Materials Science and Engineering I

Chapter Outline

- **Review of Atomic Structure**
  Electrons, Protons, Neutrons, Quantum number of atoms, Electron states, The Periodic Table
- **Atomic Bonding in Solids**
  Bonding Energies and Forces
- **Periodic Table**
- **Primary Interatomic Bonds**
  Ionic, Covalent, Metallic
- **Secondary Bonding (Van der Waals)**
  Three types of Dipole Bonds
- **Molecules and Molecular Solids**
  Understanding of interatomic bonding is the first step Towards understanding/explaining materials properties

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Structure of Atoms

ATOM

Basic Unit of an Element

Diameter : 10^{-10} m.

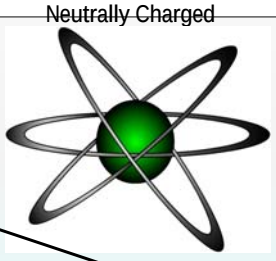
Neutrally Charged

Nucleus

Diameter : 10^{-14} m

Accounts for almost all mass

Positive Charge

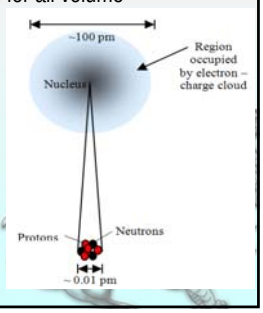


Electron Cloud

Mass : 9.109×10^{-28} g

Charge : -1.602×10^{-9} C

Accounts for all volume



Proton

Mass : 1.673×10^{-24} g

Charge : 1.602×10^{-19} C

Neutron

Mass : 1.675×10^{-24} g

Neutral Charge

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Review of Atomic Structure

Atoms = nucleus (protons and neutrons) + electrons

Charges:

Electrons and protons have negative and positive charges of the same magnitude, 1.6×10^{-19} Coulombs. Neutrons are electrically neutral.

Masses:

Protons and Neutrons have the same mass, 1.67×10^{-27} kg. Mass of an electron is much smaller, 9.11×10^{-28} kg and can be neglected in calculation of atomic mass.

The atomic mass (A) = mass of protons + mass of neutrons

 # protons gives chemical identification of the element

 # protons = atomic number (Z)

 # neutrons defines isotope number

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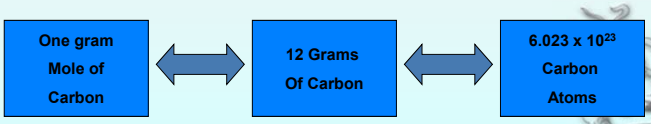
Atomic Number and Atomic Mass

- **Atomic Number** = Number of Protons in the nucleus
- Unique to an element
  - Example :- Hydrogen = 1, Uranium = 92
- **Relative atomic mass** = Mass in grams of 6.02×10^{23} (*Avagadro Number*) Atoms.
  - Example :- Carbon has 6 Protons and 6 Neutrons. Atomic Mass = 12.
- One Atomic Mass unit is $1/12^{th}$ of mass of carbon atom.
- One gram mole = Gram atomic mass of an element.
  - Example :-



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Example Problem

- A 100 gram alloy of nickel and copper consists of 75 wt% Cu and 25 wt% Ni. What are percentage of Cu and Ni Atoms in this alloy?

  Given:- 75g Cu Atomic Weight 63.54

  25g Ni Atomic Weight 58.69

- Number of gram moles of Cu = $\frac{75\ g}{63.54\ g/mol} = 1.1803\ mol$
- Number of gram moles of Ni = $\frac{25\ g}{58.69\ g/mol} = 0.4260\ mol$
- Atomic Percentage of Cu = $\frac{1.1803}{(1.1803 + 0.4260)} \times 100 = 73.5\%$
- Atomic Percentage of Ni = $\frac{0.4260}{(1.1803 + 0.4260)} \times 100 = 25.5\%$

Example Problem 2.2

An intermetallic compound has the chemical formula Ni_xAl_y, where x and y are simple integers, and consists of 42.04 wt% nickel and 57.96 wt% aluminum. What is the simplest formula of this nickel aluminide?

■ **Solution**

We first determine the mole fraction of nickel and aluminum in this compound. Using a basis of 100 g of the compound, we have 424.04 g of Ni and 57.96 g of Al. Thus,

No. of moles of Ni = 42.04 g Ni × (1 mol Ni /58.71 g Ni) = 0.7160 mol
No. of moles of Al = 57.96 g Al × (1 mol Al /26.98 g Al) = 2.148 mol
Total = 2.864 mol

Thus,

mole fraction of Ni = 0.1760 / 2.864 = 0.25
mole fraction of Al = 2.148 / 2.864 = 0.75

The simplest formula in terms of gram-mole fraction becomes $Ni_{0.25}Al_{0.75}$. To express this in integer form we multiply both fractions by four, resulting in $NiAl_3$.

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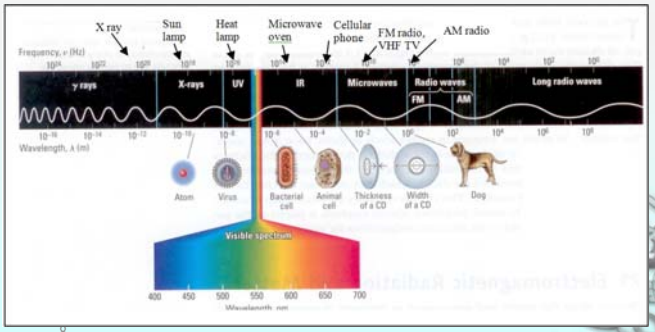
Planck's Quantum Theory

- Max Planck, discovered that atoms and molecules emit energy only in certain discrete quantities, called quanta.
- James Clerk Maxwell proposed that the nature of visible light is in the form of electromagnetic radiation.
- **$E = h\upsilon = hc/\lambda$**
- Energy is always released in integer multiples of hυ



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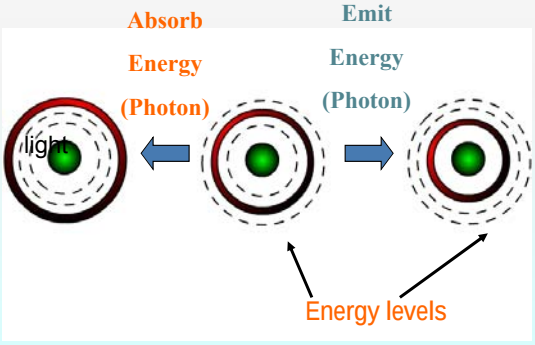
Electron Structure of Atoms

