

研究成果報告書

異なる三手法を適用したニオブおよびタンタル
シリサイドの標準生成自由エネルギー測定

1 4 5 5 0 7 2 2

平成 1 4 年度～平成 1 7 年度科学研究費補助金
(基盤研究(C)) 研究成果報告書

平成 1 8 年 5 月

研究代表者 藤原 弘 康
京都大学 工ネルギー科学研究科 助教授

はしがき

本研究では起電力法、化学平衡法ならびにクヌーゼン流出法により、ニオブおよびタンタルのシリサイドの標準生成自由エネルギーを実測することを当初目的とした。

起電力法：溶融リチウムケイ酸塩電解質を用いたシリコン濃淡電池をニオブ-シリコン系に適用したところ、シリコンポテンシャルの実測に成功し所期の目的を達成した。タンタル-シリコン系については電解質構成成分と五酸化ニタンタルが中間化合物を形成するため、所期の平衡関係が保たれないことが明らかになった。化学平衡法：銀-シリコン合金と金属-シリコン2成分系の2固相間のシリコン分配平衡実験を行なったが、平衡の到達に相当な時間を要し、実験手法として現実性に課題があると判断された。クヌーゼン流出法：特に起電力法で標準生成自由エネルギーが得られていないタンタル-シリコン系を主たる対象として実測を試みたが、装置上のトラブルから安定な蒸気圧が得られなかった。

研究計画遂行の初期段階において溶融リチウムケイ酸塩電解質を用いた起電力法について、その実験手法としての有効性が確認されたため、研究の目標に若干の修正を加えて、同実験手法をニオブ、タンタルと同様に耐熱性金属として広く利用されているモリブデンまたはタングステンとシリコンとの2成分系に発展的に適用することとした。これらの測定対象系についても成功裏に起電力測定を完了した。以上の実験結果として、2つのニオブシリサイド、2つのタングステンシリサイドおよび3つのモリブデンシリサイドの標準生成自由エネルギーの実測値を得た。さらに、得られた値に第3法則法を適用して、これらのシリサイドの298Kにおける標準生成エンタルピーを得た。

研究組織

研究代表者：藤原弘康（京都大学・エネルギー科学研究科・助教授）

研究分担者：植田幸富（京都大学・エネルギー科学研究科・助手）

海外共同研究者：Alok Awasthi (Bhabha Atomic Research Center(India)・Material Processing Division・Scientific officer (E))

交付決定額 (配分額)

(金額単位 : 円)

	直接経費	間接経費	合計
平成 1 4 年度	1,200,000	0	1,200,000
平成 1 5 年度	700,000	0	700,000
平成 1 6 年度	800,000	0	800,000
平成 1 7 年度	400,000	0	400,000
総 計	3,100,000	0	3,100,000

研究発表

(1) 学会誌等

- H. Fujiwara, Y. Ueda, A. Awasthi, N. Krishnamurthy and S. P. Garg; "Determination of standard free energy of formation for niobium silicides by EMF measurements using lithium silicate liquid electrolytes"; Journal of Electrochemical Society, vol.150, (2003), No.8, pp.J43/J48
- H. Fujiwara, Y. Ueda, A. Awasthi, N. Krishnamurthy and S. P. Garg; "Thermodynamic study on refractory metal silicides"; Journal of Physics and Chemistry of Solids, vol.66, (2005), pp.298/302
- H. Fujiwara, Y. Ueda, A. Awasthi, N. Krishnamurthy and S. P. Garg; "Determination of the standard free energies of formation for tungsten silicides by EMF measurements using lithium silicate liquid electrolyte "; Journal of Alloys and Compounds, vol.391, (2005) , pp.307/312
- H. Fujiwara and Y. Ueda; "Thermodynamic properties of molybdenum silicides by molten electrolyte EMF measurements", Journal of Alloys and Compounds 投稿済

(2) 口頭発表

- H. Fujiwara, Y. Ueda, A. Awasthi, N. Krishnamurthy and S. P. Garg; "Thermodynamic Study on Refractory Metal Silicides"; International IUPAC conference on High Temperature Materials Chemistry -XI, 19-23 May 2003
- 有井一哉; "起電力法によるモリブデンシリサイドの標準生成自由エネルギー測定", 資源素材学会関西支部若手研究者のための研究発表会, 平成 1 6 年 1 0 月 2 6 日

(3) 出版物

該当なし。

研究成果による工業所有権の出願・取得状況

該当なし。

研究成果

研究成果については既に学会誌に公表している 3 論文の別刷りおよび公表のため学会誌に投稿済みの論文原稿をもって本報告に代える。これらの論文に関する情報は本報告、研究発表 (1) 学会誌等に記載した。

Title:

Thermodynamic properties of molybdenum silicides by molten electrolyte
EMF measurements.

Authors:

Hiroyasu FUJIWARA^{*)} and Yukitomi UEDA^{**)}

^{*)} Corresponding author

Graduate School of Energy Science, Kyoto University, Yoshida-
honmachi, Sakyo-ku, 606-8501 Kyoto, JAPAN

TEL/FAX: +81-75-753-5437

E-mail: fujiwara@energy.kyoto-u.ac.jp

^{**)} Graduate School of Energy Science, Kyoto University, Yoshida-
honmachi Sakyo-ku, Kyoto 606-8501, JAPAN

Keywords:

transition metal alloys and compounds; electromotive force, EMF;
thermodynamic properties

Abstract

EMF measurements on silicon concentration cell were carried out using molten lithium silicate electrolyte in the temperature range 1305 to 1507 K. Using the EMF-temperature relations, the standard free energies of formation for Mo_3Si , Mo_5Si_3 and MoSi_2 have been obtained as functions of temperature: $\Delta_f G^\circ(\text{Mo}_3\text{Si})/\text{kJmol}^{-1} = -122.1 + 0.0027 (T/\text{K}) \pm 0.15$, $\Delta_f G^\circ(\text{Mo}_5\text{Si}_3)/\text{kJmol}^{-1} = -312.9 - 0.0064 (T/\text{K}) \pm 0.26$ and $\Delta_f G^\circ(\text{MoSi}_2)/\text{kJmol}^{-1} = -146.3 + 0.0096 (T/\text{K}) \pm 0.22$, respectively. Combining the results with thermodynamic data, the standard enthalpies of formation for these silicides at 298 K have been calculated as $\Delta_f H^\circ(\text{Mo}_3\text{Si}, 298)/\text{kJmol}^{-1} = -122.1 \pm 6.0$, $\Delta_f H^\circ(\text{Mo}_5\text{Si}_3, 298)/\text{kJmol}^{-1} = -313.5 \pm 12.0$ and $\Delta_f H^\circ(\text{MoSi}_2, 298)/\text{kJmol}^{-1} = -135.8 \pm 4.5$, respectively.

