Chemistry

Model Set - 1

Academic Year: 2020-2021 Marks: 70
Date: April 2021
Duration: 3h

1. The question paper is divided into four sections.
2. **Section A**: Q. No. 1 contains Ten multiple-choice type of questions carrying One mark each.
3. **Section A**: Q. No. 2 contains Eight very short answer type of questions carrying One mark each.
4. **Section B**: Q. No. 3 to Q. No. 14 contains Twelve short answer type of questions carrying Two marks each. **(Attempt any Eight)**.
5. **Section C**: Q. No.15 to Q. No. 26 contains Twelve short answer type of questions carrying Three marks each. **(Attempt any Eight)**.
6. **Section D**: Q.No. 27 to Q. No. 31 contains Five long answer type of questions carrying Four marks each. **(Attempt any Three)**.
7. Use of log table is allowed. Use of calculator is not allowed.
8. Figures to the right indicate full marks.
9. For each MCQ, correct answer must be written along with its alphabet. e.g., (a) ..... / (b) .... / (c) .... / (d) ..... Only first attempt will be considered for evaluation.
10. Draw well labeled diagrams and write balanced equations wherever necessary.
11. Given data:
    Atomic mass of C = 12, H = 1, O = 16
    Atomic number (Z): Mn = 25, Fe = 26, Ce = 58, Ar = 18,
    R = 8.314 J K^{-1} mol^{-1} or 0.083 L bar K^{-1} mol^{-1}

Q. 1 | Select and write the correct answer:

1.i Bottom ash of thermal power stations can be used as raw material for cement and brick industry. This example illustrates which of the following principle of green chemistry?

1. Atom economy.
2. Designing safer chemicals.
3. Design for energy efficiency.
4. Prevention of waste or by products.

1.ii The sugar component of nucleotide unit in RNA is _______________

1. α-deoxy-D-ribose
2. D-ribose
3. L-ribose

4. 2-deoxy-L-ribose

1.iii The theory which explain amphoteric nature of water is _____.

1. Arrhenius theory
2. Lewis theory
3. Ostwald theory
4. Bronsted-Lowry theory

1.iv The charge on metal ion in $[Fe(CN)_6]^{4-}$ is ________

1. +2
2. +3
3. +4
4. +5

1.v An intensive property amongst the following is _____.

1. Mass
2. Volume
3. Number of moles
4. Temperature

1.vi Acidic strength of halogen acids increases in the order of ______.

1. HF > HCl > HBr > HI
2. HCl > HF > HBr > HI
3. HBr > HCl > HF > HI
4. HI > HBr > HCl > HF

1.vii The following electronic configuration of elements shows highest oxidation state

1. $3d^5 4s^2$
2. $3d^5 4s^1$
3. $3d^{10} 4s^2$
4. $3d^{10} 4s^1$

1.viii Which of the following is the product of reaction of ethane nitrile with Grignard reagent followed by acid hydrolysis?

1. a ketone
2. an aldehyde
3. an acid
4. an acid chloride

1.ix The pK_b of weak base BOH $[K_b(BOH) = 1 \times 10^{-5}]$ will be _____.

1. -5
2. 5
3. 1
4. 10^{-5}

1.x Sodium crystallizes in bcc structure. If the edge length of unit cell is 4.3 × 10^{-8} cm, the radius of Na atom is ______.

1. 86 × 10^{-8} cm
2. 52 × 10^{-8} cm
3. 15 × 10^{-8} cm
4. 3 × 10^{-8} cm

Q. 2 | Answer the following:

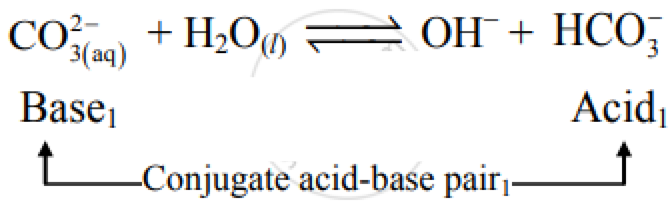
2.i Name the catalyst used to manufacture of H_2SO_4 by contact process.

Ans. Platinised asbestos is used as a catalyst in the manufacture of H_2SO_4 by contact process.

2.ii Label the one conjugate acid-base pair in the following reaction.

$$CO^{2-}_{3(aq)} + H_2O_{(l)} \rightleftharpoons OH^- + HCO_3^-$$

Ans.



$$\underset{\text{Base}_1}{CO^{2-}_{3(aq)}} + H_2O_{(l)} \rightleftharpoons OH^- + \underset{\text{Acid}_1}{HCO_3^-}$$

Conjugate acid-base pair$_1$

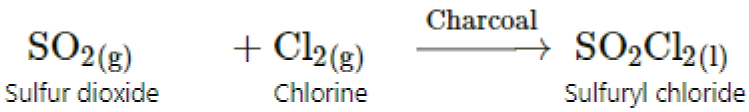
2.iii Write the type of isomerism exhibited by $[Co(NH_3)_5(NO_2)]^{2+}$ and $[Co(NH_3)_5ONO]^{2+}$ pair of complex ion.

Ans. The type of isomerism exhibited is linkage isomerism.

2.iv Complete the following reaction:

$$SO_{2(g)} + Cl_{2(g)} \xrightarrow{\text{Charcoal}} ?$$

Ans.



$$\underset{\text{Sulfur dioxide}}{SO_{2(g)}} + \underset{\text{Chlorine}}{Cl_{2(g)}} \xrightarrow{\text{Charcoal}} \underset{\text{Sulfuryl chloride}}{SO_2Cl_{2(l)}}$$

2.v Write the order of ionic character of halides with monovalent metal (M).

Ans. The ionic character of halides with monovalent metal (M) decreases in the order: MF > MCl > MBr > MI.

2.vi Write formula to calculate magnetic moment.

Ans. The spin-only formula to calculate magnetic moment is:

$$\mu = \sqrt{n(n + 2)}\ \text{BM}$$

2.vii Write chemical formula of ore of zinc.

Ans. Chemical formula of zinc ore (zink blende): ZnS

2.viii The vapour pressures of pure liquids A and B are 0.600 bar and 0.933 bar respectively, at a certain temperature.
What is the mole fraction of liquid B in the solution when the total vapour pressure of their mixture is 0.8 bar?

Ans.

