CH105
Inorganic Chemistry

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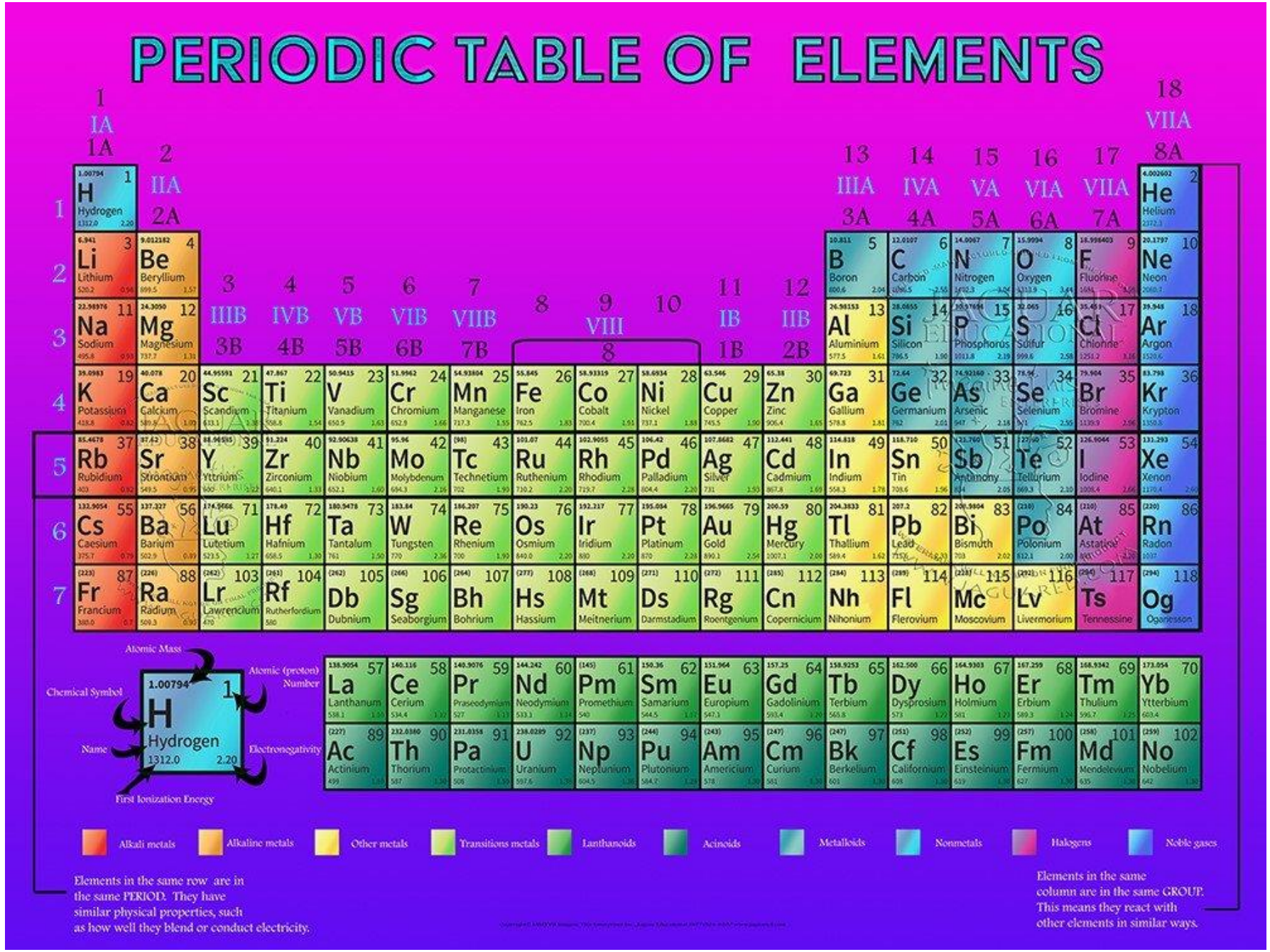

PERIODIC TABLE OF ELEMENTS
Atomic Mass
Chemical Symbol
Atomic (proton) Number
Name
Electronegativity
First Ionization Energy
1.00794
1
H
Hydrogen
1312.0
2.20
Alkali metals
Alkaline metals
Other metals
Transitions metals
Lanthanoids
Acinoids
Metalloids
Nonmetals
Halogens
Noble gases
Elements in the same row are in the same PERIOD. They have similar physical properties, such as how well they blend or conduct electricity.
Elements in the same column are in the same GROUP. This means they react with other elements in similar ways.

Interpretations, Explanations and Substantiations

Are not necessarily reflected in the slides, but are reflected in the lecture.

Please **DO NOT** miss any class

Pre-requisite (self-study topics)

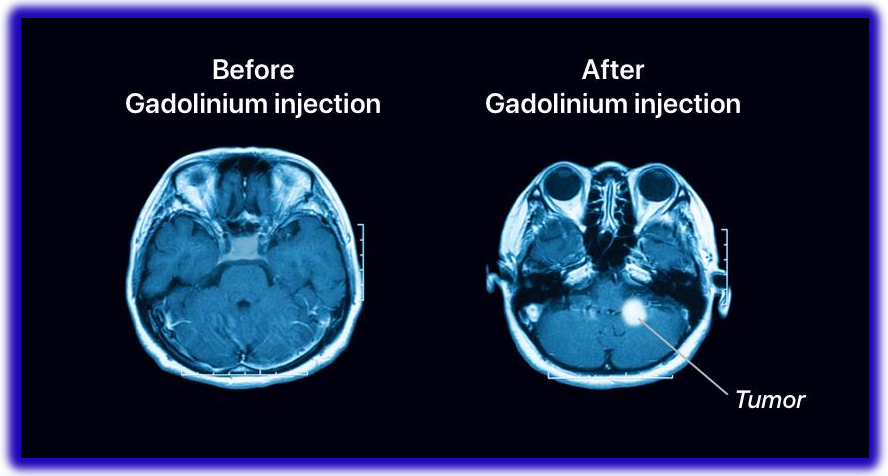
- ✓ **Electronic Configuration (s, p, d, f blocks)**
- ✓ **Penetration**
- ✓ **Shielding**
- ✓ **Effective Nuclear Charge**

Atoms and Ions

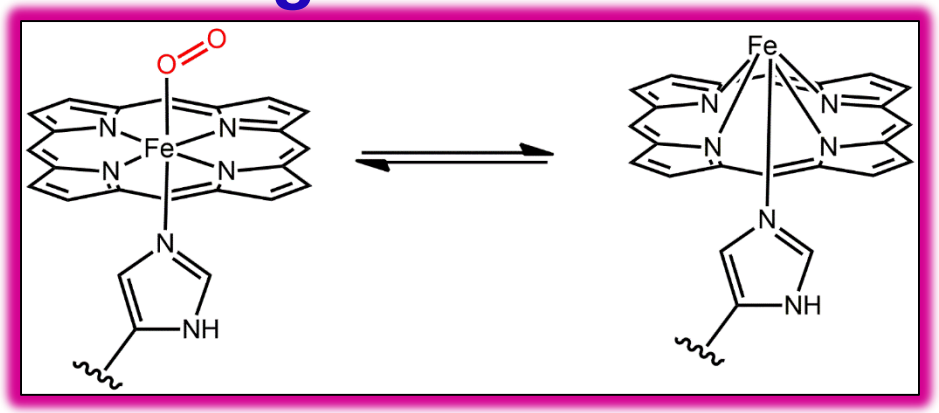
- ✓ **Size & Charge**
- ✓ **Ionization Potential**
- ✓ **Electron Affinity**
- ✓ **Electronegativity**

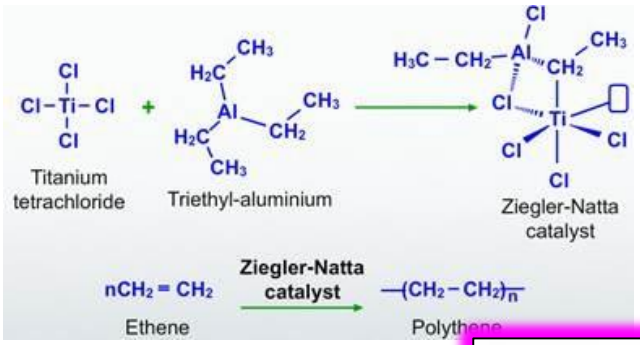
Real world applications of Inorganic complexes/materials

