Properties of Engineering Materials

Atomic Structures & Interatomic Bonding

Dr. Eng. Yazan Al-Zain
Department of Industrial Engineering
University of Jordan

Fundamental Concepts

- Each atom consists of a very small nucleus composed of protons and neutrons, which is encircled by moving electrons.
  - Both electrons and protons are electrically charged, the charge magnitude being 1.602 × 10^{-19} C, which is negative in sign for electrons and positive for protons; neutrons are electrically neutral.
- Masses for these subatomic particles are infinitesimally small; protons and neutrons have approximately the same mass, 1.67 × 10^{-27} kg, which is significantly larger than that of an electron, 9.11 × 10^{-31} kg.
- The atomic number Z (no. of protons) characterizes each element.
  - This atomic number ranges in integral units from 1 for hydrogen to 92 for uranium, the highest of the naturally occurring elements.

Fundamental Concepts

- The *atomic mass* (*A*) of a specific atom may be expressed as the sum of the masses of protons and neutrons within the nucleus.
- Atoms of some elements have two or more different atomic masses, which are called **isotopes.**
    - This is because Although the number of protons is the same for all atoms of a given element, the number of neutrons (*N*) may be variable.
- The **atomic weight** of an element corresponds to the weighted average of the atomic masses of the atom’s naturally occurring isotopes.

Fundamental Concepts

- The **atomic mass unit (amu)** may be used to compute atomic weight.
  - A scale has been established whereby 1 amu is defined as of the atomic mass of the most common isotope of carbon, carbon 12 (^{12}C) (*A* 12.00000).
- Within this scheme, the masses of protons and neutrons are slightly greater than unity, and

$$A \cong Z + N$$

Fundamental Concepts

- The atomic weight of an element or the molecular weight of a compound may be specified on the basis of amu per atom (molecule) or mass per mole of material.
    - In one **mole** of a substance there are 6.022 × 10^{-23} (Avogadro's number) atoms or molecules. These two atomic weight schemes are related through the following equation:

      1 amu/atom (or molecule) = 1 g/mol

- For example, the atomic weight of iron is 55.85 amu/atom, or 55.85 g/mol.

Electrons in Atoms

Atomic Models

- **Bohr atomic model "an early outgrowth of quantum mechanics":** is one in which in which electrons are assumed to revolve around the atomic nucleus in discrete orbitals, and the position of any particular electron is more or less well defined in terms of its orbital.

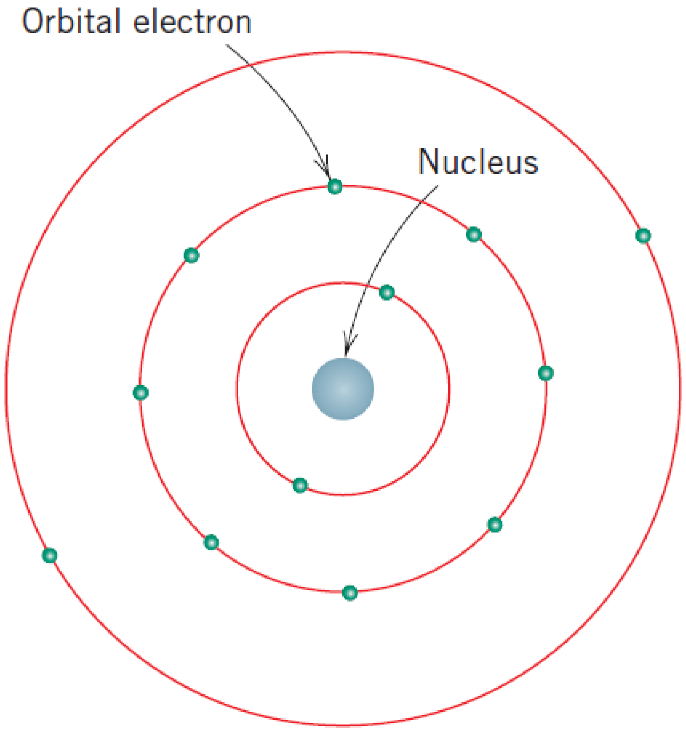


Fig. 1: Schematic representation of the Bohr atom.

Electrons in Atoms

Atomic Models

- Another important quantum-mechanical principle stipulates that the energies of electrons are quantized; that is,
  - Electrons are permitted to have only specific values of energy.
- An electron may change energy, but in doing so it must make a quantum jump either to an allowed higher energy (with absorption of energy) or to a lower energy (with emission of energy).
  - Allowed electron energies being associated with *energy levels* or *states*.

Electrons in Atoms

Atomic Models

These energies are taken to be negative, whereas the zero reference is the unbound or free electron.

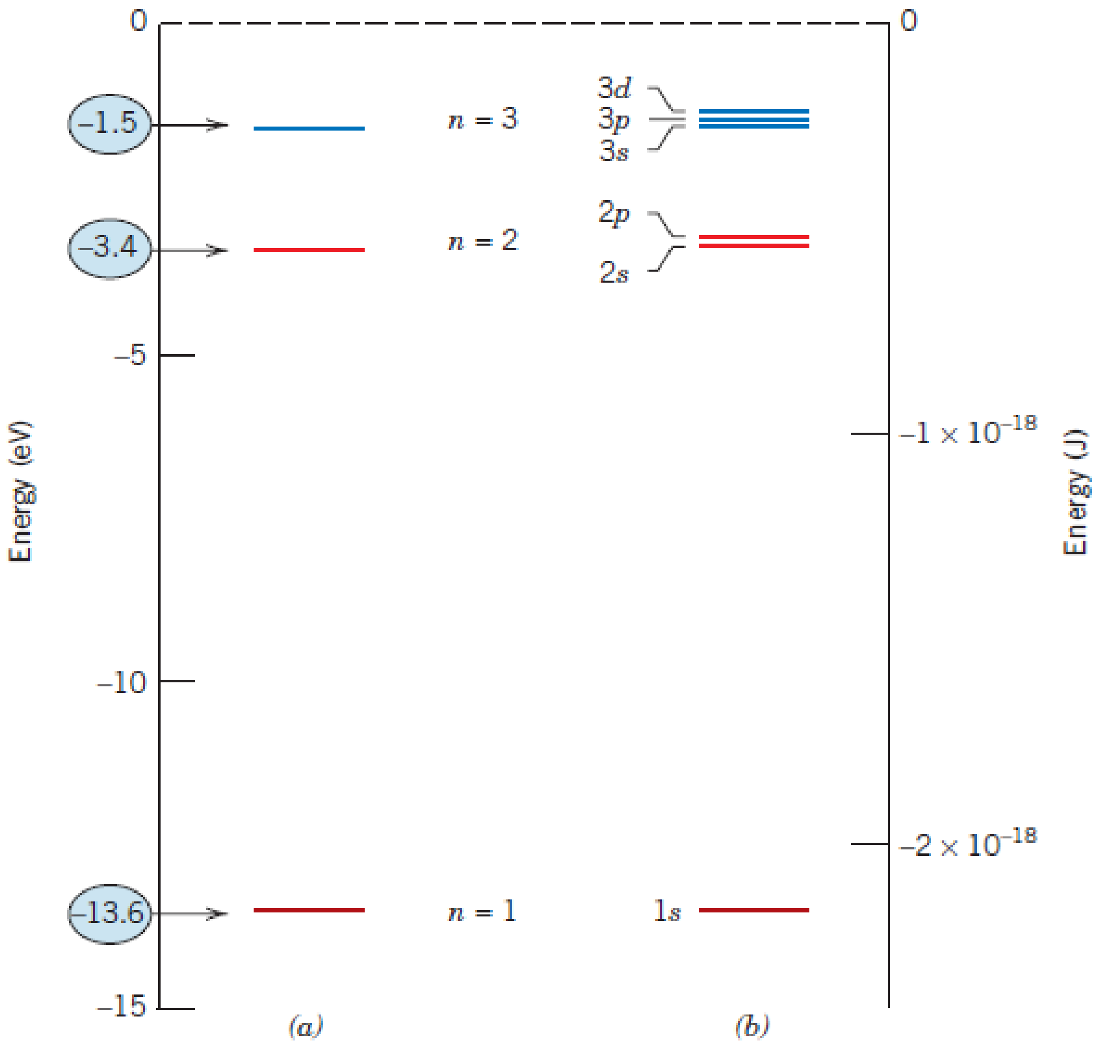


Fig. 2: (*a*) The first three electron energy states for the Bohr hydrogen atom. (*b*) Electron energy states for the first three shells of the wave-mechanical hydrogen atom.

