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Thermodynamic Study of Some Solid Solutions in the CaO–ZrO_2 System by emf Method

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The thermodynamic properties of some solid solutions in the CaO–ZrO_2 system have been investigated by using solid electrolyte galvanic cells of the type: O_2, Pt|CaO, CaF_2|CaF_2 (t_F=1)| δCaO(1 − δ)ZrO_2, CaF_2|Pt, O_2. The influence of CaF_2 added in electrodes on the thermodynamic equilibrium was investigated. It was shown that the heterogeneous field with cubic solid solution reaches the composition $x = 0.17$ mole of CaO. The results indicate that addition of ZrO_2 to the saturated solid solution produces a significant decrease in the activity of CaO. Measured data were used to calculate thermodynamic parameters of reactions with saturated solid solutions $Ca_{0.17}$ $Zr_{0.83}$ $O_{1.83}$, ZrO_2, and $CaZrO_3$. At temperatures below 820°C, saturated solid solutions have a tendency to decompose into $CaZrO_3$ and ZrO_2. A comparison of the thermodynamic results with available data on phase relationships in the CaO–ZrO_2 system is presented. High thermodynamic stability of $SrZrO_3$ and $BaZrO_3$ is one of the reasons for the absence of cubic solid solutions in the system *Me*O–ZrO_2 (*Me*–Sr, Ba).

Introduction

Thermal stability and reactivity of compounds in the ZrO_2 and alkaline earth oxide systems, and consequently, the possibility of their practical use is determined by their thermodynamic properties. The thermodynamic properties of stoichiometric zirconates of Ba, Sr, and Ca have been determined (*1*–*5*) and are reliably established. However, there is a paucity of reliable high temperature enthalpies and Gibbs energies of formation of the solid solutions in the systems *Me*O_2–CaO and ZrO_2–Re_2O_3 (*Me*–Zr, Th, and Re–Y, Sc etc.). For this reason, and also in connection with the results of investigations (*8*–*17*), it was important to gain more information about the basic thermodynamic properties of these systems. In the present paper the thermodynamic properties of some lime + zirconia solid solutions are reported.

Experimental

For the determination of the thermodynamic properties of solid solutions the emf of cells of type

$$(-)\,O_2, Pt/CaO, CaF_2/CaF_2/$$
$$\delta CaO(1-\delta)ZrO_2, x\,CaF_2/Pt, O_2\,(+)$$

($t_{F^-} = 1$; 1 atm O_2) have been measured, where δ is the molar fraction of CaO in the solid solution and x is the number of moles of CaF_2 added to the electrodes studied. The reliability of the heats and Gibbs energies of formation of refractory double oxides obtained from the emf's of such cells and the electrochemical behavior of CaF_2 as a solid electrolyte under high oxygen pressures were discussed in (*5*–*7*). Samples containing 15, 19, 21, 25, and 40 mole% CaO were prepared. Some of the samples were prepared from ZrO_2 and $CaCO_3$ "pure for analysis" carefully

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mixed and pressed into tablets under pressures of 150–200 atm.

The tablets were annealed in air at 1400°C for about 200hr and *in vacuo* at 1600°C for 50hr. After annealing they were cooled slowly. After such treatment tablets were heated for the second time in air for 100 hr at 1000°C.

Another batch of samples was prepared differently. Titrated solutions of calcium and zirconium nitrates were mixed in calculated proportions and evaporated. The residue was carefully dried and annealed for about 30 min at 400–600°C to full decomposition of the nitrates. Compact mixtures obtained in this way were annealed in the form of tablets at 1100°C for about 200hr and at 1500°C for 8hr.

X-ray analysis in a Guinier camera of the solid solution of 19, 21, 25, and 40 mole% CaO showed the formation of a mixture of two phases: $CaZrO_3$ and cubic solid solution of CaO in ZrO_2 in equilibrium with the $CaZrO_3$. The measured lattice parameters of the saturated solid solution ($a_0 = 5.144 \pm 0.001$ Å) were in good accord with data given in the literature (*10*).

