Thermodynamics of Solid Transition-Metal Silicides

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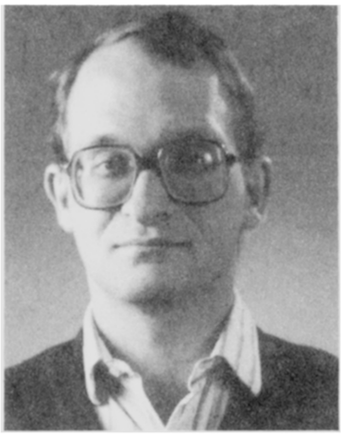
Contents

I. Introduction

The silicides formed by reaction with transition-metal elements (groups IB–VIIIB in the periodic table) have been of interest to the practicing metallurgist for some time, due to their considerable stability and oxidation resistance. This stability was first noticed in the examination of equilibria in steel-making systems[1] and led to some of the first research on the thermodynamic properties of these compounds. A more general use of a transition-metal silicide came about when molybdenum disilicide elements were developed for high-temperature furnaces.[2] More recently, the extensive development of intermetallic materials in general has yielded other potential applications of these compounds. Their low electrical resistivity and compatibility with silicon substrates has furthered their use as contacts and interconnects in integrated circuits,[3] and several silicides have potential value in thermoelectric energy conversion.[4-6] The oxidation resistance and stability of these compounds lends to their further employment as high-temperature coatings.[7] As in the case with other intermetallic compounds, the transition-metal silicides also have impressive high-temperature tensile strength (and poor ductility); this has fostered continuing efforts toward development of silicide-bearing cermets and other composites.[8,9]

The thermodynamic properties of the transition-metal silicides have an obvious bearing on their usefulness in these various applications. Greater thermodynamic stability means greater resistance to oxidation in high-temperature applications, and less likelihood of decomposition in composite structures.[8] Wagner and Simkovich,[10] for example, have shown that the stability of CoSi plays an important role in determining the effectiveness of silicon nitride additions in reducing the high-temperature oxidation of Co–Cr alloys. The thermodynamic characteristics of these compounds largely determine their feasibility in electronic applications as well; Pretorius has illustrated how heat of formation values can be used to predict which silicide phases will form (and in what order) in metal film/silicon reaction couples,[11] and Bernard et al. have demonstrated the importance of accurate free energies of formation in engineering proper chemical vapor deposition procedures.[12] Gas et al. have shown that compound heats of formation can also help determine the rate-controlling process in silicide formation in such systems.[13] Such considerations have fostered the generation of a considerable (though inadequate) body of research on transition-metal silicide thermodynamics, spread somewhat unevenly across the various elements in this group.

As the literature background in this field has developed, occasional reviews or compilations of the work have appeared, either as background to new experimental results or as specifically composed critiques. Most of the review papers have been limited to a specific metal–silicon system, but occasional general reviews have appeared as well.[14-16] However, the most recent comprehensive critical review of transition-metal silicide thermodynamics is that published by Chart in 1972.[17] Since that time, the database in this field has grown noticeably, particularly with respect to solid-state properties; the new data include the first significant



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efforts at determining rare-earth and platinum group metal silicide properties, as well as attempts to clear up confusion over the values of these properties for the more thoroughly investigated compounds of chromium, manganese, titanium, and vanadium. As a result of this new work, and of the increased interest in these compounds, it is felt that an updated review of the thermodynamics of the transition-metal silicides is in order. The available body of work is now sizable enough to recommend limitation of this review to the solid compounds (excluding technetium and the actinides); the most recent general review dealt with both solid and liquid silicide properties[17] and is recommended to those interested in the latter.

II. Analytical Methods

A. Modeling Techniques

Since the literature background on some of the subject silicide compounds is (as will be seen) rather scanty, a number of techniques have been developed for estimating their thermodynamic properties, based on such experimental data as exists. The most commonly estimated parameters are compound heat capacities and enthalpies of formation; however, some attempts have also been made to model free energies of formation as well. Just as actual experimental techniques have improved in accuracy with time, the various proposed models have also shown steady improvement with regard to both applicability and accuracy of results.

The most widely used "model" in silicide thermodynamics estimation has been the Neumann–Kopp rule (Kopp's rule/law, the principle of additivity, Dulong and Petit's additive law[18,19]), which states that the change in heat capacity resulting from the formation of a solid chemical compound from the solid elements is equal to zero, e.g.

$$C_p(M_xSi_y) = xC_p(M) + yC_p(Si) \qquad (1)$$

The heat capacities of silicon and most of the transition-metal elements are well-known, so this rule is easy to apply. In addition to allowing the calculation of enthalpy increments, the Neumann–Kopp rule has also been used for second- and third-law estimation of ambient-temperature heats of formation of some silicides from high-temperature $\Delta H°_T$ and $\Delta G°_T$ experimental data.[8,20-23]

In general, the Neumann–Kopp rule would appear to provide a relatively accurate first approximation of the heat capacities of transition-metal silicides, provided that no dramatic changes in C_p for either the compound or elements occur. Figure 1 illustrates the ratio of experimental heat capacities for three chromium silicides to those calculated using the Neumann–Kopp rule as a function of temperature; the experimental data are taken from the results of Kalishevich et al.[19,24] and the elemental heat capacities from the compilation by Pankratz.[25] The agreement, generally within 5%, is acceptable; however, the reader will notice, at higher temperatures, the ratio "takes off" for Cr_5Si_3. This is due to a rapid increase in $C_p(Cr_5Si_3)$ caused by disordering, a major limitation on the usefulness of the Neumann–Kopp rule. Phase changes in the silicide or constituent elements are another such limit; and most investigators have found significant discrepancies between experimental and additive results for subambient heat capacities.[26-29] This latter discrepancy in turn means that the entropy of formation for most silicides is not equal to zero, introducing a source of error into those third-law enthalpy of formation estimates made with use of this approach. A final note on this "model" is that most of the measured heat capacities used for comparison have been performed on less stable silicides, which are in fact likely to have a smaller entropy of formation, and thus a ΔC_p closer to zero. For the silicides of groups IIIB and IVB elements, this approach should be less applicable still.

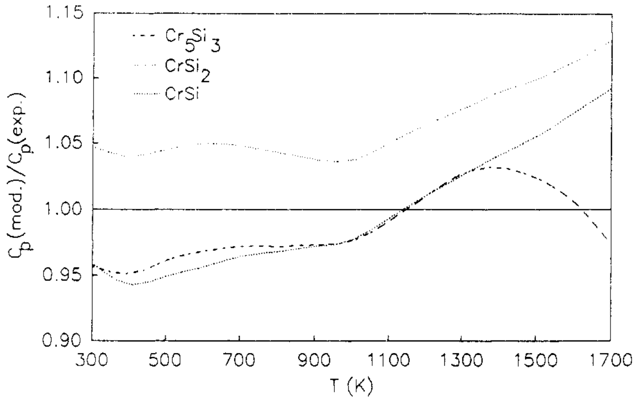

Figure 1. Ratio of "model-calculated" (Neumann–Kopp rule) heat capacities for chromium silicides divided by the experimental values of Kalishevich et al.,[19,24] plotted against temperature.

Perhaps the earliest estimation technique for transition-metal silicide heats of formation is that described in 1956 by Brewer and Krikorian.[30,31] By determining the temperature range over which equilibrium existed in a silicide-bearing M–Si–O or M–Si–N system, a range of possible $\Delta G°_T$ values could be calculated. Once this range of values was established, the Neumann–Kopp rule was used to calculate a similar range for $\Delta H°_{298}$. The heat of formation ranges established by this approach (for silicides of Ce, Mo, Nb, Re, Ta, Ti, W and Zr) are considerable in some cases and are based on phase equilibria results of some uncertainty. Similar comments can be applied to the "limiting values" of $\Delta G°$ determined for Nb_5Si_3 by Schäfer and Dohmann[32] and for other silicides by Wengert and Spanoudis.[33] Using more accurate thermodynamic data for the species in equilibrium with the silicide compound, Freund and Spear have more recently used a similar technique to estimate $\Delta G°_{1100}$ for vanadium silicides using the V–Si–O phase diagram[34] and assessed the existing experimental data in light of these results.

More recent modeling efforts have focused on the use of metal physics theory to determine the energetics of silicide formation, usually as a part of more general work on intermetallic compound thermodynamics. The most notable of these is the model proposed by Miedema and co-workers,[35] based on the Wigner–Seitz cell approach to alloy theory. Niessen and de Boer have described the "finished" expression for estimating the heat of formation of an intermetallic solution or compound:[36]

$$\Delta H = \frac{f(x)\{-P(\Delta\phi^*)^2 + Q(\Delta n_{ws}^{1/3})^2 - R\}}{(n_{ws}^{-1/3})_{av}} \qquad (2)$$

P, Q, and R are constants applicable to specific groups of A–B systems, $\Delta\phi^*$ represents the electronegativity difference, $\Delta n_{ws}^{1/3}$ is a differential in electron densities, and $f(x)$ is a function of composition. In the case of metal–metalloid compounds, an extra term is added to represent the enthalpy requirement for "metalizing" the latter element (for Si, this value is equal to 33 kJ/mol). The model is semiempirical, and the values of the various parameters are somewhat uncertain; but heat of formation calculations using this approach have shown reasonable agreement with experimental data for a large number of experimental systems. Estimated heat of formation values for several transition-metal silicides calculated with this model have been published and will be referred to throughout this review.

More recently, Machlin has focused on obtaining improved values of R in eq 2,[37] which is described as a correction related to d–p hybridization in the various compounds. The improvement in enthalpy of formation prediction for several monosilicides resulting from this is apparent, as well as for some tersilicides. Pasturel and co-workers have also developed a model for predicting silicide heats of formation, based on d-band considerations;[38] their results compare well with experimental data for cobalt, iron, and nickel silicides.

As earlier mentioned, the phase equilibria calculations of Brewer and Krikorian allow the estimation of free energies as well as enthalpies of formation of transition-metal silicides.[20] More sophisticated solution-modeling techniques, as well as improved data for M–Si liquid solutions, have facilitated development of free energy estimation techniques of this sort, most notably the "coupling" of phase diagram and thermochemical data demonstrated by Kaufman.[39] Similar techniques have been demonstrated for the Cu–Si and Ni–Si systems by Lüdecke and an Mey, respectively.[40,41] However, this type of modeling generally requires some simplifying assumptions, including strict stoichiometry and minimized solid solubility ranges for the solid silicides and the use of the Neumann–Kopp rule where experimental C_p data are not available. As a result, while phase diagrams calculated using this general approach correlate fairly well with the "real thing", estimated heats and free energies of formation of the various silicide compounds can differ considerably. Further improvement in modeling techniques (as well as in the comparable experimental data) should yield improvements in this area in the future.

B. Experimental Techniques

Just as the modeling techniques used to estimate the thermodynamic properties of transition-metal silicides can be divided into those used to calculate heat capacities and heats and free energies of formation, so too can the experimental work. Reviews by Bruzzone and Sommer describe recent advances in instrumentation for thermodynamic analysis of intermetallic systems,[42,43] and that by Kubaschewski recounts much of the history of this field of research;[44] the reader is recommended to these sources.

As might be suspected, research on the heat capacities of transition-metal silicides is divisible into two categories, subambient- and high-temperature work. Several silicides exhibit unusual low-temperature properties,[27] especially V_3Si, which becomes a superconductor at what used to be a high value of T_c (17 K).[45] This has provided greater than usual incentive for subambient C_p analysis. Research work of this type has been conducted on the same adiabatic-type instruments used for other materials,[46] with the same degree of reliability; in his review work, Chart placed considerable reliance on entropy values obtained with this approach.[15,17] However, little of the subambient data is of recent vintage; in several cases, the low-temperature limit of the published studies is 50 K or more.[19,26-29,47,48] As a result, the accuracy of some S^0_{298} determinations made by subambient calorimetry is somewhat suspect, and the user is advised to examine experimental details carefully.

While adiabatic calorimeters have been the unanimous choice of instrument of low-temperature heat capacity measurements, high-temperature work has been conducted by both adiabatic and drop (isothermal, mixing) calorimetry. Drop calorimetry is the older of the two techniques, having been used to determine silicide heat capacities as far back as 1910.[49,50] Kubaschewski and co-workers,[51,52] reviewing previous work in drop calorimetry, have pointed out that its results are less likely to be accurate for alloys (or compounds) "dropped" from temperatures above those at which a phase change or significant disordering occurs. Another expressed concern with regard to this technique is the slower thermal response of drop calorimeter metal blocks, which can result in lower than actual enthalpy measurements. The use of adiabatic calorimetry to determine silicide heat capacities stems from the early 1960s[48] and is perhaps a more appropriate choice, especially for compounds undergoing phase changes or disordering. However, the last heat capacity measurements of any sort for transition-metal silicides were published over 15 years ago;[53] since that time, a variety of improved high-temperature techniques have been made available, as illustrated by Bruzzone.[42] As will be seen, the gaps in the present database remaining to be filled by these experimental apparati are considerable.

A variety of calorimetric techniques have also been used by researchers attempting to determine the heats of formation of silicide (and other intermetallic) compounds. The earliest was the isothermal mixing technique demonstrated by Oelsen and co-workers,[54-56] which involved simultaneously pouring specified amounts of molten silicon and a transition metal (Co, Fe, Ni) into a sand-lined steel cylinder at 1873 K, plunging it into a bucket of water, and measuring the temperature increase.[44] Taking into account the enthalpies of heating the elements and the resultant alloy to the reaction temperature allows calculation of the heat of formation of the alloy phase at both 1873 K and ambient temperature. Although the analytical equipment has improved since this technique was first demonstrated in 1936, the principle behind it remains a valuable approach to intermetallic alloy thermodynamic measurements, as recent work shows.[57] However, the previously mentioned comments by Kubaschewski and Hultgren with regard to drop calorimetry enthalpy measurements through transition zones (such as incongruent freezing) apply to this type of experiment as well,[51] and so results obtained in this fashion should be viewed with some caution.

Another popular heat of formation determination method has been bomb combustion calorimetry, used to determine ΔH°_{298} for several metal silicides.[58-60] The "oxidant" used in this type of experimental work has usually been O_2, but Golutvin et al. have recently mixed scandium silicides with poly(tetrafluoroethylene) to demonstrate an indirect fluoride combustion technique.[61] Kubaschewski and Hultgren note,[51] however, that enthalpies of formation determined by this method are extremely sensitive to small degrees of uncertainty and the potential for forming silicates rather than oxides in the combustion process is another potential source of error. As a result, Chart tends to discount values obtained by this method.[15,17]

In using calorimetric techniques for ΔH°_T determination, kinetics can be a significant factor in the accuracy of experimental results. This is especially true for silicides, where for the most part experimental regimes have involved solid-state formation or decomposition of the compounds. Santandrea et al. have recently demonstrated the influence of kinetics on the measured solid-state heats of formation of nickel aluminides,[62] showing how differential scanning calorimetry results varied according to the shape of the elemental powder particles reacted. As a result, calorimetric techniques with faster reaction rates are likely to yield more accurate results. This in part explains why acid solution calorimetry is not well regarded as an experimental method for silicides,[15,17,51,52] although it has been occasionally used. Kinetic concerns are especially likely to have affected the experimental results when HCl was used as the solvent,[61] leaving behind a residue layer of solid silica. HF has also been used,[63-65] but this requires accurate measurement of SiH_4 and H_2 vapor formation rates, another likely source of uncertainty.

