2025 DHS Preliminary Examination
H2 Chemistry 9729 Paper 1
Suggested Solutions

Answer Key

1	2	3	4	5	6	7	8	9	10
D	B	A	C	D	A	B	D	A	C

11	12	13	14	15	16	17	18	19	20
D	C	B	A	C	B	B	D	D	A

21	22	23	24	25	26	27	28	29	30
D	C	D	C	A	C	D	B	A	C

1	D	
×	A	Since both particles have a positive angle of deflection, they are deflected in the same direction towards the same plate. Similar to $^4He^{2+}$, **X** must be positively charged.
×	B	The beam of positively charged particles **X** travels in a curved path towards the negatively charged plate.
×	C	Charge to mass ratio of $^{12}C^+ = +\frac{1}{12}$ Charge to mass ratio of $^4He^{2+} = +\frac{2}{4} = +\frac{1}{2}$ Since angle of deflection is proportional to charge to mass ratio, the angle of deflection of $^{12}C^+$ is expected to be $\frac{1}{6}(1°) = +0.17°$
✓	D	None of the above options are correct.

2	B
	1. Determine the number of neutrons in Sr (find proton number of Sr using *Data Booklet*.) ⇒ 84 – 38 = 46 2. Find number of electrons present in Sr^{2+} (using proton number of Sr given in Data Booklet.) ⇒ 38 – 2 = 36 ⇒ **W** has 36 electrons 3. Find number of protons present in **W** **W**: 36 protons 4. Calculate the nucleon number of **W** **W**: 36 + 46 = 82 The outer electronic configuration of **W** is $4s^24p^6$ and hence a total of four orbitals (one 4s and three 4p) are occupied in the valence shell.

3	**A** (1, 2 and 3 only)	
	The molecules have the following linear structures: O=C=O, S=C=S and O=C=S	
✓	1	C=O and C=S are polar covalent bonds due to the difference in electronegativity between the atoms.
✓	2	Each C=O and C=S bond contains one sigma and one pi bond so each molecule contains two sigma and two pi bonds.
✓	3	The dipole moments of the polar bonds are equal and opposite in O=C=O and S=C=S molecules so they cancel out and the molecules are non-polar. There exists only instantaneous dipole–induced dipole (id–id) interactions between these non–polar molecules. As O is more electronegative than S, C=O bond is more polar than C=S bond and there is a net dipole moment in O=C=S. Hence, COS molecule is polar and it has both id–id and permanent dipole–permanent dipole interactions between molecules.
×	4	O=C=S has a smaller, less polarisable electron cloud than S=C=S. Hence, O=C=S has weaker id-id interactions between molecules than S=C=S.

4	C	
×	A	Ice has a simple molecular structure with hydrogen bonds between water molecules. There are covalent bonds between atoms in the water molecules.
×	B	Iodine, I_2, has a simple molecular structure and is a non-polar molecule. There exists instantaneous dipole–induced dipole (id–id) interactions between molecules and covalent bond between iodine atoms in a molecule.
✓	C	Sodium nitrate, $NaNO_3$, has a giant ionic structure with ionic bonds between oppositely charged Na^+ and NO_3^- ions. Within the NO_3^- ion, there are covalent bonds between N and O atoms.
×	D	Manganese has a giant metallic structure with metallic bonds between the positively charged metal cations and sea of delocalised electrons.

5	D
	$2H_2S + 3O_2 \rightarrow 2SO_2 + 2H_2O$ $CS_2 + 3O_2 \rightarrow CO_2 + 2SO_2$ Hence, $SO_2 : CO_2$ will be 4 : 1. ⇒ Options **A** & **C** are incorrect. In the 60 cm^3 mixture, there is 40 cm^3 of H_2S and 20 cm^3 of CS_2. 40 cm^3 of H_2S will form 40 cm^3 of SO_2. 20 cm^3 of CS_2 will form 20 cm^3 of CO_2 and 40 cm^3 of SO_2. Hence, total volume of acidic gases, CO_2 and SO_2, = 40 + 20 + 40 = 100 cm^3 These acidic gases will react with NaOH(aq) and cause a reduction in gas volume.

6	A	
✓	A	$pV = nRT = mRT/M \Rightarrow$ density = $m/V = pM/RT$ Since density = pM/RT and M, T and R are constants, density is directly proportional to p ⇒ graph of density against p is an upward sloping straight line starting from the origin This graph does not represent the behaviour of a fixed mass of an ideal gas.

×	B	Since $pV = nRT$ and n, p and R are constants, V is directly proportional to T (in K) ⇒ graph of V against T is an upward sloping straight line starting from the origin
×	C	Since $pV = nRT$ and n and R are constants, pV/T = constant ⇒ graph of pV/T against p is a horizontal straight line.
×	D	Since $pV = nRT$ and n, V and R are constants, p/T = constant ⇒ graph of p against p/T is a vertical straight line.

7	B	
	Oxidation half-equation: $Fe^{2+} \rightarrow Fe^{3+} + e^-$ $Fe^{2+} \equiv e^-$ amount of electrons transferred $= \frac{30.0}{1000} \times 0.200 = 0.00600$ mol $\frac{\text{amount of electrons}}{\text{amount of nitrate ions}} = \frac{0.00600}{0.00200} = \frac{3}{1}$ The oxidation state of nitrogen decreases by 3 from +5 in NO_3^- to +2.	
×	A	The oxidation state of N in N_2 is 0.
✓	B	The oxidation state of N in NO is +2.
×	C	The oxidation state of N in NO_2^- is +3.
×	D	The oxidation state of N in NO_2 is +4.

8	D
	K is phosphorus as the P^{3-} has the largest ionic radii amongst the Period 3 ions. The cations are smaller has they have one less shell of electrons compared to the anions. Amongst the isoelectronic anions, P^{3-} has the lowest nuclear charge hence the weakest electrostatic forces of attraction for its valence electrons. **L** is silicon. Large amount of energy is required to break the strong and extensive covalent bonds between Si atoms in the 3-dimensional network structure. **M** is magnesium. It has the second highest number of delocalised electrons in its solid lattice, hence the second highest electrical conductivity behind aluminium. In order of increasing atomic number: **M** (magnesium) < **L** (silicon) < **K** (phosphorus)

9	A (1 and 2 only)	
✓	1	Electronegativity decreases down every group as the number of electron shells increases. This leads to an increase in screening effect. Despite the increase in nuclear charge, the ability of the atom to attract bonding electrons decreases.
✓	2	Reducing power of Group 2 elements increases as $E^{\ominus}(M^{2+}/M)$ gets increasingly negative.
×	3	As the size of electron cloud increases down the group, polarisability increases. More energy is required to overcome the stronger instantaneous dipole–induced dipole interactions between X_2 molecules. Boiling point increases and volatility (ease of vaporisation) decreases.

10	C	
×	A	$2Na(s) + \frac{1}{2}O_2(g) \rightarrow Na_2O(s)$ The number of moles of gases decreases from ½ to 0 per mole of $Na_2O(s)$ formed from its constituent elements at standard conditions.
×	B	$Mg(s) + \frac{1}{2}O_2(g) \rightarrow MgO(s)$ The number of moles of gases decreases from ½ to 0 per mole of MgO(s) formed from its constituent elements at standard conditions. The $\Delta S_f^{\ominus}$ of MgO(s) is expected to be similar to that of $Na_2O(s)$ since the change in number of gaseous particles is the same for both reactions.
✓	C	$Si(s) + O_2(g) \rightarrow SiO_2(s)$ The number of moles of gases decreases from 1 to 0 per mole of $SiO_2(s)$ formed from its constituent elements at standard conditions. The $\Delta S_f^{\ominus}$ of $SiO_2(s)$ is the most negative as its formation results in the largest decrease in number of gaseous particles.
×	D	$S(s) + O_2(g) \rightarrow SO_2(g)$ The number of moles of gases does not change as one mole of $SO_2(g)$ is formed from its constituent elements at standard conditions.

11	D	
	The magnitude of lattice energy of an ionic compound is dependent on the product of ionic charge and the sum of ionic radii: $\lvert L.E.\rvert \propto \left\lvert \frac{q_+ q_-}{r_+ + r_-} \right\rvert$	
×	A	For TiF_3, $\lvert L.E.\rvert \propto \left\lvert \frac{(+3)\times(-1)}{0.067 + 0.136} \right\rvert = 14.8$
×	B	For FeF_3, $\lvert L.E.\rvert \propto \left\lvert \frac{(+3)\times(-1)}{0.055 + 0.136} \right\rvert = 15.7$
×	C	For TiO, $\lvert L.E.\rvert \propto \left\lvert \frac{(+2)\times(-2)}{0.086 + 0.140} \right\rvert = 17.7$
✓	D	For FeO, $\lvert L.E.\rvert \propto \left\lvert \frac{(+2)\times(-2)}{0.061 + 0.140} \right\rvert = 19.9$

12	C
	heat transferred to water = $mc\lvert\Delta T\rvert$ $= 500 \times 4.18 \times 7.5 = 15675$ J heat released by combustion $= \frac{100}{70} \times 15675 = 22392$ J = 22.392 kJ energy released per gram of fuel burnt $= 22.392 \div 0.7 = 32.0$ kJ g^{-1}

13	B
	Removal of aspirin $x\,(100\%) \xrightarrow{t_{1/2}} \frac{x}{2}(50\%) \xrightarrow{t_{1/2}} \frac{x}{4}(25\%) \xrightarrow{t_{1/2}} \frac{x}{8}(12.5\%)$ $3\ t_{1/2} = 6$ h $t_{1/2} = 2$ h rate constant, $k = \ln 2 / t_{1/2}$ $= (\ln 2) / 2$ $= 0.347\ h^{-1}$

14	A
	From the slow step, rate = $k[P_2][Q]$ However, P_2 is an intermediate and should not appear in the rate equation. From the fast step, $K_c = \frac{[P_2]}{[P]^2}$ $[P_2] = K_c[P]^2$ Thus, rate = $kK_c[P]^2[Q]$ rate = $k'[P]^2[Q]$

15	C	
✗	A	Addition of catalyst does not shift the position of equilibrium as it increases the rate of both forward and backward reaction to the same extent. K_c remains unchanged as it is temperature dependent.
✗	B	Addition of inert gas at constant volume does not change the partial pressure of the gaseous reactants and products. Hence position of equilibrium will not shift. K_c remains unchanged as it is temperature dependent.
✓	C	Decrease in temperature will shift the position of equilibrium to the right to favour exothermic reaction to release heat. Hence, there is an increase in [products] and decrease in [reactants]. K_c will increase.
✗	D	Decrease in volume of vessel will increase the partial pressures of all gases, hence shift position of equilibrium to the right to decrease the number of gaseous particles. K_c remains unchanged as it is temperature dependent.

16	B (1 and 2 only)

solution	concentration / mol dm^{-3}	pH	$[H^+]$	$[OH^-]$
E	1.0	4.0	10^{-4}	
F	1.0	5.8		
G	0.01	12.0	10^{-12}	0.01
H	0.01	2.0	0.01	

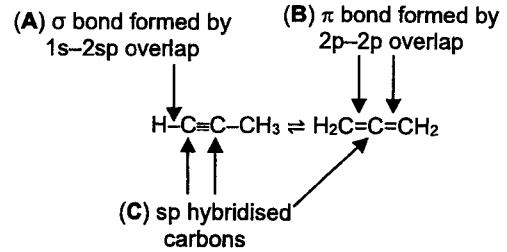
Since $[H^+]$ << [**E**] and $[H^+]$ << [**F**], **E** and **F** are weak acids or acidic salts that dissociate partially. **E** and **F** are CH_3COOH and NH_4Cl.
Since $[H^+]$ = [**H**], **H** is a strong acid, HCl, that dissociates fully.

		Since $[OH^-]$ = [**G**], **G** is a strong base, NaOH, that dissociates fully.
✓	1	Statement is correct as explained above.
✓	2	amount of **E** = $\frac{10}{1000} \times 1.0$ = 0.01 mol amount of **G** = $\frac{500}{1000} \times 0.01$ = 0.005 mol Resulting solution contains excess **E** (weak acid) and its salt. Hence, a buffer solution is produced.
✗	3	Resulting solution is a strong acid and a weak acid. Hence, a buffer solution is not formed.

