1 (a) $H^+(aq) + OH^-(aq) \longrightarrow H_2O(l)$ [1]

Comments:
Students should not give the molecular equation. Many students forgot to include state symbols in their equations.

(b) Justification for the volume of HNO_3 required [1]

Assuming 20.00 cm^3 of $Ba(OH)_2$ was used for the reaction,

No of moles of $Ba(OH)_2$ used = $\frac{20.00}{1000} \times 1.00$ = 0.0200 mol

No of moles of HNO_3 required = 0.0200 x 2 = 0.0400 (2 $HNO_3 \equiv$ 1 $Ba(OH)_2$)

Minimum volume of HNO_3 required for complete neutralisation = $\frac{0.0400}{1.50} \times 1000$
= 26.7 cm^3

The maximum temperature change should occur when equal number of moles of hydroxide and acid reacts.
Hence, there should be at least 3 convenient volumes that are less than 26.7 cm^3, and at least 3 convenient volumes that are more than 26.7 cm^3, so as to obtain 3 points each to plot for the 2 straight line graphs.

(accept other suitable volumes of $Ba(OH)_2$ used, e.g. 10.00 cm^3)

volume of $Ba(OH)_2$ used = 20.00 cm^3

[1]

initial burette reading / cm^3	final burette reading / cm^3	volume of HNO_3 added / cm^3	initial temperature / ^oC	highest temperature of mixture / ^oC
0.00		8.00	**a**	**b**
		16.00	–	
		24.00	–	
		32.00	–	
		40.00	–	
		48.00	–	

[1]: appropriate volumes of HNO_3 added. (Accept 3 convenient volumes before/after 26 cm^3.)

Procedure [3]

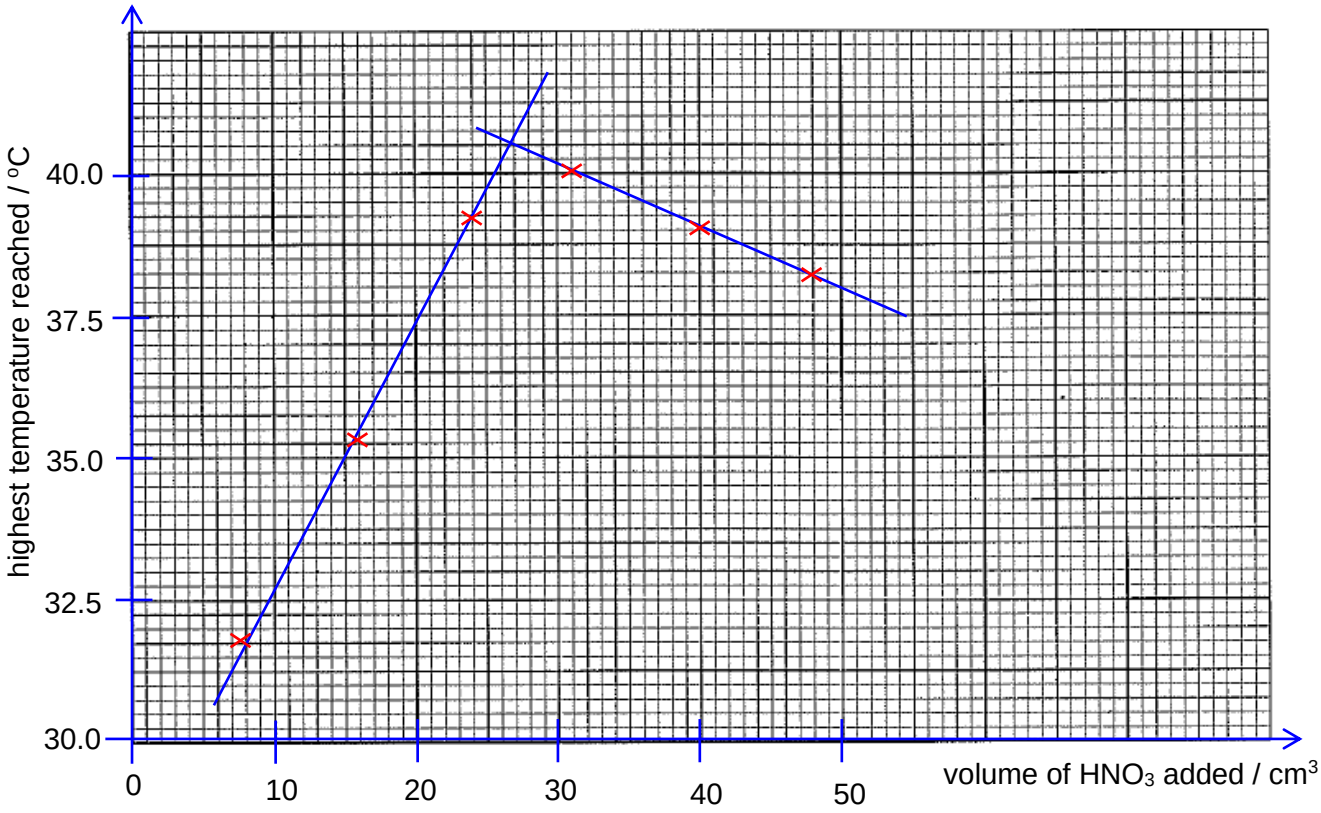
1. Using a 50.00 cm^3 burette, transfer 20.00cm^3 of $Ba(OH)_2$ into a Styrofoam cup.
2. Place the Styrofoam cup in a 250 cm^3 beaker to prevent it from toppling.
3. Fill up another 50.00 cm^3 burette with HNO_3.
4. Take the initial temperature of the solution in the Styrofoam cup. Record the value.
5. Take the initial burette reading and record the value into the table.
6. Add 8.00 cm^3 of HNO_3 from the burette into the Styrofoam cup.
7. Stir the mixture gently with the thermometer, measure and record the highest temperature reached.
8. Immediately, add another 8.00 cm^3 of HNO_3 from the burette into the Styrofoam cup. For every 8.00 cm^3 of HNO_3 added, stir the mixture gently, and measure and record its highest temperature reached.

