Application of Double Knudsen Cell Mass Spectrometry to Measure on Thermodynamic Properties of Calcium Phosphates

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Background

De-phosphorization reaction in steelmaking

$$nCaO + 2P(in\ iron) + \frac{5}{2}O_2 = (CaO)_n P_2O_5 (in\ slag)$$

Products of de-phosphorization reaction $(CaO)_4P_2O_5$ $(CaO)_3P_2O_5$

Many researchers reported on thermodynamic data of these compounds obtained by various method, but the data were different from each other.

Double Knudsen cell mass spectrometry

A new method to measure thermodynamic properties at high temperature

easy Investigation on thermodynamic properties of metals and alloys

difficult Investigation on thermodynamic properties of oxide difficult

Objective

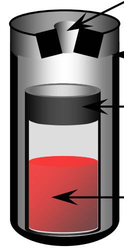
Application of double Knudsen cell mass spectrometry to investigate the thermodynamic properties of oxide systems

Measurement of thermodynamic data of $(CaO)_4P_2O_5$ and $(CaO)_3P_2O_5$ by double Knudsen cell mass spectrometry

Knudsen Cell Mass Spectrometry

Knudsen cell

Knudsen cell is a container, which has a small orifice.



Knudsen cell

Effusion rate from an orifice ➡ Vapor pressure of sample

Mass spectrometry

$$p_i = b\frac{I_i}{\sigma_i}T$$

- p_i : Partial pressure of i
- T : Temperature
- b : Device constant
- σ_i : Ionized cross section of i
- I_i : Ion current of i

Detect vapor pressures as ion current which is proportional to vapor pressure

Device constant influences Results

Device constant changes in each measurements

➡ Decreasing accuracy of measurement

Double Knudsen Cell Mass Spectrometry

Double Knudsen cell mass spectrometry

This method employees two Knudsen cells.

Cell 1: Sample

Cell 2: Reference substance (mixture)

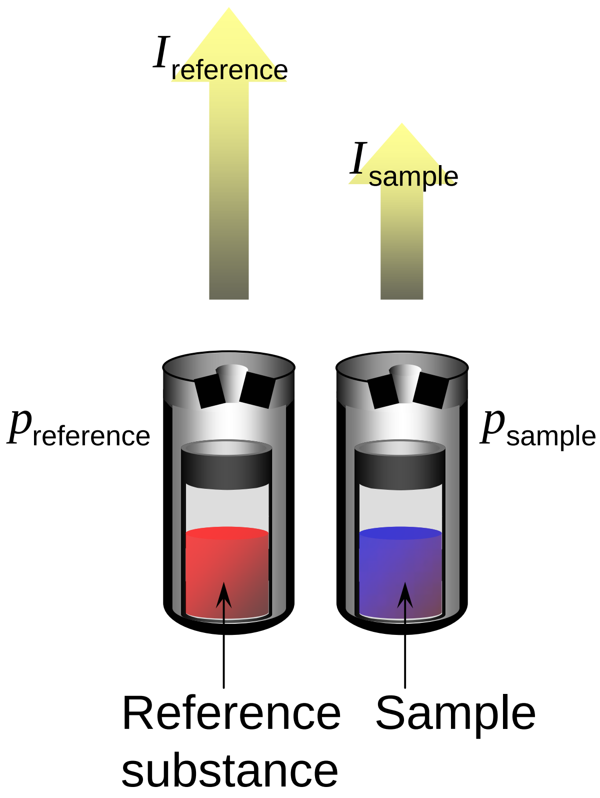
Reference substance (mixture) has well known pressure of objects of measurement.

Compare ion currents from sample and reference substance

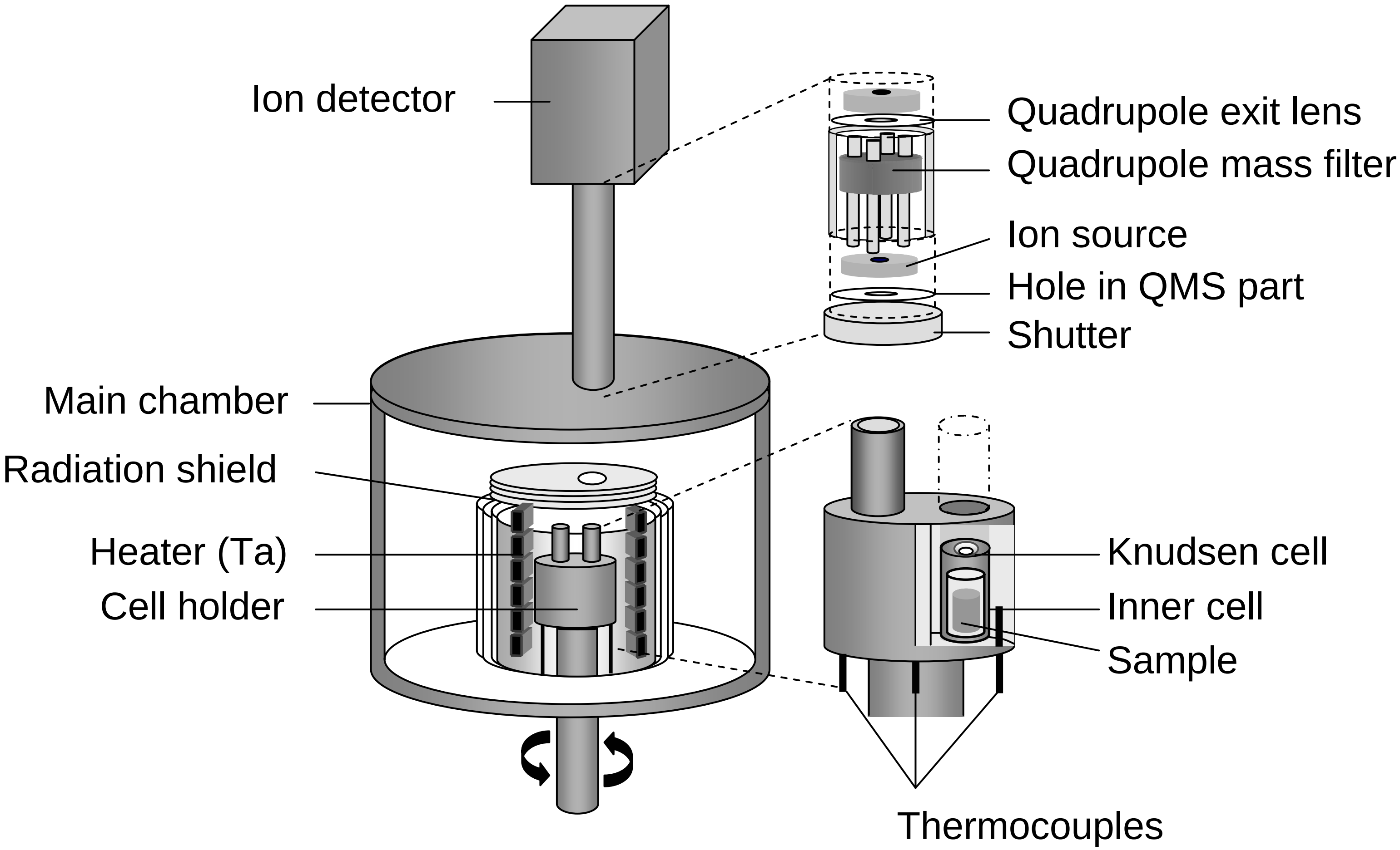
$$\frac{p_{\text{sample}}}{p_{\text{reference}}} = \frac{I_{\text{sample}}}{I_{\text{reference}}}$$

