Grade 12 Chemistry Model Paper 1

ANSWER KEY

Full marks 75 · 3 hours

Give the marks for the points in the marking scheme; an answer in other words that says the same is right.

A practice paper by Science Playground, made to CDC's Specification Grid 2078, Grade 12 Chemistry (Che. 302); not an official CDC or NEB paper.

Group A Multiple choice — 11 marks

Question 1 — 11 × 1 = 11

a. **(iv)** 49

b. **(iii)** 12.0

c. **(ii)** 12.5%

d. **(i)** Zinc is oxidized at the anode, and the zinc rod slowly gets thinner.

e. **(iv)** Zn^{2+}

f. **(ii)** Zinc is more electropositive than silver, so it displaces silver from the complex.

g. **(ii)** toluene (methylbenzene)

h. **(iii)** The strongly basic alkoxide removes a hydrogen and gives an alkene by elimination.

i. **(ii)** It is a condensation polymer of hexane-1,6-diamine and hexanedioic acid (adipic acid), formed with loss of water.

j. **(iii)** to size the paper, so that ink does not spread or soak through it

k. **(i)** The charcoal is really older than 11,460 years.

Group B Short answers, each on one content area — 40 marks

Question 2 — 5 marks

a. In any spontaneous process the total entropy of the universe (the system and its surroundings together) increases: $\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} > 0$. **[1]**

Marking scheme

- The entropy of the universe increases in every spontaneous process ($\Delta S_{\text{univ}} > 0$).

b. **[2]**

$$\Delta H^\circ = \sum \Delta H_f^\circ(\text{products}) - \sum \Delta H_f^\circ(\text{reactants})$$

$$\Delta H^\circ = [(-634.9) + (-393.5)] - (-1207.6) = -1028.4 + 1207.6 = \mathbf{+179.2\ kJ\ mol^{-1}}$$

The reaction is endothermic: the kiln has to supply heat.

Marking scheme

- $\Delta H^\circ = \sum \Delta H_f^\circ(\text{products}) - \sum \Delta H_f^\circ(\text{reactants})$ with the values.
- $\Delta H^\circ = +179.2\ \text{kJ mol}^{-1}$.

c. **[2]**

$$\Delta S^\circ = (38.1 + 213.8) - 91.7 = +160.2\ \text{J K}^{-1}\text{mol}^{-1} = 0.1602\ \text{kJ K}^{-1}\text{mol}^{-1}$$

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$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = 179.2 - 298 \times 0.1602 = +131.5 \text{ kJ mol}^{-1}$$

ΔG° is positive at 25 °C, so limestone does not break up on its own at room temperature. Because ΔS° is positive (a gas is formed), $-T\Delta S^\circ$ grows as T rises, and ΔG° becomes negative above

$$T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{179.2}{0.1602} \approx 1119 \text{ K} \approx \mathbf{846\ °C}$$

That is why the kiln is run at about 900 °C or more.

Marking scheme

- $\Delta S^\circ = +160.2$ J K^{-1} mol^{-1} and $\Delta G^\circ = +131.5$ kJ mol^{-1} at 25 °C: positive, so not spontaneous at room temperature.
- $\Delta G^\circ < 0$ above $T = \Delta H^\circ / \Delta S^\circ \approx 1119$ K (about 846 °C), so strong heating is needed.

OR

a. The **order** of a reaction is the sum of the powers to which the concentrations of the reactants are raised in the experimentally found rate law. For rate $= k[\text{A}]^x[\text{B}]^y$, the order is $x + y$. **[1]**

Marking scheme

- The sum of the powers of the concentration terms in the experimental rate law.

b. For a first-order reaction, **[2]**

$$k = \frac{2.303}{t} \log \frac{[\text{A}]_0}{[\text{A}]} = \frac{2.303}{30} \log \frac{0.80}{0.20} = \frac{2.303 \times 0.602}{30} = \mathbf{0.0462\ min^{-1}}$$

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.0462} = \mathbf{15\ min}$$

(The concentration has halved twice, $0.80 \to 0.40 \to 0.20$, in 30 minutes: two half-lives of 15 minutes.)