A more promising approach to calorimetric determination of silicide heats of formation is the use of molten metals as a solvent. Jounel et al. used liquid Al as a solvent for FeSi,[66] and Topor and Kleppa have recently published the results of a series of experiments using Cu, Pd, Pt, and Pd–Ge alloys in the same role.[67-71] When both pure metals (in proper proportion) and the corresponding silicide are mixed at 298 K into the molten solvent metal at a higher temperature, the heat of formation of the silicide can be determined at 298 K directly, without use of heat capacity data (or the Neumann–Kopp rule). However, kinetics can be a concern here as well; silicides are not classified as refractory compounds without cause, and some dissolve in molten alloys less willingly than others, as Topor and Kleppa have shown.[70] As a result, the choice of solvent metal is not one that can be made casually.

The high stability of several transition-metal silicides suggests that in some cases measurement of the heat flux associated with their formation rather than dissolution might be kinetically advantageous. In fact, the formation of some silicides generates enough heat to sustain the reaction, allowing their manufacture by self-propagating high-temperature synthesis (SHS).[72,73] As a result, ΔH°_T determination for these silicides by direct-reaction calorimetry is on occasion a viable technique, and some of the earliest measurements of this parameter for IVB–VIIB silicides were in fact made via this approach.[74] However, direct-reaction calorimetry works best only when the reaction goes to completion and when the "start-up" assistance of a thermite reaction (and the corresponding heat input) can be avoided. Most of the existing direct-reaction calorimetric work was beset with one or both of these concerns,[73-75] thus limiting its accuracy. However, in some cases these results are useful, especially for the more exothermic silicides.

Free energies of formation of transition-metal silicides have generally been determined by two steps of experimental technique: vapor pressure determinations and EMF measurements. Vapor pressure methods can in turn be categorized into those experiments that measure the dissociation or vaporization rates of the silicide in question and those that look at the results of reaction equilibria with one or more non-silicide gaseous species. Studies in the latter category are not common but have some value with regard to the most stable silicides, which exhibit appreciable vaporization rates only at extraordinarily high temperatures. In particular, Chart has shown how oxidation of the Si content in silicides by reaction with SiO_2 can be used to determine a_{Si}, through measurement of the partial pressure of SiO vapor generated as a result.[23,76] Rossemyr and Rosenqvist have demonstrated a similar technique, using HCl vapor to oxidize manganese in various silicides to $MnCl_2$ vapor.[77] However, ΔG°_T measurements made by this approach are highly sensitive to accurate determination of equilibrium vapor pressures, and the more complex the reaction, the greater the likelihood of error. As a result, some results from this type of experiment are more reliable than others, as will be seen.

The merit of using dissociative vapor pressures as an experimental technique has been augmented by the addition of mass spectroscopy to the procedure. In comparison with earlier "weight loss" techniques, mass spectroscopy allows the accurate determination of species activities at lower partial pressures, and thus lower experimental temperatures. The use of lower temperatures in turn (a) minimizes the effect of silicon vapor interaction with tungsten effusion cells, a problem in older dissociation experiments,[21] and (b) often allows the direct use of high-temperature heat capacity data for the particular silicide to determine ΔH°_{298}, instead of extrapolation or use of the Neumann–Kopp rule. Other advantages of mass spectroscopy over the weight loss technique include the ability to ascertain exactly what is volatilizing (rather than making assumptions)[78] and increased reliability of results. As a result, dissociation vapor pressure measurements are becoming an increasingly popular method for thermodynamic investigations, not just with regard to silicides but to intermetallic systems in general.[44]

The use of EMF techniques to study transition-metal silicide thermodynamics is the most recent of the major groupings but has quickly become a favorite. EMF data have good reliability and reproducibility and can be obtained at lower temperatures than vapor pressure investigations. However, there are concerns associated with this approach as well. For less stable silicides (such as those of the VIIIB metals), measured EMF values can be small and the resulting degree of uncertainty in the results large, as Vecher et al. have noted with respect to Fe–Si alloys.[79] Furthermore, several EMF investigations of transition-metal silicides were conducted with molten salt electrolytes; as Wagner and Werner have noted,[80] errors can arise in analytical results from

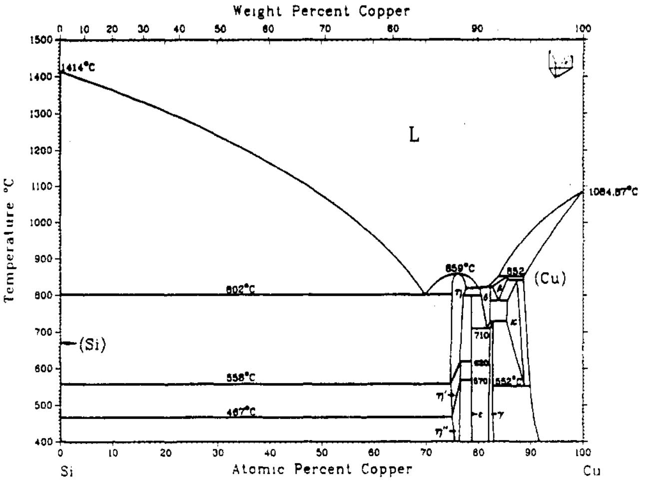

Figure 2. Copper–silicon phase diagram. Reprinted from ref 86. Copyright 1986 ASM International.

this system as a result of displacement reactions, especially in measurements on less ionic compounds (such as silicides). The use of reduced-activity "reference electrodes" deals with the latter concern, but at the expense of exacerbating the former.[81-83] Nevertheless, EMF techniques are a worthy approach, especially for the more ionic silicides, and the development of solid electrolyte cells promises to make the technique more useful for analyzing less stable compounds as well.[22,84,85] As a result, much of the more recent work on transition-metal silicide thermodynamics has been performed with use of EMF methods.

III. Specific Systems

A. IB and IIB Elements

It is somewhat misleading to begin a review of the database on the thermodynamic properties of transition-metal silicides with this group of elements, as only one of the six—copper—actually forms stable silicides. Figure 2 shows the Cu–Si phase diagram,[86] which features several stable high-Cu phases: β (nominally "$Cu_{17}Si_3$"), γ ("$Cu_{56}Si_{11}$"), δ ("$Cu_{33}Si_7$"), ϵ ("Cu_4Si"), η ("$Cu_{19}Si_6$" or "Cu_3Si"), and κ ("$Cu_{87}Si_{13}$"). Only γ, ϵ, and η are stable at room temperature; η also exhibits two polymorphs. Slight homogeneity ranges have been detected for most of these phases.

Although several investigations of liquid Cu–Si alloys are reported in the literature, the only available information concerning solid compounds is the ambient-temperature C_p value for "Cu_3Si" reported by Schimpff in 1910.[49] This leaves modeling efforts as the only source of thermodynamic "data" for the solid compounds. The most ambitious of these is that of Lüdecke,[40] who used a Redlich–Kister polynomial to model the liquid solution, followed by a least-squares fit to determine invariant points and the thermodynamic characteristics of the intermetallic phases. His assumptions include use of the Neumann–Kopp rule and strict stoichiometry for the intermetallic phases; while the modeling results closely approximate the actual phase diagram, it is doubtful whether complete confidence in the resulting five-term $\Delta G°_T$ equations for the silicide compounds is justified. Kaufman has similarly modeled the system,[39] and the Miedema approach described above can also be used to estimate the heats of formation of copper silicide compounds.[36] Table 1 shows the predicted $\Delta H°_{298}$ values for γ, ϵ, and η from these three models; as Lüdecke has pointed out, those predicted by Kaufman differ considerably. The low electronegativity and atomic size differences between copper and silicon suggest that the intermetallic compounds in this system are among the least stable in the group; as a result, the heats of formation estimated by Lüdecke or by Miedema's model are likely to be closer to the actual value, with Lüdecke's results being preferred here.

TABLE 1. Estimated $\Delta H°_{298}$ for Copper Silicides (kJ/mol of Atoms)[a]

	γ ($C_{56}Si_{11}$)	ϵ (Cu_4Si)	η ($Cu_{19}Si_6$)
Kaufman[39]	−29.4	−29.3	−26.3
Niessen and de Boer[36]	−2	−3	−3
Lüdecke[40]	−1.67*	−2.23*	−2.66*

[a] Asterisk indicates a recommended value.

TABLE 2. Experimental and Estimated Values of $\Delta H°_{298}$ for Scandium Silicides (kJ/mol of Atoms)

	Sc_5Si_3	ScSi	Sc_5Si_3
Golutvin et al.[61 a]	−161.0	−117.2	−71.1
Topor and Kleppa[71 a]	−89.0*[c]		
de Boer et al.[89 b]	−69	−80	−72
$\Delta S°_{298}$ (J/mol·K)[90]	−2.48		

[a] Experimental. [b] Modeled. [c] Asterisk indicates a recommended value.

B. IIIB Elements (Rare Earths)

Although efforts were made to determine the thermodynamic properties of IIIB silicide compounds as much as 30 years ago,[87] most of the experimental work in this area is of relatively recent vintage. Controversy still exists over what phases exist in some *Ln*–Si systems, and melting points for several compounds are as yet undetermined. As a result, the thermodynamic properties of these silicides are still largely a mystery. As a rule, however, rare-earth silicide compounds are characterized by high melting points and minimal nonstoichiometry, which suggest especially high degrees of stability. However, much work remains to be done in these systems.

The IIIB–silicon system for which the most thermodynamic information exists is that of scandium; the current state of that literature illustrates how much remains to be discovered. The most recent investigation of the Sc–Si phase diagram reports three stable compounds:[88] congruently melting Sc_5Si_3, peritectic ScSi, and a peritectic Sc_2Si_3 that decomposes below 1198 K. This flies in the face of previous claims (and in fact reported thermodynamic data) for a stable Sc_3Si_5;[61,69] "$ScSi_2$" has also been reported, and rejected. Considerable variation is also apparent in the results of the two thermodynamic investigations of the system published to date. Table 2 lists the enthalpy of formation for Sc_5Si_3 determined by Topor and Kleppa with metal solution calorimetry,[71] the values for all three "proven" silicides that Golutvin et al. obtained by a combination of oxide and fluoride combustion and aqueous solution calorimetry,[61] and estimates interpolated from the Miedema model results published by de Boer et al.[89] It should be noted that the results of Golutvin et al. also contain an oxide combustion generated $\Delta H°_{298}$ value for scandium oxide that differs substantially from the literature value.[25] Furthermore, this work assumes that the phases resulting from oxide combustion of scandium silicides were Sc_2O_3 and SiO_2, although the generation of a scandium silicate would seem a very real possibility. This, along with the model-calculated values, leads to a recommendation of the result of Topor and Kleppa for $\Delta H°_{298}(Sc_5Si_3)$ over that of Golutvin et al. The only other thermodynamic data available for this system are the low-temperature enthalpy measurements of Sychev et al.[90] This work reported an entropy at 298.15 K of 209.8 J/mol·K for Sc_5Si_3; using entropy data for the elements from the compilation of Pankratz,[25] $\Delta S°_{298}$ for this compound is calculated as −19.8 J/mol·K, and combination with the experimental heat of formation results of Topor and Kleppa yields $\Delta G°_{298} = -706.4$ kJ/mol. The variance of the modeling results from the experimental data for Sc_5Si_3 does not lend confidence to its use for ScSi or "Sc_5Si_3"; similar comments apply to the other results of Golutvin et al.

The only other published heat capacity data on IIIB silicides are the low-temperature results for Y_5Si_3 reported by Safonov et al. ($S°_{298} = 265.0$ J/mol·K, $\Delta S°_{298} = -13.7$),[91] and no $\Delta H°_T$ or $\Delta G°_T$ data exist for this phase. The Ce–Si–N phase equilibria reported by Brewer and Krikorian have been employed by Searcy to estimate $\Delta H°_{298}$ for $CeSi_2$ of −210 kJ/mol,[8,30] but a large degree of uncertainty is attached to this figure. Samsonov et al. have investigated the reduction of several rare-earth oxides by elemental silicon to produce the silicide and SiO vapor[92] and report a similar value for CeSi.[16] The same work has also produced the only reported experimental values of $\Delta H°_{298}$ for lanthanum and yttrium monosilicide (−125.4 and −134.6 kJ/mol, respectively); as is the case for scandium silicides, these are somewhat less exothermic than the model-estimated values of Niessen and de Boer.[36]

Recent reports describe the results of EMF investigations on the thermodynamic properties of rare-earth "disilicides".[81-83] The experiments were conducted over a roughly 100 °C temperature range in a molten salt electrolyte, measuring the EMF between the Si-saturated silicide and a tin-saturated stannide of the same rare-earth element. (The use of the stannide instead of the pure element minimized the exchange-reaction difficulty associated with molten salt EMF experiments described above.[80]) Previous knowledge of the free energy of formation of the stannide "reference electrode" allowed calculation of the same property for the disilicide, and the EMF vs temperature slope was used to calculate $\Delta H°_T$. For $Gd_{0.33}Si_{0.67}$, this latter value was −79.3 kJ/mol at 885 K; for β-$NdSi_2$ ($Nd_{0.36}Si_{0.64}$), −89.0 at 1000 K; and for $La_{0.37}Si_{0.64}$, −99.1 at 1000 K. Calculated entropies of formation for these compounds were also considerable: −22.2, −20.1, and −28.4 J/mol·K, respectively. (The use of silicon saturation means that these are presumably the highest stable silicides in the system. This in turn would suggest that stoichiometric lanthanum and neodymium disilicides are in fact not part of the La–Si and Nd–Si systems, yet another source of confusion.) This particular group of silicides remains a fertile field for further experimental work.

C. Titanium

Unlike the previously discussed elements, the titanium–silicon system is well characterized and extensively studied. Figure 3 illustrates the system,[86] which was recently reviewed by Murray.[93] The Ti–Si system features five stable intermetallic phases; however, thermodynamic properties have been reported only for Ti_5Si_3, TiSi, and $TiSi_2$. Ti_5Si_3 is the only compound with any significant homogeneity range; a possible allotropic transformation in $TiSi_2$ at 1473 K is the only polymorphism in the system.

