論文・Paper

Vapor Pressure of ZnO over the Spinel Solid Solutions in the ZnO-CoO-Al₂O₃ and ZnO-NiO-Al₂O₃ Systems Determined by Knudsen Effusion Method

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The vapor pressures of ZnO over the spinel solid solutions in the ZnO-CoO-Al₂O₃ and ZnO-NiO-Al₂O₃ systems were measured by Knudsen effusion method at 1330° to 1530°C.

The equation combining the vapor pressure of ZnO with the concentrations of Zn²⁺ ions and cation vacancies and their distribution over the two kinds of crystallographically equivalent cation sites in the spinel lattice was derived according to the method proposed by Nakano for ionic solids. The dependence of the vapor pressure of ZnO over the spinel solid solutions on the concentration of cation vacancies was explained satisfactorily by the equation.

The further experimental results for the relationship between the vapor pressure of ZnO and its concentration were not easily understood by the present derived equation, and it was proposed that the efforts should be made to relate the enthalpy term in the equation with the crystal structure of a solid.

The possible mechanisms for the vaporization of ZnO were also discussed on the basis of the enthalpy data.

[Received August 22, 1979]

クヌーゼン分子流出法による ZnO-CoO-Al₂O₃ 及び ZnO-NiO-Al₂O₃ 系スピネル固溶体の ZnO の蒸気圧

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ZnO-CoO-Al₂O₃ 及び ZnO-NiO-Al₂O₃ 系スピネル固溶体の ZnO の蒸気圧を、クヌーゼン分子流出法により 1330°~1530°C の温度範囲で測定した。Zn イオン、陽イオン空位の濃度と、スピネル格子中での分布を ZnO の蒸気圧と関係づける式を、中野の方法に従って導き、この式により陽イオン空位濃度に対する ZnO 蒸気圧の依存性が満足に説明された。また蒸発エンタルピーの値から、ZnO の蒸発メカニズムに対する二、三の推論を行った。更に、ZnO の濃度と蒸気圧の関係を調べる実験を行ったが、ここで導出した式では簡単に結果が説明できず、式中のエンタルピー項を結晶構造と関連づける努力が必要であることを提案した。

(1979年8月22日受付)

Key-words : Vapor pressure, Zinc oxide, Spinel solid solution, Cation vacancy, Cation distribution

1. Introduction

As to the incongruent vaporization of a solid solution, the vapor pressure of a volatile component might be a function of the concentration and the distribution of volatile ions and defects in the crystal lattice. An approximate thermodynamical treatment for ionic solid solutions with composition-dependent vacancies was undertaken by Nakano¹⁾ in compliance with the site relation rule and the electrical neutrality condition. The composition dependence of experimental values

reported previously in such problems as the vapor pressure of ionic solid solutions, the partial pressure of oxygen in equilibrium with transition metal oxide systems, and the interdiffusion of cations in the spinel solid solutions with a gradient of vacancy concentration, was interpreted successfully by her expression for the chemical potential. In the case of the spinel solid solution, $\text{AO} \cdot n \text{B}_2\text{O}_3 = (3n+1)/4 \text{A} \frac{4}{3n+1} \text{B} \frac{8n}{3n+1} \square \frac{n-1}{3n+1} \text{O}_4$, her expressions for the partial pressures of components are :

$$\log P_{\text{AO}} = \frac{h_{\text{AO}} - K_{\text{AO}}}{2.303RT} + \log \frac{4}{3(3n+1)} \left\{ \frac{n-1}{3(3n+1)} \right\}^{-1/4} \quad (1)$$

$$\log P_{\text{B}_2\text{O}_3} = \frac{2h_{\text{B}_2\text{O}_3} - K_{\text{B}_2\text{O}_3}}{2.303RT} + \log \left\{ \frac{8}{3(3n+1)} \right\}^2 \left\{ \frac{n-1}{3(3n+1)} \right\}^{1/4} \quad (2)$$

and she predicted that these equations were to be applicable, for instance, to the vapor pressures of components in $\text{MgO} \cdot n(\text{Al}, \text{Cr})_2\text{O}_3$ which is important for the vaporization of refractory materials.

However, the above equations were derived on the assumption that cations and cation vacancies distributed randomly at tetrahedral and octahedral sites at high temperatures. Therefore, these equations cannot be applied to the vapor pressure of ZnO in the spinel solid solutions in the $\text{ZnO-CoO-Al}_2\text{O}_3$ and $\text{ZnO-NiO-Al}_2\text{O}_3$ systems in which the distribution of cations and cation vacancies is not random even at 1750°C^{21} . Consequently, modified expressions for the vapor pressures of components of the spinel solid solutions with preferred distribution of cations and cation vacancies were derived in the present paper, introducing the "distribution coefficient" to each type of cations and cation vacancies. The dependence of the vapor pressure of ZnO in the spinel solid solutions on the concentration of the composition-dependent cation vacancies was interpreted satisfactorily by using the present derived equation.

A few possible mechanisms for the vaporization of ZnO were discussed on the basis of the enthalpy data. It was also noted that the dependence of the vapor pressure of ZnO on its concentration could not be elucidated without expressing the enthalpy term in the present derived equation as a function of the concentration of ZnO and/or other variables.

