

The Disilicides of Tungsten, Molybdenum, Tantalum, Titanium, Cobalt, and Nickel, and Platinum Monosilicide: A Survey of Their Thermodynamic Properties

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A critical evaluation is presented of the thermodynamic properties of six disilicides and one monosilicide that are important in the manufacture of very large scale integrated circuits. Values of the standard molar enthalpies of formation $\Delta_f H_m^\circ$ at $T = 298.15$ K and $p^\circ = 0.1$ MPa are recommended as follows: WSi_2 , $-(79 \pm 5)$ $\text{kJ}\cdot\text{mol}^{-1}$; MoSi_2 , $-(137 \pm 4)$ $\text{kJ}\cdot\text{mol}^{-1}$; TiSi_2 , $-(171 \pm 11)$ $\text{kJ}\cdot\text{mol}^{-1}$; CoSi_2 , $-(103 \pm 15)$ $\text{kJ}\cdot\text{mol}^{-1}$; NiSi_2 , $-(88 \pm 12)$ $\text{kJ}\cdot\text{mol}^{-1}$; TaSi_2 , $-(120 \pm 20)$ $\text{kJ}\cdot\text{mol}^{-1}$; and PtSi , $-(119 \pm 7)$ $\text{kJ}\cdot\text{mol}^{-1}$. Equations are given for the molar enthalpy increments of some of the silicides along with a few evaluated standard Gibbs free energies of formation. Brief descriptions of methods of synthesis and limited structural information have also been included.

Key words: chemical thermodynamics; cobalt disilicide; enthalpy increments; evaluated properties; molybdenum disilicide; nickel disilicide; platinum monosilicide; standard enthalpies of formation; standard Gibbs free energies of formation; tantalum disilicide; titanium disilicide; tungsten disilicide.

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1. Introduction

There is a revival of interest in the chemistry of transition-metal disilicides as a result of their use as interconnects and gate materials in very-large-scale integrated (VLSI) circuits.¹ Considerable R&D efforts have been

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expended in the preparation and measurement of the electrical properties of thin films of these disilicides, but much less attention has been paid to their thermodynamic properties. Without reliable thermodynamic information for these materials, any long-term compatibility evaluation is of little value.

Schlesinger² recently surveyed in a general way the thermodynamic properties of metal silicides. His review covered literature references exhaustively, but critical estimates of the uncertainties in the selected values are lacking. The only other comprehensive review of the thermochemical properties of metal silicides was published about 20 years ago by Chart.^{3,4}

In the present assessment, a thorough search was made of the literature of the thermodynamic properties of the crystalline disilicides of tungsten, molybdenum, tantalum, titanium, cobalt, and nickel, and of the monosilicide of platinum, because those substances appear to predominate in modern VLSI designs. The thermochemical properties: standard molar enthalpy of formation at $T = 298.15$ K, molar enthalpy increments relative to $T = 298.15$ K, and standard molar Gibbs free energies of formation are tabulated and appraised, and selected values are recommended. That is the main thrust of the effort. In addition, for each disilicide, we have included short, by no means exhaustive, sections that list methods of synthesis, structural information, and some details of the phase diagram.

2. Tungsten Disilicide

2.1. Preparative Methods

Tungsten disilicide, in common with the other disilicides discussed in this survey, is generally prepared by directly heating mixtures of stoichiometric amounts of pure specimens of Si and the appropriate second element in a vacuum or inert atmosphere to about 1500 K, followed by quenching to room temperature. Bondarenko *et al.*⁵ prepared single-phase WSi_2 by the diffusion impregnation in vacuum of a tablet or thin sheet of tungsten with silicon. A number of workers⁶⁻¹¹ used CVD techniques to deposit thin (≤ 50 μm) films of WSi_2 on silicon substrates. Hammar *et al.*⁶ laid tungsten films on predeposited polycrystalline Si in a CVD system at $p = 47$ Pa and $T = 623$ K, followed by annealing at 1073 K. Rode

and Harshbarger⁷ calculated the equilibrium compositions under CVD conditions for deposition of WSi_2 from two different feed gases: ($WF_6 + SiH_4 + H_2$) and ($WF_6 + SiH_2Cl_2 + H_2$) at temperatures between 473 K and 1073 K at $p = 67$ Pa. They showed that WSi_2 film was the only silicide phase formed in both cases. Blanquet *et al.*⁸ examined the optimum thermodynamic conditions for CVD deposition of WSi_2 at $p = 0.1$ MPa by means of *in situ* chlorination of W-films followed by reaction with ($SiH_4 + H_2$). Dobkin *et al.*⁹ obtained high-quality films of WSi_2 by CVD from ($WF_6 + Si_2H_6$) or ($SiH_4 + H_2 + N_2$) at $p = 0.1$ MPa and temperatures of the substrate between 563 K and 583 K. Zhang *et al.*¹⁰ obtained WSi_x by low-pressure CVD from ($WF_6 + SiH_4 + Ar$), and WSi_2 by annealing on Si substrates W films formed from WF_6 .¹¹ Tungsten disilicide and similar films prepared by CVD are usually characterized by standard surface techniques including Rutherford back-scattering.

2.2. Thermodynamic Properties

A recent assessment of the (W + Si) phase diagram by Nagender Naidu *et al.*¹² showed WSi_2 to be a congruently-melting intermediate phase that crystallized in tetragonal form (tI6, space group I4/mmm, $a = 0.3211$ nm, $c = 0.7868$ nm; melting temperature 2433 ± 4 K). The only other solid phase observed in this system was the congruently melting (at $T = 2593 \pm 10$ K) tetragonal W_3Si_3 , which has a small compositional homogeneity. Apparently, W_3Si does not exist.

