The Oxygen Potential of the Systems $Fe + FeCr_2O_4 + Cr_2O_3$ and $Fe + FeV_2O_4 + V_2O_3$ 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-$YO_{1.5}$ electrolytes, the chemical potentials of oxygen over the systems Fe + $FeCr_2O_4$ + Cr_2O_3 and Fe + FeV_2O_4 + V_2O_3 were calculated. The values may be represented by the equations:

$$2Fe(s, 1) + O_2(g) + 2Cr_2O_3(s) \rightarrow 2FeCr_2O_4(s)$$

$$\Delta\mu_{O_2} = -151{,}400 + 34.7T\ (\pm 300)\ \text{cal} = -633{,}400 + 145.5T\ (\pm 1250)\ \text{J (750 to 1536°C)}$$

$$\Delta\mu_{O_2} = -158{,}000 + 38.4T\ (\pm 300)\ \text{cal} = -661{,}000 + 160.5T\ (\pm 1250)\ \text{J (1536 to 1700°C)}$$

$$2Fe(s, 1) + O_2(g) + 2V_2O_3(s) \rightarrow 2FeV_2O_4(s)$$

$$\Delta\mu_{O_2} = -138{,}000 + 29.8T\ (\pm 300)\ \text{cal} = -577{,}500 + 124.7T\ (\pm 1250)\ \text{J (750 to 1536°C)}$$

$$\Delta\mu_{O_2} = -144{,}600 + 33.45T\ (\pm 300)\ \text{cal} = -605{,}100 + 140.0T\ (\pm 1250)\ \text{J (1536 to 1700°C).}$$

At the oxygen potentials corresponding to Fe + $FeCr_2O_4$ + Cr_2O_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 (MX_2O_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^{3+} 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,[1] Kunnmann *et al.*,[2] Katsura and Muan,[3] Novokhatski and Lenev,[4] and Chen and Chipman,[5] using gas-equilibrium methods, while solid oxide galvanic cells were employed by Tretjakow and Schmalzried,[6] Rezukhina *et al.*[7] and Fruehan.[8] 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[1-4,6,7] cannot be reconciled with the value obtained from thermal data.[9,10]

The standard free energy of formation of iron vanadite has been measured by Kunnmann *et al.*[2] below the melting point of iron, and by Chipman and Dastur,[11] Karasev et al.,[12] Narita,[13] and Kay and Kontopoulos[14] above the melting point. The values obtained by Chipman and Dastur[11] and Narita[13] agree at 1600°C, while that of Karasev *et al.*[12] is 3.7 kcal gr mole^{-1} (15.5 kJ gr mole^{-1}) more positive and that of Kay and Kontopoulos[14] 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.*[2] It will be shown later that the temperature coefficients of the free energy of formation obtained from the data of Karasev *et al.*,[12] and Kay and Kontopoulos[14] 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 + $FeCr_2O_4$ + Cr_2O_3 and Fe + FeV_2O_4 + V_2O_3 were measured with solid oxide galvanic cells incorporating ZrO_2-CaO and ZrO_2-CaO in combination with ThO_2-

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$YO_{1.5}$ as electrolyte, using Fe + 'FeO' and Mo + MoO_2 mixtures as reference electrodes, 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_2O_3 and V_2O_3) were obtained from Alfa Inorganics and were 99.9 pct pure. Iron chromite ($FeCr_2O_4$) and vanadite (FeV_2O_4) were prepared by prolonged heating at 1100°C for 3 to 4 days of pressed pellets containing Fe, Fe_2O_3 and Cr_2O_3 (or V_2O_3) 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 pct CaO. Thoria pellets doped with 15 mole pct yttria were prepared from mixed nitrate solutions by evaporation and subsequent decomposition. The resulting powder was pressed into pellets at a pressure of 30 tons sq $in.^{-1}$ and sintered under an atmosphere of 90 pct N_2 + 10 pct H_2 at 1800°C. The argon gas used as the atmosphere for the emf runs was 99.98 pct pure and was dried and then deoxidized by passing through a column of titanium granules maintained at 900°C.

Apparatus and Procedure

The method of preparation of the electrodes was similar to that described earlier.[15] 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.[15] The voltages of the following cells were measured as a function of temperature:

$$\text{Pt, Fe + 'FeO'} \,\|\, \text{CaO-}ZrO_2 \,\|\, \text{Fe + } FeCr_2O_4 + Cr_2O_3\text{, Pt} \quad [1]$$

$$\text{Pt, Fe + 'FeO'} \,\|\, \text{CaO-}ZrO_2 \,|\, YO_{1.5}\text{-}ThO_2 \,\|\, \text{Fe + } FeCr_2O_4 + Cr_2O_3\text{, Pt} \quad [2]$$

$$\text{Pt, Mo + } MoO_2 \,\|\, \text{CaO-}ZrO_2 \,\|\, \text{Fe + } FeCr_2O_4 + Cr_2O_3\text{, Pt} \quad [3]$$

$$\text{Pt, Mo + } MoO_2 \,\|\, \text{CaO-}ZrO_2 \,|\, YO_{1.5}\text{-}ThO_2 \,\|\, \text{Fe + } FeCr_2O_4 + Cr_2O_3\text{, Pt} \quad [4]$$

