

Determination of Gibbs free energy of formation of Cr₃P by double Knudsen cell mass spectrometry

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Abstract

The vapor pressure of phosphorus in equilibrium with a mixture of elemental Cr and Cr₃P at (1523 to 1623) K was estimated by double Knudsen cell mass spectrometry with a Cu–P alloy as a reference substance. The Gibbs free energy of formation of Cr₃P was calculated from the vapor pressure as follows:



$$\Delta_f G^\circ = -261,000 + 83.0(T/\text{K}) \pm 6800 \text{ J} \cdot \text{mol}^{-1} \quad (1523 < T/\text{K} < 1623)$$

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1. Introduction

Thermodynamic information on the Cr–P system is of great importance for both theoretical and practical applications. It forms a scientific foundation for the development of new metallic materials with required physicochemical properties and also for the development of new technologies for refining stainless steels and alloys.

According to the phase diagram in figure 1 [1], intermediate compounds of Cr₃P, Cr₁₂P₇, CrP, and CrP₂ are reported to exist in this system. However, there are many uncertainties concerning this phase diagram, and thermodynamic properties of these compounds.

The thermodynamic data for the Cr–P system available in the literature consist primarily of two investigations. The two methods are similar and based on vapor pressure mea-

surement generated by decomposing lower phosphides. Myers *et al.* [1] reported the Gibbs free energies of formation of Cr₃P, Cr₁₂P₇, and CrP determined by a Knudsen effusion technique. Zaitsev *et al.* [2] obtained those of Cr₃P and Cr₁₂P₇ by Knudsen cell mass spectrometry with some metals as reference substances. The Gibbs free energies they reported differ considerably from each other [3]. One reason could be that several of experiments by Myers *et al.* were performed at higher temperatures than the Cr–Cr₃P eutectic point, 1643 K. The accuracy of the data of Zaitsev *et al.* is also disputable because their data were derived using calibration method and an ionized cross-section of phosphorus gas, which generally results in large errors. Thus, it is necessary to confirm the data.

In this study, the Gibbs free energy of formation of Cr₃P was determined by the vapor pressure measurement of phosphorus in equilibrium with a mixture of elemental Cr and Cr₃P at (1523 to 1623) K using double Knudsen mass spectrometry with Cu–P alloy as a reference substance. This method allows us to obtain the

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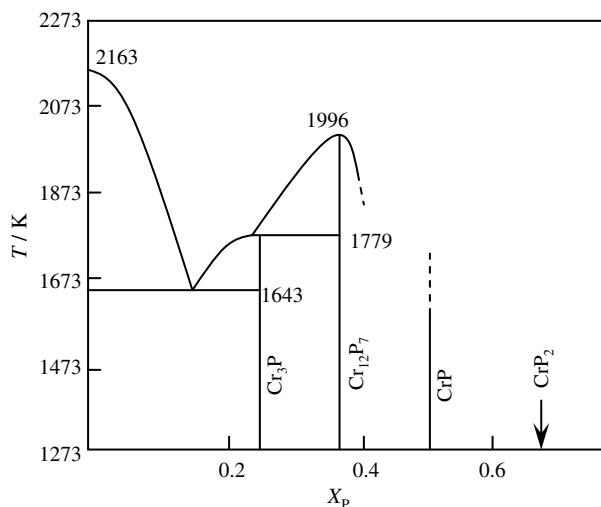
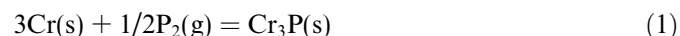


FIGURE 1. Phase diagram of the chromium and phosphorus binary system.

thermodynamic data without use of device constants and ionized cross-sections.

