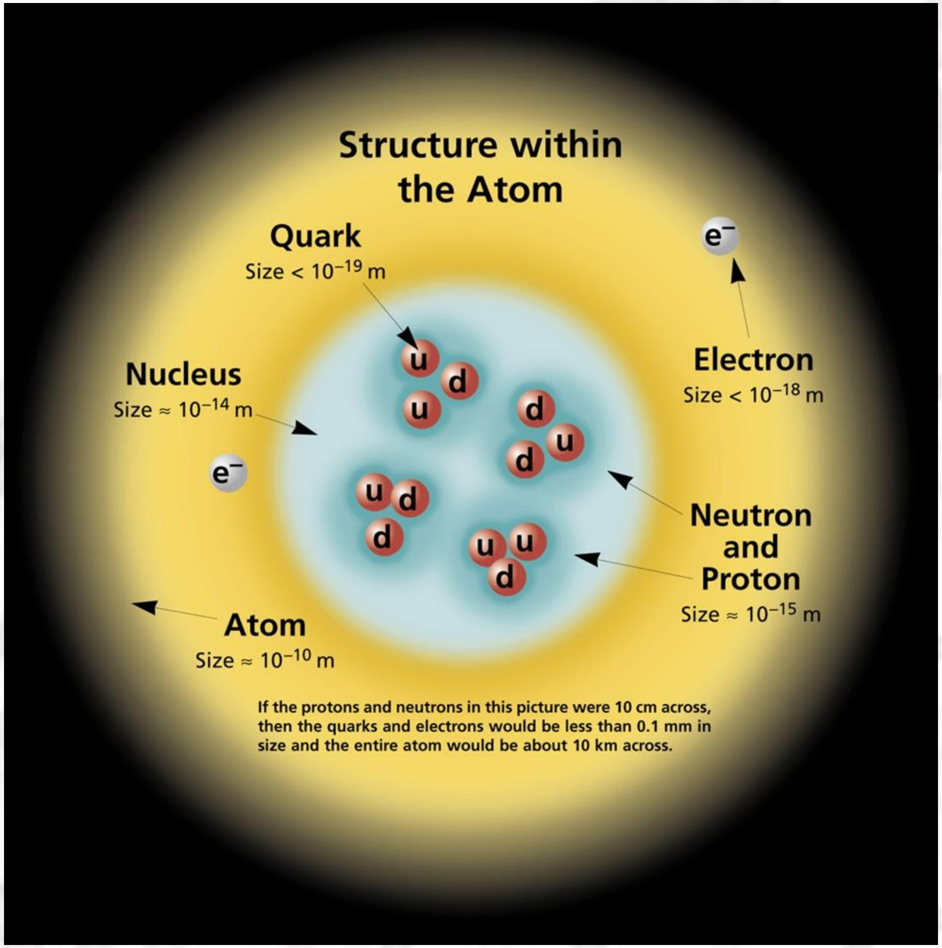


Chapter 2

ATOMIC STRUCTURE AND INTERATOMIC BONDING

Electronegativity

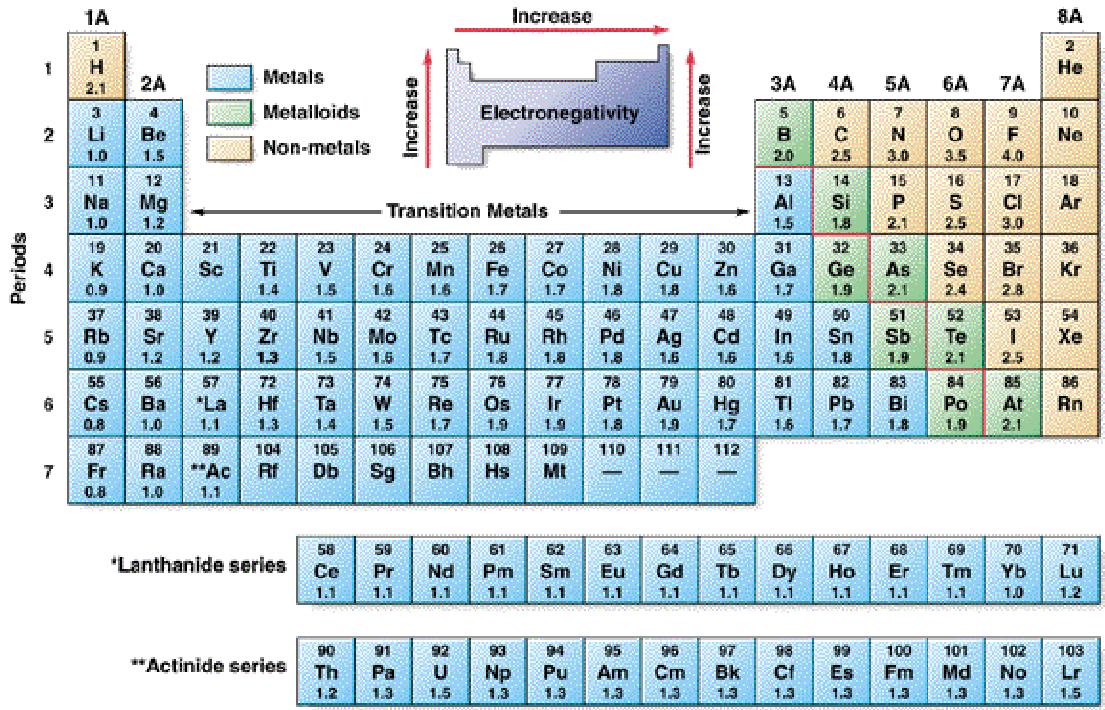
- **Electronegativity**, symbol χ, is a chemical property that describes the ability of an atom to attract electrons towards itself in a covalent bond. First proposed by Linus Pauling in 1932 as a development of valence bond theory, it has been shown to correlate with a number of other chemical properties.
- Electronegativity cannot be directly measured and must be calculated from other atomic or molecular properties. Several methods of calculation have been proposed and, although there may be small differences in the numerical values of the electronegativity, all methods show the same periodic trend between elements.
- The difference in electronegativity between atoms A and B is given by:

$$\chi_A - \chi_B = (eV)^{-1/2}\sqrt{E_d(AB) - [E_d(AA) + E_d(BB)]/2}$$

where the dissociation energy, *E*d, of the A–B, A–A and B–B bonds are expressed in electron volts, the factor (eV)−½ being included to ensure a dimensionless result. Hence, the difference in Pauling electronegativity between hydrogen and brome is 0.7 (dissociation energies: H–Br, 3.79 eV; H–H, 4.52 eV; Br–Br 2.00 eV)