Electrons in Atoms
Atomic Models

- Bohr model: imposes limitations as electrons are treated as a particle.

- Resolution: **wave-mechanical model**, the electron is considered to exhibit both wavelike and particle-like characteristics.

    - With this model, an electron is no longer treated as a particle moving in a discrete orbital; rather, position is considered to be the probability of an electron’s being at various locations around the nucleus.

Electrons in Atoms

Atomic Models

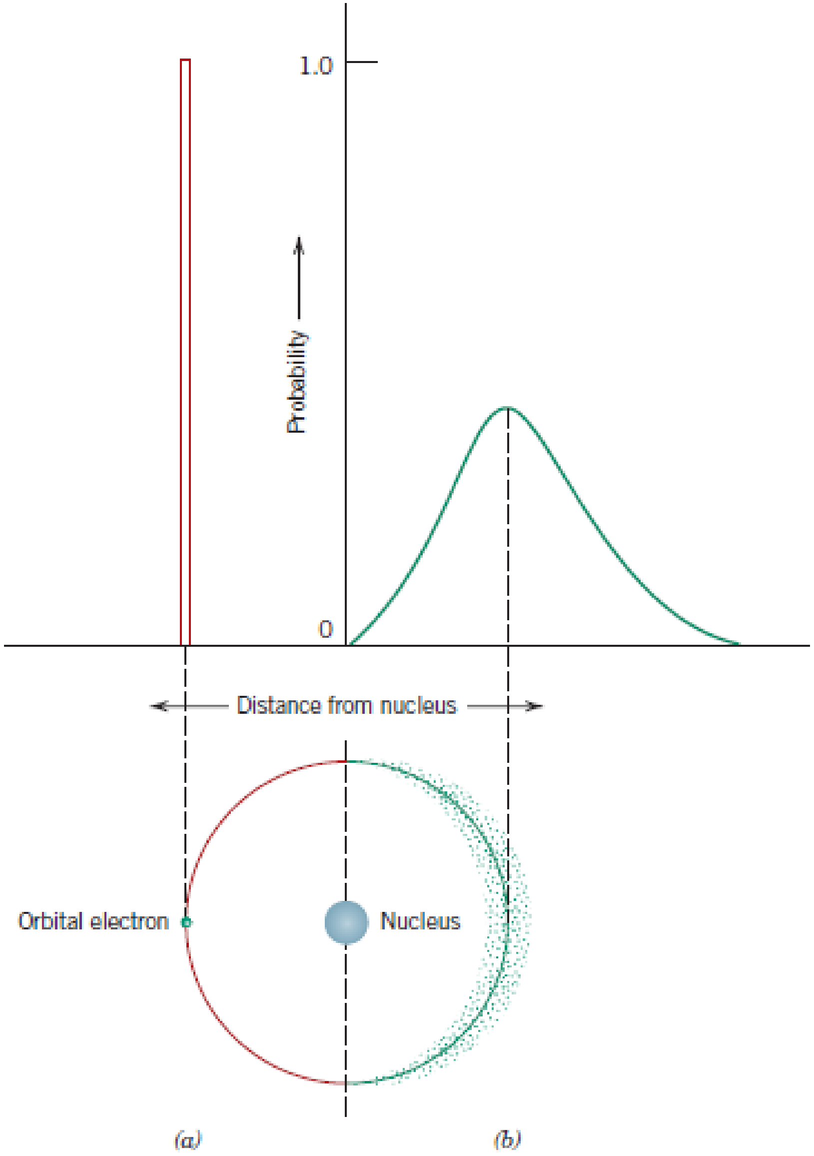


Fig. 3: (*a*) Comparison of the (*a*) Bohr and (*b*) wave mechanical atom models in terms of electron distribution.

Electrons in Atoms

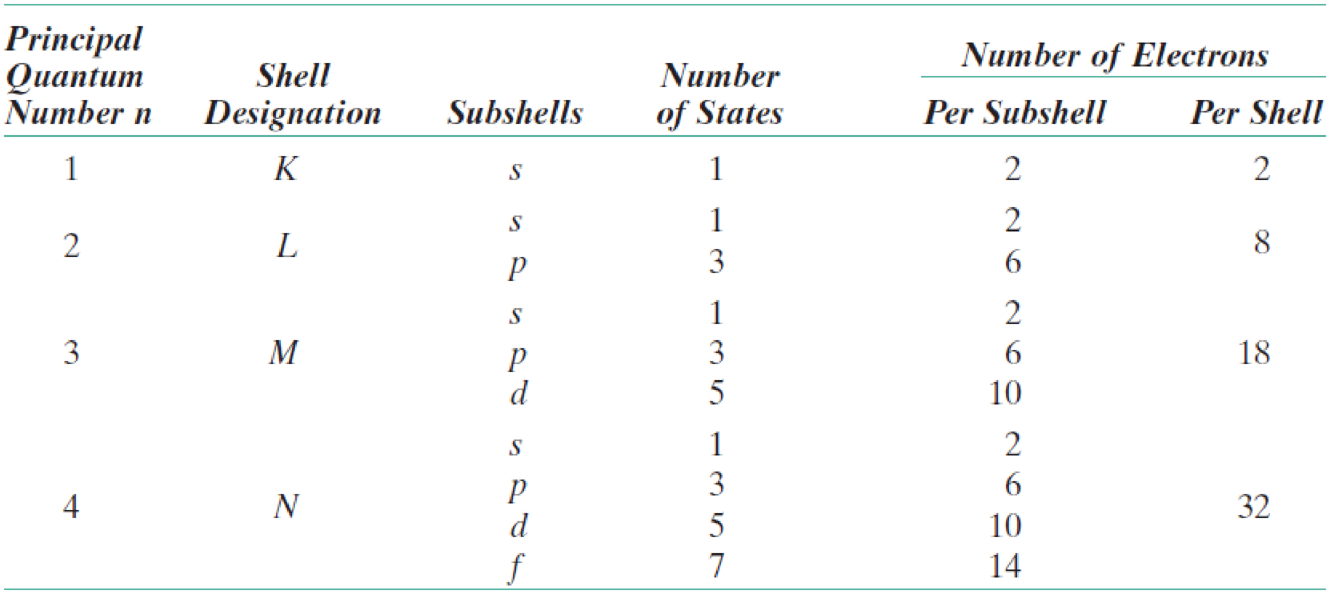
Quantum Numbers

- Using wave mechanics, every electron in an atom is characterized by four parameters called **quantum numbers.**
- The size, shape, and spatial orientation of an electron's probability density are specified by three of these quantum numbers.
- Bohr energy levels separate into electron subshells, and quantum numbers dictate the number of states within each subshell.
- Shells are specified by a *principal quantum number n*, which may take on integral values beginning with unity; sometimes these shells are designated by the letters *K*, *L*, *M*, *N*, *O*, and so on, which correspond, respectively, to $n = 1, 2, 3, 4, 5$, etc.

Electrons in Atoms

Quantum Numbers

Table 1: The Number of Available Electron States in Some of the Electron Shells and Subshells.



Principal Quantum Number n	*Shell Designation*	*Subshells*	*Number of States*	*Number of Electrons*	
				Per Subshell	*Per Shell*
1	*K*	*s*	1	2	2
2	*L*	*s*	1	2	8
		p	3	6	
3	*M*	*s*	1	2	18
		p	3	6	
		d	5	10	
4	*N*	*s*	1	2	32
		p	3	6	
		d	5	10	
		f	7	14	

- The second quantum number, *l*, signifies the subshell, which is denoted by a lowercase letter—an *s*, *p*, *d*, or *f*; it is related to the shape of the electron subshell (the number of these subshells is restricted by the magnitude of *n*).

