Chem 104
RR #1
July 11, 2022

Ch. 12 – Solids

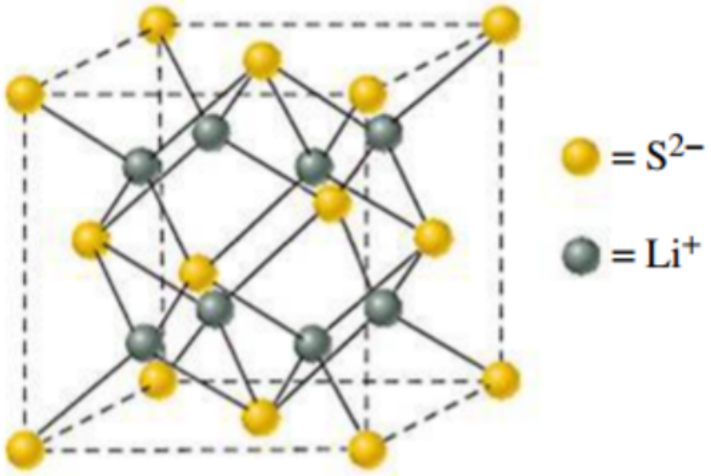
1. Tungsten has a body-centered cubic crystal structure. Using a metallic radius of 139 pm for the W atom, calculate the density of tungsten.

The body diagonal of a cube has length $\sqrt{3}l$, where *l* = length of one edge of the cube. The length of this body diagonal also equals 4r, where r is the radius of the atom in the structure. Hence, 4r = $\sqrt{3}l$ or *l* = 4r ÷ $\sqrt{3}$. The volume of a cube is l^3 and $\sqrt{3} = 1.732$.

$$\text{density} = \frac{\text{mass}}{\text{volume}} = \frac{\dfrac{2\ \text{W atoms}}{1\ \text{unit cell}} \times \dfrac{1\ \text{mol W}}{6.022 \times 10^{23}\ \text{W atoms}} \times \dfrac{183.85\ \text{g W}}{1\ \text{mol W}}}{\left(\dfrac{4 \times 139\ \text{pm}}{1.732} \times \dfrac{1\ \text{m}}{10^{12}\ \text{pm}} \times \dfrac{100\ \text{cm}}{1\ \text{m}}\right)^3} = 18.5\ \text{g}/\text{cm}^3$$

This compares well with a tabulated density of 19.25 g / cm³ .

2. The crystal structure of lithium sulfide (Li_2S), is pictured here:



The length of the unit cell is 5.88×10^2 pm. For this structure, determine

   a. The number of formula units in the unit cell
   b. The density of Li_2S

(a) 8 Li^+ cations in body.

8 S^{2-} anions in corners × 1/8 = 1 S^{2-} anion

6 S^{2-} anions on faces × 1/2 = 3 S^{2-} anions

Total: 8 Li^+, 4 S^{2-} = 4 Li_2S = 4 units

(b) $588\text{ pm} = 5.88 \times 10^{-8}\text{ cm}$

$$\text{Volume} = (5.88 \times 10^{-8}\text{ cm})^3 = 2.03 \times 10^{-22}\text{ cm}^3$$

$$4\text{ units } Li_2S \times \frac{1\text{ mol } Li_2S}{6.022 \times 10^{23}\text{ units}} \times \frac{45.94\text{g}}{1\text{ mol } Li_2S} = 3.052 \times 10^{-22}\text{ g}$$

$$\text{density} = \frac{\text{mass}}{\text{volume}} = \frac{3.052 \times 10^{-22}\text{g}}{2.03 \times 10^{-22}\text{ cm}^3} = 1.50\text{ g/cm}^3$$

3. Calcium metal crystallizes in a face-centered cubic unit cell. The density of the solid is 1.54 g/cm^3. What is the radius of a calcium atom?

