CBSE Class 12 Chemistry: Sample Paper 1: Marking Scheme and Solutions

Based on NCERT · the board's 2026-27 pattern | Time: 3 hours · **Maximum marks: 70**

Section A (16 × 1 mark)

1. Which statement about order and molecularity is correct? [1]

(a) Molecularity is found by measuring the rate at different concentrations.
(b) Molecularity can be zero for a reaction on a metal surface.
(c) Order has meaning only for elementary reactions.
(d) Order can be zero or a fraction, but molecularity cannot.

Answer: (d) Order is an experimental quantity and may be zero or fractional; molecularity counts colliding species in an elementary step, so it is a whole number and has no meaning for a complex reaction.

2. Given E°/V: $Na^+|Na$ −2.71, $Mg^{2+}|Mg$ −2.36, $Al^{3+}|Al$ −1.66, $Zn^{2+}|Zn$ −0.76. The strongest reducing agent among the four metals in aqueous solution is [1]

(a) Zn
(b) Na
(c) Mg
(d) Al

Answer: (b) The lower the standard electrode potential, the stronger the metal as a reducing agent; sodium has the lowest E° of the four.

3. Which of the following isomers of $C_5H_{13}N$ has the highest boiling point? [1]

(a) N,N-dimethylpropan-1-amine
(b) N-methylbutan-1-amine
(c) pentan-1-amine
(d) N-ethyl-N-methylethanamine

Answer: (c) Primary amines have two N–H hydrogens for hydrogen bonding and associate most; secondary amines have one; tertiary amines, (a) and (d), have none. So the boiling point order of isomers is 1° > 2° > 3°.

4. How many structurally different monochloro products can form when 2,3-dimethylbutane, $(CH_3)_2CH–CH(CH_3)_2$, undergoes free radical chlorination? [1]

(a) 1
(b) 2
(c) 3
(d) 4

Answer: (b) The molecule is symmetrical: all twelve CH_3 hydrogens are equivalent and the two CH hydrogens are equivalent. Two types of hydrogen give two monochlorides: $ClCH_2CH(CH_3)CH(CH_3)_2$ and $(CH_3)_2CClCH(CH_3)_2$.

5. 2.8 g of KOH (56 g mol^{-1}) is dissolved in water and the solution is made up to 250 mL. Its molarity is [1]

(a) 0.0112 M
(b) 0.050 M
(c) 0.20 M
(d) 2.0 M

Answer: (c) Moles of KOH = 2.8/56 = 0.050 mol; volume = 0.250 L; M = 0.050/0.250 = 0.20 M. 0.050 M forgets the volume; 0.0112 divides grams by millilitres.

6. Which carbon–halogen bond has the lowest bond enthalpy? [1]

(a) $CH_3–F$ (b) $CH_3–Cl$

(c) $CH_3–Br$ (d) $CH_3–I$

Answer: (d) Down the group the halogen grows and the C–X bond lengthens, from 139 pm (C–F) to 214 pm (C–I); the bond enthalpy falls accordingly, 452, 351, 293 and 234 kJ mol^{-1}. $CH_3–I$ has the longest bond and the lowest enthalpy.

7. 2-Methylpent-2-ene, $(CH_3)_2C=CH–CH_2CH_3$, is treated with ozone and then with zinc dust and water. The products are [1]

(a) propanone and propanoic acid (b) ethanal and butan-2-one

(c) two molecules of propanal (d) propanone and propanal

Answer: (d) Ozonolysis cleaves the C=C and puts C=O on each carbon: $(CH_3)_2C=$ gives $(CH_3)_2C=O$, propanone; $=CH–CH_2CH_3$ gives $OHC–CH_2CH_3$, propanal. Zinc dust prevents oxidation of the aldehyde to the acid.