[1]: appropriate sequence of procedure [S]
[1]: appropriate apparatus and their respective capacities [T]
[1]: ensuring reliability of results (i.e: stir gently, immediately) [R]

How to recognise if the equivalence–point has passed [1]

The equivalence point has passed if the temperature of solution shows a decrease.

Graph expected to be obtained



[1]: rough sketch of points, with T_{max} at around 26.70 cm^3.

Explanation of the shape of the graph [1]

- before equivalence point, HNO_3 is the limiting reagent.
- with each addition of HNO_3, n_{H2O} increases and hence temperature of solution increases.
- after equivalence point, $Ba(OH)_2$ has been completely neutralised and HNO_3 is in excess.
- Temperature of solution decreases due to (i) cooling, (ii) increase in the total volume.

Determination of the concentration of nitric acid [1]

The equivalence point can be obtained by finding the volume of HNO_3 added at the intersection of the 2 lines.

Let the equivalence volume be **x** cm^3

$$[HNO_3] = \frac{1.00 \times \frac{20.00}{1000} \times 2}{\frac{x}{1000}} \quad \left(\text{or } \frac{1.00 \times 20.00 \times 2}{x}\right)$$

$$= \frac{40}{x} \text{ mol dm}^{-3}$$

Determination of the ΔH_n for the reaction [1]

The maximum temperature, T_{max}, corresponds to the temperature at the intersection of the 2 lines in the graph.

maximum temperature rise, $\Delta T = T_{max}$ – initial temperature = **y** ^oC

number of moles of H_2O formed
= 2 x number of moles of $Ba(OH)_2$

$$= 1.00 \times \frac{20.00}{1000} \times 2 = 0.0400 \text{ mol}$$

Taking density of reaction mixture to be that of water (1.0 g cm^{-3})
m = (volume of $Ba(OH)_2$ + volume of HNO_3 used at equivalence pt)
= (20.00 + **x**)

$$\Delta H_c = -\frac{mc\Delta T}{n_{H2O}}$$

$$= -\frac{(20.00 + x)(4.18)(y)}{0.0400(1000)} \text{ kJ mol}^{-1}$$

Comments:
Students were expected to describe how to use the appropriate apparatus of the correct precision for a given step, rather than just outlining generally what had to be done. For thermometric experiments, the use of some type of insulated container is usually necessary.

