



Oxford Cambridge and RSA

A Level Chemistry B (Salters)

H433/01 Fundamentals of Chemistry

Tuesday 5 June 2018 – Afternoon

Time allowed: 2 hours 15 minutes



You must have:

- the Data Sheet for Chemistry B (Salters)
(sent with general stationery)

You may use:

- a scientific or graphical calculator



First name										
Last name	StemUp Model Solution									
Centre number						Candidate number				

INSTRUCTIONS

- Use black ink. You may use an HB pencil for graphs and diagrams.
- Complete the boxes above with your name, centre number and candidate number.
- Answer **all** the questions.
- Write your answer to each question in the space provided. If additional space is required, you should use the lined page(s) at the end of this booklet. The question number(s) must be clearly shown.
- Do **not** write in the barcodes.

INFORMATION

- The total mark for this paper is **110**.
- The marks for each question are shown in brackets [].
- Quality of extended responses will be assessed in questions marked with an asterisk (*).
- This document consists of **36** pages.

2
SECTION A

You should spend a maximum of 40 minutes on this section.

Write your answer to each question in the box provided.

Answer **all** the questions.

1 Which equation represents a possible fusion reaction?

- A** ${}_1\text{H} + {}_1\text{H} \rightarrow {}_2\text{H}$
- B** ${}_1\text{H} + {}_3\text{H} \rightarrow {}_4\text{He}$
- C** ${}_1\text{H} + {}_1\text{H} \rightarrow {}_2\text{He}$
- D** ${}_1\text{H} + {}_2\text{He} \rightarrow {}_3\text{Na}$

Your answer

C

[1]

2 Which solutions when mixed would give a solution of a salt?

- A** barium hydroxide and sulfuric acid
- B** lead nitrate and sulfuric acid
- C** silver nitrate and hydrochloric acid
- D** lithium hydroxide and hydrochloric acid

Your answer

D

[1]

3 Which statement about an atomic emission spectrum is correct?

- A** It occurs when electrons absorb energy.
- B** The wavelength of a line is proportional to the energy lost by electrons.
- C** The wavelengths of the lines are the same as in an absorption spectrum of the same element.
- D** The lines in the emission spectrum of lithium give a yellow colour to a lithium flame.

Your answer

C

[1]

4 Which statement about NO_x pollution is correct?

- A It is only produced in petrol engines.
- B It can cause acid rain.
- C It is not removed at all by catalytic converters.
- D It consists mainly of NO_3 gas.

Your answer

B

[1]

5 Which statement about a by-product of an industrial reaction is correct?

- A It is formed in the same reaction as the product.
- B It is formed when the reactants react in a different way.
- C It is in the equation for the reaction.
- D It is a minor reactant in the reaction.

Your answer

B

[1]

6 What is the volume of CO_2 (in dm^3) measured at RTP when 20g CaCO_3 completely decompose?

- A 0.20
- B 2.4
- C 4.8
- D 24

Your answer

C

[1]

- 7 Chlorine reacts with bromide ions in sea water, producing bromine. Which statement about this process is **not** correct?

- A Bromide ions are oxidised.
- B The chlorine is obtained from sea water.
- C Bromine forms because it is more reactive than chlorine.
- D Chlorine molecules are reduced.

Your answer

C

[1]

- 8 Which formula has the correct systematic name?

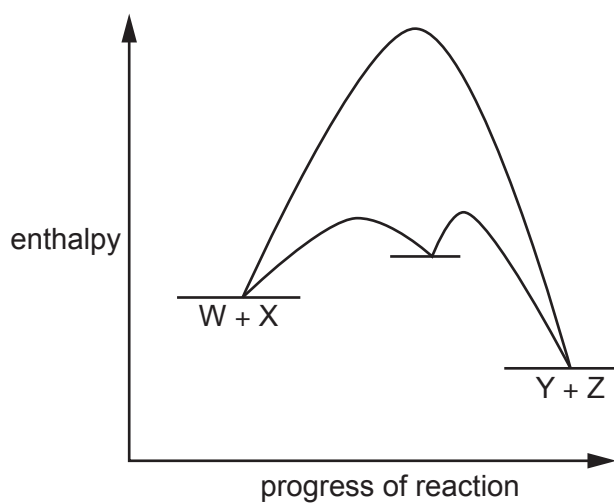
	Formula	Systematic name
A	Na_2SO_3	sodium sulfate(VI)
B	NaClO_3	sodium chlorate(III)
C	Cu_2S	copper(I) sulfide
D	$\text{Pb}(\text{NO}_3)_2$	lead(II) nitrate(III)

Your answer

C

[1]

- 9 The enthalpy profiles for the reaction $W + X \rightleftharpoons Y + Z$ are shown below, with and without a catalyst.



Which statement is correct?

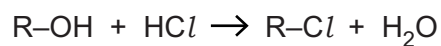
- A The catalyst increases the yield of Y.
- B Increasing the temperature shifts the position of equilibrium to the products side.
- C The catalyst does not take part in the reaction.
- D The reverse reaction is speeded up by the catalyst.

Your answer

D

[1]

- 10 The reaction below produces a chloroalkane.



Which row shows the steps to purify the liquid product in the correct order?

A	Use a separating funnel	Distil	Dry	Remove unreacted HCl
B	Remove unreacted HCl	Use a separating funnel	Dry	Distil
C	Remove unreacted HCl	Use a separating funnel	Distil	Dry
D	Use a separating funnel	Remove unreacted HCl	Distil	Dry

Your answer

B

[1]

- 11 What is **not** correct for the reaction between aqueous OH⁻ ions and bromoethane?

- A** OH⁻ ions behave as nucleophiles.
- B** An alcohol is produced.
- C** The reaction is faster if chloroethane is used.
- D** The reaction occurs because of a polar C–Br bond.

Your answer

C

[1]

- 12 Colorimetry is used to find the concentration of an orange solution of iodine. Which statement is correct?
- A The more concentrated the solution the more light is transmitted.
 - B A yellow coloured filter should be used.
 - C The absorbance of solutions of known concentration should be measured to get a calibration curve.
 - D Orange light is absorbed.

Your answer

C

[1]

- 13 What is correct for the complex $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$?

- A The charge on each ligand is 2-.
- B The co-ordination number of the metal ion is 3.
- C The oxidation state of the iron is +2.
- D The ligand is monodentate.

Your answer

A

[1]

- 14 Which statement about p-orbitals is correct?

- A A p-orbital is spherical in shape.
- B A p-orbital can contain two electrons.
- C There are six p-orbitals in a p-subshell.
- D An element with outer configuration p^2 has both electrons in the same p-orbital.

Your answer

B

[1]

15 Which row is correct?

	Species	Protons	Neutrons in isotope	Electrons
A	F ⁻	9	10	11
B	Ne	10	10	10
C	Na ⁺	11	10	11
D	Mg ²⁺	14	10	12

Your answer

B

[1]

16 Which statement about the rate determining step of a reaction is correct?

- A It is the fast step.
- B It cannot involve a catalyst.
- C It does not involve zero order reagents.
- D It is always between two first-order reagents.

Your answer

C

[1]

17 An unsaturated carboxylic acid has an M_r of 280.
70g of the acid is saturated by 1.0g of hydrogen.

How many C=C bonds are there in one molecule of the acid?

