Grade 12 Chemistry Model Paper 2

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.

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Group A Multiple choice — 11 marks

Question 1 — 11 × 1 = 11

a. **(iii)** 0.2 N

b. **(iv)** 3.2×10^{-11}

c. **(i)** -33.2 kJ

d. **(iii)** It gives a path of lower activation energy, so both the forward and backward reactions go faster.

e. **(iii)** iron

f. **(ii)** Its standard reduction potential is positive, so it cannot reduce H^+ ions to hydrogen.

g. **(ii)** a mixture of ethanol with petrol, used as a motor fuel

h. **(ii)** N-phenylhydroxylamine

i. **(ii)** PPC gives out less heat as it sets, so a thick mass cracks less, and it resists water and sulphates better.

j. **(iii)** antipyretic and analgesic

k. **(iii)** It is uranium-234, with 4 fewer neutrons than uranium-238.

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

Question 2 — 5 marks

a. The **standard electrode potential** of an electrode is its potential measured against the standard hydrogen electrode (taken as 0 V) when all the substances are in their standard states: ions at 1 M concentration, gases at 1 atm (1 bar), at 25 °C (298 K). **[1]**

Marking scheme

- The potential against the SHE with ions at 1 M, gases at 1 atm, at 25 °C.

b. Nickel has the lower reduction potential, so it is the **anode** (oxidized), and silver the **cathode**: **[2]**

$$\underset{\text{anode}}{\text{Ni(s)} \mid \text{Ni}^{2+}(1\,\text{M})} \parallel \underset{\text{cathode}}{\text{Ag}^{+}(1\,\text{M}) \mid \text{Ag(s)}}$$

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} = 0.80 - (-0.26) = \mathbf{1.06\,V}$$

The cell reaction is $\text{Ni} + 2\,\text{Ag}^+ \longrightarrow \text{Ni}^{2+} + 2\,\text{Ag}$.

Marking scheme

- Cell notation $\text{Ni} \mid \text{Ni}^{2+} \parallel \text{Ag}^+ \mid \text{Ag}$, with nickel the anode and silver the cathode.
- $E^\circ_{\text{cell}} = 0.80 - (-0.26) = 1.06$ V.

c. **No.** Aluminium (-1.66 V) has a lower reduction potential than zinc (-0.76 V), so it is the stronger reducing agent and gives electrons to the zinc ions: **[2]**

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$$2\,Al + 3\,Zn^{2+} \longrightarrow 2\,Al^{3+} + 3\,Zn \qquad E^\circ_{cell} = -0.76 - (-1.66) = +0.90\ V$$

E°_{cell} is positive (so $\Delta G°$ is negative): the reaction is spontaneous. The can would dissolve and zinc would be deposited, so the solution would be spoiled and the can holed.

Marking scheme

- No: Al (-1.66 V) is a stronger reducing agent than Zn (-0.76 V) and displaces it.
- The reaction

$$2\,Al + 3\,Zn^{2+} \longrightarrow 2\,Al^{3+} + 3\,Zn$$

has $E^\circ = +0.90$ V, positive, so spontaneous.

OR

a. Substances always react with each other in the ratio of their equivalent weights: one gram-equivalent of one substance reacts with exactly one gram-equivalent of another. So in a titration, at the equivalence point, $N_1V_1 = N_2V_2$. **[1]**

Marking scheme

- Substances react in equal numbers of gram-equivalents ($N_1V_1 = N_2V_2$).

b. **[2]**

$$\text{HCl taken} = N \times V = 0.50 \times 50.0 = 25.0\ \text{meq}$$

$$\text{HCl left over} = \text{NaOH used} = 0.40 \times 25.0 = 10.0\ \text{meq}$$

$$\text{HCl used by } CaCO_3 = 25.0 - 10.0 = \mathbf{15.0\ meq}$$

Marking scheme

- HCl taken 25.0 meq and HCl left over (= NaOH) 10.0 meq.
- HCl used by $CaCO_3$ = 15.0 meq.

