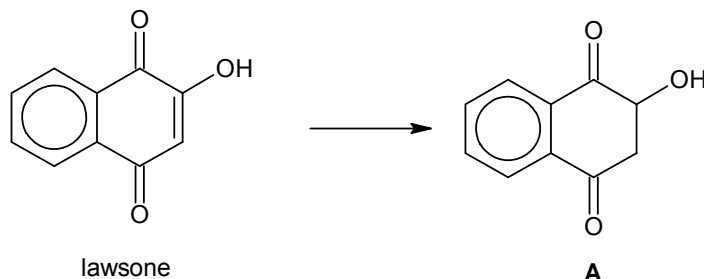


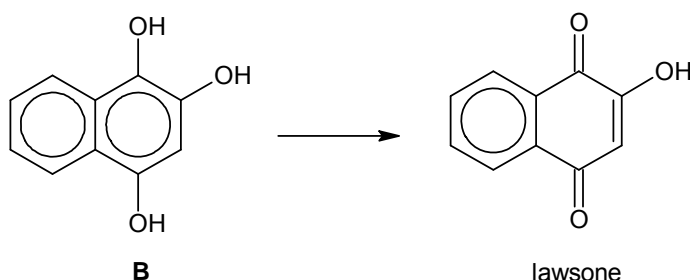
DUNMAN HIGH SCHOOL
Preliminary Examination 2014

H2 CHEMISTRY (9647/03)

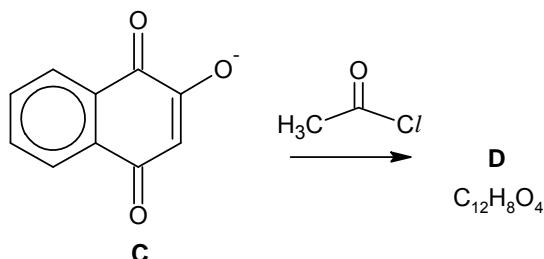
- 1 (a) Lawsone is the dye that is extracted from the henna plant, *Lawsonia inermis*. Although its natural colour is yellow, lawsone reacts with the proteins in hair and skin to produce the characteristic brown henna colour. Compound A is a derivative of lawsone.



- (i) Name two functional groups in A, other than the phenyl group.
- (ii) Describe a reaction, with reagent and condition(s), to confirm one of the functional groups in A. Describe the observations you would make.
- (iii) Only one organic compound can be formed when lawsone is reacted with aqueous Br_2 , through the loss of one water molecule. Suggest the structural formula of this compound.
- (b) Compound B can be oxidised to lawsone by acidified $\text{K}_2\text{Cr}_2\text{O}_7$ involving two moles of electrons lost per mole of B. [4]

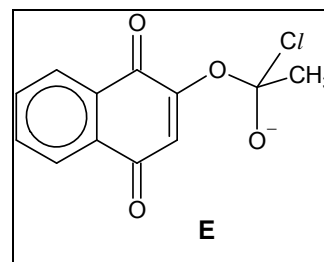


- (i) With the use of the *Data Booklet*, construct a balanced half-equation for the oxidation of B and a balanced equation for the overall reaction. You are to use the molecular formulae of lawsone ($\text{C}_{10}\text{H}_6\text{O}_3$), B ($\text{C}_{10}\text{H}_8\text{O}_3$) and $\text{Cr}_2\text{O}_7^{2-}$ in your equations.
- (ii) Calculate the concentration of a solution of compound B given that 20.0 cm^3 of this solution required 12.50 cm^3 of $0.050 \text{ mol dm}^{-3}$ $\text{K}_2\text{Cr}_2\text{O}_7$ solution to reach end-point. [4]
- (c) When lawsone is reacted under suitable condition, compound C is produced. Reacting C with ethanoyl chloride produces a neutral compound D, with molecular formula $\text{C}_{12}\text{H}_8\text{O}_4$.



- (i) The production of D occurs via a two-step mechanism.

Step I: B and ethanoyl chloride reacts to form an intermediate E as shown.



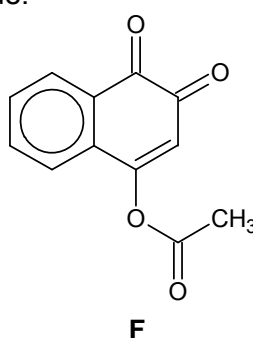
Step II: A chloride ion is eliminated to form D.

Outline the two mechanism steps by drawing relevant curly arrows, partial charges and lone pair of electrons in your answer. Label the steps clearly.

