

## GIBBS FREE ENERGIES OF FORMATION OF $\text{ZnAl}_2\text{O}_4$ AND $\text{ZnCr}_2\text{O}_4$

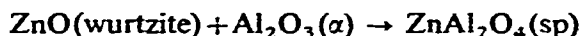
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### ABSTRACT

The standard free energies of formation of zinc aluminate and chromite were determined by measuring the oxygen potential over a solid Cu–Zn alloy, containing 10 at.-% Zn, in equilibrium with  $\text{ZnO}$ ,  $\text{ZnAl}_2\text{O}_4 + \text{Al}_2\text{O}_3(\alpha)$  and  $\text{ZnCr}_2\text{O}_4 + \text{Cr}_2\text{O}_3$ , in the temperature range 700–900°C. The oxygen potential was monitored by means of a solid oxide galvanic cell in which a  $\text{Y}_2\text{O}_3\text{–ThO}_2$  pellet was sandwiched between a CaO– $\text{ZrO}_2$  crucible and tube. The temperature dependence of the free energies of formation of the interoxidic compounds can be represented by the equations,



$$\Delta G^\circ = -10,750 + 1.57T (\pm 150) \text{ cal}$$



$$\Delta G^\circ = -15,000 + 2.05T (\pm 150) \text{ cal}$$

The heat of formation of the spinels calculated from the measurements by the “Second Law method” is found to be in good agreement with calorimetrically determined values. Using an empirical correlation for the entropy of formation of cubic spinel phases from oxides with rock-salt and corundum structures and the measured high temperature cation distribution in  $\text{ZnAl}_2\text{O}_4$ , the entropy of transformation of ZnO from wurtzite to rock-salt structure is evaluated.

### INTRODUCTION

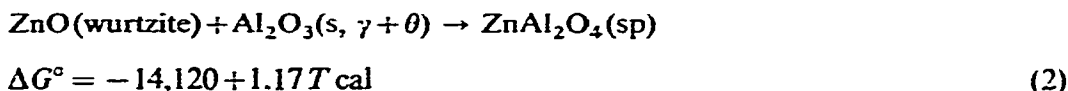
Thermodynamic data for  $\text{ZnAl}_2\text{O}_4$  are of interest in determining the conditions under which molten brass and other zinc-containing alloys react with high alumina refractories. Microprobe analysis<sup>1</sup> of alumina refractories from copper alloy melting channel induction furnaces have shown the presence of  $\text{ZnAl}_2\text{O}_4$  in the matrix and bauxite grains. It has been suggested<sup>1</sup> that the formation of the zinc spinel is an expansive reaction, which causes the disruption of bauxite/matrix bond, opening up channels for metal penetration around the grain and in the matrix.

Gilbert and Kitchener<sup>2</sup> have measured the equilibrium pressure of zinc and water produced by the reduction of zinc aluminate with hydrogen, according to the

equation,



in the presence of excess  $\alpha$ -alumina from 710 to 1044°C. They have derived the free energy of formation of the aluminate by combining the measurements with earlier studies on the reduction of zinc oxide and values for the standard free energy of formation of water vapor given in the literature. For



Alumina, obtained as a product in the reduction experiments, was a mixture of  $\gamma$  and  $\theta$  modifications which are less stable than the  $\alpha$  modification. Since values for the standard free energy of formation of the  $\alpha$  phase are not available in the literature and the ratio of  $\gamma/\theta$  modifications in the reduction product was not accurately determined, there is some uncertainty in the free energy of formation of  $\text{ZnAl}_2\text{O}_4$  given by eqn (2). Recently Navrotsky and Muan<sup>3</sup> have determined the compositions of CoO-ZnO solid solutions in equilibrium with  $\text{CoAl}_2\text{O}_4$ - $\text{ZnAl}_2\text{O}_4$  solid solutions at 1050°C. The activities of component oxides in CoO-ZnO solid solutions were determined independently. For the reaction,



