Bull. Chem. Soc. Jpn., **69**, 353—357 (1996)

Mass Spectrometric Investigation of the Vapor over the $LnCl_3$–KCl Equimolar Melt (Ln=Nd, Er) at High Temperatures

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(Received July 19, 1995)

Vaporization of the $LnCl_3$–KCl (Ln = Nd and/or Er) equimolar molten mixture was investigated at 1018—1273 K by means of Knudsen effusion mass spectrometry. The vapor species KCl, K_2Cl_2, $NdCl_3$, and $KLnCl_4$ were found in the vapor over the melt, and their vapor pressures were evaluated for the $NdCl_3$–KCl system. Volatility enhancement of $NdCl_3$ by the formation of the vapor complex $KNdCl_4$ decreases with increase in temperature. A relatively small enthalpy change, -10 ± 21 kJ mol^{-1}, of the isomolecular exchange $KNdCl_4(g)+KCl(g)=NdCl_3(g)+K_2Cl_2(g)$ suggests that the structural change of the reaction is not drastic and that the $KNdCl_4(g)$ complex has two bridging and two terminal chlorine atoms.

Various kinds of metal halides form halogen-bridged vapor complexes with other volatile halides such as aluminium, iron, and alkali halides.[1,2] Rare earth halides also give the vapor complexes and the apparent volatilities of rare earth halides are enhanced by the formation of the complexes. The vapor complexes of the rare earth halides with alkali halides have been well investigated for the iodide systems, because the iodide system is important for high intensity metal halide lamps; some lamps using the ScI_3–NaI and DyI_3–NdI_3–CsI mixtures have already been manufactured commercially. Recently, the iodide systems have been systematically investigated by means of Knudsen effusion mass spectrometry.[1,3,4] On the other hand, though volatile chloride complexes, $ALnCl_4(g)$ (Ln = rare earths, A = alkali metals), are also known to form,[5] study of the chloride complexes using the mass spectroscopy is rather limited.[6] Vapor complexes of the $LnCl_3$–ACl system have been applied for a high temperature extraction and separation process for rare earths using a chemical vapor transport reaction.[7,8]

In the present work, the vapor species over the $NdCl_3$–KCl quasi-binary melt were investigated at high temperatures up to 1273 K, which is a usual operating temperature for the chemical vapor transport of rare earths, by means of the Knudsen effusion mass spectroscopy, and the vapor pressures of the gaseous species were estimated. Furthermore, a qualitative observation of the vapor over the $ErCl_3$–KCl quasi-binary and the $NdCl_3$–$ErCl_3$–KCl quasi-ternary melts was carried out using the method.

Experimental

High purity anhydrous $NdCl_3$ and $ErCl_3$ (Shin-Etsu Chemical Co., Ltd.) were used without any pretreatment. Potassium chloride (Wako Chemical, 99.9%) was dried by heating at 773 K in vacuo for 12 h. All chemicals were handled in an argon filled glove box. These chlorides were weighted, well-mixed with an agate mortar and a pestle, and loaded in a cylindrical molybdenum Knudsen cell (inner diameter 10 mm, length 30 mm) which has an orifice of 0.5 mm diameter.

The apparatus for recording the mass spectra consists of a quadrupole mass spectrometer with a cross-beam ion source and the molybdenum Knudsen cell (see Fig. 1). The cell was placed in an ultrahigh vacuum chamber (ca. 10^{-9}—10^{-10} Torr; 1 Torr = 133.322 Pa). The chamber was evacuated by a turbo molecular pump with a rotary pump and baked for two days. An ion pump was then operated to evacuate the chamber; then the cell was heated by an rf generator up to 673 K in order to degas the sample. The temperature of the cell was measured with both a thermocouple and an optical pyrometer.

Gaseous species effusing from the cell were ionized by electron impact at an electron energy of about 15 eV; the energy was calibrated by a known ionization potential of neutral species. A shutter installed between the cell and the ion-source was used to distinguish the effused gas from residual gases. The partial pressure, $p(i)$, of species i at the temperature, T, was determined in a usual manner, based on a relation

$$p(i)=\sum_j k\frac{I_j(i)T}{\sigma(i)\gamma_j\Delta E_j} \quad (1)$$

where k is the proportionality constant, $I_j(i)$ the intensity of the ions j which were generated from the species i, $\sigma(i)$ the relative ionization cross section, γ_j the multiplier gain of the detector for the ions j, and ΔE_j the difference between the appearance potential for ions j and the energy of an impacted electron. The ionization cross sections for monomeric species, KCl and $NdCl_3$, were computed by taking the sum of Mann's atomic cross section[9] of the component atoms, while those for complexes, K_2Cl_2 and $KNdCl_4$, were calculated as 0.75 times the sum of those for monomers.[10] The multiplier gain of the detector was obtained from a calibration curve.

