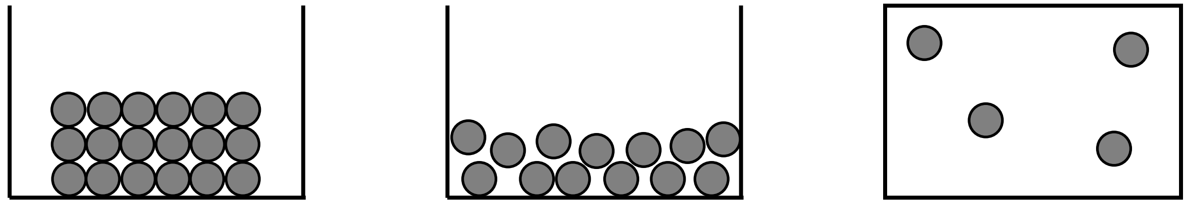
Outline

- Solids and Liquids
- Molecular Substances
- Network Substances
- Changes of State
- Phase Diagrams

Solids and Liquids



Solid – Definite shape, definite volume

Liquid – Indefinite shape, definite volume

Gas – Indefinite shape, indefinite volume

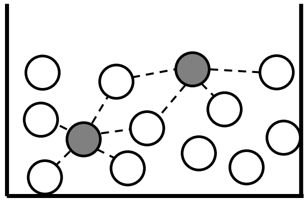
If the kinetic energy of the particles is great enough to overcome the attractive forces, the substance will be in the gas phase

If the attractive forces are great enough to overcome the kinetic energy of the particles, the substance will be in the liquid or solid phase

Liquid State

Surface Tension

The resistance of a liquid to an increase in its surface area

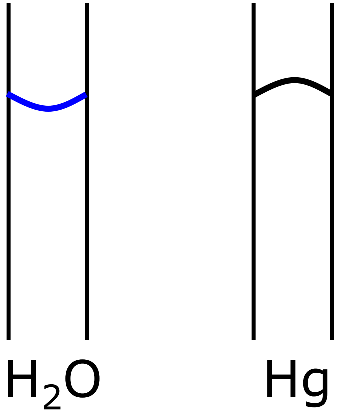


The stronger the attractive forces, the stronger the surface tension

Capillary Action

The rising of a liquid in a narrow tube

Occurs when there are strong attractive forces between the liquid particles and the container



Viscosity

A measure of a liquid's resistance to flow

The stronger the attractive forces the more viscous the liquid

Pitch Drop Experiment – "Longest Running Experiment"

Started in 1930

One drop of tar falls every decade (or so)

9th drop "fell" 4/24/2014

The University of Queensland - Physics

Solid State

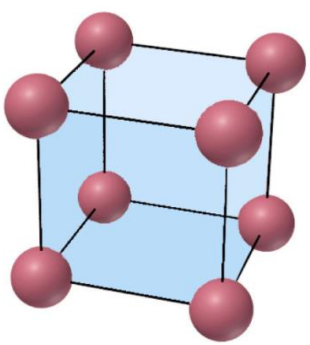
Amorphous Solid

A random particle arrangement (glass, wax,...)

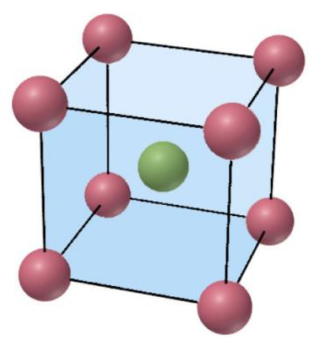
Crystalline Solid

A regular particle arrangement (called the crystal lattice)

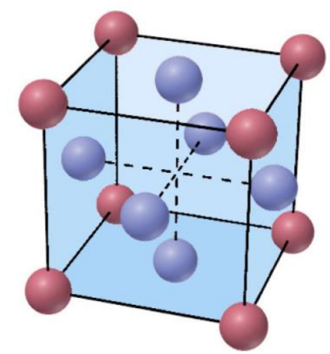
The unit cell is the smallest repeating unit of the lattice



simple cubic

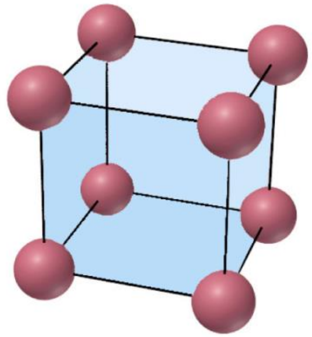


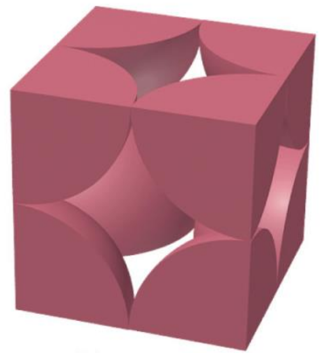
body-centered cubic



face-centered cubic

Simple Cubic





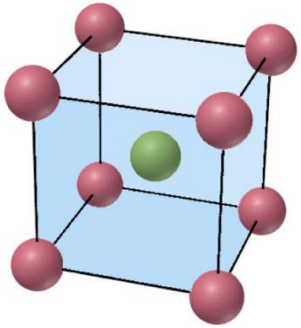
Full atoms in the unit cell:

