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Thermodynamic properties of vapor complex Na_2ZrCl_6

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Abstract: Thermodynamic studies were carried out for the vapor complex of sodium chloride with zirconium tetrachloride at 718−778 K and 0.5−2.5 kPa by using high temperature phase equilibrium-quenching experiments, taking closed Pyrex glass ampoules as the reaction containers. The results show that the sole predominant vapor complex is Na_2ZrCl_6 for the $ZrCl_4$-NaCl system under the experimental conditions. The thermodynamic equilibrium constants and other thermodynamic functions of the reaction $2NaCl(s)+ZrCl_4(g)=Na_2ZrCl_6(g)$ have been derived from the measurements. The results for the changes in enthalpy and entropy are $\Delta H^0=(-70.1\pm1.5)$ kJ/mol and $\Delta S^0=(-105.9\pm2.0)$ J/(mol·K) in the temperature range.

Key words: $ZrCl_4$; NaCl; Na_2ZrCl_6; vapor complex; phase equilibrium-quenching experiment

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1 Introduction

Transition metal halide vapor complexes have been used as key constituents chemically transported in the high temperature processes such as chemical synthesis, catalysis, extraction and separation, high-intensity discharge lamps, and lasers. To understand the nature of these high temperature processes, it is necessary to know their stoichiometry, structure and thermodynamic properties. There have been relatively more experimental and theoretical studies on the structure, properties and applications of the rare earth (ⅢB group metal) halide vapor complexes (see, for example, Refs.[1−12] and references therein). However, the same information is relatively few for the stoichiometry, structure and thermodynamic properties of the ⅣB group metal halide vapor complexes.

We have determined the thermodynamic properties of the vapor complexes in the $AlCl_3$-$LnCl_3$ systems from Ln=Sc to Ln=Lu at 588−838 K[13−16] and of the $NbCl_5$-NaCl and $NbCl_5$-KCl binary systems at 580−680 K[17] by using the high temperature phase equilibrium-quenching experiments. In this study, we report the formation thermodynamics of the vapor complex Na_2ZrCl_6 in the $ZrCl_4$-NaCl system determined by the same quenching experiments.

We try to extend the same measurements to the vapor complex K_2ZrCl_6 in $ZrCl_4$-KCl system. Unfortunately, however, the vapor complex is very unstable and its yield is too low to be quantitatively determined under the same experimental conditions by this method, which makes us unable to report the thermodynamic data for the K_2ZrCl_6 vapor complex.

2 Experimental

The chemicals used in this study were of 99.5% purity for anhydrous $ZrCl_4$ and of 99.99% purity for NaCl and KCl from Aldrich Chemical Co. The anhydrous $ZrCl_4$ was further purified by repeated sublimations under vacuum. NaCl and KCl were further crystallized using double-distilled water and then dried under vacuum over P_2O_5. The experiments were carried out in closed ampoules made from Pyrex glass with a special shape as shown in Fig.1. The volumes of the ampoules were determined to be 50−60 mL.

The quenching experiments employed in this study were similar to those described in Refs.[13−16]. An excess of NaCl or KCl, and less $ZrCl_4$ were placed in the deep ditch of the ampoule (see 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

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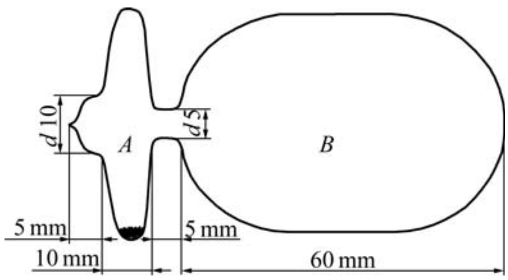

Fig.1 Schematic of ampoule

isothermal samples with different initial amounts of anhydrous $ZrCl_4$ and NaCl or $ZrCl_4$ and KCl resulted in a set of isothermal complexation data at different pressures. The temperature was kept constant within ±0.5 K measured with a Pt-$PtRu_{10}$ thermocouple so as to ensure the four samples to be at the same temperature during each run. The maximum temperature difference in the container was always smaller than 1.0 K.

