

Thermodynamic Evaluation and Optimization of the Ca-Si System

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All available phase equilibria and thermodynamic data for the Ca-Si system were collected and critically evaluated. In a first step, the thermodynamic properties of Ca(g) were obtained from experimental vapor pressure data over pure Ca. The new vapor pressure of calcium over pure solid and liquid was used as a new reference to model the thermodynamic properties of the intermediate stoichiometric Ca-Si compounds together with other thermodynamic and phase diagram data found in the literature (liquidus temperatures, heat capacities, pressures of Ca, and heats of reaction). Optimization was performed to obtain the parameters of one set of model equations for the different solid and liquid phases to best reproduce all the experimental data simultaneously. In this way, the data are rendered self-consistent, discrepancies among the data are identified, and extrapolations and interpolations can be performed. For the liquid phase, the Modified Quasichemical Model in the Pair Approximation for short-range ordering was used.

Keywords Ca-Si system, Modified Quasichemical Model, thermodynamic database, thermodynamic modeling

1. Introduction

Calcium and silicon are both important industrial materials. Calcium is used as a deoxidizer in the manufacture of steels, as a reducing agent in the preparation of metals like chromium, thorium, zirconium, and uranium. Calcium is also used for removal of bismuth from lead. Elemental silicon and its intermetallic compounds are used as alloying elements to provide more mechanical resistance to aluminum-magnesium or magnesium-copper alloys. Metallurgical silicon with 98-99% purity is used in the manufacture of organosilicic and silicon resins, seals, and oils. Silicon chips are used in integrated circuits. Photovoltaic cells for direct conversion of solar energy use thin cut slices of simple silicon crystals of electronic grade. Big silicon crystals are used for piezoelectric glasses. A colloidal dispersion of silicon in water is used as a coating agent and as an ingredient for certain enamels. Calcium silicide, CaSi, prepared in an electric oven from lime, silica, and reducing carbonated agents, is useful as a steel-deoxidizing agent.

A thermodynamic database for the Al-Mg-Ca-Si system is under development to study the corrosion reactions between molten Al-Mg-Si alloys and Al₂O₃-SiO₂-CaO refractory materials. The present system is an important subsystem because Ca-Si interactions have very negative deviations from ideality.

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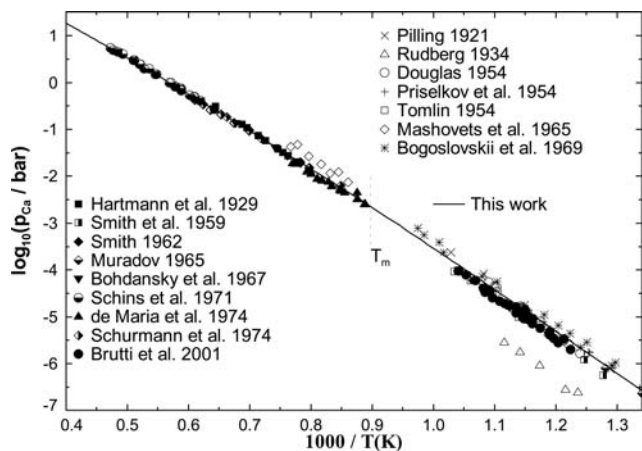


Fig. 1 Experimental and optimized partial pressure of Ca over pure Ca

2. Ca(g)

The thermodynamic properties of pure calcium gas were evaluated after reviewing all available experimental data found in the literature. Reported partial pressures of Ca over pure calcium are presented in Fig. 1.

A critical review of the reported experimental pressures of calcium over pure solid and liquid calcium was made. A new value for $H_{298}^0 - H_0^0$ was obtained by taking S_{298}^0 and $C_p = f(T)$ from [1985Cha].

Values of the partial pressure of calcium at the melting temperature obtained by extrapolation of the experimental values of different authors are shown in Fig. 2. Clearly, there is a strong disagreement between the different authors. [1921Pil] used calcium containing 1.62 wt.% Mg. The composition of the gaseous phase was not analyzed, and [1921Pil], who used a Langmuir evaporation method, probably measured a more important weight loss because Mg is

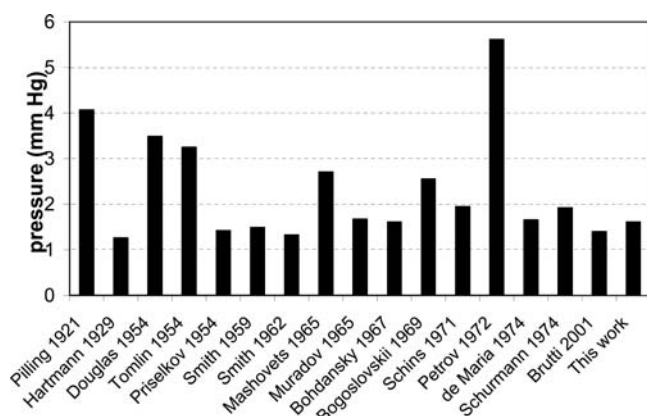


Fig. 2 Pressure of Ca(g) over pure Ca at the melting temperature ($T=1115$ K); values are extrapolated from reported experimental data

more volatile than Ca. Thermodynamic calculations in the same range of temperatures showed that the total pressure over {Ca+Mg} is 10-20 times higher than that of pure Ca. Douglas [1954Dou] and Tomlin [1954Tom] used a condensation Knudsen effusion method. They did not use a direct technique to determine the partial pressure of calcium. Determination of the amount of escaping vapor by total weight loss is preferable to weighting or analyzing a condensed fraction of the escaped vapor because errors arising from solid angle considerations, condensing efficiency, and analytical techniques are eliminated. Moreover, Douglas and Tomlin also used calcium polluted with Mg. Pressures obtained by Rudberg [1934Rud] were not taken into account because this author made some mistakes in Clausius coefficients, as mentioned by Tomlin [1954Tom], that led to smaller pressures (Fig. 1). High-temperature data seem to be consistent except for the data of Mashovets et al. [1965Mas]. This author did not use a direct determination (like [1954Dou]) and the purity of Ca was 99.3 wt.%. The data of Bogoslovskii [1969Bog] were discarded due to the discrepancies of the measurements (Knudsen effusion method) and also because the purity of the materials used was not mentioned. Since the pressures measured by Bogoslovskii are higher than the pressures measured by all other authors, the presence of some impurities like Mg may be assumed. Petrov [1972Pet] used a Knudsen technique to measure the pressure of Ca, but the purity of the calcium sample used can be questioned because Mg is reported.

