Thermodynamic Measurement for Cr-P Alloy with Double Knudsen Cell Mass Spectrometry

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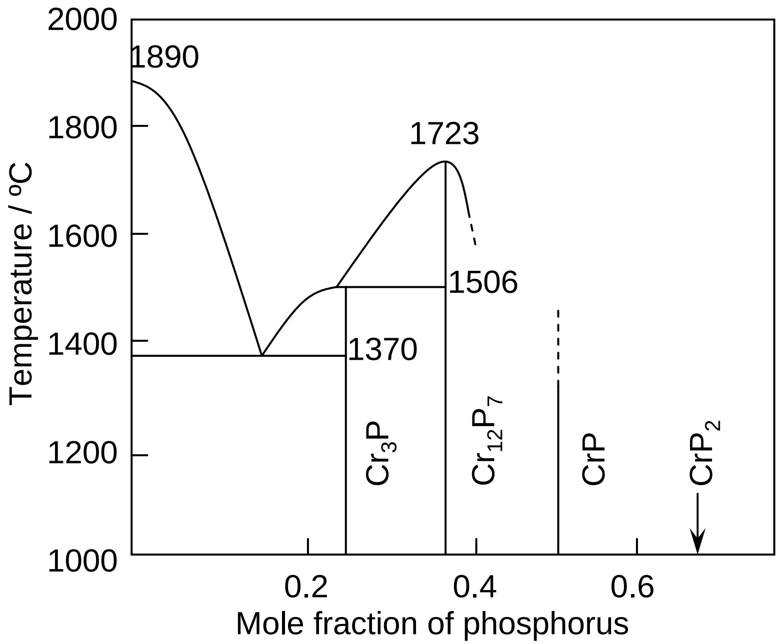
Background

Thermodynamic data of Cr-P system

Development of new technologies

Refining stainless steel and alloys

It is known that this system has some stoichiometric compounds.



Phase diagram of Cr-P

The investigation on these compounds is not enough.

Available thermodynamic data of these compounds is limited.

Previous study on Cr_3P

Myers[1]

Zaitsev et al.[2]

Measurement on P_2 pressure in equiliblium with the mixture of Cr and Cr_3P

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Gibbs energy of formation of Cr_3P

Knudsen effusion technique

Single Knudsen cell mass spectrometry

difference

$$\Delta G_{\mathrm{f}}^{0} = -132000 + 40.5T \quad \Leftrightarrow \quad \Delta G_{\mathrm{f}}^{0} = -244000 + 71.0T$$

[1] C. E. Myers, G. A. Kisacky, and J. K. Klingert; J. Electrochem. Soc., 132 (1985), p. 236.
[2] A. I. Zaitsev, N. E. Shelkova, A. D. Litvina B. M. Mogutnov, and Zh. V. Dobrokhotova; J. Phase Equilib., 19 (1998) p. 191.

Objective

To measure thermodynamic properties of Cr_3P with double Knudsen cell mass spectrometry

Principle of Measurement on thermodynamic data of Cr_3P

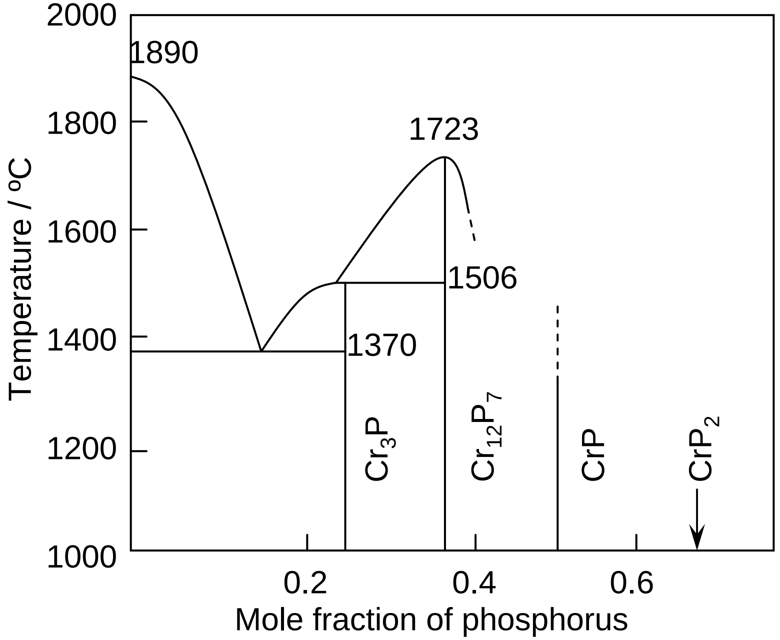
$$3\mathrm{Cr(s)} + \frac{1}{2}\mathrm{P_2(g)} = \mathrm{Cr_3P(s)}$$

