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The Si–C–O system

Part I *Representation of phase equilibria*

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Accurate data allow one to draw a precise pressure – P_{CO}/P_{SiO} ratio – temperature (PRT) diagram taking into account the mass balance of the independent components in the Si–C–O system. The existence of a congruent point for the mixture $2SiO_2 + 1SiC$ is shown, when the total pressure is lower than 36 700 Pa. From the PRT diagram it is possible to construct the phase diagrams at all temperatures and pressures.

1. Introduction

Thermodynamic study of the Si–C–O system is of great importance to understand and improve the processes of silicon and silicon carbide preparation. This system has been already studied from the point of view of equilibria between phases or of their evolution with temperature or pressure. Equilibria between phases can be represented as various diagrams:

(i) By isobaric–isothermal sections of the ternary phase diagram drawn in coordinates X_C, X_{Si} and X_O (atomic fractions of the elements) [1–4]. These diagrams allow an easy reading of the nature, composition and ratio of the phases found in the system but do not allow one to foresee the system's evolution with temperature T and pressure P. In order to describe thoroughly the system and its evolution with T and P, a double infinity of these diagrams would be necessary, one in T, other in P.

(ii) By predominance area diagrams. One (or several) variables of the system are selected. In a $P_{SiO}(T)$ diagram, Schei and Larsen [5] and Rosenqvist [6] fixed the total pressure. Berdnikov *et al.* [7, 8] drew the mole fraction of SiO in the gas, x_{SiO}, versus T at a total given pressure or at a given CO/SiO ratio. Nagamori *et al.* [9] represented the evolution of P_{CO} versus P_{O_2} or a_C at given P and T. Minster [10] drew $P_{SiO}(P_{CO})$ diagrams at various temperatures. As for the previous isobaric–isothermal sections, an infinity of diagrams would be necessary for a thorough description of the system.

In addition to this inconvenience, the results obtained by the various authors, or calculated from various sources of data, are scattered. For example, the equilibrium temperature between Si, SiO_2, SiC and gas under atmospheric pressure lies between 1960 and 2120 K according to different authors, and the corresponding P_{CO}/P_{SiO} ratio from 0.33 to 2.

The purpose of this work is to reduce these uncertainties by using coherent and accurate data, and by choosing graphical representations taking into account all the parameters involved in the phase equilibria. It will then be possible (in Part II) to foresee the isobaric evolution of the Si–C–O system when the temperature rises and, using the mass and heat balances, to calculate the energy consumption of an electric furnance for the production of silicon (Part III).

2. Thermodynamics of the Si–C–O system

2.1. Definition of the system

The state of a ternary system such as Si–C–O depends on four intensive variables: T, P and two composition variables such as X_C, X_{Si} or X_O (the atomic fractions of the elements in the solid phase). For reasons of practical interest, this study has been restricted to the following intervals:

$$P(10^5\ \text{Pa}) \in [0.02, 2];\ T(\text{K}) \in [1400, 2300];$$
$$3X_{Si} + 2X_C > 1$$

The last conditions excludes the equilibria of the O_2–CO–SiO_2 triangle. The five phases which can exist in this system between 1400 and 2300 K are

(i) C: solid graphite,
(ii) SiC: β silicon carbide,
(iii) Si: solid or liquid silicon ($T_f = 1685$ K),

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TABLE I $C_{i,k}$ coefficient values for $G_i^0(T) = -R_G T[(C_1/T^2) + (C_2/T) + C_3 + C_4 T + C_5 T^2 + C_6 \log_e T]$

Species	$-C_1(10\,K^2)$	$C_2(10^{-2}\,K)$	$-C_3(10^{-5})$	$C_4(10^{-8}\,K^{-1})$	$-C_5(10^{-11}\,K^{-2})$	$C_6(10^{-5})$
C	19 198	186 481	1 973 791	7 774	89	282 452
SiC	19 615	1 167 075	3 802 082	31 311	1541	568 722
Si, s	2125	98 174	1 650 475	23 007	− 43	274 605
Si, l	0	− 485 449	1 655 948	0	0	327 095
SiO_2, s	17 230	11 261 922	5 361 778	10 066	623	86 1467
SiO_2, l	0	11 435 003	6 728 082	0	0	1 031 606
CO	6512	1 469 870	91 533	32 538	2112	360 057
SiO	8660	1 386 834	478 401	3628	112	478 401

(iv) SiO_2: high-temperature cristobalite or liquid ($T_f = 1996\,K$), and

(v) gas.

