Vapor Pressure Measurements for the FeCl$_2$–ZnCl$_2$ System by the Transpiration Method

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The vapor pressures of FeCl$_2$ and ZnCl$_2$ in the FeCl$_2$–ZnCl$_2$ system were measured by the transpiration method at 873 K and 917 K. The vapor pressure data were interpreted to indicate the formation of complex ions in the FeCl$_2$–ZnCl$_2$ melts. It is presumed that the complex molecule FeZnCl$_4$ as well as FeCl$_2$ and ZnCl$_2$ exists in the vapors in equilibrium with molten FeCl$_2$–ZnCl$_2$ mixtures. The activities in the FeCl$_2$–ZnCl$_2$ system show a negative deviation from Raoult’s law. These results suggest that the complex ions such as ZnCl$_4^{2-}$ are formed in molten FeCl$_2$–ZnCl$_2$ mixtures.

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1. Introduction

Recently recycling processes of dust and fly ash generated in the steelmaking industry and municipal waste incineration process have been receiving much concern with environmental pollution and resource recycling. These dusts contain a lot of metallic elements such as Fe, Zn, Pb and Cd with small amounts of halogens. The presence of zinc and other impurities with halogens in dusts prevents from recycling directly to steelmaking industry because of their evaporation and condensation behavior.

Various methods have been proposed for the treatment of these dusty.$^{1-4}$ Both pyrometallurgical and hydrometallurgical, but the majority is disposed of as landfill. Hydrometallurgical treatment is difficult for these dusts due to the presence of insoluble chloride compounds such as ZnO–ZnCl$_2$–nH$_2$O which prevent from electrowinning.$^{3}$ These dusty are treated mainly by pyrometallurgical processes such as Waeltz kiln and Mitsui furnace (MF) process due to the high contents of halogen elements. In pyrometallurgical processes such as Waeltz kiln and Mitsui furnace (MF) process, halogen elements react with alkali or heavy metal and evaporate easily as halides and/or oxyhalide compounds.

Hara et al.$^{11}$ reported that zinc oxide in Electric arc furnace (EAF) dust was almost reduced and vaporized as metallic zinc in pilot plant tests for EAF dust recycling. They showed that zinc and iron could be separately recovered. The recovery of metallic elements such as Zn, Pb and Cd from iron based steelmaking dusts as volatile chlorides by using air and chlorine mixtures have been investigated.$^{5-8}$ Tailoka and Fray$^{7}$ studied the use of waste polyvinyl chloride (PVC) as a source of chlorinating agent under oxidizing atmosphere for steelmaking dust recycling. The similar works in the low oxygen potential regions have done by Hiratsuka.$^{8}$ They showed the possibility of separation of non-metallic element from steelmaking dust by chlorination of their oxides.

However, the behavior of these halogen compounds in pyrometallurgical process is not well known yet. As the first step, in the present work, the vapor pressures for the FeCl$_2$–ZnCl$_2$ system were measured to investigate the fundamental knowledge on thermodynamics as well as the behavior of halides in pyrometallurgical process.

2. Experimental

The transpiration method was employed to measure the vapor pressure for the FeCl$_2$–ZnCl$_2$ system. In this method, vapor pressure of each vapor species can be calculated from Dalton’s law

\[
p_i = P \frac{n_i}{(n_i + n_{	ext{carrier}})} \quad (1)
\]

where $n_i$ and $n_{	ext{carrier}}$ are the number of moles of vapor species and carrier gas, respectively and $P$ is the total pressure in the reaction tube ($1.013 \times 10^5$ Pa). The FeCl$_2$ and ZnCl$_2$ vapors contain dimer species and the dimerization reactions for FeCl$_2$ and ZnCl$_2$ are given by

\[
2\text{FeCl}_2(g) = \text{Fe}_2\text{Cl}_4(g) \quad (2)
\]

\[
\Delta G^0 = -142381 + 121T \quad (J/mol)^9
\]

\[
2\text{ZnCl}_2(g) = \text{Zn}_2\text{Cl}_4(g) \quad (3)
\]

\[
\Delta G^0 = -152716 + 184T \quad (J/mol)^9
\]

The relationship between mole number of each vapor species and the weight loss observed by transpiration technique is expressed by eq. (4).

\[
W_{\text{T,loss}} = W_{\text{ZnCl}_2} + W_{\text{Zn}_{2}\text{Cl}_4} + W_{\text{FeCl}_2} + W_{\text{Fe}_{2}\text{Cl}_4}
\]

\[
= M_{\text{ZnCl}_2} n_{\text{ZnCl}_2} + M_{\text{Zn}_{2}\text{Cl}_4} n_{\text{Zn}_{2}\text{Cl}_4}
\]

\[
+ M_{\text{FeCl}_2} n_{\text{FeCl}_2} + M_{\text{Fe}_{2}\text{Cl}_4} n_{\text{Fe}_{2}\text{Cl}_4}
\]

where $M$ is molecular weight of each vapor species, $n$ is the number of moles of species and $W_{\text{T,loss}}$ is the weight loss of sample. The vapor pressures of each vapor species were calculated by combining eqs. (1) through (4).