The proportionality constant, k, was obtained from the comparison of the $p(KCl)^2/p(K_2Cl_2)$ ratio over pure KCl solid with reported equilibrium constant for the $K_2Cl_2(g)=2\,KCl(g)$ reaction obtained

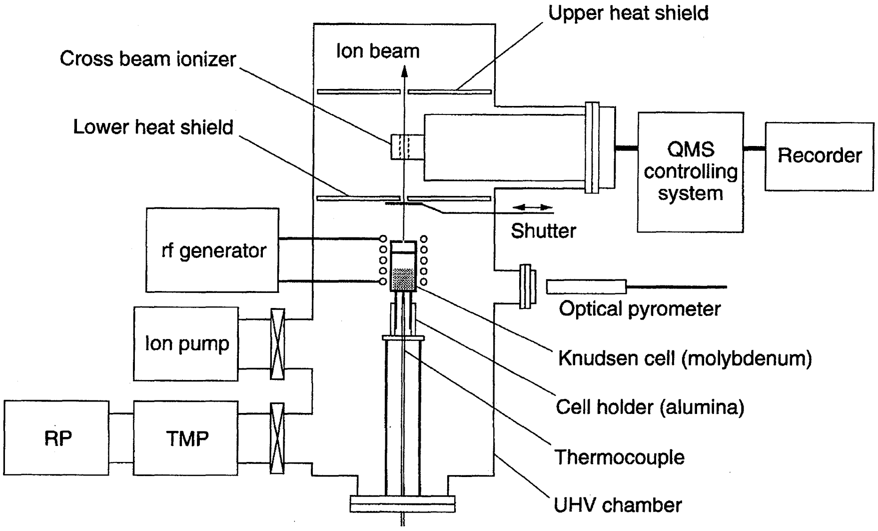

Fig. 1. Assemble of mass spectrometer equipped with Knudsen cell.

from the thermodynamic data:[11)]

$$K_p/\text{atm} = p(\text{KCl})^2/p(\text{K}_2\text{Cl}_2) = 1115708\ \exp(-21991T^{-1}). \quad (2)$$

On ionizing at an electron energy of 15.0 eV, the ions K^+, KCl^+, and K_2Cl^+ were observed, whereas $K_2Cl_2^+$ ion was not found. This is explained on the basis of a general rule that $M_mX_{n-1}{}^+$ ions are formed preferentially with large relative abundances on ionizing metal halides $M_mX_n(g)$ by electron impact.[1,3)] The fact that the appearance potentials obtained by means of extrapolated voltage difference method[12)] were 9.0, 8.4, and 9.4 eV for K^+, KCl^+, and K_2Cl^+, suggested that the ion K^+ does not originate from metallic K(g). Both the K^+ and KCl^+ ions were assigned to KCl(g), while K_2Cl^+ was assigned to the K_2Cl_2(g) dimer in analogy with other mass spectrometric studies of the vapor over alkali halide-containing melts.[3)] A mean value of the k from measurements at various temperatures was $(1.72\pm0.15)\times10^{-12}$ atm K^{-1}.

Table 1. Ion Intensities Determined upon Investigating the Vapor over the $NdCl_3$–KCl Equimolar Melt

T/K	I_{K^+}	I_{KCl^+}	I_{K^+}/I_{KCl^+}	$I_{K_2Cl^+}$	$I_{NdCl_2{}^+}$	$I_{KNdCl_3{}^+}$
1018	6.0×10^2	2.8×10	22	2.0		
1037	1.0×10^3	4.2×10	25	4.0		
1063	2.0×10^3	7.4×10	26	4.7		
1063	2.1×10^3	7.6×10	27	4.7		
1093	4.0×10^3	1.3×10^2	30	8.6	9.9	
1113	6.7×10^3	2.0×10^2	33	1.4×10	1.2×10	
1143	1.0×10^4	2.8×10^2	35	1.9×10	1.8×10	5.5
1169	1.6×10^4	3.6×10^2	44	2.7×10	2.6×10	1.1×10
1198	2.3×10^4	4.8×10^2	47	3.8×10	3.2×10	1.2×10
1223	3.2×10^4	6.5×10^2	49	5.2×10	3.9×10	1.9×10
1256	4.8×10^4	9.2×10^2	53	7.8×10	5.9×10	2.3×10
1273	5.8×10^4	1.1×10^3	55	8.3×10	8.6×10	2.9×10