FCC = 4 Ca atoms

$$4\text{ Ca atoms} \times \frac{1\text{ mol}}{6.022 \times 10^{23}\text{ atoms}} \times \frac{40.078\text{ g}}{1\text{ mol Ca}} = 2.662 \times 10^{-22}\text{ g}$$

$$2.662 \times 10^{-22}\text{ g} \times \frac{1\text{ cm}^3}{1.54\text{ g}} = 1.73 \times 10^{-22}\text{ cm}^3 = \text{Volume} = d^3$$

$$\sqrt[3]{1.73 \times 10^{-22}\text{ cm}^3} = d = 5.57 \times 10^{-8}\text{ cm}$$

$$f^2 = (4r)^2 = 2d^2 \rightarrow 16r^2 = 2(5.57 \times 10^{-8}\text{ cm})^2$$

$$8r^2 = 3.103 \times 10^{-15}\text{ cm}^2$$

$$r = \sqrt{\frac{3.103 \times 10^{-15}}{8}} = 1.97 \times 10^{-8}\text{ cm}$$

$$\boxed{r = 197\text{ pm}}$$

4. The melting points of NaF, NaCl, NaBr, and NaI are 988, 801, 755, and 651°C respectively. Can you explain this trend?

We expect forces in ionic compounds to increase as the size of ions gets smaller (decreasing radius) and as ionic charges become greater. As the forces between ions become stronger, a higher temperature is required to melt the crystal. In the series of NaF, NaCl, NaBr, and NaI, the anions (F$^-$, Cl$^-$, Br-, and I$^-$) are progressively larger and thus the ionic forces become weaker. We expect the melting points to decrease as the ionic forces decrease.

5. Without calculations, explain how you would expect the lattice energies of LiCl(s), KCl(s), RbCl(s), and CsCl(s) to compare with the value of -787 kJ/mol determined for NaCl.

Hint: assume the enthalpies of sublimation of the alkali metals are comparable in value. Which atomic properties from Ch. 9 should you compare?

Lattice energies of a series will vary approximately with the size of the cation. A smaller cation will produce a more exothermic lattice energy, thus the lattice energy for LiCl (s) should be the most exothermic, and CsCl (s) should be the least, with NaCl (s) being in the middle.

6. Determine the lattice energy of KF(s) from the following data:
$\Delta H_f°[KF(s)]$ = -567.3 kJ/mol; enthalpy of sublimation of K(s) = 89.24 kJ/mol; enthalpy of dissociation of $F_2(g)$ = 159 kJ/mol; I_1 for K(g) = 418.9 kJ/mol; EA for F(g) = -328 kJ/mol.

① $\underline{K^+_{(g)} + F^-_{(g)} \longrightarrow KF_{(s)} \qquad \Delta H = ?}$

② $K(s) + \frac{1}{2}F_2(g) \rightarrow \boxed{KF(s)} \qquad \Delta H_1 = -567.3 \text{ kJ/mol}$

$K(g) \rightarrow K(s) \qquad \Delta H_2 = -89.24 \text{ kJ/mol}$

$F(g) \rightarrow \frac{1}{2}F_2(g) \qquad \Delta H_3 = \frac{1}{2}(-159) \text{ kJ/mol}$

③ $\boxed{F^-(g)} \rightarrow F_{(g)} + e^- \qquad \Delta H_4 = +328 \text{ kJ/mol}$

$\boxed{K^+(g)} + e^- \rightarrow K(g) \qquad \Delta H_5 = -418.9 \text{ kJ/mol}$

④ $\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 + \Delta H_5$

$\Delta H = -567.3 - 89.24 - \frac{159}{2} + 328 - 418.9 = -827 \text{ kJ}$

Steps:
① Write balanced equation
② Write component equations and known enthalpy values
③ Cross off molecules/ions that appear on both sides of arrow (I have boxed what is left)
④ Add enthalpies of all component equations to find ΔH

7. From this list of terms—electrical conductor, insulator, semiconductor—choose the one that best characterizes the following materials:

Stainless steel	Electrical conductor
Solid sodium chloride	Insulator
Sulfur	Insulator
Germanium	Semiconductor
Seawater	Electrical conductor
Solid iodine	Insulator

8. Which of the following substances, when added in trace amounts to silicon, would produce a *p*-type semi-conductor? Explain.

