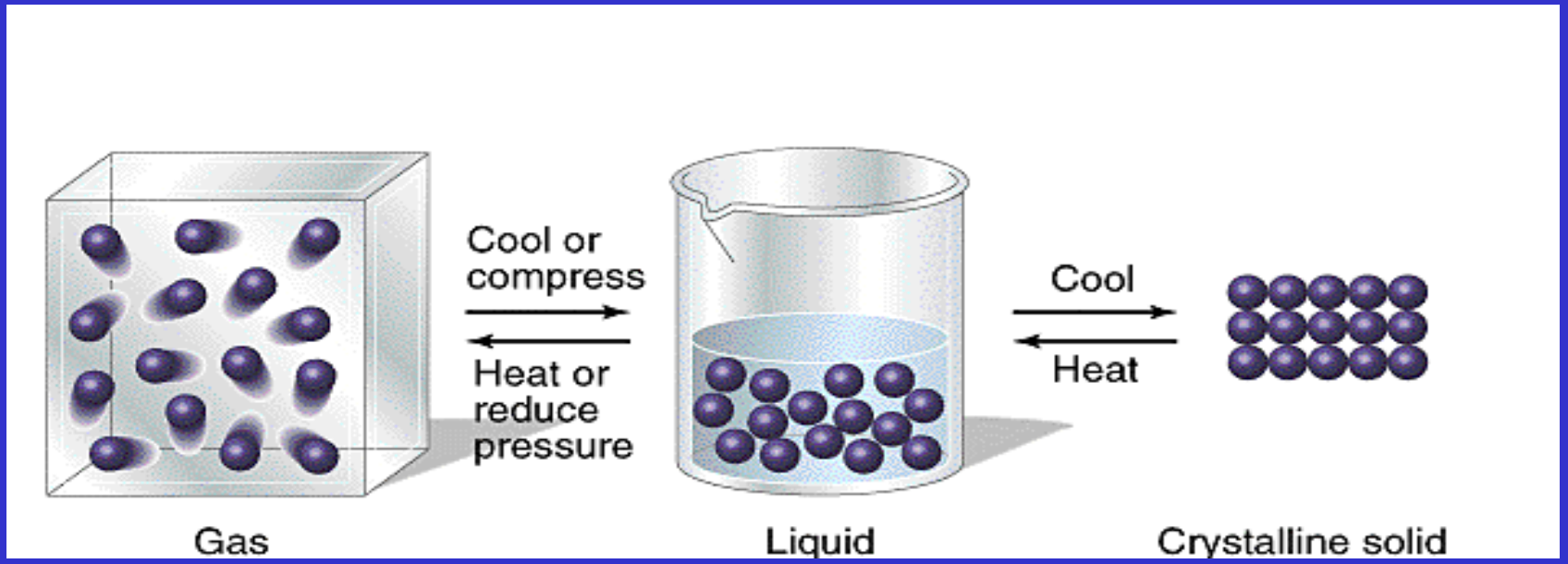
States of Matter

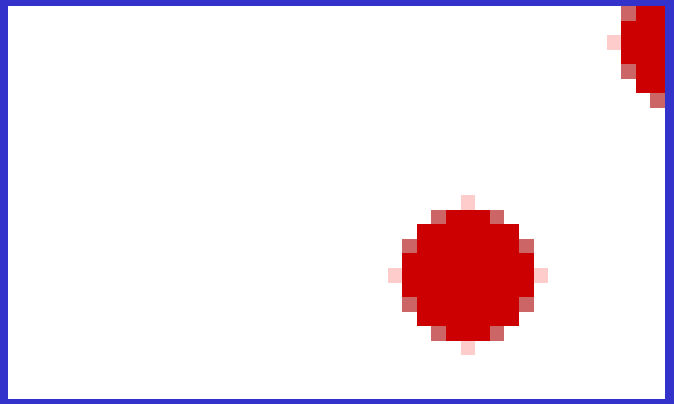


Gas
Random
Free space
Free movement
Far apart

Liquid
Disordered
Free movement of particles of groups of particles
Closer

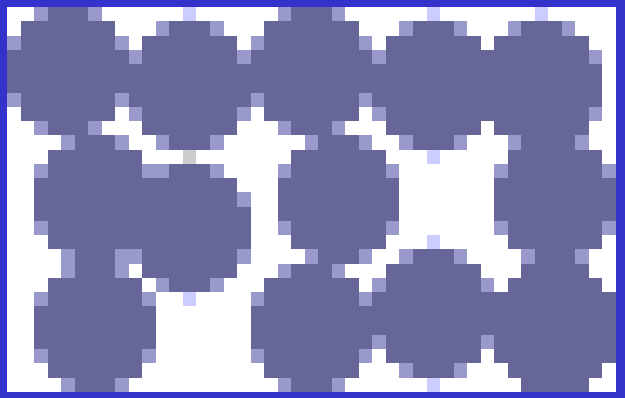
Solid
Ordered
Fixed positions
Close distances

States of Matter

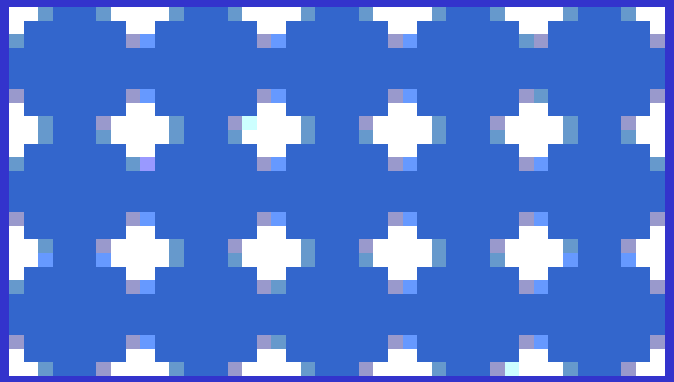


Gas

Water	Temp, ^{o}C (press 1 bar)	Density, g cm^{-1}
Solid	0	0.9168
Liquid	25	0.9971
Vapor	400	$3.26\ 10^{-4}$

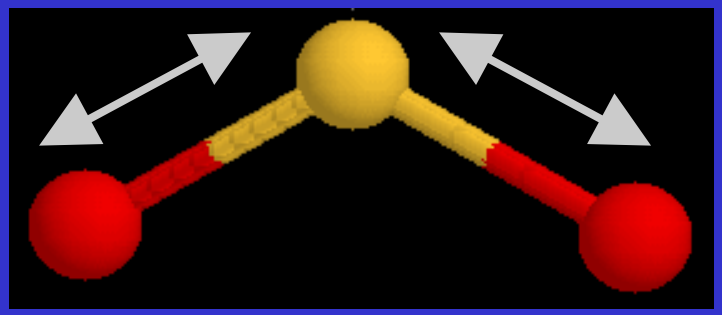


Liquid

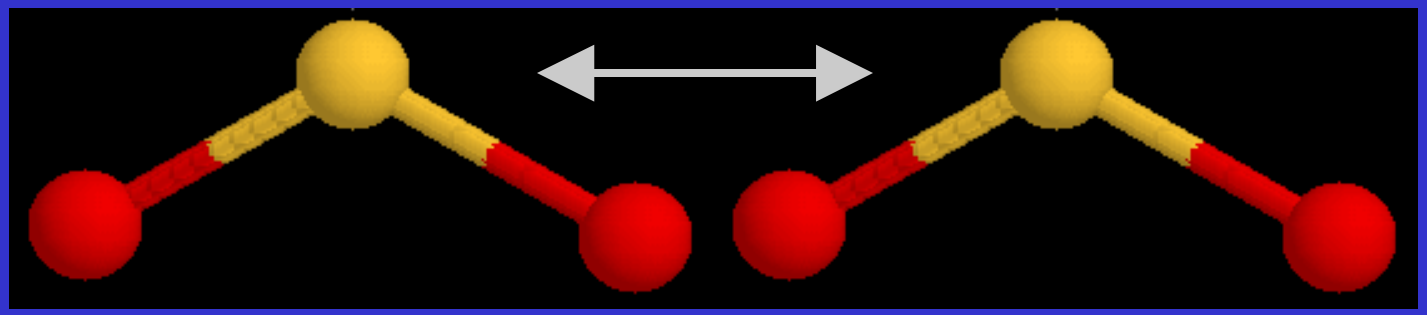


Molecular Crystal

Covalent Bond vs Intermolecular Forces

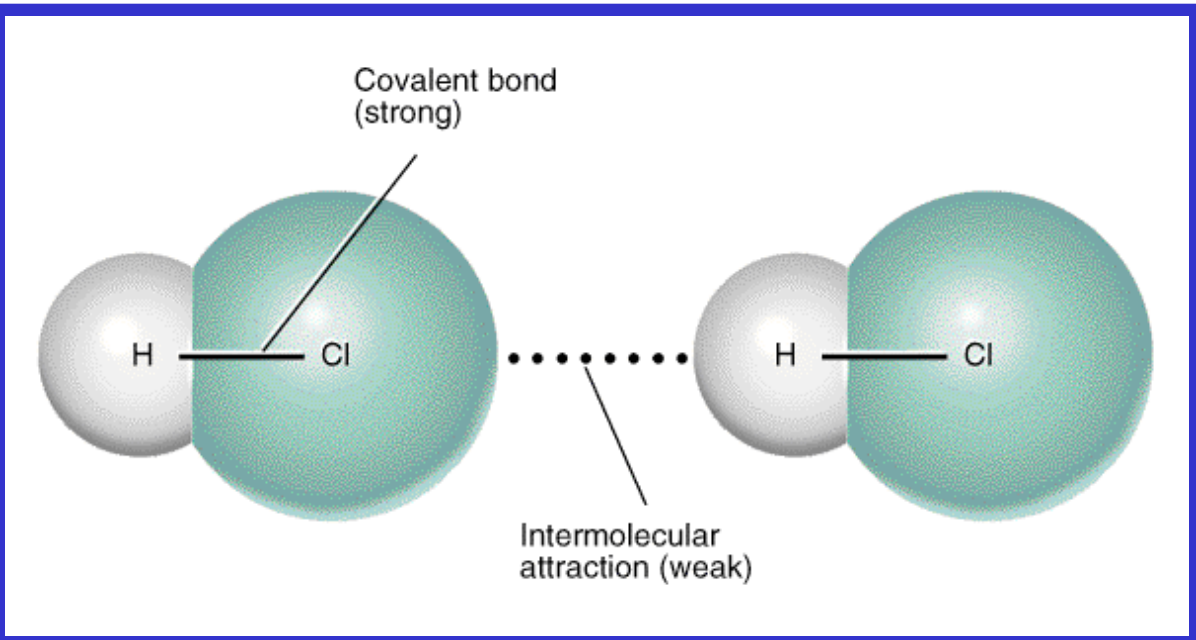


$H_2O \rightarrow 2H + O \quad \Delta H = + 920\ kJ\ mol^{-1}$



$H_2O(l) \rightarrow H_2O(g)$ při 100 $^oC \quad \Delta H = + 41.2\ kJ\ mol^{-1}$

Bond Type	Energy, kJ mol^{-1}
Covalent	200 – 1000
H-bond	10 – 50 (100)
Dipole-dipole	2 – 10
London dispersion	> 5



Van der Waals Interactions

J. D. van der Waals
(1837- 1923)
NP in Chemistry 1910

ion – ion Coulombic interactions

ion – dipole interactions

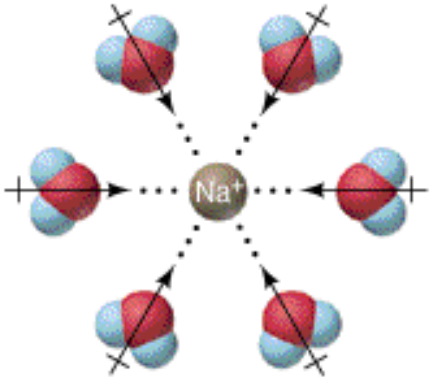
dipole – dipole → orientation, Keesom

dipole – induced dipole → induction, Debye

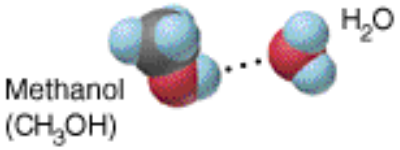
ion – induced dipole

induced dipole – induced dipole → dispersion, London

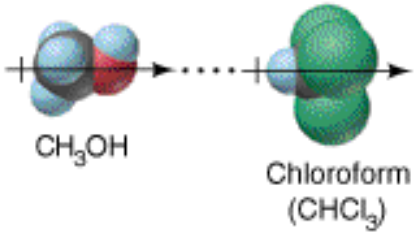
van der Waals repulsion



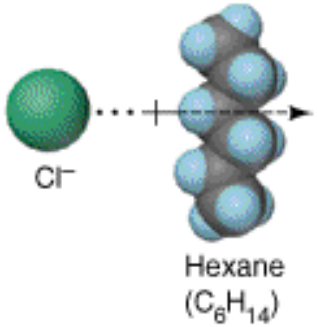
Ion-dipole



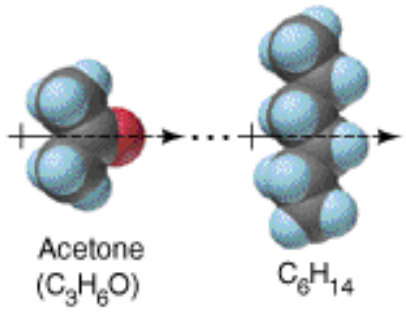
H bond



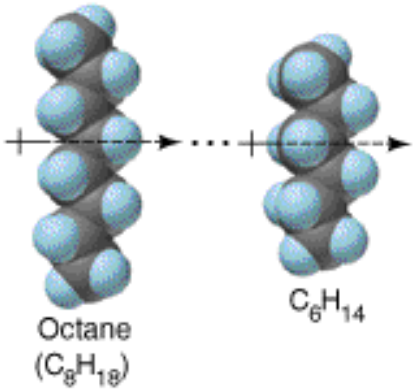
Dipole-dipole



Ion-induced dipole



Dipole-induced dipole



Dispersion

Ion – Ion Coulombic Interactions

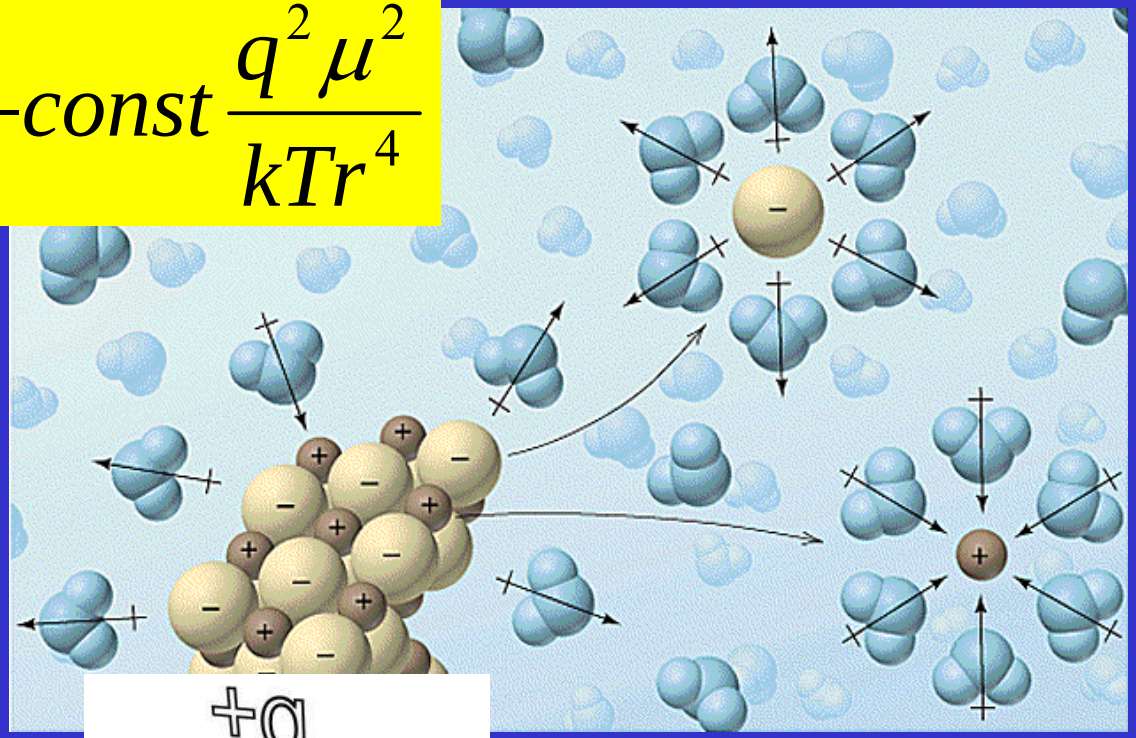
Coulomb's Law

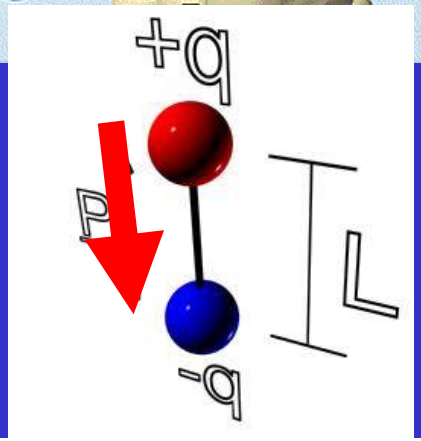
$$E = \frac{1}{4\pi\varepsilon_0}\frac{q_1 q_2}{r}$$

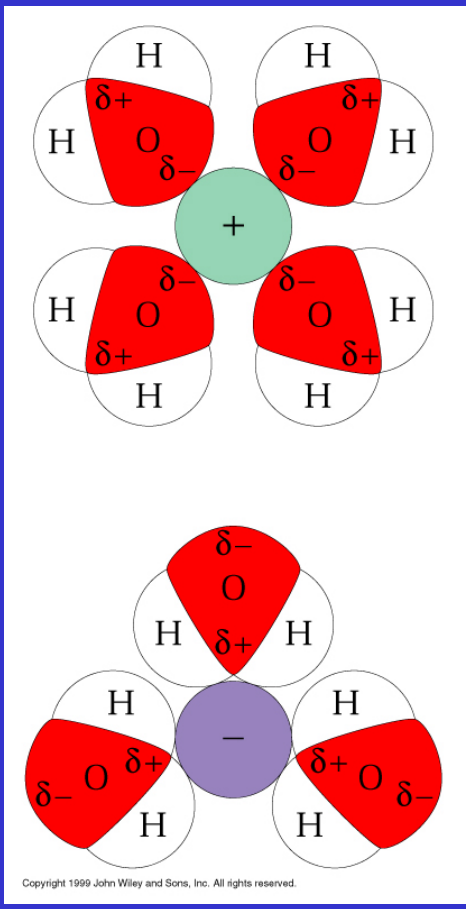
E = interaction energy
q = ion charge
r = interionic distance

Ion – Dipole Interactions

$$E = -const\,\frac{q^2\mu^2}{kTr^4}$$







E = interaction energy
q = ion charge
r = distance
μ = dipole moment
T = temp
k = Boltzmann const.

Hydration/Solvation of Ions

Interaction decreases with increasing ion size

$[Li(H_2O)_4]^+$
$[Na(H_2O)_x]^+$
K^+ weak
Rb^+ zero
Cs^+ negative

Interaction decreases

Interaction increases with increasing ion charge

$[Na(H_2O)_x]^+$ $[Mg(H_2O)_6]^{2+}$ $[Al(H_2O)_6]^{3+}$

Ion-dipole

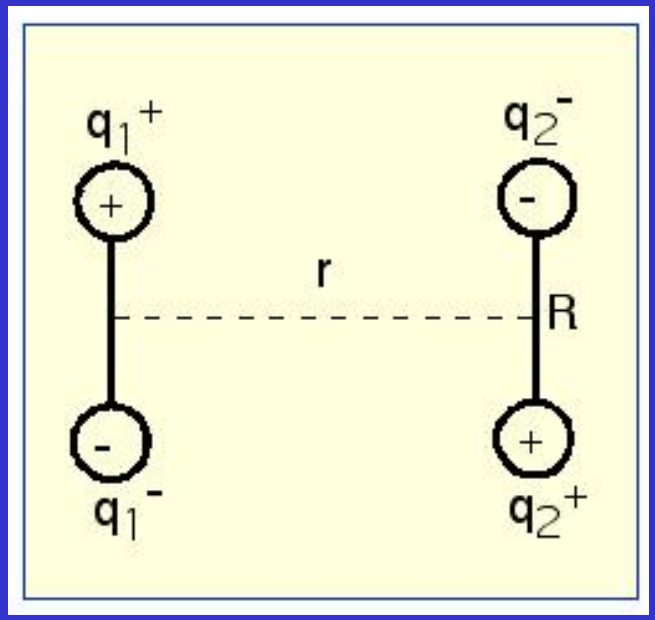
Polar coord. bond

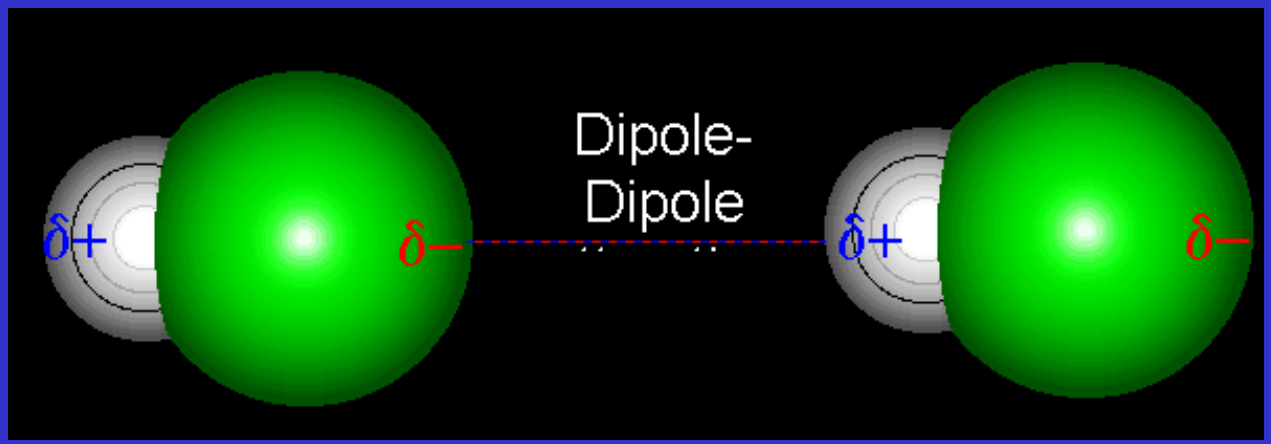
Interaction increases

Dipole - Dipole Interactions

Keesom

$$E = -const\,\frac{\mu_A^2 \times \mu_B^2}{kTr^6}$$





E = interaction energy
r = distance
μ = dipole moment
T = temp
k = Boltzmann const.

