Roll No. ☐☐☐☐☐☐☐☐

Q.P. Code 56/1/1

CHEMISTRY (THEORY)

CBSE Class XII Board Examination 2024 — with answers

Time allowed: 3 hours **Maximum Marks: 70**

General Instructions:

1. The paper has 33 questions in five sections (A to E); all of them must be answered.
2. Section A: Q1–16, multiple choice (including Assertion-Reason), 1 mark each.
3. Section B: Q17–21, very short answer, 2 marks each.
4. Section C: Q22–28, short answer, 3 marks each.
5. Section D: Q29–30, case-based, 4 marks each.
6. Section E: Q31–33, long answer, 5 marks each.
7. There is no overall choice, but some questions in Sections B to E offer an internal choice (OR). Calculators are not allowed.

SECTION A

Q1–16 are multiple choice questions of 1 mark each (Q13–16 are Assertion-Reason).

1. Among these first-row transition elements, which one should have the highest third ionisation enthalpy? **1**

(A) Iron (Z = 26)

(B) Manganese (Z = 25)

(C) Chromium (Z = 24)

(D) Vanadium (Z = 23)

ANSWER

(B) Manganese

Third ionisation removes an electron from the M^{2+} ion.

Mn^{2+} is $3d^5$ – a stable half-filled configuration. Removing a third electron breaks this stability, so a very large energy is needed.

Fe^{2+} ($3d^6$) actually becomes $3d^5$ after losing an electron, so its third IE is lower; Cr^{2+} ($3d^4$) and V^{2+} ($3d^3$) are not specially stable.

Hence Mn has the highest third ionisation enthalpy.

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2. Which of these compounds gives a ketone when oxidised with chromic anhydride (CrO_3)? **1**

(A) $(CH_3)_2CH–CH_2OH$

(B) $CH_3CH_2CH_2OH$

(C) $(CH_3)_3C–OH$

(D) $CH_3–CH_2–CH(OH)–CH_3$

ANSWER

(D) $CH_3CH_2CH(OH)CH_3$ (butan-2-ol)

Only a secondary alcohol is oxidised to a ketone.

(A) and (B) are primary alcohols → aldehydes/acids; (C) is tertiary → not oxidised easily.

(D) butan-2-ol is secondary: $CH_3CH_2CH(OH)CH_3 \rightarrow CH_3CH_2COCH_3$ (butan-2-one).

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3. A DNA nucleotide is made of three parts. Two of them are β-D-2-deoxyribose and a heterocyclic base. What is the third part? **1**

(A) Adenine

(B) Phosphoric acid

(C) Sulphuric acid

(D) Uracil

ANSWER

(B) Phosphoric acid

A nucleotide = sugar + nitrogenous base + phosphate group.

The phosphate comes from phosphoric acid; it links the sugars to form the sugar-phosphate backbone.

Adenine is itself a base, and uracil is found in RNA, not DNA.

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4. When a solute associates in a solvent, its van't Hoff factor i is: **1**

(A) always greater than one

(B) negative

(C) zero

(D) always less than one

ANSWER

(D) always less than one

i = (number of particles actually present) / (number of particles expected).

On association, several molecules join into one, so the number of particles decreases.

Therefore i < 1 (e.g. ethanoic acid dimerising in benzene, i ≈ 0.5).

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5. For the reaction X + 2Y → P, which differential rate expression is correct? **1**

(A) $\frac{2\,d[P]}{dt} = \frac{-d[Y]}{dt}$

(B) $\frac{-d[P]}{dt} = \frac{-d[X]}{dt}$

(C) $\frac{+d[X]}{dt} = \frac{-d[P]}{dt}$

(D) $\frac{-2\,d[Y]}{dt} = \frac{+d[P]}{dt}$

ANSWER

(A) 2 d[P]/dt = −d[Y]/dt

Rate = $-\frac{d[X]}{dt} = -\frac{1}{2}\frac{d[Y]}{dt} = +\frac{d[P]}{dt}$.

From the last two terms: $-\frac{d[Y]}{dt} = 2\frac{d[P]}{dt}$, which is option (A).

Common mistake: reactant terms carry a minus sign and each term is divided by its stoichiometric coefficient.

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6. Which compound undergoes SN1 reaction fastest? **1**

(A) 3-Bromocyclohexene (Br on the ring carbon next to the ring C=C, i.e. allylic)

(B) (Bromomethyl)cyclohexane, $C_6H_{11}–CH_2Br$

(C) Bromocyclohexane, $C_6H_{11}–Br$

(D) Bromobenzene, $C_6H_5–Br$

ANSWER

(A) 3-bromocyclohexene (allylic bromide)

SN1 rate depends on the stability of the carbocation formed in the slow step.

(A) gives an allylic carbocation stabilised by resonance with the C=C → most stable → fastest.

(B) would give a primary carbocation, (C) a simple secondary one.

