Grade 12 Chemistry Model Paper 3

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)** 300 mL

b. **(ii)** 20 min

c. **(ii)** −115.8 kJ

d. **(ii)** BF_3

e. **(iii)** cinnabar

f. **(iii)** They can change their oxidation states easily and provide a surface on which reactants are adsorbed.

g. **(ii)** chlorine (or bromine) with a little red phosphorus

h. **(iii)** Phenol is a weaker acid than carbonic acid, so it cannot set carbon dioxide free from a hydrogencarbonate.

i. **(ii)** Its C–F bonds are very strong, so it is chemically inert and stable when heated, and food does not stick to it.

j. **(ii)** It gives out penetrating gamma rays, which can be aimed at a tumor from outside the body.

k. **(ii)** A resin that joins neighboring fibers by covalent bonds, which water cannot break.

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

Question 2 — 5 marks

a. **Bond enthalpy** is the energy needed to break one mole of a particular bond in gaseous molecules into gaseous atoms (for bonds that occur in many compounds, an average over them). **[1]**

Marking scheme

- Energy needed to break one mole of a bond, in the gas phase (averaged over compounds).

b. Bonds broken: one C=C and one H–H (the four C–H bonds of ethene stay): **[2]**

$$612 + 436 = 1048 \text{ kJ}$$

Bonds made: one C–C and two new C–H bonds:

$$347 + 2 \times 413 = 1173 \text{ kJ}$$

$$\Delta H = \sum(\text{bonds broken}) - \sum(\text{bonds formed}) = 1048 - 1173 = \mathbf{-125\ kJ\ mol^{-1}}$$

Marking scheme

- Bonds broken 1048 kJ and bonds formed 1173 kJ (or all bonds counted on both sides).

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- $\Delta H = -125\ \text{kJ mol}^{-1}$.

c. The value from **enthalpies of formation**, $-136\ \text{kJ mol}^{-1}$, is the more reliable: those enthalpies are measured for ethene and ethane themselves, and Hess's law combines them exactly. **[2]**

The value from bond enthalpies is only an estimate, because the bond enthalpies are **averages** over many compounds. The real bonds in these two molecules are not exactly average: a bond's strength depends on the rest of the molecule (a C–H bond on the sp^2 carbon of ethene is stronger than one in ethane), yet the calculation took the four C–H bonds of ethene as unchanged and the two new ones as average.

Marking scheme

- The enthalpy-of-formation value is more reliable: measured for these very substances and combined exactly by Hess's law.
- Bond enthalpies are averages over many compounds, while the real bonds in ethene and ethane differ from the average (e.g. ethene's C–H bonds taken as unchanged).

OR

a. A **fuel cell** is a galvanic cell that turns the chemical energy of a fuel (such as hydrogen) and an oxidant (oxygen) directly into electrical energy, the reactants being supplied continuously from outside. **[1]**

Marking scheme

- A cell that converts the energy of a continuously supplied fuel and oxygen directly into electricity.

b. Anode (oxidation): **[2]**

$$2\,H_2\,(g) + 4\,OH^-\,(aq) \longrightarrow 4\,H_2O\,(l) + 4\,e^-$$

Cathode (reduction):

$$O_2\,(g) + 2\,H_2O\,(l) + 4\,e^- \longrightarrow 4\,OH^-\,(aq)$$

Together they give $2\,H_2 + O_2 \longrightarrow 2\,H_2O$.

Marking scheme

- Anode: $2\,H_2 + 4\,OH^- \longrightarrow 4\,H_2O + 4\,e^-$.
- Cathode: $O_2 + 2\,H_2O + 4\,e^- \longrightarrow 4\,OH^-$.

c. For one mole of H_2, two electrons pass ($n = 2$): **[2]**

$$\Delta G^\circ = -nFE^\circ = -2 \times 96{,}485 \times 1.23 \approx \mathbf{-237\ kJ\ mol^{-1}}$$

ΔG is the most useful work a reaction can give. A fuel cell turns the reaction's free energy **directly** into electrical work, so most of it is used. An engine first turns the energy into **heat**, and a heat engine can convert only part of heat into work (the rest is lost to the exhaust and surroundings), so its efficiency is much lower.

Marking scheme

- $\Delta G^\circ = -2 \times 96{,}485 \times 1.23 \approx -237$ kJ per mole of H_2.
- The cell converts ΔG directly into electrical work; an engine goes through heat, of which only part can become work.