Dipole - Dipole Interactions

Compound	Butane	Acetone
M_r	58	58
Boiling point, °C	– 0.5	57
Dipole moment, C m	0	$9.3\ 10^{-30}$

Ion – Induced Dipole and Dipole – Induced Dipole Interactions

$\mu(ind) = \alpha E$

α = polarizability

***E* = electr. field intensity**

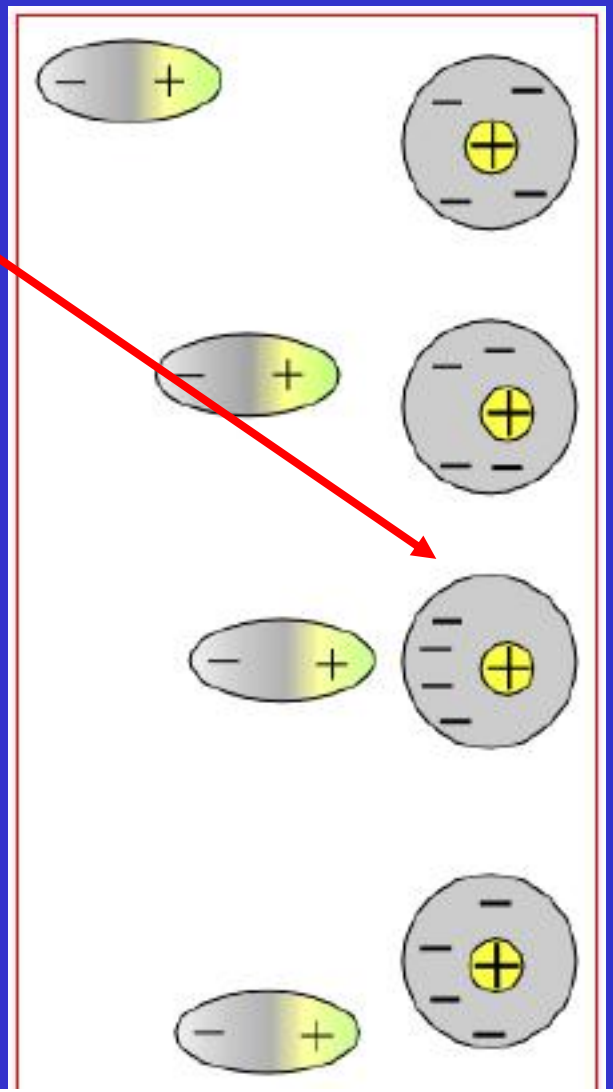
Ion – Induced Dipole

$$E = -const \frac{q^2 \alpha}{r^4}$$

Dipole – Induced Dipole , Debye

$$E = -const \frac{\mu^2 \alpha}{r^6}$$

α = polarizability
μ = dipole moment
E = interaction energy
q = ion charge
r = distance

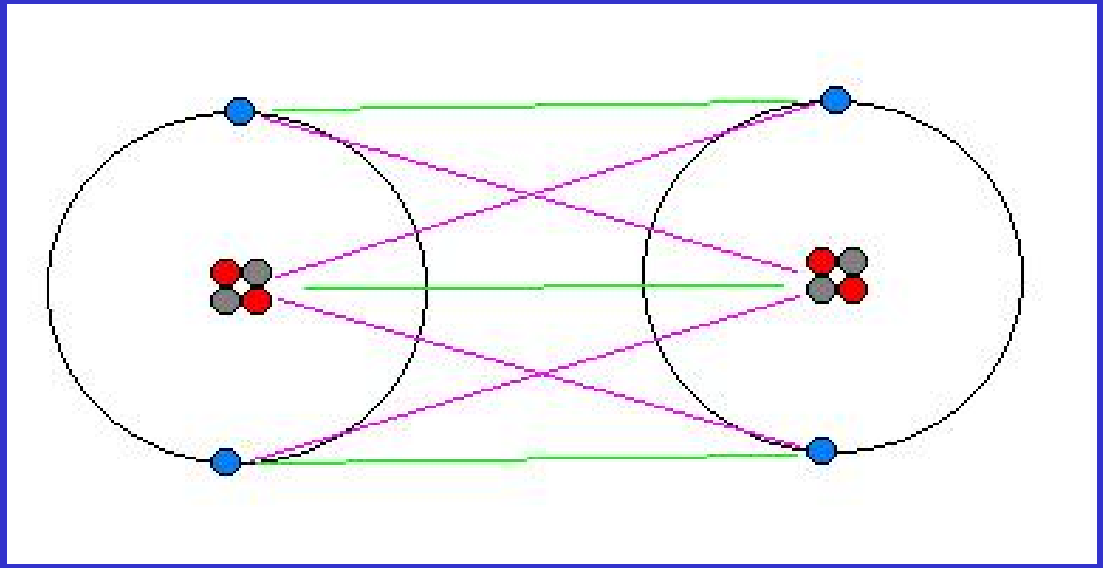


Polarizability, α, m^3

Group	Polarizability, $cm^3\ 10^{24}$	v.d.W radius, Å	Atomic Radius, r, Å
O	0.63	1.5	0.66
CH_2	1.80	2.0	-
S	3.00	1.8	1.04

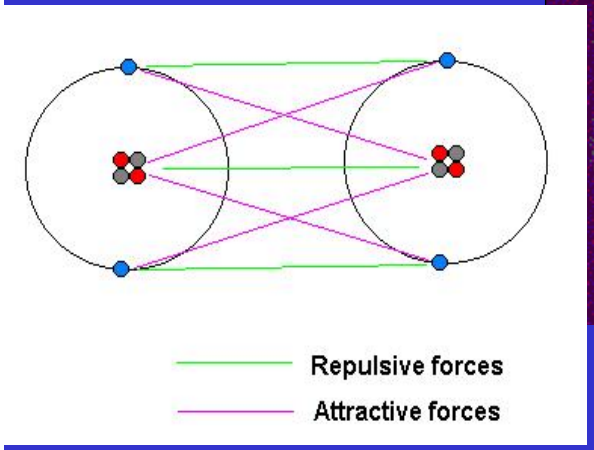
Molecule	Polarizability ($Å^3$)	T_{boil} (K)	Dipole moment (D)
He	0.20	4.216	0
Ne	0.39	27.3	0
Ar	1.62	87.3	0
Kr	2.46	119.9	0
H_2O	1.48	373.15	1.85
H_2S	3.64	212.82	1.10
CCl_4	10.5	349.85	0
C_6H_6	25.1	353.25	0
CH_3OH	3.0	338	1.71
CH_3F	3.84	195	1.81
$CHCl_3$	8.50	334.85	1.01

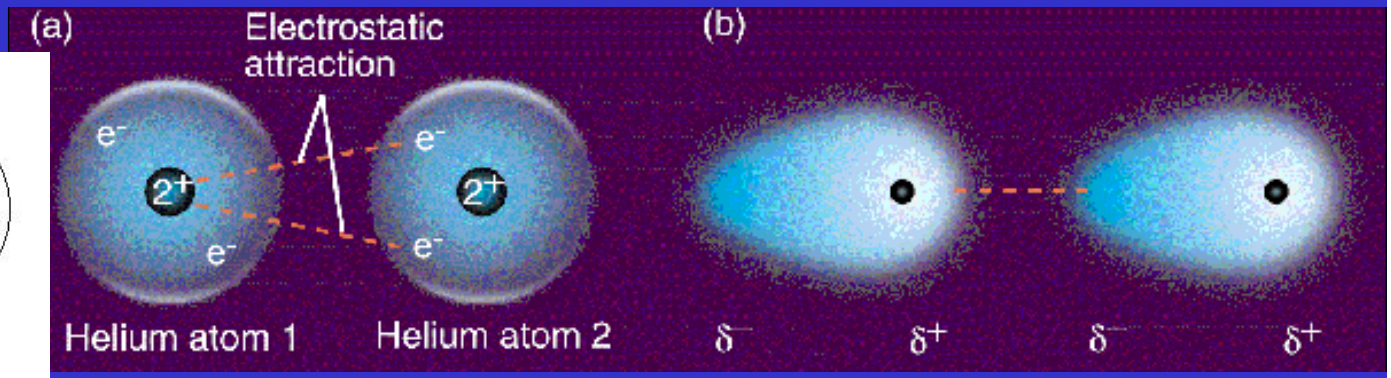
Induced Dipole – Induced Dipole Interactions



Repulsion **Attraction**

London's Dispersion Forces



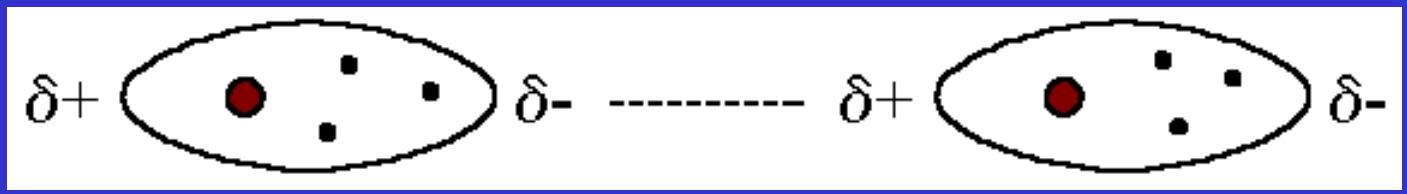


$$E = -const \times \frac{IE \times \alpha^2}{r^6}$$

IE = ionisation energy

α = polarizibility

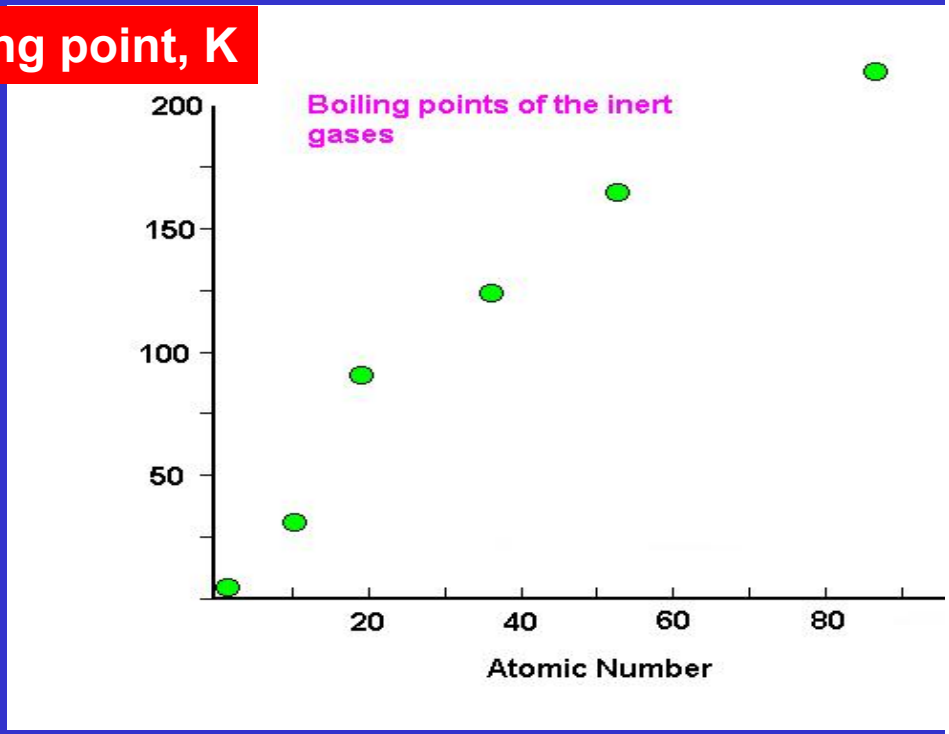
r = distance



London's Dispersion Forces and Polarizibility

London's Dispersion Forces and state of halogens and rare gases

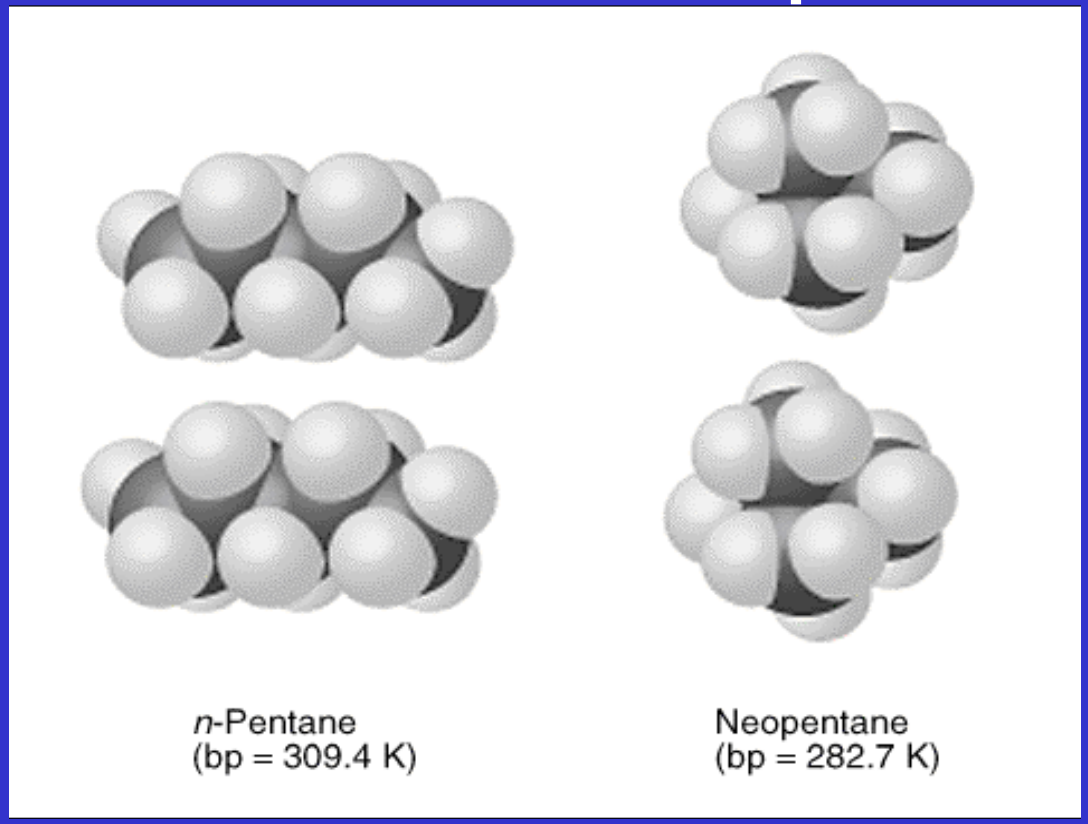
Polarizibility increases with molecular size



	Boiling point, K
F_2	85.1
Cl_2	238.6
Br_2	332.0
I_2	457.6

	Boiling point, K
He	4.6
Ne	27.3
Ar	87.5
Kr	120.9

London's Dispersion Forces and Molecular Shape

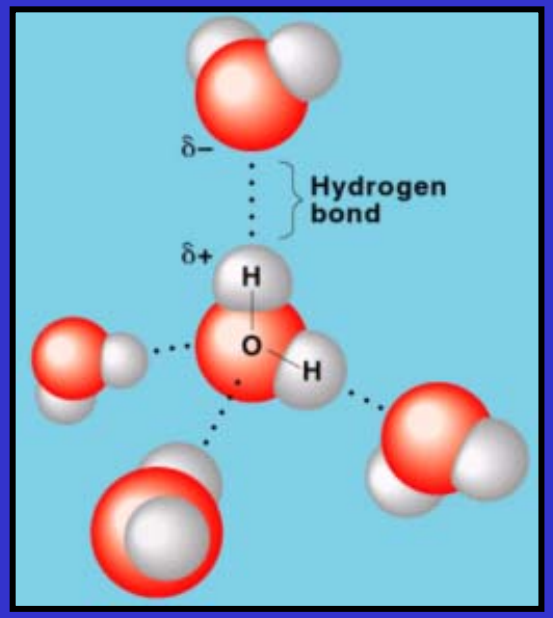


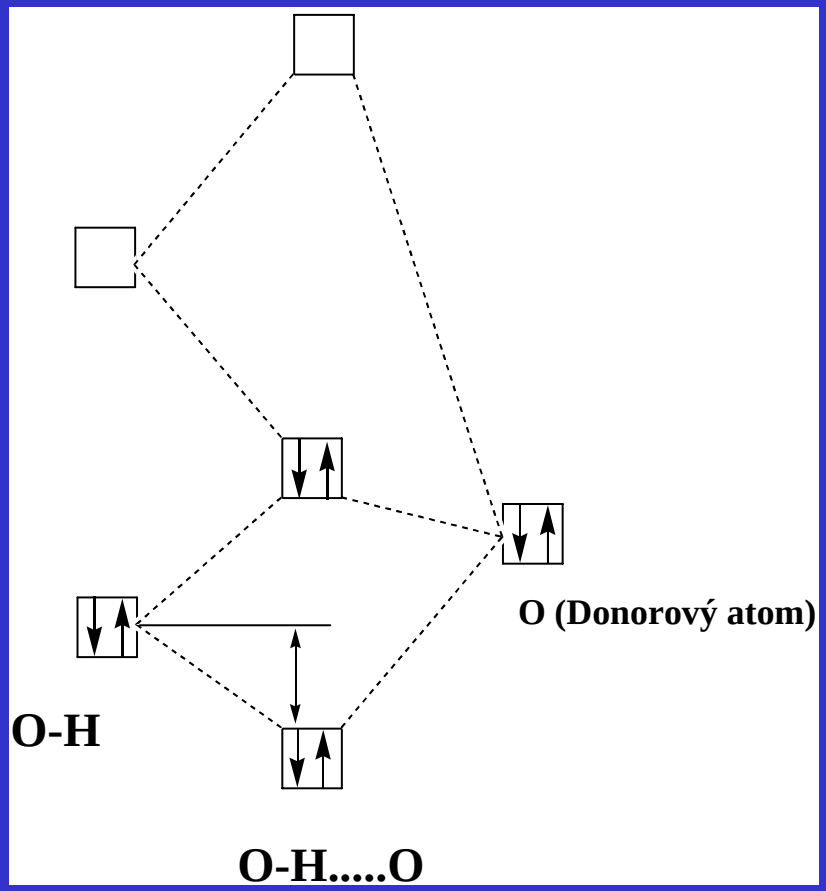
Same M_r

Larger contact area

Hydrogen Bond

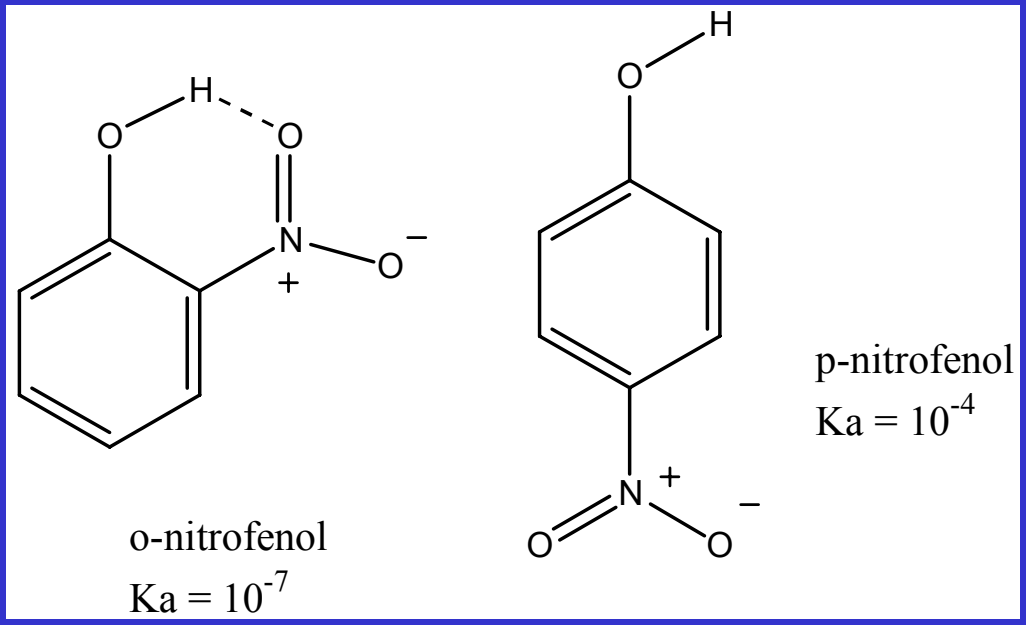
H with electronegative atoms (F, O, N, C,…)





Hydrogen Bond

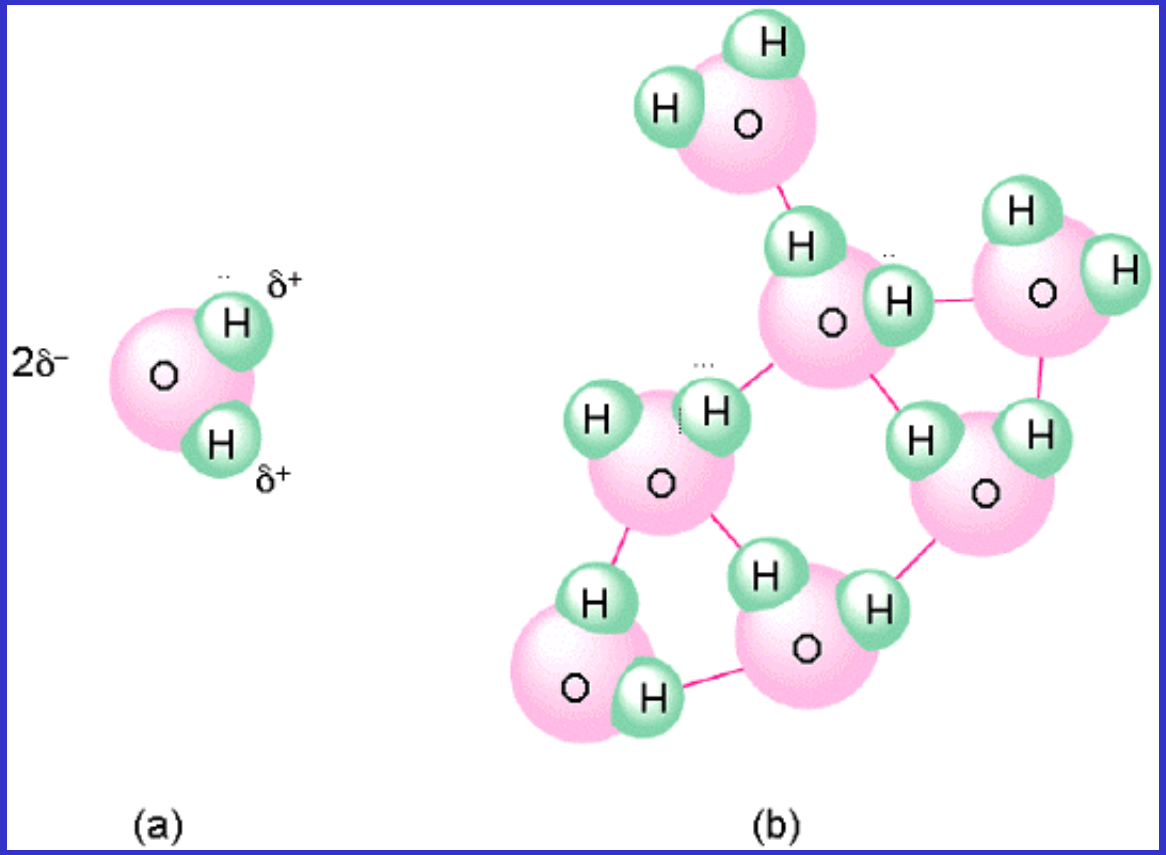
Intramolecular hydrogen bond



Lower acidity of the OH group
As a results of hydrogen bond formation

Hydrogen Bond

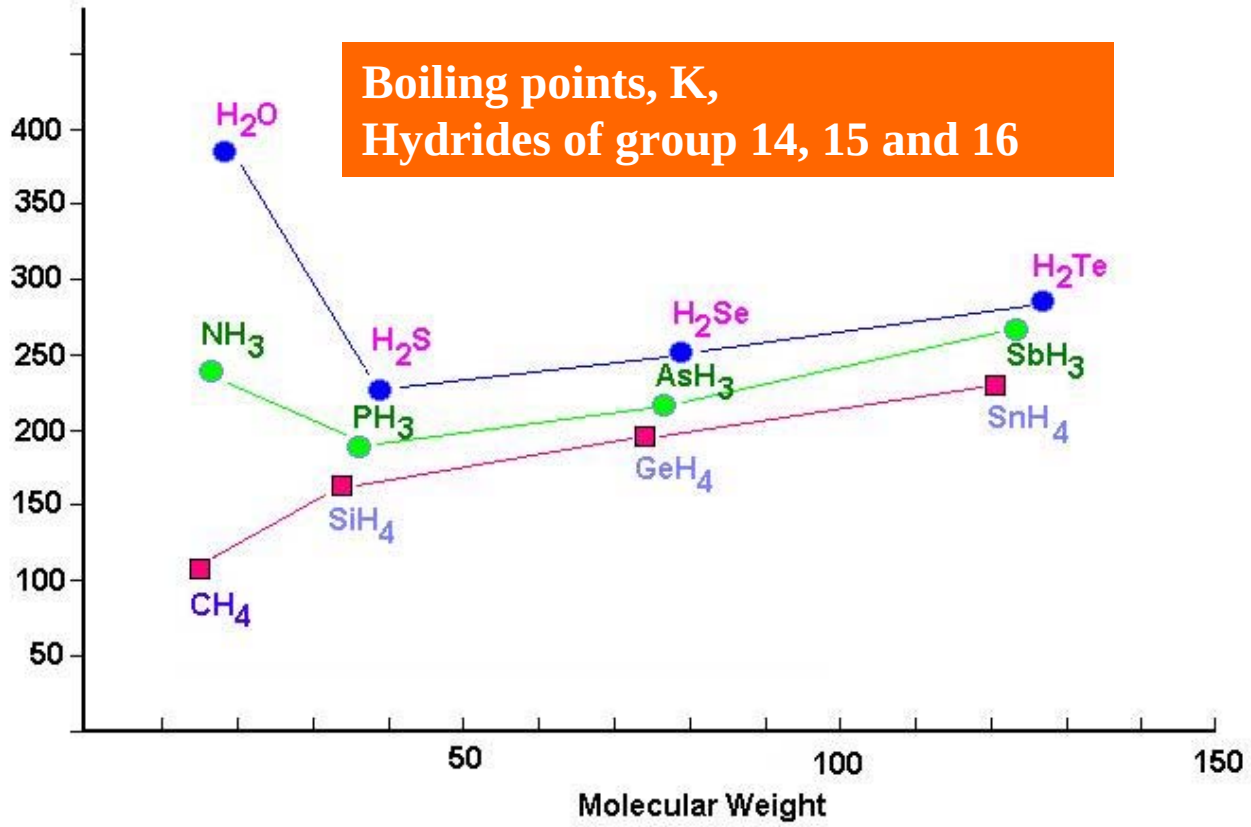
Intermolecular



Hydrogen Bond

Bond	Distance (Å)	Range (Å)
N-H...N	3.10	2.88-3.38
N-H...O		
- Amide NH	2.93	2.55-3.04
- Amino NH	3.04	2.57-3.22
N-H...F	2.78	2.62-3.01
N-H...Cl	3.21	2.91-3.52
O-H…N	2.80	2.62-2.93
O-H...O		
- Alcohol OH	2.74	2.55-2.96
- Water OH	2.80	2.65-2.93
O-H...Cl	3.07	2.86-3.21