2. Theory

Let us consider the ionic crystals such as spinel, perovskite, etc., which have only one kind of anion sites and two kinds of equivalent cation sites, A- and B-sites. Let n_{sa} , n_{sb} , and n_4 be the numbers of A-, B-sites, and anion sites, respectively, with the ratio of $n_{\text{sa}} : n_{\text{sb}} : n_4 = 1 : r_1 : r_2$. Also let n_1 , n_2 , n_3 , and n_v be the numbers of cations of type 1, 2, 3, and cation vacancies. We now introduce α , β , γ , and λ as the distribution coefficients for cations of type 1, 2, 3, and cation vacancies at A-site (Table 1), respectively. The following equations hold from the site relation rule :

Table 1. Distribution of cations and cation vacancies.

A-site	B-site	anion site
αn_1	$(1-\alpha)n_1$	n_4
βn_2	$(1-\beta)n_2$	
γn_3	$(1-\gamma)n_3$	
λn_v	$(1-\lambda)n_v$	
n_{sa}	$n_{\text{sb}} (=r_1 n_{\text{sa}})$	$n_4 (=r_2 n_{\text{sa}})$

$$\alpha n_1 + \beta n_2 + \gamma n_3 + \lambda n_v = n_{\text{sa}} = n_4 / r_2 \quad (3)$$

$$(1-\alpha)n_1 + (1-\beta)n_2 + (1-\gamma)n_3 + (1-\lambda)n_v = n_{\text{sb}} = r_1 n_4 / r_2 \quad (4)$$

The number of distinguishable arrangements of cations and cation vacancies, W , may be expressed as follows :

$$W = \frac{n_{\text{sa}}!}{(\alpha n_1)!(\beta n_2)!(\gamma n_3)!(\lambda n_v)!} \times \frac{n_{\text{sb}}!}{\{(1-\alpha)n_1\}!\{(1-\beta)n_2\}!\{(1-\gamma)n_3\}!\{(1-\lambda)n_v\}!} \times \frac{1}{\{(1-\lambda)n_v\}!} \quad (5)$$

The electrical neutrality condition requires the equation :

$$z_1 n_1 + z_2 n_2 + z_3 n_3 - |z_4| n_4 = 0 \quad (6)$$

where z_1 , z_2 , z_3 and z_4 are ionic valences of cations of type 1, 2, 3, and anion of type 4, respectively. From Eqs. (3), (4), (5) and (6), the expression for W follows :

$$W = \frac{\left(\frac{z_1 n_1 + z_2 n_2 + z_3 n_3}{r_2 |z_4|}\right)!}{(\alpha n_1)! (\beta n_2)! (\gamma n_3)! \left(\frac{z_1 n_1 + z_2 n_2 + z_3 n_3}{r_2 |z_4|} - \alpha n_1 - \beta n_2 - \gamma n_3\right)!} \times \frac{\left(\frac{z_1 n_1 + z_2 n_2 + z_3 n_3}{(r_2/r_1) |z_4|}\right)!}{\{(1-\alpha) n_1\}! \{(1-\beta) n_2\}! \{(1-\gamma) n_3\}! \left\{\frac{z_1 n_1 + z_2 n_2 + z_3 n_3}{(r_2/r_1) |z_4|} - (1-\alpha) n_1 - (1-\beta) n_2 - (1-\gamma) n_3\right\}!} \quad (7)$$

The contribution of mixing term to the entropy is given by $k \ln W$. When the other entropy term such as vibration is taken as S and the enthalpy term as H , the Gibbs' free energy is expressed in the form :

$$G = H - kT \ln W - TS \quad (8)$$

Following Nakano's definition for the partial molar enthalpy and the chemical potential for each ion, the next equation for the cation of type 1 can be derived using Stirling's formula :

$$\mu_1 + \frac{z_1}{|z_4|} \mu_4 = h_{(14)} + RT \ln \left(\frac{\alpha n_1}{n_{sa}} \right)^\alpha \left\{ \frac{(1-\alpha) n_1}{n_{sb}} \right\}^{1-\alpha} \left\{ \frac{\lambda n_v}{n_{sa}} \right\}^{\frac{z_1}{r_2 |z_4|} - \alpha} \left\{ \frac{(1-\lambda) n_v}{n_{sb}} \right\}^{\frac{z_1}{(r_2/r_1) |z_4|} - (1-\alpha)} - NT \left(\frac{\partial S}{\partial n_1} \right)_{n_2, n_3, P, T} \quad (9)$$

where N is the Avogadro's number and $h_{(14)} = N \left(\frac{\partial H}{\partial n_1} \right)_{n_2, n_3, \left(n_1 - \frac{z_1 n_4}{|z_4|} \right), P, T}$. The similar equations to Eq. (9) may be easily obtained for the cations of type 2 and 3.

When Eq. (9) is applied to the vaporization for a component AO in a spinel solid solution ($A_x^{2+} B_{1-x}^{2+}$)O· n M₂O₃, $z_1=2$ and $z_4=-2$. The spinel structure consists of cubic close-packed oxygen ions with 1/8 of tetrahedral and 1/2 of octahedral interstices occupied by cations and cation vacancies, so that $r_1=2$ and $r_2=4$. Then the following equation holds from Eq. (9) :

$$\mu_{A^{2+}} + \mu_{O^{2-}} = h_{AO} + RT \ln \left(\frac{4 x \alpha}{3 n + 1} \right)^\alpha \left\{ \frac{4 x (1-\alpha)}{2 (3 n + 1)} \right\}^{1-\alpha} \left\{ \frac{(n-1) \lambda}{3 n + 1} \right\}^{1/4-\alpha} \left\{ \frac{(n-1) (1-\lambda)}{2 (3 n + 1)} \right\}^{\alpha-1/2} + S' \quad (10)$$

where $S' = -NT (\partial S / \partial n_A)_{n_B, n_M, P, T}$.

