ELECTROCHEMICAL DETERMINATION OF THERMODYNAMIC PROPERTIES OF INTERMEDIATE COMPOUND IN Mo-O SYSTEM

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The Gibbs free energy of formation of Mo_4O_{11} has been determined by using the cell
$$Co,\ CoO\ |\ ZrO_2(MgO)\ |\ MoO_2,\ Mo_4O_{11}$$
over temperature range from 873K to 1073K. The result was
$$\Delta G^\circ_{Mo_4O_{11}} = -2679 + 0.7877\ T \quad \pm 5\ (KJ/mol.)$$
which is consistent with that obtained by Kleykamp, et al.[7] The above data and other intermediate compound data in Mo-O system have been discussed by virtue of a thermodynamic principle.

1. INTRODUCTION

There exist a series of intermediate compounds in some binary systems such as the systems constituted by metals and nonmetals (e.g., V-O, Ti-O, Mo-O and rare earth-oxygen, etc.), and the systems constituted by metals and other metals (e.g., Zr-Zn, Ni-Al, Ni-Se and so forth). A lot of thermodynamic properties of intermediate compounds so far have not yet been known. Obviously, it is quite important to make them clear.

Before 1960, the determination of the thermodynamic properties for most metallurgical systems were using the chemical equilibrium approach. After that, since such great progress was made regarding the investigation of solid electrolytes, the electrochemical method using solid electrolytes to measure thermodynamic properties has been used more and more widely. This method has some special advantages due to its simplicity and quickness during the measurement. The results obtained from this method are also reliable.

Molybdenum-Oxygen binary system is an important system for metallurgists. There are four kinds of intermediate compounds, i.e., MoO_2, Mo_4O_{11}, Mo_9O_{26}, and MoO_3, which have

been confirmed in phase diagram by many investigators.[1] Their thermodynamic properties have also been measured many times with different experimental methods. Cosgrove and Snyder[2], Mah[3], Staskiewicz[4] and other investigators have determined the thermodynamic property of MoO_3. The thermodynamic properties of MoO_2 have been studied in more detail.[5-9] Nevertheless, less investigations have been made for the systems of Mo_4O_{11} and Mo_9O_{26}. Kleykamp and Supawan[7] have determined the free energy of formation of Mo_4O_{11}, and Zhukovskii, et al[10] have measured the thermodynamic properties of Mo_9O_{26}. Those data have not yet been confirmed by other experiments.

In this study we took ZrO_2 as an electrolyte and designed the following cell

$$Co,\ CoO\ |\ ZrO_2\ (MgO)\ |\ MoO,\ Mo_4O_{11} \qquad (1)$$
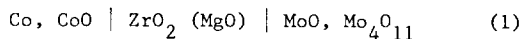
to investigate Mo_4O_{11} thermodynamic properties.

2. EXPERIMENTAL APPARATUS AND PROCEDURES

The cell assembly is shown in Fig. 1. This cell consisted of two ZrO_2 tubes which were imerged into a graphite crucible filled with liquid tin. One ZrO_2 tube contained the mixture of Co and CoO powders, another one was MoO_2

and Mo_4O_{11}. The upper portion of the tubes was filled with Al_2O_3 powder and sealed with refractory cement. There were two Ni-Cr wires as a leading wire inserting into ZrO_2 tubes used to measure the electromotive force of the cell. The entire assembly was put in the constant temperature zone of a furnace. The temperature of assembly was measured by a Pt--Pt Rh thermocouple and controlled by a DWT-702
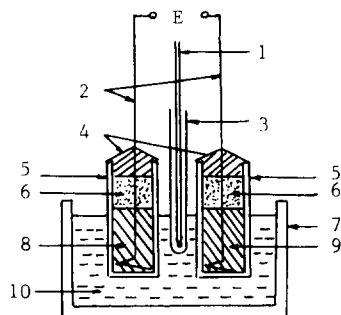

FIGURE 1
Cell Assembly

1. Pt-PtRh thermocouple, 2. Leading wire of electrode, 3. Al_2O_3-tube, 4. Refractory cement, 5. ZrO_2-tube,   6. Al_2O_3 powder, 7, Graphite crucible, 8. Co+CoO powder, 9. MoO_2+ Mo_4O_{11} powder, 10. Liquid Tin.

type of controller with an accuracy of ± 0.5 degree. The entire furnace was protected by Argon atmosphere to avoid the system oxidation.

The Co, Mo powders contained in the ZrO_2 tubes were prereduced by Hydrogen at 700C and 1000C, respectively. Afcer that, they were sifted through a 300 mech seive along with stave Co_2O_3 and MoO_3 powders. The homogeneous mixtures of Co and Co_2O_3 in a weight ratio of 8 to 1 as well as Mo and MoO_3 in a weight ratio of 1 to 5.25, were filled with two ZrO_2 (stabilized by MgO) tubes and cold-pressed respectively.