(D) Aryl halides do not undergo SN1 (C–Br bond has partial double-bond character; phenyl cation is very unstable).

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7. What is formed when acetic acid reacts with PCl_5? **1**

(A) Cl–CH_2–COCl

(B) Cl–CH_2–COOH

(C) CH_3–COCl

(D) CCl_3–COOH

ANSWER

(C) CH_3COCl

PCl_5 replaces the –OH of a carboxylic acid by –Cl:
$CH_3COOH + PCl_5 \rightarrow CH_3COCl + POCl_3 + HCl$.
The α-hydrogens are not substituted (that needs Cl_2/red P – the HVZ reaction).

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8. Formation of a cyanohydrin from an aldehyde is an example of: **1**

(A) nucleophilic addition

(B) electrophilic addition

(C) nucleophilic substitution

(D) electrophilic substitution

ANSWER

(A) nucleophilic addition

CN^- (nucleophile) attacks the electrophilic carbonyl carbon, the C=O π bond breaks and the alkoxide is protonated: $RCHO + HCN \rightarrow RCH(OH)CN$.
Nothing is replaced, so it is addition, started by a nucleophile.

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9. In the Arrhenius equation, a graph of log k against 1/T is a straight line. Its slope and intercept are: **1**

(A) slope A/R, intercept E_a

(B) slope A, intercept $-E_a/R$

(C) slope $-E_a/RT$, intercept log A

(D) slope $-E_a/(2.303\ R)$, intercept log A

ANSWER

(D) slope = $-E_a/2.303R$, intercept = log A

k = A e^($-E_a$/RT) → $\log k = \log A - \frac{E_a}{2.303\,R} \cdot \frac{1}{T}$.
Compare with y = c + mx, where y = log k and x = 1/T.
Slope = $-E_a/2.303R$ and intercept = log A.

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10. The reaction of an alkyl halide with a sodium alkoxide to give an ether is called: **1**

(A) Wurtz reaction

(B) Reimer-Tiemann reaction

(C) Williamson synthesis

(D) Kolbe reaction

ANSWER

(C) Williamson synthesis

$R–X + R'–O^-Na^+ \rightarrow R–O–R' + NaX$ is the Williamson ether synthesis (SN2 attack of alkoxide on the alkyl halide; works best with primary halides).

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11. Choose the correct order of ease of dehydration with conc. H_2SO_4: **1**

(A) **$(CH_3)_3C–OH > (CH_3)_2CH–OH > CH_3CH_2–OH$**

(B) $(CH_3)_2CH–OH > CH_3CH_2–OH > (CH_3)_3C–OH$

(C) $CH_3CH_2–OH > (CH_3)_2CH–OH > (CH_3)_3C–OH$

(D) $(CH_3)_2CH–OH > (CH_3)_3C–OH > CH_3CH_2–OH$

ANSWER

(A) 3° > 2° > 1°

Acid-catalysed dehydration goes through a carbocation.
Carbocation stability: 3° > 2° > 1°, so tertiary alcohols dehydrate most easily.
Order: tert-butyl alcohol > isopropyl alcohol > ethanol.

12. Which groups of glucose react with each other to give the cyclic hemiacetal (pyranose) form? **1**

(A) Aldehyde group and –OH at C-4

(B) **Aldehyde group and –OH at C-5**

(C) Ketone group and –OH at C-4

(D) Ketone group and –OH at C-5

ANSWER

(B) –CHO and the –OH at C-5

Glucose is an aldose, so it has a –CHO group (not a ketone).
The –OH on C-5 adds to the C-1 aldehyde, forming a six-membered ring (5 C + 1 O) = pyranose, a cyclic hemiacetal.

13. Assertion (A): Adding NaCl to water lowers its freezing point. **1**
Reason (R): NaCl dissociates in water.

(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

(B) Both true, R not the correct explanation

A is true: any non-volatile solute lowers the vapour pressure and hence the freezing point (a colligative effect).
R is true: $NaCl \rightarrow Na^+ + Cl^-$.
But the depression is caused by the presence of solute particles; dissociation only makes it larger (i = 2). A non-electrolyte like glucose also depresses the freezing point. So R does not explain A (official answer: B).

14. Assertion (A): Zr and Hf are hard to separate. **1**

Reason (R): Because of lanthanoid contraction, Zr and Hf have almost the same radii.

(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

(A) Both true, R explains A

Lanthanoid contraction cancels the expected size increase from 4d to 5d, so Zr (160 pm) and Hf (159 pm) have nearly equal radii.
Same size + same valence configuration → almost identical chemistry → separation is difficult. R correctly explains A.

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15. Assertion (A): Ethanoic acid has a lower pK_a than $Cl–CH_2–COOH$. **1**

Reason (R): Chlorine's electron-withdrawing (–I) effect increases the acidity of $Cl–CH_2–COOH$.

