Chem 1045 Chemistry & Chemical Reactivity
Lecture Notes Kotz/Treichel/Townsend, 8th Ed

These Notes are to SUPPLEMENT the Text. They do NOT Replace reading the Text Material. Additional material that is in the Text will be on your tests! To get the most information, READ THE CHAPTER prior to the Lecture, bring in these lecture notes and make comments on these notes. These notes alone are NOT enough to pass any test! The author is not responsible for typos in these notes.

Chapter 13 The Chemistry of Solids DRAFT COPY

Lithium, $^{7}_{3}$Li. It is used as lubricating grease and in Lithium-Ion batteries. Most of the worlds supply of Lithium comes from Chile and Bolivia.

13.1 Crystal Lattice and Unit Cells.

In liquids and gases, the molecules can move freely. In solids, the molecules cannot change their relative positions. Solids are a 3D lattice of atoms, ions or molecules. Crystalline solids have a **Unit Cell** which is the smallest repeating unit that has all the symmetry characteristics of arrangements in the solid.

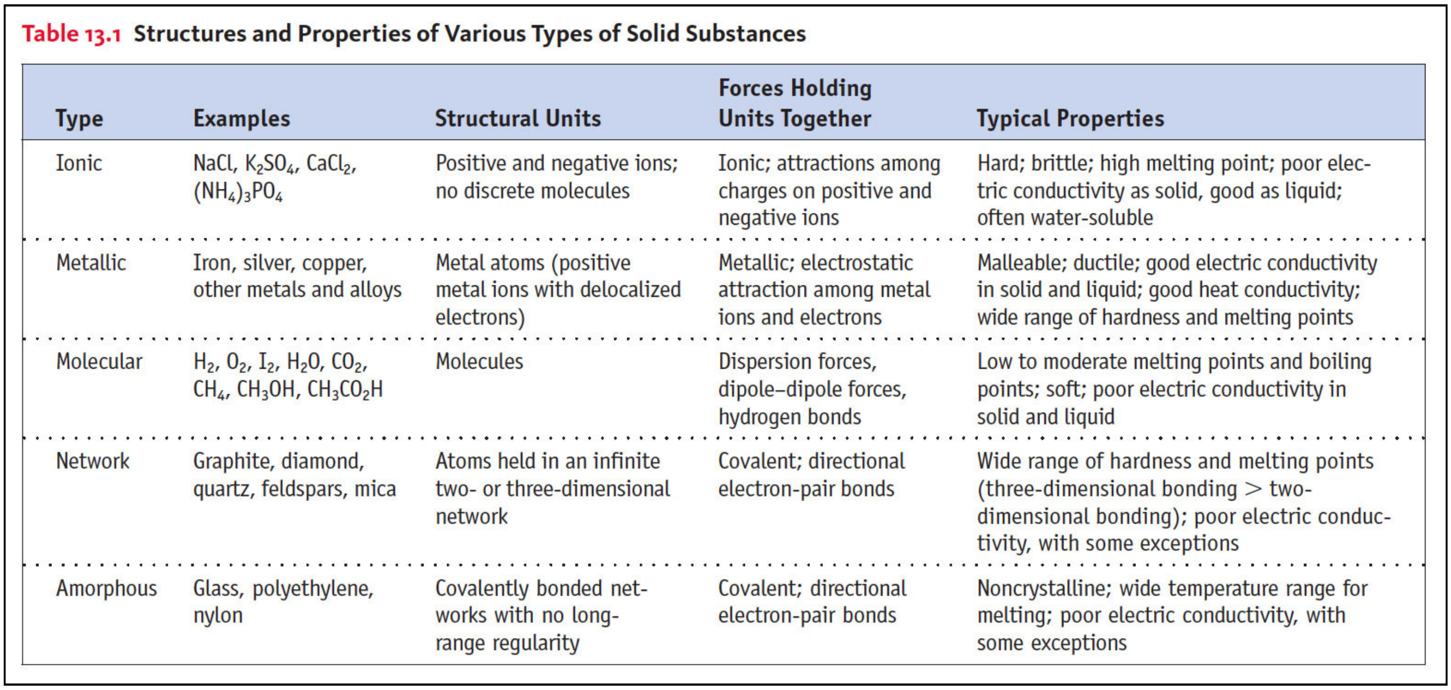
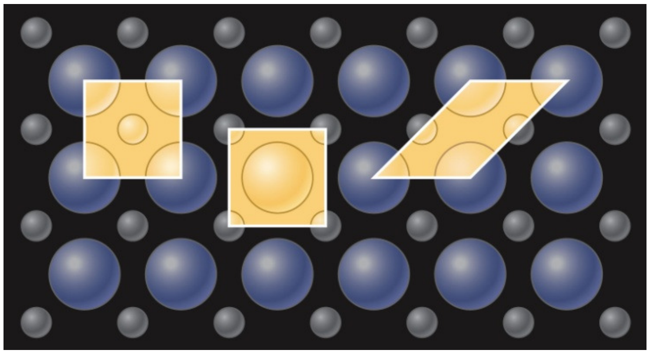