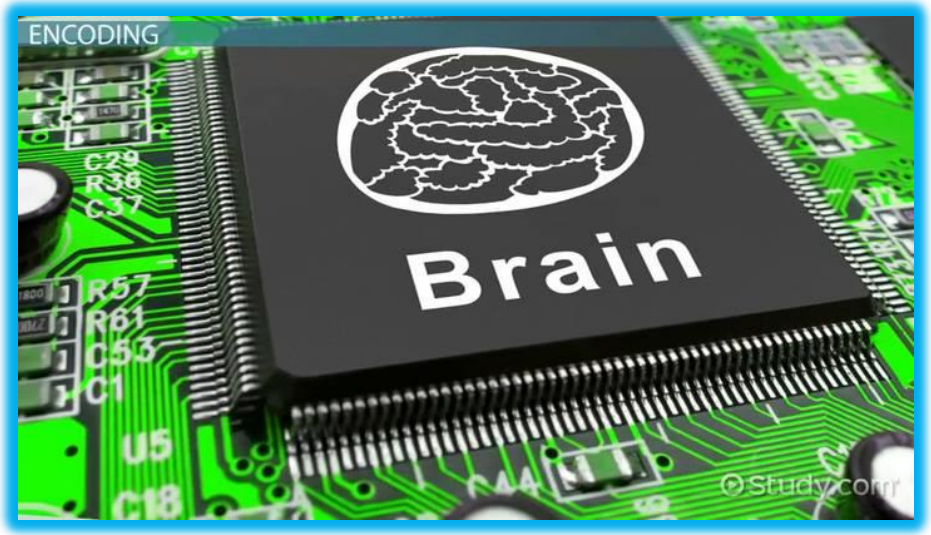
Biomedical



Bioinorganic

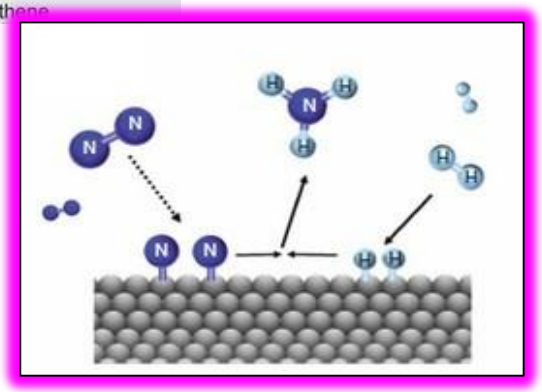






Encoding, Storage, Retrieval

Catalyst

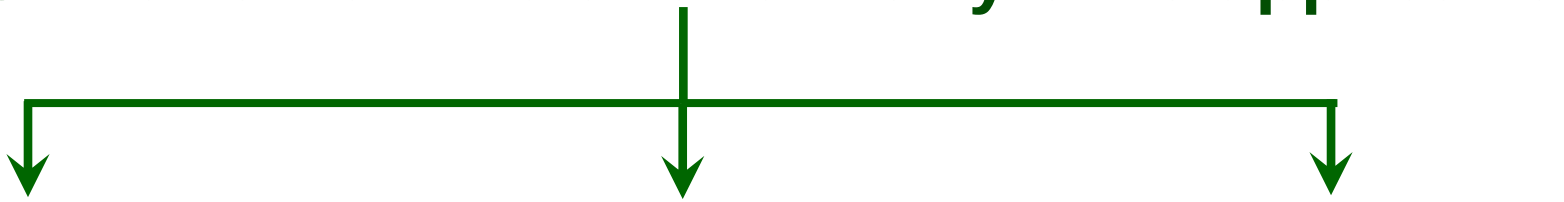


Topics Covered In This Course

Topic 1. Properties of elements & compounds

Topic 2. Basic principles of extraction of metals from ores & purification

Topic 3. Transition metal chemistry & its applications



At the end of the course: we will celebrate by conducting an exam

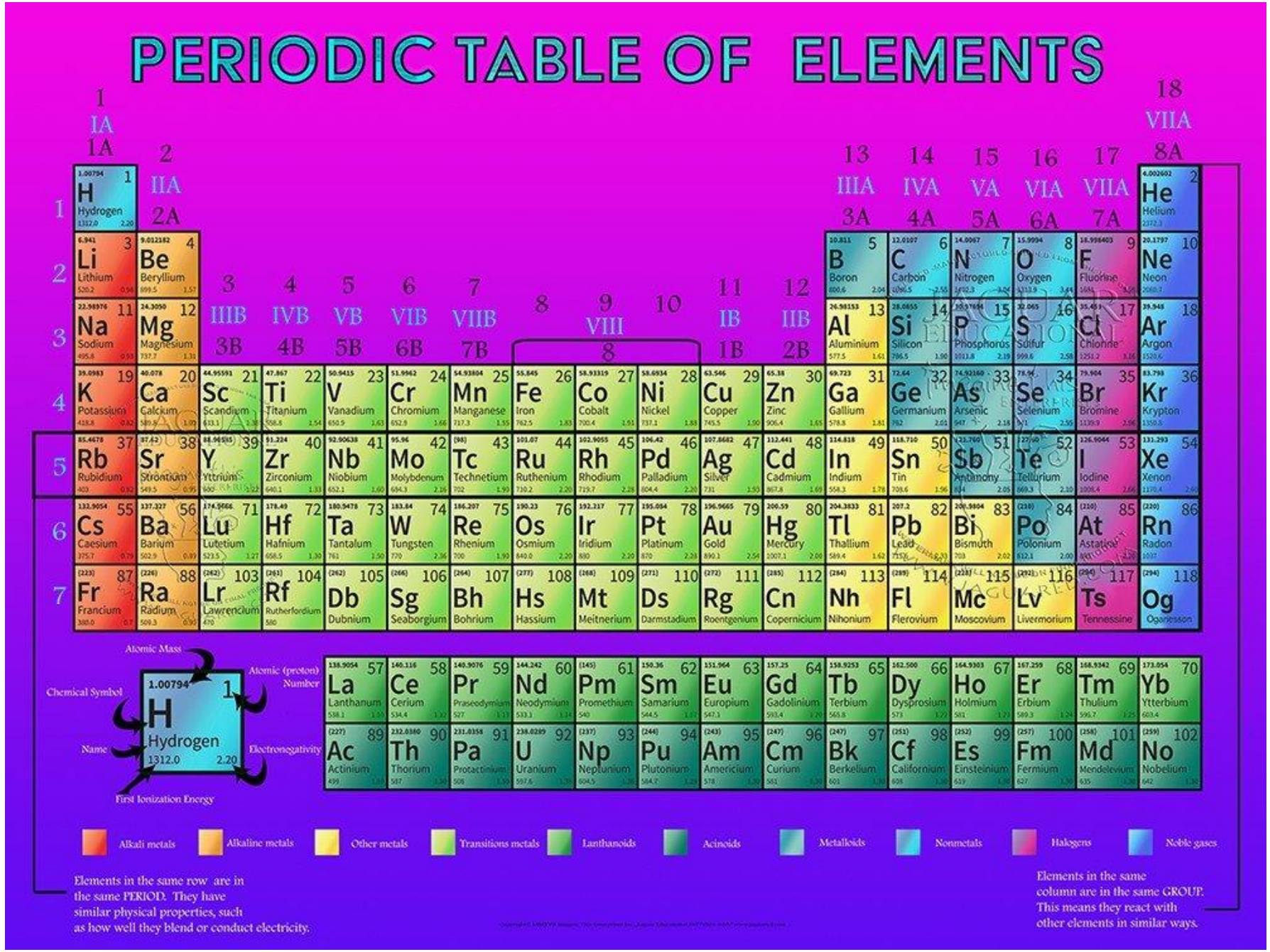
Recommended Text Books

(1) Concise Inorganic Chemistry - J.D. Lee

(2) Shriver & Atkins' Inorganic Chemistry P. Atkins, T. Overton, J. Rourke, M. Weller, F. Armstrong

(3) Chemistry 4th Edition, Catherine E. Housecroft Edwin C. Constable

Topic 1:
Properties of elements & compounds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To Understand The Change in Reactivity!

- ✓ Electronic Configuration (s, p, d, f blocks)
- ✓ Penetration
- ✓ Shielding
- ✓ Effective Nuclear Charge

Atoms and Ions

- ✓ Size & Charge
- ✓ Ionization Potential
- ✓ Electron Affinity
- ✓ Electronegativity

- ✓ **Hard Soft Acid Base (HSAB)**
- ✓ **Polarizability**
- ✓ **Importance of Weak Interaction**

Reactivity of alkali/alkaline earth metals with water
Video (You tube)

Videos are taken from sources for education purpose only
https://www.youtube.com/watch?v=dUbjn3ix3ds

https://www.youtube.com/watch?v=ytxx95g-kiA

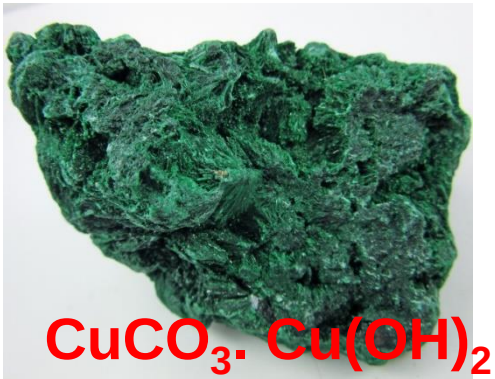
Does Nature Know Chemistry Better?

Various Metal Ores available in earth crust

- ✓ Cinnabar (HgS)
- ✓ Magnetite (Fe_3O_4)
- ✓ Hematite (Fe_2O_3)
- ✓ Argentite (Ag_2S)
- ✓ Galena (PbS)
- ✓ Chalcopyrite (CuFeS)
- ✓ Chalcocite (Cu_2S)
- ✓ Malachite ($CuCO_3$. $Cu(OH)_2$)

HgS

Fe_3O_4



$CuCO_3$. $Cu(OH)_2$

Why certain elements prefer to exist in oxide form and others in sulphide form?

Let us look at this situation…..

$AgF(s) + H_2O(aq) \longrightarrow Ag^+(aq) + F^-(aq)$ $K_{sp} = 205$

$AgCl(s) + H_2O(aq) \longrightarrow Ag^+(aq) + Cl^-(aq)$ $K_{sp} = 1.8 \times 10^{-10}$

$AgBr(s) + H_2O(aq) \longrightarrow Ag^+(aq) + Br^-(aq)$ $K_{sp} = 5.2 \times 10^{-13}$

$AgI(s) + H_2O(aq) \longrightarrow Ag^+(aq) + I^-(aq)$ $K_{sp} = 8.3 \times 10^{-17}$

Why is this?

- Solvation of ions plays significant role

- More importantly stability of metal complex responsible for this solvation effect (i.e. interaction of Ag^+ and halides)

Something more to it?

Acid and Base?

Based on Lewis's electron concept, one which accepts electron classified as acid (usually metal ions), one which donates electron classified as base (donor ligands)

What is a Hard Acid and Soft Acid?

S.No	Hard Acid	Soft Acid
1.	Large positive charge	Small positive charge
2.	Small in size (due to strong attraction)	Larger in size
3.	Polarization (disturbing the charge cloud) is difficult	Easy to polarize
4	d-electrons or orbitals are **NOT** available for π-bonding	d-electrons or orbitals are available for π-bonding

What is a Hard Base and Soft Base?

S.No 1	Hard Base	Soft Base
1.	The most electronegative atom (F^-)	Electronegativity will be less (I^-)
2.	Small in size	Large in size
3.	Polarization (disturbing the charge cloud) is difficult	Easy to polarize
4	π-bonding is weaker or no π-bonding	Involved in π-bonding

To form stable complex:

Hard acid bonding with Hard Base is favourable

Soft acid bonding with Soft Base is favourable

Hard-Hard interaction ⟶ **Columbic or electrostatic (ionic in nature)**

Soft-Soft interaction ⟶ **Covalent in nature**

Rationale For Distinct K_{sp}?

$AgF(s) + H_2O(aq) \longrightarrow Ag^+(aq) + F^-(aq)$ $K_{sp} = 205$

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$AgI(s) + H_2O(aq) \longrightarrow Ag^+(aq) + I^-(aq)$ $K_{sp} = 8.3 \times 10^{-17}$

- Ag^+ is a soft acid and iodide is a soft base
- Due to the strong stability of AgI(s), solvation or dissolution leads to extremely small concentration of Ag^+ and I^- in solution.

Stability Constant for various Metal Halide complexes

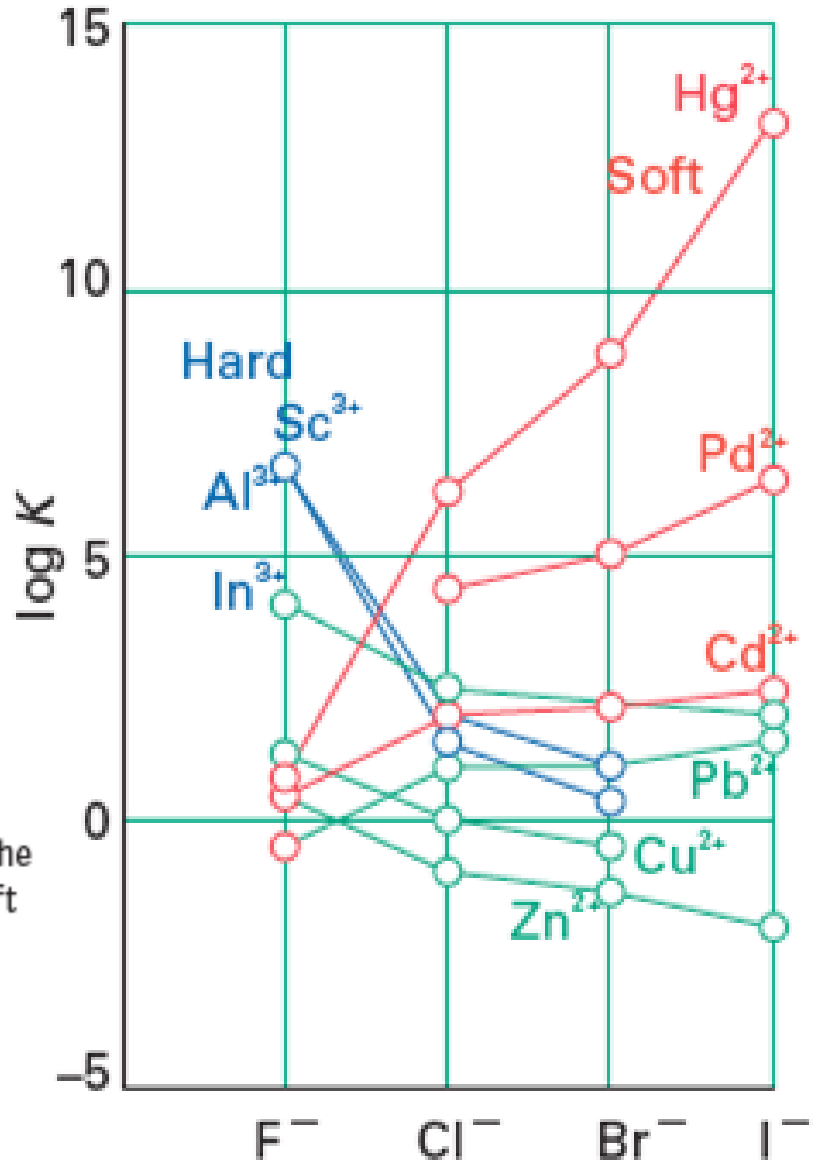


Figure 4.12 The trends in stability constants for complex formation with a variety of halide ion bases. Hard ions are indicated by the blue lines, soft ions by the red line. Borderline hard or borderline soft ions are indicated by green lines.

