3.3.5. Formal Charges on Lewis Structures

Application: Where there is more than one Lewis structure possible (resonance structure) on the basis of the octet rule, formal charges provide a method to determine the most stable, lowest energy structure.

Rules

1. Formal charges on individual atoms in the molecule must sum to the overall charge on the molecule.
2. The most stable structure: (i) has a formal charge of zero on all atoms or the minimum possible charge separation, (ii) places negative charge on the most electronegative atoms.

Note: Formal charges do not necessarily represent real charges on atoms.

Calculation of Formal Charge

valence - lone pair - bond pair

Formal Charge (FC) = (number of valence electrons in uncombined atom) - (number* of lone pair electrons on bound atom) – ½(number of electrons in bonds to the atom)

*Note: If there is one lone pair that is counted as 2 electrons (i.e. don't put '1' into the equation).

Example 1: Determination of formal charge on N in NH_3

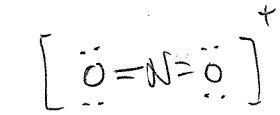
N has a electronic configuration of $[He]2s^22p^3$ giving 5 valence electrons; N has a single lone pair (2 electrons), there are 6 electrons in the bonds to N. The formal charge is thus calculated as:

no of valence e = 5
e⁻ lone pair = 2
½ Bond electrons = 3

$FC = (5 - 2) - ½ (6)$

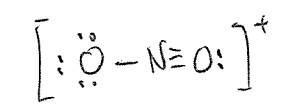
$FC = 0$

Example 2: Determination of formal charges in two alternative Lewis structures of NO_2^+

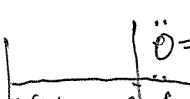
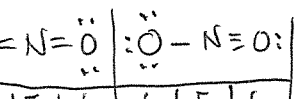


FC=
no. of valence e⁻ = 5
e⁻ lone pair = 0
½ bond pair e⁻ = 4

FC = 5-0-4 = 1



FC:
no. of valence e⁻ = 5
e⁻ lone pair = 0
½ bond pair = 4

					
Valence e	6	5	6	6	5	6
lone pair e	4	0	4	6	0	2
½ bond pair	2	4	2	1	4	3
FC	0	1	0	-1	1	1

1 more stable
↳ least charge separation
0, 1, 0 => 1
-1, 1, 1, => 2

CHEM 10021: Bonding & Molecular Structure, Dr Gareth Law

Lecture 4: VSEPR Theory and Bond Polarity (Semester 1, week 2)

LEARNING OUTCOMES

After learning the material introduced in this lecture, you should be able to:

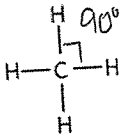
- Recognise that VSEPR theory is a useful method for predicting the geometry of molecules;
- Appreciate that the starting point for application of VSEPR theory to a molecule is to draw the Lewis structure of that molecule;
- Apply VSEPR theory to any given molecule in order to predict its shape;
- Include assumptions needed about chemical bonding in your application of VSEPR theory to a given molecule;
- Recognise polar bonds and identify whether molecules will have a dipole, taking into account the shape of the molecule.

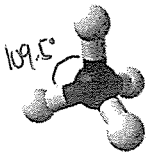
LECTURE NOTES

4. Molecular Geometry: VSEPR Theory and Bond Polarity

4.1. VSEPR - Background

- The shape of a molecule plays a large part in determining its function (reactivity).
- This is true for small molecules as it is for larger macromolecules (see PABA example given on Blackboard; note this is optional reading and as such won't be examined).
- VSEPR is a method for predicting molecular shape (geometry).
- VSEPR stands for Valence Shell Electron Pair Repulsion.
- The central concept in VSEPR theory is that valence electrons in a molecule repel each other because of their like charge (i.e. negative charge). Because of this they want to get as far away from each other at possible.
- Take the Lewis structure of CH_4 (methane) as an example. In the Lewis structure (below) the valence electrons in each bonding pair are at 90° to each other. Is this as far away from each other as they can get? In short, no, and VSEPR gives us a way to find a better geometry (e.g. the below tetrahedra).





4.2. VSEPR Assumptions and Rules

4.2.1. Assumptions

- Atoms in a molecule are bonded together by electron pairs (further more than one pair may bind two atoms i.e. multiple bonding);
- Atoms in a molecule can possess electron pairs that are not involved in bonding (lone pairs).

4.2.2. Rules

- Bonding pairs (bp) and lone pairs (lp) around an atom adopt positions in which their interactions with other electron pairs are minimised.
- A lone pair occupies more space than a bp.
- Multiple bonds (i.e. double and triple bonds) occupy more space than a single bond.

4.3. Procedure for Predicting Molecular Geometry using VSEPR Theory

(i) Draw a Lewis structure of the molecule or ion;

(ii) Count the number of bp's and lp's on the central atom (count multiple bonds as single electron pairs during this step but don't forget about the multiple bond(s) in step (iv));

(iii) Establish the geometry of the electron pairs around the central atom (i.e. points of negative charge around the atom). Assign this to an available geometry (this is called the parent geometry). (The available options are detailed in section 5 of these lecture notes);

(iv) Establish factors that would cause distortion away from ideal angles (the ideal angles for each geometry are shown in section 5 of these notes). (The factors that can cause distortion are listed in section 4 of these lecture notes);

(v) Assign the final molecular geometry based on the positions of the atoms.