(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

(D) A false, R true

–I effect of Cl stabilises the carboxylate ion, so chloroacetic acid is the stronger acid (R true).
Stronger acid → lower pK_a. So chloroacetic acid ($pK_a \approx 2.9$) has a lower pK_a than ethanoic acid (≈ 4.8). A is false.

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16. Assertion (A): Aniline is more basic than ammonia. **1**

Reason (R): In aniline the lone pair on nitrogen is delocalised into the ring by resonance, so it is less available for protonation.

(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

(D) A false, R true

R is true: the N lone pair is in conjugation with the benzene ring.
Because of this, aniline is a weaker base than ammonia (pK_b 9.4 vs 4.75). So A is false.

SECTION B

Q17–21 are very short answer questions of 2 marks each.

17. Find the electrode potential of an iron electrode dipped in 0.01 M Fe^{2+} solution at 298 K. ($E°(Fe^{2+}/Fe) = -0.45$ V; log 10 = 1) **2**

ANSWER

E = −0.509 V

Electrode reaction: $Fe^{2+} + 2e^- \rightarrow Fe$, n = 2.

Nernst: $E = E^\circ - \frac{0.059}{n} \log \frac{1}{[Fe^{2+}]}$

E = −0.45 − (0.059/2) log (1/0.01) = −0.45 − 0.0295 × 2

E = −0.45 − 0.059 = −0.509 V.

Mistake to avoid: [Fe(s)] = 1, so only $[Fe^{2+}]$ goes in the denominator.

18. What is meant by molecularity of a reaction? Give one condition under which a bimolecular reaction can behave kinetically as first order. **2**

ANSWER

Molecularity = number of species colliding in an elementary step; a bimolecular reaction is first order when one reactant is in large excess.

Molecularity: the number of reacting species (atoms, ions or molecules) that must collide at the same time in an elementary reaction for it to occur. (Always a whole number, never zero.)

Condition: if one of the two reactants is present in large excess (e.g. water in hydrolysis of an ester), its concentration stays almost constant, so the rate depends only on the other reactant → pseudo first-order reaction.

Example: $CH_3COOC_2H_5 + H_2O$ (excess) → $CH_3COOH + C_2H_5OH$, rate = k'[ester].

19. What is formed when D-glucose is treated with: **2**

(a) HI (prolonged heating)

(b) conc. HNO_3

ANSWER

(a) n-hexane (b) saccharic (glucaric) acid

(a) On prolonged heating with HI, all –OH groups and the –CHO are reduced: glucose → $CH_3(CH_2)_4CH_3$ (n-hexane). This shows the six carbons are in a straight chain.

(b) Conc. HNO_3 oxidises both the –CHO and the primary $–CH_2OH$ groups to –COOH: glucose → HOOC–$(CHOH)_4$–COOH (saccharic acid). This shows glucose has a primary alcohol group.

20. Draw the major monohalo product in each reaction: **2**

(i) Styrene (C_6H_5–CH=CH_2) + HBr →

(ii) Cyclohexene + Br_2 in UV light →

ANSWER

(i) C_6H_5–CH(Br)–CH_3 (ii) 3-bromocyclohexene

(i) Electrophilic addition, Markovnikov's rule: H^+ adds to the terminal CH_2, giving the resonance-stabilised benzylic carbocation C_6H_5–C^+H–CH_3; Br^- then attacks it → (1-bromoethyl)benzene, $C_6H_5CH(Br)CH_3$.

(ii) In UV light Br_2 forms Br• radicals; at low Br_2 concentration substitution occurs at the allylic position (the allylic radical is resonance-stabilised) → 3-bromocyclohexene (Br on the carbon next to C=C, double bond kept).

OR

Give reasons:

(i) Grignard reagents must be prepared in anhydrous conditions.

(ii) With aqueous KOH alkyl halides give alcohols, but with alcoholic KOH they give alkenes.

ANSWER

(i) RMgX reacts with water to give alkane (ii) aqueous OH^- acts as nucleophile (substitution); alcoholic RO^-/OH^- acts as strong base (elimination)

(i) Grignard reagents are very reactive; any moisture protonates them: RMgX + H_2O → RH + Mg(OH)X. The reagent is destroyed, so dry ether and dry apparatus are used.

(ii) In water, OH^- is strongly solvated and acts mainly as a nucleophile → substitution: R–X + OH^- → R–OH.

In alcohol, alkoxide ions (RO^-) are formed; they are stronger bases and remove a β-hydrogen → β-elimination (dehydrohalogenation) to an alkene.

21. Write the chemical equation when: **2**

(a) butan-2-one is treated with Zn(Hg) and conc. HCl

(b) two molecules of benzaldehyde are treated with conc. NaOH

ANSWER

(a) Butane (Clemmensen) (b) Benzyl alcohol + sodium benzoate (Cannizzaro)

(a) Clemmensen reduction converts C=O into CH_2:

$CH_3COCH_2CH_3$ + 4[H] → (Zn-Hg, conc. HCl) → $CH_3CH_2CH_2CH_3$ + H_2O.

