

1. (5%) What is the coordination number of each sphere in (a) a simple cubic cell, (b) a body-centered cubic cell, and (c) a face-centered cubic cell? Assume the spheres are all the same.

Sol.

(a) In a simple cubic structure each sphere touches **six** others on the $\pm x$, $\pm y$ and $\pm z$ axes.

(b) In a body-centered cubic lattice each sphere touches **eight** others. Visualize the body-center sphere touching the eight corner spheres.

(c) In a face-centered cubic lattice each sphere touches **twelve** others.

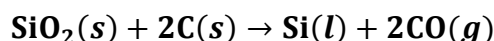
2. (6%) Explain why diamond is harder than graphite. Why graphite is an electrical conductor but diamond is not?

Sol.

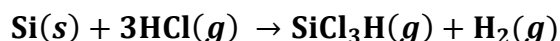
In diamond, each carbon atom is covalently bonded to four other carbon atoms. Because these bonds are strong and uniform, diamond is a very hard substance. In graphite, the carbon atoms in each layer are linked by strong bonds, but the layers are bound by weak dispersion forces. As a result, graphite may be cleaved easily between layers and is not hard.

In graphite, all atoms are sp^2 hybridized; each atom is covalently bonded to three other atoms. The remaining unhybridized $2p$ orbital is used in pi bonding forming a delocalized molecular orbital. The electrons are free to move around in this extensively delocalized molecular orbital making graphite a good conductor of electricity in directions along the planes of carbon atoms.

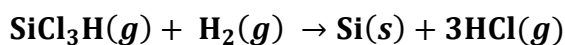
3. (15%) Silicon used in computer chips must have an impurity level below 10^{-9} (that is fewer than one impurity atom for every 10^9 Si atoms). Silicon is prepared by the reduction of quartz (SiO_2) with coke (a form of carbon made by the destructive distillation of coal) at about 2000°C :



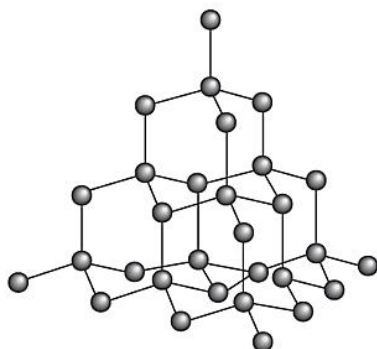
Next, solid silicon is separated from other solid impurities by treatment with hydrogen chloride at 350°C to form gaseous trichlorosilane (SiCl_3H):



Finally, ultrapure Si can be obtained by reversing the above reaction at 1000°C:



- (a) What types of crystals do Si and SiO₂ form?
- (b) Silicon has a diamond crystal structure as following figure. Each cubic unit cell (edge length $a = 543 \text{ pm}$) contains eight Si atoms. If there are 1.0×10^{13} boron atoms per cubic centimeter in a sample of pure silicon, how many Si atoms are there for every B atoms in the sample? Does this sample satisfy the 10^{-9} purity requirement for the electronic grade silicon?



Sol.

- (a) From Section 6.3 of the text, we see that SiO₂ forms a covalent crystal. Silicon, like carbon in Group 4A, also forms a covalent crystal. The strong covalent bonds between Si atoms (in silicon) and between Si and O atoms (in quartz) account for their high melting points and boiling points.
- (b) To test the 10^{-9} purity requirement, we need to calculate the number of Si atoms in 1 cm^3 . We can arrive at the answer by carrying out the following three steps:
- (1) Determine the volume of an Si unit cell in cubic centimeters, (2) determine the number of Si unit cells in 1 cm^3 , and (3) multiply the number of unit cells in 1 cm^3 by 8, the number of Si atoms in a unit cell.