Sulfur	No. S is in group 6 & has more valence electrons than Si (group 4).
Arsenic	No. As is in group 5 & has more valence electrons than Si.
Lead	No. Pb is in group 4 & has the same number of valence electrons as Si.
Boron	Yes. B is in group 3 and has fewer valence electrons than Si.
Gallium Arsenide	No. GaAs has an average of 4 valence electrons (Ga is group 3, As is group 5) so there is neither excess nor deficiency of electrons compared to Si.
Gallium	Yes. Ga is in group 3 so has fewer valence electrons than Si.

9. The conductivity of an intrinsic semiconductor increases with increasing temperature. How can this be explained?

As temperature increases, there's more energy available to promote electrons from valence band to conducting band.

10. Diamond-based semiconductors are currently of enormous interest in the research community. Although diamond itself is an insulator, the addition of a dopant will narrow the band gap. One semiconductor system has diamond with boron as a dopant. Is this a *p*- or an *n*-type semiconductor?

Carbon is in group 4. B is in group 3. B has fewer valence electrons than C, so it's a p-type semiconductor.

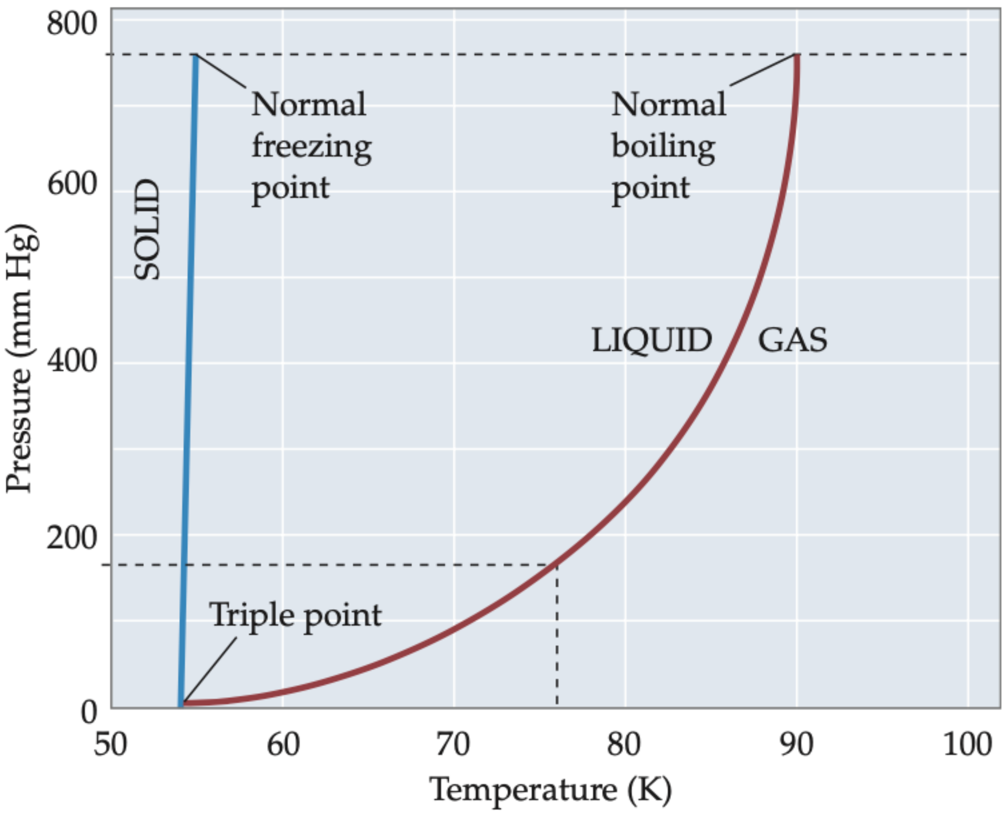
11. Molecular solids, network solids, and amorphous solids all contain atoms that are joined together by covalent bonds. However, these classes of compounds are very different in overall structure and this leads to different physical properties associated with each group. Describe how the overall structures of these classes of solids differ from each other.

