The Application of Oxygen Concentration Cells with the Solid Electrolyte, $\text{ZrO}_2\cdot\text{CaO}$ to Basic Research Works in Iron and Steel Making*

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Synopsis

Concerning the application of oxygen concentration cells with the electrolyte, $\text{ZrO}_2\cdot\text{CaO}$, which provides a pure anion conduction due to the migration of oxygen defects, to the basic research works of process metallurgy, the following four experimental works have been introduced in this report:

(1) The standard free energies of formation of FeO , Fe_3O_4 , SnO , PbO , Cu_2O , CuO and Ta_2O_5 have been measured at 500° to $1,300^\circ\text{C}$ and expressed by the functions of temperature with the comparison with the data in literatures¹⁾.

(2) The oxygen pressure in liquid $\text{PbO}\text{-SiO}_2$ solution has been measured at 800° , 900° , $1,000^\circ$ and $1,100^\circ\text{C}$, being equilibrated with liquid lead. The chemical activities of PbO and SiO_2 , and the other thermodynamical properties of $\text{PbO}\text{-SiO}_2$ solution have been obtained²⁾.

(3) K. Gotō and G. R. St. Pierre³⁾ have measured the chemical activity of tin in liquid $\text{Pb}\text{-Sn}$ binary solution at 700° , 800° , and 900°C . The thermodynamical properties of $\text{Pb}\text{-Sn}$ alloys were also calculated.

(4) Also, K. Gotō and G. R. St. Pierre⁴⁾ have developed an oxygen gauge to measure the partial pressure of oxygen in the high temperature gases in the range of $\text{PO}_2=10^{-1}\sim 10^{-20}$ atm. and $500^\circ\sim 1,300^\circ\text{C}$. The self-consistent and reproducible EMF against the gas compositions of $\text{CO}\text{-CO}_2$ or $\text{Ar}\text{-O}_2$ gas mixtures have been obtained with the several reference electrodes. The reversibility of the EMF against the changes of the atmosphere, temperature and the externally applied potential, was carefully examined.

In addition, the other possibilities for applying oxygen concentration cells to the basic study of process metallurgy have been suggested and industrial application has also been discussed.

I. Introduction and Principle of Experiments

Iron is commonly associated with oxygen in ores. Although the naturally occurring minerals are often very complex, the chemistry of metallic oxides is of great importance in the study of iron and steel manufacturing. In most metallurgical processes, the reduction of metallic oxides and the control of oxygen partial pressure are of paramount consideration. When complex oxide systems are subjected to low oxygen partial pressure at elevated temperature, two immiscible liquid phases generally are formed. One phase, often designated as the slag, consists of a solution of highly stable metal oxides, while the other is a metallic solution formed from the metals with less stable oxides.

From this sample description of a broad class of metallurgical processes, it is clear that a thorough knowledge of the chemical stabilities of metallic oxides and the chemical potentials within metallic solutions and slags relating to the partial pressure of oxygen is essential to metallurgists.

From the above viewpoint, the oxygen concentra-

tion cells with solid electrolyte, $\text{ZrO}_2\cdot\text{CaO}$ have been extensively studied at high temperature to apply this rather new method to the study of metal-oxygen systems.

In this respect, four main experimental works will be introduced to a limited extent, namely (1) the standard free energies of formation of FeO , Fe_3O_4 , Cu_2O , CuO , SnO , PbO and Ta_2O_5 ,¹⁾ (2) oxygen pressure in liquid $\text{PbO}\text{-SiO}_2$ system and the thermodynamic properties of the system,²⁾ (3) the chemical activities in liquid $\text{Pb}\text{-Sn}$ system³⁾ and (4) direct measurement of oxygen pressures in high temperature gases.⁴⁾ The last two works had been carried out by one of the present authors in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the graduate school of the Ohio State University under the supervision of Dr. George Rolland St. Pierre.

An oxygen concentration cell consists of two electrodes separated by an electrolyte through which the transference of electrical charge is accomplished by the migration of oxygen ions. Schematically, the cell can be shown as follows:

The electron flowing through the circuit is matched by O^{2-} migration.

It has been known⁵⁾⁻⁹⁾ that the $\text{ZrO}_2\cdot\text{CaO}$ solid electrolyte provides pure oxygen anion conduction due to oxygen vacancies at high temperatures. Thus, the study of the oxygen concentration cells with this electrolyte may have great significance in metallurgical research at high temperature (above 500°C). The experimental principles of the four works are as follows.

1. Measurement of the Standard Free Energies of Formation of Various Metal Oxides at Elevated Temperature from the Standard Free Energies of the Reactions between the Metal and the Oxide of a Different Metal

This method was used by Kiukkola and Wagner⁸⁾ using the following type of cell:

In the case that all substances are immiscible and

* This article is in reference to the lectures delivered before the 65th, 66th and 67th Grand Lecture Meetings of The Iron & Steel Institute of Japan held in April 1963 in Tokyo, October 1963 in Nagoya and April 1964 in Tokyo, respectively. Japanese texts were separately received on April 25, April 26, November 7, 1963 and December 1, 1964; and printed respectively in *Tetsu-to-Hagané* (Journal, Iron & Steel Institute, Japan), **49** (1963), 12, 1760-1765; 13, 1873-1879; **50** (1964), 8, 1167-1175 and **50** (1964), 3, 470-473.