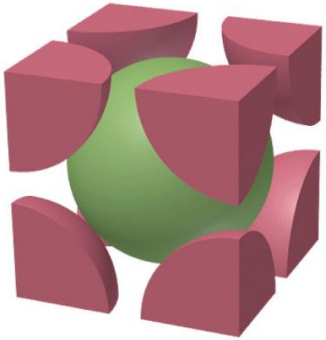
$8 \times {}^{1}/_{8} = 1$

Length of 1 side of the unit cell:

$side = 2r$ (r = radii of one particle)

Body-Centered Cubic





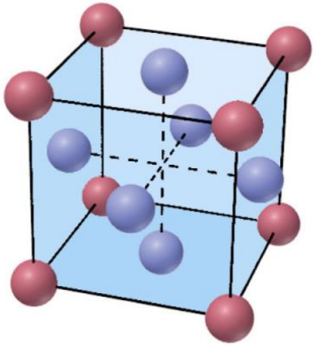
Full atoms in the unit cell:

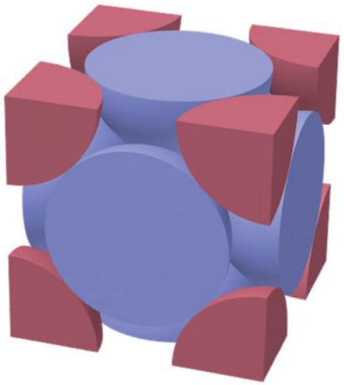
$(8 \times {}^{1}/_{8}) + 1 = 2$

Length of 1 side of the unit cell:

$$side = \frac{4}{\sqrt{3}} r$$

Face-Centered Cubic





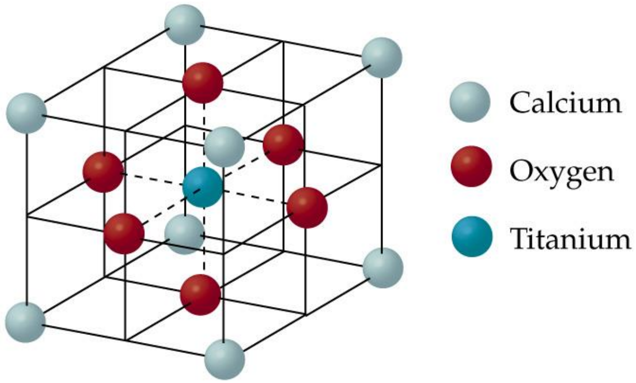
Full atoms in the unit cell:

$(8 \times {}^{1}/_{8}) + (6 \times {}^{1}/_{2}) = 4$

Length of 1 side of the unit cell:

$$\text{side} = \sqrt{8}\,\text{r}$$

Determine the formula for a mineral containing calcium, oxygen, and titanium, which crystallizes in the following cubic unit cell:



$$\text{Calcium Atoms} = (8 \times {}^{1}/_{8}) = 1$$

$$\text{Oxygen Atoms} = (6 \times {}^{1}/_{2}) = 3$$

$$\text{Titanium Atoms} = (1 \times 1) = 1$$

Chemical Formula: $CaTiO_3$

Barium has a bcc structure. Calculate the density of barium if the atomic radius of barium is 222 pm.

$$222\ \text{pm} \times \frac{1 \times 10^{-12}\ \text{cm}}{1 \times 10^{-2}\ \text{pm}} = 2.22 \times 10^{-8}\ \text{cm}$$

$$\text{mass} = 2\ \text{atoms} \times \frac{1\ \text{mol}}{6.022 \times 10^{23}\ \text{atoms}} \times \frac{137.3\ \text{g}}{1\ \text{mol}} = 4.561 \times 10^{-22}\ \text{g}$$

$$\text{vol} = (\text{side})^3 = \left(\frac{4}{\sqrt{3}} r\right)^3 = \left(\frac{4}{\sqrt{3}} \cdot 2.22 \times 10^{-8}\ \text{cm}\right)^3 = 1.35 \times 10^{-22}\ \text{cm}^3$$

$$\text{density} = \frac{\text{mass}}{\text{volume}} = \frac{4.561 \times 10^{-22}\ \text{g}}{1.35 \times 10^{-22}\ \text{cm}^3} = \underline{3.38\ \text{g cm}^{-3}}$$

Silver forms a fcc structure. Determine the radius, in pm, of a silver atom if the density of silver is 10.5 g cm^{-3}.

$$\text{mass} = 4\text{ atoms x } \frac{1\text{ mol}}{6.022 \text{ x } 10^{23}\text{ atoms}} \text{ x } \frac{107.9\text{ g}}{1\text{ mol}} = 7.167 \text{ x } 10^{-22}\text{ g}$$