The direct-reaction calorimetric determination of the standard molar enthalpy of formation $\Delta_f H_m^\circ(WSi_2, 298.15$ K) by Robins and Jenkins¹³ was, for many years, the only experimental result for this quantity. O'Hare¹⁴ has recently determined $\Delta_f H_m^\circ$ by fluorine-combustion calorimetry. Several estimates¹⁵⁻¹⁸ of $\Delta_f H_m^\circ(WSi_2)$ have been published. Chart¹⁹ deduced the molar Gibbs free energy of formation from Knudsen-effusion measurements. Bondarenko *et al.*^{5,20} obtained the high-temperature enthalpy increments (1200 K to 2200 K) from measurements with a drop calorimeter.

All the values of the enthalpies of formation are collected in Table 1.

Robins and Jenkins¹³ deduced $\Delta_f H_m^\circ(WSi_2)$ from the measured total enthalpy changes when compacted samples of powdered tungsten and silicon with mole ratio

TABLE 1. The standard molar enthalpy of formation of $WSi_2(\text{cr}, 298.15$ K)

Source	$-\Delta_f H_m^\circ / \text{kJ}\cdot\text{mol}^{-1}$	Method
Robins and Jenkins ¹³	93.2 ± 7.3	reaction calorimetry
O'Hare ¹⁴	79 ± 5	reaction calorimetry
Chart ^{3,4}	93 ± 8.8	assessment
Searcy ¹⁵	93.6	assessment
Niessen and de Boer ¹⁶	33	prediction
Kaufman ¹⁷	174	prediction
This work	79 ± 5	assessment

$n(\text{W})/n(\text{Si}) = 0.5$ were made to combine inside a calorimetric vessel. They reported the results of three such experiments. The standard deviation, $\pm 7.3 \text{ kJ}\cdot\text{mol}^{-1}$, did not allow for any systematic errors. Additional effects of the enthalpy of a Thermit reaction (a pellet of aluminum and chromium sesquioxide that initiated the calorimetric reaction), the electrical energy to ignite the Thermit, and the energy of reaction of a (silicon + zirconium) cladding used to promote combination of tungsten and silicon were all included in the calorimetric measurements. Uncertainties in the enthalpies of those reactions and the identity of the zirconium silicide formed, of effects due to possible inhomogeneities in the WSi_2 product, and of impurities in the W and Si starting materials, must all be added to the standard deviation. In the absence of such important experimental details, it is very difficult to evaluate those systematic errors. Our best estimate of $\Delta_f H_m^\circ(\text{WSi}_2)$ from the study of Robins and Jenkins¹³ is $-(93 \pm 20) \text{ kJ}\cdot\text{mol}^{-1}$.

A very recent investigation of the energy of combustion of high-purity, completely analyzed $\text{WSi}_{2.06}$ in a fluorine-bomb calorimeter by O'Hare¹⁴ has given the result: $\Delta_f H_m^\circ(\text{WSi}_{2.06}, \text{cr}, 298.15 \text{ K}) = -(80.4 \pm 4.7) \text{ kJ}\cdot\text{mol}^{-1}$, and for the exactly stoichiometric compound, $\Delta_f H_m^\circ(\text{WSi}_2)$ was estimated to be $-(79 \pm 5) \text{ kJ}\cdot\text{mol}^{-1}$. This value is close to that of Robins and Jenkins, but it is more precise and is preferred because the calorimetric materials and experimental procedures have been described in much greater detail.

Bondarenko *et al.*⁵ calculated enthalpy increments, $H_m^\circ(T) - H_m^\circ(298.15 \text{ K})$, for WSi_2 and W_5Si_3 from drop-calorimetric measurements between $T = 1173 \text{ K}$ and $T = 2118 \text{ K}$. The following equation,²⁰ with the molar mass of WSi_2 taken to be $240.02 \text{ g}\cdot\text{mol}^{-1}$, is selected as the most reliable (± 5 per cent) available at present:

$$[H_m^\circ(T) - H_m^\circ(298.15 \text{ K})]/(\text{J}\cdot\text{mol}^{-1}) = 34.294(T/\text{K}) + 15.41 \cdot 10^{-3}(T/\text{K})^2 - 5.856 \cdot 10^6(\text{K}/T) + 8065. \quad (1)$$

Chart¹⁹ used Knudsen-effusion techniques to measure the pressure of $\text{SiO}(\text{g})$ generated by the reaction between metal silicides and quartz cells; at the mean experimental temperature, $\Delta_f G_m^\circ(\text{WSi}_2, \text{cr}, 1500 \text{ K}) = -(81 \pm 8) \text{ kJ}\cdot\text{mol}^{-1}$.

3. Molybdenum Disilicide

Even before transition-metal silicides were considered as interconnects and contacts for VLSI, molybdenum disilicide, because of its great resistance to air oxidation, was being studied as a high-temperature material and had been used as a heating element under the commercial name of Super Kanthal. Even so, published thermodynamic information^{2,3,13} for MoSi_2 is not satisfactory. Of the seven values listed by Schlesinger² for $\Delta_f H_m^\circ(\text{MoSi}_2)$, only two are experimental in origin, and of those, one investigation²¹ is described in such meager detail that the results cannot be assessed authoritatively.

3.1. Preparative Methods

Bulk MoSi_2 is usually synthesized by heating ($\text{Mo} + 2\text{Si}$) at $T \approx 1273 \text{ K}$ in a vacuum or inert atmosphere. Bondarenko *et al.*²² prepared single-phase MoSi_2 by the reaction of ≈ 0.1 -mm thick Mo plates with $\text{Si}(\text{g})$ in a vacuum chamber. Thin films of MoSi_2 were formed²³⁻²⁷ by CVD methods from (silane + hydrogen + a volatile molybdenum halide) and also by the following techniques: sputtering from bulk MoSi_2 substrate; coevaporation of Mo and Si in a vacuum chamber; or by sequential deposition of Mo and Si, followed by annealing. Beyers²⁸ and Donald and Nemanich²⁹ examined the compatibility and mechanism of formation of such silicide films.

