

## **University of Mumbai**

Program: \_First Year (All Branches) Engineering- SEM-II

Curriculum Scheme: Rev 2019

Engineering Chemistry-II

### **Question Bank**

***NOTE: Atomic Weights: C = 12, H = 1, O = 16, N = 14, S = 32, Na=23 and Br=80***

<b>Q1.</b>	<b>Choose the correct option for following questions. All the Questions are compulsory and carry equal marks(2 marks each)</b>
1.	Which of the following spectroscopy can be used to quantify the concentration of protein and DNA in solution
Option A:	Infra-Red spectroscopy
Option B:	UV spectroscopy
Option C:	NMR spectroscopy
Option D:	Raman spectroscopy
2.	The standard emf of the following cell is 0.012V $\text{Sn(s)} \mid \text{Sn}^{2+}(\text{aq})(1\text{M}) \parallel \text{Pb}^{2+}(\text{aq})1\text{M} \mid \text{Pb(s)}$ Calculate standard electrode potential of Sn electrode, if standard electrode potential for Pb electrode is -0.125V.
Option A:	-0.137
Option B:	-0.113
Option C:	-0.005
Option D:	-0.245
3.	In greener synthesis of indigo, traditionally used Aniline is replaced by the following substrate.
Option A:	D-glucose
Option B:	Benzene
Option C:	Toluene
Option D:	L-tryptophan

4.	Galvanization is preferred to tinning since, i) Zinc is more electro positive than iron ii) Zinc coating protects iron sacrificially iii) Punctured tin coating causes intense corrosion
Option A:	Only (i)
Option B:	Only (iii)
Option C:	(i), (ii) &(iii)
Option D:	Only (ii)
5.	Corrosion in welded stainless steel is an example of .....
Option A:	Galvanic corrosion
Option B:	Pitting corrosion
Option C:	Waterline corrosion
Option D:	Inter granular corrosion
6.	A sample of coal has following composition by mass C = 70 %, O = 8 %, H = 10 %, N = 3 %, S = 2%, Ash = 7 %. Calculate H.C.V. using Dulong formula
Option A:	8805.80kcal/kg
Option B:	8277.80 kcal/kg
Option C:	8877.80 kcal/kg
Option D:	8205.80 kcal/kg
7.	Arrange n-octane, naphthalene and isoocetane in the increasing order of their knocking tendency.
Option A:	n-octane < Naphthalene < isoocetane
Option B:	Naphthalene < isoocetane< n-octane
Option C:	Isooctane < Naphthalene < n-octane
Option D:	Isooctane = n-octane < Naphthalene
8.	A cell is constructed from Ni+ 2 / Ni and Cu+2/ Cu half cells . The standard potential of the cell is ----- . Given E0Ni = - 0.257 V and E0Cu = 0.337 V
Option A:	- 0.594 V
Option B:	0.008 V
Option C:	- 0.008 V
Option D:	0.594 V
9.	Which of the following reactions are Green in nature: Addition reactions, Substitution reactions, Elimination reactions, Rearrangement reactions
Option A:	Addition and Substitution reactions
Option B:	Rearrangement and Elimination reactions
Option C:	Rearrangement and Addition reactions
Option D:	Substitution and Elimination reactions
10.	An iron object is plated with a coating of Nickel to protect against corrosion. Does the Nickel protect iron by cathodic protection? Give suitable reason for your answer.
Option A:	No. The oxidation potential of Ni/Ni+2 is lower than that for Fe/Fe+2
Option B:	Yes. The oxidation potential of Ni/Ni+2 is lower than that for Fe/Fe+2
Option C:	No. The oxidation potential of Fe/Fe+2 is lower than that for Ni/Ni+2
Option D:	Yes. The oxidation potential of Fe/Fe+2 is lower than that for Ni/Ni+2
11.	In quantum Mechanics, a set of rule exist, known as ‘Selection rules’ that basically explains which transitions are ‘allowed transitions’. Which amongst the following statements is an ‘allowed transitions’?
Option A:	The spin quantum number of an electron doesnot change during the absorption or

	emission of light in an ‘allowed transition’.
Option B:	The change in orbital quantum number during an ‘allowed transition’ is zero.
Option C:	There is no change in magnetic quantum number during an ‘allowed transition’.
Option D:	The change in magnetic quantum number during a ‘forbidden transition’ is either zero, or +1, or -1.
12.	Small anodic area and large cathode area results in -
Option A:	Slow corrosion because of decreased demand of electrons by the small anode.
Option B:	Intense corrosion because of huge demand of electrons by the small anode.
Option C:	Slow corrosion because of decreased demand of electrons by the large cathode.
Option D:	Intense corrosion because of huge demand of electrons by the large cathode.
13.	Selection rule to produce rotational spectra is
Option A:	Dipole moment of molecule must change during vibrations
Option B:	Molecule must have permanent dipole moment
Option C:	Presence of chromophore in a molecule
Option D:	Presence of unpaired electron in a molecule
14.	Benzene is an important industrial solvent which is classified as
Option A:	Non-toxic
Option B:	Non-flammable
Option C:	Biodegradable
Option D:	Carcinogenic
15.	Which of the following statement is incorrect about an electrochemical cell
Option A:	Oxidation occurs at anode and reduction at cathode
Option B:	Chemical energy is converted into electrical energy
Option C:	Cell can work indefinitely
Option D:	Salt bridge maintains electrical neutrality of the electrolytes
16.	If a metal rod exhibits holes on its surface due to corrosion, the type of corrosion is
Option A:	Waterline
Option B:	Galvanic
Option C:	Pitting
Option D:	Stress
17.	A good fuel has
Option A:	Low ignition temperature and high calorific value
Option B:	Low ignition temperature and low calorific value
Option C:	High ignition temperature and high calorific value
Option D:	Moderate ignition temperature and high calorific value
18.	Spin multiplicity for the two unpaired electrons in excited singlet state is
Option A:	3
Option B:	2
Option C:	1
Option D:	4
19.	Which of the following green chemistry principles are applicable to the alternate synthesis of ibuprofen?
Option A:	Maximize atom economy, preventaion of waste and use of renewable feedstock
Option B:	Maximize atom economy, preventaion of waste and reduce unnecessary derivatisatation
Option C:	Maximize atom economy, use of auxillary substances and increases energy effieciency
Option D:	Prevention of waste, renewable feedstock and increased energy efficiency.
20.	Proximate analysis of coal is used to determine
Option A:	% of Nitrogen
Option B:	% of Sulphur
Option C:	% of Hydrogen

Option D:	% of Moisture
21.	Season cracking is a special case of
Option A:	Chemical corrosion
Option B:	Stress corrosion
Option C:	Concentration cell corrosion
Option D:	Waterline corrosion
22.	By which process does the knocking starts in diesel engine?
Option A:	Due to sudden spontaneous combustion of last portion of fuel
Option B:	Due to delay in spontaneous combustion of last portion of fuel
Option C:	Due to the rise in temperature of diesel engine
Option D:	Due to the presence of straight chain paraffins in the diesel
23.	Which of the metallic structure will require more impressed current density for cathodic protection?
Option A:	Water boiler
Option B:	a ship hull
Option C:	Series of underground gas pipes
Option D:	an iron pipe buried in the soil
24.	In impressed current cathodic protection, anode is provided with a gypsum backfill because
Option A:	It enhances the rate of reaction
Option B:	It decreases metal to metal contact
Option C:	It enhances electrical contact with surrounding soil
Option D:	It decreases electrical contact with soil
25.	Zn metal is corroding in the presence of acid. After sometimes corrosion stops. The reason is
Option A:	addition of few drops of CuSO <sub>4</sub>
Option B:	Increased Hydrogen overvoltage of Zn
Option C:	Decreased Hydrogen Overvoltage of Zn
Option D:	Increased diffusion of H <sup>+</sup> ions
26.	As per Pilling- Bedworth rule, Greater the specific volume ratio,
Option A:	Higher is the oxidation corrosion
Option B:	Higher is the electrochemical corrosion
Option C:	Lower is the oxidation corrosion
Option D:	Lower is the electrochemical corrosion
27.	Calculate the emf of a concentration cell at 25°C consisting of two Ag electrodes immersed in solutions of Ag <sup>+</sup> ions of 0.2M and 0.01M concentrations
Option A:	0.777V
Option B:	-0.077V
Option C:	0.0385V
Option D:	0.077V
28.	The number of waves which can pass through a point in one second. This statement justifies, from the following
Option A:	Wavelength
Option B:	Frequency
Option C:	Wave number
Option D:	Acceleration
29.	Which is not the selection rule for the electronic transitions from the following
Option A:	Spin selection rule
Option B:	Symmetry rule
Option C:	Hund's rule

Option D:	Angular momentum rule
30.	To calculate the net calorific value, the products are _____
Option A:	cooled
Option B:	collected
Option C:	allowed to escape
Option D:	heated
31.	Which one of the following is not applicable to a green reaction?
Option A:	Should not use hazardous reagents in manufacture of products.
Option B:	All the atoms of the reactants should be incorporated to give only the atoms of products
Option C:	Should not use hazardous reagents but can produce toxic products
Option D:	Should prevent accidents in chemical industries
32.	The device in which electrical energy from an external source can be used to produce chemical reactions, such device is known as _____
Option A:	Voltaic Cell
Option B:	Electrolytic Cell
Option C:	Concentration Cell
Option D:	Fuel Cell
33.	From the following which is not used as a reference electrode
Option A:	Hydrogen electrode
Option B:	Calomel electrode
Option C:	Silver/Silver chloride electrode
Option D:	Glass electrode
34.	Mechanism of electrochemical corrosion occurs due to evolution of hydrogen gas when
Option A:	Corrosive environment is acidic
Option B:	Corrosive environment is alkaline
Option C:	Corrosive environment is neutral
Option D:	Corrosive environment is alkaline and neutral
35.	Moisture and volatile matter free 3.3 gm of coal sample was ignited in muffle furnace to a constant weight of 0.252 gm of residue. What will be the percentage of ash in coal sample
Option A:	1.84 %
Option B:	11.31 %
Option C:	8.00 %
Option D:	6.63 %
36.	Which of the following metallic coating method involves hot dipping?
Option A:	Metal cladding
Option B:	Metal Spraying
Option C:	Galvanizing
Option D:	cementation
37.	For estimation of moisture content in coal sample silica crucible is heated at _____ degree Celsius
Option A:	120 degree Celsius
Option B:	105-110 degree Celsius
Option C:	925 degree Celsius
Option D:	750 degree Celsius
38.	Caustic embrittlement is which type of electrochemical corrosion?
Option A:	Waterline corrosion
Option B:	Stress corrosion
Option C:	Pitting Corrosion
Option D:	Galvanic cell corrosion

39.	_____ is not the green chemistry principle from the following
Option A:	High atom economy
Option B:	Use of catalyst
Option C:	Use of Non-renewable feedstock
Option D:	Use of green solvent
40.	Nobel metals do not undergo oxidation corrosion because it forms _____
Option A:	Unstable oxide film
Option B:	Non-porous oxide film
Option C:	Porous stable film
Option D:	Volatile oxide film
41.	Which is used as a green solvent from the following?
Option A:	Alcohol
Option B:	Acetone
Option C:	Supercritical CO <sub>2</sub>
Option D:	Concentrated Sulphuric acid ( H <sub>2</sub> SO <sub>4</sub> )
42.	Dulong's Pettit formula is used for the theoretical calculations of
Option A:	Rating of coal
Option B:	Saponification value
Option C:	Calorific value
Option D:	Sulphur from coal
43.	In which spectrum, molecule falls from excited state to ground state with the emission of photon energy?
Option A:	Electromagnetic spectra
Option B:	Absorption spectra
Option C:	Emission spectra
Option D:	Scattering spectra
44.	Which of the following is not synthesized by greener way?
Option A:	Acetic acid
Option B:	Adipic acid
Option C:	Indigo
Option D:	Carbaryl
45.	<b>Identify the true statement of the following:-</b>
Option A:	EMF series includes non metals, metals and their alloys
Option B:	EMF series predicts the corrosion characteristics of metals and alloys correctly
Option C:	position of metals in EMF series changes with the change in the environment
Option D:	It talks about the relative displacement tendencies of metals and non metals
46.	Electromagnetic spectrum is nothing but the arrangement of electromagnetic radiations according to

Option A:	Increasing order of wavelength & Decreasing order of frequency
Option B:	Decreasing order of frequency & Decreasing order wave length
Option C:	Increasing order of wavelength & Increasing order of frequency
Option D:	Not related to frequency and wavelength order
47.	Which of the following is not a principle of proper designing?
Option A:	Avoid the contact of dissimilar metals
Option B:	Anode should be smaller than cathode
Option C:	Corrosion should not be localized but uniform
Option D:	Anode should not be painted.
48.	In galvanic cell ----- energy is converted into ----- energy.
Option A:	Chemical into electrical energy
Option B:	Electrical into Chemical energy
Option C:	Chemical into Chemical energy
Option D:	Electrical into Electrical energy
49.	Corrosion between two dissimilar metals in electrical contact is which type of corrosion
Option A:	Differential aeration corrosion
Option B:	Galvanic corrosion
Option C:	Liquid metal corrosion
Option D:	Oxygen concentration cell corrosion
50.	Standard Hydrogen electrode is arbitrarily assigned ----- potential
Option A:	Zero
Option B:	Two
Option C:	One
Option D:	Three
51.	When cathodic area is large and anodic area is small then corrosion is known as
Option A:	Galvanic corrosion
Option B:	Concentration cell corrosion
Option C:	Pitting corrosion
Option D:	Dry corrosion

