The Oxygen Potential of the Systems
Fe + FeCr$_2$O$_4$ + Cr$_2$O$_3$ and Fe + FeV$_2$O$_4$ + V$_2$O$_3$

in the Temperature Range 750-1600°C

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From electromotive force (emf) measurements using solid oxide galvanic cells incorporating ZrO$_2$-CaO and ThO$_2$-Y$_2$O$_3$ electrolytes, the chemical potentials of oxygen over the systems Fe + FeCr$_2$O$_4$ + Cr$_2$O$_3$ and Fe + FeV$_2$O$_4$ + V$_2$O$_3$ were calculated. The values may be represented by the equations:

2Fe(s, l) + O$_2$(g) + 2Cr$_2$O$_3$(s) → 2FeCr$_2$O$_4$(s)

$\Delta\mu _{O_2} = -151,400 + 34.7T$ (cal) = $-633,400 + 145.5T$ (J) (750 to 1536°C)

$\Delta\mu _{O_2} = -158,000 + 38.4T$ (cal) = $-661,000 + 160.5T$ (J) (1536 to 1700°C)

2Fe(s, l) + O$_2$(g) + 2V$_2$O$_3$(s) → 2FeV$_2$O$_4$(s)

$\Delta\mu _{O_2} = -138,000 + 29.8T$ (cal) = $-577,500 + 124.7T$ (J) (750 to 1536°C)

$\Delta\mu _{O_2} = -144,600 + 33.4T$ (cal) = $-605,100 + 140.0T$ (J) (1536 to 1700°C).

At the oxygen potentials corresponding to Fe + FeCr$_2$O$_4$ + Cr$_2$O$_3$ equilibria, the electronic contribution to the conductivity of ZrO$_2$-CaO electrolyte was found to affect the measured emf. Application of a small 60 cycle A.C. voltage with an amplitude of 50 mv across the cell terminals reduced the time required to attain equilibrium at temperatures between 750 to 950°C by approximately a factor of two. The second law entropy of iron chromite obtained in this study is in good agreement with that calculated from thermal data. The entropies of formation of these spinel phases from the component oxides can be correlated to cation distribution and crystal field theory.

The spinel phases play an important role in the oxidation of alloys, formation of inclusions in cast metals and in refining operations in pyrometallurgy. Accurate information on the thermodynamic properties of the spinel phases would permit a more precise description of these metallurgical phenomena. A normal spinel structure ($M_2$X$_2$O$_4$) can be described as a close-packed cubic arrangement of anions with one-eighth of the tetrahedral holes filled with $M^{2+}$ cations and one-half of the octahedral holes filled with $X^{2-}$ cations. At high temperatures, cations can exchange positions, the magnitude of cation mixing being determined by the difference in "site preference energies". Relationships between thermodynamic parameters and structural information would be useful both for the estimation of values where measurements are lacking, and for the evaluation of thermochemical data when a large body of experimental information is available.

The standard free energy of formation of iron chromite has been measured by Boericke and Bangert, Boericke and Bangert, Kunnmann et al., Kunnmann et al., Katsura and Muan, Novokhatkski and Lenev, and Chen and Chipman, using gas-equilibrium methods, while solid oxide galvanic cells were employed by Tretjakow and Schmalzried, Rezukhina et al., and Fruehan. The results show a spread of 8.6 kcal gr mole$^{-1}$ (36 kJ gr mole$^{-1}$) of chromite at 1000°C. Furthermore, the second law entropies obtained from the free energy measurements cannot be reconciled with the value obtained from thermal data.

