

# Thermodynamic Analysis of the Formation of Carbon Nitrides under Pressure

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A thermodynamic analysis of the formation of carbon nitrides under pressure is presented. Integration of the pressure–volume equations of state of carbon, nitrogen, and candidate carbon nitride structures show that under pressures achievable with current technology the free energies of reactions to form carbon nitrides can change more than 1000 kJ/mol of  $C_3N_4$ . These changes are greater than the positive free energies estimated for the formation reactions at ambient pressure, indicating that formation of carbon nitrides under pressure should be feasible. The large change in free energy of reaction under pressure is due to the large volume of molecular nitrogen. Because greater changes in free energy of reaction occur with increasing nitrogen content, pressure favors the formation of nitrogen-rich compounds. However, nitrogen-rich compounds tend to have more nitrogen lone-pair repulsions and contain weaker bonds, destabilizing them with respect to compounds that contain less nitrogen. The structure and composition favored under high pressure will be determined by the balance between these opposing factors.

## Introduction

The synthesis of new solids composed of carbon and nitrogen is of considerable current interest. Theoretical calculations on a carbon nitride with the structure of  $\beta$ - $Si_3N_4$  suggest that  $\beta$ - $C_3N_4$  could have sufficient cohesive energy to be metastable and a bulk modulus comparable to diamond.<sup>1,2</sup> Materials with very large bulk moduli typically exhibit extreme hardness. More recently, a transition under high pressure from the  $\beta$ - $C_3N_4$  structure to a new, potentially superhard, phase with a bulk modulus significantly larger than diamond or  $\beta$ - $C_3N_4$  has been found theoretically.<sup>3</sup> These predictions of potentially useful properties have stimulated a number of attempts to prepare carbon nitrides with the  $\beta$ - $C_3N_4$  structure,<sup>4–7</sup> which has carbon atoms in a tetrahedral,  $sp^3$ -bonded configuration. Amorphous  $sp^2$ -bonded carbon nitride with a composition of  $C_3N_4$  has been synthesized.<sup>8</sup> Crystalline carbon nitride phases in films prepared by deposition techniques have also been reported,<sup>4,5</sup> but thorough characterization of these nitrides has been difficult because the crystalline phases are embedded in an amorphous carbon–nitrogen matrix. Though the bulk composition of the films has been determined, the nitrogen content of the crystalline phases has not, leaving their composition uncertain. The bonding state ( $sp^2$  vs  $sp^3$ ) of the carbon in the crystalline phases, information that may be obtained from electron

energy loss spectroscopy (EELS),<sup>9</sup> is also uncertain. The primary evidence for the formation of  $C_3N_4$  solids has been electron diffraction data. Polycrystalline electron diffraction patterns consistent with the  $\beta$ - $C_3N_4$  structure, if significant preferred orientation is assumed, have been reported.<sup>4,5</sup> However, accurate identification of phases by powder electron diffraction is often difficult in the absence of other chemical or structural information.<sup>4,10</sup> Single-crystal X-ray or electron diffraction studies on the carbon nitrides could provide definitive structural information. Thus, to better characterize carbon nitride solids, it is desirable to have single-phase, single-crystal samples.

Static high-pressure synthesis has the potential to prepare single-phase, single-crystal carbon nitride solids, which have positive free energies of formation under ambient conditions. High-pressure synthesis allows phase diagrams to be examined under equilibrium conditions, in contrast to deposition techniques that prepare metastable phases by kinetic control of the reaction products.<sup>11</sup> Very large changes in free energies (>500 kJ/mol)<sup>12</sup> are possible at pressures achievable with current diamond anvil cell<sup>13</sup> (>200 GPa, 1 GPa  $\sim$  10 000 ATM) and large volume cubic or octahedral press ( $\sim$ 40 GPa) technology.<sup>14</sup> With laser heating, temperatures in excess of 3000 °C can be achieved in the diamond cell,<sup>15</sup> allowing kinetic barriers to reaction to

