

CH105

Inorganic Chemistry

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Or via moodle

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)

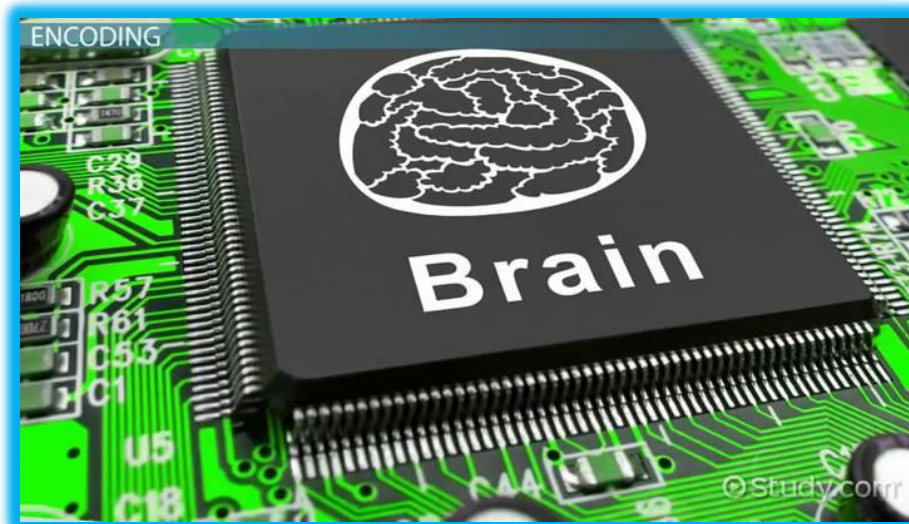
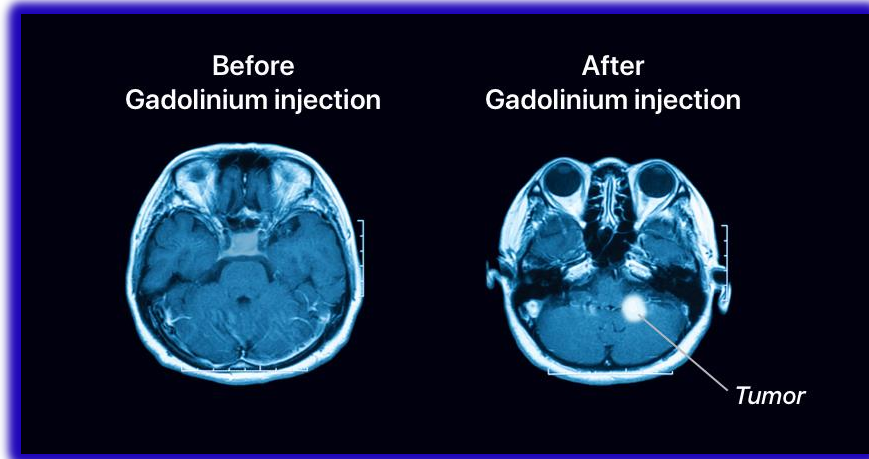
- ✓ Electronic Configuration (s, p, d, f blocks)
- ✓ Penetration
- ✓ Shielding
- ✓ Effective Nuclear Charge

Atoms and Ions

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

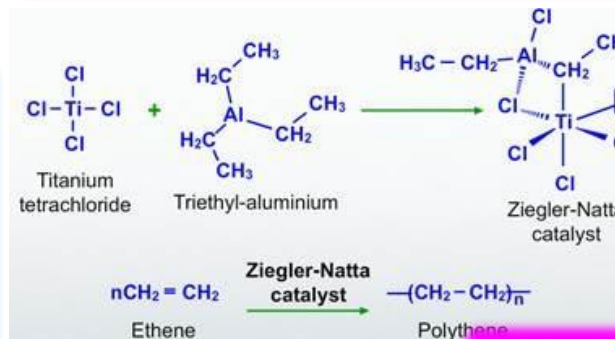
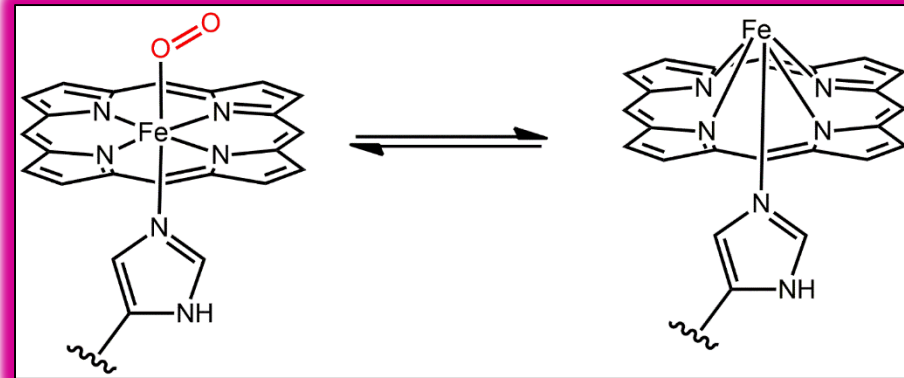
Real world applications of Inorganic complexes/materials

Biomedical

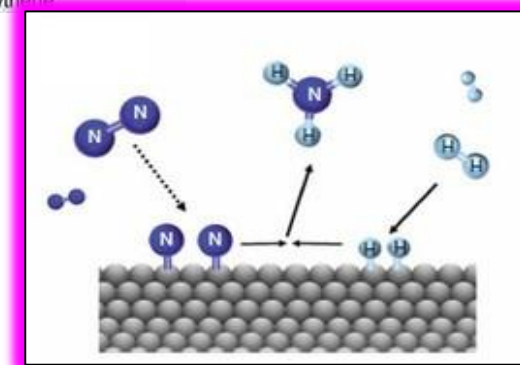


Encoding, Storage, Retrieval

Bioinorganic



Catalyst

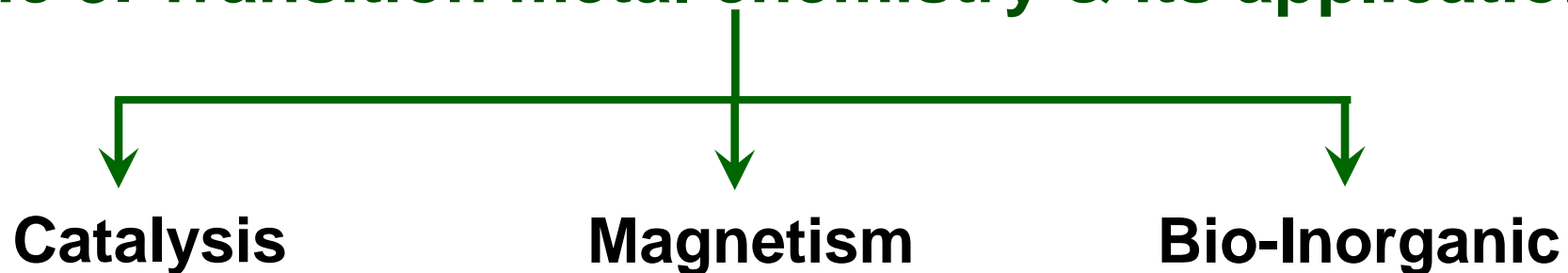


Topics Covered In This Course

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

PERIODIC TABLE OF ELEMENTS

PERIODIC TABLE OF ELEMENTS																			
1 IA 1A		2 IIA 2A												13 IIIA 3A	14 IVA 4A	15 VA 5A	16 VIA 6A	17 VIIA 7A	18 VIIIA 8A
1 1 H Hydrogen 1.00794 1.008 2.20		3 2 Li Lithium 6.941 6.94 0.94	4 2 Be Beryllium 9.012282 9.012 1.57											5 13 B Boron 10.811 10.81 2.04	6 14 C Carbon 12.0107 12.01 2.55	7 15 N Nitrogen 14.0067 14.01 3.04	8 16 O Oxygen 15.9994 16.00 3.44	9 17 F Fluorine 18.998403 19.00 3.98	10 18 Ne Neon 20.1797 20.18
11 3 Na Sodium 22.989769 22.99 0.93	12 2 Mg Magnesium 24.3050 24.31 1.31											13 13 Al Aluminium 26.9815385 27.00 1.61	14 14 Si Silicon 28.0855 28.09 1.90	15 15 P Phosphorus 30.9737615 31.00 2.19	16 16 S Sulfur 32.065 32.07 2.58	17 17 Cl Chlorine 35.453 35.45 3.16	18 18 Ar Argon 39.948 39.95		
19 4 K Potassium 39.0983 39.1 0.82	20 2 Ca Calcium 40.078 40.08 1.09	21 3 Sc Scandium 44.955912 44.96 1.36	22 4 Ti Titanium 47.867 47.87 1.54	23 5 V Vanadium 50.9415 50.94 1.63	24 6 Cr Chromium 51.9962 52.00 1.66	25 7 Mn Manganese 54.938044 54.94 1.55	26 8 Fe Iron 55.845 55.85 1.83	27 9 Co Cobalt 58.933195 58.93 1.88	28 10 Ni Nickel 58.6934 58.69 1.91	29 11 Cu Copper 63.546 63.55 1.90	30 12 Zn Zinc 65.38 65.38 1.95	31 13 Ga Gallium 69.723 69.72 1.83	32 14 Ge Germanium 72.64 72.64 2.01	33 15 As Arsenic 74.92160 74.92 2.18	34 16 Se Selenium 78.96 78.96 2.55	35 17 Br Bromine 79.904 79.90 2.96	36 18 Kr Krypton 83.798 83.80 2.95		
37 5 Rb Rubidium 85.4678 85.47 0.82	38 2 Sr Strontium 87.62 87.62 0.95	39 3 Y Yttrium 88.90584 88.91 1.33	40 4 Zr Zirconium 91.224 91.22 1.33	41 5 Nb Niobium 92.90638 92.91 1.60	42 6 Mo Molybdenum 95.94 95.94 1.66	43 7 Tc Technetium 98.90625 98.91 1.70	44 8 Ru Ruthenium 101.07 101.07 1.80	45 9 Rh Rhodium 102.9055 102.91 2.20	46 10 Pd Palladium 106.42 106.42 2.20	47 11 Ag Silver 107.8682 107.87 1.93	48 12 Cd Cadmium 112.411 112.41 1.69	49 13 In Indium 114.818 114.82 1.78	50 14 Sn Tin 118.710 118.71 1.96	51 15 Sb Antimony 121.757 121.76 2.05	52 16 Te Tellurium 127.60 127.60 2.30	53 17 I Iodine 126.90544 126.91 2.66	54 18 Xe Xenon 131.29 131.30 2.60		
55 6 Cs Caesium 132.90545 132.91 0.79	56 2 Ba Barium 137.327 137.33 0.89	57 3 La Lanthanum 138.90547 138.91 1.10	58 4 Ce Cerium 140.12 140.12 1.10	59 5 Pr Praseodymium 140.90768 140.91 1.13	60 6 Nd Neodymium 144.242 144.24 1.14	61 7 Pm Promethium 144.91274 144.91 1.13	62 8 Sm Samarium 150.36 150.36 1.17	63 9 Eu Europium 151.964 151.96 1.20	64 10 Gd Gadolinium 157.25 157.25 1.20	65 11 Tb Terbium 158.92535 158.93 1.20	66 12 Dy Dysprosium 162.500 162.50 1.22	67 13 Ho Holmium 164.93033 164.93 1.23	68 14 Er Erbium 167.259 167.26 1.24	69 15 Tm Thulium 168.93421 168.93 1.25	70 16 Yb Ytterbium 173.054 173.05 1.25	71 17 Lu Lutetium 174.967 174.97 1.25	72 18 Hf Hafnium 178.49 178.5 1.30		
87 7 Fr Francium 223 223 0.7	88 2 Ra Radium 226 226 0.9	89 3 Ac Actinium 227 227 1.1	90 4 Th Thorium 232.0377 232.04 1.30	91 5 Pa Protactinium 231.03688 231.04 1.30	92 6 U Uranium 238.02891 238.03 1.31	93 7 Np Neptunium 237.04817 237.05 1.36	94 8 Pu Plutonium 244.06422 244.06 1.28	95 9 Am Americium 243.06138 243.06 1.30	96 10 Cm Curium 247.07647 247.08 1.30	97 11 Bk Berkelium 247.07031 247.07 1.30	98 12 Cf Californium 251.08328 251.08 1.30	99 13 Es Einsteinium 252.08321 252.08 1.30	100 14 Fm Fermium 257.10371 257.10 1.30	101 15 Md Mendelevium 258.10386 258.10 1.30	102 16 No Nobelium 259.10386 259.10 1.30	103 17 Lr Lawrencium 262.10386 262.10 1.30	104 18 Rf Rutherfordium 261 261 1.30		
<div>Atomic Mass</div> <div>Chemical Symbol</div> <div>Name</div> <div>First Ionization Energy</div> <div>Atomic (proton) Number</div> <div>Electronegativity</div>																			
<div>Alkali metals</div> <div>Alkaline metals</div> <div>Other metals</div> <div>Transitions metals</div> <div>Lanthanoids</div> <div>Actinoids</div> <div>Metalloids</div> <div>Nonmetals</div> <div>Halogens</div> <div>Noble gases</div>																			