Condensed phases have been considered as pure substances though liquid silicon in equilibrium with SiC would contain a slight amount of dissolved SiC [11]. The gaseous phase is an ideal mixture of all species. At first 17 gaseous species have been considered: SiO, CO (major species) and C_{1-5}, Si_{1-3}, O_{1-2}, CO_2, SiC_{1-2}, Si_2C, SiO_2 (minor species). The sum of the partial pressures of the minor species is always lower than 0.04% of the total gas pressure and the error in x_{SiO} or x_{CO} (mole fractions of these components in the gaseous phase) is below 3×10^{-4} when the minor species are missed out in the overall equilibria. Thus, the atomic fraction of oxygen in the gas, x_O, can be considered as equal to 0.5.

For accurate equilibrium calculations, thermodynamic data must be complete, coherent and exact. The data of Turkdogan [12] or of Kubaschewsky and Alcock [13], from which the free energies of compound formation as a function of T depend only on two or three constants, do not allow one to obtain the required precision. Nagamori *et al.* [9], using several sources of data, justified the existence of the hypothetical SiO condensed species and found results very far from industrial practice as previously reported by Rosenqvist and Tuset [14]. We have used a unique and critical source of data, supplied by Thermodata (Grenoble, France) and based on the second edition JANAF tables [15]. The third edition, less complete, leads to numerical results very close to those obtained from the second edition, e.g. the difference of temperatures for the equilibrium between Si, SiO_2, SiC and gas is below 1.4 K at normal pressure.

The evolution of the standard Gibbs free energy, $G_i^0(T)$, versus T, for the formation of the component i ($i \in [1, 21]$ in the complete calculation, $i \in [1, 6]$ in the simplified calculation) is

$$G_i^0(T) = -R_G T(C_{i,6} \log_e T + \sum_{k=1}^{5} C_{i,k} T^{k-3}) \tag{1}$$

with $R_G = 8.3142\,J\,mol^{-1}\,K^{-1}$. The $C_{i,k}$ coefficient values are summarized in Table I. The use of Equation 1 results in a difference between the calculated G_i^0 and those supplied by Thermodata which is lower than $10^{-5}\,J\,mol^{-1}$.

2.2. Construction of the equilibrium pressure – P_{CO}/P_{SiO} ratio – temperature (PRT) diagram

For a system of three independent components such as Si–C–O, the maximal variance is equal to 3: the system containing only gas (SiO + CO, when the minor species are disregarded) would have a variance equal to 4, but the atomic fraction, x_O, of oxygen in this gas is then given and equal to 0.5, decreasing the variance by one unit. Thus, the stability domains of the different components of the system can be represented in a tridimensional space. The following independant variables have been chosen: total pressure P, temperature T and ratio $R = P_{CO}/P_{SiO}$. In such a diagram, volumes, surfaces and curves represent respectively a system with two (or one for gas alone), three and four phases. The following reactions were considered:

$$2C + SiO \rightleftharpoons SiC + CO \tag{2a}$$

$$SiC + 2SiO_2 \rightleftharpoons 3SiO + CO \tag{2b}$$

$$Si + SiO_2 \rightleftharpoons 2SiO \tag{2c}$$

$$SiC + SiO \rightleftharpoons 2Si + CO \tag{2d}$$

$$C + SiO_2 \rightleftharpoons SiO + CO \tag{2e}$$

The reaction $SiO + C \rightleftharpoons Si + CO$ has not been taken into account because C and Si would react one to another to form SiC.

At a given pressure, the Gibbs free energies of Reactions 2a–e have been calculated using Table I data. At equilibrium, using $\Delta G^0 = -R_G T \log_e K$, where K is the equilibrium constant, the $T(R)$ curves corresponding to each reaction can be drawn (Fig. 1). The curves representing the equilibria of Reactions 2a–e are called respectively A′A″, AB, BD, B′B″ and AH in Fig. 1. The curves A′A″, AB, AH intersect at the point A and B′B″, AB, BD at the point B. The curve BD intersect the T axis ($R = 0$) at the point D. The point H represents the equilibrium between C and CO. The variance at the points A, B and D is equal to one: at a given P, T and R are determined.