Afterward different amounts of CaF_2 were added in the electrode mixtures and pressed tablets were annealed again *in vacuo* (1×10^{-5}–5×10^{-6} Torr) at 1000–1100°C for about 150hr.

In order to elucidate the influence of CaF_2 on the establishment of electrochemical equilibrium in the cells, the quantity of CaF_2 added in the electrodes studied was varied from 0 to 30 mole% CaF_2. X-ray investigation of electrodes after annealing *in vacuo* and after electrochemical measurements did not show any noticeable interaction of the equilibrium phases of electrodes with CaF_2 and with the electrolyte. Descriptions of the apparatus and experimental techniques used are given in (*5*, *13*). The errors in the equations,

$$E(\pm t_{0.05} \times S_0) = (a \pm t_{0.05} \times \alpha) + (b \pm t_{0.05} \times \beta)\,T,$$

are given with a confidence interval of 95% probability, where S_0 is the mean-square error of the calculated value of E; α and β are the errors in a and b; and $t_{0.05}$, Student's criterion, equals 2 for the number of experimental values of E, which was equal to or more than 20.

Results and Discussion

Analysis of the kinetic curves of the cell experiments shows that equilibrium values of potentials were established within 2–3hr after the introduction of oxygen into the reactor. The values were stable in the temperature interval investigated for 60–200hr. The apparatus was held at a constant value of the emf for 2–12hr. During that time interval the maximum deviation of the measured potentials from the mean value did not exceed ±0.0019 V).

As may be seen in Fig. 1, the values of the emf of the cell studied did not depend on the amount of CaF_2 added to the electrode. This fact shows the absence of any influence of CaF_2 on the possible decomposition of the metastable solid solutions at lime concentrations higher than 15 mole% CaO and was taken as a test for reliability of the emf data.

The temperature dependence of the cell emf for all of the compositions investigated is shown in Fig. 2. Each set of results represented in Fig. 2 was subjected to a least-squares analysis using a standard computer program, and the resulting linear relationships between cell emf and temperature are in-

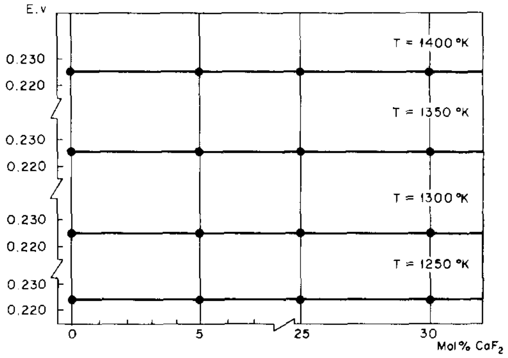

FIG. 1. Dependence of the potentials of the cell O_2, Pt/CaO, $CaF_2/CaF_2/\delta CaO \times (1-\delta)ZrO_2$, $xCaF_2$/Pt,O_2 on the amount of CaF_2 added to the right electrode ($\delta = 40$ mole% CaO) at various temperatures.

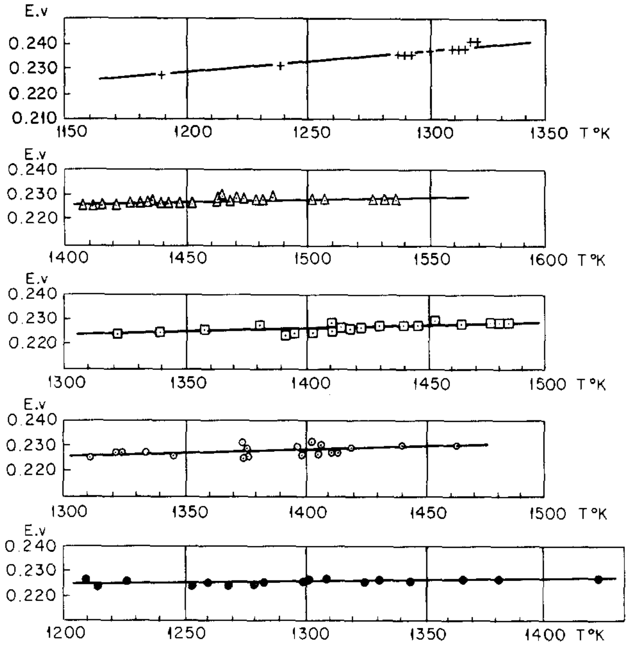

FIG. 2. The temperature dependence of the emf of the cell O_2, Pt/CaO, $CaF_2/CaF_2/\delta CaO \times (1-\delta)\ ZrO_2$, CaF_2/Pt,O_2. ●, 40 mole%; ○, 25 mole%; □, 21 mole%; △, 19 mole%; +, 15 mole% CaO.

cluded in Table I together with their corresponding standard deviations.