Hydrogen Bond



HF_2^- Hydrogendifluoride

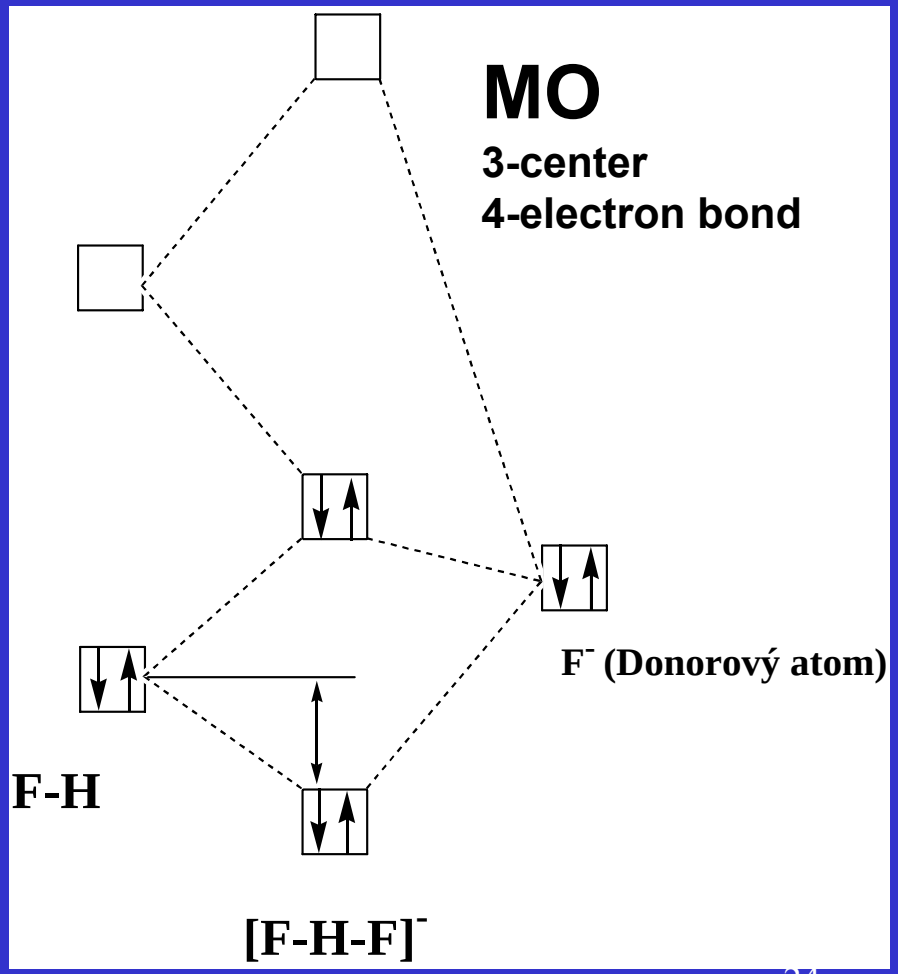
Strongest known H-bond

155 kJ mol^{-1}

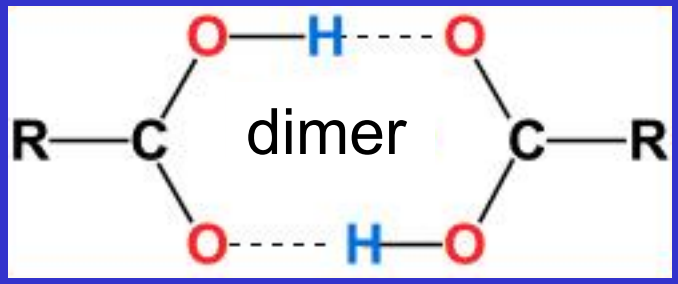
Symmetrical bond distances
H-F 114 pm

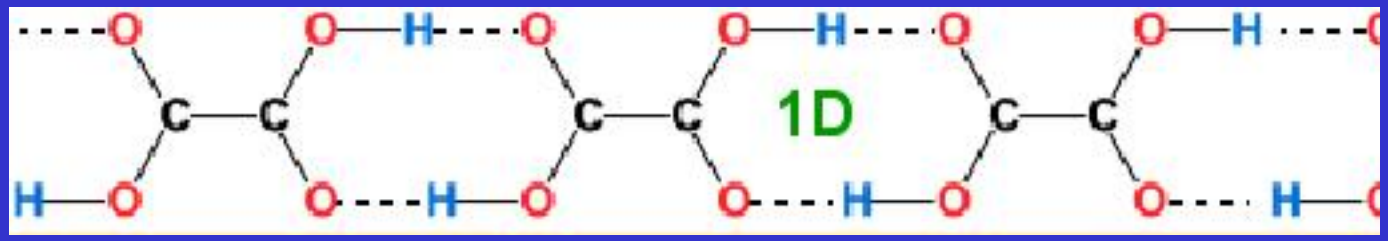
Bond angle
F-H-F = 180°

Autodissociation HF
2 HF $\leftrightarrow$ $H_2F^+ + HF_2^-$



Hydrogen Bond





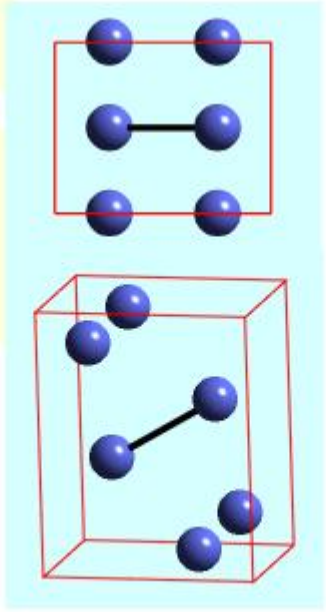
Crystal engineering
Self-assembly

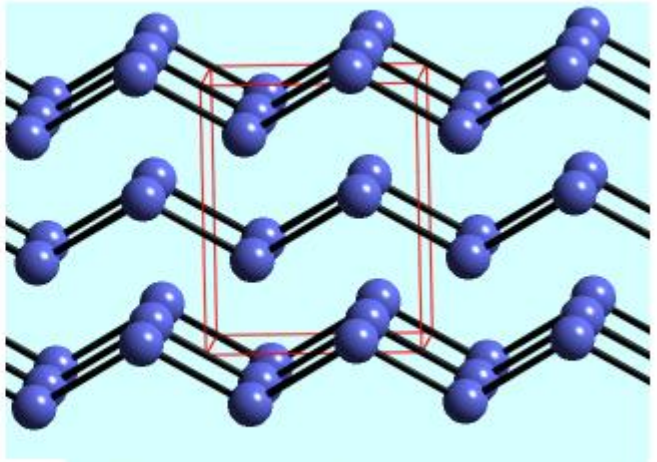
Structure of HF

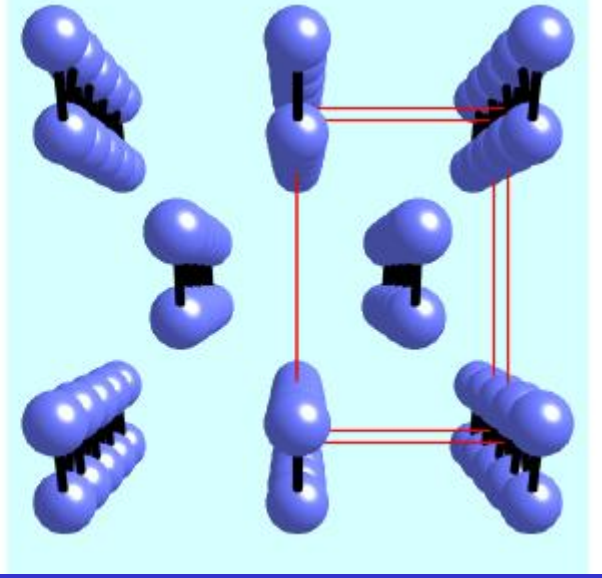
1D. HF

Ortorrómbico: B mmb	
a (Å)	3.42
b (Å)	4.32
c (Å)	5.41
V (Å^3)	79.9
Z	4
Dx (gcm^{-3})	1.66

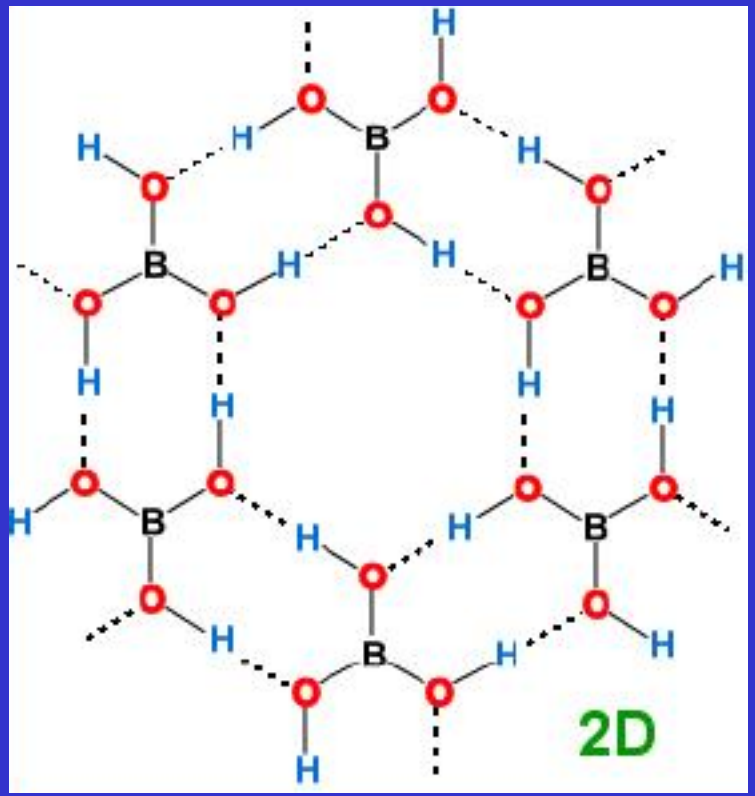
F-H (Å)	-
F···F (Å)	2.49
H···F (Å)	-
F-H···F (°)	180°