(ii) Hence or otherwise, draw the structural formula of D.

[3]

(d) Another compound F, in addition to D, is also produced in the above reaction involving C and ethanoyl chloride.



(i) Draw the structure of the nucleophile, G, involved in the formation of F.

(ii) Hence, suggest with the use of curly arrows, to show how G is formed from C.

[2]

(e) When added to silver nitrate solution, ethanoyl chloride forms a white precipitate, while ethanoyl bromide forms a cream precipitate.

(i) Identify the precipitates.

(ii) Write an equation for the formation of white precipitate from ethanoyl chloride.

(iii) State and explain which of the two precipitate will be soluble in aqueous ammonia.

[7]

[Total: 20]

- 2 (a) Over 80% of all lead produced ends up in lead–acid batteries, with lead metal and lead(IV) oxide used in them. In addition to starter batteries for road vehicles, lead and lead(IV) oxide are also used for zero emission and hybrid vehicles. The extraction of lead from its ore, galena (which is lead(II) sulfide, PbS), involves several processes.

Firstly, lead(II) sulfide is roasted in air to form lead(II) oxide (PbO) and sulfur dioxide. The lead(II) oxide is heated with coke (carbon) and air in a blast furnace. Some of the coke forms carbon monoxide, both carbon and carbon monoxide react with lead(II) oxide to form lead.

- (i) Write an equation for the reaction that occurs during roasting.
- (ii) What is the compound that can be formed when sulfur dioxide is added to water? Determine the colour of universal indicator in the solution obtained when this compound is added to water.
- (iii) Identify the type of reaction that occurs to lead(II) oxide in the blast furnace.
- (iv) Deduce two equations for the reactions in which lead is formed in the blast furnace.

[6]

- (b) Silver is an impurity present in lead obtained from the blast furnace. It is removed by a technique known as the Parkes process. In one of the steps, zinc is added to the lead and silver mixture. The mixture is then heated to a certain temperature, T, so that silver dissolves in zinc to form an alloy crust that floats. This separates silver from lead, allowing silver to be removed.

The Parkes process depends on the following:

- lead and zinc are almost immiscible just above their melting points
- silver is much more soluble in zinc than in lead
- silver/zinc alloys have higher melting points than pure zinc

Use the following data to answer the following questions:

metal	melting point /°C	boiling point /°C	density of metal at melting point /g cm ⁻³
lead	328	2023	10.7
silver	1233	2435	9.32
zinc	693	1180	6.57

- (i) Give a reason why lead and zinc are almost immiscible above zinc's melting point.
- (ii) Suggest a suitable value for temperature T.
- (iii) Suggest how silver can be recovered from the silver–zinc alloy crust.
- (iv) At a constant temperature, silver distributes itself between two immiscible solvents in such a way that the ratio of its concentration in two solvents is a constant. At 800 °C, this constant is given as:

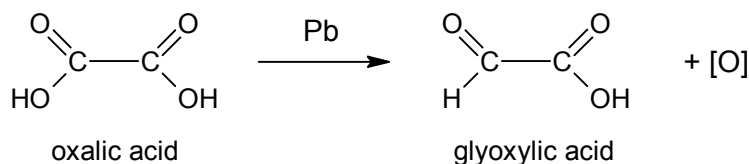
$$\frac{\text{concentration of Ag in molten zinc}}{\text{concentration of Ag in molten lead}} = 300$$

where concentration is measured in g cm⁻³.

Determine the mass of silver that can be extracted with zinc when 2% zinc by mass is added to 1 kg of the lead mixture containing 0.2% silver by mass as impurity. Assume that densities of zinc and lead at 800 °C are the same as that given in the table.

[6]

- (c) Lead cathodes are used with an acidic electrolyte in the organic synthesis of glyoxylic acid from oxalic acid.



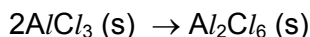
- (i) Give the IUPAC name of oxalic acid.
- (ii) Glyoxylic acid has a $\text{p}K_{\text{a}}$ value of 3.32. Define $\text{p}K_{\text{a}}$ and hence determine the acid dissociation constant of glyoxylic acid, giving its unit.
- (iii) Which is a stronger acid, glyoxylic or ethanoic acid? Explain your answer.
- (iv) Name the type of reaction involved when glyoxylic acid reacts with hydrocyanic acid, HCN in the presence of trace amount of sodium cyanide. Describe the mechanism of this reaction with relevant equations, partial charges and arrows showing movement of electrons.

