Thermodynamic Study on the Systems of Metals and Their Oxides by EMF Measurements Using Solid Electrolyte

By

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Emf of the following galvanic cell employing solid electrolyte were measured at the temperature range of 700°～1100°C.

Pt/Ni · NiO/O^{--}/Air/Pt
Pt/Ni · NiO/O^{--}/Cu · Cu$_2$O/Pt
Pt/Ni · NiO/O^{--}/Co · CoO/Pt
Pt(Fe · FeO/O^{--}/Ni · NiO/Pt
Pt/Fe · Fe$_{1-x}$O/O^{--}/Fe$_{1-y}$O · Fe$_3$O$_4$/Pt
Pt/Ni · NiO/O^{--}/Fe$_3$O$_4$ · Fe$_2$O$_3$/Pt

From those results the equilibrium oxygen pressures of Ni·NiO, Cu·Cu$_2$O, Co·CoO, Fe·FeO, FeO·Fe$_3$O$_4$ and Fe$_3$O$_4$·Fe$_2$O$_3$, and the standard free energy of formation of NiO, Cu$_2$O, CoO, FeO, FeO·Fe$_3$O$_3$ and Fe$_2$O$_3$ were estimated.

Based on these experimental results it is shown that

1) stabilized zirconia and thoria could be used as a solid electrolyte under the conditions of 700°～1100°C and partial pressure of oxygen between 1 atm. and 10^{-20} atm., and a little impurity in electrolyte did not have an unfavorable effect on the determination of equilibrium partial oxygen pressure of metal-metallic oxide systems

2) alumina and magnesia could not be used as a solid electrolyte of the present emf measurements

3) one might conclude that emf measurements using a solid electrolyte could obtain the same thermodynamic values as the other reliable equilibrium methods.

1. Introduction

Such solid electrolytes as zirconia doped with calcia were first used by Kiukkola and Wagner1) in galvanic cells for the determination of standard free energy of formation of some metallic oxides at high temperatures.

After that, various oxides and their solid solutions exhibiting oxygen ionic conductivity at high temperatures have been used for the determination of

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thermodynamic quantities of metal-oxygen systems and their physical properties have been studied with considerable accuracy by many investigators[2)~5)].

The purpose of this work is to determine the equilibrium oxygen potentials of various metal-metallic oxides and standard free energy of those metallic oxides.

In addition to the results of this work the influence of such experimental conditions as the kinds of solid electrolytes and cell atmosphere on the emf values have been discussed.

2. Experimental Principle

2.1 The emf of oxygen concentration cell

$Pt/O_2(\mu'_{O_2})/O^{--}$ (solid electrolyte)$/O_2(\mu''_{O_2})/Pt$ (I)

According to Wagner[6)], the emf of the cell (I) is related to the transport number of oxygen ion

$$E = \frac{1}{4\mathbf{F}} \int_{\mu''_{O_2}}^{\mu''_{O_2}} t_{ion}\, d\mu_{O_2} \qquad (1)$$

where E; emf of the cell (I)

t_{ion}; transport member of oxygen ion in the solid electrolyte

μ'_{O_2}, μ_{O_2}''; the oxygen chemical potential of each half-cell

F ; the Faraday constant

Since the transport number of oxygen ions in solid electrolytes, such as stabilized zirconia and thoria, can be taken as almost unity[2)~3)], the integration of equation (1) gives

$$E = (\mu_{O_2}'' - \mu'_{O_2})/4\mathbf{F} \qquad (2)$$

Noting that

$$\mu_{O_2} = \mu^0_{O_2} + RT\, l_n\, P_{O_2}$$

where $\mu^0_{O_2}$ is standard chemical potential of oxygen, R the gas constant, T the absolute temperature and P_{O_2} is the partial oxygen pressure, the electromotive force is given by

$$E = RT(P_{O_2}''/P'_{O_2})/4\mathbf{F} \qquad (3)$$

According to equation (3), the partial oxygen pressure of one half-cell could be calculated from the partial oxygen pressure of the standard electrode and the emf of the cell (I)

2·2 Measurement of equilibrium partial oxygen pressure of binary metal-metallic oxide system

If a metal A is in equlibrium with its oxide AO at a constant temperature, the equilibrium partial oxygen pressure must be constant. Using this value, the standard free energy of the formation of metallic oxide (2AO) could be estimated by equation (4)

$$\varDelta F^0_{2AO} = RT \ln P_{O_2} \qquad (4)$$

If E is the emf of cell (II), the relation of standard free energy of formation of AO and BO is shown by equation (5)

$$\mathrm{Pt/A \cdot AO/O^{--}/B \cdot BO/Pt} \quad \text{cell (II)}$$

$$\varDelta F^0_{2AO} = \varDelta F^0_{2BO} - 4EF \qquad (5)$$

According to equation (5), standard free energy of formation of any metallic oxide AO could be estimated from the emf of cell (II) and the known standard free energy of formation of one metallic oxide BO.