A schematic diagram of the experimental apparatus used in the transpiration technique is shown in Fig. 1. Experiments were carried out in a silicon carbide resistance furnace with a mullite reaction tube. Two or three grams of FeCl$_2$ and ZnCl$_2$ were held in an alumina boat. The alumina boat with the sample was inserted into an electric furnace. Purified Ar gas...
was used as carrier gas and flow rate was controlled by mass flow controller. The boat temperature was measured with Pt/Pt–13%Rh thermocouple and controlled at 873 K and 917 K within ±1 K. After reaching thermal equilibrium in 5 min, experimental time was counted with constant flow rate of Ar gas. Reagent grade of FeCl$_2$ and ZnCl$_2$ were dried at 523 K under dehydrated Ar gas atmosphere. After 10 to 35 min, the alumina boat was withdrawn from the furnace, quenched in an Ar gas stream, and weighed to measure the weight loss of the sample. The iron and zinc contents in sample were analyzed by Inductively Coupled Plasma emission spectrometry. As preliminary experiment, the vapor pressures of pure ZnCl$_2$ were measured as a function of the flow rate of Ar gas at 817 K and 916 K.

3. Results and Discussion

Figure 2 shows the vapor pressures of ZnCl$_2$ as a function of the flow rate of Ar gas at 817 K and 916 K. Two horizontal lines in Fig. 2 represent its literature values at each temperature. The saturated vapor pressures of ZnCl$_2$ were obtained for several flow rates of Ar gas. These results are in good agreement with the literature. Therefore, the transpiration method was used to measure the vapor pressure for the FeCl$_2$–ZnCl$_2$ system.

Figure 3 shows the relationship between the weight loss of FeCl$_2$ and ZnCl$_2$ and the flow rate of Ar gas in the FeCl$_2$–ZnCl$_2$ system. Bloom and Hastie showed the effect of the formation of vapor complexes of the type ABX$_{m+n}$ in ZnCl$_2$ system at 917 K. The triangle symbols in Fig. 3 represent the ratio of weight loss of FeCl$_2$ to ZnCl$_2$. The weight losses of sample were to be independent of the flow rate of Ar gas over the range of 145 cm$^3$/min to 170 cm$^3$/min at 917 K. These results in Fig. 3 show all much higher than the ideal value. These results in Fig. 3 indicate that FeCl$_2$ and ZnCl$_2$ vaporize under equilibrium between 15 min and 35 min of experimental time.

From the results of transpiration method shown in Figs. 3 and 4 the vapor pressures of each vapor species for the FeCl$_2$–ZnCl$_2$ system were calculated as shown in Fig. 5. The vapor pressures of ZnCl$_2$ in the FeCl$_2$–ZnCl$_2$ system show a negative deviation from Raoult’s law, however, those of FeCl$_2$ show all much higher than the ideal value. These results imply the formation of vapor complexes in this system. Bloom and Hastie showed the effect of the formation of gaseous CsPbCl$_3$ complex species confirmed by the mass spectrometry. Mcphail et al. summarized enhancement of the equilibrium vapor concentration due to the formation of vapor complexes of the type ABX$_{m+n}$ in
binary salt systems. They explained that there is no possibility of enhancement in non-alkali metal halide systems because the free energies of complex formation are very low. Hastie \(^{13}\) has shown that binary halide mixtures having both cations with valences greater than unity do not interact to form complex species unless the pure dimers are also present.