It can be noticed that the equilibria of Reactions 2a and d are independent of the pressure according to the Le Chatelier law, in contrast with 2b, c and e. However, the $P(T)$ curves connected with 2b, c and e are monotonous and, at a given ratio R the total pressure, $P_{CO} + P_{SiO}$, decreases continuously with T. Thus, it is easy to project a great number of curves on to the

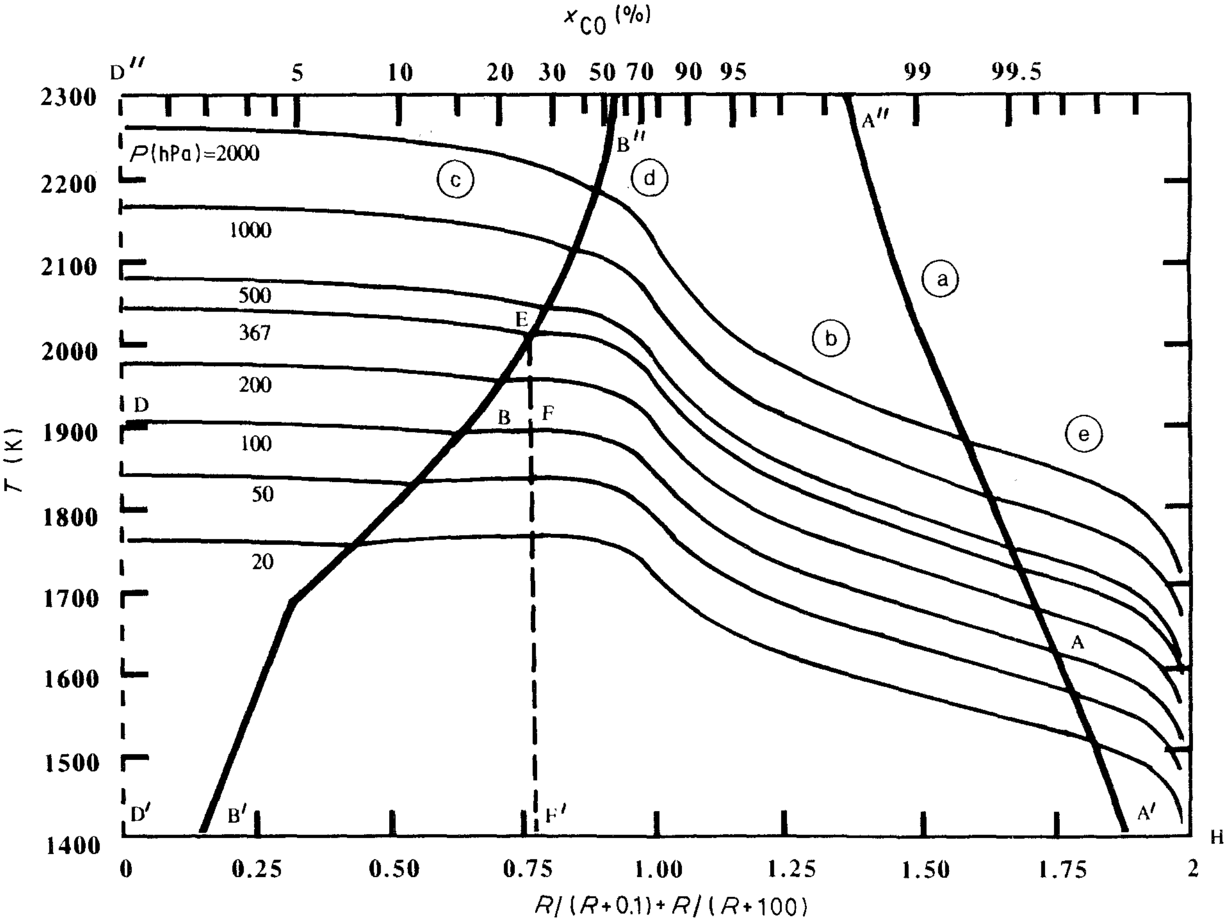


Figure 1 PRT diagram (pressure, P_{CO}/P_{SiO} ratio, temperature) of the Si–C–O system; (——) and (– – –): lines for the locus of the univariant points with respectively four or three phases; (——) isobaric lines (the non-linear abscissa $R/(R+0.1)+R/(R+100)$, allows us to distend the diagram extremities). Reactions: (a) $2C + SiO \rightleftharpoons SiC + CO$, (b) $SiC + 2SiO_2 \rightleftharpoons 3SiO + CO$, (c) $2SiO \rightleftharpoons Si + SiO_2$, (d) $SiC + SiO \rightleftharpoons 2Si + CO$, (e) $C + SiO_2 \rightleftharpoons SiO + CO$.