3.2. Thermochemical Properties

An assessment of the phase diagram of ($\text{Mo} + \text{Si}$) was published recently.³⁰ The intermediate MoSi_2 phase crystallizes in the tetragonal form (tI6, space group I4/mmm, $a = 0.3202 \text{ nm}$, $c = 0.7851 \text{ nm}$) and melts congruently at $T = (2293 \pm 10) \text{ K}$.

Since the critical reviews of the thermodynamic properties by Chart^{3,4} in the early seventies, only two^{21,31} additional measurements of $\Delta_f H_m^\circ$ of molybdenum disilicide have been performed.

As with WSi_2 , it is difficult to estimate the uncertainty to be attached to the $\Delta_f H_m^\circ(\text{MoSi}_2)$ determined by Robins and Jenkins¹³ by synthesis calorimetry. Unlike the ($\text{W} + 2\text{Si}$) experiments, an auxiliary ($\text{Zr} + \text{Si}$) reaction was not required to promote the formation of MoSi_2 . For that reason, and even though the final product contained minor quantities of a compound now known to be Mo_5Si_3 , the result should be less uncertain than that for WSi_2 . Thus, we select $\Delta_f H_m^\circ(\text{MoSi}_2) = -(131 \pm 15) \text{ kJ}\cdot\text{mol}^{-1}$, close to Chart's³ recommendation of $-(132 \pm 9) \text{ kJ}\cdot\text{mol}^{-1}$.

Maslov *et al.*²¹ electrically heated a mixture of Mo (99.47 mass per cent, with 0.24 mass per cent of oxygen and other miscellaneous contaminants) and Si (99.0 mass per cent, with the balance composed of Fe, Al, and Ca, and no reference to an oxygen impurity, although the reactants were stated to contain approximately 0.6 mass per cent of oxygen) to form MoSi_2 in a Calvet-type calorimeter. Surprisingly, no impurity correction appears to have been applied to the $\Delta_f H_m^\circ$ result. Furthermore, there seems to be an inconsistency between the oxygen contents of the starting materials and product silicide. We adjusted the reported result to $\Delta_f H_m^\circ(\text{MoSi}_2) = -(143 \pm 3) \text{ kJ}\cdot\text{mol}^{-1}$ to reflect the current molar mass of MoSi_2 . It is not clear whether this value came from one experiment or was the average of several. Nevertheless, the estimated uncertainty is probably optimistic in light of the quantity of impurities in the starting materials and the difference between the X-ray diffraction pattern of the product and that published for authentic MoSi_2 , as discussed in Ref. 31.

O'Hare³¹ recently used fluorine-combustion calorimetry to determine $\Delta_f H_m^\circ$ for a molybdenum silicide of com-

position $\text{MoSi}_{2.067 \pm 0.002}$, from which $\Delta_f H_m^\circ(\text{MoSi}_2)$ was estimated to be $-(137.1 \pm 4.5) \text{ kJ}\cdot\text{mol}^{-1}$. This result is believed to be the most reliable to date, because the sample was thoroughly characterized and the experimental procedure was documented fully.

The estimates of Searcy,¹⁵ Searcy and Finnie,³² Hultgren *et al.*,¹⁸ and Chart^{3,4} were all based in one way or another upon the determination of Robins and Jenkins.¹³ All the other approximations in Table 2 were calculated.

Four high-temperature measurements that lead to the heat capacity of MoSi_2 have been reported.^{20,22,33,34} Bondarenko *et al.*²² measured directly the heat capacity of the silicide in an adiabatic calorimeter, and the three other studies involved drop calorimetry. Douglas and Logan³³ used an ice calorimeter to determine $H_m^\circ(T) - H_m^\circ(273.15 \text{ K})$, where $T \leq 1173 \text{ K}$, and thence derived the heat capacity as a function of T . In that research, the sample contained approximately 2 mass per cent of impurities. In addition, the authors observed some oxidation of the sample container, which contributed about ± 0.7 per cent to the overall uncertainty. Their enthalpy-increment results are approximated by the relation:

$$[H_m^\circ(T) - H_m^\circ(298.15 \text{ K})]/(\text{J}\cdot\text{mol}^{-1}) = 70.8937(T/\text{K}) + 5.4559 \cdot 10^{-3}(T/\text{K})^2 - 6356.31 \lg(T/\text{K}) - 5895.3. \quad (2)$$

Walker *et al.*³⁴ measured the enthalpy increments relative to 303.15 K from 383 K to 1173 K with a copper-block calorimeter. Their sample had a purity of 97.8 mass per cent and was contained in a 347 stainless-steel capsule. There are several errors in their equations for the specific enthalpy increments, which we now correct. They gave two enthalpy-increment-against-temperature relations; the terms in T^0 were interchanged, and there is an erroneous sign in the first equation. We have used a molar mass of $152.11 \text{ g}\cdot\text{mol}^{-1}$ for MoSi_2 , and $[H_m^\circ(303.15 \text{ K}) - H_m^\circ(298.15 \text{ K})] = 0.32 \text{ kJ}\cdot\text{mol}^{-1}$ from Bondarenko *et al.*²² to reconstruct the following ($328 \leq (T/\text{K}) \leq 623$):

$$[H_m^\circ(T) - H_m^\circ(298.15 \text{ K})]/(\text{kJ}\cdot\text{mol}^{-1}) = 8.48 \cdot 10^{-2}(T/\text{K}) - 13.892 \lg(T/\text{K}) + 9.10 \quad (3)$$

and ($598 \leq (T/\text{K}) \leq 1148$):

$$[H_m^\circ(T) - H_m^\circ(298.15 \text{ K})]/(\text{kJ}\cdot\text{mol}^{-1}) = 8.94 \cdot 10^{-2}(T/\text{K}) - 20.32 \lg(T/\text{K}) + 24.21. \quad (4)$$

