CONCEPT MAP

REACTIVE INTERMEDIATES

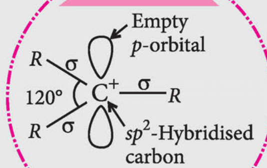
Intermediates which are short-lived species generated during conversion of reactants to products in a chemical reaction. They play an important role in various organic synthesis as well as in biological world.

Class XI | Class XII

Carbocation ($\rangle C^+$)

Carbon species carrying +ve charge on carbon having only six electrons in its valence shell.

Structure



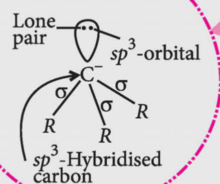
Stability

- More the number of alkyl/aryl groups present, greater is the stability.
- Electron donating groups increase the stability whereas electron withdrawing groups decrease the stability.
- The decreasing order of the stabilities of carbocations :
$(Ph)_3\overset{+}{C} \approx (R)_2\overset{+}{C}\text{–}CH{=}CH_2 > (Ph)_2\overset{+}{C}H \approx R\overset{+}{C}HCH{=}CH_2 > R_3C^+ > Ph\overset{+}{C}H_2 >$
$(R)_2\overset{+}{C}H > \overset{+}{C}H_2CH{=}CH_2 > R\overset{+}{C}H_2 > \overset{+}{C}H_3 > \overset{+}{C}H{=}CH_2 > \overset{+}{P}h$ or $\overset{+}{A}r$

Carbanion ($\rangle\bar{C}:$)

Carbon species carrying –ve charge on carbon having eight electrons in its valence shell.

Structure



Stability

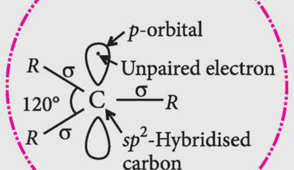
- More the number of alkyl groups present, lower is the stability.
- Electron withdrawing groups increase stability whereas electron donating groups decrease stability.
- The order of stability of carbanions :
$(C_6H_5)_2\bar{C}H > (C_6H_5)_3\bar{C} > C_6H_5\bar{C}H_2 >$ allyl $> \bar{C}H_3 >$ 1°alkyl > 2°alkyl > 3°alkyl

Note : Carbanions are sp^3-hybridised with pyramidal geometry. Due to steric hindrance of three phenyl (Ph–) groups, and to acquire pyramidal geometry, lots of energy is required due to which Ph_3C^- is less stable than Ph_2CH^-.

Free Radical ($\rangle\dot{C}$)

Atom or a group of atoms having odd or unpaired electron having seven electrons in its valence shell. They are highly unstable, electrically neutral and short-lived species.

Structure



Stability

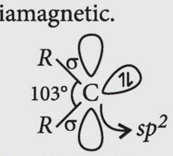
- More the number of alkyl groups present, greater is the stability.
- Allyl and benzyl free radicals are more stable than alkyl free radicals due to resonance effect.
- Greater the number of phenyl groups, more stable is the free radical.
- The order of the stability of free radicals is
$(C_6H_5)_3\dot{C} > (C_6H_5)_2\dot{C}H > C_6H_5\dot{C}H_2 > CH_2{=}CH\dot{C}H_2 >$
3°alkyl > 2°alkyl > 1°alkyl > $\dot{C}H_3 > CH_2{=}\dot{C}H > HC{\equiv}\dot{C}$

Carbene ($:CH_2$)

Neutral, divalent carbon species in which two non-bonding electrons are present along with two bonding pairs (*i.e* having sextet of electrons).

Singlet

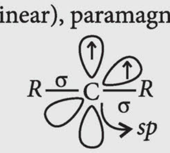
sp^2-hybridised (bent), diamagnetic.



Electrophile

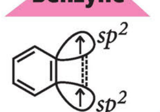
Triplet

sp-hybridised (linear), paramagnetic



Diradical (more stable)

Benzyne

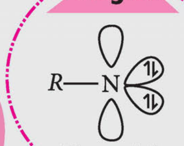


An additional bond is formed between two neighbouring carbon atoms by side ways overlapping of two sp^2-orbitals. The new bond orbital lies along with side of the ring and has little interaction with the π-electron cloud lying above and below the ring. This sideways overlapping is weak and thus, makes the benzyne more reactive.

Nitrenes or Imidogens ($R-\ddot{N}$)

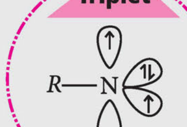
Neutral, univalent nitrogen species in which nitrogen has a sextet of electrons. They are highly reactive and act as strong electrophiles

Singlet



Electrophile

Triplet



Diradical

SOME COMMERCIAL CELLS (BATTERIES)

Batteries are cleverly engineered devices that are based on the same fundamental laws as galvanic cells. A storage cell is a galvanic cell that contains all the reactants needed to produce electricity whereas fuel cell is a galvanic cell that requires a constant external supply of one or more reactants to generate electricity.

CONCEPT MAP

PRIMARY CELLS

Cells once exhausted cannot be used again therefore, they are not chargeable.

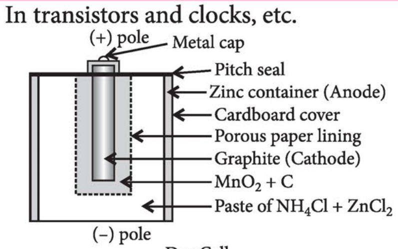
DRY CELL

Anode : $Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^-$

Cathode : $2NH^+_{4(aq)} + 2MnO_{2(s)} + 2e^- \rightarrow 2MnO(OH) + 2NH_3$

Net reaction : $Zn_{(s)} + 2NH^+_{4(aq)} + 2MnO_{2(s)} \rightarrow Zn^{2+}_{(aq)} + 2MnO(OH) + 2NH_3$

Uses : In transistors and clocks, etc.



