1 Planning (P)

Calcium salts are used in many industrial processes. Calcium oxide is used in the production of cement while calcium nitrate is sometimes used to accelerate the setting of concrete.

Calcium oxide is a white hygroscopic solid. Calcium oxide can react with water and as such can cause severe irritation when in contact with skin, eyes or if inhaled.

Calcium nitrate is also a white hygroscopic solid. Calcium nitrate decomposes on heating to form the oxide, nitrogen dioxide and oxygen.

(a) Write a balanced equation, including state symbols, for the thermal decomposition of calcium nitrate.

$Ca(NO_3)_2(s)$ ® $CaO(s) + 2NO_2(g) + ½ O_2(g)$ [1]

(b) Calculate the change in mass of the solid you would expect if 1.00 mol of calcium nitrate underwent thermal decomposition.

Loss in mass = Mass of NO_2 and O_2

= 2(14.0 + 2(16.0)) + ½(2(16.0))

= 108 g [1]

(c) A container of calcium nitrate was contaminated with calcium oxide. Design an experiment to determine the percentage purity of calcium nitrate by a gravimetric method. You are provided with about 2 g of the impure calcium nitrate.

(In gravimetric methods, the objective is to form a thermally stable solid so that the mass can be determined accurately for analysis.)

Your plan should include the following:

- A full description of the procedure.
- Details of how you would calculate the percentage purity from the measurements made.

[M_r of $Ca(NO_3)_2$ = 164]

1. Weigh accurately a clean and dry crucible (Accept: hard glass tube). Add the sample and weigh the crucible with its contents.
2. Heat the crucible strongly for about five minutes to decompose the calcium nitrate.
3. Place crucible in a dessicator to cool. Then weigh the crucible and its contents.
4. Repeat the heating, cooling and weighing process until the mass of the crucible and its contents is consistent within 0.05 g in difference.

Loss in mass = initial mass of crucible and contents – final mass of crucible and contents after final heating [8]

Amount of $Ca(NO_3)_2$ = loss in mass / 108

Mass of $Ca(NO_3)_2$ = amount of $Ca(NO_3)_2$ × 164

% purity = mass of $Ca(NO_3)_2$ / initial mass of solid × 100%

(d) State and explain clearly one precaution you would take to improve the accuracy of your results.

Sample should be stored in dessicator while cooling to prevent absorption of water from the air. [1]

(e) Identify one potential safety hazard in this experiment and state how you would minimise the risk.

NO_2 is toxic. Perform experiment in fume cupboard.

OR

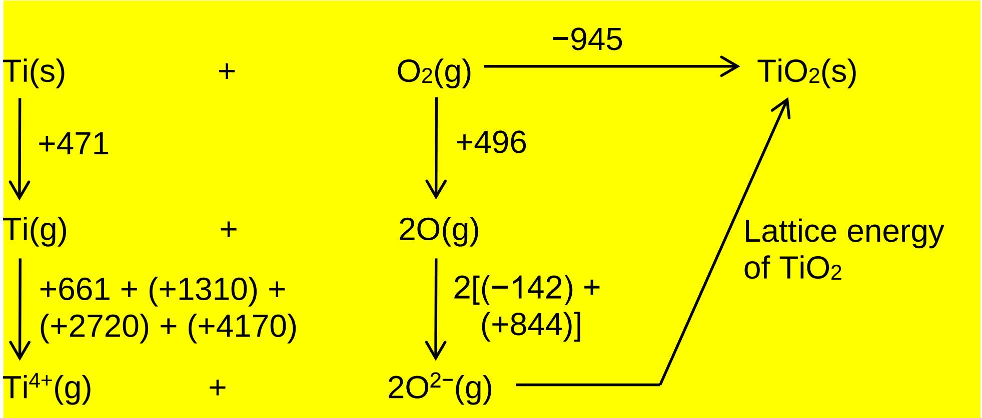
CaO causes skin / eye irritation / irritation if inhaled. Wear gloves, mask etc. [1]

[Total: 12]

2 Titanium(IV) oxide TiO_2 is the naturally occurring oxide of titanium. It is the main ingredient in sunscreen lotion due to its high refractive index and strong UV-light absorbing capability.