(b) Cannizzaro reaction (benzaldehyde has no α-H): one molecule is oxidised, the other reduced:

2 C_6H_5CHO + conc. NaOH → $C_6H_5CH_2OH$ + C_6H_5COONa.

SECTION C

Q22–28 are short answer questions of 3 marks each.

22. A conductivity cell filled with 0.05 M KCl shows a resistance of 100 Ω at 25 °C. The same cell filled with 0.02 M $AgNO_3$ shows 90 Ω. Find the conductivity and molar conductivity of the $AgNO_3$ solution. **3**

(Conductivity of 0.05 M KCl = $1.35 \times 10^{-2}\ \Omega^{-1}\ cm^{-1}$)

ANSWER

$\kappa = 0.015\ S\ cm^{-1}$; $\Lambda m = 750\ S\ cm^2\ mol^{-1}$

Step 1 – cell constant: $G^* = \kappa \times R = 1.35 \times 10^{-2} \times 100 = 1.35\ cm^{-1}$.

Step 2 – conductivity of $AgNO_3$: $\kappa = G^*/R = 1.35/90 = 0.015\ S\ cm^{-1}$.

Step 3 – molar conductivity: $\Lambda_m = \frac{\kappa \times 1000}{C} = \frac{0.015 \times 1000}{0.02} = 750\ S\ cm^2\ mol^{-1}$.

Keep the units: marks are cut for missing/wrong units.

23. For $2NO(g) + Br_2(g) \rightarrow 2NOBr(g)$, the initial rates measured were: **3**

Expt 1: [NO] = 0.05, $[Br_2]$ = 0.05 mol L^{-1}, rate = 1.0×10^{-3} mol $L^{-1}\ s^{-1}$

Expt 2: [NO] = 0.05, $[Br_2]$ = 0.15, rate = 3.0×10^{-3}

Expt 3: [NO] = 0.15, $[Br_2]$ = 0.05, rate = 9.0×10^{-3}

(a) Find the order with respect to NO and Br_2.

(b) Find the rate constant k.

(c) Find the rate when [NO] = 0.4 M and $[Br_2]$ = 0.2 M.

ANSWER

(a) 2 in NO, 1 in Br_2 (b) $k = 8\ L^2\ mol^{-2}\ s^{-1}$ (c) 0.256 mol $L^{-1}\ s^{-1}$

Let rate = $k[NO]^p[Br_2]^q$.

(a) Expt 2 ÷ Expt 1: $[Br_2]$ tripled, rate tripled → $3 = 3^q$ → q = 1.

Expt 3 ÷ Expt 1: [NO] tripled, rate ×9 → $9 = 3^p$ → p = 2.

Rate = $k[NO]^2[Br_2]$ (overall order 3).

(b) From Expt 1: $k = 1.0 \times 10^{-3} / (0.05^2 \times 0.05) = 1.0 \times 10^{-3} / 1.25 \times 10^{-4} = 8\ L^2\ mol^{-2}\ s^{-1}$.

(c) Rate = $8 \times (0.4)^2 \times 0.2 = 8 \times 0.16 \times 0.2 = 0.256$ mol $L^{-1}\ s^{-1}$ (2.56×10^{-1}).

24. (a) Write the formula of potassium tetrahydroxidozincate(II). **3**

(b) Put these in increasing order of conductivity of their solutions: $[Cr(NH_3)_5Cl]Cl_2$, $[Cr(NH_3)_3Cl_3]$, $[Cr(NH_3)_6]Cl_3$

(c) Name the isomerism shown by: (i) $[Co(NH_3)_5NO_2]^{2+}$ (ii) $[Co(en)_3]Cl_3$

ANSWER

(a) $K_2[Zn(OH)_4]$ (b) $[Cr(NH_3)_3Cl_3] < [Cr(NH_3)_5Cl]Cl_2 < [Cr(NH_3)_6]Cl_3$ (c) (i) linkage (ii) optical

(a) $Zn^{2+} + 4\ OH^-$ gives charge -2 on the complex, so two K^+: $K_2[Zn(OH)_4]$.

(b) Conductivity depends on the number of ions produced:

$[Cr(NH_3)_3Cl_3] \rightarrow$ 0 ions (non-electrolyte);

$[Cr(NH_3)_5Cl]Cl_2 \rightarrow$ 3 ions;

$[Cr(NH_3)_6]Cl_3 \rightarrow$ 4 ions.

Order: $[Cr(NH_3)_3Cl_3] < [Cr(NH_3)_5Cl]Cl_2 < [Cr(NH_3)_6]Cl_3$.

(c)(i) NO_2^- is ambidentate (binds through N as nitrito-N or through O as nitrito-O) → linkage isomerism.