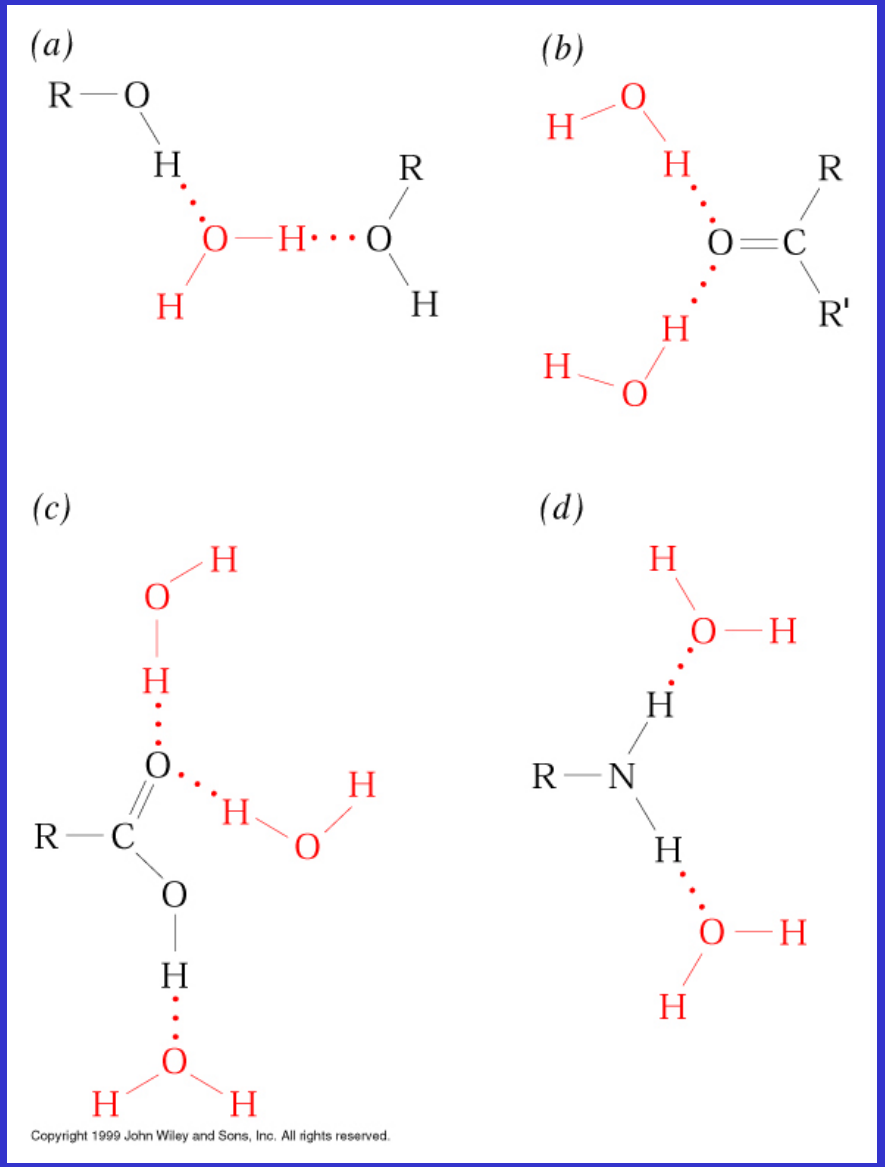




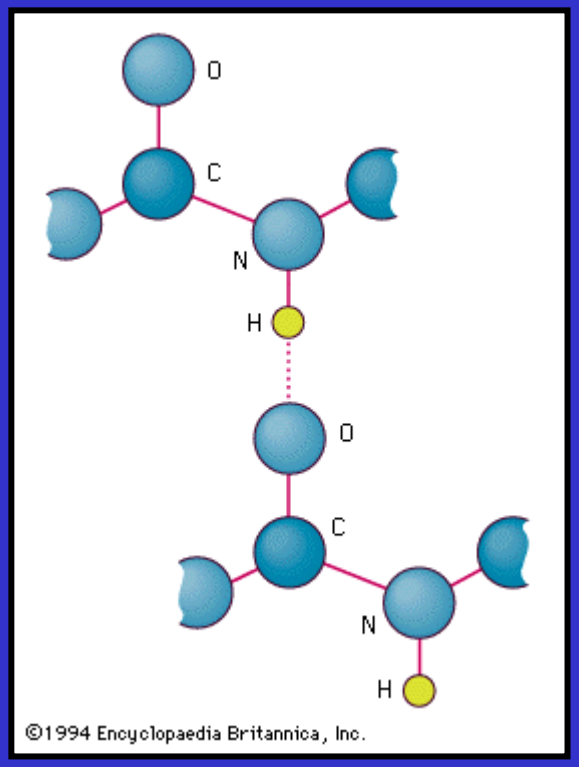


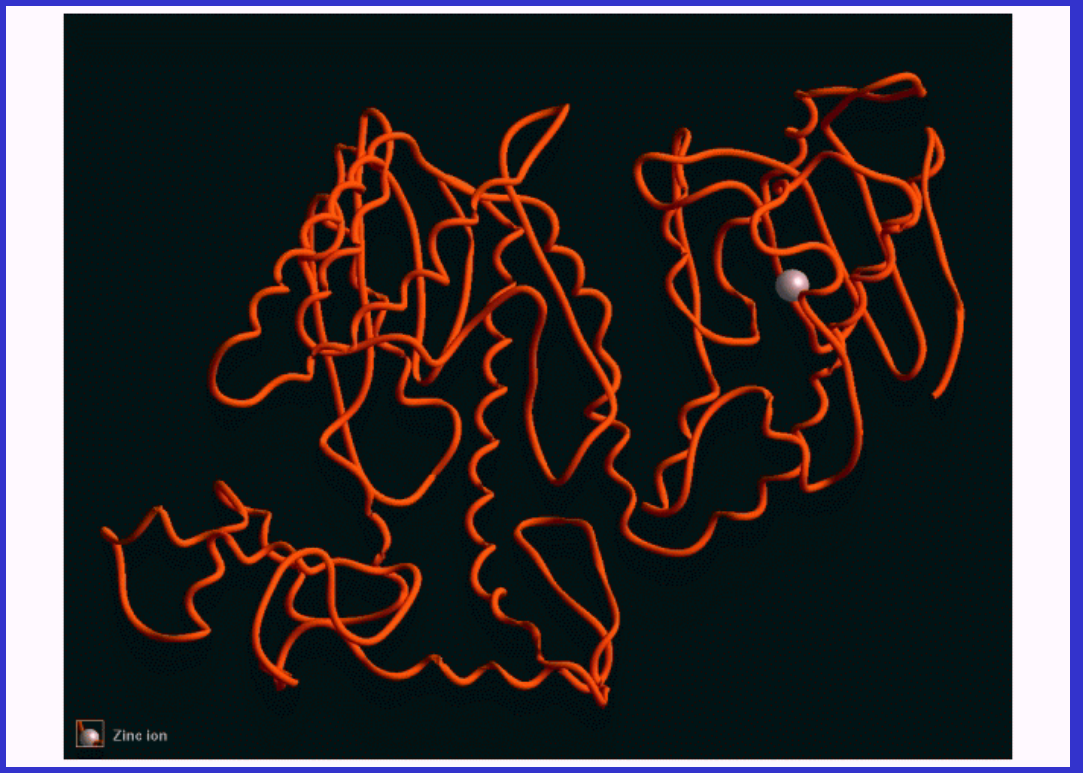
Boric Acid



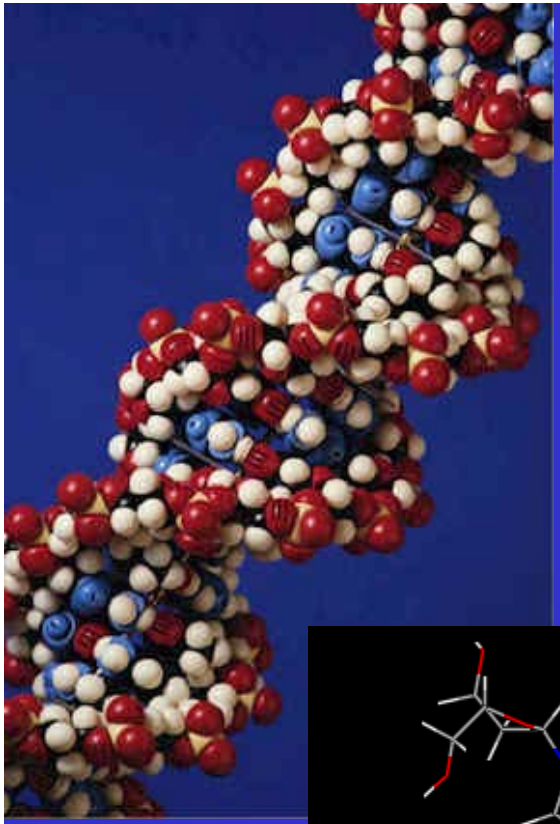


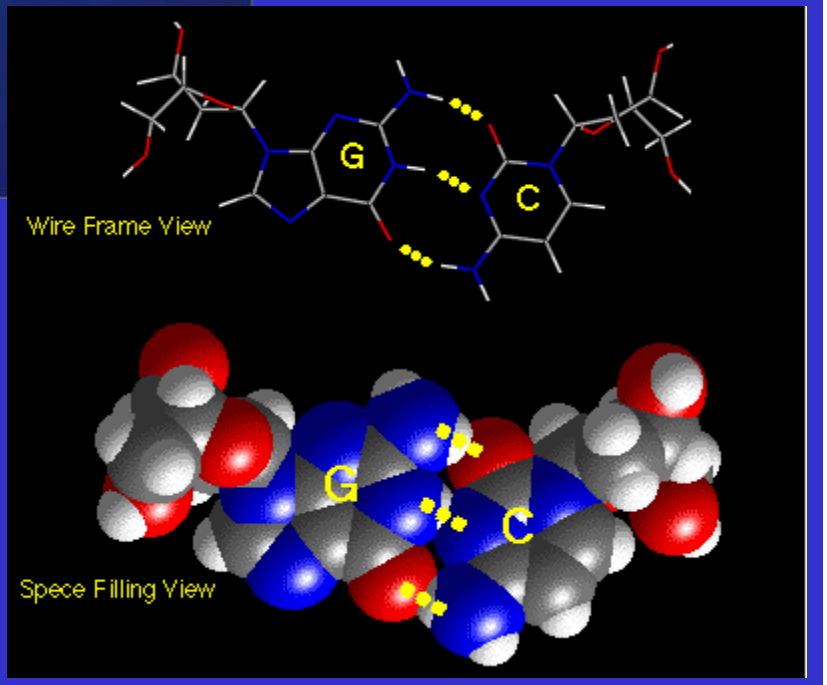
Structure of Proteins

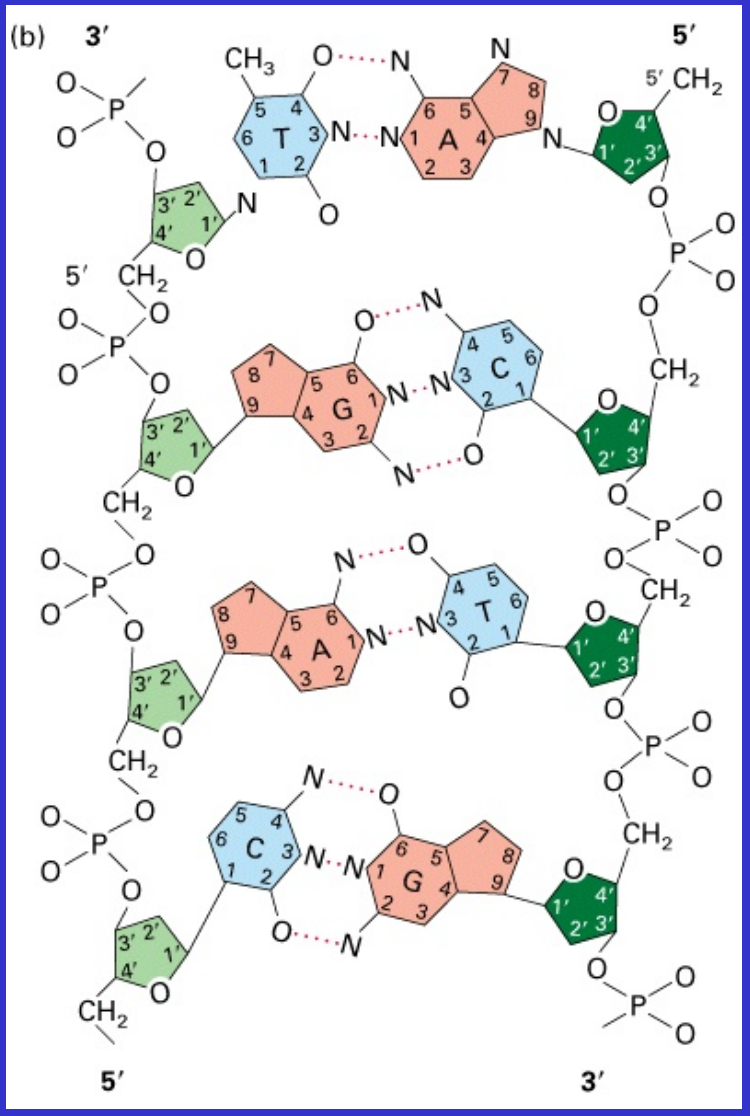


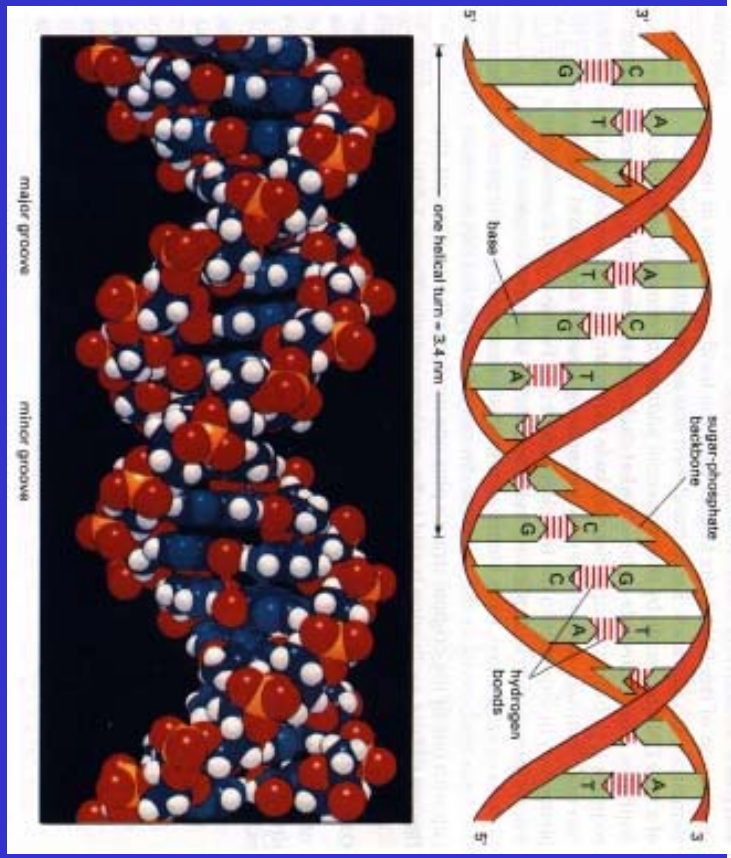


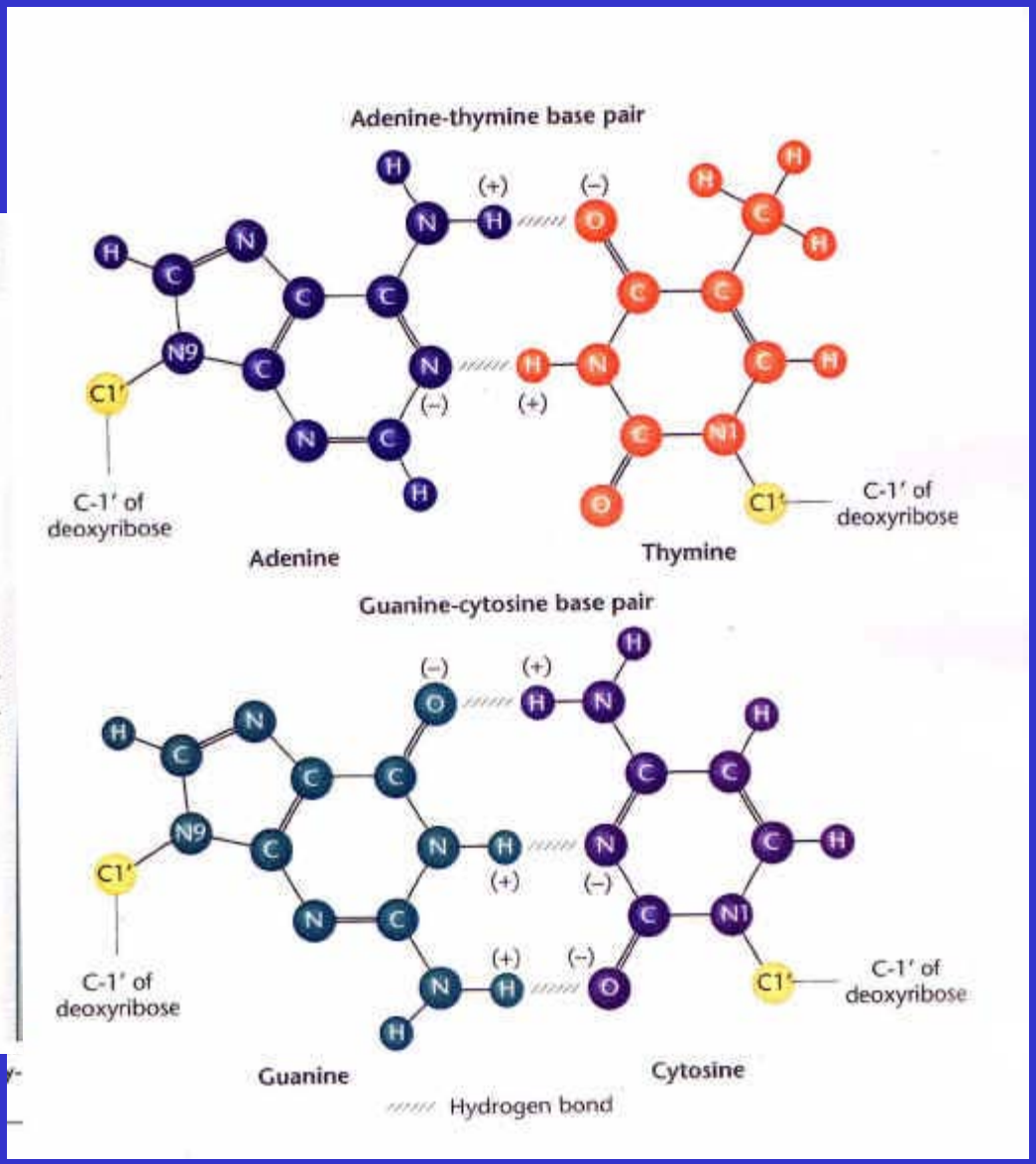
Structure of DNA








major groove
minor groove
one helical turn = 3.4 nm
base
sugar-phosphate backbone
hydrogen bonds
5'
3'

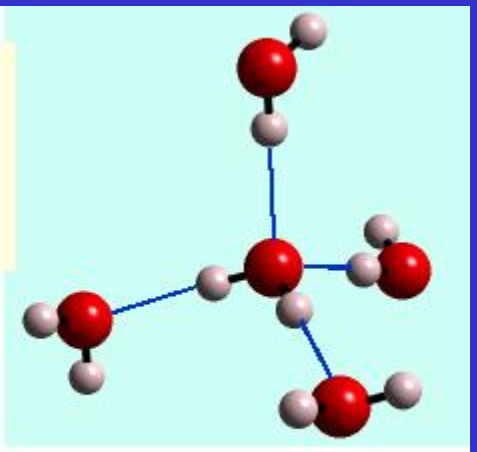

Adenine-thymine base pair
C-1′ of deoxyribose
Adenine
Thymine
C-1′ of deoxyribose
Guanine-cytosine base pair
C-1′ of deoxyribose
Guanine
Cytosine
C-1′ of deoxyribose
Hydrogen bond

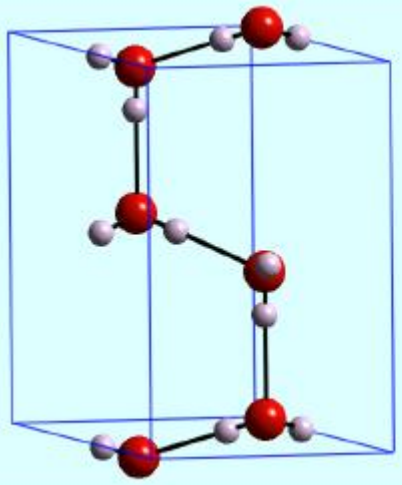
Structure of Ice

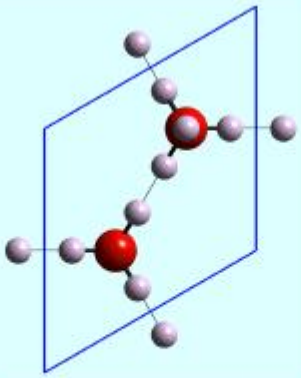
3D. H_2O

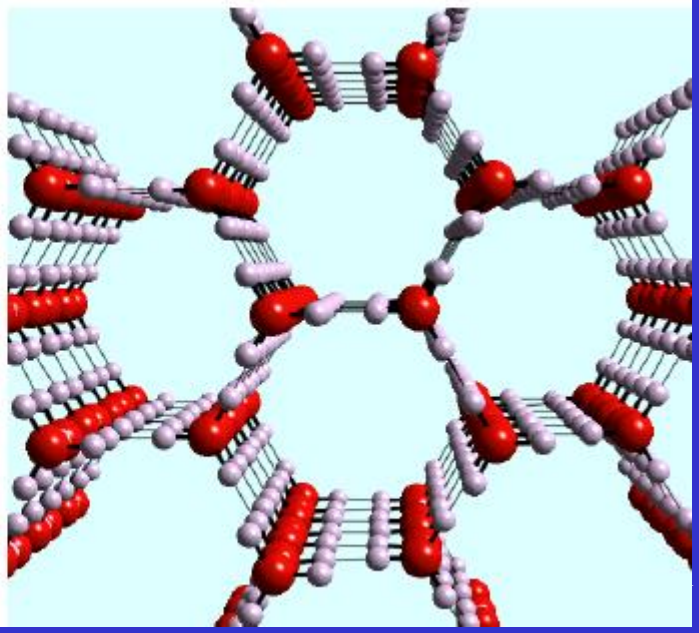
Hexagonal: $P6_3/mmc$	
a (Å)	4.5227
c (Å)	7.3671
V (Å^3)	121.9
Z	3
Dx (gcm^{-3})	0.74

O-H (Å)	0.82, 0.86
O···O (Å)	2.765, 2.773
H···O (Å)	1.91, 1.95
O-H···O (°)	180°

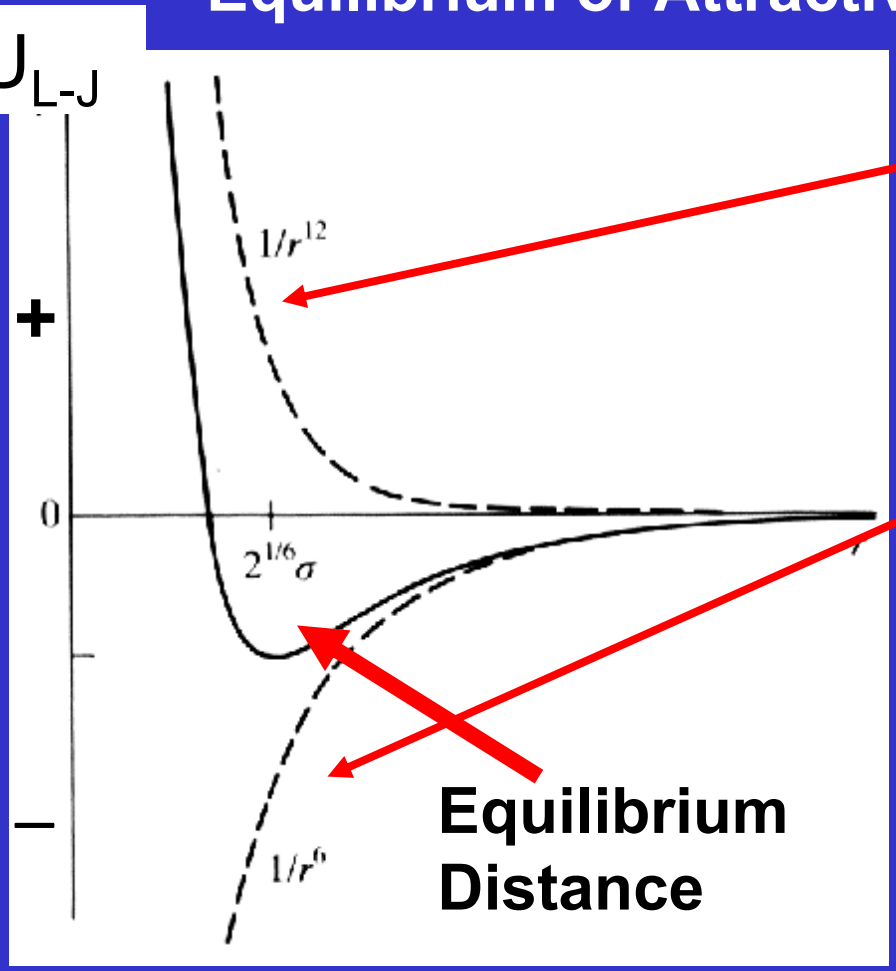








Equilibrium of Attractive and Repulsive Forces



Repulsive Forces **(Pauli)**
Repulsion of electron clouds
$U = 1/ r^{12}$

Attractive Forces**(v.d. Waals)**
$U = -1/ r^6$

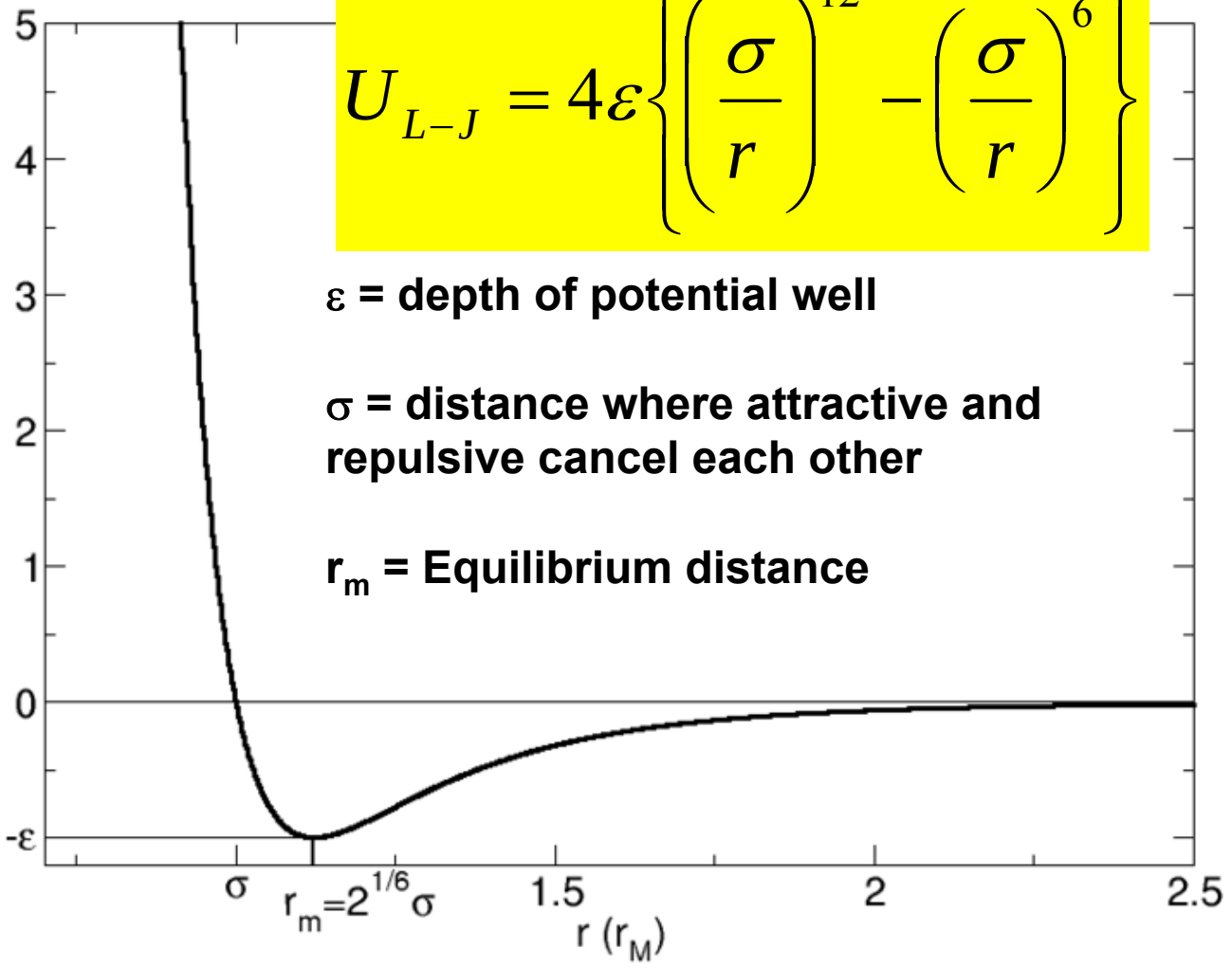
Lennard-Jones Potential

$$U_{L-J} = A\frac{1}{r^{12}} - B\frac{1}{r^6}$$

A, B = constants depending on electric properties of molecules

Lennard-Jones Potential

$$U_{L-J} = 4\varepsilon\left\{\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right\}$$



ε = depth of potential well

σ = distance where attractive and repulsive cancel each other

r_m = Equilibrium distance

Van der Waals Radii, Å

Atomic radius O 0.73 Å
Ionic radius O^{2-} 1. 40 Å

Ag 1.72	Ar 1.88	As 1.85	Au 1.66
Br 1.85	C 1.70	Cd 1.58	Cl 1.75
Cu 1.40	F 1.47	Ga 1.87	H 1.20
He 1.40	Hg 1.55	I 1.98	In 1.93
K 2.75	Kr 2.02	Li 1.82	Mg 1.73
N 1.55	Na 2.27	Ne 1.54	Ni 1.63
O 1.52	P 1.80	Pb 2.02	Pd 1.63
Pt 1.72	S 1.80	Se 1.90	Si 2.10
Sn 2.17	Te 2.06	Tl 1.96	U 1.86
Xe 2.16	Zn 1.39		

Solids

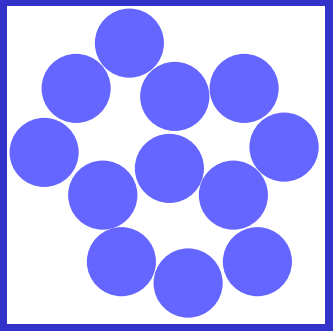
Amorphous

- **Random internal order**
- ***isotropic* physical properties**
- **thermodynamically metastabile**

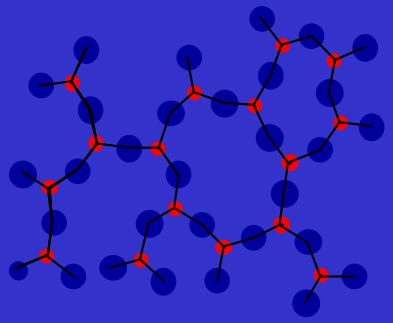
Crystalline

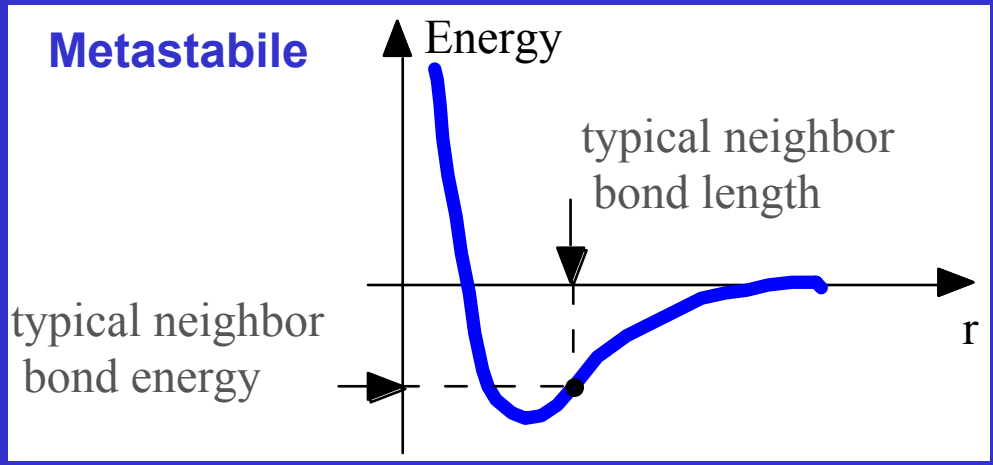
- **Regular internal order**
- ***anisotropic* physical properties = different in different directions**
  (for symmetry lower than cubic)

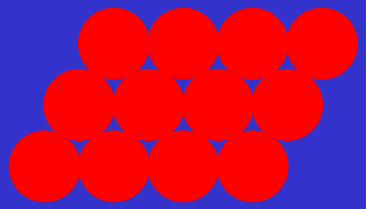
Solids



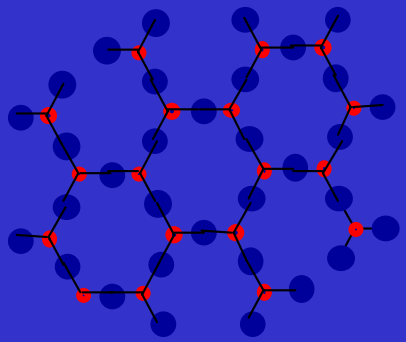
Amorphous

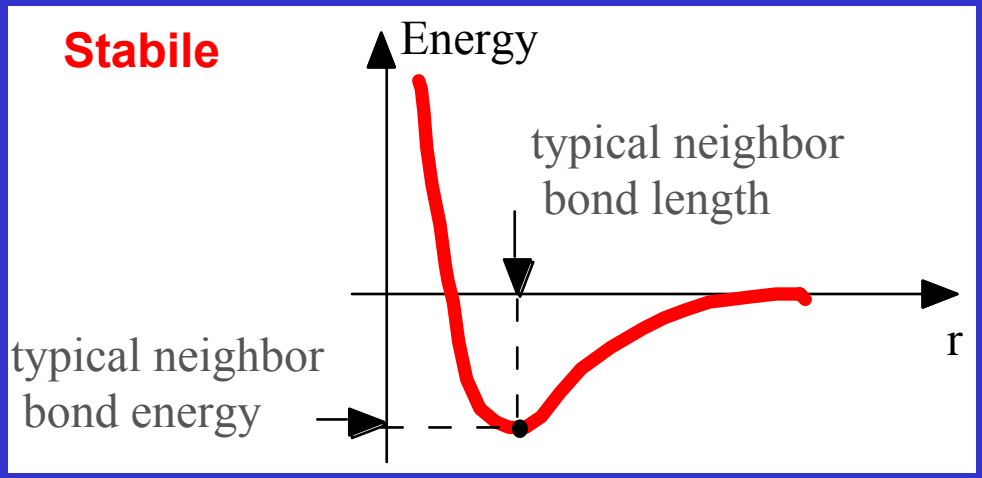






Crystalline





Crystalline Structures

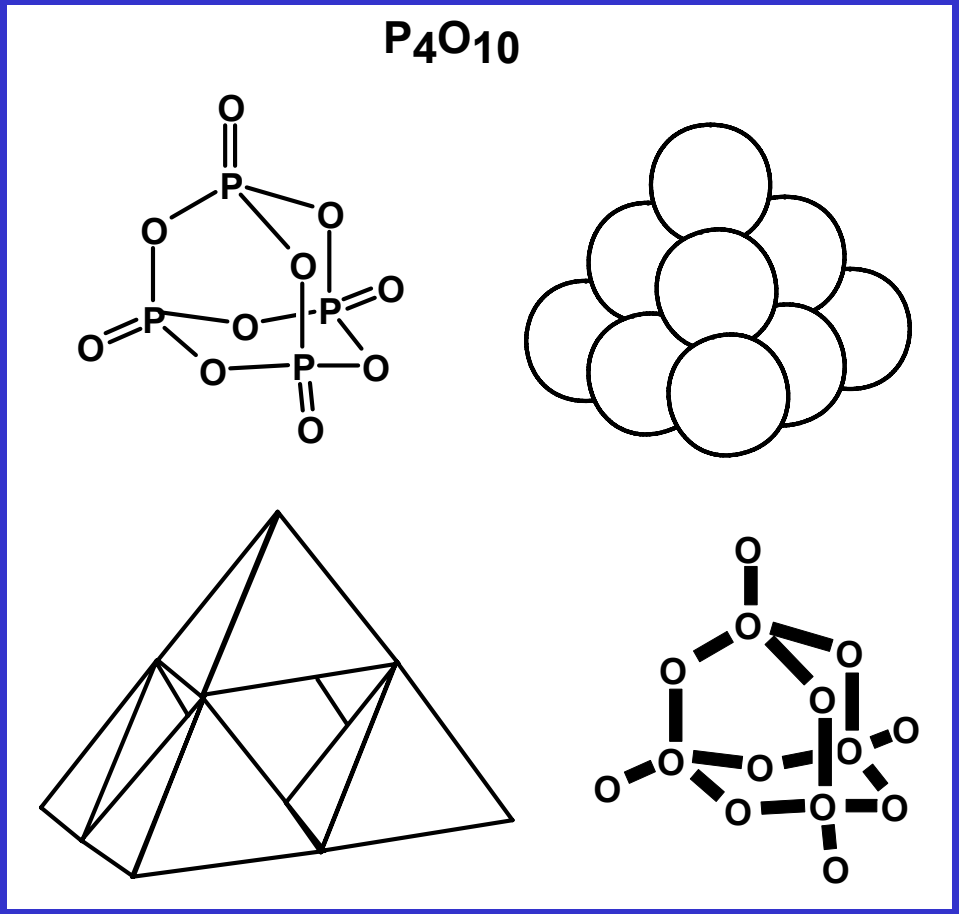
- Metallic (Cu, Fe, Au, Ba, alloys CuAu)
  metal atoms, metallic bond