NOTE: It is important that you learn and become comfortable with applying the below procedure. In the exam if you are asked to apply VSEPR to predict molecular geometry, you must include working using the below procedure; failure to do this could result in a loss of marks.

4.4. Factors Causing Distortion of Bond Angles

- Where all bonds are single, a sequence of repulsion strength applies which takes the following order: lp-lp > lp-bp > bp-bp.

4.8. More VSEPR Exercises

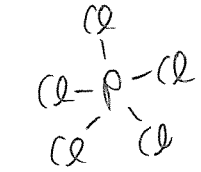
Below are two more VSEPR problems that I want you to complete in your own time. The answer to these will be uploaded in the 'annotated' version of these lecture notes. We will also do more VSEPR exercises in the next PASS session and in the next quiz.

Finally, here is the URL to a website that may help if you struggle with this content:

http://www.shef.ac.uk/chemistry/vsepr

Problems:

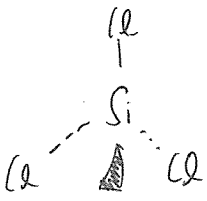
(A) Determine the molecular geometry of PCl_5



5 bond pair
0 lone pair
no distortion factors
Parental geometry
↳ trigonal bipyramidal

∴ trigonal bipyramidal

(B) Determine the molecular geometry of $SiCl_4$



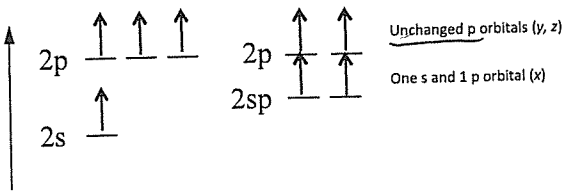
tetrahedral

4 bond pairs
0 lone pair
no distortion factors
Parental geometry
↳ tetrahedral

5.5.3. Bonding in Alkynes – ethyne (C_2H_2) as an example

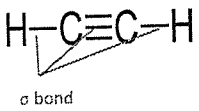
H—C≡C—H

- Triple bonds occur occasionally in natural molecules.
- Carbon forms TWO equivalent σ bonds to TWO other atoms (linear).

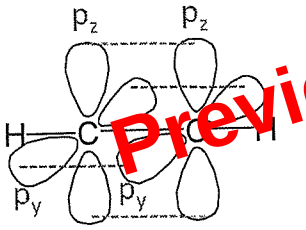


electron promotion → sp hybrid state

- sp hybrid orbitals have a greater degree of s character due to 50 % s and 50 % p.
- Linear geometry of σ bonds around carbon.

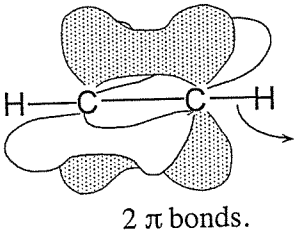


What about the remaining two 2p orbitals and their unpaired electrons?



These are perpendicular to each other and to the direction of the sp orbitals.

overlap



2 π bonds.

If assume p_x forms the hybrid orbital then p_z & p_y overlap to form 2 π bonds.

Triple bond = σ bond + 2 π bonds

- In general, you can expect that carbon will be sp hybridised when directly bonded to 2 other atoms.

Summary

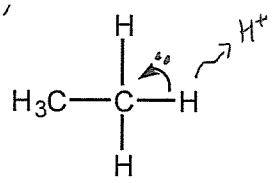
- In the orbital hybridisation model, *hybrid atomic orbitals* are formed such that an atom has a number of *equivalent* AOs;

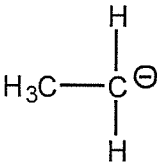
6.2.2. The Acidity of Hydrocarbons

- Consider alkanes, alkenes and alkynes (sp^3, sp^2 and sp hybridised respectively); as s character increases, it is ___easier___ to remove a proton (H^+). Importantly, the more 's' character of the resulting carbanion – the more acidic it is (it holds tightly to the available LP).

The greater the S character, the closer is the electrons.

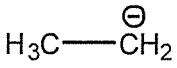
Conjugate base more stable

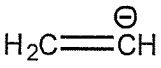


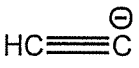


carbanion

conjugate base

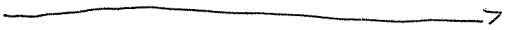






furthest from nucleus

closest to nucleus



"S" character / acidity ↑ as conjugate base stability ↑

NOT because of ease of removal of H^+

↳ non-carbon atoms which are confined an organic molecules.

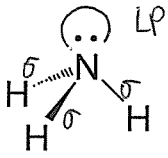
6.3. Heteroatoms in Organic Molecules (N, O, S and halogens)

6.3.1. Molecules Containing sp^3 Hybridised N

Example: Ammonia (NH_3)

- N is ___sp^3___ hybridised.

LP also contained in hybrid orbitals approach

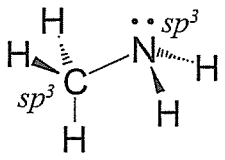


- Substitution on ammonia → amines. ↳ has a lone pair of e^- on nitrogen atom

↳ R groups

- VSEPR theory can predict geometry. Orbital hybridisation accounts for this geometry (4 equivalent sp^3 orbitals around N, one of them the lone pair).

e.g. methylamine



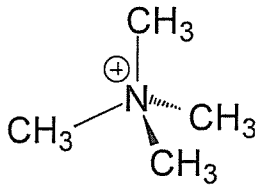
Primary amine or 1° amine (1 C attached to N)

Reactivity of N

- In the previous amine examples, the N lone pair is available (in an sp^3 orbital) to interact with an electrophilic (electron-deficient) species to form a covalent bond.