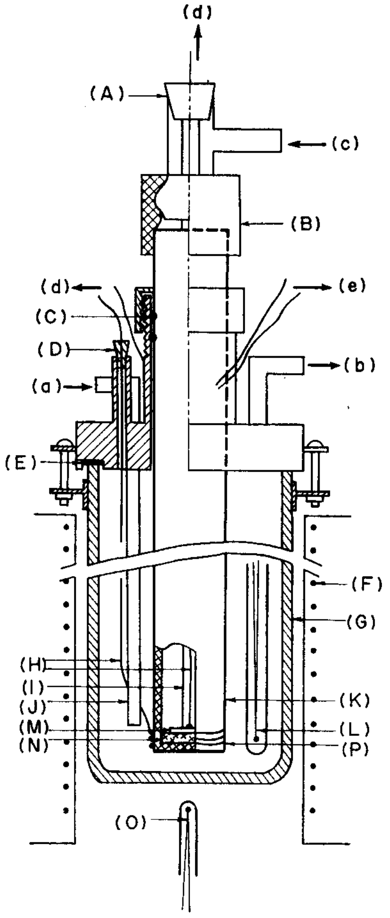
3. Experimental Method

Stabilized zirconia doped with CaO, alumina, magnesia and stabilized thoria doped with Y_2O_3 were used as a solid electrolyte in order to compare the emf values obtained by using those solid electrolytes. Stabilized zirconia were two kinds of high pure and commercial grade and the other materials were commercial pure grade. High pure stabilized zirconia was made of ZrO_2 (99.9%) and CaO (99.9%). The tablets (10 mmϕ × 1.5 mm) consisted of stabilized thoria manufactured by Toda-Chotaikabutsu Co. Ltd. and the other tablets by Nihonkagakutogyo Co. Ltd.

The metal-metallic oxide tablets used as half-cell were prepared by mixing metals and oxides powders, pressing into tablets of 10 mmϕ × 1.5 mm at 4 ton/cm², being envelopped in the silica tube in vacuum, sintering at 1000°C for 10 hours except for 72 hours in the case of Co-CoO and then being quenched in water.

These mixtures consisted of nearly equal weights of metals and oxides, and these starting materials were the powders of chemical reagent grade but the wüstite and hematite were prepared by respective decomposition of ferrous oxalate in vacuum and ferric nitrate in air at 900°C. The $FeO \cdot Fe_3O_4$ and $Fe_3O_4 \cdot Fe_2O_3$ half cell were prepared from chemical reagent grade iron powder and the above hematite.

The cell designs used for emf measurements are shown in Fig. (1) and Fig. (2).



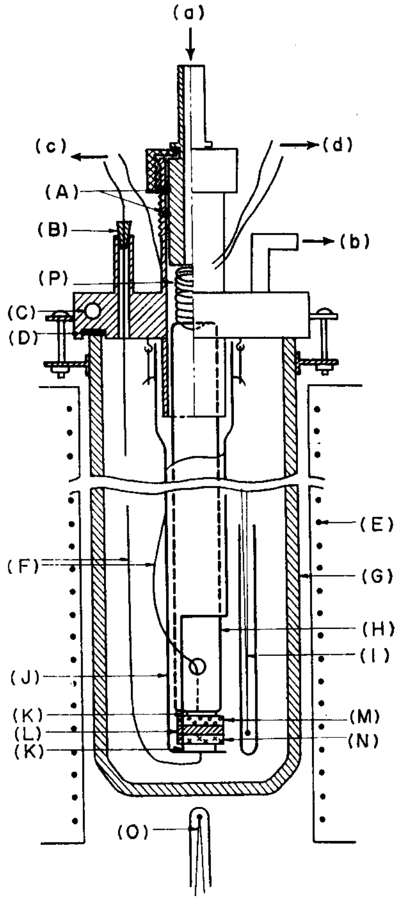
A)	Silicon Rubber Plug
B)	Rubber Tube
C)	O-ring Seal
D)	Silicon Rubber Plug
E)	Rubber Pucking
F)	Ni-Cr Resistance Furnace
G)	Quzrtz Reaction Tube
H)	Platinum Leads
I)	Quartz Tube
J)	Air Guiding Quartz Tube
K)	Stabilized Zirconia Tube
L)	Thermocuple for Specimen
M)	Platinum Disk
N)	Specimen
O)	Thermocuple for Temperature Controller
P)	Platinum Lead for Gas Electrode
(a)	Inlet for Air
(b)	Outlet for Air
(c)	Inlet for Argon
(d)	To Potentiometer
(e)	To Pyrometer

Fig. 1. Shematic diagram of cell assembly

Fig. (1) shows the cells containing a gaseous reference halfcell in which the platinum wire was connected with the outside of the zirconia tube exposed to air flow and the other half-cell was the disk placed in the bottom of the zirconia tube which was connected with a platinum plate and pressed by quartz push rod to ensure good contact with the surface of solid electrolyte.