$$\Delta G_f^0 = -RT \ln\left(\frac{a_{\mathrm{Cr_3P}}}{a_{\mathrm{Cr}}^3 \cdot p_{\mathrm{P_2}}^{\frac{1}{2}}}\right)$$

The solubility phosphorus to chromium is insignificant.

Cr_3P is stoichiometric compound under eutectic temperature.

Activity of Cr and Cr_3P in the mixture of Cr and Cr_3P could be set to unity.



Phase diagram of Cr-P

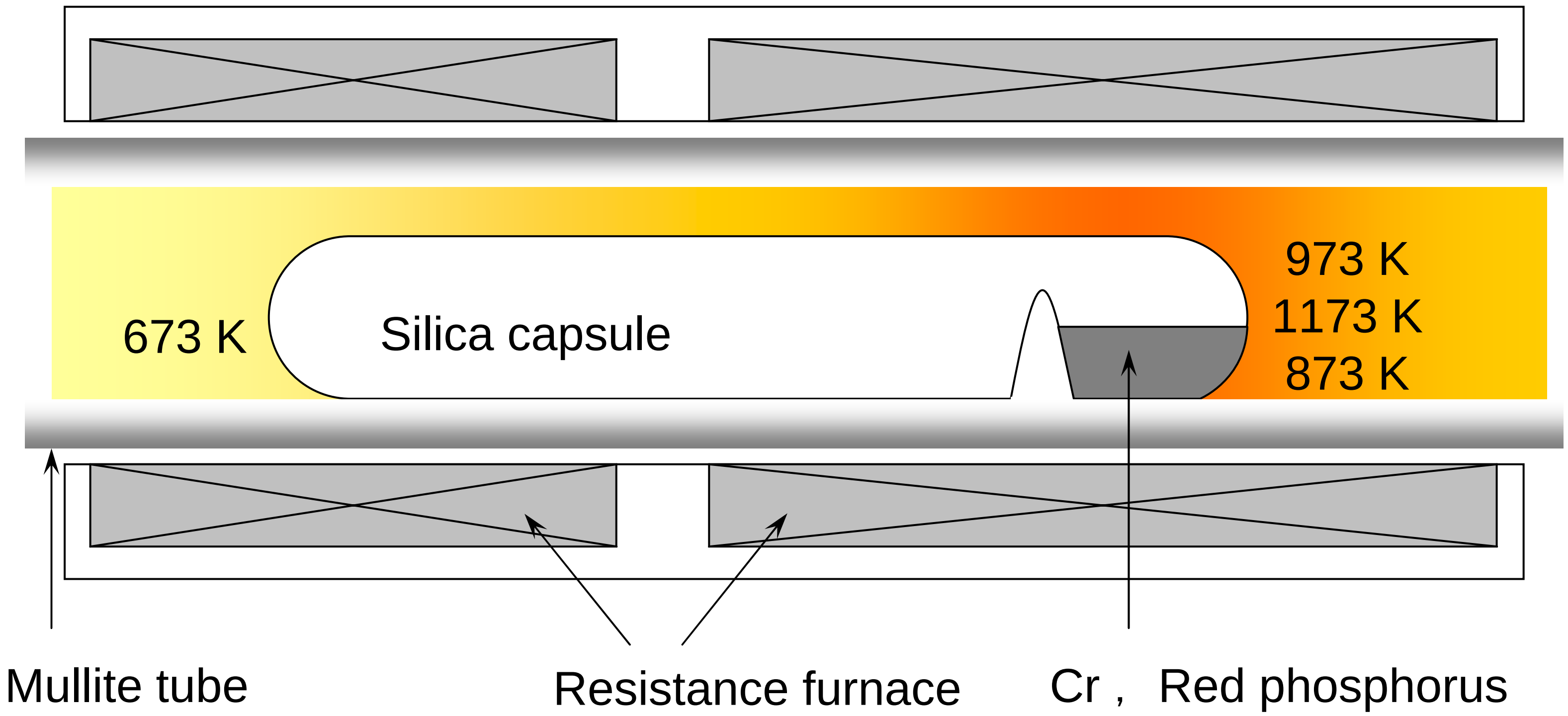
Therefore, the Gibbs energy of formation of Cr_3P can be obtained by measurement on P_2 pressure in equilibrium with the mixture of Cr and Cr_3P.