$$\text{Pt, Fe + 'FeO'} \,\|\, \text{Ca-}ZrO_2 \,\|\, \text{Fe + } FeV_2O_4 + V_2O_3\text{, Pt} \quad [5]$$

$$\text{Pt, Fe + 'FeO'} \,\|\, \text{CaO-}ZrO_2 \,|\, YO_{1.5}\text{-}ThO_2 \,\|\, \text{Fe + } FeV_2O_4 + V_2O_3\text{, Pt} \quad [6]$$

$$\text{Pt, Mo + } MoO_2 \,\|\, \text{CaO-}ZrO_2 \,\|\, \text{Fe + } FeV_2O_4 + V_2O_3\text{, Pt} \quad [7]$$

$$\text{Pt, Mo + } MoO_2 \,\|\, \text{CaO-}ZrO_2 \,|\, YO_{1.5}\text{-}ThO_2 \,\|\, \text{Fe + } FeV_2O_4 + V_2O_3\text{, Pt} \quad [8]$$

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-$YO_{1.5}$ 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_2O_4 + V_2O_3 at 1600°C was measured by dipping a closed end ZrO_2-CaO tube containing a Mo + MoO_2 reference electrode into 10 g of liquid iron equilibrated with 6 g of FeV_2O_4 and 4 g of V_2O_3 for 3 to 5 h. The liquid iron was contained in an alumina crucible, which was lined inside with V_2O_3. Molybdenum wires were used to make electrical contact with liquid iron and the Mo + MoO_2 reference electrode. Similar experiments were not carried out with the Fe + $FeCr_2O_4$ + Cr_2O_3 system, since earlier studies[11,16] 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. ripple with 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-$YO_{1.5}$ pellet was used adjacent to the Fe + $FeCr_2O_4$ + Cr_2O_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 + $FeCr_2O_4$ + Cr_2O_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[17] the emfs corresponding to the plateau may be taken to represent the equilibrium values, and are plotted in Fig. 1.

The temperature dependences of the emf of cells 3, 4, 7 and 8 are shown in Fig. 3. Again the emf of cell 3 is 2 to 6 mv below that of cell 4. The emf of cells 2, 4, 5, 6, 7 and 8 were reproducible on repeated temperature cycling. The difference in the emf of cells 1 and 2, 3 and 4, 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 + $FeCr_2O_4$ + Cr_2O_3. The values of the emf of cells 5 and 6 shown in Fig. 4 are the

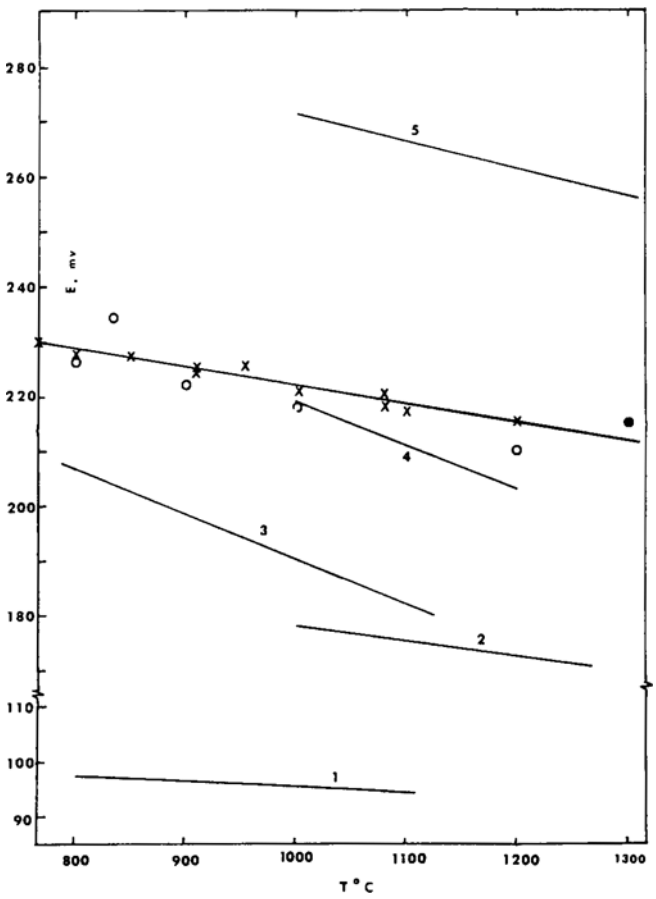

Fig. 1—The temperature dependence of the emf of cell 1 (○) and cell 2 (×) obtained in this study. 1 Kunnmann *et al.*,[2] 2 Boericke and Bangert,[1] 3 Tretjakow and Schmalzried,[6] 4 Rezukhina *et al.*,[7] 5 Novokhatski and Lenev,[4] ● Katsura and Muan.[3]

same within experimental error (±3 mv). These results indicate that at the oxygen potential corresponding to the Fe + FeV_2O_4 + V_2O_3 equilibrium, there is no significant electronic contribution (t_e < 0.01) to the conductivity of ZrO_2-CaO. The temperature dependence of the emf for the various cells can be represented by the equations,