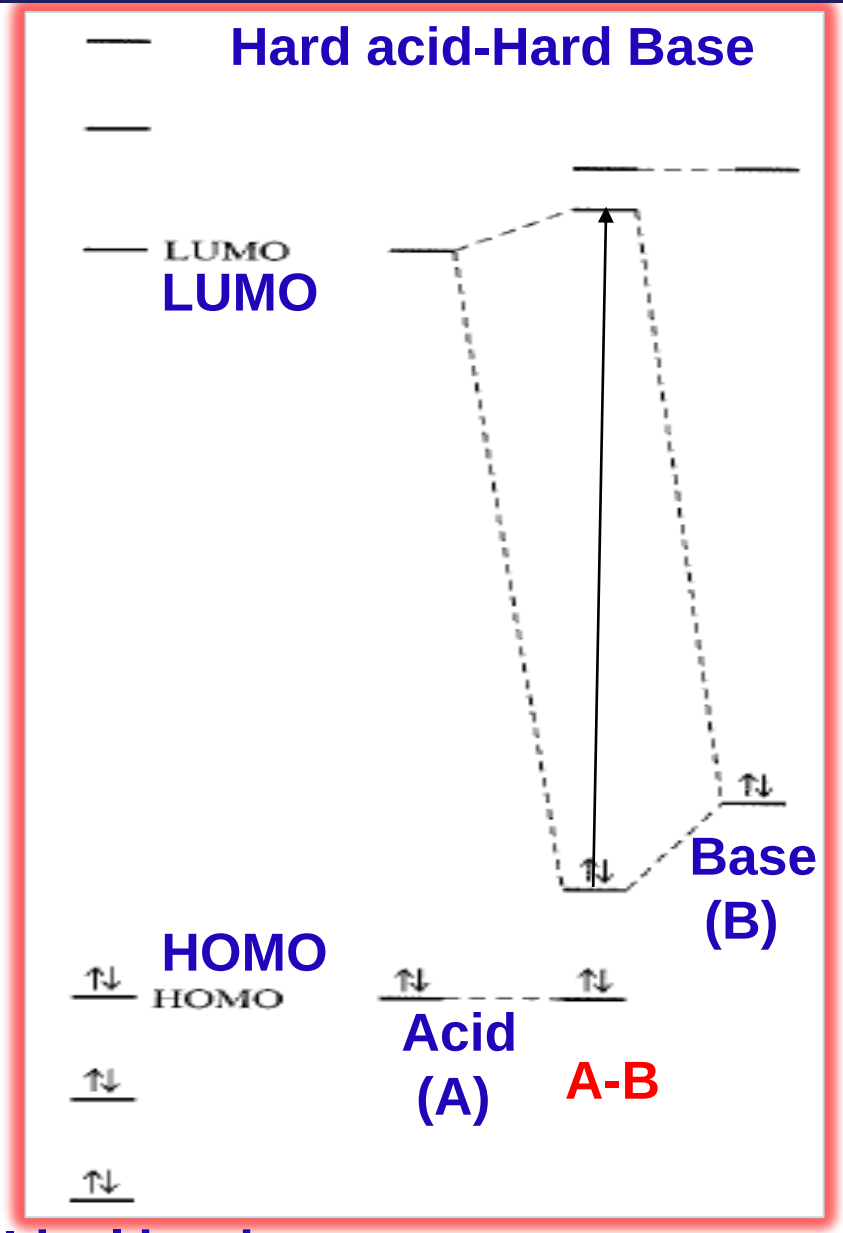
Examples for Hard-Soft Acid-Base

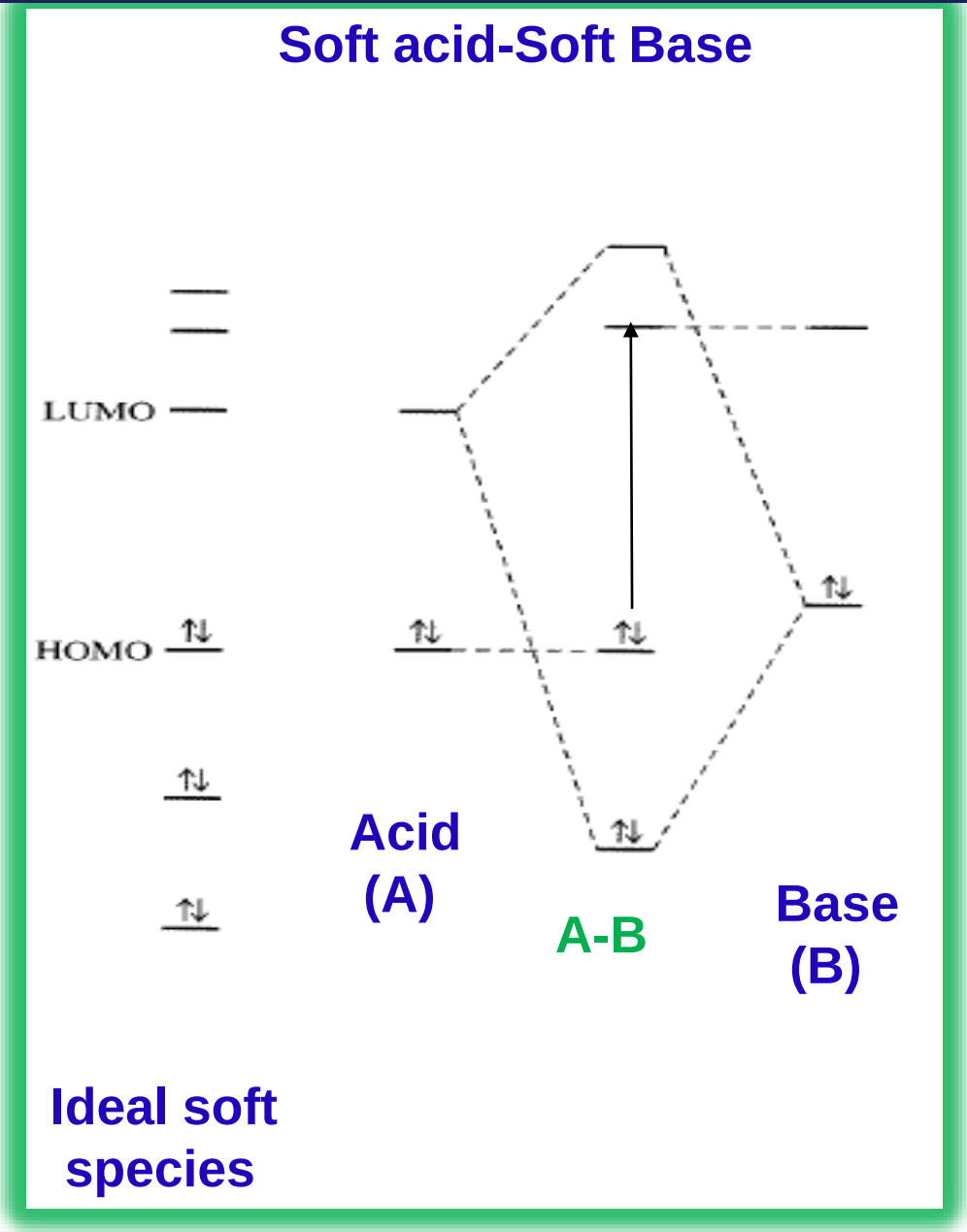
Table 4.5 The classification of Lewis acids and bases*

Hard	Borderline	Soft
Acids		
H^+, Li^+, Na^+, K^+	Fe^{2+}, Co^{2+}, Ni^{2+}	Cu^+, Au^+, Ag^+, Tl^+, Hg_2^{2+}
Be^{2+}, Mg^{2+}, Ca^{2+}	Cu^{2+}, Zn^{2+}, Pb^{2+}	Pd^{2+}, Cd^{2+}, Pt^{2+}, Hg^{2+}
Cr^{2+}, Cr^{3+}, Al^{3+}	SO_2, BBr_3	BH_3
SO_3, BF_3		
Bases		
F^-, OH^-, H_2O, NH_3	NO_2^-, SO_3^{2-}, Br^-	H^-, R^-, $\underline{C}N^-$, CO, I^-
CO_3^{2-}, NO_3^-, O^{2-}	N_3^-, N_2	$S\underline{C}N^-$, R_3P, C_6H_5
SO_4^{2-}, PO_4^{3-}, ClO_4^-	C_6H_5N, $SC\underline{N}^-$	R_2S

* The underlined element is the site of attachment to which the classification refers.

Theory of Hard-Soft Acid-Base





A Classical metathesis (HSAB) reaction

$BeI_2 + HgF_2 \rightarrow HgI_2 + BeF_2$ (Exothermic reaction)

Complex	Bond dissociation energy ($kJ\ mol^{-1}$)
Be-F	632
Hg-I	145

- It is **NOT** the large Hg–I bond energy that ensures that the reaction is exothermic but the strong bond between Be and F, which is an example of a hard–hard interaction.

- In HSAB concept, generally, the hard–hard interactions form stronger bonds relative to the soft–soft interactions.

Quantitative Determination of HA

Hard acid or base is correlated to its fundamental property of Ionization energy and electron affinity (in eV unit).

$$\text{Absolute Hardness } (\eta) = \frac{I_{base} - A_{acid}}{2}$$

Electron affinity (**A**): Electron affinity assumed to measure the energy of LUMO (tendency to attract electrons (i.e the added electron will occupy in LUMO)

Ionization energy (**I**): Ionization energy assumed to measure the energy of HOMO (removal of an electron from valence orbital)

$$\text{On the other hand, Mulliken's electronegativity } (\chi) = \frac{I + A}{2}$$

Hardness Parameters (eV)

Ion	*I*	*A*	χ	η
Al^{3+}	119.99	28.45	74.22	45.77
Li^{+}	75.64	5.39	40.52	35.12
Mg^{2+}	80.14	15.04	47.59	32.55
Na^{+}	47.29	5.14	26.21	21.08
Ca^{2+}	50.91	11.87	31.39	19.52
Sr^{2+}	43.6	11.03	27.3	16.3
K^{+}	31.63	4.34	17.99	13.64
Zn^{2+}	39.72	17.96	28.84	10.88
Hg^{2+}	34.2	18.76	26.5	7.7
F^{-}	17.42	3.40	10.41	7.01
OH^{-}	13.17	1.83	7.50	5.67
CN^{-}	14.02	3.82	8.92	5.10
Cl^{-}	13.01	3.62	8.31	4.70
Br^{-}	11.84	3.36	7.60	4.24
NO_2^{-}	>10.1	2.30	>6.2	>3.9
I^{-}	10.45	3.06	6.76	3.70

SOURCE: Data from R. G. Pearson, *Inorg. Chem.*, **1988**, *27*, 734.

NOTE: The anion values are calculated from data for the radicals or atoms.

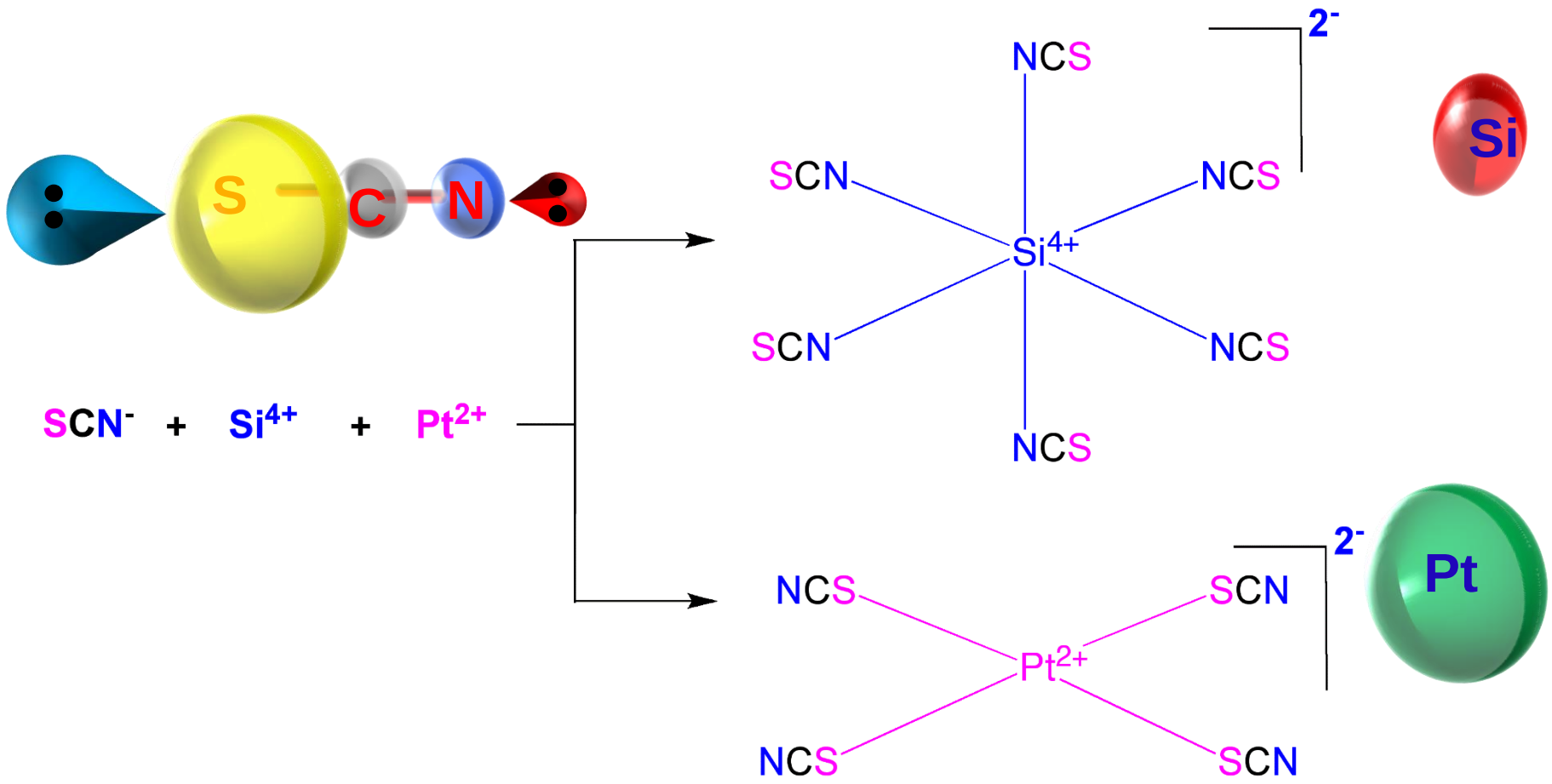
$$(\chi) = \frac{IE+EA}{2}$$

$$(\eta) = \frac{IE-EA}{2}$$

Softness (σ) is a measure of inverse of hardness

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

Ambipolar Ligand: Selectivity For Hard-Soft Acid



Trends are exhibited, by keeping the metal same and changing the anion/ligand. By keeping the anion/ligand same and changing the metal

