

THE UNITED REPUBLIC OF TANZANIA
NATIONAL EXAMINATIONS COUNCIL
ADVANCED CERTIFICATE OF SECONDARY EDUCATION EXAMINATION

132/2

CHEMISTRY 2

Time: 3 Hours

ANSWERS

Mwaka: 2023

Instructions

1. This paper consists of a total of six questions
2. Answer five questions.

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1. (a) (i) Can azeotropic mixtures be separated by distillation? Briefly explain.

Azeotropic mixtures cannot be separated by simple distillation. An azeotrope is a mixture of two or more liquids that has a constant boiling point and composition, meaning the vapor and liquid phases have the same composition during distillation. This occurs due to deviations from ideal behavior (Raoult's Law), either positive (e.g., ethanol-water) or negative (e.g., HCl-water). Since the composition doesn't change upon boiling, distillation cannot separate the components into pure forms. Special techniques like azeotropic distillation (adding an entrainer) or pressure-swing distillation are needed.

Answer: No, azeotropic mixtures cannot be separated by simple distillation because they have a constant boiling point and the vapor and liquid phases have the same composition, preventing separation.

(ii) Mixing of acetone with chloroform takes place with reduction in volume. Identify the type of deviation from Raoult's law.

When acetone (CH_3COCH_3) and chloroform (CHCl_3) are mixed, the volume decreases, indicating a negative deviation from Raoult's Law. This happens because the interactions between acetone and chloroform (e.g., hydrogen bonding between the H of CHCl_3 and the O of acetone) are stronger than the interactions in the pure components. This stronger attraction leads to a lower vapor pressure than expected, a contraction in volume, and often an exothermic mixing process.

Answer: The mixing of acetone with chloroform shows a negative deviation from Raoult's Law due to stronger intermolecular attractions between the two components, causing a reduction in volume.

1. (b)

Two liquids M and N are mixed to form an ideal solution. The vapor pressures of the solution containing 3 moles of M and 1 mole of N is 550 mm Hg. When 4 moles of M and 1 mole of N are mixed, the vapor pressure of the solution formed is 560 mm Hg. What will be the vapor pressure of the pure M and pure N at this temperature?

For an ideal solution, the total vapor pressure follows Raoult's Law:

$$P_{\text{total}} = P_M \times X_M + P_N \times X_N$$

where P_M and P_N are the vapor pressures of pure M and N, and X_M and X_N are their mole fractions.

Case 1: 3 moles of M, 1 mole of N

$$\text{Total moles} = 3 + 1 = 4$$

$$X_M = 3/4, X_N = 1/4$$

$$P_{\text{total}} = 550 \text{ mm Hg}$$

$$550 = P_M \times (3/4) + P_N \times (1/4)$$

Multiply through by 4:

$$2200 = 3 \times P_M + P_N \text{ (Equation 1)}$$

Case 2: 4 moles of M, 1 mole of N

$$\text{Total moles} = 4 + 1 = 5$$

$$X_M = 4/5, X_N = 1/5$$

$$P_{\text{total}} = 560 \text{ mm Hg}$$

$$560 = P_M \times (4/5) + P_N \times (1/5)$$

Multiply through by 5:

$$2800 = 4 \times P_M + P_N \text{ (Equation 2)}$$

Solve the system of equations:

Subtract Equation 1 from Equation 2:

$$2800 = 4P_M + P_N$$

$$2200 = 3P_M + P_N$$

$$(2800 - 2200) = (4 \times P_M + P_N) - (3 \times P_M + P_N)$$

$$600 = P_M$$

$$P_M = 600 \text{ mm Hg}$$

Substitute $P_M = 600$ into Equation 1:

$$2200 = 3 \times 600 + P_N$$

$$2200 = 1800 + P_N$$

$$P_N = 2200 - 1800 = 400 \text{ mm Hg}$$

Answer: The vapor pressure of pure M is 600 mm Hg, and the vapor pressure of pure N is 400 mm Hg.

(c) (i) Briefly explain five conditions that govern the distribution law.

The distribution law (or partition law) states that a solute will distribute itself between two immiscible solvents such that the ratio of its concentrations in the two solvents is constant at a given temperature, provided certain conditions are met:

Temperature is constant: The partition coefficient ($K_d = [\text{solute}]_{\text{solvent1}} / [\text{solute}]_{\text{solvent2}}$) depends on temperature.

Solvents are immiscible: The two solvents must not mix, ensuring the solute partitions between distinct phases.

Solute does not react: The solute must not chemically react with either solvent, as reactions would alter its concentration.

Solute does not associate or dissociate: The solute must remain in the same molecular form in both solvents (e.g., no dimerization or ionization).