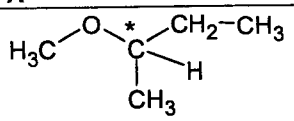
17	B
	$[H^+] = 10^{-7.4} = 3.981 \times 10^{-8}$ mol dm^{-3} $[OH\text{-}] = K_w \div [H^+] = 2.4 \times 10^{-14} \div 3.981 \times 10^{-8}$ $= 6.03 \times 10^{-7}$ mol dm^{-3}

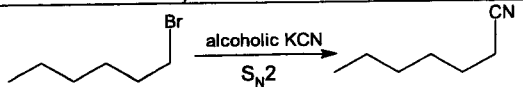
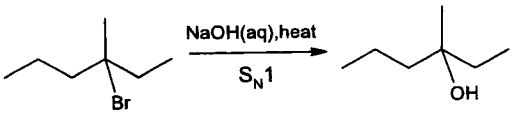
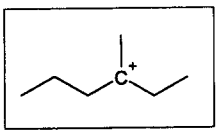
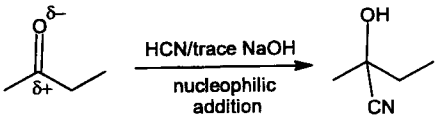
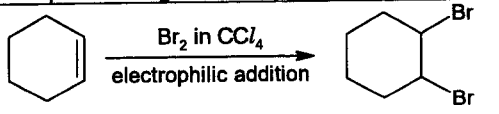
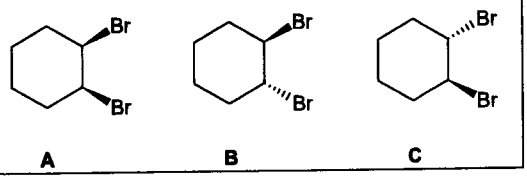
18	D (2 and 3 only)	
✗	1	In a solution saturated with **both** $BaSO_4$ and $PbSO_4$, let the solubility of $BaSO_4$ and $PbSO_4$ be x' and y' mol dm^{-3} respectively. Due to common ion effect, $x' < x$ and $y' < y$ $[Ba^{2+}] = x'$ mol dm^{-3} $[Pb^{2+}] = y'$ mol dm^{-3} $[SO_4^{2-}] = (x' + y')$ mol dm^{-3} < $(x + y)$ mol dm^{-3} $= [Ba^{2+}] + [Pb^{2+}]$
✓	2	$BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)$ In the presence of common ion SO_4^{2-}, position of above equilibrium will shift to the left to decrease $[SO_4^{2-}]$, hence solubility of $BaSO_4$ will decrease. $[Ba^{2+}] < x$ mol dm^{-3}
✓	3	Refer to statement **1** for explanation.

19	D

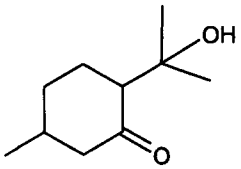


D is incorrect as the C–C single bond in propyne is sp–sp^3 overlap, while that in propane (CH_3–CH_2–CH_3) is sp^3–sp^3 overlap. The bond length in propyne is shorter as sp orbital has more s character, resulting in more effective overlap.

20	A
	

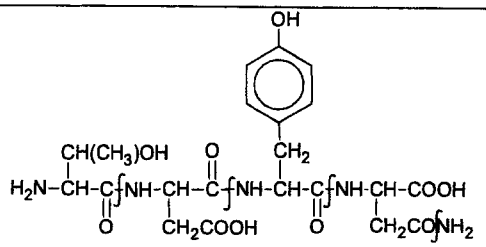
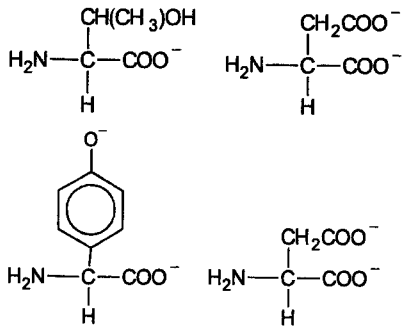
21	D (none of the above)	
×	1	 The molecule does not have a chiral carbon, so the product does not rotate plane polarised light.
×	2	 intermediate:  OH^- nucleophile attacks the positively charged carbon which is trigonal planar from the top and the bottom of the plane with equal probability. A racemic mixture is formed and does not rotate plane polarised light.
×	3	 CN^- nucleophile attacks the electron deficient trigonal planar carbonyl carbon from the top and the bottom of the plane with equal probability. A racemic mixture is formed and does not rotate plane polarised light.
×	4	 Br_2 electrophile attacks the trigonal planar C=C carbon to form a carbocation intermediate. In the fast step, the Br^- nucleophile attacks the trigonal planar carbocation from the top and the bottom of the plane with equal probability. A mixture of three stereoisomers, **A**, **B** and **C** are formed. **A** is a meso compound with an internal plane of symmetry. It is optically inactive. **B** and **C** are enantiomers that are formed in a 1:1 ratio. The resulting product mixture does not rotate plane polarised light.  **A** **B** **C**

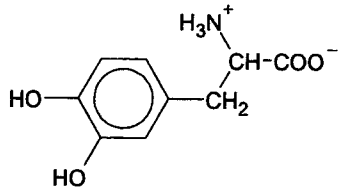
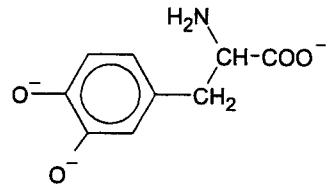
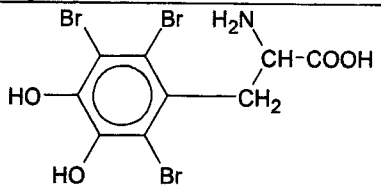
22	C	
	From the rate of formation of ppt, **P** is $C_6H_5CH_2Br$, **Q** is $X–C_6H_4CH_3$, **R** is $C_6H_5CH_2I$, **S** is $C_6H_5CH_2Cl$.	
×	**A**	**R** should have the longest and weakest C–X bond since it is the most reactive.
×	**B**	Reacting Cl_2 with methylbenzene in the presence of UV light (Free Radical Substitution reaction) gives **S**, $C_6H_5CH_2Cl$ not **R**, $C_6H_5CH_2I$.
✓	**C**	**Q** can be $BrC_6H_4CH_3$ formed from $C_6H_5CH_3$ + Br_2 in the presence of $AlBr_3$. This is an electrophilic substitution reaction and the product is $Br–C_6H_4CH_3$.
×	**D**	Only **P**, **R** and **S** give benzoic acid upon side-chain oxidation.

23	D	
	Compound **E** has the following structure: 	
×	**A**	NaOH(alcoholic) will react with neither compound since there is no R–X (X = Cl, Br or I) group for elimination to occur.
×	**B**	2,4–DNPH will only react with **E** since carbonyl group is present in **E**.
×	**C**	Warm alkaline aqueous iodine will react with neither compounds. (negative triidomethane test) since both do not have $–COCH_3$ or $–CH(OH)CH_3$.
✓	**D**	Both compounds have adjacent H and OH to undergo elimination with hot alumina (i.e., heat with Al_2O_3) to form alkene.

24	C
	Sodium hydroxide reacts with phenols and carboxylic acids: $C_6H_5OH \equiv NaOH$ [Note: NaOH does not react with alcohols.] Therefore, 1 mol of saligenin reacts with 1 mol of NaOH. Sodium metal reacts with alcohols, phenols and carboxylic acids: $ROH \equiv Na$ $C_6H_5OH \equiv Na$ Equations: $ROH + Na \rightarrow RO^-Na^+ + ½ H_2$ $C_6H_5OH + Na \rightarrow C_6H_5O^-Na^+ + ½ H_2$ Saligenin contains a ROH (primary alcohol) and a C_6H_5OH (phenolic group). Therefore, 1 mol of saligenin requires 2 mol of Na to produce 1 mol of H_2.

25	A	
✓	A	Has both alcohol group and aliphatic aldehyde group
×	B	Has an aliphatic aldehyde group only. Aromatic aldehyde group also present.
×	C	Has an alcohol group only. Aliphatic ketone group also present.
×	D	Has an aliphatic aldehyde group only. Phenol group also present but does not react with PCl_5

26	C	
		 compound **Z**
✓	A	**Z** undergoes basic hydrolysis to form 4 carbon containing products, out of which two of them are the same. 
✓	B	Primary amide undergoes basic hydrolysis to produce basic NH_3 gas.
×	C	Three moles of CH_3COCl are required (one mole with secondary alcohol, one mole with phenol and one mole with primary amine). All of these functional groups undergo condensation with CH_3COCl.
✓	D	One mole of Na_2CO_3 is required to undergo acid–base reaction with two moles of RCOOH (carboxylic acid) in **Z**. $Na_2CO_3 + 2RCOOH \rightarrow 2RCOO^-Na^+ + CO_2 + H_2O$

27	D (2 and 3 only)	
T	1	 zwitterionic form of dopamine Able to form ion–dipole interactions with water, allowing it to be soluble in water
F	2	At a high pH of 14, all acidic groups on dopamine are deprotonated:  ionic form of dopamine at pH 14 As it has an overall negative charge (of –3), it is attracted to the anode (positive electrode) of an electrolytic cell.
F	3	 product when reacted with $Br_2(aq)$ As there are three electron–withdrawing Br atoms on the benzene ring, the negative charge of the carboxylate group is dispersed to a larger extent. This makes the carboxylate ion more stable, increasing the acid strength.

28	B
	As **Y** is the negative electrode, electrons are released at **Y** and **Y** is the anode. Oxidation of **Y** to Y^{3+} occurs $Y \rightarrow Y^{3+} + 3e^-$ As **X** is the positive electrode, electrons are gained at **X** and **X** is the cathode. Reduction of X^{2+} to **X** occurs $X^{2+} + 2e^- \rightarrow X$ $E^\ominus(X^{2+}/X)$ is more positive than $E^\ominus(Y^{3+}/Y)$ $\Rightarrow X^{2+}$ is more readily reduced than Y^{3+} $\Rightarrow X^{2+}$ is a stronger oxidising agent than Y^{3+} $\Rightarrow$ **Y** is a stronger reducing agent than **X**

29	A
	$Q = It$ $= 2 \times 9 \times 60 \times 60$ $= 64800$ C amount of e^- passed $= 64800 \div 96500$ $= 0.67150$ mol $Al^{3+} + 3e^- \rightarrow Al$ mass of Al produced $= \frac{1}{3} \times 0.67150 \times 27.0$ $= 6.04$ g

30	C	
×	A	**G** is $Cu(OH)_2(s)$. NH_3 is acting as a Bronsted–Lowry base, accepting H^+ from H_2O to produce $OH^-(aq)$. Reaction I is a precipitation reaction. $NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$ $Cu^{2+}(aq) + 2OH^-(aq) \rightarrow Cu(OH)_2(s)$
×	B	**H** is $[Cu(NH_3)_4(H_2O)_2]SO_4(aq)$ and has a deep blue colour. Reaction II involves the formation

✓	C	of a complex. There is no change in oxidation state i.e., not a redox reaction.
✗	D	Reaction III is a ligand exchange reaction and $EDTA^{4-}$ is a hexadentate ligand. $[Cu(NH_3)_4(H_2O)_2]^{2+}(aq) + EDTA^{4-}(aq)$ $\rightleftharpoons [Cu(EDTA)]^{2-}(aq) + 4NH_3(aq) + 2H_2O(l)$ As there is an increase in number of aqueous species, entropy increases.

Suggested Solutions

DUNMAN HIGH SCHOOL
Preliminary Examination
Year 6

H2 CHEMISTRY

9729/02

Paper 2 Structured Questions

18 September 2025
2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your centre number, index number, name and class at the top of this page.
Write in dark blue or black pen.
You may use an HB pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper.

The use of an approved scientific calculator is expected, where appropriate.
You may lose marks if you do not show your working or if you do not use appropriate units.

A Data Booklet is provided.

The number of marks is given in brackets [ ] at the end of each question or part question.

For Examiner's Use	
1	/15
2	/17
3	/12
4	/10
5	/21
Total	/75

This document consists of **16** printed pages.

[Turn over

Answer **all** the questions in the spaces provided.

1 (a) Fig. 1.1 shows the relative first ionisation energies of six consecutive elements, **A** to **F**, in the Periodic Table with atomic number less than 20.

The letters are **not** the symbols of the elements.

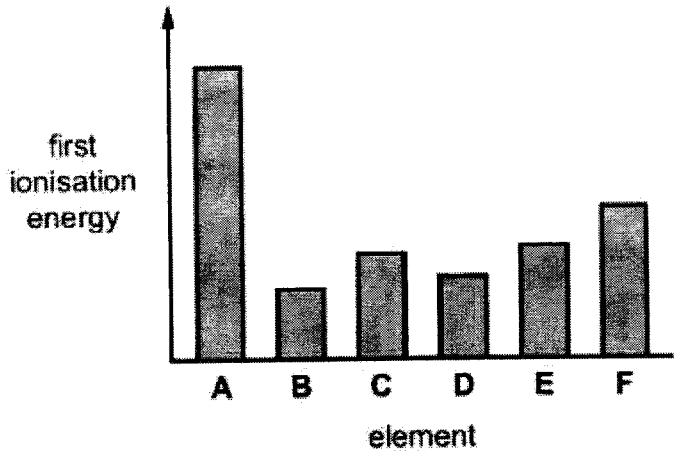


Fig. 1.1

(i) Write an equation to represent the first ionisation energy of **A**.

[1]

$A(g) \rightarrow A^+(g) + e^-$

(ii) Explain why the first ionisation energy of **F** is more than that of **E**.

[1]

Both elements have similar shielding effect. However, F has a greater nuclear charge. Hence, F has a greater effective nuclear charge than E. The attraction between the nucleus and the outermost electron is stronger in F.

(iii) Which element has the highest 4th ionisation energy? Explain your answer.

[1]

Element D. It is in Group 13 with outermost shell electronic configuration of $ns^2 np^1$. The 4th ionisation energy involves removal of an electron from an inner electron shell. Or 4th valence electron is removed from an inner electron shell.