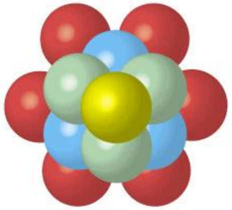
$$\text{vol} = \frac{\text{mass}}{\text{density}} = \frac{7.167 \text{ x } 10^{-22}\text{ g}}{10.5\text{ g cm}^{-3}} = 6.83 \text{ x } 10^{-23}\text{ cm}^3$$

$$\text{side} = \sqrt[3]{\text{vol}} = \sqrt[3]{6.83 \text{ x } 10^{-23}\text{ cm}^3} = \sqrt{8}\,\text{r} \quad \Rightarrow \quad \text{r} = 1.45 \text{ x } 10^{-8}\text{ cm}$$

$$1.77 \text{ x } 10^{-8}\text{ cm x } \frac{1 \text{ x } 10^{-2}\text{ pm}}{1 \text{ x } 10^{-12}\text{ cm}} = \underline{177\text{ pm}}$$

The two most efficient ways to pack atoms:

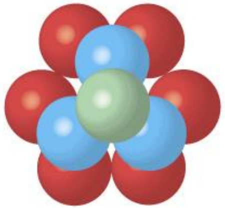
1. Cubic closest packing (ccp)



Makes face-centered cubic unit cells

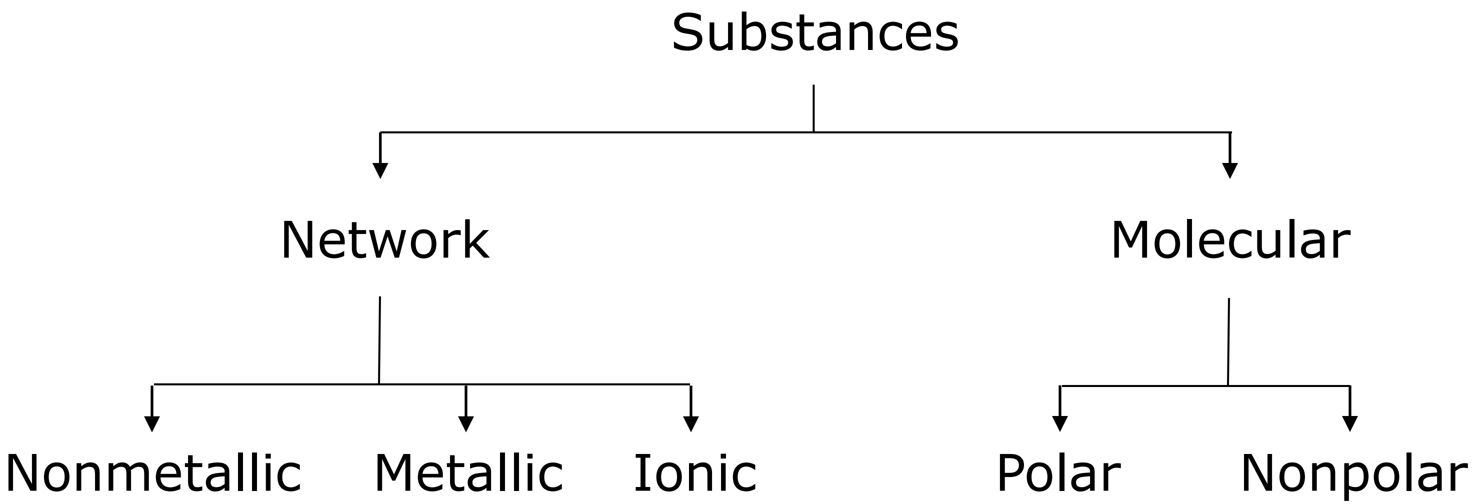
Three layers, atoms do not lie directly above atoms in other layers

2. Hexagonal closest packing (hcp)



Makes hexagonal prism unit cells

Two layers, atoms do not lie directly above atoms in other layer


Substances
Network
Molecular
Nonmetallic
Metallic
Ionic
Polar
Nonpolar

Molecular Substances

Nonpolar Molecular

Matter composed of nonpolar molecules, held together by weak intermolecular attractions

Examples:

O_2, S_8, P_4	molecules of only 1 element
CH_4, C_8H_{18}	all hydrocarbons
CO_2, BH_3	molecules with $\mu = 0$
Ne, Ar	noble gases

Attractive forces between nonpolar molecules:

London Dispersion Forces

The Nature of London Dispersion Forces (LDFs):

1. At large distances (>0.5 nm), no forces

2. At intermediate distances (0.1 – 0.5 nm), the electrons in 1 molecule polarize the electrons in a neighboring molecule creating an attraction

3. At short distances (<0.1 nm), overlapping electron clouds result in repulsion

MPs and BPs: low

MPs and BPs depend on the strength of the LDFs between the molecules, not the strength of the molecular covalent bonds

The strength of the LDFs depend on…

1. Number of electrons

The more electrons in molecules, the more polarizing they are, the stronger the LDFs