- Ionic (NaCl, CsCl, CaF_2, ...)
  cations and anions, electrostatic interactions

- Covalent (C-diamond, graphite, SiO_2, AlN,...)
  atoms, covalent bonds

- Molecular (Ar, C_{60}, HF, H_2O, CO_2, organic compounds sloučeniny, proteins)
  molecules, van der Waals and H-bonds

Models of Structures



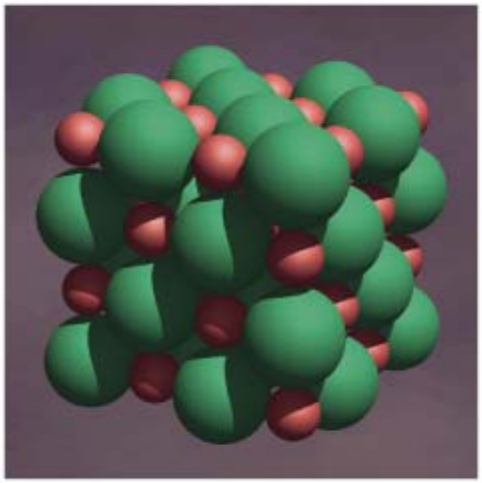
Atoms fill space

Coordination polyhedra

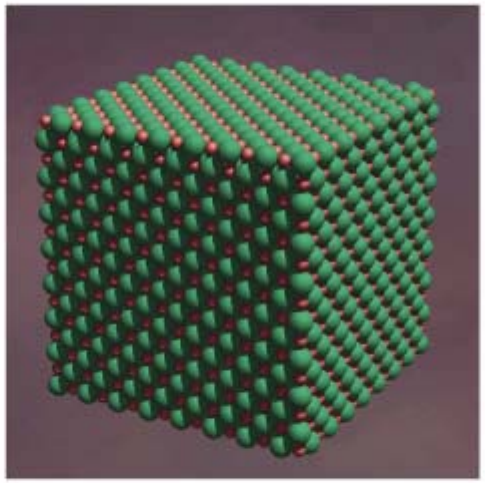
Atoms and bonds

Crystalline Structures

Regular internal order



(a)

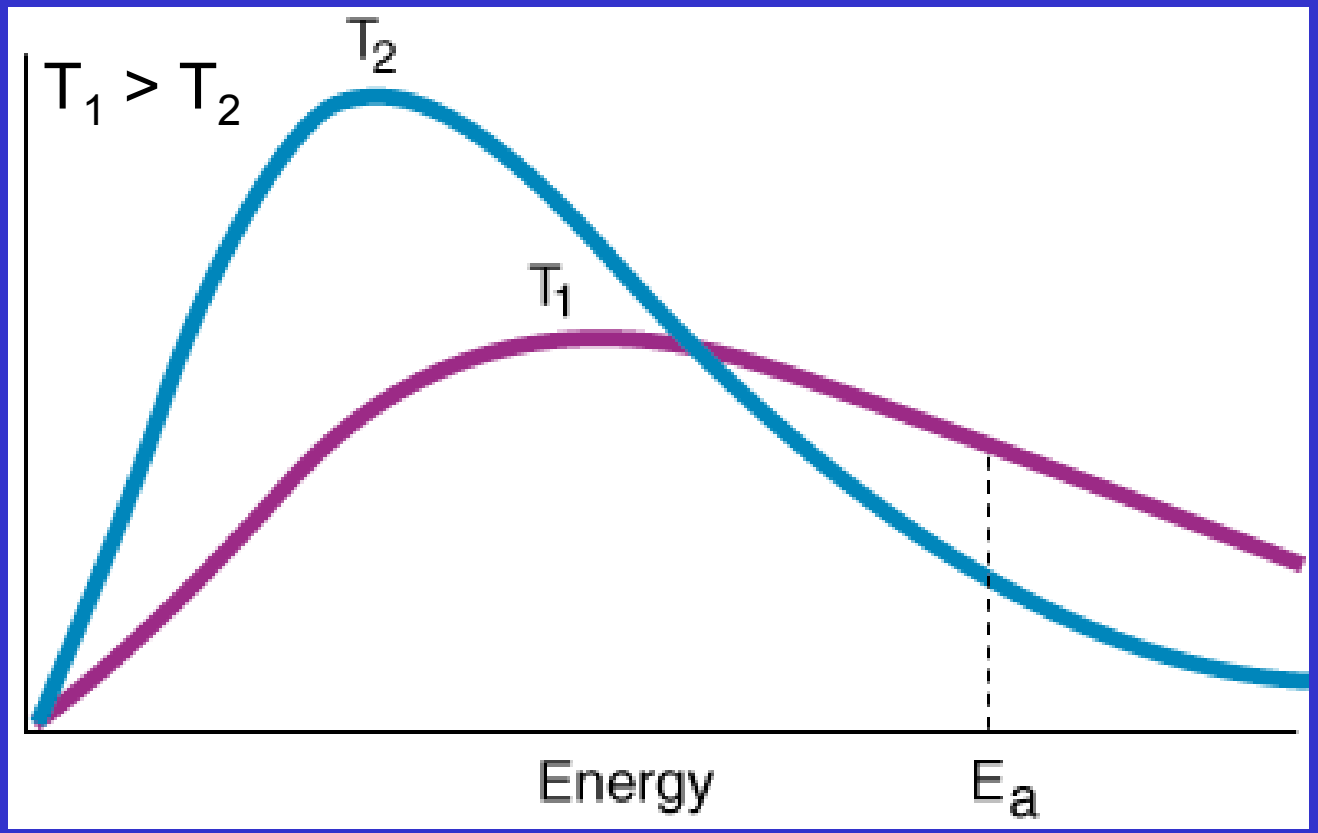


(b)

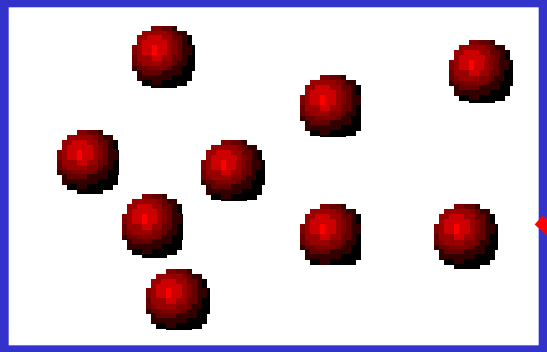
(c)

Solidification

Boltzman distribution – kinetic energy decreases during cooling



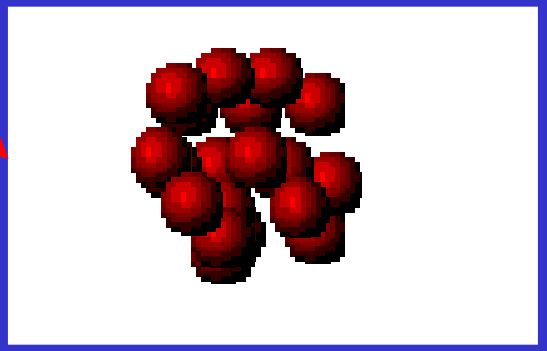
Formation of Crystallization Nuclei



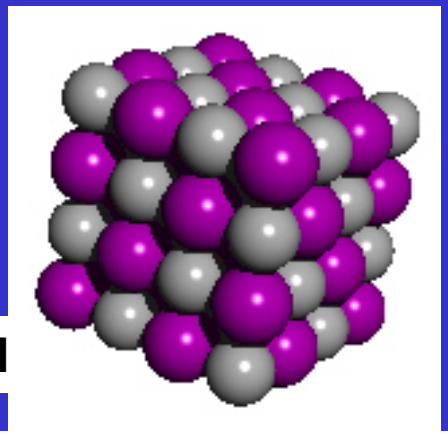
Solution or Melt

kinetic energy decreases during cooling

cooling – nucleation = random formation of crystallization nucleus



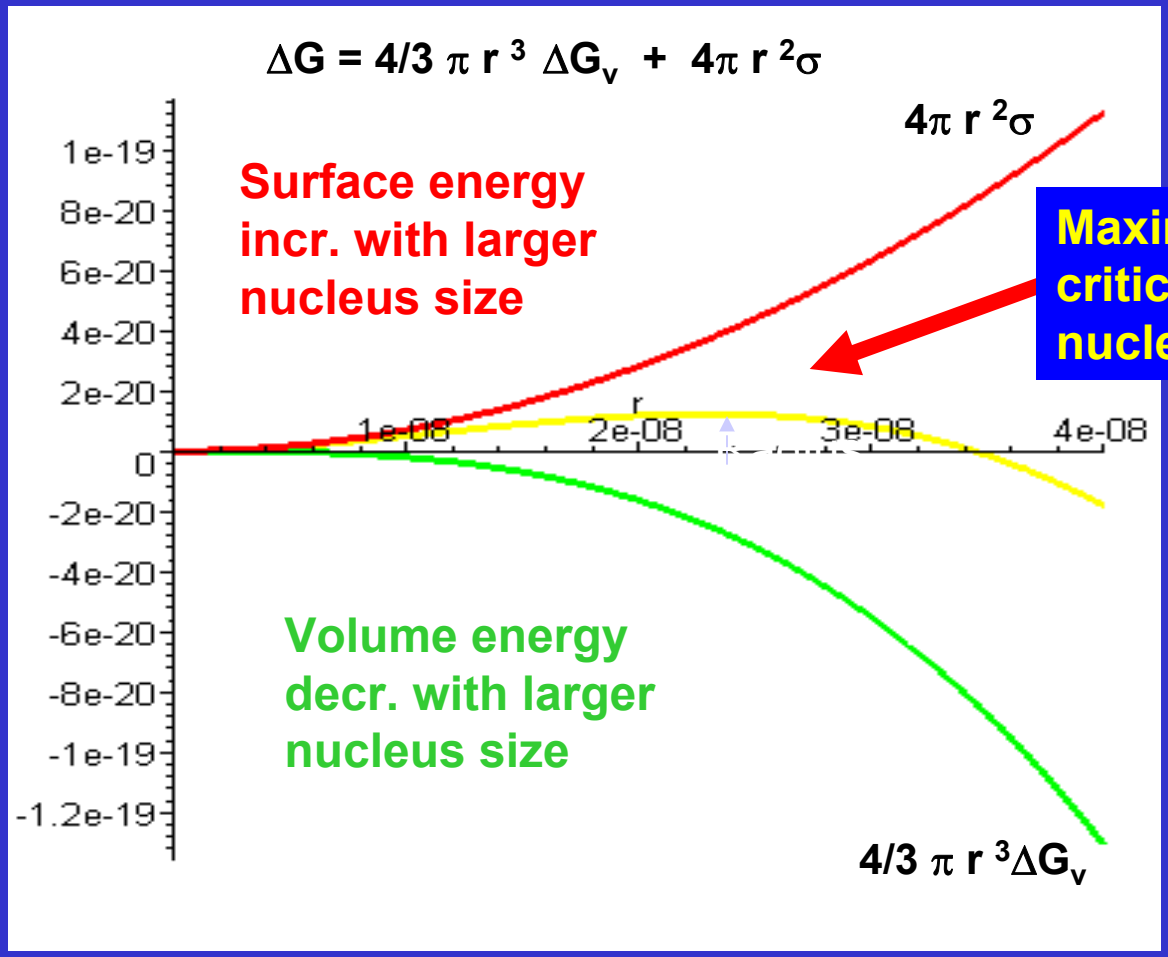
Crystallization nucleus



Crystal

Nucleation

$\Delta G_{Nucleation}$



Monocrystal Synthesis

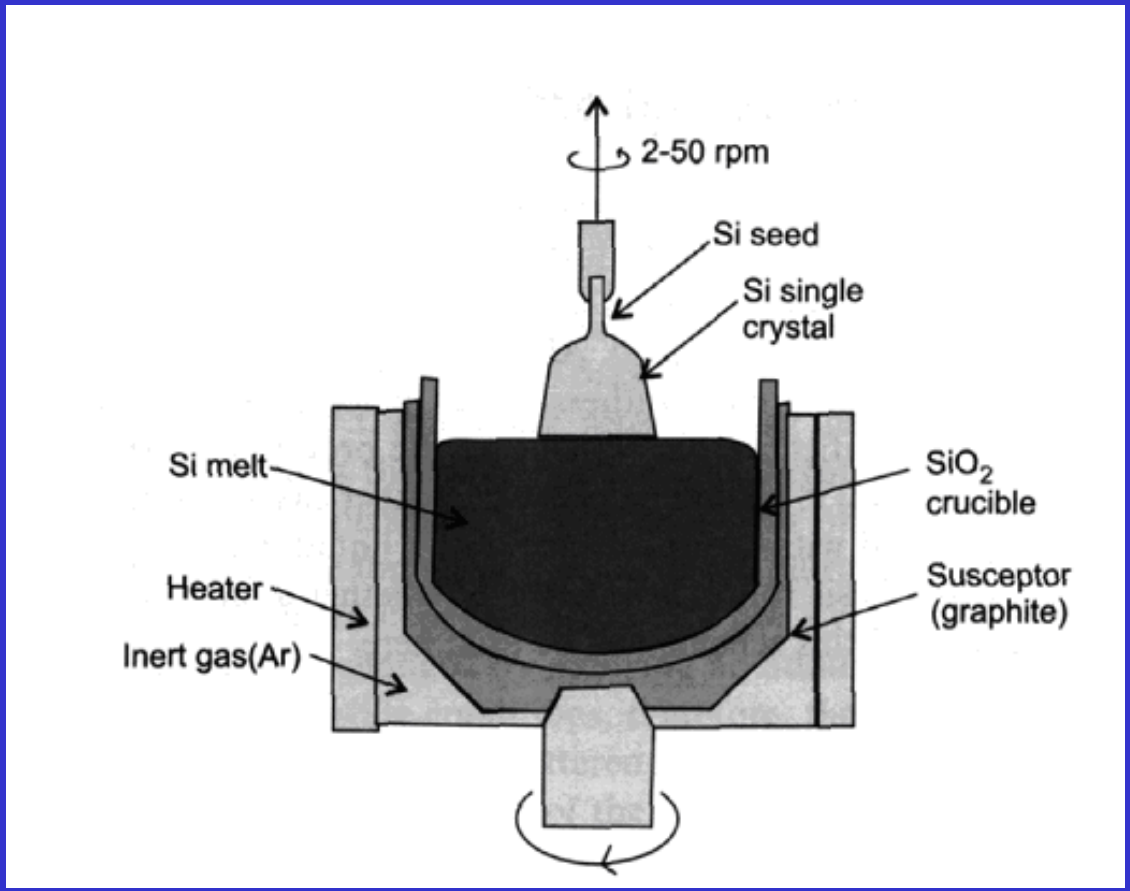
High-temperature methods
Czochralski

Medium-temperature methods
Hydrothermal method
Sublimation

Low-temperature methods
Crystallization from solution

Monocrystal Synthesis

Jan Czochralski
(1885–1953)

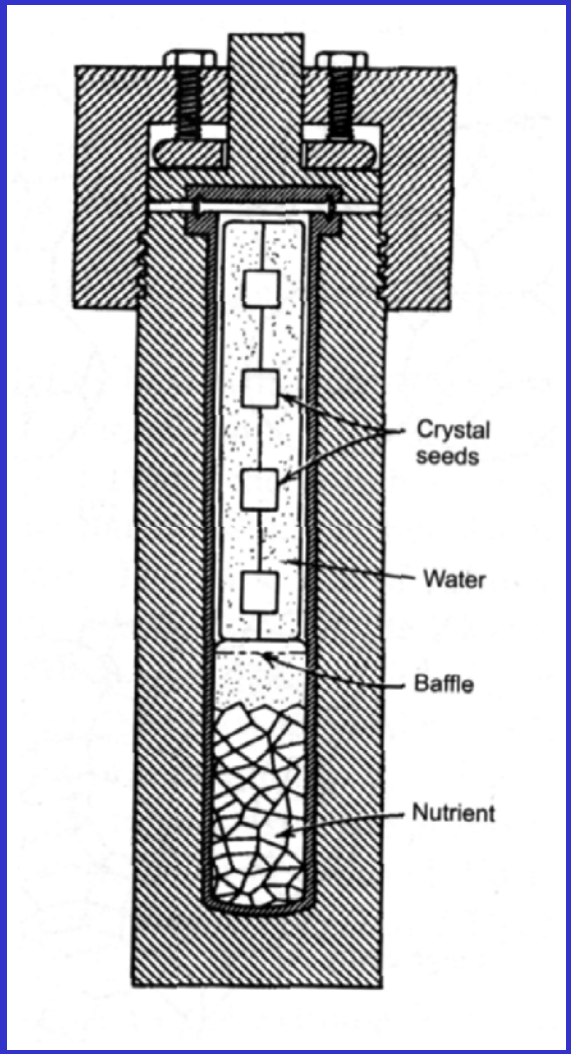


Si Monocrystal Synthesis

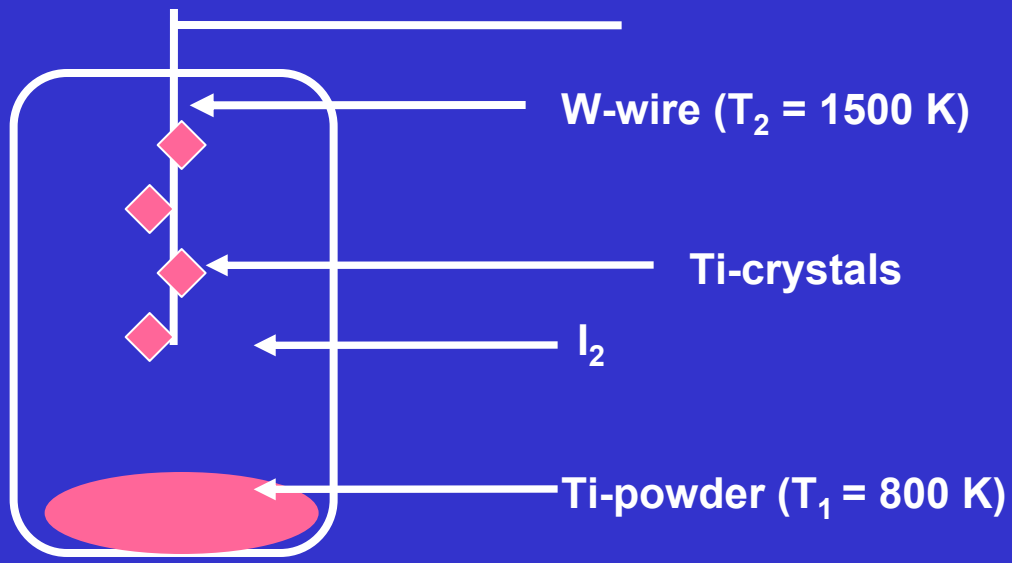
D = 300 mm
l = 2 m
m = 265 kg

Hydrothermal Method

Temperature gradient



Van Arkelova Method



$Ti + 2I_2 = TiI_4 \quad \Delta H = -376\ kJ\ mol^{-1}$

exothermal: transport from cold to hot end

Crystallization from Solution

KDP crystals

(KH_2PO_4)