c. The equivalent weight of $CaCO_3$ is $100/2 = 50$, so 15.0 meq of it weighs $15.0 \times 50 = 750$ mg $= 0.75$ g. **[2]**

$$\%\ CaCO_3 = \frac{0.75}{1.25} \times 100 = \mathbf{60\%}$$

This is a **back titration**. Limestone is insoluble and reacts slowly with the acid, so its end point could not be seen in a direct titration. Dissolving it in a known excess of acid lets the reaction finish, and the excess is then titrated easily.

Marking scheme

- Mass of $CaCO_3 = 15.0 \times 50$ mg $= 0.75$ g, so 60%.
- Back titration because limestone is insoluble and reacts slowly; a direct end point cannot be seen.

Question 3 — 5 marks

a. A **pseudo-first-order** reaction is one that has a higher molecularity (here two molecules react) but behaves as first order, because one reactant (here water, the solvent) is in such large excess that its concentration hardly changes during the reaction. **[1]**

Marking scheme

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- A reaction of higher order that behaves as first order because the other reactant is in large excess (its concentration stays constant).

b. After 40 min, 70% of the ester is left, so $[A]_0/[A] = 100/70$. **[2]**

$$k = \frac{2.303}{t}\log\frac{[A]_0}{[A]} = \frac{2.303}{40}\log\frac{100}{70} = \frac{2.303 \times 0.155}{40} = \mathbf{8.92 \times 10^{-3}\ min^{-1}}$$

Marking scheme

- The first-order equation with $[A]_0/[A] = 100/70$ (not 100/30).
- $k = 8.92 \times 10^{-3}$ min^{-1}.

c. For 90% hydrolysis, 10% is left: $[A]_0/[A] = 10$, and $\log 10 = 1$. **[2]**

$$t_{90\%} = \frac{2.303}{k}\log 10 = \frac{2.303}{8.92 \times 10^{-3}} \approx \mathbf{258\ min}$$

She is wrong. In a first-order reaction the time to use up a given fraction depends only on k: $t = \frac{2.303}{k}\log\frac{[A]_0}{[A]}$, and the ratio $[A]_0/[A]$ for 90% is 10 whatever the starting concentration. With twice the ester the rate is twice as great at every stage, but there is twice as much to use up, so it still takes 258 minutes.

Marking scheme

- $t_{90\%} = (2.303/k)\log 10 \approx 258$ min.
- No: for a first-order reaction the time for a given fraction is independent of the initial concentration (the ratio is 10 either way).

Question 4 — 5 marks

a. Any two of: **haematite**, Fe_2O_3; **magnetite**, Fe_3O_4; **limonite**, $2\,Fe_2O_3 \cdot 3\,H_2O$; **siderite**, $FeCO_3$; iron pyrites, FeS_2 (not used for extraction). **[2]**

Marking scheme

- One ore named with its correct formula.
- A second ore named with its correct formula.

b. Limestone is a **flux**. It breaks up into lime, which combines with the sandy impurity (silica) of the ore to form a fusible **slag**, calcium silicate, that floats on the molten iron and is run off: **[1]**

$$CaCO_3 \longrightarrow CaO + CO_2 \qquad CaO + SiO_2 \longrightarrow CaSiO_3$$

Marking scheme

- Flux: CaO from limestone removes silica as calcium silicate slag (both equations).

c. The iron is not burnt off, so its mass stays the same; only the carbon falls, and the total mass falls with it. **[2]**

Iron in 1.00 t of pig iron = 96.00% of 1000 kg = **960 kg**. In the steel this iron is 99.50% of the mass:

$$\text{mass of steel} = \frac{960}{0.995} = 964.8\ \text{kg} \qquad \text{carbon left} = 964.8 - 960 = 4.8\ \text{kg}$$

$$\text{carbon burnt off} = 40.0 - 4.8 = \mathbf{35.2\ kg}$$

(Taking 4.00% − 0.50% = 3.50% of 1000 kg, 35.0 kg, forgets that the steel weighs less than the pig iron.)