Step 1: The volume of the unit cell, V , is

$$V = a^3$$

$$V = (543 \text{ pm})^3 \times \left(\frac{1 \times 10^{-12} \text{ m}}{1 \text{ pm}} \times \frac{1 \text{ cm}}{1 \times 10^{-2} \text{ m}} \right)^3 = 1.60 \times 10^{-22} \text{ cm}^3$$

Step 2: The number of cells per cubic centimeter is given by:

$$\text{number of unit cells} = 1 \text{ cm}^3 \times \frac{1 \text{ unit cell}}{1.60 \times 10^{-22} \text{ cm}^3} = 6.25 \times 10^{21} \text{ unit cells}$$

Step 3: Since there are 8 Si atoms per unit cell, the total number of Si atoms is:

$$\text{number of Si atoms} = \frac{8 \text{ Si atoms}}{1 \text{ unit cell}} \times (6.25 \times 10^{21} \text{ unit cells}) = 5.00 \times 10^{22} \text{ Si atoms}$$

Finally, to calculate the purity of the Si crystal, we write:

$$\frac{\text{B atoms}}{\text{Si atoms}} = \frac{1.0 \times 10^{13} \text{ B atoms}}{5.00 \times 10^{22} \text{ Si atoms}} = \mathbf{2.0 \times 10^{-10}}$$

Since this number is smaller than 10^{-9} , the purity requirement is **satisfied**.

4. (4%) When X-rays of wavelength 0.85 \AA are diffracted by a metallic crystal, the angle of first-order diffraction ($n = 1$) is measured to be 14.8° . What is the distance (in pm) between the layers of atoms responsible for the diffraction?

Sol.

$$d = \frac{n\lambda}{2 \sin \theta} = \frac{\lambda}{2 \sin \theta} = \frac{0.085 \text{ nm} \times \frac{1000 \text{ pm}}{1 \text{ nm}}}{2 \sin 14.8} = \mathbf{166.38 \text{ pm}}$$

5. (10%) Given that the density of solid CsCl is 3.97 g cm^{-3} , calculate the density between adjacent Cs^+ and Cl^- ions. ($\text{Cs} = 132.9 \text{ g mol}^{-1}$, $\text{Cl} = 35.45 \text{ g mol}^{-1}$)

Sol.

The crystal structure of CsCl is shown in Figure 6.25. There is one CsCl unit in each cubic unit cell. Thus, the density can be determined from the mass of one CsCl unit ($132.9 \text{ u} + 35.45 \text{ u} = 168.4 \text{ u}$) divided by the volume of a unit cell, which, in terms of the unit cell edge length a , is equal to a^3 . Equating this to the density given in the problem gives

$$\frac{(168.4 \text{ u})(1.66054 \times 10^{-24} \text{ g u}^{-1})}{a^3} = 3.97 \text{ g cm}^{-3}$$

$$a^3 = 7.04 \times 10^{-23} \text{ cm}^3$$

$$a = 4.13 \times 10^{-8} \text{ cm} = 413 \text{ pm}$$

From Figure 6.25(a) we see that the distance between a Cl^- ion and a Cs^+ ion in CsCl is equal to one half of the body diagonal length of the unit cell. The body diagonal of a cube of side length a is equal to $\sqrt{3} a$, so

$$\text{Cl}^-/\text{Cs}^+ \text{ distance} = \left(\sqrt{3} / 2\right) a = 0.866 (413 \text{ pm}) = \mathbf{358 \text{ pm}}$$

6. (6%) without referring to a chemistry handbook, decide which of the following is denser: diamond or graphite.

Sol.

The carbon atoms in diamond are arranged in a three-dimensional network. Each carbon atom in this network is tetrahedrally bonded to four other carbon atoms [See Figure 6.27(a)]. The carbon atoms in graphite are arranged into two-dimensional hexagonal sheets in which each carbon atom is bonded to three others. These sheets are separated from one another by a distance of 3.35 Å [see Figure 6.27(b)]. This separation is more than twice as long as a typical C–C bond ($\sim 1.5 \text{ Å}$), such as that present in diamond. Thus, the carbon atoms in graphite are less densely packed than those in diamond and we expect diamond to be denser than graphite.

7. (5%) State whether silicon would form *n*-type or *p*-type semiconductors with the following elements: Ga, Sb, Al, or As.

Sol.

Doping silicon with Ga and Al would form *p*-type semiconductors because Ga and Al are both from Group 3A (three valence electrons). Such atoms form an electron deficient site (*p*-type) in the normally four-coordinated Si lattice. Similarly, doping with Sb and As would form *n*-type semiconductors because both Sb and As are from group 5A (five valence electrons).