- Electron rotates at definite energy levels.
- Energy is absorbed to move to higher energy level.
- Energy is emitted during transition to lower level.
- Energy change due to transition = $\Delta E = \frac{hc}{\lambda}$



h=Planks Constant
= 6.63 x 10^{-34} J.s
c= Speed of light
λ = Wavelength of

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Energy in Hydrogen Atom

- Hydrogen atom has one proton and one electron
- Energy of hydrogen atoms for different energy levels is given by (n=1,2…..) *principal quantum numbers*

$$E = -\frac{13.6}{n^2} ev$$

- **Example:-** If an electron undergoes transition from n=3 state to n=2 state, the energy of photon emitted is

$$\Delta E = -\frac{13.6}{3^2} - \frac{13.6}{2^2} = 1.89 ev$$

- Energy required to completely remove an electron from hydrogen atom is known as *ionization energy*

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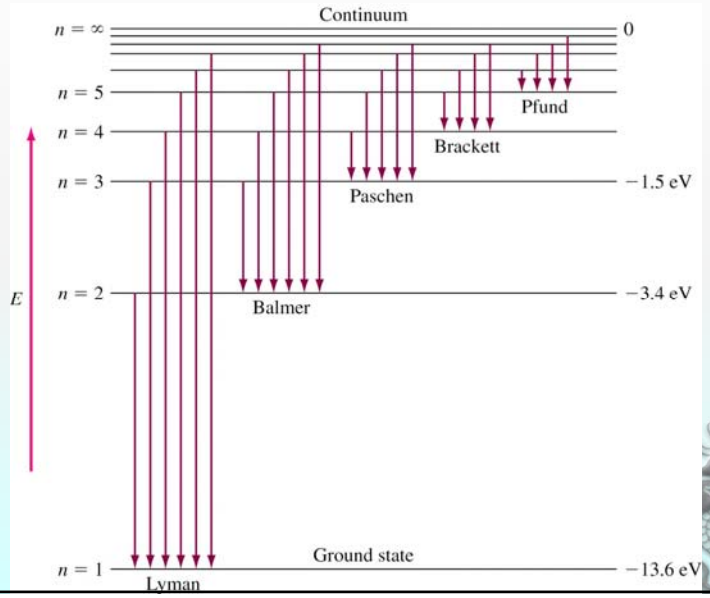
Energy-Level diagram for the line spectrum of hydrogen



Example Problem 2.3

A hydrogen atom exists with its electron in the $n = 3$ state. The electron undergoes a transition to $n = 2$ state. Calculate (a) the energy of the corresponding photon, (b) its frequency, and (c) its wavelength. (d) Is the energy absorbed or emitted, and (e) which series does it belong to and what specific type of emission does it represent?

■ **Solution**

a. Energy of the photon emitted is

$$E = \frac{-13.6\ \text{eV}}{n^2} \tag{2.3}$$

$$\Delta E = E_3 - E_2$$

$$= \frac{-13.6}{3^2} - \frac{-13.6}{2^2} = 1.89\ \text{eV} \blacktriangleleft$$

$$= 1.89\ \text{eV} \times \frac{1.60 \times 10^{-19}\ \text{J}}{\text{eV}} = 3.02 \times 10^{-19}\ \text{J} \blacktriangleleft$$

b. The frequency of the photon is

$$\Delta E = h\nu$$

$$\nu = \frac{\Delta E}{h} = \frac{3.02 \times 10^{-19}\ \text{J}}{6.63 \times 10^{-34}\ \text{J} \cdot \text{s}}$$

$$= 4.55 \times 10^{14}\ \text{s}^{-1} = 4.55 \times 10^{14}\ \text{Hz} \blacktriangleleft$$

c. The wavelength of the photon is

$$\Delta E = \frac{hc}{\lambda}$$

or

$$\lambda = \frac{hc}{\Delta E} = \frac{(6.63 \times 10^{-34}\ \text{J} \cdot \text{s})(3.00 \times 10^{8}\ \text{m/s})}{3.02 \times 10^{-19}\ \text{J}}$$

$$= 6.59 \times 10^{-7}\ \text{m}$$

$$= 6.59 \times 10^{-7}\ \text{m} \times \frac{1\ \text{nm}}{10^{-9}\ \text{m}} = 659\ \text{nm} \blacktriangleleft$$

d. Energy is released as its quantity is positive, and the electron is transitioning from a higher orbit to a lower orbit.

e. The emission belongs to the Blamer series (Fig. 2.6) and corresponds to the visible red light (Fig. 2.4).

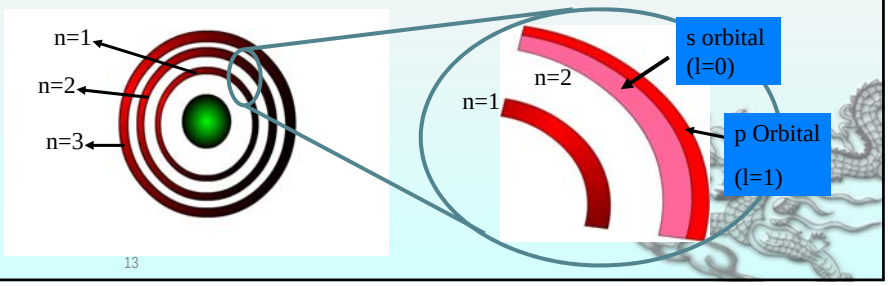
Quantum Numbers of Electrons of Atoms

Principal Quantum Number (n)

- Represents main energy levels.
- Range 1 to 7.
- Larger the 'n' higher the energy.

Subsidiary Quantum Number (l)

- Represents sub energy levels (orbital).
- Range 0…n-1.
- Represented by letters s,p,d and f.



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Quantum Numbers of Electrons of Atoms (Cont..)

Magnetic Quantum Number m_l

- Represents spatial orientation of single atomic orbital.
- Permissible values are –l to +l.
- Example:- if l=1, m_l = -1,0,+1.

  I.e. 2l+1 allowed values.
- No effect on energy.

Electron spin quantum number m_s

- Specifies two directions of electron spin.
- Directions are clockwise or anticlockwise.
- Values are +1/2 or –1/2.
- Two electrons on same orbital have opposite spins.
- No effect on energy.