(iv) Element **E** is in Period 3.
Identify element **E** and state the number of electron pairs in an atom of **E**.

[1]

element E is silicon
number of electron pairs in an atom of E is 6

(b) 10.0 cm^3 of 0.10 mol dm^{-3} aqueous bromine was added to 50.00 cm^3 of a 0.10 mol dm^{-3} sodium hydroxide solution. The products formed were Br^- and BrO_x^-.

The excess sodium hydroxide required 15.00 cm^3 of 0.20 mol dm^{-3} hydrochloric acid for complete neutralisation.

Calculate the mole ratio between aqueous bromine and sodium hydroxide in the redox reaction.

Hence write a balanced equation for the reaction and deduce the value of x.

[3]

Initial amount of NaOH = $\frac{50.00}{1000} \times 0.10 = 5.00 \times 10^{-3}$ mol

amount of NaOH reacted with HCl(aq) = $\frac{15.00}{1000} \times 0.20 = 3.00 \times 10^{-3}$ mol

amount of NaOH reacted with aqueous Br_2 = $(5.00 \times 10^{-3}) - (3.00 \times 10^{-3})$
= 2.00×10^{-3} mol

amount of Br_2 used = $\frac{10.00}{1000} \times 0.10 = 1.00 \times 10^{-3}$ mol

mole ratio of Br_2 : NaOH = 1 : 2

Balanced ionic equation:

$Br_2(aq) + 2OH^-(aq) \rightarrow Br^-(aq) + BrO^-(aq) + H_2O(l)$

x =1

(c) The halogens Cl_2 and I_2 both react similarly with H_2S. The reaction of Cl_2 with H_2S is shown in equation 1.

equation 1 $\quad Cl_2 + H_2S \rightarrow 2HCl + S$

(i) Predict which halogen, Cl_2 or I_2, has a greater reactivity when added to H_2S. Explain your answer in terms of the role of the halogen in these reactions.

[1]

Cl_2 has a greater reactivity than I_2 as Cl_2 is a stronger oxidising agent than I_2.

(ii) The white fuming gaseous products, HCl and HI, were collected in separate jars. A piece of red-hot wire was plunged into each jar and purple fumes were observed in one of them.

Explain the observation.

[2]

Purple fumes observed is iodine vapour when HI thermally decomposed

$$2HI \rightarrow H_2(g) + I_2(g)$$

Bond energy of H–I < H–Cl the covalent bond length of H–I > H–Cl.
A lower amount of energy is required to overcome the weaker H–I covalent bond.

Thermal stability of HI < HCl , HI decomposes readily in the presence of a red-hot wire to give purple iodine vapour. However, insufficient energy is provided to overcome H–Cl bond. HCl does not decompose.

(iii) Both HI(g) and HCl(g) dissolve readily in water.

Suggest a reagent, other than aqueous silver nitrate, that could be used to distinguish between the aqueous solutions of these two gases. Describe the expected observations.

[2]

Add Cl_2(aq) or Cl_2 gas into HCl(aq) and HI(aq) separately.

With HCl (aq), solution remains colourless.
With HI (aq), solution turns brown due to the formation of I_2(aq).

OR

Add Br_2(aq) into HCl(aq) and HI(aq) separately.

With HCl (aq), solution turns orange.
With HI (aq), solution turns brown due to the formation of I_2(aq).

Also accept:
Add $Pb(NO_3)_2$(aq) into HCl(aq) and HI(aq) separately.

With HCl (aq), white ppt of $PbCl_2$.
With HI (aq), yellow ppt of PbI_2.

OR
Add $Cu(NO_3)_2$(aq) into HCl(aq) and HI(aq) separately.

With HCl (aq), solution turns blue (due to Cu^{2+} present).
With HI (aq), white ppt (due to CuI) in brown solution (due to I_2)

(d) Bromine and fluorine react together to give bromine trifluoride.

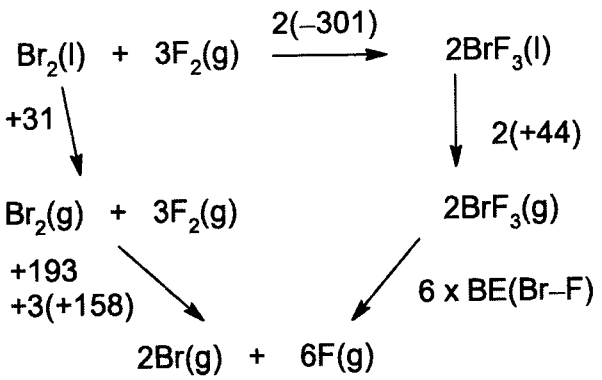
$$Br_2(l) + 3F_2(g) \rightarrow 2BrF_3(l)$$

Using the data in Table 1.1, together with data from the *Data Booklet,* construct a fully labelled energy cycle to calculate the average bond energy of the Br–F bond in BrF_3.

Table 1.1

process	$\Delta H^{\ominus}$ / kJ mol^{-1}
Standard enthalpy change of formation of BrF_3(l)	−301
Enthalpy change of vaporisation of Br_2(l)	+31
Enthalpy change of vaporisation of BrF_3(l)	+44

[3]

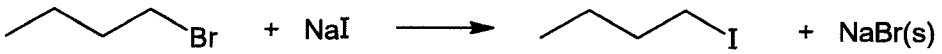


By Hess' Law,

$2(-301) = (+31) + (+193) + 3(+158) - 6BE(Br-F) - 2(+44)$
average BE(Br–F) = + 202 kJ mol^{-1}

[Total: 15]

2 The kinetics of the Finkelstein reaction between bromobutane and sodium iodide in propanone forming solid sodium bromide was studied in a series of experiments.



(a) In experiment 1, 10.0 cm^3 of 0.10 mol dm^{-3} bromobutane and 15.0 cm^3 of 1.0 mol dm^{-3} sodium iodide were mixed.

Fig. 2.1 shows the concentration of bromobutane against time, *t*, for this experiment.

(i) Use the graph in Fig. 2.1 to determine the order of reaction with respect to bromobutane. Show your working clearly.

[2]

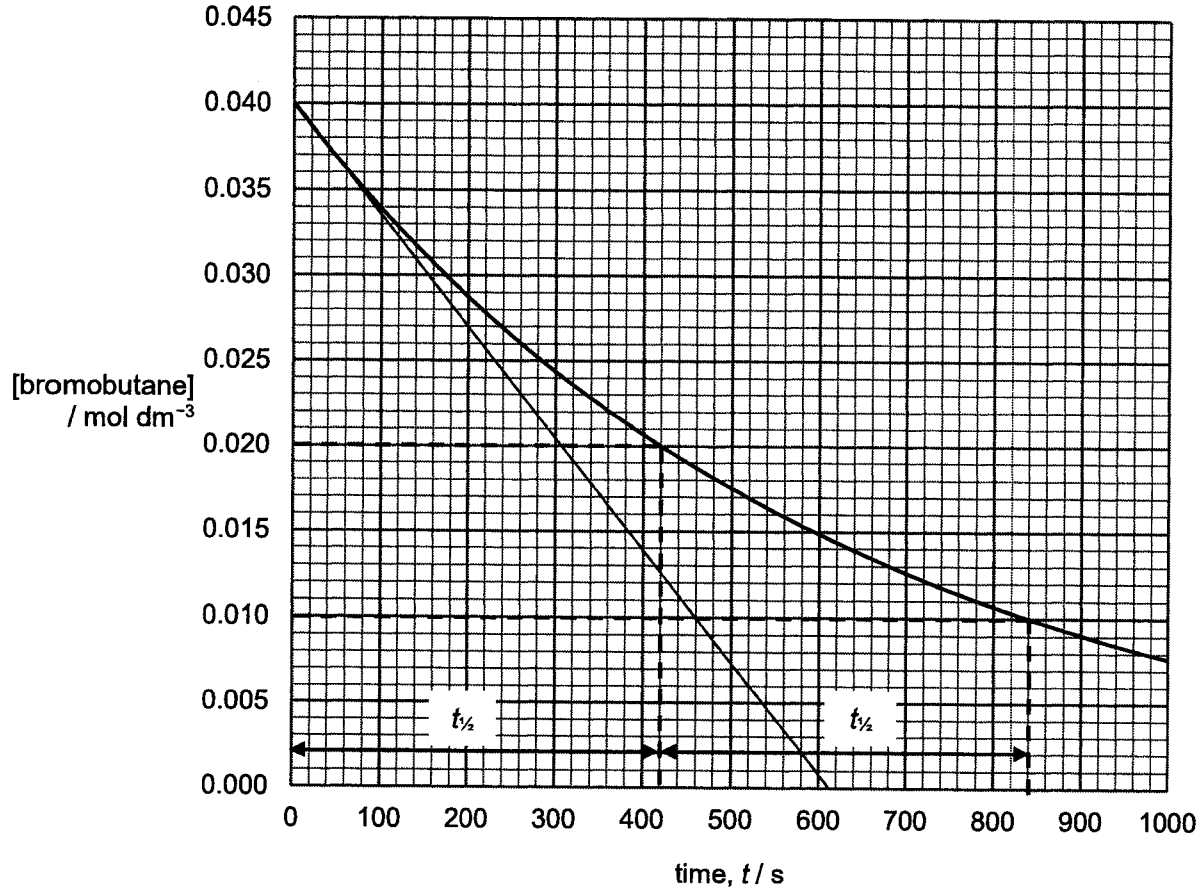


Fig. 2.1

Since $t_{½}$ is constant at 420 s, the reaction is first order wrt bromobutane.

(ii) By drawing a tangent at *t* = 0 s, determine the initial rate of reaction. Include its units.

[2]

$$\text{rate of reaction} = \frac{0.04}{610} = 6.56 \times 10^{-5} \text{ mol dm}^{-3} \text{ s}^{-1}$$

(b) In experiments 2 and 3, the time taken for a small and fixed amount of NaBr(s) to be formed was measured. The results obtained are found in Table 2.1.

Table 2.1

experiment	initial [bromobutane] / mol dm^{-3}	initial [sodium iodide] / mol dm^{-3}	time / s
2	0.60	0.60	21
3	0.40	0.40	47

(i) Use Table 2.1 to determine the order of reaction with respect to sodium iodide. Show your working clearly.

[1]

Since the extent of reaction is kept constant, relative rate $\propto \frac{1}{t}$.

Let the order of reaction w.r.t. NaI be x.
Comparing the rate of experiments 2 and 3,

$$\frac{\text{rate}_2}{\text{rate}_3} = \frac{k[\text{bromobutane}][\text{NaI}]^x}{k[\text{bromobutane}][\text{NaI}]^x}$$

$$\frac{1/21}{1/47} = \frac{k \times 0.60 \times (0.60)^x}{k \times 0.40 \times (0.40)^x}$$

$$1.49 = \left(\frac{0.60}{0.40}\right)^x$$

$x = 1$ (to nearest whole number)

(ii) Use your answers to **(a)(i)** and **(b)(i)** to write the rate equation for the reaction between bromobutane and sodium iodide.
State the units of the rate constant, k.

[1]

rate = k[bromobutane][NaI]
units of k = $mol^{-1}\ dm^3\ s^{-1}$

(iii) Hence use the initial rate of reaction from **(a)(ii)** to calculate the value of the rate constant, k.

[2]

For experiment 1,

$$\text{initial [NaI]} = \frac{15.0 \times 1.0}{25.0} = 0.60 \text{ mol dm}^{-3}$$

rate = k[bromobutane][NaI]

$$6.56 \times 10^{-5} = k \times 0.040 \times 0.60$$
$$k = 2.73 \times 10^{-3} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$$

(c) The Finkelstein reaction is a nucleophilic substitution reaction that can occur via the S_N1 or S_N2 mechanism.

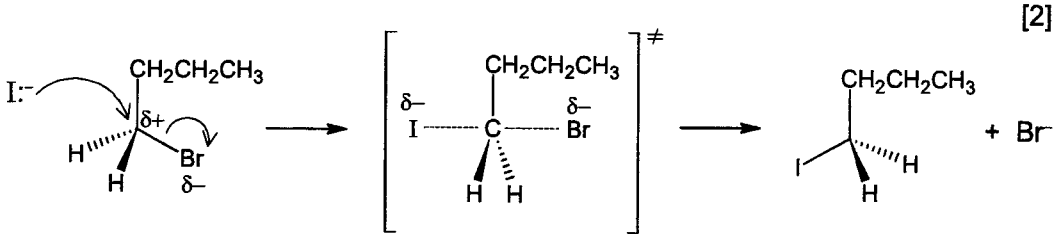
(i) Using your answer to **(b)(ii)**, identify the mechanism for the reaction between bromobutane and sodium iodide. Suggest a reason why this is the predominant mechanism.

[1]

The reaction goes by S_N2 mechanism. Bromobutane is a primary alkyl halide with little steric hindrance around the electrophilic (δ+) C, hence the I^- nucleophile is able to approach the relatively-unhindered electrophilic (δ+) C easily.

(ii) Hence draw the mechanism for the reaction between bromobutane and sodium iodide. Use curly arrows to show the movement of electrons, and include relevant dipoles and lone pair of electrons.

