Electromotive Force Measurements Using CaF_2 Cell - Heats of Formation of Calcium Chromite

K.V. Rajagopalan, R. Kalyanaraman and M. Sundaresan

Analytical Chemistry Division, BARC, Trombay, Bombay 400 085, India

Electromotive force measurements are reported on the following galvanic cell:

$$Pt, Ca(CrO_2)_2\ Cr, Cr_2O_3\ , CaF_2\ /\ CaF_2/\ Co, CoF_2, Pt \qquad (1)$$

as a function of temperature between 700-1000°K in an atmosphere of pure dry argon. The component of the two half cells were thoroughly mixed, pelletised and sintered at suitable temperatures to obtain ready pellets while the solid electrolyte was a single crystal of calcium fluoride. The optimum proportion of each component in the chromium composite pellet (left hand side half cell) was chosen after several experiments. The system was calibrated by checking the measured e.m.f. values of the cell:

$$Co, CoF_2\ /\ Ca\ F_2\ /\ Ni, NiF_2 \qquad (2)$$

against literature values. The performance of cell (1) was improved upon by using different reference electrodes on the right hand side. E.m.f. measurements were taken in both the ascending and desending orders of temperature. A linear relationship between e.m.f. and temperature was obtained and this data was used to compute the thermodynamic parameters associated with the formation of calcium chromite.

Liquid sodium is used as the coolant in fast breeder reactors. The usual containment materials for liquid sodium are stainless steels of the series 300, where the principal constituents are iron, chromium and nickel. Calcium is an important impurity in liquid sodium. During the manufacture it gets deposited along with sodium from the electric melt containing calcium chloride. The solubility of calcium in liquid sodium is neither very significant, nor does it form intermetallic compounds with sodium. However, in the presence of oxygen in liquid sodium the solubility may increase and can lead to formation of double oxides of calcium with the constituent materials of the container. An evaluation of the solubilities of these double oxides can be obtained from the knowledge of their thermodynamic properties.

The principal compounds so formed are $CaFe_2O_4$, $Ca_2Fe_2O_5$, $CaCr_2O_4$ and $CaNiO_2$. The purpose of this work is to determine the thermodynamic properties of these double oxides by measuring the e.m.f of appropriate cells with solid CaF_2 electrolyte using a modified procedure. The present work deals with calcium chromite and forms the first part of this research programme.

No experimental determination of the heats of the formation of calcium chromite has been reported in literature. Kanteeva (1) has estimated this quantity from theoretical considerations on the basis of values of similar compounds. In the present work, the e.m.f. of the cell

$$Pt/Cr, Cr_2O_3, CaCr_2O_4, CaF_2/CaF_2/Co, CoF_2/Pt \qquad (1)$$

has been measured as a function of temperature between 700 - 1000° K in an atmosphere of pure argon.

EXPERIMENTAL

High purity chemicals (99.99%) were used for the preparation of the compounds as well as the reference electrodes. Calcium chromite ($CaCr_2O_4$) was prepared by mixing stoichiometric amounts of calcium carbonate with chromium oxide (Cr_2O_3), homogenising the mixture by thorough grinding and then heating at 1500°C for around 30 hours (2). At each stage of eight hours, the mixture was taken out and homogenised again. The resultant compound was analysed chemically for calcium and chromium. X-ray diffraction pattern of the compound showed all the lines for $CaCr_2O_4$ while the lines of CaO and Cr_2O_3 were absent which confirmed the complete conversion.

$$CaCO_3 + Cr_2O_3 \xrightarrow[30\ hours]{1500°C} CaCr_2O_4 + CO_2$$

The calcium fluoride solid electrolyte was a single crystal of dimensions 10 mm diameter and 6 mm thickness. and was obtained form the Technical Physics Division, BARC.

The electrode pellets of 10 mm dia and thickness 4-6 mm were prepared by mixing the components, homogenising pelletising and sintering. For preparing the mixed calcium chromite pellets, several proportions of the components were were tried and it was found that the optimum quantity of metallic chromium was about 50%. At such proportion, the pellets were found to be sufficiently strong. All the sintering were done at 700°C in pure argon atmosphere for periods ranging from 10 to 24 hours. Prior to use, the flat surfaces were polished on fine emery to get a mirror finish.