When 2 F of electricity are passed through the cell, 1 mole of CaO is transferred from the left electrode to the right one and the cell reaction for solid solutions and binary system can be written as

$$CaO_{(a=1)} \rightarrow CaO_{S.S.} \quad (1)$$

$$CaO_{(a=1)} + \frac{1}{1-2\delta'}(\delta' CaO(1-\delta')ZrO_2) \rightarrow \frac{1-\delta'}{1-2\delta'} CaZrO_3 \quad (2)$$

where δ' is the mole fraction of CaO in the saturated solid solution. Then, the activities of CaO in the system CaO–ZrO$_2$ at T°K may be calculated from the equation:

$$\Delta G^\circ = \mu_{CaO} - \mu^\circ{}_{CaO} = -2\ FE = RT \ln a_{CaO}$$

Literature data for the value of the δ' limit of the saturated cubic solid solution are very contradictory. These values vary from 10 to 40 mole% CaO, depending on the method of investigation and preparation of the samples. From Fig. 3 and Table I we see that the values of emf for the electrodes containing 40, 25, 21,

TABLE I

THE EXPERIMENTAL RESULTS FOR THE EMF OF THE CELL O_2, Pt/CaO, $CaF_2/CaF_2/CaO$[a]

CaO (mole%)	$a \pm t_{0.05} \times \alpha$	$(b \pm t_{0.05}\beta) \times 10^{+5}$	$\pm t_{0.05} \times S_0$	T_1 (°K)	T_2 (°K)	$\overline{\Delta S^\circ_T}$
40	0.2091 ± 0.0088	1.25 ± 0.68	0.0016	1200	1430	0.6 ± 0.3
25	0.1843 ± 0.0285	3.17 ± 2.07	0.0036	1300	1450	1.5 ± 1.0
21	0.1856 ± 0.0124	2.93 ± 0.88	0.0019	1310	1550	1.4 ± 0.4
19	0.1909 ± 0.0076	2.46 ± 0.53	0.0010	1400	1550	1.1 ± 0.2
15	0.1138 ± 0.0116	9.57 ± 0.89	0.0010	1190	1320	4.4 ± 0.4

[a] $(1-\delta)ZrO_2$, CaF_2/Pt, O_2 fitted to the equation $E_v = a + b\ T$°K; also given are the 95% confidence limits $\pm t_{0.05} \times \alpha$, $\pm t_{0.05} \times \beta$, and $\pm\ t_{0.05}\ S_0$ for the quantities E, a, and b and the temperature range T_1 and T_2 of the measurements.

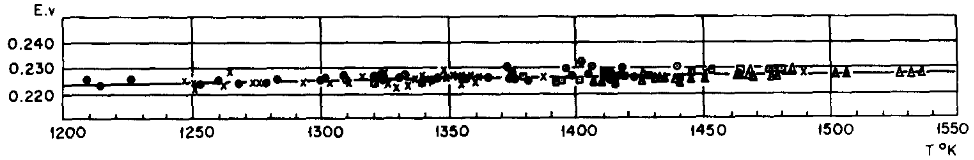

FIG. 3. Temperature dependence of emf of the cell O_2, Pt/CaO, $CaF_2/CaF_2/\delta CaO(1-\delta)\ ZrO_2$, CaF_2/pt, O_2. ●, 40 mole%; ⊙, 25 mole%; □, 21 mole%; and △, 19 mole% CaO. X represents values of E obtained during gradual temperature changes (20 to 30°K hr^{-1}).