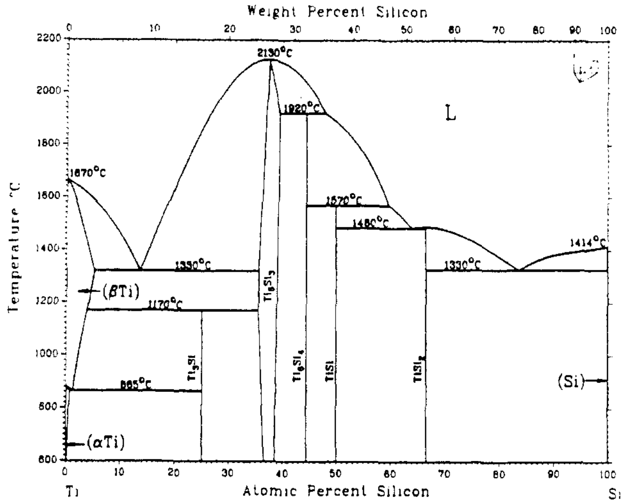

Figure 3. Titanium–silicon phase diagram. Reprinted from ref 86. Copyright 1986 ASM International.

The high electronegativity difference between Ti and Si suggests that these silicides should be among the more stable of those formed by transition metals; as a result, the compound formation calorimetric techniques described above for determining $\Delta H°_{298}$ ought to be more appropriate for this system. In fact, a variety of calorimetric experiments have been performed on titanium silicides, from the combustion technique demonstrated in 1956 by Golutvin to the 1986 metal solution work of Topor and Kleppa.[58,68] Robins and Jenkins and Maslov et al. have demonstrated the use of direct-reaction calorimetry in this system,[72,74] and Polyachenok et al. and Savin have employed indirect-reaction techniques to determine $\Delta H°_{298}$ values.[94,95] Heat capacity results are harder to come by; Sychev et al.'s results for Ti_5Si_3 are the only low-temperature data available,[90] and above-ambient work is limited to that reported for all three silicides by Golutvin and for $TiSi_2$ by Bondarenko et al.[53,96] Several modeling efforts have also been published.[37,39,89]

Two attempts at determining $\Delta G°_T$ for the titanium silicides have also been made, both dependent on the vapor pressure of reaction products. The first of these involves the reduction of TiO_2 with elemental silicon to form the silicide and SiO vapor:[97]

$$5TiO_2 + 13Si = Ti_5Si_3 + 10SiO \quad (3)$$

(Similar reactions can be written for the formation of TiSi and $TiSi_2$.) By measuring the partial pressure of SiO (or the level of vacuum necessary to make the reaction happen) at a given temperature, and assuming unit activity of the condensed-phase compounds, the free energy of eq 3 can be determined,[16] and thus $\Delta G°_T$ for the particular silicide. The second free energy experimental approach, that of Kozlov et al.,[98] employed

TABLE 3. Experimental and Estimated Values of $\Delta H°_{298}$ for Titanium Silicides (kJ/mol of Atoms)

	Ti_3Si	Ti_5Si_3	Ti_5Si_4	TiSi	$TiSi_2$
Robins and Jenkins[74 a]		−72.5		−65.0	−45.0
Golutvin[58 a]		−76.9		−82.0	−59.8
Polyachenok et al.[94 a]		−72.7			
Savin[95 a]		−76.5		−78.6*	−60.2
Maslov et al.[72 a]		−72.4*[c]			
Topor and Kleppa[68 a]					−57.0*
Kaufman[39 b]		−72.4		−64.9	−44.8
Machlin[37 b]				−64.7	
de Boer et al.[89 b]	−53*	−74	−81*	−82	−61
$\Delta S°_{298}$[90]		−4.67			

[a] Experimental. [b] Modeled. [c] Asterisk indicates recommended value.

coreduction of titanium and silicon chloride vapors with H_2:

$$5TiCl_4 + 3SiCl_4 + 16H_2 = Ti_5Si_3 + 32HCl \quad (4)$$

In both cases, the determined free energy is highly dependent on accurate measurement of partial vapor pressures, and the high-temperature thermodynamic properties of some of the vapor species are not as reliable as might be desired. As a result, the results of these investigations are not recommended for use in second-law determinations of $\Delta G°_T$ and $\Delta H°_T$ for the titanium silicides.

Table 3 illustrates $\Delta H°_{298}$ for the five stable titanium silicides, as determined by the five experimental and three modeling studies published to date. For Ti_5Si_3, the modeling and experimental results are all remarkably similar; the direct-reaction calorimetry figure generated by Maslov et al. is recommended over the others, being the result of a more appropriate experimental technique.[72] However, the degree of disagreement for the mono- and disilicides is considerable, and made more so by the fact that there is a modeling result available to support each of the experimental values. As a result, recommending a "most likely" heat of formation value for TiSi and $TiSi_2$ requires rejecting one or more of the experimental results. In both of these cases, the data reported by Robins and Jenkins are substantially different from the trend of more recent (and more numerous) studies.[74] This particular study was conducted with direct-reaction calorimetry for a solid-state reaction, and the authors pointed out that the TiSi and $TiSi_2$ that formed as a result was not in fact pure. As a result, it may be that this particular set of results is a victim of the kinetics concern described earlier. Looking at the remaining data, the combustion calorimetry results of Golutvin may in part reflect the formation of a titanium silicate;[58] as a result, this is less favored as a recommended value for the heat of formation of TiSi than that published by Savin,[95] who measured the heat effect of coreducing the chlorides with magnesium metal to form the monosilicide and $MgCl_2$. $TiSi_2$ is less stable than the other silicides and, as a result, more easily dissolved in metal solutions; as a result, the $\Delta H°_{298}$ value published by Topor and Kleppa for this compound is preferred.[68] The modeling results of de Boer et al. compare well with the recommended experimental values for Ti_5Si_3, TiSi, and $TiSi_2$[89] and so are likely to be good heat of formation estimates for Ti_3Si and Ti_5Si_4 as well.

Sychev et al. report an entropy value of 104.5 J/mol·K for Ti_5Si_3 at 298.15 K ($\Delta S°_{298} = -37.4$); applying this to the recommended heat of formation in Table III yields a $\Delta G°_{298}$ value of −590336 J/mol. Theoretically, the high-temperature heat capacity of data of Golutvin could now be added to this data to yield $\Delta G°_T$ and $\Delta H°_T$ functions for Ti_5Si_3 and $\Delta H°_T$ for TiSi and $TiSi_2$.[96] However, as Figure 4 demonstrates, Golutvin's data may not be particularly trustworthy. Comparison of the C_p values derived from Golutvin's work against those reported for higher temperatures by Bondarenko illustrates substantial differences.[53] Other heat capacity results published by Golutvin and co-workers have also been called into question.[5,19,26,99] As a result, more complete thermodynamic data for the titanium silicides cannot be recommended with any degree of confidence.

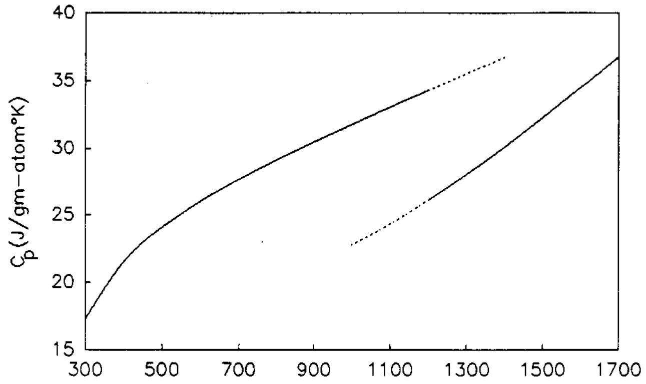

Figure 4. Heat capacity of titanium disilicide vs temperature, from the data of Golutvin (low-temperature) and Bondarenko (high-temperature).[53,96]

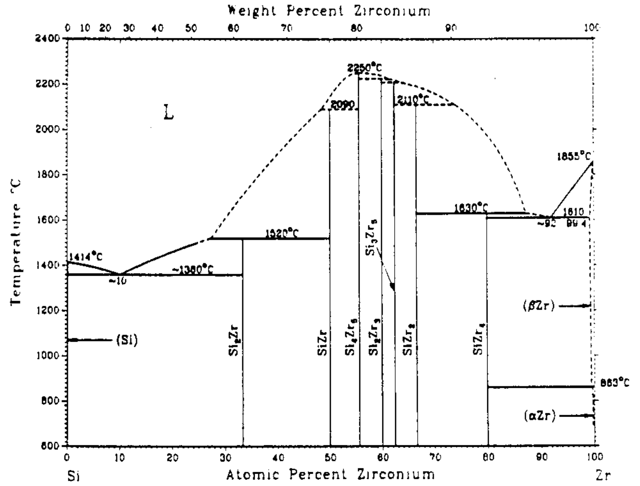

Figure 5. Silicon–zirconium phase diagram. Reprinted from ref 86. Copyright 1986 ASM International.

D. Hafnium and Zirconium

Figure 5, the zirconium–silicon phase diagram,[86] illustrates features common to both it and the Hf–Si system—several intermetallic phases, which in general exhibit minimal nonstoichiometry and a series of especially stable phases with (Hf, Zr)/Si ratios ranging between 1.00 and 2.00. There is some uncertainty concerning high-temperature equilibria in both systems, along with lack of complete agreement on just how many phases actually exist, but the extraordinarily high stability range of most of the silicides suggest these as materials worth further investigation. Sorrell and McCartney have recently reviewed the Zr–Si system.[100]

TABLE 4. Experimental and Estimated Values of ΔH°_{298} for Hafnium and Zirconium Silicides (kJ/mol of Atoms)

	Hf_2Si	Hf_5Si_3	HfSi	Zr_2Si	Zr_5Si_3	Zr_5Si_4	ZrSi	$ZrSi_2$
Robins and Jenkins[74 a]					-76.5		-73.8	-49.9
Maslov et al.[72 a]							-74.9*[c]	-51.3*
Golutvin and Maslennikova[64,65 a]	-65.3	-70.3	-71.1	-111.3	-111.3	-90.8		-63.8
Searcy and Finnie[20 b]				-69.9	-76.6		-77.4	-53.1
Machlin[37 b]			-77.9				-70.2	
Niessen and de Boer[36 b]	-74	-82	-93	-81	-90	-100	-103	-85
ΔS°_{298}[91,101]					-5.68			-2.60

[a] Experimental. [b] Modeled. [c] Asterisk indicates a recommended value.

Unfortunately, the large number of stable phases coincides with considerable *in*stability in the thermodynamic study of hafnium and zirconium silicides. No free energy studies have yet been performed, and only four investigations have resulted in published values of ΔH°_{298} for compounds in the two systems. These include the direct-reaction calorimetry experiments on zirconium silicides performed by Robins and Jenkins and Maslov et al.[72,74] and the acid solution calorimetry data for Zr–Si and Hf–Si alloys obtained by Golutvin and co-workers.[64,65] The difficulties concerning the lack of complete reaction in the alloys manufactured by Robins and Jenkins have already been mentioned in the discussion on titanium silicides; similar problems were observed in the formation of zirconium compounds. In addition, the "compounds" studied by Robins and Jenkins include "Zr_6Si_5", which is nonexistent in the actual phase diagram. The limitations of the use of acid solution calorimetry for silicide heat of formation determination have also been discussed previously. Additionally, the "phases" described by Golutvin et al. also occasionally fail to mesh with the phase diagram. The direct-reaction calorimetry results of Maslov et al. for ZrSi and $ZrSi_2$ would seem the most reliable of those published and are recommended to the reader. Otherwise, the conclusion reached by Chart that no reliable experimental values of ΔH°_{298} exist for the hafnium or zirconium disilicides remains valid today.[15] This conclusion includes the modeling results of Machlin and of Niessen and de Boer,[36,37] listed in Table 4 along with the various experimental results.

Some heat capacity work has also been published for both hafnium and zirconium silicides. Low-temperature results include those for zirconium disilicide reported by Khriplovich et al. (S°_{298} = 68.20 J/mol·K for "$ZrSi_{1.96}$", $\Delta S^\circ_{298} = -7.70$)[101] and for Zr_5Si_3 by Safonov et al. (S°_{298} = 221.6 J/mol·K, $\Delta S^\circ_{298} = -45.4$).[91] However, reported high-temperature C_p data for these systems exists only at temperatures above 1100 K,[53,102,103] and only for the two disilicides. Clearly, a more substantial research effort on these systems is mandated for the future.

E. Vanadium

TABLE 5. Experimental and Estimated Values of ΔH°_{298} for Vanadium Silicides (kJ/mol of Atoms)

	V_3Si	V_5Si_3	VSi_2
Golutvin and Kozlovskaya[59 a]	-28.2	-50.2	-104.6
Gorelkin and Mikhailov[75 a]	-35.2	-58.0*[d]	-41.6
Gorelkin et al.[110 a]		-58.6	-50.2
Topor and Kleppa[68 a]			-37.5
Chart[15,17 b]	-34.3	-57.7	-41.8
Eremenko et al.[107-109 b]	-35.2	-58.0	-41.2
Freund and Spear[34 b]	-41.4	-49.2	-40.3
Smith[99 b]	-43.1	-53.8	-40.7
Storms and Myers[104 b]	-44.9	-52.5	-40.7
Myers and Kematick[105 b]	-44.6	-52.6	
Machlin[37 c]			-29.5
de Boer et al.[89 c]	-32	-44	-29
this work	-45.2*		-40.2*
ΔS°_{298}	-3.33[45]		-2.70

[a] Experimental. [b] Assessed. [c] Modeled. [d] Asterisk indicates a recommended value.

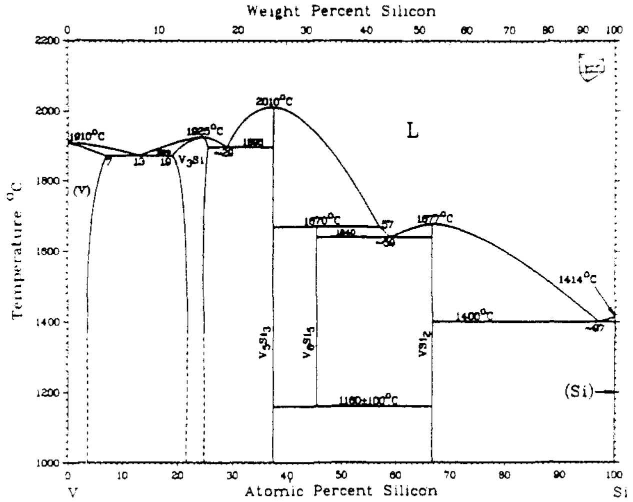

Figure 6. Vanadium–silicon phase diagram. Reprinted from ref 86. Copyright 1986 ASM International.

No transition metal–silicide system has been studied more thoroughly than that of vanadium; yet unanswered questions remain about even this phase diagram. The most recent assessment, illustrated here as Figure 6,[86] shows four stable intermetallic compounds, only one of which (V_3Si) shows any solid solubility range. The most significant issue yet to be resolved in this system is the upper and lower stability limits of V_6Si_5; the phase diagram suggests incongruent melting of this compound at 1943 K, and Storms and Myers have used their Knudsen effusion results to determine a low-temperature limit of 1160 K.[104] However, the degrees of uncertainty in both values are considerable. Smith has published a review of this system including a discussion of the thermodynamic information reported through 1980,[99] which is highly recommended to the reader.

