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Gibbs' Free Energy of Formation of Magnesium Stannate

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The thermodynamic properties of the spinel Mg_2SnO_4 have been determined by emf measurements on the solid oxide galvanic cell,

$$\text{Pt, W, MgO} + Mg_2SnO_4 + \text{Sn}/Y_2O_3\text{–}ThO_2/\text{Sn} + SnO_2\text{, W, Pt}$$

in the temperature range 600 to 1000°C. The Gibbs' free energy of formation of Mg_2SnO_4 from the component oxides can be expressed as

$$2\text{MgO (r.s)} + SnO_2\text{ (rut)} \rightarrow Mg_2SnO_4\text{ (sp)},$$
$$\Delta G^\circ = 1420 - 2.96T\ (\pm 100)\text{ cal mole}^{-1}.$$

These values are in good agreement with the information obtained by Jackson *et al.* [*Earth Planet. Sci. Lett.* **24**, 203 (1974)] on the high pressure decomposition of magnesium stannate into component oxides at different temperatures. The thermodynamic data suggest that the spinel phase is entropy stabilized, and would be unstable below 207 (±25)°C at atmospheric pressure. Based on the information obtained in this study and trends in the stability of aluminate and chromite spinels, it can be deduced that the stannates of nickel and copper(II) are unstable.

Introduction

In an earlier study (*1*) it was found that two stannates, $CaSnO_3$ with the orthorhombic perovskite structure, and Ca_2SnO_4 with the Sr_2PbO_4 structure, exist as stable phases in the CaO–SnO_2 system. Because of the smaller ionic radius of the Mg^{2+} ion (0.86 Å, CN = 6) compared to the Ca^{2+} ion (1.14 Å, CN = 6) on the Shannon–Prewitt scale, the compound Mg_2SnO_4 has the spinel structure. Poix (*2*) has shown that one Mg^{2+} ion is situated at the tetrahedral site, while the octahedral site contains one Mg^{2+} and one Sn^{4+} ion in samples quenched from 1200°C. Recently Jackson *et al.* (*3*) have studied the high pressure decomposition of Mg_2SnO_4 into its component oxides between 800 and 1200°C, and have discussed their implications for the earth's mantle. The temperature dependence of the decomposition pressure may be represented by the equation,

$$P = -24{,}300 + 40T\ (\pm 2500)\text{ bar.} \qquad (1)$$

The decomposition has been shown to be reversible (*3*). Since

$$\Delta S^\circ = \Delta V^\circ (dP/dT) \qquad (2)$$

and

$$\Delta G^\circ = -\int_1^P \Delta V\, dP, \qquad (3)$$

it appears that the heat of formation of Mg_2SnO_4 from its component oxides with rock-salt and rutile structures is positive (2240 cal mole^{-1}), and the high temperature stability of the spinel arises from its relatively large positive entropy of formation (3.7 cal deg^{-1}

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mole^{-1}), which is probably due to the mixing of cations on the octahedral sites. The error in the temperature dependence of the decomposition pressure is given as ± 10 kbar deg^{-1} by Jackson *et al.* (*3*) and frequently the accuracy of such data is poorer than the stated statistical uncertainty. In order to provide an independent check of the findings of Jackson *et al.* (*3*), the free energy of formation of Mg_2SnO_4 has been measured by a solid oxide galvanic cell in the temperature range 600 to 1000°C. Phase identification by the X-ray diffraction technique was undertaken to ensure that there is no other compound in the MgO–SnO_2 system at atmospheric pressure.

Experimental Methods

Materials. The stannic oxide used in this study was supplied by the British Drug House Limited and was 99.95% pure. The magnesium oxide powder, 99.9% pure, was obtained from Research Inorganic/Organic Corp. The dimagnesium stannate (Mg_2SnO_4) was prepared by mixing the component oxides in the required ratio, compacting the powder into pellets, and heating at 1210°C in air for 24 hr. Yttria-doped thoria tube containing 7 mole% Y_2O_3 and closed at one end was supplied by Cerac Inc. This composition is close to that of maximum ionic conductivity. 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

The apparatus used in this study was identical to that described earlier (*1*). The reversible emf of the cell,

$$\mathrm{Pt, W, MgO + Mg_2SnO_4 + Sn/Y_2O_3\text{–}ThO_2/Sn + SnO_2, W, Pt} \qquad \mathrm{(I)}$$

was measured as a function of temperature. The $Sn + SnO_2$ electrode was placed inside a vertical yttria-doped thoria tube, which dipped into the $Sn + Mg_2SnO_4 + MgO$ mixture held in a zirconia crucible. The electrical contact to the electrodes was made with tungsten wires, 2 cm long. One end of the tungsten wires was connected to platinum leads. Since the two tungsten–platinum contacts were kept at the same temperature, there was no thermoelectric contribution to the measured emf.