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both the thermal and chemical equilibria are attained at both electrodes, the EMF is simply determined by the equation:

$$\Delta F^\circ = -nE\mathcal{F} \dots\dots\dots (1)$$

where ΔF° is the difference between the standard free energies of formation of both the metal oxides, n is valance of oxygen, E is the reversible electro-motive force, and $\mathcal{F}$ is Faraday's constant.

$$\text{At Electrode I, } M_A + \frac{1}{2}O_2 = M_AO \quad \Delta F_A^\circ \dots\dots (2)$$

$$\text{At Electrode II, } M_B + \frac{1}{2}O_2 = M_BO \quad \Delta F_B^\circ \dots\dots (3)$$

$$(2)-(3), \quad M_A + M_BO = M_B + M_AO \quad \Delta F^\circ \dots (4)$$

Thus, if ΔF_A° is known, ΔF_B° can be calculated from the measured EMF according to the equation (4).

In the present work, the mixture of pure nickel powder and nickel oxide (NiO) powder was used as the standard electrodes for the following reasons.

(a) The standard free energy of formation of NiO is accurately given in the compilation by Elliott and Gleiser¹⁰⁾.

(b) The observed EMF with the Ni-NiO electrode against CO-CO₂ gas mixtures agreed very well with the calculated EMF¹¹⁾.

(c) The mutual solubility of NiO or Ni with the ZrO₂-CaO electrolyte is negligibly small.

(d) The melting points of Ni and NiO are high.

(e) The life time of the standard electrode Ni+NiO was long and the Ni+NiO combination provided very stable and constant oxygen pressure in the temperature range of 500°~1,430°C.

2. The Oxygen Pressure in Liquid Oxide Slags and the Chemical Activities of the Components

The following Galvanic cell is used to measure the oxygen pressure in liquid slags and the chemical activities of the components.

An expression for the EMF can be obtained as follows from the consideration of the equilibrium existing within each electrode.

$$EMF = \frac{RT}{2\mathcal{F}} \log \frac{P_{O_2}^\dagger(\text{Standard electrode})}{P_{O_2}^\dagger(\text{Slag+metal phase})} \dots (5)$$

Within the standard electrode, the equilibrium oxygen

pressure is uniquely determined at the constant temperature, if the metal, M_A and metal oxide, M_AO are co-existent as pure components, that is:

$$M_A + \frac{1}{2}O_2 = M_AO$$

$$\Delta F_f^\circ = -RT \log \frac{a_{M_AO}}{a_{M_A} \cdot P_{O_2}^\dagger} = RT \log P_{O_2}^\dagger \dots\dots\dots (6)$$

$$\text{If } a_{M_AO} = a_{M_A} = 1$$

On the other hand, the equilibrium oxygen pressure within the (slag+metal electrode) is determined by the following reaction equilibrium:

$$M_B + \frac{1}{2}O_2 = M_BO \text{ (in slag)} \dots\dots\dots (7)$$

$$\Delta F^\circ = -RT \ln \frac{a_{M_BO}}{P_{O_2}^\dagger} \dots\dots\dots (8)$$

This ΔF° of the equation (8) is equal to the standard free energy of M_BO formation.

Thus, $P_{O_2}^\dagger$ in the equation (5) is given by measuring the EMF and temperature, provided that the oxygen pressure in the standard electrode is known.

Furthermore, if the standard free energy of M_BO formation has been measured, one can calculate the chemical activity of M_BO in liquid M_BO - M_CO solution, using the equation (8). In the present work, the standard free energy of PbO had been measured, and then the oxygen pressure in liquid PbO-SiO₂ solution equilibrated with Pb was measured. The activity of PbO was calculated by the above procedure. Also, one can obtain the thermodynamical properties by Gibbs-Duhem relation and other thermodynamic formula.

3. Oxygen Pressure in Solid or Liquid Alloys and the Chemical Activity of the Components in Alloys

To measure the oxygen pressure in solid or liquid alloys, the following Galvanic cell is conceivable.

An expression for the EMF of the above cell can be given as follows from the consideration of the equilibrium existing within each electrode.

$$EMF = -\frac{RT}{n\mathcal{F}} \ln \frac{P_{O_2}^\dagger(\text{Electrode I})}{P_{O_2}^\dagger(\text{Electrode II})} \dots\dots (9)$$

If the combination of $M_A + M_AO$ is used as the standard electrode in the above cell, the EMF can be simply given as follows:

$$EMF = -\frac{RT}{nF} \ln a_{MA} \dots\dots\dots (10)$$

The thermodynamical formulation is exactly the same as that of the oxide slag systems.

Gotô and St. Pierre measured the chemical activity of Sn in liquid Sn-Pb solutions³⁾, using this principle.

4. Partial Pressure of Oxygen in High Temperature Gases

One can conceive the following cell to measure the partial pressure of oxygen in the range of 10⁻¹~10⁻³⁰ atm. and of 500°~1,400°C.

Provided that the equilibrium oxygen pressure in the standard electrode is known, the partial pressure of oxygen around the gas electrode is determined by the measurement of EMF and temperature, according to the equation (9).

Gotô and St. Pierre⁴⁾ successfully obtained the calibration curves of the EMF and the gas composition of CO-CO₂ gas mixture or Ar-O₂ gas mixtures in the range of P_{O_2} =10⁻¹~10⁻²⁰ atm. and of 500°~1,300°C, using the combinations of Fe+FeO, Cu+Cu₂O, and Ni+NiO as the standard electrode.