[2]



(d) The graph of *pV/RT* against *p* for one mole of iodobutane gas at 200 °C is shown in Fig. 2.2.

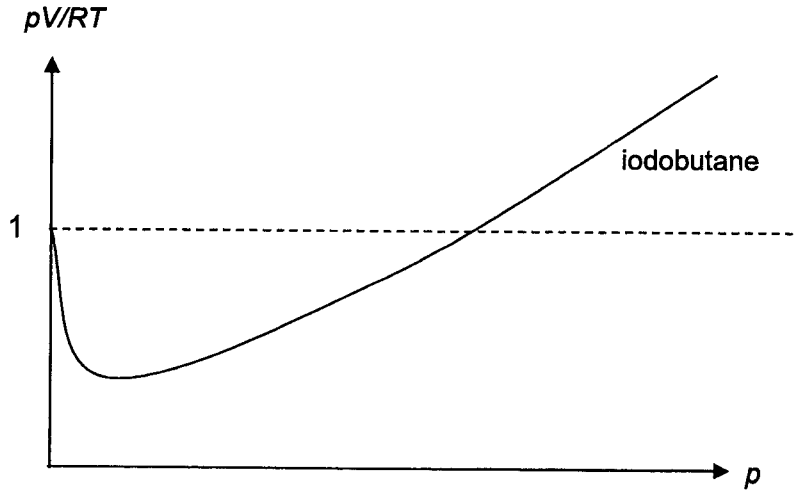


Fig. 2.2

(i) State two basic assumptions of the kinetic theory as applied to an ideal gas.

[2]

The gas particles have negligible volume compared to that of the container.
There are negligible intermolecular forces of attraction between gas particles.

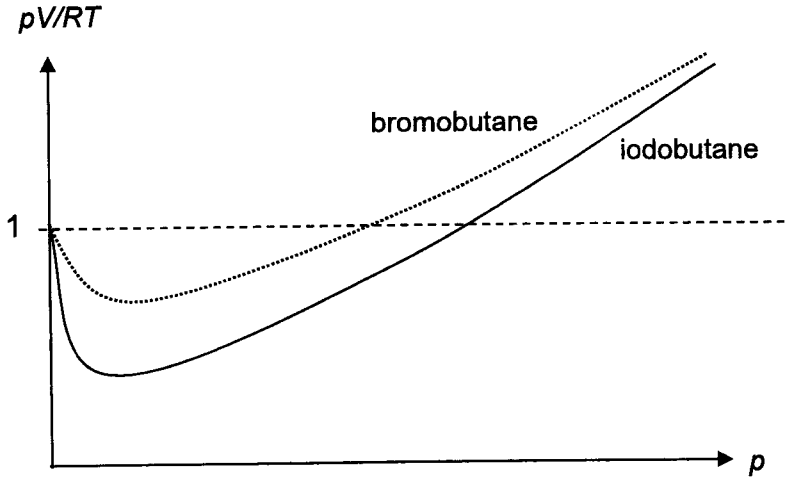
The boiling points of bromobutane and iodobutane are given in Table 2.2.

Table 2.2

	boiling point / °C
bromobutane	101
iodobutane	131

(ii) Hence show in Fig. 2.2 how one mole of bromobutane will behave at the same temperature.

[1]



Freon–11 was one of the most widely used chlorofluorocarbon (CFC) before its use was phased out by the Montreal Protocol.

(e) 1.868 g of freon–11 gas occupied 356 cm^3 at 200 °C and 1.5 bar. Assuming freon–11 gas behaves ideally, calculate its molar mass.

Hence deduce the molecular formula of freon–11, given that each molecule of freon–11 contains one carbon atom only. Show your working clearly.

[3]

$$pV = nRT$$
$$pV = \frac{m}{M}RT$$
$$M = \frac{mRT}{pV}$$
$$= \frac{1.868 \times 8.31 \times (200+273)}{\left(1.5 \times 10^5\right) \times \left(356 \times 10^{-6}\right)}$$
$$= 137.5 \text{ g mol}^{-1} \text{ (to 1 d.p.)}$$

By trial and error, the molecular formula of freon–11 is CCl_3F.

$$12.0 + (3 \times 35.5) + 19.0 = 137.5$$

[Total: 17]

3 Transition elements show typical properties that distinguish them from s-block elements, such as calcium. These include variable oxidation states in their compounds, and the formation of coloured complexes.

[1]

(a) An ion of vanadium has one electron in its 3d subshell. Deduce the oxidation state of this vanadium ion.

V atom has 23 electrons.
Electronic configuration of V is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^3 4s^2$

Since only one electron remains in the 3d subshell, hence 4 outermost electrons are lost. The oxidation state of V is **+4**.

(b) Table 3.1 gives data about some physical properties of the elements calcium, iron and copper.

Table 3.1

property	calcium	iron	copper
relative atomic mass	40.1	55.8	63.5
atomic radius (metallic) / nm	0.197	0.126	0.128
ionic radius (2+) / nm	0.099	0.076	0.069
density / g cm^{-3}	1.54	7.86	8.92

(i) Suggest why the atomic radius of iron is smaller than that of calcium.

[1]

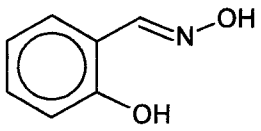
Atomic radius of Fe < Ca due to its higher nuclear charge and poor shielding by 3d electrons. Hence higher effective nuclear charge for Fe, resulting in smaller radius.

(ii) Explain why the densities of iron and copper are significantly greater than that of calcium.

[1]

Both iron and copper have greater atomic mass packed into a smaller volume as the atomic radii of Fe and Cu are smaller than Ca.

(c) Compound **M** is formed through the condensation reaction between a suitable aldehyde **A** and hydroxylamine, H_2NOH.



M

(i) Write an equation to show the formation of **M** from **A** and H_2NOH.

[1]

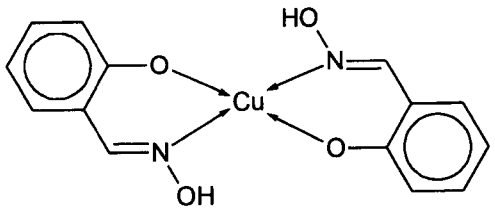
A **M**

The phenolic group in **M** can be deprotonated to form a bidentate ligand. Copper can be extracted by forming an uncharged square planar complex with deprotonated **M**.

(ii) The oxygen atom of the phenoxide group and the nitrogen atom in deprotonated **M** act as donor sites in the formation of the copper complex.

Draw a structure of the complex, clearly showing the geometry around the copper centre.

[1]



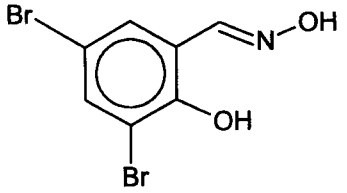
(iii) State the oxidation number and coordination number of copper in the complex. [1]

Oxidation number: +2
Coordination number: 4

Compound **M** was reacted separately with aqueous bromine and aqueous sodium carbonate.

(iv) Complete Table 3.2 by predicting the observations that could be obtained with these reagents and the structure of the organic product (if any) formed. You can assume that the –C=NOH group in **M** is inert. [2]

Table 3.2

reagent	observations	structure of organic product
aqueous bromine	orange $Br_2(aq)$ decolourised + white ppt	
aqueous sodium carbonate	**no effervescence** of CO_2	nil

(d) **(i)** The yellowish mineral pyrite mainly contains iron and sulfur. Table 3.3 gives the oxidation numbers of the elements in pyrite.

Table 3.3

element in pyrite	oxidation number of element in pyrite
Fe	+2
S	−1

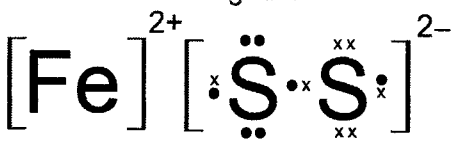
The anion in pyrite has an approximate M_r of 64.

Draw a 'dot-and-cross' diagram to show the type(s) of bonding present within a formula unit of pyrite. [2]

Anion in pyrite has an approximate M_r of 64.
$\Rightarrow$ anion is S_2^{2-}

Hence ionic bonding is present within a formula unit of pyrite, FeS_2.

Dot-and-cross diagram:



(ii) Pyrite ore contains impurities such as copper, arsenic, nickel, cadmium and cobalt. It tends to form iron(III) hydroxide along with other sulfur containing products such as sulfur dioxide when exposed to air and water.

State the type of reaction pyrite undergoes in the presence of air and water and suggest the impact on the environment when water moves through a pyrite-bearing rock.

[2]

Oxidation.
SO_2 can be dissolved in water to give sulfurous acid. This increases the acidity level that endanger aquatic lives. Or other environmental concerns such as

- 'acid rain', which can damage limestone buildings and monuments
- acidification of soil, decreasing its pH and making it less suitable for plant growth.
- Pyrite contains other heavy metals ions that can be released and these ions can contaminate water sources, enter the food chain, and pose health risks to humans and animals.

[Total: 12]

4 (a) Compound **P** is an intermediate formed in the synthesis of Vitamin A. It has molecular formula $C_{15}H_{22}O$ and it reacts with Fehling's reagent to form a brick red precipitate.

When **P** is treated with excess hot concentrated $KMnO_4$, three organic molecules are formed:

- $CH_3CO(CH_2)_3C(CH_3)_2COCO_2H$
- **Q**, $C_3H_4O_3$
- **R**, HOOC–COOH

R is further oxidised to form CO_2.

(i) State two functional groups present in **P**.

[1]

aliphatic aldehyde and alkene

P is reduced to $C_{15}H_{24}O$ by excess reagent **S**.

(ii) Suggest a possible identity of **S**.

[1]

$NaBH_4$ OR $LiAlH_4$

P exists as a mixture of cis-trans isomers.

(iii) Describe two features in the molecule of **P** that allows it to exhibit cis-trans isomerism.

[2]

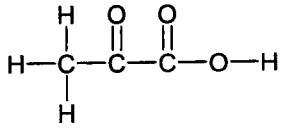
Restricted rotation due to C=C or rigid ring

Two different atoms or groups of atoms attached to each carbon of the C=C bond

(b) When **Q** is added to alkaline aqueous iodine, a pale yellow precipitate forms. When **Q** is added to aqueous sodium carbonate, effervescence is observed.

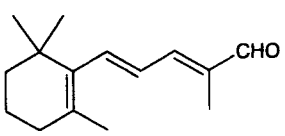
(i) Draw the displayed formula of **Q**.

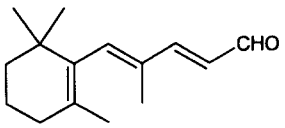
[1]

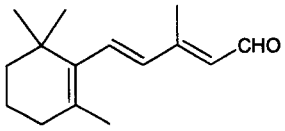


(ii) Given that the molecule of **P**, $C_{15}H_{22}O$, contains a 6-membered ring, suggest a possible structure of **P**.

[1]







any one possible structure

(c) Similar to propanone, **Q** reacts with HCN at pH 10.

(i) Name the type of reaction occurring when **Q** reacts with HCN.

[1]

Nucleophilic addition

(ii) Suggest a reason why **Q** reacts slower than propanone under the same reaction conditions.

[1]

The $-COO^-$ group is larger than the methyl group, exerting greater steric hindrance to the approaching CN^- nucleophile.

OR

The carboxylic acid group is deprotonated under basic conditions, hence the carboxylate anion repels the negatively charged CN^- nucleophile.

(d) The pK_a values of ethanoic acid and **R**, HOOC–COOH, are found in Table 4.1.

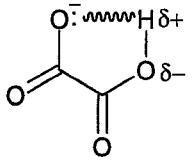
Table 4.1

	pK_{a1}	pK_{a2}
ethanoic acid	4.76	-
HOOC–COOH	1.27	4.28

(i) The pK_{a1} value of HOOC–COOH is lower than that of ethanoic acid due to an intramolecular interaction. Draw a labelled diagram to show this intramolecular interaction.

[1]

hydrogen bonding



(ii) Suggest a reason why the pK_{a2} value of HOOC–COOH is higher than its pK_{a1} value.

[1]

The removal of an H^+ from $HO_2CCO_2^-$ that already carries a negative charge would be unfavourable.

OR

The stabilisation of the mono-anion by hydrogen bonding would be destroyed when the second $–CO_2H$ group ionises. Hence pK_{a2} of HOOC–COOH is higher than its pK_{a1} value.

[Total: 10]

5 This question is about the chemistry of Group 2 elements and their compounds.

(a) The carbonates of Group 2 elements are sparingly soluble in water. The carbonates also decompose upon strong heating. Some of the properties of Group 2 carbonates are given in Table 5.1.

Table 5.1

compound	molar mass / g mol^{-1}	solubility at 25 °C / g dm^{-3}	enthalpy change of thermal decomposition / kJ mol^{-1}
magnesium carbonate	84.3	0.18	+117
calcium carbonate	100.1	0.0066	+178
strontium carbonate	147.6	0.0034	?
barium carbonate	197.3	0.014	+267

(i) Write the equation, including state symbols, for the thermal decomposition of calcium carbonate.

[1]

$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$

(ii) Describe and explain the trend of the decomposition temperatures of the Group 2 carbonates.

