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**THERMOCHEMICAL STABILITY DIAGRAMS FOR  
CONDENSED PHASES AND TABULATION OF VOLATILE SPECIES  
OVER CONDENSED PHASES FOR THIRTEEN METAL-OXYGEN-  
SILICON SYSTEMS AT 1000 AND 1250 K**

January 31, 1989

Final Report - Volume II

Prepared by:

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under

Subcontract Number 19X-43346-C

Program Manager: R. R. Judkins

for

OAK RIDGE NATIONAL LABORATORY  
Oak Ridge, Tennessee 37831  
operated by  
MARTIN MARIETTA ENERGY SYSTEMS, INC.  
for the  
U.S. DEPARTMENT OF ENERGY  
under Contract No. DE-AC05-48OR21400

Printed in the United States of America. Available from  
National Technical Information Service  
U.S. Department of Commerce  
5285 Port Royal Road, Springfield, Virginia 22161  
NTIS price codes - Printed Copy: A05 Microfiche A01

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## ABSTRACT

Thermochemical stability diagrams for oxide and silicide phases in mixed oxidation and silicide forming reactions are useful for the interpretation of the high temperature oxidation reactions which occur. In addition an analysis of the volatile metal and oxide species which develop at the several interfaces are useful in a complete analysis of high temperature oxidation.

This work begins with a literature survey of the high temperature oxidation of metal silicides. The major part of the report is a description of the stability diagrams and the volatile species in the Ca-O-Si, C-O-Si, Fe-O-Si, Mn-O-Si, Mo-O-Si, Ni-O-Si, Nb-O-Si, Ta-O-Si, Ti-O-Si, V-O-Si, W-O-Si and Zr-O-Si systems.

Log  $p_{O_2}$  vs log  $a_{Si}$  diagrams are developed to show the stability regions for the several metal, oxide and silicide phases for 1250K. For the Cr-O-Si, Fe-O-Si and Ni-O-Si systems diagrams are developed also for 1000K.

The importance of forming an  $SiO_2(s)$  film, the volatility of metal and oxide species, the melting points of the condensed phases and the formation of  $SiO(g)$  are discussed with regard to the high temperature oxidation of the metal silicides.

Key words:  $SiO_2$  film, Metal-Oxygen-Silicon, Thermochemical Stability diagram, Volatile species.

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## 1.0 INTRODUCTION

The reaction of metal-silicon alloys, particularly metal silicides with oxygen is of scientific and technical importance. This interest started from the use of compounds such as  $\text{MoSi}_2$  as high temperature heating elements and later from the use of silicide coatings to protect refractory metals from oxidation. More recently particularly in Europe, silicide coatings have been used on superalloys. Thin films of silicides on silicon and silica are finding increased uses as interconnects in microelectronic devices since they have higher electrical conductivity than polycrystalline silicon and can be oxidized to form a passive silica film.

In these applications the oxidation behavior varies greatly for bulk silicides and silicide coatings. The behavior of the latter depends strongly on the nature of the substrate under the coatings.

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## 2.0 Literature

The early work on the silicides, the crystal chemistry of the binary silicides, the two metal silicides and the properties and application of silicides was reviewed by Goldschmidt<sup>(1)</sup> in 1967. More recent work on the oxidation behavior will be briefly reviewed in the following.

### 2.1 Refractory Metal Silicides in High Temperature Applications

Monolithic  $\text{MoSi}_2$  heating elements initially form  $\text{SiO}_2$  and Mo-oxides but the latter evaporates leaving a protective  $\text{SiO}_2$  film. This film results in usable lives in excess of 2000 hr at  $1650^\circ\text{C}$ <sup>(2)</sup>. Similarly, disilicide coatings formed on refractory metals such as Mo can provide improved oxidation resistance due to the formation of a  $\text{SiO}_2$  film. In this case, however, removal of Si to form the oxide results in conversion of the disilicide to a lower silicide immediately below the oxide. For example,  $\text{Mo}_5\text{Si}_3$  forms between a  $\text{SiO}_2$  scale and  $\text{MoSi}_2$ <sup>(2)</sup> and (Nb, W)  $\text{Si}_2$  in complex silicided coatings on Nb-alloys is converted to (Nb, W)<sub>5</sub>  $\text{Si}_3$  during oxidation<sup>(3)</sup>. The lower silicides of the refractory metals are generally found to be unable to maintain protective  $\text{SiO}_2$  films, presumably due to the reduced activity of Si.

The refractory metal silicides are also subject to degradation by silicide "pest" attack<sup>(2)</sup>. This form of degradation, which is associated with the penetration of oxidant into the silicide, becomes severe at intermediate temperatures. Thus complex disilicides on Ta-W alloys are degraded at extremely rapid rates in air at  $870^\circ\text{C}$  while they remain very protective at temperatures well above  $1000^\circ\text{C}$ <sup>(4)</sup>.

### 2.2 Silicide Coatings on Superalloys

Some of the silicides of Ni and Fe are extremely resistant to oxidation due to the formation of an  $\text{SiO}_2$  film. For example,  $\text{Ni}_2\text{Si}$  shows oxidation rates

comparable with  $\text{Al}_2\text{O}_3$  - forming alloys<sup>(5)</sup> and  $\text{Fe}_3\text{Si}$  oxidizes slower in air than  $\text{Cr}_2\text{O}_3$  - forming alloys such as ferritic stainless steels<sup>(6,7)</sup>. The preparation of silicide coatings on Ni - or Fe - base alloys by pack cementation is difficult. However,  $\text{CrSi}_2$  -  $\text{NiSi}_2$  coatings have been successfully applied to Ni-base superalloys by a slurry fusion technique<sup>(7)</sup>. Such coatings have exhibited slow oxidation rates at  $1000^\circ\text{C}$ .

### 2.3 Thin Silicide Films in Microelectronic Devices

Thin silicide layers are being used as contacts and interconnections in silicon integrated circuit technology because they have lower electrical resistivity than polycrystalline silicon and are compatible with the silicon substrates. Also, the passivation of these films by oxidation to form  $\text{SiO}_2$  films has resulted in renewed interest in the oxidation properties of silicides. Oxidation behavior of the following silicides formed on a Si base recently has been reviewed<sup>(8)</sup>.

$\text{TiSi}_2$	$\text{FeSi}_2$	$\text{NiSi}$
$\text{ZrSi}_2$	$\text{Ru}_2\text{Si}_3$	$\text{NiSi}_2$
$\text{HfSi}_2$	$\text{CoSi}_2$	$\text{Pd}_2\text{Si}$
$\text{NbSi}_2$	$\text{RhSi}$	$\text{PdSi}$
$\text{TaSi}_2$	$\text{Rh}_3\text{Si}_4$	$\text{PtSi}$
$\text{CrSi}_2$	$\text{Ir}_3\text{Si}_3$	
$\text{MoSi}_2$	$\text{IrSi}_3$	
$\text{WSi}_2$		

Oxidation of silicide films on Si generally results in formation of  $\text{SiO}_2$  while the silicide layer is preserved by diffusion of Si from the underlying substrate. Only silicides for which the metal forms oxides considerably more stable than  $\text{SiO}_2$ , e.g.  $\text{ZrSi}_2$  and  $\text{HfSi}_2$ , are metal oxides formed in the films. Ternary phase diagrams describing the oxidation of the silicides of Mo, W, Ta, and Ti have recently been

calculated<sup>(9)</sup>. The oxidation data for the disilicides of these metals have been fitted to a linear-parabolic kinetic expression<sup>(10)</sup> similar to that derived by Deal and Grove<sup>(11)</sup> for pure Si.

$$x^2 + Ax = B(t + \tau)$$

where  $x$  is the oxide thickness,  $B$  is the parabolic rate constant,  $B/A$  is the linear rate constant, and  $\tau$  is a fitting parameter to account for initial oxide growth. The parabolic rate constants for the silicides were equal to those for pure Si while the linear rate constants were significantly higher for the silicides.

The oxidation of silicide films on  $\text{SiO}_2$  substrates leads to depletion of Si from the films followed by the appearance of metal oxides in the films as the Si activity decreases<sup>(8)</sup>.

#### 2.4 Thermochemical Stability Diagrams

In five<sup>(12-16)</sup> earlier reports we have developed thermochemical diagrams for the metals involved in nickel and cobalt based superalloys for the condensed and volatile species for the metal - oxygen - sulfur, metal - oxygen - carbon, metal oxygen - nitrogen and metal - oxygen - chlorine systems.

### 3.0 THERMOCHEMICAL ANALYSES

Standard Gibbs free energy data  $\Delta G_f^0$ , free energy data, f.e.f., and equilibrium constant data,  $\log K_p$ , are used to evaluate (1) the thermochemical stability of the several condensed metal, oxide and silicide phases as a function of temperature and the oxygen potential of the reactive gas and gas mixtures, (2) the oxidizing potential of the reactive gas and gas mixtures and (3) the equilibrium pressures of the volatile metal and oxide species over the condensed phases as a function of temperature and of the oxygen potentials of the gas mixtures.

Special diagrams have been developed to present the complex equilibria which occurs in gas-metal reactions at high temperature. For the condensed phases in the M-O-Si systems we use  $\log a_{Si}$  vs  $\log p_{O_2}$  diagrams. The equivalent  $\log p_{H_2}/p_{H_2O}$  values are added for  $\log p_{O_2}$ . The diagrams include  $\log a_{Si}$  and  $\log p_{O_2}$  conditions for forming  $SiO_2(s)$  films on the various alloys. The  $\log a_{Si}$  and  $\log p_{O_2}$  conditions also are given for forming  $SiO(g)$ . Maximum pressures of  $SiO(g)$  occur for the equilibria

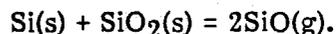


Table 1 and 2 shows details of the oxygen pressure of  $H_2/H_2O$  gas mixtures at several temperatures.

Table A1 and A2 of the Appendix gives the physical properties of the oxides and the silicides. Included are a listing of the condensed phases and volatile species.

Table A3 of the Appendix shows the thermochemical data for the oxide and silicide condensed phases of the thirteen elements of interest in this report together with their melting points and references. Data are given for 900, 1000, 1150, 1250, 1342 and 1450 K.

Table A-4 of the Appendix shows the thermochemical data for the H-O-Si system together with their melting points and references for the same temperatures as for Table A-3

An attempt will be made in this report to use thermochemical diagrams to give a clear and simple presentation of the thermochemical information on the various metal-oxygen-silicon systems. The diagrams only include compounds where thermochemical data are known.

TABLE 1

Reactive Gas Mixture				
<u>Gas Mixture</u>	<u>Equation</u>	<u>Equilibrium Expression</u>	<u>Log <math>k_p</math> at</u>	<u>T K</u>
			1150	1250
H <sub>2</sub> /H <sub>2</sub> O	H <sub>2</sub> (g) + $\frac{1}{2}$ O <sub>2</sub> (g) = H <sub>2</sub> O(g)	$\log p_{O_2} = k_p^{-2} (p_{H_2}/p_{H_2O})^{-2}$	8.373	7.467

TABLE 2

Oxygen Potential of Gas Mixture				
<u>Gas Mixture</u>	<u>1150K</u>	<u>1250K</u>	<u>1342K</u>	<u>1450K</u>
		log p <sub>O<sub>2</sub></sub> at TK		
H <sub>2</sub> /H <sub>2</sub> O = 1	-16.75	-14.93	-13.51	-12.05

#### 4.0 Volatile Species in Oxidation

Gulbransen and Jansson<sup>(17)</sup> have shown that volatile species are important in the high temperature oxidation of molybdenum, silicon and carbon. Six types of oxidation phenomena were identified: (1) at low temperature, diffusion of oxygen and metal species through a compact oxide and metal species through a compact oxide film, (2) at moderate and high temperatures a combination of oxide formation and oxide volatility, (3) at moderate and high temperatures, the formation of volatile species at the metal - oxide interface and rapid transport of the volatile species through cracks and defects in the oxide layer, (4) at high temperature the direct formation of volatile species without oxide film formation, (5) at high temperature, gaseous diffusion of oxygen through a barrier layer of volatilized oxide vapors and (6) at high temperatures, spalling of metal and oxide particles.

In addition if the oxide melts, the oxide may drop off. Rapid transport of oxygen to the metal by convection can occur if liquid oxide is formed.

For alloys where  $\text{SiO}_2$  films are formed volatile species can play an additional role. (1)  $\text{SiO}(\text{g})$  can form by reaction of the silicide  $\text{M}_x\text{Si}_y$  with the  $\text{SiO}_2(\text{s})$  film. This  $\text{SiO}(\text{g})$  can diffuse to cracks and defects in the  $\text{SiO}_2(\text{s})$ , film react with oxygen, and heal the crack or defect. Loss of adhesion may also occur by this reaction.

## 5.0 RESULTS AND DISCUSSION

### 5.1 The Calcium - Oxygen - Silicon System

#### 5.1.1. Phase Diagram Information

Three oxides are reported, CaO, CaO<sub>2</sub> and CaO<sub>4</sub><sup>(18, 19, 21)</sup>. CaO has a melting temperature of 2898K. Ca-CaO forms a eutectic at 0.15 a/o oxygen with a melting temperature of 1107K. The solubility of oxygen in liquid Ca is 10 a/o at 1623K<sup>(20)</sup>.

Three silicides are reported<sup>(21, 22)</sup> Ca<sub>2</sub>Si, CaSi and CaSi<sub>2</sub>. The melting temperature of CaSi is given as about 1518K. A recent survey<sup>(23)</sup> shows no CaSi phase.

#### 5.1.2. Thermochemical Diagram Condensed Phases 1250K.

Table 3 shows the chemical equations for equilibria over the four condensed phases in the Ca-O-Si system.

Figure 1 shows the log a<sub>Si</sub> vs log pO<sub>2</sub> diagram. Ca(l) is the stable phase for log pO<sub>2</sub> ≤ -42.18 and log a<sub>Si</sub> ≤ -7.48. Ca<sub>2</sub>Si(s) is formed for log a<sub>Si</sub> = -7.48 to -3.312 and for log pO<sub>2</sub> = -42.18 to -38.0. CaSi(s) is formed for log a<sub>Si</sub> = 3.312 to 0 and for log pO<sub>2</sub> = -38.0 to -31.4. CaSi<sub>2</sub>(s) is not formed for log a<sub>Si</sub> ≤ 0.

The line at the top of the diagram labelled Si(s) is for log a<sub>Si</sub> = 0. Here the equilibrium pressure of silicon is the vapor pressure. At 1250K log p<sub>Si</sub> = -11.111 atm.

CaO(s) forms over a wide range of log pO<sub>2</sub> values from log pO<sub>2</sub> = -42.18 to 0. The heavy diagonal line marked SiO<sub>2</sub>(s) shows the log a<sub>Si</sub> and log pO<sub>2</sub> values for forming SiO<sub>2</sub>(s).

TABLE 3

---

Chemical Equations for the Condensed Phases in the Ca-O-Si Systems.

Si(s) and O<sub>2</sub>(g) Reactions 900° to 1450K

---

1. Equilibrium over Ca(l)
  - a.  $\text{Ca(l)} + \frac{1}{2} \text{O}_2\text{(g)} = \text{CaO(s)}$
  - b.  $2 \text{Ca(l)} + \text{Si(s)} = \text{Ca}_2\text{Si(s)}$
2. Equilibria over CaO(s)
  - a. Same as 1a.
  - b.  $2 \text{CaO(s)} + \text{Si(s)} = \text{Ca}_2\text{Si(s)} + \text{O}_2\text{(g)}$
  - c.  $\text{CaO(s)} + \text{Si(s)} = \text{CaSi(s)} + \frac{1}{2} \text{O}_2\text{(g)}$
3. Equilibria over Ca<sub>2</sub>Si
  - a. Same as 1b.
  - b. Same as 2b.
  - c.  $\text{Ca}_2\text{Si(s)} + \text{Si(s)} = 2 \text{CaSi(s)}$
4. Equilibria over CaSi
  - a. Same as 2c.
  - b. Same as 3c.

CaO(s) is the stable oxide which forms on the two silicides. The light dashed lines are for the equilibria of  $\text{Si(s)} + \frac{1}{2}\text{O}_2(\text{g}) = \text{SiO(g)}$ . Lines are drawn for  $\log p_{\text{SiO}} = -7$  and  $-10$ .

The lower triple point is shown at A where Ca(l) is in equilibrium with CaO(s) and Ca<sub>2</sub>Si(s). The point A' is the triple point for an alloy where calcium is present at  $\log a_{\text{Ca}} = -2$ .

SiO(g) is not an important volatile specie in the Ca-O-Si system since SiO<sub>2</sub>(s) is not formed in the system and the silicides cannot react with CaO(s) to form SiO(g).

Table 4 shows the important thermochemical information for the Ca-O-Si system at 1250K. Included are the volatile species formed at the various interfaces and the possible silicon reactions with CaO(s). Ca(g) is the major volatile specie in the system.

TABLE 4

Summary Ca-O-Si System		1250K
1. Oxide	CaO(s)	
2. Lower triple point	$\log p_{O_2} = -42.18, \log a_{Si} = -7.48$	
3. Volatile Species		
	<u>Interface</u>	<u>Species</u> <u>Log p (atm.)</u>
a.	Si(log a = -3.312)/SiO <sub>2</sub> (s)	SiO <sub>2</sub> Not Formed                      ---
b.	Ca(l)/CaO(s)	Ca(g)                                      -1.927
		CaO(g)                                    -19.38
c.	CaO(s)/O <sub>2</sub> 1 atm	Ca(g)                                      -23.02
		CaO(g)                                    -19.38
4. Silicon Reactions	Log a <sub>Si</sub> = 0	
a.	Si(s) + 2 CaO(s) = 2 Ca(l) + SiO <sub>2</sub> (s)	log K <sub>R</sub> = -13.46
b.	Si(s) + CaO(s) = Ca(l) + SiO(g)	log K <sub>R</sub> = -12.412

## 5.2 The Carbon - Oxygen Silicon System

### 5.2.1. Phase Diagram Information

Two gaseous oxides  $\text{CO}(\text{g})$  and  $\text{CO}_2(\text{g})$  are formed<sup>(24)</sup>.

One silicide  $\text{CSi}(\text{s})$  is formed<sup>(21)</sup>. The decomposition temperature is given as about 2973K. A recent survey<sup>(23)</sup> gives a melting temperature of 2818K. The solubility of C in  $\text{Si}(\text{s})$  at 1633K is 1.40 a/o<sup>(19)</sup>.  $\text{CSi}$  exists in many different crystal forms<sup>(19, 21)</sup>.

### 5.2.2 Thermochemical Diagram Condensed Phases 1250K.

Figure 2 shows the  $\log a_{\text{Si}}$  vs  $\log p_{\text{O}_2}$  diagram. For  $\text{CO}(\text{g})$  at  $\log p_{\text{CO}} = 0$   $\text{C}(\text{s})$  is the stable phase for  $\log a_{\text{Si}} \leq -2.654$  and  $\log p_{\text{O}_2} \leq -18.566$ .  $\text{SiC}(\text{s})$  is formed for  $\log a_{\text{Si}} \geq -2.654$  to 0.00 and for  $\log p_{\text{O}_2} = -18.566$  to  $-13.25$ . Lines are also shown for the existence of the  $\text{C}(\text{s})$  and  $\text{SiC}(\text{s})$  phases for  $\log p_{\text{CO}} = -2, -4$  and  $-6$ .

The  $\text{SiO}_2(\text{s})$  line shows that a  $\text{SiO}_2(\text{s})$  film is formed on  $\text{SiC}(\text{s})$  for  $\log p_{\text{CO}} = 0$  and  $-2$ . For  $\log p_{\text{CO}} = -6$  and  $\text{SiO}_2(\text{s})$  film is formed for  $\log a_{\text{Si}} > -1$  and no  $\text{SiO}_2(\text{s})$  film for  $\log a_{\text{Si}} < -7$ .

The lower triple point is shown at A. Table 5 shows the important thermochemical information for  $\text{SiC}(\text{s})$  at 1250K. Included are the volatile species at the  $\text{SiC}(\text{s}) - \text{C}(\text{s})$  interface for several pressures of  $\log p_{\text{CO}}$ .  $\text{CO}(\text{g})$  and  $\text{SiO}(\text{g})$  are the important volatile species. The formation of an  $\text{SiO}_2(\text{s})$  film depends on  $\log p_{\text{CO}}$ . Removal of the  $\text{CO}(\text{g})$  surrounding the  $\text{SiC}(\text{s})$  sample can lead to the reaction of  $\text{SiC}(\text{s})$  with  $\text{SiO}_2(\text{s})$  to form  $\text{SiO}(\text{g})$  and active oxidation.

TABLE 5

---

 Summary C - O - Si System      1250K.
 