$T(R)$ diagram without their intersecting. The sections at constant R and T do not show this property: the $P(R)$ curves at constant T or the $P(T)$ curves at constant R intersect each other at various points and the superposition of several sections on the same diagram would soon make the latter unreadable.

In Fig. 1 the curves BD, AB and AH divide the diagram into two parts. In the temperature domains under these curves the gaseous phase does not exist and R has no significance, whatever the condensed phases considered. Above these curves, the phases present are different according to whether the atomic fraction of oxygen in the system, X_O, is superior, equal or inferior to 0.5 (Fig. 2):

(i) For $X_O = 0.5$, a unique domain exists with gas alone because the atomic fraction of oxygen in the gas, x_O, is also equal to 0.5.

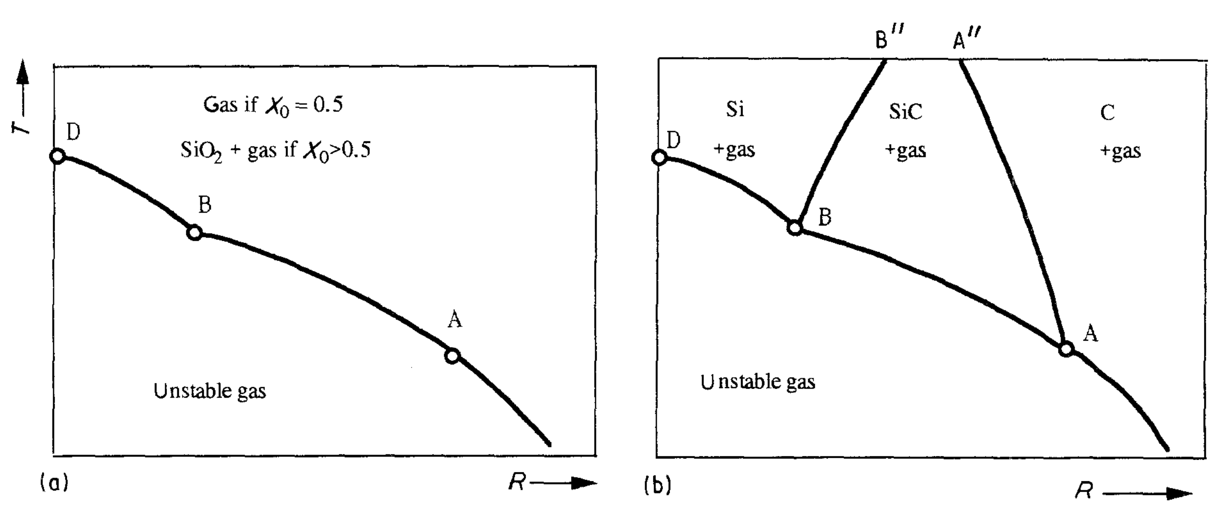


Figure 2 Schematic isobaric sections of the PRT diagram at $P > P_E = 0.367 \times 10^5$ Pa; A, B, D: are univariant points. (a) $X_O \geq 0.5$, (b) $X_O < 0.5$ (if $P < P_E$ the domains remain the same but the curve AB exhibits a maximum).