(a) Using the following information as well as relevant data from the *Data Booklet*, draw a Born-Haber cycle for the formation of TiO_2(s) and calculate the lattice energy of TiO_2(s).

Standard enthalpy change of formation of TiO_2(s)	-945 kJ mol^{-1}
Standard enthalpy change of atomisation of Ti	$+471$ kJ mol^{-1}
1st electron affinity of oxygen	-142 kJ mol^{-1}
2nd electron affinity of oxygen	$+844$ kJ mol^{-1}



[3]

By Hess' Law,

$-945 = +471 + (+661) + (+1310) + (+2720) + (+4170) + (+496) + 2[(-142) + (+844)] + \mathrm{LE}(TiO_2)$

$\mathrm{LE}(TiO_2) = -12177 \text{ kJ mol}^{-1}$
$= -1.22 \times 10^4 \text{ kJ mol}^{-1}$

(b) Crude titanium(IV) oxide is purified via the Chloride process. In this two-step process, the crude ore (containing at least 70% titanium(IV) oxide) is first reacted with carbon and chlorine, represented by the equation shown below.

$$TiO_2(s) + C(s) + 2Cl_2(g) \rightarrow TiCl_4(l) + CO_2(g)$$

Standard enthalpy change of formation of $TiCl_4(l)$	-804 kJ mol^{-1}
Standard enthalpy change of formation of $CO_2(g)$	-394 kJ mol^{-1}
Standard molar entropy of $TiO_2(s)$	$+49.9 \text{ J mol}^{-1} \text{ K}^{-1}$
Standard molar entropy of C(s)	$+5.7 \text{ J mol}^{-1} \text{ K}^{-1}$
Standard molar entropy of $Cl_2(g)$	$+223 \text{ J mol}^{-1} \text{ K}^{-1}$
Standard molar entropy of $TiCl_4(l)$	$+252 \text{ J mol}^{-1} \text{ K}^{-1}$
Standard molar entropy of $CO_2(g)$	$+214 \text{ J mol}^{-1} \text{ K}^{-1}$

Using the above information, as well as relevant data from **(a)** and the *Data Booklet*, calculate, for the first step of the Chloride process,

(i) the standard enthalpy change of reaction,

Standard enthalpy change of reaction

$= [(-804) + (-394)] - [(-945) + 0 + 2(0)]$

$= -253 \text{ kJ mol}^{-1}$

(ii) the standard entropy change of reaction.

Note: $\Delta S^\circ = \Sigma S^\circ(\text{products}) - \Sigma S^\circ(\text{reactants})$

Standard entropy change of reaction

$= [(+252) + (+214)] - [(+49.9) + (+5.7) + 2(+223)]$

$= -35.6 \text{ J mol}^{-1} \text{ K}^{-1}$ [2]

(c) Using your answers in **(b)**, determine if the first step of the Chloride process is spontaneous at 2000 K.

$\Delta G = \Delta H - T\Delta S$

$\Delta G = (-253) - (2000)(-35.6/1000)$

$\Delta G = -182 \text{ kJ mol}^{-1} < 0$

Hence, the reaction is spontaneous at 2000 K. [1]

(d) The second step of the Chloride process involves the titanium(IV) chloride being distilled off and oxidised in a pure oxygen flame to give pure titanium(IV) oxide and chlorine gas.

Write an equation for the reaction in the second step.

$TiCl_4 + O_2 \rightarrow TiO_2 + 2Cl_2$ [1]

[Total: 7]

3 Neidong Forest Recreation National Park, located in the Wulai District in Taipei, has the highest concentration of anions in Taiwan due to the numerous waterfalls and lush forestation in the park. Anions are said to help boost the immune system, among other health benefits.

(a) Bromide ions are thought to be one of the anions present in abundance. The concentration of bromide ions in the river waters can be used as an estimate of the concentration of the ions in the park.

