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An EMF Study of Certain Orthoferrites: $YFeO_3$, $GdFeO_3$ and $SmFeO_3$

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Synopsis. The EMF of a solid electrolyte galvanic cell on the formation of orthoferrites, $LnFeO_3$, was measured for Ln=Y, Gd and Sm at 1200—1400 K. The free energy change of the $(1/2)Fe_2O_3+(1/2)Ln_2O_3 \rightarrow LnFeO_3$ reaction was calculated.

Since the pioneering work by Kiukkola and Wagner,[1] many studies have been carried out in an effort to obtain free energy data from the EMF of a solid electrolyte galvanic cell. The present investigation aims to obtain, by means of the EMF method, thermodynamic data relevant to the formation of orthoferrites, which have attracted much attention as magnetic materials.

Experimental

The orthoferrites were synthesized by a solid-state reaction of ferric oxide and rare earth sesquioxide. A pellet of a mixture of 99.99% pure Fe_2O_3 and Ln_2O_3 was fired at 1300 °C to form orthoferrite. The product was ground to powder and pressed to a pellet at 5 kg/cm^2. Then it was fired again at 1400 °C.

A high-temperature galvanic cell was constructed by using a stabilized zirconia tube as an electrolyte. The arrangement of the cell is shown in Fig. 1. The open end of the stabilized zirconia tube(e) was kept at room temperature and connected to a stainless steel head(h) with a O-ring vacuum seal fitting(g). A mixture of Ni and NiO powders was used as a reference electrode (b), which was placed inside the zirconia tube. The test electrode of mixed powders(a) was placed outside the electrolyte. O-ring vacuum seal fittings(g) were used to separate the gas atmospheres inside and outside the zirconia tube(e) and the quartz glass tube (c). After the cell was arranged as is shown in Fig. 1, the whole system was evacuated to 10^{-4}—10^{-5} Torr through Pyrex tubings(i,j). Then the cell was vacuum-sealed and disconnected from the evacuation system.

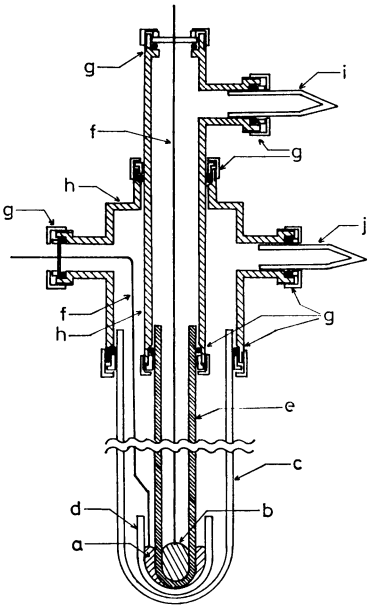

Fig. 1. Arrangement of cell.
a: test electrode powder, b: reference electrode powder, c: quartz glass tube, d: quartz glass container of test electrode powder, e: calcia-stabilized zirconia tube, f: platinum lead wire, g: O-ring vacuum seal fittings, h: stainless steel head, i: Pyrex tubing for an evacuation of reference electrode compartment, j: Pyrex tubing for an evacuation of test electrode compartment.

The cell was heated in a resistance furnace, controlled to ±0.5 °C. The cell temperatures were measured using a Pt/0.13Rh+Pt thermocouple. The EMF of the cell and that of the thermocouple were measured by using a Yokogawa high-precision potentiometer, Model 2722.

As a preliminary run, the EMF of the

$$Pt|Fe,\ FeO|ZrO_2\text{-}CaO|Ni,\ NiO|Pt \text{ cell} \qquad (I)$$

was measured. The observed values agreed within 0.5 mV with the reported ones.[2-5]

Results

The EMF of the

$$Pt|Fe,\ Ln_2O_3,\ LnFeO_3|ZrO_2\text{-}CaO|Ni,\ NiO|Pt \text{ cell} \qquad (II)$$
$$(Ln=Y,\ Gd \text{ and } Sm)$$

was reproducible at 1200—1400 K. The results are given in Fig. 2 and the first column of Table 1.

From the EMF data of the cell (II), the free energy change, ΔG°_1, of the reaction:

$$Fe + (3/2)NiO + (1/2)Ln_2O_3 \longrightarrow (3/2)Ni + LnFeO_3 \qquad (1)$$

was calculated. The results are shown in the second

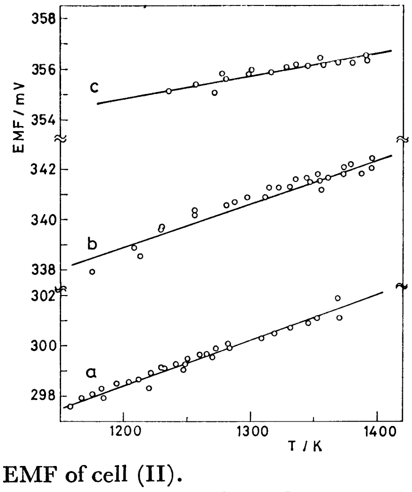

Fig. 2. EMF of cell (II).
a: $YFeO_3$, b: $GdFeO_3$, c: $SmFeO_3$.

