Chemistry (Theory) – Code 043

CBSE Class 12 Board Examination 2027 – Practice Paper No. 2

Model Answer Paper

Time: 3 hours **Max. Marks: 70**

Model answers show one correct method; any other correct method gets full marks.

SECTION A Questions 1 to 16 are multiple choice questions. Only one of the choices is correct. Select and write the correct choice as well as the answer to these questions. **[16]**

1 Which of the following units of concentration of a solution does **not** change when the temperature of the solution changes?

(A) Molarity (B) Molality

(C) Mass by volume percentage (w/V) (D) Volume percentage (V/V)

Answer (1 mark)
(B) Molality
Molality = moles of solute per kg of solvent. It uses masses only, and mass does not change with temperature. Molarity, w/V % and V/V % all use a volume, which expands or contracts with temperature.

2 A student fills a conductivity cell of cell constant 1.2 cm^{-1} with a solution and measures its resistance as 300 Ω. The conductivity of the solution is:

(A) 4.0×10^{-3} S cm^{-1} (B) 2.5×10^{2} S cm^{-1}

(C) 3.6×10^{2} S cm^{-1} (D) 2.8×10^{-3} S cm^{-1}

Answer (1 mark)
(A) 4.0×10^{-3} S cm^{-1}
$\kappa = G^*/R = 1.2\ cm^{-1}/300\ \Omega = 4.0 \times 10^{-3}$ S cm^{-1}.

3 The rate constant of a reaction is 3.0×10^{-4} mol^{-1} L s^{-1}. The overall order of the reaction is:

(A) zero (B) one

(C) two (D) three

Answer (1 mark)
(C) two
For an n^{th} order reaction the unit of k is $(mol\ L^{-1})^{1-n}\ s^{-1}$. With n = 2 this is mol^{-1} L s^{-1}.

4 Transition metals form interstitial compounds with small atoms such as H, C and N. Which of the following statements about these compounds is **incorrect**?

(A) Their melting points are higher than those of the pure metals. (B) They are very hard.

(C) They retain metallic conductivity. (D) They are chemically very reactive.

Answer (1 mark)
(D) They are chemically very reactive.
Interstitial compounds are chemically inert. Statements (A), (B) and (C) are true.

5 Which of the following lanthanoid ions has the electronic configuration [Xe] $4f^7$? (Atomic numbers: Sm = 62, Eu = 63, Gd = 64, Tb = 65)

(A) Sm^{3+} (B) Eu^{3+}

(C) Gd^{3+} (D) Tb^{3+}

Answer (1 mark)

(C) Gd^{3+}

Gd = [Xe] $4f^7 5d^1 6s^2$; removing the 6s and 5d electrons gives Gd^{3+} = [Xe] $4f^7$. (Sm^{3+} = $4f^5$, Eu^{3+} = $4f^6$, Tb^{3+} = $4f^8$.)

6 Which of the following is a **homoleptic** complex?

(A) $[Co(NH_3)_4Cl_2]^+$ (B) $K_3[Cr(C_2O_4)_3]$

(C) $[Pt(NH_3)_2Cl_2]$ (D) $[Co(en)_2(NO_2)Cl]^+$

Answer (1 mark)

(B) $K_3[Cr(C_2O_4)_3]$

In a homoleptic complex the metal is bound to only one kind of donor group. Here Cr^{3+} carries only oxalate ligands; the other three complexes have two kinds of ligands (heteroleptic).

7 Phenol is treated with chloroform in the presence of aqueous sodium hydroxide, and the product is then acidified. The main product is:

(A) benzoic acid (B) salicylaldehyde (2-hydroxybenzaldehyde)

(C) salicylic acid (2-hydroxybenzoic acid) (D) benzaldehyde

Answer (1 mark)

(B) salicylaldehyde

This is the Reimer–Tiemann reaction: a –CHO group is introduced at the ortho position of the ring. (Salicylic acid is formed in Kolbe's reaction, with CO_2.)

8 Ethanenitrile (CH_3CN) is reduced with stannous chloride and hydrochloric acid, and the product is then hydrolysed with water. The organic compound finally obtained is:

(A) ethanal (B) ethanamine

(C) ethanoic acid (D) ethanol

Answer (1 mark)

(A) ethanal

This is the Stephen reaction: $SnCl_2$/HCl reduces the nitrile to the imine $CH_3CH{=}NH$, which is hydrolysed to CH_3CHO. (Ethanamine is formed when the nitrile is reduced with $LiAlH_4$ or H_2/Ni; ethanoic acid when it is hydrolysed directly with acid.)

9 In the industrial reduction of nitrobenzene to aniline, iron scrap and hydrochloric acid are preferred because:

(A) iron is a stronger reducing agent than any other metal

(B) the $FeCl_2$ formed is hydrolysed and releases HCl, so only a small amount of acid is needed

(C) iron reduces nitrobenzene to azobenzene, which then changes to aniline

(D) aniline formed by this method is free from water

Answer (1 mark)

(B)

$FeCl_2$ formed in the reaction gets hydrolysed to release hydrochloric acid, so only a small

amount of HCl is needed to start the reaction.

10 A patient's blood takes an unusually long time to clot after a small cut. Deficiency of which vitamin is the most likely cause?

(A) Vitamin A

(B) Vitamin B_{12}

(C) Vitamin C

(D) Vitamin K

Answer (1 mark)
(D) Vitamin K
Deficiency of vitamin K increases the blood clotting time. (A → night blindness/xerophthalmia; B_{12} → pernicious anaemia; C → scurvy.)

11 The molar mass of ethanoic acid (CH_3COOH, 60 g mol^{-1}) found from the depression in freezing point is nearly 120 g mol^{-1} in benzene, but slightly less than 60 g mol^{-1} in water. This is because ethanoic acid:

(A) dissociates in benzene and associates in water

(B) associates (forms dimers) in benzene and dissociates slightly in water

(C) associates in both solvents

(D) reacts with benzene to form a heavier compound

Answer (1 mark)
(B)
In benzene, molecules of ethanoic acid form dimers through hydrogen bonding ($i \approx 0.5$), so fewer particles are present and the observed molar mass is about double. In water it ionises slightly ($i > 1$), so the observed molar mass is a little less than 60 g mol^{-1}.

12 For many reactions the rate constant nearly doubles for a 10 K rise in temperature. The main reason is that:

(A) the activation energy of the reaction decreases on heating

(B) the fraction of molecules having energy equal to or greater than the activation energy increases sharply

(C) the total number of collisions per second doubles

(D) the enthalpy change of the reaction becomes more negative

Answer (1 mark)
(B)
A small rise in temperature shifts the Maxwell–Boltzmann distribution so that the fraction of molecules with energy $\geq E_a$ nearly doubles. E_a itself does not change, and the collision frequency increases only by a few per cent.

13 **Assertion (A):** On dilution, the molar conductivity of a weak electrolyte such as ethanoic acid increases steeply.
Reason (R): On dilution, the number of ions per unit volume of the solution increases.
Select the most appropriate answer from the options given below:

(A) Both A and R are true, and R is the correct explanation of A.

