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Gibbs Free Energy of Reactions Involving SiC, Si_3N_4, H_2, and H_2O as a Function of Temperature and Pressure

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GIBBS FREE ENERGY OF REACTIONS INVOLVING SiC, Si_3N_4, H_2, AND H_2O AS A FUNCTION OF TEMPERATURE AND PRESSURE

INTRODUCTION

Silicon carbide (SiC) and silicon nitride (Si_3N_4) are being considered as materials for coatings[1] and structural components[2] in hot sections of advanced propulsion systems using hydrogen (H_2) as working fluid. Possible applications include coatings for turbine and nozzle components. Advanced propulsion systems, including nuclear thermal, will most likely employ a feed system composed of a turbine and pump. Hot hydrogen will turn the turbine which drives the pump.[3]

A multiplicity of propulsion system designs is under consideration, yet no single design has been explicitly defined as the engine which will carry future craft on interplanetary flight.[4] Near-term designs[5] consider turbine inlet temperatures up to 521 °C [5] and pressures up to 130 bars.[6] Nozzle temperature may reach 2,427 °C in the chamber[7] and pressure may be as great as 92 bars.[6][7] Higher pressures and temperatures generally contribute to higher engine efficiency and better performance. Higher temperatures across the feed system allow higher overall engine temperatures, contributing to more efficient operation. Higher reactor chamber pressure enhances performance through greater thrust.[5][7]

Several investigators have demonstrated strength reduction and weight loss in SiC and Si_3N_4 exposed to flowing H_2 as a function of temperature.[1][8-10] Variation in moisture content affects material degradation, and a high enough level of moisture in H_2 may retard degradation by the formation of a silica (SiO_2) scale. Still, at constant moisture level, chemical reactions are temperature dependent with more severe degradation generally occuring at higher temperatures.[9][10]

System total pressure affects reaction equilibria. Misra[2] theoretically examined the stability of various ceramic materials in hydrogen gas at different temperatures, total pressures, and P_{H_2O}. The partial pressure of gaseous products can be divided into discrete regions depending on moisture content of the hydrogen gas. Region I corresponds to a $\log(P_{H_2}/P_{H_2O})$ greater than about 10^5. In region II $\log(P_{H_2}/P_{H_2O})$ is between about 10^2 and 10^4. Silicon carbide and silicon nitride are generally reactive in region I, and they are actively oxidized to silicon monoxide (SiO) in region II.[2]

For SiC at all temperatures and pressures, methane (CH_4) is the major gaseous product in region I. In region II, SiO predominates at higher temperatures and lower pressures, while CH_4 predominates at lower temperatures and higher pressures.[2]

In reactions of Si_3N_4 with H_2, nitrogen gas (N_2) predominates at higher temperatures and lower pressures in both regions I and II. As temperature decreases and pressure increases, SiH_4 is favored slightly over SiO as the gaseous product.[2]

A relatively wet atmosphere (designated region III[1][2][10]) is required to form a protective SiO_2 layer on either SiC or Si_3N_4. Misra[2] has calculated that the moisture level required increases as total

system pressure increases. It decreases slightly for SiC and increases for Si_3N_4 as temperature increases.

Reactions relevant to the decomposition of SiC and Si_3N_4 in H_2 and H_2/H_2O are therefore

$$SiC+2H_2 = Si+CH_4 \qquad (1)$$

$$SiC+H_2O+H_2 = SiO+CH_4 \qquad (2)$$

$$Si_3N_4 = 3Si+2N_2 \qquad (3)$$

$$Si_3N_4+6H_2 = 3SiH_4+2N_2 \qquad (4)$$

$$2SiC+2H_2O+2H_2 = Si+SiO_2+2CH_4 \qquad (5)$$

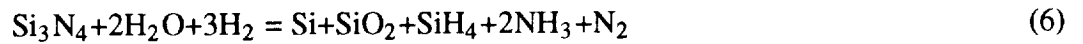$$Si_3N_4+2H_2O+3H_2 = Si+SiO_2+SiH_4+2NH_3+N_2 \qquad (6)$$

Table 1 lists these reactions according to the conditions under which they are most likely to occur.