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S, p and d Orbitals

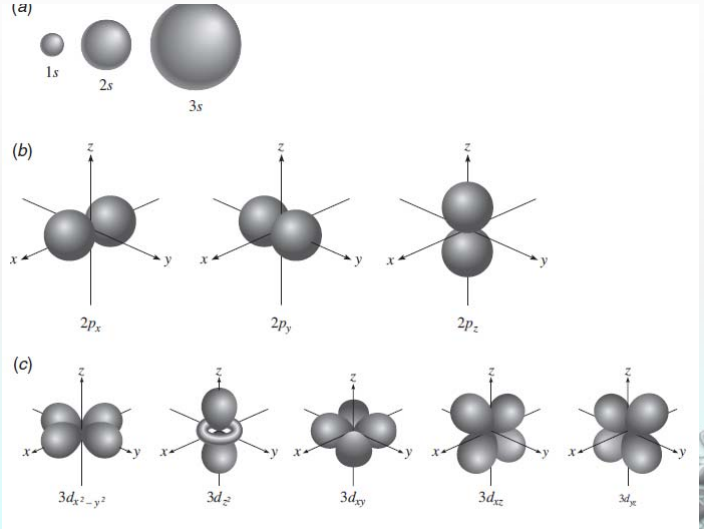
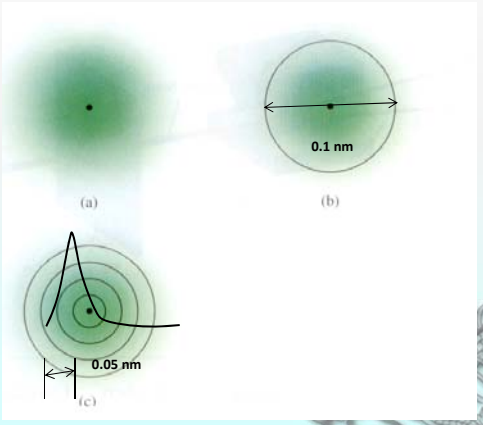


Figure 2.8.
Schematic diagram of (*a*) s, (*b*) p, and (*c*) d orbitals.

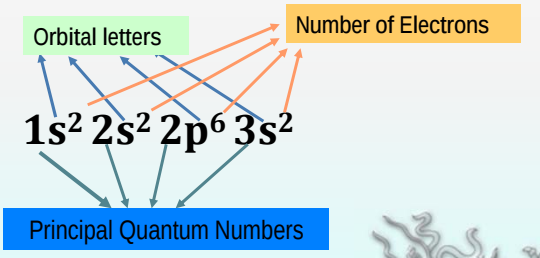
Electron Density

- Solution of the wave equation is in terms of a wave function, ψ (**orbitals**).
- The square of the wave function represents electron density.
- Boundary surface representation.
- Total probability



Electron Structure of Multielectron Atom

- Maximum number of electrons in each atomic shell is given by $2n^2$.
- Atomic size (radius) increases with addition of shells.
- **Electron Configuration** lists the arrangement of electrons in orbitals.
  - Example :-



  - For Iron, (Z=26), Electronic configuration is
    $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^6\ 4s^2$

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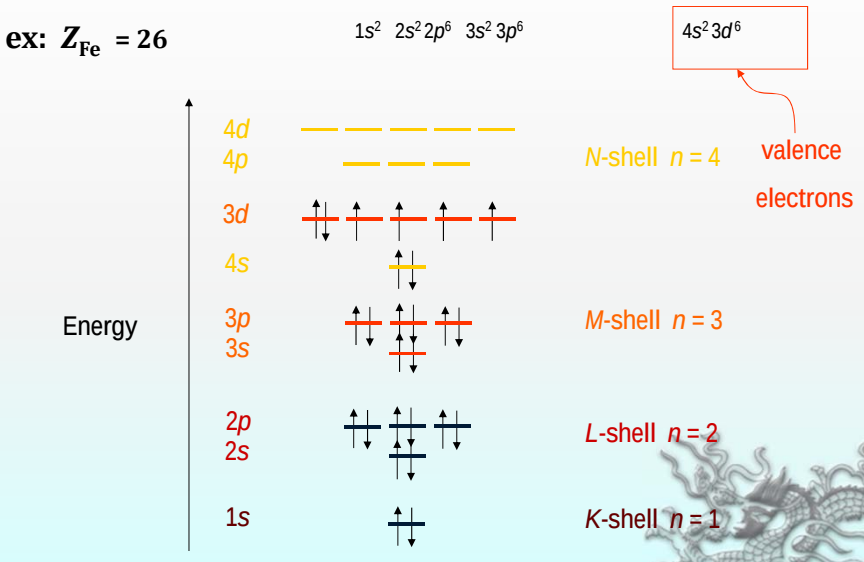
Electronic Configurations

ex: $Z_{Fe} = 26$



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Orbital Box Diagram

- Elements are classified according to their ground state electron configuration.

	Electron Configuration	Orbital Box Diagram (1s 2s 2p)
H	$1s^1$	↑
He	$1s^2$	↑↓
Li	$1s^2 2s^1$	↑↓ ↑
Be	$1s^2 2s^2$	↑↓ ↑↓
B	$1s^2 2s^2 2p^1$	↑↓ ↑↓ ↑ □ □
C	$1s^2 2s^2 2p^2$	↑↓ ↑↓ ↑ ↑ □
N	$1s^2 2s^2 2p^3$	↑↓ ↑↓ ↑ ↑ ↑
O	$1s^2 2s^2 2p^4$	↑↓ ↑↓ ↑↓ ↑ ↑
F	$1s^2 2s^2 2p^5$	↑↓ ↑↓ ↑↓ ↑↓ ↑
Ne	$1s^2 2s^2 2p^6$	↑↓ ↑↓ ↑↓ ↑↓ ↑↓

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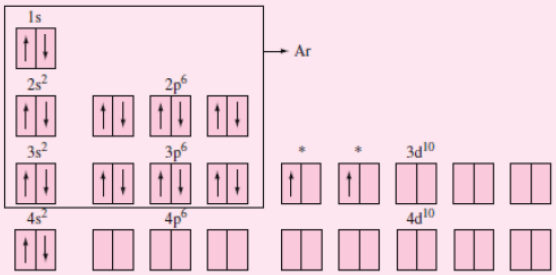
Example Problem 2.6

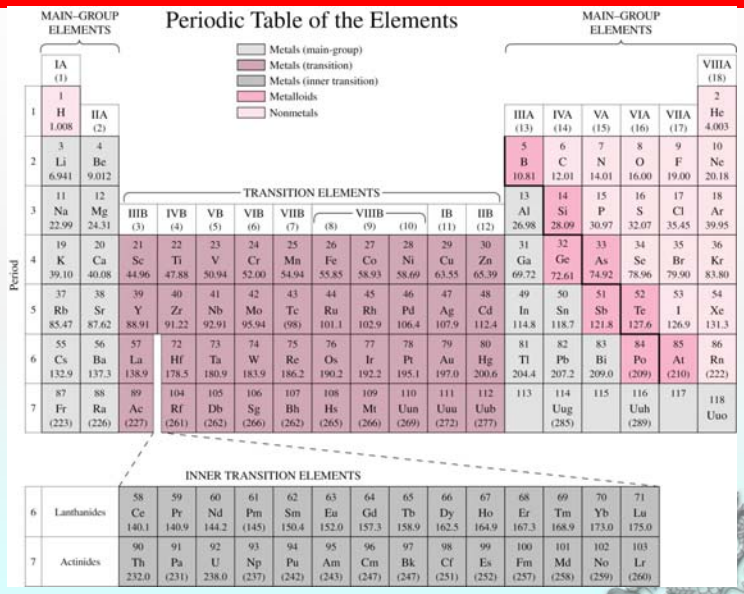
Show the electronic structure of the atom titanium (Ti) using the orbital box diagram.