Electrons in Atoms

Quantum Numbers

- The number of energy states for each subshell is determined by the third quantum number, m_l.
    - For an *s* subshell, there is a single energy state, whereas for *p*, *d*, and *f* subshells, three, five, and seven states exist, respectively.
- Related to this spin moment is the fourth quantum number, m_s, for which two values are possible (+1/2 1nd -1/2) one for each of the spin orientations.
- Thus, the Bohr model was further refined by wave mechanics, in which the introduction of three new quantum numbers gives rise to electron subshells within each shell (See Fig. 2).

Electrons in Atoms

Quantum Numbers

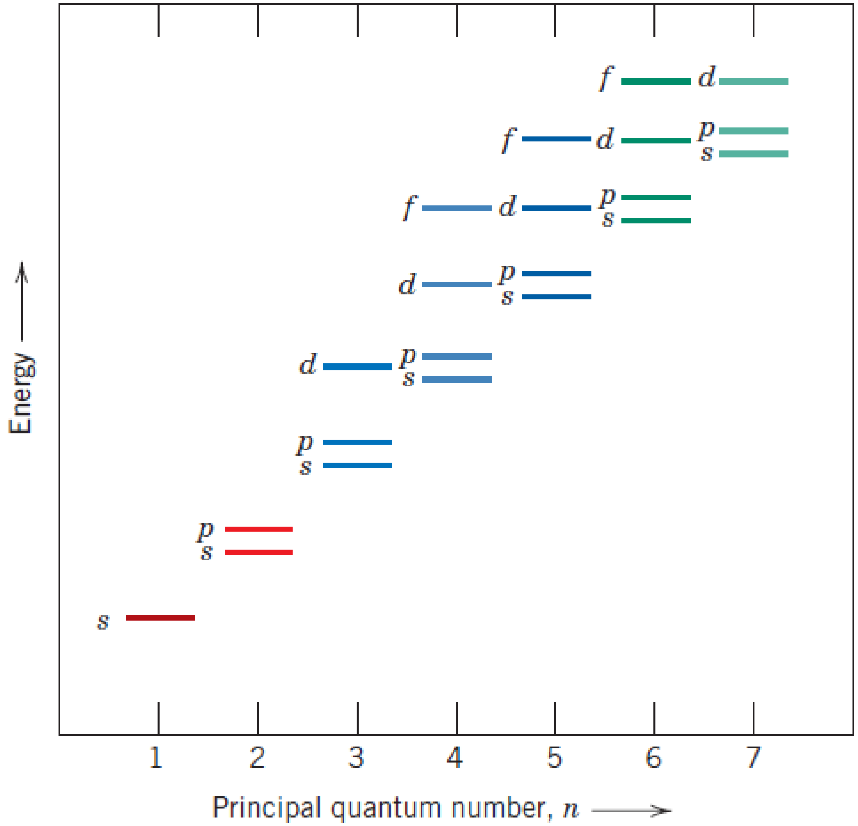


Fig. 4: Schematic representation of the relative energies of the electrons for the various shells and subshells.

3 important notes

1. The smaller the principal quantum number, the lower the energy level; for example, the energy of a 1*s* state is less than that of a 2*s* state.

2. Within each shell, the energy of a subshell level increases with the value of the *l* quantum number. For example, the energy of a 3*d* state is greater than a 3*p*.

3. There may be overlap in energy of a state in one shell with states in an adjacent shell, which is especially true of *d* and *f* states; for example, the energy of a 3*d* state is generally greater than that for a 4*s*.

Electrons in Atoms

Quantum Numbers

Table 2: A Listing of the Expected Electron Configurations for Some of the Common Elements.

Element	Atomic #	Electron configuration	
Hydrogen	1	$1s^1$	
Helium	2	$1s^2$	(stable)
Lithium	3	$1s^2 2s^1$	
Beryllium	4	$1s^2 2s^2$	
Boron	5	$1s^2 2s^2 2p^1$	
Carbon	6	$1s^2 2s^2 2p^2$	
...		...	
Neon	10	$1s^2 2s^2 2p^6$	(stable)
Sodium	11	$1s^2 2s^2 2p^6 3s^1$	
Magnesium	12	$1s^2 2s^2 2p^6 3s^2$	
Aluminum	13	$1s^2 2s^2 2p^6 3s^2 3p^1$	
...		...	
Argon	18	$1s^2 2s^2 2p^6 3s^2 3p^6$	(stable)
...	...	...	
Krypton	36	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$	(stable)

Electrons in Atoms

Electron Configurations

- **Pauli exclusion principle:** used to determine the manner in which electron states are filled with electrons.

- This principle stipulates that each electron state can hold no more than two electrons, which must have opposite spins.

  - Thus, *s*, *p*, *d*, and *f* subshells may each accommodate, respectively, a total of 2, 6, 10, and 14 electrons.

Electrons in Atoms
Electron Configurations

- For most atoms, the electrons fill up the lowest possible energy states in the electron shells and subshells, two electrons (having opposite spins) per state.

- The energy structure for a sodium atom is represented schematically in Figure 5.

- When all the electrons occupy the lowest possible energies, an atom is said to be in its **ground state.**

Electrons in Atoms

Electron Configurations

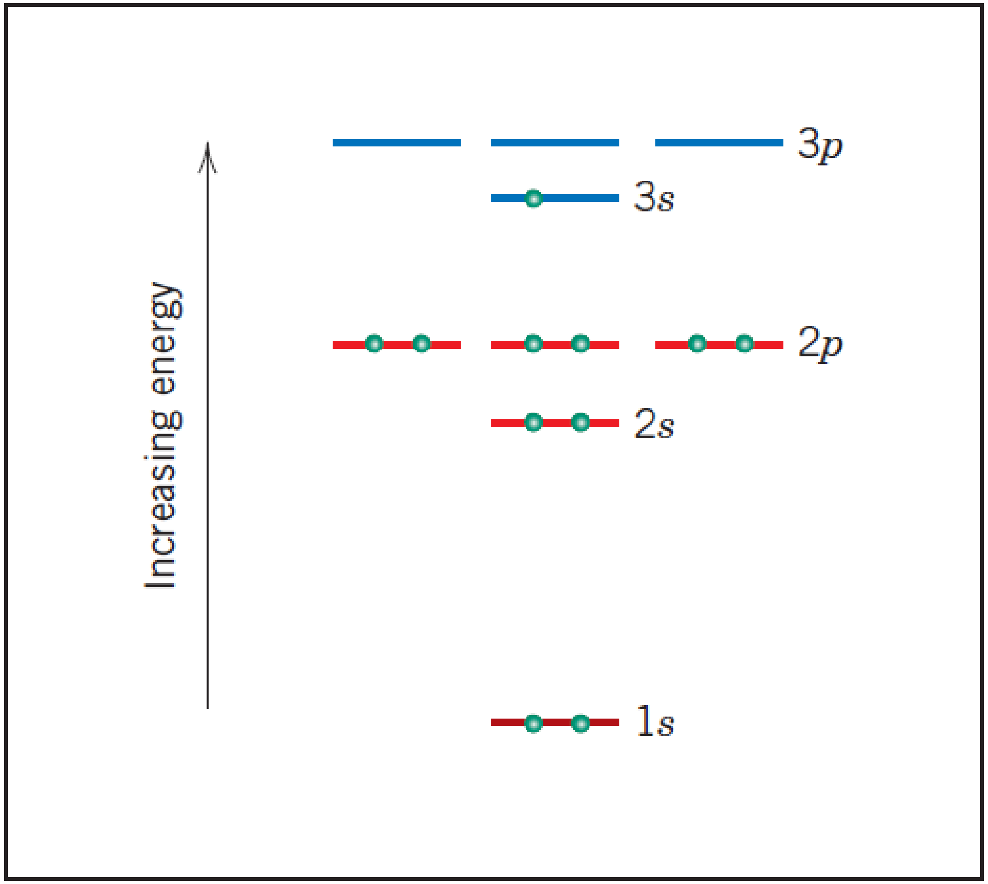


Fig. 5 Schematic representation of the filled and lowest unfilled energy states for a sodium atom