Results and Discussion

A. The $NdCl_3$–KCl Binary System. Vapor Species over the $NdCl_3$–KCl Melt. On ionizing at an electron energy of 13.8 eV, five ions: K^+, KCl^+, K_2Cl^+, $NdCl_2{}^+$, and $KNdCl_3{}^+$, were observed over the $NdCl_3$–KCl equimolar melt. Table 1 lists the intensity of each ion. In this case, molecular ions such as $K_2Cl_2{}^+$, $NdCl_3{}^+$, and $KNdCl_4{}^+$ were not found. The appearance potentials were as follows: 9.0 eV (K^+); 8.4 eV (KCl^+); 9.4 eV (K_2Cl^+); 10.8 eV ($NdCl_2{}^+$); 10.1 eV ($KNdCl_3{}^+$). The appearance potential of $KNdCl_3{}^+$ was almost the same as that of a similar complex ion $NaGdCl_3{}^+$ (10.1±0.5 eV) reported by Ciach et al.[13)] Ionization efficiency curves of the five ions did not exhibit any irregular threshold.

Consequently, the KCl^+ ion was considered to originate from KCl(g), while the K_2Cl^+, $NdCl_2{}^+$, and $KNdCl_3{}^+$ ions were assigned to K_2Cl_2, $NdCl_3$, and $KNdCl_4$ species, respectively, according to the general rule mentioned above. Based on the rule and the result for pure KCl, it seemed natural that the K^+ ion was assigned to KCl. However, the intensity ratio I_{K^+}/I_{KCl^+} largely increases with the increase of the temperature (see Table 1), suggesting K^+ was generated not only from KCl, since the ions originating from the same neutral molecule generally show the same temperature dependencies.[1)] Therefore, the K^+ ion was considered to originate also from another K-containing species, $KNdCl_4$.

The intensity of K^+ ion, I_{K^+}, in Table 1 was divided into that from KCl, I_{K^+}(KCl), and that from $KNdCl_4$ complex, $I_{K^+}(KNdCl_4)$, in the following manner. First, the I_{K^+}(KCl) values were calculated from the intensities of KCl^+ and K_2Cl^+ ions, I_{KCl^+}(KCl) and $I_{K_2Cl^+}(K_2Cl_2)$, by using Eqs. 1 and 2, assuming that the proportionality constant, k, and the equilibrium constant, K_p, of the reaction $K_2Cl_2(g)=2\,KCl(g)$ are the same as those obtained for the measurement of pure KCl. Then, resulting I_{K^+}(KCl) values were subtracted from I_{K^+} values to obtain $I_{K^+}(KNdCl_4)$ values: $I_{K^+}(KNdCl_4)=I_{K^+}-I_{K^+}(KCl)$.

The equilibrium partial pressures of KCl(g), K_2Cl_2(g), $NdCl_3$(g), and $KNdCl_4$(g) are shown in Fig. 2 as a function of reciprocal temperature. The pressures are represented in Eqs. 3, 4, 5, and 6 for the temperature range between 1018 and 1273 K:

$$\log[p(\text{KCl})/\text{atm}] = -(9.09\pm0.11)\times10^3T^{-1} + (3.53\pm0.03), \quad (3)$$