Chemical Symbol: **H**

Name: **Hydrogen**

Atomic Mass: **1.00794**

Atomic (proton) Number: **1**

Electronegativity: **2.20**

First Ionization Energy: **1312.0**

Alkali metals Alkaline metals Other metals Transition metals Lanthanoids Actinoids 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.

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?

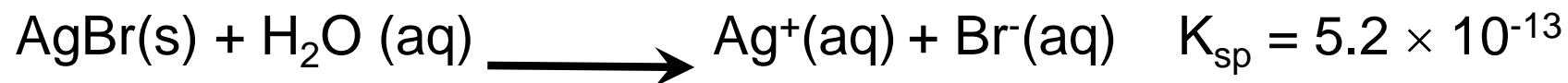
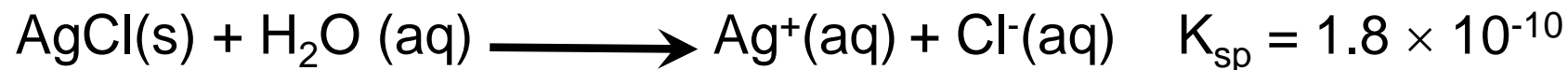
Various Metal Ores available in earth crust

- ✓ Cinnabar (HgS)
- ✓ Magnetite (Fe_3O_4)
- ✓ Hematite (Fe_2O_3)
- ✓ Argentite (Ag_2S)
- ✓ Galena (PbS)
- ✓ Chalcopyrite (CuFeS)
- ✓ Chalcocite (Cu_2S)
- ✓ Malachite ($\text{CuCO}_3 \cdot \text{Cu(OH)}_2$)



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

Let us look at this situation.....



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	Hard Base	Soft Base
1		
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:

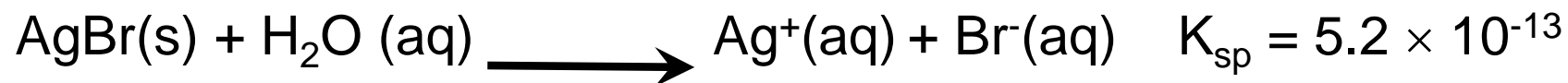
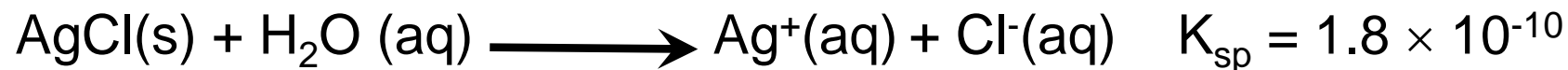
Hard acid bonding with Hard Base is favourable

Soft acid bonding with Soft Base is favourable

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

Soft-Soft interaction \longrightarrow **Covalent in nature**

Rationale For Distinct K_{sp} ?



❖ 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

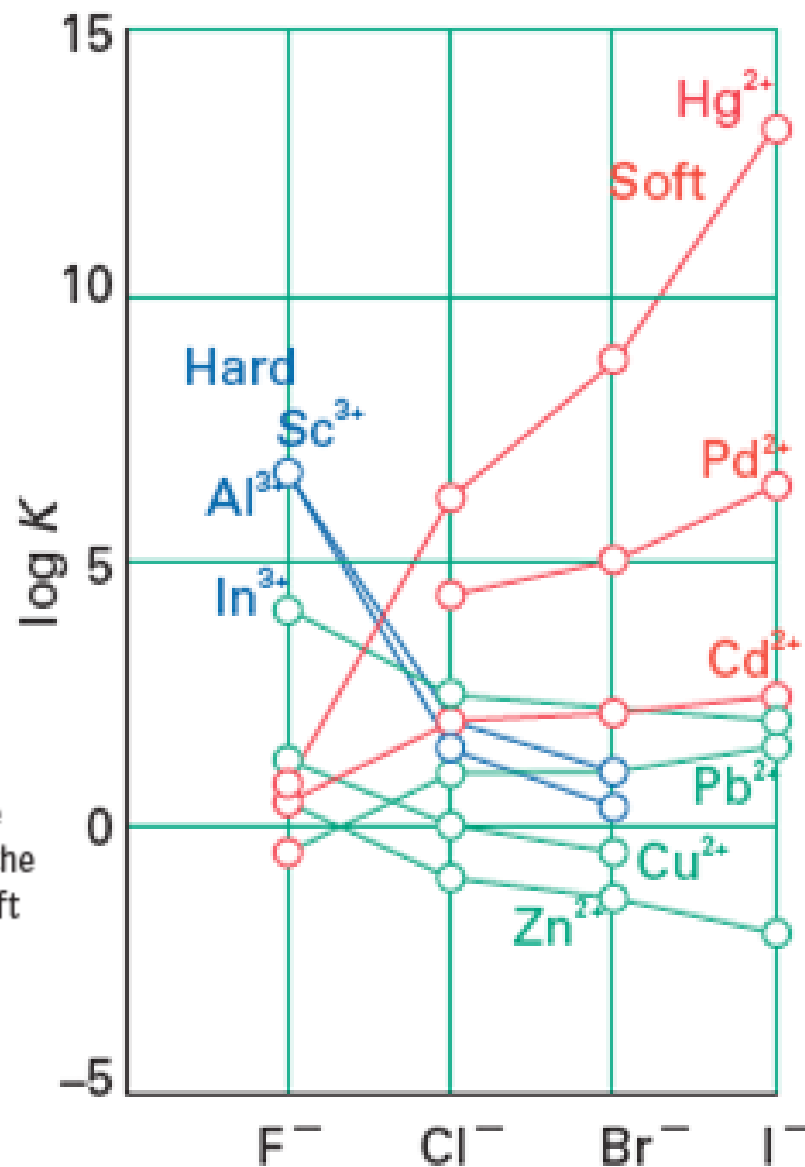


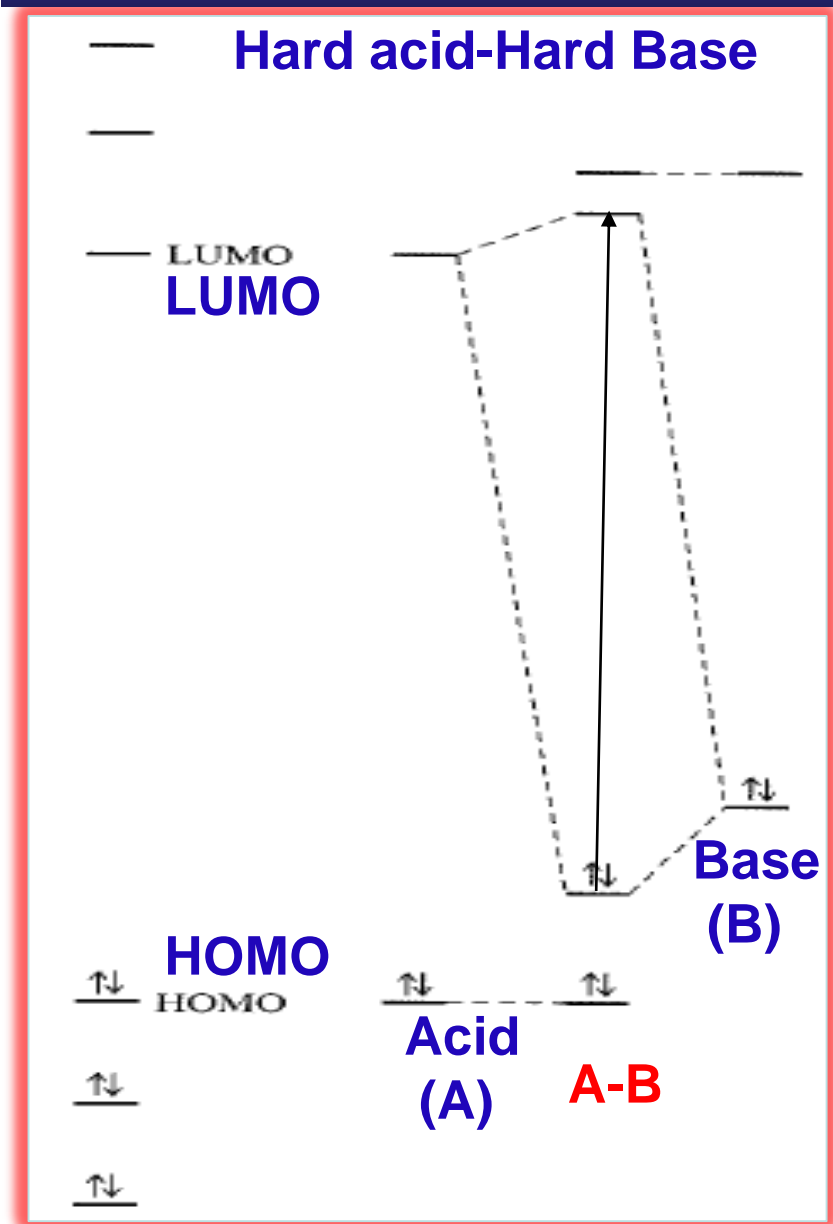
Figure 4.12 The trends in stability constants for complex formation with a variety of halide ion bases. Hard ions are indicated by the blue lines, soft ions by the red line. Borderline hard or borderline soft ions are indicated by green lines.

