# CBSE Class 12 Chemistry: Sample Paper 2: 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.** The IUPAC name of $HO{-}CH_2{-}CH(OH){-}CH_2{-}CH_3$ is [1]

(a) butan-1,2-diol
(b) butane-1,2-diol
(c) butane-3,4-diol
(d) 1,2-dihydroxybutane

**Answer: (b)** For a polyhydric alcohol the 'e' of the alkane is kept and 'di' goes before 'ol'; the chain is numbered to give the −OH groups the lowest locants: butane-1,2-diol. (a) drops the 'e'; (c) numbers from the wrong end; (d) treats −OH as a prefix.

**2.** The letter D in D-(+)-glucose tells us that [1]

(a) glucose is dextrorotatory
(b) the −OH on C-5, the lowest asymmetric carbon, is on the right in the Fischer projection, as in (+)-glyceraldehyde
(c) the −OH on C-2 is on the right in the Fischer projection
(d) every −OH in the Fischer projection is on the right

**Answer: (b)** D gives the configuration relative to glyceraldehyde, judged at the lowest asymmetric carbon (C-5) with −CHO at the top; the sign of rotation is shown separately by (+). In D-glucose the −OH on C-3 is on the left, so not every −OH is on the right.

**3.** The oxidation state of iron in $Na_2[Fe(CN)_5(NH_3)]$ is [1]

(a) +2
(b) +3
(c) +5
(d) +1

**Answer: (b)** Two $Na^+$ counter ions make the entity $[Fe(CN)_5(NH_3)]^{2-}$. $NH_3$ is neutral and each $CN^-$ is −1: $x + 5(-1) + 0 = -2$, so $x = +3$.

**4.** Oxidation of 3-methylbutan-2-ol, $CH_3CH(OH)CH(CH_3)_2$, with acidified $K_2Cr_2O_7$ gives [1]

(a) 3-methylbutanal
(b) 3-methylbutan-2-one
(c) 3-methylbutanoic acid
(d) 2-methylbut-2-ene

**Answer: (b)** It is a secondary alcohol (−OH on C-2, which carries one H); secondary alcohols are oxidised to ketones: $CH_3COCH(CH_3)_2$, 3-methylbutan-2-one.

**5.** For a salt X, $\Delta_{sol}H = +18\ kJ\ mol^{-1}$. A nearly saturated solution of X is in contact with excess solid. When the temperature is raised, the solubility of X [1]

(a) first increases and then decreases
(b) decreases, since heat drives solute out of solution
(c) does not change, since solids are incompressible
(d) increases, since the equilibrium shifts in the endothermic direction

**Answer: (d)** $\Delta_{sol}H > 0$, so dissolution absorbs heat. By Le Chatelier's principle, raising the temperature favours the endothermic change, dissolution, and solubility rises. Incompressibility is the reason pressure, not temperature, has little effect.

**6.** The IUPAC name of $CH_3CH_2CH_2–NH–CH_2CH_3$ is [1]

(a) N-propylethanamine (b) N-ethylpropan-2-amine

(c) ethylpropylamine (d) N-ethylpropan-1-amine

**Answer: (d)** The longer chain on nitrogen, propyl, gives the parent propan-1-amine; the ethyl group on nitrogen takes the locant N. Ethylpropylamine is the common name, not the IUPAC name; (a) takes the shorter chain as parent; (b) puts the nitrogen on C-2.

**7.** $CH_3CH_2CH_2CHCl_2$ is best described as [1]

(a) a vic-dihalide, 1,2-dichlorobutane (b) a gem-dihalide, 1,1-dichlorobutane

(c) a gem-dihalide, 2,2-dichlorobutane (d) a vic-dihalide, 1,1-dichlorobutane

**Answer: (b)** Both chlorine atoms sit on the same (terminal) carbon, so the compound is geminal (an alkylidene halide, butylidene chloride); its IUPAC name is 1,1-dichlorobutane. Vicinal would need the two halogens on adjacent carbons.

**8.** The IUPAC name of $Na_2[Zn(CN)_4]$ is [1]

(a) tetracyanidozincate(II) sodium (b) sodium tetracyanidozinc(II)

(c) sodium tetracyanidozincate(IV) (d) sodium tetracyanidozincate(II)

**Answer: (d)** The cation is named first. The entity $[Zn(CN)_4]^{2-}$ is an anion, so the metal name ends in -ate; $x + 4(-1) = -2$ gives Zn(II).

