

Inorganic Chemistry

CH2113

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Fall 2020

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1 Pre Midsem

1.1 Lecture 1

Acids and Bases

01 September 2020
19:29

A Variety of chemical species Can be classified as Acids & Bases

Several concepts of acid and bases exist. Which is correct? Not a concern.
Which applies better to a particular case or situation.

All concepts need to be understood so that we can tackle different cases - aqueous, organic reactions, non-aqueous etc.

In this lecture we will see how they take part in proton transfer reactions

Proton transfer equilibria => acidity constants

Classifying the strength of acids and bases



Types of acids and bases- concepts

Wednesday, September 02, 2020

Arrhenius concept

Aids increases the conc. H^+ ions
Bases increases the conc. OH^-

Bronsted - lowry \rightarrow Proton acceptor & proton donor
could fit to any protic systems.



Lan - flood \rightarrow Oxide donor - acceptor \Rightarrow Nucleophilic systems.

Lewis acid - base \rightarrow Electron pair acceptor & donor
or accepts cations & electrons

Uspenskih - acids react with bases & gives up cations

Arrhenius acids and bases

01 September 2020
20:07

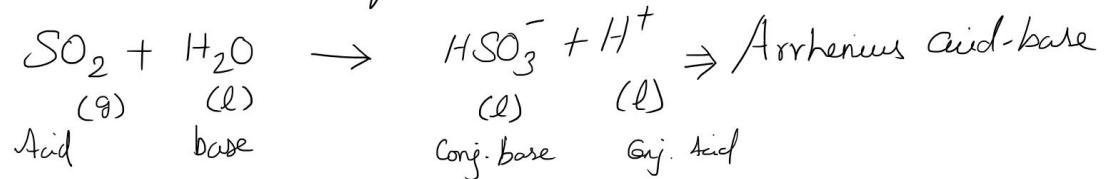


Arrhenius acids =>

Those that produce hydronium ions or hydrogen ions in water.

Bases produce or increase the OH- ions concentration in water

Acid base reactions are quite common



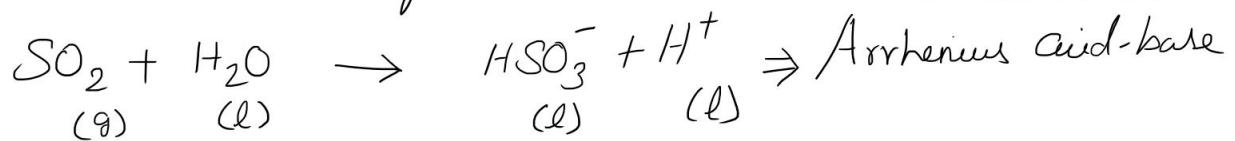
Bronsted acids and bases

01 September 2020
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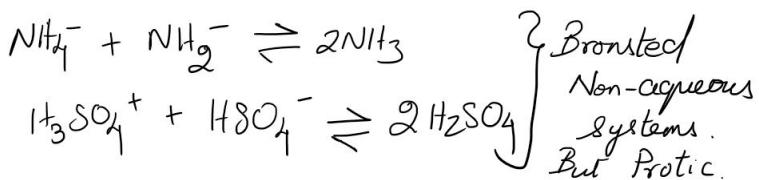
Bronsted acids and...
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Acid base reactions are quite common



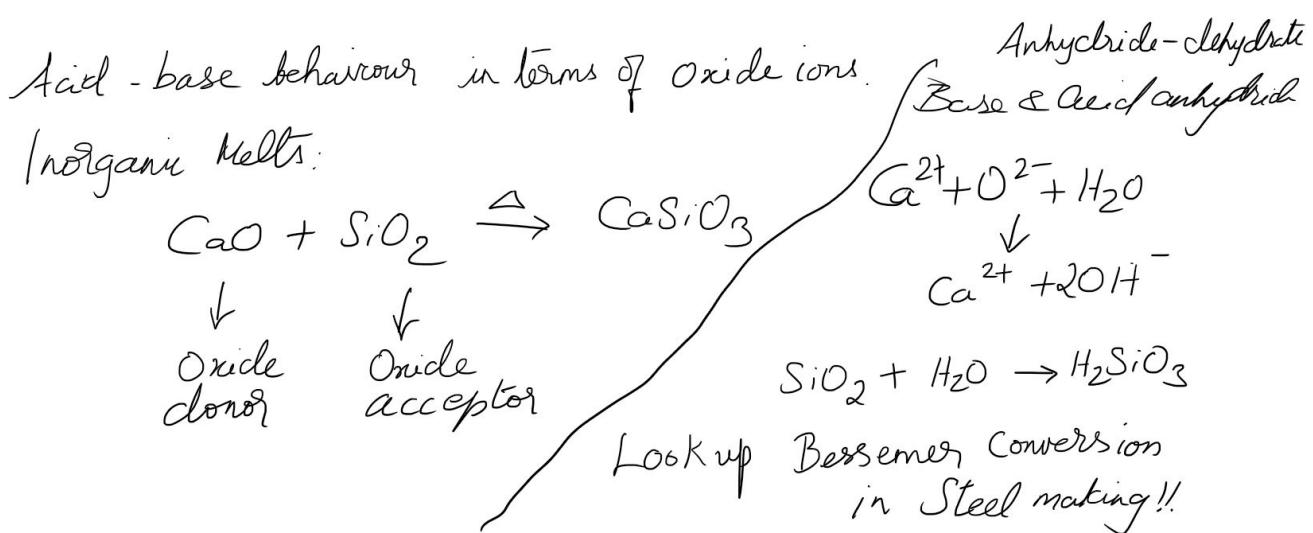
Bronsted acids = H^+ donor

Bronsted base = OH^- donor or OH^- acceptor.



Lux-Flood acid-bases

Wednesday, September 02, 2020
11:11 AM

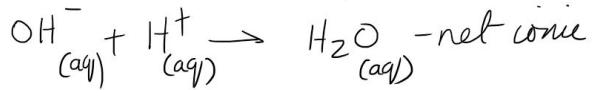




Lewis Acid-Base

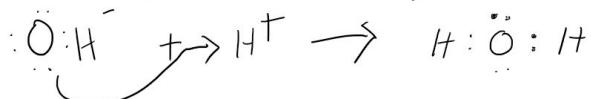
Wednesday, September 02, 2020
12:26 PM

Acid accepts electron pair → $HCl + NaOH \rightarrow NaCl + H_2O$
Base donates electron pair



OH^- → donates electron to form the octet in H_2O

H^+ → accepts electron to form the octet in H_2O



The Lewis view of the reaction focuses on the electrons. When HCl dissociates into ions, the hydrogen ion loses an electron to the chlorine ion. When NaOH dissociates, the hydroxide ion gains an electron from the sodium ion. The hydroxide ion is made up of an oxygen atom with six electrons in its outer electron shell and a hydrogen atom with one electron. It has the extra hydroxide ion electron for a total of eight electrons available for chemical bonding. Two of them are shared with the hydrogen atom in a covalent bond while the other six are unbonded pairs. In the Lewis view, the hydroxide ion donates an electron pair to the hydrogen ion to form a second covalent bond, producing a water molecule. For Lewis acid-base reactions, an acid is any substance that accepts electrons while a base donates electrons.

From <<https://sciencing.com/what-happens-in-a-lewis-acid-base-reaction-13710548.html>>

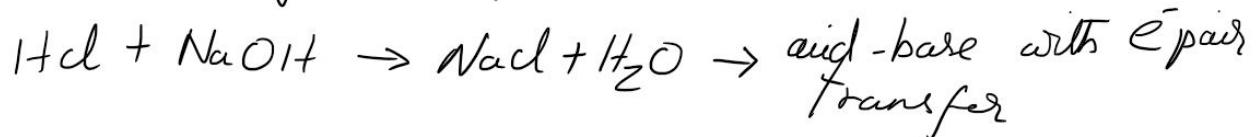
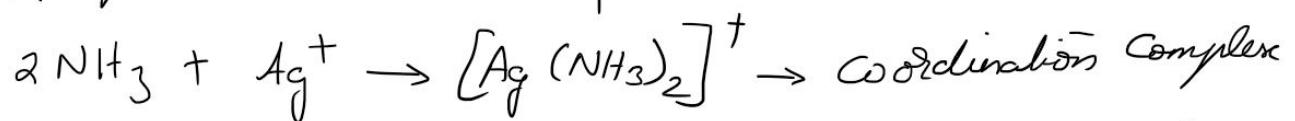
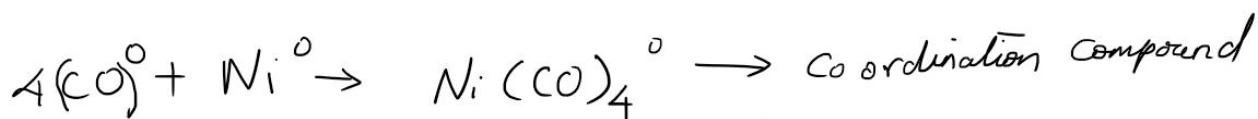
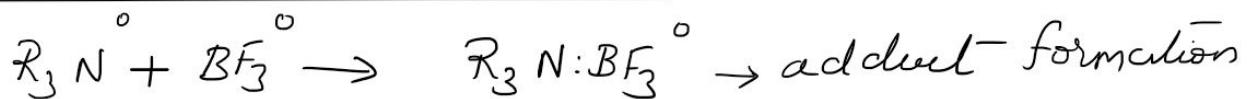
Lewis acid-base contd....

Wednesday, September 02, 2020

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No ions formed & no H^+ transferred



Acidity constant- an equilibrium constant

01 September 2020
20:36

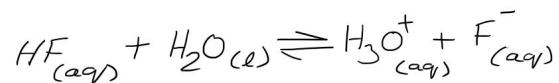


How fast the equilibrium is reached
this decides the speed of the
proton transfer reaction.



Strength of acids and bases

For Brønsted acid such as HF it is given by
its **acidity constant**.



$$K_a = \frac{[H_3O^+] [F^-]}{[HF]}$$

$[F^-]$ = Molar concentration

If the conc. of HF is 0.001 mol/Lit
then $[HF] = 0.001$



Understanding the acidity constant

01 September 2020
20:53



$$K_a = \frac{[H_3O^+][F^-]}{[HF]}$$

When $K_a \ll 1 \Rightarrow [HF] \gg [F^-]$

K_a for HF = 3.5×10^{-4}

What does this mean?



Understanding K_a

Thursday, September 03, 2020

5:02 PM

K_a = acidity constant or acid equilibrium constant

$$pK_a = -\log_{10} K_a$$

\therefore If $K_a = 3.5 \times 10^{-4}$ for HF

$$pK_a = -\log_{10} 3.5 \times 10^{-4} = 3.46$$

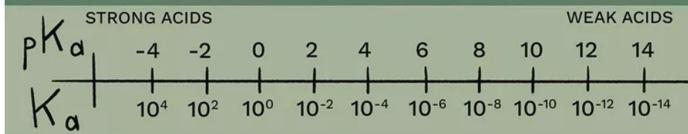


What Is pK_a in Chemistry?

The pK_a value is the negative base-10 logarithm of the acid dissociation constant (K_a) of a solution.

The smaller the value of pK_a , the stronger the acid.

$$pK_a = -\log_{10} K_a$$



ThoughtCo.

ThoughtCo / Hilary Allison

The Smaller the
Value of " pK_a ",
the Stronger the Acid.

Utilizing pKa and pH to solve acid-base problems

01 September 2020

20:53

$$pH = -\log[H_3O^+] \Rightarrow [H_3O^+] = 10^{-pH}$$

$$\therefore [H_3O^+] = 10^{-2.8} = 1.6 \times 10^{-3} \text{ mol/litre}$$

$$[H_3O^+] = [CH_3COO^-], [CH_3COOH] = 0.145 - 1.6 \times 10^{-3} \\ = 0.143$$

$$K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]} = \frac{(1.6 \times 10^{-3})^2}{0.143} = 1.8 \times 10^{-5}$$

$$pK_a = -\log[1.8 \times 10^{-5}] = 4.75$$

The pH of 0.145M acetic acid(aq) is 2.8. Calculate K_a of acetic acid

1.2 Lecture 2

Concept of pH

Tuesday, September 08, 2020
3:54 PM

Aim: To express the strength of an acid
The strength is always relative.

When an acidic species dissolves in water it releases protons, H^+ . So, how many H^+ it releases decides its strength.

i.e. $[H^+]$ or $[H_3O^+]$ gives quantification of the acid strength in moles/litre.

$$pH = -\log_{10} [H_3O^+]$$

Calculate pH of an acid

01 September 2020
20:56

The pH of 0.145M acetic acid(aq) is
2.8. Calculate K_a of acetic acid

$$\text{pH} = -\log[H_3O^+] \Rightarrow [H_3O^+] = 10^{-\text{pH}}$$
$$\therefore [H_3O^+] = 10^{-2.8} = 1.6 \times 10^{-3} \text{ mol/litre}$$

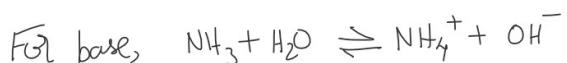
$$[H_3O^+] = [CH_3COO^-], [CH_3COOH] = 0.145 - 1.6 \times 10^{-3} \\ = 0.143$$

$$K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]} = \frac{(1.6 \times 10^{-3})^2}{0.143} = 1.8 \times 10^{-5}$$

$$pK_a = -\log[1.8 \times 10^{-5}] = 4.75$$

Calculating the strength of a base, K_b

01 September 2020
22:12



$$K_b = \frac{[\text{NH}_4^+] [\text{OH}^-]}{[\text{NH}_3]} \quad \text{Now if } K_b \ll 1 \text{ it is a weak base}$$

e.g. $\text{NH}_3 \quad K_b = 1.8 \times 10^{-5}$ Only very few NH_4^+ prevails

So in general, $K_a \ll 1$ or $K_b \ll 1$ indicate weak acid or base

pH : HF 1 mM 10 mM 100 mM

pKa : HF HCl HBr HT
 3.1 -6.0 -9.0 -9.5

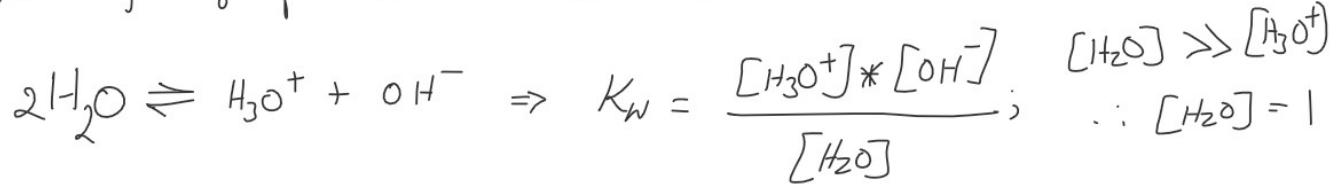
More negative stronger the acid

Note: pH of neutral solution of water is 7. Anything below is acidic & anything above is basic.

Autoprotolysis- Example water

01 September 2020
22:22

Water being amphoteric undergoes autoprotolysis. It is very fast H^+ transfer. But only very few H_2O molecules undergo this.



Given, $pH = 7$. K_w .

$$pH = -\log [H_3O^+] \Rightarrow 10^{-7} = [H_3O^+] = 1 \times 10^{-7} M/L$$

$$\therefore K_w = [1 \times 10^{-7}] [1 \times 10^{-7}] = 10^{-14} \text{ mol/L}$$

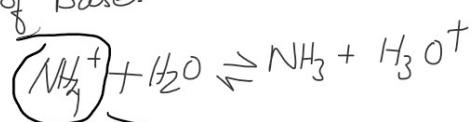
Expressing acidity of bases

01 September 2020
22:31



Expressing acidity of bases

$$K_a K_b = K_w$$



Conjugate

Note. If K_a is large K_b is small \Rightarrow for strong acid acid

K_b of $\text{NH}_3 = 1.8 \times 10^{-5}$ then K_a of NH_4^+ (conjugate)

$$K_a = \frac{K_w}{K_b} = \frac{1 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$$

$$pK = -\log K$$

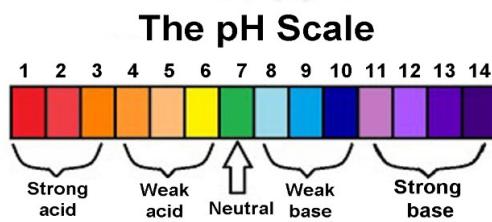
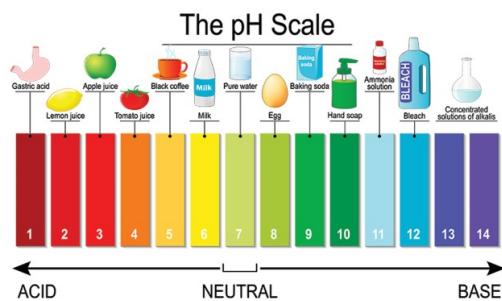
$$\therefore pK_a + pK_b = pK_w \quad / \quad pK_{\text{tot}}$$

Practical pH Scale

Wednesday, September 09, 2020

10:39 AM

$$pH = -\log_{10} [H^+]$$



A pH scale extends from 1 to 14. It is a relative value. Water which is amphoteric & has an ability to auto-protolyze. The pH for this is set at 7.

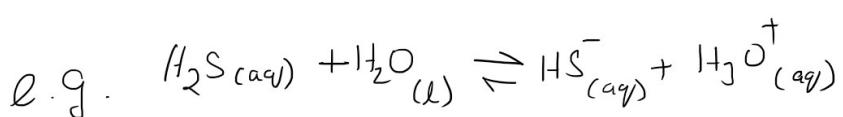
Polyprotic acids

5:22 PM

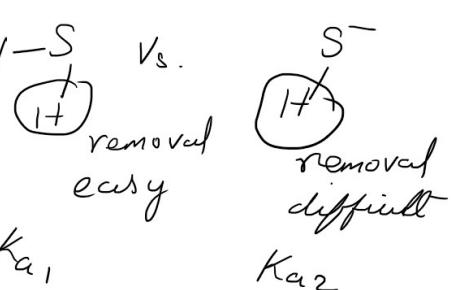
Polyprotic acids lose protons in succession.

Successive deprotonation is progressively less favored.

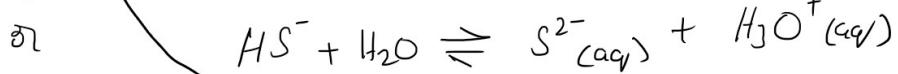
This is due to progressively increasing electrostatic attraction between the bound proton and the negatively charged centre.



$$K_{a_1} = \frac{[\text{HS}^-][\text{H}_3\text{O}^+]}{[\text{H}_2\text{S}]}$$



Always, $K_{a_2} < K_{a_1}$



$$K_{a_2} = \frac{[\text{S}^{2-}][\text{H}_3\text{O}^+]}{[\text{HS}^-]}$$

$K_{a_2} < K_{a_1}$

$\text{p}K_{a_1} < \text{p}K_{a_2}$

Distribution diagram for polyprotic acids, H_3PO_4 as an example

Tuesday, September 08, 2020, 5:43 PM

Representation of the core of different species that are formed during the successive proton transfer equilibria

Triprotic acid, H_3PO_4

fraction of H_3PO_4 molecule present in the solution.

$$f(\text{H}_3\text{PO}_4) = \frac{[\text{H}_3\text{PO}_4]}{[\text{H}_3\text{PO}_4] + [\text{H}_2\text{PO}_4^-] + [\text{HPO}_4^{2-}] + [\text{PO}_4^{3-}]}$$

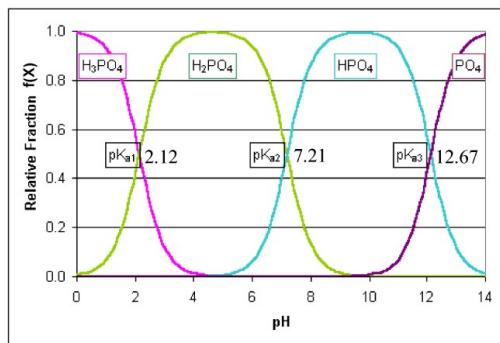
Similar $f(\text{H}_2\text{PO}_4^-)$

$f(\text{HPO}_4^{2-})$ & $f(\text{PO}_4^{3-})$ can be written.

Contd.

Distribution diagram of polyprotic acid

Wednesday, September 09, 2020, 10:10 AM



The concentration of H_3PO_4 is max. at $\text{pH} = 0 \Rightarrow$ Highly acidic condition
It drops to zero at $\text{pH} = 4.2 \Rightarrow$ relatively weakly acidic.

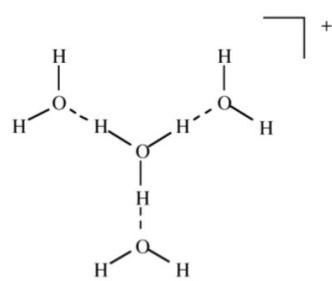
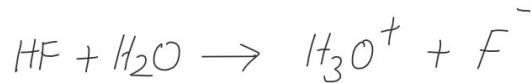
At this $\text{pH} = 4.2$, mostly we will have H_2PO_4^- as the predominant species

At a basic condition 8.8-9.2, HPO_4^{2-} is the predominant species

Note: The $\text{H}_3\text{PO}_4 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{PO}_4^- + \text{H}_3\text{O}^+$ has a $\text{pK}_{\text{a}1} = 2.12$ so $\text{H}_3\text{PO}_4 : \text{SO}_4^{2-} + \text{H}_2\text{PO}_4^-$

Comment on the Structure of Water

01 September 2020, 20:30

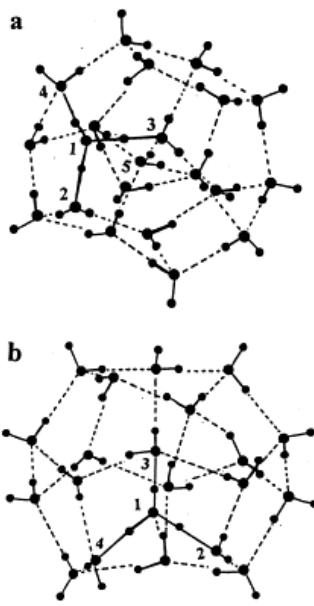


Water is amphoteric

H_3O^+ is simplified

$(H_9O_4)^+$ or $(H_2O)_{21}H^+$ are known

Pentagonal
dodecahedral



$(H_2O)_{21}H^+$

1.3 Lecture 3

L3 S1- Generalized concept of acids and bases

12 September 2020 16:34

Generalized concept of Acid & Base

Acid : Donates a proton or a cation

Accepts a pair of e^- s or anionic Solvents
or oxide ions

Base : Donates an anionic species or
accepts a cation. or donates
a pair of e^- s, oxide ions.

L3 S2

12 September 2020 16:37

Acid generally increases the cation concentration

Base increases the anion concentration

Generalized A-B concept explained in the previous slide

helps correlate A-B strength with

Electron density & Molecular structure.

and empirical observations.

Basicity of Metal Oxides

For e.g., take BeO , MgO , CaO , SrO & BaO

All are in same group and the cation is ⁱⁿ $+2$ oxidation.

BeO is amphoteric but all others below it in the group are

Basic Why??

Here the charge is packed in smaller volume in BeO compared to others. Hence the charge / size ratio impacts the "positiveness" of the cation & thereby the oxide

- Related to Fajula's Polarizability

Acidity of Non-metal oxides.

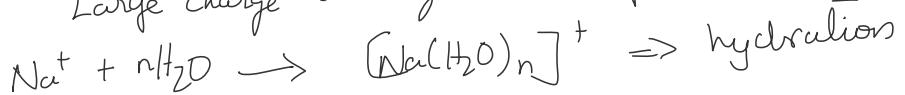
With increasing covalency of the M-O bond the acidity increases

The acidities and basicities are directly related to the electronegativity

Non metal oxides are anhydrides of their corresponding acids

Hydration Vs Hydrolysis

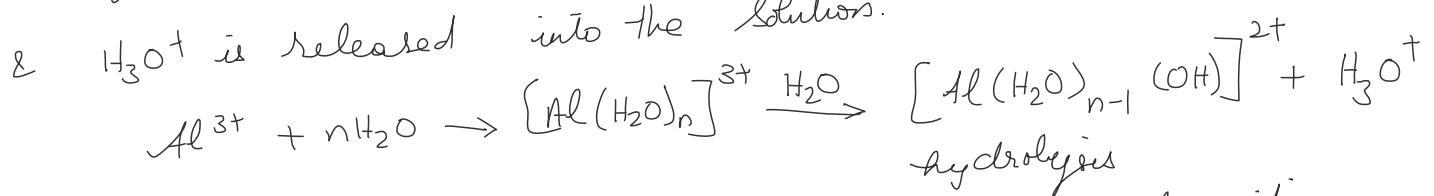
Large charge-to-size ratio for cations increase hydration energies



Contd.. .

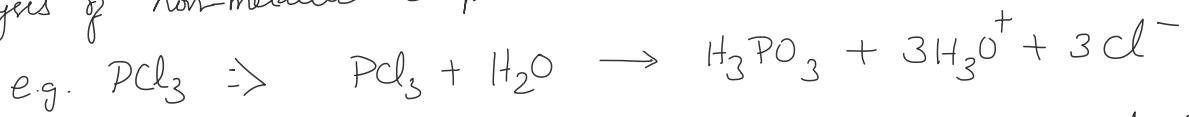
If the charge-to-size ratio is very high e.g. Al^{3+} , then in the hydrate due to the ~~only~~ acidity of the cation the $-\text{O}-\text{H}$ bond ruptures. The generated H_3O^+ & OH^- stays bound to the Cationic Metal

The generated H_3O^+ is released into the solution.



Generally small cations or highly charged cations are highly acidic
 (Be^{2+}) $(\text{Fe}^{3+} \text{ or } \text{Sr}^{4+})$

Hydrolysis of non-metallic compounds

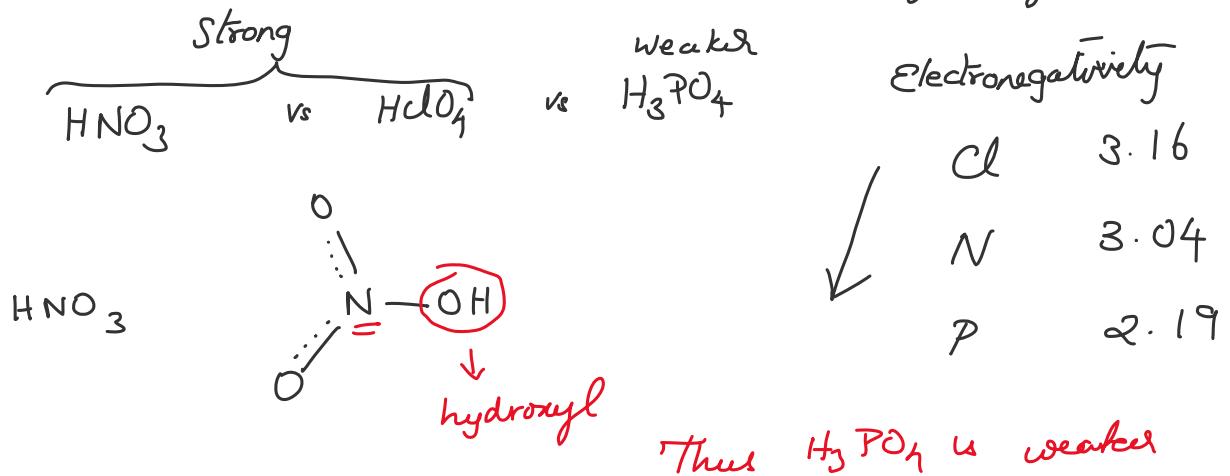


Here the "inductive effect" from the electro-withdrawing Cl species makes the "P" centre highly charged and its size being small makes it very prone to hydrolysis at the P-Cl bond.

How does hydrolysis of PCl_5 compare to PCl_3 ??

Try to get the answer

Acidity of oxyacids . Strength = inductive effect of the central atom
on the "hydroxyl" group

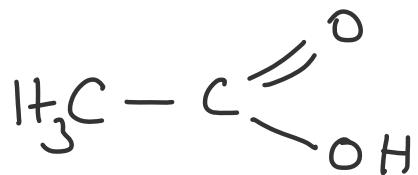


L3 - S8

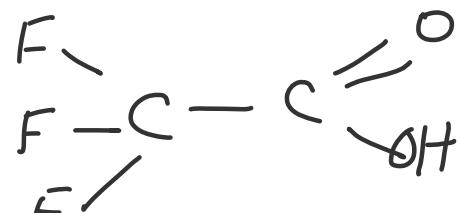
12 September 2020

17:47

Substituent effects

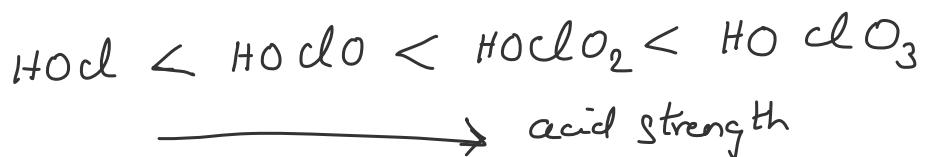


weak acid



stronger acid

Number of 'O' atoms bound to the central atom



$$pK_a = 10.5 - 5n - \chi_x \quad \text{for acids expressed as } X(\text{OH})_m \text{ O}_n$$

where χ_x is the electronegativity

The empirical rule nicely includes both central atom as well as the surrounding atom effects.

L3 - S10

Sunday, September 13, 2020 1:32 PM

Basicity of Substituted Amines.

NH_3 a weak base in water

$-\text{OH}$ or $-\text{NH}_2$ e^- withdrawing \Rightarrow Less basic

pK_b for $\text{NH}_3 = 4.74$, pK_b for $\text{NHT}_2\text{OH} = 7.97$

pK_b for $\text{NHT}_2\text{NH}_2 = 5.77$

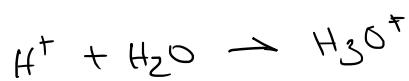
$\text{CH}_3 \quad \text{CH}_3\text{CH}_2 \Rightarrow e^-$ donating

$\text{NH}_2\text{CH}_3 \quad pK_b = 3.36$

$\text{NHT}_2\text{CH}_2\text{CH}_3 \quad pK_b = 3.25$

Charge-to-size ratio the atoms with the smallest size and high charge would be the strongest acid.

H^+ is the highest c-t-s ratio containing species



will never exist or co-exist with a base without reacting

Any species with reactive e^- is a base.

H^- , F^- - bases

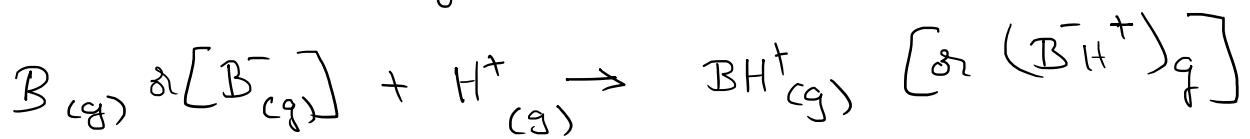
e^- is the strongest base.

There are cases e^- 's can exist alone and become the strongest

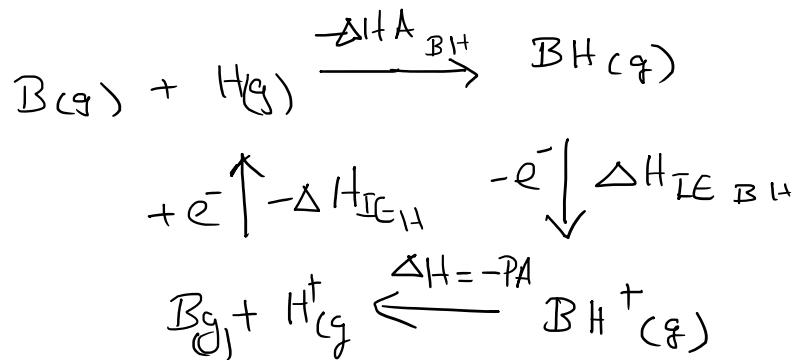
L3 S12

Sunday, September 13, 2020 2:04 PM

Most fundamental measure of basicity = Proton affinity



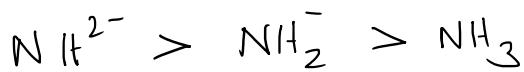
Born-Haber cycle



ion cyclotron resonance Spectroscopy (ICRS)

Proton affinity

N^{3-} has the highest proton affinity



pA decreases

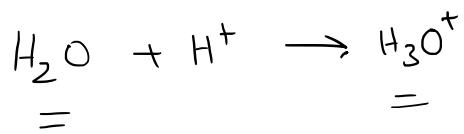
$$\text{NF}_3 = 604 \text{ kJ mol}^{-1}$$

(ΔH)

$$\text{NH}_3 = 872 \text{ kJ mol}^{-1}$$

$$(\text{CH}_3)_3\text{N} = 974 \text{ kJ mol}^{-1}$$

H_3O^+ - its ability to hold a proton



$$\text{HF} \quad \text{PA}_{\text{F}^-} = 1554 \text{ kJ mol}^{-1}$$



the more endothermic the weaker the acid is



$$\text{PA}_{\text{CH}_3\text{COO}^-} = +1459 \text{ kJ/mol} \quad \text{PA}_{\text{FCOO}^-} = +1351 \text{ kJ/mol}$$

If e^- affinity is going to be considered as the analogue of H^+ affinity.

The e^- affinity should provide an inherent gas-phase measure of acidity for any non-protonic gaseous species.

The e^- affinity $K \rightarrow K^+ + e^- \Rightarrow$ ionization energy of K .



Drago and co-workers

$$\Delta H \text{ with contributions from acids & bases}$$

$$-\Delta H = (E_A E_B) + (C_A C_B)$$

Electrostatic contributions
Covalent contributions

ΔH - enthalpy of a Lewis A-B adduct formation

Pyridine & Iodine reaction

$$E_B = 1.78$$

$$f = 0.5$$

$$-\Delta H_{\text{calc}} = E_A E_B + C_A C_B$$

$$C_B = 3.54$$

$$C = 2.0$$

$$= (0.5 \times 1.78 + 2 \times 3.54)$$

$$= 7.97 \text{ kcal mol}^{-1} \text{ or } 33.3 \text{ kJ mol}^{-1}$$

$$-\Delta H_{\text{exp}} = 7.8 \text{ kcal mol}^{-1} \text{ or } 32.6 \text{ kJ mol}^{-1}$$

Table 8.5 Acid and base parameters^a

| Acid | E_A | C_A | R_A | Acid | E_B | C_B |
|--------------------------------------|-------|-------|-------|---------------------------------------|------------------|-------------------|
| H_2 | 0.50 | 2.00 | — | H^+ | 45.00 | 13.03 |
| H_2O | 1.54 | 0.13 | 0.20 | CH_3^+ | 19.70 | 12.61 |
| SO_4^{2-} | 0.56 | 1.52 | 0.85 | Li^+ | 11.72 | 1.45 |
| HF^+ | 2.03 | 0.30 | 0.47 | K^+ | 3.78 | 0.10 ^b |
| HCN^+ | 1.77 | 0.50 | 0.54 | NO_3^- | 0.1 ^b | 6.86 |
| CH_3OH | 1.25 | 0.75 | 0.39 | NH_3^{+b} | 4.31 | 4.31 |
| H_2S^2- | 0.77 | 1.46 | 0.56 | $(\text{CH}_3)_2\text{NH}_2^{-b}$ | 3.21 | 0.70 |
| HCl^b | 3.69 | 0.74 | 0.55 | $(\text{CH}_3)_2\text{N}^+$ | 1.96 | 2.36 |
| $\text{C}_2\text{H}_5\text{OH}$ | 2.27 | 1.07 | 0.39 | $\text{C}_2\text{H}_5\text{NH}^+$ | 1.81 | 1.33 |
| $(\text{CH}_3)_2\text{COH}$ | 1.36 | 0.51 | 0.48 | $(\text{C}_2\text{H}_5)_2\text{NH}^+$ | 2.43 | 2.05 |
| HCCl_3 | 1.49 | 0.46 | 0.45 | $(\text{CH}_3)_2\text{NH}^+$ | 2.60 | 1.33 |
| $\text{CH}_3\text{CO}_2\text{H}^b$ | 1.72 | 0.86 | 0.63 | H_2O^+ | 13.27 | 7.89 |
| $\text{CF}_3\text{CH}_2\text{OH}$ | 2.07 | 1.06 | 0.38 | $(\text{H}_2\text{O}_2)\text{H}^+$ | 11.39 | 6.03 |
| $\text{C}_2\text{H}_5\text{OH}$ | 1.34 | 0.69 | 0.41 | $(\text{H}_2\text{O}_2)\text{H}^+$ | 11.21 | 4.66 |
| $i\text{-C}_4\text{H}_9\text{OH}$ | 1.14 | 0.90 | 0.46 | $(\text{H}_2\text{O}_2)\text{H}^+$ | 10.68 | 4.11 |
| PF_5^+ | 0.61 | 0.56 | 0.87 | $(\text{CH}_3)_2\text{Sn}^+$ | 7.05 | 3.15 |
| $\text{Bi(OCH}_3)_3^+$ | 0.54 | 1.22 | 0.84 | $(\text{C}_2\text{H}_5)_2\text{N}^+$ | 11.88 | 3.49 |
| AsF_6^- | 1.48 | 1.14 | 0.78 | $(\text{CH}_3)_2\text{NH}^+$ | 2.18 | 2.38 |
| Fe(CO)_6^b | 0.10 | 0.27 | 1.00 | | | |
| CH_3^+ | 1.32 | 0.91 | 0.27 | | | |
| $\text{B}(\text{C}_2\text{H}_5)_3^+$ | 1.70 | 2.71 | 0.61 | | | |

Possibility of adduct formations
using these values can be done.

1.4 Lecture 4

$\Delta H^\circ_{\text{exp}} = -32.6 \text{ kJ/mol}$

14

Bulky substituent group:

Rotate randomly & occupying huge volume of space. These volumes overlap unacceptable "F-strain"

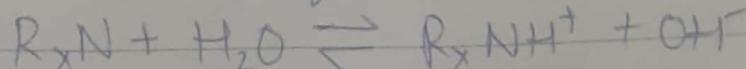
R_3N bonds well with BF_3 when 'N' centre adopts a tetrahedral geometry- sp^3 hybridization

Every R-group on "N" opens up the bond angle values $> 109^\circ$. They tend to increase the "s" character of N-R bonds. But it weakens "s" character of orbit when the lone pair is residing. Hence it is more 'p' in character, which is orthogonal to the BF_3 's orbital hence they overlap poorly. (called B-strain)

| | H_3N | $(\text{CH}_3)_2\text{NH}_2$ | $(\text{CH}_3)_2\text{HN}$ | $(\text{CH}_3)_3\text{N}$ |
|--------|----------------------|------------------------------|----------------------------|---------------------------|
| pK_b | 4.75 | 3.36 | 2.83 | 1.3 |
| PA (D) | 872 | 919 | 954 | 974 |

PAGE NO. 10 Date: 13/10/2018
Ans. No. 13
Name: Koushik

→ Why is pK_b of $(\text{CH}_3)_3\text{N}$ higher than dimethylamine or why is it a weaker base?



The charged molecules get very efficiently solvated by H_2O molecules through H-bonding

∴ $\text{R}_3\text{NH}^+ < \text{R}_2\text{NH}_2^+ < \text{RNH}_3^+$ → solvation energy
Opp. trend compared to "Inductive effect"
when " H " in ammonia is replaced by CH_3 , the hydration energy is lowered by 30 KJ/mol

→ Solvent levelling

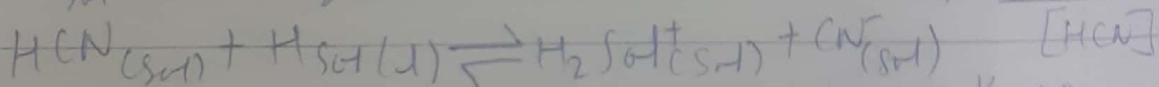
Any species that can exhibit autoprotolysis
 $\text{HI} \rightleftharpoons \text{H}^+ + \text{I}^-$ which is stronger acid in water?

Water becomes levelling solvent as it dissociates both HI & HBr . Any acid stronger than H_3O^+ gets levelled in water.

We choose a solvent that can make HF & HBr behave as weak acid - e.g. acetic acid

H_{sol} is a general solvent

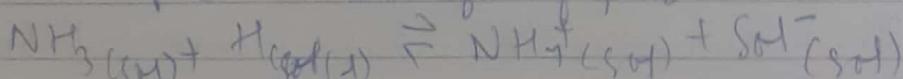
$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$



→ $\text{KNH}_2_{(\text{sol})}$ & $\text{Li}_2(\text{CH}_3)_4_{(\text{sol})}$ they get levelled by water

\Rightarrow acid instead of base
otherwise

Clarified as strong if $pK_b < 0$



$$pK_a + pK_b = pK_{\text{sol}} \Rightarrow pK_a > pK_{\text{sol}} \text{ in } \text{H}_{\text{sol}}$$

→ Effective pH in water (table in note)

for All acids with $pK_a < 0$ will be levelled

All bases with $pK_b > 0$ will be levelled

All acids and bases within the pK_a window of $pK_a = 0$ to pK_{sol} will not be levelled

DMSO has a wide window in discriminating acid & base. Water has narrow window (then why it's preferred)

1.5 Lecture 5a

Why is water the universal solvent for many acid-base reactions?

The answer lies in the solvation effects.

Rationalized from an "electrostatic model" where

- ① Solvent - continuous dielectric medium
- ② Solvation of a gas phase species is exothermic
- ③ Magnitude of $\Delta H_{\text{sol}}^{\ominus}$ depends on radius 'r' of the ion and the permittivity ' ϵ_i ' of the solvent
- ④ $\Delta F_{\text{sol}}^{\ominus}$ depends also on potential to H-bond.

$\Delta G_i^{\ominus} = \Delta H_i^{\ominus}$ in gas phase

Entropy of gas phase ion is negligible $\therefore \Delta G_i^{\ominus} = \Delta H_i^{\ominus}$ in gas phase

But this is not negligible in solvent.

In solvent, $\Delta G_{\text{solv}}^{\ominus}$ is given by an electrostatic model

$$\Delta G_{\text{solv}}^{\ominus} = - \frac{N_A e^2 \epsilon}{8\pi \epsilon_0} \left(1 - \frac{1}{\epsilon_r} \right)$$

$$\epsilon = \frac{e^2}{r}$$

\Downarrow
electrostatic
parameters

ϵ_0 = permittivity
in Vacuum

ϵ_r = relative
permittivity
 \Downarrow
dielectric
constant



$$\Delta G_{\text{solv}}^{\ominus} \propto \epsilon$$

Small & highly charged ions
get high solvation stability

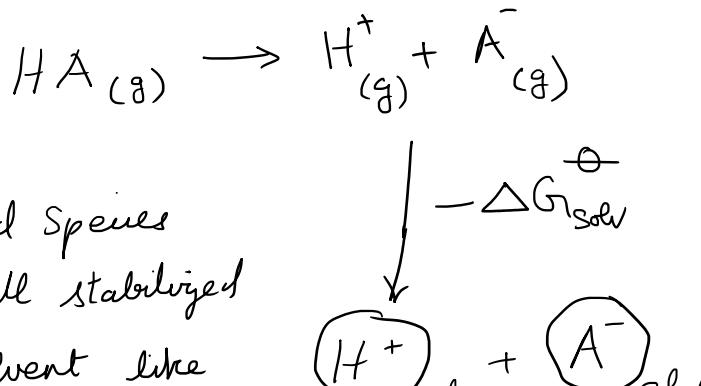
Large ϵ_r gives large $-\text{ve } \Delta G$

\therefore Water with $\epsilon_r = 80$ is
super solvent compared to many
organic ones with ϵ_r as low as 2.

L5 S3

Wednesday, September 23, 2020 5:18 PM

Born's method or Equation



Charged Species
are well stabilized
by solvent like
water - capable of
H-bonding

This is true for polar solvents.