The two electrodes were flushed with separate streams of purified argon gas. The emf was measured by a "Solatron" digital voltmeter, which had an input impedance of 10^{12} ohms. Times varying from 3 hr to 30 min were found necessary to attain a steady emf depending on temperature. The reversibility of the cell was checked by passing a small current ($\simeq 50$ μA) through the cell for 2–5 min in either direction; it was found that the emf returned to the initial value in a few minutes, after which it remained constant for up to 24 hr. The emf was independent of the flow rate of the inert gas around the electrodes.

Preliminary studies indicated that at temperatures near 1000°C calcia-stabilized zirconia electrolyte was corroded by stannic oxide in equilibrium with tin. Microscopic examination of a cross section of this electrolyte revealed almost complete penetration of the zirconia tube after about 10 hr of contact with stannic oxide. The yttria-doped thoria electrolyte remained intact till 950°C, with a very slight surface discoloration at higher temperatures. This electrolyte material has an oxygen transport number greater than 0.99 at the temperatures and oxygen partial pressures encountered in this study (*4*).

In an attempt to establish the presence or absence of other phases in the MgO–SnO_2 system, pellets containing an intimate mixture of SnO_2 and MgO in the molar ratios 1:4, 2:3, 3:2, and 4:1 were heated at 1200°C for 48 hr and then quenched to room temperature. Microscopic examination and X-ray diffraction analysis indicated that pellets contained either $Mg_2SnO_4 + SnO_2$ or $Mg_2SnO_4 + MgO$ mixture. The diffraction patterns of Mg_2SnO_4, MgO, and SnO_2 in these phase mixtures were identical to those of the pure phases, suggesting the absence of significant solid solubility between the phases in equilibrium.

Results and Discussion

The reversible emf of cell I is plotted as a function of temperature in Fig. 1. The least-mean-squares regression analysis suggests the following equation for the temperature dependence of the measured emf.

$$E = -15.4 + 0.032T\,(\pm 0.8)\,\text{mV}. \quad (4)$$

This emf is directly related to the standard free energy change for the reaction,

$$2MgO(r.s) + SnO_2(rut) \rightarrow Mg_2SnO_4(sp),$$
$$\Delta G^\circ = -nFE = 1420 - 2.96T\,(\pm 80)\,\text{cal}, \quad (5)$$

where $n = 4$, E is the emf in volts, and F is the Faraday's constant (23 063 cal V^{-1} $mole^{-1}$). At a mean temperature of 800°C, the free energy of formation of Mg_2SnO_4 from its component oxides obtained in this study is -1755 cal $mole^{-1}$, and agrees well with the value of -1715 cal $mole^{-1}$ calculated from the high pressure studies of Jackson *et al.* (*3*) using a value of $\Delta V^\circ = 3.854$ cm^3 $mole^{-1}$ evaluated from the lattice parameters of the oxides. The heat and entropy of formation of Mg_2SnO_4 obtained in this study (1420 ± 250 cal $mole^{-1}$ and 2.96 ± 0.25 cal deg^{-1} $mole^{-1}$) are slightly smaller than those derived from the variation of the decomposition pressure with temperature (*3*) (i.e., 2240 ± 900 cal $mole^{-1}$ and 3.7 ± 0.9 cal deg^{-1} $mole^{-1}$, respectively). Because of the good reproducibility and reversibility of the cell emf, the results obtained in this study are considered to be more reliable.

