

## The formation of boron, silicon and calcium containing molecular species in a graphite furnace in Ar/O<sub>2</sub> mixtures

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The composition of the Ar/O<sub>2</sub>/C gas system in the presence of traces of either B, Si or Ca was calculated under the assumption of thermal equilibrium in the temperature range 500–5500 K. The mole concentration of oxygen was taken to be 1–4 %. Two sets of calculations were carried out. In the first one the presence of solid phase (graphite) was ignored and the calculations were performed for a single-phase (gas) system, at variable ratios C/O (0.5, 0.96, 1 and 2). In the second set of calculations the presence of solid carbon (graphite) was taken into account and the composition of the gas system in equilibrium with solid carbon, at  $p = 1$  atm, was determined. The results presented show that the equilibrium composition, particularly the concentration of different compounds involving the trace elements, is very sensitive to the amounts, and the ratio of the amounts of oxygen and carbon. Increasing the O/C ratio results in increasing partial pressures of molecular and atomic oxygen, which favours the formation of oxides of the trace elements and moves their atomization temperatures to higher values. On the other hand, increasing the C/O ratio ( $C/O > 1$ ) favours atomization, but also carbide formation in the lower-temperature region. It was found that, over a relatively wide temperature interval ( $1000 < T < 3500$  K), the composition of the Ar/O<sub>2</sub>/C/X ( $X = B, Si, Ca$ ) system, with comparable amounts of oxygen and carbon ( $C/O = 1$ ), does not significantly depend on the presence of the solid phase. The results of calculations enable a reasonable interpretation of numerous experiments carried out on similar systems.

*Keywords:* atomization in a graphite furnace, thermal equilibrium.

### INTRODUCTION

The formation of molecular species plays an important role in the atomization mechanism of elements in a graphite furnace. This subject has been extensively studied both experimentally and theoretically. In a graphite furnace, besides the sample to be analyzed, the presence of carbon and oxygen (and depending on the experimental conditions, also of other species), arising as impurities in the purge gas but also due to ingress from the ambient atmosphere,<sup>1</sup> has to be taken into account. This means that besides the atomization and, at higher temperatures, also ionization processes, chemical reactions leading to the formation of oxides and carbides of the analyzed elements and the reverse dissociation reactions take place.

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The partial pressure ratios of oxides and/or carbides to atomic forms of the investigated element at equilibrium are determined by the equilibrium constants for the reactions in question and the oxygen/carbon partial pressures. The effect of added  $O_2$ , CO and  $CO_2$  to the purge gas (usually Ar) on the appearance temperature, as well as on the height of the absorbance signal of the analyzed element, was studied in a series of papers.<sup>2-7</sup> The influence of the content of  $O_2$  on the appearance temperatures of different elements (Pb, Si, Sn, Al, ...) was investigated experimentally and theoretically in Ref. 2. It was found that a change in the  $O_2$  content in the purge gas from 0.005 % to 1 % caused an increase in the appearance temperature of about 400 (Si), 200 (Pb) and 100 (Al) K. In several studies<sup>3,6,7</sup> special attention was paid to the investigation of the behaviour of boron and silicon, as elements extremely sensitive to the presence of oxygen and of low sensitivity for determination by graphite furnace atomic absorption spectrometry. Boron signals measured below 2200 K in an electrothermal vaporization inductively coupled mass spectrometre<sup>6</sup> were attributed to boron molecular species. In Ref. 7 the influence of added  $O_2$ , CO and  $CO_2$  on the atomic silicon absorbance signal, as well as on the absorbance corresponding to the SiO and  $SiC_2$  molecular species, was investigated experimentally. It was found that increasing the  $O_2$  content of the internal argon purge gas caused a decrease of the atomic silicon absorbance peak in proportion to the content of oxygen, and an increase of the silicon oxide (SiO) molecular absorbance peak. The addition of CO (5 %) into the argon purge gas caused a depression of the SiO molecular absorbance peak, but an increase of the absorbance peak of  $SiC_2$ . The effect of added  $CO_2$  was found to be very similar to the effect of added oxygen. A number of papers was devoted to the estimation of the CO and  $O_2$  (O) partial pressures in graphite furnaces. In Refs. 1 and 4 the CO partial pressure was determined experimentally and the partial pressures of  $O_2$  (O) were calculated using single- and two-phase thermodynamic equilibrium models.<sup>9</sup>

On the basis of previous experimental and theoretical investigations it is clear that the concentration of atomic species in a graphite furnace and, thus, the detectability of the corresponding elements is strongly influenced by the presence and amount of impurities such as oxygen and carbon. The subject of the present paper is the calculation of the equilibrium composition of the gas systems normally encountered in experimental praxis. Particular attention was paid to the analysis of the applicability of two thermodynamical models usually assumed in the theoretical handling of these systems: i) the single-phase (gas) model; ii) the two-phase model involving the gas mixture in equilibrium with solid carbon (graphite). The results of the present study should contribute to the elucidation of processes taking place in graphite furnaces and their effect on the detectability of the trace elements.

