CH 2113 - PRINCIPLES OF INORGANIC CHEMISTRY

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PRINCIPLES OF INORGANIC CHEMISTRY

CH 2113 – Semester 03

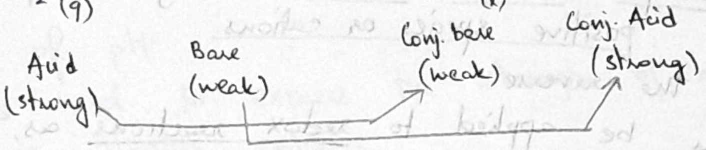
6/8

Acids and Bases
Lecture 01

There are several concepts defining acids and bases – we choose the one which applies best to a particular case or situation – aqueous, non-aqueous, organic etc

1. Arrhenius concept : Acids – increase the conc. of H^+
   Bases – increases conc. of OH^- in water

Eg: (1) $SO_{2(g)} + H_2O \longrightarrow HSO_{3(l)}^- + H^+_{(l)}$



2. Bronsted – Lowry Concept.
   Acid : Proton donor   Base : Proton acceptor
   This concept can fit any protic system

Eg: $\underset{A}{\overset{\text{Ammonium}}{NH_4^+}} + \underset{B}{\overset{\text{amine}}{NH_2^-}} \rightleftharpoons 2NH_3$

$H_3SO_4^+ + HSO_4^- \rightleftharpoons 2H_2SO_4$

} Non-aqueous but protic system

This concept doesn't explain Eg. (1) well

3. Lux – Flood Concept Base
   This is in terms of oxide ions.
   Acid: Oxide ion acceptor   Base: Oxide ion donor
   This applies to high T reactions that occur in inorganic melts → no involvement on H^+.

Eg: $\underset{\text{oxide donor}}{CaO} + \underset{\text{oxide acceptor}}{SiO_2} \xrightarrow{\Delta} CaSiO_3$

This is derived from their basic properties –

$Ca^{2+} + O^{2-} + H_2O \longrightarrow Ca^{2+} + 2OH^-$; $SiO_2 + H_2O \longrightarrow H_2SiO_3$

Eg 2) Bessemer Reaction in steel making

4. Lewis Acid-Base Theory

Acid : Electron pair / anion acceptor

Base : Electron pair donor

Eg: Neutralisation reaction of HCl and NaOH

$$\underset{e^-\text{ donor}}{:\ddot{O}H^-} + \underset{e^-\text{ acceptor}}{H^+} \longrightarrow H_2O$$

This concept also explains reactions where no ions are formed and no H^+ is transferred

Examples – $R_3N: + BF_3 \longrightarrow R_3N:BF_3$ Adduct formation

$4.CO + Ni \longrightarrow Ni(CO)_4$ Coordination compound

$2NH_3 + Ag^+ \longrightarrow [Ag(NH_3)_2]^+$ —"—

$HCl + NaOH \longrightarrow NaCl + H_2O$ e^- pair transfer.

5. Usanovich Concept

Acid : accepts electrons, anions or negative species or donat positive species or cations.

Base : the reverse

This can be applied to redox reactions as a special case of acid-base reactions.

Acidity constant - an Equilibrium constant

The relative capacity of molecules to donate a proton to a common base (H_2O) under identical conditions is quantified by K_a.

To express it more conveniently, we use $\boxed{pK_a = -\log_{10} K_a}$

pK_a ranges from -10 to 50.

How fast the equilibrium is reached decides the speed of proton transfer but not strength.

Eg: $HF_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + F^-_{(aq)}$

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

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

$pK_a = 3.46$

If K_a is very small, its a weak acid

Strong acids can have K_a in range of 10^{+1} to 10^{+9}

Eg: For HBr, $K_a = 10^9$

* Smaller the value of pK_a, stronger the acid.

Power of an acid

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

For any aqueous acid-base reaction, if K_a or pK_a and pH are supplied, we can calculate one from the others.

Eg: pH of 0.145 M acetic acid is 2.8. Calculate K_a

$pH = 2.8 \Rightarrow [H_3O^+] = 10^{-2.8} = 1.6 \times 10^{-3}\ mol\ L^{-1}$

$$CH_3COOH_{(aq)} + H_2O \rightleftharpoons CH_3COO^- + H^+$$

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

$\rightarrow [CH_3COOH] = 0.145 - [CH_3COO^-] = 0.143$

$$K_a = \frac{2.56 \times 10^{-6}}{0.143} \approx 1.8 \times 10^{-5} \Rightarrow pK_a \approx 4.75$$

9/9/20

Lecture 02

Concept of pH

pH is used to express the strength of an acid, which is always relative

$$HA + H_2O \rightarrow H_3O^{\oplus} + A^-$$

The strength is proportional to the amount of H^+ it releases

$[H_3O^+]$ quantifies the strength in mol/L

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

Calculating pH

pH of 0.145 M CH_3COOH is 2.8. Calculate K_a

$pH = 2.8 = -\log[H^+] \Rightarrow [H^+] = 10^{-2.8} = 1.6 \times 10^{-3}\ mol\ L^{-1}$

$[H_3O^+] = [CH_3COO^-] \Rightarrow [CH_3COOH] = 0.145 - 0.0016 \approx 0.143$

$$\therefore K_a = \frac{(1.6 \times 10^{-3})^2}{0.143} = 1.8 \times 10^{-5} \Rightarrow pK_a = 4.75$$

Calculating Strength of a Base

Eg $$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

For NH_3, $K_b = 1.8 \times 10^{-5} \Rightarrow$ Weak base $\because K_b \ll 1$

pH of HF at diff conc :-

1 mM - 3.27
10 mM - 2.65
100 mM - 2.12

pKa	3.1	-6.0	-9.0	-9.5
	HF	HCl	HBr	HI

$\xrightarrow{\hspace{3cm}}$ stronger the acid

pH of water is nuetral i.e. 7
< 7 : Acidic > 7 : Basic

Autoproteolysis

Water is amphoteric - acts as both acid and base
Only very few H_2O undergo autoproteolysis -

$$H_2O + H_2O \rightleftharpoons H_3O^+ + H^+$$

$$K_w = \frac{[H_3O^+]\cdot[H^+]}{[H_2O]} \quad \text{where } [H_2O] = 1$$

Since pH = 7 $\Rightarrow$ $[H^+] = 10^{-7}$ mol L^{-1}
$\therefore$ $K_w = 10^{-14}$ mol L^{-1} (at 25 °C).

Expressing acidity of bases

We can express it in terms of its conjugate acid.

$$NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$$

$\boxed{K_a K_b = K_w}$ K_b for $NH_3 = 1.8 \times 10^{-5}$

K_a of $NH_4^+ = \frac{10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$

$\therefore \boxed{pK_a + pK_b = pK_w}$

If K_a is large ($\Rightarrow$ strong acid) then K_b of its conjugate base is small.

pH Scale

It runs from 1 to 14. Its a relative value.
Water is nuetral and its pH is set at 7

Polyprotic acids

They have multiple protons which they lose in succession, in water or in presence of a base.
Each successive loss of proton is less favored as the negative charge increases and makes it very difficult to take anther H^+

$H_2A + H_2O \rightleftharpoons HA^- + H_3O^+$: pKa_1

$HA^- + H_2O \rightleftharpoons A^{2-} + H_3O^+$: pKa_2

$pKa_1 < pKa_2$
$\Rightarrow Ka_1 > Ka_2$

pKa of H_2A : $pKa = pKa_1 + pKa_2 \Rightarrow Ka = Ka_1 \times Ka_2$

Example for this : H_2S

Distribution diagram of polyprotic acids

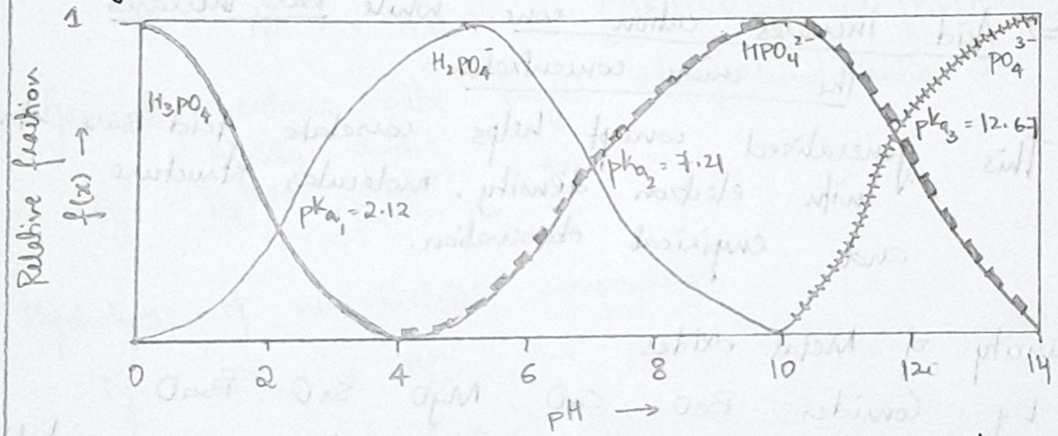
Eg: Phosphoric acid : H_3PO_4 – triprotic

Representation of conc of different species that are formed during successive proton transfer equilibria can be done through fraction of molecule present in the solution

$$f(H_3PO_4) = \frac{[H_3PO_4]}{[H_3PO_4] + [H_2PO_4^-] + [HPO_4^{2-}] + [PO_4^{3-}]}$$

Similarly $f(HPO_4^{2-})$ and etc. can be written.

Diagram –



Conc. of H_3PO_4 is maximum at pH = 0 ⇒ Highly acidic condition

It drops to zero at 4.2 ⇒ relatively weak acid

At pH = 4.2, $H_2PO_4^-$ is the predominant species.

At basic cond^n (8.8 – 9.2) HPO_4^{2-} is predominant species.

In $H_3PO_4 + H_2O \rightleftharpoons H_2PO_4^- + H_3O^+$ has $pKa_1 = 2.12$

At this point, ratio of $H_2PO_4^-$: H_3PO_4 is 1:1.

Structure of Water

H_3O^+ ion is a very simplified structure

Protonated water exists in clusters with several other water molecules as seen by spectroscopy measurements.

$(H_9O_4)^+$ and $(H_2O)_{21}H^+$ are more commonly known.

Here proton is solvated by 21 molecules and it has a pentagonal dodecahedral structure.

19/9/20

Lecture 03

Generalised concept of Acid & Base –

Acid – Donates proton or cation
Accepts an e^- pair or anionic solvents or oxide ion

Base – Donates anionic species, a pair of e^- or oxide ion
Accepts a proton or cation

⇒ Acid increases cation conc. while Base increases the anion concentration

This generalised concept helps correlate Acid-Base strength with electron density, molecular structure and empirical observation.

Basicity of Metal oxides

E.g: Consider BeO, CaO, MgO, SrO, BaO

They belong to same group and have same oxidation number – +2.

Here, BeO is amphoteric and all others are basic. Why?

→ In BeO, the charge is packed in a small volume, while in other compounds its a bigger volume.

⇒ Charge/size ratio is greatest for BeO

It imparts the 'positiveness' or 'cation richness' of the cation and hence its also slightly acidic ⇒ its amphoteric.

This is related to Fajan's Polarisability.

Acidity of non-metal oxides

(?) With increasing covalency of M – O bond, the acidity increases ⇒ increases conc. of protons.

⇒ Acidities and basicities are directly related to electronegativity

Non-metals oxides are acidic anhydrides.

Hydration vs. Hydrolysis.

* Large charge/size for cations increases hydration energy

Eg: $Na^+ + n.H_2O \longrightarrow [Na(H_2O)_n]^+ \rightarrow$ Hybration.

* If ratio is very high, like Al^{3+} – then they hydrate first & this hydration energy.

The –OH bond becomes very polarised and ruptures. While –OH remains binded to cationic metal, the H_3O^+ is released into the solution, creating an acidic solution.

$$Al^{3+} + nH_2O \longrightarrow [Al(H_2O)_n]^{3+} \longrightarrow [Al(H_2O)_{n-1}(OH)]^{2+} + H^+$$

Generally cations with large charge/size ratio are highly acidic.

Eg: Be^{2+}, Fe^{3+}, Sn^{4+}

Hydrolysis of non-metallic compounds

Eg: $PCl_3 + H_2O \longrightarrow H_3PO_3 + 3H_3O^+ + 3Cl^-$

Here, the –I (inductive) effect of $e^{\ominus}$ withdrawing Cl species makes the P centre highly charged.

* As, P is a small atom, the charge/size ratio is large and makes it prone to hydrolyses at the P–Cl bond.

Hydrolysis of PCl_5 –

$PCl_5 + H_2O \rightarrow POCl_3 + 2HCl$

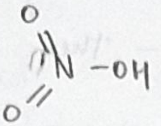
$POCl_3 + 3H_2O \longrightarrow H_3PO_4 + 3HCl$.

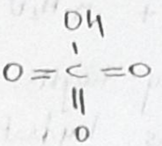
Acidity of oxy-acids

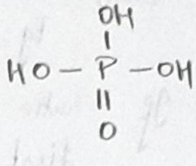
Strength of oxy-acids depends on the -I effect of the central atom and how it impacts on the 'hydroxyl' bond.

Comparing –

	HNO_3	$HClO_4$	H_3PO_4
	strong	strong	weak
χ	N : 3.04	Cl : 3.16	P : 2.19

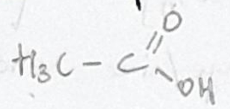




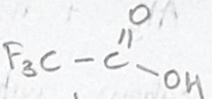


Since electronegativity (χ) of P is lesser than Cl & N, its a weaker acid than HNO_3 & $HClO_4$

* **Substituent effects**



weak



strong

Since, F is very electronegative when compared to H, its -I effect will make carbon very $e^\ominus$ deficient thus weakening the -O-H bond & making acid stronger

* Strength of oxy-acids

No. of O atoms bound to central chlorine atom increases the acidity (⇒ Resonance).

⇒ HOCl < HOClO < $HOClO_2$ < $HOClO_3$

$\xrightarrow{\hspace{6em}}$ increasing ā strength

Empirical formula for calculating pK_a –

$\boxed{pK_a = 10.5 - 5_n - \chi_x}$ for acids expressed as $\boxed{X(OH)_m O_n}$

χ_x : electronegativity of central atom.

This includes both central atom and effects of surrounding atoms.

Basicity of Substituted amines

NH_3 is a weak base in water.

★ If $-H$ is substituted with EWG like $-OH$ or $-NH_2$, it becomes less basic —

pK_b for NH_3 :- 4.74 , NH_2OH :- 7.97 , NH_2NH_2 :- 5.77

★ If its substituted with electron donating groups like $-CH_3$ or $-C_2H_5$, they are more basic —

NH_2CH_3 : $pK_b = 3.36$, $NH_2C_2H_5$: $pK_b = 3.25$

→ This happens because the s-character between N−R increases and this reduces the s-character of the lone pair. WHY ?

★★ When NH_3 is substituted with bulky alkane ($-R$) group, the s-character of lp orbital of nitrogen decreases and basicity ↓ decreases despite being attached to +I groups

Bond between an alkyl group is greater if s-character of bond is more i.e. $sp > sp^2 > sp^3$. For bulky group, to form a strong bond, the bond should have maximum overlap i.e it needs more s-orbital. So, s-char of bond increases and of the bond decreases.

The atom is highest charge/size ratio i.e. large charge, small size would be the strongest acid.

H^+ has the highest charge/size ratio.

But in never exists alone — it combines with the solvent or any base, if present. → it'll never coexist without reacting.

$$H^+ + H_2O \longrightarrow H_3O^+$$

So, e^- is the strongest base even in comparison to H^- and F^-. There are cases where electrons can exist alone and hence they're called the strongest base.

The solvents interfere while measuring the strength of acidity or basicity of species.

So, to measure it precisely, species are ionized to gases ~~and~~ ~~then~~ in Gas Phase Spectroscopy that'll allow us to measure the strength accurately.

Most fundamental measure of basicity (absolute value) is its proton affinity in the gas phase —

$$B_{(g)} \text{ or } B^-_{(g)} + H^+_{(g)} \longrightarrow BH^+_{(g)} \text{ or } BH_{(g)}$$

Born-Haber Cycle :

$$\begin{tikzcd}
B_{(g)} + H_{(g)} \arrow[r, "-\Delta H_{BH}"] & BH_{(g)} \arrow[d, "-e^{\ominus}"', "\Delta H_{IE_{BH}}"] \\
B_{(g)} + H^+_{(g)} \arrow[u, "-\Delta H_{IE_H}", "+e^{\ominus}"'] & BH^+_{(g)} \arrow[l, "\Delta H = -PA"']
\end{tikzcd}$$

→ Enthalpy of formation

→ Enthalpy of ionisation

The enthalpies are measured using an ion cyclotron resonance spectroscopy (icrs) which allows us to measure the proton affinity.

It's been experimentally measured that N_3^- (nitride) has the highest proton affinity.

$NH^{2-} > NH_2^- > NH_3$

$\longrightarrow$ Proton Affinity (PA) decreases.

$NF_3 : \Delta H = 604$ kJ mol^{-1} $NH_3 : \Delta H = 872$ kJ mol^{-1}

$N(CH_3)_3 : \Delta H = 974$ kJ mol^{-1}.

Proton affinity of a cation is defined as its ~~ad~~ ability to hold a proton i.e. its measured as the enthalpy of its conjugate base.

Eg: H_3O^+ : $H_2O + H^+ \longrightarrow H_3O^+$ i.e. PA of H_2O.

For HF : $PA_{F^-} = 1554$ kJ mol^{-1}

$HF \longrightarrow F^- + H^+$ $\Delta H = +1554$ kJ mol^{-1}

⇒ The more endothermic the reaction, the weaker the acid —

HF < HCl < HBr < HI

These gas phase measurements ~~agg~~ agree with the solvent measurements.

$PA_{CH_3COO^-} = +1459$ kJ mol^{-1} $PA_{F_3CCOO^-} = +1351$ kJ m^{-1}

If $e^\ominus$ affinity is going to be considered as the analogue of H^+ affinity, then $e^\ominus$ affinity should provide an inherent gas-phase measure of acidity for any non-protic gaseous species.

$K \rightarrow K^+ + e^\ominus$: Ionisation energy of K ↳ positive

The $e^\ominus$ affinity of potassium — (?)

$K^+ + e^\ominus \longrightarrow K$ EA $= \ominus 419$ kJ mol^{-1}

$Co^{3+} + e^\ominus \longrightarrow Co^{2+}$ EA $= +3232$ kJ mol^{-1}

This shows that transition element metal cations are more acidic that alkali / alkali earth metal cations.

Interaction of Lewis acids and bases

By Drago et. al – Ways of expressing enthalpies of reactions in terms of contributing parameters of acids and bases –

$$\boxed{-\Delta H = E_A E_B + C_A C_B}$$

ΔH : Enthalpy of Lewis A-B adduct formation

$E_A E_B$: Electrostatic contributions

$C_A C_B$: Covalent contributions.

An acid with greater electrostatic affinity (E_A) will combine with a base which has a large E_B and similarly acid with large C_A combines with a base with large C_B.

Eg: Reaction of pyridine and iodine.

For pyridine – $E_B = 1.78$, $C_B = 3.54$

For iodine – $E = 0.5$, $C = 2.0$.

$$-\Delta H_{calc} = E_A E_B + C_A C_B = 7.97 \text{ kcal mol}^{-1} = 33.3 \text{ kJ mol}^{-1}$$

$$-\Delta H_{exp} = 7.9 \text{ kcal mol}^{-1} = 32.6 \text{ kJ mol}^{-1}$$

Hence, knowing the E_i, C_i values, we can find out the possibility of adduct formation.

28/9

Discussion

For a dilute acid which has really less K_a (weak acid), the acidity of water comes into play

$$K_w = [H^+][OH^-] \qquad K_a = \frac{[A^-][H^+]}{[HA]}$$

$[HA]_0 = [HA] + [A^-]$ – Material balance

og conc

$[H^+] = [A^-] + [OH^-]$ – charge balance

$[A^-] = [H^+] - [OH^-] = [H^+] - \frac{K_w}{[H^+]}$

This comes from –

$$H_2O \rightleftharpoons H^+ + OH^-$$

$$HA \rightleftharpoons A^- + H^+$$

$$K_a = \frac{[H^+][A^-]}{[HA]} = \boxed{\frac{[H^+]^2 - K_w}{[HA]_0 - \frac{[H^+]^2 - K_w}{[H^+]}}}$$

If $[H^+]^2 \gg K_w$, then its a weak acid in sufficient conc. Uncertainity in $K_a < 1\%$. We don't need to include $[H^+]$ from water.

[H⁺] conc. determined for a weak acid in low conc should be at least 100 times greater than Kw.

$\Rightarrow 100 \times 1\times10^{-14} = 10^{-12} = K_a$ if $[HA] = 1$

$\Rightarrow [H^+] = \sqrt{10^{-12}} = 1\times10^{-6}$; Minimum concentration

28/9

Lecture 04

Bulky functional groups on central atom can affect the acidity / basicity of the molecule.

Because: 1) The alkyl groups attached ~~randomly~~ ~~can~~ rotate randomly occupying a huge volume of space and being sterically unstable.

These volumes overlap ~~unacceptability~~ unacceptably and strain the adduct : F-strain.

The bulkiness of substituents decreases acidity & basicity

$H_3N \rightarrow BF_3$ $(CH_3)_2NH$ $B(et)_3$

2) R_3N bonds well with BF_3 only when N-centre adopts a tetrahedral geometry i.e. sp³ hybridised

Every R group opens up the bond angle (due to steric hinderance) to values > 109°. This increases the Bulky groups s-character of N-R bonds

⇒ But this weakens the s-character of the lone pair orbital. Which means it has more p-character, which is orthogo ? to BF_3's orbital, making the overlap poorer.

This is called the B-strain.

Consider :	NH_3	$(CH_3)_2HN$	$(CH_3)_3N$	$(CH_3)H_2N$
pK_b	4.75	3.26	4.13 Anamoly	3.36
Proton affinity	872	954	974	919

↳ No anamoly in gas phase

- $(CH_3)_3N$ is a weaker base than $(CH_3)_2HN$. by H-bonding

$R_xN + H_2O \rightleftharpoons R_x\overset{+}{N}H + OH^-$

$R_x\overset{+}{N}H$ is highly charged & such charged molecules are very efficient in getting solvated in H_2O.

The efficiency of the stabilisation is — due to

$R_3\overset{+}{N}H < R_2\overset{+}{N}H_2 < R\overset{+}{N}H_3$: Solvation energy

- This trend is exactly opposite to the trend of inductive effect in each molecule.

The secondary amine is the strongest base because its solvation energy (overcomes the inductive effect.) ×⑤ is high as is its inductive effect.

- When 'H' in ammonia is replaced by $-CH_3$, the hydration energy is lowered by $30\ kJ\ mol^{-1}$

Solvent Levelling

Any species that can exhibit autoprotolysis can be seen as a solvent.

Eg: H_2O, NH_3, ~~HI~~, ~~HBr~~

- Consider HI and HBr. Both acids are strong in water because they undergo complete dissociation. H_2O dissociates both. Hence, its called a levelling solvent i.e it brings both their strength to H_3O^+ : levelling
- Choose a solvent that can make HI and HBr behave as weak acids — Eg: CH_3COOH.

  In this solvent, we can see that HI dissociates more than HBr.
- H_{sol} is a general solvent.

$$HCN_{(sol)} + H_{sol\,(l)} \rightleftharpoons H_2sol^+_{(sol)} + CN^-_{(sol)}$$

Here, $K_a = \dfrac{[H_2sol^+][CN^-]}{[HCN]}$

If $pK_a < 0$ ⇒ its an acid in Hsol.

- Solvent levelling of bases

  Any base that can get entirely protonated by water produces the same no. of OH^- ions.

  Consider $KNH_{2\,(s)}$ and $Li_4(CH_3)_{4\,(s)}$. They both produce equal no. of OH^- in water i.e. they get levelled by water.

Consider Hsol to be a general solvent
A base dissolved in Hsol is classified as strong if $pK_b < 0$ where $K_b = \frac{[NH_4^+][sol^-]}{[NH_3]}$

for: $NH_{3(sol)} + Hsol_{(l)} \rightleftharpoons NH^+_{4(sol)} + sol^-_{(sol)}$

Here, $pK_a + pK_b = pK_{sol}$

i.e if $pK_a > pK_{sol}$ in H_{sol} then we can call it a base

In general, $\overset{\text{i.e. } pK_b < 0}{\text{we}}$ can say that an acid is levelled in that solvent if its $pK_a < 0$.

For any general solvent, its respective pK_{sol} can be used as follows -

- All acids with $pK_a < 0$ will be levelled
- All bases with $pK_a > 0$ $\Rightarrow pK_b < 0$ will be levelled

All acids and bases within pK_a window of $pK_a = 0$ to pK_{sol} will not be levelled. ↳ Eg, H_2SO_4 (strong ā) to PH_3 (weak ā)

DMSO has a wide window ⇒ it can be used to discriminate a wide variety of acids and bases.

Water has a narrow window. Why is water still preferred?

11/10

Lecture 05

Why is water universal solvent for acid-base reactions?

Ans: Solvation effects, rationalized from an 'Electrostatic Model' where -

1. Solvent - continuous dielectric medium
2. Solvation of gas phase species is always exothermic
3. Magnitude of ΔH_{sol} depends on -
    - radius 'r' of the ion.
    - permittivity ε_r of solvent
    - potential to form H-bonds.

Entropy of gas phase is negligible ⇒ $\Delta G = \Delta H_{sol}$ in gas phase but its not negligible in solvent.

The electrostatic model gives us the ΔG involved in taking a gas phase ion of radius r and placing it in a solvent of permittivity ε_r.