8. The coordination number of cobalt in $[Co(en)_2(NO_2)Cl]^+$ is [1]

(a) 4 (b) 6

(c) 5 (d) 3

Answer: (b) Each en is didentate and gives two donor N atoms (2 × 2 = 4); NO_2^- and Cl^- give one each: 4 + 1 + 1 = 6. Counting ligands instead of donor atoms gives 4.

9. 1-Bromobutane is heated in a sealed tube at 373 K with a large excess of ethanolic ammonia, and the salt is then treated with NaOH. The amine obtained as the major product is [1]

(a) tetrabutylammonium hydroxide (b) N-butylbutan-1-amine

(c) N,N-dibutylbutan-1-amine (d) butan-1-amine

Answer: (d) Ammonolysis can run on to 2°, 3° amines and the quaternary salt, because each amine formed is itself a nucleophile; a large excess of ammonia makes it far more likely that the halide meets NH_3, so the primary amine is the major product.

10. Which of the following dissolves readily in benzene but hardly at all in water? [1]

(a) sodium chloride (b) anthracene

(c) sugar (d) potassium chloride

Answer: (b) Like dissolves like: non-polar anthracene dissolves in non-polar benzene. NaCl, KCl and sugar are polar or ionic and dissolve in water, not benzene.

11. An aqueous solution of a salt of which of the following ions is pink? [1]

(a) Ni^{2+} (b) Cr^{3+}

(c) Mn^{2+} (d) Cu^{2+}

Answer: (c) Aquated Mn^{2+} is pink; Ni^{2+} is green, Cr^{3+} violet and Cu^{2+} blue.

12. Which of the following is a tertiary alcohol? [1]

(a) $(CH_3)_2CH–CH_2–OH$ (b) $CH_3–CH_2–C(CH_3)(OH)–CH_2–CH_3$

(c) $CH_3–CH(OH)–CH(CH_3)_2$ (d) $C_6H_5–CH_2–CH_2–OH$

Answer: (b) In $CH_3CH_2C(CH_3)(OH)CH_2CH_3$ the –OH is on a carbon bonded to three other carbons: tertiary. (a) and (d) have –OH on a $–CH_2–$ carbon (primary); in (c) the –OH carbon carries one hydrogen and two carbons (secondary).

13. Assertion (A): 1-Chloro-3-nitrobenzene is converted to 3-nitrophenol by aqueous NaOH only under conditions about as severe as those for chlorobenzene. Reason (R): A nitro group at the meta position cannot take up, by resonance, the negative charge that develops on the ring when OH^- attacks the carbon carrying chlorine. [1]

(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) Attack of OH^- puts the negative charge on the carbons ortho and para to the site of attack. A nitro group placed there withdraws and stabilises it; at meta it sits on a carbon that never carries the charge, so it has no activating effect. Both are true and R explains A.

14. Assertion (A): The metal–carbon bond in $[Cr(CO)_6]$ has both σ and π character. Reason (R): Carbon of CO donates a lone pair into a vacant metal orbital, while the metal donates a filled d pair into the vacant antibonding π* orbital of CO. [1]

(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 are true. The lone-pair donation is the σ part of the M–C bond and the metal-to-π* donation the π part, so R explains A; the two reinforce each other (synergic bonding).

15. Assertion (A): Potassium dichromate is used as a primary standard in volumetric analysis. Reason (R): The chromate ion is tetrahedral. [1]

(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 statements are true, but the shape of the chromate ion has nothing to do with $K_2Cr_2O_7$'s use as a primary standard, which rests on its being a strong oxidant obtained as a pure, weighable crystalline salt.

16. Assertion (A): Aniline reacts with bromine water at room temperature to give a white precipitate of 2,4,6-tribromoaniline. Reason (R): The $-NH_2$ group is a powerful activating group that makes the ortho and para positions centres of high electron density. [1]

(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, and R explains A: the strongly activating $-NH_2$ makes all three ortho and para positions react with bromine without a catalyst.