#### METHOD OF CALCULATION OF THE EQUILIBRIUM COMPOSITION

The calculation of the equilibrium gas mixture compositions under the condition of constant pressure was carried out using the method developed by White *et*

*al.*<sup>10</sup> It is based on the fact that the equilibrium of the system corresponds to its minimum energy state. The free energy,  $G$ , of a system is the sum of the chemical potentials,  $\mu_i$ , multiplied by the mole fractions,  $x_i$ , of its components:

$$G = \sum_{i=1}^n x_i \mu_i \quad (1)$$

where  $n$  is the number of chemical species and  $x_i$  their mole fractions to be determined. The set of  $x_i$  values leading to the equilibrium can be obtained by solving the equation

$$\delta G = 0 \quad (2)$$

under fulfillment of the mass balance condition

$$\sum_{i=1}^n a_i x_i = b_j; \quad j = 1, 2, \dots, m \quad (3)$$

where  $m$  represents the number of elements in the system,  $a_i$  is the number of atoms of element  $j$  in molecule  $i$ , and  $b_j$  is a coefficient proportional to the percentage of the element  $j$  in the system. The quasineutrality of a system also containing charged species is ensured by the condition

$$\sum_{i=1}^n q_i x_i = 0 \quad (4)$$

where  $q_i$  represents the charge of species  $i$ . According to the method of White *et al.*,<sup>10</sup> the mole fractions  $x_i$  are calculated by an iterative procedure. One starts with any set of positive numbers  $x_{i0}$  which satisfy Eqs. (3) and (4) and builds the zeroth-order approximation for  $G$ . The free energy is then expanded into a Taylor series up to the quadratic terms in  $x_i - x_{i0}$ . The conditions (3) and (4) are taken into account with the help of Lagrange multipliers  $\pi_j$ . Minimization of the free energy leads to a system of linear equations which determine the improved values for  $x_i$  and, thus, a new approximation for  $G$ . The procedure is repeated until convergence is achieved. It should be noticed that the dimension of the system is  $(m+1)$ , *i.e.*, it depends only on the number of elements in the system. The concentrations of the trace species can be calculated using the equation:

$$z_i = \exp \left[ - \left( \frac{F}{RT} \right)_i - \ln p + \sum_i a_i \pi_j \right] \quad (5)$$

where  $p$  is the total pressure in the system. In the case of the two-phase calculations, an additional constraint is introduced, namely that the concentration of gaseous carbon ( $C$ ,  $C_2$ ,  $C_3$ , *etc.*) in equilibrium with the solid phase is determined by its vapor pressure, being function of temperature only.

## RESULTS OF THE CALCULATIONS

The composition of the Ar/O<sub>2</sub>/C system in presence of B, Si and Ca, as traces elements (0.0001 %), was calculated under the assumption of thermal equilibrium. For comparison, several computations are undertaken in which the oxygen was replaced by an equal amount of a nitrogen-oxygen mixture having the same mole ratio as in air. Two sets of calculations were performed:

1. The Ar/O<sub>2</sub>/C/X systems (X = B, Si, Ca) were considered as a single-phase system with the following mole ratios: Ar : O : X = 1 : 0.01 : 0.000001. The calculations were carried out for different total carbon to oxygen ratios (C/O = 0.5, 0.96, 1 and 2), covering the range encountered under usual experimental conditions. The ratio C/O = 0.96 was chosen to represent the situation with a small excess of oxygen relative to the stoichiometric quantities in the key compound, CO, over the broad range of temperatures of interest.

2. Ar/O<sub>2</sub>/C/X systems were treated as two-phase systems (gas in equilibrium with solid graphite) with the following mole ratios:

2a. Ar : O : X = 1 : 0.01 : 0.000001;

2b. Ar : O : X = 1 : 0.04 : 0.000001.

In the two-phase calculations, the equilibrium partial pressures of the C<sub>n</sub> species (C<sub>1</sub>, C<sub>2</sub>, C<sub>3</sub>, C<sub>4</sub>,...) are functions of temperature only and are equal to corresponding vapor pressure values arising from the process C<sub>s</sub> → C<sub>g</sub> [where C<sub>s</sub> represents solid carbon (graphite) and C<sub>g</sub> atomic carbon in the gas phase]. The values of the partial pressures of all other species were obtained using a computing procedure which minimizes the free energy of the system.