For all the reasons mentioned above, the data of [1921Pil], [1954Dou], [1954Tom], [1934Rud], [1965Mas], [1969Bog], and [1972Pet] were discarded. The value of H_{298}^0 of Ca(g) was obtained by performing a second and third law analysis of the selected experimental data from [1929Har], [1954Pri], [1959Smi], [1962Smi], [1965Mur], [1967Boh], [1971Sch], [1974Mar], [1974Sch2], and [2001Bru], assuming the same S_{298}^0 and C_p functions as [1985Cha].

From the measured equilibrium constants, the two calculations using the second and third laws of thermodynamics [1985Cha], [2005Dro] give the standard enthalpies of the measured reactions at 298.15 K. These calculations are

based on the relation that defines the free energy of a reaction:

$$\Delta_r G^0(T) = -RT \ln K_p = \Delta_r H^0(T) - T\Delta_r S^0(T) \quad (\text{Eq 1})$$

The second law calculations are based on the following equation to determine the enthalpy difference associated with the considered reaction at the median temperature T :

$$\frac{d \ln K_p}{d(1/T)} = -\frac{\Delta_r H(T)}{R} \quad (\text{Eq 2})$$

This application presumes that $\Delta_r H(T)$ is constant in a given temperature interval, and then the standard enthalpy at 298.15 K is calculated using enthalpy increments. Based on the determination of the slope, this method remains sensitive to experimental errors and especially to systematic ones that are not necessarily reflected by the standard deviation. For determinations performed in rather good experimental conditions, an estimated uncertainty of 3-5% can be assumed in high temperature chemistry for all experimental points. In this work, 5% uncertainty was taken for second law calculations.

The third law calculations are derived from the same relation (Eq 1), with the basic assumption that the entropy of pure components is equal to 0 at 0 K (Nernst law or third law of thermodynamics). Generally, the Gibbs energy function is introduced:

$$gef(T) = [G^0(T) - H^0(298.15 \text{ K})]/T \quad (\text{Eq 3})$$

which could also be written

$$gef(T) = -S^0(T) + [H^0(T) - H^0(298.15 \text{ K})]/T \quad (\text{Eq 4})$$

So,

$$\Delta_r H^0(298.15 \text{ K}) = -RT \ln K_p - T\Delta_r gef(T) \quad (\text{Eq 5})$$

Note that Δ signifies Σ products - Σ reactants.

In these calculations, each individual determined K_p data point gives an enthalpy value at 298.15 K, which must be distributed around a mean value. Plotting these values as a function of temperature allows the observation of any anomalous trend. This trend, if occurring, can come either from errors in the determinations or from erroneous Gibbs energy functions. In case of no trend, third law analysis can produce very low standard deviations, about 1/10 of those issued from second law. The total uncertainty can be more easily estimated from each cause of uncertainty and generally third law enthalpies are known with lower uncertainties (about 1-2%) than second law enthalpies. When systematic causes of error or misinterpretation are discarded, the two calculations must be compatible [2005Dro] in their uncertainty ranges. The results of these calculations are shown in Table 1.

Section I: Basic and Applied Research

Table 1 Standard enthalpy $H_{298}^0 - H_0^0$ of Ca(g) obtained by second and third law calculations

Authors, reference	T median, K	2nd law at median T , kJ mol ⁻¹	2nd law at 298.15 K, kJ mol ⁻¹ (a)	$H_{298}^0 - H_0^0$; Ca, g; 2nd law; kJ mol ⁻¹ (a)	3rd law at 298.15 K, kJ mol ⁻¹ (b)	$H_{298}^0 - H_0^0$; Ca, g; 3rd law; kJ mol ⁻¹ (b)
[1929Har]	1366.6	171.1	186.3 ± 9.3	194.0 ± 9.3	169.0 ± 1.1	176.8 ± 1.1
[1954Pri]	832.6	163.6	168.3 ± 8.4	169.3 ± 8.4	173.4 ± 0.6	174.5 ± 0.6
[1959Smi]	875.5	177.3	182.6 ± 9.1	183.6 ± 9.1	176.4 ± 0.7	177.4 ± 0.7
[1962Smi]	910.4	172.1	178.0 ± 8.9	179.0 ± 8.9	176.2 ± 0.2	177.2 ± 0.2
[1965Mur]	767.7	172.2	176.0 ± 8.8	177.1 ± 8.8	174.4 ± 0.1	175.5 ± 0.1
[1965Mur]	671.7	172.2	175.0 ± 8.8	175.0 ± 8.8	177.6 ± 0.1	177.6 ± 0.1
[1967Boh]	1666.8	153.7	173.1 ± 8.7	180.9 ± 8.7	169.0 ± 0.3	177.2 ± 0.3
[1971Sch]	1815.0	149.7	171.2 ± 8.6	179.0 ± 8.6	168.7 ± 0.6	176.5 ± 0.6
[1974Mar]	1205.8	140.7	153.6 ± 7.7	161.3 ± 7.7	170.7 ± 0.8	178.5 ± 0.8
[1974Sch2]	1460.5	148.6	165.1 ± 8.3	172.9 ± 8.3	169.6 ± 0.7	177.4 ± 0.7
[2001Bru]	879.3	172.5	177.9 ± 8.9	178.9 ± 8.9	175.8 ± 0.9	176.9 ± 0.9
Average value	177.4 ± 8.7	...	176.9 ± 1

(a) The uncertainty was taken to 5% for second law calculations. (b) The uncertainty was taken as the standard deviation of the measurements of partial pressures.