1. Introduction

Silicides of transition metals are well-known for their oxidation resistance. For example, molybdenum disilicide is used as heating element in oxidizing atmosphere for achieving high temperature. Although thermodynamic properties of molybdenum silicides indicate applicability for various practical uses, direct measurements of the standard free energies of formation for molybdenum silicides have been reported only to a limited extent. Chart[1] reported these values for Mo_3Si , Mo_5Si_3 and MoSi_2 , by measuring the vapor pressure of SiO at temperatures from 1410 to 1675 K by Knudsen effusion method. EMF measurements using zirconia electrolyte were performed by Ohmori et al.[2] and they reported these values for Mo_3Si and Mo_5Si_3 at temperatures 1150 to 1450 K. However, the results of these works do not agree with each other. Additionally, assessed and calculated values of the standard free energies of formation for these silicides by Hultgren et al.[3], Barin[4] and Tomasziewicz et al.[5,6] are also inconsistent. The standard enthalpies of formation at 298 K, $\Delta_f H^\circ(298)$, for these three silicides were reported by Searcy and Tharp[7] and Chart[1]. Searcy and Tharp[7] measured the silicon vapor pressure at temperatures from 1926 to 2261 K by Knudsen effusion method and obtained values by combining the heat capacity data. Robbins and Jenkins[8], Maslov et al.[9], Tomasziewicz et al.[5,6], O'Hare[10] and Meschel and Kleppa[11] used calorimetric method for determination of $\Delta_f H^\circ(298)$ values. However, difference in these results is not negligible.

The EMF measurements have been widely used for determination of thermodynamic activity. However, application of these measurements to refractory metal silicide systems has not been so popular, because of high reactivity of silicon and low partial pressure of oxygen determined by Si/SiO₂ equilibrium. In the previous works by the authors[12,13], molten lithium silicate electrolyte was utilized for EMF measurements of the silicon concentration cells for determination of the standard free energies of formation for niobium and tungsten silicides. Because of the potential utility of the method adopted in the previous work, this has been applied for molybdenum silicides in the present study. The temperature range investigated is 1305 to 1507 K. Based on the results, the standard enthalpies of formation at 298 K for Mo₃Si, Mo₅Si₃ and MoSi₂ have also been obtained.

2. Experimentals

2.1 Phase relation and potential diagram

In Figure 1, phase diagram of the Mo – Si binary system [10] is shown together with the isothermal section of the Mo - Si - O ternary system at 1400 K. According to the binary phase diagram, three molybdenum silicides, i.e., Mo₃Si, Mo₅Si₃ and MoSi₂, exist in this system. In this figure, a polymorphic transformation of MoSi₂ at high temperature(2173 K) is omitted. The isothermal section is constructed based on the potential diagram shown in figure 2. In calculation of the relations in

figure 2, present results of EMF measurement (Sec.3.1) and Barin's[4] data of the standard free energy of formation for oxides were used. The solid lines in figure 2 correspond to the two-phase equilibrium except for the lines for SiO_2 and Si (these are represented as gray lines). The points **A**, **B**, **C**, **D** and **Q** in figure 2 correspond to the three-phase triangles **A**, **B**, **C**, **D** and **Q** in the isothermal section shown in figure 1. No ternary compounds have been reported in the literature in the quadrangle Mo-MoO₂-SiO₂-Si for the isothermal section (figure 1). In addition to this, the partial pressure of oxygen at point **Q** is calculated to be much higher than that at point **A** (figure 2). Thus, SiO₂ coexists with each of the phases in the Mo - Si binary system, i.e., Mo, Mo₃Si, Mo₅Si₃ and MoSi₂, at this temperature.

In this study, EMF measurements have been carried out, for the three-phase regions of **A**, **B** and **C**. It should be noted here that solid solubility is estimated to be less than 1 mol % Si in Mo phase at the present experimental temperatures[14]. In addition to this, non-stoichiometry of Mo₅Si₃ phase is not negligible and this phase is assumed to be stable from the stoichiometric composition of Mo₅Si₃: $x(\text{Si}) = 0.375$ to the silicon rich composition: $x(\text{Si}) = 0.400$ within the experimental temperature range[14], where $x(\text{Si})$ is the mole fraction of silicon in the Mo - Si binary system. Thus, consideration of these phase equilibria has been applied in calculation of the standard free energy of formation for the silicides from the EMF values measured (in Sec. 3.2).

2.2 Configuration of the cells

Three kinds of cells were used for EMF measurements, i.e.,

cell(**A**): (-)Mo, Si+(Ag alloy or MoSi₂)+SiO₂ / electrolyte /

Mo+Mo₃Si+SiO₂, Mo(+)

.....(1)

cell(**B**): (-)Mo, Si+(Ag alloy or MoSi₂)+SiO₂ / electrolyte /

Mo₃Si+Mo₅Si₃+SiO₂, Mo(+)

.....(2)

cell(**C**): (-)Mo, Si+(Ag alloy or MoSi₂)+SiO₂ / electrolyte /

Mo₅Si₃+MoSi₂+SiO₂, Mo(+)

.....(3)

The activity of silicon was fixed as unity in the reference electrode of these cells. For this purpose, liquid silver alloy saturated with Si and SiO₂ was chosen. However, three-phase mixture of Si, SiO₂ and MoSi₂ was used for some of the initial experiments[13]. Right hand sides of the cells (**A**) to (**C**) correspond to the three-phase equilibria of **A** to **C** in figures 1 and 2, respectively. Oxide melts of the Li₂O - SiO₂ binary system saturated with SiO₂ were used as electrolyte in all the cells. The ionic conductivity of this electrolyte can be assumed unity[15]. The electrolyte composition was 86 mass%SiO₂. This composition corresponds to the SiO₂-liquidus at 1573 K in the Li₂O - SiO₂ binary phase diagram[16].

2.3 Procedure and Materials

Details on the experimental procedure have been reported

elsewhere[12,13]. Mo₃Si, Mo₅Si₃ and MoSi₂ were synthesized by vacuum heating of the compacted mixture of pure elements(Mo powder: 99.9%, less than 74 μm, Si powder: 99.999%, less than 50 μm, Furuuchi Chemical Co.) at 1473 K for 7.2 ks and at 1873 K for 7.2 ks, respectively. Lithium silicate used as electrolyte was prepared from Li₂CO₃ and SiO₂. The mixture of Li₂CO₃ and SiO₂ was de-carbonated at 1173 K in platinum crucible for 43.2 ks and pre-melted at 1473 K in graphite crucible. Surface carbon of the pre-melted drop of lithium silicate was eliminated by heating at 1273 K in air.