The apparatus used (Fig 1) was a 40 cm long quartz tube, one side closed and the other side fitted with a B-45 cone and closed with a socket. The socket is provided with inlet and outlet tubes for purified argon and has provision for introducing a thermocouple and two platinum lead wires for measurement of e.m.f. without any air leak. The calcium fluoride electrolyte pellet was sandwiched between the test and reference pellets and then tightened with platinum contacts properly insulated, in a specially fabricated S.S. 316 cell as shown in the figure. The temperature was measured by a calibrated Pt- 10% Rh-Pt thermocouple and the e.m.f. by means of a high impedence electrometer. The apparatus was evacuated, baked several times and then filled with 99.999% argon. Experiments were conducted under a slow dynamic atmosphere of argon. The temperatures were changed in the ascending and descending orders several times and readings of e.m.f. which were constant for 5 to 8 hours only were recorded.

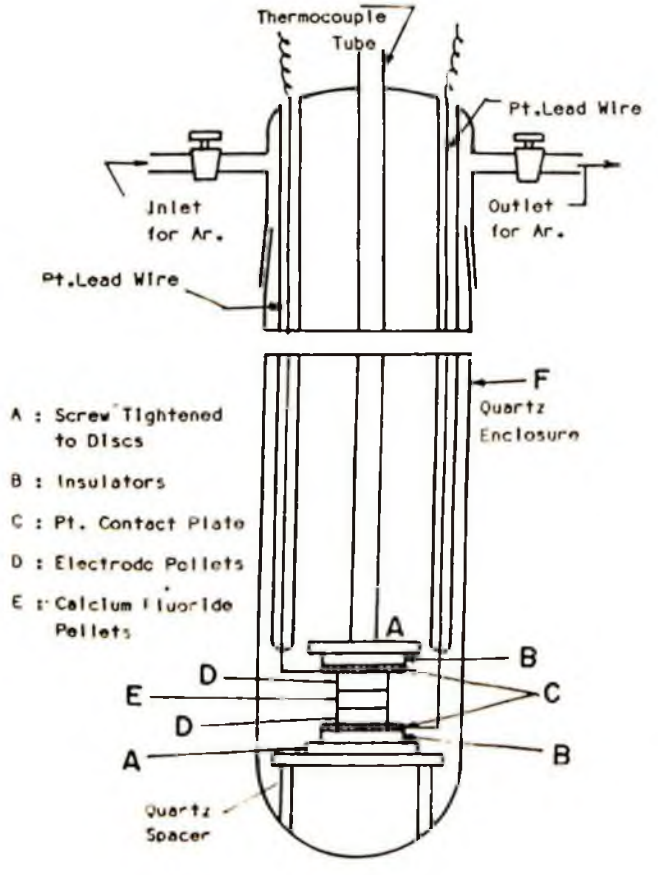


Fig. 1 Schematic Diagram of the CaF Cell Assembly

The apparatus was first calibrated by measuring the e.m.f. of the cell:

$$Pt/Co, CoF_2 / Ni, NiF_2 / Pt - cell \qquad (2)$$

as function of temperature. The e.m.f. temperature relationship of this cell has been determined by several researchers (3-6). Our data exhibited close agreement with that of Skelton and Patterson (6).

RESULTS AND DISCUSSION

The linear relationship between e.m.f. and temperature of cell (1) is shown in Fig. 2. The best fit was obtained by the least squares method. The corresponding relationship between e.m.f. and temperature was computed to be

$$E(mV) = 70.75 + 0.256\ T$$

where the root mean square deviation of the measured E values from the straight line being