The electromotive force of Galvanic cell was measured by a UJ-24 type electropotential meter. During the experiment, the circuit had been

closed for 15 seconds, then we measured its emf sequentially. The experimental results showed that the electromotive force could be recovered to its original equilibrium value only after 2-3 minutes. The cell exhibited a very good reversibility. The reproducibility was also good and the experimental errors were within ± 2 mv.

3. RESULTS

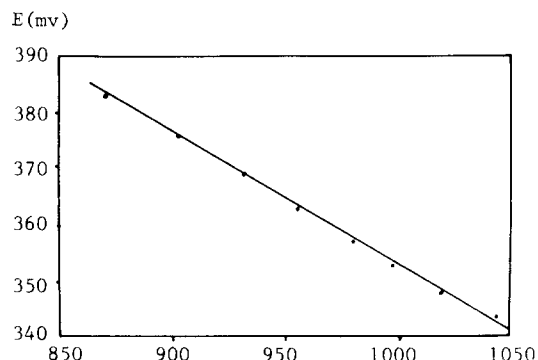The dependence of emf upon T are shown in Fig. 2.

FIGURE 2
The dependence of EMF of the cell on temperature.

After a least square treatment, we obtain

$$E = 0.5898 - 2.355*10^{-4}T \qquad (2)$$

with a correlation coefficient of 0.9979, where E represents the emf of the cell. The corresponding Gibbs free energy change is

$$\Delta G^\circ = -226.9 + 0.09089 \, T \text{ kJ/mole} \qquad (3)$$
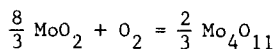
After regressing the JANAF's data[11] of reaction

$$2Co + O_2 = 2CoO \qquad (4)$$

we obtain the Gibbs free energy change versus temperature as follows,

$$\Delta G^\circ = -469.2 + 0.1419 \, T \ (298-1400K) \qquad (5)$$

which has a good agreement with the data provided by Kubaschewski and Alcock.[12] Subtracting Eq. (3) from Eq. (5) yields the Gibbs

free energy change of reaction

$$\frac{8}{3} MoO_2 + O_2 = \frac{2}{3} Mo_4O_{11}$$

which is equal to

$$\Delta G^\circ = -242.4 + 0.05101\ T \tag{6}$$

It is necessary to know the value of the Gibbs free energy of formation of MoO_2 so as to evaluate the Gibbs free energy of formation of Mo_4O_{11}. The Barbi's result,[12] namely

$$\Delta G^\circ_{Mo_4O_2} = -578.9 + 0.1778\ T\ (KJ/mol.)$$
$$(840-1100k) \tag{7}$$

has been used here, because the temperature range of their experiment was narrow and approached our temperature range.

Thus, the Gibbs free energy of formation of Mo_4O_{11} is

$$\Delta G^\circ_{Mo_4O_{11}} = -2679 + 0.7877\ T\ (KJ/mole)$$
$$(873-1073K) \tag{8}$$

and as T=1000K, $\Delta G^\circ_{Mo_4O_{11}} = -1892$ KJ/mole. This result has a good agreement with that provided by Kleykamp and Supawan,[7]

$$\Delta G^\circ_{Mo_4O_{11}} = -2743 + 0.853\ T\ (840-1090K)$$
$$(KJ/mole) \tag{9}$$

when T=1000K, it gives $\Delta G^\circ_{Mo_4O_{11}} = -1890$KJ/mole.

In order to analyze and discuss the data of intermediate compounds in Mo-O binary systems, a thermodynamic principle, so called "the progressive increase regulation of the Gibbs free energy of formation about the intermediate compounds" was used. Here is its headline.

4. A THERMODYNAMIC PRINCIPLE

Suppose A-B binary system involves a series of intermediate compounds, which locate in a phase diagram according to the following order:

$$A_{m_1}B_{n_1},\ A_{m_2}B_{n_2},\ \ldots\ldots,\ A_{m_{i-1}}B_{n_{i-1}},\ A_{m_i}B_{n_i},\ldots\ldots$$
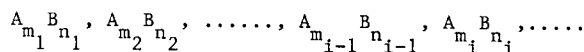
The coefficients of m_i, n_i observe the following regulation, $\frac{n_1}{m_1} < \frac{n_2}{m_2} < \frac{n_3}{m_3} < \ldots\ldots < \frac{n_{i-1}}{m_{i-1}} < \frac{n_i}{m_i} < \ldots\ldots$. The reactions of adjacent

intermediate compounds and its corresponding free energy change are listed below, respectively,

$$\frac{m_1}{n_1 m_0 - m_1 n_0} A_{m_0}B_{n_0} + B = \frac{m_0}{n_1 m_0 - m_1 n_0} A_{m_1}B_{n_1} \qquad \Delta G^\circ_1$$

$$\frac{m_2}{n_2 m_1 - m_2 n_1} A_{m_1}B_{n_1} + B = \frac{m_1}{n_2 m_1 - m_2 n_1} A_{m_2}B_{n_2} \qquad \Delta G^\circ_2$$

$$\frac{m_i}{n_i m_{i-1} - m_i n_{i-1}} A_{m_{i-1}}B_{n_{i-1}} + B = \frac{m_{i-1}}{n_i m_{i-1} - m_i n_{i-1}} A_{m_i}B_{n_i}$$
$$\Delta G^\circ_i$$
$$\tag{10}$$

where $m_o = 1$, $n_o = 0$. Since every two intermediate compounds involved in a reaction are adjacent to each other in the phase diagram, it is easy to obtain the following conclusions:[14]