ELECTRONEGATIVITY

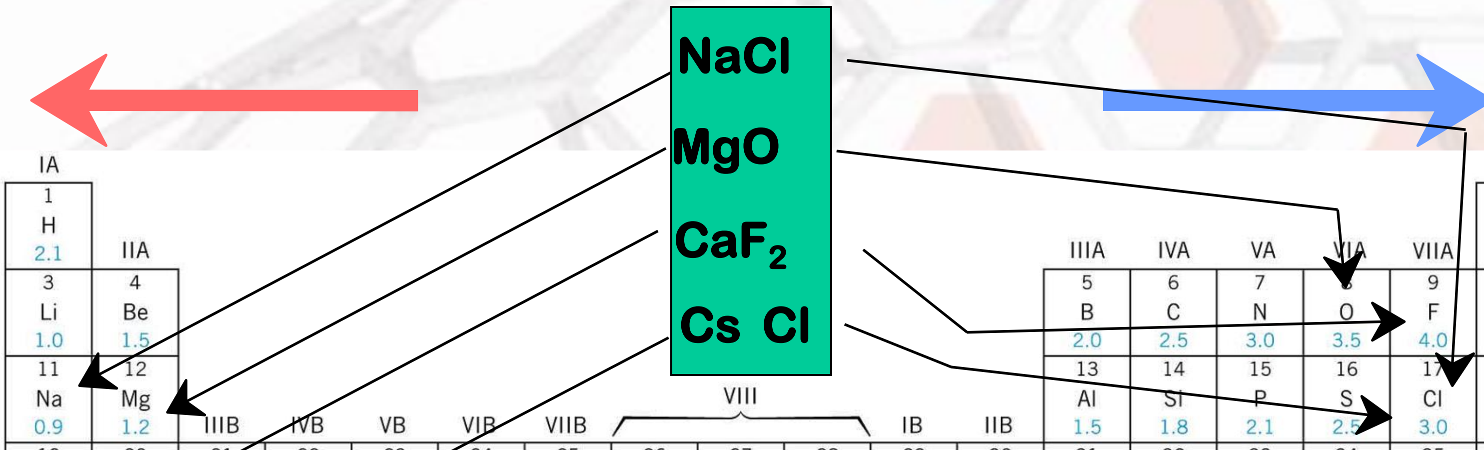
Armold, Essentials of General, Organic and Biological Chemistry
Figure 3.7



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

Electronegative elements:
Readily acquire electrons
to become - ions.