Representative Application of HSAB

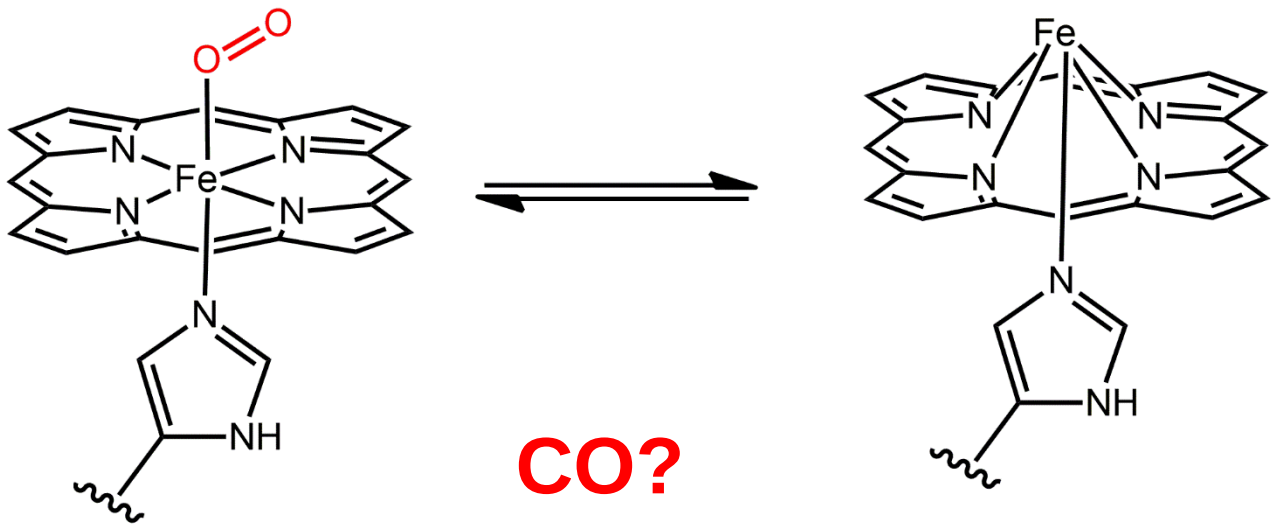
For the targeted synthetic approach

$$BeI_2 + HgF_2 \longrightarrow BeF_2 + HgI_2$$

Chemistry for commercial application

$$\underset{\text{(impure)}}{Ti} + I_2 \longrightarrow TiI_4\ (gas) \xrightarrow{Heat} \underset{\text{(pure)}}{Ti} + \text{Impurity}$$

Chemistry for life cycle (Breathing)



Reversible binding of Oxygen

Fe(II) → border line acid,

O_2 → hard base

Polarizability

Polarizability (α):

Distortion of electron cloud of an atom by the electric field generated by the neighboring atom or ion.

- **Large size**
- **Less Charge or less electronegative atom**
- **Cations not possessing noble gas e- configuration are easily polarized**

- **Small size & highly charged cations have greater polarizing ability**

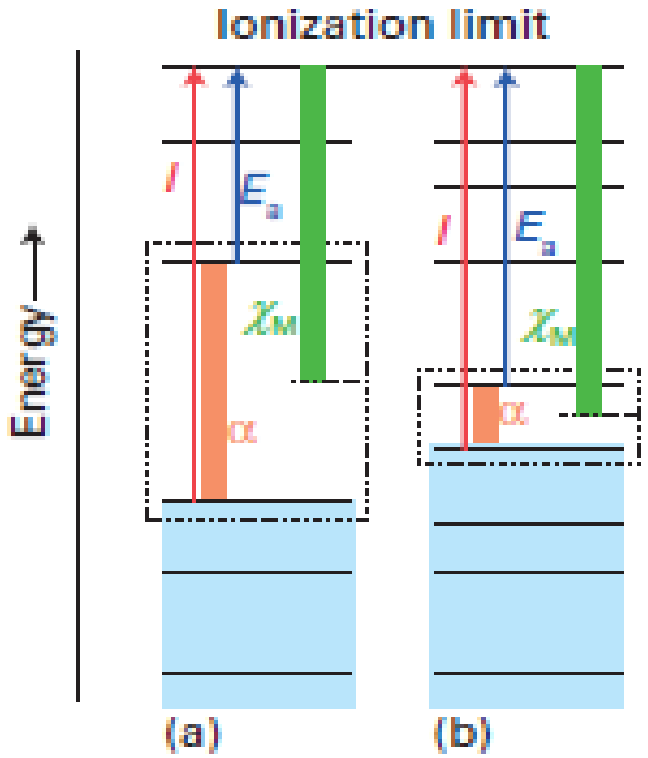
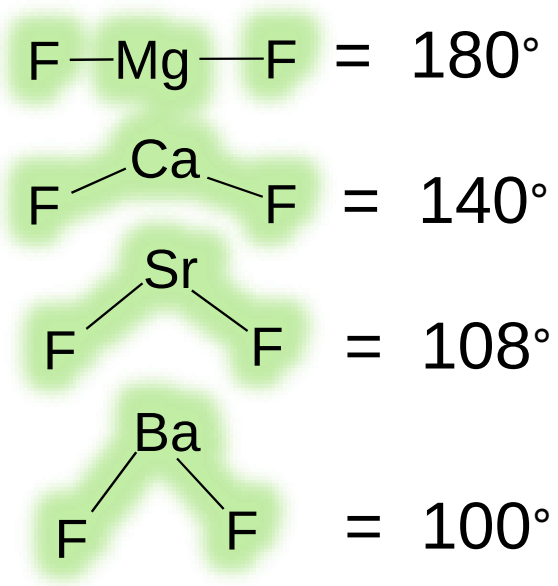
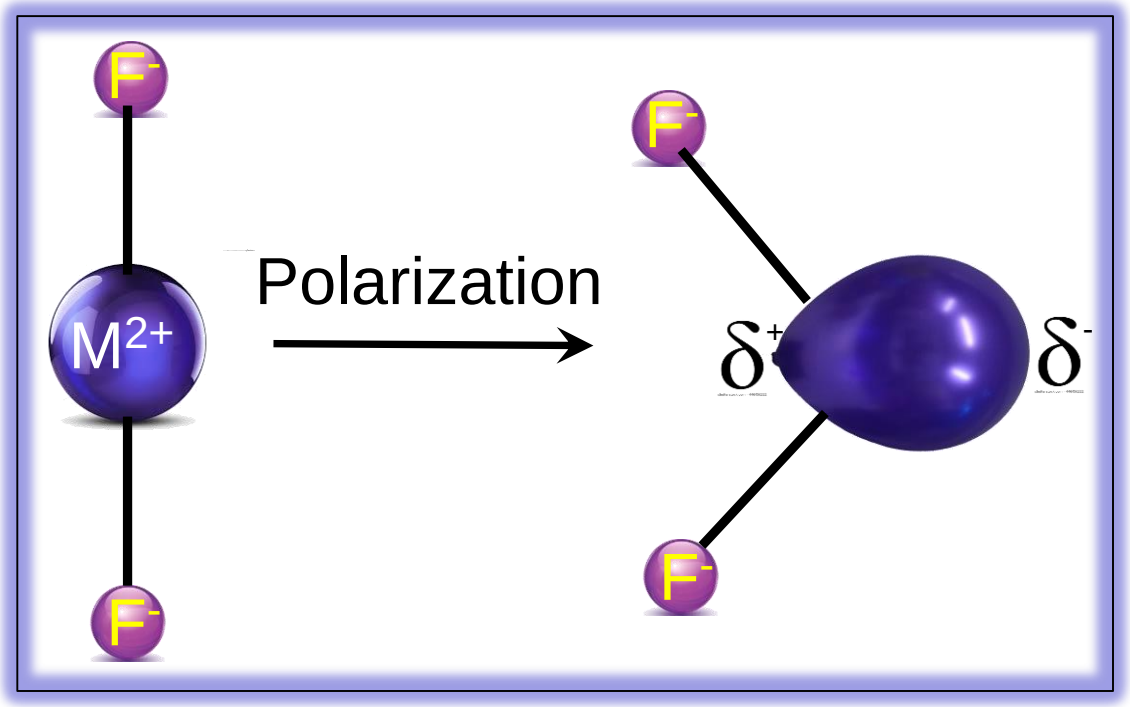


Figure 1.28 The interpretation of the electronegativity and polarizability of an element in terms of the energies of the frontier orbitals (the highest filled and lowest unfilled atomic orbitals). (a) Low electronegativity and polarizability; (b) high electronegativity and polarizability.

Polarizability: A Case Study in Group 2 Fluorides



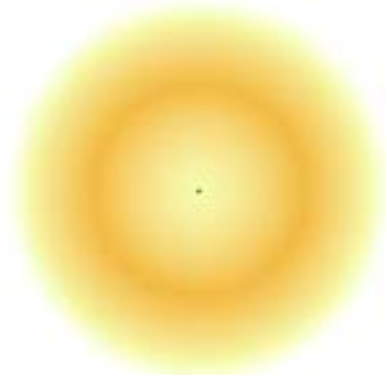


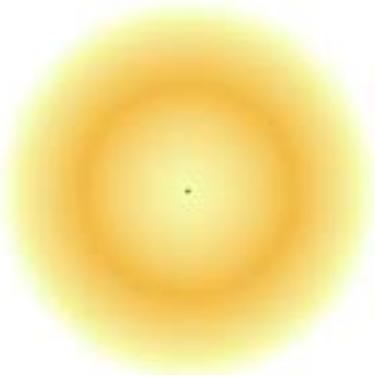
The negatively charged ligands polarize the electron cloud of the central atom and deforms its spherical symmetry. The repulsion between the ligand charges and the dipoles thus generated is minimized when the molecule has a *bent structure* (gaseous state)

Weak Intermolecular Interactions

Proof for Existence of Weak Interactions

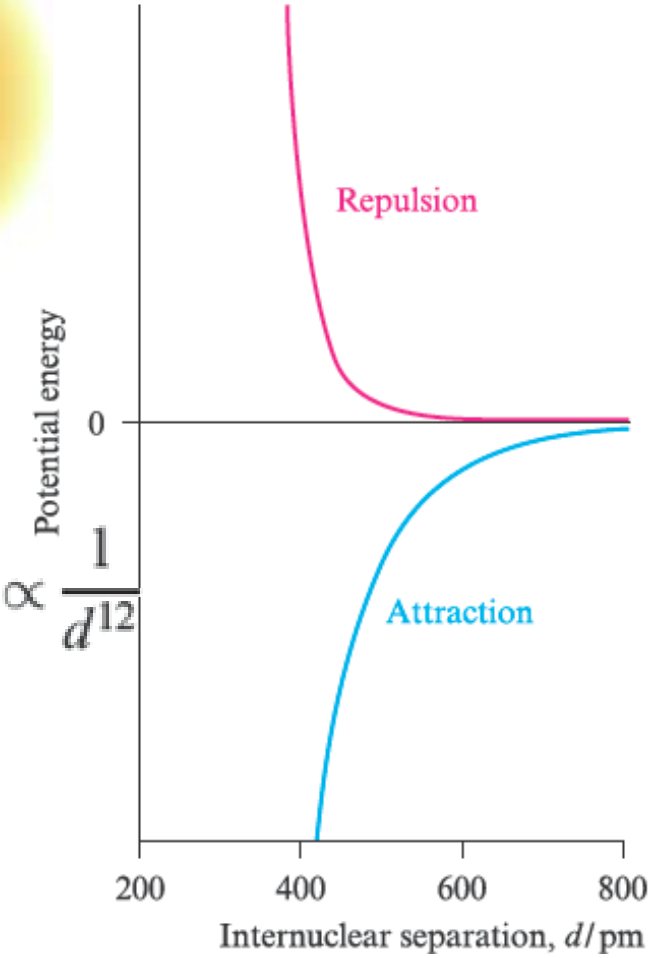
The melting point of Ne (24.5 K) and Ar (84.5 K)