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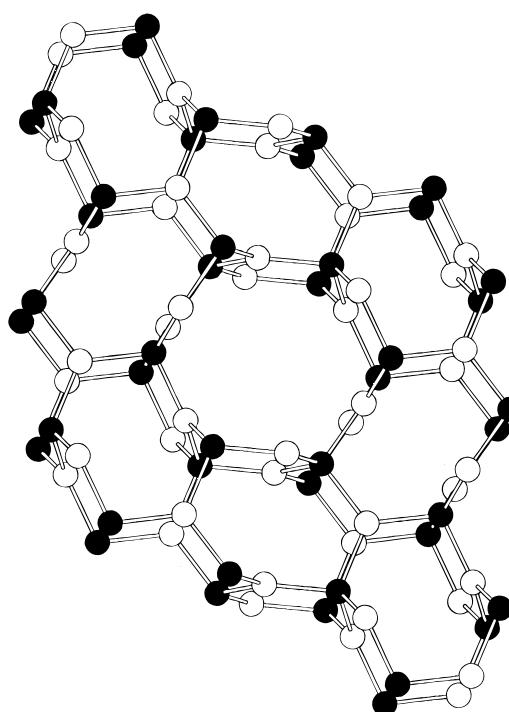
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be overcome. Synthesis of diamond that consists of single crystals of sufficient size to exhibit spot patterns in selected area transmission electron diffraction has been achieved. Since the bonds in carbon nitrides are quite strong, phases synthesized under high pressure may be quenchable to ambient pressure. Techniques are available to characterize samples both at high pressure and after quenching to ambient conditions.<sup>9,16</sup> Knowledge of which phases form in the C–N phase diagram should provide valuable “targets” for synthesis via deposition techniques.<sup>17</sup>

The driving force for the formation of carbon nitrides under pressure is the large volume of molecular nitrogen compared to covalently bonded solids. However, no quantitative information has been reported about the thermodynamics of the formation of carbon nitrides under pressure. To guide efforts at synthesis, we present here a thermodynamic analysis of the stability of carbon nitrides at high pressure. We use the cohesive energy of candidate carbon nitride structures to estimate the enthalpy of reaction at ambient pressure. The entropies of reaction are estimated using the method of Latimer.<sup>18</sup> The changes in the free energies in the products and reactants are determined by integration of the pressure–volume ( $PV$ ) equations of state ( $\Delta G = \int V dP$ ) of the products and reactants at 298 K. From the reaction stoichiometry, the changes in the free energies of reaction under pressure are then calculated. The pressure at which the Gibbs free energy of reaction curve crosses zero provides an estimate of the pressure required to induce reaction at 300 K. Finally, the effect of high temperatures, which will likely be necessary to increase reaction rates, is examined. The results obtained suggest that the shifts in reaction equilibria with pressure are large enough to allow the synthesis of  $C_3N_4$  with current pressure technology.

Since there are significant differences in the chemistry of carbon and nitrogen and the chemistry of silicon and nitrogen,<sup>19</sup> it is possible there will be differences in the structural chemistry of carbon nitrides and silicon nitrides. For comparison with  $C_3N_4$ , we also present an analysis of the thermodynamics of formation of a carbon nitride with stoichiometry  $C_4N_3$  that incorporates some of the structural features typically found in molecules containing carbon and nitrogen.<sup>20</sup>

To determine the heats of formation of carbon nitrides, it is necessary to have accurate values for the cohesive energies. The local density approximation (LDA) method used by Liu and Cohen<sup>1</sup> to investigate carbon nitrides and by Liu and Wentzcovitch<sup>21</sup> in subsequent structural optimization work has been successful in predicting properties and the relative energetics of solid-state structures with similar types of bonding. However, it has been less successful in predicting cohesive energies. This is primarily because of difficulties associated with determining the energy of the isolated atoms.<sup>22</sup> Accurate prediction of cohesive ener-



**Figure 1.** Structure of  $\beta$ - $C_3N_4$ , which is derived from  $\beta$ - $Si_3N_4$ . The hexagonal  $c$  axis is tilted slightly from vertical. Tetrahedral carbons (black) are bonded only to trigonal planar nitrogens (unshaded). Space group  $P6_3/m$ .

gies is in general a challenging problem. Well-converged LDA calculations typically overestimate the cohesive energy of solids composed of elements from the second period by 1 eV/atom (96 kJ/mol) or more.<sup>22,23</sup> Furthermore, there are significant differences ( $\sim$ 2760 kJ/mol of  $C_3N_4$ ) between the cohesive energies reported for  $C_3N_4$  in refs 1 and 21. Thus it is desirable to have another method for estimating cohesive energies for comparison with the results from LDA.