8. (12%) Construct a table with the headings q , w , ΔU , and ΔH . For each of the following processes, deduce whether each of the quantities listed is positive (+), negative (-), or zero.

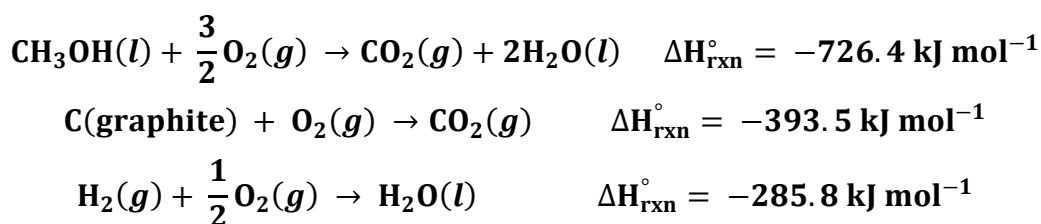
- (a) Freezing of benzene.
- (b) Compression of an ideal gas at constant temperature.
- (c) Reaction of sodium with water.
- (d) Boiling liquid ammonia.
- (e) Heating a gas at constant volume.
- (f) Melting of ice.

Sol.

q	w	ΔU	ΔH	
(a)	—	+	—	—
(b)	—	+	0	0
(c)	—	—	—	—
(d)	+	—	+	+
(e)	+	0	+	+
(f)	+	+	+	+

In (b), the internal energy of an ideal gas depends only on temperature. Since temperature is held constant, $\Delta U = 0$. Also, $\Delta H = 0$ because $\Delta H = \Delta U + \Delta(PV) = \Delta U + \Delta(nRT) = 0$.

9. (5%) From the following heats of combustion,



Calculate the standard enthalpy (in kJ mol^{-1}) of formation of methanol (CH_3OH) from its elements.

Sol.

<u>Reaction</u>	<u>ΔH° (kJ mol⁻¹)</u>
$\text{CO}_2(g) + 2\text{H}_2\text{O}(l) \rightarrow \text{CH}_3\text{OH}(l) + \frac{3}{2}\text{O}_2(g)$	726.4
$\text{C}(\text{graphite}) + \text{O}_2(g) \rightarrow \text{CO}_2(g)$	-393.5
$2\text{H}_2(g) + \text{O}_2(g) \rightarrow 2\text{H}_2\text{O}(l)$	2(-285.8)
<hr/>	
$\text{C}(\text{graphite}) + 2\text{H}_2(g) + \frac{1}{2}\text{O}_2(g) \rightarrow \text{CH}_3\text{OH}(l)$	$\Delta H_{\text{rxn}}^\circ = -238.7 \text{ kJ mol}^{-1}$

We have just calculated an enthalpy at standard conditions, which we abbreviate $\Delta H_{\text{rxn}}^\circ$. In this case, the reaction in question was for the formation of *one* mole of CH_3OH *from its elements* in their standard state.

Therefore, the $\Delta H_{\text{rxn}}^\circ$ that we calculated is also, by definition, the standard heat of formation $\Delta H_{\text{f}}^\circ$ of CH_3OH (-238.7 kJ mol⁻¹).

10. (5%) Consider the reaction



If 2.0 moles of $\text{H}_2\text{O}(g)$ are converted to $\text{H}_2(g)$ and $\text{O}_2(g)$ against a pressure of 1.0 bar at 125°C, what is ΔU (in kJ) for this reaction?

Sol.

We can calculate ΔU using Equation (7.16) of the text.