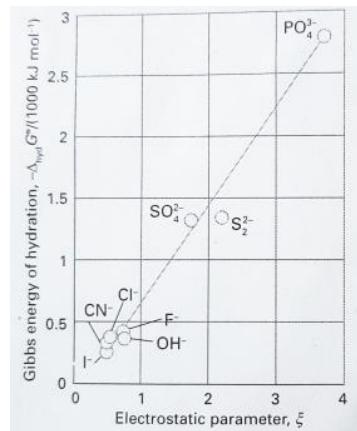
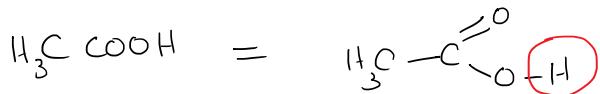


Figure 4.3 The correlation between $\Delta_{\text{solv}} G^\ominus$ and the electrostatic parameter ξ of selected anions. To obtain ξ as a small dimensionless number we have used $\xi = 100z^2/(r/\text{pm})$.

This figure shows how highly charged small ions gain high $\Delta G_{\text{solv}}^{\ominus}$ as the ξ increases.

Classifying acids:

A donatable proton is called "acidic proton"



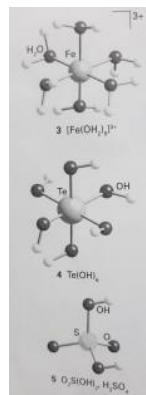
Three class of acidic protons:

① An aqua acid, acidic proton on a water molecule coordinated to a metal or a central ion e.g. $\text{Fe}(\text{OH}_2)_6^{3+}$

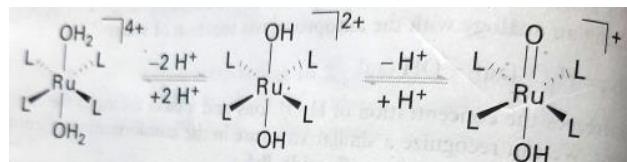
② A hydroxo acid, acidic proton is on a hydroxyl group without any neighbouring "oxo" group on the central atom

e.g. $\text{Te}(\text{OH})_6$ acidic proton is on a hydroxyl group with an oxo group attached

③ An Oxoacid, acidic proton is on a hydroxyl group with an oxo group attached to the same central atom e.g. HNO_3 , H_2SO_4 etc.



The three classes of acids can be generated successively from a single species e.g. A d-block metal in intermediate oxidation state.



Aqua acids are formed by central atoms in low oxid. states, e.g. s & d-block metals and metals left to the p-block.

Oxo acids are formed by central atoms in high oxid. state. Elements to the right of p-block.

Strength of acid $\propto \frac{Z}{r^+}$

but if deviations occur it points to covalency.

Metal cation is a sphere of radius r^+ & carries Z^{+ve} charge

This is ionic model.

Looking at the graph you can see

Cr^{3+} , Fe^{2+} are closer to the predicted

acidities - linear line.

While Fe^{3+} , Tl^{3+} etc. deviate a lot. This means these ions deviate the proton even more. Or they are more acidic. This is bcs the even more. Or they are more acidic. This is bcs the

$\text{M}-\text{O}(\text{H})$ -acidic proton
↳ more covalent. The positive charge is disposed over the ligand oxygen too.

Thus for d- and p-block elements like Cu^{2+} & Sr^{4+} known to form

covalent M-O bonds the acidity is higher than predicted by ionic model.

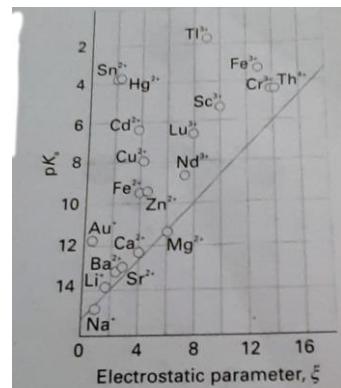


Figure 4.5 The correlation between acidity constant and the electrostatic parameter ξ of aqua ions.

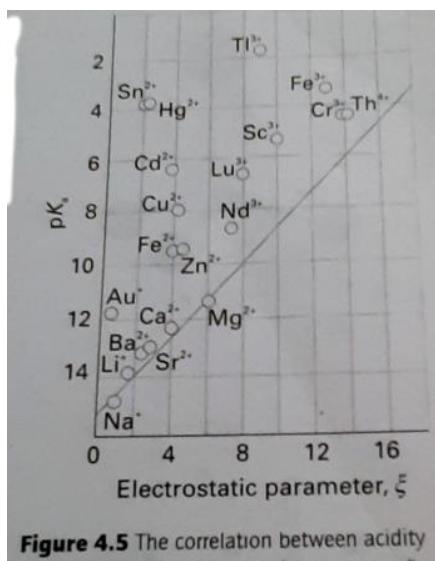


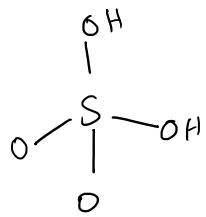
Figure 4.5 The correlation between acidity constant and the electrostatic parameter ξ of aqua ions.

Comparing $\text{Hf}(\text{H}_2\text{O})_6\text{I}^{3+}$ vs. $\text{Hg}(\text{OH}_2)^{2+}$

While the $\text{Hf}(\text{H}_2\text{O})_6\text{I}^{3+}$ obeys the ionic model due to its high charge/size ratio.

But Hg^{2+} is a complete failure of ionic model. This is because the complex has a large transfer of +ve charge to Oxygen due to the covalent nature of $\text{Hg}-\text{O}$ bonds.

O_xO acids: Example sulfurous acid

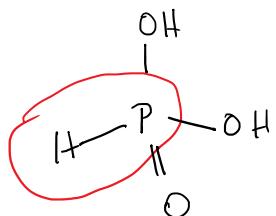


Substituents on hydroxyl group sites.

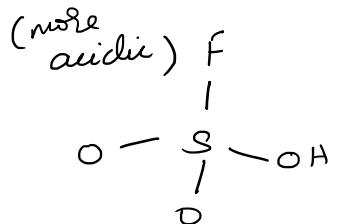
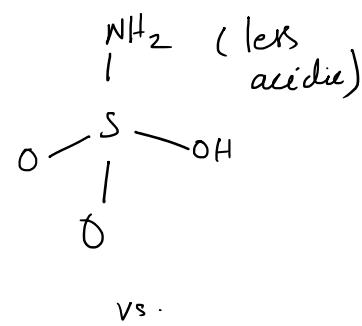
This structure is not always found.

Exception:

Phosphorous acid (H_3PO_3)



↓
Not acidic as 'P' is much less electronegative than 'O'.



L5 S9

Monday, October 05, 2020 11:30 AM

Some points on oxoacids:

① Acids with most 'oxo' groups are stronger.

e.g. HNO_3 is stronger than HNO_2

H_2SO_4 is stronger than H_2SO_3

② Resonance Stabilization of the conjugate

e.g. H_2SO_4 vs. H_2SO_3^-

\downarrow
3-resonance str. 2-resonance str.

③ Pauling's Empirical rule for oxoacids:

i) For $\text{O}_p\text{E}(\text{OH})_q$, $pK_a = 8 - 5p$

ii) The successive pK_a of polyprotic acids increase by "5" units.

Pauling rules contd ...

Rule 1 predicts neutral hydronium acids like $\text{Ti}(\text{OH})_4$ will have a $pK_a \approx 8$. Those with one oxo group like H_2CO_3 will have a $pK_a \approx 3$. Those with two oxo groups like HNO_3 will have a $pK_a \approx -2$.

These rules are only approximate. //

L5 S11

Monday, October 05, 2020 11:44 AM

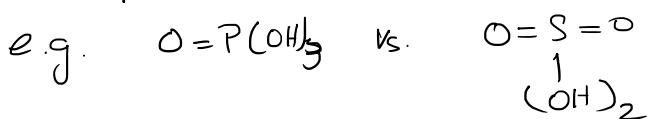
Looking at the table where acids are arranged w.r.t "p" values.

① The variation of acid strength shows the group is not much.

② Across the period it is significant

The effect of change in oxidation state of the central atom is taken care by the # of O atoms attached to it.

For example, the Group 15 with Oxid. state of +5 requires "one" O atoms, while the Group 16 with oxid. state of +6 requires "two" O atoms



| The structure and pK_a values of oxoacids | | | | |
|--|---|--|---|---|
| $p=0$ | $p=1$ | $p=2$ | $p=3$ | |
| $\text{HO}-\text{Cl}$ 7.2 | $\text{HO}-\overset{\text{O}}{\underset{\text{C}}{\text{ }}}-\text{OH}$ 3.6 | $\text{HO}-\overset{\text{O}}{\underset{\text{N}}{\text{ }}}-\text{OH}$ -1.4 | | |
| | | | | |
| $\text{HO}-\overset{\text{O}}{\underset{\text{Si}}{\text{ }}}-\text{OH}$ 10 | $\text{HO}-\overset{\text{O}}{\underset{\text{P}}{\text{ }}}-\text{OH}$ 2.1, 7.4, 12.7 | $\text{HO}-\overset{\text{O}}{\underset{\text{Cl}}{\text{ }}}-\text{O}$ 2.0 | $\text{HO}-\overset{\text{O}}{\underset{\text{S}}{\text{ }}}-\text{OH}$ -2.0, 1.9 | $\text{O}-\overset{\text{O}}{\underset{\text{Cl}}{\text{ }}}-\text{OH}$ -10 |
| | | | | |
| $\text{HO}-\overset{\text{O}}{\underset{\text{Te}}{\text{ }}}-\text{OH}$ 7.8, 11.2 | $\text{HO}-\overset{\text{O}}{\underset{\text{I}}{\text{ }}}-\text{OH}$ 1.6, 7.0 | $\text{HO}-\overset{\text{O}}{\underset{\text{P}}{\text{ }}}-\text{OH}$ 1.8, 6.6 | $\text{O}-\overset{\text{O}}{\underset{\text{Cl}}{\text{ }}}-\text{OH}$ -1.0 | |
| | | | | |
| $\text{HO}-\overset{\text{O}}{\underset{\text{B}}{\text{ }}}-\text{OH}$ 9.1 ^t | $\text{HO}-\overset{\text{O}}{\underset{\text{As}}{\text{ }}}-\text{OH}$ 2.3, 6.9, 11.5 | $\text{HO}-\overset{\text{O}}{\underset{\text{Se}}{\text{ }}}-\text{O}$ 2.6, 8.0 | | |
| | | | | |

* is the number of non-protonated O atoms

^t See Table 5-1

Some anomalies answered through Pauling's

① H_2CO_3 the pK_a is observed from experiment to be ≈ 6.4

But the Pauling's rule predicts $\text{pK}_a \approx 3.0$

This is answered by considering the poor dissociation.

Only 1% of dissolved CO_2 stays as H_2CO_3 , if this is considered, the value would be $\text{pK}_a \approx 3.6$, which agrees.

② For H_2SO_3 reported experimental value is ≈ 1.8 .

But expected is ≈ 3.0 .

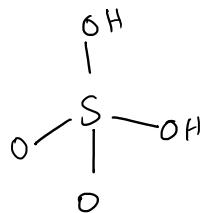
This is because of the other species such as HSO_3^- , S^+ , $\text{S}_2\text{O}_5^{2-}$ which all make the solution more acidic. Other examples, CO & OSO_4^{2-}

1.6 Lecture 5b

L5 S8

Monday, October 05, 2020 11:06 AM

O_xO acids: Example sulfurous acid

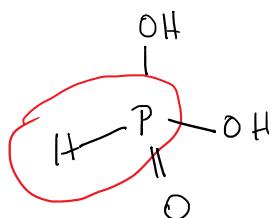


Substituents on hydroxyl group sites.

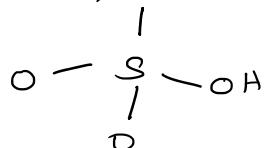
This structure is not always found.

Exception:

Phosphorous acid (H_3PO_3)



(more acidic) F



vs.

↓
Not acidic as 'P' is much less electronegative than 'O'.



Audio recording started: 12:36 PM Wednesday, October 07, 2020

Some points on oxoacids:

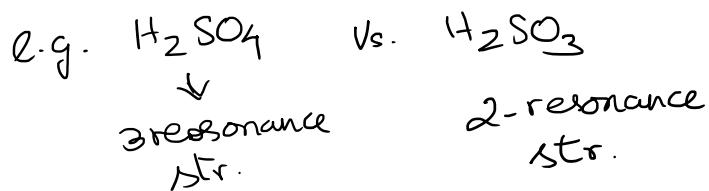
① Acids with most 'oxo' groups are stronger.

e.g. HNO_3 is stronger than HNO_2

H_2SO_4 is stronger than H_2SO_3



② Resonance Stabilization of the Conjugate



③ Pauling's Empirical rule for oxoacids:

i) For $\text{O}_p\text{E}(\text{OH})_q$, $\text{pK}_a = 8 - 5p$

ii) The successive pK_a of polyprotic acids increase by "5" units.

L5 S10

Monday, October 05, 2020 11:39 AM

Pauling rules contd ...

Rule 1 predicts neutral hydron acids like $\text{Ti}(\text{OH})_4$ will have a $pK_a \approx 8$. Those with one Oxo group like H_2CO_3 will have a $pK_a \approx 3$. Those with two Oxo groups like HNO_3 will have a $pK_a \approx -2$.

These rules are only approximate. //



L5 S10

Audio recording started: 1:02 PM Wednesday, October 07, 2020

L5 S11

Monday, October 05, 2020 11:44 AM

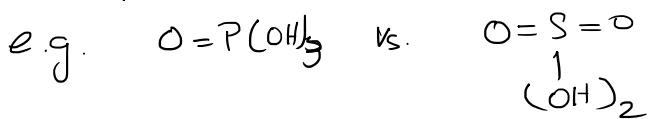
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| | | | | |
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| | | | | |
| $\text{HO}-\overset{\text{O}}{\underset{\text{Te}}{\text{ }}}-\text{OH}$ 7.8, 11.2 | $\text{HO}-\overset{\text{O}}{\underset{\text{I}}{\text{ }}}-\text{OH}$ 1.6, 7.0 | $\text{HO}-\overset{\text{O}}{\underset{\text{P}}{\text{ }}}-\text{OH}$ 1.8, 6.6 | $\text{HO}-\overset{\text{O}}{\underset{\text{Cl}}{\text{ }}}-\text{OH}$ -1.0 | |
| | | | | |
| $\text{HO}-\overset{\text{O}}{\underset{\text{B}}{\text{ }}}-\text{OH}$ 9.1 ^t | $\text{HO}-\overset{\text{O}}{\underset{\text{As}}{\text{ }}}-\text{OH}$ 2.3, 6.9, 11.5 | $\text{HO}-\overset{\text{O}}{\underset{\text{Se}}{\text{ }}}-\text{OH}$ 2.6, 8.0 | | |
| | | | | |

* is the number of non-protonated O atoms

^t See Table 5.1



L5 S11

Audio recording started: 1:20 PM Wednesday, October 07, 2020

Audio recording started: 1:25 PM
Wednesday, October 07, 2020

Some anomalies answered through Pauling's

① H_2CO_3 the pK_a is observed from experiment to be ≈ 6.4

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Only 1% of dissolved CO_2 stays as H_2CO_3 , if this is considered, the value would be $\text{pK}_a \approx 3.6$, which agrees.

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But expected is ≈ 3.0 .

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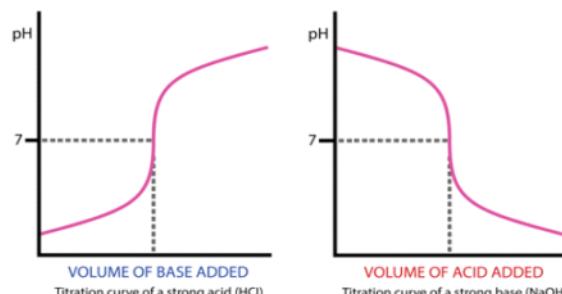
1.7 Lecture 6

Lecture 6 - S1

24 October 2020 19:02

A simple titration curve.

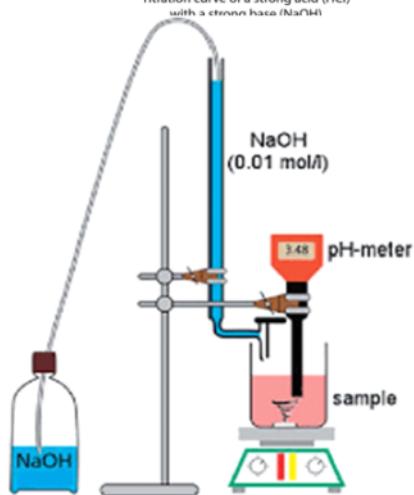
- ① pH rises slowly and
- ② increases rapidly at equivalence point.



- ③ It again becomes a gradual rise once we go past equivalence point.

$$\text{Equivalence point} \Rightarrow [\text{H}_3\text{O}^+] = [\text{OH}^-]$$

For strong acid vs. strong base Equivalence point = 7



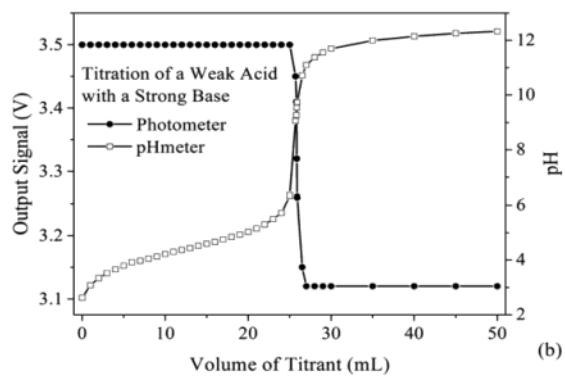
When equivalence point is reached the indicator changes color

Titration weak acid vs. strong base

a)

weak base vs. Strong acid

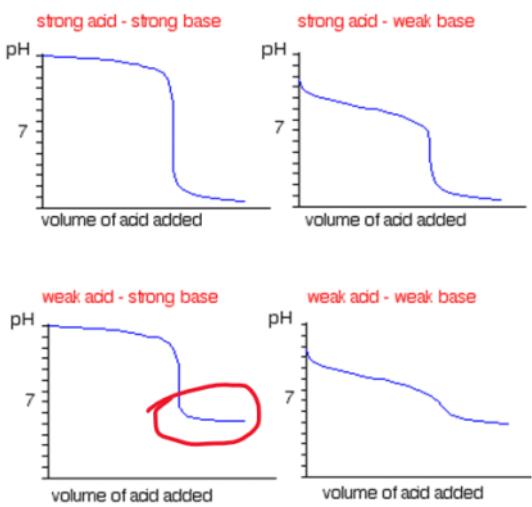
- ① The profile or the shape of the curve will be the same
- ② equivalence point changes
- ③ Weak acid - strong base $\Rightarrow E.P > 7.0$
- ④ Weak base - strong acid $\Rightarrow E.P < 7.0$



Lecture 6 - S3

24 October 2020 19:06

Titration curves & Comparisons



Consider a case where we add acetic acid to NaOH

When the NaOH is in excess the curve will look same as how it will look for HCl addition but after crossing equivalence point the conc. of CH_3COO^- increases changing the curve to be different.

Change: Part EP,

we have $\text{CH}_3\text{COOH} + \text{CH}_3\text{COONa} \Rightarrow$ Buffer results change in pH.

Lecture 6 - S4

24 October 2020 19:06

02 October 2020
17:17

Buffer : A buffer is a solution that keeps the pH unchanged when acid or base is added.

Indicator is a special case - a colored buffer.

Buffer solution can be prepared for any pH range.

Buffer has a pH range and capacity before the pH of the overall solution changes.

This is important to study several biological and chemical processes at a fixed pH.

For example, the kinetics of a reaction can be studied at a pH. Stability of intermediates at specific pH.

Lecture 6 - S5

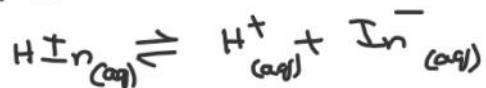
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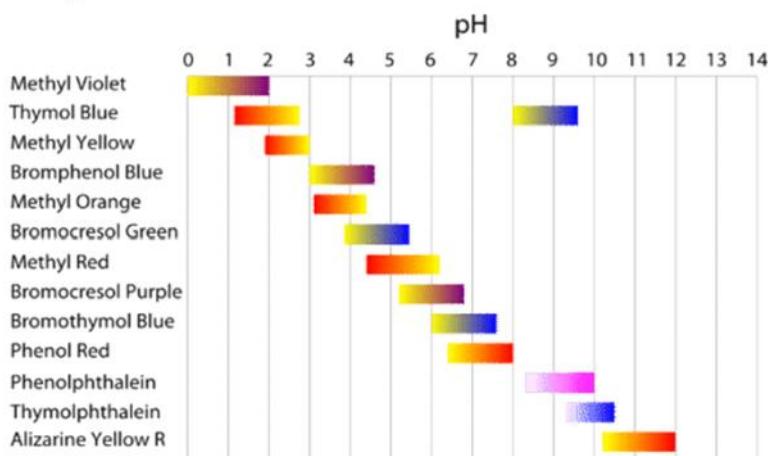
Indicators \rightarrow they are buffers. They resist pH change in a small pH window ~ 2.0 .

The protonated indicator = HIn ; deprotonated = In^-

We can write



Now if a strong acid is added in small amounts the In^- reacts and generates HIn and this keeps the overall pH of the solution the same.



Different Indicators operate in different pH windows and you can see that typically all have a pH window ~ 2.0

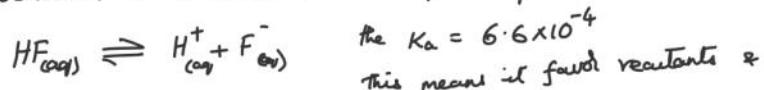
Lecture 6 - S6

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L6 S7

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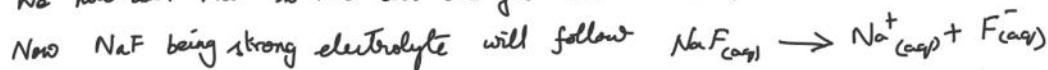
Take HF and NaF as an example to create a buffer solution.
Being a weak acid HF in water dissociates partially.



$K_a = 6.6 \times 10^{-4}$

This means it favours reactants & not the products.

Now add NaF to this till we get the desired pH and volume of buffer.



Since Na^+ is cation from a strong base $NaOH$ it will not react, so won't change pH. But F^- will be a stronger base & can react to form HF.

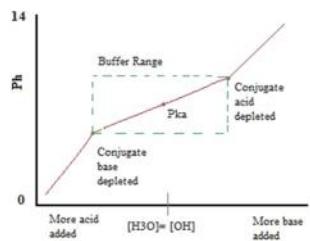
This would mean by Le Chatelier's principle the presence of F^- will make HF even less dissociative.

Thus there will be good amount of both HF & F^- in the medium.

This buffering action is seen from the titration curve.

Note: This works because the K_a for $F^- + H_3O^+ = 1.5 \times 10^{-3}$

Hence it will resist pH change when acid is added & will work until all the F^- is consumed.



Lecture 6 - S7

24 October 2020 19:09

02 October 2020
18:54

Henderson - Hasselbach equation

This equation helps us to experimentally determine the pK_a of an acid or base.

$$pH = pK_a + \log_{10} \left[\frac{\text{Conj. base}}{\text{weak acid}} \right]$$

It is derived from acid dissociation constant.



$$\text{Now, } K_a = \frac{[H_3O^+][A^-]}{[HA]} \Rightarrow [H_3O^+] = \frac{K_a[H_A]}{[A^-]}$$

$$\text{Taking log, } \log[H_3O^+] = \log K_a + \log \frac{[HA]}{[A^-]}$$

$$\text{Substituting again, } -\log[H_3O^+] = -\log K_a + \log \frac{[A^-]}{[HA]} \rightarrow \text{skipped}$$

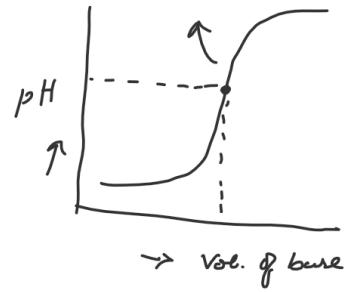
$$\text{By definition, } pH = pK_a + \log \frac{[A^-]}{[HA]}$$

When $[A^-] = [HA]$ the acid is 50% dissociated & then $pH = pK_a$

This does not work well at high dilutions as water autoproteolysis kicks in
early

Experimental
 $pH = pK_a$

50% HA : $50\% A^-$



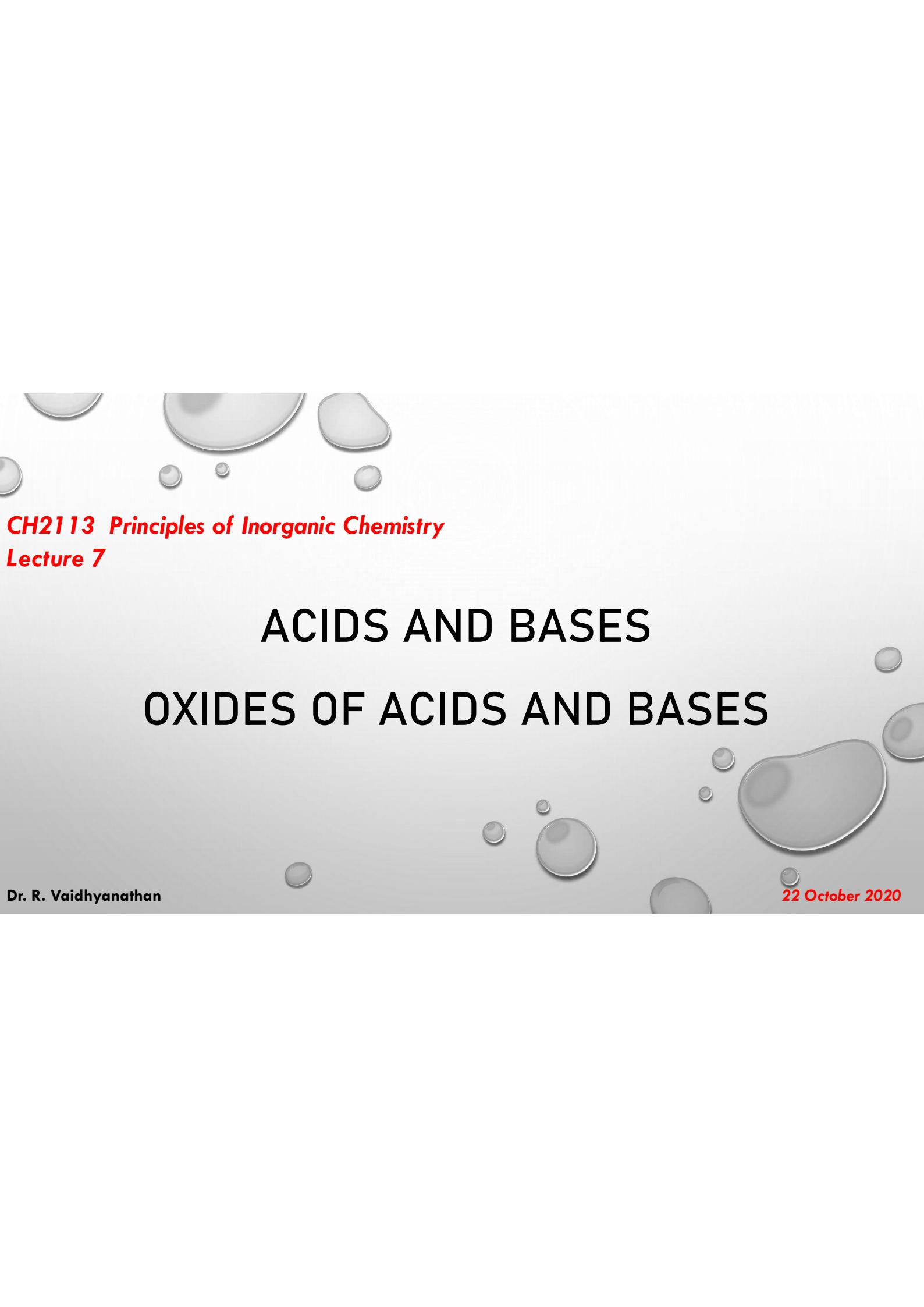
Thus when conc. reaches 1×10^{-5} mol/litre or lower it fails, pH deviates significantly.

H-H equations work well

when conjugate base/acid ratio is between 0.1 to 10

Also, when the molarity of the buffer is 100 times greater than K_a .

1.8 Lecture 7



CH2113 Principles of Inorganic Chemistry
Lecture 7

ACIDS AND BASES

OXIDES OF ACIDS AND BASES

Dr. R. Vaidhyanathan

22 October 2020

Three types of acids

1. Aqua acids, $[M(H_2O)_n]^{x+}$
2. Hydroxo acids, $[M(OH)_n]$
3. Oxoacid, $[O_yM(OH)_x]$

Refer to Lecture 5.

Anhydrous oxides

Oxoacids are derived from deprotonation of aqua acids. Corollary- we can consider aqua acids and oxoacids as being generated from the hydration of the oxides of the central atom.

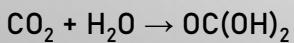
Oxides can be classified as acids and bases and can be correlated with the location in the periodic table

Acidic oxides

An acidic oxide upon dissolution in water, binds to an H₂O and releases proton into the solvent

Non-metallic elements generally form acidic oxides

Example,

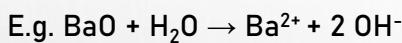


Note: Acidic oxide can react with an aqueous base to form acid.

Basic oxide

A basic oxide dissolved in water, grabs or abstracts a proton.

Metallic oxides are generally basic



Note: A basic oxide reacts with acid to neutralize it



Many properties of oxides are related to their acidic or basic character. This helps predict a wide range of properties

In a number of cases, the basic oxides are largely ionic while the acidic oxides are covalent in character.

Acidic oxides form volatile covalent halides

Basic oxides form solid ionic halides

There are elements that lie right in between acidic and basic oxide forming central elements- these are amphoteric

An amphoteric oxide is an oxide that reacts with both acids and bases.

E.g. aluminium

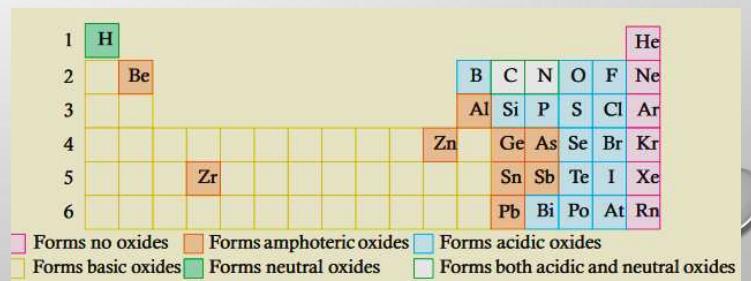
Write the equations for the reaction of Al_2O_3 with acid and base.

Amphotermism is observed for small sized elements in Group 2 and 13

E.g. BeO , Al_2O_3 and Ga_2O_3

The table below shows the elements that form amphoteric oxides in their most stable characteristic group oxidation state

| IA | IIA | IIB | IIIA | IVA | VA | VIA | VIIA |
|--------|-----|-----|------|------------|----|-----|------|
| Li | Be | | B | C | N | O | F |
| Na | Mg | | Al | Si | P | S | Cl |
| K | Ca | Zn | Ga | Ge | As | Se | Br |
| Rb | Sr | Cd | In | Sn | Sb | Te | I |
| Cs | Ba | Hg | Tl | Pb | Bi | Po | At |
| BASIC | | | | AMPHOTERIC | | | |
| ACIDIC | | | | | | | |



Important guidelines:

The onset of amphoterism correlates to the significant degree of covalent character in the central atom-Oxygen bond.

Because the metal ion is small and strongly polarizing – eg. Be²⁺

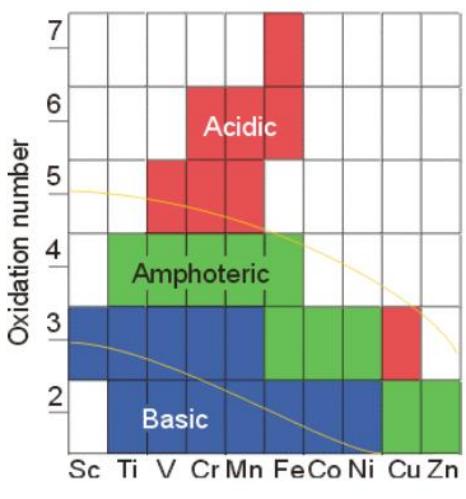
Or because the metal ion gets polarized strongly by the oxygen atom bound to it- eg. Sb

In transition metals, the amphotericism is dependent on the oxidation state of the metal.

| IA | IIA | IIB | IIIA | IVA | VA | VIA | VIIA |
|-------|-----|-----|------------|-----|----|--------|------|
| Li | Be | | B | C | N | O | F |
| Na | Mg | | Al | Si | P | S | Cl |
| K | Ca | Zn | Ga | Ge | As | Se | Br |
| Rb | Sr | Cd | In | Sn | Sb | Te | I |
| Cs | Ba | Hg | Tl | Pb | Bi | Po | At |
| BASIC | | | AMPHOTERIC | | | ACIDIC | |

| | | | | | | | | |
|---|----|--|----|----|----|----|----|----|
| 1 | H | | | | | | | He |
| 2 | Be | | B | C | N | O | F | Ne |
| 3 | | | Al | Si | P | S | Cl | Ar |
| 4 | | | Zn | | Ge | As | Se | Br |
| 5 | Zr | | | | Sn | Sb | Te | I |
| 6 | | | | | Pb | Bi | Po | At |
| | | | | | | | | Rn |

█ Forms no oxides
 █ Forms amphoteric oxides
 █ Forms acidic oxides
█ Forms basic oxides
 █ Forms neutral oxides
 █ Forms both acidic and neutral oxides



Oxidation states for which TM show amphoteric Oxide character.

From Titanium to Iron, they all are amphoteric in +4 oxidation state.

Oxidation states higher than this show acidic oxides

Oxidation states lower than +4 show basic oxides

The elements to the right of the block form amphoteric oxides in lower oxidation state – e.g. Cu and Zn

While Co and Ni form amphoteric oxides in +3 oxidation state

Typically metal when in higher oxidation state (+4 and above) tend to polarize the bonds with oxygen more making it covalent. Hence acidic.

Acidity and basicity related to the central atom's position in periodic table and the Number of oxygen bound to the it.

| Formula | Na_2O | MgO | Al_2O_3 | SiO_2 | P_2O_5 | SO_3 | Cl_2O_7 |
|--------------|-------------------------|--------------|-------------------------|----------------|--|----------------|---|
| Ratio | 2:1 | 2:2 | 2:3 | 2:4 | 2:5 | 2:6 | 2:7 |
| Bonding | Ionic | Ionic | Highly Polar Covalent | Polar Covalent | Polar Covalent | Polar Covalent | Polar Covalent |
| pH | Basic | Basic | Amphoteric | Weakly Acidic | Acidic | Acidic | Acidic |
| Other Oxides | Na_2O_2 | | | | P_2O_3 & P_4O_{10} | SO_2 | Cl_2O_2 & Cl_2O |
| Conduct? | Molten & Aq. | Molten & Aq. | Weak Conduct | Weak Conduct | No conduct | No conduct | No conduct |

Trend of Increasing Acidity →

Polyoxo anions

Acids containing -OH group condense (eliminate water) to form polyoxoanions

Polyoxoanions ($O_3CrOCrO_3$)²⁻(aq)) form polymers as the pH is lowered

Whereas aqua ions (e.g. $Fe^{3+}(H_2O)_6$) form polymers as the pH is raised.

Groups 1 and 2 do not form anything beyond the *discrete* M^+ and M^{2+} aqua species.

In contrast, the amphoteric oxides, for example Al_2O_3 and Fe_3O_4 form routine hexaaqua complex in acidic solutions
But when the pH is raised > 4 they precipitate as gelatinous hydroxides.

These precipitated hydroxides are colloidal in size (1nm to 1 μ M), and the Al forms a 3D polymeric structure, while the Fe forms more linear polymers.

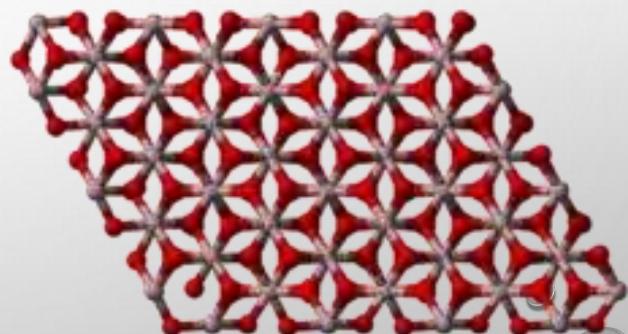
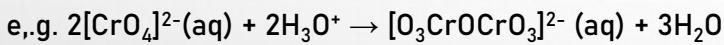


Figure 1. A 3D polymeric structure of Al_2O_3

Polyoxanions formed by condensation of oxoanion

The oxoanions are species that are formed by the elimination of water and they have multiple metal nuclei

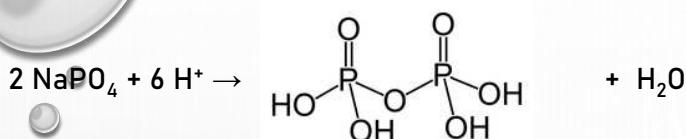
Polyoxo anions form from this when the oxo atoms are protonated at low pH and they eliminate as water making the polyoxo anions to form more polymers structure



d-block elements in high oxidation states like Mo(VI), W(VI), Nb(V), Ta(V) and Cr(VI) in a basic medium form polyoxoanions

Non-metals form polyoxoanions and they have a cage like or chain like structures. E.g. MgSiO_3 , $\text{Zn}_3(\text{PO}_4)_3$

Simplest polyoxoanion → Pyrophosphate

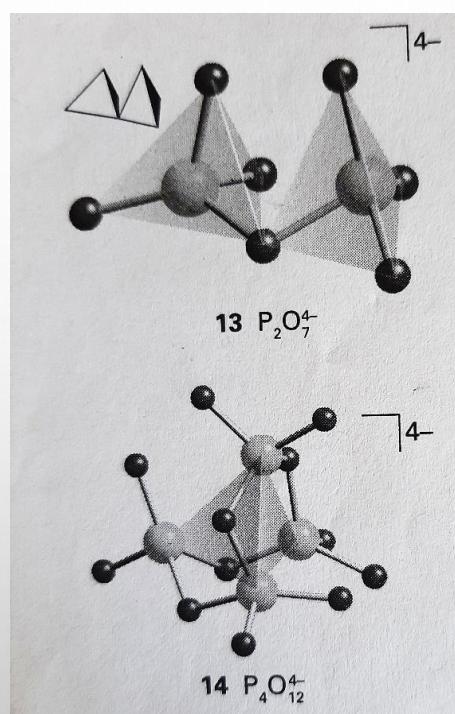


Note, the elimination of water consumes proton and decreases the formal charge of both P to -2. The structure has corner-shared tetrahedron.

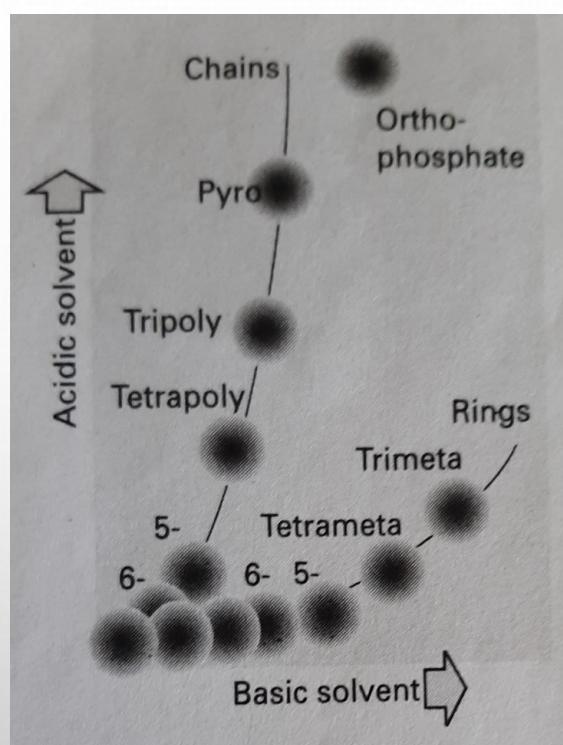
By having lowered amount of water in the medium the phosphoric acid can be made to condense into metaphosphate, $[\text{P}_4\text{O}_{12}]^{4-}$

In fact, when phosphorous pentoxide is treated with acidic or basic water many polymeric

Polyoxoanionic species form with number of P atoms ranging from 2 to 50, and these can be separated by chromatography



Picture of a pyrophosphate and metaphosphate represented as tetrahedra

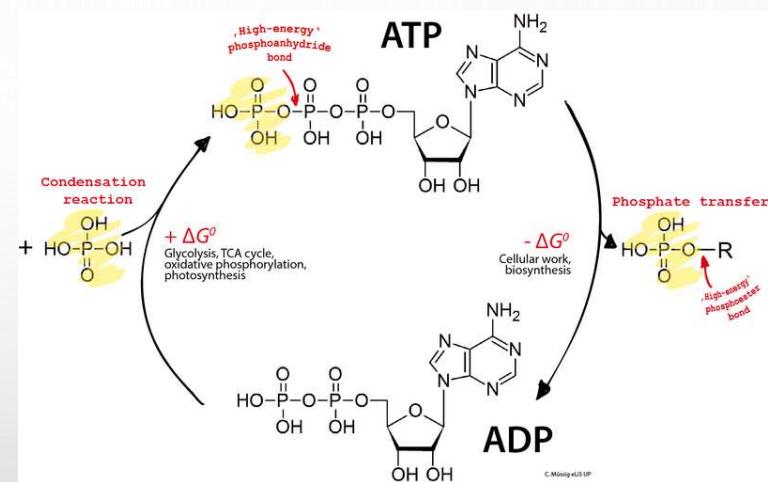


The polyphosphates being made of P-O-P bonds are very crucial in biological systems

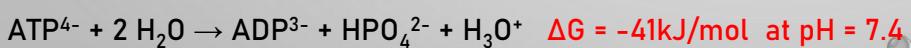
At physiological pH, 7.4, these P-O-P bonds are prone to hydrolysis.

P-O-P bonds when hydrolysed it provides the Gibbs Energy for driving a reaction.

Same way a P-O-P bond can be formed to store a required Gibbs Energy.



Energy flow in biological system is thus controlled by the hydrolysis of ATP to ADP:



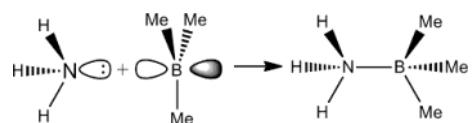
1.9 Lecture 8

Lecture 8- S1: Introduction

02 November 2020 09:56

Lewis acid: Accepts a pair of electrons

Lewis base: Donates a pair of electrons



Good example, adduct formation: Where $A + :B = A-B$ formed by sharing of electrons supplied by the base.

H^+ is an acid as it always accepts a pair of electrons

Any Bronsted acid which supplies a proton is a Lewis acid too. Thus Bronsted acid is a special case of Lewis acid

Same way NH_3 is a Lewis base as it donates an electron pair while forming NH_4^+

Molecules without a proton can also transfer electron pairs and this is what a Lewis concept encompasses- a wide range of substances

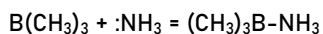
LA and LB are used in describing equilibrium properties; while, in the context of reaction rates they are referred to as nucleophile and electrophile

Lecture 8- S2: Different Lewis acid-base adducts

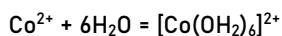
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Possibilities of Lewis acid base adducts or conditions for the formation of A-B adducts

1. A molecule with an incomplete octet



2. A metal cation can accept electron pair in a coordination compound

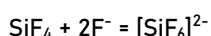


3. A molecule with complete octet may be able to rearrange its valence electron to accept a pair of electrons

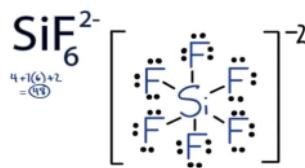


Try writing this rearrangement?