Since service conditions may vary in temperature and pressure for SiC and Si_3N_4 as structural materials and coatings, and degradation modes may vary with temperature and pressure, a fuller understanding of reactions operating at various temperatures and pressures is necessary. Flowing hydrogen gas creates a situation in which equilibrium is never reached. Fresh reactant is introduced continuously into the chemical reaction. Examination of the conditions under which SiC and Si_3N_4 might preferentially decompose in H_2 is instructive.

THEORY

Reactions proceed spontaneously where differences between Gibbs free energy of products and reactants is negative. If ΔG for a reaction is positive, the reverse of the reaction proceeds. Change in Gibbs free energy is a function of temperature and pressure such that

$$dG = (\delta G/\delta p)_T \, dp + (\delta g/\delta T)_p \, dT . \qquad (7)$$

Since $(\delta G/\delta p)_T = V$ and $(\delta G/\delta T)_p = -S$, equation (7) becomes

$$dG = Vdp - SdT . \qquad (8)$$

For molar quantities

$$dGm = Vm \, dp - Sm \, dT , \qquad (9)$$

where the subscript m denotes molar quantity. The integral taken over the ranges of temperature and pressure of interest is the total change in Gibbs free energy.

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The change in molar volume of solids and liquids is negligible over a broad range of pressures. For practical purposes it can be considered constant. The molar volume of gases changes significantly with pressure. For an ideal gas

$$Vm = RT/p .$$ (10)

Computation of molar entropy is similar for solids, liquids, and gases. It is

$$Sm = Cpm/T$$ (11)

for solids and liquids, and

$$Sm = Cpm/T–R/p$$ (12)

for ideal gases.[11] Cpm is the molar heat capacity of the substance at constant pressure.

The total derivative of molar Gibbs free energy with respect to temperature and pressure is then

$$dGm(T,p) = Vm \, dp–Cpm/T \, dT$$ (13)

for solids and liquids, and

$$dGm(T,p) = RT/p \, dp–Cpm/T \, dT+R/p$$

$$= R(T+1)/p \, dp–Cpm/T \, dT$$ (14)

for ideal gases.

The Gibbs free energy of a substance at any temperature or pressure is found by integrating over the ranges of temperature and pressure of interest. If Gibbs free energy is determined with reference to the standard state (T = 298.15 K, p = 1 bar), it is the change in Gibbs free energy (ΔG) that is calculated. Integration gives

$$\Delta G(T,p) = \Delta G^o + Vm(p–p0)–Cpm \, ln(T/T0)$$ (15)

for solids and liquids, and

$$\Delta G(T,p) = \Delta G^o + R(T+1) \, ln(p/p0)–Cpm \, ln(T/T0)$$ (16)

for ideal gases. Where ΔG^o is the change in Gibbs free energy of the substance in the standard state. Heat capacity at constant pressure is itself a function of temperature and can be approximated by an equation of the form

$$Cpm = a+bT+cT^2+dT^3 .$$ (17)

Molar entropy is Cpm/T so that

$$Cpm/T = a/T+b+cT+dT^2 .$$ (18)

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Integrating with respect to T gives

$$\Delta Cpm = a \ln(T/298) + b(T-298) + \tfrac{1}{2} c(T^2 - 298^2) + \tfrac{1}{3} d(T^3 - 298^3) . \qquad (19)$$

A surface describing ΔG for a chemical reaction, as a function of temperature and pressure, will show the regions of temperature and pressure in which the reaction is spontaneous.

PROCEDURE

The JANAF Thermochemical Tables[12] provide data for elements and compounds based on a reference state of 1 bar and 298.15 K. Values for heat capacity are given at a pressure of 1 bar in the temperature range of 0 to 6,000 K for most substances. Using an appropriate number of simultaneous equations, coefficients for best-fit curves were calculated from Cp values for species in the range of 298.15 to 1,500 K. Species chosen were those included in equations (1) to (6). Best-fit curves were of the form

$$Cpm = a + bT + cT^{\pm 2} + dT^{\pm 3} . \qquad (20)$$

Coefficients of T, as well as molar volume and standard Gibbs free energy change for species, are listed in table 2.