Marking scheme

- $k = \frac{2.303}{t} \log \frac{[\text{A}]_0}{[\text{A}]} = 0.0462$ min^{-1}.
- $t_{1/2} = 0.693/k = 15$ min.

c. From the Arrhenius equation, **[2]**

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$$

with $k_2/k_1 = 2$, $T_1 = 298$ K, $T_2 = 308$ K:

$$E_a = \frac{2.303 \times 8.314 \times \log 2 \times 298 \times 308}{10} = \frac{2.303 \times 8.314 \times 0.301 \times 91{,}784}{10}$$

$$E_a \approx 52{,}900 \text{ J mol}^{-1} = \mathbf{52.9\ kJ\ mol^{-1}}$$

Only collisions with energy E_a or more react, and they are a small fraction of all collisions, $e^{-E_a/RT}$, in the far

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tail of the energy distribution. A small rise in temperature makes that tail much larger: here the fraction with at least 52.9 kJ mol^{-1} doubles, although the average energy (proportional to T, 308/298) rises by only 3%.

Marking scheme

- The Arrhenius equation in two-temperature form with $k_2/k_1 = 2$, 298 K and 308 K, giving $E_a \approx 52.9$ kJ mol^{-1}.
- The fraction of collisions with energy $\geq E_a$ ($e^{-E_a/RT}$) doubles, though the average energy rises only slightly.

Question 3 — 5 marks

a. A **standard solution** is a solution whose concentration (strength) is known exactly, made by dissolving a known mass of a primary standard substance in a known volume of solution, or found by titration against one. **[1]**

Marking scheme

- A solution of exactly known concentration.

b. Oxalic acid is dibasic (and in this reaction each molecule gives 2 electrons), so its equivalent weight is $126/2 = 63$. **[2]**

$$N = \frac{\text{mass}}{E \times V(\text{L})} = \frac{0.63}{63 \times 0.100} = \mathbf{0.1\ N}$$

Marking scheme

- Equivalent weight of the crystals $= 126/2 = 63$.
- $N = \dfrac{0.63}{63 \times 0.100} = 0.1$ N.

c. By the normality equation, $N_1V_1 = N_2V_2$: **[2]**

$$0.1 \times 20.0 = N_2 \times 25.0 \quad \Rightarrow \quad N_2 = \mathbf{0.08\ N}$$

In acid, $E(\text{KMnO}_4) = 158/5 = 31.6$, so strength $= 0.08 \times 31.6 = \mathbf{2.53\ g/L}$.

With hydrochloric acid the result would be **too low**. Permanganate oxidizes chloride ions to chlorine as well as oxidizing the oxalic acid, so more than 25.0 mL would be run in before the pink color lasts. A larger V_2 in $N_2 = N_1V_1/V_2$ gives a smaller normality than the true one.

Marking scheme

- $N(\text{KMnO}_4) = 0.1 \times 20.0/25.0 = 0.08$ N and strength $= 0.08 \times 31.6 = 2.53$ g/L.
- Too low: KMnO_4 also oxidizes Cl^- to Cl_2, so a larger volume is used and N_1V_1/V_2 comes out smaller.

Question 4 — 5 marks

a. A **ligand** is an ion or molecule with a lone pair of electrons that it gives to the central metal atom or ion to form a coordinate bond; in $[\text{Fe(CN)}_6]^{3-}$ the ligands are the six cyanide ions, CN^-. **[2]**

The **coordination number** is the number of coordinate bonds the ligands form with the central metal ion; in $[\text{Fe(CN)}_6]^{3-}$ it is **6**.

Marking scheme

- Ligand: a species that donates a lone pair to the central metal ion (here CN^-).
- Coordination number: the number of coordinate bonds to the central ion (here 6).

b. In a complex, the ligands split the metal ion's d orbitals into two sets of slightly different energy. If the d orbitals are partly filled, an electron can absorb visible light of just the energy of the gap, Δ_o, and jump to the higher set (a **d–d transition**). The light that is not absorbed reaches our eyes, so we see the complementary color. **[1]**

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Marking scheme

- Partly filled d orbitals split by the ligands; a d–d transition absorbs part of the visible light, and the complementary color is seen.

c. In an octahedral field the d orbitals split into a lower t_{2g} set (three orbitals) and an upper e_g set (two), Δ_o apart. **[2]**

- $[Fe(H_2O)_6]^{3+}$: water is a weak-field ligand, so Δ_o is smaller than the pairing energy P. The electrons fill singly first: $t_{2g}^3 e_g^2$, **high spin**, with **5 unpaired electrons** (strongly paramagnetic).
- $[Fe(CN)_6]^{3-}$: cyanide is a strong-field ligand, $\Delta_o > P$, so all five electrons pair up in the lower set: $t_{2g}^5 e_g^0$, **low spin**, with **1 unpaired electron** (weakly paramagnetic).