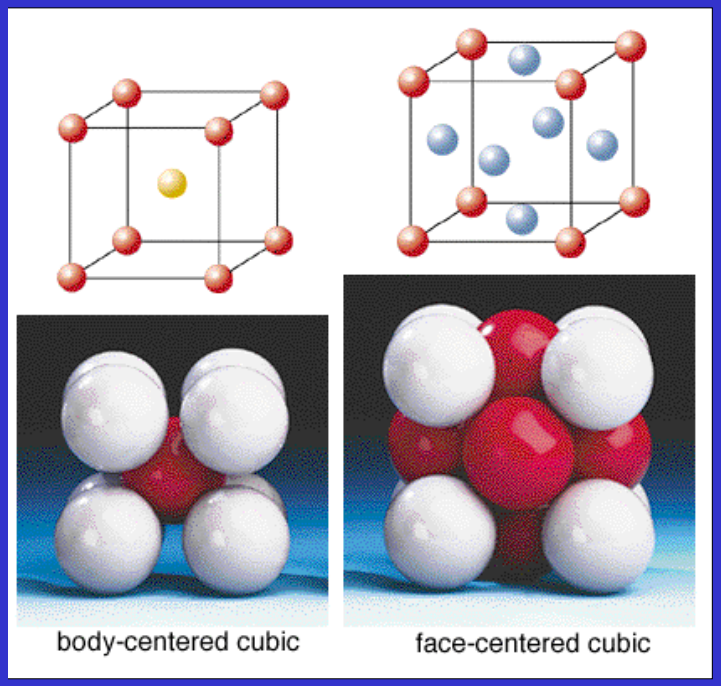
Supersaturated solution

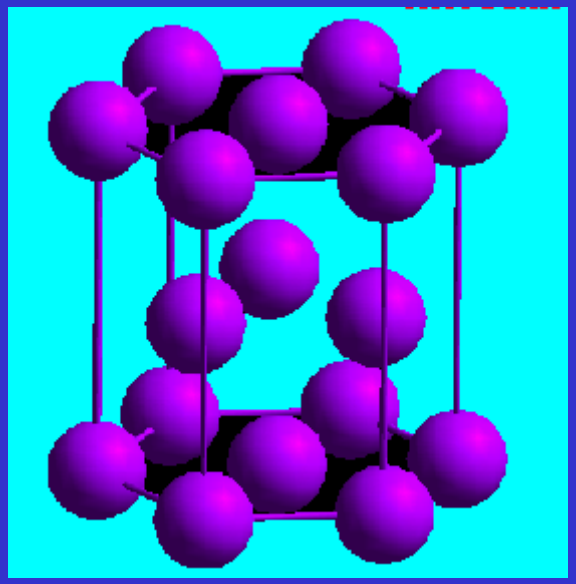
Nucleation with crystals

Slow cooling

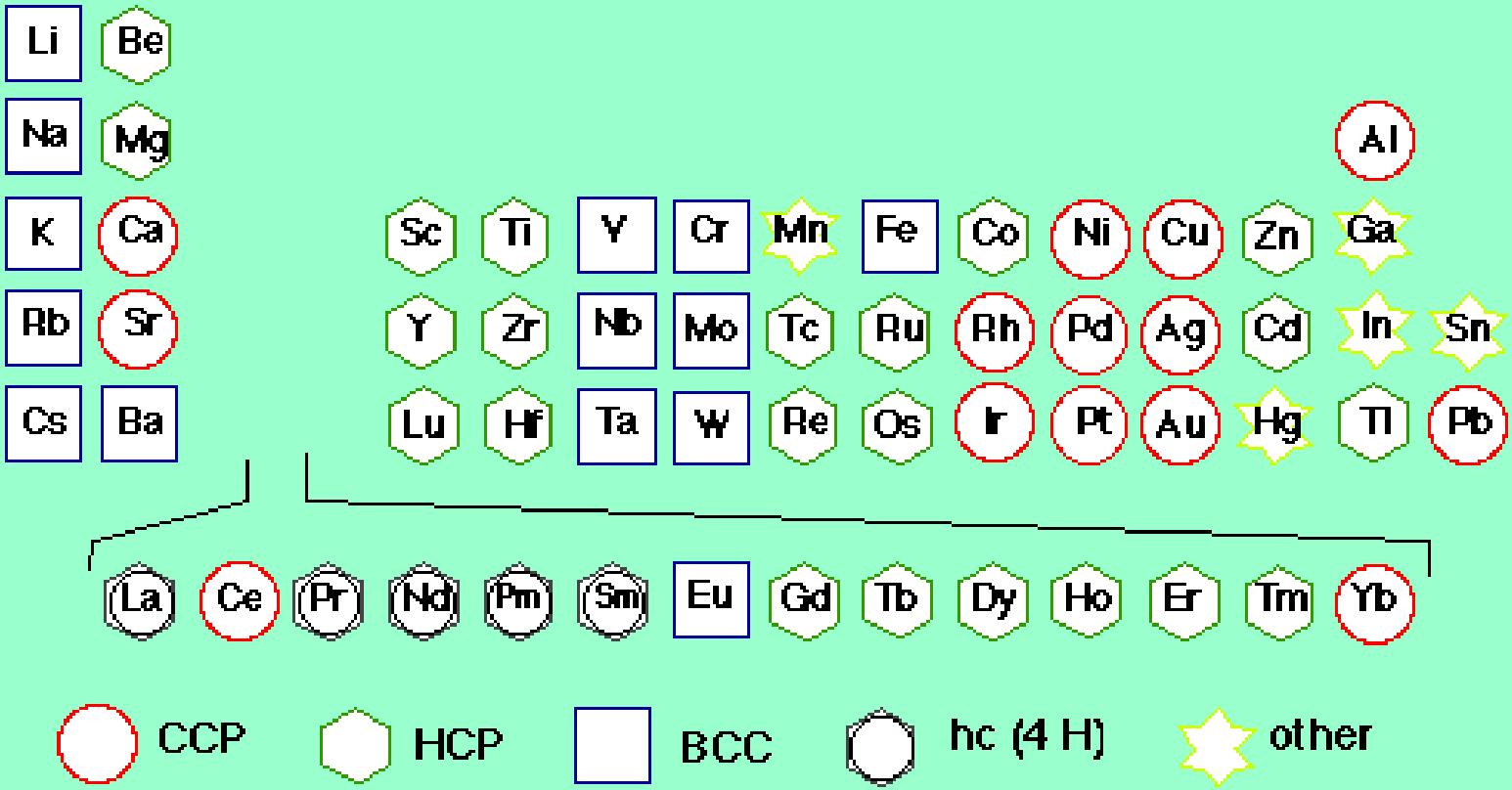
Structure of Metals

- Cubic Close Packing = Face Centered Cubic
- Hexagonal Close Packing
- Body Centered Cubic



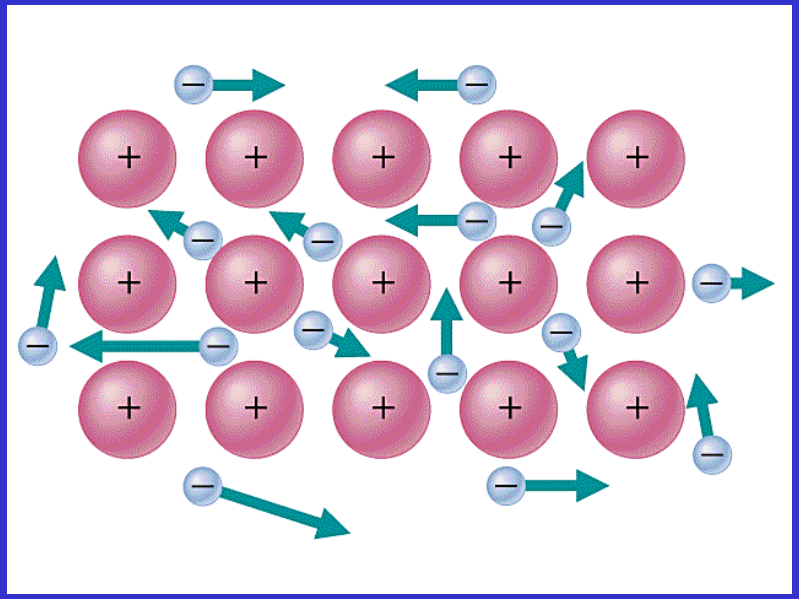


Periodic Table of Metal Structures



Cubic Close Packing = Face Centered Cubic
Hexagonal Close Packing
Body Centered Cubic

Electron Gas



Electrical conductivity:

Electrons move freely in positive charge field of nuclei

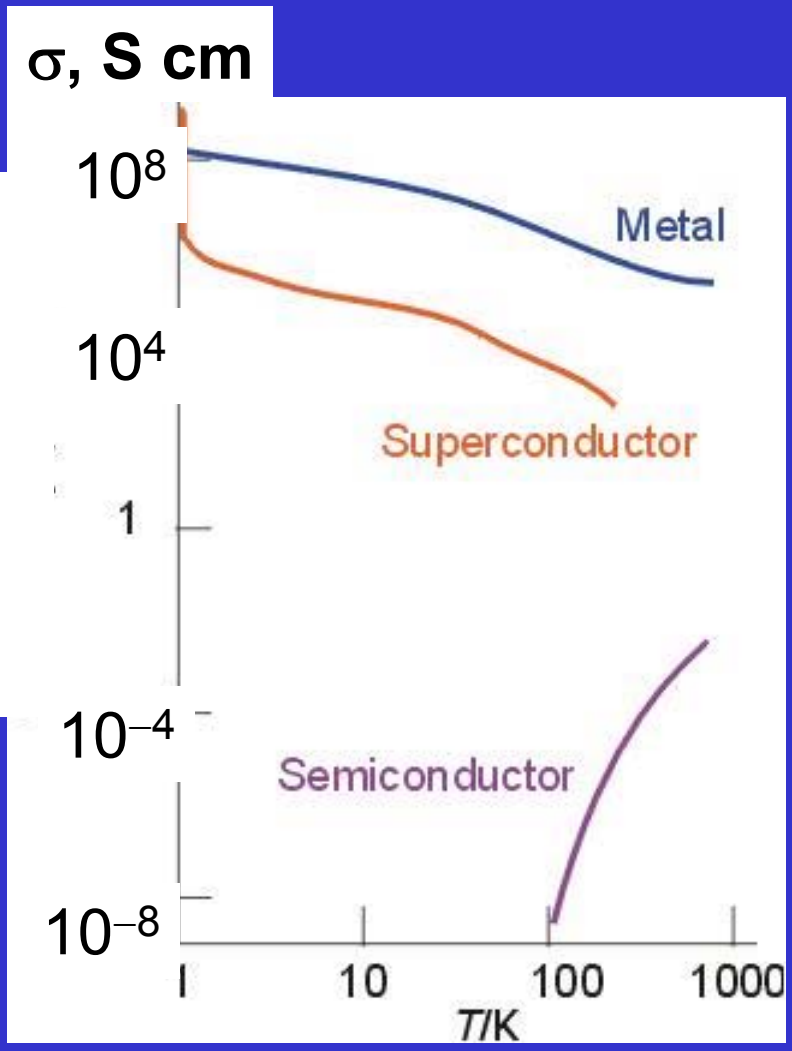
Electrical resistance of metals increases with temperature – larger atom vibrations

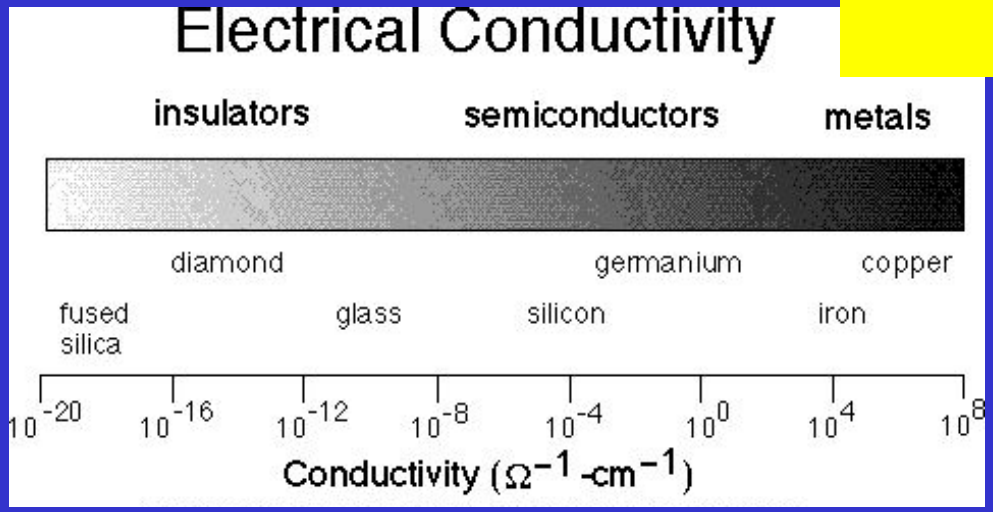
Electrical resistance of metals increases with impurity concentration – hinder electron movement

Thermal conductivity :
Transfer of energy by electrons

Electrical Conductivity S and Resistance R

$$R = \frac{1}{\Sigma}$$





$$R = \rho \frac{l}{A}$$

$$\rho = \frac{1}{\sigma}$$

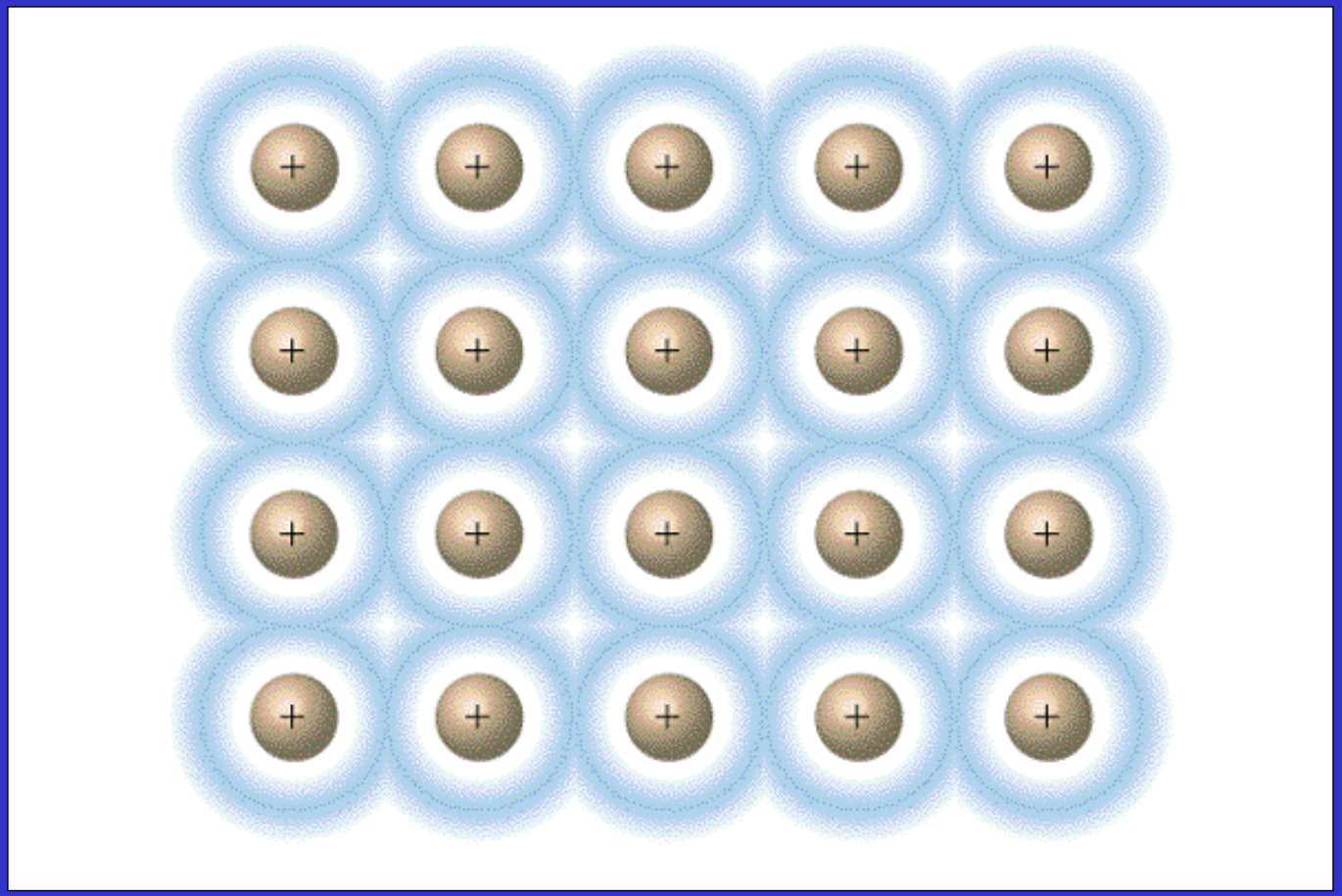
R = electrical resistance , Ω

ρ = specific resistivity , Ω m

L = conductor length, m

A = conductor cross area, m^2

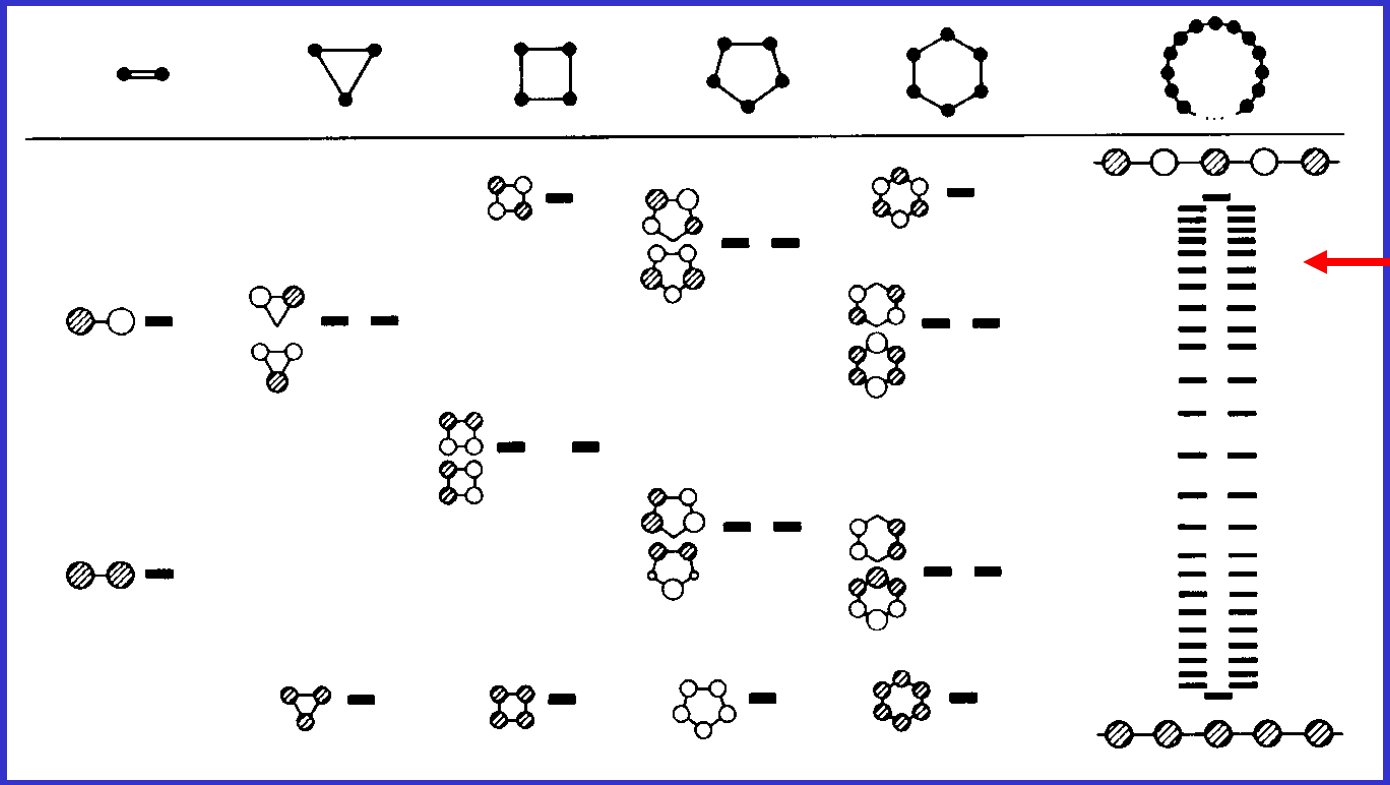
Metallic Bond



Band Theory

MO for 2, 3, 4,....N_A atoms

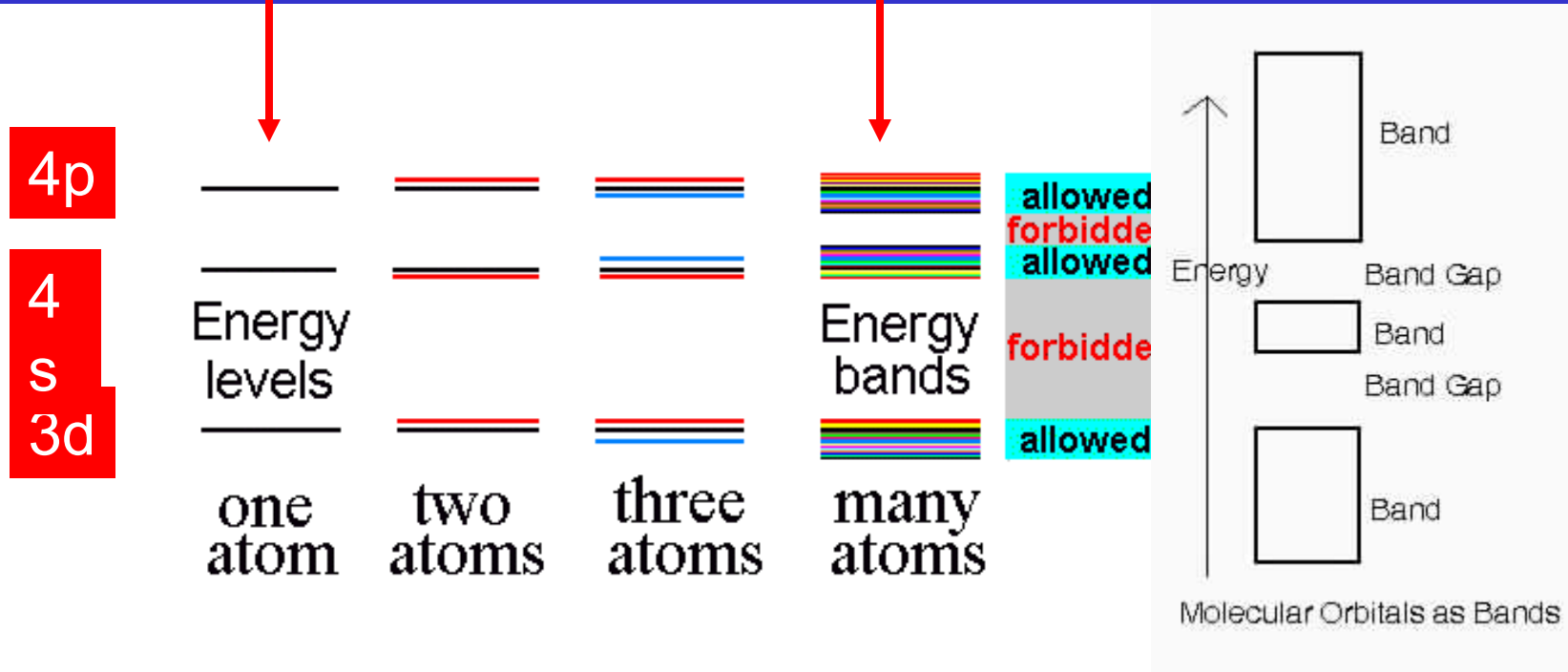
Antibonding orbitals = conduction band



Many closely spaced energy levels overlap and form a band

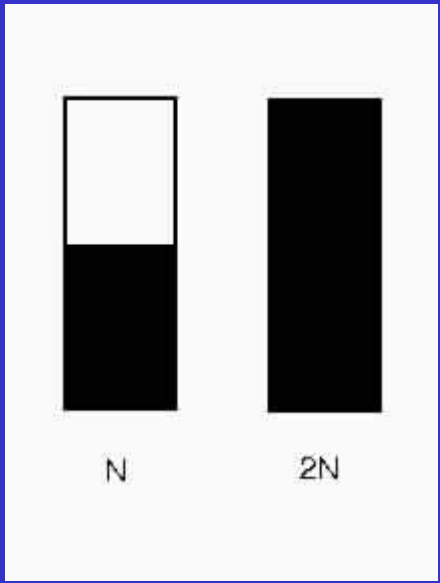
Bonding orbitals = valence band

Band Theory



Electron energies quantized = only some energies allowed, can occupy only allowed levels, forbidden bands = band gap