- In doing so N effectively loses one electron and becomes positively charged.

e.g.



Tetramethylammonium ion: a quarternary ammonium ion.

- The N in amines can act as a Lewis base;
- The availability of lone pair is an important factor in the reactivity of amines;
- sp^3 hybrid orbital has low s character, therefore electrons on average are further from nucleus and thus are more available;
- sp^3 hybridisation at N makes lone pair more available and therefore a stronger base.

Hybridisation and Lone Pair Availability

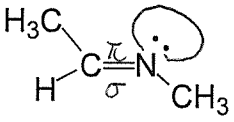
Compare:

Amines > Imines > Nitriles

sp^3 sp^2 sp

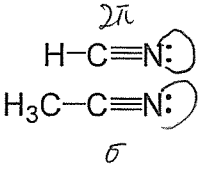
→ s character ↑

Imines ⇒ double bond between C & N



- Both C & N are sp^2 hybridised (both planar geometry);
- σ bond from sp^2 orbital overlap; (axial overlap)
- π bond from remaining p orbital overlap;
- Lone pair is in an sp^2 orbital;
- Reflecting this, imine is less basic than amines (electron pair less available).

Nitriles ⇒ triple bond between C & N



- Both C & N are sp hybridised (both linear);
- Lone pair occupies sp orbital;
- Nitrile less basic than amines and imines.

• lone pair of electrons less available

Part 2: Non-covalent Bonding Interactions

6.4. General

Non-covalent bonding interactions can be extremely important interactions in chemistry and biology:

- Can occur inter- or intramolecularly; ↳ between diff molecules ↳ within 1 molecules
- Intramolecular interactions influence shape and stability of a macromolecule;
- Intermolecular interactions affect physiochemical properties and are the basis for selective molecular recognition between molecules.
- Two general types of non-covalent interaction: Non-polar and polar.
  ↳ molecules w/ ort molecular dipole ↳ molecules with molecular dipole

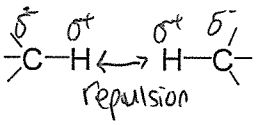
6.5. Non-Polar (Hydrophobic) Interactions

Dispersion forces and Van der Waals interactions : 0.4 kJ mol^{-1}
↳ London dispersion force

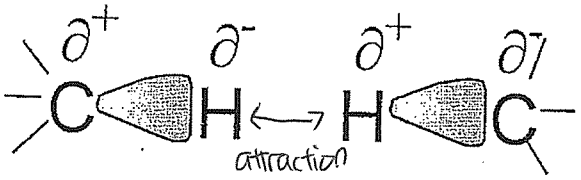
- Proximity of another molecule can affect the charge separation between a nucleus and electrons of an atom at a given instant in time:

C – 2.4 δ⁻
H – 2.2 δ+

e.g.



- The C—H bonds of the neighbouring molecules generally repel each other; however, the bonds are moderately ___(repulsive)___.



- If on one molecule, the electron density shifts closer to the H atom at a given instant, this has an effect on the other molecule e.g. electron density shifts closer to C atom. Thus a dipole in one molecule can induce a temporary dipole in another molecule. This can cause a net ___attractive___ force.

CHEM 10021: Bonding & Molecular Structure, Dr Gareth Law

Lecture 7: Chemical Bonding III – Molecular Orbital Theory (Semester 1, week 4)

LEARNING OUTCOMES

After learning the material introduced in this Lecture, you should be able to:

- Know that the number of MOs formed is equal to the number of AOs that combine to form them;
- Appreciate that the phases of atomic orbitals must be considered in the molecular orbital theory of chemical bonding;
- Know the type of MOs that can form from in-phase or out-of-phase linear combination of AOs;
- Draw orbital diagrams depicting how σ MOs are formed from s AOs;
- Describe the criteria for formation of a stable molecule using molecular orbital theory;
- Draw diagrams depicting how particular MOs are formed from p AOs; both σ, σ* and π, π* MOs;
- Draw energy level diagrams showing formation of σ and σ* orbitals from linear combination of s, p, or hybrid orbitals, and show their electron occupation;
- Draw energy level diagrams showing formation of π and π* MOs from p orbitals;
- Draw energy level diagrams depicting molecular orbitals formed for simple diatomic molecules, showing their electron occupation.

LECTURE NOTES

7. Chemical Bonding III – Molecular Orbital Theory

Note: Some extra reading is highly recommended to reinforce learning of Molecular Orbital Theory – See Bruice, 4th Ed. page 20 – 25 and also other 1st year chemistry texts like Ebbing and Gammon 'General Chemistry', 9th Ed. page 399 – 405.

7.1. General Information on Molecular Orbital Theory and a Comparison

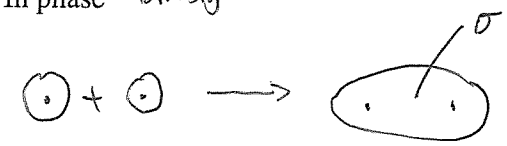
- Bonding and molecular structure has been covered in several ways between L3-6: Lewis Structures; VSEPR theory; VBT with HOA;
- VBT: bonds result from the sharing of electrons in overlapping orbitals between two atoms (centres) – i.e. bonding electrons are confined between two atoms in a molecule;
- The treatment of electrons in Molecular Orbital Theory (MOT for short) is different;
- In MOT we postulate that the combination of AO's on different atoms in a molecule form molecular Orbitals (MO's);
- The MOT model results in electrons in molecules occupying MO's (electrons belong to the molecule as a whole or shared between several atoms in the molecule);
- Molecular orbitals are formed by a linear combination of atomic orbitals (LCAO);
- VBT and MOT are alternative descriptions of bonding in molecules and each has its strengths and weaknesses (thus you must learn both techniques).