A computer code was written to construct a three-dimensional surface of the change in Gibbs free energy of reactions (1) to (6) as functions of temperature and pressure. The generation of the surface is by equation (15) for solid species and equation (16) for gaseous species. Both equations (15) and (16) use equations of the form of equation (19) for the molar entropy term. In this program, temperature ranges from 298 to 1,500 K, and pressure ranges from 1 bar to 500 bars. The surface showing change in Gibbs free energy of a reaction subtracts $\Sigma \Delta G(T,p)$ of reactants from $\Sigma \Delta G(T,p)$ of products.

RESULTS AND DISCUSSION

Figures $1a$ to $4a$ show changes in Gibbs free energy of the reactions assumed relevant. The plots are surfaces as functions of temperature and pressure. Figure $1a$ is a plot of reaction 1:

$$SiC + 2H_2 = Si + CH_4. \qquad (1)$$

Except at lower temperatures and pressures, the reaction is spontaneous. Silicon is the stable solid, and CH_4 is the gaseous product. The reaction is favored by increases in temperature and pressure. Initially, an increase in pressure decreases ΔG dramatically at all temperatures. At pressures greater than about 20 to 70 bars, the effect is less pronounced. Temperature has a significant effect at all pressures as well, and the effect is greater at higher pressures. This is consistent with Herbell et al.[1] Silicon carbide (SiC) should decompose at an increasing rate with increasing total pressure in that ΔG becomes more negative as pressure increases over the range of temperatures they considered. However, the rate is markedly less at higher pressures. Clearly, both temperature and pressure act in concert to enhance the decomposition of SiC in pure H_2.

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Figure 2a shows reaction 2:

$$SiC+H_2O+H_2 = SiO+CH_4. \qquad (2)$$

A change in temperature has only a slight effect, and this reaction is not spontaneous at any temperature or pressure considered here. Silicon carbide is stable over the entire ranges of both parameters. It is interesting to speculate that the reaction is spontaneous at extremely high pressure, though this is extrapolation from the model. Should the trend continue, figure 2 suggests that, at extremely high pressures, SiC would convert to SiO and CH_4 in a hydrogen/water atmosphere. Solving for p in

$$0 = \Delta G^o(SiO)+RT\ ln(p)+\Delta G^o(CH_4)+RT\ ln(p)-\Delta G^o(H_2O)-RT\ ln(p)$$

$$- \Delta G^o(H_2)-RT\ ln(p)-Vm(SiC)(p-1),$$

the reaction would reach equilibrium at 40 kbars.

The decomposition of Si_3N_4

$$Si_3N_4 = 3Si+2N_2 \qquad (3)$$

is shown in figure 3a. This reaction is also not spontaneous at any temperature or pressure under consideration. In contrast to the previous reactions, this one is not favored by increasing temperature or pressure. In fact, figure 3a suggests that the reaction will proceed only at very low temperatures and pressures. The pressure effect appears dominant at less than approximately 50 bars. Below 50 bars ΔG, for the reaction, drops steeply and approaches zero only at much less than 1 bar. This is in keeping with Misra's[2] statement that reducing the pressure at constant temperature is equivalent to increasing the temperature at 1 atm. It is also a consequence of the fact that ΔG generally increases where the number of moles of product gases is greater than that of reactant gases.

In the high-pressure range, temperature has a larger effect on ΔG than pressure. In this region, the change in entropy is of greater magnitude than the change in molar volume of constituents.

Figure 4a depicts reaction (4):

$$Si_3N_4+6H_2 = 3SiH_4+2N_2. \qquad (4)$$

The plot for this reaction is similar in appearance to those involving SiC, though products of this one are not stable over the ranges of temperature and pressure considered. Again, however, the reaction is favored by increasing temperature and pressure.

Figure 5a plots a possible reaction where SiO_2 forms on SiC:

$$2SiC+2H_2O+2H_2 = Si+SiO_2+2CH_4. \qquad (5)$$

The change in Gibbs free energy is the most negative of any reaction considered. It is therefore most likely to proceed. Except at low pressures, it is more dependent on temperature than pressure. As temperature increases, the change in entropy determines the reaction more than change in molar volume. Comparing figures 1a and 5a, if SiC is unstable in pure H_2, a wetter atmosphere provides some stability by allowing the formation of a protective SiO_2 scale.