■ **Solution**

Ti has 22 electrons. Therefore, the inner core electrons will have the structure of the noble gas argon, $\mathbf{1s^2 2s^2 2p^6 3s^2 3p^6}$, accounting for 18 of the 22 electrons. Four electrons remain. After the 3p orbital is filled, according to Fig. 2.9, the next orbital to be filled is not 3d and is instead 4s. As explained previously this is because the energy level of the 4s orbital is lower than the 3d orbital. The next two electrons (nineteenth and twentieth) occupy $4s^1$ and $4s^2$. Finally, the last two electrons (*twenty-first and *twenty-second) will then fill the available slots in d orbital as shown in the figure, $[Ar]4s^2 3d^2$.



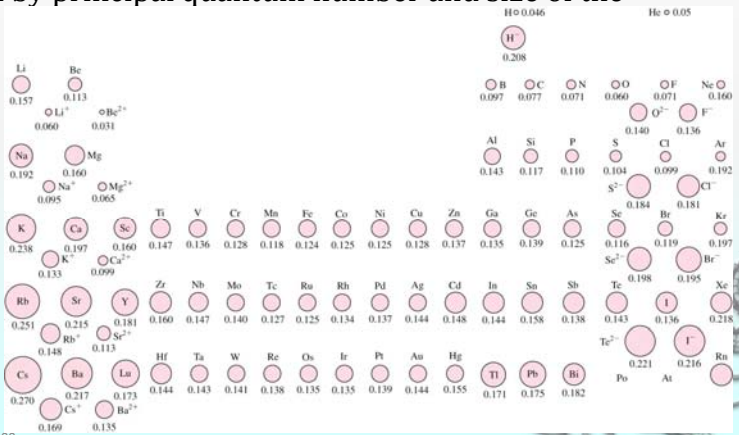
Periodic Table



Source: Davis, M. and Davis, R., Fundamentals of Chemical Reaction Engineering, McGraw-Hill, 2003

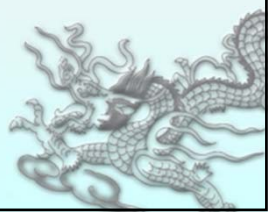
Periodic Variations in Atomic Size

- Atomic size: half the distance between the nuclei of two adjacent atoms (metallic radius) OR identical (covalent radius).
- Affected by principal quantum number and size of the nucleus.



Atomic Structure

- **Valence electrons** determine all of the following properties
  1) Chemical
  2) Electrical
  3) Thermal
  4) Optical



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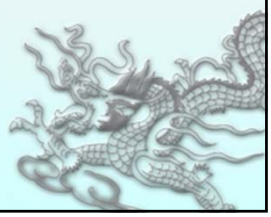
Electron Structure and Chemical Activity

- **Except Helium, most *noble gasses* (Ne, Ar, Kr, Xe, Rn) are chemically very stable**
  - **All have s^2 p^6 configuration for outermost shell.**
  - **Helium has $1s^2$ configuration**
- **Electropositive elements give electrons during chemical reactions to form *cations*.**
  - **Cations are indicated by positive oxidation numbers**
  - **Example:-**

    Fe : $1s^2$ $2s^2$ sp^6 $3s^2$ $3p^6$ $3d^6$ $4s^2$

    Fe^{2+} : $1s^2$ $2s^2$ sp^6 $3s^2$ $3p^6$ $3d^6$

    Fe^{3+} : $1s^2$ $2s^2$ sp^6 $3s^2$ $3p^6$ $3d^5$



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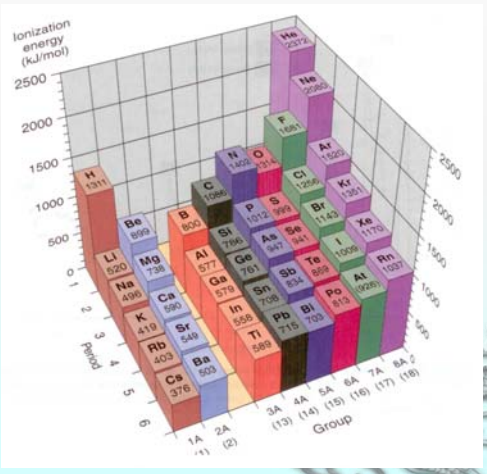
Trends in Ionization Energy

- Energy required to remove an electron from its atom.
- **First ionization energy** plays the key role in the chemical reactivity.
- As the atomic size decreases it takes more energy to remove an electron.
- as the first outer core electron is removed, it takes more energy to remove a second outer core electron



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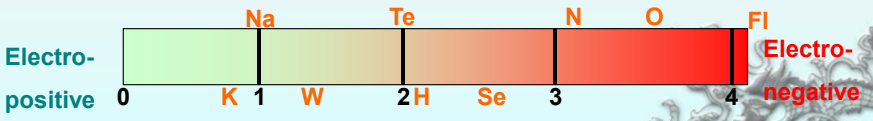
Electron Structure and Chemical Activity (Cont..)

- **Electronegative elements accept electrons during chemical reaction.**
- **Some elements behave as both electronegative and electropositive.**
- **Electronegativity is the degree to which the atom attracts electrons to itself**
  - **Measured on a scale of 0 to 4.1**
  - **Example :- Electronegativity of Fluorine is 4.1**
    Electronegativity of Sodium is 1.



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Electronegativity

- Ranges from χ = 0.7 to 4.0, dimensionless!
- Large values: tendency to acquire electrons.

IA																	0
H 2.1	IIA											IIIA	IVA	VA	VIA	VIIA	He –
Li 1.0	Be 1.5											B 2.0	C 2.5	N 3.0	O 3.5	F 4.0	Ne –
Na 0.9	Mg 1.2	IIIB	IVB	VB	VIB	VIIB	VIII			IB	IIB	Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0	Ar –
K 0.8	Ca 1.0	Sc 1.3	Ti 1.5	V 1.6	Cr 1.6	Mn 1.5	Fe 1.8	Co 1.8	Ni 1.8	Cu 1.9	Zn 1.6	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8	Kr –
Rb 0.8	Sr 1.0	Y 1.2	Zr 1.4	Nb 1.6	Mo 1.8	Tc 1.9	Ru 2.2	Rh 2.2	Pd 2.2	Ag 1.9	Cd 1.7	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5	Xe –
Cs 0.7	Ba 0.9	La–Lu 1.1–1.2	Hf 1.3	Ta 1.5	W 1.7	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9	Tl 1.8	Pb 1.8	Bi 1.9	Po 2.0	At 2.2	Rn –
Fr 0.7	Ra 0.9	Ac–No 1.1–1.7															

TM: Uniformly low EN

Larger electronegativity

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The Periodic Table

Metal

Nonmetal

Intermediate

IA																	0
1 H	IIA											IIIA	IVA	VA	VIA	VIIA	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg	IIIB	IVB	VB	VIB	VIIB	VIII			IB	IIB	13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	Rare earth series	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	Acti-nide series	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds								

Electropositive elements:
Readily give up electrons
to become + ions.