The cell consisted of both solid half-cell as shown in Fig. (2) and a couple of specimen, zirconia tablet and Ni–NiO reference electrode, was placed between the two platinum disks connected to platinum leads, and those kept good contact by a spring.

Nichrome resistance furnace was utilized for heating and its temperature was



A)	O-ring Seal
B)	Silicon Rubber Plug
C)	Water Path
D)	Rubber Packing
E)	Ni-Cr Resistance Furnace
F)	Platinum Leads
G)	Quartz Reaction Tube
H)	Quartz Tube
I)	Thermocuple for Specimen
J)	Specimen Holder
K)	Platinum Disk
L)	Solid Electrolyte
M)	Standard Electrode
N)	Specimen
O)	Thermocuple for Temperature Controller
(a)	Inlet for Argon
(b)	Outlet for Argon
(c)	To Potentiometer
(d)	To Pyrometer

Fig. 2. Shematic diagram of cell assembly

controlled automatically in the range of ±1°C. The emf measurements were carried out at the temperature range of 700°~1100°C in a stream of purified argon gas and the emf values were read with an accuracy of ± 0.1 mV by the precision potentiometer.

After the entire cell was assembled, the system was first evacuated at about 200°C in order to dehydrate, purified argon gas was introduced in it and then the cell was heated up to the desired temperature. The first emf was measured after maintaining the cell at a constant temperature for about 3 hours. The temperature was alternately increased and decreased and the emf was measured at each new temperature.

4. Experimental Results and Discussions

In a series of preliminary experiments, it was found that the high pressure of disk-making and the longer sintering time needed the short time for the obtainment of the equlibrium emf. On the other hand, the samples made by low sintering pressure and short sintering time were influenced sensibly by surrounding atmosphere, which resulted in the instability of emf measurements.

And it was also confirmed that the emf of cell constructed with the same half-cell was nearly zero.

The emf measurements of the following cells (A)~(C) were carried out in the temperature range 700°~1100°C and results were shown in Fig (3) ~(5)

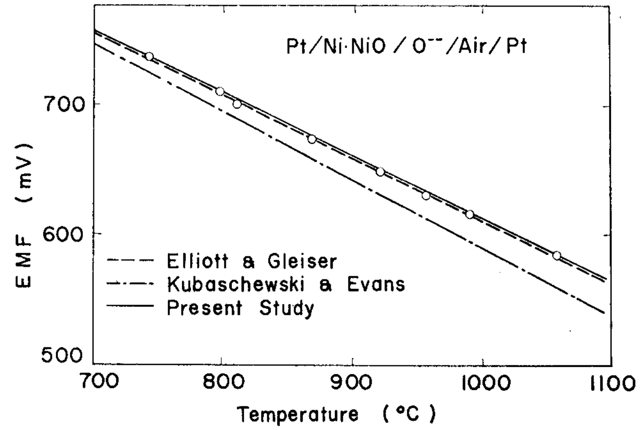


Fig. 3. Temperature dependence of emf for the cell (A)
$E = -0.489T + 1240$
T; absolute temperature
E; mV