4. A molecule may be able to expand its valence shell to accept electron pairs



Common in heavier p-blocks, e.g. SiX_4 , AsX_3 , PX_5 (X = halide).



Lecture 8- S3: Periodic trends

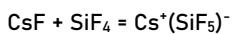
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Trends

Group 1:

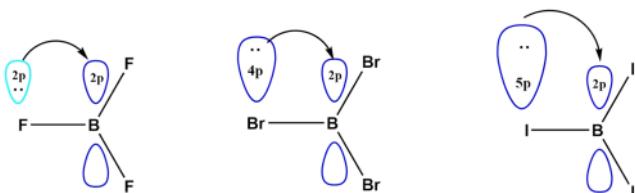
Alkali and alkaline earths: Na^+ , Cs^+ etc exist as hydrates in water showing their Lewis acidity

However, their halides can act as Lewis bases



BeCl_2 form polymeric chains by reacting among themselves where Cl^- from one unit transfers electron into the sp^3 orbitals of the Be.

Group 13 elements form excellent Lewis acids



Strong 2p-2p interaction
Back bonding

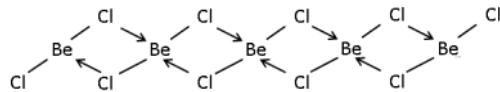
Acidity trend: $\text{BF}_3 < \text{BCl}_3 < \text{BBr}_3$ – Follows pi-bonding correlation and not the e- withdrawing power

These are planar molecules with a vacant p-orbital lying perpendicular the plane of the molecule

They have incomplete octets; they accept electron pair from Lewis bases and the adduct formation make these B acids to become pyramidal

Thermodynamic stability of complexes with NR_3 : $\text{BF}_3 < \text{BCl}_3 < \text{BBr}_3$. Explain?

BF_3 is an industrial catalyst for generating carbo cations. Used by dissolving the gas in diethyl ether.



Lecture 8 - S4: Periodic trends

02 November 2020 10:29

Group 14 Lewis acids with expandable shells - hyper valence

Unlike Carbon, Silicon atom can expand its valence shell to become hypervalent



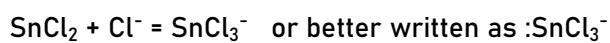
Ge and Sn can also expand

Why is the HF dangerous for glasses?

The acidity trend of Si halides: $\text{SiI}_4 < \text{SiBr}_4 < \text{SiCl}_4 < \text{SiF}_4$ - Correlates with e- withdrawing power

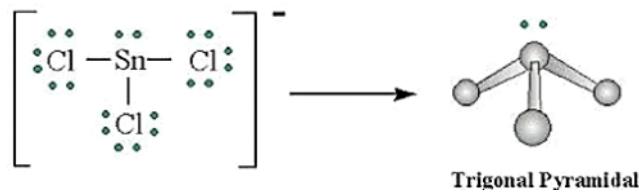
This is opposite of Boron.

SnCl_2 is an amphoteric Lewis acid and Lewis base.



It can act as a base, $(\text{CO})_5\text{Mn}-\text{SnCl}_3$

SnCl_4 is a Lewis acid, Strength of Lewis acidity: $\text{SnF}_4 > \text{SnCl}_4 > \text{SnBr}_4 > \text{SnI}_4$



Trigonal Pyramidal

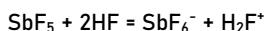
Lecture 8- S5: Periodic trends

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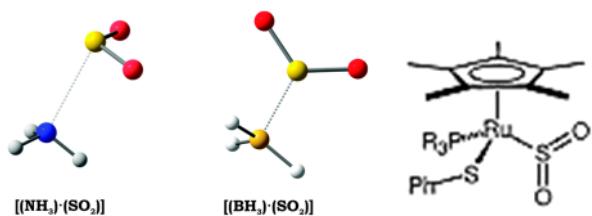
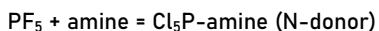
Group 15:

Antimony halides

Heavier element of the N group forms super acids

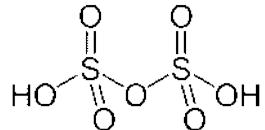
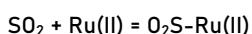
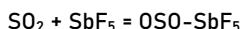


Phosphorous halides form strong adducts with organic reagents



Group 16:

Sulfur dioxide as amphoteric species



Sulfur trioxide is a strong Lewis acid and a weak Lewis base. How is this exploited in sulfuric acid preparation? Hint: $\text{H}_2\text{S}_2\text{O}_7$

Lecture 8-S6: Hard and soft acid-base

02 November 2020 11:24

In acids and bases two classes are observed with opposite order of strengths as measured by their equilibrium constant, K_f - formation of complex.

Hard acids bond in the order: $I^- < Br^- < Cl^- < F^-$

Soft acids bond in the order: $F^- < Cl^- < Br^- < I^-$

Figure shows the trend in the halide (Lewis base) adduct formation of different metal ions (Lewis acids)

The K_f for complex formation,

For Hg^{2+} it increases steeply from F^- to I^- = Soft

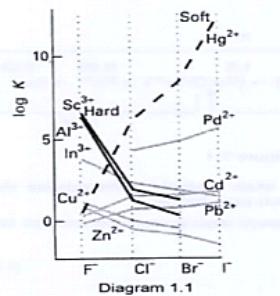
For Pb^{2+} same trend but less steep - less softer - borderline soft base

For Zn^{2+} the same trend is opposite but equally less steep - borderline hard acid

For Al^{3+} steep drop indicates strong binding to F^- and weak binding to I^- - hard acid

Hard acids cations form complexes where the bonds are ionic, while the soft cations form more covalent bonding.

Based on diagram 1.1, explain the trends in stability constants and the classification of cations as hard, borderline and soft acids with which they form complexes with halide ion bases. Borderline ions are indicated by gray lines and may be borderline soft or borderline hard.



Lecture 8- S7: Hard and soft acids

02 November 2020 12:12

Neutral hard and soft acids

Phenol with ether vs. thioether

I₂ with ether vs. thioether

In general,

Hard acids bind in the order: R₃P << R₃N, R₂S << R₂O

Soft acids bind in the order: R₂O << R₂S, R₃N << R₃P

Soft bases: CO and CN⁻

HARD-SOFT ACIDS & BASES CHARACTERISTICS & DIFFERENCES

| HARD ACID | SOFT ACID |
|---|--|
| Small ionic radius High positive charge Low electronegativity High energy LUMO | Large ionic radius Low positive charge Intermediate electronegativity Low energy LUMO |
| HARD BASE | SOFT BASE |
| Small radius High electronegativity Weak polarizability High energy HOMO | Large radius Intermediate electronegativity High polarizability Low energy HOMO |

σ donor and π acceptors - 'σ' bond through HOMO and 'π' acceptance through LUMO

Hence there is electron sharing making the bonds highly covalent -soft bases also called as π-acids

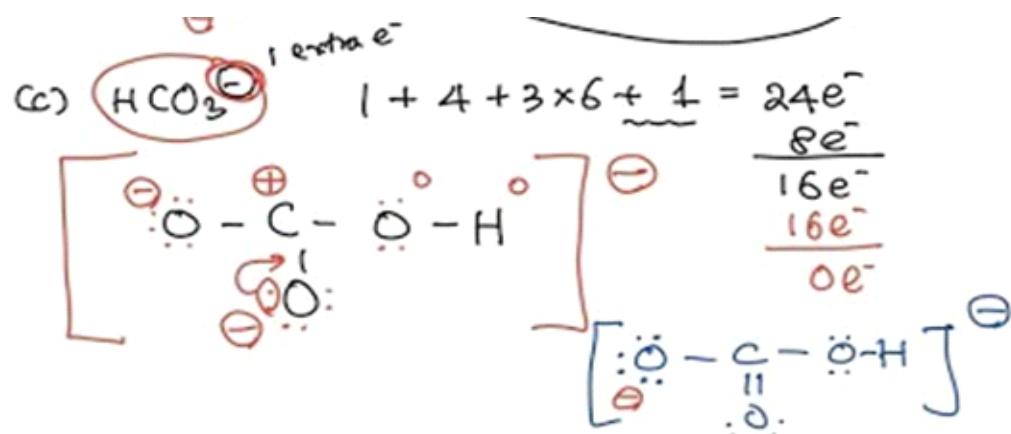
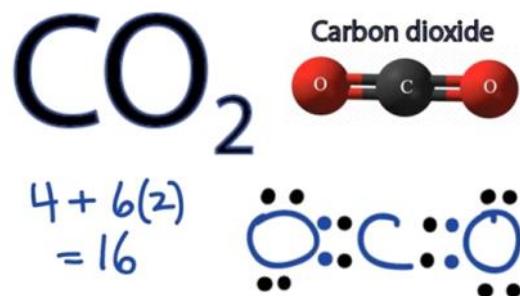
| | Soft | Borderline | Hard |
|--------------|---|---|---|
| Bases | H ₂ S, C ₂ H ₄ , RSH, R ₂ S, CO, CN ⁻ , RCN, H ₂ ⁻ , R ₃ P, C ₆ H ₆ , RS ⁻ , I ⁻ | C ₆ H ₅ NH ₂ , C ₅ H ₅ N, C ₃ H ₄ N ₂ N ₂ , Br ⁻ , N ₃ ⁻ | ROH, RO ⁻ , HO ⁻ , R ₂ O, N ₂ H ₄ , R-NH ₂ , H ₂ O, CO ₃ ²⁻ , F ⁻ , Cl ⁻ |
| Acids | Cd ²⁺ , Cu ⁺ , Ag ⁺ , carbenes, I ₂ , Hg ²⁺ | SO ₂ , Bi ³⁺ , Ni ²⁺ , Zn ²⁺ , C ₆ H ₅ ⁺ , Pb ²⁺ , Cu ²⁺ | CO ₂ , SO ₃ , H ⁺ , Li ⁺ , Mg ²⁺ , Al ³⁺ , Co ³⁺ , Ga ³⁺ , Ti ⁴⁺ , La ³⁺ , In ³⁺ , Zr ⁴⁺ |

Appendix

02 November 2020 15:15

List of Hard and Soft Lewis Acids and Bases

| Hard acids (non-metals) | Borderline acids (non-metals) | Soft acids (non-metals) |
|---|---|---|
| H ⁺ , B(OR) ₃ , BF ₃ , BCl ₃ , RCO ⁺ , CO ₂ , NC ⁺ , R ₃ Si ⁺ , Si ²⁺ , RPO ₂ ⁺ , ROPO ₂ ⁺ , As ³⁺ , RSO ₂ ⁺ , ROSO ₂ ⁺ , SO ₃ , Se ¹⁺ , Cl ²⁺ , I ²⁺ , F ²⁺ | BR ₃ , R ⁺ (softer CH ₃ ⁺ > RCH ₂ ⁺ > R ₂ CH ⁺ > R ₃ C ⁺ > vinyl ⁺ = C ₆ H ₅ ⁺ = RC=C ⁺ harder), RCHO, R ₂ CO, R ₂ C=NR, NO ⁺ , SO ₂ | BH ₃ , Ar-Z, C=C-Z, quinones, carbenes, H O ⁺ , RO ⁺ , RS ⁺ , RSe ⁺ , RTe ⁺ , Br ₂ , Br ⁺ , I ₂ , I ⁺ |
| Hard acids (metals) | Borderline acids (metals) | Soft acids (metals) |
| Li ⁺ , Na ⁺ , K ⁺ , BeMe ₂ , Be ²⁺ , RMgX, Mg ²⁺ , Ca ²⁺ , Sr ²⁺ , AlCl ₃ , AlMe ₃ , AlH ₃ , Al(OR) ₃ , Al ³⁺ , GaMe ₃ , Ga ³⁺ , InMe ₃ , In ³⁺ , SnR ₃ ⁺ , SnMe ₂ ²⁺ , Sn ²⁺ , Sc ³⁺ , La ³⁺ , Ti(OR) ₄ , Ti ⁴⁺ , Zr ⁴⁺ , VO ₂ ⁺ , Cr ³⁺ , Fe ³⁺ , Co ³⁺ , Ir ³⁺ , Th ⁴⁺ , UO ₂ ²⁺ , Pu ⁴⁺ , Yb ³⁺ | GaH ₃ , Sn(OR) ₄ , SnCl ₄ , Pb ²⁺ , Sb ³⁺ , Bi ³⁺ , Sc(OH) ₃ , ScCl ₃ , Fe ²⁺ , Co ²⁺ , Ni ²⁺ , Cu ²⁺ , RZn ⁺ , Zn ²⁺ , Yb(OH) ₃ , YbCl ₃ | Cs ⁺ , TiMe ₂ , Ti ⁺ , Ti ³⁺ , Pd(PAr ₃) ₂ , Pd(PAr ₃) ₂ ²⁺ , Pd ²⁺ , Pt ²⁺ , Cu ⁺ , Ag ⁺ , Au ⁺ , CdR ⁺ , Cd ²⁺ , HgR ⁺ , Hg ²⁺ , Hg ³⁺ , M ⁰ |
| Hard bases | Borderline bases | Soft bases |
| NH ₃ , RNH ₂ , R ₂ N ⁺ , N ₂ H ₄ , H ₂ O, OH ⁻ , ROH, RO ⁻ , R ₂ O, RCO ₂ ⁻ , CO ₃ ²⁻ , NO ₃ ⁻ , PO ₄ ³⁻ , SO ₄ ²⁻ , ClO ₄ ⁻ , F ⁻ , Cl ⁻ | AlH ₄ ⁻ , N ₂ , N ₃ ⁻ , PhNH ₂ , R ₃ N, C ₆ H ₅ N, R ₂ C=NR, NO ₂ ⁻ , SO ₃ ²⁻ , Br ⁻ | H ⁻ , BH ₄ ⁻ , R ⁻ (softer RC=C ⁻ > vinyl ⁻ > R ₃ C ⁻ harder), C ₆ H ₆ , R ₂ C=CR ₂ , RC=CR, CN ⁻ , RNC, CO, PR ₃ , P(OR) ₃ , AsR ₃ , RS ⁻ , SCN ⁻ , RSH, R ₂ S, S ₂ O ₃ ²⁻ , RSe ⁻ , I ⁻ |



1.10 Lecture 9



CH2113 Principles of Inorganic Chemistry

Lecture 9

Oxidation and Reduction

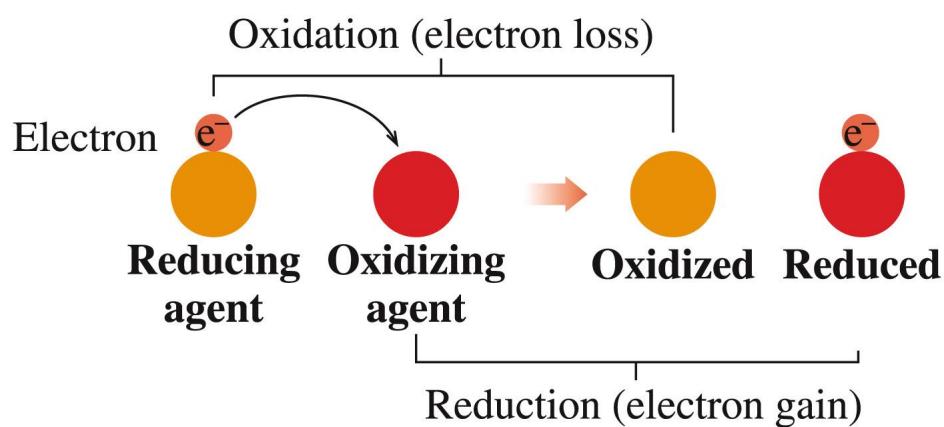
Dr. R. Vaidhyanathan

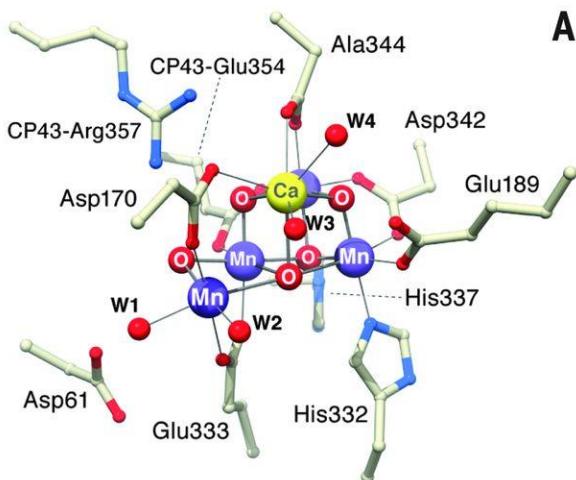
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*Few examples of **REDOX** systems*

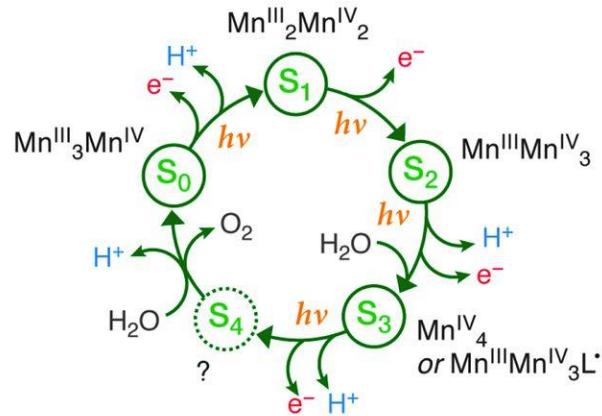
Inorganic Oxidation and Reduction

- Atoms that lose electrons during a chemical reaction are said to undergo **oxidation**.
- Atoms that gain electrons during a chemical reaction are said to undergo **reduction**.
- The oxidized species is also known as the reducing agent, and the reduced species is the oxidizing agent.





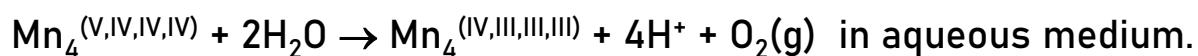
A



B

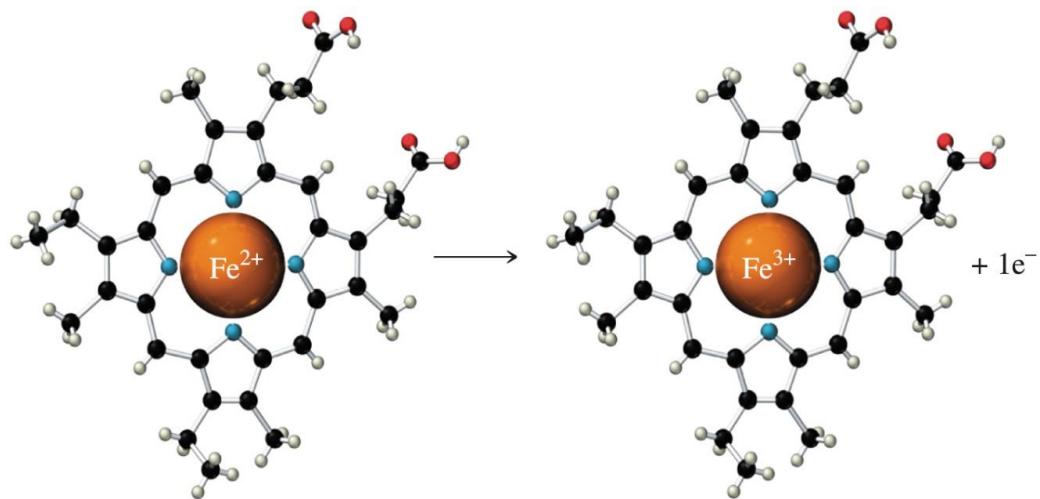
Biological system:

Production of oxygen from water by a Mn₄ cofactor



Biochemical Oxidation and Reduction

- In biological systems, cells oxidize and reduce metals.
- A protein called cytochrome c plays an important role in ATP production.
- This protein contains an Fe^{2+} that undergoes oxidation to Fe^{3+} followed by reduction back to Fe^{2+} . The iron ion is held in place on a small organic molecule called a **heme**.



Oxidation and Reduction: **in cells**

- We fuel our bodies with nutrients that are broken down through oxidation.
- In the body, the process of combustion occurs through a chemical pathway, transferring energy as it goes.
- The series of reactions through which glucose is combusted is cellular respiration.
- Ethanol is oxidized to the aldehyde ethanal, also called acetaldehyde.
- In the case of ethanol oxidation, the reduced molecule is nicotinamide adenine dinucleotide, NAD⁺.
- NAD⁺, and flavin adenine dinucleotide (FAD) are two important molecules used in metabolic oxidation-reduction reactions.

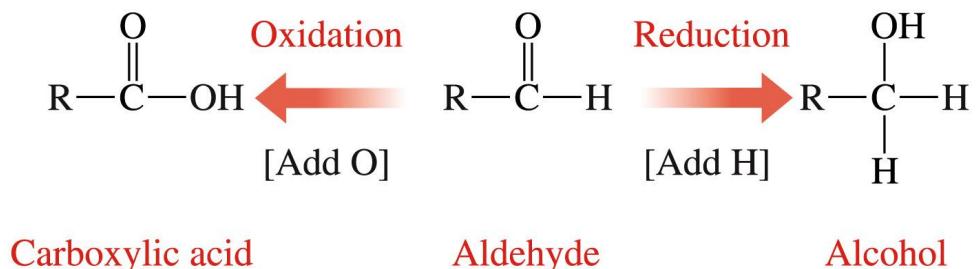
Oxidation and Reduction: in organic reactions

Organic Oxidation and Reduction

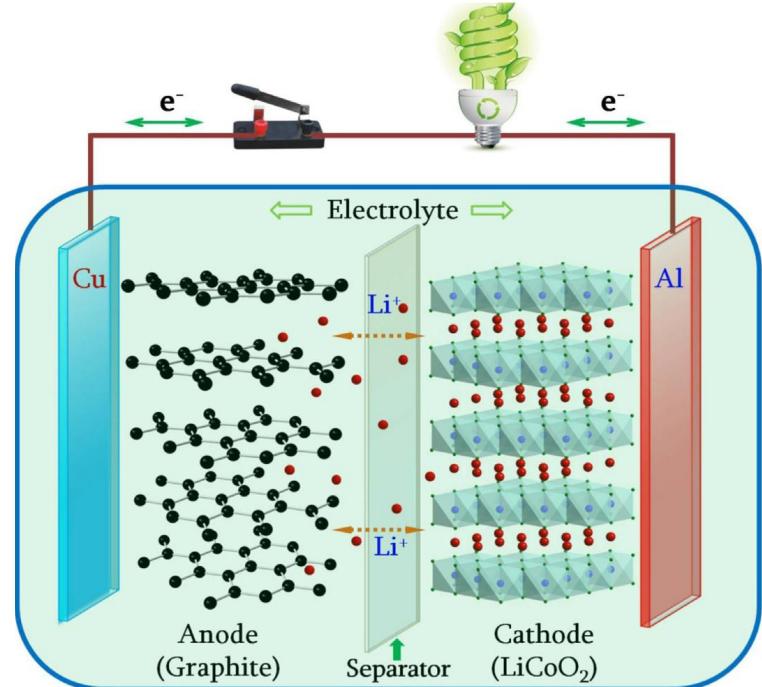
- An organic molecule is oxidized if it gains O or loses H and is reduced if it gains H or loses O.

TABLE 5.6 Characteristics of Oxidation and Reduction Reactions

| Oxidation | |
|-------------------|--|
| Always Involves | May Involve |
| Loss of electrons | Addition of oxygen Loss of hydrogen |
| Reduction | |
| Always Involves | May Involve |
| Gain of electrons | Loss of oxygen Gain of hydrogen |



In battery



In a Li-ion battery



Does this represent a redox reaction? Debatable? Why?

Oxidation and Reduction

Inorganic Oxidation and Reduction

- Metal atoms generally lose electrons to form cations becoming oxidized.
- Nonmetals gain electrons to form anions becoming reduced.
- Oxidation and reduction reactions are always coupled.
- A mnemonic device for remembering what is happening to the electrons in a redox reaction is to remember the letters in the words “OIL RIG.”

| | | | | | |
|---|---|---|---|---|---|
| O | I | L | R | I | G |
| X | S | O | e | s | a |
| i | | S | d | | i |
| d | | S | u | | n |
| | | | c | | |
| | | | t | | |
| | | | i | | |
| | | | o | | |
| | | | n | | |

Redox reaction happens in gas phase, or liquid phase or solid phase or in interfaces.

Formal rule: Oxidation increases oxidation number

Reduction decreases oxidation number

Li oxidizes to Li_2O in air

Cl^- reduces to CaCl_2

Osmium can take oxidation states from -2 to +8. TM are known for variable oxidation states.

Reduction potential: Electrochemical methods help us measure the ability of a species to transfer electrons.

Each chemical species' electron transfer can be studied under standard thermodynamic conditions

This sets up – **Standard Potential (SP)**

Now tendency of electron to migrate from one species to the other can be expressed in terms of the differences in SP.

Redox reaction: $A + B \rightarrow A^+ B^-$

Now this is a full redox reaction

Can be expressed as two half reactions: $A \rightarrow A^+$ (oxidation) and $B \rightarrow B^-$ (reduction)

These two constitute a redox couple: $A/A^+:B/B^-$

Now take an example: $2H^{+}_{(aq)} + 2e^- \rightarrow H_2(g)$ and $Zn(s) \rightarrow Zn^{2+}_{(aq)} + 2e^-$

Note: The physical state (g, s, l) of electron is never assigned as it is in transit.

Many of these redox reactions release great deal of energy

To identify this for this redox couple, $H+/H_2:Zn/Zn^{2+}$

Both reactions are expressed as reduction: $Zn^{2+} + 2e^- \rightarrow Zn$; $2H^{+} + 2e^- \rightarrow H_2$

Now take the difference in the reduction potentials of these half-cell reaction under the same standard electrochemical conditions. This tells you the energy of the reaction.

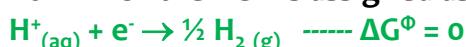
Standard potentials and spontaneity

A full-cell redox reaction is thermodynamically favourable if the equilibrium constant $K > 1$, if the $E^\ominus > 0$, where E^\ominus is the difference between the standard potentials of the two half-cell reactions that make up the full-cell reactions.

Thermodynamic requirement is that at constant temperature and pressure, the reaction Gibbs energy change, ΔG^\ominus , is negative.

We have $\Delta G^\ominus = -RT \ln K$. Thus a negative value of $\Delta G^\ominus \Rightarrow K > 1$, The product dominates the reactants at equilibrium.

For convenience and to normalize, the ΔG^\ominus for any half-cell reaction is reported relative to a reduction reaction for which the ΔG^\ominus is assigned as zero. And this happens to be



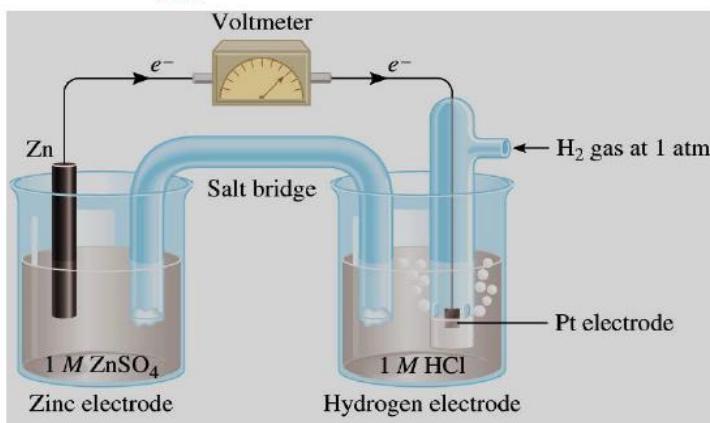
Now, consider $Zn^{2+}_{(aq)} + H_{(g)} \rightarrow Zn(s) + 2H_{(aq)}^+$, the ΔG^\ominus for this reaction is determined electrochemically to be $\Delta G^\ominus = +147 \text{ kJ/mol}$

Because the H^+ reduction half-cell reaction makes no contribution to this, it follows that



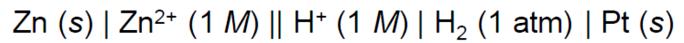
A Galvanic Cell or measuring standard free energies of redox reactions

$$E_{cell}^0 = 0.76 \text{ V}$$



Standard emf (E_{cell}^0)

$$E_{cell}^0 = E_{cathode}^0 - E_{anode}^0$$



$$E_{cell}^0 = E_{\text{H}_2\text{H}_2}^0 - E_{\text{Zn}^{2+}\text{Zn}}^0$$

$$0.76 \text{ V} = 0 - E_{\text{Zn}^{2+}\text{Zn}}^0$$

$$E_{\text{Zn}^{2+}\text{Zn}}^0 = -0.76 \text{ V}$$



The potential difference between the electrodes, E, is measured in “Volts”

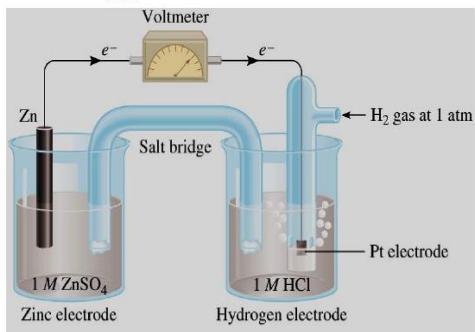
To determine the ΔG° , the potential is measured when no current is flowing

The reactions Gibbs Free Energy is given by $\Delta G^\circ = -nFE$, where E - measured potential, F- Faraday constant; n - number of electrons transferred.

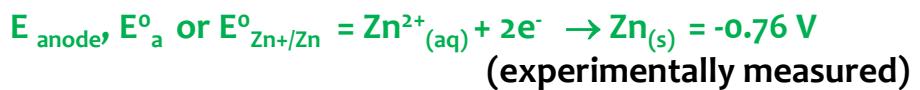
Since ΔG° for H^+/H_2 couple is arbitrarily set at zero, and is zero at all temperatures.

A Galvanic Cell or measuring standard free energies of redox reactions

$$E_{\text{cell}}^{\circ} = 0.76 \text{ V}$$



For the couple shown the E_{cell} is given by $E_{\text{cathode}} - E_{\text{anode}}$



$$E_{\text{Cell}}^{\circ} = E_{\text{H+}/\text{H}_2}^{\circ} - E_{\text{Zn+}/\text{Zn}}^{\circ} = 0 - (-0.76) = +0.76 \text{ V}$$

Note: A positive $E_{\text{cell}}^{\circ} \Rightarrow K > 1$, spontaneity.

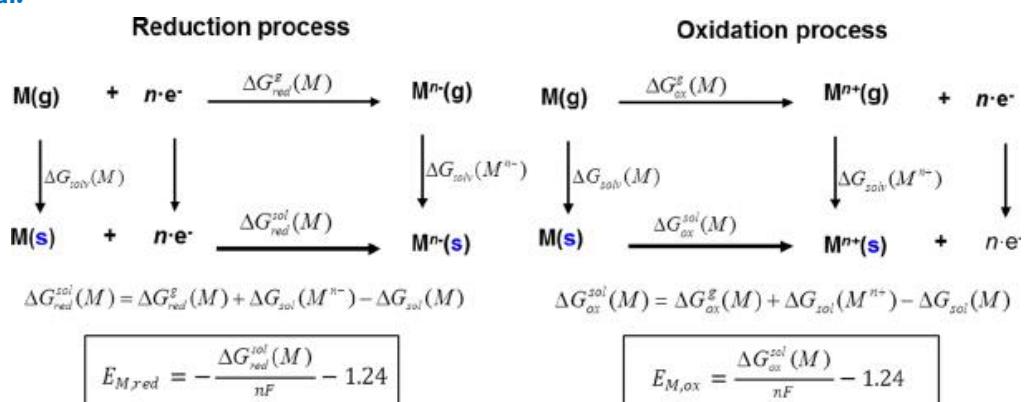
Thus Zinc dissolves in H^+ to reduce it. And this is measured at $\text{pH} = 0$ (1 M acid) and 1 bar pressure.

This is true for any metal that has a negative standard potential.



Relating thermodynamic cycle of a cell to the electrochemical potential:

The atomization and ionization of elements or metal and the hydration enthalpy of the ions all contribute to the value of the Standard Potential.



Enthalpy (for example $\Delta H^\circ = +147 \text{ kJ/mol}$ for Zn^{2+}), outweighs the entropy ($T\Delta S^\circ \sim 20-50 \text{ kJ/mol}$), hence entropy contribution is omitted.

We do not use the ΔH° of $H^+/H_2 = 0$, in this case, instead we use the absolute values, which is obtained by considering the formation of an H atom from $1/2 H_{2(g)}$ (+218 kJ/mol), ionization to $H_{(g)}^{+}$ (+1312 kJ/mol), and hydration of $H_{(g)}^{+}$ (~ -1085 kJ/mol). This will give an absolute value of +445 kJ/mol for ΔH of H^+/H_2 half cell.

Why is Lithium preferred over other metals for metal-ion battery? Is there a trend in a periodic group?

This can be answered by considering the thermodynamic contributions to the E_{cell}

In Group 1, Cs is less electronegative than Li. Hence it would be expected that it should have a more favourable half cell potential.

Cs^+/Cs ($\chi = 0.79$, $E = -2.94$ V) vs. Li^+/Li ($\chi = 2.20$, $E = -3.04$)

Also, Lithium has higher enthalpy of sublimation and ionization energy than Cs.

All this would mean the Lithium is expected to have lower standard potential.

However, Li has high enthalpy of solvation (hydration) owing to its smaller ionic radii (90pm) vs. Cs (181pm) and has stronger electrostatic interaction with water. This outweighs every other thermodynamic factor leading to $\text{Li} \rightarrow \text{Li}^+$ has a superior Standard Potential.

Electrochemical series:

A **negative standard potential ($E < 0$)** of signifies that the couple (for e.g. Zn^{2+}/Zn) **can reduce H^+ ions under standard conditions in an aqueous solution.**

Implies, $E_{\text{cell}}(\text{Ox,red}) < 0$. Based on this, different elements have been arranged in a

Electrochemical series.

Important: Any couple or half-cell that lies below in the series can reduce a couple that lies above it.

The classification considers only thermodynamic aspects (K and G) hence even a favoured couple may not be working due to slow kinetics.

2 Post Midsem

2.1 Lecture 1

Molecular structure and Bonding

Interpretation of structures and reactions based on qualitative and semi-quantitative models

- For example, **Lewis and VSEPR descriptions** are the pure pictorial representation of bonding and are examples of qualitative models
- Semi-quantitative models: **CFT, V. B and M.O. Theory** which can also be represented by pictorial models for simple understanding

True molecular structure is arrived by an interplay between qualitative and semi-quantitative methods

Inorganic chemistry → **correlating electronic structure with chemical properties**

Most elementary discussion of covalent bonding → **Sharing a pair of electrons**

Introduced by G. N. Lewis → Since then our understanding is greatly enriched by various theories

Modern theories capture some of its essence and go far beyond!

Molecular structure and Bonding: main group elements

Lewis Theory

Covalent bond is formed by sharing a pair of electrons denoted by
 $A-B$, $A=B$ and $A\equiv B$

Unshared pair of V. E.'s are called lone pairs → Do not directly contribute to the bonding but influence the shape of the molecule and its chemical properties

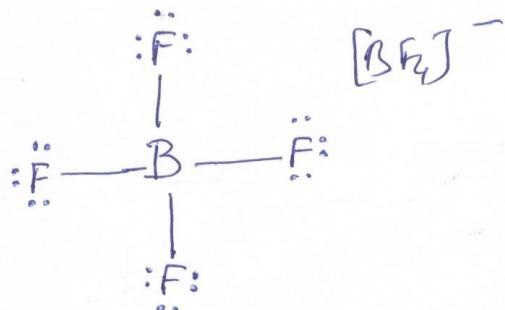
The Octet Rule → Lewis accounts the existence of wide range of molecules
States that “Each atom shares electrons with neighboring atoms to achieve a total of 8-valence electrons”

Octet rule → Simple way of constructing Lewis structures ; Diagrams that show the patterns of bond pairs and lone pairs in a molecule

Steps for constructing Lewis Structures

1. Decide the number of electrons to be included in the structure by adding together the number of valence electrons provided by the atoms. Each negative charge → one electron plus; each positive charge → one electron minus
 2. Write the chemical symbol of the atoms in the arrangement showing them to be bonded together
 3. Informed guess → Mostly less electronegative element is the central atom (exceptions possible for ex. H₂O and NH₃)
- Distribute the electron pairs so that there is one pair of electron between each pair of atoms bonded and then supply electron pairs to form lone pairs or multiple bonds until each atom has an octet.
- Each bonding pair is represented by a single line
- The net charge of the polyatomic ion is assumed to be possessed by the ion as a whole

Examples

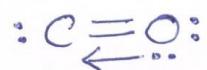


B \Rightarrow 3 e^{0s}
F \Rightarrow 7 e^{0s}, 1 e^{for bonding}
6 e^{0s} as b.p.s



3 V.E. shared on each
'N'

one b.p. & 2 in N'



1 b.p. & 3 b.p.



Further concepts

Resonance:

A single Lewis structure is often an inadequate representation of the molecule.

Ex. The Lewis structure of O₃



Both the O-O bonds are identical in length. Mere Lewis structure can not predict this. Resonance averages the bond characteristics over the molecule. The energy of the resonance hybrid structure is lower than that of any single contributing structure.

Try the resonance structure for [NO₃]⁻

Further concepts

Formal Charge:

The formal charge is the charge of an atom if electron pairs were shared equally.

The decision about which Lewis structure is likely to have lowest energy and hence contribute predominantly to the resonance is possible by finding formal charges on each atom.

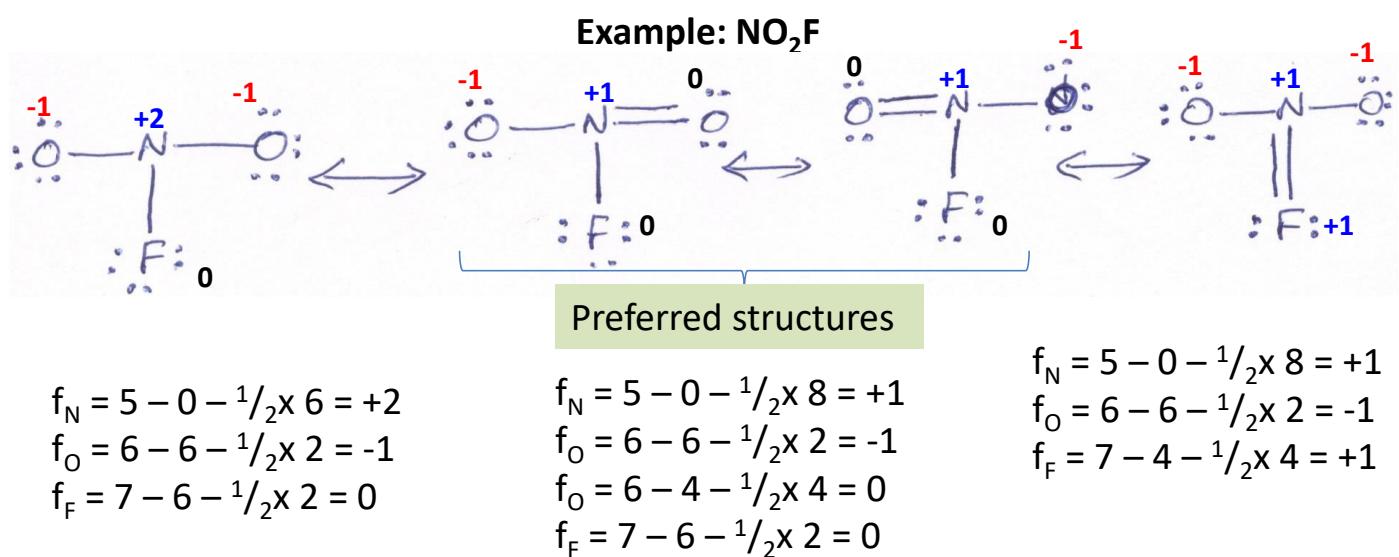
Assuming perfect covalent bonding and each shared pair being shared equally....that is...

Each atom is assumed to own one electron of a bonding pair and each lone pair of electrons belongs wholly to the atom on which it resides, formal charge can be calculated by the formula

$$f = V - L - \frac{1}{2}P \quad f = \text{Formal charge of an atom}; V = \text{Number of valence electrons}$$

L = Number of lone pair electrons and P = Number of shared electrons in the Lewis structure

Example for calculating the formal charge and determining lowest energy resonance structure



Lewis structures with low formal charges typically have the lowest energy

The Lowest energy structure is the one with

1. The lowest formal charge on the atoms
2. The structure in which the more electronegative element is assigned a formal negative charge and the less electronegative element is assigned a formal positive charge

Further concepts

Oxidation Number:

Formal charge is a parameter derived by exaggerating the covalent character of a bond

Oxidation number is a parameter derived by exaggerating the ionic character of a bond

In this formalism the more electronegative element of a bond acquires two negative charge and given the oxidation number of -2. And the more electropositive element acquires the a positive charges equivalent to its Valency.

$[\text{NO}_3]^-$ is treated as $[\text{N}^{5+}] [\text{O}^{2-}]_3$ The Valency of nitrogen is denoted as N(V).

Main-Group and Transition-Metal Chemistry

The Valance Shell Electron Pair Repulsion (VSEPR) Model

Primary assumption: Enhanced regions of electron density by which we mean bonding pairs, lone pairs or the concentration of electrons associated with multiple bonds, take up positions as far as possible so that repulsions between them are minimized.

For example:

Four regions: at the corners of a tetrahedron

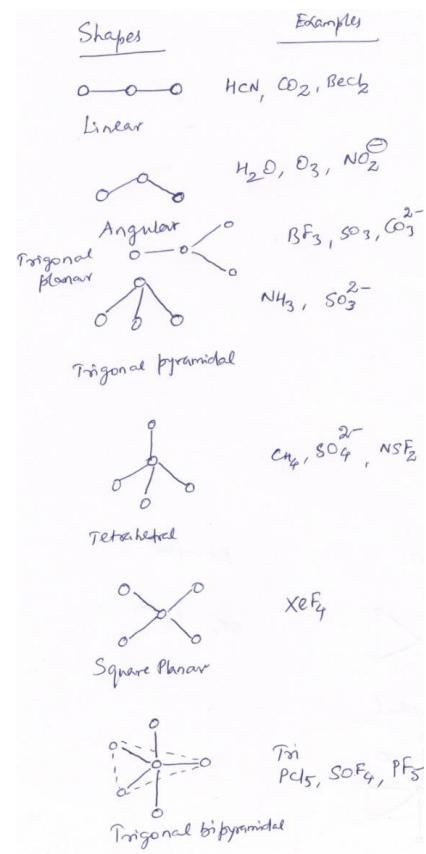
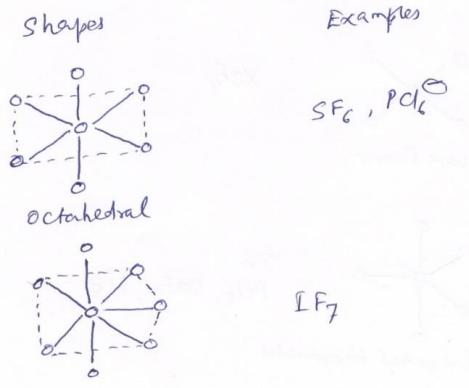
Five regions: at the corners of TBP geometry

Steps for obtaining the Basic shapes

1. Count the valance electrons on the central and peripheral atoms that participate in the bonding
2. Identify the number of electron pairs and the basic shapes
3. Assign the location of sigma bonds, lone-pairs and multiple bonds
4. Multiple bonds are treated as another region of enhanced electron density (along the given sigma-bond). Example: Structures of POCl_3 and COCl_2

Basic arrangement of the regions of electron density

| No. of e ⁻ s | Arrangement |
|-------------------------|------------------------|
| 2 | Linear |
| 3 | Trigonal planar |
| 4 | Tetrahedral |
| 5 | Trigonal bipyramidal |
| 6 | Octahedral |
| 7 | Pentagonal Bipyramidal |



Steps for constructing VSEPR models



P → 5 V.E.