Electronegative elements:
Readily acquire electrons
to become - ions.

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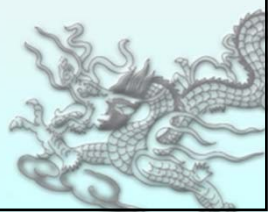
Trends in Electron Affinity

- **Electron affinity**: Tendency to accept one or more electrons and release energy.
- Electron affinity increases (more energy is released after accepting an electron) as we move to the right across a period and decreases as we move down in a group.
- Groups 6A and 7A have in general the highest electron affinities.



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Types of Bonding

Primary bonding: e- are transferred or shared

Strong (100-1000 KJ/mol or 1-10 eV/atom)

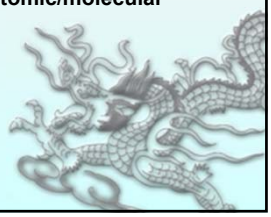
Three primary bonding combinations : 1) metal-nonmetal, 2) nonmetal-nonmetal, and 3) metal-metal

- **Ionic: Strong Coulomb interaction among negative atoms (have an extra electron each) and positive atoms (lost an electron). Example - Na^+Cl^-**
- **Covalent: electrons are shared between the molecules, to saturate the valency. Example -H_2**
- **Metallic: the atoms are ionized, loosing some electrons from the valence band. Those electrons form a electron sea, which binds the charged nuclei in place**

Secondary Bonding: no e- *transferred or shared* Interaction of atomic/molecular dipoles

Weak (< 100 KJ/mol or < 1 eV/atom)

- **Fluctuating Induced Dipole (inert gases, H_2, Cl_2…)**
- **Permanent dipole bonds (polar molecules - H_2O, HCl...)**



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Ionic Bonding (I)

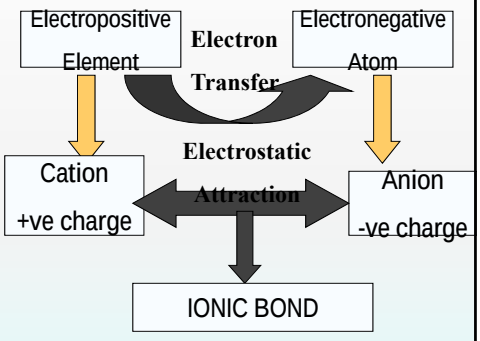
Formation of ionic bond:

1.Mutual ionization occurs by electron transfer (remember electronegativity table)

- **Ion = charged atom**
- **Anion = negatively charged atom**
- **Cation = positively charged atom**

2. Ions are attracted by strong coulombic interaction

- **Oppositely charged atoms attract**
- **An ionic bond is non-directional (ions may be attracted to one another in any direction**



Ionic Bonding - Example

Ionic bond – metal + nonmetal

donates electrons

accepts electrons

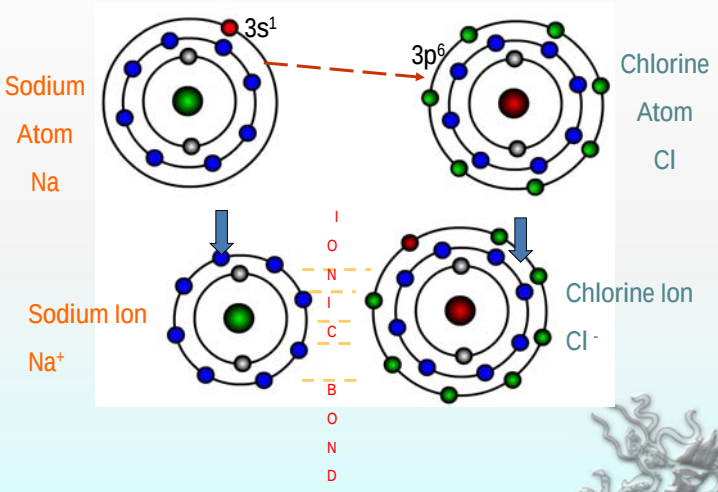
ex: MgO Mg $1s^2\ 2s^2\ 2p^6\ 3s^2$ O $1s^2\ 2s^2\ 2p^4$

[Ne] $3s^2$

Mg^{2+} $1s^2\ 2s^2\ 2p^6$ [Ne]

O^{2-} $1s^2\ 2s^2\ 2p^6$ [Ne]

Ionic Bonding - Example



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Ionic Force for Ion Pair

- Nucleus of one ion attracts electron of another ion.
- The electron clouds of ion repulse each other when they are sufficiently close.

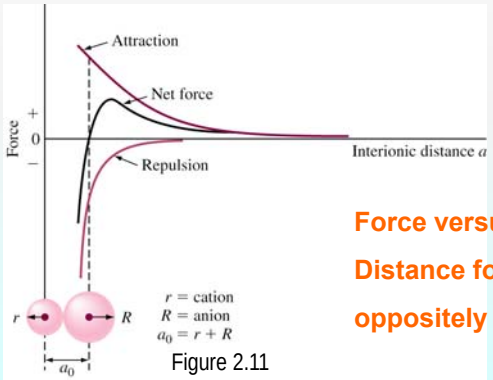

Figure 2.11

Force versus separation Distance for a pair of oppositely charged ions

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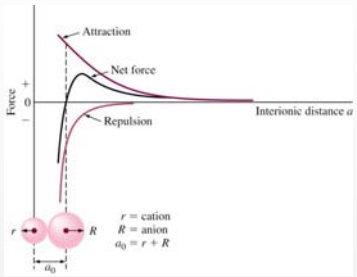
Ion Force for Ion Pair (Cont..)

$$F_{attractive} = -\frac{(Z_1 e)(Z_2 e)}{(4\pi\varepsilon_0 a^2)} = -\frac{Z_1 Z_2 e^2}{(4\pi\varepsilon_0 a^2)}$$