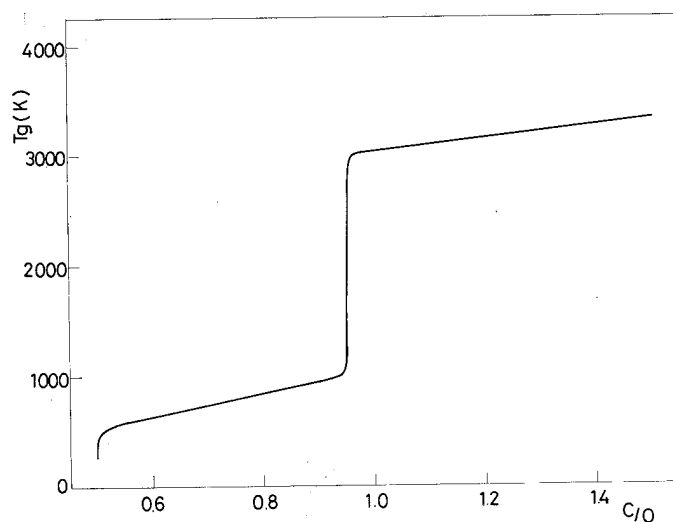
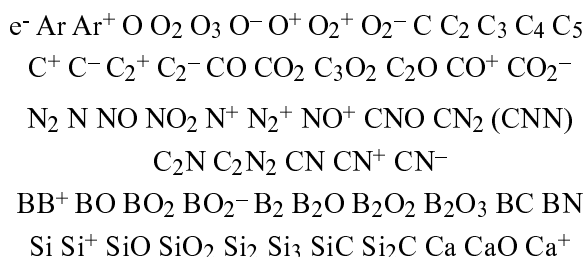


Fig. 1. Temperature  $T_g$ , at which the partial pressure of carbon in the gas phase with a given C/O ratio is equal to the vapor pressure of carbon in equilibrium with solid graphite, as a function of the C/O ratio.

The equilibrium partial pressures of up to 54 species (atoms, ions, electrons, molecules, radicals), whose Gibbs (free) energy data were available,<sup>11</sup> were calculated in the temperature range between 500–5500 K for the single-phase system, and 500–3500 K for the two-phase system. The species considered in the computation are listed in Table I.

TABLE I Species considered in the computations



The two sets of calculations designated above were performed as previous investigations did not give an unambiguous answer to the question of whether the gas phase in the graphite furnace is really in equilibrium with the solid phase or not. Depending on this, one set of the results of the calculations will be more reliable than the other. The temperature,  $T_g$ , at which, for a given C/O ratio in the gas phase, the partial pressure of the carbon atoms obtained in the single-phase calculations equals to the vapor pressure of carbon at the same temperature may serve (Fig. 1) as a quantitative criterion for the reliability of single- or two-phase results. At temperatures below  $T_g$ , *ie.*, in the region below the curve displayed in Fig. 1, the partial pressure of the carbon atoms calculated using the single-phase model is higher than the corresponding vapor pressure and, thus, in this zone the single gas phase is "oversaturated" with the carbon. Consequently, the results of the single-phase calculations are in this region unreliable if the gas phase is in equilibrium with the solid carbon. The curve shown in Fig. 1 exhibits two discontinuities corresponding to the C/O ratios with the values 1 and 2. As will be shown below, this is a consequence of the predominant formation of  $\text{CO}_2$  and  $\text{CO}$ , respectively, in the gas phase.

$\text{Ar}/\text{O}_2/\text{C}/\text{X}$  ( $\text{X} = \text{B}, \text{Si}, \text{Ca}$ ) considered as a single-phase system.

This type of calculations was performed assuming the following mole ratios:  $\text{Ar} : \text{O} : \text{X} = 1 : 0.01 : 0.000001$ , at different total carbon amount to total oxygen amount (C/O) ratios. The equilibrium partial pressures (precisely  $\log(p/p_0)$  where  $p_0$  is the total pressure, in our case 1 atm) of the main components,  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{O}$  and  $\text{O}_2$ , of the  $\text{Ar}/\text{O}_2/\text{C}/\text{X}$  gas system at  $\text{C}/\text{O} = 0.5, 0.96, 1$  and  $2$  are presented as functions of temperature in Fig. 2. It can be seen that, at the ratios  $\text{C}/\text{O} > 1$ , the most abundant species over the whole temperature region considered (1000–6000 K) is  $\text{CO}$ . An excess of oxygen over carbon ( $\text{C}/\text{O} = 0.5$ ) causes an increase of the partial pressures of oxygen in atomic and molecular form and favours the formation of  $\text{CO}_2$ , which appears as the main component at lower temperatures ( $T < 2500$  K).