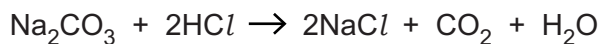
- A 1
- B 2
- C 4
- D 8

Your answer

B

[1]

- 18 Sodium carbonate reacts with hydrochloric acid as shown in the equation.



What mass (in grams) of Na_2CO_3 will react exactly with 50 cm^3 of 2.0 mol dm^{-3} HCl ?

- A 0.05
- B 5.3
- C 10.6
- D 21.2

Your answer

B

[1]

- 19 Which compound will react with acidified potassium dichromate(VI)?

- A $\text{CH}_3\text{CH}(\text{OH})\text{COOH}$
- B $(\text{CH}_3)_3\text{COH}$
- C CH_3COOH
- D CH_3COCH_3

Your answer

A

[1]

- 20 Which statement is **not** correct about amines?

- A The lone pair on the nitrogen allows them to act as nucleophiles.
- B They react with carboxylic acids to form amides.
- C They form hydrogen bonds with water.
- D They accept protons from water molecules.

Your answer

B

[1]

- 21 The methane concentration in the atmosphere has increased from 0.722 ppm in pre-industrial times to $1.80 \times 10^{-4} \%$ now.

What is the % increase in methane concentration?

- A 40%
- B 60%
- C 67%
- D 150%

Your answer

D

[1]

- 22 Which observation is correct?

- A A solution of bromine water forms a purple layer when hexane is added.
- B Aqueous silver nitrate forms a yellow precipitate when added to sodium bromide solution.
- C When iodobutane and chlorobutane are separately refluxed with aqueous silver nitrate, a precipitate forms faster with iodobutane.
- D Steamy fumes of hydrogen bromide are formed as the only gas when concentrated sulfuric acid is warmed with sodium bromide.

Your answer

C

[1]

- 23 Which row gives the correct appearances of the products of the reactions?

	$[\text{Fe}(\text{H}_2\text{O})_6]^{3+}(\text{aq})$ and sodium hydroxide solution	$[\text{Cu}(\text{H}_2\text{O})_6]^{2+}(\text{aq})$ and excess conc. ammonia solution
A	Green precipitate	Green solution
B	Orange precipitate	Blue/violet solution
C	Orange precipitate	Green precipitate
D	Orange solution	Yellow solution

Your answer

B

[1]

24 Which statement about the Arrhenius equation is correct?

- A A plot of $\ln k$ against T gives a straight line.
- B When T is very large $\ln k$ almost equals $\ln A$.
- C E_a is the gradient of a plot of $\ln k$ against $1/T$.
- D A plot of k against $1/T$ gives a straight line.

Your answer

B

[1]

25 Which molecule will **not** be made when water is eliminated from $\text{CH}_3\text{CH}_2\text{C}(\text{CH}_3)(\text{OH})\text{CH}_2\text{CH}_2\text{CH}_3$?

- A $\text{CH}_3\text{C}(\text{CH}_3)=\text{CHCH}_2\text{CH}_2\text{CH}_3$
- B $\text{CH}_3\text{CH}=\text{C}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{CH}_3$
- C $\text{CH}_2=\text{C}(\text{CH}_2\text{CH}_3)\text{CH}_2\text{CH}_2\text{CH}_3$
- D $\text{CH}_3\text{CH}_2\text{C}(\text{CH}_3)=\text{CHCH}_2\text{CH}_3$

Your answer

A

[1]

26 Which statement about a strong base at 298 K is correct?

- A It is partially ionised.
- B Its pH is given by $\text{pH} = 14 + \log[\text{OH}^-]$.
- C It will not react with weak acids.
- D It has the same pH as a weak base of the same concentration.

Your answer

B

[1]

27 Which row correctly shows the main products in electrolysis using graphite electrodes?

	Electrolyte	Product at the anode	Product at the cathode
A	MgBr ₂ (l)	bromine	magnesium
B	CuSO ₄ (aq)	oxygen	hydrogen
C	NaCl(aq)	chlorine	sodium
D	PbS(l)	hydrogen sulfide	lead

Your answer

A

[1]

28 Which statement/s is/are correct about solutions of amino acids with the general formula RCH(NH₂)COOH?

- 1 They contain zwitterions.
- 2 They react with sodium hydroxide.
- 3 They react with hydrochloric acid.

- A** 1, 2 and 3
- B** Only 1 and 2
- C** Only 2 and 3
- D** Only 1

Your answer

A

[1]

29 Which statement/s is/are a result of delocalisation in benzene?

- 1 Benzene undergoes substitution reactions.
- 2 Benzene reacts faster with bromine than alkenes do.
- 3 The enthalpy change of hydrogenation of benzene is three times that of cyclohexene.

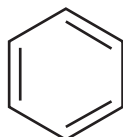
- A** 1, 2 and 3
B Only 1 and 2
C Only 2 and 3
D Only 1

Your answer

D

[1]

30 Kekulé represented benzene as:



Which statement/s follow/s from this structure?

- 1 All the carbon-carbon bonds are of equal length in benzene.
- 2 The C–C–C bond angle in benzene is 120° .
- 3 Benzene has a planar structure.

- A** 1, 2 and 3
B Only 1 and 2
C Only 2 and 3
D Only 1

Your answer

C

[1]

SECTION B

Answer **all** the questions.

- 31** Long chain alkanes can be cracked to provide better fuels and raw materials for the chemical industry. One such cracking reaction is shown in **equation 31.1**.



- (a) In a cracking reaction 1.50 tonnes of dodecane ($\text{C}_{12}\text{H}_{26}$) produce 478 kg of hexane (C_6H_{14}).

Calculate the percentage yield of the reaction in **equation 31.1**.

$$M_r(\text{C}_{12}\text{H}_{26}) = 170.0; \quad M_r(\text{C}_6\text{H}_{14}) = 86.0$$

$$n(\text{C}_{12}\text{H}_{26}) = 1.50 \times 10^6 \text{ g} \div 170.0 = 8.824 \times 10^3 \text{ mol}$$

$$1 \text{ mol } \text{C}_{12}\text{H}_{26} \text{ gives } 1 \text{ mol } \text{C}_6\text{H}_{14}, \text{ so theoretical mass of hexane} = 8.824$$

$$\times 10^3 \times 86.0 = 7.589 \times 10^5 \text{ g} = 758.9 \text{ kg}$$

$$\% \text{ yield} = 478 \div 758.9 \times 100 = 63.0\%$$

percentage yield = ... **63.0** % **[3]**

- (b) Some students want to investigate the usefulness of hexane as a fuel.

- (i) Describe an experiment they could use to determine the enthalpy change of combustion of liquid hexane in the laboratory.

..Burn a known mass of hexane in a spirit burner under a (copper) calorimeter.....
 ..containing a known mass of water; measure the temperature rise of the.....
 ..water and the mass of hexane burnt (weigh the burner before and after)..... **[1]**

- (ii) Show how the result would be calculated from the measurements made when carrying out the experiment in part (b)(i).

..Energy to water $q = mc\Delta T$ ($c = 4.18 \text{ J g}^{-1} \text{ K}^{-1}$); $n(\text{hexane}) = \text{mass burnt}$
 .. $\div 86.0$; $\Delta_c H = -q \div n(\text{hexane})$ (in kJ mol^{-1})..... **[1]**

- (iii) Describe **two** ways in which the students could make the basic experiment more accurate.