Section B (5 × 2 marks)

17. A 2.0 kg sample of water from a hill stream contains 16 mg of dissolved oxygen. Express this concentration in ppm by mass, and state why ppm is used here rather than mass percentage. [2]

ppm = (mass of O_2 / mass of solution) × 10^6 = (0.016 g / 2000 g) × 10^6 = 8.0 ppm. The solute is present in trace quantity; as a percentage it would be an awkward 0.0008%.

- 8.0 ppm with working (1)
- ppm is used for a solute in trace quantity (1)

18. Carnallite, $KCl{\cdot}MgCl_2{\cdot}6H_2O$, and $K_4[Fe(CN)_6]$ each contain two simple salts combined in a fixed ratio. Classify each as a double salt or a coordination compound, and name the ions each gives in aqueous solution. [2]

Carnallite is a double salt: in water it dissociates completely into K^+, Mg^{2+} and Cl^-. $K_4[Fe(CN)_6]$ is a coordination compound: it gives K^+ and the complex ion $[Fe(CN)_6]^{4-}$, which stays intact, so no free Fe^{2+} or CN^- is present.

- carnallite a double salt, giving K^+, Mg^{2+} and Cl^- (1)
- $K_4[Fe(CN)_6]$ a coordination compound, giving only K^+ and $[Fe(CN)_6]^{4-}$ (no free Fe^{2+} or CN^-) (1)

19. Write the two steps by which 1-phenylethan-1-one, $C_6H_5COCH_3$, is converted to ethylbenzene by the Wolff–Kishner reduction. [2]

Or *Write the equation for the conversion of butan-2-one into butane by the Clemmensen reduction, giving the reagents.*

Step 1: $C_6H_5COCH_3 + NH_2NH_2 \rightarrow C_6H_5C(CH_3)=N{-}NH_2 + H_2O$ (the hydrazone). Step 2: $C_6H_5C(CH_3)=N{-}NH_2 \rightarrow C_6H_5CH_2CH_3 + N_2$ on heating with KOH in ethylene glycol.

- hydrazone formation with NH_2NH_2 (1)
- heating with KOH in ethylene glycol gives $C_6H_5CH_2CH_3$ and N_2 (1)

Or:

$CH_3COCH_2CH_3 + 4[H] \rightarrow CH_3CH_2CH_2CH_3 + H_2O$, with zinc amalgam and concentrated hydrochloric acid; the C=O becomes CH_2.

- reagents Zn–Hg and conc. HCl (1)
- correct equation: butanone to butane and water (1)

20. Write the equation for the manufacture of methanol today, with the catalyst and conditions, and state the main use of methanol. [2]

$CO + 2H_2 \rightarrow CH_3OH$, over $ZnO{-}Cr_2O_3$ at 200–300 atm and 573–673 K (catalytic hydrogenation of carbon monoxide). Methanol is used chiefly to make formaldehyde; it is also a solvent for paints and varnishes.

- equation with $ZnO{-}Cr_2O_3$ and high pressure and temperature (1)
- chief use: formaldehyde (1)

21. A first order reaction has $k = 6.93 \times 10^{-3}$ min^{-1}. How long will it take for 87.5% of the reactant to be used up? [2]

$t_{1/2} = 0.693/k = 0.693/(6.93 \times 10^{-3}) = 100$ min. 87.5% used means 12.5% = ⅛ remains: three half-lives. $t = 3 \times 100 = 300$ min.

- $t_{1/2} = 100$ min (1)
- ⅛ remaining is three half-lives, 300 min (1)

Section C (7 × 3 marks)

22. Ethyl ethanoate can be made from ethanol (i) with ethanoic acid and a little concentrated H_2SO_4, or (ii) with ethanoyl chloride in pyridine. Write both equations. Why is water removed as it forms in (i), and what is the role of pyridine in (ii)? [3]

(i) $C_2H_5OH + CH_3COOH \rightleftharpoons CH_3COOC_2H_5 + H_2O$ (H^+). (ii) $C_2H_5OH + CH_3COCl \rightarrow CH_3COOC_2H_5 + HCl$ (pyridine). Reaction (i) is reversible, so removing water shifts the equilibrium towards the ester. In (ii) pyridine, a base, neutralises the HCl formed and so shifts the equilibrium to the right.