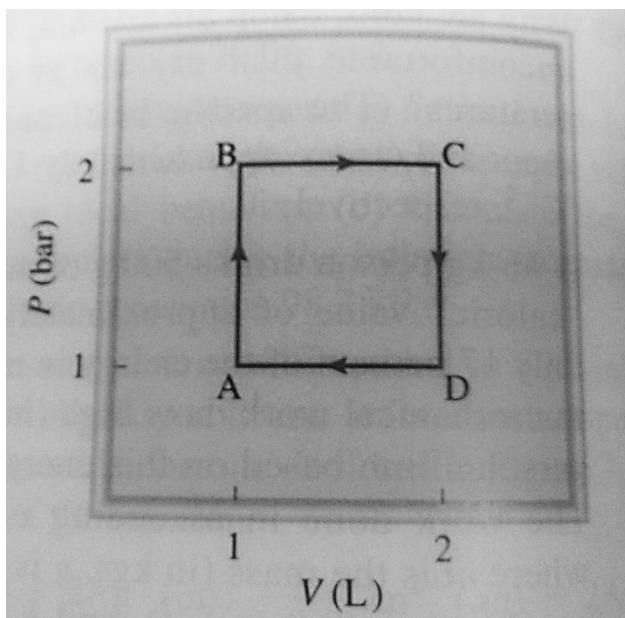
$$\Delta U = \Delta H - RT\Delta n$$

We initially have 2.0 moles of gas. Since our products are 2.0 moles of H_2 and 1.0 mole of O_2 , there is a net gain of 1 mole of gas (2 reactant \rightarrow 3 product). Thus, $\Delta n = +1$. Looking at the equation given in the problem, it requires 483.6 kJ to decompose 2.0 moles of water ($\Delta H = 483.6 \text{ kJ}$).

Substituting into the above equation:

$$\begin{aligned} \Delta U &= 483.6 \times 10^3 \text{ J} - (8.314 \text{ J mol}^{-1} \text{ K}^{-1})(398 \text{ K})(+1 \text{ mol}) \\ \Delta U &= 4.80 \times 10^5 \text{ J} = 4.80 \times 10^2 \text{ kJ} \end{aligned}$$

11. (10%) Starting at A, an ideal gas undergoes a cyclic process involving expansion and compression at constant temperature as shown. Calculate the total work done. Does your result support the notion that work is not a state function?



Sol.

A \rightarrow B $w=0$, because $\Delta V=0$

B \rightarrow C $w=-P\Delta V=-(2 \text{ bar})(2-1)\text{L}=-2 \text{ L bar}$

C \rightarrow D $w=0$, because $\Delta V=0$

D \rightarrow A $w=-P\Delta V=-(1 \text{ bar})(1-2)\text{L}=+1 \text{ L bar}$

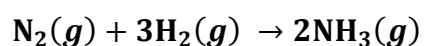
The total work done = $(-2 \text{ L bar}) + (1 \text{ L bar}) = -1 \text{ L bar}$

Converting to units of joules,

$$-1 \text{ L bar} \times \frac{100 \text{ J}}{1 \text{ L bar}} = -100 \text{ J}$$

In a cyclic process, the change in a state function must be zero. We therefore conclude that work is not a state function. Note that the total work done equals the area of the enclosure.

12. (8%) Consider the equation



$$\Delta H_{\text{rxn}}^{\circ} = -91.8 \text{ kJ mol}^{-1}$$

If 2.0 moles of N₂ react with 6.0 moles of H₂ to form NH₃, calculate the work done (in joules) against a pressure of 1.0 bar at 25°C. What is ΔU° for this reaction? Assume the reaction goes to completion.

Sol.

We initially have 8 moles of gas (2 of nitrogen and 6 of hydrogen). Since our product is 4 moles of ammonia, there is a net loss of 4 moles of gas (8 reactant → 4 product). The corresponding volume loss is

$$V = \frac{nRT}{P} = \frac{(4.0 \text{ mol})(0.08314 \text{ L bar mol}^{-1} \text{ K}^{-1})(298 \text{ K})}{1 \text{ bar}} = 99 \text{ L}$$

$$w = -P\Delta V = -(1 \text{ bar})(-99 \text{ L}) = 99 \text{ L bar} \cdot \frac{100 \text{ J}}{1 \text{ L bar}} = 9.9 \times 10^3 \text{ J} = 9.9 \text{ kJ}$$

$$\Delta H = \Delta U + P\Delta V \text{ or } \Delta U = \Delta H - P\Delta V$$

Using ΔH as −185.2 kJ = (2 × −92.6 kJ), (because the question involves the formation of 4 moles of ammonia, not 2 moles of ammonia for which the standard enthalpy is given in the question), and −PΔV as 9.9 kJ (for which we just solved):

$$\Delta U = -185.2 \text{ kJ} + 9.9 \text{ kJ} = \mathbf{-175.3 \text{ kJ}}$$

13. (5%) Calculate the work done (in joules) when 1.0 mole of water vaporizes at 1.0 atm and 100°C. Assume ideal gas behavior and that the volume of liquid water is negligible compared with that of steam at 100°C.