(B) Both A and R are true, but R is not the correct explanation of A.

(C) A is true but R is false.

(D) A is false but R is true.

Answer (1 mark)
(C) A is true but R is false.
For a weak electrolyte, Λ_m increases steeply on dilution because the degree of dissociation

increases, so the total number of ions in the solution increases. But the number of ions **per unit volume** decreases on dilution (this is why conductivity κ decreases), so R is false.

14 **Assertion (A):** The C–Cl bond length in chlorobenzene is shorter than that in chloromethane.
Reason (R): In chlorobenzene the carbon atom attached to chlorine is sp^2 hybridised.
Select the most appropriate answer from the options given below:

(A) Both A and R are true, and R is the correct explanation of A.
(B) Both A and R are true, but R is not the correct explanation of A.
(C) A is true but R is false.
(D) A is false but R is true.

Answer (1 mark)
(A) Both A and R are true, and R is the correct explanation of A.
In chlorobenzene the carbon of the C–Cl bond is sp^2 hybridised. With greater s-character it is more electronegative and holds the bonding pair of the C–Cl bond more tightly than the sp^3 carbon of chloromethane, so the C–Cl bond is shorter (169 pm against 177 pm). NCERT gives exactly this hybridisation argument for the shorter bond, so R correctly explains A. (Partial double bond character from resonance also shortens the bond; that is an additional reason and does not make R a wrong explanation.)

15 **Assertion (A):** Carboxylic acids do not give the characteristic reactions of the carbonyl group, such as the formation of oximes with hydroxylamine.
Reason (R): Carboxylic acids exist as hydrogen-bonded dimers in the vapour phase and in aprotic solvents.
Select the most appropriate answer from the options given below:

(A) Both A and R are true, and R is the correct explanation of A.
(B) Both A and R are true, but R is not the correct explanation of A.
(C) A is true but R is false.
(D) A is false but R is true.

Answer (1 mark)
(B) Both A and R are true, but R is not the correct explanation of A.
A is true because the carbonyl carbon of –COOH is less electrophilic: the lone pair on the –OH oxygen is delocalised onto the C=O group by resonance. R is a true fact, but dimer formation does not explain the absence of carbonyl reactions.

16 **Assertion (A):** All naturally occurring α-amino acids are optically active.
Reason (R): Most naturally occurring α-amino acids have the L-configuration.
Select the most appropriate answer from the options given below:

(A) Both A and R are true, and R is the correct explanation of A.
(B) Both A and R are true, but R is not the correct explanation of A.
(C) A is true but R is false.
(D) A is false but R is true.

Answer (1 mark)
(D) A is false but R is true.
Glycine ($H_2N–CH_2–COOH$) has two H atoms on the α-carbon, so it has no chiral carbon and is optically inactive. Hence A is false. R is true.

SECTION B Questions 17 to 21 are very short answer questions carrying 2 marks each. **[10]**

17 (A) (I) Write the IUPAC name of $[Pt(NH_3)_4(NO_2)Cl]SO_4$.

(II) Write the formula of tetraamminecopper(II) tetrachloridoplatinate(II). Name the type of isomerism it shows with $[Pt(NH_3)_4][CuCl_4]$.

OR

(B) (I) Low spin tetrahedral complexes are rarely observed. Give reason.

(II) Write the formula and the IUPAC name of the ionisation isomer of $[Pt(NH_3)_4Cl_2]Br_2$.

Answer (2 marks)

(A) (I) Tetraamminechloridonitrito-N-platinum(IV) sulphate

(Ligands in alphabetical order: ammine, chlorido, nitrito; oxidation state of Pt: x + 0 − 1 − 1 = +2, so x = +4.)

(II) $[Cu(NH_3)_4][PtCl_4]$

In this compound NH_3 is bound to Cu^{2+} and Cl^- to Pt^{2+}; in $[Pt(NH_3)_4][CuCl_4]$ the ligands are interchanged between the cationic and anionic entities of the two metal ions: **coordination isomerism**.

OR

(B) (I) In a tetrahedral field the splitting is small: $\Delta_t = (4/9)\,\Delta_o$. Δ_t is almost always less than the pairing energy P, so electrons occupy the higher orbitals before pairing. Hence tetrahedral complexes are high spin and low spin ones are rarely observed.

(II) $[Pt(NH_3)_4Br_2]Cl_2$: tetraamminedibromidoplatinum(IV) chloride

(Br^- is now a ligand and Cl^- is the counter ion, so the two isomers give different ions in solution.)

Marking: (A) (I) Correct IUPAC name with oxidation state (IV) – 1 mark · (A) (II) Correct formula – ½ mark; coordination isomerism – ½ mark · (B) (I) $\Delta_t = (4/9)\Delta_o$ is smaller than pairing energy – 1 mark · (B) (II) Formula – ½ mark; IUPAC name – ½ mark

Examiner tip: Find the oxidation state from the charge of the counter ion first: SO_4^{2-} makes the complex ion 2+, so Pt is +4, not +2. Write 'nitrito-N' because NO_2^- is ambidentate.

18 (I) Enzymes are needed only in very small amounts in the body. How does an enzyme increase the rate of a reaction? Name the enzyme that catalyses the hydrolysis of maltose and name the product.

(II) Thyroxine is a hormone produced in the thyroid gland. Of which amino acid is it a derivative? Why does a diet poor in iodine lead to enlargement of the thyroid gland, and how is this condition commonly prevented?

Answer (2 marks)

(I) Like other catalysts, an enzyme lowers the magnitude of the activation energy (it provides an alternative path with lower E_a), so many more molecules can react at body temperature.

Maltose is hydrolysed by the enzyme **maltase**: $C_{12}H_{22}O_{11}$ (maltose) + $H_2O \rightarrow 2C_6H_{12}O_6$ (glucose).

(II) Thyroxine is an iodinated derivative of the amino acid **tyrosine**. A low level of iodine in the diet lowers thyroxine production (hypothyroidism), and the thyroid gland enlarges. It is prevented by using iodised salt (table salt with added sodium iodide).

Marking: (I) Lowering of activation energy – ½ mark; maltase and glucose – ½ mark · (II) Tyrosine – ½ mark; iodine deficiency → less thyroxine → enlarged thyroid, prevented by iodised salt – ½ mark

Examiner tip: Say 'lowers the activation energy'. Writing only 'speeds up the reaction' repeats the question and earns no mark.

19 (I) Write the equation for the preparation of 2-fluoropropane from 2-bromopropane using silver fluoride. Name the reaction.
(II) Alkyl chlorides are made by replacing the –OH group of alcohols with HCl, but chlorobenzene cannot be prepared from phenol in this way. Why?

Answer (2 marks)

(I) $CH_3CH(Br)CH_3 + AgF \rightarrow CH_3CH(F)CH_3 + AgBr$

This is the **Swarts reaction** (an alkyl bromide or chloride is heated with a metallic fluoride such as AgF, Hg_2F_2, CoF_2 or SbF_3).

