



Oxford Cambridge and RSA

Monday 19 June 2023 – Afternoon

A Level Chemistry B (Salters)

H433/02 Scientific literacy in chemistry

Time allowed: 2 hours 15 minutes



You must have:

- a clean copy of the Advance Notice Article (inside this document)
- the Data Sheet for Chemistry B

You can use:

- a scientific or graphical calculator
- an HB pencil



Please write clearly in black ink. **Do not write in the barcodes.**

Centre number

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Candidate number

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First name(s)

Last name

StemUp Model Solution

INSTRUCTIONS

- Use black ink. You can use an HB pencil, but only for graphs and diagrams.
- Write your answer to each question in the space provided. If you need extra space use the lined pages at the end of this booklet. The question numbers must be clearly shown.
- Answer **all** the questions.
- Where appropriate, your answer should be supported with working. Marks might be given for using a correct method, even if your answer is wrong.

INFORMATION

- The total mark for this paper is **100**.
- The marks for each question are shown in brackets [].
- Quality of extended response will be assessed in questions marked with an asterisk (*).
- This document has **24** pages.

ADVICE

- Read each question carefully before you start your answer.

- 1 The element bromine is extracted from seawater.

Bromide ions are present in seawater in very low concentrations compared with chloride ions.

- (a) (i) Excess chlorine is added to acidified seawater, forming aqueous bromine.

Write an **ionic** equation for the reaction of chlorine with bromide ions and explain how it shows that chlorine is more reactive than bromine.



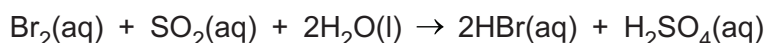
Explanation: *...chlorine gains electrons from bromide ions (oxidises Br^-), so
...chlorine displaces bromine.*

[2]

- (ii) Air is blown through the mixture to remove the bromine as a vapour.

Sulfur dioxide is then added, and the mixture is dissolved in water.

Bromine reacts to form concentrated HBr.



What is the oxidising agent in this reaction?

Explain your answer using oxidation states.

Bromine, Br_2 , is the oxidising agent.
*The oxidation state of Br decreases from 0 in Br_2 to -1 in HBr, so
bromine gains electrons (is reduced). The oxidation state of S increases
from +4 in SO_2 to +6 in H_2SO_4 .*

[2]

- (iii) Concentrated Br_2 is made from the concentrated HBr by displacement using chlorine.

Complete the table to give the properties of chlorine, bromine and iodine.

Halogen	Colour at room temperature	Physical state at room temperature
chlorine	<i>green</i>	<i>gas</i>
bromine	<i>red-brown</i>	<i>liquid</i>
iodine	<i>grey-black</i>	<i>solid</i>

[2]

- (b) Some of the hazards of transporting bromine are similar to those of transporting chlorine.

Suggest **two** hazards of transporting bromine in a road tanker.

Hazard 1 *Bromine is toxic (poisonous), especially if its vapour is breathed in after a leak.*

Hazard 2 *Bromine is corrosive: it causes chemical burns to skin and eyes.*

[2]

- (c) Some students add aqueous silver nitrate to a sample of seawater.

They expect to see a cream precipitate of silver bromide but the precipitate is pure white.

- (i) Write an **ionic** equation for the reaction of silver ions with **bromide** ions.

Show state symbols.



[2]

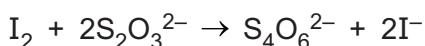
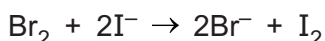
- (ii) Suggest why the students do **not** get the result they expect.

The white precipitate is silver chloride, AgCl.

Seawater contains much more Cl^- than Br^- , so the Ag^+ ions react with the chloride ions and the white AgCl hides any cream AgBr.

[2]

- (d) The students titrate 25.0 cm^3 of a solution of bromine with sodium thiosulfate in the presence of excess iodide ions.



They find that 24.65 cm^3 of $0.380 \text{ mol dm}^{-3}$ sodium thiosulfate is required to reach the end point.

Calculate the concentration of Br_2 in mol dm^{-3} .

$$n(\text{S}_2\text{O}_3^{2-}) = 24.65 \times 0.380 \div 1000 = 9.37 \times 10^{-3} \text{ mol}$$

$$n(\text{Br}_2) = n(\text{I}_2) = 9.37 \times 10^{-3} \div 2 = 4.68 \times 10^{-3} \text{ mol}$$

$$[\text{Br}_2] = 4.68 \times 10^{-3} \times 1000 \div 25.0 = 0.187 \text{ mol dm}^{-3}$$

concentration = *0.187* mol dm^{-3} [2]

- (e) The students have another solution containing 20 g dm^{-3} bromine.