2. Principle of measurement

The Gibbs free energy of formation of Cr_3P can be determined by measuring P_2 pressure in equilibrium with a mixture of solid Cr and Cr_3P based on the following equilibrium:



$$\Delta_f G^\circ = -R(T/\text{K}) \ln \left(\frac{a_{\text{Cr}_3\text{P}}}{a_{\text{Cr}}(p_{\text{P}_2}/p^\circ)^{1/2}} \right) \quad (2)$$

Since the solubility of phosphorus to solid Cr is negligible [1], and Cr_3P exists as a stable phase, the activities of Cr and Cr_3P could be set as unity under $T = 1643$ K. Equation (2) can, therefore, be simplified to

$$\Delta_f G^\circ = \frac{1}{2} R(T/\text{K}) \ln(p_{\text{P}_2}/p^\circ) \quad (3)$$

Double Knudsen cell mass spectrometry (Twin Knudsen cell mass spectrometry) was used for the measurement of vapor pressure [4–7]. A mass spectrometer detects ion current of a species in proportion to vapor pressure of the species. Therefore, in the double Knudsen cell mass spectrometry, the vapor pressure of a species can be obtained according to equation (4) by comparing the ion current of a sample with that of a reference substance for which the vapor pressure is known:

$$p_i \text{ in sample} / p_i \text{ in reference} = I_i \text{ in sample} / I_i \text{ in reference} \quad (4)$$

where p_i and I_i are the vapor pressure and the ion current of species i in equilibrium with a sample or a reference substance, respectively.

The reference substance is usually a pure substance. However, when measuring vapor pressures of phosphorus,

pure condensed phosphorus cannot be used as a reference specimen since the vapor pressure of phosphorus is too high to be measured by the Knudsen method at experimental temperature. In this study, Cu–0.90mass%P alloy was used as the reference substance instead of pure phosphorus. A previous study confirmed that the vapor pressure of P_2 in Cu–P alloys could be accurately measured by Knudsen cell mass spectrometry, and P in molten alloy conforms to Henry's law in the range of P content less than 2.21 mass% [4]. The partial pressure of P_2 in equilibrium with this alloy at the experimental temperature, p_{P_2} in reference, can be calculated by using the following data [8]:

$$1/2\text{P}_2(\text{g}) = \underline{\text{P}} \text{ (1 wt\% in liquid copper)} \quad (5)$$

$$\Delta G_5^\circ = -125,000 + 0.54(T/\text{K})(\pm 5500) \text{ J} \cdot \text{mol}^{-1} \quad (6)$$

3. Experimental

A mixture of Cr and Cr_3P was prepared, consulting the preparation of compounds between Co and P by Myers [9]. Pure Cr powder (99.9%) and red phosphorus powder (99.9%) were mixed at the ratio of the stoichiometric composition of Cr_3P and sealed in a silica capsule 15 mm in diameter and approximately 220 mm length under vacuum (figure 2). One end of the capsule where the mixed powder was placed was heated at 973 K for 30 h, subsequently at 1173 K for 7 h, and then, at 873 K for 30 h in an electric resistance furnace. The other end of the capsule was maintained at about 673 K to be the lowest temperature part. This temperature gradient is required to prevent a catastrophic buildup of phosphorus pressure, since the sublimation pressure of phosphorus reaches $1 \cdot 10^5$ Pa at about 673 K.

Phosphorus concentration of the sample obtained after the above-mentioned procedure was analyzed by inductively coupled plasma atomic spectroscopy (ICP-AES, SPS-4000, Seiko Instruments Inc.), and determined to be (12.4 to 12.7) mass%, which is smaller than the stoichi-

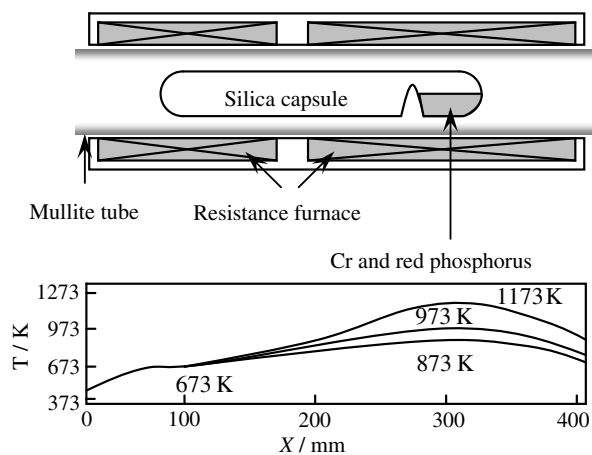


FIGURE 2. Schematic configuration of the apparatus for preparation of Cr_3P .

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