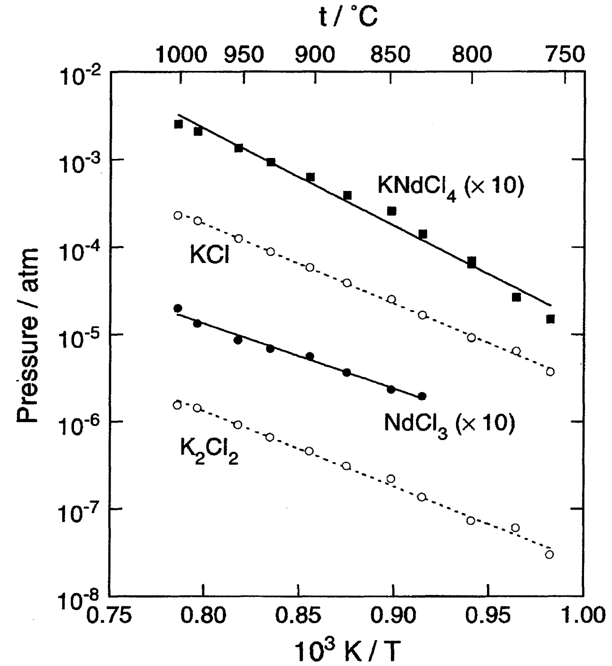

Fig. 2. Partial pressures of gaseous species over the NdCl$_3$–KCl equimolar melt as a function of the reciprocal temperature.

$$\log[p(\mathrm{K_2Cl_2})/\mathrm{atm}] = -(8.62\pm0.23)\times10^3T^{-1}+(1.02\pm0.05), \quad (4)$$

$$\log[p(\mathrm{NdCl_3})/\mathrm{atm}] = -(7.45\pm0.35)\times10^3T^{-1}+(0.09\pm0.04), \quad (5)$$

$$\log[p(\mathrm{KNdCl_4})/\mathrm{atm}] = -(11.1\pm0.4)\times10^3T^{-1}+(5.21\pm0.10). \quad (6)$$

The pressures of KCl(g), NdCl$_3$(g), and KNdCl$_4$(g) at 1273 K, which is a usual reaction temperature for the rare earth separation process using vapor complex formation,[7,8] were 2.5×10^{-4}, 1.7×10^{-6}, and 3.1×10^{-4} atm. This means that the rate of vaporization of K-containing species is almost twice as fast as that of Nd-containing ones, since the pressures of KCl(g) and KNdCl$_4$(g) are nearly equal to each other. Therefore, composition of the KCl–NdCl$_3$ melt gradually shifts to a NdCl$_3$-rich side during keeping at high temperatures. This phenomenon was observed also during the rare earth separation process using the LnCl$_3$–KCl (Ln=Pr and Nd; Pr/Nd=1/1) equimolar mixture as a raw material; here the change of the composition lowered the transport efficiency of LnCl$_3$.[14] In other words, the deviation of the melt to a NdCl$_3$-rich side lowers the vapor pressure of KNdCl$_4$(g).

Since the NdCl$_3$–KCl mixture is expected to be molten completely above ca. 820 K,[15] the $\log p(i)$ vs. $1/T$ plot should be linear for all vapor species. However, the vapor pressure curve of KNdCl$_4$(g) displayed slight upward curvature. One reason for such curvature is that the vapor species in the cell might not be completely equilibrated. In order to attain equilibrium, however, the cell temperature was monitored by both thermocouple and pyrometer and kept constant for about 10 min before each measurement. We did not try to keep the cell temperature for a longer time, because, as mentioned above, the composition of the sample is changing every moment at high temperatures.

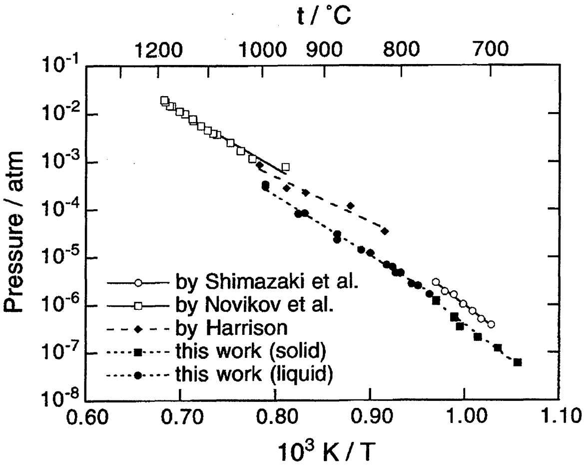

Fig. 3. Vapor pressure of NdCl$_3$(g) over pure NdCl$_3$ solid and liquid as a function of the reciprocal temperature.