They find that 160 cm^3 of this solution reacts exactly with 0.80 g of a hydrocarbon with a molecular formula of C_6H_8 .

Suggest a structure for the hydrocarbon.

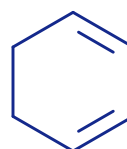
$$\text{amount Br}_2 = (160 \div 1000 \times 20) \div 159.8 = 0.0200 \text{ mol}$$

$$\text{amount C}_6\text{H}_8 = 0.80 \div 80.0 = 0.0100 \text{ mol}$$

$\text{Br}_2 : \text{C}_6\text{H}_8 = 2 : 1$, so there are 2 $\text{C}=\text{C}$ double bonds per molecule

C_6H_8 has one more degree of unsaturation, so it also has a ring:

a cyclohexadiene, e.g. cyclohexa-1,3-diene

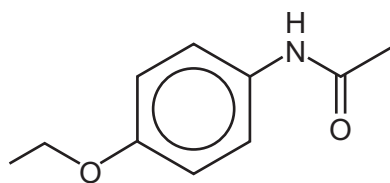


[4]

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Turn over for the next question

- 2 Phenacetin was used as a pain-relieving medicine until its harmful side-effects were discovered.



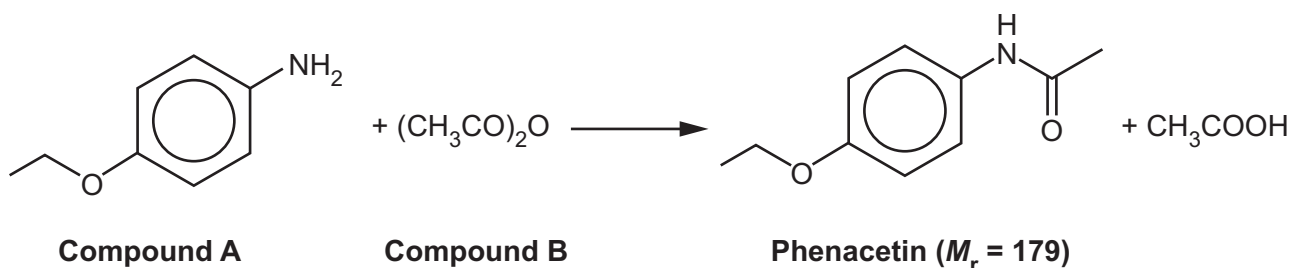
Phenacetin

- (a) Phenacetin has a secondary amide group attached to a benzene ring. It also has one other functional group.

Name this functional group.

ether..... [1]

- (b) Some students set out to make phenacetin from compound **A**, using the reaction shown.



- (i) Give the systematic name of compound **B**.

ethanoic anhydride..... [1]

- (ii) The students use 14 g of both compound **A** and compound **B**.

Calculate the amounts of each (in mol) that show that compound **B** is in excess.

$$M_r(A), C_8H_{11}NO = 137 \qquad M_r(B), C_4H_6O_3 = 102$$

$$\text{amount } A = 14 \div 137 = 0.102 \text{ mol}$$

$$\text{amount } B = 14 \div 102 = 0.137 \text{ mol}$$

A and B react 1 : 1, and 0.137 > 0.102, so B is in excess

amount of compound **A** = ... 0.102 mol

amount of compound **B** = ... 0.137 mol
[2]

- (iii) The students recrystallise their crude phenacetin using water and obtain 20 g of solid product. They calculate their percentage yield.

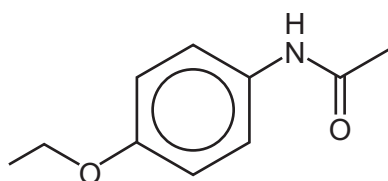
What advice would you give them?

