THERMODYNAMIC PROPERTIES OF DICALCIUM FERRITE BY CALCIUM FLUORIDE GALVANIC CELLS

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Galvanic cells using CaF_2 as the solid electrolyte were fabricated as follows

$$Pt / Fe, Fe_2O_3, Ca_2Fe_2O_5, CaF_2 / CaF_2 / Ni, NiF_2 / Pt$$

$$Pt / Fe, Fe_2O_3, Ca_2Fe_2O_5, CaF_2 / CaF_2 / Co, CoF_2 / Pt$$

and the resultant emf was measured as a function of temperature between 600 to 1000°K under a slow dynamic argon atmosphere. These values have been utilised to determine Gibbs free energy and enthalpy relations for the formation of dicalcium ferrite.

Interoxidic compounds of the alkaline earth metals with the transition metals are of great importance to ferrous industries. Combinations of such oxides give rise to low melting mixtures which are used as slags and as additives to sintering products. There are combinations giving rise to high melting mixtures which are used as refractories. $Ca_2Fe_2O_3$(2 CaO, Fe_2O_5) is one such identified slag.

Further the presence of clacium as an impurity in liquid sodium which, used as a coolant in fast breeder reactors, can lead to the formation of $Ca_2Fe_2O_5$ as one of the corrosion products in presence of oxygen which is present as sodium oxide. With these points in view, the study of the thermodynamic properties of $Ca_2Fe_2O_5$ as a function of temperature between 600 to 1000°K has been pursued. The data arising out of the present study will augment the information in the compilation of the thermodynamic constants of this compound and will be useful for further calculations and design of machinary in reactor systems and steel industry.

Rezukhina et al [1] investigated the cell

$$Pt, O_2 / CaO / CaF_2 / CaFe_2O_4 + Ca_2Fe_2O_5 / O_2 Pt$$

for the determination of the free energies of formation of $Ca_2Fe_2O_5$ in the range of 1100 to 1350°K. The study, however, did not yield any fruitful results due to the complicated nature of the cells. Eremenko and Phillipov [2] have studied the dissociation pressures of dicalcium ferrite from emf measurements between 900 to 1300°K of the cell

$$Pt / FeO, Fe_3O_4 / ZnO_2CaO / (O) pt$$

where (O) was the oxide phase taken for sinters and slages, mixtures of (2 CaO, Fe_2O_3), (CaO, FeO, Fe_2O_3) and (CaO, 3 FeO, Fe_2O_3, Fe_3O_4). This study pertained to mixtures of interoxidic compounds and not to $Ca_2Fe_2O_5$ alone. The work of Bratchikov and Toponischev [3], who determined the heat of formation of $Ca_2Fe_2O_5$ from the oxides, suffers from the inherent weakness that the heat value has been compounded from the small heat changes accompanying the formation of the compounds from the oxides which, themselves, have large heats of formation. Kubaschavski [4] has, by some theoretical considerations deduced that the heat of formation of $Ca_2Fe_3O_5$ from the oxides is 40.16 ± 4.18 KJ/mole . The present work aims at a computation of the free energies and enthalpies of formation of $Ca_2Fe_2O_5$ using the data obtained from the solid electrolyte galvanic cells of the type.

$$Pt/ Fe,Fe_2O_3, Ca_2Fe_2O_5, CaF_2/CaF_2/ Ni, NiF_2/Pt \quad ...(1)$$

$$Pt/ Fe,Fe_2O_3, Ca_2Fe_2O_5, CaF_2/CaF_2/ Co, CoF_2/Pt \quad ...(2)$$

EXPERIMENTAL

Dicalcium ferrite was prepared[5] by sintering a homogenised mixtures of stoichiometric proportions of $CaCO_3$ and Fe_2O_3 at 1150°C for about 30 hours in several stages in a slow stream of oxygen. The resultant compound was analysed chemically for calcium and iron.

