Technical Section

ACTIVITY MEASUREMENTS IN CoO - MgO SOLID SOLUTIONS BY THE SOLID-STATE GALVANIC CELL TECHNIQUE

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ABSTRACT

The activity of CoO in CoO–MgO solid solutions has been measured in the temperature range 800–1000°C by the solid-state, galvanic cell technique. The cell used is of the type

Pt | Co,CoO | ThO_2–Y_2O_3 | (Co,Mg)O,Co | Pt.

The results indicate that the system shows a slight positive deviation from Raoult's law and conforms to regular solution model. These results are corraborated by the measurement of the enthalpies of formation by acid–solution calorimetry using 6N hydro chloric acid as the solvent.

A knowledge of the activities in simple, binary, metal–oxide systems is helpful in understanding the thermo–dynamic behaviour of a number of complex systems of interest in metallurgy and the cation distribu, tion in such systems. Till recently the measurement of the thermodynamic activities in the case of oxide systems by high-temperature, solid – state, galvanic cell technique has not received much attention and till the initiation of the present work, this system was not investigated by the EMF technique. The applicability of this technique for activity measurement in oxide systems has now been well established. [1,2]

The system CoO – MgO has been reported [3,4,5] to exhibit complete solid solubility. Aukrust and Muan[5] have determined the activity of CoO in this system at 1200 °C by equilibra - ting the system CO_2/H_2 or CO_2 /CO gas– mixtures and found the system to obey Raoult's law.

The present report deals with the determination of the activities of CoO in the solid solutions existing in the system CoO – MgO by the EMF technique in the temperature range 800 – 1000 C. The cell used is of the type.

Pt | Co, CoO | ThO_2–Y_2O_3 | (Co, Mg)O, Co | Pt

The solid – electrolyte yttria estabilized thoria, has been reported by Steele and Alcock[6] to be an almost pure anion conductor in this temperature range and between the oxygen partial pressures of 10^{-0} and 10^{-25} atm. as can be seen from the chart given by these authors showing the oxygen partial pressure ranges at which various solid – electrolytes exhibit almost pure anionic conduction. This chart has been reproduced in Fig. 1. It is seen that at the Co – CoO equilibrium oxygen partial pressure in the temperature range 800 – 1000°C ($\sim 10^{-12}$atm.) ThO_2 – Y_2O_3 electrolytes are suitable for galvanic cell measurements.

The EMF of the cell is given by

$$E = -\frac{RT}{2F} \ln a_{CoO}$$

where R is the gas constant, T is the absolute temperature and , F, the Farady constant.

The heats of formation of CoO – MgO solid solutions were determined by measuring their heats of solution in 6N. hydrochloric acid.

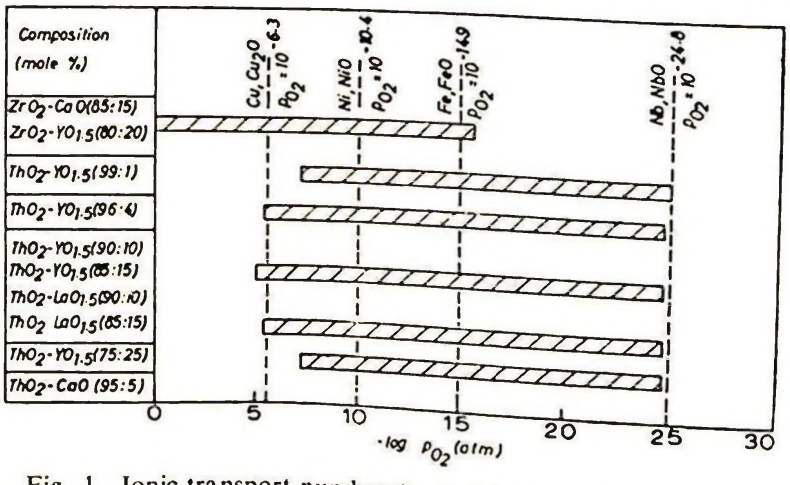


Fig. 1 Ionic transport number ($t_{ion} > 0.99$) as a function of composition and oxygen pressure at 1000°C[6].