$$E_2 = 270 - 3.75 \times 10^{-2} T \text{ mv}$$

$$E_4 = 138 + 5.72 \times 10^{-2} T \text{ mv}$$

$$E_5 = E_6 = 125.2 + 1.583 \times 10^{-2} T \text{ mv}$$

$$E_7 = E_8 = -6.3 + 11.06 \times 10^{-2} T \text{ mv}.$$

The emf of cell 7 was 200 (±4) mv at 1600°C and 194 (±4) mv at 1589°C. The emfs above the melting point of iron were constant for 5 to 10 min after immersion of the electrolyte tube. The difference in oxygen potential between the two electrodes is related to the emf by the relation

$$\Delta\mu_{O_2} = RT \ln \frac{p'_{O_2}}{p''_{O_2}} = -4FE \qquad [9]$$

where F = 23,063 cal V^{-1} $mole^{-1}$, E is the emf in volts and the chemical potential is expressed in cal. The oxygen potential corresponding to the reference electrodes are given by the equations,[15,18]

$$\text{Mo} + \text{MoO}_2\text{: } \Delta\mu_{O_2} = -138{,}600 + 40.0T \text{ cal} = -579{,}900 + 167.4T \text{ J} \qquad [10]$$

$$\text{Fe} + \text{'FeO'}\text{: } \Delta\mu_{O_2} = -126{,}470 + 31.26T \text{ cal} = -529{,}150 + 130.8T \text{ J} \qquad [11]$$

When Eqs. [9], [10] and [11] are combined with the measured emf, the following equations are obtained for the oxygen potential of the three phase mixtures:

$$2\text{Fe}(s, 1) + \text{O}_2(g) + 2\text{Cr}_2\text{O}_3(s) \rightarrow 2\text{FeCr}_2\text{O}_4(s)$$

$$\Delta G^\circ = -151{,}400 + 34.7T (\pm 300) \text{ cal} = -633{,}400 + 145.5T (\pm 1250) \text{ J (750 to 1536°C)} \qquad [12]$$

$$\Delta G^\circ = -158{,}000 + 38.4T (\pm 300) \text{ cal} = -661{,}000 + 160.5T (\pm 1250) \text{ J (1536 to 1700°C)} \qquad [13]$$

$$2\text{Fe}(s, 1) + \text{O}_2(g) + 2\text{V}_2\text{O}_3(s) \rightarrow 2\text{FeV}_2\text{O}_4(s)$$

$$\Delta G^\circ = -138{,}000 + 29.8T (\pm 300) \text{ cal} = -577{,}500 + 124.7T (\pm 1250) \text{ J (750 to 1536°C)} \qquad [14]$$

$$\Delta G^\circ = -144{,}600 + 33.45T (\pm 300) \text{ cal} = -605{,}100 + 140.0T (\pm 1250) \text{ J (1536 to 1700°C)} \qquad [15]$$

Throughout this paper cal = 4.184 J. For the purpose of internal consistency and in view of the uncertainty limits, four significant figures are used for representing the numerical terms in the above equations. The quoted uncertainty limits on the standard free energy changes were obtained by combining the uncertainties in measured emf and the oxygen potential of the reference electrodes. The equations for the temperature range 1536 to 1700°C are derived by using the heat of fusion of iron[19] (3.3 kcal or 13.8 kJ). The values obtained in this manner for Fe + FeV_2O_4 + V_2O_3 are in good agreement with the direct measurements at 1600°C. Strictly, the variation of the free energy with temperature in the range 750 to 1536°C should exhibit small changes in slope at points corresponding to the solid-state phase transitions in iron. However, the results using Fe + 'FeO' and Mo + MoO_2 reference electrodes agree within the experimental error (± 3 mv) and indicate that a linear equation may be used for this temperature range. The iron chromite and vanadite phases might exhibit nonstoichiometry; the values quoted in this study correspond to the Cr_2O_3 or V_2O_3 saturated compositions. The following equations characterize the formation of the spinel phases from the component oxides:

$$\text{Fe}_{0.946}\text{O}(s) + \text{Cr}_2\text{O}_3(s) + 0.054\,\text{Fe}(s) \rightarrow \text{FeCr}_2\text{O}_4(s)$$

$$\Delta G^\circ = -12{,}450 + 1.73T (\pm 250) \text{ cal} = -52{,}100 + 7.24T (\pm 1000) \text{ J (750 to 1300°C)} \qquad [16]$$

$$\text{Fe}_{0.946}\text{O}(s) + \text{V}_2\text{O}_3(s) + 0.054\,\text{Fe}(s) \rightarrow \text{FeV}_2\text{O}_4(s)$$

$$\Delta G^\circ = -5{,}780 - 0.73T (\pm 250) \text{ cal} = -24{,}160 - 3.06T (\pm 1000) \text{ J (750 to 1300°C)} \qquad [17]$$

DISCUSSION

The results obtained in this study for iron chromite are compared with those reported in the literature in