Table 13.1 Structures and Properties of Various Types of Solid Substances

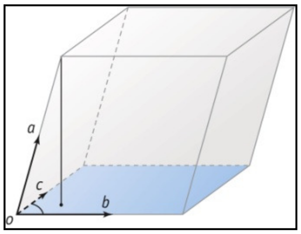
Type	Examples	Structural Units	Forces Holding Units Together	Typical Properties
Ionic	NaCl, K_2SO_4, $CaCl_2$, $(NH_4)_3PO_4$	Positive and negative ions; no discrete molecules	Ionic; attractions among charges on positive and negative ions	Hard; brittle; high melting point; poor electric conductivity as solid, good as liquid; often water-soluble
Metallic	Iron, silver, copper, other metals and alloys	Metal atoms (positive metal ions with delocalized electrons)	Metallic; electrostatic attraction among metal ions and electrons	Malleable; ductile; good electric conductivity in solid and liquid; good heat conductivity; wide range of hardness and melting points
Molecular	H_2, O_2, I_2, H_2O, CO_2, CH_4, CH_3OH, CH_3CO_2H	Molecules	Dispersion forces, dipole–dipole forces, hydrogen bonds	Low to moderate melting points and boiling points; soft; poor electric conductivity in solid and liquid
Network	Graphite, diamond, quartz, feldspars, mica	Atoms held in an infinite two- or three-dimensional network	Covalent; directional electron-pair bonds	Wide range of hardness and melting points (three-dimensional bonding > two-dimensional bonding); poor electric conductivity, with some exceptions
Amorphous	Glass, polyethylene, nylon	Covalently bonded networks with no long-range regularity	Covalent; directional electron-pair bonds	Noncrystalline; wide temperature range for melting; poor electric conductivity, with some exceptions

From the above chart, there are 5 types of solids: Ionic, Metallic, Molecular, Network and Amorphous. We will be studying the crystal forms of Ionic Solids.



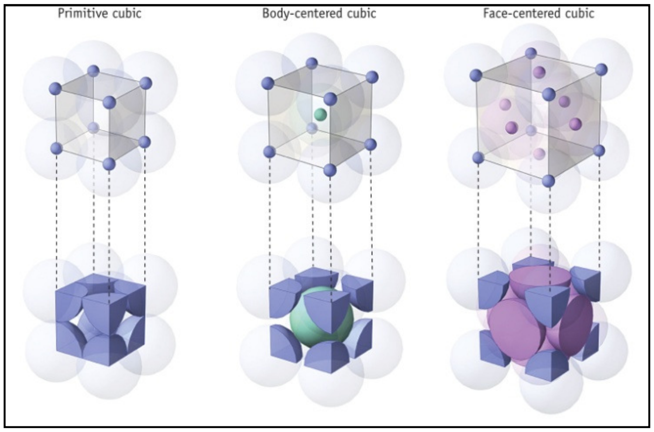
Starting with a flat or 2D picture above shows the repeating unit cells. We are to select the appropriate Unit Cell, or repeating unit that has all of the symmetry characteristics of arrangements in the solid.

