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Thermochemical Analysis for Purification of Polysilicon Melts

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Thermochemical Analysis for Purification of Polysilicon Melts

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Abstract

Chemical equilibrium calculations are presented that are relevant to the purification of molten silicon by gas-blowing. The equilibrium distributions of silicon, boron, phosphorus carbon and iron among the solid, liquid and gas phases are reported for a variety of added chemicals, temperatures and total pressures. The identities of the dominant chemical species for each element in each phase are also provided for these conditions. The added gases examined are O₂, air, water, wet air, HCl, Cl₂, Cl₂/O₂, SiCl₄, NH₃, NH₄OH, and NH₄Cl. These calculations suggest possible purification schemes, although kinetic or transport limitations may prove to be significant.

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Thermochemical Analysis for Purification of Polysilicon Melts

I. Introduction

The availability of polysilicon feedstock has become a major issue for the photovoltaic (PV) industry in recent years. Most of the current polysilicon feedstock is derived from rejected material from the semiconductor industry. However, during expansions in the integrated-circuit industry, the reject material became rare and more expensive [1]. Although economic downturns in the integrated-circuit industry periodically increase the availability of the reject material to the PV industry, the continued rapid expansion of the PV crystalline-silicon industry will eventually require a dedicated supply of polysilicon feedstock.

The photovoltaic industry can accept a lower purity polysilicon feedstock ("solar-grade") compared to the semiconductor industry. The purity requirements and potential production techniques for solar-grade polysilicon have been reviewed [2]. One interesting process from previous research involves reactive gas blowing of the molten silicon charge. In early work, Dosaj, *et al.* reported a reduction of metal and boron impurities from silicon melts using reactive gas blowing with O_2 and Cl_2 [3]. The same authors later reassessed their data and the literature, and concluded that Cl_2 and O_2/Cl_2 gas blowing are only effective for removing Al, Ca, and Mg from the silicon melt [4]. Khattak and Schmid [5] have reported that the combination of vacuum, slagging, moist argon blowing and directional solidification reduced impurity levels, including B and P. More recently, researchers from Kawasaki Steel Corp. reported removal of B and C from silicon melts using reactive gas blowing with an O_2/Ar plasma torch [6]. Processes that purify the silicon melt are believed to be potentially much lower cost compared to present production methods that purify gas species.

In this report, we describe chemical equilibrium calculations relevant to the removal of C, B, P and Fe from silicon melts. The purpose of the calculations is to help guide experimental investigations that will be described elsewhere, and to understand the purification process. Preliminary results from these calculations have been presented elsewhere [7], as well as similar work by other researchers [8]. This type of analysis provides information as to which chemical

species are likely to form when various gases are blown over molten silicon. If these species are gases, they could be pumped out of the system during the blowing process. If these species are solid, they might be separable from the liquid or solid silicon, depending on the relative densities. These calculations are fairly limited in that they only examine the effects of thermochemistry on the composition of the system as a function of total pressure and temperature. The assumption of chemical equilibrium means that relative rate effects are ignored and complete mixing takes place. Kinetic or mass transport effects will only decrease the amount of a reaction product relative to the results presented here.

II. **Calculational Methods**

These studies used the code EQUIL [9], which is part of the CHEMKIN Collection of software[10], and is a CHEMKIN implementation of STANJAN [11]. This code uses a minimization-of-free-energy method to determine the equilibrium composition of the mixture. This method for determining chemical equilibrium treats all possible reactions between all chemical species included in the calculation, in contrast with other methods which involve specifying a set of reactions between a limited set of chemical species. Through Surface Chemkin, EQUIL can handle multiple phases, including condensed phases. Each phase can contain multiple species, but they are treated ideally. Although treating the gas-phase as ideal is a fairly good approximation, this will be less true for the condensed phases. Treating these systems as ideal is quite common in these sorts of calculations, and generally results from a lack of data about non-ideal effects. The approach taken here, however, should be adequate for the present purpose of screening possible chemical systems for silicon purification.

A standard starting mixture was chosen for these calculations based on information on the composition of metallurgical-grade silicon of interest. For 1 mole of silicon, levels for each of the impurities of most interest were set for carbon at the 1000 ppm level, boron and phosphorus at the 2.5 ppm level, and iron at the 1000 ppm level. To evaluate the effects of blowing gas over the molten silicon, various reactants were included in the calculation, generally at the 0.05 mole level. This represents a substantial gas exposure, as it corresponds to blowing 5 SLM of gas for 80 minutes over a 10 kg sample of silicon. Argon was also included in the equilibrium

calculations at the 0.01 mole level to ensure that there would always be some gas present. [If the input gas reacts to form solid products, the absence of gaseous species can cause numerical problems in the calculations. A constant pressure and temperature is specified, so the loss of gas leads to an extremely small volume in the simulation, which in turn can cause convergence problems.]

Although the various "blowing gas" additions are discussed in terms of specific chemical species being input (i.e. water or O_2), the equilibrium analysis is actually only dependent on the ratios of the different elements that are input into the system. In other words, the composition of the system at equilibrium will be the same if one mole of water is specified in the input file or one mole of H_2 plus half a mole of O_2 is specified in the input file. Kinetically, there may be a large difference, and the amount of heat released when these gases react with silicon can be quite different, but the chemical composition at equilibrium is the same.

For a specified input gas mixture, the equilibrium composition of the system was calculated for a range of pressures and temperatures. The furnace system to be used for the experiments is vacuum capable, so pressures of 0.001 to 1 atm were investigated. Silicon melts at $1410^\circ C$ (1683K) and the various forms of silicon dioxide in the range of $1610^\circ C$ to $1703^\circ C$ (1883K to 1976 K), so results at temperatures of 1450, 1550, and $1650^\circ C$ are reported in this study. The distribution of the impurity elements among the solid, liquid and gas phases should correlate with the likelihood of being able to remove the impurity either by pumping away gaseous byproducts, or separation of solids from the liquid silicon.

Table 1 lists the chemical species considered in these calculations, along with the source of the thermochemical data used. In general, a species was considered if it was composed of the relevant elements and thermochemical data for that species was straightforwardly accessible in the polynomial-fit format used by CHEMKIN. More gas-phase species than condensed phase species were considered, primarily because of the availability of data.

Table 1. Chemical species considered in equilibrium calculations.

References for thermochemical data:

C = CHEMKIN-III Thermodynamic Data Base, v 3.0, Jan. 1997 [12, 23]

J = fits to data from JANAF Tables [19]

B = BAC-MP4 calculations [13-18]

Na = NASA Data Base [20, 23]

Bu = Burcat Data Base [21, 23]

No = Noring Data Base [22, 23]

O = Other, see text for details

Species	Ref.	Species	Ref.	Species	Ref.	Species	Ref.	Species	Ref.	Species	Ref.
H	C	H ₂	C	O	C	O ₂	C	O ₃	C		C
OH	C	H ₂ O	C	HO ₂	C	H ₂ O ₂	C				
Cl	C	Cl ₂	C	HCl	C	HOCl	C				
Si	C	SiH	C	SiH ₂	C	SiH ₃	C	SiH ₄	C		C
Si ₂	C	Si ₂ H ₂	C	Si ₂ H ₃	C	H ₃ SiSiH	C	H ₂ SiSiH ₂	C		C
Si ₂ H ₅	C	H ₃ SiSiH ₃	C	Si ₃	C	Si ₃ H ₈	C				
SiClH ₃	C	SiCl ₃ H	C	SiCl ₂ H ₂	C	SiH ₂ Cl	C	SiHCl ₂	C		C
HSiCl	C	SiCl	C	SiCl ₂	C	SiCl ₃	C	SiCl ₄	C		C
HCl ₂ SiSiCl ₂ H	C	Si ₂ Cl ₅ H	C	Si ₂ Cl ₆	C	Si ₂ Cl ₅	C	Cl ₂ SiSiCl ₂	C		C
Cl ₃ SiSiCl	C	Cl ₃ SiSi	C	Cl ₂ SiSiCl	C	Cl ₂ SiSi	C	ClSiSiCl	C		C
ClSiSi	C	HSiSiCl	C								
C	C	C ₂	C	C ₃	C	C ₄	C	C ₅	C		C
CH	C	CH ₂	C	CH ₃	C	CH ₄	C	C ₂ H	C		C
C ₂ H ₂	C	C ₂ H ₃	C	C ₂ H ₄	C	C ₂ H ₅	C	C ₂ H ₆	C		C
C ₃ H ₂	C	C ₃ H ₄	C	C ₃ H ₆	C	C ₃ H ₈	C	C ₄ H	C		C
C ₄ H ₂	C	C ₄ H ₆	C	C ₄ H ₈	C	C ₄ H ₁₀	C	C ₅ H	C		C
C ₅ H ₂	C	C ₅ H ₅	C	C ₅ H ₆	C	C ₅ H ₁₂	C	C ₆ H	C		C
C ₆ H ₂	C	C ₆ H ₃	C	C ₆ H ₄	C	C ₆ H ₅	C	C ₆ H ₆	C		C
C ₆ H ₇	C	C ₆ H ₁₀	C	C ₆ H ₁₄	C	C ₈ H	C	C ₈ H ₂	C		C
CH ₂ CHCCH	C	CH ₂ CHCCH ₂	C	CH ₂ CHCH ₂	C	CH ₂ CHCHCH	C	CH ₂ CHCHCH ₂	C		C
CH ₃ CC	C	CH ₃ CCCH ₂	C	CH ₃ CCCH ₃	C	CH ₃ CCH ₂	C	CH ₃ CHCH	C		C

Species	Ref.	Species	Ref.	Species	Ref.	Species	Ref.	Species	Ref.	Species	Ref.
CH ₃ CH ₂ CCH	C	CH ₃ CH ₂ CH ₂ CH ₃	C	HCCCHCCH	C	HCCCHCCH	C	HCCCHCCH	C	H ₂ CCCCCH	C
H ₂ CCCCCH	C	H ₂ CCCCCH ₂	C	H ₂ CCCCCH	C	H ₂ CCCCCH	C	H ₂ CCC	C	CHCl	C
CCl	C	CCl ₂	C	CCl ₃	C	CCl ₃	C	CCl ₄	C	CH ₃ Cl	C
CHCl ₂	C	CH ₂ Cl	C	CHCl ₃	C	CHCl ₃	C	CH ₂ Cl ₂	C	C ₂ HCl ₅	C
C ₂ Cl ₃	C	C ₂ Cl ₅	C	C ₂ Cl ₆	C	C ₂ Cl ₆	C	C ₂ HCl	C	CH ₂ CCl	C
CCl ₂ CH	C	CCl ₃ CClH ₂	C	CCl ₃ CH ₂	C	CCl ₃ CH ₂	C	CCl ₃ CHCl	C	CH ₂ ClCH ₂ Cl	C
CH ₂ CCl ₂	C	CH ₂ CHCl	C	CH ₂ ClCCl ₂	C	CH ₂ ClCCl ₂	C	CH ₂ ClCH ₂	C	CH ₃ CCl ₃	C
CH ₂ ClCHCl	C	CH ₂ ClCHCl ₂	C	CH ₃ CCl	C	CH ₃ CCl	C	CH ₃ CHCl ₂	C	CHCl ₂ CH ₂	C
CH ₃ CH ₂ Cl	C	CH ₃ CHCl	C	CH ₃ CHCl ₂	C	CH ₃ CHCl ₂	C	CHCl ₂ CCl ₂	C	CHClCHCl	C
CHCl ₂ CHCl	C	CHCl ₂ CHCl ₂	C	CHClCCl	C	CHClCCl	C	CHClCH	C		
Cl ₂ CCCl ₂	C	Cl ₂ CCCHCl	C	ClCCCl	C	ClCCCl	C	HCCCl	C		
CO	C	CO ₂	C	C ₂ O	C	C ₂ O	C	C ₃ O ₂	C	H ₂ C ₄ O	C
CH ₂ O	C	CH ₂ OH	C	CH ₃ O	C	CH ₃ O	C	CH ₃ OH	C		
HCO	C	HCOOH	C	HOCH ₂ OH	C	HOCH ₂ OH	C	HOCO	C	OC(OH) ₂	C
HCCO	C	HCCOH	C	OCHCHO	C	OCHCHO	C	CH ₂ CO	C	CH ₂ HCO	C
H ₂ CCH ₂ OH	C	H ₂ CCHO	C	CH ₃ CH ₂ O	C	CH ₃ CH ₂ O	C	CH ₃ CHOH	C	CH ₃ OCH ₃	C
CH ₃ CO	C	CH ₃ HCO	C	C ₆ H ₅ O	C	C ₆ H ₅ O	C	C ₆ H ₅ OH	C		
Cl ₂ CO	C	Cl ₂ COH	C	Cl ₂ HCO	C	Cl ₂ HCO	C	Cl ₃ CO	C	Cl ₃ COH	C
ClCO	C	ClCOH	C	ClH ₂ CO	C	ClH ₂ CO	C	ClHCO	C	ClOCl	C
ClO	C	ClOO	C	CCl ₂ CClO	C	CCl ₂ CClO	C	CCl ₂ CClOH	C	CCl ₂ HOO	C
CCl ₂ OHCH ₂	C	CCl ₂ OHCHCl	C	CCl ₃ CClO	C	CCl ₃ CClO	C	CCl ₃ CHO	C	CCl ₃ OO	C
CClH ₂ OO	C	CH ₂ CClOH	C	CH ₂ ClCClO	C	CH ₂ ClCClO	C	CH ₂ ClCHO	C	CH ₂ OHCCl ₂	C
CH ₂ OHCHCl	C	CH ₃ C(O)Cl	C	CH ₃ CClO	C	CH ₃ CClO	C	CH ₃ OCl	C	CHClCClOH	C
CHClCHOH	C	CHClOH	C	CHClOHCH ₂	C	CHClOHCH ₂	C	CHClOHCHCl	C	CHCl ₂ CClO	C
CHOHClCCl ₂	C	ClCH ₂ OH	C	Cl ₂ CHOH	C	Cl ₂ CHOH	C	HClCCClO	C	HClCCCHO	C
H ₂ CCClO	C	Cl ₂ CCHO	C	Cl ₃ CCO	C	Cl ₃ CCO	C	ClCCO	C		
SiC	C	SiCH	C	SiCH ₂	C	SiCH ₂	C	SiCH ₃	C	SiC ₂	C
HSiC	C	HSiCH ₂	C	HSiCH ₃	C	HSiCH ₃	C	Si ₂ C	C	SiCCH	C
H ₂ SiC	C	H ₂ SiCH	C	H ₂ SiCH ₂	C	H ₂ SiCH ₂	C	H ₂ SiCH ₃	C		
H ₃ SiC	C	H ₃ SiCH	C	H ₃ SiCH ₂	C	H ₃ SiCH ₂	C	H ₃ SiCH ₃	C		