and 19 mole% CaO in the limits of error are in good agreement with one another and with the emf values obtained at high temperatures for cells with 27, 21.7, and 19.8 mole% CaO (*9*). This is a proof that in the interval of compositions studied the chemical potential of CaO does not change. The dependence $E = f(T)$ found in (*9*) for the composition 17 mole% CaO has a steeper temperature dependence. This at $T < 1300$°K leads to a certain decrease of values of emf for this composition in comparison with the data represented in Fig. 3. The authors (*9*) do not give the errors in their initial equations $E = f(T)$. Nevertheless, since the values of a_{CaO} calculated in (*9*) for 17 mole% CaO in the interval 1300–1550°K lie within the limits of maximal errors in emf values of the present investigation, they were used to obtain the isotherms of activity in this temperature interval. Plots of the activity of CaO at six temperatures vs the mole fraction of this oxide are shown in Fig. 4. As can be seen the activity of CaO does not depend on its concentration being higher than 17 mole% CaO. Beginning from the composition of 15 mole% CaO a noticeable negative deviation from Raoult's law is observed. It appears, therefore, that there exist strong interactions between the ions of CaO and ZrO_2 in the solid solutions. At concentrations of 11 and 10 mole% CaO, the values of a_{CaO} given in (*9*) are increasing again and within the limits of error given coincide with values of a_{CaO} at higher concentrations of CaO. This circumstance does not allow us to decide, in our opinion, if this is a specific property of the CaO–ZrO_2 system in this interval of concentration or if this is connected with experimental errors in the emf measurements in (*9*).

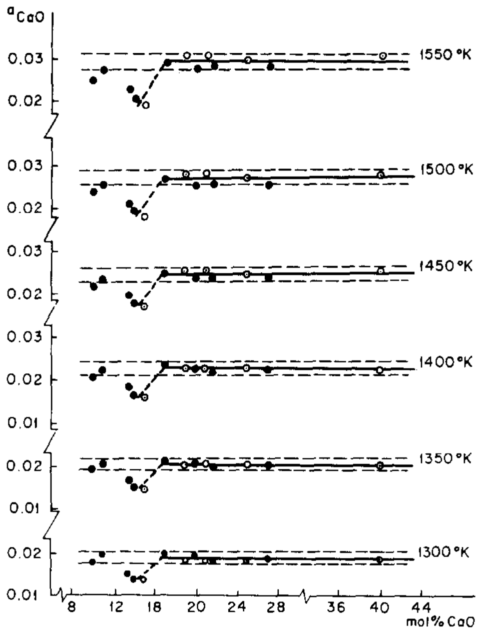

FIG. 4. The dependence of the activity of CaO in stabilized zirconia as a function of line content. ⊙, present work; ●, data of (*9*).

In (*10–12*) indications are given of the possibility of formation at high temperatures and long-time annealing of a phase $CaZr_4O_9$, which can be treated as an ordered solid solution in this system. We could not find such a compound by direct synthesis at 1500°C for 500hr. It may be seen from Table I that the values of the partial molar entropies calculated for the compositions studied agree within the limits of error given. The dependence of $\overline{\Delta S_T^\circ} = f$ (mole% CaO) does not show any discontinuity of the entropy at $\delta = 0.2$ corresponding to the phase $CaZr_4O_9$, previously discovered as a stable phase in the zirconia + lime system (*10*). More precise thermodynamic measurements for composition near 20 mole% CaO are needed.

In agreement with all the data published on the phase diagram of the $CaO–ZrO_2$ system, the composition with 40 mole% CaO corresponds to a heterogeneous mixture of $CaZrO_3$ and saturated cubic solution. Therefore, based on the data (*9*) and our results on the activity of CaO in the field of 17–40 mole% CaO, we state that in the temperature interval studied, the heterogeneous region with saturated cubic solid solution reaches the composition of 17 mole% CaO.