7.2. Atomic Orbitals and Wave Functions - Consequences For the Construction of Molecular Orbitals

(ii) Diagrams of AO surface boundary overlap:

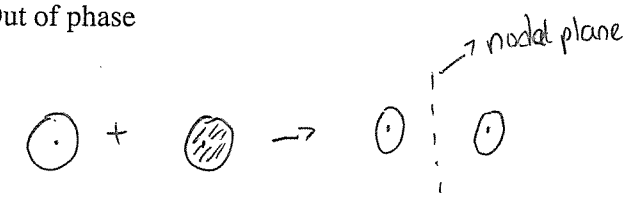
σ and σ* orbitals

(a) In phase – form sigma bond



Building up of electron density between nuclei – forms a σ bonding MO.

(b) Out of phase



Point of zero electron density between nuclei – form a σ* antibonding MO.

π orbitals – see page 69 of Bruice (and also later in Lecture notes and in Fleming and Gammon).

In summary: * antibonding

(a) Combination of AO's in phase

- Bonding MO;
- Build up of electron density between nuclei;
- Symbol σ (electron density build up on bonding axis between nuclei);
- Symbol π (electron density build up alongside bonding axis between nuclei; see later in lecture).

(b) Combination of AO's out of phase

- Antibonding MO;
- Node (point of zero electron density) between nuclei;
- Symbol σ * or π* (for π* see later in lecture).

7.4. Properties of Molecular Orbitals

- The number of MOs generated is equal to the number of AOs from which they arise i.e. 2 x AOs give 2 x MOs (very important to remember);
- MOs have different energy levels;
- MOs are filled in order of increasing energy, and AUFBAU, Hund's Rules, and the Pauli exclusion principle are all obeyed (i.e. fill MO's from bottom (lowest energy), fill MO's singly before pairing, 2 electrons (opposite spin) can occupy each MO).

1.6 Key Features of Resonance Structures (Summary)

If a molecule or ion can be represented by 2 or more structural formulae that can be interconverted, by just interchanging bonds, it is more stable.

The different contributing structures are known as resonance structures and are linked by a resonance arrow. resonance form

Resonance structures are also known as ~~canonical~~ canonical structures.

Resonance structures must have the same total number of electrons.

Delocalisation of electrons in overlapping p orbital requires contributing orbitals to be in plane.

Resonance structures are not always equal (*i.e.* contribute equally to the average).

Where they do, then the stabilisation afforded by resonance is greater. Neutral (minimise separation of charge) resonance structures are the major contributors.

Molecules with localised charges contribute less. Out of such structures, those with negative charge on the more electronegative atom will contribute more.

minor contributor

major contributor

To Sum up…

The examination may require the following skills and knowledge.

1. Be able to draw simple equilibria between *acids and their conjugate anions* and between *ammonium cations and the corresponding neutral amines*.
2. Describe the concept of resonance and realise that resonance is the delocalisation of electrons within a p-system.
3. Describe the hydridisation and geometry of a molecule involved in resonance.
4. Be able to draw curved arrows showing the interrelation of resonance structures.
5. Recognise that greater delocalisation results in greater stability.
6. Identify, giving reasons, the most stable resonance structure.

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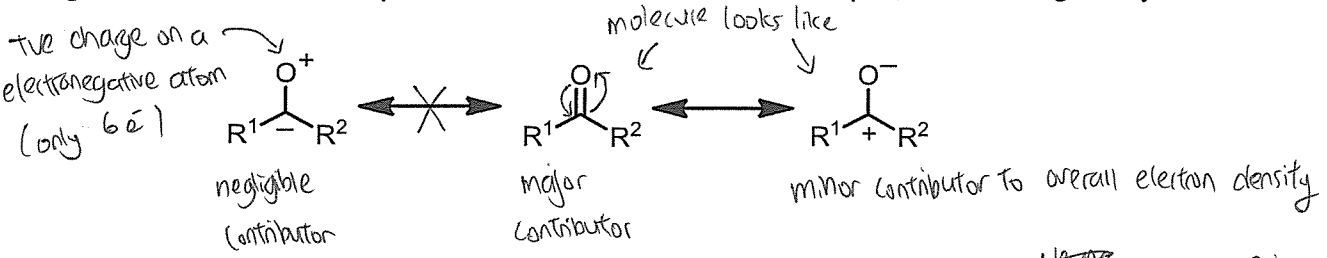
MIB 2.014

Lecture 2:
Resonance - The Chemistry of Unsaturated Functional Groups

2.1 Some Further Examples of Resonance

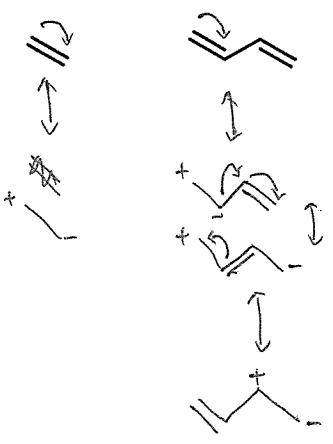
Resonance is characteristic of **π-systems** - double bonds, triple bonds, lone pairs.
Charge distribution will depend on other factors, for example, electronegativity.