Filling Bands with Electrons



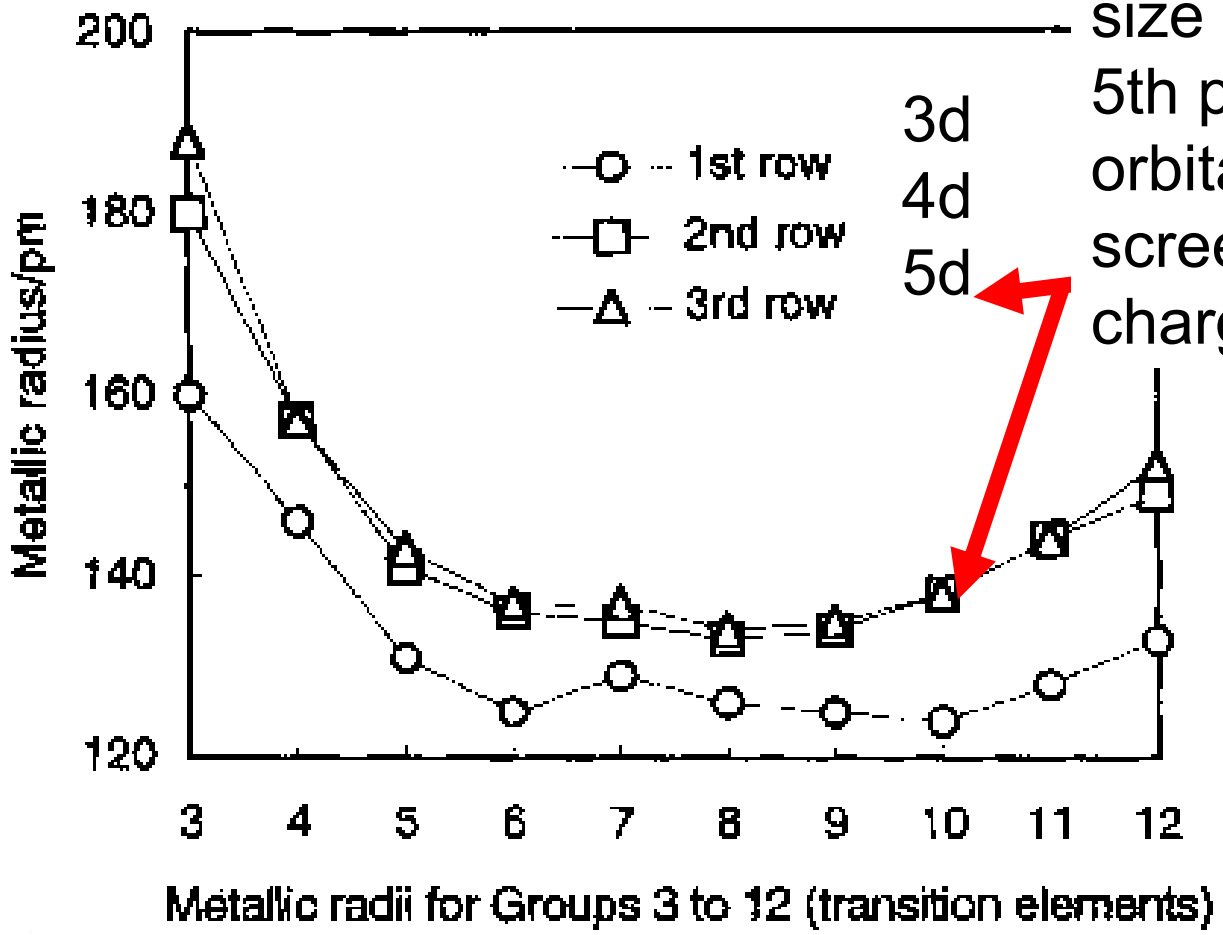
N atoms, each with 1 electron

N levels in a band

Occupied by pairs of electrons

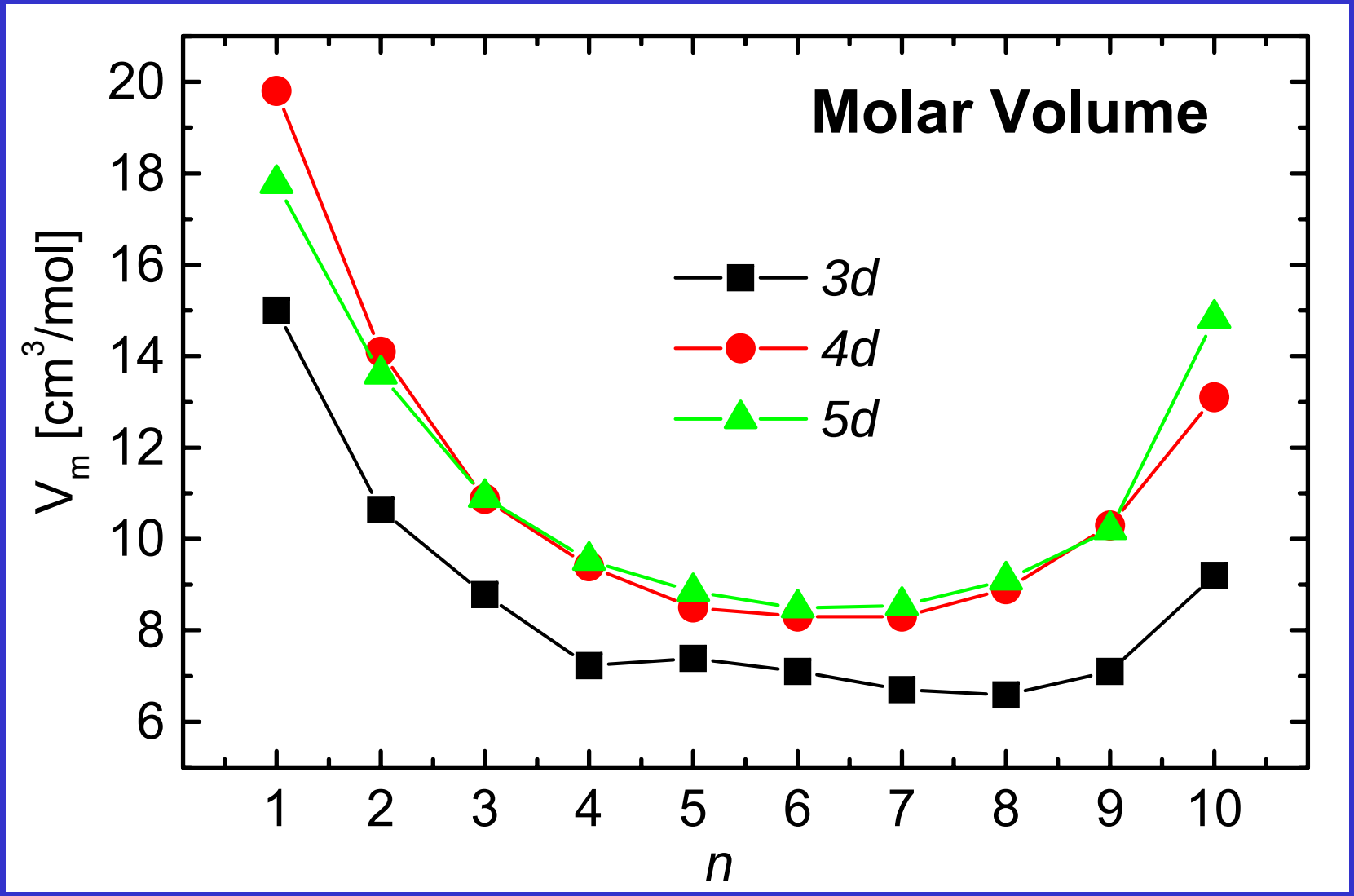
N/2 levels filled
N/2 levels empty

Atomic Radii of TM, pm

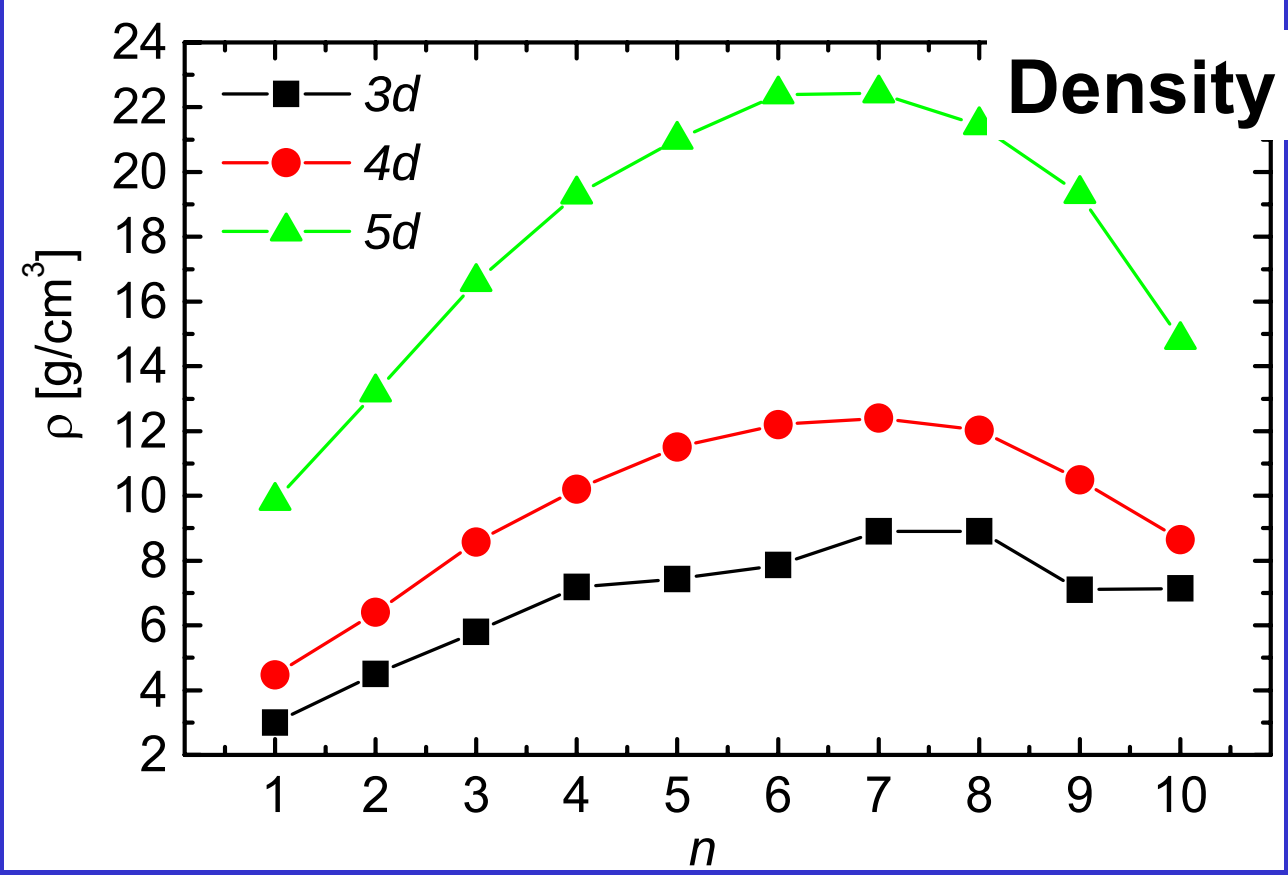


Small incr of atom size down from 4th to 5th period – filled f-orbitals of lanthanides screen poorly nuclear charge

Molar Volume of TM

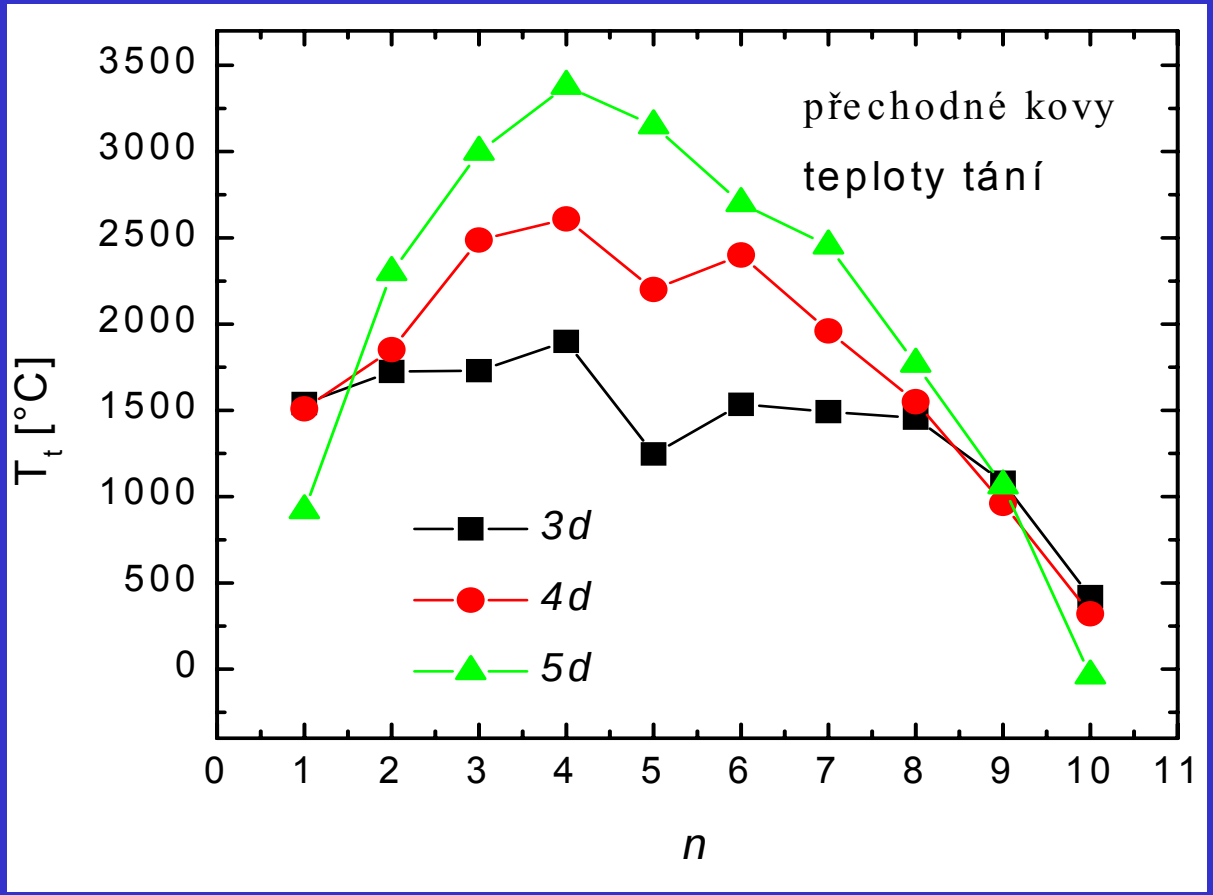


Density of TM



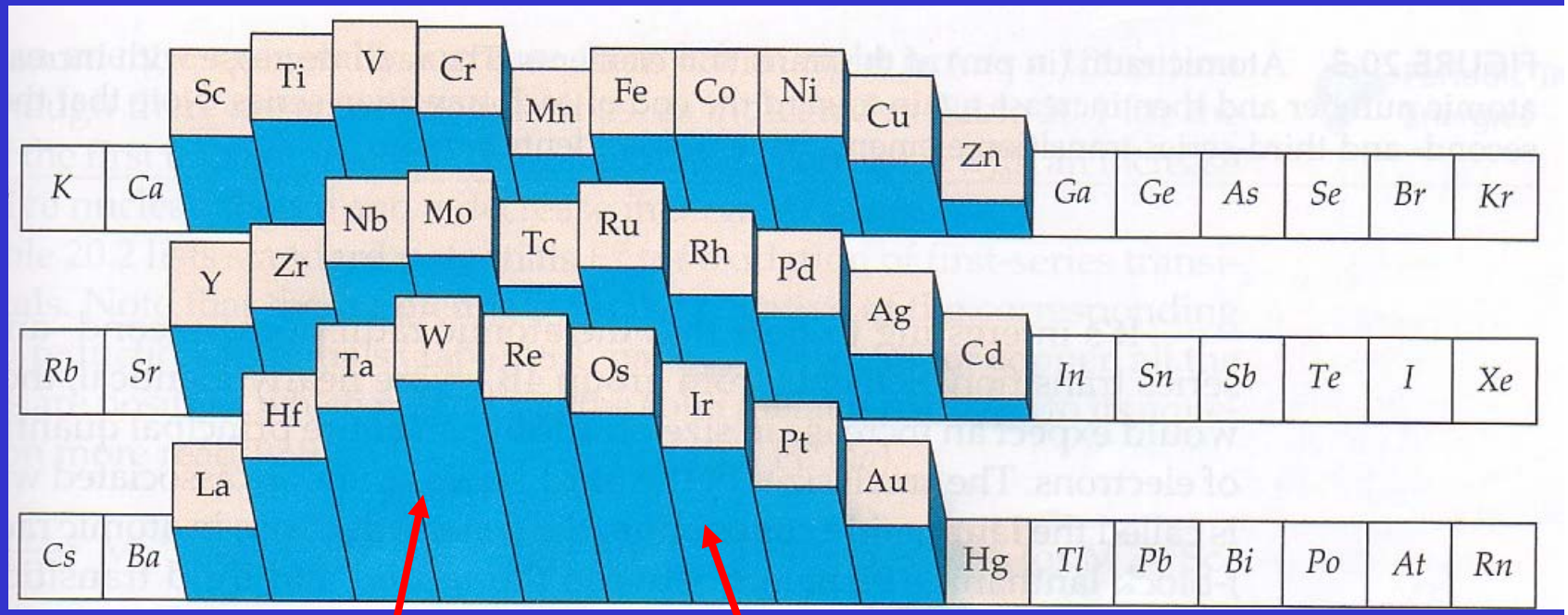
Os 22.5 g cm^{-3}
Ir 22.4 g cm^{-3}

Melting Points of TM



Melting Point = Strength of Metallic bond

Melting Points of TM



Filling of bonding orbitals t_{2g} (bands)

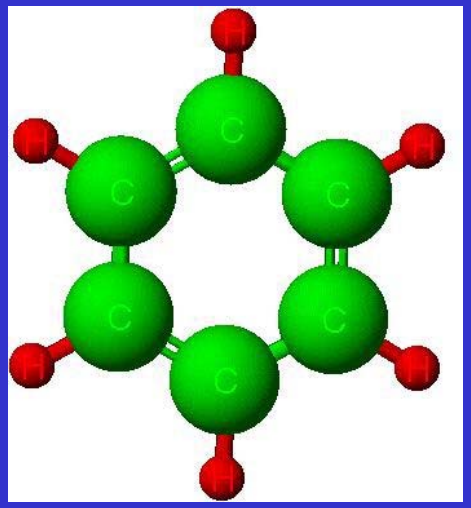
Filling of antibonding orbitals e_g (bands)

Liquid Hg

Metal	El. conf.	T_{melt}, °C	ΔH_{melt}, kJ mol $^{-1}$
Au	$5d^{10}\,6s^{1}$	1064	12.8
Hg	$5d^{10}\,6s^{2}$	–39	2.3

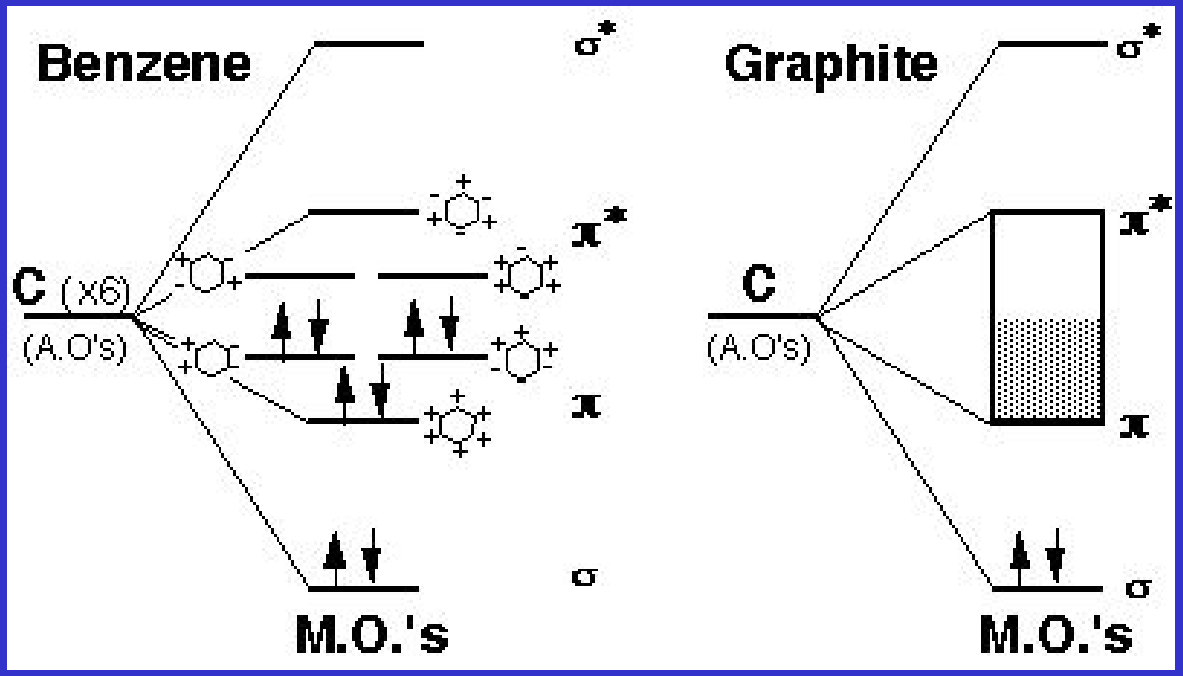
Lanthanide contraction, decr energy of 6s band, 6s further from 6p band.

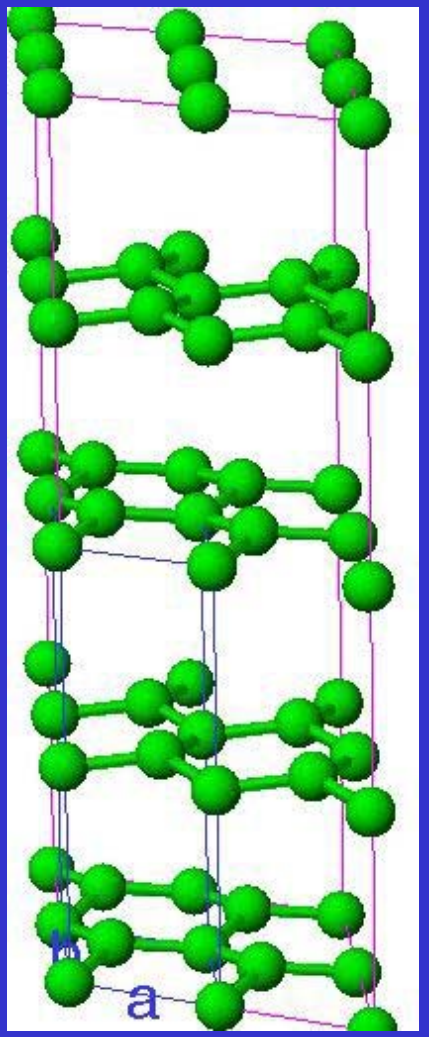
$6s^2$ inert pair



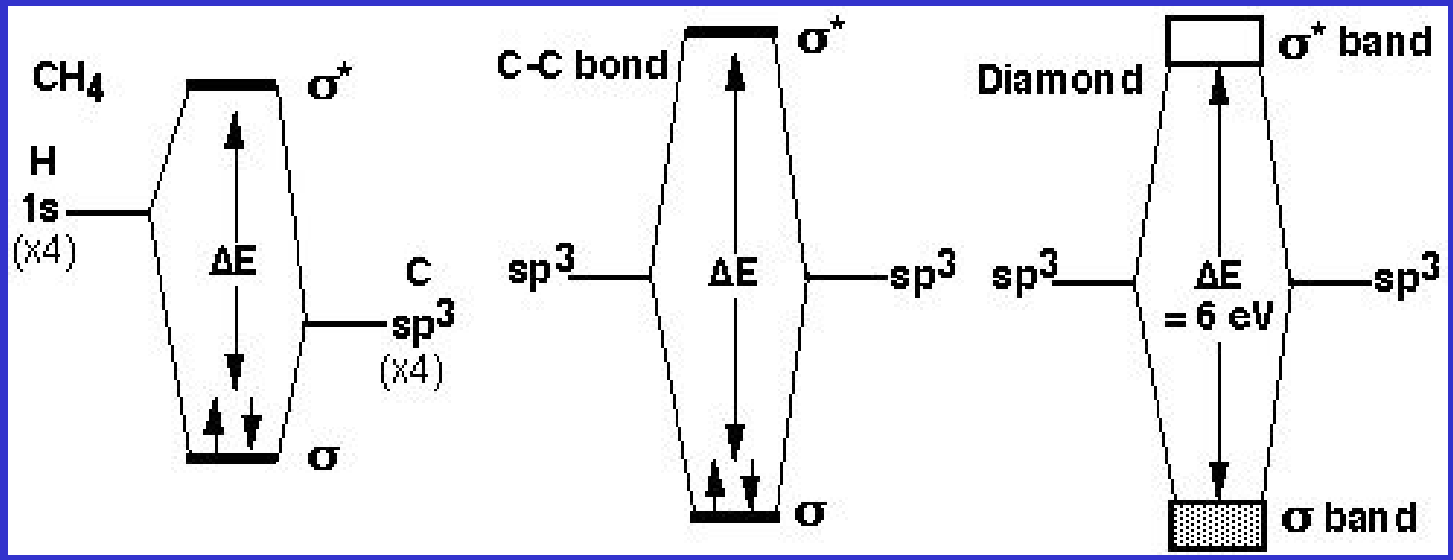
Graphite Bands

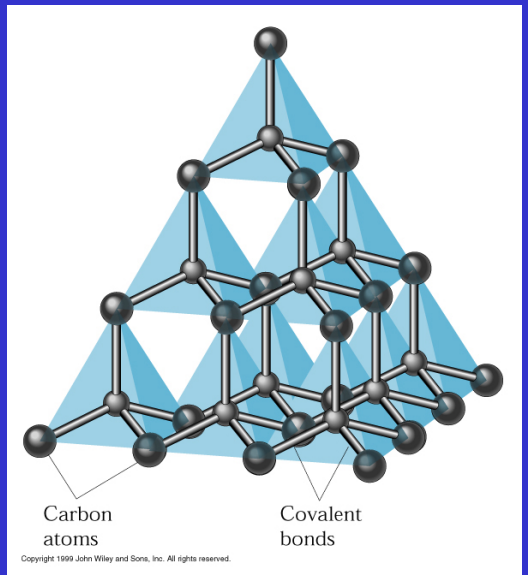
Graphite is a electrical conductor
Conductivity in layers