Marking scheme

- The iron (960 kg) stays constant and is 99.5% of the steel: steel 964.8 kg, carbon left 4.8 kg.

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- Carbon burnt off $= 40.0 - 4.8 = 35.2$ kg.

Question 5 — 5 marks

a. Any two of: they show **variable oxidation states**; they form **colored** ions and compounds; they form **complexes**; they and their compounds are good **catalysts**; many are **paramagnetic**; they are hard metals with high melting points; they form **alloys** and interstitial compounds. **[2]**

Marking scheme

- One characteristic property.
- A second characteristic property.

b. $2(+1) + 2x + 7(-2) = 0$, so $x = \mathbf{+6}$. Chromium is [Ar] $3d^5\,4s^1$, six electrons beyond argon; in the +6 state all six are used, so it has **no 3d electrons** ($3d^0$). **[1]**

Marking scheme

- Cr is +6 ($2 + 2x - 14 = 0$), with $3d^0$.

c. $\sqrt{n(n+2)} = 5.92$ gives $n(n+2) = 35$, so $\mathbf{n = 5}$ unpaired electrons: in a weak field the ion is $3d^5$, one electron in each d orbital. A +2 ion has lost the two 4s electrons, so the atom is [Ar] $3d^5\,4s^2$: M is **manganese** ($Z = 25$). **[2]**

Mn^{2+} ($3d^5$) has a **half-filled** d subshell, which is especially stable; Mn^{3+} would be $3d^4$, losing that arrangement. So Mn^{3+} is **less stable** than Mn^{2+}, and manganese(III) compounds are readily reduced to manganese(II).

Marking scheme

- $n(n + 2) = 35$, so $n = 5$, the ion is $3d^5$ and M is manganese.
- Mn^{3+} ($3d^4$) is less stable than Mn^{2+}, whose half-filled $3d^5$ is especially stable.

Question 6 — 5 marks

a. $CH_3CHBrCH_3$. The carbon carrying the bromine is joined to two other carbons, so it is a **secondary** haloalkane. **[1]**

Marking scheme

- $CH_3CHBrCH_3$, secondary.

b. Lucas reagent is **anhydrous zinc chloride in concentrated hydrochloric acid**. Shaken with it at room temperature, an alcohol turns into a chloroalkane, which does not dissolve and makes the mixture cloudy: **[2]**

$$CH_3CH(OH)CH_3 + HCl \xrightarrow{ZnCl_2} CH_3CHClCH_3 + H_2O$$

Propan-2-ol (secondary) turns cloudy in about **5 minutes**; **propan-1-ol** (primary) stays clear at room temperature (it reacts only on heating). (A tertiary alcohol would turn cloudy at once.)

Marking scheme

- Lucas reagent: anhydrous $ZnCl_2$ in conc. HCl; the alcohol forms an insoluble chloroalkane (turbidity).
- Propan-2-ol turns cloudy in about 5 minutes; propan-1-ol stays clear at room temperature.

c. With excess HI an ether R–O–R′ gives two iodoalkanes, RI and R′I. Only one organic product means the two groups are the same: X is a **symmetrical** ether. The ethers $C_4H_{10}O$ are ethoxyethane, 1-methoxypropane and 2-methoxypropane, and only ethoxyethane has two equal groups, so X is **ethoxyethane** (diethyl ether), and the product is iodoethane: **[2]**

$$C_2H_5OC_2H_5 + 2\,HI \xrightarrow{\Delta} 2\,C_2H_5I + H_2O$$

Marking scheme

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- One product means a symmetrical ether: of the $C_4H_{10}O$ ethers, X is ethoxyethane.
- $C_2H_5OC_2H_5 + 2\,HI \longrightarrow 2\,C_2H_5I + H_2O$.