This type of “oxygen gauge” has been used to measure the oxidation and reduction rates of iron and iron oxides through CO-CO₂ gas mixture by Matsushita and Gotô¹¹⁾ and the applicability of the oxygen gauge to the continuous measurement of P_{O_2} in the waste gas of an open hearth furnace is under investigation by Matsushita et al.¹²⁾

II. Experimental Apparatus and Procedure

The experimental apparatus for the study of oxygen concentration cell is composed of (1) gas cleaning and flow-rate controlling systems for CO, CO₂, Ar, and O₂ gases, (2) the reaction chambers and heating furnaces with the heating elements of platinum ribbon, nichrom wires, silicon carbide, or Globar heating elements, (3) various types of the oxygen concentration cells, and (4) the potentiometer with the external Galvanometer. Photo 1 shows the gas trains for carbon monoxide, carbon dioxide, and argon.

Commercial carbon monoxide was cleaned through concentrated H₂SO₄, platinum asbestos, soda lime, CaCl₂, and P₂O₅. Carbon dioxide was cleaned through concentrated H₂SO₄, CaCl₂, and P₂O₅ and argon was cleaned through copper and titanium chips held at 700°~800°C, concentrated H₂SO₄, CaCl₂, and P₂O₅.

The flow rates of all these three gases were regulated

Photo 1. An experimental apparatus

Fig. 1. Schematic diagram of gas trains

by capillary flow meters and bubbling bleeders, and then mixed with a gas mixer. The schematic diagram of the gas trains is shown by Fig. 1.

The oxygen concentration cells used for the measurement of the standard free energy of metal oxide formation are as follows:

- (1) Pt·Ni·NiO | ZrO₂·CaO | Pb·PbO·Pt
- (2) Pt·Ni·NiO | ZrO₂·CaO | Sn·SnO·Pt
- (3) Pt·Ni·NiO | ZrO₂·CaO | Fe·FeO·Pt
- (4) Pt·Ni·NiO | ZrO₂·CaO | FeO·Fe₃O₄·Pt
- (5) Pt·Ni·NiO | ZrO₂·CaO | Cu·Cu₂O·Pt
- (6) Pt·Ni·NiO | ZrO₂·CaO | CuO·Cu₂O·Pt
- (7) Pt·Ni·NiO | ZrO₂·CaO | Ta·Ta₂O₅·Pt
- (8) Ni·Pt(I)·NiO | ZrO₂·CaO | Mo(O)·Pt(II) | ZrO₂·CaO | Mn·Pt(III)·MnO | ZrO₂·CaO | FeO·Pt(IV)·Fe₃O₄
(This cell is with four electrodes.)
- (9) Ni·Pt(I)·NiO | ZrO₂·CaO | Mn·Pt(II)·MnO | ZrO₂·CaO | Fe·Pt(III)·FeO | ZrO₂·CaO | Cu·Pt(IV)·Cu₂O
(This cell is also with four electrodes.)

The oxygen concentration cell used for the measurement of the oxygen pressure in liquid PbO-SiO₂ is as follows:

- (10) Ni·NiO·Pt | ZrO₂·CaO | Pb(l)·(PbO+SiO₂) slag

The cell used for the measurement of the chemical activity of Sn is as follows:

- (11) Sn·SnO₂ | ZrO₂·CaO | (Pb+Sn) alloy·SnO₂

The cells used to measure the oxygen pressure in high temperature gases are as follows:

- (12) CO·CO₂ : FeO(solvent)·Pt | ZrO₂·CaO | Fe·FeO·Pt
- (13) CO·CO₂ : Pt | ZrO₂·CaO | Ni·NiO·Pt
- (14) CO·CO₂ : FeO(solvent)·Pt | ZrO₂·CaO | Cu·Cu₂O·Pt
- (15) Air or Ar+O₂ : Pt | ZrO₂·CaO | Ni·NiO·Pt

Fig. 2(a) shows the construction of the cell with four electrodes and Fig. 2(b) shows the construction of the cell used to measure the oxygen pressure in PbO-SiO₂ slag.

Also, Fig. 3 shows the “oxygen gauge” to measure the partial pressure of oxygen in high temperature gases.

All the metals and the oxides used in the above cells were in a state of powder under 100 mesh with purity

Fig. 2. Constructions of various oxygen concentration cells

of chemical reagent grade.

The zirconia stabilized with lime contained about 0.15~0.08 moles of CaO, traces of Fe₂O₃, TiO₂ and ignition loss.

There was no observable difference in the performance of the electrolyte as pure anion conductor due to the migration of oxygen vacancies, when the stabilized zirconia manufactured in the United States, West Germany, Japan, as well as in the laboratory was used as the electrolyte of the above cells. Particularly, some of the experimental runs of Pb-Sn system were carried out in a crucible made by one of the authors from zirconyl nitrate to compare the performances of the commercial crucibles with the home-made pure zirconia-lime crucibles. The procedure for preparing the pure ZrO₂·CaO crucible was as follows:

- (1) Mixing of ZrO(NO₃)₂ solution (20%) and dilute nitric acid solution of CaCO₃.
- (2) Drying in a water bath and heating at 120°C for two nights to decompose the ZrO(NO₃)₂ and volatilize NO₂ gas.
- (3) Sintering at 1,350° to 1,400°C for two days.

Fig. 3. Schematic diagram of the oxygen gauge

(4) Pressing the sintered powder to a 1.0 inch diameter block under 15,000 psi.

(5) Boring the block with a drill to form the cavity and finishing into a crucible shape.

(6) Sintering the crucible at 1,500° to 1,700°C in a high frequency induction furnace under a reducing atmosphere for 3 hours.

(7) Sintering the crucible at 800° to 900°C for 1 to 2 hours in an oxidizing atmosphere to oxidize the absorbed carbon.

The chemical analyses of the samples have been carried out according to the methods by Japan Industrial Standards and American Standards of Testing Materials.