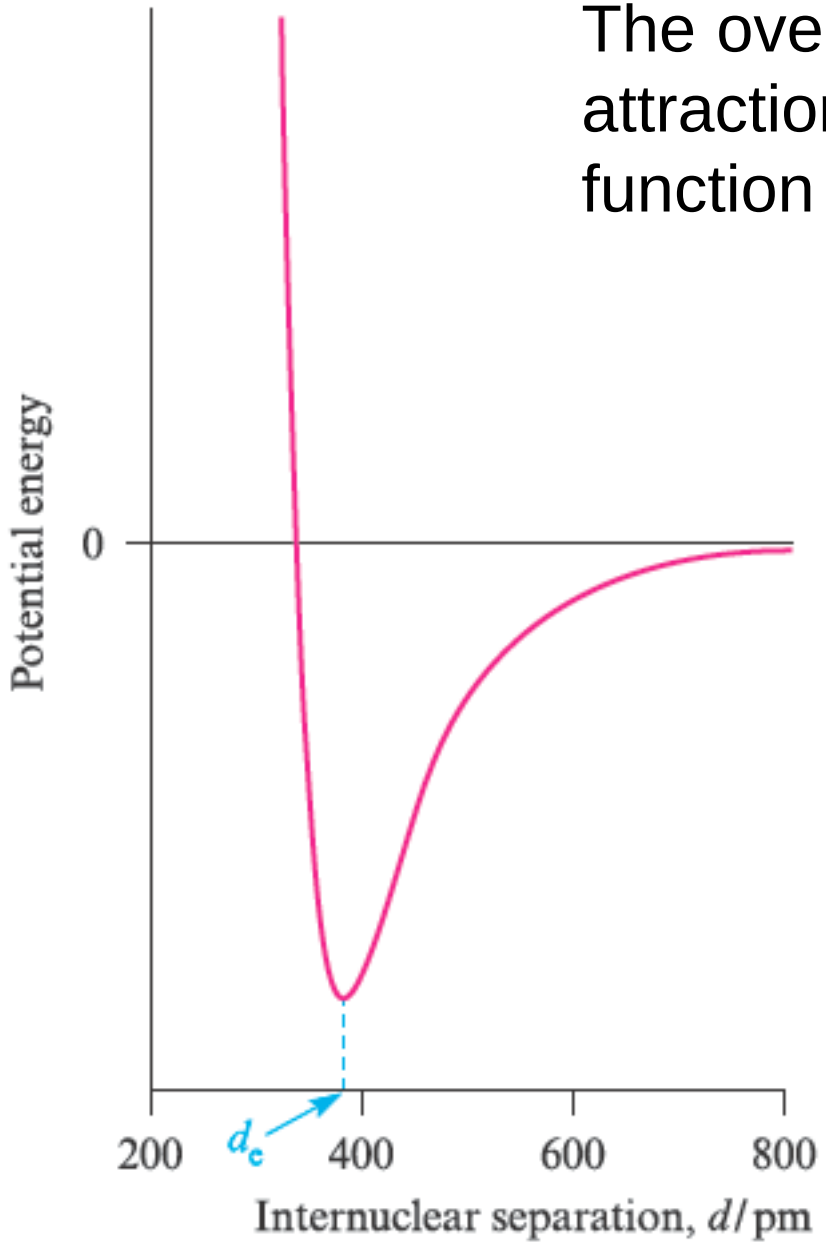


$$\text{Potential energy due to repulsion between atoms} \propto \frac{1}{d^{12}}$$

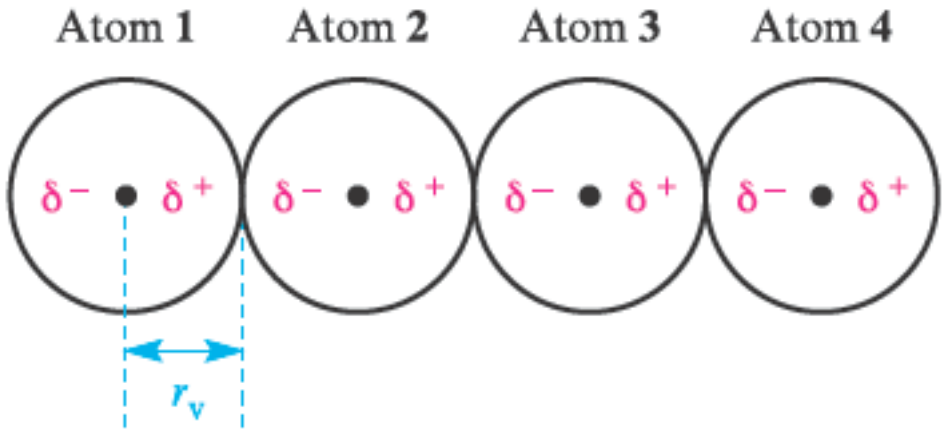
$$\text{Potential energy due to attraction between atoms} \propto \frac{1}{d^{6}}$$



Proposed Mechanism For The Attraction



The overall potential energy (repulsion plus attraction) between the argon atoms as a function of the internuclear separation, *d*



Instantaneous dipole created in a molecule will induce dipole on the adjacent molecule. Thus electrostatic attraction.

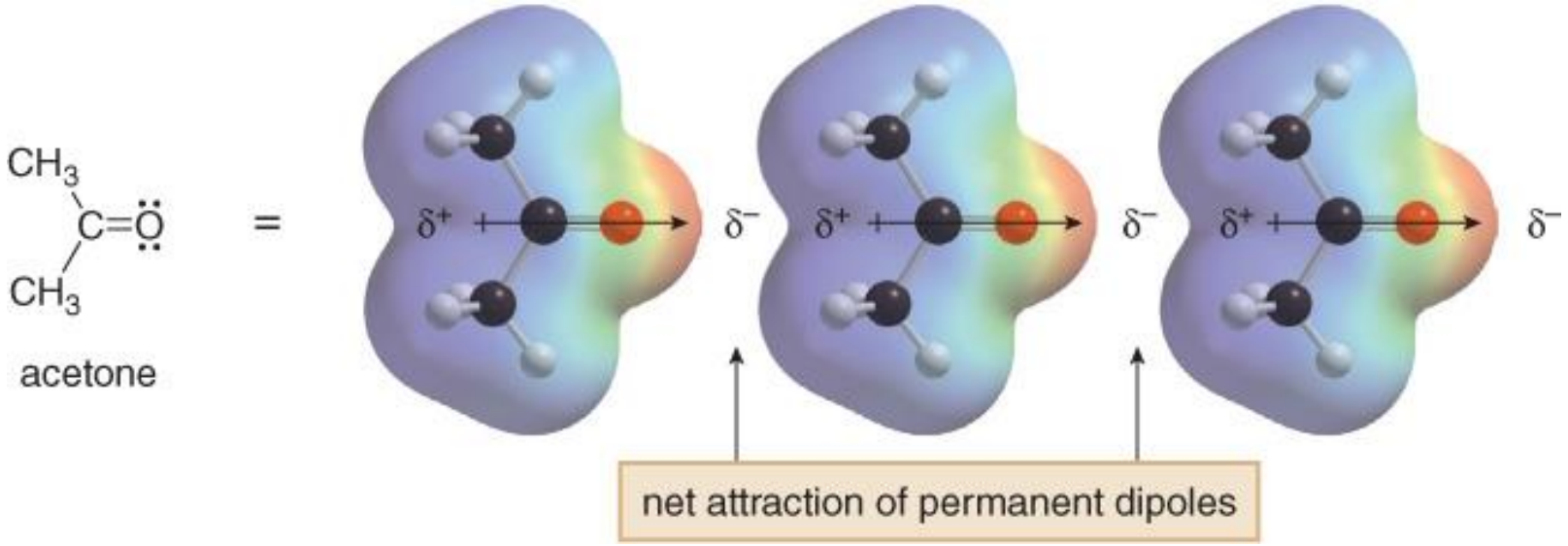
van der Waals Interaction

- Dipole – Dipole Interactions
- Ion-Dipole interaction
- Dipole – Induced Dipole Interactions
- Induced Dipole – Induced Dipole
  (London dispersion Forces)

Weak interactions are more important and dominant particularly at Low temperature

Dipole-Dipole Interaction

Dipole—dipole interactions are the attractive forces between the **polar** molecules with permanent dipole moment.



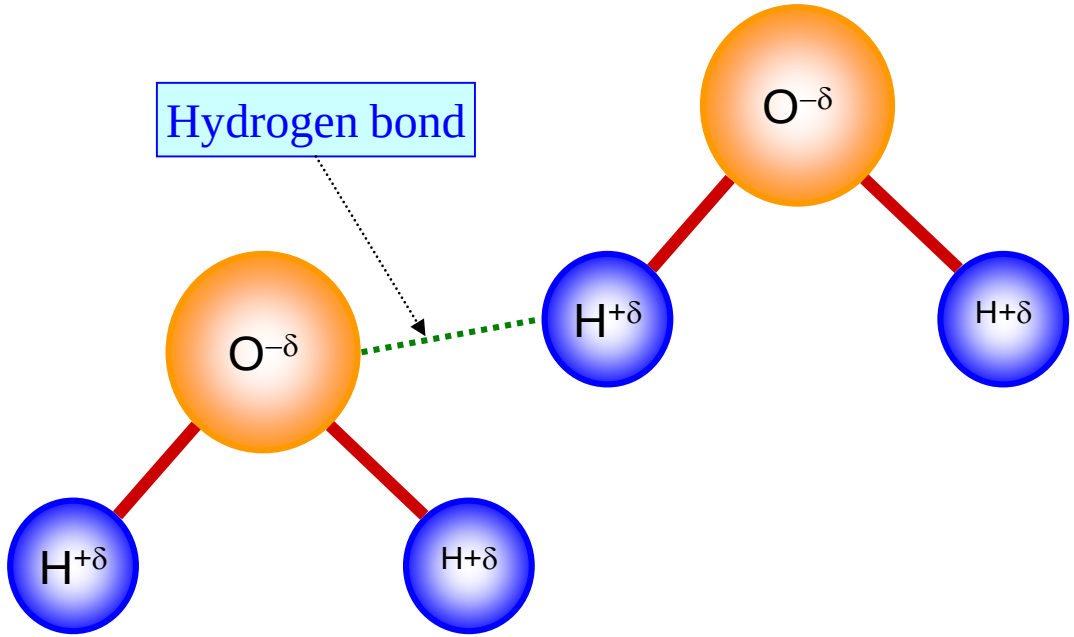
Significant difference in electronegativity of the atoms within the molecule responsible for permanent dipole.

Example includes: HCl, H_2O, Carboxylate

Phase Transition

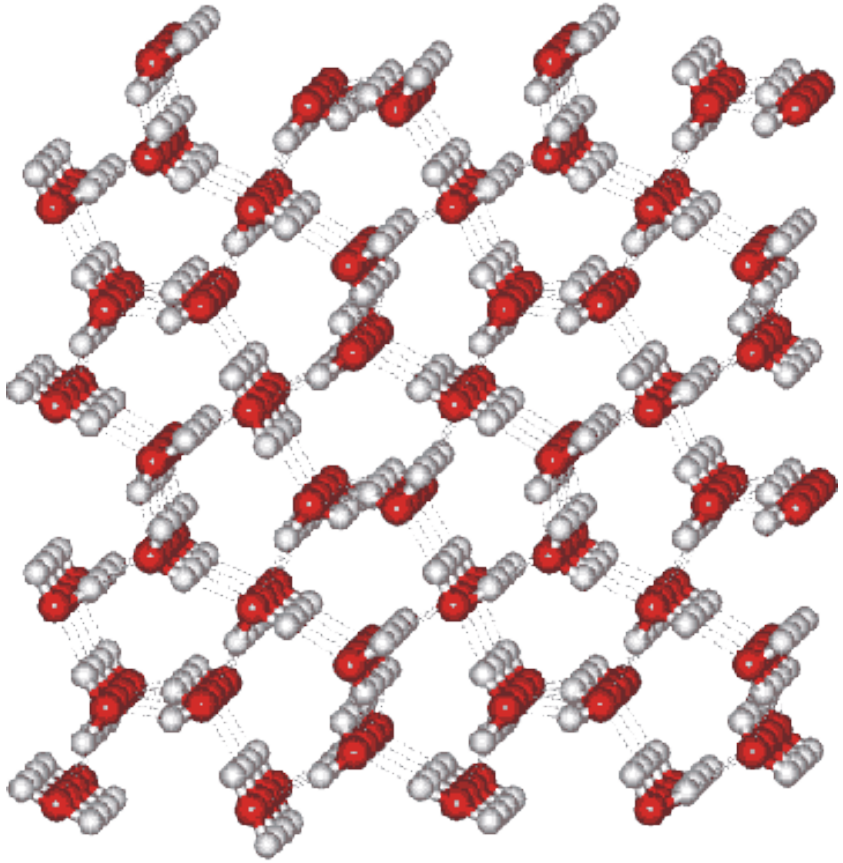
When the weak interaction becomes dominant → Induces phase transition