Figure 6a shows a plot of the reaction forming SiO_2 on Si_3N_4:

$$Si_3N_4 + 2H_2O + 3H_2 = Si + SiO_2 + SiH_4 + 2NH_3 + N_2. \tag{6}$$
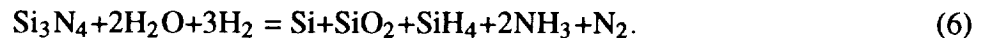
Change in Gibbs free energy is not negative, so the reaction does not proceed as written. Instead, the opposite of the reaction proceeds. Again, Si_3N_4 appears to be stable, though ΔG decreases with temperature. It is also apparent that ΔG for this reaction is the lowest for all reactions involving Si_3N_4 in this study. This is most likely due to the great stability, hence negative ΔG of formation of SiO_2 over a broad range of temperatures. A positive ΔG for the reaction notwithstanding, it is less positive than for other reactions due to the possibility of SiO_2 as a product.

Mathematical models do not generally reflect real processes completely accurately, yet models such as the one described here are illustrative and some tentative conclusions can be drawn. In a closed system, only SiC in pure H_2 will decompose. Where moisture is present in the same proportion as hydrogen gas, SiC is stable up to moderate temperatures and pressures. Silicon nitride is stable in pure H_2 at all but the lowest pressures. This suggests that where temperatures are less than 1,500 K and pressures less than 500 bars, SiC will decompose quite readily in pure H_2 while Si_3N_4 remains stable. Reliability of structural components and coatings in turbopumps and nozzles would be better served by using silicon nitride.

A real structural material employs various sintering and binding aids which may engage in reactions with H_2 and H_2O where the parent material would not. Also, it can be argued that treatment of gases as ideal introduces error. Due to attraction between molecules, the molar volume of a real gas is less than that expected for an ideal gas. A smaller contribution by gaseous molar volume to overall Gibbs free energy might favor all of the above reactions as written. However, if the scale of energy change in reactions is large enough, the effect of additional terms may be immeasurably small.

As an example, consider gases to behave as van der Waals gases, with molar volume derived in the following manner:[13] The compressibility factor is $Z = pVm/RT$ for ideal gases. If $p = RT/(Vm-b) - a/Vm^2$ for a van der Waals gas, $Z = Vm/(Vm-b) - a/RT$. Dividing numerator and denominator by Vm gives

$$Z = 1/[1-(b/Vm)] - a/VmRT. \tag{21}$$

At very low pressures, Vm is large and b/Vm is very small. A power series in Vm can be generated for the term $1/[1-(b/Vm)]$ to give

$$Z = 1 + b/Vm + (b/Vm)^2 + ... - a/VmRT$$

$$= 1 + (b - a/RT)(1/Vm) + (b/Vm)^2 + ... \tag{22}$$

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Since $Z = pV_m/RT$, then $V_m = ZRT/p = RT/p+RT/p(b-a/RT)(p/RTZ)$. More simply,

$$V_m = RT/p+b-a/RT \ . \tag{23}$$

Integrating with respect to p gives

$$V_m(p) = RT \ ln(p/p0)+(b-a/RT)(p-p0) \ . \tag{24}$$

If the units of the gas constant are kJ/mol K and the units of $(b-a/RT)(p-p0)$ are m^3 bar/mol, the latter term must be multiplied by 100 to convert m^3 bar to kJ.

Using equation (24) for molar volume in Gibbs free energy change for gases gives figures 1*b* to 6*b* for the reactions investigated here. Table 3 gives van der Waals constants for gaseous species.

In the range of temperature and pressure considered here, where ΔG is measured in kJ, there is no discernable difference in reactions where gases are treated as ideal or van der Waals gases. The implication is that gases behave ideally on the scale of energy changes considered here and can be modeled as such. At low pressure and/or high temperature, van der Waals attractive and repulsive forces have negligible effect, and a gas behaves very nearly ideal. However, where Gibbs free energy of reactions is calculated in kJ, the effect of van der Waals forces is simply too small to detect at temperatures and pressures investigated here.

CONCLUSIONS

On the basis of change in Gibbs free energy of reactions, Si_3N_4 is more stable than SiC at all pressures and temperatures likely to be encountered in near-term advanced propulsion feed systems. Silicon carbide is more stable in a wet hydrogen atmosphere due to the formation of a SiO_2 scale. Reactant and product gases can be treated as ideal for the purpose of reaction thermodynamics involving SiC, Si_3N_4, and H_2/H_2O.