The MoSi_2 studied by Bondarenko *et al.*²² was the purest (99.95 mass per cent) sample used in the drop-calorimetric investigations, and they measured the heat capacity directly with an adiabatic calorimeter. Therefore, the selected heat capacity (± 2 per cent) is taken directly from their work:

$$C_{p,m}^\circ/(\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}) = 67.487 + 15.522 \cdot 10^{-3}(T/\text{K}) - 7.406 \cdot 10^5(\text{K}/T)^2. \quad (5)$$

We have integrated Eq. (5) to obtain the following expression:

$$[H_m^\circ(T) - H_m^\circ(298.15 \text{ K})]/(\text{kJ}\cdot\text{mol}^{-1}) = 67.487 \cdot 10^{-3}(T/\text{K}) + 7.761 \cdot 10^{-6}(T/\text{K})^2 + 7.406 \cdot 10^2(\text{K}/T) - 23.295. \quad (6)$$

Above 1200 K, the only enthalpy increments available were reported by Bondarenko²⁰ on the basis of drop-calorimetric experiments. His results are represented by the following:

$$[H_m^\circ(T) - H_m^\circ(298.15 \text{ K})]/(\text{kJ}\cdot\text{mol}^{-1}) = 26.359 \cdot 10^{-3}(T/\text{K}) + 1811.63 \cdot 10^{-8}(T/\text{K})^2 - 7469(\text{K}/T) + 15.606. \quad (7)$$

Enthalpy-increment values obtained by different workers are summarized in Table 3; the agreement, usually within approximately 2 per cent, is reasonable considering the difference in sample purities and techniques.

Searcy and Tharp³⁵ and Chart³⁶ deduced the relative partial molar Gibbs free energy of Si from their Knudsen effusion studies. Searcy and Tharp measured the equilibrium partial pressures of Si(g) over MoSi_2 by means of the total mass loss method. The relatively small partial pressures required that the measurements be performed at quite high temperatures and that, in turn, caused interactions of the silicide with the container, sintering of the sample, and lack of equilibrium in the effusion cell. For

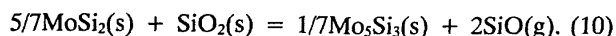
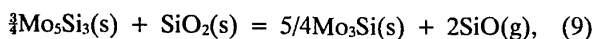
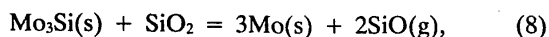
TABLE 2. The standard molar enthalpy of formation of $\text{MoSi}_2(\text{cr}, 298.15 \text{ K})$

Source	$-\Delta_f H_m^\circ/\text{kJ}\cdot\text{mol}^{-1}$	Method
Robins and Jenkins ¹³	131 ± 10	reaction calorimetry
Maslov <i>et al.</i> ²¹	143 ± 3	reaction calorimetry
O'Hare ³¹	137 ± 4	reaction calorimetry
Hultgren <i>et al.</i> ¹⁸	131 ± 6.2	assessment
Searcy ¹⁵	113.7	assessment
Niessen and de Boer ¹⁶	48	prediction
Kaufman ¹⁷	216	prediction
Chart ³	132 ± 9	assessment
This work	137 ± 4	assessment

those reasons, their derived $\Delta_f H_m^\circ$ at $T = 298.15$ K is not believed to be reliable.

Chart, on the other hand, measured the partial pressures of SiO(g) formed in reactions between MoSi₂ and SiO₂. He then derived the relative partial molar Gibbs free energies of Si in the silicide and, with the help of the Gibbs-Duhem relation, calculated $\Delta_f G_m^\circ(\text{MoSi}_2, \text{cr}) = -(128.3 \pm 7.5) \text{ kJ}\cdot\text{mol}^{-1}$. He also recalculated the $\Delta_f G_m^\circ(\text{MoSi}_2, \text{cr})$ result of Searcy and Tharp and found it to be between 2 to 3 $\text{kJ}\cdot\text{mol}^{-1}$ less negative than his own.

A careful examination of the experimental details of Chart's work indicates that his estimates of the uncertainties of $\Delta_f G_m^\circ(\text{MoSi}_2)$ were rather optimistic. He measured vapor pressures over just three alloy compositions: $x(\text{Si}) = 0.20, 0.35, \text{ and } 0.69$. Each alloy sample was a two-phase mixture. In other words, he measured the equilibrium constants of the reactions:



Thus, in the evaluation of the partial molar Gibbs free energy of MoSi₂, not only must the errors from the measurement of $p(\text{SiO})$ in reaction (8) be included, so also must those from reactions (9) and (10). Pressures varied with effusion orifice area, which suggests that thermodynamic equilibrium conditions were not realized in the effusion cells. No corrections were made to compensate for this effect. Chart's estimated uncertainties in the physical quantities that contributed to the values of $p(\text{SiO})$ were: 1 to 2 per cent in the orifice area; ± 1.5 per cent in the Clausing factor; 0.1 to 1 per cent in mass loss; and ± 1.5 K in the cell temperature. These estimates are optimistic, in our opinion, when one considers that the loss in mass of the cell was the experimental parameter measured. Implicit in this method is an assumption that effusion fluxes obey the cosinc distribution; such rarely happens for the total-mass-loss procedure. Chart also assumed that, in

converting the measured partial pressures to Gibbs free energies, the constant errors in pressure values were cancelled. It is difficult to justify that assumption. Errors in the measurement of orifice area, temperature, mass loss rates, or the Clausing factors are not cancelled when the activities of Si are computed from two experiments, one with pure Si and the other with the silicides. Because oxygen solubility is small in the terminal solid phases, Mo(cr) and Si(cr), Chart assumed that the partial molar Gibbs free energies of Si in the silicides were not affected by the solubility of oxygen in the silicide phases. This assumption is also difficult to accept without some additional proof. In the light of these observations, the selected value $\Delta_f G_m^\circ = -(129 \pm 20) \text{ kJ}\cdot\text{mol}^{-1}$ is much more uncertain than that originally given by Chart.