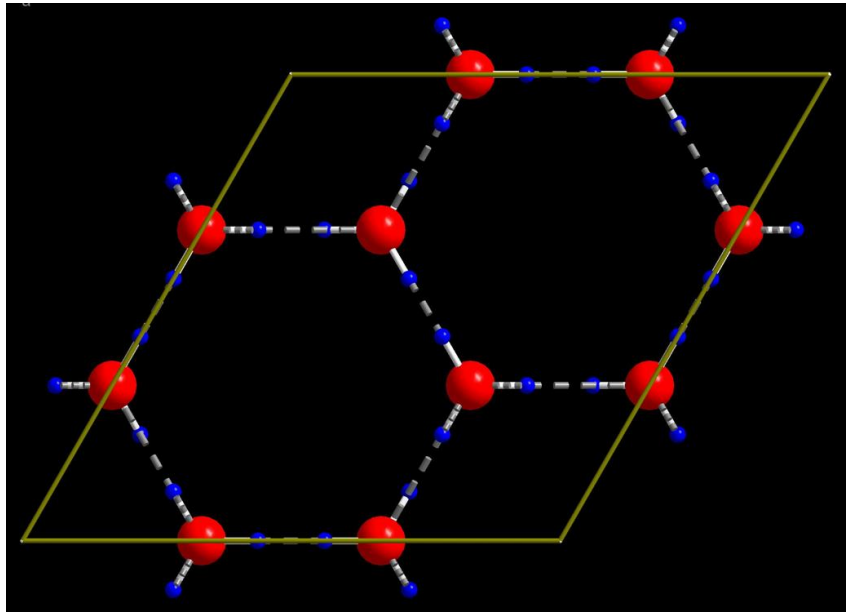
Example: H_2O (l) → H_2O (s)



Hydrogen sulfide and **water boil** at -60.7 °C and +100.0 °C

H-Bonding Network

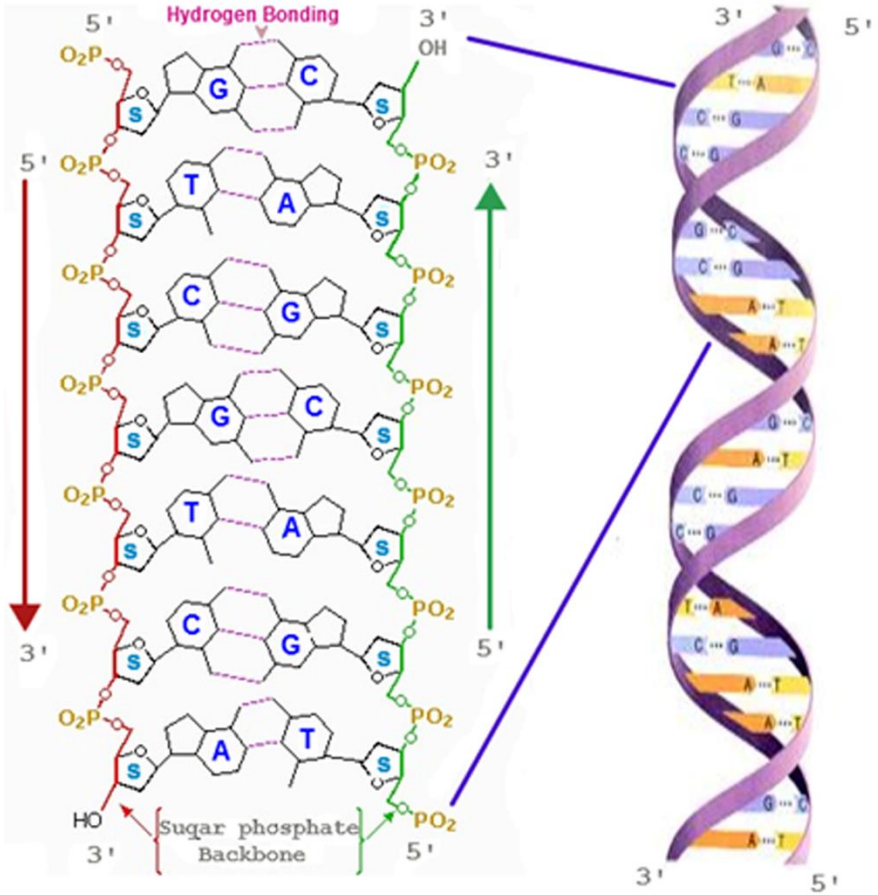


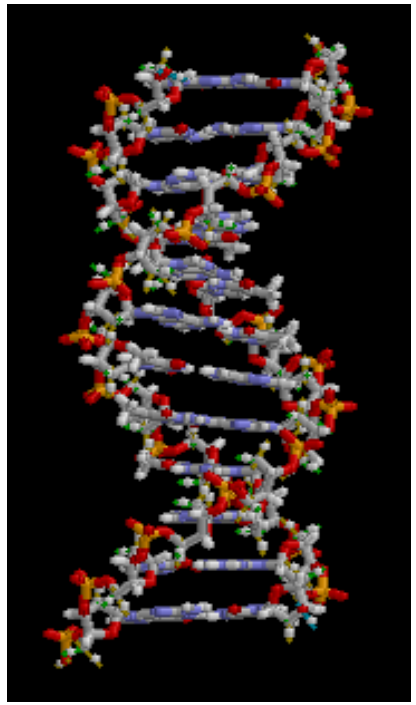


H-Bonding is a classic example of Dipole-Dipole interaction

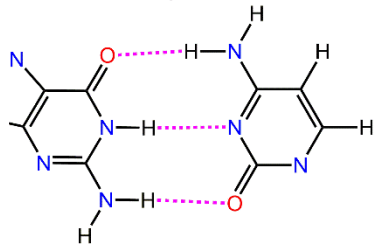
Importance of Weak Interaction In Biology

Molecular Structure of Deoxyribonucleic acid

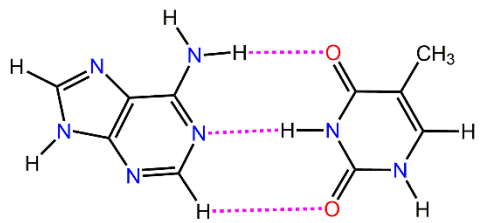




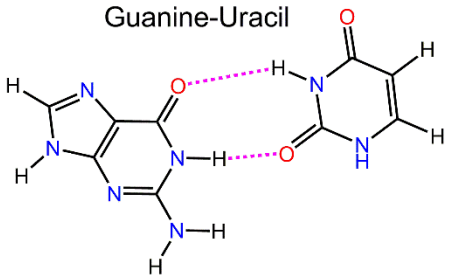
Guanine-Cytosine



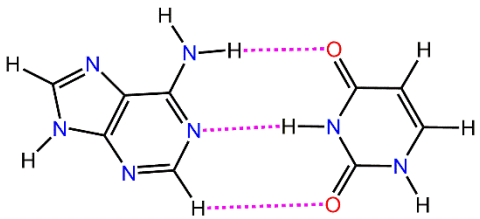
Adenine-Thymine



Guanine-Uracil



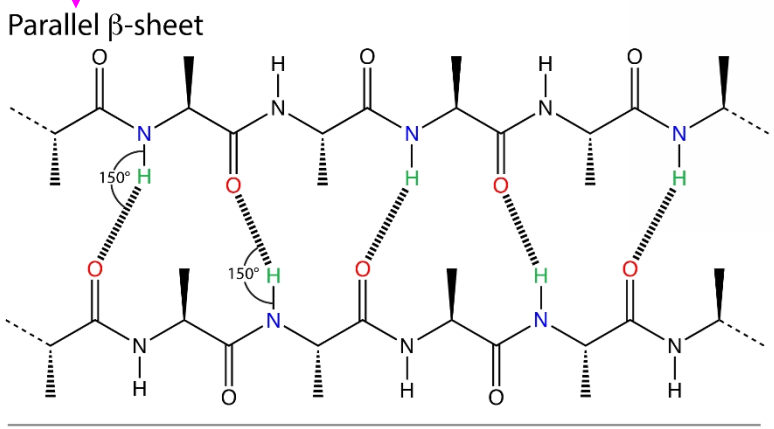
Adenine-Uracil

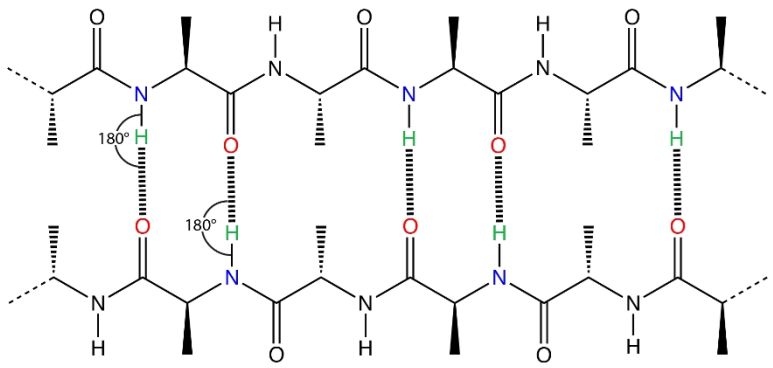


What Will Happen If You Destroy H-Bonding?

Intramolecular

Intermolecular or
Inter-strand





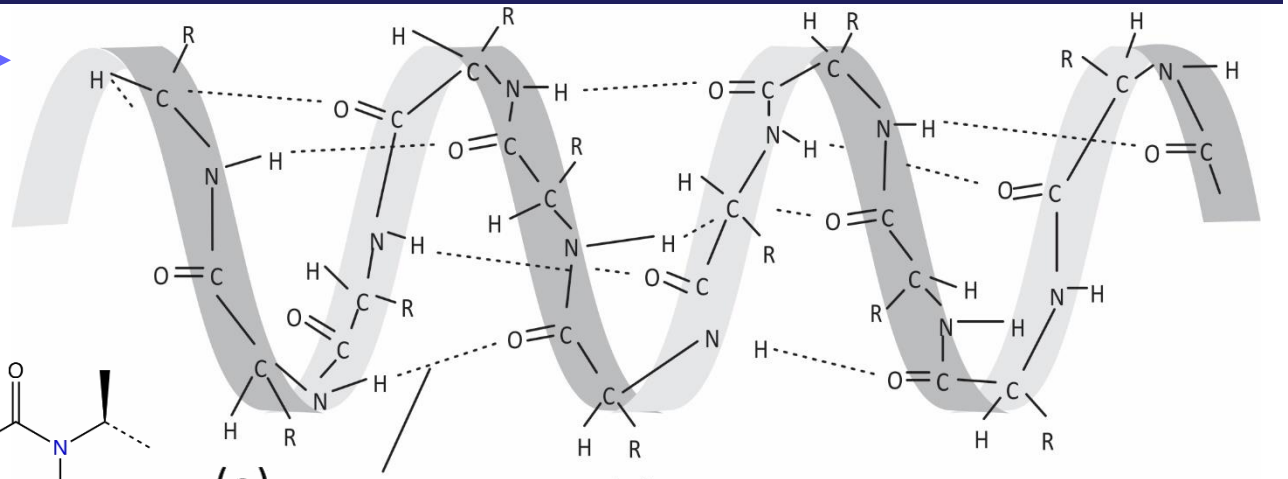
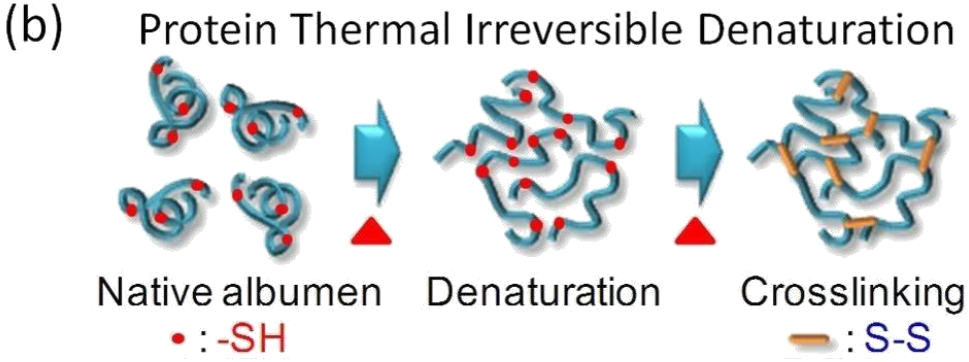