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Table 1. Reactions of SiC and Si_3N_4 with H_2 and H_2/H_2O.

	Region I	Region II	Region III	Ref.
High T, Low p	$SiC+2H_2=Si+CH_4$	$SiC+H_2O+H_2=SiO+CH_4$		
Low T, High p	$SiC+2H_2=Si+CH_4$	$SiC+2H_2=Si+CH_4$	$2SiC+2H_2O+2H_2=Si+SiO_2$ $+2CH_4$	1, 2, 8, 11
High T, Low p	$Si_3N_4=3Si+2N_2$	$Si_3N_4=3Si+2N_2$		
Low T, High p	$Si_3N_4+6H_2=3SiH_4+2N_2$	$Si_3N_4+6H_2=3SiH_4+2N_2$	$Si_3N_4+2H_2O+3H_2=SiO_2+$ $SiH_4+2NH_3+N_2$	1, 2

Table 2. Thermochemical data.

			Cp Coefficients			
Species*	**$\Delta G^{\underline{o}}$ (kJ/mol)**	**Vm (m³/mol)**	**a**	**b**	**c**	**d**
H_2 (1)	0.0	-	3.029×10^{-2}	-3.216×10^{-6}	3.102×10^{-9}	-2.045×10^4
N_2 (1)	0.0	-	2.487×10^{-2}	1.018×10^{-5}	-2.360×10^{-9}	3.794×10^4
Si (3)	0.0	1.205×10^{-5}	2.283×10^{-2}	3.839×10^{-6}	-3.536×10^2	0.0
SiC (2)	-69.139	1.249×10^{-5}	-6.131×10^{-4}	1.174×10^{-4}	-9.356×10^{-8}	2.578×10^{-11}
Si_3N_4 (1)	-647.343	4.412×10^{-5}	6.738×10^{-2}	1.241×10^{-4}	-3.326×10^{-8}	-5.002×10^4
SiO (2)	-127.305	-	2.363×10^{-2}	2.520×10^{-5}	-1.746×10^{-8}	4.357×10^{-12}
SiO_2 (3)	-853.636	2.590×10^{-5}	7.278×10^{-2}	1.285×10^{-6}	-4.141×10^3	0.0
SiH_4 (1)	56.827	-	2.107×10^{-2}	9.134×10^{-5}	-2.781×10^{-8}	-7.957×10^4
H_2O (1)	-228.582	-	2.823×10^{-2}	1.388×10^{-5}	-8.739×10^{-10}	3.445×10^4
CH_4 (2)	-50.768	-	2.229×10^{-2}	3.716×10^{-5}	3.095×10^{-3}	-1.811×10^{-11}
NH_3 (2)	-16.367	-	2.634×10^{-2}	3.028×10^{-5}	4.560×10^{-9}	-4.581×10^{-12}

* Numbers in parentheses denote form of integrated equation used in entropy calculations.
(1): a $ln(T)$ + b$(T-T0)$ + c/2(T^2-T0^2) - d/3$(T^{-3}-T0^{-3})$
(2): a $ln(T)$ + b$(T-T0)$ + c/2(T^2-T0^2) + d/3(T^3-T0^3)
(3): a $ln(T)$ + b$(T-T0)$ + c/2$(T^{-2}-T0^{-2})$

Table 3. Van der Waals constants for gaseous species.

Species	$a\ (m^6\ bar/mol^2)$	$b\ (m^3/mol)$
H_2	2.476×10^{-7}	2.661×10^{-5}
N_2	1.408×10^{-6}	3.913×10^{-5}
SiO	8.698×10^{-6}	8.582×10^{-6}
SiH_4	2.478×10^{-6}	3.275×10^{-5}
H_2O	5.536×10^{-6}	3.049×10^{-5}
CH_4	2.283×10^{-6}	4.278×10^{-5}
NH_3	4.225×10^{-6}	3.707×10^{-5}