Given: Vapour pressure of pure liquid A $\left(P_1^0\right)$ = 0.600 bar

Vapour pressure of pure liquid B $\left(P_2^0\right)$ = 0.933 bar

Total pressure (P) = 0.8 bar

To find: Mole fraction of liquid B in the solution

Formula: $P = \left(P_2^0 - P_1^0\right) x_2 + P_1^0$

$$0.8\text{ bar} = (0.933\text{ bar} - 0.600\text{ bar})\, x_2 + 0.600\text{ bar}$$

$$\therefore 0.8 - 0.600 = 0.333\, x_2$$

$$\therefore x_2 = \frac{0.2}{0.333} = 0.6$$

Mole fraction of liquid B in the solution is 0.6.

Q. 3 | Attempt any Eight:

Complete and write the following table

Reation	Name of catalyst
i) Manufacture of HDPE polymer	______________
ii) ______________	V_2O_5

Ans.

Reaction	Name of catalyst
i) Manufacture of HDPE polymer	**Ziegler-Natta catalyst**
ii) **Manufacture of H_2SO_4 by contact process**	V_2O_5

Q. 4 Write the name of raw material used for preparation of nylon 6, 6 polymer.

Ans. Raw material used for preparation of nylon 6, 6 polymer are adipic acid and hexamethylenediamine.

Q. 5 Give two points to explain why vapour pressure of solvent is lowered by dissolving nonvolatile solute into it.

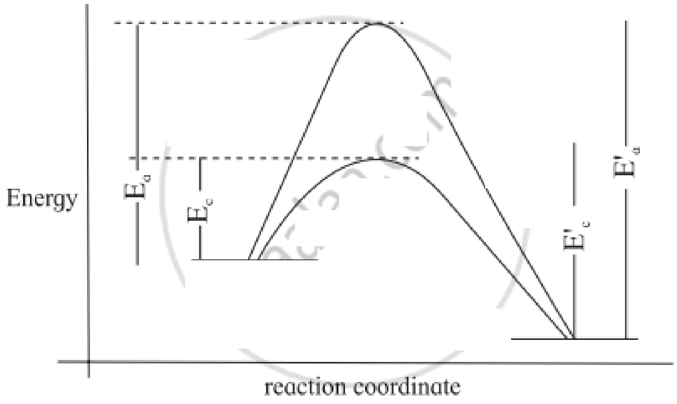
Ans.

1. Vapour pressure of a liquid depends on the ease with which the molecules escape from the surface of liquid. When nonvolatile solute is dissolved in a solvent, some of the surface molecules of solvent are replaced by nonvolatile solute molecules. These solute molecules do not contribute to vapour above the solution.
2. Thus, the number of solvent molecules available for vaporization per unit surface area of a solution is less than the number at the surface of pure solvent. As a result the solvent molecules at the surface of solution vaporize at a slower rate than pure solvent. This results in lowering of vapour pressure.

Q. 6 Explain with the help of a potential energy diagram that the catalyst increases the rate of the reaction.

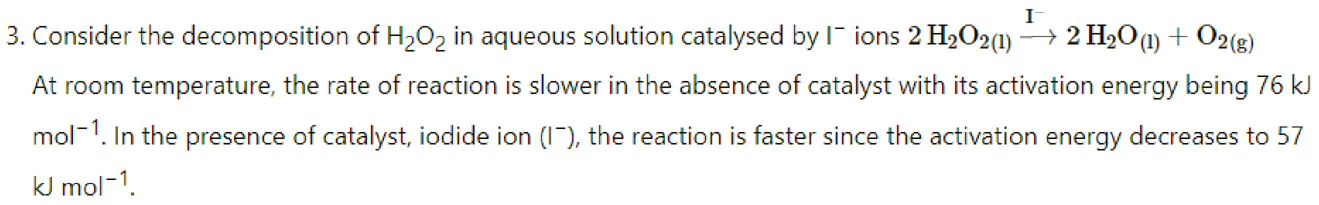
Ans.

1. A catalyst provides alternative pathway associated with lower activation energy.



Potential energy barriers for catalyzed and uncatalyzed reactions

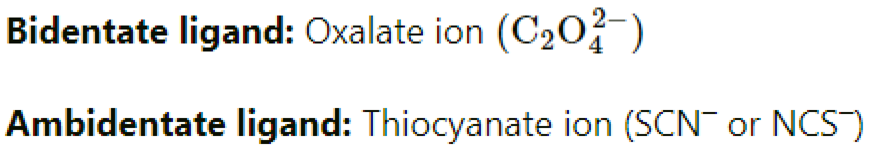
2. The potential energy diagram compares the potential energy barriers for the catalysed and uncatalysed reactions. The barrier for uncatalysed reaction (E_a) is larger than that for the same reaction in the presence of a catalyst E_a.



3. Consider the decomposition of H_2O_2 in aqueous solution catalysed by I^- ions $2\,H_2O_{2(l)} \xrightarrow{I^-} 2\,H_2O_{(l)} + O_{2(g)}$ At room temperature, the rate of reaction is slower in the absence of catalyst with its activation energy being 76 kJ mol^{-1}. In the presence of catalyst, iodide ion (I^-), the reaction is faster since the activation energy decreases to 57 kJ mol^{-1}.

Q. 7 Write one example of each of bidentate and ambidentate ligand.

Ans.



Bidentate ligand: Oxalate ion ($C_2O_4^{2-}$)

Ambidentate ligand: Thiocyanate ion (SCN^- or NCS^-)

Q. 8. A Define the Standard enthalpy of combustion.

Ans. A The standard enthalpy of combustion of a substance is the standard enthalpy change accompanying a reaction in which one mole of the substance in its standard state is completely oxidized.

Q. 8. B Define the Enthalpy of sublimation.

Ans. Enthalpy of sublimation is the enthalpy change for the conversion of one mole of solid directly into vapour at constant temperature and pressure.

Q. 9 Elements of group 16 have lower ionization enthalpy values compared to those of group 15 elements. Explain why?

Ans. Group 15 elements have extra stable, half-filled p-orbitals with outer electronic configuration ($ns^2\ np^3$). Therefore, more amount of energy is required to remove an electron compared to that of the partially filled orbitals ($ns^2\ np^4$) of group 16 elements of the corresponding period. Hence, elements of group 16 have lower ionization enthalpy values compared to those of group 15 elements.

Q. 10 Manganese in the +2 oxidation state is more stable than +3 oxidation state where as iron is stable at +3 oxidation state than +2 oxidation state. Explain why?

Ans.

