MSE2711

Materials Science

Hakan Yılmazer

Lecture 2. Atomic Structure and Interatomic Bonding

Objectives of Lecture 2

- The goal is to describe the underlying physical concepts related to the structure of matter.
- To examine the relationships between structure of atoms-bonds-properties of engineering materials.
- To learn about different levels of structure i.e. atomic structure, nanostructure, microstructure, and macrostructure.

Outline

- The Structure of Materials: Technological Relevance
- The Structure of the Atom
- Electrons in Atoms
- The Periodic Table
- Atomic Bonding
- Binding Energy and Interatomic Spacing

3

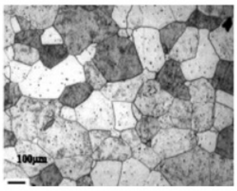
The Structure of Materials: Technological Relevance

Level of Structure	Example of Technologies	
Atomic Structure	Diamond – edge of cutting tools	
Atomic Arrangements: Long-Range Order (LRO)	Lead-zirconium-titanate [$Pb(Zr_x Ti_{1-x})$] (PZT) – gas igniters	
Atomic Arrangements: Short-Range Order (SRO)	Amorphous silica - fiber optical communications industry	

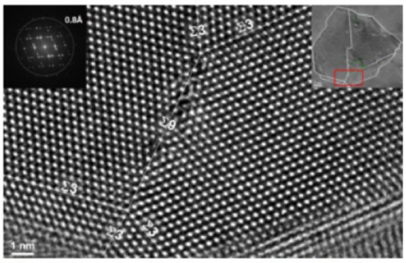
4

The Structure of Materials: Technological Relevance

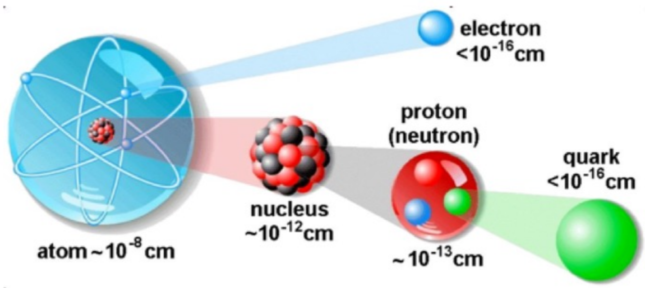
Level of Structure	Example of Technologies
Nanostructure (~10^{-9} to 10^{-7} m, 0.1 to 100 nm)	Nano-sized particles of iron oxide – ferrofluids
Microstructure (~>10^{-7} to 10^{-4} m, 0.1 to 100 μm)	Mechanical strength of metals and alloys
Macrostructure (~>10^{-4} m, ~>100 000 nm)	Paints for automobiles for corrosion resistance



The Structure of the Atom



HRTEM image-Nanocrystalline Palladium



- ☐ The atomic number of an element is equal to the number of electrons or protons in each atom.
- ☐ The atomic mass/weight of an element is equal to the average number of protons and neutrons in the atom.
- ☐ The Avogadro number of an element is the number of atoms or molecules in a mole.
- ☐ The atomic mass unit of an element is the mass of an atom expressed as 1/12 the mass of a carbon atom.

Example 2.1
Calculate the Number of Atoms in Silver

Calculate the number of atoms in 100 g of silver.

The atomic mass, or weight, of silver: *107.868 g/mol*.
Avogadro number: 6.023×10^{23} atoms/mol

Example 2.1 SOLUTION

The number of silver atoms = (100 g/*107.868 g/mol*) x 6.023×10^{23} *atoms/mol*

= 5.58×10^{23} atoms

Example 2.2
Nano-Sized Iron-Platinum Particles For Information Storage

Nano-particles as iron-platinum (Fe-Pt)

- magnetic materials
- ultrahigh density data storage.
- Arrays of such particles potentially can lead to storage of trillions of bits of data per square inch—a capacity
- 10 to 100 times higher than computer hard disks.

Q: If the scientists considered iron (Fe) particles that are 3 nm in diameter, what will be the number of atoms in one such particle?

Density of Fe: 7.8 g/cm^3.
Atomic mass of Fe: 56 g/mol.
Avogadro number: 6.023×10^{23} atoms/mol

Example 2.2 SOLUTION

The radius of a Fe particle is 1.5 nm.

Volume of each iron (Fe) magnetic nano-particle

$= (4/3)\pi(1.5 \times 10^{-7}\ cm)^3$

$= 1.4137 \times 10^{-20}\ cm^3$

Mass of each iron nano-particle

$= 7.8\ g/cm^3 \times 1.4137 \times 10^{-20}\ cm^3$

$= 1.102 \times 10^{-19}$ g.

1 mole Fe = 56 g Fe = 6.023 × 10^{23} atoms,

The number of atoms in one Fe nano-particle = 1186.

Electrons in Atoms

Quantum mechanics

Atomic spectra

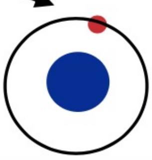
- Bunsen, Kirchhoff, 1860
  - 1st spectroscope
  - 1st line spectrum
- Lockyer, 1868
  - He in solar system
- Balmer,1885
  - H line spectrum

Quantum theory

- Plank, 1900
  - Black body radiation
- Einstein, 1905
  - Photoelectric effect
- Heisenberg, 1925
  - Heisenberg Uncertainty Principles
- Schrodinger, 1926
  - Wave theory

Atomic structure

- Dalton, 1803
  - atomic nature
- Faraday, 1834
  - Electricity & Mag.
- Thompson, 1807
  - electrons e/m
- Millikan, 1911
  - oil drop
- Rutherford, 1911
  - gold foil/nucleus



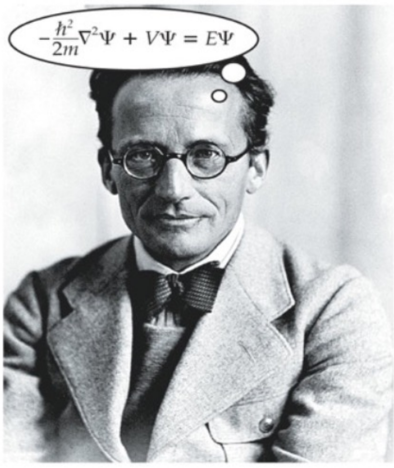
Bohr, 1913

- Applied to atom structure

10

Electrons in Atoms

The electrons form a cloud around the nucleus, of radius of 0.05 – 2 nm.



Schrödinger

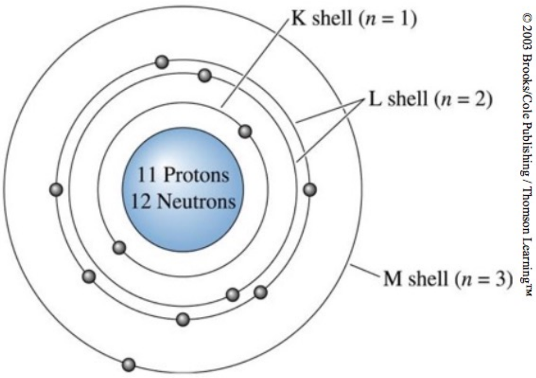
Bohr model looks like a mini planetary system. But quantum mechanics tells us that this analogy is not correct:

Quantum mechanics

- Each electron can be explained using a standing wave equation (wavefunction) (Heisenberg and Schrödinger)
- Quantized frequency corresponds to quantized Energy (Debroglie, Plank, etc.)

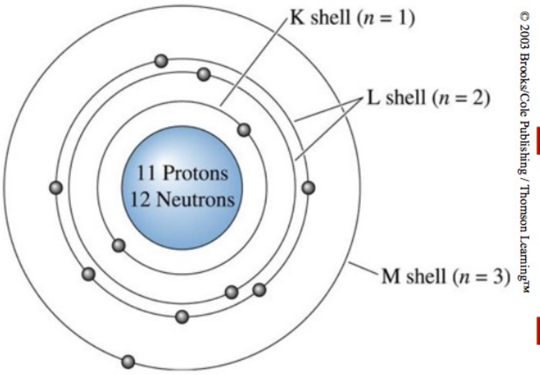
Integer values are critical to this description: ***Quantum numbers.***

Electrons in Atoms



- Quantum numbers are the numbers that assign electrons in an atom to discrete energy levels
- Solving the wave equation gives a set of wave functions, or orbitals, and their corresponding energies.
- Each orbital describes a distribution of electron density.
- An orbital is described by a set of quantum numbers.