Figure 1. Change in Gibbs free energy for the reaction $SiC+2H_2 = Si+CH_4$ as a function of temperature and pressure. (a) Using ideal gas molar volume, (b) using van der Waals molar volume.
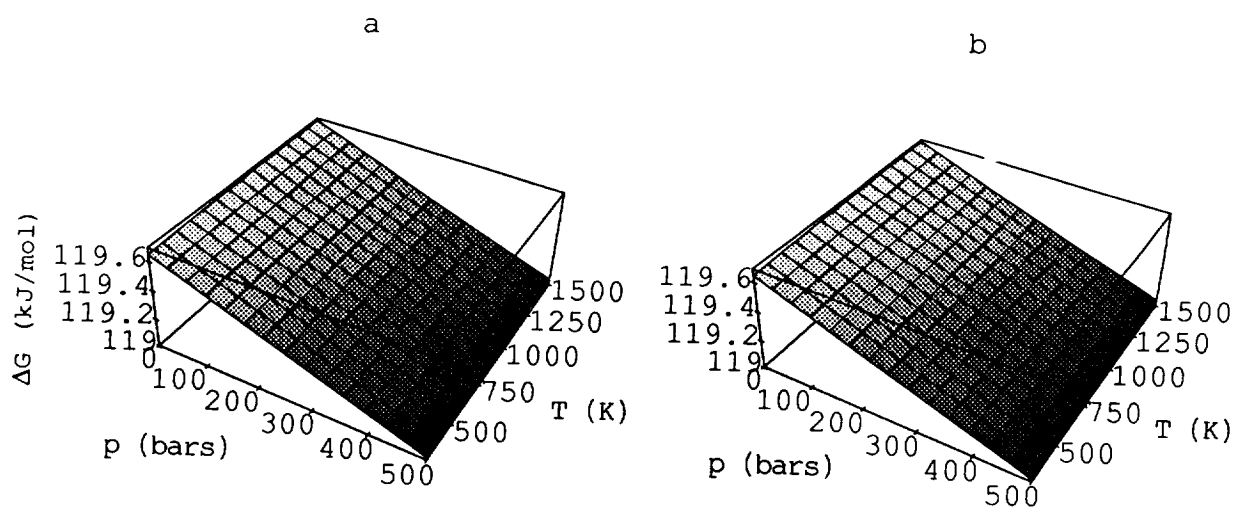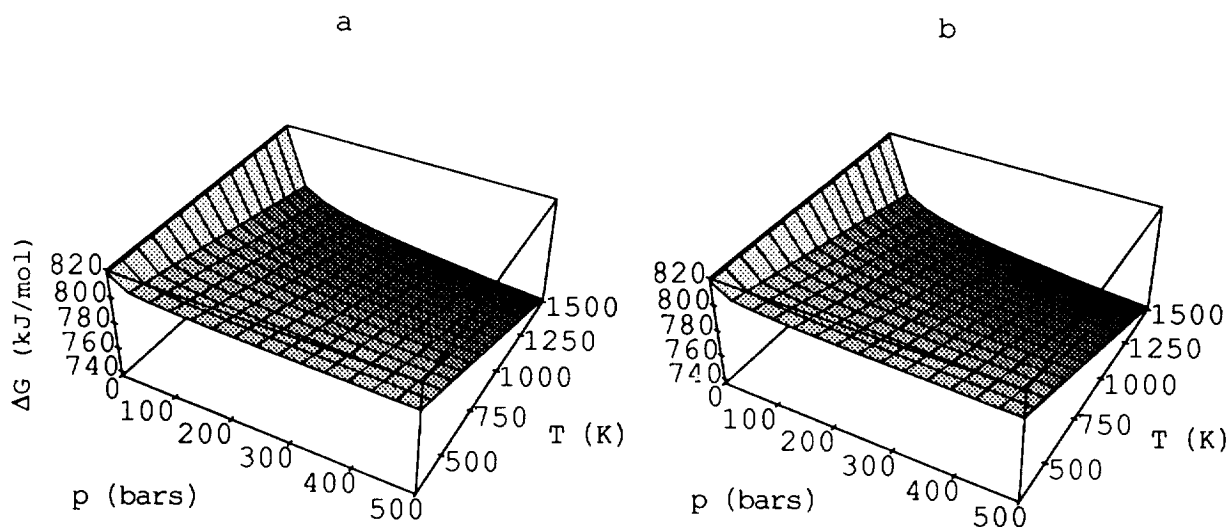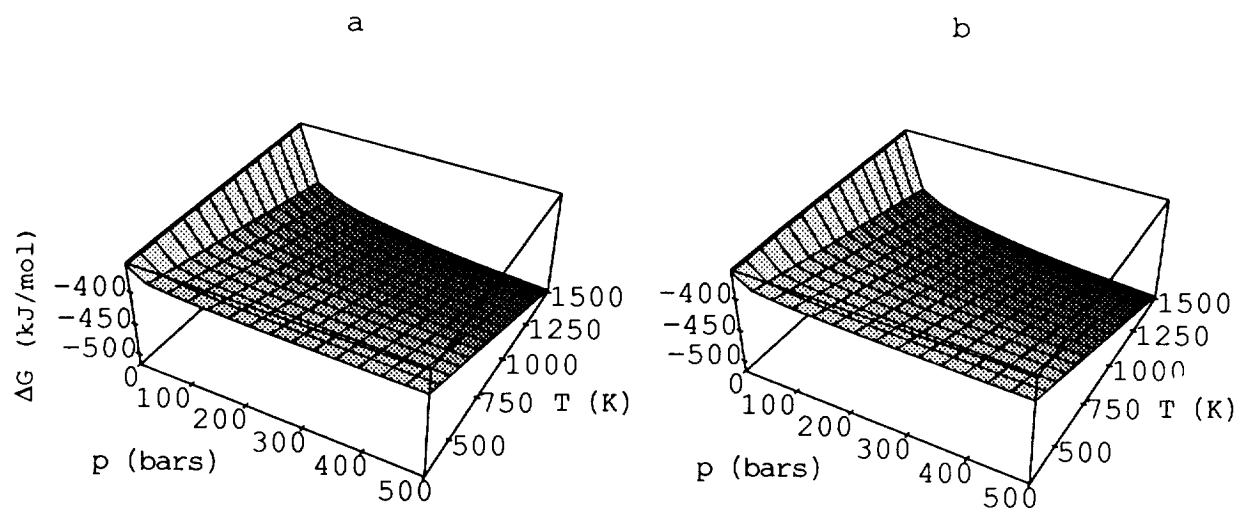