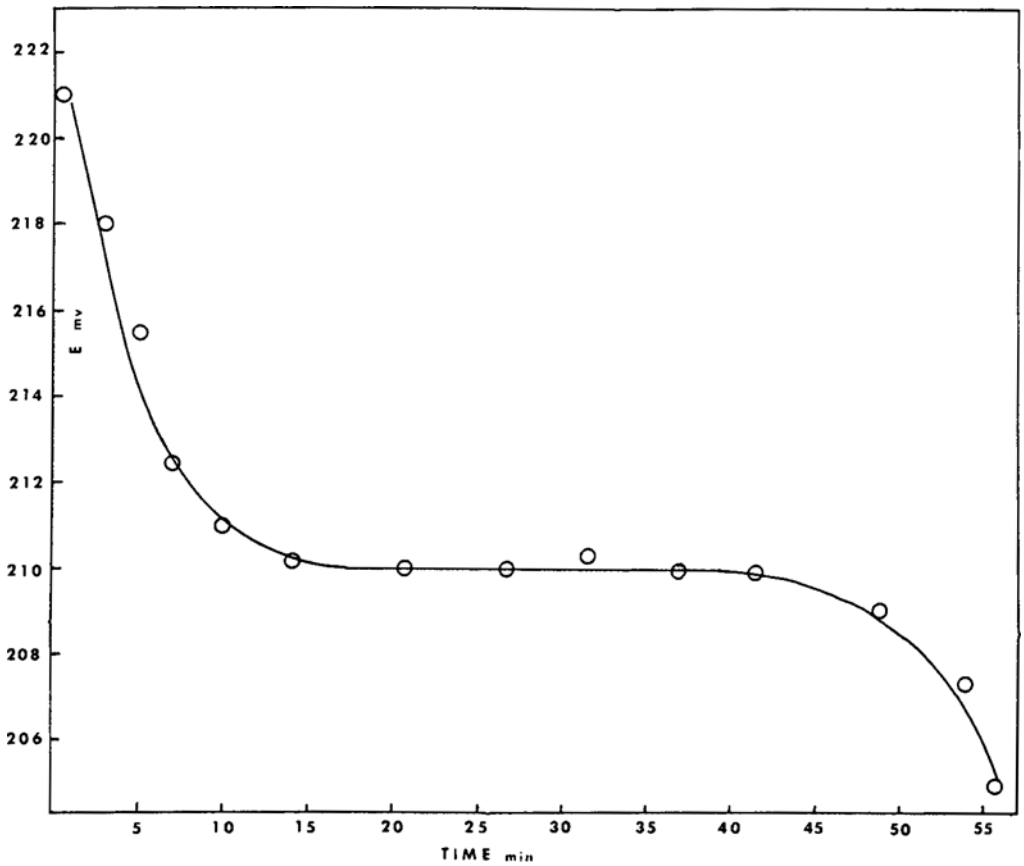

Fig. 2—The time dependence of the emf of cell 1 at 1200°C.

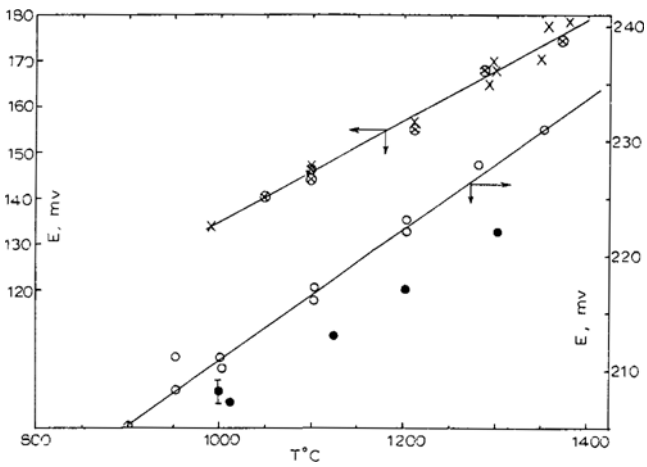

Fig. 3—The variation of emf with temperature: ● cell 3; ○ cell 4; ⊗ cell 7; × cell 8.

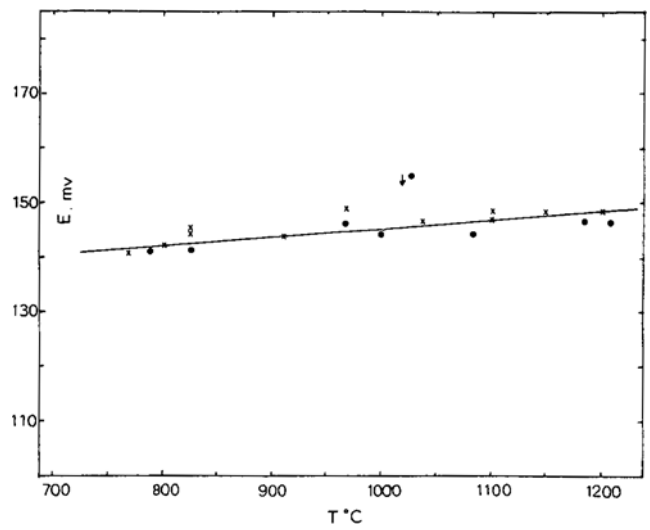

Fig. 4—The temperature dependence of emf of cells 5 (●) and 6 (×).