3. Results and discussion

3.1 EMF and activity of the three-phase equilibria

EMF of the cells, $E(\mathbf{A})$, $E(\mathbf{B})$ and $E(\mathbf{C})$, are shown in figure 3. The EMF-temperature relations obtained by the linear regression are:

$$E(\mathbf{A})/\text{mV} = + 319.0 - 0.0090 (T/\text{K}) \pm 0.08 \quad \text{.....(4)}$$

$$E(\mathbf{B})/\text{mV} = + 212.7 + 0.0211 (T/\text{K}) \pm 0.13 \quad \text{.....(5)}$$

$$E(\mathbf{C})/\text{mV} = + 153.4 - 0.0212 (T/\text{K}) \pm 0.40 \quad \text{.....(6)}$$

respectively. The errors in these equations are estimated by the 95% confidence interval for the least square regression. These equations indicate that the temperature dependence of EMF is relatively small for all three cells. This is expected since only condensed phases are involved in the overall cell reactions, for which the entropy change is small. EMF measurements were carried out by increasing and

decreasing temperature, showing no systematic errors in the results. The EMF values obtained with either of the reference electrodes (Sec. 2.2) agree with each other. The X-ray diffraction analysis of the used electrodes showed the presence of the solid phases according to corresponding three-phase equilibrium.

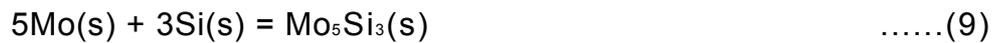
Because the activity of silicon, $a(\text{Si})$, at the reference electrode is unity, the EMF values, $E(\mathbf{A})$, $E(\mathbf{B})$ and $E(\mathbf{C})$, are given as:

$$4FE = -RT \ln a(\text{Si}) \quad \text{.....(7)}$$

Silicon activities at these three-phase equilibria were obtained as functions of temperature within the experimental temperature range (figure 3).

3.2 Standard free energy of formation for silicide

By using the following formation reactions for each molybdenum silicide:



the standard free energy of formation for these silicides, $\Delta_f G^\circ(\text{silicide})$, can be related to the activity of i , $a(i)$, respectively, by the following Eqs.:

$$\Delta_f G^\circ(\text{Mo}_3\text{Si}) = -RT \ln \frac{a(\text{Mo}_3\text{Si})}{a(\text{Mo})^3 a(\text{Si})} \quad \text{.....(11)}$$

$$\Delta_f G^\circ(\text{Mo}_5\text{Si}_3) = -RT \ln \frac{a(\text{Mo}_5\text{Si}_3)}{a(\text{Mo})^5 a(\text{Si})^3} \quad \text{.....(12)}$$

$$\Delta_f G^\circ(\text{MoSi}_2) = -RT \ln \frac{a(\text{MoSi}_2)}{a(\text{Mo}) a(\text{Si})^2}, \quad \dots\dots(13)$$

where the reference states of the activities are pure solid elements and stoichiometric solid compounds. As shown in figure 1, non-stoichiometry of Mo_3Si and MoSi_2 is negligibly small. Then, $a(\text{Mo}_3\text{Si})$ and $a(\text{MoSi}_2)$ for all the cells can be regarded as unity. On the other hand, the Mo_5Si_3 phase is stable within the relatively wide composition range. However, as the composition of the Mo-rich boundary of this phase is nearly consistent with the stoichiometric composition of Mo_5Si_3 : $x(\text{Si})=0.375$, $a(\text{Mo}_5\text{Si}_3)$ for the cell(**B**) can be regarded as unity. The values of $a(\text{Si})$ for the cells (**A**) to (**C**) are obtained directly by Eq.(7) from the EMF values measured. Accordingly, $\Delta_f G^\circ(\text{Mo}_3\text{Si})$, $\Delta_f G^\circ(\text{Mo}_5\text{Si}_3)$ and $\Delta_f G^\circ(\text{MoSi}_2)$ can be obtained by the given values of the activity of molybdenum, $a(\text{Mo})$, using Eqs.(11) to (13), respectively.

For the case of cell(**A**), i.e. Eq.(11), the value of $a(\text{Mo})$ cannot be taken as unity, because solid solubility of silicon is not negligible. In literatures[17-20], solid solubilities within the temperature range from 1589 to 2298 K are available. Based on these data, the solid solubility was extrapolated to experiment temperatures by assuming the Raoult's law for $a(\text{Mo})$, the Henry's law for $a(\text{Si})$ and a linear relation between temperature and the partial molar free energy of mixing for silicon. Further, using the obtained solid solubility, the partial molar free energy of mixing for Mo at region **A**, $RT \ln a(\text{Mo}, \text{at } \mathbf{A})$, is summarized by least square regression as:

$$\{RT \ln a(\text{Mo}, \text{at } \mathbf{A})\} / \text{kJ} = 0.33 - 0.00027 T / \text{K}. \quad \dots\dots(14)$$

This correction yields 0.02 to 0.08 kJ negative value for 1 mole of

molybdenum at experiment temperatures.

For the case of cell(**B**), i.e. Eq. (12), because of stoichiometric Mo₃Si saturation for cell (**B**), $a(\text{Mo})$ can be simply related to $\Delta_f G^\circ(\text{Mo}_3\text{Si})$ and $a(\text{Si at B})$, i.e. $E(\mathbf{B})$, by using Eq. (11):

$$\{RT \ln a(\text{Mo, at } \mathbf{B})\} / \text{kJ} = \{ - (1/3)\Delta_f G^\circ(\text{Mo}_3\text{Si}) - (4/3)FE(\mathbf{B})\} / \text{kJ} \quad \text{.....(15)}$$

For the case of cell(**C**), i.e. Eq. (13), because non-stoichiometry of Mo₅Si₃ is apparent in the phase diagram, Gibbs - Duhem integration is carried out within the composition range of homogeneous Mo₅Si₃ phase. As mentioned in Sec. 2.2, the stability range of composition for Mo₅Si₃ phase is assumed to be constant: $x(\text{Si}) = 0.375$ to 0.400 within the experimental temperature range. The boundary values of $a(\text{Si})$ are given by Eq. (7) and that of $a(\text{Mo})$ is calculated using Eqs. (12) and (7). A linear relation between $RT \ln a(\text{Si})$ and $x(\text{Si})/x(\text{Mo})$, which is the integrated term in Gibbs-Duhem integration, is also assumed for Mo₅Si₃ phase. Thus, $RT \ln a(\text{Mo, at } \mathbf{C})$ could be given as a function of temperature as:

$$\{RT \ln a(\text{Mo, at } \mathbf{C})\} / \text{kJ} = - 27.82 - 0.00673 T / \text{K} \quad \text{.....(16)}$$

The value of $RT \ln a(\text{Mo, at } \mathbf{C})$ becomes 1.47 to 1.58 kJ lower at experimental temperatures due to correction.