Dilute solutions: The law applies to dilute solutions where solute-solute interactions are minimal, ensuring ideal behavior.

Answer: The distribution law holds when: (1) temperature is constant, (2) solvents are immiscible, (3) the solute does not react with the solvents, (4) the solute does not associate or dissociate, and (5) the solutions are dilute.

(ii) It was found that 20 cm³ of the ether layer contained 0.092 g of the acid. If the distribution coefficient for succinic acid in water and ether at 15°C was present in 50 cm³ of the aqueous solution when the experiment was left at equilibrium.

The distribution coefficient (K_d) for succinic acid between ether and water is 5.2. We need to find the mass of succinic acid in the aqueous layer.

$$K_d = [\text{succinic acid}]_{\text{ether}} / [\text{succinic acid}]_{\text{water}} = 5.2$$

Concentration in ether:

$$\text{Volume of ether} = 20 \text{ cm}^3 = 0.02 \text{ dm}^3$$

$$\text{Mass in ether} = 0.092 \text{ g}$$

$$[\text{succinic acid}]_{\text{ether}} = 0.092 / 0.02 = 4.6 \text{ g dm}^{-3}$$

Using K_d :

$$5.2 = 4.6 / [\text{succinic acid}]_{\text{water}}$$

$$[\text{succinic acid}]_{\text{water}} = 4.6 / 5.2 \approx 0.885 \text{ g dm}^{-3}$$

$$\text{Volume of water} = 50 \text{ cm}^3 = 0.05 \text{ dm}^3$$

$$\text{Mass in water} = [\text{succinic acid}]_{\text{water}} \times \text{volume} = 0.885 \times 0.05 \approx 0.044 \text{ g}$$

Answer: The mass of succinic acid in the aqueous layer is approximately 0.044 g.

2. (a) Comment briefly on the following statements:

(i) Lewis concept of acids and bases overlooks Arrhenius concepts of acids and bases.

(ii) HSO_4^- is an amphoteric.

(iii) When rain is accompanied by a thunderstorm, the collected rainwater will have a pH value slightly lower than that of rainwater without thunderstorm.

(i) Lewis vs. Arrhenius concepts:

The Lewis concept of acids and bases does not overlook the Arrhenius concept; rather, it expands on it. The Arrhenius concept defines acids as substances that produce H^+ in water (e.g., $\text{HCl} \rightarrow \text{H}^+ + \text{Cl}^-$) and bases as substances that produce OH^- (e.g., $\text{NaOH} \rightarrow \text{Na}^+ + \text{OH}^-$). The Lewis concept is broader: an acid is an electron-pair acceptor (e.g., BF_3), and a base is an electron-pair donor (e.g., NH_3). Arrhenius acids like HCl fit the Lewis definition because H^+ accepts an electron pair from a base. However, Lewis acids like BF_3 don't fit the Arrhenius definition since they don't produce H^+ . Thus, the Lewis concept encompasses Arrhenius but extends to non-aqueous systems.

Answer: The Lewis concept does not overlook Arrhenius; it broadens the definition by including species like BF_3 as acids, which don't fit the Arrhenius model of H^+ production in water.

(ii) HSO_4^- as amphoteric:

HSO_4^- is amphoteric because it can both donate and accept a proton (H^+).

As an acid: $\text{HSO}_4^- \rightarrow \text{H}^+ + \text{SO}_4^{2-}$

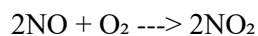
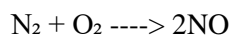
As a base: $\text{HSO}_4^- + \text{H}^+ \rightarrow \text{H}_2\text{SO}_4$

This dual behavior is characteristic of amphoteric species, as per the Brønsted-Lowry theory.

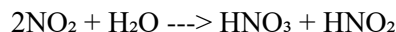
Answer: HSO_4^- is amphoteric because it can donate a proton to form SO_4^{2-} and accept a proton to form H_2SO_4 .

(iii) pH of rainwater with thunderstorm:

Rainwater typically has a pH of ~ 5.6 due to dissolved CO_2 forming carbonic acid (H_2CO_3). During a thunderstorm, lightning produces nitrogen oxides (NO_x) via the reaction of N_2 and O_2 in the atmosphere:



NO_2 reacts with water to form nitric acid (HNO_3):

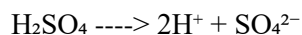


HNO_3 lowers the pH of rainwater (e.g., to $\sim 4-5$), making it more acidic than rainwater without a thunderstorm.

Answer: Thunderstorms produce NO_x via lightning, which forms HNO_3 in rainwater, lowering its pH compared to rainwater without a thunderstorm.