In solvent,

$$\Delta G_{solv} = \frac{-N_A e^2 \xi}{8\pi \varepsilon_0}\left(1 - \frac{1}{\varepsilon_r}\right) \quad \text{where} \quad \xi = \frac{z^2}{r}$$

ε_0 : Permittivity in vacuum ε_r : Relative permittivity of solvent

$$\Rightarrow \boxed{\Delta G_{solv} \propto \xi} \quad \text{(electrostatic component)}$$

Small r highly charged ions get very well solvated

ΔG also depends of ε_r

Large value of ε_r gives large -ve value of ΔG

Hence, water with $\varepsilon_r = 80$ is a great solvent compared to organic solvents ($\varepsilon_r \sim 2$).

Born's method / equation

$$\begin{tikzcd} HA_{(g)} \arrow[r] & H^+_{(g)} + A^-_{(g)} \arrow[d, "-\Delta G_{sol}"] \\ & H^+_{sol} + A^-_{sol} \end{tikzcd}$$

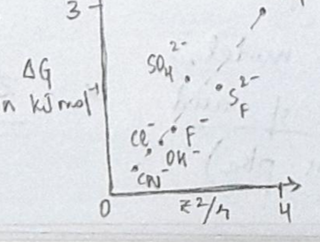
* ΔG indicates the free energy released when a gas phase ion is solvated.

The degree to which the conjugate acid of HA (ie. H_3O^+) is stabilised decides value of $-\Delta G_{sol}$

Charged species are well stabilized by polar-protic solvents like water because they can for H-bonds

Eg: $\overset{+}{NH_4}$ in water.

"Ones with high charge/mass ratio tend to be stable"



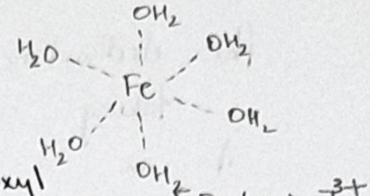
SOOOD CONFUSED. whaat?

Classifying acids

A donatable proton is called an 'Acidic proton'.

Three class of acid protons

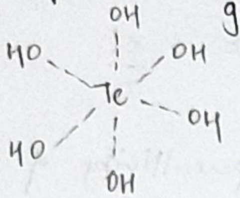
1. Aqua acid - acidic proton on a water molecule when its coordinated to a inorganic cation



Eg: $[Fe(H_2O)_6]^{3+}$

2. Hydroxo acid - acidic proton is on an hydroxyl group without any neighbouring 'oxo' group on the central atom.

They're less acidic than aqua acids.



$Te(OH)_6$

3. Oxoacid - Acidic group is on a hydroxyl group with an oxo group attached to same central atom.

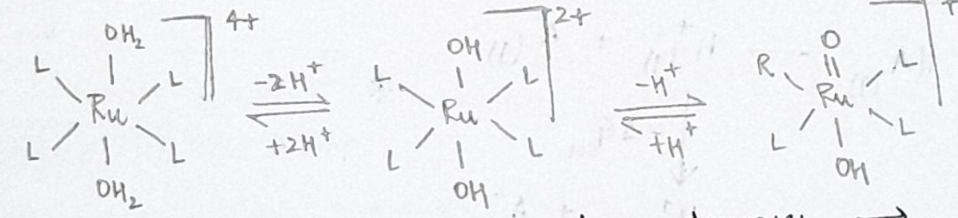
Due to high χ of oxo group, it increases acidity.

Eg: HNO_3, H_3PO_4.

These three classes of acid can be generated from a single species -

Aqua $\xrightarrow{-H^+}$ Hydroxy $\xrightarrow{-H^+}$ Oxo

Eg: D-Block metal in intermediate oxidation state : Ruthenium



Oxidation state of central atom decreases →

* Aqua acids - central atom in low oxd^n state

Eg: s & d-block metals & metals to left of Fe p-block

Oxo-acids - central atom in high oxd^n state

Eg: Elements to right of p-block - N, S, P, Se

In electrostatic model,

strength of acid (in pKa) $\propto$ Z^2/r^+

r^+, radius of cation

Z : +ve charge

But if deviations occurs, it points to covalency

Refer : Graph in L5 S6

- Cr^{3+}, Fe^{2+} (?) [Also, Na^+, Mg^{2+}] are closer to predicted acidities and fall closer to the linear line
  ⇒ They follow Born's electrostatic model
- Fe^{3+}, Tl^{3+} deviate a lot. This means they're more acidic — this is because it's bonds have greater covalent character.
  $M-O$

* $\underset{\text{covalent}}{\underset{\downarrow}{M}} - O - H$ ⇒ The positive charge of central atom is spread over the ligand oxygens, so they try to lose the hydrogen ⇒ more acidic.

Eg: Cu^{2+}, Sn^{4+}

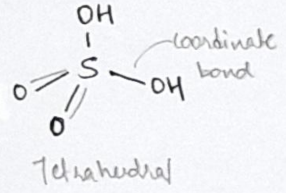
Hence, more the covalency, more the acidity

Comparing $Al(H_2O)_6]^{3+}$ & $Hg(H_2O)]^{2+}$ —

* $Al(H_2O)_6]^{3+}$ obeys ionic model because of high $\frac{\text{charge}}{\text{mass}}$ ratio.

But $Hg(H_2O)]^{2+}$ shows a great deviation because of $\boxed{\text{covalency}}$ of Hg−O bonds.

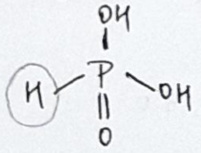
Oxo acid : Sulfuric acid



These oxo-groups are very electronegative, making the S very $\delta+$
⇒ Acidity is very high.

If we substitute the −OH by $-NH_2$, the acidity decreases & if substituted by −F, it becomes more acidic

Exception : H_3PO_3 - Phosphonic acid



: Only 2 acidic protons
The −H attached to P is not very acidic as P is not very electronegative

Features —

* Acids with the most 'oxo' groups are stronger
i.e $H_2SO_4 > H_2SO_3$, $HNO_3 > HNO_2$

* Resonance stabilization of conjugate base (more oxo group ⇒ more resonance strs ⇒ stronger ā)
H_2SO_4 - 3 resonance str. H_2SO_3 - 2 resonance str.

* Pauling's emperical rule for oxoacids —

- For $O_pE(OH)_q$, $\boxed{pK_a = 8 - 5p}$
- Successive pKa of polyprotic oxoacids increases 5-fold

i.e. $pKa_1 = x$ $pKa_2 = 5x$

Predictions of rule 1.

	pKa
$Ti(OH)_4$	~8
H_2CO_3	~3
HNO_3	~ -2

Rules are only approximate.

Refer : Table in L5 S11

Observations —

* ~~Variation~~ Acid strength down the 'group' (same p value) doesn't vary much because structure of acids changes to accommodate & pKa remains somewhat same.

* Across the 'period', pKa varies significantly (from L→R)
The effect of change in oxdⁿ state of central atom is taken care of by no. of oxo atoms attached

Eg: $O\overset{+5}{P}(OH)_3$ vs $O_2\overset{+6}{S}(OH)_2$ vs $O_3\overset{+7}{Cl}(OH)$

Some anatholies explained —

- Eg: $H_2CO_3 \equiv OC(OH)_2$ $pK_{a\,\underset{erimental}{(exp)}} \simeq 6.4$

But Pauling's rule predicts $pK_a \simeq 3$

This is due to poor ~~dissociation~~ dissolution.
Only 1% of CO_2 dissolves and stays as H_2CO_3. If this is considered, the value would have been ≃ 3.6.

- $H_2SO_3 \equiv OS(OH)_2$ $pK_{a\,\underset{erimental}{(exp)}} = 1.8$ $\underset{predicted}{pK_a} \simeq 3.0$

When H_2SO_3 is in water, other species such as HSO_3^-, SH^-, $S_2O_5^{2-}$ which all make the solution more acidic.

- Other anamolies : CO, OsO_4

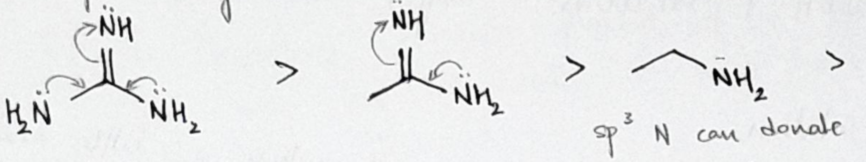
19/10

Tutorial

Quiz 2 solutions

3) $H_3\overset{\oplus}{N}CH_2COO^-$ is NOT a conjugate base of H_2NCH_2COOH as the H^+ is not lost, rather its picked up by the same molecule in its zwitter ion form.

6) Order of basicity

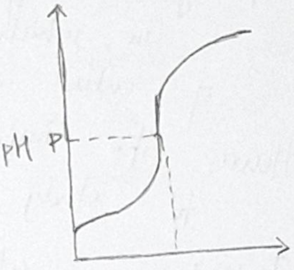


sp^3 N can donate e^- better than sp^2 N

9/10

Lecture 06

Titration Curve



Volume of base added (to a solution of acid)

- To find the strength of an acid, we slowly add and stir a ~~known~~ base of known strength and measure the pH.
- The pH rises slowly and increases rapidly at equivalence point, and then becomes a gradual rise again
- At equivalence point, $[H_3O^+] = [OH^-]$

  For a pair of strong acid & strong base, equivalence point = 7.

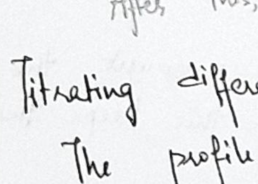
  After this, color of indicator changes.

Titrating different pairs of acids and bases i.e. weak vs strong. The profile of curve will remain the same, but the E.P changes. For –

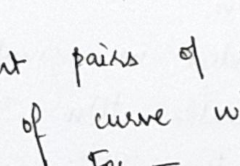
- Weak acid – strong base : EP > 7
- Strong acid – weak base : EP < 7

X-axis: vol. of acid added

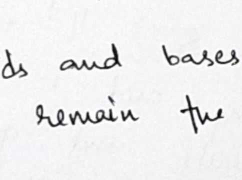
I



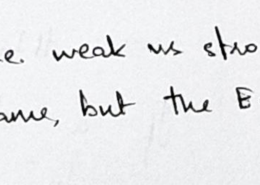
II



III



IV



Compare figure I and III — (CH_3COOH & HCl with $NaOH$)
Curves are similar till they reach E.P (till $NaOH$ is present in considerable amount). After crossing EP, conc of CH_3COOH / HCl increases, changing the curves to be different.

With weak acid - strong base curve, we have -
CH_3COOH + CH_3COONa : Buffer solution

Buffer solution
It keeps the pH unchanged when a little amount of acid or base is added.
Combination of weak acid and its salt with a strong base
A given buffer solution has a certain pH range & capacity in which it can resist change, after which pH of entire solution changes.
Hence, its important in biological systems & its important to study reactions at a fixed pH.
Indicators — colored buffer ~~then~~ how can it tell the pH accurately?

Indicators
They're buffers which can resist pH change in window ~ pH
Consider : Protonated : HIn   Deprotonated : In^-

$$\Rightarrow HIn_{(aq)} \rightleftharpoons H^+ + In^-$$

If a strong acid is added in small amount, the In^- reacts and generates HIn & this keeps the overall pH of solution the same.
Different operators operate in different pH windows.

Example —
Take HF and NaF to make a buffer solution.
We know HF is a weak acid

$$\Rightarrow HF \rightleftharpoons H^+ + F^- \quad K_a = 6.6 \times 10^{-14}$$

Now we add NaF to this till we get the desired pH and volume of buffer (important if it needs to resist a lot of acid)

NaF is a strong electrolyte,

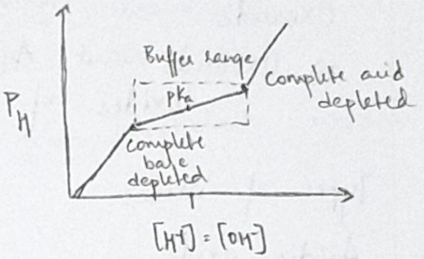
$$NaF \longrightarrow Na^+_{(aq)} + F^-_{(aq)} \longrightarrow \text{strong conj. base}$$

Since Na^+ is a cation from a strong base (NaOH), it won't react, so it won't change pH.

But F^- is a strong base and it abstracts protons.

By Le Chatalier's principle, presence of F^- will make HF even less dissociative ⇒ we'll have a good amt. of both HF and F^-

Buffering action can be ~~change~~ seen in titration curve where pH changes at a slower rate in the window than outside



This works because F^- is very good at abstracting protons - $K_a = 1.5 \times 10^3$

$$F^- + H_3O^+ \longrightarrow HF + H_2O$$

⇒ It'll resist pH change when acid is added and will work until all F^- is gone.

Henderson - Hasselbach Equation.

It helps determine pK_a of an acid or base -

$$\boxed{pH = pK_a + \log_{10} \frac{[\text{conj. base}]}{[\text{weak acid}]}}$$

It is derived from dissociation constant

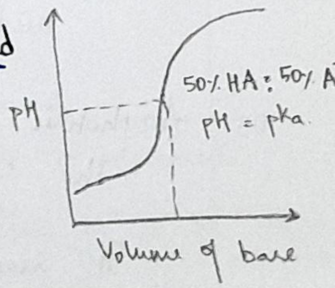
$$H_2O + HA \rightleftharpoons H_3O^+ + A^-$$

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

Taking log on both sides

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

This point can be experimentally determined in a titration curve



- This eqⁿ doesn't work well at high dilutions as water autoprotolysis kicks in & it doesn't agree with expt values. ㉔
  ⇒ When conc. reaches 10^{-5} mol L^{-1}, it fails
- It works well when
  - $[A^-] : [HA]$ is between 0.1 to 1
  - Molarity of buffer is 100x greater than Ka.

2/11/20

Lecture 07 - Just from slides.

Anhydrous oxides

Oxoacids are derived from deprotonation of aqua acids.

⇒ Oxoacids and Aquaacids are derived from hydration of oxides of central atom.

Types of oxides

01. Acidic oxide

Upon dissolution in water, it binds to H_2O & releases proton into solvent. Reacts with aqueous base to form acid. ?

Eg: Non-metallic elements form acidic oxides.

$$CO_2 + H_2O \longrightarrow OC(OH)_2$$

$$OC(OH)_2 + H_2O \longrightarrow H_3O^+ + O_2COH^-$$

02. Basic oxide

When it dissolves in water, it abstracts a proton

Eg: Metallic oxides

$$BaO + H_2O \longrightarrow Ba^{2+} + 2OH^-$$

Basic oxide reacts with acid & neutralizes it

$$BaO + H_2SO_4 \longrightarrow BaSO_4 + H_2O$$

Mostly, basic oxides are ionic in nature, form solid ionic halides.

acidic oxides are covalent & form volatile covalent halides

03. Amphoteric oxide

The central atom lie between acidic & basic oxide forming central atoms.

It reacts with both acids and bases.

Eg: Amphoterism is observed in small size elements of Group 2 and 13

⇒ Al_2O_3 , BeO , Ga_2O_3 Also – Zr, Zn, Ge, Sn, Pb, As, Sb

Amphoterism arises due to increase in covalent nature of the central atom – oxygen bond

This is because metal ion is • small • strongly polarising – Eg. Be
(OR) • gets strongly polarised by O – Eg. Sb

In transition metals, amphoterism is dependent on oxidation state

- from Titanium to Iron – { Amphoteric at O.S : +4
  Acidic at O.S > +4
  Basic at O.S < +4 }
- Elements to the right of the block form amphoteric oxides at lower O.S
  Eg. Cu and Zn. – +2.
- Cobalt & Nickel form amphoteric oxides at +3 O.S.

Higher oxidation state ⇒ polarize the oxygen bond ⇒ acidic
make it covalent

Acidity and basicity based on central atom.

	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	Cl_2O_7
Bonding	← Ionic →		Highly Polar covalent	← Polar covalent →			
pH	← Basic →		Amphoteric	Weakly acidic	← Acidic →		
Conduct?	← In molten & aq. →		← weak conduct. →		← No Conduction →		

Polyoxo anions.

→ Acids containing –OH groups condense (eliminate H_2O) to form polyoxo anions.

- $(O_3CrOCrO_3)^{2-}_{(aq)}$ form polymers when pH is decreased
- Aqua ions – $Fe(H_2O)_6^{3+}$ form polymers when pH is increased
- Groups 1 & 2 don't form anything beyond discrete M^+ & M^{2+} aqua species.

- Amphoteric oxides, Al_2O_3, Fe_3O_4, form routine hexa-aqua complex in acidic solution.

  When pH > 4, they precipitate as gelatinous hydroxides, which are colloidal in size (1nm - 1μm).

  Al - 3D polymeric structure

  Fe - linear polymeric structure

→ Polyoxoanions can be formed from oxoanions by protonating them at low pH & they eliminate water, forming a polymeric structure.

Eg: $$CrO_{4\,(aq)}^{2-} + 2H_3O^+ \longrightarrow (O_3CrOCrO_3)^{2-}_{(aq)} + 3H_2O$$

- D-Block elements in high oxidation states form polyoxoanions in a basic medium

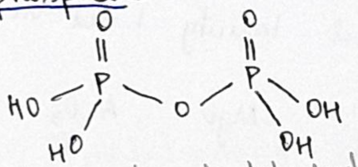
  Eg: Mo (VI), W (VI), Nb (V), Ta (V), Cr (VI).

- Non-metals form polyoxoanions & they have cage or chain-like structures.

  Eg: $MgSiO_3$, $Zn_3(PO_4)_3$

→ Simplest polyoxoanion: Pyrophosphate

$2Na_{3?}PO_4 + 6H^+ \longrightarrow$



$+ H_2O$

Corner shared tetrahedron - $P_2O_7^{4-}$

- Elimination of water consumes a proton and decreases formal charge of both P to -2.

- Lowering the amount of water in the medium, H_3PO_4 can be made to condense into metaphosphate ($P_4O_{12}^{4-}$)

- When P_2O_5 is treated with acidic or basic water, many polymeric polyoxoanionic species form (with 2-50 P atoms) and they can be seperated by chromatography.

Polyphosphates made of <u>P – O – P bonds</u> are very crucial in biological systems i.e. ADP – ATP.

At physiological pH, 7.4, these bonds are prone to hydrolysis and when hydrolysed, it provides Gibbs Energy for driving a reaction.

Same way, P–O–P bond can be formed to store energy

Energy flow in biological system is controlled by hydrolysis of ATP to ADP –

$$ATP^{4-} + 2H_2O \longrightarrow ADP^{3-} + HPO_4^{2-} + H_3O^+ \quad \Delta G = -41\ kJ/mol$$

at pH = 7.4.

2/4

Lecture 08

Lewis Acids and Bases

Encompasses a wide range. Bronsted acids & bases are special cases.

H^+ is always a Lewis acid.

<u>Adduct</u> : Formed by sharing of electrons supplied by base

$$A + :B \rightarrow A-B$$

In context of <u>reaction rates,</u> they're referred to as nucleophile and electrophile.

Possibilities of LA - LB adduct –

1. Molecule with incomplete octet

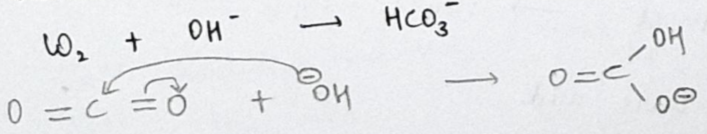
$$\underset{\text{Planar}}{B(CH_3)_3} + NH_3 \longrightarrow \underset{\text{Pyramydal}}{(CH_3)_3B-NH_3}$$

2. Metal cation accepts e^- pair to form coordinate bond

$$Co^{2+} + 6H_2O \longrightarrow [Co(OH_2)_6]^{2+}$$

3. Molecule with complete octet maybe able to re-arrange its valence electron to accept $e^{\ominus}$ pair.

Eg: $CO_2 + OH^- \longrightarrow HCO_3^-$



4. Molecule maybe able to <u>expand its valence shell</u> to accept $e^{\ominus}$

$$SiF_4 + 2F^- \longrightarrow SiF_6^{2-}$$

Common in <u>heavier p-block elements</u> – SiX_4, AsX_3, PX_5

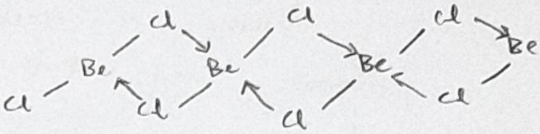
Periodic trends.

- Alkali & Alkali earth metals exist as hydrates in water, showing their Lewis acidity.

However, their halide can act as Lewis bases

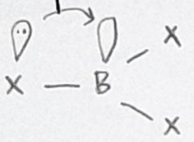
$CsF + SiF_4 \longrightarrow Cs^+(SiF_5)^-$

- $BeCl_2$ forms a polymeric chain



- Group 13 elements form Lewis acids

Acidity trend : $BF_3 < BBr_3 < BI_3$: Doesn't follow the e-withdrawing power.



• Planar structure with vacant p-orbital lying perpendicular to plane

strong 2p-2p interaction back bonding

When X = F, the back-bonding is strong

But for X = I, the overlap of p orbitals is less ⇒ back-bonding is weak.

• BX_3 accepts e^- pair from LB & adduct formation make the BX_3 pyramidal.

• BF_3 is an industrial catalyst for generating carbocation. Used by dissolving gas in diethyl ether.

- Group 14 element - expandable valence shell

• Si, Ge, Sn can expand its valence shell - becomes hypervalent.

$SiF_4 + 2F^- \longrightarrow SiF_6^{2-}$ trigonal bipyramidal / octahedral

(in aq. medium)

⇒ HF is dangerous for glass because its made of silicates.

• Acidity trend : $SiI_4 < SiBr_4 < SiCl_4 < SiF_3$

correlates with e^- withdrawing power

• $SnCl_2$ is an amphoteric compound.

$\underset{LA}{SnCl_2} + \underset{LB}{Cl^-} \longrightarrow :SnCl_3^-$ → Acts as base.

$SnCl_4$ is a Lewis acid

Trend : $SnF_4 > SnCl_4 > SnBr_4 > SnI_4$

Also correlates to electronegativity and $e^\ominus$ withdrawing power

Group 15

- Heavier elements of G15 forms super acids -

$$SbF_5 + 2HF \longrightarrow SbF_6^- + \underline{H_2F^+}$$

- P halides form strong adducts with organic reagents

PF_5 + amine/ether $\longrightarrow$ F_5P – amine/ether   N-donor/O-donor

Group 16

- SO_2 is amphoteric : $[(H_3N)\cdot(SO_2)]$ LA , $[(BH_3)\cdot(SO_2)]$ LB

$SO_2 + SbF_5 \longrightarrow OSO - SbF_5$ Can donate by both O and S

$SO_2 + Ru(II) \longrightarrow O_2S - Ru(II)$

- Sulfur trioxide is a strong LA & weak LB. This feature is exploited in industrial preperation of H_2SO_4.

Dissolving SO_3 in H_2O is very exothermic ⇒ very dangerous.

When mixed with H_2SO_4, SO_3 acts as Lewis base and forms $H_2S_2O_7$ (oleum). When watered down with water, it forms $2H_2SO_4$ & this process isn't very exothermic.

Hard and Soft acid - base

Empirical concept : In both acids and bases, two classes (hard and soft) ~~based~~ are observed with opposite order of strength as measured by their equilibrium constant,

K_f : formation of complex.

Hard acids bond in order : $\boxed{I^- < Br^- < Cl^- < F^-}$

Soft acids bond in the opposite order.

Eg: Hg^{2+} : soft - rate increases from F^- to I^- borderline soft base ?

Pb^{2+} : less soft ∵ less steep increase

Zn^{2+} : borderline hard acid - curve decreases slowly from F^- to I^-

Al^{3+} : Hard acid.

Hard acid cations form ionic bonds, while soft cations form more covalent bonding.

To detect covalent vs ionic bonding, check for colligative properties

In general,

Hard acids bind in order : $\boxed{R_3P \ll R_3N \ , \ R_2S \ll R_2O}$

Soft acids bind in the opposite order

Soft base : CO and CN^-

They're good σ donors (i.e. l·p donor through HOMO) and π acceptors through LUMO [π acids]

⇒ There's high covalency in their bond ⇒ Soft species.

HARD ACID

- Small ionic radius
- Low electronegativity
- High +ve charge
- High energy LUMO

HARD BASE

- Small ionic radius
- High electronegativity
- Weak polarizability
- High energy HOMO

SOFT ACID

- Larger ionic radius
- Intermediat electronegativity
- Low +ve charge
- Low energy LUMO

SOFT BASE

- ~~Sm~~ Larger ionic radius
- Intermediate electronegativity
- High polarizability
- Low energy HOMO.

* Something about hard acids react better with hard bases, & soft acids react with soft bases (Hg - poisonous ∵ S and P in proteins)

(31) A

CH 2113 - Part II

9/11

Lecture 01

Molecular Structure and Bonding

Interpretation of structures & reactions based on qualitative (Lewis & VSEPR - pure pictorial representation) and semi-quantitative (CFT, VB and MO Theory) models.

considers energy of system

True molecular structure is arrived at by an interplay between qualitative & semi-quantitative models.

Inorganic chemistry - correlates electronic structure with chemical properties.

Covalent bonding - sharing a pair of electrons - introduced by GN Lewis

Lewis Dot Structure

Lewis Theory : Covalent bond is formed by sharing a pair of electrons by A-B, A=B, A≡B

~~Unpaired~~ Lone pair electrons influence the shape & chemical properties.

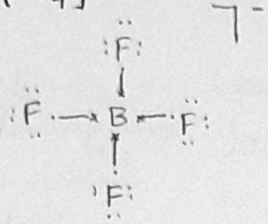
Octet rule : "Each atom shares electrons with neighboring atoms to acheive a total of 8 valence electrons"

This is used to construct Lewis structures.