O → 2 V.E.

3 × Cl → 3 V. E.

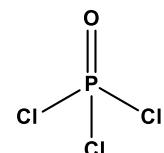
Total 10 V. E.

10 V. E. → 5 electron pairs

Less 1 electron pair for double bond

Basic shape for 4 electron pair:

Tetrahedral



S → 6 V.E.

3 × O → 6 V.E.

Total 12 V. E.

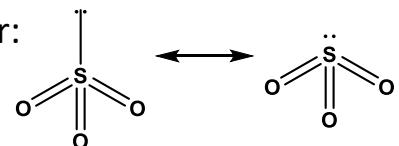
10 V. E. → 5 electron pairs

Less 3 electron pair for =O or oxide ion

Basic shape for 4 electron pair:

Tetrahedral

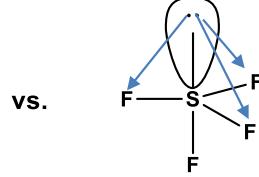
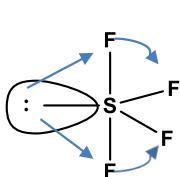
Actual shape: Trigonal pyramidal



Modifications to the Basic Shape

- Once the number of electron pairs has been used to identify the basic shape, minor adjustments are made by taking into account the differences in electrostatic repulsions between them
- The repulsion order is l.p./l.p. > l.p./b.p. > b.p./b.p
- Elementarily, the greater repelling power of lone pairs is explained by supposing that it is on average closer to the nucleus than bond pairs and therefore it repels other electron pairs more strongly.
- Hence, Lone pairs require larger sites, for examples equatorial sites in TBP.
- If all sites are equal → Trans to each other.

SF_4
 $\text{S} \rightarrow 6 \text{ V.E.}$
 $4 \times \text{F} \rightarrow 4 \text{ V.E.}$
 $10 \text{ V. E.} = 5 \text{ pairs}$
Basic shape: TBP



Two 90 ° interactions vs. Three 90 ° interactions
Distortions to the axial bond

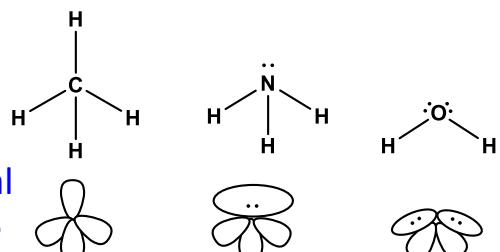
Modifications to the Basic Shape

Tetrahedral modifications

$\text{CH}_4 \rightarrow$ No l.p., 109.5° , perfect tetrahedral angles

$\text{NH}_3 \rightarrow$ 1 l.p., 107° , acute angles in trigonal pyramidal

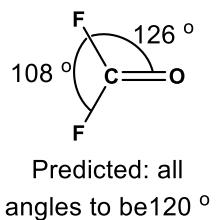
$\text{H}_2\text{O} \rightarrow$ 2 l.p., 104.5° , more acute angles in bent shape



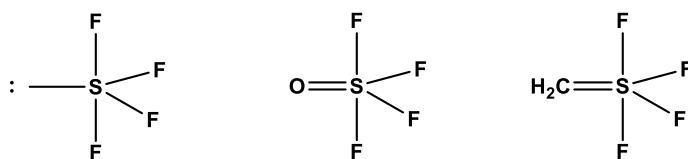
Trigonal modifications:

$\text{COF}_2 \rightarrow$ Because of the double bond, C=O distance is shortened.

Hence, =O requires more angular volume (higher angle)



TBP modifications:



Axial F-S-F angle: 179°

Equatorial F-S-F angle: 103°

178.5°

110°

170°

97°

Summary of VSEPR Rules

- Electron pair tend to minimize repulsion
- The repulsion order is l.p./l.p. > l.p./b.p. > b.p./b.p
- When lone pairs are there, bond angles are smaller than predicted
- Lone pairs choose larger sites
- Double bonds occupy more space
- Electro negative substituents occupy less space than electro positive elements (Bent's rule)

2.2 Lecture 2

The Valance Bond (V.B.) Theory

The V.B. theory of bonding is the first quantum mechanical theory of bonding to be developed and can be regarded as a way of expressing Lewis's concepts in wave functions

But , the M.O. theory largely superseded V. B. theory

The Hydrogen Molecule

The two electron wave function for two widely separated H-atoms is $\Psi = \chi_A(1) \chi_B(2)$

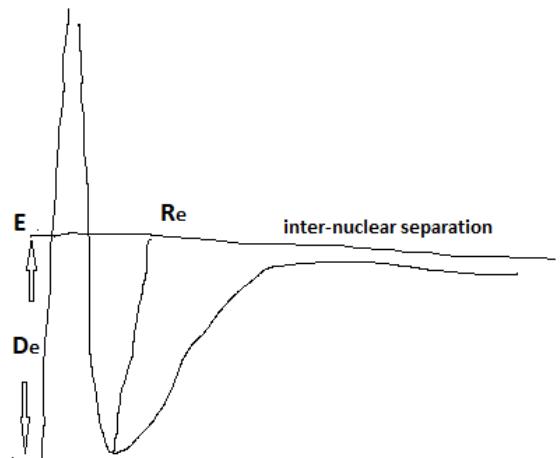
When the atoms are close, it is not possible to know whether it is that electron 1 is on atom A or electron 2 is on atom B or vice versa

When two outcomes are equally possible, Quantum mechanics instructs that the true state of the system as a superposition of the wave function for each probability and can be written as

$\Psi = \chi_A(1) \chi_B(2) + \chi_A(2) \chi_B(1)$ → This eqn. is the un-normalized wave function of the H-H bond.

The Hydrogen Molecule

- Molecular potential energy curve → total energy of a molecule varies as the inter-nuclear separation is changed.
- E = 0 is the energy of the free atom
- The energy falls suddenly when the two separated H-atoms were brought within bonding distance and each electron is free to migrate each others orbitals.



But, when the two atoms are brought further closer coulombic repulsions between the two positively charged nuclei increases rapidly.

The Deeper the minimum, stronger the atoms are bonded together

According to Pauli's principle, only electrons with paired spins can be described by the wave function shown above and can contribute to the σ-bond in V. B. Theory

The σ-bond has cylindrical symmetry and electrons in it has zero orbital angular momentum around the inter-nuclear axis.

The Homonuclear diatomic Molecule

Same description can be applied....

For ex. $N_2 \rightarrow$ To construct the V.B. description of N_2 , we consider the V.E.s of each N-atom.

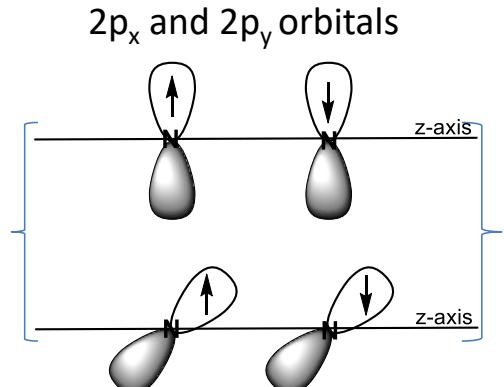
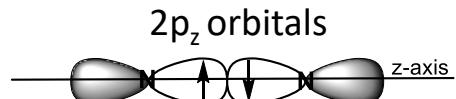
$2s^2 2p_x^1 2p_y^1 2p_z^1 \rightarrow$ consider z as the inter-nuclear axis.

Imagine $2p_z$ of one atom point towards to that of another atom with $2p_x$ and $2p_y$ orbitals perpendicular to the axis

σ -bond is formed by spin pairing between 2-electrons in the opposing p_z -orbitals

The remaining $2p$ - orbitals can not merge to give σ -bonds \rightarrow don't have cylindrical symmetry around the inter-nuclear axis.

Electrons in them approach side-by-side to give two π -bonds



Polyatomic Molecules

- Each σ -bond in a polyatomic molecule is formed by the spin pairing of electrons in any neighboring atomic orbital with cylindrical symmetry about the relevant inter-nuclear axis.
- Similarly, the π -bonds \rightarrow formed with orbitals of appropriate symmetry.
- But there are some discrepancies....
Consider H_2O , O \rightarrow $2s^2 2p_x^2 2p_y^1 2p_z^1$; the $2p_y$ and $2p_z$ orbitals with one unpaired electron each will interact with H-1s electrons forming O-H bonds
- Since the $2p_y$ and $2p_z$ orbitals both lie at 90° , their O-H bonds also should lie at 90° . But the actual angle is 104.5° .
- Similarly for $\text{NH}_3 \rightarrow 107^\circ$ not 90°
- What is the origin of this discrepancy?

Promotion

In H_2O and NH_3 the $2s^2$ orbital is not participating in bonding and hence they remain in their divalent and trivalent states.

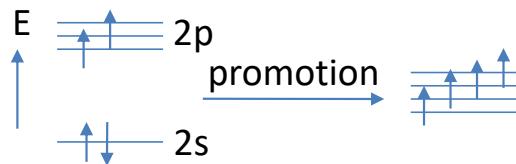
Along these line, C-atom has to divalent; but in contrast it is in tetravalent state.

This is due to promotion of its electron(s) to a higher energy.

“Although electron promotion requires an investment of energy, it is worthwhile if the energy can be more than recovered from the greater strength of the number of bonds that is allowed to be formed.”

In carbon, promotion lead to $\rightarrow 2s^1 2p_x^1 2p_y^1 2p_z^1$

This promotion energy is quite small and carbon gains energy by forming 4 bonds (ex. CH_4) as well as by relaxing the electron-electron repulsions in the 2s level, which also brings down the energy.

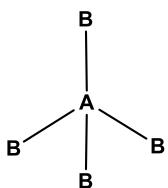


Hybridization

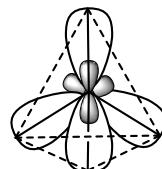
Consider the type AB_4 (ex. CH_4)

Expected: 3 σ -bonds of one type (from χ_B and $\chi_A 2p$) and a 4th one (from χ_B and $\chi_A 2s$). But all the evidences, bond-length, strength and shape point to the equivalence of all 4 bonds.

This problem is overcome by realizing that the electron density distribution in the promoted atom is equivalent to the electron density in which each electron occupies a hybrid orbital formed by interference between A_{2s} and A_{2p} orbital (interference of wave ripples) → leading to 4 new shapes due to constructive and destructive interference



| | |
|--------------------------|--------------------------|
| $h_1 = s + px + py + pz$ | $h_2 = s - px - py + pz$ |
| $h_3 = s - px + py - pz$ | $h_4 = s + px - py - pz$ |



Each hybrid orbital now consists of a large lobe pointing in the direction of one corner of a tetrahedron and a smaller lobe at the origin of tetrahedron.

The angle between the axis of the hybrid orbitals is

$\cos(1/3) = 109.47^\circ \rightarrow \text{sp}^3 \text{ hybrid} \rightarrow \text{four equivalent A-B } \sigma\text{-bonds}$

Hybridization

- Important aspect of hybridization → pronounced directional character → enhanced amplitude in the inter-nuclear region
- This gives rise to higher bond strengths to sp^3 hybrids compared to the bonds formed from s & p orbitals alone.
- Similarly, Hybrid orbitals of different composition were used to match different geometry

| C.N. | Shape/Arrangement | Composition |
|------|----------------------|-----------------|
| 2 | Linear | sp, pd, sd |
| 2 | Angular | sp, pd, sd |
| 3 | Trigonal planar | Sp^2, p^2d |
| 3 | Trigonal pyramidal | Sp^2, p^2d |
| 4 | tetrahedral | sp^3, sd^3 |
| 4 | Square planar | P^2d^2, sp^2d |
| 5 | Trigonal bipyramidal | Sp^3d, spd^3 |
| 6 | Octahedral | sp^3d^2 |
| 6 | Trigonal prismatic | Spd^4, pd^6 |

Compositions of the Hybrid Orbitals

Most Hybridization result in equivalent hybrid orbitals → all the hybrid orbitals are identical in composition with respect to each other both in terms of the %s & %p character and in spacial orientation.

For ex. Tetrahedral and octahedral molecules → very high shape

In case of dsp^3 TBP structure, the resulting hybrid orbitals are not equivalent → three strong equatorial bonds (sp^2 trigonal orbitals) and two weaker axial bonds (dp linear orbitals).

Similarly for the square pyramidal geometry dsp^3 → square planar dsp^2 set + a p_z orbital

Compositions of the Hybrid Orbitals

The relationship between hybridization and bond angles is simple for s-p hybrids. For two or more equivalent orbitals, the %s and %p character is given by the relationship

$$\cos \theta = \frac{S}{S-1} = \frac{P-1}{P}$$

where θ is the angle between two equivalent orbitals ($^{\circ}$) and the %s and %p characters are expressed in decimal fractions.

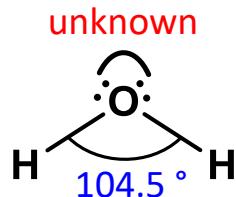
For CH_4 , the hybridization is sp^3

$$\cos \theta = \frac{S}{S-1} = \frac{0.25}{0.25-1} = \frac{0.25}{-0.75} = -0.333$$

Therefore $\theta = \cos^{-1}(-0.333)$ which is $\theta = 109.5^{\circ} \rightarrow$ case of an equivalent hybrid.

Non Equivalent Hybrids

- No equivalent hybrids (for ex. H₂O) exhibits **fractional s & p character**. It uses its bonding orbitals midway between pure p and sp³.
- For such molecules in sp³ hybridization, their 4 orbitals can be divided into bonding subsets and non-bonding subsets.

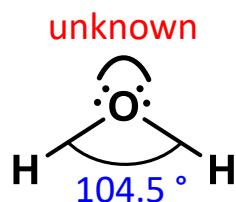


For H₂O, the angle between the orbitals of bonding subsets is 104.5 °. However, the angle between the orbitals of non-bonding subsets is experimentally unknown and can be deduced as follows.

The angle between the bonding subsets $\theta = 104.5^\circ$

$$\cos 104.5^\circ = -0.25 = \frac{s}{s-1} = \frac{0.20}{0.20-1} = \frac{0.20}{-0.80} \rightarrow \%s = 20\% \text{ and } \%p = 80\%$$

Non Equivalent Hybrids



The total p-character summed over all 4 orbitals must be 3 and s-character must be 1.

$$\text{Total p-character} = (0.80+0.80+x+x) = 3; 2x = 3 - 1.6 = 1.4 \rightarrow x = 0.7 \rightarrow \%p \text{ (non-bonding)} = 70\%$$

$$\text{Total s-character} = (0.20+0.20+y+y) = 1; 2y = 1 - 0.4 = 0.6 \rightarrow y = 0.3 \rightarrow \%p \text{ (non-bonding)} = 30\%$$

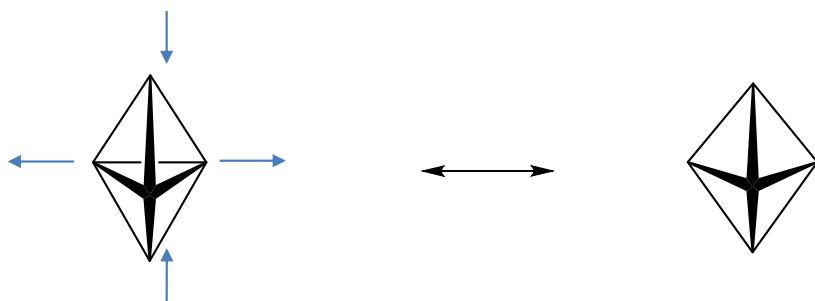
The angle θ between the non-bonding subsets is computed to be

$$\cos \theta = \frac{s}{S-1} = \frac{0.30}{0.30-1} = \frac{0.30}{-0.70} = -0.4285 = 115.37^\circ$$

Non Equivalent Hybrids

For AB_5 molecules, unlike 2, 3, 4, 6 coordination numbers, there is no unique highly symmetric set of equivalent orbitals that can be considered for 5 coordination.

Also, the two possibilities of TBP and SP are inter-linked.



The calculation of s & p character is more difficult if either d-orbitals participate in hybridization or if none of the orbitals is equivalent to another to form a subset.

Take home exercise: Please find the %s and %p characters of the molecule ammonia both for the bonded and non-bonded subsets.

Hypervalence

Elements of period 2 obeys octet rule, but the elements of later periods shows deviations from it.

'P-atom' in PCl_5 requires 10 electrons in valance shell. S-atom must have 12 electrons in SF_6 . Presence of such electrons exceeding octet configuration → Hypervalence or Hyper-coordination

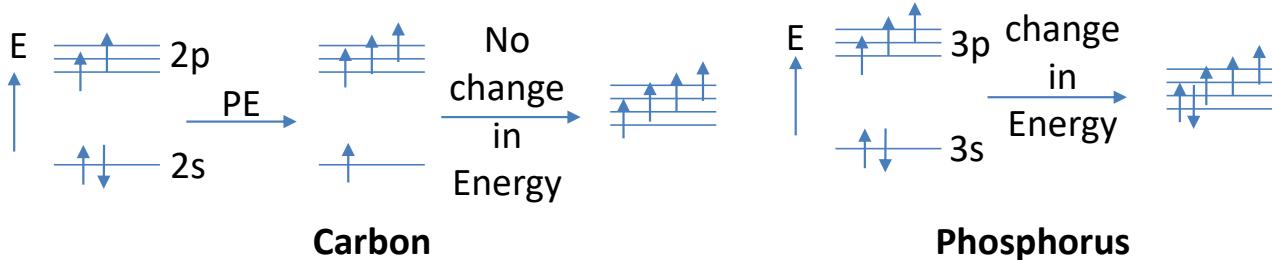
Traditional Explanation → Availability of Low-lying d-orbitals
P-atom can accommodate more than 8-electrons if it uses the 3d-orbitals.

However, the absence of the 2d-shell alone is not responsible for the rarity of hypervalence in period 2 elements. Reasons such as geometrical difficulty of packing more than four atoms around a small central atom might also limit the existence of hypervalency in them.

The Molecular Orbital Theory efficiently describes the hypervalent compounds without invoking the participation of d-orbitals

Bent's Rule and the Energies of Hybridization

- When a set of hybrid orbitals is constructed from a set of atomic orbitals, the energy of the resultant hybrids is the weighted average of the energies of the atomic orbitals
- For ex. When carbon forms 4-covalent bonds, although there is a promotion energy (P.E.), this is independent of the hybridization to the valance state.
- In P-atom, there is little (no) P.E. Hybridization will cost energy as the filled 3s orbital is raised and half filled 3p orbital is lowered in energy.



This energy of hybridization is of the order of the magnitude of bond energy and thus be important in determining the structure of the molecule. It is also responsible for the tendency of some of the lone pairs to occupy the spherical and non-stereochemically active s-orbital rather than the stereochemically active sp hybrid orbital.

Bent's Rule and the Energies of Hybridization

Energy factors determines the most stable arrangement of atoms. Variation of bond energy with hybridization

For ex.: It costs around 600 KJ/mol to hybridize a central P-atom alone. Other higher congeners will have subsequent higher energies

When there is higher P.E. and better overlap, then the hybrid will be rich in s-character

Poor overlap and lower P.E. leads to P-rich character

The sp^3d hybrid orbital set may be considered to be a combination of $p_zd_z^2$ hybrids and sp_xp_y hybrids

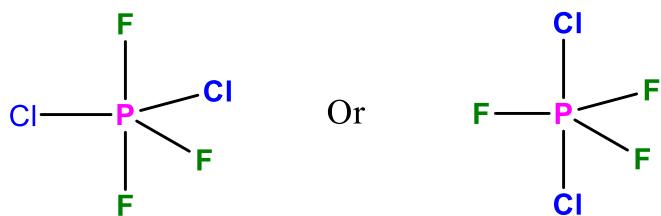
$p_zd_z^2 \rightarrow$ Two linear hybrid orbitals binding axially \rightarrow weaker
 $sp^2 \rightarrow$ Three trigonal equatorial bonds \rightarrow stronger

Bent's Rule and the Energies of Hybridization

When the electronegativity of the substituents on the P-atom differs ($\text{PCl}_x\text{F}_{5-x}$), it is experimentally observed that, the more electronegative substituent occupies the axial position and the less electronegative substituent is equatorially situated. → This is an example of a Bent's Rule.



Which str. Is favoured?



Bent's Rule states that "More electronegative substituents prefer hybrid orbitals having less 's' character and more electropositive substituents prefer hybrid orbitals having more 's' character."

Take home example:

Consider the molecule CH_2F_2 . Explain the bond-angles in this molecule using both VSEPR and Bent's Rules.

2.3 Lecture 3+4

Molecular Orbital Theory

Key points: Molecular orbitals are constructed as linear combinations of atomic orbitals; there is a high probability of finding electrons in atomic orbitals that have large coefficients in the linear combination; each molecular orbital can be occupied by up to two electrons.

Approximations of the Theory

Orbital Approximation

$$\Psi = \Psi(1) \Psi(2) \dots \Psi(N_e)$$

- The electron 1 is described by $\Psi(1)$ and electron 2 by $\Psi(2)$ and so on.
- These one-electron wavefunctions are the molecular orbitals of the theory
- The square of a one-electron wavefunction gives the probability distribution for that electron in the molecule.
- An electron can be found where the orbital has a large amplitude and not found at any of the nodes

Linear Combination of Atomic Orbitals (LCAO)

- When an electron is close to the nucleus of one atom → its wavefunction resembles its atomic orbital
- Therefore, a reasonable first approximation to the molecular orbital can be constructed by superimposing the atomic orbitals contributed by each atom → LCAO approximation.
- A Linear combination is a sum with various weighted coefficients.
- In simple terms → combination of atomic orbitals of contributing atoms give the M.O.s that extend over the entire molecule

Fundamental of the Molecular Orbitals

The most elementary form of the theory, the valance shell of the atomic orbitals (χ) are used for the Mos. Thus, for H_2

$$\Psi = C_A \chi_A + C_B \chi_B$$

The coefficient C is the linear combination shows extend to which the atomic orbitals contribute to the MOs

- To interpret the coefficients, we note that C_A^2 is the probability of the electron in χ_A and C_B^2 is that of the electron in χ_B .
- Since both atomic orbitals contribute to the MO, there is interference between them where their amplitudes are non-zero.
- The probability distribution is given by $\Psi^2 = C_A^2 \chi_A^2 + 2C_A C_B \chi_A \chi_B + C_B^2 \chi_B^2$
- The term $2C_A C_B \chi_A \chi_B$ represents the contributions to the probability density due the interference

Fundamental of the Molecular Orbitals

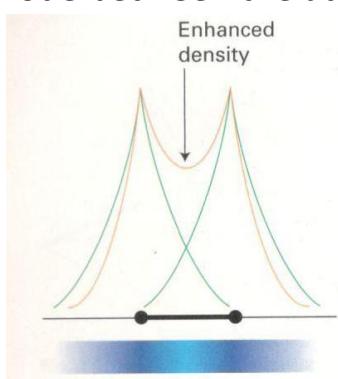
- For H_2 , its electrons are equally likely to be found near each nucleus. So the linear combination that gives the lowest energy will have equal contribution from each 1s orbital.
- Therefore, $C_A^2 = C_B^2$, leaving open the possibility that
 $C_A = + C_B$ or $C_A = - C_B$
- Ignoring normalization, the two molecular orbitals are

$$\Psi_{\pm} = \chi_A \pm \chi_B$$

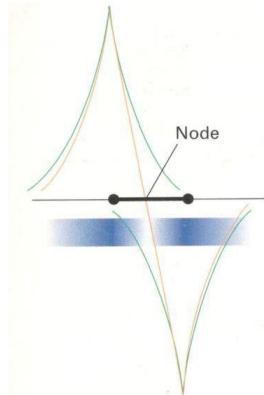
- The relative signs of the coefficients of the LCAOs play a very important role in determining the energies of the orbitals.

Fundamental of the Molecular Orbitals

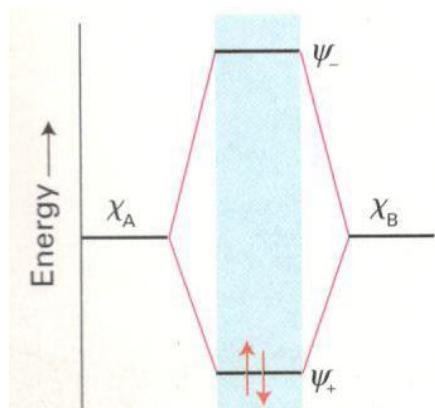
A bonding orbital arises from the constructive interference of neighbouring atomic orbital; an antibonding orbital arises from their destructive interference, as indicated by a node between the atoms



Constructive interference:
enhancement of electron density
in the inter-nuclear region



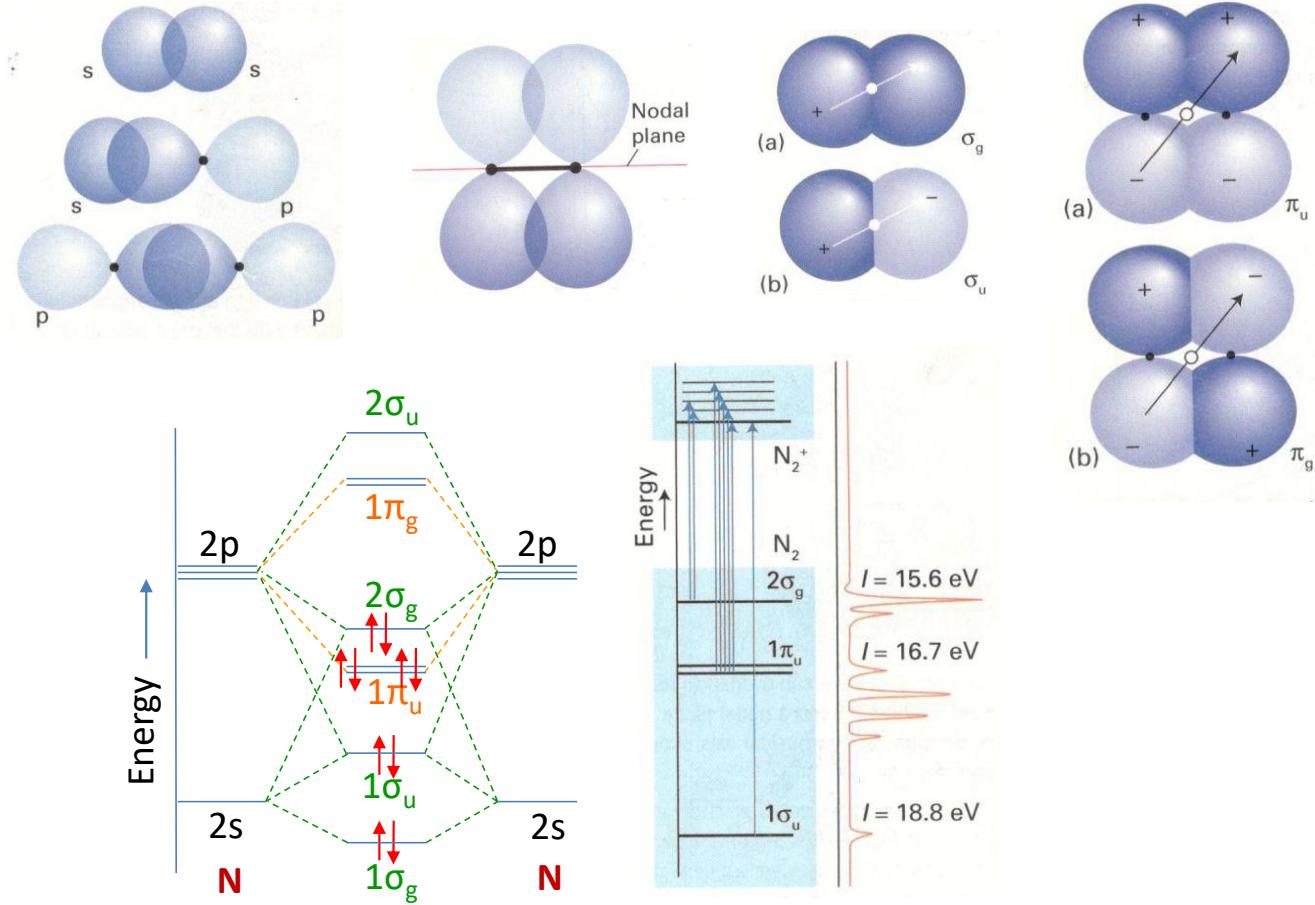
**Destructive interference: nodal
surface in an antibonding
molecular orbital**



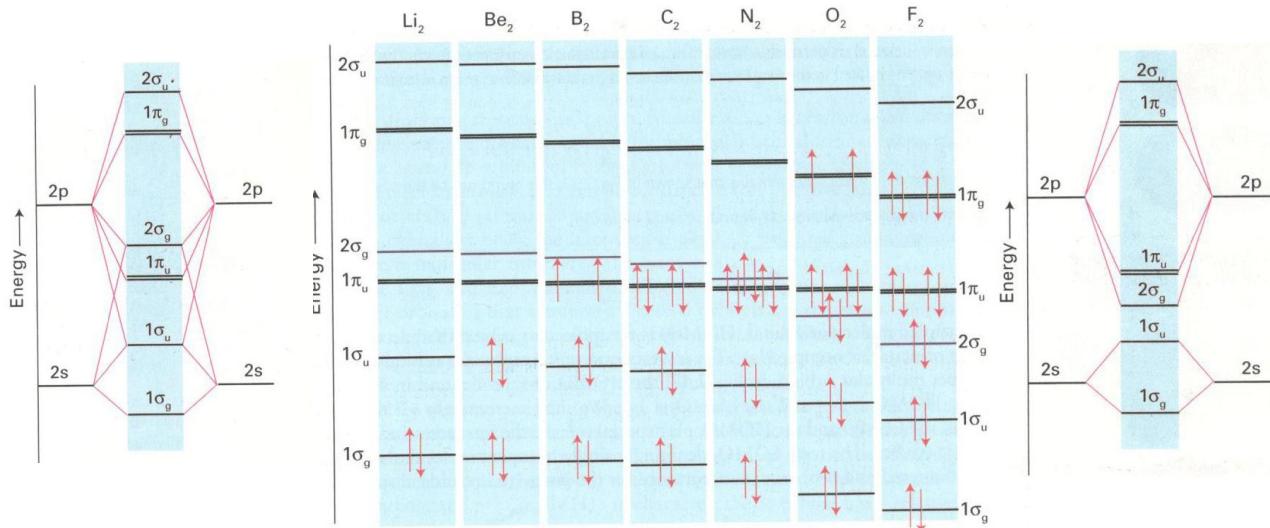
**Molecular orbital energy level diagram for
 H_2 and analogous molecules**

- Experimental energy gap between the two Mos.: Spectroscopic absorption in H_2 is 11.4 eV → transition of an electron from bonding to antibonding orbital.
- The dissociation energy of H_2 is 4.5 eV (434 KJ/mol) → indication of the location of bonding orbital relative to the separated atoms

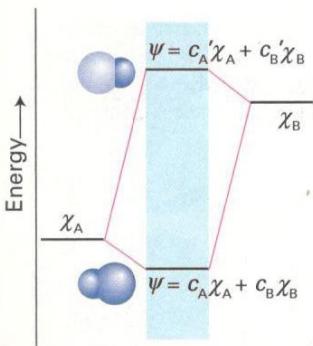
Homonuclear Diatomic Molecules: case of N₂



Homonuclear Diatomic Molecules



- Eight M.O.s are constructed from four atomic orbitals on each atom
- 4 σ-bond orbitals and 4 π-bond orbitals
- The 4 σ-orbitals span a range of energy: one strongly bonding and another strongly antibonding and two lie between these extremes
- The 4 π-orbitals form a two doubly degenerate pairs of bonding and antibonding orbitals



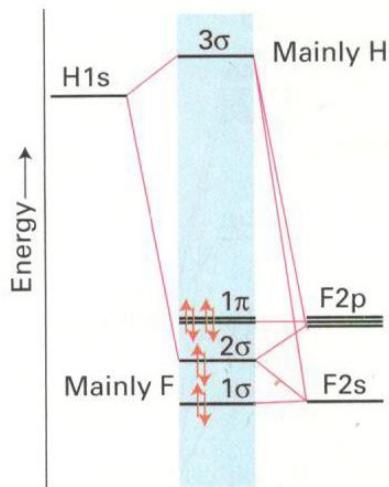
Hetero-nuclear Diatomic Molecules

Differs from homonuclear diatomic molecules due to unequal contributions from each atomic orbitals

Each M.O. has the form $\Psi = C_A\chi_A + C_B\chi_B + \dots$

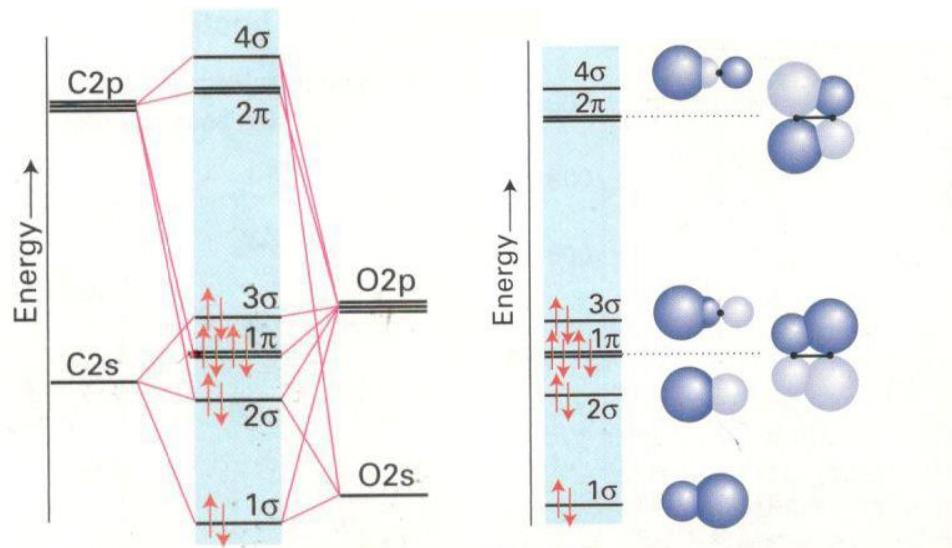
- Greater contribution to the bonding M.Os. → Electronegative atoms
- Contribution to the antibonding M.Os. → Less Electronegative atoms
- Second difference between homo- and heteronuclear M.Os. → Energy mismatch of their corresponding atomic orbitals
- Energy separation of such A.Os. implies less pronounced overlaps
- However, A—B bonds are not always weaker than A—A bonds as other factors such as orbital size and closeness of approach decides the strength
- Bond enthalpy of CO (1070 KJ/mol) is higher than its isoelectronic counter part N₂ (946 KJ/Mol)

Heteronuclear Diatomic Molecules: HF



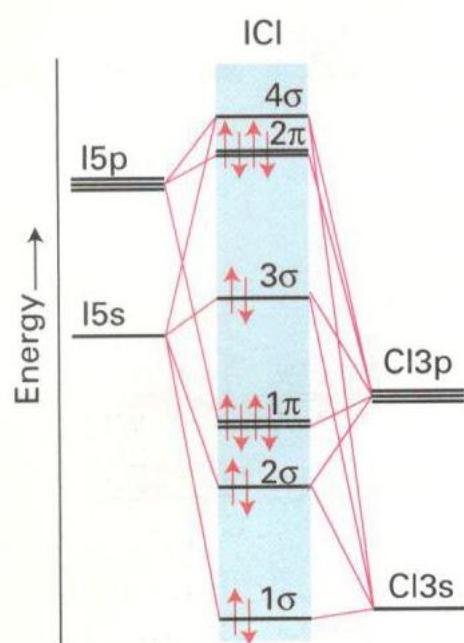
- Three σ -orbitals can be constructed : from H1s, F2s and F2pz orbitals
 - The F2px and F2py orbitals are unaffected due to the unavailability of the matching orbitals and have π -symmetry → Examples of a non-bonding orbital
 - Note that there is no centre of inversion in heteronuclear diatomic molecule and so g, u classifications are not used.
-
- Total 8 V. E.s: Two occupy the 2σ , which is the bonding orbital
 - The six electrons occupy the 1σ and 1π orbitals which are largely non-bonding.
 - Note that all electrons occupy the orbitals that are predominantly on the F-atom. This makes HF to be polar with a partial negative charge on the F-atom.

Heteronuclear Diatomic Molecules: CO



- $1\sigma \rightarrow$ Localized on O-atom \rightarrow non-bonding; $2\sigma \rightarrow$ bonding
- $1\pi \rightarrow$ bonding \rightarrow mainly O2p; $3\sigma \rightarrow$ largely bonding \rightarrow HOMO of CO \rightarrow C2pz
- $2\pi \rightarrow$ LUMO \rightarrow C2p character.
- The presence of both HOMO and LUMO orbitals on C-atom facilitate its coordination to metal ions through C-atoms \rightarrow σ -donation and π -back-donation

Heteronuclear Diatomic Molecules: ICl



- ICl molecule: Try yourself

Molecular Orbital Theory of Polyatomic Molecules

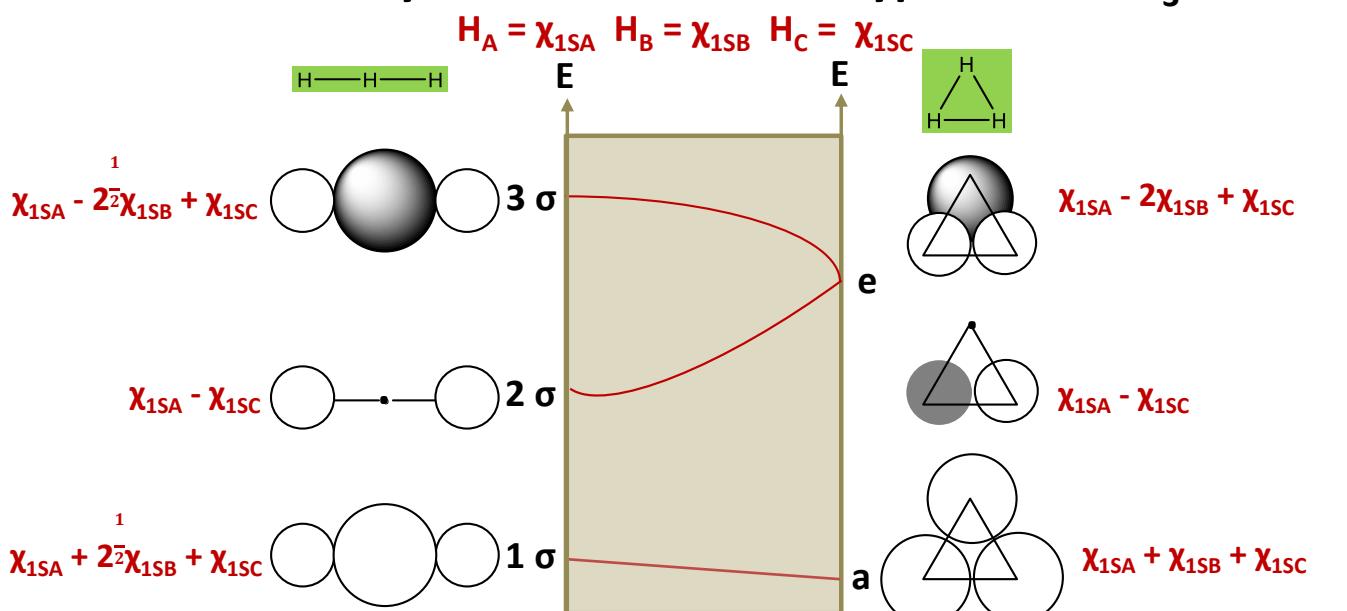
- MOT → Useful to discuss the electronic structure of triatomic molecules, finite group of atoms and almost the infinite arrays of atoms
- Mostly resemble that of diatomic molecules → only difference that the orbitals are built from a more extensive basis sets → from 'N' A.O.s 'N' M.O.s can be built
- Similar to diatomic molecules, we can write the M.O.s of a given symmetry (say, the σ -orbitals of a linear molecule) as a sum of all the overlapping A.O.s

$\Psi = \sum c_i \chi_i$ → The index 'i' runs over all the atomic orbitals of appropriate symmetry

Then

1. The greater the number of nodes in a M.O., the greater the anti-bonding character and higher the symmetry
2. Orbitals constructed from lower energy orbitals lie lower in energy ('s' is lower in energy than 'p' in a given shell)
3. Interactions between non-nearest neighbor atoms are weakly bonding or weakly antibonding depending upon the signs of their lobes.

MOT of Polyatomic Molecules: Hypothetical H₃



1σ = Bonding between HA & HB and HB & HC

2σ = Bonding between HA & HC; negligible interaction between them

3σ = Anti-bonding between HA & HB and HB & HC

1σ = Bonding between HA & HB, and HB & HC and HA & HC

But 2σ and 3σ will now have same energy. 2σ = anti-bonding for HA & HC: **rise in E.** 3σ = Anti-bonding between HA & HB and HB & HC but bonding for HA & HC: **decrease in E.**

MOT of Polyatomic Molecules

It is always not-appropriate to use the notation σ and π in polyatomic systems as in linear molecules. However, they are often convenient to use to represent the local form of an orbital, its shape etc. → Example of how the language of VBT survives in MOT.

Note that

- a, b denote a nondegenerate orbital
- e denotes a doubly degenerate orbital (two orbitals of the same energy)
- t denotes a triply degenerate orbital (three orbitals of the same energy).

Subscripts and superscripts are sometimes added to these letters, as in a_1 , b'' , e_g , and t_2 because it is sometimes necessary to distinguish different a, b, e, and t orbitals according to a more detailed analysis of their symmetries.

MOT of Polyatomic Molecules: NH₃

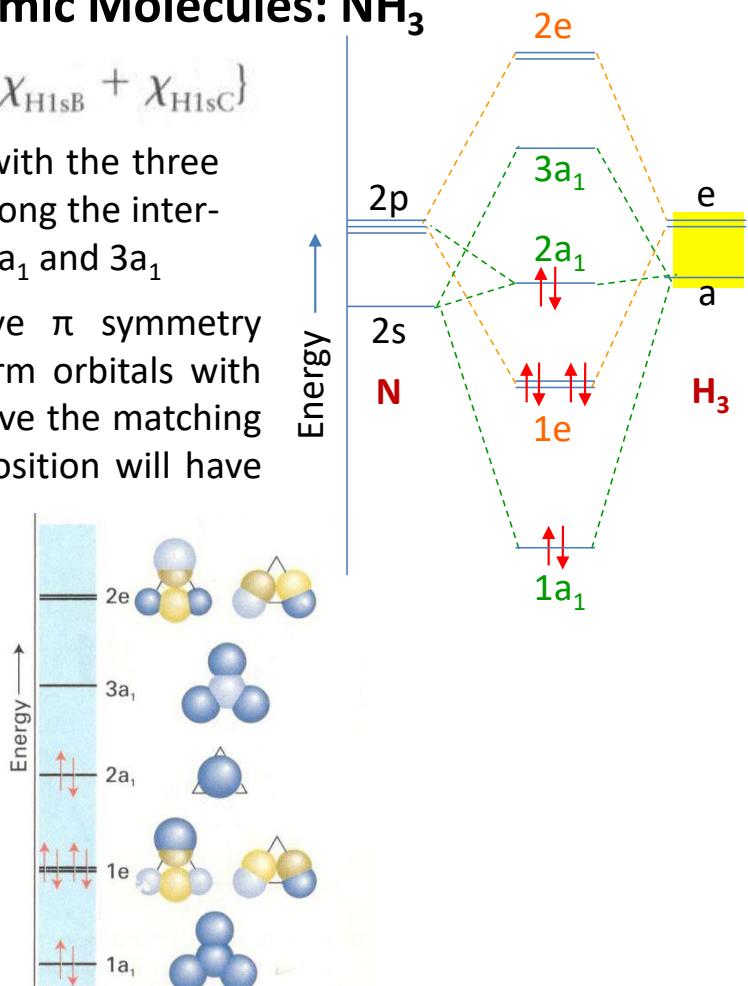
$$\psi = c_1 \chi_{N2s} + c_2 \chi_{Np_z} + c_3 \{\chi_{H1sA} + \chi_{H1sB} + \chi_{H1sC}\}$$

N2s and N2pz orbitals superimpose with the three H1s orbitals to give three σ orbitals along the inter-nuclear axis \rightarrow 3 MOs. Labelled 1a₁, 2a₁ and 3a₁

The N2px and N2py orbitals have π symmetry orbitals w.r.t. z-axis and used to form orbitals with combinations of H1s orbitals that have the matching symmetry. For example one superposition will have the form

$$\psi = c_1 \chi_{N2p_x} + c_2 \{\chi_{H1sA} + \chi_{H1sB}\}$$

The eight electrons occupy the M.O.s in the increasing order of energy.