52.	In atmospheric corrosion, which film is developed over Aluminum, Titanium and Vanadium
Option A:	Stable porous film
Option B:	Volatile film
Option C:	Unstable film
Option D:	Stable Non porous film
53.	Intergranular corrosion is also known as
Option A:	Galvanic corrosion
Option B:	Dry corrosion
Option C:	Grain boundary corrosion
Option D:	Wet corrosion
54.	Which of the following constituent is measured in both proximate and ultimate analysis?
Option A:	Moisture
Option B:	Ash
Option C:	Volatile matter
Option D:	Nitrogen
55.	Which of the following are principal constituents of fuel
Option A:	Carbon and Hydrogen
Option B:	Oxygen and hydrogen
Option C:	Sulphur and Oxygen
Option D:	Sulphur and Hydrogen
56.	Quality of petrol is decided by it's
Option A:	Cetane number
Option B:	Octane number
Option C:	Carbon number
Option D:	Hydrogen number
57.	Which of the following method is used for nitrogen estimation
Option A:	Precipitation method
Option B:	Combustion method

Q.B

1) Opt-B

2)  $E_{\text{cell}}^{\circ} = 0.012 \text{ V}$ ;  $\text{Sn} | \text{Sn}^{2+}(\text{aq}) \parallel \text{Pb}^{2+} | \text{Pb}(\text{aq})$   
 $E_{\text{Pb}}^{\circ} = -0.125 \text{ V}$ ;  $E_{\text{Sn}}^{\circ} = ?$

$$E_{\text{cell}}^{\circ} = E_{\text{right}}^{\circ} - E_{\text{left}}^{\circ} \quad (\text{where both are redn pot})$$

$$0.012 = -0.125 - E_{\text{Sn}}^{\circ}$$

$$E_{\text{Sn}}^{\circ} = -0.125 - 0.012$$

$$= -0.137 \text{ V} \quad (\text{A})$$

3) Opt-D

4) All of these (c)

5) opt-D

6)  $C = 70\%$ ,  $O = 8\%$ ,  $H = 10\%$ ,  $N = 3\%$ ,  $S = 2\%$

$$\text{GCV} = \frac{1}{100} \left( 8080 \times C + 34500 \left( H - \frac{O}{8} \right) + 2240 \times S \right)$$

$$= \frac{1}{100} \left( 8080 \times 70 + 34500 \left( 10 - \frac{8}{8} \right) + 2240 \times 2 \right)$$

$$= \frac{1}{100} \left( 8080 \times 70 + 34000(9) + 2240 \times 2 \right)$$

opt-A

7) opt-D

8)  $E_{\text{Ni}}^{\circ} = -0.257$ ;  $E_{\text{Cu}}^{\circ} = 0.337$   
 $\text{Ni} | \text{Ni}^{2+} \parallel \text{Cu}^{2+} | \text{Cu}$

$$E_{\text{cell}}^{\circ} = E_{\text{Cu}}^{\circ} - E_{\text{Ni}}^{\circ} \Rightarrow 0.337 - (-0.257)$$

$$\Rightarrow 0.594 \text{ V} \quad (\text{opt-D})$$

9) Addition - more atom economy  
elimination - less atom economy.

→ (C) Rearrangement of Addition.

10) Ni lies below Fe - (opt-A)

11) opt - A

12) opt - D (cathode requires more electron)

13) opt - A

14) opt - D

15) opt - C

16) opt - C

17) opt - D

(for single electron)

$$18) (2s+1) \Rightarrow 2 \times \frac{1}{2} + 1 = 2$$

19) opt - B

20) opt - D

21) opt - B

22) opt - B

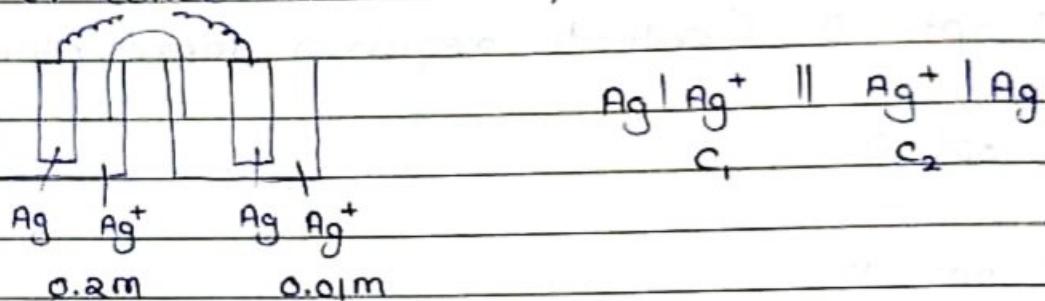
23) opt - c (current density = large surface area)

24) opt - c

25) opt - B (overvoltage / / corrosion)

26) opt - c

27) For concentration cell,



Applying Nernst equation to above cell,  
 $E = E^\circ - \frac{0.0591}{n} \log_{10} \frac{c_2}{c_1} \quad (c_1 > c_2)$

\* For the above cell  $E_{\text{cell}}^\circ$  is always "zero"

$$\begin{aligned} \therefore E &= 0 - \frac{0.0591}{n} \log_{10} \left( \frac{0.01}{0.2} \right) \\ &= -0.0591 \log_{10} ( ) \\ &= 0.077 \quad (\text{opt-D}) \end{aligned}$$

28) opt - B ( $\lambda_{\text{max}} = 1/\lambda$ )

29) opt - c

30) opt - c (allowed to escape bcoz Net < GCV)

- 31) opt-C
- 32) opt-B
- 33) opt-D (Indicator electrode rest are reference)
- 34) opt-A (acidic medium = evolution of hydrogen)
- 35) Wt. of coal = 3.3 gm  
Wt. of ash = 0.252 gm
- % Ash =  $\frac{\text{Wt. of ash}}{\text{Wt. of coal}} \times 100$  i.e.  $0.252 \times 100 / 3.3$   
= 7.63% (Opt-D) \* Correction.

36) opt C (chart)

(37) opt-B

(38) opt-B

39) opt-C

40) opt-B

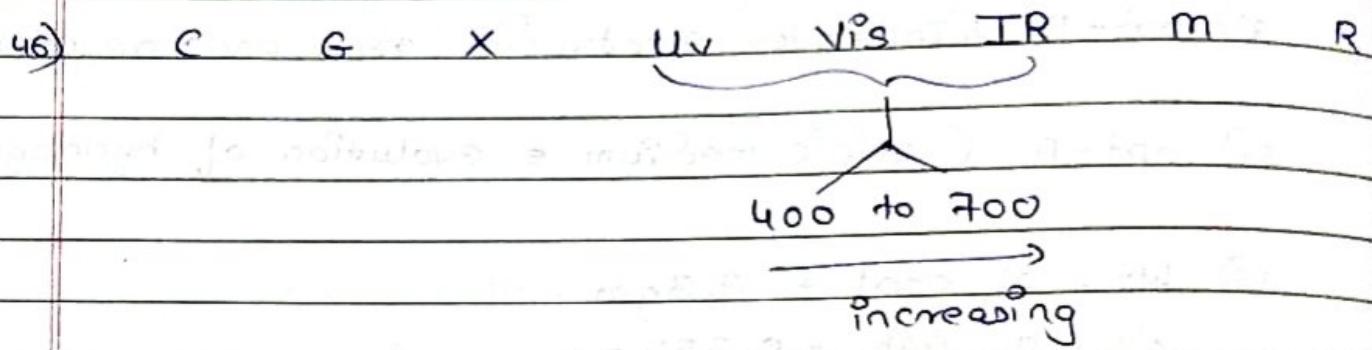
41) opt-C [Green = Renewable ; Non = non-renewable]

42) opt-C

43) opt-C

44) opt - A

45) opt - D



$$\because E = h\nu = hc \quad \nu \propto 1/\lambda$$

(opt - A)

47) opt - B

48) opt - A

49) opt - B

50) opt - A

51) opt - A [ Concentration cell  $\equiv$  similar 3 ]

52) opt - D

53) opt - C

54) opt - B

55) opt - A

56) opt - B ( Diesel  $\rightarrow$  cedane)

57) opt - C ( Preci = 'S' , Comb = C & H , Tidration = All )

Option C:	Kjeldahl's method
Option D:	Titration method

## Descriptive Section

1.	A sample of coal has the following composition by mass: C = 85%, H = 6%, O = 8%, S = 0.5% and Ash = 0.5%. Calculate HCV and LCV using Dulong's Formula. Given Atomic Weights: C=12, H = 1, S = 32, O = 16
2.	Discuss differential aeration corrosion with the help of a suitable example.
3.	Explain the conventional and Green route of manufacturing Carbaryl. Highlight the green chemistry principle involved.
4.	Define Spectroscopy and Electromagnetic spectrum. Also explain the origin of spectrum.
5.	The standard emf of the following cell is 0.462 V. $Cu(s) / Cu^{+2} (aq)(1M) // Ag^+(aq)(1M) / Ag(s)$ Write the cell reaction. If the standard potential of Cu electrode is 0.337 V, what is the standard potential of Ag electrode?
6.	What is cathodic protection? What are the two types of cathodic protection? Discuss any one with the help of a suitable diagram.
7.	Calculate the percentage atom economy for the following reaction with respect to acetanilide. $C_6H_5NH_2 + (CH_3CO)_2O \longrightarrow C_6H_5NHCOCH_3 + CH_3COOH$ Given Atomic Weights: C = 12, H = 1, O = 16, N = 14
8.	Calculate the volume of air required for complete combustion of 1m <sup>3</sup> of gaseous fuel having the following composition: CO = 5%, C <sub>2</sub> H <sub>4</sub> = 10%, CH <sub>4</sub> = 40%, N <sub>2</sub> = 2.5 %, H <sub>2</sub> = 35%, CO <sub>2</sub> = 2%, O <sub>2</sub> = 2.5% Given Atomic Weights: C = 12, H = 1, O = 16, N = 14
9.	How do the following factors affect the rate of corrosion: (i) relative areas of anodic to cathodic part (ii) position of metal in galvanic series.
10.	(i) Distinguish between anodic and cathodic coating. (ii) What is Biodiesel? Give the trans-esterification reaction of the preparation of Biodiesel.
11.	Explain the conventional and Green route of manufacturing Adipic acid. Highlight the green chemistry principle involved.
12.	Give in tabular form the relation between electromagnetic spectrum, types of spectroscopy and corresponding energy changes.

13.	What is an electrochemical cell? What are the types of electrochemical cell? Briefly discuss the different types.
14.	What is green chemistry? Explain the principle of ‘Designing safer chemicals and products’ and the principle of ‘Use of renewable feedstocks’.
15.	(i) 1 g of coal sample was used for determination of nitrogen by Kjeldhal’s method. The ammonia evolved was passed into 50 ml of 0.1 N $\text{H}_2\text{SO}_4$ . The excess acid required 42 mL of 0.1 N NaOH for neutralisation. Calculate the percentage of N in the sample.  (ii) One of the design and material selection principle is ‘ the anodic material should not be painted or coated’ . Give reason for the same.
16.	Discuss season cracking.
17.	What are ‘oxygenates’ used in the fuel industry? Where and why are they added? Explain by giving examples.
18.	By kjeldahl’s method 3 gm of coal sample was analysed. The ammonia evolved was absorbed in 40 ml of 0.5 N $\text{H}_2\text{SO}_4$ . After absorption, the excess $\text{H}_2\text{SO}_4$ required 18.5 ml of 0.5N KOH for neutralization. A coal sample was subjected to ultimate analysis 2.45 g of coal on combustion in a Bomb-Colorimeter gave 0.67 of $\text{BaSO}_4$ . Calculate percentage of Nitrogen and sulphur.
19.	Discuss Bimetallic corrosion with the help of a suitable example
20.	Explain the conventional and Green route of manufacturing indigo dye. Mention the green chemistry principles involved.
21.	Explain construction and working of SHE with neat and labeled diagram.
22.	Explain different types of electromagnetic radiations.
23.	Draw a diagram of a cell made up of aluminium and silver half cells. Give representation of the cell along with electrode reactions.
24.	Calculate the volume and weight of air required for complete combustion of 1m <sup>3</sup> of gaseous fuel having the following composition: CO = 10%, $\text{C}_3\text{H}_8$ = 12%, CH 4 = 30%, N 2 = 3 %, H 2 = 40%, $\text{CO}_2$ = 3%, O2 = 2.0% (Molecular weight of air =28.949).
25.	How do the following factors related to nature of environment affect corrosion? i) Anodic and Cathodic area ii) Purity of metal
26.	$\begin{array}{ccc} \text{CH}_3 & & \text{CH}_3 \\   & &   \\ \text{H}_3\text{C} - \text{C} - \text{CH}_3 & \xrightarrow{\text{NaO C}_2\text{H}_5} & \text{H}_3\text{C} - \text{C} = \text{CH}_2 + \text{C}_2\text{H}_5\text{OH} + \text{NaBr} \\   & &   \\ \text{Br} & & \end{array}$ Find atom economy of the reaction with respect to 2-methyl propene.
27.	Explain ‘Selection rules’ that basically decide which transitions are ‘allowed or forbidden’ in spectroscopy
28.	Distinguish between Octane number and Cetane number
29.	i) Explain the principle of ‘use of catalytic reagent’ with respect to green chemistry. ii) How would you synthesize benzimidazole using green catalyst.
30.	Calculate the minimum amount of air required for the complete combustion of 1 kg of fuel containing C= 80%, H= 6%, O=8%, S= 1.5%, $\text{H}_2\text{O}= 1.0\%$ , N= 1.5% and ash= rest.
31.	Explain why a “pure Zinc metal rod half immersed in saline water starts corroding at the bottom” Explain with neat diagram, reactions & corrosion product formation.
32.	Explain construction and working of a reference electrode which is used in pH meter.
33.	Write cell reaction and calculate the standard emf of the following cell.