Marking scheme

- $[Fe(H_2O)_6]^{3+}$: weak field, $t_{2g}^3 e_g^2$, high spin, 5 unpaired electrons.
- $[Fe(CN)_6]^{3-}$: strong field, t_{2g}^5, low spin, 1 unpaired electron.

Question 5 — 5 marks

a. The chief ore is **zinc blende**, ZnS. After concentration by froth flotation it is roasted in excess air: **[2]**

$$2\,ZnS + 3\,O_2 \xrightarrow{\Delta} 2\,ZnO + 2\,SO_2\uparrow$$

Marking scheme

- Zinc blende, ZnS.
- $2\,ZnS + 3\,O_2 \longrightarrow 2\,ZnO + 2\,SO_2$, balanced.

b. Zinc oxide is mixed with coke and heated to about 1400 °C in a retort; the zinc distils off as vapor and is condensed: **[1]**

$$ZnO + C \xrightarrow{1400\,^\circ C} Zn(g) + CO\uparrow$$

Marking scheme

- $ZnO + C \longrightarrow Zn + CO$ with coke at about 1400 °C.

c. Zinc has the more negative reduction potential, so it is more easily oxidized than iron. Where the iron is exposed and wet, the zinc and iron form a small cell in which zinc is the **anode** and is oxidized ($Zn \longrightarrow Zn^{2+} + 2\,e^-$), while the iron is the **cathode** and receives the electrons, so it is not oxidized. The zinc corrodes in place of the iron: **sacrificial (cathodic) protection**, which lasts as long as zinc remains near the scratch. **[2]**

Marking scheme

- Zinc (−0.76 V) is more easily oxidized than iron (−0.45 V), so zinc becomes the anode.
- Zinc corrodes instead of the iron, which is the cathode and is protected (sacrificial protection).

Question 6 — 5 marks

a. **2-Bromo-2-methylpropane** (tert-butyl bromide). The carbon carrying the bromine is joined to three other carbons, so it is a **tertiary** haloalkane. **[1]**

Marking scheme

- 2-Bromo-2-methylpropane, tertiary.

b. Hydrolysis gives a primary alcohol, **butan-1-ol**: **[2]**

$$CH_3CH_2CH_2CH_2Br + KOH(aq) \xrightarrow{\Delta} CH_3CH_2CH_2CH_2OH + KBr$$

A primary alcohol is oxidized first to an aldehyde and, with excess oxidizing agent, to the carboxylic acid, **butanoic acid**:

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$$CH_3CH_2CH_2CH_2OH \xrightarrow{K_2Cr_2O_7/H^+} CH_3CH_2CH_2CHO \xrightarrow{K_2Cr_2O_7/H^+} CH_3CH_2CH_2COOH$$

Marking scheme

- Hydrolysis to butan-1-ol, equation.
- Oxidation (through butanal) to butanoic acid, equation.

c. $(CH_3)_3CBr$ reacts by the **SN1** mechanism. Its slow step is the ionization of the C–Br bond to a **tertiary carbocation**, $(CH_3)_3C^+$, which is stabilized by the three electron-donating methyl groups (and its crowded carbon is hard for a nucleophile to reach from behind). The nucleophile joins only in the fast second step. **[2]**

So the rate depends only on the haloalkane: rate $= k[(CH_3)_3CBr]$, a first-order reaction, and adding more OH^- does not change it. 1-Bromobutane would give an unstable primary carbocation, so it reacts by the slower SN2 path instead.