Species	Ref.	Species	Ref.	Species	Ref.	Species	Ref.	Species	Ref.
HSiCCH	C	H ₂ SiCCH	C	H ₃ SiCCH	C	SiH ₃ SiH ₂ CH ₃	C	CH ₃ SiH ₂ SiH	C
H ₂ CCHSi	C	H ₂ CCHSiH	C	H ₂ CCHSiH ₂	C	H ₂ CCHSiH ₃	C	CH ₃ SiH ₂ SiH ₂ CH ₃	C
H(CH ₃)SiCH ₂	C	H ₂ Si(CH ₃) ₂	C	H ₂ Si(CH ₃)CH ₂	C	HSi(CH ₃) ₂ CH ₂	C	Si(CH ₃) ₃ CH ₂	C
HSi(CH ₃) ₂	C	HSi(CH ₃) ₃	C	Si(CH ₃) ₂	C	Si(CH ₃) ₃	C	Si(CH ₃) ₄	C
CSiCl	C	CSiCl ₂	C	CSiHCl	C	CSiCl ₃	C	CSiHCl ₂	C
CSiH ₂ Cl	C	CHSiCl	C	CHSiCl ₂	C	CHSiHCl	C	CHSiCl ₃	C
CHSiHCl ₂	C	CHSiH ₂ Cl	C	CH ₂ SiCl	C	CH ₂ SiCl ₃	C	CH ₂ SiHCl ₂	C
CH ₂ SiH ₂ Cl	C	CH ₃ SiCl	C	CH ₃ SiHCl ₂	C	HClSiCH ₂	C	HClSiCH ₃	C
HCl ₂ SiCH ₃	C	Cl ₂ SiCH ₂	C	Cl ₂ SiCH ₃	C	Cl ₃ SiCH ₃	C	H ₂ ClSiCH ₃	C
ClSi(CH ₃) ₂	C	Cl ₂ Si(CH ₃) ₂	C	ClSi(CH ₃) ₃	C	HClSi(CH ₃) ₂	C	H ₂ ClSiSiCl ₃	C
ClSi(CH ₃) ₂ CH ₂	C	Cl ₂ Si(CH ₃)CH ₂	C	HClSi(CH ₃)CH ₂	C	Cl(CH ₃)SiCH ₂	C		
SiCl ₃ CH ₂ CH	C	H ₂ CCH(SiCl ₂ H)	C	HCCSiCl ₂ H	C				
SiO	B	SiO ₂	B	-SiOSiO-	B	Si ₃ O ₃	B	Si ₄ O ₄	B
HOSi	B	HSiOH	B	HSi=O	B	SiOOH	B	Si(OH) ₂	B
SiH ₂ OH	B	SiH(OH) ₂	B	Si(OH) ₃	B	H ₂ SiO	B	H ₃ SiO	B
H ₃ SiOH	B	SiH ₂ (OH) ₂	B	SiH(OH) ₃	B	Si(OH) ₄	B	O=Si(OH) ₂	B
HOSi=O	B	HSi(=O)O	B	HSiOO	B	HSiOOH	B	HSiO ₂	B
SiH ₃ O ₂	B	H ₂ SiOOH	B	HSi(O)OH	B	H ₂ SiO ₂	B	SiH ₂ OH ₂	B
SiH ₂ (OH)O	B	SiH(OH) ₂ O	B	SiH ₃ OOH	B	HOSiO ₂	B	Si(OH) ₃ O	B
SiH ₃ OSiH ₃	B	-SiH ₂ OSiO-	B	H ₂ Si(O) ₂ SiH ₂	B	(HSiO(OH)) ₂	B		
CH ₃ OSiO ₂	B	CH ₃ OSiO	B	CH ₃ OSi	B	CH ₃ OSiOH	B	CH ₂ OSi(OH) ₃	B
CH ₃ OSi(OH) ₃	B	Si(OCH ₃) ₂ (OH) ₂	B	Si(OCH ₃) ₃ OH	B	Si(OCH ₃) ₄	B	CH ₃ OSi(OH) ₂ O	B
Si(OH) ₂ OCH ₃	B	SiOH(OCH ₃) ₂	B	Si(OCH ₃) ₃	B	Si(OCH ₃) ₃ O	B	Si(OCH ₃) ₂	B
(CH ₃) ₃ SiOH	B	(CH ₃) ₃ SiO	B	-Si(OH) ₂ OCH ₂ -	B	O=SiHOCH ₃	B	O=Si(OCH ₃) ₂	B
Si(OC ₂ H ₅) ₄	B	Si(OC ₂ H ₅) ₃ OH	B	Si(OC ₂ H ₅) ₂ (OH) ₂	B	C ₂ H ₅ OSi(OH) ₃	B	Si(OC ₂ H ₅) ₃ H	B
C ₂ H ₅ OSiH ₃	B	O=Si(OC ₂ H ₅) ₂	B						
N	C	N ₂	C	N ₃	C	NH	C	NH ₂	C
NH ₃	C	NNH	C	N ₂ H ₂	C	N ₂ H ₃	C	N ₂ H ₄	C
HN ₃	C								
CN	C	CN ₂	C	CNN	C	C ₂ N	C	C ₂ N ₂	C

Species	Ref.	Species	Ref.	Species	Ref.	Species	Ref.	Species	Ref.
HCN	C	HCNH	C	H ₂ CN	C	HNC	C	HNCN	C
H ₂ CNH	C	HNCNH	C	H ₂ CNCH ₂	C	C ₄ N ₂	J	C'CN	J
NO	C	NO ₂	C	NO ₃	C	N ₂ O	C	N ₂ O ₃	J
N ₂ O ₄	C	N ₂ O ₅	J	HNO	C	HNO ₂	C	HNO ₃	C
HNOH	C	HONO	C	HONO ₂	C	H ₂ NO	C	HNNO	C
H ₂ NOH	C	HN(OH) ₂	C	H ₂ NNO	C	HNNHO	C	HNNONO	C
ONHNHO	C	ONHNOH	C						
CNO	C	HCNO	C	HNCO	C	HOCN	C	H ₂ CNO	C
CH ₃ NO	C	CH ₃ NO ₂	C	CH ₃ ONO	C	CH ₃ ONO ₂	C	H ₃ CONHO	C
H ₂ CNCH ₂ O	C	H ₂ CNCHO	C	H ₂ CONO	C	H ₂ CNO ₂	C		
H ₂ CNNHO	C	H ₂ CNNO	C	H ₂ CNNO ₂	C	OCHNNHO	C		
SiN	C	SiNH	C	SiNH ₂	C	Si ₂ N	J		
HSiN	C	HSiNH	C	HSiNH ₂	C				
H ₂ SiN	C	H ₂ SiNH	C	H ₂ SiNH ₂	C	H ₂ SiNH ₃	C		
H ₃ SiN	C	H ₃ SiNH	C	SiH ₃ NH ₂	C	H ₂ Si(NH ₂) ₂	C	HSi(NH ₂) ₂	C
HSi(NH ₂) ₃	C	Si(NH ₂) ₃	C	Si(NH ₂) ₄	C	SiH ₃ NHSiH ₃	C	SiH ₃ NSiH ₃	C
B	C	B ₂	Na	BH	B	BH ₂	B	BH ₃	B
BO	Na	BO ₂	Na	B ₂ O	Na	B ₂ O ₂	Na	B ₂ O ₃	Na
HBO	B	HBO	B	HBOH	B	H ₂ BO	B	HOBHO	B
BH ₂ OH	B	HB(OH) ₂	B	B(OH) ₃	B	B ₃ O ₃ H ₃	Na	H ₃ B ₃ O ₆	Na
BCl	C	BCl ₂	C	BCl ₃	C	B ₂ Cl ₄	J		
HBCl	B	BHCl ₂	B	BH ₂ Cl	B	BC	J		
BOCl	Na	B ₃ O ₃ Cl ₃	Na	B ₂ H ₄ O ₄	J	HBN	B	HBNH	B
BN	B	BNH	B	BNH ₂	B	H ₂ BNH	B	H ₃ BNH ₃	B
HBNH ₂	B	H ₂ BN	B	H ₂ BNH	B	B ₃ H ₆ N ₃	J		
B(NH ₂) ₂	B	B(NH ₂) ₃	B	HB(NH ₂) ₂	B	CIBNH	B	C'BNH ₂	B
C'BN	B	Cl ₂ BN	B	BNCl ₂	B				
HCIBNH ₂	B	Cl ₂ BNH	B	Cl ₃ BNH ₃	B				
BCl ₂ NH ₂	B	BCl(NH ₂) ₂	B	NH ₂ BCl ₂ NH ₃	B				

Species	Ref.	Species	Ref.	Species	Ref.	Species	Ref.	Species	Ref.	Species	Ref.
H ₃ SiBH ₂	B	H ₂ SiBH ₂	B	HSiBH ₂	B	SiBH ₂	B	SiBH ₂	B	H ₃ SiBH	B
H ₂ SiBH	B	HSiBH	B	SiBH	B	H ₃ SiB	B	H ₃ SiB	B	H ₂ SiB	B
SiB	B	HSi(H ₂)BH ₂	B	Si(H ₂)BH ₂	B	HSi(H ₂)BH ₂	B	HSi(H ₂)BH ₂	B	Si(H ₂)BH	B
Si(H ₂)B	B	Si(H ₂)BH ₂	B	H ₃ SiSiH ₂ BH ₂	B	HB(SiH ₃) ₂	B	H ₂ SiBHSiH ₃	B	H ₂ SiBHSiH ₃	B
H ₃ SiBSiH ₃	B	Si(H ₂)BSiH ₃	B	H ₂ SiBHSiH ₂	B	H ₂ SiBHSiH ₂	B	H ₃ SiSiBH ₂	B	H ₃ SiSiBH ₂	B
HSiBHSiH ₃	B	H ₃ SiSiHBH	B	H ₂ SiBSiH ₃	B	H ₂ SiBSiH ₂	B	HSiBHSiH ₂	B	HSiBHSiH ₂	B
Si(H ₂)BHSiH	B	HSi(H ₂)BHSiH	B	SiBHSiH ₂	B	Si(H ₂)BSiH	B	Si(H ₂)BSiH	B	Si(H ₂)BHSiH	B
HSiBSiH ₂	B	HSiBHSiH	B	H ₂ Si(BH ₂) ₂	B	HSi(BH ₂) ₂	B	HSi(BH ₂) ₂	B		
HBSiH ₂ BH ₂	B	-H ₂ SiBHBH-	B	Si(BH ₂) ₂	B	HSi(H ₂)BHCl	B	HSi(H ₂)BHCl	B		
H ₃ SiBHCl	B	H ₂ ClSiBH ₂	B	ClSi(H ₂)BH ₂	B	HSi(H ₂)BHCl	B	HSi(H ₂)BHCl	B	HClSiBH ₂	B
H ₂ SiBHCl	B	ClSi(H ₂)BH ₂	B	Si(H ₂)BHCl	B	H ₃ SiBCl	B	H ₃ SiBCl	B	HSi(H ₂)BHCl	B
H ₂ ClSiBH	B	Si(H ₂)BCl	B	ClSiBH ₂	B	HSiBHCl	B	HSiBHCl	B	H ₂ SiBCl	B
HClSiBH	B	SiBCl ₂	B	ClSiBCl	B	SiBHCl	B	SiBHCl	B	HSiBCl	B
ClSiBH	B	HClSiB	B	SiBCl	B	ClSiB	B	ClSiB	B		
P	C	P ₂	C	P ₄	C	PH	Na	PH	Na	PH ₂	B
PH ₃	Na	PCl	J	PCl ₃	Na	PCl ₅	J	PCl ₅	J	OPCl ₃	J
PO	Na	PO ₂	Na	P ₄ O ₆	Bu	P ₄ O ₁₀	Na	P ₄ O ₁₀	Na		
CP	J	CHP	J	PN	J						
Fe	Na	FeCl	Na	FeCl ₂	Na	FeCl ₃	Na	FeCl ₃	Na	Fe ₂ Cl ₄	Na
Fe ₂ Cl ₆	Na	FeO	Na	FeC ₃ O ₅	Na	Fe(OH) ₂	Na	Fe(OH) ₂	Na		
Si(L)	C	SiO ₂ (L)	Na	B(L)	Na	B ₂ O ₃ (L)	Na	B ₂ O ₃ (L)	Na	B ₄ C(L)	J
P(L)	Na	N ₂ H ₄ (L)	C								
Fe(L)	Na	FeCl ₂ (L)	Na	FeCl ₃ (L)	Na	FeO(L)	Na	FeO(L)	Na	FeC ₅ O ₅ (L)	Na
Si(S)	C	SiO ₂ (S)	O	C(S)	C	SiC(B)	C	SiC(B)	C	Si ₃ N ₄ (A)	Na
B(S)	Na	B ₄ C(S)	J	B ₂ O ₃ (S)	J	B ₃ O ₃ H ₃ (cr)	Na	B ₃ O ₃ H ₃ (cr)	Na	BN(cr)	C
P(cr)	Na	P ₄ O ₁₀ (S)	Na	NH ₄ Cl(s)	Na	FeCl ₃ (s)	Na	FeCl ₃ (s)	Na	FeO(s)	No
Fe(α-δ)	No	Fe(γ)	No	FeCl ₂ (s)	No	Fe ₂ O ₃ (s)	No	Fe ₂ O ₃ (s)	No		
Fe(OH) ₂ (s)	Na	Fe(OH) ₃ (s)	Na	Fe ₂ O ₃ (s)	Na						

The CHEMKIN Thermodynamic Database [10,12] provided data for many gas-phase species, particularly molecules comprised of C, H, O and N. For most of the silicon-containing species, thermochemical data were obtained from quantum chemistry calculations using the BAC-MP4 method. This involves a combination of empirically-based corrections with relatively high-level *ab initio* electronic structure calculations (see the original papers for details). For the Si-H-Cl [13], Si-C-H-Cl, [14] and Si-N-H [15] species, the thermochemical parameters from the BAC-MP4 calculations had already been incorporated into the CHEMKIN Thermodynamic Database. For the other systems, Si-O-H-C [16], Si-B-H-Cl [17] and B-H-N-Cl [18], the thermochemical data had to be compiled separately. In other cases, thermochemical data in the necessary format were obtained by extracting and fitting data from the JANAF Thermochemical Tables [19], or obtained from the NASA [20], Burcat [21] or Noring [22] Databases on the CHEMKIN Web Site on Sandia's intranet [23]. For SiO₂(S), thermochemical data were obtained from work by Babushkin, *et al.* [24]. For the liquid and solid species, information on the bulk density was also needed as input, and are given in Table 2. The data were generally obtained from the CRC [25] or guessed based on related compounds. The calculations do not consider the free energy of mixing of the impurities in the silicon (such data generally do not exist).