Assuming that only a vapor phase is in equilibrium with the solid phase and the vapor phase contains AO which behaves as ideal gas, the equilibrium condition is,

$$\mu_{AO}(g) = \mu_{A^{2+}}(s) + \mu_{O^{2-}}(s) = K_{AO} + RT \ln P_{AO} \quad (11)$$

where $\mu_{AO}(g)$ is the chemical potential of AO in the vapor phase and $K_{AO} (= \mu_{AO}^\circ(g) - RT \ln P_{AO}^\circ)$ is a constant independent of composition at temperature T , $\mu_{AO}^\circ(g)$ and P_{AO}° being the standard chemical potential of AO gas and the vapor pressure of pure AO solid, respectively. But if the vaporization of AO in the spinel solid solution occurs by decomposition to elements, the equilibrium condition is,

$$\mu_A(g) + 1/2 \mu_{O_2}(g) = \mu_{A^{2+}}(s) + \mu_{O^{2-}}(s) = K_A + 1/2 K_{O_2} + RT \ln P_A P_{O_2}^{1/2} \quad (12)$$

where $\mu_A(g)$ and $\mu_{O_2}(g)$ are the chemical potentials of A and O₂ in the vapor phase, respectively, and K_A and K_{O_2} are constants. Thus, from Eqs. (10), (11) and (12), the relationships between the vapor pressures of AO or A+1/2O₂ and the sum of the chemical potentials of ions in the solid phase can be expressed as follows :

for $AO(s) = AO(g)$;

$$\ln P_{AO} = \frac{h_{AO} - K_{AO}}{RT} + \ln \left(\frac{4 x \alpha}{3 n + 1} \right)^\alpha \left\{ \frac{4 x (1-\alpha)}{2 (3 n + 1)} \right\}^{1-\alpha} \left\{ \frac{(n-1) \lambda}{3 n + 1} \right\}^{1/4-\alpha} \left\{ \frac{(n-1) (1-\lambda)}{2 (3 n + 1)} \right\}^{\alpha-1/2} + S' \quad (13)$$

and for $AO(s) = A(g) + 1/2 O_2(g)$;

$$\ln P_A \cdot P_{O_2}^{1/2} = \frac{h_{AO} - K_A - 1/2 K_{O_2}}{RT} + \ln \left(\frac{4 x \alpha}{3 n + 1} \right)^\alpha \left\{ \frac{4 x (1-\alpha)}{2 (3 n + 1)} \right\}^{1-\alpha} \left\{ \frac{(n-1) \lambda}{3 n + 1} \right\}^{1/4-\alpha} \left\{ \frac{(n-1) (1-\lambda)}{2 (3 n + 1)} \right\}^{\alpha-1/2} + S' \quad (14)$$

3. Experimental procedure

3.1 Material

The spinel powders with the compositions $(\text{Zn}_x\text{Co}_{1-x})\text{O} \cdot n\text{Al}_2\text{O}_3$ and $(\text{Zn}_x\text{Ni}_{1-x})\text{O} \cdot n\text{Al}_2\text{O}_3$ ($x=0, 0.2, 0.5, 0.8, 1.0$; $n=1.0, 1.1, 1.2, 1.3$) were synthesized from zinc carbonate, cobalt carbonate, nickel carbonate and gibbsite of reagent grade following the procedure described previously²⁾. The powders obtained were identified as spinels by X-ray diffraction. They were passed through screens to obtain 250~325 mesh particles. The average size of primary particles observed under an optical microscope was approximately $1\text{ }\mu\text{m}$ for all the samples.

3.2 Knudsen cell

The Knudsen cells were fabricated from platinum containing 10% rhodium because of its low reactivity with zinc oxide. The shape and size of the cell is shown in **Fig. 1**. The bottom cap was sealed with the upper cell by heliarc welding. The cap design allowed alternate opening and resealing of the crucible for a number of experiments. To examine the reliability of the orifice size (diameter and thickness) and gas-tightness of the welded part of the cell, the vapor pressures of pure zinc oxide were measured as they were already known as a function of temperature. The results shown in **Fig. 2** agree fairly well with those reported by other workers³⁾⁻⁵⁾, so that it was considered that the orifice size was approximately correct and the cell could be made gas-tight by heliarc welding.

3.3 Thermogravimetric measurements

The Knudsen cell was loosely filled with the spinel powder (approximately 0.5 g), sealed, put in a platinum basket, installed in the apparatus. This was followed by a bakeout at 600°C for at least 30 min to achieve a stable background pressure in the range of 3×10^{-5} to 2×10^{-4} Torr. The procedure before a vaporization run was almost the same with that for the free vaporization experiments previously performed⁶⁾⁻⁷⁾. At a prescribed temperature the cell was equilibrated to obtain constant weight loss rates. The constancy of weight loss rates was fairly good, so that the vaporization times of about 8~10 min at higher temperatures and 10~15 min at lower temperatures were taken in the temperature range of 1330° to 1530°C . The total weight loss ranging

Fig. 1. Knudsen cell.

Fig. 2. Temperature dependence of the total vapor pressure of pure ZnO as compared with other workers' results.

from 0.5 to 0.6 mg was considered enough judging from the accuracy of $\pm 0.1 \mu\text{g}$ of the microbalance (Cahn 1000).