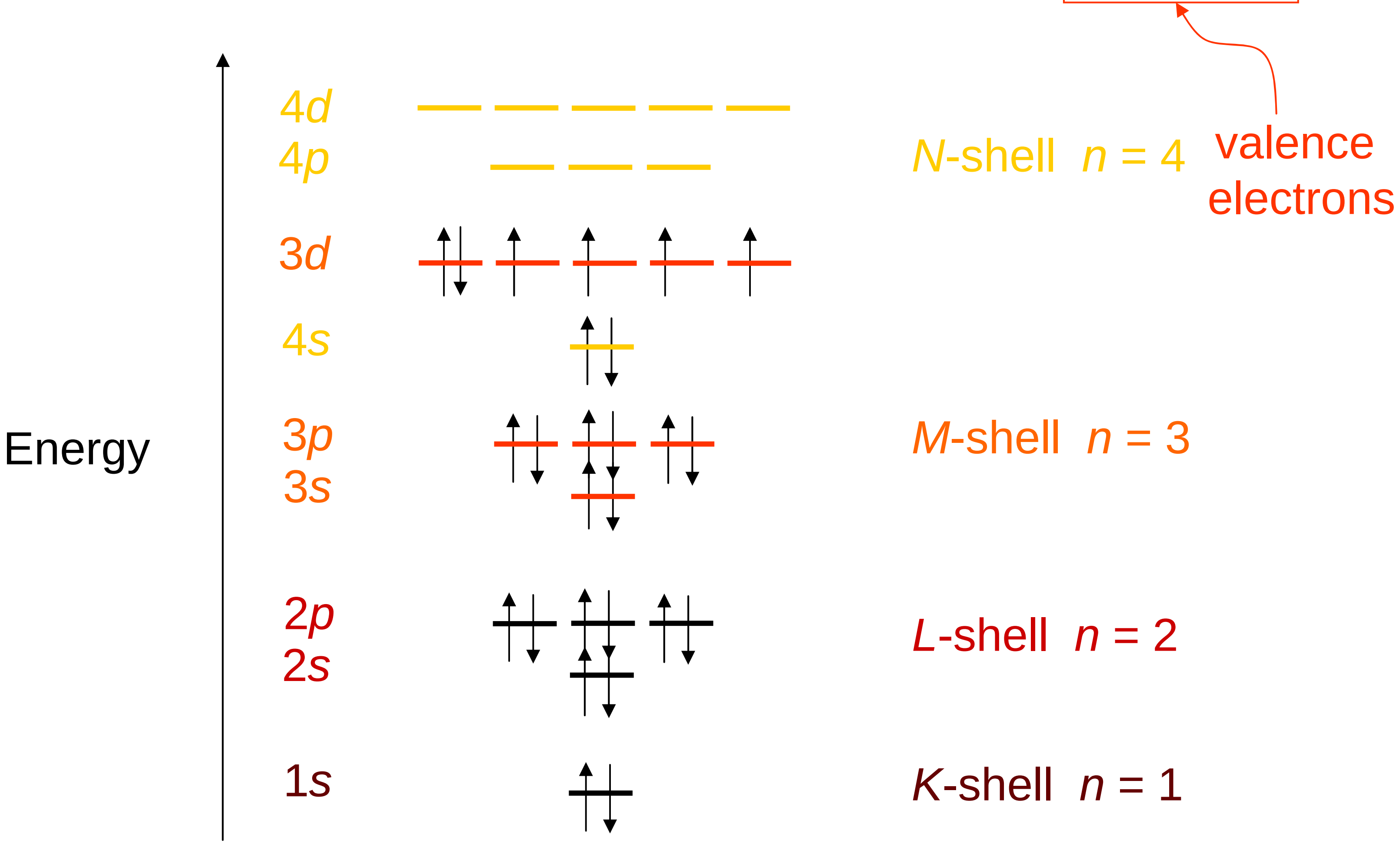
Electrons in Atoms
Electron Configurations

- comments regarding these electron configurations are necessary.
    - First, the **valence electrons** are those that occupy the outermost shell. These electrons are extremely important; they participate in the bonding between atoms to form atomic and molecular aggregates. Furthermore, many of the physical and chemical properties of solids are based on these valence electrons.
    - Second, inert atoms have what are termed *stable electron configurations;* that is, the states within the outermost or valence electron shell are completely filled. (Ne, Ar, Kr, and He).
    - Some atoms of the elements that have unfilled valence shells assume stable electron configurations by gaining or losing electrons to form charged ions, or by sharing electrons with other atoms. This is the basis for some chemical reactions, and also for atomic bonding in solids.