Preparation of Cr_3P

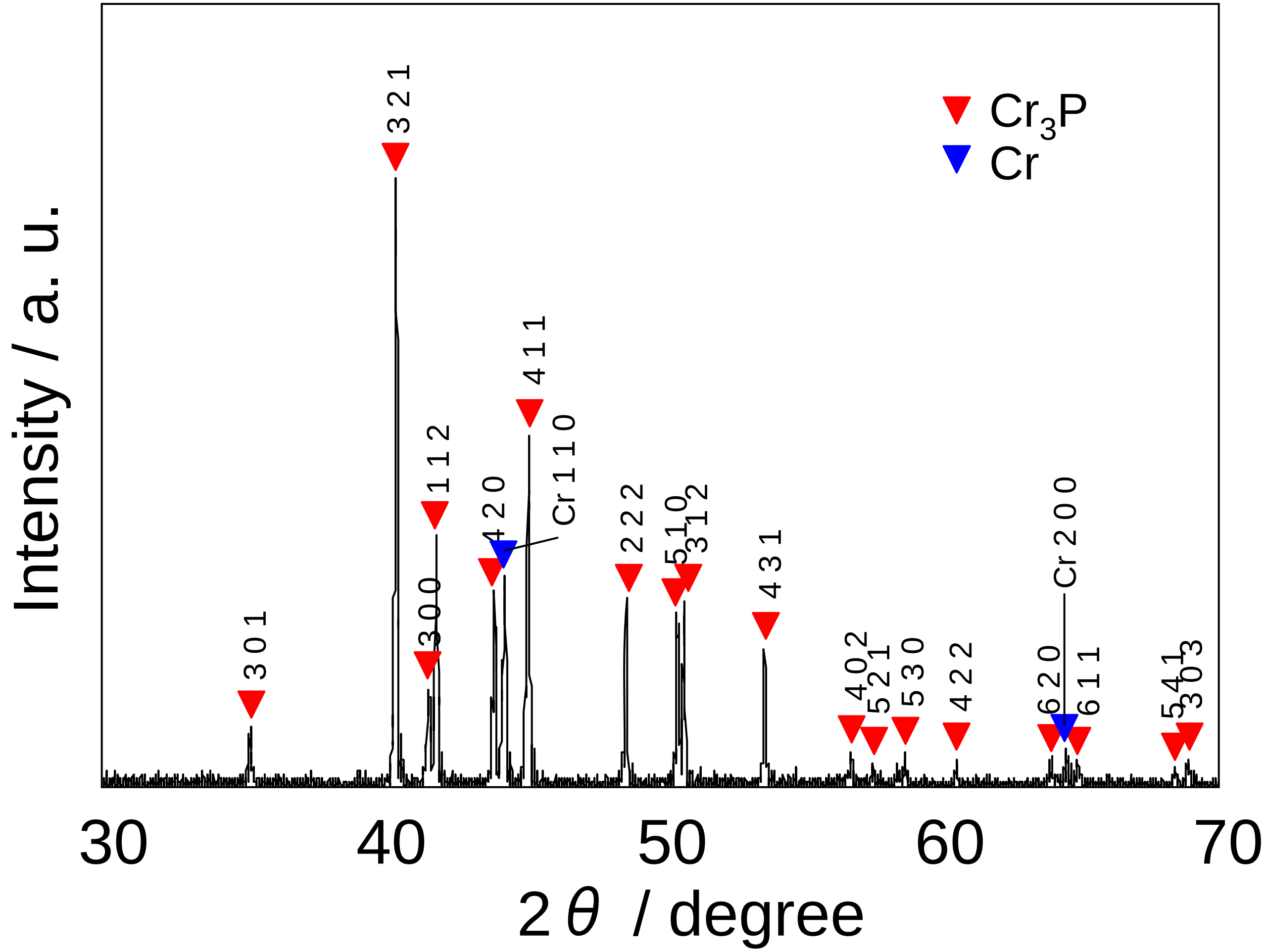
Material : Pure Cr (3N), Red Phosphorus(3N)