To make the cell, $\text{Ni} \cdot \text{NiO} \cdot \text{Pt} | \text{ZrO}_2 \cdot \text{CaO} | \text{Pb} \cdot (\text{PbO} \cdot \text{SiO}_2)$, for example, the small hole was bored at the very bottom of the $\text{ZrO}_2 \cdot \text{CaO}$ tube with one closed end by a diamond cutter. The iron lead wire, which has no mutual solubility with the liquid Pb, was inserted into the Pb electrode, on which the mixture of PbO and SiO_2 powder of minus 100 mesh was stamped with a small amount of binder of water. The homogeneous and transparent slag was observed on the lead metal when each experimental run was finished. On the other hand, the standard electrode of $\text{Ni} + \text{NiO}$ combination was made by winding platinum wire on the outside of the $\text{ZrO}_2 \cdot \text{CaO}$ tube, on which the mixture of NiO and Ni powder was stamped with the binder of water.

Fig. 4. Standard free energies of formation of oxides

When the construction of the cell was completed, it was set into the reaction chamber. The electric power of the furnace was turned on after flushing in the reaction chamber with argon gas passed through the cleaning train. The cells were kept at a given temperature for 10~20 minutes to attain equilibrium at both electrodes. When the EMF stabilized, both the temperature and the EMF were read with the potentiometers several times.

The EMF of the above fifteen types of the cells was ranged in 20~1,200 mV. The sensitivity of the potentiometers used to measure the EMF was ± 0.00001 volt.

The temperature of the cells was measured by Pt-13% Rh-Pt thermocouple, the hot junction of which was located within 5 mm from the cell. The temperature of the cell might be kept constant within $\pm 1^\circ\text{C}$.

The electric furnace with platinum resistance ribbon was used for the $\text{PbO} \cdot \text{SiO}_2$ work. The electric furnace with SiC heating elements was used for the work on the standard free energy of formation. The electric furnace with Globar heating elements was used for the Pb-Sn work and the work on "oxygen gauge". Always, the automatic controllers were used to maintain the constant temperature.

The reaction chambers were of glazed silica tube, of sintered alumina tube, and of porcelain tube with water-cooled brass caps or rubber caps. In the "oxygen gauge" work, the commercial stabilized zirconia tubes, which are supposed to be gas tight up to 10^{-6} mmHg and up to 1,000°C, have been used as the solid electrolyte. This one closed end tube was 2 feet long, 3/4 inch outside diameter and 5/8 inch inside diameter.

III. Experimental Results and Discussions

The standard free energies of formation of the metal oxides have been obtained as follows and as shown in Fig. 4.

- (1) $\text{Fe}(\alpha) + \frac{1}{2}\text{O}_2(\text{g}) = \text{FeO}(\text{s})$
 $\Delta F_f^\circ = -57,610 + 14.13 T (^\circ\text{C}) \pm 300 \text{ cal}$
 (500°C ~ up to trans. point of $\alpha \rightarrow \gamma$ iron)
- (2) $3\text{Fe}(\alpha) + 2\text{O}_2(\text{g}) = \text{Fe}_3\text{O}_4(\text{s})$
 $\Delta F_f^\circ = -236,600 + 63.33 T (^\circ\text{C}) \pm 1,000 \text{ cal}$
 (500°C ~ up to trans. point of $\alpha \rightarrow \gamma$ iron)
- (3) $\text{Pb}(l) + \frac{1}{2}\text{O}_2(\text{g}) = \text{PbO}(\text{s or } l)$
 $\Delta F_f^\circ = -45,710 + 23.47 T (^\circ\text{C}) \pm 100 \text{ cal}$
 (500°C ~ M.P. of PbO)
 $\Delta F_f^\circ = -40,840 + 17.82 T (^\circ\text{C}) \pm 100 \text{ cal}$
 (M.P. of PbO ~ 1,150°C)
- (4) $\text{Sn}(l) + \frac{1}{2}\text{O}_2(\text{g}) = \text{SnO}(\text{s})$
 $\Delta F_f^\circ = -61,000 + 23.72 T (^\circ\text{C}) \pm 50 \text{ cal}$
 (500°C ~ 1,100°C)
- (5) $\text{Cu}(\text{s}) + \frac{1}{2}\text{O}_2(\text{g}) = \text{CuO}(\text{s})$

Recently, Elliott and Gleiser¹⁰⁾ have published an excellent compilation of thermodynamic data which include the thermodynamical properties of many metals and many metal oxides. The present authors believe that the data in this compilation are most up-to-date and reliable, and ΔF_f° from this compilation is given by broken lines in Fig. 4 for the comparison with the present works.

Except for the data on Ta_2O_5 , the present results, in general, agreed quite well with the data in the compilation. The reproducibility of the EMF was so good and the range of scattering was within $\pm 1,000$ cal at most. Particularly, the ΔF_f° of FeO was completely coincident with the data in the compilation which were measured much more accurately than the ΔF_f° of the other oxides, by many investigators, such as Humphrey, King, and Kellog¹³⁾, Darken and Gurry¹⁴⁾, Schenk, Dingmann, Kirscht, and Wasselkock¹⁵⁾, Gokcen¹⁶⁾, Coughlin, King, and Bonnickson¹⁷⁾, and so on.

The complete coincidence of the present ΔF_f° of FeO with the previous data suggests two significant meanings. Namely, (1) it is the right thing to use the $\text{Ni}+\text{NiO}$ combination as the standard electrode and (2) regardless of whether the structures of the cells have two or four electrodes, the commercial stabilized zirconia performs as the pure anion conductor.