Examples for Hard-Soft Acid-Base

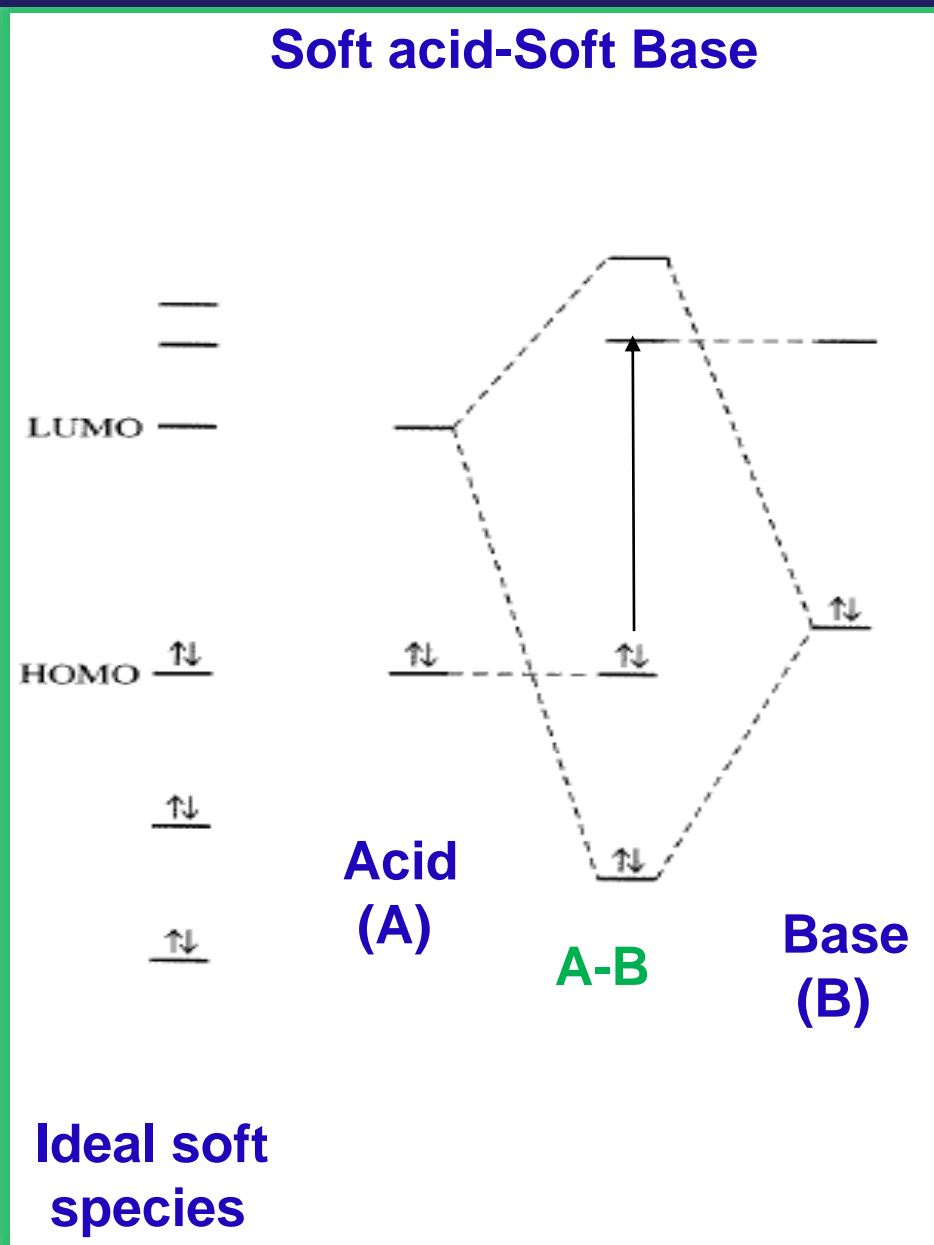
Table 4.5 The classification of Lewis acids and bases*

Hard	Borderline	Soft
<i>Acids</i>		
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		
<i>Bases</i>		
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	$\underline{S}CN^-, R_3P, C_6H_5$
$SO_4^{2-}, PO_4^{3-}, ClO_4^-$	$C_6H_5N, \underline{S}CN^-$	R_2S
* The underlined element is the site of attachment to which the classification refers.		

Theory of Hard-Soft Acid-Base



Ideal hard species



A Classical metathesis (HSAB) 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).

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

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)

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

Hardness Parameters (eV)

<i>Ion</i>	<i>I</i>	<i>A</i>	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.

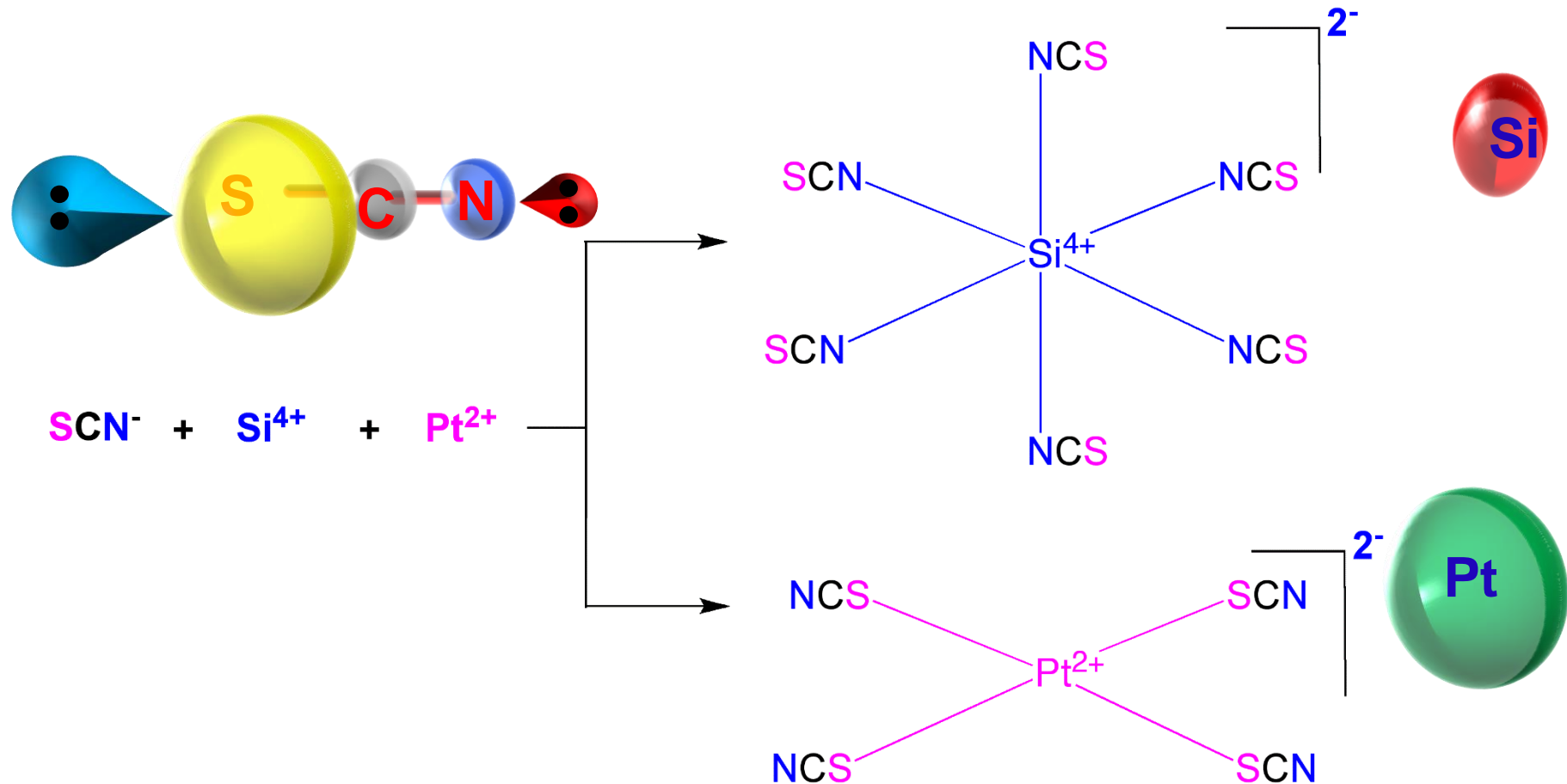
$$(\chi) = \frac{IE + EA}{2}$$

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

Softness (σ) is a measure of
inverse of hardness

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

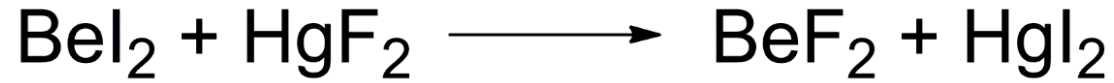
Ambipolar Ligand: Selectivity For Hard-Soft Acid



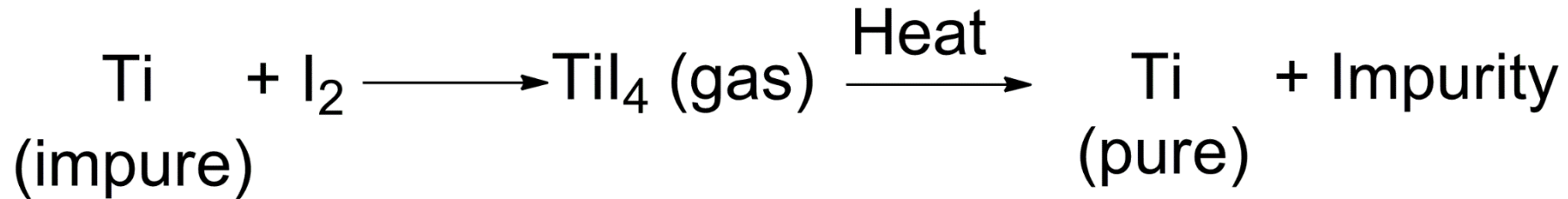
Trends are exhibited, by keeping the metal same and changing the anion/ligand. By keeping the anion/ligand same and changing the metal

Representative Application of HSAB

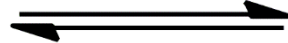
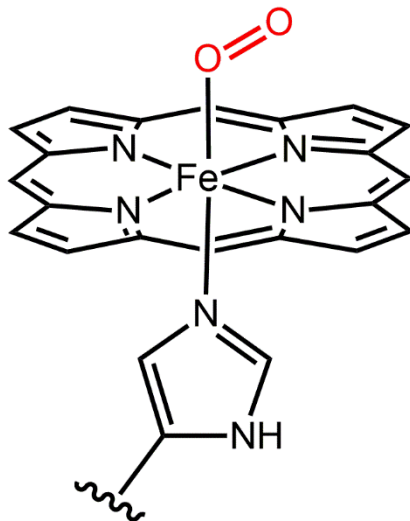
For the targeted synthetic approach



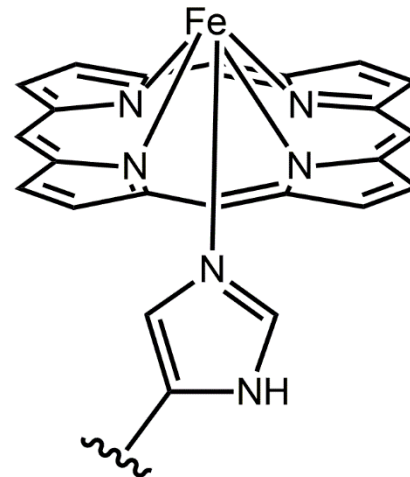
Chemistry for commercial application



Chemistry for life cycle (Breathing)



CO?