	Cd(s)   Cd +2 (aq)(1M)    Ni2+ (aq)(1M)   Ni(s) If the standard potential of Cd electrode is -0.40 V and the standard potential of Ni electrode is -0.25 V
34.	Write a note on Catalytic converter with the help of chemical reactions.
35.	i) Give significance of determination if moisture in coal. ii) What is season cracking?
36.	Which molecule is used as a component in various therapeutic drugs? Give any one traditional and green synthesis of the same.
37.	Write the Nernst Equation and calculate Emf of the following cell at 298K: Mg(s)/Mg2+(0.001M)    Cu2+(0.0001M)/Cu(s). <i>Given:</i> $E_{Cu2+/Cu}^0 = 0.34$ V and $E_{Mg2+/Mg}^0 = -2.37$ V
38.	With the help of traditional and green synthesis of ibuprofen, list the principles of green chemistry involved in it.
39.	What is knocking? How is knocking of gasoline related to chemical structure of hydrocarbons present in it? Define octane rating.
40.	A sample of coal was found to contain C = 80%, H = 5%, O = 1%, N = 2%, Ash=12%. Calculate the minimum amount of air required for complete combustion of 1kg of coal sample.
41.	Draw the energy level diagram showing various molecular energies and explain why molecular spectra contains broad bands whereas atomic spectra consist of sharp lines.
42.	A cell uses Zn2+/Zn and Ag+/Ag electrodes. Write the cell representation, Half-cell reactions, Net cell reactions and calculate the standard Emf of the cell. <i>Given:</i> $E_{Zn2+/Zn}^0 = -0.76$ V and $E_{Ag+/Ag}^0 = 0.8$ V
43.	Define Green chemistry. As per Green chemistry Principles, why is it essential to design energy efficient process. Explain with suitable examples.
44.	What is oxidation corrosion. Name the different types of oxide layer formed and state which oxide layers are non-protective in nature. Explain with suitable examples.
45.	Determine C, H, N elements as % from the following observations in experiments of analysis of coal. 0.25g coal on burning in a combustion tube and passing the gases through tubes containing anhydrous CaCl2 and KOH increases their weight by 0.09 g and 0.8g respectively. In Kjeldahl's method, ammonia evolved by 0.42g coal was absorbed in 49.5ml of 0.12 N HCl solution. After absorption, the excess acid required 36.5ml of 0.12 N NaOH for neutralization.
46.	What are antiknocking agents? Explain the factors affecting antiknocking characteristics of a compound
47.	What is electrochemistry? Write the cell reaction and Calculate the standard emf of the following cell $Zn_{(s)}   Zn^{2+}_{(aq)} (1M)     Cu^{2+}_{(aq)} (1M)   Cu_{(s)}$ <i>Given:</i> $E_{Zn}^0 = -0.763$ V and $E_{Cu}^0 = 0.337$ V
48.	What is Green Chemistry? Calculate percentage atom economy for the following reaction with respect to acetophenone (5)  $\text{C}_6\text{H}_6 + \text{CH}_3\text{COCl} \longrightarrow \text{C}_6\text{H}_5\text{COCH}_3 + \text{HCl}$ <b>Acetophenone</b> (Atomic weights: C=12, H=1, O=16, Cl=35.5)
49.	Define corrosion. Explain sacrificial anode method with suitable diagram. (5)
50.	Calculate the weight and volume of air required for complete combustion of 1 kg of coal containing C=65%, H=4%, O=7%, N=3%, moisture=15% and remaining is ash. (molecular weight of air=28.94 gm) (5)
51.	Give the classification of Spectroscopy based on atomic level of study. Distinguish between absorption and emission spectra. (2+3)
52.	What is metallic coating? Differentiate between Galvanizing and Tinning. (5)
53.	List 12 principles of Green Chemistry. Explain Biodiesel as a Green fuel (5)

54.	List the factors affecting the rate of corrosion. Explain Galvanic cell Corrosion (5)
55.	3.2 gm of coal in Kjeldahl's experiment evolved $\text{NH}_3$ gas was absorbed in 40 ml of 0.5 N $\text{H}_2\text{SO}_4$ . After absorption the excess acid required 16 ml of 0.5N NaOH for complete neutralization. 2.5 gms of coal sample in quantitative analysis gave 0.42 gm $\text{BaSO}_4$ . Calculate the % N and S. (5)
56.	Define spectroscopy and explain different regions of electromagnetic spectrum with the help of diagram
57.	What is Electrochemistry? Differentiate between electrolytic cell and Galvanic cell
58.	List the 12 Principles of Green chemistry and calculate % atom economy for the following reaction with respect chlorobenzene $\text{C}_6\text{H}_6 + \text{Cl}_2 \longrightarrow \text{C}_6\text{H}_5\text{Cl} + \text{HCl}$ Atomic weight C = 12, H = 1, Cl = 35.5
59.	What is Electrochemical corrosion? Explain Hydrogen evolution mechanism with the help of diagram
60.	Calculate the amount of air needed for complete combustion of 1Kg of coal containing C = 65%, H = 13 %, O = 6 %, N = 2% S = 4%
61.	Give construction and working of hydrogen-oxygen fuel cell with the help of diagrams and reactions.
62.	What is standard potential? Calculate standard emf of following cell $\text{Zn(s)} \text{Zn}^{2+}_{(\text{aq})}(1\text{M}) \parallel \text{Cu}^{2+}_{(\text{aq})}(1\text{M}) \text{Cu}_{(\text{s})}$ Given $E^{\circ} \text{ Zn} = -0.763 \text{ V}$ and $E^{\circ} \text{ Cu} = 0.337 \text{ V}$
63.	Explain the mechanism of 'Rusting of iron in water' with the help of diagram and reactions.
64.	Explain sacrificial anode method for prevention of corrosion with the help of diagram and also distinguish between Galvanizing and Tinning
65.	What is Fuel? and what are ideal characteristics of fuel. Give classification of fuels.

Q1

Given: C = 85%.

H = 6%.

O = 8%.

S = 0.5%.

Ash = 0.5%.

Weight  $\rightarrow$  C = 12

H = 1

S = 32

O = 16

Formulae:

$$H.C.V = \frac{1}{100} [8080C + 34500(H - O) + 2240S]$$

$$L.C.V = [H.C.V - \frac{q}{100} H \times 587]$$

$$\text{solution: } H.C.V = \frac{1}{100} [8080C + 34500(H - O) + 2240S]$$

$$= \frac{1}{100} [8080 \times 85 + 34500 \times \left(6 - \frac{8}{8}\right) + 2240 \times 0.5]$$

$$= \frac{1}{100} [686800 + 172500 + 1120]$$

$$= \frac{1}{100} [860420]$$

$$H.C.V = \underline{8604.2 \text{ kcal/kg}}$$

$$L.C.V = [H.C.V - \frac{q}{100} H \times 587]$$

$$= [8604.2 - \frac{q}{100} \times 6 \times 587] = [8604.2 - 316.98]$$

$$L.C.V = \underline{8287.22 \text{ kcal/kg}}$$

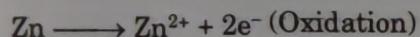
## ~~Q3~~ 4.2 Concentration Cell (Differential Aeration) Corrosion

MU - May 15

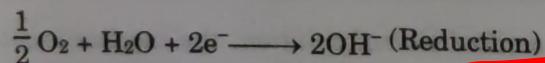
(May 15, 5 Marks)

Q Write a note on differential aeration corrosion.

- This type of corrosion is due to the electrochemical attack on the metal surface, which is exposed to an electrolyte of varying concentrations or of varying aeration.
- The variation is caused due to local difference in metal ion concentration caused by,
  - (i) Local difference in temperature
  - (ii) Inadequate agitation
  - (iii) Slow diffusion of metal ions, produced by oxidation at anode.
- It is the most common type of corrosion, and it occurs when one part of the metal is exposed to a different air concentration from the other part.
- *This causes a difference in potential between differently aerated areas.* It has been found that *poor oxygenated parts are anodic and rest are cathodic*. Consequently, differential aeration of metal causes a flow of current, called *differential current*.
- For Example, Metal (Iron) tank/drum storing water or a strip of zinc metal partially dipped in dilute solution of salt; like NaCl and if solution is not agitated properly then the parts of the strip above and closely adjacent to the water line are more strongly aerated; because they have more supply of oxygen while remaining parts of the same strip which are immersed to greater depth have less supply of oxygen and these are poorly aerated and show lower oxygen concentration or lesser access of oxygen, and thus they become anodic.
- Thus, difference of potential is created which causes a flow of current between the two differently aerated areas of the same metal. Zinc will dissolve at anodic areas as,



O<sub>2</sub> will take up electrons at the cathodic areas to form OH<sup>-</sup> ions.



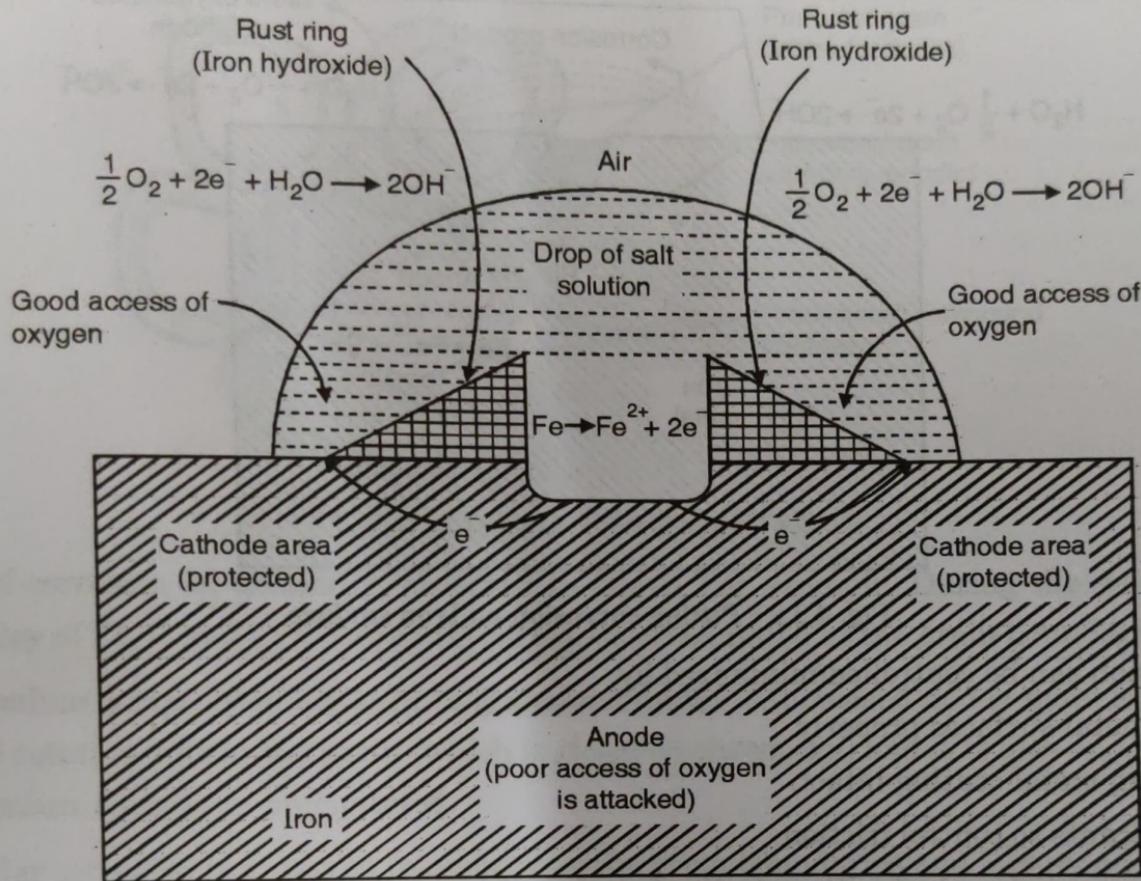
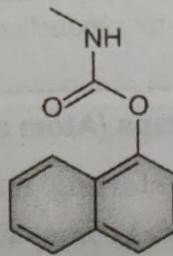


Fig. 4.3.1 : Concentration cell corrosion

#### 5.4.4 Synthesis of Carbaryl

MU - Dec. 17, Dec. 18

- Q3.** Explain conventional and Green route of manufacturing of Carbaryl. By this reaction which principle of Green Chemistry is shown.  
(Dec. 17, Dec. 18, 4 Marks)

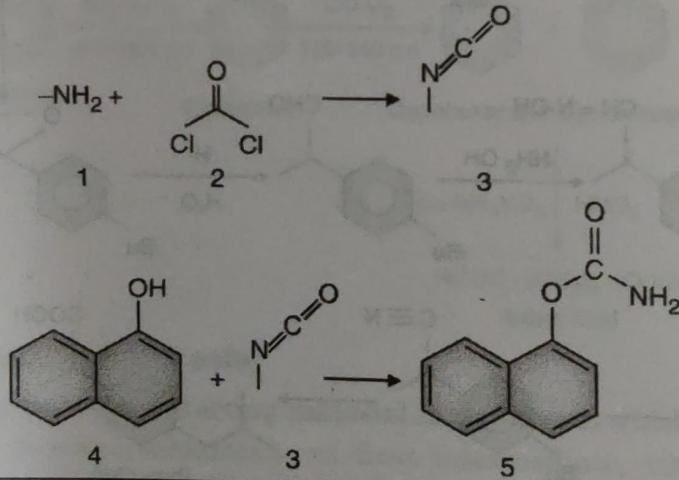


Structure of Carbaryl

##### 1. Conventional route of synthesis

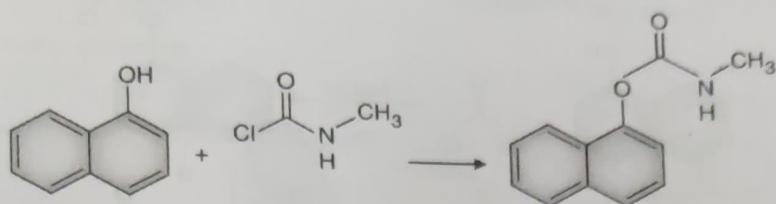
###### (I) With using naphtol-1 and methyl-isocyanate

Carbaryl is prepared on large scale by treating methyl-isocyanate [compound 3] with 1-naphthol [compound 4], Amine is treated with Phosgene to get methyl-isocyanate.