↓

Avoid influence of device constant



Equipment for Double Knudsen Cell Mass Spectrometry

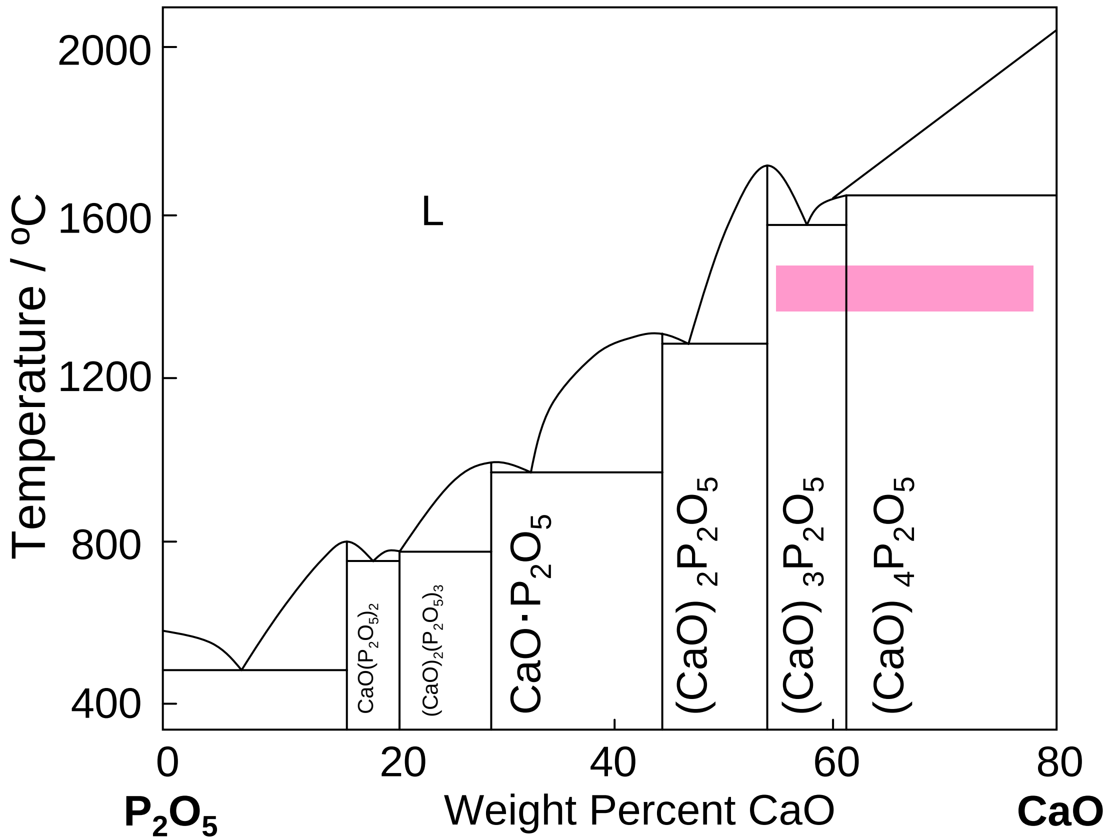


Equipment for Double Knudsen Cell Mass Spectrometry

Measurement of CaO-P_2O_5 Compounds

CaO-P_2O_5 system has many stoichiometric compounds.