Since Smith's review,[99] several noteworthy investigations of vanadium silicide thermodynamics have been reported. These include the metal solution calorimetry study of VSi_2 by Topor and Kleppa,[68] the modeling results of de Boer et al.,[89] and the vaporization studies of Myers and co-workers.[104,105] Table 5 summarizes the results of the various experimental studies, thermodynamic assessments, and modeling efforts with regard to ΔH°_{298} for the three stable silicides at that temperature; although exact agreement is not apparent, a

TABLE 6. Parameters for ΔH°_T and ΔG°_T Calculations for Vanadium Silicides (J/mol of Atoms)

phase	std states V	std states Si	temp range, K	*a*	*b*	*c*	*d*	*e*
VSi_2	sol	sol	298–1687	−39 957	0.37	−0.030	−0.33	0.016
VSi_2	sol	liq	1687–1950	−74 636	−1.54	0.95	−2.42	13.568
V_3Si	sol	sol	298–1650	−45 614	0.63	−1.77	−1.25	7.212

TABLE 7. Recommended Thermodynamic Values for Solid VSi_2 (per Mole of Atoms)

temp, K	$H_T - H_{298}$, J	S°_T, J/K	ΔH°_T, J	ΔG°_T, J
298.15	0	19.51	−40 181	−39 376
400	2 292	26.11	−40 192	−39 100
500	4 667	31.41	−40 216	−38 825
600	7 129	36.90	−40 245	−38 544
700	9 661	39.80	−40 278	−38 258
800	12 257	43.26	−40 313	−37 967
900	14 911	16.39	−40 351	−37 672
1000	17 622	49.25	−40 391	−37 372
1100	20 387	51.98	−40 430	−37 068
1200	23 205	54.33	−40 472	−36 761
1300	26 076	56.63	−40 514	−36 450
1400	28 999	58.80	−40 557	−36 136
1500	31 974	60.85	−40 602	−35 818
1600	35 000	62.80	−40 646	−35 498
1687	37 674	64.43	−40 686	−35 217
1687	37 674	64.43	−74 387	−35 217
1700	38 076	64.67	−74 366	−34 913
1800	41 204	66.50	−74 196	−32 581
1900	44 383	68.17	−74 005	−30 260
1950	45 991	69.01	−73 903	−29 103

TABLE 8. Recommended Thermodynamic Values for Solid V_3Si (per Mole of Atoms)

temp, K	$H_T - H_{298}$, J	S°_T, J/K	ΔH°_T, J	ΔG°_T, J
298.15	0	24.55	−45 163	−44 170
400	2 298	31.18	−45 331	−43 804
500	4 658	36.44	−45 490	−43 404
600	7 088	40.87	−45 663	−42 971
700	9 578	44.70	−45 860	−42 507
800	12 120	48.10	−46 085	−42 013
900	14 711	51.15	−46 340	−41 489
1000	17 349	53.93	−46 627	−40 935
1100	20 031	56.48	−46 947	−40 351
1200	22 759	58.86	−47 300	−39 736
1300	25 530	61.07	−47 687	−39 090
1400	28 344	63.16	−48 109	−38 413
1500	31 202	65.13	−48 565	−37 705
1600	34 102	67.00	−49 056	−36 965
1650	35 568	67.91	−49 314	−36 583

"grouping" of values can be seen for each compound, suggesting the approximate range of the "correct" ΔH°_{298}. It is also apparent that the modeling results of de Boer et al. do not compare well with the experimental heats of formation.[89]

Smith points that reliable heat capacity data exists for two of these compounds, V_3Si and VSi_2.[47,99,106] By using this data and the EMF results of Eremenko and co-workers,[107–109] a second-law analysis could be performed to determine the assessed values of ΔH°_{298} listed in Table 5. However, this EMF work was performed with use of molten salt electrolytes, bringing up the experimental concerns mentioned earlier. As a result, the subsequently published vaporization results have proved useful in generally confirming the EMF data;[104,105] by combining this and the appropriate heat capacity data, detailed expressions for ΔG°_T and ΔH°_T can be derived. In the case of VSi_2, the C_p expression reported by Smith has been combined with those listed for Si and V in the recent compilation by Pankratz to generate continuous functions for $\Delta C_p(VSi_2)$ below and above the melting point of Si:[25]

$$\Delta C_p(VSi_2) = -1.11 - 0.180 \times 10^3 T + 0.99 \times 10^5 T^{-2} \text{ (J/mol·K) (298–1687 K)} \quad (5)$$

$$\Delta C_p(VSi_2) = -4.62 + 5.7 \times 10^{-3} T - 7.26 \times 10^5 T^{-2} \text{ (1687–1950 K)} \quad (6)$$

Storms and Myers have illustrated the excellent agreement between the determined free energies of VSi_2 from their work and that of Eremenko et al.;[100,107] ΔG°_T values at 1000 K from the latter work and at 1650 K from the former allow calculation of the remaining constants in the standard free energy equation:

$$\Delta G^\circ_T = a - bT \ln T - 10^{-3} cT^2 - 10^5 (d/2) T^{-1} + eT \text{ (J/mol)} \quad (7)$$

From these, the standard enthalpy of formation coefficients can be determined:

$$\Delta H^\circ_T = a + bT + 10^{-3} cT^2 - 10^5 d T^{-1} \text{ (J/mol)} \quad (8)$$

Table 6 lists recommended values for *a*, *b*, *c*, *d*, and *e* for the formation of VSi_2 from the elements, along with the appropriate temperature ranges. The resultant ΔH°_T and ΔG°_T values, along with S°_T and $H_T - H_{298}$, are tabulated in Table 7. The value of ΔH°_{298} for VSi_2 calculated from eq 8, −120 543 J/mol, is slightly less exothermic than most of those listed in Table 6, but well within the various margins of error; the calculated ΔS°_{298} of −8.10 compares reasonably well with that determined by Smith,[99] using the experimental results of Kalishevich et al.[47]

The approach used to determine eqs 5–8 cannot be exactly replicated for V_3Si, as the ΔG°_T results of Eremenko et al. and the vapor pressure studies are not in good agreement.[104] However, the availability of highly accurate C_p results in both low-temperature and high-temperature ranges allows a third-law derivation. Smith has used the low-temperature data of Knapp et al. to determine an S°_{298} value of 98.20 J/mol·K,[45,100] and thus $\Delta S^\circ_{298} = -13.32$. The high-temperature results of Pankratz and Kelley and previously employed C_p expressions for elemental V and Si result in[25,106]

$$\Delta C_p(V_3Si) = 2.52 - 14.16 \times 10^{-3} T - 6.00 \times 10^5 T^{-2} \text{ (J/mol) (298–1500 K)} \quad (9)$$

(The upper limit is defined by that of the V_3Si heat capacity data.) The conformation in separate experiments of the results of Myers and co-workers recommends those particular data for use in completing the analysis.[104,105] At 1650 K, ΔG°_T for V_3Si is equal to −146 332 J/mol; the previously listed value of ΔS°_{298} for V_3Si can be used to solve for the constant in the last term of the standard ΔG°_T expression, leaving only the temperature-independent constant to be determined by

TABLE 9. Experimental and Estimated Values of $\Delta H°_{298}$ for Niobium and Tantalum Silicides (kJ/mol of Atoms)

	Nb_5Si_3	$NbSi_2$	"Ta_9Si_2"	Ta_2Si	Ta_5Si_3	$TaSi_2$
Robins and Jenkins[74a]					-39.7	-38.8
Gorelkin et al.[110a]	-63.8					
Myers and Searcy[116b]			-27.1	-40.9	-41.8	-32.4
Chart[15,17b]	-60.7	-46.0		-41.8	-41.8	-39.7
Searcy and Finnie[20c]	-46.0	-44.8	-27.2	-42.3	-37.7	-33.5
Kaufman[39c]	-65.3	-90.7				
Niessen and de Boer[36c]	-58	-46	-28	-51	-56	-44

[a] Experimental. [b] Assessed. [c] Modeled.

comparison against the published free energy value. The resultant *a*, *b*, *c*, *d*, and *e* values are also listed in Table 6, and the calculated thermodynamic properties are tabulated in Table 8. It should be noted that use of the vapor pressure $\Delta G°_T$ results implies the extrapolation of the heat capacity data of Pankratz and Kelley to higher temperatures, an inherent source of uncertainty; however, the calculated $\Delta H°_{298}$ value of −180 652 J/mol is a result similar to much of the experimental data listed in Table 5, as well as that resulting from Smith's assessment.[96]

As Smith points out,[99] no reliable experimental heat capacity data exists for either V_5Si_3 or V_6Si_5 (since the latter is unstable below 1160 K, it is not hard to understand why). An estimating technique was used to instead to derive the given expressions for these compounds in Smith's assessment; however, the accuracy of the estimating technique is not well documented. As a result, the derivation of reliable expressions for $\Delta G°_T$ and $\Delta H°_T$ for the intermediate vanadium silicides is not feasible. However, it should be pointed out that the EMF and vapor pressure results for the free energies of formation of both compounds are in good agreement,[104] and hence higher temperature $\Delta G°_T$ values may be taken from the graph published by Storms and Myers with a reasonable degree of confidence. Improved heat capacity work on V_5Si_3 would help complete the picture, in addition to better information on the low-temperature stability limit of V_6Si_5. In the meantime, the two experimental heats of formation for V_5Si_3 obtained by Gorelkin and co-workers,[75,110] using different experimental methods, are in sufficient agreement to recommend their use as a value of $\Delta H°_{298}$ for this compound.

F. Niobium and Tantalum

Figures 7 and 8 illustrate the Nb–Si and Ta–Si phase diagrams,[86] which have in common a relatively small number of compounds, with melting/transformation temperatures high enough to make characterization a considerable challenge. Kocherzhinskii et al. report a slight homogeneity range for Nb_3Si_2 and an allotropic transformation occurring between 2023 and 2213 K,[111] and some discussion exists of a possible Nb_4Si.[112] Research by the same group on the Ta–Si system rejects the Ta_9Si_2 postulated in Figure 8 but adds a peritectic Ta_3Si and moves the transformation temperature of Ta_5Si_3 from 1973 to 2433 K.[113] Melting points and eutectic temperatures also vary considerably between the proposed diagrams.

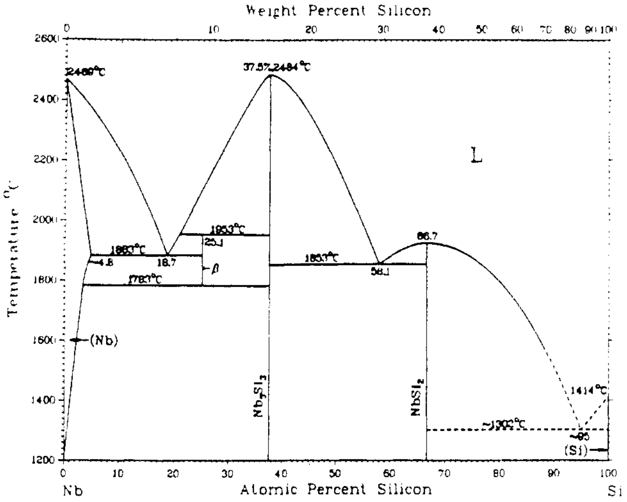

Figure 7. Niobium–silicon phase diagram. Reprinted from ref 86. Copyright 1986 ASM International.

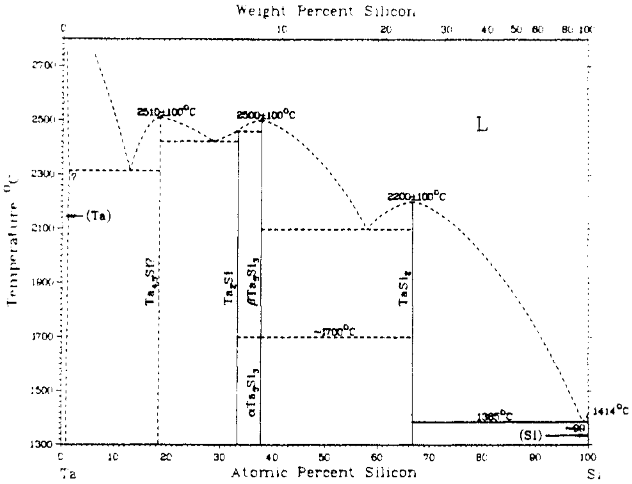

Figure 8. Tantalum–silicon phase diagram. Reprinted from ref 86. Copyright 1986 ASM International.

The thermodynamic properties of the two systems are not well characterized, either. The only published experimental heat of formation of a niobium silicide is that for Nb_5Si_3 reported by Gorelkin et al.,[110] obtained by direct-reaction calorimetry set off with a thermite reaction. A large degree of uncertainty is attached to the result, as well as to the $\Delta H°_{298}$ values for Nb_5Si_3 and $NbSi_2$ resulting from Chart's assessment.[15,17] Modeling results have also been published by Kaufman and by Niessen and de Boer[36,39] and are summarized along with the others in Table 9. The previously illustrated poor results of the modeling efforts in the V–Si system and the considerable uncertainty in the assessed and experimental results make the specification of a "recommended" value difficult. Kozlov et al. have used the chloride coreduction experimental approach described above for titanium silicide preparation to produce Nb_5Si_3 and $NbSi_2$ as well (along with Ta_2Si, β-Ta_5Si_3, and $TaSi_2$),[98] and the free energies of these reactions are summarized by Samsonov and Vinitskii;[16]

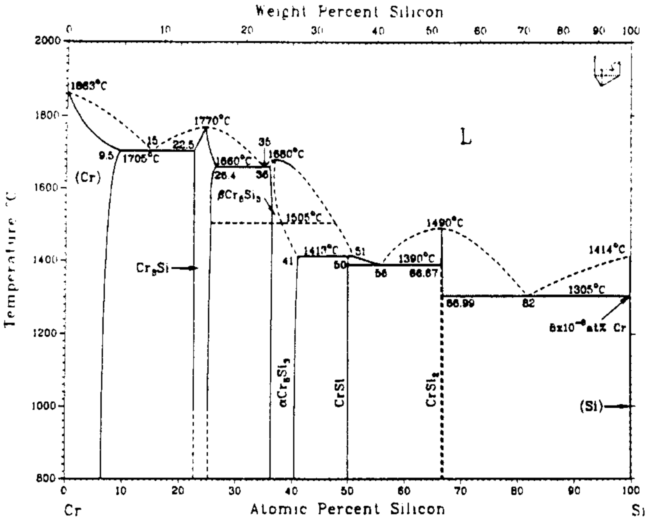

Figure 9. Chromium–silicon phase diagram. Reprinted from ref 86. Copyright 1986 ASM International.