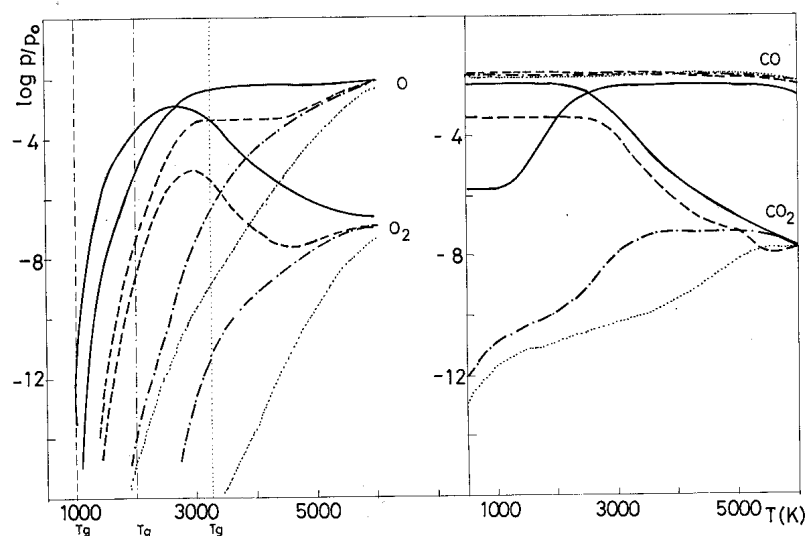


Fig. 2. Partial pressures of the main components of the Ar/O<sub>2</sub>/C system obtained employing the single-phase calculation model, as functions of temperature. Solid lines: C/O = 0.5; dashed lines: C/O = 0.96; dash-dotted lines: C/O = 1; dotted lines: C/O = 2.

The equilibrium partial pressures of boron containing compounds obtained in the computations with C/O = 2, 1, 0.96 and 0.5 as functions of temperature are shown in Figs. 3 and 4. It can be noticed that the curves for C/O = 0.5 and 0.96 (*i.e.*, C/O < 1)

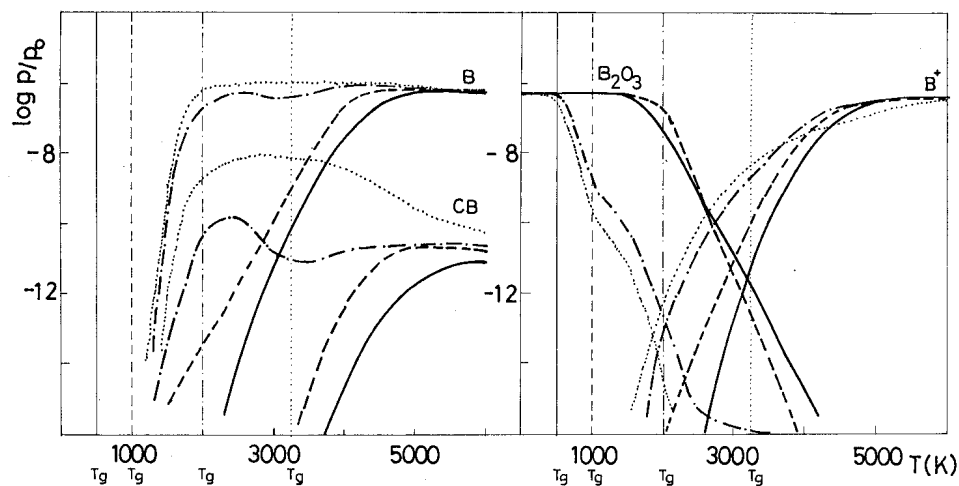


Fig. 3. Partial pressures of boron containing species in the Ar/O<sub>2</sub>/C/B gas system, calculated in the framework of the single-phase model, as functions of temperature. Solid lines: C/O = 0.5; dashed lines: C/O = 0.96; dash-dotted lines: C/O = 1; dotted lines: C/O = 2. Vertical lines correspond to temperature  $T_g$  defined in the text and in the legend to Fig. 1 (see also Fig. 4).

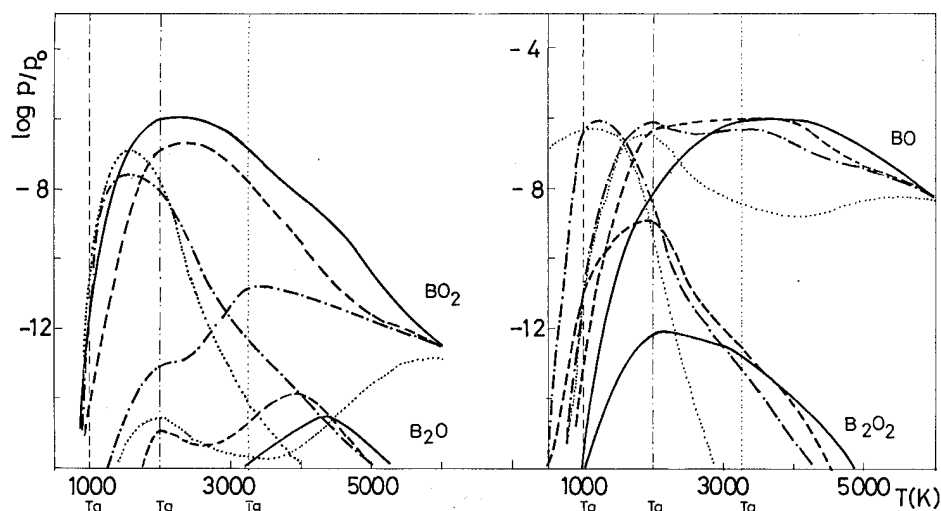


Fig. 4. Partial pressures of boron containing species in the Ar/O<sub>2</sub>/C/B gas system, calculated in the framework of the single-phase model, as functions of temperature. For the key to the notation see Fig. 3.