Reversible
binding of
Oxygen

Fe(II) →
border line
acid,
O₂ → 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

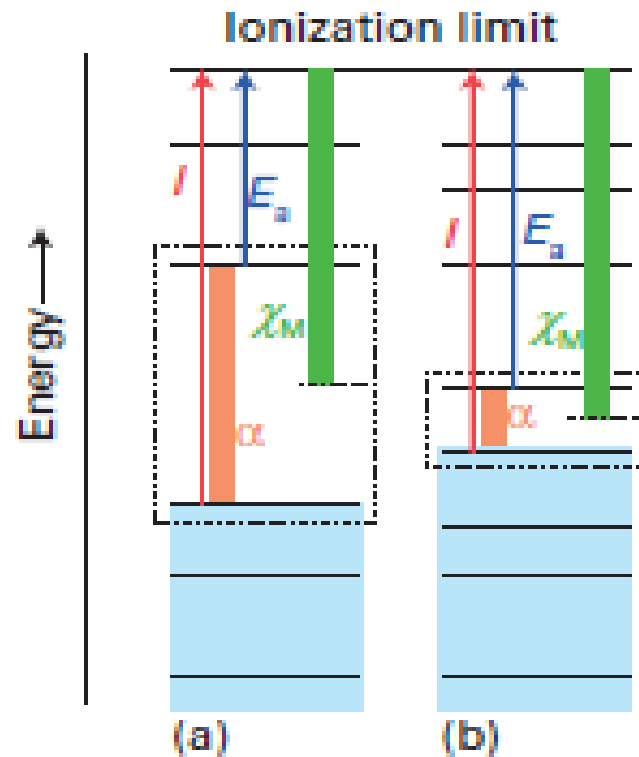
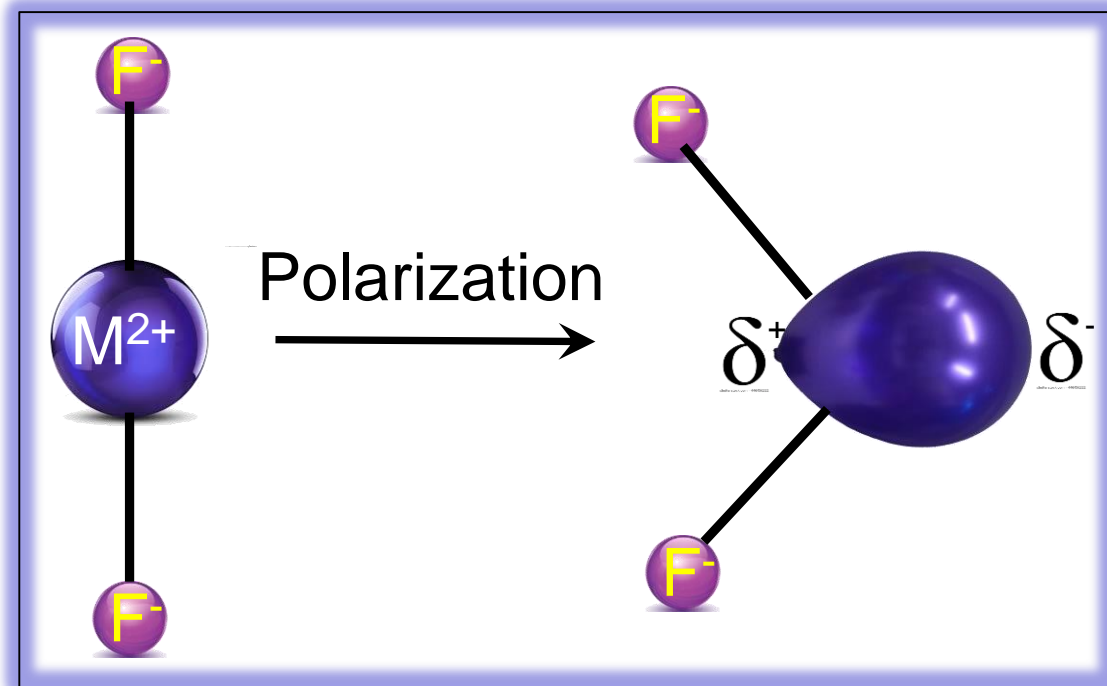
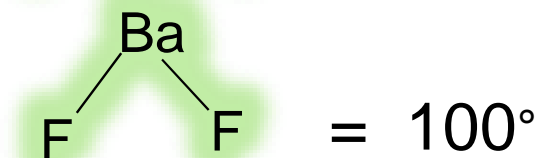
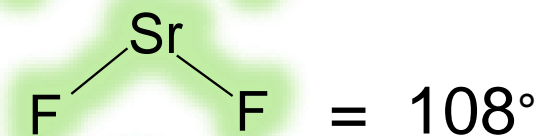
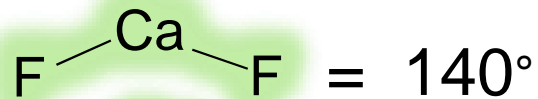
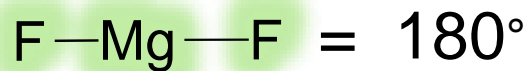


Figure 1.28 The interpretation of the electronegativity and polarizability of an element in terms of the energies of the frontier orbitals (the highest filled and lowest unfilled atomic orbitals). (a) Low electronegativity and polarizability; (b) high electronegativity and polarizability.

Polarizability: A Case Study in Group 2 Fluorides

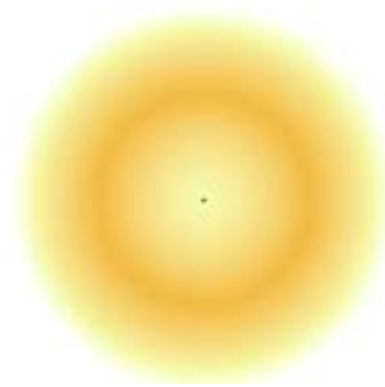
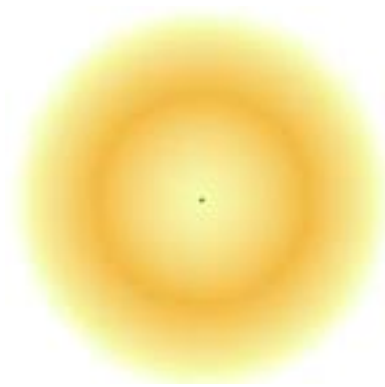


The negatively charged ligands polarize the electron cloud of the central atom and deforms its spherical symmetry. The repulsion between the ligand charges and the dipoles thus generated is minimized when the molecule has a ***bent structure*** (gaseous state)

Weak Intermolecular Interactions

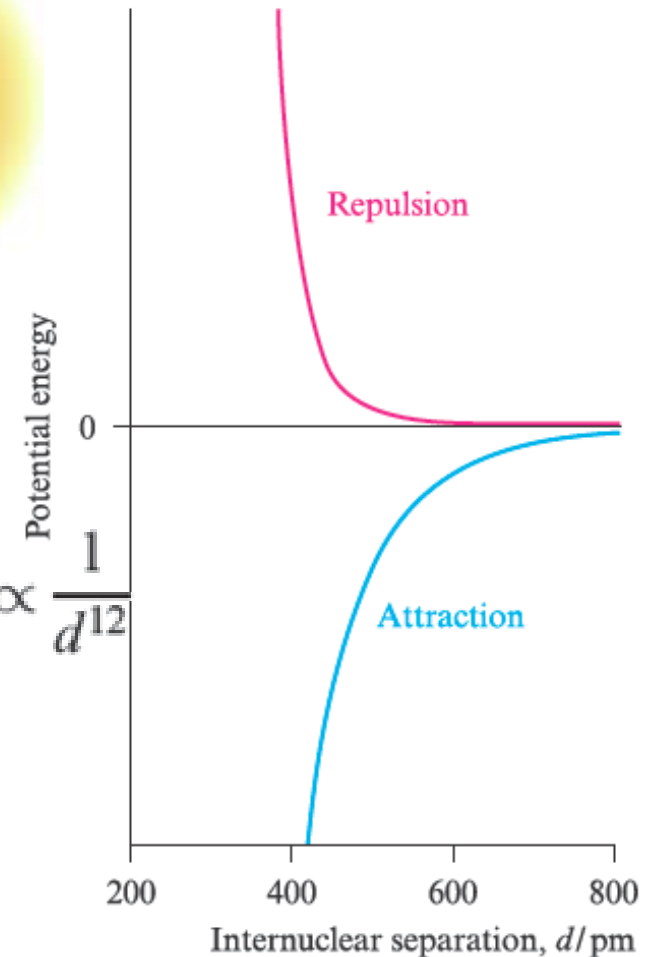
Proof for Existence of Weak Interactions