(ii) $[Co(en)_3]^{3+}$ is an octahedral complex with three didentate ligands; it has no plane of symmetry and exists as d and l forms → optical isomerism.

25. (a) Which one is an allylic halide: (i) $CH_3–CH=CH–Br$ or (ii) $CH_2=CH–CH(Br)–CH_3$? **3**

(b) Which is more reactive towards nucleophilic substitution – chlorobenzene or 2,4,6-trinitrochlorobenzene – and why?

(c) Which isomer of C_4H_9Cl has the lowest boiling point?

ANSWER

(a) (ii) (b) 2,4,6-trinitrochlorobenzene (c) 2-chloro-2-methylpropane (tert-butyl chloride)

(a) In an allylic halide the halogen is on the sp^3 carbon next to C=C. In (ii) Br is on C-3, adjacent to the double bond → allylic. In (i) Br is on the sp^2 carbon itself → vinylic.

(b) 2,4,6-Trinitrochlorobenzene. The three $–NO_2$ groups at ortho and para positions withdraw electrons, making the ring carbon electron-poor and stabilising the negatively charged intermediate (Meisenheimer complex) by resonance. Chlorobenzene has no such help.

(c) $(CH_3)_3C–Cl$. Among isomers, more branching → more spherical shape → smaller surface area → weaker van der Waals forces → lowest boiling point.

26. (a) Write the mechanism of: $CH_3CH_2OH \rightarrow (H^+, 443\ K) \rightarrow CH_2=CH_2$ **3**

(b) Write the main product:

(i) $CH_3–CH_2–CH=CH_2$ treated with (a) B_2H_6 and then (b) H_2O_2/OH^-

(ii) Phenol treated with (a) aq. NaOH and then (b) CO_2, H^+

ANSWER

(a) Protonation → carbocation → loss of H^+ (b)(i) Butan-1-ol (ii) Salicylic acid (2-hydroxybenzoic acid)

(a) Step 1 – protonation of alcohol (fast): $CH_3CH_2–OH + H^+ \rightleftharpoons CH_3CH_2–OH_2^+$.
Step 2 – loss of water (slow, rate-determining): $CH_3CH_2–OH_2^+ \rightarrow CH_3CH_2^+ + H_2O$.
Step 3 – loss of a β-proton: $CH_3CH_2^+ \rightarrow CH_2=CH_2 + H^+$.
(b)(i) Hydroboration–oxidation adds water in an anti-Markovnikov way: $CH_3CH_2CH_2CH_2OH$ (butan-1-ol).
(ii) Kolbe's reaction: phenol → sodium phenoxide; phenoxide + CO_2 → sodium salicylate; acidification → o-hydroxybenzoic acid (salicylic acid).

27. Answer any three: **3**

(a) What is a peptide linkage?

(b) What bonds hold the two strands of the DNA double helix together?

(c) Which of these is a polysaccharide: sucrose, glucose, starch, fructose?

(d) Give one example each of a water-soluble and a fat-soluble vitamin.

ANSWER

(a) –CO–NH– amide bond between amino acids (b) Hydrogen bonds (c) Starch (d) Vitamin C (or B); Vitamin A (or D, E, K)

(a) The amide bond –CO–NH– formed when the –COOH of one amino acid reacts with the $–NH_2$ of another, with loss of water.
(b) Hydrogen bonds between complementary base pairs (A=T two H-bonds, G≡C three H-bonds).
(c) Starch – a polymer of α-D-glucose. Sucrose is a disaccharide; glucose and fructose are monosaccharides.
(d) Water-soluble: vitamin B group or C. Fat-soluble: vitamin A, D, E or K.

28. Compound A ($C_6H_{12}O_2$) is reduced by $LiAlH_4$ to two compounds B and C. Oxidation of B with PCC gives D. D with dilute NaOH followed by heating gives E. Catalytic hydrogenation of E gives C. Further oxidation of D gives F, a monobasic acid of molar mass 60. Identify A to F. **3**

ANSWER

A = ethyl butanoate ($CH_3CH_2CH_2COOC_2H_5$); B = ethanol; C = butan-1-ol; D = ethanal; E = but-2-enal; F = ethanoic acid

F is a monobasic acid of molar mass 60 → CH_3COOH. So D (oxidised to F) is CH_3CHO and B (oxidised by PCC to D) is CH_3CH_2OH.

D + dil. NaOH → aldol $CH_3CH(OH)CH_2CHO$; on heating it loses water → E = $CH_3CH{=}CHCHO$ (but-2-enal, crotonaldehyde).

E + H_2/catalyst (both C=C and C=O reduced) → C = $CH_3CH_2CH_2CH_2OH$ (butan-1-ol).

An ester giving ethanol and butan-1-ol with $LiAlH_4$ must be ethyl butanoate: $CH_3CH_2CH_2COOCH_2CH_3$ → $CH_3CH_2CH_2CH_2OH$ + CH_3CH_2OH. Check: $C_6H_{12}O_2$ ✓.