Volatility Enhancement of NdCl$_3$ by Forming KNdCl$_4$(g) Complex. The vapor pressure of NdCl$_3$(g) over a pure NdCl$_3$ is also measured by the same operations. The pressures over pure NdCl$_3$ solid (947—1030 K) and liquid (1039—1268 K) are represented as follows:

$$\log[p(\mathrm{NdCl_3}\ \text{over solid})/\mathrm{atm}] = -(15.2\pm0.6)\times10^3T^{-1}+(8.79\pm0.05), \quad (7)$$

$$\log[p(\mathrm{NdCl_3}\ \text{over liquid})/\mathrm{atm}] = -(12.5\pm0.2)\times10^3T^{-1}+(6.30\pm0.06). \quad (8)$$

These vapor pressures are the same level as those measured by means of other techniques[16—18] (see Fig. 3).

The overall concentration of the neodymium in the vapor phase over the NdCl$_3$–KCl equimolar melt, that is the sum of the p(NdCl$_3$) (Eq. 5) and p(KNdCl$_4$) (Eq. 6), was compared with the vapor pressure of NdCl$_3$(g) over pure NdCl$_3$ (Eqs. 7 and 8), as shown in Fig. 4. Around 1273 K, the concentration of the neodymium over the NdCl$_3$–KCl melt is almost equal to NdCl$_3$(g) pressure over the pure NdCl$_3$ liquid. Therefore, apparent volatility enhancement of the NdCl$_3$ by the formation of the vapor complex was not so large. On the contrary, the volatility enhancement becomes remarkable at lower temperatures, below the melting point of NdCl$_3$ (ca. 1030 K). According to the extrapolation of the $\log p(i)$ vs. $1/T$ plots, the volatility enhancement is estimated to be 31 at 823 K, above which the NdCl$_3$–KCl equimolar mixture is completely molten.[15] The phenomenon of the volatility enhancement can be expressed qualitatively as follows. Coordination of Cl$^-$ ion around Nd^{3+} ion in pure NdCl$_3$ solid and liquid are nine[19] and six,[20] respectively, while Nd^{3+} in NdCl$_3$(g) has a 3-fold coordination. Therefore, the vaporization of pure NdCl$_3$ needs to overcome three to six Nd–Cl bonds. On the other hand, the Nd^{3+} ion in the NdCl$_3$–KCl equimolar melt has 6-fold coordination,[20] while KNdCl$_4$(g) complex contains Nd^{3+} coordinated by four Cl$^-$ ions (see below). Hence, on vaporization of the KNdCl$_4$(g) from the melt, fewer Nd–Cl bonds, i.e. two Nd–Cl interactions, need

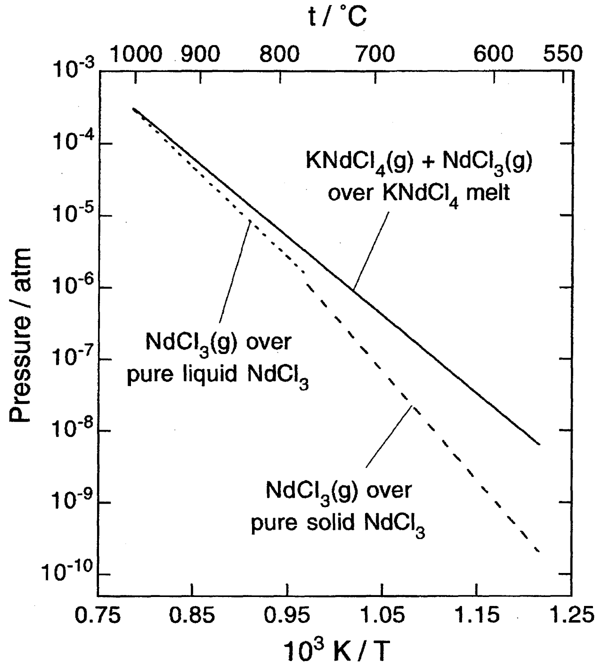

Fig. 4. Comparison of vapor pressures of Nd-containing species over the $NdCl_3$–KCl equimolar melt, pure $NdCl_3$ liquid, and pure $NdCl_3$ solid.

to be broken. At higher temperatures around 1200 K, it becomes easy even for pure $NdCl_3$ to obtain enough energy to overcome Nd–Cl bonds; thus, the volatility enhancement is decreased. The enhancement increases with decrease in temperature are generally observed for many complex forming halide systems.