Electrons in Atoms

Electron Configurations

ex: Fe - atomic # = 26 $1s^2$ $2s^2\,2p^6$ $3s^2\,3p^6$ $\boxed{3d^6\ 4s^2}$

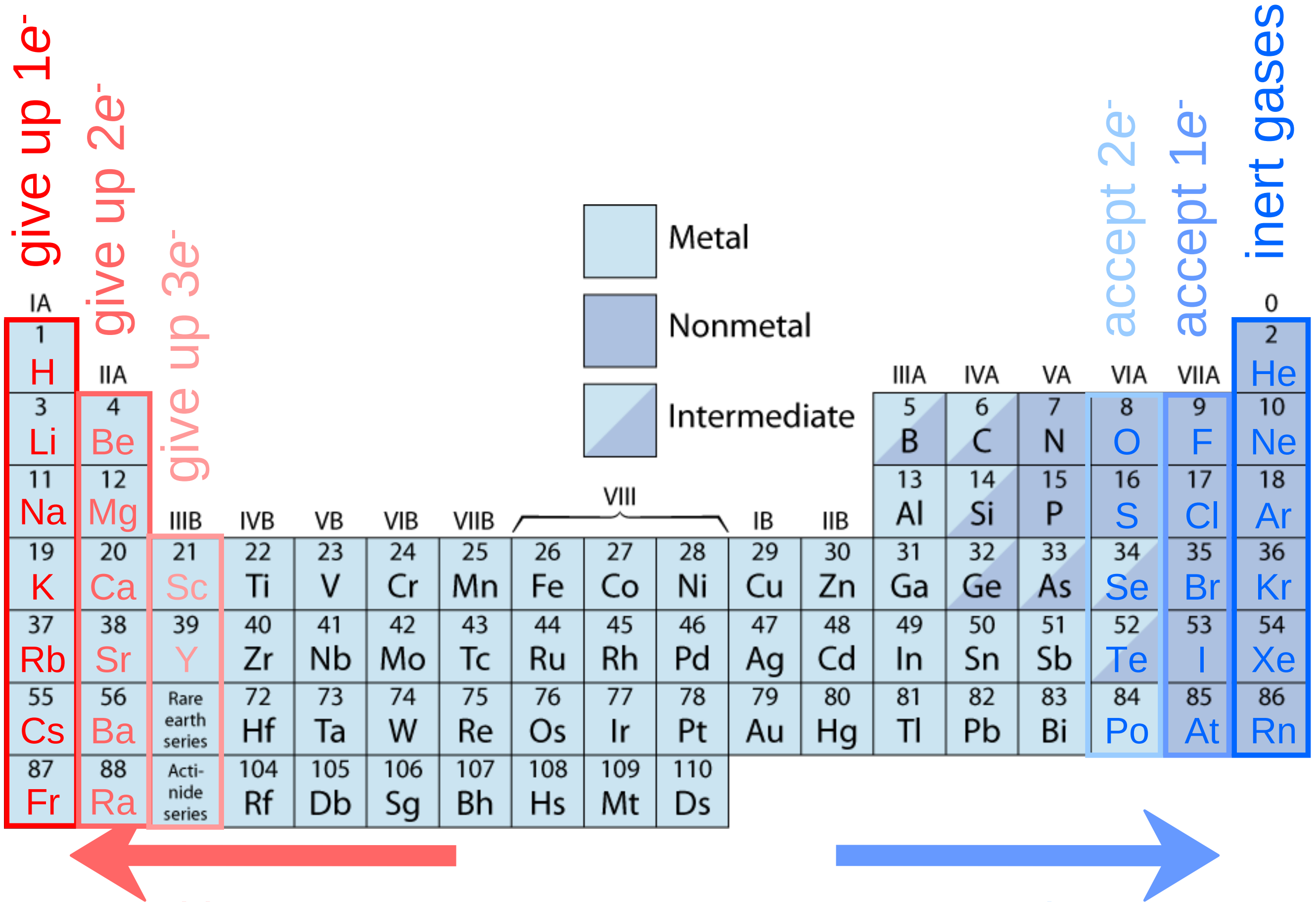


The Periodic Table

- In the periodic table, the elements are situated, with increasing atomic number, in seven horizontal rows called periods.
  - The arrangement is such that all elements arrayed in a given column or group have similar valence electron structures, as well as chemical and physical properties.
  - These properties change gradually, moving horizontally across each period and vertically down each column.

The Periodic Table

Fig. 6: Periodic Table



IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIII	VIII	VIII	IB	IIB	IIIA	IVA	VA	VIA	VIIA	0
1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											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	Actinide series	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds								

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

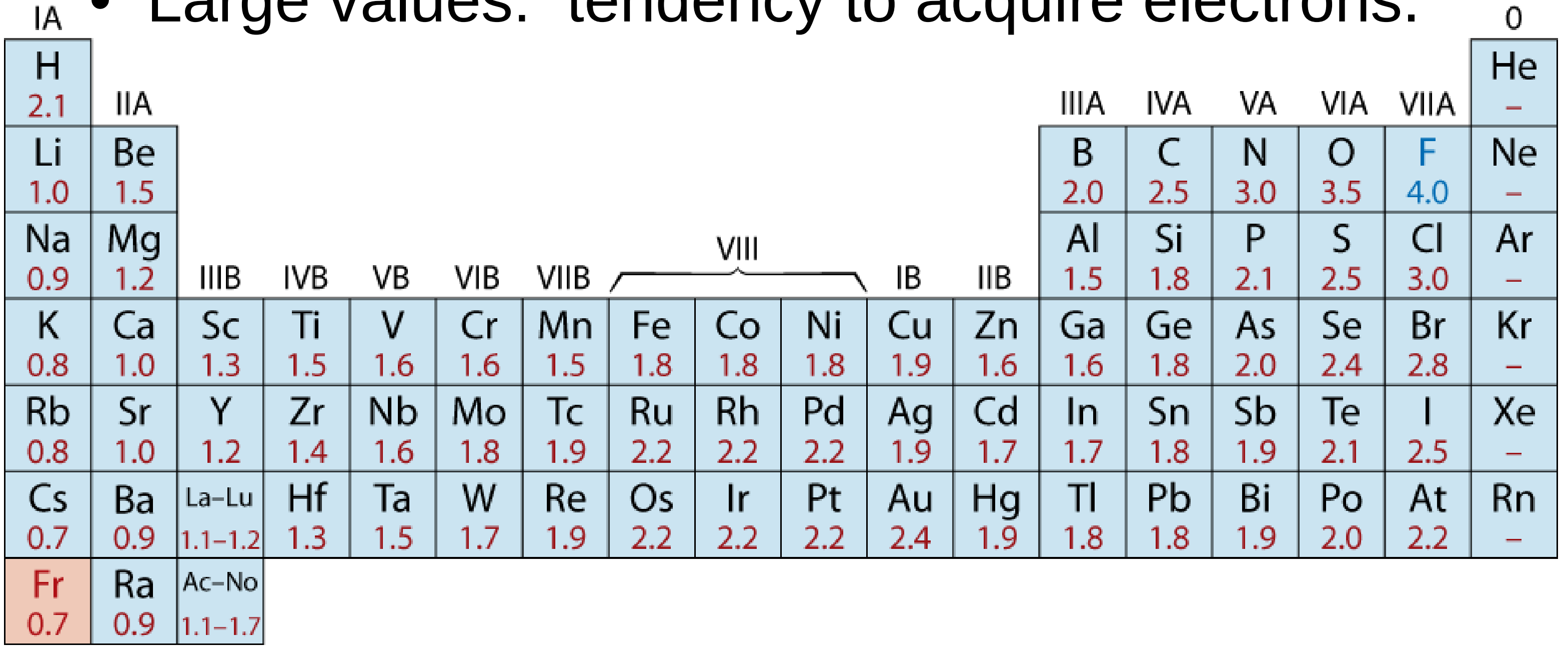
Electronegative elements: Readily acquire electrons to become - ions.

The Periodic Table

Electronegativity

Fig. 7: The electronegativity values for the elements

- Ranges from 0.7 to 4.0,
- Large values: tendency to acquire electrons.

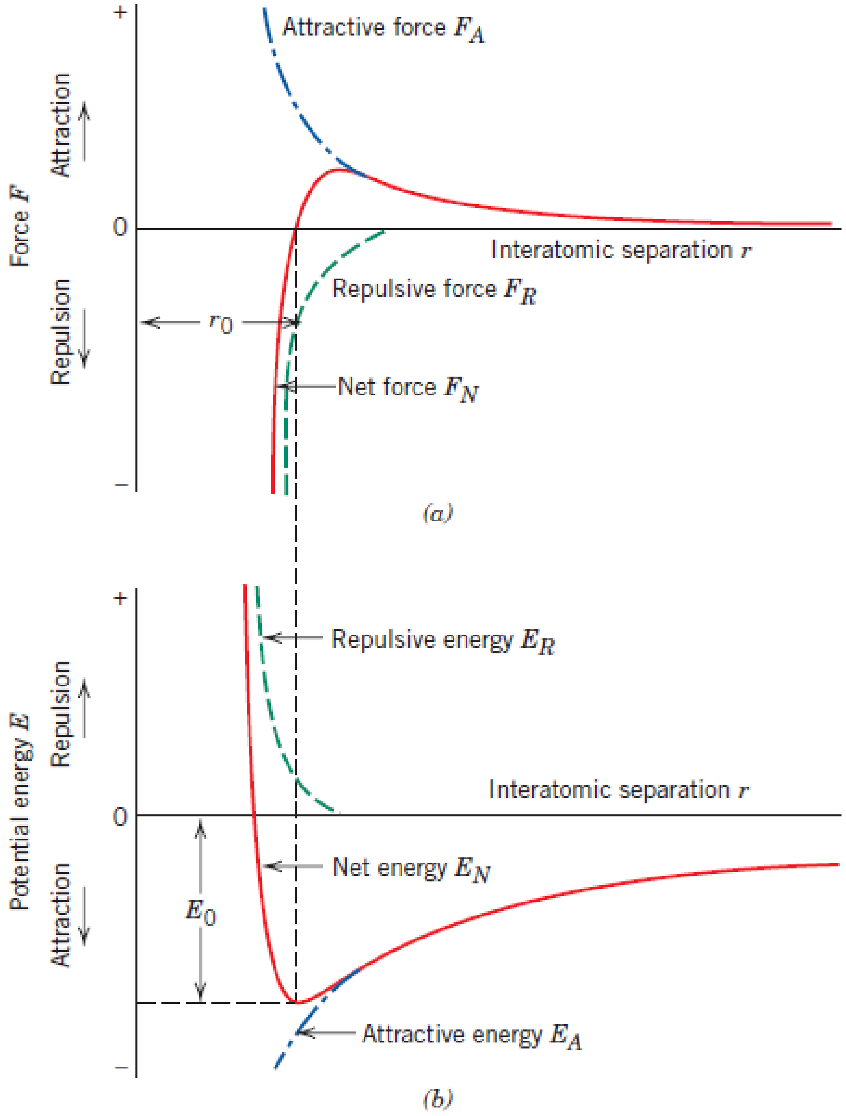


IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIII			IB	IIB	IIIA	IVA	VA	VIA	VIIA	0
H 2.1																	He –
Li 1.0	Be 1.5											B 2.0	C 2.5	N 3.0	O 3.5	F 4.0	Ne –
Na 0.9	Mg 1.2											Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0	Ar –
K 0.8	Ca 1.0	Sc 1.3	Ti 1.5	V 1.6	Cr 1.6	Mn 1.5	Fe 1.8	Co 1.8	Ni 1.8	Cu 1.9	Zn 1.6	Ga 1.6	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															

Smaller electronegativity

Larger electronegativity

Bonding Forces & Energies



- Attractive force depends on type of bonding.