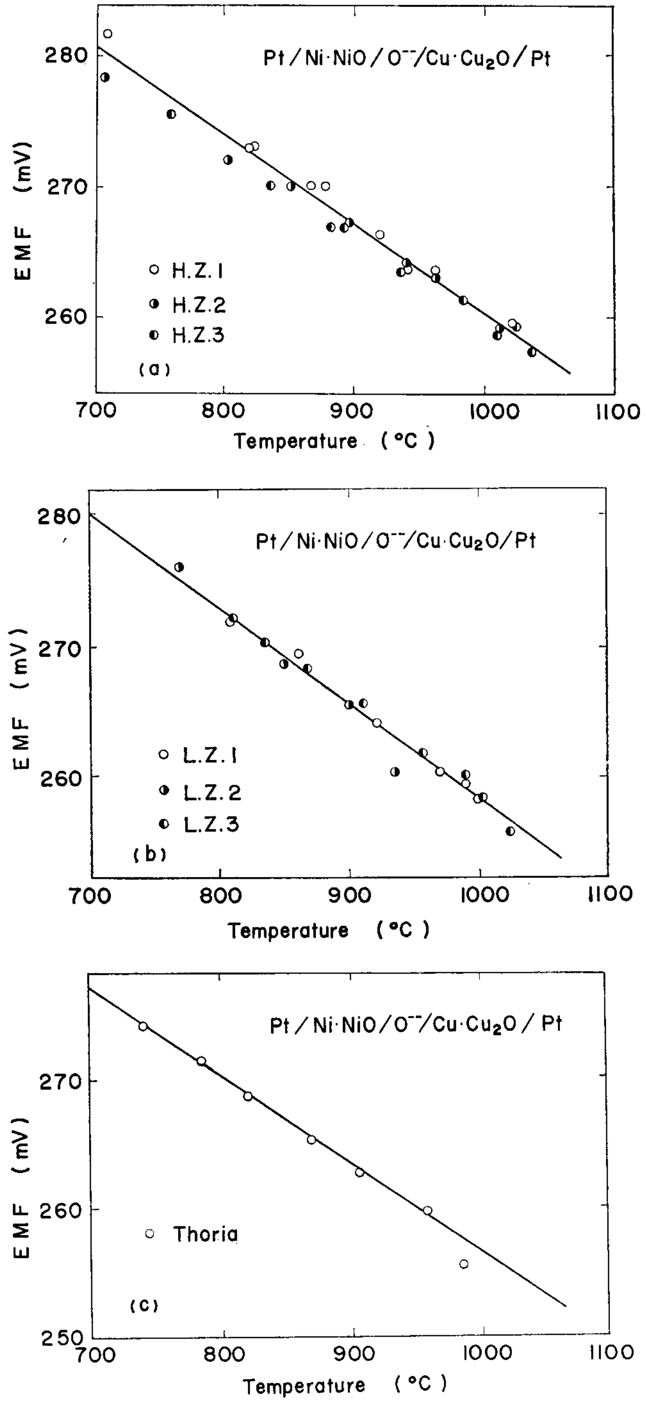
$Pt/Ni\cdot NiO/O^{--}/Air/Pt$ (A)

$Pt/Ni\cdot NiO/O^{--}/Cu\cdot Cu_2O/Pt$ (B)

$Pt/Ni\cdot NiO/O^{--}/Co\cdot CoO/Pt$ (C)

From these figures it was found that the emf plots against temperature were nearly linear. This linear relation indicates that the same emf could be observed when a particular temperature was attained from higher or lower temperature and the emf ought hardly to vary during several hours.

It could be regarded as one evidence for cell reversiblity, that is, the effect of irreversible pheomena such as contamination could be considered to be negligible.



a) measured by using high pure zirconia
$E=-6.90\times10^{-2}T+348$
H.Z. 1, 2, 3,; high pure zirconia

b) measured by using less pure zirconia
$E=-7.20\times10^{-22}T+350$
L.Z. 1, 2, 3,; less pure zirconia

c) measured by using thoria
$E=-6.85\times10^{-2}T+344$

Fig. 4. Temperature dependence of emf for the cell (B)

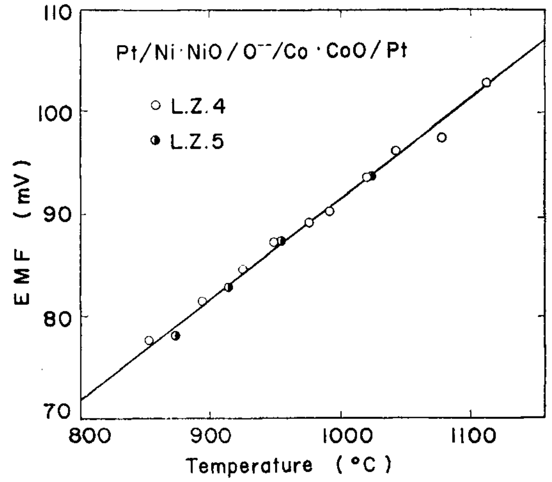


Fig. 5. Temperature dependence of emf for the cell (C)
$E = 8.87 \times 10^{-2}T - 22.2$
L.Z. 4, 5; less pure zirconia