EXAMPLES: IONIC BONDING

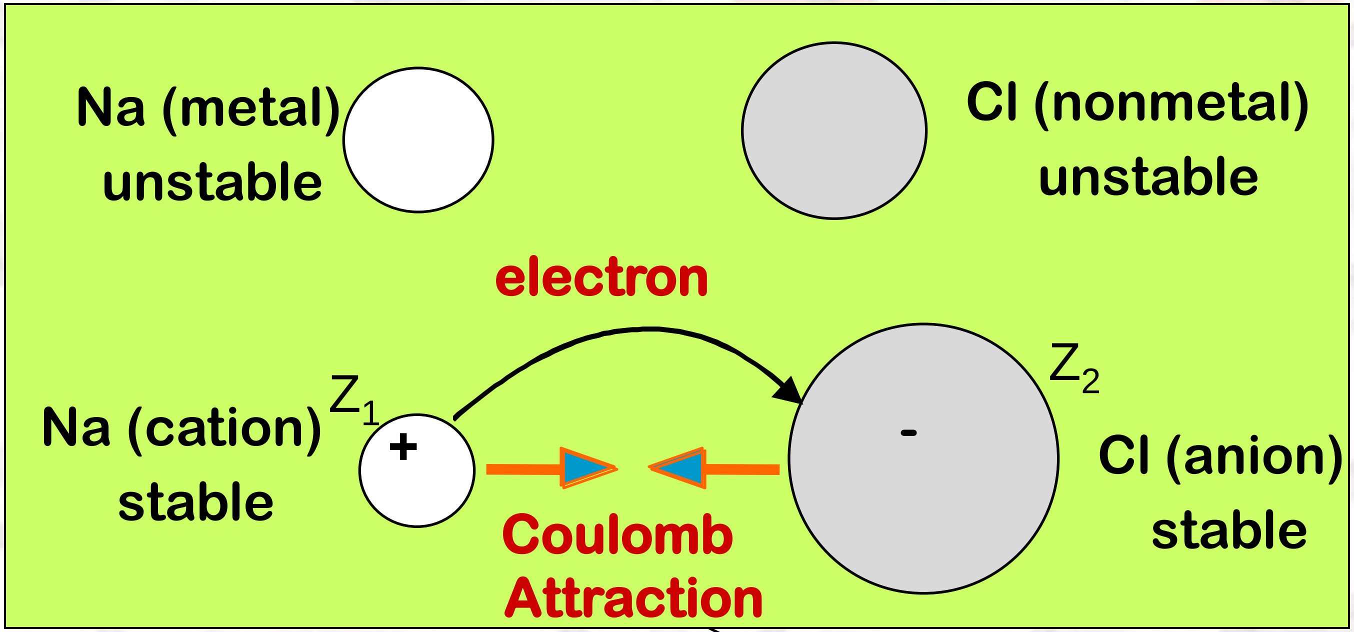


IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIII			IB	IIB	IIIA	IVA	VA	VIA	VIIA	0
1 H 2.1																	2 He –
3 Li 1.0	4 Be 1.5											5 B 2.0	6 C 2.5	7 N 3.0	8 O 3.5	9 F 4.0	10 Ne –
11 Na 0.9	12 Mg 1.2											13 Al 1.5	14 Si 1.8	15 P 2.1	16 S 2.5	17 Cl 3.0	18 Ar –
19 K 0.8	20 Ca 1.0	21 Sc 1.3	22 Ti 1.5	23 V 1.6	24 Cr 1.6	25 Mn 1.5	26 Fe 1.8	27 Co 1.8	28 Ni 1.8	29 Cu 1.9	30 Zn 1.6	31 Ga 1.6	32 Ge 1.8	33 As 2.0	34 Se 2.4	35 Br 2.8	36 Kr –
37 Rb 0.8	38 Sr 1.0	39 Y 1.2	40 Zr 1.4	41 Nb 1.6	42 Mo 1.8	43 Tc 1.9	44 Ru 2.2	45 Rh 2.2	46 Pd 2.2	47 Ag 1.9	48 Cd 1.7	49 In 1.7	50 Sn 1.8	51 Sb 1.9	52 Te 2.1	53 I 2.5	54 Xe –
55 Cs 0.7	56 Ba 0.9	57–71 La–Lu 1.1–1.2	72 Hf 1.3	73 Ta 1.5	74 W 1.7	75 Re 1.9	76 Os 2.2	77 Ir 2.2	78 Pt 2.2	79 Au 2.4	80 Hg 1.9	81 Tl 1.8	82 Pb 1.8	83 Bi 1.9	84 Po 2.0	85 At 2.2	86 Rn –
87 Fr 0.7	88 Ra 0.9	89–102 Ac–No 1.1–1.7															

- **Ionic bonding energy** is relatively large:
  600-1500 kJ/mol (3-8 eV/atom; 1eV=1.602 x 10^{-19} J)
- The ionic materials typically have **high melting point**, are **hard** and **brittle** as well as electrically and thermally **insulators**
- Example: Ceramics (MgO, SiO_2 etc.)

IONIC BONDING (1)

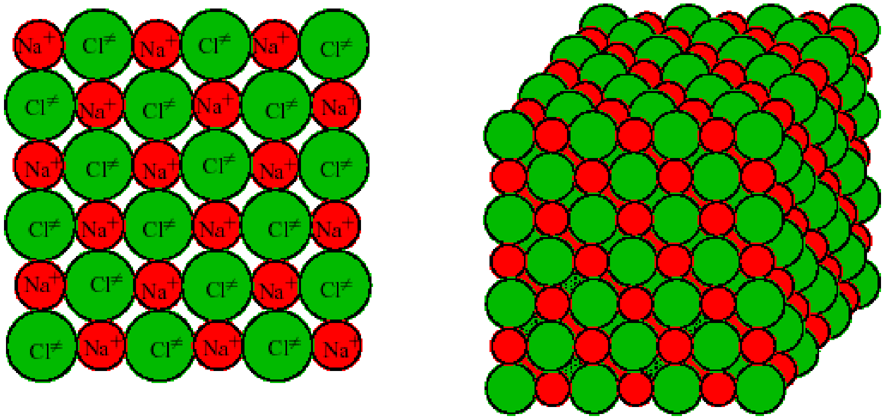
- Occurs between + and - ions.
- Requires **electron transfer**.
- Large difference in electronegativity required.
- Example: NaCl



$$E_A = \frac{(Z_1 e)(Z_2 e)}{4\pi\varepsilon_0} \cdot \frac{1}{r}$$

ε_0 – a vacuum permittivity ($8.85 \cdot 10^{-12}$ F/m)

IONIC BONDING (2)



(a) (b)

Fig. 1.9: (a) A schematic illustration of a cross section from solid NaCl. NaCl solid is made of Cl^- and Na^+ ions arranged alternatingly so that the oppositely charged ions are closest to each other and attract each other. There are also repulsive forces between the like-ions. In equilibrium the net force acting on any ion is zero. (b) Solid NaCl.