**9.** A reaction goes by three elementary steps. Run on its own, step 1 is over in about 2 s, step 2 takes about 40 min and step 3 about 5 s. The overall rate of the reaction is decided by [1]

(a) step 2, because it is the slowest (b) step 1, because it comes first

(c) step 3, because it gives the products (d) the sum of the three rates

**Answer: (a)** The slowest step is the rate determining step; the overall reaction cannot go faster than it, as a relay team is held to its slowest runner.

**10.** The IUPAC name of $CH_3–CH_2–CH(CH_3)–CH_2–CH_2–OH$ is [1]

(a) 3-methylpentan-1-ol (b) 3-methylpentan-5-ol

(c) 3-ethylbutan-1-ol (d) 1-hydroxy-3-methylpentane

**Answer: (a)** The longest chain has five carbons and is numbered from the end nearest –OH: OH on C-1, $CH_3$ on C-3; the 'e' of pentane becomes 'ol': 3-methylpentan-1-ol. Numbering from the other end (b) gives the –OH a higher locant; (c) uses a four-carbon chain; (d) names –OH as a prefix.

**11.** In the cell notation $Al(s) \mid Al^{3+}(aq) \parallel Sn^{2+}(aq) \mid Sn(s)$, the double vertical line stands for [1]

(a) the boundary between a metal and its solution (b) a platinum wire

(c) a salt bridge (d) the voltmeter

**Answer: (c)** A single line separates a metal from its electrolyte; the double line is the salt bridge joining the two half-cells.

**12.** A colourless sample of aniline turns brown after some weeks in a half-filled bottle. The change is due to [1]

(a) reaction with nitrogen of the air, giving an azo dye (b) absorption of water, giving anilinium hydroxide

(c) oxidation by the air in the bottle (d) conversion into nitrobenzene by light

**Answer: (c)** Arylamines are usually colourless but become coloured on storage through atmospheric oxidation.

**13.** Assertion (A): The amount of oxygen dissolved in a pond falls on a hot afternoon. Reason (R): Dissolution of a gas in a liquid is an exothermic process. [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)** Dissolving a gas evolves heat, like condensation; by Le Chatelier's principle a rise in temperature shifts the equilibrium back, so solubility falls. R explains A.

**14.** Assertion (A): Propan-1-amine dissolves in water. Reason (R): Propan-1-amine gives a foul-smelling isocyanide when heated with chloroform and ethanolic KOH. [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 true. A lower aliphatic amine dissolves because it hydrogen bonds with water; the carbylamine reaction shows only that it is primary and does not explain its solubility.

**15.** Assertion (A): Phenol dissolves in aqueous sodium hydroxide, forming sodium phenoxide. Reason (R): Phenol is a stronger acid than water. [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. Because phenol is a stronger acid than water, it gives up its proton to $OH^-$: $C_6H_5OH + NaOH \rightarrow C_6H_5ONa + H_2O$. R explains A.

**16.** Assertion (A): The time taken by a first order reaction to fall from 0.8 M to 0.4 M equals the time it takes to fall from 0.2 M to 0.1 M. Reason (R): For a first order reaction $t_{½} = 0.693/k$, which does not contain the initial concentration. [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 intervals are one half-life; $t_{½} = 0.693/k$ is independent of $[R]_0$, which is exactly why the two times are equal.

## Section B (5 × 2 marks)

**17.** Write the equation for the preparation of a Grignard reagent from 1-bromopropane, and the equation for its reaction with water. Which atom of the C–Mg bond carries the partial negative charge? [2]

**Or** *Bromocyclohexane is warmed with magnesium in dry ether and the product is then treated with methanol. Write the two equations and name the final organic product.*

$CH_3CH_2CH_2Br + Mg \rightarrow CH_3CH_2CH_2MgBr$ (dry ether). $CH_3CH_2CH_2MgBr + H_2O \rightarrow CH_3CH_2CH_3 +$ Mg(OH)Br. In the C–Mg bond the carbon is δ−: it pulls electrons from the electropositive magnesium.