A 25.0 cm^3 sample of river water was collected and 50.0 cm^3 of 1.00 mol dm^{-3} $Pb(NO_3)_2$ was added. The precipitate formed was filtered off and 3.00 g of precipitate was collected. The filtrate can be regarded as a saturated solution of $PbBr_2$.

(i) Calculate the concentration of Pb^{2+} ions in the filtrate.

Amount of $PbBr_2$ collected $= \dfrac{3.00}{207 + 2(79.9)}$

$= 8.18 \times 10^{-3}$ mol

Amount of Pb^{2+} in filtrate $= \left(\dfrac{50}{1000} \times 1.00\right) - \left(8.18 \times 10^{-3}\right)$

$= 0.0418$ mol

$$[Pb^{2+}] \text{ in filtrate} = \frac{0.0418}{0.075}$$

$$= \underline{\mathbf{0.557\ mol\ dm^{-3}}}$$

(ii) Write an expression for the solubility product, K_{sp}, of $PbBr_2$.

$K_{sp} = [Pb^{2+}][Br^{-}]^2$

(iii) The numerical value for the K_{sp} of $PbBr_2$ is 3.9×10^{-5}. Determine the concentration of bromide ions in the sample of river water.

$$[Br^{-}] \text{ in filtrate} = \sqrt{\frac{3.9 \times 10^{-5}}{0.557}}$$

$$= 8.37 \times 10^{-3} \text{ mol dm}^{-3}$$

Total amount of Br^{-} in sample of river water

= Amount of Br^{-} in filtrate + Amount of Br^{-} in ppt

$$= (8.37 \times 10^{-3} \times \frac{75}{1000}) + (8.18 \times 10^{-3} \times 2)$$

= 0.0170 mol

$$[Br^{-}] \text{ in sample of river water} = 0.0170 \div \frac{25}{1000}$$

$$= \underline{\mathbf{0.680\ mol\ dm^{-3}}}$$ [5]

(b) Another anion, **W**, found in Neidong National Park can be formed when the oxide of a Period 3 element reacts with an alkali. When dilute nitric acid is added to a solution containing **W**, a colourless and pungent gas that turns acidified potassium dichromate(VI) from orange to green is evolved.

(i) Suggest an identity for anion **W**.

SO_3^{2-}/HSO_3^{-}

(ii) Write an equation for the formation of **W** from the reaction of a Period 3 oxide with an alkali.

$SO_2 + 2OH^{-} \rightarrow SO_3^{2-} + H_2O$

OR $SO_2 + OH^{-} \rightarrow HSO_3^{-}$ [2]

[Total: 7]

4 The lead–acid accumulator is a storage battery used in cars because it can be recharged. It consists of a series of cells containing lead plate anodes, lead dioxide plate cathodes and an electrolyte of 6 mol dm^{-3} sulfuric acid.

When it is operating, the reactions that occur at the electrodes are

$Pb^{2+}(aq) + 2e^{-} \rightleftharpoons Pb(s)$ $\qquad E^{\ominus} = -0.13$ V

$PbO_2(s) + 4H^{+}(aq) + 2e^{-} \rightleftharpoons Pb^{2+}(aq) + 2H_2O(l)$ $\qquad E^{\ominus} = +1.47$ V

(a) Write the overall equation for the reaction during discharge and calculate the voltage delivered by the battery.

$Pb(s) + PbO_2(s) + 4H^{+}(aq) \rightarrow 2Pb^{2+}(aq) + 2H_2O(l)$

$E^{\ominus}_{cell} = 1.47 - (-0.13) = \mathbf{+1.60V}$ [2]

(b) However, it is noted that the actual voltage is 2.0 V as compared to the value that you have calculated in **(a)**. Explain why the actual voltage differs from the calculated voltage.

During discharging, $Pb^{2+}(aq)$ is removed as it precipitates out as $PbSO_4(s)$. This cause the equilibrium position of $PbO_2 + 4H^{+} + 2e^{-} \rightleftharpoons Pb^{2+} + 2H_2O$ to shift to the right, hence, $E(PbO_2/Pb^{2+})$ is more positive than +1.47 V.