---

1. Oxide       $\text{SiO}_2$ 2. Lower triple point  $\log p_{\text{O}_2} = -18.566$ ,  $\log a_{\text{Si}} = -2.654$ 

3. Volatile Species

	<u>Interface</u>	<u>Species</u>	<u>Log p (atm.)</u>
a.	Si( $\log a = -2.654$ )/ $\text{SiO}_2(\text{s})$ $\log p_{\text{CO}} = 0$	SiO(g)	-7.00
b.	Si( $\log a = -2.654$ )/ $\text{SiO}_2(\text{s})$ $\log p_{\text{CO}} = -2$	SiO(g)	-7.00
c.	Si( $\log a = -2.654$ )/ $\text{SiO}_2(\text{s})$ $\log p_{\text{CO}} = -4$	SiO <sub>2</sub> Not Formed SiO(g)	-7.00

### 5.3 The Chromium - Oxygen - Silicon System

#### 5.3.1 Phase Diagram Information

Four condensed oxides exist,  $\text{Cr}_2\text{O}_3$ <sup>(21)</sup>,  $\text{CrO}_2$ <sup>(18)</sup>,  $\text{CrO}_3$ <sup>(18, 25)</sup> and  $\text{CrO}_6$ <sup>(25)</sup>. The highest melting temperature for  $\text{Cr}_2\text{O}_3$  is given as 2697K.  $\text{CrO}_6$  has a melting temperature of 470K.  $\text{CrO}_2$  is reported to be stable at an oxygen partial pressures greater than 100 bars<sup>(18)</sup>.  $\text{CrO}_3$  has a melting temperature of about 453K. The O solubility in Cr is reported as 0.0025 a/o at 1373K and 0.043 a/o at 1773K<sup>(19)</sup>.

Four condensed silicides are reported<sup>(22, 23)</sup>  $\text{Cr}_3\text{Si}$ ,  $\text{Cr}_5\text{Si}_3$ ,  $\text{CrSi}$ , and  $\text{CrSi}_2$ . The following approximate melting points are given;  $\text{Cr}_3\text{Si}$  -2003K,  $\text{CrSi}$  -1873K and  $\text{CrSi}_2$  -1823K.

#### 5.3.2 Thermochemical Diagrams Condensed Phases 1250K.

Figure 3 shows the  $\log a_{\text{Si}}$  vs  $\log p_{\text{O}_2}$  diagram. Cr(s) is the stable phase for  $\log p_{\text{O}_2} \leq -22.48$  and  $\log a_{\text{Si}} \leq -4.263$ .  $\text{Cr}_3\text{Si}(s)$  is formed for  $\log a_{\text{Si}} = -4.263$  to  $-2.156$  and for  $\log p_{\text{O}_2} = -22.48$  to  $-21.50$ . Three additional silicides are formed for  $\log a_{\text{Si}}$  between  $-2.156$  and  $0.00$  and for  $\log p_{\text{O}_2} = -21.50$  to  $-18.187$ .

The line labelled  $\text{SiO}_2(s)$  shows  $\text{SiO}_2(s)$  is the stable oxide formed for  $\log a_{\text{Si}} > -6.05$  and  $\text{Cr}_2\text{O}_3(s)$  for  $\log a_{\text{Si}} < -6.05$ . The light dashed lines show the conditions for forming  $\text{SiO}(g)$  for  $\log p_{\text{SiO}} = -7$  and  $-10$ . At point B for the equilibrium between  $\text{CrSi}_2(s)$  and  $\text{CrSi}(s)$   $\log a_{\text{SiO}} = -6.07$  atm.

The lower triple point is shown at A. The point labelled A' is for an alloy with a Cr content of  $\log a_{\text{Cr}} = -2$ .

Table 6 shows the thermochemical information for the Cr-O-Si system at 1250K.  $\text{SiO}(g)$ ,  $\text{Cr}(g)$  and  $\text{CrO}_3(g)$  are the important volatile species.

Silicon can also react with  $\text{Cr}_2\text{O}_3(\text{s})$  to form  $\text{SiO}_2(\text{s})$  and  $\text{SiO}(\text{g})$  at  $\log p_{\text{SiO}} = -2.562$  atm.

Volatile species are important in the oxidation of Cr-Si alloys at 1250K;  $\text{Cr}(\text{g})$  by short circuiting normal diffusion processes,  $\text{CrO}_3(\text{g})$  by loss of  $\text{Cr}_2\text{O}_3$  and  $\text{SiO}(\text{g})$  by diffusion to cracks and defects in the  $\text{SiO}_2(\text{s})$  film where reaction with oxygen can occur and healing of the crack and defect.

TABLE 6

Summary Cr-O-Si System

1250K

1. Oxide  $\text{SiO}_2(\text{s})$   $\log a_{\text{Si}} > -6.05$ ,  $\text{Cr}_2\text{O}_3$   $\log a_{\text{Si}} < -6.05$ 2. Lower triple point  $\log p_{\text{O}_2} = -22.48$ ,  $\log a_{\text{Si}} = -4.263$ 

3. Volatile Species

	<u>Interface</u>	<u>Species</u>	<u>Log p (atm.)</u>
a.	Si( $\log a = -.774$ )/ $\text{SiO}_2(\text{s})$	SiO(g)	-6.069
b.	Cr(s)/ $\text{Cr}_2\text{O}_3$	Cr(g)	-8.96
		CrO(g)	-19.12
		CrO <sub>2</sub> (g)	-17.82
		CrO <sub>3</sub> (g)	25.08
c.	$\text{Cr}_2\text{O}_3/\text{O}_2$ (1 atm)	Cr(g)	-25.82
		CrO(g)	-13.50
		CrO <sub>2</sub> (g)	-11.90
		CrO <sub>3</sub> (g)	-8.22

4. Silicon Reactions  $\log a_{\text{Si}} = 0$ a.  $\text{Si}(\text{s}) + 2/3 \text{Cr}_2\text{O}_3(\text{s}) = 4/3 \text{Cr}(\text{s}) + \text{SiO}_2(\text{s})$   $\log K_{\text{R}} = 6.24$ b.  $\text{Si}(\text{s}) + 1/3 \text{Cr}_2\text{O}_3(\text{s}) = 2/3 \text{Cr}(\text{s}) + \text{SiO}(\text{g})$   $\log K_{\text{R}} = -2.562$

### 5.3.3 Thermochemical Diagram Condensed Phases 1000K

Figure 4 shows the  $\log a_{\text{Si}}$  vs  $\log p_{\text{O}_2}$  diagram. Cr(s) is the stable phase for  $\log a_{\text{Si}} < -5.366$  and  $\log p_{\text{O}_2} < -30.291$ .  $\text{Cr}_3\text{Si(s)}$  is formed where  $\log a_{\text{Si}} = -5.366$  to  $-2.488$  and  $\log p_{\text{O}_2} = -30.291$  to  $-29.01$ . Three additional silicides are formed  $\text{Cr}_5\text{Si}_3\text{(s)}$ ,  $\text{CrSi(s)}$  and  $\text{CrSi}_2\text{(s)}$  for  $\log a_{\text{Si}}$  between  $-2.488$  and  $0.00$  and  $\log p_{\text{O}_2} = -29.01$  to  $-24.819$ .

The  $\text{SiO}_2\text{(s)}$  line shows an  $\text{SiO}_2\text{(s)}$  film to form for  $\log a_{\text{Si}} > -8$  and a  $\text{Cr}_2\text{O}_3$  film to form for  $\log a_{\text{Si}} < -8$ . The light dashed lines show conditions for forming  $\text{SiO(g)}$  for  $\log p_{\text{SiO}} = -5$  and  $-10$ . At point B  $\log p_{\text{SiO}} = -9.29$ .

The lower triple point is shown at A. Point A' is the triple point for an alloy having a chromium content of  $\log a_{\text{Cr}} = -2$ .

Table 7 shows the thermochemical information for the Cr - O - Si system at 1000K. Neither Cr(g) or the  $\text{Cr}_x\text{O}_y\text{(g)}$  volatile species are important.  $\text{SiO(g)}$  with  $\log p_{\text{SiO}} = -9.29$  is of a very minor importance in the oxidation of Cr - Si alloys at 1000K.

TABLE 7

Summary Cr - O - Si System		1000K	
1. Oxide $\text{SiO}_2(\text{s})$ $\log a_{\text{Si}} > -8$ , $\text{Cr}_2\text{O}_3$ $\log a_{\text{Si}} < -8$			
2. Lower triple point $\log p_{\text{O}_2} = -30.291$ $\log a_{\text{Si}} = -5.366$			
3. Volatile Species			
	<u>Interface</u>	<u>Species</u>	<u>Log p (atm.)</u>
a.	$\text{Si}(\log a = -1.104)/\text{SiO}_2$	$\text{SiO}(\text{g})$	-9.29
b.	$\text{Cr}(\text{s})/\text{Cr}_2\text{O}_3$	$\text{Cr}(\text{g})$	-13.039
		$\text{CrO}(\text{g})$	-19.287
		$\text{CrO}_2(\text{g})$	-24.469
		$\text{CrO}_3(\text{g})$	-33.896
c.	$\text{Cr}_2\text{O}_3/\text{O}_2$ (1 atm)	$\text{Cr}(\text{g})$	-35.757
		$\text{CrO}(\text{g})$	-26.86
		$\text{CrO}_2(\text{g})$	-16.896
		$\text{CrO}_3(\text{g})$	-10.980
4. Silicon Reactions $\log a_{\text{Si}} = 0$			
a.	$\text{Si}(\text{s}) + 2/3 \text{Cr}_2\text{O}_3(\text{s}) = 4/3 \text{Cr}(\text{s}) + \text{SiO}_2(\text{s})$		$\log K_{\text{R}} = 7.859$
b.	$\text{Si}(\text{s}) + 1/3 \text{Cr}_2\text{O}_3(\text{s}) = 2/3 \text{Cr}(\text{s}) + \text{SiO}(\text{g})$		$\log K_{\text{R}} = -5.358$

## 5.4 Iron - Oxygen - Silicon System

### 5.4.1 Phase Diagram Information

Three condensed oxides are formed,  $\text{Fe}_{0.947}\text{O}$ ,  $\text{Fe}_3\text{O}_4$  and  $\text{Fe}_2\text{O}_3$ <sup>(24, 21, 18, 19)</sup>.  $\text{Fe}_{0.947}\text{O}$  has a melting temperature of 1650K and  $\text{Fe}_3\text{O}_4$  has a melting temperature of 1870K.  $\text{Fe}_2\text{O}_3$  decomposes above 1735K. The solubility of oxygen in  $\alpha$ -Fe is invariant with temperature, i.e. 0.0024 a/o at both 973 and 1153K. In  $\gamma$ -Fe at 1273K O solubility is  $1.3 \times 10^{-3}$  a/o<sup>(20)</sup>.

Four condensed silicides exist<sup>(21)</sup>,  $\text{Fe}_3\text{Si}$ ,  $\text{Fe}_5\text{Si}_3$ ,  $\text{FeSi}$  and  $\text{FeSi}_2$ . The melting temperature of  $\text{FeSi}$  is 1683K. The solubility of Si in Fe is 13.2 a/o and the solubility of Fe in Si is  $1.1 \times 10^{-8}$  a/o both at 1373K.

Thermochemical data only exists for the  $\text{Fe}_5\text{Si}_3$  and  $\text{FeSi}$  phases<sup>(26)</sup>.

### 5.4.2 Thermochemical Diagram Condensed Phases 1250K

Figure 5 shows the  $\log a_{\text{Si}}$  vs  $\log p_{\text{O}_2}$  diagram. Fe(s) is the stable phase for  $\log a_{\text{Si}} \leq -3.321$  and  $\log p_{\text{O}_2} \leq -15.32$  at 1250K.  $\text{Fe}_5\text{Si}_3(\text{s})$  is formed for  $\log a_{\text{Si}} = -3.321$  to  $-2.359$ .  $\log p_{\text{O}_2}$  has values of  $-15.32$  to  $-14.23$ .  $\text{FeSi}(\text{s})$  is formed for  $\log a_{\text{Si}} = -2.359$  to  $0$  and for  $\log p_{\text{O}_2} = -14.23$  to  $-10.59$ .

The  $\text{SiO}_2(\text{s})$  line shows that  $\text{SiO}_2(\text{s})$  is the stable oxide for all silicon activities shown.

The lower triple point is shown at A. Point A' is the triple point for an iron concentration of  $\log a_{\text{Fe}} = -2$ . The line labelled Si(s) is for  $\log a_{\text{Si}} = 0$ . Here the equilibrium pressure is the vapor pressure. At 1250K  $\log p_{\text{Si}} = -11.111$  atm. The dashed lines for  $\log p_{\text{SiO}}$  indicate a pressure for point B of  $\log p_{\text{SiO}} = -6.682$ .

Table 8 gives the thermochemical information for the Fe-O-Si system at 1250K. Included are the volatile species formed at the several interfaces and the possible silicon reactions with  $\text{Fe}_{0.947}\text{O}(\text{s})$ .  $\text{SiO}(\text{g})$  is the important

volatile specie in the system. Also silicon can react with  $\text{Fe}_{0.947}\text{O}(\text{s})$  to form  $\text{SiO}_2(\text{s})$  and  $\text{SiO}(\text{g})$ . The  $\text{SiO}(\text{g})$  can diffuse to cracks and defects in the  $\text{SiO}_2(\text{s})$  film and react with oxygen to repair the crack or defect.

TABLE 8

Summary Fe-O-Si System		1250K
1. Oxide	SiO <sub>2</sub> (s)	
2. Lower triple point	log p <sub>O<sub>2</sub></sub> = -15.32, log a <sub>Si</sub> = -3.321	
3. Volatile Species		
	<u>Interface</u>	<u>Species</u> <u>Log p (atm.)</u>
a.	Si(log a = -2.36)/SiO <sub>2</sub> (s)	SiO(g)                              -6.682
b.	Fe(s)/Fe <sub>0.947</sub> O(s)	Fe(g)                                -9.64
		FeO(g)                              -12.76
c.	Fe <sub>2</sub> O <sub>3</sub> (s)/O <sub>2</sub> (g)	Fe(g)                                -20.10
		FeO(g)                              -15.56
4. Silicon Reactions	Log a <sub>Si</sub> = 0	
a.	Si(s) + 2 Fe <sub>0.947</sub> O(s) = 1.894 Fe(s) + SiO <sub>2</sub> (s)	log K <sub>R</sub> = 13.40
b.	Si(s) + Fe <sub>0.947</sub> O(s) = 0.947 Fe(s) + SiO(g)	log K <sub>R</sub> = 1.08

### 5.4.3 Thermochemical Diagram Condensed Phases 1000K

Figure 6 shows the  $\log a_{\text{Si}}$  vs  $\log p_{\text{O}_2}$  diagram. Fe(s) is the stable phase for  $\log a_{\text{Si}} < -4.078$  and  $\log p_{\text{O}_2} < -20.842$ .  $\text{Fe}_5\text{Si}_3(\text{s})$  is formed where  $\log a_{\text{Si}} = -4.078$  to  $-3.223$  and  $\log p_{\text{O}_2} = -20.842$  to  $-19.942$ . One additional silicide is formed,  $\text{FeSi}(\text{s})$ , for  $\log a_{\text{Si}} = -3.223$  to  $0.00$  and for  $\log p_{\text{O}_2} = -19.942$  to  $-15.107$ .

The  $\text{SiO}_2(\text{s})$  line shows an  $\text{SiO}_2(\text{s})$  film forms on the iron silicides for all conditions shown on the diagram. The light dashed line is for  $\log p_{\text{SiO}} = -10$ . At point B for the  $\text{Fe}_5\text{Si}_3(\text{s}) - \text{FeSi}(\text{s})$  equilibria  $\log p_{\text{SiO}} = -10.90$ . The lower triple point is shown at A. The point labelled A' is the triple point for an alloy with an Fe content of  $\log a_{\text{Fe}} = -2$ .

Table 9 shows the important thermochemical data for 1000K. Included are the volatile species at the several interfaces and the silicon reactions with  $\text{Fe}_{0.947}\text{O}(\text{s})$ .

Volatile species do not play an important role in the oxidation of Fe-Si alloys at 1000K. The silicon reaction with  $\text{Fe}_{0.947}\text{O}(\text{s})$  to form  $\text{SiO}_2(\text{s})$  is favorable thermochemically. The reaction to form  $\text{SiO}(\text{g})$  gives  $\log p_{\text{SiO}} = -.634$ . The kinetics of this reaction at 1000K may be slow.

TABLE 9

Summary Fe-O-Si System		1000K
1. Oxide	SiO <sub>2</sub> (s)	
2. Lower triple point	log p <sub>O<sub>2</sub></sub> = -20.842, log a <sub>Si</sub> = -4.078	
3. Volatile Species		
	<u>Interface</u>	<u>Species</u> <u>Log p (atm.)</u>
a.	Si(log a = -3.223)/SiO <sub>2</sub> (s)	SiO(g)                              -10.90
b.	Fe(s)/Fe <sub>0.947</sub> O	Fe(g)                                -13.87
		FeO(g)                              -17.98
c.	Fe <sub>2</sub> O <sub>3</sub> (s)/O <sub>2</sub>	Fe(g)                                -28.55
		FeO(g)                              -22.24
4. Silicon Reactions	Log a <sub>Si</sub> = 0	
a.	Si(s) + 2 Fe <sub>0.947</sub> O(s) = 1.894 Fe(s) + SiO <sub>2</sub> (s)	log K <sub>R</sub> = 17.308
b.	Si(s) + Fe <sub>0.947</sub> O(s) = 0.947 Fe(s) + SiO(g)	log K <sub>R</sub> = -0.634

## 5.5 Manganese - Oxygen - Silicon System

### 5.5.1 Phase Diagram Information

Six condensed oxides are reported<sup>(19)</sup>. Thermochemical data exist<sup>(27)</sup> for MnO(s), Mn<sub>3</sub>O<sub>4</sub>(s) and Mn<sub>2</sub>O<sub>3</sub>(s). The melting temperature of MnO is 2115 ± 10K. At 1173K the homogeneity range of MnO is 47.4 - 52.4 a/o O. Mn<sub>3</sub>O<sub>4</sub> has a melting temperature of 1840 ± 4K. The homogeneity range for O in Mn<sub>3</sub>O<sub>4</sub> is from 57 to 58.4 a/o. Mn<sub>2</sub>O<sub>3</sub> exists in the temperature range of 873 -1073K and not above 1173K. MnO<sub>2</sub> converts to α - Mn<sub>2</sub>O<sub>3</sub> above 723K. From 873 -1213K Mn<sub>3</sub>O<sub>4</sub> reacts with MnO<sub>2</sub> to form Mn<sub>2</sub>O<sub>3</sub>. Above 1213K Mn<sub>2</sub>O<sub>3</sub> breaks down to Mn<sub>3</sub>O<sub>4</sub> and O<sub>2</sub>.

Seven condensed silicides exist<sup>(18)</sup>, Mn<sub>6</sub>Si, Mn<sub>9</sub>Si<sub>2</sub>, Mn<sub>3</sub>Si, Mn<sub>5</sub>Si<sub>2</sub>, Mn<sub>5</sub>Si<sub>3</sub>, MnSi and MnSi<sub>1.9</sub>. The melting temperature of Mn<sub>5</sub>Si<sub>3</sub> is given as 1558K and 1548K for MnSi. At 1333K the solubility of Si in β Mn is 16.7 a/o.

### 5.5.2 Thermochemical Diagram Condensed Phases 1250K.

Figure 7 shows the log a<sub>Si</sub> vs log p<sub>O<sub>2</sub></sub> diagram. Mn(s) is the stable phase for log a<sub>Si</sub> < -3.122 and log p<sub>O<sub>2</sub></sub> < -24.576 at 1250K. Mn<sub>5</sub>Si<sub>3</sub>(s) is formed where log a<sub>Si</sub> = -3.132 to -0.94. Log p<sub>O<sub>2</sub></sub> has values of -24.576 to -21.946. MnSi(s) and MnSi<sub>1.7</sub>(s) are formed for log a<sub>Si</sub> = -0.94 to 0 and for log p<sub>O<sub>2</sub></sub> = -21.946 to -19.258 at log a<sub>Si</sub> = 0.

The line labelled SiO<sub>2</sub>(s) indicates SiO<sub>2</sub>(s) to form for log a<sub>Si</sub> > -4.1 and MnO(s) for log a<sub>Si</sub> < -4.1. The light dashed lines are for log p<sub>SiO</sub> = -7 and -10. At point B log p<sub>SiO</sub> = -5.96 atm.

The lower triple point is shown at A. The point labelled A' is the triple point for a Mn-Si alloy with log a<sub>Mn</sub> = -2.

Table 10 gives the important thermochemical information for the Mn-O-Si system at 1250K. Included are the volatile species formed at the various interfaces and the silicon reactions with MnO(s) to form SiO<sub>2</sub>(s) and SiO(g). Mn(g) and SiO(g) are the important volatile species. The silicon reaction with MnO(s) to form SiO<sub>2</sub>(s) is favorable. The reaction to form SiO(g) gives a low pressure of SiO(g). Volatile species are very important in the oxidation of Mn-O-Si alloys at 1250K. SiO(g) can diffuse to cracks and defects to react with oxygen and heal the crack or defect. Mn(g) at  $\log p_{\text{Mn}} = -4.55$  is sufficiently high to play a major role in the oxidation of Mn-Si alloys.