—where the brackets denote solid solutions—the equilibrium constant was found to have a constant value,  $K = 0.174 (\pm 0.015)$ , when the activities of the spinel components in the spinel solid solution were set equal to their mole fractions. This suggests that the spinel solid solution is approximately ideal. From the value of the equilibrium constant and the known standard free energy of formation of  $\text{CoAl}_2\text{O}_4$  a value of  $-8.06 (\pm 0.5) \text{ kcal mol}^{-1}$  is obtained for the standard free energy of formation of  $\text{ZnAl}_2\text{O}_4$  from the component oxides  $\text{ZnO}(\text{wurtzite})$  and  $\text{Al}_2\text{O}_3(\alpha)$  at 1050°C. This value is  $4.5 \text{ kcal mol}^{-1}$  more positive than that suggested by Gilbert and Kitchener<sup>2</sup>. The heat of formation of  $\text{ZnAl}_2\text{O}_4$  from  $\text{ZnO}(\text{wurtzite})$  and  $\text{Al}_2\text{O}_3(\alpha)$  has been determined by Navrotsky and Kleppa<sup>4</sup> at 700°C as  $-10.56 \text{ kcal mol}^{-1}$ . Müller and Kleppa<sup>5</sup> have obtained a value of  $-15.05 \text{ kcal mol}^{-1}$  for the heat of formation of  $\text{ZnCr}_2\text{O}_4$  from component oxides at 900°C by oxide melt solution calorimetry.

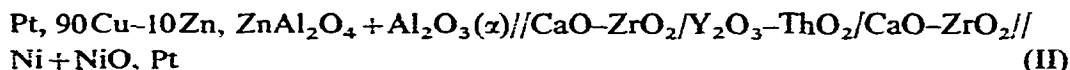
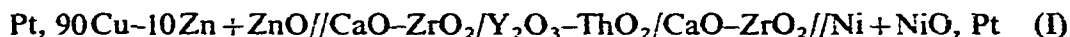
When cubic spinel phases are formed from component oxides having rock-salt and corundum structures, the entropy of formation can be expressed as  $-1.75 + \Delta S^M + \Delta S^{\text{rand}} \text{ cal deg}^{-1} \text{ mol}^{-1}$  (refs. 6 and 7), where  $\Delta S^M$  is the entropy of cation mixing in the interstitial sites of the spinel structure and  $\Delta S^{\text{rand}}$  is the entropy of randomization of orbital orientation for spinels that exhibit tetragonal Jahn-Teller distortions at low temperatures. Cooley and Reed<sup>8</sup> have determined the fraction of  $\text{Zn}^{2+}$  ions in the tetrahedral interstitial sites of  $\text{ZnAl}_2\text{O}_4$  as 0.96 and 0.94 at 905 and 1197°C, respectively, by high temperature X-ray diffraction. These values are in good

agreement with an estimated value of 0.965 at  $1000^{\circ}\text{C}$  from octahedral "site preference energies" for  $\text{Zn}^{2+}$  (0 kcal) and  $\text{Al}^{3+}$  ( $-18.6$  kcal) obtained from crystal field theory and measured cation distribution in  $\text{NiAl}_2\text{O}_4$ <sup>6</sup>. Therefore the entropy of formation of the spinels  $\text{ZnAl}_2\text{O}_4$  and  $\text{ZnCr}_2\text{O}_4$  from  $\text{ZnO}$ ,  $\text{Al}_2\text{O}_3$  and  $\text{Cr}_2\text{O}_3$  which have the wurtzite and corundum structures, respectively, is of interest.

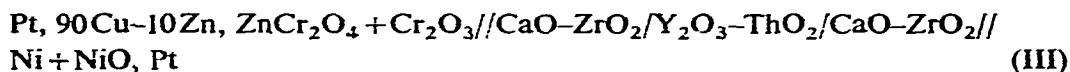
## EXPERIMENTAL

### Technique

The oxygen potentials over the mixtures Cu-10 at.-% Zn + ZnO, Cu-10 at.-% Zn +  $\text{ZnAl}_2\text{O}_4$  +  $\text{Al}_2\text{O}_3$  and Cu-10 at.-% Zn +  $\text{ZnCr}_2\text{O}_4$  +  $\text{Cr}_2\text{O}_3$  were measured in the temperature range  $700$ – $900^{\circ}\text{C}$ , using reversible solid oxide galvanic cells. Because of the high vapor pressure of pure zinc, it was necessary to have it at low activity as an alloy with copper. The electromotive force (emf) of the following cells were measured, for both increasing and decreasing temperatures;



and



The precautionary use of yttria doped thoria electrolyte ensures that the electrolyte has an oxygen ion transport number greater than 0.995 under the experimental conditions. The difference in the emf of cells I and II is directly related to the free energy of formation of  $\text{ZnAl}_2\text{O}_4$  from component oxides, while the difference in emf of cells I and III is related to the free energy of formation of  $\text{ZnCr}_2\text{O}_4$ .