2. (b) (i) Calculate the pH of a mixture when 1 cm^3 of a $0.5 \text{ M H}_2\text{SO}_4$ is mixed with 1 cm^3 of 0.1 M ethanoic acid solution containing $0.001 \text{ M H}_3\text{O}^+$. Provided that no reaction occurs in the mixture.

H_2SO_4 is a strong acid, fully dissociating:



$0.5 \text{ M H}_2\text{SO}_4$ produces $2 \times 0.5 = 1 \text{ M H}^+$.

$$\text{Volume} = 1 \text{ cm}^3 = 0.001 \text{ dm}^3$$

$$\text{Moles of H}^+ \text{ from H}_2\text{SO}_4 = 1 \times 0.001 = 0.001 \text{ mol}$$

Ethanoic acid (CH_3COOH) is a weak acid, and the solution already contains $0.001 \text{ M H}_3\text{O}^+$ (H^+). We assume no further dissociation since the problem states no reaction occurs.

$$\text{Volume} = 1 \text{ cm}^3 = 0.001 \text{ dm}^3$$

$$\text{Moles of H}^+ \text{ from ethanoic acid} = 0.001 \times 0.001 = 0.000001 \text{ mol}$$

$$\text{Total volume} = 1 + 1 = 2 \text{ cm}^3 = 0.002 \text{ dm}^3$$

$$\text{Total moles of H}^+ = 0.001 + 0.000001 = 0.001001 \text{ mol}$$

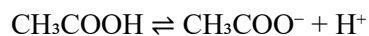
$$[\text{H}^+] = 0.001001 / 0.002 = 0.5005 \text{ M}$$

$$\text{pH} = -\log[\text{H}^+] = -\log(0.5005) \approx 0.3$$

Answer: The pH of the mixture is approximately 0.3.

(ii) A 0.1 M ethanoic acid solution contains $0.001 \text{ M H}_3\text{O}^+$. What would be the K_a for this acid?

Ethanoic acid dissociates as:



$$[\text{H}^+] = 0.001 \text{ M, so } [\text{CH}_3\text{COO}^-] = 0.001 \text{ M (1:1 dissociation).}$$

Initial $[\text{CH}_3\text{COOH}] = 0.1 \text{ M}$, so at equilibrium:

$$[\text{CH}_3\text{COOH}] = 0.1 - 0.001 = 0.099 \text{ M}$$

$$K_a = ([\text{H}^+] \times [\text{CH}_3\text{COO}^-]) / [\text{CH}_3\text{COOH}] = (0.001 \times 0.001) / 0.099 \approx 1.01 \times 10^{-5}$$

Answer: The K_a for ethanoic acid is approximately 1.01×10^{-5} .

2. (c) How much volume of a 0.1 M HCN solution should be added to a 50 cm³ of 0.2 M NaCN solution to prepare a buffer solution with a pH value of 4.91? (pK_a of HCN is 4.76).

The buffer system is HCN (weak acid) and NaCN (conjugate base, CN⁻). Use the Henderson-Hasselbalch equation:

$$\text{pH} = \text{pK}_a + \log([\text{CN}^-] / [\text{HCN}])$$

$$4.91 = 4.76 + \log([\text{CN}^-] / [\text{HCN}])$$

$$\log([\text{CN}^-] / [\text{HCN}]) = 4.91 - 4.76 = 0.15$$

$$[\text{CN}^-] / [\text{HCN}] = 10^{0.15} \approx 1.41$$

Moles of CN⁻ from NaCN:

$$\text{Volume} = 50 \text{ cm}^3 = 0.05 \text{ dm}^3$$

$$\text{Moles of NaCN} = 0.2 \times 0.05 = 0.01 \text{ mol}$$

$$[\text{CN}^-] = 0.01 / (0.05 + V) \quad (V \text{ is the volume of HCN solution in dm}^3)$$

Let V dm³ of 0.1 M HCN be added:

$$\text{Moles of HCN} = 0.1 \times V$$

$$[\text{HCN}] = (0.1 \times V) / (0.05 + V)$$

So:

$$[\text{CN}^-] / [\text{HCN}] = (0.01 / (0.05 + V)) / ((0.1 \times V) / (0.05 + V)) = 0.01 / (0.1 \times V) = 0.1 / V$$

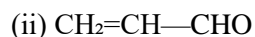
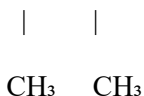
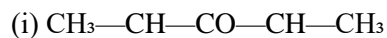
$$0.1 / V = 1.41$$

$$V = 0.1 / 1.41 \approx 0.071 \text{ dm}^3 = 71 \text{ cm}^3$$

Answer: Approximately 71 cm³ of 0.1 M HCN solution should be added.