[3]

Decomposition temperature increases from $MgCO_3$ to $BaCO_3$
Ionic radius of metal cation increases from Mg^{2+} to Ba^{2+} / down the group
Charge density / polarising power of metal cation decreases from Mg^{2+} to Ba^{2+} / down the group

Extent of polarisation / distortion of electron cloud of CO_3^{2-} by metal cation decreases from Mg^{2+} to Ba^{2+} / down the group
Extent of weakening of covalent bonds in CO_3^{2-} decreases from Mg^{2+} to Ba^{2+} / down the group
More energy is required for the decomposition of Group 2 carbonates from $MgCO_3$ to $BaCO_3$

(iii) Hence suggest a value for the enthalpy change of thermal decomposition of strontium carbonate.

[1]

+235 (kJ mol^{-1})

(iv) Write the solubility product expression for barium carbonate, including the units.

[1]

$K_{sp} = [Ba^{2+}][CO_3^{2-}]$
$mol^2\ dm^{-6}$

(v) Using the data in Table 5.1 and your answer in **(a)(iv)**, calculate the solubility product for barium carbonate.

[2]

solubility of $BaCO_3 = 0.014 \div 197.3$
$= 7.0958 \times 10^{-5}$ mol dm^{-3}
K_{sp} of $BaCO_3 = (7.0958 \times 10^{-5})^2$
$= 5.04 \times 10^{-9}$ $mol^2\ dm^{-6}$

(b) The hydroxides of Group 2 elements are also sparingly soluble in water. The solubility of calcium hydroxide is 1.03 g dm^{-3} at 25 °C.

(i) Calculate the concentration of calcium ions, in mol dm^{-3}, in a saturated solution of calcium hydroxide at 25 °C.

[1]

Solubility of $Ca(OH)_2$
$= 1.03 \div 74.1$
$= 0.013900$
$= 0.0139$ mol dm^{-3}

$[Ca^{2+}] = 0.0139$ mol dm^{-3}

(ii) Hence, calculate the pH of a saturated solution of calcium hydroxide at 25 °C.

[2]

$[OH^-] = 2 \times 0.0139$
$= 0.0278$ mol dm^{-3}
$pOH = -lg\ 0.0278$
$= 1.5556$
$pH = 14 - 1.5556$
$= 12.4$

(c) When carbon dioxide was bubbled into a saturated solution of calcium hydroxide, a white precipitate of calcium carbonate was formed. However, upon further bubbling of carbon dioxide into the mixture, the precipitate dissolved and a colourless solution of calcium hydrogencarbonate, $Ca(HCO_3)_2$, was obtained.

(i) Write an ionic equation for the formation of hydrogencarbonate ions.

[1]

$CO_3^{2-}(aq) + CO_2(g) + H_2O(l) \rightarrow 2HCO_3^-(aq)$

(ii) Use Le Chatelier's Principle to explain why calcium carbonate dissolves when excess carbon dioxide was bubbled into the mixture.

[1]

By Le Chatelier's Principle, the decrease in $[CO_3^{2-}]$ results in the position of equilibrium of "$CaCO_3 \rightleftharpoons Ca^{2+} + CO_3^{2-}$" to shift to the right (to increase $[CO_3^{2}]$). Hence, the white precipitate dissolves.

(d) Magnesium chloride is a supplement used to increase dietary magnesium intake.

(i) Describe the reaction of magnesium chloride with water. Write an equation for the reaction and state the pH of the resultant solution.

[2]

$MgCl_2$ dissolves in water and undergoes partial hydrolysis to give a slightly acidic solution with pH 6.5.

$$[Mg(H_2O)_6]^{2+} + H_2O \rightleftharpoons [Mg(H_2O)_5(OH)]^{+} + H_3O^{+}$$

Some enthalpy changes relating to magnesium chloride are found in Table 5.2.

Table 5.2

	value / kJ mol^{-1}
lattice energy of $MgCl_2$(s)	–2540
standard enthalpy change of hydration of Mg^{2+}(g)	–1980
standard enthalpy change of hydration of Cl^-(g)	–364

(ii) Define the term *lattice energy of magnesium chloride*.

[1]

It is is the energy evolved when one mole of solid magnesium chloride is formed from its constituent gaseous ions, Mg^{2+} and Cl^-, under standard conditions.

(iii) Suggest a reason for the sign of the standard enthalpy change of hydration of Mg^{2+}(g).

[1]

Energy is released upon formation of ion–dipole interactions between Mg^{2+} ions and water molecules.

(iv) Using data from Table 5.2, calculate the standard enthalpy change of solution, $\Delta H_{sol}^{\ominus}$, of magnesium chloride.

[1]

$$\Delta H_{sol}^{\ominus}(MgCl_2) = -\text{L.E.}(MgCl_2) + \Delta H_{hyd}^{\ominus}(Mg^{2+}) + 2\Delta H_{hyd}^{\ominus}(Cl^-)$$
$$= -(-2540) + (-1980) + 2(-364)$$
$$= -168 \text{ kJ mol}^{-1}$$

(v) Given that the standard Gibbs free energy change of solution of magnesium chloride is –126 kJ mol^{-1}, use your answer in **(d)(iv)** to calculate the standard entropy change of solution, $\Delta S_{sol}^{\ominus}$, of magnesium chloride at 298 K.

[1]

$$\Delta G_{sol}^{\ominus} = \Delta H_{sol}^{\ominus} - T\Delta S_{sol}^{\ominus}$$

$$-126 = -168 - [298 \times \Delta S_{sol}^{\ominus}(MgCl_2)]$$

$\Delta S_{sol}^{\ominus}$ ($MgCl_2$) = –0.14094 kJ mol^{-1} K^{-1}

= –141 J mol^{-1} K^{-1}

(vi) Predict, with reasoning, how the spontaneity of the dissolution of magnesium chloride will change with increasing temperature.

[2]

When temperature increases, $-T\Delta S_{sol}$ becomes more positive.

Since $\Delta G_{sol} = \Delta H_{sol} - T\Delta S_{sol}$, ΔG_{sol} will become less negative / more positive with increasing temperature. Hence, the dissolution is less spontaneous at higher temperatures.

[Total: 21]

Suggested Solutions

DUNMAN HIGH SCHOOL
Preliminary Examination
Year 6

H2 CHEMISTRY

9729/03

Paper 3 Free Response Questions

25 September 2025
2 hours

Candidates answer on the Question Paper.
Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your centre number, index number, name and class at the top of this page.
Write in dark blue or black pen.
You may use an HB pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper. If additional space is required, you should use the pages at the end of this booklet. The question number must be clearly shown.

Section A
Answer **all** questions.

Section B
Answer **one** question.

A Data Booklet is provided.
The use of an approved scientific calculator is expected, where appropriate.

The number of marks is given in brackets [ ] at the end of each question or part question.

For Examiner's Use	
Section A	
1	20
2	20
3	20
Section B	
4 / 5	20
Total	80

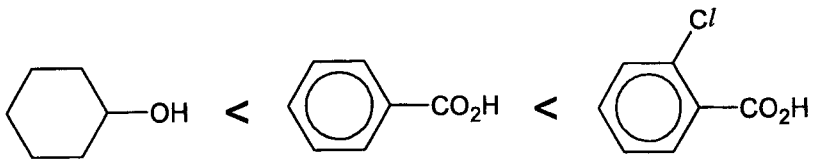
This document consists of **22** printed pages.

[Turn over

Section A

Answer **all** the questions in this section.

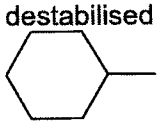
1 (a) The order of increasing Brønsted-Lowry acidity of cyclohexanol, benzoic acid and 2–chlorobenzoic acid is shown. Explain this order.



cyclohexanol benzoic acid 2-chlorobenzoic acid

[3]

Cyclohexanol is the least acidic because its conjugate base, is destabilised by the electron-donating effect of the cyclohexyl/alkyl group,



which intensifies the negative charge on the oxygen in the conjugate base.

Both 2-chlorobenzoic acid and benzoic acid are more acidic than cyclohexanol because their conjugate bases are resonance-stabilised by the delocalisation of negative charge over two highly electronegative oxygen atoms.

In 2-chlorobenzoic acid, presence of electron withdrawing *Cl* atom helps to disperse the negative charge, making its conjugate base (2-chlorobenzoate ion) more stable than benzoate.

Hence, 2-chlorobenzoic dissociates to the largest extent and cyclohexanol to the least extent.

(b) BF_3 acts as a Lewis acid in its reaction with dimethylether, CH_3OCH_3, to form product **P**.

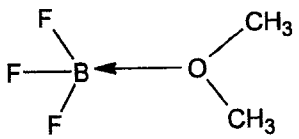
(i) Describe how BF_3 acts as a Lewis acid in this reaction.

[1]

The electron deficient B atom in BF_3 accepts the (lone) electron pair from O in CH_3OCH_3.

(ii) Draw a structure for **P** to show the bonding present.

[1]



(c) Dimethylether, CH_3OCH_3, can be formed from the reaction between carbon monoxide, CO, and hydrogen, H_2, as shown by equation 1.

equation 1 $3CO(g) + 3H_2(g) \rightleftharpoons CH_3OCH_3(g) + CO_2(g)$

A mixture of CO and H_2 was introduced into a 10 m^3 sealed vessel at 500 K. The initial total pressure was 40 atm.

After dynamic equilibrium was established at 500 K, the total pressure in the vessel decreased to 28 atm.

(i) Write an expression for the equilibrium constant, K_p, for this reaction, and state its units.

[1]

$K_p = \dfrac{P_{CH_3OCH_3} P_{CO_2}}{(P_{CO})^3 (P_{H_2})^3}$ units: atm^{-4} OR Pa^{-4}

(ii) *Use of the Data Booklet is relevant to this question.*

The amount of CH_3OCH_3 at equilibrium was found to be 732 mol. Show that the equilibrium partial pressure of CH_3OCH_3 in the sealed vessel is 3 atm.

[1]

$pV = nRT$
$p = nRT/V$

partial pressure of CH_3OCH_3 at equilibrium $= \dfrac{732 \times 8.31 \times 500}{10} = 304146$ Pa

$= \dfrac{304146}{101325} = 3.0017$ atm

$= 3$ atm (shown)

OR

n = pV/RT

total moles of gases at equilibrium $= \dfrac{28 \times 101325 \times 10}{8.31 \times 500} = 6828.2$ mol

partial pressure of CH_3OCH_3 at equilibrium $= \dfrac{732}{6828.2} \times 28 = 3.0017$ atm

$= 3$ atm (shown)

(iii) At equilibrium, it was found that 60% of the CO had been converted to the products. Calculate the equilibrium partial pressures of CO and H_2 in atm. Hence, determine the value of K_p for the reaction.

[3]

Let the initial partial pressure of CO be x.

	$3CO(g)$	$+ 3H_2(g)$	$\rightleftharpoons$	$CH_3OCH_3(g)$	$CO_2(g)$
initial / atm	x	40 – x		0	0
change / atm	–0.6x	–0.6x		+3	+3
equilibrium/ atm	0.4 x	40 – 1.6x		3	3

$3CO(g) \equiv 1CH_3OCH_3(g)$
Change in partial pressure of CO = (3)(3) = 9 atm
$\therefore$ 0.6x = 9 atm
x = 15 atm

Equilibrium partial pressure of CO = 0.4x
= 0.4 (15)

= 6.0 atm

OR

$(0.4\ x) + (40 - 1.6x) + 3 + 3 = 28$
$x = 15$ atm

Equilibrium partial pressure of H_2 = 28 – 6 – 3 – 3
= 16.0 atm

$$K_p = \frac{P_{CH_3OCH_3} P_{CO_2}}{(P_{CO})^3 (P_{H_2})^3}$$

$$= \frac{(3)(3)}{(6)^3(16)^3}$$

$$= 1.02 \times 10^{-5}\ atm^{-4}$$

(iv) The volume of the vessel is reduced from 10 m^3 to 5 m^3 and the system is allowed to reach equilibrium.

Explain the effect this will have on the partial pressures of the individual gases and the composition of the reaction mixture.

[2]

A reduction in volume causes partial pressures of all gas components at equilibrium to double, position of equilibrium shifts to the right, favouring the side with fewer moles of gaseous particles, to reduce the pressure. At new equilibrium, the mixture contains more moles of products, CH_3OCH_3 and CO_2 and less moles of the reactants, CO and H_2 than that before the reduction in volume.

(d) NH_3 is commonly used as a nucleophile in organic chemistry. In some instances, it adds to the C=C bond as shown in Fig. 1.1.

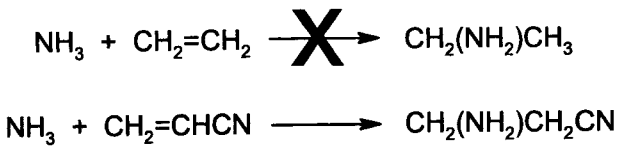


Fig. 1.1

(i) Suggest reasons to explain Fig. 1.1.

Use concepts of electronegativity and electronic effects in your answer.

[2]

Ethene is non-polar.
There are no electron deficient sites in ethene to attract the NH_3 nucleophile OR NH_3 is a nucleophile and is repelled by the electron-rich C=C bond in ethene.