Steps :
1. Decide no. of electrons in molecule by adding the valence e's of each atom, adding 1 for a negative charge & subtracting 1 for a positive charge
2. Write chemical symbol of atoms in arrangement, showing them to be bonded together.
3. Arrange by informed guess : Heavier or less electronegative atom is the central atom
4. Distribute electron pairs so that there's one pair of e^- between each pair of bonded atoms (represented by a single line) and other e^- pairs form lone pairs or multiple bonds.
5. Net charge of polyatomic ion is assumed to be possessed by the ion as a whole, and not individual atoms.

Examples -

$[BF_4]^-$



F - 7 valence e^- - 1 bonding
6 lp e^-

B - 3 valence e^-

N_2

$:N \equiv N:$

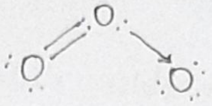
N - 5 valence e^-
2 lp e's

CO

$:C \equiv O:$

2 covalent bond,
1 dative bond
⇒ Neutral molecule.

O_3



Dative bond ⇒ neutral

Drawback: Lewis structures are just pictorial representations / diagrams it doesn't correspond to the actual structure.

To improve this, we need other concepts -

⇒ Resonance

Eg: O_3 : $\ddot{O}=\ddot{O}-\ddot{O}: \leftrightarrow :\ddot{O}-\ddot{O}=\ddot{O} \equiv O \text{---} O \text{---} O$

Both the O-O bonds are equal in length

Resonance averages the bond characteristics & the energy of the hybrid structure is lower than the canonical forms.

⇒ Formal charge

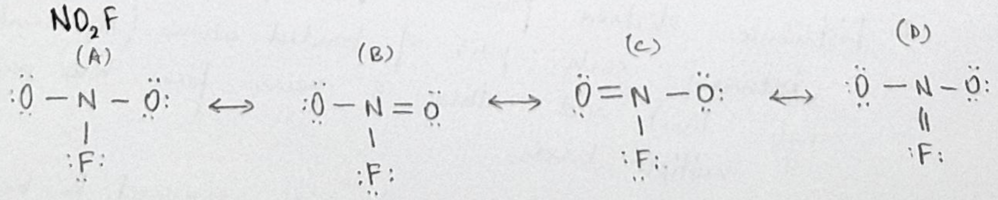
Its the charge of an atom if the electron pairs were shared equally.

This helps to identify the lewis structure that contributes the most to resonance i.e. lowest energy.

Assuming perfectly covalent bonding,

$$\boxed{FC = \text{Valence electrons} - \left(\text{Lone pair } e^-\text{s} + \frac{1}{2} \text{ Shared } e^-\text{s}\right)}$$

Eg: NO_2F



	(A)	(B)	(C)	(D)
N	+2	+1	+1	+1
O	2(-1)	-1, 0	0, -1	2(-1)
F	0	0	0	+1

B Lowest energy structure is the one with -

1. Lowest formal charge on the atoms
2. more electronegative element has a -ve formal charge and less electronegative element has a +ve formal charge.

Structure A is ruled out (∵ reason ①) and D is out ∵ reason ②.

∴ Structures C and D contribute more.

⇒ Oxidation number.

Its a parameter derived by exagerating the ionic character of a bond. Here, more electronegative element of a bond acquires two negative charge and given oxdⁿ no. -2.

less electronegative element acquires positive charge equivalent to its valency.

Eg: $[NO_3]^-$ is treated as $[N^{5+}][O^{2-}]_3$

Lecture 02

VSEPR Model

Its an extension of Lewis' ideas and its very successful in predicting the shapes of polyatomic molecules.

Basic shapes

Primary assumption : Enhanced region of e^- density (lone pairs and bonding pairs) take up positions so that they experience minimized repulsion.

4 :	Tetrahedron	CH_4, SO_4^{2-}, H_2O, NH_3
5 :	Trigonal bipyramidal	PCl_5, PF_5, SOF_4
6 :	Octahedral	SF_6, PCl_6^-, XeF_4
7 :	Pentagonal bipyramidal	IF_7
3 :	Trigonal planar	BF_3, SO_3, CO_3^{2-}, O_3 (angular), NO_2^-
2 :	Linear	HCN, CO_2, $BeCl_2$

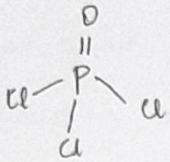
Modified shapes - Angular, pyramidal, square planar etc

Constructing VSEPR model -

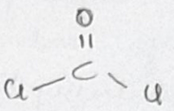
1. Count valence e^- on central atom & peripheral atoms that participate in bonding
2. Identify e^- pairs and the basic shape
3. Assign sigma bond, multiple bond and lone pairs
4. Multiple bonds are treated as another region of e^- density along the given σ bond

Example :

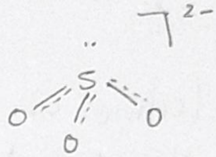
★ $POCl_3$ – 5 e^- pairs, 1 double bond ⇒ Basic shape: Tetrahedral



★ $COCl_2$ 3e^- pairs Trigonal planar



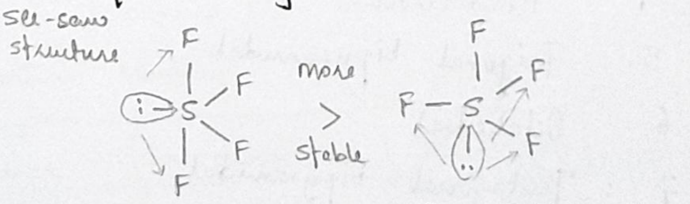
★ SO_3^{2-} S – 6e^- + O – 3 (2e^-) + 2e^-
⇒ 14e^- i.e 7e^- pair – 3e^- pair
= 4 e^- pair : Tetrahedral (Basic shape)
Pyramidal (Modified shape)



Modifications -

- Repulsion order : lp-lp > lp-bp > bp-bp
- Greater repelling power of lp is explained by supposing that they're closer to the nucleus than bp and hence it repels other lp more strongly
- So lp require larger site eg. equatorial site in TBP. If all sites are equal, they're trans to each other

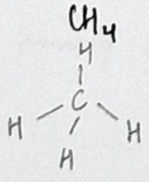
Eg: SF_4
S – 6e^- F – 4(1e^-)
⇒ 5$e^\ominus$ pair ⇒ TBP



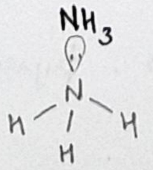
Two 90° interactn Three 90° interaction

▸ Tetrahedral

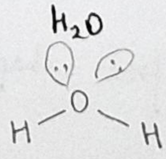
CH_4 109.5° Tetrahedral



NH_3 107° Pyramidal

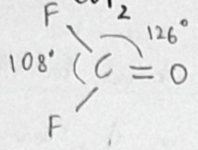


H_2O 104.5° Angular



▲ Trigonal planar

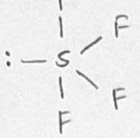
COF$_2$

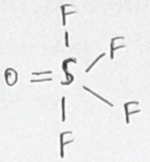


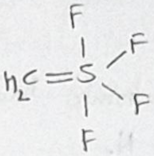
Predicted angle : 120°

C=O distance is shorter ⇒ it requires more volume (higher angle).

▸ Trigonal bipyramidal







Axial F-S-F	179°	178.5°	170°
Eq. F-S-F	103°	110°	97°

N :

- Double bonds occupy more space
- Bent's rule : Electropositive substituents occupy ~~less~~ MORE space than electronegative elements
- Complexes of As (III), Sb (III) and Bi (III) [$d^{10}s^2p^3$] with polydentate ligands have been found to have stereochemically active lone pairs.

12/11

Lecture 03

Valence Bond Theory

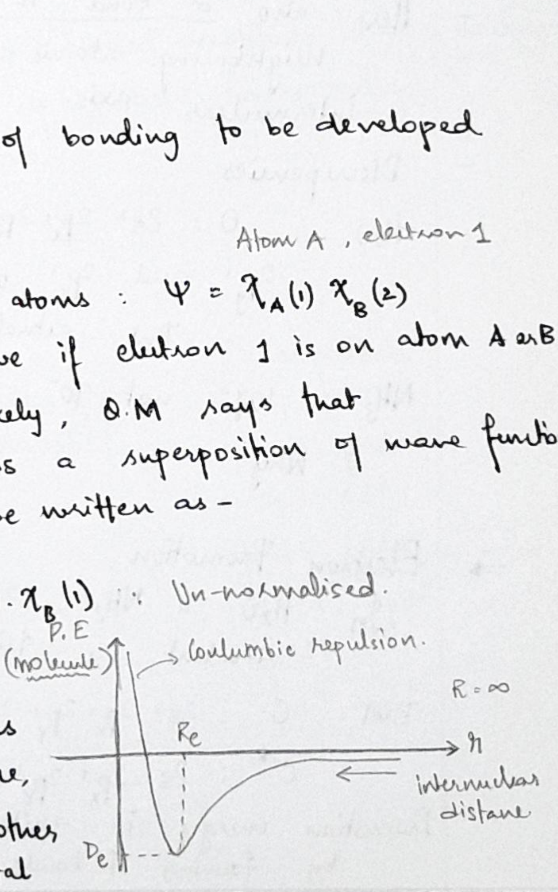
First quantum mechanical theory of bonding to be developed

⇒ The Hydrogen Molecule

Atom A, electron 1

- Wave fn for two widely separated H atoms : $\Psi = \chi_A(1)\,\chi_B(2)$
  When atoms are close together, we if electron 1 is on atom A or B.
- When two outcomes are equally likely, Q.M says that true state of the system is a superposition of wave function for each probability & can be written as -

$$\Psi = \chi_A(1)\,\chi_B(2) + \chi_A(2)\cdot\chi_B(1) \quad \because \text{Un-normalised.}$$

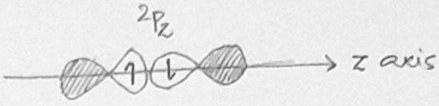


- E = 0 : Free atom
  PE suddenly falls when two H-atoms are brought within bonding distance, & each electron is free to migrate into other atom's orbital

i.e bond starts forming

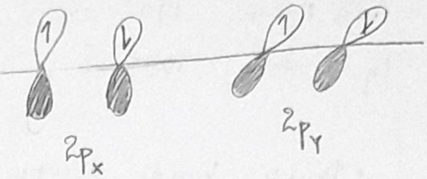
- De : Energy minima is found at Re : molecular radius
  Deeper the minimum, stronger the bond
- Pauli's principle : only e⁻s with paired spins can be described by ψ & can contribute to σ bond in VB Theory
  σ bond has cylindrical symmetry – electrons in it have 0 orbital angular momentum around the internuclear axis.

⇒ Homonuclear Diatomic Molecule



Eg: Nitrogen – N_2

- Consider V.Es : $2s^2$, $2p_x^1$ $2p_y^1$ $2p_z^1$
- Consider z-axis as internuclear axis.
  σ-bond is formed by spin-pairing between 2 e⁻s in opposing p_z orbital



- Electrons in $2p_x$ and $2p_y$ approach side-by-side (laterally) to give π bond
  ✱ They can't form σ bond ∵ they're not cylindrically symmetric about internuclear axis.

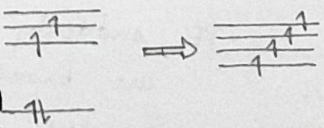
Polyatomic molecules
- Here also, σ bond is formed by spin pairing of e⁻s in neighboring atomic orbitals with cylindrical symmetry about internuclear axis.
- Discrepencies
  H_2O : O : $2s^2$ $2p_x^2$ $2p_y^1$ $2p_z^1$
  $2p_y^1$ and $2p_z^1$ orbitals form O–H bond ⇒ Bond angle should be 90°
  But, actual angle : 104.5°
  NH_3 : 107° not 90°
  Why?

⇒ Electron Promotion

In H_2O & NH_3, $2s^2$ doesn't participate in bonding. So they're divalent & trivalent respectively.

BUT C : $2s^2$ $2p_x^1$ $2p_y^1$ $2p_z^0$ is in tetravalent state due to promotion

C^* : $2s^1$ $2p_x^1$ $2p_y^1$ $2p_z^1$



Promotion energy is quite small & C gains energy by forming 4 bonds & relaxing e⁻–e⁻ repulsion in 2s orbital

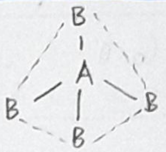
Hybridisation

Consider a molecule of type AB_4

- Expected : 3 σ-bond of one type ($\chi_B + \chi_A 2p$) & one σ-bond of another type ($\chi_B + \chi_A 2s$).

But all bond characteristics point to <u>4 equivalent bonds</u>.

- This is because –
  Electron density distribution in promoted atom is equivalent to electron density in which each electron occupies a <u>hybrid orbital</u> formed by interference of A_{2s} & A_{2p} orbitals
- Leads to 4 new shapes due to <u>constructive & destructive interference</u>



- $h_1 = s + p_x + p_y + p_z$ $h_2 = s - p_x - p_y + p_z$

  $h_3 = s - p_x + p_y - p_z$ $h_3 = s + p_x - p_y - p_z$
- Each of the 4 equivalent hybrid orbitals consists of a large lobe pointing towards corner of tetrahedron & a smaller lobe at the origin of tetrahedron.
- Angle between orbitals : $\boxed{\mathrm{Cos}-\left(\frac{1}{3}\right) = 109.47^\circ} \rightarrow sp^3$ hybridisation.
- Important aspects of hybridisation –
  ★ Pronounced directional character ★ ⟹ enhanced amplitude in inter-nuclear region
- This gives higher <u>bond strength</u> to sp^3 hybrids (<u>more overlap</u>) than s & p orbitals alone

Composition – Geometry table

Coordination No.	Shape/Arrangement	Composition
2	Linear, Angular ← extra lp.	sp, pd, sd
3	Trigonal planar, Pyramidal	sp^2, p^2d
4	Tetrahedral	sp^3, sd^3
	Square planar	p^2d^2, sp^2d → more common
5	Trigonal bipyramidal, Sq. py	sp^3d, spd^3
6	Octahedral	sp^3d^2
	Trigonal prismatic	spd^4, pd^6

Lecture 04 12/11

Composition of Hybrid Orbitals

- Most hybridization result in equivalent hybrid orbital i.e. all are identical shape in terms of % s & % p character and spatial orientation
  Eg: tetrahedral and octahedral
- Non-equivalent : TBP - dsp^3 $\langle$ → 3 strong equatorial bond (sp^2 trigonal) → 2 axial weaker bonds (dp linear)

Relationship b/w hybridization and bond angle is simple for s-p hybrids –

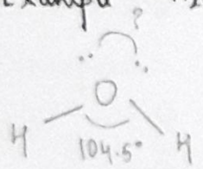
$$\boxed{\cos\theta = \frac{s}{s-1} = \frac{p-1}{p}}$$

θ : Angle b/w orbitals
% s & % p characters are expressed in decimal fraction.

Eg: For CH_4, $\cos\theta = \frac{0.25}{0.25-1} = -\frac{1}{3} \Rightarrow \theta = 109.47$

⇒ Non-equivalent hybrids

- They exhibit fractional s & p character i.e. bonding orbitals are midway b/w pure p & sp^3.
- For such molecules in sp^3 hybridisation, the 4 orbitals can be divided into bonding & non-bonding subset.
- Example H_2O



We can't compute the angle b/w lp.
WKT, angle b/w bonding subsets, θ = 104.5°

$\Rightarrow \cos\theta = -0.25 = \frac{0.20}{0.20-1} = \frac{0.2}{-0.8}$

$\Rightarrow s = 0.2$, $p = 0.8$ – bonding

For non-bonding subset

Ratio of total p-character to total s-character, summed over all 4 orbitals is 3 : 1

$\Rightarrow$ Total p : $3 = 0.8 + 0.8 + x + x \Rightarrow x = 0.7$
Total s : $1 = 0.2 + 0.2 + y + y \Rightarrow y = 0.3$
} Non-bonding subset.

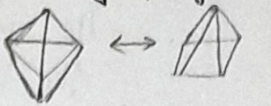
⇒ θ' : angle between l.p. can be computed by –

$\cos\theta' = \frac{s}{s-1} = \frac{0.3}{-0.7} \Rightarrow \theta' = 115.37°$

For NH_3 : Bonding subset $\cos(107°) = -0.29 = \frac{s}{s-1} \Rightarrow s = 0.22$, $p = 0.78$ | Non-bonding subset $s = 0.34$, $p = 0.66$

REVISE

▸ For AB_5 (unlike CN 2, 4, 3, 6), there's no unique, highly symmetrical set of equivalent orbitals.



Possibilities of TBP and SP are interlinked.

Calculation of s & p character is more difficult if d orbitals participate in hybridisation.

→ Hypervalence

Many molecules defy octet rule – they have more than 8 electrons. This is hypervalence/hypercoordination.

* Period 2 obeys octet rule.

Example : PCl_5, SF_6

Traditional explanation: Octet expansion is explained by availability of low-lying 3d orbitals

Just the absence of 2d shell is not the only reason for absence of hypervalence of in Period 2 – it might also be due to geometrical difficulty of packing 4+ atoms around a small central atom.

Why don't we observe PF_5 and PI_5?

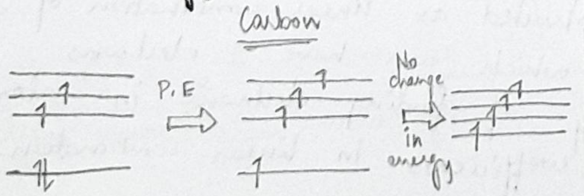
PF_5 – Due to electronegativity of F, Cl (3) the electrons are withdrawn towards halogen, away from orbitals of P.
So even if octet is satisfied in PCl_3, P is e⁻ deprived.
So PCl_5 is the 'perfect octet' for P

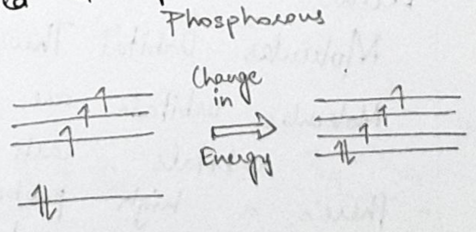
PI_5 – I is too bulky.

→ Bent's Rule : Energy of Hybridisation

- ↳ When a set of hybrid orbitals are constructed from a set of atomic orbitals, energy of resultant hybrid is the weighted average of energies of atomic orbitals.
- The Promotion Energy in carbon is independent of hybridisation

In phosphorus, there's no promotion, rather hybridisation costs energy as 3s orbital is raised & 3p lowered in energy.



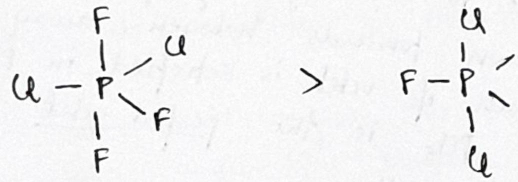


- This energy of hybridisation is of order of bond energy
  ∴ - Its important in determining the structure
  - Also responsible for tendency of some l.p to occupy spherical and non-stereochemically inactive s-orbital rather than stereochemically active hybrid sp orbital.
- Energy factors determine the most stable arrangement of atoms
- It costs 600 kJ mol^{-1} to hybridize a central P-atom.
  Other congeners (As, Sb, Bi) will have higher energies
- Higher P.E & better overlap : Hybrid has more s-character

* Lower P.E & weaker overlap : Hybrid has more p-character

- Consider : sp^3d^2 – Considered a combination of $P_z d_z$ ② ? & sP_xP_y
  Weaker ← Two linear hybrid orbitals → axial ↵
  Stronger ← More directionality ← 3 trigonal equatorial bonds ←
- Eg: When χ of substituents on P-atom differs, its experimentally observed that, more χ element occupies the axial positions (∵ they have more p-character ∴ they're not hybridised) and less electronegative one occupies equatorial bond

⇒



∴ Bent's Rule: More electronegative elements prefer hybrid orbitals having less s-character & vice versa

- Eg: Bond angle of CH_2F_2 — Refer Shriver Atkins
  Can be explaind through VSEPR & Bent's rules.

18/11/20

Lecture 05

Molecular Orbital Theory

- Molecular orbitals are constructed as linear combination of atomic orbitals, each of which can have 2 electrons
- There's a high probability of finding electrons in atomic orbitals that have large coefficients in linear combination.

Approximations of the Theory -

Orbital Approximation:

- Wavefunction of a molecule can be written as product of one-electron wave functions -

$$\psi = \psi(1).\psi(2) \cdots \psi(N)$$

They are molecular orbitals of theory

- $|\psi(i)|^2$ gives the probability distribution for that electron in the molecule
- Electrons are found where amplitude is large & they're never found at nodes.

Linear Combination of Atomic Orbitals (LCAO)

- When electron is close to the nucleus of one atom, its wavefunction resembles its atomic orbital
- LCAO Approximation: Reasonable first approximation of M.O can be constructed by superimposing Atomic orbitals of each atom i.e its a sum with various weighted coefficients

Fundamentals

- In elementary form of theory, valence shell of A.O (χ) are used to construct MO -

$$\psi = C_A \chi_A + C_B \chi_B \quad : \text{For } H_2$$

- C_A, C_B : Coefficients which show the extent to which atomic orbitals contribute

C_A^2, C_B^2 : Probability that e^- is in χ_A, χ_B respectively

- Probability distribution -

$$\psi^2 = C_A^2 \chi_A^2 + \underbrace{2C_A C_B \chi_A \chi_B}_{\text{Contribution to Prob density due to interference of } \chi_A, \chi_B} + C_B^2 \chi_B^2$$

- For H_2 - ▸ electrons are equally likely to be found near each nucleus
  - ▸ Linear combination with least energy will have equal contribution from each 1s orbital.

$$\Rightarrow C_A^2 = C_B^2 \quad \Rightarrow C_A = \pm C_B$$ ✱

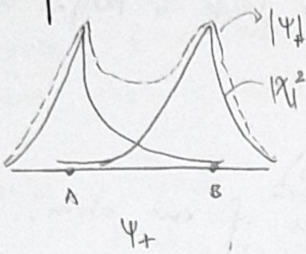
After normalisation, we'd get - $\psi_+ = \chi_A + \chi_B \qquad \psi_- = \chi_A - \chi_B$

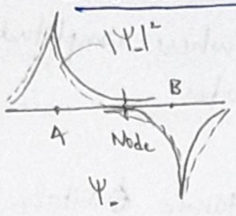
The relative sign of coefficients of LCAOs play an important role in determining energies of orbitals

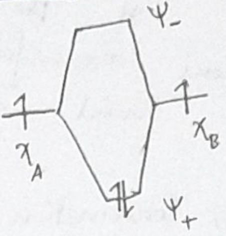
Also, n atomic orbitals combine to give n molecular orbitals.

Bonding

Bonding MO arises from constructive interference of wave funtions of neighboring atoms & conversely ABMOs are formed through destructive interference, as indicated by a node.







* Experimental energy gap between two MOs is measured by absorption spectrum in H_2

11.4 eV (~109 nm) - transition of e^- from BMO to ABMO

* Dissociation energy of H_2 is 4.5 eV (434 kJ mol^{-1}). This is an indication of location of BMO relative to seperated atoms.

*BMO is stabilising while ABMO is destabilizing.

Homonuclear diatomic molecule: N_2

N: $2s^2\ 2p^3$

The atomic orbitals can combine in several ways

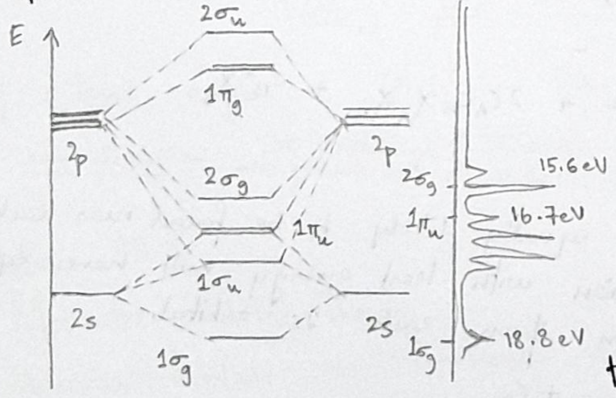
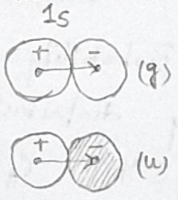
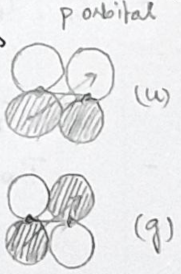


Photo ejection by UV-Visible photoelectron spectroscopy





g: gerade - even

u: ungerade - odd

This is based on symmetry of the signs of the lobes when compared to the opposite one (across the midpoint of internuclear axis)

(43) 6 - To find the energy levels of MOs, we excite the electron to its excited state by shining UV-Visible radiation.
↓ Max E ~ 21 eV

* ~~F~~ X-Ray for inner shells or other molecules.

- From the energy diagram, we can see that there are 3 levels that can be probed — first ionisation occurs from $2\sigma_g$ at 15.6 eV and so on.
- The second level ($1\pi_u$) has multiple vibrational levels.

Other homonuclear diatomic molecules

* As we go across the period, the energy of BMO goes on decreasing.

REVISE

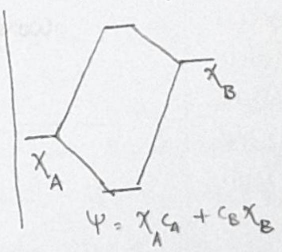
* There's an anamoly in energy level of MO in O_2 and F_2 — $2\sigma_g < 1\pi_u$ unlike other molecules.
This is because energy of 2p and 2s varies significantly in Oxygen & Fluorine

* 8 MOs are formed from A.O. In that —
- 4 σ-orbitals span a range of energy : one strongly bonding, another strongly anti-bonding
- 4 π-orbitals form 2 doubly-degenerate pairs of BMO & ABMO.