Fig. 1. Values reported by Katsura and Muan,[3] and Rezukhina *et al.*[7] are in fair agreement with the results of this study. Tretjakow and Schmalzried[6] used a calcia stabilized zirconia electrolyte and air as the reference electrode. The presence of electronic conduction in the electrolyte would explain the lower emfs obtained in their study. Kunnmann *et al.*[2] measured the CO/CO_2 ratio required for the synthesis of the chromite from iron and chromium sesquioxide. The presence of kinetic restrictions on the formation reaction would require the presence of a more oxidizing gas mixture for the synthesis than that observed under equilibrium conditions. The oxygen potential obtained from Kunnmann *et al.* is considerably more positive and suggests that these measurements may not reflect equilibrium conditions. No obvious reasons can be found for the discrepancy between the present results and those of Boericke and Bangert,[1] and Novokhatski and Lenev.[4]

Chen and Chipman[5] and Fruehan[8] have measured the free energy change at 1600°C for the reaction

$$Fe\,(l) + 2Cr\,(l) + 4\,\underline{O} \rightarrow FeCr_2O_4\,(s)$$

where $\underline{O}$ denotes oxygen dissolved in liquid iron. Their

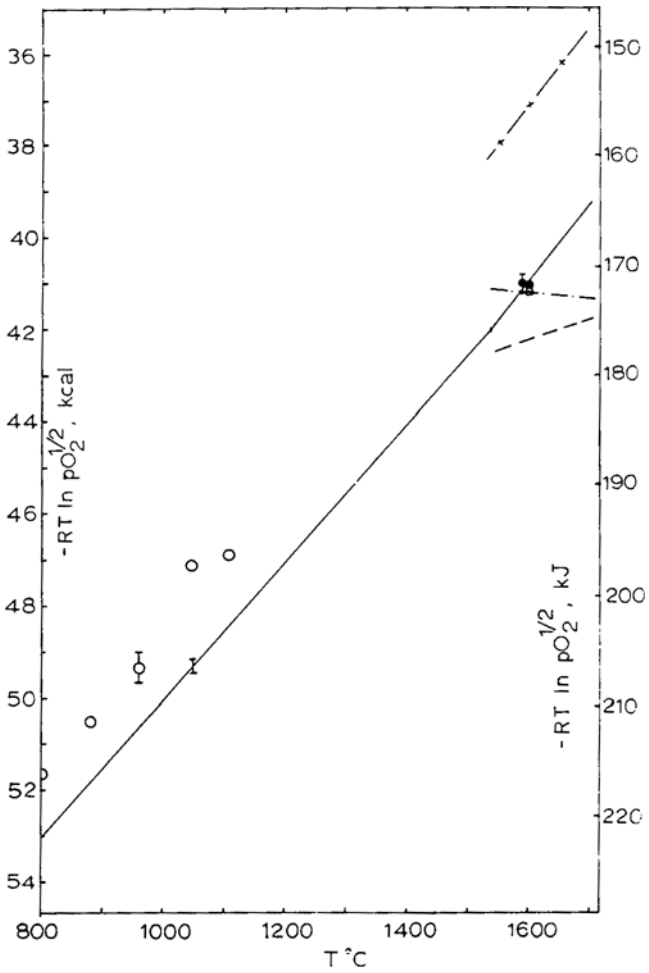

Fig. 5—The variation of $RT \ln p_{O_2}^{1/2}$ with temperature for the system Fe + FeV_2O_4 + V_2O_3:
——, ● this study; –·–·– Narita;[13]
– – – – Kay and Kontopoulos;[14]
–×– Karasev *et al.*;[12] ○ Kunnmann *et al.*;[2]
□ Chipman and Dastur.[11]

values are combined with the free energy of solution of oxygen in iron,[20] the free energy of formation of Cr_2O_3[21] and the free energy of fusion of Cr[19] to obtain the free energy change for the reaction,

$$2Fe\,(l) + O_2(g) + 2Cr_2O_3(s) \rightarrow 2FeCr_2O_4(s)$$

$\Delta G^\circ_{1873} = -85{,}430$ cal $= -357{,}450$ J — Chen and Chipman

$\Delta G^\circ_{1873} = -82{,}370$ cal $= -344{,}626$ J — Fruehan.

These values compare with a value of $-86{,}100$ (± 300) cals ($-360{,}400$ J) obtained from the results of this study (Eq. [13]).

The heat capacity measurements of Shomate[9] (53 to 298 K) and Naylor[10] (298 to 1780 K) can be used to calculate a value of 93.56 (± 0.6) cal deg^{-1} mole^{-1} for the entropy of $FeCr_2O_4$ at 1300 K. The second law entropy of formation of $FeCr_2O_4$ (Eq. [12] or [16]) obtained in this study can be combined with the entropy of $Cr_2O_3(s)$, Fe(s) and $O_2(g)$ or 'FeO'(s)[19] to give a value of 94.17 (± 1.0) cal deg^{-1} mole^{-1} or 394 J deg^{-1} mole^{-1} at 1300 K. The second law entropy of $FeCr_2O_4$ is in good agreement with that calculated from thermal data. The third law heat of formation of $FeCr_2O_4$ at 298 K is $-11{,}800$ (± 350) cal mole^{-1} or $-49{,}370$ ($\pm 1{,}460$) J mole^{-1}.

