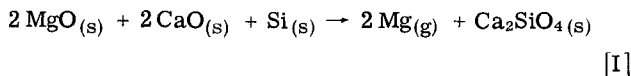


Equilibria in the Silicothermic Reduction of Calcined Dolomite

J. R. WYNNYCKYJ AND L. M. PIDGEON

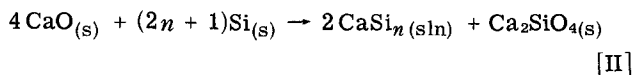
When a mixture of calcium oxide and silicon is heated to above 1000°C a liquid Ca-Si alloy is formed. When magnesium metal is produced by reacting calcined dolomite with silicon, the alloy still forms and is the effective reducing agent for magnesium oxide. In this investigation the thermodynamic data on the Ca-Si alloys have been related to the magnesium-producing reaction, the calcium pressures over mixtures CaO + Si were measured using a Knudsen cell, and the magnesium and calcium pressures over the mixtures CaO + MgO + Si were measured using the transportation method. The magnesium content of the equilibrium alloy was determined isopiastically and the identity of the silicate was established. The results constitute a complete and consistent definition of the equilibria in the magnesium production reaction, and have also yielded an improved value of the free energy of formation of calcium orthosilicate.

THE reduction of calcined dolomite¹⁻³ by a reactive metal or metalloid continues to be an important route for the production of magnesium metal. The reducing agent used industrially is ferrosilicon containing usually about 75 to 80 pct Si. The present paper reports on a study of the chemistry and the equilibria which govern the basic reaction



Schneider *et al.*⁴ have drawn attention to the fact that a spontaneous reaction occurs between solid silicon and calcium oxide⁸ to form a liquid Ca-Si alloy and a silicate at above 1000°C, *i.e.* temperatures of interest in the industrial process in its present embodiments.^{1,3} When magnesium oxide is reacted with silicon in the absence of calcium oxide the magnesium vapor pressure^{5,6} is an order of magnitude lower and the reaction rate⁷ is substantially less. The solid product is then the magnesium orthosilicate.⁶

The spontaneous reaction between calcium oxide and silicon may be represented by

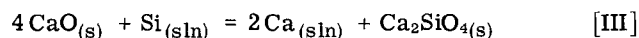


where n indicates the ratio of silicon to calcium in the liquid alloy. Reaction [II] must continue to the right until either solid silicon or solid calcium oxide are consumed (depending on which is supplied in excess). A CaO/Si-mixture with Reaction [I] stoichiometry contains an excess of calcium oxide and the phases present at equilibrium must be CaO_(s), Ca₂SiO_{4(s)}, and the liquid alloy CaSi _{n} . In accordance with the phase rule,⁹ the composition of the alloy is fixed for a given temperature, *i.e.* n is a single-valued function of the temperature.

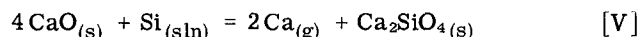
The condition at equilibrium is described by the equations

J. R. WYNNYCKYJ, formerly Graduate Student, University of Toronto, Toronto, Ontario, Canada, is now Associate Professor, Department of Chemical Engineering, University of Waterloo, Waterloo, Ontario. L. M. PIDGEON is Professor, Department of Metallurgy and Materials Science, University of Toronto.

Manuscript submitted August 31, 1970.

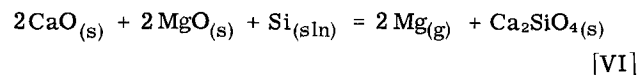


Addition of [III] and [IV] gives



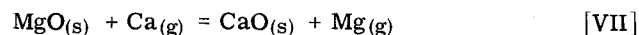
which relates the gas phase with the solid and liquid phases.

Reaction [II] will occur regardless of whether magnesium oxide is present or not and the equilibrium condition corresponding to Reaction [I] is to be represented as



where the subscript (sln) in Si_(sln) is to emphasize the fact that silicon is in the form of a liquid alloy. Measurements to determine the composition of this alloy will be described below, whereby use will be made of the activity composition data for the Ca-Si system reported in Ref. 10. The equilibrium magnesium pressure as measured for example by Pidgeon and King,⁵ refers to Reaction [VI] and not to Reaction [I] as is usually suggested in the literature.^{5,11,12} Similarly, silicon activities in Si-Fe alloys obtained with the help of Eq. [VI]²² are not based on pure silicon as the standard state.

An assumption implicit in writing Eq. [VI] is that the equilibrium calcium pressure produced by the concurrent Reaction [V] is very much lower than the magnesium pressure and can, therefore, be neglected. The equilibrium



will, nevertheless, be established if both solid MgO and solid CaO are present.

The equilibrium constants for Reactions [V], [VI], and [VII] can be written as

$$K_V = \frac{a_{\text{Ca}_2\text{SiO}_4} \cdot p_{\text{Ca}}^2}{a_{\text{CaO}}^4 \cdot a_{\text{Si}}} = \frac{p'_{\text{Ca}}{}^2}{a'_{\text{Si}}} \quad [1]$$

$$K_{\text{VI}} = \frac{a_{\text{Ca}_2\text{SiO}_4} \cdot p_{\text{Mg}}^2}{a_{\text{CaO}}^2 \cdot a_{\text{MgO}}^2 \cdot a_{\text{Si}}} = \frac{p''_{\text{Mg}}{}^2}{a''_{\text{Si}}} \quad [2]$$

$$K_{VII} = p_{Mg}'' / p_{Ca}'' \quad [3]$$

where p and a are pressures and activities, respectively; the superscript (') denotes the system $CaO_{(s)}$, $Ca_2SiO_4_{(s)}$, alloy (Ca, Si); and superscript (") the system $CaO_{(s)}$, $Ca_2SiO_4_{(s)}$, alloy (Ca, Si, Mg) + $MgO_{(s)}$. Henceforth these systems will be referred to as system (') and system ("), respectively. The activities of the solid phases, a_{MgO} , a_{CaO} , and $a_{Ca_2SiO_4}$ have been set equal to unity as there is no evidence of appreciable mutual solubility.

