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Investigation of the CaO–MnO System

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A series of solid solutions $Ca_xMn_{1-x}O$ was studied thermodynamically in the range from 1000 to 1200 K by solid-state galvanic cells involving β''-alumina electrolytes conducting calcium and manganese ions, respectively. The experimental procedure allowed us to determine the CaO and MnO activities directly from the emf measurements. The solutions exhibited strong positive deviation from ideal behavior. They could be regarded as regular solutions. © 1992 Academic Press, Inc.

Introduction

CaO and MnO belong to the oxides with rock salt structure. They mix in the solid state to form a complete series of solid solutions $Ca_xMn_{1-x}O$ ($0 < x < 1$). A study of the thermodynamic properties of these solid solutions is useful in understanding the interactions involving metals and slags as well as metals and refractories. The thermodynamic data published so far are very fragmentary and often contradictory. The first investigation by Schenck *et al.* (*1*) allowed to make assumption of ideality in the system CaO-MnO. Then, Driessens (*2*) considering the properties of some rock salt structure solid solutions assigned $Ca_xMn_{1-x}O$ to ideal solutions. Brezny *et al.* (*3*) estimated the activity data for the system CaO-MnO from the tie lines in the ternary systems CaO-MnO-CoO and CaO-MnO-NiO in the temperature range 1373 K to 1573 K. As an experimental method they used a CO/CO_2 gas equilibrium technique. The $Ca_xMn_{1-x}O$ appeared to be a non-ideal solution with a strong positive deviation from ideality. A similar estimation of the activities at 1373 K was made by Tiberg and Muan (*4*). Finally, the information about a non-ideal behavior of $Ca_xMn_{1-x}O$ solid solutions can be found in the review article by Davies and Navrotsky (*5*). The authors modeled data for all binary oxide solid solutions having rock salt structure, using a regular solution approach.

The purpose of the present work is to determine the thermodynamic functions of mixing directly from emf measurements as well as the activities for $Ca_xMn_{1-x}O$ solid solutions. The investigations were carried out by a solid-electrolyte galvanic cell method. Calcium β''-alumina and manganese β''-alumina were used as solid electrolytes. These electrolytes are known to be calcium and manganese(II) ions conductors. They belong to the family of divalent ion exchanged sodium β''-alumina compounds (*6*). Many of them were applied successfully in reversible galvanic cells (*7–13*).

The solid-electrolyte cells were of the type

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$$\mathrm{Pt}|\mathrm{O_2, CaO}||\mathrm{Ca}\text{-}\beta''\text{-alumina}|\,|\mathrm{Ca_xMn_{1-x}O, O_2}|\mathrm{Pt} \quad (1)$$

$$\mathrm{Pt}|\mathrm{O_2, MnO}||\mathrm{Mn(II)}\text{-}\beta''\text{-alumina}|\,|\mathrm{Ca_xMn_{1-x}O, O_2}|\mathrm{Pt}. \quad (2)$$

Experimental

The samples of $Ca_xMn_{1-x}O$ solid solutions were prepared in the following way. From the aqueous solutions of appropriate amounts of calcium and manganese nitrates the mixture of calcium and manganese carbonates were precipitated. The mixtures were carefully washed and then dried at 380 K. After calcination at 1070 K for 2 h they were heated at 1270 K in an atmosphere of deoxygenated dry argon for 24 h. The compositions of the solid solutions were determined by both gravimetric and volumetric methods. The results obtained were comparable. For all the samples X-ray powder diagrams were performed. The lattice parameters calculated by us were slightly different from those determined by Schenck *et al.* (*1*). Vegard's law appeared to be fulfilled for all compositions of the solid solution. The solid solutions as well as pure CaO and MnO powders were pressed into pellets 2 mm thick and 8 mm in diameter.