Many of the species listed in Table 1 are unimportant under the conditions of interest. To avoid carrying lots of unimportant species throughout the analysis, this list was reduced substantially using the following process. For a given subset of the elements of interest, for example Si, O, H and B, equilibrium calculations were done using the full set of chemical species comprised of those elements for the extremes of pressure and temperature (i.e. 1700 and 2000K, 0.001 and 1.0 atm). If a species was present in any given phase only at low mole fractions (MF) for all these cases, it generally was dropped from further calculations. The thresholds for dropping a species depended on its composition, and were set at $MF < 10^{-10}$ for species containing B or P, $MF < 10^{-8}$ for species containing C, or $MF < 10^{-7}$ for species comprised of Si, O, H, N, Cl only. Fe containing compounds were few enough that reduction was not an issue. Table 3 gives the reduced list of 153 chemical species actually used in the equilibrium analysis.

Table 2. Densities for condensed phases species

Species	Density (g/cm ³)	Data Source *
Si(L)	2.52	CRC, at melting point
B(L)	2.08	CRC, at melting point
B ₂ O ₃ (L)	2.0	guess
B ₄ C(L)	2.3	guess
P(L)	2.0	guess
SiO ₂ (L)	2.0	guess
N ₂ H ₄ (L)	1.011	CRC
Fe(L)	7.08	CRC, at melting point, average of seven numbers
FeC ₅ O ₅ (L)	1.457	CRC
FeCl ₂ (L)	3.1	guess from solid
FeCl ₃ (L)	3.0	guess from solid
FeO(L)	5.0	guess from solid
Si(S)	2.33	CRC
SiO ₂ (S)	2.19	CRC, lechatelierite
B(S)	2.35	CRC, average of two numbers
B ₄ C(S)	2.52	CRC
B ₂ O ₃ (S)	1.812	CRC, glass
B ₃ O ₃ H ₃ (cr)	2.0	guess
C(S)	2.25	CRC, graphite
SiC(B)	3.217	CRC
P(cr)	2.34	CRC, red phosphorus,
P ₄ O ₁₀ (S)	2.39	CRC
Si ₃ N ₄ (A)	3.44	CRC
BN(cr)	2.25	CRC
NH ₄ Cl(a)	1.527	CRC
NH ₄ Cl(b)	1.527	CRC
Fe(α - δ)	7.86	CRC
Fe(γ)	7.86	CRC
FeCl ₂ (s)	3.16	CRC
FeCl ₃ (s)	2.898	CRC
FeO(s)	5.7	CRC, wuestite
Fe(OH) ₂ (s)	3.4	CRC
Fe(OH) ₃ (s)	3.0	guess from above
Fe ₂ O ₃ (s)	5.24	CRC, hematite
Fe ₃ O ₄ (s)	5.18	CRC, magnetite

* CRC = Ref. [25]

Table 3. Chemical species actually used in equilibrium calculations.

GASES					
Ar	Si	Si ₂	Si ₃		
H	H ₂	Cl	Cl ₂	HCl	
SiH	SiH ₂	SiH ₃	SiH ₄		
SiClH ₃	SiCl ₃ H	SiCl ₂ H ₂	HSiCl	SiH ₂ Cl	SiHCl ₂
SiCl	SiCl ₂	SiCl ₃	SiCl ₄		
Si ₂ Cl ₅	Si ₂ Cl ₅ H	Si ₂ Cl ₆	HCl ₂ SiSiCl ₂ H	Cl ₂ SiSiCl ₂	Cl ₃ SiSiCl
Cl ₃ SiSi	Cl ₂ SiSiCl	Cl ₂ SiSi	ClSiSiCl	ClSiSi	
O ₂	OH	H ₂ O			
CO	CO ₂	CH ₃	CH ₄	C ₂ H ₂	
SiC	SiC ₂	SiCH	SiCH ₂	Si ₂ C	
CH ₂ SiCl ₃	CH ₃ SiCl	Cl ₃ SiCH ₃	H ₂ ClSiSiCl ₃		
HSi=O	HOSi	SiO	-SiOSiO-		
N	N ₂	NH	NH ₂	NH ₃	
NO	CN	HCN	HNC	ClCN	
SiN	SiNH	SiNH ₂	Si ₂ N		
B	BO	B ₂ O ₂	HBO	HOBO	BH ₂ OH
BH	BH ₂	BH ₃	BCl	BCl ₂	BCl ₃
HBCl	BHCl ₂	BH ₂ Cl	BOCl		
BN	BNH	BNH ₂	B(NH ₂) ₂	B(NH ₂) ₃	B ₃ N ₃ H ₆
H ₂ BN	H ₂ BNH	H ₂ BNH ₂	H ₃ BNH ₃	HB(NH ₂) ₂	
HBN	HBNH	HBNH ₂	ClBNH	BCl ₂ NH ₂	
SiBH	SiBCl	SiBCl ₂			
P	P ₂	PH	PH ₂	PH ₃	
PCl	PCl ₃	PO	CP	CHP	PN
Fe	FeCl	FeCl ₂	FeCl ₃	Fe ₂ Cl ₄	Fe ₂ Cl ₆
FeO	FeC ₅ O ₅	Fe(OH) ₂			
LIQUIDS					
Si(L)	SiO ₂ (L)				
B(L)	B ₂ O ₃ (L)				
P(L)					
Fe(L)	FeCl ₂ (L)	FeCl ₃ (L)	FeO(L)		
SOLIDS					
Si(S)	SiO ₂ (S)	SiC(B)	Si ₃ N ₄ (A)		
B(S)	B ₂ O ₃ (S)	BN(cr)			
C(S)					
P(cr)					
NH ₄ Cl(a)	NH ₄ Cl(b)				
Fe(s,a-d)	Fe(s,gamma)	FeCl ₂ (s)	FeCl ₃ (s)		
FeO(s)	Fe(OH) ₂ (s)	Fe(OH) ₃ (s)	Fe ₂ O ₃ (s)	Fe ₃ O ₄ (s)	

III. Results

The EQUIL code outputs a list of the species with significant mole fractions in the starting and equilibrium mixtures, followed by the number of moles and lists of the full species mole fractions for each of the phases (gas, liquid, solid). The Appendix gives an example of an EQUIL output file. These outputs were post-processed by adding up the number of moles of species containing a given element (Si, B, P, C or Fe) in each of the liquid and solid phases, then normalizing them to the input number of moles of that element. The remainder was assumed to be in the gas phase.

The subsections below discuss the effects of adding a variety of gases to the standard silicon/impurities mixture. Each subsection includes figures showing the equilibrium distribution between the gas, liquid and solid phases of silicon, boron, phosphorus, carbon and iron, as well as the overall mole fraction for a variety of temperatures and total pressures. These figures show a few general features. As expected, the overall mole fraction distribution generally mirrors that of silicon, the primary component of the mixture, and is primarily molten. (Note that the over all mole fraction distribution always contains the 0.01 mole of inert argon included in the input mixture.) Lower total pressures and higher temperatures favor the gas phase, whereas higher total pressures and lower temperatures favor the condensed phases. Phosphorus and iron vaporize to a certain extent at high temperature and low pressure, independent of the added gases.

Tables listing the identity of the dominant chemical species containing Si, B, P, C and Fe in each phase are also given. This information is useful in separating chemical effects from simple vaporization or melting, although the latter may be useful as purification processes. Somewhat arbitrarily, a "dominant" species has been defined as one accounting for at least ~20% of that element in that phase. For completeness, the tables include entries even in cases where a given phase is only present to a very minor extent.

A. Oxygen Addition

Figure 1 gives the equilibrium distribution of the overall MF, Si, B, P, C and Fe among the gas, liquid and solid phases for exposure to oxygen at 1450°C and total pressures of 0.001, 0.01, 0.1 and 1.0 atmospheres. Figure 2 gives the corresponding results at 1550°C and Figure 3 the results at 1650°C. Table 4 gives information on chemical species identities for the same sets of conditions.

These figures show that at the higher pressures, the C and Fe are generally solids, the P is generally liquid along the Si, and the B is mostly liquid with some solid. In all cases, the input O_2 reacts away almost completely. At the lower pressures, and particularly at the higher temperatures, more vapor-phase species are present, dominated by SiO, which represents loss of silicon. However, substantial fractions of the C can be converted to CO, while significant amounts of P and Fe can vaporize. Small amounts of BO are formed, but the conversion is quite low for the purposes of a purification process, given that the total amount of oxygen exposure will be limited by the concomitant loss of silicon via SiO formation. The C in the solid phase is primarily silicon carbide, which is only somewhat denser than silicon. Overall, it appears that O_2 is a good candidate for removing C by oxidation to CO, but is unlikely to be a good route for vaporizing the other impurities.

Figure 1. Distribution of elements among phases: $O_2 = 0.05$, $Ar = 0.01$, $1450^\circ C$.

Figure 2. Distribution of elements among phases: $O_2 = 0.05$, $Ar = 0.01$, $1550^\circ C$.

Figure 3. Distribution of elements among phases: $O_2 = 0.05$, $Ar = 0.01$, $1650^\circ C$.

Table 4. Dominant* chemical species for silicon and impurities with O₂/Ar addition.

Temp. (°C)	Pressure (atm)	Phase	Si	B	P	C	Fe
1450	0.001 – 1.0	Gas Liquid Solid	SiO Si(L) Si(S)	BO B(L) B(S)	P ₂ P(L) P(cr)	CO -- SiC(B)	Fe Fe(L) Fe(α,δ,γ)
1550	0.001	Gas Liquid Solid	SiO Si(L) Si(S)	BO B(L) B(S)	P ₂ , P P(L) P(cr)	CO -- SiC(B)	Fe Fe(L) Fe(α,δ,γ)
1550	0.01 – 1.0	Gas Liquid Solid	SiO Si(L) Si(S)	BO B(L) B(S)	P ₂ P(L) P(cr)	CO -- SiC(B)	Fe Fe(L) Fe(α,δ,γ)
1650	0.001	Gas Liquid Solid	SiO Si(L) --	BO B(L) --	P ₂ , P P(L) --	CO -- --	Fe Fe(L) --
1650	0.01	Gas Liquid Solid	SiO Si(L) Si(S)	BO B(L) B(S)	P ₂ , P P(L) P(cr)	CO -- SiC(B)	Fe Fe(L) Fe(α,δ,γ)
1650	0.1 – 1.0	Gas Liquid Solid	SiO Si(L) Si(S), SiC(B)	BO B(L) B(S)	P ₂ , P P(L) P(cr)	CO -- SiC(B)	Fe Fe(L) Fe(α,δ,γ)

* Chemical species are listed for each phase in order of decreasing mole fraction as a function of temperature and pressure. If multiple species are listed, each represents at least ~20% of the element in that phase.

B. Air Addition

Air is simple to obtain and straightforward to handle experimentally. Figure 4 through Figure 6 and Table 5 give the equilibrium results for reaction of the silicon/impurities mixture with air. As for the case of oxygen exposure presented above, the oxygen reacts away to form SiO, CO and small amount of BO. Air is only 20% oxygen, so the total amount of C converted to CO, even at the highest temperature and lowest pressure, is lower than for the O₂ case. The presence of nitrogen, however, results in PN formation in the gas at low pressures, and in BN(cr) formation at higher pressures. The latter conditions also result in significant Si₃N₄(A) formation, which would result in loss of silicon. With the caveat that N₂ is very likely to have kinetic barriers that will hinder reaction, it appears that air has potential for removal of C, P and some B if the solid is separable from the silicon.

Figure 4. Distribution of elements among phases: $O_2 = 0.01$, $N_2 = 0.04$, $Ar = 0.01$, $1450^\circ C$.

Figure 5. Distribution of elements among phases: $O_2 = 0.01$, $N_2 = 0.04$, $Ar = 0.01$, $1550^\circ C$.

Figure 6. Distribution of elements among phases: $O_2 = 0.01$, $N_2 = 0.04$, $Ar = 0.01$, $1650^\circ C$.

Table 5. Dominant* chemical species for silicon and impurities with O₂/N₂/Ar addition.