The equilibrium constants are related to the standard free energies of the reactions, ΔG_i^0 , by the familiar relationship

$$K_i = \exp^{-\Delta G_i^0 / RT} \quad [4]$$

Combining Eqs. [1] to [4] and solving for the pressures, one can write

$$p_{Ca}' = a_{Si}'^{1/2} \exp^{-\Delta G_V^0 / 2RT} \quad [5]$$

$$p_{Mg}'' = a_{Si}''^{1/2} \exp^{-\Delta G_{VI}^0 / 2RT} \quad [6]$$

$$p_{Ca}'' = p_{Mg}'' / K_{VII} \quad [7a]$$

Also

$$p_{Ca}'' = a_{Si}'^{1/2} \frac{K_{VI}^{1/2}}{K_{VII}} = a_{Si}''^{1/2} \exp^{-\Delta G_V^0 / 2RT} \quad [7b]$$

since $K_{VI}^{1/2} / K_{VII} = K_V^{1/2}$. It follows from comparing [5] and [7b] that the calcium pressures in the two systems, p_{Ca}' and p_{Ca}'' , differ only in as much as the silicon activities a_{Si}' and a_{Si}'' differ from each other. A difference can, however, arise only as a result of solution of magnesium in the liquid alloy. Should the extent of

this solution be small, a_{Si}' and a_{Si}'' and, therefore, also p_{Ca}' and p_{Ca}'' would be expected to be about equal.*

*A direct reaction between silicon and magnesium oxide to form an alloy (analogous to Reaction [II]) does not occur. The magnesium-silicon phase diagram¹³ indicates a liquids composition of 35 at. pct Mg in equilibrium with solid silicon at 1000°C. This is the lowest magnesium content that a liquid alloy could have. Magnesium pressures over Mg-Si alloys have recently been determined¹⁴ and the magnesium pressure over such an alloy is 50 torr. This pressure is substantially above the 10.2 torr⁵ over Reaction [VI]. It follows that a liquid Mg-Si alloy cannot form by reduction of MgO in the absence of CaO. In the presence of CaO, once a liquid alloy is formed by Reaction [II], some magnesium can dissolve.

Another assumption implicit in writing Eq. [VI] is that the silicate forming in the presence and in the absence of magnesium oxide is Ca_2SiO_4 . Earlier literature favors this assumption,^{1,4} but unequivocal evidence is as yet lacking. In a recent paper,¹⁵ Hughes *et al.* report identifying the compound $Ca_3Mg(SiO_4)_2$ (the mineral merwinite) in the reaction residues and propose that the reaction to which the measured⁵ magnesium pressure corresponds produces $Ca_3Mg(SiO_4)_2$. Attention is devoted to this question later.

1) EXPERIMENTAL

a) Materials

The dolomite used in the investigations was from the Grenville¹⁶ series supplied in calcined form by Dominion Magnesium Ltd. Its chemical analysis in wt pct was 38.9 MgO, 59.0 CaO, 0.32 ternary oxides, and 1.2 loss on ignition. Magnesium oxide and silica were obtained from Fischer Scientific, Toronto (lot numbers 754-282