### Materials

The spinel phases  $\text{ZnAl}_2\text{O}_4$  and  $\text{ZnCr}_2\text{O}_4$  were synthesized by heating pressed pellets of equimolar mixtures of the component oxides at  $1200$ – $1300^{\circ}\text{C}$  in air for 2–3 days. Formation of the ternary compounds was confirmed by X-ray diffraction analysis.  $\text{ZnO}$ ,  $\text{Al}_2\text{O}_3(x)$ ,  $\text{Cr}_2\text{O}_3$ , Ni and NiO powders used in this study were 99.99% pure. A Cu-Zn alloy containing 10 at.-% Zn was prepared by melting a mixture of Cu and Zn, each of 99.999+ purity, in closed zirconia crucibles under argon gas. The alloy was quenched and subsequently homogenized at  $1000^{\circ}\text{C}$  for 8 h. Chemical analysis indicated that the zinc concentration was 10.01 ( $\pm 0.03$ ) at.-%. A fine powder of the alloy was prepared by filing. Iron particles in the powder were removed magnetically. Impervious calcia stabilized zirconia tubes supplied by the Zirconia Corporation of America contained 7.5 mol % CaO. Thoria pellets doped with 15 mol %  $\text{YO}_{1.5}$  were supplied by Cerac Inc. This composition is close to that of maximum

ionic conductivity<sup>9</sup>. The argon gas used as the atmosphere for the emf experiments was 99.99% pure and was dried and then deoxidized by passing through a column of titanium granules maintained at 900°C.

#### *Apparatus and procedure*

A schematic diagram of the cell assembly is shown in Fig. 1. The test electrode containing the Cu-Zn alloy was placed in a CaO-ZrO<sub>2</sub> crucible and covered by a polished alumina disc. The reference electrode containing Ni and NiO in equimolar

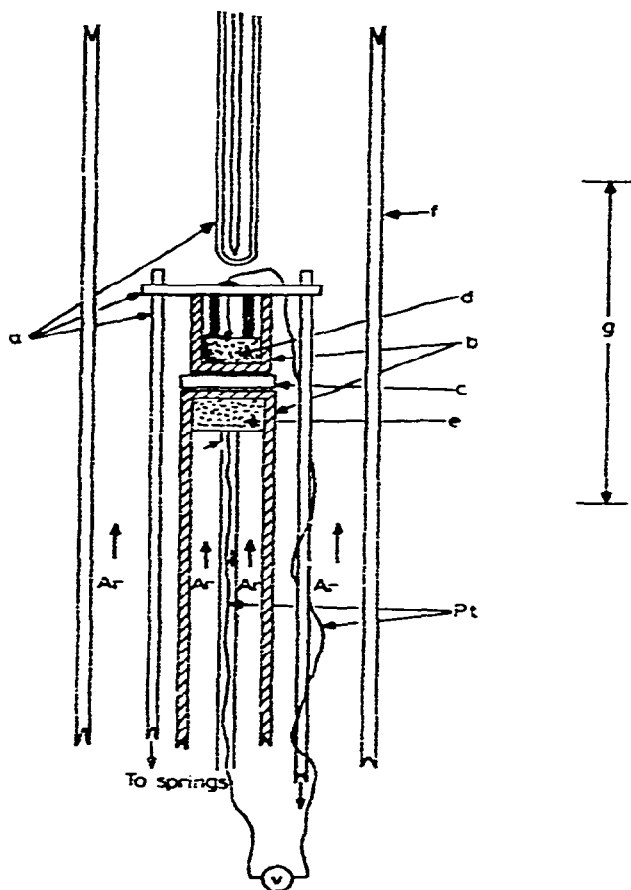


Fig. 1. Schematic diagram of the cell assembly. (a) alumina; (b) CaO-ZrO<sub>2</sub>; (c) Y<sub>2</sub>O<sub>3</sub>-ThO<sub>2</sub>; (d) test electrode; (e) Ni+NiO; (f) reaction tube (Al<sub>2</sub>O<sub>3</sub>); and (g) zone of constant temperature ( $\pm 1.0^\circ\text{C}$ ).