The analysis of reaction gas was carried out to confirm the vapor species by Mass spectrometer. However, the confirmation of vapor species was difficult because of the adsorption of chloride gas in the capillary tube connecting the Mass spectrometer. Therefore, gaseous FeZnCl\(_4\) is assumed to be formed in the present system according to the reaction (5).

\[
\text{FeCl}_2(g) + \text{ZnCl}_2(g) = \text{FeZnCl}_4(g) \tag{5}
\]

In this case eq. (4) can be rewritten as eq. (6).

\[
W_{\text{T,loss}} = W_{\text{ZnCl}_2} + W_{\text{Zn}_2\text{Cl}_4} + W_{\text{FeCl}_2} + W_{\text{Fe}_2\text{Cl}_4} + W_{\text{FeZnCl}_4} \tag{6}
\]

The total weight loss of FeCl\(_2\) is expressed by eq. (7).

\[
W_{\text{loss,FeCl}_2, (\text{total})} = W_{\text{loss,FeCl}_2, (\text{actual})} + W_{\text{loss,FeZnCl}_4, (\text{actual})} + W_{\text{loss,FeZnCl}_4, (\text{actual})} \tag{7}
\]

where \(W_{\text{loss,X, (total)}}\) is total weight loss of X and \(W_{\text{loss,X, (actual)}}\) is actual weight loss of X. The total weight loss of FeCl\(_2\) can be regarded as the actual weight loss of FeZnCl\(_4\) in vapor because the vapor pressures of FeCl\(_2\) are much higher than ideal values as shown in Fig. 5. The relationship can be written by eq. (8).

\[
W_{\text{loss,FeCl}_2, (\text{total})} \approx W_{\text{loss,FeZnCl}_4, (\text{actual})} \tag{8}
\]

The actual weight loss of ZnCl\(_2\) is thus given by eq. (9).

\[
W_{\text{loss,ZnCl}_2, (\text{total})} = W_{\text{loss,ZnCl}_2, (\text{actual})} + W_{\text{loss,Zn}_2\text{Cl}_4, (\text{actual})} + W_{\text{loss,FeZnCl}_4, (\text{actual})} \approx W_{\text{loss,ZnCl}_2, (\text{actual})} + W_{\text{loss,Zn}_2\text{Cl}_4, (\text{actual})} + W_{\text{loss,FeCl}_2, (\text{total})} \tag{9}
\]

The vapor pressure of ZnCl\(_2\) can be recalculated by combining eqs. (3), (6) and (9). The vapor pressures of FeCl\(_2\) and FeZnCl\(_4\) were calculated by using the Gibbs-Duhem relationship and eq. (10), respectively.

\[
p_{\text{FeZnCl}_4} = p_{\text{FeCl}_2, (\text{total})} / C_{0} p_{\text{FeCl}_2, (\text{actual})} \tag{10}
\]

Figures 6 and 7 show the recalculated vapor pressure of each species for the FeCl\(_2\)–ZnCl\(_2\) system at 917 K and 873 K. The vapor pressures of FeZnCl\(_4\) are shown higher than those of FeCl\(_2\). The vapor pressure curve of FeZnCl\(_4\) in Fig. 6 is not symmetrical about the equimolar composition and hence there could be at least one other complex species containing more than one mole of ZnCl\(_2\) for each molecule of FeCl\(_2\). The formation of other complex species such as FeZn\(_2\)Cl\(_6\) above molten FeCl\(_2\)–ZnCl\(_2\) mixture could be considered.
From the vapor pressure data of FeCl$_2$ and ZnCl$_2$ at 873 K and 917 K, the activities for the FeCl$_2$–ZnCl$_2$ system were calculated as shown in Fig. 8. Two vertical straight lines in Fig. 8 represent the composition of FeCl$_2$ saturation at each temperature from the phase diagram. The activities in this system show a negative deviation from Raoult’s law. Raman spectra of molten ZnCl$_2$ and ZnCl$_2$-alkali chloride mixtures have been studied by many authors, and it has been demonstrated that molten ZnCl$_2$ consists not only of single ions but also of large complex anions such as ZnCl$_2$$^2$ or ZnCl$_2$$^{-n}$. The negative deviation from Raoult’s law in Fig. 8 suggests that complex ions such as ZnCl$_2$$^2$ in molten FeCl$_2$–ZnCl$_2$ mixtures are formed by a strong interaction between FeCl$_2$ and ZnCl$_2$.

4. Conclusions

The vapor pressures of FeCl$_2$ and ZnCl$_2$ for the FeCl$_2$–ZnCl$_2$ system were measured by the transpiration method at 873 K and 917 K. The vapor pressures of FeCl$_2$ and ZnCl$_2$ were calculated based on the assumption of the formation of FeZnCl$_4$ complex species in vapors. The vapor pressure data imply the presence of some complex species as well as FeCl$_2$, ZnCl$_2$, and FeZnCl$_4$ in the vapors with molten FeCl$_2$–ZnCl$_2$ mixtures. The activities for the FeCl$_2$–ZnCl$_2$ system show a negative deviation from Raoult’s law. These results are interpreted by the formation of complex ions such as ZnCl$_2$$^2$ in molten FeCl$_2$–ZnCl$_2$ mixtures.

REFERENCES