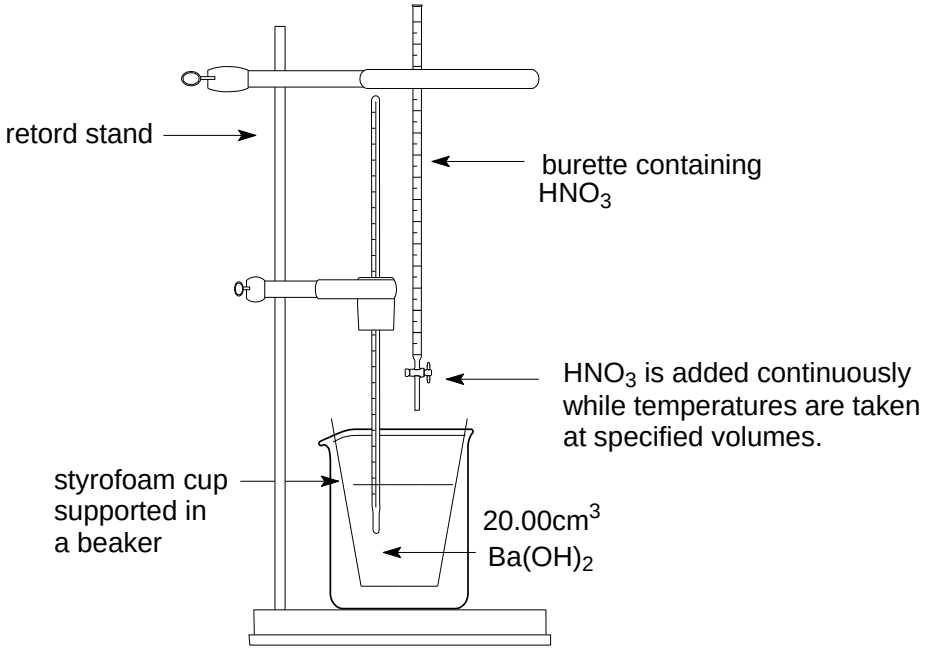
In this experiment, the subsequent addition of acid had to be done in small enough portions to give sufficient points on the graph to draw two straight lines. Ideally, the titrant (HNO_3) should be continuously added and the temperatures are taken at the specified volumes to prevent heat loss (NOT add-stir-read cycle).

Students are required to show clearly on the graph that the maximum temperature reached corresponded with the correct volume of HNO_3 added (i.e. around 26.70 cm^3, depending on the initial volume of $Ba(OH)_2$ used). Subsequently, they need to indicate how ΔT was obtained from their graph.

(c) $\Delta H_c = -\frac{mc\Delta T}{n_{H2O}}$ [1]

If the volume of acid and hydroxides are used was doubled, <u>volume of reaction mixture</u> will <u>double</u> while the <u>amount of heat evolved</u> from the reaction will also <u>double</u> [since now twice the n(H_2O) will be formed].
Hence, there will be <u>no change in maximum temperature rise</u>.

<u>FYI</u>
Experimental set-up



2 (a) (i) Mg^{2+} and SO_4^{2-} [1]

(ii) Fe^{2+}, Mn^{2+}, Cu^{2+} [1]

Comments:
Hint for (i): concentration of ions should decrease to 0.0 in the hydrothermal vent water.
Hint for (ii): there should be an increase in concentration of ions from 0.0 in normal sea water. As zinc is not a transition metal, Zn^{2+} should not be included.

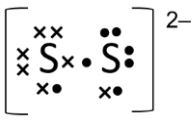
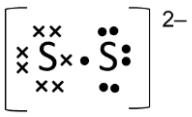
(b) In normal seawater,
$[H^+] = 10^{-7.8}$
$= \mathbf{1.58 \times 10^{-8}\ mol\ dm^{-3}}$ [1]

In hydrothermal vent water,
$[H^+] = 10^{-4.3}$
$= \mathbf{5.01 \times 10^{-5}\ mol\ dm^{-3}}$ [1]

(c) $\mathbf{SO_4^{2-} + 10H^+ + 8e^- \longrightarrow H_2S + 4H_2O}$ [1]

(d) (i) oxidised = **sulfur** (from –2 in H_2S to –1 in FeS_2) [1]

reduced = **hydrogen** (from +1 in H_2S to 0 in H_2)

(ii)  OR  [2]

[1]: correct dot-and-cross
[1]: clear distinction of electrons from the two sulfur atoms

(iii) Electronic configuration of Fe^{2+} is $[Ar]3d^6$ and it has partially filled 3d–orbitals. [3]

In the presence of ligands, the partially filled 3d–orbitals of Fe^{2+} are split into two (non–degenerate) levels with a small energy gap (ΔE) (d orbitals splitting) between them.

When energy is absorbed from the visible light region, an electron is promoted from the d orbital of a lower energy level to a d orbital of higher energy level (d-d transition) The colour of Fe^{2+} is the complement of the colour absorbed. This energy corresponds to violet light from the visible light region. The yellow colour observed is the complementary colour of the violet light absorbed.