Nonpolar Substance	MP (^oC)	BP (^oC)
He	- - - -	-269
O_2	-218	-183
CO_2	-157	-79

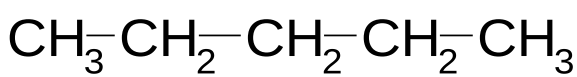
These are gases to very low temperatures

Nonpolar molecules with many electrons may have strong enough LDFs to be solids or liquids at room temperature

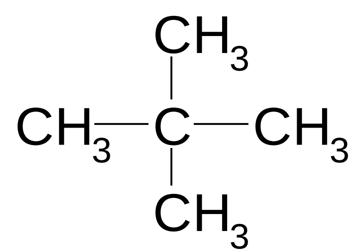
Nonpolar Substance	MP (^oC)	BP (^oC)
CCl_4	-23	77
C_6H_6	6	80
P_4	44	280
S_8	112	445

2. Molecular Shape

The greater the area of contact between molecules, the more polarizing they are, the stronger the LDFs



BP 36 ^oC



BP 10 ^oC

Explain:

F_2	gas	CH_4	gas
Cl_2	gas	C_3H_8	gas
Br_2	liquid	C_8H_{18}	liquid
I_2	solid	$C_{20}H_{42}$	solid

F_2 (gas) $\rightarrow$ I_2 (solid)

Greater molar mass implies greater numbers of electrons and, therefore, stronger dispersion forces!

CH_4 (gas) $\rightarrow$ $C_{20}H_{42}$ (solid)

Larger molecules will have greater contact and, therefore, stronger dispersion forces!

Additional properties of nonpolar molecules…

H_2O Solubility: low

Electrical Conductivity: none

Electrical conductivity is the movement of charged particles

Molecules are neutral particles, so their movement (in the liquid or gaseous state) would not result in conduction

As a solid, particles can’t move, so no conduction

Polar Molecular

Matter is composed of polar molecules held together by weak intermolecular attractions

Examples:

SO_2, H_2O molecules with $\mu \neq 0$

Attractive forces between polar molecules:

LDFs plus the attraction of oppositely charged ends of the molecules

This extra attractive force is called the dipole-dipole interaction

Relative strengths of attractive forces:

covalent bond	400	kJ/mol
dipole-dipole interaction	1	kJ/mol
London dispersion force	0.1	kJ/mol

MPs and BPs: low, but higher than similar nonpolar molecules due to the extra attractive force

Substance	Polar/Non	MP(^oC)	BP(^oC)
SiH_4	N	-185	-112
PH_3	P	-133	-88

MPs and BPs of polar molecules depend primarily on the strength of the LDFs, not the dipole-dipole interaction

Polar Substance	MP(^oC)	BP(^oC)
H_2Te	-49	-2
H_2Se	-60	-42
H_2S	-86	-61
H_2O	0	100

Molecules with H bonded to highly electronegative atom form weak hydrogen bonds (~20 kJ/mol) between molecules

highly electronegative atoms: N, O, and F

This extra attractive force increases MPs and BPs of these substances

Network Substances

Ionic Network

Matter composed of positive and negative ions held together by strong chemical bonds

Examples:

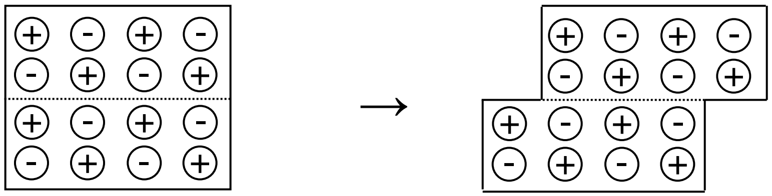
NaCl, $Mg(NO_3)_2$ metal / nonmetal ions

Attractive forces between ions:

Ionic Bonds

MPs and BPs: high, due to the strength of ionic bonds (~400 kJ/mol)

Ionic crystals are brittle due to repulsion between ions



H_2O Solubility: high

Electrical Conductivity:

As a solid… The positive and negative ions are not free to move, so no!

As a liquid or dissolved in H_2O…The positive and negative ions are free to move, so yes!