Question 3 — 5 marks

a. A **conjugate acid–base pair** is an acid and the base it becomes by losing one proton (they differ by one H^+). In **[1]**

$$HCOOH + H_2O \rightleftharpoons HCOO^- + H_3O^+$$

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$HCOOH$ and $HCOO^-$ are one pair (and H_3O^+ and H_2O the other).

Marking scheme

- A pair differing by one proton; $HCOOH$ and $HCOO^-$ (or H_3O^+ and H_2O).

b. For a weak acid, $[H^+] = \sqrt{K_a C}$: **[2]**

$$[H^+] = \sqrt{1.8 \times 10^{-4} \times 0.10} = \sqrt{1.8 \times 10^{-5}} = 4.24 \times 10^{-3}\ \text{M}$$

$$\text{pH} = -\log(4.24 \times 10^{-3}) = \mathbf{2.37}$$

(The degree of ionization is 4.2%, under 5%, so the shortcut holds; the exact quadratic gives 2.38.)

Marking scheme

- $[H^+] = \sqrt{K_a C} = 4.24 \times 10^{-3}$ M.
- pH = 2.37 (2.38 by the quadratic also accepted).

c. At 0.10 M: $\alpha = \sqrt{K_a/C} = \sqrt{1.8 \times 10^{-4}/0.10} = 0.042$, that is **4.2%**. **[2]**

At 0.0010 M the shortcut would give $\sqrt{0.18} = 0.42$, over 5%, so the full form is used: $K_a = \dfrac{C\alpha^2}{1-\alpha}$, that is $0.0010\alpha^2 + 1.8 \times 10^{-4}\alpha - 1.8 \times 10^{-4} = 0$, giving $\alpha = 0.34$, about **34%**.

By **Ostwald's dilution law**, for a weak electrolyte $\alpha \approx \sqrt{K_a/C}$: as the concentration falls, the degree of ionization rises. On dilution the ions are farther apart and recombine less, so more of the acid ionizes, though the solution as a whole is less acidic.

Marking scheme

- $\alpha = 4.2\%$ at 0.10 M and about 34% at 0.0010 M (0.42 by the shortcut, accepted with a note that it overestimates).
- Ostwald's law: $\alpha \propto 1/\sqrt{C}$; dilution increases the degree of ionization.

Question 4 — 5 marks

a. Copper pyrites (chalcopyrite) is $CuFeS_2$. Being a sulphide ore, it is concentrated by the **froth flotation process**, in which the ore particles, wetted by pine oil, rise with the froth and the earthy gangue sinks. **[2]**

Marking scheme

- Formula $CuFeS_2$.
- Froth flotation.

b. Roasting leaves much of the iron as iron(II) oxide (and FeS is turned into FeO in the furnace). Silica is a **flux** that combines with it to form a fusible **slag**, iron(II) silicate, which floats on the molten matte and is run off: **[1]**

$$FeO + SiO_2 \longrightarrow FeSiO_3$$

Marking scheme

- Silica removes iron as $FeSiO_3$ slag (equation).

c. Air blown through the molten matte oxidizes part of the copper(I) sulphide to copper(I) oxide, which then reacts with the rest of the sulphide: **[2]**

$$2\,Cu_2S + 3\,O_2 \longrightarrow 2\,Cu_2O + 2\,SO_2 \qquad 2\,Cu_2O + Cu_2S \longrightarrow 6\,Cu + SO_2$$

In the second reaction copper goes from **+1** (in Cu_2O and Cu_2S) to **0**: copper is reduced. Sulphur goes from **−2**

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in Cu_2S to **+4** in SO_2: it is oxidized, giving up the electrons the copper takes. So the reducing agent is the copper(I) sulphide itself (its sulphide ion), and no carbon is needed: the ore reduces itself.

Marking scheme

- The two equations, part of Cu_2S oxidized to Cu_2O, which reacts with the rest of the Cu_2S.
- Cu $+1 \rightarrow 0$ (reduced); S $-2 \rightarrow +4$ (oxidized), so Cu_2S (sulphide) is the reducing agent.