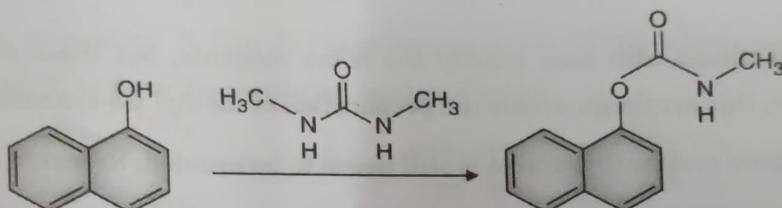


Note : This process was carried out in Bhopal, by Union Carbide where leakage of MIC mishap took place in 1984

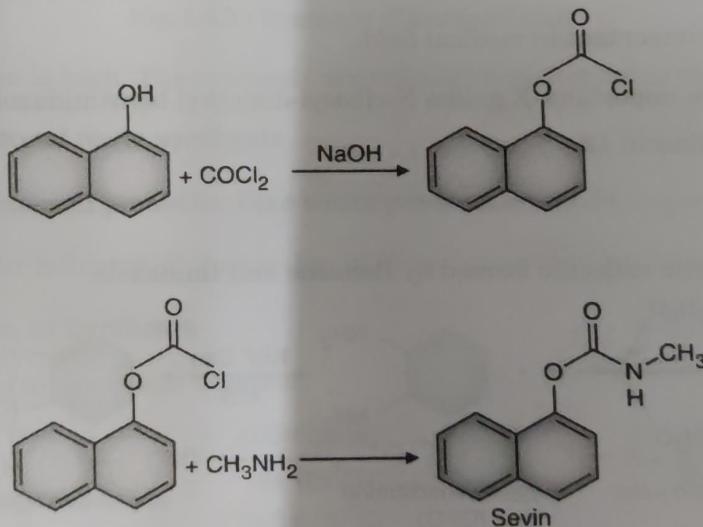
## (III) With using naphtol-1 and methylcarbamoylchloride



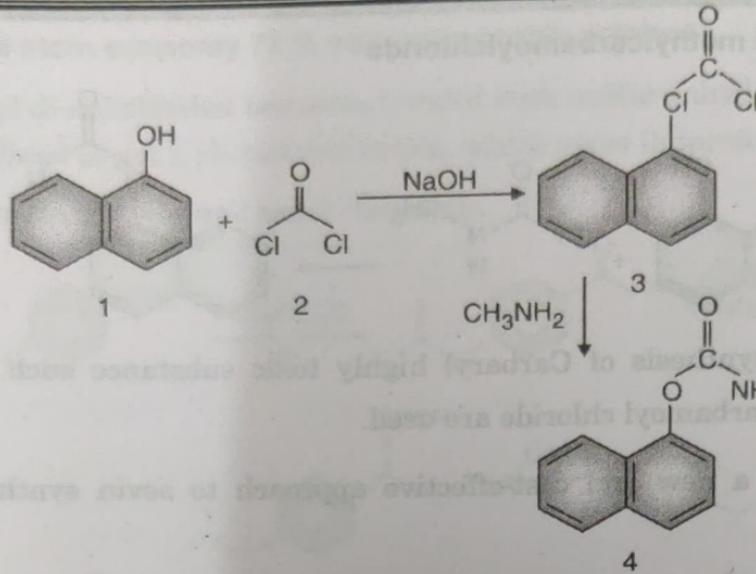
- In these routes of synthesis of Carbaryl highly toxic substance such as phosgene, methyl isocyanate and methylcarbamoyl chloride are used.
- We have developed a new and cost-effective approach to sevin synthesis without using toxic reagents.

**Routes of sevin synthesis**

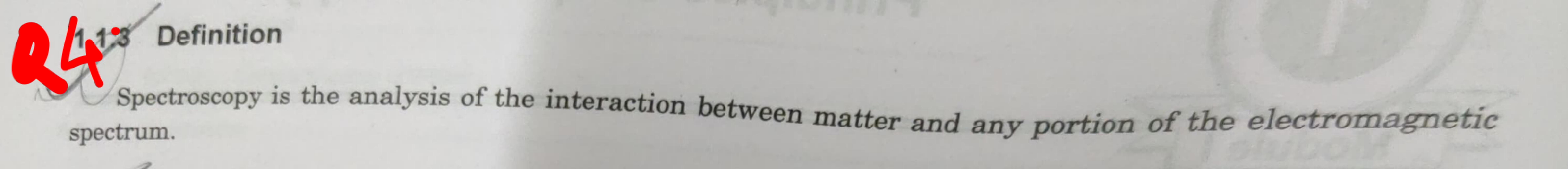
## (I) By using naphtol-1 and phosgene

**2. Green route of synthesis**

- 1-naphthol [compound 1] treated directly with equal quantity of phosgene [compound 2] in alkaline medium to get chloroformate [compound 3], which is then treated with methyl amine to give Carbaryl [compound 4]
- Alternatively, 1-naphthol [compound 1] is first converted to its chloroformate [compound 3], which is then treated with methylamine to give the desired product [compound 4].



- Greene route synthesis also uses exactly the same reagents, but these are taken in a different sequence. Hence, this synthesis avoids the preparation of methyl iso-cyanate.
- But use of phosgene and methyl amine is still needs to be avoided. Research is in progress.



**Q4** 113

## Definition

Spectroscopy is the analysis of the interaction between matter and any portion of the *electromagnetic spectrum*.

The electromagnetic spectrum is the range of frequencies of electromagnetic radiation and their respective wavelengths and photon energies.

spectrum.

### 1.1.4 Origin of Spectrum

The first spectroscope was invented in 1859 by the German chemist Robert Wilhelm Bunsen and the German physicist Gustav Robert Kirchhoff. It was used to identify materials that emit light when heated.

A spectroscope transforms light into a spectrum using a prism that can be observed through a small telescope.

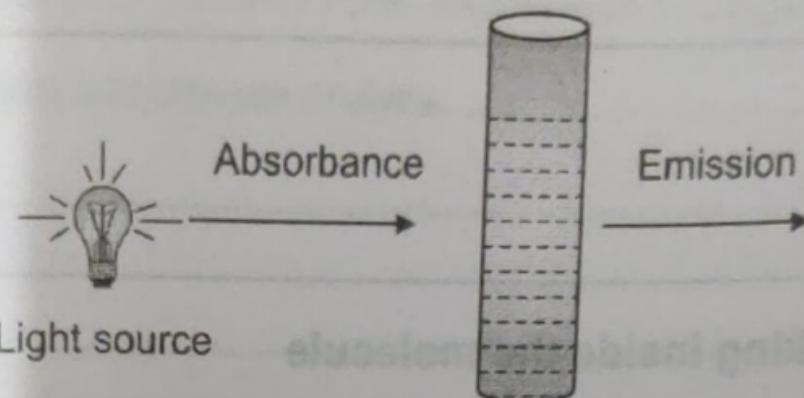


Fig. 1.1.1 : Typical Setup in Spectroscopy

#### 4.5.3 Cathodic Protection Method

MU - May 15, May 18

Q6

What is cathodic protection ?

(May 15, May 18, 6 Marks)

Cathodic protection is nothing but a method used to reverse the flow of current between the two dissimilar metals, under corroding environment thereby reversing the action of the metals in contact. This is achieved by applying the external circuit and forcing the anodic metal to behave as a cathode.

- Anodic protection involves suppression of anodic reaction by adjusting the potential of the more reactive metal, i.e. making metal passive in the working environment.

#### Methods of cathodic protections

Cathodic protection can be achieved by two different method as :

- (i) By using sacrificial anode method/Auxiliary anode method
- (ii) By using impressed current method.

Both the methods are discussed here in detail.

#### 4.5.3(A) Sacrificial Anode

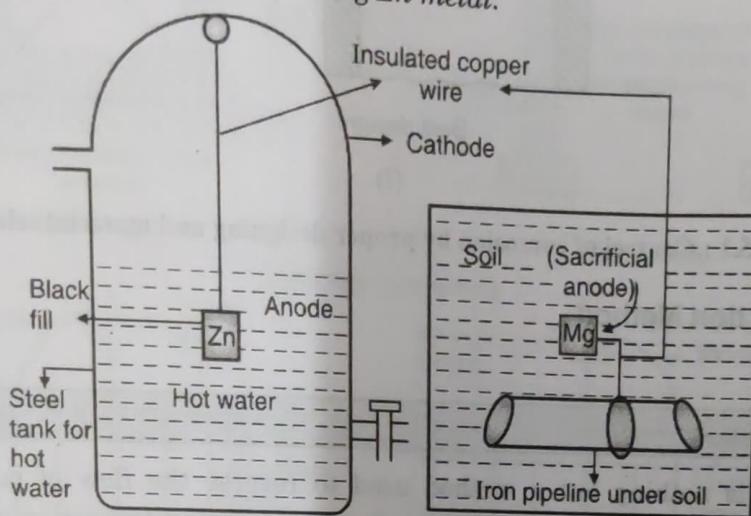
MU - Dec. 17

Q. Discuss in brief sacrificial anode method of corrosion protection.

(Dec. 17, 3 Marks)

- To achieve protection by *sacrificial anode* method, the metal to be protected from corrosion is connected by a wire to another piece of metal which is *more reactive* than the *base metal* itself.

- This results in the corrosion of the piece of metal connected, thereby saving base metal.
- Since the more active metal sacrifices itself, by undergoing corrosion and saving the base metal, the method is named as *sacrificial anode or auxiliary anode method*.
- When the piece of more active metal gets corroded completely, it is simply replaced by new piece.
- The metals normally used are Mg, Zn or Al.
- This method is used normally to protect pipelines carrying water or industrial wastes, and which are normally embedded under the soil, thereby facing the conditions of soil corrosion as well as microbiological corrosion.
- Applications of this method are seen to protect *cables or iron pipelines*, by connecting them to Mg-blocks; and in case of *marine structures, ships are protected by using Zn-plates as sacrificial anode*. Even *water tanks, boilers* are protected by using Zn metal.



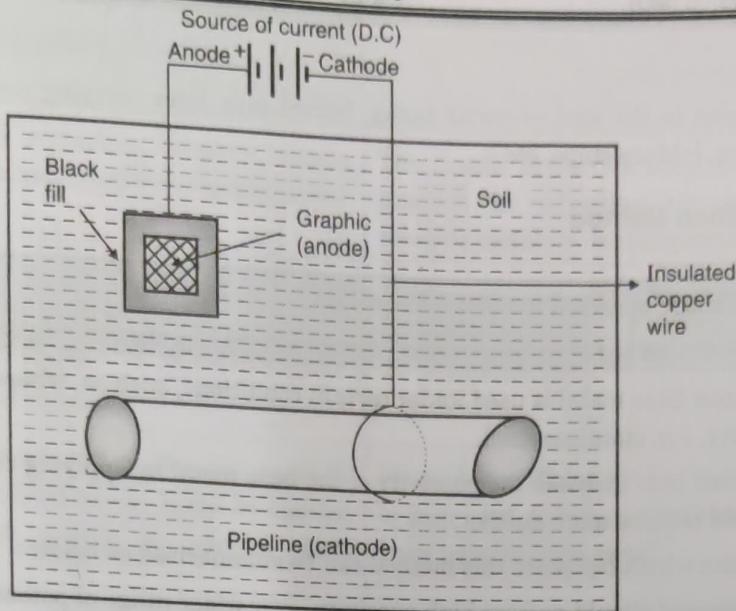
**Fig. 4.5.2 : Corrosion control by sacrificial anode method**

#### 4.5.3(B) Impressed Current

MU - May 15, May 17, Dec. 17

Q. Explain impressed current method of corrosion control.	(May 15, 5 Marks)
Q. Explain the method of impressed current cathodic protection.	(May 17, 3 Marks)
Q. A metal rod half immersed in water starts corroding at the bottom. Give reasons.	(Dec. 17, 2 Marks)

- In impressed current method, a current is applied in the opposite direction to that of corrosion current, thereby nullifying the effect of the latter one on the base metal, i.e. converting the base metal, to cathode from an anode.



**Fig. 4.5.3 : Corrosion control by impressed current method**

- Such an impressed current can be obtained by using D.C. source such as battery or dry cell along with an insoluble anode such as platinum, stainless-steel, graphite etc.
- In this method, as shown in Fig. 4.5.3, the insoluble anodic metal used (i.e. platinum, steel, scrap iron etc.) is normally embedded underground. To this, with the help of D.C. current source, the impressed current is applied, and whole of this assembly is connected to the metallic structure to be protected.
- The connections are done by using wires.
- The insoluble anode is kept inside back-fill made up of gypsum or any such material, which can help in increasing the electrical contact with the soil.
- Such an anode can be single, if the area of the metallic structure to be protected is small.
- There can be many such anodes, connected in series if the area of the metallic structure to be protected is wider, i.e. long pipeline etc.

#### Advantages

- (i) This method is highly useful, because it can protect the long length structures for a long term, thereby reducing frequency of monitoring as well as maintenance cost.
- (ii) These both methods are most widely used, because the protection provided to the base metal is long term and maintenance is easy.

#### Disadvantage

Due to the application of the impressed current, the anode deteriorates and hence, it has to be replaced from time to time.



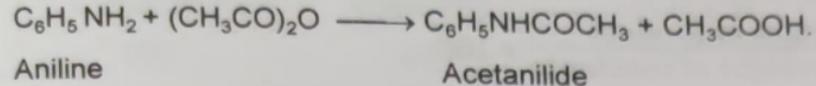
## Application

This method are seen in the case of water tanks, buried pipe lines carrying water or oil, condensers, transmission line towers, laid-up ships, etc.