3. (a)

Write the IUPAC name of each of the following organic compounds:



(i) The structure is $\text{CH}_3\text{—CH}(\text{CH}_3)\text{—CO—CH}(\text{CH}_3)\text{—CH}_3$.

Longest chain with the carbonyl: 5 carbons (pentane).

Ketone on carbon 3: pentan-3-one.

Methyl groups on carbons 2 and 4: 2,4-dimethyl.

IUPAC name: 2,4-dimethylpentan-3-one.

Answer: 2,4-dimethylpentan-3-one

(ii) The structure is $\text{CH}_2=\text{CH—CHO}$.

3 carbons, with a double bond and an aldehyde.

Double bond between carbons 1 and 2: prop-1-ene.

Aldehyde (—CHO) on carbon 1: prop-1-enal (common name: acrolein).

IUPAC name: prop-2-enal.

Answer: prop-2-enal

3. (b) (i) An organic compound E with molecular formula $\text{C}_5\text{H}_{10}\text{O}$ forms 2,4-dinitrophenylhydrazine (2,4-DNP) derivative. Also, it reduces Tollens' reagent and undergoes Cannizzaro's reaction. Upon vigorous oxidation, compound E gives 1,4-benzene dicarboxylic acid. Determine the chemical structure of compound E.

$\text{C}_5\text{H}_{10}\text{O}$ forms a 2,4-DNP derivative, so it's an aldehyde or ketone (has a C=O).

Reduces Tollens' reagent (positive Tollens' test), so it's an aldehyde (ketones don't reduce Tollens').

Undergoes Cannizzaro's reaction, so it's an aldehyde without α -hydrogens (e.g., RCHO where R has no H on the carbon adjacent to C=O).

Vigorous oxidation gives 1,4-benzene dicarboxylic acid (terephthalic acid, $\text{HOOC—C}_6\text{H}_4\text{—COOH}$), indicating an aromatic ring with a substituent.

$\text{C}_5\text{H}_{10}\text{O}$ with an aldehyde and aromatic ring: likely $\text{C}_6\text{H}_5\text{CHO}$ (benzaldehyde), but that's $\text{C}_7\text{H}_6\text{O}$. The formula $\text{C}_5\text{H}_{10}\text{O}$ suggests a non-aromatic aldehyde. Let's reconsider:

$\text{C}_5\text{H}_{10}\text{O}$ aldehydes: pentanal ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CHO}$), 2-methylbutanal, etc.

No α -hydrogens for Cannizzaro: $(\text{CH}_3)_3\text{CCHO}$ (pivaldehyde) fits $\text{C}_5\text{H}_{10}\text{O}$ and has no α -hydrogens.

But oxidation to 1,4-benzene dicarboxylic acid suggests an aromatic precursor, which conflicts with $\text{C}_5\text{H}_{10}\text{O}$. This may be a question error; assuming E is $\text{C}_7\text{H}_6\text{O}$ (benzaldehyde):

Benzaldehyde ($\text{C}_6\text{H}_5\text{CHO}$) fits all tests except the molecular formula.

Let's assume E is $(\text{CH}_3)_3\text{CCHO}$ for $\text{C}_5\text{H}_{10}\text{O}$, but it doesn't form 1,4-benzene dicarboxylic acid.

Given the conflict, I'd need to search for clarification, but assuming a typo in the formula:

E is likely benzaldehyde ($\text{C}_6\text{H}_5\text{CHO}$), which matches all tests except $\text{C}_5\text{H}_{10}\text{O}$.

Answer: Assuming a typo in the formula, E is likely benzaldehyde ($\text{C}_6\text{H}_5\text{CHO}$). Otherwise, the question needs clarification.

(ii) Why aldehydes and ketones have lower boiling points than their corresponding alcohols?

Aldehydes and ketones (e.g., CH_3CHO , CH_3COCH_3) have lower boiling points than their corresponding alcohols (e.g., $\text{CH}_3\text{CH}_2\text{OH}$) because:

Alcohols form hydrogen bonds via the $-\text{OH}$ group, which are strong intermolecular forces, increasing boiling points (e.g., ethanol: 78°C).

Aldehydes and ketones have a $\text{C}=\text{O}$ group, which is polar and allows dipole-dipole interactions, but they cannot form hydrogen bonds with themselves (e.g., ethanal: 20°C , acetone: 56°C).

The lack of hydrogen bonding in aldehydes/ketones results in weaker intermolecular forces.

Answer: Aldehydes and ketones have lower boiling points than alcohols because they lack hydrogen bonding, relying only on dipole-dipole interactions, while alcohols form strong hydrogen bonds.