Strong, brittle materials

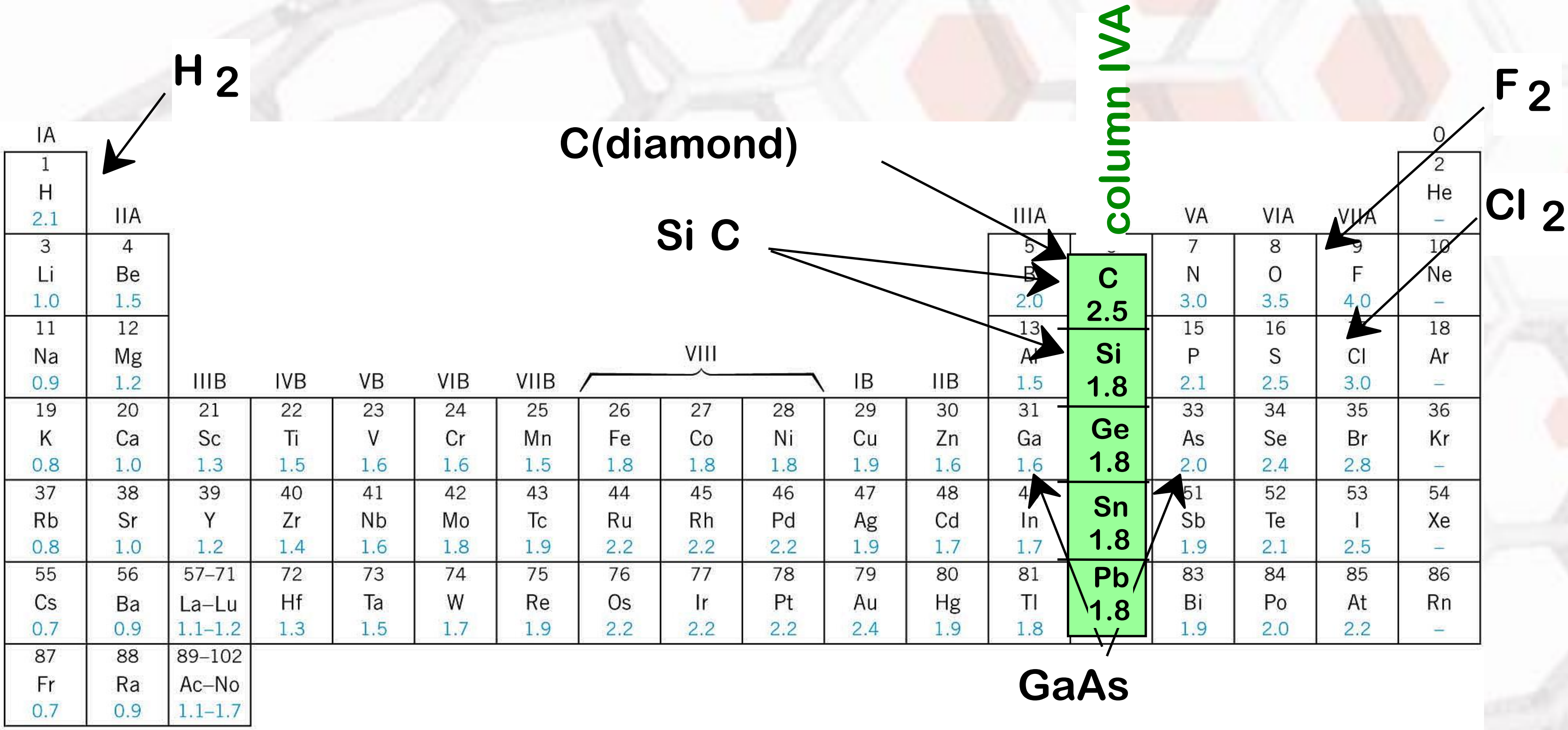
High melting points

Soluble in polar liquids like water

Electrical isolators

Low thermal conductivity

EXAMPLES: COVALENT BONDING



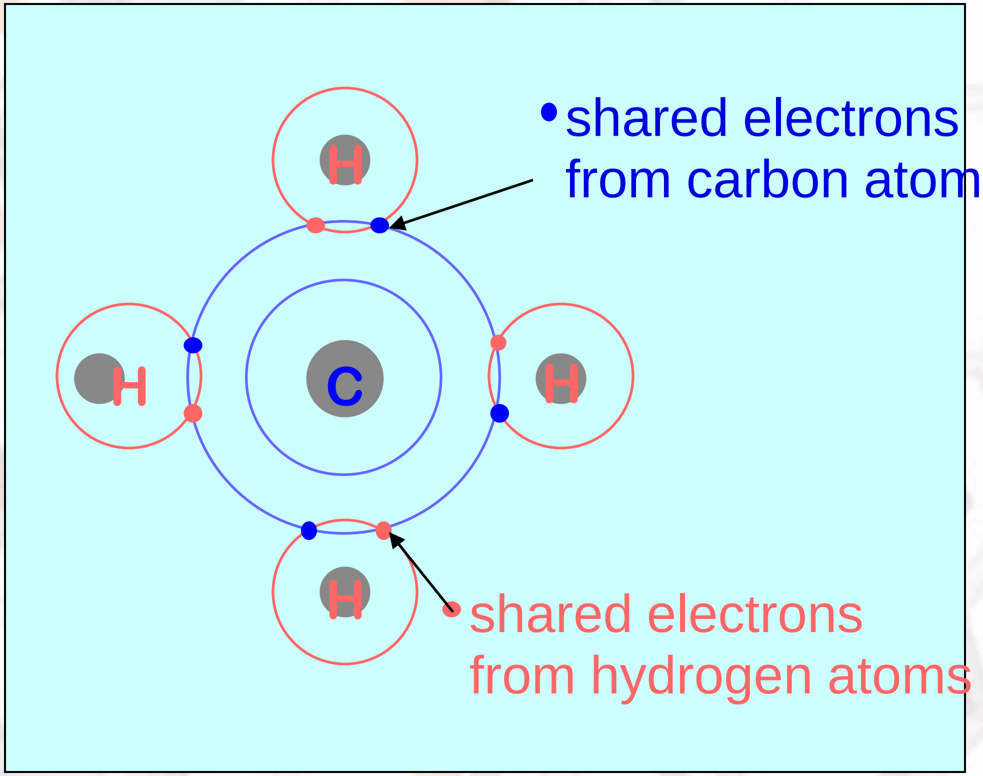
- ***Nonmetallic*** Molecules: H_2, Cl_2, F_2
- Molecules with ***dissimilar atoms***: CH_4, HNO_3, HF
- ***Elemental solids*** (e.g. column IVA: C, Si, Ge, etc,)
- ***Compound*** solids (columns IIIA, IVA, VA: SiC, GaAs, InSb)
- ***Polymeric Materials***

COVALENT BONDING (1)

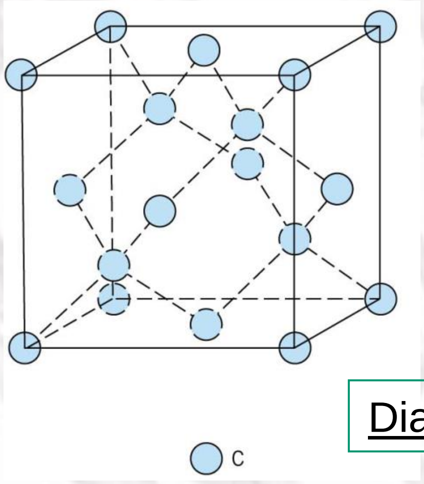
- Requires **shared electrons**
- Electronegativities are ***comparable***

- The number of covalent bonds that is possible for a specific atom is determined by ***number of valance electrons*** (N_v):
Number of covalent bonds = 8-N_v

Examples: Carbon – N_v=4 → Number of covalent bonds = 8 –4 = 4



Methane (CH_4): Carbon has 4 **valence** e and needs 4 more, while H has 1 **valence** e, and needs 1 more



Diamond: each carbon atom covalently bonds with 4 other C atoms.