Electrons in Atoms

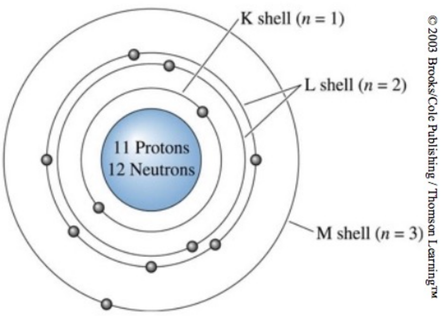


Principal Quantum Number, *n*

- The principal quantum number, *n*, describes the **energy level** on which the orbital resides.
- Largest E difference is between E levels
- The values of *n* are integers > 0.
- 1, 2, 3,...n.

13

Electrons in Atoms



Azimuthal Quantum Number, *l*

- Defines **shape** of the orbital.
- Allowed values of *l* are integers ranging from 0 to *n* − 1.

Azimuthal Quantum Number, *l = 0, 1...,n-1*

Value of *l*	0	1	2	3
Type of orbital	*s*	*p*	*d*	*f*

So each of these letters corresponds to a shape of orbital.

14

Electrons in Atoms

Magnetic Quantum Number, m_l

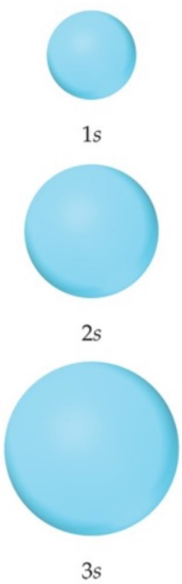
- Describes the **three-dimensional orientation** of the orbital.
- Values are integers ranging from -*l* to *l*:

$$-l \leq m_l \leq l.$$

- Therefore, on any given energy level, there can be up to:
- 1 *s* (*l*=0) orbital (m_l=0),
- 3 *p* (*l*=1) orbitals, (m_l=-1,0,1)
- 5 *d* (*l*=2) orbitals, (m_l=-2,-1,0,1,2)
- 7 *f* (*l*=3) orbitals, (m_l=-3,-2,-1,0,1,2,3)

Electrons in Atoms

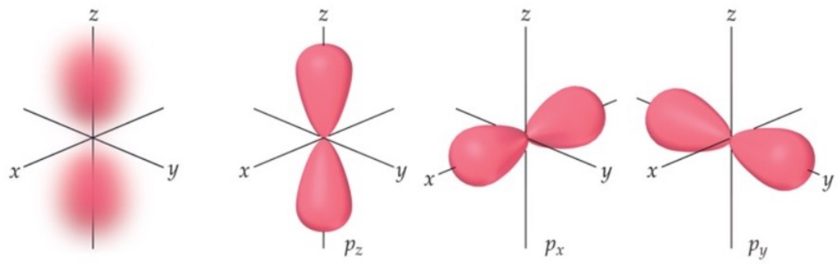
s Orbitals



- Value of *l* = 0.
- Spherical in shape.
- Radius of sphere increases with increasing value of *n*.

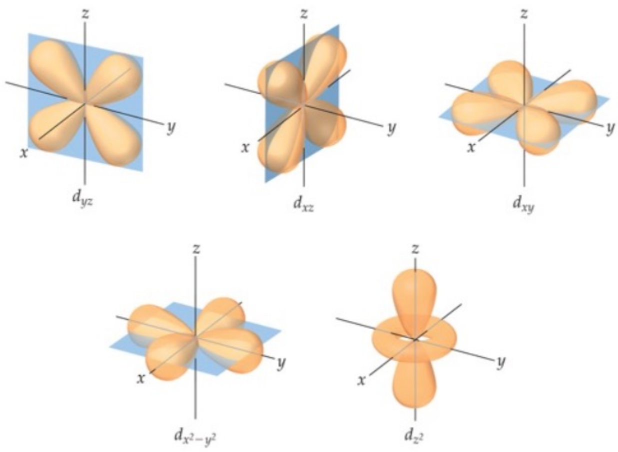
Electrons in Atoms
p Orbitals

- Value of *l* = 1.
- Have two lobes with a nodal plane between them.



Note: always 3 p orbitals for a given n

Electrons in Atoms
d Orbitals

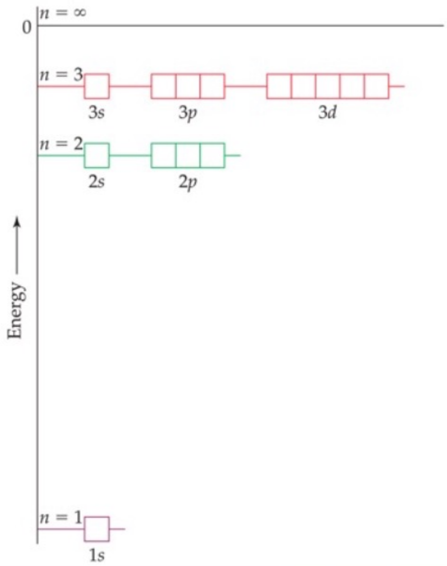


- Value of *l* is 2.
- 2 nodal planes
- Four of the five orbitals have 4 lobes; the other resembles a *p* orbital with a doughnut around the center.

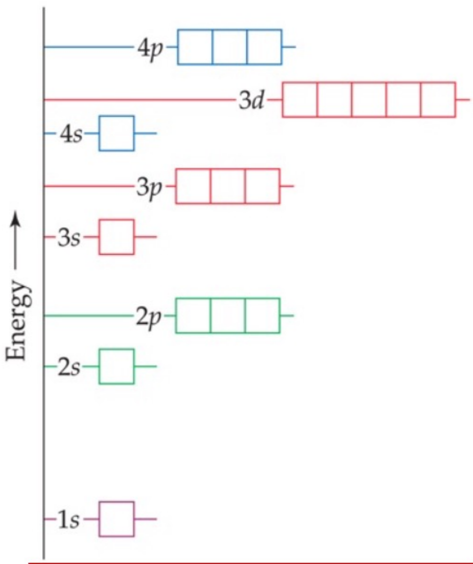
Note: always 5 d orbitals for a given n.

Energies of Orbitals

- For a one-electron hydrogen atom, orbitals on the same energy level have the same energy.
- That is, they are degenerate.

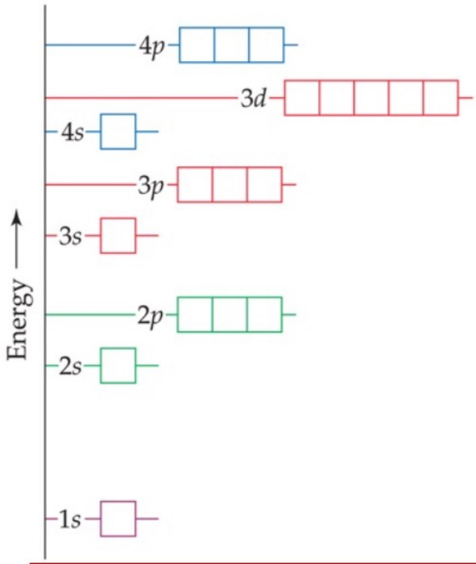


Energies of Orbitals



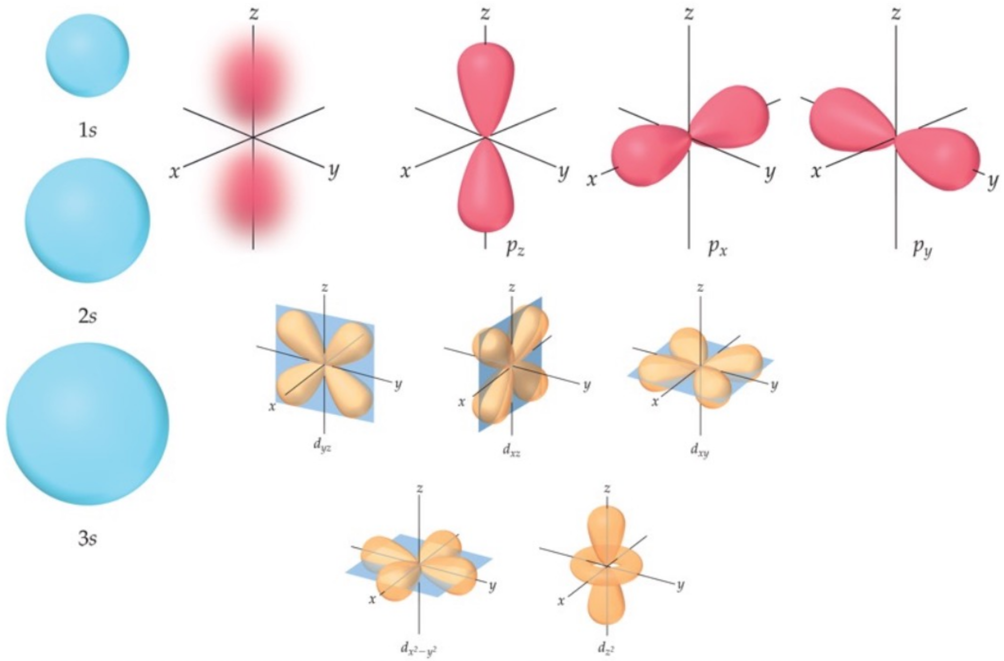
- As the number of electrons increases, though, so does the repulsion between them.
- Therefore, orbitals on the same energy level are no longer degenerate in many-electron atoms.