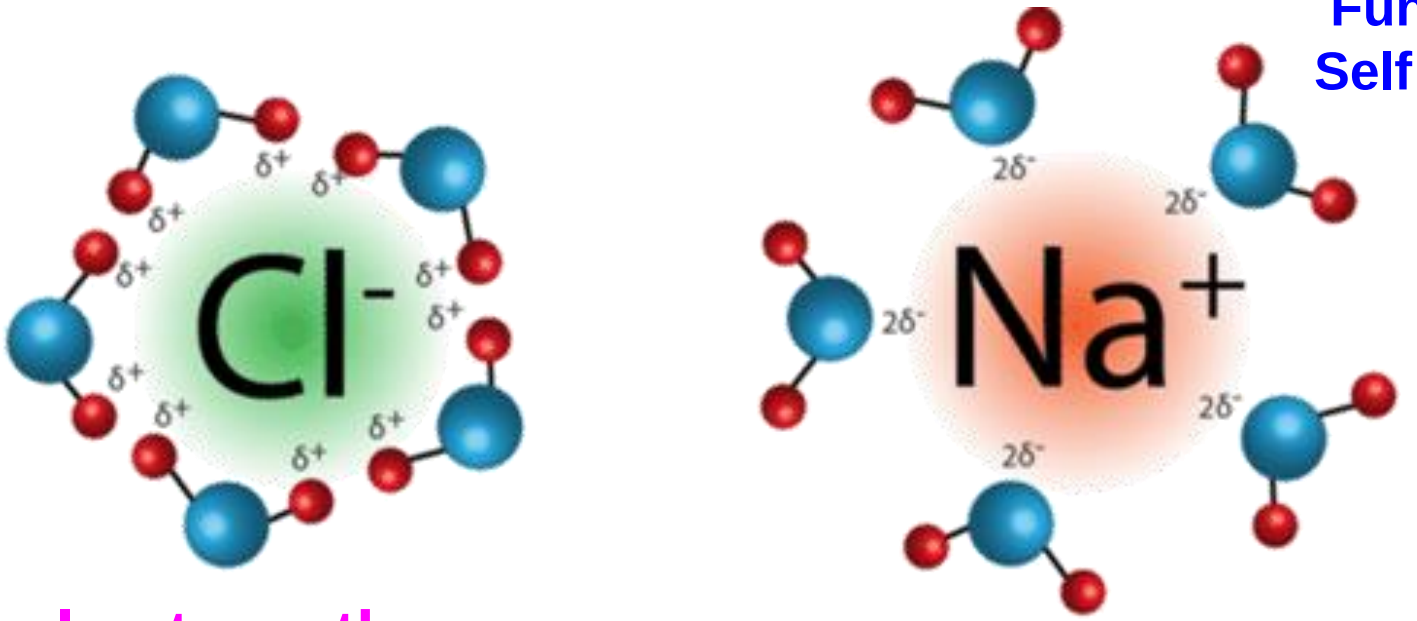
Fig.



Ion-Dipole (ID) Interaction

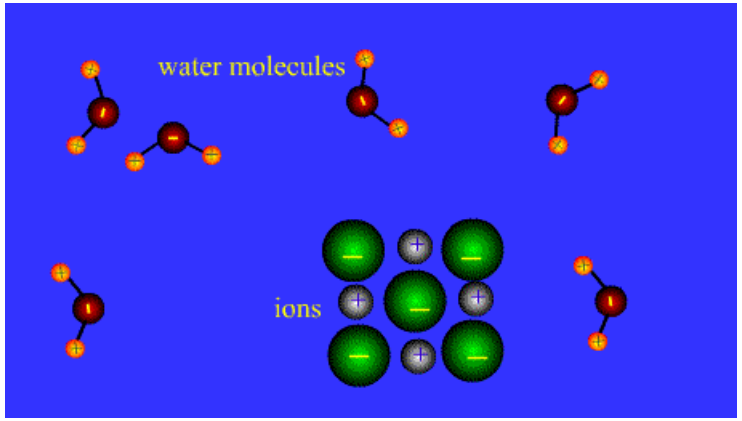
- Permanent dipole interacts with an ion.
- Example: NaCl in water.

ID importance in biological Functions: Self reading



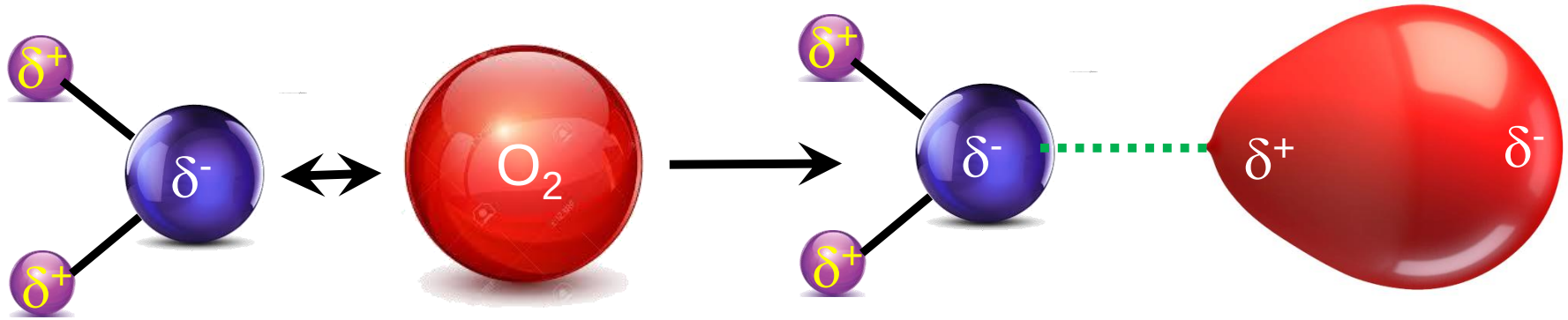
Ion-Dipole strength

- Increases with increasing charge of the ion and magnitude of dipole
- Decreases with increasing distance between the ion and the dipole.



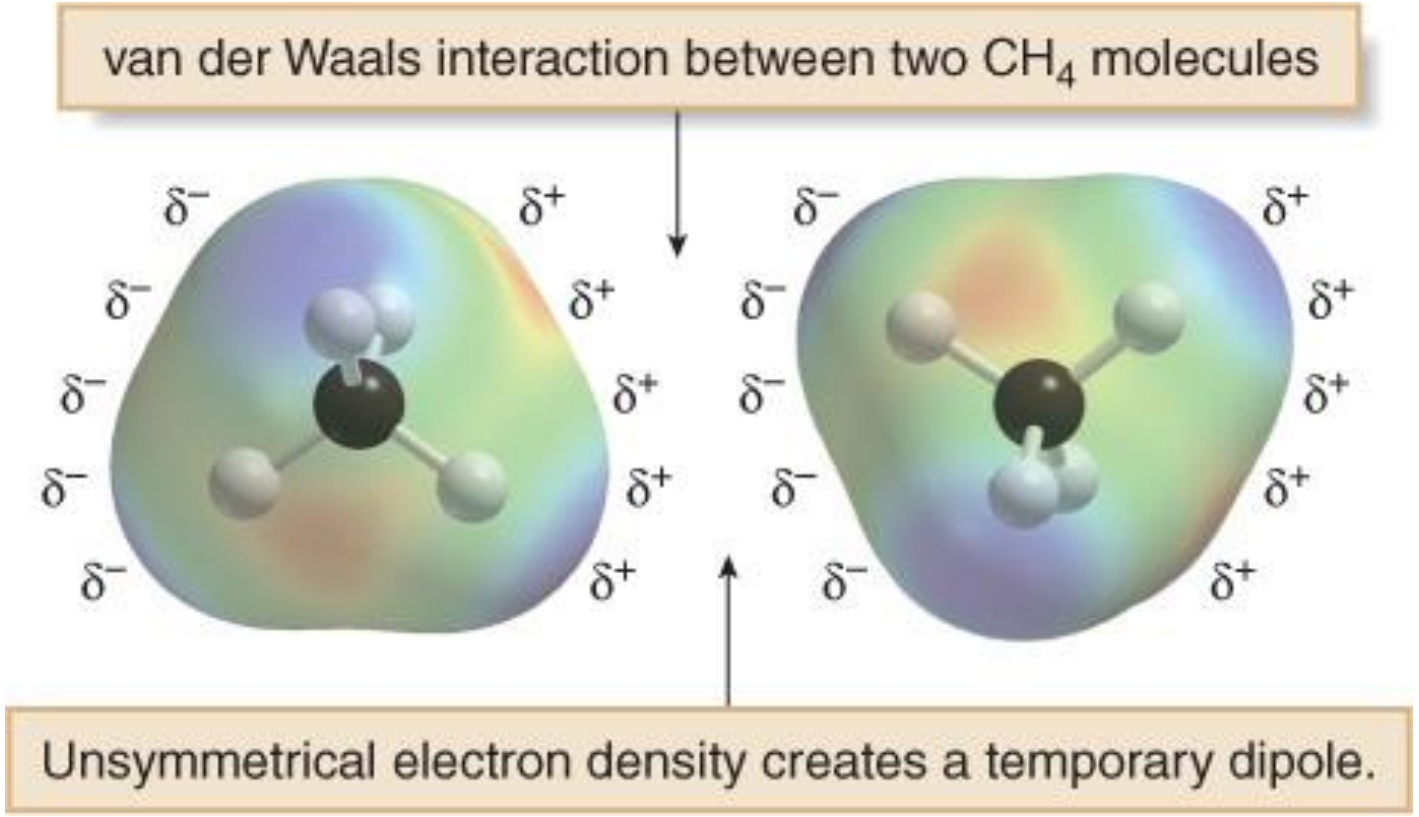
Dipole- Induced Dipole Interaction

When a non-polar molecule approaches a polar molecule (with permanent dipole), a dipole will be induced in the non-polar molecule.



Induced Dipole-Induced Dipole Interaction

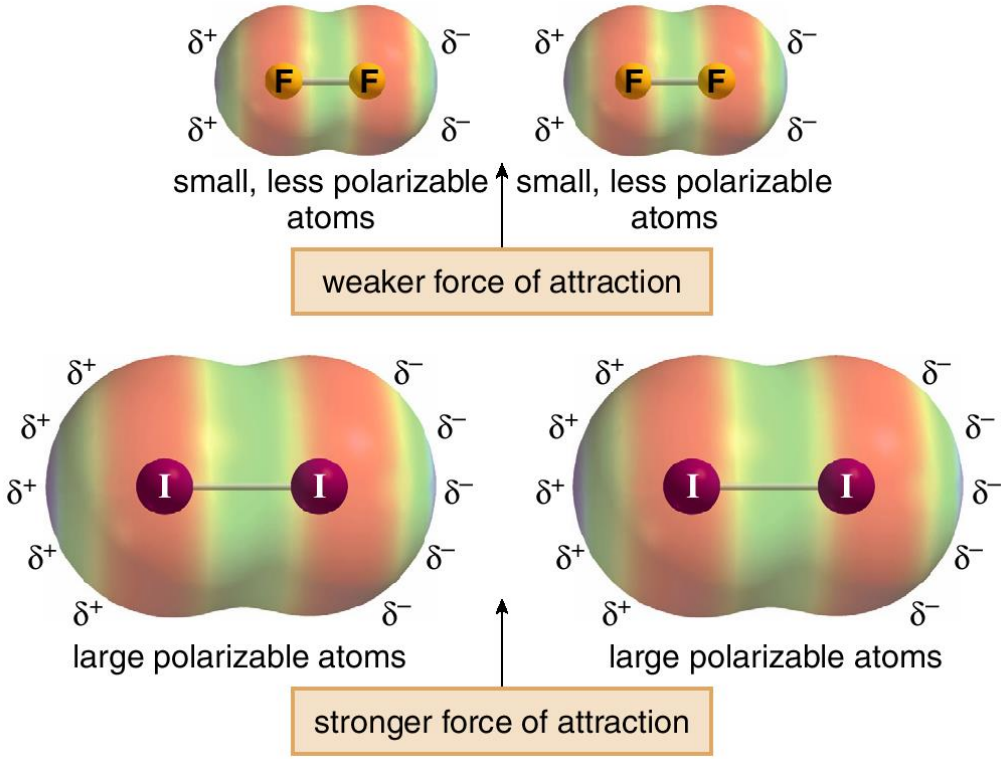
Attractive force exist between **non-polar** molecules due to the momentary induced dipole.



Induced dipole-Induced dipole interaction is also known as **London dispersion force**

Induced Dipole-Induced Dipole Interaction Ex:2

	Size	MP (°C)	BP (°C)	State
F_2		-220	-118	gas
Cl_2		-110	-34	gas
Br_2		-7	59	liquid
I_2		114	184	solid



Larger atoms, like iodine, which have more loosely held valence electrons, are more polarizable than smaller atoms like fluorine, which have more tightly held electrons. Thus, two F_2 molecules have little attractive force between them since the electrons are tightly held and temporary dipoles are difficult to induce. This is correlated to their boiling point.