Question 5 — 5 marks

a. **Tetraamminecopper(II) sulphate**; the coordination number of copper is **4** (four ammonia ligands). **[2]**

Marking scheme

- Tetraamminecopper(II) sulphate.
- Coordination number 4.

b. Two chloride ions are outside the brackets, so the complex ion is $[Co(NH_3)_5Cl]^{2+}$. Ammonia is neutral and the chlorido ligand is -1: $x + 5(0) + (-1) = +2$, so $x = \mathbf{+3}$. **[1]**

Marking scheme

- The complex ion is $[Co(NH_3)_5Cl]^{2+}$; $x + 0 - 1 = +2$, so $x = +3$.

c. In $[Ni(CN)_4]^{2-}$ the strong-field cyanide ligands make the eight d electrons **pair up**, leaving one d orbital empty for the square planar arrangement: no unpaired electrons, so it is **diamagnetic**. **[2]**

In $[NiCl_4]^{2-}$ the weak-field chloride ligands do not pair them, so, as in the free Ni^{2+} ion, **two electrons are unpaired**: it is **paramagnetic**.

$$\mu = \sqrt{n(n+2)} = \sqrt{2 \times 4} = \sqrt{8} = \mathbf{2.83\ BM}$$

Marking scheme

- $[NiCl_4]^{2-}$ (weak field, tetrahedral) has two unpaired electrons and is paramagnetic; $[Ni(CN)_4]^{2-}$ (strong field) has all paired, diamagnetic.
- $\mu = \sqrt{n(n+2)} = \sqrt{8} = 2.83$ BM.

Question 6 — 5 marks

a. An **ambident nucleophile** is a nucleophile that can attack through two different atoms, because both carry a lone pair: for example the cyanide ion, CN^-, which has a lone pair on both its carbon and its nitrogen and can bond through either (or the nitrite ion, through nitrogen or oxygen). **[1]**

Marking scheme

- A nucleophile that can bond through two different atoms; e.g. CN^- (or NO_2^-).

b. With potassium cyanide: **propanenitrile** (ethyl cyanide): **[2]**

$$C_2H_5Br + KCN \xrightarrow{\text{alc.}} C_2H_5CN + KBr$$

With silver cyanide: **ethyl isocyanide** (ethyl carbylamine):

$$C_2H_5Br + AgCN \longrightarrow C_2H_5NC + AgBr$$

Marking scheme

- KCN: propanenitrile, C_2H_5CN.
- AgCN: ethyl isocyanide, C_2H_5NC.

c. **KCN** is ionic, so it gives free CN^- ions in solution. The ion attacks through its **carbon** atom, the more nucleophilic end, and the stronger C–C bond is formed: a nitrile. **[2]**

AgCN is largely covalent: the carbon of the cyanide is already bonded to silver (Ag–C≡N), so only the lone pair on **nitrogen** is free to attack the haloalkane, and an isocyanide (C–N bond) forms. Silver also helps pull

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off the bromide, as insoluble AgBr.

Marking scheme

- KCN is ionic: free CN^- attacks through carbon, giving the nitrile.
- AgCN is covalent (Ag–C bond): only the N lone pair is free, giving the isocyanide.

OR

a. Benzoic acid is C_6H_5COOH (a carboxyl group on a benzene ring); toluene is oxidized to it by **alkaline potassium permanganate** (followed by acid). **[1]**

Marking scheme

- C_6H_5COOH, from toluene with alkaline $KMnO_4$ (then acid).

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

$$C_6H_5CH_3 + 3\,[O] \xrightarrow[H_3O^+]{\text{alk. } KMnO_4} C_6H_5COOH + H_2O$$

(ii)

$$C_6H_5COONa + NaOH \xrightarrow[\Delta]{CaO} C_6H_6 + Na_2CO_3$$

The product is benzene (decarboxylation).

Marking scheme

- Oxidation of toluene to benzoic acid.
- Decarboxylation of sodium benzoate with soda lime to benzene.

c. The –COOH group withdraws electrons from the ring, by induction and by resonance (its C=O pulls the ring's π electrons), so the ring is **deactivated**: it reacts more slowly than benzene and needs concentrated acids and heat. **[2]**

The withdrawal by resonance leaves positive charge at the **ortho and para** positions, so they are the most electron-poor, and the electrophile NO_2^+ attacks the **meta** position, the least deactivated: 3-nitrobenzoic acid.