[1]: partially filled 3d–orbital; small energy gap
[1]: d–d transition
[1]: absorption of violet (complementary to yellow)

Comments:
For (iii), clarity must be shown in the description of d–d transition. Electrons are being promoted to a higher energy level d orbital with the absorption of the photon, and not the other way around.

(e) **(i)** Relative atomic mass of an element is the weighted average of the mass of its isotopes, relative to $\frac{1}{12}$ the mass of one atom of ^{12}C. [1]

(ii) Let the percentage of ^{3}He be x%. [2]
So the percentage of ^{4}He is (100 – x)%.

$$A_r \text{ of He} = \frac{3.0160293x + 4.0026033(100 - x)}{100}$$

$$400.25959 = 3.0160293x + 400.26033 - 4.0026033x$$

$$x = 7.50 \times 10^{-4}$$

∴Percentage of ^{3}He is **7.50×10^{-4} %**

Comments:
For (i), students are to state that it is an average mass of the isotopes, and that it is relative to 1/12 the mass of carbon–12.

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3 (a) (i) Assuming ideal gas behavior, $pV = nRT$ [1]

$$[CO_2(g)] = \frac{p}{RT}$$
$$= \frac{250000}{8.31 \times 298}$$
$$= 101 \text{ mol m}^{-3}$$
$$= \mathbf{0.101 \text{ mol dm}^{-3}}$$

[1]: substitution & conversion of units for *p* and T
[1]: final answer in mol dm^{-3}

Comments:
Students are expected to apply the knowledge learnt in a novel context.
Since pressure and temperature is given in the question, to calculate the concentration of gas (no. of moles of gas per unit volume), the ideal gas equation can be used here.

Note:
- *Convert pressure from kPa to Pa and temperature from ^oC to K (SI units).*
- *The SI units for no. of moles, is mol, and volume, is m^3. Thus, conversion of concentration from mol m^{-3} to mol dm^3 is necessary.*
  i.e. $\frac{101\text{mol}}{1\text{m}^3} = \frac{101\text{mol}}{1000\text{ dm}^3}$ *= 0.101 mol* dm^{-3}

Final answer should be expressed to 3 significant figures.

(b) (i) $K_c = \frac{[H_2CO_3]}{[CO_2]}$ [1]

$[H_2CO_3] = 1.70 \times 10^{-3} \times 0.084$
$= \mathbf{1.43 \times 10^{-4} \text{ mol dm}^{-3}}$ [1]

(ii) When the bottle is opened, the gas pressure decreases and $[CO_2(g)]$ decreases. [1]

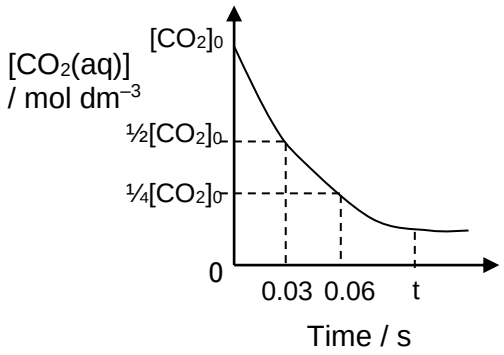
Position of equilibrium (P.O.E.) for reaction 1 shifts left to increase the $[CO_2(g)]$, resulting in a decrease in $[CO_2(aq)]$. Thus, P.O.E. for reaction 2 shifts left to increase $[CO_2(aq)]$. [1]
This results in a decrease in $[H_2CO_3]$ which in turns cause the P.O.E. for reaction 3 to shift left.

Hence there will be a decrease in $[H^+]$ and pH increases when the bottle is opened. [1]

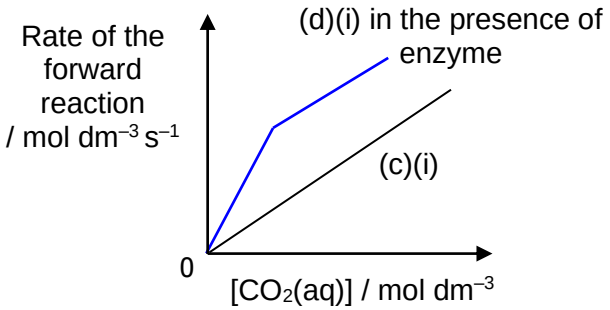
Comments:
Note: $[H_2O]$ is not included in the equilibrium constant expression.