Table 2 Standard enthalpies of formation of the compounds in the Ca-Si system (kJ/mol atoms, $T = 298.15$ K)

Reference	Ca ₂ Si	Ca ₅ Si ₃	CaSi	Ca ₃ Si ₄	Ca ₁₄ Si ₁₉	CaSi ₂	Method
[1949Kub]	-69.0 ± 4.2	...	-75.3 ± 4.2	-50.2 ± 2.5	Calorimetry at 940 K
[1962Shc]	-161.8 ± 2.8	Dissolution calorimetry
[1968Zvi]	-51.5	emf
[1967Mur]	-84.9	...	-90.2	-63.8	Effusion
[1971Wyn]	-46 (a)	-36.7(a)	Effusion
[2001Bru]	-56.1 ± 3.1	-55.3 ± 3.5	-49.6 ± 2.2	-40.6 ± 1.5	-44.4 ± 2.3	-37.8 ± 1.6	Knudsen cell mass spectrometry
This work	-47.1	-49.2	-43.5	-40.4	-38.7	-31.2	...

(a) Estimated by Anglezio et al. [1994Ang] but not mentioned in Wynnyckyj et al. [1971Wyn]

3. Thermodynamic Data for the Ca-Si System

Two calorimetric studies are available in the literature for the Ca-Si system. Kubaschewski et al. [1949Kub] determined calorimetrically the heats of formation of solid Ca₂Si, CaSi, and CaSi₂ (Table 2). The heat of formation of Ca₂Si was also measured by dissolution calorimetry by Shchukarev et al. [1962Shc] (Table 2).

Wynnyckyj et al. reported in two different papers [1971Wyn] and [1972Wyn2] vapor pressure measurements over calcium-silicon alloys in the silicon-rich region (50-76 at.% Si), and for one composition in the Ca-rich region of the phase diagram (40.8 at.% Si, 930-1220 °C). A direct weighing Knudsen cell was used, and the activities of the components in the liquid were derived. Because of the incomplete knowledge of the phase diagram (mentioned in [1972Wyn1]), a correct attribution of the vapor pressures to well-defined two-phase equilibria was not possible. Data from Wynnyckyj are shown in Fig. 3 and 4. A similar argument applies to previous effusion data by Muradov et al. [1967Mur]. Electromotive force (emf) measurements for solid CaSi₂ phase were made by Zviadadze et al. [1968Zvi] in the temperature range 660-810 °C (Table 2).

Sudavtsova et al. [1988Sud] used dissolution calorimetry

to determine the partial and integral mixing enthalpies in the Si-rich liquid at 1835 K (Fig. 5). Esin et al. [1985Esi] also measured by calorimetry the enthalpy of mixing of the liquid at 1773 K (Fig. 5). Discrepancies are observed between the two authors (Fig. 5). Schürmann et al. [1975Sch] made total pressure measurements over the liquid at different compositions for temperatures close to 1350 °C (Table 5). The partial pressure of Ca was assumed to be equal to the total pressure. Impurities of 0.1-0.3 wt.% Mg were reported.

Affronte et al. [1998Aff] measured at low temperature (1.6-15 K) heat capacities of solid CaSi and CaSi₂. Canepa et al. [2000Can] measured the heat capacities by adiabatic calorimetry of solid Ca₃Si₄, Ca₁₄Si₁₉, and CaSi₂ in the temperature range 3-300 K.

Brutti et al. [2001Bru] measured the partial pressure of calcium (Fig. 3 and 4) by high-temperature mass spectrometry and a vacuum microbalance technique in the composition range 20-75 at.% Si. Brutti et al. derived from these measurements the enthalpies of formation of solid calcium silicides.

4. Phase Diagram Data

Tamaru [1909Tam] was the first author to report experimentally the Ca-Si phase diagram. He used calcium with a

purity of 99.17 wt.% (with 0.55 wt.% of Al and Fe and 0.28 wt.% of Si). The silicon used consisted of 92.48 wt.% (with 1.74 wt.% Al and 6.08 wt.% Fe). The proposed phase diagram showed only one invariant reaction: liquid (L) + Si \leftrightarrow CaSi₂. The data of Tamaru (Fig. 6) were not considered in the present optimization because the raw materials used contained large proportions of impurities.

The Ca-Si phase diagram was measured by thermal analysis and electrical conductivity by [1921Wöh] and [1926Wöh]. Data of [1926Wöh] are shown in Fig. 6.

Using metallographic, x-ray diffraction (XRD), and electron microprobe analyses, Wynnyckyj [1972Wyn1] estab-

lished the existence of two unknown calcium silicides with stoichiometry reported as Ca₃Si and Ca₃Si₄.

Schürmann et al. [1974Sch1] studied the Ca-Si system over the entire composition range by thermal analysis, metallography, and electron microprobe analysis (Fig. 6). The raw materials used were Ca 99.8% purity (major impurity: Mg) and Si 99.99% purity. Liquidus temperatures higher than those reported previously by Hansen [1958Han] were found. Schürmann et al. confirmed the existence of Ca₂Si, CaSi, and CaSi₂. Ca₂Si (1305 °C) and CaSi (1315 °C) were found to melt congruently, and CaSi₂ (1033 °C) was found to melt incongruently. Schürmann et al. also estimated the three eutectic compositions as X(Si) = 0.056 at 782 °C for L \rightarrow Ca + Ca₂Si, 0.402 at 1259 °C for L \rightarrow Ca₂Si + CaSi, and 0.694 at 1023 °C for L \rightarrow CaSi₂ + Si.

Lee [1986Lee] measured thermal arrests for two alloys with compositions near the Ca₂Si compound to determine which of the reported phase diagrams of Hansen [1958Han] and Schürmann [1974Sch1] was correct. Lee measured liquidus temperatures (Fig. 6) higher than those of Hansen and concluded that Schürmann's phase diagram was correct.

Anglezio et al. [1994Ang] measured by differential thermal analysis (DTA) a eutectic temperature of 1020 °C for Si + Si₂Ca alloys. This compares well to the temperature of 1023 °C obtained by Schürmann et al. [1974Sch1].