- Repulsive force arises from the negatively charged electron cloud for the 2 atoms.

- Equilibrium spacing: r_0.

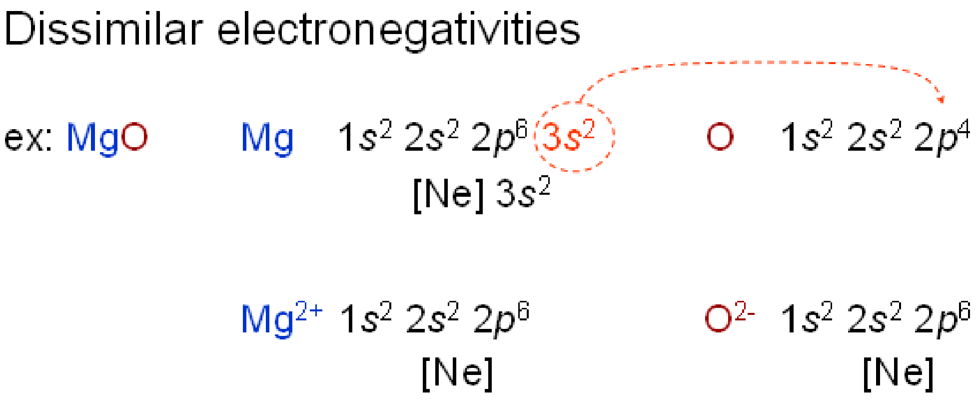
- Minimum energy to separate atoms (bonding energy): E_0.

Fig. 8: (*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.

Primary Interatomic Bonds

Ionic Bonding

- It is always found in compounds that are composed of both metallic and nonmetallic elements.
- Atoms of a metallic element easily give up their valence electrons to the nonmetallic atoms.
  - ☐ In the process all the atoms acquire stable or inert gas configurations and, in addition, an electrical charge; that is, they become ions.



Dissimilar electronegativities

ex: MgO

Mg $1s^2\ 2s^2\ 2p^6\ 3s^2$

$[\mathrm{Ne}]\ 3s^2$

O $1s^2\ 2s^2\ 2p^4$

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

[Ne]

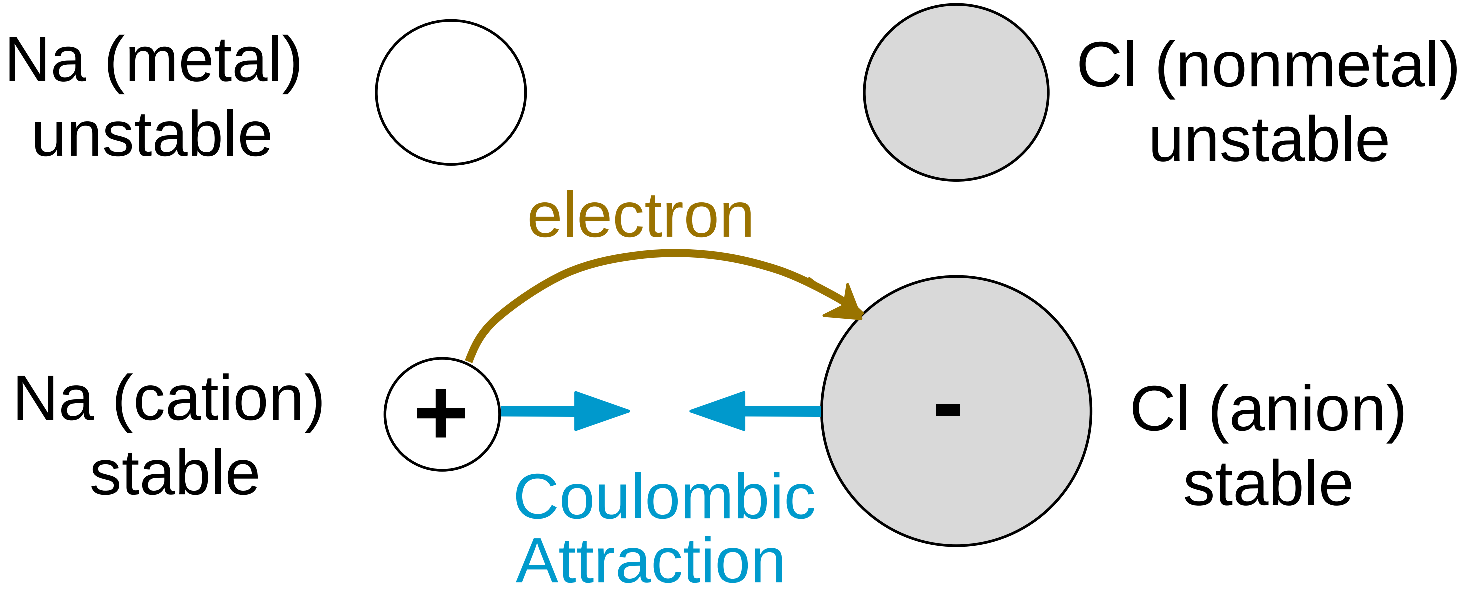
O^{2-} $1s^2\ 2s^2\ 2p^6$

[Ne]

Primary Interatomic Bonds

Ionic Bonding

- Sodium chloride (NaCl) is the classic ionic material.