Students are expected to explain and predict how the pH will change. When the bottle is opened, the gas escapes/ the gas pressure decreases. Thus, the concentration of $CO_2(g)$ decreases. In order to explain how the pH changes, students should refer to the $[H^+]$ in the equilibrium in reaction 3. Since it is found that $[CO_2(g)]$ decreases, students should deduce the impact of this change on the P.O.E. of all three reactions, and then conclude that $[H^+]$ increased. It is incorrect to think that the CO_2 concentration increases due to CO_2 from the air dissolving into the drink.

(b) **(i)** [2]



Graph **A**



Graph **B**

[1]: Graph A – downward sloping curve; clear labeling on axes with at least 2 half-life shown; curve does not drop completely to zero.
[1]: Graph B – straight line passing through origin

(ii) [2]

$$k = \frac{\ln 2}{t_{1/2}}$$

$$= \frac{\ln 2}{0.030}$$

$$= \mathbf{23.1\ s^{-1}}$$

[1]: correct answer
[1]: correct unit

(iii) When carbonic acid reaches 99% of its eqm concentration, 1% of CO_2 is left to react before equilibrium concentration is reached. [1]

$$1 \longrightarrow \frac{1}{2} \longrightarrow \frac{1}{4} \longrightarrow \frac{1}{8} \longrightarrow \longrightarrow \frac{1}{100}\ [(\frac{1}{2})^n]$$

Hence $\frac{1}{100} = (\frac{1}{2})^n$, n = no. of half-life

$$n = \ln 0.01 \div \ln(\frac{1}{2})$$

$$\approx 6.64$$

Time taken for carbonic acid to reach 99% its eqm concentration
= 6.64 x 0.03
= **0.199 s**

(accept 7 x 003 = 0.21 s because $\frac{1}{100} = (\frac{1}{2})^7$)

Comments:
Graph A: [CO_2] reaches a constant (not zero) when the reaction reaches equilibrium after time t.
Graph B: Since rate is directly proportional to the concentration of CO_2, rate increases when the concentration of CO_2 increases. Note: when [CO_2] = 0, rate = 0 must be shown.

For a 1st order reaction, the concentration of the reactant at time t (C_t) can be determined using this formula $\frac{C_t}{C_o} = (\frac{1}{2})^n$ *where C_o is the initial concentration and n is the no. of half-life undergone.*

(d) **(i)** [1]: first order kinetics at low [CO_2] & rate is greater than the corresponding rate in **(c)(i)** [2]
[1]: zero order kinetics at high [CO_2] & rate is same as the corresponding rate in **(c)(i)**

(ii) At low [CO_2], rate increases proportionally with [CO_2] as the frequency of effective collisions increases when the number of CO_2 molecules per unit volume increases. [1]
At high [CO_2], all active sites of enzyme molecules are occupied by CO_2 molecules and rate becomes independent of [CO_2] and will be the same as when there is no enzyme molecules added. [1]

Comments:
Recall enzyme kinetics (where the substrate is CO_2):
*Initially, the rate rises rapidly with increasing [CO_2]. The rate should be faster than the graph shown in **(c)(i)** at each concentration because catalyst increases the rate of reaction. Above a certain concentration, all the active sites on the enzymes are saturated, thus the reaction becomes zero order with respect to CO_2.*

It is insufficient to describe the relationship between rate and [CO_2], as the question required students to "explain" the relationship. The explanation of how enzyme increases the rate of reaction is not required.

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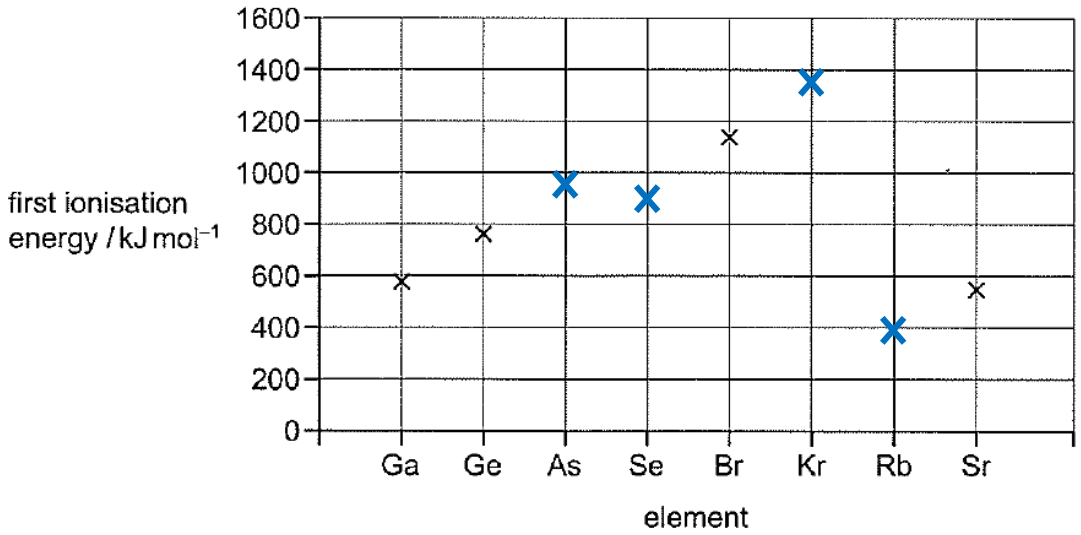
4 (a) [2]