Temp. (°C)	Pressure (atm)	Phase	Si	B	P	C	Fe
1450	0.001	Gas Liquid Solid	SiO Si(L) Si(S)	BO B(L) BN(cr)	PN P(L) P(cr)	CO -- SiC(B)	Fe Fe(L) Fe(α, δ, γ)
1450	0.01– 1.0	Gas Liquid Solid	SiO Si(L) Si(S), Si ₃ N ₄ (A)	BO B(L) BN(cr)	PN P(L) P(cr)	CO -- SiC(B)	Fe Fe(L) Fe(α, δ, γ)
1550	0.001	Gas Liquid Solid	SiO Si(L) Si(S)	BO B(L) BN(cr)	PN P(L) P(cr)	CO -- SiC(B)	Fe Fe(L) Fe(α, δ, γ)
1550	0.01– 1.0	Gas Liquid Solid	SiO Si(L) Si(S), Si ₃ N ₄ (A)	BO B(L) BN(cr)	PN P(L) P(cr)	CO -- SiC(B)	Fe Fe(L) Fe(α, δ, γ)
1650	0.001	Gas Liquid Solid	SiO Si(L) Si(S), SiC(B)	BO B(L) BN(cr), B(S)	PN P(L) P(cr)	CO -- SiC(B)	Fe Fe(L) Fe(α, δ, γ)
1650	0.01	Gas Liquid Solid	SiO Si(L) Si(S), SiC(B)	BO B(L) BN(cr)	PN P(L) P(cr)	CO -- SiC(B)	Fe Fe(L) Fe(α, δ, γ)
1650	0.1 – 1.0	Gas Liquid Solid	SiO Si(L) Si ₃ N ₄ (A), Si(S)	BO B(L) BN(cr)	PN P(L) P(cr)	CO -- SiC(B)	Fe Fe(L) Fe(α, δ, γ)

* Chemical species are listed for each phase in order of decreasing mole fraction as a function of temperature and pressure. If multiple species are listed, each represents at least ~20% of the element in that phase.

C. Water Addition

Water vapor is generally considered more reactive than O_2 in terms of kinetics. From an equilibrium point of view, the presence of hydrogen allows the formation of additional compounds that may offer routes to impurity removal. Figure 7 through Figure 9 and Table 6 give the equilibrium results for reaction of the silicon/impurities mixture with water vapor. Some of the differences between the results obtained for water and oxygen result from the fact that one mole of water provides one mole of oxygen atoms whereas one mole of O_2 provides two moles of oxygen atoms. The most interesting difference between water and oxygen, however, is the formation of noticeable amounts of HBO in the gas phase with water. There are also some differences in the identities of the gas-phase phosphorus-containing species, but these are present in negligible quantities. Thus, water vapor appears to be roughly comparable to oxygen from the standpoint of C removal, but has potential for B removal also.

Figure 7. Distribution of elements among phases: $H_2O = 0.05$, $Ar = 0.01$, $1450^\circ C$.

Figure 8. Distribution of elements among phases: $H_2O = 0.05$, $Ar = 0.01$, $1550^\circ C$.

Figure 9. Distribution of elements among phases: $H_2O = 0.05$, $Ar = 0.01$, $1650^\circ C$.

Table 6. Dominant* chemical species for silicon and impurities with H₂O/Ar addition.

Temp. (°C)	Pressure (atm)	Phase	Si	B	P	C	Fe
1450	0.001– 0.1	Gas Liquid Solid	SiO Si(L) Si(S)	HBO B(L) B(S)	P ₂ P(L) P(cr)	CO -- SiC(B)	Fe Fe(L) Fe(α,δ,γ)
1450	1.0	Gas Liquid Solid	SiO Si(L) Si(S)	HBO B(L) B(S)	P ₂ , PH ₃ P(L) P(cr)	CO -- SiC(B)	Fe Fe(L) Fe(α,δ,γ)
1550	0.001	Gas Liquid Solid	SiO Si(L) Si(S)	HBO B(L) B(S)	P ₂ , P P(L) P(cr)	CO -- SiC(B)	Fe Fe(L) Fe(α,δ,γ)
1550	0.01	Gas Liquid Solid	SiO Si(L) Si(S)	HBO B(L) B(S)	P ₂ P(L) P(cr)	CO -- SiC(B)	Fe Fe(L) Fe(α,δ,γ)
1550	0.1	Gas Liquid Solid	SiO Si(L) Si(S)	HBO B(L) B(S)	P ₂ , CHP P(L) P(cr)	CO -- SiC(B)	Fe Fe(L) Fe(α,δ,γ)
1550	1.0	Gas Liquid Solid	SiO Si(L) Si(S)	HBO B(L) B(S)	CHP, P ₂ P(L) P(cr)	CO -- SiC(B)	Fe Fe(L) Fe(α,δ,γ)
1650	0.001	Gas Liquid Solid	SiO Si(L) --	HBO B(L) --	P ₂ , P P(L) --	CO -- --	Fe Fe(L) --
1650	0.01	Gas Liquid Solid	SiO Si(L) Si(S)	HBO B(L) B(S)	P ₂ , P P(L) P(cr)	CO -- SiC(B)	Fe Fe(L) Fe(α,δ,γ)
1650	0.1	Gas Liquid Solid	SiO Si(L) Si(S)	HBO B(L) B(S)	P ₂ , CHP P(L) P(cr)	CO -- SiC(B)	Fe Fe(L) Fe(α,δ,γ)
1650	1.0	Gas Liquid Solid	SiO Si(L) Si(S), SiC(B)	HBO B(L) B(S)	CHP P(L) P(cr)	CO -- SiC(B)	Fe Fe(L) Fe(α,δ,γ)

* Chemical species are listed for each phase in order of decreasing mole fraction as a function of temperature and pressure. If multiple species are listed, each represents at least ~20% of the element in that phase.

D. Wet Air Addition

Using a combination of water vapor (20%) and air gives the results shown in Figure 10 through Figure 12 and Table 7. The results in these figures are very similar to those shown in section III.B. above for air. Although the presence of the water vapor leads to the formation of HBO rather than BO in the gas phase, this is a relatively small effect. Under most of the conditions, the boron is BN(cr) formed by reaction with N₂. From a thermodynamic viewpoint, wet air offers only a small advantage for boron removal over dry air, but there may be kinetic advantages that are not addressed here.

Figure 10. Distribution of elements among phases: $H_2O = 0.01$, $O_2 = 0.008$, $N_2 = 0.032$, $Ar = 0.01$, $1450^\circ C$.

Figure 11. Distribution of elements among phases: $H_2O = 0.01$, $O_2 = 0.008$, $N_2 = 0.032$, $Ar = 0.01$, $1550^\circ C$.

Figure 12. Distribution of elements among phases: $H_2O = 0.01$, $O_2 = 0.008$, $N_2 = 0.032$, $Ar = 0.01$, $1650^\circ C$.

Table 7. Dominant* chemical species for silicon and impurities with H₂O/O₂/N₂/Ar addition.

Temp. (°C)	Pressure (atm)	Phase	Si	B	P	C	Fe
1450	0.001	Gas Liquid Solid	SiO Si(L) Si(S)	HBO B(L) BN(cr)	PN P(L) P(cr)	CO -- SiC(B)	Fe Fe(L) Fe(α,δ,γ)
1450	0.01– 1.0	Gas Liquid Solid	SiO Si(L) Si(S), Si ₃ N ₄ (A)	HBO B(L) BN(cr)	PN P(L) P(cr)	CO -- SiC(B)	Fe Fe(L) Fe(α,δ,γ)
1550	0.001	Gas Liquid Solid	SiO Si(L) Si(S)	HBO B(L) BN(cr)	PN P(L) P(cr)	CO -- SiC(B)	Fe Fe(L) Fe(α,δ,γ)
1550	0.01– 1.0	Gas Liquid Solid	SiO Si(L) Si(S), Si ₃ N ₄ (A)	HBO B(L) BN(cr)	PN P(L) P(cr)	CO -- SiC(B)	Fe Fe(L) Fe(α,δ,γ)
1650	0.001	Gas Liquid Solid	SiO Si(L) Si(S), SiC(B)	HBO B(L) BN(cr), B(S)	PN P(L) P(cr)	CO -- SiC(B)	Fe Fe(L) Fe(α,δ,γ)
1650	0.01	Gas Liquid Solid	SiO Si(L) Si(S), SiC(B)	HBO B(L) BN(cr)	PN P(L) P(cr)	CO -- SiC(B)	Fe Fe(L) Fe(α,δ,γ)
1650	0.1 – 1.0	Gas Liquid Solid	SiO Si(L) Si ₃ N ₄ (A), Si(S)	HBO B(L) BN(cr)	PN P(L) P(cr)	CO -- SiC(B)	Fe Fe(L) Fe(α,δ,γ)

* Chemical species are listed for each phase in order of decreasing mole fraction as a function of temperature and pressure. If multiple species are listed, each represents at least ~20% of the element in that phase.

E. HCl Addition

Many of the elements of interest in this study have volatile chlorides, so the use of HCl for purification is worth examining. Chloride chemistry is commonly used for the production and purification of silicon, although it introduces experimental complications because of its corrosive nature. Figure 13 through Figure 15 and Table 8 give the equilibrium results for this system. In this case almost no volatile carbon compounds are formed, in sharp contrast with the oxidizing chemical systems discussed above. The carbon stays in the solid phase as silicon carbide for the entire range of conditions explored. The HCl system also exhibits volatile Fe species (FeCl_2) over a much wider range of pressure and temperature conditions than in sections III.A. – D., where Fe volatilized as the atomic vapor. In this system, there is some vaporization of phosphorus as P_2 , especially at high temperatures and low pressures, but no significant chemical reaction. Formation of volatile boron compounds (BCl , BCl_3 and BHCl_2), occurs to a roughly comparable extent as HBO formation from water. Overall, HCl appears to offer a good route to Fe removal, with some potential for B removal. But HCl does not volatilize C and appears to offer no advantage over vacuum for P removal.

Figure 13. Distribution of elements among phases: $\text{HCl} = 0.05$, $\text{Ar} = 0.01$, 1450°C .

Figure 14. Distribution of elements among phases: $\text{HCl} = 0.05$, $\text{Ar} = 0.01$, 1550°C .

Figure 15. Distribution of elements among phases: $\text{HCl} = 0.05$, $\text{Ar} = 0.01$, 1650°C .

Table 8. Dominant* chemical species for silicon and impurities with HCl/Ar addition.

Temp. (°C)	Pressure (atm)	Phase	Si	B	P	C	Fe
1450	0.001	Gas	SiCl ₂	BCl	P ₂	CHP, Si ₂ C	FeCl ₂
		Liquid	Si(L)	B(L)	P(L)	--	Fe(L)
		Solid	Si(S)	B(S)	P(cr)	SiC(B)	Fe(α,δ,γ)
1450	0.01	Gas	SiCl ₂	BCl, BCl ₃	P ₂	CHP	FeCl ₂
		Liquid	Si(L)	B(L)	P(L)	--	Fe(L)
		Solid	Si(S)	B(S)	P(cr)	SiC(B)	Fe(α,δ,γ)
1450	0.1	Gas	SiCl ₂	BCl ₃ , BHCl ₂	P ₂	CHP	FeCl ₂
		Liquid	Si(L)	B(L)	P(L)	--	FeCl ₂ (L), Fe(L)
		Solid	Si(S)	B(S)	P(cr)	SiC(B)	Fe(α,δ,γ)
1450	1.0	Gas	SiCl ₂ , SiCl ₄	BCl ₃ , BHCl ₂	P ₂	CH ₄	FeCl ₂
		Liquid	Si(L)	B(L)	P(L)	--	FeCl ₂ (L)
		Solid	Si(S)	B(S)	P(cr)	SiC(B)	Fe(α,δ,γ)
1550	0.001	Gas	SiCl ₂	BCl	P ₂ , P	Si ₂ C, CHP	FeCl ₂
		Liquid	Si(L)	B(L)	P(L)	--	Fe(L)
		Solid	Si(S)	B(S)	P(cr)	SiC(B)	Fe(α,δ,γ)
1550	0.01	Gas	SiCl ₂	BCl	P ₂	CHP, Si ₂ C	FeCl ₂
		Liquid	Si(L)	B(L)	P(L)	--	Fe(L)
		Solid	Si(S)	B(S)	P(cr)	SiC(B)	Fe(α,δ,γ)
1550	0.1	Gas	SiCl ₂	BCl ₃ , BHCl ₂	P ₂	CHP	FeCl ₂
		Liquid	Si(L)	B(L)	P(L)	--	FeCl ₂ (L), Fe(L)
		Solid	Si(S)	B(S)	P(cr)	SiC(B)	Fe(α,δ,γ)
1550	1.0	Gas	SiCl ₂ , SiCl ₄	BCl ₃ , BHCl ₂	CHP, P ₂	CH ₄ , CHP	FeCl ₂
		Liquid	Si(L)	B(L)	P(L)	--	FeCl ₂ (L)
		Solid	Si(S)	B(S)	P(cr)	SiC(B)	Fe(α,δ,γ)

Temp. (°C)	Pressure (atm)	Phase	Si	B	P	C	Fe
1650	0.001	Gas	SiCl ₂ , SiCl	BCl	P ₂ , P	Si ₂ C, CHP	FeCl ₂ , Fe
		Liquid	Si(L)	B(L)	P(L)	--	Fe(L)
		Solid	Si(S)	B(S)	P(cr)	SiC(B)	Fe(α,δ,γ)
1650	0.01	Gas	SiCl ₂	BCl	P ₂ , CHP, P	Si ₂ C, CHP	FeCl ₂
		Liquid	Si(L)	B(L)	P(L)	--	Fe(L)
		Solid	Si(S)	B(S)	P(cr)	SiC(B)	Fe(α,δ,γ)
1650	0.1	Gas	SiCl ₂	BCl, BCl ₃ , BHCl ₂	CHP, P ₂	CHP, Si ₂ C	FeCl ₂
		Liquid	Si(L)	B(L)	P(L)	--	FeCl ₂ (L), Fe(L)
		Solid	Si(S)	B(S)	P(cr)	SiC(B)	Fe(α,δ,γ)
1650	1.0	Gas	SiCl ₂	BCl ₃ , BHCl ₂	CHP, P ₂	CHP, CH ₄	FeCl ₂
		Liquid	Si(L)	B(L)	P(L)	--	FeCl ₂ (L)
		Solid	Si(S)	B(S)	P(cr)	SiC(B)	Fe(α,δ,γ)

* Chemical species are listed for each phase in order of decreasing mole fraction as a function of temperature and pressure. If multiple species are listed, each represents at least ~20% of the element in that phase.