Currao et al. [1996Cur] synthesized Ca₁₄Si₁₉ by mixing Ca (99.8% purity) and Si (99.99% purity) in a ratio close to Ca₃Si₄. Upon heating of the mixture, they observed by DTA three endothermic effects: two effects at 1210 and 1370 K corresponding to a peritectoid and peritectic decomposition (reported as CaSi + Ca₁₄Si₁₉ \leftrightarrow Ca₃Si₄, and L + CaSi \leftrightarrow

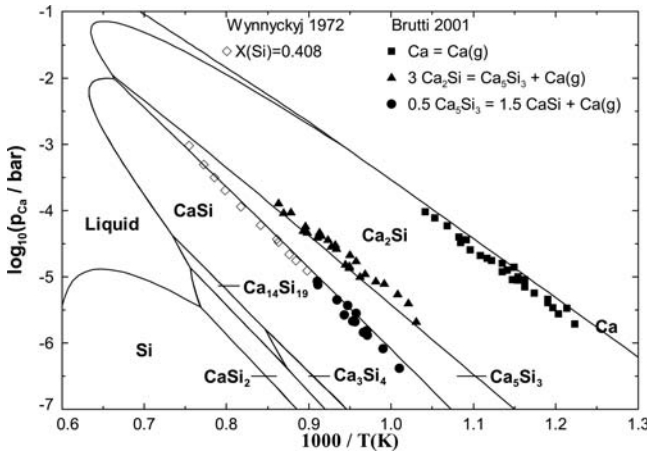


Fig. 3 Calculated pressures of Ca versus 1000/T with experimental data from [1972Wyn2] and [2001Bru] in the Ca-rich part of the Ca-Si system

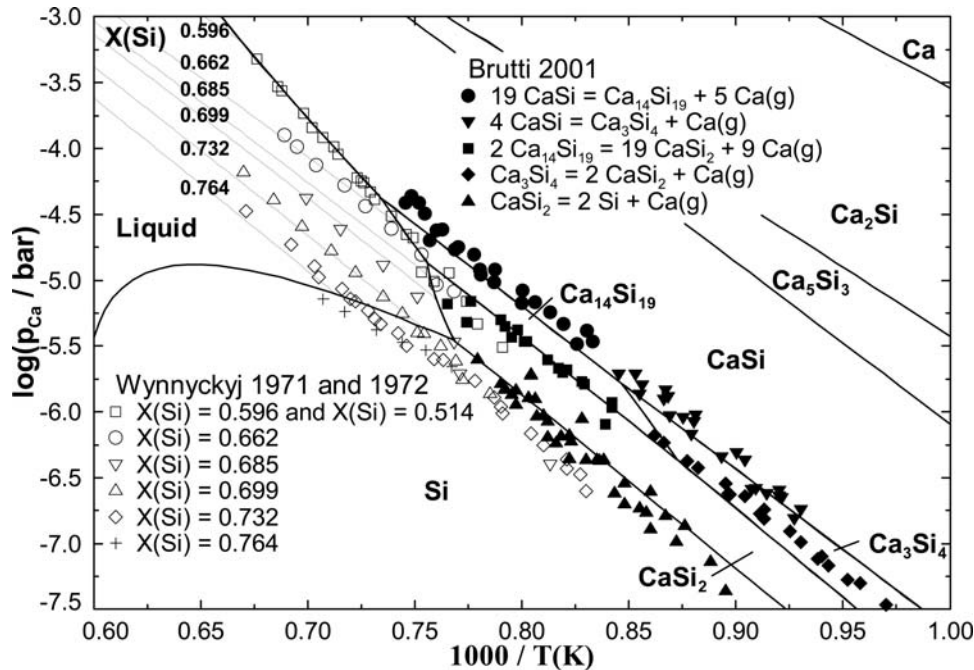


Fig. 4 Calculated pressures of Ca versus 1000/T with experimental data from [1971Wyn], [1972Wyn2], and [2001Bru] in the Si-rich part of the Ca-Si system

Section I: Basic and Applied Research

Ca₁₄Si₁₉, respectively), and one effect at 1580 K corresponding to the congruent melting point of CaSi.

Manfrinetti et al. [2000Man] studied the Ca-Si phase diagram in the composition range 0-70 at.% Si using DTA, metallographic analysis, XRD, and electron microscopy (Fig. 6). Commercial elemental calcium (purity 99.5 wt.%) and silicon (purity 99.999 wt.%) were used. The accuracy of the temperature measurements is reported to be $\pm 5^\circ$. Problems of undercooling were encountered in the silicon-rich side of the system, and thus a precise determination of the “horizontal” temperatures was not possible. Manfrinetti et al. confirmed the existence of the five intermediate phases: Ca₂Si, Ca₅Si₃, CaSi, Ca₁₄Si₁₉, and CaSi₂, and reported a new compound, the Zintl-phase Ca₃Si₄ (which had already

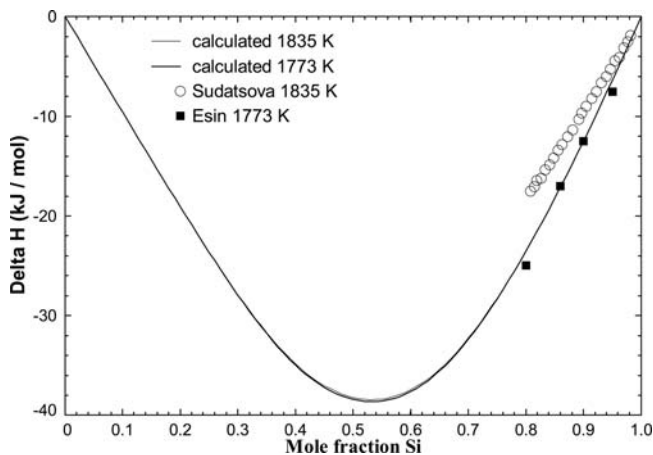


Fig. 5 Calculated enthalpy of mixing of the Ca-Si liquid at 1773 and 1835 K

been suggested by Wynnyckyj et al. [1972Wyn1]). Three eutectics were reported at $X(\text{Si}) = 0.035$ (795 °C), 0.425 (1230 °C), and 0.72 (1020 °C) (Table 3).

Only one author measured the solubility of calcium in solid silicon [1982Sig]. This solubility is reported to be small ($< 1.6 \times 10^{-4}$ in molar fraction at $T = 1100^\circ\text{C}$).

The characteristic points of the Ca-Si phase diagram are listed and compared with the results of the present optimization in Table 3.

5. Previous Assessments

Lee [1986Lee] derived thermodynamic parameters from phase diagram data. He represented the excess Gibbs energy of the liquid phase using three polynomial equations for different composition ranges. His results cannot be used for calculations in a Ca-Si based multicomponent system.

