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Determination of the thermodynamic activities in $\{x\mathrm{CaO} + (1 - x)\mathrm{CdO}\}(\mathrm{s,sln})$ from a solid electrolyte galvanic cell in the temperature range 823–1303 K

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Abstract

The thermodynamic activities of CaO in the solid solutions which can exist in the system CaO–CdO were determined in the temperature range 823–1303 K by the high temperature solid electrolyte galvanic cell technique with calcium fluoride as the solid electrolyte. The conventional cell arrangement of sandwiching the electrolyte in direct contact with the electrodes was not found to give stable reproducible EMF values at temperatures above 1123 K. For the higher temperatures a modified technique has been introduced, which permits the establishment of an equilibrium through the gas phase. In the temperature range of study, the system was observed to show near ideal behaviour. The results are in agreement with the near zero enthalpies of mixing reported in the literature and also with the theroretical models available for predicting the mixing enthalpies in such systems.

INTRODUCTION

Calcium fluoride has been shown to be an ionic conductor [1] and has been used [2–4] as a solid electrolyte in high temperature solid state galvanic cells for determination of chemical potentials of CaO in metal oxide systems. A similar technique has been used in the present work for determining the thermodynamic activities of CaO in the NaCl-type solid solutions $\{x\mathrm{CaO} + (1 - x)\mathrm{CdO}\}(\mathrm{s,sln})$ in the temperature range 823–1303 K. There is very little literature available on the thermodynamic

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properties of the solid solutions which can exist in the system CaO–CdO. The system CaO–CdO has been reported to form a complete series of solid solutions [5]. It is possible to measure the activity of CaO in the solid solutions that can exist in this system by setting up the cell

$$O_2(g),Pt|CaO,CaF_2||CaF_2||\{xCaO + (1-x)CdO\}(s,sln),CaF_2|Pt,O_2(g)$$

The EMF is due to the reaction

$$CaO(s) \rightarrow CaO(s,sln) \tag{1}$$

where CaO(s,sln) represents CaO in the solid solution at the temperature of interest. The reactions at the two electrodes can be represented as follows, in accordance with Benz and Wagner [6] for a similar cell. At the reference electrode where pure CaO is in contact with CaF_2 electrolyte

$$CaO(s) + 2F^- \rightarrow CaF_2 + (1/2)O_2(g) + 2e^- \tag{2}$$

At the working electrode, where $\{xCaO + (1-x)CdO\}$(s,sln) is in contact with the CaF_2 electrolyte

$$CaF_2 + (1/2)O_2(g) + 2e^- \rightarrow CaO(s,sln) + 2F^- \tag{3}$$

Therefore, the measured EMF E is related to the activity a(CaO) of CaO in the solid solution by the expression

$$-2EF = RT \ln a(CaO) \tag{4}$$

where F is the Faraday constant.

These cell reactions clearly indicate that oxygen is necessary for the operation of the cell. If the same oxygen pressure prevails at the electrodes, the overall reaction is as given by eqn. (1). An atmosphere of dry CO_2-free oxygen gas was provided throughout the working period of the cell.

EXPERIMENTAL

Materials

Calcium fluoride for use as the solid electrolyte and as an additive to improve the conductivity of the electrodes was prepared from reagent grade calcium carbonate and hydrofluoric acid by the method described by Taylor and Schmalzried [8]. The electrolyte was prepared by pressing the powder to a pressure of 235 MPa in a cylindrical die. The green pellet was then sintered in an atmosphere of CO_2-free dry oxygen gas at 1323 K for 4 h. Calcium oxide was prepared by calcining $CaCO_3$ (AR) at 1373 K. Cadmium oxide was prepared from the reagent acetate by heating in oxygen at 973 K. Solid solutions of CaO and CdO were prepared by mixing the appropriate quantities of $CaCO_3$ and CdO and heating the mixture in dry CO_2-free oxygen at 973 K for 12 h. The product was mixed thoroughly, compacted into pallets and again sintered at 1073 K for 12 h. The product was again ground, compacted and sintered for 12 h at 1173 K for compositions rich in CdO. For compositions rich in CaO the final sintering was performed at 1373 for 24 h. Control experiments showed that there was no loss of CdO due to decomposition and volatilisation during the long hours of sintering. The formation of true solid solutions was confirmed by X-ray diffraction. The electrode pellets were prepared by adding about 15 wt.% calcium fluoride to the solid solutions, pressing the mixed powder into a cylindrical pellet and sintering at 1313 K in dry CO_2-free oxygen before use.

Cell operation

The assembly used in the present work was similar to that described earlier [9]. The performance of the polycrystalline CaF_2 as a solid electrolyte was checked by operating the cell

$O_2(g),Pt|CaO,CaF_2||CaF_2||MgO,MgF_2|Pt,O_2(g)$

in the temperature range 1173–1273 K. The performance of the apparatus was checked by these measurements. The EMFs obtained in the present work for the above cell agreed with those reported by Pizzini and Morlotti [4].