We estimate cohesive energies from bond enthalpies derived from organic molecules. This method is simple and often gives accurate estimates for the cohesive energy of covalently bonded solids such as diamond, boron oxide ( $B_2O_3$ ) and cubic boron nitride.<sup>18</sup> The cohesive energy estimated for diamond by this method (694 kJ/mol vs 717 kJ/mol experimental)<sup>18</sup> is more accurate than the value obtained from LDA (833 kJ/mol).<sup>24</sup> We assume bond additivity, which is examined for covalently bonded structures by Johnson.<sup>18</sup> In the structures considered, there are short nonbonded nitrogen–nitrogen contacts, resulting in significant lone pair repulsion. Ab initio calculations have been performed to estimate the destabilization due to the nonbonded repulsions as a function of the distance between nitrogens.<sup>20</sup> We use the results of these calculations to estimate the effect of nonbonded repulsions on the cohesive energies.

## Structures

The  $\beta$ - $C_3N_4$  structure is derived from  $\beta$ - $Si_3N_4$  (Figure 1).<sup>1</sup> It is a network of tetrahedrally-bonded ( $sp^3$ ) carbon

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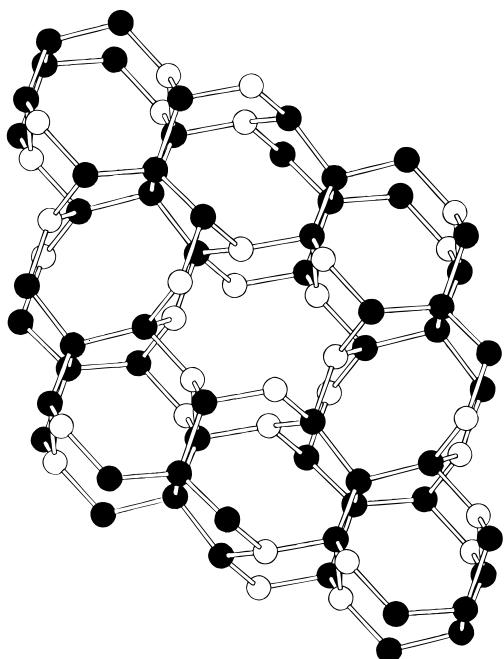
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**Figure 2.** Structure of  $\text{C}_4\text{N}_3$ . The hexagonal  $c$  axis is tilted slightly from vertical. Like all carbon nitrides with very large bulk moduli, it has tetrahedral,  $\text{sp}^3$  carbon (black). It is obtained by replacing pairs of nitrogens (unshaded) along the 3-fold axis of the  $\beta\text{-C}_3\text{N}_4$  structure with pairs of carbons. The nitrogens have undergone a small pyramidal distortion into the larger cavity in the center. This increases the nonbonded nitrogen–nitrogen distances and reduces the lone-pair repulsion. Space group  $P\bar{3}$ .

and 3-fold coordinated ( $\text{sp}^2$ ) nitrogen with only C–N bonds. One-quarter of the nitrogens (N1) have trigonal planar coordination and are stacked along a three-fold axis with a N1–N1 nonbonded distance of 2.46 Å. The other three-quarters (N2) are in a slightly distorted trigonal planar environment. N2–N2 nonbonded distances are 2.69 Å. In  $\text{C}_3\text{N}_4$ , the nitrogen–nitrogen lone-pair repulsions are larger than for  $\text{Si}_3\text{N}_4$  because the N–N nonbonded distances are smaller.<sup>20</sup> Furthermore, though trigonal-planar coordination for nitrogen is common when it is bonded to silicon, the trigonal-pyramidal configuration for nitrogen is typically found when it is bonded to carbon.<sup>19</sup> However, stable organic molecules containing nitrogen bonded to three carbons and constrained to be trigonal planar by steric effects are known.<sup>25</sup> Stable organic molecules containing tetrahedral carbon bonded to four nitrogens, as found in  $\beta\text{-C}_3\text{N}_4$ , are also known.<sup>26</sup>

A structure that incorporates less nitrogen lone-pair repulsion has been proposed.<sup>20</sup> The structure (Figure 2) can be derived from the  $\text{C}_3\text{N}_4$  structure by replacing pairs of N1 trigonal planar nitrogens with tetrahedrally bonded carbons and allowing the N2 nitrogens to distort slightly to a trigonal-pyramidal coordination, increasing the N2–N2 distance and reducing lone-pair repulsion. There are five-, six-, and eight-membered rings. Little strain appears to be introduced by replacing the pairs of nitrogen atoms with carbon atoms. However, structural optimization will be necessary to confirm this. The amount of pyramidal distortion will be determined by the balance between strain induced by the pyramidal

distortion and the reduction in lone pair repulsion. The structure incorporates both C–C and C–N bonds and less nitrogen than  $\text{C}_3\text{N}_4$ , with stoichiometry  $\text{C}_4\text{N}_3$ . Since  $\text{C}_4\text{N}_3$ , like  $\text{C}_3\text{N}_4$ , has short, strong bonds and a high number density of atoms, it should also have a very large bulk modulus. Structures with nitrogen stoichiometries intermediate between  $\text{C}_3\text{N}_4$  and  $\text{C}_4\text{N}_3$  have been proposed. These structures have only partial substitution of pairs of N1 atoms by carbon, perhaps allowing a balance between the strain energy associated with carbon pairing and the repulsive energy between N1 lone pairs.<sup>20</sup>