The equlibrium oxygen pressures of Ni•NiO, Cu•Cu_2O and Co•CoO were calculated from the following equation (6) using the present emf measurements. These results were shown in Fig(6)~(8)

$$\log P_{O_2} = \log 0.21 - 4EF/2.303\ RT \qquad (6)$$

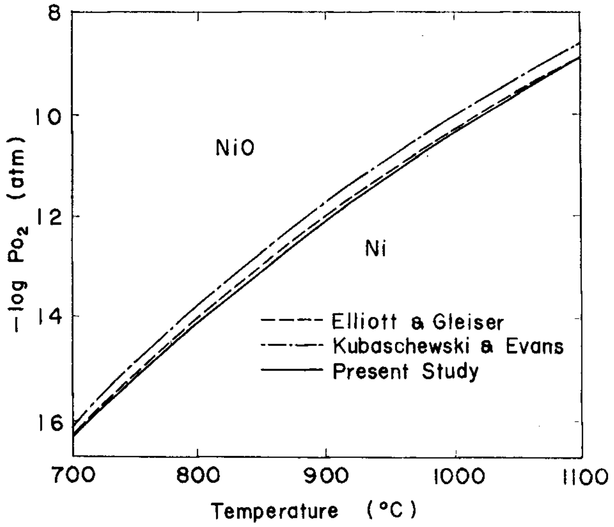


Fig. 6. Temperature dependence of the equilibrium partial oxygen pressure of Nickel-Nickeloxide mixture

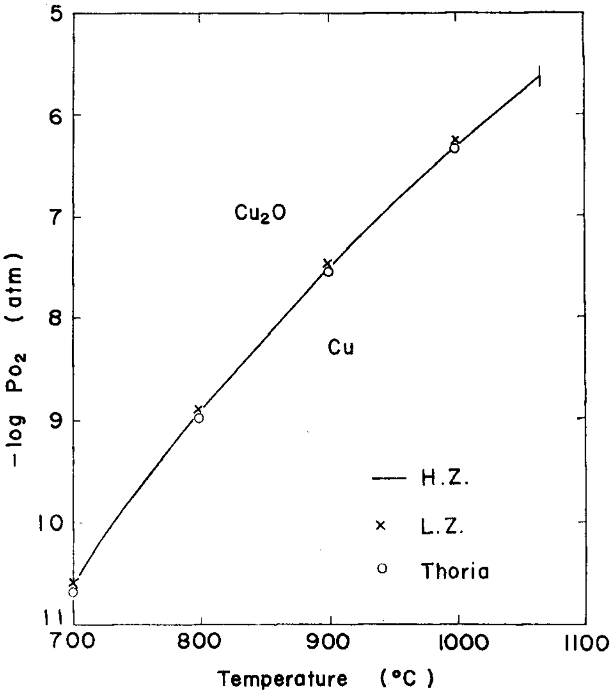


Fig. 7. Temperature dependence of the equilibrium partial oxygen pressure of Copper-Cuprous oxide mixture
H.Z.; high pure zirconia
L.Z.; less pure zirconia

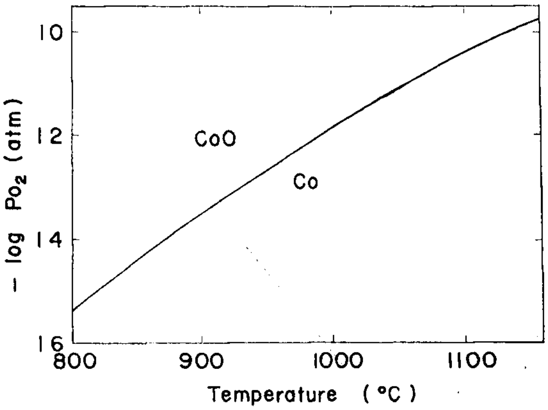


Fig. 8. Temperature dependence of equilibrium partial oxygen pressure of Cobalt-Cobalt Oxide mixture

The solid electrolyte used for the cells (A) and (C) was commercial stabilized zirconia, but several solid electrolytes such as high purity stabilized zirconia, commercial pure stabilized thoria, alumina and magnesia were also used in cell (B) in order to compare their emf values.

From these experiments it was found that alumina and magnesia could not be used as an electrolyte in these experimental conditions and the discrepancy of emf in the case of the other three different kinds of electrolytes was not observed beyond experimental error.

For the Fe-O system, the emf measurements were carried out on the three following cells (D)~(F) and these results were shown in Fig. (9)~(11). In the

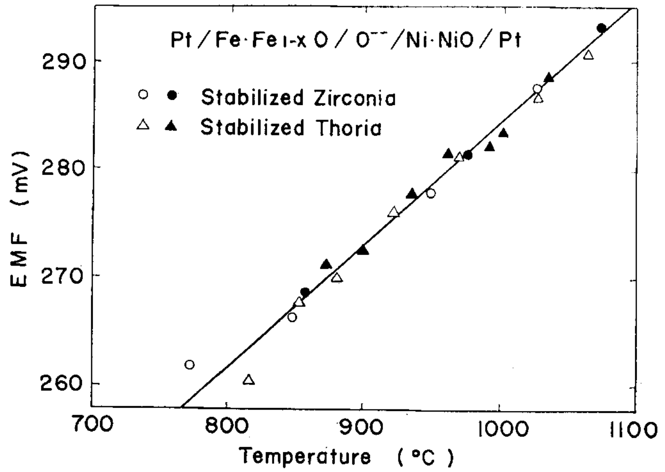


Fig. 9. Temperature dependence of emf for the cell (D)
$E=1.12\times10^{-1}T+141$