F. Cl_2 Addition

Cl_2 is an alternate source of chlorine, although experimentally it is somewhat more difficult to handle than HCl . Each mole of chlorine gas provides twice as many chlorine atoms as a mole of HCl , so on a "per sccm" basis, it is a more intense Cl source. Figure 16 through Figure 18 and Table 9 give the equilibrium results for adding Cl_2 to this system. As expected, these results are quite similar to those for HCl addition. There is somewhat higher volatilization of Fe as FeCl_2 , B as BCl_x ($x=1, 3$), and Si as SiCl_x ($x=2, 4$) as a result of the higher Cl content of the system. The absence of H in the system leads to differences in the identity of some of the gas-phase species, but this is a minor effect. There is some evaporation of P as P_2 at lower pressures and higher temperatures, but the C remains in the solid as silicon carbide. As for HCl , Cl_2 offers advantages for Fe removal and probably B removal, but not C or P .

Figure 16. Distribution of elements among phases: $\text{Cl}_2 = 0.05$, $\text{Ar} = 0.01$, 1450°C .

Figure 17. Distribution of elements among phases: $\text{Cl}_2 = 0.05$, $\text{Ar} = 0.01$, 1550°C .

Figure 18. Distribution of elements among phases: $Cl_2 = 0.05$, $Ar = 0.01$, $1650^\circ C$.

Table 9. Dominant* chemical species for silicon and impurities with Cl₂/Ar addition.

Temp. (°C)	Pressure (atm)	Phase	Si	B	P	C	Fe
1450	0.001	Gas Liquid Solid	SiCl ₂ Si(L) Si(S)	BCl B(L) B(S)	P ₂ P(L) P(cr)	Si ₂ C -- SiC(B)	FeCl ₂ Fe(L) Fe(α,δ,γ)
1450	0.01	Gas Liquid Solid	SiCl ₂ Si(L) Si(S)	BCl ₃ , BCl B(L) B(S)	P ₂ P(L) P(cr)	Si ₂ C -- SiC(B)	FeCl ₂ Fe(L), FeCl ₂ (L) Fe(α,δ,γ)
1450	0.1	Gas Liquid Solid	SiCl ₂ Si(L) Si(S)	BCl ₃ B(L) B(S)	P ₂ P(L) P(cr)	Si ₂ C -- SiC(B)	FeCl ₂ FeCl ₂ (L) Fe(α,δ,γ)
1450	1.0	Gas Liquid Solid	SiCl ₄ , SiCl ₂ Si(L) Si(S)	BCl ₃ B(L) B(S)	P ₂ P(L) P(cr)	Si ₂ C -- SiC(B)	FeCl ₂ FeCl ₂ (L) Fe(α,δ,γ)
1550	0.001	Gas Liquid Solid	SiCl ₂ Si(L) Si(S)	BCl B(L) B(S)	P ₂ P(L) P(cr)	Si ₂ C -- SiC(B)	FeCl ₂ Fe(L) Fe(α,δ,γ)
1550	0.01	Gas Liquid Solid	SiCl ₂ Si(L) Si(S)	BCl, BCl ₃ B(L) B(S)	P ₂ P(L) P(cr)	Si ₂ C -- SiC(B)	FeCl ₂ Fe(L), FeCl ₂ (L) Fe(α,δ,γ)
1550	0.1 – 1.0	Gas Liquid Solid	SiCl ₂ Si(L) Si(S)	BCl ₃ B(L) B(S)	P ₂ P(L) P(cr)	Si ₂ C -- SiC(B)	FeCl ₂ FeCl ₂ (L) Fe(α,δ,γ)
1650	0.001	Gas Liquid Solid	SiCl ₂ Si(L) Si(S)	BCl B(L) B(S)	P ₂ P(L) P(cr)	Si ₂ C -- SiC(B)	FeCl ₂ Fe(L) Fe(α,δ,γ)
1650	0.01	Gas Liquid Solid	SiCl ₂ Si(L) Si(S)	BCl B(L) B(S)	P ₂ P(L) P(cr)	Si ₂ C -- SiC(B)	FeCl ₂ Fe(L), FeCl ₂ (L) Fe(α,δ,γ)
1650	0.1	Gas Liquid Solid	SiCl ₂ Si(L) Si(S)	BCl ₃ , BCl B(L) B(S)	P ₂ , P P(L) P(cr)	Si ₂ C -- SiC(B)	FeCl ₂ FeCl ₂ (L) Fe(α,δ,γ)
1650	1.0	Gas Liquid Solid	SiCl ₂ , SiCl ₄ Si(L) Si(S)	BCl ₃ B(L) B(S)	P ₂ , PCl, P P(L) P(cr)	Si ₂ C -- SiC(B)	FeCl ₂ FeCl ₂ (L) Fe(α,δ,γ)

* Chemical species are listed for each phase in order of decreasing mole fraction as a function of temperature and pressure. If multiple species are listed, each represents at least ~20% of the element in that phase.

G. Cl₂/O₂ Addition

Figure 19 through Figure 21 and Table 10 give results for Cl₂ plus O₂ addition. As expected, they show a combination of the features seen in sections III.A. and III.F. Especially at the lower pressures and higher temperatures, iron is vaporized as FeCl₂ by reaction with the Cl₂, and carbon is vaporized as CO by reaction with the O₂. The phosphorus that does vaporize is primarily P₂ or P; only a small amount reacts to form PCl at the higher pressures and temperature. A moderate amount of boron is vaporized as BCl_x (x=1, 3), again at the higher pressures and temperatures. The gaseous silicon-containing compounds are primarily SiO at the lower pressures and the SiCl_x (x=2, 4) compounds at higher pressures. In both cases, most of the chlorine and the oxygen input into the system reacts with silicon, but at the higher pressures, the oxide is liquid rather than gaseous. Overall, the thermochemistry of Cl₂ and O₂ addition appears offer good potential for removal of Fe and C from Si, especially at the lower pressures and higher temperatures. The same conditions should remove some B, as well as P by evaporation.

Figure 19. Distribution of elements among phases: $\text{Cl}_2 = 0.025$, $\text{O}_2 = 0.025$, $\text{Ar} = 0.01$, 1450°C .

Figure 20. Distribution of elements among phases: $\text{Cl}_2 = 0.025$, $\text{O}_2 = 0.01$, 1550°C .

Figure 21. Distribution of elements among phases: $\text{Cl}_2 = 0.025$, $\text{O}_2 = 0.01$, $\text{Ar} = 0.01$, 1650°C .

Table 10. Dominant* chemical species for silicon and impurities with Cl₂/O₂/Ar addition.

Temp. (°C)	Pressure (atm)	Phase	Si	B	P	C	Fe
1450	0.001	Gas Liquid Solid	SiO, SiCl ₂ Si(L) Si(S)	BCl B(L) B(S)	P ₂ P(L) P(cr)	CO -- SiC(B)	FeCl ₂ Fe(L) Fe(α,δ,γ)
1450	0.01	Gas Liquid Solid	SiO, SiCl ₂ Si(L) Si(S)	BCl ₃ , BCl B(L) B(S)	P ₂ P(L) P(cr)	CO -- SiC(B)	FeCl ₂ Fe(L), FeCl ₂ (L) Fe(α,δ,γ)
1450	0.1	Gas Liquid Solid	SiCl ₂ Si(L) Si(S)	BCl ₃ B(L) B(S)	P ₂ P(L) P(cr)	CO -- SiC(B)	FeCl ₂ FeCl ₂ (L), Fe(L) Fe(α,δ,γ)
1450	1.0	Gas Liquid Solid	SiCl ₂ , SiCl ₄ Si(L) Si(S)	BCl ₃ B(L) B(S)	P ₂ P(L) P(cr)	CO -- SiC(B)	FeCl ₂ FeCl ₂ (L) Fe(α,δ,γ)
1550	0.001	Gas Liquid Solid	SiO, SiCl ₂ Si(L) Si(S)	BCl B(L) B(S)	P ₂ , P P(L) P(cr)	CO -- SiC(B)	FeCl ₂ Fe(L) Fe(α,δ,γ)
1550	0.01	Gas Liquid Solid	SiO, SiCl ₂ Si(L) Si(S)	BCl B(L) B(S)	P ₂ P(L) P(cr)	CO -- SiC(B)	FeCl ₂ Fe(L) Fe(α,δ,γ)
1550	0.1	Gas Liquid Solid	SiCl ₂ , SiO Si(L) Si(S)	BCl ₃ B(L) B(S)	P ₂ P(L) P(cr)	CO -- SiC(B)	FeCl ₂ FeCl ₂ (L), Fe(L) Fe(α,δ,γ)
1550	1.0	Gas Liquid Solid	SiCl ₂ , SiCl ₄ Si(L) Si(S), SiC(B)	BCl ₃ B(L) B(S)	P ₂ P(L) P(cr)	CO -- SiC(B)	FeCl ₂ FeCl ₂ (L) Fe(α,δ,γ)
1650	0.001	Gas Liquid Solid	SiO, SiCl ₂ Si(L) --	BCl B(L) --	P ₂ , P P(L) --	CO -- --	FeCl ₂ , Fe Fe(L) --
1650	0.01	Gas Liquid Solid	SiO, SiCl ₂ Si(L) --	BCl B(L) --	P ₂ , P P(L) --	CO -- --	FeCl ₂ Fe(L) --
1650	0.1	Gas Liquid Solid	SiCl ₂ , SiO Si(L) Si(S), SiC(B)	BCl ₃ , BCl B(L) B(S)	P ₂ , P P(L) P(cr)	CO -- SiC(B)	FeCl ₂ FeCl ₂ (L), Fe(L) Fe(α,δ,γ)
1650	1.0	Gas Liquid Solid	SiCl ₂ , SiCl ₄ Si(L) Si(S), SiC(B)	BCl ₃ B(L) B(S)	P ₂ , PCl, P P(L) P(cr)	CO -- SiC(B)	FeCl ₂ FeCl ₂ (L) Fe(α,δ,γ)

* Chemical species are listed for each phase in order of decreasing mole fraction as a function of temperature and pressure. If multiple species are listed, each represents at least ~20% of the element in that phase.

H. SiCl_4 Addition

Figure 22 through Figure 24 and Table 11 gives results for the addition of SiCl_4 to the silicon and impurity elements. As expected, they closely resemble the results for Cl_2 addition, with the variations expected given that, on a "per sccm" basis, SiCl_4 provides twice as many chlorine atoms. Compared with the results for Cl_2 and HCl , SiCl_4 addition leads to more vaporization of Fe and B for a given pressure and temperature. The distribution of silicon among the phases is quite similar for Cl_2 and SiCl_4 addition, as are the identity of the dominant chemical species. So, although there should be kinetic, safety, or operational differences (e.g. from the fact that SiCl_4 is a liquid), from a chemical equilibrium point of view, SiCl_4 and Cl_2 addition are effectively the same.

Figure 22. Distribution of elements among phases: $\text{SiCl}_4 = 0.05$, $\text{Ar} = 0.01$, 1450°C .

Figure 23. Distribution of elements among phases: $\text{SiCl}_4 = 0.05$, $\text{Ar} = 0.01$, 1550°C .

Figure 24. Distribution of elements among phases: $\text{SiCl}_4 = 0.05$, $\text{Ar} = 0.01$, 1650°C .

Table 11. Dominant* chemical species for silicon and impurities with SiCl₄/Ar addition.