- Grignard formation in dry ether (1)
- hydrolysis to propane, Mg(OH)Br; carbon δ− (1)

*Or:*

$C_6H_{11}Br + Mg \rightarrow C_6H_{11}MgBr$ (cyclohexylmagnesium bromide, dry ether). $C_6H_{11}MgBr + CH_3OH \rightarrow C_6H_{12} + Mg(OCH_3)Br$. Methanol, like water, is a proton source, so the Grignard reagent is converted to the hydrocarbon cyclohexane.

- Grignard formation in dry ether (1)
- protonation by methanol gives cyclohexane (1)

**18.** Write the equation for the conversion of butanoic acid into 2-chlorobutanoic acid and name the reaction. [2]

$CH_3CH_2CH_2COOH + Cl_2 \rightarrow CH_3CH_2CH(Cl)COOH + HCl$, with a little red phosphorus. Hell–Volhard–Zelinsky reaction: halogenation at the α-carbon of an acid that has an α-hydrogen.

- correct equation with $Cl_2$ and red phosphorus, Cl on the α-carbon (1)
- names the Hell–Volhard–Zelinsky reaction (1)

**19.** Give two differences between the order and the molecularity of a reaction. [2]

Order is the sum of the powers of concentration terms in the experimental rate law; it can be 0, a fraction or a whole number. Molecularity is the number of species colliding simultaneously in an elementary step; it is a whole number (1, 2 or 3), never 0 or a fraction. Order applies to elementary and complex reactions; molecularity has meaning only for an elementary reaction.

- one difference, correctly stated for both quantities (e.g. 0 or fraction allowed for order only) (1)
- a second difference (e.g. experimental against theoretical, or complex against elementary) (1)

**20.** Patient P's red blood cells are unusually fragile, and P has a loss of muscle strength. Patient Q has cheilosis and a burning sensation of the skin. Name the vitamin each patient lacks and state whether it is fat soluble or water soluble. [2]

P lacks vitamin E, whose deficiency causes increased fragility of red blood cells and a loss of muscle strength; E is fat soluble. Q lacks vitamin $B_2$ (riboflavin), whose deficiency causes cheilosis, digestive disorders and a burning sensation of the skin; $B_2$ is water soluble.

- P: vitamin E, fat soluble (1)
- Q: vitamin $B_2$ (riboflavin), water soluble (1)

**21.** What is meant by the denticity of a ligand? State the denticity of (i) the oxalate ion, $C_2O_4^{2-}$, and (ii) $N(CH_2CH_2NH_2)_3$. [2]

Denticity is the number of donor atoms through which a ligand binds the central atom (the number of its ligating groups). (i) Oxalate binds through two O atoms: didentate. (ii) $N(CH_2CH_2NH_2)_3$ binds through its central N and three $NH_2$ nitrogens: tetradentate (polydentate).

- denticity: the number of donor atoms of a ligand bound to the metal (1)
- oxalate 2 (didentate); $N(CH_2CH_2NH_2)_3$ 4 (polydentate) (1)

## Section C (7 × 3 marks)

**22.** 2-Bromo-2-methylbutane is hydrolysed in water. Write the mechanism in two numbered steps with equations, the rate expression, and one reason why the reaction is fast. [3]

**Or** *3-Chloro-3-ethylpentane, $(C_2H_5)_3CCl$, is warmed in aqueous ethanol. Write the mechanism in two numbered steps with equations, the rate expression, and why a polar protic solvent helps.*

Step 1 (slow, reversible): $(CH_3)_2CBrCH_2CH_3 \rightleftharpoons (CH_3)_2C^+CH_2CH_3 + Br^-$; the energy to break C–Br comes from solvation of the ions by water. Step 2 (fast): $(CH_3)_2C^+CH_2CH_3 + H_2O \rightarrow (CH_3)_2C(OH)CH_2CH_3 + H^+$, giving 2-methylbutan-2-ol. Rate = $k[(CH_3)_2CBrCH_2CH_3]$, first order: only the halide is in the slow step. The reaction is fast because the carbocation is tertiary and stabilised by three alkyl groups.