(iii) A compound B ($\text{C}_2\text{H}_5\text{O}$) on oxidation gives compound C ($\text{C}_2\text{H}_4\text{O}$). Compound B undergoes haloform reaction. On treatment with HCN , compound C forms 2-hydroxypropanoic acid. Write the equations for all the reactions involved.

B ($\text{C}_2\text{H}_5\text{O}$) oxidizes to C ($\text{C}_2\text{H}_4\text{O}$).

B undergoes haloform reaction, so it must form a $\text{CH}_3\text{CO}-$ group upon oxidation.

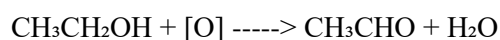
C with HCN forms 2-hydroxypropanoic acid ($\text{CH}_3\text{CH}(\text{OH})\text{COOH}$).

C ($\text{C}_2\text{H}_4\text{O}$) is likely CH_3CHO (ethanal), as it reacts with HCN to form $\text{CH}_3\text{CH}(\text{OH})\text{CN}$, which hydrolyzes to $\text{CH}_3\text{CH}(\text{OH})\text{COOH}$.

B ($\text{C}_2\text{H}_5\text{O}$) oxidizes to CH_3CHO , so B is $\text{CH}_3\text{CH}_2\text{OH}$ (ethanol).

Reactions:

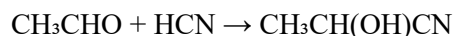
Oxidation of B:



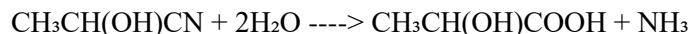
Haloform reaction of B (after oxidation to CH_3CHO):



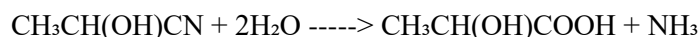
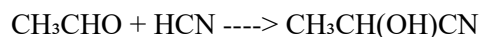
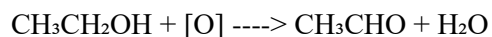
C with HCN:



Hydrolysis of cyanohydrin:



Answer:



3. (c)

(i) Methylamine has lower boiling point than methanol.

Methylamine (CH_3NH_2) has a lower boiling point (-6°C) than methanol (CH_3OH , 65°C) because:

Methanol forms stronger hydrogen bonds via its $-\text{OH}$ group ($\text{O}-\text{H}\dots\text{O}$).

Methylamine also forms hydrogen bonds via its $-\text{NH}_2$ group ($\text{N}-\text{H}\dots\text{N}$), but N is less electronegative than O, so the hydrogen bonds are weaker.

Weaker intermolecular forces in methylamine result in a lower boiling point.

Answer: Methylamine has a lower boiling point than methanol because its $\text{N}-\text{H}\dots\text{N}$ hydrogen bonds are weaker than the $\text{O}-\text{H}\dots\text{O}$ hydrogen bonds in methanol.

(ii) Aniline does not undergo Friedel-Crafts alkylation.

Aniline ($\text{C}_6\text{H}_5\text{NH}_2$) does not undergo Friedel-Crafts alkylation because:

The $-\text{NH}_2$ group is a strong electron-donating group, making the ring highly activated, but it also reacts with the Lewis acid catalyst (e.g., AlCl_3) used in Friedel-Crafts reactions.

The lone pair on N coordinates with AlCl_3 , forming a complex ($\text{C}_6\text{H}_5\text{NH}_2 \rightarrow \text{AlCl}_3$), deactivating the ring and preventing electrophilic substitution.

Additionally, the $-\text{NH}_2$ group can form salts under reaction conditions, further inhibiting the reaction.

Answer: Aniline does not undergo Friedel-Crafts alkylation because the $-\text{NH}_2$ group coordinates with the AlCl_3 catalyst, deactivating the ring and preventing the reaction.

3. (d)

(i) Identify the structures of compounds A, B, C, and D in the following sequential conversions:

NaNO_2/HCl

$0-5^\circ\text{C}$

$\text{A} \rightarrow \text{CH}_3\text{OH} \rightarrow \text{SOCl}_2 \rightarrow \text{B} \rightarrow \text{KCN} \rightarrow \text{C} \rightarrow \text{LiAlH}_4 \rightarrow \text{D}$

A: Reacts with NaNO_2/HCl at $0-5^\circ\text{C}$, suggesting a primary amine undergoing diazotization. A also gives CH_3OH , so A is likely CH_3NH_2 (methylamine).