Marking scheme

- –COOH withdraws electrons (−I, −R): the ring is deactivated, so nitration is difficult.
- Ortho and para positions are most electron-poor, so substitution is at meta.

Question 7 — 5 marks

a. **1-Chloro-4-nitrobenzene** (p-chloronitrobenzene), with 1-chloro-2-nitrobenzene as the minor product. **[1]**

Marking scheme

- 1-Chloro-4-nitrobenzene.

b. Sulphuric acid is the stronger acid: it protonates nitric acid, which then loses water to give the **nitronium ion**, NO_2^+, the electrophile that attacks the ring: **[2]**

$$HNO_3 + 2\,H_2SO_4 \rightleftharpoons NO_2^+ + H_3O^+ + 2\,HSO_4^-$$

$$C_6H_6 + NO_2^+ \longrightarrow C_6H_5NO_2 + H^+$$

It also absorbs the water formed, which would otherwise slow the reaction.

Marking scheme

- H_2SO_4 protonates HNO_3 to give the electrophile NO_2^+ (equation).

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- NO_2^+ substitutes on the ring (equation; H_2SO_4 also takes up the water).

c. The $-NO_2$ group withdraws electrons so strongly that a hydrogen on the carbon next to it (an **α-hydrogen**) becomes weakly acidic: a base can remove it as H^+, and the nitroalkane dissolves in NaOH as a salt. 1-Nitrobutane, a primary nitroalkane, has two α-hydrogens, so it dissolves. **[2]**

X does not dissolve, so it has **no α-hydrogen**: the carbon carrying $-NO_2$ is joined to three other carbons, a **tertiary** nitroalkane. With four carbons in all, the only one is **2-methyl-2-nitropropane**, $(CH_3)_3CNO_2$.

Marking scheme

- Nitroalkanes with an α-hydrogen dissolve in NaOH (the H next to $-NO_2$ is acidic); X has none, so it is tertiary.
- X = 2-methyl-2-nitropropane, $(CH_3)_3CNO_2$, the only tertiary $C_4H_9NO_2$.

Question 8 — 5 marks

a. $K[PtCl_3(C_2H_4)]$ (potassium trichlorido(ethene)platinate(II)), usually as its monohydrate. **[1]**

Marking scheme

- $K[PtCl_3(C_2H_4)]$.

b. (i) Two molecules lose one water between them: **ethoxyethane** (diethyl ether): **[2]**

$$2\,C_2H_5OH \xrightarrow[140\,^\circ C]{\text{conc. } H_2SO_4} C_2H_5OC_2H_5 + H_2O$$

(ii) Each molecule loses water (elimination): **ethene**:

$$C_2H_5OH \xrightarrow[170\,^\circ C]{\text{conc. } H_2SO_4} CH_2{=}CH_2 + H_2O$$

Marking scheme

- At 140 °C with excess alcohol: ethoxyethane (equation).
- At 170 °C: ethene (equation).

c. An ether has no hydrogen on oxygen, so its molecules **cannot hydrogen-bond to each other**; only weak dipole and dispersion forces hold them, and it boils low. Butan-1-ol molecules are joined by O–H···O hydrogen bonds, which take much energy to break. **[2]**

But the ether's oxygen has lone pairs, so it can **accept hydrogen bonds from water** molecules, as the alcohol can; so both dissolve to about the same small extent (about 6–8 g per 100 g of water).

Marking scheme

- No H-bonding between ether molecules (no O–H), so low b.p.; butan-1-ol molecules are H-bonded.
- The ether's O accepts H-bonds from water, so its solubility is similar to the alcohol's.

Question 9 — 5 marks

a. **Limestone** (calcium carbonate, the source of lime) and **clay** or shale (the source of silica, alumina and iron oxide); gypsum is added only at the grinding stage. **[1]**

Marking scheme

- Limestone and clay (shale).

b. In the **dry process** the raw materials are crushed, dried and ground to a fine powder (raw meal), which is preheated and fed into the kiln. In the **wet process** they are ground with water into a slurry, which is fed into the kiln. **[2]**

In the wet process all that water must be evaporated in the kiln, which takes a great deal of fuel. The dry process saves this energy (and gives out less carbon dioxide), so it is cheaper and better for the environment.