Also, it was known that the oxide-oxide combinations such as $\text{FeO}+\text{Fe}_3\text{O}_4$ or $\text{Cu}_2\text{O}+\text{CuO}$ could provide the stable equilibrium oxygen pressure.

The difference of ΔF_f° of Ta_2O_5 from that in the compilation was also observed by Foster and St. Pierre¹⁸⁾ when they tried to obtain ΔF_f° of Ta_2O_5 by the oxygen concentration cell method.

The authors think that this discrepancy may be due to the electronic conduction in $\text{ZrO}_2\text{-CaO}$ electrolyte, because the equilibrium oxygen pressure over Ta and Ta_2O_5 is so small, as compared with that of other cases. Schmalzried¹⁹⁾ explained this situation as follows.

The relation between the electron concentration, C_θ and the oxygen pressure, P_{O_2} , is expressed by the next equations, when the oxygen pressure is much smaller than 1.

$$2\theta + \frac{1}{2}\text{O}_2 + \text{O}_{\square}'' = 2\text{O}^{2-}(\text{lattice}) \quad \dots\dots (11)$$

$$\therefore C_\theta = k'(T) \cdot C_{\text{O}_{\square}''}^{-\frac{1}{2}} \cdot P_{\text{O}_2}^{-\frac{1}{4}} \quad \dots\dots (12)$$

$$= k(T) \cdot P_{\text{O}_2}^{-\frac{1}{4}} \quad \dots\dots (13)$$

where $k(T)$ is the constant for the constant temperature. The above equation means that the electron concentration C_θ is proportional to $P_{\text{O}_2}^{-\frac{1}{4}}$.

On the other hand, the transference number of ion, t_{ion} is defined by,

$$t_{\text{ion}} = \frac{\sigma_{\text{ion}}}{\sigma_{\text{ion}} + \sigma_\theta} = \frac{\sigma_{\text{ion}}}{\sigma_{\text{ion}} + aC_\theta} \quad \dots\dots (14)$$

where, σ_{ion} and σ_θ are the electric conductivity by ions and electrons respectively and a is the electron mobility. $(\partial\sigma_{\text{ion}}/\partial P_{\text{O}_2})_T = 0$.

Furthermore, t_{ion} can be expressed by the equation (15), inserting, $a'(T) = a/\sigma_{\text{ion}}$.

$$t_{\text{ion}} = \frac{1}{1 + a'C_\theta} \quad \dots\dots (15)$$

If the oxygen pressure for $t_{\text{ion}} = \frac{1}{2}$ is denoted by $P_{\text{O}_2}^*$, $P_{\text{O}_2}^*(T)$ is equal to $(a'k)^4$ and this relation results in,

$$t_{\text{ion}} = \frac{1}{1 + (P_{\text{O}_2}^*/P_{\text{O}_2})^4} \quad \dots\dots (16)$$

The EMF of the cell, $P_{\text{O}_2}' \cdot \text{Pt} | \text{ZrO}_2\text{-CaO} | \text{Pt} \cdot P_{\text{O}_2}''$, can be expressed as follows:

$$E = \frac{1}{4f} \int_{P_{\text{O}_2}'}^{P_{\text{O}_2}''} t_{\text{ion}} d\mu_{\text{O}_2} \quad \dots\dots (17)$$

Therefore,

$$E = \frac{RT}{4f} \ln \frac{P_{\text{O}_2}''}{P_{\text{O}_2}'} + \frac{RT}{f} \ln \frac{t_{\text{ion}}(P_{\text{O}_2}')}{t_{\text{ion}}(P_{\text{O}_2}'')} \quad \dots\dots (18)$$

The second term of the right hand of the above equation may be considered as the correction term, when t_{ion} is not the unit.

By the rough calculation, t_{ion} becomes about 0.8~0.9 in the case of Ta_2O_5 , so that the second term of the equation (18) can not be neglected.

Therefore, it is clear that the oxygen concentration cells with the $\text{ZrO}_2\text{-CaO}$ electrolyte are not appropriate for use in measuring the standard free energies of formation of such oxides as Al_2O_3 , Ta_2O_5 , CaO , ZrO_2 , MgO and so on, because the oxygen pressure over these oxides and metals is too small.

The reversibility of the EMF was carefully examined with respect to the atmosphere in the reaction chamber, the temperature and the applied potential.

For example, if the small amount of CO gas was mixed in argon gas flown in the reaction chamber, the

EMF suddenly changed but it again returned to the equilibrium EMF when the mixing of CO gas was stopped and only argon gas was flown in.

The EMF was, of course, completely reversible with respect to the temperature.

The relation between the current and the externally applied potential was obtained by the several cells. When the applied potential was not so different from the equilibrium EMF of the cell, the relation between the current and the applied potential was linear, but not linear, when the applied potential was much different from the equilibrium EMF, possibly due to the polarization effect.

However, the EMF was reversible with respect to the externally applied potential.

The six EMF were recorded with the four-electrode cell at the constant temperature and their relation was also considered.

Fig. 5 shows the oxygen pressure in the liquid PbO-SiO₂ solutions equilibrated with pure lead.

From the figure, it is clear that the oxygen pressure of PbO-SiO₂ solutions increases at the higher temperature and decreases with the increase of the silica content.

The oxygen ions in silicate melts may be considered to be divided into three kinds, that is, (1) completely bridged oxygen ions like $\text{--}\underset{\cdot}{\text{Si}}\text{--O--}\underset{\cdot}{\text{Si}}\text{--}$ (designated by O[°]), (2) half bridged ions like $\text{--}\underset{\cdot}{\text{Si}}\text{--O--}$ (designated by O⁻) and (3) completely free ions (designated by O⁼).