Due to presence of electronegative N / electron-withdrawing -CN group, electron density is withdrawn away from the C=C bond. This causes the carbon of the terminal alkene to be electron deficient, hence susceptible to nucleophilic attack by NH_3.

Ammonia or primary amines react with aldehydes and ketones to produce imines as shown in Fig. 1.2.

The reaction is carried out at carefully controlled pH of between 4 and 5.
In Fig. 1.2, R_1, R_2 and R_3 represent alkyl groups or hydrogen atoms.

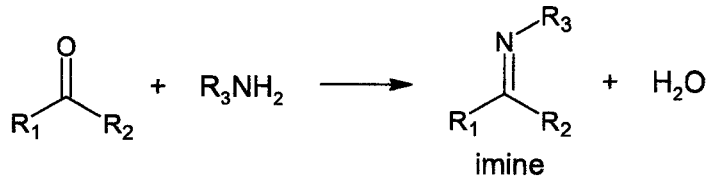
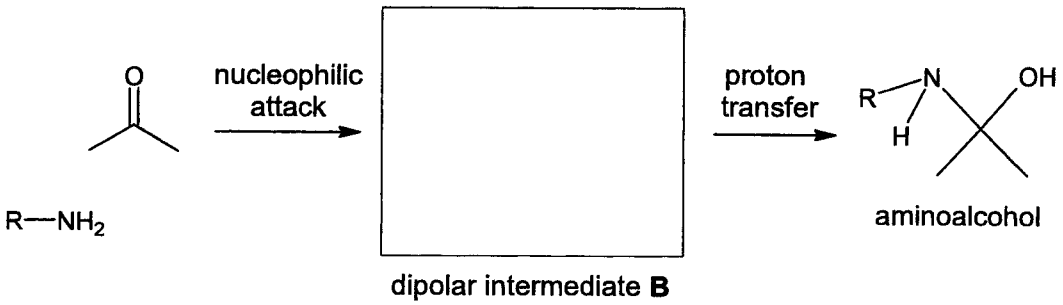


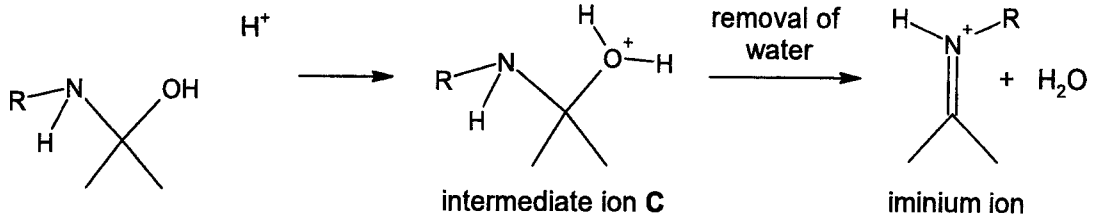
Fig. 1.2

The mechanism for the formation of an imine between a primary amine and propanone is shown in Fig. 1.3.

Stage 1: Formation of aminoalcohol



Stage 2: Formation of iminium ion intermediate



Stage 3: Formation of imine via deprotonation

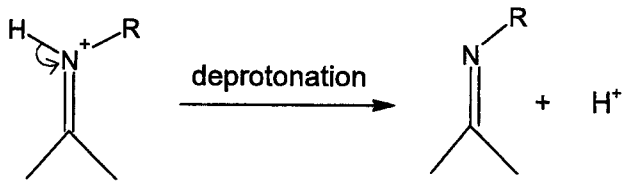
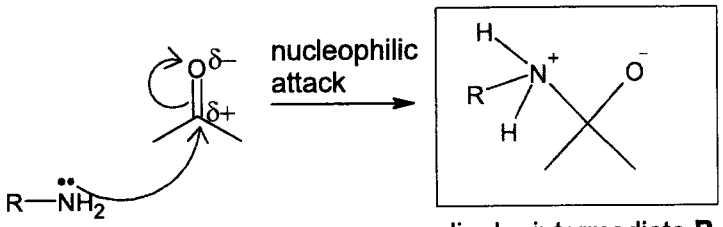


Fig. 1.3

(ii) Complete the mechanism for the formation of **B** in Fig. 1.3 by

- adding curly arrows, a lone pair and a dipole to show how the nucleophilic attack occurs between the primary amine and propanone.
- drawing the structure of the dipolar intermediate **B** in the box provided.

[2]

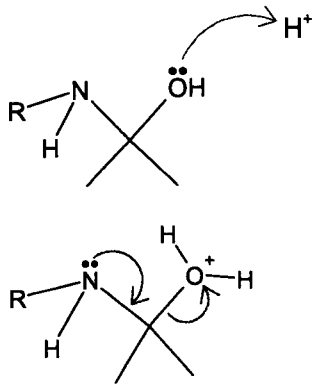


dipolar intermediate **B**

(iii) Complete the mechanism for stage 2 in Fig. 1.3 by

- adding a curly arrow and a lone pair to show protonation of the aminoalcohol.
- adding a lone pair and curly arrows on intermediate ion **C** to show how the iminium ion is formed.

[2]



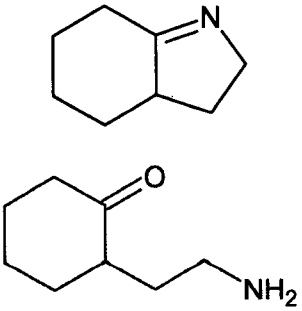
intermediate ion **C**

(iv) By considering stage 1, suggest why the reaction is slower at pH lower than 4.

[1]

At pH < 4, the primary amine is protonated and does not have a lone pair of electrons available for nucleophilic addition. This leads to a slower rate of reaction as there is lower concentration of amine available.

(v) Suggest the reactant used to form the following product by a similar reaction to that shown in Fig. 1.2.



[1]

[Total: 20]

2 (a) Phenylamine can be made in the laboratory using the method given below.

Nitrobenzene is heated under reflux with a mixture of tin and concentrated hydrochloric acid.

Once the reaction mixture has cooled, concentrated sodium hydroxide solution is added until the mixture is alkaline. Pure phenylamine can be obtained from this mixture.

The reaction between tin and concentrated hydrochloric acid produces $SnCl_2$ and H_2 gas. Nitrobenzene then reacts with $SnCl_2$, in the presence of concentrated hydrochloric, to form $C_6H_5NH_3^+$ and $[SnCl_6]^{2-}$ ions.

(i) Describe the roles of tin and concentrated hydrochloric acid when they are added together to form $SnCl_2$ and H_2 gas. Explain your answer in terms of electron transfer.

[2]

Tin acts as a reducing agent while concentrated hydrochloric acid as an oxidising agent in the reaction.

Electrons are lost from tin and gained by concentrated hydrochloric acid.

(ii) Construct a half–equation for the formation of $C_6H_5NH_3^+$ from nitrobenzene. State symbols are **not** required.

[1]

$C_6H_5NO_2 + 7H^+ + 6e^- \rightarrow C_6H_5NH_3^+ + 2H_2O$

(iii) Using the relevant theory of acids and bases, explain how the phenylamine can be recovered from the mixture by adding concentrated sodium hydroxide solution.

[1]

$C_6H_5NH_3^+$ loses a proton to OH^- to obtain $C_6H_5NH_2$ via a Brønsted-Lowry acid-base reaction.

OR

OH^- gains a proton from $C_6H_5NH_3^+$ to obtain $C_6H_5NH_2$ via a Brønsted-Lowry acid-base reaction.

(iv) Describe a simple chemical test you could carry out to confirm the presence of phenylamine in the product. State what you would observe.

[2]

Add $Br_2(aq)$ to the mixture.
The presence of phenylamine will result in the decolourisation of orange $Br_2(aq)$ and the formation of a white precipitate.

(b) (i) Table 2.1 gives the pK_b values of some nitrogen-containing compounds at 25 °C.

Table 2.1

name	structure	pK_b
phenylamine	$C_6H_5NH_2$	9.40

phenylalanine	$C_6H_5CH_2CH(NH_2)CO_2H$	4.87 (α-amino group)
propylamine	$CH_3CH_2CH_2NH_2$	3.46

Explain the relative basicities of the compounds in Table 2.1 in terms of their structures.

[3]

$C_6H_5NH_2$ is the least basic as the lone pair of electrons on N delocalises into the benzene ring and is the least available for donation / dative bonding with a proton.

The α-amino group in phenylalanine is less basic than propylamine as the electron-withdrawing $-CO_2H$ group / electron-withdrawing oxygen atoms decreases the electron density on the N atom, making the lone pair of electrons on N less available for donation / dative bonding with a proton.

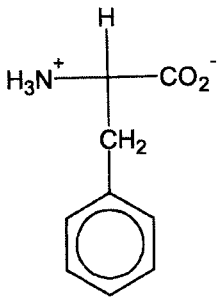
Propylamine is more basic than the α-amino group in phenylalanine as the electron-donating alkyl / propyl group increases the electron density on the N atom, making the lone pair of electrons on N more available for donation / dative bonding with a proton.

(ii) Use Table 2.2 to draw the predominant species of phenylalanine at pH 8.

Table 2.2

name	structure	pK_a at 25 °C	
		α-carboxyl group	α-amino group
phenylalanine	$C_6H_5CH_2CH(NH_2)CO_2H$	1.83	9.13

[1]



(c) Arecoline, $C_8H_{13}NO_2$, is a compound found in the Taiwanese betel nut.

Arecoline has three different functional groups, does not display cis-trans isomerism and does not contain a chiral centre. It contains a six-membered ring comprising one nitrogen and five carbon atoms.

Table 2.3 shows the organic products formed, and other information, when arecoline and compound **F**, $C_8H_{15}NO_2$, are added to different reagents under specific conditions.

Table 2.3

test	reactant	reagents and conditions	organic products formed	other information
1	arecoline	excess H_2 / Ni	**F**, $C_8H_{15}NO_2$	**F** contains one chiral centre.
2	arecoline	2,4-DNPH	no reaction	[redacted]
3	arecoline	Na_2CO_3(aq)	no reaction	
4	arecoline	ethanoyl chloride	no reaction	
5	arecoline	excess CH_3Cl in ethanol, heat	**G**, $C_9H_{16}NO_2Cl$	**G** is an ionic compound.
6	**F**	excess HCl(aq), heat	**H**, $C_7H_{14}NO_2^+$, and **J**	[redacted]
7	**F**	excess acidified $KMnO_4$, heat	**H** only	effervescence observed.

For each of the seven tests, state the type of reaction occurring, if any. For each compound, state what the information in Table 2.3 tells you about the functional groups it contains. Include your reasoning.

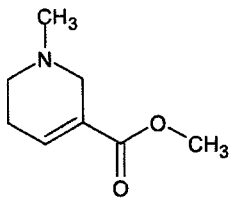
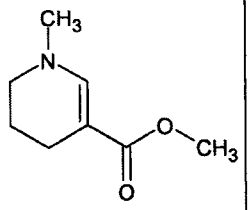
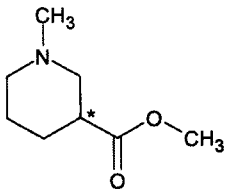
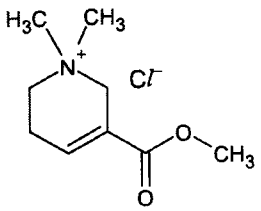
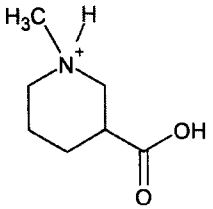
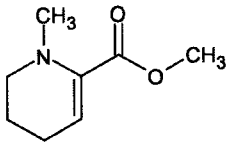
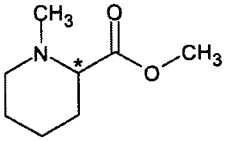
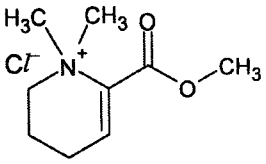
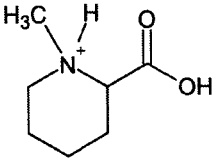
Suggest possible structures for **F**, **G**, **H** and **J**. Hence deduce a possible structure for arecoline.

[10]

test	type of reaction	functional group
1	reduction	arecoline contains alkene / C=C bond or ketone or aldehyde
2	no reaction	ketone and aldehyde are absent
3	no reaction	carboxylic acid is absent
4	no reaction	alcohol, primary and secondary amine are absent
5	nucleophilic substitution	**G**, $C_9H_{16}NO_2Cl$, is a quaternary ammonium salt while arecoline contains a tertiary amine

6	acid hydrolysis	**F**, $C_8H_{15}NO_2$, contains an ester **H**, $C_7H_{14}NO_2^+$, contains the carboxylic acid and protonated amine / quaternary ammonium group **J** contains an alcohol group
7	acid hydrolysis and oxidation	**J** contains a primary alcohol group

J = CH_3OH / methanol

arecoline	**F**, $C_8H_{15}NO_2$	**G**, $C_9H_{16}NO_2Cl$	**H**, $C_7H_{14}NO_2^+$
 OR 			
			

[Total: 20]

3 **(a)** Aqua regia (a mixture of 25% nitric acid and 75% hydrochloric acid by volume) is highly corrosive. Only noble metals like iridium are inert to this solution. A 5 g sample of platinum–iridium alloy required 24.6 cm^3 of aqua regia for complete reaction. Platinum was completely oxidised to platinum(IV) ions by nitric acid and 0.5 g of the remaining metal was recovered.