OR

a. **Esterification** is the reaction of a carboxylic acid with an alcohol, in the presence of an acid catalyst (concentrated sulphuric acid), to form an ester and water. **[1]**

Marking scheme

- Acid + alcohol $\rightarrow$ ester + water, with an acid catalyst.

b. **[2]**

$$CH_3COOH + C_2H_5OH \overset{\text{conc. } H_2SO_4}{\rightleftharpoons} CH_3COOC_2H_5 + H_2O$$

Alkaline hydrolysis (saponification) gives the salt of the acid and the alcohol:

$$CH_3COOC_2H_5 + NaOH \xrightarrow{\Delta} CH_3COONa + C_2H_5OH$$

Marking scheme

- Esterification equation (with conc. H_2SO_4, reversible).
- Saponification equation: sodium ethanoate and ethanol.

c. Esterification is **reversible** and slow. Concentrated sulphuric acid is a **catalyst** (it protonates the acid's C=O, making the carbon easier for the alcohol to attack), so equilibrium is reached faster; it is also a **dehydrating agent**, taking up the water formed. **[2]**

Removing water and using an **excess of alcohol** both push the equilibrium to the right (Le Chatelier's principle), so more of the acid turns into ester.

Marking scheme

- Conc. H_2SO_4 catalyzes the slow reaction and removes water (dehydrating agent).
- The reaction is reversible; excess alcohol (and removing water) shift the equilibrium towards the ester.

Question 7 — 5 marks

a. The **Sandmeyer reaction**: **[1]**

$$C_6H_5N_2{}^+Cl^- \xrightarrow{CuCl/HCl} C_6H_5Cl + N_2$$

Marking scheme

- Sandmeyer reaction.

b. Chlorine is more electronegative than carbon, so it pulls electrons out of the ring through the σ bond (**−I effect**). This lowers the electron density of the whole ring, so electrophiles attack it more slowly: the ring is **deactivated**. **[2]**

But chlorine also has lone pairs, which it gives back into the ring by resonance (**+R effect**). This puts extra electron density at the **ortho and para** positions only, so of the positions left, those are attacked: chlorine is an ortho/para director. The −I effect is stronger overall, the +R effect decides the positions.

Marking scheme

- −I effect of Cl lowers the ring's electron density: deactivated.
- +R effect of Cl's lone pairs raises the density at ortho and para positions: o/p directing.

c. **[2]**

$$C_6H_5OH + 3\,Br_2\,(aq) \longrightarrow C_6H_2Br_3OH \downarrow + 3\,HBr$$

The white precipitate is 2,4,6-tribromophenol.

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The –OH group gives electrons to the ring by resonance, so the ring of phenol is strongly **activated**, especially at the two ortho and the para positions. In water phenol is partly ionized to the phenoxide ion, more activated still, and the polar water helps polarize the bromine, so no catalyst is needed and all three positions are substituted at once. Benzene's ring has no such group, so it needs $FeBr_3$ to make a strong electrophile, Br^+.

Marking scheme

- The equation, giving 2,4,6-tribromophenol.
- –OH strongly activates the ring (o/p) by resonance, so no catalyst is needed and three Br atoms enter; benzene needs $FeBr_3$.

Question 8 — 5 marks

a. **N,N-Dimethylethanamine**: the nitrogen carries three alkyl groups, so it is a **tertiary (3°)** amine. **[1]**

Marking scheme

- N,N-Dimethylethanamine, tertiary.

b. **[2]**

$$C_2H_5NH_2 + HNO_2 \longrightarrow C_2H_5OH + N_2 \uparrow + H_2O$$

The main organic product is **ethanol** (in practice with some alkene and other products), and bubbles of **nitrogen** gas are given off (brisk effervescence), the reliable sign of a primary aliphatic amine.