The yellow area on the left has the one small sphere and ¼ of the large spheres at each corner. This would be the desired unit cell as the atoms are placed at the corners of the cube, **Lattice Points.**



The types of cells are:
Cubic: All angles are 90^{o}, and all sides are equal
Tetragonal: All angles are 90^{o}, side a length = side b length ≠ side c length
Tetragonal: No angle = 90^{o}, all sides are different lengths

Cubic Cells can have 3 different cell symmetries

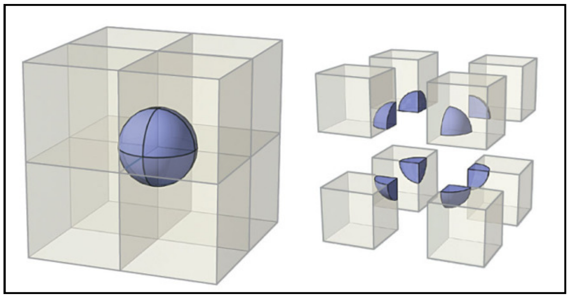


Primitive Cubic (PC) has atoms at the corners of a cubic cell

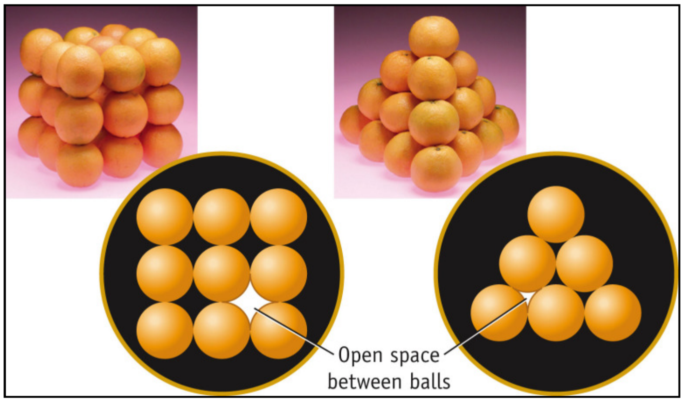
Body-Centered Cubic (BCC) has atoms at the corners of a cubic cell and an additional atom in the center of the cube.

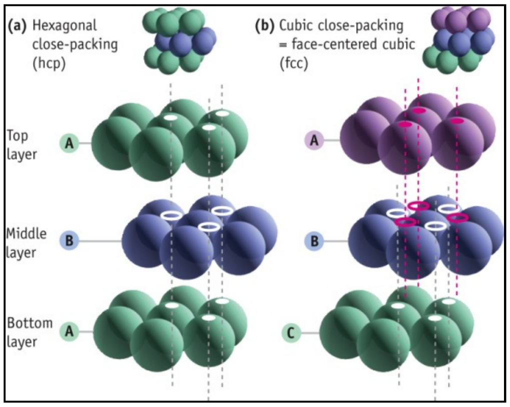
Face-Centered Cubic (FCC) has atoms at the corners of a cubic cell and an additional atoms at the center of each of the 6 faces of the cube.