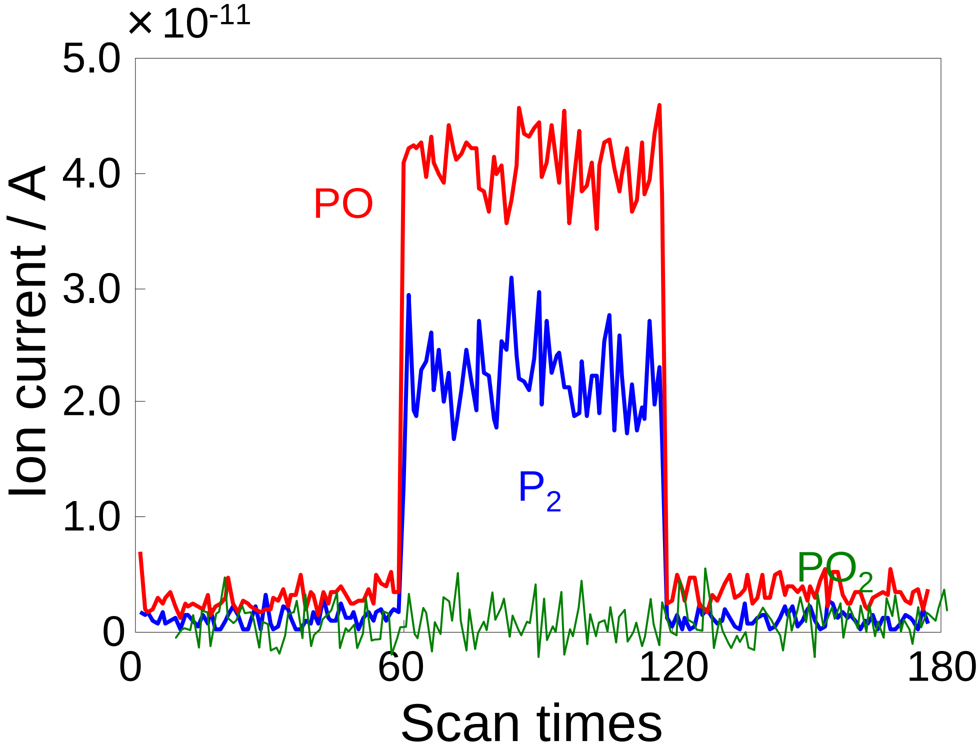
In this study,
equilibrium between $(CaO)_4P_2O_5$ and CaO,
equilibrium between $(CaO)_4P_2O_5$ and $(CaO)_3P_2O_5$
were investigated
at 1523 – 1623 K.



Phase diagram of CaO-P_2O_5 system

Investigation on Gas Species

Measurement on equilibrium between $(CaO)_4P_2O_5$ and CaO



Ion currents from a mixture of $(CaO)_4P_2O_5$ and CaO

Ion currents of 47, 62

PO, P_2

P_2 and PO in equilibrium with P_2O_5 in the mixture could be detected

Kambayashi et al. reported

In the case of PbO-P_2O_5, FeO-P_2O_5

Ion current of PO, P_2, and PO_2 was detected by mass spectrometer. P_2O_5 in oxide system was in equilibrium with these gases.

Ref. S. Kambayashi, H. Awaka and E. Kato: Tetsu-to-Hagane, 71, 1985, pp. 1911-1918.

Principle of Measurement

It can be assumed that the activities of tetra-calcium phosphate ($(CaO)_4P_2O_5$) and calcium oxide (CaO) in the mixture set to unity, since the compounds are stoichiometric.

If pressures of PO and P_2 in equilibrium with the mixture of tetra-calcium phosphate ($(CaO)_4P_2O_5$) and calcium oxide (CaO) can be measured, free energy change of following reaction can be obtained.

$$4\mathrm{CaO(s)} + 5\mathrm{PO(g)} = \mathrm{(CaO)_4P_2O_5(s)} + \frac{3}{2}\mathrm{P_2(g)}$$

$$\Delta G^0 = -RT \ln \frac{a_{\mathrm{(CaO)_4P_2O_5}} \cdot p_{\mathrm{P_2}}^{\frac{3}{2}}}{a_{\mathrm{CaO}}^4 \cdot p_{\mathrm{PO}}^5}$$

⬇

Gibbs energy of formation of $(CaO)_4P_2O_5$

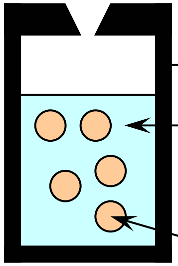
Principle of Measurement

P_2 pressure Fixed by charging Cu-P alloy with sample

Calculate with the data in literature

$$\frac{1}{2}P_2 = P\,(1\,\text{wt\% in liquid Cu})$$

$$\Delta G^0 = -125000 + 0.54T \quad \text{J/mol}$$



Assembly of sample

Ref. M. Iwase, E. Ichise, and N. Yamada; Steel. Res., 56, 1985, pp. 319-326.