1. Any subshell having a half-filled or completely filled electronic configuration has extra stability.
2. The electronic configuration of Mn^{2+} is [Ar] $3d^5$ while that of Mn^{3+} is [Ar] $3d^4$. Hence, manganese in the +2 oxidation state is more stable than +3 oxidation state due to half-filled d-orbitals.

3. The electronic configuration of Fe^{3+} is [Ar] $3d^5$ while that of Fe^{2+} is [Ar] $3d^6$. Hence, iron is stable at +3 oxidation state than +2 oxidation state due to half-filled d-orbitals.

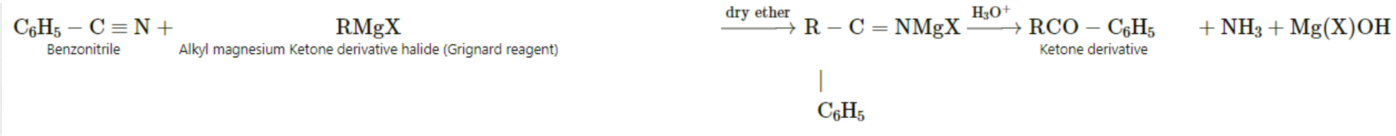
Q. 11 Carboxylic acids have higher boiling points than those of ethers. Give reason.

Ans.

i. In the liquid phase, carboxylic acids form a dimer in which two molecules are held by two hydrogen bonds.
ii. Acidic hydrogen of one molecule forms a hydrogen bond with the carbonyl oxygen of the other molecule.
iii. This doubles the size of the molecule resulting in an increase in intermolecular van der Waals forces, which in turn results in a high boiling point.
iv. Therefore, carboxylic acids have higher boiling points than those of ethers of comparable mass.

Q. 12 What is the action of Grignard reagent on benzonitrile?

Ans. Benzonitrile on reaction with the Grignard reagent in the dry ether as solvent followed by acid hydrolysis will form corresponding ketone derivative.

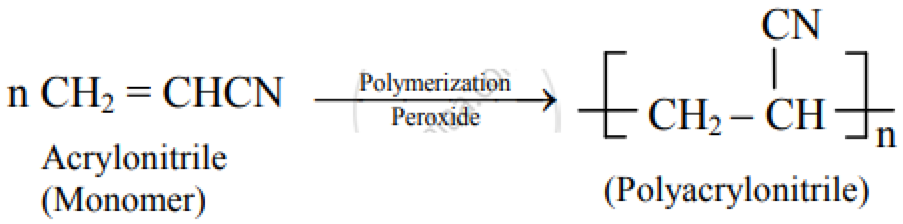


$$\underset{\text{Benzonitrile}}{C_6H_5-C\equiv N} + \underset{\text{Alkyl magnesium Ketone derivative halide (Grignard reagent)}}{RMgX} \xrightarrow{\text{dry ether}} \underset{\substack{|\\ C_6H_5}}{R-C}=NMgX \xrightarrow{H_3O^+} \underset{\text{Ketone derivative}}{RCO-C_6H_5} + NH_3 + Mg(X)OH$$

Q. 13 Write chemical reaction for the preparation of the following polymer.

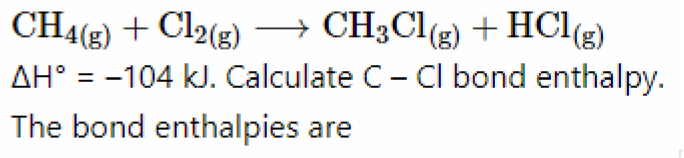
Polyacrylonitrile

Ans.



$$\underset{\substack{\text{Acrylonitrile}\\ \text{(Monomer)}}}{n\,CH_2=CHCN} \xrightarrow[\text{Peroxide}]{\text{Polymerization}} \underset{\text{(Polyacrylonitrile)}}{\left[CH_2-\overset{\overset{CN}{|}}{CH} \right]_n}$$

Q. 14 The enthalpy change of the following reaction



$CH_{4(g)} + Cl_{2(g)} \longrightarrow CH_3Cl_{(g)} + HCl_{(g)}$

ΔH° = −104 kJ. Calculate C – Cl bond enthalpy.

The bond enthalpies are

Bond	C – H	Cl – Cl	H – Cl
ΔH°/kJ mol⁻¹	414	243	431

Ans. Given: $\Delta_rH°$ = –104 kJ
ΔH° (C – H) = 414 kJ mol^{-1}
ΔH° (Cl – Cl) = 243 kJ mol^{-1}
ΔH° (H – Cl) = 431 kJ mol^{-1}

To find: C – Cl bond enthalpy, ΔH° (C–Cl)

Formula: $\Delta_rH° = \sum\Delta H°(\text{reactant bonds}) - \sum\Delta H° (\text{product bonds})$

Calculation: $\Delta_rH° = \Sigma\ \Delta H°\ (\text{reactant bonds}) - \Sigma\ \Delta H°\ (\text{product bonds})$

$= [4\ \Delta H°(C - H) + \Delta H°(Cl - Cl)] - [3\ \Delta H°(C - H) + \Delta H°(C - Cl) + \Delta H°(H - Cl)]$

$= \Delta H°(C - H) + \Delta H°(Cl - Cl) - \Delta H°(C - Cl) - \Delta H°(H - Cl)$

$\therefore -104\ kJ = 1\ mol \times (414\ kJ\ mol^{-1}) + 1\ mol \times (243\ kJ\ mol^{-1}) - \Delta H°(C - Cl) - 1\ mol \times (431\ kJ\ mol^{-1})$

$\therefore -104\ kJ = 226\ kJ - \Delta H°(C - Cl)$

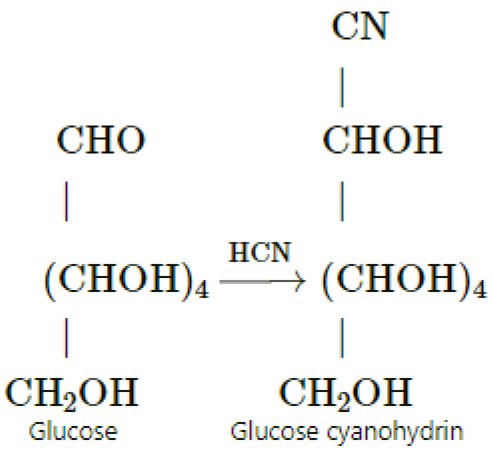
$\therefore \Delta H°(C - Cl) = 226\ kJ + 104\ kJ$

$\therefore \Delta H°(C - Cl) = 330\ kJ\ mol^{-1}$

C – Cl bond enthalpy is **330 kJ mol⁻¹**.