Temperature, Time (Sample end) : 973 K 30 hr, 1173 K 7 hr, 873 K 30 hr

Temperature (The other end) : 673 K



XRD Pattern of product



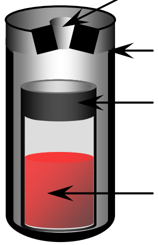
The mixture of Cr and Cr_3P was obtained.

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

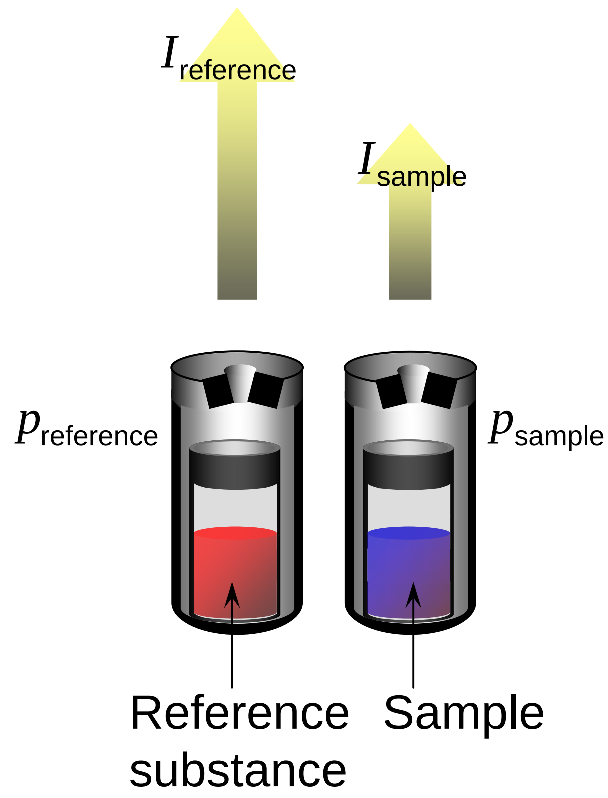
Cell 1: Reference substance

Reference substance has well known pressure of objects of measurement.