on the one hand, and those for  $C/O = 1$  and  $2$  ( $C/O > 1$ ) on the other hand, lie close to each other. It can also be seen that different boron oxides appear at considerable concentrations over a wide temperature region ( $500 < T < 5500$  K). An excess of oxygen ( $C/O = 0.96, 0.5$ ) causes an extension of the temperature region in which boron oxides appear, and a consequential depression of boron in the atomic form. This results in the atomization temperature, the lowest temperature,  $T_a$ , at which boron is considerably atomized (we use 60 % as the quantitative criterion), being shifted to higher values with increasing amount of oxygen (Table II).

TABLE II. Atomization temperature of B, Si and Ca at different C/O ratios obtained using the single-phase (sp) and two-phase (tp) calculation models

	(sp) C/O = 0.5	(sp) C/O = 0.96	(sp) C/O = 1	(sp) C/O = 2	(tp) 1 % O	(tp) 4 % O
(B) $T_a/K$	4750	4250	2500	1900	2400	2600
(Si) $T_a/K$	4600	4000	2300	1800	2400	2550
(Ca) $T_a/K$	3250	1000	1000	2000	1000	1200

The equilibrium partial pressures of silicon and calcium containing compounds for the ratios  $C/O = 1$  and  $0.96$  (Si) and  $C/O = 2, 1, 0.96$  and  $0.5$  (Ca) are presented in Figs. 5 and 6. (left-hand side). The curves representing the partial pressures of silicon containing compounds at  $C/O = 0.5$  and  $2$  are omitted for clarity since they lie close to the curves for the ratios  $C/O = 0.96$  and  $2$ , respectively. At the ratio  $C/O = 1$ , the dominating compounds containing silicon are at lower temperatures (below 1500 K) SiO and Si<sub>2</sub>C. At 2500 K, approximately 50 % of the silicon

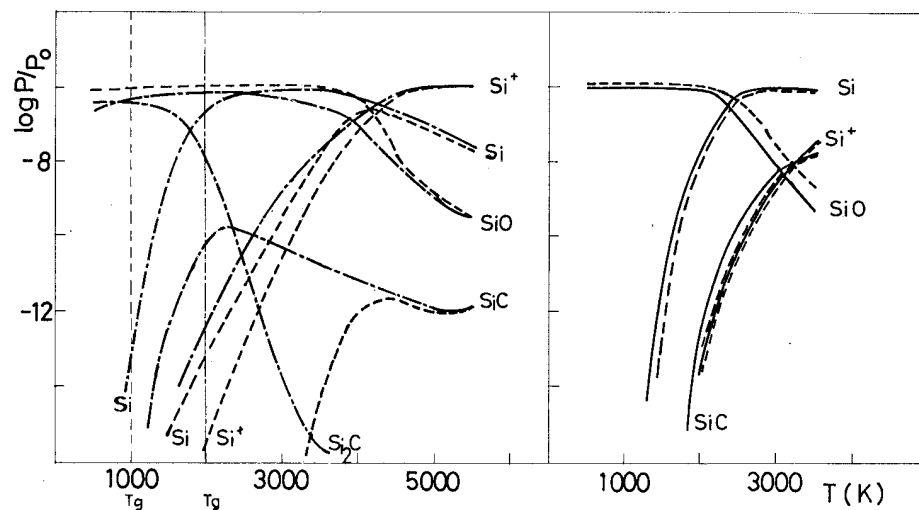


Fig. 5. Partial pressures of silicon containing species in the Ar/O<sub>2</sub>/C/Si gas system, as functions of temperature. Left: single-phase calculation; dashed lines: C/O = 0.96; dash-dotted lines: C/O = 1. Right: two-phase model; solid lines: 1% O; dashed lines: 4% O.

is in the atomic and 50 % in the SiO form. At higher temperatures, the concentrations of silicon carbides, Si<sub>2</sub>C and SiC, are relatively low (that of SiC also at lower temperatures). An excess of oxygen (C/O = 0.96) favours the formation of SiO, and the silicon becomes considerably atomized (>60 %) only at temperatures higher