A is limiting: 100% yield = $0.102 \times 179 = 18.3$ g of phenacetin

(20 g, if pure, would be $20 \div 179 = 0.112$ mol, more than 0.102 mol)

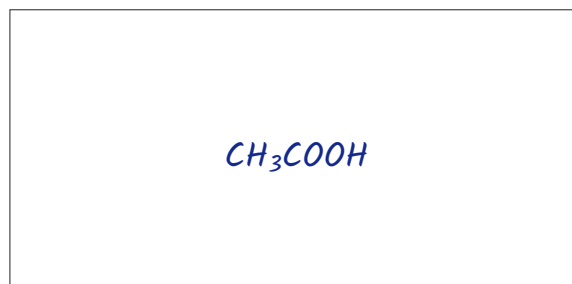
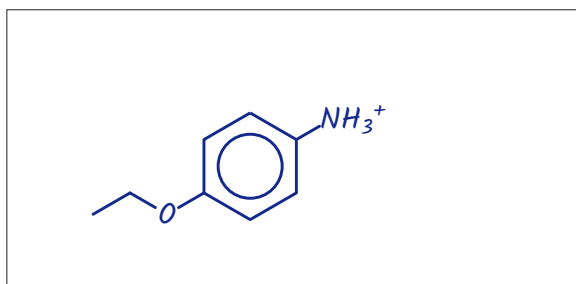
*20 g is more than the 100% yield of 18.3 g, so their yield is over
100%; the product is still wet or impure. Dry it fully, recrystallise
again and reweigh.* [3]

- (c) The students boil some phenacetin with aqueous acid.



Phenacetin

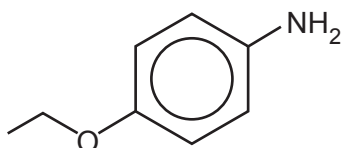
Draw the structures of the **two** products formed in the boxes below.



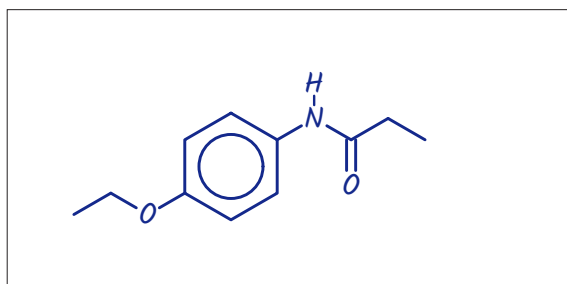
[2]

- (d) Compound **A** reacts with propanoyl chloride.

Draw the **skeletal** formula of the organic compound formed in the box below.