Marking scheme

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- Dry: raw materials ground dry to a raw meal; wet: ground with water to a slurry.
- The dry process needs far less fuel (no water to evaporate), so it is preferred.

c. 24 days is 24/8 = 3 half-lives, so $\left(\frac{1}{2}\right)^3 = \mathbf{1/8}$ (12.5%) is left. **[1]**

Marking scheme

- 3 half-lives, so 1/8 is left.

d. Nylon-6,6 is a polyamide: its chain is held together by **amide links**, –CO–NH–, and an amide is hydrolyzed by acid (as ethanamide is), so the chains are slowly cut and the rope weakens. Polythene's chain has only **C–C and C–H bonds**, which dilute acid does not attack. **[1]**

Marking scheme

- Acid hydrolyzes nylon's amide (–CO–NH–) links and cuts its chains; polythene has only C–C and C–H bonds, which acid does not attack.

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

Question 10 — 8 marks

a. By **collision theory**, molecules must collide to react, but a collision is **effective** only if two conditions are met: **[3]**

1. The colliding molecules must have at least a minimum energy, the **activation energy** E_a, enough to break the old bonds and reach the activated complex.
2. They must collide in the right **orientation**, with the reacting atoms facing each other.

Most collisions fail one or both, so only a small fraction react. Raising the temperature by 10 °C increases the molecules' speed only a little (about 2%), but it greatly increases the **fraction of molecules with energy above** E_a, the tail of the energy distribution, often about doubling it, so the rate roughly doubles.

Marking scheme

- Effective collisions need energy at least equal to the activation energy.
- And the proper orientation; so only a small fraction react.
- A 10 °C rise greatly increases the fraction of molecules with energy above E_a (not just the number of collisions), so the rate about doubles.

b. Experiments 1 and 2: [A] doubles, [B] fixed, rate rises 4 times = 2^2: **second order in A**. **[3]**

Experiments 1 and 3: [B] doubles, [A] fixed, rate doubles = 2^1: **first order in B**.

Rate law: rate $= k[\mathrm{A}]^2[\mathrm{B}]$, overall order 3. From experiment 1:

$$k = \frac{2.0 \times 10^{-3}}{(0.10)^2(0.10)} = \mathbf{2.0\ L^2\ mol^{-2}\ s^{-1}}$$

Marking scheme

- Second order in A (rate × 4 when [A] doubles).
- First order in B; rate = k[A]²[B], overall third order.
- k = 2.0 L² mol⁻² s⁻¹.

c. (i) Halving the volume **doubles the concentration** of each gas (the same number of moles in half the volume): **[2]**

$$\text{new rate} = k(2[\mathrm{A}])^2(2[\mathrm{B}]) = 8k[\mathrm{A}]^2[\mathrm{B}]$$

The rate becomes **8 times** as fast, because the reaction is third order overall ($2^3 = 8$).

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(ii) The rate **does not change**. The rate law depends on the concentrations of A and B, and at the same volume their moles per liter are unchanged; the argon raises the total pressure but takes no part in the reaction.

Marking scheme

- Halving the volume doubles both concentrations: rate $\times 2^2 \times 2 = 8$ times (third order).
- Argon at the same volume leaves [A] and [B] unchanged, so the rate is unchanged.

OR

a. **[3]**

- **Mohr's salt** is stable in air, does not lose water of crystallization and is not easily oxidized, so it can be weighed pure. Iron(II) sulphate crystals, $FeSO_4 \cdot 7\,H_2O$, slowly lose water and are oxidized by air to iron(III), so their exact mass of iron(II) is unknown.
- **Dilute sulphuric acid** stops the iron(II) salt from hydrolyzing and being oxidized by air, and supplies the H^+ ions the dichromate reaction needs.
- Dichromate is orange and its product, Cr^{3+}, green: the change is not sharp enough to see the end point, so an **indicator** (diphenylamine, which turns violet-blue with the first excess of dichromate) is used. Permanganate is a self-indicator, purple to colorless.

Marking scheme

- Mohr's salt is stable and not oxidized by air ($FeSO_4 \cdot 7H_2O$ is efflorescent and oxidized), so it is a primary standard.
- Dilute H_2SO_4 prevents hydrolysis and air oxidation of Fe^{2+} and supplies H^+.
- Dichromate (orange to green) is not a self-indicator, so diphenylamine is needed.

b. Mohr's salt gives one electron ($Fe^{2+} \rightarrow Fe^{3+}$), so its equivalent weight is 392: **[3]**

$$N_1 = \frac{3.92}{392 \times 0.250} = 0.040\ \text{N}$$

$$N_2 = \frac{N_1 V_1}{V_2} = \frac{0.040 \times 25.0}{20.0} = 0.050\ \text{N}$$

Dichromate takes six electrons (2 Cr: $+6 \rightarrow +3$), so E = 294/6 = 49, and strength $= 0.050 \times 49 =$ **2.45 g/L**.