TABLE 10. Experimental and Estimated Values of $\Delta H°_{298}$ for Chromium Silicides (kJ/mol of Atoms)

	Cr_3Si	Cr_5Si_3	CrSi	$CrSi_2$
Golutvin and Chin-k'uei[60 a]	–34.7	–41.0	–39.7	–40.2
Topor and Kleppa[69 a]				–25.8*
Bolgar et al.[160 b]	–33.9			
Chart[15,17 b]	–23.0	–26.4	–26.6	–26.6
Eremenko et al.[107,122,123 b]	–34.4*[d]	–34.4	–29.8	–26.6
Chart[76 b]	–26.4	–27.9	–27.4	–26.7
Lukashenko et al.[121 b]	–34.9	–34.8	–31.0	–26.9
Myers et al.[78 b]	–28.2	–28.1	–26.6	–27.9
Kaufman[39 c]	–34.2	–42.9	–51.5	–55.6
Machlin[37 c]	–22.7		–30.3	
de Boer et al.[118 c]	–24	–31	–30	–15
this work		–35.0*	–30.2*	
$\Delta S°_{298}$		–2.14	–0.09	–2.06

[a] Experimental. [b] Assessed. [c] Modeled. [d] Asterisk indicates a recommended value.

but the objections to this approach remain the same. Good heat capacity data exists for all three niobium silicide phases,[53,101,114,115] but only at temperatures above 1200 K; at lower temperatures (including subambient), no results are available. As a result, this is one of the transition metal–silicide systems where new thermodynamic information would be most welcome.

The circumstances in the Ta–Si system are somewhat better. The only directly obtained $\Delta H°_{298}$ results are those for Ta_5Si_3 and $TaSi_2$ in the previously discussed work of Robins and Kenkins;[74] but two $\Delta G°_T$ determinations have been reported, both of some interest. The first is that of Myers and Searcy,[116] obtained by measuring the vapor pressure of Si from dissociating two-phase mixtures at high (1900–2500 K) temperatures; the other is that of Levine and Kolodney,[22] obtained by EMF measurement of the O_2 partial pressure in equilibrium with two-phase mixtures at 1173–1373 K, using a thoria-stabilized zirconia electrolyte. Levine and Kolodney claim good agreement between their results and those of Myers and Searcy for Ta_9Si_2, Ta_2Si, and Ta_5Si_3; however, their means of comparison involved use of the Neumann–Kopp rule and apparently neglected any compensation for the solid-state transformation of Ta_5Si_3. Again, the available heat capacity data are inadequate for more rigorous comparison. The only available data are for the disilicide,[53,102,115,117] the compound whose free energy of formation is most subject to dispute, and the "$TaSi_2$" tested by Mezaki et al. contained considerable amounts of impurity carbon.[117] Again, the results of Bondarenko et al. are valid only above 1200 K.[102,115,125] In addition to the estimates for niobium silicides, Table 9 also lists those reported experimental, modeled, and assessment-derived values of $\Delta H°_{298}$ for the various tantalum–silicide compounds; as before, the accuracy of the modeling results is questionable.[39,118]

G. Chromium

As Figure 9 shows,[86] the compounds of the Cr–Si system display more solid solubility than those of the transition metal–silicide systems illustrated previously. Although the liquidus surface is not well-defined, this phase diagram is in general a settled issue and is accompanied by an estimable body of thermodynamic research on the various compounds as well. Similar to vanadium, the relatively advanced state of knowledge on the thermodynamic properties of this system has facilitated an element-specific review by Gokhale and Abbaschian,[5] which is recommended to the reader.

Only two investigations have directly determined enthalpies of formation in solid Cr–Si alloys. These include the heat of combustion results reported for all four silicides by Golutvin and Chin-k'uei[60] and the more recent metal solution calorimetry study of $CrSi_2$ performed by Topor and Kleppa.[69] Otherwise, $\Delta H°_{298}$ for these compounds have been determined either by modeling[37,39] or by second/third-law analysis of the results of $\Delta G°_T$ determinations, which are more numerous. Performing this type of analysis requires accurate high-temperature heat capacity data, which are available for all compounds but Cr_3Si from the results of Kalishevich et al.;[19,24] the previously obtained data of Davydov et al. and Golutvin and Chin-k'uei are held in less regard.[60,119] Kalishevich and co-workers have also generated low-temperature C_p data for the four silicides;[19,29,120] the low-temperature limit of 50 K in the former investigation limits its use for third-law analysis. For Cr_3Si, reliable high-temperature data are not available and the Neumann–Kopp rule has been used instead.[23] Table 10 illustrates the experimental, assessed, and model-calculated values of $\Delta H°_{298}$ for the chromium silicides; with the exception of the experimental results of Golutvin and Chin-k'uei, the agreement among the various experimental and assessed values generally improves with the Si content of the compound.

Both EMF and vapor pressure investigations have been used to determine $\Delta G°_T$ in this system, the most recent being the nonreactive vaporization results of Myers et al.[78] However, as these investigators have pointed out, there is considerable disagreement among the published results and reasons for concern over the accuracy of each investigation. The early EMF studies summarized by Eremenko et al. and more recently repeated by Lukashenko et al. were both performed with use of molten salt electrolytes and a pure Cr reference electrode,[107,121] implying a possible exchange reaction concern. In addition, the use of two-phase "alloys" as the sample implies the use of chromium- or silicon-saturated compounds in the experimental regime, another possible source of difference with other results. A similar nonstoichiometry concern affects the reactive

TABLE 11. Experimental Values of ΔG°_{1650} for Chromium Silicides (kJ/mol of Atoms)

	Eremenko et al.[107,122,123]	Chart[76]	Lukashenko et al.[121]	Myers et al.[78]
Cr_3Si	-28.8	-21.9	-27.7	-28.2
Cr_5Si_3	-33.0	-28.0	-31.3	-30.4
CrSi	-31.8	-27.4	-31.4	-29.2
$CrSi_2$	-28.1	-24.3		-23.3

effusion results of Chart,[23] along with the presence of some Cr in the effusate from $Cr-Cr_3Si$ mixtures heated with SiO_2, which ideally would have produced only SiO vapor. The nonreactive vaporization experiments performed by Myers et al. were also performed in two-phase regions, and the ΔG°_T values calculated for the various silicides vary by up to 5% depending on which adjacent region is the source of Cr and Si activities used in the calculation. Table 11 compares the experimental or extrapolated values of ΔG°_{1650} from these four studies; the degree of disagreement is substantial (though possibly exaggerated by the sizable temperature extrapolation of the EMF results to the common temperature).

However, the metal solution calorimetry heat of formation for $CrSi_2$ reported by Topor and Kleppa compares well with the second-law estimates generated from the EMF results.[69] If this process is performed in the opposite temperature direction, using the heat capacity for $CrSi_2$ reported by Kalishevich et al. and the elemental C_p values compiled by Pankratz,[19,25] the calculated ΔH°_T value at 1023 K (-76 461 J/mol) is in good agreement with the experimentally determined value at that temperature from the work of Eremenko et al. (-77 820 J/mol).[122] This in turn provides a somewhat tentative recommendation for the EMF results over the others and allows derivation of ΔH_T and ΔG_T expressions for $CrSi_2$, CrSi, and Cr_5Si_3, using Topor and Kleppa's ΔH°_{298} value for $CrSi_2$ and published ΔH°_T values from the EMF works for the other two compounds,[123] in addition to the ΔG°_T figures. The resulting equation parameters are published as Table 12; the unusual equation format for Cr_5Si_3 at temperatures above 1300 K is due to a different heat capacity expression, brought on in turn by increased disordering in this substance above this level.[19] Standard thermodynamic charts for the three chromium silicides are included as Tables 13–15. The lack of good heat capacity data for Cr_3Si prevents completion of the picture; Eremenko and co-workers suggest that the entropy of formation of this compound may be substantial,[107,121,123] which would mean that the Neumann–Kopp rule is inappropriate. Because of the shorter temperature extrapolation, the estimates of ΔH°_{298} for the tersilicide given by Eremenko et al. in Table 10 are recommended over other estimates.

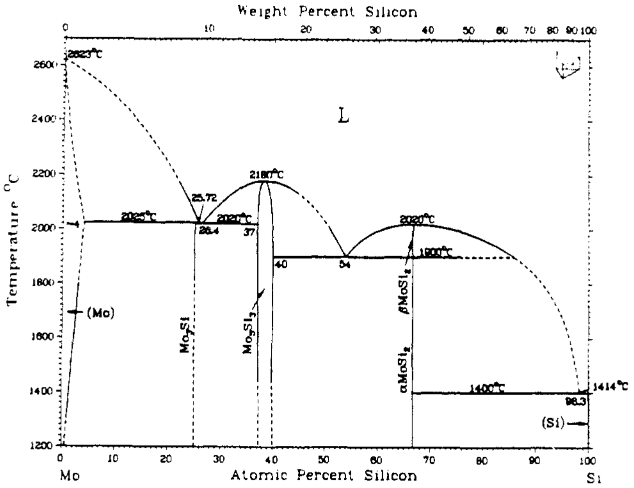

Figure 10. Molybdenum–silicon phase diagram. Reprinted from ref 86. Copyright 1986 ASM International.

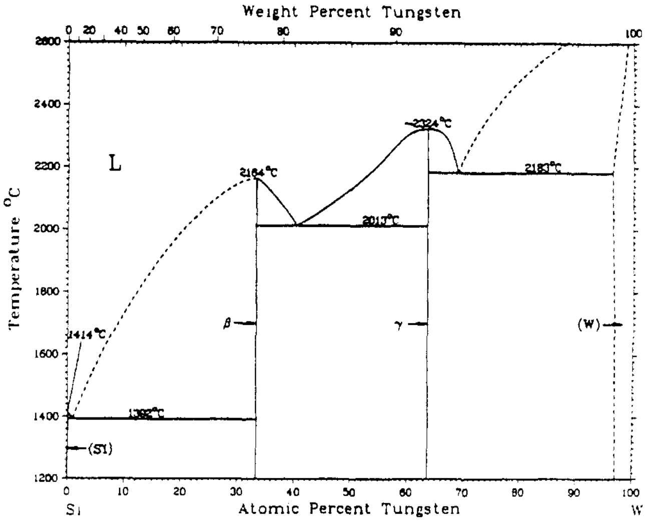

Figure 11. Silicon–tungsten phase diagram. Reprinted from ref 86. Copyright 1986 ASM International.

H. Molybdenum and Tungsten

The early commerical use of $MoSi_2$ has resulted in considerable interest in this particular phase diagram and in the similar tungsten–silicon system. Figures 10 and 11 illustrate the most recent versions of these diagrams;[86] Kocherzhinskii et al. propose a small homogeneity range for γ (W_5Si_3),[124] along with different

TABLE 12. Parameters for ΔH°_T and ΔG°_T Calculation for Chromium Silicides (J/mol of Atoms)

	std states							
phase	Cr	Si	temp range, K	*a*	*b*	*c*	*d*	*e*
$CrSi_2$	sol	sol	298–311.5	-27 220	9.95	-16.8	0.159	54.48
$CrSi_2$	sol	sol	311.5–1687	-25 823	-0.049	-0.27	-0.030	-2.363
$CrSi_2$	sol	liq	1687–1730	-53 523	-1.22	1.2	-2.778	7.772
CrSi	sol	sol	298–311.5	-34 401	20.0	-28.0	-2.149	118.6
CrSi	sol	sol	311.5–1687	-32 314	5.00	-2.3	-2.434	33.60
CrSi	sol	liq	1687–1700	-58 332	4.12	-1.56	-4.495	43.69
Cr_5Si_3	sol	sol	298–311.5	-39 400	23.3	-34.2	-1.655	138.5
Cr_5Si_3	sol	sol	311.5–1300	-36 786	4.52	-2.16	-2.010	32.29
Cr_5Si_3	sol	sol	1300–1687	-57 855	53.1	-39.2	-1.190	356.3[a]
Cr_5Si_3	sol	liq	1687–1930	-77 355	52.4	-38.6	-0.356	364.0[a]

[a] Add $9.39 \times 10^{-6}T^3$ to ΔH°_T expression (eq 8); add $4.70 \times 10^{-6}T^3$ to ΔG°_T expression (eq 7).

TABLE 13. Recommended Thermodynamic Values for Solid $CrSi_2$ (per Mole of Atoms)

temp, K	$H_T - H_{298}$, J	$S°_T$, J/K	$\Delta H°_T$, J	$\Delta G°_T$, J
298.15	0	22.49	−25 800	−26 413
311.5	287	23.42	−25 802	−26 446
400	2 275	29.03	−25 792	−26 604
500	4 670	34.37	−25 774	−26 782
600	7 183	38.95	−25 750	−26 953
700	9 496	42.98	−25 721	−27 118
800	12 500	46.53	−25 686	−27 277
900	15 288	49.87	−25 645	−27 290
1000	18 159	52.69	−25 599	−27 576
1100	21 110	55.70	−25 547	−27 717
1200	24 140	58.34	−25 490	−27 852
1300	27 248	60.83	−25 428	−27 981
1400	30 433	63.19	−25 360	−28 104
1500	33 695	65.44	−25 287	−28 221
1600	37 034	67.59	−25 208	−28 333
1687	40 000	69.40	−25 135	−28 426
1687	40 000	69.40	−52 005	−28 426
1700	40 449	69.66	−51 696	−28 244
1730	41 488	70.27	−51 885	−27 826

TABLE 14. Recommended Thermodynamic Values for Solid CrSi (per Mole of Atoms)

temp, K	$H_T - H_{298}$, J	$S°_T$, J/K	$\Delta H°_T$, J	$\Delta G°_T$, J
298.15	0	21.14	−30 206	−30 179
331.5	771	23.59	−30 198	−30 176
400	2 444	28.17	−30 074	−30 186
500	5 029	33.94	−29 902	−30 234
600	7 729	38.86	−29 736	−30 316
700	10 512	43.15	−29 593	−30 424
800	13 364	46.95	−29 482	−30 551
900	16 276	50.39	−29 407	−30 690
1000	19 243	53.51	−29 370	−30 835
1100	22 263	56.39	−29 376	−30 981
1200	25 332	59.06	−29 423	−31 125
1300	28 450	61.56	−29 514	−31 264
1400	31 616	63.91	−29 648	−31 394
1500	34 828	66.12	−29 827	−31 512
1600	38 086	68.23	−30 050	−31 618
1687	40 958	69.97	−30 280	−31 697
1687	40 958	69.97	−55 555	−31 697
1700	41 390	70.23	−55 572	−31 513

TABLE 15. Recommended Thermodynamic Values for Solid Cr_5Si_3 (per Mole of Atoms)

temp, K	$H_T - H_{298}$, J	$S°_T$, J/K	$\Delta H°_T$, J	$\Delta G°_T$, J
298.15	0	19.69	−34 950	−34 311
331.5	311	20.71	−34 942	−34 282
400	2 475	26.81	−34 820	−34 110
500	5 075	32.61	−34 663	−33 950
600	7 790	37.53	−34 515	−33 822
700	10 597	41.88	−34 390	−33 716
800	13 485	45.74	−34 300	−33 627
900	16 447	49.22	−34 342	−33 546
1000	19 480	52.42	−34 223	−33 470
1100	22 581	55.37	−34 243	−33 394
1200	25 748	58.13	−34 302	−33 315
1300	29 007	60.72	−34 403	−33 229
1400	32 314	63.17	−34 552	−33 132
1500	35 728	65.52	−34 694	−33 027
1600	39 309	67.84	−34 775	−32 915
1687	42 603	69.84	−34 751	−32 817
1687	42 603	69.84	−53 707	−32 817
1700	43 112	70.14	−53 675	−32 656
1800	47 194	72.47	−53 317	−31 432
1900	51 611	74.86	−52 716	−30 235
1930	53 010	76.59	−52 480	−29 883

melting points for this and WSi_2. No other phases beyond those illustrated in Figures 10 and 11 have been recently proposed.