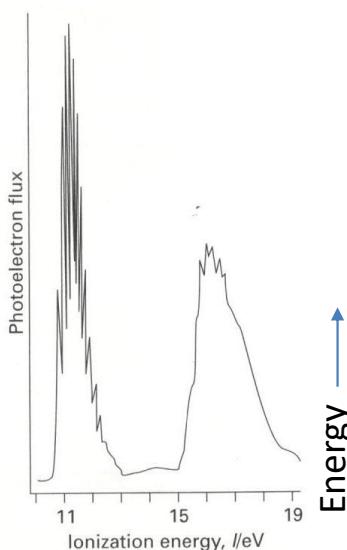
CH-2113: Introductory Inorganic Chemistry
Instructor: R. Boomie Shankar

MOT of Polyatomic Molecules: NH₃

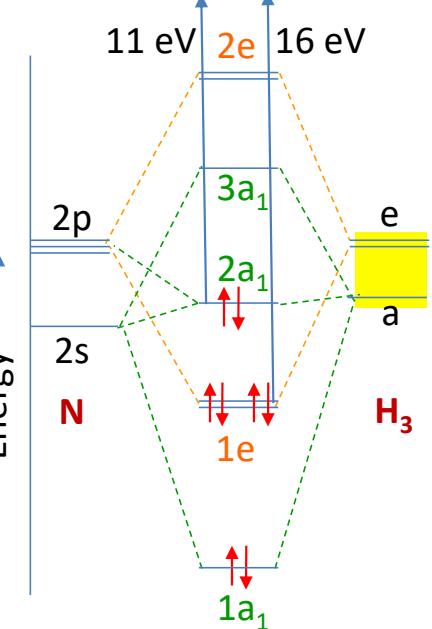
The actual location of the orbitals can be found by detailed computation or by identifying the orbitals responsible for the photoelectron spectrum.

The 11 eV and 16 eV peaks are assigned to the 2a₁ and 1e orbitals.

The 1a₁ orbital is out of range for the 21 eV radiation used to obtain the spectrum.



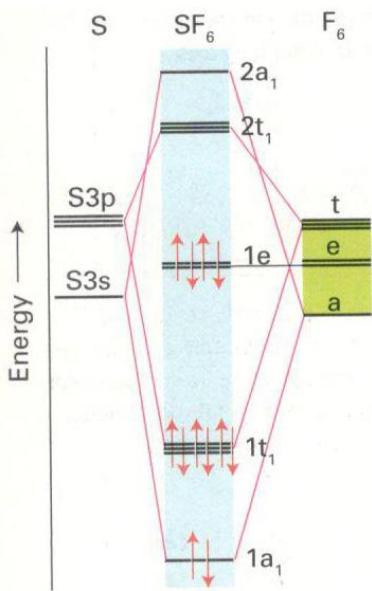
Excited state: photo-ejection of electrons



The HOMO is 2a₁, which is largely confined to the N-atom and makes only small contribution to the bonding → consistent with the fact that the lone pairs play a considerable role in determining the shape of the molecule. The vibration structure for the 11 eV transition is due to distortions to the shape of the molecule upon removal of the electron from the l.p.

Hypervalence in the context of molecular orbitals: SF_6 example

VBT explains hypervalence by using d orbitals



In SF_6 this can be explained easily by using the available bonding, non-bonding and anti-bonding molecular orbitals

In the octahedral geometry, the six F-ions can give rise to six ligand-group orbitals of non-degenerate, doubly degenerate and triply degenerate sets.

The S3s interacts with the ligand a-orbitals to give one bonding and one non-bonding orbitals.

The S3p interacts with the t-set of orbitals to give two sets of triply degenerate orbitals.

There is no matching for the ligand e orbitals → so non-bonding

The 12-valence electrons of SF_6 can be accommodated in the bonding (1a_1 , 1t_1) and non-bonding (1e) orbitals and all the anti-bonding orbitals are free. Therefore the molecule is stable.

Localization

Striking feature of VB approach to Chemical bonding → Chemical instinct → identifies something that can be called as A-B bonding.

For example, both OH bonds in H_2O are treated as localized, equivalent structures because each one consists of an electron pair shared between O and H.

This feature seems to absent from MO theory → MOs are delocalized and electrons occupy them bind all atoms together.

The concept of an A-B bond existing independently of other bonds in the molecule, transferable from one molecule to another seems to be lost in MOT.

Lets now see that how the MO description is mathematically almost equivalent to a localized description of the overall electron distribution.

...and how the linear combinations of MOs can be formed in the same overall electron distribution, but the individual orbitals can be different.

Localization

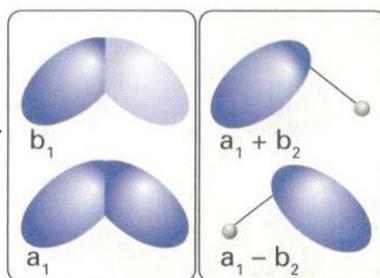
Consider the MO of $\text{H}_2\text{O} \rightarrow$ The two occupied MOs. in the delocalized description are $1a_1$ and $1b_2 \rightarrow$ The sums and differences of these orbitals create the localized orbitals.

In the additive sum of $1a_1 + 1b_2$, the negative lobe of $1b_2$ cancels half of $1a_1$ orbital, leaving a localized orbital between O and other H.

Likewise, the other half of $1a_1$ orbital is cancelled for $1a_1 + 1b_2$, the difference between these orbitals giving rise to the localized description for the other OH group.

Localized and delocalized descriptions \rightarrow Two equivalent ways of describing the same overall electron populations \rightarrow one can not be better than the other.

The two occupied MOs of H_2O , $1a_1$, $1b_2$ and their sum and difference. In each case, we form a fully delocalized orbital between a pair of atoms



Localization

See table below for some suggestions to select a delocalized description or a localized description

A delocalized description is suggested for describing the global properties of the entire molecule.

A localized description is adopted for describing the properties of a fragment of an entire molecule, because it focusses on the distribution of electrons in and around a particular bond.

A General Indication of the properties for which localized and delocalized descriptions are appropriate

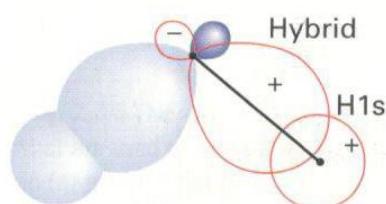
| Localized appropriate | Delocalized appropriate |
|---|---|
| Bond Strengths | Electronic Spectra |
| Force constants | Photoionization |
| Bond lengths | Magnetism |
| Bronsted Acidity | Standard Potentials |
| VSEPR Description of Molecular Geometry | Walsh Description of Molecular Geometry |

Localized bonds and Hybridization

The description of localized MO bonds can be further expressed by invoking the concepts of hybridization.

MOs are typically formed from the AOs of appropriate symmetry → However, it is convenient to form a mixture of orbitals on one atom ('O' in water) and then use these hybrids to construct the localized molecular orbitals → for example each OH bond can be regarded as formed by the overlap of an H1s orbital and a hybrid orbital composed of O2s and O2p orbitals

In this procedure, once the hybrid orbitals have been selected, the localized molecular orbital descriptions can be constructed → For ex. the four CF₄ bonds can be formed by building bonding and antibonding localized orbitals by overlap of each hybrid orbital with one F2p orbital directed towards it.



2.4 Lecture 5+6

Main Group Chemistry

- The most fascinating aspect of inorganic chemistry and its most difficult problem is the diversity of reactions and structures encountered over one hundred elements.
- The challenge is to be able to treat adequately the chemistry of non-metals and noble gases, transition metals and inner transition metals.
- The tool that the inorganic chemist uses to systematize elemental relationships is the periodic table.
- Within a given family there are increases in size and decreases in ionization energy, electron affinity, electronegativity, etc.
- Increasing the atomic number across a given period results in concomitant increase in ionization, electron affinity and electronegativity, but a decrease in size.
- The change in effective nuclear charge within a period is reasonably smooth, but the various periods differ in length (8, 18, and 32 elements).
- Another aspect of Periodic trends: Pronounced differences in similar elements. For example, between the first ten, H-Ne, and those immediately following Na-Ar. → not completely obvious why? May be lighter elements utilize only 1s, 2s and 2p orbitals.

A representative information on the Periodic trends: Group 13 elements

- Group 13 elements → B, Al, Ga, In and Tl
- Boron is the only nonmetal in this group; Aluminium is the most abundant element → Results in a diversity of chemical properties and some distinctive trends → increase in the metallic character from B to Tl
- Alteration effects are seen in the electronegativities of the metals Al, Ga and In → Ga being more electronegative than Al (and In, as expected)
- The chemical properties of 'B' are distinct from those of the rest of the series, however 'B' shows diagonal relationship with 'Si'
 - 'B' and 'Si form acidic oxides, B_2O_3 and SiO_2 ; 'Al' forms amphoteric oxide Al_2O_3 .
 - Both 'B' and 'Si' form many polymeric oxide structures and glasses → reason for the existence of borosilicate glasses
 - 'B' and 'Si form flammable, gaseous hydrides; Aluminium hydride is a solid.

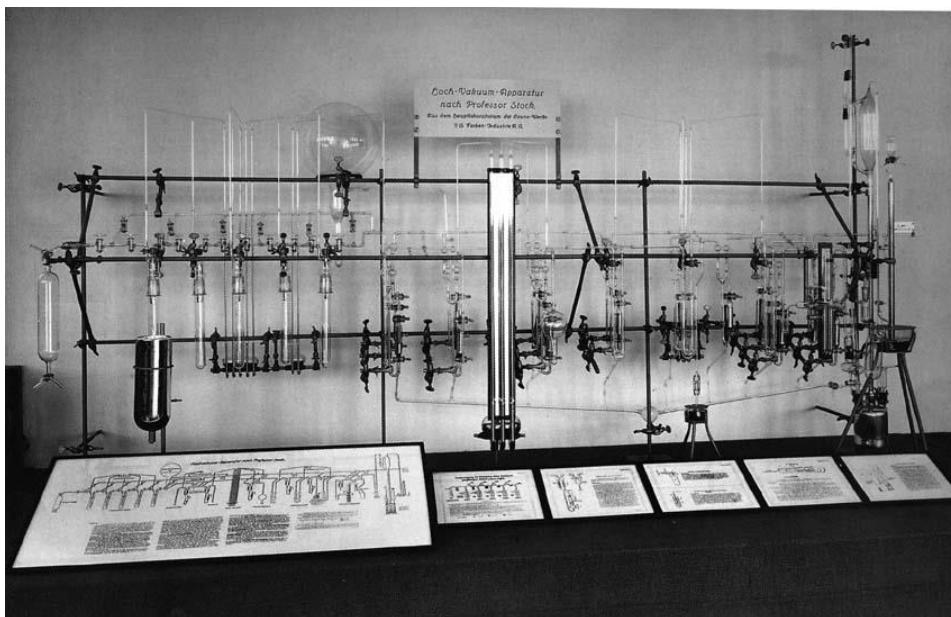
Most of the Group 13 elements adopt the +3 oxidation state; Tl preferable adopt the +1 oxidation state → due to inert pair effect

Main group Chemistry: Topics of Interest

Ability of their compounds to form various structures: Cages, Clusters, Rings, Chains and Frameworks and Polymers

- Cages and Clusters: Boron-hydrides, Zintl compounds, Phosphorus and its oxides and sulfides
- Rings, macrocycles and polymers: B-N, P-N and S-N compounds
- Chains and Frameworks: Silicon compounds and Silicates
- Introduction to Low-valent compounds and main-group organometallic Chemistry

Cages and Clusters: Boron Hydrides



**Alfred Stock
1912**

**father of
boron
hydrides**

Alfred Stock prepared a series of boron hydrides including B_2H_6 and separated them using the first sophisticated vacuum manifold. Due to their very high air and moisture sensitivity and flammability, till then they were not separable. He published his work in 1933.

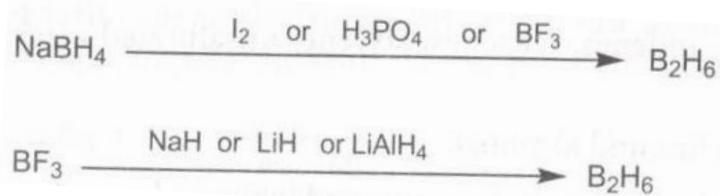
| B. P |
|----------------------|
| B_2H_6 -92.5 °C |
| B_4H_{10} 16 °C |
| B_5H_9 58 °C |
| B_5H_{11} 65 °C |
| B_6H_{10} 108 °C |
| $B_{10}H_{14}$ 213°C |
| m.p. 99.7 °C |



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Boron Hydrides: Diborane

- Boranes are very interesting class of molecules for their structure and bonding
- In the 1950s, USA and USSR spent a lot to explore their chemistry and develop them as rocket fuels
- Lower boranes are difficult to handle, catch fire on exposure to air with green flame
- Diborane can now be prepared in several methods as shown below.

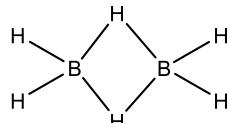


Structure of Diborane

$2 \times B = 6$ electrons

$6 \times H = 6$ electrons

Total 12 electrons

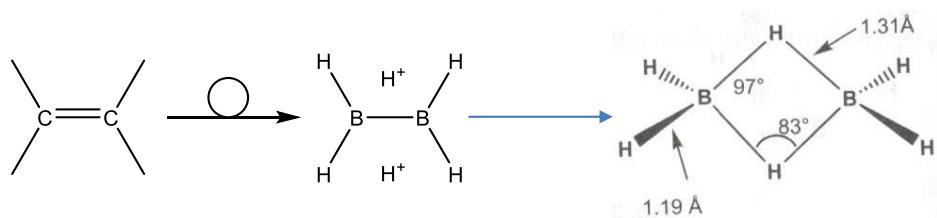


4 B-H terminal bonds = 6 electrons

4 bridging bonds requires 8 electrons,
but only 4 electrons are left.

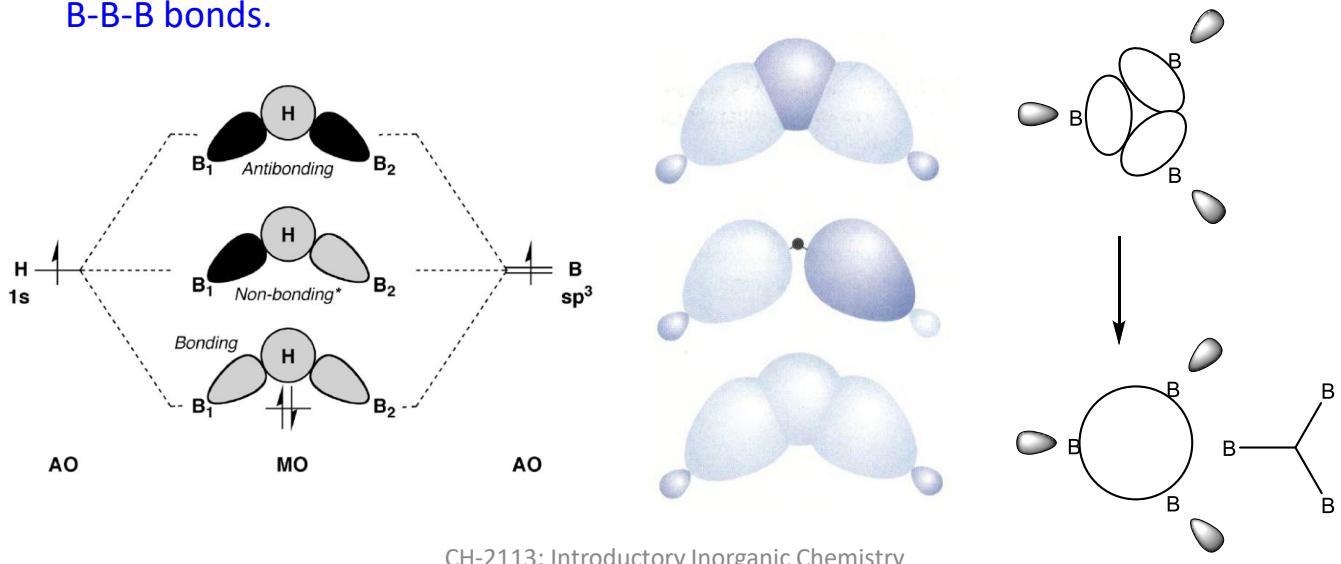
Hence the molecule is electron deficient

- A number of approaches has been used to rationalize the structure of diborane
- Earlier prediction assumes $[B_2H_4]^{2-}$ is isoelectronic to C_2H_4 and two H^+ ions are located above and below the plane of B-B bond
- This argument was later refined by the 3-centre-2-electron bond (3c-2e⁻) model.



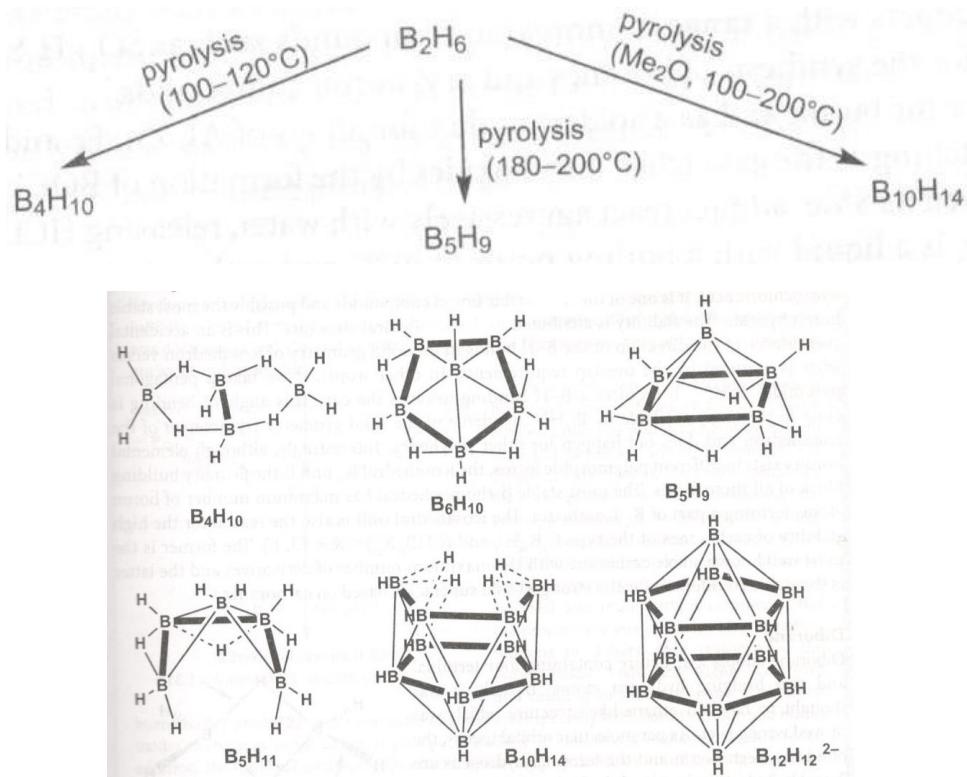
Structure of Diborane

- Each B-H-B bridge involves a delocalized 3c-2e⁻ bonds as follows.
- The atomic orbitals of two 'H's and one 'B' combine to give three orbitals, one bonding, one nonbonding and one antibonding for each B-H-B unit.
- Each B-H-B bridge accepts 2e⁻ in the respective bonding orbital and form the 3c-2e⁻ bonds to rationalize the dimer with four terminal B-H bonds and two bridging B-H-B bonds.
- Two other bonds are important for higher boranes: 2c-2e⁻ B-B bonds and 3c-2e⁻ B-B-B bonds.



Boron Hydrides: Polyhedral Boranes

- Most of the higher boranes can be prepared from diboranes by controlled pyrolysis reactions or by chemical reactions in the presence of hard and soft bases

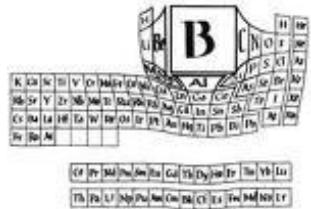
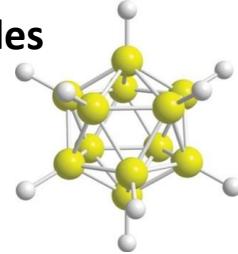


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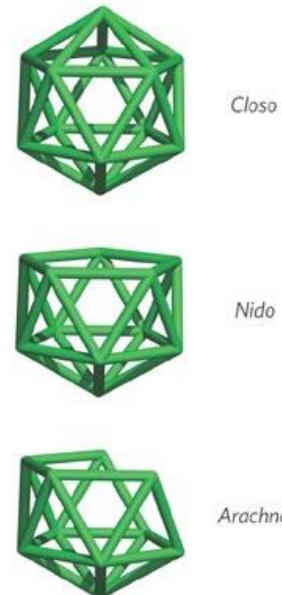


Polyhedral Boranes: Wade's Rules 1971

Ken Wade,
Durham



For borane and carborane clusters, the structures are based on **deltaahedra**, which are polyhedra in which **every face is triangular**. The clusters are classified as *closo*-, *nido*-, *arachno*- or *hypho*-, based on whether they represent a complete (*closo*-) deltaahedron, or a deltaahedron that is missing one (*nido*-), two (*arachno*-) or three (*hypho*) vertices.



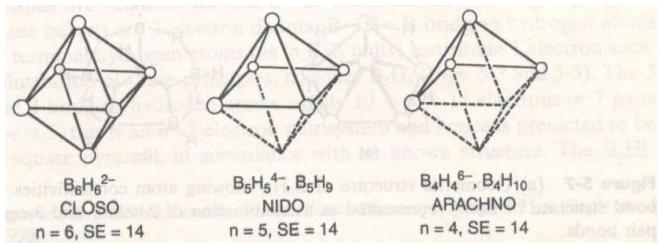
| Boron hydride | Name | No. of skeletal electron pairs | Examples |
|---|---------|--------------------------------|--|
| $[\text{B}_n\text{H}_n]^{2-}$ or B_nH_{n+2} | Closo | $n+1$ | $\text{B}_6\text{H}_6^{2-}, \text{B}_{12}\text{H}_{12}^{2-}$ |
| B_nH_{n+4} | Nido | $n+2$ | $\text{B}_2\text{H}_6, \text{B}_5\text{H}_9, \text{B}_{10}\text{H}_{14}$ |
| B_nH_{n+6} | Arachno | $n+3$ | B_4H_{10} |
| B_nH_{n+8} | Hypho | $n+4$ | $\text{B}_5\text{H}_{12}^-$ |

Each BH unit furnishes 2 skeletal bonding electrons; Each additional H furnishes 1 skeletal bonding electron; Ionic charges must be included in the electron count

Wade's Rules: Examples

| Boron hydride | Name | No. of skeletal electron pairs | Examples |
|---------------------------------|-------------|---------------------------------------|----------------------------------|
| $[B_nH_n]^{2-}$ or B_nH_{n+2} | Ccloso | $n+1$ | $B_6H_6^{2-}, B_{12}H_{12}^{2-}$ |
| B_nH_{n+4} | Nido | $n+2$ | $B_2H_6, B_5H_9, B_{10}H_{14}$ |
| B_nH_{n+6} | Arachno | $n+3$ | B_4H_{10} |
| B_nH_{n+8} | Hypno | $n+4$ | $B_5H_{12}^-$ |

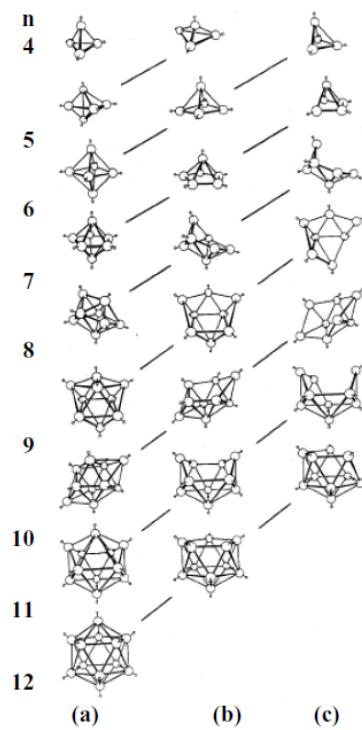
Polyhedral Relationships



Boron frameworks based on a 6-vertex, 14-skeletal electron octahedral cluster

Electron Counts for closed deltahedral clusters

| n | Polyhedron | p-block VEC | d-block VEC | NFE |
|----|------------------------------|-------------|-------------|-----|
| 5 | Tigonal bipyramidal | 22 | 72 | 12 |
| 6 | Octahedron | 26 | 86 | 14 |
| 7 | Pentagonal bipyramidal | 30 | 100 | 16 |
| 8 | Dodecahedron (cuboctahedron) | 34 | 114 | 18 |
| 9 | Tiicapped trigonal prism | 38 | 128 | 20 |
| 10 | Bicapped square antiprism | 42 | 142 | 22 |
| 11 | Octadecahedron | 46 | 156 | 24 |
| 12 | Icosahedron | 50 | 170 | 26 |



Deltahedra and deltahedral fragments for boranes and borane anions.

(a) The Closو boranes containing n boron atoms (b) Corresponding nido boranes (c) Corresponding arachno boranes]

Diagonal lines show the fragmentation patterns leading to the structures of the nido and arachno boranes

Zintl Compounds

Electropositive cationic element (alkali metal and alkaline earth metal, main group metal etc.) and an anionic element of moderate electronegativity

Resembles ionic solids in composition but are quite different

- Metallic property especially metallic luster
- Not full-value metals, not malleable and ductile but brittle
- Electrical properties: semiconductivity or moderate metallic conductors
- Obeys the 8-N rule

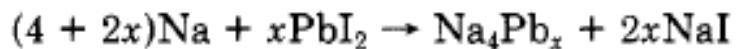
| | |
|-------------|---------------|
| VEC(X) < 8: | Polyanionic |
| VEC(X) = 8: | Simple ionic |
| VEC(X) > 8: | Poly cationic |

$$\text{VEC (X)} = \mathbf{m} \cdot \mathbf{e(M)} + \mathbf{x} \cdot \mathbf{e(X)}/\mathbf{x}$$

“Due to the ionic nature the structures of these compounds are driven by cationic or anionic nature of the main group elements in the zintl phase”

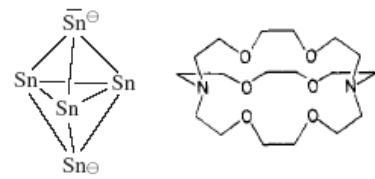
Zintl Clusters

- The first evidence for Zintl ions was reported by Joannis in 1891 from studies of the reaction of sodium in liquid ammonia with a variety of metals.
- He observed a blue solution of sodium which colored the ammonia solution to green (presence of dissolved electrons in NH_3) with excess lead giving new solids.
- More attention was given to the solid precipitates which were found to have the compositions NaPb_4 or NaPb_2 depending on conditions.



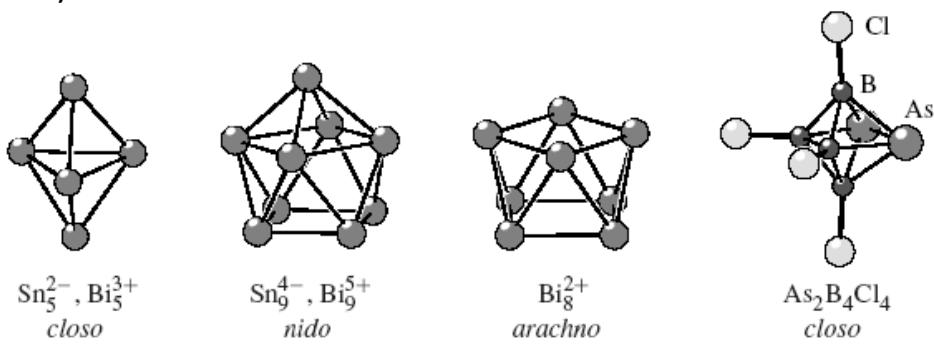
The isolation of any solid derivative of the Zintl anions has only been accomplished in the last 40 years.

Intact cage like anions can be extracted from the solids by offering a complexing ligand to the cations. The Na^+ ions in Na_2Sn_5 can be captured by cryptand molecules $[\text{N}(\text{C}_2\text{H}_4\text{OC}_2\text{H}_4\text{OC}_2\text{H}_4)\text{N}]$ as $[\text{NaCrypt}]_2\text{Sn}_5$



Zintl Clusters and Wade's Rule

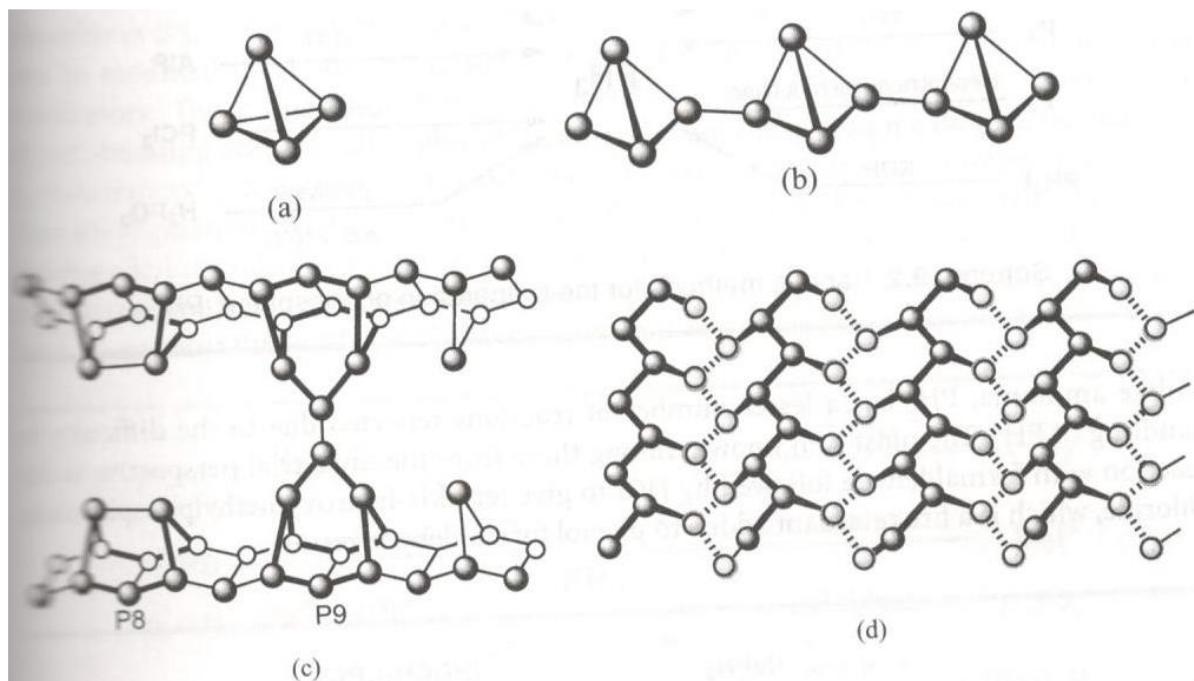
- The WADE's rules can be applied to ligand-free cluster compounds of main-group elements. If we postulate one lone electron pair pointing outwards on each of the n atoms, then $g - 2n$ electrons remain for the polyhedron skeleton (g = total number of valence electrons)



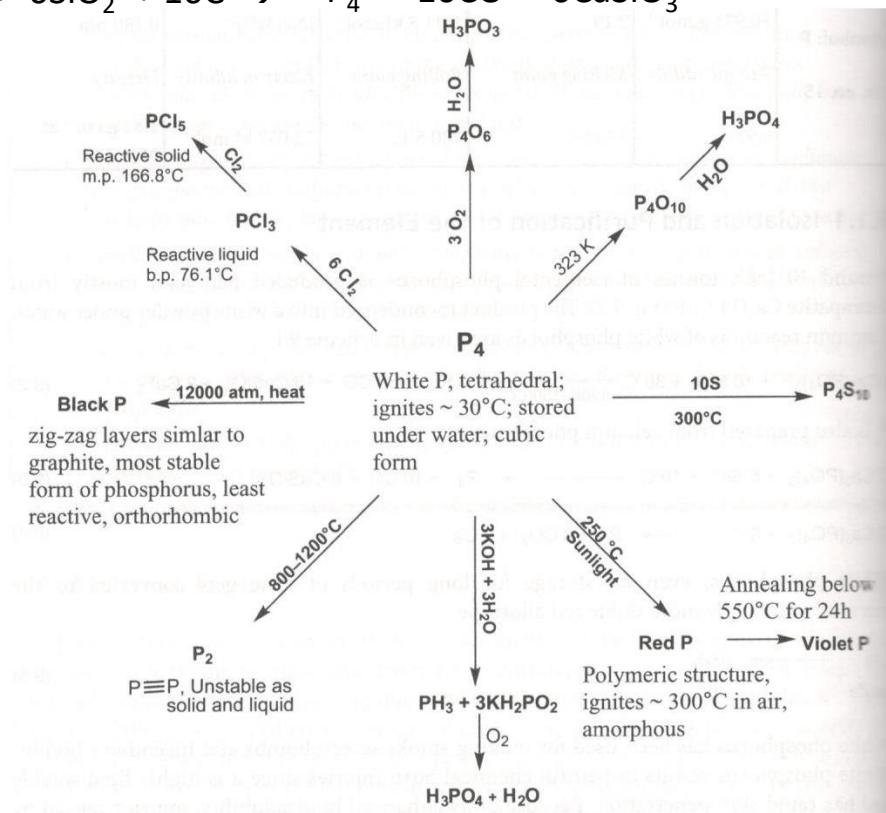
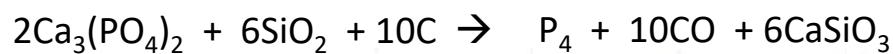
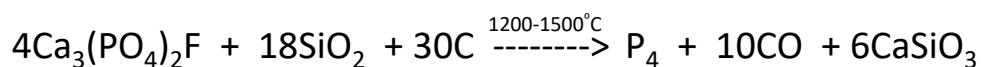
| | n | g | $g - 2n$ | | cluster type |
|--------------------------------------|-----|-----|----------|------------|----------------|
| $\text{Sn}_5^{2-}, \text{Bi}_5^{3+}$ | 5 | 22 | 12 | $= 2n + 2$ | <i>closo</i> |
| Tl_6^{8-} | 6 | 26 | 14 | $= 2n + 2$ | <i>closo</i> |
| $\text{Sn}_9^{4-}, \text{Bi}_9^{5+}$ | 9 | 40 | 22 | $= 2n + 4$ | <i>nido</i> |
| Bi_8^{2+} | 8 | 38 | 22 | $= 2n + 6$ | <i>arachno</i> |
| $\text{As}_2\text{B}_4\text{Cl}_4$ | 6 | 26 | 14 | $= 2n + 2$ | <i>closo</i> |

The calculation also works if some of the atoms bear ligands (instead of lone pairs) and others have no ligands but lone electron pairs.

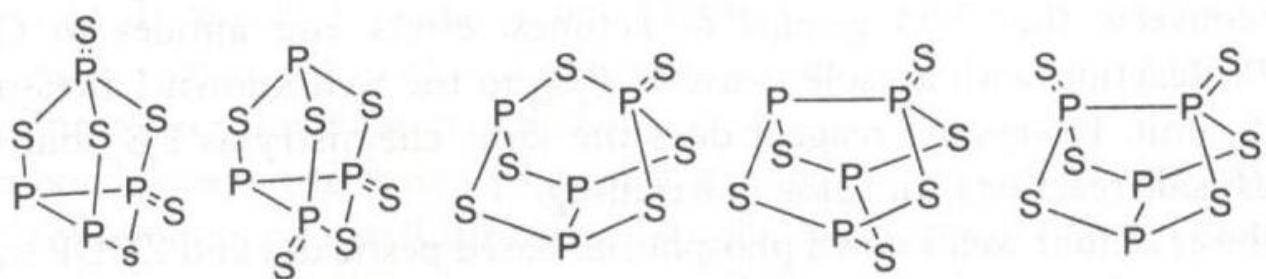
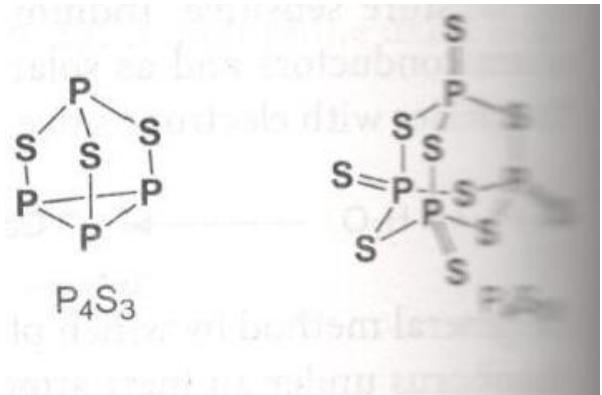
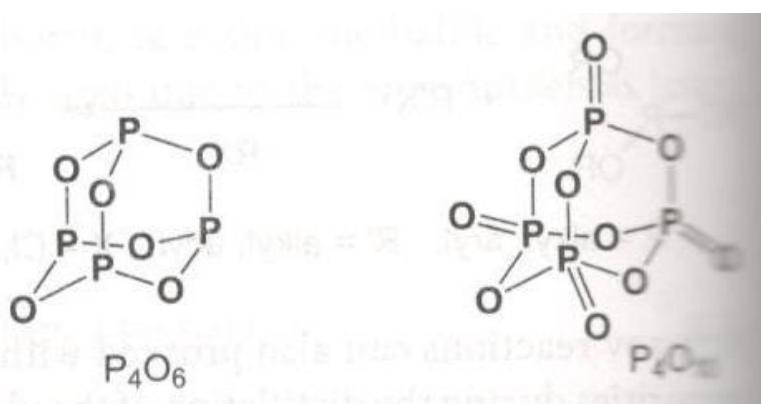
Cages and Clusters of phosphorus compounds



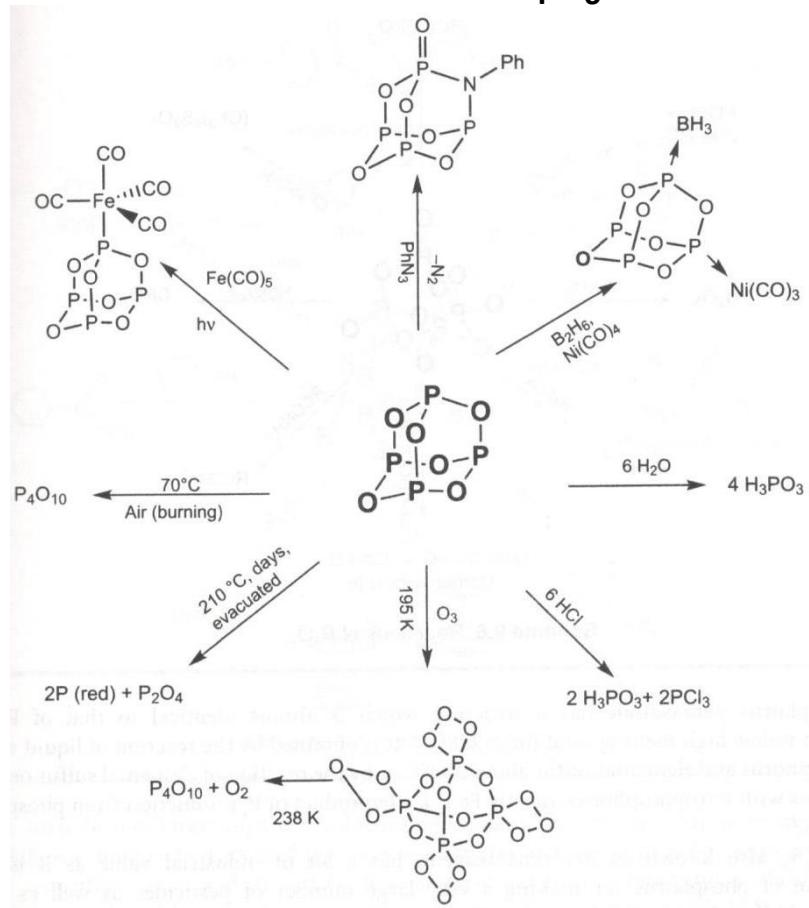
White phosphorus and its reactions



Phosphorus oxides and sulfides

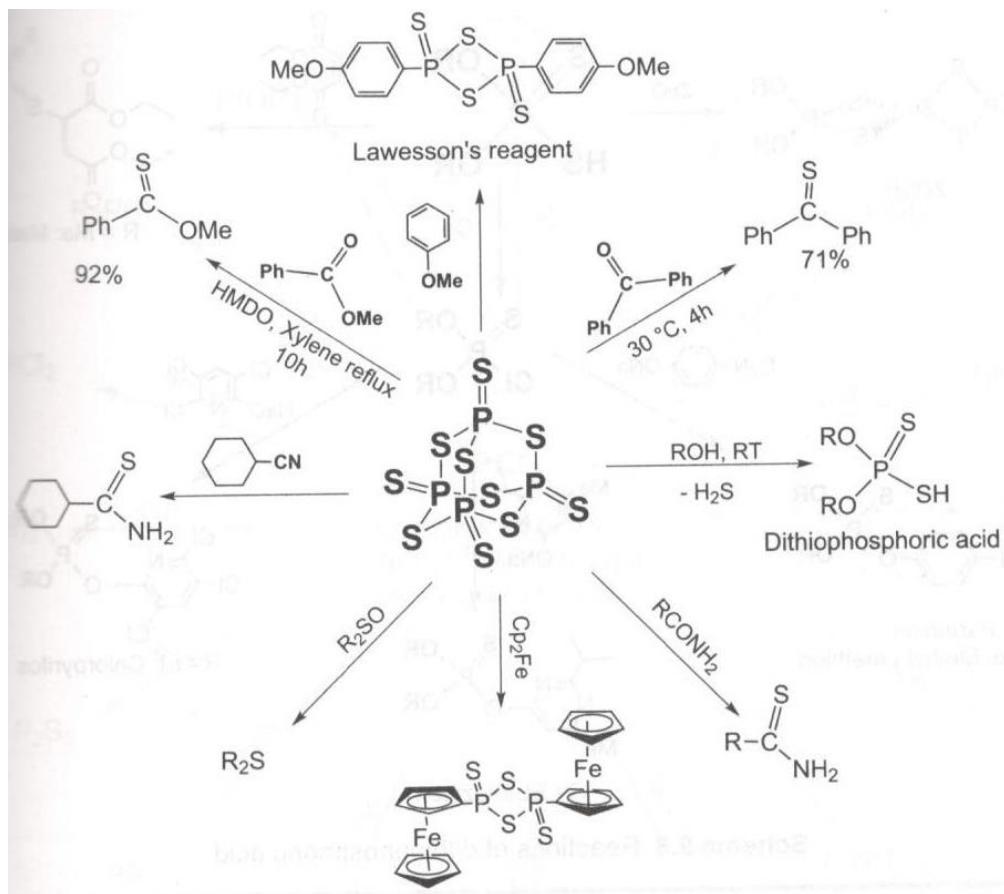


Reactions of P_4O_6



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Reactions of P_4S_{10}



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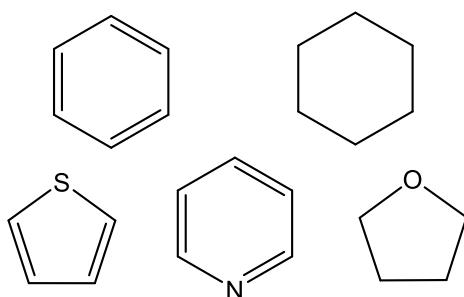
2.5 Lecture 7

Main Group Chemistry: rings, macrocycles and polymers

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Organic Ring Systems

- Very Important Branch of Organic Chemistry
- Benzene: Pre-eminent example; provided important insights into delocalized bonding
- Cycloalkanes: Another prominent class; form a homologous series $(CH_2)_n$ ($n= 3$ to >30)
- Heterocycles: Replacement of one or more carbon atoms with another p-block element in a homocyclic compound. This process can be continued with the replacement of two or more C-atoms with p-block elements.
- Approx. half of known organic compounds contain at least one heterocyclic ring and so this branch of organic chemistry is vast.