[8]
[Total: 20]

- 3 (a) The standard enthalpy change of formation of solid Al_2Cl_6 is found to be $-1364.2 \text{ kJ mol}^{-1}$ using the following data:

	$\Delta H^\circ / \text{kJ mol}^{-1}$
$\text{Al}_2\text{Cl}_6(\text{s}) \rightarrow \text{Al}_2\text{Cl}_6(\text{aq})$	- 650
$\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightarrow 2\text{HCl}(\text{g})$	-184
$\text{HCl}(\text{g}) \rightarrow \text{HCl}(\text{aq})$	-72.7
$2\text{Al}(\text{s}) + 6\text{HCl}(\text{aq}) \rightarrow \text{Al}_2\text{Cl}_6(\text{aq}) + 3\text{H}_2(\text{g})$	-1026

- (i) State Hess' Law.
 - (ii) Use the set of data and an appropriate energy cycle to verify the standard enthalpy change of formation value of solid Al_2Cl_6 . Label the ΔH° values clearly in your cycle.
- [4]
- (b) Dimerisation of AlCl_3 in the gaseous state produces Al_2Cl_6 .
 - (i) Draw the structure of Al_2Cl_6 .
 - (ii) Given that the standard enthalpy change of formation of solid AlCl_3 is $-705.6 \text{ kJ mol}^{-1}$, calculate the standard enthalpy change for the following reaction.



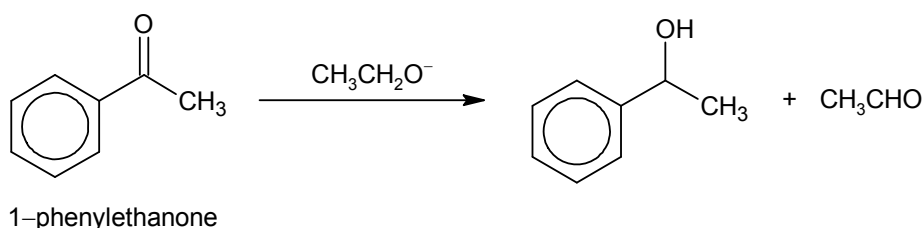
- (iii) Consider your answer in (i) and suggest with reasoning if the enthalpy value that you have determined in (ii) is as expected.
- (iv) The standard entropy change of reaction for the dissociation of Al_2Cl_6 molecules into AlCl_3 molecules is $+88.0 \text{ J mol}^{-1} \text{ K}^{-1}$. Use your answer in (ii) to determine ΔG° of the dimerisation reaction. What is the significance of the sign of your answer?

[5]

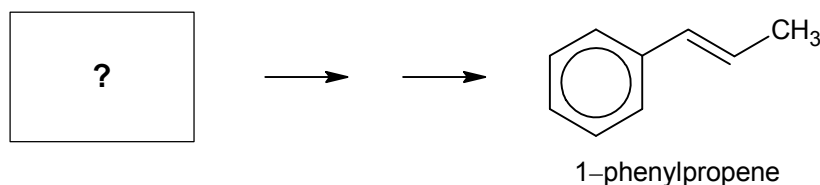
- (c) Aluminium sulfate is the active ingredient in styptic pencils, which can be used to stop bleeding from small cuts. The Al^{3+} ions induce coagulation in the blood, which facilitates formation of a blood clot.
- (i) Suggest how Al^{3+} ions induce coagulation in blood.
- (ii) It is also possible that the low pH of an aqueous solution of Al^{3+} brings about blood clotting. Write an equation to account for the low pH and explain how this happens.
- (iii) Hence determine the equilibrium constant for the reaction in (ii) for a 0.10 mol dm^{-3} aqueous solution of Al^{3+} with a pH of 2.95.

[5]

- (d) Alcohols can react with aluminium in the same way as it does with sodium metal.
- (i) Write the structural formula of the organic product obtained with propan-1-ol reacts with aluminium.
- (ii) In the Meerwein–Ponndorf–Verley reaction shown below, ethoxide ($CH_3CH_2O^-$) reduces 1-phenylethanone to an alcohol and itself oxidised to an aldehyde.



Use this reaction to devise a 2-step synthesis of 1-phenylpropene, starting from a suitable phenylketone and propan-1-ol. Include in your answers, suitable reagents and conditions and any organic compounds formed.



- (iii) 1-phenylpropene reacts with both HCl and HBr at different rates. Predict, with reasoning, which halide will react faster.