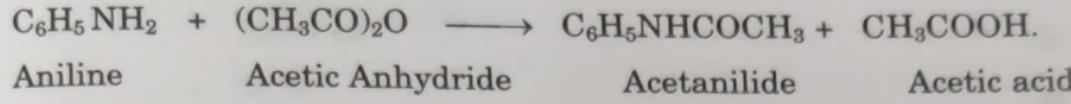
**Q7** Ex. 5.5.5.

Calculate the percentage atom economy for the following reaction with respect to acetanilide :



**Soln. :**

**Reaction given**



$$\begin{aligned}\% \text{ Atom economy} &= \frac{\text{Molecular weight of product}}{\text{Total molecular weight of reactants}} \times 100 \\ &= \frac{123}{(93 + 102)} \times 100 \\ &= \frac{92}{128.5} \times 100 = 51.5\% \\ &= \frac{123}{195} \times 100 = 63.07\%\end{aligned}$$

$$\% \text{ Atom economy} = 63.07\%$$

...Ans.

the theoretical reversible value of the same solution is called the overvoltage or overpotential".

**Q9.**

#### Areas Occupied by the Anode and Cathode

If two *dissimilar* metals are in contact, one forming anode while another forming cathode, then the corrosion of the anodic metal (part) is directly proportional to the ratio of the areas occupied by the cathode and anode.

Thus, corrosion at anode,  $\alpha = \frac{\text{Area of cathodic part}}{\text{Area of anodic part}}$

Hence, if cathode is large and anode is small, then corrosion at anode is higher and vice-versa.

**Purity of the Metal**

## 4. Position of Metal in the Galvanic Series

In a corroding environment, the position of metal in the galvanic series determines its rate of corrosion. If two dissimilar metals are in contact with each other in a corrosive medium, the metal which is more active in the galvanic series undergoes corrosion, i.e. it acts as an anode.

# Q10.

## Table 4.5.2 : Comparison between Anodic and Cathodic Coatings

Sr. No.	Anodic coating	Cathodic coating
1.	This type of coatings protect base metal "sacrificially".	This type of coatings protect the base metal because of <b>high corrosion resistance and noble behaviour</b> .
2.	The coating metal is at lower electrode potential than base metal.	The coating metal is at higher electrode potential than base metal.



Sr. No.	Anodic coating	Cathodic coating
3.	Corrosion of base metal does not enhance even on breaking “anodic coating”, as it heals its film.	Corrosion of base metal enhances, if there is small cut / break in coating.
4.	E.g. Galvanizing, i.e. Zn coating on iron / steel.	E.g. Tinning, i.e. Tin coating on iron / steel / copper / brass.

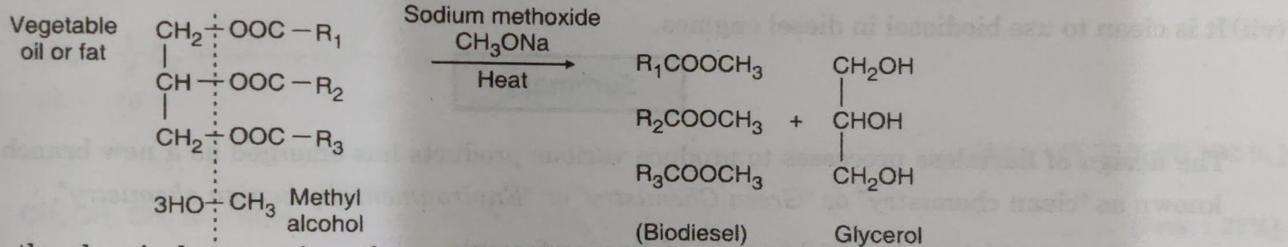
**5.6 Biodesel****Q 10****MU - May 15, Dec. 17, May 18, May 19**

- Q. What is Bio-diesel? Explain the trans-esterification method for its synthesis. Mention advantages of biodiesel as fuel. (May 15, 6 Marks)
- Q. What is biodiesel ? Discuss the method to obtain biodiesel. What are the advantages of biodiesel ? (Dec. 17, 4 Marks)
- Q. Define Bio-Diesel and give its advantages. (May 18, May 19, 2 Marks)

Chemically biodiesel is the methyl esters of long chain carboxylic acids. Biodiesel is obtained by transesterification of vegetable oil or animal fats with methyl alcohol using sodium metal or sodium methoxide, as catalyst.

### Transesterification

- Transesterification is the process of converting one ester to another ester.
- A molecule of oil or fat is the triester of glycerol and three molecules of long chain carboxylic acids. This triester is converted into methyl esters of the fatty acids.



- During the chemical conversion of vegetable oil to biodiesel we get water soluble glycerol and a small amount of sodium soaps.
- The water soluble part can be easily separated from biodiesel by washing the mixture with water.
- The alkaline sodium methoxide catalyst, saponifies some small amount of oil to give soap.
- Compounds present in biodiesel are like,

Methyl palmitate  $\text{H}_3\text{C}-(\text{CH}_2)_{14}-\text{COOCH}_3$

Methyl stearate  $\text{H}_3\text{C}-(\text{CH}_2)_{16}-\text{COOCH}_3$

Methyl oleate  $\text{H}_3\text{C}-(\text{CH}_2)_7-\text{CH}=\text{CH}-(\text{CH}_2)_7-\text{COOCH}_3$

Methyl linoleate  $\text{H}_3\text{C}-(\text{CH}_2)_5(\text{CH}=\text{CH}_2)-( \text{CH}_2)_7-\text{COOCH}_3$

## ~~Q~~ 5.4.2 Synthesis of Adipic Acid

MU – May 15, May 17, May 19

Q. Explain conventional and green synthesis of adipic acid. Mention the green chemistry principle involved.

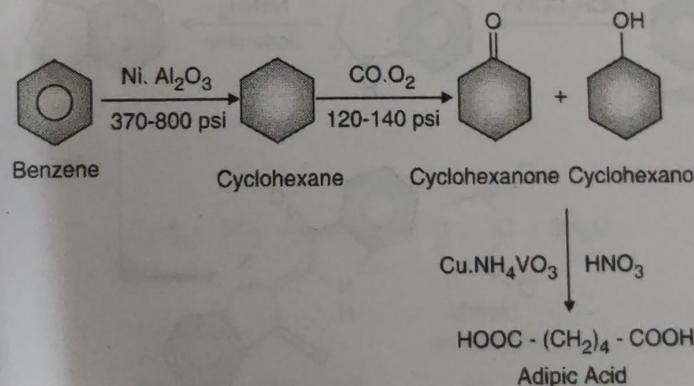
(May 15, 5 Marks)

Q. Explain conventional and green route of manufacturing of Adipic acid.

(May 17, May 19, 4 Marks)

### 1. Conventional route using Benzene (Carcinogenic solvent)

- For synthesizing adipic acid molecule, starting material is benzene, treated with Ni/alumina catalyst at high pressure to get a saturated cyclic hydrocarbon, cyclohexane.
- This is treated with carbon monoxide in presence of oxygen at medium pressure to get mixture of cyclohexanone and cyclohexanol as intermediate which are converted into adipic acid.

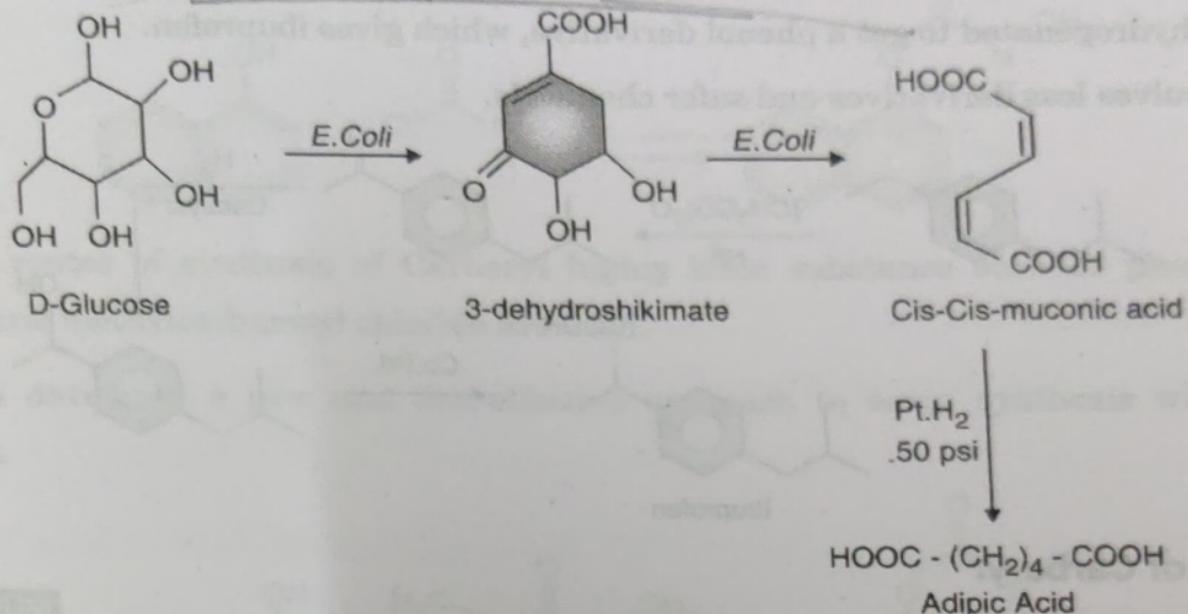


### 2. Green route using glucose (absolutely safe)

- To get adipic acid by green route, starting material is D glucose, which is simply fed with *E. Coli* in specified dose to get 3-dehydroshikimate as first intermediate, cis-cis muconic acid as second intermediate. Further it is catalytically with Pt.-hydrogen catalyst at pressure 50 psi to give adipic acid.



- This route is inexpensive, fast with high atom economy.
- This is example of avoid hazardous chemicals and also avoid derivatization.



# **Q13** Types of Electrochemical Cells

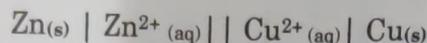
Electrochemical cells are device in which chemical energy converted into electrical energy, (and in reverse direction electrical energy may be converted into chemical energy).



- In Electrochemical cells electricity obtained with the help of oxidation and reduction reaction. Electrochemical cell generally consists of two half-cells, each containing an **electrode** in contact with an electrolyte. The electrode is an electronic conductor or a semiconductor. Current flows through the electrodes through the movement of electrons.
- Electrochemical cells are of two types. These cells are known as Galvanic cells or voltaic cell and Electrolytic cells.
- The chemical reaction responsible for production of electricity takes place in two separate compartments.

### 3.3.1 Galvanic Cell (Voltaic Cells)

- Each compartment consists of a suitable electrolyte solution and a metallic conductor. The metallic conductor acts as an electrode (half-cells). When the two compartments are connected by a salt bridge and electrodes are joined by a wire through galvanometer the electricity begins to flow. This is the simple form of voltaic cell.



- A galvanic cell produces an electrical charge from the flow of electrons. The electrons move due to the Redox reaction.
- Zn oxidizes to  $\text{Zn}^{2+}$ , while  $\text{Cu}^{2+}$  reduces to Cu.

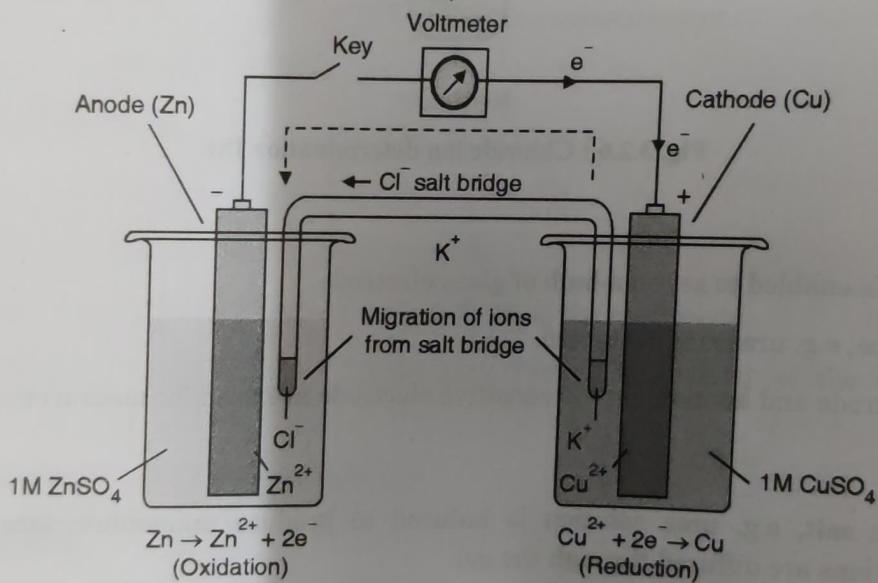
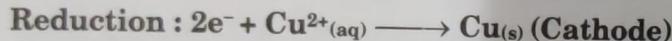
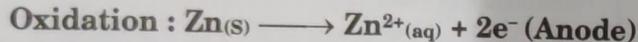


Fig. 3.3.1 : Galvanic Cell (Voltaic Cells)

### 3.3.2 Electrolytic Cell

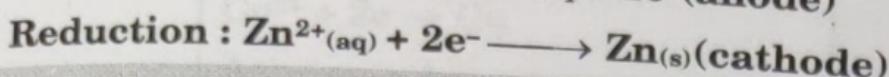
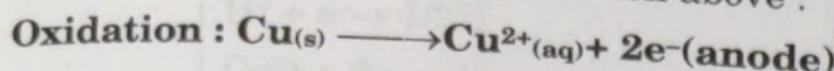
- Electrolytic cell is "a cell which requires an outside electrical source to initiate the redox reaction". The process of how electric energy drives the non-spontaneous reaction is called electrolysis.
- Galvanic cell is "a cell which uses a redox reaction to make electrons flow, the electrolytic cell uses electron movement (in the source of electricity) to cause the redox reaction."
- In an electrolytic cell, electrons are forced to flow in the opposite direction. Since the direction is reversed of the voltaic cell, the  $E^{\circ}_{\text{cell}}$  for electrolytic cell is negative.