Based on these assumptions and experimentally obtained EMFs, the following relations have been obtained:

$$\Delta_f G^\circ(\text{Mo}_3\text{Si})/\text{kJ} = - 122.1 + 0.0027(T/\text{K}) \pm 0.15 \quad \text{.....(17)}$$

$$\Delta_f G^\circ(\text{Mo}_5\text{Si}_3)/\text{kJ} = - 312.9 - 0.0064(T/\text{K}) \pm 0.26 \quad \text{.....(18)}$$

$$\Delta_f G^\circ(\text{MoSi}_2)/\text{kJ} = -146.3 + 0.0096(T/\text{K}) \pm 0.22 \quad \text{.....(19)}$$

In calculation of the standard free energy of formation, solid solubilities of oxygen in the binary Mo - Si phases should be considered. However, oxygen solubilities in Mo and Si phases are negligibly small[14].

Although there are no reports on oxygen solubilities in the silicide phases, the partial pressures of oxygen of the three phase regions **A** to **D** were calculated to be lower than 10^{-20} at 1400 K in figure 2. Therefore, the effect of oxygen addition to the Mo - Si binary system is considered limited in this study.

Figure 4 shows the temperature dependence of the standard free energy of formation for silicides, together with the literature data. Chart[1] reported $\Delta_f G^\circ(\text{Mo}_3\text{Si})$, $\Delta_f G^\circ(\text{Mo}_5\text{Si}_3)$, $\Delta_f G^\circ(\text{MoSi}_2)$ at 1500 K and summarized the results in a set of data: the standard enthalpies and entropies of formation at 298 K and the heat capacities. The present results for Mo_3Si , Mo_5Si_3 and MoSi_2 fairly agree with the reported values by Chart[1]. The value of $\Delta_f G^\circ(\text{Mo}_3\text{Si})$ and $\Delta_f G^\circ(\text{Mo}_5\text{Si}_3)$ by Ohmori et al.[2] is about 16 to 19 kJmol^{-1} higher than the present results. Assessed value by Barin[4] for Mo_5Si_3 shows relatively high temperature dependence. The difference between the value reported by Tomaszkiwicz et al.[5,6] and the present results are less than 10 kJ for Mo_3Si and Mo_5Si_3 . The difference between these assessed data and the present results might have been caused by the selection of the heat capacity and the standard enthalpy of formation for each silicides.

Figure 5 shows the composition dependence of the integral Gibbs energy of Mo - Si alloy at 1400 K. Because two phase equilibria of Mo +

Mo₃Si and Mo₃Si + Mo₅Si₃ appear up to 2293 K in the phase diagram (figure 1), the Gibbs energy of the alloy of $x(\text{Si})=0.25$ must be lower than that of the mixture of Mo and the alloy of $x(\text{Si})=0.375$. This is found valid up to 3500 K by extrapolating the present results. Although the change in the composition of the phase boundary is ignored in this extrapolation, it indicates that the present results do not contradict the phase diagram.

3.3 The standard enthalpy of formation for silicide

By applying the third law method, the standard enthalpy of formation for silicide at 298 K, $\Delta_f H^\circ(\text{silicide}, 298)$, is given as:

$$\Delta_f H^\circ(\text{silicide}, 298) = \Delta_f G^\circ(\text{silicide}, T) - \Delta f_{ef} * T, \quad \dots\dots(20)$$

where Δf_{ef} is the change in the free energy function for the formation reactions of the silicides. The f_{ef} values for the elements are taken from JANAF table[21] and those for the silicides are calculated from the estimated values by Chart[1]. The results of this calculation and the literature data are listed in Table 1. The estimation of errors listed in this table was made by using the error in $\Delta_f G^\circ(\text{silicide}, T)$ represented by Eqs. (17) to (19) and that in f_{ef} . Assuming that the error in f_{ef} for 1 mol of alloy is $1 \text{ JK}^{-1}\text{mol}^{-1}$, the error in $\Delta_f H^\circ(\text{silicide}, 298)$ is estimated to be 6.0, 12.0 and 4.5 kJmol^{-1} for Mo₃Si, Mo₅Si₃ and MoSi₂, respectively. As the difference in calculated values by using the free energy values of 1300 and 1500 K was less than 1.2 kJmol^{-1} , the average of them is indicated in the table. The present results for all the three silicides are in fair agreement with the recent calorimetric results by Tomaszkiwicz[5,6] and O'Hare[10] and

Meschel and Kleppa[11], thus establishing the reliability of the present study.

4. Conclusions

The standard free energies of formation for molybdenum silicides at temperatures from 1305 to 1507 K were determined by EMF measurements by using lithium silicate electrolyte. The results are summarized as follows:

(i) The EMF-temperature relations are

$$E/\text{mV} = + 319.0 - 0.0090 (T/\text{K}) \pm 0.08$$

(-)Mo, Si+(Ag alloy or MoSi₂)+SiO₂ / electrolyte / Mo+Mo₃Si+SiO₂, Mo(+)

$$E/\text{mV} = + 212.7 + 0.0211 (T/\text{K}) \pm 0.13$$

(-)Mo, Si+(Ag alloy or MoSi₂)+SiO₂ / electrolyte / Mo₃Si+Mo₅Si₃+SiO₂,
Mo(+)

$$E/\text{mV} = + 153.4 - 0.0212 (T/\text{K}) \pm 0.40$$

(-)Mo, Si+(Ag alloy or MoSi₂)+SiO₂ / electrolyte / Mo₅Si₃+MoSi₂+SiO₂,
Mo(+)