Energies of Orbitals



- For a given energy level (n):
- Energy: s<p<d<f
- s lowest energy, where electrons go first
- Next p
- Then d

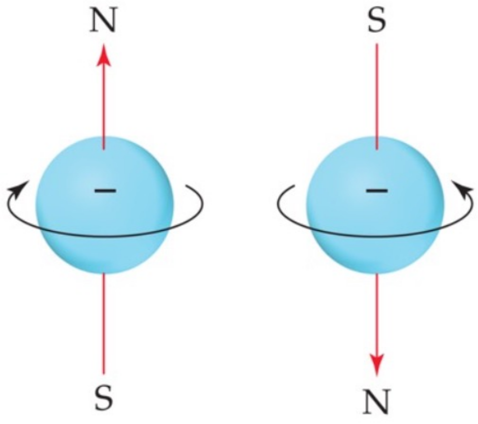
Why?



The closer to the nucleus, the lower the energy

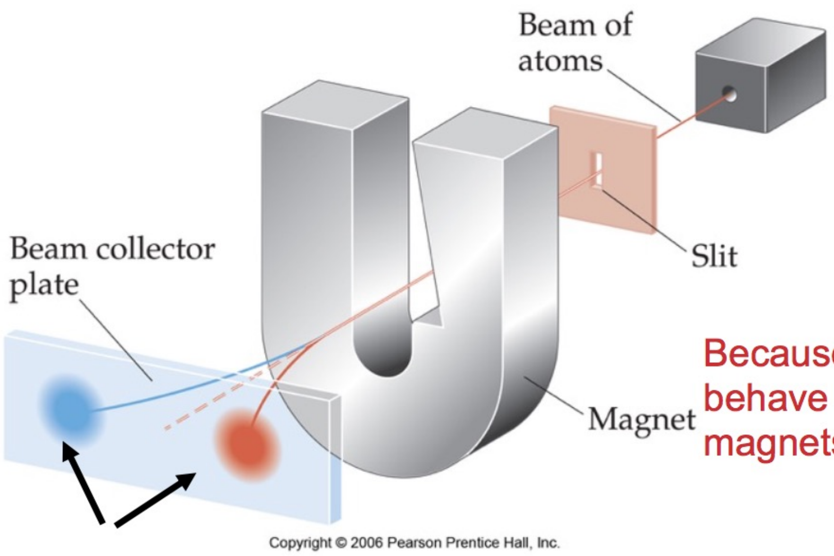
Electrons in Atoms

Spin Quantum Number, m_s



- This leads to a fourth quantum number, the spin quantum number m_s.
- The spin quantum number has only 2 values **+1/2 and -1/2**
- **Describes magnetic field vector of electron**

Why do we call it "spin"

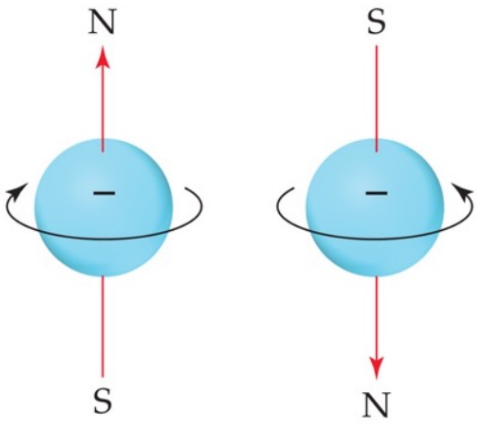


Because electrons behave like little magnets

Note: apparently only two values for the magnetic field

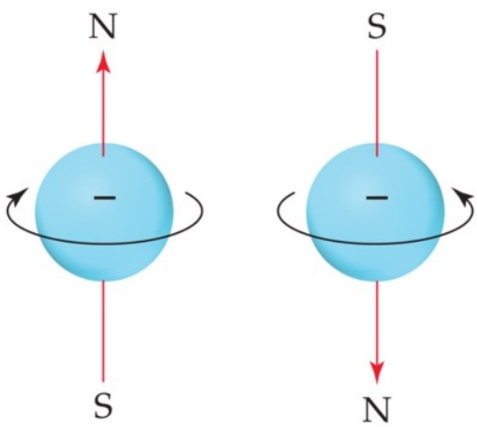
Why do we call it "spin"

- And charges that spin produce magnetic fields



Pauli Exclusion Principle

- No two electrons can have exactly the same energy in the same atom.
- For example, no two electrons in the same atom can have identical sets of quantum numbers.



Properties of Quantum Numbers

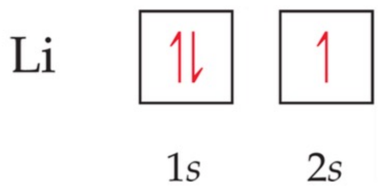
Symbol	Name	Values	Role
n	principal	1,2,3,.....	determines the energy (size)
ℓ	angular momentum	0,1,2,...n-1	contributes to angular dependence (shape) and to a lesser extent energy
m_l	magnetic	0,±1,±2,...±ℓ	determines the orientation in space
m_s	spin	±1/2	describes the electron spin (magnetic moment)

ℓ	0	1	2	3
	s	p	d	f

TABLE SHOWING PROPERTIES OF QUANTUM NUMBERS

Orbital Diagrams

- Each box represents one orbital.
- Half-arrows represent the electrons.
- The direction of the arrow represents the spin of the electron.

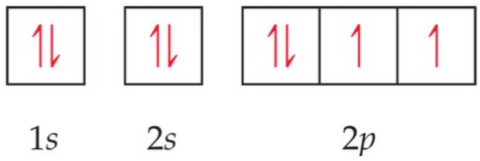


$1s^2 2s^1$

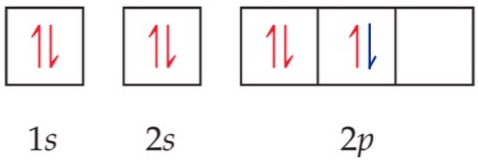
Hund's Rule

(of maximum multiplicity)

"For degenerate orbitals, the lowest energy is attained when the number of electrons with the same spin is maximized."



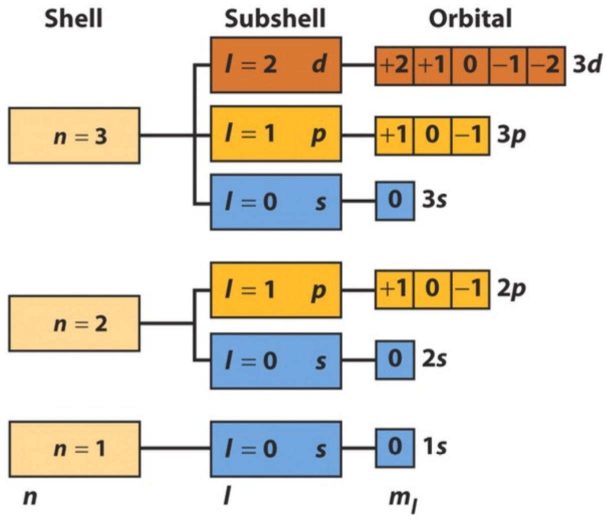
NOT:



Aufbau principle:
fill lowest energy orbital first

Electron configurations

shell = all orbitals with the same value of n
subshell = all orbitals with the same value of n and *l*
an **orbital** is fully defined by three quantum numbers, n, *l*, and m_l



Valence Electrons

- The electrons the occupy the highest energy level of an atom.
- Valence electrons play a key role in the chemical properties of an element.