proportions was presintered inside a 18 in. long, flat end, CaO-ZrO<sub>2</sub> tube. A Y<sub>2</sub>O<sub>3</sub>-ThO<sub>2</sub> pellet was sandwiched between the CaO-ZrO<sub>2</sub> tube and crucible. The assembly was firmly held together between alumina rods by a spring loading arrangement. The springs were connected to a water-cooled end cap. Separate streams of argon were used to flush the reaction tube and the reference electrode. A Pt-Pt (13% Rh)

thermocouple placed immediately above the cell assembly measured the cell temperature. Another such thermocouple placed outside the reaction tube activated a solid-state temperature controller which maintained the cell temperature constant to within  $\pm 0.5^\circ\text{C}$ .

The test electrode was prepared by mixing the Cu-10% Zn alloy powder and the oxides in equimolar ratios, compacting the mixture into 1 cm diameter pellets and sintering at  $1000^\circ\text{C}$  in closed CaO-ZrO<sub>2</sub> crucibles at  $1000^\circ\text{C}$  under argon gas for 1-2 h prior to the emf experiments. Chemical analysis of the test electrode showed that the vaporization loss of zinc from the alloy was less than 0.02% during a typical experiment. The cell emf was measured using a Keithley Model 630 potentiometric electrometer with a minimum impedance of  $10^{12}\ \Omega$ . Times varying from 2 to 3 h after the attainment of thermal equilibrium were required to obtain steady reversible emfs. The rapid attainment of equilibrium in the present experiments compared to earlier studies on spinel phases containing Fe<sup>2+</sup> ions<sup>6,10</sup>, suggests that the presence of a slightly volatile component in the electrode can be beneficial, provided the cell is designed to minimize composition changes resulting from volatilization. To check for reversibility, the cell was occasionally shorted out for 10 to 30 sec; emf variation caused by this procedure was always reversed to within 0.5 mV of the original emf in 30 to 40 min. X-ray diffraction analysis of the pellets after a typical experiment confirmed the absence of any significant change in the composition of the electrodes.

## RESULTS AND DISCUSSION

The emfs of cells I, II, and III are shown in Fig. 2 as a function of temperature. The upper temperature limit of the experiments was determined by the vapor pressure of zinc. Reproducible emfs could not be obtained once the cells were heated above  $950^\circ\text{C}$ . The lower temperature limit was set by the resistance of the electrolyte assembly. The following equations were obtained by least mean-squares regression analysis of the emf data:

$$E_{\text{I}} = 436.2 - 0.148 T (\pm 1.8) \text{ mV} \quad (4)$$

$$E_{\text{II}} = 669.3 - 0.182 T (\pm 2.2) \text{ mV} \quad (5)$$

$$E_{\text{III}} = 761.4 - 0.192 T (\pm 2.2) \text{ mV} \quad (6)$$

The difference in oxygen potential between the two electrodes is related to the emf by the relation,

$$\Delta\mu_{\text{O}_2} = RT \ln \frac{P'_{\text{O}_2}}{P''_{\text{O}_2}} = -4FE \quad (7)$$

where  $F = 23,063 \text{ cal V}^{-1} \text{ mol}^{-1}$ ,  $E$  is the emf in volts,  $R$  is the gas constant,  $T$  is the absolute temperature, and the chemical potential is expressed in calories. The oxygen potential corresponding to the Ni + NiO reference electrode is given by <sup>11</sup>,