Ca-β''-alumina and Mn-β''-alumina electrolytes were prepared from MgO stabilized sodium-β''-alumina by ion exchange in an appropriate molten salt. The method of sodium-β''-alumina preparation was described in (*13, 14*). The exchange experiment with Ca^{2+} ions was performed in an α-alumina crucible filled with a $Ca(NO_3)_2-CaCl_2$ eutectic mixture. The Na-β''-alumina pellets (3 mm thick and 12 mm in diameter) were dipped in the fused salt at 850 K in air and held there for over 24 h. After the exchange the surface of the samples was cleaned from solidified eutectic melt by immersing it into molten $CaCl_2$. Then the samples were treated with anhydrous ethyl alcohol to remove any residue of the salt. The extent of ion exchange as determined by weighing pellets before and after exchange was greater than 96%. The exchange with Mn^{2+} ions was described in details in (*14*).

The half-cells and electrolyte pellets were assembled in a simple spring-loaded alumina holder according to the respective galvanic cell arrangement. The cell was placed in the furnace and heated to the measurement temperature. The emf's were monitored with a high resistance digital voltmeter. A purified dry argon flow was passed through the furnace during the emf measurements. Five independent series of emf measurements for each composition of the solid solution were performed in the temperature range 1000–1200 K. The time taken for the cell to attain equilibrium did not exceed 0.5 h.

Results and Discussion

The emf of the cells (1) and (2) is a result of a difference in the activity of Me ions (Me = Ca or Mn) at the electrodes. The overall cell reaction for the cells (1) and (2) can be written as

$$\mathrm{MeO} = (\mathrm{MeO})_{\mathrm{s.s.}}, \quad (3)$$

where $(MeO)_{s.s.}$ denotes the appropriate oxide in the solid solution. The work of the cell (1) considered, then, in transferring CaO, whereas that one of the cell (2) in transferring MnO to the solid solution.

From the values of emf to cell (1), E_1, the partial molar Gibbs free energy of CaO, $\overline{G}_{CaO}$, and the activity of CaO, a_{CaO} in the solid solutions were calculated

$$\overline{G}_{CaO} = -2FE_1 = RT \ln a_{CaO} \quad (4)$$

In a similar way the partial molar Gibbs free energy, $\overline{G}_{MnO}$, and the activity of MnO, a_{MnO}, were obtained

$$\overline{G}_{MnO} = -2FE_2 = RT \ln a_{MnO} \quad (5)$$

(E_2 is the emf of cell (2)).

The emf of both cells appeared to vary

TABLE I

EMF of Cell (1) as a Function of Temperature $E_1 = A_1 + B_1\,(10^{-3}\,T)$ at Various Compositions of $Ca_xMn_{1-x}O$ Solid Solution

x	A_1/mV	B_1/(mV · K^{-1})
0.14	−59.0 ± 1.5	81.4 ± 1.6
0.34	−36.4 ± 0.9	45.4 ± 1.0
0.50	−21.0 ± 1.1	29.9 ± 0.8
0.68	−8.4 ± 0.6	16.5 ± 0.9
0.76	−4.7 ± 0.8	11.6 ± 0.7

linearly with temperature in the range under study. The coefficients A_i and B_i (i = 1, 2) of the straight line $E_i = A_i + B_i\,(10^{-3}\,T)$, calculated by least-squares method, are given in Tables I and II.

The emf's of the cell (1) for x = 0.90 and those of the cell (2) for x = 0.14 were too small to measure them with a sufficient precision. In terms of the partial molar Gibbs free energy, the Gibbs free energy change due to the formation of 1 mole of the solid solution (the Gibbs free energy of mixing) is

$$G^M = x\overline{G}_{CaO} + (1 - x)\overline{G}_{MnO} \qquad (6)$$

Taking into account the linearity of emf with composition, and the equations (4) and (5), the equation for G^M can be represented as

$$G^M = \alpha + \beta T \qquad (7)$$

where

$$\alpha = -2F\,[xA_1 + (1 - x)A_2] \qquad (8)$$

$$\beta = -2{*}10^{-3}F\,[xB_1 + (1 - x)B_2] \qquad (9)$$

The calculated values of the α and β coefficients (see Eqs. (8) and (9)) are given in Table III.