Q. 15 | Attempt any Eight:

Write a chemical reaction to convert glucose into glucose cyanohydrin.
Ans. Glucose forms cyanohydrin on reaction with hydrogen cyanide:



$$\begin{array}{c} CHO \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \\ \text{Glucose} \end{array} \xrightarrow{HCN} \begin{array}{c} CN \\ | \\ CHOH \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \\ \text{Glucose cyanohydrin} \end{array}$$

Q. 16 Derive the equation which implies that the degree of dissociation of weak acid is inversely proportional to the square root of its concentration.

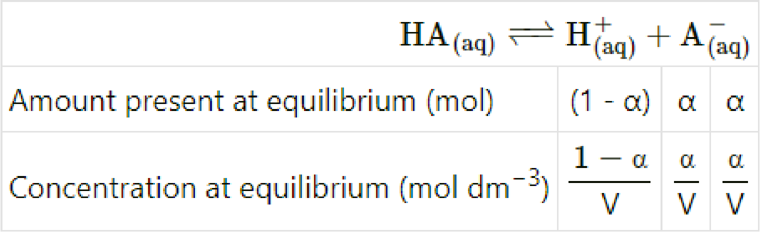
Ans. Consider an equilibrium of weak acid HA that exists in solution partly as the undissociated species HA and partly H^+ and A^- ions. Then

$$HA_{(aq)} \rightleftharpoons H^+_{(aq)} + A^-_{(aq)}$$

The acid dissociation constant is given as:

$$K_a = \frac{[H^+][A^-]}{HA} \quad .....(1)$$

Suppose 1 mol of acid HA is initially present in volume V dm^3 of the solution. At equilibrium, the fraction dissociated would be α, where α is a degree of dissociation of the acid. The fraction of an acid that remains undissociated would be (1 − α).



	$HA_{(aq)} \rightleftharpoons$	$H^+_{(aq)}$ +	$A^-_{(aq)}$
Amount present at equilibrium (mol)	(1 - α)	α	α
Concentration at equilibrium (mol dm^{-3})	$\frac{1-\alpha}{V}$	$\frac{\alpha}{V}$	$\frac{\alpha}{V}$

Thus, at equilibrium [HA] = $\frac{1-\alpha}{V}$ mol dm^{-3}

$[H^+] = [A^-] = \frac{\alpha}{V}$ mol dm^{-3}

Substituting these in equation (1),

$$K_a = \frac{(\alpha/V)(\alpha/V)}{(1-\alpha)/V} = \frac{\alpha^2}{(1-\alpha)V} \quad ....(2)$$

If c is the initial concentration of an acid in mol dm^{-3} and V is the volume in dm3 mol^{-1} then c = 1/V. Replacing 1/V in equation (2) by c, we get

$$K_a = \frac{\alpha^2 c}{1-\alpha} \quad ....(3)$$

For the weak acid HA, α is very small, or (1 − α) ≅ 1.

With this equation (2) and (3) becomes:

$K_a = \alpha^2/V$ and $k_a = \alpha^2 c$ ....(4)

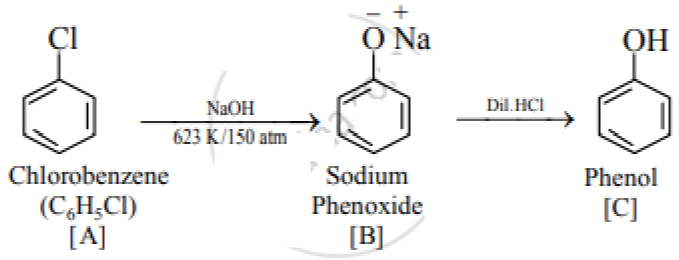
$$\alpha = \frac{\sqrt{K_a}}{c} \text{ or } \alpha = \sqrt{K_a \cdot V} \quad ....(5)$$

The equation (5) implies that the degree of dissociation of a weak acid is inversely proportional to the square root of its concentration.

Q. 17 Compound 'A' with molecular formula C_6H_5Cl is fused with NaOH at high temperature under pressure to give compound 'B'. Compound 'B' on treatment with dil.HCl gives compound C having characteristic carbolic odour. Write the chemical equations in support of this. Name the process and give uses of compound C.

Ans.

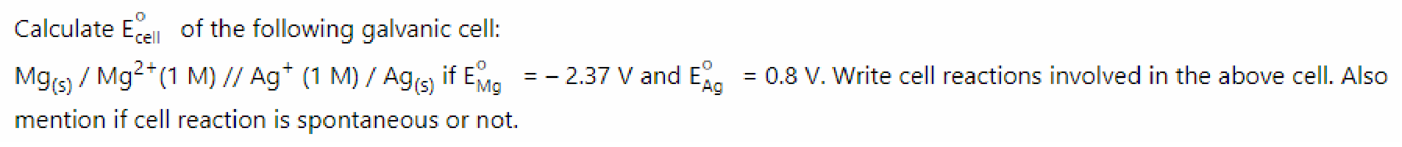
i. The chemical equation can be represented as:



ii. The process involved in the Dow process.

iii. **Uses of phenols:**
a. Phenol is used in the preparation of phenol-formaldehyde resin. For example, bakelite.
b. Phenols are used as antiseptic in common products like air fresheners, deodorants, mouthwash, calamine lotions, floor cleaners, etc.

Q. 18



Calculate E^{o}_{cell} of the following galvanic cell:

$Mg_{(s)} / Mg^{2+}(1\ M) // Ag^{+}\ (1\ M) / Ag_{(s)}$ if $E^{o}_{Mg} = -2.37$ V and $E^{o}_{Ag} = 0.8$ V. Write cell reactions involved in the above cell. Also mention if cell reaction is spontaneous or not.

Ans.

Given: E^{o}_{Mg} = – 2.37 V and E^{o}_{Ag} = 0.8 V

To find: Standard cell potential

Formula: $E^{o}_{cell} = E^{o}_{cathode} - E^{o}_{anode}$

Calculation: $E^{o}_{cell} = E^{o}_{cathode} - E^{o}_{anode}$

$E^{o}_{cell} = E^{o}_{Ag} - E^{o}_{Mg}$

= (0.8 V) - (- 2.37 V) = 3.17 V

The standard cell potential for the reaction is **3.17 V**.