Also, in order to force the electrons to flow in the opposite direction, the electromotive force that connects the two electrode-the battery must be larger than the magnitude of  $E^\circ_{\text{cell}}$ .

This additional requirement of voltage is called overpotential.

Electrolytic cell reactions for the cell above :



In short,

➤ **Galvanic cell** : Turns chemical energy into electrical energy.

➤ **Electrolytic Cell** : Turns electrical energy into chemical energy.

➤ **Example** : The most common form of Electrolytic cell is the rechargeable battery (cell phones, mp3's, etc.)

or electroplating. While the battery is being used in the device it is a galvanic cell function (using the redox energy to produce electricity). While the battery is charging it is an electrolytic cell function (using outside electricity to reverse the completed redox reaction).

used for manufacture.

A new branch commonly known as “clean chemistry” or “Green Chemistry” has emerged as a new branch commonly known as “clean chemistry” or “Green Chemistry”.

Q 14

## 5.2.4 Design Safer Chemicals and Products

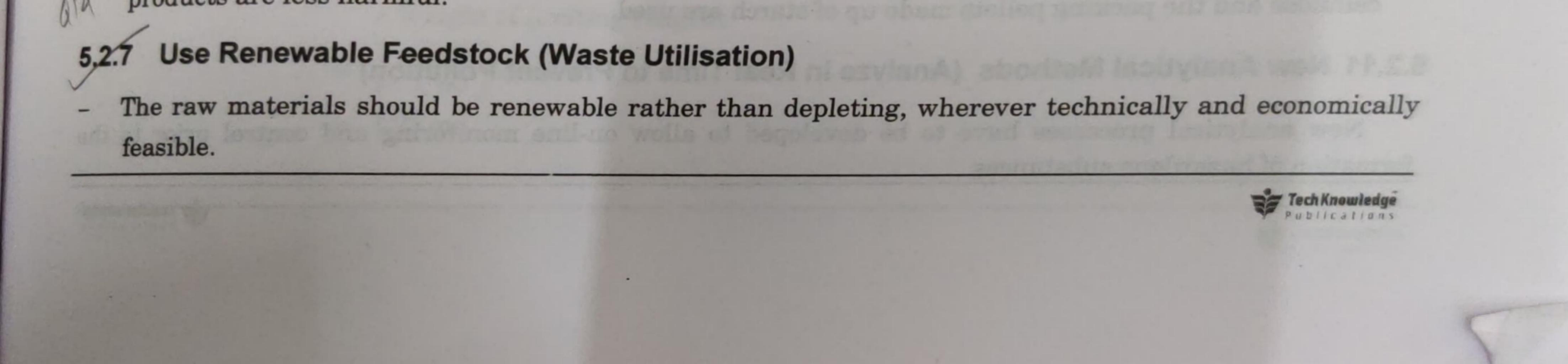
MU – May 18

**Q.** Why is it essential to design safer chemicals and products w.r.t. green chemistry principle? Explain with an example.  
**(May 18, 3 Marks)**

- The chemical products should be designed to preserve the efficiency of desired function while reducing toxicity.



- When any medicinal formulations are to be put in market, they are put first on trials to check their toxic effects on humans. If found to be toxic then alternatives are prepared keeping in mind the function of the medicine but only toxicity reduced.
- Similarly in many insecticides like *DDT*, *gammexane*, *aldrin* etc. which are found to be *toxic to humans*, the use of these is *curtailed* and alternatively *biological pesticides* are more in use.
- *Thus green chemistry emphasizes to design chemical products to be fully effective, yet have little or no toxicity.*



products are less harmful.

### 5.2.7 Use Renewable Feedstock (Waste Utilisation)

- The raw materials should be renewable rather than depleting, wherever technically and economically feasible.



- Renewable feedstock are often made from agricultural products or are the wastes of other processes; depleting feedstock are made from fossil fuels (petroleum, natural gas, or coal) or are mined.
- For example, A new method is developed to prepare adipic acid from glucose obtained from corn starch or cellulose. This is green process because it *replaces benzene* as starting material for production of same product. *Benzene* is a known *carcinogen*.

1. **Seasonal cracking** : Seasonal cracking is a term applied to stress corrosion of copper alloys, mainly brasses. Pure copper is immune to stress corrosion, but presence of small amounts of alloying element (like P, As, Sb, Zn, Al, Si) result in marked sensitivity. For examples, alpha brass (which when highly stressed) undergo intergranular cracking in an atmosphere, containing traces of ammonia or amines.

**Ex. 6.5.3:**

3 g of coal was heated in Kjeldahl's flask and  $\text{NH}_3$  gas evolved was absorbed in 40 ml of 0.5 N  $\text{H}_2\text{SO}_4$ .

After absorption, the excess acid required 18.5 ml of 0.5 N KOH for exact neutralization. 2.3 g of coal sample in quantitative analysis gave 0.35 g  $\text{BaSO}_4$ . Calculate percentage of N and S in coal sample.

**Soln. :**

### Calculation of % nitrogen

**Given Data**

Weight of sample = 3.0 gms

KOH consumed = 18.5 ml

Normality of  $\text{H}_2\text{SO}_4$  and KOH = 0.5 N

Quantity of  $\text{H}_2\text{SO}_4$  = 40 ml.

$$\begin{aligned}\text{Amount of } \text{H}_2\text{SO}_4 \text{ used} &= (40 - 18.5) \text{ ml.} \\ &= 21.5 \text{ ml.}\end{aligned}$$

$$\begin{aligned}\text{Equivalents of } \text{H}_2\text{SO}_4 &= 21.5 \times 0.5 = 10.75 \\ &= 10.75 \times 10^{-3} \text{ milli equivalents}\end{aligned}$$

$$\therefore \text{Weight of Nitrogen} = 10.75 \times 10^{-3} \times 14 = 0.1505 \text{ gms}$$

$$\begin{aligned}\therefore \% \text{ Nitrogen} &= \frac{\text{Weight of Nitrogen}}{\text{Weight of Coal sample}} \times 100 \\ &= \frac{0.1505}{3} \times 100\end{aligned}$$

$$\therefore \% \text{ Nitrogen} = 5.01\%.$$

## Calculation of % sulphur

### Given data

Weight of sample = 2.3 gm

Weight of BaSO<sub>4</sub> = 0.35 gms

$$\% \text{ Sulphur} = \frac{\text{Weight of BaSO}_4 \text{ ppt}}{\text{Weight of coal sample}} \times \frac{32}{233} \times 100$$

$$= \frac{0.35}{2.3} \times \frac{32}{233} \times 100$$

$$\% \text{ Sulphur} = \frac{1120}{535.9} = 2.09 \%$$

*Percentage of nitrogen in coal sample = 5.01%.*

*Percentage of sulphur = 2.09 %*

...Ans.

## 5.4 Conventional and Green Synthesis of Chemical Compounds

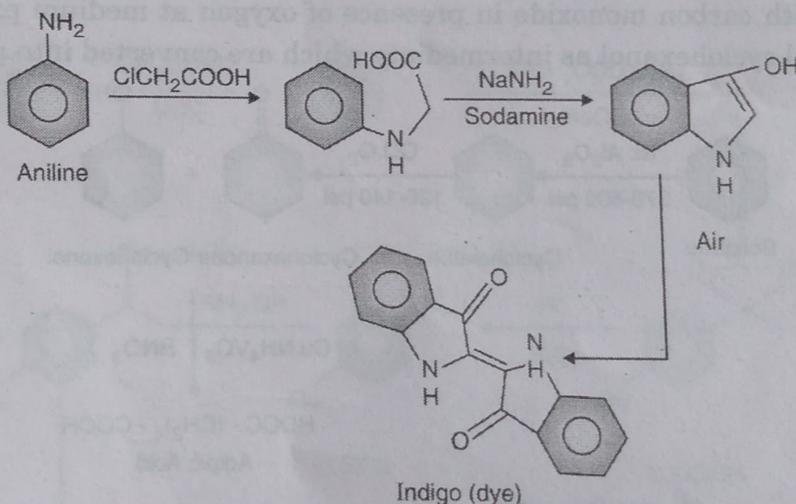
### 5.4.1 Synthesis of Indigo

MU – Dec. 15, May 16

Q. Explain conventional and green synthesis of Indigo dye. Mention the green chemistry principle involved.

(Dec. 15, May 16, 5 Marks)

#### 1. Conventional route using hazardous Aniline

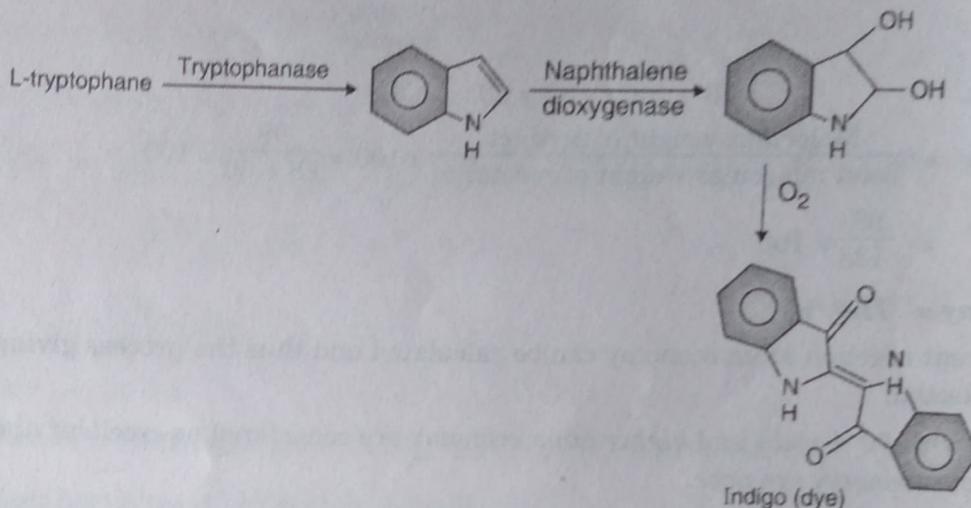


- In conventional method, aniline is treated with chloroacetic acid and the resultant heterocyclic carboxylic acid which is treated with sodamine to get a heterocyclic phenol.
- This is followed by coupling reaction in air to result in cyclisation forming indigo dye.



## 2. Green route using enzyme

- Greener route involves enzyme reaction starting with L-tryptophane treated with tryptophanase to get heterocyclic compound, which is treated with naphthalene in dioxygenase to get a heterocyclic di-phenol which is oxygenated to form indigo dye.



The above example is to meet with green chemistry principle of "Avoid use of hazardous chemicals"

### 5.4.2 Synthesis of Adipic Acid

#### 4. Areas Occupied by the Anode and Cathode

If two *dissimilar* metals are in contact, one forming anode while another forming cathode, then the corrosion of the anodic metal (part) is directly proportional to the ratio of the areas occupied by the cathode and anode.

Thus, corrosion at anode,  $\alpha = \frac{\text{Area of cathodic part}}{\text{Area of anodic part}}$

Hence, if cathode is large and anode is small, then corrosion at anode is higher and vice-versa.

#### 5. Purity of the Metal

- If the metals are impure, then the impurities present in them cause heterogeneity, which *gives rise to small electro-chemical cells* at the sites where metal and impurities are exposed, to the corrosive environment and thus, the corrosion starts, which then affects the entire metal.
- For Example, Zinc metal, if with the impurities of Fe or Pb, undergoes corrosion at the sites where the impurities are exposed because of the formation of local small electrochemical cell. *Thus more the percentage of impurity, higher is the corrosion of zinc metal.*

Q28

Table 6.7.1 : Comparison between octane and cetane number

Sr. No.	Octane number	Cetane number
1.	“Octane Number” expresses knocking character of petrol.	“Cetane Number” expresses knocking character of diesel.
2.	<p><b>Definition :</b></p> <p>“It is % of iso-octane in the mixture of iso-octane and n-heptane, which has similar knocking to the petrol sample”</p>	<p><b>Definition :</b></p> <p>“It is % of n-hexa-decane in the mixture of n-hexadecane and 2-methyl naphthalene which has same ignition character like the ignition character of the diesel under test.”</p>



Sr. No.	Octane number	Cetane number
3.	Octane number of good petrol should be atleast 85 for motor cycles and cars 100 for aeroplanes and helicopters.	Cetane number of good diesel should be 25 for low speed engine, 35 for medium speed engine and 45 for high speed engines.
4.	Octane number of petrol can be increased by adjusting compression ratio suitably, or by adding benzene or toluene, or alkylate fraction etc.	Cetane number of diesel can be increased by adding organic compounds containing oxygen atom, e.g. ethyl nitrate / nitrite, , acetone , peroxide etc.

### **5.2.9 Use Catalysts (Not Stoichiometric Reagents)**

The catalytic reagents which are selective in their reaction are preferred, over stoichiometric reagents.

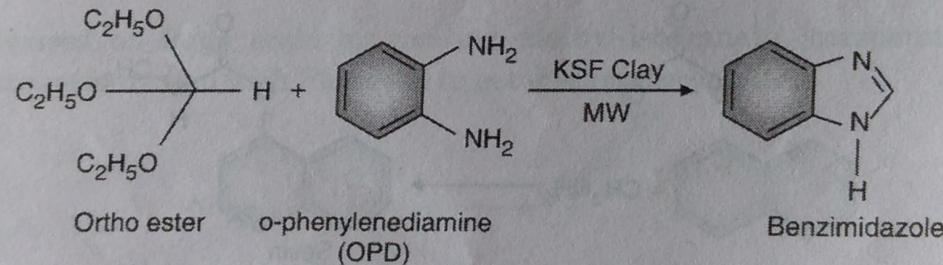
- Minimize waste by using *catalytic reactions*.
- Many times *catalysts* are used in small amounts and can carry out a single reaction.
- They are preferable to *stoichiometric reagents*, which are used in excess and work *only once*.
- Catalytic *reactions are faster* and hence require less energy.
- In recent years many processes have been developed which use *non toxic recoverable catalysts and also biocatalysis*.