It may be seen in Fig. 4, that the limit of saturated cubic solid solution in the temperature interval studied practically does not depend on temperature. This fact contradicts the results obtained for the phase diagram $CaO–ZrO_2$ in the interval 17–20 mole% CaO (*9*, *17*, *23*, *24*) and is in good agreement with the phase diagram data, published recently (*12*). Based on what was said before and taking for the interval 1200–1550°K the value $\delta' = \text{const} = 0.17$, the cell reaction (*2*) may be written as

$$CaO + 1.515\,(0.17\,CaO \times 0.83\,ZrO_2) \rightarrow 1.258\,CaZrO_3. \quad (3)$$

Treating together 85 measured values of the emf of cells for the compositions studied (Fig. 3) we obtain

$$E(\pm 0.002) = (0.1919 \pm 0.0049) + (2.474 \pm 0.97) \times 10^{-5}\,T, \text{v}.$$

Using this equation one finds

$$\Delta G^\circ_3(\pm 100\ \text{cal}) = -8850 - 1.14\,T,$$

where

$$\Delta H^\circ_{1375^\circ K} = -8850 \pm 230\ \text{cal};$$

$$\Delta S^\circ_{1375^\circ K} = 1.14 \pm 0.45\ \text{e.u.}$$

Thermodynamic data for $CaZrO_3$, published in the literature (*1*, *2*, *19*), enable us to calculate thermodynamic parameters of some of the reactions taking place in the $CaO–ZrO_2$ system. The results obtained are presented in Table II. The equation:

$$\Delta G^\circ_4 = -(7810 \pm 830) - (2.09 \pm 0.45) \times T\ \text{cal/mole}$$

for the reaction

$$CaO + ZrO_2 \rightarrow CaZrO_3 \quad (4)$$

needed for calculation was obtained using the thermochemical data given in (*1*, *18*, and *19*).[1] From the analysis of the Gibbs energies at different temperatures, which are presented in Table II, it is readily concluded that in the temperature interval studied the formation of 1 mole of zirconate from CaO and ZrO_2 is preferred in comparison to the reaction of formation of 1 mole of $CaZrO_3$ from CaO and the saturated solid solution. The data obtained indicate that during the synthesis of stabilized zirconia, $CaZrO_3$ must be formed first, and then the $CaZrO_3$ reacts at high temperatures with the remainder of ZrO_2 according to the reaction of the type:

$$0.17\,CaZrO_3 + 0.66\,ZrO_2 \rightarrow (Ca_{0.17}\,Zr_{0.83}\,O_{1.83}). \quad (5)$$

The enthalpy of this reaction has a small positive value and a decrease in Gibbs energy is connected with the entropy term. The last may be considered as a small increase of the entropy of the system connected with destroying the ordered structures $CaZrO_3$ and ZrO_2 and forming a defect solid solution $Ca\delta Zr_{1-\delta}O_{2-\delta}\square_\delta$.

Owing to the low speed of phase transformations at low temperatures, reliable data on equilibrium phase relations in the $CaO–ZrO_2$ system below 1000°C are lacking. Analysis of the dependence $\Delta G_5 = f(T)$ for reaction (5) shows that for the interaction considered Gibbs energy values are small and this reaction is thermodynamically possible at temperatures higher than 820°C. The temperature of the eutectoidal decomposition of the cubic solid solution found in this work is in good agreement with the value ~850°C determined experimentally in (*12*, *20–22*). At lower temperatures the saturated solid solution has a tendency to decompose into $CaZrO_3$ and monoclinic ZrO_2. Thus, the formation of $CaZrO_3$ must proceed intensively at intermediate temperatures (1000–

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[1] The high temperature heat capacity of $CaZrO_3$ is lacking in the literature. In our calculations we supposed that $\Delta C_p4(T) = \Delta C_p(T)$ for a reaction of the same type, $SrO + ZrO_2 \rightarrow SrZrO_3$, for which reliable values of heat capacities are given in the literature (*3*, *19*).