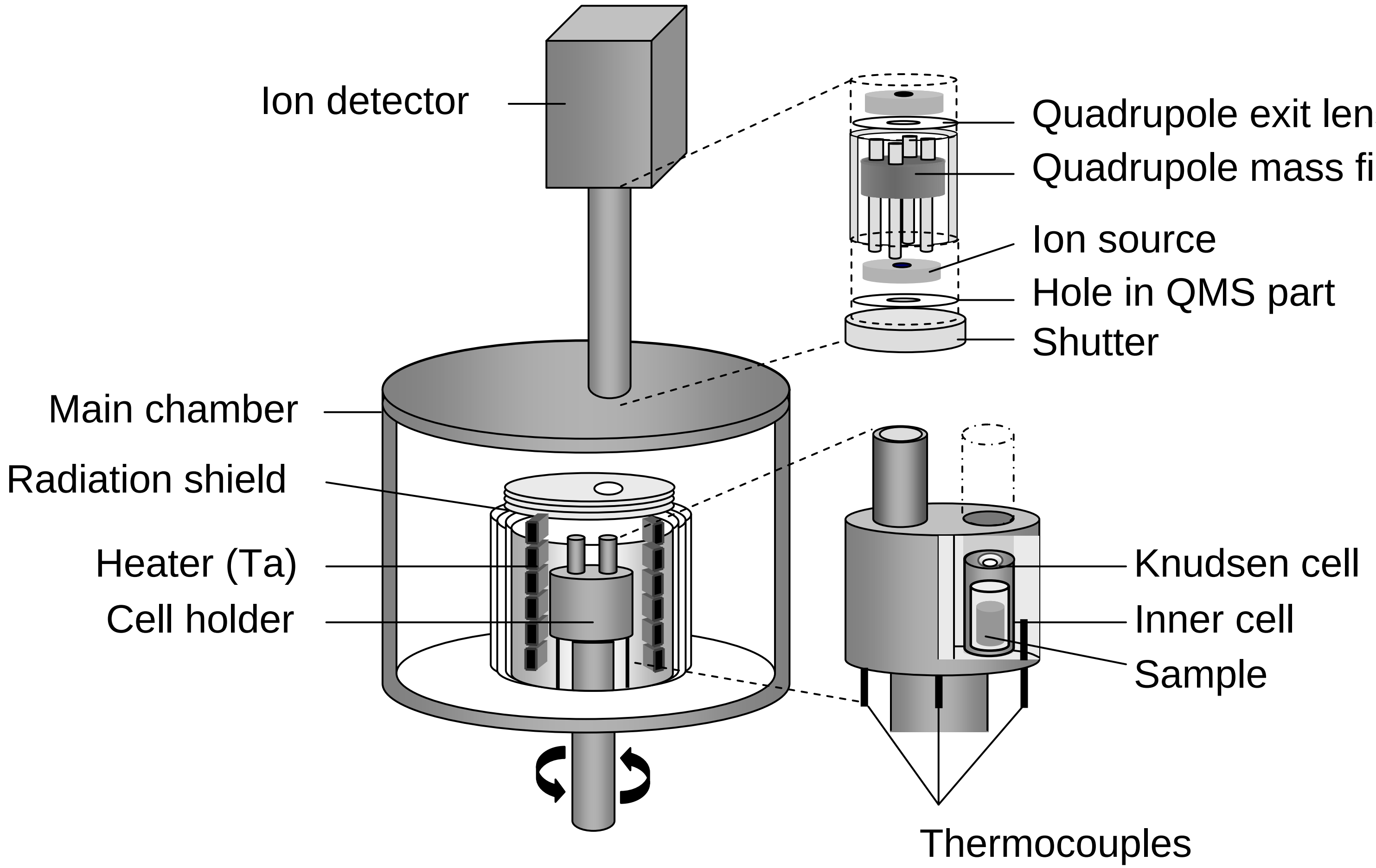
Compare ion currents from sample and reference substance