Cell reactions:

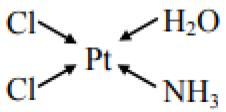
Electrode reactions are

At anode:	$Mg_{(s)} \longrightarrow Mg^{2+}_{(aq)} + 2\,e^{-}$
At cathode:	$Ag^{+}_{(aq)} + e^{-} \longrightarrow Ag_{(s)}$
Overall cell reaction- $Mg_{(s)} + 2\,Ag^{+}_{(aq)} \longrightarrow Mg^{2+}_{(aq)} + 2\,Ag_{(s)}$	

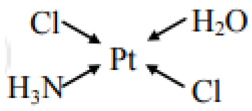
Since the standard cell potential is positive, the cell reaction is spontaneous.

Q. 19 Draw the geometrical isomers of the following complexes $[Pt(NH_3)(H_2O)Cl_2]$ and $[Co(NH_3)_4Cl_2]^+$

Ans. Geometrical isomers of $[Pt(NH_3)(H_2O)Cl_2]$:

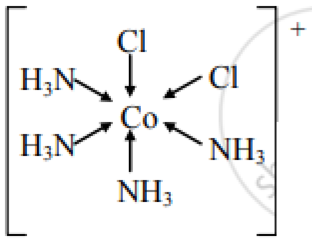


Cis isomer

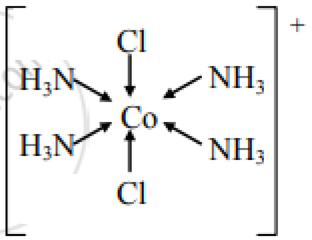


Trans isomer

Geometrical isomers of $[Co(NH_3)_4Cl_2]^+$:



Cis isomer

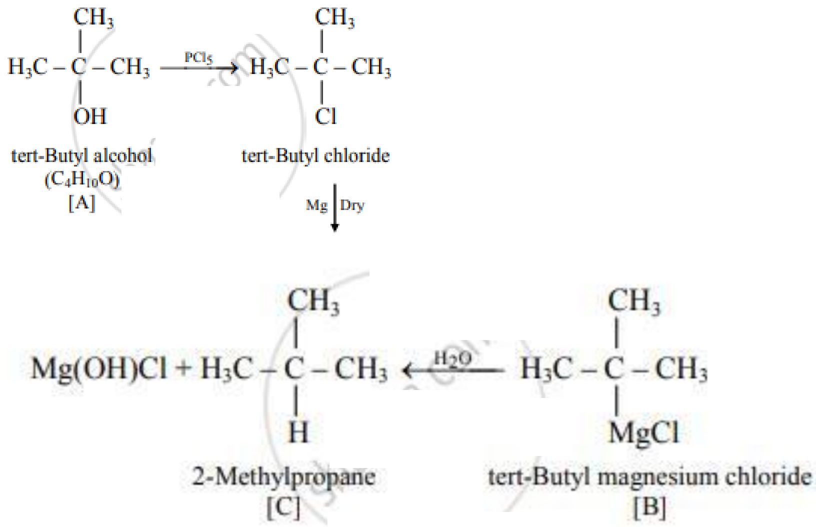


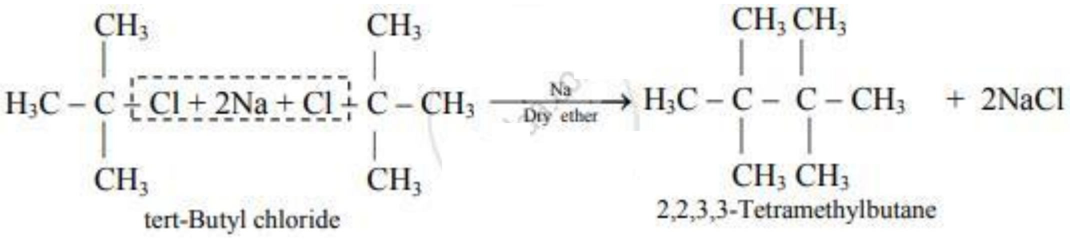
Trans isomer

Q. 20 An organic compound A with molecular formula $C_4H_{10}O$ on treatment with phosphorus pentachloride gives alkyl chloride. Alkyl chloride on treatment with Mg in presence of dry ether gives a highly reactive compound B.

Compound B reacts with water to give hydrocarbon C. Alkyl chloride on treatment with Na in dry ether as a solvent gives alkane, 2,2,3,3-tetramethylbutane. Identify ‘A’, ‘B’, ‘C’

Ans.





∴ **Compound (A):** tert-Butyl alcohol;
Compound (B): tert-Butyl magnesium chloride;
Compound (C): 2-Methylpropane

Q. 21 Derive the expression for work done in chemical reaction. Write the relationship between ΔH and ΔU for an isochoric process

Ans. Expression for work done in a chemical reaction:

The work done by a system at constant temperature and pressure is given by

$W = P_{ext} \Delta V$ .....(1)

Assuming $P_{ext} = P$,

$W = - P\Delta V$

$= - P (V_2 - V_1) W$

$= - PV_2 + PV_1$ ......(2)

If the gases were ideal, at constant temperature and pressure.,

$PV_1 = n_1RT$ and $PV_2 = n_2RT$ ...(3)

Substitution of equation (3) into equation (2) yields

$W = - n_2RT + n_1RT$

$= - (n_2 - n_1) RT$

$= - \Delta n_g RT$ ...(4)

Equation (4) gives the work done by the system in chemical reactions.

Relationship between ΔH and ΔU for an isochoric process:

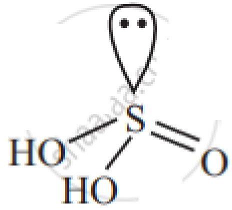
For an isochoric process, $\Delta V = 0$.

$\Delta H = \Delta U + P\Delta V = \Delta U + 0 = \Delta U$

∴ $\Delta H = \Delta U$

Q. 22. A What is the oxidation state of sulfur in the following?
Sulfurous acid

Ans. A Sulfurous acid, H_2SO_3:



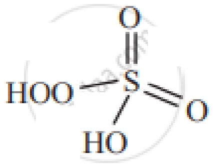
$2 \times (+1) + (\text{Oxidation state of S}) + 3 \times (-2) = 0$

$2 + (\text{Oxidation state of S}) - 6 = 0$

Hence, oxidation state of 'S' in H_2SO_3 = **+4**

Q. 22. B What is oxidation state of sulfur in the following?
Peroxymonosulfuric acid

Ans. Peroxymonosulfuric acid, H_2SO_5:



2 × (+1) + (Oxidation state of S) + 3 × (−2) + 2 × (−1) = 0

2 + (Oxidation state of S) − 6 − 2 = 0

Hence, oxidation state of 'S' in H_2SO_4 = **+6**

Q. 23. A What are rare earth elements?

Ans.