- both equations (1)
- (i) reversible; removing water drives it forward (1)
- (ii) pyridine neutralises HCl (1)

23. A student sets up the cell Zn(s) | Zn^{2+}(0.10 M) || Ni^{2+}(aq) | Ni(s) and reads its emf at 298 K as 0.451 V. Write the cell reaction and the Nernst equation for the cell, and find the concentration of Ni^{2+} in the cathode compartment. Given $E°(Zn^{2+}|Zn) = -0.76$ V, $E°(Ni^{2+}|Ni) = -0.25$ V, 2.303RT/F = 0.059 V. [3]

Or *A student sets up the cell Fe(s) | Fe^{2+}(0.0010 M) || Cu^{2+}(aq) | Cu(s) and reads its emf at 298 K as 0.839 V. Write the cell reaction and the Nernst equation for the cell, and find the concentration of Cu^{2+} in the cathode compartment. Given $E°(Fe^{2+}|Fe) = -0.44$ V, $E°(Cu^{2+}|Cu) = 0.34$ V, 2.303RT/F = 0.059 V.*

Zn(s) + Ni^{2+}(aq) → Zn^{2+}(aq) + Ni(s), n = 2. $E°cell = -0.25 - (-0.76) = 0.51$ V. $Ecell = E°cell - (0.059/2)\log([Zn^{2+}]/[Ni^{2+}])$, so $0.451 = 0.51 - 0.0295\log(0.10/[Ni^{2+}])$; $\log(0.10/[Ni^{2+}]) = 0.059/0.0295 = 2$, so $0.10/[Ni^{2+}] = 100$ and $[Ni^{2+}] = 1.0 \times 10^{-3}$ M.

- cell reaction with n = 2 and E°cell = 0.51 V (1)
- Nernst equation with $Q = [Zn^{2+}]/[Ni^{2+}]$ and log Q = 2 (1)
- $[Ni^{2+}] = 1.0 \times 10^{-3}$ M (1)

Or:

Fe(s) + Cu^{2+}(aq) → Fe^{2+}(aq) + Cu(s), n = 2. $E°cell = 0.34 - (-0.44) = 0.78$ V. $Ecell = E°cell - (0.059/2)\log([Fe^{2+}]/[Cu^{2+}])$, so $0.839 = 0.78 - 0.0295\log(0.0010/[Cu^{2+}])$; $\log(0.0010/[Cu^{2+}]) = -0.059/0.0295 = -2$, so $0.0010/[Cu^{2+}] = 0.01$ and $[Cu^{2+}] = 0.10$ M.

- cell reaction with n = 2 and E°cell = 0.78 V (1)
- Nernst equation with $Q = [Fe^{2+}]/[Cu^{2+}]$ and log Q = −2 (1)
- $[Cu^{2+}] = 0.10$ M (1)

24. A student has 4-methylaniline and methylbenzene dissolved together in ether. Describe, with equations, how she separates them and recovers the amine. [3]

Shake the ether solution with dilute HCl: $CH_3-C_6H_4-NH_2 + HCl \rightarrow CH_3-C_6H_4-NH_3^+Cl^-$. The salt is soluble in water but insoluble in ether, so it passes into the aqueous layer; methylbenzene, not basic, stays in the ether layer. Separate the layers. Add NaOH to the aqueous layer: $CH_3-C_6H_4-NH_3^+Cl^- + NaOH \rightarrow CH_3-C_6H_4-NH_2 + H_2O + NaCl$; the free amine separates and can be extracted into fresh ether.