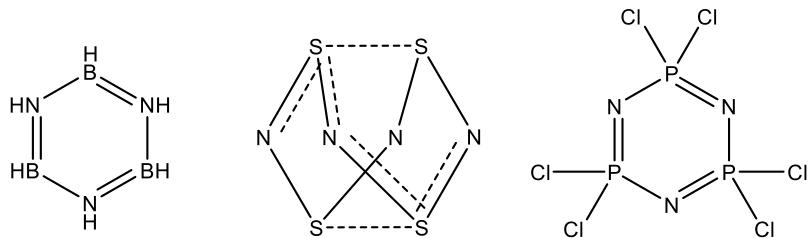


Inorganic Heterocycles

- The extension of the substitution process to the complete replacement of all carbon atoms
- This branch of heterocycles together with the polymers derived from them are some of the subjects of this lecture.
- Elemental Sulfur: quintessential inorganic ring system. Cyclo-S₈.
- In common with cycloalkanes, homocyclic sulfur rings (cyclo-S_n) can range in size from n = 6 to around 24.
- Cyclosilanes (R₂Si)_n for n = 3-35 are known in the family of saturated inorganic ring systems: extended family of homologous systems
- An intriguing example of inorganic heterocycle is the Arsenic based drug “Salvarsan”: Forerunner of chemotherapy; used in early 20th century for treating syphilis
- Recently, Salvarsan was shown to primarily contain a mixture of three- and five-membered rings, (RAs)_n (n = 3, 5; R = 3-NH₂-4-OHC₆H₃)

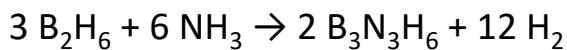
Historical Background

- The first inorganic heterocycle cyclotriphosphazene ($\text{NPCl}_2)_3$ was described in 1834 and the second example tetrasulfur tetrinitride S_4N_4 was reported a year later.
- The structures of these compounds comprised of six-membered ring and folded cage structure was established about a century ago.
- These structural determinations raised fundamental questions about nature of bonding in inorganic heterocyclic rings: Became a major force.
- Borazine $\text{B}_3\text{N}_3\text{H}_6$ was discovered in 1926. Because of its isoelectronic relationship to C_6H_6 it is referred to as inorganic benzene.
- But debate over its aromaticity of this six-membered ring is continued even today.
- An extensive homologous series exists for cyclophosphazenes ($\text{NPX}_2)_n$ ($X = \text{Cl}, \text{F}; n = 3-40$), but not for borazine.

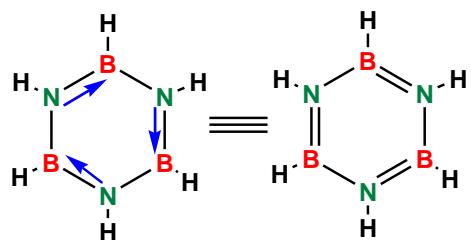


Borazine: The Inorganic Benzene

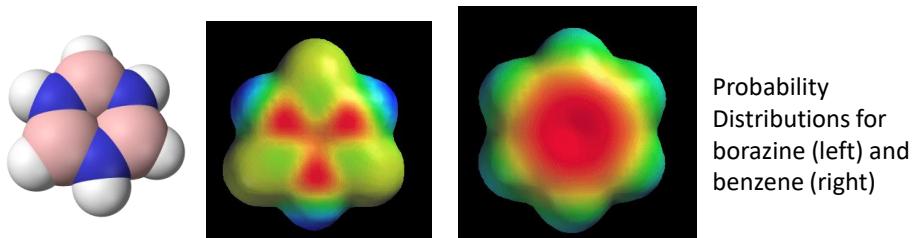
First reported in 1926 by Alfred Stock and Pohland



An alternative more efficient route



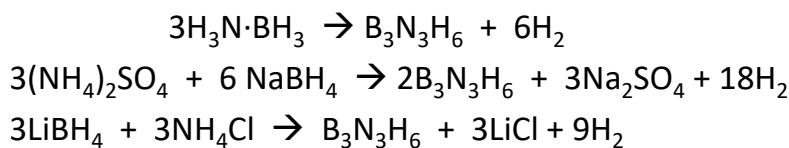
Borazine is isostructural with benzene. The six B-N bonds have length of 1.436 Å. The carbon-carbon bond in benzene is shorter length at 1.42 Å. The boron-nitrogen bond length is between that of the B-N (1.51 Å) and the B=N (1.31 Å). This suggests partial delocalization of nitrogen lone pair.



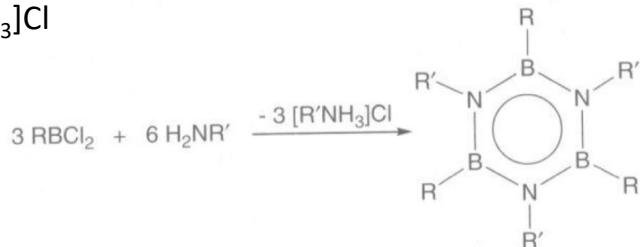
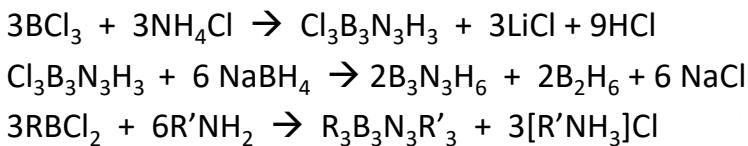
Borazine has the same colligative properties as benzene, however the two are very different chemically. The electron density along the boron-nitrogen bond is not distributed evenly, due to the difference in electro negativities between the two atoms. Therefore, the molecular orbitals of the system are lumpy in appearance. This uneven distribution makes borazine prone to addition reactions.

Boron-Nitrogen Rings

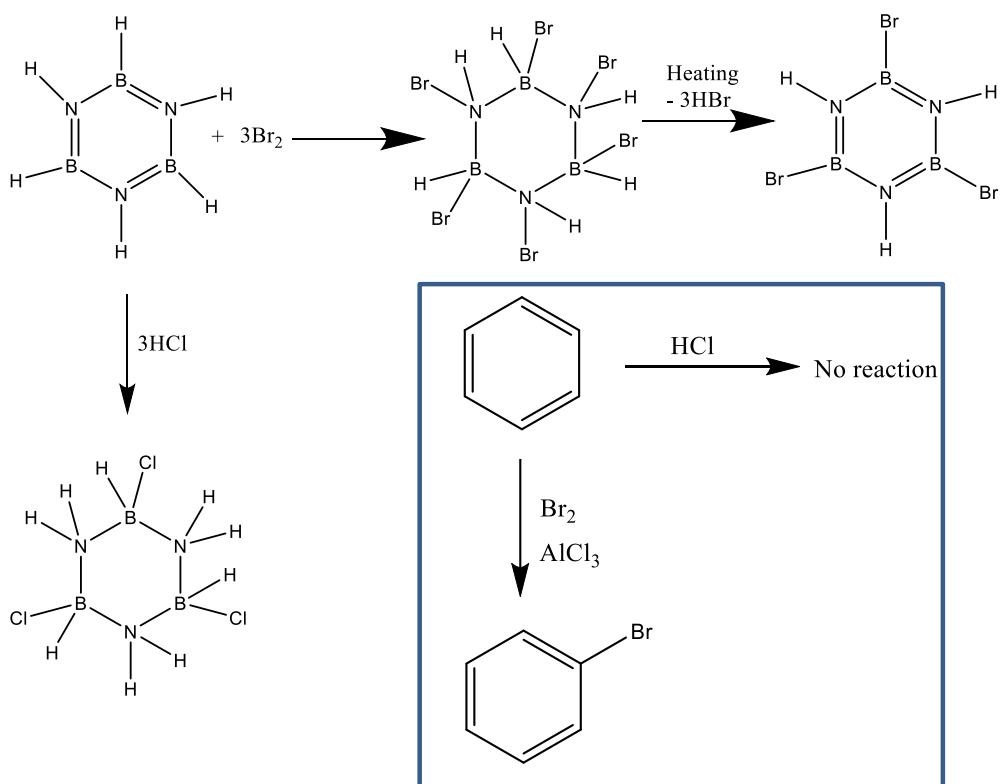
- Iminonoranes $\text{RB}\equiv\text{NR}'$ are isoelectronic with alkynes
- However, $\text{RB}\equiv\text{NR}'$ cyclooligomerize: Nature of substituents on B and N atoms
- $(\text{RB}\equiv\text{NR}')_n$ rings analogous to cyclobutadiene, benzene and cyclooctatetrenes are commonly encountered oligomers: Trimer more prevalent
- Borazine first prepared by the thermolysis of diborane-ammonia adduct $[(\text{BH}_2)(\text{NH}_3)_2]^+[\text{BH}_4]^-$
← How do you get this compound?
- The convenient methods are as below



B and N substituted Borazines

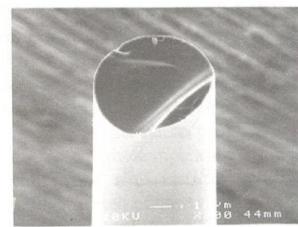
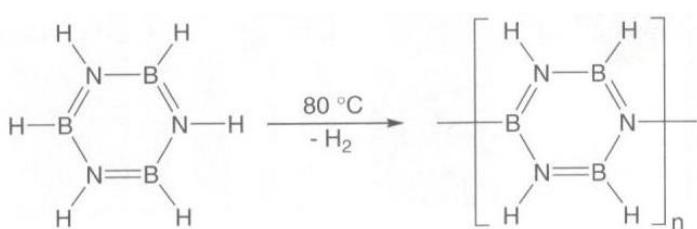


Reactions of borazine



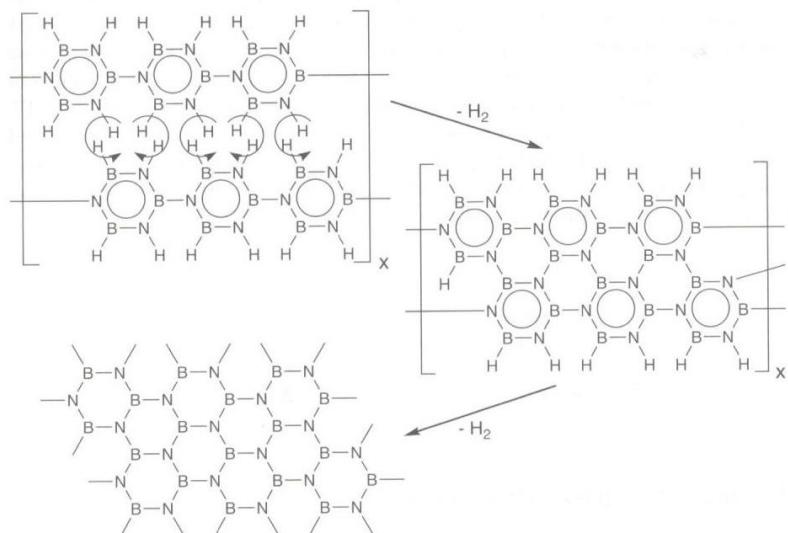
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Boron-Nitrogen Polymer



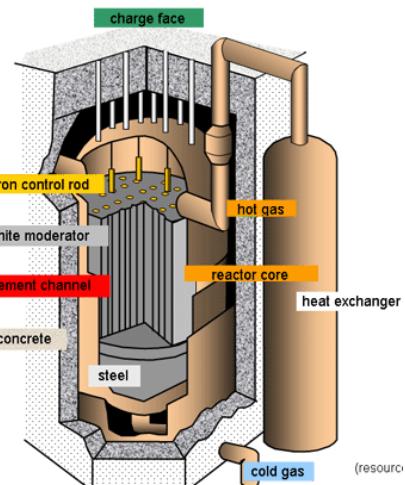
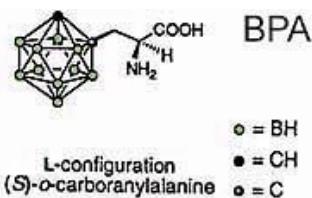
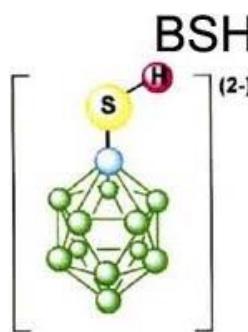
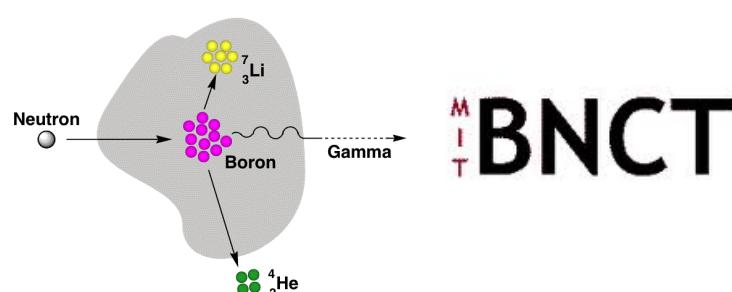
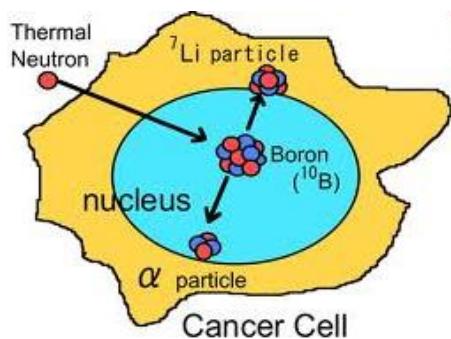
(a)
BN fibres formed from Polyaminoborazyles prepared by substituting borazines with NR_2 groups and by subjecting them to melt extrusion followed by Pyrolysis at $1200\text{ }^{\circ}\text{C}$

- Low-temp thermally induced dehydropolymerization of Borazine gives a cyclo-linear polymer ($M_w = \sim 7600$)
- Pyrolysis at $1200\text{ }^{\circ}\text{C}$ yielded white boron nitride in 85-93% yield.
- Borazine can also be used to grow B-N thin films on to surface

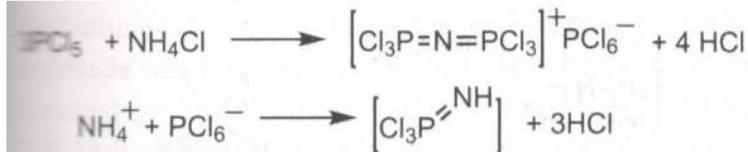
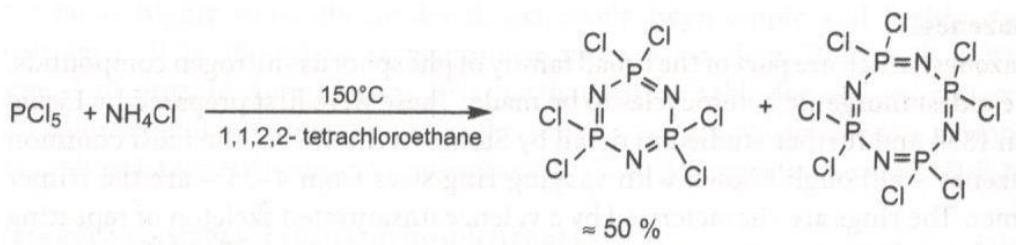


Nuclear Applications of Boron and Boranes

1935 H J Taylor

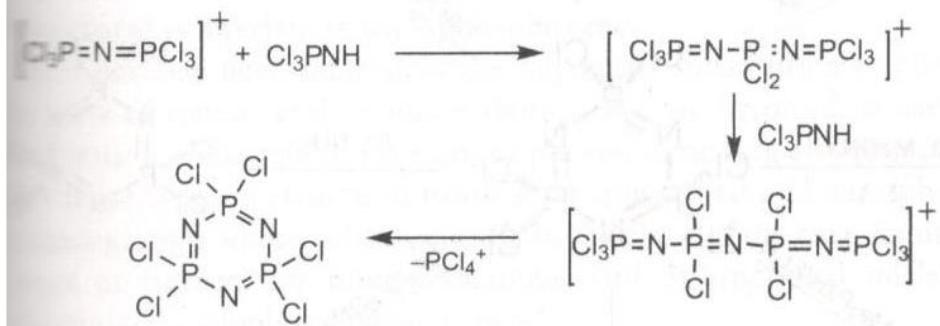


Cyclic P-N compounds: Cyclophosphazenes

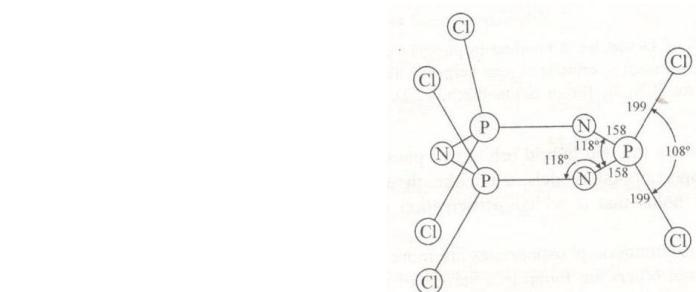
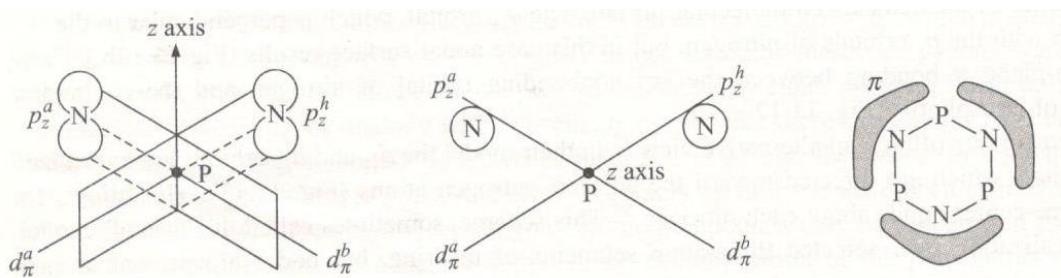
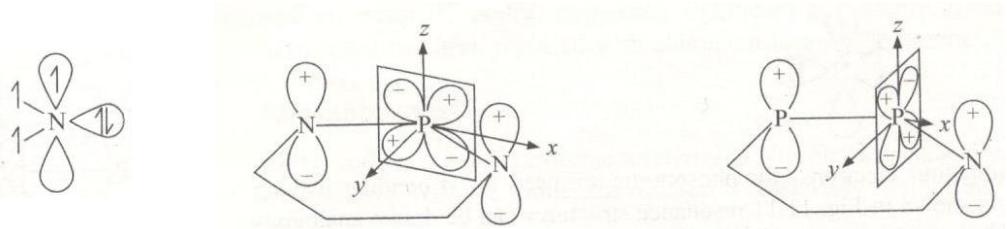


Cl_3PNH has not been isolated but analogous compound

$\text{Cl}_3\text{PNSiMe}_3$ has been made and characterised



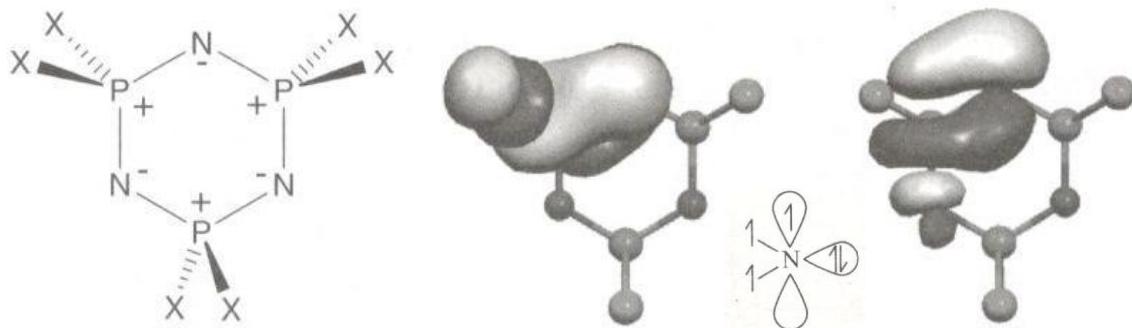
Dewar Model of Bonding in Cyclophosphazenes: p_{π} - d_{π} overlap



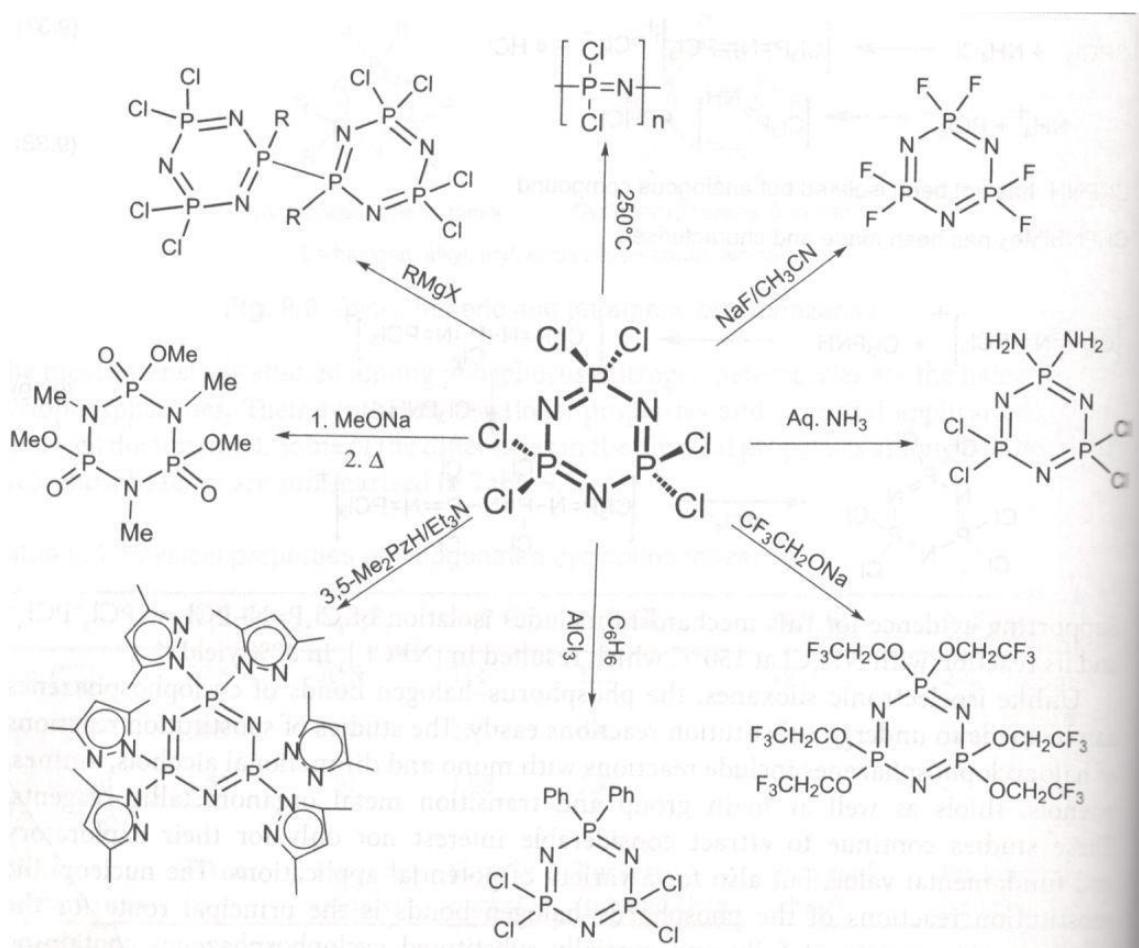
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Zwitterionic and Negative Hyperconjugation in Cyclophosphazenes

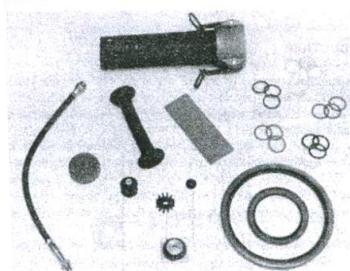
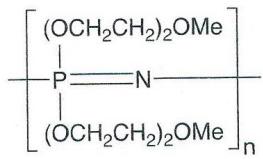
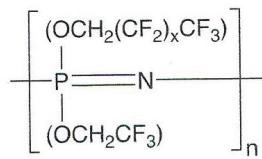
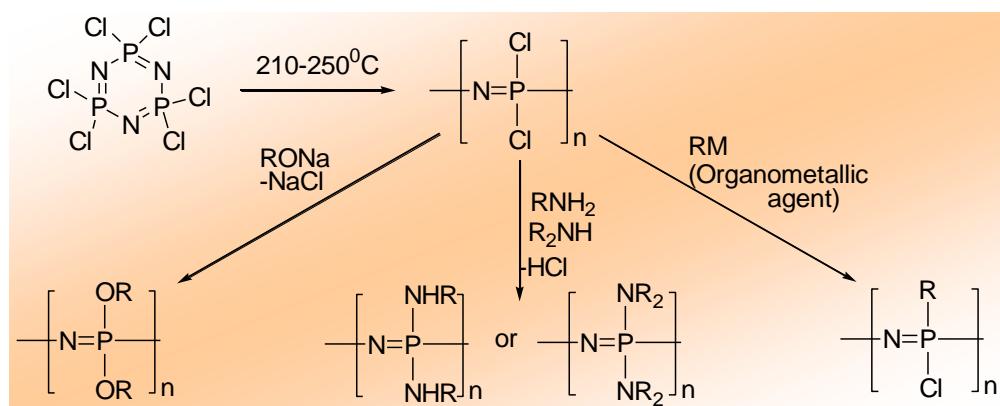
- A topological analysis of electron density distribution reveals a significant ionic character in the P-N bond and the Zwitterionic model is one of the well-accepted model of bonding in cyclophosphazenes
- A natural bond order analysis indicates a subsidiary bonding contribution is provided by negative hyperconjugation.
- This involves the interaction of in-plane and out-of-plane lone pair orbitals with the σ^* (P-N) and σ^* (P-X) orbitals, respectively.
- The latter contribution is enhanced as the electronegativity of the substituents X increases.
- So the bonding in cyclophosphazenes is described by ionic contributions and negative hyperconjugation and not by valance d-orbital participation → not considered to be aromatic systems for their homologous series



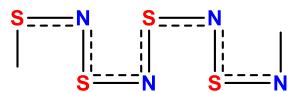
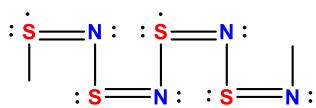
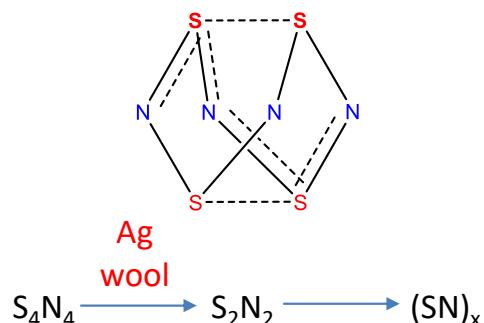
Reactivity of Cyclotriphosphazenes



Polyphosphazenes



Sulfur-Nitrogen Rings



2.6 Lecture 9+10+11

Transition Metal Chemistry: Structure and Bonding

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Historic Background

Coordination compounds were identified in the early nineteenth century → challenge to the inorganic chemists in those days → hence called as complexes

The modern study of these compounds began with two people: Alfred Werner and Sophus Mads Jorgensen → both had different approaches and supporting experiments.

Finally Werner's interpretation were widely accepted and he is the first inorganic chemist to be awarded the noble prize.

His first experiments were based on four complexes of cobalt(III) chloride with ammonia → named according to their colours

$\text{CoCl}_3 \cdot 6\text{NH}_3$ (yellow); $\text{CoCl}_3 \cdot 5\text{NH}_3$ (purple);

$\text{CoCl}_3 \cdot 4\text{NH}_3$ (green); $\text{CoCl}_3 \cdot 4\text{NH}_3$ (violet) → identical formula; distinct properties

He also noted the difference in the reactivities of the chloride ions in these complexes with AgNO_3 .



Historic Background

Werner postulated that cobalt exhibits constant coordination number in this series and when ammonia molecules are removed they are replaced by chloride ions in which they are covalently bonded to cobalt rather than free ions.

To describe the complex chemistry of cobalt → not only the oxidation state but also its coordination number must be considered. He has also noticed conductivities typical of 1:1, 1:2 and 1:3 electrolytes for these complexes.

Werner also identified that the bonds to the ligands were fixed in space and hence noted that they can be treated by application of structural principles. He was able to predict the correct geometric structure to many coordination compounds

For example, for the octahedral $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$, two isomers were observed; one violet and one green. Similarly for Pt(VI) octahedral geometry with the possibilities of isomers and for Pd(II) and Pt(II) MA_2B_2 structures with two isomers were identified.

Bonding in coordination compounds

A lot of work has been done to formulate the theories of bonding in coordination compounds and to predict and rationalize their properties.

1. Valance Bond Theory → first successful model by Linus Pauling in the 1930s
2. Crystal Field Theory → By Bethe and Van Vleck in the 1950s and 1960s and its Modifications known as Ligand Field Theory
3. Molecular Orbital Theory

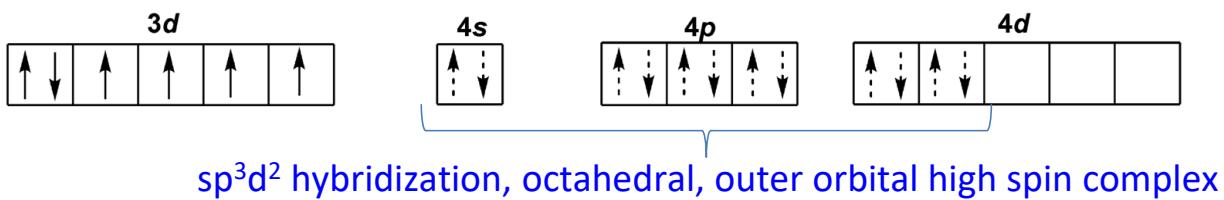
Although both the valance bond theory and crystal field theories were largely displaced by molecular orbital theory, they have been applied as working models for the practicing inorganic chemists and continue to contribute to current discussions of coordination compounds.

Valence Bond Theory

- Formation of a complex → considered as a series of hypothetical steps
- Lets consider the case of Co^{3+} . The outer electronic configuration of a Co atom is $3d^74s^2$. So for Co^{3+} it will have the structure $3d^6$

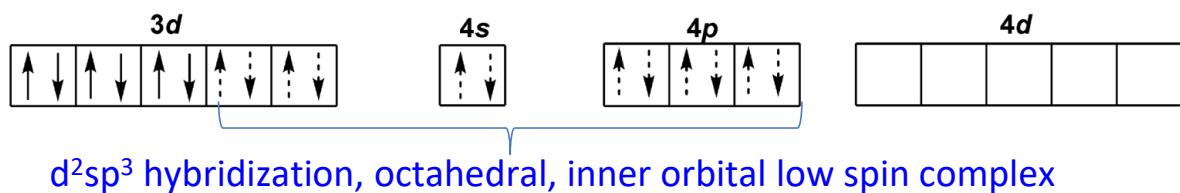


- To form an octahedral complex with six ligands, six empty orbitals are required and hence it uses the 4s, 4p and 4d orbitals. A ligand orbital having a lone pair of electrons is used to form a coordinate bond by overlapping with the empty hybrid orbitals ($4dx^2-y^2$ and $4dz^2$) on the metal. In this way a σ -bond is formed with each ligand. Due to the use of 4d orbitals → outer sphere complex. The energy of these orbitals are quite high and so the complex will be reactive or labile. Due to the high number of unpaired electrons in its $3d^6$ configuration → high-spin or spin-free complex → paramagnetic.



Valence Bond Theory

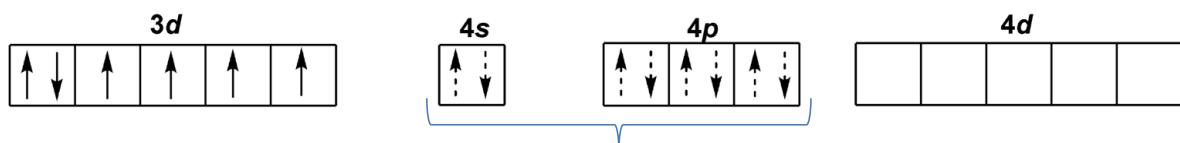
- An alternate arrangement is possible when the electrons on the metal ion are rearranged as below.
- Since the low-energy 3d orbitals are used \rightarrow inner-sphere complexes



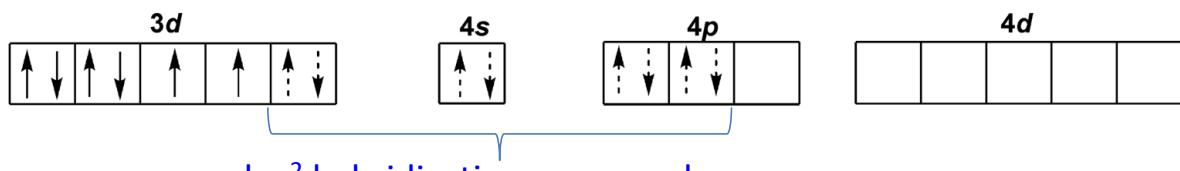
- Such complexes are more stable than outer-sphere complexes. The unpaired electrons on the metal ion are forced to pair up \rightarrow low-spin or spin-paired complexes \rightarrow diamagnetic

Valence Bond Theory

- Four-coordinate complexes are also possible for the metal ions in two different arrangements
- Remember that hybrid orbitals do not actually exist. Hybridization is a mathematical representation for the wave equations for the atomic orbitals participating in the bonding.



sp^3 hybridization, tetrahedral



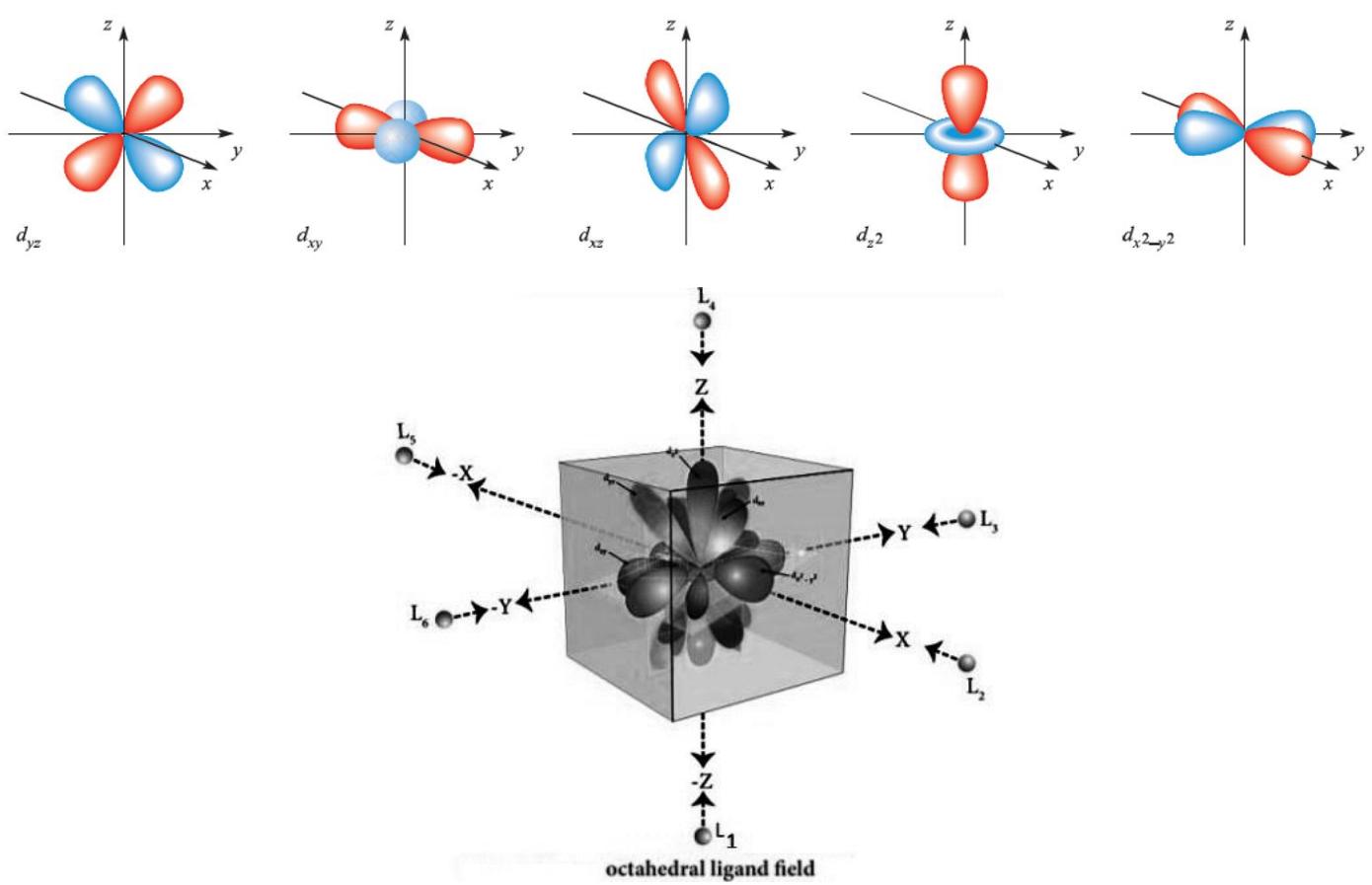
- This theory does not explain the colour of the spectra or the kinetic inertness
- It shows the stereochemical arrangements and number of unpaired electrons \Rightarrow magnetic moment can be calculated. It can not however explain the variations in the magnetic moment with T

Crystal Field Theory

Crystal field theory is much more widely accepted than VBT. The following assumptions are made in this theory

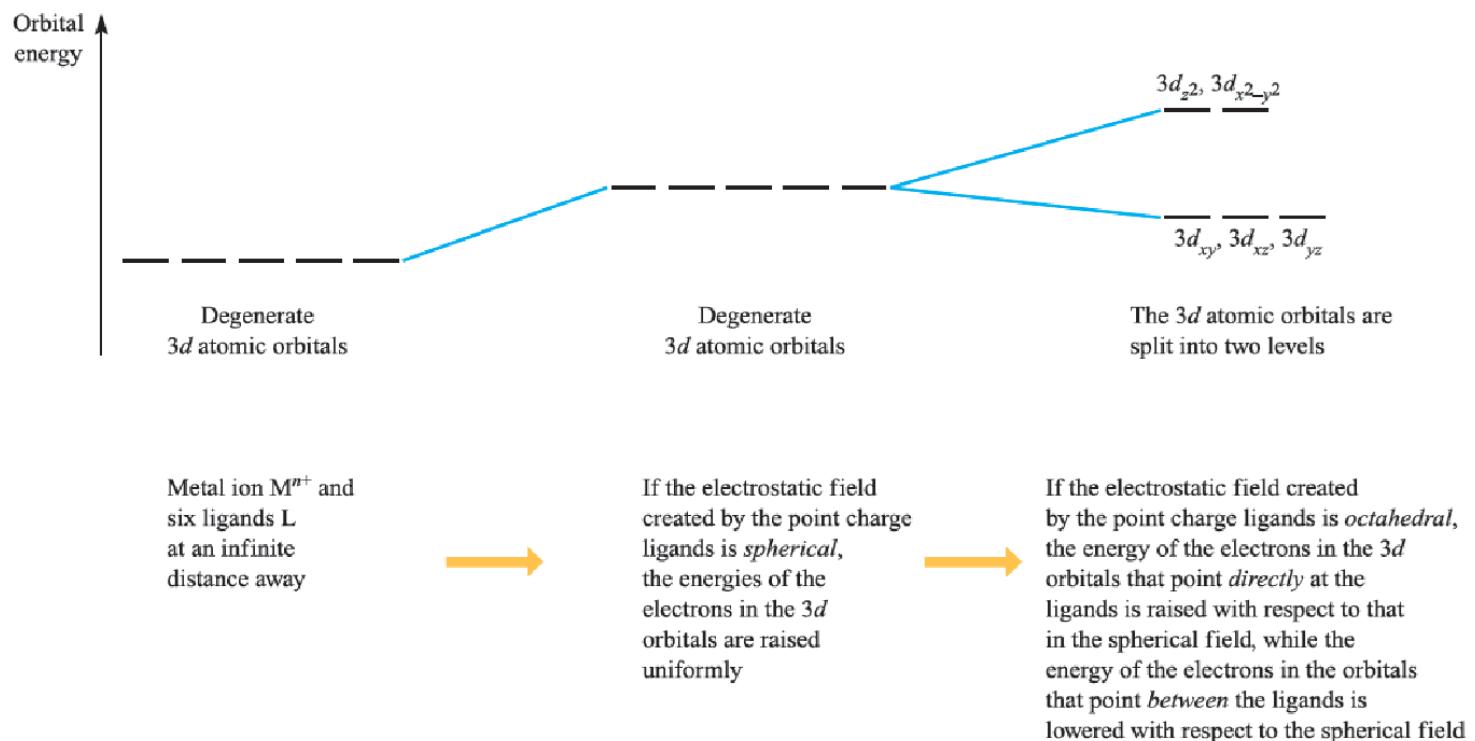
1. The attraction between the central metal and the ligands in a complex is purely electrostatic. The metal ion of the complex is positively charged equal to the oxidation state. The ligands (neutral or negatively charged) are treated as point charges → negative end of its dipole is directed towards the metal ion. The electrons of the central atom are under repulsive forces from those on the ligands.
2. There is no interaction between the meal orbitals and ligand orbitals
3. All the d-orbitals of the metal have same energy in the free atom. When the complex is formed the ligands destroy the degeneracy of these orbitals.

Octahedral Crystal Field

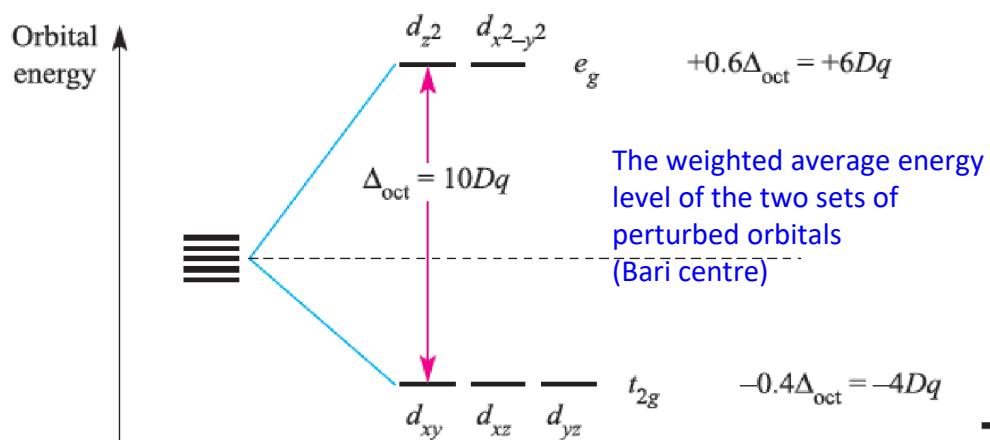


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Octahedral complexes



Octahedral complexes



d-d transition peak at 20300 cm^{-1}

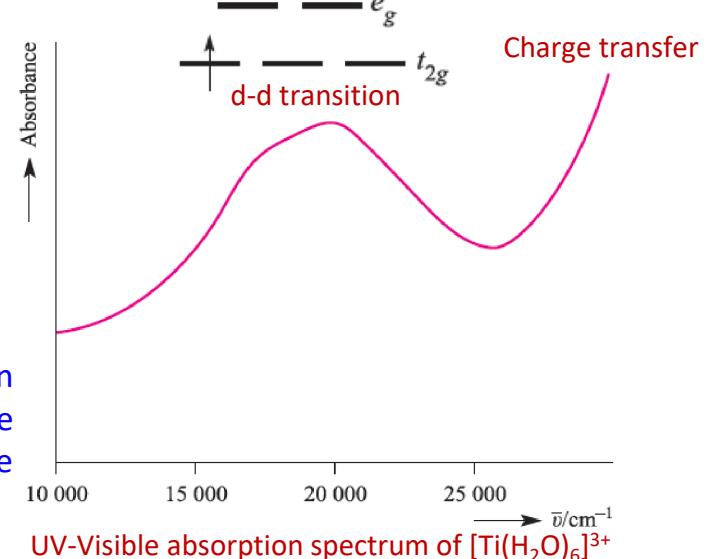
$$1 \text{ KJmol}^{-1} = 83.7 \text{ cm}^{-1}$$

$$\text{The value of } \Delta_0 = 243 \text{ KJmol}^{-1}$$

Similar to the energy of many normal single bonds.

