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The Si–C–O system

Part II *Isobaric evolution of the system*

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In a reactor where the pressure is held constant by expulsion of the gas produced by the reactions, the evolution of the Si–C–O system with temperature occurs in several steps, although the main transformations happen at the univariant points shown in a PRT diagram (pressure, P_{CO}/P_{SiO} ratio, temperature). The path followed by the system depends on the ratio of reactants initially present in the reactor. When the gas is expelled, the theoretical SiC yield from a $C + SiO_2$ mixture is close to 100%. The Si yield remains low, although it increases rapidly with the imposed pressure. The gas must be recirculated to obtain a higher yield.

1. Introduction

In Part I [1], a PRT diagram (Pressure, P_{CO}/P_{SiO} Ratio, Temperature) of the Si–C–O system was drawn using a unique and precise source of data [2]. This diagram (Fig. 1) shows the curves of equilibria between the components of the system at various pressures.

The purpose of this paper is to describe the evolution of the Si–C–O system with temperature when the equilibria between phases are achieved at constant pressure in an ideal reactor (i.e. where P and T are homogeneous) starting from a mixture of SiO_2 and C. It will be shown that the transformations occur almost wholly at the univariant points. A mass balance allows the determination of the path followed by the system and the calculation of the amount of each component in the reactor at a given pressure and temperature.

2. Definition of the system

Different types of complexes (i.e. sets of components) can coexist in a domain of a PRT diagram. (i) the inert bivariant complexes: their transformation is impossible whatever the conditions of temperature or pressure may be, C, SiC, Si, SiO_2, C + SiC and SiC + Si; (ii) the bivariant complexes formed by condensed phases which can react with each other to give a gaseous phase, $C + SiO_2$, $SiC + SiO_2$, $Si + SiO_2$, $C + SiC + SiO_2$ and $SiC + SiO_2 + Si$, and (iii) the evolutive complexes formed by the previous components and a gaseous phase (SiO + CO), which can be univariant, bivariant or trivariant.

In a closed system (n_C, n_{Si} and n_O – the moles number of C, Si and O – are constant), the reactions are possible only between transformable complexes of different types, or, in the case of the evolutive complexes, between complexes having different variances. Fig. 2 shows the various possibilities of evolution from one complex to another; these possibilities depend on the pressure, the temperature and the atomic fraction of the components in the system.

Now consider a reactor containing the condensed transformable reactants and, initially, an inert gas. The pressure is held constant by means of a regulating valve which allows gas evacuation as soon as the pressure reaches a preset pressure, P^*. The number of gas moles inside the reactor will be considered as negligible compared to the number of moles, n_i, of each component i, that is:

$$n_i \gg P^* V / R_G T \quad (1)$$

where V and R_G are the volume of the reactor and the perfect gas constant respectively. The reactor is heated so that the temperature is homogeneous.

3. Evolution of the system with temperature

Under heating, the initial complexes evolve in several steps to give the products shown in Fig. 3 at high temperatures.

3.1. Step 1

As long as inert gas remains in the reactor, the pressure, $\pi = P_{CO} + P_{SiO}$, of the gas produced by the reactions is lower than the imposed pressure, P^*. The ratio

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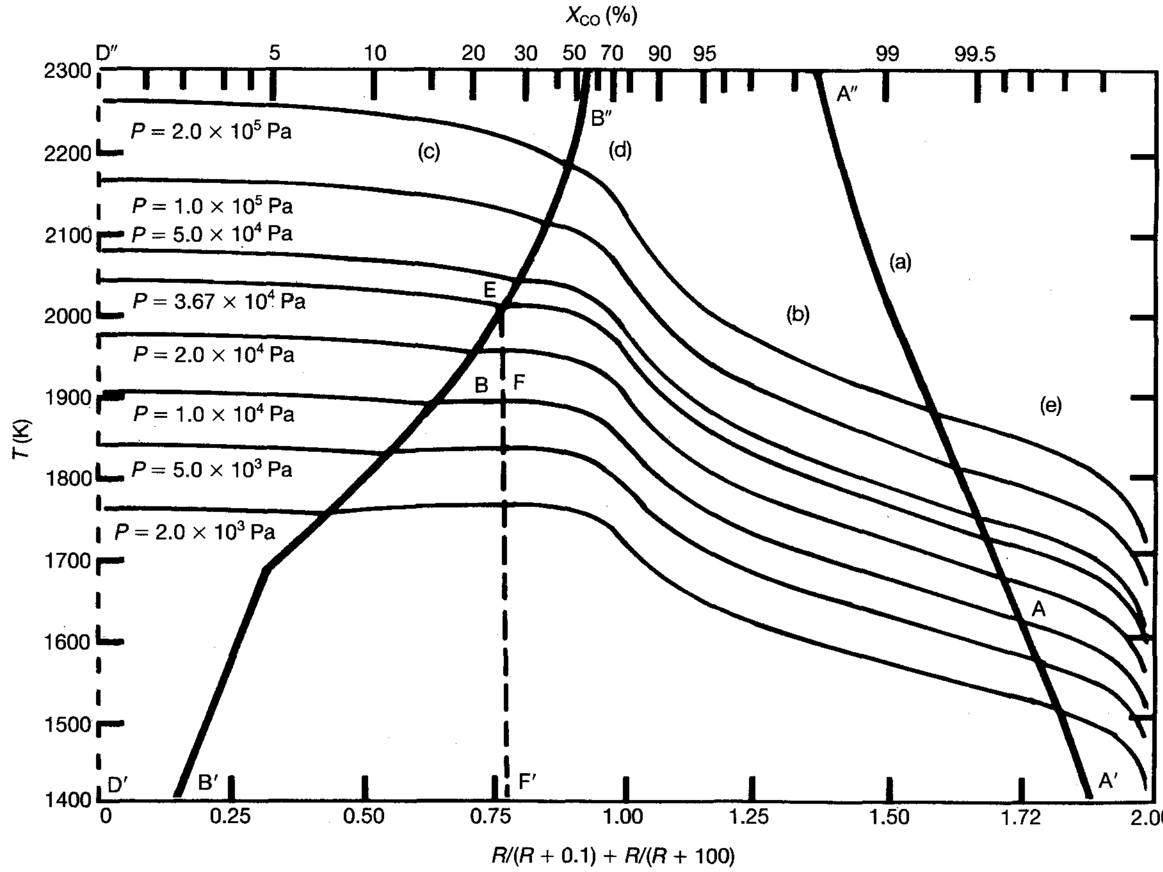