- 1 *Put a lid on the calorimeter and use draught excluders / insulate its sides to reduce heat loss to the surroundings.*
- 2 *Cover (cap) the wick of the burner when it is not in use, to reduce evaporation of the fuel, so the mass burnt is accurate.* [2]

- (c) The students are given some enthalpy changes of formation and use them to check the accuracy of their answer.

Calculate the standard enthalpy change of combustion of hexane from the data given.

Substance	$\Delta_f H^\ominus / \text{kJ mol}^{-1}$
$\text{CO}_2(\text{g})$	-393
$\text{H}_2\text{O}(\text{l})$	-286
$\text{C}_6\text{H}_{14}(\text{l})$	-199



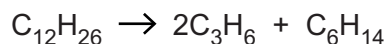
$$\Delta_c H = \Sigma \Delta_f H(\text{products}) - \Sigma \Delta_f H(\text{reactants})$$

$$\Delta_c H = (6 \times -393) + (7 \times -286) - (-199)$$

$$= -2358 - 2002 + 199 = -4161 \text{ kJ mol}^{-1}$$

$$\Delta_c H^\ominus \text{ hexane} = \dots\dots\dots -4161 \dots\dots\dots \text{kJ mol}^{-1} \text{ [2]}$$

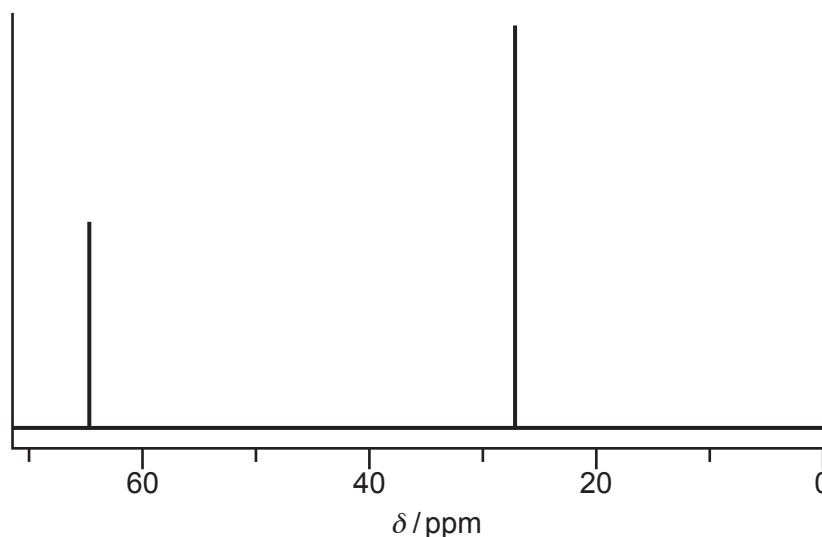
- (d) The propene produced in **equation 31.1** has many uses in the chemical industry.



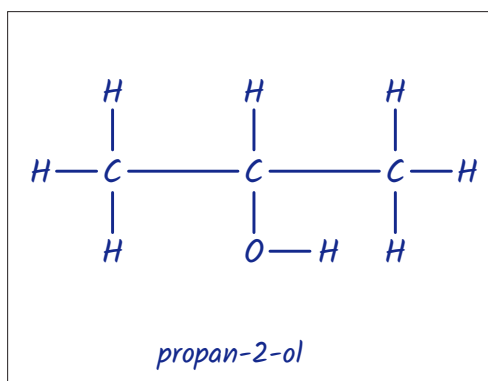
Equation 31.1

One of the substances produced from propene is an alcohol used as a cleaner and de-icer.

The ^{13}C NMR spectrum of this alcohol is shown below.



Draw the **full** structural formula of the alcohol in the box below, giving your reasoning.



Reasoning *Propan-2-ol, CH₃CH(OH)CH₃. The ^{13}C spectrum has only 2 peaks, so there are only 2 carbon environments: the two CH₃ carbons are equivalent ($\delta \approx 27$ ppm) and the C bonded to O is at $\delta \approx 64$ ppm.* [2]

- (e) The alcohol from (d) can be oxidised to a carbonyl compound.

Give the reagents and conditions to carry out this oxidation.

Reagents *acidified potassium dichromate(VI), K₂Cr₂O₇ / H₂SO₄*

Conditions *heat (high temperature)*

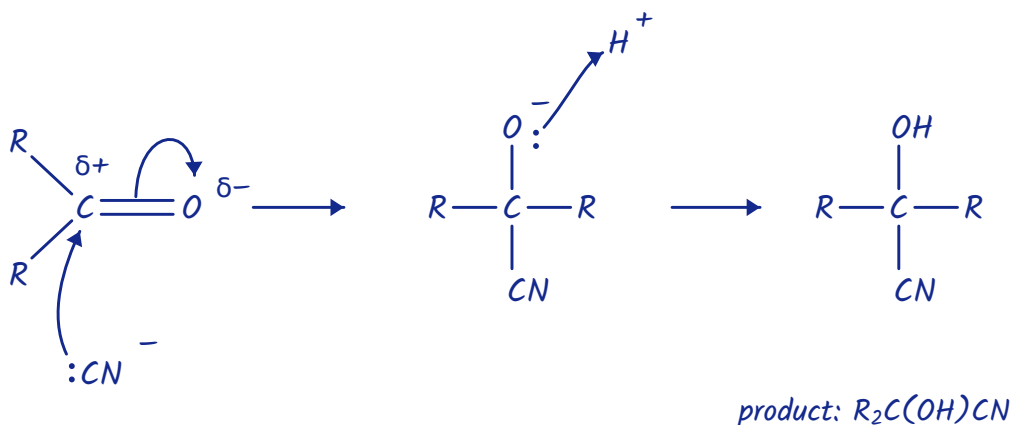
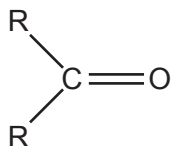
[1]

- (f) The carbonyl compound from (e) can be reacted further to produce other raw materials. For example, it reacts with HCN.

The formula of a carbonyl compound is shown below.

Give the mechanism for the reaction of this compound with cyanide ions followed by H^+ . Show curly arrows, relevant dipoles and charges and give the formula of the product.

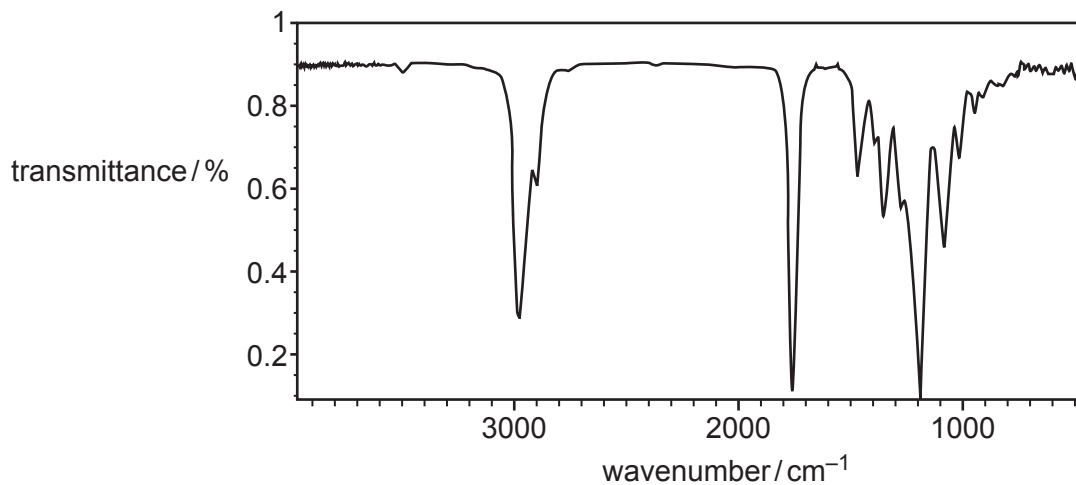
Name the type of reaction.