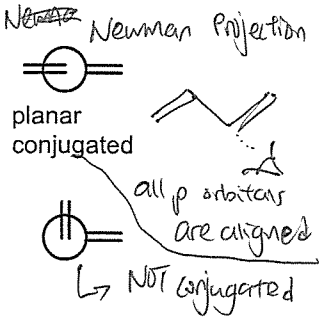


Conjugated Double Bonds
Adjacent π-systems extends the overall MO.

↑ no of resonance forms
↑ ē delocalisation
↑ stability of ions

Ethane **Butadiene** **1,4-Pentadiene**





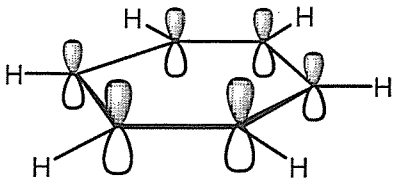
MO Theory Explanation of C_6H_6 Stability

Huckel's rule can be generalised to the number of electrons for benzene-like behaviour being **(4n + 2)** π-electrons (where n = 0, 1, 2, 3 *etc*).

Benzene, n=1 → 6π electrons

Huckel proposed a delocalised model for the benzene structure which explains the dependence on electron numbers.

Linear: n=0



↳ all p AOs are in phase

Regular hexagon of 6 sp^2-hybridised C-atoms .

σ-framework (C-C and C-H): sp^2 hybrids and hydrogen 1s AOs.

π-framework: delocalised MOs from the 6 p-AOs on the carbon atoms.

The Huckel formalism for planar regular conjugated arrays always has one low energy orbital and the others paired in energy as far as possible.

In this case the scheme generates *three bonding MOs* and *three antibonding MOs*.

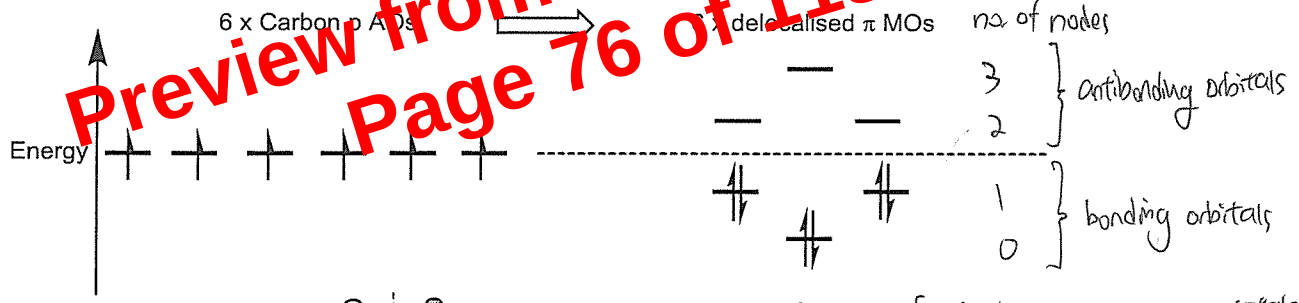
The MO *energy* increases as the number of *nodes* increases.

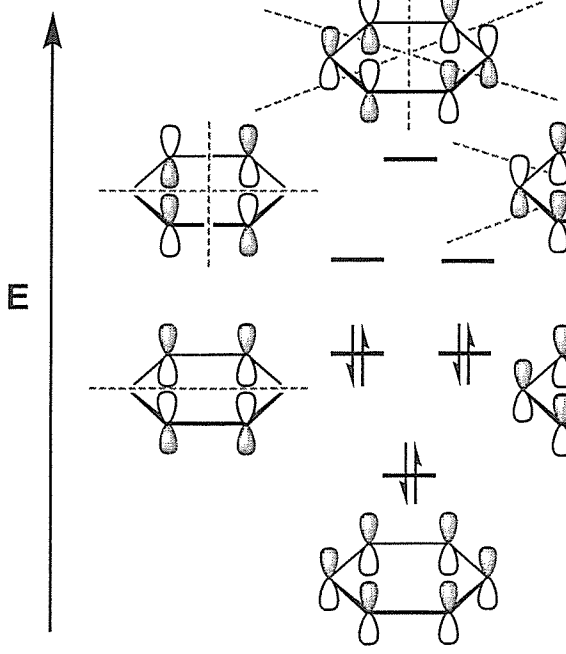
↳ change of phase in MO

With 6 electrons, only the bonding MOs are populated.

*In benzene, all electrons are in bonding orbitals, hence all e⁻ are in low energy MO, hence ... ↓ Stability

↳ nodes, ↓ sharing / delocalisation





↳ no sharing of electrons as all p orbitals NOT in phase at all.