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X-ray diffraction pattern of the compound showed all the lines for $Ca_2Fe_2O_5$ while lines for CaO and Fe_2O_3 were absent.

$$2\ CaCO_3 + Fe_2O_3 \xrightarrow[30\ hrs]{1150^\circ C} Ca_2Fe_2O_5 + 2\ CO_2$$

The apparatus, construction of the cell and mode of operation are described in our earlier publication [6]. The coexistance electrodes were prepared by mixing iron metal powder, haematite, dicalcium ferrite with calcium fluoride and sintering at 700°C in pure argon for around 24 hours. The method of operation and further calculations are based on Chiotti et al [7].

RESULTS AND DISCUSSION

The relationship between emf and temperature was obtained by least squares method to be

$(E \pm 8.0)$ mV = 463.6 + 0.333 T for cell (1)

$(E \pm 10.1)$ mV = 425.6 + 0.316 T for cell (2)

and are depicted in Fig 1. Internal consistancy between data of cells using the reference electrodes Ni, NiF_2 and Co, CoF_2 was good. The nickel electrode cells behaved better than the cobalt electrode cells. The emf can be attributed to the reactions,

$$2Fe + \tfrac{3}{2} Ca_2Fe_2O_5 + 3NiF_2 \longrightarrow 3CaF_2 + 3Ni + \tfrac{5}{2} Fe_2O_3$$

$$2Fe + \tfrac{3}{2} Ca_2Fe_2O_5 + 3CoF_2 \longrightarrow 3CaF_2 + 3Co + \tfrac{5}{2} Fe_2O_3$$

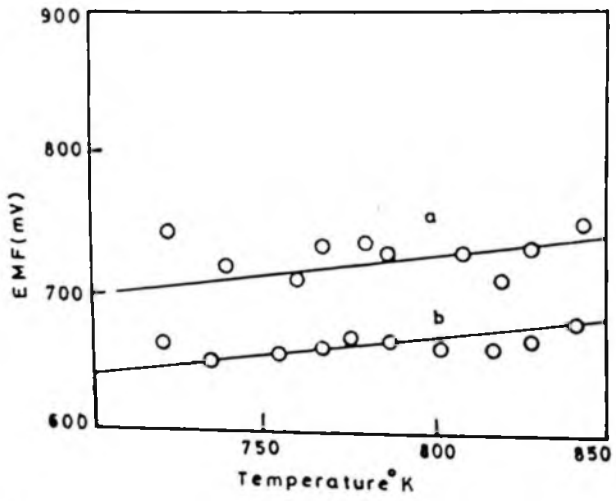


Fig. 1 EMF - Temperature Relationship of cell (1) & (2)

The free energies of these reactions which is equal to the difference in the summation of the energies of the products and the reactants can be expressed as

$$\Delta G_{T(R)} = -nFE = 3\Delta G^f_{T(CaF_2)} + \tfrac{5}{2}\Delta G^f_{T(Fe_2O_3)} - (\tfrac{3}{2}\Delta G^f_{T(Ca_2Fe_2O_5)} + 3\Delta G^f_{T(NiF_2)})$$

In this equation all the terms other than $\Delta G^f_{T(Ca_2Fe_2O_5)}$ are known from the literature and hence can be calculated at any temperature using the experimental values on the left hand side. On calculation, the values of $\Delta G^f_{T(Ca_2Fe_2O_5)}$ as a function of temperature from cells (1) and (2) works out to be -2259.3 + 0.2187 T and 2283.4 + 0.5864 T KJ/mole respectively.

From this data the enthalpy of formation of dicalcium ferrite at 298 K, $\Delta H^f_{298(Ca_2Fe_2O_5)}$ was calculated to be -2071.4 KJ/mol. The mode of calculation has been published [6] earlier. In this context, it is worthwhile mentioning that Bratchikov and Toponischev [4] had determined the enthalpy of formation of dicalcium ferrite at 298°K from the oxides. On the basis of these values, the enthalpy of formation of dicalcium ferrite can be calculated as -2130.1 KJ/mole as against the present value of -2071.4 KJ/mole. The deviation from the calculated value should be deemed due to the inherent error and assumptions in the theoretical computation of the function. The experimental value should be accepted for the compilation.