## 5.4.5 Synthesis of Benzimidazole

- Benzimidazole is a heterocyclic aromatic organic compound.
- This compound is very important in medical field.
- Its derivatives are more important. E.g. like N-ribosyl-dimethyl benzimidazole which is highly useful as a ligand for cobalt in vitamin 12.

### **Structure**

- Benzimidazole is a bicyclic molecule formed by Benzene and Imidazole.



**Fig. 5.4.1 : Structure of benzimidazole with numbering of carbons**

- Pharmacologically this compound plays a vital role as most important nuclei in several drugs with beneficial therapeutic actions as shown below.

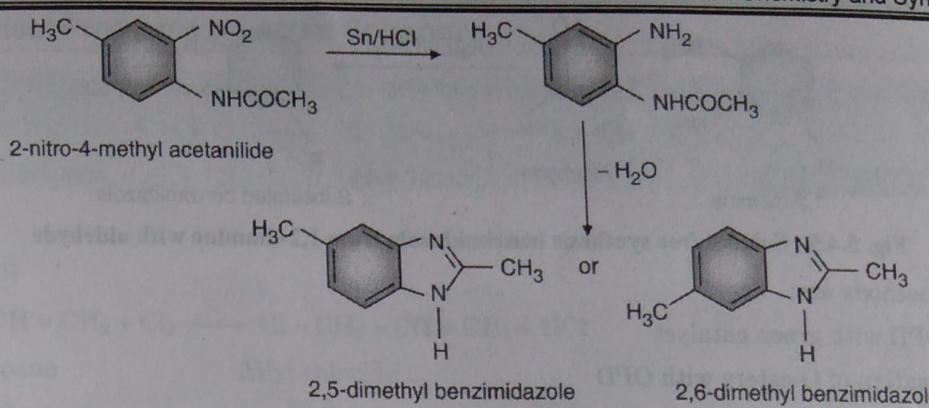


Fig. 5.4.2 : Pharmacological applications of benzimidazole

**(A) Synthesis by conventional chemical pathway**

- Benzene analogues possessing N like O-Phenylenediamines (OPD) which are reactive with various carboxylic acids readily, to form 2-substituted benzimidazoles.

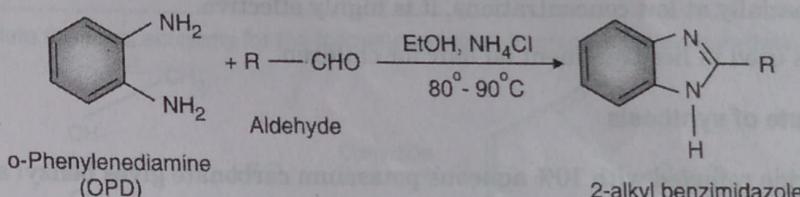


Fig. 5.4.3 : Synthesis of benzimidazole

- The yield of the reaction is high. The reactants are refluxed together using steam bath.

**Disadvantages of conventional route synthesis**

- Causes severe environmental problems. Like waste generation and its disposal.
- Hence E Factor rises for industry (E Factor- kgs of Waste generated per kg of the desirable product).

**(B) Alternative green route of Synthesis**

## 1. By condensation of o-phynylene diamine

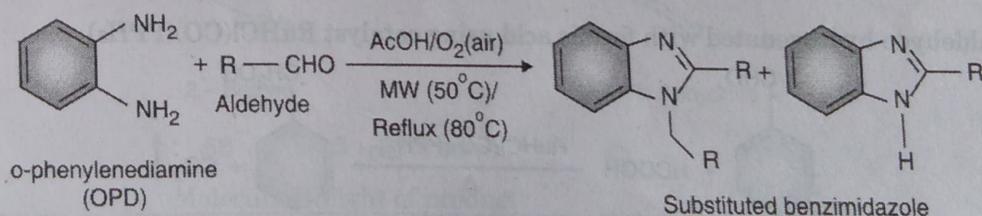
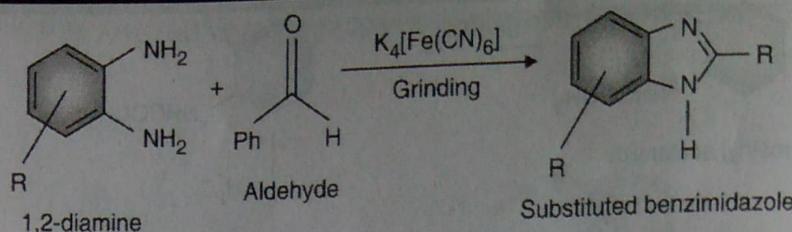


Fig. 5.4.4 : Microwave assisted benzimidazole synthesis

- 2. Solvent free synthesis 1,2-diamine is treated with aromatic aldehyde using metal coordinate complex like potassium ferrocyanide catalyst  $\text{K}_4[\text{Fe}(\text{CN})_6]$ .

This process inexpensive as carried out in solvent free conditions via oxidation of C-N bond. This provides green route under milder conditions giving good yield.



**Fig. 5.4.5 : Solvent free synthesis benzimidazole from 1,2-diamine with aldehyde**

Few more methods are;

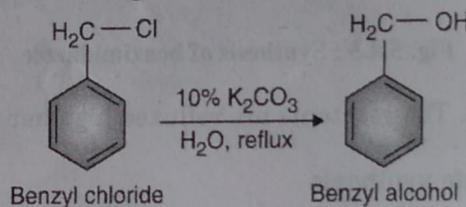
1. From OPD with green catalyst
2. Condensation of O-esters with OPD

#### 5.4.6 Synthesis of Benzyl Alcohol

- Benzyl alcohol is aromatic primary alcohol  $C_6H_5CH_2OH$ . It is polar in nature, with low toxicity and low vapour pressure and hence is highly useful in many reactions.
- It is also useful as a bacteriostatic preservative for several cosmetics, drugs and intravenous medications, especially at low concentrations, it is highly effective.
- Its 5% solution is used in lice treatment on hair for children.

##### (A) Conventional route of synthesis

- Benzyl Chloride refluxed with 10% aqueous potassium carbonate gives benzyl alcohol.

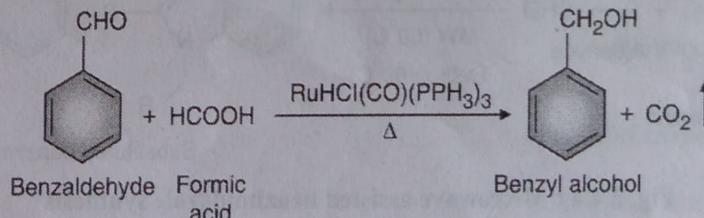


**Fig. 5.4.6 : Conventional process to manufacture Benzyl Alcohol**

- The method is highly expensive.
- The by-products are harmful which are generated due to low atom economy of the reaction.

##### (B) Alternative green route of synthesis

- Benzaldehyde hydrogenated with formic acid using catalyst RuHCl(CO)(PPh<sub>3</sub>)<sub>3</sub>



**Fig. 5.4.7 : Alternative green route process to manufacture Benzyl Alcohol**

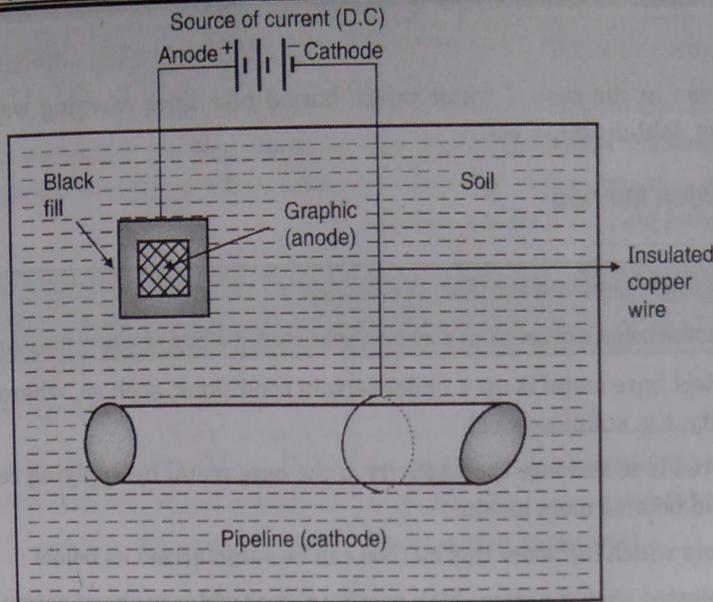
- It is microwave assisted by constant irradiation of microwaves.
- The time taken is just 7 minutes.
- The by-product is CO<sub>2</sub> which gets evaporated.

#### 4.5.3(B) Impressed Current

MU - May 15, May 17, Dec. 17

- Q. Explain impressed current method of corrosion control. (May 15, 5 Marks)
- Q. Explain the method of impressed current cathodic protection. (May 17, 3 Marks)
- Q. A metal rod half immersed in water starts corroding at the bottom. Give reasons. (Dec. 17, 2 Marks)

- In impressed current method, a current is applied in the opposite direction to that of corrosion current, thereby nullifying the effect of the latter one on the base metal, i.e. converting the base metal, to cathode from an anode.



**Fig. 4.5.3 : Corrosion control by impressed current method**

- Such an impressed current can be obtained by using D.C. source such as battery or dry cell along with an insoluble anode such as platinum, stainless-steel, graphite etc.
- In this method, as shown in Fig. 4.5.3, the insoluble anodic metal used (i.e. platinum, steel, scrap iron etc.) is normally embedded underground. To this, with the help of D.C. current source, the impressed current is applied, and whole of this assembly is connected to the metallic structure to be protected.
- The connections are done by using wires.
- The insoluble anode is kept inside back-fill made up of gypsum or any such material, which can help in increasing the electrical contact with the soil.
- Such an anode can be single, if the area of the metallic structure to be protected is small.
- There can be many such anodes, connected in series if the area of the metallic structure to be protected is wider, i.e. long pipeline etc.

#### **Advantages**

- (i) This method is highly useful, because it can protect the long length structures for a long term, thereby reducing frequency of monitoring as well as maintenance cost.
- (ii) These both methods are most widely used, because the protection provided to the base metal is long term and maintenance is easy.

#### **Disadvantage**

Due to the application of the impressed current, the anode deteriorates and hence, it has to be replaced from time to time.

### 3.2.1 Measurement of Electrode Potential

#### 3.2.1(A) Reference Electrodes

##### 1. Gas Electrode (Normal/Standard Hydrogen Electrode- NHE/SHE)

- It consists of gas bubbling over an inert metal wire or foil immersed in a solution containing ions of the gas.
- Standard hydrogen electrode is the primary reference electrode, whose electrode potential at all temperature is taken as zero arbitrarily.

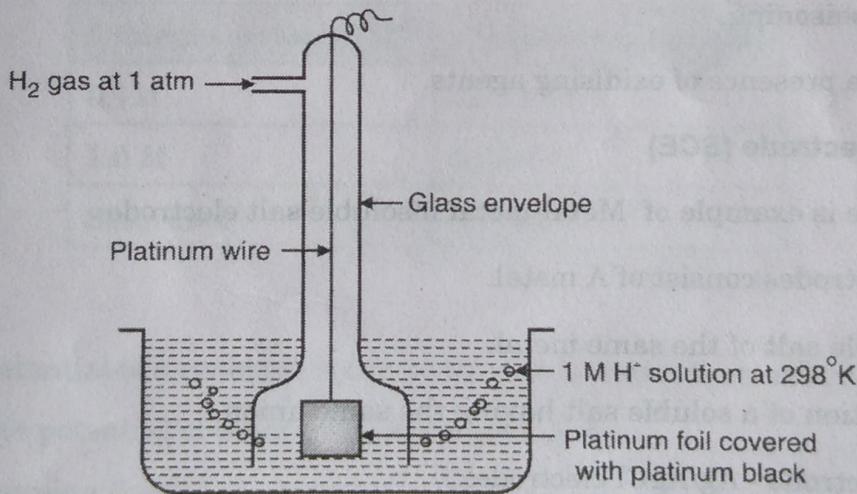


Fig. 3.2.2 : Gas electrode (Normal/Standard Hydrogen Electrode- NHE/SHE)



**Representation :** Pt, H<sub>2(g)</sub>/ H<sup>+</sup>

**Electrode reaction :** H<sup>+</sup> + e<sup>-</sup> → 1/2 H<sub>2(g)</sub>

- The electrode reaction is reversible as it can undergo either oxidation or reduction depending on the other half cell.
- If the concentration of the H<sup>+</sup> ions is 1M, pressure of H<sub>2</sub> is 1atm at 298°K it is called as Standard Hydrogen Electrode (SHE).

## Applications

- To determine electrode potential of other unknown electrodes.
- To determine the pH of a solution.

$$\begin{aligned} E &= E^\circ - \frac{RT}{nF} \log [H_2]_{1/2}/[H^+] \\ &= 0 - 0.0591 \log 1/[H^+] \\ &= -0.0591 \text{pH}. \end{aligned}$$

Cell Scheme: Pt, H<sub>2</sub>, H<sup>+(x)</sup> // SHE

- The emf of the cell is determined.

$$\begin{aligned} E_{\text{(cell)}} &= E_{\text{(c)}} - E_{\text{(A)}} \\ &= 0 - (-0.0592 \text{ pH}) \end{aligned}$$

$$E_{\text{(cell)}} = 0.0592 \text{ pH}$$

$$\text{pH} = E_{\text{(cell)}} / 0.0592$$

## Limitations

- Construction and working is difficult.
- Pt is susceptible for poisoning.
- Cannot be used in the presence of oxidising agents.