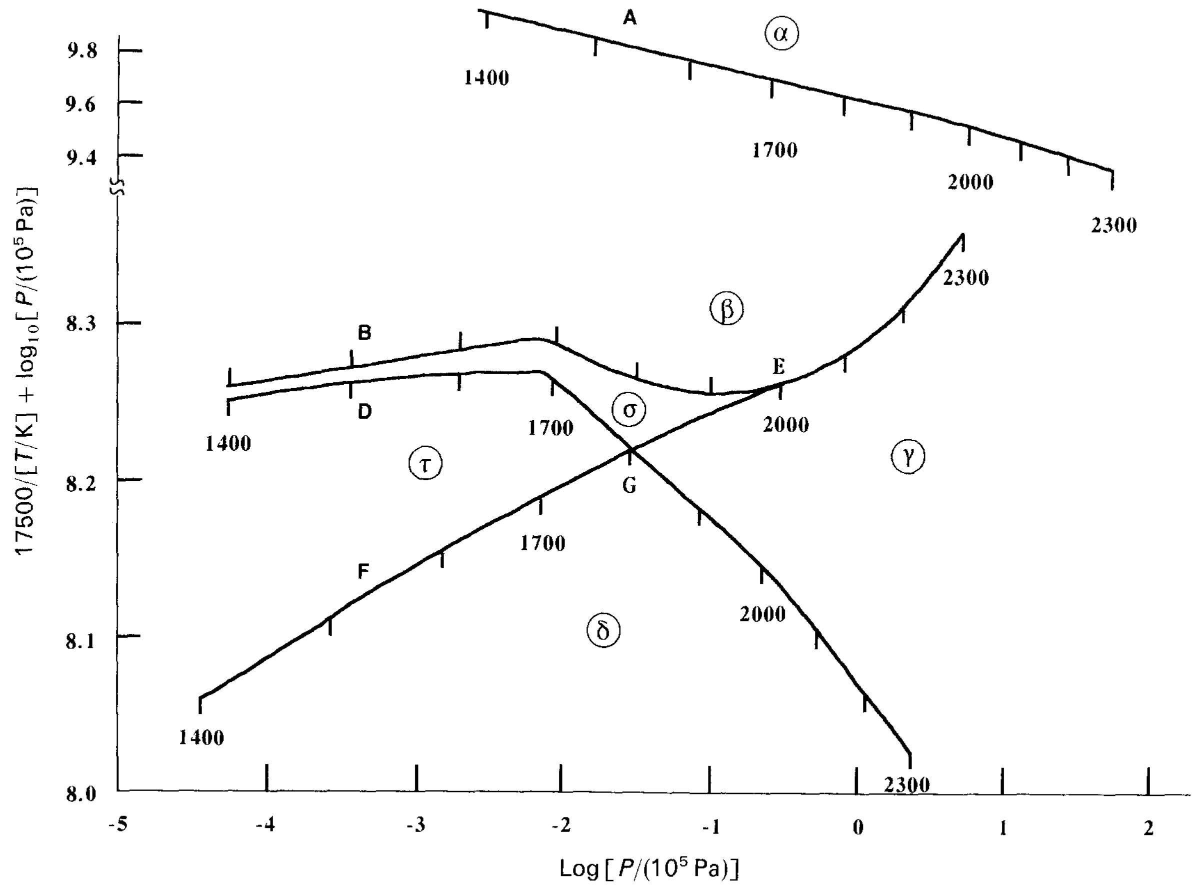


Figure 3 Locus of the univariant points A, B, D, F in a modified $P(T)$ diagram showing the existence domains of the six phase configurations: α, β, γ, δ, σ, τ.

(ii) For $X_O > 0.5$ this domain also contains SiO_2, which is the only condensed component containing oxygen.

(iii) For $X_O < 0.5$ there are three domains, limited by the curves BD–BB″, B″–AB–AA″ and AA″–AH and representing respectively the existence domains of Si + gas, SiC + gas and C + gas.

In Fig. 1 the $T(R)$ curves, whatever the given pressure may be, are always monotonous for Reactions 2a and 2c–e: $dT/dR > 0$ for 2d and $dT/dR < 0$ for 2a, c and e. It is the same for 2b ($dT/dR < 0$) when the pressure is above $P_E = 0.367 \times 10^5$ Pa ($T_E = 2011$ K, $R_E = 1/3$). On the other hand, below P_E the $T(R)$ curves for Reaction 2b show a maximum called F ($R_F = 1/3$); $dT/dR > 0$ between B and F and $dT/dR < 0$ between F and A. Thus, T_F is greater than T_B (and than T_D if $P < 336$ Pa) as can be seen in Fig. 3, showing the temperature evolution versus pressure for the univariant points A, B, D and F.