25/4

Lecture 06 [Live lecture - 19 Nov]

Heteronuclear Diatomic Molecules (~ 30 mins)



* It differs from homonuclear molecule due to unequal contribution from each atomic orbitals

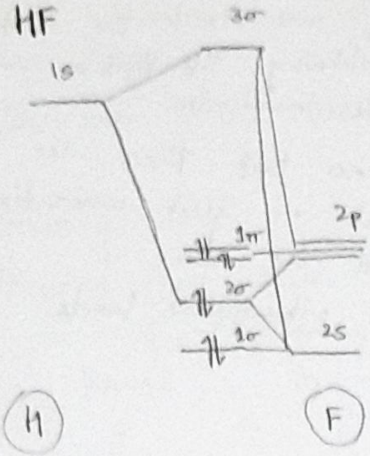
$$\psi = c_A \chi_A + c_B \chi_B + \cdots$$

* There is also energy mismatch of corresponding atomic orbitals
More electronegative → Lower energy → More contribution to BMO

* Due to this energy separation of A.O.s, it implies less pronounced overlaps. But not always, since bond strength also depends on orbital size and closeness of approach.
Eg: CO (1070 kJ mol⁻¹) > N_2 (946 kJ mol⁻¹)

\# There's no center of inversion
⇒ g, u notations are not used

1. HF

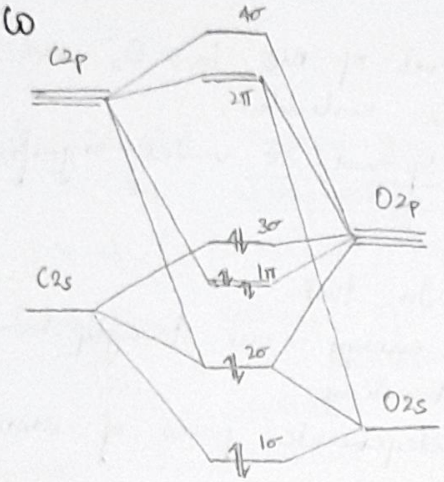


- 3 σ orbitals are constructed from H 1s, F 2s, F $2p_z$
- F $2p_x$ and $2p_y$ have π symmetry and are non-bonding orbitals (1π)
- Total 8 V.Es : 2 e's occupy 2σ : BMO
  6e's occupy 1σ, 1π : NBMO
- All electrons occupy orbitals that are mostly on F-atom.

⇒ HF is polar with δ-ve charge on F

HF is a strong Bronsted ā ?!

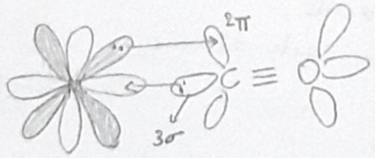
2. CO



- The orbital size of C is less than that of O – they can approach closer and form a good overlap.
- 1σ/2σ : localised on Oxygen / ~~carbon atom~~
  ⇒ non-bonding
  2σ – bonding MO. – many AOs are contributing to it
  ↳ from O2p
- 1π → bonding → mainly O2p
- 3σ → more contribution from C2p
  lp on carbon is the 3σ orbital of CO
  3σ : HOMO of CO. So, it binds to metals through C atom, not O.

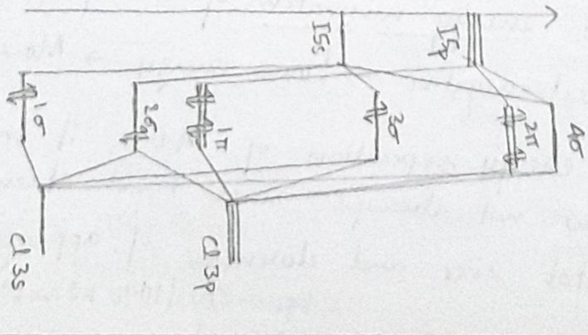
- 2π → mainly from C2p → LUMO
- Presence of both HOMO and LUMO on C-atom facilitate its coordination to metal ions through σ-donation & π-back-donation

Shrives
Atkins
UV-PE
graph



$:C\equiv O$
δ- δ+

3. ICl



Do it yourself ?!

Lecture 07 [Live lecture - 23 Nov] 14/12/20

Polyatomic Molecules

The MOs are similar to that of diatomic molecules, just that orbitals are built from a more extensive basis set

We can write the MO of a given symmetry as a sum of overlapping AOs –

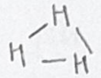
$$\psi = \sum c_i \chi_i$$

Then – fundamental assumptions.

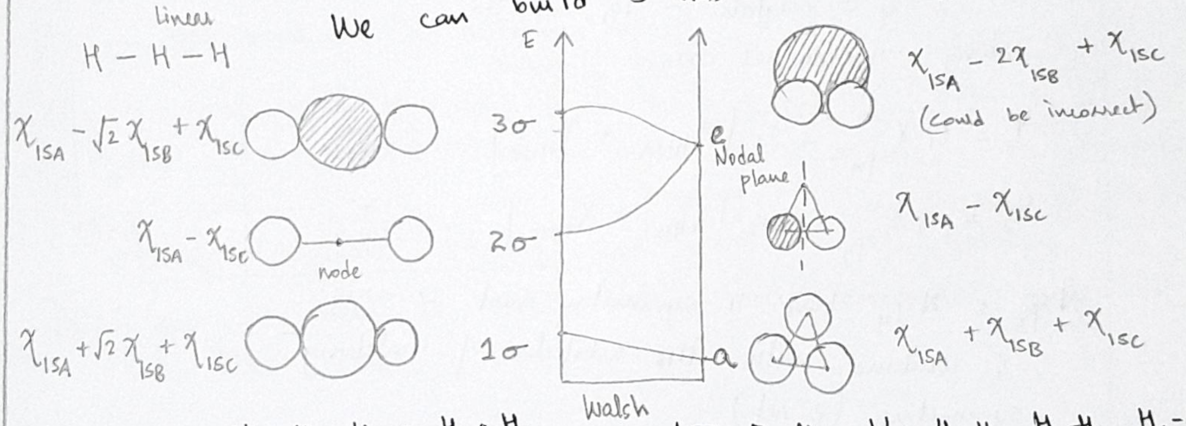
1. Greater the no. of nodes in a MO, greater the anti-bonding character and higher the symmetry (?) & energy.
2. MOs constructed from lower energy AOs are lower in energy
3. Interactions b/w non-nearest neighbor atoms are weakly bonding or ~~non~~ anti-bonding based on the signs of their lobes

Hypothetical H_3

$H_A = \chi_{1SA}$ $H_B = \chi_{1SB}$ $H_C = \chi_{1SC}$ cyclic



We can build 3 MOs –



1σ: Bonding b/w H_A & H_B & H_B & H_C

2σ: Bonding b/w H_A & H_C (negligible)

3σ: Anti-bonding b/w H_A-H_B & H_B-H_C (∵ signs of lobes)

1σ: Bonding b/w H_A-H_B, H_B-H_C, H_A-H_C

$(1\sigma)_{cyclic} \underset{stronger}{>} (1\sigma)_{linear}$

Degenerate → 2σ and 3σ have same energy

2σ: Antibonding b/w H_A-H_C ⇒ ↑E

3σ: Antibonding b/w H_A-H_B, H_B-H_C but bonding b/w H_A-H_C ⇒ ↓E

Becomes anti-bonding instead of non-bonding

Walsh / Correlation diagram: shows the variation in energy as the bond angle changes.

In the cyclic molecule, the lower energy orbital is "a-symmetry" and the other two orbitals are called "e-symmetry".

It's not always appropriate to use σ and π in polyatomic systems, but they're convenient ⇒ remnant of VBT.

Note that –

- a, b : non-degenerate orbital (point group symmetries)
- e : doubly degenerate orbitals
- t : triply degenerate orbitals

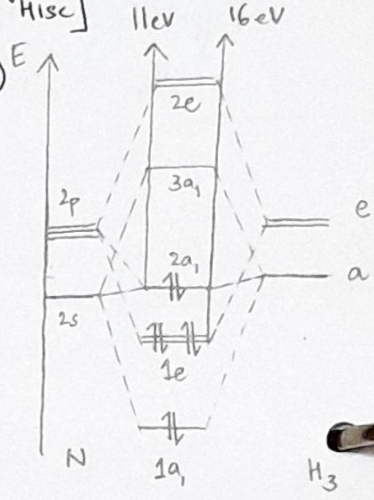
Subscripts and superscripts are added (a_1, b'', e_g, t_2) to distinguish different orbitals according to more detailed analysis of their symmetries

\# A, B, E, T – capital letters used to describe electronic terms Useful in absorption spectroscopy

Ammonia : NH_3

$$\psi_1 = c_1 \chi_{N2s} + c_2 \chi_{N2p_z} + c_3 \left[\chi_{H1sA} + \chi_{H1sB} + \chi_{H1sC} \right]$$

- N2s, $N2p_z$ and 3 H1s combine to give (a orbital) 3 ~~a~~ σ orbitals – $1a_1$, $2a_1$, $3a_1$ along internuclear axis



- $$\psi_2 = c_1 \chi_{2p_x} + c_2 \left[\chi_{H1sA} + \chi_{H1sB} \right]$$ – 2 MOs

$$\psi_3 = c_1 \chi_{2p_y} + c_2 \left[\chi_{H1sB} + \chi_{H1sC} \right]$$ – 2 MOs

$N2p_x$ & $N2p_y$ have π-symmetry wrt z-axis & combine with H1s orbitals of matching symmetry. (e set)

3 Hydrogen atoms in the plane give rise to 3 ligand group orbitals* – a & e sets.

Actual location of orbitals can be found by detailed computation or photoelectron spectrum –

- 11 eV – $2a_1$ orbital – sharper signal
- 16 eV – 1e orbital – broader signal

\# $1a_1$ orbital is out of range for 21 eV photo electron spectrum
Maybe X-ray

* Also called "Symmetry adapted linear combination"

- ★ HOMO - $2a_1$ - non-bonding orbital ∵ it's mostly confined to N-atom & doesn't contribute to bonding.

  ⇒ consistent with fact that lp play role in determining shape.

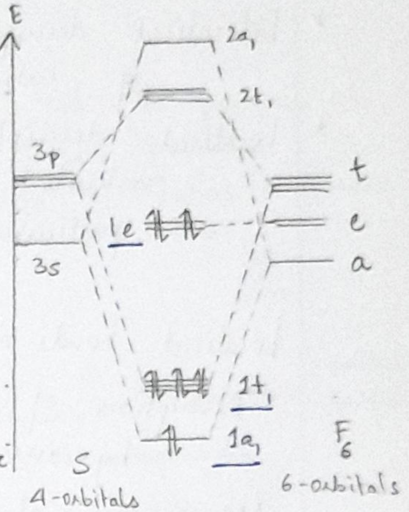
- ★ 11eV Vibration structure is due to distortions to the shape of the molecule upon removal of electron from lp

- ★ Broad nature of 16 eV signal is ∵ there are many vibration levels in 1e

Hypervalence : SF_6

VBT explains by invoking d-orbitals

In octahedral geometry, 6 F^- ions give rise to 6 ligand group orbitals — t, e, a



Very stable ∵ all e^-s are in BMOs

S_{3s} + a → $1a_1$ (bonding) + $2a_1$ (antibonding)

S_{3p} + t → $1t_1$ (bonding) + $2t_1$ (antibonding)

e → non-bonding ∵ no matching set of orbitals on S

↳ We don't need to split them in P_x, P_y, P_z because they all fall along the axis and combine nicely with the bonding triply degenerate orbitals

This can be used to explain other octet-expanded molecules like PCl_5

Exam ↑

Localisation

→ In VBT, both O-H bonds are treated as localised i.e equivalent structures where O & H share a pair of e^-

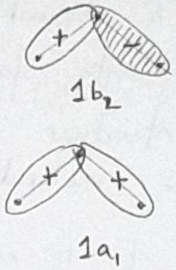
→ MOs are delocalised i.e. electrons occupy them and bind them all together. No concept of A-B bond existing independently of other bonds in the molecule.

→ But, linear combinations of MOs can be formed in the same overall electron distribution, but individual orbitals can be different

MO description is mathematically equivalent to a localized description of overall electron distribution.

Consider MO description of H_2O

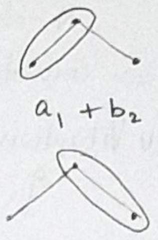
- Occupied MOs in delocalised description are – $1a_1$ & $1b_2$
- Linear combination of these orbitals creates localised descriptions between O and H atoms
- In each case, we form a fully delocalised orbital between a pair of atoms.



$1b_2$

$1a_1$

Delocalised



$a_1 + b_2$

$a_1 - b_2$

Localised description

* Delocalised description is suggested for describing global properties of entire molecule (Magnetism, Electronic spectra, Walsh descript^n^)

* Localised description used for properties of a fragment of entire molecule, to focus on distribution of e⊖ in and around a particular bond (Bond length, strength, VSEPR description).

Localised bonds and hybridisation

Description of localised MO bonds can be further expressed by invoking concepts of hybridization.

MOs can also be constructed from hybrid orbitals i.e O–H bond can be overlap of H1s and hybrid orbital composed of O2s and O2p.

15

Lecture – Live (26th Nov)

Main Group Chemistry

Challenge is to treat adequately the chemistry of all these various elements.

Periodic table is used to systemize elemental relationships

Across a period : Increasing At. No. : ↑ ionization E, e⊖ affinity & electronegativity
↓ size

Change in effective nuclear charge is also reasonably smooth but varies in diff. periods

Another anamoly – pronounced differences in similar elements

Maybe ∵ lighter elements use only 1s, 2s & 2p

Group 13 – B, Al, Ga, In, Tl

- B : only nonmetal

  Al: Most abundant element ⇒ Diversity of chemical properties
- Increasing metallic character, B → Tl

  1.81 1.68, 1.78
- Electronegativity : alternation is observed i.e. Ga > Al, Tl

  ∵ Ga has 4p & 3d electrons which sheild it
- Properties of Boron are different from rest of group. Shows diagonal relationship with Si –
  - forms acidic oxide
  - B & Si form polymeric oxide structures & glasses ⇒ easily formed borosilicate glasses
  - Both form flammable, gaseous hydrides
- Most G13 elements adopt +3 oxd^n state, but Tl prefers +1

  ∵ Inert pair effect – down the group, there's increased suppression b/w s and p orbitals, where s orbital is more stabilised

Topics of Interest –

- Cages & Clusters : Boron hydrides, Zintl compounds, Phosphorous (oxides sulfide)
- Rings, macrocycles & polymers : B-N, P-N & S-N compounds
- Chains & frameworks : Si compounds, silicates & zeolites
- Low-valent compounds & organometallic chemistry.

Boron Hydrides

Alfred Stock (1912) – Father of Boron hydrides

Prepared as series of boron hydrides, including B_2H_6 using first sophisticated vacuum manifold.

They're one of the oldest known cage structures

They weren't seperable till then due their flammability and air & moisture sensitivity.

B_2H_6 - gas BP = -92.5°C

B_4H_{10} – B_6H_{10} : liquids BP: 16°C – 108°C

$B_{10}H_{14}$ - solid mp = 99.7°c

(?) Apparatus : Schlenk tubes?

→ Diborane

1950s, USA & USSR explored borane chemistry to develop them as rocket fuel

But they're difficult to handle & catch on fire with green flame (too conspicuous)

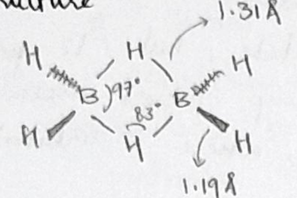
Now their application is found in other feilds – boron-neutron capture therapy.

Synthesis –

* $NaBH_4 \xrightarrow{I_2 \text{ or } H_3PO_4 \text{ or } BF_3} B_2H_6$ catalising agent – oxidising agent

* $BF_3 \xrightarrow{NaH \text{ or } LiH \text{ or } LiAlH_4} B_2H_6$

Structure



2 × B = 6
6 × H = 6
⇒ 12 electrons

The molecule is electron deficient

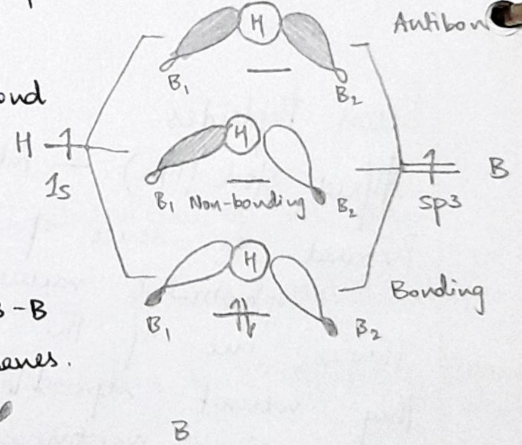
\# BH_3 can be stabilised in gaseous form

- 4 B-H terminal bonds – 8 electrons

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

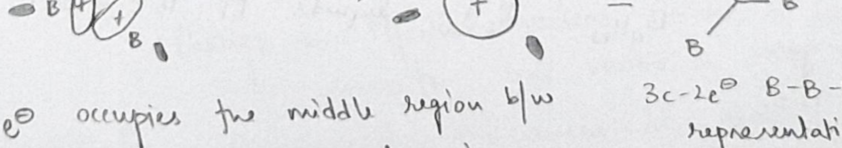
- Earlier hypothesis: $[B_2H_4]^{2-}$ is isoelectronic to C_2H_4 & 2 H^+ ions are located above and below plane of B–B

- The 3-centre-2-electron model was developed in 1970s with MO theory –
  - Each B-H-B bridge involves delocalised $3c-2e^\ominus$ bonds
  - H 1s and B sp^3 (2) combine to form 3 MOs
  - Each B-H-B accepts 2 e^- in its bonding MO & form $3c-2e^\ominus$ bond to rationalise the dimer.



\# $(MeLi)_4$ – $4c-2e^\ominus$ bond

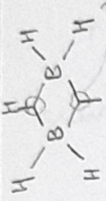
- $2c-2e^\ominus$ B–B and $3c-2e^\ominus$ B–B–B are important for higher boranes.



$3c-2e^\ominus$ B–B–B representation

\# The $e^\ominus$ occupies the middle region b/w 3 B atoms – no C atom in the representation

Accurate :



$e^\ominus$ are located here

\# BF_3 has backbonding – no need to dimerise

(51) → # Polyhedral Boranes

P₁

Higher boranes can be prepared from B_2H_6 by controlled pyrolysis or chemical reaction in presence of hard and soft bases.

\# If there's a small contamination, B_2H_6 can catch fire
Even if B_2H_6 is stored for looong time, it dimerises to form B_4H_{10}

$$B_2H_6 \xrightarrow{100-120^\circ c} B_4H_{10}$$

$$B_2H_6 \xrightarrow{180^\circ-200^\circ c} B_5H_9$$

$$B_2H_6 \xrightarrow[100-200^\circ c]{Me_2O} B_{10}H_{14}$$

The biggest, single unit borane : $\boxed{B_{12}H_{12}^{2-}}$ (no bridging H)
Above, B_{12}, the boranes start forming conjuncto-clusters i.e joined or fused borane clusters.

Wade's Rule – Ken Wade (1971)

Diborane in presence of soft bases (Me_2N, Et_2O) gets cleaved symmetrically to produce 2 BH_3 – Base

$$B_2H_6 \xrightarrow{Et_2N} 2.\ \text{Base}-BH_3$$

$$B_2H_6 \xrightarrow[\text{Hard base}]{NH_3} BH_4^-\ [BH_2(NH_3)_2]^+ \quad \text{Asymmetrical cleavage}$$

$$\#\quad B_2H_6 \xrightarrow{Et_2O} BH_3 \cdot Et_2O \xrightarrow{NH_3} BH_3 \cdot NH_3$$

$$B_4H_{10} \xrightarrow[\text{cleavage}]{\text{Base mediated}} B_3H_8 + \cdots$$

$$B_2H_6 + 2\,Et_3N \longrightarrow 2.\ Et_3N.BH_3 \xrightarrow{B_4H_{10},\ 190^\circ c} [Et_3NH]_2^+\ [B_{12}H_{12}]^{2-}$$

Structures of borane clusters are based on deltahedra (polyhedra in which all faces are triangular). Clusters are classified –

$[B_nH_n]^{2-}$ or B_nH_{n+2}	Closo – complete	n+1	$B_6H_6^{2-}$, $B_{12}H_{12}^{6-}$
B_nH_{n+4}	(1) Nido – basket	n+2	B_2H_6, B_5H_9, $B_{10}H_{14}$
B_nH_{n+6}	(2) Arachno – spider web	n+3	B_4H_{10}, B_5H_{11}
B_nH_{n+8}	(3) Hypho – net ↳ very rare	$\underbrace{n+4}_{\text{No. of } e^\ominus \text{ skeletal pairs}}$	$B_5H_{12}^-$ hypothetical

1 missing vertex

REVISE

Each BH unit furnishes 2 skeletal bonding $e^\ominus$

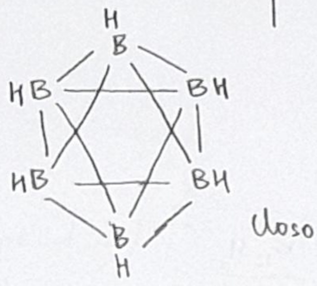
* additional H· furnishes 1 skeletal bonding $e^\ominus$

ionic charge must be included in $e^\ominus$ count

This allows us to calculate no. of skeletal electron pairs from molecular formula ⇒ we can predict the structure

Example —

1) $B_6H_6^{2-}$



Closo

$6B \times 3 = 18$

$6H \times 1 = 6$

$24 + 2\, e^\ominus$

$\Rightarrow 26\, e^-$

$- 12\, e^-$ (BH)

$7\, e^\ominus$ pairs ⇒ closo structure

$B_{12}H_{12}^{2-}$ is another closed cluster — icosahedron

2) B_2H_6

$2B \times 3 = 6$

$6H \times 1 = 6$

$12\, e^-$

$-(2\times2)\, e^-$

$\Rightarrow 4\, e^-$ pairs $= n+2$

∴ Nido structure

3) $B_{10}H_{14}$

$10B \times 3 = 30$

$14H \times 1 = 14$

$44\, e^-$

$-20\, e^-$

$\Rightarrow 12\, e^\ominus$ pair $= n+2$

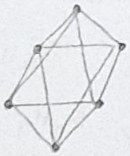
Nido structure

Note: According to MO, the extra electrons in B_nH_{n+x} boranes occupy the ABMOs, so the bridging bonds are broken ⇒ structure is more and more open.

Polyhedral Relationships.

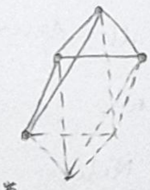
Boron frameworks based on 6-vertex, 14 skeletal $e^\ominus$ octahedral clusters.

Similarly,
12 Closo — 11 Nido — 10 Arachno



$B_6H_6^{2-}$

* $B_5H_5^{4-}$ or B_5H_9



* $B_4H_4^{6-}$ or B_4H_{10}

$\text{Closo} \xrightarrow{\text{1 vertex less}} \text{Nido} \xrightarrow{\text{1 vertex less}} \text{Arachno}$

$n = 6$ SE $= 7$ $n = 5$ SE $= 7$ $n = 4$ SE $= 7$

SE: no. of skeleton $e^\ominus$ pairs

* Hypothetical molecules — H^+ added to make it equivalent

Lecture - Live 2nd Dec 16/12

Recall : Using Wade's rules to reconstruct structures.

Eg : ★ B_4H_{10} - n + 3 skeletal $e^{\ominus}$ pairs.

$4B \times 3 = 12$

$10H \times 1 = 10$

22

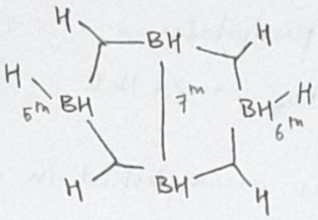
-8

$7 e^-$ pairs

4 $e^{\ominus}$ pairs : B-H-B

5th & 6th e pair : -H

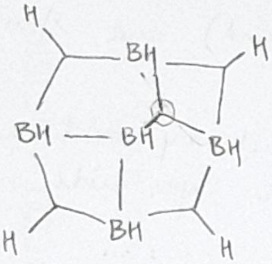
7 $e^{\ominus}$ pair : B - B



Butterfly shaped

4 B-H → 4 $e^{\ominus}$ pairs
6 H → 3 $e^{\ominus}$ pairs } gives
= 7 $e^{\ominus}$ pairs.

★ B_5H_{10}



Nido structure (n+2) = 7 $e^{\ominus}$ pairs

BH - 5 $e^{\ominus}$ pairs
4 H - 2 $e^{\ominus}$ pairs } gives
= 7 $e^{\ominus}$ pairs

B-H-B - 4 $e^{\ominus}$ pairs
2 B-B - 2 $e^{\ominus}$ pairs
B-B-B - 1 $e^{\ominus}$ pair.

4 borons in basal plane

The apical boron should be connected to all borons in basal plane. To make this happen, a 3c 2$e^{\ominus}$ B-B-B bond is formed

⇒ Zintl Compounds

They are alloy-like compounds made of electropositive cationic element and an anionic element of moderate electropositivity

Resembles ionic solids but different wrt -

- Metallic property, especially metallic luster
- Brittle, not malleable or ductile
- Semiconductivity or moderate metallic conductors
- Obeys $\boxed{\text{8-N rule}}$: -

Valence $e^{\ominus}$ concentration

M_mX_x # of electrons

x > m

VEC(x) < 8 - Polyanionic

VEC(x) = 8 - simple ionic

VEC(x) > 8 - Polycationic 10% of the time

m > x

$VEC(x) = m.e(M) + x.e(x) / X$

Some Zintl clusters obey Wade's rule

Due to ionic nature, they are driven by cationic or anionic nature of main group elements in zintl phase

* Discovery - Joannis in 1891 - studying rxn of Na in ammonia with a variety of metals

Red^n react^n

He observed blue sol^n of Na, which colored NH_3 sol^n to green (presence of dissolved e⊖ in NH_3) with excess lead giving new solids

More attention was given to solid precipitates -

$$(4+2x)Na + x\,PbI_2 \longrightarrow Na_4Pb_x + 2x\,NaI$$

* Isolation of solid derivative has been accomplished in last 40 years

Intact cage-like anions can be extracted by offering a complexing ligand to cations. Na^+ in Na_2Sn_5 are captured by cryptand (chelating, complexing ligand) and structure of Sn_5^{2-} was discovered

Polycationic zintl structures can be formed by oxidising reactions through reagents like bronsted & super acids

Wade's Rules

They can be applied to ligand-free cluster compounds.