(i) All of ΔG°_i expressed in the above formulae are negative;

(ii) $\Delta G^\circ_1 < \Delta G^\circ_2 < \ldots\ldots < \Delta G^\circ_{i-1} < \Delta G^\circ_i \ldots\ldots$ \qquad (11)

(iii) The Gibbs free energy of formation of an intermediate compound can be calculated in terms of the following equation

$$\Delta G^\circ_{A_{m_i}B_{n_i}} = m_i \sum_{k=1}^{i} \left(\frac{n_k}{m_k} - \frac{n_{k-1}}{m_{k-1}} \right) \Delta G^\circ_k \tag{12}$$

If we design a cell corresponding to the above reaction, then Eq. (12) can also be expressed as:

$$\Delta G^\circ_{A_{m_i}B_{n_i}} = -m_i F \sum_{k=1}^{i} \left(\frac{n_k}{m_k} - \frac{n_{k-1}}{m_{k-1}} \right) E_k \tag{13}$$

where E_k denotes the electromotive force and F Faraday constant.

(iv) The Gibbs free energy of formation of an intermediate compound divided by corresponding coefficient m_i satisfies a progress decrease principle, i.e.,

$$\frac{\Delta G^\circ_{A_{m_1}B_{n_1}}}{m_1} > \frac{\Delta G^\circ_{A_{m_2}B_{n_2}}}{m_2} > \cdots > \frac{\Delta G^\circ_{A_{m_{i-1}}B_{n_{i-1}}}}{m_{i-1}} >$$

$$\frac{\Delta G^\circ_{A_{m_i}B_{n_i}}}{m_i} > \cdots \qquad (14)$$

5. DISCUSSION

Based on the thermodynamic theory provided in the last section, let's analyze the thermodynamic data of the intermediate compounds in Mo-O system obtained so far. The Gibbs free energies of formation of intermediate compounds are listed in the second column of Table 1.

TABLE 1
The Gibbs Free Energies of Formation of Intermediate Compound in Mo-O System (1000 K)

Reaction	ΔG°(J/mole)	$\Delta G^\circ/m_i$(J/mol)	Ref.
$Mo+O_2=MoO_2$	-401100	-401100	Barbi[8]
$4Mo+\frac{11}{2}O_2$	-1890000	-472500	Kleykamp[7]
$= Mo_4O_{11}$	-1891000	-472750	This study
$9Mo+13O_2$	-43680000	-485300	Cal. from Zhukovskii's data[10]
$= Mo_9O_{26}$			
$Mo+\frac{3}{2}O_2$	-494200	-494200	JANAF[11]
$= MoO_3$			

The value of the Gibbs free energy of formation of Mo_9O_{26} was calculated from the data provided by Zhukovskii, et al[10] and the JANAF Table.[13] The above results show that a good agreement is obtained about the Gibbs free energies of formation between ours and Kleykamp's.[7] Taking a glance at Table 1, it is hard to find any regulation in the free energies of formation. However, the values of $\Delta G^\circ_{A_{m_i}B_{n_i}}/m_i$ (column III) exhibits a progressive decrease regulation which is consistent with our theory presented in the last paragraph.

Our data can also be inspected based on the progressive increasing principle of Gibbs free energy change of the reaction involving two adjacent intermediate compounds (Eq. (10)). Let's list these values in Table 2.

TABLE 2
The Gibbs Free Energy Change of the Reactions of Intermediate Compounds with One Mole Oxygen (1000 K)

No.	Reaction	ΔG°(J/mole)	Ref.
1.	$Mo + O_2 = MoO_2$	-401100	Barbi[8]
2.	$\frac{8}{3}MoO_2 + O$	(-190400)	Kleykamp[7]
	$= \frac{2}{3}Mo_4O_{11}$	-191100	This study
3.	$\frac{18}{5}Mo_4O_{11}$	-181500	Calculated by Eq. (12)
	$= \frac{8}{5}Mo_9O_{26}$		
4.	$2Mo_9O_{26}+O_2$	-15900	Zhukovskii[10]
	$= 19\,MoO_3$		

The second column of Table 2 lists the reactions of intermediate compound with one mole Oxygen. And the third column gives the Gibbs free energies of the corresponding reactions. The value of the third reaction was calculated in terms of Eq. (12), the others were obtained from experiments.

Table 2 shows that the free energy changes of reactions concerned satisfy the regulation mentioned above. It seems clear that our data are reasonable. The principle used here will be very useful in checking and calculating thermodynamic data for a series of intermediate compounds in a binary system.

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