

SOLIDS

A. PROPERTIES OF SOLIDS

1. Not compressible
2. Have definite shape and volume
3. Flow or diffuse very slowly, if at all
4. Relatively high density
5. Expand only slightly when heated

B. TYPES OF SOLIDS

1. Crystalline solids - have highly regular arrangement of particles – ordered structure
2. Amorphous solids - considerable disorder in their structure

C. CRYSTALLINE SOLIDS

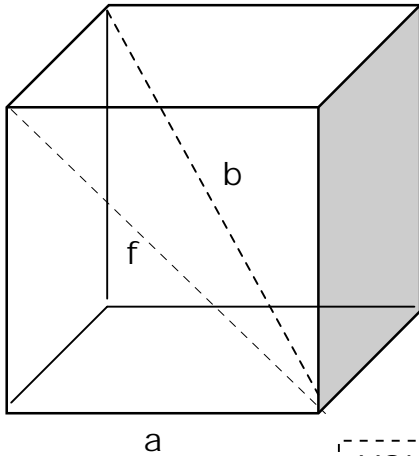
1. X-ray diffraction
2. Lattice
 - a. Crystal Lattice: three dimensional array of points (lattice points) which is the pattern of particles in the crystal.
 - b. Unit Cell: the basic repeating unit of the lattice; the smallest portion of the lattice which includes all the positions of each type of particle the crystal.
 - (1) All the properties of the lattice are contained in the properties of its unit cell.
 - (2) All unit cells have 8 corners.
 - (3) Unit cells differ in edge lengths: a , b , c
 - (4) Unit cells differ in angles opposite the edges.
 - c. Only 14 different kinds of lattices are possible. These can be divided into seven basic crystal systems.

cubic	hexagonal
tetragonal	rhombohedral
orthorhombic	triclinic
monoclinic	

D. CUBIC CRYSTAL SYSTEMS

1. Review of some geometrical relationships

CUBE



a = edge

b = body diagonal

f = face diagonal

$$\text{VOLUME OF CUBE} = a^3$$

Relationship between f and a

$$f = a \sqrt{2} \quad \text{or} \quad a = \frac{f}{\sqrt{2}}$$

Derivation of relationship between f and a

$$f^2 = a^2 + a^2$$

$$f^2 = 2 a^2$$

$$f = a \sqrt{2}$$

Relationship between b and a

$$b = a \sqrt{3} \quad \text{or} \quad a = \frac{b}{\sqrt{3}}$$

Derivation of relationship between b and a

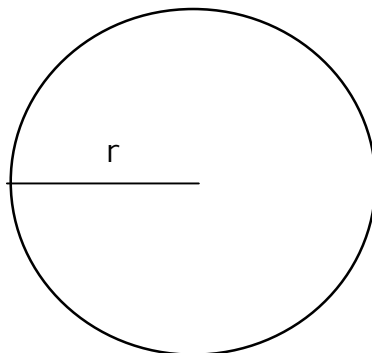
$$b^2 = f^2 + a^2$$

$$b^2 = 2 a^2 + a^2$$

$$b^2 = 3 a^2$$

$$b = a \sqrt{3}$$

SPHERE



r = radius

d = diameter = 2r

VOLUME OF SPHERE

$$\frac{4}{3} \pi r^3 \quad \text{or} \quad \frac{1}{6} \pi d^3$$

D. Cubic Crystal Systems, continued

2. Three Cubic Crystal Systems

In each of the three types of crystal systems:

- The unit cell is cubic
- The particles (atoms, etc.) occupying the unit cell are assumed to be spherical.

a. SIMPLE CUBIC UNIT CELL

Determining Unit Cell Volume

The spherical particles inside the cubic unit cell are in contact along a , the edge of the cube. The length of a is $2r$, where r is the radius of the spherical particle.

$$a = 2r$$

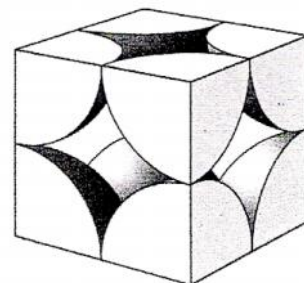
$$\text{Volume of unit cell} = a^3$$

Determining Occupied Volume

Number of spherical particles inside unit cell: there are 8 corners of the unit cell, each occupied by one-eighth of a sphere. $8 \times 1/8 = 1$.