PO pressure Measured by double Knudsen mass spectrometry

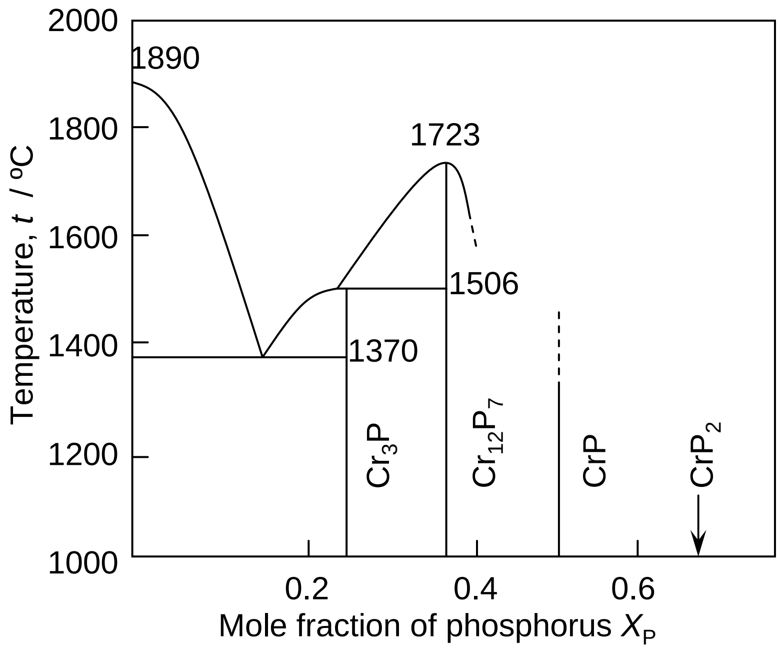
Reference Mixture

Reference substance of PO: **Mixture of Cr, Cr_3P, and Cr_2O_3**

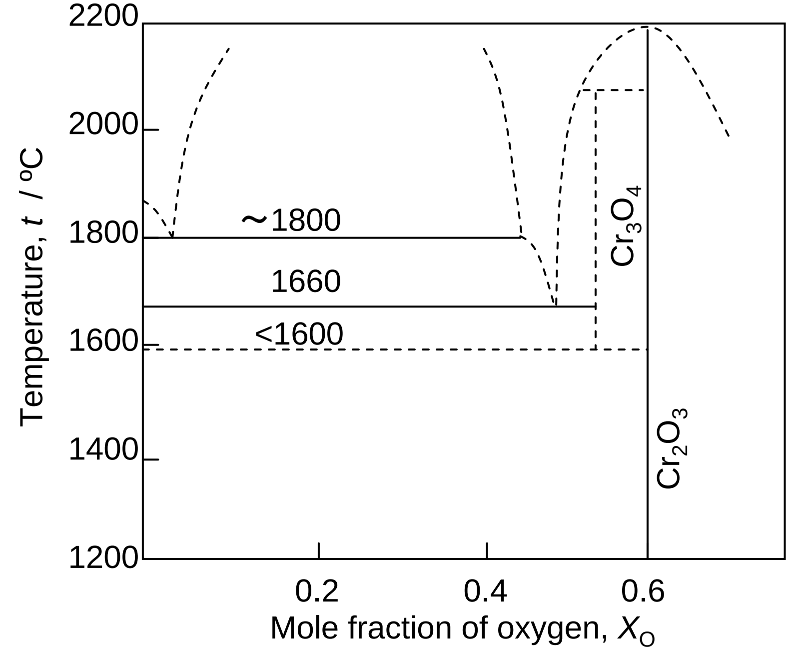
Solubility of oxygen and phosphorus to chromium is insignificant.

Cr_2O_3 and Cr_3P are stoichiometric compound.

Pressure of PO and P_2 in equilibrium with a mixture of Cr, Cr_3P, and Cr_2O_3 can be calculated with Gibbs energy of formation of Cr_3P and Cr_2O_3

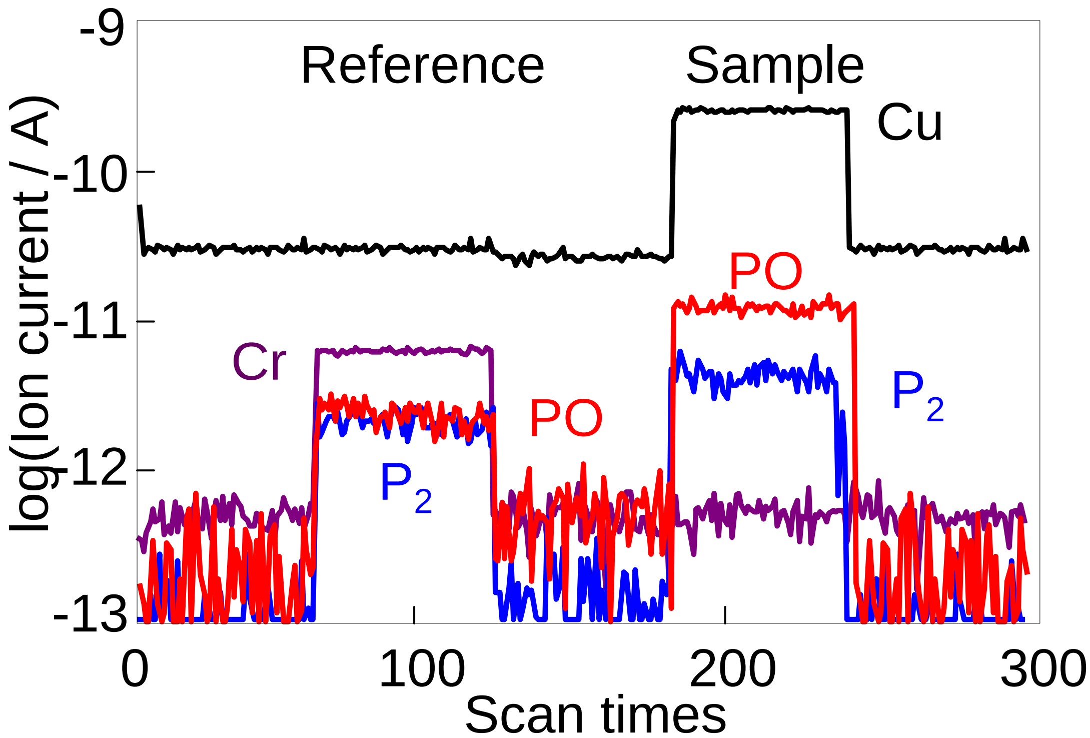


Phase diagram of Cr-P



Phase diagram of Cr-O

Results - Ion Current from Specimen



Ion currents during measurement on the mixture of $(CaO)_4P_2O_5$ and CaO

Detection of Ion Currents

Reference (Cr, Cr_3P, Cr_2O_3)

Mass-to-ratio (*e*/*z*) 47, 52, 62

PO, Cr, P_2

Sample (CaO-P_2O_5 compounds with Cu-P alloy)