Marking scheme

- SN1: the slow step is ionization to a stable tertiary carbocation (stabilized by three methyl groups), which a primary haloalkane cannot form.
- The nucleophile is not in the slow step, so rate = k[RBr], independent of $[OH^-]$.

OR

a. Anisole is **methoxybenzene**, $C_6H_5OCH_3$. **[1]**

Marking scheme

- Methoxybenzene, $C_6H_5OCH_3$.

b. Sodium phenoxide and iodomethane (or bromomethane): **[2]**

$$C_6H_5ONa + CH_3I \longrightarrow C_6H_5OCH_3 + NaI$$

The $-OCH_3$ group activates the ring, so bromine in ethanoic acid substitutes it without a catalyst, mainly at the para position, giving **4-bromoanisole** (1-bromo-4-methoxybenzene), with some 2-bromoanisole:

$$C_6H_5OCH_3 + Br_2 \xrightarrow{CH_3COOH} BrC_6H_4OCH_3 + HBr$$

Marking scheme

- Williamson's synthesis from sodium phenoxide and iodomethane:

$$C_6H_5ONa + CH_3I \longrightarrow C_6H_5OCH_3 + NaI$$

- Bromination to 4-bromoanisole (main product), with HBr.

c. The violet color shows **phenol**, and the iodoalkane is iodoethane, so Z has a phenyl and an ethyl group on its oxygen: Z is **ethoxybenzene**, $C_6H_5OC_2H_5$ ($C_8H_{10}O$). **[2]**

$$C_6H_5OC_2H_5 + HI \xrightarrow{\Delta} C_6H_5OH + C_2H_5I$$

HI first protonates the ether's oxygen, and the iodide ion then attacks a carbon next to the oxygen by SN2: the **ethyl** carbon, which can be reached from behind, so that C–O bond breaks. The bond between oxygen and the **ring** has partial double-bond character (a lone pair of the oxygen is delocalized into the ring), and an sp^2 ring carbon cannot be attacked from behind, so no iodobenzene forms.

Marking scheme

- Z is ethoxybenzene, $C_6H_5OC_2H_5$ (phenol from the $FeCl_3$ test, two-carbon iodoalkane), with the equation.
- I^- attacks the ethyl carbon (SN2); the ring C–O bond, partly double by resonance, with an sp^2 carbon, is not broken.

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Question 7 — 5 marks

a. A **violet** color appears, from a complex of iron(III) with phenoxide. **[1]**

Marking scheme

- A violet color.

b. When phenol loses H^+, the negative charge of the **phenoxide ion** is spread over the oxygen and the ortho and para carbons of the ring by resonance, which stabilizes the ion, so phenol ionizes to a small extent ($K_a \approx 10^{-10}$). **[2]**

In the **ethoxide ion** the charge stays on the oxygen, and the electron-donating ethyl group even pushes more electron density onto it, so the ion is less stable and ethanol hardly ionizes at all.

Marking scheme

- Phenoxide ion is stabilized by resonance (charge delocalized into the ring).
- Ethoxide has no resonance, and the +I ethyl group destabilizes it further, so ethanol is the weaker acid.

c. The –OH group of phenol gives electrons to the ring by resonance, so the ring is **activated** (attacked easily, under mild conditions), and the extra electron density is at the ortho and para positions, so it is an **ortho/para director**. **[2]**

The $-NO_2$ group of nitrobenzene withdraws electrons from the ring by resonance and induction, so the ring is **deactivated** (attacked only under harsh conditions), and the ortho and para positions are made the most electron-poor, so the new group goes to the **meta** position.

Marking scheme

- –OH donates electrons: ring activated, mild conditions, ortho and para products.
- $-NO_2$ withdraws electrons: ring deactivated, harsh conditions, meta product.