The relation of these three kinds of ions may be

Fig. 5. Partial pressure of oxygen in PbO-SiO₂ melts

expressed by,

and, the oxygen pressure of the melts may be given by,

$$\frac{1}{2}\text{O}_2(\text{g}) = \text{O}^= \dots\dots\dots (20)$$

Toop and Samis²⁰⁾ reported the relative amounts of the oxygen ions of these three kinds in ZnO-SiO₂ melts. The free ions, O⁼ decreased with the increase of the silica content, while completely bridged ions, O[°] increased. The half bridged ions, O⁻ have a maximum concentration at $N_{\text{SiO}_2} \approx 0.4$. The similar discussion will be valid in PbO-SiO₂ binary solutions. Assuming the equation (20), the free ions, O⁼ may decrease with the increase of the silica content in PbO-SiO₂ slags, because the oxygen pressure of PbO-SiO₂ decreased with the silica content.

Fig. 6 gives the chemical activities of PbO and SiO₂ at 900°, 1,000° and 1,100°C.

The activity coefficient of SiO₂, γ_{SiO_2} was calculated by the Gibbs-Duhem relation as follows:

$$\ln \gamma_{\text{SiO}_2} = -\alpha_{\text{PbO}} \cdot N_{\text{SiO}_2} \cdot N_{\text{PbO}} - \int_{N_{\text{SiO}_2}=1}^{N_{\text{SiO}_2}} \alpha_{\text{PbO}} dN_{\text{SiO}_2} \quad (21)$$

$$\text{Where, } \alpha_{\text{PbO}} = \frac{\ln \gamma_{\text{PbO}}}{(1 - N_{\text{PbO}})^2}$$

The scattering of the so-called α -plot was very

Fig. 6. Activity of PbO and SiO₂ in the system PbO-SiO₂ at 900°, 1,000° and 1,100°C

small.

From the figure, it is known that the activity of PbO deviated in a negative direction from ideality and the degree of the deviation increased with decreasing temperature, while the activity of SiO₂ deviated in a negative direction from ideality if the silica content was less than 0.38 mole fraction, above which the activity of SiO₂ deviated in a positive direction. The deviation becomes less at the higher temperature.

Richardson and Webb²¹⁾, and Sawamura²²⁾ et al. measured the chemical activity of PbO and SiO₂ by other methods, the results of which seemed to nearly agree with the present results.

The free energy of mixing, the enthalpy, and the entropy of mixing of the liquid PbO-SiO₂ solution were calculated by the following equations respectively and shown by Fig. 7.

$$\Delta F^{\text{mix}} = RT(N_{\text{PbO}} \ln a_{\text{PbO}} + N_{\text{SiO}_2} \ln a_{\text{SiO}_2}) \dots (22)$$

$$\Delta H^{\text{mix}} = \left(\frac{\partial \Delta F^{\text{mix}}}{\partial 1/T} \right)_{P, N_{\text{PbO}}, N_{\text{SiO}_2}} \dots (23)$$

$$\Delta S^{\text{mix}} = \left(\frac{\partial \Delta F^{\text{mix}}}{\partial T} \right)_{P, N_{\text{PbO}}, N_{\text{SiO}_2}} \dots (24)$$

The diagrams of $\Delta F^{\text{mix}}/T$ vs. $1/T$ and of ΔF^{mix} vs. T are not presented here because of the limited papers, but their relations were exactly linear for the temperatures of 900°, 1,000° and 1,100°C.

Fig. 7. Free energy, enthalpy and entropy of mixing in the system PbO-SiO₂

From Fig. 7, it is clear that the free energy of mixing of PbO-SiO₂ system has the minimum values at $N_{\text{SiO}_2} = 0.38$, $\Delta F^{\text{mix}} = -2.2$ kcal/mole, -2.3 kcal/mole, and -2.45 kcal/mole at 900°, 1,000° and 1,100°C, respectively. The minimum enthalpy of mixing is about -700 cal/mole at $N_{\text{SiO}_2} = 0.32$ and the maximum entropy of mixing is about 1.3 entropy unit/mole at $N_{\text{SiO}_2} = 0.38$.

The slags were chemically analyzed after the experiment according to Japan Industrial Standards and the chemical analysis of the slags agreed with the charge composition within $\pm 1\%$ PbO.

Particularly, ZrO₂-CaO in the slags was examined by X-ray spectroscopy and it was known that the slags after the experimental runs contained only the trace amount of ZrO₂. The electrolyte, ZrO₂-CaO was not attacked by the liquid slags. The solubility limit of SiO₂ in PbO, was determined by Krrakau, Mukhin, and Heinrich²³⁾. Gotō and St. Pierre³⁾ measured the activity of tin in liquid lead-tin alloys with the following cell:

Fig. 8 shows the activity of Sn and Pb at 700°, 800° and 900°C. The activity of Pb was calculated by Gibbs-Duhem equation as explained above.

However, the valence, n was 2 for the calculation of the activity of tin, possibly because the virtual electrode reaction was $\text{Sn} + \frac{1}{2}\text{O}_2 = \text{SnO}$, although the used tin oxide was SnO₂. This fact may imply that the stable oxide with metallic tin is SnO at the experimental temperature. This deduction may be also supported by the fact that the standard free energy of formation of SnO by the cell, $\text{Sn} \cdot \text{SnO} \mid \text{ZrO}_2 \cdot \text{CaO} \mid \text{Ni} \cdot \text{NiO}$ agreed quite well with that in the compilation by Elliott and Gleiser¹⁰⁾.