- salt formation with HCl, equation (1)
- salt in water, insoluble in ether; methylbenzene stays in ether (1)
- NaOH frees the amine, equation (1)

25. A sugar Y, $C_5H_{10}O_5$, shows the following: (i) on prolonged heating with HI it gives n-pentane; (ii) it forms an oxime with hydroxylamine; (iii) bromine water oxidises it to a monocarboxylic acid with five carbon atoms; (iv) with acetic anhydride it gives a stable tetraacetate. Deduce what each observation shows, write the open-chain structure of Y and classify it. [3]

(i) n-Pentane: the five carbons are in a straight chain. (ii) An oxime: Y has a carbonyl group. (iii) Oxidation by a mild oxidising agent without loss of carbon: the carbonyl group is an aldehyde group. (iv) A tetraacetate: four −OH groups; since it is stable, they are on different carbon atoms. Y is $CHO-(CHOH)_3-CH_2OH$, an aldopentose.

- (i) straight chain and (ii) carbonyl group (1)
- (iii) aldehyde group and (iv) four −OH on different carbons (1)
- structure $CHO-(CHOH)_3-CH_2OH$, aldopentose (1)

26. One mole of $IrCl_3 \cdot 4NH_3$ gives one mole of AgCl at once with excess $AgNO_3$(aq). Iridium has coordination number 6 in it. (a) Write its formula. (b) State the primary and the secondary valence of iridium and what each corresponds to today. (c) How many geometrical isomers can the complex ion have? [3]

(a) Only one Cl^- is ionisable, so two Cl^- join four NH_3 inside the sphere: $[Ir(NH_3)_4Cl_2]Cl$. (b) Primary valence 3, the ionisable valence, read today as the oxidation state +3; secondary valence 6, the non-ionisable valence, the coordination number. (c) $[Ir(NH_3)_4Cl_2]^+$ is octahedral $[MX_2L_4]$: two isomers, cis (Cl at 90°) and trans (Cl at 180°).

- $[Ir(NH_3)_4Cl_2]Cl$ (1)
- primary 3 = oxidation state; secondary 6 = coordination number (1)
- two: cis and trans (1)

27. Write the major product and the reagents for (i) bromination of bromobenzene and (ii) Friedel–Crafts acetylation of bromobenzene. (iii) Why are harsher conditions needed than for benzene? [3]

(i) Br_2 with anhydrous $FeBr_3$ (or Fe): 1,4-dibromobenzene major, 1,2-dibromobenzene minor. (ii) CH_3COCl with anhydrous $AlCl_3$: 4-bromoacetophenone, 1-(4-bromophenyl)ethanone, major; the ortho isomer minor. (iii) Bromine withdraws electrons by its −I effect, which outweighs its resonance release and destabilises the carbocation intermediate, so the ring is deactivated; resonance still makes ortho and para the preferred positions.

- 1,4-dibromobenzene, $Br_2/FeBr_3$ (1)
- 4-bromoacetophenone, $CH_3COCl/AlCl_3$ (1)
- −I deactivates; resonance directs o,p (1)

28. For water, T_f = 273.15 K and Δfus H = 6.01 kJ mol^{-1}. Calculate K_f of water from these data and compare it with the tabulated value. (R = 8.314 J mol^{-1} K^{-1}, M_1 = 18 g mol^{-1}) [3]

$K_f = R \times M_1 \times T_f^2/(1000 \times \Delta\text{fus H}) = (8.314 \times 18 \times 273.15^2)/(1000 \times 6010) = 1.86$ K kg mol^{-1}, in agreement with the tabulated 1.86 K kg mol^{-1}.