TABLE II

THERMODYNAMIC PARAMETERS OF SOME REACTIONS IN THE SYSTEM $MeO-ZrO_2$ (*Me*–Ca, Sr, Ba)

		$\Delta G_T^\circ = \Delta H_T^\circ - T\Delta S_T^\circ$ (kcal/mole)					
No.	Reaction	ΔH_T° (kcal/mole)	ΔS_T° (e.u.)	1100°K	1300°K	1500°K	1700°K
1	$CaO + 1.515\,Ca_{0.17}Zr_{0.83}O_{1.83} \rightarrow 1.258\,CaZrO_3$	−8.85 ± 0.23	1.14 ± 0.45	−10.1	−10.3	−10.6	−10.8
2	$CaO + ZrO_2 \rightarrow CaZrO_3$	−7.81 ± 0.83	2.09 ± 0.45	−10.1	−10.5	−10.9	−11.4
3	$0.795\,CaO + 1.204\,Ca_{0.17}Zr_{0.83}O_{1.83} \rightarrow CaZrO_3$	−7.03 ± 0.20	0.91 ± 0.36	−8.0	−8.2	−8.4	−8.6
4	$0.17\,CaO + 0.83\,ZrO_2 \rightarrow Ca_{0.17}Zr_{0.83}O_{1.83}$	−0.65 ± 0.70	0.98 ± 0.48	−1.7	−1.9	−2.1	−2.3
5	$0.17\,CaZrO_3 + 0.66\,ZrO_2 \rightarrow Ca_{0.17}Zr_{0.83}O_{1.83}$	+0.69 ± 0.57	0.63 ± 0.42	0.0	−0.1	−0.25	−0.4
6	$SrO + ZrO_2 \rightarrow SrZrO_3$	−19.5 ± 3.1	0.87 ± 2.46	−20.5	−20.6	−20.8	−21.0
7	$O.17\,SrZrO_3 + 0.66\,ZrO_2 \rightarrow Sr_{0.17}Zr_{0.83}O_{1.83}$	+2.7	0.8	+1.8	+1.7	+1.5	+1.3
8	$BaO + ZrO_2 \rightarrow BaZrO_3$	−32.1 ± 1.5	0.47 ± 1.60	−32.6	−32.7	−32.8	−32.9
9	$0.17\,BaZrO_3 + 0.66\,ZrO_2 \rightarrow Ba_{0.17}Zr_{0.83}O_{1.83}$	+4.8	0.9	+3.6	+3.6	+3.5	+3.3

1300°C), whereas higher temperatures and longer annealing times are required to form the solid cubic solutions.

The existing data about phase diagrams of the $SrO-ZrO_2$ and $BaO-ZrO_2$ systems do not indicate any solid solutions in these systems. We are not aware of any attempts to account for this fact from thermodynamic and structural points of view. That is why we tried to estimate the thermodynamic probability of formations of solid solutions in these systems. It was supposed that the hypothetical solid solution, $Me_{0.17}\,Zr_{0.83}\,O_{1.83}$ (where $Me =$ Sr, Ba), has thermodynamic characteristics of formation from *Me*O and ZrO_2 which are close to those of the solution, $Ca_{0.17}\,Zr_{0.83}\,O_{1.83}$. Following this supposition and using thermodynamic properties of $SrZrO_3$ and $BaZrO_3$ determined in (*5*), values of ΔG_T° for some reactions in the $SrO-ZrO_2$ and $BaO-ZrO_2$ systems involving the hypothetical solid solution $Me_{0.17}\,Zr_{0.83}\,O_{1.83}$, $MeZrO_3$ and ZrO_2, were calculated. The thermodynamic parameters of two of these reactions are presented in Table II. It may be readily seen that in the temperature range studied, solid solutions in the $SrO-ZrO_2$ and $BaO-ZrO_2$ systems are unstable and should dissociate into $MeZrO_3$ and ZrO_2. As the negative values of ΔG_T° of formation of $MeZrO_3$ from oxides increase in the series $CaZrO_3 \rightarrow SrZrO_3 \rightarrow BaZrO_3$, the probability of dissociation of the solid solution $Me_{17}\,Zr_{0.83}\,O_{1.83}$ on $MeZrO_3$ and ZrO_2 increases. Thus, considerable (in comparison with $CaZrO_3$) thermodynamic stability of $SrZrO_3$ and especially of $BaZrO_3$ are, evidently, one of the causes of the absence of solid solutions in these systems.

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