COVALENT BONDING (2)

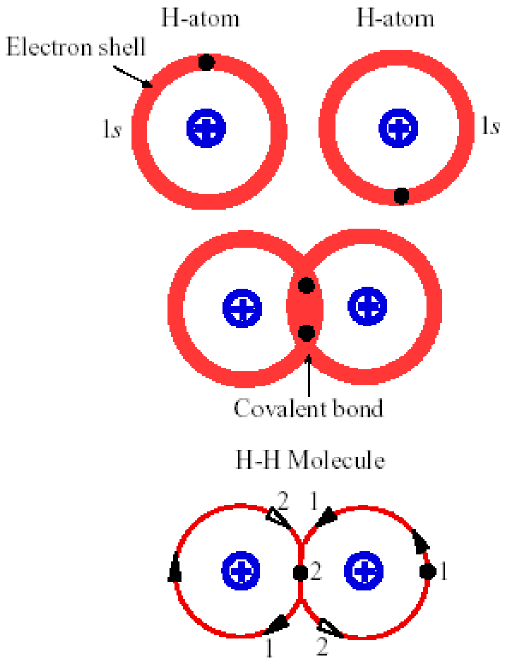


Fig. 1.4: Formation of a covalent bond between two H atoms leads to the H_2 molecule. Electrons spend majority of their time between the two nuclei which results in a net attraction between the electrons and the two nuclei which is the origin of the covalent bond .

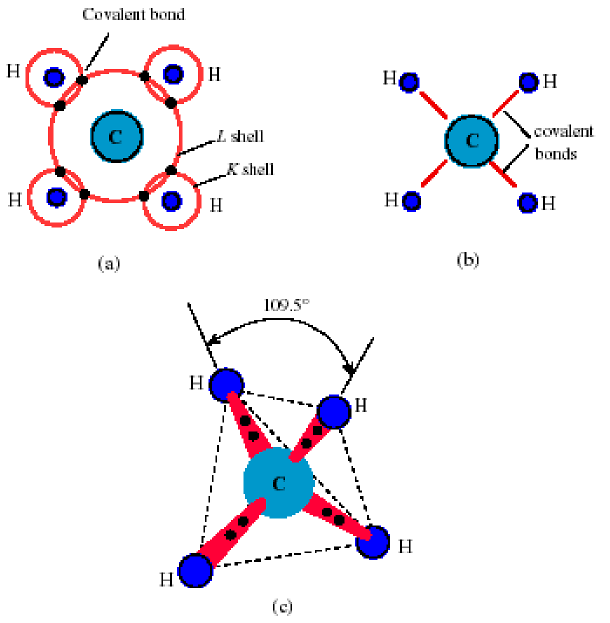


Fig. 1.5: (a) Covalent bonding in methane, CH_4, involves four hydrogen atoms sharing electrons with one carbon atom. Each covalent bond has two shared electrons. The four bonds are identical and repel each other. (b) Schematic sketch of CH_4 on paper. (c) In three dimensions, due to symmetry, the bonds are directed towards the corners of a tetrahedron.

COVALENT BONDING (3)

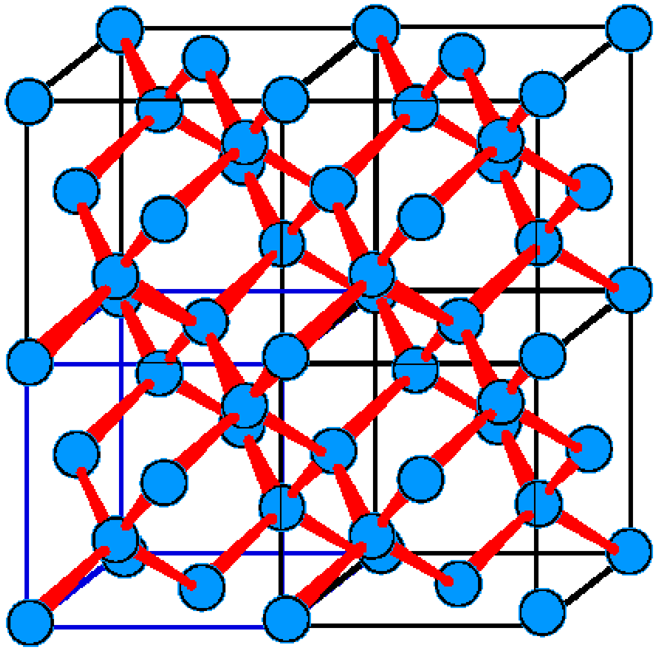


Fig. 1.6: The diamond crystal is a covalently bonded network of carbon atoms. Each carbon atom is bonded covalently to four neighbors forming a regular three dimensional pattern of atoms which constitutes the diamond crystal.

Covalent Bonds are strong:

Hard material
High melting points
Insoluble in most solvents
Nonmalleable
Poor conductors

Mixing Bonds

- Very few compounds exhibit pure ionic or covalent bonding
- The degree of either bond type depends on the different in their **electronegativities** (i.e. relative element position in the periodic table):

  - the greater the difference in electronegativity – the more ionic bond

  - the smaller the difference in electronegativity (i.e. closer the atoms together in periodic table) – the greater the degree of covalent bonds.

To estimate the % of ionic bonds between elements A and B one can use the following expression:

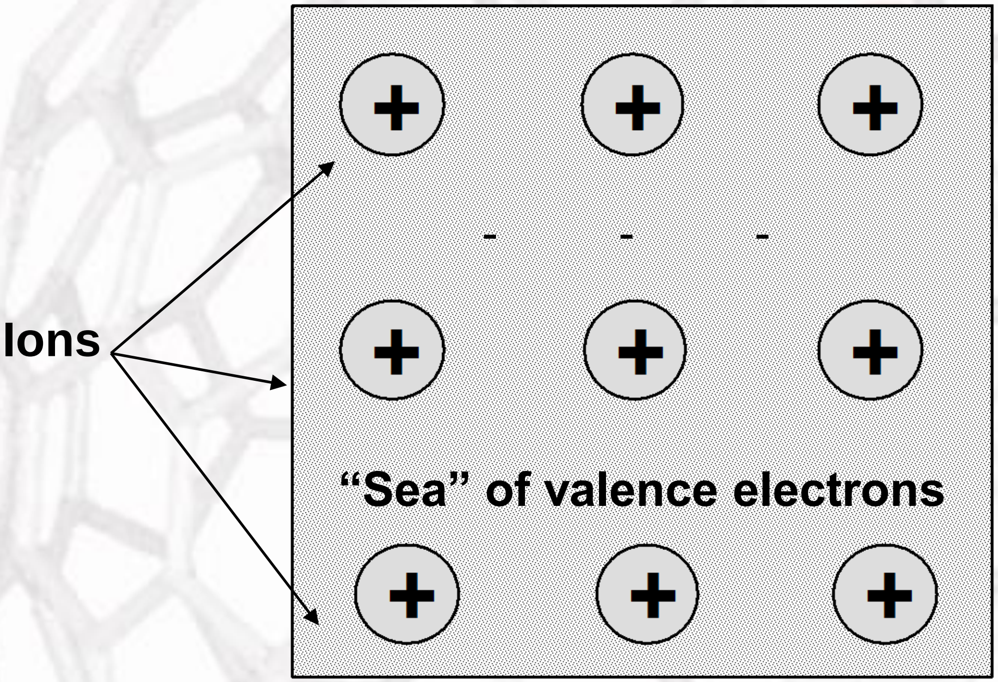
$$\% \text{ ionic character} = \{1-\exp[-0.25(X_A-X_B)^2]\} \times 100$$

where Xa and X_B are elements electronegativity.

http://www.youtube.com/watch?v=Ibr63AjnEoQ

METALLIC BONDING (1)

- Arises from a sea of **donated valence electrons** (1, 2, or 3 from each atom).



- Metallic bonding: for ***Group IA and IIA*** of periodic table and all metals

Bonding energy: ***wide range***
E(Hg)= 0.7eV/at   E(W)=8.8.eV/at

- Properties: good electro/thermal conductors (electron “sea”!) and ductile materials (Chapter 7)

- Primary bond for **metals** and their **alloys**

METALLIC BONDING (2)

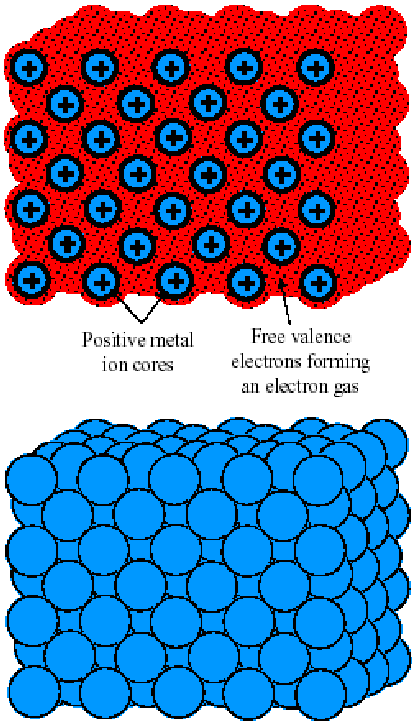


Fig. 1.7: In metallic bonding the valence electrons from the metal atoms form a "cloud of electrons" which fills the space between the metal ions and "glues" the ions together through the coulombic attraction between the electron gas and positive metal ions.

Delocalized valence electrons

Electron gas or cloud

Non-directional bonds

Close-packed ions with electron glue

Thus metals are:
Ductile
High electrical conduction
High thermal conduction

EXAMPLES: METALLIC BONDING

Metal

Nonmetal !!!

Intermediate

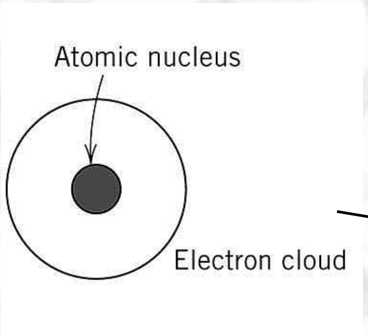
Key: 29 ← Atomic number; Cu ← Symbol; 63.54 ← Atomic weight

IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIII	VIII	VIII	IB	IIB	IIIA	IVA	VA	VIA	VIIA	0
1 H 1.0080																	2 He 4.0026
3 Li 6.939	4 Be 9.0122											5 B 10.811	6 C 12.011	7 N 14.007	8 O 15.999	9 F 18.998	10 Ne 20.183
11 Na 22.990	12 Mg 24.312											13 Al 26.982	14 Si 28.086	15 P 30.974	16 S 32.064	17 Cl 35.453	18 Ar 39.948
19 K 39.102	20 Ca 40.08	21 Sc 44.956	22 Ti 47.90	23 V 50.942	24 Cr 51.996	25 Mn 54.938	26 Fe 55.847	27 Co 58.933	28 Ni 58.71	29 Cu 63.54	30 Zn 65.37	31 Ga 69.72	32 Ge 72.59	33 As 74.922	34 Se 78.96	35 Br 79.91	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc (99)	44 Ru 101.07	45 Rh 102.91	46 Pd 106.4	47 Ag 107.87	48 Cd 112.40	49 In 114.82	50 Sn 118.69	51 Sb 121.75	52 Te 127.60	53 I 126.90	54 Xe 131.30
55 Cs 132.91	56 Ba 137.34	Rare earth series	72 Hf 178.49	73 Ta 180.95	74 W 183.85	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.09	79 Au 196.97	80 Hg 200.59	81 Tl 204.37	82 Pb 207.19	83 Bi 208.98	84 Po (210)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra (226)	Acti-nide series															

Rare earth series	57 La 138.91	58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm (145)	62 Sm 150.35	63 Eu 151.96	64 Gd 157.25	65 Tb 158.92	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.04	71 Lu 174.97
Actinide series	89 Ac (227)	90 Th 232.04	91 Pa (231)	92 U 238.03	93 Np (237)	94 Pu (242)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (249)	99 Es (254)	100 Fm (253)	101 Md (256)	102 No (254)	103 Lw (257)

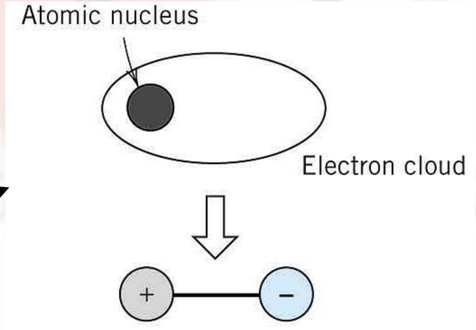
SECONDARY (van der Waals) BONDING (1)