35

31

The Modern Periodic Table

- The Periodic Table is a listing of all the known elements.
- The elements are organized by:
  - Atomic number
  - Chemical Properties

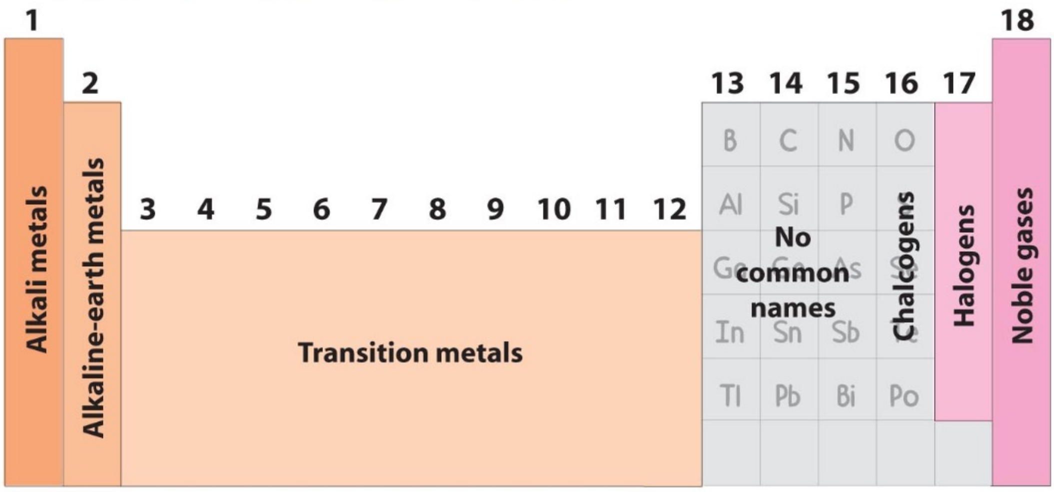
36

Groups and Periods

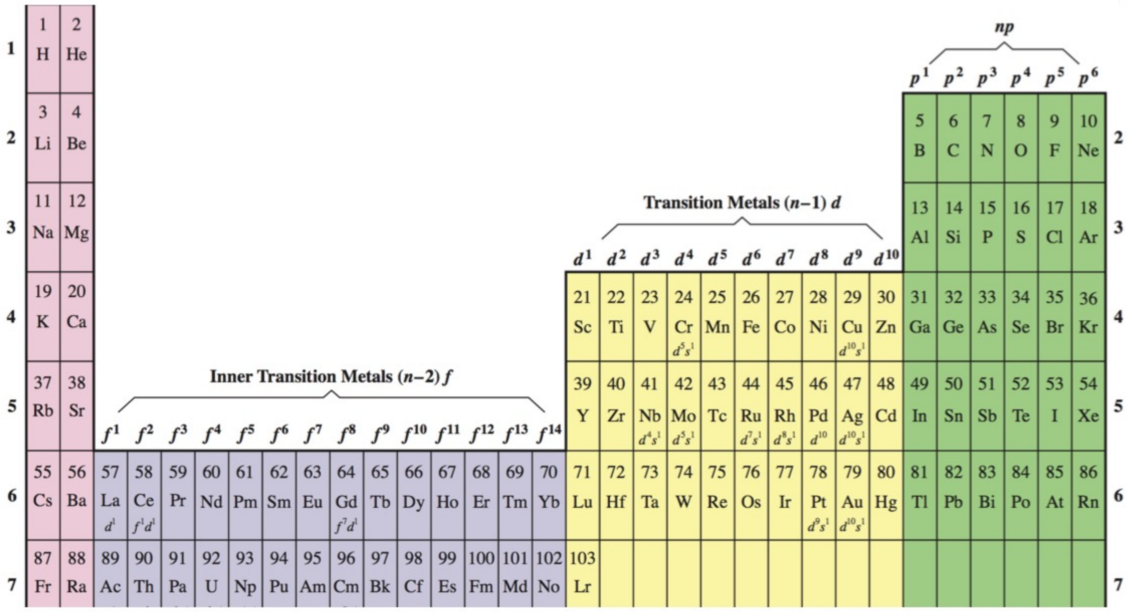
- **Group**(or Family): a vertical column. Elements in groups have similar chemical properties.
  - There are 7 periods
- **Period**: a horizontal row.
  - There are 18 numbered columns

37

The Periodic Table



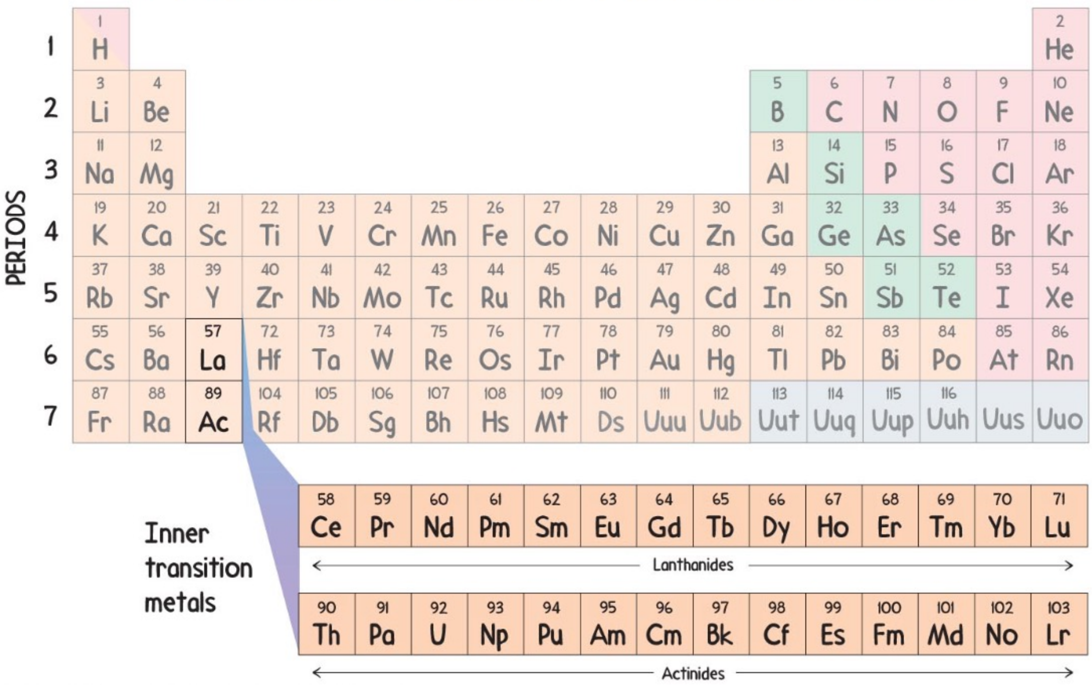
38



39

35

Actinides and Lanthanides



36

Ionization energy (IE)

Period	1	2	13/III	14/IV	15/V	16/VI	17/VII	18/VIII
1	H 1310							He 2370
2	Li 519	Be 900	B 799	C 1090	N 1400	O 1310	F 1680	Ne 2080
3	Na 494	Mg 736	Al 577	Si 786	P 1011	S 1000	Cl 1255	Ar 1520
4	K 418	Ca 590	Ga 577	Ge 784	As 947	Se 941	Br 1140	Kr 1350
5	Rb 402	Sr 548	In 556	Sn 707	Sb 834	Te 870	I 1008	Xe 1170
6	Cs 376	Ba 502	Tl 590	Pb 716	Bi 703	Po 812	At 1037	Rn 1036

Ionization energy ($kJ \cdot mol^{-1}$): 2001–2500; 1501–2000; 1001–1500; 501–1000; 1–500

The ionization energy (IE) of an atom is the minimum energy required to remove an electron from an atom.

$$X(g) \longrightarrow X^{+}(g) + e^{-}$$

Periodic trends ionization energies of the representative elements:

41

Electron affinity (EA)

Period	1	2	13/III	14/IV	15/V	16/VI	17/VII	18/VIII
1	H +73							He <0
2	Li +60	Be ≤0	B +27	C +122	N −7	O +141 −844	F +328	Ne <0
3	Na +53	Mg ≤0	Al +43	Si +134	P +72	S +200 −532	Cl +349	Ar <0
4	K +48	Ca +2	Ga +29	Ge +116	As +78	Se +195	Br +325	Kr <0
5	Rb +47	Sr +5	In +29	Sn +116	Sb +103	Te +190	I +295	Xe <0
6	Cs +46	Ba +14	Tl +19	Pb +35	Bi +91	Po +174	At +270	Rn <0

Electron affinity ($kJ \cdot mol^{-1}$): >300; 200–300; 100–200; 0–100; <0

The electron affinity (EA) of an atom is the energy change which occurs when an atom gains an electron.