(II) In phenol the C–O bond has partial double bond character (the lone pair on oxygen is in conjugation with the benzene ring), and the carbon is sp^2 hybridised. This C–O bond is difficult to break, so –OH cannot be replaced by Cl.

Marking: (I) Balanced equation – ½ mark; Swarts reaction – ½ mark · (II) Partial double bond character of C–O bond (difficult to break) – 1 mark

Examiner tip: Swarts reaction makes alkyl fluorides; Finkelstein reaction (NaI in dry acetone) makes alkyl iodides. Do not mix up the two names.

20 Write the chemical equations for the following and name the organic product formed:
(I) Phenol is treated with concentrated nitric acid.
(II) Salicylic acid (2-hydroxybenzoic acid) is treated with acetic anhydride in the presence of a few drops of conc. H_2SO_4.

Answer (2 marks)

(I) $C_6H_5OH + 3HNO_3$ (conc.) $\rightarrow C_6H_2(NO_2)_3OH + 3H_2O$

Product: **2,4,6-trinitrophenol (picric acid)**. The –OH group strongly activates the ring, so three $–NO_2$ groups enter at the 2, 4 and 6 positions.

(II) o-$HOC_6H_4COOH + (CH_3CO)_2O \xrightarrow{-H^+}$ o-$CH_3COOC_6H_4COOH + CH_3COOH$

Product: **acetylsalicylic acid (aspirin)**, formed by acetylation of the phenolic –OH group.

Marking: (I) Balanced equation – ½ mark; 2,4,6-trinitrophenol/picric acid – ½ mark · (II) Equation – ½ mark; aspirin (acetylsalicylic acid) – ½ mark

Examiner tip: In (II) only the phenolic –OH is acetylated; the –COOH group stays as it is. Show CH_3COOH as the by-product.

21 (I) Write the equations for the preparation of propan-1-amine by the Gabriel phthalimide synthesis.
(II) Write the equation for the reaction of ethanamine with ethanoyl chloride. Why is this reaction carried out in the presence of pyridine?

Answer (2 marks)

(I) Phthalimide + KOH (ethanolic) $\rightarrow$ potassium phthalimide + H_2O

Potassium phthalimide + $CH_3CH_2CH_2Br \rightarrow$ N-propylphthalimide + KBr

N-propylphthalimide + 2NaOH(aq) $\xrightarrow{\text{–heat}}$ $CH_3CH_2CH_2NH_2$ (propan-1-amine) + sodium phthalate

(II) $CH_3CH_2NH_2 + CH_3COCl \rightarrow CH_3CH_2NHCOCH_3$ (N-ethylethanamide) + HCl

Pyridine is a base stronger than the amine. It removes the HCl formed and shifts the equilibrium to the right (otherwise HCl would form a salt with unreacted amine).

Marking: (I) Formation of potassium phthalimide and N-alkylation with 1-bromopropane – ½ mark; alkaline hydrolysis to propan-1-amine – ½ mark · (II) Equation – ½ mark; role of pyridine (removes HCl, shifts equilibrium) – ½ mark

Examiner tip: In the Gabriel synthesis use a primary alkyl halide (1-bromopropane). Name the acylated product as N-ethylethanamide, not 'ethyl acetamide'.

SECTION C Questions 22 to 28 are short answer questions carrying 3 marks each. **[21]**

22 A cell is set up at 298 K as follows:

$Zn(s) \mid Zn^{2+}(0.10\ M) \mid\mid H^+(aq) \mid H_2(g, 1\ bar) \mid Pt(s)$

Its emf is found to be 0.6715 V.

Given: $E°(Zn^{2+}/Zn) = -0.76$ V, $2.303RT/F = 0.059$ V.

(I) Write the cell reaction.

(II) Calculate the pH of the solution in the hydrogen electrode compartment.

(III) The solution in the hydrogen electrode compartment is replaced by a solution of pH 3, everything else remaining the same. Calculate the new emf of the cell.

Answer (3 marks)

(I) Anode: $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$; Cathode: $2H^+(aq) + 2e^- \rightarrow H_2(g)$

Cell reaction: $Zn(s) + 2H^+(aq) \rightarrow Zn^{2+}(aq) + H_2(g)$; n = 2

(II) $E°_{cell} = E°_{cathode} - E°_{anode} = 0.00 - (-0.76) = 0.76$ V

$E_{cell} = E°_{cell} - (0.059/2) \log ([Zn^{2+}]\ p_{H2}/[H^+]^2)$

$0.6715 = 0.76 - 0.0295 \log (0.10/[H^+]^2)$

$\log (0.10/[H^+]^2) = 0.0885/0.0295 = 3.0$

$0.10/[H^+]^2 = 10^3$, so $[H^+]^2 = 10^{-4}$ and $[H^+] = 10^{-2}$ M

pH = 2

(III) At pH 3, $[H^+] = 10^{-3}$ M

$E_{cell} = 0.76 - 0.0295 \log (0.10/(10^{-3})^2) = 0.76 - 0.0295 \log 10^5 = 0.76 - 0.0295 \times 5 = 0.76 - 0.1475$

E_{cell} = 0.6125 V ≈ 0.61 V (lower than before, because fewer H^+ ions are available for reduction at the cathode)

Marking: (I) Correct cell reaction with n = 2 – ½ mark · (II) $E°_{cell} = 0.76$ V and Nernst equation with correct Q – ½ mark; solving log term = 3 – ½ mark; pH = 2 – ½ mark · (III) Nernst equation with $[H^+] = 10^{-3}$ M – ½ mark; $E_{cell} = 0.6125$ V – ½ mark

Examiner tip: $[H^+]$ is squared in Q because two H^+ ions appear in the balanced equation. In (III), raising the pH by 1 lowers the emf by $2 \times 0.0295 = 0.059$ V.

23 (I) Write the equation for the reaction of chlorobenzene with methyl chloride in the presence of anhydrous $AlCl_3$ and name the major product.

(II) Write the equation for the reaction that takes place when bromobenzene is treated with sodium metal in dry ether. Name the reaction and the product.

(III) Which of the two compounds, $C_6H_5CH(Cl)CH_3$ and $C_6H_5CH_2CH_2Cl$, undergoes S_N1 hydrolysis faster? Give reason.

Answer (3 marks)

(I) Friedel–Crafts alkylation:

$C_6H_5Cl + CH_3Cl$ –anhyd. $AlCl_3$→ 1-chloro-4-methylbenzene (major) + 1-chloro-2-methylbenzene (minor) + HCl

Major product: **1-chloro-4-methylbenzene** (p-chlorotoluene).

(II) $2C_6H_5Br + 2Na$ –dry ether→ $C_6H_5–C_6H_5 + 2NaBr$

This is the **Fittig reaction**: two aryl groups are joined together. The product is **biphenyl (diphenyl)**.