(Butyl ethanoate, $CH_3COOC_4H_9$, would also give the same two alcohols and is accepted.)

SECTION D

Q29–30 are case-based questions of 4 marks each (choice in part (c)).

29. Batteries and fuel cells are practical galvanic cells. A useful battery must be light, compact and give a nearly constant voltage. Primary batteries work only once, while secondary batteries can be recharged. Fuel cells convert the energy of combustion of a fuel directly into electricity (one was used in the Apollo space programme). **4**

(a) How do primary batteries differ from secondary batteries? (1)

(b) A mercury cell gives 1.35 V that stays constant throughout its life. Why? (1)

(c) Write the reactions that take place when a lead storage battery is recharged. (2)

ANSWER

(a) Primary – not rechargeable; secondary – rechargeable (b) Overall reaction has no ions in solution whose concentration changes (c) $2PbSO_4 + 2H_2O \rightarrow Pb + PbO_2 + 2H_2SO_4$

(a) In a primary battery the reaction occurs only once and the cell cannot be reused (e.g. dry cell, mercury cell). A secondary battery can be recharged by passing current in the opposite direction and reused many times (e.g. lead storage battery).

(b) Overall reaction: $Zn(Hg) + HgO(s) \rightarrow ZnO(s) + Hg(l)$. It involves no ion in solution whose concentration changes during use, so by the Nernst equation the cell potential stays constant.

(c) During charging the cell works as an electrolytic cell and the discharge reaction is reversed:

At the electrode that becomes Pb: $PbSO_4(s) + 2e^- \rightarrow Pb(s) + SO_4^{2-}(aq)$

At the electrode that becomes PbO_2: $PbSO_4(s) + 2H_2O(l) \rightarrow PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^-$

Overall: $2PbSO_4(s) + 2H_2O(l) \rightarrow Pb(s) + PbO_2(s) + 2H_2SO_4(aq)$.

OR

(c) Write two advantages of fuel cells over other galvanic cells.

ANSWER

High efficiency (~70%) and pollution-free

1. High efficiency – fuel cells convert chemical energy directly into electricity with about 70% efficiency, compared with about 40% for thermal power plants.
2. Pollution-free – an H_2–O_2 fuel cell gives only water as product.

(Also: fuel is supplied continuously, so the cell does not run down like a battery.)

30. Valence bond theory explains formation, magnetism and shape of complexes, while crystal field theory looks at how ligands (taken as point charges) split the degenerate d-orbitals of the metal. The splitting gives different electron arrangements in strong and weak fields, and d–d transitions explain the colour of complexes. Complexes are used in metallurgy, analysis and medicine. **4**

(a) What is crystal field splitting energy? (1)

(b) Explain the violet colour of $[Ti(H_2O)_6]^{3+}$ using crystal field theory. (1)

(c) Explain why $[Cr(NH_3)_6]^{3+}$ is paramagnetic but $[Ni(CN)_4]^{2-}$ is diamagnetic. [Cr = 24, Ni = 28] (2)

ANSWER

(a) Energy gap between split d-levels (Δ) (b) d^1 electron $t_2g \rightarrow e_g$ absorbs yellow-green light, violet seen (c) Cr^{3+} t_2g^3 has 3 unpaired e^-; Ni^{2+} d^8 paired by strong-field CN^- (dsp^2)

(a) When ligands approach in a definite geometry, the five degenerate d-orbitals split into sets of different energy; the energy difference between these sets is the crystal field splitting energy (Δ_o for octahedral).

(b) Ti^{3+} is $3d^1 \rightarrow t_2g^1e_g^0$. The electron absorbs visible light (around 498 nm, green-yellow) and jumps from t_2g to e_g (d–d transition). The complementary colour, violet, is seen.

(c) Cr^{3+}: $3d^3 \rightarrow t_2g^3$ (d^2sp^3). Three unpaired electrons → paramagnetic.

Ni^{2+}: $3d^8$. CN^- is a strong-field ligand; it pairs the electrons so that one 3d orbital is empty → dsp^2 square planar; no unpaired electrons → diamagnetic.

OR

(c) Explain why $[Fe(CN)_6]^{3-}$ is an inner orbital complex while $[Fe(H_2O)_6]^{3+}$ is an outer orbital complex. [Fe = 26]

ANSWER

CN^- (strong) pairs Fe^{3+} electrons → d^2sp^3 (inner); H_2O (weak) does not → sp^3d^2 (outer)

$Fe^{3+} = 3d^5$.

$[Fe(CN)_6]^{3-}$: CN^- is a strong-field ligand; it forces pairing, leaving two 3d orbitals empty (t_2g^5, 1 unpaired e^-). These inner (n−1)d orbitals are used → d^2sp^3 hybridisation → inner orbital (low-spin) complex.