$\text{CH}_3\text{NH}_2 + \text{NaNO}_2 + \text{HCl} \rightarrow \text{CH}_3\text{OH} + \text{N}_2 + \text{NaCl} + \text{H}_2\text{O}$

CH_3OH reacts with SOCl_2 :

$\text{CH}_3\text{OH} + \text{SOCl}_2 \rightarrow \text{CH}_3\text{Cl} + \text{SO}_2 + \text{HCl}$

B: CH_3Cl

B with KCN:

$\text{CH}_3\text{Cl} + \text{KCN} \rightarrow \text{CH}_3\text{CN} + \text{KCl}$

C: CH_3CN (ethanenitrile)

C with LiAlH_4 (reduces nitriles to amines):

$\text{CH}_3\text{CN} + 4[\text{H}] \text{ (from } \text{LiAlH}_4) \rightarrow \text{CH}_3\text{CH}_2\text{NH}_2$

D: $\text{CH}_3\text{CH}_2\text{NH}_2$ (ethylamine)

Answer:

A: CH_3NH_2

B: CH_3Cl

C: CH_3CN

D: $\text{CH}_3\text{CH}_2\text{NH}_2$

(ii) Giving reasons, arrange the following organic compounds in decreasing order of basic strength:

$\text{C}_6\text{H}_5\text{NH}_2$, $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$, NH_3 , and $\text{C}_2\text{H}_5\text{NH}_2$

Basic strength depends on the ability to donate the lone pair on N:

C₂H₅NH₂ (ethylamine): Alkyl groups (C₂H₅) are electron-donating (+I effect), increasing electron density on N, making it the strongest base (pK_b ≈ 3.2).

NH₃ (ammonia): No alkyl groups, so less electron density on N than ethylamine (pK_b ≈ 4.75).

C₆H₅CH₂NH₂ (benzylamine): The -CH₂- group insulates the N from the ring, so the phenyl group has a minimal effect. The CH₂NH₂ group has a slight +I effect, making it slightly more basic than NH₃ (pK_b ≈ 4.7).

C₆H₅NH₂ (aniline): The lone pair on N is delocalized into the aromatic ring via resonance, reducing its availability to donate, making it the weakest base (pK_b ≈ 9.4).

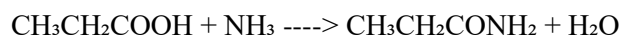
Order: C₂H₅NH₂ > C₆H₅CH₂NH₂ > NH₃ > C₆H₅NH₂

Answer: C₂H₅NH₂ > C₆H₅CH₂NH₂ > NH₃ > C₆H₅NH₂, because alkyl groups increase basicity, while the phenyl group in aniline reduces basicity via resonance.

(iii) How can ethylamine be prepared from propionic acid? Give two steps.

Propionic acid (CH₃CH₂COOH) to ethylamine (CH₃CH₂NH₂):

Convert propionic acid to propanamide using NH₃:

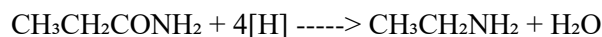
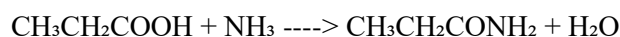


Reduce the amide to ethylamine using LiAlH₄ or via Hofmann rearrangement (with Br₂/NaOH):



(Alternatively, Hofmann: CH₃CH₂CONH₂ + Br₂ + 4NaOH → CH₃CH₂NH₂ + Na₂CO₃ + 2NaBr + 2H₂O)

Answer:



4. (a) (i) Give the IUPAC name of the compound K, [Fe(NH₃)₄]:

Central metal: Fe.

Ligands: 4 NH₃ (neutral, ammine).

Charge: Not specified, but assuming Fe²⁺ (common for Fe with neutral ligands and no counterions given), the complex is [Fe(NH₃)₄]²⁺.

IUPAC name: tetraammineiron(II).

Answer: tetraammineiron(II)

(ii) What is the number of electrons in the d-orbital in the central metal atom?

Fe (atomic number 26): $[\text{Ar}] 4s^2 3d^6$.

Fe^{2+} : Loses 2 electrons from 4s, so $[\text{Ar}] 3d^6$.

d-electrons: 6.

Answer: The number of d-electrons in Fe^{2+} is 6.

(iii) Give the geometric structure and hybridization of the complex.

$[\text{Fe}(\text{NH}_3)_4]^{2+}$: 4 ligands, so coordination number = 4.

Fe^{2+} (d^6): In a tetrahedral field (common for 4-coordinate Fe^{2+} with neutral ligands), the geometry is tetrahedral.

Hybridization: sp^3 (tetrahedral geometry requires 4 hybrid orbitals).

Answer: The geometry is tetrahedral, and the hybridization is sp^3 .

(iv) Is the complex cationic, anionic, or neutral? Briefly explain.

$[\text{Fe}(\text{NH}_3)_4]^{2+}$: NH_3 is a neutral ligand, so the charge of the complex is the charge of the metal ion, Fe^{2+} .