Question 8 — 5 marks

a. A **Grignard reagent** is an alkylmagnesium (or arylmagnesium) halide, made by treating a haloalkane with magnesium in dry ether: general formula **RMgX**, for example CH_3MgBr. **[1]**

Marking scheme

- An alkyl or aryl magnesium halide, RMgX.

b. (i) With methanal, a primary alcohol with one more carbon, **ethanol**: **[2]**

$$HCHO + CH_3MgBr \longrightarrow CH_3CH_2OMgBr \xrightarrow{H_2O/H^+} CH_3CH_2OH + Mg(OH)Br$$

(ii) With carbon dioxide (dry ice), a carboxylic acid, **ethanoic acid**:

$$CO_2 + CH_3MgBr \longrightarrow CH_3COOMgBr \xrightarrow{H_2O/H^+} CH_3COOH + Mg(OH)Br$$

Marking scheme

- With methanal: ethanol, equation.
- With CO_2: ethanoic acid, equation.

c. The test is the **carbylamine (isocyanide) test**, which only a primary amine gives. Two amines have the formula C_2H_7N: ethanamine, $CH_3CH_2NH_2$ (primary), and N-methylmethanamine, $(CH_3)_2NH$ (secondary). Y gives no isocyanide, so Y is **N-methylmethanamine**. Its isomer, ethanamine, gives the foul-smelling ethyl isocyanide: **[2]**

$$CH_3CH_2NH_2 + CHCl_3 + 3\,KOH \xrightarrow{\Delta} CH_3CH_2NC + 3\,KCl + 3\,H_2O$$

Marking scheme

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- Only primary amines give the carbylamine test; of the two C_2H_7N amines, Y is the secondary one, N-methylmethanamine, $(CH_3)_2NH$.
- The balanced equation for ethanamine.

Question 9 — 5 marks

a. **Clinker** is the hard, greyish lumps (nodules) that come out of the rotary kiln when the raw mix of limestone and clay is heated to about 1400–1500 °C; it is mostly calcium silicates and aluminates, and it is ground with a little gypsum to make cement. **[1]**

Marking scheme

- The fused lumps from the kiln (limestone and clay heated to about 1450 °C), ground with gypsum to give cement.

b. Cement does not harden by drying: its compounds react with water (**hydration**). The calcium silicates form a gel of calcium silicate hydrate, which binds the sand and gravel together, and calcium hydroxide: **[2]**

$$2\,Ca_3SiO_5 + 6\,H_2O \longrightarrow 3\,CaO \cdot 2\,SiO_2 \cdot 3\,H_2O + 3\,Ca(OH)_2$$

Tricalcium silicate reacts in hours and days, giving the early strength; dicalcium silicate reacts over weeks and months, giving the later strength, so concrete keeps getting stronger.

Marking scheme

- Setting and hardening are hydration reactions of the calcium silicates, giving a binding gel (calcium silicate hydrate) and $Ca(OH)_2$.
- Tricalcium silicate gives early strength (days), dicalcium silicate later strength (weeks to months).

c. 100 g of $CaCO_3$ gives 56 g of CaO, so 1000 kg gives $1000 \times \dfrac{56}{100} = \mathbf{560\ kg}$ of CaO (and 440 kg of carbon dioxide). **[1]**

Marking scheme

- $1000 \times 56/100 = 560$ kg of CaO.

d. Concrete hardens by the hydration of the calcium silicates, which needs water for days and weeks. If the slab dries out, the reaction stops for want of water and the concrete stays weak and may crack; keeping it wet (**curing**) lets the hydration go on. **[1]**

Marking scheme

- Hardening is hydration, which needs water; curing keeps the reaction going so the concrete gains full strength.

Group C Long answers, each on one content area — 24 marks

Question 10 — 8 marks

a. The solution holds a large reserve of both the weak acid, CH_3COOH, and its conjugate base, CH_3COO^- (from the fully ionized salt). **[3]**

When a little acid is added, the ethanoate ions take up the H^+ ions and form weakly ionized ethanoic acid:

$$CH_3COO^- + H^+ \longrightarrow CH_3COOH$$

When a little base is added, the ethanoic acid neutralizes the OH^- ions:

$$CH_3COOH + OH^- \longrightarrow CH_3COO^- + H_2O$$

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Either way the added ions are removed and only the ratio $[CH_3COO^-]/[CH_3COOH]$ changes slightly, so the pH hardly changes.