Na (metal)
unstable

Cl (nonmetal)
unstable

electron

Na (cation)
stable

+

-

Cl (anion)
stable

Coulombic
Attraction

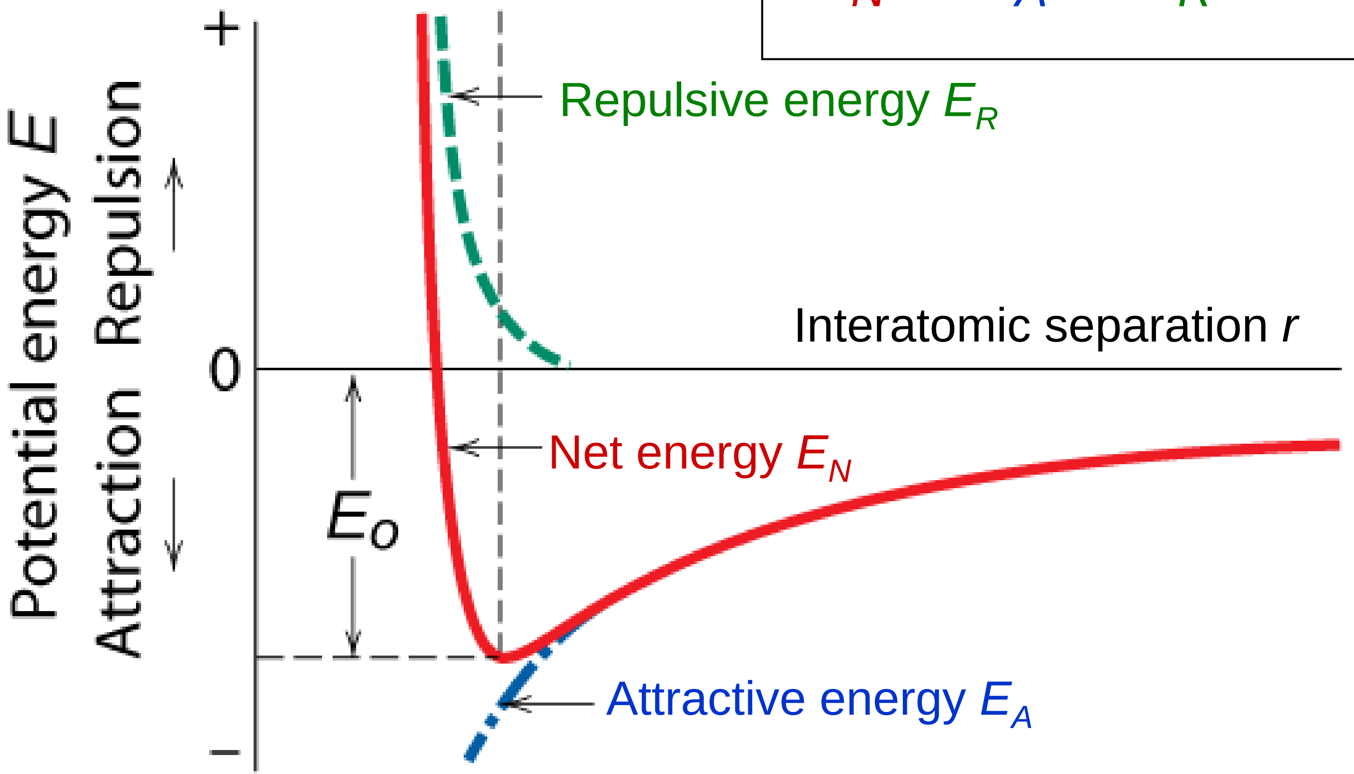
Fig. 9: Ionic bonding in NaCl

Primary Interatomic Bonds

Ionic Bonding

- Energy – minimum energy most stable
  - Energy balance of attractive and repulsive terms

$$E_N = E_A + E_R = -\frac{A}{r} + \frac{B}{r^n}$$



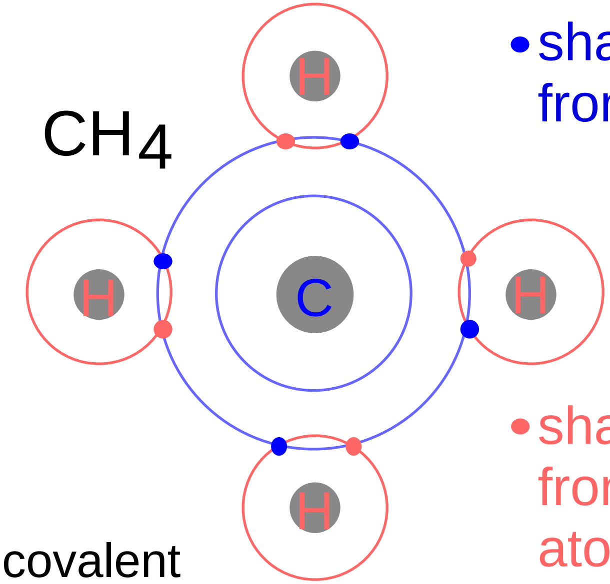
Primary Interatomic Bonds
Covalent Bonding

- stable electron configurations are assumed by the sharing of electrons between adjacent atoms.
  - Two atoms that are covalently bonded will each contribute at least one electron to the bond, and the shared electrons may be considered to belong to both atoms.

C: has 4 valence e^-,
needs 4 more

H: has 1 valence e^-,
needs 1 more

Electronegativities
are comparable.



- shared electrons from carbon atom
- shared electrons from hydrogen atoms

Fig. 10: Schematic representation of covalent bonding in a molecule of methane (CH_4).

Primary Interatomic Bonds
Ionic- Covalent Mixed Bonding

- It is possible to have interatomic bonds that are partially ionic and partially covalent.
  - In fact, very few compounds exhibit pure ionic or covalent bonding.
- For a compound, the degree of either bond type depends on the difference in their electronegativities.
- The greater the difference in electronegativity, the more ionic the bond, and the smaller the difference the greater the degree of covalency.

Primary Interatomic Bonds
Ionic- Covalent Mixed Bonding

- Ionic-Covalent Mixed Bonding

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

where X_A & X_B are Pauling electronegativities

Ex: MgO

$X_{Mg} = 1.2$
$X_O = 3.5$

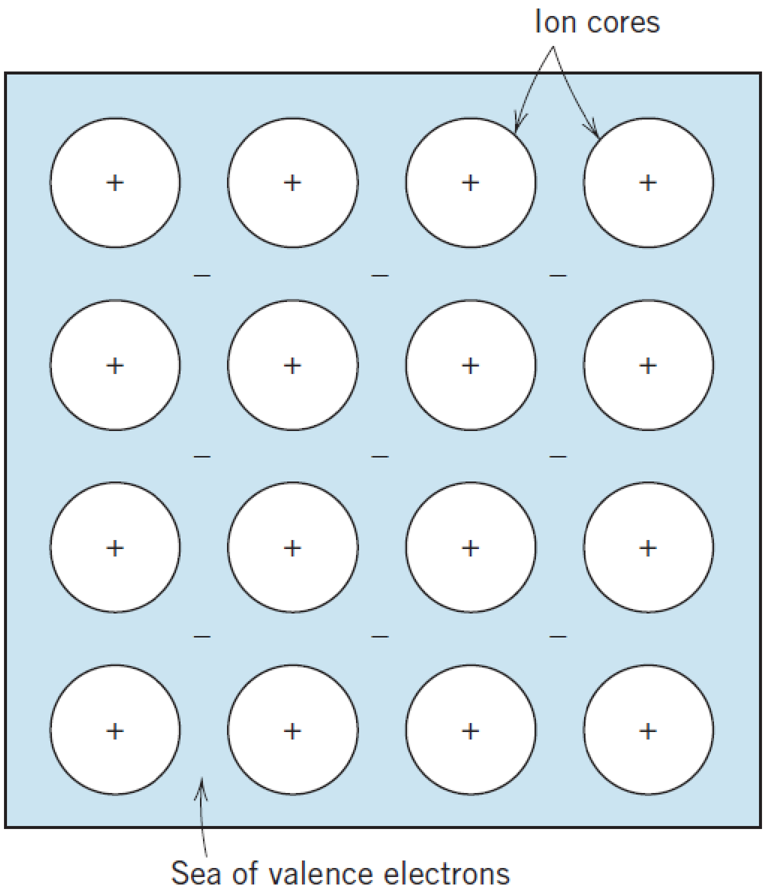
$$\%\text{ ionic character} = \left(1 - e^{-\frac{(3.5 - 1.2)^2}{4}}\right) \times (100\%) = 73.4\%\text{ ionic}$$

Primary Interatomic Bonds
Metallic Bonding

- Found in metals and their alloys.
  - Metallic materials have one, two, or at most, three valence electrons.
- In a proposed model, these valence electrons are not bound to any particular atom in the solid and are more or less free to drift throughout the entire metal.
  - They may be thought of as belonging to the metal as a whole, or forming a “sea of electrons” or an “electron cloud.”
- The remaining non-valence electrons and atomic nuclei form what are called *ion cores,* which possess a net positive charge equal in magnitude to the total valence electron charge per atom.

Primary Interatomic Bonds

Metallic Bonding



The free electrons shield the positively charged ion cores from mutually repulsive electrostatic forces.

In addition, these free electrons act as a “glue” to hold the ion cores together.

Fig. 11: Schematic illustration of metallic bonding.

SECONDARY BONDING OR VANDER WAALS BONDING

- They are weak in comparison to the primary or chemical ones.
  - Bonding energies are typically on the order of only 10 kJ/mol (0.1 eV/atom).
- Secondary bonding exists between virtually all atoms or molecules, but its presence may be obscured if any of the three primary bonding types is present.
- Evidenced for the inert gases and between molecules in molecular structures that are covalently bonded.