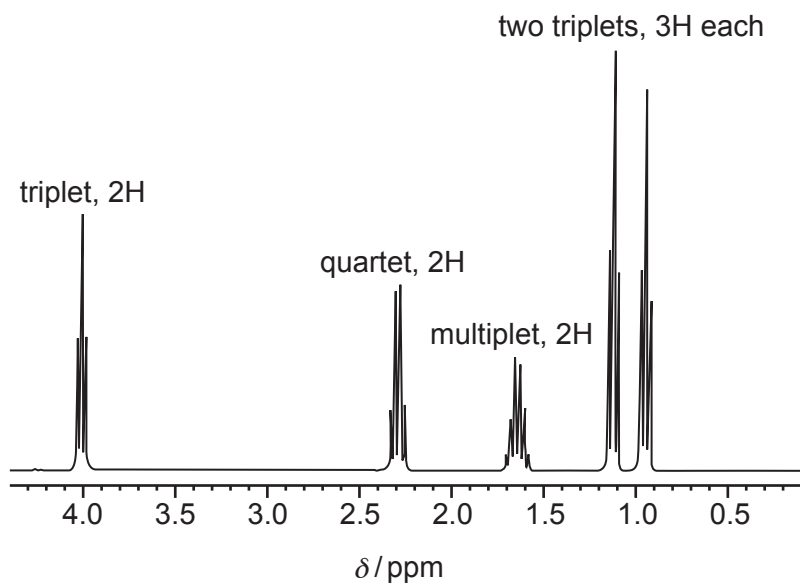
type of reaction nucleophilic addition..... [4]

- (g)* Compound **A** has six carbon atoms and can be made from propene using several steps. The infrared, proton NMR and mass spectra for compound **A** are shown.

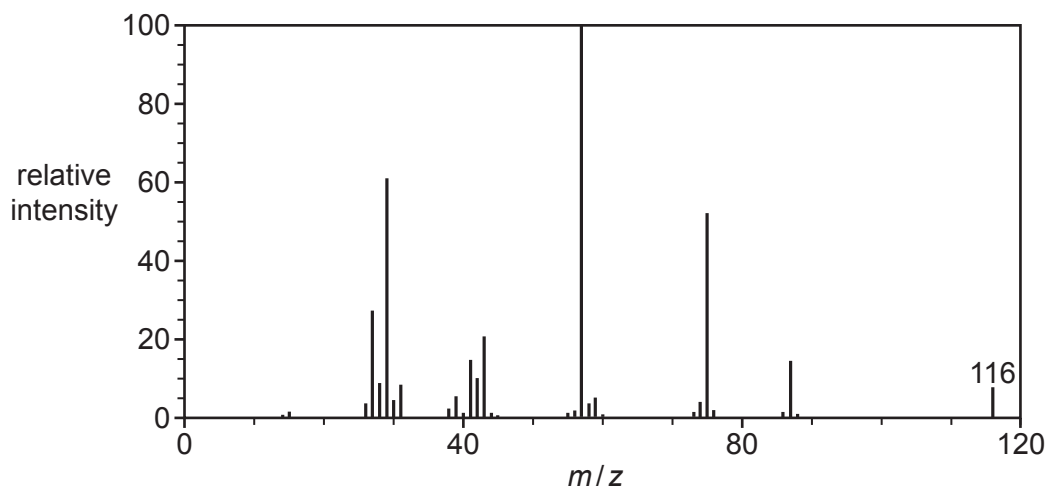
Infrared spectrum



Proton NMR spectrum



Mass spectrum



Working shown on this page will not be marked.

Use the information on page 18 to work out the structure of **compound A**.

Explain your reasoning, using evidence from each spectrum.

Mass spectrum: M^+ peak at $m/z = 116$, so $M_r = 116$. $6\text{ C} = 72$, so $116 - 72 = 44$ fits $12\text{ H} + 2\text{ O}$: $\text{C}_6\text{H}_{12}\text{O}_2$, possibly an ester. Fragments: m/z 57 is $\text{CH}_3\text{CH}_2\text{CO}^+$ and 87 is loss of CH_3CH_2 ($116 - 29$).

IR: strong absorption at about 1750 cm^{-1} is $\text{C}=\text{O}$; no broad absorption at 2500 to 3600 cm^{-1} , so no $\text{O}-\text{H}$ (not a carboxylic acid or alcohol); $\text{C}-\text{H}$ at about 2950 cm^{-1} , so A is probably an ester.

Proton NMR: 5 peaks, so 5 proton environments ($3 + 3 + 2 + 2 + 2 = 12\text{ H}$).

δ 4.0, triplet, 2H: CH_2 bonded to the ester O ($\text{H}-\text{C}-\text{O}$); triplet so 2 H on the adjacent C, i.e. $-\text{O}-\text{CH}_2-\text{CH}_2-$.

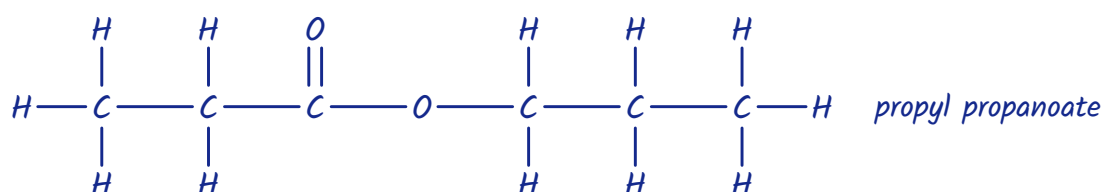
δ 2.3, quartet, 2H: CH_2 next to $\text{C}=\text{O}$ ($\text{H}-\text{C}-\text{C}=\text{O}$); quartet so 3 H on the adjacent C, i.e. $\text{CH}_3-\text{CH}_2-\text{C}=\text{O}$.

δ 1.6, multiplet, 2H: CH_2 ($\text{H}-\text{C}-\text{R}$) with H on several adjacent C, i.e. $\text{CH}_3-\text{CH}_2-\text{CH}_2-$.

δ 0.9 and 1.1, two triplets, 3H each: two CH_3 groups ($\text{H}-\text{C}-\text{R}$), each next to a CH_2 .

So A is the ester propyl propanoate, $\text{CH}_3\text{CH}_2\text{COOCH}_2\text{CH}_2\text{CH}_3$.