When measurements of CaO activities in $\{x\mathrm{CaO} + (1-x)\mathrm{CdO}\}$ solid solutions by the conventional fluoride electrolyte cell were performed, it was found that for some compositions satisfactory results could be obtained with this cell design in the temperature range 823 to 1123 K and contamination of the electrolyte by the volatile species, (namely CdO) posed problems with certain other compositions and at temperatures above 1123 K. This was avoided by adopting the modified cell arrangement [10] shown in Fig. 1. The solid electrolyte pellet A is in direct contact with the reference electrode B, whereas the solid solution electrode C is physically separated from the electrolyte by the introduction of a perforated platinum foil between these two pellets. Somewhat similar cell design with provision for establishing electrolyte-electrode contact via the gas phase has been employed by Komarov and Tretyakov [7].

The modified cell arrangement used in the present work has also been

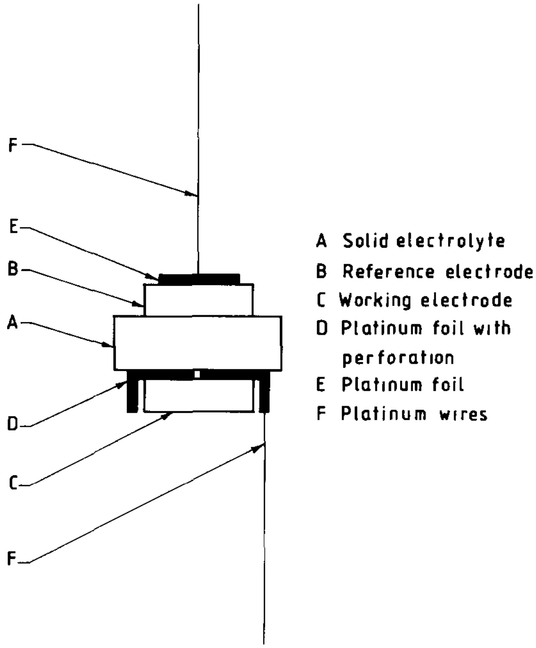

Fig. 1. Modified cell arrangement [10].

used to study $\{x\mathrm{CaO} + (1-x)\mathrm{MnO}\}$ and consistent reproducible results have been obtained [10]. For $\{x\mathrm{CaO} + (1-x)\mathrm{CdO}\}$, CdO is sufficiently volatile to suggest a reaction mechanism in terms of gas-phase equilibration. For solid solutions studied with the perforated platinum foil, several checks were performed to ensure that a true equilibrium had been established. When the cell EMFs were measured without the perforation in the platinum foil placed between the working electrode and the electroyte, EMFs close to zero were obtained. Cells with pure CaO on both sides and operated with the perforated platinum foil also gave EMFs close to zero. Changes in gas flow rate also did not affect the cell EMF. Reproducible EMFs were obtained even after an initial polarization of the cell by passing an external current. The question now arises regarding the mechanism by which the CaO formed at the interface establishes contact with CaO in the solid solution to maintain equilibrium, as represented by reaction (3). In the absence of the perforated platinum foil this occurs by physical contact and in the presence of a perforated platinum foil this could occur through the gas phase or through surface diffusion on platinum or by actual physical contact at some protruding points as the platinum foil is quite thin and a pressure has been applied on both the electrodes. The mechanism outlined assumed conductivity solely due to fluoride ions.

The in situ temperature of the cell was measured with a Pt–PtRh(13% Rh) thermocouple welded to the platinum foil in contact with the reference electrode of the cells. The platinum wire of the couple also served as the lead wire for measuring the cell EMF. The temperature of the furnace was controlled by another thermocouple to within ±3 K. The time of equilibration was dependent on the lime composition and the temperature, being 1 h at 1303 and 1278 K for the compositions studied, and varying from 4 to 10 h at lower temperatures with increasing lime content.

RESULTS

The experimental values of the EMF for five compositions measured in the temperature range 823–1303 K and the corresponding activities of CaO are listed in Table 1. The cell EMF could be read on the potentiometer correct to ±0.2 mV. The EMF was reproducible to within ±1 mV when taken through a thermal cycle. There is an uncertainty of ±3 K in the temperature measurements but this is not likely to introduce any serious error into the activities, because the variation of EMF with temperature was quite small. The uncertainty of ±1 mV in the EMF would lead to an error of ±193 J mol^{-1} in the chemical potential of the metal oxide. This uncertainty results in an uncertainty of ±0.002 for the activity at low CaO content and 0.019 at high CaO content.