3.4 Calculation of vapor pressures

That zinc oxide predominantly vaporized from the spinel solid solutions in the $\text{ZnO-CoO-Al}_2\text{O}_3$ and $\text{ZnO-NiO-Al}_2\text{O}_3$ systems has been ascertained from the free vaporization experiments^{9), 7)} and the concentration distribution of cations in the neighborhood of the surface of sintered bodies determined by the electron microprobe analysis²⁾. Then assuming the vaporization of zinc oxide by decomposition to gaseous elements just as that of pure zinc oxide⁴⁾, the total vapor pressure of zinc oxide was calculated from the measured weight losses using the Knudsen effusion equation⁸⁾,

$$P_i = \frac{m_i}{AWt} \left(\frac{2\pi RT}{M_i} \right)^{1/2} \quad (15)$$

where P_i is the partial pressure of the molecule i (dyn/cm^2), m_i/t is the weight loss rate (g/s), M_i is the molecular weight, A is the orifice area (cm^2), W is the Clausing correction factor (0.632 for the present cells)⁹⁾, R is the gas constant, and T is the absolute temperature. The partial pressures of Zn and O_2 in atm are expressed as :

$$P_{\text{O}_2} = \frac{m_{\text{O}_2}}{AWt} \cdot \frac{1}{44.33} \left(\frac{T}{M_{\text{O}_2}} \right)^{1/2} \quad (16)$$

$$P_{\text{Zn}} = \frac{m_{\text{Zn}}}{AWt} \cdot \frac{1}{44.33} \left(\frac{T}{M_{\text{Zn}}} \right)^{1/2} \quad (17)$$

From the decomposition formula of zinc oxide ($\text{ZnO(s)} = \text{Zn(g)} + 1/2\text{O}_2(\text{g})$), the equation $m_{\text{Zn}}/M_{\text{Zn}} = 2(m_{\text{O}_2}/M_{\text{O}_2})$ holds and thus,

$$P_{\text{Zn}} = 2 P_{\text{O}_2} (M_{\text{Zn}}/M_{\text{O}_2})^{1/2} \quad (18)$$

Let m_t be the total weight loss, and $m_t = m_{\text{Zn}} + m_{\text{O}_2}$. Combining Eqs. (16), (17) and (18) the following equations were derived;

$$P_{\text{O}_2} = \frac{m_t}{2AWt} \cdot \frac{32}{81.37} \cdot \frac{1}{44.33} \left(\frac{T}{32} \right)^{1/2} \quad (19)$$

$$P_{\text{ZnO}} = P_{\text{Zn}} + P_{\text{O}_2} = P_{\text{O}_2} [1 + 2(65.37/32)^{1/2}] \quad (20)$$

where P_{ZnO} is the total vapor pressure of zinc oxide. Using Eqs. (19) and (20), the total pressures of zinc oxide were calculated from the measured weight losses and temperatures. For the present temperature range the equilibrium constant for the reaction $1/2\text{O}_2(\text{g}) = \text{O(g)}$, $K_p = P_{\text{O}}/P_{\text{O}_2}^{1/2} (\text{atm}^{1/2})$ is in the range of $10^{-5} \sim 10^{-4(10), (11)}$, and the amount of oxygen atoms in the vapor phase was not taken into account.

The vapor pressures of CoO, NiO and Al_2O_3 over the spinel solid solutions were estimated from the reported values for those pure oxides³⁾; the vaporization of both CoO and NiO occurs by decomposition to elements as $\text{CoO} = \text{Co} + 1/2\text{O}_2$ and $\text{NiO} = \text{Ni} + 1/2\text{O}_2$, for which the vapor pressures of oxygen at 1500°C were calculated as $5.37 \times 10^{-6} \text{ atm}$ and $1.70 \times 10^{-6} \text{ atm}$ for CoO and NiO, respectively. Assuming the vapor pressures of CoO and NiO over the spinel solid solutions of $(\text{Zn}_{0.2}\text{Co}_{0.8})\text{O} \cdot \text{Al}_2\text{O}_3$ and $(\text{Zn}_{0.2}\text{Ni}_{0.8})\text{O} \cdot \text{Al}_2\text{O}_3$ to follow the Raoult's law, the total vapor pressures of CoO and NiO at 1500°C were calculated as $7.98 \times 10^{-6} \text{ atm}$ and $2.52 \times 10^{-6} \text{ atm}$, respectively. The total vapor pressures of ZnO obtained from the weight losses at 1500°C were $8.42 \times 10^{-4} \text{ atm}$ and $6.39 \times 10^{-4} \text{ atm}$ for $(\text{Zn}_{0.2}\text{Co}_{0.8})\text{O} \cdot \text{Al}_2\text{O}_3$ and $(\text{Zn}_{0.2}\text{Ni}_{0.8})\text{O} \cdot \text{Al}_2\text{O}_3$, respectively. The present estimation indicated that the total vapor pressures of CoO and NiO were less than 1% of that of ZnO and they were considered negligible. The vapor pressure of Al_2O_3 is less by many orders of magnitude than that of CoO or NiO, so that it was also neglected.

4. Results and discussion

4.1 Vapor pressures of ZnO over the spinel solid solutions

The Knudsen effusion data for $\text{ZnO} \cdot n\text{Al}_2\text{O}_3 (\text{ZA-}n)$, $(\text{Zn}_{0.2}\text{Co}_{0.8})\text{O} \cdot n\text{Al}_2\text{O}_3 (\text{ZCA-}n)$ and $(\text{Zn}_{0.2}\text{Ni}_{0.8})\text{O} \cdot n\text{Al}_2\text{O}_3 (\text{ZNA-}n)$ are listed in Table 2. The total vapor pressures of ZnO are shown in Fig. 3. The enthalpies, ΔH , and the entropies, ΔS , obtained by the second law analysis taking an equilibrium constant as $K = P_{\text{Zn}}P_{\text{O}_2}^{1/2}$ are also given in Table 2.