### Estimation of Cohesive Energy

First we consider the cohesive energy of  $\beta\text{-C}_3\text{N}_4$ . Removal of one nitrogen atom from  $\text{C}_3\text{N}_4$  requires three C–N bonds to be broken. Since three bonds to carbon are broken and each carbon atom has found bonds, three quarters of a carbon atom will be removed by breaking these three bonds. This results in removal of a fragment with stoichiometry  $\text{C}_{3/4}\text{N}$ . Tabulated estimates of the C–N bond enthalpy from organic compounds range from 286 to 305 kJ/mol.<sup>18,27</sup> The C–N bond enthalpy of molecules such as methyl amine ( $\text{CH}_3\text{-NH}_2$ ), which have a single nitrogen bonded to a carbon atom can be as high as 331 kJ/mol.<sup>28</sup> Adding a second nitrogen to the carbon atom reduces the C–N bond enthalpy slightly because the carbon radical formed upon breakage of the bond is stabilized by the presence of nitrogen. *N*-(aminomethyl)dimethylamine ( $\text{H}_2\text{NCH}_2\text{-N}(\text{CH}_3)_2$ ) with two nitrogens bonded to the first carbon has a C–N bond enthalpy of 321 kJ/mol, according to Benson group additivity calculations.<sup>29,30</sup> The C–N bonds in molecules containing four nitrogens bonded to carbon, the bonding situation in  $\beta\text{-C}_3\text{N}_4$ , are somewhat weaker. On the basis of semiempirical calculations on model compounds, we place a lower bound of 260 kJ/mol on the C–N bond enthalpy in this bonding environment.<sup>31</sup> Because of errors associated with the estimation of energy of the radical formed after bond dissociation, only a lower bound can be estimated; the true bond enthalpy is likely substantially higher. The tabulated range of bond enthalpies (286–305 kJ/mol)<sup>18,27</sup> appears suitable for the estimation of the cohesive energy of  $\beta\text{-C}_3\text{N}_4$ . With this range of bond enthalpies, the cohesive energy of  $\beta\text{-C}_3\text{N}_4$  ranges from 858 to 915 kJ/mol of  $\text{C}_{3/4}\text{N}$  ( $887 \pm 28$  kJ/mol). The destabilization due to nonbonded nitrogen lone-pair repulsions has been estimated to be 52 kJ/mol of  $\text{C}_{3/4}\text{N}$ ,<sup>20</sup> which decreases the cohesive energy to 806–863 kJ/mol. The C–N bond enthalpy is somewhat less than the C–C bond enthalpy (347 kJ/mol) and the Si–N bond enthalpy (333 kJ/mol),<sup>18</sup> a trend seen in bonds between second-row elements in which one or both atoms have lone pairs. The smaller bond enthalpy, together with the large cohesive energy of diamond (717 kJ/mol) and strong bond strength for diatomic nitrogen (945 kJ/mol), results in a positive  $\Delta H$  for the formation reaction of  $\text{C}_{3/4}\text{N}$ :

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**Table 1. Cohesive Energies from Bond Enthalpies, Estimated Lone-Pair Repulsions, Cohesive Energies after Subtraction of Lone-Pair Repulsions, Cohesive Energy from Theory, and  $\Delta H_f^\circ$** 

structural unit	$E_{coh}$ (kJ/mol)	lone-pair repulsion (kJ/mol)	$E_{coh}$ corrected (kJ/mol)	$E_{coh}$ theory (kJ/mol)	$\Delta H_f^\circ$ (kJ/mol)
$C_{3/4}N$	858–915	52	806–863	813	147–204
$CN_{3/4}$	947–990	16	931–974		97–140
$\frac{3}{4}C + \frac{1}{2}N_2 = C_{3/4}N$					(1)
$\Delta H_f^\circ = \frac{3}{4}(717) + \frac{1}{2}(945) - E_{coh,C_{3/4}N}$					

$\Delta H_f^\circ$  ranges from 147 to 204 kJ/mol, depending on the choice of C–N bond enthalpy (Table 1).