The standard free energy of formation of iron vanadite has been measured by Kunnmann et al., below the melting point of iron, and by Chipman and Dastur, Karasev et al., Narita, and Kay and Kontopoulos above the melting point. The values obtained by Chipman and Dastur and Narita agree at 1600°C, while that of Karasev et al. is 3.7 kcal gr mole$^{-1}$ (15.5 kJ gr mole$^{-1}$) more positive and that of Kay and Kontopoulos is 1 kcal gr mole$^{-1}$ (4.18 kJ gr mole$^{-1}$) more negative. Extrapolation of these data to temperatures below the melting point of iron does not match the measurements of Kunnmann et al. It will be shown later that the temperature coefficients of the free energy of formation obtained from the data of Karasev et al. and Kay and Kontopoulos are not consistent with the current knowledge on the statistical thermodynamics of gases and condensed phases.

In an attempt to resolve the above discrepancies, the chemical potentials of oxygen over the mixtures Fe + FeCr$_2$O$_4$ + Cr$_2$O$_3$ and Fe + FeV$_2$O$_4$ + V$_2$O$_3$ were measured with solid oxide galvanic cells incorporating ZrO$_2$-CaO and ZrO$_2$-CaO in combination with ThO$_2$.
Cells 1, 2, 5 and 6 were employed in the temperature range 750 to 1600°C.

**EXPERIMENTAL**

**Materials**

The fine powders of metallic iron and ferric oxide used in this study were of spectrographic standard and were supplied by Johnson Matthey Chemicals. Chromium and vanadium oxides (Cr$_2$O$_3$ and V$_2$O$_5$) were obtained from Alpha Inorganics and were 99.9% pure. Iron chromite (FeCr$_2$O$_4$) and vanadate (FeV$_2$O$_4$) were prepared by prolonged heating at 1100°C for 3 to 4 days of pressed pellets containing Fe, Fe$_2$O$_3$ and Cr$_2$O$_3$ (or V$_2$O$_5$) in the molar ratio (1:1:3). The pellets were contained in alumina crucibles placed inside evacuated silica capsules. Formation of the ternary compounds was confirmed by X-ray diffraction analysis.

Impervious calcia-stabilized zirconia tubes supplied by Zirconia Corporation of America contained 7.5 mole% CaO. Thoria pellets doped with 15 mole% CaO were prepared from mixed nitrate solutions and were supplied by Johnson Matthey Chemicals. The fine powders of metallic iron and ferric oxide used in this study were of spectrographic standard.

**Apparatus and Procedure**

The method of preparation of the electrodes was similar to that described earlier. Fine powders of component metals and oxides were mixed in equimolar proportions, compacted into pellets and sintered in evacuated quartz capsules at 1100°C. The apparatus and cell arrangements were identical to that used in an earlier study on iron aluminate. The voltages of the following cells were measured as a function of temperature:

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\begin{align*}
\text{Pt, Fe + 'FeO' II CaO-ZrO}_2 & \text{ II Fe + FeCr}_2\text{O}_4 + \text{Cr}_2\text{O}_3, \text{ Pt} \\
\text{Pt, Fe + 'FeO' II CaO-ZrO}_2 & \text{ II YO}_{1.5}-\text{ThO}_2 \text{ II Fe + FeCr}_2\text{O}_4 + \text{Cr}_2\text{O}_3, \text{ Pt} \\
\text{Pt, Mo + MoO}_3 & \text{ II CaO-ZrO}_2 \text{ II Fe + FeCr}_2\text{O}_4 + \text{Cr}_2\text{O}_3, \text{ Pt} \\
\text{Pt, Mo + MoO}_3 & \text{ II CaO-ZrO}_2 \text{ II YO}_{1.5}-\text{ThO}_2 \text{ II Fe + FeCr}_2\text{O}_4 + \text{Cr}_2\text{O}_3, \text{ Pt} \\
\text{Pt, Fe + 'FeO' II Ca-ZrO}_2 & \text{ II Fe + FeV}_2\text{O}_4 + \text{V}_2\text{O}_5, \text{ Pt} \\
\text{Pt, Fe + 'FeO' II Ca-ZrO}_2 & \text{ II YO}_{1.5}-\text{ThO}_2 \text{ II Fe + FeV}_2\text{O}_4 + \text{V}_2\text{O}_5, \text{ Pt} \\
\text{Pt, Mo + MoO}_3 & \text{ II Ca-ZrO}_2 \text{ II Fe + FeV}_2\text{O}_4 + \text{V}_2\text{O}_5, \text{ Pt} \\
\text{Pt, Mo + MoO}_3 & \text{ II Ca-ZrO}_2 \text{ II YO}_{1.5}-\text{ThO}_2 \text{ II Fe + FeV}_2\text{O}_4 + \text{V}_2\text{O}_5, \text{ Pt} \\
\text{Cells 1, 2, 5 and 6 were employed in the temperature range 750 to 1200°C, and cells 3, 4, 7 and 8 from 950 to 1400°C. In bielectrolyte cells, the ThO}_2-YO}_3, \text{ electrolyte was placed in contact with the electrode having the lower oxygen partial pressure. The cell temperature was measured with a Pt/Pt-13 pct Rh thermocouple. The oxygen chemical potential over Fe + FeV}_2\text{O}_4 + \text{V}_2\text{O}_5 at 1600°C was measured by dipping a closed end ZrO}_2-CaO tube containing a Mo + MoO}_3 reference electrode into 10 g of liquid iron equilibrated with 6 g of FeV}_2\text{O}_4 and 4 g of V}_2\text{O}_5 for 3 to 5 h. The liquid iron was contained in an alumina crucible, which was lined inside with V}_2\text{O}_5. Molybdenum wires were used to make electrical contact with liquid iron and the Mo + MoO}_3 reference electrode. Similar experiments were not carried out with the Fe + FeCr}_2\text{O}_4 + \text{Cr}_2\text{O}_3 system, since earlier studies have shown that the phases do not coexist under equilibrium conditions at 1600°C.

The emf was measured with either 'Solartron' or 'Keithley' digital voltmeters. The reversibility of the cells was checked by passing small external currents in either direction. In each case the emf was found to return to the original value. The time required to reach equilibrium (steady emf) varied from 16 h at 750°C to 2 h at 1400°C. The emf was also found to be independent of the flow rate of the inert gas. Application of an A.C. potential at an amplitude of 50 mV was found to shorten the time required for equilibration in the temperature range 750 to 950°C by approximately a factor of two. In each case, the cell emfs were monitored for 2 to 6 h after the removal of the A.C. potential. Application of the A.C. potential at higher temperatures was found to accelerate the corrosion of the electrolyte by the Fe + 'FeO' electrode. The phases present in the electrode pellets were established before and after experiments by X-ray diffraction. These studies showed that no changes occurred in the electrodes during the experiments.

**Results**

The variation of the emf of cells 1 and 2 with temperature is shown in Fig. 1. The emf of cell 1 using the ZrO}_2-CaO electrolyte was found to be 3 to 5 mV lower than that of cell 2, in which the ThO}_2-YO}_3, \text{ pellet was used adjacent to the Fe + FeCr}_2\text{O}_4 + \text{Cr}_2\text{O}_3 electrode. The emf of cell 1 was found to decrease gradually with time. A trace of the time dependence of the emf at 1200°C, after passing an external current to remove oxygen from the Fe + FeCr}_2\text{O}_4 + \text{Cr}_2\text{O}_3 electrode is shown in Fig. 2. The value of the 'plateau' emf was independent (+3 mV) of the amount of current passed (5 to 100 μA for 15 min to 60 min). Following the method of Diaz and Richardson, the emfs corresponding to the plateau may be taken to represent the equilibrium values, and are plotted in Fig. 1.

The temperature dependencies of the emf of cells 3, 4, 5, 6, 7 and 8 were reproducible on repeated temperature cycling. The difference in the emf of cells 2, 4, 5, 6, 7 and 8 may be attributable to the onset of electronic conductivity in the ZrO}_2-CaO electrolyte at the oxygen partial pressures corresponding to the three phase equilibrium Fe + FeCr}_2\text{O}_4 + \text{Cr}_2\text{O}_3. The values of the emf of cells 5 and 6 shown in Fig. 4 are the