Niwa et al.²⁴⁾ measured the activity of Sn at 800°C in liquid Sn-Pb solution. The results were coincident

Fig. 8. Activities of Sn and Pb in the system Sn-Pb

with the activity of tin at 800°C, by Gotō and St. Pierre³⁾.

Fig. 10 shows the free energy of mixing of Pb-Sn alloys at 700°, 800° and 900°C.

St. Pierre²⁵⁾ calculated the heat of mixing by the following elegant method from the single partial molar property.

$$\Delta H^{\text{mix}} = N_2 \int_{N_1/N_2=0}^{N_1/N_2} (\bar{H}_1 - H_1^\circ) d(N_1/N_2) \dots (25)$$

$$\text{where, } \bar{H}_1 - H_1^\circ = R \left[\frac{\partial (\ln a_1)}{\partial (1/T)} \right]_N$$

However, the calculated ΔH^{mix} values were much larger than the very careful calorimetric determination of Kleppa²⁶⁾.

In order to determine whether the lead-tin alloy is a regular solution or not, the following conditions should be considered.

- (1) Whether α is constant at a given temperature for any composition of alloys.
- (2) Whether the following relation is satisfied.

$$\left(\frac{\partial \alpha}{\partial (1/T)} \right)_{PN, N_2} - T\alpha = 0 \dots\dots\dots (26)$$

Both of the above conditions should be satisfied for

Fig. 9. Free energy of mixing of Pb-Sn alloys

Fig. 10. Calibration curves of EMF against CO₂(%) in gas phase using Ni-NiO reference electrode

a regular solution.

The tin-lead system seems to satisfy condition (1) but not (2), and it can be concluded that the lead-tin solution is not a regular solution, although the free energy of mixing seems almost symmetrical at $N_{\text{Pb}} = N_{\text{Sn}} = 0.5$.

The effect of oxygen in lead-tin alloys on the activity of tin or lead is assumed to be negligible, because the solubility of oxygen in liquid lead has been determined by Alcock²⁷⁾ to be about 0.13 atomic % at 700°C, using the Coulombmetric titrations.

The vapor pressure of tin is rather large (10^{-4} atm. at 692°C and 10^{-3} atm. at 809°C), therefore, the final tin content in Pb-Sn alloys was decreased from the charge composition.

The EMF was again very sensitive to the atmosphere over the cells. If pure CO or CO₂ was mixed with the argon atmosphere, the EMF spontaneously decreased or increased; and if pure argon flowed over the cells, the EMF returned to the original reversible EMF value in a short time. The reversibility of the EMF against the externally applied potential was also examined to be complete.

The above characteristic of the oxygen concentration cells, that the EMF was very sensitive to the atmosphere and very reversible, caused Gotō and St. Pierre⁴⁾ to suggest the development of an oxygen gauge to measure the partial pressure of oxygen in high temperature gases, which might have a big significance in industry, in general.

Fig. 10 and Fig. 11 show the calibration curves of the EMF against the gas compositions of CO-CO₂ gas mixture and Ar-O₂ gas mixture, respectively. The Ni+NiO combination was used as the standard electrode to obtain the calibration curves in Fig. 10 and Fig. 11 but the other combinations, such as Cu+Cu₂O or Fe+FeO were also successfully used. The other calibration curves may not be introduced here.

Matsushita and Gotō¹¹⁾ used the oxygen gauge to measure the oxidation and reduction rates of pure iron

Fig. 11. Calibration curve of EMF against oxygen (%) in argon-oxygen gas mixtures

and iron oxides by the gas mixture of carbon monoxide and carbon dioxide. The details of this experiment will be disclosed in future.

Also, Matsushita et al.¹²⁾ are working on the industrial application of the oxygen gauge to measure continuously the oxygen pressure in the waste gas of an open hearth furnace, using the steam ejector to take out the waste gas from an open hearth furnace. The life time of the oxygen gauge may be one of the industrial problems and it was known that the life time was longer than 80 hours at least, at $800^{\circ}\sim 1,000^{\circ}\text{C}$ and that the reproducibility of the EMF was very good.

The measurable range of the oxygen pressure is $10^{-1}\sim 10^{-30}$ atm.

As to industrial application, there might be many applications of this oxygen gauge in metallurgical furnaces. However, the following advantages and disadvantages can be expected.

(1) As far as the construction of the cells is concerned, it is rather easy to obtain the necessary materials written above.

(2) The calibration should be done by some gases, the oxygen pressure of which has been well established, such as CO-CO₂ mixture or H₂-H₂O mixture.

(3) The life time of the cells should be considered for industrial application.

(4) Temperature of the measurement should be above 800°C to insure a rapid response and a high transference number for oxygen.

(5) The oxygen diffuses through the electrolyte, although it is apparently very slow. Thus, either the metal or the metal oxide in the reference electrode may disappear eventually due to oxidation or reduction.

(6) If the output EMF is connected to the automatic recorder, the continuous measurement of the gas composition may be possible.

Weissbart and Ruka²⁸⁾ independently developed the oxygen gauge with the electrolyte, ZrO₂·CaO but the standard electrode was different from that used by Gotō and St. Pierre⁴⁾.

In addition, Matsushita and Gotō⁹⁾ carried out the experiment to measure the oxygen content in liquid iron at $1,560^{\circ}\text{C}$. The conventional methods of the oxygen analysis are by a vacuum fusion analysis with a micro-Orsat or by a fusion in a graphite crucible with an argon carrier gas, measuring the change of an electric resistance of Ba(OH)₂ solution by absorption of CO₂ gas. One of the reasons for the discrepancy of the oxygen analysis in iron may be considered due to difference of sampling methods for gas analysis. However, if the suitably designed oxygen concentration cells can determine the oxygen content in liquid iron by the EMF, the oxygen analysis in iron may possibly be done more easily than by the conventional

methods.