The cohesive energy predicted from bond enthalpies compares favorably with the value obtained from LDA by Liu and Cohen. A cohesive energy of 983 kJ/mol of  $C_{3/4}N$  (5.85 eV/atom) was obtained for  $C_3N_4$ .<sup>1</sup> To compensate for the tendency of LDA to overestimate the cohesive energy, approximately 1 eV/atom can be subtracted from this value.<sup>22</sup> This results in a corrected cohesive energy of 815 kJ/mol of  $C_{3/4}N$ , in agreement with the range of values estimated previously (806–863 kJ/mol). The LDA calculations of Liu and Wentzcovitch predict a higher cohesive energy of 982 kJ/mol of  $C_{3/4}N$  (after subtracting 1 eV/atom). A cohesive energy this large implies a bond enthalpy of 327 kJ/mol, considerably higher than expected for a C–N bond enthalpy for a carbon surrounded by four nitrogens.<sup>18</sup> Alternatively, the heat of formation can be calculated within the LDA approximation by using the LDA values for the cohesive energy of carbon and dissociation energy for nitrogen, which gives a  $\Delta H_f^\circ$  of 18 kJ/mol of  $C_{3/4}N$ .<sup>21</sup> This is substantially lower than the  $\Delta H_f^\circ$  estimated from bond enthalpies, again indicating that Liu and Wentzcovitch's LDA calculation predicts an enthalpy for the carbon–nitrogen bond substantially higher than experimentally observed in molecules.

The  $C_4N_3$  structure has both C–C and C–N bonds. Table 2 gives the simplest way to break bonds and remove atoms to estimate the cohesive energy. There are two different kinds of carbons, those bonded to nitrogen and those bonded to only carbon. All nitrogens are equivalent. Eighteen C–N bonds and seven C–C bonds can be broken to remove a  $C_8N_6$  unit. We assume a C–C bond enthalpy of 347 kJ/mol,<sup>18</sup> a little less than the bond enthalpy in diamond (356 kJ/mol), and the range of C–N bond energies used previously (286–305 kJ/mol). This gives a cohesive energy for a  $CN_{3/4}$  unit ranging from 947 to 990 kJ/mol. Because there are only three nitrogens surrounding the carbons that are bonded to nitrogen, the enthalpy of the C–N bonds in  $C_4N_3$  is likely slightly higher than enthalpy of the bonds in  $C_3N_4$ . In addition, the large repulsions present between N1 atoms in  $C_3N_4$  have been eliminated because the N1 atoms have been replaced by carbons. The repulsions between the remaining pairs of nitrogens can be decreased by a pyramidal distortion. If the nitrogens are kept at the same distance as in  $C_3N_4$  (2.69 Å), the repulsion amounts to 24 kJ/mol of  $C_{3/4}N$ . We assume a small distortion, such that the distance between nitrogens increases to about 2.9 Å and the repulsion between pairs of N2 atoms is reduced to 0.45 eV.<sup>20</sup> The repulsion amounts to 16 kJ/mol of  $C_{3/4}N$ . Including this repulsion, the cohesive energy ranges from 931 to 974 kJ/mol of

**Table 2. Simplest Means To Break Bonds To Remove a Stoichiometric Unit of the  $C_4N_3$  Structure**

atoms removed	no. of bonds broken	stoichiometry
3 C1	9 C–N, 3 C–C	$C_{3.75}N_3$
1 C2	4 C–C	$C_2$
3 N1	9 C–N	$C_{2.25}N_3$
total	18 C–N, 7 C–C	$C_8N_6$

**Table 3. Entropies and Free Energies of Formation**

structural unit	$S^\circ$ (J/K mol)	$\Delta S_f^\circ$ (J/K mol)	$\Delta H_f^\circ$ (kJ/mol)	$\Delta G_f^\circ$ (kJ/mol)
$C_{3/4}N$	19	−78	147–204	171–227
$CN_{3/4}$	19	−55	97–140	113–156

$C_{3/4}N$ , which is larger than for  $C_3N_4$  because of the presence of strong carbon–carbon bonds.  $\Delta H_f^\circ$  for the formation reaction:



$$\Delta H_f^\circ = 717 + \frac{3}{8}(945) - E_{coh,CN_{3/4}}$$

ranges from 97 to 140 kJ/mol (Table 2).