Structure of compound **A**



[6]

The 3D shape of the protein produced by the folding of the polypeptide chain

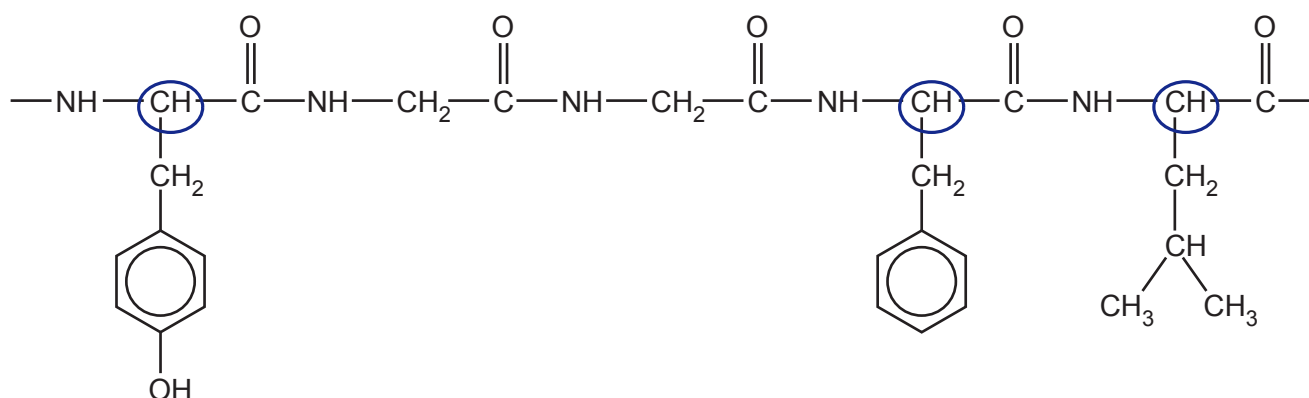
(held by interactions between R groups). [1]

1 hydrogen bonds

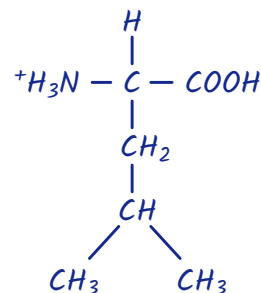
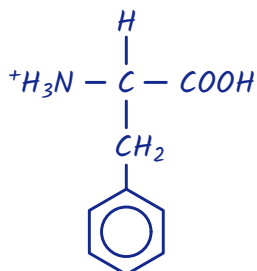
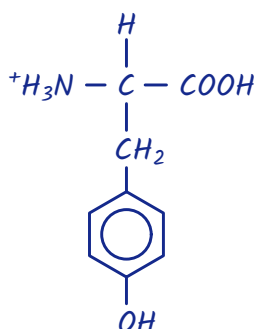
2 ionic bonds

(c) Some students hydrolyse a protein in the laboratory by refluxing it with moderately concentrated hydrochloric acid.

[1]



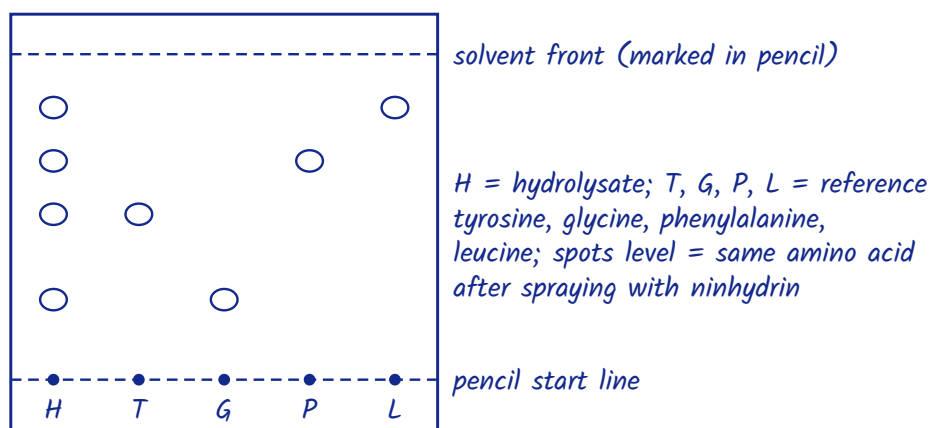
(ii) Give the organic products of the complete hydrolysis of this protein section with hydrochloric acid.



- (d)* The students use paper chromatography to confirm that the products of hydrolysis are those in part (c)(ii).

Describe how the students would **develop** and **analyse** the chromatogram to identify the products of hydrolysis.

You may include a diagram in your answer.



Put a small spot of the hydrolysate on a pencil start line near the bottom of the paper, with spots of the suspected amino acids (tyrosine, glycine, phenylalanine and leucine) alongside for reference.

Develop: stand the paper in a tank of solvent with the solvent level below the start line and put a lid on. Remove the paper when the solvent gets near the top and mark the solvent front in pencil straight away.

Dry the paper (in a fume cupboard or oven), then spray it with ninhydrin (or look under UV light), so the colourless amino acids show up as (purple) spots.

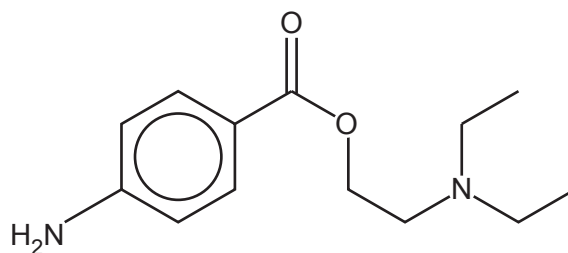
Analyse: the hydrolysate should give four spots. A spot level with a reference spot shows that amino acid is present.

Measure the distances from the start line and calculate $R_f = \text{distance moved by spot} \div \text{distance moved by solvent front}$.

Compare the R_f values of the four spots with those of the reference amino acids (or data-book values for the same solvent) to identify each product.

[6]

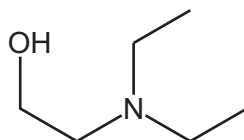
33 Procaine has been used as an anaesthetic in dentistry.



Procaine

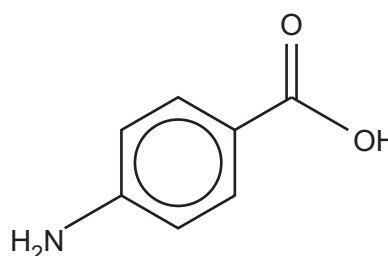
Some students reacted procaine with various reagents to see if they could make other useful substances from it.

They hydrolysed procaine, producing a solution containing compound **B** and the **sodium salt** of compound **C**.



compound B

State at room temperature: liquid



compound C

solid

(a) (i) Suggest the reagent and conditions the students used for the hydrolysis.

NaOH(aq) and heat under reflux..... [1]

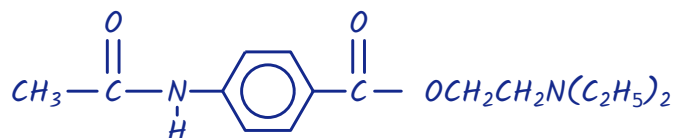
(ii) Suggest how the students could obtain a sample of compound **C** from the solution they obtained.

Add dilute hydrochloric acid until the solution is just neutral, so the sodium salt is converted back to compound C (the acid), which is a solid and precipitates.....