(III) **$C_6H_5CH(Cl)CH_3$** (1-chloro-1-phenylethane) reacts faster. It ionises to a secondary benzylic carbocation, $C_6H_5C^+HCH_3$, which is stabilised by resonance with the benzene ring. $C_6H_5CH_2CH_2Cl$ would give a primary carbocation that is not in conjugation with the ring.

Marking: (I) Equation with both products – ½ mark; major product named – ½ mark · (II) Balanced equation – ½ mark; Fittig reaction and biphenyl named – ½ mark · (III) Correct compound – ½ mark; resonance-stabilised benzylic carbocation – ½ mark

Examiner tip: In (III) the halogen in $C_6H_5CH_2CH_2Cl$ is two carbons away from the ring, so it is not benzylic. Check the position of Cl before calling a halide 'benzylic'.

24 An organic compound A (C_3H_8O) liberates hydrogen gas with sodium metal. It gives turbidity with Lucas reagent at room temperature, but not immediately. On oxidation with acidified potassium dichromate, A gives B (C_3H_6O), which gives a yellow precipitate with iodine and sodium hydroxide but does not reduce Tollens' reagent. When A is heated with concentrated phosphoric acid, it gives a gas C that decolourises bromine water.
Identify A, B and C. Write the equations for (i) the conversion of A into B, (ii) the conversion of A into C and (iii) the reaction of B with methylmagnesium bromide followed by hydrolysis.

Answer (3 marks)

A reacts with Na, so it is an alcohol. Lucas reagent gives turbidity, but not immediately, so it is a secondary alcohol. B gives iodoform but not Tollens' test, so it is a methyl ketone.

A = propan-2-ol, $CH_3CH(OH)CH_3$; **B = propanone**, CH_3COCH_3; **C = propene**, $CH_3CH{=}CH_2$

(i) $CH_3CH(OH)CH_3 + [O] \xrightarrow{-K_2Cr_2O_7/H^+} CH_3COCH_3 + H_2O$

(ii) $CH_3CH(OH)CH_3 \xrightarrow{\text{conc. } H_3PO_4,\ \text{heat}} CH_3CH{=}CH_2 + H_2O$

(iii) $CH_3COCH_3 + CH_3MgBr \rightarrow (CH_3)_3C{-}OMgBr \xrightarrow{-H_2O} (CH_3)_3C{-}OH + Mg(OH)Br$

The product is 2-methylpropan-2-ol.

Marking: Identification of A, B and C – ½ mark each (1½ marks) · Equations (i), (ii) and (iii) – ½ mark each (1½ marks)

Examiner tip: Primary alcohols give no turbidity at room temperature and tertiary alcohols give it immediately, so 'turbidity, but not immediately' points to a secondary alcohol. A Grignard reagent with a ketone gives a tertiary alcohol.

25 A student crystallised glucose in two ways. From a concentrated solution at 303 K she obtained crystals melting at 419 K. From a hot saturated solution at 371 K she obtained crystals melting at 423 K.
(I) Name these two forms of glucose. What is the term used for such isomers, and at which carbon atom do they differ?
(II) Draw the Haworth structure of the form that melts at 423 K.
(III) Glucose is written as D-(+)-glucose. What do the symbols 'D' and '(+)' indicate?

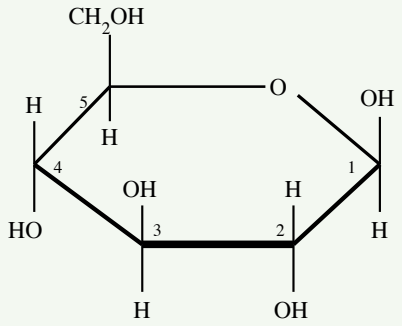
Answer (3 marks)

(I) The crystals melting at 419 K are **α-D-glucose** and those melting at 423 K are **β-D-glucose**. These two cyclic hemiacetal forms are called **anomers**. They differ only in the configuration of the –OH group at **C1** (the anomeric carbon, which was the aldehyde carbon before ring formation).

(II) β-D-glucopyranose: a six-membered ring of five carbon atoms and one oxygen atom (the –OH at C5 has added to the –CHO group). In the Haworth structure the –OH at C1 is on the same side (up) as the $-CH_2OH$ group at C5; the –OH groups at C2 and C4 point down and the –OH at C3 points up. (Structure below.)

(III) 'D' shows the configuration: the –OH group on the lowest asymmetric carbon (C5) is on the

right-hand side, as in D-(+)-glyceraldehyde. '(+)' shows that glucose is dextrorotatory (it rotates plane-polarised light to the right). The two are not related to each other.



β-D-glucopyranose: –OH at C1 on the same side as CH_2OH

Marking: (I) α and β forms identified correctly – ½ mark; anomers, differing at C1 – ½ mark · (II) Correct pyranose ring with O – ½ mark; correct positions of –OH groups and CH_2OH (β at C1) – ½ mark · (III) Meaning of D – ½ mark; meaning of (+) – ½ mark

Examiner tip: In β-D-glucose the C1–OH is on the same side as the CH_2OH group (both up). Many students draw the α-form by mistake. 'D' does not mean dextrorotatory.

26 Three isomeric amines P, Q and R have the molecular formula C_7H_9N, and each molecule contains a benzene ring.

• P reacts with nitrous acid at 273–278 K with brisk evolution of nitrogen gas and gives an alcohol of formula C_7H_8O.

• Q reacts with benzenesulphonyl chloride to give a product that is insoluble in aqueous KOH.

• R, whose $–CH_3$ group is para to the $–NH_2$ group, reacts with $NaNO_2$ and HCl at 273–278 K to give a diazonium salt that is stable at this temperature.

Identify P, Q and R and write one equation for the reaction of each described above.

Answer (3 marks)

P = phenylmethanamine (benzylamine), $C_6H_5CH_2NH_2$: the $–NH_2$ is on an alkyl carbon, so it behaves as an aliphatic primary amine, whose diazonium salt decomposes at once.

$C_6H_5CH_2NH_2 + HNO_2 \rightarrow C_6H_5CH_2OH + N_2\uparrow + H_2O$ (via the unstable $C_6H_5CH_2N_2^+$)

Q = N-methylaniline (N-methylbenzenamine), $C_6H_5NHCH_3$: a secondary amine. The sulphonamide has no H on nitrogen, so it is not acidic and does not dissolve in alkali.

$C_6H_5NHCH_3 + C_6H_5SO_2Cl \rightarrow C_6H_5SO_2N(CH_3)C_6H_5 + HCl$

R = 4-methylaniline (p-toluidine, 4-methylbenzenamine), $CH_3C_6H_4NH_2$: a primary aromatic amine, whose diazonium salt is stabilised by resonance with the ring.

$p\text{-}CH_3C_6H_4NH_2 + NaNO_2 + 2HCl \xrightarrow{–273–278\ K} p\text{-}CH_3C_6H_4N_2^+Cl^- + NaCl + 2H_2O$

Marking: Identification of P, Q and R – ½ mark each (1½ marks) · One correct equation for each of P, Q and R – ½ mark each (1½ marks)

Examiner tip: Benzylamine is C_7H_9N but behaves like an aliphatic amine, because its $–NH_2$ is not attached to the ring. Only arenediazonium salts are stable at 273–278 K.