- correct expression for K_f (1)
- Δfus H in J mol^{-1} and substitution (1)
- K_f = 1.86 K kg mol^{-1}, agreeing with the table (1)

Section D (2 × 4 marks)

29. Read the passage and answer the questions that follow. [4]

A student studies a gas-phase reaction A + B → C + D. Reactant molecules must pass through an activated complex before they form products, and the energy needed to reach it is the activation energy. The figure plots potential energy against the reaction coordinate for the reaction alone (solid curve) and for the same reaction with a catalyst added (dashed curve). Both paths start from the same reactants and end at the same products. Read the energies from the figure to answer the questions.

(a) The activation energy of the forward reaction without the catalyst is [1]

(a) 80 kJ mol^{-1} (b) 130 kJ mol^{-1}
(c) 110 kJ mol^{-1} (d) 40 kJ mol^{-1}

Answer: (a) Ea(forward) = peak − reactants = 130 − 50 = 80 kJ mol^{-1}.

(b) The enthalpy change ΔH of the reaction is [1]

(a) −30 kJ mol^{-1} (b) 30 kJ mol^{-1}
(c) −80 kJ mol^{-1} (d) −110 kJ mol^{-1}

Answer: (a) ΔH = products − reactants = 20 − 50 = −30 kJ mol^{-1}; exothermic.

(c) Find the activation energy of the backward reaction C + D → A + B along each path, and state what you notice about how the catalyst changes the forward and backward barriers. [2]

Or *Using the figure, explain why the catalyst changes neither ΔH nor the equilibrium constant of the reaction.*

Uncatalysed: 130 − 20 = 110 kJ mol^{-1}; catalysed: 90 − 20 = 70 kJ mol^{-1}. The forward barrier falls from 80 to 40 kJ mol^{-1} and the backward from 110 to 70: both are lowered by the same 40 kJ mol^{-1}, so the catalyst speeds both directions alike.

- 110 and 70 kJ mol^{-1} (1)
- both barriers lowered by the same 40 kJ mol^{-1} (1)

Or:

Both paths start at the same reactant energy (50) and end at the same product energy (20), so ΔH = −30 kJ mol^{-1} either way. The catalyst lowers the forward and backward barriers by the same 40 kJ mol^{-1}, speeding both reactions equally, so equilibrium is reached sooner but its position, and K, are unchanged.

- same end points, so ΔH unchanged (1)
- both barriers lowered equally, so K unchanged (1)

30. Read the passage and answer the questions that follow. [4]

A health camp at a school in Nashik finds four students whose symptoms point to a vitamin deficiency. The doctor notes each student's usual diet and recommends changes in food rather than vitamin pills, explaining that an excess of a vitamin can also be harmful and that pills should be taken only on a doctor's advice.

Student	Main symptom
Ravi	night blindness
Meena	bleeding gums
Arjun	convulsions
Fatima	soft bones that bend under the body's weight (rickets)

(a) Meena's diet lacks [1]

(a) vitamin C (b) vitamin D
(c) vitamin K (d) vitamin B_{12}

Answer: (a) Bleeding gums are a sign of scurvy, the deficiency disease of vitamin C (ascorbic acid).

(b) The vitamins missing in which two students can be stored in the liver and adipose tissue? [1]

(a) Meena and Arjun (b) Ravi and Fatima
(c) Ravi and Meena (d) Arjun and Fatima

Answer: (b) Ravi lacks vitamin A and Fatima vitamin D; both are fat soluble and stored in the liver and adipose tissue. Meena's vitamin C and Arjun's B_6 are water soluble.

(c) Name the vitamin Arjun lacks, give two foods that supply it, and state whether it is fat soluble or water soluble. [2]

Or *Name the vitamin Fatima lacks, give one source of it that is not a food, and name the disease its deficiency causes in adults.*

Convulsions are caused by deficiency of vitamin B_6 (pyridoxine). Sources (any two): yeast, milk, egg yolk, cereals, grams. It belongs to the B group and is water soluble.

- vitamin B_6 (pyridoxine) (1)
- two sources and water soluble (1)

Or:

Fatima lacks vitamin D. Exposure to sunlight is a source that is not a food (fish and egg yolk are food sources). In adults its deficiency causes osteomalacia.