Sharing of corner atoms: It takes 8 cubes to form a 3D whole atom

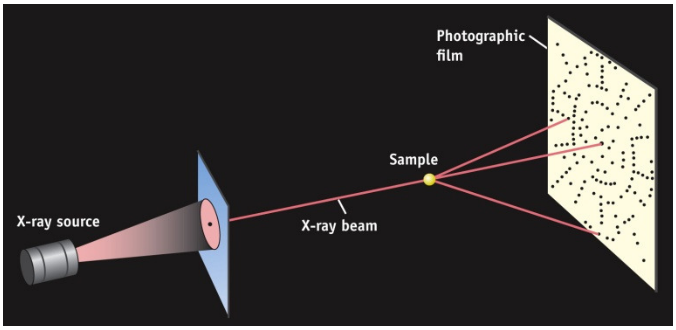


Packing Densities: If you pack oranges, you get more oranges in a box if you start packing using pyramid arrangement rather than as a box. Pyramid uses up 68% of the space, box stacking uses up 52%. The pyramid will result in an alternating hexagonal close-packing arrangement (see below).





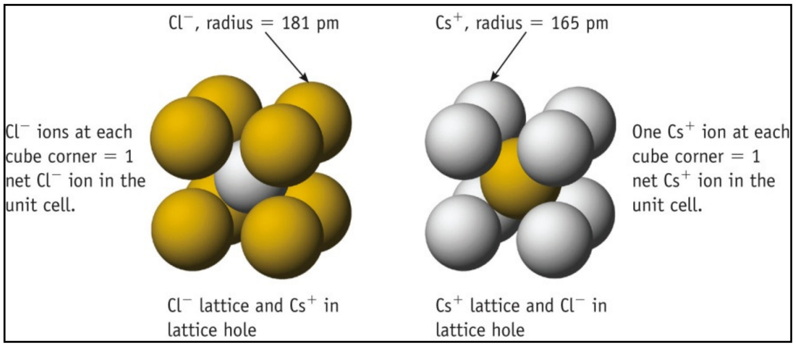
X-Ray Crystallography is used to determine the actual arrangement of atoms in a crystal. One crystal of oa compound that I had synthesized in graduate school took 2 years to calculate the atomic atom arrangements. It was the PhD thesis of a Physics Major at Wayne State U.



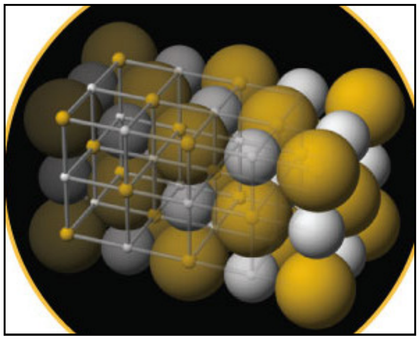
13.2 Structures and Formuale of Ionic Solids

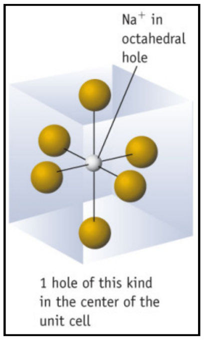
Many ionic compounds take a cubic or face centered cubic lattice of ionic structure. Smaller atoms will fill holes left by the arrangement of larger atoms.

Cesium Chloride, CsCl, is a cubic unit cell and can be shown as either of these two diagrams. Cs and Cl have similar radius.

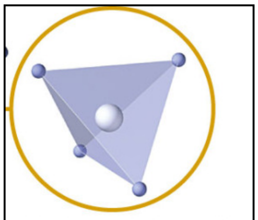


In Sodium Chloride, NaCl, Cl^- is much larger than Na^+ and uses a face-centered cubic unit cell.





Tetrahedral Holes have one ion surrounded by 4 oppositely charged ions – sort of like the structure of methane:



Single tetrahedron with a tetrahedral hole shown as a white sphere.