Marking scheme

- The balanced equation, ethanol formed.
- Nitrogen gas is evolved (effervescence).

c. **[2]**

$$C_6H_5NH_2 < NH_3 < CH_3NH_2 < (CH_3)_2NH$$

Alkyl groups push electrons towards the nitrogen (**+I effect**), making its lone pair more available for a proton, so the alkyl amines are stronger bases than ammonia, and two methyl groups more than one (in water the dimethylammonium ion is also well solvated). In aniline the lone pair is **delocalized into the benzene ring**, so it is the weakest base of the four.

Marking scheme

- The order $C_6H_5NH_2 < NH_3 < CH_3NH_2 < (CH_3)_2NH$.
- Reasons: +I effect of alkyl groups raises the lone pair's availability; aniline's lone pair is delocalized into the ring.

Question 9 — 5 marks

a. **Cellulose** (a long chain of glucose units). **[1]**

Marking scheme

- Cellulose.

b. **Mechanical pulping** grinds or tears the wood apart in water: nothing is removed, so the yield is high (about 90–95%), but the fibers are cut short and still coated with lignin. **[2]**

Kraft pulping cooks wood chips in a digester at about 160–170 °C in white liquor (sodium hydroxide and sodium sulphide), which **dissolves the lignin** and frees the cellulose fibers whole and long. The long, clean fibers bond to each other well through hydrogen bonds, so the paper is stronger and lasts longer (the yield is only about 45–50%).

Marking scheme

- Mechanical: fibers torn apart, lignin kept, short fibers, high yield.

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- Kraft: NaOH and Na_2S dissolve the lignin, leaving long, clean fibers that bond strongly, so the paper is stronger.

c. $20 \times \dfrac{45}{100} = \mathbf{9\ tonnes}$ of pulp. **[1]**

Marking scheme

- $20 \times 0.45 = 9$ t.

d. Alum is slightly acidic, and in damp air the acid slowly **hydrolyzes the cellulose chains**, so the paper browns and crumbles. Magnesium hydrogencarbonate is a mild base: it **neutralizes the acid** in the paper and, as it dries, leaves a little magnesium carbonate in the fibers to neutralize acid formed later, so the chains stop being broken. **[1]**

Marking scheme

- The base neutralizes the acid (from alum) that hydrolyzes the cellulose, so the breakdown stops (an alkaline reserve left in the paper also earns the mark).

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

Question 10 — 8 marks

a. **Entropy** (S) is a measure of the disorder (randomness) of a system. When ice melts, the ordered crystal becomes a liquid whose molecules move freely, so **ΔS is positive**. **[3]**

Whether a change is spontaneous at constant temperature and pressure is decided by the **Gibbs free energy**, $\Delta G = \Delta H - T\Delta S$: it is spontaneous when ΔG is negative. ΔH alone does not decide it.

For melting, ΔH is positive but ΔS is positive too. Above 0 °C (273 K) the term $T\Delta S$ is larger than ΔH, so ΔG is negative and ice melts by itself; below 0 °C it is smaller, ΔG is positive, and ice does not melt.

Marking scheme

- Entropy measures disorder; melting increases it ($\Delta S > 0$).
- Spontaneity is decided by $\Delta G = \Delta H - T\Delta S < 0$, not by ΔH alone.
- Above 273 K, $T\Delta S > \Delta H$, so $\Delta G < 0$ and melting is spontaneous though endothermic.

b. The equations: **[3]**

$$\mathrm{CH_4(g) + 2\,O_2(g) \longrightarrow CO_2(g) + 2\,H_2O(l)} \qquad \Delta H_c^\circ = -890.3\ \mathrm{kJ}$$

$$\mathrm{C(s) + 2\,H_2(g) \longrightarrow CH_4(g)} \qquad \Delta H_f^\circ = ?$$