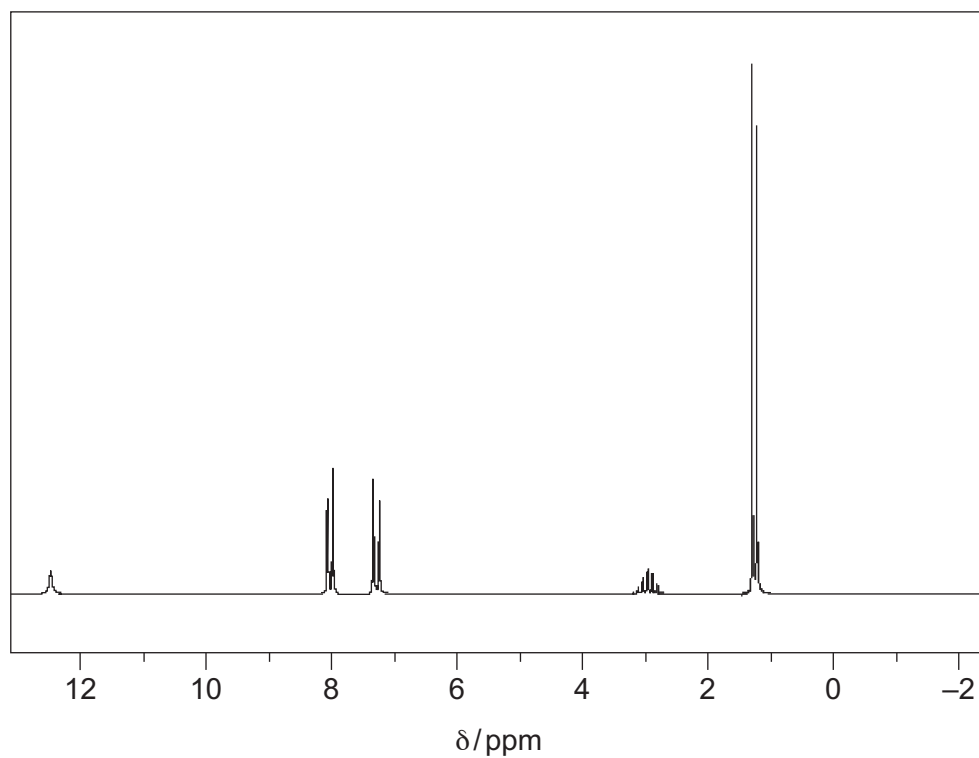
Compound A



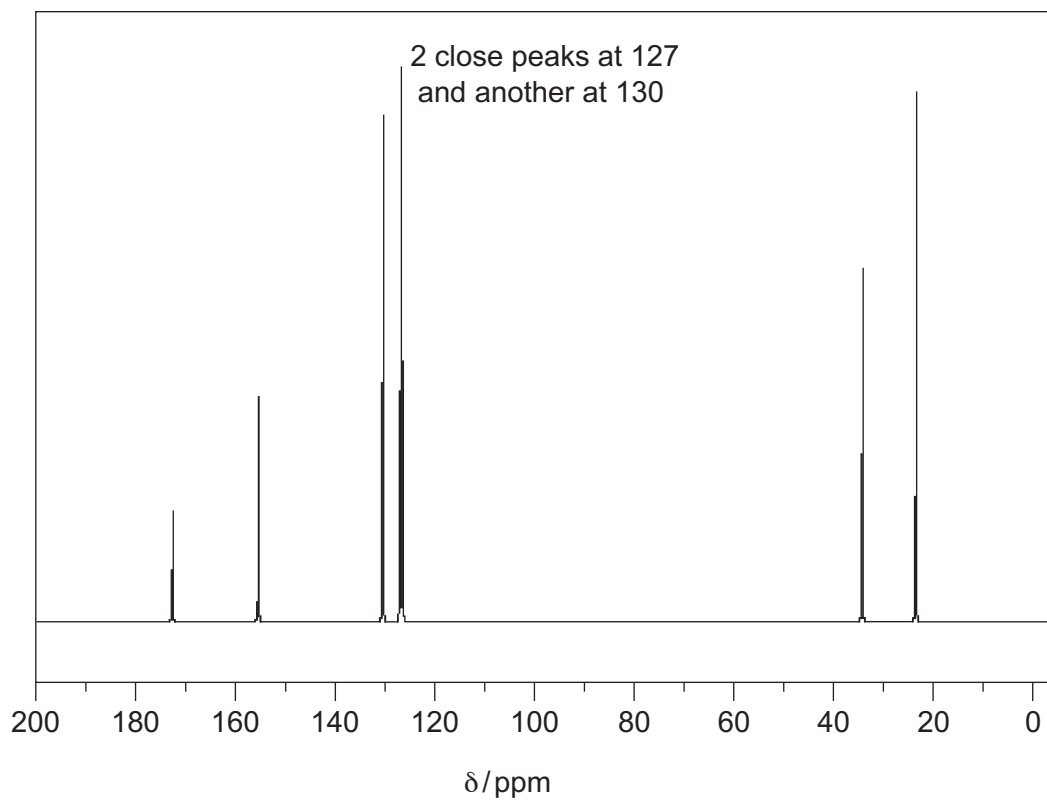
[2]

(e)* An aromatic acid has the formula $C_{10}H_{12}O_2$. Its NMR spectra are shown below.

^1H NMR



^{13}C NMR



You may do working on this page but only your answer on page 9 will be marked.

Identify the aromatic acid.

Show how evidence from **both** spectra relates to the structure.

The acid is 4-(propan-2-yl)benzoic acid, $(\text{CH}_3)_2\text{CH}-\text{C}_6\text{H}_4-\text{COOH}$, with the COOH and the $\text{CH}(\text{CH}_3)_2$ groups opposite each other (1,4-positions) on the benzene ring.

^1H NMR: 5 peaks, so 5 different H environments.

$\delta \approx 12.5$ ppm: H of the COOH group (carboxylic acid).

$\delta \approx 8.0$ and 7.3 ppm: aromatic H on the benzene ring; two peaks (doublets) show two pairs of equivalent ring H, so the ring is

1,4-disubstituted.

$\delta \approx 3.0$ ppm: a multiplet (heptet), so this CH is next to carbons with six H in total, the CH of $\text{CH}(\text{CH}_3)_2$.

$\delta \approx 1.2$ ppm: $\text{HC}-\text{C}$; a doublet, so the two equivalent CH_3 groups are next to a CH.

^{13}C NMR: 7 peaks but 10 carbons, so 7 environments; three pairs of carbons are identical.

$\delta \approx 172$ ppm: the $\text{C}=\text{O}$ carbon of COOH . [6]

Additional answer space if required:

$\delta \approx 155, 130$ and two close peaks at 127 ppm: 4 aromatic carbon environments (120 to 160 ppm); two of them are identical pairs of ring CH carbons, which fits a 1,4-disubstituted ring.

$\delta \approx 34$ ppm: the CH carbon; $\delta \approx 24$ ppm: the two identical CH_3 carbons (C-C region, 0 to 50 ppm).