Evaluation of Thermodynamic Functions. Second-law enthalpy changes, ΔH°_T, of the reactions,

$$KNdCl_4(l) = KNdCl_4(g), \tag{9}$$

$$KNdCl_4(g) + KCl(g) = NdCl_3(g) + K_2Cl_2(g), \tag{10}$$

and

$$KNdCl_4(g) = KCl(g) + NdCl_3(g), \tag{11}$$

were evaluated from the slope of $\log K_p$ vs. $1/T$ plot (Fig. 5) for each reaction. The mean enthalpy changes of the reactions (9)—(11) at 1198—1273 K were calculated as 168±4 $\mathrm{kJ\,mol^{-1}}$, −10±21 $\mathrm{kJ\,mol^{-1}}$, and 173±21 $\mathrm{kJ\,mol^{-1}}$, respectively. Novikov et al. obtained a rather bigger enthalpy change of reaction (11), $\Delta H^\circ_{1350\,\mathrm{K}}=247\pm17\ \mathrm{kJ\,mol^{-1}}$, by a calculation from overall composition and pressure.[21] However, the reason of the difference cannot be explained, since these authors did not give detailed calculations.

It is noteworthy that the enthalpy change of isomolecular exchange reaction (10) is near zero, suggesting that no drastic structure change takes place through the reaction. According to electron diffraction measurements, the $K_2Cl_2(g)$ and $NdCl_3(g)$ molecules are known to have D_{2h}-type square and C_{3v}-type pyramidal structures, respectively.[22] Therefore, the most plausible structure of $KNdCl_4(g)$ is C_{2v}-type structure as shown in Fig. 6, since only a $NdCl_3$ unit with C_{3v} symmetry is "replaced" by a linear KCl unit from left- to right-hand side of the reaction (10).

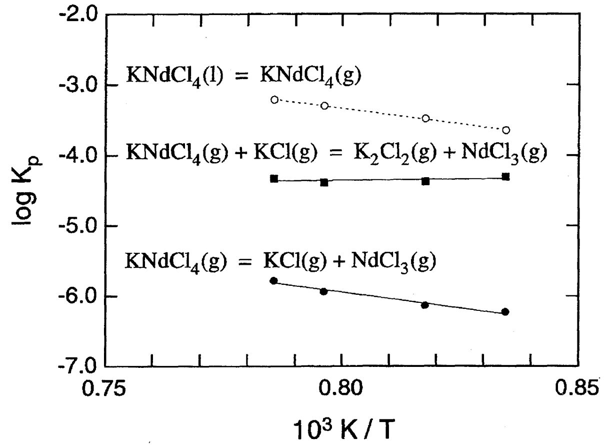

Fig. 5. Relationship between equilibrium constant of some reactions and the reciprocal temperature in the $NdCl_3$–KCl quasi-binary system.

This C_{2v}-type structure of $KNdCl_4(g)$ is supported by an enthalpy change of reactions (10) and (11) deduced from Hastie's empirical rule[23] for dissociation energy. According to the rule, dissociation energy of M–Cl^b bond, $D(\mathrm{M{-}Cl^b})$, is 0.6±0.04 times that of M–Cl^t bond, $D(\mathrm{M{-}Cl^t})$, where Cl^b and Cl^t represent bridging and terminal chloride atoms, respectively. Then, the enthalpy changes of reactions (10) and (11) were expressed as

$$\begin{aligned}\Delta H^\circ(\text{Eq. }10) &= [2D(\mathrm{Nd{-}Cl^t})+2D(\mathrm{Nd{-}Cl^b})+D(\mathrm{K{-}Cl^t})\\ &\quad +2D(\mathrm{K{-}Cl^b})]-[3D(\mathrm{Nd{-}Cl^t})+4D(\mathrm{K{-}Cl^b})]\\ &= [2D(\mathrm{Nd{-}Cl^t})+2\times0.6D(\mathrm{Nd{-}Cl^t})\\ &\quad +D(\mathrm{K{-}Cl^t})+2\times0.6D(\mathrm{K{-}Cl^t})]\\ &\quad -[3D(\mathrm{Nd{-}Cl^t})+4\times0.6D(\mathrm{K{-}Cl^t})]\\ &= 0.2D(\mathrm{Nd{-}Cl^t})-0.2D(\mathrm{K{-}Cl^t})\end{aligned} \tag{12}$$

and

$$\begin{aligned}\Delta H^\circ(\text{Eq. }11) &= [2D(\mathrm{Nd{-}Cl^t})+2D(\mathrm{Nd{-}Cl^b})+2D(\mathrm{K{-}Cl^b})]\\ &\quad -[3D(\mathrm{Nd{-}Cl^t})+D(\mathrm{K{-}Cl^t})]\\ &= [2D(\mathrm{Nd{-}Cl^t})+2\times0.6D(\mathrm{Nd{-}Cl^t})+2\\ &\quad \times0.6D(\mathrm{K{-}Cl^t})]-[3D(\mathrm{Nd{-}Cl^t})+D(\mathrm{K{-}Cl^t})]\\ &= 0.2D(\mathrm{Nd{-}Cl^t})+0.2D(\mathrm{K{-}Cl^t}).\end{aligned} \tag{13}$$