TABLE 10

Summary Mn-O-Si System		1250K
1. Oxide $\text{SiO}_2$ $\log a_{\text{Si}} > -4.1$ , $\text{MnO}$ $\log a_{\text{Si}} < -4.1$		
2. Lower triple point $\log p_{\text{O}_2} = -24.576$ , $\log a_{\text{Si}} = -3.132$		
3. Volatile Species		
	<u>Interface</u>	<u>Species</u> <span style="float:right"><u>Log p (atm.)</u></span>
a.	$\text{Si}(\log a = -0.577)/\text{SiO}_2(\text{s})$	$\text{SiO}(\text{g})$ <span style="float:right">-5.96</span>
b.	$\text{Mn}(\text{s})/\text{MnO}$	$\text{Mn}(\text{g})$ <span style="float:right">-4.55</span>
		$\text{MnO}(\text{g})$ <span style="float:right">-12.96</span>
c.	$\text{Mn}_3\text{O}_4(\text{s})/\text{O}_2(\text{g})$ 1 atm	$\text{Mn}(\text{g})$ <span style="float:right">-17.83</span>
		$\text{MnO}(\text{g})$ <span style="float:right">-13.952</span>
4. Silicon Reactions $\log a_{\text{Si}} = 0$		
a.	$\text{Si}(\text{s}) + 2 \text{MnO}(\text{s}) = 2 \text{Mn}(\text{s}) + \text{SiO}_2(\text{s})$	$\log K_{\text{R}} = 4.144$
b.	$\text{Si}(\text{s}) + \text{MnO}(\text{s}) = \text{Mn}(\text{s}) + \text{SiO}(\text{g})$	$\log K_{\text{R}} = -3.61$

## 5.6 The Molybdenum - Oxygen - Silicon System

### 5.6.1 Phase Diagram Information

Two principal condensed oxides form<sup>(18)</sup>  $\text{MoO}_2(\text{s})$  and  $\text{MoO}_3(\text{s,l})$ . In addition  $\text{Mo}_3\text{O}$  and a series of oxides in the range of  $\text{Mo}_4\text{O}_{11}$  to  $\text{Mo}_{26}\text{O}_{75}$  are formed<sup>(18)</sup>.  $\text{MoO}_2$  has a melting temperature of 1068.4K. O solubility in Mo is reported to be about  $10^{-2}$  a/o at 1273K.

Three condensed silicides are formed  $\text{Mo}_3\text{Si}$ ,  $\text{Mo}_5\text{Si}_3$  and  $\text{MoSi}_2$ <sup>(28)</sup>. The melting temperature of  $\text{Mo}_5\text{Si}_3$  is given as  $2463 \pm 20\text{K}$  and the melting temperature of  $\text{MoSi}_2$  is given as  $2303 \pm 20\text{K}$ . The solubility of Si in Mo is about 7 a/o at  $2298 \pm 40\text{K}$ .

### 5.6.2 Thermochemical Diagram Condensed Phases 1250K

Figure 8 shows the  $\log a_{\text{Si}}$  vs  $\log p_{\text{O}_2}$  diagram.  $\text{Mo}(\text{s})$  is the stable phase for  $\log a_{\text{Si}} < -4.839$  and  $\log p_{\text{O}_2} < -15.344$ .  $\text{Mo}_3\text{Si}(\text{s})$  is formed where  $\log a_{\text{Si}} = -4.839$  to  $-3.882$ .  $\log p_{\text{O}_2}$  has values of  $-15.344$  to  $-15.025$ .  $\text{Mo}_5\text{Si}_3$  is formed for  $\log a_{\text{Si}}$  of  $-3.882$  to  $-1.974$  and for  $\log p_{\text{O}_2} = -15.025$  to  $-13.880$ .  $\text{MoSi}_2$  is formed for  $\log a_{\text{Si}}$  of  $-1.474$  to  $0.00$  and for  $\log p_{\text{O}_2} = -13.880$  to  $-10.028$ .

The line  $\text{SiO}_2(\text{s})$  shows that  $\text{SiO}_2(\text{s})$  is formed on Mo-Si alloys for  $\log a_{\text{Si}}$  from 0 to  $-13$ . Molybdenum oxides are not formed except where  $\log a_{\text{Si}} < -13.3$ .  $\text{SiO}(\text{g})$  pressures are shown by the light dashed lines for  $\log p_{\text{SiO}} = -7$  and  $-10$ . At point B where  $\text{MoSi}_2(\text{s})$  is in equilibrium with  $\text{Mo}_5\text{Si}_3(\text{s})$   $\log p_{\text{SiO}} = -6.67$ .

The lower triple point is shown at A on the Figure. The point A' is the triple point for an alloy where Mo is present at  $\log a_{\text{Mo}} = -2$ .

Table 11 shows the important thermochemical information. Included are the volatile species at the several interfaces and the silicon reactions with  $\text{MoO}_2(\text{s})$  to form  $\text{SiO}_2(\text{s})$  and  $\text{SiO}(\text{g})$ . Both reactions are feasible.

Volatile species are very important in the high temperature oxidation of molybdenum.  $\text{SiO}(\text{g})$  can diffuse to cracks and defects in the  $\text{SiO}_2(\text{film})$ , react with oxygen and repair the crack or defect. If breakdown of the  $\text{SiO}_2(\text{s})$  films occurs the highly volatile  $(\text{MoO}_3)_3(\text{g})$  forms which leads to a rapid oxidation of molybdenum.

TABLE 11

## Summary Mo-O-Si System 1250K

1. Oxide  $\text{SiO}_2$   $\log a_{\text{Si}} > -13.3$

2. Lower triple point  $\log p_{\text{O}_2} = -15.344$ ,  $\log a_{\text{Si}} = -4.839$

3. Volatile Species

	<u>Interface</u>	<u>Species</u>	<u>Log p (atm.)</u>
a.	Si( $\log a = -1.974$ )/ $\text{SiO}_2(\text{s})$	$\text{SiO}(\text{g})$	-6.67
b.	Mo(s)/ $\text{MoO}_2(\text{s})$	$\text{MoO}_3(\text{g})$	-10.97
		$\text{MoO}_2(\text{g})$	-12.75
		$(\text{MoO}_3)_3(\text{g})$	-14.18
		$\text{MoO}(\text{g})$	-18.55
		$\text{Mo}(\text{g})$	-19.69
c.	$\text{MoO}_3(\text{l})/\text{O}_2$ atm	$(\text{MoO}_3)_3(\text{g})$	-0.74
		$\text{MoO}_3(\text{g})$	-6.094
		$\text{MoO}_2(\text{g})$	-15.946
		$\text{MoO}(\text{g})$	-29.415
		$\text{Mo}(\text{g})$	-38.225

4. Silicon Reactions  $\log a_{\text{Si}} = 0$

a.  $\text{Si}(\text{s}) + \text{MoO}_2(\text{s}) = \text{Mo}(\text{s}) + \text{SiO}_2(\text{s})$   $\log K_{\text{R}} = 13.376$

b.  $\text{Si}(\text{s}) + 1/2 \text{MoO}(\text{s}) + \text{SiO}(\text{g})$   $\log K_{\text{R}} = 2.012$

## 5.7 The Nickel - Oxygen - Silicon System

### 5.7.1 Phase Diagram Information

Nickel oxide is the principal condensed oxide and it exists over the composition range of  $\text{NiO}_{1.002-1.32}$ <sup>(19)</sup>.  $\text{NiO(s)}$  has a melting temperature of 2257K.  $\text{NiO}_2$  can be prepared at high temperature and has a cubic structure. O solubility in nickel is about 0.07 a/o at 1273K<sup>(20)</sup>.

Six condensed silicides are formed<sup>(21)</sup>  $\text{Ni}_3\text{Si}$ ,  $\text{Ni}_5\text{Si}_2$ ,  $\text{Ni}_2\text{Si}$ ,  $\text{Ni}_3\text{Si}_2$ ,  $\text{NiSi}$  and  $\text{NiSi}_2$ . The melting temperatures of  $\text{Ni}_5\text{Si}_2$ ,  $\text{Ni}_2\text{Si}$  and  $\text{NiSi}$  are 1555, 1591 and 1265K respectively. The solubility of Ni in Si at 1273K is 0.28 or  $0.32 \times 10^{-3}$  a/o<sup>(18)</sup>.

### 5.7.2 Thermochemical Phase Diagram Condensed Phases 1250K

Figure 9 shows the  $\log a_{\text{Si}}$  vs  $\log p_{\text{O}_2}$  diagram.  $\text{Ni(s)}$  is the stable phase for  $\log a_{\text{Si}} < -6.305$  and  $\log p_{\text{O}_2} < -10.68$ .  $\text{Ni}_3\text{Si(s)}$  is formed for  $\log a_{\text{Si}} = -6.305$  to  $-5.44$  and  $\log p_{\text{O}_2}$  values of  $-10.68$  to  $-10.104$ . Three additional silicides are formed  $\text{Ni}_5\text{Si}_2\text{(s)}$ ,  $\text{Ni}_2\text{Si(s)}$  and  $\text{NiSi(s)}$  for  $\log a_{\text{Si}} = -5.44$  to  $0.00$  and for  $\log p_{\text{O}_2}$  values of  $-10.104$  to  $-3.77$ .

The  $\text{SiO}_2\text{(s)}$  line shows  $\text{SiO}_2\text{(s)}$  is the stable oxide for all  $\log a_{\text{SiO}}$  values in the diagram. The light dashed lines show  $\log p_{\text{SiO}}$  pressures of  $-7$  and  $-10$ . Point B represents  $\log p_{\text{SiO}}$  for the equilibrium between  $\text{SiO}_2\text{(s)}$  and the  $\log a_{\text{Si}}$  of the  $\text{NiSi(s)} - \text{Ni}_2\text{Si(s)}$  equilibria. Here  $\log p_{\text{SiO}} = -6.415$ .

Point A shows the lower triple point and point A' is the triple point for an alloy having a nickel content of  $\log a_{\text{Ni}} = -2$ .

Table 12 gives the thermochemical information for the system Ni-O-Si for 1250K. Included are the pressures of the volatile species at the several interfaces and the silicon reactions with  $\text{NiO(s)}$  to form  $\text{SiO}_2\text{(s)}$  and  $\text{SiO(g)}$ .

SiO(g) is an important volatile specie in the system. Also silicon can react with NiO(s) to form SiO<sub>2</sub>(s) and SiO(g).

SiO(g) can have a beneficial effect in high temperature oxidation by diffusing to defects and cracks and reacting with oxygen to repair the SiO<sub>2</sub>(s) film. Too extensive reaction at the interface may result in loss of adhesion.

TABLE 12

Summary Ni-O-Si System		1250K
1. Oxide $\text{SiO}_2(\text{s})$		
2. Lower triple point $\log p_{\text{O}_2} = -10.68, \log a_{\text{Si}} = -6.305$		
3. Volatile Species		
	<u>Interface</u>	<u>Species</u> <u>Log p (atm.)</u>
a.	$\text{Si}(\log a = -1.466)/\text{SiO}_2(\text{s})$	$\text{SiO}(\text{g})$ -6.415
b.	$\text{Ni}(\text{s})/\text{NiO}(\text{s})$	$\text{Ni}(\text{g})$ -9.97
		$\text{NiO}(\text{g})$ -12.88
c.	$\text{NiO}(\text{s})/\text{O}_2$ 1 atm	$\text{Ni}(\text{g})$ -15.31
		$\text{NiO}(\text{g})$ -12.88
4. Silicon Reactions $\log a_{\text{Si}} = 0$		
a.	$\text{Si}(\text{s}) + 2 \text{NiO}(\text{s}) = 2 \text{Ni}(\text{s}) + \text{SiO}_2(\text{s})$	$\log K_{\text{R}} = 18.04$
b.	$\text{Si}(\text{s}) + \text{NiO}(\text{s}) = \text{Ni}(\text{s}) + \text{SiO}(\text{g})$	$\log K_{\text{R}} = 3.38$

### 5.7.3 Thermochemical Diagram Condensed Phases 1000K

Figure 10 shows the  $\log a_{\text{Si}}$  vs  $\log p_{\text{O}_2}$  diagram. Ni(s) is the stable phase for  $\log a_{\text{Si}} < -8.01$  and  $\log p_{\text{O}_2} < -15.60$ . Ni<sub>3</sub>Si(s) is formed for  $\log a_{\text{Si}} = -8.01$  to  $-6.63$  and for  $\log p_{\text{O}_2} = -15.60$  to  $-14.69$ . Three additional silicides are formed, Ni<sub>5</sub>Si<sub>3</sub>(s), Ni<sub>2</sub>Si(s) and NiSi(s) for  $\log a_{\text{Si}} = -6.63$  to  $0.00$  and for  $\log p_{\text{O}_2} = -14.69$  to  $-6.90$ .

The SiO<sub>2</sub>(s) shows an SiO<sub>2</sub>(s) film to form on Ni-Si alloys for all conditions shown on the Figure. The light dashed line shows  $\log p_{\text{SiO}} = -10$ . At point B  $\log p_{\text{SiO}} = -10.105$ .

The lower triple point is shown at A. Point A' shows the triple point for a Ni-Si alloy having a nickel content of  $\log a_{\text{Si}} = -2$ .

Table 13 shows a summary of the thermochemical information. Volatile species are not important in the oxidation of Ni-Si alloys at 1000K. However, silicon reactions with NiO(s) are favorable thermochemically to form both SiO<sub>2</sub>(s) and SiO(g). Kinetically the reactions may not occur.

TABLE 13

Summary Ni-O-Si System		1000K
1. Oxide	SiO <sub>2</sub> (s)	
2. Lower triple point	log pO <sub>2</sub> = -15.60, log a <sub>Si</sub> = -8.01	
3. Volatile Species		
	<u>Interface</u>	<u>Species</u> <u>Log p (atm.)</u>
a.	Si(log a = -1.634)/SiO <sub>2</sub>	SiO(g)                              -10.105
b.	Ni(s)/NiO(s)	Ni(g)                                -14.33
		NiO(g)                              -18.496
c.	NiO(s)/O <sub>2</sub> 1 atm	Ni(g)                                -22.13
		NiO(g)                              -18.496
4. Silicon Reactions	Log a <sub>Si</sub> = 0	
a.	Si(s) + 2 NiO(s) = 2 Ni(s) + SiO <sub>2</sub> (s)	log K <sub>R</sub> = 22.55
b.	Si(s) + NiO(s) = Ni(s) + SiO(g)	log K <sub>R</sub> = 1.987

## 5.8 The Niobium - Oxygen - Silicon System

### 5.8.1 Phase Diagram Information

Three condensed oxides are formed NbO, NbO<sub>2</sub> and Nb<sub>2</sub>O<sub>5</sub><sup>(19)</sup>. These oxides have the following melting temperatures NbO = 2218K, NbO<sub>2</sub> = 2175K and Nb<sub>2</sub>O<sub>5</sub> = 1768K. Niobium dissolves 4 a/o O at 2188K and 1.43 a/o O at 773K.

Three silicides are reported Nb<sub>3</sub>Si, Nb<sub>5</sub>Si<sub>3</sub> and NbSi<sub>2</sub><sup>(18)</sup>. Nb<sub>5</sub>Si<sub>3</sub> has a melting temperature of 2753K and NbSi<sub>2</sub> a melting temperature of 2203K. The solubility of Si in Nb is less than 3 a/o at 1273K.

### 5.8.2 Thermochemical Diagrams Condensed Phases 1250K

Figure 14 shows the log a<sub>Si</sub> vs log p<sub>O<sub>2</sub></sub> diagram. Nb(s) is the stable phase for log a<sub>Si</sub> < -6.517 and log p<sub>O<sub>2</sub></sub> < -25.66. Nb<sub>5</sub>Si<sub>3</sub> is formed where log a<sub>Si</sub> = -6.517 to -1.125 and log p<sub>O<sub>2</sub></sub> has values of -25.66 to -20.65. NbSi<sub>2</sub>(s) is formed for log a<sub>Si</sub> = -1.125 to 0.00 and for log p<sub>O<sub>2</sub></sub> = -20.65 to -18.409.

The SiO<sub>2</sub>(s) line shows SiO<sub>2</sub>(s) is formed on the silicides where log a<sub>Si</sub> > -5 and Nb<sub>x</sub>O<sub>y</sub>(s) oxides are formed for log a<sub>Si</sub> < -5,

The lower triple point is shown at A. Point A' is the triple point for an alloy with a Nb content of log a<sub>Nb</sub> = -2. The light dashed lines show log p<sub>SiO</sub> lines of -7 and -10. At point B for the equilibrium between NbSi<sub>2</sub>(s) and Nb<sub>5</sub>Si<sub>3</sub>(s) log p<sub>SiO</sub> = -6.248.

Table 14 shows the important thermochemical information for the Nb-O-Si system at 1250K. Included are the volatile species formed at the several interfaces and the possible silicon reactions with NbO<sub>2</sub>(s). SiO(g) is the only important volatile specie formed. Silicon reacts with NbO<sub>2</sub>(s) to form SiO<sub>2</sub>(s). A very low pressure of SiO(g) is formed in reaction 4b of Table 14. SiO(g) can play an important role in the oxidation of Nb-Si alloys by

diffusing to cracks and defects in the  $\text{SiO}_2(\text{s})$  film, react with oxygen and heal the crack or defect.

TABLE 14

Summary Nb-O-Si System		1250K
1. Oxide $\text{SiO}_2(\text{s})$ $\log a_{\text{Si}} > -5$ , $\text{Nb}_x\text{O}_y$ $\log a_{\text{Si}} < -5$		
2. Lower triple point $\log p_{\text{O}_2} = -25.66$ $\log a_{\text{Si}} = -6.517$		
3. Volatile Species		
	<u>Interface</u>	<u>Species</u> <u>Log p (atm.)</u>
a.	$\text{Si}(\log a = -1.125)/\text{SiO}_2(\text{s})$	$\text{SiO}(\text{g})$ -6.248
b.	$\text{Nb}(\text{s})/\text{NbO}(\text{s})$	$\text{Nb}(\text{g})$ -22.75
		$\text{NbO}(\text{g})$ -16.21
		$\text{NbO}_2(\text{g})$ -15.97
c.	$\text{Nb}_2\text{O}_5(\text{s})/\text{O}_2$ 1 atm	$\text{Nb}(\text{g})$ -51.17
		$\text{NbO}(\text{g})$ -31.80
		$\text{NbO}_2(\text{g})$ -18.73
4. Silicon Reactions $\log a_{\text{Si}} = 0$		
a.	$\text{Si}(\text{s}) + \text{NbO}_2(\text{s}) = \text{Nb}(\text{s}) + \text{SiO}_2(\text{s})$	$\log K_{\text{R}} = 4.83$
b.	$\text{Si}(\text{s}) + \frac{1}{2} \text{NbO}_2(\text{s}) = \frac{1}{2} \text{Nb}(\text{s}) + \text{SiO}(\text{g})$	$\log K_{\text{R}} = -3.267$

## 5.9 The Tantalum - Oxygen - Silicon System

### 5.9.1 Phase Diagram Information

Five oxides have been reported  $Ta_4O$ ,  $Ta_2O$ ,  $TaO$ ,  $TaO_2$  and  $Ta_2O_5$ <sup>(18)</sup>.  $Ta_2O_5$  occurs in at least five modifications<sup>(18)</sup>. The melting temperature of  $Ta_2O_5$  is given as 2150K. Oxygen solubility is 2.5 a/o at 1273K<sup>(20)</sup>.

Four condensed silicides exist  $Ta_{4.5}Si$ ,  $Ta_2Si$ ,  $Ta_5Si_3$  and  $TaSi_2$ . The melting temperatures are given as  $Ta_{4.5}Si = 2783K$ ,  $Ta_5Si_3 = 2773K$  and  $TaSi_2 = 2473K$ . The solubility of Si in Ta at 2073K is less than 1.3 a/o.

### 5.9.2 Thermochemical Diagrams Condensed Phases 1250K

Figure 12 shows the  $\log a_{Si}$  vs  $\log p_{O_2}$  diagram.  $Ta(s)$  is the stable phase for  $\log a_{Si} < -5.422$  and  $\log p_{O_2} < -25.114$ .  $Ta_2Si(s)$  is formed where  $\log a_{Si} = -5.422$  to  $-2.302$  and  $\log p_{O_2}$  has values of  $-25.114$  to  $-23.87$ .  $Ta_5Si_3(s)$  and  $TaSi_2(s)$  are formed for  $\log a_{Si} = -2.302$  to  $0.00$  and  $\log p_{O_2} = -23.87$  to  $-22.07$ .

The  $SiO_2(s)$  line shows an  $SiO_2(s)$  film is formed for  $\log a_{Si} > -4.0$  and a  $Ta_2O_5(s)$  film for  $\log a_{Si} < -4.0$ . The light dashed lines shows  $\log p_{SiO}$  lines of  $-7$  and  $-10$ . At point B for the  $TaSi_2/Ta_5Si_3$  equilibria  $\log p_{SiO} = -5.99$ .