The enthalpies for ZA-*n*, ZCA-*n* and ZNA-*n* are similar to that of the pure zinc oxide (114 kcal/mol), when *n* is larger than unity. The mechanism for the vaporization of PbO from PZT(Pb(Zr, Ti)O₃) has been reported by Northrop¹²⁾ as,

from the fact that the enthalpy for the vaporization of PbO from PZT and from pure PbO showed good agreement. For the cases of ZA-*n* and ZCA-*n* with *n* larger than unity, ZnO may have formed on the solid surface before decomposing to elements. However, the enthalpies for

Table 2. Knudsen effusion data for the spinel solid solutions.

(a)

Sample	T(°C)	m/t(g/s) x10 ⁶	P _{O₂} (atm) x10 ⁵	P _{ZnO} (atm) x10 ⁴	P _{Zn} ^{1/2} _{O₂} x10 ⁷	ΔH(kcal/mol)	ΔS(e.u.)
ZA-1.0	1315	2.183	5.498	2.121	11.65	78.2	21.3
	1350	2.375	6.046	2.333	13.44		
	1400	3.333	8.615	3.324	22.86		
	1450	5.806	15.22	5.786	53.67		
	1500	8.972	23.87	9.211	105.4		
ZA-1.1	1310	1.722	4.330	1.671	8.145	119	46.5
	1335	2.014	5.103	1.969	10.42		
	1360	2.767	7.065	2.726	16.98		
	1400	5.042	13.03	5.028	42.52		
	1430	7.333	19.12	7.378	75.57		
	1460	10.97	28.85	11.13	140.1		
	1500	19.05	50.68	19.55	326.0		
ZA-1.2	1330	2.148	5.435	2.097	11.45	125	52.3
	1360	2.938	7.501	2.894	18.57		
	1390	4.690	12.09	4.664	38.00		
	1420	7.667	19.93	7.691	80.43		
	1450	11.13	29.20	11.27	142.6		
	1480	17.13	45.31	17.48	275.7		
	1510	25.57	68.23	26.33	509.5		
ZA-1.3	1330	2.019	5.107	1.970	10.43	124	50.1
	1350	2.625	6.682	2.587	15.61		
	1380	4.381	11.25	4.343	34.11		
	1410	6.786	17.59	6.787	66.70		
	1440	10.53	27.55	10.63	130.7		
	1470	15.96	42.10	16.24	246.9		
	1500	24.17	64.30	24.81	466.1		

(b)

Sample	T(°C)	m/t(g/s) x10 ⁶	P _{O₂} (atm) x10 ⁵	P _{ZnO} (atm) x10 ⁴	P _{Zn} ^{1/2} _{O₂} x10 ⁷	ΔH(kcal/mol)	ΔS(e.u.)
ZCA-1.0	1330	2.667	6.746	2.603	15.84	70.5	16.7
	1350	2.703	6.883	2.656	16.32		
	1380	3.357	8.625	3.328	22.90		
	1410	4.190	10.86	4.191	32.35		
	1440	5.119	13.39	5.166	44.29		
	1450	5.625	14.75	5.693	51.21		
	1500	6.233	16.44	6.345	61.26		
ZCA-1.1	1360	1.000	2.553	0.985	3.687	115	40.9
	1390	1.556	4.008	1.547	7.253		
	1420	2.063	5.362	2.069	11.22		
	1465	4.357	11.48	4.429	35.16		
	1500	6.458	17.18	6.630	64.37		
	1530	8.917	23.92	9.231	105.8		
ZCA-1.2	1360	1.259	3.215	1.241	5.211	116	42.7
	1390	1.854	4.778	1.844	9.441		
	1415	2.852	7.404	2.857	18.21		
	1450	4.452	11.68	4.506	36.08		
	1500	8.333	22.17	8.555	94.36		
	1525	10.38	27.81	10.73	132.6		
ZCA-1.3	1350	1.282	3.263	1.259	5.328	115	41.9
	1380	1.944	4.994	1.927	10.09		
	1410	3.019	7.827	3.020	19.79		
	1450	4.728	12.40	4.786	39.47		
	1480	6.936	18.35	7.079	71.06		
	1500	8.581	22.83	8.810	98.61		

(c)

Sample	T(°C)	m/t(g/s) x10 ⁶	P _{O₂} (atm) x10 ⁵	P _{ZnO} (atm) x10 ⁴	P _{Zn} P _{O₂} ^{1/2} x10 ⁷	ΔH(kcal/mol)	ΔS(e.u.)
ZNA-1.0	1330	1.000	2.530	0.976	3.638	112	39.7
	1350	1.146	2.917	1.125	4.503		
	1380	1.479	3.800	1.466	6.700		
	1410	2.143	5.555	2.143	11.84		
	1440	3.238	8.468	3.268	22.27		
	1470	4.667	12.31	4.750	39.04		
	1500	6.389	17.00	6.559	63.36		
ZNA-1.1	1335	0.667	1.689	0.652	1.984	115	41.1
	1350	1.061	2.700	1.042	4.010		
	1370	1.133	2.903	1.120	4.471		
	1400	1.854	4.792	1.849	9.482		
	1430	2.852	7.436	2.869	18.34		
	1460	4.063	10.69	4.123	31.59		
	1500	6.750	17.96	6.930	68.80		
ZNA-1.2	1360	1.185	3.026	1.168	4.758	115	41.1
	1390	1.700	4.381	1.690	8.289		
	1420	2.521	6.554	2.529	15.17		
	1450	3.542	9.289	3.584	25.59		
	1480	4.286	13.73	5.299	46.00		
	1510	7.472	19.94	7.693	80.49		
ZNA-1.3	1350	0.803	2.044	0.789	2.640	115	40.7
	1380	1.222	3.140	1.212	5.030		
	1410	1.917	4.968	1.917	10.00		
	1440	2.881	7.534	2.907	18.69		
	1470	4.167	10.99	4.241	32.94		
	1500	5.917	15.74	6.074	56.45