Figure 1 PRT diagram (pressure, P_{CO}/P_{SiO} ratio, temperature) showing the locus of the univariant points with: (—) four phases and (- - -) three phases; and (—) isobaric curves. For reactions: (a) $2C + SiO \rightleftarrows SiC + CO$, (b) $SiC + 2SiO_2 \rightleftarrows 3SiO + CO$, (c) $2SiO \rightleftarrows Si + SiO_2$, (d) $SiC + SiO \rightleftarrows 2Si + CO$, and (e) $C + SiO_2 \rightleftarrows SiO + CO$.

$R = P_{CO}/P_{SiO}$ evolves rapidly until reaching a value given by a curve (a dashed line in Fig. 3) corresponding to the locus of the univariant points A, B, D or F (Fig. 1) [1] according to the initial complex: curve AA* if the initial complex is $C + SiO_2$ or $C + SiO_2 + SiC$, curve BB* for $SiC + SiO_2 + Si$ (or $SiC + SiO_2$ if $P^* > P_E = 36700$ Pa), curve FF* for $SiC + SiO_2$ if $P^* < P_E$, or curve DD* for $Si + SiO_2$. With a temperature increase, the inert gas is expelled, and the pressure π increases up to P^* at the univariant points A*, B*, D* or F*.

3.2. Step 2

At the univariant points, the gas is at equilibrium with two (in D* or F*) or three (in A* or B*) condensed phases. The gas composition and the corresponding temperature, T_{M^*} ($T_{M^*} = T_{A^*}, T_{B^*}$, T_{D^*} or T_{F^*}), are given by Fig. 1. The temperature can then increase only after total consumption of one condensed phase (or two if the reactants are in a stoichiometric ratio). Thus, above T_{M^*}, the remaining complex is either bivariant (two condensed phases and gas, step 3) or trivariant (no condensed phase or one condensed phase and gas, step 4).

3.3. Step 3

Above T_{A^*}, the remaining condensed phases are either $SiC + C$ or $SiC + SiO_2$ depending on whether C or SiO_2 is initially in excess. Thus, the system evolution is illustrated by the following curves: A*A″ for $SiC + C +$ gas, A*F* for $SiC + SiO_2 +$ gas if $P^* < P_E$, and A*B* for $SiC + SiO_2 +$ gas if $P^* > P_E$.

Above T_{B^*}, the system evolution follows the curves: B*B″ for $Si + SiC +$ gas if $P^* > P_E$, B*F* for $SiO_2 + SiC +$ gas if $P^* < P_E$, and B*D* for $Si + SiO_2 +$ gas if $P^* > P_E$.

3.4. Step 4

After total consumption of one or two condensed reactants above T_{F^*} or T_{D^*} and two condensed reactants above T_{A^*} or T_{B^*}, the system is constituted by a gas and one condensed component (SiC for $T > T_{A^*}$, Si for $T > T_{B^*}$, Si or SiO_2 for $T > T_{D^*}$, SiO_2 or SiC for $T > T_{F^*}$), or by a gas only.

When Si is in excess in B* or D*, or when SiO_2 is in excess in D* or F*, no change in the system is observed above the corresponding temperature, T_{M^*}. In Fig. 3, this corresponds to a vertical line starting from the univariant point and crossing the stability domain of the component located above this point. On the contrary, when SiC is in excess, above A*, the system composition follows the curve A*A″, i.e. the limit of the stability domain of SiC. Above F*, no change in the system composition is observed up to T_E. Then the gas composition is given by EB″; the curve BB″ is the other limit of the stability domain of SiC.