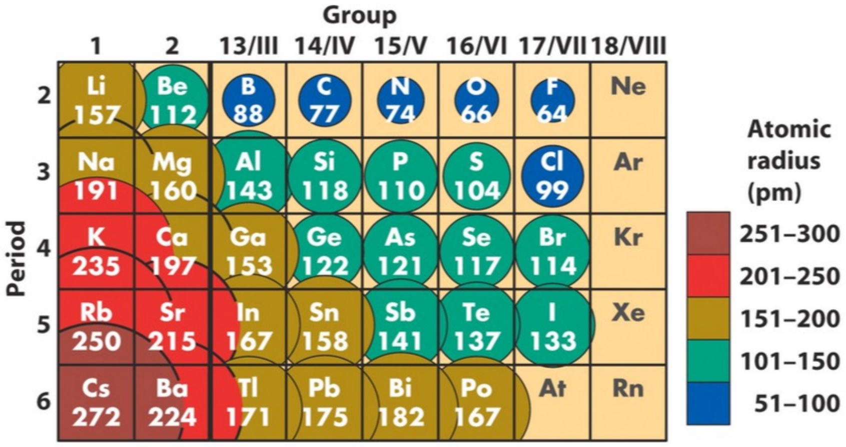
$$X(g) + e^{-} \longrightarrow Xe^{-}(g)$$

42

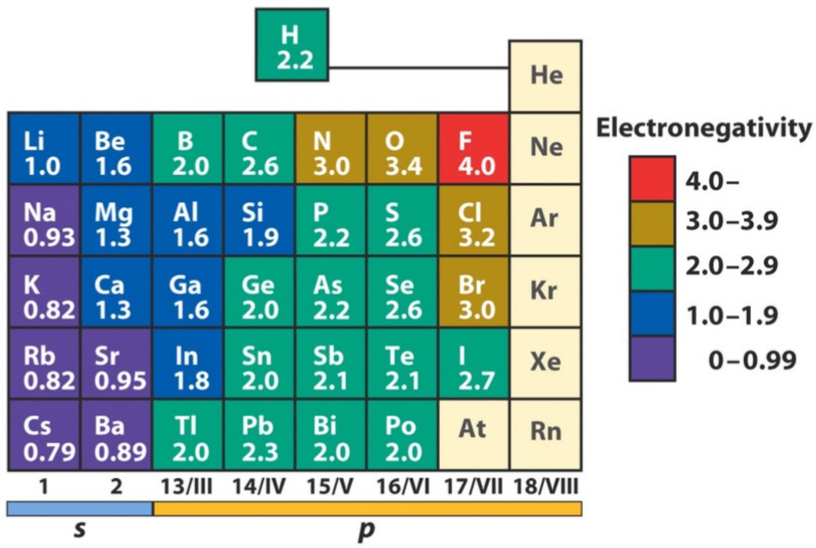
Periodic properties of atomic radius

General Rule:

The size of an atom decreases in a row the nuclear charge increases and the size of an atom increases in a column as the nuclear charge increases



Electronegativity (EN)

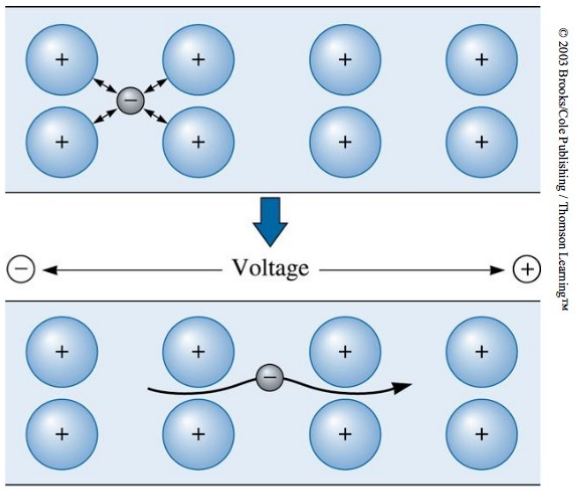


A measure of the ability of an atom to attract electrons to itself in competition with other atoms

Atomic Bonding

- Metallic bond,
- Covalent bond,
- Ionic bond,
- Intermolecular Forces
  - van der Waals Interaction
  - Dipole Dipole Interactions

Metallic Bonding



When voltage is applied to a metal, the electrons in the electron sea can easily move and carry a current

Metallic Bonding

Characteristics

Non-directional

High Electrical and thermal conductivity

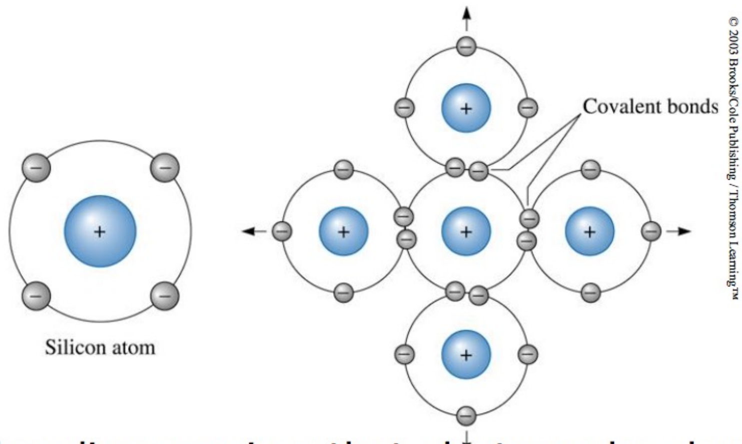
Low spesific heat

High melting and boiling point

Strength of bond proportional with numbers of free electron per atom

High Stiffness vs. bond energy

Covalent Bonding



Covalent bonding requires that electrons be shared between atoms in such a way that each atom has its outer *sp* orbital filled. In silicon, with a valence of four, four covalent bonds must be formed

Covalent Bonding

- Sharing valance electrons
- Covalent bonds are **directional**. In silicon, a tetrahedral structure is formed, with angles of 109.5° required between each covalent bond

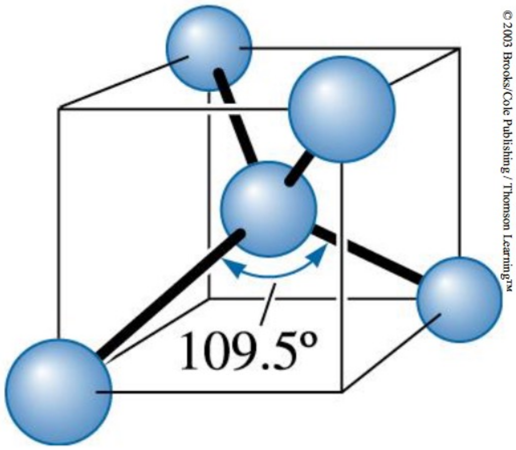
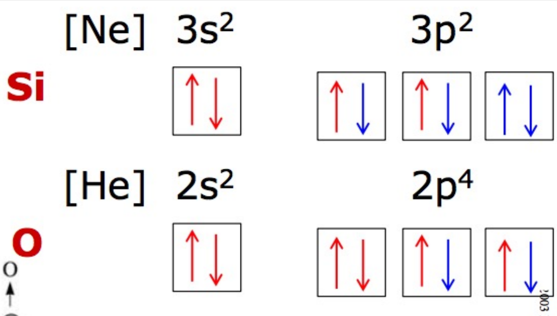


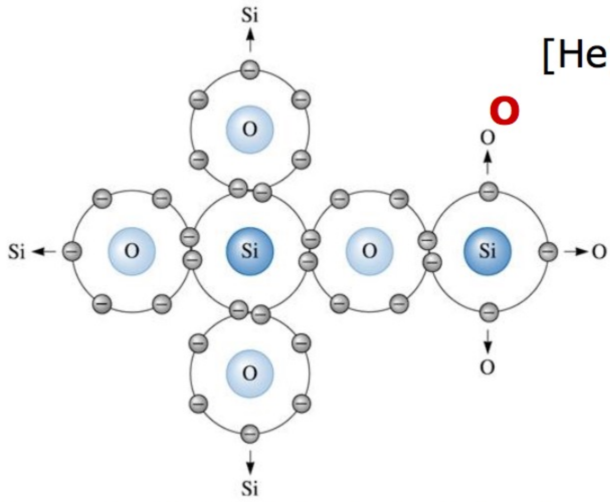
Figure 2.15 illustration of structure of Silicon ($Si0_2$)

Example 2.6
How Do Oxygen and Silicon Atoms Join to Form Silica?

Assuming that silica (SiO_2) has 100% covalent bonding, describe how oxygen and silicon atoms in silica (SiO_2) are joined.