Fig. 3. Temperature dependence of the total vapor pressure of ZnO over the spinel solid solutions. (a) : $\text{ZnO} \cdot n \text{Al}_2\text{O}_3$, (b) : $(\text{Zn}_{0.2}\text{Co}_{0.8})\text{O} \cdot n \text{Al}_2\text{O}_3$, (c) : $(\text{Zn}_{0.2}\text{Ni}_{0.8})\text{O} \cdot n \text{Al}_2\text{O}_3$; ● : $n=1.0$, ▲ : $n=1.1$, ■ : $n=1.2$, ○ : $n=1.3$.

ZA-1.0 and ZCA-1.0 were found smaller than others, which might indicate the other mechanism controlling the reaction.

Altman¹³⁾ has reported the vapor pressures of MgO over MgAl_2O_4 and obtained the results which could not be elucidated unless the activity of solid Al_2O_3 was smaller than unity for the reaction, $\text{MgAl}_2\text{O}_4(\text{s}) = \text{Mg}(\text{g}) + 1/2\text{O}_2(\text{g}) + \text{Al}_2\text{O}_3(\text{s})$. He suggested a kind of quasi-equilibrium reaction for the vaporization of MgO accompanied by the solid solution formation reaction of Al_2O_3 with MgAl_2O_4 . By the present experimental method the concentration of ZnO is considered to have changed during the course of a vaporization run. In spite of this concentration change the weight loss was observed linear with respect to time and this fact may support the quasi-equilibrium vaporization in a Knudsen cell. Thus, the solid solution formation reaction was supposed to have occurred parallel with the vaporization of ZnO, which means that ZnO vaporized with the spinel structure being maintained within the range of solubility limit.

In ZA- n and ZCA- n with n larger than unity, Zn^{2+} ions occupy A-site and cation vacancies occupy B-site, and the cation vacancies formed by the vaporization of Zn^{2+} ions from A-site may also gather at B-site with the site exchange reaction with Al^{3+} ions^{2), 14)}. Then the total vapori-

zation reaction may be written for these spinels as;

where V denotes cation vacancy and () and [] are for A- and B-sites, respectively. For the cases of ZA-1.0 and ZCA-1.0 on the other hand, the cation vacancies formed by the vaporization of Zn^{2+} ions from A-site may be able to occupy A-site to some extent, as will be clear in the later discussion and the total vaporization reaction may be expressed as;

The enthalpy of the reaction of Eq. (21) must be larger than that of the reaction of Eq. (22), because of the excess energy required for the site exchange reaction of Al^{3+} ions (B-site to A-site) in spite of their octahedral site preference¹⁴⁾.

Both Zn^{2+} ions and the composition-dependent cation vacancies occupy A-site in $\text{ZNA}-n^{23)}$, so that the cation vacancies formed by the vaporization of Zn^{2+} ions from A-site may be able to occupy A-site without any site exchange reaction of Al^{3+} or Ni^{2+} ions. Thus, the vaporization may have occurred according to Eq. (22) and the enthalpy was observed about the same for both perfect and defective spinels.

In spite of the possibilities mentioned above, mechanisms for the vaporization of ZnO from the spinel solid solutions could not be explained totally. It is proposed that further efforts should be made to relate the present data with other possible information to determine the mechanism.

4.2 Relationship between the vapor pressures of ZnO and the composition-dependent cation vacancies

Assuming the vaporization of ZnO to occur by decomposition to elements, the relationship between the vapor pressure and the concentration of cation vacancies for the spinel solid solutions may be expressed by Eq. (14). Putting Zn equal to A in Eq. (14), $\log P_{\text{Zn}}P_{\text{O}_2}^{1/2}$ is plotted against the concentration of cation vacancies in Fig. 4. For the cases of ZA- n and ZCA- n , $\log P_{\text{Zn}}P_{\text{O}_2}^{1/2}$ increased with increase in the concentration of cation vacancies, while it showed a tendency to decrease in the case of ZNA- n . The calculation of $\log P_{\text{Zn}}P_{\text{O}_2}^{1/2}$ using Eq. (14), taking into account of various combinations of n , α and λ values ($n: 1.05 \sim 1.35$, $\alpha: 0.5 \sim 0.99$, $\lambda: 0.01 \sim 0.99$), and taking arbitrary constants for $(h_{\text{ZnO}} - K_{\text{Zn}} - 1/2 K_{\text{O}_2})/RT + S'$, showed that $\log P_{\text{Zn}}P_{\text{O}_2}^{1/2}$ increases with increase in n values for some combination of α and λ and decreases for other combinations. According to Nakano's equation (Eq. (1)), the vapor pressure of AO always decreases with increase in n values, but it is clear that this is not the case when the distribution coefficients of cations and cation vacancies are introduced into the derivation of the equation combining the vapor pressure and the concentration of cation vacancies.