- slow ionisation to the tertiary carbocation (1)
- fast attack, 2-methylbutan-2-ol (1)
- first-order rate law, tertiary cation stability (1)

*Or:*

Step 1 (slow, reversible): $(C_2H_5)_3C–Cl \rightleftharpoons (C_2H_5)_3C^+ + Cl^-$. Step 2 (fast): $(C_2H_5)_3C^+ + H_2O \rightarrow (C_2H_5)_3C–OH + H^+$, giving 3-ethylpentan-3-ol. Rate = $k[(C_2H_5)_3CCl]$, first order. A polar protic solvent such as water or alcohol solvates the ions formed in step 1, supplying the energy needed to break the C–Cl bond.

- slow ionisation to the tertiary carbocation (1)
- fast attack, 3-ethylpentan-3-ol (1)
- first-order rate law, solvation of the ions (1)

**23.** For the lead storage battery while it is being discharged, write (i) the anode reaction, (ii) the cathode reaction, and (iii) explain why the density of the electrolyte can be used to tell how far the battery has run down. [3]

(i) Anode: $Pb(s) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) + 2e^-$. (ii) Cathode: $PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \rightarrow PbSO_4(s) + 2H_2O(l)$. (iii) Overall $Pb + PbO_2 + 2H_2SO_4 \rightarrow 2PbSO_4 + 2H_2O$: sulphuric acid is used up and water formed, so the acid becomes more dilute and its density falls as the battery discharges.

- anode reaction (1)
- cathode reaction (1)
- $H_2SO_4$ consumed and water formed, so density falls (1)

**24.** 2-Methylpropan-2-ol is dehydrated by 20% $H_3PO_4$ at 358 K, whereas ethanol needs concentrated $H_2SO_4$ at 443 K. Write, as numbered steps, the mechanism of dehydration of 2-methylpropan-2-ol, and use it to explain the difference. [3]

1. The alcohol is protonated: $(CH_3)_3C–OH + H^+ \rightarrow (CH_3)_3C–OH_2^+$. 2. Water leaves, giving the carbocation $(CH_3)_3C^+$; this is the slowest, rate-determining step. 3. A proton is lost from a $CH_3$ group: $(CH_3)_2C=CH_2 + H^+$, and the acid is regenerated. Because step 2 decides the rate and the tertiary carbocation is the most stable, it forms easily; ethanol would have to form a much less stable primary carbocation, so it needs harsher conditions.

- step 1: protonation of the alcohol (1)
- step 2: $(CH_3)_3C^+$ formed, rate determining (1)
- step 3: loss of $H^+$ to 2-methylpropene; tertiary carbocation most stable, so easier (1)

**25.** Explain the role of a coordination compound in each of the following: (i) fixing a developed black-and-white photographic film, (ii) electroplating an article with silver, (iii) the hydrogenation of alkenes. [3]

(i) Hypo (sodium thiosulphate) dissolves the unexposed AgBr as the complex $[Ag(S_2O_3)_2]^{3-}$: AgBr + $2Na_2S_2O_3 \rightarrow Na_3[Ag(S_2O_3)_2]$ + NaBr. (ii) Silver plates more smoothly and evenly from a solution of $[Ag(CN)_2]^-$ than from simple $Ag^+$ ions. (iii) Wilkinson catalyst, $[(Ph_3P)_3RhCl]$, a rhodium complex, catalyses the hydrogenation of alkenes.

- hypo dissolves AgBr as $[Ag(S_2O_3)_2]^{3-}$ (1)
- smooth plating from $[Ag(CN)_2]^-$ (1)
- Wilkinson catalyst $[(Ph_3P)_3RhCl]$ (1)

**26.** Vanadium forms the oxides $V_2O_3$, $V_2O_4$ and $V_2O_5$. (i) State the acid–base nature of each. (ii) What does $V_2O_4$ give when it dissolves in acids? (iii) Why does the acidic character increase from $V_2O_3$ to $V_2O_5$? [3]

(i) $V_2O_3$ is basic, $V_2O_4$ less basic, $V_2O_5$ amphoteric though mainly acidic (it gives $VO_4^{3-}$ and $VO_2^+$ salts). (ii) $VO^{2+}$ salts. (iii) The oxidation number rises from +3 to +5; ionic character falls as the oxidation number rises, and the higher, more covalent oxides are acidic.