Experimental :

Materials :

Cobalt oxide :

CoO was prepared by decomposing cobalt nitrate (A. R.) in a platinum dish. It was then heated for 6 hours at 1050°C and cooled in purified argon.

Magnes. .m oxide :

Magnesium oxide (A. R.) was calcined at 1100°C before use.

Solid solutions ;

The oxide mixtures of required composition, made into compacts, were sintered at 1250°C for 60 hours in argon in two stages, powering and mixing them well, in between. X-ray powder patterns with iron radiation were taken to confirm the formation of true solid solutions.

Metal-metal oxide electrodes :

The Co-CoO electrode was an equimolar mixture of cobalt and cobalt oxide powders packed inside the electrolyte in the form of a crucible. The (Co, Mg)O-Co electrode was prepared by compacting an equimolar mixture of the metal and the solid solution.

Solid electrolyte :

The ThO_2–Y_2O_3 electrolyte used was in the form of a crucible of 1 cm. diameter and 1½ cm. height.

The cell assembly :

The galvanic cell assembly, incorporating the solid electrolyte crucible is shown in Fig. 2. The ThO_2–Y_2O_3 crucible 'A' has been packed inside with an equimolar mixture of cobalt metal and cobalt oxide 'B', with a coil of platinum wire 'C' embedded in the same and this formed the reference electrode. A platinum-13% rhodium wire 'D' has been attached to the platinum wire to measure the 'insitu' temperature of the cell. The platinum-rhodium wire passes through an alumina tube and taken out. A 'T'-joint 'F' attached to the alumina tube at the top, enables the passage of argon through the same.

The other electrode consisting of a mixture of the solid solutions and cobalt metal, is kept in the form of a compact 'G' over a silica rod 'H' with the platinum foil 'J' at the top. A platinum lead wire 'K', welded to the foil, is taken out through the bottom after coiling around the quartz rod The rod rests on a small spring 'L' kept at the bottom of a brass block 'M' and is kept vertical by means of the centralising ring 'N'. A 'T' joint 'P' is provided at the bottom to take out the platinum wire and to pass argon gas. The outer sillimanite tube 'Q' encloses the whole assembly and is closed at the bottom by 'O' ring seals and at the top by a rubber stopper 'R'. The gas outlet is provided at the top. The cell is heated by means of a vertical, kanthal-wound tube furnae 'S'.

Measurements :

The EMF measurements were made in an atmosphere of argon gas purified by passing over copper turnings at 400°C and titanium chips at 850°C. The gas was allowed to flow both from the top and the bottom of the cell assembly, so that, the direct gas-phase