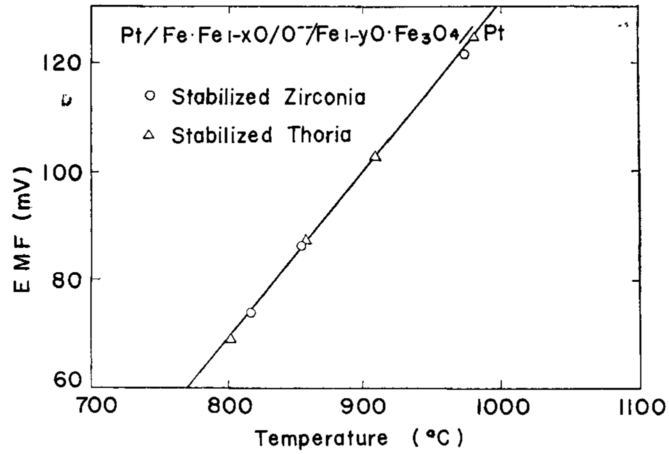


Fig. 10. Temperature dependence of emf for the cell (E)
$E=3.11\times10^{-1}T-264$

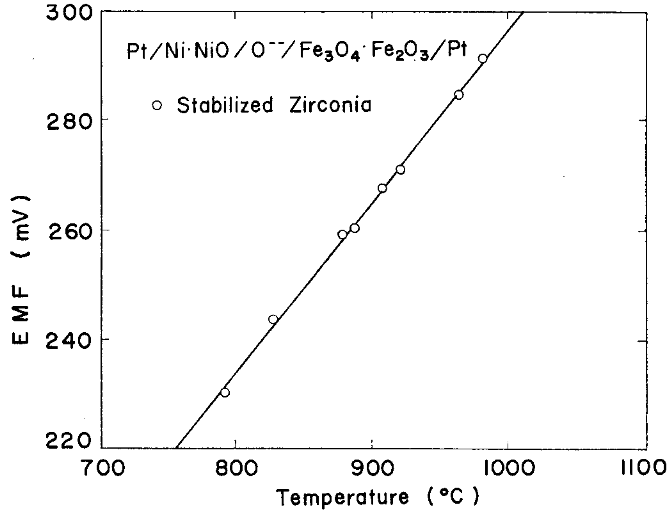


Fig. 11. Temperature dependence of emf for the cell (F) $E=3.19\times10^{-1}T-108.7$

case of cells (D) and (E), both commercial stabilized thoria and commercial stabilized zirconia were used as solid electrolyte. From the results of Fig(9) and (10), the difference in emf values could not be observed in those two kinds of solid electrolytes under these experimental conditions.

$$\mathrm{Pt/Fe\cdot Fe_{1-x}O/O^{--}/Ni\cdot NiO/Pt} \qquad \text{(D)}$$

$$\mathrm{Pt/Fe\cdot Fe_{1-x}O/O^{--}/Fe_{1-y}\cdot Fe_3O_4/Pt} \qquad \text{(E)}$$

$$\mathrm{Pt/Ni\cdot NiO/O^{--}/Fe_3O_4\cdot Fe_2O_3/Pt} \qquad \text{(F)}$$

Based on these emf values, the equilibrium oxygen pressures for the following reactions (7) (10) were calculated

$$2\mathrm{Fe}+\mathrm{O_2} = 2\mathrm{FeO} \qquad (7)$$

$$6\mathrm{FeO}+\mathrm{O_2} = 2\mathrm{Fe_3O_4} \qquad (8)$$

$$4\mathrm{Fe_3O_4}+\mathrm{O_2} = 6\mathrm{Fe_2O_3} \qquad (9)$$

From these equilibrium oxygen pressures the oxygen pressure (P_{O_2})-temperature (T) diagram of Fe-O system was made as shown in Fig. (12).

The standard free energies of reactions (7)~(12) were estimated based on previous results and listed in the equation (13)~(18) and shown as a function of temperature in Fig. (13) with the data of other investigators[7)][8)].