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

Avoid influence of device constant

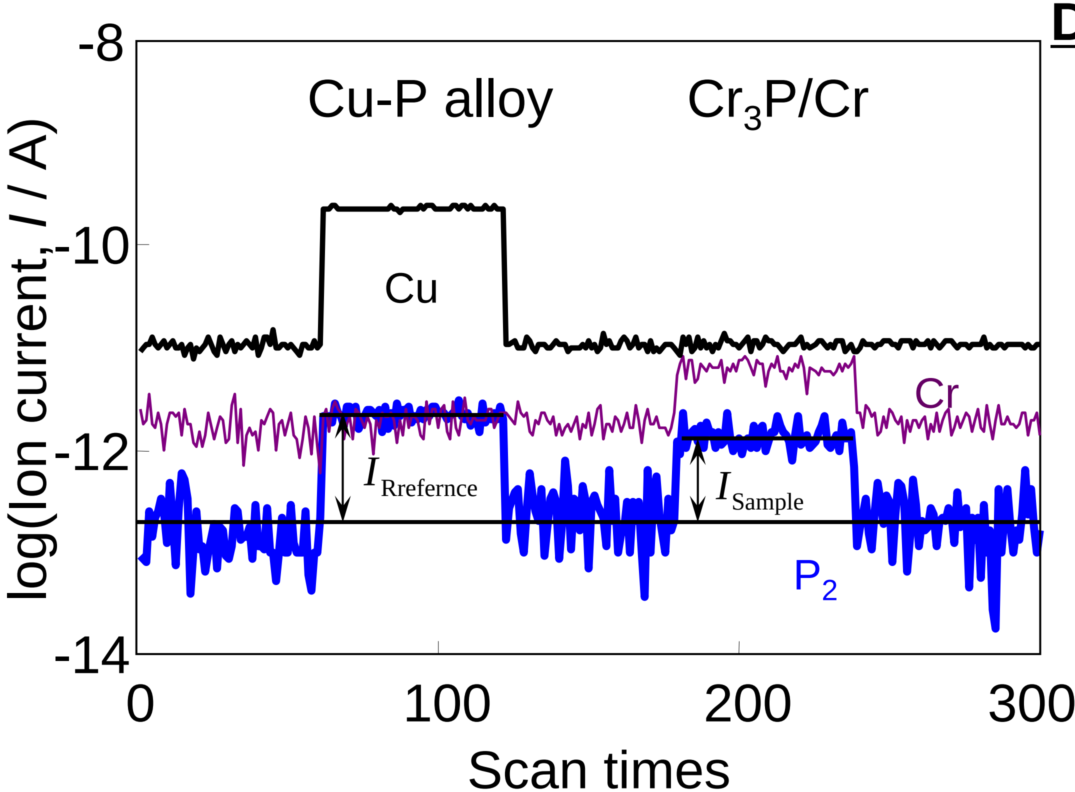


Equipment for Double Knudsen Cell Mass Spectrometry



Equipment for Double Knudsen Cell Mass Spectrometry

Results - Ion Current from Samples



Ion currents during measurement

Reference substance Cu-P alloy P : 0.90 wt%

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

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

Detection of Ion Currents

Sample (Cr and Cr_3P)

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

^{52}Cr, $^{31}P_2$

Reference (Cu-P alloy)