The oxygen potential over the Fe + FeV_2O_4 + V_2O_3 system is plotted in Fig. 5. The values reported by other investigators are also shown for comparison. The results of this study are in good agreement with the measurements of Chipman and Dastur[11] and Narita[13] at 1600°C. The temperature dependence of the oxygen potential is negative according to Narita.[13] This is not in accord with the statistical thermodynamics of gases and condensed phases. For the reaction,

$$Fe\,(l) + \tfrac{1}{2}O_2(g) + V_2O_3(s) \rightarrow FeV_2O_4(s)$$

the main contribution to the entropy change arises from the entropy of the gaseous reactant, which combines with the solid phases to form a solid product. The entropy change would therefore be negative and greater than 10 cal deg^{-1} mole^{-1} (42 J deg^{-1} mole^{-1}). The free energy of formation of FeV_2O_4 obtained by Karasev *et al.*[12] is 3.7 kcal (15.5 kJ) more positive than that obtained in this study. The results of Kay and Kontopoulos[14] are 1.3 to 2.7 kcal (5.4 to 11.3 kJ) more negative and the temperature coefficient of their free energy indicates an entropy change of -4.4 cal deg^{-1} mole^{-1} (18.4 J deg^{-1} mole^{-1}). The free energy of formation of FeV_2O_4 obtained by Kunnmann *et al.*[2] at lower temperatures is 1.3 kcal (5.4 kJ) more positive than that obtained in this study. As discussed earlier, this discrepancy probably arises from kinetic restrictions in the synthesis of FeV_2O_4 from Fe, V_2O_3 and CO + CO_2 mixtures.

ENTROPY OF FORMATION OF SPINELS

Since the entropy arising from the mixing of cations in the tetrahedral and octahedral sites of the spinel structure would make a significant contribution to the total entropy of a spinel at high temperatures, information on the cation distribution is required to account for the entropies of formation of spinels from component oxides which were obtained in this study. Dunitz and Orgel[22] have discussed the distribution of transition-metal ions among tetrahedral and octahedral sites in oxides from the viewpoint of crystal field theory. When a transition-metal ion is surrounded by an octahedron of negative ions, the d orbitals are split by the electrostatic field into a triply degenerate t_{2g} orbital which is stabilized and a doubly degenerate e_g orbital which is destabilized relative to the mean d orbital. In the tetrahedral field, the situation is similar but the e_g orbitals are more stable than the t_{2g} orbitals. Dunitz and Orgel[22] have calculated the magnitude of the stabilization energies for the transition-metal ions in tetrahedral and octahedral sites from optical and magnetic measurements. The difference between the stabilization energies in the two competing sites gives the 'site preference energy', which is shown in Table I. If the mixing of cations on each type of site is ideal, the cation distribution can be obtained by equating the difference in octahedral site preference energy for the two cations to the product of absolute temperature and the ideal entropy of mixing.

Navrotsky and Kleppa[23] have used the mass-action law treatment to derive an empirical scale of octahedral site preference energies from available high

Table I. Octahedral Site Preference Energies for Various Ions from Crystal Field Theory[22]

Ion	Octahedral Site Preference Energy	
	kcal	kJ
Fe^{2+}	−4.0	−16.7
Ni^{2+}	−20.6	−86.2
Co^{2+}	−7.4	−31.0
Cu^{2+}	−15.2	−63.6
Mn^{2+}	0	0
V^{3+}	−12.8	−53.6
Cr^{3+}	−37.7	−157.7
Fe^{3+}	0	0
Al^{3+}	(−18.6)*	(−77.8)*

*Based on the value for Ni^{2+} and measured cation distribution in $NiAl_2O_4$.

Table II. Cation Distribution in Spinels

Spinel (MX_2O_4)	ΔH_{ex} kcal	ΔH_{ex} kJ	Cation Distribution: Fraction of M on Tetrahedral Site (x) Calculated 1200 K	Measured
$FeAl_2O_4$	14.6	61.1	0.936	0.923 (1473 K)[24]
$NiAl_2O_4$	−2.0	−8.4	0.21	0.20 (1300 K)[25]
$CoAl_2O_4$	11.2	46.9	0.89	0.95 (1123 K)[24,25]
$CuAl_2O_4$	3.4	14.2	0.54	0.4 (1100 K)[26]
$MnAl_2O_4$	18.6	77.8	0.972	0.958 (1272 K)[24]
FeV_2O_4	8.8	36.8	0.81	–
$FeCr_2O_4$	33.7	141	0.999	–
$FeFe_2O_4$	−4.0	−16.7	0.11	–

temperature crystallographic information on cation distribution in spinels and a value for Al^{3+} obtained from calorimetric data on the transformation of α-alumina to γ-alumina. However, lack of accurate cation distribution data on vanadites, prevents the estimation of an octahedral site preference energy of V^{3+} using this procedure. Although the values on Navrotsky and Kleppa's empirical scales are generally about 8 to 10 kcal (33.5 to 42 kJ) more negative for a given cation than those obtained from crystal field theory, the difference in the energy values for two cations (which determines the distribution) is approximately the same on both scales.