Example 2.6 SOLUTION





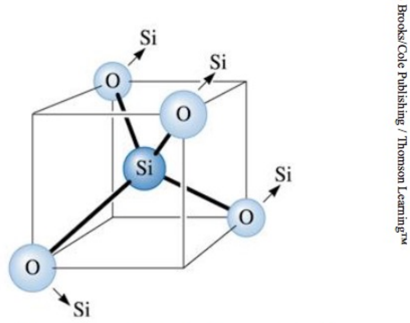


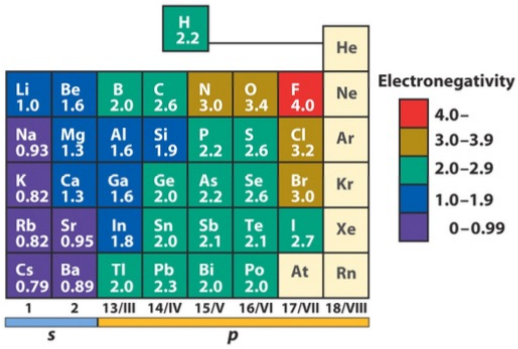
Figure 2.16 The tetrahedral structure of silica (SiO_2), which contains covalent bonds between silicon and oxygen atoms (for Example 2-6)

Covalent Bonding

Characteristics
Directional
Completely full valance band
Insulator

Ionic Bonding

- An ionic bond is created between two unlike atoms with **different electronegativities**.
- Give and Take valence electrons



When sodium donates its valence electron to chlorine, each becomes an ion; attraction occurs, and the ionic bond is formed

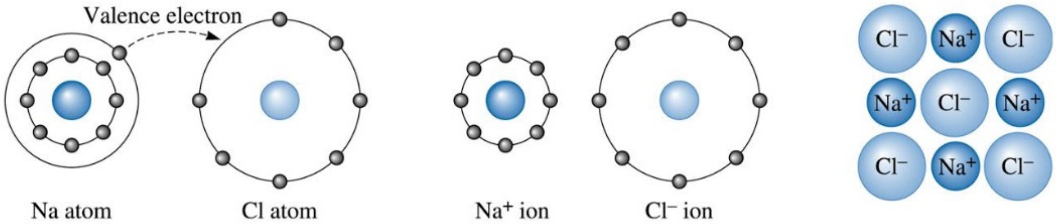


Figure 2.18 Sodium chloride formation

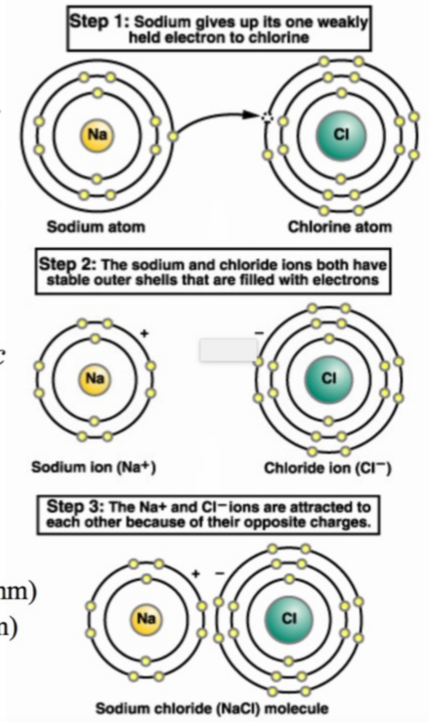
Ionic Bonding

- **Ion**: an atom or molecule that *gains* or *loses* electrons (acquires an electrical charge). Atoms form **cations** (+charge), when they lose electrons, or **anions** (-charge), when they gain electrons.
- **Ionic bonds** are *strong bonds* formed when *oppositely charged ions are attrac to each other*.
- Ionic bonds are **non-directional** (ions may be attracted to one another in any direction)

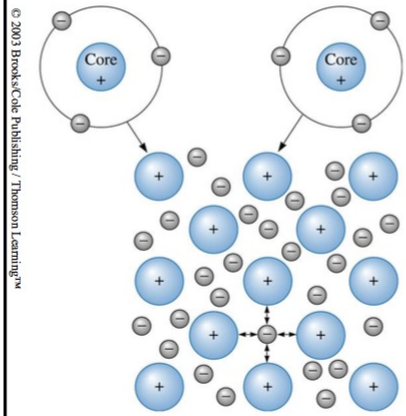
Example:

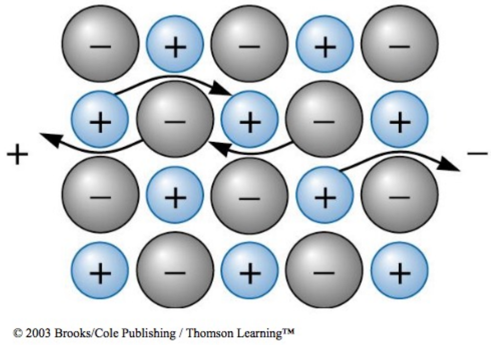
Atomic Radius: Na (r = 0.192nm) Cl (r = 0.099nm)

Ionic Radius : Na (r = 0.095nm) Cl (r = 0.181nm)



Electrical conductivity for Ionic Bonded materials



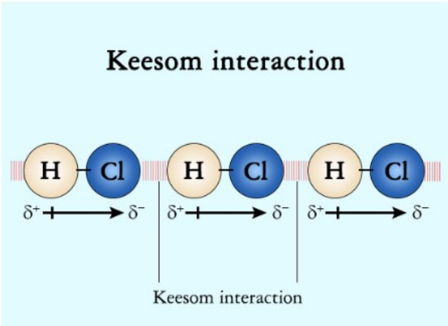


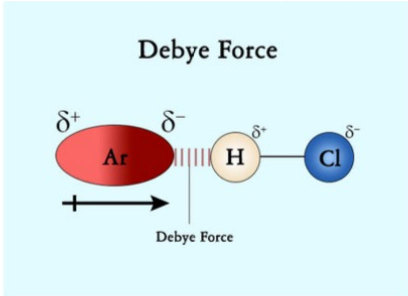
When voltage is applied to an ionic material, entire ions must move to cause a current to flow. Ion movement is slow and the electrical conductivity is poor

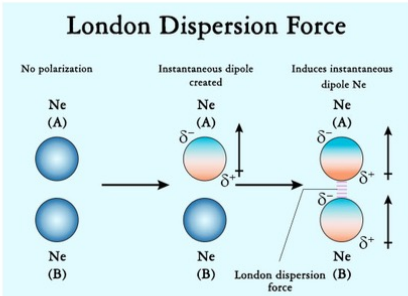
Intermolecular Forces

- van der Waals Interaction
  - Keesom interactions
  - Debye Force
  - London Dispersion force
- Dipole Dipole Interactions
  - Ion-dipole forces
  - Ion-induced dipole forces
  - Hydrogen bonds

Van der Walls Interaction

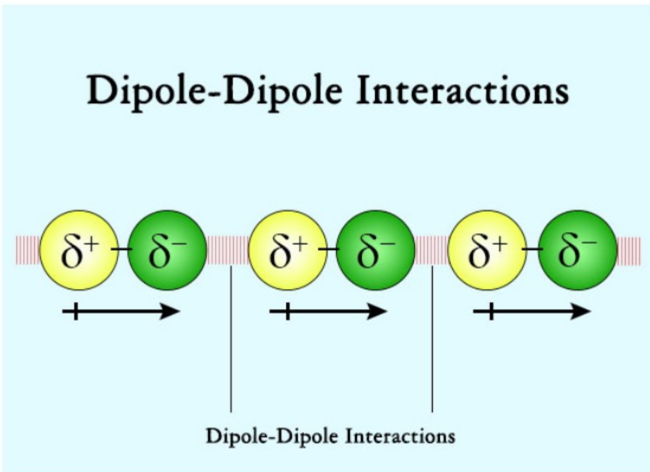






56

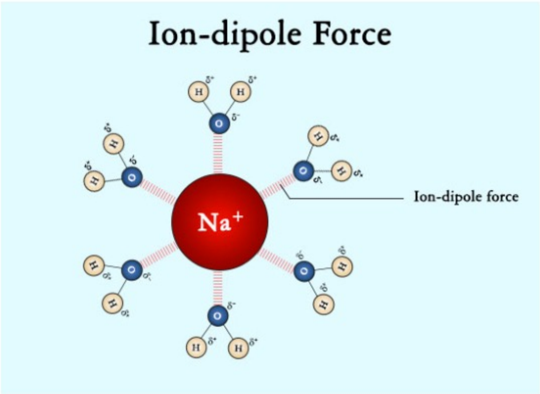
53



These interactions are formed due to uneven distribution of electrons in a molecule. This gives rise to a partial positive (δ^+) and a partial negative (δ^-) charge in a molecule that, as a whole, is neutral. Polar molecules tend to orient themselves in such a way that the δ^+ part of the molecule is close to the δ^- part of the molecule, such that there is minimum repulsion and maximum attraction between the molecules.