Marking scheme

- N(Mohr's salt) = 0.040 N (E = 392).
- N(dichromate) = 0.050 N.
- E($K_2Cr_2O_7$) = 49, strength = 2.45 g/L.

c. **[2]**

$$Cr_2O_7^{2-} + 6\,Fe^{2+} + 14\,H^+ \longrightarrow 2\,Cr^{3+} + 6\,Fe^{3+} + 7\,H_2O$$

Too high. Standing in air without acid, some of the Fe^{2+} is oxidized to Fe^{3+}, which dichromate does not react with. So 25.0 mL of the solution holds less Fe^{2+} than the 0.040 N it was made to, less dichromate is needed to reach the end point, and the calculation $N_2 = N_1 V_1 / V_2$, still using 0.040 N, divides by a smaller V_2.

Marking scheme

- The balanced ionic equation.
- Too high: air oxidizes some Fe^{2+} to Fe^{3+}, so less dichromate is used (smaller V_2) while N_1 is still taken as 0.040 N.

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Question 11 — 8 marks

a. The mixture is treated with **diethyl oxalate**, $(COOC_2H_5)_2$; each amine reacts according to how many hydrogens its nitrogen carries. **[3]**

- The **primary** amine (two H on N) reacts with both ester groups and gives a **solid** dialkyloxamide, $(CONHC_2H_5)_2$.
- The **secondary** amine (one H) reacts with one ester group only and gives a **liquid** oxamic ester, $(C_2H_5)_2NCOCOOC_2H_5$.
- The **tertiary** amine (no H on N) does not react.

The tertiary amine is distilled off, the solid is filtered from the liquid, and each product is boiled with KOH to give back its amine.

Marking scheme

- Primary amine gives a solid dialkyloxamide with diethyl oxalate.
- Secondary amine gives a liquid oxamic ester.
- Tertiary amine does not react and is distilled off; KOH regenerates the amines from the products.

b. (i) With sodium and ethanol (Mendius reduction) or $LiAlH_4$: **[2]**

$$CH_3CN + 4\,[H] \xrightarrow{Na/C_2H_5OH} CH_3CH_2NH_2$$

(ii) Ammonolysis, in a sealed tube with excess ammonia:

$$C_2H_5Br + NH_3 \longrightarrow C_2H_5NH_2 + HBr$$

(The HBr forms ammonium bromide with the excess ammonia; some secondary and tertiary amines form too.)

Marking scheme

- Reduction of ethanenitrile to ethanamine.
- Ammonolysis of bromoethane to ethanamine.

c. A yellow oil (an N-nitrosamine) and no nitrogen gas: X is a **secondary amine**, with two carbon groups on its nitrogen. Three carbons can be shared between two groups only as one methyl and one ethyl, so X is **N-methylethanamine**, $CH_3NHC_2H_5$. (The other amines of formula C_3H_9N are primary, propan-1-amine and propan-2-amine, which give nitrogen gas, or tertiary, N,N-dimethylmethanamine, which gives no oil.) **[3]**

$$CH_3NHC_2H_5 + HNO_2 \longrightarrow CH_3N(NO)C_2H_5 + H_2O$$

The product is N-methyl-N-nitrosoethanamine.

Marking scheme

- A yellow oily nitrosamine without N_2 shows a secondary amine.
- X = N-methylethanamine, $CH_3NHC_2H_5$ (the only secondary amine C_3H_9N).
- The equation forming the N-nitrosamine.

Question 12 — 8 marks

a. Oxygen is much more electronegative than carbon, so the C=O bond is **polar**: $C^{\delta+}=O^{\delta-}$. The electron-poor carbon is attacked by **nucleophiles** (and the oxygen then takes up H^+). **[2]**

The C=C bond of an alkene is non-polar, with an electron-rich π cloud between the carbons, so it attracts **electrophiles**.