Figure 2. Change in Gibbs free energy for the reaction $SiC+H_2O+H_2 = SiO+CH_4$ as a function of temperature and pressure. (a) Using ideal gas molar volume, (b) using van der Waals molar volume.
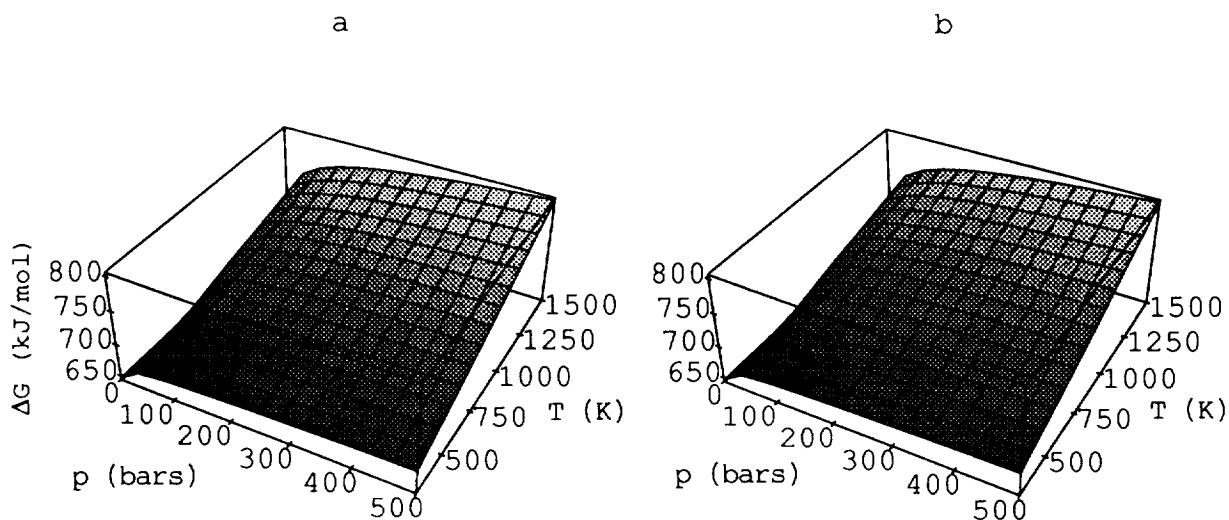
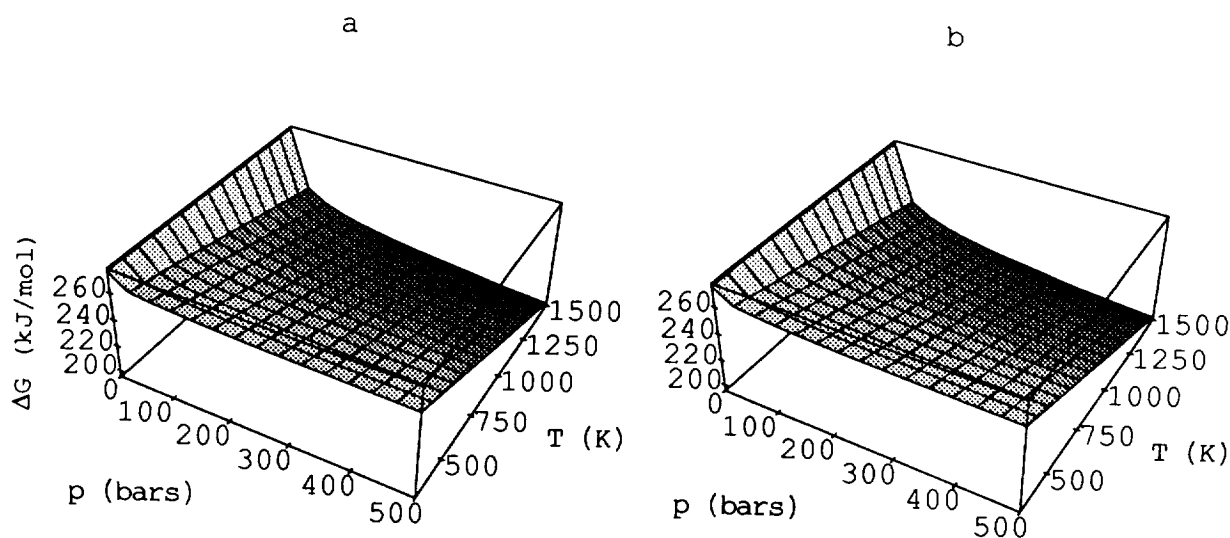Figure 3. Change in Gibbs free energy for the reaction $Si_3N_4 = 3Si+2N_2$ as a function of temperature and pressure. (a) Using ideal gas molar volume, (b) using van der Waals molar volume.