Sol.

Strategy: The work done in gas expansion is equal to the product of the external, opposing pressure and the change in volume.

$$w = -P\Delta V$$

We assume that the volume of liquid water is zero compared to that of steam. How do we calculate the volume of the steam? What is the conversion factor between L bar and J?

Solution: First, we need to calculate the volume that the water vapor will occupy (V_f).

Using the ideal gas equation:

$$V_{\text{H}_2\text{O}} = \frac{n_{\text{H}_2\text{O}}RT}{P} = \frac{(1 \text{ mol})(0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1})(373 \text{ K})}{(1.0 \text{ atm})} = 31 \text{ L}$$

It is assumed that the volume occupied by liquid water is negligible. Therefore,

$$\Delta V = V_f - V_i = 31 \text{ L} - 0 \text{ L} = 31 \text{ L}$$

Now, we substitute P and ΔV into Equation (7.1) of the text.

$$w = -P\Delta V = -(1.0 \text{ atm})(31 \text{ L}) = -31 \text{ Latm}$$

The problem asks for the work done in units of joules:

$$w = -31 \text{ L atm} = \frac{101.325 \text{ J}}{1 \text{ L atm}} = -3.1 \times 10^3 \text{ J}$$

Check: Because this is gas expansion (work is done by the system on the surroundings), the work done has a negative sign.

14. (10%) Determine the equipartition predictions for the heat capacities of CO, N₂O, O₃, and H₂CO both including and excluding the vibrational contribution. Compare these to the experimental values at 25°C. How important are the vibrational contributions in each case?

Sol.

Use the expressions in Table 7.3 in the text and the expression $\bar{C}_p = \bar{C}_v + R$ to compute \bar{C}_p for each substance. The actual values are found in Appendix 2. Use

$$R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}. \text{ Use } \bar{C}_p(\text{H}_2\text{CO}(g), 298 \text{ K}) = 35.39 \text{ J mol}^{-1} \text{ K}^{-1}$$

(webbook.nist.gov).

CO (linear):

$$\text{No vibrations: } \bar{C}_p = \frac{3}{2}R + R + R = \frac{7}{2}R = 29.10 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$\text{With vibrations: } \bar{C}_p = \frac{3}{2}R + R + R + R = \frac{9}{2}R = 37.41 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$\text{Actual: } \bar{C}_p = 29.1 \text{ J mol}^{-1} \text{ K}^{-1}$$

The vibrations make an insignificant contribution at 298 K.

N₂O (linear):

$$\text{No vibrations: } \bar{C}_p = \frac{3}{2}R + R + R = \frac{7}{2}R = 29.10 \text{ J mol}^{-1} \text{ K}^{-1}$$

With vibrations: $\overline{C_p} = \frac{3}{2}R + R + 4R + R = \frac{15}{2}R = 62.36 \text{ J mol}^{-1} \text{ K}^{-1}$

Actual: $\overline{C_p} = 38.6 \text{ J mol}^{-1} \text{ K}^{-1}$

The vibrations make a significant contribution at 298 K, but the contribution is less than that predicted by the equipartition theorem.

O₃ (nonlinear):

No vibrations: $\overline{C_p} = \frac{3}{2}R + \frac{3}{2}R + R = 4R = 33.27 \text{ J mol}^{-1} \text{ K}^{-1}$

With vibrations: $\overline{C_p} = \frac{3}{2}R + \frac{3}{2}R + 3R + R = 7R = 58.20 \text{ J mol}^{-1} \text{ K}^{-1}$

Actual: $\overline{C_p} = 39.2 \text{ J mol}^{-1} \text{ K}^{-1}$

The vibrations make a significant contribution at 298 K, but the contribution is less than that predicted by the equipartition theorem.