It must be noted that the transformations occurring during steps 1, 3 and 4 are extremely limited, since to a slight transformation of the condensed phases cor-

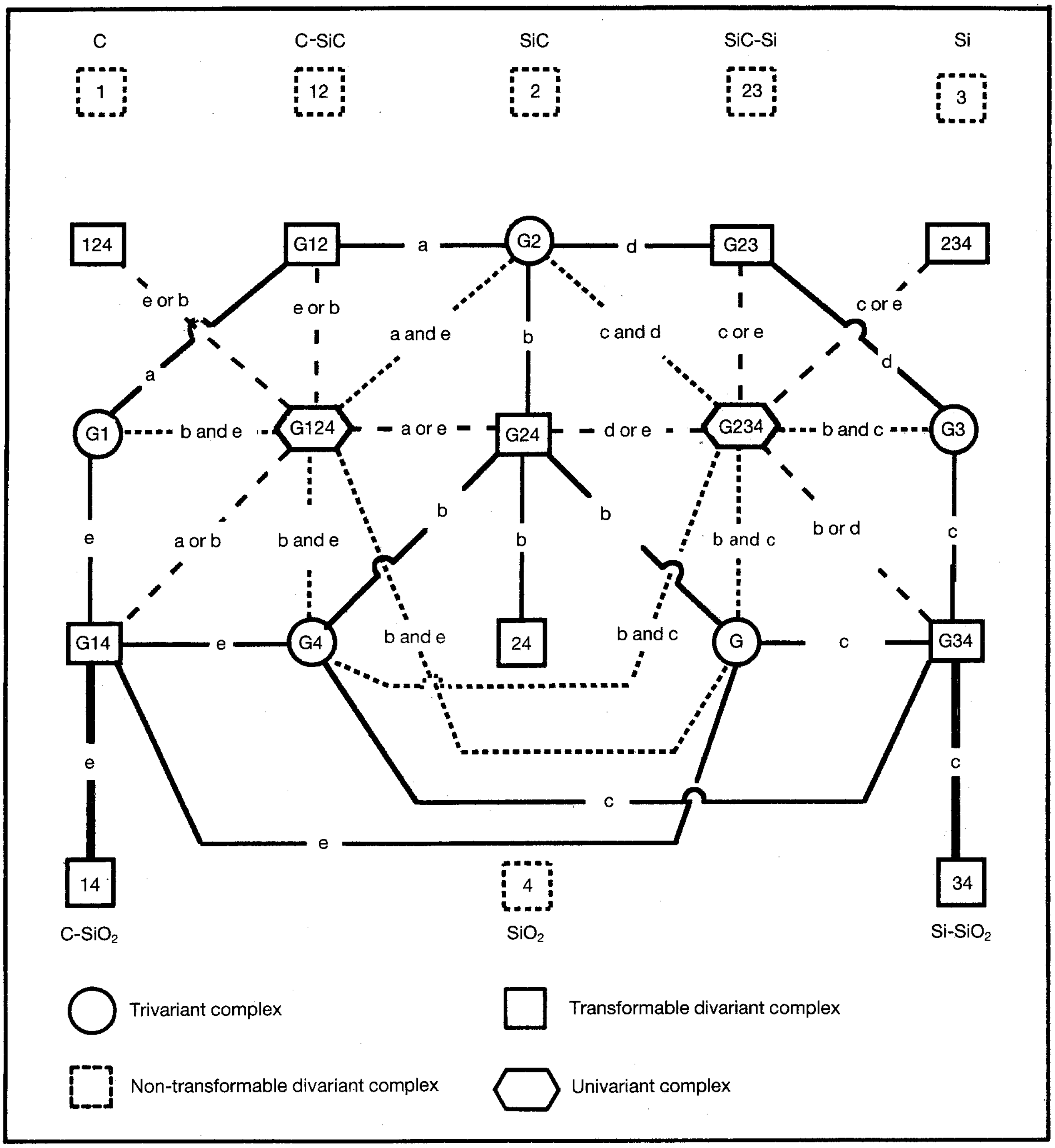

Figure 2 The various complexes and their transformation. G = gas, 1 = C, 2 = SiC, 3 = Si, 4 = SiO_2, (a–e) are the reactions listed in Fig. 1.

responds a great volume of gas: according to Equation 1, the amount of condensed phases does not vary significantly. Thus, the composition of the gas, which is expelled from the reactor in a major part, changes rapidly from one univariant point to another and the transformations arise almost wholly in these points. Therefore, the evolution of the system with temperature depends on the mass balance at the univariant points.

This evolution with temperature is valid only for an isobaric reactor. Previous experimental studies [3, 4] about the carbothermic reduction of SiO_2 under an inert gaseous flux are difficult to interpret because the reacting-gas pressure (of CO, SiO) varies during the experiments.

4. Mass balance

The stoichiometric coefficient, ν_{i,M^*} (i = C, SiC, Si, SiO_2, CO and SiO; M* = A*, B*, D* and F*), of the reactions occurring at a univariant point are deduced from the balance per element (Si, C, O) and from the ratio $R_{M^*} = \nu_{CO,M^*}/\nu_{SiO,M^*}$. For example, at the point A*, these balances are:

$$n^0_{C,A^*} = n_{CO,A^*} + n_{SiC,A^*}$$

$$n^0_{SiO_2,A^*} = n_{SiC,A^*} + n_{SiO,A^*}$$

$$2n^0_{SiO_2,A^*} = n_{CO,A^*} + n_{SiO,A^*}$$

where n^0_{i,M^*} and n_{i,M^*} are, respectively, the number of moles of i (C, SiC, Si, SiO_2, CO or SiO) consumed or produced at the point M* = A*, B*, D* or F*.