TABLE 1

Experimental EMFs and activities a(CaO) from 823–1303 K for {xCaO + $(1-x)$CdO}(s,sln)

T/K	x(CaO)									
	0.25		0.4		0.5		0.6		0.75	
	E/mV	a(CaO)	E/mV	a(CaO)	E/mV	a(CaO)	E/mV	a(CaO)	E/mV	a(CaO)
823	50.6	0.24	32.0	0.405	–	–	–	–	–	–
873	54.4	0.235	–	–	–	–	–	–	–	–
1023	–	–	40.9	0.395	–	–	22.9	0.595	–	–
1073	–	–	40.1	0.420	33.9	0.48	–	–	–	–
1123	–	–	46.2	0.385	36.5	0.47	23.5	0.615	–	–
1208	–	–	–	–	–	–	–	–	14.5	0.757
1243	–	–	48.4	0.405	35.5	0.516	26.9	0.604	14.1	0.768
1278	–	–	47.6	0.422	37.3	0.508	27.6	0.607	15.3	0.757
1303	–	–	50.0	0.410	38.7	0.502	29.5	0.592	16.00	0.752

DISCUSSION

The CaO activities calculated from the EMF data obtained are plotted in Fig. 2. It is seen that in the temperature range 823–1303 K, the system CaO–CdO shows nearly ideal thermodynamic behaviour. This has been substantiated by the nearly zero enthalpies of mixing of the solid solutions reported by Prasad [11]. The cationic sizes $r(Ca^{2+}) = 99$ pm, $r(Cd^{2+}) = 97$ pm [12] are nearly the same and there is no contribution to crystal-field stabilization. The enthalpies of mixing can be calculated using

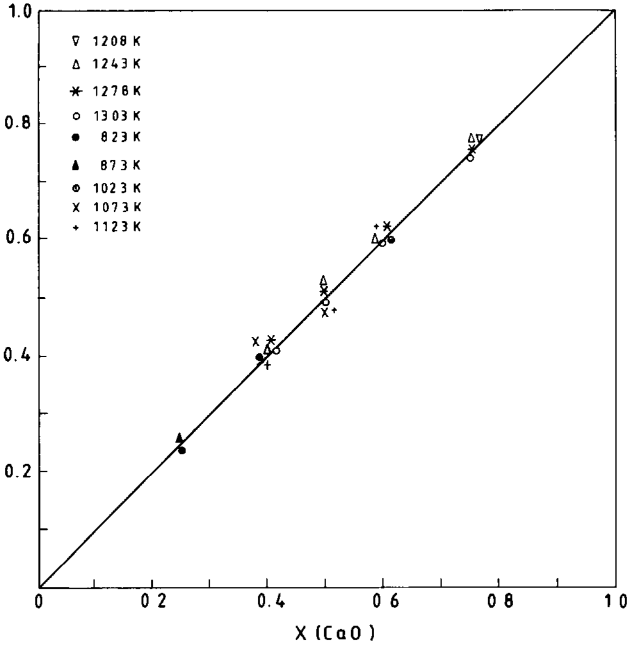

Fig. 2. Activities of CaO for compositions at 823–1303 K.

the model proposed by Wasastjerna [13] based on ionic size differences. The values so calculated are in reasonable agreement with the experimental values obtained in the present work and by calorimetry [11].

REFERENCES

1 R.W. Ure, J. Chem. Phys., 26 (1957) 1263.
2 T.N. Rezukhina and Ya. Baginska, Electrokhimiya, 3 (1967) 1148.
3 S. Raghavan and K.P. Abraham, J. Electrochem. Soc. India, 22 (1973) 149.
4 S. Pizzini and R. Morlotti, J. Chem. Soc., Faraday Trans., 68 (1972) 1601.
5 Natta and L. Passerini, Gazz. Chim. Ital., 59 (1929) 139.
6 R. Benz and C. Wagner, J. Phys. Chem., 65 (1961) 1308.
7 V.F. Komarov and Y.D. Tretyakov, in Physics of Electrolytes, Vol. II, Academic Press, London, 1970.
8 R.W. Taylor and H. Schmalzried, J. Phys. Chem., 68 (1964) 2444.
9 D.V. Vecher and A.A. Vecher, Zh. Fiz. Khim., 41 (1967) 2916.
10 S. Raghavan, G.N.K. Iyengar and K.P. Abraham, Trans. Indian Inst. Met., 33 (1980) 51.
11 K.K. Prasad, Ph.D. Thesis, Indian Institute of Science, Bangalore, 1971.
12 N.N. Greenwood, in Ionic Crystals, Lattice Defects and Non-stoichiometry, Butterworths, London, 1968.
13 J.A. Wasastjerna, Soc. Sci. Fenn. Comment. Phys. Math., 15 (1949) 1.