(ii)The standard free energies of formation for molybdenum silicides are:

$$\Delta_f G^\circ(\text{Mo}_3\text{Si})/\text{kJ} = - 122.1 + 0.0027(T/\text{K}) \pm 0.15$$

$$\Delta_f G^\circ(\text{Mo}_5\text{Si}_3)/\text{kJ} = - 312.9 - 0.0064(T/\text{K}) \pm 0.26$$

$$\Delta_f G^\circ(\text{MoSi}_2)/\text{kJ} = -146.3 + 0.0096(T/\text{K}) \pm 0.22$$

(iii)The standard enthalpies of formation for molybdenum silicides at 298 K are:

$$\Delta_f H^\circ(\text{Mo}_3\text{Si}, 298)/\text{kJmol}^{-1} = - 122.1 \pm 6.0$$

$$\Delta_f H^\circ(\text{Mo}_5\text{Si}_3, 298)/\text{kJmol}^{-1} = - 313.5 \pm 12.0$$

$$\Delta_f H^\circ(\text{MoSi}_2, 298)/\text{kJmol}^{-1} = - 135.8 \pm 4.5$$

Acknowledgment

This study was financially supported by Grant in aid of Japanese Ministry of Education, Culture, Sports and Technology(#14550722). The experimental works by K. Aii (previously graduate school of Kyoto University) are acknowledged.

References

- [1] T. G. Chart; *Met. Sci.* 8(1974) 344-348.
- [2] S. Ohmori, Y. Hashimoto and K. Kohyama; *J High Temp. Soc. Jpn.*(in Japanese) 8(1982),113-118
- [3] R. Hultgren, PD. Desai, DT. Hawkins, M. Gleiser and K. K. Kelly; *Selected values of the thermodynamic properties of binary alloys*, ASM international Metals park(USA), 1973
- [4] I. Barin; *Thermodynamic data of pure substances*, third. Ed., VCH verlagsgesellschaft mbH, Weinheim(FRG), 1995.
- [5] I. Tomaszkiwicz, G.A. Hope, Charles M. Beck II and P.A.G. O'Hare; *J. Chem. Thermodynamics*, 29(1997), 87-98
- [6] I. Tomaszkiwicz, G.A. Hope, Charles M. Beck II and P.A.G. O'Hare; *J. Chem. Thermodynamics*, 28(1996), 29-42
- [7] A. W. Searcy and A. G. Tharp; *J. Phys. Chem.*, 64(1960), 1539-1542
- [8] D. A. Robbins and I. Jenkins; *Acta Metall.*, 3(1955), 598-604
- [9] V. M. Maslov, A. S. Neganov, I. P. Borovinskaya and A. G. Merzhanov; *Fizika Goreniya Vzryvz*, 14(1978), 73-82
- [10] P. A. G. O'Hare; *J. Chem. Thermodynamics*, 25(1993), 1333-43
- [11] S. V. Meschel and P. J. Kleppa; *J. Alloys and Comps.* 274(1998), 193-200
- [12] H. Fujiwara, Y. Ueda, A. Awasthi N. Krishnumurthy and S. P. Garg; *J. Electrochem. Soc.* 150(2003), J43-J48.
- [13] H. Fujiwara, Y. Ueda, A. Awasthi N. Krishnumurthy and S. P. Garg; *J.*

Alloy and Comp. 391(2005), 307-312

[14] T. B. Massalski, H. Okamoto, P. R. Subramanian and L. Kacprzak; Binary Alloy Phase Diagrams, second ed., ASM international, Metals park(USA), 1990.

[15] J. D. Mackenzie; Chem. Rev. 56(1956), 445-70

[16] E. M. Levin, C. R. Robbins and F. McMurdie; Phase Diagrams for Ceramists, vol. 1, The American Ceramic Society, Ohio, 1964.

[17] J. L. Ham; Trans. AIME, 73(1951), 723

[18] R. Kieffer and E. Cerwenka; Z. Metallkd. 43(1952)

[19] V. N. Svechnikov, Yu. A. Kocherzhinskii and L. M. Yupko; Diagrammy Sostoyaniya Metal Sistem Nauka, (1971), 116

[20] A. B. Gokhale and G. J. Abbaschian; J. Phase Equilibria, 12(1991), 493

[21] M. W. Chase, Jr.; NIST-JANAF Thermochemical Tables, 4th ed., ACS, AIP and NIST, New York(USA), 1998.

Captions

Figure 1 Phase diagram of the Mo - Si binary system and the isothermal section of the Mo - Si - O ternary system at 1400 K. Each of the three-phase regions of **A** to **D** and **Q** corresponds to the point **A** to **D** and **Q** in figure 2.

Figure 2 Potential diagram of Mo - Si - O ternary system at 1400 K. Points **A** to **D** and **Q** correspond to the three-phase regions shown in figure 1.

Figure 3 Observed EMF of the cells (**A**), (**B**) and (**C**) plotted against temperature.

Figure 4 The standard free energies of formation for Mo_3Si , Mo_5Si_3 and MoSi_2 compared with the literature data.

Figure 5 Composition dependence of the integral Gibbs energy of the alloy at 1400 K.

Table 1 Comparison of the standard enthalpies of formation for Mo_3Si , Mo_5Si_3 and MoSi_2 reported by various authors.