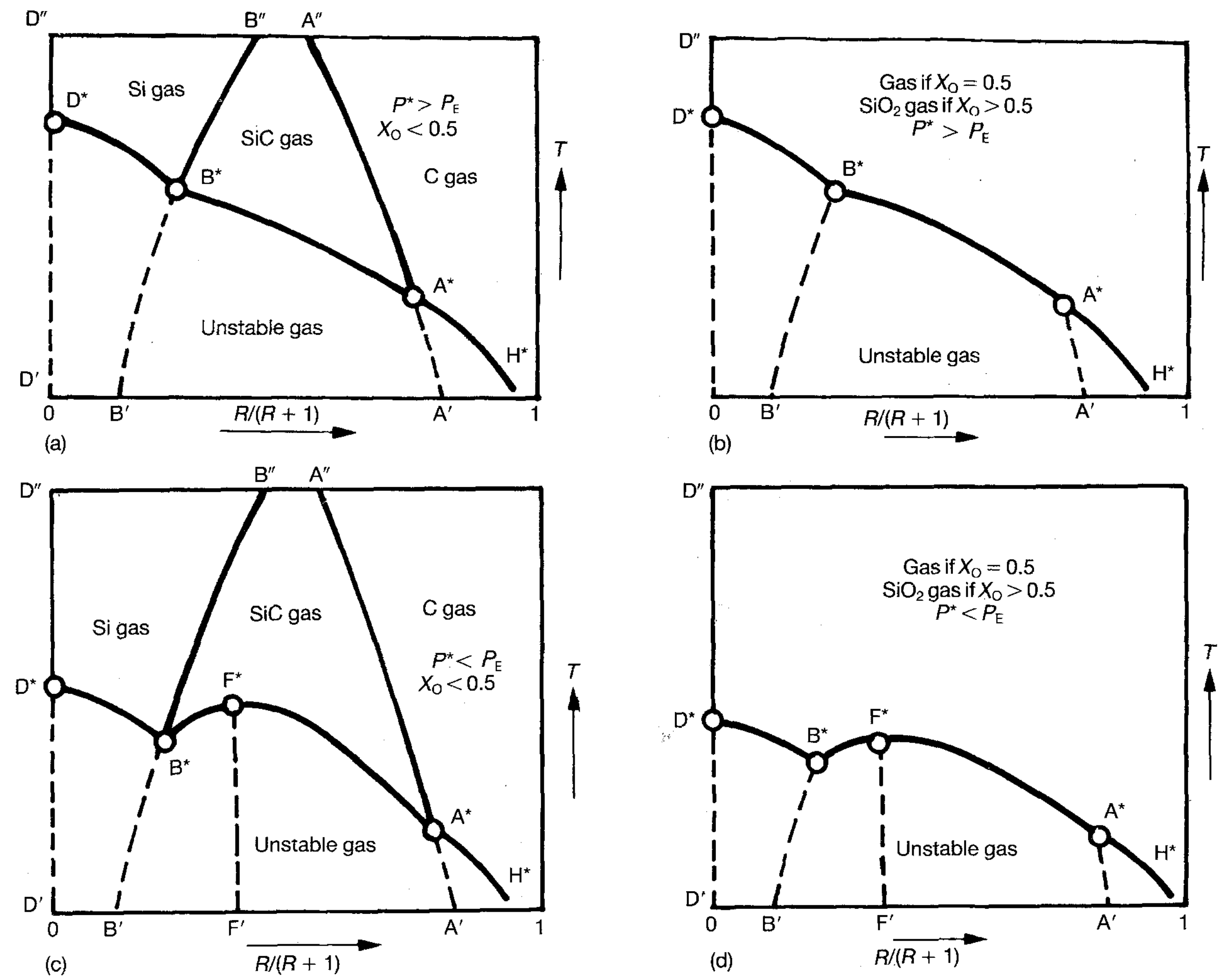

Figure 3 Schematic predominance area isobaric diagrams: (—) divariant curves limiting the predominance domains, (O) univariant points at the considered pressure P^*, (- - -) locus of the univariant points at $P < P^*$. $P_E = 36700$ Pa.

Arbitrarily choosing one of the stoichiometric coefficients (for example, $\nu_{SiO,A^*} = 2$), the reaction in A* can be written as follow:

$$(3R_{A^*} - 1)C + (R_{A^*} + 1)SiO_2 \rightleftarrows (R_{A^*} - 1)SiC + 2R_{A^*}CO + 2SiO \quad (2a)$$

In the same way in B*

$$(R_{B^*} + 1)SiO_2 + 2R_{B^*}SiC \rightleftarrows (3R_{B^*} - 1)Si + 2R_{B^*}CO + 2SiO \quad (2b)$$

in D*

$$Si + SiO_2 \rightleftarrows 2SiO \quad (2c)$$

in F*

$$SiC + 2SiO_2 \rightleftarrows 3SiO + CO \quad (2d)$$

The number of moles of reactants remaining (or of products formed) above M* is equal to:

$$n_{i,M^*} = n^0_{i,M^*} + \nu_{i,M^*}\alpha_{M^*} \quad (3)$$

where ν_{i,M^*} is negative for the reactants and positive for the products and α_{M^*} is the progress of the reactions 2a–2d.