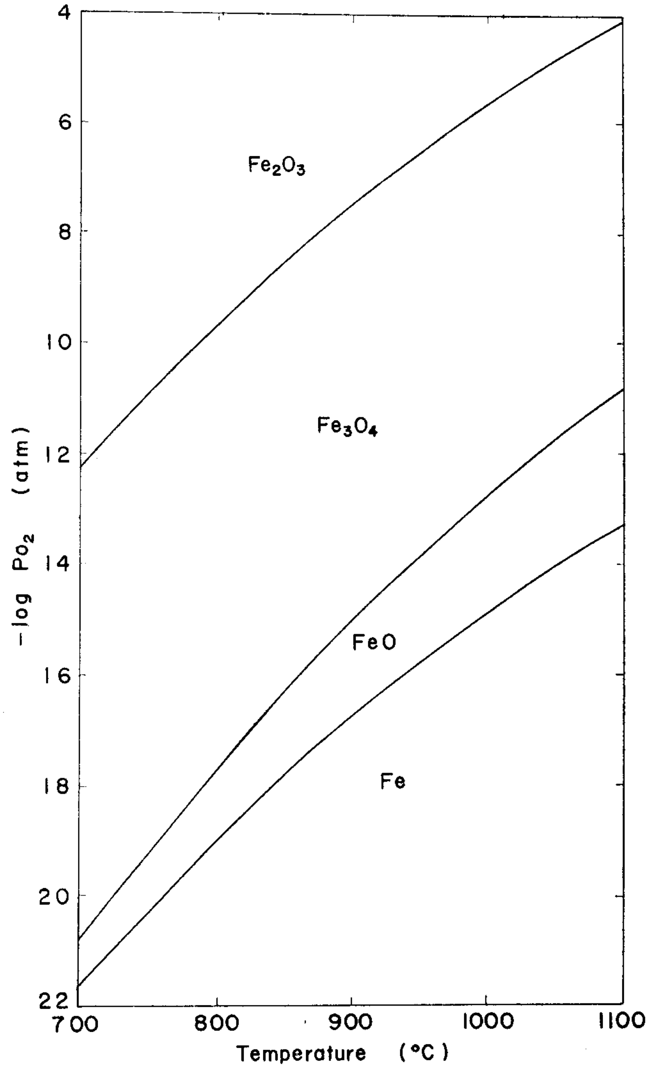


Fig. 12. Temperature dependence of the equilibrium partial oxygen pressures of iron-wüstite mixture, wüstite-magnetite mixture and magnetite-hematite mixture

$$2Ni+O_2 = 2NiO \tag{10}$$

$$4Cu+O_2 = 2Cu_2O \tag{11}$$

$$2Co+O_2 = 2CoO \tag{12}$$

$$\Delta F^0_{NiO} = 42.01T-114,000 \tag{13}$$

$$\Delta F^0_{Cu_2O} = 35.37T- 81,700 \tag{14}$$

$$\Delta F^{o}_{CoO} = 33.83T - 112{,}000 \tag{15}$$

$$\Delta F^{0}_{FeO} = 31.68T - 127{,}100 \tag{16}$$

$$\Delta F^{0}_{Fe_3O_4} = 60.37T - 151{,}400 \tag{17}$$

$$\Delta F^{0}_{Fe_2O_3} = 71.40T - 124{,}000 \tag{18}$$

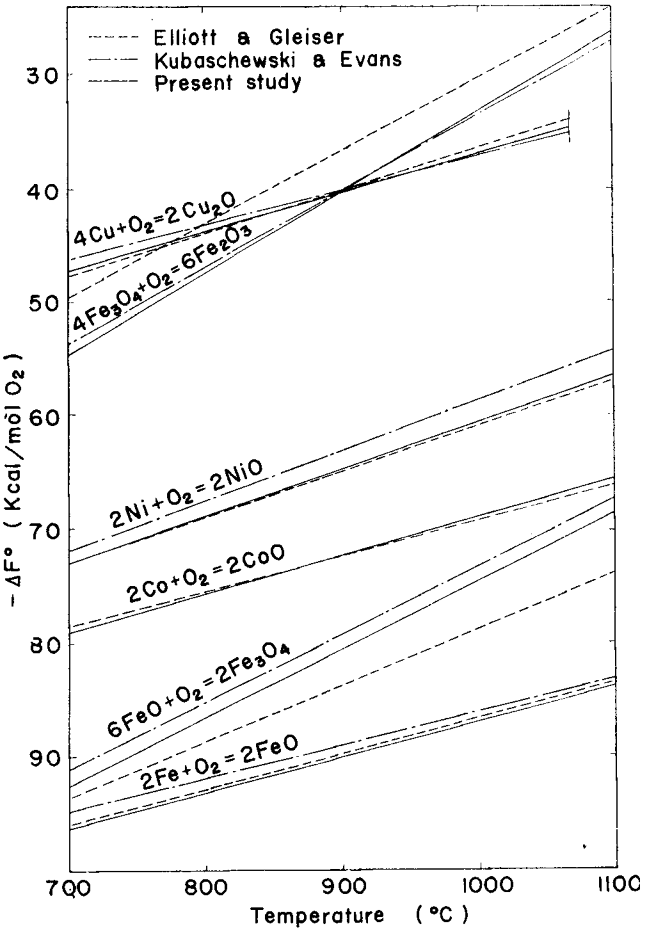


Fig. 13. The standard free energy of formation of oxide

where ΔF^{0}_{MxOy} is standard free energy of formation of M_xO_y in cal/mole of O_2 and T is temperature in °K. From Fig. (13) the present values were found to be a good agreement with the values by Elliott et al.