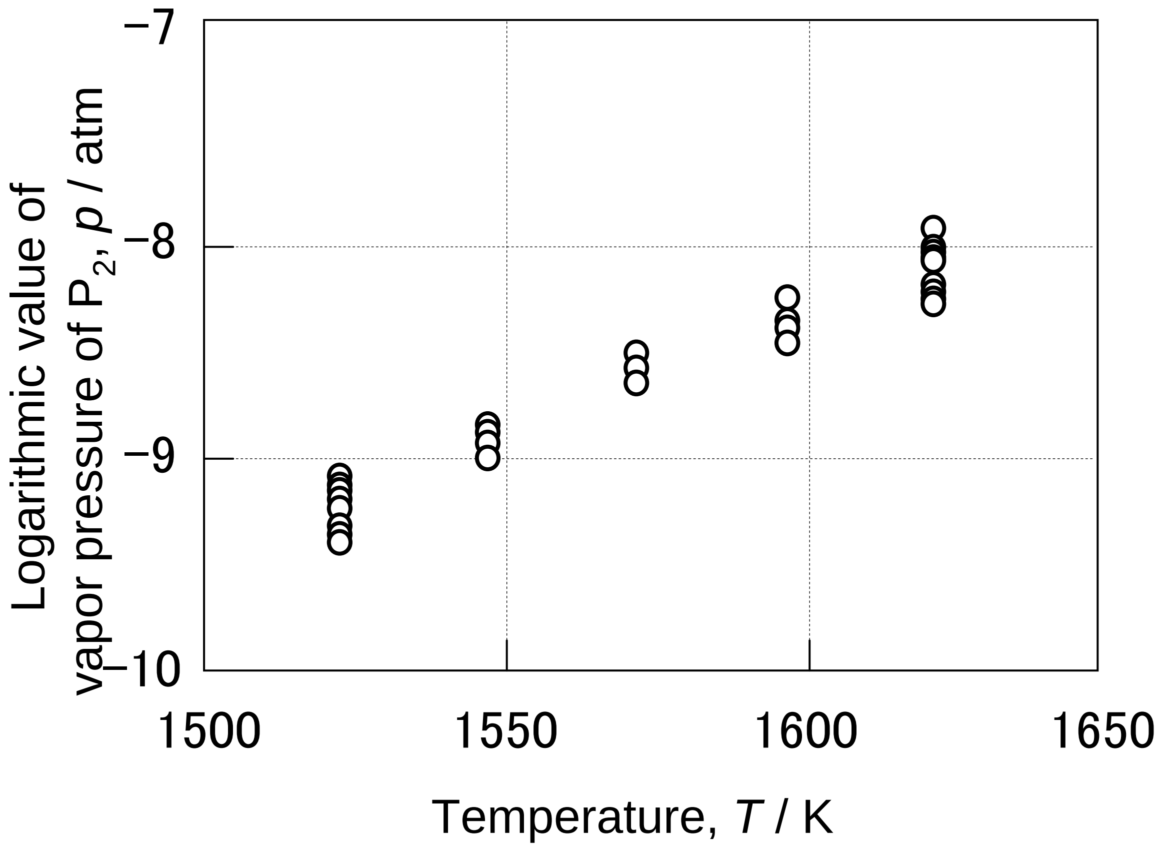
Mass-to-ratio (e/z), 62, 63, 65

$^{31}P_2$, ^{63}Cu, ^{65}Cu

$$\frac{p_{P_2\ \mathrm{in\ sample}}}{p_{P_2\ \mathrm{in\ reference}}} = \frac{I_{P_2\ \mathrm{in\ sample}}}{I_{P_2\ \mathrm{in\ reference}}}$$