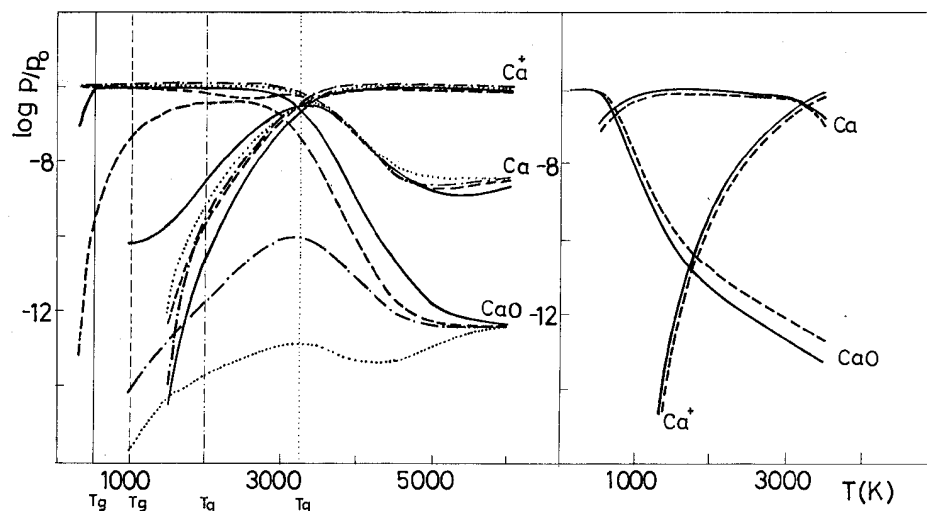


Fig. 6. Partial pressures of calcium containing species in the Ar/O<sub>2</sub>/C/Ca gas system, as functions of temperature. Left: single-phase calculation; solid lines: C/O = 0.5; dashed lines: C/O = 0.96; dash-dotted lines: C/O = 1; dotted lines: C/O = 2. Right: two-phase model; solid lines: 1% O; dashed lines: 4% O.



than 4000 K. On the other hand, at  $T < 3000$  K calcium is present predominantly in the atomic form if  $C/O > 1$ , and in form of CaO if oxygen is present in excess (Fig. 6). The atomization temperatures of calcium (as well as of boron and silicon) at all the C/O ratios considered are presented in Table II. At temperatures higher than 3000 K, calcium is mainly present as the  $Ca^+$  ion.

Ar/O<sub>2</sub>/C/X (X = B, Si and Ca) considered as a two-phase system.

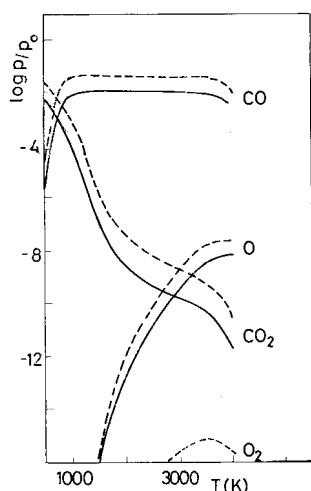


Fig. 7. Partial pressures of the main components of the Ar/O<sub>2</sub>/C gas systems in equilibrium with solid carbon, as functions of temperature. Solid lines: 1 % O, dashed lines: 4 % O.

The equilibrium partial pressures of the main components of the Ar/O<sub>2</sub>/C/X system, treated as a gas phase system in equilibrium with solid graphite, are presented in Fig. 7. The results, corresponding to two different total amounts of

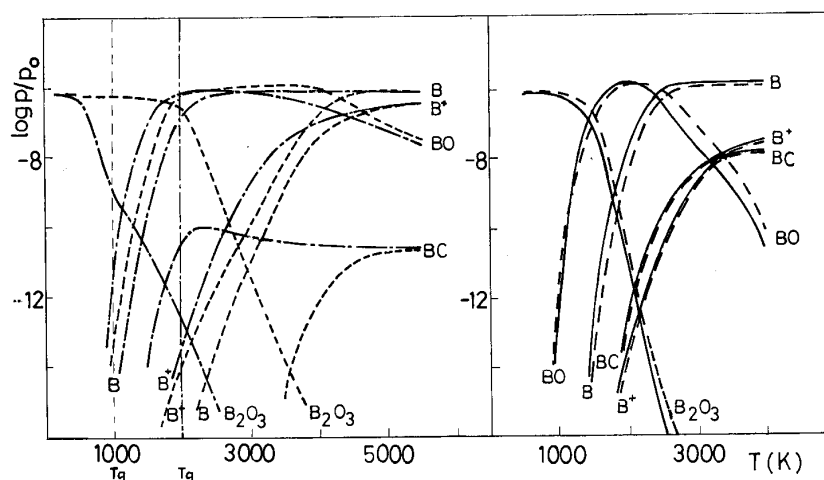


Fig. 8. Partial pressures of boron containing species in the Ar/O<sub>2</sub>/C/B gas system, as functions of temperature. Left-hand side: single-phase calculation; dashed lines: C/O = 0.96; dash-dotted lines: C/O = 1. Right-hand side: two-phase model; solid lines: 1 % O; dashed lines: 4 % O. Note that the content of the left-hand side is also included in Figs. 3 and 4.

oxygen (1 % and 4 %), show that in the low-temperature region ( $T < 1000$  K) the most abundant species is  $\text{CO}_2$ , whereas the dominating compound at higher temperatures, (1000–4000 K) is CO. The temperature dependence of the partial pressures of boron, silicon and calcium compounds are presented in Figs. 8, 5 and 6 (right-hand sides), respectively. Analogous calculations on the  $\text{Ar}/\text{O}_2+\text{N}_2/\text{C}/\text{X}$  systems, with the O/N ratio corresponding to that in air, gave similar results for most of the compounds involving the trace elements. The main difference caused by the presence of nitrogen is that  $\text{N}_2$  becomes one of the dominating compounds over a wide temperature region (500–3500 K); at temperatures higher than 2500 K, CN and  $\text{C}_2\text{N}$  reach considerable concentrations, continuously increasing with increasing temperature.