Z_1, Z_2 = Number of electrons removed or added during ion formation

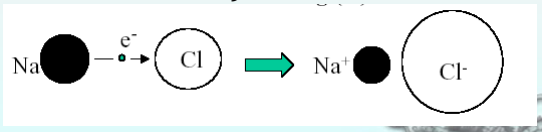
e = Electron Charge

a = Interionic seperation distance

ε = Permeability of free space ($8.85 \times 10^{-12} c^2/Nm^2$)

$$F_{repulsive} = -\frac{nb}{a^{n+1}}$$

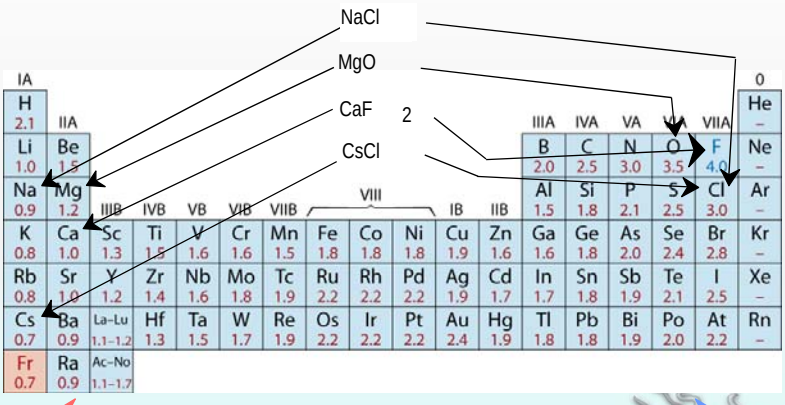
(n and b are constants)



$$F_{net} = -\frac{Z_1 Z_2 e^2}{(4\pi\varepsilon_0 a^2)} - \frac{nb}{a^{n+1}}$$

Attraction Force — Repulsion Force

- Predominant bonding in Ceramics



Adapted from Fig. 2.7, *Callister 7e.* (Fig. 2.7 is adapted from Linus Pauling, *The Nature of the Chemical Bond*, 3rd edition, Copyright 1939 and 1940, 3rd edition. Copyright 1960 by Cornell University.

Interionic Force - Example

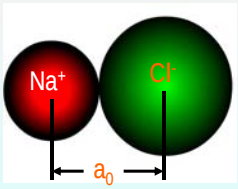
Force of attraction between Na^+ and Cl^- ions

Z_1 = +1 for Na^+, Z_2 = -1 for Cl^-

e = 1.60 x 10^{-19} C , ε_0 = 8.85 x 10^{-12} C^2/Nm^2

a_0 = Sum of Radii of Na^+ and Cl^- ions

= 0.095 nm + 0.181 nm = 2.76 x 10^{-10} m



$$F_{attraction} = -\frac{Z_1 Z_2 e^2}{(4\pi\varepsilon_0 a^2)} = -\frac{(+1)(-1)(1.60\times10^{-19}C)^2}{4\pi(8.85\times10^{-12}\ C^2/Nm2)(2.76\times10^{-10}\ m)} = +3.02\times10^{-9}N$$

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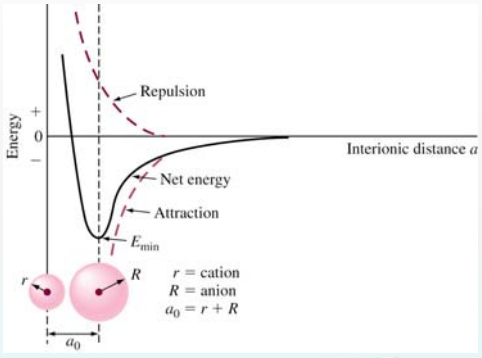
Interionic Energies for Ion Pairs

- **Net potential energy for a pair of oppositely charged ions =**

$$E_{net} = \underbrace{\frac{Z_1 Z_2 e^2}{(4\pi\varepsilon_0 a)}}_{\text{Attraction Energy}} + \underbrace{\frac{b}{a^n}}_{\text{Repulsion Energy}}$$

Attraction Energy → Energy Released

Repulsion Energy → Energy Absorbed



- **E_{net} is minimum when ions are at equilibrium seperation distance a_0**

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Example Problem 2.7

If the attractive force between Mg^{2+} and S^{2-} ions at equilibrium is 1.49×10^{-9} N, calculate (a) the corresponding interionic distance. If S^{2-} ion has a radius of 0.184 nm, calculate (b) the ionic radius for Mg^{2+} and (c) the repulsion force between the two ions at this position.

■ **Solution**

The value of a_0, the sum of the Mg^{2+} and S^{2-} ionic radii, can be calculated from a rearranged form of Coulomb's law.

a.
$$a_0 = \sqrt{\frac{-Z_1 Z_2 e^2}{4\pi\epsilon_0 F_{\text{attraction}}}}$$

$$Z_1 = +2 \text{ for } Mg^{2+} \qquad Z_2 = -2 \text{ for } S^{2-}$$
$$|e| = 1.60 \times 10^{-19}\,\text{C} \qquad \epsilon_0 = 8.85 \times 10^{-12}\,\text{C}^2/(\text{N}\cdot\text{m}^2)$$
$$F_{\text{attractive}} = 1.49 \times 10^{-9}\,\text{N}$$

Thus,
$$a_0 = \sqrt{\frac{-(2)(-2)(1.60 \times 10^{-19}\,\text{C})^2}{4\pi[8.85 \times 10^{-12}\,\text{C}^2/(\text{N}\cdot\text{m}^2)](1.49 \times 10^{-8}\,\text{N})}}$$
$$= 2.49 \times 10^{-10}\,\text{m} = 0.249\,\text{nm}$$

b.
$$a_0 = r_{Mg^{2+}} + r_{s^{2-}}$$

or
$$0.249\,\text{nm} = r_{Mg^{2+}} + 0.184\,\text{nm}$$
$$r_{Mg^{2+}} = 0.065\,\text{nm} \blacktriangleleft$$

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Example Problem 2.8

The repulsion force between Na^+ ($r = 0.095$ nm) and Cl^- ($r = 0.181$) ions at equilibrium is -3.02×10^{-9} N. Calculate (a) the value of constant b using the repulsive force section of Eq. 2.8, and (b) the bonding energy, E_{min}. Assume $n = 9$.

■ **Solution**

a. To determine the b value for a NaCl ion pair,

$$F = -\frac{nb}{a^{n+1}} \qquad (2.6)$$

The repulsive force between a Na^+Cl^- ion pair is -3.02×10^{-9} N.
Thus,
$$-3.02 \times 10^{-9}\,\text{N} = \frac{-9b}{(2.76 \times 10^{-10}\,\text{m})^{10}}$$
$$b = 8.59 \times 10^{-106}\,\text{N}\cdot\text{m}^{10} \blacktriangleleft$$

b. To calculate the potential energy of the Na^+Cl^- ion pair,

$$E_{Na^+Cl^-} = \frac{+Z_1 Z_2 e^2}{4\pi\epsilon_0 a} + \frac{b}{a^n}$$
$$= \frac{(+1)(-1)(1.60 \times 10^{-19}\,\text{C})^2}{4\pi[8.85 \times 10^{-12}\,\text{C}^2/(\text{N}\cdot\text{m}^2)](2.76 \times 10^{-10}\,\text{m})} + \frac{8.59 \times 10^{-106}\,\text{N}\cdot\text{m}^{10}}{(2.76 \times 10^{-10}\,\text{m})^9}$$
$$= -8.34 \times 10^{-19}\,\text{J}^* + 0.92 \times 10^{-19}\,\text{J}^*$$
$$= -7.42 \times 10^{-19}\,\text{J} \blacktriangleleft$$