On the other hand, as $PbSO_4$ is precipitated out, the equilibrium position of $Pb^{2+} + 2e^{-} \rightleftharpoons Pb$ shifts to the left, resulting in $E(Pb^{2+}/Pb)$ to be more negative than - 0.13 V.

Hence actual voltage is 2.0V

[2]

(c) Explain why the battery is rechargeable.

When an external current is applied, it will recharge the battery by driving the cell reaction in the reverse direction. [1]

(d) State **one** disadvantage of the lead-acid accumulator battery.

1) Rather large and heavy due to the lead, hence produces low power for its mass.
2) $PbSO_4$ deposits on the electrodes in a finely divided form during discharge. If a discharged battery stands for a long time, the small grains of $PbSO_4$ may grow into large crystals that fall from the electrodes. If too much $PbSO_4$ is lost, the cell cannot be recharged and results in a loss of capacity.
3) Lead is toxic. [1]

[Total: 6]

5 This question is about the chemistry of halogens and the halide ions.

(a) Aqueous bromine is decolourised when added to aqueous sodium thiosulfate. When excess of aqueous barium nitrate is added to the resulting solution, a white precipitate is observed. This precipitate is filtered off, leaving a colourless filtrate.

(i) Write a balanced ionic equation for the reaction between bromine and sodium thiosulfate.

$4Br_2 + S_2O_3^{2-} + 5H_2O \rightarrow 8Br^- + 2SO_4^{2-} + 10H^+$

(ii) To the colourless filtrate in **(i)**, aqueous silver nitrate is added, followed by concentrated ammonia solution.

Describe what is observed and write balanced equations for the reaction that occur.

Cream ppt formed when $AgNO_3$ is added.

Upon adding concentrated NH_3, cream ppt is soluble in concentrated NH_3

$Ag^+(aq) + Br^-(aq) \rightarrow AgBr(s)$
$AgBr(s) + 2NH_3(aq) \rightarrow [Ag(NH_3)_2]^+(aq) + Br^-(aq)$

(b) In a separate experiment, aqueous bromine is added to aqueous potassium iodide. To the resulting mixture, an equal volume of an organic solvent is added.

What will be the colour of the organic layer? Write equations for any reactions that occur.

Colour: Purple

Equation: $Br_2(aq) + 2KI(aq) \rightarrow 2KBr(aq) + I_2(aq)$ [6]

(c) Iodide ions react with peroxodisulfate ions in the presence of Fe^{3+} catalyst. The overall equation for the reaction is shown below.

$$2I^-(aq) + S_2O_8^{2-}(aq) \rightarrow I_2(aq) + 2SO_4^{2-}(aq)$$

(i) Fe^{3+} ions are added to lower the high activation energy so that the reaction can proceed at a higher rate. Explain why the activation energy is high for the reaction between the iodide and peroxodisulfate ions if no Fe^{3+} ions are added.

Energy is required to overcome the repulsion between two reactant anions before the ions can react.

(ii) With reference to the *Data Booklet*, suggest a mechanism for [4] this reaction in the presence of Fe^{3+}.

$S_2O_8^{2-}(aq) + 2e^- = SO_4^{2-}(aq)$ E› = +2.01 V

$Fe^{3+}(aq) + e^- = Fe^{2+}(aq)$ E› = +0.77 V

$I_2(aq) + 2e^- = 2I^-(aq)$ E› = +0.54 V

Step 1: $2Fe^{3+}(aq) + 2I^-(aq)$ ® $2Fe^{2+}(aq) + I_2(aq)$

E›$_{cell}$ = +0.77 - (+0.54) = + 0.23 V > 0 V

Reaction in step 1 is energetically feasible.

Step 2: $2\,Fe^{2+}(aq) + S_2O_8^{2-}(aq)$ ® $2Fe^{3+}(aq) + 2SO_4^{2-}(aq)$

E›$_{cell}$ = +2.01 - (+0.77) = + 1.24 V > 0 V

Reaction in step 2 is energetically feasible.

[Total: 10]

6 Chromium is a hard grey metal which is widely used in the manufacture of stainless steel due to its good corrosion-resistant properties.