Marking scheme

- The buffer holds large amounts of the weak acid and of its conjugate base (from the salt).
- Added H^+ is removed by CH_3COO^- (equation).
- Added OH^- is removed by CH_3COOH (equation), so the ratio and the pH change very little.

b. **[3]**

$$pK_a = -\log(1.75 \times 10^{-5}) = 4.76$$

By the Henderson–Hasselbalch equation:

$$\text{pH} = pK_a + \log\frac{[\text{salt}]}{[\text{acid}]} = 4.76 + \log\frac{0.15}{0.10} = 4.76 + 0.18 = \mathbf{4.93}$$

Marking scheme

- $pK_a = 4.76$.
- $pH = pK_a + \log([\text{salt}]/[\text{acid}])$ (Henderson–Hasselbalch).
- $pH = 4.93$.

c. In pure water, $K_{sp} = s^2$, so $s = \sqrt{1.8 \times 10^{-10}} = 1.34 \times 10^{-5}$ mol/L. **[2]**

In 0.010 M NaCl, $[Cl^-] \approx 0.010$ M (the chloride from AgCl is negligible), so $s' = \dfrac{K_{sp}}{0.010} = 1.8 \times 10^{-8}$ mol/L.

$$\frac{s}{s'} = \frac{1.34 \times 10^{-5}}{1.8 \times 10^{-8}} \approx \mathbf{750}$$

AgCl is about 750 times less soluble in the salt solution: the **common ion** Cl^- pushes the equilibrium $AgCl(s) \rightleftharpoons Ag^+ + Cl^-$ to the left.

Marking scheme

- Solubility in water $= \sqrt{K_{sp}} = 1.34 \times 10^{-5}$ mol/L.
- In 0.010 M NaCl, $s' = K_{sp}/0.010 = 1.8 \times 10^{-8}$ mol/L: about 750 times less (common ion effect).

OR

a. The **standard hydrogen electrode** is a platinum foil coated with platinum black, dipped in a solution of H^+ ions of 1 M concentration (activity 1), with pure hydrogen gas at 1 atm (1 bar) bubbled over it at 25 °C: $Pt,\ H_2(1\,\text{atm}) \mid H^+(1\,\text{M})$. Its potential is taken as **exactly 0 V**. **[3]**

To find E° of zinc, a zinc rod in 1 M Zn^{2+} solution is joined to the SHE through a salt bridge and a voltmeter: $Zn \mid Zn^{2+}(1\,\text{M}) \,||\, H^+(1\,\text{M}) \mid H_2(1\,\text{atm}),\ Pt$. The cell's emf is 0.76 V, and the zinc is found to be the negative electrode (anode), so $E^\circ_{Zn^{2+}/Zn} = 0 - 0.76 = -0.76$ V.

Marking scheme

- SHE: platinized platinum in 1 M H^+ with H_2 at 1 atm, 25 °C.
- Its potential is taken as 0 V (the reference).
- Zinc in 1 M Zn^{2+} is coupled with the SHE; the measured emf (0.76 V) with zinc as the anode gives E° = −0.76 V.

b. **[3]**

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} = 0.34 - (-0.76) = 1.10\ \text{V}$$

The cell reaction is $Zn + Cu^{2+} \longrightarrow Zn^{2+} + Cu$, with n = 2. By the Nernst equation:

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$$E\text{cell} = E^\circ\text{cell} - \frac{0.0592}{n}\log\frac{[Zn^{2+}]}{[Cu^{2+}]} = 1.10 - \frac{0.0592}{2}\log\frac{0.10}{0.0010} = 1.10 - 0.0296\times 2 = \mathbf{1.04\ V}$$

Marking scheme

- $E^\circ\text{cell} = 1.10$ V.
- The Nernst equation with n = 2 and $Q = [Zn^{2+}]/[Cu^{2+}] = 100$.
- $E\text{cell} = 1.04$ V.

c. **[2]**

$$\Delta G^\circ = -nFE^\circ\text{cell} = -2\times 96{,}485\times 1.10 = -212{,}267\ \text{J} \approx \mathbf{-212\ kJ\ mol^{-1}}$$

$$\Delta G = -nFE\text{cell} = -2\times 96{,}485\times 1.04 \approx \mathbf{-201\ kJ\ mol^{-1}}$$

Both are negative, so the reaction is spontaneous either way. In Nischal's cell the product ion, Zn^{2+}, is a hundred times more concentrated than the reactant ion, Cu^{2+} (Q = 100 > 1). The reaction is already some way towards its products, so it has less tendency to go on: $\Delta G = \Delta G^\circ + RT\ \ln Q$ is less negative, and the emf is lower.