MX compounds usually have one of the following 3 crystal structures:

CsCl	Primitive Cubic
NaCl	Na^+ is in the Octahedral Holes of a Face-centered cube
ZnS	Zn^{2+} is in half of the tetrahedral holes of a Face-centered cube

13.3 Bonding in Metals and Semiconductors BSOTC

Semiconductors BSOTC

13.4 Bonding in Ionic Compounds: Lattice Energy

Coulombs' Law $U_{\text{ion pr}} = C * [(n^+e)(n^-e)] / d$

$U_{\text{ion pr}}$ = the attractive energy between a pair of ions
C is a constant
d = distance between ion centers
n^+e = cation charge n^-e= anion negative charge

The attractive force is directly related to the charges and indirectly to the distance between the ion centers.

MgO $\Delta_{\text{lattice}}H = -4050$ kJ/mol NaF $\Delta_{\text{lattice}}H = -926$ kJ/mol
Mg is Mg^{2+}, O is O^{2-} Na is Na^+ and F is F^-

13.5 The Solid State: Other Types of Solid Molecules

Molecular Solids: molecules rather than atoms or ions are packed in a regular 3D fashion. HOH and CO_2 are examples. The shape of the crystal lattice depends on the shape of the molecules and the type of molecular interaction – such as hydrogen bonding as in water.

Network Solids: 3D array of covalently bonded atoms such as carbon/graphite, carbon/diamond, elemental silicon.

Graphite consists of carbon atoms bonded together in sheets. The layers can slip so graphite is a good lubricant.

Diamonds have carbon bonded to 4 other carbons in a tetrahedron. Diamond is a good conductor of heat and is transparent to UV, Vis and IR light.

Silicates, SiO compounds, are tetrahedral silicon atoms covalently bonded to oxygen in a 3D lattice. Sand, quartz, talc and mica are examples.

Amorphous Solids are crystalline solids with well defined crystals with smooth flat faces. They had a specific MP – Ice melts at 0 °C, asprin at 135 °C, lead at 327.5 °C and NaC at 901 °C.

Glass is an amorphous solid without a regular structure.

13.6 Phase Changes Involving Solids

Melting: Conversion of Solid into a Liquid

The MP of a solid is the temperature at which the lattice collapses and the solid is converted to a liquid. This energy is called the Enthalpy of Fusion, $\Delta_{fusion}H$ (kJ/mole). Freezing is going from liquid to solid and is called the Enthalpy of Crystallization, - $\Delta_{fusion}H$ (kJ/mole). Note Tungsten (W) below has the highest MP, except for Carbon, off all the elements. Non polar compounds usually have low melting points. Except as the size of the molecule increases, London forces get larger and the MP may increase. Ionic compounds have very high melting points due to the strong forces due to the ionic charges.

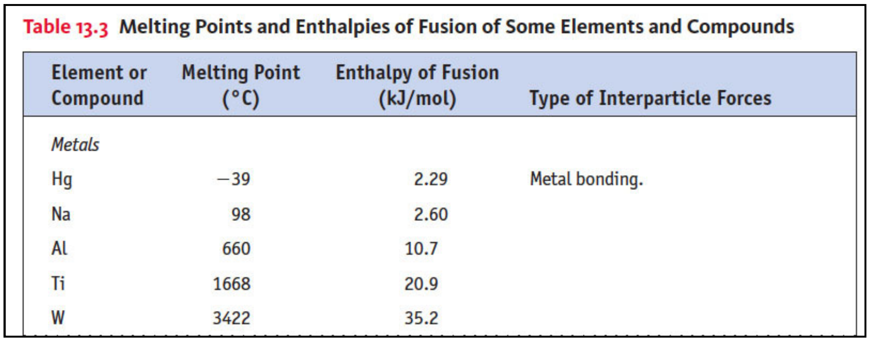


Table 13.3 Melting Points and Enthalpies of Fusion of Some Elements and Compounds

Element or Compound	Melting Point (°C)	Enthalpy of Fusion (kJ/mol)	Type of Interparticle Forces
Metals			
Hg	−39	2.29	Metal bonding.
Na	98	2.60	
Al	660	10.7	
Ti	1668	20.9	
W	3422	35.2	