### Entropies of Reaction

To determine the free energies of reaction, the entropies of reaction under standard conditions are required. Entropies of solids can be estimated with the empirical rules of Latimer,<sup>18</sup> which assign constants to each element that can be summed to give the total entropy. The best accuracy is obtained when the entropy is calculated as a difference from an analogous reference structure. As a reference structure, we use  $Si_3N_4$ , which has an entropy of 113 J/K mol at 298 K.<sup>32</sup> Subtracting 102 ( $3 \times 34$ ) J/K mol for Si and adding 66 ( $3 \times 22$ ) for carbon<sup>18</sup> gives an entropy of 77 J/K mol for  $C_3N_4$ . Using the standard values for the entropy of diamond (2.4 J/K mol) and molecular nitrogen (192 J/K mol)<sup>18</sup> the entropy of reaction 1 is −78 J/K mol. At 298 K  $T\Delta S$  is −23 kJ/mol, giving a free energy of reaction ( $\Delta G_f^\circ$ ) ranging from 171 to 227 kJ/mol (Table 3).

There is no reference structure to estimate the entropy for  $C_4N_3$ . According to Latimer's rules, the entropy contributions for carbon and nitrogen in solid-state compounds tend to be similar.<sup>18</sup> We assume an entropy similar to that of  $C_3N_4$ , 77 J/K mol. With this entropy,  $\Delta S^\circ$  for reaction 2 becomes −55 J/K mol and  $\Delta G_f^\circ$  ranges from 113 to 156 kJ/mol (Table 3).

### Changes in Free Energy under Pressure

To determine the effect of pressure on the Gibbs free energy of reaction, the Gibbs–Duhem relation ( $dG = -S dT + V dP$ )<sup>33</sup> must be integrated at constant temperature. Except for nitrogen, we derive the pressure–volume ( $PV$ ) relation from the Birch–Murnaghan equation of state (EOS):<sup>34</sup>

$$P = \frac{3}{2}K_0(x^7 - x^5)[1 + \frac{3}{4}(K_0' - 4)(x^2 - 1)]$$

where

$$x = (V_0/V)^{1/3}$$

which is characterized by the ambient pressure (0.1

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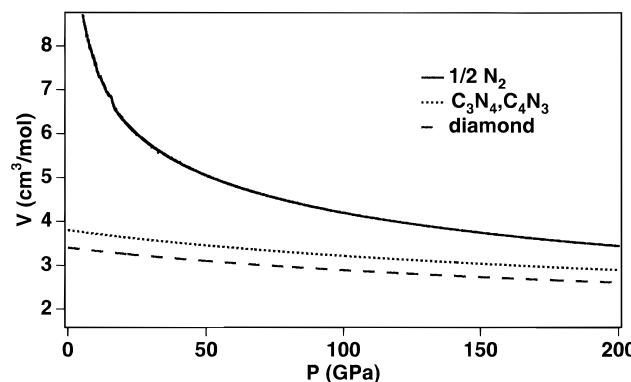
**Table 4. Ambient Pressure Volumes, Bulk Moduli, and Derivatives of Bulk Moduli for Structures Considered**

structure	$V_0$	$K_0$	$K_0'$
$\text{C}_3\text{N}_4$	3.8	427	4
$\text{C}_4\text{N}_3$	3.8	427	4
Diamond	3.4	443	4

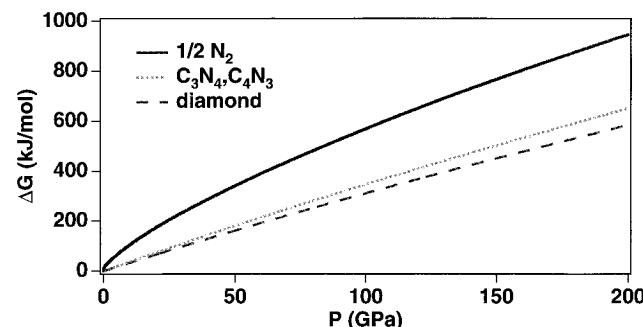
MPa) volume ( $V_0$ ), the ambient pressure bulk modulus ( $K_0$ ), and the derivative of the bulk modulus ( $K_0'$ , Table 4). An equation of state for diamond is available.<sup>35,36</sup> The EOS for  $\text{C}_3\text{N}_4$  has been calculated with LDA.<sup>1</sup> Since the composition of  $\text{C}_4\text{N}_3$  is only slightly different from  $\beta\text{-C}_3\text{N}_4$ , we assume it has a bulk modulus and volume similar to those of  $\beta\text{-C}_3\text{N}_4$ . Because the materials under consideration are very incompressible, small variations in the bulk modulus or volume at zero pressure have a small effect on the volume at high pressure.