There are two reports of the enthalpies of mixing of liquid Mo with Si. Arpaci and Frohberg³⁷ used levitation calorimetry to measure those quantities at $T = 3087$ K for $0 \leq x(\text{Si}) \leq 0.4$. They estimated the enthalpies of mixing to be uncertain by ± 12 per cent. From an examination of their results and the problems associated with accurate determination of the temperature of liquid drops and the loss by vaporization of Si during the mixing process, it may be concluded that the systematic errors are larger than Arpaci and Frohberg believed. Sudavtsova *et al.*³⁸ also determined enthalpies of mixing in an isothermally jacketed calorimeter. Insufficient details are given in their paper to assess critically the accuracy of the measurements.

4. Titanium Disilicide

The (Ti + Si) phase diagram, probably one of the better understood for transition-metal silicides, was assessed recently by Murray.³⁹ The orthorhombic α -TiSi₂ (oF24, space group Fddd, $a = 0.8252$ nm, $b = 0.4783$ nm, $c = 0.8540$ nm) is the stable reference state from room temperature to $T = 1603$ K. The crystal structure of the high-temperature β -TiSi₂ modification has not yet been established.

TABLE 3. Enthalpy increments for MoSi₂(cr)

T/K	$[H_m^\circ(T) - H_m^\circ(298.15 \text{ K})]/\text{kJ}\cdot\text{mol}^{-1}$			
	Douglas & Logan ³³	Walker <i>et al.</i> ³⁴	Bondarenko <i>et al.</i> ⁵	Bondarenko ²⁰
400	6.79 \pm 0.14	6.87 \pm 0.12	6.79 \pm 0.14	67.1 \pm 1.3 (1200 K)
500	13.76 \pm 0.28	14.01 \pm 0.24	13.87 \pm 0.28	74.7 \pm 1.5 (1300 K)
600	20.95 \pm 0.42	21.39 \pm 0.39	21.23 \pm 0.42	82.7 \pm 1.7 (1400 K)
700	28.32 \pm 0.57	28.98 \pm 0.57	28.81 \pm 0.58	90.9 \pm 1.8 (1500 K)
800	35.86 \pm 0.71	36.74 \pm 0.69	36.59 \pm 0.73	99.5 \pm 2.0 (1600 K)
900	43.55 \pm 0.87	44.64 \pm 0.88	44.57 \pm 0.89	108.4 \pm 2.4 (1700 K)
1000	51.38 \pm 1.03	52.65 \pm 1.01	52.71 \pm 1.05	117.8 \pm 2.6 (1800 K)
1100	59.36 \pm 1.19	60.75 \pm 1.18	61.03 \pm 1.22	127.2 \pm 2.7 (1900 K)
1200	67.46 \pm 1.35	68.92 \pm 1.30	69.51 \pm 1.39	137.1 \pm 2.9 (2000 K)

4.1. Preparative Methods

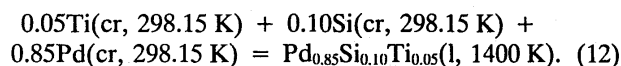
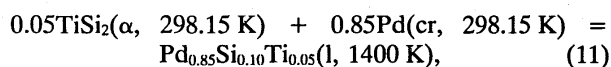
Bulk TiSi₂ is generally prepared by direct heating of stoichiometric amounts of the elements in a vacuum or inert atmosphere. Trambukin and Munir⁴⁰ synthesized titanium silicides by the self-propagating high-temperature combination of Ti and Si in which the exothermicity of the reaction was sufficient to carry the process to completion. Thin films of TiSi₂ have been prepared by CVD methods. The most common procedure is to deposit first a thin layer of Ti and then Si or to codeposit Ti and Si by means of titanium chloride, hydrogen, silicon chloride, or silane mixtures. Generally, the deposition of these layers is followed by annealing. Variations of this procedure have been described recently. Maex *et al.*⁴¹ examined the thermodynamic criteria for the deposition of thin films of TiSi₂ or CoSi₂ on boron- or arsenic-doped substrates. Their calculations showed the absence of any stable tie-lines between TiSi₂(cr) and solid solutions of B or As in Si. They studied the redistribution of dopants during the formation of TiSi₂ film. This analysis underscores the importance of thermodynamic information for silicides used as gates or interconnects on VLSI circuits. Richter *et al.*⁴² studied the formation of thin films of TiSi₂ on silicon and the effects of either furnace annealing or rapid thermal annealing on the final structures. Mercier *et al.*⁴³ deposited TiSi₂ layers from mixtures of TiCl₄, SiH₄, and H₂ without any consumption of the silicon substrate. Dahan *et al.*⁴⁴ studied the formation of layers of a ternary phase, (Ti,Ta)Si₂, by sputter depositing Ti and Ta on silicon wafers followed by annealing.

4.2. Thermodynamic Properties

The standard molar enthalpy of formation $\Delta_f H_m^\circ(\text{TiSi}_2)$ was determined in four calorimetric,^{13,45-47} and one equilibrium⁴⁸ study. Four other assessments or estimates of this quantity have also been published.^{17,18,49} Table 4 contains a summary of these values.