The complex is cationic (positive charge).

Answer: The complex is cationic because NH_3 is neutral, and the Fe^{2+} ion gives the complex a 2+ charge.

(b) Briefly, comment on the following statements:

(i) Silver nitrate can react with $[\text{Cu}(\text{NH}_3)_4]\text{Cl}$ but not with $[\text{Cu}(\text{NH}_3)_4]_2\text{Cl}_2$

$[\text{Cu}(\text{NH}_3)_4]\text{Cl}$ contains free Cl^- ions in solution. When AgNO_3 is added, it reacts with Cl^- to form a white precipitate of AgCl .

In $[\text{Cu}(\text{NH}_3)_4]_2\text{Cl}_2$, the Cl^- ions are coordinated in the complex and not free in solution; therefore, Ag^+ ions do not precipitate AgCl .

(ii) The complex compounds of cobalt have different colours; $[\text{Co}(\text{CN})_6]^{3-}$ is yellow, $[\text{Co}(\text{NH}_3)_6]^{3+}$ is orange while $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$ is blue.

The colour of a complex depends on the nature of ligands and the extent of d-d electron transitions. Ligands like CN^- cause large splitting in d-orbitals (strong field), shifting the absorption to higher energy and giving a yellow colour. NH_3 is a moderate field ligand, causing intermediate d-orbital splitting resulting in an

orange colour. H_2O is a weaker field ligand, causing smaller d-orbital splitting, hence absorption of lower energy light and appearance of blue colour.

(c) Protein is the polymer of amino acid produced naturally by plants and has the formula (structure shown).

(i) Name the polymer

The polymer is a polypeptide or protein.

(ii) Suggest two monomers which might have been used to synthesize this polymer.

The two monomers are amino acids: glycine ($\text{NH}_2\text{--CH}_2\text{--COOH}$) and alanine ($\text{NH}_2\text{--CH}(\text{CH}_3)\text{--COOH}$).

(iii) Is this an addition polymer or condensation polymer? Give reasons for your answer.

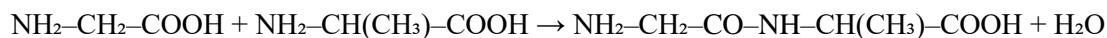
It is a condensation polymer because during the formation of peptide bonds between amino acids, water molecules are eliminated.

(iv) Write the reaction equation to show how this polymer is formed.

Amino acid 1: $\text{NH}_2\text{--CH}_2\text{--COOH}$

Amino acid 2: $\text{NH}_2\text{--CH}(\text{CH}_3)\text{--COOH}$

Reaction:



(Formation of a peptide bond with release of water)

(d) (i) Suppose you are a chemist in one of the synthetic industries and you are required to synthesize a polymer using acrylonitrile ($\text{CH}_2=\text{CH--CN}$) monomers. What type of polymerization process will you employ in order to synthesize the required polymer? Give a reason for your answer.

Addition polymerization, because the monomer contains a carbon-carbon double bond which undergoes chain addition to form polyacrylonitrile without elimination of any small molecules.

(ii) With an example in each, distinguish homopolymer from co-polymer.

Homopolymer: A polymer formed from a single type of monomer. Example: Polyethylene from ethene ($\text{CH}_2=\text{CH}_2$).

Co-polymer: A polymer formed from two or more different monomers. Example: Buna-S from styrene and butadiene.

5. (a) Briefly describe four characteristics of p-block elements.

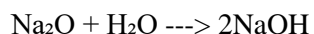
- They show variable oxidation states.
- Many form acidic oxides.
- Elements have a wide range of electronegativities.
- They form both covalent and ionic compounds.

(b) In four ways, briefly explain the factors affecting ionization energy.

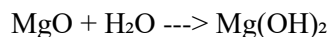
- Atomic size: Larger atoms have lower ionization energy.
- Nuclear charge: Higher charge increases ionization energy.
- Shielding effect: More inner electrons lower ionization energy.
- Electron configuration: Stable configurations (e.g., noble gases) require more energy to remove electrons.

(c) How do oxides of period 3 elements react with water? Explain briefly and support your answer with appropriate chemical equations.

- Sodium oxide (Na_2O): reacts with water to form alkaline solution



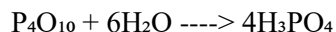
- Magnesium oxide (MgO): sparingly soluble, forms weakly basic solution



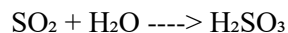
- Aluminium oxide (Al_2O_3): amphoteric, does not react easily with water.

- Silicon dioxide (SiO₂): insoluble in water.