*1J = 1N·m

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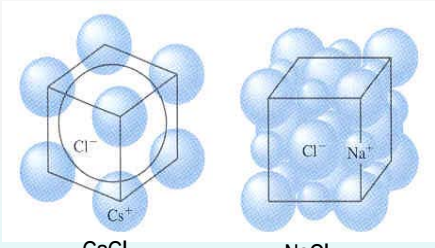
Ion Arrangements in Ionic Solids

- Ionic bonds are *Non Directional*
- Geometric arrangements are present in solids to maintain electric neutrality.
  - Example:- in NaCl, six Cl- ions pack around central Na+ Ions



CsCl NaCl

Figure 2.13

Ionic packing In NaCl and CsCl

2-20 41

Bonding Energies

- Lattice energies and melting points of ionically bonded solids are high.
- Lattice energy decreases when size of ion increases.
- Multiple bonding electrons increase lattice energy.

  - Example :-

NaCl	Lattice energy = 766 KJ/mol
	Melting point = 801°C
CsCl	Lattice energy = 649 KJ/mol
	Melting Point = 646°C
BaO	Lattice energy = 3127 KJ/mol
	Melting point = 1923°C

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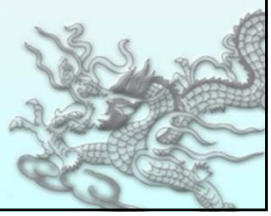
Bonding Energy

- Consider production of LiF: result in the release of about 617 kJ/mole.
- **Step 1.** Converting solid Li to gaseous Li ($1s^2 2s^1$): 161 kJ/mole of energy.
- **Step 2**. Converting the F_2 molecule to F atoms: 79.5 kJ/mole.
- **Step 3.** Removing the $2s^1$ electron of Li to form a cation, Li^+: 520 kJ/mole.
- **Step 4.** Transferring or adding an electron to the F atom to form an anion, F^-: -328 kJ/mole.
- **Step 5.** Formation of an ionic solid from gaseous ions: **lattice energy ,** unknown=-617 kJ – [161 kJ + 79.5 kJ + 520 kJ – 328 kJ] = *-1050 kJ*

Hess law $\triangle H^0 = \triangle H^1 + \triangle H^2 + \triangle H^3 + \triangle H^4 + \triangle H^5$

$\triangle H^5 = \triangle H^0 - \triangle H^1 + \triangle H^2 + \triangle H^3 + \triangle H^4 = -1050$ kj



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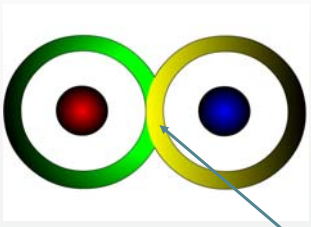
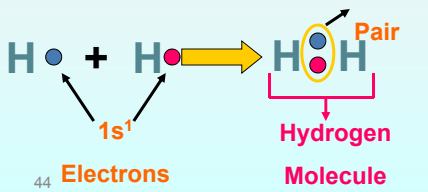
Covalent Bonding

- **In covalent bonding, outer s and p electrons are shared between two atoms to obtain noble gas configuration.**
- **Takes place between elements with small differences in *electronegativity* and close by in periodic table.**
- **In Hydrogen, a bond is formed between 2 atoms by sharing their $1s^1$ electrons**



Overlapping Electron Clouds



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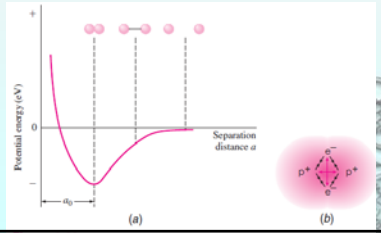


Covalent Bonding - Examples

In case of F_2, O_2 and N_2, covalent bonding is formed by sharing p electrons

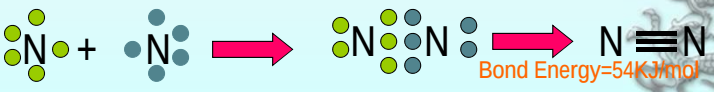
- Fluorine gas (Outer orbital – $2s^2\ 2p^5$) share one p electron to attain noble gas configuration.



- Oxygen (Outer orbital - $2s^2\ 2p^4$) atoms share two p electrons



- Nitrogen (Outer orbital - $2s^2\ 2p^3$) atoms share three p electrons



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Covalent Bonding

Formation of covalent bonds:

- Cooperative sharing of valence electrons
- Can be described by orbital overlap
- Covalent bonds are HIGHLY directional
- Bonds - in the direction of the greatest orbital overlap
- Covalent bond model: an atom can covalently bondwith at most 8-N', N' = number of valence electrons

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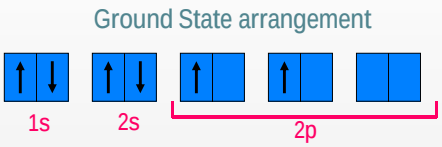
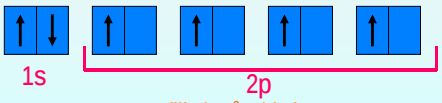
Covalent Bonding in Carbon

- Carbon has electronic configuration $1s^2\ 2s^2\ 2p^2$



Indicates carbon Forms two Covalent bonds

- *Hybridization* causes one of the 2s orbitals promoted to 2p orbital. Result ⇒ four sp3 orbitals.



Indicates four covalent bonds are formed

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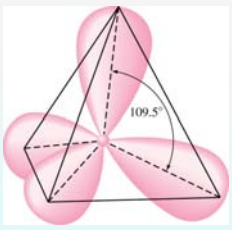
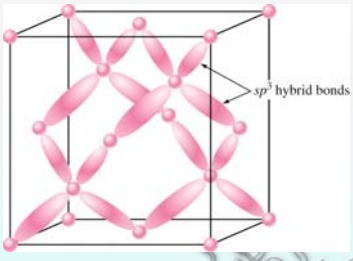
Structure of Diamond

- Four sp^3 orbitals are directed *symmetrically* toward corners of regular tetrahedron.
- This structure gives high hardness, high bonding strength (711KJ/mol) and high melting temperature (3550°C).