- Ion-dipole forces
- Ion-induced dipole forces
- Hydrogen bonds

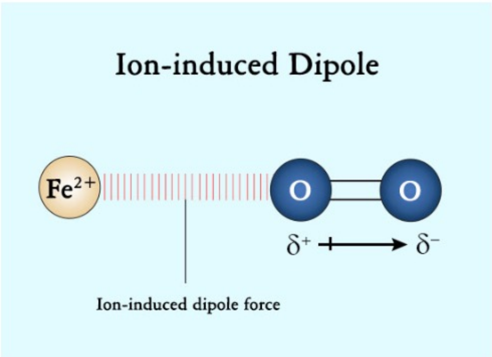
57



The force of attraction between a polar molecule and an ion that may lie in its vicinity is called an ion-dipole force.

- NaCl

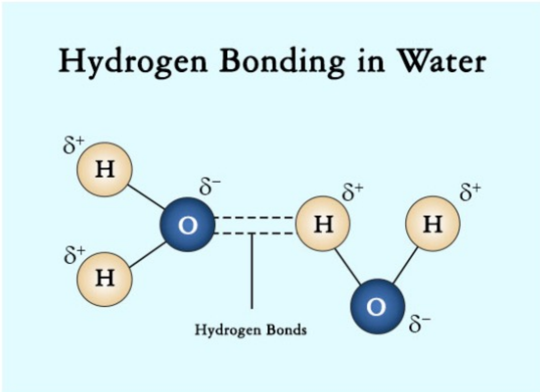
58



The force of attraction between a non-polar molecule and an ion that may lie in its vicinity is called ion-induced dipole force.

- Hemoglobin in the blood cells

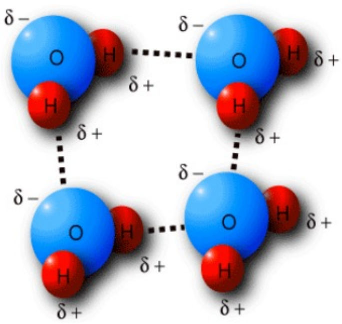
59

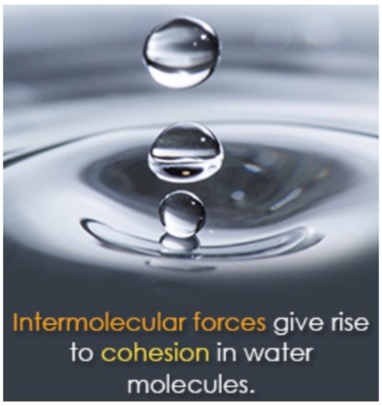


The force of attraction between the lone pair of electrons in an electronegative atom (atoms in a covalent bond that tend to pull the shared pair of electrons towards themselves) and a hydrogen atom that is covalently attached to either nitrogen, fluorine, or oxygen is called a hydrogen bond.

Keesom Interactions

The Keesom interactions are formed as a result of polarization of molecules or groups of atoms.





In water, electrons in the oxygen tend to concentrate away from the hydrogen. The resulting charge difference permits the molecule to be weakly bonded to other water molecules

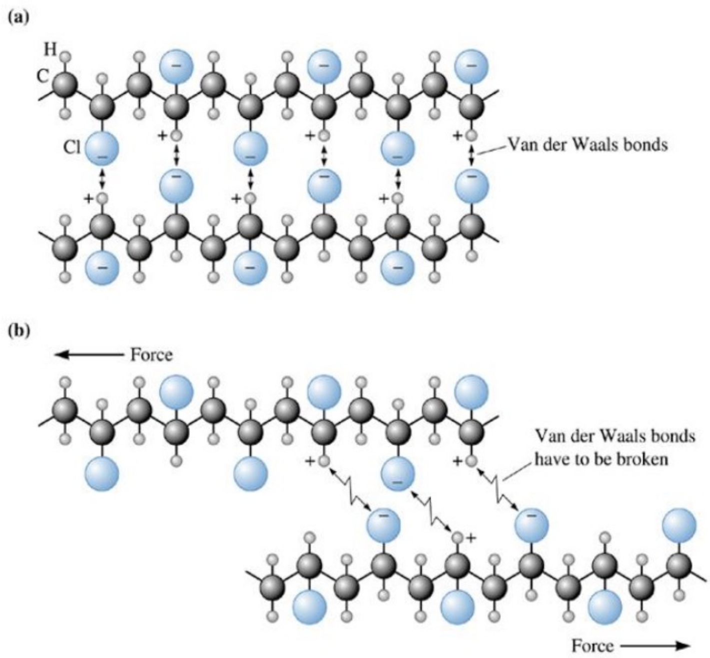
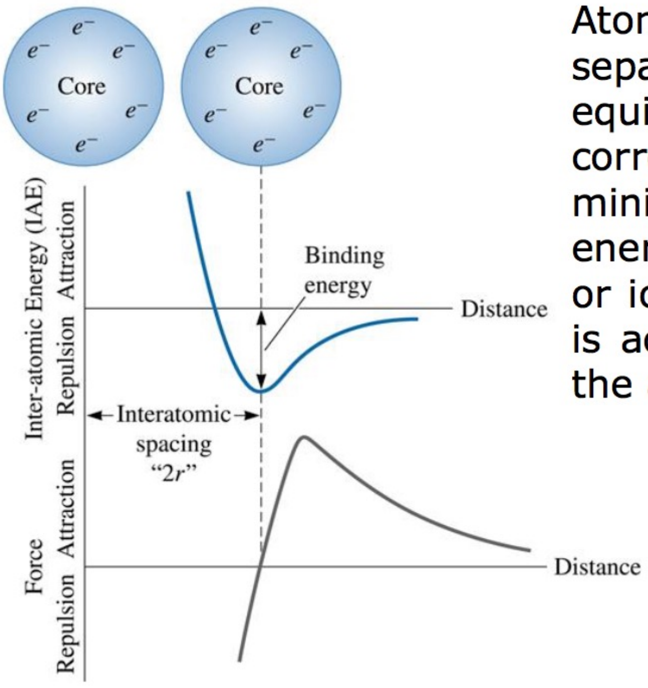


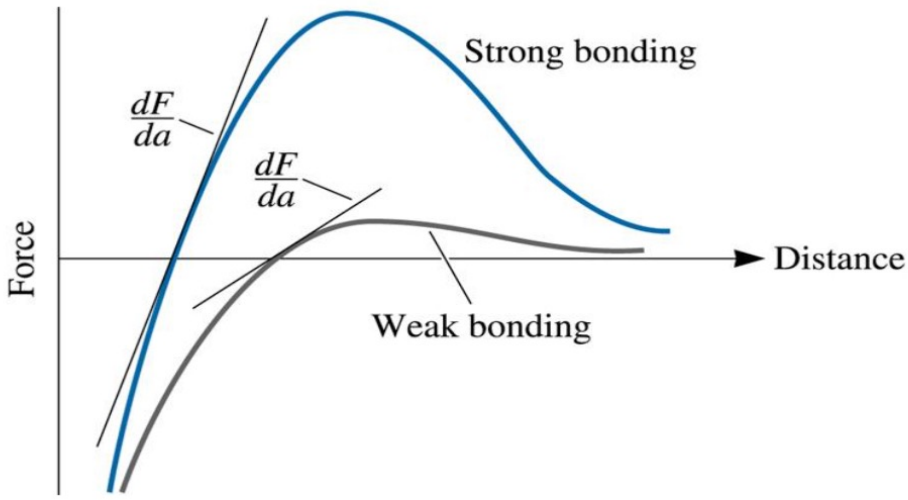
Figure 2.22 (a) In polyvinyl chloride (PVC), the chlorine atoms attached to the polymer chain have a negative charge and the hydrogen atoms are positively charged. The chains are weakly bonded by van der Waals bonds. This additional bonding makes PVC stiffer, (b) When a force is applied to the polymer, the van der Waals bonds are broken and the chains slide past one another

Binding Energy and Interatomic Spacing

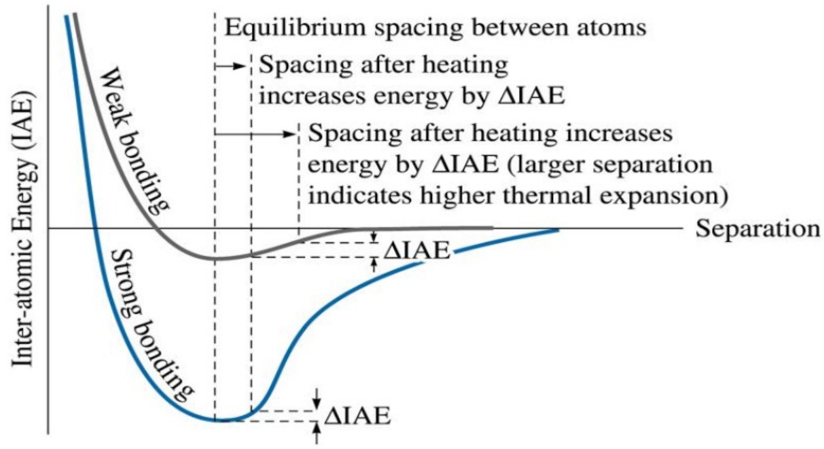
- Interatomic spacing is the equilibrium spacing between the centers of two atoms.
- Binding energy is the energy required to separate two atoms from their equilibrium spacing to an infinite distance apart.