- nature of all three (1)
- $VO^{2+}$ salts (1)
- rising oxidation number, falling ionic character (1)

**27.** The concentration of a reactant in a zero order reaction falls from 0.50 mol $L^{-1}$ to 0.38 mol $L^{-1}$ in 30 min. Calculate (i) k, (ii) the time at which the reactant is used up completely, and (iii) the half-life for the initial concentration of 0.50 mol $L^{-1}$. [3]

(i) $k = ([R]_0 - [R])/t = (0.50 - 0.38)/30 = 4.0 \times 10^{-3}$ mol $L^{-1}$ $min^{-1}$. (ii) [R] = 0 when $t = [R]_0/k = 0.50/0.004 = 125$ min. (iii) $t½ = [R]_0/2k = 0.50/0.008 = 62.5$ min.

- $k = 4.0 \times 10^{-3}$ mol $L^{-1}$ $min^{-1}$ (1)
- 125 min to completion (1)
- t½ = 62.5 min (1)

**28.** Starting from 1-bromopropane: (a) write equations to prepare propan-1-amine free of secondary and tertiary amines; (b) state what heating 1-bromopropane with ethanolic ammonia in a sealed tube would give, and why. (c) To make the reaction in (b) go faster, would you replace 1-bromopropane by 1-chloropropane or by 1-iodopropane? Give the order of reactivity on which you decide. [3]

(a) Gabriel synthesis: phthalimide + ethanolic KOH → potassium phthalimide; with $CH_3CH_2CH_2Br$ on heating → N-propylphthalimide; hydrolysis with NaOH(aq) → $CH_3CH_2CH_2NH_2$ + the disodium salt of phthalic acid. Only a primary amine can form. (b) A mixture of propan-1-amine, N-propylpropan-1-amine, tripropylamine and the quaternary salt $(CH_3CH_2CH_2)_4N^+Br^-$, because each amine formed is itself a nucleophile and reacts further with the halide. (c) 1-Iodopropane: the reactivity of halides with amines is RI > RBr > RCl, so the iodide reacts faster and the chloride slower.

- (a) Gabriel route with the three stages (1)
- (b) mixture of 1°, 2°, 3° amines and quaternary salt, with reason (1)
- (c) 1-iodopropane, RI > RBr > RCl (1)

## Section D (2 × 4 marks)

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

A student is given five white carbohydrate samples, P to T. She tests each with Tollens' reagent and then hydrolyses it completely with dilute acid, identifying the monosaccharides formed. Sample T dissolves in hot water. Her teacher adds that T was separated from a natural mixture whose other, water-insoluble component also gives only glucose on hydrolysis but has a branched chain.

| Sample | Tollens' reagent | Products of complete hydrolysis |
|---|---|---|
| P | silver mirror | not hydrolysed |
| Q | no change | glucose and fructose, equimolar |
| R | silver mirror | glucose only, two units per molecule |
| S | silver mirror | galactose and glucose |
| T | no change | glucose only, several hundred units in an unbranched chain |

(a) Sample Q is [1]

(a) maltose (b) lactose
(c) sucrose (d) cellulose

**Answer: (c)** Q is a non-reducing sugar giving equimolar glucose and fructose: sucrose. Maltose gives only glucose, lactose galactose and glucose, cellulose many glucose units.

(b) In sample R the two units are joined between [1]

(a) C1 of β-D-galactose and C4 of β-D-glucose (b) C1 of α-D-glucose and C2 of β-D-fructose
(c) C1 of one α-D-glucose and C4 of the other (d) C1 of one α-D-glucose and C6 of the other

**Answer: (c)** R is maltose: two α-D-glucose units, C1 of one to C4 of the other. (a) is lactose (sample S), (b) sucrose (Q), (d) a branch point of amylopectin.

(c) Explain why R gives a silver mirror with Tollens' reagent but Q does not. [2]

**Or** *Identify T and the water-insoluble component the teacher describes, and state how their chains differ.*

In Q, sucrose, the glycosidic linkage joins C1 of α-D-glucose to C2 of β-D-fructose, so the reducing groups of both units are bonded and none is free. In R, maltose, C1 of the first glucose is joined to C4 of the second; C1 of the second unit is free and a free aldehyde group can form there in solution, which reduces Tollens' reagent.