These clusters are small chunks of metal clusters - to get the structure, they need to be stripped off by by giving extra electrons.

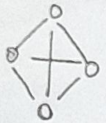
Postulate: One lone electron pair pointing outwards on each of the n-atoms, then, g - 2n electrons remain for polyhedron skeleton (g: total no. of valence electrons).

Type	n	g	g-2n		Example
Closo	5, 6	22, 26	12, 14	= 2n+2	Sn_5^{2-}, Bi_5^{3+}
Nido	9	40	22	= 2n+4	Sn_9^{4-}, Bi_9^{5+}
Arachno	8	38	22	= 2n+6	Bi_8^{2+}

Calculation also works if some of atoms bear ligands, instead of lone pairs.

REVISE

Cages and Clusters of Phosphou



White phosphorus and its reactions

White P

Reduction process

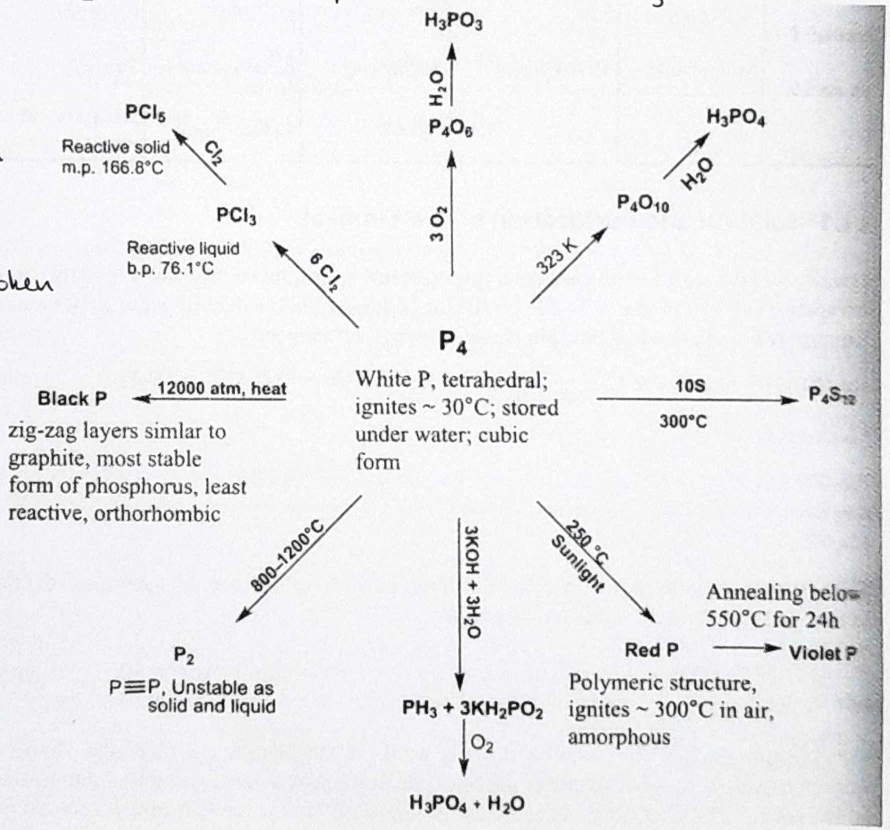
$$4Ca_3(PO_4)_2F + 18SiO_2 + 30C \xrightarrow{1200\text{-}1500^\circ C} P_4 + 10CO + 6CaSiO_3$$

Apetite

$$2Ca_3(PO_4)_2 + 6SiO_2 + 10C \rightarrow P_4 + 10CO + 6CaSiO_3$$

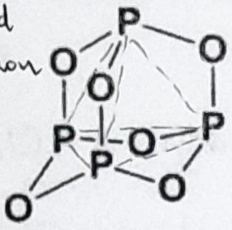
There are 4 kinds –

- White : solitary clusters
- Red: Tetrahedral clusters connected by single bonds
- Voilet : Tetrahedral shape is broken Cross-chain links
- Black: Puckered-layer structure (2D



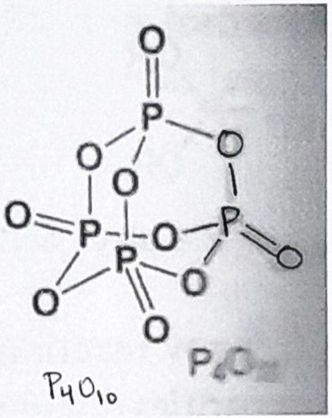
Phosphorus oxides and sulfides

Extended tetrahedron



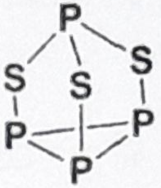
P_4O_6

Phosphorus trioxide

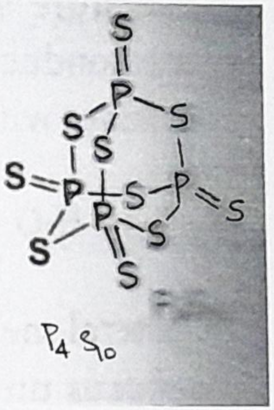


P_4O_{10}

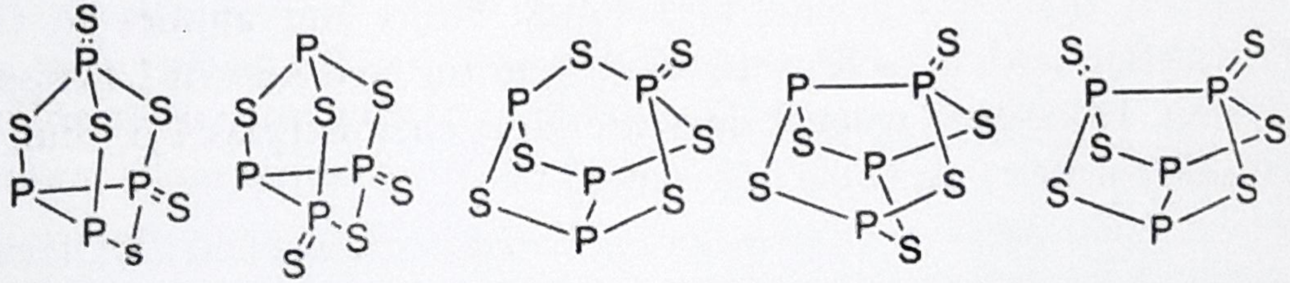
Phosphorous pentoxide



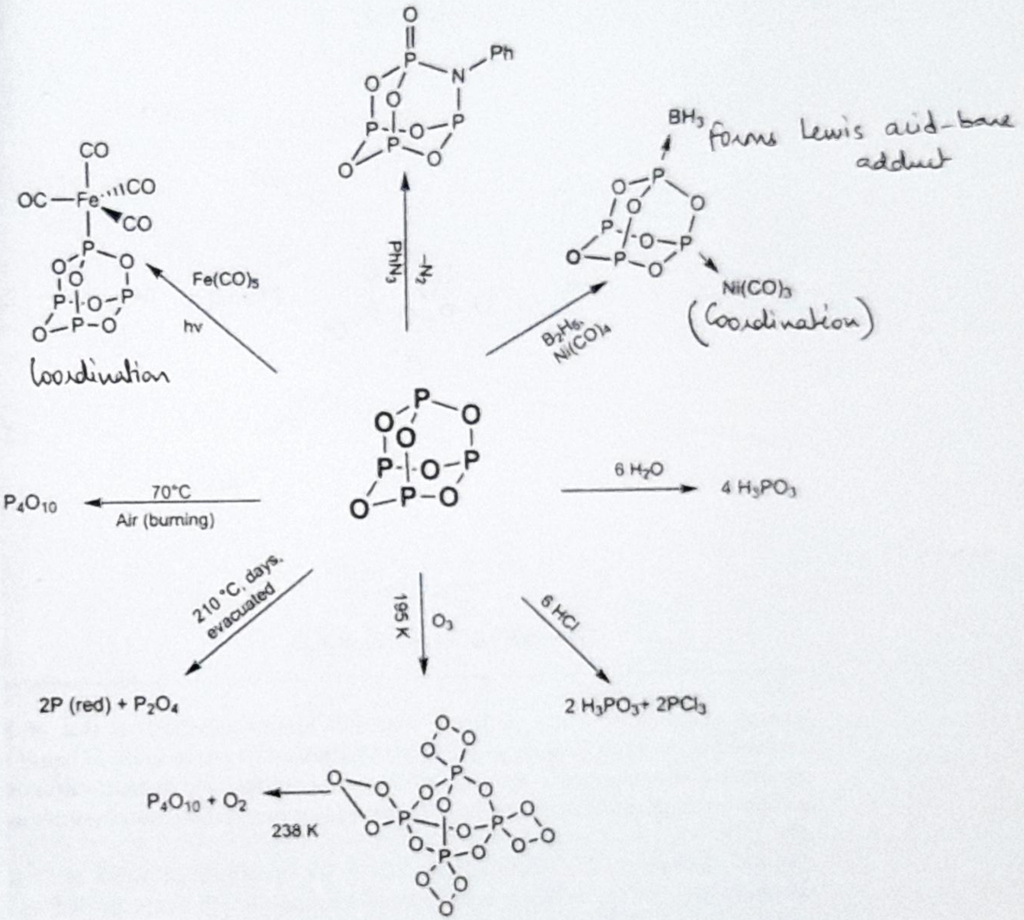
P_4S_3



P_4S_{10}



Reactions of P_4O_6



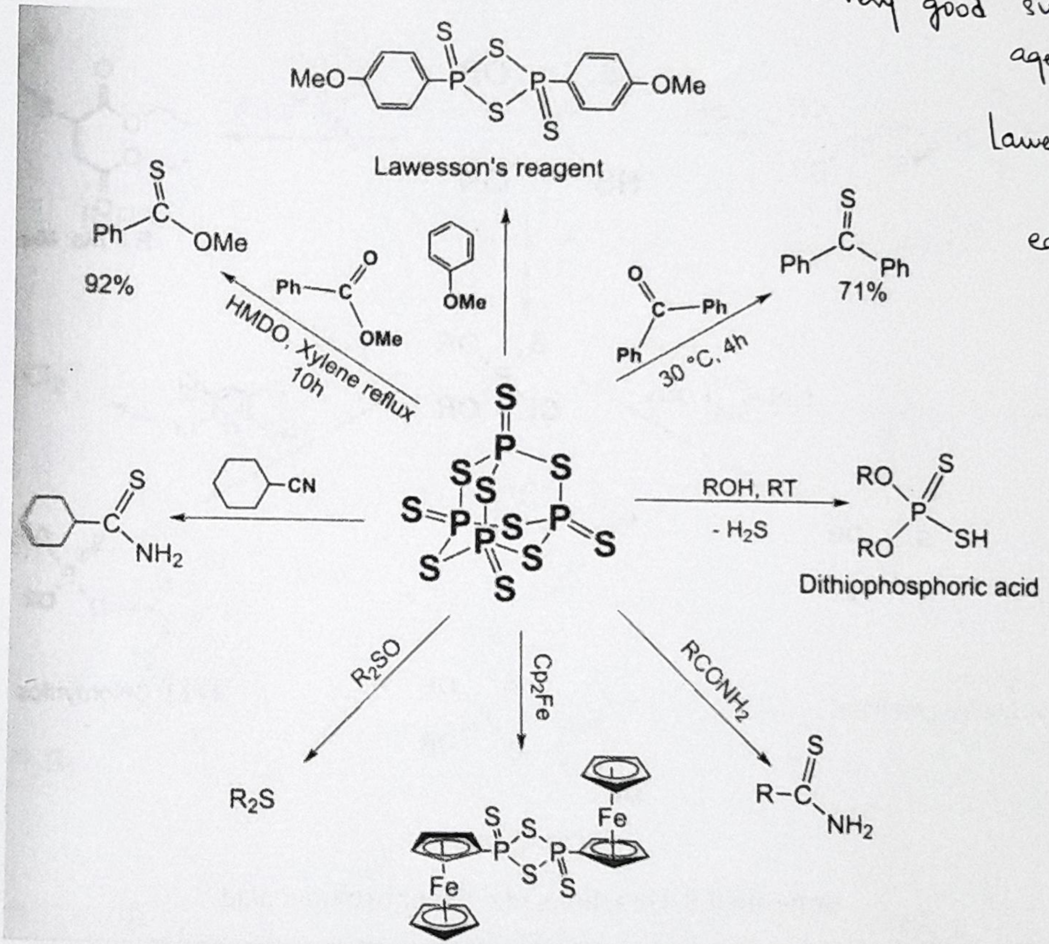
Coordination

Forms Lewis acid-base adduct

(Coordination)

Reactions of P_4S_{10}

→ Very good sulfurising agent



Lawesson's reagent – better sulfurising agent

easier to handle ∵

less smelly & toxic,

more stable

Lecture - Live (3rd Dec) 214/12

Rings, macrocycles and polymers

Organic Ring systems

Very important - Benzene, cycloalkanes (homologous series - 3 to 30)

Heterocycles - replacing one or more C with p-block element in in a homocyclic compound (very vast).

Eg. Pyridines, furans etc.

Inorganic heterocycles

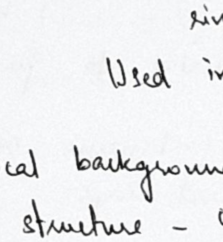
- Extension of substitution process to replace <u>all</u> C atoms with other p-block elements
- Elemental sulphur (S_8) : Cyclo-S_8 : quintessential inorganic rings
  Homocyclic sulfur rings (cyclo-S_n) from $n = 6$ to 24
- Cyclosilanes $(R_2Si)_n$ for $n = 3-35$ - Saturated inorganic ring system
- Salvarsan - arsenic based drug - mixture of 3 and 5 membered rings : $(RAs)_n$ where $n = 3, 5$ $R = 3\text{-}NH_2\text{-}4\text{-}OHC_6H_3$
  Used in chemotherapy, treating syphilis.

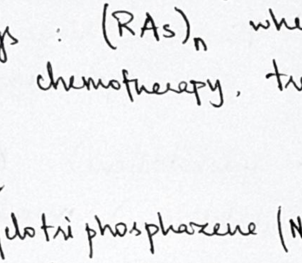
Historical background

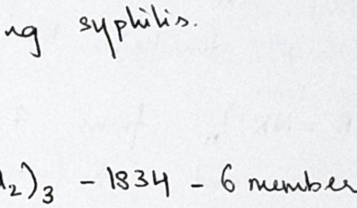
* First structure - cyclotriphosphazene $(NPCl_2)_3$ - 1834 - 6 membered ring
  tetrasulfur tetranitride (S_4N_4) - 1835 - folded cage structure

* Structural determinations were the major motivation to to figure out the nature of bonding in inorganic heterocycline ring.

* Borazine - $B_3N_3H_6$ - 1926 - Inorganic benzene
  Debate over its aromaticity continues till today.







* ∃ an extensive homologous series for cyclophosphazenes $(NPX_2)_n$
  $n = 3 - 40$

⇒ Borazine

Reported by Alfred Stock and Pohland –

$3 B_2H_6 + 6NH_3 \longrightarrow 2B_3N_3H_6 + 12H_2$

More Efficient : $3LiBH_4 + 3NH_4Cl \longrightarrow B_3N_3H_6 + 3LiCl + 9H_2$

Borazene is isostructural with benzene & their colligative properties are same but they differ –

- π electrons are completely delocalised in C_6H_6. In borazine, the lp of nitrogen forms a dative bond with boron – partial delocalisation of N lone pair. Boron – Nitrogen bond length (1.436 Å) is between B–N (1.51 Å) & B=N (1.31 Å)
- ⇒ Electron density is not distributed evenly, due to χ difference. ∴ MOs of system are lumpy in appearance. This uneven distribution makes it prone to addition reactions.

B–N Rings

* RB≡NR' : Iminoboranes – similar / isoelectronic to alkynes & R–C≡N
Just like R–C≡N form tri-azine rings, (∵ ≡ can't hold the* e⊖ density) RB≡NR' also cyclo oligomerize to form rings.

* $(RB=NR')_n$ form 4 (~ cyclobutadiene), 6 (~ benzene : more prevalent) and 8 (~ cyclo-octatetraene) membered rings

* Borazine first prepared by thermolysis of diborane-ammonia adduct

$3H_3N \cdot BH_3 \longrightarrow B_3N_3H_6 + 6H_2$

$3(NH_4)_2SO_4 + 6NaBH_4 \longrightarrow 2B_3N_3H_6 + 3Na_2SO_4 + 18H_2$

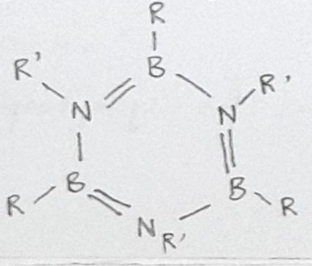
$3NH_4Cl + 3LiBH_4 \longrightarrow B_3N_3H_6 + 3LiCl + 9H_2$

* Substituted borazines –

- $3BCl_3 + 3NH_4Cl \longrightarrow Cl_3B_3N_3H_3 + 9HCl$

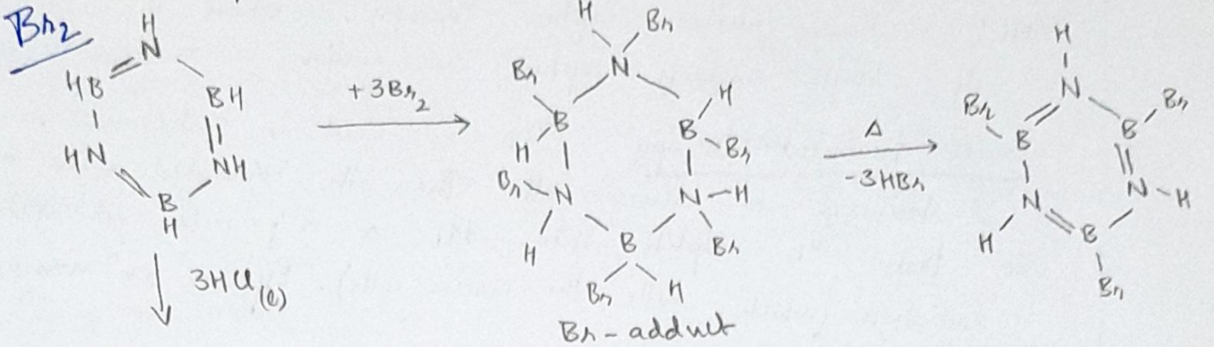
$Cl_3B_3N_3H_3 + 6NaBH_4 \longrightarrow 2B_3N_3H_6 + 6NaCl + 2B_2H_6$

- $3RBCl_2 + 6R'NH_2 \longrightarrow R_3B_3N_3R'_3 + 3[R'NH_3]Cl$

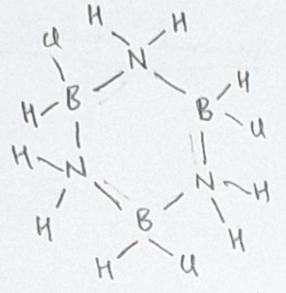


Reactions of Borazine

Br_2



Br - adduct



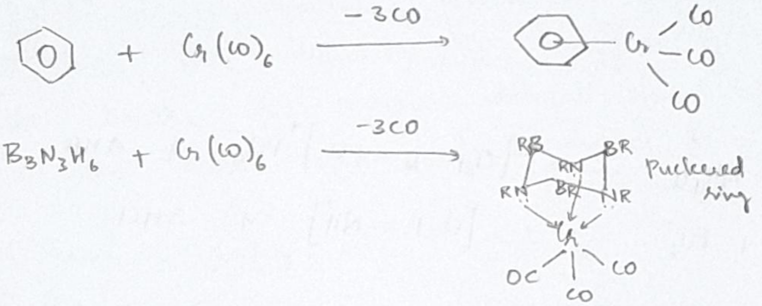
HCl - adduct

Benzene doesn't react with HCl
In presence of Lewis acid it reacts with Br_2 to undergo Nucleophilic substitution.

Some reactions are similar -

Eg:

CO



I Complex ?

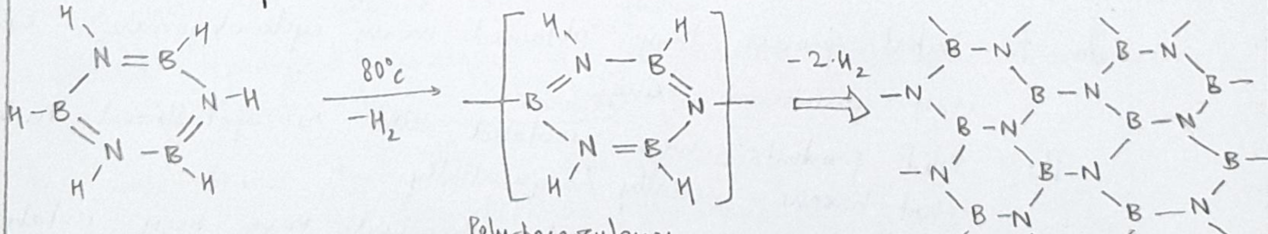
$B_3N_3H_6 + Cr(CO)_6 \xrightarrow{-3CO}$

⇒ Delocalisation is not uniform

⇒ B-N Polymers

Borazine can be used to make B-N polymers and ceramics

- Low T thermally induced dehydropolymerisation of $N_3B_3H_6$ gives a cyclo-linear polymer $(-H_2)$



Poly-borazylanes

- Pyrolysis at 1200°c yeilded white boron nitride in 85 - 93% yeild
- Borazine can also be used to grow B-N thin films on to surface to the thickness we want.
- NR_2 is a better leaving group than H_2.

Nuclear application of Boron & boranes –

BNCT : Boron neutron capture therapy - boron is used for its large neutron capture cross-section in nuclear reactors

* Cancer treatment therapy – ^{10}B in used in carboranes and delivered to cancer cells. Then its bomarded with neutrons so that ^{10}B splits into ^7Li, α-particle and gamma radiation (which kills the cancer cells). Effective on non-operable brain tumors.

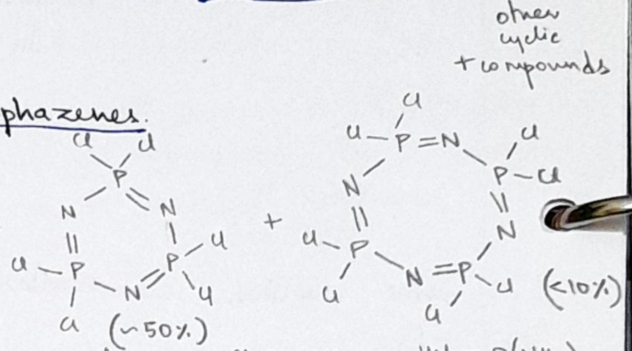
water soluble → BSH & BPA

* In nuclear reactors, boron rods absorb thermal neutrons

Cyclic P-N compounds : Cyclophosphazenes.

$$PCl_5 + NH_4Cl \xrightarrow[\text{Tetrachloroethane}]{150^\circ C}$$

High-boiling non-polar solvent



\# They were cheking rxn of PCl_5 with ammonia – resulted in mixture of moisture sensitive compounds ~ $Cl_3P{=}NH$ & $HN{=}P(NH_3)_3$ very reactive

$$3PCl_5 + NH_4Cl \longrightarrow [Cl_3P{=}N{=}PCl_3]^+PCl_6^- + 4HCl$$

$$\overset{+}{N}H_4 + PCl_6^- \longrightarrow [Cl_3P{=}NH] + 3HCl$$

$[Cl_3P{=}NH]$ → (Hasn't been isolated)

$$[N(PCl_3)_2]^+ \xrightarrow[-HCl]{Cl_3PNH} [Cl_3P{=}N{-}PCl_2{=}N{-}PCl_3]^+ \xrightarrow{Cl_3PNH} \left[Cl_3P{=}N{-}\overset{Cl}{\underset{Cl}{P}}{=}N{-}\overset{Cl}{\underset{Cl}{P}}{=}N{-}\overset{+}{P}Cl_3\right]^+$$

Polyphosphazene

$$N_3P_3Cl_6 \text{ – Cyclophosphazene} \xleftarrow{\;-\overset{+}{P}Cl_4\;}$$

In the initial process, they obtained many cyclo-oligomers – upto ~24 membered rings.

The solid products were isolated and re-crystallized in hot-hexane serially / sequentially.

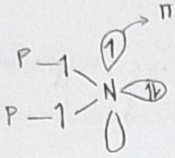
Through this many ~~the~~ cyclic compounds have been isolated. The trimer is the major product i.e. max yeild

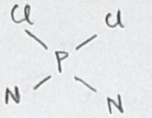
$$\star\quad [Cl_3P{=}\overset{+}{N}{=}PCl_3] \longleftrightarrow [Cl_3P{=}N{-}\overset{+}{P}Cl_3]$$

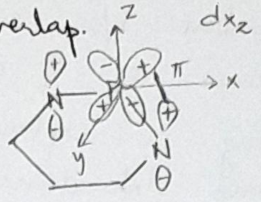
The resonance form is important for cyclisation. If + charge was just on N, it would lead to branching.

When its on P, the other end of polyphosphazene attacks, removes $^+PCl_4$ and forms cyclic compound

Dewar model of bonding : $P_\pi - d_\pi$ overlap.