Filter off the solid C, wash with a little cold water and dry it..... [2]

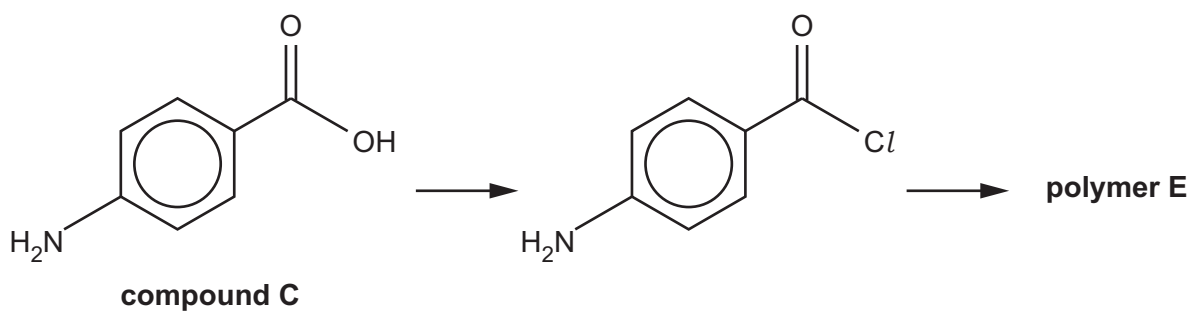
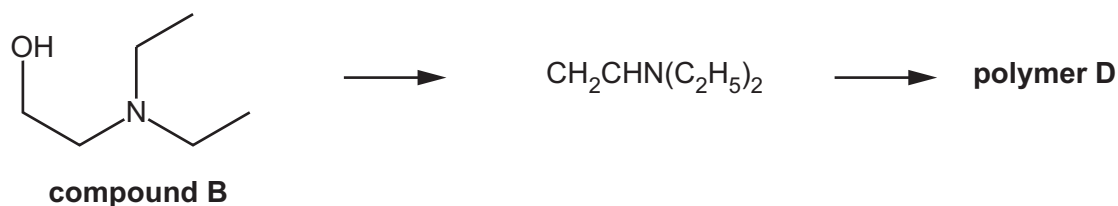
(iii) The students reacted procaine with ethanoyl chloride.

Give the formula of the organic product formed.

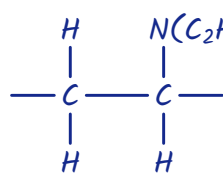
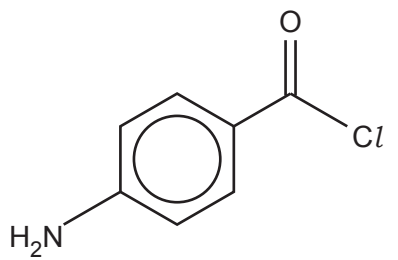
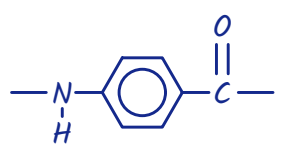


[1]

(b) Compounds **B** and **C** can be turned into monomers for polymerisation reactions.



Give the structural formula for the repeat units of polymers **D** and **E** and give the **type** of polymerisation occurring in each case.

Monomer	Repeat unit of the polymer	Type of polymerisation
$\text{CH}_2\text{CHN}(\text{C}_2\text{H}_5)_2$	Polymer D 	<i>addition</i>
	Polymer E 	<i>condensation</i>

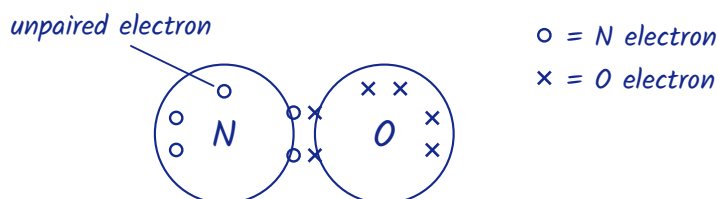
[2]

- 34 The use of cars can affect the concentration of ozone in the troposphere. Tropospheric ozone causes respiratory problems and photochemical smog.

Tropospheric ozone is formed in a series of reactions involving carbon monoxide, oxides of nitrogen and volatile organic compounds, all of which are present in exhaust emissions.

- (a) NO is a radical.

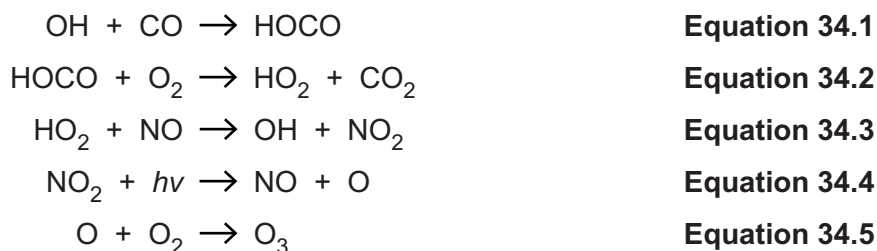
Draw a 'dot-and-cross' diagram of NO and explain why it is called a radical.
Show outer electron shells only.



..NO has an unpaired (single) electron on the N atom, so it is a radical.....

[1]

- (b) A series of reactions producing ozone from carbon monoxide, hydroxyl radicals and NO are shown in **equations 34.1 – 34.5** below.



- (i) Explain why the reaction in **equation 34.3** is classed as a propagation step.

..A radical (HO_2) reacts and another radical (OH) is produced, so the number
..of radicals stays the same and the chain reaction continues..... [1]

- (ii) Write in the box the overall equation for the reaction sequence in **equations 34.1 – 34.5**.



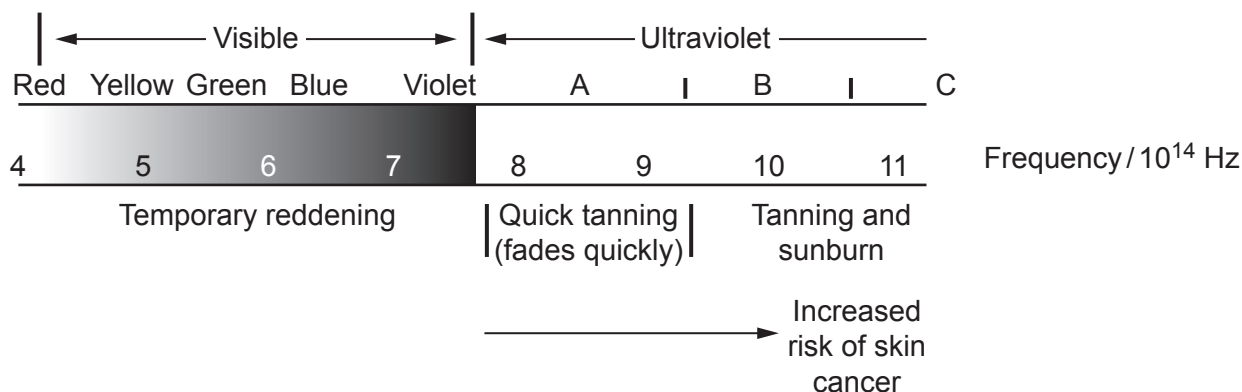
[1]

- (c) Years ago, the air conditioning in cars used CFC-12, CCl_2F_2 .