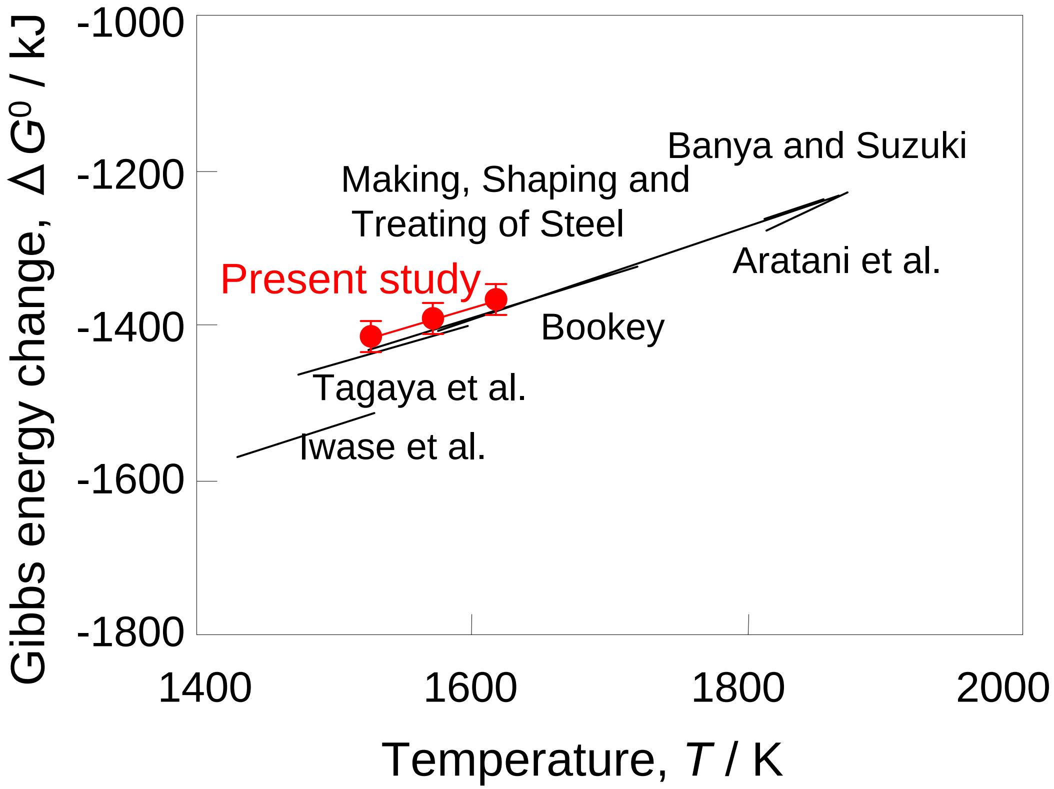
Mass-to-ratio (*e*/*z*) 47, 62, 63

PO, P_2, Cu

$$\frac{p_{\text{PO in sample}}}{p_{\text{PO in reference}}} = \frac{I_{\text{PO in sample}}}{I_{\text{PO in reference}}}$$

The Gibbs energy of formation of $(CaO)_4P_2O_5$ was estimated with these pressure.

Results - Thermodynamic Data of $(CaO)_4P_2O_5$



$$4CaO(s) + P_2(g) + \frac{5}{2}O_2(g) = (CaO)_4P_2O_5(s)$$

$$\Delta G^0 = -2211000 + 520T(\pm 15000) \text{ J}$$

$$4CaO(s) + 5PO(g) = (CaO)_4P_2O_5(s) + \frac{3}{2}P_2(g)$$

$$\Delta G^0 = -RT \ln \frac{a_{(CaO)_4P_2O_5} \cdot p_{P_2}^{\frac{3}{2}}}{a_{CaO}^4 \cdot p_{PO}^5}$$

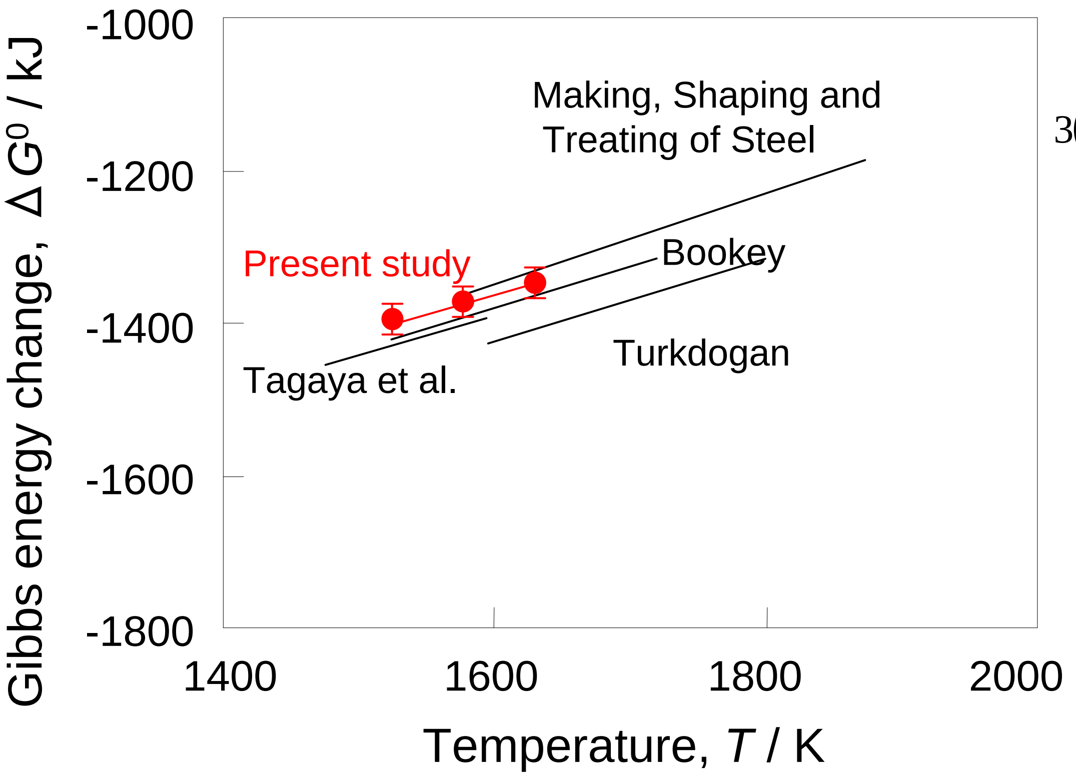
$$a_{(CaO)_4P_2O_5} = a_{CaO} = 1$$

p_{PO} Measured value

p_{P_2} Calculated value

$$\Delta G^0 = 1827000 - 597T(\pm 15000)$$

Results - Thermodynamic Data of $(CaO)_3P_2O_5$



$$3(CaO)_4P_2O_5(s) + 5PO(g) = 4(CaO)_3P_2O_5(s) + \frac{3}{2}P_2(g)$$

$$\Delta G^0 = -RT \ln \frac{a^4_{(CaO)_3P_2O_5} \cdot p^{\frac{3}{2}}_{P_2}}{a^3_{(CaO)_4P_2O_5} \cdot p^5_{PO}}$$