- **Arises from interaction between dipoles**
- ***Week*** physical bonding: E ~0.1 eV/atom



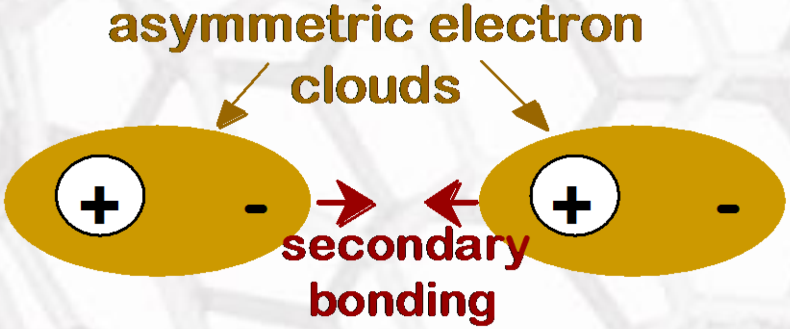
an electrically symmetric atom

an induced atomic dipole

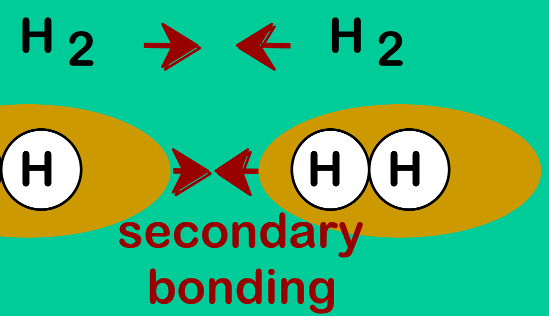


Short –lived distortion of the electrical symmetry by thermal vibration motion

- ***Fluctuating-induced* dipoles bonding**

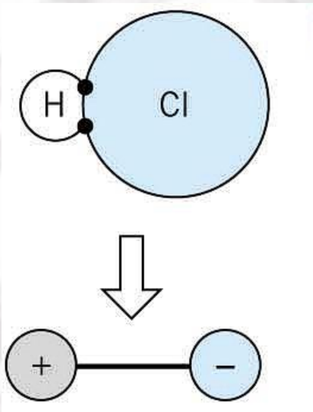


Example: liquid H_2



SECONDARY (van der Waals) BONDING (2)

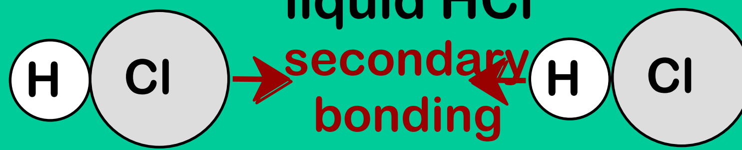
- **Permanent** dipoles - molecule induced



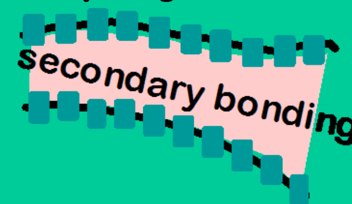
Asymmetrical arrangement of the electrical field for ***polar*** molecules

Examples:

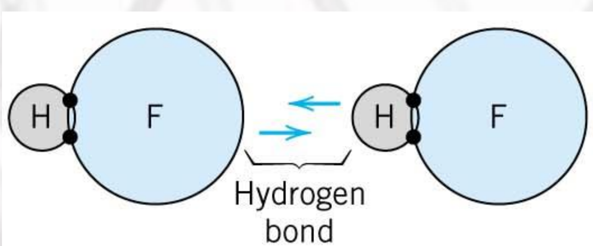
liquid HCl



polymer



• Special and the strongest (E~0.5eV/atom) type of polar molecule bond is so-called ***hydrogen bond***



In molecule where H is covalently bonded (i.e. ***shared*** electron) to Fluorine (e.g. HF), Oxygen (e.g. H_2O) and nitrogen (e.g. NH_3). The H end of the molecule is highly ***positively*** charged – provides strong attractive interaction with the ***negative*** end of the adjacent molecule.

SECONDARY (van der Waals) BONDING (3)

Permanent dipoles

Induced dipoles

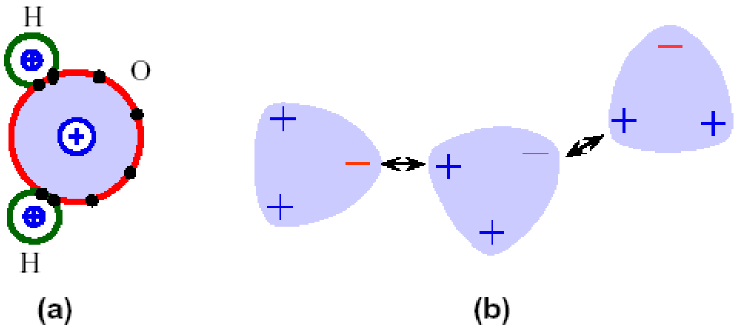
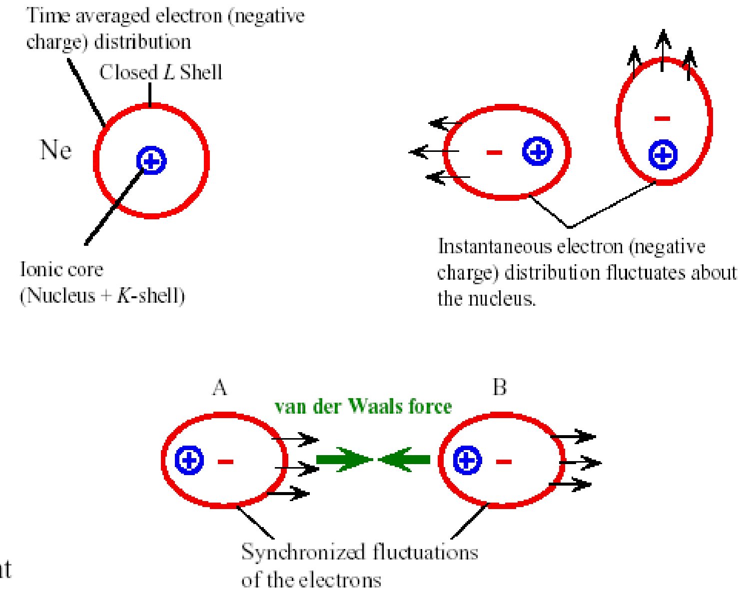


Fig. 1.12: The origin of van der Waals bonding between water molecules. (a) The H_2O molecule is polar and has a net permanent dipole moment. (b) Attractions between the various dipole moments in water gives rise to van der Waals bonding.