The values for octahedral site preference energy from crystal field theory were used to compute the cation distribution in FeV_2O_4 and $FeCr_2O_4$. The value for Al^{3+} in Table I is obtained relative to that for Ni^{2+} using the measured equilibrium distribution of Ni^{2+} and Al^{3+} in $NiAl_2O_4$ at 1300 K.[25] In a spinel crystal of the composition $M_xX_{1-x}[M_{(1-x)}X_{(1+x)}]O_4$ in thermal equilibrium, the free energy change for the exchange reaction, $M + [X] \rightarrow [M] + X$, is zero. The change in enthalpy for the exchange reaction can therefore be equated to the product of absolute temperature and change in configurational entropy. The partial molar entropy of a cation on any site is equal to $-R \ln N_i$, where N_i is the mole ionic fraction of the cation i on that site

$$\Delta H_{ex} = -RT \ln \frac{N_{[M]}N_X}{N_{[X]}N_M}$$

$$= -RT \ln \frac{(1-x)^2}{x(1+x)} \quad [18]$$

where [ ] indicates atoms in octahedral position and

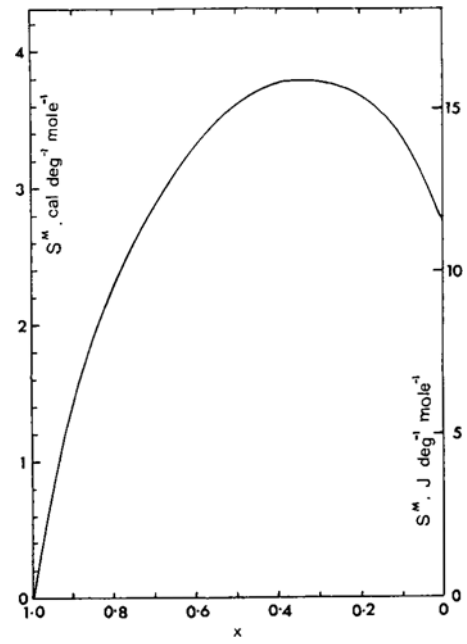

Fig. 6—The configurational entropy of mixing of cations in 2-3 spinels; × is the fraction of divalent cation in tetrahedral site.

Table III. Comparison of Entropies and Heats of Formation with Entropies of Mixing of Cations of Spinels Containing Fe^{2+}

Spinel	ΔS^* cal deg^{-1} mole^{-1}	ΔS^* J deg^{-1} mole^{-1}	ΔS^M cal deg^{-1} mole^{-1}	ΔS^M J deg^{-1} mole^{-1}	ΔH^* kcal mole^{-1}	ΔH^* kJ mole^{-1}
$FeFe_2O_4(Fe_3O_4)$	1.47[27]	6.15[27]	3.42	14.31	−5.1[27]	−21.3[27]
FeV_2O_4	0.73	3.05	2.20	9.20	−5.78	−24.2
$FeAl_2O_4$	−0.78[15]	−3.26[15]	1.04	4.35	−6.66[15]	−27.9[15]
$FeCr_2O_4$	−1.73	−7.24	0.03	0.13	−12.45	−52.1

*For the reaction $Fe_{0.95}O(s) + 0.05\ Fe(s) + X_2O_3(s) \rightarrow FeX_2O_4(s)$.

x is the fraction of divalent metal M in tetrahedral position. The exchange energies derived from the values in Table I for various spinels are shown in Table II, along with calculated cation distribution at 1200 K. Comparison of the calculated cation distribution with crystallographic information (Table II) illustrates the accuracy of the estimations. The extent of cation mixing increases from $FeCr_2O_4$ to $FeAl_2O_4$ and FeV_2O_4. The configurational entropy of mixing of cations may be calculated using Temkin's ionic fraction approach,[23]

$$\Delta S^M = -R\left[x \ln x + (1-x) \ln (1-x) + (1-x) \ln \frac{(1-x)}{2} + (1+x) \ln \frac{(1+x)}{2}\right]. \quad [19]$$

The variation of ΔS^M with x is illustrated in Fig. 6. The mixing contribution to the entropy of the three spinel phases containing Fe^{2+} are shown in Table III, along with their entropies of formation from component oxides obtained in this study. It is apparent that the differences in the measured entropies of formation are mainly due to differences in cation distribution and the corresponding mixing entropies.

This close correspondence probably arises from the fact that the differences in lattice parameter and the degree of covalent bonding in the three Fe^{2+} spinels

are paralleled by corresponding differences in the properties of the trivalent oxides which have the corundum structure. It is also clear from Fig. 6 that drop calorimetric techniques for heat capacity measurements would not be suitable in computing entropies at high temperatures of spinels with significant cation mixing. The disorder on the cation sites increases with temperature, and the entropies obtained in this study are average values for the temperature range covered.

The heat of formation of the spinel phases from component oxides shown in Table III decreases with increasing cation mixing. This is in line with the calculations of Verwey *et al.*,[28] who have shown that Madelung constant and electrostatic stability decrease as the fraction of M^{2+} ions in octahedral position increases. The Madelung constant is also sensitive to the oxygen parameter,[29] u, which is a measure of the departure from the ideal spinel structure. Unfortunately, the values for this parameter are not known accurately for all the phases listed in Table III.

