SOLIDS – Chapter 12

(We are only covering a small amount of the material in this chapter. I do not recommend that you read the entire chapter – just the sections mentioned below.)

Structure and Type of Solids

Amorphous solids have a disorder in their arrangement; noncrystalline; can be best pictured as a solution in which the components have become frozen in place before they could reach any orderly arrangement. Ex. Glass (Fig. 12.2)

Crystalline solids have a highly regular arrangement of their components.

The positions of the components are represented by a lattice, a three-dimensional system of points designating the positions of the components (molecules, ions or atoms) that make up the substance.

Fig. 12.4, 12.5, 12.6, 12.7

The smallest repeating unit of the lattice is the unit cell.

Three common unit cells are the cubic unit cells: (see page 477 and 479)

1. Simple cubic
2. body-centered cubic
3. face-centered cubic

The structure of crystalline solids is determined by X-ray diffraction. (page 478) (Fig 12.9)

Types of crystalline solids:

- Ionic solids - have ions at the lattice points (Fig 12.25)
  - → held together by ionic bonds
  - high boiling pt & melt. pt. Strong!
  - ex: NaCl
  - (Fig 12.24) • brittle • nonconductors of electricity
- Molecular solids - have molecules at the lattice points
  - → held together by IMFs
  - • low m.p. + b.p (Fig 12.28)
  - ex: ice $H_2O_{(s)}$
    sugar $C_{12}H_{22}O_{11}{(s)}$
    dry ice $CO_{2}{(s)}$
- Atomic solids - have atoms at the lattice points

Atomic solids include:

- Metallic solids – exhibit delocalized, non-directional, covalent bonding
  - → metallic bonding is created by delocalized electrons → nonspecific sharing (Fig. 12-20)
  - • strong w/o being brittle • conduct electricity
  - ex: $Cu_{(s)}$, $K_{(s)}$, $Pb_{(s)}$
  - (Fig 12.11, 12.12)
  - * alloys → substitional → interstitial (Fig 12.15) (Table 12.2)

* CHEMISTRY PUT TO WORK - p. 485 → Interesting info about gold.

- Network solids (Network covalent solids)– strong, directional, covalent bonds that lead to giant "molecules"
  ex: carbon, silicon, germanium; quartz (SiO_2), SiC, BN

- Group 18 (Group 8A) solids – atoms of noble gas elements held together by LDFs.
  ex: $Ar_{(s)}$

Carbon and Silicon

similar to molecules

Network Solids - atomic solids that contain strong covalent bonds and that can be viewed as "giant molecules"

- different from metals because of the way electrons are shared.

Carbon

Two common forms of carbon, diamond and graphite, are typical covalent network solids. They are also allotropes. also charcoal, graphene, fullerenes

What are allotropes? forms of an element differing in crystal or molecular structure

B
C, Sn
P, As
S, Se

- Diamond
  - Hardest naturally occurring substance
  - Each C atom is surrounded by a tetrahedral arrangement of other C atoms to form a huge molecule (see figure 12.29). The C atoms are covalently bonded together by the overlap of sp^3 orbitals (Fig 12.29)
  - Does not conduct electric current; is an insulator of current
  - one of best-known thermal conductors
- Graphite
  - Slippery, black, and a good electrical conductor
  - Structure is based on layers of carbon atoms arranged in fused six-membered rings. Each carbon atom is surrounded by three other carbons in a trigonal planar with sp^2 hybridization (see figure 12.29).
    - One p orbital remains unhybridized, these electrons are responsible for the conductivity of graphite and also form weak bonds between the layers. (delocalized π bonding) → good electrical conductor
    - Graphite is slippery because the layers slide past one another easily.
      → used as a lubricant

Silicon

Silicon is an important constituent of the earth's crust. The fundamental silicon – oxygen compound is silicon dioxide, SiO_2, is also known as silica. Silicon dioxide is a covalent **network solid** (as is diamond). Quartz is essentially pure silicon dioxide.

SiO_2 bonds very differently than CO_2. Silicon cannot use its 3p orbitals to form strong pi bonds with oxygen. This is primarily due to the large size of the silicon orbitals which results in less effective overlap with the smaller oxygen orbitals.

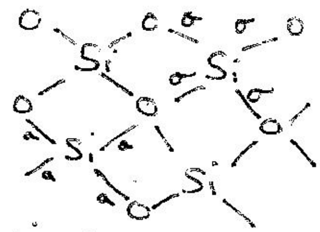
CO_2

C O → Both in same period ∴ the p-orbitals are similar size

SiO_2 →

Si

Cannot ~~effectively~~ π bond because p-orbitals are different sizes



Si → sp^3

Empirical formula for silica is SiO_2. The actual structure is a network of SiO_4 tetrahedral. (See silicates, page 973-974, Figure 22.32)

If cools slowly, quartz forms.

Glass is formed by heating silica above its melting point and then cooling rapidly. This results in a good deal of disorder and creates an amorphous solid.

Additives to glass can dramatically change its properties. Chemical glassware is borosilicate glass (Pyrex, Kymex). B_2O_3 allows glass to undergo large changes in temperature with little expansion and contraction.

Solids that don't fit neatly into a category:

1) Polymers – long chains of atoms held together by covalent bonds, where the adjacent chains are held together by weak intermolecular forces. (Table 12.5) (Fig. 12.35)
   - stronger and have higher mp than molecular solids
   - more flexible than ionic, metallic, or covalent network solids

2) Nanomaterials – solids in which the size of the individual crystals has been reduced to 1–100 nm.

(Fig 12.49)

	Crystal Type	Structural Particles (lattice points)	Principal Attractive Forces Between Particles	Characteristics of the Crystal	Examples
ionic solids	Ionic Crystals	Positive and negative ions	Electrostatic attractions between ions → ionic bonds!	Hard, brittle; moderate to high melting points; nonconductors as solids, but conductors as liquids; many dissolve in water	KCl, CaF_2, CsBr, MgO, $BaCl_2$, NaCl
atomic solids	Covalent Network Crystals	Atoms	Covalent bonds	Very hard; insoluable in most ordinary liquids; sublime or melt at high temperatures; most are nonconductors	C (diamond), C (graphite), SiC, BN, SiO_2
atomic solids	Metallic Crystals	Positive ions and delocalized, mobile valence electrons → "sea of electrons"	Metallic bonds	Hardness varies from very soft to very hard; melting point varies from very low to very high; lustrous; malleable; ductile; high thermal and electrical conductivity	Na, Mg, Cu, Al, Zn, Fe, Li, W, Pt, Cr, Ag, Pb, Au, Hg
molecular solids	Polar Molecular Crystals	Polar molecules	Dispersion forces and dipole–dipole attractions	Low to moderate melting points; soluble in some polar and nonpolar liquids	HCl, $CHCl_3$, H_2S
molecular solids	Hydrogen-bonded Molecular Crystals	Molecules with H bonded to O, N, F	Hydrogen bonds and dispersion forces	Low to moderate melting points; soluble in some hydrogen-bonded and some polar liquids	H_2O, NH_3, HF, CH_3OH
molecular solids	Nonpolar Molecular Crystals	Atoms or nonpolar molecules	Dispersion forces	Extremely low to moderate melting points; soluble in nonpolar solvents	Ar, Cl_2, H_2, CH_4, I_2, CO_2, CCl_4