Both the results of this investigation and the high pressure measurements of Jackson *et al.* (*3*) show that dimagnesium stannate is an entropy stabilized compound, whose heat of formation from component oxides is positive. At temperatures below 207 (±25)°C, the standard free energy of formation of this compound is positive, and it can exist only as a metastable phase whose decomposition is hindered by kinetic factors. The high entropy of Mg_2SnO_4 arises mainly from the mixing of cations on the octahedral sites of the spinel

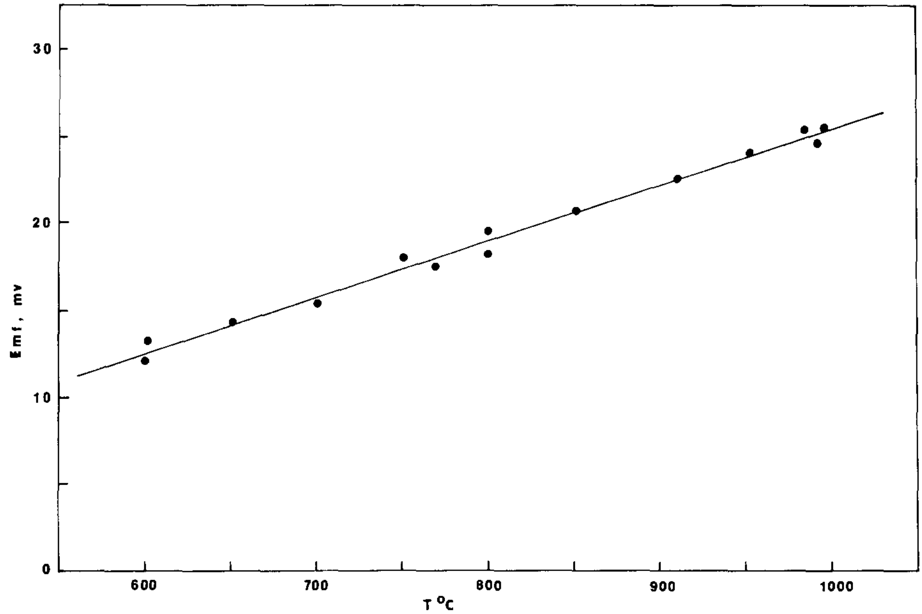

FIG. 1. The temperature dependence of the reversible emf of cell I.

structure. The ideal contribution from the mixing of cations for an inverse spinel is 2.75 cal deg^{-1} $mole^{-1}$ (*5*).

A recent study (*6*) of the thermodynamic properties of Zn_2TiO_4, which also has the inverse spinel structure, showed that its entropy of formation from component oxides according to the scheme,

$$2ZnO\ (wurtz) + TiO_2\ (rut) \rightarrow Zn_2TiO_4\ (sp) \quad (6)$$

is $\Delta S° = 2.46\ (\pm 0.2)$ cal deg^{-1} $mole^{-1}$, in the temperature range 650 to 800°C. The entropy of transformation of ZnO from the wurtzite to rock-salt structure has been evaluated as -0.4 (± 0.2) cal deg^{-1} $mole^{-1}$ (*7*). Therefore, for the reaction,

$$2ZnO\ (r.s) + TiO_2\ (rut) \rightarrow Zn_2TiO_4\ (sp), \quad (7)$$

the entropy change can be estimated as

$$\Delta S° = 3.26\ (\pm 0.28)\ cal\ deg^{-1}\ mole^{-1}.$$

This is close to the value for the entropy of formation of Mg_2SnO_4 by an isostructural reaction obtained in this study. For Mg_2TiO_4, which is a similar compound with the inverse spinel structure, the entropy of formation from component oxides is 3.36 cal deg^{-1} $mole^{-1}$ (*8*). The only exception from this trend is the entropy of formation of Co_2TiO_4 which is -0.15 cal deg^{-1} $mole^{-1}$ (*9*, *10*, *16*). If this value for Co_2TiO_4 can be confirmed, it might be indicative of short range order on the octahedral site and/or electronic contributions. The slightly higher entropy of formation of titanate spinels, Zn_2TiO_4 and Mg_2TiO_4, from component oxides with rock-salt and rutile structures, compared to the value for Mg_2SnO_4 obtained in this study, probably arises from a greater departure from the inverse cation distribution for the titanates. Because the configurational contribution to the entropy of the spinel phase has a maximum value at the random composition (*5*), $(M_{0.33}X_{0.67})_{tet}\ [M_{0.67}X_{1.33}]_{oct}\ O_4$, the cation distribution of inverse spinels will approach that of the random composition with increasing temperature. The rate of change of cation distribution with temperature is governed by the relative octahedral site preference energies of the cations involved. In Co_2TiO_4 the ionic fraction of the Co^{2+} ion on the tetrahedral site is 0.9 at 1200°C (*2*), while in Fe_2TiO_4 the ionic fraction of the Fe^{2+} ion is 0.92 at 1100°C (*11*). Using a simple model (*5*) for ion exchange between tetrahedral and octahedral sites, a value of -11.6 (± 2) kcal $mole^{-1}$ can be derived for the octahedral site preference energy of the Ti^{4+} ion, relative to those of Co^{2+} and Fe^{2+} obtained from crystal field theory (*12*). Since Co_2SnO_4 has 0.95 ions of Co^{2+} on the tetrahedral site (*2*), the octahedral site preference energy of Sn^{4+} ion is -15.7 (± 2) kcal $mole^{-1}$.