The possibility of the side reaction of iron metal powder reacting with haematite in the left hand side of the cells to form wustite could not be discounted. However a realistic assessment can be made by calculating the free energy of this reaction at 800°K. For this, the free energy of formation of haematite was not available in literature and was computed by the following calculation.

$3Fe_2O_3 \rightarrow 2Fe_3O_4 + \frac{1}{2}O_2$, ΔG_R = 299.5 - 0.1407 x T KJ/mole

$Fe_3O_4 \longrightarrow 3FeO + \frac{1}{2}O_2$, ΔG_R = 312.2 - 0.1251 x T KJ/mole

$FeO \longrightarrow Fe + \frac{1}{2}O_2$, ΔG_R = 264.9 - 0.0654 x T KJ/mole

By appropriate manipulation, one obtains from

these equations $\Delta G^{f}_{(Fe_2O_3)} = -809.6 + 0.2554 \times T$ KJ/mole. Using this value, the free energy of the reaction of iron metal with haematite was found to be -37.3 KJ/mole at 800 K. This value is not significant enough to be considered for practical purposes even though the reaction is thermodynamically possilble. As the reaction is electrochemically inactive, even if it occurs, it will not hinder the electrochemical reaction. X-ray diffraction and chemical analysis of the used pellets for ferrous iron did not reveal any significant formation of wustite

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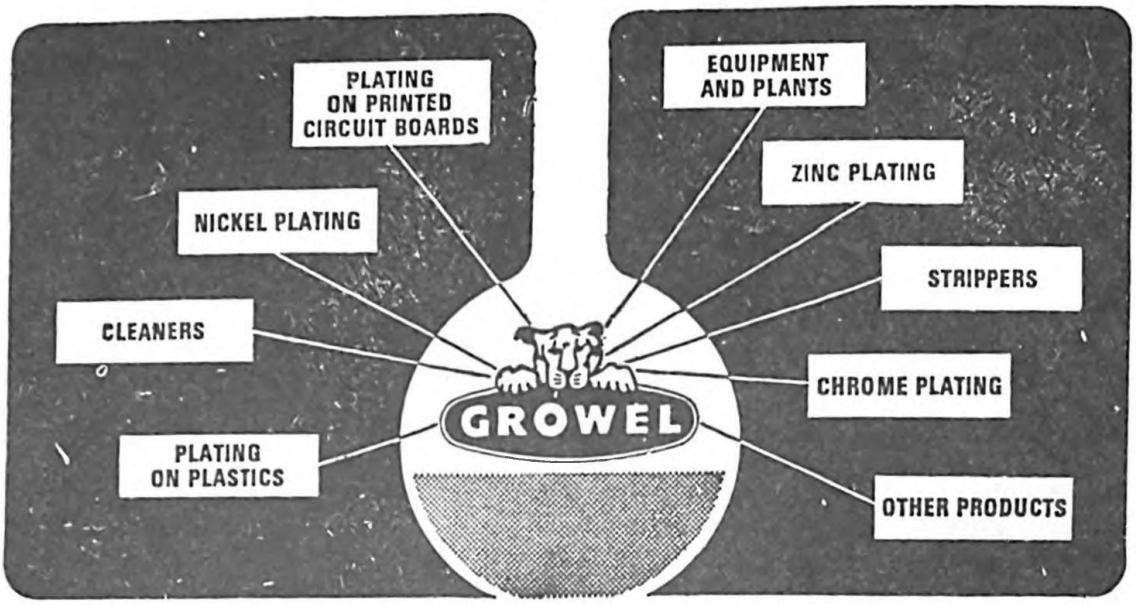
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