27 (A) Write the main organic product and name the reaction in each of the following:

(I) $C_6H_6 + CO + HCl$ –(anhydrous $AlCl_3/CuCl$)→ ?

(II) $C_6H_5COONa + NaOH$ –(CaO, heat)→ ?

(III) $C_6H_5CHO + CH_3COCH_3$ (equimolar) –(dil. NaOH)→ ?

OR

(B) (I) Give a simple chemical test to distinguish between pentanal and pentan-3-one.

(II) Chloroethanoic acid is a stronger acid than ethanoic acid. Explain.

(III) Write the equation for the preparation of ethyl ethanoate from ethanoic acid. What is the role of concentrated H_2SO_4 in this reaction?

Answer (3 marks)

(A) (I) C_6H_5CHO (**benzaldehyde**); **Gattermann–Koch reaction**.

(II) $C_6H_5COONa + NaOH$ –CaO, Δ→ C_6H_6 (**benzene**) + Na_2CO_3; **decarboxylation** (heating with soda-lime).

(III) $C_6H_5CHO + CH_3COCH_3 \rightarrow C_6H_5CH{=}CH{-}COCH_3 + H_2O$; product **4-phenylbut-3-en-2-one** (benzalacetone); **cross aldol condensation** (Claisen–Schmidt). The α-hydrogen of propanone adds to the C=O of benzaldehyde, and the β-hydroxy ketone formed loses water.

OR

(B) (I) Tollens' test: warm each with Tollens' reagent. Pentanal gives a silver mirror; pentan-3-one does not.

$CH_3(CH_2)_3CHO + 2[Ag(NH_3)_2]^+ + 3OH^- \rightarrow CH_3(CH_2)_3COO^- + 2Ag\downarrow + 2H_2O + 4NH_3$

(Alternatively, Fehling's test: pentanal gives a red-brown precipitate of Cu_2O; pentan-3-one does not. The iodoform test does not work here, because neither compound has a $CH_3CO–$ group.)

(II) Cl is an electron-withdrawing group (–I effect). It pulls electron density away from the carboxylate group and disperses its negative charge, so $ClCH_2COO^-$ is more stable than CH_3COO^-. The acid therefore ionises more, and chloroethanoic acid is stronger.

(III) $CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$ (conc. H_2SO_4, heat)

Conc. H_2SO_4 acts as a catalyst: it protonates the carbonyl oxygen of the acid, which makes the carbonyl carbon more electrophilic, so the alcohol can attack it.

Marking: (A) Each correct product with the name of the reaction – ½ + ½ mark × 3 · (B) (I) Correct test with result for both compounds – 1 mark · (B) (II) –I effect of Cl stabilising the carboxylate ion – 1 mark · (B) (III) Equation – ½ mark; role of H_2SO_4 as catalyst (protonation) – ½ mark

Examiner tip: In a cross aldol between benzaldehyde and propanone, only propanone has α-hydrogens, so it supplies the carbanion and benzaldehyde is the electrophile. Write the dehydrated product, $C_6H_5CH{=}CHCOCH_3$.

28 How will you bring about the following conversions? Write the chemical equations with reagents and conditions.

(I) 2-Bromopropane to 2-methylpropanoic acid

(II) Toluene to benzaldehyde (through side chain chlorination)

(III) Ethanoyl chloride to propanone

Answer (3 marks)

(I) $(CH_3)_2CHBr + Mg$ –dry ether→ $(CH_3)_2CHMgBr$

$(CH_3)_2CHMgBr + CO_2$ (dry ice) → $(CH_3)_2CHCOOMgBr$ $–H_3O^+\rightarrow$ $(CH_3)_2CHCOOH + Mg(OH)Br$

(The carboxyl carbon comes from CO_2, so the chain grows by one carbon.)

(II) $C_6H_5CH_3 + 2Cl_2$ –hν (or heat)→ $C_6H_5CHCl_2$ (benzal chloride) + 2HCl

$C_6H_5CHCl_2 + H_2O$ –373 K→ $C_6H_5CHO + 2HCl$

(III) Dimethylcadmium is prepared from a Grignard reagent: $2CH_3MgBr + CdCl_2 \rightarrow (CH_3)_2Cd + 2Mg(Br)Cl$

$2CH_3COCl + (CH_3)_2Cd \rightarrow 2CH_3COCH_3 + CdCl_2$

Marking: (I) Grignard reagent formation – ½ mark; reaction with CO_2 and hydrolysis – ½ mark · (II) Side chain chlorination to benzal chloride – ½ mark; hydrolysis to benzaldehyde – ½ mark · (III) Preparation of dimethylcadmium – ½ mark; reaction with ethanoyl chloride – ½ mark

Examiner tip: Chlorination of toluene in the side chain needs sunlight/heat with no Lewis acid; with $FeCl_3$ in the dark the ring is chlorinated instead. Dialkylcadmium (not a Grignard reagent) stops at the ketone stage.

SECTION D Questions 29 and 30 are case-based questions carrying 4 marks each. **[8]**

29 Electrolysis of brine in a chlor-alkali plant

Chlor-alkali plants near Thane and in other industrial areas of India pass electricity through concentrated aqueous sodium chloride (brine). Three useful products are obtained: chlorine gas at the anode, hydrogen gas at the cathode, and sodium hydroxide, which collects in the solution. Chlorine is used to disinfect drinking water and to make PVC; sodium hydroxide is used in making soap, paper and textiles. In an electrolytic cell, the products depend on the species present and on their electrode potentials. Some processes, though feasible, are so slow that an extra potential, called overpotential, is needed.

(Given: $E°(Na^+/Na) = -2.71$ V, $E°(H^+/½H_2) = 0.00$ V, $E°(½Cl_2/Cl^-) = 1.36$ V, $E°(O_2, H^+/H_2O) = 1.23$ V; 1 F = 96500 C mol^{-1}; Na = 23, O = 16, H = 1, Cl = 35.5 g mol^{-1})

Answer the following questions:

(I) Hydrogen, and not sodium, is obtained at the cathode because:

(A) Na^+ ions move towards the anode

(B) reduction of H^+ (from water) has a much higher E° value than reduction of Na^+

(C) E° of Na^+/Na is more positive than that of $H^+/½H_2$

(D) hydrogen has a lower molar mass than sodium

(II) Going by the E° values (1.23 V is lower than 1.36 V), water should be oxidised at the anode more easily than Cl^- ions, yet chlorine and not oxygen is the main product. This is because of:

(A) the overpotential of oxygen

(B) the higher molar mass of chlorine

(C) the reaction of oxygen with sodium hydroxide

(D) the greater solubility of chlorine in brine

(IIIA) A current of 2.5 A is passed through brine for 64 minutes 20 seconds. Calculate the mass of chlorine liberated at the anode and the mass of sodium hydroxide formed.