$$\text{Volume of one sphere: } \frac{4}{3} \pi r^3$$

$$\text{Occupied Volume} = 1 \text{ sphere per U.C.} \times \text{volume per sphere}$$



b. BODY-CENTERED CUBIC UNIT CELL

Determining Unit Cell Volume

The spherical particles inside the cubic unit cell are in contact along b , the body diagonal of the cube. The length of b is $4r$, where r is the radius of the spherical particle.

$$b = 4r$$

$$\text{Also, } a = \frac{b}{\sqrt{3}} \quad \text{therefore } a = \frac{4r}{\sqrt{3}}$$

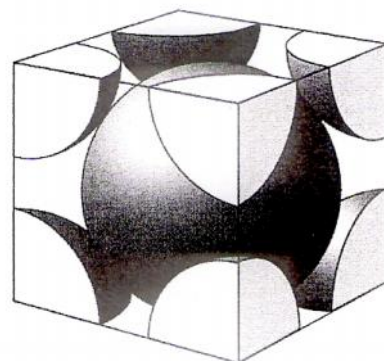
$$\text{Volume of unit cell} = a^3$$

Determining Occupied Volume

Number of spherical particles inside unit cell: there are 8 corners, each occupied by one-eighth of a sphere, plus one whole sphere at the center. $(8 \times 1/8) + 1 = 2$

$$\text{Volume of one sphere: } \frac{4}{3} \pi r^3$$

$$\text{Occupied Volume} = 2 \text{ spheres per U.C.} \times \text{volume per sphere}$$



c. FACE-CENTERED CUBIC UNIT CELL

Determining Unit Cell Volume

The spherical particles inside the cubic unit cell are in contact along f , the face diagonal of the cube. The length of f is $4r$, where r is the radius of the spherical particle. $f = 4r$

$$\text{Also, } a = \frac{f}{\sqrt{2}} \quad \text{therefore } a = \frac{4r}{\sqrt{2}}$$

$$\text{Volume of unit cell} = a^3$$

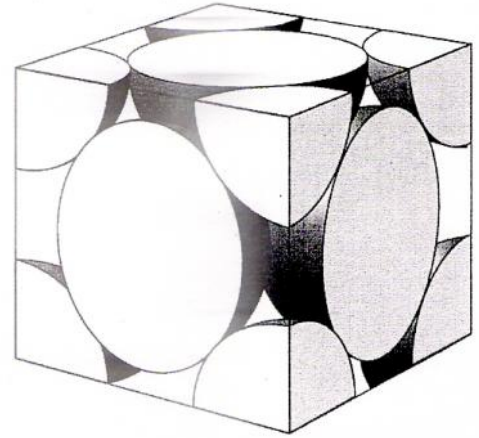
Determining Occupied Volume

Number of spherical particles inside unit cell: there are 8 corners, each occupied by one-eighth of a sphere, plus one half sphere at each of the six faces of the cube.

$$(8 \times 1/8) + (6 \times 1/2) = 4$$

$$\text{Volume of one sphere: } \frac{4}{3} \pi r^3$$

$$\text{Occupied Volume} = 4 \text{ spheres per U.C.} \times \text{volume per sphere}$$



3. Packing Efficiency (Percent Occupied Volume)

E. CUBIC UNIT CELL PROBLEMS

1. Ag has atomic radius of 144 pm. What would be the % occupied volume of Ag if it were to crystallize in the following structures: (a) simple cubic (b) body-centered cubic (c) face-centered cubic

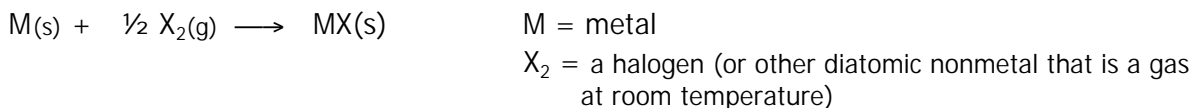
2. Metallic Na has a body-centered cubic crystalline structure and has a density of 0.970 g/cm^3 .
 - a. Calculate the length of the edge of its unit cell.
 - b. Calculate the volume of the sodium atom.