These maxima in F are only slightly marked and one can wonder if they really exist or if they are a consequence of a lack of accuracy in the data. To prove their existence, it can be noted that one cannot question the fact that vertical line the $R = 1/3$ intersects the curve BB″ (at the point E). On the other hand, let us assume that a mixture of two moles of SiO_2 and one mole of SiC ($X_O = 0.5$) are heated under a given pressure lower than P_E. At the temperature T_F on the isobaric curve AB, SiO_2 and SiC react up to total disappearance because the oxygen fraction in the condensed phases is the same as in the produced gas ($X_O = x_O = 0.5$). Thus, the point F is really a congruent point of the system. However, the presence of these maxima induces slight modifications in the construction of the phase diagram (see below), as well as in the evolution of the Si–C–O system versus T (to be considered in Part II). The 1Si + 1SiO_2 system is also congruent because $X_O = x_O = 0.5$.

Univariant points (A, B, D and F) are important in the scope of a study of the system's evolution since, at these points, the nature of the phases in equilibrium changes. To calculate T and R versus P at A, B, D and F, the following relationships, obtained by non-linear regression, can be used:

$$10^4/T_A = 5.5214 - 0.283 \log_e P - 3.8 \times 10^{-5} \log_e^2 P; \quad P(10^5\ \text{Pa}) \in [0.02, 2] \tag{3}$$

$$\log_e R_A = 5.161 - 0.264 \log_e P \tag{4}$$

$$10^4/T_B = 4.7348 - 0.2317 \log_e P + 5.1 \times 10^{-3} \log_e^2 P; \quad (10^5\ \text{Pa}) \in [0.367, 2] \tag{5}$$

$$\log_e R_B = -0.61765 + 0.46917 \log_e P - 1.05 \times 10^{-2} \log_e^2 P \tag{6}$$

$$10^4/T_F = 4.7336 - 0.2389 \log_e P - 0.36 \times 10^{-3} \log_e^2 P \tag{7}$$

$$R_F = 1/3 \tag{8}$$

$$10^4/T_D = 4.6225 - 0.2722 \log_e P - 0.53 \times 10^{-3} \log_e^2 P; \quad T < T_f(SiO_2) \tag{9}$$

$$10^4/T_D = 4.6150 - 0.2383 \log_e P - 1.11 \times 10^{-3} \log_e^2 P; \quad T > T_f(\mathrm{SiO_2}) \qquad (10)$$

$$R_D = 0 \qquad (11)$$

These R_A, R_B and T_B values will be compared with those calculated by other authors in the second part of this work.

3. Ternary phases diagrams at constant *T* and *P*

Let us call a "complex" the set of coexisting phases in a domain with two (surfaces), three (curves) or four (univariant points) phases in the PRT diagram (Fig. 1).

In the phase diagram (Gibbs–Rooseboom triangle at constant T and P), each component is represented by one point, a two-phase complex (or a one-phase complex for a gaseous mixture) by a straight line, and a three-phase complex by a triangle. A four-phase complex (as $SiO_2 + SiC + C +$ gas at the point A in Fig. 1) is represented by a quadrilater but the amount of each phase in the system can be calculated only if supplementary data (such as the volume of the system or the heat supplied to the system) are known.

The phase diagrams corresponding to the six configurations α, β, γ, δ, σ and τ shown in Fig. 4 have been considered. Each of them is determined from the intersection between an isotherm and the isobaric $T(R)$ section of the (P, R, T) diagram. According as the isobaric curve AB exhibits or not a maximum at F, the isotherm can intersect AB at two points M and N (configuration σ or τ: Fig. 4b and c) or in only one point M (configuration β: Fig. 4a–c). The configuration τ corresponds to the case $T_F > T_D$, i.e. $P < 336$ Pa (Fig. 4c).

In Fig. 5, the existence domains of the complexes of the phase diagram, for the various configurations, have been qualitatively represented. The exact position of the points A, B, L, M, N, Q on the SiO–CO line are directly deduced from Fig. 1. On the modified $P(T)$ diagram (Fig. 3) the existence domains of configurations α, β, γ, δ, σ, τ, limited by the loci of the univariant points A, B, D or F, are shown.

TABLE II Phase diagram configurations, according to the literature, at various temperatures and pressures

Configuration	$P(10^5$ Pa)	T(K)	Ref.
α	1	1700	[1, 2, 4]
	5	1900	[1]
β	1	1900	[1, 4]
γ	1	2100	[3, 4][a]
δ	0.01	1700	[1][a]
		1900	[1]
		2500	[1, 2]
	1	2300	[4]
		2500	[1, 4]
		2700	[4]
		2900	[4]
	5	2500	[1]

[a] Configuration β according to our calculations.