The lower triple point is shown at A. Point A' is the triple point for an alloy having a Ta content of  $\log a_{Ta} = -2$ .

Table 15 shows the important thermochemical information for 1250K. Included are the volatile species formed at the several interfaces and the silicon reaction with  $Ta_2O_5(s)$  to form  $SiO_2(s)$  and  $SiO(g)$ .  $SiO(g)$  is the important volatile specie for the system at 1250K. The reaction of silicon with  $Ta_2O_5(s)$  to form  $SiO_2$  is feasible. The reaction of silicon with  $Ta_2O_5(s)$  to form  $SiO(g)$  gives  $\log p_{SiO} = -3.88$ .  $SiO(g)$  can be important in the high

temperature oxidation of Ta-Si alloys by diffusion to cracks and defects where reaction with oxygen can occur to form  $\text{SiO}_2(\text{s})$  and heal the crack or defect.

TABLE 15

Summary Ta-O-Si System		1250K
1. Oxide $\text{SiO}_2$ $\log a_{\text{Si}} > -4.0$ $\text{Ta}_2\text{O}_5$ $\log a_{\text{Si}} < -4.0$		
2. Lower triple point $\log p_{\text{O}_2} = -25.114$ , $\log a_{\text{Si}} = -5.422$		
3. Volatile Species		
	<u>Interface</u>	<u>Species</u> <u>Log p (atm.)</u>
a.	$\text{Si}(\log a = -0.614)/\text{SiO}_2(\text{s})$	$\text{SiO}(\text{g})$ -5.99
b.	$\text{Ta}(\text{s})/\text{Ta}_2\text{O}_5(\text{s})$	$\text{Ta}(\text{g})$ -25.311
		$\text{TaO}(\text{g})$ -15.838
		$\text{TaO}_2(\text{g})$ -15.237
c.	$\text{Ta}_2\text{O}_5(\text{s})/\text{O}_2$ 1 atm	$\text{Ta}(\text{g})$ -56.704
		$\text{TaO}(\text{g})$ -34.673
		$\text{TaO}_2(\text{g})$ -21.515
4. Silicon Reactions $\log a_{\text{Si}} = 0$		
a.	$\text{Si}(\text{s}) + 2/5 \text{Ta}_2\text{O}_5(\text{s}) = 4/5 \text{Ta}(\text{s}) + \text{SiO}_2(\text{s})$	$\log K_{\text{R}} = 3.606$
b.	$\text{Si}(\text{s}) + 1/5 \text{Ta}_2\text{O}_5(\text{s}) = 2/5 \text{Ta}(\text{s}) + \text{SiO}(\text{g})$	$\log K_{\text{R}} = -3.879$

## 5.10 The Titanium - Oxygen - Silicon System

### 5.10.1 Phase Diagram Information

The condensed oxide phases are complex<sup>(18, 19, 24)</sup>. Four oxides are reported for the Ti(s) - TiO(s) region: Ti<sub>6</sub>O, Ti<sub>3</sub>O, Ti<sub>2</sub>O and Ti<sub>3</sub>O<sub>2</sub>. Five oxides exist in the TiO(s) - TiO<sub>2</sub>(s) region: TiC, TiO<sub>2</sub>, Ti<sub>2</sub>O<sub>3</sub>, Ti<sub>3</sub>O<sub>5</sub> and Ti<sub>4</sub>O<sub>7</sub>.

The limiting oxygen content of  $\alpha$  - Ti is TiO<sub>0.48</sub> (32.4 a/o)<sup>(19)</sup>. TiO has two modifications:  $\alpha$  < 1265K and  $\beta$  > 1265K.  $\beta$  - TiO has a melting temperature of 2023  $\pm$  20K. Ti<sub>2</sub>O<sub>3</sub> has a melting temperature of 2115  $\pm$  10K. The melting temperature of Ti<sub>3</sub>O<sub>5</sub> is 2050  $\pm$  20K. Ti<sub>3</sub>O<sub>5</sub> has two modifications;  $\alpha$  < 450K and  $\beta$  > 450K. Ti<sub>4</sub>O<sub>7</sub> has a melting temperature of 1950  $\pm$  60K. Rutile has a melting temperature of 2130  $\pm$  20K.

Five condensed silicides exist<sup>(30)</sup>. Ti<sub>3</sub>Si, Ti<sub>5</sub>Si<sub>3</sub>, Ti<sub>5</sub>Si<sub>4</sub>, TiSi and TiSi<sub>2</sub>. Ti<sub>5</sub>Si<sub>3</sub> has a melting temperature of 2403K and TiSi<sub>2</sub> has a melting temperature of 1773K. The solubility of Si in Ti at 1613K is about 5 a/o.

### 5.10.2 Thermochemical Diagram Condensed Phases 1250K

Figure 13 shows the log  $a_{Si}$  vs log  $p_{O_2}$  diagram. Ti(s) is the stable phase for log  $a_{Si} \leq 8.223$  and log  $p_{O_2} \leq -35.40$ . Ti<sub>5</sub>Si<sub>3</sub>(s) is formed where log  $a_{Si} = -8.223$  to  $-1.185$  and log  $p_{O_2}$  has values of  $-35.40$  to  $-27.16$ . TiSi(s) is formed for log  $a_{Si} = -1.185$  to  $0.00$  and for log  $p_{O_2} = -27.16$  to  $-25.59$

The SiO<sub>2</sub>(s) line shows that SiO<sub>2</sub>(s) forms on Ti-Si alloys for log  $a_{Si} > -1.5$  and a series of titanium oxides for log  $a_{Si} < -1.5$ .

The light dashed lines are the log  $p_{SiO}$  lines for  $-7$  and  $-10$ . At point B where TiSi(s) is in equilibrium with Ti<sub>5</sub>Si<sub>3</sub>(s) log  $p_{SiO} = -6.27$ .

The lower triple point is shown at A. Point A' is the triple point for Ti-Si alloys where log  $a_{Ti} = -2.0$

Table 16 shows the important thermochemical information for 1250K. Included are the volatile species and pressures for the several interfaces and the possible reactions of Si(s) with TiO(s) to form SiO<sub>2</sub>(s) and SiO(g). Neither reaction is feasible. SiO(g) can only play a role in the high temperature oxidation of Ti-Si alloys for  $\log a_{\text{Si}} > -1.5$ . For these values SiO(g) can diffuse to cracks and defects, react with oxygen and tend to heal the defects and cracks.

TABLE 16

Summary Ti-O-Si System		1250K
1. Oxide $\text{SiO}_2$ $\log a_{\text{Si}} > -1.5$ , $\text{Ti}_x\text{O}_y$ $\log a_{\text{Si}} < -1.5$		
2. Lower triple point $\log p_{\text{O}_2} = -35.40$ , $\log a_{\text{Si}} = -8.223$		
3. Volatile Species		
	<u>Interface</u>	<u>Species</u> <u>Log p (atm.)</u>
a.	Si(log a = -1.185)/SiO <sub>2</sub> (s)	SiO(g) -6.27
b.	Ti(s)/TiO(s)	Ti(g) -12.146
		TiO(g) -15.046
		TiO <sub>2</sub> (g) -21.894
c.	TiO <sub>2</sub> (s)/O <sub>2</sub> 1 atm	Ti(g) -42.48
		TiO(g) -27.366
		TiO <sub>2</sub> (g) -16.314
4. Silicon Reactions $\log a_{\text{Si}} = 0$		
a.	$\text{Si(s)} + 2 \text{TiO(s)} = 2 \text{Ti(s)} + \text{SiO}_2\text{(s)}$	$\log K_R = -6.68$
b.	$\text{Si(s)} + \text{TiO(s)} = \text{Ti(s)} + \text{SiO(g)}$	$\log K_R = -9.022$

## 5.11 The Vanadium - Oxygen - Silicon System

5.11.1 Twelve condensed oxide phases are reported<sup>(19, 21)</sup>. These exist in two regions of the phase diagram, V-VO and VO - V<sub>2</sub>O<sub>5</sub>. Two oxides exist in the V-VO region, V<sub>2</sub>O and VO. VO has a wide range of homogeneity and a melting temperature of 2063 ± 10K. Ten oxides exist in the VO - V<sub>2</sub>O<sub>5</sub> range: V<sub>2</sub>O<sub>3</sub>, V<sub>3</sub>O<sub>5</sub>, VO<sub>1.75</sub>, VO<sub>1.8</sub>, VO<sub>1.84</sub>, VO<sub>1.86</sub>, VO<sub>1.87</sub>, VO<sub>2</sub>, V<sub>6</sub>O<sub>13</sub> and V<sub>2</sub>O<sub>5</sub>. V<sub>2</sub>O<sub>3</sub> has a melting temperature of 2340 ± 20K. VO<sub>2</sub> has a melting of 1818 ± 15K and V<sub>2</sub>O<sub>5</sub> has a melting temperature of 943 ± 10K. O solubility in V is reported as 10.7 a/o at 1273K.

Four condensed silicides are reported<sup>(30)</sup>. V<sub>3</sub>Si, V<sub>5</sub>Si<sub>3</sub>, V<sub>6</sub>Si<sub>5</sub> and VSi<sub>2</sub>. The melting temperatures are as follows, V<sub>3</sub>Si 2198, V<sub>5</sub>Si<sub>3</sub> 2283, and VSi<sub>2</sub> 1950K. The Si solubility in V at 2143K is 7 a/o.

### 5.11.2 Thermochemical Diagram Condensed Phases 1250K

Figure 14 shows a log a<sub>Si</sub> vs log p<sub>O<sub>2</sub></sub> diagram. V(s) is the stable phase for log a<sub>Si</sub> < -7.034 and log p<sub>O<sub>2</sub></sub> < -27.08. V<sub>5</sub>Si<sub>3</sub>(s) is formed for log a<sub>Si</sub> = -7.034 to -1.239 and log p<sub>O<sub>2</sub></sub> values of -17.08 to -20.503. VSi<sub>2</sub> is formed for log a<sub>Si</sub> = -1.239 to 0.00 and log p<sub>O<sub>2</sub></sub> values of -20.503 to -17.2.

The SiO<sub>2</sub>(s) line shows SiO<sub>2</sub>(s) to form on the silicides for log a<sub>Si</sub> > -4.5 and the vanadium oxides VO(s) and V<sub>2</sub>O<sub>3</sub>(s) for log a<sub>Si</sub> < -4.5.

The light dashed lines show log p<sub>SiO</sub> lines of -7 and -10. At point B for the equilibrium between VSi<sub>2</sub>(s) and V<sub>5</sub>Si<sub>3</sub>(s) log p<sub>SiO</sub> = -6.302.

The lower triple point is shown at A. Point A' is the triple point for V-Si alloy having a V content of log a<sub>V</sub> = -2.

Table 17 shows the important thermochemical information for 1250K. Included are the volatile species at the several interfaces and the possible reactions between Si(s) and V<sub>2</sub>O<sub>3</sub>(s) to form SiO<sub>2</sub>(s) and SiO(g). SiO(g) is the

important volatile specie. The Si(s) reaction with  $V_2O_3(s)$  is feasible. The reaction of Si(s) with  $V_2O_3(s)$  forms SiO(g) at a pressure of  $\log p_{SiO} = -3.892$ .

SiO(g) can play an important role in the high temperature oxidation of V-Si alloys by diffusing to cracks and defects in the  $SiO_2(s)$  film reacting with oxygen to repair cracks and defects in the film. The formation of the low melting temperature oxide  $V_2O_5$  indicates rapid oxidation of V-Si alloys above 943K.

TABLE 17

Summary V-O-Si System		1250K
1. Oxide	$\text{SiO}_2 \log a_{\text{Si}} > -4.5, \text{V}_x\text{O}_y \log a_{\text{Si}} < -4.5$	
2. Lower triple point	$\log p_{\text{O}_2} = -27.08 \log a_{\text{Si}} = -7.034$	
3. Volatile Species		
	<u>Interface</u>	<u>Species</u> <u>Log p (atm.)</u>
a.	Si(log a = -1.239)/SiO <sub>2</sub> (s)	SiO(g)                              -6.302
b.	V(s)/VO(s)	V(g)                                -13.62
		VO(g)                              -14.011
		VO <sub>2</sub> (g)                           -16.02
c.	V <sub>2</sub> O <sub>5</sub> (s)/O <sub>2</sub> 1 atm	V(g)                                -35.44
		VO(g)                              -22.291
		VO <sub>2</sub> (g)                          -10.765
4. Silicon Reactions	Log a <sub>Si</sub> = 0	
a.	Si(s) + 2/3 V <sub>2</sub> O <sub>3</sub> (s) = 4/3 V(s) + SiO <sub>2</sub> (s)	log K <sub>R</sub> = 3.58
b.	Si(s) + 1/3 V <sub>2</sub> O <sub>3</sub> (s) = 2/3 V(s) + SiO(g)	log K <sub>R</sub> = -3.892

## 5.12 The Tungsten - Oxygen - Silicon System

### 5.12.1 Phase Diagram Information

Five condensed oxides are formed  $WO_2$ ,  $WO_{2.72}$ ,  $WO_{2.90}$ ,  $WO_{2.96}$  and  $WO_3$ <sup>(24)</sup>.  $WO_3$  has a melting temperatures of 1744K. The solubility of O in W is 0.06 a/o at 1973K.

Two condensed silicides are formed  $W_3Si_2$  and  $WSi_2$ <sup>(21)</sup>.  $W_3Si_2$  has a melting temperature of 2623K and  $WSi_2$  a melting temperature of 2438K. A more recent study indicates  $W_3Si_2$  is probably  $W_5Si_3$  with a melting temperature of 2643K<sup>(21)</sup>. The solubility of Si in W is 5.3 a/o at 2073K.

### 5.12.2 Thermochemical Diagrams Condensed Phases 1250K

Figure 15 shows the  $\log a_{Si}$  vs  $\log p_{O_2}$  diagram. W(s) is the stable phase for  $\log a_{Si} \leq -2.394$  and  $\log p_{O_2} \leq -15.238$ .  $W_5Si_3$  is formed for  $\log a_{Si} = -2.394$  to  $-1.485$  and  $\log p_{O_2}$  has values of  $-15.238$  to  $-14.693$ .  $WSi_2$ (s) is formed for  $\log a_{Si} = -1.485$  to  $0.00$  and  $\log p_{O_2}$  has values of  $-14.693$  to  $-12.444$ .

The  $SiO_2$ (s) line shows  $SiO_2$ (s) to form on the tungsten silicides for all conditions shown on the diagram. The light dashed lines show  $\log p_{SiO} = -7$  and  $-10$ . Point B for the equilibrium between  $W_5Si_3$ (s) and  $WSi_2$ (s) shows a  $\log p_{SiO}$  of  $-6.245$ .

The lower triple point is shown at A. Point A' is the value of the triple point for an alloy having a tungsten content of  $\log a_W = -2$ .

Table 18 shows the important thermochemical information. Included are the volatile species and pressures at the several interfaces and the equilibrium constants for the silicon reaction with  $WO_2$ (s) to form  $SiO_2$ (s) and  $SiO$ (g). Both reactions are favorable thermochemically.

Volatile species play an important role in the high temperature oxidation of W-Si alloys.  $\text{SiO(g)}$  can form at the silicide - silica interface, diffuse to cracks and defects, react with oxygen and repair the crack or defect.  $(\text{WO}_3)_3(\text{g})$  is the other important oxide volatile specie. At the  $\text{WO}_3(\text{s}) - \text{O}_2$  interface this gas can volatilize due to the high value of  $\log P(\text{WO}_3)_3 = -7.05$ .

TABLE 18

## Summary W-O-Si System 1250K

1. Oxide  $\text{SiO}_2$
2. Lower triple point  $\log p_{\text{O}_2} = -15.238$ ,  $\log a_{\text{Si}} = -2.394$
3. Volatile Species

	<u>Interface</u>	<u>Species</u>	<u>Log p (atm.)</u>
a.	Si(log a = -1.485)/ $\text{SiO}_2(\text{s})$	$\text{SiO}(\text{g})$	-6.425
b.	W(s)/ $\text{WO}_2(\text{s})$	$(\text{WO}_3)_3(\text{g})$	-9.74
		$(\text{WO}_3)_2(\text{g})$	-10.064
		$\text{W}_3\text{O}_8(\text{g})$	-10.612
		$(\text{WO}_3)_4(\text{g})$	-11.75
		$\text{WO}_3(\text{g})$	-13.497
		$\text{WO}_2(\text{g})$	-16.195
		$\text{WO}(\text{g})$	-19.90
		$\text{W}(\text{g})$	-28.11
c.	$\text{WO}_3(\text{s})/\text{O}_2$ atm	$(\text{WO}_3)_3(\text{g})$	-7.05
		$(\text{WO}_3)_4(\text{g})$	-8.180
		$(\text{WO}_3)_2(\text{g})$	-8.27
		$\text{W}_3\text{O}_8(\text{g})$	-15.04
		$\text{WO}_3(\text{g})$	-12.60
		$\text{WO}_2(\text{g})$	-22.917
		$\text{WO}(\text{g})$	-34.24
		$\text{W}(\text{g})$	-50.07

4. Silicon Reactions  $\log a_{\text{Si}} = 0$ 

- a.  $\text{Si}(\text{s}) + \text{WO}_2(\text{s}) = \text{W}(\text{s}) + \text{SiO}_2(\text{s})$   $\log K_{\text{R}} = 13.482$
- b.  $\text{Si}(\text{s}) + 1/2 \text{WO}_2(\text{s}) = 1/2 \text{W}(\text{s}) + \text{SiO}(\text{g})$   $\log K_{\text{R}} = 1.059$

## 5.13 The Zirconium - Oxygen - Silicon System

### 5.13.1 Phase Diagram Information

ZrO<sub>2</sub> is the principal oxide<sup>(19, 20)</sup>. Below ZrO<sub>2</sub> suboxides exist Zr<sub>3</sub>O, Zr<sub>5.6</sub>O, Zr<sub>3.7</sub>O, Zr<sub>3.1</sub>O, Zr<sub>3</sub>O and Zr<sub>2.7</sub>O. Zr<sub>2</sub>O and ZrO are also formed. The melting point of ZrO<sub>2</sub> is given as 2950K<sup>(27)</sup>. The solubility limit of O in α -Zr is 30 a/o at 673 -1073K<sup>(20)</sup>.

Seven condensed silicides are formed Zr<sub>3</sub>Si, Zr<sub>2</sub>Si, Zr<sub>5</sub>Si<sub>3</sub>, Zr<sub>3</sub>Si<sub>2</sub>, Zr<sub>5</sub>Si<sub>4</sub>, ZrSi, ZrSi<sub>2</sub><sup>(19, 22)</sup>. The melting temperature of Zr<sub>2</sub>Si is 2488K and Zr<sub>5</sub>Si<sub>4</sub> is 2523K. The solubility of Si in Zr is very limited, less than 0.3 a/o in α -Zr and less than 0.65 a/o in β - Zr.

### 5.13.2 Thermochemical Diagram Condensed Phases 1250K

Figure 16 shows the log a<sub>Si</sub> vs log p<sub>O<sub>2</sub></sub> diagram. Zr(s) is the stable phase for log a<sub>Si</sub> < -8.725 and log p<sub>O<sub>2</sub></sub> < -35.98. Zr<sub>2</sub>Si is formed where log a<sub>Si</sub> = -8.725 to -4.757 and log p<sub>O<sub>2</sub></sub> has values of -35.98 to -34.00. Zr<sub>5</sub>Si<sub>3</sub>(s) and ZrSi(s) are formed for log a<sub>Si</sub> = -4.757 to 0.00 and log p<sub>O<sub>2</sub></sub> has values of -34 to -29.605.

The SiO<sub>2</sub>(s) line shows ZrO<sub>2</sub>(s) is the oxide formed for all log a<sub>Si</sub> given on the Figure. The light dashed lines show log p<sub>SiO</sub> = -7 and -10. Since the silicides are not in contact with SiO<sub>2</sub>(s), SiO(g) is not formed.

The lower triple point is shown at A. The point labelled A' shows the triple point for an alloy with a Zr content of log a<sub>Zr</sub> = -2.

Table 19 shows the important thermochemical information. Included are the volatile species at the several interfaces and the possible reaction of Si(s) with ZrO<sub>2</sub>(s) to form SiO<sub>2</sub>(s) and SiO(g). SiO(g) does not play a role in the high temperature oxidation of Zr-Si alloys.