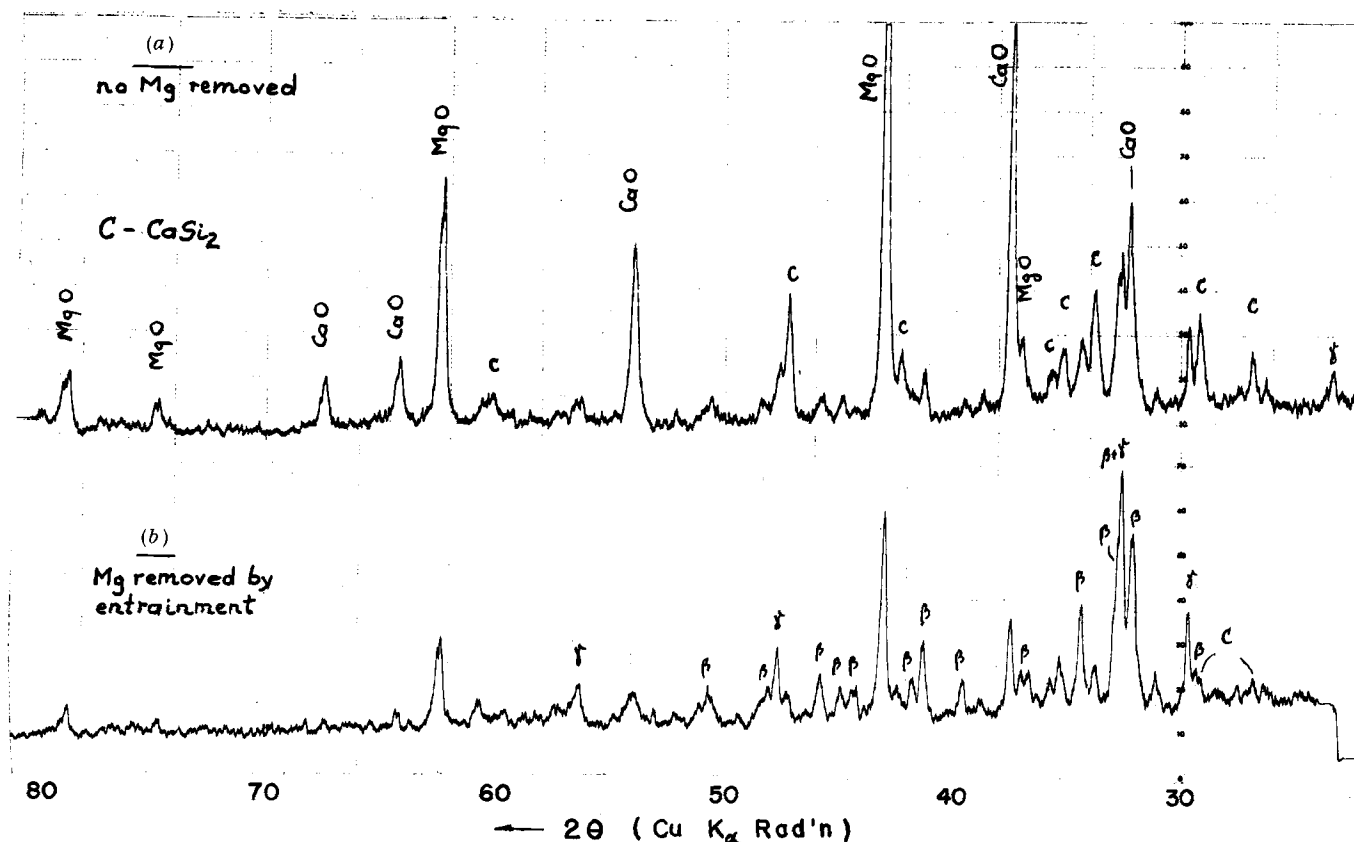


Fig. 1—X-ray diffractograms of a 2.2/1 calcined-dolomite/silicon mixture reacted at 1150°C. (a) only Reaction [II] took place; (b) some magnesium removed by entrainment in argon via Reaction [VI].

and 745-015, respectively). Calcium oxide was prepared by heating the carbonate at about 900°C for 2 hr followed by 24 hr at 1150°C. The carbonate was from Fischer Scientific analyzing less than 0.01 Mg and alkali-metal oxides and 0.01 sulfates. Reaction mixtures of oxides were prepared, after prior mixing, by pressing into $\frac{3}{4}$ in. diam by about $\frac{3}{16}$ in. pellets. Solid $\text{Ca}_3\text{Mg}(\text{SiO}_4)_2$ was prepared by heating to 1150°C a stoichiometric mixture of oxides in an argon atmosphere containing a low partial pressure of magnesium. Under such conditions (as compared to air) the reaction rate was found to be substantially enhanced. The charge for the determination of p'_{Ca} (Reaction [V]) was prepared by mixing the calcined carbonate with -100 mesh silicon and pressing into $\frac{3}{4}$ in. pellets which were subsequently broken down into about $\frac{3}{16}$ in. pieces. Prior to Knudsen cell measurements the volatile impurities were removed by streaming argon through a bed of the CaO + Si fragments in the transportation apparatus, for 3 days followed by another 2 days at 1150°C.

b) Apparatus and Procedure

The transportation apparatus which was used for the measurement of p''_{Mg} and p''_{Ca} as well as the isopiestic method (see results) for the study of oxide reactions and alloy composition are described elsewhere.¹⁷ The calcium pressure for Reaction [V] was measured by the Knudsen apparatus described in Ref. 10.

II) RESULTS

a) Nature of the Silicate Formed by Reactions [II] and [VI]

If Reaction [VI] is carried out in a transportation apparatus^{5,17} presumably nearly reversible conditions exist. Considering a fresh charge of effectively infinite length, magnesium evolves principally near the carrier gas entrance, because as the gas passes through the charge it becomes progressively more saturated until, eventually, no further magnesium evolves. The residue at the exit will still contain all of the magnesium originally charged. Reaction [II], on the other hand, will have been free to occur at any point in the charge. Accordingly the silicate found at the exit will be a product of Reaction [II] while at the entrance it will be both [II] and [VI].

Figs. 1(a) and (b) shows two X-ray diffractograms of residues sampled at a point near the exit (a) and near the entrance (b). To be noted in Fig. 1(a) are the peaks of β - Ca_2SiO_4 but also weaker peaks of γ - Ca_2SiO_4 as well as CaSi_2 . Fig. 1(b) shows much stronger peaks of β - and γ - Ca_2SiO_4 as the only silicates.* (The in-

*The presence of both β - and γ - Ca_2SiO_4 indicates that the allotropic transformation [18] from the high-temperature β - Ca_2SiO_4 to the low-temperature γ -form has taken place only for a part of the silicate. Absence of the transformation appears to be common both in the case of the silicothermic process residue as well as the silicate prepared from the oxides. While no explanation is offered here it is known that many factors can affect this transformation.

tensity of the MgO, CaO and CaSi_2 peaks, has decreased, consistent with extensive reaction via [VI]. Fig. 1 is representative of more than ten other diffractograms. The characteristic peaks of $\text{Ca}_3\text{Mg}(\text{SiO}_4)_2$ were not observed in any of these. Diffractograms of residues of Reaction [V] show Ca_2SiO_4 .

Table I. Products of Reacting Lime and Silica in Various Reducing Atmospheres

5 to 8 hr at 1150°C unless otherwise noted		
Atmosphere	Test Charge	Product*
1) Air	MgO + 3 CaO + 2 SiO ₂ CaO + SiO ₂	-Ca ₂ SiO ₄ + MgO + CaO -Ca ₂ SiO ₄ + SiO ₂ some CaSiO ₃
2) MgO + Si	CaO + SiO ₂ MgO + 3 CaO + 2 SiO ₂	α -CaSiO ₃ Ca ₃ Mg(SiO ₄) ₂
3) MgO + CaO + Si	a) 3 CaO + SiO ₂ CaO + SiO ₂ 2 CaO + SiO ₂ 2 CaO + MgO + SiO ₂	-Ca ₂ SiO ₄ + CaO -Ca ₂ SiO ₄ + Si -C ₁₂ SiO ₄ -Ca ₂ SiO ₄ + MgO
	b) Merwinite† α -CaSiO ₃ †	-Ca ₂ SiO ₄ +MgO + CaSi ₂ + Si -Ca ₂ SiO ₄ +CaSi ₂ + Si
	c) Temp. 1300°C 3 CaO + SiO ₂	Ca ₃ SiO ₅
4) MgO + CaO + Al	3 CaO + SiO ₂	CaO + MgO + CaSi

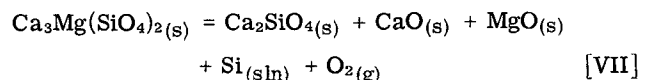
*Identified by X-ray diffraction.

†Prepared prior to charging.