#### DISCUSSION AND CONCLUSIONS

Over a wide temperature region, 1000–3500 K, the most abundant component of the  $\text{Ar}/\text{O}_2/\text{C}/\text{X}$  gas system (at the ratios of total amounts of the components as assumed in the present study) in equilibrium with solid carbon is the CO molecule – only at temperatures below 1000 K does the  $\text{CO}_2$  molecule predominates. Consequently, the ratio of the total amounts of carbon and oxygen in the gas phase at temperatures between 1000 and 3500 K is about one. This means that the presence of oxygen in the gas phase favours the process of carbon evaporation until practically all the available oxygen is bound into CO ( $\text{CO}_2$  at low temperatures). The precise C/O ratios resulting from the two-phase model calculations are presented in Table III. The results given in this Table show that the above statements remain valid if oxygen is replaced by an oxygen/nitrogen mixture.

TABELE III. C/O ratios resulting from the two-phase calculation model

T/K	C/O		
	AIR ( $\text{N}_2 + \text{O}_2$ )	1 % O	4 % O
298	0.4999	0.4999	0.5000
500	0.5003	0.5001	0.5000
1000	0.9944	0.9943	0.9796
1500	0.9996	0.9998	0.9999
2000	0.9999	0.9999	1.0000
2500	1.0026	1.0002	1.0000
3000	1.1795	1.0904	1.0233
3500	10.152	8.6861	2.9784
4000	650.48	623.00	160.98

The computed partial pressures of oxygen in atomic and molecular forms are quite low (see Fig. 7 and Table IV), but the calculations show that boron, silicon and calcium oxides are nevertheless formed in considerable amounts. The atomization temperatures of B and Si obtained in the framework of the two-phase model

(Table II) are in agreement with the corresponding experimentally estimated values,<sup>2,6</sup> while the theoretical result for Ca is an underestimation of its experimentally determined value. The same results for the atomization temperatures of B, Si and Ca are obtained in the calculations in which the presence of air instead of oxygen is assumed.

TABELE IV. Partial pressures (in atm) of oxygen in atomic and molecular forms obtained using the two-phase (tp) and single-phase (sp) calculation models

$T/K$	(tp) 1% O		(sp) C/O = 0.5		(sp) C/O = 0.96		(sp) C/O = 1	
	O	O <sub>2</sub>	O	O <sub>2</sub>	O	O <sub>2</sub>	O	O <sub>2</sub>
1500	$1.0 \times 10^{-16}$	$1.0 \times 10^{-21}$	$3.5 \times 10^{-6}$	$1.0 \times 10^{-8}$	$8.2 \times 10^{-13}$	$4.1 \times 10^{-14}$	$8.0 \times 10^{-20}$	$4.0 \times 10^{-28}$
2000	$2.5 \times 10^{-13}$	$1.0 \times 10^{-19}$	$1.0 \times 10^{-5}$	$1.6 \times 10^{-4}$	$3.7 \times 10^{-8}$	$3.1 \times 10^{-9}$	$1.2 \times 10^{-14}$	$3.3 \times 10^{-22}$
2500	$1.9 \times 10^{-11}$	$2.0 \times 10^{-18}$	$5.6 \times 10^{-4}$	$1.0 \times 10^{-3}$	$2.1 \times 10^{-5}$	$2.1 \times 10^{-6}$	$3.5 \times 10^{-11}$	$5.9 \times 10^{-18}$
3000	$4.0 \times 10^{-10}$	$1.6 \times 10^{-17}$	$3.0 \times 10^{-3}$	$1.0 \times 10^{-3}$	$3.0 \times 10^{-4}$	$7.2 \times 10^{-6}$	$4.0 \times 10^{-8}$	$1.2 \times 10^{-13}$
3500	$3.8 \times 10^{-9}$	$6.2 \times 10^{-17}$	$4.0 \times 10^{-3}$	$1.0 \times 10^{-4}$	$3.9 \times 10^{-4}$	$6.3 \times 10^{-7}$	$3.3 \times 10^{-6}$	$4.5 \times 10^{-11}$

The atomization temperatures of B, Si and Ca obtained in the single-phase computation model (Table II) are highly dependent on the assumed ratio of the total carbon and total oxygen amounts. They increase with increasing partial pressures of atomic and molecular oxygen, presented in Table IV for C/O ratios of 0.5, 0.96 and 1.0. The increase of the atomization temperatures in presence of oxygen is a consequence of the fact that the temperature region in which the oxides of the investigated elements appear is extended considerably to higher values [up to 4000 K, see Figs. 8, 5 and 6 (left-hand sides) and Table II], even in the case of a slight excess of oxygen (C/O = 0.96) for B and Si, and at C/O = 0.5 for Ca. In a gas mixture with oxygen but without carbon (Ar/O/X), the atomization temperatures of Si and B should be about 5000 K.