From the dissociation energies of K–Cl^t and Nd–Cl^t, i.e. $D(\mathrm{K{-}Cl^t})=425\ \mathrm{kJ\,mol^{-1}}$ and $D(\mathrm{Nd{-}Cl^t})=464\ \mathrm{kJ\,mol^{-1}}$,[11,24]

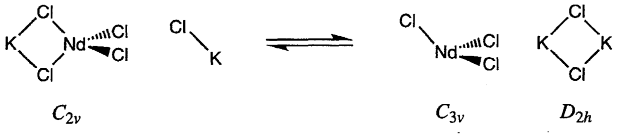

Fig. 6. Structure model for $KNdCl_4(g)$ complex molecule deduced from structures of $K_2Cl_2(g)$ and $NdCl_3(g)$ together with a relatively small enthalpy change of an isomolecular exchange $KNdCl_4(g)+KCl(g)=NdCl_3(g)+K_2Cl_2(g)$.

the ΔH°(Eq. 10) and ΔH°(Eq. 11) are calculated as 8 and 178 kJ mol^{-1}, which almost agree with the above experimental values, -10 ± 24 and 173 ± 21 kJ mol^{-1}.

B. The $ErCl_3$–KCl Binary and the $NdCl_3$–$ErCl_3$–KCl Ternary Systems. On ionizing at an electron energy of ca. 15 eV, six ions, K^+, KCl^+, K_2Cl^+, $ErCl_2^+$, $ErCl_3^+$, and $KErCl_3^+$, were observed over the $ErCl_3$–KCl equimolar melt. However, the sample in the Knudsen cell was exhausted much faster than the case of the $NdCl_3$–KCl mixture, and quantitative measurements up to 1273 K were impossible. This phenomenon agrees with the fact that vapor complexes containing rare earth with larger atomic number, or with smaller ionic radius, have higher volatility.[7]

Vapor over the $NdCl_3$–$ErCl_3$–KCl ($Nd/Er/K=1/1/2$) ternary melt was also investigated. These ions: K^+, KCl^+, K_2Cl^+, $LnCl_2{}^+$, $LnCl_3{}^+$, and $KLnCl_3{}^+$ (Ln=Nd, Er), were observed. In this case, intensities of Er-containing ions diminished much faster than those of Nd-containing ones, also indicating the larger volatility of the $KErCl_4$(g) complex.

Conclusion

Vapor over the $NdCl_3$–KCl equimolar molten mixture was investigated at 1018—1273 K by means of Knudsen effusion mass spectrometry. The vapor species KCl, K_2Cl_2, $NdCl_3$, and $KNdCl_4$ were present in the vapor over the melt and their vapor pressures were evaluated. Volatility enhancement of Nd-containing species by the formation of the vapor complex $KNdCl_4$ decreases with the increase of temperature. Enthalpy change of the isomolecular exchange $KNdCl_4(g)+KCl(g)=NdCl_3(g)+K_2Cl_2(g)$ was relatively small, -10 ± 21 kJ mol^{-1}, suggesting that the structual change of the reaction is not drastic and the $KNdCl_4$(g) complex has a C_{2v} type configuration. Qualitative observation of the vapor over the $ErCl_3$–KCl and $NdCl_3$–$ErCl_3$–KCl mixtures where $Ln/K=1/1$ suggested that Er-containing species vaporize much faster than Nd-containing ones.

The present work is supported by Grants-in-Aid for Scientific Research Nos. 06241106, 06241107 (Priority Areas "New Development of Rare Earth Complexes"), and 051298 from the Ministry of Education, Science, Sports and Culture. One of the authors (K. M.) is in receipt of a Fellowship of the Japan Society for the Promotion of Science for Japanese Junior Scientists.

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