At $T_{M^*}(P^*)$, the transformation is achieved when the minority reactant is completely consumed, i.e. $(n_{i,M^*})_{minor.} = 0$. Let us call α_{i,M^*} the maximal reaction progress (the index i indicates that the progress is limited by the disappearance of i). Using Equation 3:

$$\alpha_{i,M^*} = -n^0_{i,M^*}/\nu_{i,M^*} \quad (4)$$

The component i disappearing in M* has the lowest α_{i,M^*}-value. When the two reactants have the same α_{i,M^*}-value, both disappear.

Above T_{A^*}, C or SiO_2 or both are consumed depending on whether $\alpha_{C,A^*} = n^0_{C,A^*}/(3R_{A^*} - 1)$ is inferior, superior or equal to $\alpha_{SiO_2,A^*} = n^0_{SiO_2,A^*}/(R_{A^*} + 1)$. Thus SiO_2 + SiC, C + SiC or SiC (Fig. 4) will remain.

Above T_{B^*}, with $T_{B^*} > T_E$, there are also three possibilities according to the respective values of $\alpha_{SiC,B^*} = n^0_{SiC,B^*}/2R_{B^*}$ and $\alpha_{SiO_2,B^*} = n^0_{SiO_2,B^*}/(1 + R_{B^*})$. Si, Si + SiC, or Si + SiO_2 will remain.

When $T_{B^*} < T_E$ (i.e. $R_{B^*} \leqslant 1/3$), $\nu_{Si,B^*} = 3R_{B^*} - 1$ is negative and Si must be regarded as a reactant. Thus, in this case, it is not possible to produce Si from a SiC + SiO_2 mixture and the initial Si will be consumed by heating. The remaining complexes are SiC + SiO_2 ($\alpha_{Si,B^*} < \alpha_{SiC,B^*}$ or $\alpha_{Si,B^*} < \alpha_{SiO_2,B^*}$), SiO_2 ($\alpha_{Si,B^*} = \alpha_{SiC,B^*} < \alpha_{SiO_2,B^*}$), SiC ($\alpha_{Si,B^*} = \alpha_{SiO_2,B^*} < \alpha_{SiC,B^*}$) or no condensed phase ($\alpha_{Si,B^*} = \alpha_{SiC,B^*} = \alpha_{SiO_2,B^*}$) in addition to the previous complexes formed in the case $T_{B^*} > T_E$.

Above the congruent points, F* and D*, where the reactants are, respectively, SiC + SiO_2 and Si + SiO_2,