degenerate orbitals
↳ same no. of node(s)
↳ same energy

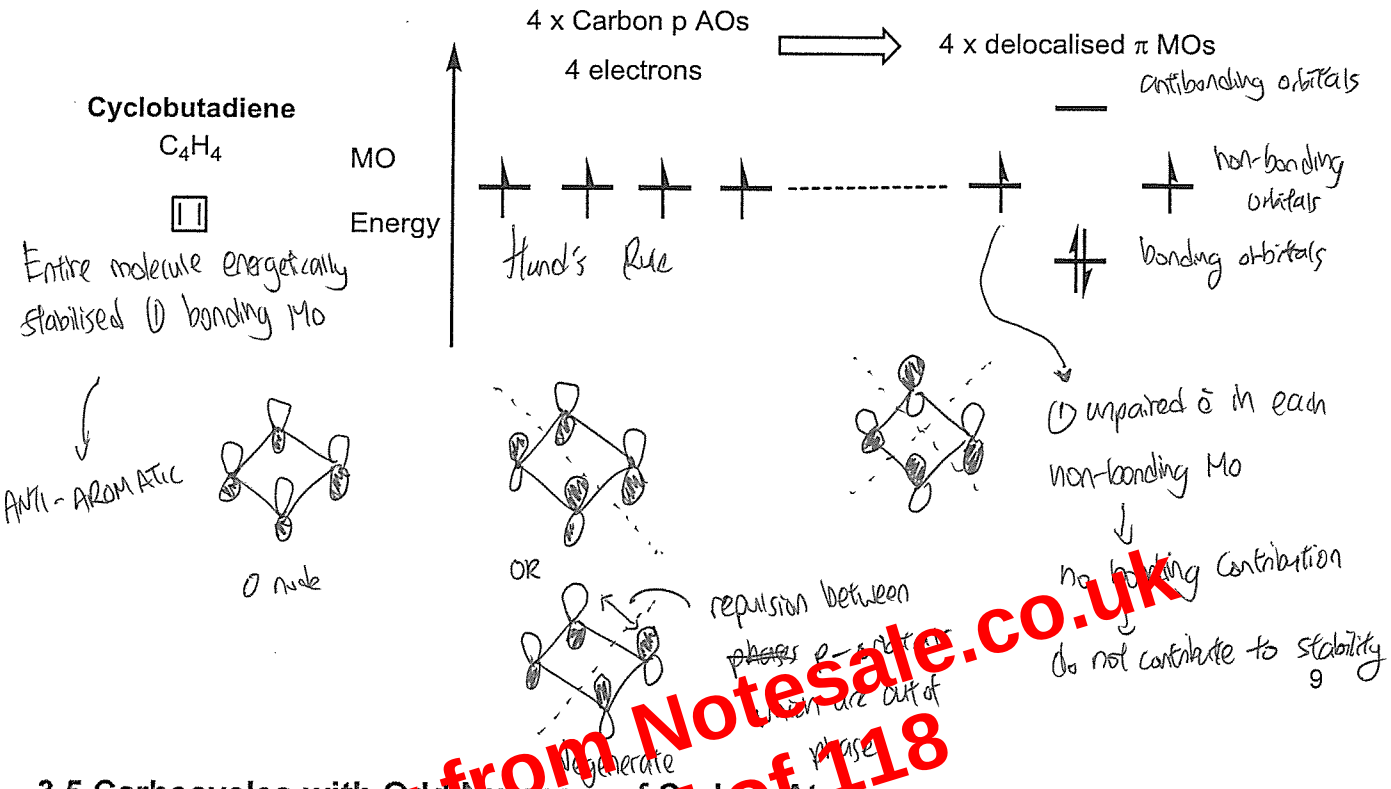
less delocalisation / sharing when compared to 0 nodes

↳ Most stable as all p orbitals are in phase

↳ 4n π electrons system n≥1

3.4 Anti-Aromatic Stuctures

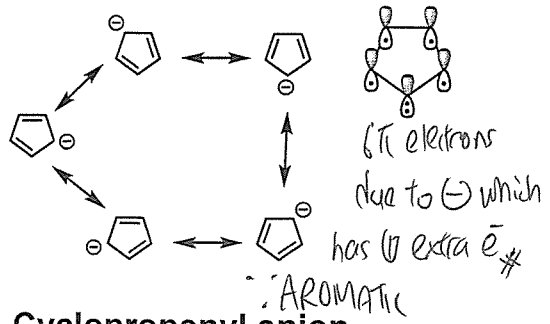
Conjugated cycloalkenes have different numbers of p AO making up their π-array, *e.g.* cyclobutadiene. Analysis of the MOs can reveal why aromatic stabilisation is absent.



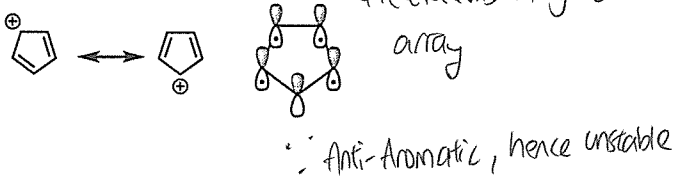
3.5 Carbocycles with Odd Numbers of Carbon Atoms

Fully conjugated species must be charged.
Counting the electrons will help decide which charged cyclic hydrocarbons display enhanced stability and which might be especially unstable.

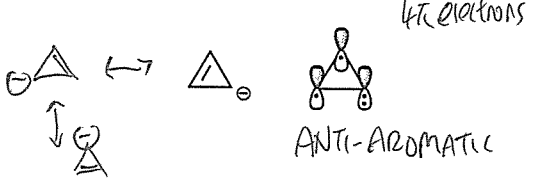
1. Cyclopentadienyl anion



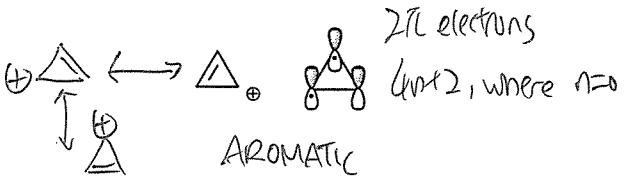
2. Cyclopentadienyl cation



3. Cyclopropenyl anion



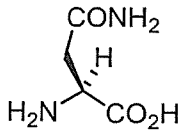
4. Cyclopropenyl cation



The answers are based on Huckel's (4n + 2) rule. Do not learn these structures but be able to work out whether or not the given structure is aromatic.