Preliminary experiments showed that the glass ampoule broke easily when quenching from an equilibrium pressure higher than 0.25 MPa at high temperature. Ref.[18] showed that the normal sublimation temperature is 605 K and the melting point is 710 K for $ZrCl_4$. Moreover, Ref.[19] showed that the solid and liquid phases might coexist in the $ZrCl_4$-NaCl system at temperatures higher than 812 K, where the activities of $ZrCl_4$ and NaCl are unknown. Therefore, the formal experiments were carried out at pressures lower than 0.25 MPa and at temperatures lower than 800 K but higher than 715 K for the $ZrCl_4$-NaCl system to ensure the complete evaporation of $ZrCl_4$ and the existence of pure solid NaCl in the deep ditch of the ampoule in this study.

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 covered with asbestos, then quenched with ice water. Thus the equilibrium gas phase was rapidly and uniformly condensed all over the ampoules. The amounts of substance of Zr^{4+} and Na^+ condensed in part *B* of the ampoules could then be determined by spectrophotometry and atomic absorption spectrophotometry, respectively.

3 Results and discussion

At temperatures below 800 K, the equilibrium pressure of pure solid NaCl is negligible. On the other hand, however, the Na^+ ions are condensed in part *B* of the ampoule after quenching. It is known [20] that there is a dimerization reaction in the $ZrCl_4$ vapor but with the thermodynamic equilibrium constant only in the magnitude of 10^{-13}. Therefore, the Na^+ ions condensed in part *B* of the ampoule may reasonably be assumed to all belong to the vapor complexes $Na_uZr_vCl_{u+4v}(g)$ in the $ZrCl_4$-NaCl system formed by the reaction:

$$u\text{NaCl(s)}+v\text{ZrCl}_4\text{(g)}=\ \text{Na}_u\text{Zr}_v\text{Cl}_{u+4v}\text{(g)} \tag{1}$$

with the equilibrium constant

$$K_{p(uv)}=(p_{c(uv)}/p^0)/(p(\text{ZrCl}_4)/p^0)^v \tag{2}$$

which yields

$$\ln(p_{c(uv)}/p^0)=\ln K_{p(uv)}+v\ln(p(\text{ZrCl}_4)/p^0) \tag{3}$$

where p^0 =0.1 MPa, p_i denotes the partial pressure of *i*, $c(uv)$ and $K_{p(uv)}$ denote the vapor complex $Na_uZr_vCl_{u+4v}$ and its equilibrium constant, respectively. The relationships between p_i and the analysis results of Zr^{4+} and Na^+ may be given by

$$p_{c(uv)}=n_{c(uv)}RT/V \tag{4}$$

$$p(\text{ZrCl}_4)=n(\text{ZrCl}_4)RT/V \tag{5}$$

$$n(\text{Zr}^{4+})=n(\text{ZrCl}_4)+\sum_{u=2}^{u'}\sum_{v=1}^{v'}vn_{c(uv)} \tag{6}$$

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

and the total pressure may be given by

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

where *T* is the temperature, *V* is the volume of part *B* of the ampoule, n_i is the amounts of substance of the component *i*. After calculating the quantities from the analysis results of $n(Zr^{4+})$ and $n(Na^+)$, the molar Gibbs energy (ΔG^0), molar enthalpy (ΔH^0) and molar entropy (ΔS^0) of reaction (1) may be determined by

$$\Delta G^0=-RT\ln K_{p(uv)}=\Delta H^0-T\Delta S^0 \tag{9}$$

The Refs.[19,21−24] suggested the Na_2ZrCl_6 to be the sole solid and liquid complex in the $ZrCl_4$-NaCl system. Therefore, one may assume the Na_2ZrCl_6 (or $Na_2Zr_vCl_{4v+2}$) 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 Eqns.(6) and (7) may be simplified to

$n(\mathrm{Zr}^{4+})=n(\mathrm{ZrCl_4})+vn_c$ (10)

$n(\mathrm{Na}^{+})=2n_c$ (11)

The calculation results of Eqns.(3)−(5) and (9)−(11) should lead to the straight lines of $\ln(p_c/p^0)$ vs $\ln(p(\mathrm{ZrCl_4})/p^0)$ with the slope of v and of $R\ln K_p$ vs $1/T$ for the $\mathrm{ZrCl_4}$-NaCl system.