So the molecule has an aromatic ring, a COOH group and a propan-2-yl group, $\text{C}_{10}\text{H}_{12}\text{O}_2$, which fits all the evidence from both spectra.

- 3 There is concern about the amount of carbon dioxide produced when methane is burned in domestic gas boilers.

Hydrogen is being investigated as an alternative gas that could be delivered through adaptations of the present gas pipes to adapted boilers.

- (a) The traditional source of industrial hydrogen uses two processes that have the overall equation shown in **Equation 3.1**.



A high temperature is needed to obtain a reasonable yield of hydrogen in a reasonable time.

- (i) A student says that a **low pressure** is best for the industrial manufacture of hydrogen in **Equation 3.1**.

Discuss the student's statement.

Use relevant chemistry to support your answer.

A low pressure gives a greater equilibrium yield of hydrogen; there are 3 moles of gas on the left and 5 on the right, so lowering the pressure moves the equilibrium to the right (more gas molecules). However, at low pressure the molecules are further apart (less concentrated), so there is a lower rate of collision and the reaction is slower. So the student is right about yield but not rate; a compromise pressure is needed. [4]

Equation 3.1 is repeated.



$$K_c = \frac{[\text{CO}_2] [\text{H}_2]^4}{[\text{CH}_4] [\text{H}_2\text{O}]^2}$$

- (ii) A mixture of $1.00 \text{ mol dm}^{-3} \text{ CH}_4(\text{g})$ and $1.00 \text{ mol dm}^{-3} \text{ H}_2\text{O}(\text{g})$ is allowed to reach equilibrium at 673 K in a container of volume 1.00 dm^3 .

The equilibrium concentration of H_2 is found to be $0.0705 \text{ mol dm}^{-3}$.

Calculate a value for the equilibrium constant, K_c , for Equation 3.1 at 673 K and give its units.

$$[\text{CO}_2] = 0.0705 \div 4 = 0.0176 \text{ mol dm}^{-3}$$

$$[\text{CH}_4] = 1.00 - 0.0176 = 0.982 \text{ mol dm}^{-3}$$

$$[\text{H}_2\text{O}] = 1.00 - 2 \times 0.0176 = 0.965 \text{ mol dm}^{-3}$$

$$K_c = (0.0176 \times 0.0705^4) \div (0.982 \times 0.965^2)$$

$$K_c = 4.76 \times 10^{-7}$$

$$\text{units: } (\text{mol dm}^{-3})^5 \div (\text{mol dm}^{-3})^3 = \text{mol}^2 \text{ dm}^{-6}$$

$$K_c = 4.76 \times 10^{-7} \text{ units mol}^2 \text{ dm}^{-6} \quad [4]$$

- (iii) K_c for the reaction is then measured again at an increased pressure.

Would the value of K_c be larger, smaller or the same?

Give a reason for your answer.

The same: K_c does not vary with pressure, it only varies with temperature. [1]

Equation 3.1 is repeated.



(iv) The table shows some entropy data.

Substance	$S^\circ / \text{J mol}^{-1} \text{K}^{-1}$
$\text{CH}_4(\text{g})$	186
$\text{CO}_2(\text{g})$	214
$\text{H}_2(\text{g})$	130
$\text{H}_2\text{O}(\text{g})$	189

Use the data to show that $\Delta S^\circ_{\text{sys}} = +170 \text{ J mol}^{-1} \text{K}^{-1}$ for the reaction in Equation 3.1.

$$\begin{aligned} \Delta S^\circ_{\text{sys}} &= \Sigma S^\circ(\text{products}) - \Sigma S^\circ(\text{reactants}) \\ &= (214 + 4 \times 130) - (186 + 2 \times 189) = 734 - 564 \\ &= +170 \text{ J mol}^{-1} \text{K}^{-1} \end{aligned}$$

[1]

(v) Use calculations to determine if the forward reaction in Equation 3.1 is feasible at 750°C .

Give a reason for your answer.

$$T = 750 + 273 = 1023 \text{ K}$$

$$\Delta S_{\text{surr}} = -\Delta H \div T = -165\,000 \div 1023 = -161 \text{ J mol}^{-1} \text{K}^{-1}$$

$$\Delta S_{\text{total}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = +170 - 161 = +8.7 \text{ J mol}^{-1} \text{K}^{-1}$$

It is feasible at 750°C , because ΔS_{total} is positive.

[3]

(vi) The carbon dioxide produced by the process in Equation 3.1 is a greenhouse gas.