TABLE 19

Summary Zr-O-Si System		1250K
1. Oxide	ZrO <sub>2</sub>	
2. Lower triple point	log pO <sub>2</sub> = -35.98, log a <sub>Si</sub> = -8.725	
3. Volatile Species		
	<u>Interface</u>	<u>Species</u> <u>Log p (atm.)</u>
a.	Si(log a = -3.83)/SiO <sub>2</sub> (s)	SiO <sub>2</sub> not formed
b.	Zr(s)/ZrO <sub>2</sub> (s)	Zr(g)                                      -18.56
		ZrO(g)                                    -16.323
		ZrO <sub>2</sub> (g)                                -22.79
c.	ZrO <sub>2</sub> (s)/O <sub>2</sub> 1 atm	Zr(g)                                      -54.54
		ZrO(g)                                    -34.313
		ZrO <sub>2</sub> (g)                                -22.79
	4. Silicon Reactions Log a <sub>Si</sub> = 0	
a.	Si(s) + ZrO <sub>2</sub> (s) = Zr(s) + SiO <sub>2</sub> (s)	log K <sub>R</sub> = -7.36
b.	Si(s) + 1/2 ZrO <sub>2</sub> (s) = 1/2 Zr(s) + SiO(g)	log K <sub>R</sub> = -9.312

## 6.0 APPENDIX

6.1 Table A-1 Physical Properties of the Element and Their Oxide

Element	M.P.K. B.P.K.		Condensed Oxides M.P.K.	See Table A-3 for References Volatile Species
	M.P.K.	B.P.K.		
Ca	1112	1767	CaO 2887 CaO <sub>2</sub> CaO <sub>4</sub>	Ca, CaO
C				C <sub>1</sub> , C <sub>2</sub> , C <sub>3</sub>
Cr	2176	2915	Cr <sub>2</sub> O <sub>3</sub> 2603±15  CrO <sub>2</sub> CrO <sub>3</sub> CrO <sub>4</sub> CrO <sub>6</sub>	Cr, CrO, CrO <sub>2</sub> , CrO <sub>3</sub>
Fe	1809	3145	Fe <sub>0.947</sub> O 1650 Fe <sub>3</sub> O <sub>4</sub> 1870 Fe <sub>2</sub> O <sub>3</sub> d	Fe, FeO
Mn	1517	2314	MnO 2058 Mn <sub>3</sub> O <sub>4</sub> 1833 Mn <sub>2</sub> O <sub>3</sub> d	Mn, MnO
Mo	2892	4919	MoO <sub>2</sub>  MoO <sub>3</sub> 1074	Mo, MoO, MoO <sub>2</sub> , MoO <sub>3</sub> (MoO <sub>3</sub> ) <sub>3</sub>
Ni	1725	> 3,000	NiO 2223	Ni, NiO
Nb	2750	3156	NbO 2210 NbO <sub>2</sub> 2175 Nb <sub>2</sub> O <sub>5</sub> 1783	Nb, NbO, NbO <sub>2</sub>
Si	1685	3492	SiO <sub>2</sub> 1996	Si, Si <sub>2</sub> , Si <sub>3</sub> , SiO, SiO <sub>2</sub>
Ta	3258	5786	Ta <sub>2</sub> O <sub>5</sub> 2058±30	Ta, TaO, TaO <sub>2</sub>
Ti	1933	3591	Sub-Oxides (Ti <sub>6</sub> O, Ti <sub>3</sub> O Ti <sub>2</sub> O, Ti <sub>3</sub> O <sub>2</sub> ) TiO 2023 Ti <sub>2</sub> O <sub>3</sub> 2115 Ti <sub>3</sub> O <sub>5</sub> 2050 Ti <sub>4</sub> O <sub>7</sub> 1950 TiO <sub>2</sub> 2130	Ti, TiO, TiO <sub>2</sub>

APPENDIX

Table A-1 (Cont) Physical Properties of the Element and Their Oxides

See Table A-3 for References

Element	M.P.K.	B.P.K.	Condensed Oxides M.P.K.	Volatile Species
V	2190	3694	V <sub>2</sub> O VO 2063 V <sub>2</sub> O <sub>4</sub> 2340 Intermediates (V <sub>3</sub> O <sub>5</sub> , VO <sub>1.75</sub> , VO <sub>1.8</sub> , VO <sub>1.84</sub> , VO <sub>1.86</sub> , VO <sub>1.87</sub> ) V <sub>2</sub> O <sub>4</sub> V <sub>2</sub> O <sub>5</sub>	V, VO, VO <sub>2</sub>
W	3680	5936	WO <sub>2</sub> d 1977  WO <sub>2.72</sub> WO <sub>2.90</sub> WO <sub>2.96</sub> WO <sub>3</sub> 1745	W, WO, WO <sub>2</sub> , W <sub>3</sub> O <sub>8</sub> , WO <sub>3</sub> , (WO <sub>2</sub> ) <sub>2</sub> (WO <sub>3</sub> ) <sub>3</sub> , (WO <sub>3</sub> ) <sub>4</sub>
Zr	2126	4777	ZrO <sub>2</sub> 2950	Zr, ZrO, ZrO <sub>2</sub>

APPENDIX

6.2 Table A-2 Physical Properties of the Elements and Their Silicides

See Table A-3 for References

Element	M.P.K. B.P.K.		Condensed Silicide M.P.K.	Volatile Species
Ca	1112	1767	Ca <sub>2</sub> Si CaSi 1513 CaSi <sub>2</sub>	Ca
C			CSi 3259	
Cr	2176	2915	Cr <sub>3</sub> Si 2043 Cr <sub>5</sub> Si <sub>3</sub> 1920 CrSi 1730 CrSi <sub>2</sub> 1730	Cr
Fe	1809	3145	Fe <sub>5</sub> Si <sub>3</sub> FeSi	Fe
Mn	1517	2314	Mn <sub>3</sub> Si 1348 Mn <sub>5</sub> Si <sub>3</sub> 1513 MnSi 1548 MnSi <sub>1.7</sub> 1425	Mn
Mo	2892	4919	Mo <sub>3</sub> Si 2298 Mo <sub>5</sub> Si <sub>3</sub> 2463 MoSi <sub>2</sub> 2383	Mo
Ni	1725	> 3,000	Ni <sub>3</sub> Si Ni <sub>5</sub> Si <sub>2</sub> Ni <sub>2</sub> Si 1560 NiSi 1265 Ni <sub>1.04</sub> Si <sub>1.93</sub> 1245	Ni
Nb	2750	3156	Nb <sub>5</sub> Si <sub>3</sub> NbSi <sub>2</sub>	Nb
Ta	3258	5786	Ta <sub>2</sub> Si Ta <sub>5</sub> Si <sub>3</sub> TaSi	Ta
Ti	1933	3591	Ti <sub>5</sub> Si <sub>3</sub> TiSi	Ti

APPENDIX

Table A-2 (Cont) Physical Properties of the Element and Their Silicides

See Table A-3 for References

Element	M.P.K. B.P.K.		Condensed Silicides	Volatile Species
	M.P.K.	B.P.K.	M.P.K.	
V	2190	3694	V <sub>3</sub> Si V <sub>5</sub> Si <sub>3</sub> VSi <sub>2</sub> 1950	V
W	3680	5936	W <sub>5</sub> Si <sub>3</sub> 2593 WSi <sub>2</sub> 2433	W
Zr	2126	4777	Zr <sub>2</sub> Si Zr <sub>5</sub> Si <sub>3</sub> ZrSi ZrSi <sub>2</sub>	Zr

## 6.3 TABLE A-3

6.3 Table A-3 Thermochemical Data M-O-Si System 900-1450K

Compound	Ref.	M.P.K.	log K <sub>p</sub> at T K					1450
			900	1000	1150	1250	1342	
Calcium								
Ca <sub>2</sub> Si(s)	22		11.010	9.762	28.25	7.48*	6.63*	---
CaSi(s)	22	1513	7.937	7.049	5.986	5.396	4.929	4.460
CaSi <sub>2</sub> (s)	22		7.262	6.379	5.328	4.745	4.30*	3.85*
CaO(s)	29	3200 ± 50	31.42	27.75	23.42	21.09	19.25	17.39
CaO(g)	31		1.196	1.406	1.620	1.708	1.773	1.836
Ca(g)	24	1112	-4.653	-3.652	-2.510	-1.927	-1.470	-1.012
Carbon								
CSi(s)	24	3259	3.837	3.414	2.919	2.654	2.445	2.233
CO(g)	24		11.108	10.459	9.694	9.083	8.956	8.623
Chromium								
Cr <sub>3</sub> Si(s)	22	2043	5.983	5.366	4.649	4.263	3.957	3.648
Cr <sub>5</sub> Si <sub>3</sub> (s)	22	1920	13.512	12.261	10.772	9.979	9.352	8.719
CrSi(s)	22	1730	3.309	3.000	2.640	2.446	2.293	2.138
CrSi <sub>2</sub> (s)	22	1730 ‡	4.507	4.104	3.507	3.220	2.950	2.717
Cr <sub>2</sub> O <sub>3</sub> (s)	29	2603 ‡ 15	51.961	45.436	37.80	33.72	30.50	27.25
CrO <sub>6</sub> (l)	29	470	22.7	19.5	15.76	13.75	12.22	10.53
Cr(g)	29	2176	-15.32	-13.039	-10.38	-8.96	-7.84	-6.72
CrO(g)	29		-5.201	-4.142	-2.91	-2.26	-1.75	-1.24
CrO <sub>2</sub> (g)	29		6.292	5.822	5.26	4.96	4.71	4.46
CrO <sub>3</sub> (g)	29		13.456	11.738	9.72	8.64	7.78	6.91

\* extrapolated

‡ peritectic

TABLE A-3

Table A-3 (Cont.) Thermochemical Data M-O-Si System 900-1450K

Compound	Ref.	M.P.K.	log K <sub>p</sub> at T K					1342	1450
			900	1000	1150	1250	1342		
Iron									
Fe <sub>5</sub> Si <sub>3</sub> (s)	26		13.497	12.235	10.754	9.963	---	---	
FeSi(s)	26		4.18	3.736	3.214	2.936	---	---	
Fe <sub>0.947</sub> O(s)	24	1650	11.947	10.421	8.63	7.66	6.90	6.18	
Fe <sub>3</sub> O <sub>4</sub> (s)	24	1870	47.754	41.422	33.98	29.99	26.86	23.67	
Fe <sub>2</sub> O <sub>3</sub> (s)	24		34.055	29.364	23.87	20.91	18.60	16.25	
Fe(g)	24	1809	-16.25	-13.87	-11.11	-9.64	-8.49	-7.33	
FeO(g)	24		-8.96	-7.56	-5.95	-5.10	14.44	-3.77	
Manganese									
Mn <sub>3</sub> Si(s)	22	1348	4.171	3.731	3.22*	2.94*	2.72*	---	
Mn <sub>5</sub> Si <sub>3</sub> (s)	22	1513	12.846	11.653	10.187	9.395	8.763	---	
MnSi(s)	22	1548	3.279	2.921	2.488	2.258	2.070	---	
MnSi <sub>1.7</sub> (s)	27	1425	3.953	3.501	2.956	2.659	2.422	1.877	
MnO(s)	27	2058	18.517	16.289	13.692	12.285	11.173	10.047	
Mn <sub>3</sub> O <sub>4</sub> (s)	27	1833	62.334	54.316	44.876	39.845	35.886	31.852	
Mn <sub>2</sub> O <sub>3</sub> (s)	27	dec.	42.058	36.531	30.03	26.568	23.845	---	
Mn(g)	33	1517	-9.06	-7.486	-5.605	-4.551	-3.882	-3.129	
MnO(g)	34		-2.553	-1.861	-1.069	-0.670	-0.352	-0.043	
Molybdenum									
Mo <sub>3</sub> Si(s)	22	2298	6.769	6.080	5.273	4.839	4.497	4.151	
Mo <sub>5</sub> Si <sub>3</sub> (s)	22	2463	18.311	16.499	14.378	13.241	12.348	11.440	
MoSi <sub>2</sub> (s)	22	2383	7.555	6.784	5.882	5.412	4.998	4.628	
MoO <sub>2</sub> (s)	24		24.728	21.362	17.431	15.344	13.699	12.045	

\* extrapolated

TABLE A-3  
Table A-3 (cont.) Thermochemical Data M-O-Si System 900-1450K

Compound	Ref	M .P.K	log K <sub>p</sub> at T K					
			900	1000	1150	1250	1342	
Molybdenum (continued)								
MoO <sub>3</sub> (s,l)	24	1074	30.058	25.799	20.955	18.536	16.607	14.672
Mo(g)	24	2892	-30.304	-26.505	-22.063	-19.689	-17.817	-15.931
MoO(g)	24		-17.062	-14.846	-12.259	-10.879	-9.792	-8.699
MoO <sub>2</sub> (g)	24		2.887	2.784	2.66	2.59	2.55	2.46
MoO <sub>3</sub> (g)	24		17.92	15.82	13.36	12.04	11.00	9.95
$\frac{1}{3}$ (MoO <sub>3</sub> ) <sub>3</sub> (g)	32		28.49	24.90	20.55	18.29	16.50	14.67
Nickel								
Ni <sub>3</sub> Si(s)	26		8.945	8.006	6.902	6.305	---	---
Ni <sub>5</sub> Si <sub>3</sub> (s)	26		17.354	15.554	13.44	12.32	---	---
Ni <sub>2</sub> Si(s)	35	1560	7.914	7.066	6.073	5.544	5.128	---
NiSi(s,l)	35	1265	4.86	4.35	3.744	3.455	3.282	---
Ni <sub>1.04</sub> Si <sub>1.93</sub> (s,l)	35	1245	5.06	4.533	3.917	3.67	---	---
NiO(s)	36	2223	9.17	7.80	6.20	5.34	4.67	4.00
Ni(g)	33	1725	-16.77	-14.33	-11.49	-9.97	-8.78	-7.57
NiO(g)	35		-12.465	-10.696	-8.637	-7.536	-6.671	-5.802
Niobium								
Nb <sub>5</sub> Si <sub>3</sub> (s)	22		26.860	24.243	21.198	19.550	18.229	16.921
NbSi <sub>2</sub> (s)	22		7.751	6.939	5.989	5.481	5.081	4.669
NbO(s)	29	2210	19.586	17.168	14.34	12.83	11.64	10.44
NbO <sub>2</sub> (s)	29	2175	36.586	32.025	26.713	23.89	21.67	19.43
Nb <sub>2</sub> O <sub>5</sub> (s)	29	1785	87.336	76.413	63.65	56.83	51.46	46.04
Nb(g)	29	2750	-34.65	-30.39	-25.40	-22.75	-20.62	-18.50
NbO(g)	29		-6.50	-5.38	-4.07	-3.38	-2.83	-2.28
NbO <sub>2</sub> (g)	29		13.03	11.84	10.4	9.69	9.10	8.50

TABLE A-3

Table A-3 (Cont.) Thermochemical Data M-O-Si System 900-1450K

Compound	Ref	M.P.K.	log K <sub>p</sub> at T K					
			900	1000	1150	1250	1342	1450
Tantalum								
Ta <sub>2</sub> Si(s)	22		7.458	6.729	5.678	5.422	5.063	4.700
Ta <sub>5</sub> Si <sub>3</sub> (s)	22		20.178	18.220	15.932	14.706	13.740	12.765
TaSi <sub>2</sub> (s)	22		5.732	5.041	4.234	3.801	3.459	3.144
Ta <sub>2</sub> O <sub>5</sub> (s)	29	2058+30	95.632	83.868	70.124	62.785	57.005	51.179
Ta(g)	29	3258	-37.978	-33.451	-28.148	-25.311	-23.071	-20.808
TaO(g)	29		-6.302	-5.217	-3.953	-3.280	-2.750	-2.218
TaO <sub>2</sub> (g)	29		13.229	12.036	10.633	9.878	9.280	8.674
Titanium								
Ti <sub>5</sub> Si <sub>3</sub> (s)	22		34.131	30.767	26.824	24.670	22.959	21.237
TiSi(s)	22		7.520	6.769	5.888	5.408	5.027	4.644
TiO(s)	29	2023	26.448	23.321	19.66	17.70	16.16	14.62
Ti <sub>2</sub> O <sub>3</sub> (s)	29	2115	73.586	64.870	54.66	49.20	44.91	40.57
Ti <sub>3</sub> O <sub>5</sub> (s)	29	2050	119.183	105.077	88.53	79.69	72.70	65.66
Ti <sub>4</sub> O <sub>7</sub> (s)	29	1950	164.787	145.178	122.18	109.90	100.22	90.44
TiO <sub>2</sub> (s)	29	2130	45.297	39.842	33.44	30.02	27.33	24.60
Ti(g)	24	19.33	-19.722	-17.002	-13.83	-12.146	-10.822	-9.49
TiO(g)	29		1.899	2.182	2.498	2.654	2.771	2.886
TiO <sub>2</sub> (g)	29		18.797	16.990	14.86	13.706	12.789	11.861
Vanadium								
V <sub>3</sub> Si(s)	22		8.441	7.552	6.504	5.94	5.499	---
V <sub>5</sub> Si <sub>3</sub> (s)	22		27.974	25.467	22.600	21.102	19.945	18.795
VSi <sub>2</sub> (s)	22	1950	7.998	7.268	6.413	5.955	5.592	5.225
VO(s)	29	2063	20.428	17.960	15.08	13.54	12.34	11.12
V <sub>2</sub> O <sub>3</sub> (s)	29	2340	57.23	50.243	42.06	37.71	34.29	30.83

TABLE A-3

Table A-3 (Cont.) Thermochemical Data M-O-Si System 900-1450K

Compound	Ref	M.P.K.	log K <sub>p</sub> at T K					
			900	1000	1150	1250	1342	1450
Vanadium (cont)								
V <sub>2</sub> O <sub>4</sub> (s)	29	1818	65.164	57.035	47.52	42.45	38.48	34.45
V <sub>2</sub> O <sub>5</sub> (s,l)	29	943	67.565	58.885	48.93	43.64	39.48	35.28
V(g)	29	2190	-21.952	-18.971	-15.483	-13.62	-12.151	-10.670
VO(g)	29		-2.424	-1.7	-0.903	-0.471	-0.135	0.201
VO <sub>2</sub> (g)	29		14.936	13.553	11.93	11.06	10.36	9.66
Tungsten								
W <sub>5</sub> Si <sub>3</sub> (s)	27	2593	9.241	8.456	7.543	7.182	7.083	---
WSi <sub>2</sub> (s)	27	2433	5.038	4.434	3.857	3.515	3.243	2.969
WO <sub>2</sub> (s)	24	d.1977	24.658	21.281	17.32	15.238	13.58	11.92
WO <sub>2.72</sub> (s)	24		32.918	28.444	23.222	20.44	18.24	16.033
WO <sub>2.92</sub> (s)	24		34.488	29.792	24.311	21.386	19.084	16.766
WO <sub>2.96</sub> (s)	24		35.118	30.336	24.756	21.778	19.435	17.075
WO <sub>3</sub> (s)	24	1745	35.422	30.596	24.94	21.96	19.60	17.22
W(g)	24	3680 <sub>+20</sub>	-42.01	-37.05	-31.23	-28.11	-25.65	-23.14
WO(g)	24		-19.08	-16.65	-13.80	12.28	-11.08	-9.87
WO <sub>2</sub> (g)	24		-2.12	-1.70	-1.21	-0.957	-0.758	-0.557
WO <sub>3</sub> (g)	24		14.13	12.42	10.43	9.36	-8.52	-7.66
(WO <sub>3</sub> ) <sub>2</sub> (g)	24		54.26	47.60	39.81	35.65	32.38	29.06
(WO <sub>3</sub> ) <sub>3</sub> (g)	24		91.24	79.64	66.08	58.83	53.14	47.36
(WO <sub>3</sub> ) <sub>4</sub> (g)	24		124.50	108.44	89.68	79.66	71.79	63.80
W <sub>3</sub> O <sub>8</sub> (g)	24		77.73	67.93	56.46	50.84	45.53	40.64

TABLE A-3

Table A-3 (Cont.) Thermochemical Data M-O-Si System 900-1450K

Compound	Ref	M.P.K.	log K <sub>p</sub> at T K					
			900	1000	1150	1250	1342	1450
Zirconium								
Zr <sub>2</sub> Si(s)	22		12.216	10.986	9.527	8.725	8.088	7.445
Zr <sub>5</sub> Si <sub>3</sub> (s)	22		33.830	30.431	26.400	24.191	22.436	20.664
ZrSi(s)	22		8.94	8.042	6.963	6.375	5.909	5.438
ZrSi <sub>2</sub> (s)	22		8.905	7.958	6.840	6.229	5.744	5.255
ZrO <sub>2</sub> (s)	24	2950	53.72	47.38	39.96	35.98	32.84	29.67
Zr(g)	24	2126	-28.58	-24.99	-20.79	-18.56	-16.80	-15.03
ZrO(g)	24		0.852	1.153	1.450	1.667	1.799	1.931
ZrO <sub>2</sub> (g)	24		17.97	16.27	14.27	13.19	12.33	11.46