Systematic studies on the stability of aluminate and chromite spinels (*5*, *13–18*) suggest that for each family of spinels the stability decreases in the sequence

$$Zn^{2+} > Mn^{2+} > Co^{2+} > Fe^{2+} \approx Mg^{2+} > Ni^{2+} > Cu^{2+}$$

as shown in Fig. 2. Similar trends are exhibited by germanate and titanate spinels (*16*), although accurate information is not available on all the compounds of these series. On the basis of this trend and the measured heat of formation of Mg_2SnO_4, it appears that nickel and copper(II) stannates would have large positive heats of formation, and hence would not form at any temperature. Stannates of cobalt, manganese, and zinc are expected to be stable at all temperatures, while iron(II) stannate may only be stable at moderate temperatures (~350°C) because of entropy stabilization.

Note added in proof. Dr. A. Navrotsky has drawn the attention of the authors to a recent calorimetric study [A. Navrotsky and R. P. Kasper, *Earth Planet. Sci. Lett.* **31**, 247–54 (1976)] on the spinel compounds Mg_2SnO_4 and Co_2SnO_4. The heats of formation of Mg_2SnO_4 and Co_2SnO_4 from their component oxides are $+1.13$ (± 0.48) kcal $mole^{-1}$ and -2.31 (± 0.28) kcal $mole^{-1}$, respectively. Their value for Mg_2SnO_4 is in excellent agreement with the "second law" heat of formation obtained in this study, while their value for

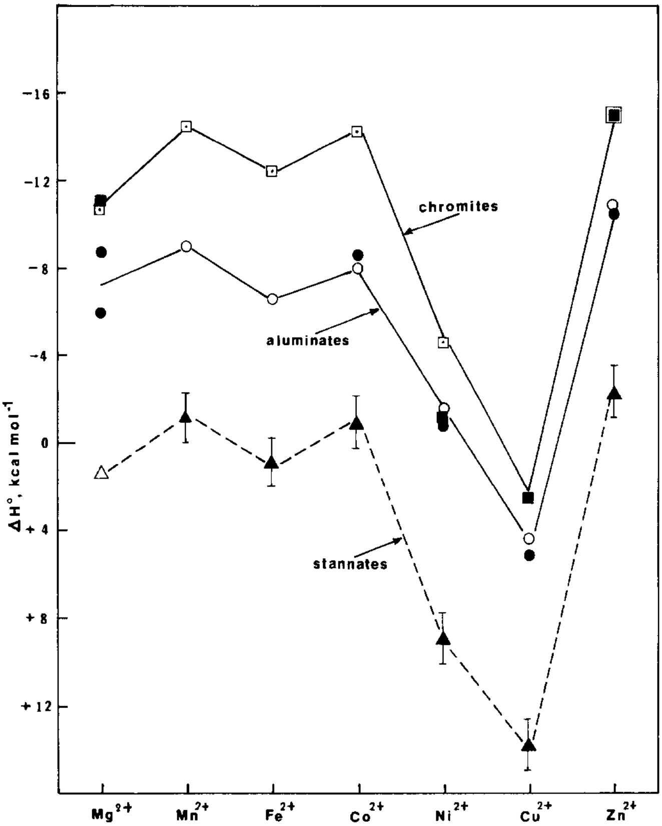

FIG. 2. Heats of formation of aluminate, chromite, and stannate spinels: aluminates. emf ○ (*5*, *7*, *13–15*), calorimetry ● (*16*, *17*); chromites. emf □ (*5*, *7*, *15*), calorimetry ■ (*18*); stannates, △ emf (Mg_2SnO_4—this study), ▲ estimated values with uncertainty limits. All values correspond to the formation of spinels from their component oxides at high temperatures.

Co_2SnO_4 is in fair agreement with that estimated in Fig. 2. The entropy of formation of Co_2SnO_4 has been evaluated as −0.95 cal deg^{-1} $mole^{-1}$, analogous to Co_2TiO_4.

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