Metallic Network

Matter composed of metal atoms held together by strong chemical bonds

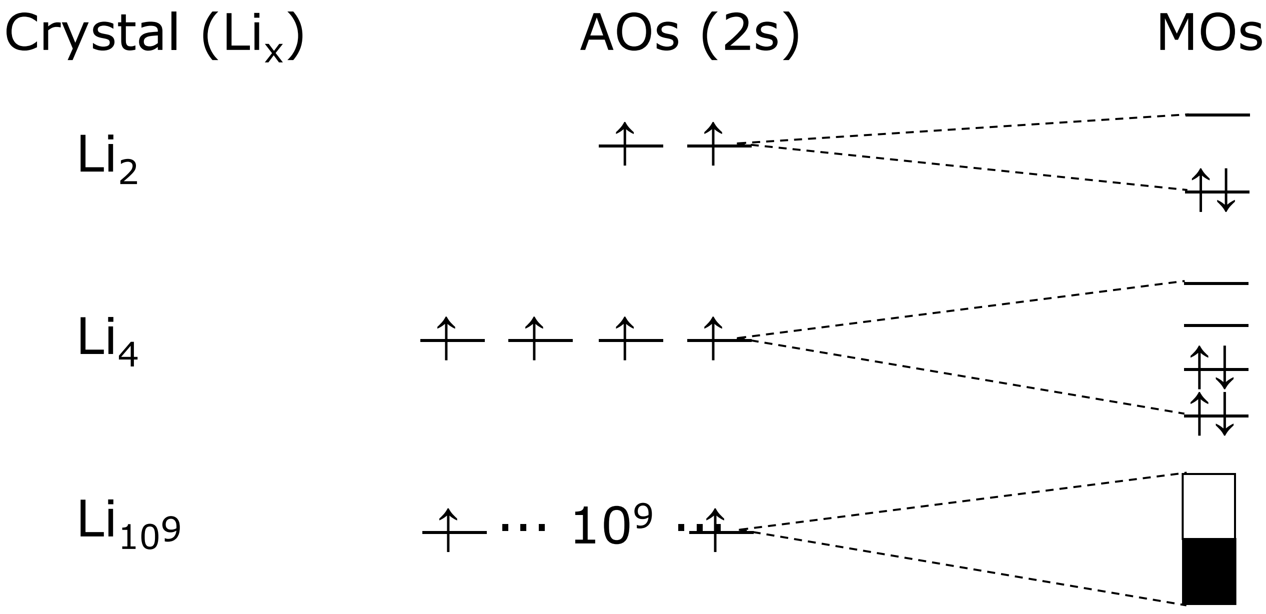
Examples:

Fe, Au, bronze (Cu + Sn)   only metals

Attractive forces between metal atoms:

Metallic Bonds (delocalized covalent bonds)

The valence electrons are contained in delocalized molecular orbitals



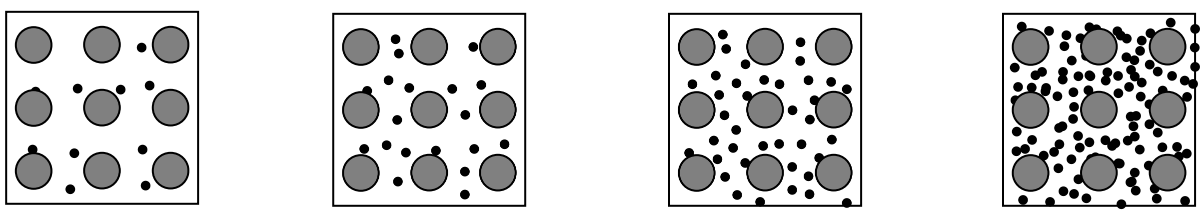
The 10^9 MOs are so close in energy they seem to form a continuous band

Applying molecular orbital theory to metallic solids is called band theory

MPs and BPs: high, due to strength of metallic bonds (~ 400 kJ/mol)

The strength of metallic bonds depends on:

1. The net number of bonding e^-



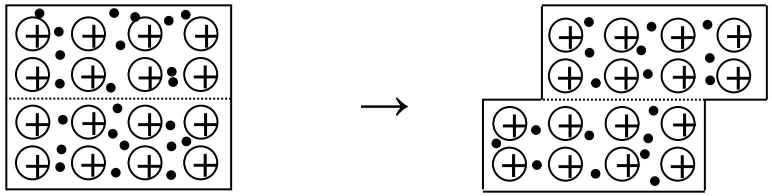
Metal	Cs	Ba	W	Au
MPs (^oC)	29	725	3410	1064

2. Metal ion size

the smaller the ions, the greater the charge density, the greater the attraction between the ions and the valence electron cloud

Metal	MP (^{o}C)
Li	180
Na	98
K	64
Rb	39
Cs	29
Fr	?

Metals are malleable and ductile because shifts in the crystal do not result in repulsive forces