Describe **two** ways in which greenhouse gases in the troposphere cause warming when they are irradiated by infrared radiation from the Earth.

1 The molecules absorb IR, so their bonds vibrate more (increased vibrational energy); this energy is passed on in collisions, so molecules move faster (more kinetic energy).

2 The molecules re-emit IR radiation in all directions, so some of it goes back towards the Earth and warms the surface.

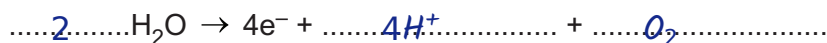
[3]

(b) A potentially 'greener' method of making hydrogen is by electrolysis of acidified water.

(i) The equation for the reaction at the cathode is shown.



Complete and balance the equation for the reaction at the anode:



[2]

(ii) A mole of electrons is 96 500 coulombs. A coulomb is 1 amp flowing for 1 second.

How long (in hours) would it take for a current of 100.0 amps to produce 20.0 g of hydrogen by electrolysis?

Assume 100% efficiency.

$$n(\text{H}_2) = 20.0 \div 2.0 = 10.0 \text{ mol}$$

$$n(\text{e}^-) = 2 \times 10.0 = 20.0 \text{ mol}$$

$$Q = 20.0 \times 96\,500 = 1\,930\,000 \text{ C}$$

$$t = Q \div I = 1\,930\,000 \div 100.0 = 19\,300 \text{ s}$$

$$t = 19\,300 \div 3600 = 5.36 \text{ hours}$$

time = ... 5.36 hours [3]

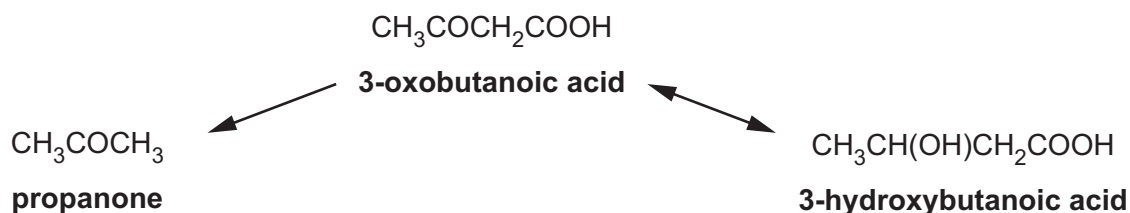
(iii) A student says that producing hydrogen by electrolysis is **not** 'green' because fossil fuels are used to make the electricity.

Discuss this statement.

True if the electricity is made by burning fossil fuels; they are not renewable and produce CO₂, so the process is not carbon neutral. But the electricity can come from a green source, e.g. wind or solar power, so it can be green. [2]

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- 4 3-oxobutanoic acid is formed from carboxylic acids in the liver in the human body. It is then broken down to produce propanone and 3-hydroxybutanoic acid.



These three compounds are known as 'ketone bodies' and are always present in human blood.

- (a) Name the **type** of reaction by which 3-oxobutanoic acid is converted to 3-hydroxybutanoic acid.

reduction [1]

- (b) A concentration of greater than $6 \times 10^{-4} \text{ mol dm}^{-3}$ of ketone bodies in the bloodstream is known as 'ketosis'.

Calculate the **mass** of propanone (M_r 58) (in grams) in 100 cm^3 of blood that contains $6 \times 10^{-4} \text{ mol dm}^{-3}$ of propanone.

Give your answer to an **appropriate** number of significant figures.

$$n = 6 \times 10^{-4} \times 100 \div 1000 = 6 \times 10^{-5} \text{ mol}$$

$$\text{mass} = 6 \times 10^{-5} \times 58 = 3.48 \times 10^{-3} \text{ g} = 3 \times 10^{-3} \text{ g (1 s.f.)}$$

$$\text{mass} = \dots\dots\dots 3 \times 10^{-3} \dots\dots\dots \text{ g [2]}$$

- (c) Ketosis can be detected by the presence of propanone in the breath.

Propanone can be recognised from its mass spectrum.

- (i) State a method of separating propanone vapour from human breath, allowing it to be analysed by a mass spectrometer.

gas chromatography (GLC) [1]

- (ii) Peaks are found at m/z values 15, 43 and 59 in the mass spectrum of propanone (M_r 58).

Give the origin of these peaks.