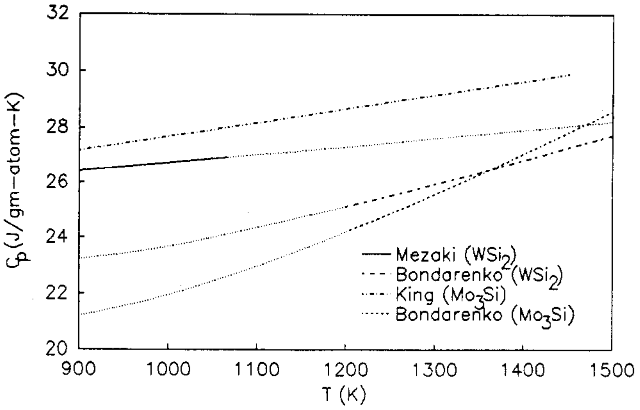

Figure 12. Heat capacities of Mo_3Si and WSi_2 vs temperature, from the data of Bondarenko et al.,[53,102,125,126] King and Christensen,[127] and Mezaki et al.[117]

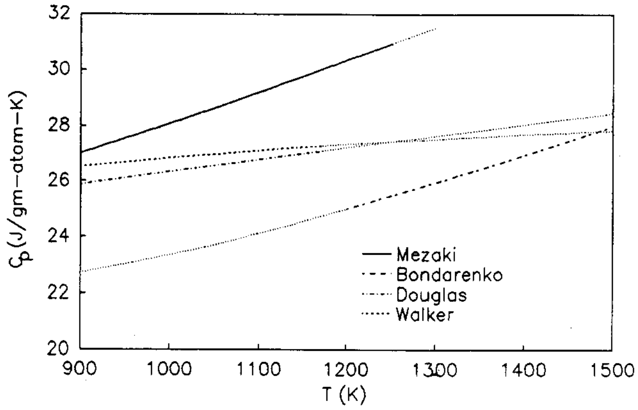

Figure 13. Heat capacity of $MoSi_2$ vs temperature, from the data of Bondarenko et al.,[53,102,125] Douglas and Logan,[127] Mezaki et al.,[117] and Walker et al.[18]

Because of the use of $MoSi_2$ for high-temperature furnace windings, the thermodynamic properties of this phase are among the earliest reported for transition-metal silicides and similar research on the other silicides has followed. In particular, the above-ambient heat capacities of these compounds have been well researched; published reports include those of Bondarenko et al. (all five compounds, 1100–2200 K),[53,101,125,126] Douglas and Logan ($MoSi_2$, 298–1173 K),[127] King and Christensen (Mo_3Si, 50–1450 K),[128] Mezaki et al. ($MoSi_2$ and WSi_2, 298–1252 K),[117] and Walker et al. ($MoSi_2$, 298–1173 K).[18] However, most of this research is not of recent vintage, and improvements in both instrumentation and available compound purity have rendered some of the results suspect. Figure 12 shows the results of C_p determinations for Mo_3Si and WSi_2, comparing earlier results with those summarized by Bondarenko et al.; while the degree of agreement for WSi_2 is reasonable, such is not the case for the tersilicide. Figure 13 similarly illustrates the data for $MoSi_2$, again demonstrating glaring differences. While the agreement between the results of Douglas and Logan and of Walker et al. is encouraging, the disilicide material used in these two studies also contained the greatest levels of impurities, thus suggesting that the agreement is at best fortuitous. The results of Bondarenko and coworkers are the most recent of those listed, and possibly the most reliable;[15] however, their confirmation at lower temperatures would be of value.

Only two $\Delta H°_{298}$ experimental determinations have been made for compounds in these systems, both by direct-reaction calorimetry. Robins and Jenkins give enthalpy of formation values for the two disilicides and a nonexistent "Mo_3Si_2",[74] while Maslov et al. list a more

TABLE 16. Experimental and Estimated Values of $\Delta H°_{298}$ for Molybdenum and Tungsten Silicides (kJ/mol of Atoms)

	Mo_3Si	Mo_5Si_3	$MoSi_2$	W_5Si_3	WSi_2
Robins and Jenkins[74 a]			-32.8		-23.4
Maslov et al.[72 a]			-47.4*[d]		
Searcy and Tharp[21 b]	-24.5	-35.5	-36.3		
Chart[15,17 b]	-29.1	-38.7	-43.9	-16.9	-31.0
Searcy[8 c]	-22.0	-34.5	-37.9	-23.5	-31.2
Niessen and de Boer[36 c]	-20	-28	-16	-23	-11
Kaufman[39 c]	-39.5	-55.3	-72.1	-33.5	-58.0
Machlin[37 c]	-26.6				

[a] Experimental. [b] Assessed. [c] Modeled. [d] Asterisk indicates a recommended value.

TABLE 17. Experimentally Derived $\Delta G°_{1500}$ for Molybdenum Silicides (kJ/mol of Atoms)

	Mo_3Si	Mo_5Si_3	$MoSi_2$
Chart[76]	-29.0	-39.9	-42.8
Omori et al.[84]	-21.9		
Omori et al.[85]	-25.6	-37.9	

negative value for $MoSi_2$.[72] Other $\Delta H°_{298}$ estimates have been obtained either from modeling work,[36,37,39] assessment,[15,17] or from second- or third-law analysis of various free energy studies, using the Neumann–Kopp rule or "combined" C_p data, as in the case of Chart's work with the molybdenum silicides.[21,23,76] Unfortunately, analyses of the latter type depend on either accurate $\Delta H°_{298}$ or $S°_{298}$ results: In the former case, difficulties with the results of Robins and Jenkins have been previously pointed out and the work of Maslov et al. remains unconfirmed, while in the latter case, the only low-temperature heat capacity data are those for Mo_3Si reported by King and Christensen,[128] which have a low-temperature limit of 50 K. As before, the results of Maslov et al. are recommended over the other suggested values for $MoSi_2$; otherwise, the listing of reliable recommended values is not feasible. Table 16 lists the various reported experimental and estimated values of $\Delta H°_{298}$ for the molybdenum and tungsten silicides.

The only published information on the free energies of formation of tungsten silicides is that reported in 1975 by Chart,[23] using the previously described reactive-effusion method. Tungsten effusion rates from these silicides were minimal, and this combined with the lack of nonstoichiometry in this system suggests that these results should be seen as more reliable than those for the Cr–Si system discussed earlier. Chart has also published similar work for the Mo–Si system,[76] although the phase diagram published in this work does not illustrate the solid solution range for Mo_5Si_3 illustrated in Figure 10. More recent solid electrolyte EMF measurements by Omori and co-workers have yielded $\Delta G°_T$ values for Mo_3Si and Mo_5Si_3 that are less negative than those of Chart;[84,85] however, the scatter in these results is substantial. Table 17 illustrates the results of these three studies, along with $\Delta G°_{1500}$ values calculated from the elemental effusion results of Searcy and Tharp.[21]

I. Manganese

Figure 14, the Mn–Si phase diagram,[86] illustrates several characteristics that become increasingly apparent as the nobility of the transition metals in such systems increases. Most notable is the considerable terminal solid solution range in the pure metal; the increasing metal content in the stable silicides is also apparent, as are increasing degrees of instability and nonstoichiometry. (A comparison with Figure 2, the Cu–Si phase diagram, further illustrates these characteristics.) The increasing complexity of the Mn–Si system means that the number of unanswered questions is larger as well; the three most significant issues are the effect of dissolved Si on the equilibria between β-Mn and γ-Mn, the solid solution range for Mn_9Si_2, and the existence of stable Mn_5Si_2. The most recent investigation of the latter issue suggests that this latter phase is in fact not stable in equilibrium systems.[129]

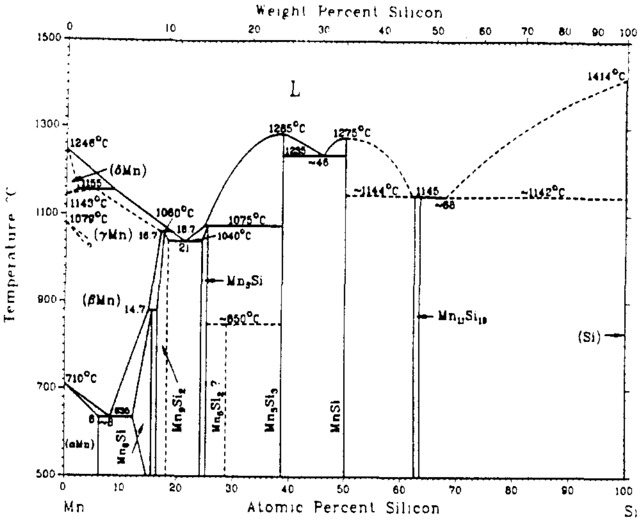

Figure 14. Manganese–silicon phase diagram. Reprinted from ref 86. Copyright 1986 ASM International.

As part of his 1977 vapor pressure investigation,[4] Nowotny et al. reviewed the previous work on the thermodynamic properties of solid Mn–Si alloys; since that time, Lukashenko and co-workers have performed two EMF studies on the system[129,130] and three modeling efforts have included $\Delta H°_{298}$ estimates as well.[37,39,118] With the exceptions of chromium and vanadium, no transition metal–silicide system has been studied as thoroughly, or, as Nowotny et al. and Letun and Gel'd have illustrated,[26] with as wildly varying results. While data exist for all six compounds (excluding Mn_5Si_2), most of the existing work deals with the four higher silicides ($Mn_{11}Si_{19}$, MnSi, Mn_5Si_3, Mn_3Si).

This is particularly true of heat capacity measurements, of which four studies have been performed. These include the drop calorimetry measurements of Davydov et al. and Golutvin et al.[63,119] and the adiabatic high- and low-temperature results reported in various places by Letun and co-workers.[26,27,131,132] Letun and Gel'd have shown that their high-temperature results are similar to those reported by Davydov et al., but not to those of the other drop calorimetry investigation; it will be recalled that other C_p data from Golutvin and co-workers have been called into question as well. As a result, most reviewers have chosen the high-temperature results of Letun et al. for analytical use,[4,15,17,129] a conclusion repeated here. The low-temperature values reported by the same group, however, were obtained with a low-temperature limit of 50 K, a cause for some concern in their use for third-law analysis.

Table 18 illustrates the various published $\Delta H°_{298}$ values for the manganese silicides. Only the results of Golutvin et al. and of Gertman and Gel'd are the

TABLE 18. Experimental and Estimated Values of ΔH°_{298} for Manganese Silicides (kJ/mol of Atoms)

	Mn_1Si	Mn_9Si_2	Mn_3Si	Mn_5Si_3	MnSi	$Mn_{11}Si_{19}$
Gertman and Gel'd[133][a]			−28.5	−33.1	−35.6	−33.5
Golutvin et al.[63][a]			−34.3	−28.9	−48.5	−13.0
Gel'd et al.[131][a]						−35.9
Rossemyr and Rosenqvist[77][b]				−19.0	−24.8	−20.7
Chart[15,17][b]			−19.9	−25.1	−30.3	−28.0
Muradov[134][b]	(−17.6)	−26.4	−36.4	−42.3	−40.6	−35.1
Eremenko et al.[107,135,136][b]			−26.9	−34.2	−39.8	−35.4
Nowotny et al.[4][b]			−27.6	−30.5	−32.6	−27.2
Lukashenko and Sidorko[130][b]			−26.6			
Kaufman[39][c]	−18.8	−22.1	−29.2	−43.0	−52.6	
Machlin[37][c]					−29.3	
de Boer et al.[118][c]	(−15)	−23	−31	−41	−42	−29
this work			−25.9*[d]	−30.2*		−35.9*
ΔS°_{298}			−1.02	4.01		−7.80

[a] Experimental. [b] Assessed. [c] Modeled. [d] Asterisk indicates a recommended value.

TABLE 19. Experimentally Derived ΔG°_{1350} for Manganese Silicides (kJ/mol of Atoms)

	Mn_3Si	Mn_5Si_3	MnSi	$Mn_{11}Si_{19}$
Eremenko et al.[107,135,136]	−25 571	−33 321	−32 104	−24 824
Nowotny et al.[4]	−26 814	−34 707	−29 808	−24 202

product of actual experimental heat of formation experiments,[63,133] the former performed by acid solution and the latter by combustion calorimetry. The other listed values are the result of either assessment, estimation, or second- or third-law analysis of ΔG°_T values. The only experimentally derived ΔH°_{298} values for Mn_9Si_2 and Mn_6Si are those reported by Muradov;[134] in the absence of heat capacity data, it is presumed that the Neumann–Kopp rule was applied to the ΔG°_T data from which these values were obtained. (The figures in parentheses for "Mn_6Si" in Table 18 represent the manganese-saturated composition, roughly equal to $Mn_{7.3}Si$.) The variation in the various suggested heats of formation is considerable; it is noteworthy that the assessed values of Chart tend to be less exothermic than most of the experimentally derived figures.[15,17] The modeling results show a reasonable degree of agreement with experimental results, given the wide spread in the latter.

Some of the discrepancies in Table 18 may be a result of limitations in the experimental methods used to obtain the original ΔH°_{298} and ΔG°_T data. The objections to the two employed calorimetric techniques have previously been discussed; in less exothermic alloys such as these, the validity of those objections increases. The same statement is true with regard to the molten salt electrolytes used in the EMF investigations conducted by Lukashenko and co-workers.[107,130,135,136] Observation of the vapor equilibrium results illustrated by Rossemyr and Rosenqvist (also described earlier) reveals considerable scatter in some of the data;[77] furthermore, "corrections" have subsequently been made to these results to correct for the reporting of results for "$MnSi_2$" rather than the actual $Mn_{11}Si_{19}$ (the corrected results are those displayed in Table 14).[4,15,17] The relatively high vapor pressure of manganese makes the use of elemental vapor pressure measurements a good experimental choice in this system;[4,134] however, Nowotny et al. have illustrated how the choice of effusion technique affected their results, causing some uncertainty.