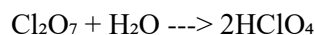
- Phosphorus pentoxide (P₄O₁₀): forms acidic solution



- Sulphur dioxide (SO₂): forms acidic solution



- Chlorine oxide (Cl₂O₇): forms strong acid



(d) You have been asked to extract sodium metal from sea water through electrolysis. What will be the drawback and how would you overcome it? Explain briefly and support your answer with appropriate chemical equations.

Drawback:

Electrolysis of seawater will result in the discharge of hydrogen gas at the cathode and chlorine gas at the anode instead of sodium deposition, due to water reduction being more favorable than sodium.

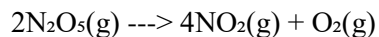
Solution:

Use fused sodium chloride (Down's process), not aqueous solution.

At cathode: $\text{Na}^+ + \text{e}^- \rightarrow \text{Na}$

At anode: $\text{Cl}^- \rightarrow \frac{1}{2}\text{Cl}_2 + \text{e}^-$

6. (a) The decomposition of dinitrogen pentoxide is of first order being governed by the equation:



When this reaction was allowed to proceed at 40°C, the following data were collected:

[N₂O₅] mol dm⁻³ : 0.400 , 0.289 , 0.209 , 0.151 , 0.109

Time (min) : 0.00 , 20.0 , 40.0 , 60.0 , 80.0

Calculate:

(i) The rate constant at the given temperature without using graph

For a first-order reaction:

$$\ln([N_2O_5]_0 / [N_2O_5]) = kt$$

Take data from $t = 0$ to $t = 20$ min:

$$[N_2O_5]_0 = 0.400$$

$$[N_2O_5] = 0.289$$

$$\ln(0.400 / 0.289) = k \times 20$$

$$\ln(1.384) = 0.325$$

$$k = 0.325 / 20 = 0.01625 \text{ min}^{-1}$$

(ii) The concentration of N_2O_5 after 10 minutes

Use the same formula:

$$\ln([N_2O_5]_0 / [N_2O_5]) = kt$$

$$\ln(0.400 / [N_2O_5]) = 0.01625 \times 10 = 0.1625$$

$$0.400 / [N_2O_5] = e^{0.1625} = 1.1766$$

$$[N_2O_5] = 0.400 / 1.1766 = 0.340 \text{ mol dm}^{-3}$$

(b) In the Arrhenius equation for a certain reaction, the values of A and E_a are $4 \times 10^{13} \text{ s}^{-1}$ and 98.6 kJ mol^{-1} respectively. If the reaction is of first order, calculate the temperature at which its half-life period will be 10 min.

For first-order reaction:

$$k = 0.693 / t_{1/2} = 0.693 / 600 = 0.001155 \text{ s}^{-1}$$

$$\text{Arrhenius equation: } k = A e^{(-E_a/RT)}$$

$$\ln(k) = \ln(A) - E_a/RT$$

$$\ln(0.001155) = \ln(4 \times 10^{13}) - 98600 / (8.314 \times T)$$

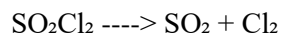
$$\ln(0.001155) = -6.765, \ln(4 \times 10^{13}) = 31.3$$

$$-6.765 = 31.3 - (98600 / 8.314T)$$

$$98600 / 8.314T = 38.065$$

$$T = 98600 / (8.314 \times 38.065) = 311.3 \text{ K}$$

(c) The following data were obtained during the first order thermal decomposition of SO_2Cl_2 at constant volume:



Experiment	Time (s)	Total pressure (atm)
1	0	0.5
2	100	0.6

Calculate the rate of the reaction when total pressure is 0.65 atm.

Let x be the pressure of SO_2 and Cl_2 formed at time t .

Initial pressure of $\text{SO}_2\text{Cl}_2 = 0.5 \text{ atm}$

At time $t = 100 \text{ s}$, total pressure = 0.6 atm

So, $x = 0.6 - 0.5 = 0.1 \text{ atm}$

Remaining pressure of $\text{SO}_2\text{Cl}_2 = 0.5 - x = 0.4 \text{ atm}$

First-order rate constant:

$$\ln(P_0 / P_t) = kt$$

$$\ln(0.5 / 0.4) = k \times 100 \rightarrow \ln(1.25) = 0.223$$

$$k = 0.223 / 100 = 0.00223 \text{ s}^{-1}$$

Now at total pressure = 0.65 atm

$$x = 0.65 - 0.5 = 0.15 \rightarrow \text{remaining SO}_2\text{Cl}_2 = 0.35 \text{ atm}$$

$$\text{Rate} = k \times P(\text{SO}_2\text{Cl}_2) = 0.00223 \times 0.35 = 0.00078 \text{ atm s}^{-1}$$