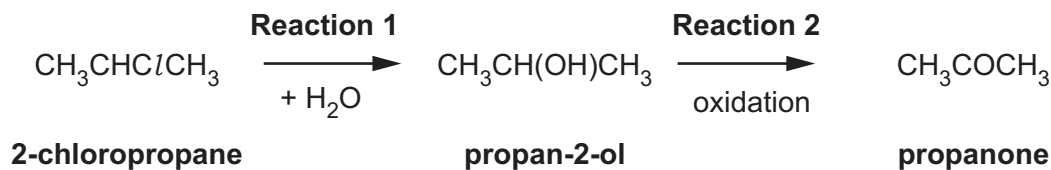
15 *CH_3^+*

43 *CH_3CO^+*

59 *M^+ (molecular ion) containing one ^{13}C atom*

[3]

(d) A student proposes a reaction sequence for the formation of propanone.

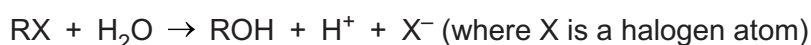


(i) Name the **mechanism** of **Reaction 1**.

nucleophilic substitution [1]

(ii)* In **Reaction 1** the haloalkane is hydrolysed.

The general equation is:



The rate of this reaction for different halogens could depend on either the bond enthalpy or the bond polarisation of the C–X bond.

It is not possible to predict which by chemical theory.

Explain how the bond enthalpy **and** how the bond polarisation could affect the rate.

Design suitable laboratory experiments to show if bond enthalpy or bond polarisation has the greater effect on the rate.

Band enthalpy: the C–X bond gets weaker from C–Cl to C–Br to C–I, so if bond enthalpy matters most, the C–I bond is broken most easily and the iodoalkane reacts fastest (then bromo, then chloro).

Bond polarisation: Cl is more electronegative than Br and I, so C–Cl is the most polar bond and its C is the most δ^+ . Attack by the nucleophile (H_2O or OH^-) is easiest, so C–Cl breaks most easily and the chloroalkane would react fastest.

Experiment: put equal volumes (e.g. 5 drops) of 2-chloropropane, 2-bromopropane and 2-iodopropane in three test tubes, each with the same volume of ethanol as a solvent.

Add the same volume of aqueous AgNO_3 of the same concentration (e.g. 1 cm^3 of 0.10 mol dm^{-3}) to each, all at the same temperature in a water bath (e.g. 50°C).

As X^- ions form they react with Ag^+ to give a precipitate of silver [6]

Additional answer space if required:

halide (AgCl white, AgBr cream, AgI yellow). Time how long until the precipitate appears: shorter time, faster rate.
If the iodoalkane is fastest ($I > Br > Cl$), bond enthalpy has the greater effect; if the chloroalkane is fastest, bond polarisation has the greater effect.

- (e) Classify propan-2-ol, $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$, as primary, secondary or tertiary and give a reason for your answer.

Classification (primary, secondary or tertiary) secondary

Reason: the carbon atom bonded to the OH group is attached to two other carbon atoms (two alkyl groups).

[2]

- (f) Propan-1-ol is oxidised to an aldehyde rather than a ketone.

Describe a laboratory test, and its result, that would distinguish this aldehyde from propanone.

Warm each with Tollens' reagent (ammoniacal silver nitrate) in a water bath.

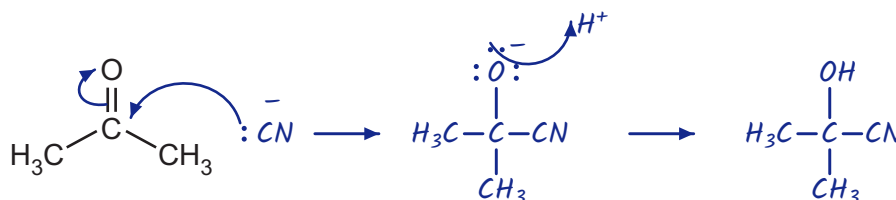
The aldehyde (propanal) gives a silver mirror; propanone gives no silver mirror (no change).

[2]

- (g) Propanone reacts with CN^- ions in the presence of acid.

- (i) Complete the mechanism for this reaction.

Show curly arrows, charges, lone pairs and the product.



[3]

- (ii) Name the functional group formed in the product from (i).

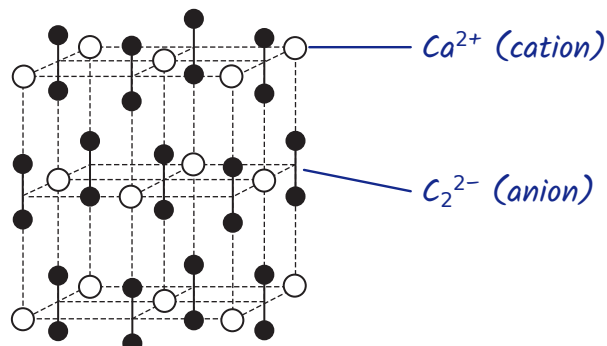
hydroxynitrile (cyanohydrin)

[1]

- 5 This question concerns the Advance Notice Article 'Calcium carbide' that is included as an insert with this paper.