Marking scheme

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- C=O is polar (Cδ+), so nucleophiles attack the carbon.
- C=C is non-polar and electron-rich (π cloud), so electrophiles attack it.

b. (i) **[3]**

$$C_6H_5CH_3 \xrightarrow[H_2O]{CrO_2Cl_2/CS_2} C_6H_5CHO$$

(chromyl chloride in carbon disulphide, then water)

(ii)

$$C_6H_5COCl + H_2 \xrightarrow{Pd/BaSO_4} C_6H_5CHO + HCl$$

(palladium on barium sulphate, partly poisoned so that the aldehyde is not reduced further)

(iii)

$$2\,C_6H_5CHO \xrightarrow[\text{ethanol}]{KCN} C_6H_5CH(OH)COC_6H_5$$

(benzoin)

Marking scheme

- Étard reaction: toluene → benzaldehyde with CrO_2Cl_2.
- Rosenmund reduction: $C_6H_5COCl + H_2$ ($Pd/BaSO_4$) → benzaldehyde.
- Benzoin condensation: 2 C_6H_5CHO with KCN → benzoin.

c. P is **acetophenone** (1-phenylethan-1-one), $C_6H_5COCH_3$. **[3]**

- The 2,4-DNP precipitate shows a C=O group; no silver mirror shows it is a **ketone**, not an aldehyde.
- The iodoform test shows a CH_3CO^- group:

$$C_6H_5COCH_3 + 3\,I_2 + 4\,NaOH \longrightarrow C_6H_5COONa + CHI_3 \downarrow + 3\,NaI + 3\,H_2O$$

- Oxidation to benzoic acid shows a benzene ring with a single side chain; with eight carbons, the side chain is $-COCH_3$.

Marking scheme

- C=O present (2,4-DNP) and ketone (no Tollens' mirror).
- CH_3CO- group (iodoform test, equation or explanation).
- Monosubstituted benzene ring (benzoic acid on oxidation): P = acetophenone, $C_6H_5COCH_3$.

OR

a. In the carboxyl group a lone pair of the –OH oxygen is delocalized onto the C=O by **resonance** (in one form the carbonyl oxygen carries a negative charge and the –OH oxygen a positive one, joined to the carbon by a double bond). This makes the carbonyl carbon much **less positive** and gives the C=O partial single-bond character, so nucleophiles such as 2,4-DNP do not add to it as they do to an aldehyde or ketone. **[2]**

Marking scheme

- Resonance of the –OH lone pair with C=O in the carboxyl group.
- The carbonyl carbon is less electrophilic, so typical carbonyl addition does not occur.

b. (i) **[3]**

$$CH_3COOH + NaHCO_3 \longrightarrow CH_3COONa + H_2O + CO_2 \uparrow$$

(ii)

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$$CH_3COOH + SOCl_2 \longrightarrow CH_3COCl + SO_2 \uparrow + HCl \uparrow$$

(iii)

$$CH_3COONa + NaOH \xrightarrow[\Delta]{CaO} CH_4 + Na_2CO_3$$

Marking scheme

- With $NaHCO_3$: sodium ethanoate, water and CO_2.
- With $SOCl_2$: ethanoyl chloride, SO_2 and HCl.
- With soda lime: methane and Na_2CO_3.

c. **[3]**

$$CH_3CH_2COOH < CH_3COOH < ClCH_2COOH < FCH_2COOH$$

An acid is stronger the more stable its anion, $RCOO^-$. A halogen on the α-carbon withdraws electrons through the σ bonds (**−I effect**), spreading the negative charge and stabilizing the anion, so the halogenated acids are the strongest. Fluorine is more electronegative than chlorine, so its pull is stronger and fluoroethanoic acid is the strongest of the four (pK_a about 2.6, against 2.9 for chloroethanoic acid).

Alkyl groups push electrons (**+I effect**), adding to the negative charge and destabilizing the anion. An ethyl group pushes a little more than a methyl group, so propanoic acid (4.87) is weaker than ethanoic acid (4.76).

Marking scheme

- The order $CH_3CH_2COOH < CH_3COOH < ClCH_2COOH < FCH_2COOH$.
- −I effect of the halogen stabilizes the carboxylate; F is more electronegative than Cl, so fluoroethanoic acid is strongest.
- +I effect of alkyl groups destabilizes it, ethyl more than methyl, so propanoic acid is weakest.

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