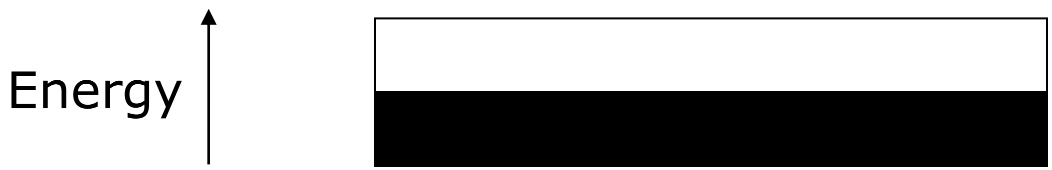


H_2O Solubility: low

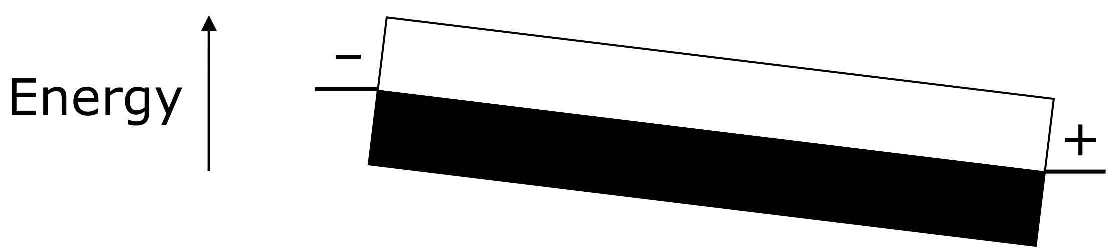
Electrical Conductivity: yes

Valence electrons are the mobile charge particles allowing metals to conduct

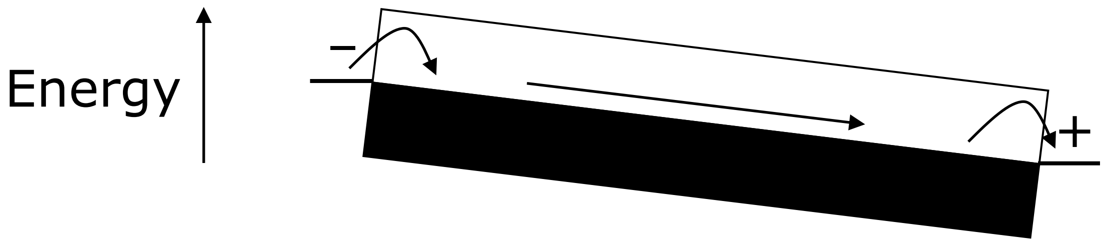
Valence electrons in metals are found in the delocalized MOs called the valence band



When a negative potential is applied to a metal, close MOs increase in energy, and when a positive potential is applied to a metal, close MOs decrease in energy



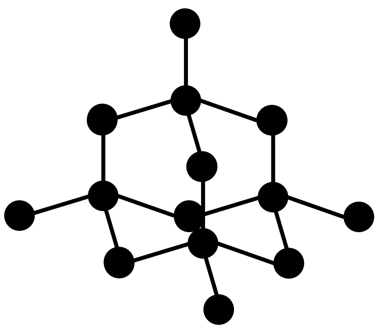
Electrons in the valence band near the negative potential move in the more stable conduction band near the positive potential



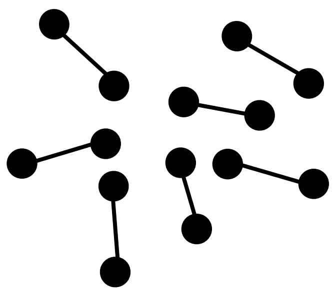
This movement of electrons through the metal is electrical conduction

Nonmetallic Network

Matter composed of nonmetal atoms all held together by strong chemical bonds



Nonmetallic Network
(diamond)



Molecular Substance
(iodine)

Examples:	MP (^{o}C)
C_x (diamond)	3550
Si_x	1410
B_x	2075
$(SiO_2)_x$	1723

Attractive forces between nonmetal atoms:

Covalent Bonds

MPs and BPs: high, due to the strength of covalent bonds (~ 400 kJ/mol)

The strength of covalent bonds depends on:

1. The bond order of the covalent bonds

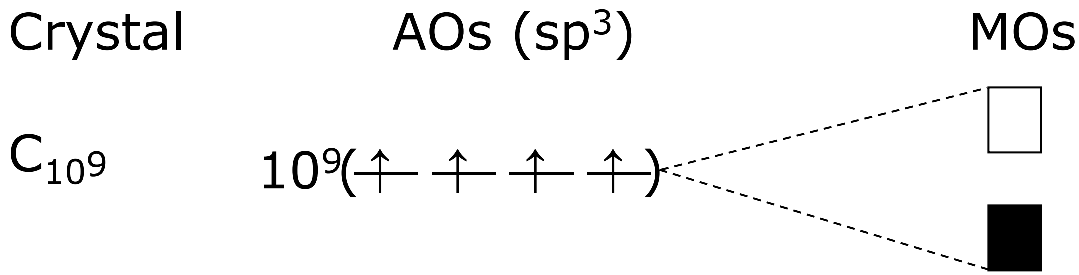
   Triple bonds are stronger than double bonds, double bonds are stronger than single bonds

2. Atom size

   The smaller the atoms, the smaller the bonding MOs, the greater the electron density in the MOs, the greater the attraction to the nuclei of the bonding atoms

H_2O Solubility: low

Electrical Conductivity: no



This energy gap between the bonding and antibonding MOs is called the band gap, or forbidden zone, and is the reason nonmetallic networks don’t conduct electricity

Too much energy would be required to move electrons from the valence band into the conduction band

Nonmetallic networks are insulators

Metalloids have a small band gap so they don't require a lot of energy to promote electrons into the antibonding MOs (conduction band)