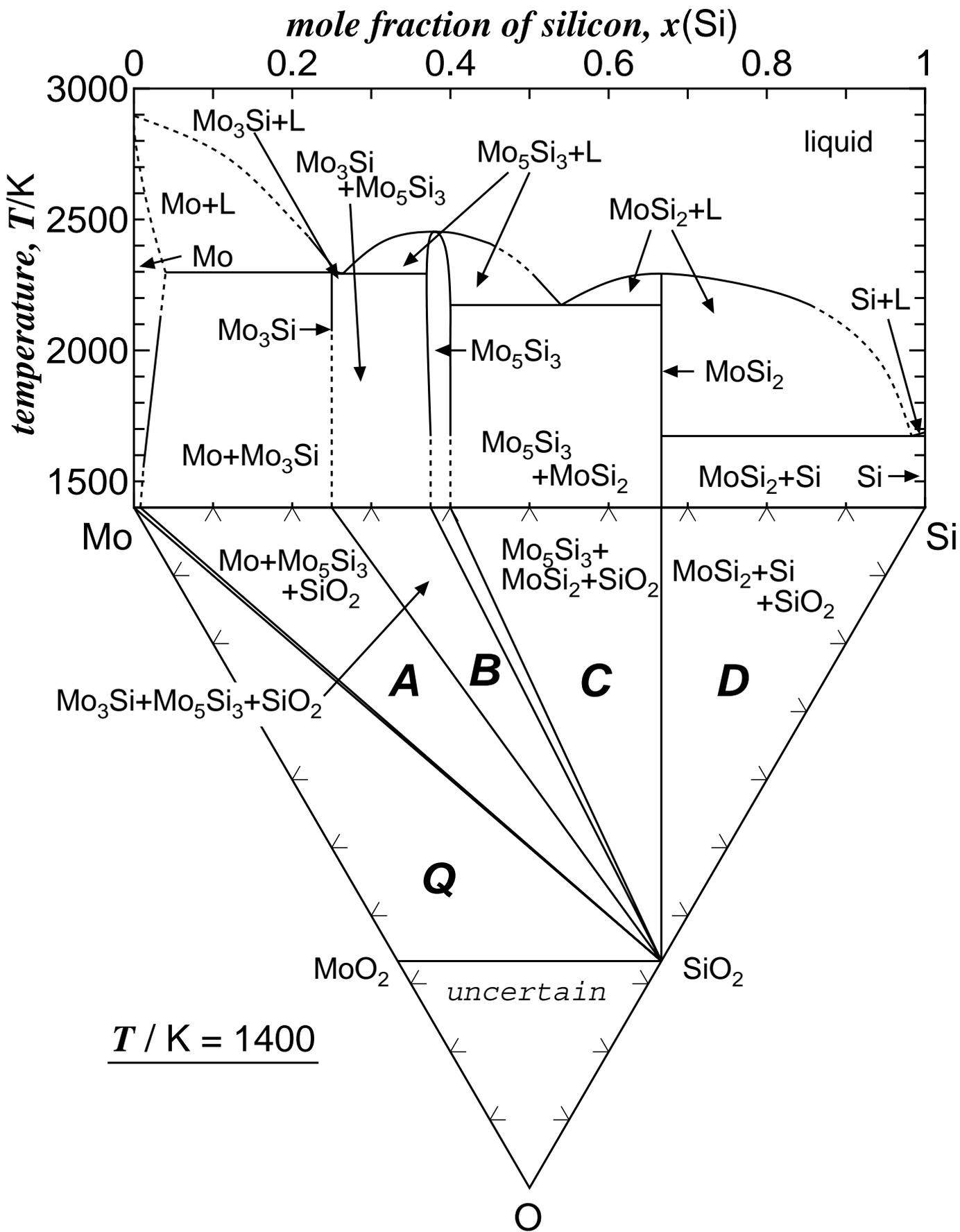


Fig. 1, H. Fujiwara

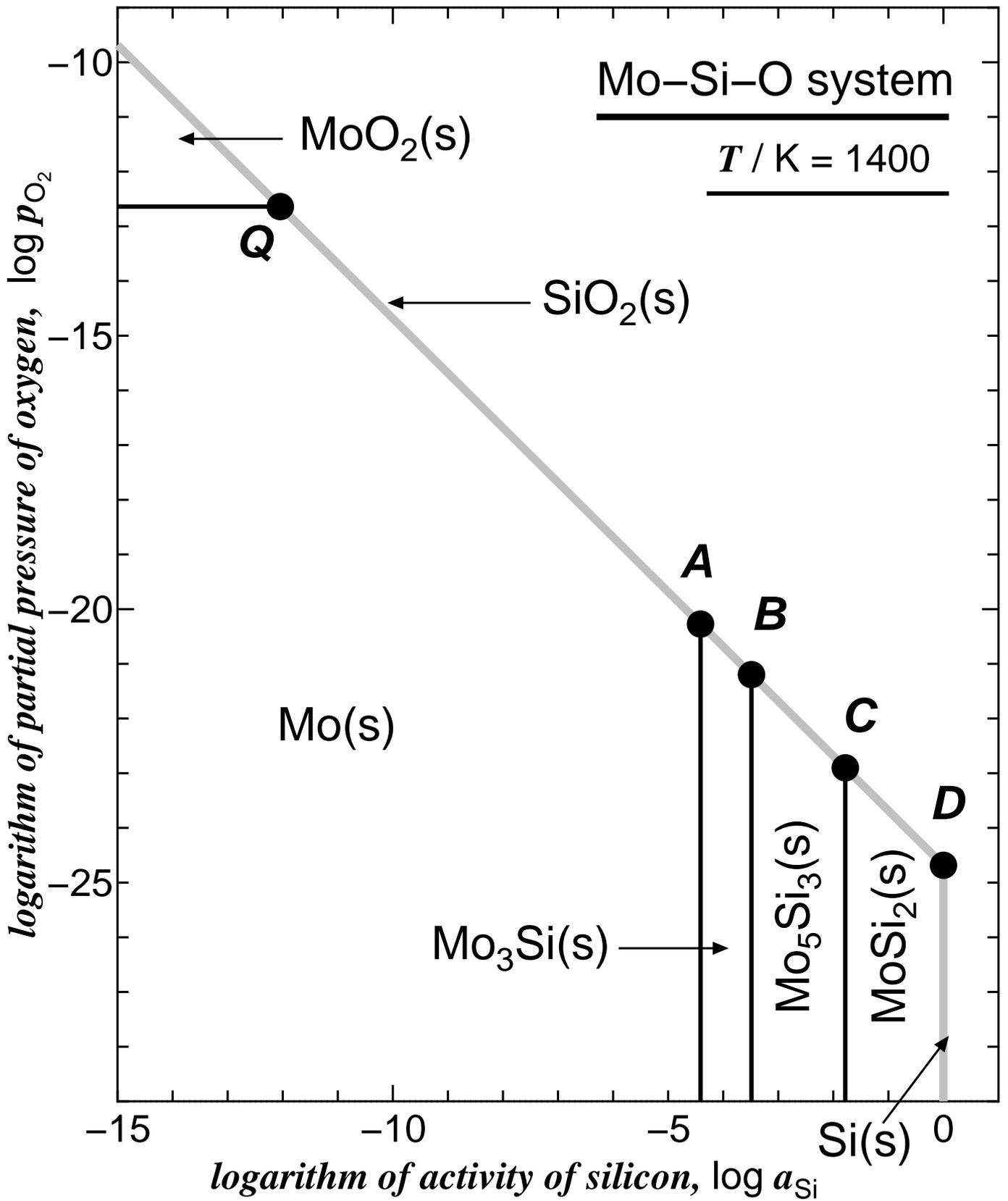


Fig. 2, H. Fujiwara

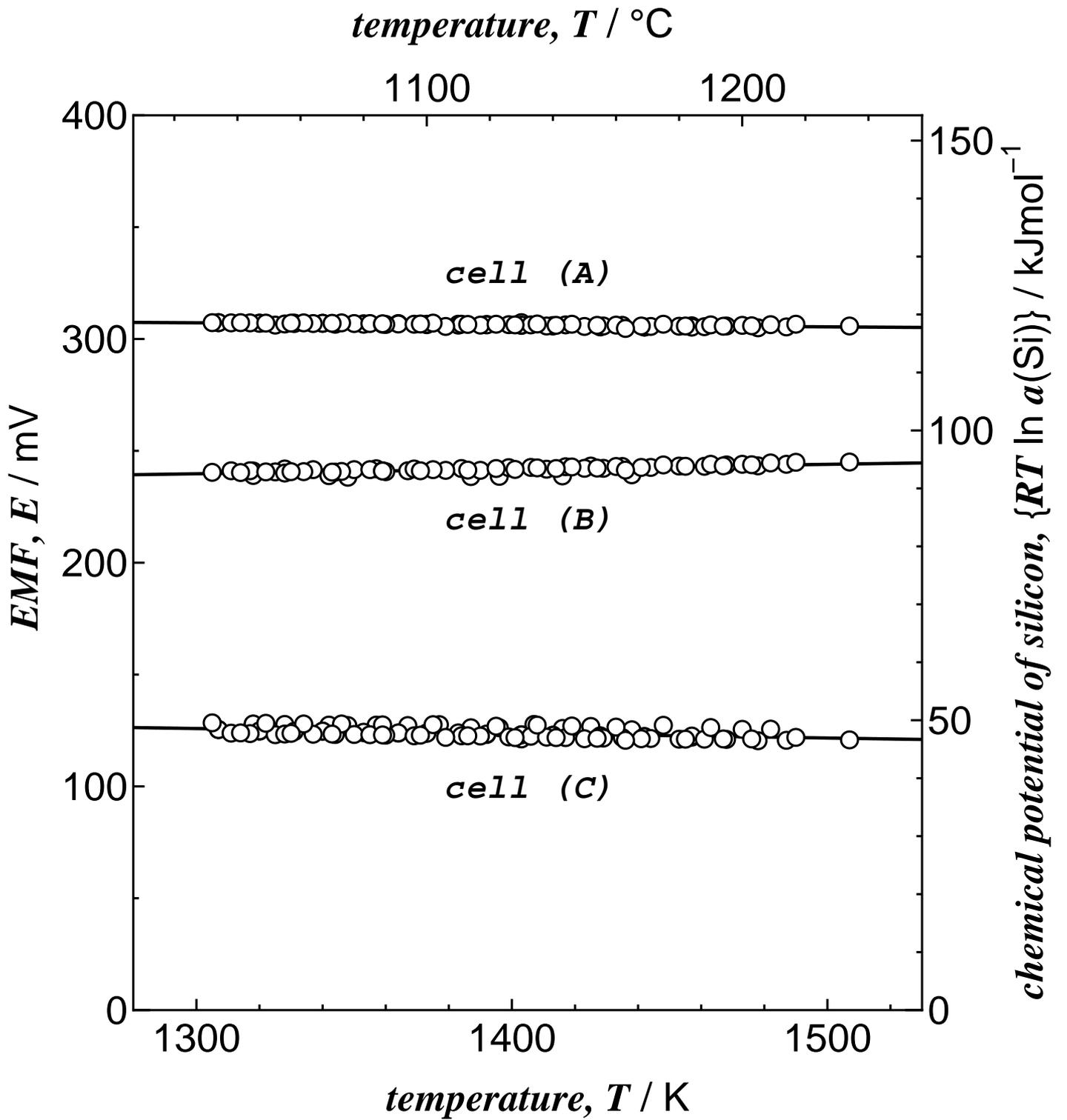


Fig. 3, H. Fujiwara

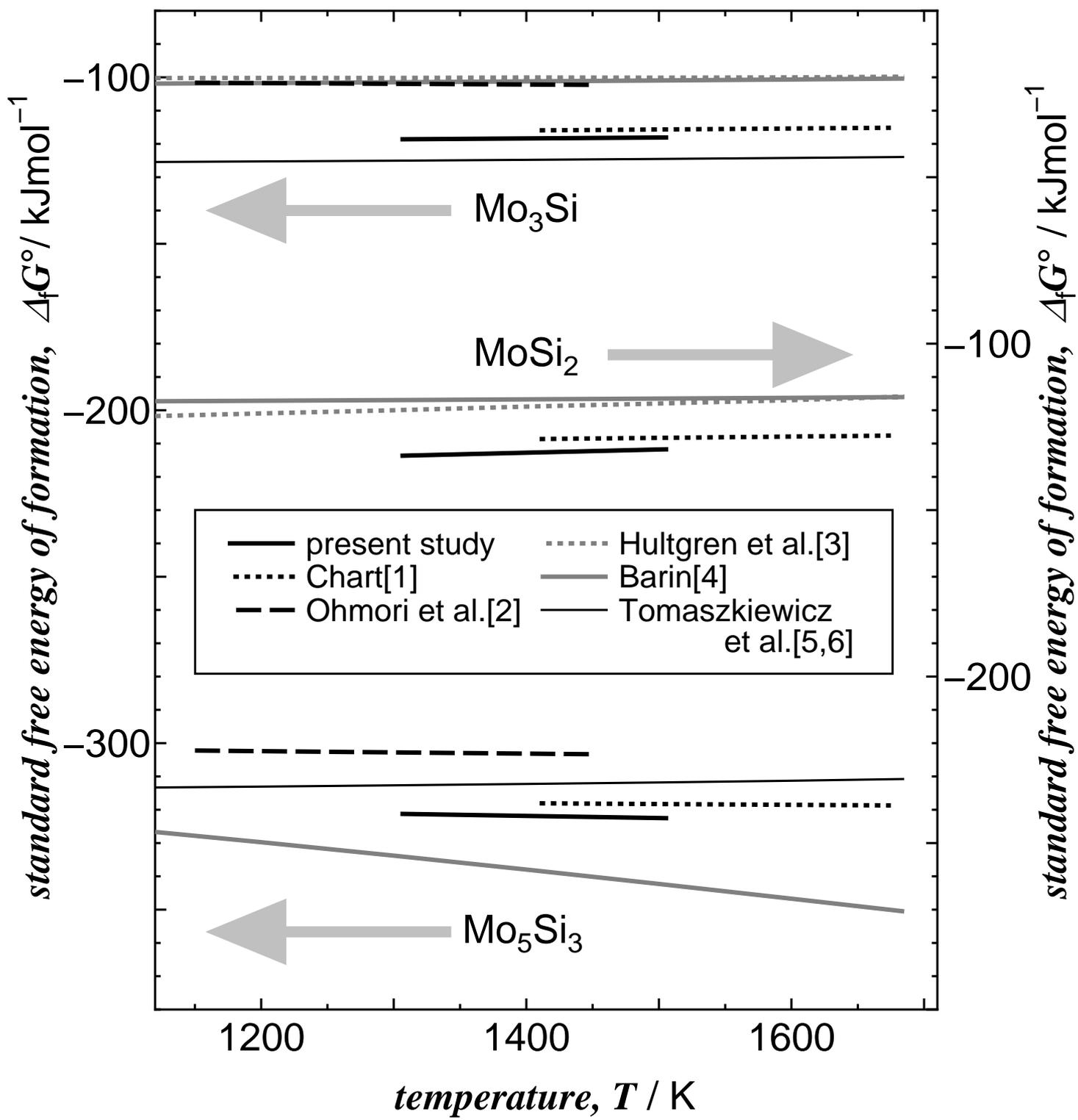


Fig. 4, H. Fujiwara

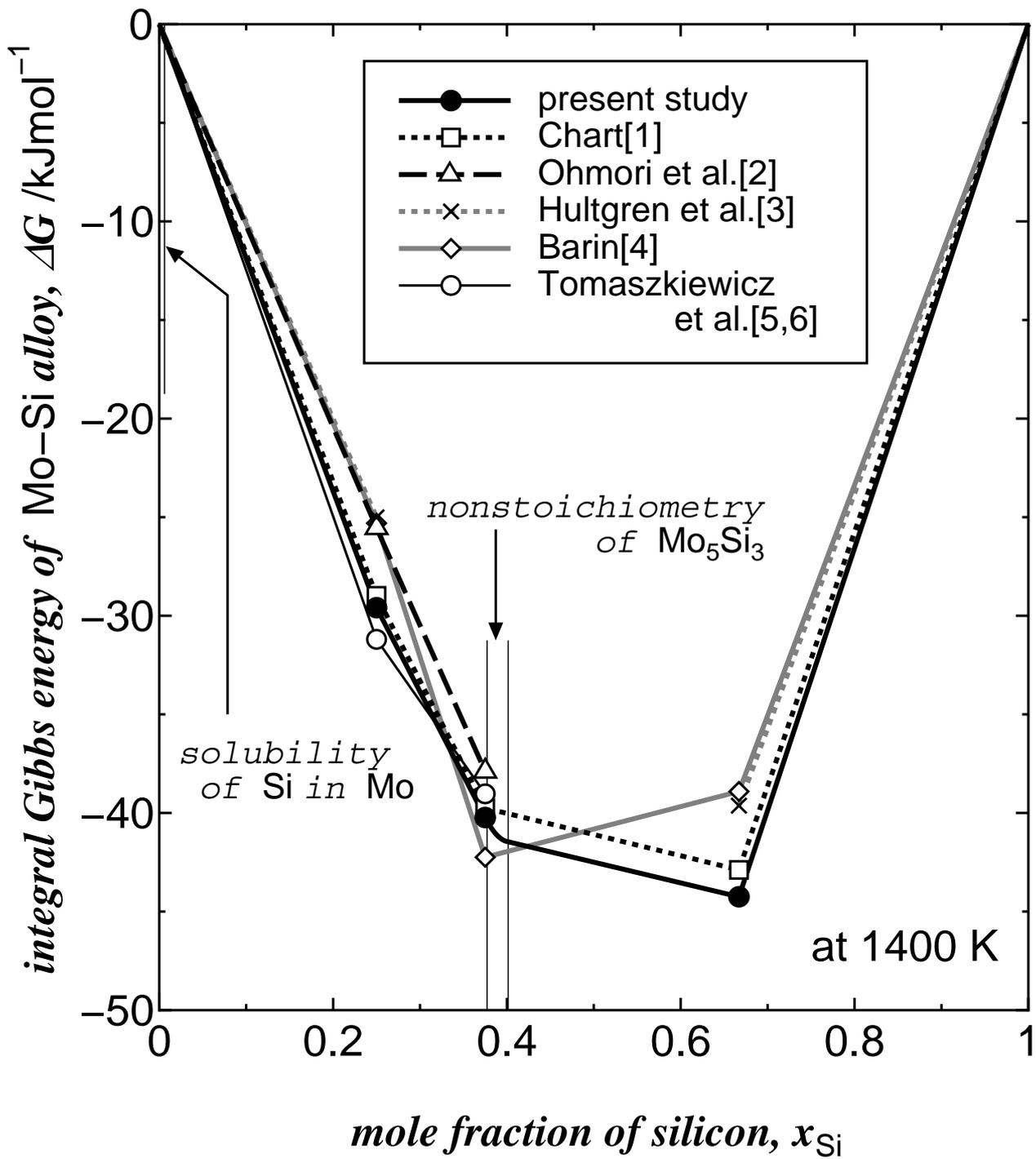


Fig. 5, H. Fujiwara

Table 1 Comparison of the standard enthalpies of formation for Mo₃Si, Mo₅Si₃ and MoSi₂ reported by various authors