1. Although, historically, lanthanoids are termed as rare earth elements, they are fairly abundant in earth's crust.
   e.g. Thulium is found more in abundance than silver (4.5×10^{-5} vs 0.79 × 10−5 percent by mass).
2. The names rare earth elements was coined because of difficulty in extracting them economically in pure form from other lanthanoids having similar chemical properties. Now, due to newer separation methods like ion exchange resins, the separation of these elements has become easier and more economical.

Q. 23. B Write any two properties actinides.

Ans. Properties of actinides:

1. Similar to lanthanoids, they appear silvery-white in colour.
2. These are highly reactive radioactive elements.
3. Except promethium (Pm), all are nonradioactive in nature.
4. They experience decrease in the atomic and ionic radii from actinium (Ac) to lawrencium (Lr), known as actinoid contraction.
5. They usually exhibit +3 oxidation state. Elements of the first half of the series usually exhibit higher oxidation states.

Q. 23. C Write any two uses of actinides.

Ans. Uses of actinides:

1. The half-lives of natural thorium and uranium isotopes are so long that we get very negligible radiation from these elements. So, we find them in everyday use.
2. Th(IV) oxide, ThO2 with 1% CeO_2 was used as a major source of indoor lighting before incandescent lamps came into existence only because these oxides convert heat energy from burning natural gas to intense light. Even today, there is a great demand for these lights for outdoor camping.

Q. 24. A What is the action of following reagents on ethanoic acid?

$SOCl_2$/heat

Ans. Ethanoic acid on heating with $SOCl_2$ gives the corresponding acyl chloride.

$$\underset{\text{Ethanoic acid}}{CH_3COOH} + \underset{\text{Thionyl chloride}}{SOCl_2} \xrightarrow{\Delta} \underset{\text{Acetyl chloride}}{CH_3COCl} + HCl\uparrow + SO_2\uparrow$$

Q. 24. B What is the action of following reagents on ethanoic acid?

sodalime/heat

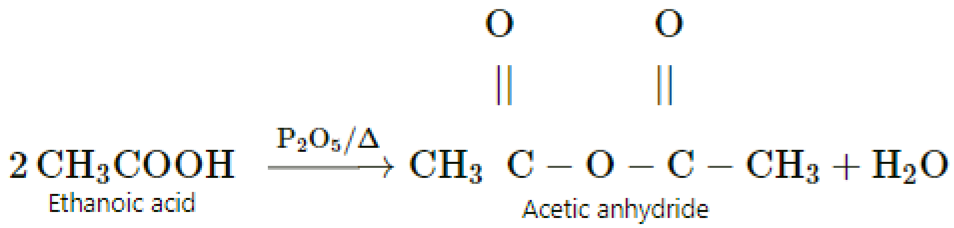
Ans. Sodium salts of ethanoic acid on heating with soda lime give methane which contains one carbon atom less than the ethanoic acid.

$$\underset{\text{Ethanoic acid}}{CH_3-COOH} \xrightarrow{NaOH} \underset{\text{Sodium acetate}}{CH_3-COO^-\ Na^+} + NaOH \xrightarrow[\Delta]{CaO} \underset{\text{Methane}}{CH_4} + Na_2CO_3$$

Q. 24. C What is the action of following reagents on ethanoic acid?

P_2O_5/heat

Ans. Ethanoic acid on heating with strong dehydrating agent P_2O_5 forms acetic anhydride.



$$\underset{\text{Ethanoic acid}}{2\,CH_3COOH} \xrightarrow{P_2O_5/\Delta} \underset{\text{Acetic anhydride}}{CH_3\ \overset{\overset{O}{||}}{C}-O-\overset{\overset{O}{||}}{C}-CH_3} + H_2O$$

Q. 25 A solution containing 3 g of solute A (M = 60 g/mol) in 1 L solution is isotonic with a solution containing 8.55 g of solute B in 500 mL solution. What is the molar mass of B?

Ans. Given: Mass of solute A = $(W_2)_A$ = 3 g
Volume = V_A = 1 L
Molar mass of solute A = $(M_2)_A$ = 60 g mol$_{-1}$
Mass of solute B = $(W_2)_B$ = 8.55 g
Volume = V_B = 500 mL = 0.5 L

To find: Molar mass of solute B = $(M_2)_B$

Formula: $\pi = \dfrac{W_2RT}{M_2V}$

Calculation: For solution containing 3 g of solute A,

$$\pi_A = \frac{(W_2)_A RT}{(M_2)_A V_A} \quad .....(i)$$

For solution containing 8.55 g of solute B,

$$\pi_B = \frac{(W_2)_B RT}{(M_2)_B V_B} \quad .....(ii)$$

Since both the solutions are isotonic, $\pi_A = \pi_B$

$$\therefore \frac{(W_2)_A RT}{(M_2)_A V_A} = \frac{(W_2)_B RT}{(M_2)_B V_B}$$

$$\therefore (M_2)_B = \frac{(W_2)_B \times (M_2)_A \times V_A}{(W_2)_A \times V_B}$$

$$= \frac{8.55 \times 60 \times 1}{3 \times 0.5} = 342 \text{ g mol}^{-1}$$

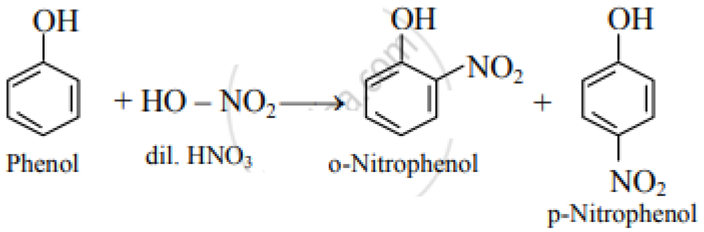
The molar mass of solute B is 342 g mol^{-1}

Q. 26 What is the action of following on phenol at low temperature?

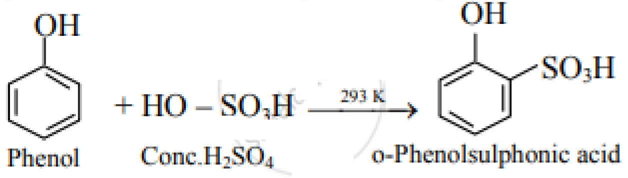
a. dil. HNO_3
b. conc. H_2SO_4
c. Br_2/CS_2

Ans.