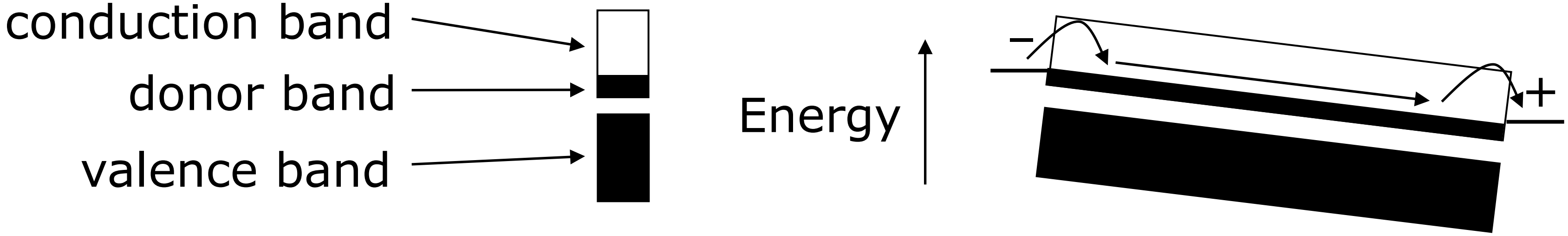
Crystal	Band Gap (kJ/mol)
C_x (diamond)	502
Silicon	105
Germanium	59
Tin	8

Metalloids are also called <u>semiconductors</u>

The conductivity of semiconductors can be increased by adding impurities

Silicon “doped” with phosphorus

The extra phosphorus electrons occupy a high energy level than the valence band, called the donor band

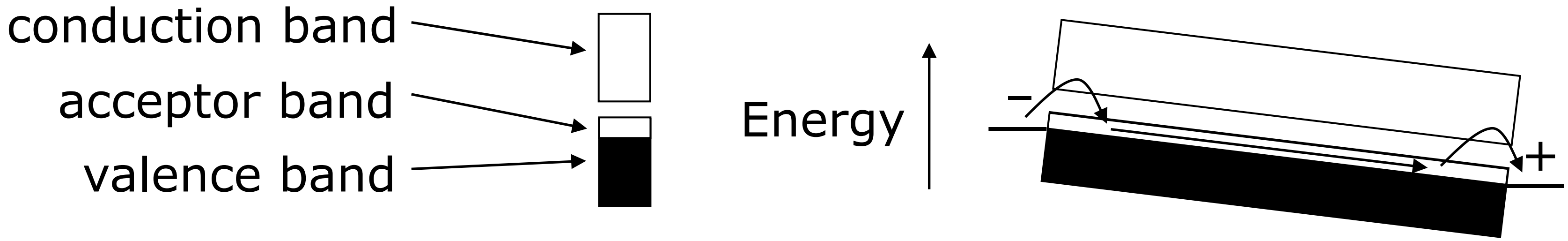


The donor band electrons can move in the conduction band toward the positive potential

Because of the extra negative electrons, these materials are called N-type conductors

Silicon “doped” with boron

The lack of boron electrons form a band higher in energy than the valence band, called the acceptor band



The valence band electrons can move in the acceptor band towards the positive potential

Because of the lack of negative electrons, these materials are called P-type conductors

Changes of State

Vaporization

- Liquid particles overcoming all attractive forces
- Through collisions, surface molecules can acquire enough kinetic energy to overcome attractive forces and vaporize

When vaporization and condensation rates are equal, a dynamic equilibrium is established

In a closed container, a vapor in equilibrium with it liquid exerts an <u>equilibrium vapor pressure</u>

- The EVP only changes with temperature

Boiling Point

The temperature at which the equilibrium vapor pressure above the liquid equals atmospheric pressure

Normal BP: The BP at 1 atm pressure

Heat of Vaporization (ΔH_{vap}) is the heat required to vaporize a liquid at its boiling point

Clausius-Clapeyron Equation:

$$Ln\left(\frac{P_{vap,T_1}}{P_{vap,T_2}}\right) = \frac{\Delta H_{vap}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \qquad R = 8.314 \text{ J/mol K}$$

Melting Point

The temperature at which the EVP of the solid equals the EVP of the liquid

Normal MP: The MP at 1 atm pressure

Heat of Fusion (ΔH_{fus}) is the heat required to melt a solid at its melting point

Sublimation

Solid particles overcoming all attractive forces (to become a gas)

In a closed container a solid and its vapor reach equilibrium

How much heat is needed to convert 50.0 g of ice at -20.0 ^oC to steam at 120.0 ^oC?