Marking scheme

- $\Delta G^\circ = -nFE^\circ = -212$ kJ mol^{-1} and $\Delta G = -nFE = -201$ kJ mol^{-1}.
- Less negative because Q = $[Zn^{2+}]/[Cu^{2+}] = 100 > 1$: more product and less reactant than in the standard cell.

Question 11 — 8 marks

a. The Cannizzaro reaction is given only by aldehydes with **no α-hydrogen** (no hydrogen on the carbon next to the C=O). Benzaldehyde has none (its CHO is joined to the ring), so with concentrated alkali two molecules react: one is oxidized to the acid (as its salt) and the other reduced to the alcohol (a **disproportionation**): **[3]**

$$2\,C_6H_5CHO + NaOH(\text{conc}\cdot) \longrightarrow C_6H_5COONa + C_6H_5CH_2OH$$

The products are sodium benzoate and phenylmethanol (benzyl alcohol). Ethanal has three α-hydrogens, so with alkali it gives the aldol reaction instead.

Marking scheme

- Only aldehydes without α-hydrogen give the Cannizzaro reaction; benzaldehyde has none, ethanal has three.
- The balanced equation.
- Products sodium benzoate and benzyl alcohol: one molecule oxidized, the other reduced (disproportionation).

b. Aldol condensation (addition): two molecules of ethanal join: **[2]**

$$2\,CH_3CHO \xrightarrow{\text{dil. NaOH}} CH_3CH(OH)CH_2CHO$$

The product is **3-hydroxybutanal** (aldol). On warming it loses water to give but-2-enal.

Marking scheme

- The equation $2\,CH_3CHO \longrightarrow CH_3CH(OH)CH_2CHO$.
- The product named, 3-hydroxybutanal (aldol).

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c. The 2,4-DNP test shows a C=O group, and the iodoform test a CH_3CO^- group. The only carbonyl compounds C_4H_8O are butanal, 2-methylpropanal and butan-2-one, and only the ketone has a CH_3CO^- group, so P is a methyl ketone: **butan-2-one**, $CH_3COCH_2CH_3$. **[3]**

The yellow precipitate is iodoform (the iodoform test):

$$CH_3COCH_2CH_3 + 3\,I_2 + 4\,NaOH \longrightarrow CHI_3 \downarrow + CH_3CH_2COONa + 3\,NaI + 3\,H_2O$$

P is a **ketone**: it has no hydrogen on its carbonyl carbon, so it cannot be oxidized by a mild oxidizing agent like Tollens' reagent, and the silver ions are not reduced to silver.

Marking scheme

- P is butan-2-one, $CH_3COCH_2CH_3$ (C=O from 2,4-DNP, CH_3CO- from the iodoform test).
- The balanced iodoform equation (CHI_3 the yellow precipitate).
- A ketone has no H on the carbonyl carbon, so it is not oxidized by Tollens' reagent.

Question 12 — 8 marks

a. Both form hydrogen bonds, but a carboxylic acid forms two hydrogen bonds between each pair of molecules (its O–H to the other's C=O, both ways), so the molecules exist as **dimers** even in the vapor. These dimers behave as larger units, and more energy is needed to separate them, so the boiling point is higher than that of the alcohol, whose molecules are joined by single, weaker hydrogen bonds. **[2]**

Marking scheme

- Ethanoic acid forms two hydrogen bonds per pair of molecules (cyclic dimers).
- The dimers need more energy to separate than the singly H-bonded alcohol molecules, so the b.p. is higher.

b. **[3]**

1. With ammonia, ethanoic acid gives ammonium ethanoate: $CH_3COOH + NH_3 \longrightarrow CH_3COONH_4$
2. Heating the ammonium salt removes water and gives ethanamide:

$$CH_3COONH_4 \xrightarrow{\Delta} CH_3CONH_2 + H_2O$$

3. Hofmann bromamide reaction with bromine and potassium hydroxide gives methanamine, one carbon shorter:

$$CH_3CONH_2 + Br_2 + 4\,KOH \longrightarrow CH_3NH_2 + K_2CO_3 + 2\,KBr + 2\,H_2O$$