$[Fe(H_2O)_6]^{3+}$: H_2O is a weak-field ligand; no pairing occurs (5 unpaired e^-), so the outer 4d orbitals are used → sp^3d^2 hybridisation → outer orbital (high-spin) complex.

SECTION E

Q31–33 are long answer questions of 5 marks each.

31. (i) At the same temperature CO_2 is more soluble in water than O_2. Which gas has the higher Henry's constant K_H, and why? **5**

(ii) What happens to the size of red blood cells placed in an aqueous solution containing more than 0.9% (mass/volume) NaCl?

(iii) A 1 molal aqueous solution of electrolyte A_2B_3 is 60% ionised. Find the boiling point of the solution. (K_b of water = 0.52 K kg mol^{-1})

ANSWER

(i) O_2 (higher K_H = lower solubility) (ii) Cells shrink (iii) T_b = 374.768 K (≈ 101.77 °C)

(i) Henry's law: p = K_H·x, so for a given pressure, solubility x ∝ 1/K_H. O_2 is less soluble, so O_2 has the higher K_H.

(ii) The solution is hypertonic; water moves out of the cells by osmosis and the cells shrink (crenation).

(iii) $A_2B_3 \rightarrow 2A^{3+} + 3B^{2-}$, so n = 5 ions.

$\alpha = (i - 1)/(n - 1) \rightarrow 0.6 = (i - 1)/4 \rightarrow i = 3.4$.

$\Delta T_b = i \cdot K_b \cdot m = 3.4 \times 0.52 \times 1 = 1.768$ K.

T_b = 373 + 1.768 = 374.768 K (using 373.15 K gives 374.918 K).

OR

(i) At 25 °C the vapour pressures of pure A and B are 75 mm Hg and 25 mm Hg. A and B are mixed so that the mole fraction of A in the liquid is 0.4. Find the mole fraction of B in the vapour.

(ii) Define a colligative property. Which colligative property is preferred for finding the molar mass of macromolecules?

(iii) Why are equimolar solutions of NaCl and glucose not isotonic?

ANSWER

(i) y_B = 1/3 ≈ 0.33 (ii) Depends only on number of solute particles; osmotic pressure (iii) NaCl dissociates (i = 2), glucose does not

(i) x_A = 0.4, x_B = 0.6.

p_A = 75 × 0.4 = 30 mm Hg; p_B = 25 × 0.6 = 15 mm Hg; P_total = 45 mm Hg.

y_B = p_B/P_total = 15/45 = 1/3 ≈ 0.33 (a mole fraction has no unit).

(ii) A colligative property depends only on the number of solute particles in a given amount of solvent, not on their nature. Osmotic pressure is preferred for macromolecules: it is measured at room temperature (proteins not damaged) and gives a measurable value even for very dilute solutions, using molarity instead of molality.

(iii) $\pi = iCRT$. $NaCl \rightarrow Na^+ + Cl^-$ (i ≈ 2) while glucose does not dissociate (i = 1). So at equal concentration NaCl gives about twice the osmotic pressure; they are not isotonic.

32. Answer any five: **5**

(a) Why is N,N-diethylbenzenesulphonamide insoluble in alkali?

(b) Why does aniline not undergo Friedel-Crafts reaction?

(c) Give a simple chemical test to tell methylamine from aniline.

(d) Write the reaction(s) of Gabriel phthalimide synthesis.

(e) How will you convert aniline into p-bromoaniline?

(f) Complete: benzenediazonium chloride treated with (i) HBF_4, then (ii) $NaNO_2$/Cu, heat →

(g) Benzoic acid is heated with NH_3 to give A; A with Br_2 + NaOH gives B. Write A and B.

ANSWER

(a) No H on N (b) Forms salt with $AlCl_3$ (c) Azo-dye test: aniline gives orange dye (d) Phthalimide → K-salt → N-alkyl → RNH_2 (e) Acetylate, brominate, hydrolyse (f) Nitrobenzene (g) A = benzamide, B = aniline

(a) In $C_6H_5SO_2N(C_2H_5)_2$ the nitrogen carries no hydrogen, so there is no acidic N–H to react with alkali; hence it is insoluble (basis of Hinsberg test for 3° amines' product from 2° amines).
(b) Aniline is a Lewis base and forms a salt with the Lewis acid catalyst $AlCl_3$. The N becomes positively charged, strongly deactivating the ring, so the reaction fails.
(c) Azo-dye test: with HNO_2 ($NaNO_2$ + HCl) at 273–278 K aniline gives benzenediazonium chloride, which couples with alkaline β-naphthol to give an orange-red dye. Methylamine gives an unstable aliphatic diazonium salt that releases N_2 and gives no dye.
(d) Phthalimide + ethanolic KOH → potassium phthalimide; + R–X → N-alkylphthalimide; alkaline hydrolysis (NaOH) → R–NH_2 + sodium phthalate.
(e) $C_6H_5NH_2$ + $(CH_3CO)_2O$ (pyridine) → $C_6H_5NHCOCH_3$ (acetanilide, activation reduced); + Br_2/CH_3COOH → p-bromoacetanilide; hydrolysis (H^+ or OH^-) → p-bromoaniline. Direct bromination would give 2,4,6-tribromoaniline.
(f) $C_6H_5N_2^+Cl^-$ + HBF_4 → $C_6H_5N_2^+BF_4^-$; this with $NaNO_2$/Cu, heat → $C_6H_5NO_2$ (nitrobenzene) + N_2 + $NaBF_4$.
(g) C_6H_5COOH + NH_3 → (heat) $C_6H_5CONH_2$ (A, benzamide); Hoffmann bromamide degradation: $C_6H_5CONH_2$ + Br_2 + 4NaOH → $C_6H_5NH_2$ (B, aniline) + Na_2CO_3 + 2NaBr + $2H_2O$.