CFC-12 absorbs some UV radiation when it breaks down.

The most harmful UV radiation from the Sun that causes damage to cells is in the range 10.1×10^{14} to 14.0×10^{14} Hz. Ozone in the stratosphere absorbs radiation in this range.

The diagram below shows the effects of different frequencies of UV on human skin.



Carry out some calculations, using the bond enthalpies below, and comment on the ability of CFC-12 to remove harmful UV when it breaks down.

Bond	Bond enthalpy / kJ mol^{-1}
C-Cl	+346
C-F	+467

$$E \text{ per C-Cl bond} = 346\,000 \div 6.02 \times 10^{23} = 5.75 \times 10^{-19} \text{ J}$$

$$\nu = E \div h = 5.75 \times 10^{-19} \div 6.63 \times 10^{-34} = 8.67 \times 10^{14} \text{ Hz}$$

$$E \text{ per C-F bond} = 467\,000 \div 6.02 \times 10^{23} = 7.76 \times 10^{-19} \text{ J}$$

$$\nu = 7.76 \times 10^{-19} \div 6.63 \times 10^{-34} = 11.7 \times 10^{14} \text{ Hz}$$

Breaking C-Cl absorbs UV of 8.67×10^{14} Hz, below the harmful range, so this does not remove harmful UV. Breaking C-F absorbs 11.7×10^{14} Hz, which is in the harmful range (10.1 to 14.0×10^{14} Hz), so CFC-12 removes some harmful UV, but not across the whole range as ozone does. [3]

- 35 A company was investigating the corrosion of metal parts used in oil rigs in the North Sea.

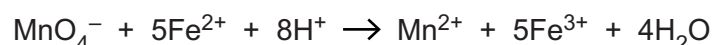
Chemists took two identical bolts. One was unused and the other had been exposed to the seawater for several weeks. They reacted each bolt with dilute sulfuric acid. All the unreacted iron was converted to $\text{Fe}^{2+}(\text{aq})$ ions and the rust reacted to form $\text{Fe}^{3+}(\text{aq})$.

- (a) Describe how the chemists would dissolve one bolt and make the solution up to 1.00 dm^3 .

Dissolve the bolt in excess warm dilute sulfuric acid in a beaker.
Transfer the solution to a 1.00 dm^3 volumetric flask, add the washings from
rinsing the beaker, then make up to the mark with distilled water and invert to
mix. [2]

- (b) The chemists then titrated 10.0 cm^3 portions of their solutions with a solution of $0.200 \text{ mol dm}^{-3}$ potassium manganate(VII).

The MnO_4^- ions oxidise the Fe^{2+} to Fe^{3+} and the Fe^{3+} ions do not react.
 The equation for the reaction is given below.



Use the titration results below to find the mass of the bolt that had rusted away.

Type of bolt	Average volume of $0.200 \text{ mol dm}^{-3}$ KMnO_4 used in the titration / cm^3
Unused bolt	17.92
Rusted bolt	9.75

$$\text{titre difference} = 17.92 - 9.75 = 8.17 \text{ cm}^3$$

$$n(\text{MnO}_4^-) = 0.200 \times 8.17 \div 1000 = 1.634 \times 10^{-3} \text{ mol}$$

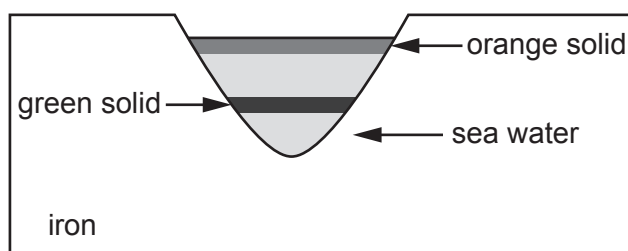
$$n(\text{Fe rusted}) \text{ in } 10.0 \text{ cm}^3 = 5 \times 1.634 \times 10^{-3} = 8.17 \times 10^{-3} \text{ mol}$$

$$\text{in } 1.00 \text{ dm}^3: 8.17 \times 10^{-3} \times 100 = 0.817 \text{ mol}$$

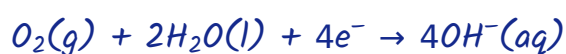
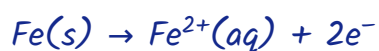
$$\text{mass rusted away} = 0.817 \times 55.8 = 45.6 \text{ g}$$

$$\text{mass of bolt that had rusted away} = \dots\dots\dots 45.6 \dots\dots\dots \text{ g [3]}$$

- (c) The iron rusted in small dips in the surface. The chemists noticed a green solid that turned orange at the surface of the water.



- (i) Give the half-equations for the processes occurring during the rusting.



[2]

- (ii) What are the **formulae** of the green and orange solids?

Green solid $\text{Fe}(\text{OH})_2$

Orange solid $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$

[1]

- (iii) Suggest why rusting takes place faster in seawater than in rainwater.

...Seawater contains more dissolved ions (salt), so it is a better electrolyte

... (conductor) for the ions to move between the anode and cathode areas

[1]

- (d) Give the electron configuration of the Fe^{2+} ion.

... $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6$

[1]

The chemists investigated making the bolts from a nickel-copper alloy that has high strength and resistance to corrosion.

They reacted the alloy with sulfuric acid and filtered off the unreacted solid, which they found was copper.

(e) Use the electrode potentials in the table below to explain why only the nickel reacts.

Half reaction	$E^\ominus / \text{V}$
$\text{Ni}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Ni}(\text{s})$	- 0.25
$2\text{H}^+(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{H}_2(\text{g})$	0.00
$\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Cu}(\text{s})$	+ 0.34

$E^\ominus(\text{Ni}^{2+}/\text{Ni}) = -0.25 \text{ V}$ is more negative than $E^\ominus(\text{H}^+/\text{H}_2) = 0.00 \text{ V}$, so H^+ ions can oxidise Ni to Ni^{2+} (and are reduced to H_2): $\text{Ni} + 2\text{H}^+ \rightarrow \text{Ni}^{2+} + \text{H}_2$.
 $E^\ominus(\text{Cu}^{2+}/\text{Cu}) = +0.34 \text{ V}$ is more positive than 0.00 V , so H^+ cannot oxidise Cu to Cu^{2+} ; copper does not react.

[2]

(f) The solution they obtained was green due to $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$. The chemists added some EDTA^{4-} solution and the colour changed to blue. EDTA^{4-} is a polydentate ligand.

(i) Suggest why the colour changes as the EDTA^{4-} is added and name the type of reaction taking place.

Ligand substitution (exchange): EDTA^{4-} replaces the H_2O ligands. The new ligand splits the d-orbitals differently (different ΔE), so a different frequency of light is absorbed.

[1]

(ii) In a separate experiment, 25.0 cm^3 of a $0.250 \text{ mol dm}^{-3}$ $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ solution is found to react exactly with 41.7 cm^3 of $0.150 \text{ mol dm}^{-3}$ EDTA^{4-} solution.