According to VBT, the 5th electron in P will be put in a d-orbital to form the $P_\pi - d_\pi$ overlap

* Craigg & Paddock model

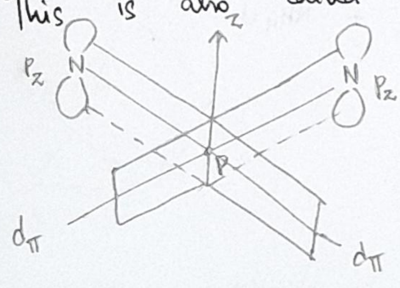
The electron in N p-orbital forms a π bond with an electron present in d_{xz} or d_{yz} orbital

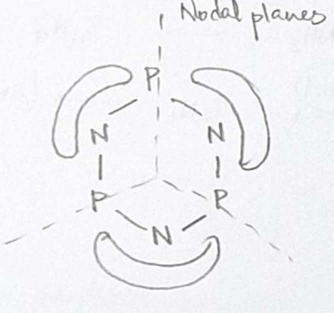
(?) The d_{xz} $e^{\ominus}$ would react with one neighboring N, while the d_{yz} would interact with other. This predicts a delocalised π bond, that doesn't match with the actual structure

* Dewar model

Here, the d_{xz} and d_{yz} will combine to form a pair of hybridized d orbitals, which are represented as orthogonals π orbitals. They lead to the formation of a nodal plane which breaks the complete delocalisation in the molecule

This is also called the island model (of π cloud)

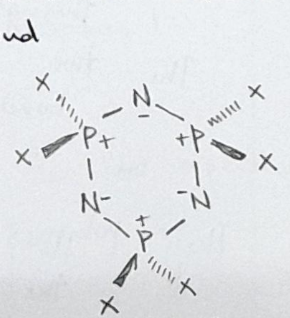




* Zwitterionic and Negative Hyperconjugation

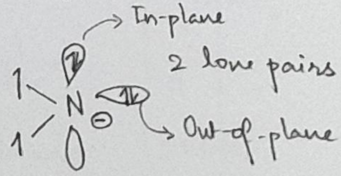
Detailed topological analysis of $e^{\ominus}$ density distribution reveals a significant ionic character in P–N bond

It was found that there are no double bonds i.e no delocalisation. The molecule can take planar structure or puckered ring structure



N^- has two lone pairs, one of which participates in negative hyperconjugation

⇒ In plane (p_z) and out-of-plane (p_x) lone pairs interact with σ* (P–N) and σ* (P–X) orbitals respectively.



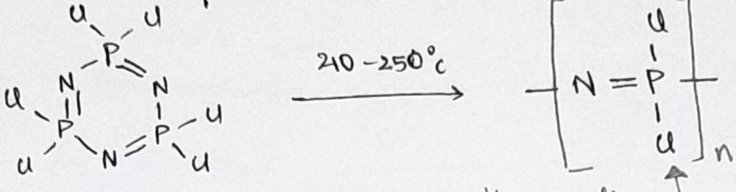
The interaction b/w out of plane lp and σ* (P–X) increases as χ of X increases.

So bonding is explained by ionic and negative hyperconjugation ~~reactions~~ interactions. Compound is not considered ionic anymore.

Reactivity of Cyclotriphosphazenes

There are many reactions that can be carried out

Polymerisation of polyphosphazenes –



Very reactive

Cl can be substituted with other substituents – –OR, –NR$_2$, –R

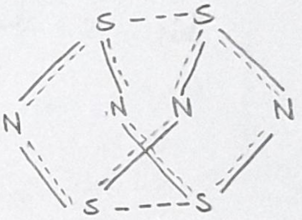
Sulfur Nitrogen rings

S_4N_4 – interlocked cage structure

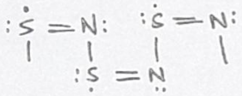
$$6S_2Cl_2 + 16NH_3 \longrightarrow S_4N_4 + S_8 + 12NH_4Cl$$

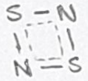
$$S_4N_4 \xrightarrow[\text{Heat}]{\boxed{\text{Ag wool}}} S_2N_2 \longrightarrow (SN)_x$$

weak van-der Waals interaction



ne-dimensional conductor





Lewis structure can't be written for this structure

Except for bonded e⊖, all other e⊖s are completely delocalised through the molecule.

The two S molecules form a weak van der Waals' bond due to their proximity & presence of odd electron on S because – it has 6 valence e⊖s but only 3 bonds.

The polymer $(SN)_x$ is considered a conductor because of the delocalisation of the odd electron.

Live Lecture - 9th Dec

23/12

Silicon compounds and silicates

Elemental Si

- Prod^n & purification
  from SiO_2, sand, ~~qtz~~ quartz in an electric arc furnace and use coke as reducing agent. We get 98% purity.
- Further purified by converting Si into volatile silane compounds, which are isolated by fractional distillation, after which its reduced to Si by red^n at 1000°C by H_2.

$$SiO_2 + 2C \longrightarrow Si + 2CO$$

Siemens Process

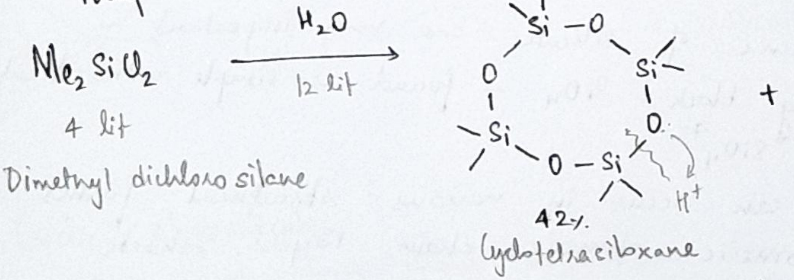
$$Si + 3HCl \longrightarrow \underbrace{SiHCl_3}_{\text{chlorosilane}} + H_2 + \text{impurities}$$

$$SiHCl_3 + H_2 \longrightarrow \underbrace{Si}_{\sim 99\%\ \text{pure}} + 3HCl$$

- To produce semiconductor grade silicon -
  Crystal growth / Czochralski technique - heating Si to 1500°C in a silica crucible under inert atmosphere using a rotating seed crystal.
  Other techniques - Bridgeman technique (Also used to make i.e grow AsGa and InP semiconductors)

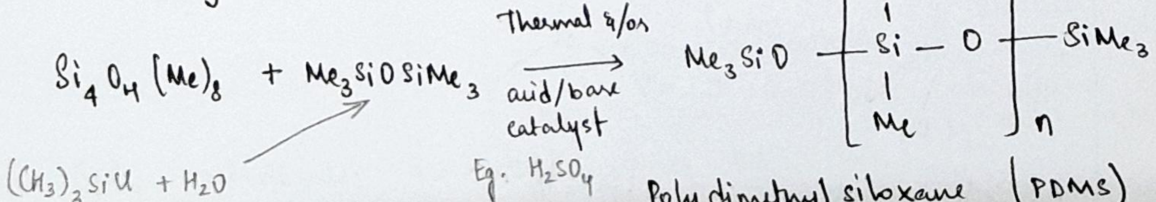
Silicone polymers

They were invented + worked on by F. Stanley Kipping.



+ Trimer (0.5%)
Pentamer (7%)
Hexamer (2%)

The products are all viscous oils, so they can be seperated by distillation



$$Si_4O_4(Me)_8 + Me_3SiOSiMe_3 \xrightarrow[\text{acid/base catalyst}]{\text{Thermal \&/or}} Me_3SiO\left[\begin{matrix}Me\\ |\\ Si-O\\ |\\ Me\end{matrix}\right]_n SiMe_3$$

$(CH_3)_3SiCl + H_2O$

Eg. H_2SO_4

Polydimethyl siloxane (PDMS)

PDMS are silicone polymers (∵ they're considered analogues of ketomes – $R_2C=O$ :: $R_2Si=O$)

In $R_2Si=O$, the $e^{\ominus}$ density can't be contained so it ends up forming oligomers and polymers.

Industrial success of silicone

Rochow Mueller Process (1943)

$$CH_3Cl + Si \xrightarrow{Cu} (CH_3)_2SiCl_2 \longrightarrow \text{cyclotetrasiloxane + dimer} \longrightarrow \text{PDMS}$$

$$+ (CH_3)_3SiCl$$

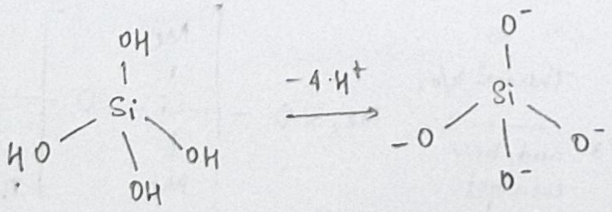
World silicone demand (2010) – \$ 12.4 billion.

Playing around with the ratio of the tetramer and dimer allows us to create polymers of different hardness and texture, which has many, many applications.

Silicates and Metal silicates

- * ↳ 90% of earth's crust. Silicates are ionic compounds that contain silicon oxanion along with metal cation.
- * Silicates are major constituents of pottery (from clay materials) and glass (transparent, supercooled & infinitely viscous liquid of metal silicates).
- * Clay is a mixture of various hydrated silicates of aluminium – benetonite, kaolinite, hanoysite etc
- * Structural patterns of silicates are very important – Basic building block : SiO_4 – found as simple orthosilicate anion – SiO_4^{4-}

Silicate units can occur in various structural forms such as monomeric, dimeric, chain, layers, sheets and cage structures.



Orthosilicic acid

$[SiO_4]^{4-}$

(67) → Orthosilicate anion $[SiO_4]^{4-}$

- Rare, not found in many minerals. Strong base ⇒ cannot persist in aqueous solution
- Occurs in nature as insoluble salts of acidic cations
- Eg: Phenacite (Be_2SiO_4), Willemite (Zn_2SiO_4), Zircon ($ZrSiO_4$)

  Garnets - $(M^{2+})_3(M^{3+})_2(SiO_4)_3$ (Ca, Mg, Fe ; Al, Cr, Fe)

  Olivine - Mg_2SiO_4 or Fe_2SiO_4

  Isomorphous substitution is very common. So the formula is written as $(Fe, Mg)SiO_4$.

  They can substitute each other in any proportion
- ~~Sti~~ These minerals are found in magma and buried deep under desert soil (∵ less rain ⇒ less solid). Also found in newly-formed soil.

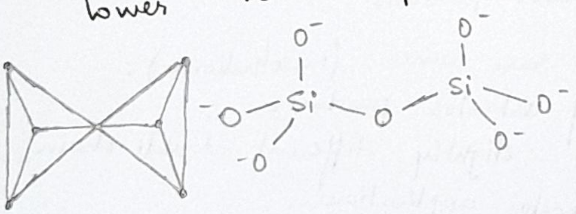
→ Chain oligosilicates

Linking 2 simple silicate units : (~ neutralisation reaction)

$2SiO_4^{4-} + \underset{acid}{2H^+} \longrightarrow [O_3Si-O-SiO_3]^{7-} + H_2O$ ↗ Reason for its polymerisat

[More efficient : $3LiBH_4 + 3NH_4Cl \rightarrow B_3N_3H_6 + \cancel{3LiCl + 9H_2}$] ×

Basic structural unit : $SiO_{3.5}^{3-}$: ½ vacant coordination site per unit. This is less basic than SiO_4^{4-} ∵ it has lower -ve charge density.

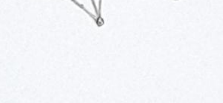


The Si-O-Si angle is determined by the bulkiness of the cation.

→ Cyclic oligosilicates

Ends of long chain oligosilicates come together to eliminate oxide ions and form cyclic silicates.

$Si_3O_{10}^{8-} + 2H^+ \longrightarrow cyclo-Si_3O_9^{6-} + H_2O$



Benitonite

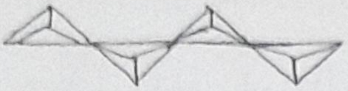
$BaTi(Si_3O_9)$

Similarly, $Si_6O_{18}^{12-}$ is also formed

Eg: Beryl : $Be_3Al_2(Si_6O_{18})$

⇒ Cyclic metasilicates are oligomers of SiO_3^{2-}. One vacant coordination site & lower -ve charge density (-2) per Si unit.

→ Chain Polysilicate – Pyroxene & Amphibole

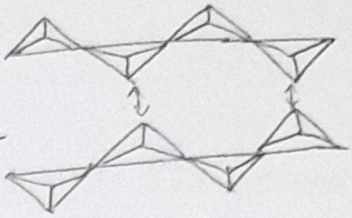


SiO_3^{2-} in pyroxene

SiO_3^{2-} in $CaSiO_3$

Enstatite ($MgSiO_3$), Diopsite ($MgCaSi_2O_6$), Spodumene ($LiAlSi_2O_6$), Pollucite ($CsAlSi_2O_6$)

- There are different types of single chain silicate polymers
- Similar charge density, basicity & formula as the cyclic analog.
- Further reduction in anion basicity & reduced charge density is acheived by formation of double-chain polysilicate by side-to-side linking of chain polymers

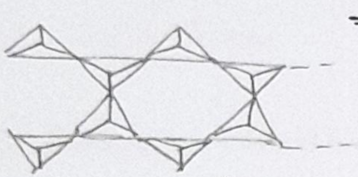


→ Double chain polysilicates : Amphiboles

Fractional structural unit : $SiO_{2.75}^{1.5-}$

Simplest formula unit : $Si_4O_{11}^{6-}$

1.25 vacant coordination sites per Si.



$Si_4O_{11}^{6-}$

HW

$[Si_6O_{17}]^{10-}$

- Eg: Crocidolite – $Na_2Fe_5(OH)_2[Si_4O_{11}]_2$ Amosite – $(Mg,Fe)_7(OH)_2[Si_4O_{11}]_2$

★ Known for their fire and heat resistant properties and for their fibrous nature.

Used for weaving of insulating & non-flammable garments & for use in +3000 products.

★ Inhaling → asbestosis & rare cancers (mesothelioma).

US-EPA banned use of asbestos products

Xenotlite – $Ca_6(OH)_2(Si_6O_{17})$ – slightly different double-chain used for asbestos applications.

→ Layered Polymeric Silicates

If side to side linking of chains is continued indefinitely, further oxide ions are eliminated.

Structural unit : $SiO_{2.5}^{-}$

1.5 vacant coordination site per Si, lower basicity

Formula : ~~Si4 10~~ $Si_4O_{10}^{4-}$ – most useful silicate.

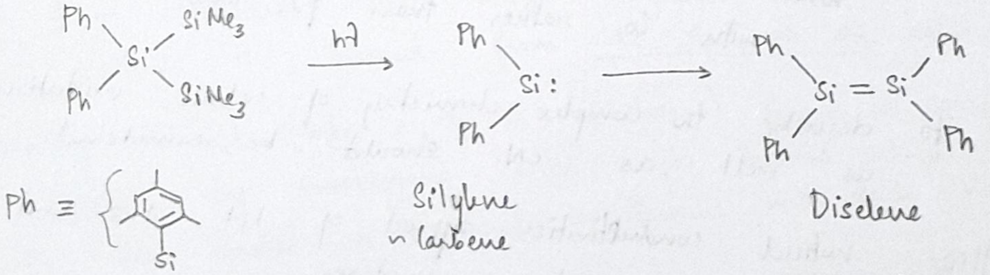
Eg: Clay minerals – Kaolinite / china clay $Al_4(OH)_8[Si_4O_{10}]$, Pyrophillite $Al_2(OH)_2(Si_4O_{10})$, Serpentine $Mg_6(OH)_8(Si_4O_{10})$.

Further removal of oxygen will lead to uncharged oxide, silica – SiO_2 – acidic nature

⇒ Silica – 3D unit

- It has 3 crystalline forms –
  - Quartz < 870°c
  - Tridymite 870° – 1470°c
  - Cristobalite 1470° – 1710°c, at which T, silica melts.
- High viscosity of molten silica makes crystallization slow. Instead of crystalling, it forms glass, which softens near 1500°c. Flash cooling of silica → glass
- Conversion of one crystalline form to another is difficult and slow even at high T ∵ it involves breaking Si–O. All forms contain SiO_4 tetrahedra, sharing oxygen atoms.
- Quartz : common form of silica. Contains helical chains of SiO_4 tetrahedra (chiral). Each full turn of helix contains 3 Si and 3 O atoms ; 6 helices combine to form overall hexagonal shape
- α - Quartz has a similar but less regular structure than β - Quartz

Si – Si Double Bond – Robert West, 1981
First stable silicon-silicon double bond



This double bond is non-classical ∵ 2 singlet silylene overlap – lp in s is given to p orbital – which gives rise to a non-planar structure

This can be compared to formation of ethylene by two triplet carbenes through pair bonding, giving rise to classical double bond & planar structure

24/12

Werner countered Jørgensen's theories with expts

Lecture - 10th Dec

Transition Metal Chemistry

- Coordination compounds were first identified ~~with~~ in 19th cent and they showed very different characteristics from regular salts. It was a challenge in those days → they were called complexes.
- Modern study began by Alfred Werner and Sophus Mads Jørgensen - both had different approaches. Werner's was widely accepted - first inorganic chemist to win the Nobel.
- His first experiments were based on 4 complexes of Cobalt (III) chloride with ammonia (at diff. concentrations)

$CoCl_3 \cdot 6NH_3$ (yellow) $CoCl_3 \cdot 5NH_3$ (purple)

$CoCl_3 \cdot 4NH_3$ (green) $CoCl_3 \cdot 4NH_3$ (violet) - same formula, distinct properties.

- He also noted the difference in reactivities of chloride ions with $AgNO_3$

$CoCl_3 \cdot 6NH_3 + Ag^+ \longrightarrow 3AgCl$

$CoCl_3 \cdot 5NH_3 + Ag^+ \longrightarrow 2AgCl$

$CoCl_3 \cdot 4NH_3 + \underset{\text{(excess)}}{Ag^+} \longrightarrow AgCl$

- Postulate : Co exhibits constant coordination number (CN) in the s When NH_3 molecules are reduced, chlorine bonds covalently with Co rather than free ions.

So to describe the complex chemistry of cobalt, oxidation state as well as CN. should be considered.

- Also noticed conductivities typical of 1:1, 1:2 and 1:3 electrolytes for these complexes.
- Werner also identified that bonds to ligands were fixed in space ⇒ they can be treated by application of structural application ⇒ he predicted the correct geometric structures of many coordinate compounds.

- Eg: For octahedral $[Co(NH_3)_4Cl_2]Cl$ two isomers were observed - voilet and green, which could be cis-trans isomers

Similarly for Pd(II) and Pt(II), MA_2B_2 structures with 2 isomers (cis, trans) were identified.

Bonding

Many theories have been proposed -

1. Valence Bond Theory - 1930s - Linus Pauling
2. Crystal feild theory - 1950s & 1960s - Hans Bethe & Van Vleck
   Later modified to Ligand Feild Theory (MO based approach to Crystal feild concepts
3. Molecular Orbital Theory - very widely applicable

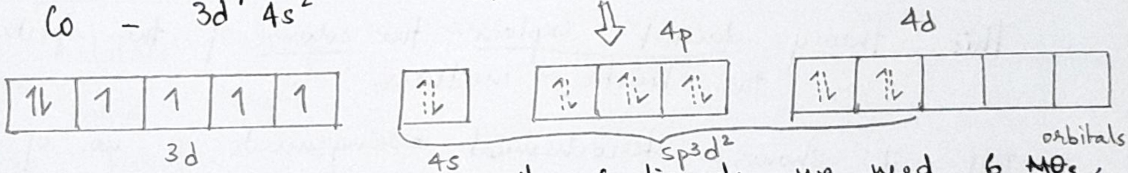
VBT and CFT are applied as working models for practicing inorganic chemistry and continue to contribute to current discussions.

Valence Bond Theory

Formation of complex is considered as a series of hypothetical steps.
↑
But in reality, all steps are happening simultaneously.

⇒ Consider the case of Co^{3+}

* Co - $3d^7 4s^2$ ⇒ Co^{3+} - $3d^6$



* To form octahedral complex with 6 ligands, we need 6 ~~MOs~~ orbitals, which are formed from 4s, 4p and 4d orbitals

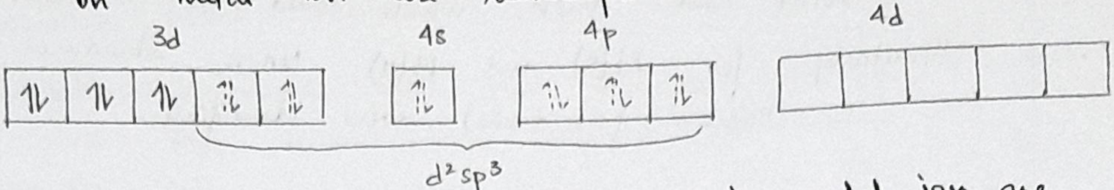
* Incoming ligand (with a lp or -ve charge) forms a coordinate bond by overlapping with empty hybrid orbitals on the metal ⇒ σ-bond is formed with each ligand.

* Due to use of 4 orbitals - outer sphere complex. Energy of these orbitals are quite high, so complex will be reactive

* Large no. of unpaired electrons in its $3d^6$ configuration ⇒ high spin complex i.e. its paramagnetic.

Eg: $[CoCl_6]^{3-}$

⇒ Alternatively, when there's a strong ligand, electrons on metal ion are rearranged as below –

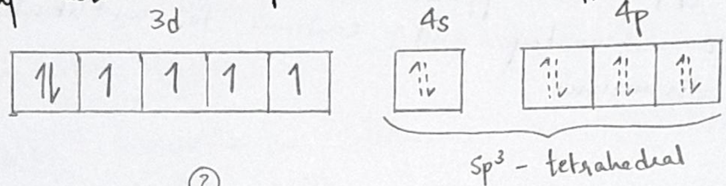


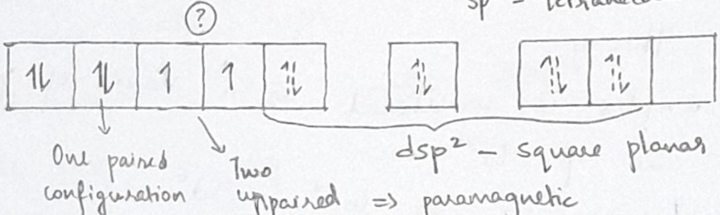
- This is because the unpaired e⁻ on the metal ion are forced to pair up ⇒ low spin complex i.e diamagnetic
- Since low energy 3d orbitals are used → inner sphere complex, which is more stable

Eg: $[Co(NH_3)_6]^{3+}$

⇒ Four coordinate complexes

They are also possible in two different arrangements –





- This theory doesn't explain the colours of the spectra or the kinetic inertness.
- But it shows stereochemical arrangements & no. of unpaired electrons ⇒ magnetic moment can be calculated.

It cannot explain variation of magnetic moment with T. i.e. the changes in spin configuration that causes it.

Crystal Feild Theory.

Assumptions –

1. Attraction b/w metal ion and ligand is purely electrostatic.

Metal ion – positively charged equal to the oxdⁿ state

Ligands – neutral or negatively charged – treated as point charges

–ve end of dipole is directed towards metal ion.

Electrons of central atom experience repulsive forces from e⁻s of ligand

2. There is no interaction b/w metal orbitals and ligand orbitals

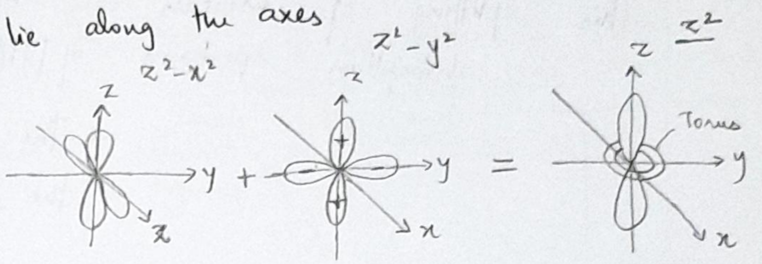
3. All d orbitals of metal have same energy in free atom. When the complex is formed, the ligands destroy the degeneracy of these orbitals (the geometry of the crystal feild determines the energies of d-orbitals)

Octahedral Crystal Feild.

In the free atom, the d-orbitals –

- d_{xy}, d_{yz}, d_{xz} – lie in between the axes
- $d_{x^2-y^2}$ and d_{z^2} lie along the axes

$d_{z^2} = d_{2z^2-x^2-y^2}$

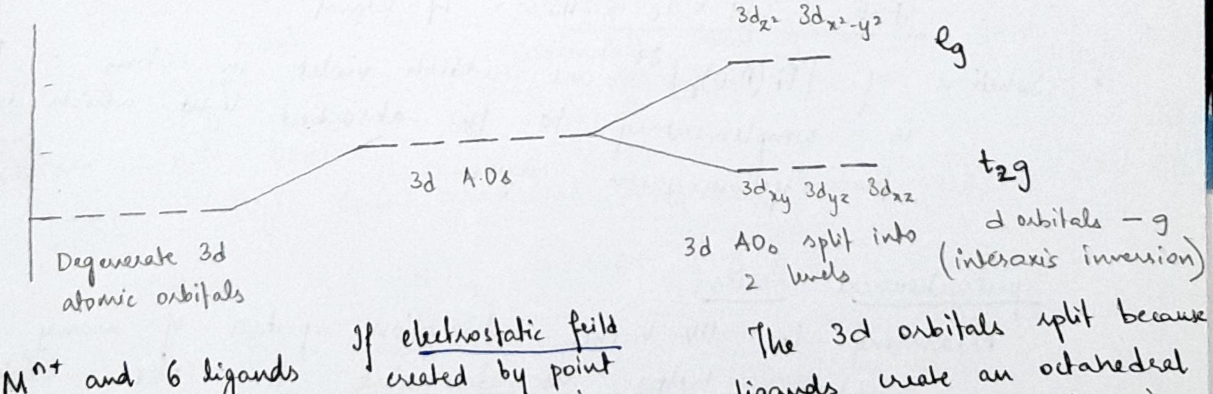


$e^\ominus$ density on the x-y plane is very weak

– diffused spherical $e^\ominus$ density cloud
Most of it is present along the z-axis.