Putting the configurational entropy term as F ,

$$F = \ln \left(\frac{4x\alpha}{3n+1} \right)^\alpha \left\{ \frac{4x(1-\alpha)}{2(3n+1)} \right\}^{1-\alpha} \left\{ \frac{(n-1)\lambda}{3n+1} \right\}^{1/4-\alpha} \left\{ \frac{(n-1)(1-\lambda)}{2(3n+1)} \right\}^{\alpha-1/2} \quad (23)$$

F is a function of α , λ and n . Thus,

Fig. 4. Comparison of calculated and observed dependence of vapor pressures on the concentration of cation vacancies. See text for discussion.

■ : $\text{ZnO} \cdot n \text{Al}_2\text{O}_3$,
● : $(\text{Zn}_{0.2}\text{Co}_{0.8})\text{O} \cdot n \text{Al}_2\text{O}_3$,
▲ : $(\text{Zn}_{0.2}\text{Ni}_{0.8})\text{O} \cdot n \text{Al}_2\text{O}_3$.

$$dF = \left(\frac{\partial F}{\partial n} \right)_{\alpha, \lambda} dn + \left(\frac{\partial F}{\partial \alpha} \right)_{n, \lambda} d\alpha + \left(\frac{\partial F}{\partial \lambda} \right)_{\alpha, n} d\lambda \quad (24)$$

Taking 0.2 for x to treat the spinel solid solutions ZCA- n and ZNA- n , Eq. (24) is written as:

$$dF = -\frac{3n-2}{(3n+1)(n-1)} dn + \ln \frac{\alpha}{1-\alpha} \cdot \frac{1-\lambda}{\lambda} d\alpha + \frac{1+\lambda-4\alpha}{4\lambda(1-\lambda)} d\lambda \quad (25)$$

Based on the observed distribution of Zn^{2+} ions and cation vacancies in ZCA- n ²⁾, it may be possible that the distribution coefficient α of Zn^{2+} ions is unchanged with the change in n values, and that the maximum amount of cation vacancies ($y = n_v/n_{sa}$) able to occupy A-site could be assumed. The concentration of cation vacancies is $(n-1)/3(3n+1)$ and the distribution coefficient of cation vacancies is λ , and then,

$$y \cdot n_{sa} : \left\{ \frac{n-1}{3(3n+1)} \times (n_{sa} + n_{sb}) - y n_{sa} \right\} = \lambda : 1-\lambda \quad (26)$$

In the spinel lattice, $n_{sb} = 2n_{sa}$, and from Eq. (26) λ is expressed as:

$$\lambda = \left(3 + \frac{4}{n-1} \right) y \quad (27)$$

Differentiating λ with respect to n ,

$$d\lambda/dn = -4y/(n-1)^2 \quad (28)$$

Substituting Eq. (28) for Eq. (25), and putting $d\alpha = 0$, the expression for dF/dn becomes;

$$dF/dn = \frac{3(3n+1)y + 4\alpha + 1 - 3n}{(3n+1)\{(n-1) - (3n+1)y\}} \quad (29)$$

When y is very small, the value for dF/dn is always positive with the condition $4\alpha + 1 > 3n$, and F increases monotonically with increase in n values. It is also obvious from Eq. (29) that the variation rate of F is subject to the values for α and y . The value for y was estimated by a trial and error method for the observed $\log P_{\text{ZnPO}_2}^{1/2}$ to agree well with the calculated values by taking 0.99 for α and arbitrary constants for the other terms than configurational entropy in Eq. (14). The calculated results are listed in **Table 3**, and also shown in Fig. 4 as solid lines.

For the case of ZNA- n , where the composition-dependent cation vacancies predominantly occupy A-site²⁾, the maximum amount of cation vacancies ($u = n_v/n_{sb}$) able to occupy B-site could be assumed. The following expressions were easily obtained by the similar derivation;

$$\lambda = 1 - \frac{2(3n+1)}{n-1} u \quad (30)$$

$$dF/dn = \frac{6(3n+1)u - 4\alpha + 4 - 3n}{(3n+1)\{(n-1) - 2(3n+1)u\}} \quad (31)$$

When u is very small, it is obvious that F decreases monotonically with increase in n values with the condition $4\alpha + 3n > 4$. However, the variation rate of F calculated by taking 0.93 for α with $\lambda > 0.8$ was larger than that of the observed values, and the appropriate value for u could not be found. Then, assuming that the introduced cation vacancies distributed at A- and B-sites with the fixed proportion ($\lambda = 0.99$) independent of n values, the calculated rate of variation agreed fairly well with the observed one. The results are shown in **Table 4** and Fig. 4 as dotted lines.

4.3 The relationship between the vapor pressure of ZnO and its concentration

According to Eq. (14), $\log P_{\text{ZnPO}_2}^{1/2}$ is also a function of the concentration of ZnO, x . The

Table 3. The change in the configurational entropy term for ZCA- n and ZA- n calculated using Eq. (23); $\alpha = 0.99$, $y = 7.5 \times 10^{-4}$.

n	λ (by Eq. (27))	2.303F
1.1	$43y \mp 0.03225$	0.600
1.2	$23y \mp 0.01725$	0.707
1.3	$13.3y \mp 0.01$	0.819

Table 4. The change in the configurational entropy term for ZNA- n ; $\alpha = 0.93$, $\lambda = 0.99$.

n	2.303F
1.1	-1.44
1.2	-1.573
1.3	-1.602

Table 5. Knudsen effusion data for the spinel solid solutions.