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



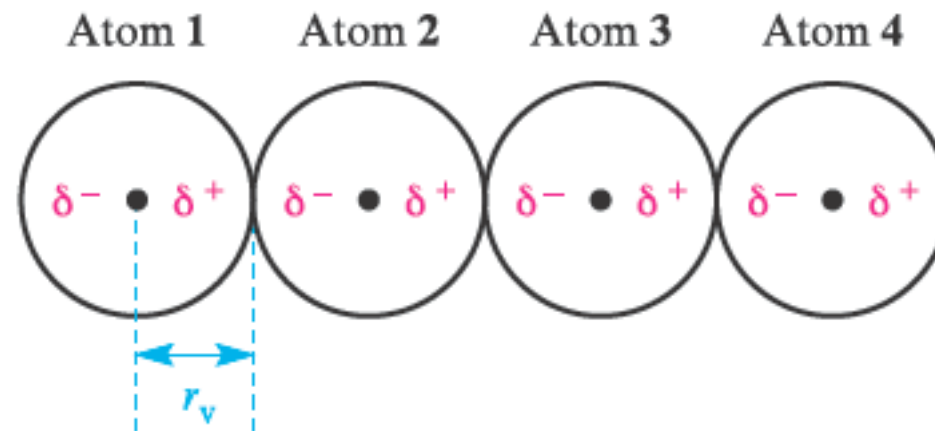
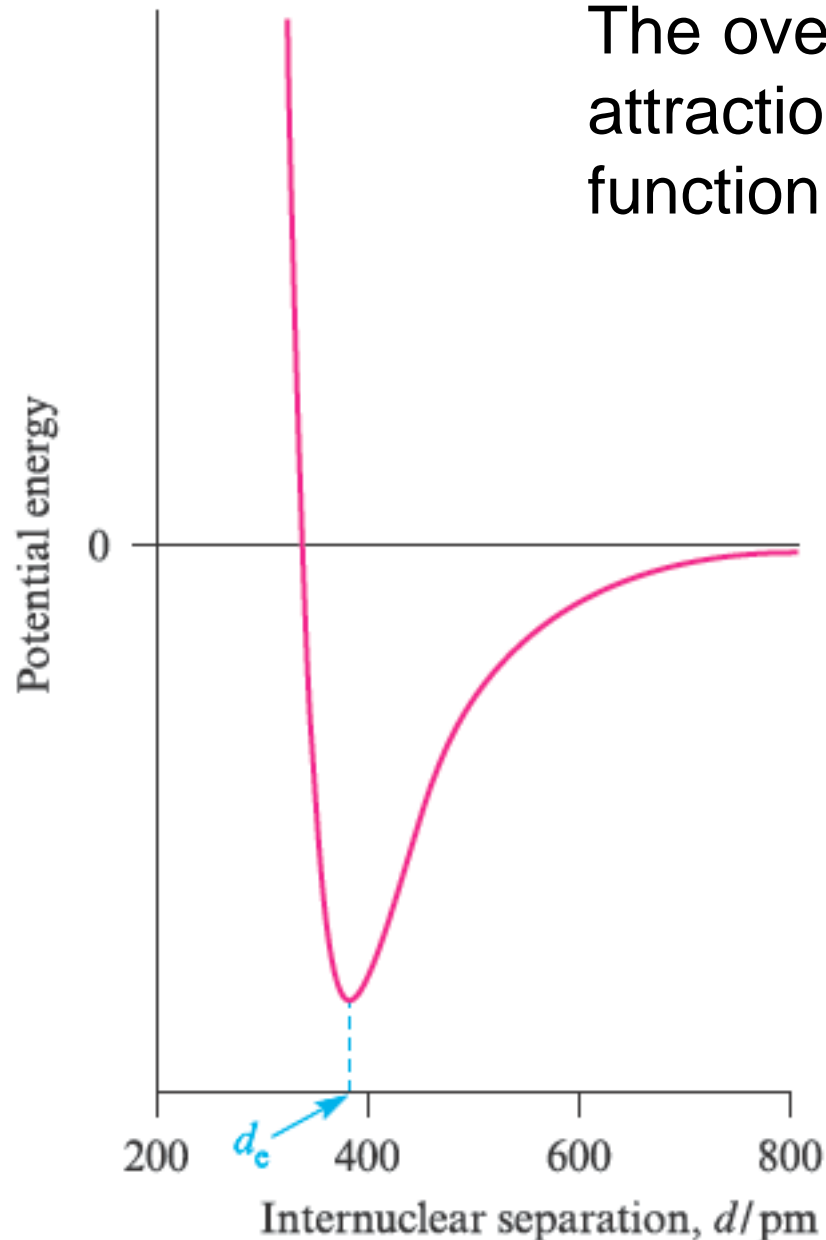
Potential energy due to repulsion between atoms $\propto \frac{1}{d^{12}}$

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.

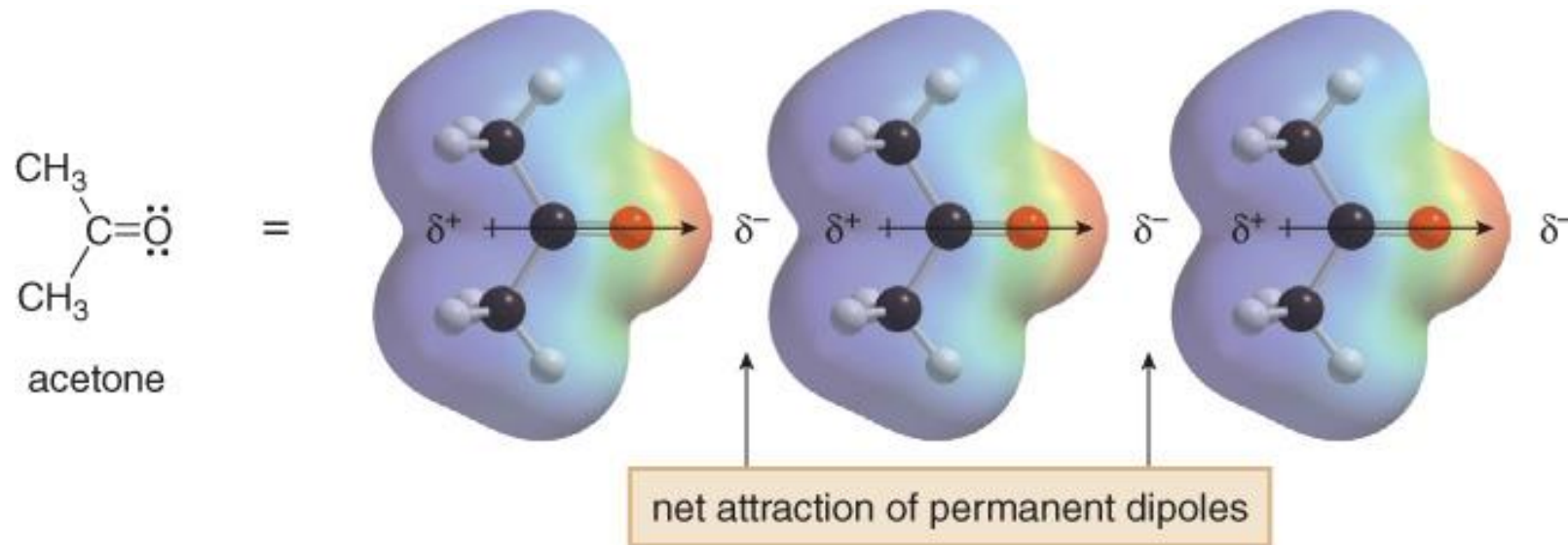
van der Waals Interaction

- ❖ 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.



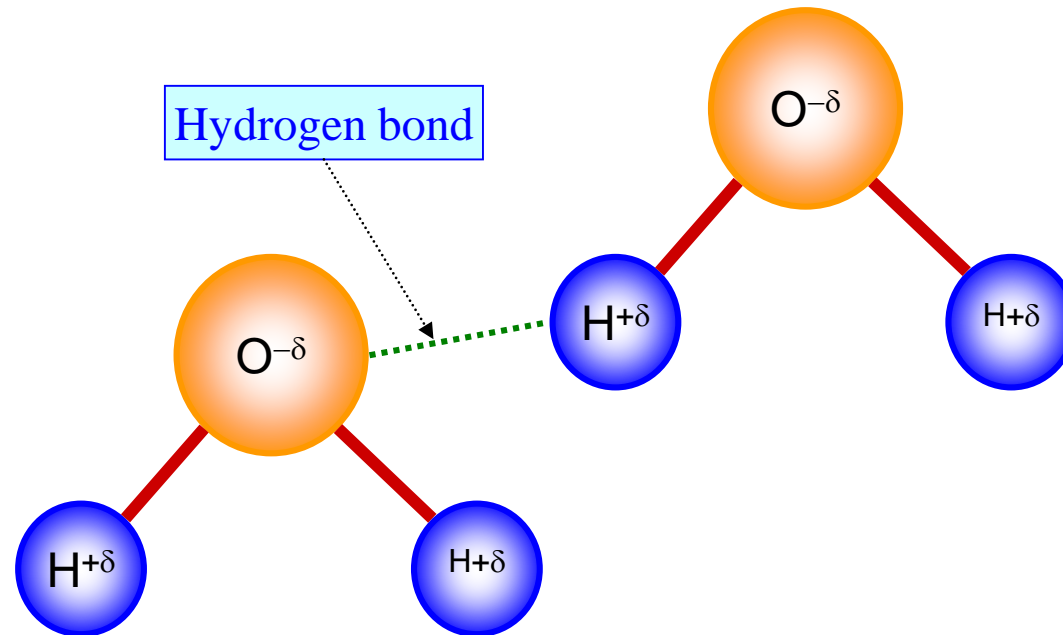
Significant difference in electronegativity of the atoms within the molecule responsible for permanent dipole.

Example includes: HCl, H₂O, Carboxylate

Phase Transition

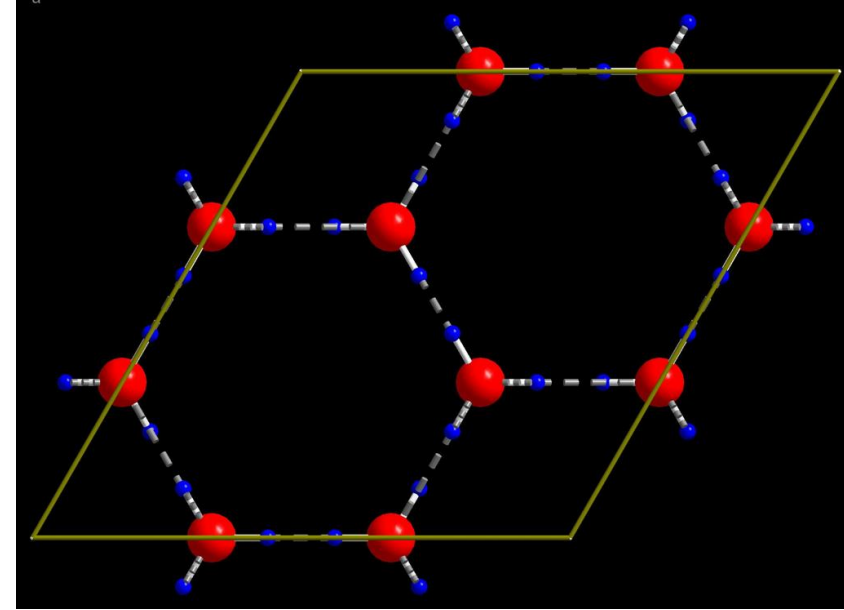
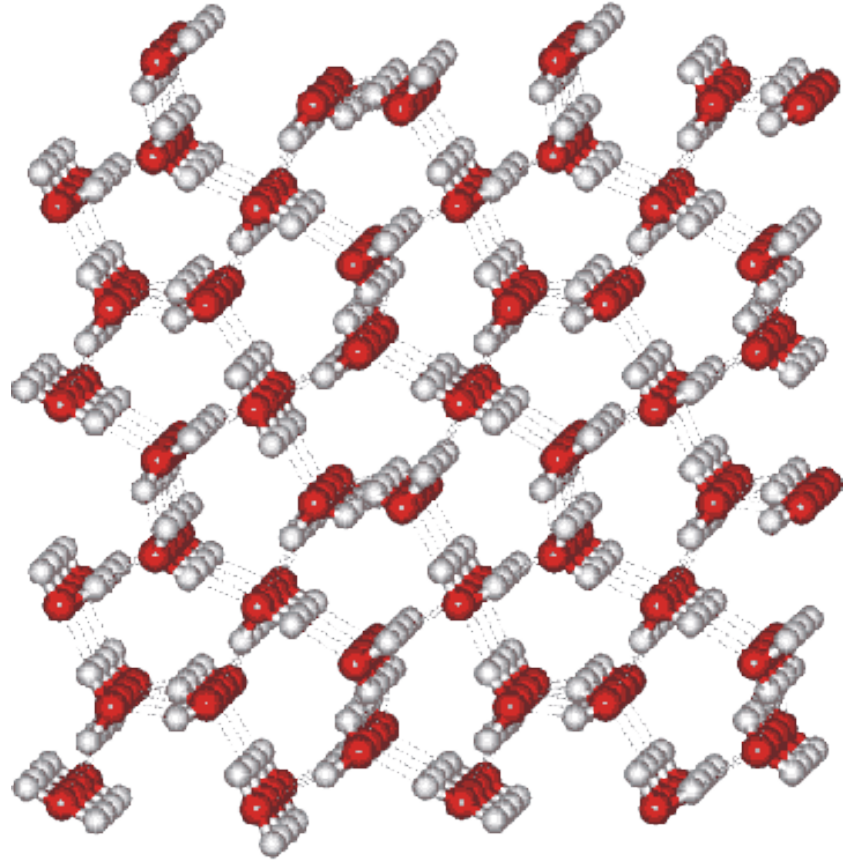
When the weak interaction becomes dominant → Induces phase transition