If all the orbitals were superimposed on the same coordinate axes, in an octahedral feild (cubic), then the ligands approach along the axes.

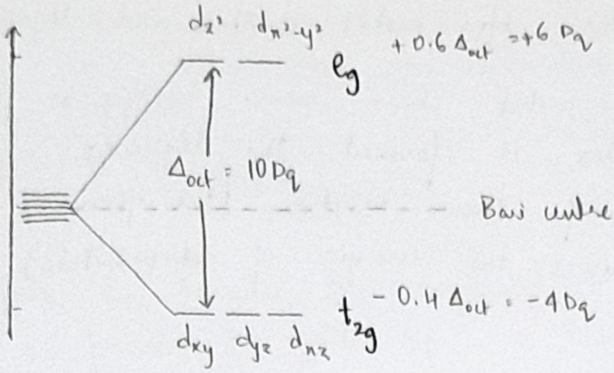
So orbitals along the axes experience more repulsion and hence, they'll increase in energy. At same time, orbitals in between the axes will reduce in energy.



M^{n+} and 6 ligands are infinitely far apart

If electrostatic feild created by point charge ligands is spherical, energies of 3d orbitals are raised uniformly

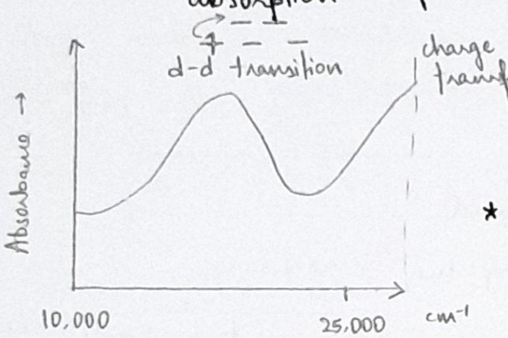
The 3d orbitals split because ligands create an octahedral feild, raising & lowering the energies of certain orbitals along & in between axes.



Bari centre
Weighted average energy level of the two sets of perturbed orbitals

-ve sign of t_{2g} orbitals is because they're stabilised i.e energy is lowered

This splitting of orbitals can be observed in the UV-Visible absorption spectrum of $[Ti(H_2O)_6]^{3+}$ —



* The peak in absorbance is for the excitation of t_{2g} electron the an e_g electron.

* The second peak (out of graph) is due to ligand → metal charge transfer.

* d-d transition peak ~ 20,300 cm^{-1}
  $\Delta_{oct} = 243$ kJ mol^{-1} (∵ 1 kJ mol^{-1} = 83.7 cm^{-1})

Similar to the energy of many, normal single bonds
⇒ during this transition, some of the bonds are activated.

Crystal Feild Stabilisation Energy —

CFSE = 0.4 × 1e^- × 243 = 97 kJmol^{-1}

Refer — JD Lee

* Solution of $[Ti(H_2O)_6]^{3+}$ are reddish violet in colour ∵ this is complementary to the absorbed light which is in the yellow-green region.

Spectrochemical series

Measuring the UV-Visible absorption spectra of many complexes helps us determine the CFSE — which is the first peak in the graph

Comparing the CFSE of similarly oxidised Cr coordinate complex –

$[CrF_6]^{3-}$	15000
$[Cr(H_2O)_6]^{3+}$	17400
$[Cr(NH_3)_6]^{3+}$	21600
$[Cr(CN)_6]^{3-}$	26600

CFSE increases with the strength of stronger ligands ∵ its creates high feild.

$I^- < Br^- < [NC\underline{S}]^- < Cl^- < F^- < [Ox]^{2-} \approx [H_2O] < [\underline{N}CS]^- < NH_3 < en < bpy < phen < CN^- < CO$

weak feild ligands $\xrightarrow[\text{Increasing } \Delta_{oct}]{}$ strong feild ligands

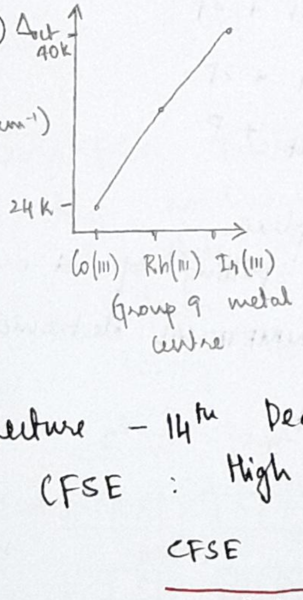
Magnitude of Δ_{oct} depends on –

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

② No. of e⁻s involved in CFSE also matters. Higher oxdⁿ state tend to stabilise the complex more (∵ more e⁻s in t_{2g} ?)

① Patterns of increasing σ-donation : Halide < O < N < C-donors

Because, the σ donation by C-donors is very strong, they end up forming a M–C covalent bond, which now comes under the study of organometallics ⇒ less coordinate bond/character

③ 

The splitting energy / CFSE increases down the group. ∵ increased seperation of s & d orbitals (?)

\# Metal ions are LA and ligands are LB and their hard-soft nature should be compatible.

* M^{2+} and M^{3+} have intermediate acidity & N-donors have intermediate basicity ⇒ they form most efficient bonds.

25|12

Lecture – 14th Dec

CFSE : High spin octahedral complexes (weak field)

$$CFSE = (-0.4\, n_{t_{2g}} + 0.6\, n_{e_g})\Delta_{oct}$$

In weak field complexes, the electrons are filled according to Hund's rule first filling 1 electron in t_{2g}, then in e_g orbitals, and then filling the 2nd electron in the same sequence

⇒ d^3, d^8 – most stable ; d^5, d^{10} – least stable.

High spin and low spin complexes

$-1.6\ \Delta_{oct}$ — d^4 system — $-0.6\ \Delta_{oct}$

LOW — HIGH

$\Delta_{oct} > P$ — $\Delta_{oct} < P$

Total stabilisation energy in low spin : $\boxed{-1.6\ \Delta_{oct} + P}$

Pairing energy consists of two terms –

i) Loss in exchange energy upon pairing

ii) Coulombic repulsion between spin paired electrons.

Spectroscopically, P can be determined by estimating the observed absorption maxima (vs. expected maxima)

Eg: $[Fe(CN)_6]^{3-}$ – Low spin : good σ-donor, good π-acceptor (lesser than CO)

The configuration is different for low spin complexes as follows –

d^4	$t_{2g}^4\ e_g^0$	$-1.6\ \Delta_{oct} + P$
d^5	$t_{2g}^5\ e_g^0$	$-2.0\ \Delta_{oct} + 2P$
d^6	$t_{2g}^6\ e_g^0$	$-2.4\ \Delta_{oct} + 2P$
d^7	$t_{2g}^6\ e_g^1$	$-1.8\ \Delta_{oct} + P$

Tetragonal distortions in octahedral complexes

Repulsion by ligands causes the splitting of d-orbitals.

d_n	t_{2g}	e_g	Nature of Ligand
✓ d_0	☐ ☐ ☐	☐ ☐	Strong / weak
d_3	↑ ↑ ↑	☐ ☐	strong / weak
d_5	↑ ↑ ↑	↑ ↑	weak
d_6	⇅ ⇅ ⇅	☐ ☐	strong
d_8	⇅ ⇅ ⇅	↑ ↑	strong / weak
✓ d_{10}	⇅ ⇅ ⇅	⇅ ⇅	strong / weak

Spherically symmetrical

SYMMETRICAL electronic arrangement (e_g)
⇒ All ligands repelled equally – no distortion

ASYMMETRICAL electronic arrangement

d_n	t_{2g}	e_g	Nature
d^4	↑ ↑ ↑	↑ ☐	weak
d^7	⇅ ⇅ ⇅	↑ ☐	strong
d^9	⇅ ⇅ ⇅	⇅ ↑	strong / weak

⇒ Some ligands are repelled more than others.

⇒ Strong distortions.

Unsymmetrical filling of t_{2g} orbitals (d_1, d_2, d_4(s), d_6(w), d_7(w)) causes smaller distortions than those of e_g because t_{2g} orbitals are in between Cartesian axes while ligands approach along the axes.

Distortions caused by asymmetrical arrangements are called Tetragonal distortions or more commonly –

Jahn-Teller Distortions

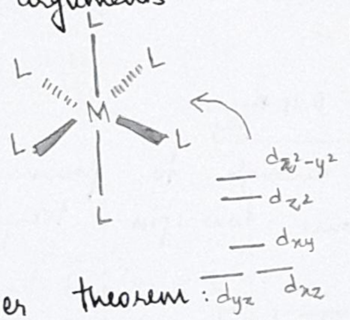
* d^9 and d^4 (w) are often distorted Eg: CuF_2 (infinite 2d structure) and $[Cr(H_2O)_6]^{2+}$. There, axial metal ligand bonds ~~age~~ are different from equatorial ones.

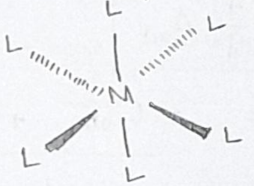
* In d^4 (w) i.e high spin, if electron is in –

* – d_{z^2} : more $e^{\ominus}$ density between metal & axial ligands
$\Rightarrow$ axial bond elongation.

– $d_{x^2-y^2}$: Maximum repulsions in equatorial ligands
$\Rightarrow$ ~~axial~~ equatorial bond compression.

Similar arguments can be made for d^9 configuration





In $[Cr(H_2O)_6]^{2+}$, d_{z^2} was found to be occupied $\Rightarrow$ axial elongation.

Jahn-Teller theorem :
Any non-linear molecular system in a degenerate electronic state will be unstable and will undergo distortion to form a system of lower symmetry & lower energy, losing its degeneracy in the process.

~ 32 : 30

Electronic Term Discussions

Explanation of Jahn-Teller – why some configurations get distorted (d_4) and why some (d^3) don't. This is because of the ground electronic term they occupy.

d^3 → A (singly degenerate) $\Rightarrow$ No distortions

d^2 → T (triply degenerate) $\Rightarrow$ Yes distortion?

Angular momentum → +2 +1 0 −1 −2

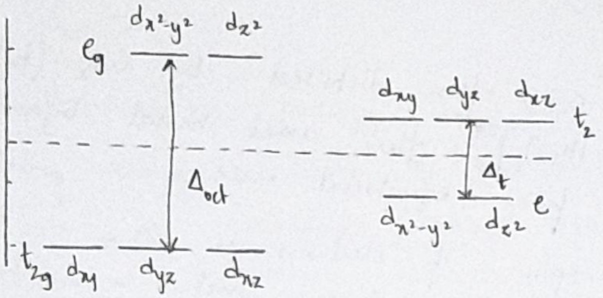
S P D F → Electronic Terms
0 +1 +2 +3

F spilts into 1 singly and 2 doubly degenerate –
A, T_{1g}, T_{2g}

Tetrahedral Crystal Field

Here, the ligands don't approach along the axes, rather in between the axes.

So, none of the d orbitals will face the ligand electrons directly. But t_{2g} orbitals are more proximal to ligand electrons, so they increase in energy.



Since there's no centre of inversion in tetrahedral structure – no 'g' or 'u' representation.

$\Delta_t < \Delta_o$ due to two main reasons –

1. Only 4 ligands (not 6), so the field is 2/3 of the size
2. Direction of orbital doesn't coincide with that of ligands. This reduces CF size by ~2/3

$$\therefore \boxed{\Delta_t = \frac{4}{9}\Delta_{oct}}$$

$$(CFSE_{tetrahedral}) = \underline{-0.6n_{e_g} + 0.4\,n_{t_{2g}}}$$

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

Rare example : $Cr[N(SiMe_3)_2]_3[NO]$ → strong π acid ligand

d^4 species with low spin complex

When are tetrahedral complexes favored?

In d^0, d^5, d^{10} – they have 0 CFSE, so both octahedral and tetrahedral complexes are equally likely.

Very weak feild ligands favor tetrahedral

For all other electronic arrangements, octahedral complexes are more stable and more common.

Despite that td complexes are formed and favoured when –

1. Ligands are <u>bulky</u> & cause crowding in Oct. complexes
2. Attainment of <u>regular shape</u> is important. For Td structures, d^0, d^2, d^5, d^7 and d^{10} are regular.

$\overset{IV}{Ti}Cl_4 - e_g^0 t_{2g}^0$

$\overset{VI}{Fe}O_4^{2-} : e_g^2 t_{2g}^0$

$CoCl_4 : e_g^4 t_{2g}^3$

$\overset{II}{Zn}Cl_4 : e_g^4 t_{2g}^6$

3. When loss of CFSE is small – d^1 and d^6 where
$CFSE_{oct} = -0.4\,\Delta_{oct}$ $CFSE_{td} = -0.26\bar{6}\,\Delta_{oct}$ ⇒ Loss ~ $0.13\,\Delta_{oct}$.

4. When ligands are weak feild, so loss in CFSE is less important.

5. When there's no CFSE – d^0, d^5, d^{10}

6. When central metal atom is in low oxd^n state, which reduces magnitude of CFSE. Eg $Ni^0(CO)_4$.

27/12

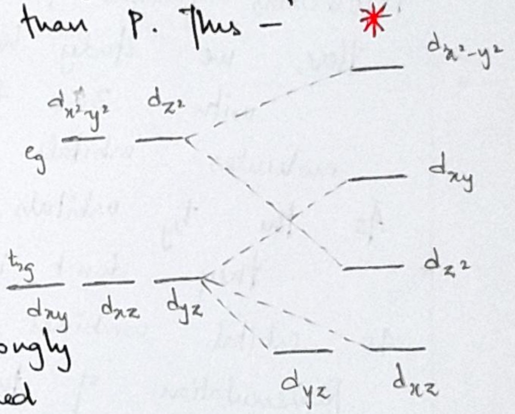
Lecture – 16th Dec

Square Planar Complexes

They're expected to be derived from octahedral complex by removal of two axial ligands. Intermediate stage (z-out) is a Jahn-Teller distortion. Square planar is considered an extreme case of tetragonal distortion

A single $e^{\ominus}$ in $d_{x^2-y^2}$ is repelled by 4 ligands, while one in d_{z^2} is repelled only by 2 ligands.

If the ligand feild is strong enough, the difference b/w
Especially
these two orbitals is more than P. Thus –



SQUARE PLANAR

- Both e_g $e^{\ominus}$s pair up and occupy lower energy d_{z^2} orbital
- 4 ligands can approach freely along X & Y ∵ $d_{x^2-y^2}$ is empty
- Ligands approaching along z are strongly repelled ⇒ No axial bond formed ∴ Square planar is formed
- Again d_{xy} orbital with more X and Y contribution more destabilized.

Crystal Feild splitting comparison

Splittings are given wrt Δ_0 related to a common barycentre

As you lower the symmetry of the molecule, the geometry of the structure changes which affects the degeneracy of its d orbitals.

Extension to allow covalency.

CFT is purely based on electrostatic attraction.

Although improbable, this successfully explains structure of complexes, their spectra and magnetic properties by simple calculations. ↳ Using Orgel diagram which uses electronic terms.

But there are evidences of covalent bonding —

- $Ni(CO)_4$ – zero oxd^n state ⇒ no electrostatic attraction. Thus, bonding must be covalent.
- Order of ligands in spectrochemical series can't be explained by electrostatic interactions alone
- Evidence of covalency by NMR (coupling b/w nucleus) and EPR (hyperfine ~~techni~~ splitting due to nuclear spin of M), showing $e^{\ominus}$ density on ligands → suggests sharing of electrons
- Racah parameter : introduced to explain the interpretation of spectra, allowing some covalency.

$B \rightarrow h + k$: covalent char. of metal & ligand

Molecular Orbital Theory.

Here, we study how the orbitals of ligands interact with 3d, 4s and 4p orbitals to form molecular orbitals.

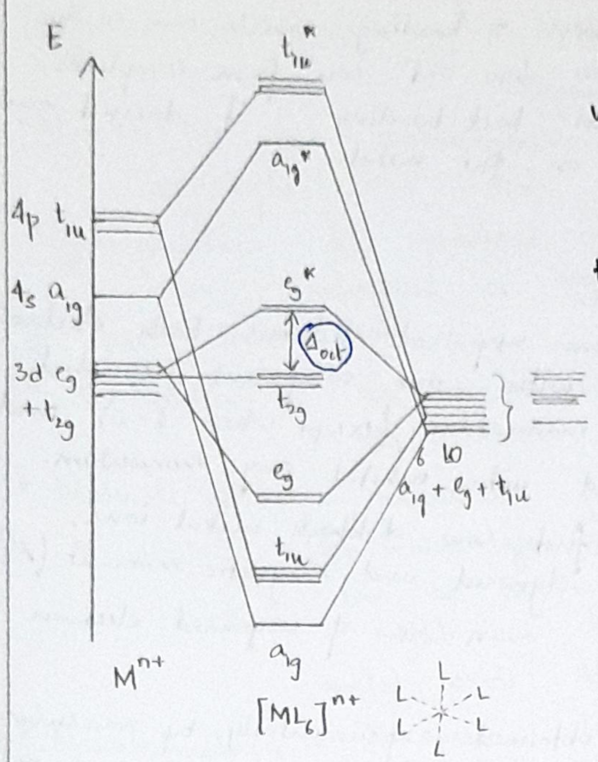
As the t_{2g} orbitals (d_{xy}, d_{yz}, d_{xz}) exist between the axes, they don't interact with L.O.

4s orbital combines with L.O to form a_{1g} and a_{1g}^* MOs.

Representation of these ligand group orbitals come from Symmetry adopted linear combination (SALC) i.e ligand orbitals take different shapes when you operate the octahedral crystal feild in the molecule

Similarly, e_g and 4p interact with LO to form corresponding bonding and anti-bonding MOs

Total : 12 molecular orbitals.



Approximate MO diagram for $[ML_6]^{n+}$ using ligand group orbital approach

Bonding only involves M–L σ-interaction in this diagram

t_{2g} : Non-bonding e^0s.

12 e^0s from ligands take up a_{1g}, t_{1u} & e_g orbitals. So, metal electrons occupy t_{2g} and e_g^*

⇒ CFT representation in CFT

→ Octahedral Co^{3+} complexes

$[Co(NH_3)_6]^{3+}$ $[CoF_6]^{3-}$

$Co^{3+} \to d^6$ ⇒ 6 electrons

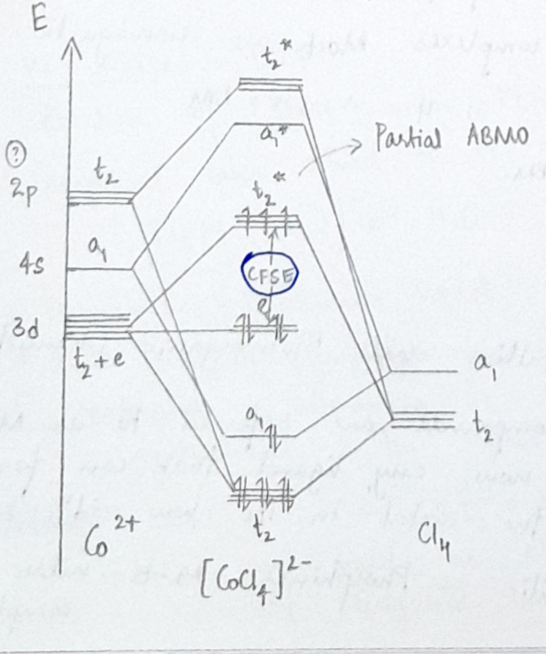
P for Co^{3+} : 19 000 cm^{-1}

Δ_0 of $Co(NH_3)_6$: 23,000 cm^{-1} ⇒ Low spin : t_{2g}^6 e_g^0

Δ_0 of CoF_6 : 13000 cm^{-1} ⇒ High spin : t_{2g}^4 e_g^2

2p t_{1u} ?

→ Tetrahedral Co^{2+} complex



e in Co^{2+} doesn't have a matching orbital set in M-L σ-bond. So its non-bonding orbital

MOT and CFT have strong resemblances but they differ fundamentally in how they describe M-L bond, with MO being more realistic and provide better quantitative prediction of properties.

MOT explains magnetic properties and spectra of complexes equally.

Both depend on spectra to measure Δ values

- MO has advantage to covers π-bonding, which can easily explain how metals in low oxd^n can form complexes. CFT can't explain such back-bonding ∵ it doesn't assume any -ve charge on the metal.

Magnetic Properties.

- Paramagnetism comes from unpaired electrons. Each electron has magnetic moment with one component associated with spin angular momentum (except when $l = 0$) and second component associated with orbital ang. momentum.
- For simple complexes of first row d-block metal ions, second component is ignored and magnetic moment (μ) –

$\boxed{\mu = \sqrt{n(n+2)}}$ n: no. of unpaired electron

- Effective magnetic moment – obtained experimentally by measuring molar magnetic susceptibility χ_m & is expressed in Bohr magnetons : $\mu_B = \frac{eh}{4\pi m_e} = 9.27 \times 10^{-24}\ JT^{-1}$

$$\mu_{eff} = \sqrt{\frac{3k\chi_m T}{L\mu_0\mu_B^2}}$$

L: Avagadro no. k: Boltzmann const.
μ_0 : vacuum permeability.

$$\mu_{eff} = 2.828\sqrt{\chi_m T}$$ (Gaussian units)

- d^8 complexes $Ni(CN)_4^{2-}$ and $NiCl_4^{2-}$ can be distinguished by their magnetic properties.

Similarly for d^7 Co^{3+} complexes. Most are diamagnetic.

$[CoF_6]^{3-}$: paramagnetic : $n = 4 \Rightarrow \mu_{calc}$ = BM

Observed μ = 5.3 BM.

28/12/20

Lecture 21st Dec

Introduction to Organometallics and Bioinorganic Chemistry

- Traditionally, organometallic compounds are referred to as M–C bonded system. But now, any ligand that can form a σ bond & stabilize the metal in its low oxd^n state is considered organometallic – Phosphines, M–B, nitric oxide complexes.

- Difference in terminology : Metal-organic ($Ti(OMe)_4$)
  Organometallic (R_4Ti) - direct M-C σ bond

M - CN is not organometallic ∵ -CN need M to be at a higher oxd^n state

- Organometallics has provided conceptual insights, useful catalysts for industrial & organic synthesis

It has links with -

* Biochemistry - use of enzymes in organometallic catalysis
Eg: Acetyl CoA synthase

* Materials science - precursors for Metal Organic Chemical Vapor Deposition (MOCVD) (for which you need volatile compounds; metal alkyls can be sublimated & when M-C bond breaks, metal ions deposit as thin film), metal and metal oxide surfaces

* Nanotechnology - to prepare electronic, magnetic & optical devices

* Green chemistry - minimizing energy & chemical waste, atom economy (simple byproducts) etc.

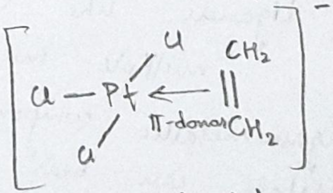
Historic Background

1. Cacodyl oxide - Cadet, 1760, Paris military pharmacy.
Discovered during Cadet's work on Co-based invisible ink containing As impurities.

$$As_2O_3 + 4CH_3COO^-K^+ \longrightarrow [(CH_3)_2As]_2O$$ - Cadet's fuming liquid

2. W.C. Zeise - 1827
Reaction of EtOH with $PtCl_2 + PtCl_4$ in presence of KCl
Compound later solved to be -

$$[Cl_3Pt(C_2H_4)]^-K^+ \cdot H_2O$$



Dewar - Chatt - Duncanson model

DCD Model

\# Et_2Zn - highly pyrophoric - hard to handle

3. E. Frankland - attempting to prove the presence of organic radical synthesized the first compound with metal-alkyl σ bond.

Attempt: $2EtI + Zn \rightarrow ZnI_2 + 2Et\bullet$ Actual: $2EtI + 2Zn \rightarrow Zn(Et)_2 + ZnI_2$

$Zn(Et)_2$ was used as alkylating reagent, later replaced by Grignard reagent (1900)

4. Ferrocene (1951)

Miller – from Fe and dicyclopentadiene

Pauson & Kealey – from $CpMgBr + FeCl_3$ – proposed a σ-bonded str.

Wilkinson & Fisher – proposed the sandwich structure η^5-Cp rings involved in π-bonding

5. Zeigler's Polymerisation (1953)

Ethylene → Polyethylene using catalyst : $TiCl_4 + \overset{\text{Promoter}}{AlEt_3} \rightarrow \underset{\text{Active catalyst}}{Ti-Et}$

Natta's group : stereoregular polymerisation of propylene and buta-diene was developed using modified catalysts.

6. Wacker's Process

Conversion of ethylene → acetaldehyde.

Both have profound impact on growing petrochemical industry

Parallely, novel, unprecedented complexes like Vaska's complex, dinitrogen compounds, carbene complexes etc were developed & potentially investigated for various other catalytic processes

↓ 2nd gen ligands ↓ Grubb's catalyst

18-electron rule

3 types of bonded systems –

i) Metal alkyl single bond – –R are σ-bonding ligands (donor) like Cl, H_2O, NH_3 etc

ii) Large variety of ligands (in organometallics) are soft and can π bond (donor) Eg: Ethylene, benzene, cyclopentadiene

iii) Ligands like CO, NO, phosphenes, carbenes etc. can bond with multiple interactions involving σ-donor & π-acceptor bonds.

Organometallic compounds are different because –

- * Metals can bear a greater -ve charge
- * M–L bonds are more covalent & can π bond
- * d-$e^\ominus$ are higher in energy & can perturb (via back donation) the electronic structure of ligands. ⇒ These ligands can be easily polarised and activated towards reactions
- * Most rudimentary basis of controlling structure & reactivity of OMC is 18-$e^\ominus$ rule and back bonding

18 $e^{\ominus}$ rule

Sidwick - 1927 - based on VB formalism of localised M-L bonds

Its an extension of octet rule - tells us whether d-block organometallic complex is stable.