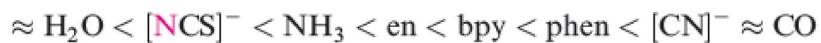
$$\text{CFSE} = 0.4 \times 243 = 97 \text{ KJmol}^{-1}$$

Solution containing $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ are reddish-violet in colour. This is because the absorbed light is in the yellow-green region which is complementary to the red-violet colour in the transmitted light



Octahedral complexes: Spectrochemical Series

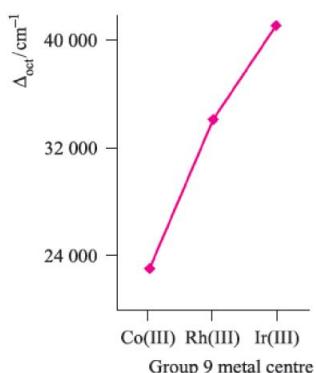
| Complex | Δ / cm^{-1} | Complex | Δ / cm^{-1} |
|--|---------------------------|--|---------------------------|
| $[\text{TiF}_6]^{3-}$ | 17 000 | $[\text{Fe(ox)}_3]^{3-}$ | 14 100 |
| $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ | 20 300 | $[\text{Fe(CN)}_6]^{3-}$ | 35 000 |
| $[\text{V}(\text{H}_2\text{O})_6]^{3+}$ | 17 850 | $[\text{Fe(CN)}_6]^{4-}$ | 33 800 |
| $[\text{V}(\text{H}_2\text{O})_6]^{2+}$ | 12 400 | $[\text{CoF}_6]^{3-}$ | 13 100 |
| $[\text{CrF}_6]^{3-}$ | 15 000 | $[\text{Co(NH}_3)_6]^{3+}$ | 22 900 |
| $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ | 17 400 | $[\text{Co(NH}_3)_6]^{2+}$ | 10 200 |
| $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$ | 14 100 | $[\text{Co(en)}_3]^{3+}$ | 24 000 |
| $[\text{Cr}(\text{NH}_3)_6]^{3+}$ | 21 600 | $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$ | 18 200 |
| $[\text{Cr}(\text{CN})_6]^{3-}$ | 26 600 | $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ | 9 300 |
| $[\text{MnF}_6]^{2-}$ | 21 800 | $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ | 8 500 |
| $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ | 13 700 | $[\text{Ni}(\text{NH}_3)_6]^{2+}$ | 10 800 |
| $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ | 9 400 | $[\text{Ni(en)}_3]^{2+}$ | 11 500 |



weak field ligands → strong field ligands
increasing Δ_{oct}

The Magnitude of Δ_{o} depends on three factors

1. Nature of the ligand
2. The charge on the metal ion
3. Location of the metal ion in the group

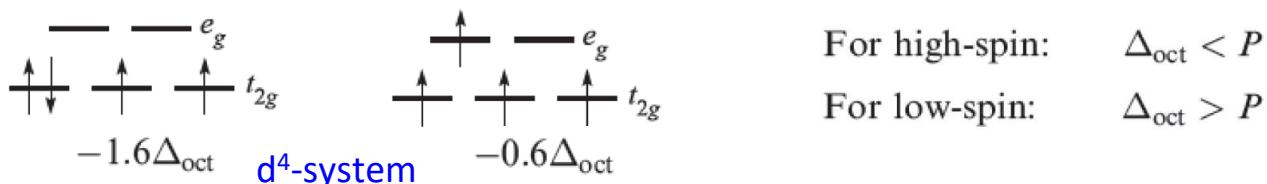


CFSE: High spin octahedral complexes

| d^n | High-spin = weak field | |
|----------|--------------------------|---------------------------|
| | Electronic configuration | CFSE |
| d^1 | $t_{2g}^1 e_g^0$ | $-0.4\Delta_{\text{oct}}$ |
| d^2 | $t_{2g}^2 e_g^0$ | $-0.8\Delta_{\text{oct}}$ |
| d^3 | $t_{2g}^3 e_g^0$ | $-1.2\Delta_{\text{oct}}$ |
| d^4 | $t_{2g}^3 e_g^1$ | $-0.6\Delta_{\text{oct}}$ |
| d^5 | $t_{2g}^3 e_g^2$ | 0 |
| d^6 | $t_{2g}^4 e_g^2$ | $-0.4\Delta_{\text{oct}}$ |
| d^7 | $t_{2g}^5 e_g^2$ | $-0.8\Delta_{\text{oct}}$ |
| d^8 | $t_{2g}^6 e_g^2$ | $-1.2\Delta_{\text{oct}}$ |
| d^9 | $t_{2g}^6 e_g^3$ | $-0.6\Delta_{\text{oct}}$ |
| d^{10} | $t_{2g}^6 e_g^4$ | 0 |

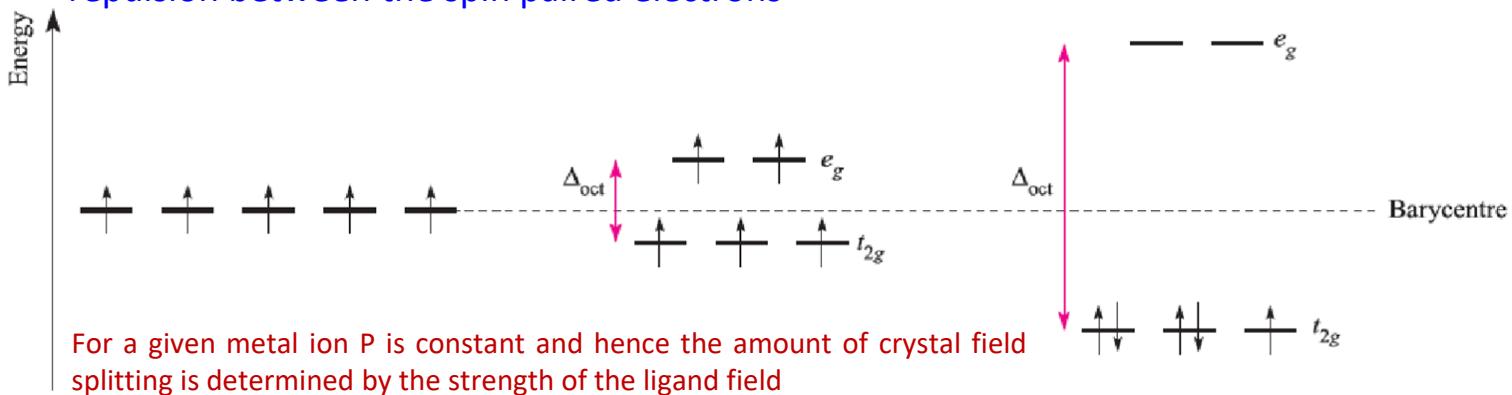
$$\text{CFSE (octahedral)} = -0.4n(t_{2g}) + 0.6n(e_g)$$

CFSE: High and Low-spin complexes



The total stabilization energy in low-spin is $-1.6\Delta_o + P$ (pairing energy)

P consists of two terms (i) loss in exchange energy upon pairing and (ii) columbic repulsion between the spin paired electrons



Gaseous ion

Weak field

(high-spin)

complex

e.g. $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$

Strong field

(low-spin)

complex

e.g. $[\text{Fe}(\text{CN})_6]^{3-}$

CFSE: High and Low-spin complexes

| d^n | High-spin = weak field | | Low-spin = strong field | |
|----------|--------------------------|---------------------------|--------------------------|--------------------------------|
| | Electronic configuration | CFSE | Electronic configuration | CFSE |
| d^1 | $t_{2g}^1 e_g^0$ | $-0.4\Delta_{\text{oct}}$ | | |
| d^2 | $t_{2g}^2 e_g^0$ | $-0.8\Delta_{\text{oct}}$ | | |
| d^3 | $t_{2g}^3 e_g^0$ | $-1.2\Delta_{\text{oct}}$ | | |
| d^4 | $t_{2g}^3 e_g^1$ | $-0.6\Delta_{\text{oct}}$ | $t_{2g}^4 e_g^0$ | $-1.6\Delta_{\text{oct}} + P$ |
| d^5 | $t_{2g}^3 e_g^2$ | 0 | $t_{2g}^5 e_g^0$ | $-2.0\Delta_{\text{oct}} + 2P$ |
| d^6 | $t_{2g}^4 e_g^2$ | $-0.4\Delta_{\text{oct}}$ | $t_{2g}^6 e_g^0$ | $-2.4\Delta_{\text{oct}} + 2P$ |
| d^7 | $t_{2g}^5 e_g^2$ | $-0.8\Delta_{\text{oct}}$ | $t_{2g}^6 e_g^1$ | $-1.8\Delta_{\text{oct}} + P$ |
| d^8 | $t_{2g}^6 e_g^2$ | $-1.2\Delta_{\text{oct}}$ | | |
| d^9 | $t_{2g}^6 e_g^3$ | $-0.6\Delta_{\text{oct}}$ | | |
| d^{10} | $t_{2g}^6 e_g^4$ | 0 | | |

Tetragonal Distortions in Octahedral Complexes

Repulsions by the ligands cause the splitting of the d orbitals. It follows the corresponding repulsions between the d-electrons and the ligands.

Symmetrical Electronic Arrangement

| d^n | t_{2g} | e_g | Nature of Ligand Field |
|----------|----------|-------|------------------------|
| d^0 | | | Strong or weak |
| d^3 | | | Strong or weak |
| d^5 | | | weak |
| d^6 | | | Strong |
| d^8 | | | weak |
| d^{10} | | | Strong or weak |

Repel all the six ligands equally

No distortions

Asymmetrical Electronic Arrangement

| d^n | t_{2g} | e_g | Nature of Ligand Field |
|--|----------|-------|------------------------|
| d^4 | | | weak |
| d^7 | | | Strong |
| d^9 | | | Strong or weak |
| Some ligands are repelled more than the others; Strong distortions | | | |
| Unsymmetrically filling of t_{2g} orbitals cause small distortions than those of e_g . | | | |

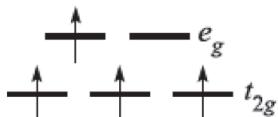
Jahn-Teller Distortions

Octahedral complexes of d^9 and high-spin (H.S.) d^4 ions are often distorted, e.g. CuF_2 (octahedrally sited Cu^{2+} centres) and $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$, so that two metal–ligand bonds (axial) are different lengths from the remaining four (equatorial).

For H.S. d^4 one e_g occupied and one is vacant. If the electron is in d_{z^2} , then most of the electron density in this orbital is concentrated between the metal and on the two axial ligands, leading to greater repulsion → result in axial elongation.

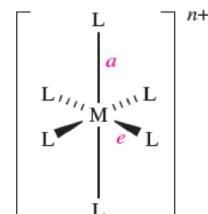
If the electron is in $d_{x^2-y^2}$ orbital, the repulsions will be maximum in the equatorial ligands → result in axial compression.

A similar argument can be put forward for the d^9 configuration in which the two orbitals in the e_g set are occupied by one and two electrons, respectively.

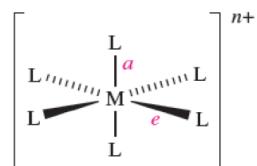


In $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$, it is $d_{xy}^1 d_{yz}^1 d_{xz}^1 d_{z^2}^1$

The *Jahn–Teller theorem* states that any non-linear molecular system in a degenerate electronic state will be unstable and will undergo distortion to form a system of lower symmetry and lower energy, thereby removing the degeneracy.

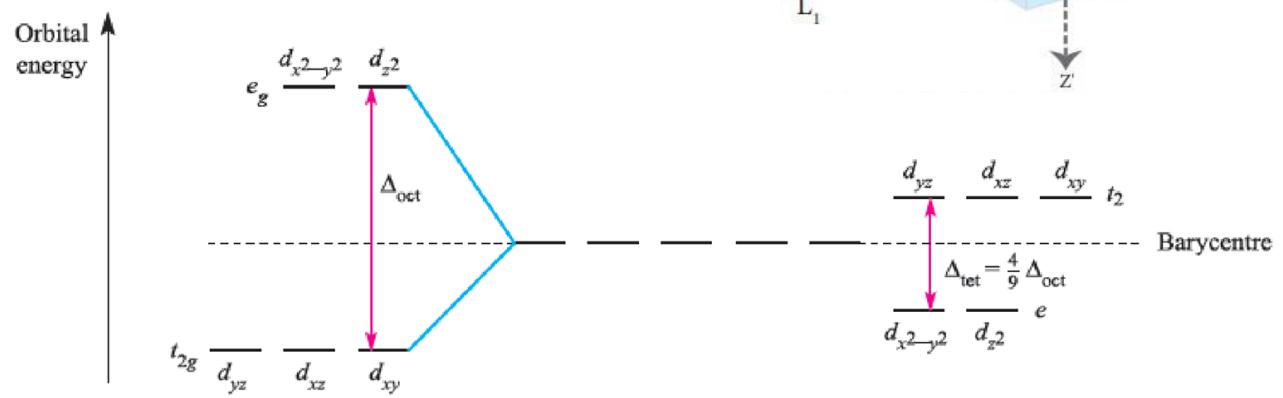
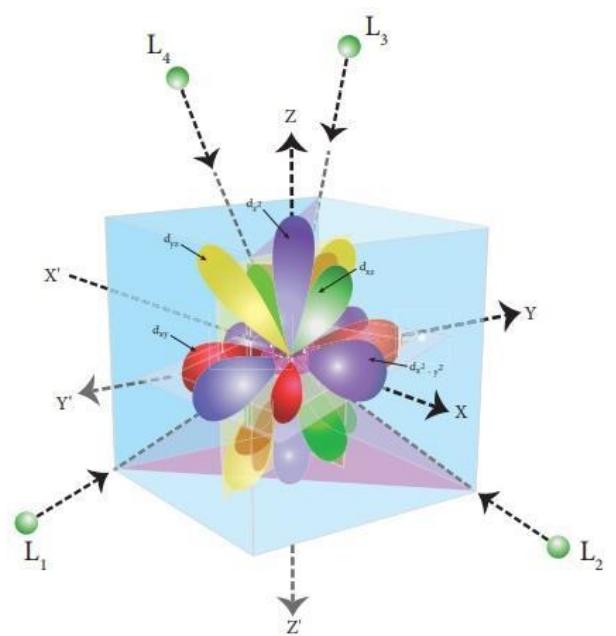
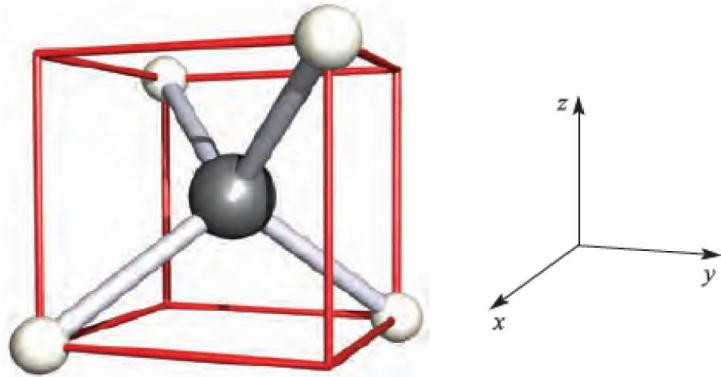


Bond length $a > e$



Bond length $a < e$

Tetrahedral Crystal Field



Tetrahedral Crystal Field: CFSE

| | | |
|----------|-------------|----------------|
| d^1 | $e^1 t_2^0$ | 0.6 Δ_t |
| d^2 | $e^2 t_2^0$ | 1.2 Δ_t |
| d^3 | $e^2 t_2^1$ | 0.8 Δ_t |
| d^4 | $e^2 t_2^2$ | 0.4 Δ_t |
| d^5 | $e^2 t_2^3$ | 0.0 Δ_t |
| d^6 | $e^3 t_2^3$ | 0.6 Δ_t |
| d^7 | $e^4 t_2^3$ | 1.2 Δ_t |
| d^8 | $e^4 t_2^4$ | 0.8 Δ_t |
| d^9 | $e^4 t_2^5$ | 0.4 Δ_t |
| d^{10} | $e^4 t_2^6$ | 0.0 Δ_t |

The magnitude Δ_t of is considerably less than Δ_o due to

1. There are only 4 ligands (vs. 6 in octahedral) so the field is only $\frac{2}{3}$ of the size.
2. The direction of the orbital does not coincide with that of the ligands. This reduces the CFS by roughly $\frac{2}{3}$ further.

Thus the Δ_t is roughly $\frac{2}{3} \times \frac{2}{3} = \frac{4}{9}$ of Δ_o

$$\text{CFSE (tetrahedral)} = -0.6n_{(e_g)} + 0.4n_{(t_{2g})}$$

The tetrahedral splitting is not enough to favour the pairing of the electrons and hence low-spin tetrahedral complexes are not common.

A rare example is $\text{Cr[N(SiMe}_3)_2]_3[\text{NO}]$

When tetrahedral complexes are favoured?

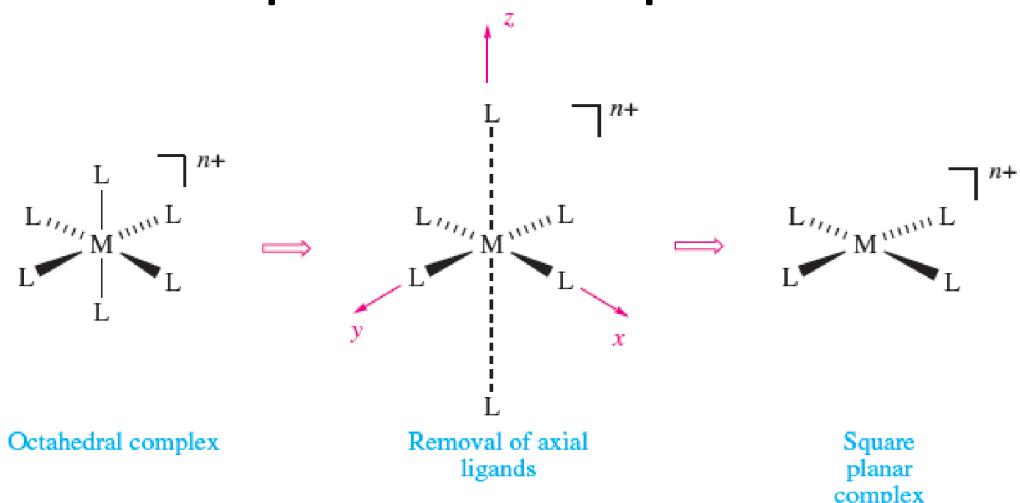
From the CFSE tables, it is evident that the d^0 , d^5 and d^{10} arrangements show zero CFSE and so both octahedral (Oh) and tetrahedral (Td) arrangements are equally likely.

For all other electronic arrangements there is some CFSE \rightarrow suggestive of octahedral complexes being more stable and more common than tetrahedral complexes.

Despite that, stable tetrahedral complexes are formed and are favoured...

1. When ligands are bulky and could cause crowding in Oh complex
2. Where attainment of regular shape is important. For Td structures d^0 , d^2 , d^5 , d^7 and d^{10} are regular.
3. When ligands are weak field and hence loss in CFSE is less important
4. When the central metal atom is in low oxidation state that reduces the magnitude of CFSE.
5. When there is no CFSE for ex. d^0 , d^5 and d^{10} arrangements
6. When the loss of CFSE is small, example, d^1 and d^6 where the loss of CFSE is $0.13 \Delta_o$

Square Planar Complexes

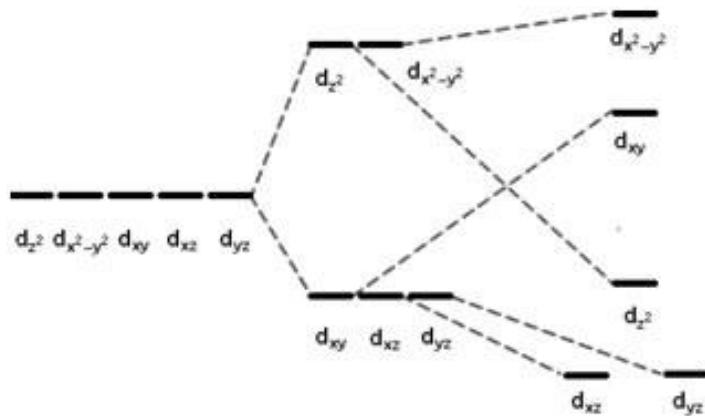


A square planar complex can be derived from an octahedral complex by the removal of two ligands, e.g. those on the z-axis; the intermediate stage is a Jahn–Teller distorted (elongated) octahedral complex.

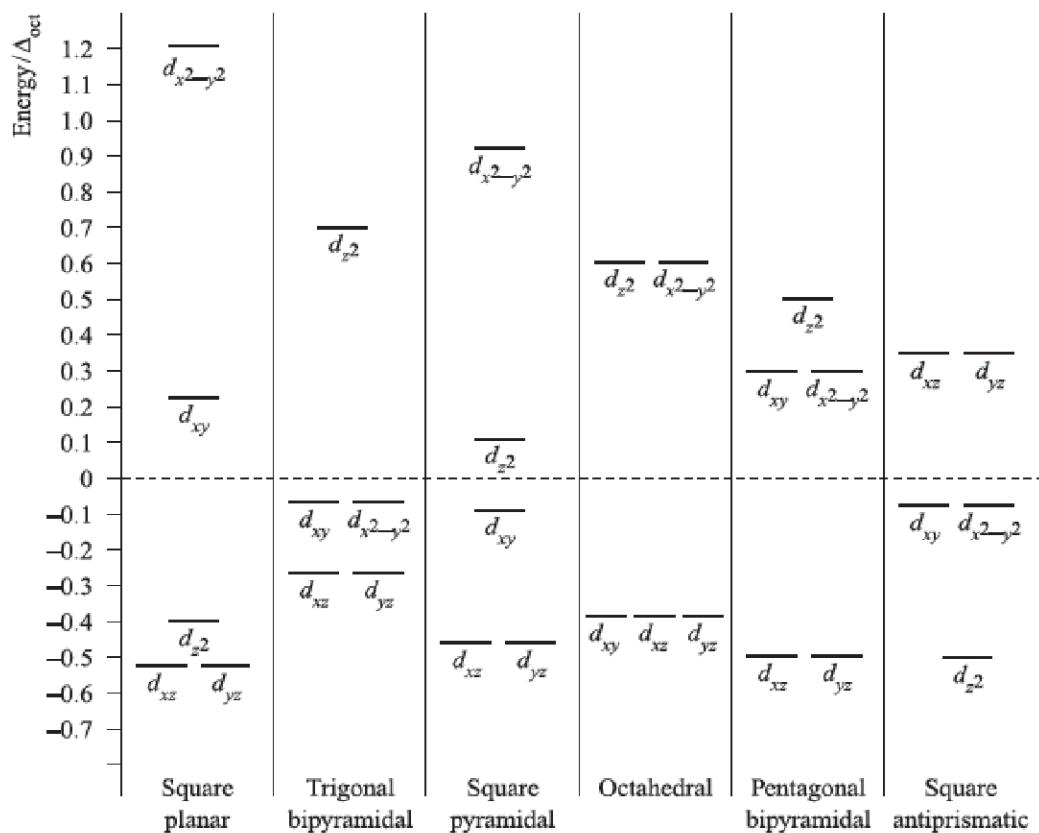
Square Planar Complexes

A single electron in $d_{x^2-y^2}$ is repelled by 4 ligands while the electron in d_{z^2} is repelled by two ligands → then energy of $d_{x^2-y^2}$ increases relative to d_{z^2} . If the ligand field is sufficiently strong the energy difference between these two orbitals is larger than the pairing energy. Thus...

- Both e_g electrons pair up and occupy the lower energy d_{z^2} orbital
- Four ligands can approach freely along the x and y directions as $d_{x^2-y^2}$ is empty
- The ligands approaching along the z direction feels stronger forces → no bonds formed and thus a square planar complex is formed.
- Again the d_{xy} orbital with more x and y contribution is more destabilized.



Crystal Field Splitting comparisons



Crystal field splitting diagrams for some common fields related to a common barycentre; splittings are given with respect to Δ_{oct} .

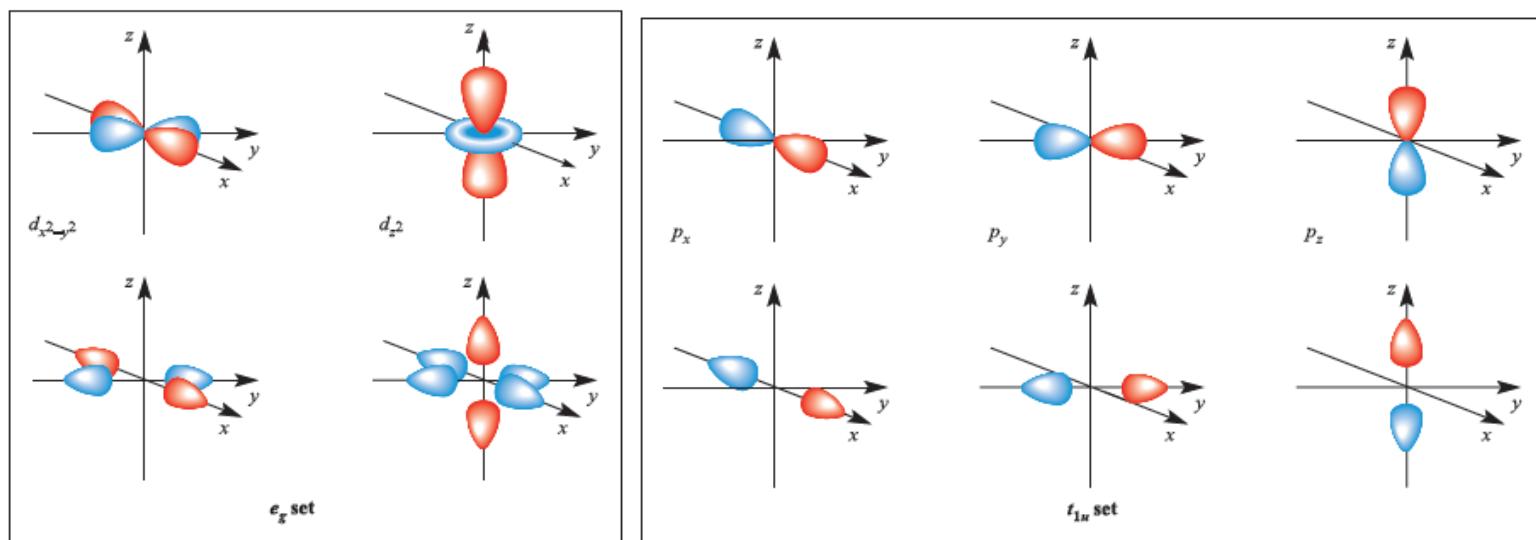
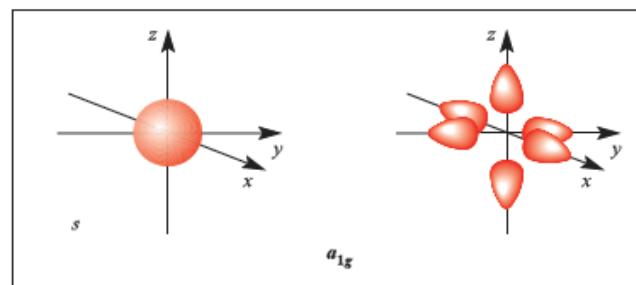
Extension of CFT to allow for some covalancy

CFT is purely based on electrostatic attractions → might sound improbable assumption. However, the theory is remarkably successful in explaining the shapes of the complexes, their spectra and magnetic properties by simple calculations. But there are evidences for some covalent bonding present in many complexes.

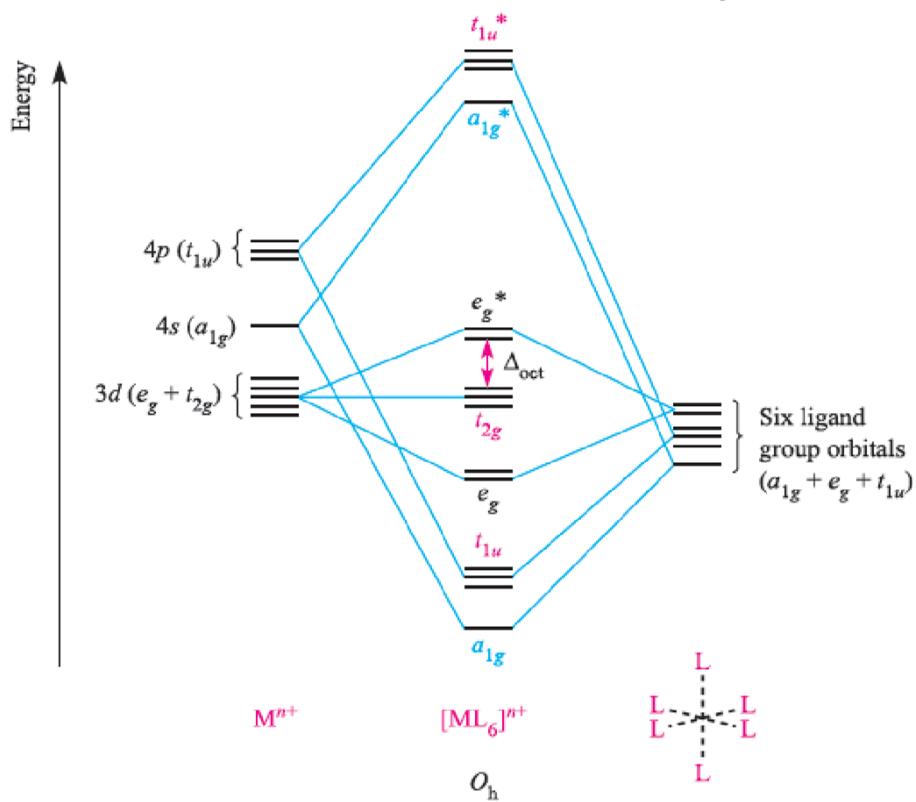
- Complexes in zero oxidation state such as $\text{Ni}(\text{CO})_4$ have no electrostatic attraction. Thus, bonding must be covalent.
- The order of ligands in the spectrochemical series can not be explained alone with electrostatic interactions
- There are evidence for covalency by NMR and EPR techniques showing some electron density on the ligands → suggests sharing of electrons and hence some covalancy.
- Another parameter called Racah parameter was introduced first to explain the interpretation of spectra allowing some covalancy → topic for the future.

But for now, lets have a quick look at the MOT of complexes

Molecular Orbital Theory

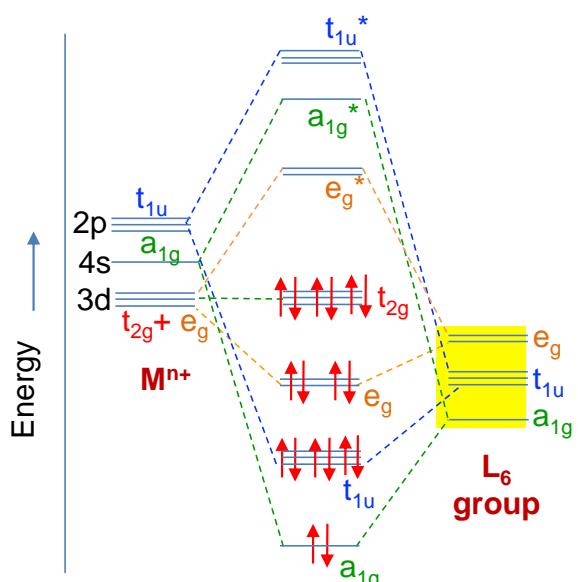


Molecular Orbital Theory

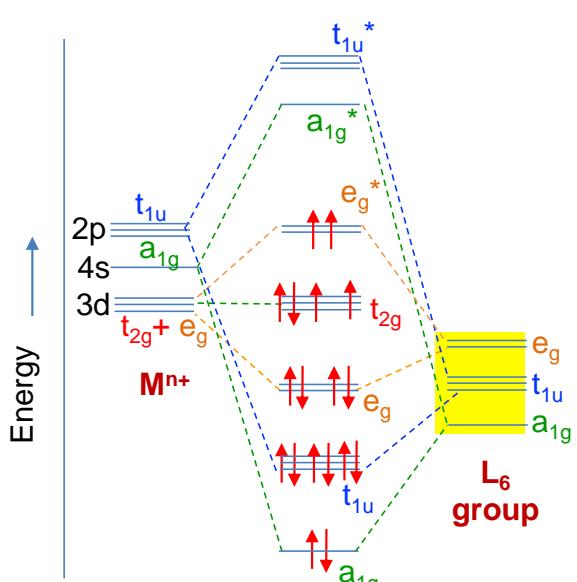


An approximate MO diagram for the formation of $[\text{ML}_6]^{n+}$ (where M is a first row metal) using the ligand group orbital approach; 12 atomic orbitals combine to give 12 molecular orbitals. The bonding only involves M-L σ -interactions in this diagram.

Molecular Orbital Theory: Octahedral Co^{3+} complexes



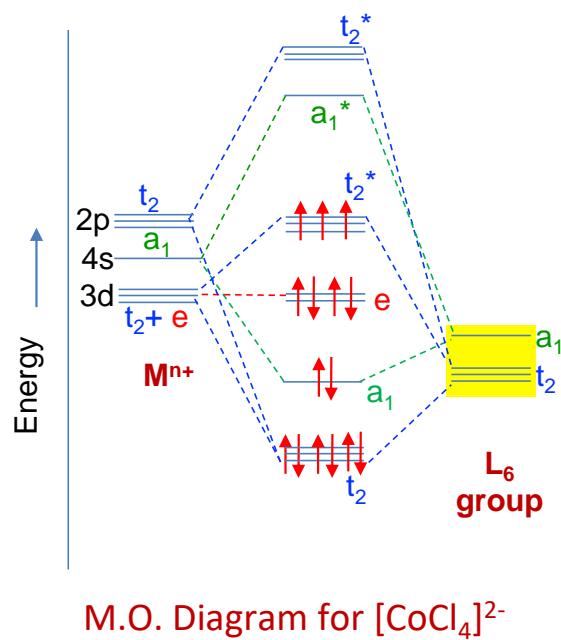
M.O. Diagram for $[\text{Co}(\text{NH}_3)_6]^{3+}$



M.O. Diagram for $[\text{CoF}_6]^{3-}$

Pairing energy for Co^{3+} ion is computed to be 19000 cm^{-1} . The Δ_o observed from electronic spectrum is 23000 cm^{-1} for $[\text{Co}(\text{NH}_3)_6]^{3+}$. Hence it's a low-spin complex. In contrast, The Δ_o observed from electronic spectrum is 13000 cm^{-1} for $[\text{CoF}_6]^{3-}$, which clearly indicates the formation of a high-spin complex.

Molecular Orbital Theory: Tetrahedral Co^{2+} complexes



M.O. Diagram for $[\text{CoCl}_4]^{2-}$

From all these MO diagrams, it should be apparent that the M.O. and CFT descriptions have strong resemblances, especially in the central portion of the MO diagram.
The two theories differ fundamentally in how they describe the metal-ligand bond, with the MO view being more realistic and provide better quantitative prediction of properties.

Molecular Orbital Theory

MOT explains the magnetic properties and spectra of complexes equally as that of CFT. Both theories depend on spectra to measure the Δ values. Hence, both theories may be used depending upon which is the most convenient for the property (dealing with metal-ligand σ -bond).

- MO theory has the advantage to cover the π -bonding. Pi bonding can easily explain how metals in low oxidation states can form complexes. CFT can not explain such back bonding because it does not assume any negative charge on the metal.

Magnetic properties

Magnetic susceptibility and the spin-only formula

Paramagnetism arises from unpaired electrons. Each electron has a magnetic moment with one component associated with the spin angular momentum of the electron and (except when the quantum number $l = 0$) a second component associated with the orbital angular momentum.

For many complexes of first row d-block metal ions, the second component is ignored and the magnetic moment μ can be derived from the number of unpaired electrons n using any one of the two related equations.

$$\mu(\text{spin-only}) = 2\sqrt{S(S+1)} \quad \mu(\text{spin-only}) = \sqrt{n(n+2)}$$

The effective magnetic moment, μ_{eff} , can be obtained from the experimentally measured molar magnetic susceptibility, χ_m , and is expressed in Bohr magnetons (BM) μ_B , where $1\mu_B = eh/4\pi m_e = 9.27 \times 10^{-24} \text{ JT}^{-1}$

The relationship between μ_{eff} and χ_m is given by the equation

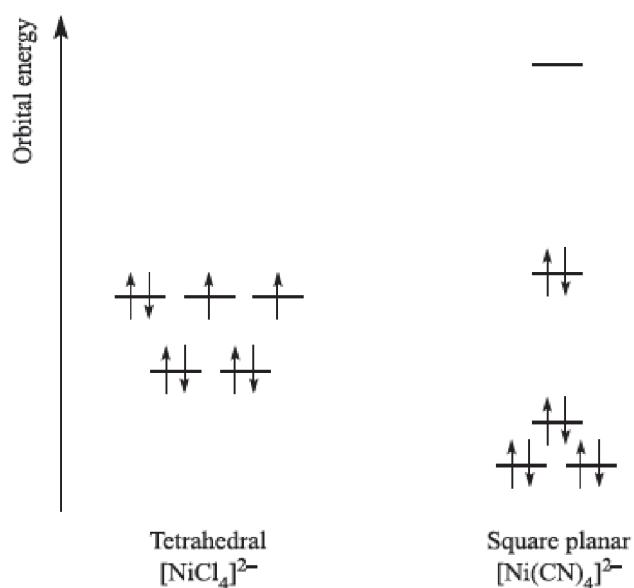
$$\mu_{\text{eff}} = \sqrt{\frac{3k\chi_m T}{L\mu_0\mu_B^2}} \quad \text{where } k = \text{Boltzmann constant; } L = \text{Avogadro number; } \mu_0 = \text{vacuum permeability; } T = \text{temperature in kelvin.}$$

$$\mu_{\text{eff}} = 2.828\sqrt{\chi_m T} \quad (\text{for use with Gaussian units})$$

Magnetic properties

The d^8 complexes $[\text{Ni}(\text{CN})_4]^{2-}$ and $[\text{NiCl}_4]^{2-}$ can be square planar and tetrahedral. These can be distinguished by magnetic properties

Similarly, the structure of four-coordinate d^7 Co^{2+} complexes can be distinguished by magnetic properties.



Tetrahedral: 3-unpaired electrons
 $\mu = \sqrt{3(3 + 2)} = \sqrt{15} = 3.87 \text{ BM}$

Square planar: 1-unpaired electrons
 $\mu = \sqrt{3(3 + 2)} = \sqrt{15} = 1.73 \text{ BM}$

Magnetic properties

Co³⁺ forms many complexes and most of them are diamagnetic (low-spin). However, [CoF₆]³⁻ is paramagnetic with an observed magnetic moment of 5.3 BM. This has been determined by magnetic measurements and correlating it with the calculated spin only value of 4.9 BM for 4 unpaired electrons.

2.7 Lecture 12+13

Transition Metal Chemistry: Introduction to Organometallics and Bioinorganic Chemistry

CH-2113: Introductory Inorganic Chemistry
Instructor: R. Boomi Shankar

Organometallics: Preface

Traditionally organometallic compounds are referred to M-C bonded systems →
Interface between organic and inorganic chemistry

There is always a difference in their terminology → Metal-Organic vs.
Organometallics, for example, $\text{Ti}(\text{OMe})_4$ and R_4Ti .

The field of organometallics has not only provided important conceptual insights but
also yielded useful catalysts for industrial and organic synthesis. It has links with...

biochemistry → use of enzymes in organometallic catalysis, for example, acetyl coA
synthase.

Materials Science → precursors for MOCVD, metal and metal-oxide surfaces

Nano-science and Nano-technology → Electronic, magnetic and optical devices and
sensors

Green Chemistry → Minimizing energy and chemical waste, atom economy (simple
by-products) etc.

Historic Background

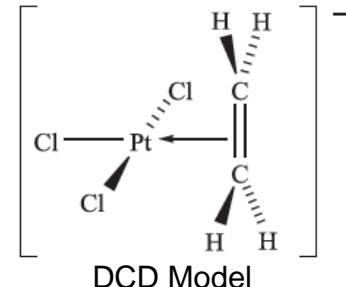
Most organometallic compounds that triggered the breakthrough research are accidental discoveries.

1. First compound Cacodyl oxide is known from 1760 in Paris Military Pharmacy → Cadet's work on cobalt based invisible inks containing Arsenic impurities.

$\text{As}_2\text{O}_3 + 4 \text{CH}_3\text{COOK} \rightarrow [(\text{CH}_3)_2\text{As}]_2\text{O}$ known as Cadet's fuming liquid

2. Second oldest compound prepared by W.C. Zeise in 1827 which involves the reaction of EtOH with a mixture of PtCl_2 and PtCl_4 in the presence of KCl

$\text{PtCl}_2(\text{C}_2\text{H}_4) \cdot \text{KCl} \cdot \text{H}_2\text{O} \rightarrow$ Bizarre compound, the structure is later solved as $[\text{Cl}_3\text{Pt}(\text{C}_2\text{H}_4)] \cdot \text{K} \cdot \text{H}_2\text{O}$



3. First compound with direct metal-alkyl σ-bond was synthesized by E. Frankland (who discovered He) in an attempt to prove the presence of organic radical.

Attempted: $2\text{EtI} + \text{Zn} \rightarrow \text{ZnI}_2 + 2\text{Et}\cdot$ Actual: $\text{EtI} + \text{Zn} \rightarrow \frac{1}{2} \text{Et}_2\text{Zn} + \frac{1}{2} \text{ZnI}_2$

Used as alkylating reagent, later replaced by Grignard reagents (again another organometallic compound, discovered in 1900)

Historic Background

The most exciting finding came in early 1950s: Ferrocene in 1951 and Zeigler process in 1953.

1. Miller synthesized it from Fe powder and dicyclopentadiene; Pauson and Kealey made it from $\text{CpMgBr} + \text{FeCl}_3$. They proposed a σ -bonded structure. Wilkinson and Fisher proposed the sandwich structure where the $\eta^5\text{-Cp}$ rings involve in π -bonding.
2. Ziegler showed the conversion of ethylene to polyethylene by a catalyst composed on $\text{TiCl}_4 + \text{AlEt}_3$. When this process was transferred to Natta's group in Italy the stereoregular polymerization of propylene and polymerization of butadiene was developed using modified catalysts → outstanding example of how a basic research can suddenly produce a worldwide industrial process.
3. Followed this process was Wacker's process for the conversion of ethylene to acetaldehyde → both have profound impact on the growing petrochemical industry.
4. In parallel, novel, unprecedented complexes like Vaska's complex, dinitrogen compounds, carbine complexes etc. were developed that are potentially investigated for various other catalytic processes.