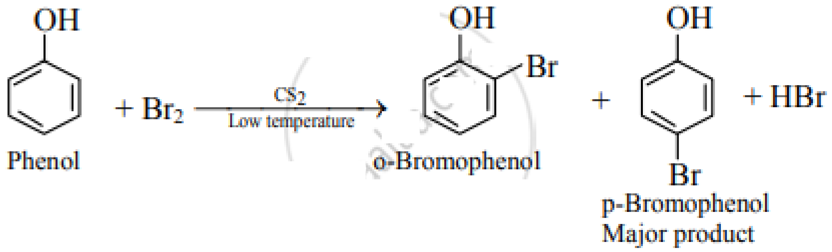
a. **Dilute HNO_3:** Phenol reacts with dilute nitric acid at low temperature to give a mixture of ortho- and para-nitrophenol.



b. **Conc. H_2SO_4:** At room temperature (298 K), phenol reacts with concentrated sulphuric acid to form o-phenolsulphonic acid.



Br_2 in CS_2: When a reaction is carried out in a solvent of lower polarity like CS_2 a mixture of ortho- and para-bromophenol is formed.



Q. 27 | Attempt any Three:

27.i What is dehydrohalogenation? State the rule for the formation of the preferred product of dehydrohalogenation.

Ans.

i. **Dehydrohalogenation reaction:** When an alkyl halide having at least one β-hydrogen is boiled with an alcoholic solution of potassium hydroxide (KOH), it undergoes elimination of hydrogen atom from β-carbon and halogen atom from α-carbon resulting in the formation of an alkene. As hydrogen and halogen are removed in this reaction, it is termed a dehydrohalogenation reaction.

ii. **Saytzeff's rule:**
Statement - "In dehydrohalogenation reaction, the preferred product is that alkene which has a greater number of alkyl groups attached to doubly bonded carbon atoms."

27.ii Write the equations for the preparation of ethyl chloride using

a. Hydrogen halide
b. ethene
c. Thionyl chloride
d. Which of these methods is preferred and why?

Ans.

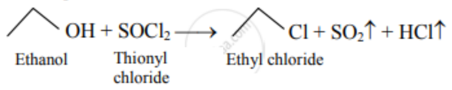
a. **Hydrogen halide:**

$$\underset{\text{Ethanol}}{CH_3CH_2-OH} + HCl \xrightarrow[ZnCl_2]{\text{anhydrous}} \underset{\text{Ethyl chloride}}{CH_3CH_2-Cl} + H_2O$$

b. **Ethene:**

$$\underset{\text{Ethene}}{CH_2=CH_2} + HCl \longrightarrow \underset{\text{Ethyl chloride}}{CH_3-CH_2-Cl}$$

c. **Thionyl chloride:**



d. The preparation of ethyl chloride using thionyl chloride will be the most preferred method.
1. Thionyl chloride reacts with straight-chain primary alcohols to give unrearranged alkyl chloride.
2. The byproducts (SO_2 and HCl) obtained during the course of the reaction are in a

gaseous state thus, there is no need to put extra effort for its separation. Hence, this method is preferred for the preparation of ethyl chloride.

Q. 28

Calculate the voltage of the cell $Sn_{(s)}$ / Sn^{2+}(0.02 M) // Ag^{+} (0.01 M) / $Ag_{(s)}$ at 25 °C.

Given: E^{o}_{Sn} = - 0.136, E^{o}_{Ag} = 0.800 V

Ans.

Given: E^{o}_{Sn} = - 0.136, E^{o}_{Ag} = 0.800 V

To find: Voltage of the cell (E_{cell})

Formulae:

1. $E^{o}_{cell} = E^{o}_{cathode} - E^{o}_{anode}$
2. $E_{cell} = E^{o}_{cell} - \frac{0.0592\ \mathrm{V}}{n} \log_{10} \frac{[\mathrm{Product}]}{[\mathrm{Reactant}]}$

Calculation: First we write the cell reaction.

$\mathrm{Sn_{(s)} \longrightarrow Sn^{2+}\ (0.02\,M) + 2\,e^{-}}$	(oxidation at anode)
[Ag^{+} (0.01 M) + e^{-} → $Ag_{(s)}$] × 2	(reduction at cathode)
Overall reaction: $\mathrm{Sn_{(s)} + 2\,Ag^{+}\ (0.01\,M) \longrightarrow Sn^{2+}\ (0.02\,M) + 2\,Ag_{(s)}}$	

Using formula (1),

$E^{o}_{cell} = E^{o}_{Ag} - E^{o}_{Sn}$ = 0.800 V - (- 0.136 V) = 0.936 V

Using formula (2),

The cell potential is given by

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0592\text{ V}}{n}\log_{10}\frac{\left[\text{Sn}^{2+}\right]}{\left[\text{Ag}^{+}\right]^{2}}$$

$$\therefore E_{\text{cell}} = 0.936\text{ V} - \frac{0.0592\text{ V}}{2}\log_{10}\frac{0.02}{(0.01)^{2}}$$

$$= 0.936\text{ V} - \frac{0.0592\text{ V}}{2}\log_{10}\ 200$$

$$= 0.936\text{ V} - \frac{0.0592\text{ V}}{2} \times 2.301$$

Calculation using log table:

0.0592×2.303

$= \text{Antilog}_{10}\,[\log_{10} 0.0592 + \log_{10} 2.303]$

$= \text{Antilog}_{10}\left[\bar{2}.7723 + 0.3623\right]$

$= \text{Antilog}_{10}\left[\bar{1}.1346\right]$

$= 0.1363$

$= 0.936\text{ V} - \dfrac{0.1363\text{ V}}{2}$ (Using log table)

$= 0.936\text{ V} - 0.0681\text{ V}$

$= 0.8679\text{ V}$

The voltage of cell is **0.8679 V**.

Q. 29 Derive an expression for the relation between half-life and rate constant for first-order reaction.
The half-life period for the first order reaction is 1.7 hrs. How long will it take for 20% of the reactant to disappear?

Ans. 1. The relation between half-life and rate constant for first-order reaction:

The integrated rate law for the first-order reaction is $k = \frac{2.303}{t}\log_{10}\frac{[A]_0}{[A]_t}$ where, $[A]_0$ is the initial concentration of reactant at t = 0. It falls to $[A]_t$ at time t after the start of the reaction.