By Hess's law, $\Delta H_c^\circ = [\Delta H_f^\circ(CO_2) + 2\Delta H_f^\circ(H_2O)] - \Delta H_f^\circ(CH_4)$, so

$$\Delta H_f^\circ(CH_4) = -393.5 + 2(-285.8) - (-890.3) = -393.5 - 571.6 + 890.3 = \mathbf{-74.8\ kJ\ mol^{-1}}$$

Marking scheme

- The combustion equation and the formation equation of methane.
- Hess's law relation between them.
- $\Delta H_f^\circ(CH_4) = -74.8\ \mathrm{kJ\ mol^{-1}}$.

c. **[2]**

$$\Delta G^\circ = -2.303RT \log K$$

$$\log K = -\frac{4700}{2.303 \times 8.314 \times 298} = -0.824 \qquad K = 10^{-0.824} \approx \mathbf{0.15}$$

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$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T} = \frac{57{,}200 - 4700}{298} = +176 \text{ J K}^{-1}\text{mol}^{-1}$$

K depends on $\Delta G^\circ/T$, not on ΔG° alone. Putting $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ into $\Delta G^\circ = -2.303RT \log K$:

$$\log K = -\frac{\Delta H^\circ}{2.303RT} + \frac{\Delta S^\circ}{2.303R}$$

The ΔS° term does not change with temperature. ΔH° is **positive**, so the first term, $-\Delta H^\circ/(2.303RT)$, becomes less negative as T rises, and K becomes **larger**. For example, at 35 °C (308 K), $\Delta G^\circ = 57{,}200 - 308 \times 176 \approx +2990$ J mol^{-1}, $\log K = -0.507$ and K ≈ 0.31, twice the value at 25 °C. Warming favors NO_2, as expected for an endothermic forward reaction, and the brown color of the gas deepens. (Had ΔH° been negative, K would fall on warming, whatever the sign of ΔS°.)

Marking scheme

- $\log K = -\Delta G^\circ/(2.303RT) = -0.824$, K ≈ 0.15.
- K grows on warming: $\log K = -\Delta H^\circ/(2.303RT) + \Delta S^\circ/(2.303R)$, and with ΔH° > 0 the first term becomes less negative as T rises (or ΔG°/T, worked out at a higher temperature, is smaller: K ≈ 0.31 at 308 K).

OR

a. **Ammonium chloride** is the salt of a weak base and a strong acid. Its ammonium ion reacts with water (**hydrolysis**) and gives H_3O^+, so the solution is acidic (pH below 7): **[3]**

$$NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$$

Sodium ethanoate is the salt of a weak acid and a strong base. Its ethanoate ion takes a proton from water and leaves OH^-, so the solution is basic (pH above 7):

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

Sodium chloride is the salt of a strong acid and a strong base. Neither Na^+ nor Cl^- reacts with water, so $[H^+] = [OH^-]$ and the solution is neutral (pH 7).

Marking scheme

- NH_4^+ hydrolyzes to give H_3O^+: acidic (equation).
- CH_3COO^- hydrolyzes to give OH^-: basic (equation).
- Na^+ and Cl^- do not hydrolyze: neutral.

b. **[3]**

$$K_h = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{1.75 \times 10^{-5}} = 5.71 \times 10^{-10}$$

$$[OH^-] = \sqrt{K_h C} = \sqrt{5.71 \times 10^{-10} \times 0.10} = 7.56 \times 10^{-6} \text{ M}$$

$$\text{pOH} = 5.12 \qquad \text{pH} = 14 - 5.12 = \mathbf{8.88}$$

Marking scheme

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- $K_h = K_w/K_a = 5.71 \times 10^{-10}$.
- $[OH^-] = \sqrt{K_h C} = 7.56 \times 10^{-6}$ M.
- pOH = 5.12, pH = 8.88.

c. **Phenolphthalein.** At the equivalence point the flask holds sodium ethanoate solution, which is basic (pH about 8.9, as found above), and the steep part of the titration curve lies roughly between pH 7 and 10. Phenolphthalein changes color within that range, exactly at the end point. **[2]**

Methyl orange would change color at pH 3–4, while plenty of ethanoic acid is still unneutralized, so it would give an end point far too early.

