub>2</sub>Cl<sub>9</sub> [9] or HoAl<sub>3</sub>Cl<sub>12</sub>-HoAl<sub>2</sub>Cl<sub>9</sub> coexistence [11].

The calculation results of Eqs.(3)-(5) and (8)-(10) are listed in Table I for the HfCl<sub>4</sub>-NaCl system. It can be seen that the values of the apparent stoichiometric factor  $v$  were within 1.01-1.07 at 712-778 K and 0.5-3.1 kPa for the HfCl<sub>4</sub>-NaCl system, being very close to the theoretical value of  $v=1.0$ . Figure 3 also shows that the plots of  $\ln(p_c/p^\circ)$  vs.  $\ln(p_{\text{HfCl}_4}/p^\circ)$  are all straight lines with a slope of  $v=1.0$ . It may be therefore concluded that the Na<sub>2</sub>HfCl<sub>6</sub> is the predominant vapor complex for the HfCl<sub>4</sub>-NaCl system at 712-778 K. The values of  $K_p$  of the reaction (1) at  $v=1.0$  can then be calculated in terms of Eq.(3) for Na<sub>2</sub>HfCl<sub>6</sub>. The results are given

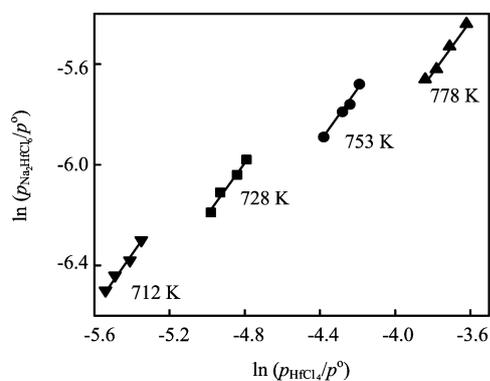


FIG. 3 Plots of  $\ln(p_c/p^0)$  vs.  $\ln(p_{\text{HfCl}_4}/p^0)$  for  $\text{HfCl}_4$ - $\text{NaCl}$  binary system.

in the last column of Table I. Plots of  $R \ln K_p$  vs.  $1/T$  are shown in Fig.4 for the  $\text{Na}_2\text{HfCl}_6$ , which are also straight lines.

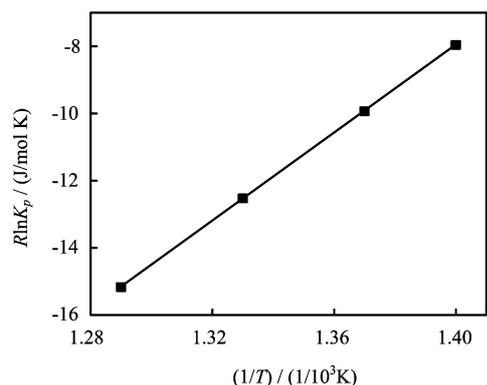


FIG. 4 Plots of  $R \ln K_p$  vs.  $1/T$  for  $\text{HfCl}_4$ - $\text{NaCl}$  binary system.

The thermodynamic quantities of reaction (1) can be determined from the experiments by a least squares computation within the reaction temperature ranges. The results are  $\Delta_r H^\circ = -65.5 \pm 1.5$  kJ/mol and  $\Delta_r S^\circ = -99.6 \pm 2.0$  J/(mol K) at about 712-778 K for the  $\text{Na}_2\text{HfCl}_6$ .

The probable overall errors of the  $\Delta_r G^\circ$ ,  $\Delta_r H^\circ$ ,  $\Delta_r S^\circ$  values should be computed from the statistical errors and the estimated probable uncertainties [8-11]. The statistical errors may be not more than  $\pm 0.2$  kJ/mol for  $\Delta_r G^\circ$  at every temperature,  $\pm 0.7$  kJ/mol for  $\Delta_r H^\circ$  and  $\pm 1.0$  J/(mol K) for  $\Delta_r S^\circ$  for the complex  $\text{Na}_2\text{HfCl}_6$  in the reaction temperature ranges shown in this study. The probable uncertainties may be estimated by assuming absolute errors of the chemical analysis for  $\text{Hf}^{4+}$  and  $\text{Na}^+$  as  $\pm 5\%$  of the volume measurement of the ampoules as  $\pm 0.5\%$ , and of the temperature measurement as  $\pm 2.0$  K. These uncertainties together with the error from the scatter of the experimental points in Fig.3 and Fig.4 may give rise to probable overall errors of  $\pm 0.5$  kJ/mol for  $\Delta_r G^\circ$  at every temperature,  $\pm 1.5$  kJ/mol for  $\Delta_r H^\circ$  and  $\pm 2.0$  J/(mol

K) for  $\Delta_r S^\circ$  for the vapor complex  $\text{Na}_2\text{HfCl}_6$  in the reaction temperature range shown in this study.

#### IV. CONCLUSION

In conclusion, the formation thermodynamics of the vapor complex in the  $\text{HfCl}_4$ - $\text{NaCl}$  and  $\text{HfCl}_4$ - $\text{NaCl}$  binary systems was determined by high temperature phase equilibrium-quenching experiments. The results show that the sole predominant vapor complex is  $\text{Na}_2\text{HfCl}_6$  formed by the reaction of solid  $\text{NaCl}$  with gaseous  $\text{HfCl}_4$ . The thermodynamic functions are  $\Delta_r H^\circ = -65.5 \pm 1.5$  kJ/mol and  $\Delta_r S^\circ = -99.6 \pm 2.0$  J/(mol K) for  $\text{Na}_2\text{HfCl}_6(\text{g})$  at about 712-778 K. The vapor complex formation ability in the  $\text{HfCl}_4$ - $\text{KCl}$  system is much lower than that in the  $\text{HfCl}_4$ - $\text{NaCl}$  system.

Thermodynamic modeling is a valuable tool to optimize the applications of vapor complexes. This implies the prerequisite of having a database with accurate thermodynamic functions of all vapor complexes involved. Thermodynamic modeling of metal vapor complexes has just begun in recent years, but it was confined to rare earth halides and alkali metal halides. Therefore research on thermodynamic functions of IIIB, IVB and VB group elements vapor complexes are very necessary. For this purpose, we are further planning to investigate the other IVB and VB group elements halides and alkali metal halides systems which may contribute to completing the database with thermodynamic functions of IIIB, IVB and VB group elements vapor complexes, to understanding the nature of high temperature processes and to optimizing the applications of IVB and VB group vapor complexes.

#### V. ACKNOWLEDGEMENT

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