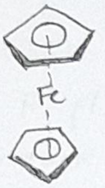
Statement : "Thermodynamically stable transition metal complexes are formed when sum of metal d-$e^{\ominus}$ and electrons conventionally regarded as being supplied by the ligand equal 18."

Very evident from its MO diagram

Conventions -

1. Intermolecular partitioning of electrons has to ensure that total charge of the complex remains unchanged

Eg:



Ionic

$2\,Cp^- - 2(6)\,e^{\ominus}$

$Fe^{2+} - 6\,e^{\ominus}$

Oxd^n state approach

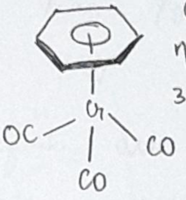
Covalent

$2\,Cp - 10\,e^{\ominus}$

$Fe - 8\,e^{\ominus}$

$18\,e^{\ominus}s$

Neutral atom approach ✓



$Cr(0) - 6\,e^{\ominus}$

η^6-$C_6H_6 - 6\,e^{\ominus}$

$3\,CO - 3(2)\,e^{\ominus}$

$18\,e^{\ominus}$

2. Metal-metal bond contributes 1 electron to the total $e^{\ominus}$ count of a metal atom

Eg: $Mn_2(CO)_{10}$ - $[Mn(CO)_5]_2$

$1.\ Mn - 7\,e^{\ominus}$

$5\ CO - 5(2)\,e^{\ominus}$

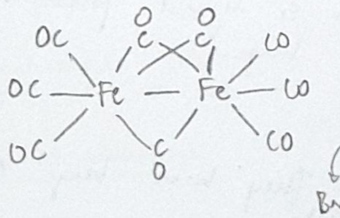
$Mn-Mn - 1\,e^{\ominus}$

} $18\,e^{\ominus}$

This rule can also be used to back-calculate no. of metal-metal bonds

3. Electron pair of the bridging ligand donates 1 electron to each of the bridging atoms.

Eg: * $Fe_2(CO)_9$



$Fe \rightarrow 8e^{\ominus}$

$Fe-Fe \rightarrow 1\,e^{\ominus}$

$3\,CO \rightarrow 6\,e^{\ominus}$

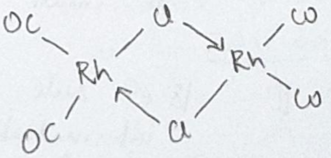
3-μ-$CO \rightarrow 3e^{\ominus}$

$18\,e^{\ominus}$

Bridging

Square planar complexes are exceptions to 18 $e^{\ominus}$ rule

* $Rh_2Cl_2(CO)_4$



Exception.

$Rh(0) \rightarrow 9\,e^{\ominus}$

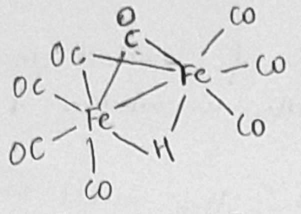
$2.\ CO \rightarrow 4\,e^{\ominus}$

μ-$Cl \rightarrow 3\,e^{\ominus}$

16 electrons

Bridging Cl gives $3\,e^{\ominus}$ - 1 to one Rh and $2\,e^{\ominus}$ to other Rh

*



$[HFe_2(CO)_8]^-$

Fe (0) → 8 $e^\ominus$

3 CO → 6 $e^\ominus$

Fe-Fe → 1 $e^\ominus$

2 μ-CO → 2 $e^\ominus$

μ-H → ½ $e^\ominus$

-1 charge → ½ $e^\ominus$ ⇒ 18 $e^\ominus$ Rule

Advantage -

Considerable predictive value to arrive at the composition of many transition metal complexes.

This rule breaks down for early & late d-block metals. 16 $e^\ominus$ complexes are favored for Rh (I), Ir (I), Pd (0) and Pt (0) compounds. Its because they majorly form square planar structures ⇒ less no. of ligands.

Consider MO diagram of octahedral complex - Pg. 81

18 electrons in $Co(CO)_6$ occupy orbitals similar to that of $[Co(NH_3)_6]^{3+}$. So, the guiding principles of 18 $e^\ominus$ rule are -

- * ABO shouldn't be occupid
- * NBO may be occupied
- * BO should be occupied

(?) # In a π bonding situation, NBO t_{2g} split into BMO & ABMOs. In σ-bonding situation, t_{2g} remains as NBO.

Based on these consideration, complexes are differentiated into -

→ Class I : 18 $e^\ominus$ rule not obeyed Eg: $[TiF_6]^{2-}$ (12), $[VCl_6]^{2-}$ (19)?, $Zn(en)_3^{2+}$ (22)

12 - 22 $e^\ominus$s They are formed when Δ_o is small & σ-donor ligands are weak field ligands.

→ Class II : 18 $e^\ominus$ rule is not exceeded & ligand fields are intermediate and Δ_o is large.

Eg: $[ZrF_6]^{2-}$

→ Class III : 18 $e^\ominus$ rule is always obeyed. They have large Δ_o and ligand fields are very strong.

Eg: CO, NO, phosphenes

Lecture 12b – recorded

29/12/20

Nature of ligands & modes of bonding : $\boxed{\sigma\text{-bonded}}$

→ Simplest ligands & bonding – σ-bonded alkyl, aryl and related ligands.

M–C bond can be described as 2c-2e⁻ interaction

Examples –

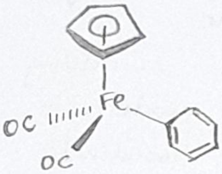
Transmetallation : $TiCl_4 + 4LiMe \xrightarrow[193K]{Et_2O} TiMe_4 + 4LiCl$

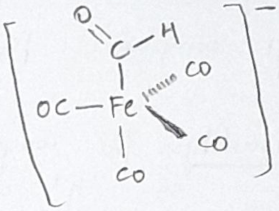
$$WCl_6 + 3Al_2Me_6 \longrightarrow WMe_6 + 3Al_2Me_4Cl_2$$

$$MoF_6 + 3ZnMe_2 \xrightarrow[143K]{Et_2O} MoMe_6 + 3ZnF_2$$

$$MoMe_6 \xrightarrow[\text{in } Et_2O,\ 258K]{\text{excess LiMe}} [Li(Et_2O)]^+[MoMe_7]^-$$

Others examples – Fe – C_{ph}





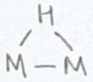
Fe – C_{CHO}

→ Hydride ligands

M – H

Terminal

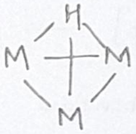
2c – 2e⁻



μ – H

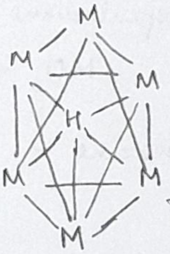
Bridging

3c – 2e⁻



μ_3H

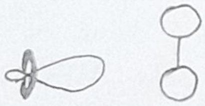
4c – 2e⁻



Endohedral or Interstitial hydride μ_7–H

7c – 2e⁻

Dihydrogen as ligand : σ complex



Vacant metal orbital – sp^3d^2

Filled σ – MO

H₂ – M donation

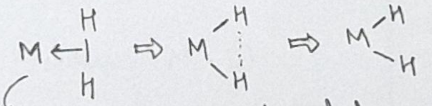
Filled metal d_{xz}

Vacant σ*

M – H₂ back donation

→ Directly $M\langle^{H}_{H}$ is formed.

Metal and H₂ can form a σ complex where H₂ acts as an edge-on ligand

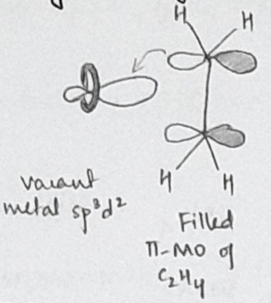


↳ When metal atom is electron poor.

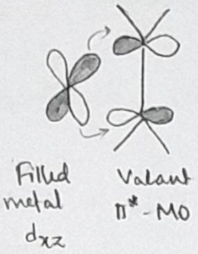
π donors

M − C bond is formed by π-electron donation of ligands

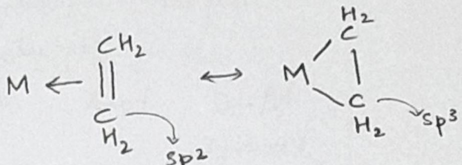
Eg: ethylene, cyclo octa-di-ene



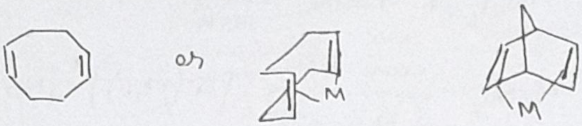
Alkene − M donation



M − alkene back donation.



Like Zeisse salt



Others examples −

1. π - allyl complex : $[C_3H_5]^-$: -ve charge is delocalised over the molecule

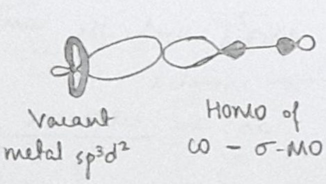
Fluxionality : The complex keeps switching between η^1 and η^3 mode

- Buta-diene can switch between coordinate complex & 5-member ring
- Cyclopentadiene − has η^1, η^3 and η^5 modes

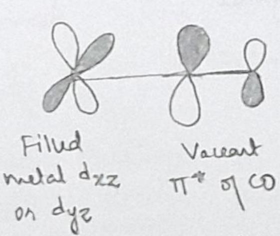
$$MCl_2 + 2Na[Cp] \longrightarrow (\eta^5\text{-}Cp)_2M + 2NaCl$$

- Benzene - Eg: bisbenzene chromium.

σ - donors and π - acceptors − CO



CO − M donation



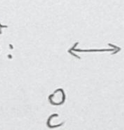
M − CO back donation.

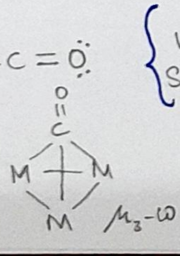
If back-bonding is very strong, a double bond is formed b/w M−C, weakening the C−O bond.

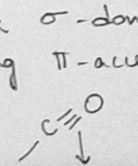
$$:\overset{-}{M} - C \equiv \overset{+}{O}: \longleftrightarrow M = C = \ddot{O}$$

{Weak σ - donor
Strong π - acceptor}

M − C≡O







Semi-briding ligand

π-e^0 cloud of C≡O donates to M

$M \equiv C = O$: Depending on M-C bond strength, the C-O bond is weakened or strengthened, bee which can be mapped using IR spectroscopy ∵ C-O bond stretches based on the strength of back-bonding.

Region : $1600\ cm^{-1}$ to $1800\ cm^{-1}$

Methods of synthesis –

$$\overset{3+}{CrCl_3} + CO + \underset{\text{Reducing agent}}{LiAlH_4} \xrightarrow[Et_2O]{390K,\ 70\ bar} \overset{0}{Cr}(CO)_6 + LiCl + AlCl_3 + H_2$$

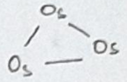
$$WCl_6 + Fe(CO_5) \xrightarrow{373K} W(CO)_6 + FeCl_2$$

$$OsO_4 + CO \xrightarrow{520K,\ 350\ bar} Os(CO)_5 + CO_2$$

$$\xrightarrow[MeOH]{400K,\ 200\ bar} Os_3(CO)_{12} \longrightarrow 48e^{\ominus}/3 = 16e^{\ominus}$$

⇒ 2 metal-metal bonds each

Total : 3 M-M



$$2Fe(CO)_5 \xrightarrow{h\nu} Fe_2(CO)_9 + CO.$$

$$\xrightarrow{\Delta} Fe_3(CO)_{12}$$

→ **Phosphine ligands**

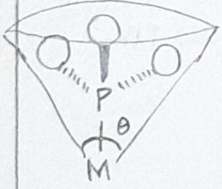
Extent of σ-donation & π-acceptance can be varied based on the substituents.

Eg $-PR_3$: poor π acceptor

$-PF_3$: poor σ-donor & strong π-acceptor (due to χ of F)

π-accepting property –

$$PF_3 > \underbrace{P(OPh)_3 > P(OMe)_3}_{\text{Phosphites}} > \underbrace{PPh_3 > PMe_3}_{\text{Phosphines}} > P^tBu_3$$

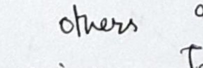


No. of phosphine ligands around a metal atom is decided by θ – cone angle parameter.

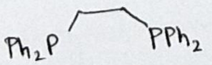
212° – $P(M_3C_6H_2)_3$

107° – $P(OMe)_3$

PPh_3 and P^tBu are more sterically demanding, while others are less so. Steric requirements are assessed using Tolman cone angle.



DPPM



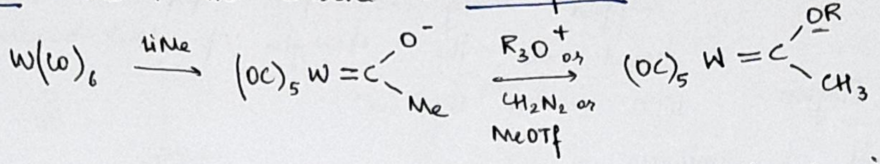
DPPE

: very strong σ-donor ⇒ firmly bound to M

✱ Phosphines and carbenes are good spectator ligands. ✱

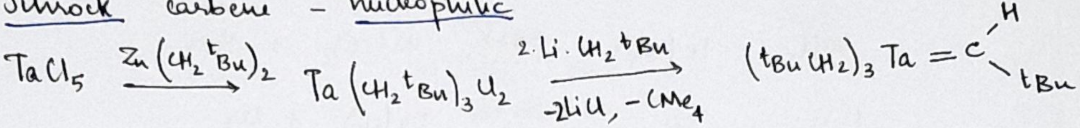
→ Carbenes

* Fisher carbene : the carbene is electrophilic



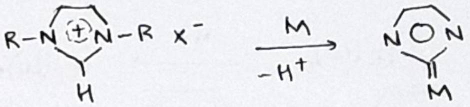
Fisher carbenes are identified by heteroatom in the indicated position

* Schrock carbene - nucleophilic



This was an accidental discovery.

* N-heterocyclic carbenes :



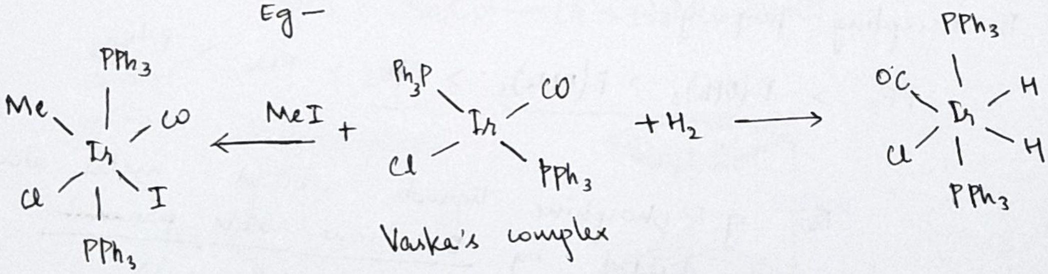
\# They're backbone for 2nd gen Grubbs catalyst.

Reactivity : Oxidative addition and Reductive elimination.

→ Oxidative addition

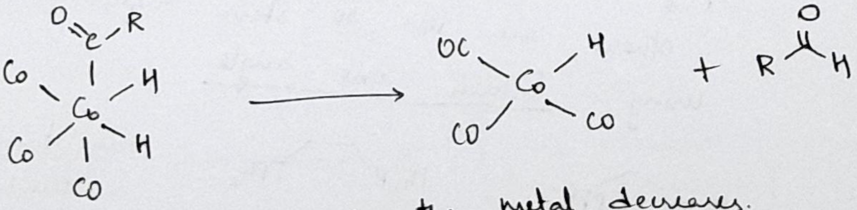
Oxdⁿ no. of M increases by 2 and C.N of metal also increases by 2

Eg -



→ Reductive elimination

Eg : Conversion of acyl group to aldehyde



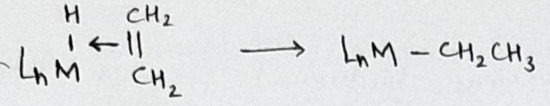
Here, the oxdⁿ no. of the metal decreases.

→ Insertion (migration)

* Alkene insertion — Oxdⁿ no. of M doesn't change

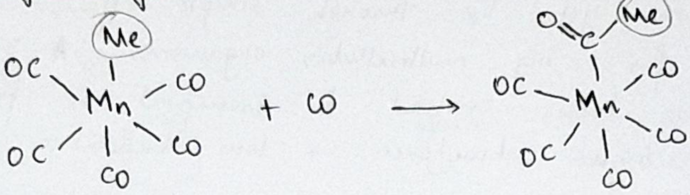
\# During insertion, metal hydride is ~~inserted with~~ reacted with alkene at some partial pressure

16e$^{\ominus}$ complex

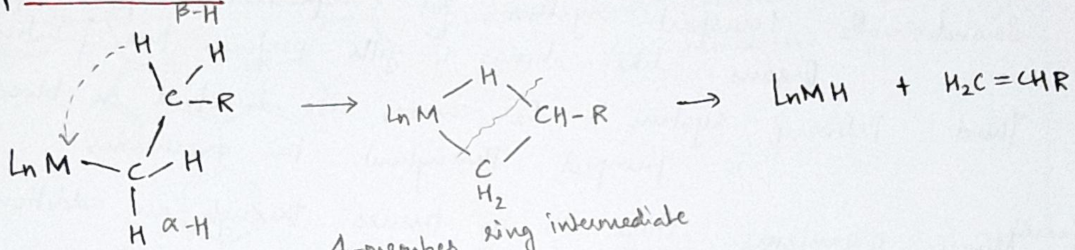


π complex

* Alkyl migration — Also elimination (~43:20). How ??



→ β - Elimination.



4-membes ring intermediate

$L_nMH\ (\eta^2 - RCH=CH_2)$

In some rare cases, the α-H is eliminated (Eg: Shrock carbene)

30/12

Live lecture - 23rd Dec

Bioinorganic chemistry

When considering chemistry of biological processes, boundary b/w inorganic and organic is blurred.

* Elements — C, H, N, O (4 most abundant)
Na, K, Ca, Mg, P, S and Cl

* C, H, N, O - fundamental elements that make up building blocks of biomolecules

P, S - ATP, DNA, cystine residue in proteins

* Role of less abundant but essential elements -

Na, K, Cl - nerve action & osmotic control

Mg^{2+} - chlorophyll & enzymes involved in phosphate hydrolysis

Ca - structural functions (bone, teeth, shell), triggering action in muscles

* Trace metals - V, Cr, Mn, Mo, Zn, Cu, Ni, Fe | Non-metals - B, Si, Se, F, I

Trace metals play a very crucial role in biological function
& Biomimetic chemistry

Oxygen metabolism

* O_2 is used in various biochemical processes. Most are consumed in the reaction : $4H^+ + O_2 + 4e^- \rightarrow 2H_2O$
— terminal step of oxidative phosphorylation.

* Small organisms get O_2 through simple diffusion. This isn't fast enough for big multicellular organisms. A 3-component system has been evolved to transport O_2 from regions of high abundance → low abundance

* First : O_2 carrier protein based on Cu or Fe active sites
Eg: Hemoglobin, hemocyanin, hemoerythrin

Second : O_2 transport system for sequestration of O_2 by the protei
Organs like lungs & gills perform this function

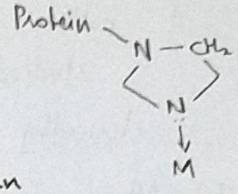
Third : Delivery system — O_2 carrier is dissolved in blood that is pumped throughout the organisms

* Many organisms store O_2 in tissues through an additional O_2-binding protein like myoglobin

Hemoglobin & Myoglobin

- Hb picks up O_2 from lungs/gills to tissues where it is stored by Mb. It serves as O_2 reserve which can be accessed during increased metabolism or O_2 deprivation
- Mb also regulates O_2 flow within cells and buffering of O_2 partial pressure within cell in response to increased or decreased O_2 ~~sy~~ supply.
- As a ligand, O_2 resembles CO, NO & N_2
It doesn't have enough dipole moment to contribute to σ-bond
So, it binds under high partial pressure
CO enhances back-bonding better than O_2.
- O_2 : soft ligand with weaker π-bonding capacity
Fe(II) wouldn't bind to ~~O_2~~ soft ligands. But symbiotic softening action of tetrapyrrole ring of porphyrin facilitates O_2 binding.
- Truly soft CO binds to heme group even more tightly ⇒ CO poisoning.

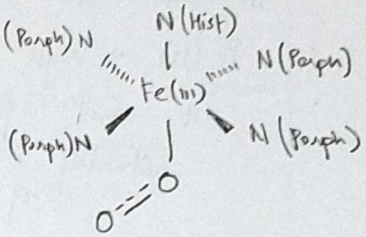
Mb – M. wt. 17,000 with 153 amino acid residues, folded about a single heme group.



Hb – M. W. 68,000, 4 hemes bound to 4 protein chains – 2α and 2β.

α – 141 amino ā   β – 146 amino ā

similar to Mb



Active site

The actual active site contains amino ā residues, carboxyl groups etc. It can be modelled through

Tetra Phenyl Porphyrin – TPP.

When they wanted to study its reaction with Fe & O_2 – The 2° amine got deprotonated and formed covalent bonds with Fe^{2+} while other two nitrogens formed coordinate bonds.

Oxygen metabolism

When PFe^{II} was made to react with O_2, it underwent irreversible oxidation & formed a μ-~~per~~oxo dimer known as hematin

$$PFe^{II} + O_2 \rightleftharpoons PFe^{II}O_2 \rightleftharpoons PFe^{III}O_2^- + PFe^{II}$$

$$\downarrow$$

$$2\,PFe^{IV}=O \longleftarrow 2.\,PFe^{III}-O^{\bullet} \longleftarrow PFe^{III}O-OFe^{III}P$$

Ferryl complex   μ-peroxo complex

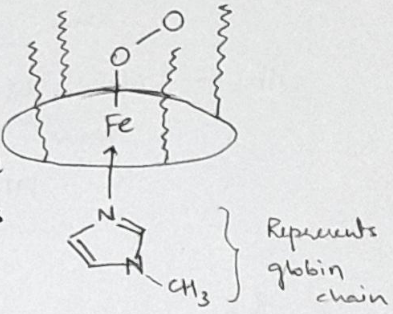
$$PFe^{IV}=O + PFe^{II} \longrightarrow PFe^{III}-O-Fe^{III}P$$

Hematin

Living systems frustrate the above reactions (otherwise all the heme would precipitate) through steric hinderance from the Globin part

First proof obtained for this by anchoring heme on a polymer matrix which reversibly bind O_2.

A better model with more steric hinderance was studied — Picket-fence heme — which had sterically hindered heme.



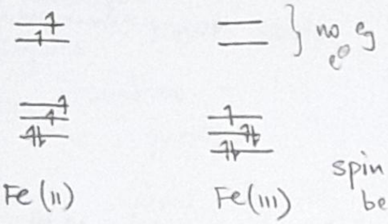
In Mb —

* Fe(II) - high spin d_6 - 92 pm, square pyramidal
  It can't fit in the porphyrin ring, its actually 42 pm above the plane of N-atoms of the ring.

* O_2 binding makes it Fe(III) and low spin. So its radius is lowered to 75 pm, which fits in the ring.

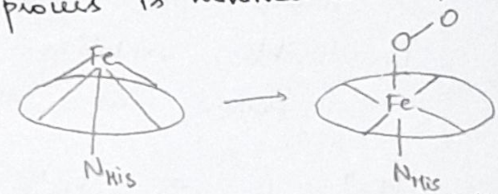
Electrons in e_g repel the ligand $e^{\ominus}$s so there's a spherical expansion of radius in Fe(II) high spin.

Spin pairing the Fe(III) radius in absence of e_g electrons.



lone $e^{\ominus}$ on Fe(III) & O_2^- com
in antiferromagnetic coupling
↑
spin-silent - no EPR signal
because ligand: O_2^-

Though the net effect of this process is minimal in Mb, its important in Hb.



O_2 binding in Hb

Four heme units in Hb bind and release O_2 in a cooperative process which is visualised as communication b/w heme groups arising from conformational changes in protein chains

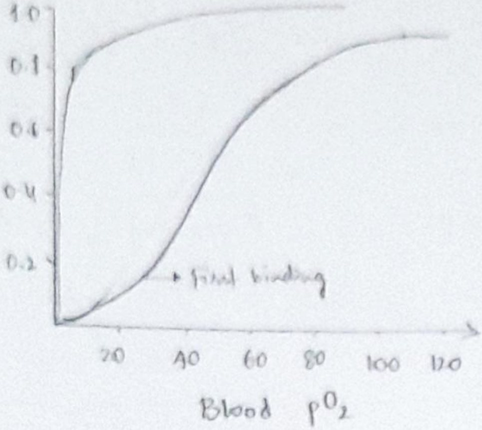
When 1st heme group binds to O_2, the iron centre (low spin Fe^{3+}) moves into plane of porphyrin ring and pulls His residue with it. This perturbs its protein chain and those of other 3 groups also. This triggers the successive 'vacant' heme groups to bind with O_2 more freely. In fact, affinity of 4th group ~300 times that of 1st one.

When O_2 is released from Hb, the loss of first O_2 molecule triggers the release of the other 3 molecules.

So, $Hb + 4O_2 \longrightarrow Hb(O_2)_4$

$Hb(O_2)_4 + 4Mb \longrightarrow 4Mb(O_2) + Hb$

When Hb release O_2, it picks up H^+, which helps in creating more HCO_3^-, helping in CO_2 [illegible] transport.



This cooperative mechanism was proposed by <u>Perutz</u>