Temp. (°C)	Pressure (atm)	Phase	Si	B	P	C	Fe
1450	0.001	Gas	SiCl ₂	BCl, BCl ₃	P ₂	Si ₂ C	FeCl ₂
		Liquid	Si(L)	B(L)	P(L)	--	Fe(L)
		Solid	Si(S)	B(S)	P(cr)	SiC(B)	Fe(α,δ,γ)
1450	0.01	Gas	SiCl ₂	BCl ₃ , BCl	P ₂	Si ₂ C	FeCl ₂
		Liquid	Si(L)	B(L)	P(L)	--	Fe(L), FeCl ₂ (L)
		Solid	Si(S)	B(S)	P(cr)	SiC(B)	Fe(α,δ,γ)
1450	0.1	Gas	SiCl ₂ , SiCl ₄	BCl ₃	P ₂	Si ₂ C	FeCl ₂
		Liquid	Si(L)	B(L)	P(L)	--	FeCl ₂ (L), Fe(L)
		Solid	Si(S)	B(S)	P(cr)	SiC(B)	Fe(α,δ,γ)
1450	1.0	Gas	SiCl ₄ , SiCl ₂	BCl ₃	P ₂	Si ₂ C	FeCl ₂
		Liquid	Si(L)	B(L)	P(L)	--	FeCl ₂ (L)
		Solid	Si(S)	B(S)	P(cr)	SiC(B)	Fe(α,δ,γ)
1550	0.001	Gas	SiCl ₂	BCl	P ₂ , P	Si ₂ C	FeCl ₂
		Liquid	Si(L)	B(L)	P(L)	--	Fe(L)
		Solid	Si(S), SiC(B)	B(S)	P(cr)	SiC(B)	Fe(α,δ,γ)
1550	0.01	Gas	SiCl ₂	BCl, BCl ₃	P ₂	Si ₂ C	FeCl ₂
		Liquid	Si(L)	B(L)	P(L)	--	Fe(L), FeCl ₂ (L)
		Solid	Si(S), SiC(B)	B(S)	P(cr)	SiC(B)	Fe(α,δ,γ)
1550	0.1	Gas	SiCl ₂	BCl ₃	P ₂	Si ₂ C	FeCl ₂
		Liquid	Si(L)	B(L)	P(L)	--	FeCl ₂ (L)
		Solid	Si(S), SiC(B)	B(S)	P(cr)	SiC(B)	Fe(α,δ,γ)
1550	1.0	Gas	SiCl ₂ , SiCl ₄	BCl ₃	P ₂ , PCl	Si ₂ C	FeCl ₂
		Liquid	Si(L)	B(L)	P(L)	--	FeCl ₂ (L)
		Solid	Si(S), SiC(B)	B(S)	P(cr)	SiC(B)	Fe(α,δ,γ)
1650	0.001	Gas	SiCl ₂	BCl	P ₂ , P	Si ₂ C	FeCl ₂
		Liquid	Si(L)	B(L)	P(L)	--	Fe(L)
		Solid	Si(S), SiC(B)	B(S)	P(cr)	SiC(B)	Fe(α,δ,γ)
1650	0.01	Gas	SiCl ₂	BCl	P ₂ , P	Si ₂ C	FeCl ₂
		Liquid	Si(L)	B(L)	P(L)	--	Fe(L), FeCl ₂ (L)
		Solid	Si(S), SiC(B)	B(S)	P(cr)	SiC(B)	Fe(α,δ,γ)
1650	0.1	Gas	SiCl ₂	BCl ₃ , BCl	P ₂ , P	Si ₂ C	FeCl ₂
		Liquid	Si(L)	B(L)	P(L)	--	FeCl ₂ (L)
		Solid	Si(S), SiC(B)	B(S)	P(cr)	SiC(B)	Fe(α,δ,γ)
1650	1.0	Gas	SiCl ₂ , SiCl ₄	BCl ₃	P ₂ , PCl, P	Si ₂ C	FeCl ₂
		Liquid	Si(L)	B(L)	P(L)	--	FeCl ₂ (L)
		Solid	Si(S), SiC(B)	B(S)	P(cr)	SiC(B)	Fe(α,δ,γ)

* Chemical species are listed for each phase in order of decreasing mole fraction as a function of temperature and pressure. If multiple species are listed, each represents at least ~20% of the element in that phase.

I. NH_3 Addition

Ammonia is generally considered more reactive than N_2 , and is worth examining as an alternate nitrogen-containing system. The results in Figure 25 through Figure 27 and Table 12 show significant formation of volatile PN, especially for lower pressures. This is similar to the results for P removal in section III.B. for air, although NH_3 appears to give somewhat more volatile PN at moderate pressures. In the presence of NH_3 , B forms a lot of $\text{BN}(\text{cr})$ with almost no volatile products. Carbon stays in the solid phase as silicon carbide for the range of conditions explored, and Fe is physically volatilized at higher temperatures and low pressures. Some silicon is lost by formation of $\text{Si}_3\text{N}_4(\text{A})$ and $\text{SiC}(\text{B})$, but no significant amount of silicon-containing volatiles are formed. Most of the gas phase is composed of H_2 and N_2 formed from the input NH_3 . Ammonia thus appears to be a good candidate for P removal, and possibly B and C if the solids can be separated from the silicon.

Figure 25. Distribution of elements among phases: $\text{NH}_3 = 0.05$, $\text{Ar} = 0.01$, 1450°C .

Figure 26. Distribution of elements among phases: $\text{NH}_3 = 0.05$, $\text{Ar} = 0.01$, 1550°C .

Figure 27. Distribution of elements among phases: $\text{NH}_3 = 0.05$, $\text{Ar} = 0.01$, 1650°C .

Table 12. Dominant* chemical species for silicon and impurities with NH₃/Ar addition.

Temp. (°C)	Pressure (atm)	Phase	Si	B	P	C	Fe
1450	0.001	Gas Liquid Solid	Si Si(L) Si(S)	BH ₃ B(L) BN(cr)	PN P(L) P(cr)	HCN -- SiC(B)	Fe Fe(L) Fe(α,δ,γ)
1450	0.01– 0.1	Gas Liquid Solid	SiNH, Si Si(L) Si(S)	BH ₃ B(L) BN(cr)	PN P(L) P(cr)	HCN, CHP -- SiC(B)	Fe Fe(L) Fe(α,δ,γ)
1450	1.0	Gas Liquid Solid	SiNH Si(L) Si(S)	BH ₃ B(L) BN(cr)	PN P(L) P(cr)	CH ₄ -- SiC(B)	Fe Fe(L) Fe(α,δ,γ)
1550	0.001	Gas Liquid Solid	Si Si(L) Si(S)	B, BH ₃ B(L) BN(cr)	PN P(L) P(cr)	HCN, Si ₂ C -- SiC(B)	Fe Fe(L) Fe(α,δ,γ)
1550	0.01	Gas Liquid Solid	Si, SiNH Si(L) Si(S)	BH ₃ B(L) BN(cr)	PN P(L) P(cr)	HCN -- SiC(B)	Fe Fe(L) Fe(α,δ,γ)
1550	0.1	Gas Liquid Solid	SiNH, Si Si(L) Si(S), Si ₃ N ₄ (A)	BH ₃ B(L) BN(cr)	PN P(L) P(cr)	HCN -- SiC(B)	Fe Fe(L) Fe(α,δ,γ)
1550	1.0	Gas Liquid Solid	SiNH Si(L) Si(S), Si ₃ N ₄ (A)	BH ₃ B(L) BN(cr)	PN P(L) P(cr)	HCN, CH ₄ -- SiC(B)	Fe Fe(L) Fe(α,δ,γ)
1650	0.001	Gas Liquid Solid	Si Si(L) Si(S), SiC(B)	B B(L) BN(cr), B(S)	PN P(L) P(cr)	Si ₂ C, HCN -- SiC(B)	Fe Fe(L) Fe(α,δ,γ)
1650	0.01	Gas Liquid Solid	Si Si(L) Si(S), SiC(B)	BH ₃ B(L) BN(cr)	PN P(L) P(cr)	HCN -- SiC(B)	Fe Fe(L) Fe(α,δ,γ)
1650	0.1	Gas Liquid Solid	SiNH, Si Si(L) Si(S), Si ₃ N ₄ (A)	BH ₃ B(L) BN(cr)	PN P(L) P(cr)	HCN -- SiC(B)	Fe Fe(L) Fe(α,δ,γ)
1650	1.0	Gas Liquid Solid	SiNH Si(L) Si ₃ N ₄ (A), Si(S)	BH ₃ B(L) BN(cr)	PN P(L) P(cr)	HCN -- SiC(B)	Fe Fe(L) Fe(α,δ,γ)

* Chemical species are listed for each phase in order of decreasing mole fraction as a function of temperature and pressure. If multiple species are listed, each represents at least ~20% of the element in that phase.

J. NH_4OH Addition

Ammonium hydroxide can be thought of as a solution of ammonia in water, and could provide an easy method of handling ammonia on a production scale. It is sold at various concentrations, and in the calculations a mixture of 0.015 moles of NH_3 and 0.035 moles of H_2O is used to represent a "30% NH_3 solution". Figure 28 through Figure 30 and Table 13 give the equilibrium results for this system. As expected, these results are a combination of the results for H_2O and NH_3 shown above in sections III.C. and I. Carbon and silicon react with oxygen, so their distributions among the phases for NH_4OH match those for H_2O . Phosphorus reacts with nitrogen, so its behavior with NH_4OH matches that for NH_3 . The boron reacts both with the water to form gas-phase HBO and with ammonia to form BN(cr). Overall, especially at low pressure and higher temperature, NH_4OH appears to be a good candidate for removal of C and P via chemical reaction, Fe by evaporation, with some B.

Figure 28. Distribution of elements among phases: $\text{NH}_3 = 0.015$, $\text{H}_2\text{O} = 0.035$, $\text{Ar} = 0.01$, 1450°C .

Figure 29. Distribution of elements among phases: $\text{NH}_3 = 0.015$, $\text{H}_2\text{O} = 0.035$, $\text{Ar} = 0.01$, 1550°C .

Figure 30. Distribution of elements among phases: $\text{NH}_3 = 0.015$, $\text{H}_2\text{O} = 0.035$, $\text{Ar} = 0.01$, 1650°C .

Table 13. Dominant* chemical species for silicon and impurities with NH₃/H₂O/Ar addition.

Temp. (°C)	Pressure (atm)	Phase	Si	B	P	C	Fe
1450	0.001– 1.0	Gas Liquid Solid	SiO Si(L) Si(S)	HBO B(L) BN(cr)	PN P(L) P(cr)	CO -- SiC(B)	Fe Fe(L) Fe(α,δ,γ)
1550	0.001	Gas Liquid Solid	SiO Si(L) Si(S)	HBO B(L) BN(cr), B(S)	PN P(L) P(cr)	CO -- SiC(B)	Fe Fe(L) Fe(α,δ,γ)
1550	0.01	Gas Liquid Solid	SiO Si(L) Si(S)	HBO B(L) BN(cr)	PN P(L) P(cr)	CO -- SiC(B)	Fe Fe(L) Fe(α,δ,γ)
1550	0.1– 1.0	Gas Liquid Solid	SiO Si(L) Si(S), Si ₃ N ₄ (A)	HBO B(L) BN(cr)	PN P(L) P(cr)	CO -- SiC(B)	Fe Fe(L) Fe(α,δ,γ)
1650	0.001	Gas Liquid Solid	SiO Si(L) Si(S), SiC(B)	HBO B(L) BN(cr), B(S)	PN P(L) P(cr)	CO -- SiC(B)	Fe Fe(L) Fe(α,δ,γ)
1650	0.01– 0.1	Gas Liquid Solid	SiO Si(L) Si(S)	HBO B(L) BN(cr)	PN P(L) P(cr)	CO -- SiC(B)	Fe Fe(L) Fe(α,δ,γ)
1650	1.0	Gas Liquid Solid	SiO Si(L) Si(S), Si ₃ N ₄ (A)	HBO B(L) BN(cr)	PN P(L) P(cr)	CO -- SiC(B)	Fe Fe(L) Fe(α,δ,γ)

* Chemical species are listed for each phase in order of decreasing mole fraction as a function of temperature and pressure. If multiple species are listed, each represents at least ~20% of the element in that phase.

K. NH_4Cl Addition

Ammonium chloride is a salt of ammonia and hydrochloric acid that is a solid at room temperature, but decomposes upon heating above $\sim 350^\circ\text{C}$. The results shown in Figure 31 – Figure 33 and Table 14 are the expected combination of the results for HCl and NH_3 in sections III.E. and I. In this case, the silicon reacts with the ammonia at the higher pressures to form noticeable amounts of solid $\text{Si}_3\text{N}_4(\text{A})$, and with the HCl to form small amounts of volatile SiCl_2 . The carbon reacts with silicon to form $\text{SiC}(\text{B})$ for most of the conditions, with negligible amounts of volatile species such as HCN. The gas phase is mostly composed of H_2 , N_2 and HCl. The phosphorus reacts with ammonia to form PN in the gas, and the iron reacts to form FeCl_2 vapor, especially at low pressures and high temperatures. The boron primarily forms $\text{BN}(\text{cr})$, especially at high pressures and low temperatures, but also forms some volatile boron chlorides (BCl , BHCl_2 and BCl_3), at low pressures and high temperatures.

Figure 31. Distribution of elements among phases: $\text{NH}_4\text{Cl} = 0.05$, $\text{Ar} = 0.01$, 1450°C .

Figure 32. Distribution of elements among phases: $\text{NH}_4\text{Cl} = 0.05$, $\text{Ar} = 0.01$, 1550°C .

Figure 33. Distribution of elements among phases: $\text{NH}_4\text{Cl} = 0.05$, $\text{Ar} = 0.01$, 1650°C .

Table 14. Dominant* chemical species for silicon and impurities with $\text{NH}_4\text{Cl}/\text{Ar}$ addition.