$$a_{(CaO)_4P_2O_5} = a_{(CaO)_3P_2O_5} = 1$$

p_{PO} Measured value

p_{P_2} Calculated value

$$\Delta G^0 = 1735000 - 580T(\pm 15000)$$

$$3CaO(s) + P_2(g) + \frac{5}{2}O_2(g) = (CaO)_3P_2O_5(s)$$

$$\Delta G^0 = -2204000 + 526T(\pm 16000) \quad \text{J}$$

Gas Introducing System

Thermodynamic measurement on oxide and oxide system

Potential of oxygen in experimental system Important factor

Control and grasp of oxygen potential ➡ Accurate measurement

Thermodynamic measurement on CaO - P_2O_5 compounds

$$nCaO(s) + P_2(g) + \frac{5}{2}O_2(g) = (CaO)_n P_2O_5(s)$$

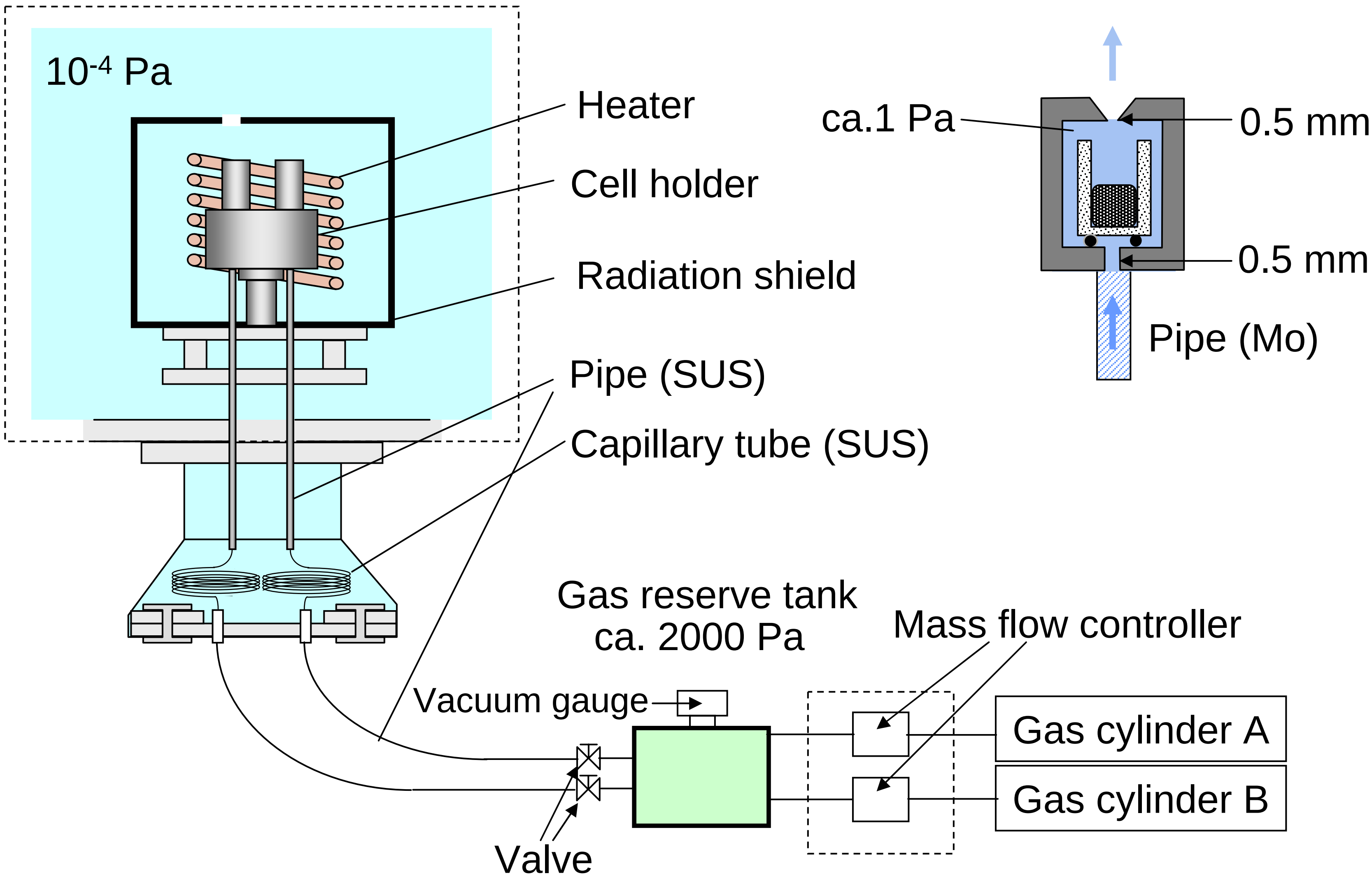
Control and grasp of oxygen potential in Knudsen cell