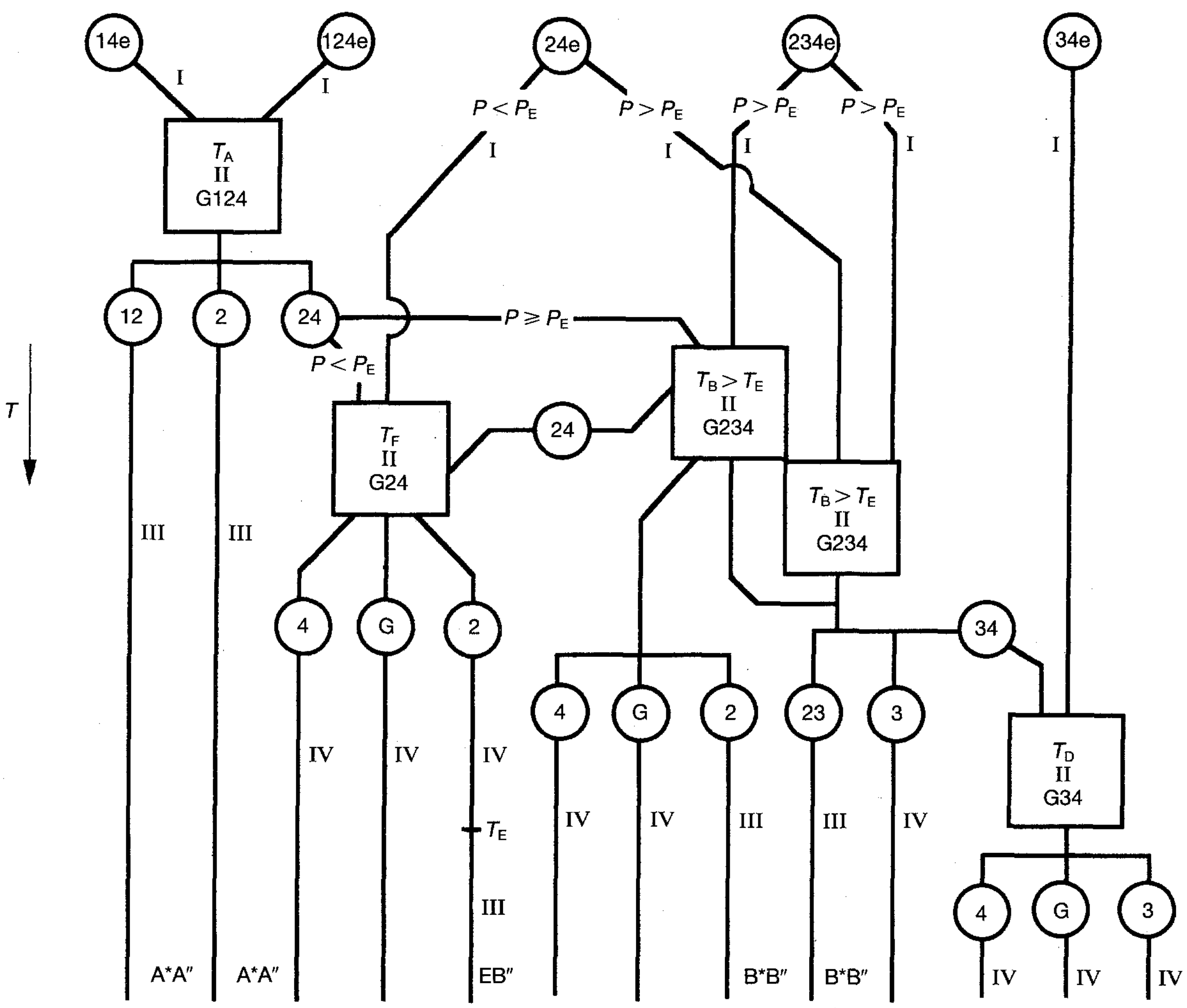

Figure 4 The various possibilities for the temperature evolution of the Si–C–O system in an isobaric reactor with expulsion of the gas. G = gas, 1 = C, 2 = SiC, 3 = Si, 4 = SiO_2 and e = inert gas. I, II, III and IV are steps 1, 2, 3, 4, respectively, (see the text).

only SiO_2 or SiC and Si or SiO_2, remain, or no condensed phases remain, depending on the respective values of α_{i,F^*} or α_{i,D^*}.

The number of moles, n_{j,M^*}, either of reactants in excess or of condensed products formed above the univariant points M* can be deduced from Equation 3

$$n_{j,M^*} = n^0_{j,M^*} + \nu_{j,M^*}\alpha_{i,M^*} \qquad (5)$$

where i represents the minority component ($\alpha_{i,M^*} < \alpha_{j,M^*}$)

All the possibilities of the evolution with temperature for the initial complexes are shown in Fig. 4. It can be seen that above the univariant points, two, one or no condensed phases are obtained, according to the temperature, the pressure and the initial number of moles of reactants. The unique two-phase complexes which cannot be transformed in a one-phase complex under heating are SiC + C above T_{A^*}, and Si + SiC above T_{B^*}, from which C and SiC, respectively, cannot be eliminated.

5. An application, SiC and Si production from C and SiO_2

From a C + SiO_2 initial complex, (14e in Fig. 4) it is possible to obtain SiC or Si by different pathways (Fig. 4) depending on the imposed pressure, the final temperature and the initial number of moles of reactants. Call $\rho = n^0_{SiO_2}/n^0_C$, the ratio of initial numbers of moles of SiO_2 and C, ρ_A and ρ_B, the ratio values which allow SiC to be obtained free from C and SiO_2 at $T > T_A$ and Si to be obtained free from SiC and SiO_2 at $T > T_B$ (Fig. 5). ρ_A can be deduced from reaction 2a:

$$\rho_A = \frac{R_A + 1}{3R_A - 1} \qquad (6)$$

Since R_A is high (Table II), ρ_A is close to 1/3. ρ_B is calculated by taking into account the excess in SiO_2 or SiC (Equation 5) formed by Reaction 2a and the

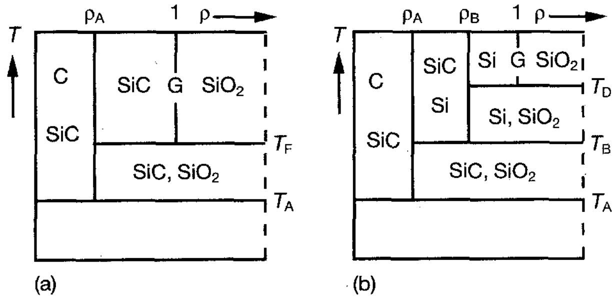

Figure 5 C–SiO_2-complex evolution with temperature as a function of the ratio $\rho = n^0_{SiO_2}/n^0_C$. G = gas alone. (a) $P^* < 0.367 \times 10^5$ Pa, (b) $P^* > 0.367 \times 10^5$ Pa.

stoichiometric coefficients of Reaction 2b:

$$\rho_B = \frac{3R_AR_B + R_A + R_B - 1}{2R_B(3R_A - 1)} \quad (7)$$

ρ_B decreases with P and T (Table I) and is superior to the ratio 1/2 given by the stoichiometry of Reaction 10.

As shown in Fig. 5, at $T > T_A$ and $\rho \neq \rho_A$, SiC will be obtained with an excess of C ($\rho < \rho_A$) or SiO_2($\rho > \rho_A$). The excess of C cannot be eliminated whatever the temperature and pressure may be. On the contrary, for $P < P_E$, the excess of SiO_2 disappears at T_F ($\rho_F = 1$) giving free SiC if $\rho_A < \rho < 1$. Likewise, for $P > P_E$ and $T > T_B$, Si is obtained with an excess of SiC ($\rho < \rho_B$) or SiO_2($\rho > \rho_B$). SiC cannot be eliminated, whereas SiO_2 disappears above T_D if $\rho_B < \rho < 1$.