author	method	$\Delta_f H^\circ(\text{Mo}_3\text{Si}, 298)$ kJmol ⁻¹	$\Delta_f H^\circ(\text{Mo}_5\text{Si}_3, 298)$ kJmol ⁻¹	$\Delta_f H^\circ(\text{MoSi}_2, 298)$ kJmol ⁻¹
present study	electromotive force, third law	- 122.1 ± 6.0	- 313.5 ± 12.0	- 135.8 ± 4.5
Chart[1]	Knudsen effusion, third law	- 116.4 ± 12	- 309.6 ± 24	- 131.7 ± 9
Searcy & Tharp[7]	Knudsen effusion, third law	- 98.3 ± 16.7	- 283.4 ± 62.8	- 108.8 ± 41.8
Robinson & Jenkins[8]	reaction calorimetry		- 293.7	- 131.4
Maslov[9]	reaction calorimetry			- 142.3 ± 2.9
Tomaszkiewicz et al.[6]	reaction calorimetry	- 125.2 ± 5.8		
Tomaszkiewicz et al.[5]	reaction calorimetry		- 314.3 ± 8.3	
O'Hare[10]	reaction calorimetry			- 137.1 ± 4.5
Meschel & Kleppa[11]	reaction calorimetry		- 305.6 ± 12.8	- 143.7 ± 16.8