The G^M obtained was compared to that one for the ideal solutions

$$G^{M,id} = \beta^{id}\,T \qquad (10)$$

where

$$\beta^{id} = R\,[x\ln x + (1 - x)\ln(1 - x)] \qquad (11)$$

The calculated β^{id} values for four compositions of the solutions under study are also given in table III.

As can be seen from Table III the β values are (in the limit of error) nearly the same as those calculated for ideal solutions. It can be concluded therefrom that the entropy of mixing for the solutions under study is equal to the configurational entropy, defined in theory of solutions (*15*). Thus, the nonzero values of α coefficient and nearly ideal entropy of formation allow to assign $Ca_xMn_{1-x}O$ to a class of regular solutions. Consequently, the excess molar free energy of the solution, G^E, as well as the enthalpy of mixing, H^M, are equal to the coefficient α.

The assumption on the regular behaviour allowed to calculate the activity values for the second component of the solid solution, for which it was not possible to measure the emf with a satisfactory precision (x = 0.14 and 0.90). At first, the interaction parameter Ω, derived in the quasi-chemical model of solutions (*15*) was calculated for all solutions studied as

$$\Omega = \frac{\alpha}{x(1 - x)} \qquad (12)$$

Its mean value was calculated as (16260 ± 820) J/mol. Then the activities were obtained directly from the following equations

$$a_{CaO} = x\exp\left[(1 - x)^2\frac{\Omega}{RT}\right] \qquad (13a)$$

TABLE II

EMF of Cell (2) as a Function of Temperature $E_2 = A_2 + B_2\,(10^{-3}\,T)$ at Various Compositions of $Ca_xMn_{1-x}O$ Solid Solution

x	A_2/mV	B_2/(mV · K^{-1})
0.34	−9.5 ± 1.0	17.7 ± 1.1
0.50	−20.6 ± 1.3	29.4 ± 1.3
0.68	−38.6 ± 1.5	49.3 ± 1.5
0.76	−48.5 ± 1.3	61.5 ± 1.6
0.90	−68.3 ± 1.9	99.3 ± 2.4

TABLE III

GIBBS FREE ENERGY OF MIXING FOR $Ca_xMn_{1-x}O$ SOLID SOLUTIONS AS A FUNCTION OF TEMPERATURE, $G^M = \alpha + \beta T$, VALUES OF α(theor) AND β^{id} OBTAINED FROM THEORETICAL CONSIDERATIONS

x	α ($J \cdot mol^{-1}$)	($-\beta$) ($J \cdot deg^{-1} mol^{-1}$)	α(theor) ($J \cdot mol^{-1}$)	($-\beta^{id}$) ($J \cdot deg^{-1} mol^{-1}$)
0.34	3598 ± 193	5.233 ± 0.193	4750	5.329
0.50	4014 ± 193	5.721 ± 0.251	5400	5.763
0.68	3486 ± 174	5.209 ± 0.289	4710	5.213
0.76	2935 ± 154	4.549 ± 0.309	3890	4.589

$$a_{MnO} = (1 - x)\exp\left[x\frac{\Omega}{RT}\right] \qquad (13b)$$

The activities of CaO and MnO in the $Ca_xMn_{1-x}O$ solid solution as functions of x at 1100 K are shown in Figure 1. Similar plots are obtained for other temperatures. Knowing the Ω-values, the G^E values for $x = 0.14$ and $x = 0.90$ were calculated. The G^E values at 1100 K for all compositions of solid solutions are presented at the top of Figure 1. As can be seen in Figure 1 the $Ca_xMn_{1-x}O$ solid solutions show significant positive deviation from Raoult's law. This fact could be related to a tendency towards immiscibility in the solid solution at lower temperatures. The critical temperature, T_{cr}, could be evaluated according to the regular solutions theory (*15*) as