Temp. (°C)	Pressure (atm)	Phase	Si	B	P	C	Fe
1450	0.001	Gas	SiCl_2	BCl	PN	$\text{HCN}, \text{Si}_2\text{C}$	FeCl_2
		Liquid	Si(L)	B(L)	P(L)	--	Fe(L)
		Solid	Si(S)	BN(cr)	P(cr)	SiC(B)	$\text{Fe}(\alpha, \delta, \gamma)$
1450	0.01	Gas	SiCl_2	$\text{BCl}, \text{BHCl}_2$	PN	HCN, CHP	FeCl_2
		Liquid	Si(L)	B(L)	P(L)	--	Fe(L)
		Solid	Si(S)	BN(cr)	P(cr)	SiC(B)	$\text{Fe}(\alpha, \delta, \gamma)$
1450	0.1	Gas	SiCl_2	$\text{BHCl}_2, \text{BCl}_3$	PN	HCN, CHP	FeCl_2
		Liquid	Si(L)	B(L)	P(L)	--	$\text{Fe(L)}, \text{FeCl}_2(\text{L})$
		Solid	Si(S)	BN(cr)	P(cr)	SiC(B)	$\text{Fe}(\alpha, \delta, \gamma)$
1450	1.0	Gas	SiCl_2	$\text{BHCl}_2, \text{BCl}_3$	PN	CH_4	FeCl_2
		Liquid	Si(L)	B(L)	P(L)	--	$\text{FeCl}_2(\text{L}), \text{Fe(L)}$
		Solid	Si(S)	BN(cr)	P(cr)	SiC(B)	$\text{Fe}(\alpha, \delta, \gamma)$
1550	0.001	Gas	$\text{SiCl}_2, \text{SiCl}$	BCl	PN	$\text{HCN}, \text{Si}_2\text{C}$	FeCl_2, Fe
		Liquid	Si(L)	B(L)	P(L)	--	Fe(L)
		Solid	Si(S)	BN(cr)	P(cr)	SiC(B)	$\text{Fe}(\alpha, \delta, \gamma)$
1550	0.01	Gas	SiCl_2	$\text{BCl}, \text{BHCl}_2$	PN	HCN	FeCl_2
		Liquid	Si(L)	B(L)	P(L)	--	Fe(L)
		Solid	Si(S)	BN(cr)	P(cr)	SiC(B)	$\text{Fe}(\alpha, \delta, \gamma)$
1550	0.1	Gas	SiCl_2	$\text{BHCl}_2, \text{BCl}$	PN	HCN	FeCl_2
		Liquid	Si(L)	B(L)	P(L)	--	$\text{Fe(L)}, \text{FeCl}_2(\text{L})$
		Solid	$\text{Si(S)}, \text{Si}_3\text{N}_4(\text{A})$	BN(cr)	P(cr)	SiC(B)	$\text{Fe}(\alpha, \delta, \gamma)$
1550	1.0	Gas	SiCl_2	$\text{BHCl}_2, \text{BCl}_3$	PN	HCN, CH_4	FeCl_2
		Liquid	Si(L)	B(L)	P(L)	--	$\text{FeCl}_2(\text{L}), \text{Fe(L)}$
		Solid	$\text{Si(S)}, \text{Si}_3\text{N}_4(\text{A})$	BN(cr)	P(cr)	SiC(B)	$\text{Fe}(\alpha, \delta, \gamma)$

Temp. (°C)	Pressure (atm)	Phase	Si	B	P	C	Fe
1650	0.001	Gas	SiCl ₂ , SiCl	BCl	PN	Si ₂ C, HCN	Fe, FeCl ₂
		Liquid	Si(L)	B(L)	P(L)	--	Fe(L)
		Solid	Si(S), SiC(B)	BN(cr), B(S)	P(cr)	SiC(B)	Fe(α,δ,γ)
1650	0.01	Gas	SiCl ₂	BCl, BHCl ₂	PN	HCN, CHP	FeCl ₂
		Liquid	Si(L)	B(L)	P(L)	--	Fe(L)
		Solid	Si(S)	BN(cr)	P(cr)	SiC(B)	Fe(α,δ,γ)
1650	0.1	Gas	SiCl ₂	BCl, BHCl ₂	PN	HCN	FeCl ₂
		Liquid	Si(L)	B(L)	P(L)	--	Fe(L), FeCl ₂ (L)
		Solid	Si(S), Si ₃ N ₄ (A)	BN(cr)	P(cr)	SiC(B)	Fe(α,δ,γ)
1650	1.0	Gas	SiCl ₂	BHCl ₂ , BCl ₃	PN	HCN	FeCl ₂
		Liquid	Si(L)	B(L)	P(L)	--	FeCl ₂ (L), Fe(L)
		Solid	Si ₃ N ₄ (A), Si(S)	BN(cr)	P(cr)	SiC(B)	Fe(α,δ,γ)

* Chemical species are listed for each phase in order of decreasing mole fraction as a function of temperature and pressure. If multiple species are listed, each represents at least ~20% of the element in that phase.

IV. Discussion

The chemical equilibrium calculations suggest that the following treatments be investigated for the purification of polysilicon melts. There may well be kinetic limitations to these treatments, which are probably best investigated experimentally, rather than theoretically.

Carbon impurities could be removed by gas treatments containing oxygen or water via oxidation to CO at higher temperatures and lower pressures. Water treatments are less likely to have kinetic limitations than O₂ treatments. If silicon carbide solid (density ~3.2) can be separated from silicon liquid (density ~ 2.5), a non-oxidizing gas treatment might also work.

Phosphorus impurities can be removed by vaporization at lower pressures and higher temperatures in the absence of any gas treatment. In the presence of nitrogen, it could form a volatile species PN, which then could be pumped away. Kinetically, NH₃ is more likely to react than N₂, although the equilibrium calculations indicate that gas treatments containing either could be effective at the lower pressures.

Boron impurities could be removed by reaction with water vapor to form HBO at moderate pressures and the higher temperatures, or by reaction with chlorine (HCl, Cl₂ or SiCl₄) to form boron chlorides (BCl, BHCl₂ and BCl₃) at lower pressures and higher temperatures. The calculations indicate that both of these treatments may be relatively inefficient, but may be workable. Solid boron nitride has a density of ~2.25, which is very close to that for silicon (2.52 liquid, 2.33 solid). But if it could be separated from the silicon, boron impurities could also be removed by reaction with N₂ or NH₃ to form BN(cr), which is favored at higher pressures and lower temperatures.

Iron impurities, like phosphorus, can apparently be removed to some degree by vaporization at lower pressures and higher temperatures in the absence of any gas treatment. Otherwise, treatment with chlorine (HCl, Cl₂ or SiCl₄), which leads to the formation of FeCl₂, should allow the removal of iron impurities over a much wider range of pressures and temperatures.

These gas treatments all involve some degree of silicon loss also. This places limits on the extent to which the gas treatment could be used to remove impurities before the loss of silicon becomes unacceptable. In the case of the oxidizing gases (O_2 and H_2O), most of the oxygen input into the system actually reacts with the silicon to form SiO , which would wind up depositing on cold surfaces in the chamber or exhaust lines. In the case of the nitrogen-containing gases (N_2 and NH_3), most of the input nitrogen also winds up reacting with the silicon to form solid silicon nitride at equilibrium. However, the reaction between silicon and N_2 is generally considered to be relatively inefficient because of kinetic barriers. In the case of HCl , Cl_2 and $SiCl_4$ treatment, silicon is lost by formation of volatile silicon chlorides. However, in some cases (higher pressure and lower temperature), silicon loss is decreased because not all the HCl and $SiCl_4$ reacts away.

It is difficult to directly compare the results from these equilibrium calculations with the experimental literature. The calculations give results for a single "batch exposure", whereas the experiments are for a system in which gases are continuously flowed into the system and pumped out. In addition, the experimental papers generally do not specify the pressure of the system, which greatly affects the equilibrium calculations. The temperature, amount of chemical blowing and/or silicon sample size are also often unavailable. But qualitative comparisons are possible, and show a reasonable level of agreement.

Recently, Sakaguchi, *et al.* [6] reported the removal of phosphorus from electron-beam melted silicon in vacuum. Although the pressure and temperatures of their system is not given, this is consistent with the equilibrium calculations showing significant amounts of P_2 at the lower pressures. These workers also reported the removal of boron by treatment with water vapor and an argon plasma torch, which is also consistent with the equilibrium results in section III. C. showing formation of volatile HBO with water addition. In these experiments, the plasma may have dissociated some of the water (the water vapor was injected separately from the argon for the plasma). This would serve to reduce kinetic limitations and possibly add heat to the system, but does not affect the comparisons with equilibrium calculations.

The work by Khattak and Schmid [5] includes experiments on directional solidification at pressures of 0.2-0.3 Torr ($\sim 3 \times 10^{-4}$ atm), as well as argon blowing and slagging. They observed that directional solidification and argon blowing reduced phosphorus impurities, but that double directional solidification under vacuum and slagging reduced it more. This effect of vacuum and blowing is consistent with the equilibrium calculations showing the evaporation of phosphorus as P_2 . They also reported that iron levels were reduced by directional solidification under vacuum and by argon blowing. This is consistent with the equilibrium calculations that show the formation of gaseous Fe at the lower pressures and higher temperatures, and/or the removal of the iron by the directional solidification. Their best results overall were attained by a combination of moist argon blowing and slagging, which reduced all the impurities studied. This was the only treatment that reduced boron, which is consistent with the equilibrium calculations that show some removal of boron by water via the formation of HBO. But this is not a very clear comparison because of combination of treatments.

An earlier study by this group [26] discusses the formation of silicon carbide particles in silicon melts that both accumulated at the bottom of the ingot and dispersed throughout it. They discuss removal of SiC by use of a silica slag, that would remove the SiC via formation of CO and/or CO_2 . This is consistent with the equilibrium calculations that show that the carbon impurities generally form SiC in the solid, but can be vaporized by CO formation in the presence of oxygen. However, as mentioned above, silicon loss by SiO formation can be considerable in oxygen-containing systems.

In 1975, Dosaj, *et al.* [3] carried out experiments on reactive gas blowing using Cl_2 , O_2 , or Cl_2/O_2 mixtures. The temperature was $\sim 1470^\circ C$, but the pressure was not given. The flow rates and duration of blowing varied by factors of three for different experiments, but they are not specified. They reported that all three gases reduced boron impurities in metallurgical grade silicon by roughly a factor of 2, but that phosphorus was not reduced. Iron was reduced by about a factor of 40 by Cl_2 refinement, but by a factor of 3.5 by the O_2 and Cl_2/O_2 treatments. Their observation that P was not reduced is completely consistent with our results shown in Figure 16 for Cl_2 , Figure 1 for O_2 , and Figure 19 for Cl_2/O_2 , if their pressure was 0.01 atm or higher. Their observation of moderate removal of boron is also consistent with the equilibrium

calculations for Cl_2 and Cl_2/O_2 , but less so for O_2 treatment, where the calculations would predict less efficient B removal than for the chlorine-containing gases, assuming comparable gas exposures. The observation that Fe is more efficiently removed than boron is consistent with the equilibrium calculations, as is the more efficient Fe removal in Cl_2 than O_2 . But the equilibrium results suggest that the Fe removal rate with Cl_2/O_2 should be closer to that with Cl_2 , and that O_2 should be quite inefficient.

In a later paper from the same group [4], however, they revised their conclusions. The final analysis of twenty experiments led to the result that reactive gas blowing using Cl_2 or Cl_2/O_2 was ineffective for Fe removal, but exhibited 10% P reduction and 40% B reduction. For Fe, this is not entirely consistent with either their earlier report or the equilibrium calculations, but the B results remain consistent, and the minor degree of phosphorus removal could be caused by evaporation as P_2 or experimental uncertainty.

In 1956, Theuerer [27] reported that treating liquid silicon with wet hydrogen led to the removal of boron, but not phosphorus. Although the pressure and temperature are not given, the experiments were probably done at a total pressure close to atmospheric and not much above the melting point of silicon, as only part of the silicon rods were molten at any given time. This is consistent with the equilibrium results in section III.C., which showed the formation of some volatile HBO at the higher pressures, but no volatile phosphorus oxides or hydroxides.

The papers by Dosaj, *et al.* [3] and by Dietl [28], also refer to earlier work on gas-blowing purification in the literature (primarily patents). These included the use of chlorine, SiCl_4 , and oxygen to reduce metal impurities, the use of water, air (O_2) and vacuum to reduce phosphorus, and the use of CO_2 to reduce carbon impurities. Attempting to do comparisons between these reports and the equilibrium calculations is not warranted, given the low level of information available. But the calculations suggest that any P removal was probably due to evaporation rather than chemical reaction. In contrast, an equilibrium calculation done with added CO_2 gave no indication of carbon removal via a reaction like $\text{CO}_2 + \text{C}(\text{S}) \rightarrow 2 \text{CO}$. Instead, the system preferred to have the oxygen react with silicon to form SiO , and the carbon react with silicon to

form SiC(B). Hence the experimental observation of carbon removal by CO₂ may be attributed to kinetic effects.

V. Conclusions

Chemical equilibrium calculations provide a useful tool for screening possible methods for removing B, P, C and Fe impurities from polysilicon melts by gas blowing. Examining the effects of a number of possible chemical additives (O₂, air, water wet air, HCl, NH₃, NH₄OH, and NH₄Cl) at 1450, 1550 and 1650°C, and total pressures of 0.001, 0.01, 0.1, and 1.0 atm, suggests the following:

1. Water vapor is a likely additive for removing carbon impurities as CO, and boron impurities as HBO, at lower total pressures and higher temperatures.
2. NH₃ (and possibly N₂) addition may provide a method of removing phosphorus impurities as PN, although evaporation as P₂ is known to work and would avoid silicon loss by Si₃N₄ formation.
3. HCl or other chlorine-containing treatments may remove iron (and possibly other metals), along with some boron.
4. Combinations of additives (such as wet air or Cl₂/O₂ or NH₄Cl) offer the best prospects for removal of multiple impurities.
5. The extent of vaporization is quite dependent on total pressure as well as on temperature. Generally the lower total pressures are much more effective, which suggests that this is an important parameter to monitor/control in purification experiments.
6. The separation of solid reaction products (boron nitride, silicon carbide or silicon nitride) from liquid silicon, offers other treatment possibilities.

This study does not address chemical kinetic and transport limitations, which have been reported to be important [5] and are probably best investigated experimentally. But it should help guide and interpret the experiments, and hopefully reduce the number required. There are, of course, other considerations for designing a polysilicon purification method, including safety, energy and economic factors, but they await more experimental demonstrations of impurity removal.

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APPENDIX: Example Output from EQUIL

EQUIL: Chemkin interface for Stanjan-III
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DOUBLE PRECISION

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KEYWORD INPUT

REAC SI(S) 1.0
REAC C(S) 0.001
REAC B(S) 2.5E-5
REAC P(cr) 2.5E-5
REAC FE(s,a-d) 0.001
REAC AR 0.01
REAC NH4CL(a) 0.05
TEMP 1923. ! Kelvin
PRES 0.001 ! Atmospheres
TP
END

Constant temperature and pressure problem.

EQUIL: Chemkin interface for Stanjan-III
CHEMKIN-III Version 3.8, 97/03/01
DOUBLE PRECISION

WORKING SPACE REQUIREMENTS

	PROVIDED	REQUIRED
INTEGER	73933	73933
REAL	383336	383336
CHAR	153	153

STANJAN: Version 3.95, September 1993
W. C. Reynolds, Stanford Univ.