Table 1. The EMF data and the derived Gibbs free energy changes

Ln	$\frac{\text{EMF}^{a)}}{\text{mV}}$	$\frac{\Delta G_1{}^{\circ b)}}{\text{cal}}$	$\frac{\Delta G_2{}^{\circ}}{\text{cal}}$
Y	$277.1+0.0178T$ (± 0.2)	$(-19170\pm 40)-(1.23\pm 0.04)T$	$-6250-0.31T$
Gd	$318.3+0.172T$ (± 0.4)	$(-22000\pm 70)-(1.19\pm 0.07)T$	$-9105-0.27T$
Sm	$344.1+0.0089T$ (± 0.4)	$(-23800\pm 140)-(0.61\pm 0.13)T$	$-10900+0.32T$

a) The values in parentheses are square roots of invariant variances. b) Uncertainties in $\Delta H_1{}^{\circ}$ and $\Delta S_1{}^{\circ}$ are the standard variations.

column of Table 1, where the constant term and the temperature coefficient correspond to $\Delta H^{\circ}{}_{1,\ 1300\text{K}}$ and $\Delta S^{\circ}{}_{1,\ 1300\text{K}}$ respectively. The standard deviations of these values were also calculated.

The oxygen partial pressure at the test electrode was the lowest for Reaction (1) of SmFeO_3. It was $10^{-17.5}$ atm at 1200 K and $10^{-13.6}$ atm at 1400 K. According to Tretyakov and Muan,[6] the electronic transport number of the calcia-stabilized zirconia electrolyte, t_e, is $10^{-4.5}$ at these temperatures and oxygen partial pressures. Etsell and Flengas[7] have reported that the t_e value is still as low as 10^{-3} at these oxygen partial pressures. Thus, the systematic error due to the electronic conduction is negligibly small.

The values of $\Delta G^{\circ}{}_2$, the free energy change of the reaction $(1/2)\text{Fe}_2\text{O}_3 + (1/2)\text{Ln}_2\text{O}_3 \longrightarrow \text{LnFeO}_3$ (2) were calculated from $\Delta G_1{}^{\circ}$. In this calculation, the equation reported by Charette and Flengas[2] was used for the free energy of the formation of NiO. An approximation was made in the calculation of the free energy of the formation of Fe_2O_3 by using this equation:

$$\begin{aligned}\Delta G^{\circ}_{\text{f.Fe}_2\text{O}_3\text{.1200--1400K}} &= \Delta H^{\circ}_{\text{f.1300K}} - T\cdot\Delta S^{\circ}_{\text{f.1300K}}\\ &= -193373 + 59.05T\ \text{(cal/mol)}\end{aligned}$$

The values of $\Delta H_f{}^{\circ}{}'_{1300\text{K}}$ and $\Delta S_f{}^{\circ}{}'_{1300\text{K}}$ were taken from the JANAF Thermochemical Tables.[8] The calculated values of $\Delta G_2{}^{\circ}$ are given in the third column of Table 1. As may easily be seen, the absolute values of $\Delta S^{\circ}{}_2$ are very small, as is to be expected from Neumann-Kopp's rule on the ΔC_p of a solid-state reaction.

References

1) K. Kiukkola and C. Wagner, *J. Electrochem. Soc.*, **104**, 308, 379 (1957).

2) G. G. Charette and S. N. Flengas, *ibid.*, **115**, 796 (1968).

3) B. C. H. Steel and C. B. Alcock, *Trans. Amer. Inst. Min. (Metall.) Engrs.*, **233**, 1359 (1965).

4) Ju. D. Tretyakov and H. Schmalzried, *Z. Elektrochem.*, **69**, 396 (1965).

5) J. Chipman, *Pure Appl. Chem.*, **5**, 669 (1962).

6) Ju. D. Tretyakov and A. Muan, *J. Electrochem. Soc.*, **116**, 331 (1969).

7) T. H. Etsell and S. N. Flengas, *ibid.*, **118**, 1980 (1971).

8) JANAF Thermochemical Tables, NSRDS-NBS 37, Office of Standard Reference Data, National Bureau of Standards, Washington, D. C. (1971).