(a) A diagram of the structure of calcium carbide is shown below.

Label a cation and an anion to show how the ions are arranged in the structure.



[2]

- (b) The industrial manufacture of calcium carbide has benefits and disadvantages for modern society.

From the article, suggest **two** benefits and **two** disadvantages.

Benefit 1 ..making acetylene (ethyne), which is used to make PVC.....

.....

Benefit 2 ..making cyanamide, which is used as a fertiliser.....

.....

Disadvantage 1 ..the process produces CO₂, a greenhouse gas.....

.....

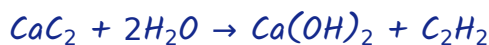
Disadvantage 2 ..it needs a very high temperature, so uses large amounts of

energy.....

[4]

- (c) 1.1 kg of a sample of impure calcium carbide produces 0.33 m^3 of acetylene (at RTP) when reacted with water.

Calculate the percentage purity of the sample.



$$n(\text{C}_2\text{H}_2) = 0.33 \times 1000 \div 24.0 = 13.75 \text{ mol} = n(\text{CaC}_2)$$

$$M(\text{CaC}_2) = 40.1 + 2 \times 12.0 = 64.1 \text{ g mol}^{-1}$$

$$\text{mass of CaC}_2 = 13.75 \times 64.1 = 881 \text{ g}$$

$$\text{percentage purity} = 881 \div 1100 \times 100 = 80 \%$$

percentage purity = ...80..... % [3]

- (d) (i) Acetylene (ethyne) burns in a carbide lamp to form carbon dioxide and water. Some unreacted carbon is also formed that glows and gives light.

Write a possible chemical equation for the combustion of acetylene to give carbon dioxide and carbon.



[1]

- (ii) Impure calcium carbide contains calcium phosphide.

The phosphide ion is P^{3-} .

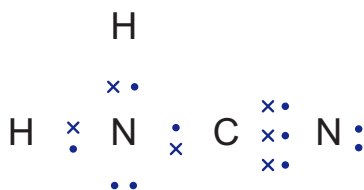
Calcium phosphide reacts with water to form PH_3 .

Suggest a chemical equation for this reaction.



[2]

- (e) (i) Complete a 'dot-and-cross' diagram for cyanamide.



[2]

- (ii) Suggest, with reasons, the bond angle for N–C–N in cyanamide.

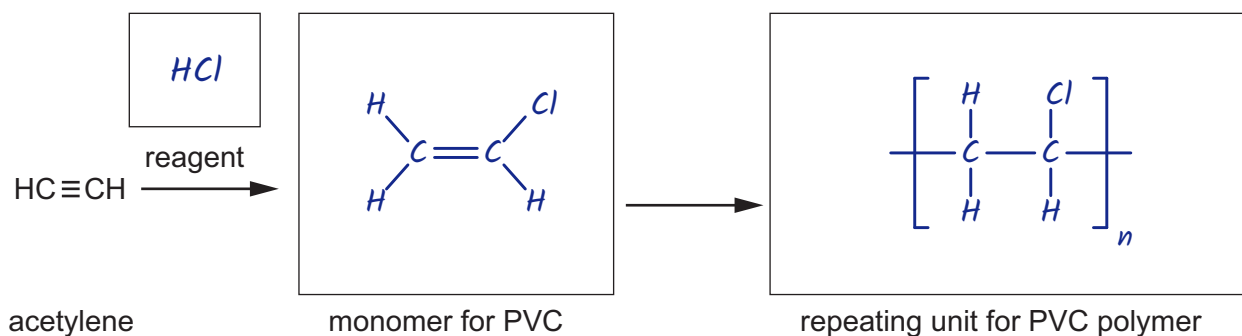
The N–C–N bond angle is 180° (linear).
Around the C atom there are two areas of electron density (the N–C single bond and the C≡N triple bond) and no lone pairs.
These repel each other and get as far apart as possible (minimise repulsion), so the angle is 180°.

[3]

- (f) PVC has the systematic name poly(chloroethene).

Complete the sequence below for the formation of PVC from acetylene.

Write a structural formula in each box.



[3]

END OF QUESTION PAPER

[illegible]

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