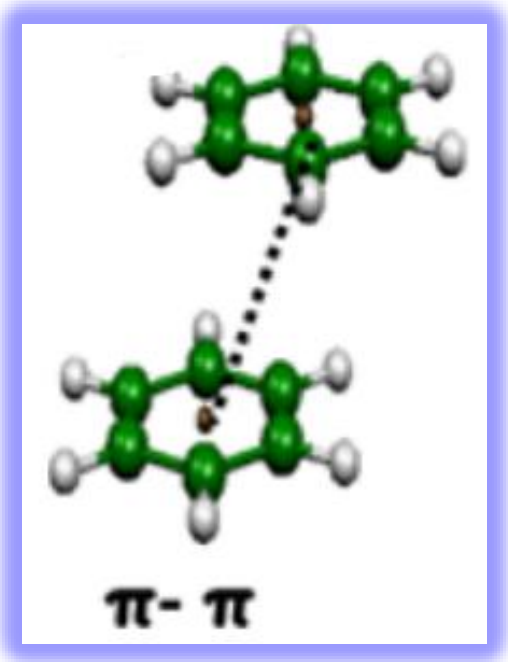
Which is Strong Among the Weak Interactions?

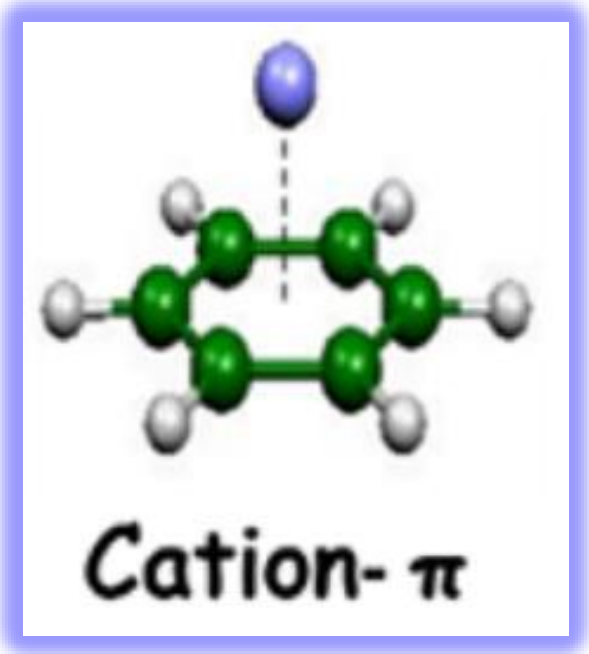
Ion-Dipole > Dipole-Dipole > Dipole-Induced dipole > London dispersion force

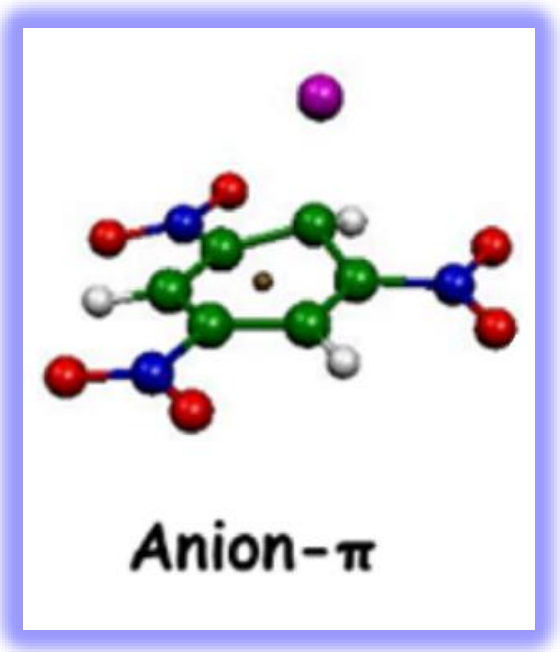
Can We Prove The Strength of The Order Given Above Experimentally?

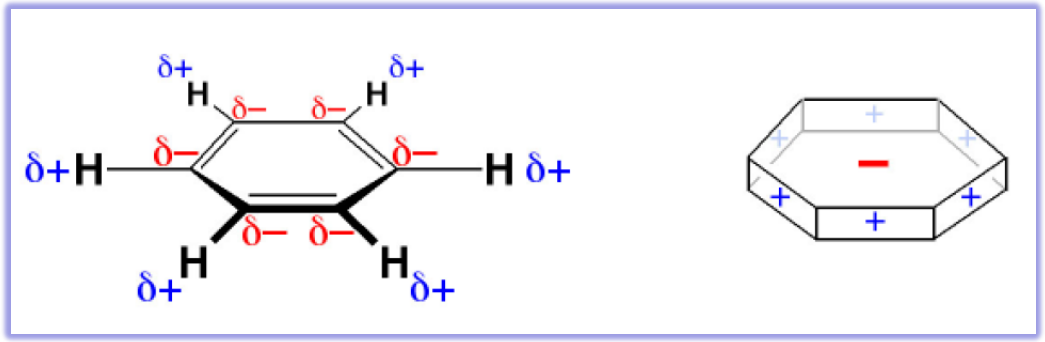
Yes!!! WATCH THE DEMONSTRATION

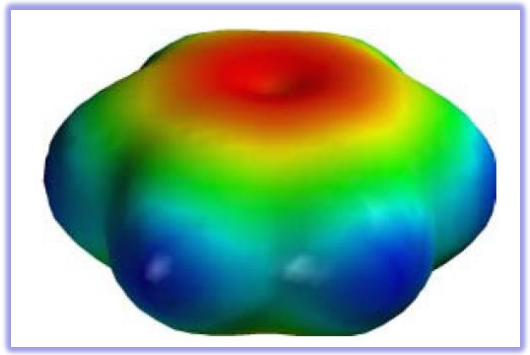
Other weak interactions





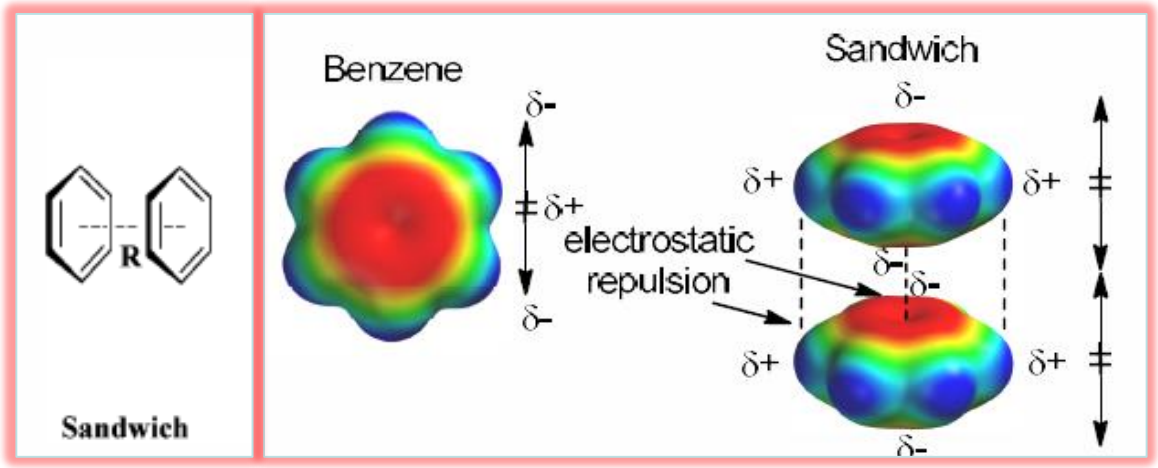


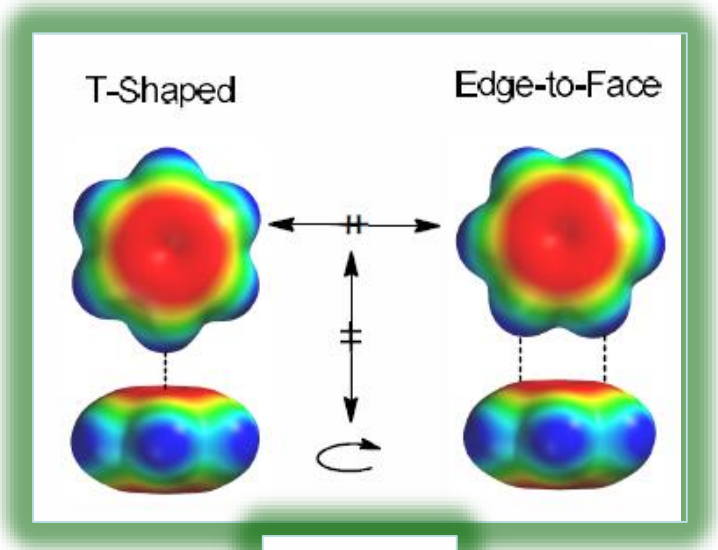


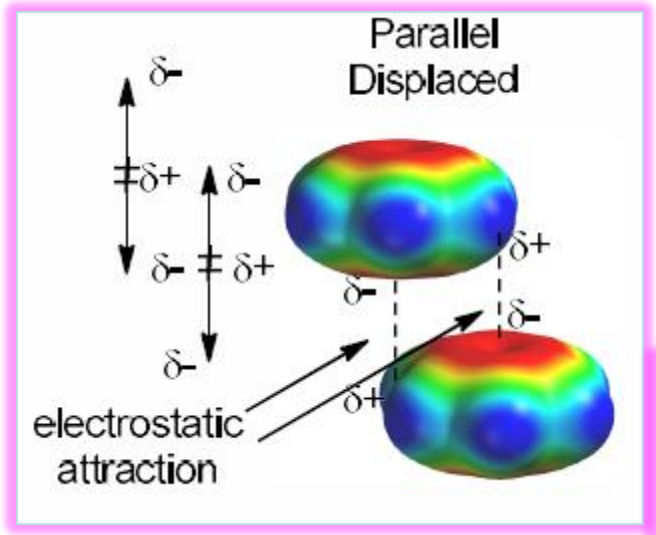


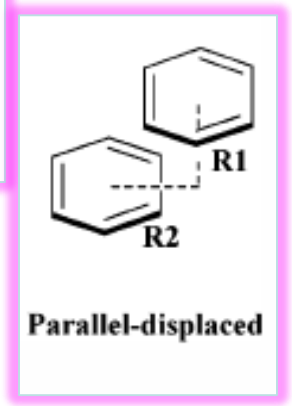
red = extreme negative; blue = extreme positive

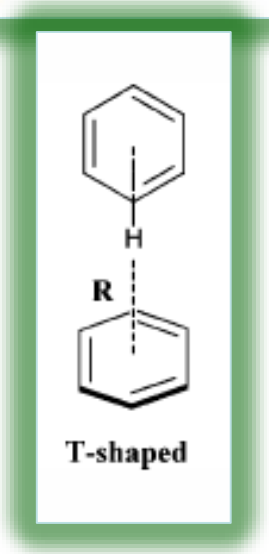
π - π interactions



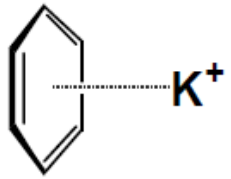


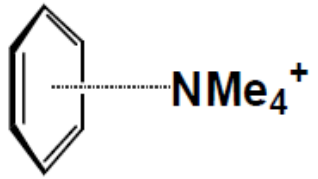






Cation-π Interactions





$-\Delta H_{exptl}$ = 19.2 kcal/mol

$-\Delta H_{exptl}$ = 9.4 kcal/mol

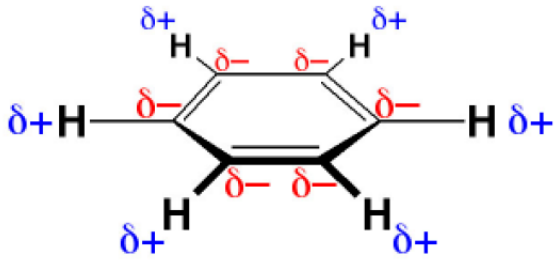
H_2O·····K^+

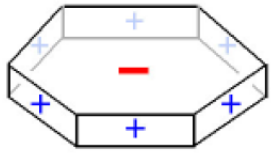
$-\Delta H_{exptl}$ = 17.9 kcal/mol

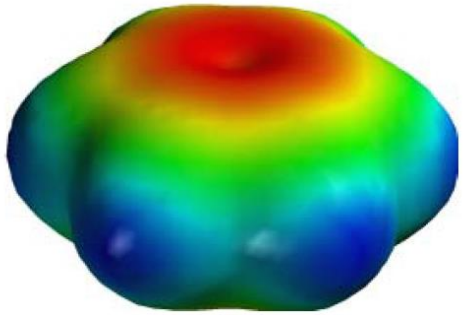
H_2O·····NMe_4^+

$-\Delta H_{exptl}$ = 9.0 kcal/mol

- **Electron clouds on the benzene binds cation stronger than the water.**







red = extreme negative; blue = extreme positive

- How is it possible to have anion-π interactions?