18-electron rule

1. Organometallic chemistry is concerned with Metal-Carbon bonds, of which the simplest is the M-C single bond of metal alkyls As σ -bonding ligands, alkyls are related to the ligands found in coordination compounds such as Cl, H₂O, NH₃ etc.
2. A large variety of ligands in organometallic chemistry of soft and can π -bond. For example, ethylene, benzene, cyclopentadienyl etc.
3. A group of ligands such as CO, NO, phosphines, carbenes etc. can bond with multiple interactions involving σ -donor and π -acceptor bonds

All these classes of compounds make this field an unique subject on its own.

Organometallic compounds differ from the traditional coordination complexes on the following grounds

1. The metals can bear a greater negative charge
2. The M-L bonds are more covalent in energy and often can π -bond
3. The d-electrons are higher in energy and can perturb (via back donation) the electronic structure of the ligands more than the coordination compounds. Hence, these ligands can be easily be polarized and activated towards reactions.
4. The most rudimentary basis of controlling the structure and reactivity of organometallic complexes is 18-electron rule and back-bonding.

18-electron rule

Proposed by Sidwick (1927) → based on V. B. formalism of localized M-L bonds

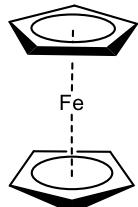
- 18-electron rule is a way to help us decide whether a given d-block organometallic complex is stable. It states that

"Thermodynamically stable transition metal complexes are formed when the sum of the metal d-electrons plus the electrons conventionally regarded as being supplied by the ligands equal 18"

In this way, the metal formally attains the electronic configuration of the subsequent noble gas in the periodic table.

While applying the 18-electron rule, the following conventions should be considered

1. The intermolecular partitioning of the electrons has to ensure that the total charge of the complex remains unchanged. For example

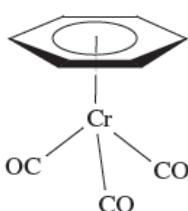


Ionic Model

2 Cp → 12 electrons
Fe²⁺ → 6 electrons
Total 18 electrons

Covalent Model

2 Cp → 10 electrons
Fe(0) → 8 electrons
Total 18 electrons



Cr(0) (group 6) contributes 6 electrons
η⁶-C₆H₆ contributes 6 electrons
3 CO contribute 3 × 2 = 6 electrons
Total = 18 electrons

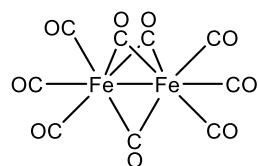
18-electron rule

2. A metal-metal bond contributes one electron to the total electron count of a metal atom.

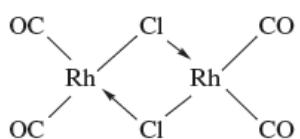
$\text{Mn}_2(\text{CO})_{10} \rightarrow \text{Mn} = 7 \text{ electrons}, 5(\text{CO}) = 10 \text{ electrons}$ and $1 \text{ Mn-Mn bond} = 1 \text{ electron}$. So the total is 18 electrons

3. The electron pair of the bridging ligand donates one electron to each of the bridging atoms.

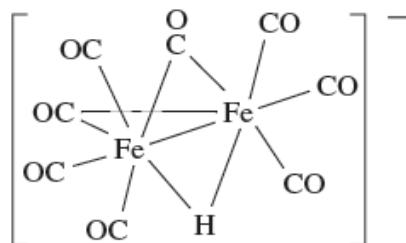
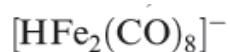
Example $\text{Fe}_2(\text{CO})_9$



Covalent Model
3 CO \rightarrow 6 electrons
3 $\mu\text{-CO}$ \rightarrow 3 electrons
 $\text{Fe}(0)$ \rightarrow 8 electrons
 Fe-Fe \rightarrow 1 electron
Total 18 electrons



$\text{Rh}(0)$ (group 9) contributes 9 electrons
 $\mu\text{-Cl}$ contributes 3 electrons (1 to one Rh and 2 to the other Rh)
2 CO contribute $2 \times 2 = 4$ electrons
Total per Rh = 16 electrons



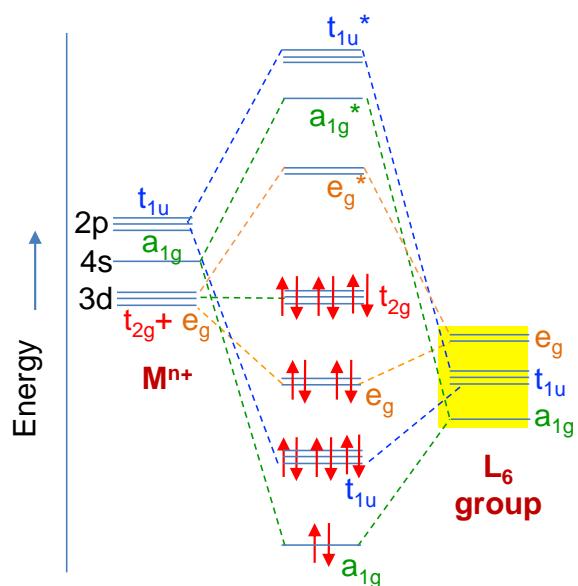
$\text{Fe}(0) = 8$ electrons
3 terminal CO = 3×2 electrons
2 $\mu\text{-CO} = 2 \times 1$ electron per Fe
Fe-Fe bond = 1 electron per Fe
 $\text{H} = \frac{1}{2}$ electron per Fe
1- charge = $\frac{1}{2}$ electron per Fe
Total = 18 electrons per Fe

18-electron rule

Considerable predictive value to arrive at the composition of many transition metal complexes → majority of the compounds with middle of the d-block metals obey. This rule often breaks down for the early and late d-block metals. For example, 16-electron complexes are favoured for Rh(I), Ir(I), Pd(0) and Pt(0) compounds

Guiding principles

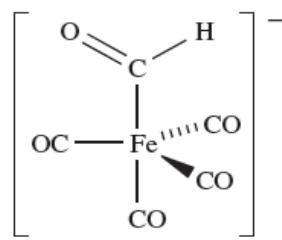
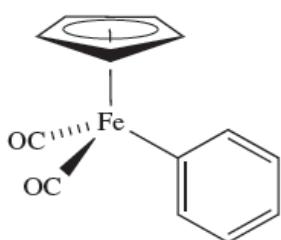
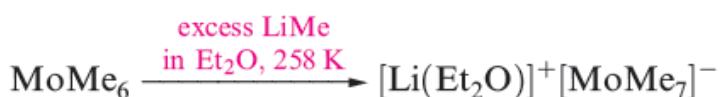
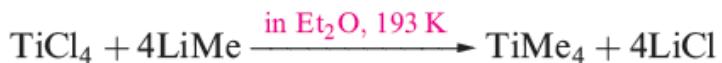
- A.B.O. should not be occupied
- N.B.O. may be occupied
- B.O. should be occupied



Nature of Ligands and Modes of Binding: σ -donors

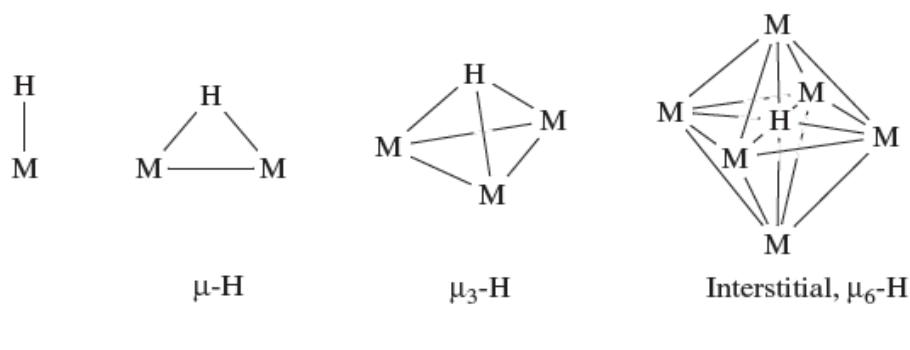
σ -Bonded alkyl, aryl and related ligands

In complexes such as WMe_6 , $[\text{MoMe}_7]^-$, TiMe_4 and $\text{MeMn}(\text{CO})_5$, the M-C_Me bond can be described as a localized 2c-2e interaction, i.e. it parallels that for the $[\eta^1-\text{Cp}]^-$ ligand. The same bonding description is applicable to the Fe-CPh bond in and the Fe-C_CHO bond in the complexes given below.

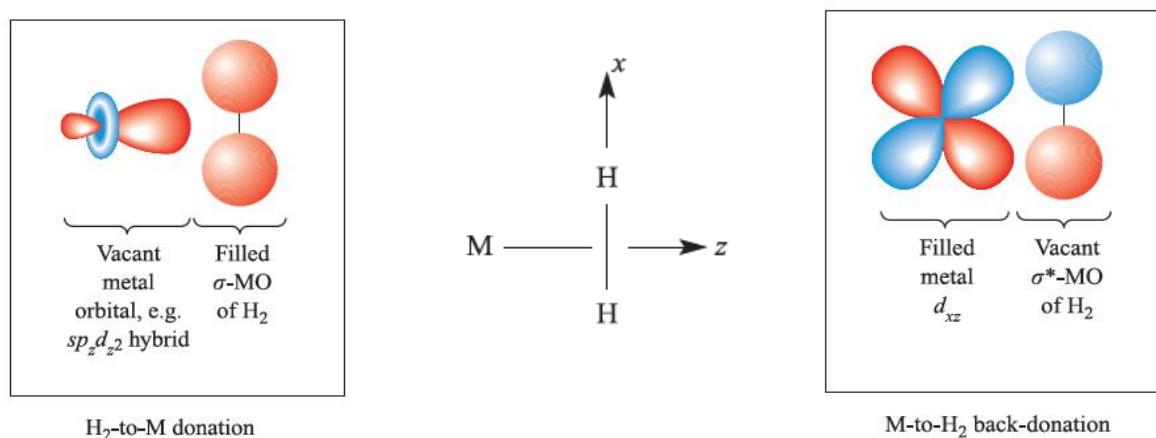


Nature of Ligands and Modes of Binding: σ -donors

Hydride ligands

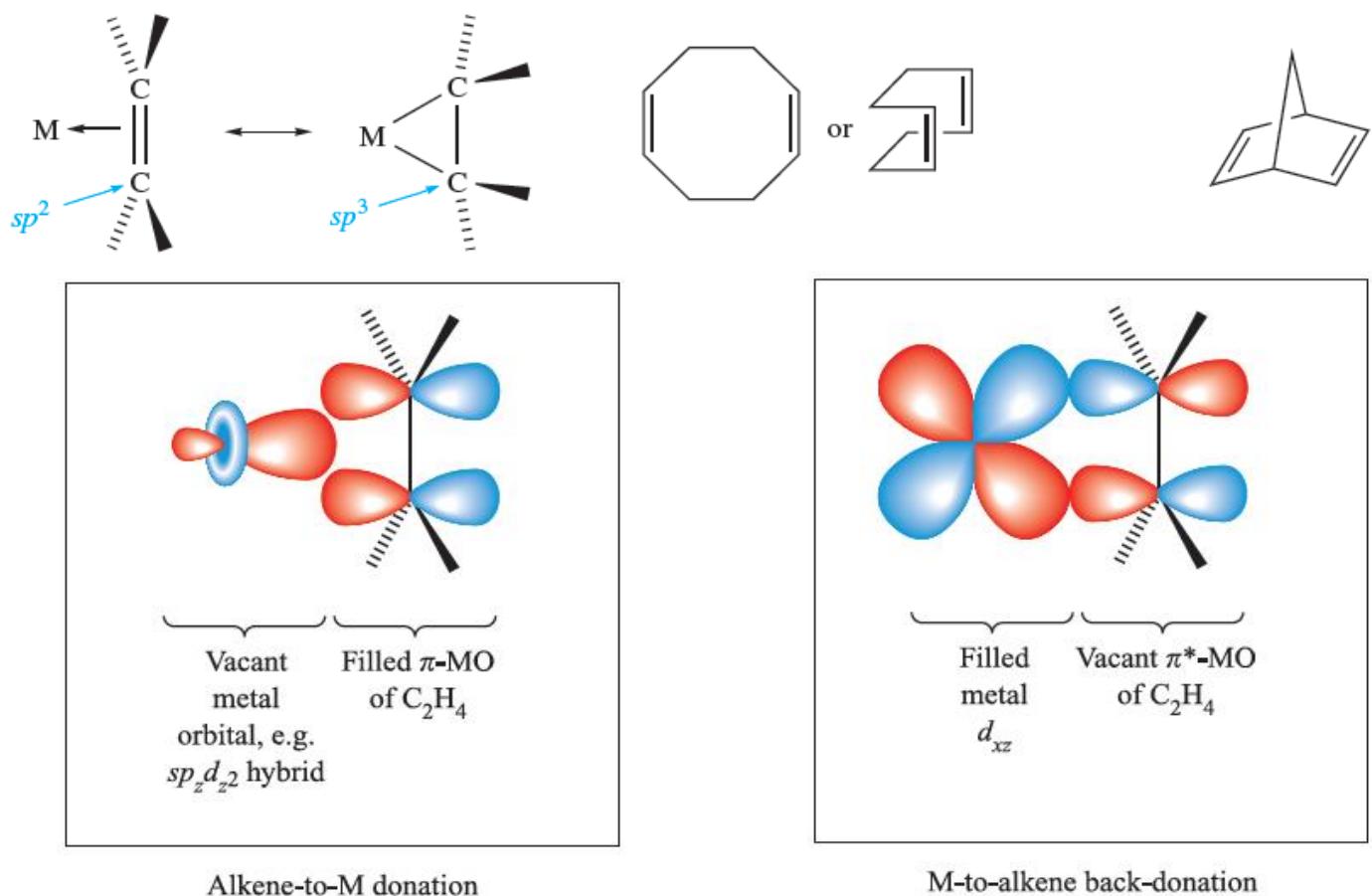


Dihydrogen as Ligand: σ -complex



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Nature of Ligands and Modes of Binding: π -donors



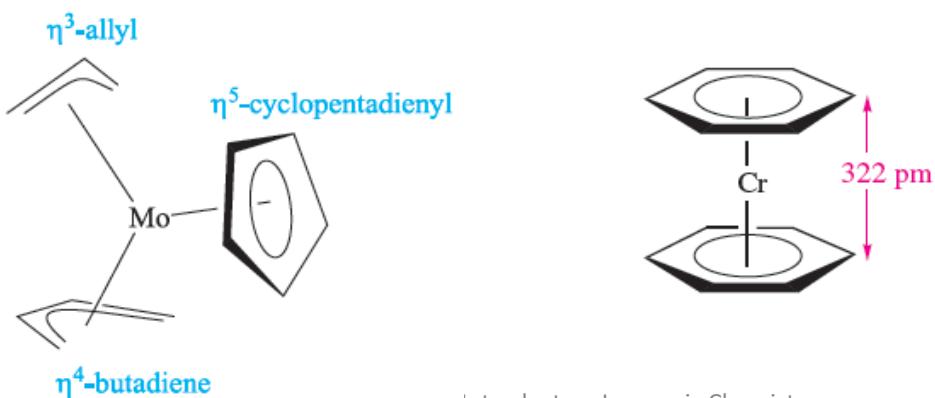
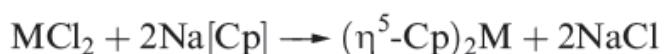
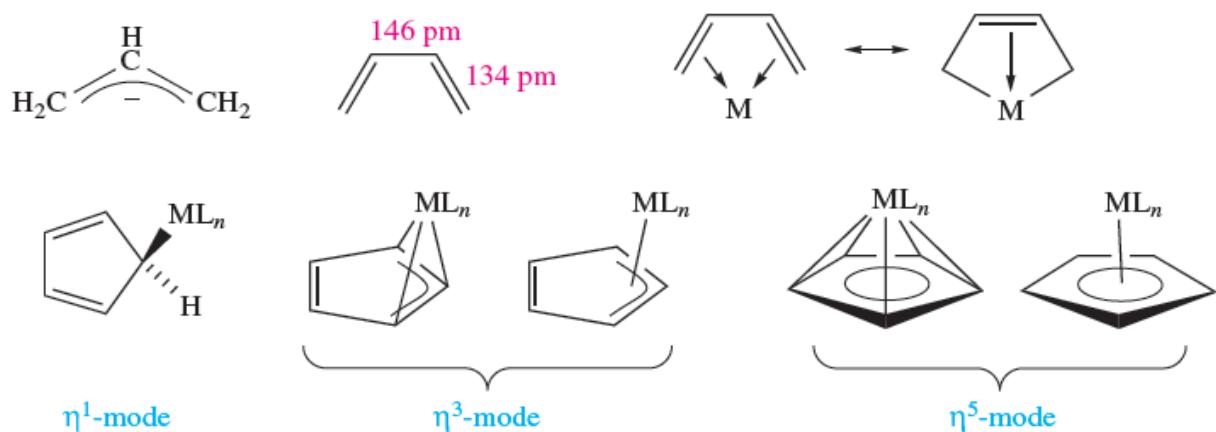
Alkene-to-M donation

M-to-alkene back-donation

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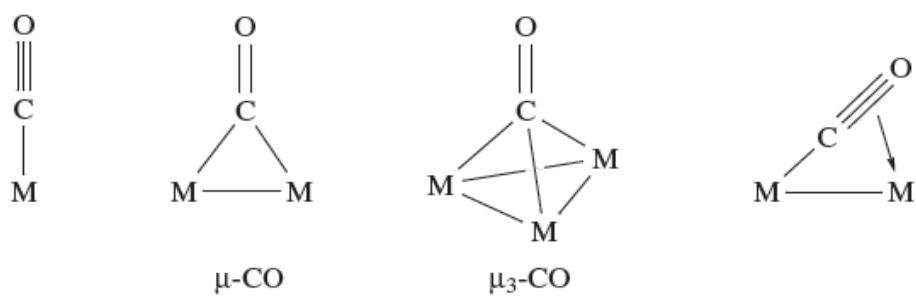
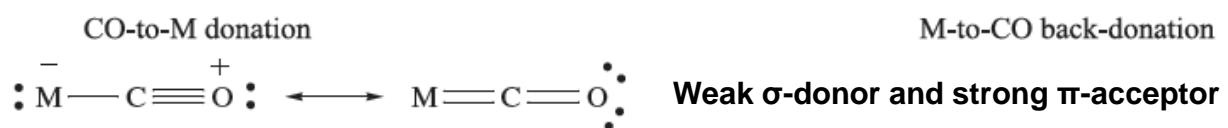
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Nature of Ligands and Modes of Binding: π -donors

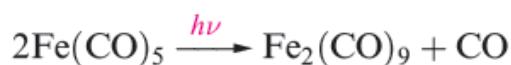
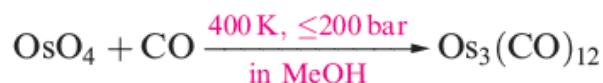
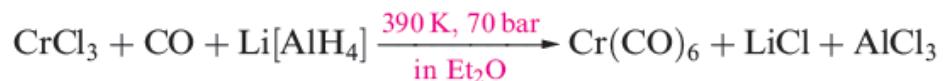


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Nature of Ligands : σ -donors and π -acceptors

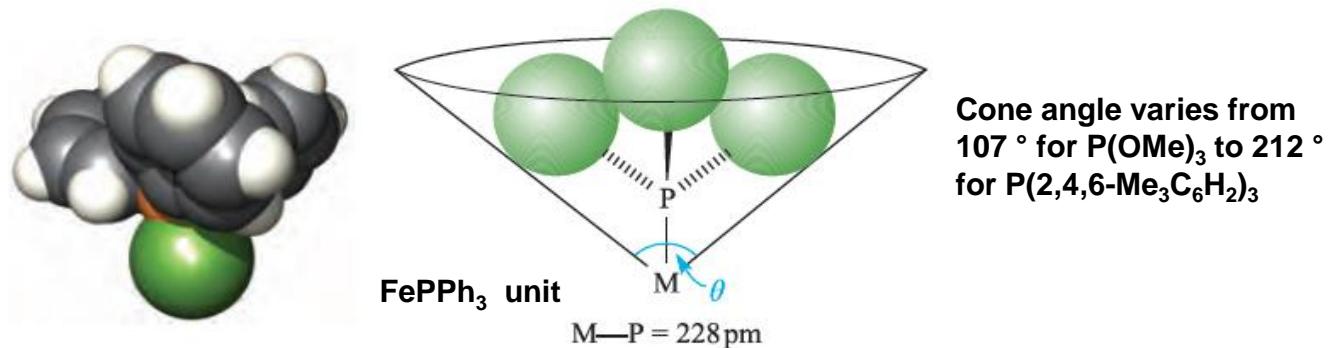
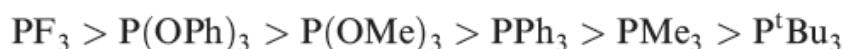


Nature of Ligands : σ -donors and π -acceptors



Nature of Ligands : σ -donors and π -acceptors

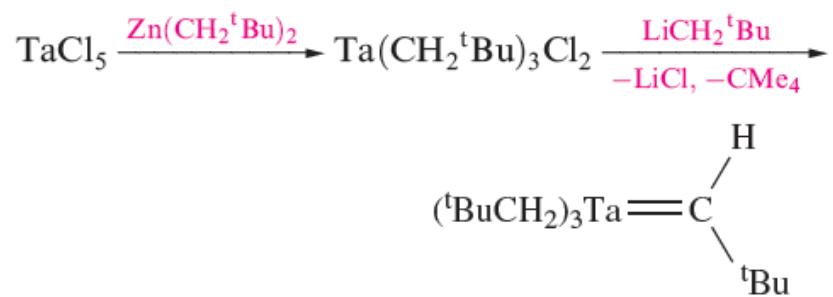
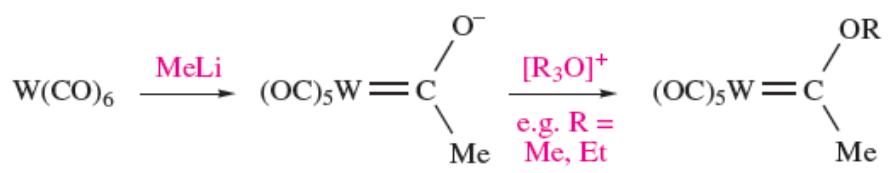
The extent of σ -donation and π -acceptance depends on the substituents, e.g. PR_3 (R = alkyl) is a poor π -acceptor, whereas PF_3 is a poor σ -donor and as strong π -acceptor as CO . The π -accepting properties of some PR_3 ligands follow the ordering:



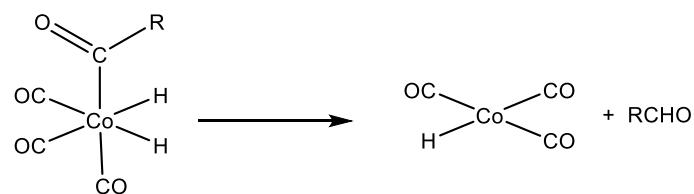
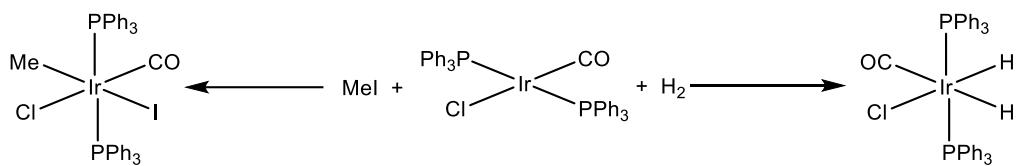
The steric requirements of a PR_3 ligand depend on the R groups. Ligands such as PPh_3 or P^tBu_3 are sterically demanding while others such as PMe_3 are less so. The steric requirements are assessed using the Tolman cone angle, found by estimating the angle of a cone that has the metal atom at its apex and encompasses the PR_3 ligand taking the van der Waals surfaces of the ligand H atoms as its boundary



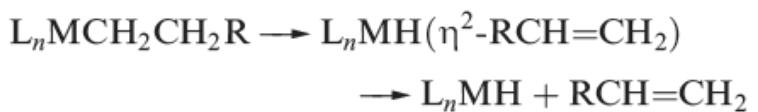
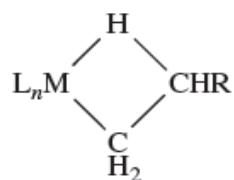
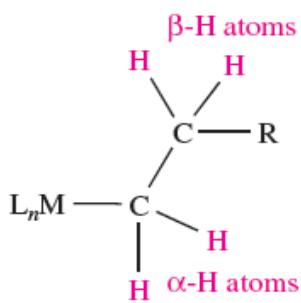
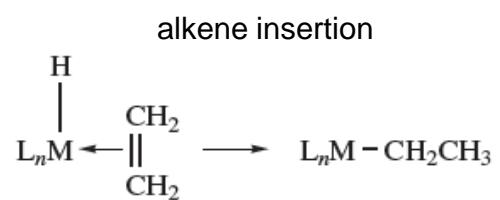
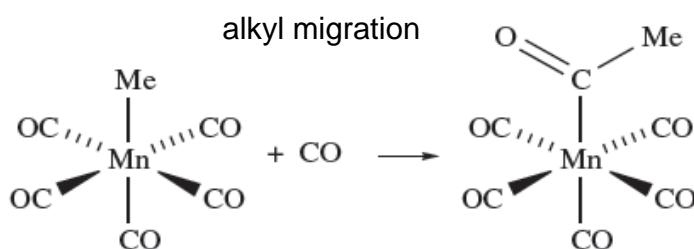
Nature of Ligands : Carbenes



Reactivity: oxidative addition and reductive elimination



Reactivity: Insertion (migration) and elimination



Metals in Life: Preface

- When one considers the chemistry of biological processes, the boundary between inorganic and organic chemistry is blurred.
- The bulk biological elements that are essential to all life include C, H, N, O (the four most abundant elements in biological systems) along with Na, K, Mg, Ca, P, S and Cl.
- The fundamental elements that make up the building blocks of biomolecules (e.g. amino acids, peptides, carbohydrates, proteins, lipids and nucleic acids) are C, H, N and O, with P playing its part in, for example, ATP and DNA and S being the key to the coordinating abilities of cysteine residues in proteins.
- The roles of the less abundant, but nonetheless essential, elements include osmotic control and nerve action (Na, K and Cl), Mg^{2+} in chlorophyll, Mg^{2+} -containing enzymes involved in phosphate hydrolysis, structural functions of Ca^{2+} (e.g. bones, teeth, shells) and triggering actions of Ca^{2+} (e.g. in muscles).
- The trace metals are V, Cr, Mn, Fe, Co, Ni, Cu, Zn and Mo, while trace non-metals comprise B, Si, Se, F and I

Summary of Trace metals in life and their biological roles

| Metal | Mass / mg | Biological roles |
|-------|-----------|---|
| V | 0.11 | Enzymes (nitrogenases, haloperoxidases) |
| Cr | 14 | Claimed (not yet proven) to be essential in glucose metabolism in higher mammals |
| Mn | 12 | Enzymes (phosphatase, mitochondrial superoxide dismutase, glycosyl transferase); photoredox activity in Photosystem II |
| Fe | 4200 | Electron-transfer systems (Fe–S proteins, cytochromes); O ₂ storage and transport (haemoglobin, myoglobin, haemerythrin); Fe storage (ferritin, transferritin); Fe transport proteins (siderophores); in enzymes (e.g. nitrogenases, hydrogenases, oxidases, reductases) |
| Co | 3 | Vitamin B ₁₂ coenzyme |
| Ni | 15 | Enzymes (urease, some hydrogenases) |
| Cu | 72 | Electron transfer systems (blue copper proteins); O ₂ storage and transport (haemocyanin); Cu transport proteins (ceruloplasmin) |
| Zn | 2300 | Acts as a Lewis acid (e.g. in hydrolysis processes involving carboxypeptidase, carbonic anhydrase, alcohol dehydrogenase); structural roles |
| Mo | 5 | Enzymes (nitrogenases, reductases, hydroxylases) |

Despite their crucial role in life, the trace metals make up only a tiny fraction of the human body-weight. Research progress in bioinorganic chemistry has been greatly assisted in recent years by the development of methods to solve protein structures using X-ray diffraction and NMR spectroscopy together with their correlation with model systems.

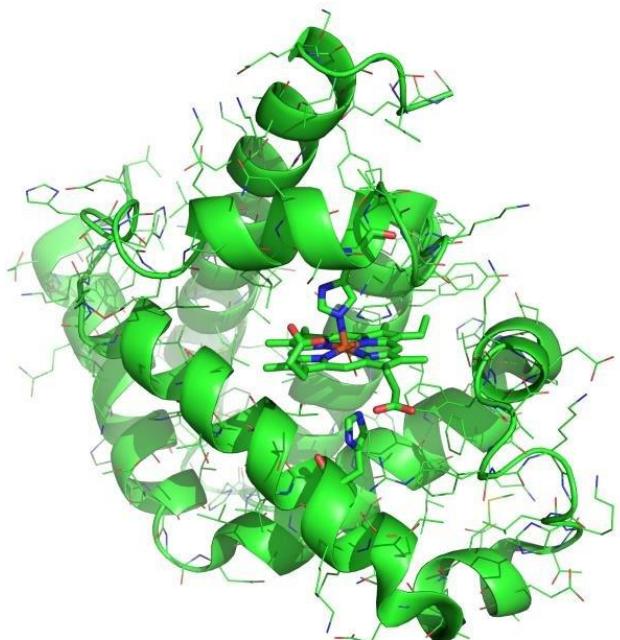
Oxygen Metabolism

- Most organisms require molecular oxygen to survive. The dioxygen is used in a variety of biochemical reactions. However, most of them are consumed in the reaction $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$, this is the terminal step of the oxidative phosphorylation.
- For small organism and plants, the oxygen is supplied by a simple diffusion process (due to large surface to volume ratio in them). Plants get it via photosynthesis.
- But this process is not fast enough in multi-cellular organisms without help. An elegant three component system evolved to transport oxygen from the regions of high abundance (air and water) to regions of low abundance and demand (interiors of the cells).
- First and central component → di-oxygen carrier protein based on Cu or Fe active sites, for ex. Hemoglobins, Hemocyanin and Hemerythrin. The second component → a O_2 transport system for the sequestration of oxygen by the protein. Special organs such as Lungs and Gills perform this function. The third component is the delivery system → The O_2 carrier is suspended/ dissolved in a fluid/blood is pumped through out the organism → by special organs such as heart.
- In many organisms, an additional O_2 -binding protein such as myoglobin is present to store O_2 in tissues

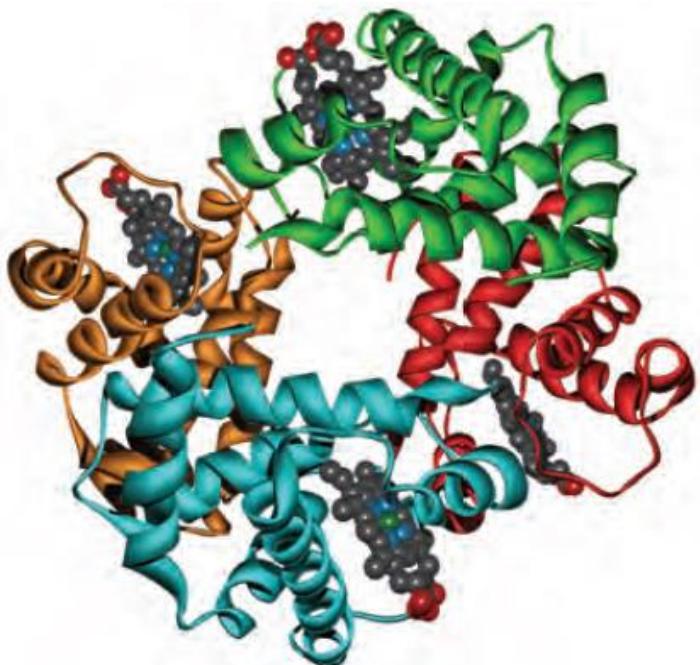
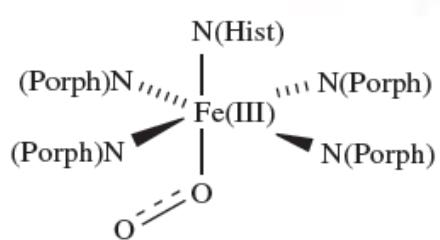
Oxygen Metabolism: Haemoglobin and myoglobin

- Hemoglobin (Hb) picks up O₂ from lungs/gills and transports it to the tissues where it is stored by Myoglobin (Mb)
- The function of Hb in red blood cells is obvious and that of Mb is subtle
- Besides serving as a repository for O₂, Mb also functions as a dioxygen reserve. The organisms can draw O₂ during increased metabolism or O₂ deprivation.
- Mb also regulates O₂ flow within cells and buffering of the O₂ partial pressures within the cell in response to increased or decreased O₂ supply.
- -----
- O₂ is not a typical ligand → resembles closely to CO, NO and N₂ → does not have significant dipole moment to contribute to σ-bond. CO enhances better back-bonding than O₂.
- O₂ is considered as a soft ligand with a weaker π-bonding capacity. Fe(II) does not bind soft ligands. But the symbiotic softening action of the tetrapyrrole ring of the porphyrin facilitates O₂ binding.
- The truly soft 'CO' binds the heme group even more tightly → CO poisoning

Oxygen Metabolism: Haemoglobin and myoglobin

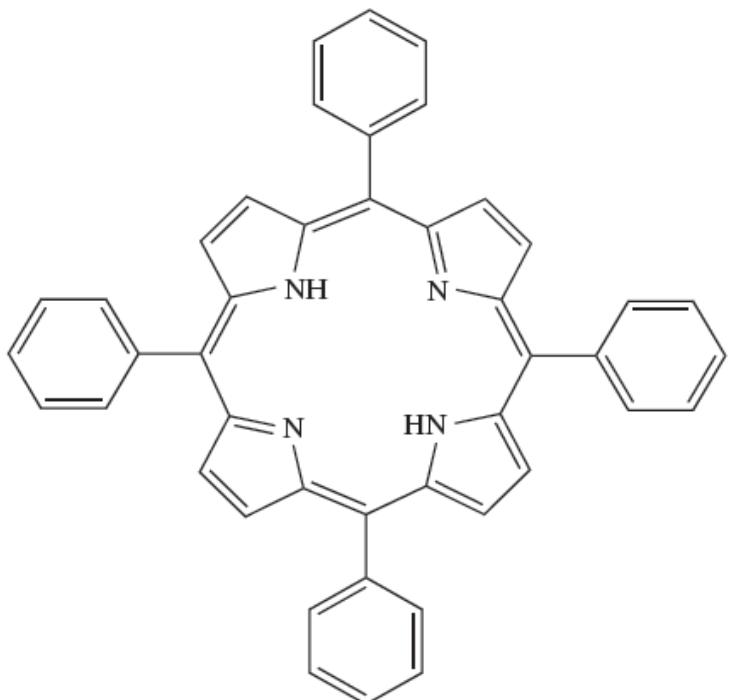
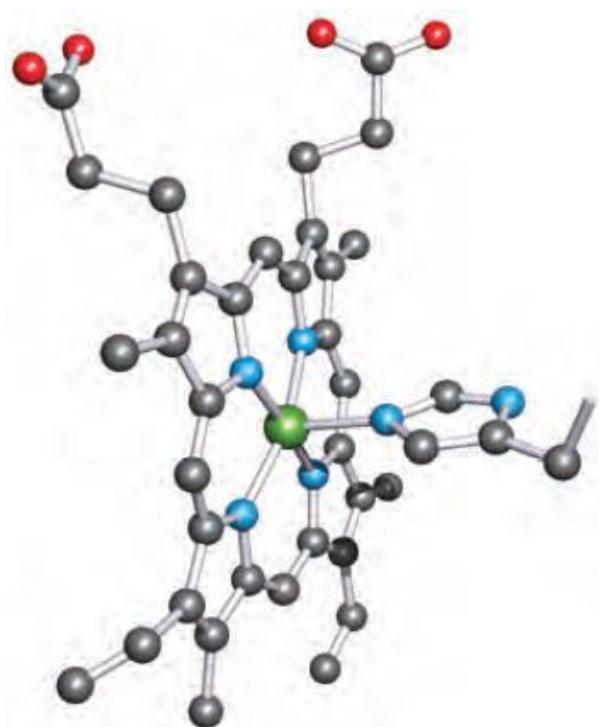


Mb → Protein of M.wt. 17000 (17 Kg/mol) with 153 amino acid residues folded about a single heme group.



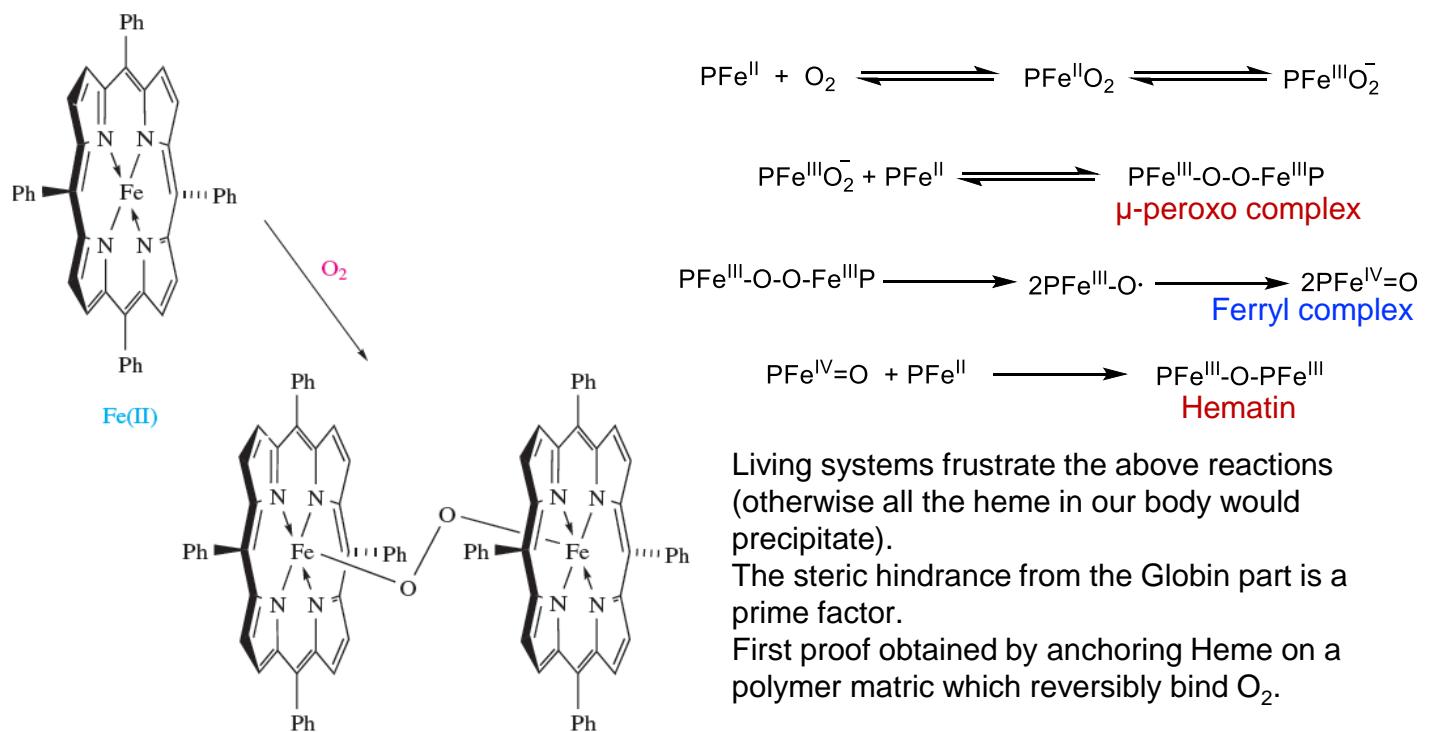
Hb → Protein of M.wt. 68000 (68 Kg/mol). Four hemes bound to four (2α and 2β type) protein chains. α -chains contain 141 amino acid residues and β -chains contain 146 amino acid residues

Active sites of Haemoglobin and myoglobin



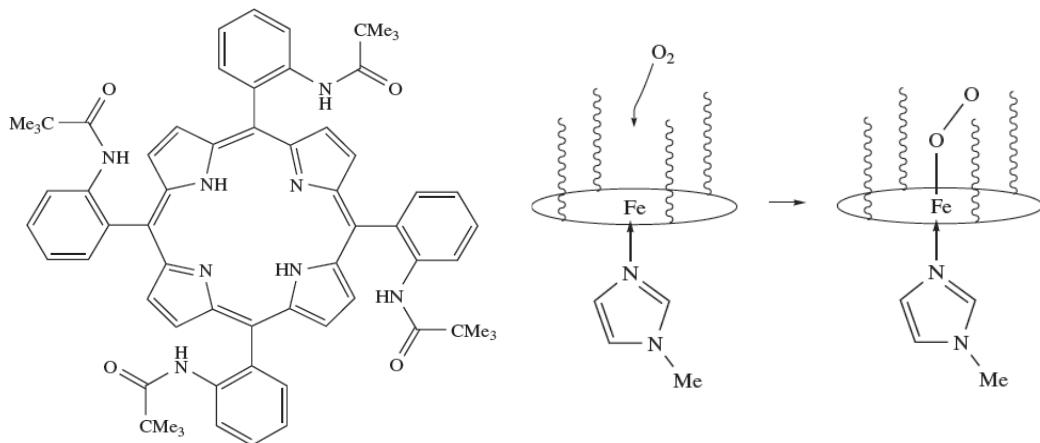
Oxygen Metabolism: Haemoglobin and myoglobin

Potential flaw in $\text{O}_2\text{-Hb}$ bonding is irreversible oxidation. If Free Heme is exposed to O_2 , it is almost immediately converted to a μ -Oxo dimer known as Hematin.



Oxygen Metabolism: Myoglobin

Same results were obtained on a model “picket-fence” heme and related compounds



In Mb, Fe(II) is high-spin d⁶, radius 92 pm, square-pyramidal

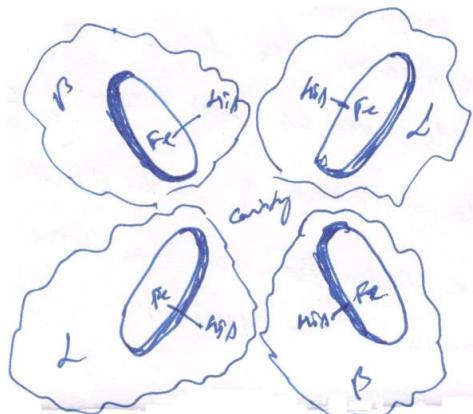
Fe → will not fit the hold of porphyrin and reside 42 pm above the plane of N-atoms of the ring.
O₂ binding makes it Fe(III) low-spin and the radius is lowered to 75 pm which fits the ring. Reason:
electrons in e_g orbital, repels ligand electrons so spherical expansion of the radius in Fe(II) high spin.
Spin pairing shrinks the Fe(III) radius in the absence of e_g electrons.

Though, the net effect of this process is minimal in Mb, it is important in Hb for the transmission of O₂ from lungs to tissues.

O₂ binding in Haemoglobin

The four heme units in haemoglobin do not operate independently and the binding (and release) of O₂ is a cooperative process, which is visualized as a communication between the heme groups arising from conformational changes in the protein chains.

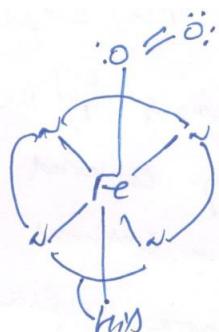
When the first heme motif binds to the O₂ molecule, the affinity of the successive 'vacant' heme groups increases. In fact, the affinity for the fourth site is ~300 times that of the first heme unit.



The heme group in its rest state contains high-spin Fe(II) lying ~40pm out of the plane of the porphyrin group and is drawn towards the His residue.

When O₂ enters the sixth coordination site, the iron centre (now low-spin Fe³⁺) moves into the plane of the porphyrin ring and pulls the His residue with it. This in turn perturbs not only the protein chain to which the His group is attached, but also the other three protein chains, and a cooperative process triggers the other heme units to successively bind O₂ more freely.

When O₂ is released from haemoglobin to myoglobin, the loss of the first O₂ molecule triggers the release of the other three molecules.



Oxygen Metabolism: cooperative mechanism