Example: $\text{H}_2\text{O (l)} \rightarrow \text{H}_2\text{O (s)}$



Hydrogen sulfide and **water boil** at $-60.7\text{ }^{\circ}\text{C}$ and $+100.0\text{ }^{\circ}\text{C}$

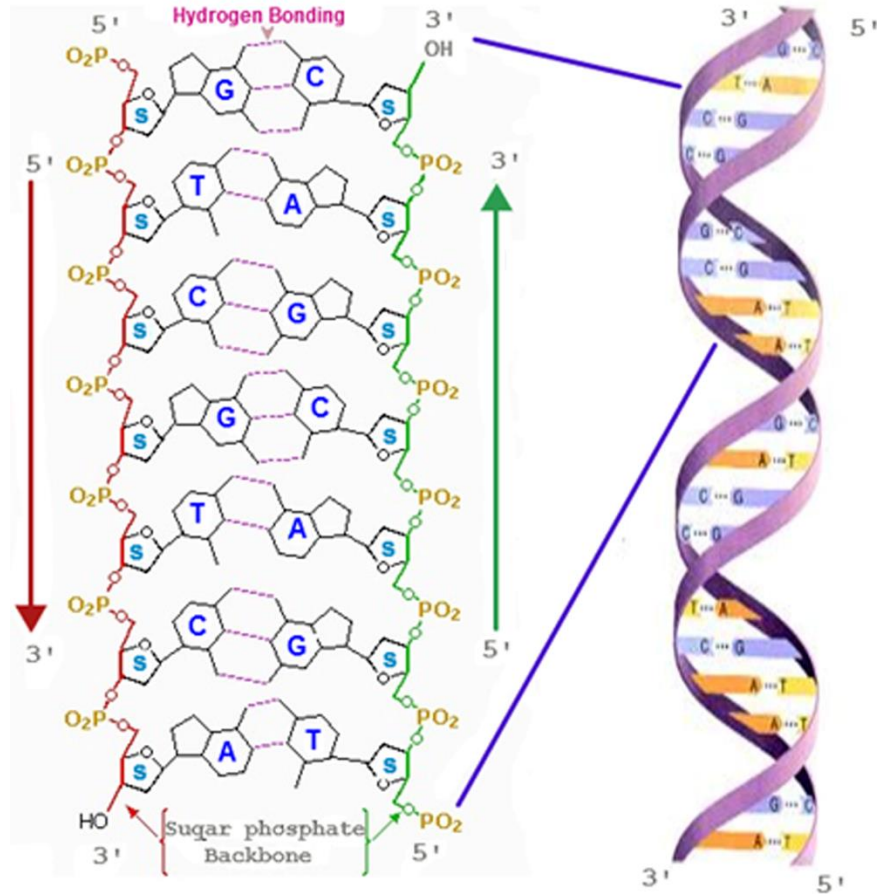
H-Bonding Network



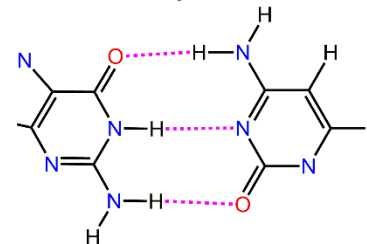
H-Bonding is a classic example of Dipole-Dipole interaction

Importance of Weak Interaction In Biology

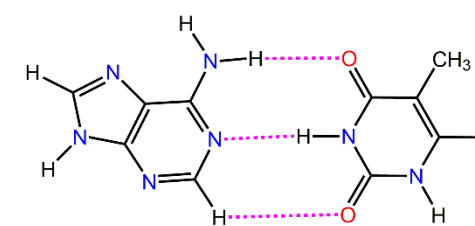
Molecular Structure of Deoxyribonucleic acid



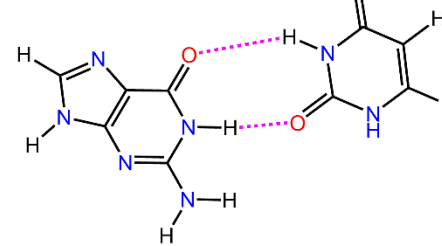
Guanine-Cytosine



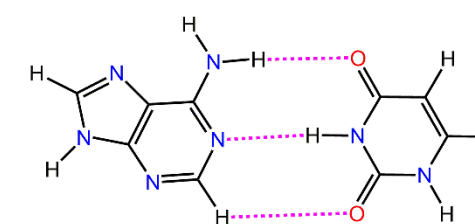
Adenine-Thymine



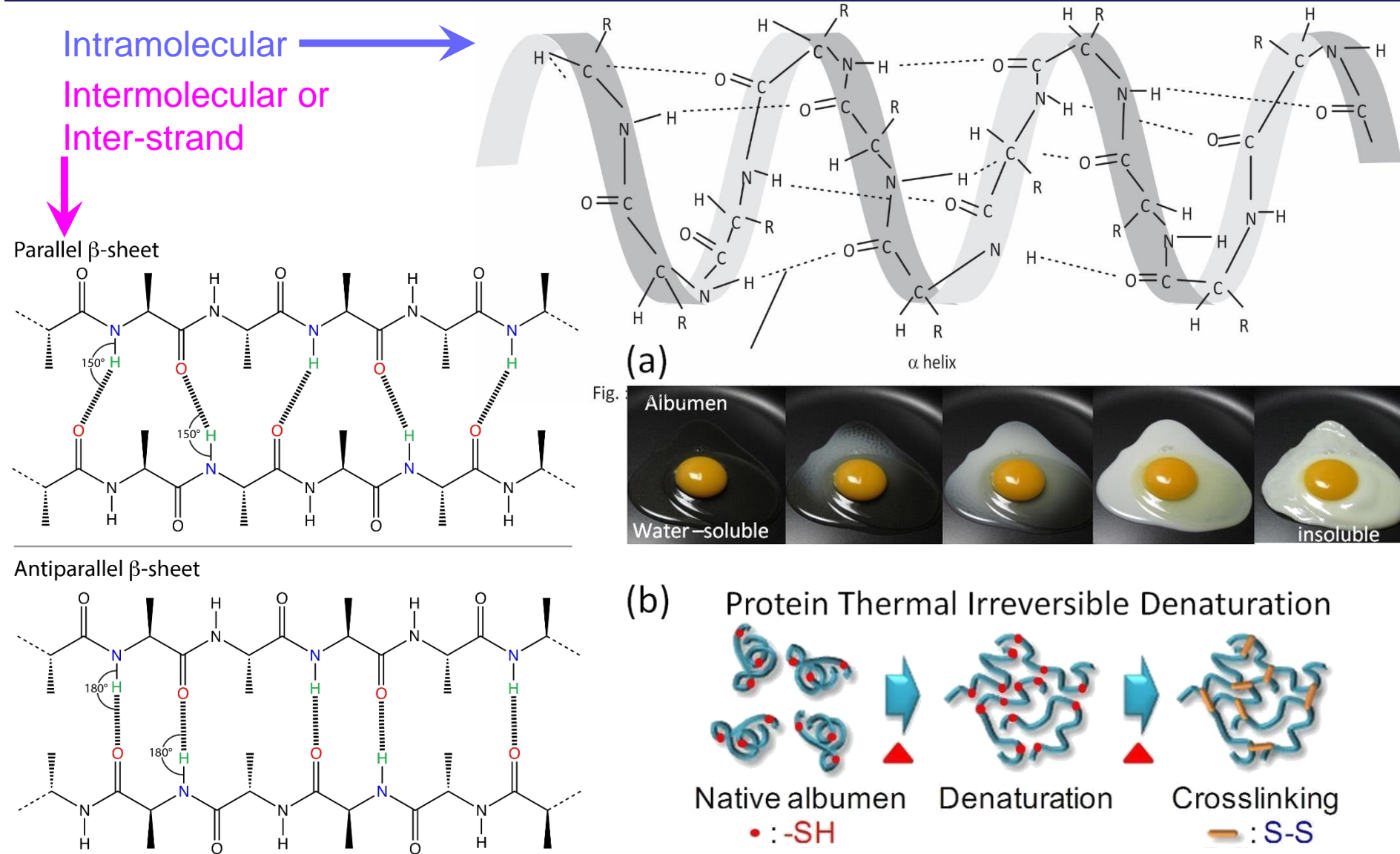
Guanine-Uracil



Adenine-Uracil



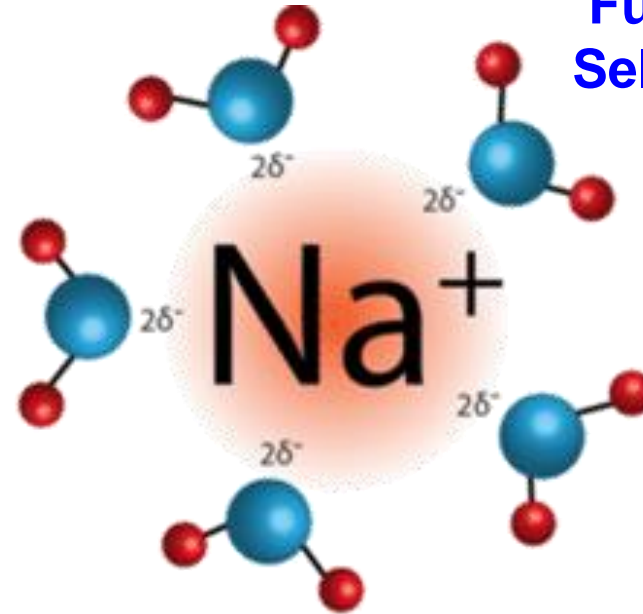
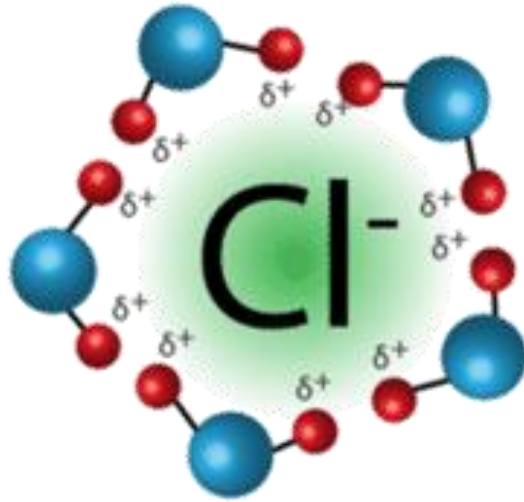
What Will Happen If You Destroy H-Bonding?