Anglezio et al. [1994Ang] made an assessment of the Ca-Si system by the Calphad method using mainly the phase diagram data of Schürmann [1974Sch1].

Gröbner et al. [2003Gro] performed an assessment of the Ca-Si system. They used the polynomial model with a Redlich-Kister expansion and a Bragg-Williams type of configurational entropy for the liquid phase. The enthalpies of formation of solid calcium silicides derived by Brutti et al. [2001Bru] and phase diagram data from Schürmann [1974Sch1] and Manfrinetti [2000Man] were used. They also used activity values derived from measurements of Wynnyckyj [1971Wyn], Schürmann [1975Sch], and Sudatsova [1988Sud]. The agreement between the calculated phase diagram of Gröbner et al. and experimental data could be improved in regard to the melting point of CaSi and the Si liquidus. The calculated partial pressures of Ca using the

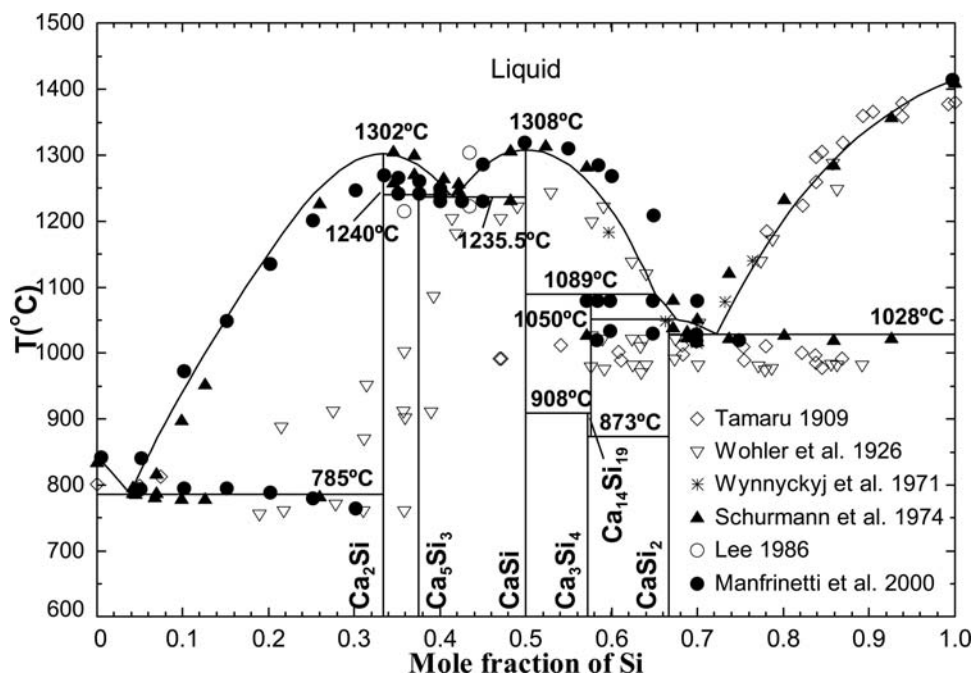


Fig. 6 Calculated Ca-Si phase diagram at 1 bar

Table 3 Characteristic points of the Ca-Si Phase Diagram

Characteristic point	Mol fraction Si	Temperature, °C	Reference
(βCa) ↔ (αCa)	0	443	This work
L ↔ (βCa) + Ca ₂ Si	...	760	[1921Woh], [1926Woh]
	0.056	782	[1974Sch1]
	0.035	795	[2000Man]
	0.039	785	This work
L ↔ Ca ₂ Si	0.333	1305	[1974Sch1]
	0.333	1270	[2000Man]
	0.333	1302	This work
L + Ca ₂ Si ↔ Ca ₅ Si ₃	0.402	1259(a)	[1974Sch1]
	0.414(b)	1240	[2000Man]
	0.412 (liquid)	1240	This work
L ↔ Ca ₅ Si ₃ + CaSi	0.425	1230	[2000Man]
	0.418	1235.5	This work
L ↔ CaSi	0.5	≈1245	[1921Woh], [1926Woh]
	0.5	1315	[1974Sch1]
	0.5	1307	[1996Cur]
	0.5	1320	[2000Man]
	0.5	1308	This work
CaSi + Ca ₁₄ Si ₁₉ ↔ Ca ₃ Si ₄	...	937	[1996Cur]
	...	≈910	[2000Man]
	...	908	This work
L + CaSi ↔ Ca ₁₄ Si ₁₉	...	1097	[1996Cur]
	0.712 (L)(b)	1085	[2000Man]
	0.650 (L)	1089	This work
Ca ₁₄ Si ₁₉ ↔ Ca ₃ Si ₄ + CaSi ₂	...	≈900	[2000Man]
	...	873	This work
L + Ca ₁₄ Si ₁₉ ↔ CaSi ₂	≈0.67	1020(c)	[1921Woh], [1926Woh]
	0.682 (L)	1033(c)	[1974Sch1]
	0.721 (L)(b)	1030	[2000Man]
	0.675 (L)	1050	This work
L ↔ CaSi ₂ + Si	...	≈990(d)	[1909Tam]
	≈0.69	980	[1921Woh], [1926Woh]
	0.694	1023	[1974Sch1]
	0.720	1020	[2000Man]

(a) Reported as Liquid ↔ CaSi₂ + CaSi; (b) read from a smoothed phase diagram; (c) reported as Liquid + CaSi ↔ CaSi₂; (d) reported as Liquid + Si ↔ CaSi₂

reported Gibbs energies of condensed phases of [2003Gro] with the Gibbs energy of Ca(g) of the present work do not fit well with the reported values of [1971Wyn], [1972Wyn2], and [2001Bru].

In this work, a new optimization of the Ca-Si system was performed using phase diagram data together with the reported partial pressures of Ca in the two-phase regions (rather than the derived enthalpy and activity values). As a result, when activities were derived by an author from pressure measurements, only the pressures (not the activities) were used in the present optimization. The optimization of the different stoichiometric compounds was done using the vapor pressures measured by Brutti et al. [2001Bru] and Schürmann et al. [1975Sch] as well as entropies at 298.15 K derived from direct integration of heat capacities determined by Canepa et al. [2000Can]. The phase diagram data from Schürmann et al. [1974Sch1] and Manfrinetti et al. [2000Man] were also considered.