The maximal SiC yields in comparison with C($\eta_{SiC/C}$) or with SiO_2 (η_{SiC/SiO_2}) are calculated as a function of the pressure using the stoichiometric coefficients of Reaction 2a and those of the reaction

$$SiO_2 + 3C \rightleftarrows SiC + 2CO \quad (8)$$

one obtains

$$\eta_{SiC/SiO_2} = \frac{n_{SiC}}{n^0_{SiO_2}} = \frac{R_A - 1}{R_A + 1} \quad (9a)$$

$$\eta_{SiC/C} = \frac{3n_{SiC}}{n^0_C} = \frac{3(R_A - 1)}{3R_A - 1} \quad (9b)$$

In the same way, the maximal Si yields, $\eta_{Si/C}$ or η_{Si/SiO_2}, obtained at $T = T_B$ with $\rho = \rho_B$, are calculated using Reaction 10 and Reaction 2b:

$$SiO_2 + 2C \rightleftarrows Si + 2CO \quad (10)$$

$$\eta_{Si/SiO_2} = \frac{(3R_B - 1)(R_A - 1)}{3R_AR_B + R_B + R_A - 1} \quad (11a)$$

$$\eta_{Si/C} = \frac{(3R_B - 1)(R_A - 1)}{R_B(3R_A - 1)} \quad (11b)$$

In Table I, temperatures T_A, T_B, ratios ρ_A, ρ_B and various yields are summarized for some pressure values between 2000 Pa and 2×10^5 Pa. Table I also shows the temperatures where the excess of SiO_2 can be consumed by gasification of SiC and SiO_2, at T_F, or Si and SiO_2 at T_D.

Fig. 6 shows the maximal mass flow per SiC mole (at T_A with $\rho = \rho_A$) or per Si mole (at T_B with $\rho = \rho_B$) produced at a constant pressure equal to 10^5 Pa.

Table I shows that the theoretical SiC yields are very high whatever the imposed pressure. However, it must be noted that if $T < T_f$ (SiO_2) the reactions at the point A occur either between solids (C + SiO_2) or through a gaseous phase produced by reactions between solids. These reactions are restricted to the contact areas and even if the solids are initially mixed intimately, the exchanges can occur only at the outset of the reaction. Thus, though thermodynamically possible, the production of SiC from solid reactants will be limited. Bessaguet [3], who attempted to produce SiC wiskers from SiO_2 and C in excess, under a slight flux of argon, obtained good yields in SiC only at a high temperature (1740 °C), i.e. above the fusion temperature of SiO_2.

With regards to the Si production, the yield remains low though it increases with pressure; for example η_{Si/SiO_2} is only equal to 23.5% under 10^5 Pa ($T = 2112$ K). Filsinger and Bourrie [4] have determined the Si yield obtained in a reactor containing SiO_2 and C, and crossed by a gaseous flux. This yield is close to zero since the pressure $P_{SiO} + P_{CO}$ is lower than 36 700 Pa (Table I). Even at atmospheric pressure, SiO_2 is transformed mainly in gaseous SiO (Fig. 6). The number of SiO moles per number of Si moles produced is equal to $(1 - \eta_{Si/SiO_2})/\eta_{Si/SiO_2}$. The total number of gaseous moles, $r = n_{SiO} + n_{CO}$ (the gas ebb rate), expelled from the reactor is:

$$r = \frac{(1 + R_B)(1 - \eta_{Si/SiO_2})}{\eta_{Si/SiO_2}} \quad (12)$$

Table II summarizes the values of R_A, R_B and T_B, under 10^5 Pa, obtained from the literature, and the gas ebb rate, r, deduced from Equations 11a and 12. According to the authors, T_B ranges between 1960 and 2120 K, the yields η_{Si/SiO_2} from 0 to 71% and r from 1.2 to infinity. The discrepency of these results indicates the importance of accuracy in the thermodynamic data.

TABLE I Temperatures of elaboration (respectively, T_A, T_B) and purification (respectively T_F, T_D) of SiC and Si, and optimal ratios ρ_A and ρ_B ($\rho = n^0_{SiO_2}/n^0_C$) and maximal yields in SiC and Si as a function of the imposed pressure (see the text)

P (10^5 Pa)	SiC					Si				
	Elaboration				Purification	Elaboration				Purification
	T_A (K)	ρ_A	$\eta_{SiC/C}$ (%)	η_{SiC/SiO_2} (%)	T_F (K)	T_B (K)	ρ_B	$\eta_{Si/C}$ (%)	η_{Si/SiO_2} (%)	T_D (K)
0.02	1510	0.3342	99.9	99.6	1766	*	*	*	*	*
0.05	1571	0.3345	99.8	99.5	1836	*	*	*	*	*
0.1	1620	0.3348	99.8	99.4	1893	*	*	*	*	*
0.2	1673	0.3349	99.7	99.3	1954	*	*	*	*	*
0.367	1723	0.3353	99.7	99.1	2011	2011	1	0	0	2044
0.5	1749	0.3355	99.7	99.0	*	2042	0.930	13.9	7.5	2080
0.75	1785	0.3356	99.6	98.9	*	2082	0.855	29.1	17.0	2130
1	1811	0.3358	99.6	98.8	*	2112	0.810	38.0	23.5	2167
1.5	1850	0.3362	99.6	98.7	*	2154	0.757	48.6	32.1	2221
2	1878	0.3364	99.5	98.6	*	2185	0.726	54.9	37.8	2261

*Impossible.