Ion-Dipole (ID) Interaction

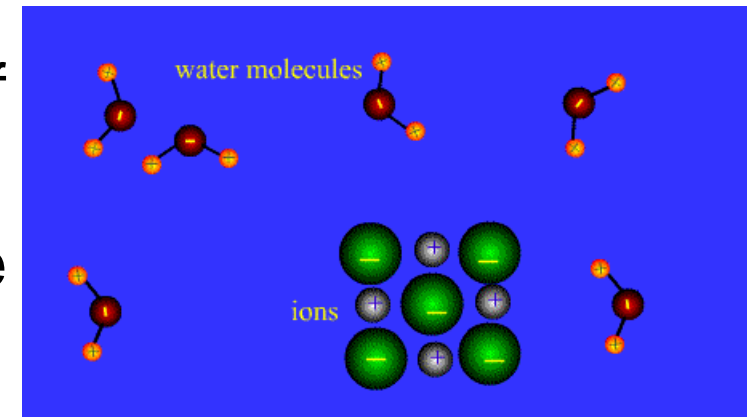
- Permanent dipole interacts with an ion.
- Example: NaCl in water.

ID importance
in biological
Functions:
Self reading



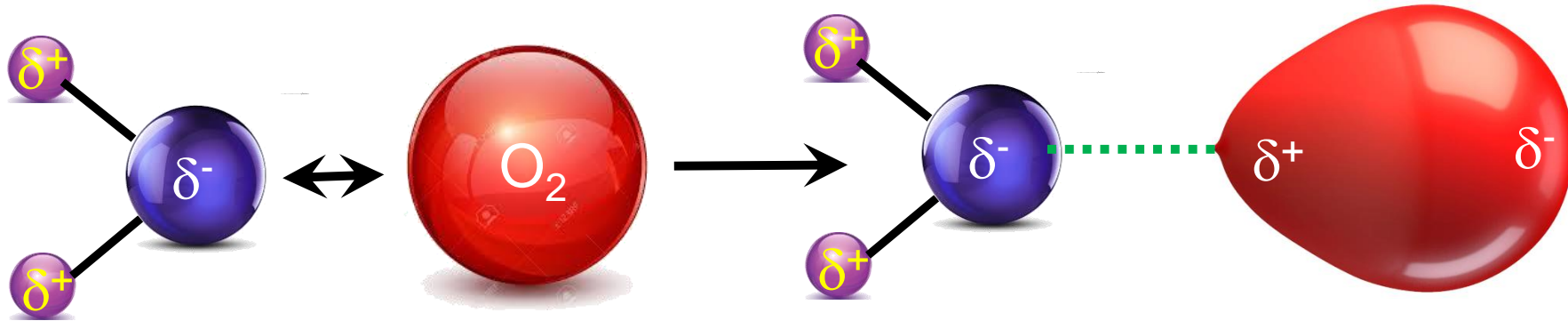
Ion-Dipole strength

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



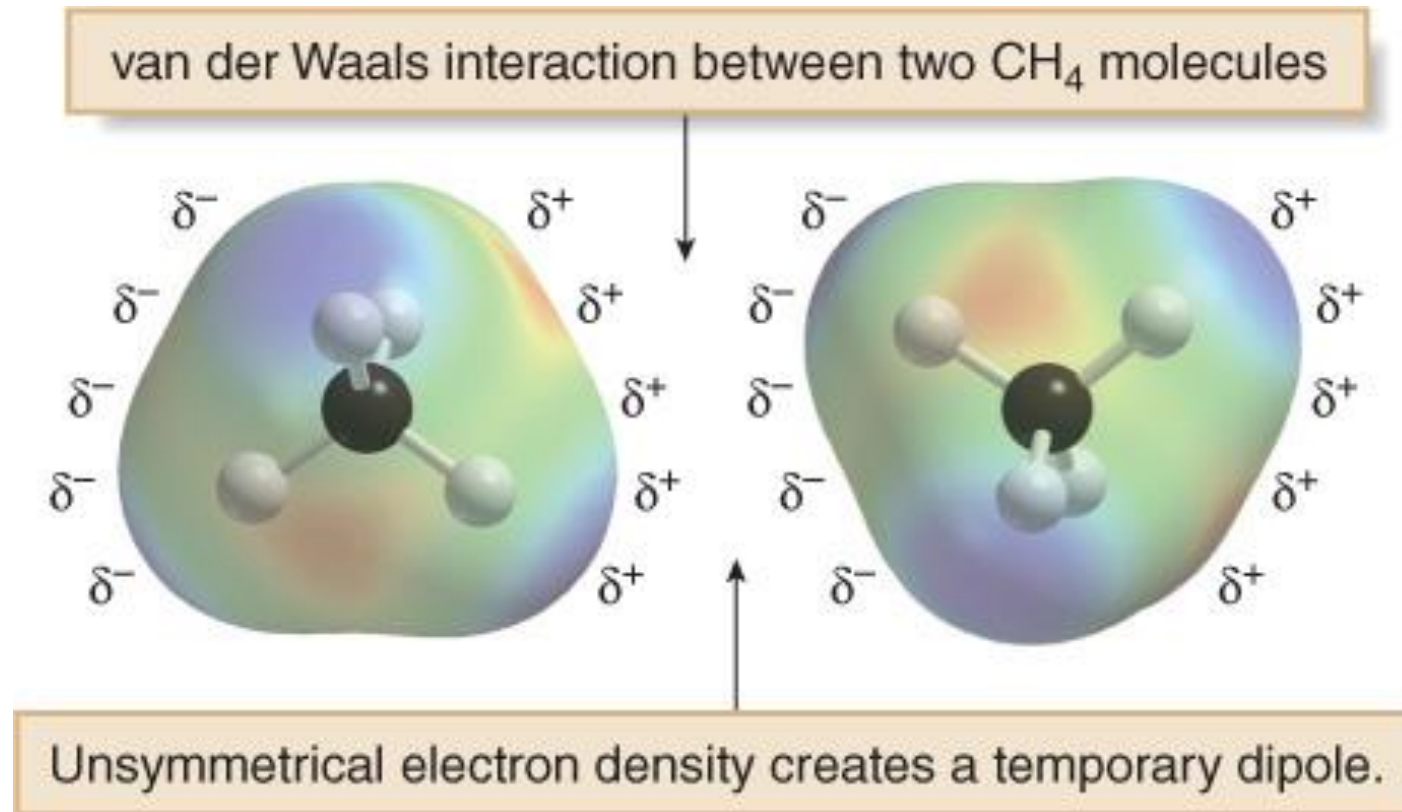
Dipole- Induced Dipole Interaction

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




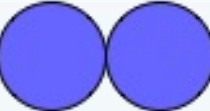
Attractive force exist between **non-polar** molecules due to the momentary induced dipole.

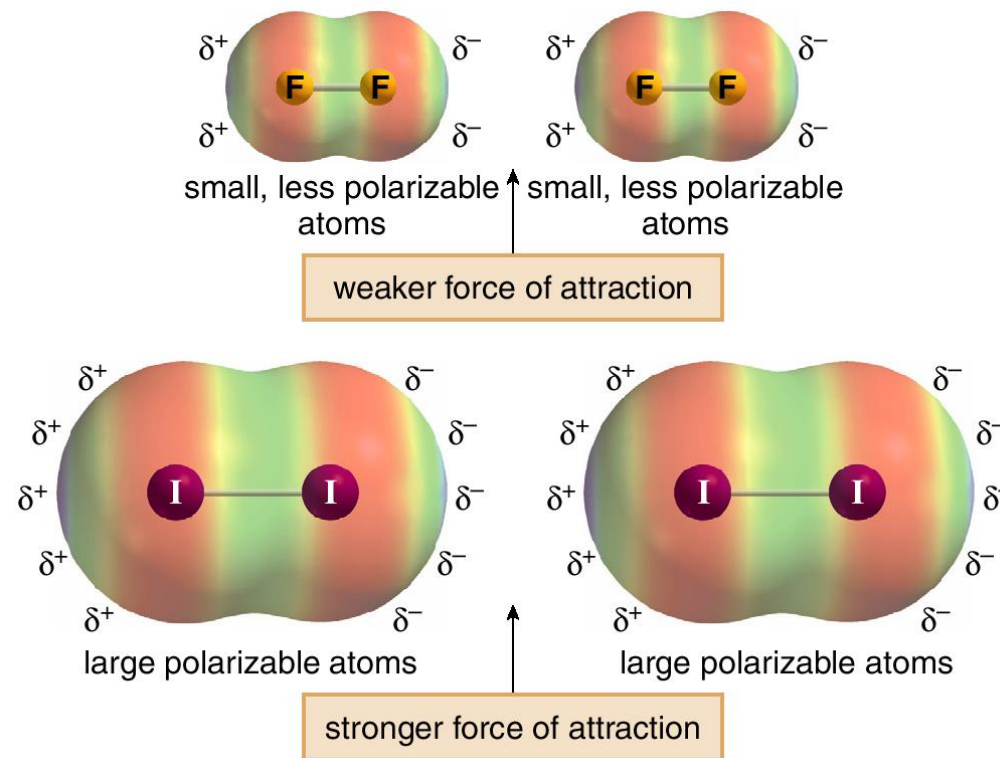


Induced dipole-Induced dipole interaction is also known as **London dispersion force**

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 F₂ 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.

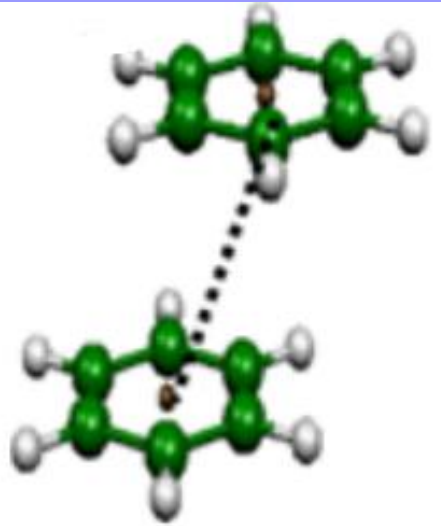
Which is Strong Among the Weak Interactions?