Calcium is a fairly soft, silvery grey metal which tarnishes quickly in air.

(a) The melting point of calcium is 843 °C while chromium melts at a much higher temperature of 1907 °C.

Explain this difference in terms of the type and strength of bonding in each metal.

Both elements have metallic bonding. In Cr, both the 4s and 3d electrons can be contributed to form mobile charge cloud as they are very close in energy. The resulting chromium ion has a higher positive charge and a smaller ionic radius. This leads to stronger metallic bonds in Cr as compared to Ca, which only contributes 2 valence electrons per Ca atom to form Ca^{2+}.

[3]

(b) Write the electronic configuration of chromium atoms and chromium(III) ions.

Cr: $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^5\,4s^1$
Cr^{3+}: $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^3$

[2]

(c) When aqueous sodium hydroxide was added to aqueous chromium(III) nitrate, a blue-green precipitate was observed. Upon addition of excess sodium hydroxide, the precipitate dissolved to give a dark green complex.

When aqueous sodium carbonate was added to aqueous chromium(III) nitrate, effervescence was observed.

(i) State the formula of the blue-green precipitate.

$Cr(OH)_3$

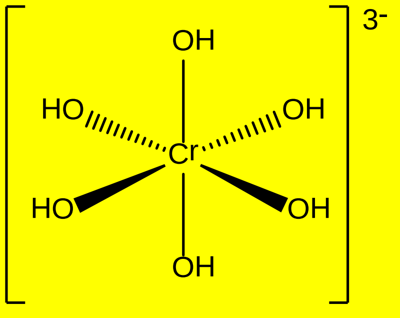
(ii) Suggest a reason why effervescence was observed when aqueous sodium carbonate was added to aqueous chromium(III) nitrate.

Aqueous chromium(III) solutions are acidic (and an acid-carbonate reaction occurred forming carbon dioxide).

(iii) Given that the formula of the soluble dark green complex is $Na_3CrO_6H_6$, state the formula of the complex ion formed.

$[Cr(OH)_6]^{3-}$

(iv) Draw the structure of the complex ion.



[4]

[Total: 9]

7 Hydrocarbons are commonly used as combustible fuel sources as well as feed materials in the petrochemical industry.

(a) Describe a simple chemical test to distinguish between but-1-ene and but-2-ene. State clearly what would be observed with each compound.

Heat with acidified $KMnO_4$ and test the gas evolved with limewater.

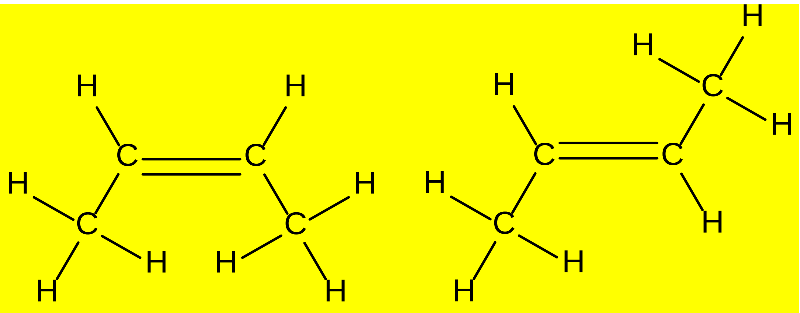
But-1-ene would (turn purple $KMnO_4$ colourless and) produce a gas that forms a white ppt with limewater, while but-2-ene (would turn purple $KMnO_4$ colourless but) would not produce a gas. [2]

(b) But-2-ene is able to exist as 2 isomers.

(i) State the type of isomerism exhibited by but-2-ene.