MIXTURE: INITIAL STATE: EQUILIBRIUM STATE:

P (atm)	1.0000E-03	1.0000E-03
T (K)	1.9230E+03	1.9230E+03
V (cm ³ /gm)	5.0530E+04	8.5146E+05
H (erg/gm)	1.4531E+10	-1.9355E+10
U (erg/gm)	1.4480E+10	-2.0218E+10
S (erg/gm-K)	2.9313E+07	4.5434E+07
W (gm/mol)	2.9404E+01	2.7122E+01
Mol Fractions		
AR	9.4158E-03	8.6848E-03
SI	.0000E+00	2.3776E-03
SI2	.0000E+00	3.9577E-06
SI3	.0000E+00	4.8118E-06
H	.0000E+00	3.0826E-03
H2	.0000E+00	7.3990E-02
CL	.0000E+00	7.0168E-04
CL2	.0000E+00	1.1585E-08
HCL	.0000E+00	2.2482E-02
SIH	.0000E+00	1.7059E-05
SIH2	.0000E+00	5.2741E-07
SIH3	.0000E+00	1.1012E-09
SIH4	.0000E+00	4.2821E-11
SICLH3	.0000E+00	1.1006E-09
SICL3H	.0000E+00	1.0624E-07
SICL2H2	.0000E+00	1.6679E-08
HSICL	.0000E+00	8.6713E-05
SIH2CL	.0000E+00	1.9360E-08
SIHCL2	.0000E+00	1.9462E-07
SICL	.0000E+00	5.1012E-03
SICL2	.0000E+00	7.3139E-03
SICL3	.0000E+00	1.7579E-06
SICL4	.0000E+00	1.4906E-07
CL2SISICL2	.0000E+00	7.8154E-11
CL3SISICL	.0000E+00	1.9559E-10
CL3SISI	.0000E+00	5.4129E-11
CL2SISICL	.0000E+00	1.8423E-10
CL2SISI	.0000E+00	3.3800E-09
CLSISICL	.0000E+00	9.6549E-09
CLSISI	.0000E+00	5.7322E-08
CH3	.0000E+00	2.2532E-10
CH4	.0000E+00	2.1901E-10
C2H2	.0000E+00	5.5132E-09
SIC	.0000E+00	2.9014E-10
SIC2	.0000E+00	1.0216E-08
SICH	.0000E+00	2.2411E-09
SICH2	.0000E+00	5.9922E-09
SI2C	.0000E+00	1.4448E-05
N	.0000E+00	5.0224E-10
N2	.0000E+00	2.1674E-02
NH	.0000E+00	9.1741E-11
NH2	.0000E+00	5.6532E-11
NH3	.0000E+00	4.8106E-10
CN	.0000E+00	5.8211E-09
HCN	.0000E+00	5.7394E-06
HNC	.0000E+00	4.5105E-07
CLCN	.0000E+00	8.1143E-10
SIN	.0000E+00	1.1261E-08
SINH	.0000E+00	3.7392E-05

SINH2	.0000E+00	3.4836E-10
SI2N	.0000E+00	1.3836E-05
B	.0000E+00	1.9017E-09
BH	.0000E+00	3.0945E-10
BH2	.0000E+00	5.1370E-11
BH3	.0000E+00	1.9334E-10
BCL	.0000E+00	4.8228E-06
BCL2	.0000E+00	8.6948E-08
BCL3	.0000E+00	7.3747E-09
HBCL	.0000E+00	1.0119E-09
BHCL2	.0000E+00	1.6642E-08
BH2CL	.0000E+00	2.6313E-09
BNH	.0000E+00	1.7588E-11
HBNH	.0000E+00	6.4430E-12
CLBNH	.0000E+00	2.9119E-10
SIBH	.0000E+00	4.5439E-11
SIBCL	.0000E+00	7.0045E-10
SIBCL2	.0000E+00	6.0418E-12
P	.0000E+00	1.1597E-06
P2	.0000E+00	1.7844E-07
PCL	.0000E+00	1.1427E-08
PH	.0000E+00	4.6782E-08
PH2	.0000E+00	6.3590E-10
PH3	.0000E+00	1.1805E-11
CP	.0000E+00	6.1431E-10
CHP	.0000E+00	5.5517E-07
PN	.0000E+00	1.6985E-05
FE	.0000E+00	5.2824E-04
FECL	.0000E+00	1.5511E-06
FECL2	.0000E+00	2.0523E-04
FECL3	.0000E+00	8.8401E-10
SI(L)	.0000E+00	8.5089E-01
B(L)	.0000E+00	1.3656E-05
B2O3(L)	.0000E+00	.0000E+00
P(L)	.0000E+00	2.5955E-06
SIO2(L)	.0000E+00	.0000E+00
FE(L)	.0000E+00	1.1398E-05
FECL2(L)	.0000E+00	3.7962E-08
FECL3(L)	.0000E+00	1.0274E-13
FEO(L)	.0000E+00	.0000E+00
SI(S)	9.4158E-01	1.7540E-03
SIO2(S)	.0000E+00	.0000E+00
B(S)	2.3539E-05	1.0136E-06
B2O3(S)	.0000E+00	.0000E+00
C(S)	9.4158E-04	3.2872E-05
SIC(B)	.0000E+00	8.1436E-04
P(cr)	2.3539E-05	1.9867E-12
SI3N4(A)	.0000E+00	1.9091E-08
BN(cr)	.0000E+00	2.1011E-06
NH4CL(a)	4.7079E-02	6.1441E-25
NH4CL(b)	.0000E+00	3.7009E-26
FE(s,a-d)	9.4158E-04	6.1373E-05
FE(s,gamma)	.0000E+00	6.0641E-05
FECL2(s)	.0000E+00	5.5187E-12
FECL3(s)	.0000E+00	.0000E+00
FEO(s)	.0000E+00	.0000E+00
FE(OH)2(s)	.0000E+00	.0000E+00

FE(OH)3(s)	.0000E+00	.0000E+00
FE2O3(s)	.0000E+00	.0000E+00
FE3O4(s)	.0000E+00	.0000E+00

GAS PHASE

Mols	1.0000E-02	1.6852E-01
W (gm/mol)	3.9948E+01	2.1410E+01
V (cm3/gm)	3.9501E+06	7.3704E+06
Mol Fractions		
AR	1.0000E+00	5.9341E-02
SI	.0000E+00	1.6245E-02
SI2	.0000E+00	2.7042E-05
SI3	.0000E+00	3.2878E-05
H	.0000E+00	2.1062E-02
H2	.0000E+00	5.0556E-01
CL	.0000E+00	4.7944E-03
CL2	.0000E+00	7.9159E-08
HCL	.0000E+00	1.5362E-01
SIH	.0000E+00	1.1656E-04
SIH2	.0000E+00	3.6036E-06
SIH3	.0000E+00	7.5239E-09
SIH4	.0000E+00	2.9258E-10
SICLH3	.0000E+00	7.5200E-09
SICL3H	.0000E+00	7.2594E-07
SICL2H2	.0000E+00	1.1397E-07
HSICL	.0000E+00	5.9249E-04
SIH2CL	.0000E+00	1.3228E-07
SIHCL2	.0000E+00	1.3298E-06
SICL	.0000E+00	3.4855E-02
SICL2	.0000E+00	4.9974E-02
SICL3	.0000E+00	1.2012E-05
SICL4	.0000E+00	1.0185E-06
SI2CL5	.0000E+00	1.0103E-12
SI2CL5H	.0000E+00	7.4492E-14
SI2CL6	.0000E+00	1.0813E-13
HCL2SISICL2H	.0000E+00	4.2565E-15
CL2SISICL2	.0000E+00	5.3400E-10
CL3SISICL	.0000E+00	1.3364E-09
CL3SISI	.0000E+00	3.6985E-10
CL2SISICL	.0000E+00	1.2588E-09
CL2SISI	.0000E+00	2.3094E-08
CLSISICL	.0000E+00	6.5969E-08
CLSISI	.0000E+00	3.9167E-07
O2	.0000E+00	.0000E+00
OH	.0000E+00	.0000E+00
H2O	.0000E+00	.0000E+00
CO	.0000E+00	.0000E+00
CO2	.0000E+00	.0000E+00
CH3	.0000E+00	1.5395E-09
CH4	.0000E+00	1.4964E-09
C2H2	.0000E+00	3.7670E-08
SIC	.0000E+00	1.9825E-09
SIC2	.0000E+00	6.9806E-08
SICH	.0000E+00	1.5313E-08
SICH2	.0000E+00	4.0943E-08
SI2C	.0000E+00	9.8722E-05
CH2SICL3	.0000E+00	7.4175E-14

CH3SICL	.0000E+00	6.3341E-12
CL3SICH3	.0000E+00	5.3727E-15
H2CLISISICL3	.0000E+00	9.3691E-15
HSI=O	.0000E+00	.0000E+00
HOSI	.0000E+00	.0000E+00
SIO	.0000E+00	.0000E+00
-SIOSIO-	.0000E+00	.0000E+00
N	.0000E+00	3.4316E-09
N2	.0000E+00	1.4809E-01
NH	.0000E+00	6.2684E-10
NH2	.0000E+00	3.8627E-10
NH3	.0000E+00	3.2870E-09
NO	.0000E+00	.0000E+00
CN	.0000E+00	3.9774E-08
HCN	.0000E+00	3.9216E-05
HNC	.0000E+00	3.0819E-06
CLCN	.0000E+00	5.5443E-09
SIN	.0000E+00	7.6946E-08
SINH	.0000E+00	2.5549E-04
SINH2	.0000E+00	2.3803E-09
SI2N	.0000E+00	9.4535E-05
B	.0000E+00	1.2994E-08
BO	.0000E+00	.0000E+00
B2O2	.0000E+00	.0000E+00
BH	.0000E+00	2.1144E-09
HBO	.0000E+00	.0000E+00
HOB0	.0000E+00	.0000E+00
BH2	.0000E+00	3.5100E-10
BH3	.0000E+00	1.3210E-09
BH2OH	.0000E+00	.0000E+00
BCL	.0000E+00	3.2953E-05
BCL2	.0000E+00	5.9409E-07
BCL3	.0000E+00	5.0389E-08
HBCL	.0000E+00	6.9142E-09
BHCL2	.0000E+00	1.1371E-07
BH2CL	.0000E+00	1.7979E-08
BOCL	.0000E+00	.0000E+00
BN	.0000E+00	3.1358E-14
BNH	.0000E+00	1.2018E-10
BNH2	.0000E+00	6.6231E-13
B(NH2)2	.0000E+00	2.6083E-22
B(NH2)3	.0000E+00	1.1405E-27
B3N3H6	.0000E+00	3.1814E-32
H2BN	.0000E+00	1.4245E-18
H2BNH	.0000E+00	8.0961E-16
H2BNH2	.0000E+00	6.0411E-15
H3BNH3	.0000E+00	5.4416E-25
HB(NH2)2	.0000E+00	1.6003E-21
HBN	.0000E+00	1.7967E-13
HBNH	.0000E+00	4.4024E-11
HBNH2	.0000E+00	1.9387E-15
CLBNH	.0000E+00	1.9896E-09
BCL2NH2	.0000E+00	8.3678E-14
SIBH	.0000E+00	3.1047E-10
SIBCL	.0000E+00	4.7860E-09
SIBCL2	.0000E+00	4.1282E-11
P	.0000E+00	7.9238E-06

P2	.0000E+00	1.2192E-06
PCL	.0000E+00	7.8077E-08
PCL3	.0000E+00	4.4444E-14
PH	.0000E+00	3.1965E-07
PH2	.0000E+00	4.3449E-09
PH3	.0000E+00	8.0661E-11
PO	.0000E+00	.0000E+00
CP	.0000E+00	4.1974E-09
CHP	.0000E+00	3.7933E-06
PN	.0000E+00	1.1606E-04
FE	.0000E+00	3.6093E-03
FECL	.0000E+00	1.0598E-05
FECL2	.0000E+00	1.4023E-03
FECL3	.0000E+00	6.0402E-09
FE2CL4	.0000E+00	6.7651E-12
FE2CL6	.0000E+00	3.9404E-23
FEO	.0000E+00	.0000E+00
FEC5O5	.0000E+00	.0000E+00
FE(OH)2	.0000E+00	.0000E+00

BULK PHASE # 1

Mols	.0000E+00	9.7978E-01
Mol Fractions		
SI(L)	.0000E+00	9.9997E-01
B(L)	.0000E+00	1.6049E-05
B2O3(L)	.0000E+00	.0000E+00
P(L)	.0000E+00	3.0503E-06
SIO2(L)	.0000E+00	.0000E+00
FE(L)	.0000E+00	1.3395E-05
FECL2(L)	.0000E+00	4.4613E-08
FECL3(L)	.0000E+00	1.2074E-13
FEO(L)	.0000E+00	.0000E+00

BULK PHASE # 2

Mols	1.0520E+00	3.1392E-03
Mol Fractions		
SI(S)	9.5053E-01	6.4334E-01
SIO2(S)	.0000E+00	.0000E+00
B(S)	2.3763E-05	3.7177E-04
B2O3(S)	.0000E+00	.0000E+00
C(S)	9.5053E-04	1.2057E-02
SIC(B)	.0000E+00	2.9870E-01
P(cr)	2.3763E-05	7.2869E-10
SI3N4(A)	.0000E+00	7.0023E-06
BN(cr)	.0000E+00	7.7065E-04
NH4CL(a)	4.7526E-02	2.2536E-22
NH4CL(b)	.0000E+00	1.3575E-23
FE(s,a-d)	9.5053E-04	2.2511E-02
FE(s,gamma)	.0000E+00	2.2243E-02
FECL2(s)	.0000E+00	2.0242E-09
FECL3(s)	.0000E+00	.0000E+00
FEO(s)	.0000E+00	.0000E+00
FE(OH)2(s)	.0000E+00	.0000E+00
FE(OH)3(s)	.0000E+00	.0000E+00
FE2O3(s)	.0000E+00	.0000E+00
FE3O4(s)	.0000E+00	.0000E+00
Total CPUtime (sec):	1.08E+00	

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