➡ Objective thermodynamic data can be estimated by P_2 pressure

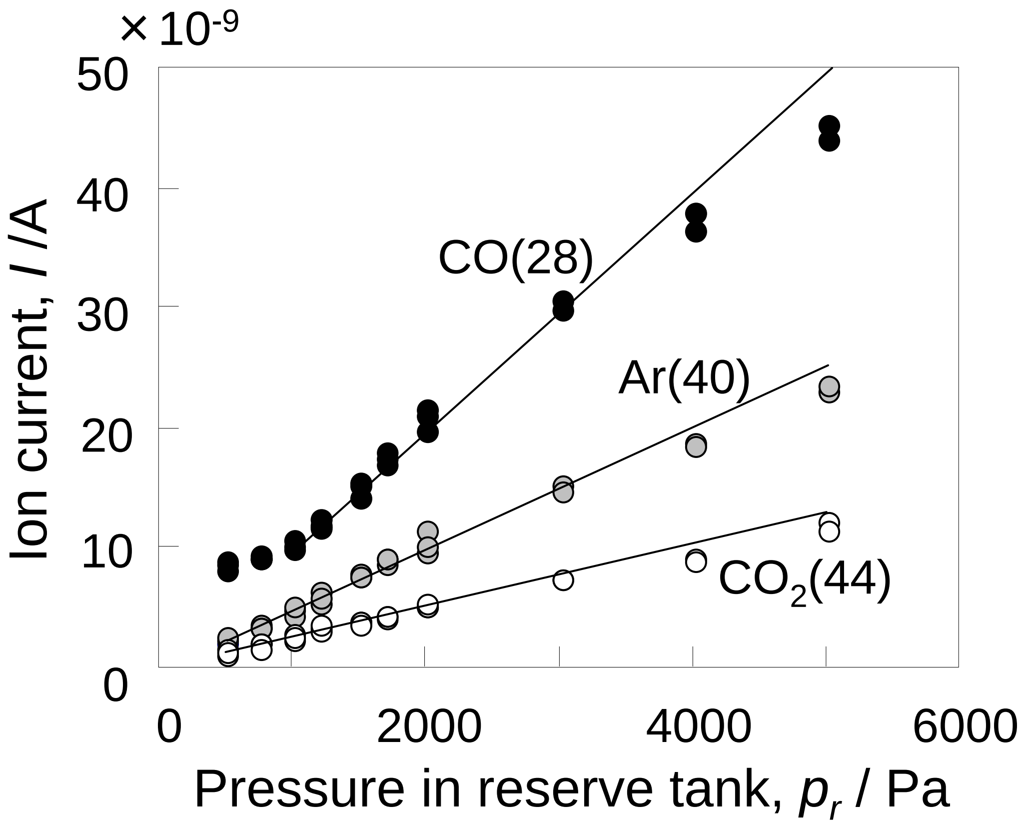
Reference of PO	$Cr/Cr_3P/Cr_2O_3$	1523 – 1623 K
Reference of P_2	Pure P, Metal – P alloys, Phosphides	

It is important to develop the equipment with introducing gas system for double Knudsen cell mass spectrometry in the sense of permitting measurement in various experimental condition.

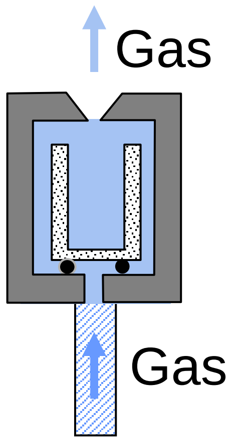
Gas Introducing System



Ion Currents Introduced Gases



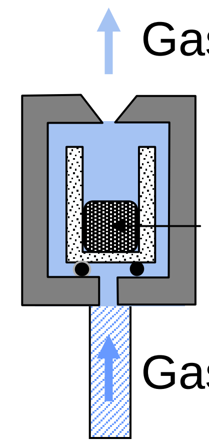
Relationship between ion current and pressure in reserve tank of introducing gas



Ion Currents form Cu-P Alloy with $CO\text{-}CO_2$ Mixture

Ion current from Cu-P alloy with introducing $CO\text{-}CO_2$ mixture

Ratio of gases ($CO:CO_2$)	Potential of O_2 p_{O_2}/p^0	Ion current, I / A 47 (PO)	62 (P_2)	63 (^{63}Cu)
—	—	—	1.88×10^{-13}	5.28×10^{-11}
CO	—	—	1.84×10^{-13}	5.53×10^{-11}
100:1	4.01×10^{-17}	1.61×10^{-12}	1.88×10^{-13}	5.27×10^{-11}
10:1	4.01×10^{-15}	2.64×10^{-11}	1.89×10^{-13}	5.35×10^{-11}
5:1	1.60×10^{-14}	8.32×10^{-11}	1.90×10^{-13}	5.17×10^{-11}
1:1	4.01×10^{-13}	4.35×10^{-10}	1.88×10^{-13}	5.22×10^{-11}
1:5	1.00×10^{-11}	1.76×10^{-9}	1.84×10^{-13}	5.50×10^{-11}
1:10	4.01×10^{-11}	1.90×10^{-9}	1.91×10^{-13}	5.45×10^{-11}
1:100	4.01×10^{-9}	2.09×10^{-9}	1.94×10^{-13}	5.51×10^{-11}
CO_2	—	2.55×10^{-9}	1.88×10^{-13}	5.27×10^{-11}



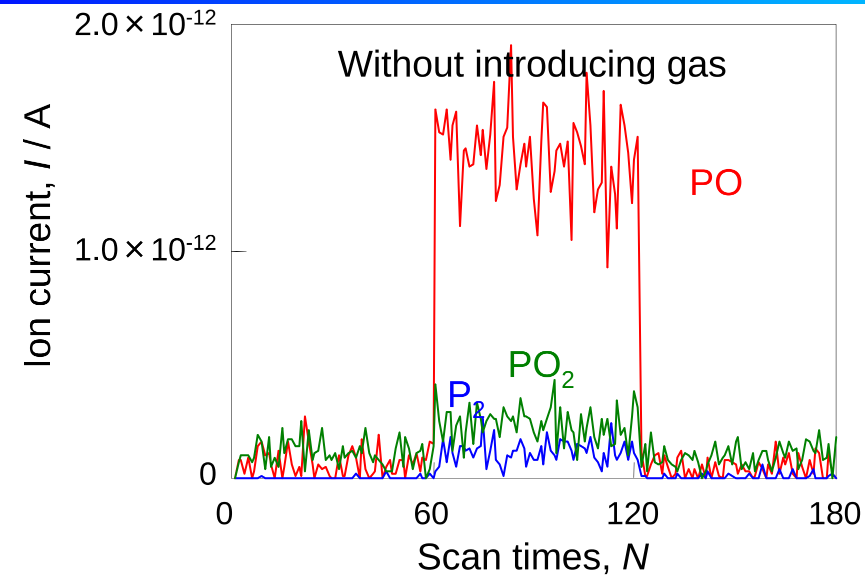
Sample, Pure Cu (l)