$$\Delta\mu_{\text{O}_2} = -111,930 + 40.58 T (\pm 250) \text{ cal} \quad (8)$$

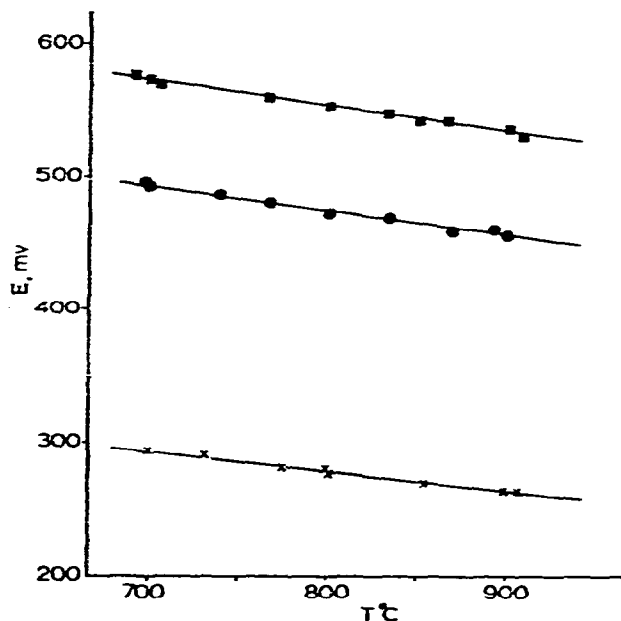
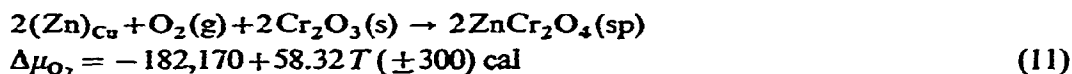
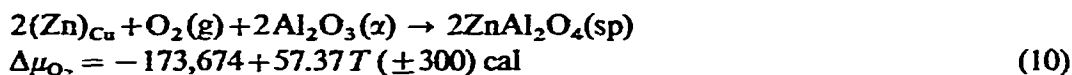
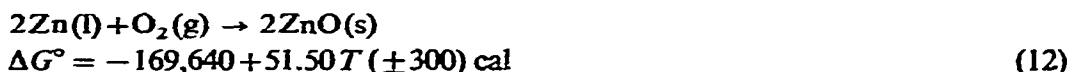


Fig. 2. Temperature dependence of the emf.  $\times$ , Cell I;  $\bullet$ , cell II;  $\blacksquare$ , cell III.

when eqns (7) and (8) are combined with the measured emf, the oxygen potential over the test electrodes are obtained:



It can readily be shown, from thermodynamic data on cupric aluminate and chromite<sup>7</sup>, that at the oxygen potentials encountered in the experiments the activities of  $\text{CuAl}_2\text{O}_4$  and  $\text{CuCr}_2\text{O}_4$  are less than  $10^{-7}$ . Significant contamination of  $\text{ZnAl}_2\text{O}_4$  and  $\text{ZnCr}_2\text{O}_4$  by  $\text{Cu}^{2+}$  ions is therefore not expected. Wilder<sup>12</sup> has recently measured the standard free energy of formation of  $\text{ZnO}(\text{s})$  using a solid oxide galvanic cell and a  $\text{Ni} + \text{NiO}$  reference electrode. When the value for the oxygen potential of the  $\text{Ni} + \text{NiO}$  electrode given by eqn (8) is combined with his emfs, for the reaction,



This equation is in good agreement with earlier studies on the free energy and heat of formation as well as heat capacity measurements on  $\text{ZnO}(\text{s})$ . By combining eqns (9)

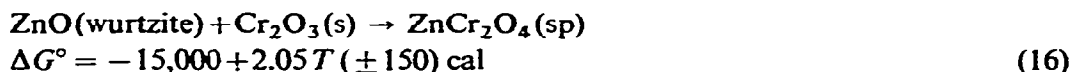
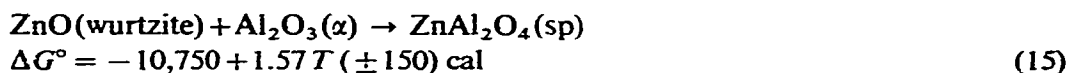
and (12), the chemical potential of Zn in Cu-10 at.-% Zn alloy, relative to liquid Zn as the standard state, is obtained;