Sublimation: Conversion of Solid into Vapour

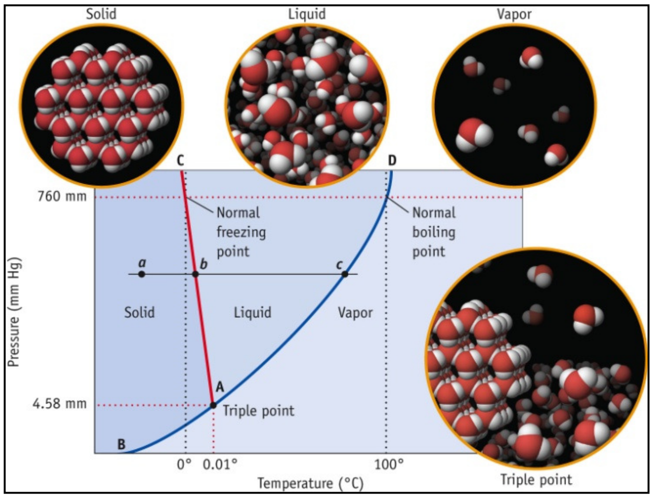
Molecules can escap directly from the solid to the gas phase and this is called sublimation.

Solid → Gas $\Delta_{sublimation}H$ (Enthalpy of Sublimation)

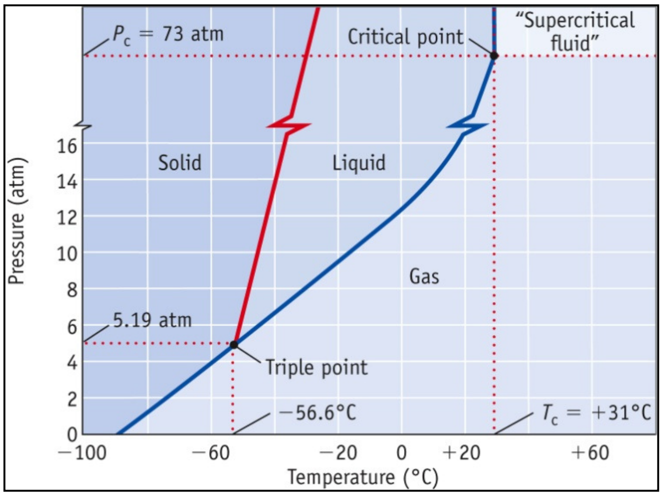
Water as solid ice → water as vapour $\Delta_{sublimation}H = 51$ kJ/mole

13.7 Phase Diagrams

Substances can usually exist as either a solid, liquid or a gas. Two or three of these conditions can occur at the same time and this is shown in a Phase Diagram:



Phase Diagram of Water



Phase Diagram of CO_2

In the left diagram, line A-B represents the boundry between solid and water vapour. A-C is the solid / liquid boundry and A-D the liquid / vapour boundry. Bottom axis is temperature, left side is pressure. So, starting at D, if you lower the pressure (follow the blue line), you also lower the boiling point. Any point on the blue line represents the existance of liquid and vapour together. The red line is solid and liquid together. Point A is the **Triple Point**, where all three phases exist together. The Triple Point for water is 4.6 mm Hg at 0.01 °C. The red A-C line represents increasing the pressure (A

➔ C) and as you increase the pressure the melting point of water decreases. Ice is less dense than water, as you increase the pressure you force ice to water so you must lower the temperture to keep ice as a solid.

The graph of CO2 on the right also shows a Critical Point in the higher temperature and pressure range. The Critical Point is the temperature and pressure where there is no boundry between liquid and vapour – they both exist together. A substance at or above the Super Critical Point exists only as a gas. On the CO2 graph, draw and follow a line from left to right at 1.0 atm. You can see that CO2 will go from solid to gas and not to a liquid state. Dry Ice is used to keep items cold during shipping (Ohama Steaks) and will dissappear – it goes directly from solid to gas.