Geometric(al) isomerism / *cis-trans* isomerism

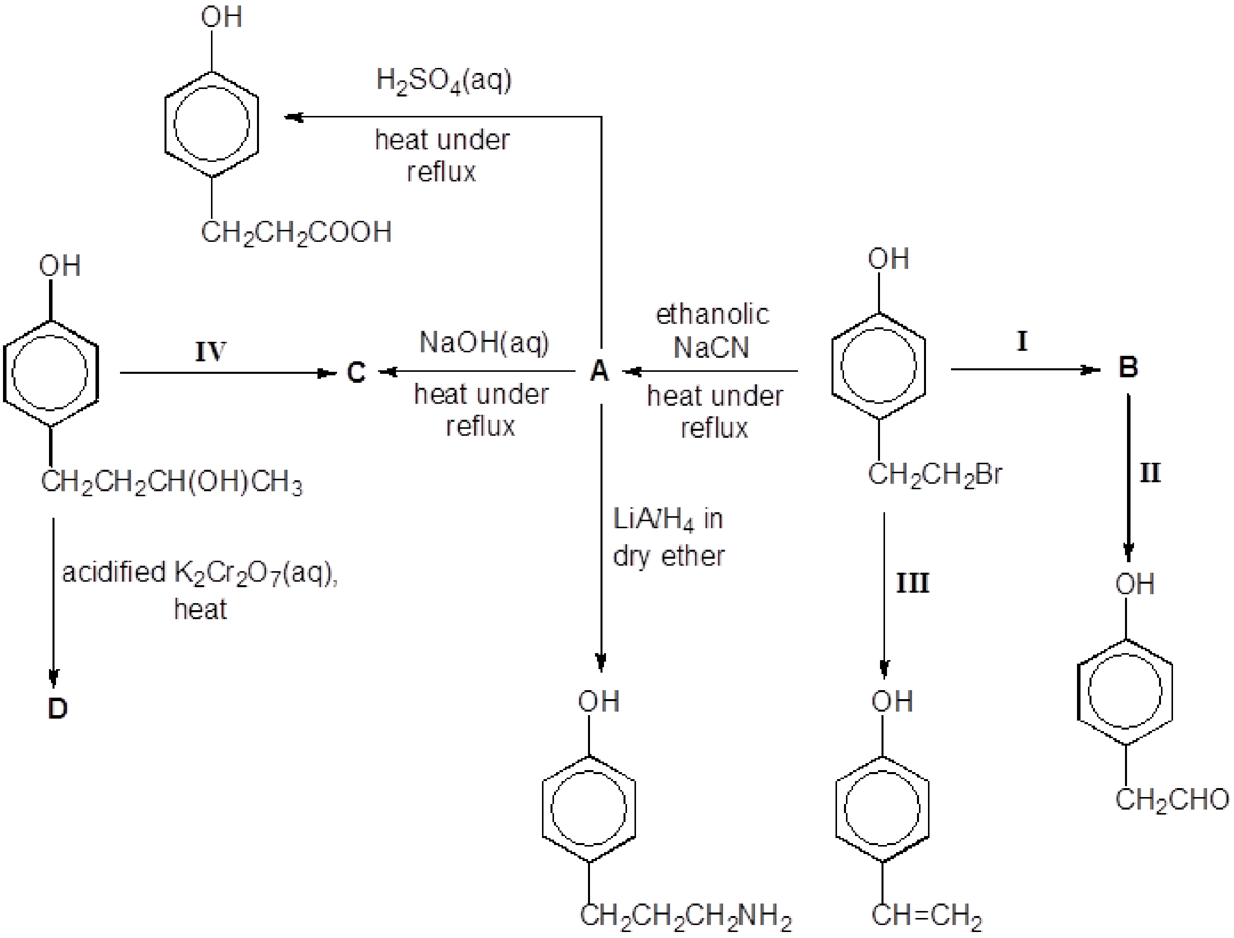
(ii) Draw the displayed structural formulae for the 2 isomers of but-2-ene.