7.8 Chirality and Life

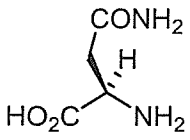
Most of the molecules of life are chiral. In general enantiomers may show entirely different physiological responses, *e.g.*



L-aspargnine

Sweet

to the taste

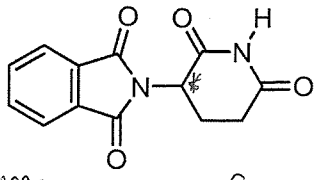


D-aspargnine

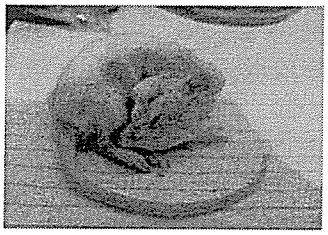
Bitter

to the taste

Thalidomide

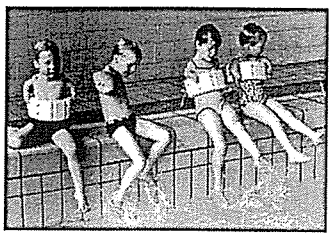


R - enantiomer



Sedative

S- enantiomer



Teratogen

The chemistry of life is highly stereoselective

Proteins comprise only *L*-amino acids, nucleic acids use only D-ribose. Enzymes only will catalyse reactions work on one enantiomer.

To Sum up…

The examination will be set to test the following skills and knowledge.

1. Define the terms: *constitutional isomers*, *stereoisomers*, *enantiomers*, *racemic mixture*, and *diastereoisomers, meso.*
2. Identify all of the possible stereoisomers of a given compound.
3. Identify stereogenic centres at carbon and non-carbon atoms.
4. Appreciate the importance of chirality to living things.
5. Assign stereoisomers of stereogenic centres witihin previously unseen molecules using the rules outlined in the lecture, *i.e.* be able to assign *R/S* as appropriate when given a structural diagram.

You do **NOT** need to learn the specific structures of molecules introduced in this lecture: you will **NOT** be asked draw structures from memory in the examination. You will be expected to carry out the tasks indicated when given a structure, *e.g.* identify a stereogenic centre, assign a stereogenic centre, draw isomers and stereoisomers.

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Integrated Rate Laws : 1st order [A → P]

$$-\frac{d[A]}{dt} = \frac{d[P]}{dt} = k[A]$$

↝ [A] decays exponentially from its initial value

↝ the expression should be in the form of ln([A]/units)

$$\ln[A] = \ln[A_0] - kt$$

$$[A] = [A_0]e^{-kt}$$

$$-\int \frac{1}{[A]} = \int k\,dt$$

$$-\ln[A] = kt + c$$

$$\ln[A] = \ln[A_0] - kt$$

Integrated Rate Laws : 2nd order

↳ equal initial concentration

A commonly used rate law for a 2nd order reaction : A+A → P $-\frac{dA}{dt} = k[A]^2$

$\int y^{-2}$

Is $-\frac{d[A]}{dt} = k[A]^2$

$$-\int [A]^{-2} = \int k\,dt$$

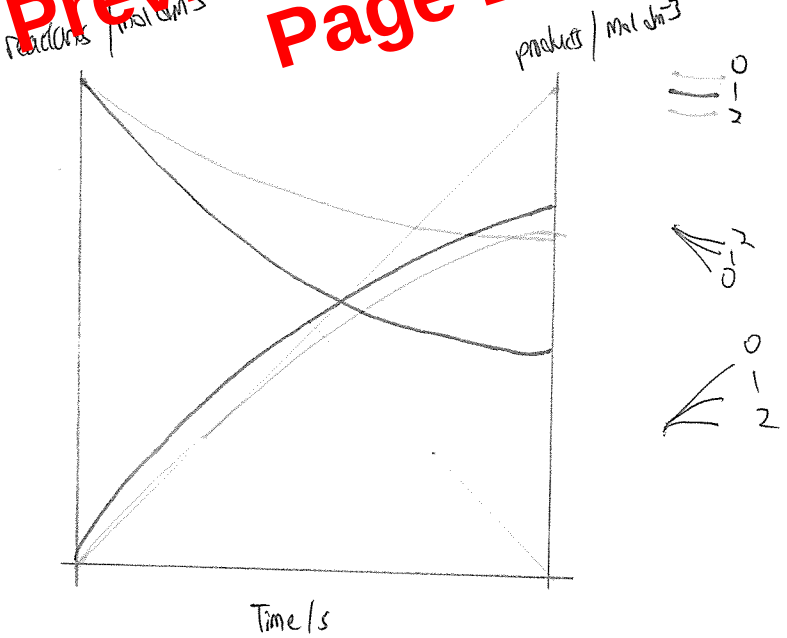
$$\frac{1}{[A]} = kt + \frac{1}{[A]_0}$$

Integration...

$$\frac{1}{[A]} = \frac{1}{[A]_0} + kt$$

* [A] is always concentration of reactants, TAKE NOTE if question is [products] instead

The same rate law applies for a 2nd order reaction [illegible] provided [A] = [B]



* only in zeroth order reaction, concentration of reactants will go to zero *

* Always write ln(A_0/mol dm-3) to cancel out the units *

=> Concentration as a function of time for different reaction orders

Notation:

A vertical bar | denotes phase boundary eg: Ag | AgCl | Cl^-

2 vertical bars || indicate connection

A redox electrode for a couple ox/red are denoted M | red, ox

Cell Potential:

The zero-current cell potential / emf is the voltage measured between LHS & RHS electrodes with no current flowing.