Table II. Magnesium Pressures and Corresponding Oxygen Pressures Produced by Metallothermic Reduction of Dolomite and of MgO

Temperature = 1150°C		
Reaction	P_{Mg} , torr	P_{O_2} , atm
MgO + Si ⁶	0.94	3.5×10^{-27}
MgO + CaO + Si ⁵	18.6	8.4×10^{-30}
MgO + CaO + Al ¹⁷	212	6.7×10^{-32}

The nature of the silicate was further investigated by the following procedure. Mixtures of powdered oxides CaO, MgO and SiO₂ were pressed into tablets and heated in atmospheres containing magnesium vapor. These atmospheres were produced by reacting magnesium oxide and/or calcined dolomite with silicon and/or aluminum in a closed system with argon as the ambient inert gas. The results are summarized in Table I. The magnesium pressures and the corresponding oxygen pressures produced by the reaction mixtures are given in Table II. The CaO/SiO₂ ratios of 3/1 and 1/1 (see Table I, Column 2) were chosen to provide an excess of either of the oxides with respect to Ca₂SiO₄. Only the latter is seen to be stable under conditions of Reaction [VI]. Row 3b shows that both Ca₃Mg(SiO₄)₂ and α -CaSiO₃ decompose to form Ca₂SiO₄, *i.e.*



Both methods, therefore, show that Ca₂SiO₄ is the solid product of Reactions [V] and [VI] under near equilibrium conditions. (Note also that Ca₂SiO₄ decomposes in the more highly reducing atmosphere offered by system CaO + MgO + Al; see Row 4.

It is noteworthy that Ca₃Mg(SiO₄)₂ does form at low magnesium pressures, Row 2. The fact that it occurs in residues when Reaction [VI] is carried out in vacuum¹⁵ presumably means that magnesium pressures are considerably below equilibrium inside the bri-

quettes under these conditions. This latter observation appears to be significant in attempts to establish the reaction mechanism, a subject beyond the scope of this paper.

b) Magnesium Content of the Liquid Alloy in the System (")

It was pointed out earlier that in the event that the magnesium content of this alloy were only a few percent, the activity of silicon a''_{Si} would not be significantly different from a'_{Si} . The magnesium content was measured by an analogous method to that just described. Ca-Si alloys were allowed to reach equilibrium with magnesium vapor produced by Reaction [VI]; they were held in magnesium oxide crucibles in a capsule containing briquetted dolomite/silicon mixtures, with argon as the inert gas at 1 atm pressure. The temperature was 1150°C and exposure times ranged from 48 to 72 hr. At the end of the heating period the capsule was quenched and the alloy analyzed for magnesium. The alloys used were prepared¹⁰ previously for the determination of calcium vapor pressure and had compositions on both sides of $x_{Si} = 0.68$ (see below). Magnesium could enter the alloy by reduction of the crucible or from the vapor phase, while calcium content adjustments had to proceed through the vapor.

The magnesium content, after equilibration, was found to be 2.4 ± 0.3 pct based on five experiments. This low concentration is consistent with the much weaker interactions between magnesium and silicon, as compared to calcium and silicon (see first footnote, p. 980). It seemed, therefore, justified to assume that the activity a''_{Si} was the same as a'_{Si} .

c) Thermodynamics of the System (')

The calcium pressures over Reaction [V], $4CaO_{(s)} + Si_{(sln)} = 2Ca_{(g)} + Ca_2SiO_4_{(s)}$ have been measured at temperatures in the range 1035° to 1230°C using the Knudsen effusion apparatus described in Ref. 10. The briquetted mixture of calcium oxide and silicon was placed directly into the titanium Knudsen cell. Results are in Fig. 2. The equation of the straight line (not shown in Fig. 2) representing the experimental points is

$$\log p'_{Ca} = -\frac{14,160}{T} + 8.441 \quad [8]$$

where p'_{Ca} is in torr and T in degrees K.

It is not possible to determine the composition of the alloy formed by Reaction [II] by direct sampling and analysis. The alloy spreads very effectively over the surface of the CaO and MgO particles (which, moreover, are intimately associated with the orthosilicate produced by [II]) and it is not possible to isolate it from these oxides. An alternate approach is provided by matching the calcium vapor pressure data obtained on a series of Ca-Si alloys, plotted against composition, with the data for p'_{Ca} . Results from Ref. 10 on the Ca-Si alloys are shown in Fig. 3. The measured values of p'_{Ca} (calculated from Eq. [8] at the temperatures shown) are shown as arrows. Their intersections with the curves give the alloy composition which exists at equilibrium. It can be seen that these intersections occur at the same alloy composition, $x'_{Si} = 0.68$ within

the accuracy of this method. No explanation is offered for the apparently fortuitous temperature independence.

The silicon activity for the composition $x'_{Si} = 0.68$ can, in turn, be read off from Fig. 5 of Ref. 10. It is shown plotted as a function of temperature in Fig. 4.

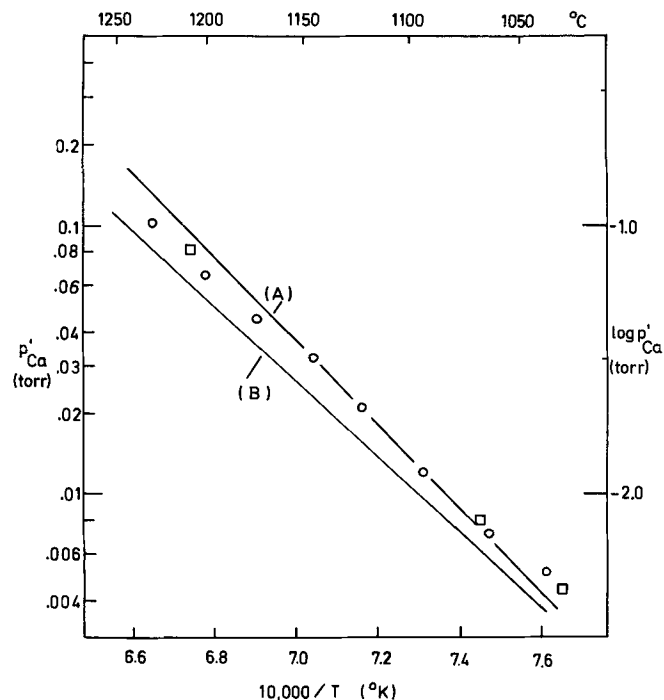


Fig. 2—Calcium vapor pressures over Reaction [V] (or [VI]). Points are experimental measurements; curve (A) is calculated from $p'_{Ca} = a'_{Si}{}^{1/2} \exp(-\Delta G^0_V/2RT)$ assuming $a'_{Si} = 1$; (B) is calculated using experimental a'_{Si} data.