- vitamin D; exposure to sunlight (1)
- osteomalacia in adults (1)

Section E (3 × 5 marks)

31. (a) Write the reduction half-reactions of permanganate ion in (i) strongly acidic and (ii) neutral solution, naming the manganese product in each. (b) 25.0 mL of an acidified iron(II) solution needs 15.0 mL of 0.020 M $KMnO_4$ for complete oxidation. Write the balanced ionic equation and calculate the molarity of the iron(II) solution. (c) Why is sulphuric acid, not hydrochloric acid, used to acidify the solution? [5]

Or *(a) Write balanced ionic equations for the oxidation, by acidified permanganate, of (i) nitrite ion and (ii) sulphite ion. (b) Calculate the volume of 0.020 M $KMnO_4$ needed to oxidise 25.0 mL of 0.040 M sodium nitrite solution in acid. (c) State the manganese product in this titration, and why the titration is not done in hydrochloric acid.*

(a)(i) $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$: manganese(II). (ii) $MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2 + 4OH^-$: manganese dioxide. (b) $5Fe^{2+} + MnO_4^- + 8H^+ \rightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$. MnO_4^- used = 15.0 × 0.020 = 0.30 mmol; Fe^{2+} = 5 × 0.30 = 1.50 mmol; molarity = 1.50/25.0 = 0.060 M. (c) Permanganate oxidises hydrochloric acid to chlorine, so some titrant would be used up by the acid.

- acid half-reaction, Mn^{2+} (1)
- neutral half-reaction, MnO_2 (1)
- balanced Fe^{2+} equation (1)
- 0.060 M from the 5 : 1 ratio (1)
- HCl oxidised to Cl_2 (1)

Or:

(a)(i) $2MnO_4^- + 5NO_2^- + 6H^+ \rightarrow 2Mn^{2+} + 5NO_3^- + 3H_2O$. (ii) $2MnO_4^- + 5SO_3^{2-} + 6H^+ \rightarrow 2Mn^{2+} + 5SO_4^{2-} + 3H_2O$. (b) NO_2^- = 25.0 × 0.040 = 1.00 mmol; MnO_4^- = (2/5) × 1.00 = 0.40 mmol; volume = 0.40/0.020 = 20.0 mL. (c) In acid permanganate is reduced to Mn^{2+} (purple colour discharged). HCl would itself be oxidised to Cl_2, using up titrant.

- nitrite equation (1)
- sulphite equation (1)
- 2 : 5 ratio, 0.40 mmol (1)
- 20.0 mL (1)
- Mn^{2+}; HCl oxidised to Cl_2 (1)

32. (a) State Faraday's first and second laws of electrolysis. (b) A current of 5.0 A is passed for 3860 s through molten $MgCl_2$. Calculate the mass of magnesium deposited at the cathode and the volume of chlorine set free at the anode (molar volume 22.7 L at 1 bar and 273 K; Mg = 24 g mol^{-1}; F = 96500 C mol^{-1}). (c) Why is magnesium made from the molten chloride and not by a chemical reducing agent? [5]

Or *(a) State Faraday's first and second laws of electrolysis. (b) Aluminium is made by electrolysing aluminium oxide dissolved in cryolite. If a current of 9.65 A is passed for 3000 s, calculate the quantity of electricity in faradays and the mass of aluminium deposited (Al = 27 g mol^{-1}, F = 96500 C mol^{-1}). (c) Why can aluminium not be deposited by electrolysing an aqueous solution of an aluminium salt?*

(a) First law: the amount of chemical reaction at an electrode is proportional to the quantity of electricity passed. Second law: the amounts of different substances liberated by the same quantity of electricity are proportional to their chemical equivalent weights (atomic mass ÷ electrons needed to reduce the cation). (b) Q = 5.0 × 3860 = 19 300 C = 0.200 F. $Mg^{2+} + 2e^- \rightarrow Mg$: 0.100 mol Mg = 2.4 g. $2Cl^- \rightarrow Cl_2 + 2e^-$: 0.100 mol Cl_2 = 2.27 L. (c) Magnesium is a very powerful reducing metal (E° −2.36 V); no suitable chemical reducing agent exists, so it is won by electrochemical reduction of the fused chloride.