## 6.4 TABLE A-4

Table A-4 Thermochemical Data H-O-Si System 900-1450K

Compound	Ref	M.P.K.	log $K_p$ at T K					
			900	1000	1150	1250	1342	1450
Si(g)	24	1683	-18.391	-15.786	-12.739	11.111	-9.83	-8.535
Si <sub>2</sub> (g)	24		-24.387	-20.994	-17.028	-14.909	-13.24	-11.558
Si <sub>3</sub> (g)	24		-26.088	-22.443	-18.189	-15.921	-14.13	-12.34
SiO <sub>2</sub> (s)	24	1996	43.406	38.150	31.99	28.72	26.12	23.53
SiO(g)	24		10.396	9.787	9.067	8.678	8.369	8.054
SiO <sub>2</sub> (g)	24		17.899	16.114	14.021	12.900	12.012	11.162
SiH(g)	37		-16.967	-13.908	-11.386	-10.038	-8.978	-7.910
SiH <sub>4</sub> (g)	31		-6.910	-6.375	-6.219	-6.134	-6.069	-6.001
H <sub>2</sub> O(g)	24		11.498	10.062	8.373	7.467	6.753	6.025

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## 8.0 LIST OF FIGURES

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- A-2 Physical Properties of the Metals and Their Silicides.
- A-3 Thermochemical Data M-O-Si Systems 900-1450K.
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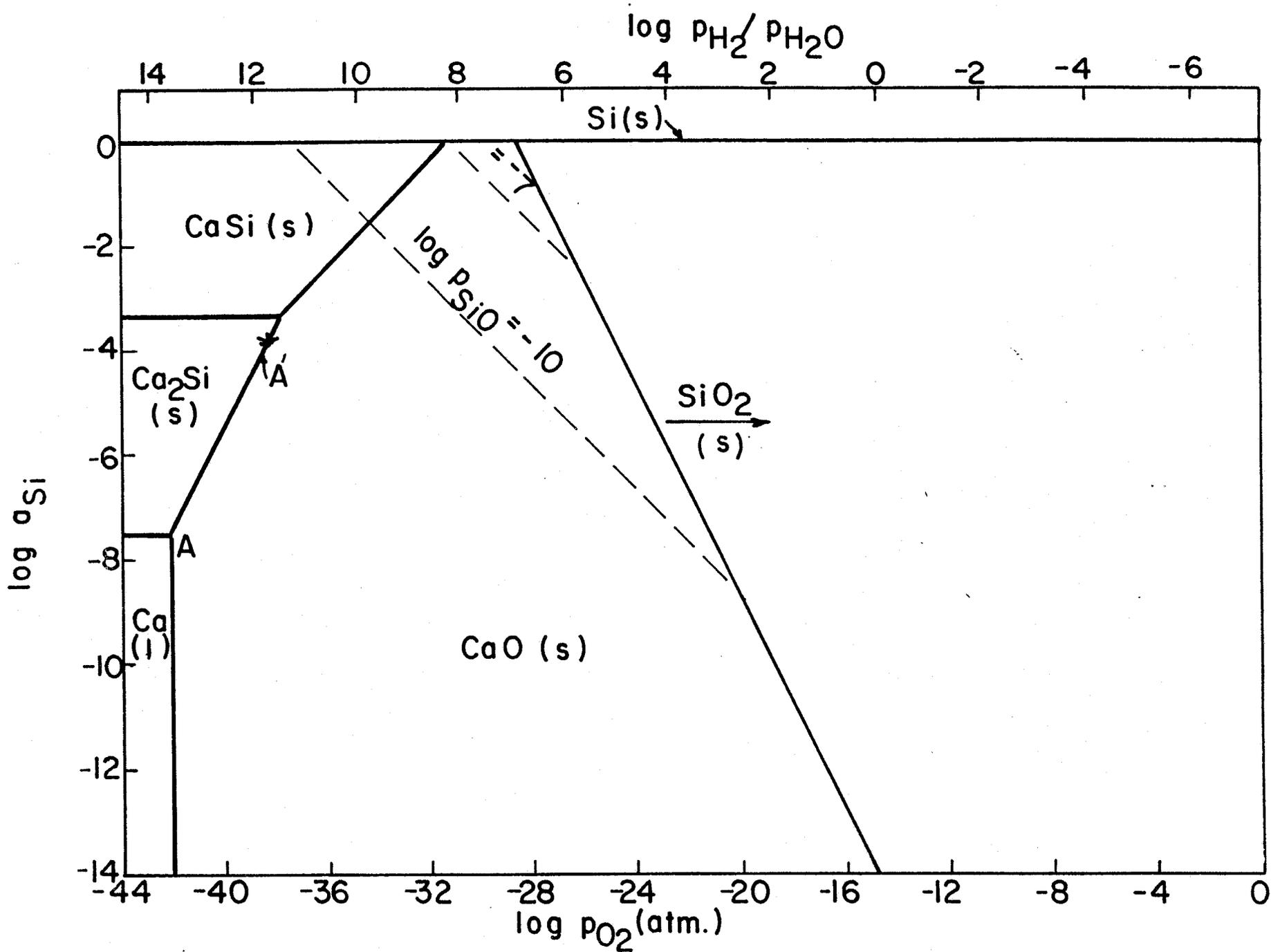