Robins and Jenkins¹³ were the first to obtain $\Delta_f H_m^\circ(\text{TiSi}_2)$ from the direct, solid-state reaction. Different sources of systematic error in their experiments, discussed earlier in the present document, are not

adequately accounted for in the standard deviation of $\pm 1.9 \text{ kJ}\cdot\text{mol}^{-1}$. Golutvin⁴⁵ derived a value of $-(179.5 \pm 18.8) \text{ kJ}\cdot\text{mol}^{-1}$ by combustion calorimetry in oxygen of a sample that had the composition Ti_{1.066}Si_{1.934} and contained 1 mass per cent of oxygen. Savin⁴⁶ reported $\Delta_f H_m^\circ(\text{TiSi}_2) = -(180.7 \pm 6.3) \text{ kJ}\cdot\text{mol}^{-1}$ from calorimetric measurements of the enthalpy of reduction with Na of (TiCl₄ + 2SiCl₄). Recently, Topor and Kleppa⁴⁷ employed a Calvet-type calorimeter operating at $T = (1400 \pm 2) \text{ K}$ to measure the enthalpy changes for the reactions:



The combined enthalpy changes of these two reactions gave $\Delta_f H_m^\circ(\text{TiSi}_2) = -170.9 \text{ kJ}\cdot\text{mol}^{-1}$, but the estimated error, $\pm 8.3 \text{ kJ}\cdot\text{mol}^{-1}$, may be too small.

Brewer and Krikorian⁴⁸ estimated $\Delta_f H_m^\circ(\text{TiSi}_2) = -(234 \pm 42) \text{ kJ}\cdot\text{mol}^{-1}$ on the basis of equilibrium studies of several metal silicides, and de Boer *et al.*⁴⁹ used a semi-empirical model to predict a value of $-183 \text{ kJ}\cdot\text{mol}^{-1}$.

The selected $\Delta_f H_m^\circ(\text{TiSi}_2, \alpha, 298.15 \text{ K}) = -(171 \pm 11) \text{ kJ}\cdot\text{mol}^{-1}$ is the result obtained by Topor and Kleppa with an expanded error limit. Note, however, that within the combined uncertainties the $\Delta_f H_m^\circ$ s obtained by Golutvin and Savin are in very good agreement with the recommended value.

There have been two measurements of enthalpy increments of TiSi₂, both by drop calorimetry. At 1200 K, the temperature of closest approach, the results of Golutvin⁵⁰ (from 407 K to 1181 K) and Bondarenko²⁰ (from 1200 K to 1700 K) shown in Table 5 agree to no better than about 5 per cent. According to the chemical analyses quoted by the authors, the titanium disilicide samples had different compositions, one being hyperstoichiometric and the other hypostoichiometric, and that could account for part, at least, of the discrepancies in the enthalpy values. "As a result of such variations," according to Schlesinger,² "more complete thermodynamic data for the titanium silicides cannot be recommended with any degree of confidence."

TABLE 4. The standard molar enthalpy of formation of TiSi₂(cr, α , 298.15 K)

Source	$-\Delta_f H_m^\circ/\text{kJ}\cdot\text{mol}^{-1}$	Method
Topor & Kleppa ⁴⁷	170.9 ± 8.3	mixing calorimetry
Robins & Jenkins ¹³	134.7 ± 1.9	reaction calorimetry
Golutvin ⁴⁵	179.5 ± 18.8	reaction calorimetry
Savin ⁴⁶	180.7 ± 6.3	reaction calorimetry
Brewer & Krikorian ⁴⁸	234 ± 42	equilibrium studies
Hultgren <i>et al.</i> ¹⁸	134.3	assessment
de Boer <i>et al.</i> ⁴⁹	183	prediction
Kaufman ¹⁷	134.4	prediction
Present work	171 ± 11	assessment

5. Cobalt and Nickel Disilicides

Disilicides of nickel (α -NiSi₂) and cobalt (CoSi₂) exhibit the fluorite structure with lattice constants only slightly different from those of Si. Thus, one would expect these two silicides to grow epitaxially on single-crystal silicon substrates, and a number of workers⁵¹⁻⁵⁵ have recently studied such growth. But the thermodynamic information available for these materials is sparse. The phase diagram of (Ni + Si) was reviewed recently,⁵⁶ and that of (Co + Si)³⁰ was critically assessed.

5.1. Preparative Methods

Disilicides of nickel and cobalt may be prepared by heating stoichiometric mixtures of the powdered components in vacuum or an inert atmosphere. Thin films are grown on silicon substrates by depositing the respective metals in vacuum followed by annealing at temperatures between 1073 K and 1173 K. Chang *et al.*⁵¹ prepared NiSi₂ films epitaxially on (111) and (100) silicon substrates by depositing nickel from a plating solution at $T = 363$ K and pH = 9, followed by annealing in dry nitrogen. Werner *et al.* prepared epitaxial NiSi₂ films on a similar substrate, followed by rapid thermal annealing. Lindner and Tekat⁵³ formed NiSi₂ on silicon by implanting 6 MeV

nickel ions into silicon, followed by annealing, while Barbour *et al.*⁵⁷ prepared layers of epitaxial CoSi₂ on silicon by ion implanting the cobalt ions and then annealing.