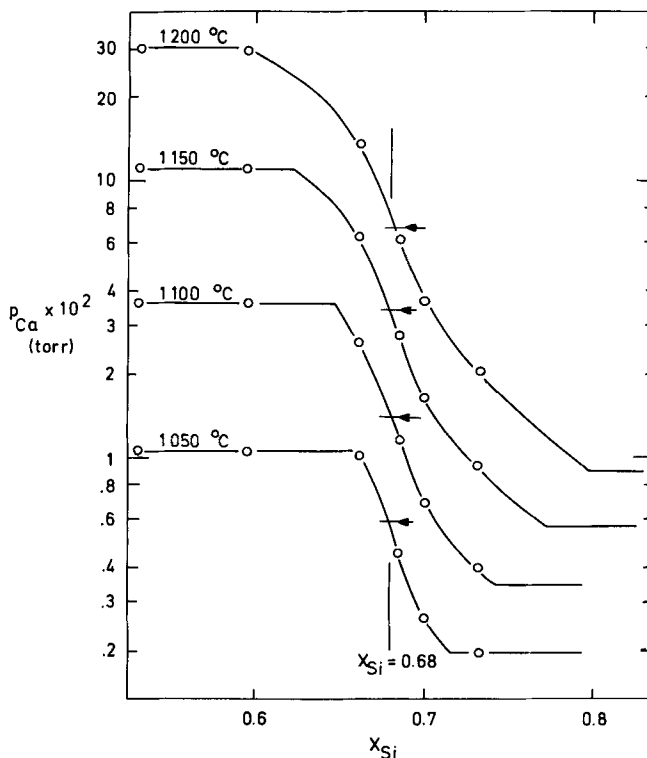


Fig. 3—Calcium pressures over Ca-Si alloys vs alloy composition. Horizontal lines with arrows represent calcium pressures for Reaction [V] at the corresponding temperatures.

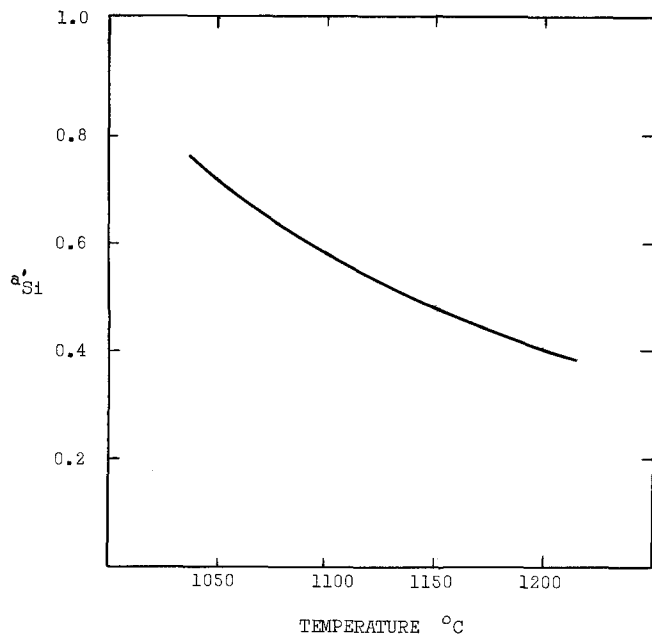


Fig. 4—Silicon activity in the alloy $x_{Si} = 0.68$ vs temperature.

The experimental calcium pressures are compared in Fig. 2 with pressures calculated using Eq. [5]. Line (A) is the calculated p'_{Ca} assuming $a_{Si} = 1$. Line (B) was obtained by using the experimental activities a'_{Si} , as given in Fig. 4. The standard free energies of formation of CaO and Ca_2SiO_4 used to calculate ΔG_i^0 , were taken from the tabulated data of Elliott and Gleiser¹⁹ modified in accordance with the new value of the heat of formation of SiO_2 .²⁰ The free energy data for vaporization of calcium is that of Hultgren *et al.*²¹

d) Thermodynamics of the System (")

The magnesium pressures produced by the reaction $2CaO_{(s)} + 2MgO_{(s)} + Si_{(sln)} = 2Mg_{(g)} + Ca_2SiO_{4(s)}$ were determined in the temperature range 1030° to 1175°C using the transportation apparatus. The pressures over the same reaction were measured previously by Pidgeon and King⁵ and also by Ellingsaeter and Rosenqvist.²² After the present study was completed unpublished data from the Norwegian Institute of Technology also become available in manuscript form.²³ The experimental points from these three sources have been plotted in Fig. 5 together with the present results, which also extend the temperature range to lower values.

Line (A) in Fig. 5 was calculated using Eq. [6], the above-mentioned free energy data and $a''_{Si} = 1$. Line (B) was also calculated using Eq. [6], except that now the experimental values of a''_{Si} , Fig. 4, were substituted.