Figure 4. Change in Gibbs free energy for the reaction $Si_3N_4+6H_2 = 3SiH_4+2N_2$ as a function of temperature and pressure. (a) Using ideal gas molar volume, (b) using van der Waals molar volume.

Figure 5. Change in Gibbs free energy for the reaction 2SiC+2H$_2$O+2H$_2$ = Si+SiO$_2$+2CH$_4$ as a function of temperature and pressure. (a) Using ideal gas molar volume, (b) using van der Waals molar volume.

Figure 6. Change in Gibbs free energy for the reaction Si$_3$N$_4$+2H$_2$O+3H$_2$ = Si+SiO$_2$+SiH$_4$+ 2NH$_3$+N$_2$ as a function of temperature and pressure. (a) Using ideal gas molar volume, (b) using van der Waals molar volume.

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Silicon carbide (SiC) and silicon nitride (Si_3N_4) are considered for application as structural materials and coating in advanced propulsion systems including nuclear thermal. Three-dimensional Gibbs free energy surfaces were constructed for reactions involving these materials in H_2 and H_2/H_2O. Free energy plots are functions of temperature and pressure. Calculations used the definition of Gibbs free energy where the spontaneity of reactions is calculated as a function of temperature and pressure.

Silicon carbide decomposes to Si and CH_4 in pure H_2 and forms a SiO_2 scale in a wet atmosphere. Silicon nitride remains stable under all conditions. There was no apparent difference in reaction thermodynamics between ideal and Van der Waals treatment of gaseous species.

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