Fig. 1 Condensed Phase Equilibria for the Ca-O-Si System 1250 K

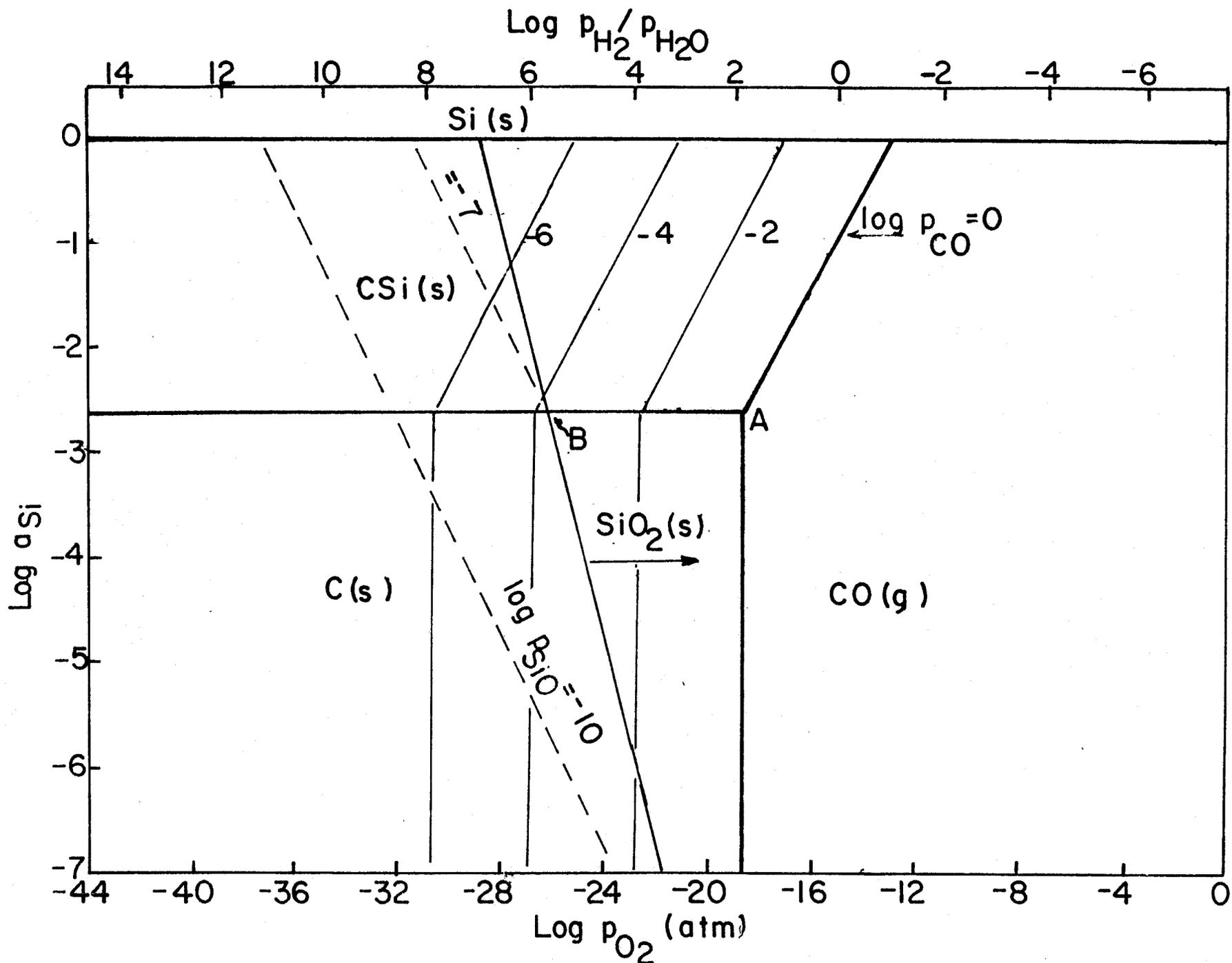


Fig.2 Condensed Phase Equilibria for the C-O-Si System 1250 K

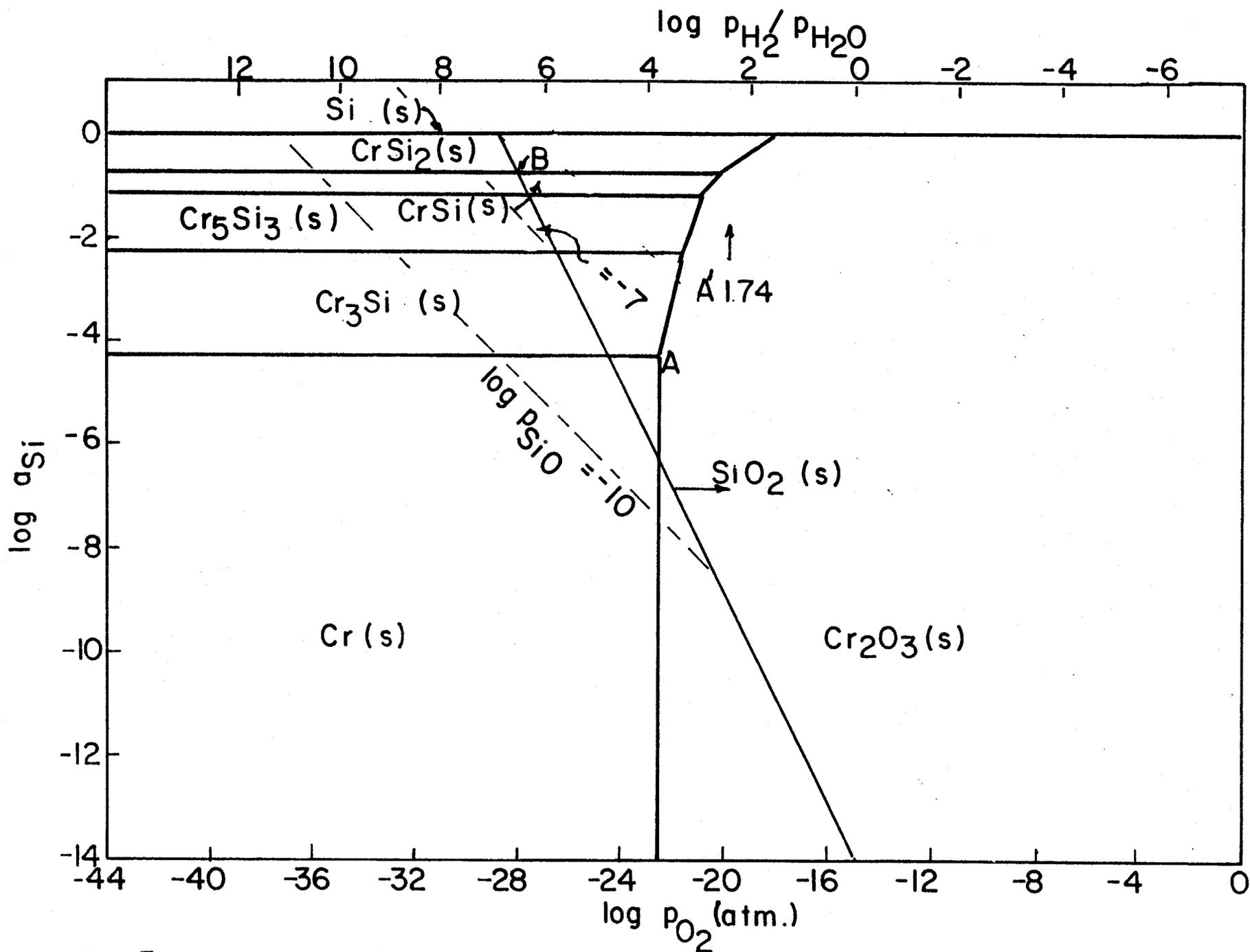


Fig. 3 Condensed Phase Equilibria for the Cr-O-Si System 1250 K

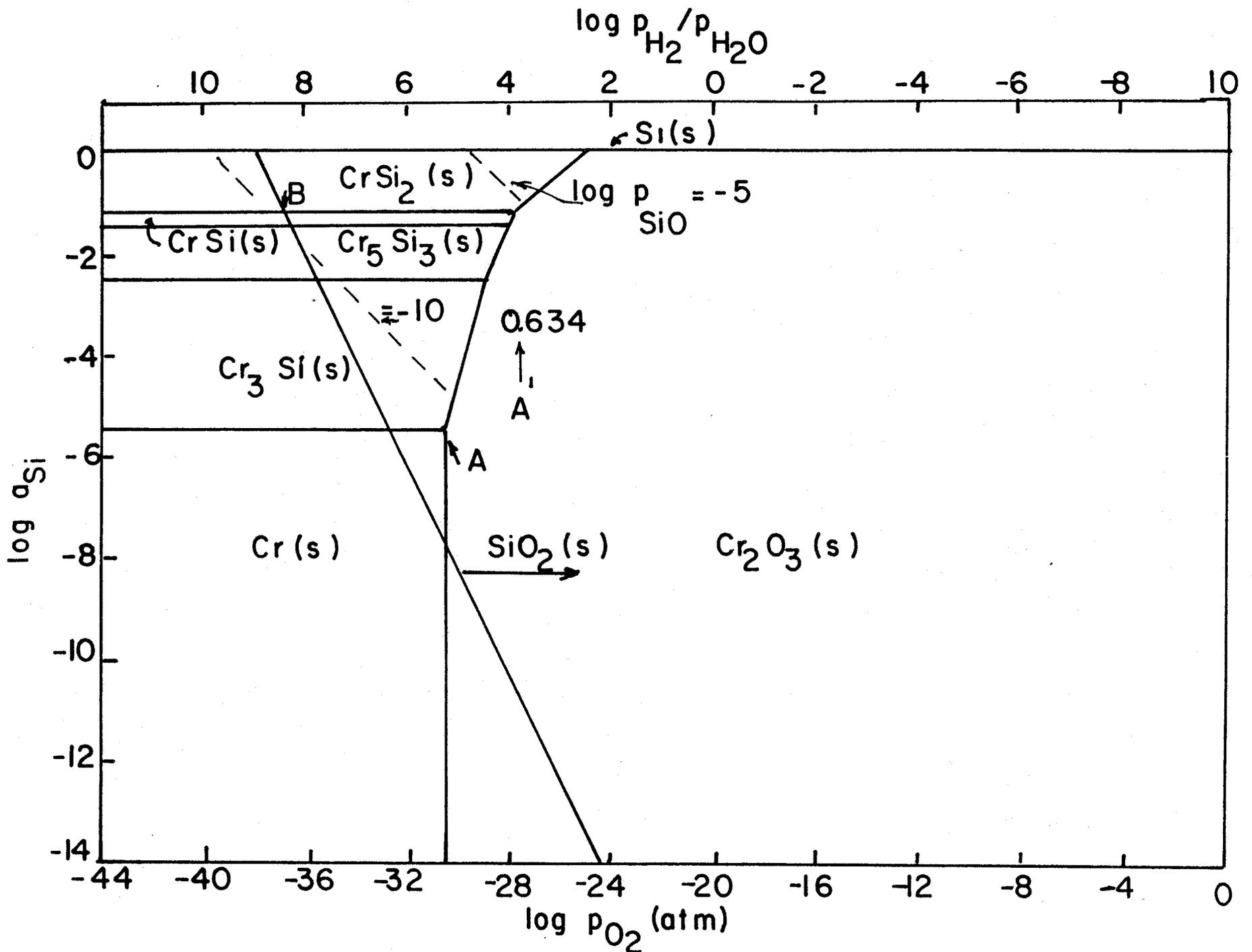


Fig.4 Condensed Phase Equilibria for the Cr-O-Si System 1000 K

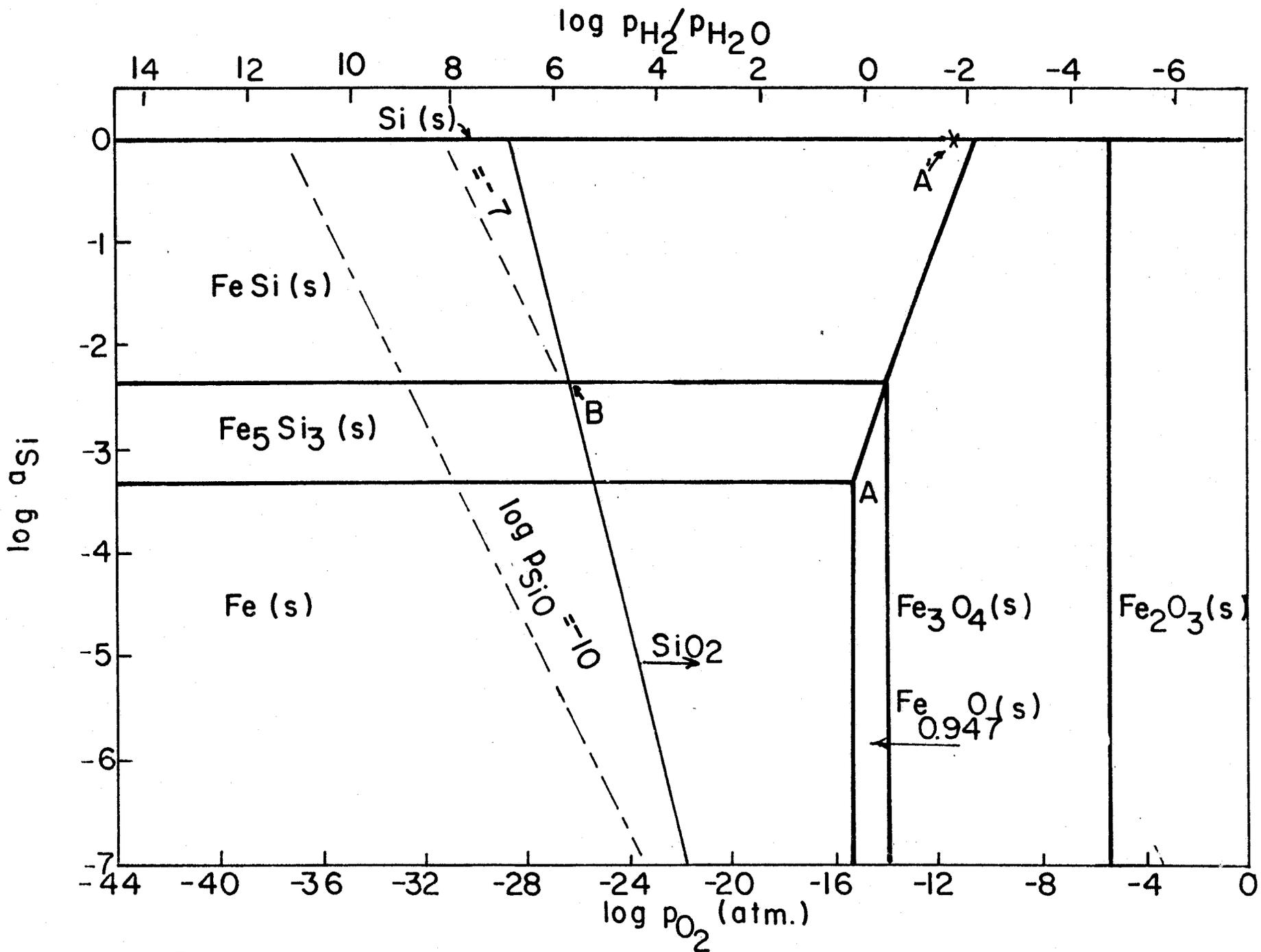


Fig. 5 Condensed Phase Equilibria for the Fe-O-Si System 1250 K

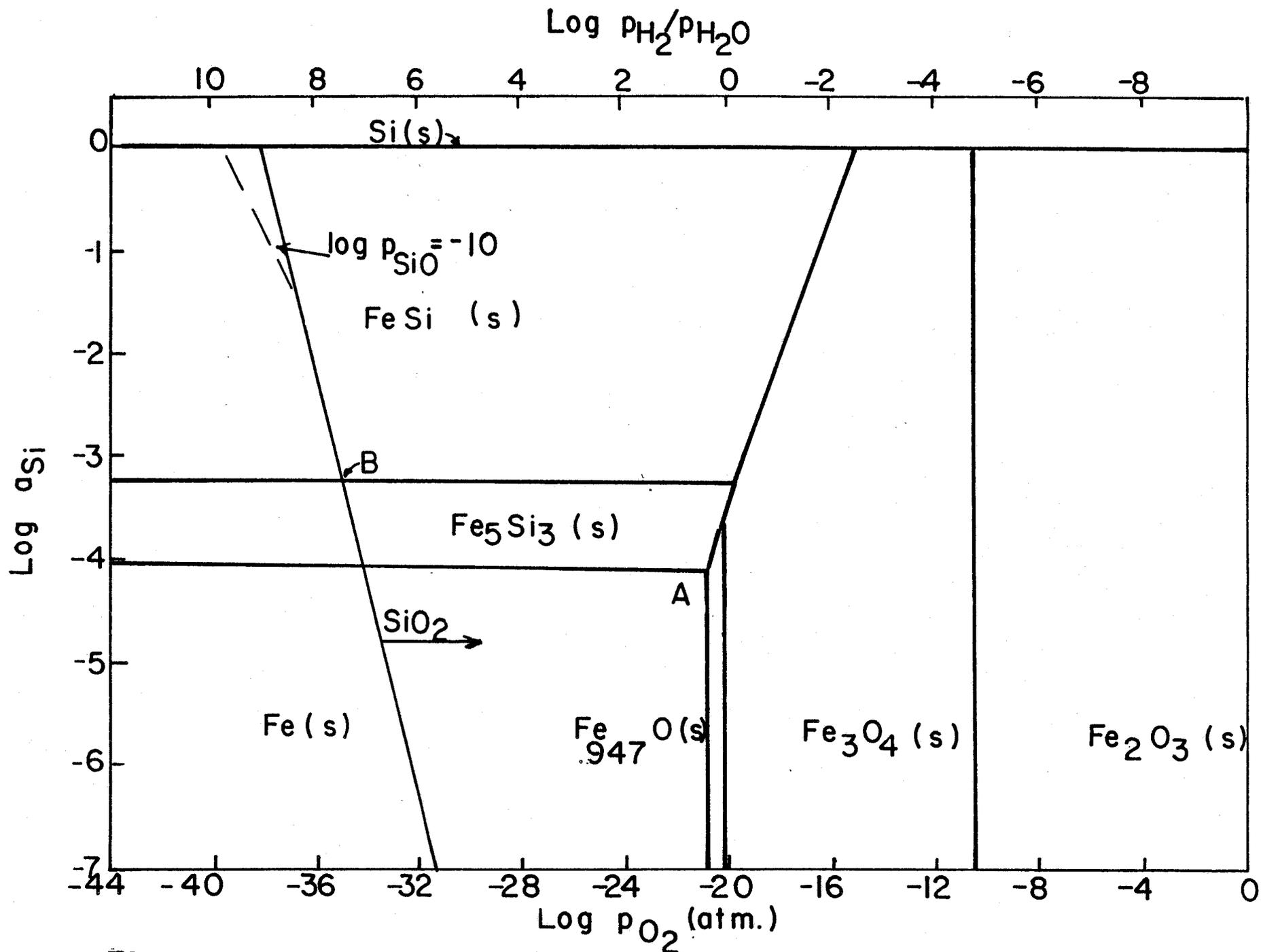


Fig 6 Condensed Phase Equilibria for the Fe-O-Si System 1000 K

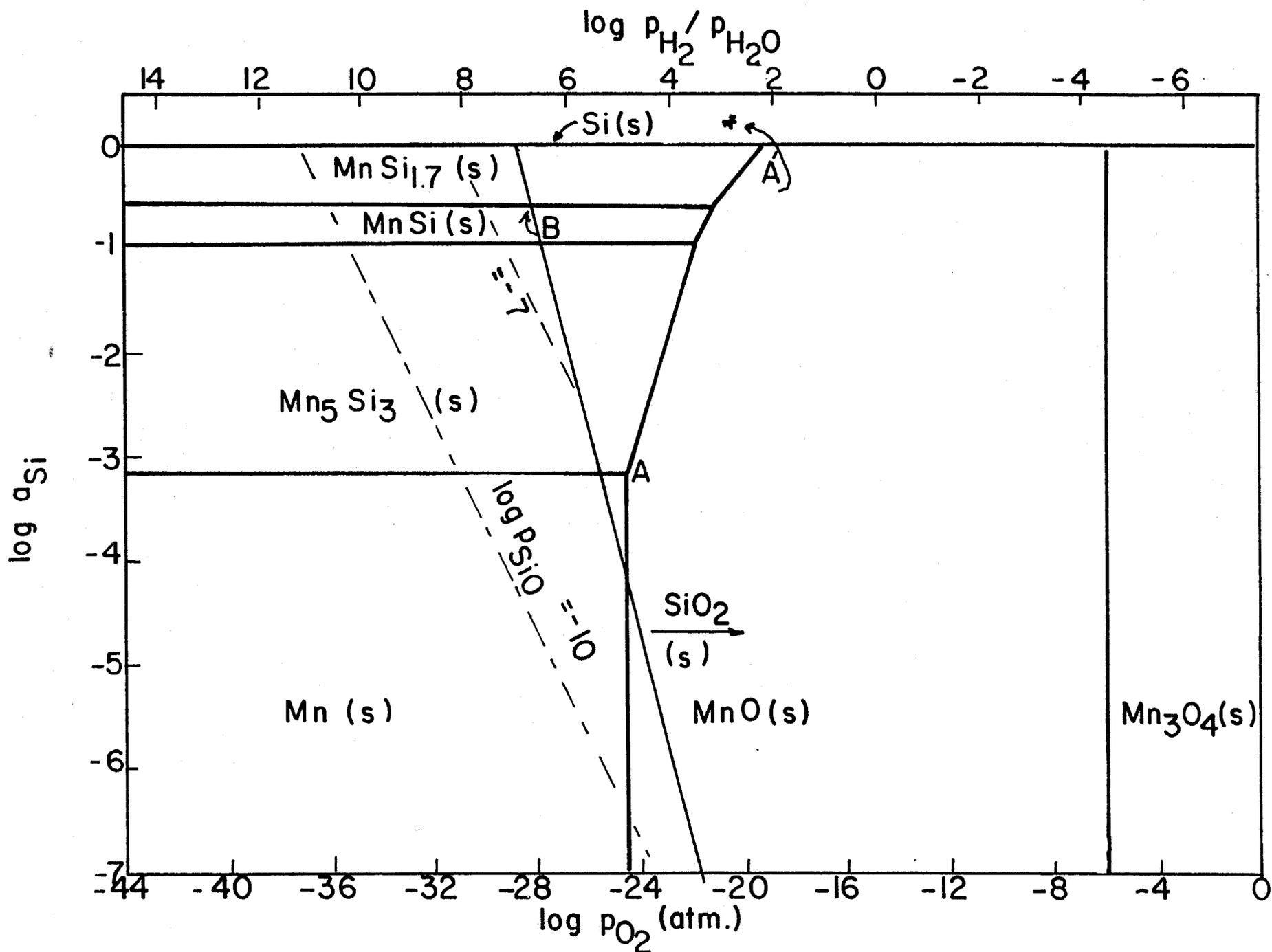


Fig. 7 Condensed Phase Equilibria for the Mn-O-Si System 1250 K

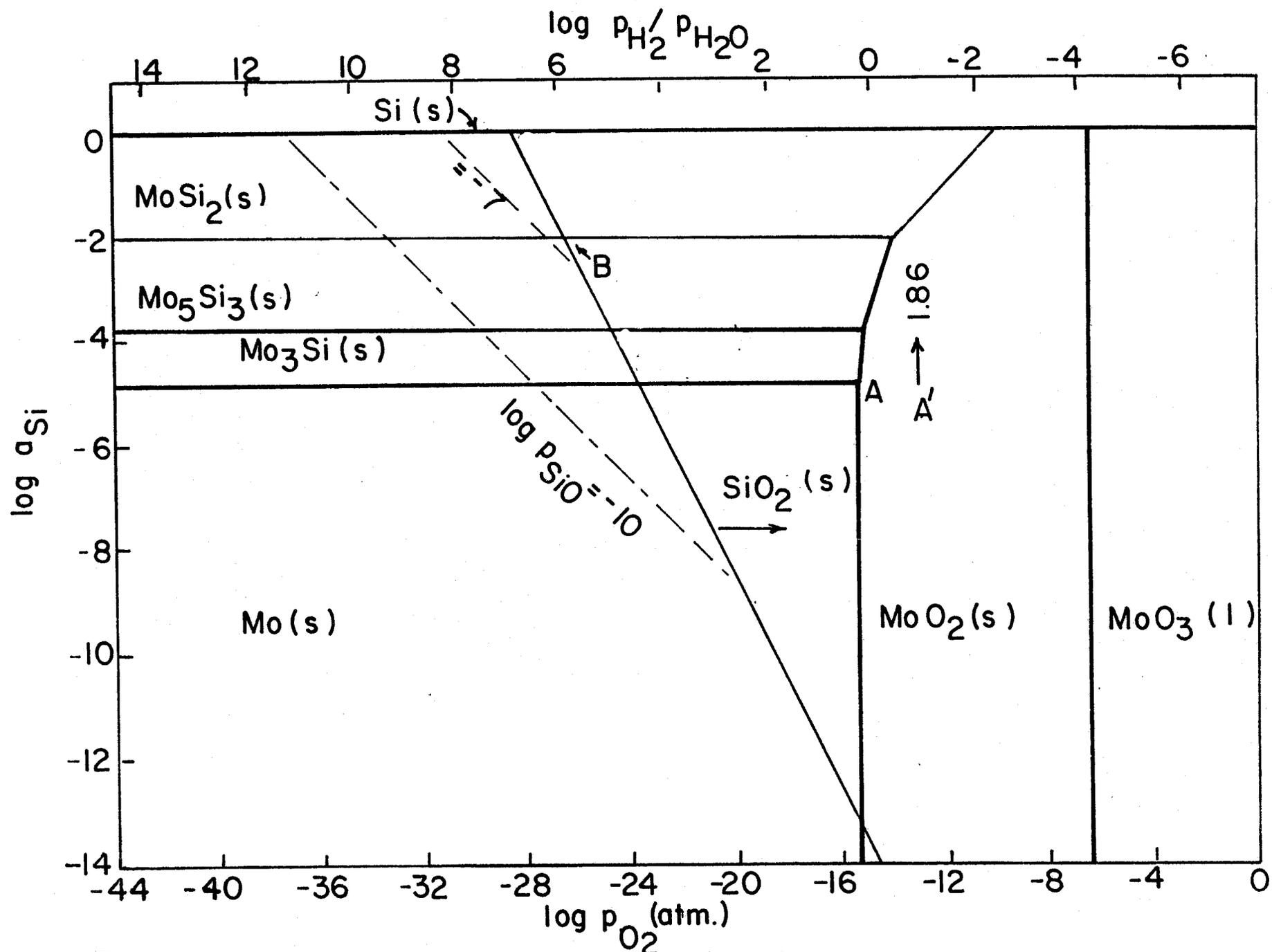


Fig. 8 Condensed Phase Equilibria for the Mo-O-Si System 1250 K

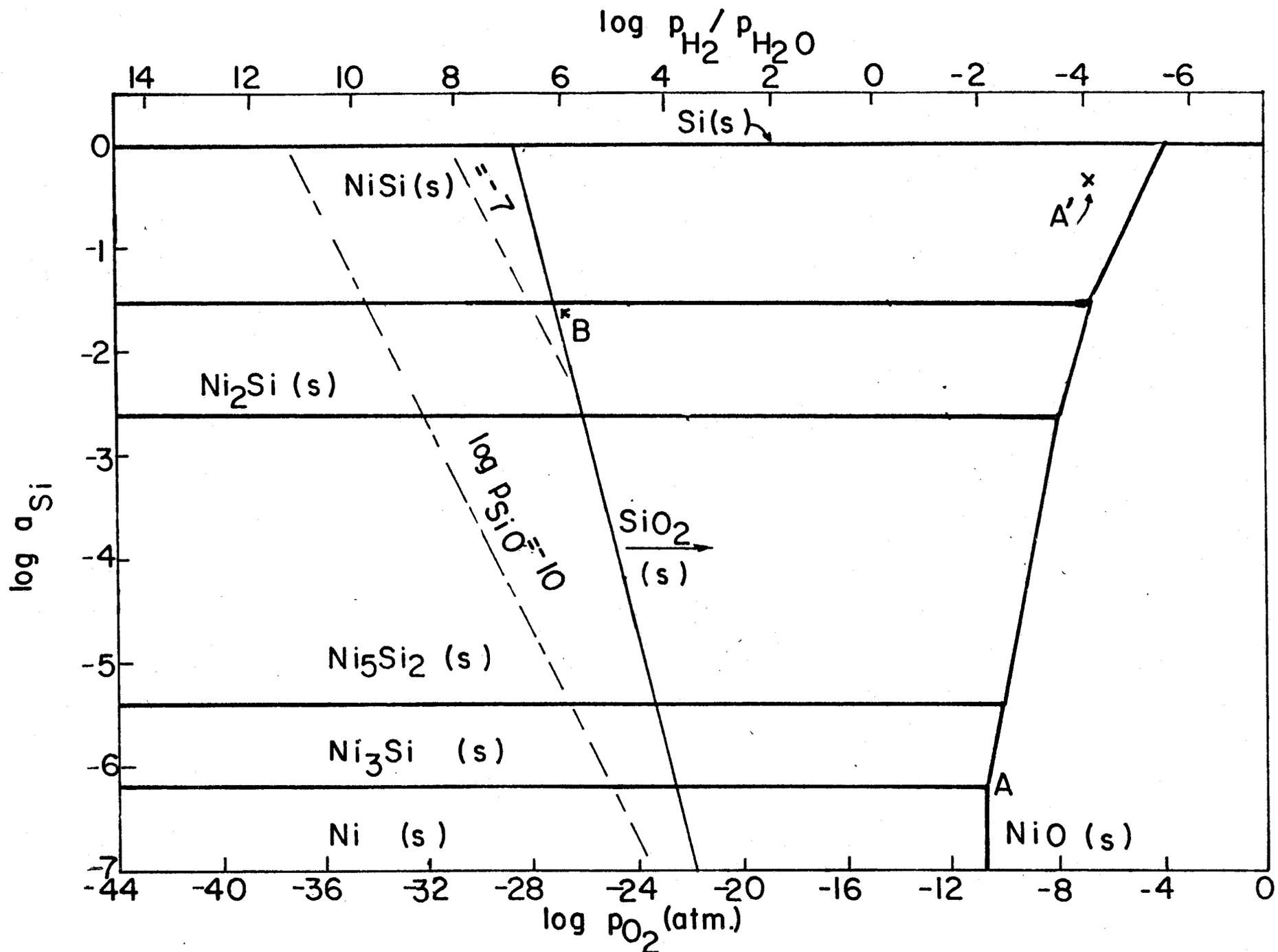