6. Calcium Silicides

Canepa et al. [2000Can] measured the heat capacities over the temperature range 3-300 K for the three calcium silicides CaSi₂, Ca₃Si₄, and Ca₁₄Si₁₉. In the present work, the C_p of the different calcium silicides were estimated as follows:

- The C_p of Ca(bcc) was extrapolated from 716 to 2000 K by using a linear extrapolation of the type A + BT.
- A similar procedure was used for the C_p of Si(diamond) from 1687 to 2000 K.
- Then, the Kopp-Neumann rule was used (i.e., the heat capacity of a compound is equal to the sum of the heat capacities of the constituent elements) to estimate the C_p of the various calcium silicides.
- Finally, the values of C_p were adjusted by introducing a constant term to obtain the values of C_p at 298.15 K

Section I: Basic and Applied Research

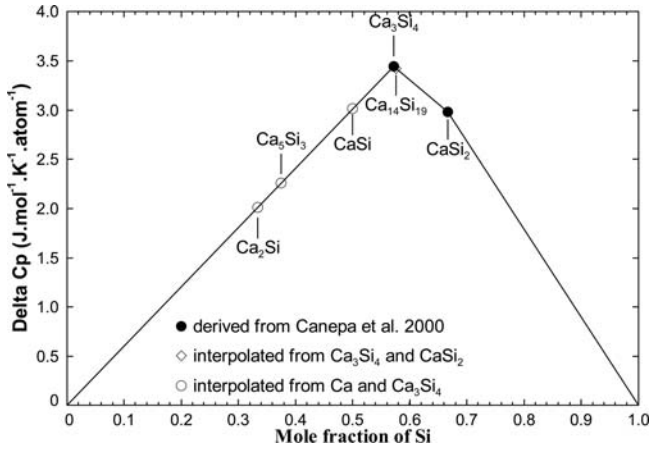


Fig. 7 Delta C_p (in $\text{J mol}^{-1} \text{K}^{-1} \text{atom}^{-1}$) of calcium silicides referred to Ca(bcc) and Si(diamond)

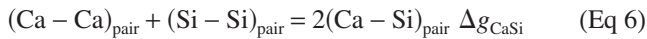
determined by Canepa et al. [2000Can] for solid CaSi_2 and Ca_3Si_4 and a linear interpolation of the ΔC_p (Fig. 7) was performed in the 2 regions Ca- Ca_3Si_4 , Ca_3Si_4 - CaSi_2 to obtain the corresponding constants for Ca_2Si , Ca_5Si_3 , CaSi , and $\text{Ca}_{14}\text{Si}_{19}$.

All standard enthalpies of formation of the stoichiometric compounds from experimental investigations are given in Table 2.

7. Liquid Phase

The Modified Quasichemical Model in the Pair Approximation [2000Pel] is used for the liquid phase. In this model, the energy of first nearest-neighbor pair formation is expanded as a polynomial in the pair fractions, rather than in the component equivalent fractions [1986Pel]. These modifications provide greater flexibility in fitting the binary data and in combining optimized binary systems into large databases for multicomponent solutions [2001Pel].

For the liquid binary solution, Ca and Si atoms are distributed over the sites of a quasilattice. The following first-nearest-neighbor pair exchange reaction is considered:



The nonconfigurational Gibbs energy change for the formation of 2 mols of (Ca-Si) pairs according to Eq 6 is Δg_{CaSi} . The analytical description of the Gibbs energy of the solution is

$$G = (n_{\text{Ca}} g_{\text{Ca}}^0 + n_{\text{Si}} g_{\text{Si}}^0) - T \Delta S^{\text{config}} + \frac{1}{2} n_{\text{CaSi}} \Delta g_{\text{CaSi}} \quad (\text{Eq 7})$$

where g_{Ca}^0 and g_{Si}^0 are the molar Gibbs energies of the pure liquid components, ΔS^{config} is the configurational entropy of mixing given by randomly distributing the (Ca-Ca), (Si-Si), and (Ca-Si) pairs in the one-dimensional Ising approximation [2000Pel], n_{Ca} and n_{Si} are the number of mols of

calcium and silicon, respectively, and n_{CaSi} is the number of mols of calcium-silicon first-nearest-neighbor pairs obtained by minimizing the Gibbs energy at constant T and P respecting the mass balance.

$$Z_{\text{Ca}} n_{\text{Ca}} = 2n_{\text{CaCa}} + n_{\text{CaSi}} \quad (\text{Eq 8})$$

$$Z_{\text{Si}} n_{\text{Si}} = 2n_{\text{SiSi}} + n_{\text{CaSi}} \quad (\text{Eq 9})$$

When Δg_{CaSi} is small, the degree of short-range ordering is small, and the solution approximates a random (Bragg-Williams) mixture of atoms on the quasilattice.

As the model parameter Δg_{CaSi} becomes progressively more negative, the reaction in Eq 6 is shifted to the right, (Ca-Si) pairs predominate, and the solution becomes progressively more ordered. Δg_{CaSi} is expanded as a polynomial in terms of the pair fractions $X_{\text{CaCa}} = n_{\text{CaCa}} / (n_{\text{CaCa}} + n_{\text{SiSi}} + n_{\text{CaSi}})$ and $X_{\text{SiSi}} = n_{\text{SiSi}} / (n_{\text{CaCa}} + n_{\text{SiSi}} + n_{\text{CaSi}})$ (where n_{CaCa} , n_{SiSi} and n_{CaSi} are the numbers of mols of each kind of pairs):

$$\Delta g_{\text{CaSi}} = \Delta g_{\text{CaSi}}^{(0)} + \sum_{i \geq 1} g_{\text{CaSi}}^{(i0)} X_{\text{CaCa}}^i + \sum_{j \geq 1} g_{\text{CaSi}}^{(0j)} X_{\text{SiSi}}^j \quad (\text{Eq 10})$$

where $\Delta g_{\text{CaSi}}^{(0)}$, $g_{\text{CaSi}}^{(i0)}$, and $g_{\text{CaSi}}^{(0j)}$ are the adjustable model parameters that can be linear functions of temperature. Composition-dependent coordination numbers are introduced: Z_{Ca} and Z_{Si} are permitted to vary with the composition as follows:

$$\frac{1}{Z_{\text{Ca}}} = \frac{1}{Z_{\text{CaCa}}} \left(\frac{2n_{\text{CaCa}}}{2n_{\text{CaCa}} + n_{\text{CaSi}}} \right) + \frac{1}{Z_{\text{CaSi}}} \left(\frac{n_{\text{CaSi}}}{2n_{\text{CaCa}} + n_{\text{CaSi}}} \right) \quad (\text{Eq 11})$$

$$\frac{1}{Z_{\text{Si}}} = \frac{1}{Z_{\text{SiSi}}} \left(\frac{2n_{\text{SiSi}}}{2n_{\text{SiSi}} + n_{\text{CaSi}}} \right) + \frac{1}{Z_{\text{SiCa}}} \left(\frac{n_{\text{CaSi}}}{2n_{\text{SiSi}} + n_{\text{CaSi}}} \right) \quad (\text{Eq 12})$$

where Z_{CaCa} and Z_{CaSi} are the values of Z_{Ca} when all nearest-neighbors of a calcium atom are calcium atoms, and when all nearest neighbors of a calcium atom are silicon atoms, respectively. Z_{SiSi} and Z_{SiCa} are defined similarly. In this work, $Z_{\text{CaCa}} = Z_{\text{SiSi}} = 6$ and $Z_{\text{CaSi}} = Z_{\text{SiCa}} = 4$.

The Gibbs free energy of Eq 6 for the liquid solution, optimized by taking into account all data discussed above, is

$$\Delta g_{\text{CaSi}} = -47,279.2 + 1.8828T + (-17,991.2)X_{\text{SiSi}} + (-1354.3 - 16.7360T)X_{\text{CaCa}} (\text{J mol}^{-1})$$

8. Results and Discussion

Thermodynamic data ($H_{298.15\text{K}}^0 - H_0^0$, $S_{298.15\text{K}}^0$, and C_p) for the condensed pure phases of the Ca-Si system are given in Table 4. Table 4 also includes optimized values from the present work.

The calculated phase diagram is compared with all available experimental data in Fig. 6. Solid solubilities were assumed to be negligible. No decomposition of the different calcium silicides occur below 600 °C.

In Fig. 8 and 9, respectively, the enthalpies of formation

Table 4 Thermodynamic properties of compounds

		T range, K	$H_{298.15\text{K}}^0 - H_{0\text{K}}^0$ J mol^{-1} (a)	$S_{298.15\text{K}}^0$ J $\text{mol}^{-1} \text{K}^{-1}$ (b)	C_p , J $\text{mol}^{-1} \text{K}^{-1}$	Reference
Ca	bcc	298.15-2000	[1991Din]
	fcc	298.15-2000	[1991Din]
	L	298.15-3000	[1991Din]
	G	298.15-1773.66	176,900	154.886	20.791789	This work and [1985Cha]
	G	1773.66-6000	[1985Cha]
Si	S	298.15-3600	[1991Din]
	L	298.15-3600	[1991Din]
	G	298.15-6000	[1985Cha]
CaSi	S	298.15-716	-87,000.1	60.4287	$57.107853 - 0.010639392 T +$ $2.7022614 \times 10^{-5} T^2 - 474,490 T^{-2}$	This work
	S	716-1687	-86,715.0	61.2048	$44.941273 + 0.025355808 T +$ $2.1312 \times 10^{-8} T^2 - 353,334 T^{-2}$	This work
CaSi ₂	S	1687-2000	-87,070.4	60.2113	$44.007128 + 0.025871666 T$	This work
	S	298.15-716	-93,724.4	77.2860	$82.851606 - 0.006813584 T +$ $2.7043926 \times 10^{-5} T^2 - 827,824 T^{-2}$	This work
	S	716-1687	-93,439.3	78.0621	$70.685026 + 0.029181616 T +$ $4.2624 \times 10^{-8} T^2 - 706,668 T^{-2}$	This work
Ca ₂ Si	S	1687-2000	-94,150.3	76.0753	$68.816736 + 0.030213334 T$	This work
	S	298.15-716	-141,227.2	93.2562	$85.360953 - 0.025104592 T +$ $5.4023916 \times 10^{-5} T^2 - 595,646 T^{-2}$	This work
Ca ₃ Si ₄	S	716-1687	-140,657.0	94.8084	$61.027793 + 0.046885808 T +$ $2.1312 \times 10^{-8} T^2 - 353,334 T^{-2}$	This work
	S	1687-2000	-141,012.4	93.8150	$60.093648 + 0.047401666 T$	This work
	S	298.15-716	-282,534.7	185.858	$200.17631 - 0.028092368 T +$ $8.1089154 \times 10^{-5} T^2 - 1,776,804 T^{-2}$	This work
Ca ₅ Si ₃	S	716-1687	-281,679.4	188.1863	$163.67657 + 0.079893232 T +$ $8.5248 \times 10^{-8} T^2 - 1,413,336 T^{-2}$	This work
	S	1687-2000	-283,101.2	184.2127	$159.93999 + 0.081956666 T$	This work
	S	298.15-716	-393,521.4	231.4300	$227.82976 - 0.060848576 T +$ $0.00013507045 T^2 - 1,665,782 T^{-2}$	This work
Ca ₁₄ Si ₁₉	S	716-1687	-392,095.8	235.3106	$166.99686 + 0.11912742 T +$ $6.3936 \times 10^{-8} T^2 - 1,060,002 T^{-2}$	This work
	S	1687-2000	-393,162.2	232.3303	$164.19442 + 0.120675 T$	This work
	S	298.15-716	-1,275,855.9	912.0040	$942.22071 - 0.12982245 T +$ $0.00037842316 T^2 - 8,409,530 T^{-2}$	This work
Ca ₁₄ Si ₁₉	S	716-1687	-1,271,864.2	922.8696	$771.88859 + 0.37411036 T +$ $4.04928 \times 10^{-7} T^2 - 6,713,346 T^{-2}$	This work
	S	1687-2000	-1,278,618.1	903.9946	$754.13983 + 0.38391166 T$	This work