5.2. Thermodynamic Properties

Schlesinger² listed five values for the enthalpy of formation of α -NiSi₂ and six for the enthalpy of formation of CoSi₂ but, in each case, only one was obtained experimentally, the others having been assessed or calculated from various models. Oelsen and coworkers^{58,59} determined $\Delta_f H_m^\circ$ for NiSi₂ and CoSi₂ by direct-reaction calorimetry. Molten Si and the appropriate molten metals were mixed together in a calorimeter at room temperature. Measurements of $\Delta_f H_m^\circ$ of Ni₂Si and NiSi were made, and from them $\Delta_f H_m^\circ(\text{NiSi}_2)$ was estimated to be ≈ -88 kJ·mol⁻¹. It is very difficult to evaluate the probable error in $\Delta_f H_m^\circ$; we have taken it to be ± 12 kJ·mol⁻¹. The Si and Ni were of technical grade and inferior purity by present-day standards. Cobalt of comparable purity was used in measurements of the reaction of molten cobalt and silicon to form CoSi₂. We have taken $\Delta_f H_m^\circ(\text{CoSi}_2) = -103$ kJ·mol⁻¹ directly from Oelsen and Middel and, as with NiSi₂, estimate the uncertainty to be ± 12 kJ·mol⁻¹. Experimental, assessed, and estimated values are summarized in Table 6.

TABLE 5. Enthalpy increments for TiSi₂

T/K	$[H_m^\circ(T) - H_m^\circ(298.15 \text{ K})]/\text{kJ}\cdot\text{mol}^{-1}$ Golubvin ⁶⁰	T/K	$[H_m^\circ(T) - H_m^\circ(298.15 \text{ K})]/\text{kJ}\cdot\text{mol}^{-1}$ Bondarenko ²⁰
407	6.37	1200	71.6
500	12.68	1300	79.6
596	20.22	1400	88.3
690	27.51	1500	97.7
804	37.57	1600	107.7
847	41.57	1700	118.4
969	49.71		
1072	58.45		
1181	75.23		

TABLE 6. The standard molar enthalpies of formation of CoSi₂(cr) and NiSi₂(α , cr) at 298.15 K

Source	CoSi ₂	NiSi ₂ (α)	Method
	$-\Delta_f H_m^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$-\Delta_f H_m^\circ/\text{kJ}\cdot\text{mol}^{-1}$	
Oelsen <i>et al.</i> ^{58,59}	103 \pm 12	88 \pm 12	calorimetry
Chart ³	99 \pm 12	94 \pm 12	assessment
Kaufman ¹⁷	201	195	prediction
Machlin ⁷⁶	118.5		prediction
Pasturel <i>et al.</i> ⁶⁰	104		prediction
Mey ⁷⁷		82	prediction
Niessen <i>et al.</i> ⁶¹	45	51	prediction
This work	103 \pm 15	88 \pm 12	assessment

Kalishevich *et al.*⁶² measured the heat capacities of NiSi₂ and CoSi₂ to 300 K. They calculated the standard molar entropies: $S_m^\circ(\text{NiSi}_2, \alpha, 298.15 \text{ K}) = (65 \pm 6) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ and $S_m^\circ(\text{CoSi}_2, 298.15 \text{ K}) = (64 \pm 6) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$. Because the lowest temperature of the measurements was only 60 K, the uncertainties in $C_{p,m}^\circ$ may be large. Kalishevich *et al.*⁶³ used drop calorimetry to determine the enthalpy increments of NiSi₂ and CoSi₂ from $T = 298.15 \text{ K}$ to $T = 1560 \text{ K}$. Chart³ reviewed these results and selected $H_m^\circ(T) - H_m^\circ(298.15 \text{ K})$ for both silicides; the assessed values in Table 7 are essentially those given by him.

A few measurements of the relative partial molar Gibbs free energies of Si are available for the liquid alloys. Those quantities were obtained by Schwerdtfeger and Engell^{64,65} for (Ni + Si)(l) and (Co + Si)(l) by means of e.m.f. techniques, and by Martin-Garin *et al.*⁶⁶ for (Co + Si)(l) by distribution measurements followed by Gibbs-Duhem integration. Such molar Gibbs free energies of formation show large negative deviations from ideal solution behavior.

6. Tantalum Disilicide

Hexagonal tantalum disilicide (hP9, space group P6222, $a = 0.47821 \text{ nm}$, $c = 0.65695 \text{ nm}$) is one of four intermediate phases in the (Ta + Si) phase equilibrium system.³⁰ Experimental thermodynamic information on TaSi₂ is sparse. Chart^{3,4} reviewed the data available in the early seventies.

6.1. Preparative Methods

Bulk samples of TaSi₂ may be prepared by heating mixtures of the elements in an inert atmosphere or in vacuum; thin films have been prepared by a number of CVD techniques. Blanquet *et al.*^{8,67} used the thermodynamic properties to calculate the optimum conditions for CVD deposition of TaSi₂. They obtained TaSi₂ films at atmospheric pressure by generating tantalum chlorides *in situ* by direct reaction of Ta and Cl₂(g) at one end of the reactor and heating with different (SiH₄ + H₂) mixtures,

followed by annealing at the other end. Several other workers⁶⁸⁻⁷⁰ prepared thin films of TaSi₂ by high-pressure and low-pressure CVD, and from (TaCl₅ + SiCl₄ + H₂) mixtures in hot-wall reactors.

6.2. Thermodynamic Properties

Table 8 gives the experimental and estimated values for $\Delta_f H_m^\circ(\text{TaSi}_2)$. As discussed previously, the measurements of Robins and Jenkins¹³ are subject to a number of systematic errors. Myers and Searcy⁷¹ measured the dissociation pressures of TaSi₂ as a function of temperature by means of the total mass loss Knudsen effusion method and calculated the molar Gibbs free energy of formation at $T = 1500 \text{ K}$. They assumed $\Delta C_{p,m}^\circ = 0$, and evaluated $\Delta_f H_m^\circ(\text{TaSi}_2)$. Levine and Kolodney⁷² calculated $\Delta_f G_m^\circ(\text{TaSi}_2)$ at $T = 1300 \text{ K}$ from galvanic cell measurements. In both determinations of $\Delta_f G_m^\circ$, more than one equilibrium constant had to be calculated and the cumulative errors make the final values somewhat uncertain. Furthermore, uncertainties introduced by estimated auxiliary thermodynamic functions are difficult to estimate. Thus, the selected $\Delta_f H_m^\circ$ shown in Table 8 has quite large error limits.