Another possible cause of the disagreements in Table 14 may stem from the choice between second- and third-law analysis of the ΔG°_T data. For example, the ΔH°_{298} estimates reported by Eremenko et al. were calculated by second-law analysis,[107] apparently with the Neumann–Kopp rule; Nowotny et al. used the heat capacity data of Letun et al. to perform their second- and third-law analyses.[4,27,132] Table 19, which lists ΔG°_T values for $Mn_{11}Si_{19}$, MnSi, Mn_5Si_3, and hypothetical solid Mn_3Si at 1350 K from the results of the two comprehensive studies, shows reasonable agreement for all but MnSi; the degree of agreement is made more impressive by the extent of temperature extrapolation of the EMF work necessary to create such a comparison. As a result, it seems reasonable to perform a second-law analysis for $Mn_{11}Si_{19}$, Mn_5Si_3, and Mn_3Si in the same manner as previously performed for the vanadium silicides, using the ΔG°_T results of Nowotny et al. at 1350 K and those of Eremenko et al. at 1000 K (a temperature within the original experimental range) and the high-temperature C_p data of Letun et al. This allows the bypassing of the questionable experimental ΔH°_{298} results described earlier, as well as the experimental S°_{298} values reported by Letun et al.,[27] the objection to

TABLE 20. Parameters for ΔH°_T and ΔG°_T Calculation for Manganese Silicides (J/mol of Atoms)

	std states							
phase	Mn	Si	temp range, K	*a*	*b*	*c*	*d*	*e*
α-Mn_3Si	α	sol	298–950	−26 692	1.588	0.788	−1.607	13.025
β-Mn_3Si	α	sol	950–970	−38 589	22.75	7.238	121.2	183.2
β-Mn_3Si	β	sol	980–1343	7 310	−29.59	10.823	118.5	−220.7
Mn_5Si_3	α	sol	298–980	−30 686	1.947	−2.098	−0.150	7.861
Mn_5Si_3	β	sol	980–1360	−29 588	−3.757	0.890	−2.420	−29.736
Mn_5Si_3	γ	sol	1360–1410	−29 516	−3.159	−0.250	−1.023	−26.932
Mn_5Si_3	δ	sol	140–1573	−28 856	−4.699	−0.080	−1.023	−38.327
$Mn_{11}Si_{19}$	α	sol	298–980	−37 158	2.953	−2.715	−1.728	26.921
$Mn_{11}Si_{19}$	β	sol	980–1360	−36 508	−0.427	−0.944	−3.073	4.679
$Mn_{11}Si_{19}$	γ	sol	1360–1410	−35 680	−0.072	−1.620	−2.246	5.735
$Mn_{11}Si_{19}$	δ	sol	1410–1517	−34 595	−0.985	−1.518	−2.246	−1.511

TABLE 21. Recommended Thermodynamic Values for Solid Mn_3Si (per Mole of Atoms)

temp, K	$H_T - H_{298}$, J	$S°_T$, J/K	$\Delta H°_T$, J	$\Delta G°_T$, J
298.15	0	23.69	-25 910	-25 607
400	2 717	31.50	-25 829	-25 513
500	5 641	38.02	-25 680	-25 450
600	8 756	43.69	-25 488	-25 422
700	12 036	48.75	-25 265	-25 428
800	15 469	53.33	-25 016	-25 468
900	19 047	57.54	-24 746	-25 541
950	20 888	59.53	-24 603	-25 589
950	22 288	61.01	-23 204	-25 589
980	23 449	62.21	-21 712	-25 689
980	23 449	62.21	-23 381	-25 689
1000	24 223	63.00	-23 302	-25 735
1100	28 116	66.71	-22 912	-25 997
1200	32 087	70.16	-22 484	-26 296
1300	36 179	73.44	-21 978	-26 634
1343	37 984	74.80	-21 729	-26 792

TABLE 22. Recommended Thermodynamic Values for Solid Mn_5Si_3 (per Mole of Atoms)

temp, K	$H_T - H_{298}$, J	$S°_T$, J/K	$\Delta H°_T$, J	$\Delta G°_T$, J
298.15	0	24.64	-30 242	-31 438
400	2 596	32.12	-30 205	-31 853
500	5 290	38.12	-30 207	-32 266
600	8 085	43.32	-30 248	-32 675
700	10 962	47.65	-30 330	-33 073
800	13 914	51.59	-30 452	-33 457
900	16 934	55.15	-30 616	-33 823
980	18 777	57.43	-30 735	-34 102
980	18 777	57.43	-32 122	-34 102
1000	20 019	58.40	-32 213	-34 141
1100	23 168	61.40	-32 424	-34 323
1200	26 379	64.49	-32 613	-34 487
1300	29 651	66.81	-32 782	-34 636
1360	31 643	68.31	-32 873	-34 720
1360	31 643	68.31	-34 199	-34 720
1400	32 984	69.08	-34 356	-34 729
1500	33 320	69.52	-34 395	-34 731
1510	33 320	69.52	-35 568	-34 731
1510	36 377	71.62	-36 016	-34 653
1573	38 892	73.62	-36 380	-34 572

which has also been noted.

As before, heat capacities and heats of transition for the elements have been taken from the compilation of Pankratz;[25] the heat of transformation for Mn_3Si at 950 K (not illustrated in the phase diagram) given by Letun et al. has also been adopted.[132] Table 20 lists the resulting coefficients for the standard $\Delta H°_T$ and $\Delta G°_T$ equations for the three solid silicides, and the appropriate temperature ranges, and Tables 21–23 report recommended thermodynamic values for Mn_5Si_3, and $Mn_{11}Si_{19}$ calculated from these coefficients. In general, the calculated heats of formation fall within the range of other listed values in Table 23, and the entropies of formation for Mn_5Si_3 and Mn_3Si are similar to those listed by Eremenko et al.;[107] however, the calculated enthalpy of formation for $Mn_{11}Si_{19}$ is more negative than those previously listed, and this results in a value of $S°_{298}$ lower than that reported by Letun et al.[30] As a result, the $S°_T$ values for the latter compound listed in Table 23 should be regarded cautiously.

J. Iron

Figure 15, the most recent Fe–Si phase diagram,[86] may prove not the last word on the subject. Confusion is still apparent over the Fe-rich end of the system, particularly with regard to the relative stabilities of the α_2 solid solutions; in this regard, Figure 15 is markedly different from the phase diagram published by Chart.[137] The rest of the system is more settled, although some transformation temperatures are not entirely set. In either case, the relative complexity of the system at high-Fe contents and increasing nonstoichiometry for the various compounds further illustrate the trends apparent in Figure 14.

TABLE 23. Recommended Thermoydnamic Values for Solid $Mn_{11}Si_{19}$ (per Mole of Atoms)

temp, K	$H_T - H_{298}$, J	$S°_T$, J/K	$\Delta H°_T$, J	$\Delta G°_T$, J
298.15	0	14.52	-35 939	-33 613
400	2 362	17.69	-35 979	-32 810
500	4 862	21.63	-36 015	-32 012
600	7 459	25.47	-36 076	-31 204
700	10 120	29.04	-36 174	-30 383
800	12 827	32.31	-36 317	-29 543
900	15 570	35.36	-36 507	-28 683
980	17 231	37.52	-36 695	-27 977
980	17 231	37.52	-37 510	-27 977
1000	18 344	38.05	-37 572	-27 782
1100	21 144	40.59	-37 841	-26 790
1200	23 969	42.95	-38 124	-25 773
1300	26 817	45.16	-38 422	-24 732
1360	28 536	46.41	-38 609	-24 096
1360	28 536	46.41	-39 394	-24 096
1400	29 686	47.23	-39 581	-23 643
1410	29 974	47.43	-39 628	-23 529
1410	29 974	47.43	-40 316	-23 529
1500	32 576	49.17	-40 812	-22 442
1517	33 069	49.49	-40 909	-22 233

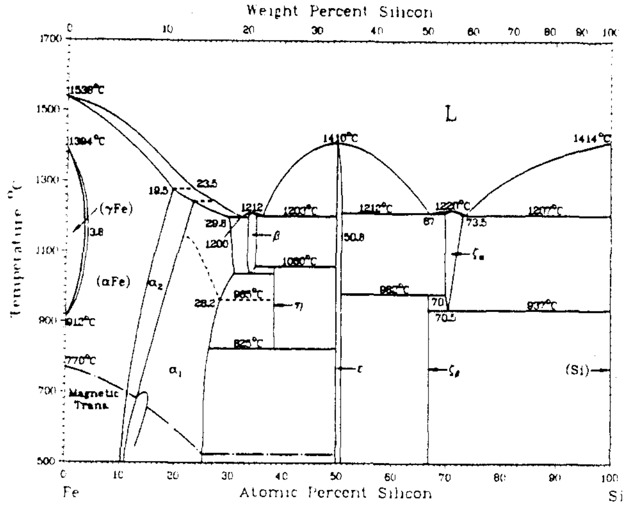

Figure 15. Iron–silicon phase diagram. Reprinted from ref 86. Copyright 1986 ASM International.

Although some work on the thermodynamic properties of this system has been performed since the 1970 review by Chart,[137] this latter work remains a worthy investment of the reader's time. The work performed since that time falls into two categories, experimental $\Delta H°_{298}$ determinations and modeling efforts. The experimental results include a 1971 combustion study by Gorelkin and Mikhailov,[75] the 1972 direct-reaction calorimetry value for FeSi of Gorelkin et al.,[110] and the metal solution calorimetry results for "Fe_3Si" (silicon-saturated α_1) of Sommer.[43] Table 24 lists the various experimental, assessed, and modeled values of $\Delta H°_{298}$ for Fe_3Si, FeSi, and β-$FeSi_2$ (the low-temperature stoichiometric form). The range of experimental values for each compound is surprisingly small, considering the potential for experimental error in a relatively nonionic system such as this; and it will be noted that a half-century of improvement in analytical instrumentation

TABLE 24. Experimental and Estimated Values of $\Delta H°_{298}$ for Iron Silicides (kJ/mol of Atoms)

	α_1 (Fe_3Si)	FeSi	$FeSi_2$
Körber and Oelsen[54 a]	-20.1	-40.2	-23.6
Jounel et al.[66 a]		-39.3*	
Gorelkin and Mikhailov[75 a]		-38.5	-30.6*
Gorelkin et al.[110 a]		-37.7	
Sommer[43 a]	-25.8*[d]		
Vecher et al.[142,143 b]	-23.4	-36.8	-27.0
Chart[137 b]	-20.0	-38.4	-26.4
Kaufman[39 c]		-61.5	
Machlin[37 c]	-18.4	-39.3	
Pasturel et al.[38 c]		-37.7	
Boom et al.[157 c]	-21	-27	-12

[a] Experimental. [b] Assessed. [c] Modeled. [d] Asterisk indicates a recommended value.

TABLE 25. Parameters for $\Delta H°_T$ Calculation for FeSi (J/mol of Atoms)

std states		temp				
Fe	Si	range, K	*a*	*b*	*c*	*d*
α	sol	298–1043	-42706	-10.73	-9.70	-3.127
γ	sol	1043–1185	6604	-81.27	33.6	1.653
δ	sol	1185–1683	-42855	-1.245	0.82	-0.837

TABLE 26. Recommended Thermodynamic Values for Solid FeSi (J/mol of Atoms)

temp, K	$H_T - H_{298}$	$\Delta H°_T$
298.15	0	-39320
400	2487	-39814
500	5019	-39141
600	7632	-39239
700	10325	-39501
800	13094	-39939
900	15940	-40559
1000	18862	-41363
1043	20142	-41767
1100	22860	-42287
1185	24467	-42658
1185	24467	-43108
1200	24933	-43098
1300	28082	-43023
1400	31306	-42931
1500	34605	-42821
1600	37979	-42695
1683	40282	-42602

and techniques does not seem to have resulted in much improvement on the 1936 $\Delta H°_{298}$ values reported by Körber and Oelsen.[54] Choosing a "recommended value" from this list would appear to be a difficult matter, since so little difference is apparent among the various experimental results. However, the nature of the system suggests that the best choice of experimental technique of those used is metal solution calorimetry; as a result, the $\Delta H°_{298}$ results of Jounel et al. for FeSi and Sommer for Fe_3Si are recommended to the reader.[42,66] The results of Gorelkin and Mikhailov are similar to those of Jounel et al. for FeSi and so are tentatively recommended as the best choice of $\Delta H°_{298}$ for $FeSi_2$.

The existing low-temperature C_p results for the iron silicides all have a low-temperature limit of 55 K,[28] making their use suspect for third-law derivations of thermodynamic properties. Additionally, the only high-temperature heat capacity results for Fe_3Si were obtained by drop calorimetry,[138,139] a cause for concern in light of both the phase change to α_2 at 1325 K and magnetic transformation at 835 K. However, the above-ambient heat capacity results for FeSi and $FeSi_2$ are more useful. Figure 16 compares C_p for FeSi from the four separate experimental studies as a function of temperature[119,138,140,141] and Figure 17 the results of two reported investigations on $FeSi_2$;[119,140] in light of previous comparisons, the degree of agreement is impressive. However, the only $\Delta G°_T$ data available for this system stem from the EMF results reported by Vecher et al., conducted in a molten salt (iodide) electrolyte;[79,142,143] Chart reiterates the previously discussed concern over this type of experimental technique,[137] by pointing out the similar values of $\Delta H°_{298}$ for the two iodides. As a result, the generation of reliable thermodynamic values for the iron silicides must wait for (a) the publication of more appropriate C_p results for Fe_3Si and (b) confirmation of either the low-temperature heat capacity work of Krentsis and Geld or the EMF data of Vecher et al., by a different experimental technique. As a result, thermodynamic expressions of the type derived for other fourth-row transition-metal silicides are infeasible. However, it is possible to derive expressions for the heat of formation of FeSi, using the recommended $\Delta H°_{298}$ value and the high-temperature heat capacities of Krentsis;[66,140] Table 25 lists the standard equation coefficients and Table 26 the resultant enthalpies and heats of formation.