Four of the configurations indicated in Fig. 5 have been previously reported in the literature but only for a few P, T couples with the exception of the σ and τ configurations which have very narrow existence domains in P, T space. Good agreement between the literature results and our results is observed in Table II except for the two cases pointed out in this table. The difference of configurations proceeds probably from a discrepancy between the Gibbs free energy values used for the formation of the components.

4. Conclusion

In the Si–C–O system the maximal variance is equal to 3. The equilibria between phases can be described in a tridimensional diagram: P, T, $R = P_{CO}/P_{SiO}$ or more simply in a $T(R)$ plane because the projections of isobaric curves on to this plane do not intersect.

The accuracy of the diagram depends on the coherence and the precision of the thermodynamic data.

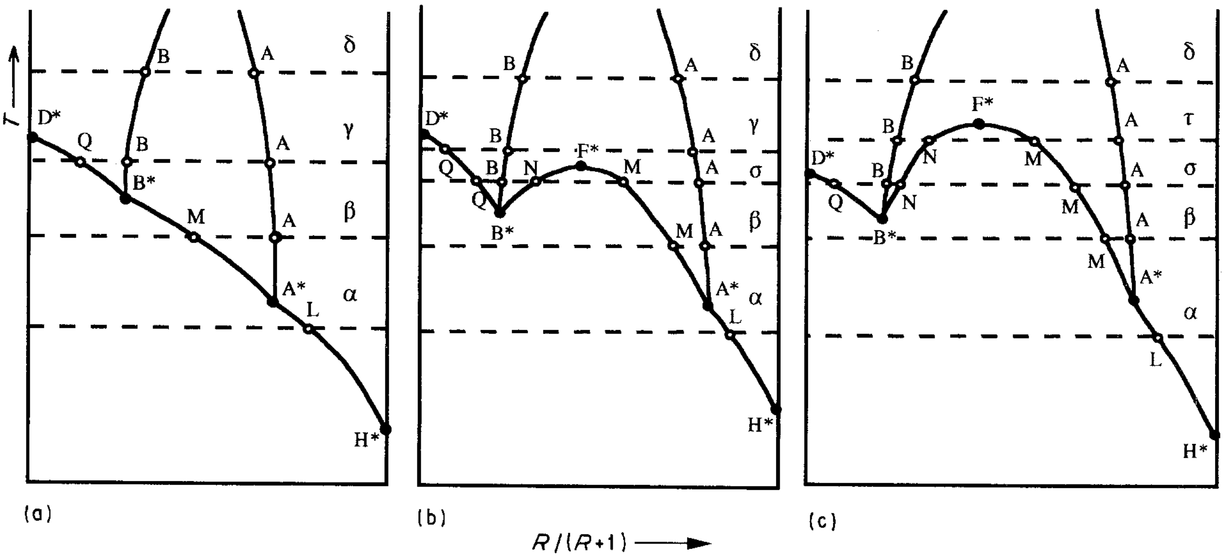
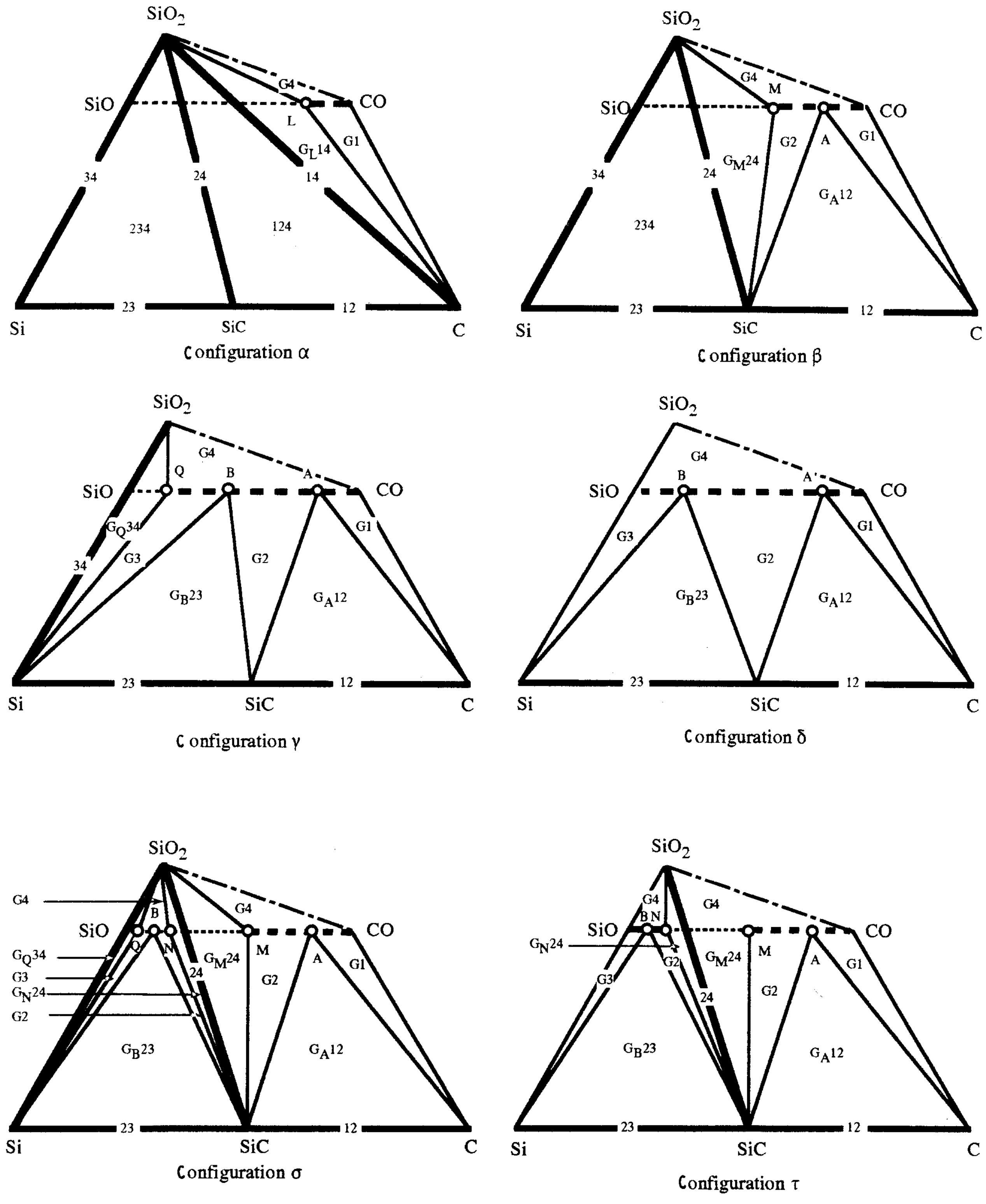