Dry Cell

MERCURY CELL (Ruben-Mallory Cell)

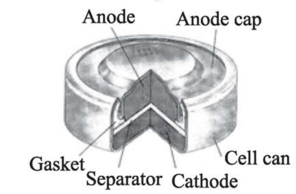
Anode : $Zn(Hg) + 2OH^-_{(aq)} \rightarrow ZnO_{(s)} + H_2O_{(l)} + 2e^-$

Cathode : $HgO_{(s)} + H_2O_{(l)} + 2e^- \rightarrow Hg_{(l)} + 2OH^-_{(aq)}$

Net reaction : $Zn(Hg) + HgO_{(s)} \rightarrow ZnO_{(s)} + Hg_{(l)}$

The cell potential is approximately 1.35 V and remains constant during its life.

Uses : In watches, hearing aids, etc.



Mercury cell
(The reducing agent is zinc and the oxidising agent is mercury (II) oxide.)

SECONDARY CELLS

Cells which can be used again and again therefore, they are chargeable.

LEAD STORAGE CELL

Cell reactions during use of battery :

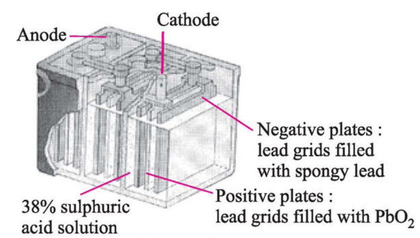
Anode : $Pb_{(s)} + SO^{2-}_{4(aq)} \rightarrow PbSO_{4(s)} + 2e^-$

Cathode : $PbO_{2(s)} + SO^{2-}_{4(aq)} + 4H^+_{(aq)} + 2e^- \rightarrow PbSO_{4(s)} + 2H_2O_{(l)}$

Net reaction :
$Pb_{(s)} + PbO_{2(s)} + 2H_2SO_{4(aq)} \rightarrow 2PbSO_{4(s)} + 2H_2O_{(l)}$

The reverse reaction takes place during recharging :
$2PbSO_{4(s)} + 2H_2O_{(l)} \rightarrow Pb_{(s)} + PbO_{2(s)} + 2H_2SO_{4(aq)}$

Uses : In automobiles and inverters.



Lead Storage Battery

NICKEL - CADMIUM CELL (or NICAD cell)

Cell reactions during use of battery :

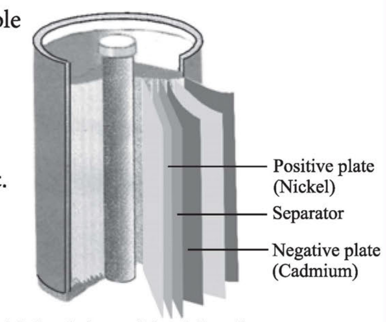
Cathode : $2Ni(OH)_{3(s)} + 2e^- \rightarrow 2Ni(OH)_{2(s)} + 2OH^-_{(aq)}$

Anode : $Cd_{(s)} + 2OH^-_{(aq)} \rightarrow CdO_{(s)} + H_2O_{(l)} + 2e^-$

Net reaction : $Cd_{(s)} + 2Ni(OH)_{3(s)} \rightarrow CdO_{(s)} + 2Ni(OH)_{2(s)} + H_2O_{(l)}$

The reverse reaction takes place during recharging :
$CdO_{(s)} + 2Ni(OH)_{2(s)} + H_2O_{(l)} \rightarrow Cd_{(s)} + 2Ni(OH)_{3(s)}$

Uses : In portable electronic devices, emergency lighting, photography equipments, etc.



A rechargeable nickel-cadmium cell in a jelly roll arrangement and separated by a layer soaked in moist sodium or potassium hydroxide.

FUEL CELLS

Cells which can convert the energy of combustion of fuels such as H_2, CO, CH_4 etc. into electrical energy.

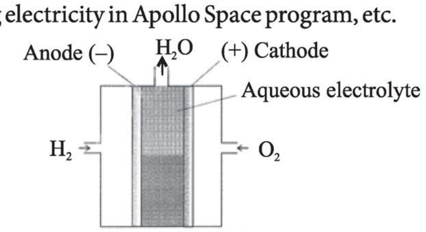
$H_2 - O_2$ FUEL CELL

Anode : $2H_{2(g)} + 4OH^-_{(aq)} \rightarrow 4H_2O_{(l)} + 4e^-$

Cathode : $O_{2(g)} + 2H_2O_{(l)} + 4e^- \rightarrow 4OH^-_{(aq)}$

Net reaction : $2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(l)}$

Uses : In automobiles on experimental basis, for producing electricity in Apollo Space program, etc.



Fuel cell using H_2 and O_2 produces electricity.

CLASSIFICATION OF FUEL CELLS

(i) Alkali fuel cells [electrolyte is $KOH_{(aq)}$] (ii) Phosphoric acid fuel cells [electrolyte is $H_3PO_{4(aq)}$]. (iii) Molten carbonate fuel cells [electrolyte is $K_2CO_{3(l)}/Li_2CO_{3(l)}$] here, methane is used as a fuel. Recently, a zinc-air fuel cell (ZAFC) is developed in USA as a source of power in automobiles in which zinc metal is used in place of hydrogen gas.