F. TYPES OF CRYSTALS

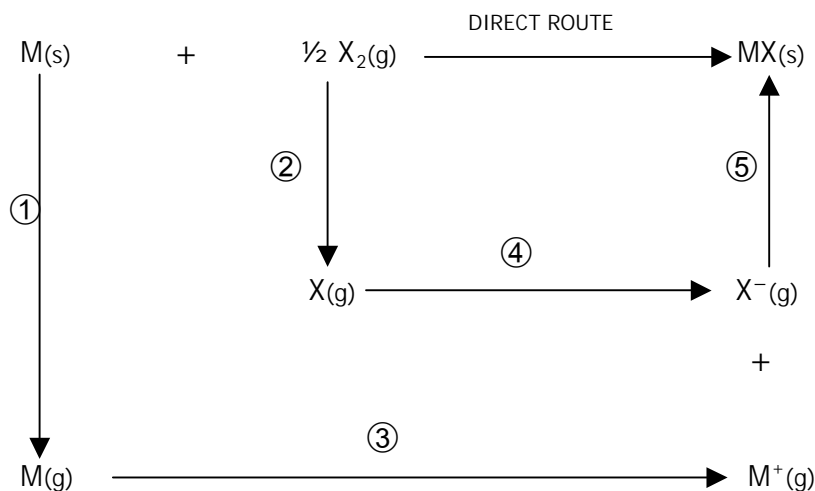
Crystal Type	Particles at Lattice Points	Attractive Forces	Properties			Examples
			Hardness & Brittleness	Melting Point	Conductivity	
Covalent Network	Atoms	Covalent bonds	Very hard	Very high	Non-conductor	C (diamond) SiC SiO ₂ AlN
Ionic	Positive ions and negative ions	Ionic bond	Hard	high	Non-conductor	NaCl KBr LiNO ₃
Molecular (polar)	Polar molecules	H-bond or dipole-dipole	Somewhat soft	Low	Poor conductor	H ₂ O SO ₂ NH ₃ C ₂ H ₆ O
Molecular (nonpolar)	Nonpolar molecules	London Forces	Very soft	Very low	Non-conductor	H ₂ Cl ₂ CH ₄ CO ₂
Metallic	Positive ions	Metallic bond	varies	varies	Good conductor	Au Cu Fe Pb Na Hg

G. BORN-HABER CYCLE

Born-Haber cycle provides a means for determining the Lattice Energy of an ionic solid (which is difficult to measure directly), using energy involved in forming an ionic solid from the elements by two different routes. Consider the formation of ionic solid, MX from the elements M and X₂:



Born-Haber cycle accomplishes the formation of the ionic solid by two different routes:



Enthalpy change, symbolized as ΔH , is change in heat energy that occurs during a chemical reaction. If the sign is negative, the reaction is exothermic. If the sign is positive, the reaction is endothermic.

DIRECT ROUTE: formation of $MX(s)$ directly from the elements $M(s)$ and $X_2(g)$
Enthalpy change for this reaction symbolized as ΔH_f

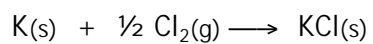
STEPWISE ROUTE:

- ① Sublimation of the metal, M. Enthalpy change symbolized ΔH_{SUB}
- ② Covalent bond between X and X broken. Enthalpy change is the bond dissociation energy (bond energy) for X_2 and is symbolized ΔH_{BE} . (Remember the definition of Bond Energy?)
- ③ Ionization of the Metal, M. Enthalpy change for this reaction is the Ionization Energy of elemental M, symbolized ΔH_{IE} . (Remember the definition of Ionization Energy?)
- ④ Ionization of Nonmetal, X. Electron(s) lost by M are transferred to X. Enthalpy change for this reaction is the Electron Affinity of elemental X, symbolized ΔH_{EA} . (Definition of Electron Affinity?)
- ⑤ Formation of the MX from the ions. Enthalpy change for this reaction corresponds to the Lattice Energy of MX, symbolized ΔH_{LE} . Lattice Energy is defined as the energy required to break solid MX into its ions. Since this process is the reverse, the enthalpy change for this process would be symbolized $-\Delta H_{LE}$.

$$\Delta H_{DIRECT\ ROUTE} = \Delta H_{STEPWISE\ ROUTE}, \text{ Where } \Delta H_{STEPWISE\ ROUTE} = \Delta H_{SUB} + \Delta H_{BE} + \Delta H_{IE} + \Delta H_{EA} + \Delta H_{LE}$$

Born-Haber cycle problems:

1. Draw the Born-Haber cycle and calculate the lattice energy for the reaction:



Enthalpy change for formation of KCl, $\Delta H_f = -104$ kcal/mole

Bond Dissociation Energy for $\text{Cl}_2 = 58$ kcal/mole Cl_2

Electron Affinity for Cl = -88 kcal/mole

Sublimation of K = 21 kcal/mole

Ionization Energy of K = 99 kcal/mole