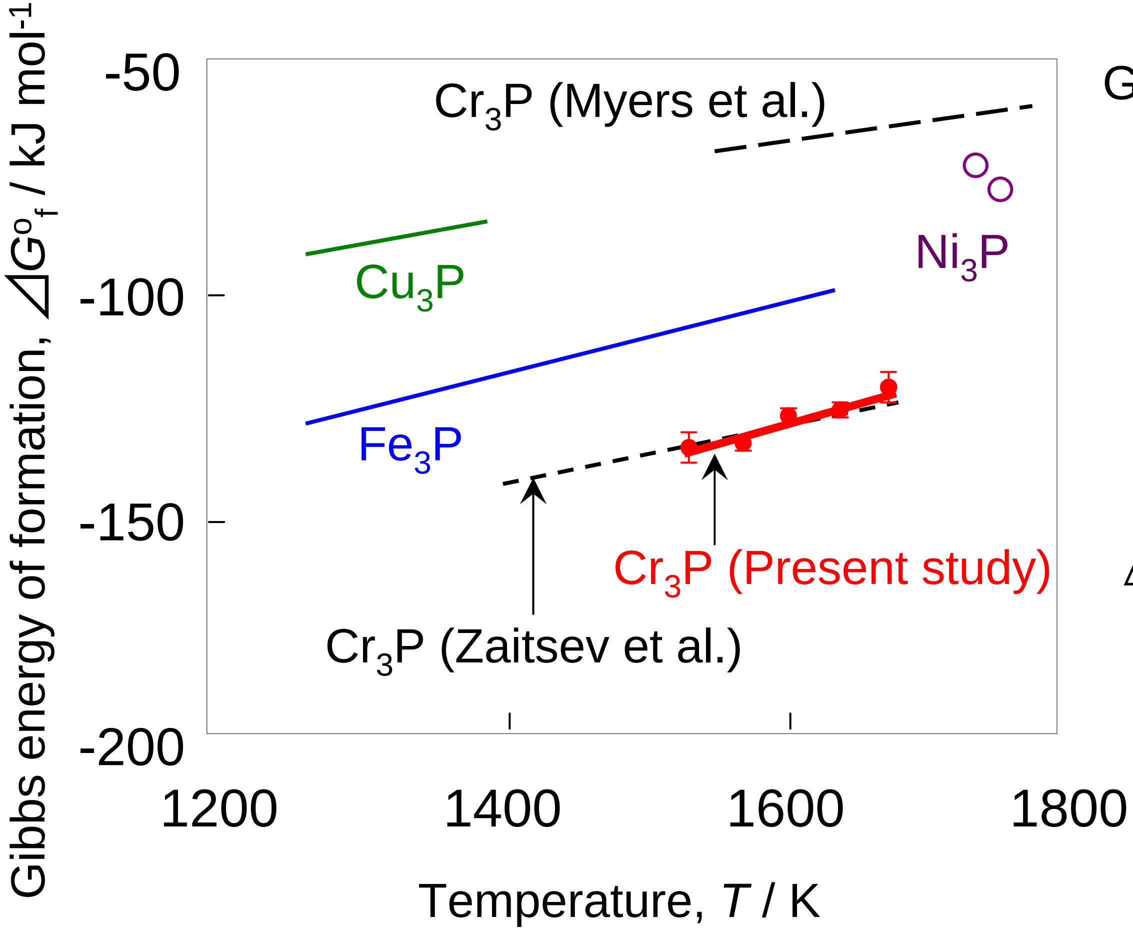
P_2 pressure in sample was obtained by comparison of ion currents.

Results - Pressure of P_2



P_2 pressure in equilibrium with a mixture of Cr and Cr_3P

Results - Gibbs Energy of Formation of Cr_3P



Gibbs energy of formation of phosphides

Gidds energy of formation of Cr_3P

$$3\mathrm{Cr(s)} + \frac{1}{2}\mathrm{P_2(g)} = \mathrm{Cr_3P(s)}$$

$$\Delta G^0_{\mathrm{f}} = -RT\ln\left(\frac{a_{\mathrm{Cr_3P}}}{a^3_{\mathrm{Cr}} \cdot p^{\frac{1}{2}}_{\mathrm{P_2}}}\right)$$

$$\Delta G^0_{\mathrm{f}} = -261000 + 83.0T\left(\pm 6800\right) \text{ J/mol}$$

Gidds energy of formation of Cr_3P is good agreement with Zaitsev's data.

The Gibbs energy of formation of Cr_3P was smaller than those of copper, iron, and nickel.

Summary

P_2 Pressure in a mixture of Cr and Cr_3P at 1523 – 1623 K was measured by double Knudsen cell mass spectrometry.

Gibbs energy of formation of Cr_3P was determined as follows:

$$3\mathrm{Cr(s)} + \frac{1}{2}\mathrm{P_2(g)} = \mathrm{Cr_3P(s)}$$

$$\Delta G_\mathrm{f}^0 = -261000 + 83.0T\left(\pm 6800\right) \quad \text{J/mol}$$