SECONDARY BONDING OR VANDER WAALS BONDING

- Secondary bonding forces arise from atomic or molecular **dipoles.**
- An electric dipole exists whenever there is some separation of positive and negative portions of an atom or molecule.
    - The bonding results from the coulombic attraction between the positive end of one dipole and the negative region of an adjacent one.
- **Hydrogen bonding,** a special type of secondary bonding, is found to exist between some molecules that have hydrogen as one of the constituents

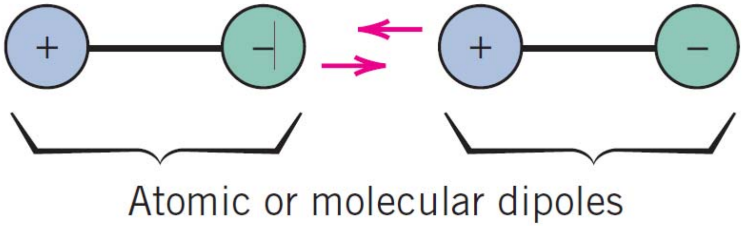
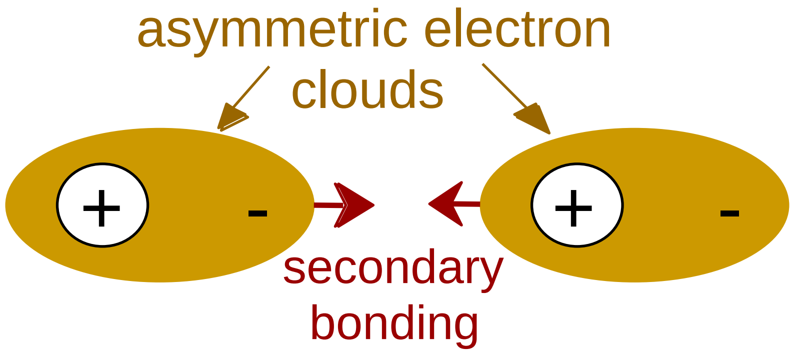


Fig. 12 Schematic illustration of van der Waals bonding between two dipoles.

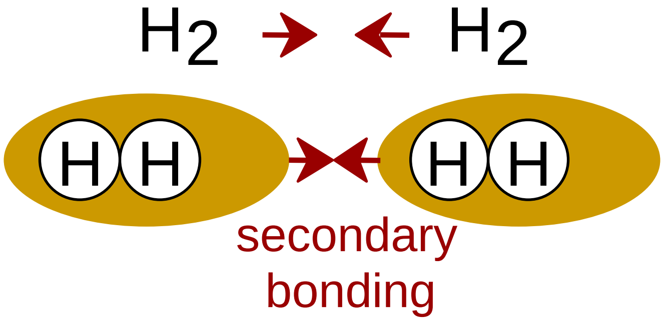
SECONDARY BONDING

- Fluctuating dipoles


asymmetric electron clouds

secondary bonding

ex: liquid H_2


H_2 → ← H_2

secondary bonding

- Permanent dipoles-molecule induced

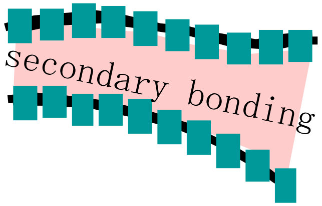
-general case:


secondary bonding

-ex: liquid HCl


secondary bonding

-ex: polymer

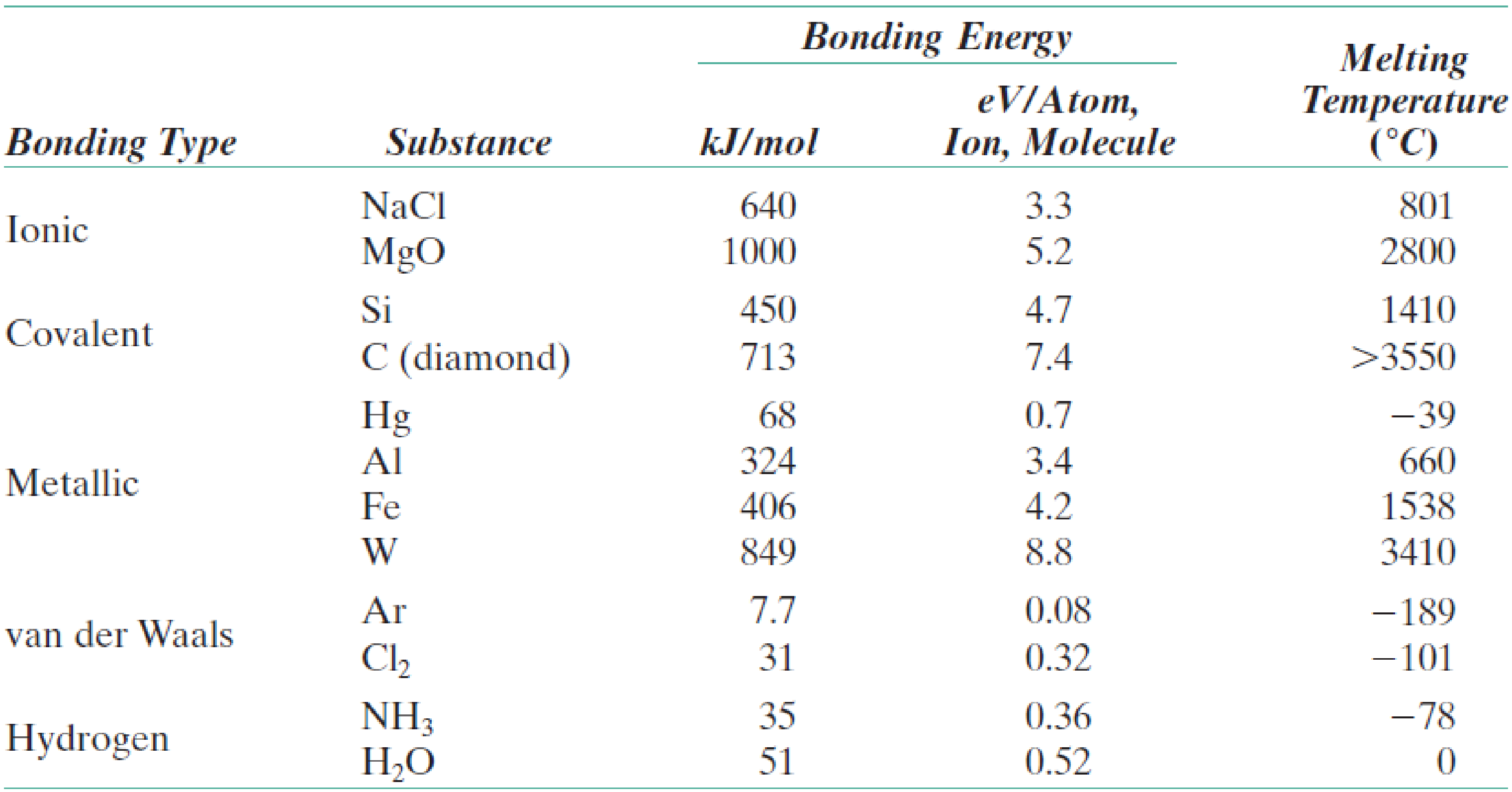


secondary bonding

Primary Interatomic Bonds

Bonding Energy

Table 3: Bonding Energies and Melting Temperatures for Various Substances.



		Bonding Energy		
Bonding Type	***Substance***	***kJ/mol***	***eV/Atom, Ion, Molecule***	***Melting Temperature (°C)***
Ionic	NaCl	640	3.3	801
	MgO	1000	5.2	2800
Covalent	Si	450	4.7	1410
	C (diamond)	713	7.4	>3550
Metallic	Hg	68	0.7	−39
	Al	324	3.4	660
	Fe	406	4.2	1538
	W	849	8.8	3410
van der Waals	Ar	7.7	0.08	−189
	Cl_2	31	0.32	−101
Hydrogen	NH_3	35	0.36	−78
	H_2O	51	0.52	0