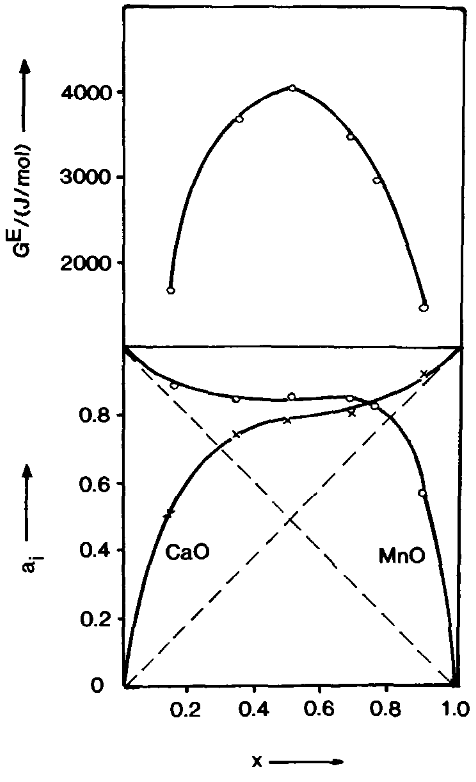

FIG. 1. Excess Gibbs free energy and activity values for $Ca_xMn_{1-x}O$ at 1100 K.

$$T_{cr} = \frac{\Omega}{2R} \qquad (14)$$

and for the solutions under study is equal to (978 ± 49) K. It is worth mentioning that our emf experiments were done in temperatures exceeding the calculated T_{cr}.

The accurate measurements of the thermodynamic properties of $Ca_xMn_{1-x}O$ solution by a solid-state electrochemical method were matched by theoretical lattice energy calculation based on the model put forward by Wasastjerna (*16*) and modified by Hovi (*17*). This treatment takes into account the difference in the electrostatic and exchange energies between the solid solutions and the pure components together with the geometric displacement due to the difference in the ionic sizes. The enthalpy of mixing of a binary solid solution is given by the relationship

$$H^M = [N_0 x(1 - x)\, A(ze)^2/d_0] \{[(V_1 + V_2)/8] + 0.5\}(\Delta d/d_0)^2 \quad (15)$$

where N_0 is the Avogadro's number, A is the Madelung's constant (1.75 for rock salt structure), z is the valence (2 in the case of $Ca_xMn_{1-x}O$ solution), e is the electronic charge, d_0 is the interionic distance in the solid solution, Δd is the difference in the interionic distances in the pure components and V_i is characteristic quantity for the pure component "i" as defined below

$$V_i = (3 + 4\gamma_i T)/[k_i A(ze)^2/(6d_i^4 - \gamma_i T)] \quad (16)$$

where γ_i is the coefficient of cubic expansion and k_i is the compressibility. The model presented above was verified in the calculations of enthalpies of mixing in various binary alkali halide solid solutions (*17, 18*) and in some oxide solid solutions (*19*). The equations (15) and (16) were employed by us for the estimation of the theoretical values of α ($\alpha = H^M$). Since the Vegard's law is applicable to the $Ca_xMn_{1-x}O$ solution, the interionic distance for the solid solution is simply related to those for the pure components. The respective lattice parameter values were found in (*20*). The values of γ_i and k_i for MnO were taken from (*19*) and those for CaO from (*21*). It should be mentioned that there is not any change in the crystal field stabilization energy in the solid solutions involving Mn^{2+} as transition metal cation (*2, 22*). The calculated α(theor) values are given in Table III along with those obtained from the emf experiments. The agreement between the theoretical and experimental values is reasonable considering the approximation in the assumption on the negligible deviation from the stoichiometry of the solutions under study.

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