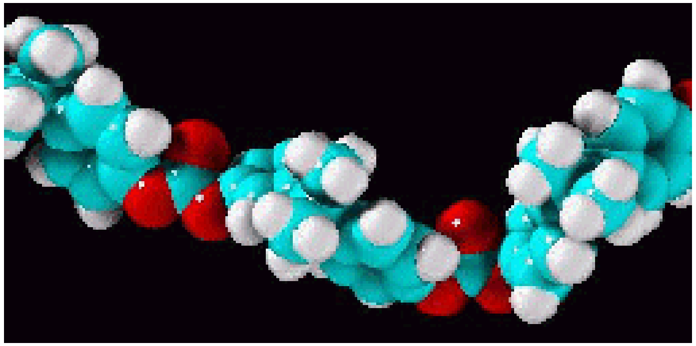


From *Principles of Electronic Materials and Devices, Second Edition*, S.O. Kasap (©McGraw-Hill, 2002)
http://Materials.Usask.Ca

Fig. 1.13: Induced dipole-induced dipole interaction and the resulting van der Waals force.

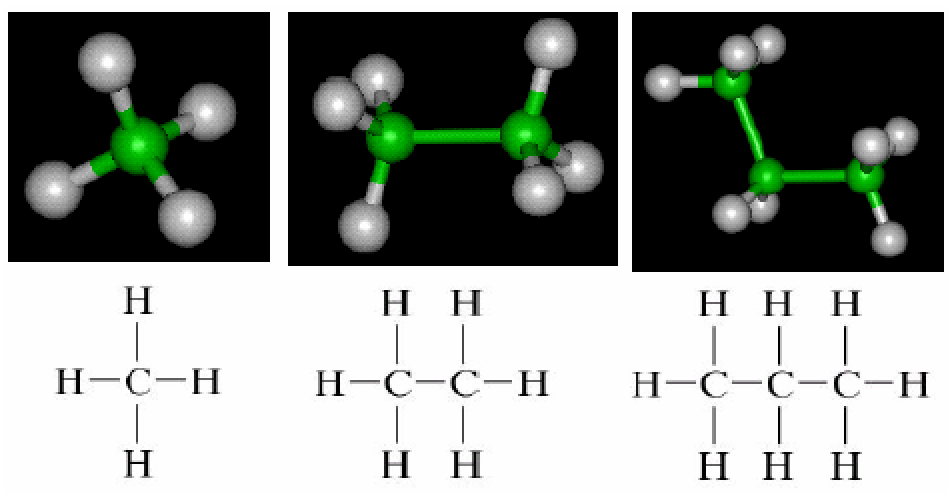
POLYMERS

- **A polymer** is a macromolecule (long molecules) built (covalently bonded !!) of small units called "mer" (from the Greek word *meros* meaning part).
- The small units are repeated successively throughout the macromolecule chain.
- The smallest unit is the **monomer** (a single *mer* unit).
- In turn these long molecules are bonded together by weak Van der Waals and hydrogen (secondary) bonds, or plus covalent cross-links.



THE STRUCTURE of POLYMERS:
Hydrocarbon Molecules

- Most polymers are organic, and formed from hydrocarbon molecules
- Each C atom has four e- that participate in bonds, each H atom has one bonding e-
- Attachment of different organic groups to the hydrocarbon backbone offers wide variety of possible polymers
- Examples of **saturated** (all bonds are single ones) hydrocarbon molecules (of type C_nH_{2n+2})



Methane, CH_4 Ethane, C_2H_6 Propane, C_3H_8

Comparison of Different Atomic Bonds

	Typical Solids	Bond Energy eV/atom	Melt. Temp. (°C)	Elastic Modulus (GPa)	Density (g cm^{-3})	Typical Properties
Ionic	NaCl, (rock salt) MgO, (magnesia)	3.2 10	801 2852	40 250	2.17 3.58	Generally electrical insulators. May become conductive at high temperatures. High elastic modulus. Hard and brittle but cleavable. Thermal conductivity less than metals.
Metallic	Cu Mg	3.1 1.1	1083 650	120 44	8.96 1.74	Electrical conductor. Good thermal conduction. High elastic modulus. Generally ductile. Can be shaped.
Covalent	Si C (diamond)	4 7.4	1410 3550	190 827	2.33 3.52	Large elastic modulus. Hard and brittle. Diamond is the hardest material. Good electrical insulator. Moderate thermal conduction, though diamond has exceptionally high thermal conductivity.
van der Waals: Hydrogen bonding	PVC, (polymer) H_2O, (ice)	- 0.52	212 0	4 9.1	1.3 0.917	Low elastic modulus. Some ductility. Electrical insulator. Poor thermal conductivity. Large thermal expansion coefficient.
van der Waals: Induced dipole	Crystalline Argon	0.09	−189	8	1.8	Low elastic modulus. Electrical insulator. Poor thermal conductivity. Large thermal expansion coefficient.

SUMMARY: BONDING

Type	Bond Energy	Comments
Ionic	Large!	Nondirectional (ceramics)
Covalent	Variable large-Diamond small-Bismuth	Directional (semiconductors, ceramics polymer chains)
Metallic	Variable large-Tungsten small-Mercury	Nondirectional (metals)
Secondary	smallest	Directional inter-chain (polymer) inter-molecular