$$\Delta\mu_{Zn} = -8640 - 1.36T (\pm 120) \text{ cal} \quad (13)$$

Activity measurements on Cu-Zn alloys have been reviewed recently by Hultgren and Desai<sup>13</sup> and compared graphically in ref. 14. The values for the chemical potential of Zn in its  $\alpha$ -solid solution with Cu reported in the literature show a scatter of 2000 cal. The value selected by Hultgren and Desai<sup>13</sup> given by the relation,

$$\Delta\mu_{Zn} = -7,510 - 0.64T \text{ cal} \quad (14)$$

is 1800 cal more positive than the value obtained in this study at a mean temperature of 800°C. By combining eqns 9, 10 and 11, the standard free energy of formation of  $ZnAl_2O_4$  and  $ZnCr_2O_4$  from component oxides with wurtzite and corundum structures, respectively, is obtained:



The value of  $-10.75 (\pm 0.4)$  kcal mol<sup>-1</sup> for this "Second Law" heat of formation of  $ZnAl_2O_4$  is in good agreement with the value of  $-10.56 (\pm 0.2)$  kcal mol<sup>-1</sup> obtained by Navrotsky and Kleppa<sup>4</sup> at 700°C. The quoted limits of error in the free energies and heat of formation obtained in this study are twice the standard deviation ( $2\sigma$ ). The calorimetric heat of formation of  $ZnCr_2O_4$  ( $15.05 \pm 0.15$  kcal mol<sup>-1</sup>) obtained by Muller and Kleppa<sup>5</sup> is the same as that obtained in this study ( $15.0 \pm 0.4$  kcal mol<sup>-1</sup>). The free energy of formation of  $ZnAl_2O_4$  at 1050°C obtained from eqn 15 is  $-8.67 (\pm 0.12)$  kcal mol<sup>-1</sup>, in fair agreement with a value of  $-8.06 (\pm 0.5)$  kcal mol<sup>-1</sup> obtained by Navrotsky and Muan<sup>3</sup> from distribution measurements in the system Co-Zn-Al-O, but 3.9 kcal mol<sup>-1</sup> more positive than the value reported by Gilbert and Kitchener<sup>2</sup>. This difference arises from the fact that a mixture of  $\gamma$  and  $\theta$  modification of  $Al_2O_3$  results from the decomposition of  $ZnAl_2O_4$  below 1250°C. The difference in the stabilities of  $\gamma$  and  $\alpha$  modifications is 2.7 kcal mol<sup>-1</sup>, while the stability of the  $\theta$  form is not accurately known. Presence of kinetic restrictions on the reduction reaction would require a more deducing mixture, and consequently a more negative value would be obtained for the free energy of formation of  $ZnAl_2O_4$ . Gilbert and Kitchener<sup>2</sup> did not study the  $H_2/H_2O$  ratios for the formation of  $ZnAl_2O_4$  from  $Al_2O_3(\alpha)$  and Zn(l).

Since  $ZnAl_2O_4$  and  $ZnCr_2O_4$  do not exhibit Jahn-Teller tetragonal distortions at low temperatures, their entropy of formation from component oxides with rock-salt and corundum structures is given by  $-1.75 + \Delta S^M \text{ cal deg}^{-1} \text{ mol}^{-1}$  ( $-1.17 \text{ cal mol}^{-1}$  for  $ZnAl_2O_4$  and  $-1.73 \text{ cal deg}^{-1} \text{ mol}^{-1}$  for  $ZnCr_2O_4$ )<sup>6</sup>. If the measured

cation distribution for  $\text{ZnAl}_2\text{O}_4$  at 905 and 1197°C is extrapolated to 800°C, the mean temperature in the present study, the ionic fraction of  $\text{Zn}^{2+}$  in the tetrahedral position is 0.97. The configurational contribution to the entropy of the spinel  $\text{ZnAl}_2\text{O}_4$ , arising from the mixing of cations in the interstitial position is 0.58<sup>6</sup>. Therefore the entropy changes for the reaction,