SUMMARY AND CONCLUSIONS

1) Solid oxide galvanic cells were used to measure the oxygen potential of the three phase mixtures Fe + $FeCr_2O_4$ + Cr_2O_3 and Fe + FeV_2O_4 + V_2O_3 in the temperature range 750 to 1600°C. The second law entropy of formation of $FeCr_2O_4$ obtained in this study is in good agreement with that calculated from thermal data.

2) Application of a small A.C. potential (50 mv) across the cell terminals was found to decrease the time required to attain equilibrium in the temperature range 750 to 950°C.

3) At the oxygen potentials corresponding to the Fe + $FeCr_2O_4$ + Cr_2O_3 equilibria, electronic contributions to the conductivity of CaO-ZrO_2 electrolyte were found to affect the measured emf.

4) The cation distribution in spinel phases at high temperatures can be evaluated from 'site preference energies' derived from crystal field theory. The entropy of formation of spinel phases from the component oxides with rock salt and corundum structures may be expressed as $-1.75 + \Delta S^M$ cal deg^{-1} mole^{-1} or $-7.25 + \Delta S^M$ J deg^{-1} mole^{-1}, where ΔS^M is the entropy of mixing of cations.

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REFERENCES

1. F. G. Boericke and W. M. Bangert: *Bur. Mines (U.S.) Rep. Invest.*, 1945, N. 3813.
2. W. Kunnmann, D. B. Rogers, and A. Wold: *J. Phys. Chem. Solids*, 1963, vol. 24, p. 1535-38.
3. T. Katsura and A. Muan: *Trans. TMS-AIME*, 1964, vol. 230, p. 77.
4. I. A. Novokhatski and L. M. Lenev: *Zh. Neorg. Khim.*, 1966, vol. 11, p. 2014.
5. H. M. Chen and J. Chipman: *Trans. ASM*, 1947, vol. 38, p. 70-113.
6. J. D. Tretjakow and H. Schmalzried: *Ber. Bunsenges. Phys. Chem.*, 1965, vol. 69, p. 396.
7. T. N. Rezukhina, V. A. Levitski, and B. A. Istomin: *Electrochemistry* (Russian), 1965, vol. 1, p. 467-71.
8. R. J. Fruehan: *Trans. TMS-AIME*, 1969, vol. 245, p. 1215-18.
9. C. H. Shomate: *Ind. Eng. Chem.*, 1944, vol. 36, p. 910.
10. B. F. Naylor: *Ind. Eng. Chem.*, 1944, vol. 36, p. 933.
11. J. Chipman and M. Dastur: *Trans. AIME*, 1951, vol. 191, p. 111-15.
12. R. A. Karasev, A. Y. Polyakov, and A. M. Samarin: *Dokl. Akad. Nauk USSR*, 1952, vol. 85, pp. 1313-16.
13. K. Narita: *Nippon Kagaku Zasshi*, 1958, vol. 79, pp. 866-72.
14. D. A. R. Kay and A. Kontopoulos: *Proceedings of the International Symposium on 'Metallurgical Chemistry: Applications in Ferrous Metallurgy,'* Sheffield, England, 1971.
15. J. C. Chan, C. B. Alcock, and K. T. Jacob: *Can. Met. Quart.*, 1973, vol. 12, pp. 439-43.
16. D. C. Hilty, W. J. Forgeng, and R. L. Folkman: *J. Metals*, 1955, vol. 7, p. 253.
17. C. M. Diaz and F. D. Richardson: *Trans. Inst. Mining Met.*, (London), 1967, vol. 76, C196-203.
18. C. B. Alcock and J. C. Chan: *Can. Met. Quart.*, 1972, vol. 11, p. 559.
19. O. Kubaschewski, E. L. Evans, and C. B. Alcock: *Metallurgical Thermochemistry*, Pergamon Press, 1967.
20. J. F. Elliott, M. Gleiser, and V. Ramakrishna: *Thermochemistry for Steelmaking*, vol. II, Addison-Wesley, 1964.
21. Y. Jeannin, C. Mannerskantz, and F. D. Richardson: *Trans. AIME*, 1963, vol. 227, p. 300.
22. J. D. Dunitz and L. E. Orgel: *J. Phys. Chem. Solids*, 1957, vol. 3, pp. 318-23.
23. A. Navrotsky and O. J. Kleppa: *J. Inorg. Nucl. Chem.*, 1967, vol. 29, p. 2701.
24. W. W. Roth: *J. Phys.*, 1964, vol. 25, p. 507.
25. H. Schmalzried: *Z. Phys. Chem. Frankf., Aust.*, 1961, vol. 28, p. 203.
26. F. Bertaut: *Compt. Rend.*, 1954, vol. 239, p. 504.
27. D. R. Stull *et al.*: JANAF Thermochemical Tables, NSRDS-NBS 37, 1971.
28. E. J. W. Verwey, F. DeBoer, and J. H. van Santen: *J. Chem. Phys.*, 1948, vol. 16, pp. 1091-92.
29. F. DeBoer, J. H. van Santen, and E. J. W. Verwey: *J. Chem. Phys.*, 1950, vol. 18, pp. 1032-34.