For this purpose, the reproducibility of the EMF against the oxygen content at a given temperature and the life time of the cells should be carefully examined and they are now under investigation by the present authors.

IV. Conclusions

By the application of the oxygen concentration cell technique with a solid electrolyte, ZrO₂·CaO, two kinds of research work have been carried out by the present authors^{1), 2)} and the other two kinds of research work have been carried out by Gotō and St. Pierre^{3), 4)}. In the first work, the various oxygen concentration cells, including the cells with four electrodes have been constructed and the standard free energies in the formation of FeO, Fe₃O₄, Cu₂O, CuO, SnO, PbO and Ta₂O₅ have been obtained at the temperature range of $500^{\circ}\sim 1,300^{\circ}\text{C}$. The accuracy of ΔF_f° seemed much better than those in the literature, except ΔF_f° of Ta₂O₅ possibly due to the effect of electronic conduction in ZrO₂·CaO.

As the standard electrode, nickel and nickel oxide have been used and their equilibrium oxygen pressure has been carefully examined¹¹⁾ by CO-CO₂ gas mixtures.

The standard free energies in the formation of the above metal oxides have been presented by the functions of the reciprocal of temperature with the ranges of the scattering of the data and with the temperature range, in which the functions are valid.

The reversibility of the equilibrium EMF was studied against the changes of the atmosphere, temperature and the externally applied potential, and proved to be complete with respect to these three factors.

Also, the possibility of electronic conduction through the electrolyte, ZrO₂·CaO was discussed. In the second work, the equilibrium oxygen pressure in liquid PbO-SiO₂ binary solution equilibrated with liquid Pb has been measured at 800° , 900° , $1,000^{\circ}$ and $1,100^{\circ}\text{C}$, with the standard electrode composed of the powder mixture of nickel and nickel oxide.

It is concluded that the equilibrium oxygen pressure in liquid PbO-SiO₂ solution decreases with the increase of the silica content in the solution and increases at the higher temperature, in possible relation to the concentration of free oxygen ions in the slag solution.

The activities of PbO and SiO₂ have been calculated. From the activity values, the thermodynamical properties of PbO-SiO₂ solution, such as the free energy of mixing, enthalpy and entropy of mixing have been calculated.

The activity of PbO deviates in a negative direction

from ideality and the degree of the deviation increased with decreasing temperature, while the activity of SiO_2 deviates in a negative direction from ideality if the silica content is less than 0.38 mole fraction, above which the activity of SiO_2 deviates in a positive direction. The deviation becomes less at higher temperature. The free energy obtained from mixing the PbO-SiO_2 system has the minimum values at $N_{\text{SiO}_2} = 0.38$, as $\Delta F^{\text{mix}} = -2.2$ kcal/mole, -2.3 kcal/mole, and -2.45 kcal/mole at 900° , $1,000^\circ$ and $1,100^\circ\text{C}$ respectively.

The minimum enthalpy of mixing is about -700 cal/mole at $N_{\text{SiO}_2} = 0.32$ and the maximum entropy of mixing is about 1.3 entropy unit/mole at $N_{\text{SiO}_2} = 0.38$.

In the third experiment, the chemical activity of tin in liquid tin-lead alloys has been measured at 700° , 800° and 900°C . The activity of lead was calculated by Gibbs-Duhem equation. Although the tin oxide used for both electrodes was SnO_2 , the valence, n was 2 for the calculation of the activity of tin, possibly because the virtual electrode reaction was $\text{Sn}(l) + \frac{1}{2}\text{O}_2(g) = \text{SnO}(s)$.

The activities of tin and lead exhibited positive deviation from ideality and the degree of deviation was smaller at higher temperature.

The normal amount of free energy of the solution as well as the excess free energy of solution was calculated from the activity data. Also, the mole quantities of lead and tin in solution were calculated.

The Pb-Sn binary system was not a regular solution, although the free energy of mixing seemed almost symmetrical at $N_{\text{Sn}} = N_{\text{Pb}} = 0.5$.

The laboratory-made $\text{ZrO}_2\cdot\text{CaO}$ was compared with the commercial stabilized zirconia as to performance as a pure anion conductor and both the electrolytes resulted in the same EMF.

In the fourth work, the oxygen gauge was developed to measure the partial pressure of oxygen in high temperature gases and the characteristics of the oxygen gauge as well as calibration data were obtained.

The self-consistent and reproducible EMF against oxygen pressure were successfully obtained by several standard electrodes for oxygen pressure in the range of 10^{-1} to 10^{-20} atm. at 500° to $1,300^\circ\text{C}$. Also, the life time of the oxygen gauge was determined and proved to be long enough for industrial purposes.

Also, in addition to the above four works, other possibilities of applying oxygen concentration cells have been discussed. These other possibilities include the measurement of oxidation or reduction rates of iron or iron oxides by CO-CO_2 gas, the waste gas of an open hearth furnace, and the measurement of the oxygen content in iron by the EMF.

V. Acknowledgements

The present authors acknowledge with the sincere appreciation the invaluable discussions with Dr. George R. St. Pierre of the Ohio State University through the private communication. Acknowledgement is made to Mr. Yu Ching Wu, Master of Engineering for his co-operation in carrying out the PbO-SiO_2 work.

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