For nitrogen, which undergoes several phase transitions under pressure, experimental PV data between atmospheric pressure and 43 GPa are used.<sup>37–42</sup> The equation of state of  $\epsilon$ -nitrogen, the phase of  $\text{N}_2$  above 16 GPa, is determined from a nonlinear least-squares fit of the Vinet equation of state<sup>43</sup> to the pressure–volume data of Olijnyk to 43 GPa.<sup>40</sup> The Vinet EOS has been shown to be superior for fitting compression data of condensed gases.<sup>44</sup> Like the Birch–Murnaghan EOS, it is characterized by  $V_0$ ,  $K_0$ , and  $K_0'$ . A plot of stress vs strain is linear for nitrogen, which indicates that the data fit the Vinet equation of state well. In our calculations, the equation of state is extrapolated from 43 to 200 GPa, a pressure range for which nitrogen is compressed by a factor of 2. Since this is a relatively small range of compression, extrapolation to 200 GPa is justified. Because  $\epsilon\text{-N}_2$  exists only above 16 GPa, and significant compression occurs between 0.1 MPa and 16 GPa, there is some uncertainty in the extrapolation of the volume to 0.1 MPa. However, since  $V_0$  is highly correlated with  $K_0$  and  $K_0'$ , the effect on the extrapolated volume to 200 GPa is small. Fits for which  $V_0$  is constrained to be  $\pm 10\%$  less than the best fit value result in less than 3% variation in the volume at 200 GPa. Phase transitions in nitrogen may occur at pressures higher than 43 GPa, but as long as a molecular structure is retained, the effect on the volume is likely to be small. Up to 200 GPa, the volume of molecular nitrogen is considerably larger than that of the carbon nitrides and diamond (Figure 3). As a result, its free energy increases much more rapidly, providing the driving force for reaction with carbon. Figure 4 shows the changes in free energy determined by integrating the equations of state.

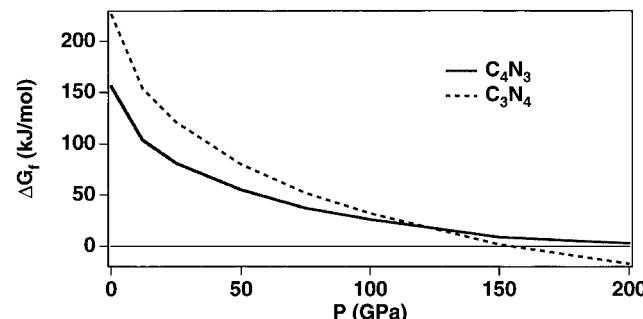
The changes in the free energies of reaction under pressure ( $\Delta G_f^P$ ) determined from the changes in the free



**Figure 3.** Volume of 1 mol of atoms as a function of pressure for molecular nitrogen and carbon nitrides. These volumes are from direct experimental measurements or from equations of state, which were theoretically predicted or experimentally measured.



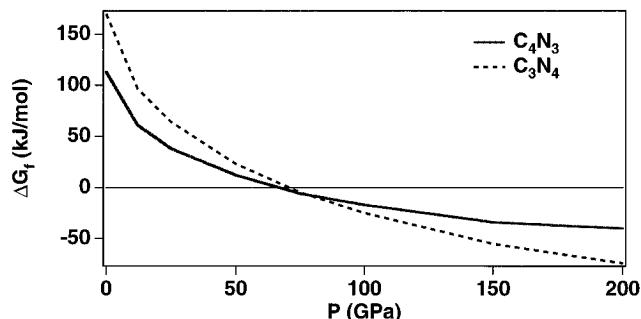
**Figure 4.** Free energy shifts per mole of atoms as a function of pressure of individual products and reactants obtained from integration of Gibbs–Duhem relation at constant temperature.  $\Delta G_f^P = \int_0^P V \, dP$ , where  $P$  is the pressure. Volumes are from Figure 3. 1 kJ = 1  $\text{cm}^3$  GPa.