(i) Find the percentage of each metal in the alloy.

[1]

Only Pt was oxidised during the reaction, Ir remains inert.

∴ 0.5 g of metal was recovered, the metal was Ir
percentage by mass of Ir in sample
$= \frac{0.5}{5} \times 100$
= 10%
Percentage by mass of Pt in sample
= (100 – 10)%
= 90%

(ii) Aqua regia was prepared using 5.0 mol dm^{-3} nitric acid. Assuming that the reaction between the sample and aqua regia is complete, calculate the number of moles of nitric acid reacted per mole of platinum.

[2]

volume of HNO_3 used
= 0.25 × 24.6
= 6.15 cm^3

amount of HNO_3 reacted
= 0.00615 × 5
= 0.03075 mol

amount of Pt reacted
$= \frac{4.5}{195.1}$
= 0.02306 mol

∴ mole ratio of HNO_3 : Pt = 1.33 : 1

(b) Gold is typically an inert metal and it does not dissolve in either hydrochloric acid or nitric acid alone. It will dissolve in aqua regia because of the unique combined action of the two acids.

In aqua regia, nitric acid converts gold to its ionic form, Au^{3+}, and hydrochloric acid provides a source of chloride which reacts with the gold cations to form stable tetrachloroaurate(III) complex, $AuCl_4^-$.

The standard reduction potential of Au^{3+} to Au is given below.

$$Au^{3+} + 3e^- \rightleftharpoons Au \qquad E^\ominus = +1.50\ V$$

(i) With the use of relevant data from the *Data Booklet*, explain why hydrochloric acid alone cannot dissolve gold.

[1]

$2Au + 6H^+ \rightarrow 3H_2 + 2Au^{3+}$
$E_{cell}^\ominus = 0.00 - (+1.50)$
$= -1.50\ V < 0$, hence reaction is not spontaneous.

(ii) Gold has the chemical properties of a typical transition element.
Explain why gold can be considered a transition element.

[1]

Gold is a d-block element that forms one or more stable ions with a partially filled d subshell.

(iii) Another method of extracting gold from low–grade ore involves converting the gold to a water–soluble dicyanoaurate(I) anionic complex, $[Au(CN)_2]^-$.

Explain why the gold complex ion, $AuCl_4^-$ in **(b)**, is coloured while the dicyanoaurate(I) complex ion, $[Au(CN)_2]^-$, is colourless.

[4]

$AuCl_4^-$: d^8 configuration for Au^{3+}
In the presence of Cl^- ligands, the d orbitals of Au^{3+} are split into two groups of different energy levels.

When white light shines on the complex, a d electron from lower energy level undergoes d–d electronic transition and is promoted to a higher energy vacant or partially filled d orbital. The colour of the solution is the complementary colour of the light absorbed.

$Au(CN)_2^-$: d^{10} configuration for Au^+ / fully filled d subshell and hence no d–d electronic transition is possible.

(c) Freshly prepared aqua regia decomposes quickly and one of the decomposition products, nitrosyl chloride, NOCl, is a yellow gas.

Nitrosyl chloride can further decompose into nitrogen, chlorine and oxygen, as shown in the equation below.

$$2NOCl(g) \rightarrow N_2(g) + Cl_2(g) + O_2(g) \qquad \Delta H = +258 \text{ kJ mol}^{-1}$$

(i) Define the term *bond energy of N=O bond.*

[1]

Energy required to break 1 mol of gaseous N=O bond to form its gaseous N and O atoms.

(ii) Using data from the *Data Booklet*, calculate the bond energy of N=O bond in NOCl.

[2]

Enthalpy change of decomposition = $\sum BE_{rxt} - \sum BE_{pdt}$
$+258 = [2BE(N=O) + 2BE(N–Cl)] – [BE(N\equiv N) + BE(Cl–Cl) + BE(O=O)]$
$+258 = [2BE(N=O) + 2(+310)] – [(+944) + (+244) + (+496)]$
$BE(N=O) = +661 \text{ kJ mol}^{-1}$

(iii) The boiling points of NOCl and NOF are –5.6 °C and –72.4 °C respectively. Suggest a reason for the difference in their boiling points.

[2]

Both NOCl and NOF have simple molecular structure with permanent dipole–permanent dipole interactions between molecules. NOCl has a larger and hence more polarisable electron cloud than NOF. Hence more energy is required to overcome the stronger instantaneous dipole–induced dipole interaction between NOCl molecules.

(iv) Copper(II) oxide, CuO, is a common catalyst used for the decomposition of NOCl. Suggest the type of catalyst CuO acts as and describe its mode of action.

[3]

Heterogeneous catalyst. Reactant molecules diffuse towards the catalyst surface and are adsorbed onto the active sites at the surface. Intramolecular bonds within the reactant molecules are weakened, thus lowering the activation energy. The adsorption process increases the concentration of the reactant molecules on the catalyst surface. Product molecule desorbs and diffuses away from the catalyst surface.

(d) *Use of the Data Booklet is relevant to this question.*

A student wanted to study the following reaction.

$$2Au^{3+} + 3Ni \longrightarrow 2Au + 3Ni^{2+}$$

He first sets up an electrochemical cell which comprises of Au^{3+}/Au and Ni^{2+}/Ni half–cells prepared under standard conditions.

When the reaction begins, $[Au^{3+}]$ starts to decrease while $[Ni^{2+}]$ increases. In the study of electrochemical cells, the *Nernst equation*, given below, can be applied to determine the cell potential under non–standard conditions.

$$E_{cell} = E^{\ominus}_{cell} - \frac{0.0592}{n} \log_{10} Q$$

where n is the number of moles of electrons transferred, Q is the reaction quotient given by $\frac{[Ni^{2+}]^3}{[Au^{3+}]^2}$ and $E^{\ominus}_{cell}$ is the standard cell potential.

(i) Using the $E^{\ominus}(Au^{3+}/Au)$ given in **(b)**, calculate the new E_{cell} using the Nernst equation, when $[Au^{3+}]$ and $[Ni^{2+}]$ are 0.02 mol dm^{-3} and 2.47 mol dm^{-3} respectively.

[2]

$E^{\ominus}_{cell} = +1.50 - (-0.25) = +1.75$ V

$$E_{cell} = +1.75 - \frac{0.0592}{6} \log_{10} \frac{(2.47)^3}{(0.02)^2} = +1.70 \text{ V}$$

(ii) Suggest and explain what happens to E_{cell} value of the electrochemical cell when the mass of nickel electrode is increased.

[1]

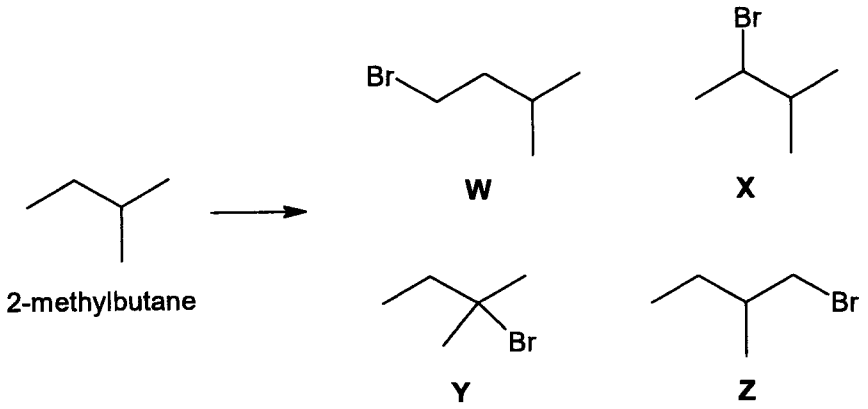
There is no change to the E_{cell} value as the increase in mass of Ni electrode will not affect the equilibrium position of $Ni^{2+} + 2e^- \rightleftharpoons Ni$

[Total: 20]

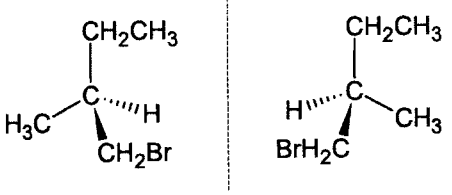
Section B

Answer **one** question from this section.

4 2-methylbutane reacts with bromine in the presence of UV light to give a mixture of products. There are four possible monobromoalkanes, **W** to **Z**, that can be formed.



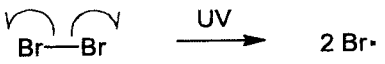
(a) **(i)** Draw both stereoisomers of **Z**. [1]



(ii) Name and draw the mechanism for the formation of **W** from 2-methylbutane using curly arrows. [3]

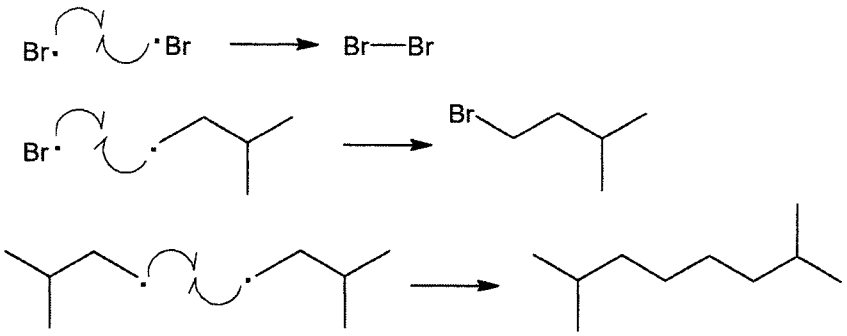
Name of mechanism: Free radical substitution

Initiation



Propagation

Termination



Empirical evidence has shown that different types of carbons have a different relative probability of being substituted by bromine. These probabilities can be found in Table 4.1.

Table 4.1

type of carbon	relative probability of substitution
primary	1
secondary	62
tertiary	1640

(iii) By considering the number of H atoms on each carbon, and information in Table 4.1, predict the relative proportions of **W**, **X**, **Y** and **Z** in the product mixture.

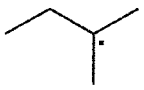
[1]

W:**X**:**Y**:**Z** = 3 : (2 × 62) : 1640 : 6 = 3 : 124 : 1640 : 6

The reaction of 2-methylbutane and bromine gas also forms a mixture of side-products with a molecular formula of $C_{10}H_{22}$.

(iv) Use Table 4.1 to deduce the identity of the most stable alkyl radical present in the reaction mixture. Draw its structure using skeletal formula.

[1]



(v) Hence name the $C_{10}H_{22}$ product that is formed in the highest proportion.

[1]

3,3,4,4-tetramethylhexane

(b) Fig. 4.1 shows a 2-step synthesis to obtain 2-methylbutan-2-ol from **X**.

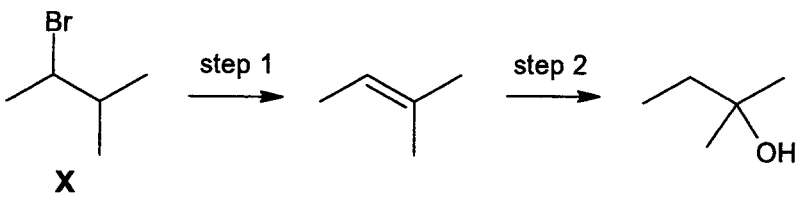


Fig. 4.1

(i) State the reagents and conditions required for each step.

[2]

step 1: alcoholic NaOH, heat

step 2: cold, concentrated H_2SO_4, followed by H_2O and heat
OR
$H_2O(g)$, heat in presence of concentrated H_3PO_4 catalyst at high temperature and pressure

Each step in the synthesis forms a mixture of products as there is more than one possible region for each reaction to occur. The term *regioselectivity* refers to the preference for a chemical reaction to occur at a specific region of a molecule to give the major product.

(ii) Explain if each step in Fig. 4.1 is regioselective for the intended product. Your answer should refer to the relative stability of relevant products or intermediates.

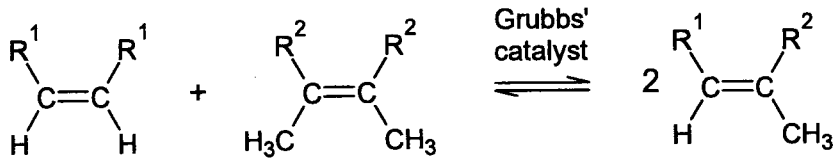
Hence conclude if the synthesis will give a good yield of 2-methylbutan-2-ol. [2]

For step 1, the tri-substituted alkene is the major product as it is lower in energy / more stable than the di-substituted alkene.
OR the more substituted alkene is more stable and hence it is the major product of step 1.

For step 2, the tertiary carbocation leading to 2-methylbutan-2-ol is more stable than the secondary carbocation leading to 3-methylbutan-2-ol as the positive charge is dispersed to a greater extent by more electron-donating alkyl groups. Hence 2-methylbutan-2-ol is the major product.