There are two reports^{73,74} that deal with the enthalpy increments of TaSi₂; both formed the basis of Chart's^{3,4} recommendations, which are accepted.

7. Platinum Monosilicide

The (Pt + Si) phase diagram is not yet completely understood, but it is clear³⁰ that PtSi is a congruently melting intermediate phase of the system.

7.1. Preparative Methods

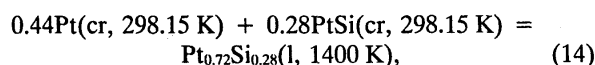
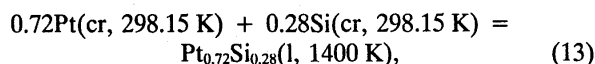
PtSi(cr) may be prepared directly by melting equimolar amounts of pure Pt and Si in a BN container at $T = 1575 \text{ K}$ under an inert gas atmosphere. This substance crystallizes in an orthorhombic habit (oP8, space group Pnma, $a = 0.5916 \text{ nm}$, $b = 0.3587 \text{ nm}$, $c = 0.5577 \text{ nm}$), and its melting temperature is $(1502 \pm 5) \text{ K}$.

TABLE 7. Enthalpy increments for CoSi₂(cr) and NiSi_{1.857}(α , cr)

T/K	$[H_m^\circ(T) - H_m^\circ(298.15 \text{ K})]/\text{kJ}\cdot\text{mol}^{-1}$	
	CoSi ₂ (cr)	NiSi _{1.857} (α , cr)
400	7.03	6.81
500	14.44	13.87
600	22.22	21.28
700	30.25	28.81
800	38.66	36.58
900	47.20	44.47
1000	55.86	52.60
1100	74.06	60.73
1200	83.35	68.98

7.2. Thermodynamic Properties

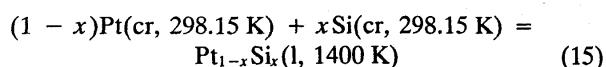
Topor and Kleppa⁷⁵ measured the enthalpy changes that occurred when appropriate amounts of (platinum + silicon) and (platinum + platinum silicide) at room temperature were dropped into a BN cup at $T = (1400 \pm 2)$ K in a Calvet-type calorimeter. From the experimental enthalpy changes of the reactions:



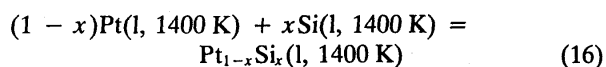
$\Delta_f H_m^\circ(\text{PtSi}, \text{cr}, 298.15 \text{ K}) = -(118.7 \pm 5.2) \text{ kJ}\cdot\text{mol}^{-1}$ was calculated. This uncertainty is the standard deviation of the measurements rather than an indication of their overall accuracy. Platinum and silicon, both of 99.99 mass per cent purity as used in the experiments of Topor and Kleppa, were sufficiently pure with respect to trace metals, but no account was taken of possible nonmetallic contaminants such as oxygen. The calibration standard was copper and its $[H_m^\circ(T) - H_m^\circ(298.15 \text{ K})]$, taken from Hultgren *et al.*,¹⁸ was arbitrarily adjusted by one per cent to allow for heat losses during its transfer from room temperature to the calorimeter at $T = 1400 \text{ K}$. Insufficient details were given to assess other systematic errors reli-

ably. Our selected $\Delta_f H_m^\circ(\text{PtSi})$ is $-(119 \pm 7) \text{ kJ}\cdot\text{mol}^{-1}$, where the uncertainty has been estimated.

Topor and Kleppa also measured the enthalpy changes of the reaction:



for $0.20 \leq x \leq 0.40$ and $0.62 \leq x \leq 0.70$. From their experiments, the enthalpy of mixing for:



was obtained as a function of composition, and a distinct minimum was observed at $x(\text{Si}) = 0.33$. They combined $\Delta_{\text{mix}} H_m^1$ with $\Delta_f H_m^\circ(\text{PtSi})$ to calculate $\Delta_{\text{fus}} H_m^\circ(\text{PtSi}) \approx 47 \text{ kJ}\cdot\text{mol}^{-1}$ and $\Delta_{\text{fus}} S_m^\circ(\text{PtSi}) \approx 31.2 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$.

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TABLE 8. The standard molar enthalpy of formation of $\text{TaSi}_2(\text{cr}, 298.15 \text{ K})$

Source	$-\Delta_f H_m^\circ/\text{kJ}\cdot\text{mol}^{-1}$	Method
Robins and Jenkins ¹³	116 ± 4	calorimetry
Myers and Searcy ⁷¹	97 ± 30	equilibrium
Chart ³	119 ± 13	assessment
Searcy and Finnie ³²	105 ± 18	prediction
Niessen and de Boer ¹⁶	132	prediction
Brewer and Krikorian ⁴⁸	107 ± 26	prediction
Levine and Kolodney ⁷²	68 ± 17	galvanic cell
This work	120 ± 20	assessment

TABLE 9. The standard molar enthalpy of formation of $\text{PtSi}(\text{cr}, 298.15 \text{ K})$

Source	$-\Delta_f H_m^\circ/\text{kJ}\cdot\text{mol}^{-1}$	Method
Topor and Kleppa ⁷⁵	118.7 ± 5.2	solution calorimetry
Chart ³	184	estimation
Searcy and Finnie ³²	58	prediction
Machlin ⁷⁶	157	prediction
Pasturel <i>et al.</i> ⁶⁰	138	prediction
Niessen and de Boer ¹⁶	166	prediction
This work	119 ± 7	assessment

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