- first law (1)
- second law (1)
- Q = 0.200 F and 2.4 g Mg (1)
- 0.100 mol Cl_2 = 2.27 L (1)
- (c) no suitable chemical reducing agent; electrolysis of fused chloride (1)

Or:

(a) First law: the amount of chemical reaction at an electrode is proportional to the quantity of electricity passed. Second law: the amounts of different substances liberated by the same quantity of electricity are proportional to their chemical equivalent weights. (b) Q = 9.65 × 3000 = 28 950 C = 0.300 F. $Al^{3+} + 3e^- \rightarrow Al$: 0.300/3 = 0.100 mol Al = 2.7 g. (c) $E^\circ(Al^{3+}|Al)$ = −1.66 V is far below that of H^+/H_2 (0.00 V), so water is reduced to H_2 at the cathode before Al^{3+}.

- first law (1)
- second law (1)
- Q = 0.300 F (1)
- 0.100 mol Al = 2.7 g (1)
- (c) water reduced in preference to Al^{3+} (1)

33. (a) Write, as numbered steps, the mechanism of the acid-catalysed esterification of propanoic acid with methanol. (b) Write the equation for the conversion of propanoic acid into propanoyl chloride with thionyl chloride, and say why this reagent is preferred. [5]

Or *(a) Write the equations for the conversion of butanoic acid into butanoyl chloride by PCl_5, PCl_3 and $SOCl_2$, and say which reagent is preferred and why. (b) Butanoic acid is heated with ethanol and concentrated H_2SO_4. Write the equation and state the role of the acid in the first step of the mechanism.*

(a) 1. H^+ protonates the carbonyl oxygen of CH_3CH_2COOH, making the carbon more electrophilic. 2. CH_3OH attacks the carbonyl carbon; a tetrahedral intermediate forms. 3. A proton moves from the $-O^+H-CH_3$ to an $-OH$, making $-OH_2^+$, a good leaving group. 4. Water leaves, giving the protonated ester. 5. Loss of H^+ gives $CH_3CH_2COOCH_3$, methyl propanoate. (b) $CH_3CH_2COOH + SOCl_2 \rightarrow CH_3CH_2COCl + SO_2 + HCl$; SO_2 and HCl are gases that escape, so the acid chloride is obtained pure.

- protonation of the carbonyl oxygen (1)
- attack of methanol, tetrahedral intermediate (1)
- proton transfer, loss of water and of H^+ to methyl propanoate (1)
- $SOCl_2$ equation (1)
- gaseous by-products escape (1)

Or:

(a) $CH_3CH_2CH_2COOH + PCl_5 \rightarrow CH_3CH_2CH_2COCl + POCl_3 + HCl$; $3CH_3CH_2CH_2COOH + PCl_3 \rightarrow 3CH_3CH_2CH_2COCl + H_3PO_3$; $CH_3CH_2CH_2COOH + SOCl_2 \rightarrow CH_3CH_2CH_2COCl + SO_2 + HCl$. $SOCl_2$ is preferred: SO_2 and HCl are gases and escape. (b) $CH_3CH_2CH_2COOH + C_2H_5OH \rightleftharpoons CH_3CH_2CH_2COOC_2H_5 + H_2O$; H^+ protonates the carbonyl oxygen, making the carbonyl carbon more electrophilic towards the alcohol.

- PCl_5 equation (1)
- PCl_3 equation (1)
- $SOCl_2$ equation and why preferred (1)
- esterification equation (1)
- protonation of carbonyl oxygen activates the carbon (1)