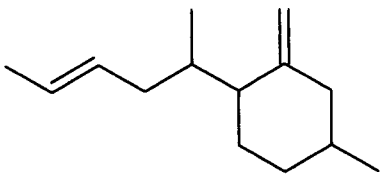
The two-step synthesis is likely to give a good yield of 2-methylbutan-2-ol as each step is regioselective for the intended product.

(c) Alkene metathesis allows the redistribution of alkene fragments.



The reaction only involves the breaking and forming of C=C bonds.

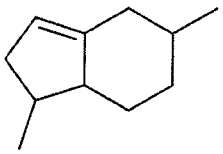
Compound **T** is shown. When compound **T** undergoes alkene metathesis, an intramolecular reaction occurs to form a small hydrocarbon and a product containing two rings.



T

Predict the small hydrocarbon and the product formed in this reaction. [2]

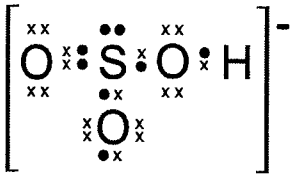
Propene, $CH_3CH=CH_2$



(d) Sodium bisulfite, $NaHSO_3$, is commonly used as a food preservative.

(i) Given that the bisulfite ion contains a O–H covalent bond, draw a dot-and-cross diagram to show the bonding in a bisulfite ion, HSO_3^-.

[1]



(ii) Hence state the shape and bond angle around the sulfur atom within the bisulfite ion. Explain your answer using the Valence Shell Electron Pair Repulsion Theory.

[2]

There are 3 bond pairs and 1 lone pair around the central S atom. According to VSEPR theory, the 4 electron pairs are arranged as far apart as possible around the central S atom to minimise repulsion. Since bond pair-bond pair repulsion is weaker than bond pair-lone pair repulsion, the ion has a trigonal pyramidal shape around the central S atom and a bond angle of 107°.

The bisulfite ion is a weak acid with a pK_a value of 6.97.

$$HSO_3^- \rightleftharpoons SO_3^{2-} + H^+$$

An aqueous mixture containing bisulfite ions, $HSO_3^-(aq)$, and sulfite ions, $SO_3^{2-}(aq)$, can act as a buffer.

(iii) Write two equations to describe how a HSO_3^-/SO_3^{2-} mixture resists pH change when a small amount of acid or base is added.

[1]

$HSO_3^- + OH^- \rightarrow SO_3^{2-} + H_2O$
$SO_3^{2-} + H^+ \rightarrow HSO_3^-$

A buffer with pH 7.5 was prepared by mixing 30.0 cm^3 of 0.500 mol dm^{-3} sodium bisulfite with 20.0 cm^3 of aqueous sodium hydroxide.

(iv) Calculate the $[SO_3^{2-}]:[HSO_3^-]$ ratio of the buffer.

[1]

$$pH = pK_a + \lg \frac{[A^-]}{[HA]}$$

$$7.5 = 6.97 + \lg \frac{[SO_3^{2-}]}{[HSO_3^-]}$$

$$\frac{[SO_3^{2-}]}{[HSO_3^-]} = 10^{0.53}$$

$$= 3.39$$

(v) Hence calculate the concentration of sodium hydroxide used in the preparation of the buffer.

[2]

Let the concentration of the sodium hydroxide be x mol dm^{-3}.

	HSO_3^- + OH^-		→	SO_3^{2-} + $H_2O(l)$	
Initial / mol	0.015	$0.02x$		0	
Change / mol	$-0.02x$	$-0.02x$		$+0.02x$	
End / mol	$0.015 - 0.02x$	0		$0.02x$	

$$\frac{0.02x}{0.015 - 0.02x} = 3.388$$

$3.388(0.015 - 0.02x) = 0.02x$

$3.388 \times 0.015 = (0.02x)(1 + 3.388)$

$0.08776x = 0.05082$

$[OH^-] = 0.579$ mol dm^{-3}

[Total: 20]

5 (a) (i) Explain the difference in pH in Table 5.1.

Table 5.1

compound	pH of a 1.0 mol dm^{-3} solution in water
NaCl	7.0
$AlCl_3$	3.0

[2]

Al^{3+} has a high charge density and polarises (or weakens the O—H bonds in) the surrounding water molecules to a large extent. Hence appreciable hydrolysis occurs to release H^+ ions and pH is 3.0.

Na^+ has a relatively low charge density and does not hydrolyse in water. Hence, no H^+ ions are released and pH is 7.0.

(ii) With the aid of relevant equation(s), describe what happens when Na_2O, SiO_2 and P_4O_{10} are separately added to water.

[3]

Na_2O reacts vigorously with water to form a basic solution.
$Na_2O(s) + H_2O(l) \rightarrow 2NaOH(aq)$

SiO_2 does not dissolves in water due to the strong and extensive covalent bonds between Si and O atoms.

P_4O_{10} reacts readily with water to form an acidic solution.
$P_4O_{10}(s) + 6H_2O(l) \rightarrow 4H_3PO_4(aq)$

(b) Strontium metal can be obtained by the electrolysis of molten strontium chloride, $SrCl_2$, using the apparatus shown in Fig. 5.1.

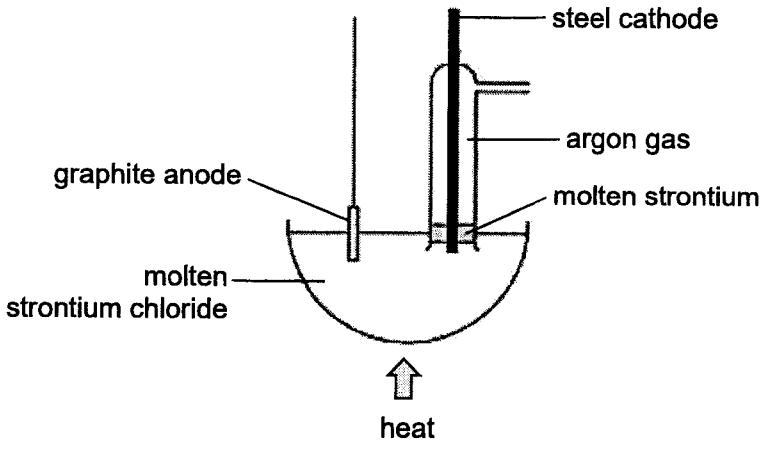


Fig. 5.1

Strontium ions are reduced at the cathode to form molten strontium metal, which is then removed from the set up.

(i) Write the half–equations, including state symbols, for the reactions at the anode and cathode.

[2]

Anode: $2Cl^-(l) \rightarrow Cl_2(g) + 2e^-$
Cathode: $Sr^{2+}(l) + 2e^- \rightarrow Sr(l)$

(ii) A current of 5.0 A was passed through molten strontium chloride for 45 min.

Calculate the mass of strontium metal formed at the cathode.

[2]

quantity of charge passed = $5.0 \times 45 \times 60$
= 13500 C

amount of electrons = $\frac{13500}{96500}$ = 0.13990 mol

amount of Sr formed = 0.13990 ÷ 2 = 0.06995 mol

mass of Sr formed = 0.06995×87.6
= 6.13 g

(c) Cyclohexylamine can be produced from benzene in a three–step synthesis as shown in Fig. 5.2.

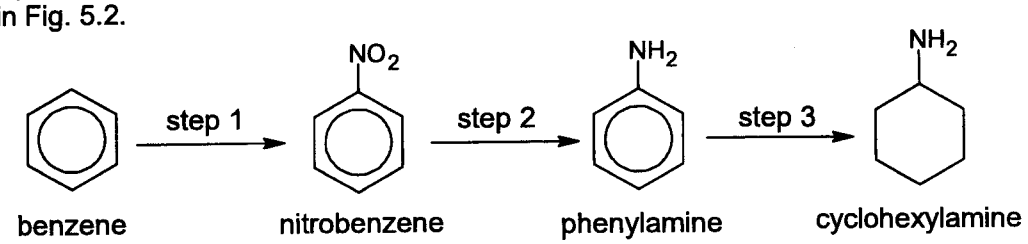


Fig. 5.2

(i) Name and draw the mechanism for step 1. Include all relevant lone pairs, curly arrows and charges. Include the structure of the organic intermediate.

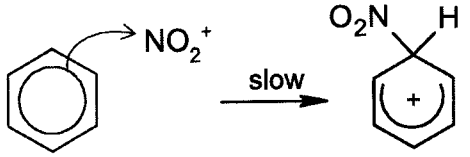
[3]

Electrophilic substitution

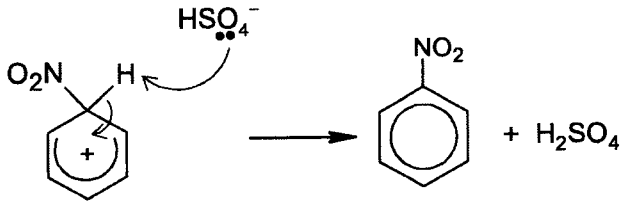
Generation of the electrophile, NO_2^+:

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

Step 1:



Step 2:



In step 3, phenylamine is converted to cyclohexylamine using hydrogen gas dissolved in supercritical carbon dioxide in the presence of rhodium catalyst supported on alumina. This was carried out at high temperature and pressure.

(ii) By considering the structure of phenylamine, suggest why its conversion to cyclohexylamine requires the use of a catalyst.

[1]

The reaction has a very high activation energy as phenylamine is resonance–stabilised / has delocalised π electrons in the ring.

(d) Glycine, $H_2NCH_2CO_2H$, is a naturally occurring α–amino acid.

It can be synthesised using bromomethane as shown in Fig. 5.3.

$$CH_3Br \xrightarrow{\text{step 1}} CH_3CN \xrightarrow{\text{step 2}} ClCH_2CN \xrightarrow{\text{step 3}} \underset{\textbf{A}}{\text{intermediate}} \xrightarrow{\text{step 4}} H_2NCH_2CO_2H$$

Fig. 5.3

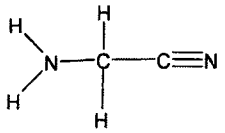
(i) State the reagents and conditions required for step 1.

[1]

KCN in ethanol, heat (under reflux)

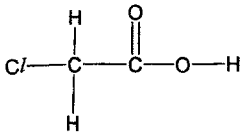
(ii) Draw the **displayed** structural formula of intermediate **A** and state the reagents and conditions required for step 3.

[2]



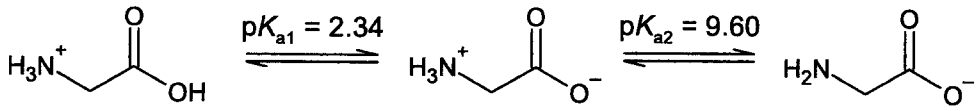
excess NH_3 (in ethanol), heat in a sealed tube

OR



dilute H_2SO_4, heat

(e) Protonated glycine acts as a dibasic weak acid.



A student adds small portions of 0.125 mol dm^{-3} NaOH(aq) to 25.0 cm^3 of 0.100 mol dm^{-3} protonated glycine. The student uses a pH meter to measure the pH of the mixture.

(i) Calculate the pH of 0.100 mol dm^{-3} protonated glycine. You may ignore the effect of pK_{a2} on the pH.

[1]

$[H^+] = \sqrt{10^{-2.34} \times 0.100} = 0.021380$ mol dm^{-3}

$pH = -\log_{10}(0.021380) = 1.67$

(ii) Calculate the volume of NaOH required to reach the first equivalence point.

[1]

amount of protonated glycine = $\frac{25.0}{1000} \times 0.100 = 0.00250$ mol

amount of NaOH required for 1st equivalence point = 0.00250 mol

volume of NaOH required = 0.00250 ÷ 0.125 = 0.0200 dm^3 (= 20.0 cm^3)

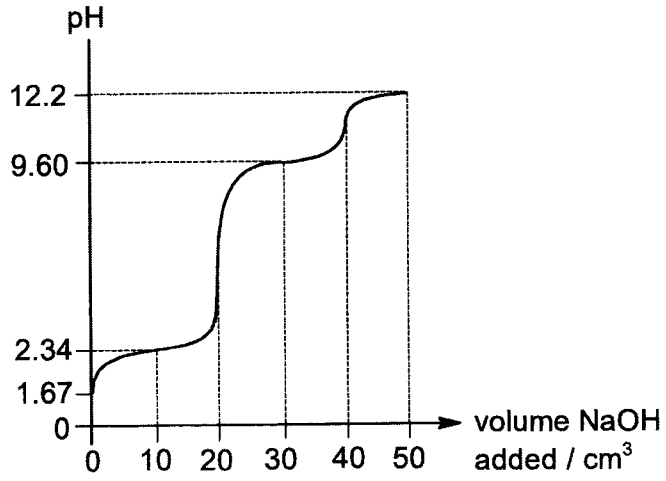
(iii) Sketch the pH-volume added curve you would expect to obtain when a total of 50 cm^3 of 0.125 mol dm^{-3} NaOH(aq) is added.

Label the following points on the curve.

- initial pH
- volume required for each equivalence point
- pH and volume at each point of maximum buffering capacity

You may assume that the pH of the solution is 12.2 upon addition of 50 cm^3 of NaOH.

[2]



[Total: 20]