Fig. 9 Condensed Phase Equilibria for the Ni-O-Si System 1250 K

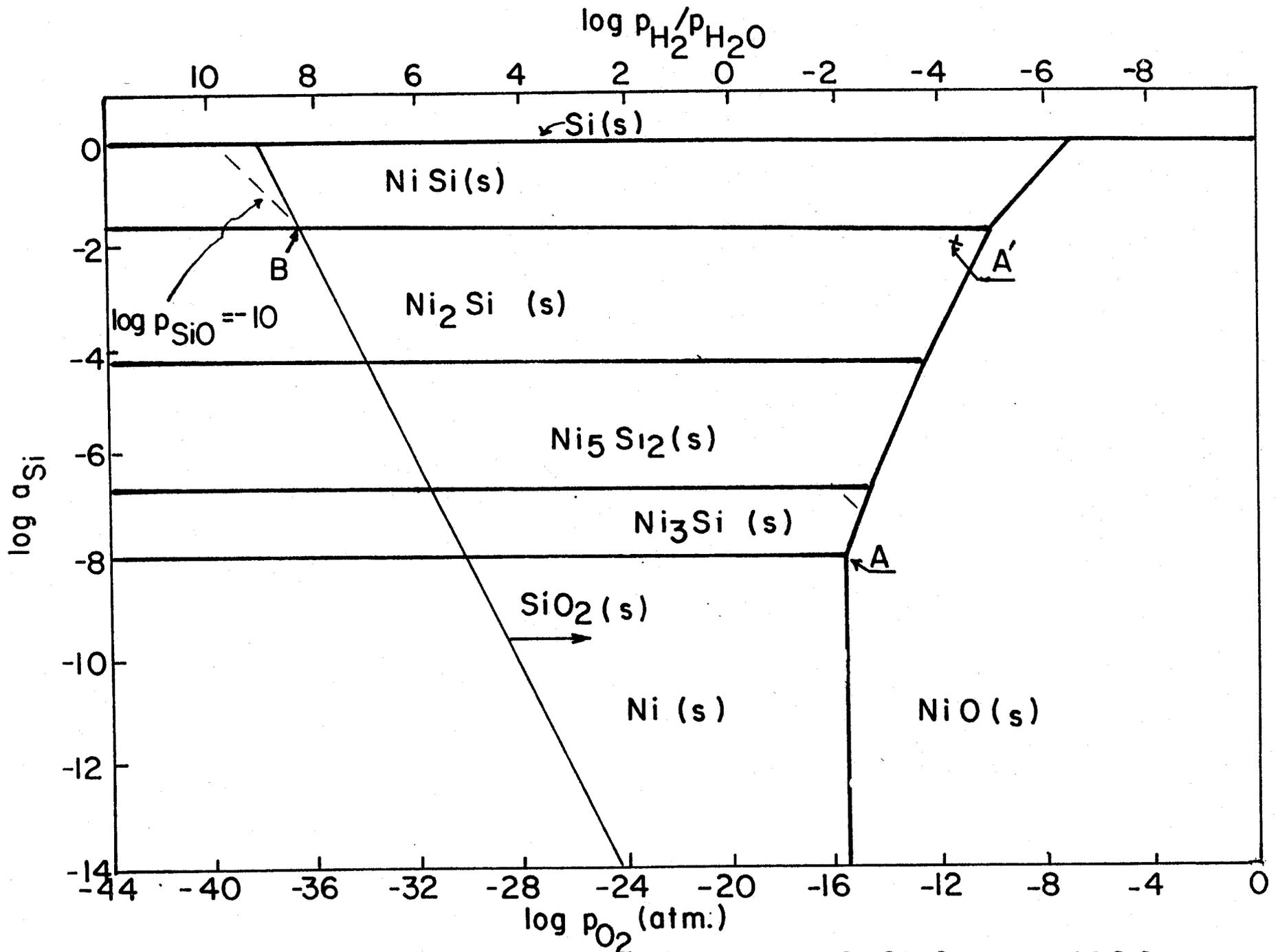


Fig.10 Condensed Phase Equilibria for the Ni-O-Si System 1000 K

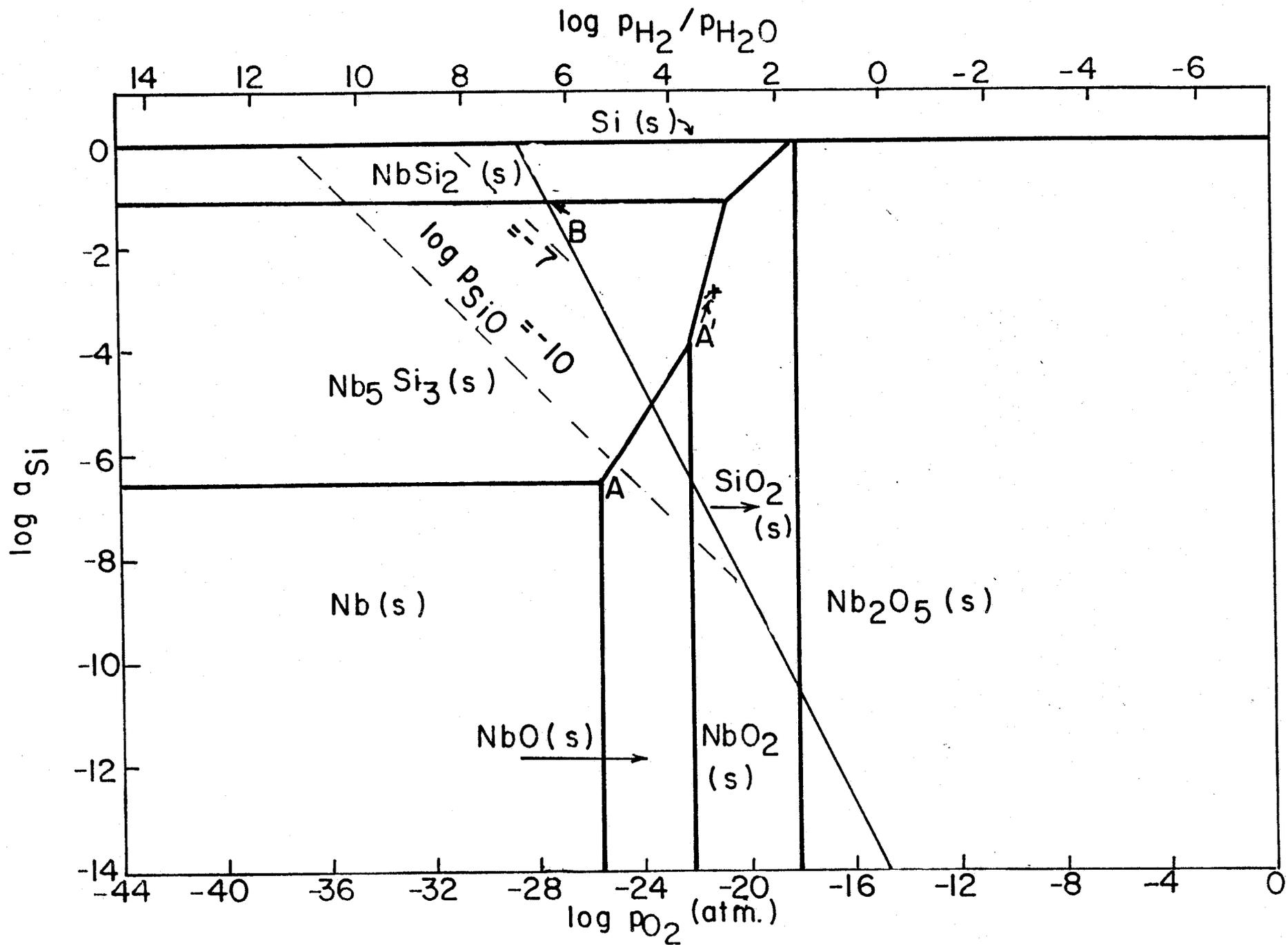


Fig.11 Condensed Phase Equilibria for the Nb-O-Si System 1250 K

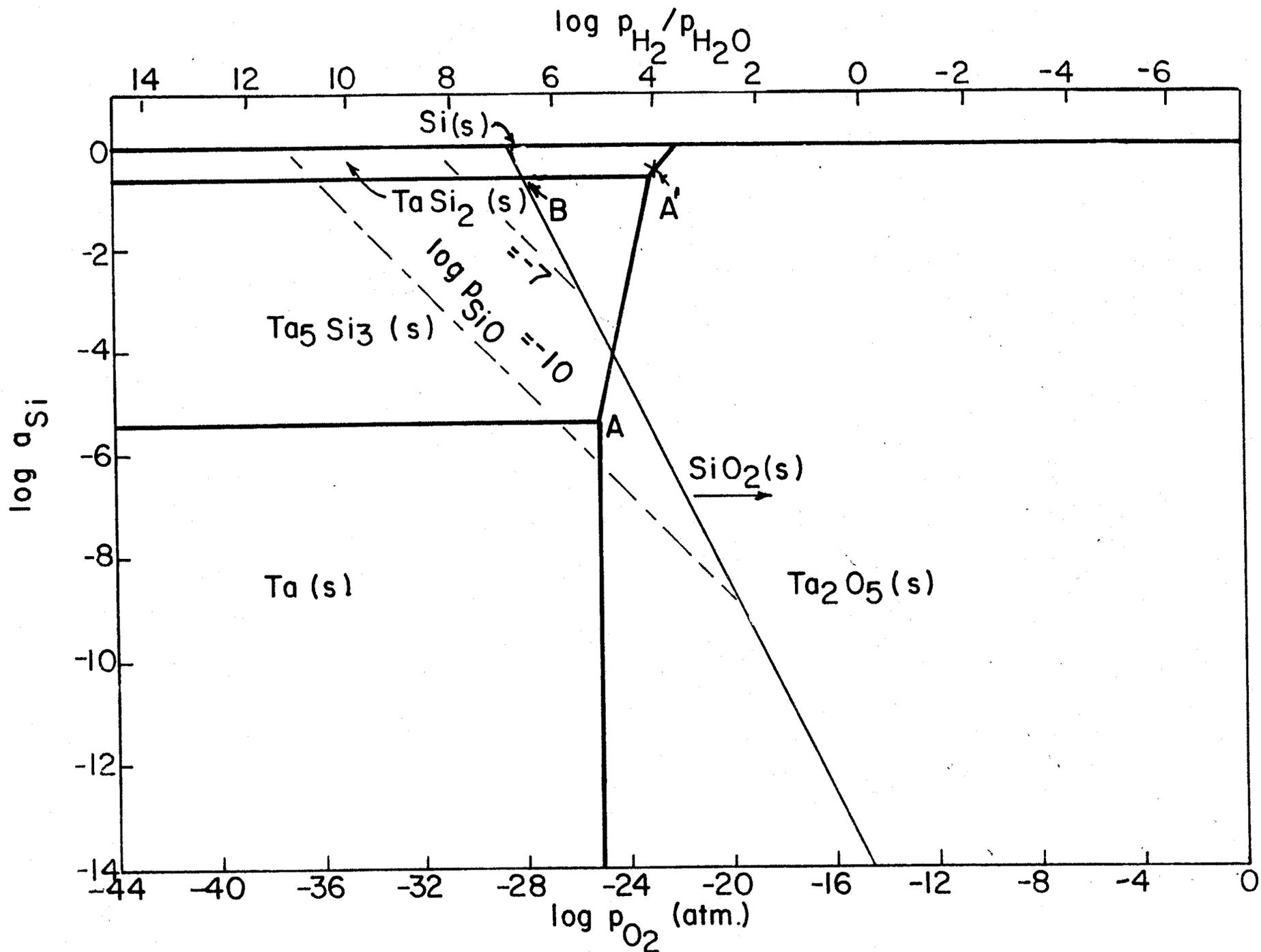


Fig.12 Condensed Phase Equilibria for the Ta-O-Si System 1250 K

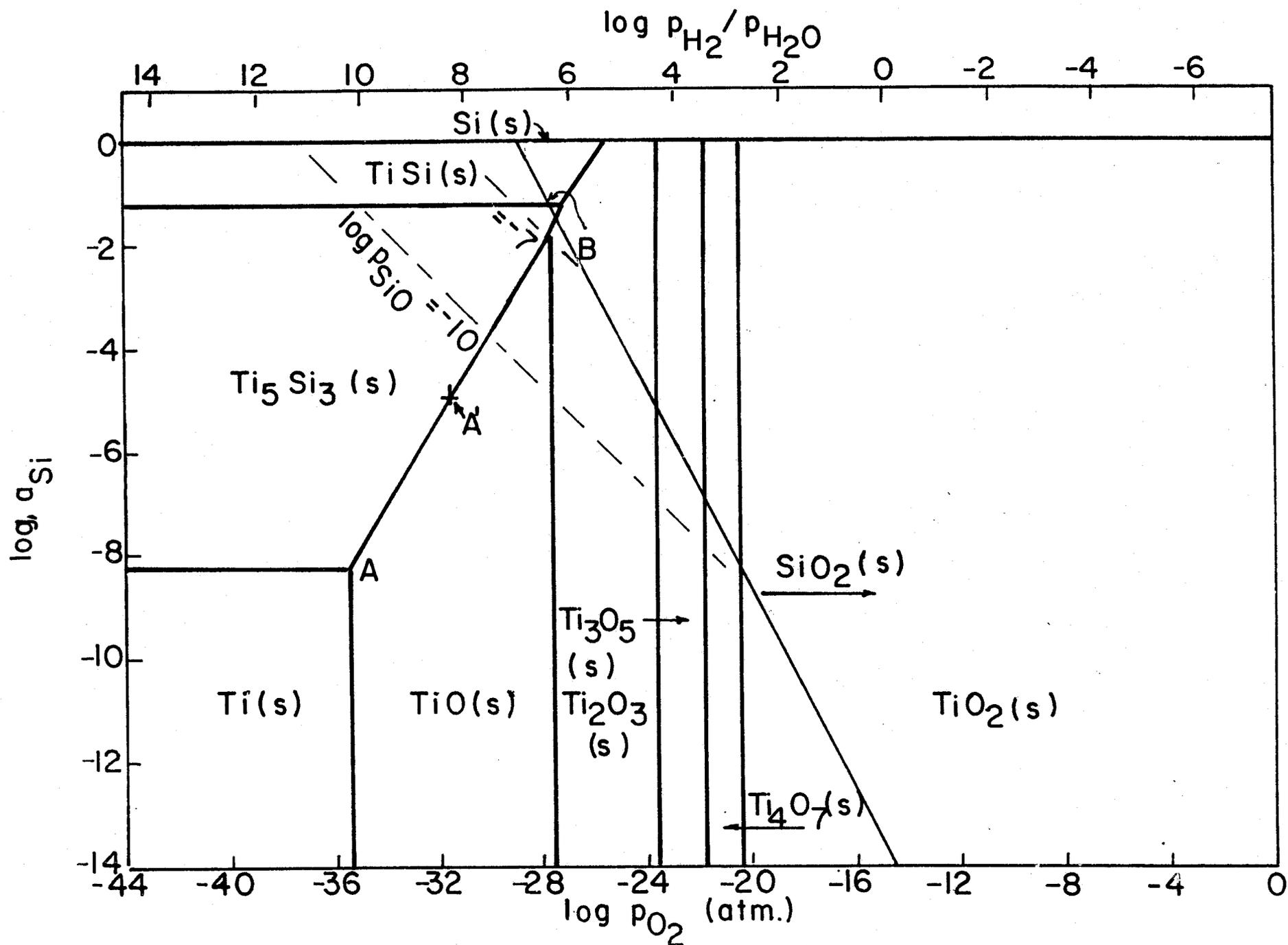


Fig. 13 Condensed Phase Equilibria for the Ti-O-Si System 1250 K

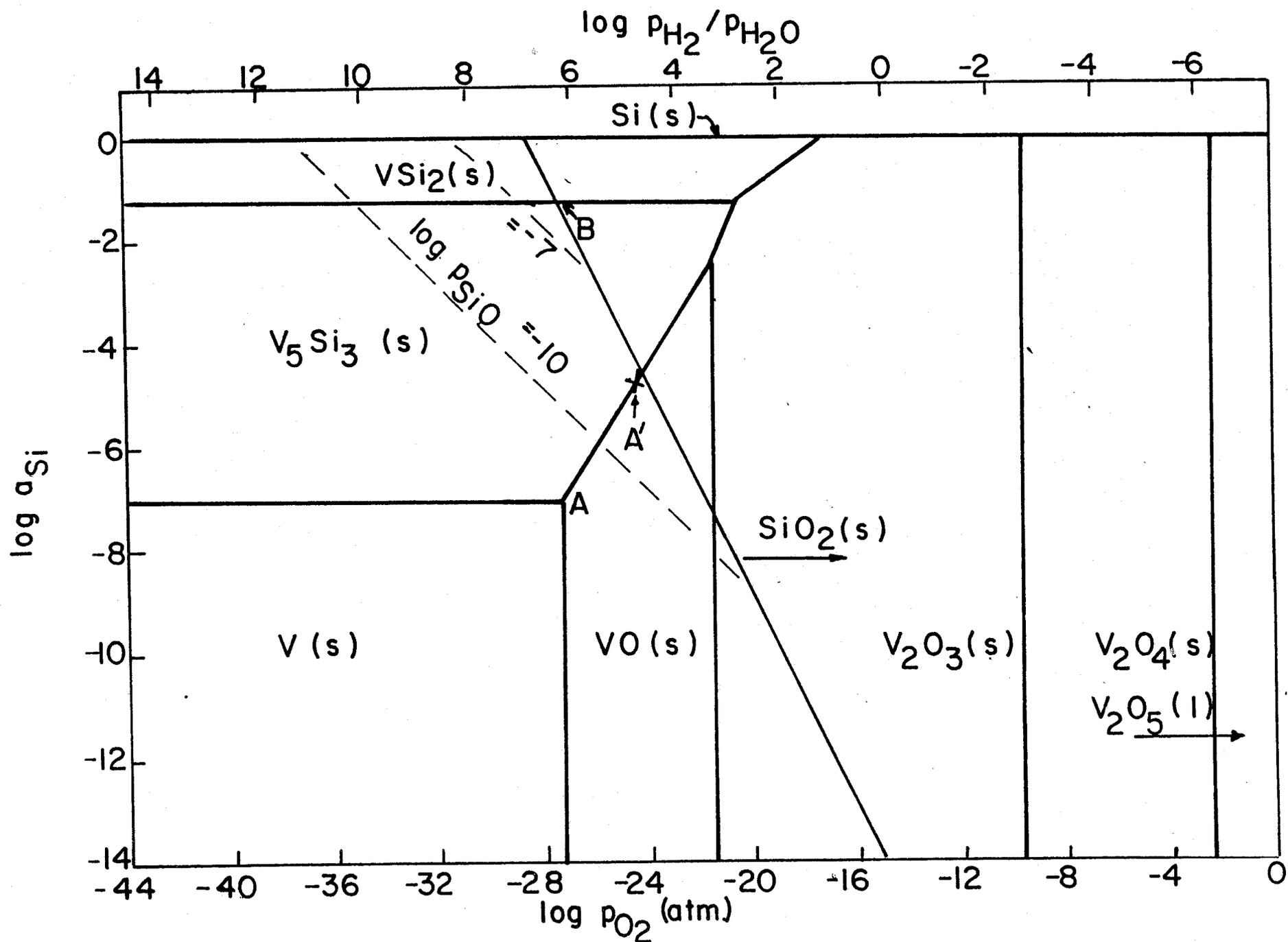


Fig.14 Condensed Phase Equilibria for the V-O-Si System 1250 K

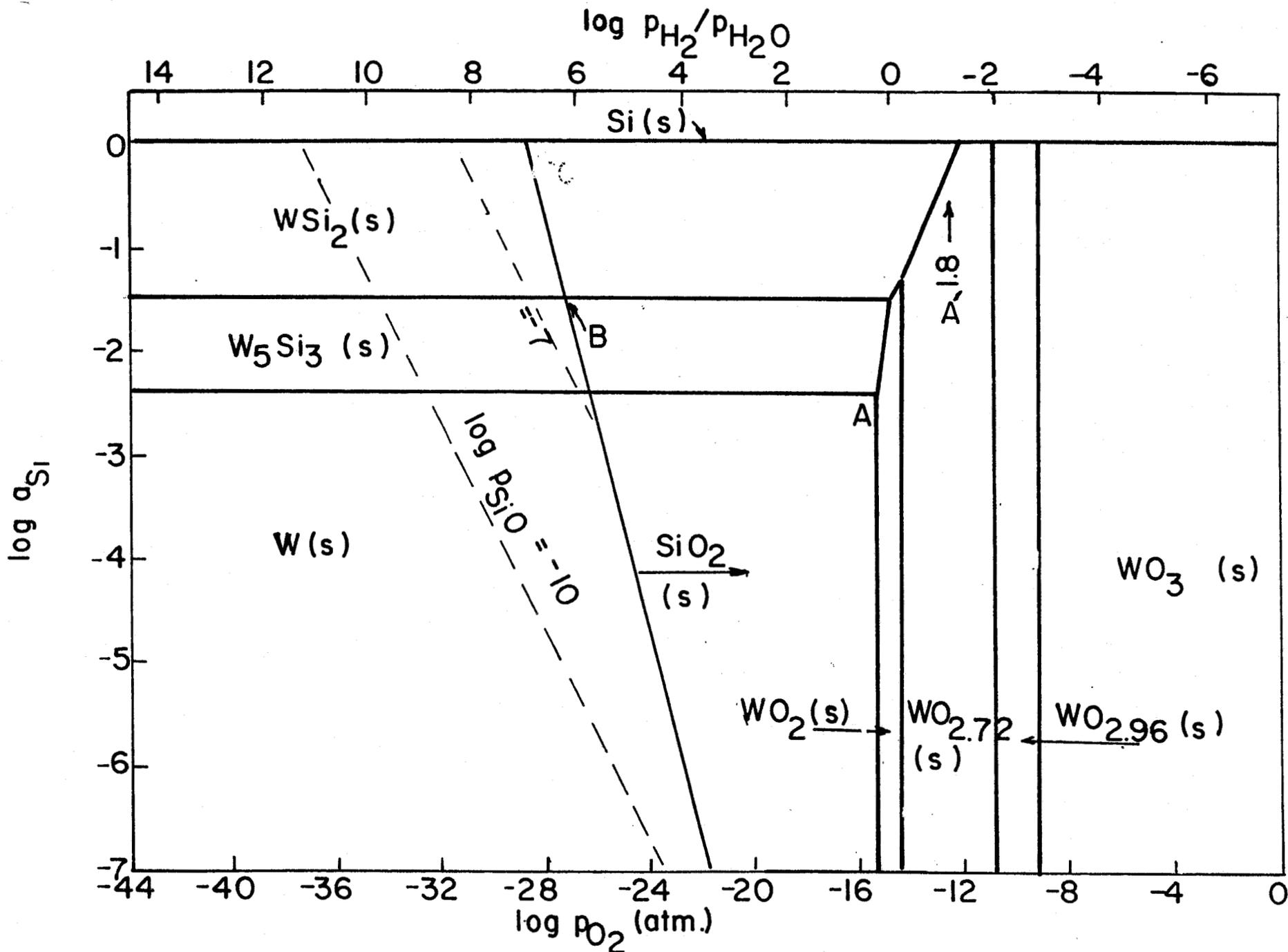


Fig.15 Condensed Phase Equilibria for the W-O-Si System 1250 K

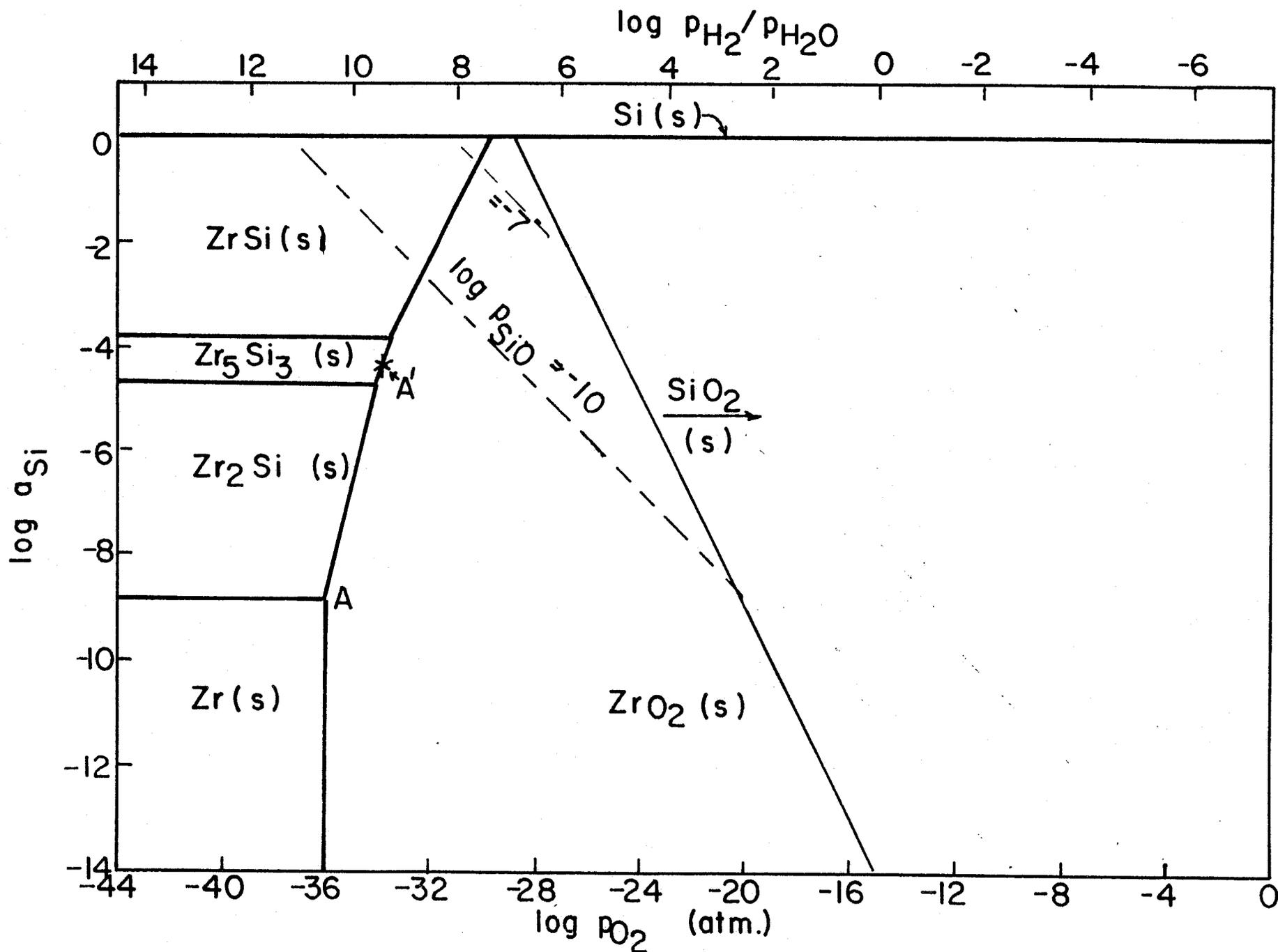


Fig.16 Condensed Phase Equilibria for the Zr-O-Si System 1250 K