## Significance/ Importance of Proximate Analysis

Q35  
Moisture

- (i) It decreases calorific value of coal largely as it does not burn and takes away heat in the form of latent heat.
- (ii) It increases ignition point of coal. Hence, a coal with lower moisture % is better quality.

Volatile matter

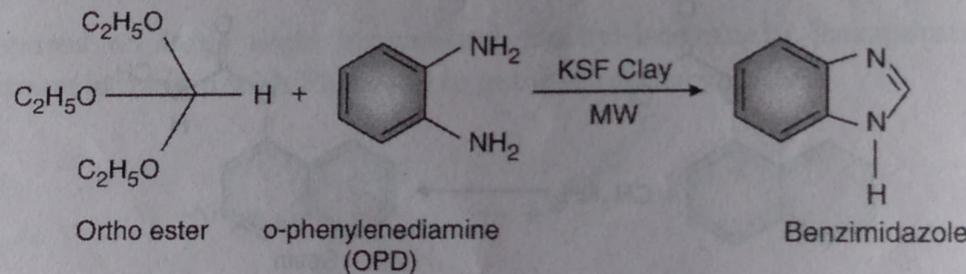
1. **Seasonal cracking** : Seasonal cracking is a term applied to stress corrosion of copper alloys, mainly brasses. Pure copper is immune to stress corrosion, but presence of small amounts of alloying element (like P, As, Sb, Zn, Al, Si) result in marked sensitivity. For examples, alpha brass (which when highly stressed) undergo intergranular cracking in an atmosphere, containing traces of ammonia or amines.

## 5.4.5 Synthesis of Benzimidazole

- Benzimidazole is a heterocyclic aromatic organic compound.
- This compound is very important in medical field.
- Its derivatives are more important. E.g. like N-ribosyl-dimethyl benzimidazole which is highly useful as a ligand for cobalt in vitamin 12.

### Structure

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**Fig. 5.4.1 : Structure of benzimidazole with numbering of carbons**

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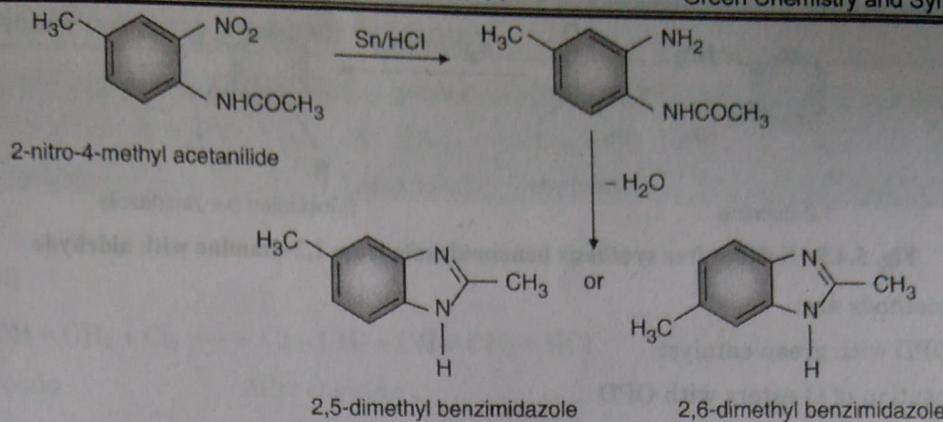


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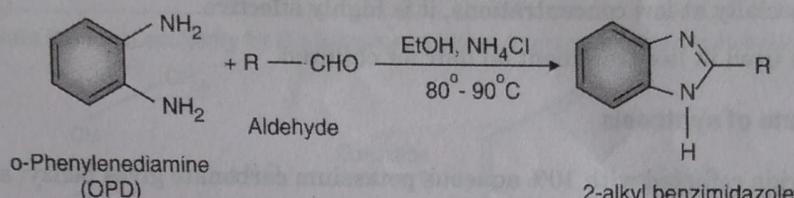


Fig. 5.4.3 : Synthesis of benzimidazole

- The yield of the reaction is high. The reactants are refluxed together using steam bath.

**Disadvantages of conventional route synthesis**

- Causes severe environmental problems. Like waste generation and its disposal.
- Hence E Factor rises for industry (E Factor- kgs of Waste generated per kg of the desirable product).

**(B) Alternative green route of Synthesis**

## 1. By condensation of o-phenylenediamine

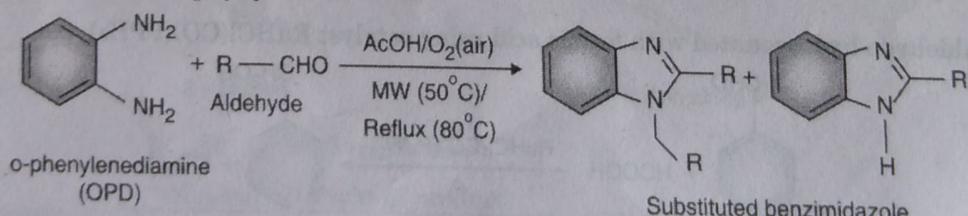
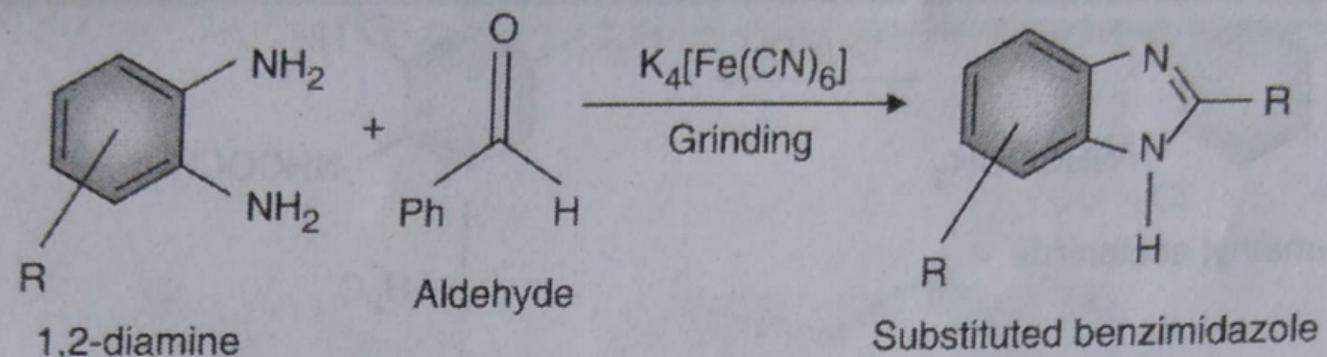


Fig. 5.4.4 : Microwave assisted benzimidazole synthesis

- 2. Solvent free synthesis 1,2-diamine is treated with aromatic aldehyde using metal coordinate complex like potassium ferrocyanide catalyst K4[Fe(CN)6].

This process inexpensive as carried out in solvent free conditions via oxidation of C-N bond. This provides green route under milder conditions giving good yield.



**Fig. 5.4.5 : Solvent free synthesis benzimidazole from 1,2-diamine with aldehyde**

Few more methods are;

1. From OPD with green catalyst
2. Condensation of O-esters with OPD

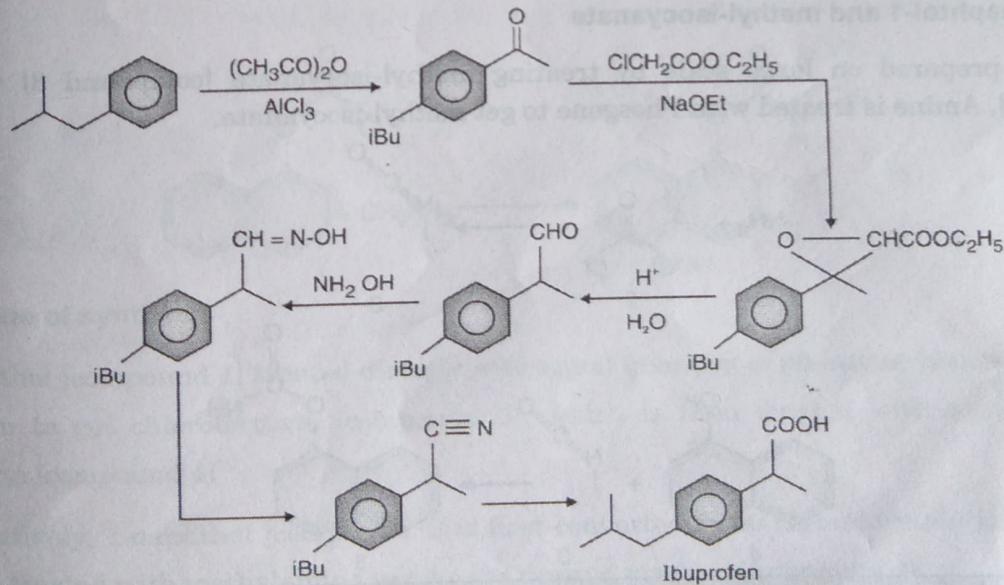
### Q.5b 5.4.3 Synthesis of Ibuprofen

MU – May 18

Q. Explain conventional and Green chemistry route for production of Ibuprofen Highlight the green chemistry principle involved. (May 18, 4 Marks)

#### 1. Conventional route with larger number of steps (Atom economy is 40 %)

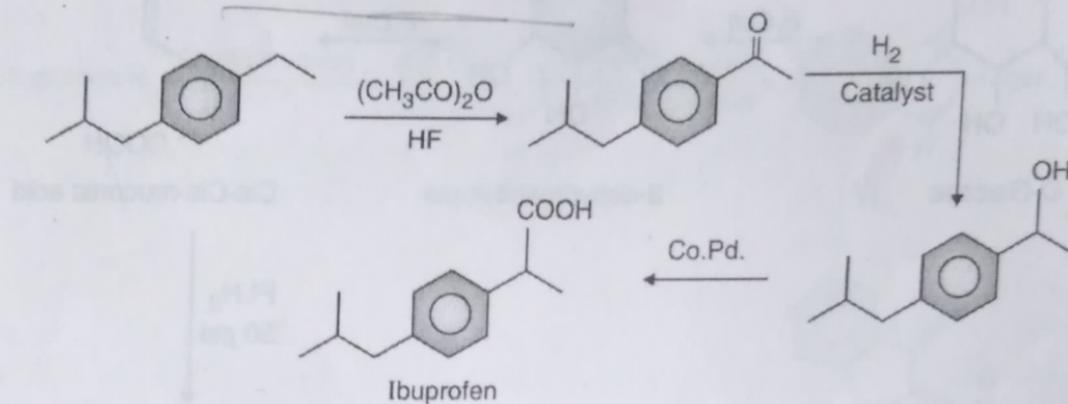
- Meta substituted benzene is used as starting material, subjected to FC reaction with acetic anhydride and aluminium chloride to give ketone, which is treated with ester in sodium ethoxide to get an intermediate. This is followed by acidic hydrolysis to get an aldehyde, which is treated with hydroxyl amine to form finally ibuprofen molecule.
- Route involves too many derivatives, and has low atom economy.





## 2. Green route with the atom economy 77 % and recoverable catalyst

- Starting with alkyl di-substituted benzene, treated with acetic anhydride to give ketone derivative, which is hydrogenated to get a phenol derivative, which gives ibuprofen.
- Route involves less derivatives and safer chemicals.



### 4.4 Synthesis of Carbaryl

**Q.** What is meant by knocking in internal combustion engine?

(Dec. 15, 5 Marks)

- Knocking is a term related to the internal combustion engine working on petrol.
- In internal combustion engine, a mixture of gasoline vapours and air is used as a fuel. The combustion or burning of a fuel is initiated by a spark in the cylinder as shown in Fig. 6.7.1.
- Due to combustion, gases are formed which move the piston down the cylinder. The rate of combustion and movement of piston depend upon the composition of fuel, temperature and design of the engine.
- The movement of the piston must be even uniform without any vibration.
- But sometimes, the rate of combustion becomes so great that the fuel on ignition, instantaneously produces sudden increase in the gaseous volume which causes uneven movement of the piston with rattling noise in the engine. It is called as knocking of the engine. The knocking results in the loss of efficiency of I.C. engine.

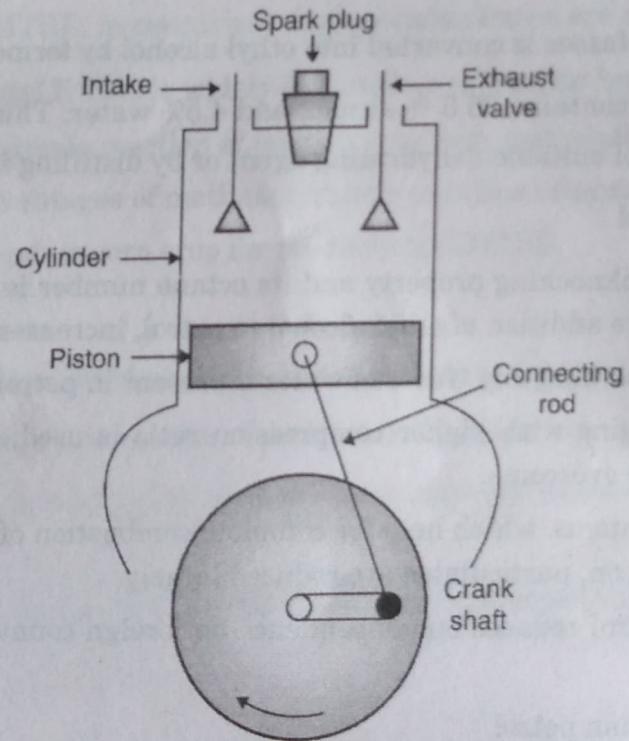


Fig. 6.7.1 : Spark in engine initiating combustion

- Thus knocking can be defined as, "a sharp metallic sound similar to rattling of hammer, which is produced in the internal combustion engine due to immature ignition of the air-gasoline mixture".
- Knocking causes (i) loss of large amount of energy (ii) damage to the piston and cylinder.