(a) Enthalpy relative to the enthalpy of the elements in their stable standard states at 298.15 K; (b) absolute (third law) entropy

and the standard absolute entropies of the various calcium silicides are represented. The calculated enthalpies of formation are more positive than those determined directly by calorimetry [1947Sch, 1949Kub] but are relatively close to the values derived by Brutti et al. [2001Bru]. For the absolute entropies of the silicides, the only available data were derived by Canepa et al. from low-temperature heat capacity measurements [2000Can]. Only the entropy values for CaSi₂ and Ca₃Si₄ were considered because Ca₁₄Si₁₉ is unstable at the low temperatures at which the heat capacity measurements were conducted. There are clearly discrepancies among the reported thermodynamic data for the calcium silicides. The enthalpies of formation determined by calorimetry [1947Sch, 1949Kub] are more negative than

those derived from pressure measurements [2001Bru]. The calorimetric measurements are largely scattered and the recent heat capacity measurements from Canepa et al. are considered to be more reliable. Consequently, the optimization was made using the latter values combined with vapor pressure values and phase diagram data. The calculated heats of formation of the calcium silicides are closer to those derived by Brutti et al. and disagree with the earlier calorimetric measurements.

The calculated enthalpies of mixing at 1773 and 1835 K of liquid Ca-Si solution are shown in Fig. 5 together with the experimental enthalpies of mixing of Esin [1985Esi] and Sudatsova [1988Sud].

The calculated pressures of Ca are compared with the

Section I: Basic and Applied Research

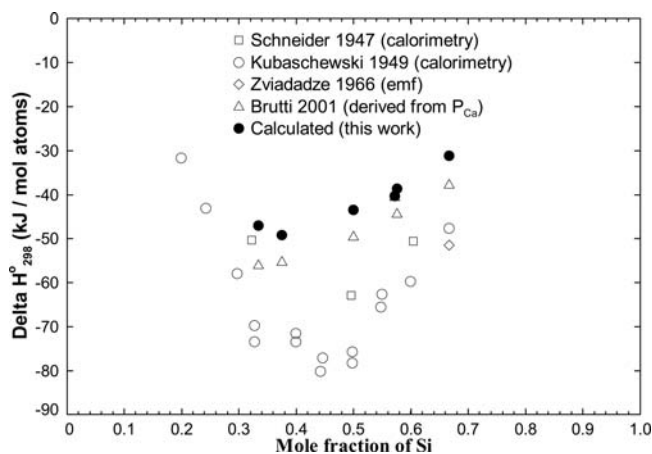


Fig. 8 Standard heats of formation at 298.15 K for the calcium silicides

Table 5 Measured total pressures in the system calcium-silicon [1975Sch] and calculated total pressures

X_{Si}	$T, ^\circ C$	Measured total pressure, torr	Calculated total pressure, torr		
			0% Mg	0.1 wt.% Mg	0.3 wt.% Mg
0.129	1356	249.6	246.1	249.2	256.2
0.208	1337	187.3	147.7	151.9	160.4
0.231	1346	187	135.1	139.6	149.9
0.248	1355	183	126.8	131.8	143.9
0.333	1347	120.2	52.8	61.3	79.7
0.329	1341	112.5	53.0	60.6	78.0
0.361	1348	95.7	38.0	47.4	68.4
0.394	1360	60.8	27.3	38.7	63.6
0.42	1362	46.7	19.8	31.4	57.0
0.43	1359	39.3	17.0	28.4	53.2
0.461	1340	26.2	9.8	19.1	39.3

measured values of Wynnyckyj [1972Wyn2] and Brutti et al. [2001Bru] in Fig. 3 and 4. A good agreement between the calculated pressures and experimental data is obtained for the solid-solid equilibria. For the liquid, some discrepancies are sometimes observed: for mole fractions of Si less than 0.662, the measured vapor pressures of Wynnyckyj et al. [1971Wyn], [1972Wyn2] are accurately reproduced, but for liquids richer in Si, only the experimental slopes (and not the absolute values) are reproduced by the model.

The calculated total pressure over various Ca-Si liquid alloys are compared with the experimental total pressure data of Schürmann et al. [1975Sch] in Table 5. For the Si-rich liquid alloys, the calculated vapor pressures of Ca are significantly lower than the measurements. Table 5 also shows total pressures calculated by taking into account impurities of Mg present in the same concentration as the Ca used by Schürmann (reported as 0.1-0.3 wt.%), in this case a better agreement is obtained.

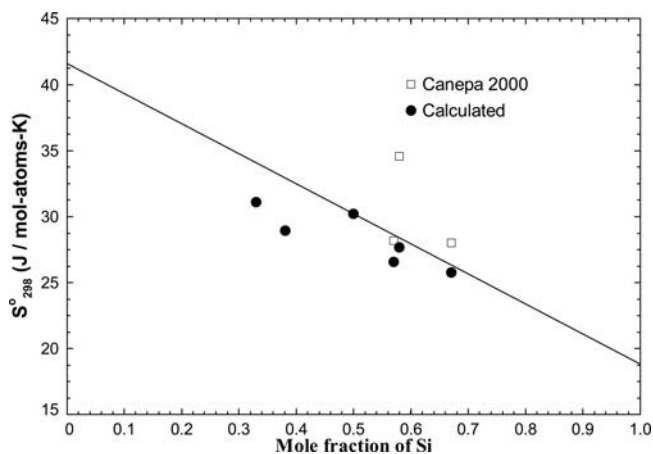


Fig. 9 Absolute standard entropy at 298.15 K for calcium silicides

9. Conclusions

The enthalpy of formation of Ca(g) was slightly adjusted to best reproduce the more accurate experimental data.

All available data for the binary Ca-Si system were collected and critically evaluated. The optimization has produced one set of model parameters for each phase that reproduce all the data simultaneously within the experimental error limits. This has also permitted discrepancies in the data to be identified, and all the data have been rendered self-consistent. The obtained parameters can be used in Gibbs free energy minimization software as FactSage [2002Bal] to interpolate and extrapolate, and to calculate all thermodynamic properties, vapor pressures, etc. at all compositions and over extended ranges of temperature and pressure.

The Modified Quasichemical Model in the Pair Approximation [2000Pel, 2001Pel] was used for the liquid phase.

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Section I: Basic and Applied Research

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