* Biological standard potential at pH = 7 *

For the cell

Pt | NADH, NAD^+, H^+ || H_2O_2, H^+, O_2 | Pt

right hand cell eqn: $O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$

left " " : $NAD^+ + H^+ + 2e^- \rightarrow NADH$

cell reaction $H^+ + NADH + O_2 \rightarrow NAD^+ + H_2O_2$

E^θ = standard potential which has the standard hydrogen electrode as LHE and the ox/red at the RHE.

$E^\circ_{cell} = E^\circ_R - E^\circ_L$ [reduction - oxidation] * A reaction high up the ECS will drive ① lower down into reverse *

$E^\circ > 0$ Spontaneous reaction

ECS - electrochemical series

Strong oxidizing agent has ↑ +ve E° values

Strong reducing agent has very -ve E° values

Cell Potentials & Thermodynamics:

For a cell reaction which transfers v electrons,

F = Faraday constant = 96485 C mol^{-1}

$\Delta_r G^\circ = -vFE^\circ$ → remember for spontaneous change, $\Delta_r G^\circ < 0$

&

$\Delta_r S^\circ = \frac{vF\,dE^\circ}{dT}$ → $\Delta_r S^\circ > 0$

The Nernst Equation for a half cell equation $Ox + Ye^- \rightarrow Red$

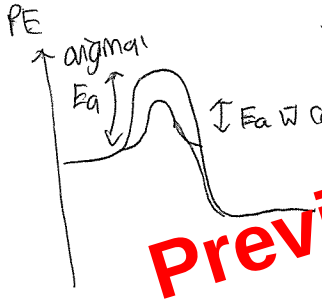
$$E = E^\circ - \frac{RT}{vF} \ln Q$$

$Q = [Red]/[Ox]$ ← for non-standard cell potentials

↳ reaction quotient

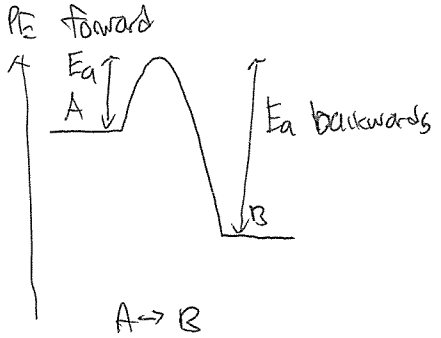
Catalysts:

- catalyst does not change ΔH, but ↓ E_a
- enzymes are biochemistry catalyst



A → B, rate of formation of B = $k_{forward}[A]$

B → A rate of decomposition = $k_{backward}[B]$



if temperature ↑, rate of backward reaction is increased more than rate of forward reaction

At equilibrium, rate of forward = rate of backward

↳ concentration of reactants & products remain the same!

net rate of formation of B molecules

$$\frac{d[B]}{dt} = k_f[A] - k_b[B]$$

At equilibrium, $\frac{dB}{dt} = 0$; no net formation of B → $k_f[A] = k_b[B]$, hence $\frac{d[B]}{dt} = 0$

equilibrium constant, $K = \frac{[B]_{equilibrium}}{[A]_{equilibrium}} = \frac{k_f}{k_b}$ → rate constant of forward reaction

Acid-Base reactions and Equilibria:

For deprotonation of an acid, dissociation constant — K_a

Strong acid, ↑ K_a
weak acid, ↓ K_a

K_a can be expressed as pK_a, $pK_a = -\log_{10} K_a$

HCl Monoprotic — pK_1
H_2SO_4 diprotic — pK_2
H_3PO_4 triprotic — pK_3

} multiple pK values

pK_1 - 1st proton
pK_2 - 2nd proton
pK_3 - 3rd proton

For amino acids, pK_1 refers to COOH group

pK_2 — NH_2

pK_3 — side chain

* Dissociation of triprotic acid, eg: phosphoric acid

$H_3A \rightarrow H^+ + H_2B^-$ $\quad K_1 = \dfrac{[H^+][H_2B^-]}{[H_3A]}$ → total $[H^+]$ in the solution, NOT just $[H^+]$ due to 2nd proton dissociation

$H_2B^- \rightarrow H^+ + HB^{2-}$ $\quad K_2 = \dfrac{[H^+][HB^{2-}]}{[H_2B^-]}$

$HB^{2-} \rightarrow H^+ + B^{3-}$ $\quad K_3 = \dfrac{[H^+][B^{3-}]}{[HB^{2-}]}$

Dissociation constant of H_2O, K_w

$K_w = [H^+][OH^-]$; $[H_2O]$ is omitted by convention. $K_w \neq K_{eq}$ as K_{eq} involves $[H_2O]$

In biochemistry, dissociation constant, K_d is an equilibrium constant that measures the propensity of a larger object to dissociate into the smaller object/components.

dissociation constant is the INVERSE of association (binding) constant

For general reaction, $A_xB_y \leftrightarrow xA + yB$

$K_d = \dfrac{[A]^x[B]^y}{[A_xB_y]}$