Calculate the formula of the complex ion that nickel forms with EDTA^{4-} .

$$n(\text{Ni}^{2+}) = 0.250 \times 25.0 \div 1000 = 6.25 \times 10^{-3} \text{ mol}$$

$$n(\text{EDTA}^{4-}) = 0.150 \times 41.7 \div 1000 = 6.26 \times 10^{-3} \text{ mol}$$

$$\text{ratio } \text{Ni}^{2+} : \text{EDTA}^{4-} = 1 : 1$$

$$\text{charge} = +2 + (-4) = -2$$

formula of the complex ion = $[\text{Ni}(\text{EDTA})]^{2-}$ [2]

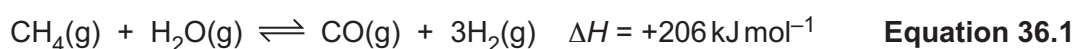
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- 36 Plants need nitrogen to synthesise proteins, but most plants cannot use atmospheric nitrogen. Ammonium nitrate is often used as a fertiliser as it contains nitrogen in a form that plants can absorb.

- (a) The first step in the process of making ammonium nitrate is the synthesis of ammonia from atmospheric nitrogen.
This synthesis reaction has a very high activation enthalpy.
Explain this in terms of the bonding in nitrogen.

N₂ has a triple bond between the N atoms, which has a very high bond enthalpy, so a lot of energy is needed to break it. [1]

- (b) The hydrogen needed to manufacture ammonia can be produced from steam and methane as shown in **equation 36.1** below.



- (i) Use the entropy values in the table below to calculate $\Delta_{\text{sys}}S$ for the forward reaction in **equation 36.1**.

Substance	Entropy $S/\text{J K}^{-1} \text{mol}^{-1}$
$\text{CH}_4(\text{g})$	186.2
$\text{H}_2\text{O}(\text{g})$	189.0
$\text{CO}(\text{g})$	197.6
$\text{H}_2(\text{g})$	130.6

$$\begin{aligned} \Delta_{\text{sys}}S &= \Sigma S(\text{products}) - \Sigma S(\text{reactants}) \\ &= (197.6 + 3 \times 130.6) - (186.2 + 189.0) \\ &= 589.4 - 375.2 = +214.2 \text{ J K}^{-1} \text{mol}^{-1} \end{aligned}$$

$$\Delta_{\text{sys}}S = +214.2 \text{ J K}^{-1} \text{mol}^{-1} \quad [1]$$

- (ii) Explain how the sign of your answer to (i) is predicted by **equation 36.1**.

Positive (entropy increases), because there are more moles of gas on the product side: 2 mol of gas $\rightarrow$ 4 mol of gas, so more ways of arranging the particles and energy. [1]

- (c) Calculate the minimum temperature required for the forward reaction in **equation 36.1** to be feasible.

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

feasible when $\Delta G = \Delta H - T\Delta_{sys}S \leq 0$, so minimum $T = \Delta H \div \Delta_{sys}S$

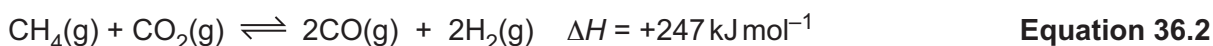
$$T = 206\,000 \text{ J mol}^{-1} \div 214.2 \text{ J K}^{-1} \text{ mol}^{-1} = 961.7 \text{ K}$$

$$= 962 \text{ K (3 s.f.)}$$

temperature = ... **962** K [2]



Another source of hydrogen is from the reaction shown in **equation 36.2**.



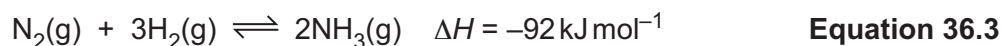
This is claimed to be a much greener process than that in **equation 36.1**.

Comment on the validity of this statement, considering:

- the raw materials used
- the operating conditions
- the mole ratios.

Raw materials: 36.2 uses up CO_2 , removing a greenhouse gas from the atmosphere, so it is greener. Conditions: both reactions are endothermic with positive ΔS , so both need a high temperature to be feasible; both go from 2 mol to 4 mol of gas, so both need a low pressure; little difference. Mole ratios: 36.2 gives only 2 mol H_2 per mol CH_4 (36.1 gives 3), so lower atom economy; less green. The claim is only partly valid. [3]

- (e) The Haber process for the manufacture of ammonia is shown in **equation 36.3**.



At a certain temperature, a mixture of nitrogen and hydrogen was allowed to reach equilibrium in a container of fixed volume. Chemists found the concentrations shown in the table.

Substance	Concentration at the start / mol dm ⁻³	Concentration at equilibrium / mol dm ⁻³
N ₂	1.00	0.90
H ₂	1.00	0.70
NH ₃	0.00	0.20

Calculate the equilibrium concentrations of H₂ and NH₃.

Use these values to calculate a value for K_c at the temperature of the experiment and give the units.

0.10 mol dm⁻³ N₂ reacts, so 0.30 mol dm⁻³ H₂ reacts and 0.20 mol dm⁻³ NH₃ forms

$$[\text{H}_2] = 1.00 - 0.30 = 0.70 \text{ mol dm}^{-3}; \quad [\text{NH}_3] = 0.20 \text{ mol dm}^{-3}$$

$$K_c = [\text{NH}_3]^2 \div ([\text{N}_2][\text{H}_2]^3) = 0.20^2 \div (0.90 \times 0.70^3)$$

$$K_c = 0.040 \div 0.3087 = 0.13 \text{ dm}^6 \text{ mol}^{-2}$$

$$K_c = \dots 0.13 \dots \text{ units } \text{dm}^6 \text{ mol}^{-2} \dots [3]$$

- (f) In order to make the ammonium nitrate fertiliser, some of the ammonia is oxidised to nitric acid in several stages shown by **equations 36.4–36.6**.



The nitric acid formed is reacted with more ammonia.



- (i) Use oxidation states or some other method to balance **equation 36.4**. [1]



- (ii) The overall yield of the reactions in equations 36.4 – 36.6 is 77%.
The yield of ammonium nitrate in equation 36.7 can be taken as 100%.

What mass (in tonnes) of ammonia is needed to make 25 tonnes of ammonium nitrate?

$$n(\text{NH}_4\text{NO}_3) = 25 \times 10^6 \text{ g} \div 80.0 = 3.125 \times 10^5 \text{ mol}$$

so $3.125 \times 10^5 \text{ mol HNO}_3$ and $3.125 \times 10^5 \text{ mol NH}_3$ needed for equation

36.7

$$\text{NH}_3 \text{ for } \text{HNO}_3 (1 : 1 \text{ overall, } 77\% \text{ yield}) = 3.125 \times 10^5 \times 100 \div 77 = 4.058$$

$$\times 10^5 \text{ mol}$$

$$\text{total } n(\text{NH}_3) = 3.125 \times 10^5 + 4.058 \times 10^5 = 7.18 \times 10^5 \text{ mol}$$

$$\text{mass} = 7.18 \times 10^5 \times 17.0 = 1.22 \times 10^7 \text{ g} = 12 \text{ tonnes}$$

mass of ammonia needed = ...12.....tonnes [4]

- (iii) Describe a test that would identify nitrate ions.

..Add NaOH(aq) and Devarda's alloy (or aluminium powder) and warm. Test.....
..the gas with damp red litmus paper: it turns blue (ammonia), showing.....
..nitrate ions are present..... [2]

END OF QUESTION PAPER

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