H₂CO (nonlinear):

No vibrations: $\overline{C_p} = \frac{3}{2}R + \frac{3}{2}R + R = 4R = 33.27 \text{ J mol}^{-1} \text{ K}^{-1}$

With vibrations: $\overline{C_p} = \frac{3}{2}R + \frac{3}{2}R + 6R + R = 10R = 83.14 \text{ J mol}^{-1} \text{ K}^{-1}$

Actual: $\overline{C_p} = 35.39 \text{ J mol}^{-1} \text{ K}^{-1}$

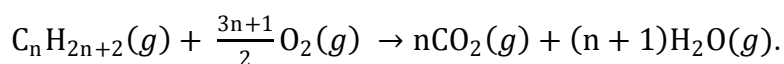
The vibrations make a small contribution at 298 K.

15. (10%) Alkanes are hydrocarbons with the general formula C_nH_{2n+2} , where n is a positive integer. Using the following table, derive general formulas for the enthalpies of combustion (in kJ g^{-1}) for gas-phase alkanes as functions of n .

Bond	Bond Enthalpy (kJ mol^{-1})	Bond	Bond Enthalpy (kJ mol^{-1})
H—H	436.4	N—N	193
H—N	393	N=N	418
H—O	460	N≡N	941.4
H—S	368	N—O	176
H—P	326	N—P	209
H—F	568.2	O—O	142
H—Cl	431.9	O=O	498.7
H—Br	366.1	O—P	502
H—I	298.3	O=S	469
C—H	414	P—P	197
C—C	347	P=P	489
C=C	620	S—S	268
C≡C	812	S=S	352
C—N	276	F—F	156.9
C=N	615	Cl—Cl	242.7
C≡N	891	Br—Br	192.5
C—O	351	I—I	151.0
C=O [†]	745	C—F	484
C—P	263	C—Cl	338
C—S	255	C—Br	276
C=S	477	C—I	238

Sol.

Write a balanced equation for the combustion reaction.



$$\begin{aligned}
 \Delta H_{rxn} &= (2n+2)\Delta H_B(C-H) + (n-1)\Delta H_B(C-C) + \left(\frac{3n+1}{2}\right)\Delta H_B(O=O) \\
 &\quad - (2n)\Delta H_B(C=O) - 2(n+1)\Delta H_B(H-O) \\
 &= (2n+2) \times 414 + (n-1) \times 347 + \left(\frac{3n+1}{2}\right) \times 498.7 - (2n) \times 745 - 2(n+1) \times 460 \\
 &= -486.95n - 1679.65 \text{ (kJ mol}^{-1}\text{)}
 \end{aligned}$$

The molar mass of the hydrocarbon is

$$12 \times n + 2n + 2 = 14n + 2$$

$$\text{So, } \Delta H_{rxn} = \frac{-486.95n - 1679.65}{14n + 2} (kJ\ g^{-1})$$

16. (5%) Show that the work required for the reversible and isothermal

expansion of n moles of a van der Waals gas ($P = \frac{nRT}{V-nb} - a\left(\frac{n}{V}\right)^2$) from an initial volume V_1 to a final volume V_2 is given by

$$w = nRT \ln \frac{V_1 - nb}{V_2 - nb} + an^2 \left(\frac{1}{V_1} - \frac{1}{V_2} \right)$$

Sol.

The van der Waals equation is equation 5.42 of the text.

$$\begin{aligned} w &= \int_{V_1}^{V_2} dw = \int_{V_2}^{V_1} P dV = \int_{V_2}^{V_1} \left(\frac{nRT}{V-nb} - a\left(\frac{n}{V}\right)^2 \right) dV \\ &= \int_{V_2}^{V_1} \frac{nRT}{V-nb} dV - \int_{V_2}^{V_1} a\left(\frac{n}{V}\right)^2 dV \\ &= nRT \int_{V_2}^{V_1} \frac{1}{V-nb} dV - an^2 \int_{V_2}^{V_1} \frac{1}{V^2} dV \\ &= nRT \ln \frac{V_1 - nb}{V_2 - nb} - an^2 \left(\frac{1}{V_2} - \frac{1}{V_1} \right) \\ &= nRT \ln \frac{V_1 - nb}{V_2 - nb} + an^2 \left(\frac{1}{V_1} - \frac{1}{V_2} \right) \end{aligned}$$