Diamond Bands

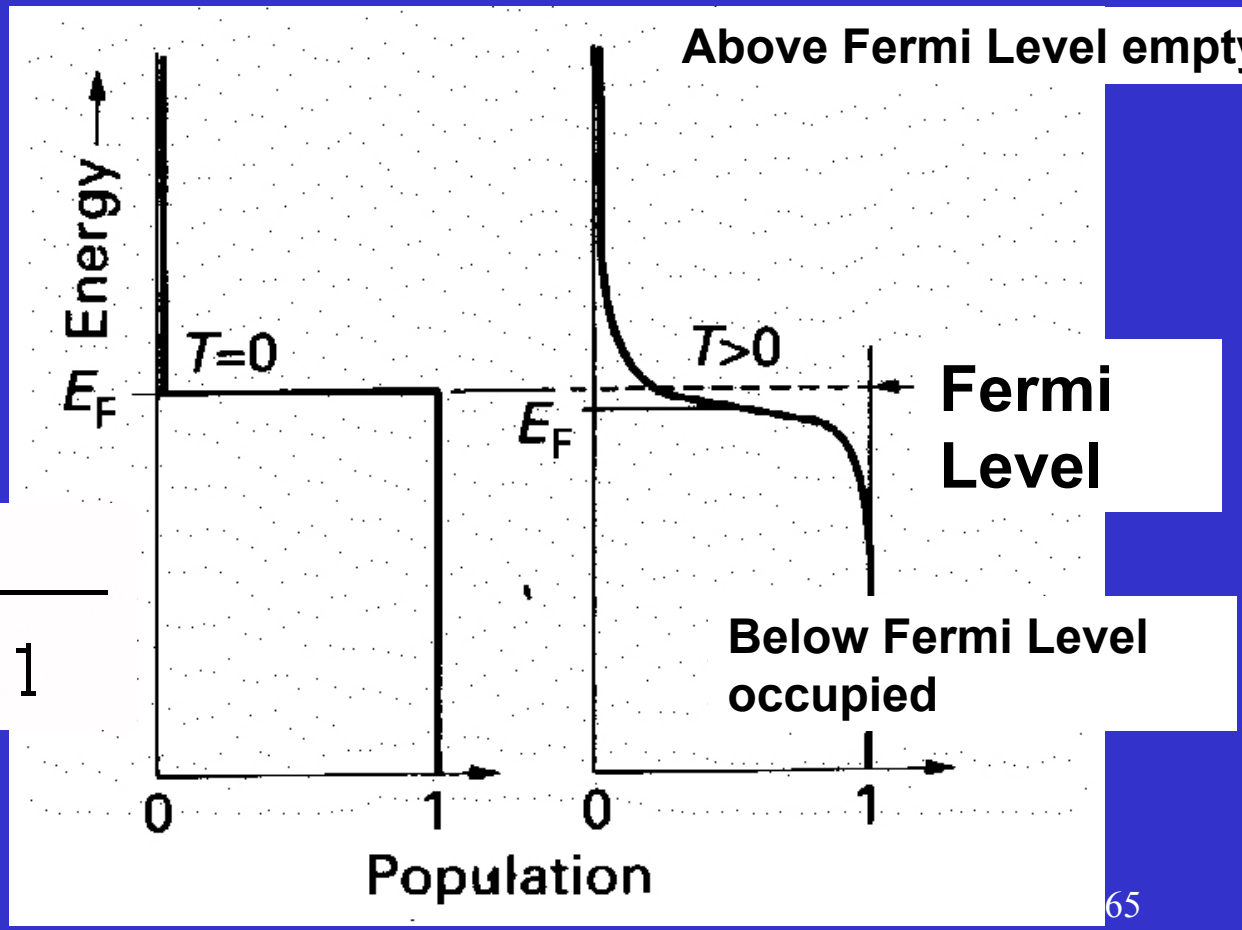




Fermi Level

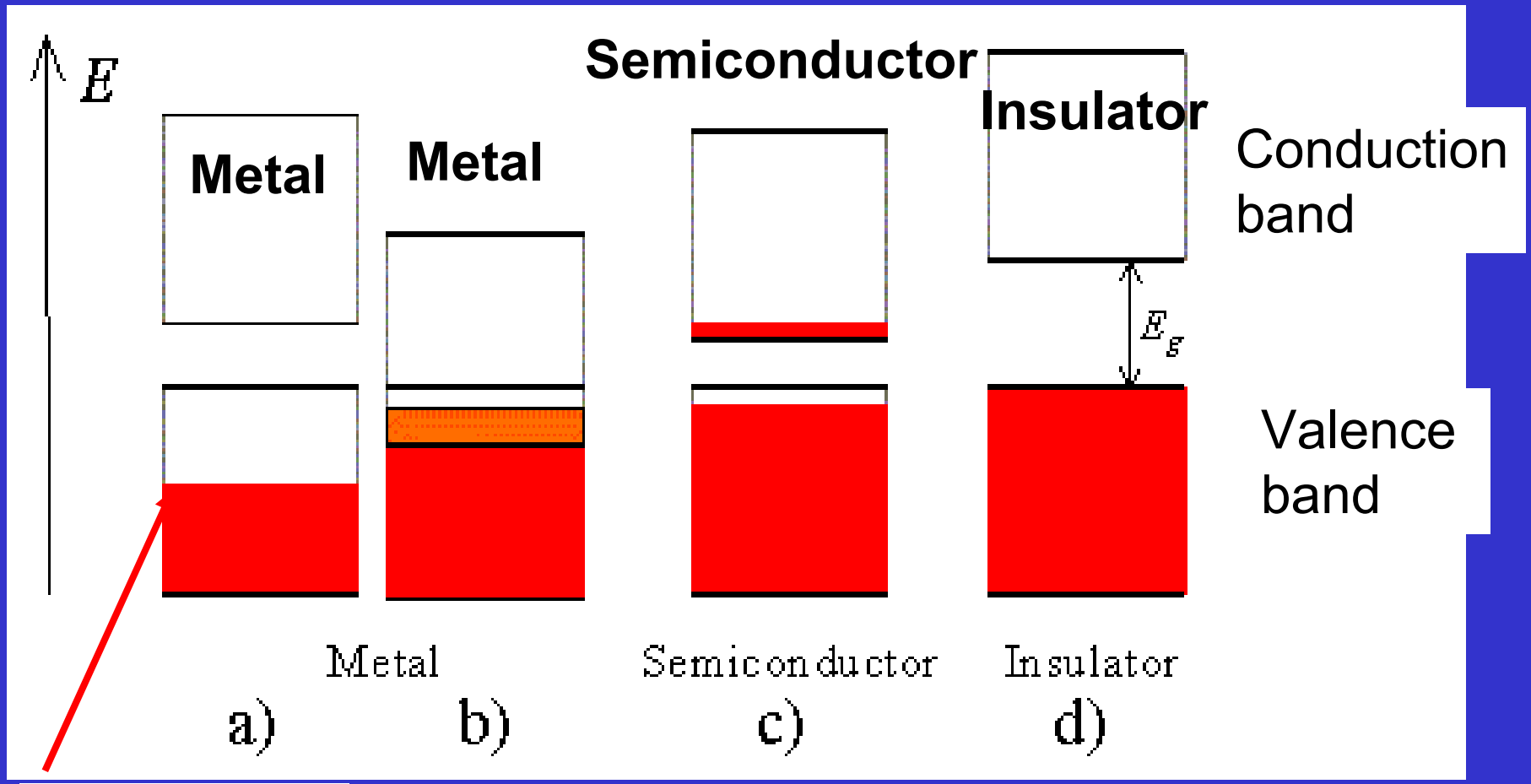
E_f – Probability of occupation is ½

Levels
$E < E_f$ occupied
$E > E_f$ empty



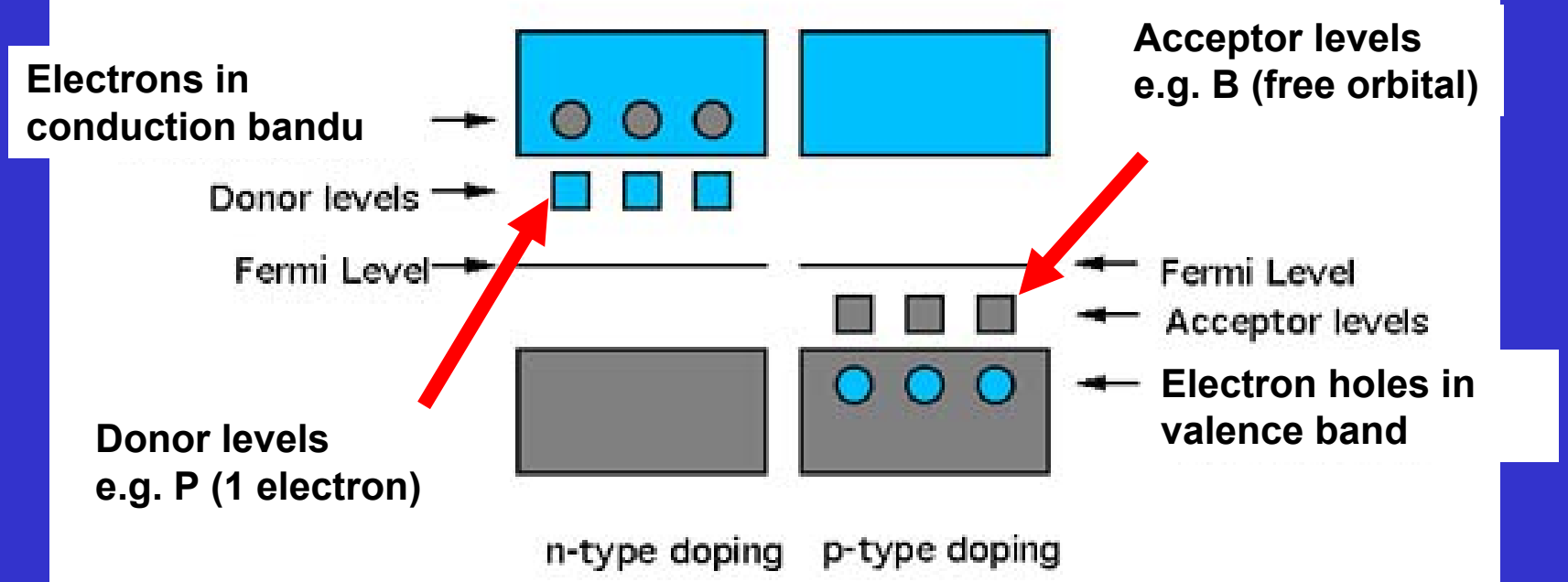
$$P = \frac{1}{e^{(E-E_f)/kT} + 1}$$

Metals, Semiconductors, Insulators



Doped Semiconductors

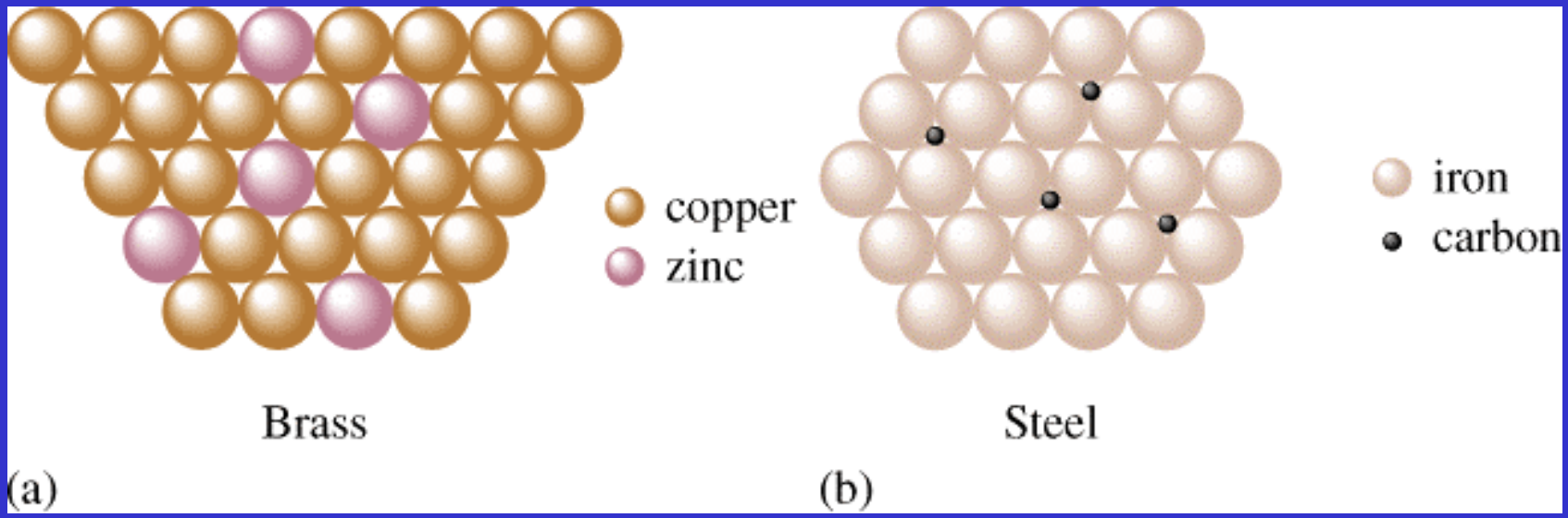
Silicon semiconductors type n and p



Alloys

Substitutional

Interstitial



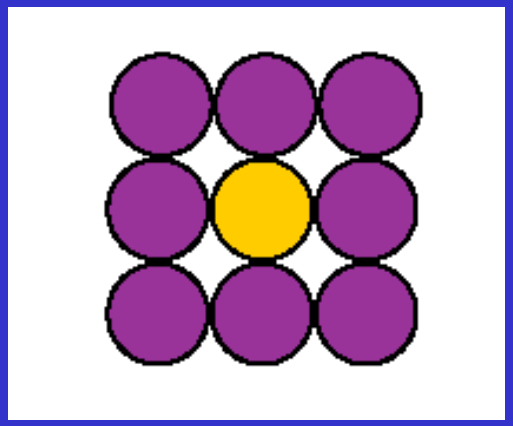
Solid solution
Similar atom size

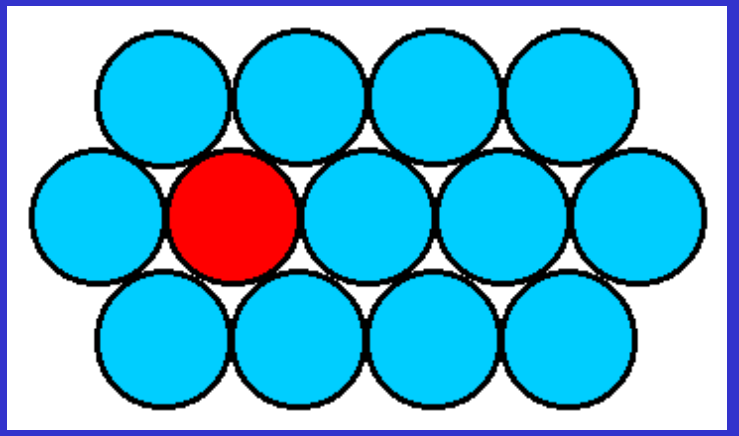
Filling voids with small atoms (C, N, H)

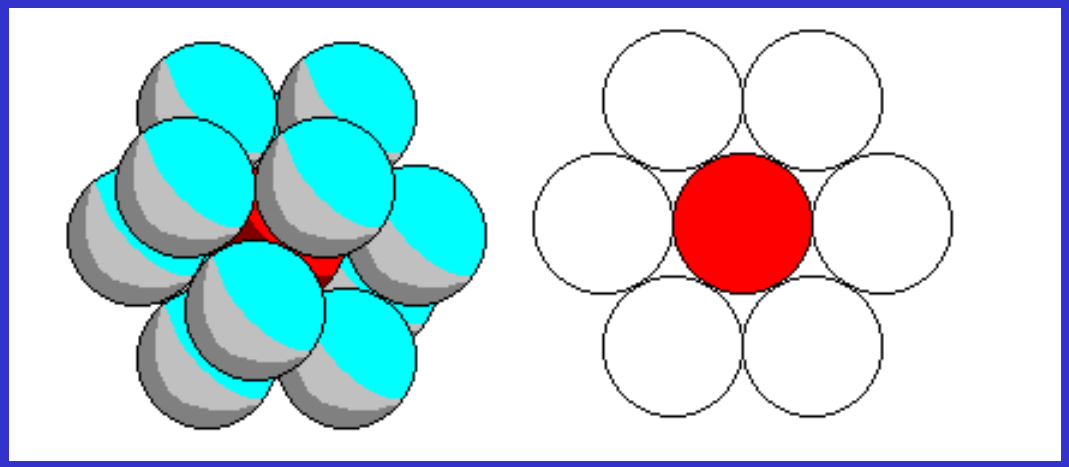
Interstitial compound (Fe_3C)
Constant ratio metal/nonmetal

Coordination Number

Coordination Number = number of closest neighbors

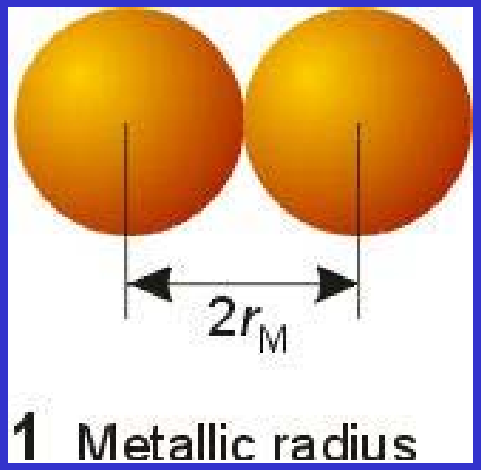


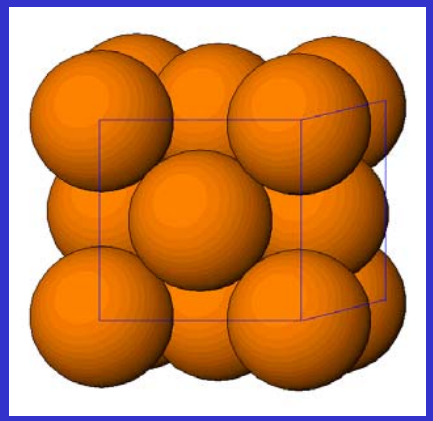




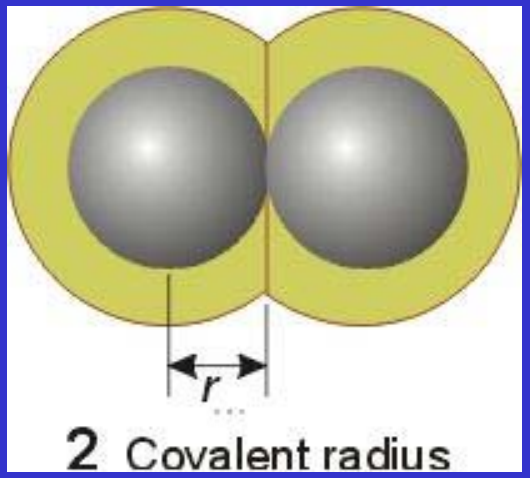
Size of Atoms and Ions

Metallic

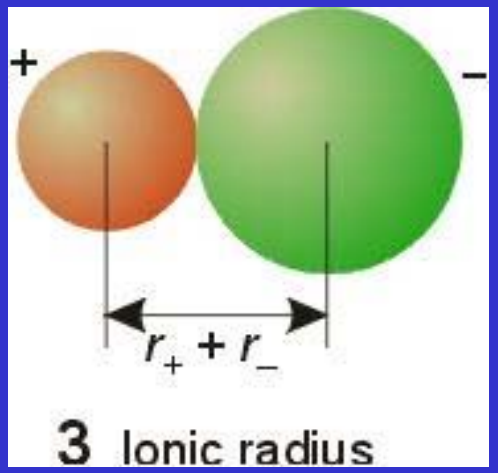




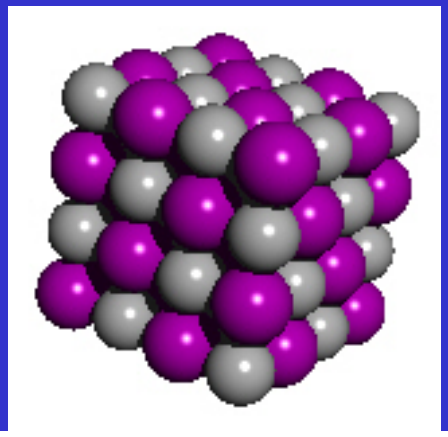
Covalent



Ionic

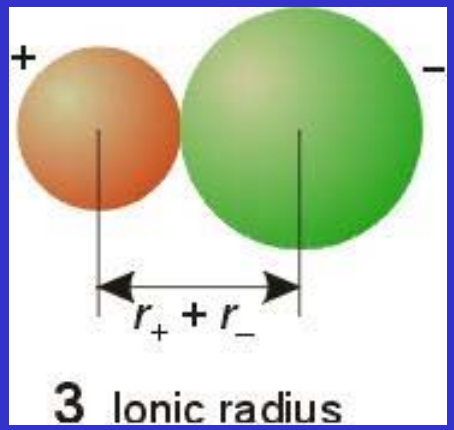


r(O) = 140 pm

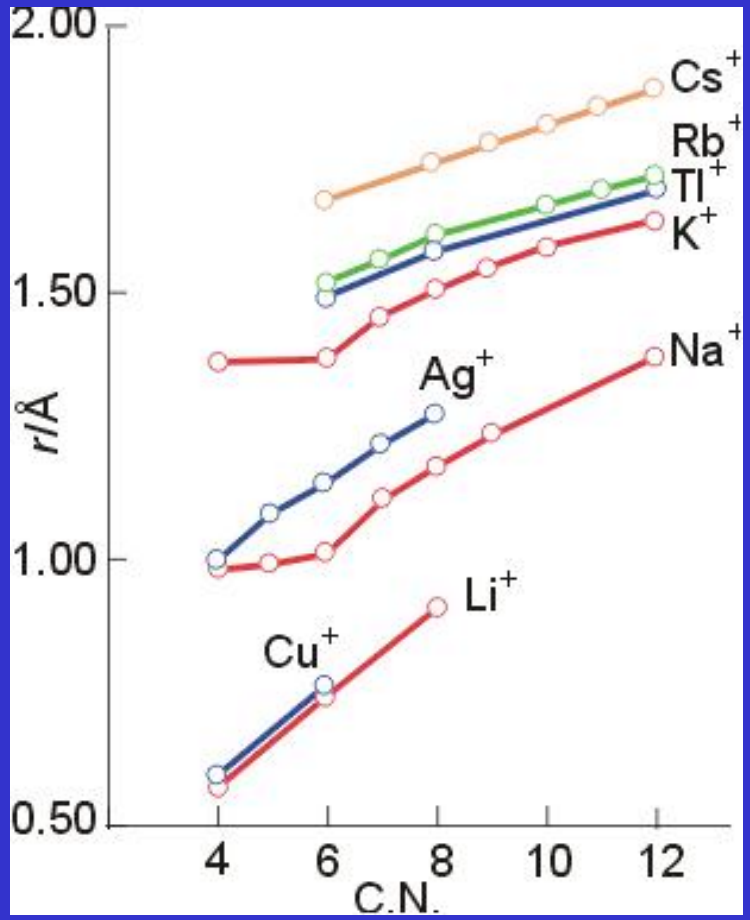


Ionic Radius

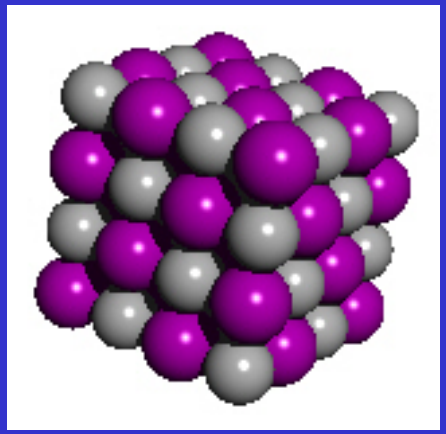
Ionic radius increases with coordination number



3 Ionic radius



Coordination number



Electron density