On the other hand, SCHÄFER[25] and PAPATHEODOROU et al[1,26] suggested the $u=v=1$ type vapor complex to be the only vapor complex in many alkali metal chloride-containing binary systems, such as $\mathrm{KMgCl_3}$, $\mathrm{NaSnCl_3}$, $\mathrm{KLuCl_4}$ and $\mathrm{NaFeCl_4}$. According to this, one may also assume the $\mathrm{Na_2ZrCl_6}$ vapor complex to coexist with the $\mathrm{NaZrCl_5}$ vapor complex in the $\mathrm{ZrCl_4}$-NaCl system. In this case, however, the calculation results of Eqns.(3)−(5) and (9)−(11) may result in the nonlinear $\ln(p_c/p^0)$—$\ln(p(\mathrm{ZrCl_4})/p^0)$ and/or $R\ln K_p$—$1/T$ relationships in the $\mathrm{ZrCl_4}$-NaCl system, similar to the situations of $\mathrm{LaAl_3Cl_{12}}$-$\mathrm{LaAl_4Cl_{15}}$ or $\mathrm{CeAl_3Cl_{12}}$-$\mathrm{CeAl_4Cl_{15}}$ coexistence[16] and of $\mathrm{DyAl_3Cl_{12}}$-$\mathrm{DyAl_2Cl_9}$[14] or $\mathrm{HoAl_3Cl_{12}}$-$\mathrm{HoAl_2Cl_9}$ coexistence[16].

The calculation results of Eqns.(3)−(5) and (8)−(10) are listed in Table 1 for the $\mathrm{ZrCl_4}$-NaCl system. It can be seen that the values of the apparent stoichiometric factor v are within 1.03−1.08 at 718−778 K for the $\mathrm{ZrCl_4}$-NaCl system, being very close to the theoretical value of v=1.0.

Fig.2 also shows that the plots of $\ln(p_c/p^0)$ vs $\ln(p(\mathrm{ZrCl_4})/p^0)$ are all straight lines with the slope of v=1. It may be therefore concluded that $\mathrm{Na_2ZrCl_6}$ is the predominant vapor complex for the $\mathrm{ZrCl_4}$-NaCl system at 718−778 K. The values of K_p of reaction (1) at v=1.0 can then be calculated in terms of Eqn.(3) for $\mathrm{Na_2ZrCl_6}$. The results are given in the last column of Table 1. The plots of $R\ln K_p$ vs $1/T$ are shown in Fig.3 for $\mathrm{Na_2ZrCl_6}$, which are also straight lines.

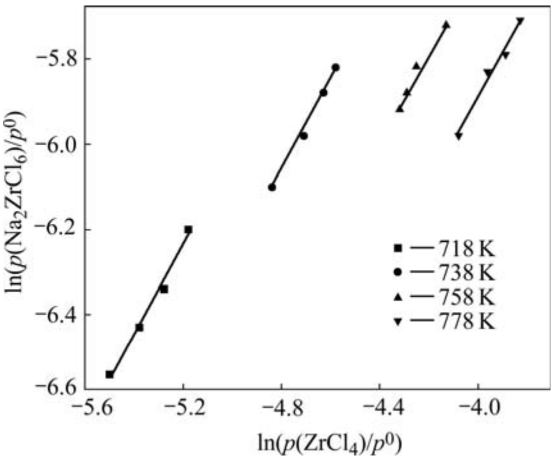

Fig.2 Plots of $\ln(p_c/p^0)$ vs $\ln(p(\mathrm{ZrCl_4})/p^0)$ for NaCl-$\mathrm{ZrCl_4}$ binary system