**Figure 5.** Less optimistic free energy of reaction curves as a function of pressure for carbon nitrides based on stoichiometries  $\text{C}_{3/4}\text{N}$  and  $\text{CN}_{3/4}$ . These curves were obtained from:  $\Delta G_f^P = \Delta G_f^\circ + \sum v_i \Delta G_P$ , where  $\Delta G_f^\circ$  is the free energy of formation at STP (positive),  $v_i$  are the stoichiometric coefficients of the formation reactions (negative for reactants, positive for products),  $\Delta G_P$  are the changes in free energy for reactants and products from Figure 4 (always positive). The least favorable estimated free energies of formation have been used.

energies of the products and reactants and the stoichiometries of the formation reactions are shown in Figure 5 and are tabulated at 50, 100, and 150 GPa in Table 5. In Figure 5, each curve has been offset by the most positive free energies of formation estimated previously (Table 3). The free energy curve for  $\text{C}_3\text{N}_4$  becomes negative at 150 GPa. The free energy curve for  $\text{C}_4\text{N}_3$  becomes negative at slightly more than 200 GPa. If the more optimistic values for the free energies of formation obtained using larger bond energies for the carbon nitrides (Table 3), the formation pressures shift into the

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**Figure 6.** Optimistic free energy of reaction curves for carbon nitrides. The most optimistic estimated free energies of formation have been used. Formation of carbon nitrides becomes favorable in the 50–100 GPa range.

**Table 5. Changes in Free Energy of Formation Reactions,  $\Delta G_f^P$ , as a Function of Pressure at 298 K**

structural unit	$\Delta G_f^P$ (kJ/mol)		
	$P = 50$ GPa	$P = 100$ GPa	$P = 150$ GPa
$\text{C}_{3/4}\text{N}$	-147	-195	-225
$\text{CN}_{3/4}$	-101	-130	-153

50–75 GPa range (Figure 6).

The calculations suggest that  $\text{C}_3\text{N}_4$  and  $\text{C}_4\text{N}_3$  form in a similar pressure range. The change in the free energy of reaction under pressure for  $\text{C}_3\text{N}_4$  is larger than for  $\text{C}_4\text{N}_3$  because of the larger nitrogen content. However, its free energy of formation at ambient pressure is also more positive. In carbon nitrides, the free energy of formation becomes more positive with increasing nitrogen content because there is increased nitrogen lone-pair repulsion, and less bonds between carbon, which are stronger than C–N bonds and N–N bonds. If another nitrogen rich structure exists that has a geometry suitable for tetrahedral carbon and trigonal nitrogen and does not have as much lone pair repulsion as  $\beta\text{-C}_3\text{N}_4$ , its formation should be favored under pressure and also in synthesis by deposition techniques.

### Effect of Temperature

To overcome kinetic barriers to reaction, it will likely be necessary to heat the reactants in a synthesis of carbon nitrides under pressure. Graphitic carbon nitrides may transform to  $\text{sp}^3$ -bonded phases at extreme pressures at room temperature. However, like the  $\text{sp}^3$ -bonded phase formed from graphite under room-temperature compression,<sup>45</sup> nitrides formed this way are not likely to be quenchable to ambient conditions. Since

both the entropies and volumes of reaction are negative, according to the Clapeyron equation:

$$\text{d}P/\text{d}T = \Delta S/\Delta V$$

the pressure required for synthesis must increase with temperature. To estimate the Clayperon slope, the entropies and volumes of reaction are required. The entropy of reaction under pressure will become less negative because nitrogen is solid above 3 GPa at room temperature. By subtracting the entropies of vaporization (72 J/K mol) and melting (11 J/K mol) from the entropy of gaseous nitrogen (191 J/K mol) an upper bound on the entropy of solid nitrogen at 300 K can be determined (108 J/K mol). The entropies of diamond and carbon nitride should change slowly under pressure because they are incompressible. Assuming an entropy of 108 J/K mol for  $\text{N}_2$  and no change in the entropies of diamond or carbon nitride, the entropy of reaction for the formation of  $\text{C}_{3/4}\text{N}$  becomes  $-37$  J/K mol. At 50 GPa, the volume of reaction is  $-1.3 \text{ cm}^3/\text{mol}$  from Figure 3. The Clayperon slope is  $(-37 \times 10^{-3} \text{ kJ/K mol})/(-1.3 \text{ cm}^3) = -0.03 \text{ GPa/K}$ .

Temperatures of at least 1300 K are required to synthesize diamond at high pressure. We assume similar temperatures are required for the synthesis of carbon nitrides from appropriate precursors. After heating at 50 GPa to 1300 K, the phase boundary between reactants and products for  $\text{C}_3\text{N}_4$  shifts by about 30 GPa. Since we have likely overestimated the entropy of reaction at 50 GPa, the shift in the phase boundary could be smaller. At still higher pressures both the entropy and volume of reaction will become smaller, tending to keep the slope of the phase boundary roughly the same. Since pressures well in excess of 200 GPa are now achievable with diamond anvil cells,<sup>13</sup> synthesis of carbon nitride phases should be possible even if our least optimistic estimates of the pressures required are correct.

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