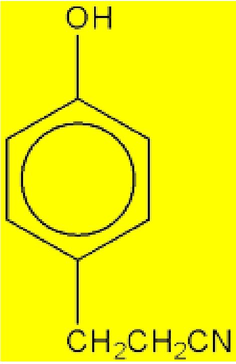
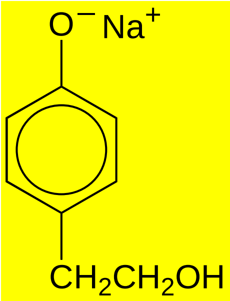
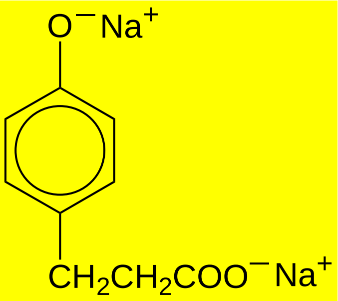
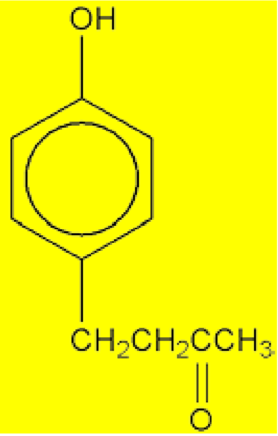


[3]

(c) Benzene is an aromatic hydrocarbon present in many compounds.

A reaction scheme involving benzene derivatives is given below. Draw the structures of **A** to **D** and give the reagents and conditions for steps **I** to **IV**.



A: 	**B:** 
C: 	**D:** 

Step **I**: NaOH(aq)/KOH(aq), heat under reflux

Step **II**: acidified $K_2Cr_2O_7$(aq), heat and distil

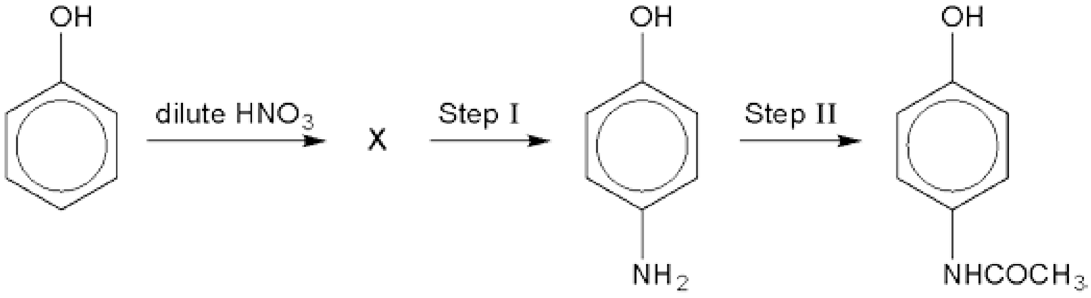
Step **III**: alcoholic NaOH/KOH, heat under reflux

Step **IV**: I_2, NaOH(aq), warm

[8]

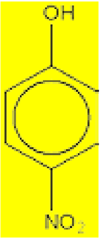
[Total: 13]

8 Students often complain of headaches when faced with a tough problem they cannot solve. A very common over-the-counter drug to combat headaches is paracetamol. The synthesis of paracetamol is shown below:



Paracetamol

(a) Draw the structure of compound **X**.



[1]

(b) Step **I** is actually a two-stage process. State the reagents and conditions for the two stages.

Stage 1: …………………………………………………………………….......

Sn, conc. HC*l*, heat

Stage 2: …………………………………………………………………….......

NaOH(aq)

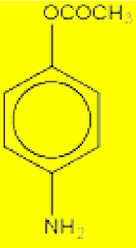
[2]

(c) Step **II** involves a condensation reaction. An organic side-product, **Y**, can be formed along with paracetamol.

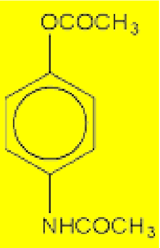
(i) State the reagent for this step.

CH_3COCl

(ii) Suggest a structure for the side-product, **Y**. [2]

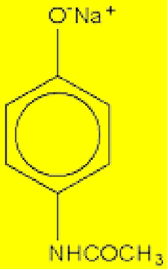


OR

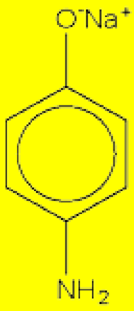


(d) Suggest the structues of all the organic products formed when paracetamol reacts with

(i) NaOH(aq) at room temperature



(ii) NaOH(aq) with heating



and $CH_3COO^-Na^+$

[3]

[Total: 8]