- Q: both reducing groups used in the C1–C2 linkage (1)
- R: free aldehyde group can form at C1 of the second glucose unit (1)

*Or:*

T is amylose, the water-soluble component of starch (about 15–20%), an unbranched chain of α-D-glucose units joined by C1–C4 glycosidic linkages. The insoluble component is amylopectin (about 80–85%), a branched polymer of α-D-glucose: its chain is formed by C1–C4 linkages and its branches by C1–C6 linkages.

- T amylose, unbranched α C1–C4 chain (1)
- amylopectin, branched, with C1–C6 linkages at the branches (1)

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

A lighter flint is made of mischmetall, an alloy of about 95% lanthanoid metals with about 5% iron. The lanthanoids in it are so alike that separating them is difficult: all are reactive metals whose atoms share the $6s^2$ configuration while the number of 4f electrons changes along the series. Their compounds are mostly of the tripositive ions, many of which give coloured solutions with sharp absorption bands. A few lanthanoids also form compounds in which they show an oxidation state other than +3, and such compounds are useful as oxidising or reducing agents in the laboratory.

(a) Which of the following tripositive ions is colourless in aqueous solution? [1]

(a) $Pr^{3+}$ (b) $Nd^{3+}$
(c) $Sm^{3+}$ (d) $Lu^{3+}$

**Answer: (d)** $Lu^{3+}$ is $4f^{14}$: with a filled f subshell no f–f transition is possible, so it is colourless. $Pr^{3+}$, $Nd^{3+}$ and $Sm^{3+}$ have partly filled 4f sets and are coloured.

(b) On going from $La^{3+}$ to $Lu^{3+}$, the ionic radius [1]

(a) increases regularly (b) decreases regularly
(c) stays the same (d) first increases, then decreases

**Answer: (b)** The lanthanoid contraction: the decrease is regular for the $M^{3+}$ ions (not quite regular for the atoms), because 4f electrons shield the rising nuclear charge poorly.

(c) $Eu^{2+}$ is a strong reducing agent while $Tb^{4+}$ is an oxidising agent. Explain both, using their electronic configurations. [2]

**Or** *$E°(Ce^{4+}/Ce^{3+})$ is +1.74 V, enough in principle to oxidise water. Explain why cerium shows the +4 state, and why Ce(IV) is nevertheless a useful analytical reagent in aqueous solution.*

Eu (Z = 63) is $[Xe]4f^7 6s^2$; $Eu^{2+}$ ($4f^7$) forms by losing the two s electrons, and it readily loses one more electron to return to the common +3 state, so it reduces other species. $Tb^{4+}$ has a half-filled $4f^7$ set, which favours its formation, but it readily gains an electron to return to +3, so it oxidises other species.

- $Eu^{2+}$ $4f^7$, gives up an electron to reach +3: reductant (1)
- $Tb^{4+}$ $4f^7$, takes an electron to reach +3: oxidant (1)

*Or:*

Ce (Z = 58) in the +4 state has a noble gas configuration ([Xe], $4f^0$), which favours $Ce^{4+}$; it is a strong oxidant that reverts to the common +3 state. Its reaction with water is very slow, so Ce(IV) solutions are kinetically stable and serve as a good analytical oxidant.

- $Ce^{4+}$ has the noble gas configuration ($4f^0$) (1)
- oxidation of water is very slow, so the reagent is usable (1)

## Section E (3 × 5 marks)

**31.** Liquids P and Q are mixed in equal numbers of moles at 300 K. Raoult's law predicts a total vapour pressure of 60 kPa over the mixture, but 72 kPa is measured. (a) Name the type of deviation shown. (b) Compare the P–Q interactions with the P–P and Q–Q interactions, and give the likely sign of Δmix H. (c) If the deviation is large, what kind of azeotrope may form, and how does its boiling point compare with those of the mixtures near it? (d) Name one pair of liquids from the chapter that behaves like P and Q, and give the reason at molecular level. [5]

**Or** *Liquids L and M are mixed in equal numbers of moles at 300 K. Raoult's law predicts a total vapour pressure of 50 kPa over the mixture, but 41 kPa is measured. (a) Name the type of deviation shown. (b) Compare the L–M interactions with the L–L and M–M interactions, and give the likely sign of Δmix H. (c) If the deviation is large, what kind of azeotrope may form? Name one such azeotrope with its approximate composition. (d) Name one pair of liquids from the chapter that behaves like L and M, and give the reason at molecular level.*

(a) The measured vapour pressure exceeds the Raoult value: positive deviation. (b) P–Q attractions are less strong than P–P and Q–Q, so molecules escape more easily; energy is absorbed on mixing, so Δmix H is usually > 0. (c) A minimum boiling azeotrope: at its composition the vapour pressure is highest, so it boils at a lower temperature than mixtures of nearby composition. (d) Ethanol and acetone: acetone molecules get between ethanol molecules and break some of their hydrogen bonds, weakening the interactions.