Marking scheme

- Phenolphthalein: the equivalence point is basic (sodium ethanoate, pH about 9), within its range.
- Methyl orange changes at pH 3–4, well before the equivalence point.

Question 11 — 8 marks

a. All four derivatives react by **nucleophilic acyl substitution**: the nucleophile adds to the C=O carbon, and then the group attached to the acyl group leaves. **[3]**

How easily this happens depends on the **leaving group**. Cl^- is a very weak base and leaves easily; and chlorine, strongly electron-withdrawing and giving back little electron density by resonance, leaves the carbonyl carbon strongly positive. So acid chlorides are the most reactive.

In an amide the nitrogen's lone pair is strongly **delocalized** onto the C=O (resonance), which makes the carbon much less positive, and NH_2^- is a very strong base and a poor leaving group. So amides are the least reactive. Overall: acid chloride > acid anhydride > ester > amide.

Marking scheme

- All react by nucleophilic acyl substitution (addition to C=O, then loss of the leaving group).
- Cl^- is a good leaving group and Cl makes the C=O carbon strongly positive, so acid chlorides are the most reactive.
- The amide's N lone pair is delocalized onto C=O and NH_2^- is a poor leaving group, so amides are least reactive (order: chloride > anhydride > ester > amide).

b. (i) **[2]**

$$CH_3COCl + H_2O \longrightarrow CH_3COOH + HCl$$

(ii)

$$CH_3COCl + C_2H_5OH \longrightarrow CH_3COOC_2H_5 + HCl$$

(ethyl ethanoate)

Marking scheme

- With water: ethanoic acid and HCl.
- With ethanol: ethyl ethanoate and HCl.

c. Since C oxidizes to B, the acid and the alcohol have the **same carbon skeleton**: three carbons each, out of six in the ester. An alcohol that is oxidized to a carboxylic acid must be **primary**, so C is propan-1-ol (not propan-2-ol, which would give propanone). So B is **propanoic acid**, C is **propan-1-ol**, and A is **propyl propanoate**, $CH_3CH_2COOCH_2CH_2CH_3$. **[3]**

$$CH_3CH_2COOCH_2CH_2CH_3 + H_2O \overset{H^+}{\rightleftharpoons} CH_3CH_2COOH + CH_3CH_2CH_2OH$$

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$$CH_3CH_2CH_2OH + 2\,[O] \xrightarrow{K_2Cr_2O_7/H^+} CH_3CH_2COOH + H_2O$$

Marking scheme

- Reasoning: B and C have the same three-carbon skeleton and C is a primary alcohol: A propyl propanoate, B propanoic acid, C propan-1-ol.
- Hydrolysis equation.
- Oxidation equation of propan-1-ol to propanoic acid.

Question 12 — 8 marks

a. **Electronic reason:** alkyl groups push electrons (+I) towards the carbonyl carbon. A ketone has two alkyl groups and an aldehyde only one, so the carbon of a ketone is less positive and attracts nucleophiles less. **[2]**

Steric reason: two alkyl groups also crowd the carbonyl carbon of a ketone more than one alkyl group and a small hydrogen do, so a nucleophile reaches it less easily, and the crowded product is less stable.

Marking scheme

- Electronic: two +I alkyl groups make a ketone's carbonyl carbon less positive.
- Steric: two alkyl groups hinder the nucleophile's approach more than in an aldehyde.

b. (i) Methanal with ethylmagnesium bromide: **[3]**

$$HCHO + C_2H_5MgBr \longrightarrow C_2H_5CH_2OMgBr \xrightarrow{H_2O/H^+} CH_3CH_2CH_2OH$$

(ii) Ethanal with methylmagnesium bromide:

$$CH_3CHO + CH_3MgBr \longrightarrow (CH_3)_2CHOMgBr \xrightarrow{H_2O/H^+} (CH_3)_2CHOH$$