In correlating the systems (') and (") the experimentally determined calcium pressure p'_{Ca} may be compared with p''_{Ca} . The latter can be either directly measured or calculated using Eq. [7], the experimentally measured magnesium pressure and the standard free energy, ΔG_V^0 , obtainable from data for MgO, CaO and vaporization of calcium metal. Note that such a calculation does not involve the silicate. Experimental measurement of p''_{Ca} is possible by analyzing the condensate from the transportation experiments for

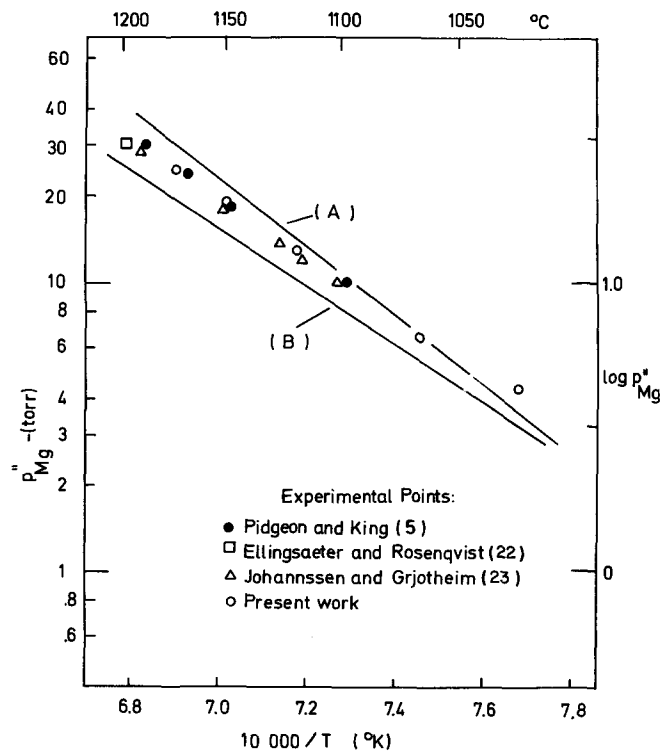


Fig. 5—Magnesium vapor pressures over Reaction [VI]. Experimental points as noted; curve (A) calculated from $p''_{Mg} = a'_{Si}{}^{1/2} \exp -\Delta G_V^0/2RT$ assuming $a'_{Si} = 1$; (B) calculated from the same equation but using experimental a'_{Si} data.

Table III. Comparison of Calcium Pressures over Systems (') and (")

Temperature 1150°C	
Source	p_{Ca} , torr
p'_{Ca} - experimental (from Figure 2)	3.2×10^{-2}
p'_{Ca} - from equation [7] and $p''_{Mg} = 19.1$ torr	3.3×10^{-2}
p''_{Ca} - experimental	2.0×10^{-2}

calcium. Six condensates obtained at 1150°C yielded 0.173 ± 0.020 wt pct Ca or a calcium pressure of 0.020 torr. Table III lists three p_{Ca} values from the different sources at 1150°C. There is very satisfactory agreement between p'_{Ca} and the calculated p''_{Ca} . The experimental p''_{Ca} agrees less satisfactorily with the others which, perhaps, is to be accounted for by the very small amounts of calcium collected in the transportation experiments.*

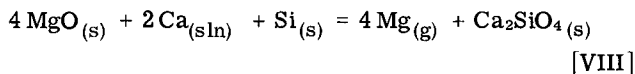
*Both plant practice as well as vacuum reaction in the laboratory yield condensates containing some calcium. The reason why earlier equilibrium measurements⁵ did not contain the element seems to be the geometry of the apparatus. Presently the condenser is connected directly to the charge container while no connecting tube was used in the previous experiments. It is likely that calcium, which condenses at appreciably higher temperatures than magnesium, was not collected, but condensed in the furnace tube.

III) DISCUSSION

The calcium pressures p'_{Ca} and magnesium pressures p''_{Mg} have been obtained by widely different methods. Moreover, the p''_{Mg} values may be considered well established. They have now been measured in four separate investigations and several additional unpublished ones.²⁴ The variation among these inves-

tigations is less than 8 pct. Since the thermodynamic data for MgO and CaO appear very reliable,²⁵ the agreement of the pressures in Table III provides a strong argument for the correctness of the analysis of the system given earlier and may, moreover, be considered a calibration of the Knudsen apparatus for the measurements of the alloy vapor pressures.

Another independent measurement to substantiate the validity and internal consistency of the results is obtained by the consideration of a mixture of MgO + CaO + Si with an excess of silicon with respect to Reaction [II], so that all CaO is consumed and solid silicon is present at equilibrium. The equilibrium may then be represented by



The composition of the alloy is fixed and must be that corresponding to the liquidus composition on the binary calcium-silicon diagram, since silicon is present as a solid (the dissolved magnesium is neglected). The equilibrium constant may then be written as equal to

$$K = p_{\text{Mg}}^* 4 / a_{\text{Ca}}^* 2 \quad \text{[9]}$$

and

$$a_{\text{Ca}}^* = p_{\text{Mg}}^* 2 \exp^{-\Delta G_{\text{VIII}}^0 / 2RT} \quad \text{[10]}$$

where the superscript (*) is to denote the equilibrium described by Reaction [VIII].

That the system indeed behaves in this way is confirmed by X-ray diffraction analysis of residues of a 1/1 dolomite-silicon mixture reacted in the transportation apparatus, Fig. 6. The ratio 1/1 still contains an

excess of CaO and lines for the latter are still present when no magnesium is removed, Fig. 6(a). Furthermore, there are no silicon lines but strong lines for CaSi₂.

When the reaction is made to proceed by removal of magnesium (see Section IIa), twice as much CaO as silicon is consumed. This leads, first, to disappearance of CaO and, thereafter, to concentration of silicon and depletion of calcium in the alloy. When the liquidus composition is reached, solid silicon precipitates. Fig. 6(b) shows the latter condition of the initially 1:1 CaO/Si mixture; there are no CaO peaks, weak CaSi₂ peaks and strong Si peaks while the γ -Ca₂SiO₄ peaks have become correspondingly stronger than in Fig. 6(a). When the initial ratio is below about 0.5 the condition shown in Fig. 6(b) is reached directly.

Six transportation measurements at 1150°C using three mixtures with CaO/Si ratio below 0.5 have yielded a magnesium pressure of 9.4 ± 0.15 torr. Substituting this value and the thermodynamic data already referred to earlier (with an adjustment of 2000 cal to be discussed below) into Eq. [10], $a_{\text{Ca}}^* = 8.2 \times 10^{-5}$ is calculated. This is in very good agreement with 8.7×10^{-5} in Table II of Ref. 10, obtained directly by measurement of the calcium pressure over the liquidus-composition alloy at 1150°C.