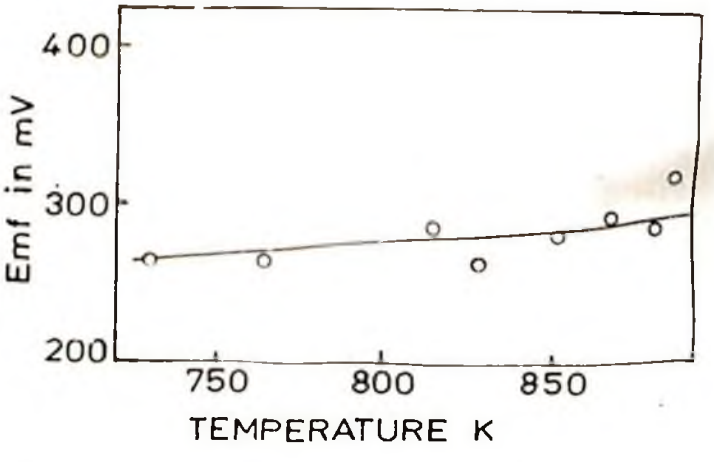


Fig. 2 Emf vs. Temperature Data for Cell I

within ± 3.1 mV. The cell reaction can be written as :

$$Cr + 3/2 CaCr_2O_4 + 3/2\ CoF_2 \rightarrow 3/2\ CaF_2 + 3/2\ Co + 2Cr_2O_3 \quad \ldots\ldots(1)$$

The free energy of this reaction can be expressed as the difference between the free energies of formation of the products and the reactants.

$$\Delta G_{T(R)} = 3/2\Delta G^{f}_{T CaF_2} + 2\Delta G^{f}_{T Cr_2O_3} - (3/2\Delta G^{f}_{T CaCr_2O_4} + 3/2\Delta G^{f}_{T CoF_2}) \ldots\ldots(2)$$

as ΔG^{f}_{T} for pure metals-chromium and cobalt - is equal to zero.

$$\Delta G_{T(R)} = -nFE_T \quad \ldots\ldots (3)$$

Where n is the number of electrons involved in the reaction, E_T is the e.m.f. of the cell in volts at temperature T and F is Faraday (96500 coulombs). The values of $\Delta G^{f}_{T CaF_2}$, $\Delta G^{f}_{T Cr_2O_3}$ and $\Delta G^{f}_{T CoF_2}$ were taken from literature. The $G^{f}_{T CaCr_2O_4}$ could thus be calculated from equations (2) and (3) and was found to be -53.19 kJ/ mole^{-1} at 800° K. The variation of e.m.f. with temperature can be correlated to the entropy of the reaction by :

$$\frac{\partial \Delta G\ (R)}{\partial T} = -nf \frac{\partial E}{\partial T} = -\Delta S \quad \ldots\ldots (4)$$

Thereafter using Gibbs Helmoltz equation, the enthalpy of reaction (1) can be calculated and was found to be -13.66 kJ/ mole^{-1} at 800 K.

Further with the knowledge of the Cp-T relationship for the products and reactants in reaction (1), $\Delta H_{298(R)}$ for the reaction can be calculated from the relation :

$$H_{298(R)} = \Delta H'_{800(R)} - \int_{298}^{800} Cp\ dT \quad \ldots. (5)$$

Where $H_{298(R)}$ and $H_{800(R)}$ are the heats of reaction at 298K and 800K and Cp is the difference between the heat capacities of the products and reactants. The value of Cp for all the terms in equation (1) were taken from literature (7-8).

The Cp values of $CaCr_2O_4$ were determined in this laboratory as they were not available in literature and will be published shortly.

Equation (5) can now be written as

$$\Delta H_{298(R)} = -13.66 - \int_{298}^{800} Cp\ dT \quad \ldots.(6)$$

and can be equated to the difference in the enthalpies of formation of the products and reactants in equation (1). Therefore,

$$\Delta H_{298(R)} = \Delta H^{f}_{298(Products)} - \Delta H^{f}_{298(Reactants)} \quad \ldots\ldots 7$$

In the above equation all the quantities are known except $H^{f}_{CaCr_2O_3}$ and hence can be calculated. Thus the heat of formation of $CaCr_2O_4$ i.e. the heat of reacation at 298K of the equation

$$Ca(s) + 2Cr\ (s) + 2O_2\ (g) \rightarrow CaCr_2O_4\ (s) \quad \ldots(8)$$

has been calculated and found to be -2096 kJ/ mole at 298K. From theoretical considerations, Kanteeva (1) has derived a value of -1952.7 kJ/mole for the heat of formation of $CaCr_2O_4$ at the same temperature. Our experimental values must be considered as more accurate even though the disparity between the experimental and theoretical values is not significant.

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