(iii) Propanone with methylmagnesium bromide:

$$(CH_3)_2CO + CH_3MgBr \longrightarrow (CH_3)_3COMgBr \xrightarrow{H_2O/H^+} (CH_3)_3COH$$

Marking scheme

- Propan-1-ol: methanal + C_2H_5MgBr, then hydrolysis.
- Propan-2-ol: ethanal + CH_3MgBr, then hydrolysis.
- 2-Methylpropan-2-ol: propanone + CH_3MgBr, then hydrolysis.

c. Both tests are mild **oxidizing agents**, which oxidize an aldehyde (with its H on the C=O) to the acid. **[3]**
Propanone is a ketone: with no H on its carbonyl carbon it is not oxidized by them, so it gives neither.

Fehling's solution (Cu^{2+} in alkaline tartrate) is a **weaker** oxidizing agent than Tollens' reagent: it oxidizes aliphatic aldehydes such as ethanal (giving red Cu_2O) but not aromatic aldehydes such as **benzaldehyde**, which still reduces Tollens' reagent. So Fehling's tells an aliphatic aldehyde from an aromatic one.

$$CH_3CHO + 2\,[Ag(NH_3)_2]^+ + 3\,OH^- \longrightarrow CH_3COO^- + 2\,Ag\downarrow + 4\,NH_3 + 2\,H_2O$$

Marking scheme

- Ketones (propanone) have no H on the C=O and are not oxidized by either reagent.
- Fehling's is weaker: it oxidizes aliphatic aldehydes but not aromatic ones like benzaldehyde, which reduces only Tollens'.
- The balanced equation for ethanal with Tollens' reagent.

OR

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a. 2,4-DNP reacts with the **carbonyl group** (C=O) of any aldehyde or ketone by addition followed by loss of water (condensation), giving a colored 2,4-dinitrophenylhydrazone. **[2]**

So it shows only that a C=O group is present. Propanal and propanone both have one, so both give the precipitate, and the test cannot tell an aldehyde from a ketone.

Marking scheme

- 2,4-DNP condenses with any C=O group (aldehyde or ketone) to give a colored hydrazone.
- Both compounds have a carbonyl group, so the test cannot distinguish them.

b. (i) Zinc amalgam and concentrated HCl reduce C=O to CH_2: **[3]**

$$CH_3COCH_3 + 4\,[H] \xrightarrow{Zn-Hg/conc.\ HCl} CH_3CH_2CH_3 + H_2O$$

The product is **propane**.

(ii)

$$CH_3CH_2CHO + HCN \longrightarrow CH_3CH_2CH(OH)CN$$

The product is **2-hydroxybutanenitrile** (propanal cyanohydrin).

(iii)

$$CH_3COCH_3 \xrightarrow[H_2O]{LiAlH_4} CH_3CH(OH)CH_3$$

The product is **propan-2-ol**.

Marking scheme

- Clemmensen: propanone → propane.
- HCN addition: propanal → 2-hydroxybutanenitrile.
- $LiAlH_4$: propanone → propan-2-ol.

c. **Iodoform test** (iodine and sodium hydroxide, warmed): propanone gives a **yellow precipitate** of iodoform, CHI_3; propanal does not. **[3]**

Tollens' test: propanal gives a **silver mirror**; propanone does not (or Fehling's: a red precipitate with propanal only).

The iodoform test needs a CH_3CO^- group (or $CH_3CH(OH)^-$, which is oxidized to it). Propanone has one; in propanal the C=O carries an ethyl group and a hydrogen, $CH_3CH_2{-}CHO$, so it has no methyl next to the carbonyl and gives no iodoform.

Marking scheme

- Iodoform test: yellow precipitate with propanone only.
- Tollens' (or Fehling's): silver mirror (red precipitate) with propanal only.
- Iodoform needs a CH_3CO- group, which propanal lacks.

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