Carbon Atom



Tetrahedral arrangement in diamond

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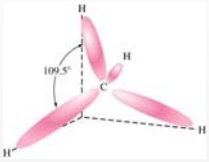
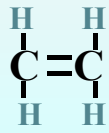
Carbon Containing Molecules

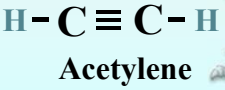
- In Methane, Carbon forms four covalent bonds with Hydrogen. (hydrocarbons)
- Molecules are very weekly bonded together resulting in low melting temperature (-183°C). **Intramolecular bonding: 1650 kl/mole; intermolecular bonding: 8kj/mole**
- Carbon also forms bonds with itself.
- Molecules with multiple carbon bonds are more reactive. –unsaturated bond
  - Examples:-



Methane molecule



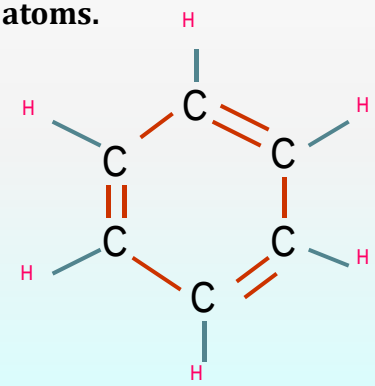
Ethylene



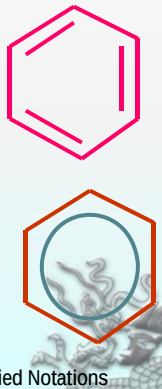
Acetylene

Covalent Bonding in Benzene

- **Chemical composition of Benzene is C_6H_6.**
- **The Carbon atoms are arranged in hexagonal ring.**
- **Single and double bonds alternate between the atoms.**



Structure of Benzene



Simplified Notations

Figure 2.23

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Metallic Bonding

- Atoms in metals are closely packed in crystal structure.
- Loosely bounded valence electrons are attracted towards nucleus of other atoms.
- Electrons spread out among atoms forming electron clouds.
- These free electrons are reason for electric conductivity and ductility
- Since outer electrons are shared by many atoms, metallic bonds are *Non-directional*

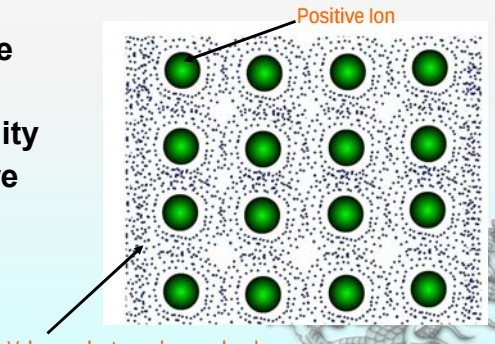

Figure 2.24

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Metallic Bonds (Cont..)

- **Overall energy** of individual atoms are lowered by metallic bonds
- Minimum energy between atoms exist at equilibrium distance a_0
- Fewer the number of valence electrons involved, more metallic the bond is.
  - Example:- Na ⇒ Bonding energy 108KJ/mol, Melting temperature 97.7°C
- Higher the number of valence electrons involved, higher is the bonding energy.
  - Example:- Ca ⇒ Bonding energy 177KJ/mol, Melting temperature 851°C

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Mixed Bonding

- Ionic-Covalent Mixed Bonding

$$\%\ \text{ionic character} = \left(1 - e^{-\frac{(\chi_A - \chi_B)^2}{4}}\right) \cdot 100\%$$

where χ_A & χ_B are Pauling electronegativities

Ex: MgO $\quad X_{Mg} = 1.3$, $X_O = 3.5$

$$\%\ \text{ionic character} = \left(1 - e^{-\frac{(3.5-1.3)^2}{4}}\right) \text{x } (100\%) = 70.2\%\ \text{ionic}$$

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Example Problem 2.9

Calculate the percentage ionic character of the semiconducting compounds GaAs (3–5) and ZnSe (2–6) by using Pauling's equation

$$\%\ \text{ionic character} = (1 - e^{(-1/4)(X_A - X_B)^2})(100\%)$$

a. For GaAs, electronegativities from Fig. 2.14 are $X_{Ga} = 1.6$ and $X_{As} = 2.0$. Thus,

$$\begin{aligned}\%\ \text{ionic character} &= (1 - e^{(-1/4)(1.6-2.0)^2})(100\%)\\ &= (1 - e^{(-1/4)(-0.4)^2})(100\%)\\ &= (1 - 0.96)(100\%) = 4\%\end{aligned}$$

b. For ZnSe, electronegativities from Fig. 2.14 are $X_{Zn} = 1.6$ and $X_{Se} = 2.4$. Thus,

$$\begin{aligned}\%\ \text{ionic character} &= (1 - e^{(-1/4)(1.6-2.4)^2})(100\%)\\ &= (1 - e^{(-1/4)(-0.8)^2})(100\%)\\ &= (1 - 0.85)(100\%) = 15\%\end{aligned}$$

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Secondary Bonding

- Secondary bonds are due to attractions of *electric dipoles* in atoms or molecules.
- Dipoles are created when positive and negative charge centers exist.

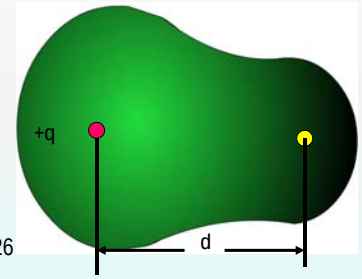

Figure 2.26

Dipole moment=μ =q.d

q= Electric charge

d = separation distance

- There two types of bond ➡ permanent and fluctuating.

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Fluctuating Dipoles

- Weak secondary bonds in noble gasses.
- Dipoles are created due to asymmetrical distribution of electron charges.
- Electron cloud charge changes with time.

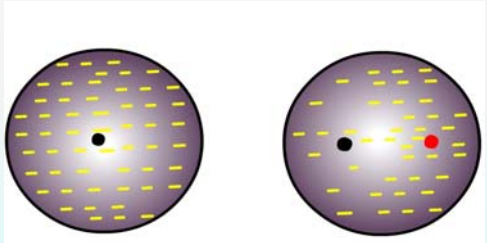


Figure 2.27

Symmetrical distribution of electron charge

Asymmetrical Distribution (Changes with time)

Permanent Dipoles

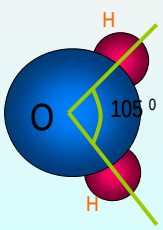
- Dipoles that do not fluctuate with time are called Permanent dipoles.
  - Examples:-

CH_4 → Symmetrical Arrangement Of 4 C-H bonds → No Dipole moment

CH_3Cl → Asymmetrical Tetrahedral arrangement → Creates Dipole

Hydrogen Bonds

- Hydrogen bonds are *Dipole-Dipole interaction* between polar bonds containing hydrogen atom.
  - Example :-
    - In water, dipole is created due to asymmetrical arrangement of hydrogen atoms.
    - Attraction between positive oxygen pole and negative hydrogen pole.



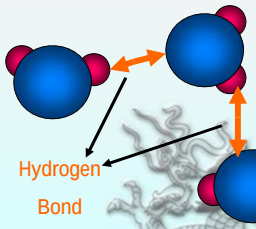


Figure 2.28