The time required for $[A]_0$ to become $\frac{[A]_0}{2}$ is denoted as $t_{1/2}$ or $[A]_t = \frac{[A]_0}{2}$ at $t = t_{1/2}$

Putting this condition in the integrated rate law we write

$$k = \frac{2.303}{t_{1/2}}\log_{10}\frac{[A]_t}{[A]_0/2} = \frac{2.303}{t_{1/2}}\log_{10}2$$

Substituting value of $\log_{10}2$,

$$k = \frac{2.303}{t_{1/2}} \times 0.3010$$

$$\therefore k = \frac{0.693}{t_{1/2}}$$

$$\therefore t_{1/2} = \frac{0.693}{k}$$

2. Given: Half life ($t_{1/2}$) = 1.7 hours, $[A]_0$ = 100%, $[A]_t$ = 100 – 20 = 80%

To find: Time for 20% of reactant to react = t

Formulae:

1. $t_{\frac{1}{2}} = \frac{0.693}{k}$
2. $t = \frac{2.303}{K}\log_{10}\frac{[A]_0}{[A]_t}$

Calculation: $t_{\frac{1}{2}} = \frac{0.693}{k}$

$$k = \frac{0.693}{t_{\frac{1}{2}}} = \frac{0.693}{1.7\ h} = 0.4076\ h^{-1}$$

$$t = \frac{2.303}{k}\log_{10}\frac{[A]_0}{[A]_t}$$

$$= \frac{2.303}{0.4076\ h^{-1}}\log\frac{100}{80}$$

$$t = \frac{2.303}{0.4076\ h^{-1}} \times 0.0969$$

$$= 0.5475 \text{ h} \times \frac{60 \text{ min}}{1\text{h}}$$

= 32.9 min

The time required for 20% of reaction to react is **0.5475 h** or **32.9 min**.

Q. 30 Derive the relationship between density of substance, its molar mass, and the unit cell edge length. Explain how you will calculate the number of particles, and a number of unit cells in x g of metal.

Ans.

- **Relationship between density of a substance, its molar mass and the unit cell edge length:**

1. If edge length of cubic unit cell is 'a', then the volume of unit cell is a^3.
2. Suppose that mass of one particle is 'm' and that there are 'n' particles per unit cell.
   ∴ Mass of unit cell = m × n .....(1)
3. The density of unit cell (ρ), which is same as density of the substance is given by:

$$\rho = \frac{\text{Mass of unit cell}}{\text{Volume of a unit cell}}$$

$$= \frac{m \times n}{a^3} = \text{Density of substance} \quad ...(2)$$

4. Molar mass (M) of the substance is given by:

M = mass of one particle × number of particles per mole

= m × N_A (N_A is Avogadro number)

$$\text{Therefore, } m = \frac{M}{N_A} \quad .....(3)$$

5. Combining equations (1) and (3), gives

$$\rho = \frac{n\ M}{a^3\ N_A} \quad .....(4)$$

The density (ρ) and molar mass (M) of metal are related to each other through unit cell parameters as given below:

$$\rho = \frac{n}{a^3} \times \frac{M}{N_A}$$

$$\therefore M = \rho \frac{a^3\ N_A}{n}$$

- where, 'n' is the number of particles in unit cell and 'a^3' is the volume of unit cell.

1. **The number of particles in x g of metallic crystal:**

∴ Molar mass, M, contains N_A particles.

∴ x g of metal contains $\frac{xN_A}{M}$ particles.

Substitution of M in the above equation gives

Number of particles in 'x' g = $\frac{xN_A}{\rho a^3 N_A / n} = \frac{x\ n}{\rho a^3}$

2. **Number of unit cells in x g of metallic crystal:**

'n' particles correspond to 1 unit cell.

∴ $\frac{xn}{\rho a^3}$ particles correspond to $\frac{xn}{\rho a^3} \times \frac{1}{n}$ unit cells.

∴ Number of unit cells in 'x' g metal = $\frac{x}{\rho a^3}$

Q. 31 Write the factors influencing the basicity of amines.

Ans. Factors influencing the basicity of amines are as follows:

i. **Influence of +I effect:**
1. Basicity of amines is related to the structural effects which influence the stabilization of various species. Greater is the stabilization of the protonated amine, that is, the conjugate acid, greater is the basicity of the amine.
2. An alkyl group exerts an electron releasing inductive effect (+I) which stabilizes the positive charge on the atom bonded to it. As we move from conjugate acid of ammonia NHX4+ to that of tertiary amine (R_3NH^+), the number of alkyl groups (R) bonded to nitrogen goes on increasing steadily. This results in increasing stabilization of the conjugate acids and thereby an increasing order of basic strength is expected.
Order of stabilization:

$$\overset{+}{N}H_4 < R - \overset{+}{N}H_3 < R_2\overset{+}{N}H_2 < R_3\overset{+}{N} - H$$

Expected order of basic strength: $NH_3 < R - NH_2 < R_2NH < R_3N$
3. The expected order of basic strength on the basis of the +I effect differs from the observed order. However, decreased basic strength of 3° amine implies that the conjugate acid of 3° amine is less stabilized even though the +I effect of three alkyl groups in R_3N^+H is expected to be large. Decreased basic strength of 3° amine implies that the conjugate acid of 3° amine is less stabilized even though the +I effect of three alkyl groups in R_3N^+H is expected to be large. This is suggestive of the existence of another influencing factor in the stabilization of conjugate acids of amines.

ii. **Influence of solvation by water:** The solvent water stabilizes the conjugate acid by hydrogen bonding through the 'H' bonded to the 'N^+'.

The number of ‘H’ atoms bonded to the ‘N^+’ decreases from 4 in NHX4+ to 1 in R_3NH^+. As a result, NHX4+ is best stabilized by solvation while the stabilization by solvation is very poor in R_3NH^+. Thus, the basic strength of 3° amines is decreased.

iii. **Combined influence of +I effect and solvation:**

1. The combined influence of both, +I effect and solvation on stabilization if conjugate acids of aliphatic amines decide the observed basic strength and pK_b value. These two influencing factors operate in opposite directions.
2. The net result is that as we move from NH_3 to RNH_2 to R_2NH, the basic strength increases due to better stabilization of the corresponding conjugate acids.
3. But, 3° amine is a weaker base than 2° amine because the stabilization of conjugate acid of 3° amine by solvation is very poor.