[6]

[Total: 20]

- 4 Iron, the most common element on Earth, has an important role in biological systems and is found in a variety of chemical compounds.

- (a) Iron can be found in seaweed as $Fe(II)$ or $Fe(III)$ cations. The total iron content of a seaweed sample can be determined in the laboratory using volumetric analysis.

Dilute sulfuric acid is added to 100 g of seaweed and the mixture is filtered. The resulting filtrate is divided into two 25.0 cm^3 portions for analysis.

The first portion is titrated with $0.0005 \text{ mol dm}^{-3} \text{ KMnO}_4$ and $1.70 \times 10^{-5} \text{ mol}$ of Fe^{2+} is found to be present. The second portion is treated with excess zinc, filtered, and titrated with the same $0.0005 \text{ mol dm}^{-3} \text{ KMnO}_4$. A total of 10.25 cm^3 is required to reach the end-point.

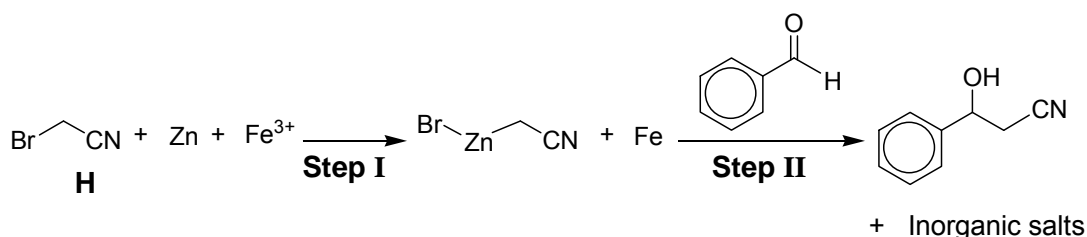
- With reference to the *Data Booklet*, explain the reaction between zinc and Fe^{3+} .
- Calculate the concentration of Fe^{3+} dissolved in dilute sulfuric acid in the second portion.
- Given that the recommended total iron content for a three-year-old child is 0.007 g , determine the mass of seaweed required daily if the child does not eat any other source of iron.

[5]

- Iron is important in biological systems as it is found in haemoglobin, the oxygen transport protein. Explain qualitatively, the toxic nature of carbon monoxide by considering its ligand exchange with oxygen.

[2]

- Iron and its compounds have also been used in organic synthesis. An example involving a nitrile compound H is shown below.



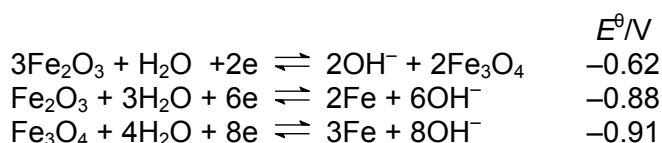
- State the type of reaction in Step II.
- The final product can exist in two isomeric forms which rotates plane polarised light in opposite directions. Using an appropriate representation, draw the isomers.
- In the presence of FeBr_3 , H and benzaldehyde can react differently to produce a disubstituted aromatic ring. The reaction mechanism is similar to the Al/Br_3 catalysed reaction of Br_2 and benzene.

Describe the mechanism of H and benzaldehyde catalysed by FeBr_3 .

[4]

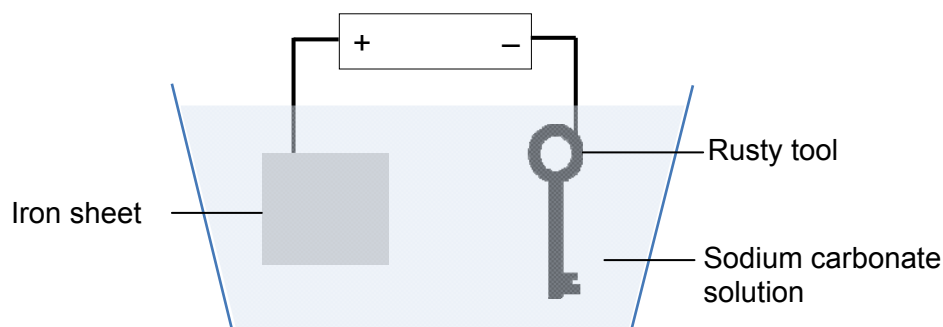
- Use of the *Data Booklet* is relevant to parts of this section.

Iron is used to make many household items. In a humid environment, rusting occurs easily. There are two forms of rust, red rust, Fe_2O_3 , and black rust, Fe_3O_4 . Red rust is responsible for “rusty” household items. The following shows some standard electrode potentials involving both forms of rust.