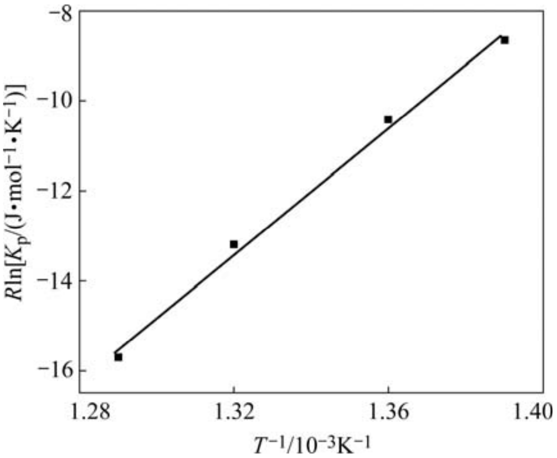

Fig.3 Plots of $R\ln K_p$ vs $1/T$ for NaCl-$\mathrm{ZrCl_4}$ binary system

Table 1 Quenching experimental results for vapor complexes $\mathrm{Na_2ZrCl_6}$

No.	T/K	V/cm^{-3}	$p(\mathrm{Na_2ZrCl_6})/p^0$	$p(\mathrm{ZrCl_4})/p^0$	p_T/p^0	v	K_p
1	718	40.77	0.002 029	0.005 628	0.007 657	1.04±0.02	0.360 5
2	718	40.22	0.001 764	0.005 092	0.006 856		0.346 4
3	718	41.40	0.001 612	0.004 608	0.006 220		0.349 8
4	718	42.44	0.001 444	0.004 087	0.005 531		0.353 3
5	738	43.07	0.002 968	0.010 26	0.013 23	1.08±0.01	0.289 3
6	738	42.62	0.002 795	0.009 755	0.012 55		0.286 5
7	738	41.75	0.002 529	0.009 005	0.01153		0.280 8
8	738	41.62	0.002 243	0.007 907	0.010 15		0.283 7
9	758	41.94	0.003 280	0.016 08	0.019 36	1.03±0.01	0.204 0
10	758	41.76	0.002 968	0.014 26	0.017 23		0.208 1
11	758	40.97	0.002 795	0.013 70	0.016 50		0.204 0
12	758	42.70	0.002 685	0.013 30	0.015 98		0.201 9
13	778	45.65	0.003 313	0.021 71	0.025 02	1.05±0.02	0.152 6
14	778	42.08	0.003 058	0.020 44	0.023 50		0.149 6
15	778	42.23	0.002 938	0.019 06	0.022 00		0.154 1
16	778	42.60	0.002 529	0.016 91	0.019 44		0.149 6

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 ΔH^0=−70.1 kJ/mol and ΔS^0= −105.9 J/(mol·K) at about 718−778 K for Na_2ZrCl_6.

The probable overall errors of the ΔG^0, ΔH^0, ΔS^0 values should be computed from the statistical errors and the estimated probable uncertainties[13−16]. The statistical errors may be not more than ±0.2 kJ/mol for ΔG^0 at every temperature, ±0.7 kJ/mol for ΔH^0 and ±1.0 J/(mol·K) for ΔS^0 for the complex Na_2ZrCl_6 in the reaction temperature ranges shown in this study. The estimated probable uncertainties may result from assuming absolute errors of the chemical analysis for Zr^{4+} and Na^+ as ±5 %, of the volume measurement of the ampoules as ±0.5%, and of the temperature measurement as ±2.0 K. These uncertainties together with the error from the scatter of the experimental points in Figs.2 and 3 may give rise to the probable overall errors of ±0.5 kJ/mol for ΔG^0 at every temperature, ±1.5 kJ/mol for ΔH^0 and ±2.0 J/(mol·K) for ΔS^0 for the vapor complex Na_2ZrCl_6 in the reaction temperature range shown in this study.

4 Conclusions

The vapor complex Na_2ZrCl_6 was formed by the reaction of solid NaCl with gaseous $ZrCl_4$. The formation thermodynamics is ΔH^0=(−70.1±1.5) kJ/mol and ΔS^0=(−105.9±2.0) J/(mol·K) for Na_2ZrCl_6(g) at 718−778 K. The vapor complex formation ability in the $ZrCl_4$-KCl system is much lower than that in the $ZrCl_4$-NaCl system.

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