33. (i) Account for: **5**

(1) Zn, Cd and Hg have low melting and boiling points.

(2) Both are d^4 species, yet Cr^{2+} is a strong reducing agent while Mn^{3+} is a strong oxidising agent.

(3) E° for Cu^{2+}/Cu is +0.34 V (positive).

(ii) Complete and balance:

(1) $KMnO_4 \rightarrow$ (heat)

(2) $Cr_2O_7^{2-} + 6I^- + 14H^+ \rightarrow$

ANSWER

(i) (1) No unpaired d-electrons → weak metallic bonding (2) Cr^{3+} (t_2g^3) and Mn^{2+} (d^5) are stable (3) High Δ_aH not balanced by ΔhydH (ii) $2KMnO_4 \rightarrow K_2MnO_4 + MnO_2 + O_2$; $Cr_2O_7^{2-} + 6I^- + 14H^+ \rightarrow 2Cr^{3+} + 3I_2 + 7H_2O$

(i)(1) Zn, Cd, Hg have completely filled d-orbitals (d^{10}) – no unpaired d-electrons to take part in metallic bonding – so bonding is weak and m.p./b.p. are low.

(2) Cr^{2+} (d^4) loses an electron to become Cr^{3+} (d^3, stable half-filled t_2g^3) → good reducing agent. Mn^{3+} (d^4) gains an electron to become Mn^{2+} (d^5, stable half-filled) → good oxidising agent.

(3) For Cu, the energy needed (high enthalpy of atomisation + first and second ionisation enthalpies) is not compensated by its hydration enthalpy, so $Cu \rightarrow Cu^{2+}$ is unfavourable and E° is positive.

(ii)(1) $2KMnO_4 \rightarrow$ (513 K) $K_2MnO_4 + MnO_2 + O_2$.

(2) $Cr_2O_7^{2-} + 6I^- + 14H^+ \rightarrow 2Cr^{3+} + 3I_2 + 7H_2O$ (check: charge $-2 -6 +14 = +6 = 2 \times 3$; O 7 = 7).

OR

(i) Which is more stable in aqueous solution, Cu_2Cl_2 or $CuCl_2$, and why?

(ii) Write the general electronic configuration of f-block elements.

(iii) Which of Sc^{3+}, Fe^{3+}, Zn^{2+} is coloured in aqueous solution, and why? [Sc = 21, Fe = 26, Zn = 30]

(iv) How is potassium dichromate obtained from sodium chromate?

(v) Why do transition metals and their compounds act as catalysts?

ANSWER

(i) $CuCl_2$ (ii) $(n-2)f^{1-14}(n-1)d^{0-1}ns^2$ (iii) Fe^{3+} (iv) Acidify to $Na_2Cr_2O_7$, then add KCl (v) Variable oxidation states, complex formation, large surface area

(i) $CuCl_2$. $Cu^{2+}(aq)$ has a much more negative hydration enthalpy, which more than compensates for the second ionisation enthalpy. Cu^+ in water disproportionates: $2Cu^+ \rightarrow Cu^{2+} + Cu$.

(ii) $(n-2)f^{1-14}$ $(n-1)d^{0-1}$ ns^2.

(iii) Fe^{3+} ($3d^5$) has unpaired electrons and shows d–d transitions → coloured. Sc^{3+} ($3d^0$) and Zn^{2+} ($3d^{10}$) cannot have d–d transitions → colourless.

(iv) Acidify: $2Na_2CrO_4 + 2H^+ \rightarrow Na_2Cr_2O_7 + 2Na^+ + H_2O$.

Then add KCl: $Na_2Cr_2O_7 + 2KCl \rightarrow K_2Cr_2O_7 + 2NaCl$ ($K_2Cr_2O_7$ is less soluble and crystallises out).

(v) They can show variable oxidation states (forming unstable intermediates), form complexes with reactants, and provide a large surface area for adsorption of reactants.

— END —

Questions restated from the CBSE Class XII Board Examination 2024 (set 56/1/1) for practice. Reading passages and map items are described, not reproduced.