In order to compare this electrochemical method with the other gas equilibrium methods for estimation of thermodynamic quantities of metal-metallic oxide systems, the present emf values were shown in Fig (14) with the emf values by several investigators[1)9)~11)] and these calculated from the standard free energy of formation by the other methods[7)12)] in the case of Cu•Cu_2O system.

From these results it was found that discrepancies of emf by using the different kinds of solid electrolytes were in the range of about ±3 mV and it must be regarded as very small. The values obtained by the other methods were found to be considerably different from the values by emf methods, but noting that an uncertainty of 1 Kcal in free energy corresponds to 10.8 mV in emf values, these difference would not be regarded as so large. One might conclude that the electrochemical method

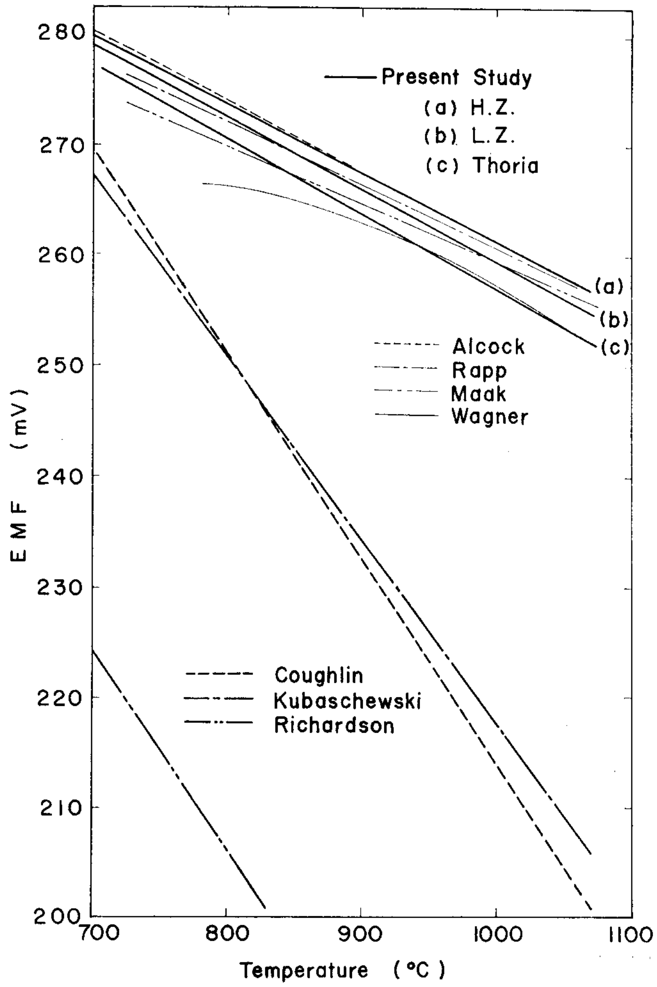


Fig. 14. Comparison of directly measured emf with other data calculated in emf
H.Z.; high pure zirconia
L.Z.; less pure zirconia

using solid electrolyte could be available for the determination of thermodynamic quantities.

5. Conclusion

The equilibrium oxygen pressures of metal-metallic oxide systems such as Ni•NiO, Cu•Cu_2O, Co•CoO, Fe•FeO, FeO•Fe_3O_4 and Fe_3O_4•Fe_2O_3 were determined by means of emf measurements employing solid electrolyte at the temperature range of 700°~1100°C.

From these results the standard free energy of formation of NiO, Cu_2O, FeO, Fe_3O_4 and Fe_2O_3 were given as function of temperature.

Based on the present experiments it was found that the transport numbers of oxygen ion in stabilized zirconia and thoria were nearly unity at the temperature range of 700°~1100°C and the oxygen pressure range of $1 \sim 10^{-20}$ atm. and the small content of impurity in the solid electrolyte had not undesirable influence in emf measurements. On the other hand Al_2O_3 and MgO could not be available as a solid electrolyte in this study.

One might conclude that emf measurement using solid electrolyte is a good method for the determination of the thermodynamic quantities of metal-oxygen system at high temperatures.

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