OR

(IIIB) (a) What are the products at the cathode and at the anode when molten NaCl is electrolysed? (b) What happens at the cathode and at the anode when aqueous $CuSO_4$ is electrolysed using copper electrodes?

Answer (4 marks)

(I) (B) The reduction with the higher E° is preferred; $H^+/½H_2$ (0.00 V) is far higher than Na^+/Na (−2.71 V). The net cathode reaction is $H_2O + e^- \rightarrow ½H_2 + OH^-$.

(II) (A) The overpotential of oxygen. Oxidation of water is kinetically slow and needs extra potential, so $Cl^- \rightarrow ½Cl_2 + e^-$ takes place.

(IIIA) $Q = I \times t = 2.5\ A \times 3860\ s = 9650\ C = 9650/96500 = 0.100\ F$

Anode: $2Cl^- \rightarrow Cl_2 + 2e^-$, so 2 F give 1 mol Cl_2.

Moles of Cl_2 = 0.100/2 = 0.0500 mol; mass = 0.0500 × 71 = **3.55 g**

Cathode: $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$, so 1 F gives 1 mol OH^-, i.e. 1 mol NaOH.

Moles of NaOH = 0.100 mol; mass = 0.100 × 40 = **4.00 g**

OR

(IIIB) (a) Molten NaCl contains only Na^+ and Cl^- ions. Cathode: $Na^+ + e^- \rightarrow Na$ (sodium metal); anode: $Cl^- \rightarrow \frac{1}{2}Cl_2 + e^-$ (chlorine gas).

(b) Cathode: $Cu^{2+} + 2e^- \rightarrow Cu$, so copper is deposited. Anode: $Cu \rightarrow Cu^{2+} + 2e^-$, so the copper anode dissolves. The concentration of $CuSO_4$ stays nearly the same (this is the basis of refining of copper).

Marking: (I) Correct option – 1 mark · (II) Correct option – 1 mark · (IIIA) Q = 9650 C = 0.100 F – ½ mark; moles of Cl_2 (0.0500) – ½ mark; mass 3.55 g – ½ mark; mass of NaOH 4.00 g – ½ mark · (IIIB) (a) Na at cathode and Cl_2 at anode – ½ + ½ mark; (b) Cu deposited at cathode, Cu anode dissolves – ½ + ½ mark

Examiner tip: One mole of Cl_2 needs 2 F but one mole of NaOH needs only 1 F. Convert the time fully into seconds: 64 min 20 s = 3860 s.

30 Why complexes of the same metal have different colours

According to crystal field theory, in an octahedral complex the five d orbitals of the metal ion split into a lower set of three (t_{2g}) and a higher set of two (e_g) orbitals. The energy gap is the crystal field splitting energy, Δ_o. Ligands that cause a larger splitting are called strong field ligands. When white light falls on the complex, an electron jumps from a t_{2g} to an e_g orbital (d–d transition) by absorbing light whose energy equals Δ_o, and the complex shows the complementary colour. A larger Δ_o means light of higher energy, i.e. shorter wavelength, is absorbed. Students in a college laboratory recorded the following for two complexes of Cr^{3+} (Z of Cr = 24):

Complex	Light absorbed	Wavelength absorbed (approx.)	Colour seen
$[Cr(H_2O)_6]^{3+}$	yellow	575 nm	violet
$[Cr(NH_3)_6]^{3+}$	blue	465 nm	yellow

Answer the following questions using only the information and data given above:

(I) Which conclusion follows from the data?

(A) Δ_o for $[Cr(NH_3)_6]^{3+}$ is larger than for $[Cr(H_2O)_6]^{3+}$, so NH_3 is a stronger field ligand than H_2O.

(B) Δ_o for $[Cr(H_2O)_6]^{3+}$ is larger, so H_2O is a stronger field ligand.

(C) Both complexes have the same Δ_o, as both contain Cr^{3+}.

(D) The colour seen is the colour of the light absorbed.

(II) Which statement is true for **both** complexes in the table?

(A) Both are diamagnetic.

(B) Both have the configuration $t_{2g}^3e_g^0$ with three unpaired electrons.

(C) $[Cr(NH_3)_6]^{3+}$ is low spin with one unpaired electron.

(D) $[Cr(H_2O)_6]^{3+}$ has two electrons in the e_g set.

(IIIA) Cr^{2+} forms $[Cr(H_2O)_6]^{2+}$ (H_2O weak field, $\Delta_o < P$) and $[Cr(CN)_6]^{4-}$ (CN^- strong field, $\Delta_o > P$). Write the t_{2g}/e_g configuration of the metal ion in each, and calculate the spin-only magnetic moment of each.

OR

(IIIB) (a) $[Co(NH_3)_6]^{3+}$ absorbs light of about 475 nm, while $[Co(NH_3)_5Cl]^{2+}$, in which one NH_3 is replaced by Cl^-, absorbs light of about 535 nm. What does this show about the field strength of Cl^- compared with NH_3? Explain.

(b) State one limitation of crystal field theory.

Answer (4 marks)

(I) (A) $[Cr(NH_3)_6]^{3+}$ absorbs at the shorter wavelength (465 nm), i.e. higher energy, so its Δ_o is larger and NH_3 is the stronger field ligand.

(II) (B) Cr^{3+} is $3d^3$. The three electrons occupy the three t_{2g} orbitals singly whatever the ligand: $t_{2g}^3e_g^0$, 3 unpaired electrons (paramagnetic, $\mu = 3.87$ BM).

(IIIA) Cr^{2+} = [Ar] $3d^4$.

$[Cr(H_2O)_6]^{2+}$: $\Delta_o < P$, so the fourth electron enters e_g: $\mathbf{t_{2g}^3e_g^1}$, n = 4 unpaired; $\mu = \sqrt{(4 \times 6)} = \sqrt{24}$ = **4.90 BM** (high spin).

$[Cr(CN)_6]^{4-}$: $\Delta_o > P$, so the fourth electron pairs in t_{2g}: $\mathbf{t_{2g}^4e_g^0}$, n = 2 unpaired; $\mu = \sqrt{(2 \times 4)} = \sqrt{8}$ = **2.83 BM** (low spin).

OR

(IIIB) (a) Replacing NH_3 by Cl^- shifts the absorption to a longer wavelength (lower energy), so Δ_o becomes smaller. Hence Cl^- is a **weaker field ligand** than NH_3 (Cl^- lies below NH_3 in the spectrochemical series).

(b) Any one: CFT treats ligands as point charges, so anionic ligands should give the largest splitting, but they actually lie at the low end of the spectrochemical series; it does not take into account the covalent character of the metal–ligand bond.

Marking: (I) Correct option – 1 mark · (II) Correct option – 1 mark · (IIIA) Each configuration – ½ mark × 2; each magnetic moment – ½ mark × 2 · (IIIB) (a) Cl^- weaker field, with reason from wavelength/energy – 1 mark; (b) any one limitation – 1 mark

Examiner tip: Shorter wavelength absorbed means larger Δ_o. Do not confuse the colour seen with the colour absorbed. For d^1–d^3 ions the number of unpaired electrons does not depend on the ligand.