Molecular solids are made of discrete molecules held together by intermolecular forces. Network and amorphous solids, on the other hand, are made of infinite two or three-dimensional covalent networks (covalent bonds extend throughout the solids). In network solids there is regularity in the network pattern (they are crystalline) while in amorphous solids there is not.

12. Construct a phase diagram for O_2 from the following information:
Normal boiling point – 90.18 K
Normal melting point – 54.8 K
Triple point – 54.34 K at a pressure of 2 mm Hg.

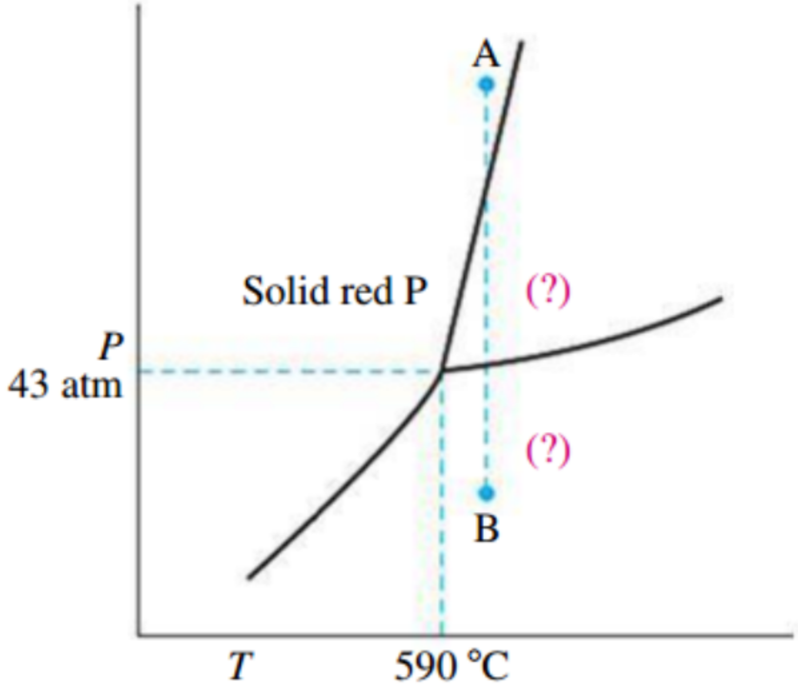
Very roughly estimate the vapor pressure of liquid O_2 at -196°C, the lowest temperature easily reached in the laboratory. Is the density of liquid O_2 greater or less than that of solid O_2?

(i) Note the slight positive slope of the solid-liquid equilibrium line. It indicates that the density of solid O_2 is greater than that of liquid O_2.
(ii) Using the diagram below, the vapor pressure of O_2 at 77 K is between 150 and 200 mm Hg.



800
600
400
200
0
Pressure (mm Hg)
SOLID
Normal
freezing
point
Normal
boiling
point
LIQUID
GAS
Triple point
50
60
70
80
90
100
Temperature (K)

13. Shown here is a portion of the phase diagram for phosphorous.



a. Indicate the phases present in the regions labeled with (?).
b. A sample of solid red phosphorous cannot be melted by heating in a container open to the atmosphere. Why?

   Melting involves converting the solid into a liquid. As the phase diagram shows, the lowest pressure at which liquid exists is at the triple point pressure (43 atm). Thus liquid cannot exist at this pressure and solid sublimes to gas instead.

c. Trace the phase changes that occur when the pressure on a sample is reduced from point A to B, at constant temperature.

   As we move from point A to B by lowering the pressure, initially nothing happens. At a certain pressure, the solid liquifies. The pressure continues to drop, with the whole sample being liquid, until even lower pressure is reached. At this lower pressure, the entire sample vaporizes. The pressure keeps dropping, with the gas becoming less dense as the pressure falls until we get to point B.