Both calculated lines in Figs. 2 and 5 agree with the experimental points within experimental error of the free energies of formation of the compounds involved in calculating ΔG_V^0 and ΔG_{VI}^0 . It is, moreover, possible to draw additional conclusions based on the following similarities between Figs. 2 and 5: First, the slopes of lines (A) differ from the slopes of the lines which can be drawn through the experimental points in both fig-

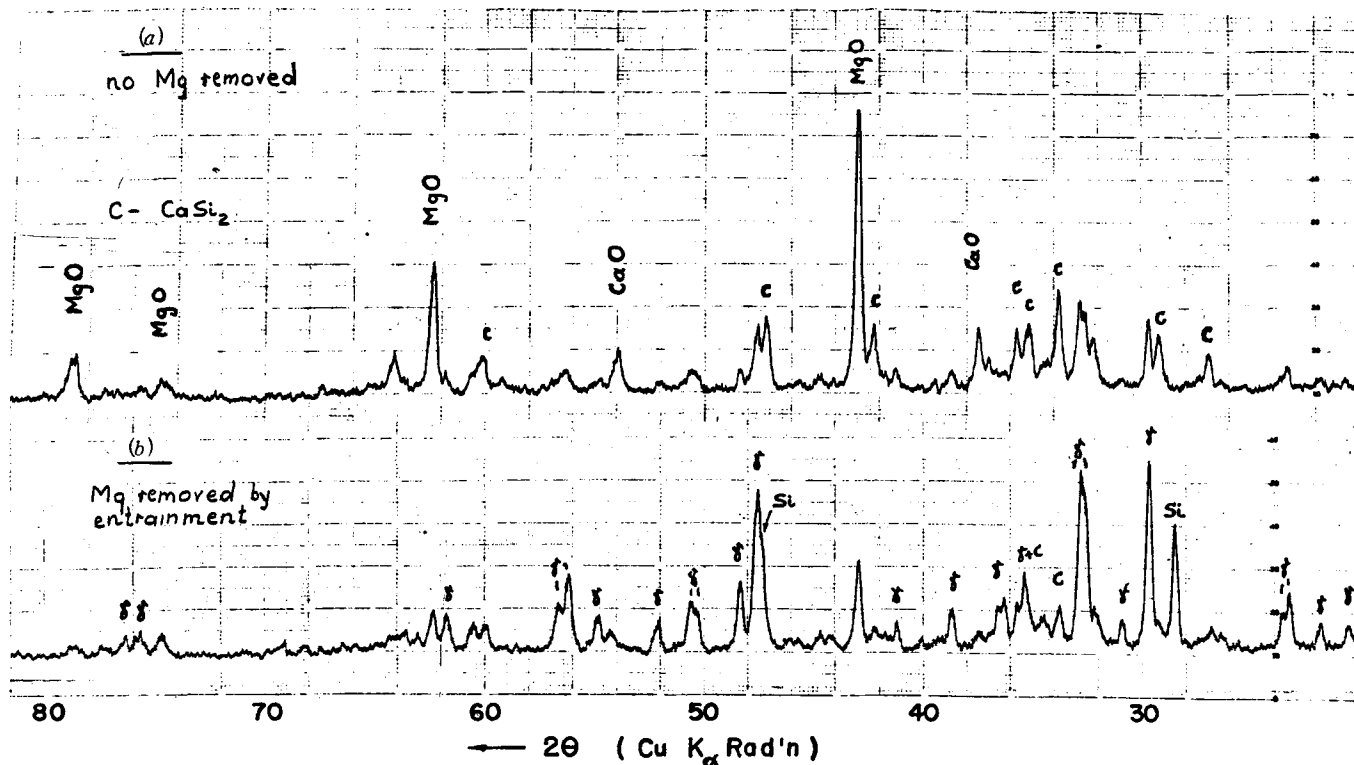


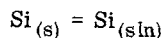
Fig. 6—X-ray diffractogram of the residue of a 1/1 calcined-dolomite/silicon mixture reacted at 1150°C. (a) no magnesium evolution, only Reaction [III] took place; (b) magnesium removed by entrainment into argon. Note absence of CaO and appearance of silicon lines.

ures. Second, lines (B) in both figures have the same slope as the lines through the points, but lie below the latter by about 30 pct. This difference is equivalent to approximately 2000 cal in the free energies ΔG_V^0 and ΔG_{VI}^0 .

The calculated lines (A) and (B) in Fig. 5 represent Reactions [I] and [VI]. Their slopes are related²⁶ to the heats of these reactions by the relationship:

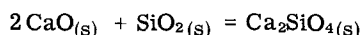
$$\frac{d \log p}{d 1/T} = - \frac{\Delta H}{4.6R}$$

The difference between the slopes represents the difference between the heats of the two reactions, *i. e.* the heat-effect of the reaction



The same arguments apply to Fig. 2. The fact that a 'correction' by the silicon activity brings the slope of (A) into agreement with the slope of (B) and, thus, with the experimental points, constitutes evidence that the equilibrium reactions, [V] and [VI], have been correctly written. This is also independent evidence that the silicon activities measured presently are reasonably accurate.

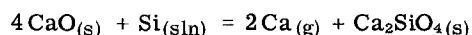
Regarding the disparity between lines (B) and the experimental points in Figs. 2 and 5 the following is to be noted i) the magnesium pressures p_{Mg}'' used in the calculations appear to be accurate to better than 10 pct; ii) the precision with which p_{Ca}'' was measured was 4 pct¹⁰ and the agreement between the two independent methods of obtaining p_{Ca}' and p_{Ca}'' (Table III) indicated absence of significant systematic errors; iii) lines (B) differ from the points by the same amount in both Figs. 2 and 5. These facts taken together suggest that an error is associated with the free energy of formation of Ca_2SiO_4 . The latter free energy has been determined²⁷ to be 900 cal per mole more negative than the calorimetric¹⁹ value at 700°C with the help of an electrochemical method using a solid electrolyte. The ability of the latter method to yield accurate results for oxide free energies has recently been demonstrated again.²⁸ Given also the present evidence, it appears that the standard free energy of the reaction



should be revised by about -1000 cal at 1400°K, to $\Delta G^0 = -33,400$ cal per mole Ca_2SiO_4 .