is given by,

$$\Delta S = -0.4 (\pm 0.2) \text{ cal deg}^{-1} \text{ mol}^{-1}$$

A similar result is obtained from the measurements on  $\text{ZnCr}_2\text{O}_4$ . The  $\text{Cr}^{3+}$  ion has an octahedral site preference energy of  $-37.7$  kcal, and there is little cation disorder in  $\text{ZnCr}_2\text{O}_4$ . The entropy of cation mixing is approximately  $0.02 \text{ cal deg}^{-1} \text{ mol}^{-1}$ . The entropy of formation of  $\text{ZnCr}_2\text{O}_4$  from oxides with rock-salt and corundum structures is therefore  $-1.73 \text{ cal deg}^{-1} \text{ mol}^{-1}$ . When this value is compared with the measured value for the entropy of formation of  $\text{ZnCr}_2\text{O}_4$  from oxides with wurtzite and corundum structures, a value of  $-0.32 \text{ cal deg}^{-1} \text{ mol}^{-1}$  is obtained for the entropy change for reaction (17).

The molar volume of ZnO in the wurtzite structure is  $14.52 \text{ cm}^3$  and in the rock salt structure it is  $11.81 \text{ cm}^3$ . A 19% decrease in molar volume is usually accompanied by an entropy decrease of 2 to 3  $\text{cal deg}^{-1} \text{ mol}^{-1}$ , provided the bonding conditions in the two structures are similar. In the wurtzite structure, each atom is tetrahedrally coordinated, corresponding to the  $\psi \text{ sp}^3$  orbitals, while the rock salt structure in which each atom has six neighbours is generally associated with greater ionic bonding<sup>15</sup>. In order to form the covalently bonded solid, the phases of orbitals on neighbouring atoms must be correlated so that they add coherently to form bonding states. In the less covalent rock-salt structure, the phases of the orbitals are more randomized. This results in higher entropy of the rock-salt phase, although the magnitude of the entropy contribution from orbital phase randomization cannot be accurately estimated because the precise extent of covalent bonding in the two structures is not known. In the limiting case when a covalently bonded tetrahedrally coordinated  $\text{A}^N\text{B}^{8-N}$  crystal converts to a metallic crystal, both bonding and anti-bonding states are equally likely to be occupied, and there are  $2^{4N}$  choices of orbital phases allowed. For this situation, Van Vechten<sup>16</sup> has estimated the 'bonding entropy' change as  $4Nk \ln 2 \text{ cal g at}^{-1} \text{ deg}^{-1}$ . The value of the entropy of transformation of ZnO from wurtzite to rock-salt phase obtained in this study results from the interaction of two opposing factors; a decrease in molar volume which makes a negative contribution to the entropy change, and a decrease in covalent bonding which makes a positive contribution to the entropy of transformation.

From activity measurements in the CoO-ZnO and NiO-ZnO systems at 1050°C and the assumption that ZnO with rock-salt structure would mix ideally with NiO and CoO, Navrotsky and Muan<sup>3</sup> have derived a value of  $5.8 \text{ kcal mol}^{-1}$  for the free energy change of reaction (17). Measurements of the approximate



temperature and pressure of wurtzite to rock salt transformation in  $\text{ZnO}^{17}$  together with molar volumes calculated from lattice constants yield a value of  $6.7 \text{ kcal mol}^{-1}$  for the free energy change of reaction (17) at  $400^\circ\text{C}$ , when compressibilities of the two polymorphic forms are neglected\*. The enthalpy change corresponding to reaction (17) may therefore be estimated as  $5.5 (\pm 0.9) \text{ kcal mol}^{-1}$ . Accumulation of information on the relative stabilities of pure oxides in different crystal structures would facilitate computer calculation of oxide phase diagrams by methods similar to those used by Kaufman and Bernstein<sup>18</sup> for refractory alloy systems.

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\* $\Delta G^\circ = P\Delta V$ . When compressibility effect is taken into consideration, the  $P\Delta V$  term must be replaced by  $\int_1^2 \Delta V dP$ . Since denser compounds are generally more incompressible,  $\Delta V$  decreases with increasing pressure and hence the transition pressure might correspond to smaller energy difference than that estimated from the linear relationship.