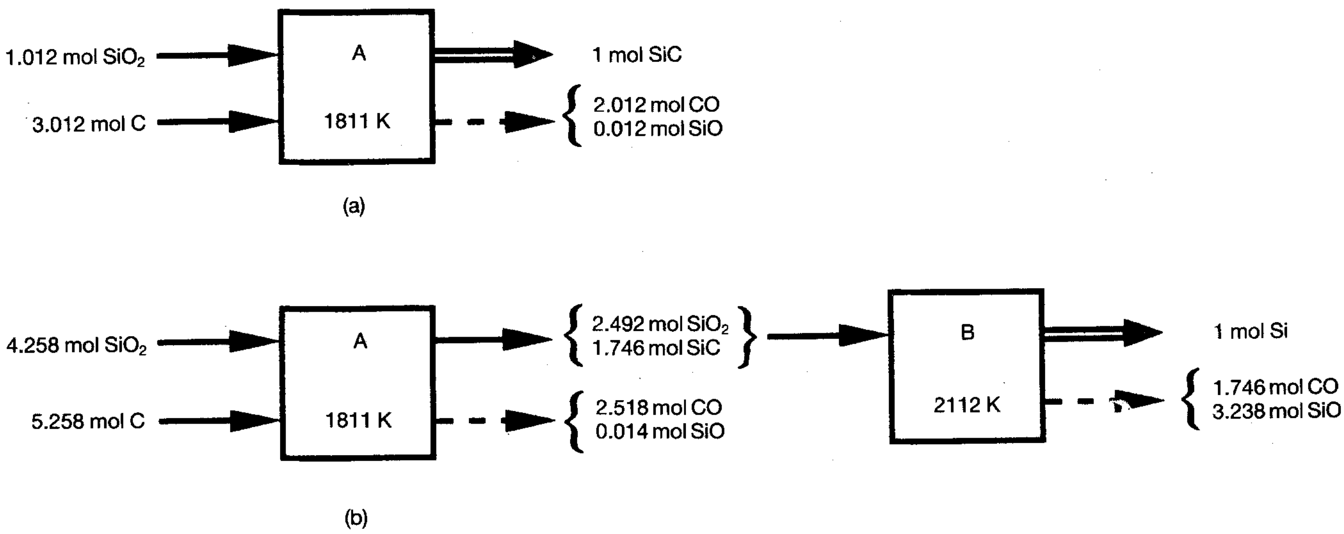

Figure 6 Mass flow under 10^5 Pa in the production, without gas recirculation, of: (a) 1 mol of SiC, or (b) 1 mol of Si.

TABLE II Literature values of R_A, T_B and R_B (see the text) under 10^5 Pa; and the yields, η_{Si/SiO_2} and gas ebb rate, r (in moles of gas per Si mole), deduced from these values

R_A	T_B (K)	R_B	η_{Si/SiO_2} (%)	r	References
90	1962	2.00	71	1.2	–[a]
44	2023	1.38	60	1.5	–[a]
540	2123	1.00	50	2.0	–[a]
100	2073	0.76	39	2.7	–[a]
184	2085	0.61	29	3.9	[5]
100	2060	1.40	61	1.5	[6]
200	2092	0.49	19	6.3	[9]
90	2046	0.90	45	2.2	This work[b]
167	2051	0.33	0	∞	This work[c]
174	2112	0.54	24	5.0	This work[d]

[a] Quoted in [5].
[b] According to data in [7].
[c] According to data in [8].
[d] According to data in [1, 2].

6. Conclusion

In an isobaric reactor from which gas is expelled at constant pressure, the evolution of a Si–C–O system with temperature occurs in several steps, but the main transformations happen at the univariant points where, in addition to the gaseous phase (CO and SiO), either three condensed phases (SiO_2, C and SiC, or SiO_2, SiC and Si) or two condensed phases at a congruent point (SiO_2 and SiC if $P < 0.367 \times 10^5$ Pa, or SiO_2 and Si) exist.

The transformations depend on the respective amounts of the initial condensed components. A mass balance, in addition to the thermodynamic study, allows the determination of the nature and the amount of products formed during a temperature rise.

From an initial mixture of C and SiO_2, it is possible to calculate the theoretical SiC and Si yields for a given ratio, $n^0_{SiO_2}/n^0_C$. The theoretical SiC yields are always very high whatever the imposed pressure, as soon as the temperature reaches that temperature corresponding to the univariant point; that is, the limitations of the practical yield are not due to thermodynamic reasons. Silicon is produced at a higher temperature only if $P > 0.367 \times 10^5$ Pa. The Si yields increase rapidly with the imposed pressure but always remain low; it is only possible to obtain Si with a high yield if the gases are recirculated, as they are in an electric arc furnace.

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