- positive deviation (1)
- P–Q less strong than P–P and Q–Q (1)
- Δmix H usually positive (1)
- minimum boiling azeotrope, lowest boiling point (1)
- ethanol + acetone, with hydrogen bonds of ethanol broken (1)

*Or:*

(a) The measured vapour pressure is below the Raoult value: negative deviation. (b) L–M attractions are stronger than L–L and M–M, so the escaping tendency falls; heat is evolved on mixing, so Δmix H is usually < 0. (c) A maximum boiling azeotrope, for example nitric acid–water at about 68% $HNO_3$ by mass, boiling at 393.5 K. (d) Chloroform and acetone: the hydrogen of chloroform forms a hydrogen bond with the oxygen of acetone, $(CH_3)_2C{=}O \cdots H{-}CCl_3$.

- negative deviation (1)
- L–M stronger than L–L and M–M (1)
- Δmix H usually negative (1)
- maximum boiling azeotrope, e.g. $HNO_3$–water about 68% (1)
- chloroform + acetone with the hydrogen bond (1)

**32.** (a) Define the cell constant of a conductivity cell and say why it is found with a KCl solution rather than by measuring l and A. (b) A conductivity cell filled with 0.010 M KCl ($\kappa = 1.41 \times 10^{-3}$ S cm$^{-1}$) has a resistance of 1000 Ω at 298 K. Filled with 0.0050 M of a monobasic weak acid HX, the same cell has a resistance of 6000 Ω. Calculate the cell constant, the conductivity and molar conductivity of the acid solution, and, given $\Lambda°m(HX) = 390$ S cm$^2$ mol$^{-1}$, its dissociation constant. [5]

**Or** *(a) State the balance condition of the Wheatstone bridge used to measure the resistance of a conductivity cell, and how κ then follows from it. (b) A conductivity cell filled with 0.100 M KCl (κ = 0.0129 S cm$^{-1}$) has a resistance of 200 Ω at 298 K. Filled with 0.0020 M of a monobasic weak acid HY, its resistance is 5160 Ω. Calculate the cell constant, the conductivity and molar conductivity of the acid solution, and, given Λ°m(HY) = 400 S cm$^2$ mol$^{-1}$, its dissociation constant.*

(a) Cell constant $G^* = l/A$, the distance between the electrodes divided by their area of cross-section (unit cm$^{-1}$). l and A cannot be measured reliably, so $G^* = R\kappa$ is found from the resistance of a KCl solution of known κ. (b) $G^* = 1000 \times 1.41 \times 10^{-3} = 1.41$ cm$^{-1}$. $\kappa(HX) = G^*/R = 1.41/6000 = 2.35 \times 10^{-4}$ S cm$^{-1}$. $\Lambda m = \kappa \times 1000/c = 2.35 \times 10^{-4} \times 1000/0.0050 = 47.0$ S cm$^2$ mol$^{-1}$. $\alpha = 47.0/390 = 0.121$; $Ka = c\alpha^2/(1 - \alpha) = 0.0050 \times 0.01452/0.879 = 8.3 \times 10^{-5}$ mol L$^{-1}$.