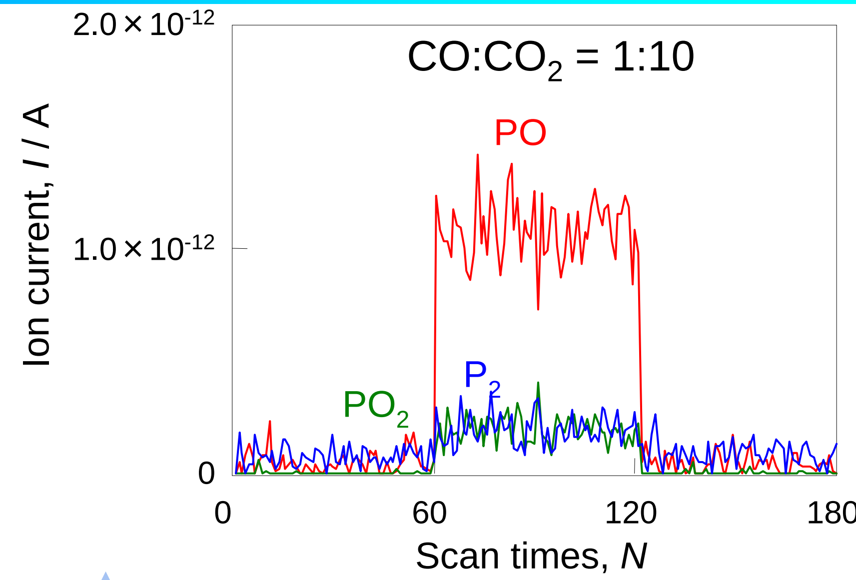
Temperature, 1373 K

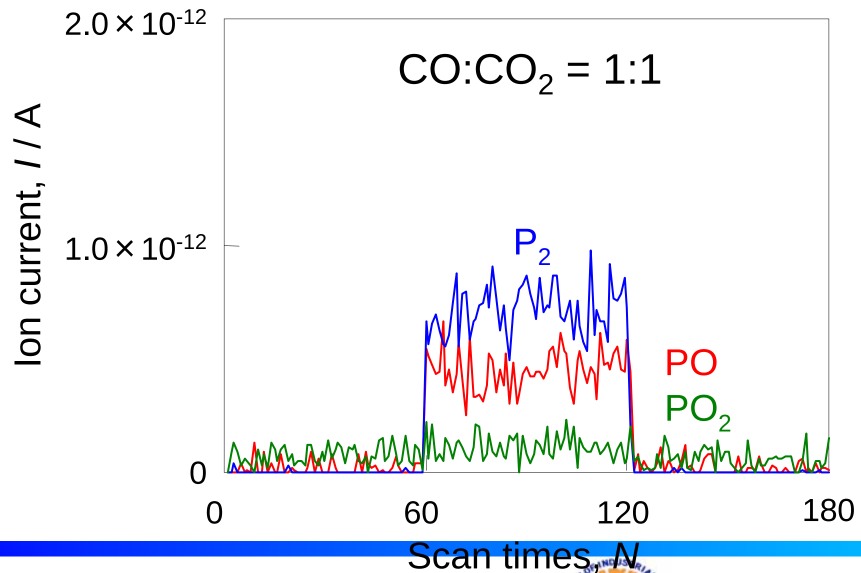
The higher oxygen potential gas was introduced, the larger ion current of PO was detected.

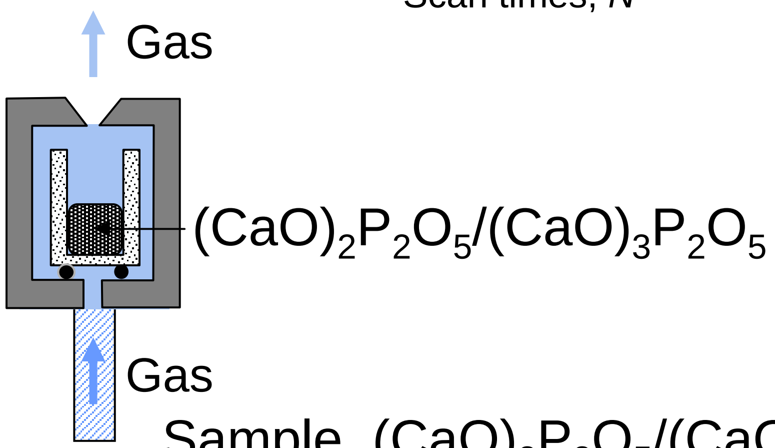
This indicates that the oxygen potential in Knudsen cell was changed by introducing gases.

Ion Currents form $CaO-P_2O_5$ with $CO-CO_2$ mixture









Sample, $(CaO)_2P_2O_5/(CaO)_3P_2O_5$

Temperature, 1173 K

Summary

Pressure of PO in equilibrium with mixtures of CaO-P_2O_5 compounds with Cu-P alloy was measured by double Knudsen cell mass spectrometry using a mixture of Cr, Cr_3P, and Cr_2O_3 as a reference substance.

Gibbs energy changes of the reactions were determined as follows:

$$4CaO(s)+P_2(g)+\frac{5}{2}O_2(g)=(CaO)_4P_2O_5(s) \qquad \Delta G^0=-2211000+520T(\pm 15000)\ \text{J/mol}$$

$$3CaO(s)+P_2(g)+\frac{5}{2}O_2(g)=(CaO)_3P_2O_5(s) \qquad \Delta G^0=-2204000+526T(\pm 16000)\ \text{J/mol}$$

Thermodynamic measurement on oxide system by double Knudsen cell mass spectrometry was successful.

The equipment for double Knudsen cell mass spectrometry with introducing gas system was produced experimentally.

It was successful to introduce gas to Knudsen cell and to change oxygen potential in the cells.