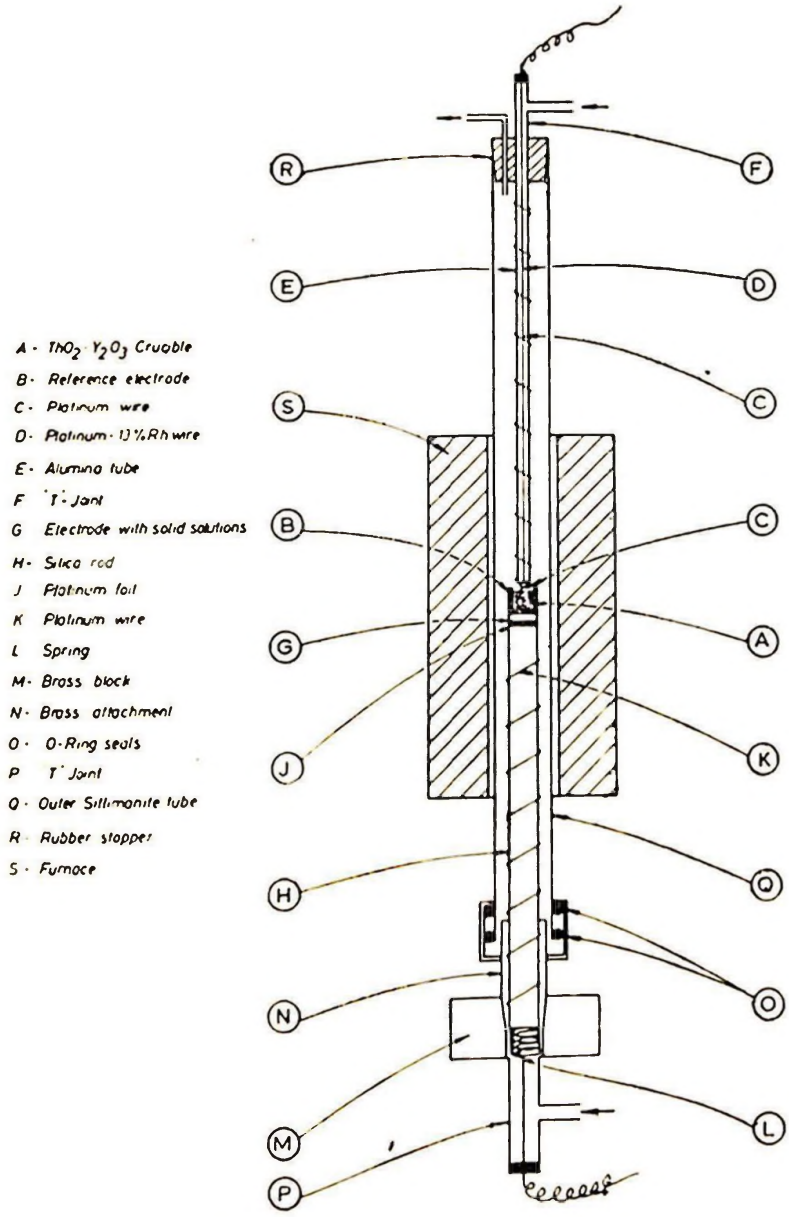


Fig. 2 The cell assembly.

oxygen transfer between the electrodes could be kept to a minimum.

The cell EMF has been measured at rising and falling temperatures with a vernier potentiometer accurate to 0.1 mv. The furnace temperature has been controlled to $\pm 2°C$. The EMF values are generally found to be steady within ± 1mv.

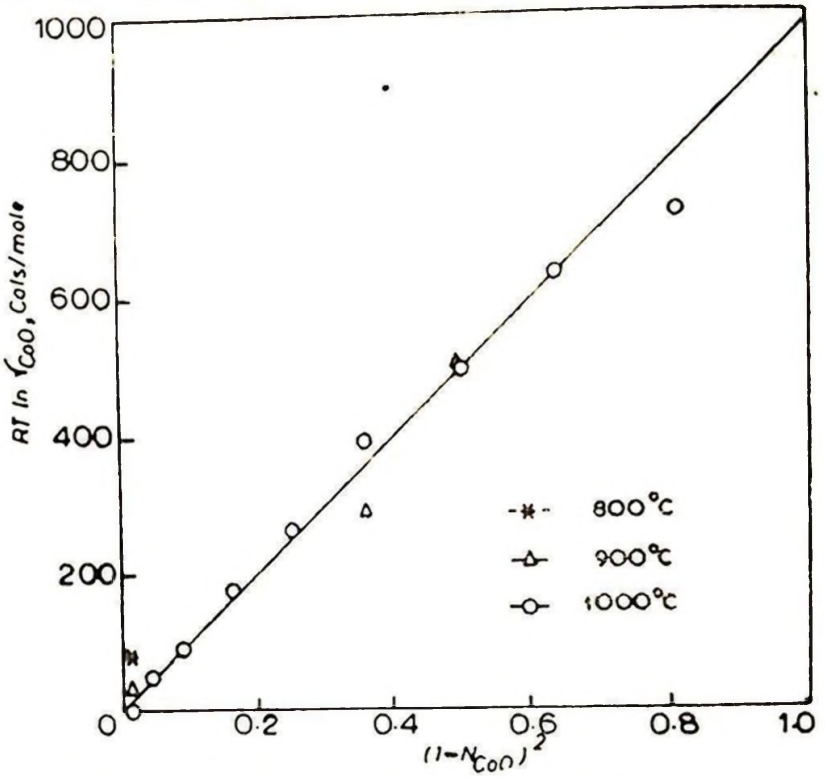
Heat of solution measurements :

The solid solution and the pure oxides are easily soluble in 6N. hydrochlorie acid at 70°C. A modified form of the submarine-type calorimeter described by Jeffes, Richardson and Pearson[7] was used for the measurement of heats of solution. The solutions were made in 6N. hydrochloric acid at 70°C and the ΔH values were calculated from the measured heats of solution.