- (a) $G^* = l/A$ and why KCl calibration ($G^* = R\kappa$) (1)
- $G^* = 1.41$ cm$^{-1}$ (1)
- $\kappa = 2.35 \times 10^{-4}$ S cm$^{-1}$ (1)
- $\Lambda m = 47.0$ S cm$^2$ mol$^{-1}$ (1)
- $\alpha = 0.121$ and $Ka = 8.3 \times 10^{-5}$ (1)

*Or:*

(a) The bridge is balanced when no current flows through the detector; then the cell's resistance $R_2 = R_1R_4/R_3$, and $\kappa = G^*/R_2$. (b) $G^* = R\kappa = 200 \times 0.0129 = 2.58$ cm$^{-1}$. $\kappa(HY) = 2.58/5160 = 5.00 \times 10^{-4}$ S cm$^{-1}$. $\Lambda m = 5.00 \times 10^{-4} \times 1000/0.0020 = 250$ S cm$^2$ mol$^{-1}$. $\alpha = 250/400 = 0.625$; $Ka = c\alpha^2/(1 - \alpha) = 0.0020 \times 0.3906/0.375 = 2.08 \times 10^{-3}$ mol L$^{-1}$.

- (a) no detector current, $R_2 = R_1R_4/R_3$, $\kappa = G^*/R$ (1)
- $G^* = 2.58$ cm$^{-1}$ (1)
- $\kappa = 5.00 \times 10^{-4}$ S cm$^{-1}$ (1)
- $\Lambda m = 250$ S cm$^2$ mol$^{-1}$ (1)
- $\alpha = 0.625$ and $Ka = 2.08 \times 10^{-3}$ (1)

**33.** (a) Benzoic acid is treated with ammonia and the salt formed is then heated strongly. Write the two equations and name the product of each. (b) Benzaldehyde is treated with conc. $HNO_3$ and conc. $H_2SO_4$ at 273–283 K. Write the structure and name of the product, and explain why the nitro group enters that position. (c) Benzoic acid gives no ketone when warmed with $CH_3COCl$ and anhydrous $AlCl_3$. Give two reasons. [5]

**Or** *(a) Phthalic acid, $C_6H_4(COOH)_2$ (benzene-1,2-dicarboxylic acid), is treated with ammonia; the ammonium salt is heated to give P, and P on strong heating gives Q. Write the structures and names of P and Q. (b) Benzaldehyde and benzoic acid are each nitrated with conc. $HNO_3$ and conc. $H_2SO_4$. Name the two products and give the one reason that explains both. (c) Benzoic acid reacts with $Br_2$ in the presence of $FeBr_3$ but gives no product with $CH_3Cl$ and anhydrous $AlCl_3$. Name the bromination product and explain the second observation.*

(a) $C_6H_5COOH + NH_3 \rightarrow C_6H_5COONH_4$, ammonium benzoate. $C_6H_5COONH_4 \rightarrow$ (strong heating) $C_6H_5CONH_2 + H_2O$, benzamide. (b) m-$O_2N$–$C_6H_4$–CHO, m-nitrobenzaldehyde (3-nitrobenzaldehyde). The –CHO group withdraws electrons from the ring, deactivating it, and directs the incoming electrophile to the meta position. (c) The –COOH group deactivates the ring towards electrophilic substitution, and the Lewis acid $AlCl_3$ bonds to the –COOH group, so the Friedel–Crafts reaction does not occur.

- (a) ammonium benzoate equation (1)
- (a) heating to benzamide, water lost (1)
- (b) m-nitrobenzaldehyde, structure and name (1)
- (b) –CHO deactivates the ring and directs meta (1)
- (c) ring deactivated, and $AlCl_3$ bonds to –COOH (1)

*Or:*

(a) $C_6H_4(COOH)_2 + 2NH_3 \rightarrow C_6H_4(COONH_4)_2$; on heating, $2H_2O$ is lost: P = $C_6H_4(CONH_2)_2$, phthalamide. On strong heating P loses $NH_3$ and closes a ring: Q = $C_6H_4(CO)_2NH$, phthalimide. (b) m-nitrobenzaldehyde and m-nitrobenzoic acid. Both –CHO and –COOH withdraw electrons from the ring, deactivate it and direct the electrophile meta. (c) m-bromobenzoic acid. The Friedel–Crafts alkylation fails because –COOH deactivates the ring and the $AlCl_3$ bonds to the –COOH group.

- (a) P phthalamide (1)
- (a) Q phthalimide, $NH_3$ lost (1)
- (b) m-nitrobenzaldehyde and m-nitrobenzoic acid (1)
- (b) both groups deactivate and direct meta (1)
- (c) m-bromobenzoic acid; Friedel–Crafts fails, deactivation and $AlCl_3$ bonding (1)