IV) CONCLUSIONS

1) The equilibrium vapor pressure of calcium for the reaction



(in torr) follows the equation

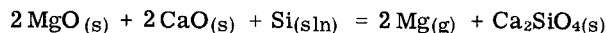
$$\log p_{\text{Ca}} = - \frac{14,160}{T} + 8.441$$

over the temperature range 1290° to 1500°K.

2) The liquid Ca-Si alloy in equilibrium with the reaction given in 1) contains 68 at. pct Si; its composition is constant in the temperature range 1050° to 1200°C

and the activity of silicon in the alloy (based on solid silicon as the standard state) varies from 0.71 at 1050°C to 0.40 at 1200°C.

3) The equilibrium between magnesium oxide and silicon in the presence of calcium oxide is represented by



The ternary alloy present at equilibrium contains 2.4 ± 0.3 pct Mg in addition to calcium and silicon; the value of the silicon activity is that given under 2) to a sufficiently close approximation.

4) The magnesium pressures for the reaction given in 3) have been redetermined and found in excellent agreement with previous workers. A comparison of the experimental calcium and magnesium pressures with those calculated from thermodynamic data shows agreement within experimental error in the free energy data. The calcium pressures in this system follow the equation given under 1).

5) Based on present evidence, a preferred value of the standard free energy of formation of calcium orthosilicate from calcium oxide and silica is -33,400 cal per mole of the silicate at 1400°K.

ACKNOWLEDGMENTS

Support of this work in the form of the University of Toronto Faculty of Applied Science Fellowship to J. R. Wynnycyk is gratefully acknowledged. The authors thank Professor C. Wagner for his helpful comments on the manuscript and Dominion Magnesium Limited for providing the calcined dolomite.

REFERENCES

1. L. M. Pidgeon and W. A. Alexander: *Trans. AIME*, 1944, vol. 159, p. 315; L. M. Pidgeon: *Trans. Can. Inst. Min. Met.*, 1944, vol. 47, p. 16.
2. A. Schneider: *Metall. Erz.*, 1942, vol. 39, p. 272.
3. C. Faure and J. Marchall: *J. Metals*, 1964, vol. 16, p. 721.
4. A. Schneider, J. F. Cordes, H. Kribbe, and H. Runge: *Z. Erzbergbau Metallhuettenw.*, 1959, vol. 12, pp. 193, 164, 224.
5. L. M. Pidgeon and J. A. King: *Discussions Faraday Soc.*, 1948, vol. 4, p. 197.
6. A. Schneider and E. Hesse: *Z. Elektrochem.*, 1940, vol. 46, p. 279.
7. J. M. Toguri and L. M. Pidgeon: *Can. J. Chem.*, 1961, vol. 39, p. 540, *Can. J. Chem.*, 1962, vol. 40, p. 1769.
8. H. Kautsky and H. Thiele: *Z. Anorg. Allgem. Chem.*, 1928, vol. 173, p. 121; also L. Woller and W. Schuff, *Z. Anorg. Allgem. Chem.*, 1932, vol. 209, p. 33.
9. J. E. Ricci: *Phase Rule and Heterogeneous Equilibrium*, Dover, New York, 1966.
10. J. R. Wynnycyk and L. M. Pidgeon: *Met. Trans.*, 1971, vol. 2, p. 975.
11. O. Kubaschewski and E. L. Evans: *Metallurgical Thermochemistry*, p. 375, Pergamon, London, 1958.
12. J. Chipman: *Pure Appl. Chem.*, 1962, vol. 5, p. 361.
13. M. Hansen: *Constitution of Binary Alloys*, 2nd ed., McGraw-Hill, New York, 1958.
14. J. M. Eldridge, E. Miller, and K. L. Komarek: *Trans. TMS-AIME*, 1967, vol. 239, p. 775.
15. W. T. Hughes, C. E. Ransley, and E. F. Emley: in *Advances in Extractive Metallurgy, Inst. Min. Met.*, London, 1968.
16. M. F. Goudge: *Limestones of Canada*, Queen's Printer, Ottawa.
17. J. R. Wynnycyk and L. M. Pidgeon: *Can. Met. Quart.*, 1971, vol. 9.
18. W. Eitel: *Physical Chemistry of the Silicates*, p. 260, McGraw-Hill, New York, 1953.
19. J. F. Elliott and M. Gleiser: *Thermochemistry of Steelmaking*, vol. I, 1960, and vol. II, 1962, Addison Wesley, Reading, Mass.
20. S. S. Wise, J. L. Margrave, H. M. Fedder, and W. M. Hubbard: *J. Phys. Chem.*, 1962, vol. 66, p. 381, W. D. Good: *J. Phys. Chem.*, 1962, vol. 66, p. 480.

21. R. Hultgren, R. L. Orr, P. B. Anderson, and K. K. Kelley: *Selected Values of Thermodynamic Properties of Metals and Alloys*, John Wiley & Sons, New York, 1963.
22. B. Ellingsaeter and T. Rosenqvist: *J. Metals*, 1956, vol. 8, p. 1111.
23. K. Johanssen: Thesis, Inst. Inorg. Chem., Norwegian Inst. of Technology, Trondheim, 1967.
24. W. J. Thoburn: M. A. Sci. Thesis, University of Toronto, 1962. S. Wilkening: M. A. Sci. Thesis, University of Toronto, 1960.
25. E. J. Huber and C. E. Holley: *J. Phys. Chem.*, 1956, vol. 60, p. 498; L. Brewer: *Chem. Rev.*, 1953, vol. 52, p. 1.
26. L. S. Darken and R. W. Gurry: *Physical Chemistry of Metals*, p. 260, McGraw-Hill, New York, 1953.
27. R. Benz and C. Wagner: *J. Phys. Chem.*, 1961, vol. 65, p. 1308.
28. G. G. Charette and S. N. Flengas: *J. Electrochem. Soc.*, 1968, vol. 115, p. 796.