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

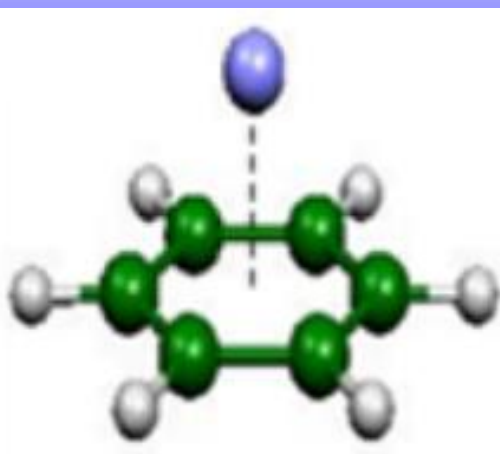
Can We Prove The Strength of The Order Given Above Experimentally?

Yes!!! WATCH THE DEMONSTRATION

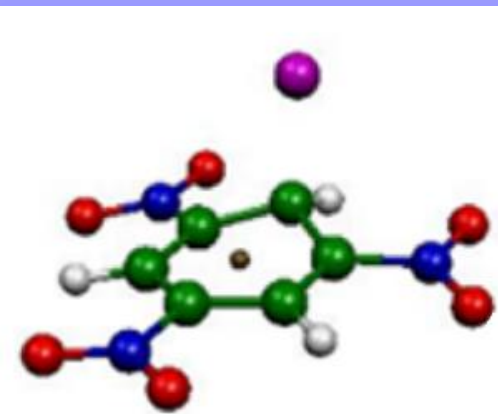
Other weak interactions



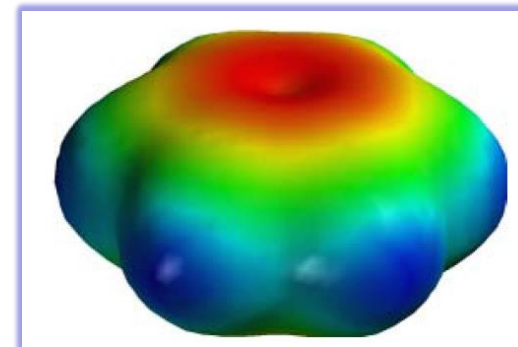
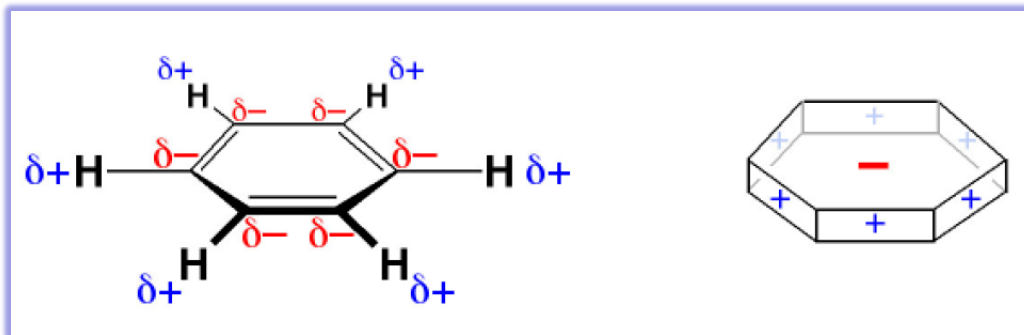
π - π



Cation- π

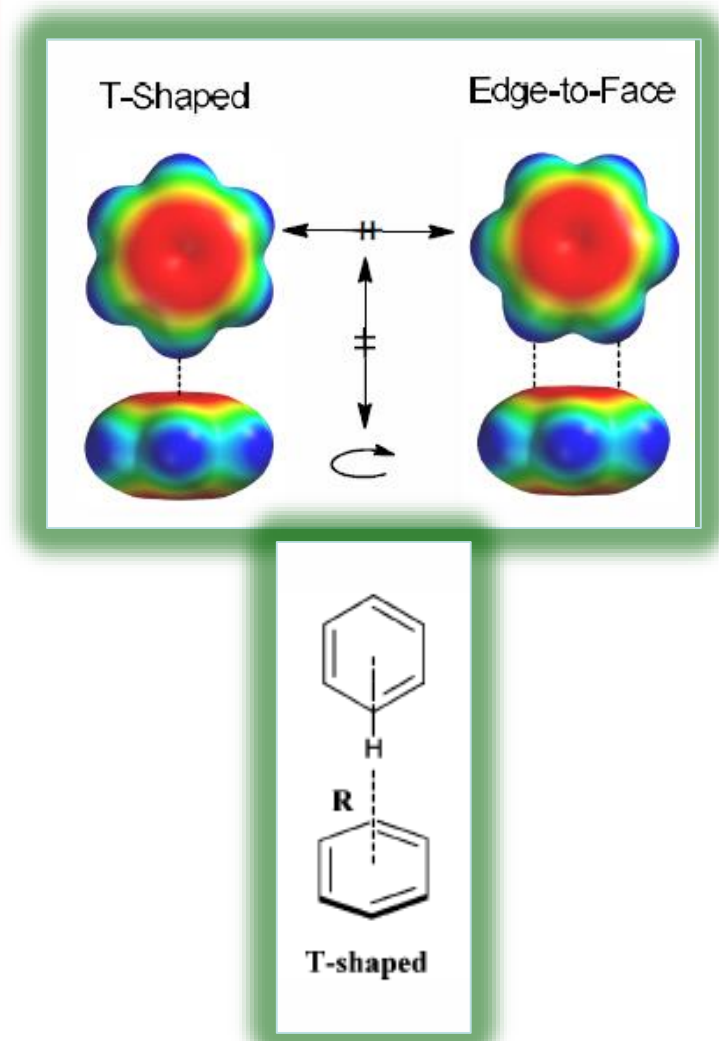
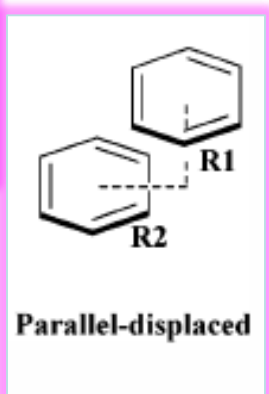
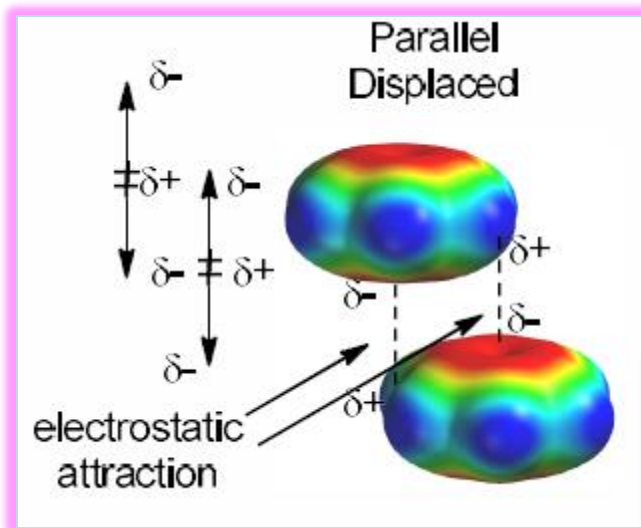
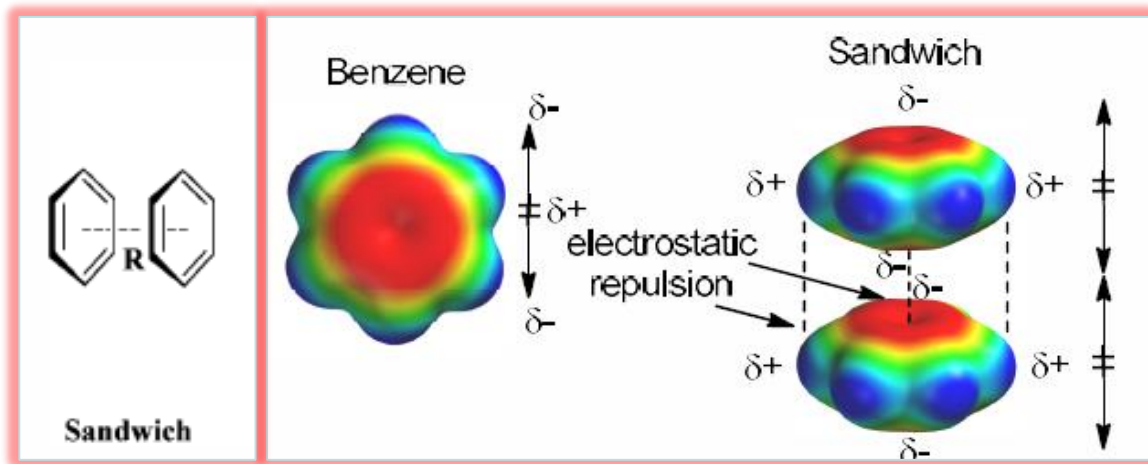


Anion- π

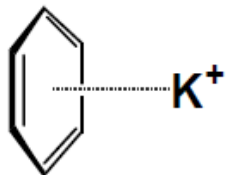


red = extreme negative; blue = extreme positive

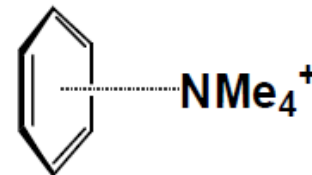
$\pi - \pi$ interactions



Cation- π Interactions



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



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

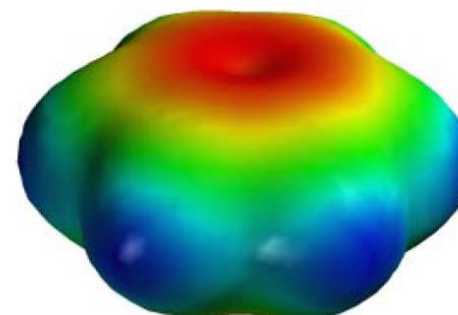
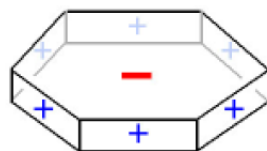
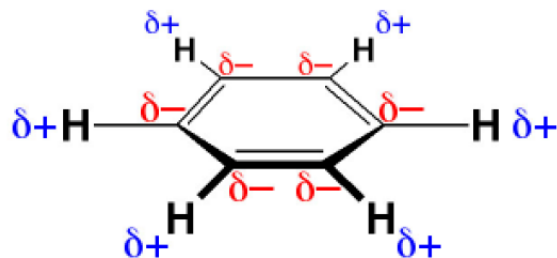


$$-\Delta H_{\text{exptl}} = 17.9 \text{ kcal/mol}$$



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

➤ **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?