When warming/cooling… $q = mC\Delta T$

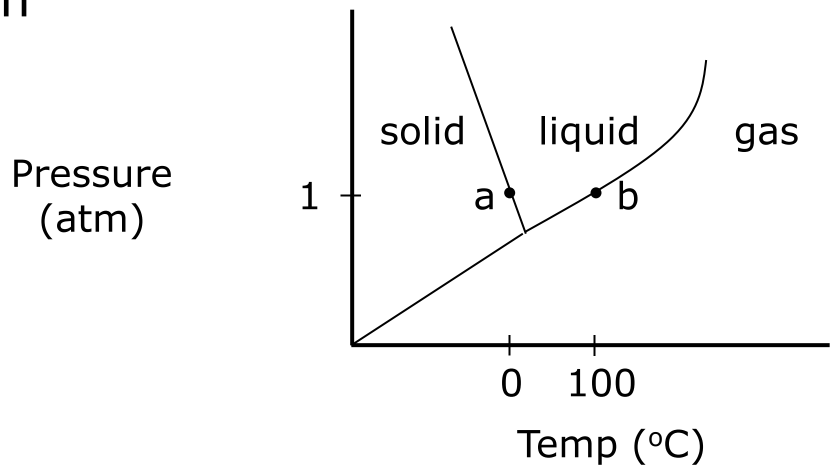
During phase change… $q = n\Delta H$ (or $m\Delta H$)

a	(2.22 J/g^{o}C)(50.0 g)(20.0 ^{o}C)	=	2220 J
b	(335 J/g)(50.0 g)	=	16<u>7</u>50 J
c	(4.18 J/g^{o}C)(50.0 g)(100.0 ^{o}C)	=	20900 J
d	(2260 J/g)(50.0 g)	=	113000 J
e	(2.01 J/g^{o}C)(50.0 g)(20.0 ^{o}C)	=	2010 J
	total	=	<u>155000 J</u>

Phase Diagrams

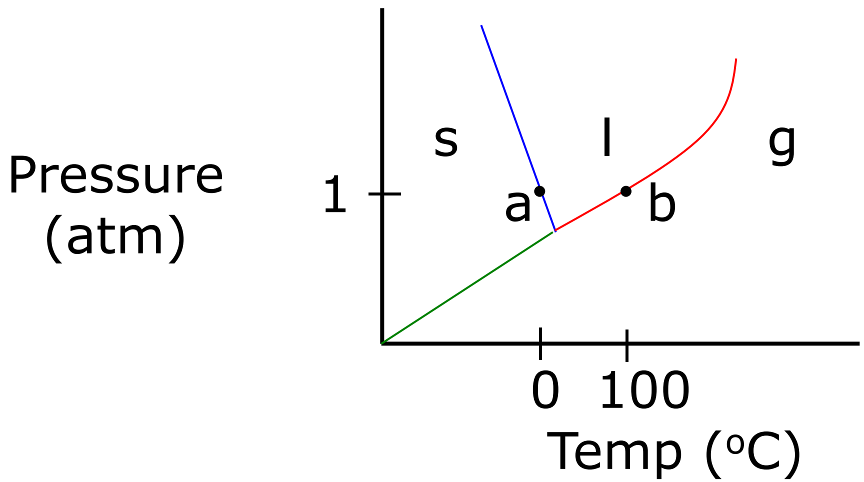
Many substances can exist as a solid, liquid, or gas, depending on the temperature and pressure

Phase Diagram



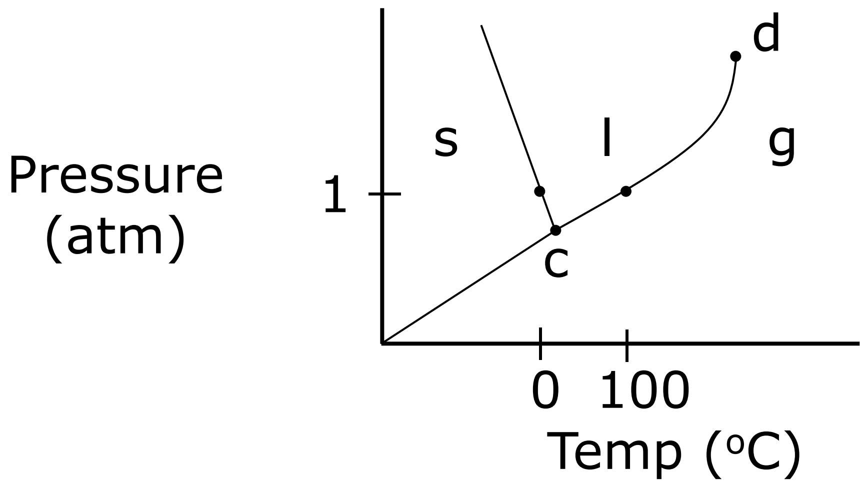
a normal melting point (T_m)

b normal boiling point (T_b)



Each line represents an equilibrium between phases

Blue Line:	solid / liquid equilibrium
Red Line:	liquid / gas equilibrium
Green Line:	solid / gas equilibrium



c the point where T and P allow solid, liquid, and gas to be in equilibrium: <u>triple point</u>

For water: T_3 = 0.0098 °C, P_3 = 0.0060 atm

d <u>Critical Point</u>

Critical Temperature is the highest temperature at which a substance can exist as a liquid

Critical Pressure is the pressure needed to make the substance a liquid at the critical temperature

For water: $T_c = 374\ ^oC$, $P_c = 218$ atm

About water...

The solid-liquid line has negative slope

Increasing the pressure will produce a more dense phase, so increasing the pressure on ice produces liquid water