Results and Discussion :

The CoO activities calculated from the EMF data at 800, 900 and 1000°C are plotted in Fig. 3. No steady values could be obtained during a number of runs carried out at temperatures below 1000°C. In view of the erratic behaviour of the cell at lower temperatures, except for the solid solutions with high CoO content, no regular trend could be observed for the variation of EMF with temperature.

The partial molar excess free energy ΔF^{xs} of CoO has been plotted with respect to $(1-N_{CoO})^2$ in Fig. 4. It can



RT ln γ_{CoO} vs. $(1-N_{CoO})^2$ for the sytem CoO-Mgo.

be seen that the plot is linear, thus indicating that the system conforms to regular solution model. The interaction parameter calculated from Fig. 4 is approximately 980 cals./mole. The integral molar enthalpies of formation calculated on the basis of the regular solution model are given in Table I. These values are estimated to have an overall error of not more than ± 150 cals.

The integral molar enthalpies obtained experimentally by calorimetric measurements are also given in Table I. Each value given is the average of two or three different calorimetric experiments. From the scatter in the results, the error in these values is estimated to be not more than ± 150 cals. The agreement between the two sets of values is reasonable considering the uncertainties involved.

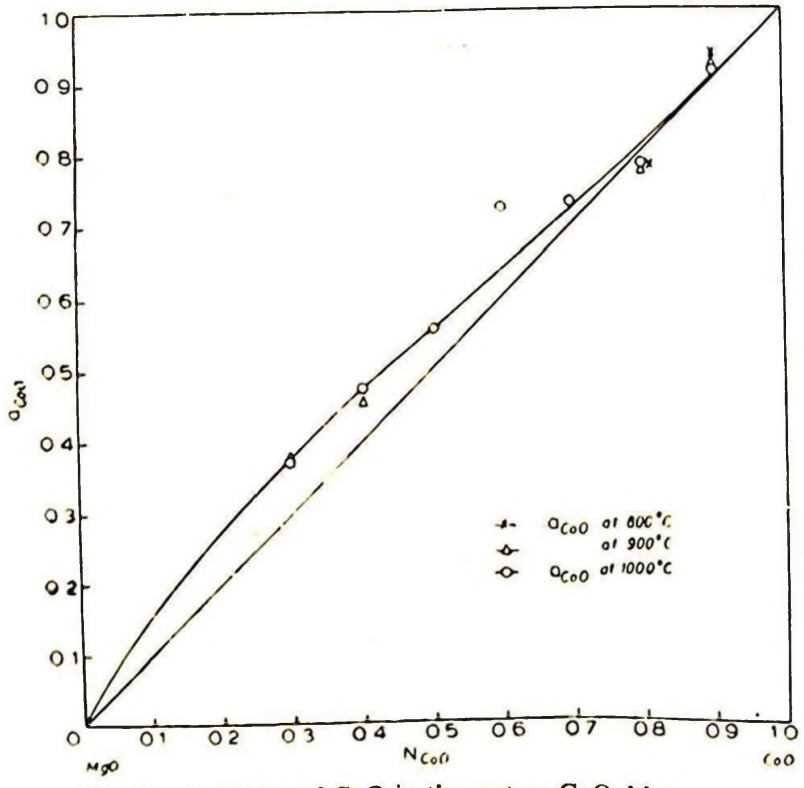


Fig. 3 Activities of CoO in the system CoO-Mgo.

TABLE – I

Comparison of the calculated (from EMF data) and calorimetric integral molar enthalpies in the system CoO–MgO.

N_{CoO} &	ΔH^M Calculated in cals./mole.	ΔH^M experimental in cals./mole.
0.5	205.8	244
0.4	235.3	594
0.5	245.0	460
0.6	235.3	378
0.7	205.8	140

The slight positive deviation obtained in the present work does not agree with the results of Aukrust and Muan who, by the gas equilibrium technique reported the system to be ideal at 1200°C.

Acknowledgement

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