Sample	T(°C)	m/t(g/s) x10 ⁶	P _{O₂} (atm) x10 ⁵	P _{ZnO} (atm) x10 ⁴	P _{ZnO} ^{1/2} x10 ⁷	ΔH(kcal/mol)	ΔS(e.u.)
ZCA-1.3 x=0.8	1350	2.125	5.409	2.087	11.37	124	49.3
	1380	3.458	8.885	3.428	23.94		
	1410	5.292	13.72	5.293	45.94		
	1440	8.139	21.29	8.213	88.80		
	1470	12.33	32.54	12.55	167.8		
	1500	18.00	47.89	18.48	299.6		
ZCA-1.3 x=0.5	1350	2.000	5.091	1.964	10.38	119	45.5
	1380	2.917	7.493	2.891	18.54		
	1410	4.250	11.02	4.251	33.07		
	1440	6.417	16.78	6.475	62.13		
	1470	9.433	24.89	9.602	112.2		
	1500	13.63	36.27	14.00	197.5		
ZNA-1.3 x=0.8	1350	2.222	6.205	2.394	13.97	117	45.1
	1380	3.704	9.515	3.671	26.53		
	1410	5.458	14.15	5.460	48.11		
	1440	8.250	21.58	8.325	90.62		
	1470	12.33	32.54	12.55	167.8		
	1500	17.50	46.56	17.97	287.2		
ZNA-1.3 x=0.5	1380	3.125	8.028	3.098	20.56	106	37.8
	1410	4.146	10.75	4.147	31.86		
	1440	5.778	15.11	5.830	53.09		
	1470	8.333	21.98	8.483	93.15		
	1500	11.67	31.04	11.98	156.3

Fig. 5. Dependence of the total vapor pressures of ZnO on its concentration.

○ : (Zn_xCo_{1-x})O · 1.3 Al₂O₃,
 △ : (Zn_xNi_{1-x})O · 1.3 Al₂O₃.

Fig. 6. Log-log plots of $P_{Zn}P_{O_2}^{1/2}$ vs. x obtained at 1500°C.

○ : (Zn_xCo_{1-x})O · 1.3 Al₂O₃,
 ▲ : (Zn_xNi_{1-x})O · 1.3 Al₂O₃.

spinel solid solutions with the compositions (Zn_xCo_{1-x})O · 1.3 Al₂O₃ (ZCA-1.3) and (Zn_xNi_{1-x})O · 1.3 Al₂O₃ (ZNA-1.3) ($x=0.2, 0.5, 0.8, 1.0$) were chosen in this work to investigate the dependence of the vapor pressure of ZnO on x (Table 5). The results obtained at 1500°C are shown in Fig. 5. The total vapor pressure P_{ZnO} deviates positively from the Raoult's law for $x < 0.65$ in ZCA-1.3 and for $x > 0.45$ in ZNA-1.3, and negatively for $x > 0.65$ in ZCA-1.3 and for $x > 0.45$ in ZNA-1.3, respectively. As far as the compositions investigated are concerned, P_{ZnO} was larger over ZCA-1.3 than over ZNA-1.3, which corresponded to the higher activity of ZnO in ZCA-1.3 than in ZNA-1.3.

Equation (14) can be rewritten as a function of x as :

$$\log P_{Zn}P_{O_2}^{1/2} = K + \log x \quad (32)$$

where K contains other parameters as n , α , λ , enthalpy and so on. If K were not to be a function of x , the gradient $\partial(\log P_{\text{Zn}}P_{\text{O}_2}^{1/2})/\partial \log x$ would be unity, but this was not the case (**Fig. 6**). The results indicated that the parameters α and/or λ and/or enthalpy were also functions of x . Though the approximate values for α and λ may be obtained from the X-ray diffraction analysis as functions of x , the enthalpy term still remains to be determined by other possible methods as a function of x and/or other variables since the results could not be explained only by the configurational term in Eq. (14). Explanation of this kind of quasi-activity data or activity data taking into account of the relationship between thermodynamic properties and crystal structure of a solid should be an important subject to be undertaken.

References

- 1) M. Nakano, *Yogyo-Kyokai-Shi*, **81**, 491 (1973).
 - 2) K. Koumoto and H. Yanagida, *ibid.*, **85**, 193 (1977).
 - 3) M.S. Chandrasekharaiah, "The Characterization of High-Temperature Vapors", ed. J.L. Margrave, John Wiley & Sons, Inc. (1967) p. 495.
 - 4) D.F. Anthrop and A.W. Searcy, *J. Phys. Chem.*, **68**, 2335 (1964).
 - 5) J.A. Kitchener and S. Ignatowicz, *Trans. Faraday Soc.*, **47**, 1278 (1951).
 - 6) K. Koumoto, H. Yanagida and S. Mizuta, *J. Am. Ceram. Soc.*, to be published.
 - 7) K. Koumoto and H. Yanagida, *Yogyo-Kyokai-Shi*, **87**, 153 (1979).
 - 8) K.D. Carlson, "The Characterization of High-Temperature Vapors", ed. J.L. Margrave, John Wiley & Sons, Inc. (1967) p. 115.
 - 9) P. Clausen, *Ann. Physik*, **12**, 961 (1932).
 - 10) D.R. Stull and G.C. Sinke, "Thermodynamic Properties of the Elements", Am. Chem. Soc., Wash. D.C., (1956).
 - 11) JANAF Thermochemical Tables, 2nd Ed.
 - 12) D.A. Northrop, *J. Am. Ceram. Soc.*, **50**, 441 (1967); *ibid.*, **51**, 357 (1968).
 - 13) R.L. Altman, *J. Chem. Phys.*, **67**, 366 (1963).
 - 14) K.T. Jacob and K. Fitzner, *J. Mater. Sci.*, **12**, 481 (1977).
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