SECTION E Questions 31 to 33 are long answer questions carrying 5 marks each. **[15]**

31 (A) (I) 1.80 g of a non-volatile non-electrolyte X is dissolved in 50.0 g of water. The boiling point of water rises by 0.208 K. Calculate the molar mass of X. Also calculate the freezing point of this solution. (K_b of water = 0.52 K kg mol^{-1}, K_f of water = 1.86 K kg mol^{-1}, freezing point of water = 273.15 K)

(II) Two liquids A and B form a solution in which the A–B attractions are stronger than the A–A and B–B attractions. State (a) the type of deviation from Raoult's law, (b) the sign of $\Delta_{mix}H$, (c) the sign of $\Delta_{mix}V$, and (d) the type of azeotrope such a pair may form.

OR

(B) (I) Methanol and ethanol form a nearly ideal solution. At a certain temperature the vapour pressures of pure methanol and pure ethanol are 16.0 kPa and 8.0 kPa respectively, and a solution of the two has a vapour pressure of 12.8 kPa at the same temperature. Calculate (a) the mole fraction of methanol in the solution, (b) the mole fraction of methanol in the vapour in equilibrium with the solution and (c) the mass of methanol that must be mixed with 46.0 g of ethanol to make this solution. (C = 12, H = 1, O = 16 g mol^{-1})

(II) (a) A beaker of pure water and a beaker of sugar solution are kept side by side in a sealed glass chamber. After some days the level of water in the first beaker falls and the level of the sugar solution rises. Explain.

(b) Why are the tanks used by scuba divers filled with air diluted with helium?

Answer (5 marks)

(A) (I) $\Delta T_b = K_b\, m = K_b \times (w_2 \times 1000)/(M_2 \times w_1)$

$M_2 = (K_b \times w_2 \times 1000)/(\Delta T_b \times w_1) = (0.52 \times 1.80 \times 1000)/(0.208 \times 50.0) = 936/10.4 =$ **90 g mol^{-1}**

Molality $m = (1.80/90)/0.0500$ kg $= 0.0200/0.0500 = 0.400$ mol kg^{-1}

$\Delta T_f = K_f\, m = 1.86 \times 0.400 = 0.744$ K

Freezing point = 273.15 − 0.744 = **272.41 K** (≈ −0.74 °C)

(II) (a) Negative deviation from Raoult's law (each component escapes less easily, so the vapour pressure is lower than expected).

(b) $\Delta_{mix}H$ is negative (heat is released, as stronger attractions are formed).

(c) $\Delta_{mix}V$ is negative (the volume of the solution is a little less than the sum of the volumes).

(d) A maximum boiling azeotrope.

OR

(B) (I) (a) By Raoult's law, $p_{total} = p°_E + (p°_M - p°_E)\, x_M$

$12.8 = 8.0 + (16.0 - 8.0)\, x_M$, so $x_M = 4.8/8.0 =$ **0.60** ($x_E = 0.40$)

(b) $p_M = x_M\, p°_M = 0.60 \times 16.0 = 9.6$ kPa; $y_M = p_M/p_{total} = 9.6/12.8 =$ **0.75**

(The vapour is richer in methanol, the more volatile component: 0.75 > 0.60.)

(c) Ethanol, C_2H_5OH = 46 g mol^{-1}: $n_E = 46.0/46 = 1.00$ mol

$x_M = n_M/(n_M + 1.00) = 0.60$, so $n_M = (0.60/0.40) \times 1.00 = 1.50$ mol

Methanol, CH_3OH = 32 g mol^{-1}: mass = $1.50 \times 32 =$ **48.0 g**

(II) (a) The vapour pressure of the sugar solution is lower than that of pure water (vapour pressure lowering by a non-volatile solute). In the sealed chamber the air becomes saturated for the solution before it is saturated for pure water, so water keeps evaporating from the pure water and condensing into the solution. The water level falls and the solution level rises.

(b) At great depth the pressure is high, so more N_2 dissolves in the blood (Henry's law). When the diver comes up, the dissolved gas forms bubbles in the blood (the bends), which is painful and dangerous. Diluting the air with helium (which is much less soluble in blood) reduces this problem and the toxic effects of high concentrations of nitrogen.

Marking: (A) (I) Formula for M_2 – ½ mark; M = 90 g mol^{-1} – 1 mark; molality 0.400 – ½ mark; ΔT_f = 0.744 K – ½ mark; freezing point 272.41 K – ½ mark · (A) (II) Each of (a), (b), (c), (d) – ½ mark × 4 · (B) (I) x_M = 0.60 – 1 mark; y_M = 0.75 – 1 mark; n_M = 1.50 mol and mass 48.0 g – 1 mark · (B) (II) (a) Lower vapour pressure of solution → transfer of water vapour – 1 mark; (b) Henry's law/bends and use of helium – 1 mark

Examiner tip: Mass of solvent must be in kg (50.0 g = 0.0500 kg). In (B)(I) the mole fraction in the vapour uses partial pressures (Dalton's law), not the liquid mole fractions; in (c) use the mole ratio $n_M : n_E = 0.60 : 0.40 = 3 : 2$.

32 (A) Answer the following:

(I) In the preparation of potassium permanganate, the green manganate ion (MnO_4^{2-}) disproportionates in a neutral or acidic solution. Write the balanced ionic equation for this change in acidic solution.

(II) Iron(III) ions catalyse the reaction between iodide and persulphate (peroxodisulphate) ions. Write the two steps that show how Fe^{3+} works as a catalyst.

(III) Transition metals readily form alloys with one another. Give reason.

(IV) Calculate the spin-only magnetic moment of Cu^{2+} (Z = 29).

(V) Chromium (Z = 24) has the configuration [Ar] $3d^5 4s^1$ and copper (Z = 29) has [Ar] $3d^{10} 4s^1$, instead of $3d^4 4s^2$ and $3d^9 4s^2$. Explain.

OR

(B) Answer the following:

(I) Write the equation for the decomposition of potassium permanganate on heating at 513 K.

(II) Why is it difficult to separate the lanthanoids from one another?

(III) Draw the structure of the dichromate ion, $Cr_2O_7^{2-}$.

(IV) Calculate the spin-only magnetic moment of Ti^{2+} (Z = 22).

(V) Complete and balance the following equation for the oxidation of a manganese(II) salt by peroxodisulphate in the laboratory:

$Mn^{2+} + S_2O_8^{2-} + H_2O \rightarrow$

Answer (5 marks)

(A) (I) $3MnO_4^{2-} + 4H^+ \rightarrow 2MnO_4^- + MnO_2 + 2H_2O$

(Mn goes from +6 to +7 in MnO_4^- and to +4 in MnO_2. Check: charge −6 + 4 = −2 on the left and −2 on the right; O: 12 = 8 + 2 + 2.)