The results obtained in the framework of the two-phase model are generally similar, particularly in the temperature range  $1000 < T < 3500$  K, to those generated in the single-phase calculations with the ratio C/O = 1.

According to some previous studies<sup>4,8</sup> there are strong reasons, based on experimental evidence, to believe that the heterogeneous equilibrium ( $C_s \rightarrow C_g$ ) is completed at temperatures higher than 2100 K. If this is really true, the two-phase computation model should be reliable for all temperatures higher than 2100 K. On the other hand, the one-phase computations of the present paper correspond to experiments carried out in a graphite furnace in presence of CO (C/O = 1), CO<sub>2</sub> (C/O = 0.5) and oxygen, if equilibrium between the gas and the solid phase is not established. In this way, the agreement or disagreement of the results of our calculations with the corresponding experimental findings offers a possibility to derive conclusions concerning the existence or nonexistence of equilibrium in the systems considered. According to the results of the calculations in the framework

of the single-phase model, an increase in the O/C ratio is followed by an increase of the oxygen ( $O_2$  and O) partial pressure (Fig. 2), which favours oxide formation and moves the atomization curves and atomization temperatures of the trace elements (B, Si and Ca, Figs. 3, 4, 5, 6 and 8) to higher values, in some proportion to the O/C ratio. Fig. 3 shows that at  $T = 2500$  K and  $C/O = 2$  boron is completely atomized: at the same temperature and  $C/O = 1$ , 40 % of the boron is atomized, while the percentages of atomized boron at  $C/O = 0.96$  and  $C/O = 0.5$  and  $T = 2500$  K are negligibly small ( $1.6 \times 10^{-4}$  % and  $5 \times 10^{-10}$  %, respectively). Similar results were obtained for silicon. These results are in agreement with the experimentally found<sup>3,7</sup> depression of the atomic absorbance signal of Si and B in the presence of  $O_2$ , CO and  $CO_2$ , detected at a graphite furnace temperature of 2400 K. The complete suppression of the atomic absorbance signal in presence of  $CO_2$  and the depression of about 65 % in the presence of  $CO_2$ , stated in Ref. 7, are also in agreement with the present calculations.

The general result of the present study is that the form in which the trace elements exist in the graphite furnace is very sensitive to the absolute and relative amounts of impurities, such as carbon and oxygen. Already a small excess of oxygen relative to carbon should cause an increase in the atomization temperatures of B and Si due to the formation of silicon and boron oxides over a large temperature region. On the other hand, an increase of the C/O ratio ( $C/O > 1$ ) favours atomization, but also carbide formation (e.g.,  $Si_2C$ ) in the lower temperature regions.

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#### ИЗВОД

#### ФОРМИРАЊЕ МОЛЕКУЛА КОЈИ САДРЖЕ БОР, СИЛИЦИЈУМ И КАЛЦИЈУМ У $Ar/O_2$ СМЕШАМА У ГРАФИТНОЈ ПЕЋИ

ЈЕЛЕНА РАДИЋ-ПЕРИЋ и МИЛАН МАРКИЋЕВИЋ

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Састав  $Ar/O_2/C$  гасног система у присуству B, Si и Ca у траговима израчунат је под претпоставком постојања термалне равнотеже у температурској области 500–5500 K. Узето је да је концентрација кисеоника 1–4 %. Извршене су две врсте прорачуна. У првој је занемарено присуство чврсте фазе (графита) и систем је третиран као једнофазни гасни систем при различитим односима C/O (0,5; 0,96; 1 и 2). У другом низу прорачуна узето је у обзир присуство чврсте фазе и добивен је састав гасне фазе у равнотежи с чврстим угљеником, при  $p = 1$  атм. Резултати прорачуна показују да је равнотежни састав, специјално концентрација различитих једињења у којима се јављају елементи присутни у траговима, врло осетљив на количине и односе количина кисеоника и угљеника. Повећање односа O/C има за последицу повећање парцијалног притиска молекулског и атомског кисеоника, што фаворизује грађење оксида елемената у траговима и помера њихове температуре атомизације ка вишим вредностима. Нађено је да у релативно широкој области температура ( $1000 < T < 3500$  K) састав  $Ar/O_2/C/X$  ( $X = B, Si, Ca$ )

система са упоредивим количинама кисеоника и угљеника ( $C/O = 1$ ) не зависи битно од присуства чврсте фазе. Резултати рачуна омогућавају разумну интерпретацију бројних експеримената извршених на сличним системима.

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