Figure 4 The various possibilities of intersections between one isotherm and the isobaric curves of the PRT diagram: (a) $P > P_E = 36\,700$ Pa, (b) $P_E > P > P_G = 336$ Pa (i.e. $T_F < T_D$), (c) $P < P_G$ (i.e. $T_F > T_D$).



Configuration α

Configuration β

Configuration γ

Configuration δ

Configuration σ

Configuration τ

Figure 5 Isobaric, isothermal phase diagrams for the Si–C–O system corresponding to the six configurations α, β, γ, δ, σ and τ shown in Fig. 4; configurations α, β, γ, δ have been previously reported. σ and τ are new configurations. 1 = C, 2 = SiC, 3 = Si, 4 = SiO_2, G_j = gas with composition j (j = A, B, L, M, N, N or Q); (▬) two condensed phases; (– – –) stable gas; (····) CO–SiO line; (–·–) limit of this study.

The use of a unique source of data and six adjustable parameters to describe the variations of the chemical standard potentials of the components, as a function of the temperature, ensures the requisite accuracy. In particular, we have shown that, under certain conditions, the complex gas + SiC + SiO_2 undergoes a congruent transformation.

The $P(T)$ curves corresponding to four univariant complexes divide this plane into six domains corresponding to six configurations of the ternary Si–C–O phase diagrams. These can be constructed at all temperatures and pressures using the P_{CO}/P_{SiO} ratio given by the PRT diagram. Such an approach can also be used for all ternary systems in which the gaseous phase, in equilibrium with pure condensed phases, contains only two main species.

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