(II) $2Fe^{3+} + 2I^- \rightarrow 2Fe^{2+} + I_2$

$2Fe^{2+} + S_2O_8^{2-} \rightarrow 2Fe^{3+} + 2SO_4^{2-}$

(Fe^{3+} is used in the first step and given back in the second; its ability to change oxidation state makes it a catalyst.)

(III) The atomic (metallic) radii of transition metals are very similar (within about 15% of each other), so atoms of one metal can easily take the place of atoms of another in the crystal lattice.

(IV) Cu^{2+} = [Ar] $3d^9$: one unpaired electron. $\mu = \sqrt{(n(n+2))} = \sqrt{(1 \times 3)} = \sqrt{3}$ = **1.73 BM**

(V) 3d and 4s orbitals have very similar energies, and exactly half-filled (d^5) and completely filled (d^{10}) sets of d orbitals have extra stability (symmetry and exchange energy). So one 4s electron moves into 3d.

OR

(B) (I) $2KMnO_4 \xrightarrow{-513\ K} K_2MnO_4 + MnO_2 + O_2$

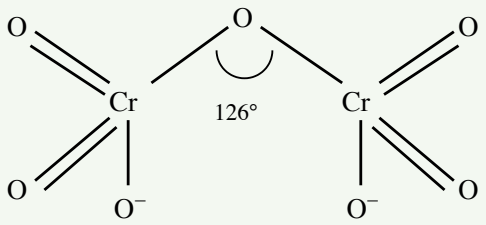
(II) Because of the lanthanoid contraction, the atomic and ionic radii of successive lanthanoids differ very little, and almost all show the +3 state. So their chemical properties are very similar, which makes their separation difficult.

(III) Two CrO_4 tetrahedra share one corner oxygen atom; the Cr–O–Cr bond angle is 126°. Each Cr is in the +6 state. (Structure below.)

(IV) Ti^{2+} = [Ar] $3d^2$: two unpaired electrons. $\mu = \sqrt{(2 \times 4)} = \sqrt{8}$ = **2.83 BM**

(V) $2Mn^{2+} + 5S_2O_8^{2-} + 8H_2O \rightarrow 2MnO_4^- + 10SO_4^{2-} + 16H^+$

(Check: charge +4 − 10 = −6 on the left; −2 − 20 + 16 = −6 on the right; O: 40 + 8 = 48 = 8 + 40.)



Marking: (A) Each part (I) to (V) – 1 mark (in (I), correct products MnO_4^- and MnO_2 ½ + balancing ½; in (II), each step ½) · (B) Each part (I) to (V) – 1 mark (in (III), two tetrahedra sharing one O – ½, bond angle/charges – ½; in (V), products ½ + balancing ½)

Examiner tip: For Cu^{2+}, remove the 4s electron first and then one 3d electron: $3d^9$, not $3d^74s^2$. In ionic equations check that the total charge is equal on both sides.

33 (A) (I) In a textile-mill effluent treatment tank, a dissolved dye is bleached by first order kinetics. Its concentration is 0.80 mg L^{-1} two hours after the treatment starts and 0.20 mg L^{-1} six hours after the treatment starts. Calculate (a) the half-life, (b) the rate constant and (c) the concentration of the dye when the treatment started (t = 0). (Given: log 2 = 0.301, log 4 = 0.602)

(II) (a) The decomposition of ammonia on a hot platinum surface is a zero order reaction at high pressure. Explain.

(b) A reaction takes place in several steps. Which step decides the overall rate of the reaction, and what is it called?

OR

(B) (I) In a zero order reaction the concentration of the reactant falls from 0.90 mol L^{-1} to 0.60 mol L^{-1} in 25 minutes. Calculate (a) the rate constant, (b) the time taken for the concentration to fall from 0.90 mol L^{-1} to 0.30 mol L^{-1} and (c) the half-life of the reaction when the initial concentration is 0.90 mol L^{-1}.

(II) (a) According to collision theory, not every collision between molecules having energy equal to or more than the threshold energy forms products. Why?

(b) The rate constant of a first order reaction is 2.31×10^{-2} min^{-1}. Calculate its half-life.

Answer (5 marks)

(A) (I) (a) From t = 2 h to t = 6 h (4 h) the concentration falls from 0.80 to 0.20 mg L^{-1}, i.e. to one-fourth = $(½)^2$. So 4 h = 2 half-lives and $\mathbf{t_{1/2} = 2.0\ h}$.

(b) $k = (2.303/t) \log ([R]_1/[R]_2) = (2.303/4\ h) \log (0.80/0.20) = (2.303 \times 0.602)/4 = \mathbf{0.347\ h^{-1}}$

(Check: $k = 0.693/t_{1/2} = 0.693/2.0 = 0.347\ h^{-1}$.)

(c) From t = 0 to t = 2 h is one half-life, so $[R]_0 = 2 \times 0.80 = \mathbf{1.60\ mg\ L^{-1}}$

(Or: $\log ([R]_0/0.80) = kt/2.303 = 0.347 \times 2/2.303 = 0.301$, so $[R]_0/0.80 = 2$.)

(II) (a) At high pressure the platinum surface is completely covered (saturated) with ammonia molecules. A further increase in pressure cannot increase the amount on the surface, so the rate stays constant: Rate = $k[NH_3]^0 = k$.

(b) The slowest step decides the overall rate; it is called the **rate determining step**.

OR

(B) (I) For zero order: $[R] = [R]_0 - kt$

(a) $k = ([R]_0 - [R])/t = (0.90 - 0.60)/25 = \mathbf{0.012\ mol\ L^{-1}\ min^{-1}}$

(b) $t = (0.90 - 0.30)/0.012 = \mathbf{50\ min}$

(c) $t_{1/2} = [R]_0/2k = 0.90/(2 \times 0.012) = \mathbf{37.5\ min}$

(II) (a) Besides having enough energy, the molecules must collide with proper orientation so that the old bonds can break and new bonds form. Collisions with improper orientation do not give products (for example, OH^- must approach CH_3Br from the side opposite to Br to form CH_3OH).

(b) $t_{1/2} = 0.693/k = 0.693/(2.31 \times 10^{-2}\ min^{-1}) = \mathbf{30.0\ min}$

Marking: (A) (I) $t_{1/2}$ = 2.0 h – 1 mark; k = 0.347 h^{-1} – 1 mark; $[R]_0$ = 1.60 mg L^{-1} – 1 mark · (A) (II) (a) Surface saturated, so rate independent of pressure – 1 mark; (b) slowest step, rate determining step – 1 mark · (B) (I) k = 0.012 mol L^{-1} min^{-1} – 1 mark; t = 50 min – 1 mark; $t_{1/2}$ = 37.5 min – 1 mark · (B) (II) (a) Proper orientation needed – 1 mark; (b) $t_{1/2}$ = 30.0 min – 1 mark

Examiner tip: In (A)(I) the time interval is 6 − 2 = 4 h, not 6 h. For a zero order reaction the half-life depends on the initial concentration, so use $t_{1/2} = [R]_0/2k$, not 0.693/k.

All the best for your exam!