Marking scheme

- Ethanoic acid + NH_3 → ammonium ethanoate.
- Heat → ethanamide ($-\,H_2O$).
- Ethanamide + Br_2 + 4KOH → methanamine (Hofmann bromamide), balanced.

c. **A is methanoic acid** and **B is ethanoic acid**. At the same concentration the lower pH belongs to the stronger acid. In ethanoic acid the methyl group pushes electrons towards the carboxylate (+I effect), which destabilizes the ethanoate ion and makes the acid weaker; methanoic acid has no alkyl group, so its anion is more stable and the acid is stronger (pK_a 3.75 against 4.76). **[3]**

Methanoic acid, HCOOH, has a hydrogen on the carbonyl carbon: it contains an **aldehyde group** (H–C=O) as well as a carboxyl group. So, like an aldehyde, it is easily oxidized, to carbon dioxide and water, and reduces the silver ions of Tollens' reagent to a **silver mirror**; ethanoic acid has a methyl group in that place and gives none. So the mirror comes from A:

$$HCOOH + 2\,[Ag(NH_3)_2]^+ + 2\,OH^- \longrightarrow 2\,Ag \downarrow + CO_2 + 2\,H_2O + 4\,NH_3$$

Marking scheme

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- A (lower pH) is methanoic acid, the stronger acid: the +I methyl group of ethanoic acid destabilizes its anion.
- Methanoic acid has an aldehyde group (H–C=O), so A gives the silver mirror (oxidized to CO_2); ethanoic acid has none.
- The balanced equation.

OR

a. A base accepts a proton with the lone pair on its nitrogen. In aniline that lone pair is **delocalized into the benzene ring** by resonance, so it is less available to take up a proton; protonating it would also lose that resonance stabilization. In ammonia the lone pair is held only on the nitrogen and is fully available, so ammonia is the stronger base (pK_b about 4.75 against 9.4 for aniline). **[2]**

Marking scheme

- The lone pair on aniline's N is delocalized into the ring by resonance.
- It is less available for a proton than ammonia's localized lone pair, so aniline is the weaker base.

b. **[3]**

1. **Diazotization**: aniline in hydrochloric acid with sodium nitrite (which gives nitrous acid) at 0–5 °C forms benzenediazonium chloride:

$$C_6H_5NH_2 + NaNO_2 + 2\,HCl \xrightarrow{0\text{–}5\ ^\circ C} C_6H_5N_2{}^+Cl^- + NaCl + 2\,H_2O$$

2. The temperature is kept at 0–5 °C because the diazonium salt decomposes (to phenol and nitrogen) when warm.
3. **Coupling**: the cold diazonium salt is added to naphthalen-2-ol in sodium hydroxide solution; the scarlet azo dye, 1-phenylazo-2-naphthol, forms:

$$C_6H_5N_2{}^+Cl^- + C_{10}H_7OH \xrightarrow{NaOH} C_6H_5N{=}N{-}C_{10}H_6OH + HCl$$

Marking scheme

- Diazotization: aniline + $NaNO_2$ + HCl → benzenediazonium chloride (equation).
- Condition 0–5 °C (the salt decomposes when warm).
- Coupling with naphthalen-2-ol in NaOH → scarlet 1-phenylazo-2-naphthol (equation).

c. The $-NH_2$ group activates the ring so strongly that all three ortho and para positions are brominated. Its effect is reduced by **protecting** it first: **[3]**

1. **Acetylation**: aniline with ethanoic anhydride (or ethanoyl chloride) gives acetanilide, $C_6H_5NHCOCH_3$. The nitrogen's lone pair is now shared with the C=O as well, so the ring is less activated, and the bulky group hinders the ortho positions.
2. **Bromination**: acetanilide with bromine in ethanoic acid gives mainly 4-bromoacetanilide.
3. **Hydrolysis**: boiling with acid or alkali removes the acetyl group and gives **4-bromoaniline**.

Marking scheme

- Protect the amino group by acetylation to acetanilide (less activating, ortho positions hindered).
- Brominate to 4-bromoacetanilide.
- Hydrolyze to 4-bromoaniline.

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