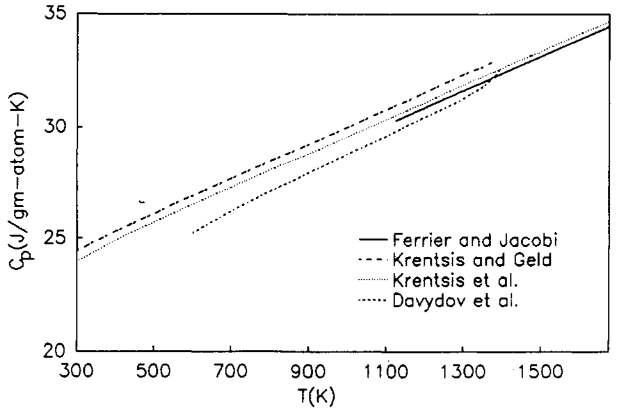

Figure 16. Heat capacity of FeSi vs temperature, from the data of Davydov et al.,[119] Ferrier and Jacobi,[141] Krentsis and Geld,[138] and Krentsis et al.[161]

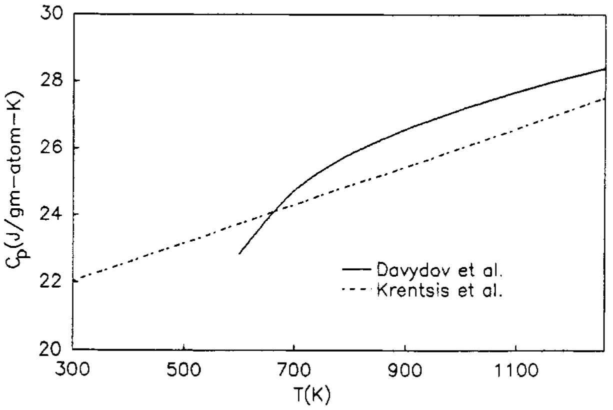

Figure 17. Heat capacity of $FeSi_2$ vs temperature, from the data of Davydov et al. and Krentsis et al.[119,139]

K. Cobalt and Nickel

The Co–Si and Ni–Si alloy systems are similar in degree of complexity to that of Cu–Si and Fe–Si, as Figures 18 and 19 illustrate. In the Ni–Si system, the "β_1" phase is normally stoichiometrized as Ni_3Si, δ as Ni_2Si, ϵ as Ni_3Si_2, and γ as $Ni_{31}Si_{12}$ or Ni_5Si_2. Figure

TABLE 27. Experimental and Estimated Values of ΔH°_{298} for Cobalt and Nickel Silicides (kJ/mol of Atoms)

	Co_2Si	CoSi	$CoSi_2$	Ni_3Si	Ni_5Si_2 ($Ni_{31}Si_{12}$)	Ni_2Si	Ni_3Si_2	NiSi	$NiSi_2$
Oelsen et al.[55,56 a]	-38.5*[d]	-50.2*	-34.3*	-37.2*	-42.3*	-46.9*	-45.2*	-43.1	-29.3*
Topor and Kleppa[67 a]								-42.4*	
Chart[15,17 b]	-37.7	-47.5	-32.8	-35.6	-42.3	-47.7	-46.4	-44.8	-31.4
Kaufman[39 c]	-58.9	-72.4	-67.0	-49.3	-55.5	-60.4	-64.9	-67.3	-65.0
Machlin[37 c]		-44.4	-39.5					-53.6	
Pasturel et al.[38 c]	-33.1	-44.8	-34.7	-41.8		-37.7		-43.9	
an Mey[41 c]					-41.3	-37.6	-37.0	-33.9	-27.3
Niessen et al.[157,158 c]	-38	-48	-15	-26	-29	-32	-35	-33	-17

[a] Experimental. [b] Assessed. [c] Modeled. [d] Asterisk indicates a recommended value.

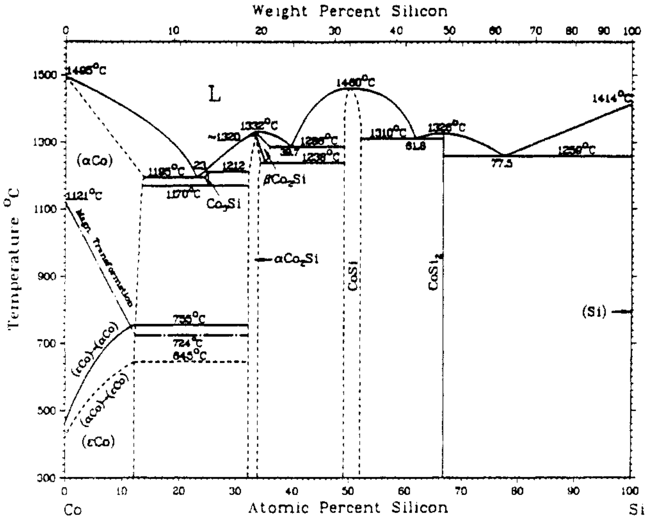

Figure 18. Cobalt–silicon phase diagram. Reprinted from ref 86. Copyright 1986 ASM International.

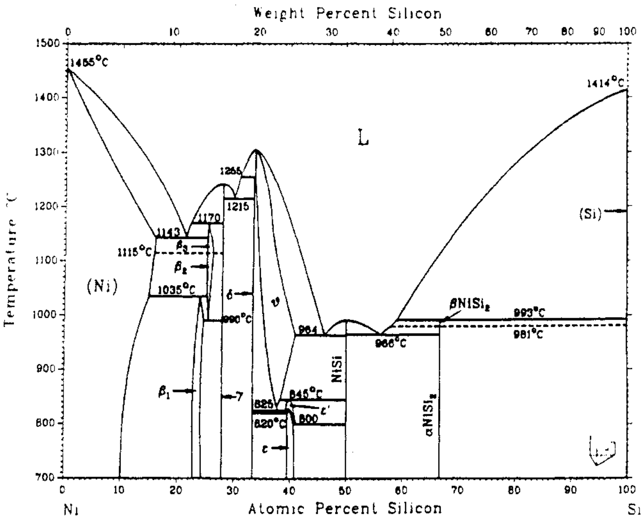

Figure 19. Nickel–silicon phase diagram. Reprinted from ref 86. Copyright 1986 ASM International.

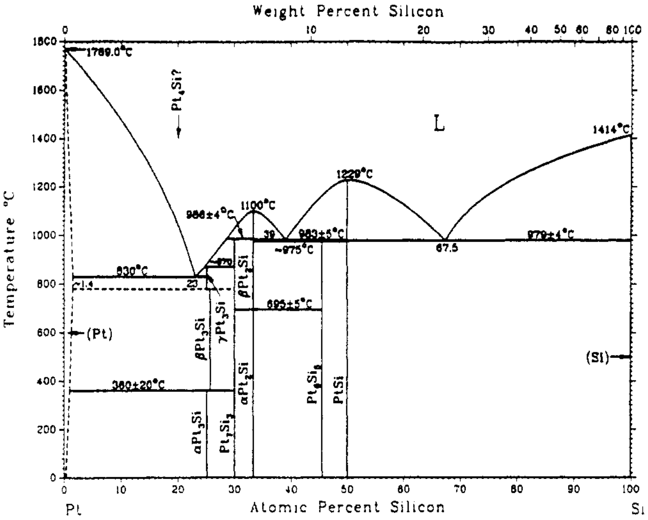

Figure 20. Platinum–silicon phase diagram. Reprinted from ref 86. Copyright 1986 ASM International.

19 has since been superseded by the assessment of Nash and Nash,[144] which also reviews the existing thermodynamic data; the complexity of the Ni-rich end of the system corresponds with a greater degree of controversy over the shape of the diagram here as well. (A review of some value has also been published by an Mey.[41]) The most recent work in the Co–Si system is that of Köster et al.,[145] published in 1973; again, equilibria in the Co-rich end of the system is the greatest source of uncertainty.

The only general experimental studies of the thermodynamics of compound formation in the Co–Si and Ni–Si systems are the 1936 and 1937 ΔH°_{298} results of Oelsen and co-workers,[55,56] determined by the direct-reaction calorimetry technique described earlier. More recently, Topor and Kleppa have used metal solution calorimetry to determine the heat of formation of NiSi,[67] arriving at a similar value. Otherwise, the only published heats of formation for these compounds are those arrived at through assessments or modeling work. Table 27 lists the various proposed values; the assessment of Chart is based in large part on the results of Oelsen and co-workers,[15,17] and so the similarity of values is no surprise. The modeling results of Pasturel et al. also show good agreement for NiSi[38] but diverge from the experimental results of Oelsen and co-workers for other compounds; as a result, while the latter are recommended as "best choice" heat of formation values, not enough confidence is placed in them to justify their use in second- or third-law analyses. Low- and high-temperature heat capacity results have also been published for some of these compounds;[47,48,146,147] the subambient work generally has a lower temperature limit of 60 K. No ΔG°_T values have been reported, outside of the assessment results for nickel silicides of an Mey and of Nash and Nash.[41,144]

L. Platinum Group Metals and Rhenium

The seven elements in this grouping have a good deal in common with the rare-earth elements, at least with regard to their silicide systems. Both groupings feature silicide compounds with considerable stability and minimal homogeneity ranges; unfortunately, both groupings also feature inadequate characterization of the actual phase diagrams. Figure 20 illustrates the

TABLE 28. Experimental and Estimated Values of ΔH°_{298} for Platinum Group and Rhenium Silicides (kJ/mol of Atoms)

	IrSi	Pd_2Si	Pt_2Si	PtSi	Re_5Si_3	ReSi	$ReSi_2$	RhSi	RuSi
Topor and Kleppa[67,70 a]	-63.8*[d]	-64.5*	-61.7*	-59.4*				-75.0*	-58.1*
Chart[15,17 b]	-67	-80	-71	-84	-19.7	-26.4	-30.1	-61	-42
Searcy and Finnie[20 b]	-33.3	-29.8	-57.7	-28.9		-25.5	-28.7	-33.7	-33.3
Machlin[37 c]	-65.5			-78.6		-32.1		-61.9	-39.2
Pasturel et al.[38 c]	-27.2	-66.1	-50.2	-69.0				-48.1	-43.9
Niessen and de Boer[36 c]	-41	-48	-61	-83	-27	-28	-16	-44	-33

[a] Experimental. [b] Assessed. [c] Modeled. [d] Asterisk indicates a recommended value.

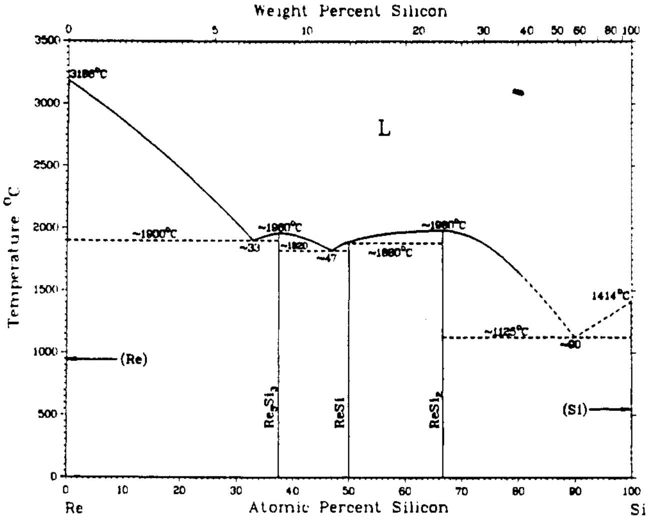

Figure 21. Rhenium–silicon phase diagram. Reprinted from ref 86. Copyright 1986 ASM International.

Pt–Si phase diagram,[86] which is still the subject of some controversy.[148] A recent reinvestigation of the Re–Si diagram shown as Figure 21 suggests different melting and eutectic points,[149] along with dissociation of ReSi below 1923 K. The phase diagrams of the Pd–Si system has also been recently updated;[150,151] the existence of several palladium silicides complicates the analysis. Phase diagrams have only recently been published for the Os–Si and Rh–Si systems,[152–54] and no accurate phase diagrams for the Ir–Si and Ru–Si systems are extant.

As demonstrated for other systems, the amount of thermodynamic information available for the silicides in these seven systems correlates closely with the degree of understanding of the phase diagram. In most cases, this means that very little information is available at all. The only reported heat capacity data are the high-temperature results for $ReSi_2$ reported by Bondarenko et al.,[53,102,103] and the investigation of ΔG°_T for the rhenium silicides conducted by Searcy and McNees (by elemental effusion) is the only such study of this property.[155] More recently, Topor and Kleppa have used metal solution calorimetry to determine ΔH°_{298}[67,70] for several platinum group silicides; Table 28 summarizes these results, comparing them with the usual assessment and model-generated estimates. Comparison of the latter with the recommended experimental results reveals none with good enough agreement to be recommended for other silicides in their own right. Obviously, a considerable amount of work remains to be performed on these systems.

IV. Conclusions and Recommendations

Commenting on his review work, Chart stated in 1972 that "the absolute accuracy of thermochemical data for transition metal-silicon systems is not high."[17] Eighteen years later, this comment remains largely valid. The available data are in agreement enough to allow the generation of reliable thermodynamic tables for only nine of the 100+ transition-metal silicide compounds, and even for one of these ($Mn_{11}Si_{19}$) the resultant entropy of formation is a cause for concern. As a result, the field remains highly fertile for future research.

Another factor encouraging further research is the at-best uneven ability of the various thermodynamic models to accurately predict these properties for silicides. Although these models appear capable of parroting trends in the various systems, such as the increasing stability of lower silicides for VIIIB elements, and the more exothermic ΔH°_{298} values in the Hf–Si and Zr–Si systems, their results often compare poorly with experimental data. (Of course, this disagreement is likely due in some cases to errors in the experimental work.) An improved experimental database would (a) improve the quality of the comparison with model-predicted results and (b) offer a basis for improvements in the models themselves.

A large part of the accuracy problem with the current database lies in the choices of experimental technique, which in many cases have not been the most fortuitous. The best choice of technique for one system may not be the same for another, depending particularly on the relative stability of the compound in question. Some techniques, such as oxide combustion calorimetry, are perhaps best left alone entirely.[51,52] Others, such as metal solution calorimetry, are perhaps best suited to less stable silicides, such as those of the VIIIB metals; the lower stability is likely to translate into higher (and quicker) solubility in molten alloy solvents. Free energy measurement methods should also vary according to system; the reactive effusion technique is most appropriate in systems where SiO is the only vapor species likely to form in appreciable quantities, and molten salt EMF methods work best in systems with large electronegativity differences between the transition-metal element and silicon (i.e., the current work with rare-earth silicides). The recent work with mass spectrometric measurement of elemental effusion rates has generally yielded reliable results[78,104,105] and has considerable promise for the future.

A good deal of experimental work with compound heat capacities also remains to be performed. In some cases, this work needs to be performed to confirm previous results, in particular the work of Bondarenko and co-workers.[53,102,103,114,115,125,126] Much of this latter work was performed at temperatures above 1200 K, and extrapolation to 298 K across this large a range is risky. Confirmation of some low-temperature results would also be of interest. In other cases, new heat capacity work is required to replace less reliable data, in particular the drop calorimetry results of Golutvin and co-workers;[60,63,96,156] the questioning of results from this group has been referenced repeatedly throughout these pages.[5,13,26,100] In the greatest number of cases, however, the need for heat capacity results stems from the lack of any such information at all for a compound or even a whole system. The Neumann–Kopp rule has demonstrated reasonable accuracy in predicting C_p for some silicide compounds (see Figure 1) but is not likely to produce accurate results from second- or third-law $\Delta H°_T$ and $\Delta G°_T$ calculations, especially over long temperature ranges. The increasing availability of adiabatic calorimetry for high-temperature work promises to make reliable experimental C_p data more widely available in the future.

The increasing applicability of intermetallic phases in general, and silicides in particular, has led to a noticeable expansion in research on the electrical, magnetic, and mechanical properties of these compounds. A revitalized research effort on their thermodynamic properties would help "complete the picture" and help to focus better the development work now occurring.

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