Atoms or ions are separated by and equilibrium spacing that corresponds to the minimum inter-atomic energy for a pair of atoms or ions (or when zero force is acting to repel or attract the atoms or ions)



The force-distance curve for two materials, showing the relationship between atomic bonding and the modulus of elasticity, a steep *dFlda* slope gives a high modulus



- The inter-atomic energy (IAE)-separation curve for two atoms.
- *Materials that display a steep curve with a deep trough have low linear coefficients of thermal expansion

$$F_N = F_A + F_R$$

(a) The dependence of repulsive, attractive, and **net forces** on interatomic separation for two isolated atoms.

(b) The dependence of repulsive, attractive, and **net potential energies** on interatomic separation for two isolated atoms.

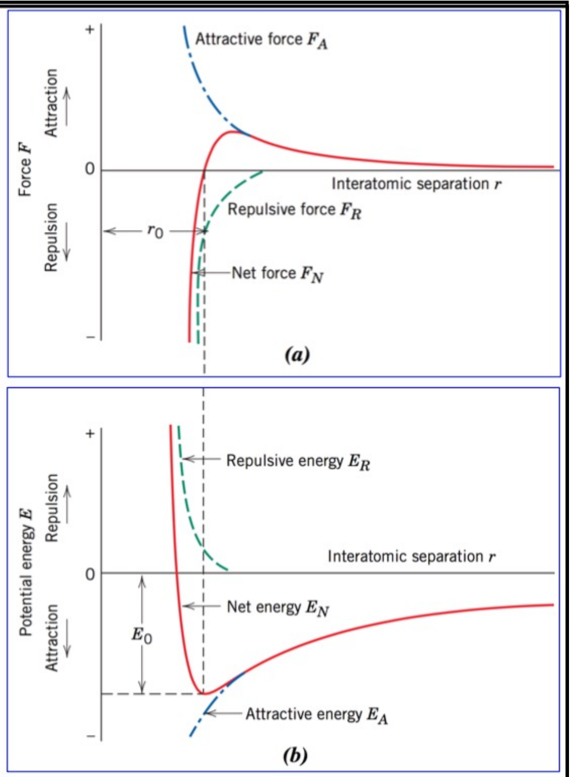
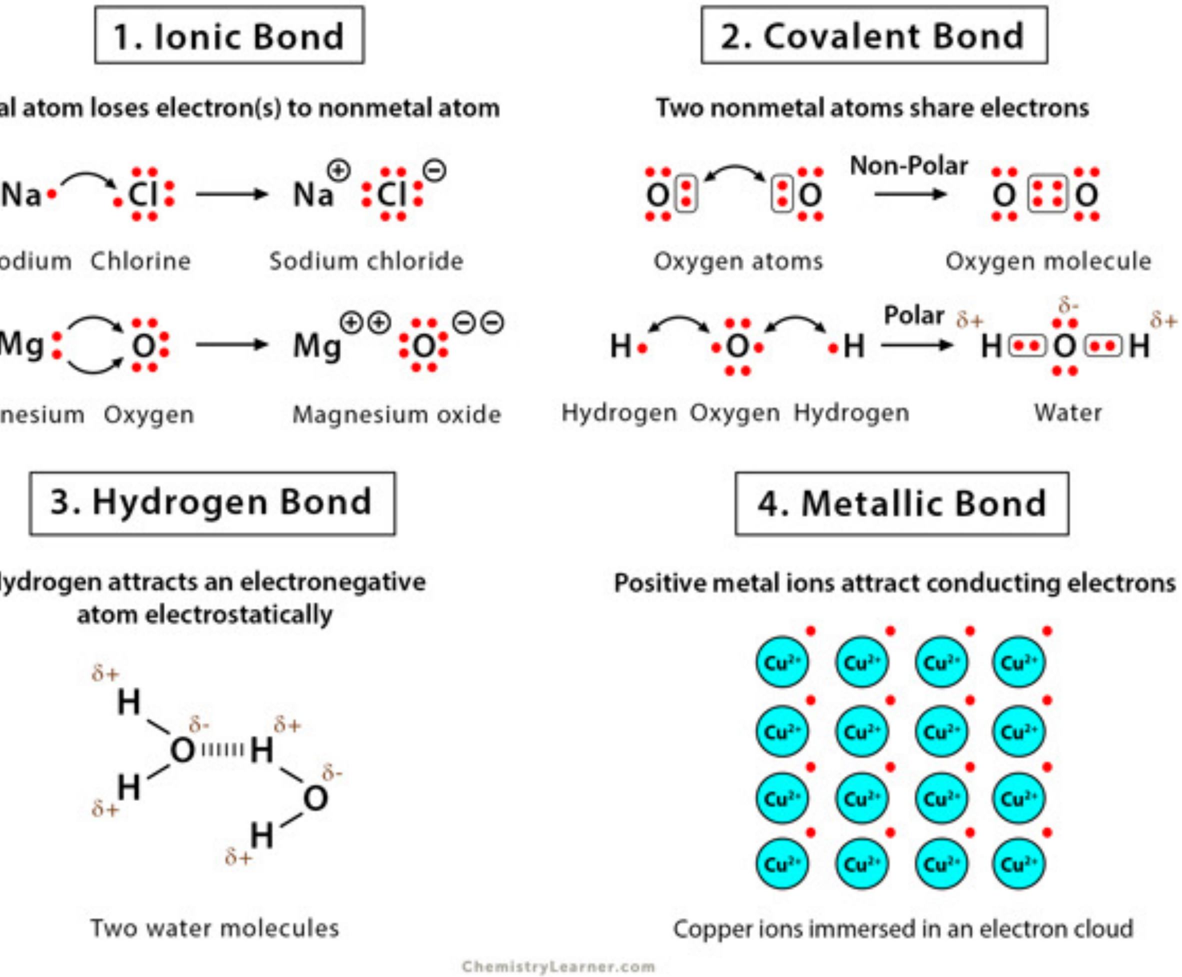


TABLE 2-3 ■ ***Binding energies for the four bonding mechanisms***

Bond	Binding Energy (kcal/mol)
Ionic	150–370
Covalent	125–300
Metallic	25–200
Van der Waals	<10

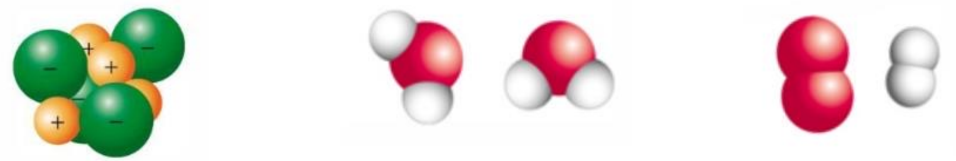
- Modulus of elasticity is the slope of the stress-strain curve in the elastic region (E).
- Yield strength is the level of stress above which a material begins to show permanent deformation.
- Coefficient of thermal expansion (CTE) is the amount by which a material changes its dimensions when the temperature changes.



Ionic Bonds | Polar Covalent Bonds | Covalent Bonds

- Electrons transferred
- Electrostatic attraction between cations & anions
- Non-directional

- Electrons shared
- Attraction between electrons and nucle
- Defined bond axis



1

TABLE 2-3 ■ ***Binding energies for the four bondi[ng] mechanisms***

Bond	Binding Energy (kcal/mol)
Ionic	150–370
Covalent	125–300
Metallic	25–200
Van der Waals	<10