The following shows a “Do-It-Yourself” setup to remove rust from household tools.

After the power has been turned on for a few hours, the iron sheet *will be sacrificed* and the rusty tool will be coated with a black layer.



Note: Iron sheet contains trace amounts of zinc and chromium impurities.

- (i) State if the iron sheet is the cathode or the anode, and explain why it *will be sacrificed* in this process.
- (ii) A handyman prepares the above setup with a 50 A power source, and turns it on for 15 hours. Determine the mass of the iron sheet *sacrificed*.
- (iii) With reference to the standard electrode potentials given above, state and explain the identity of the black layer formed after the process. Deduce if it is possible to regenerate pure iron on the household tool.
- (iv) Small amounts of chromium and zinc are also found to be coated on the tool after 15 hours. Briefly explain how the coating could have occurred.

[6]

- (e) Iron(III) fluoride is a powerful dehydrating agent and is used in the production of ceramics. Its solubility product is $1.14 \times 10^{-7} \text{ mol}^4 \text{ dm}^{-12}$.
- (i) Calculate the solubility of iron(III) fluoride in pure water.
- (ii) Determine if a precipitate will be obtained when 10 cm^3 of 0.26 mol dm^{-3} iron(III) nitrate is added to 10 cm^3 of $0.182 \text{ mol dm}^{-3}$ sodium fluoride.

[3]

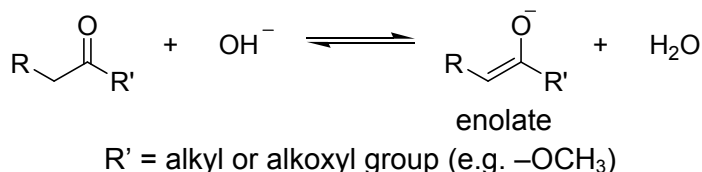
[Total: 20]

- 5 Acids and bases play a variety of roles in both organic and inorganic chemistry as exemplified by the following.

(a) Using the Bronsted–Lowry Theory, define a base, and state an example of a conjugate acid–base pair.

[2]

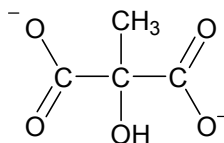
(b) Bases are common reagents in organic chemistry, and are often used in the formation of enolates. Enolates are the deprotonated anions of hydroxy alkenes. They are important intermediates in many carbon–carbon bond forming reactions, and are in equilibrium with the corresponding carbonyl compound as shown below.



- (i) In neutral conditions, the enolate concentration is very low. Suggest why reactions involving enolates are often carried out under basic conditions.
- (ii) Methyl propanoate can be converted to its lithium enolate for further carbon–carbon bond forming reactions. Draw the structure of the lithium enolate formed.
- (iii) The lithium enolate of methyl propanoate was reacted to form compound J.

J is a neutral compound which does not react with 2,4–dinitrophenylhydrazine. When refluxed with acidified K₂Cr₂O₇, a colour change and effervescence is observed. The gas liberated produces a white precipitate with aqueous calcium hydroxide. More effervescence is observed when aqueous sodium carbonate is added to the remaining products.

J decolourises liquid bromine to give K, C₆H₁₀Br₂O₂. J also reacts with cold dilute alkaline KMnO₄ to give L, C₆H₁₂O₄. When heated with aqueous alkaline iodine, hydrolysis and oxidation occurs. L then gives a yellow precipitate and 2–hydroxy–2–methyl–propandioate as products.



2–hydroxy–2–methyl–propandioate

Deduce with explanations, the structures of J, K and L.

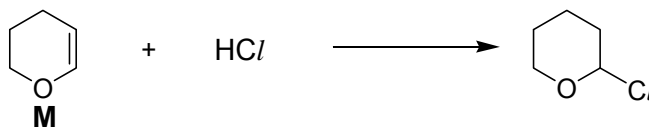
[10]

(c) Basic solutions can be formed from the reactions of Group II metals and water. Describe the reactivity and observations of Group II metals with water. Write the equation for the reaction of water with magnesium, including state symbols.

[3]

- (d) Aqueous acids can react with alkenes.

The reaction between hydrochloric acid and cyclic alkene M is as shown below.



- (i) Draw the structure of the reactive intermediate, and the hybrid orbitals of the reaction centre.
- (ii) Hence, outline the mechanism of the above reaction.
- (iii) Suggest why methanol is more soluble in water than cyclic alkene M.

[5]
[Total: 20]