[1]: shows general increase trend
[1]: shows dip for Se and Rb

Comments:
Note that there is a small drop for the Group VI element, selenium, in the first ionisation energy on the graph.

(b) The first ionisation energy of As and Kr are higher than Ge than Br respectively. [4]
There is an increase in the number of protons and hence nuclear charge increases. The number of electrons also increase but these electrons are added to the same outermost electron shell and hence number electron shell remain the same and shielding effect remains approximately constant. Electrostatic attraction between the valence electrons and the nucleus increases. Hence, the energy required to remove the valence electrons increases.

The first ionisation energy of Se is lower than As.
As: [Ar] $3d^{10}4s^24p^3$ Se: [Ar] $3d^{10}4s^24p^4$
The 4p electron to be removed from Se is a paired electron while that to be removed from As is an unpaired electron.
The paired 4p electrons in Se experience inter–electronic repulsion. Hence, less energy is required to remove one of the paired p electrons.

The first ionisation energy of Rb is much lower than Kr.
Nuclear charge of Rb is higher than Kr. Rb also has more number of electron shells, which result in valence electron further away and is more shielded. Electrostatic attraction between the valence electron and nucleus decreases. Less energy is required for the removal of the valence electron in Rb.

[1] correct explanation for each element

Comments:
It is important to base the explanation around the specific comparisons in the question.
Reasons such as the increase in number of electrons or that Kr has a full outer shell are irrelevant in explaining the increase in first I.E. from Br to Kr.

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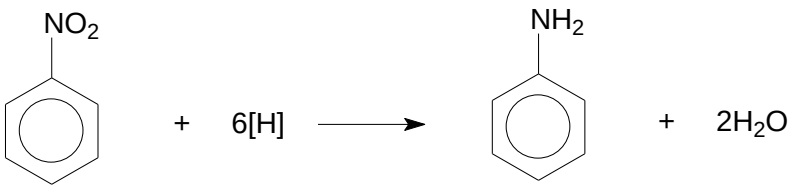
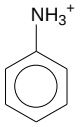
5 (a)



[2]

[1]: correct species in the equation
[1]: balanced equation

(b)

In the acidic mixture, phenylamine exists as the protonated form 

, which is soluble in aqueous solution due to ion–dipole interactions, thus making the desired product inseparable from the solution. [1]

By making the mixture alkaline, the protonated phenylamine will react with the alkali and revert back to its conjugate base form, and its solubility in water will drastically decrease, allowing the separation of phenylamine from the aqueous medium as a distinct layer. [1]

(c) Nitrobenzene is the limiting reagent in this question.

$$\text{amount of nitrobenzene} = \frac{4.84}{123.0}$$
$$= 0.03935 \text{ mol}$$

since nitrobenzene : phenylamine = 1 : 1
amount of phenylamine = amount of nitrobenzene
= 0.03935 mol [1]

theoretical mass of phenylamine to be produced = 0.03935 x 93.0
= 3.660 g

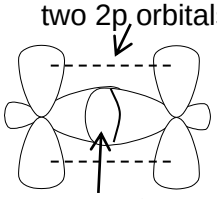
$$\% \text{ yield of phenylamine} = \frac{2.64}{3.660} \times 100\%$$
$$= \mathbf{72.1\%}$$

[1]

(d) chemical test: add aqueous bromine [1]

observation: [1]
(a) orange $Br_2(aq)$ turned colourless
(b) white precipitate of 2,4,6–tribromophenylamine is formed

6 (a) two 2p orbitals overlapping side-on to form π bond [2]

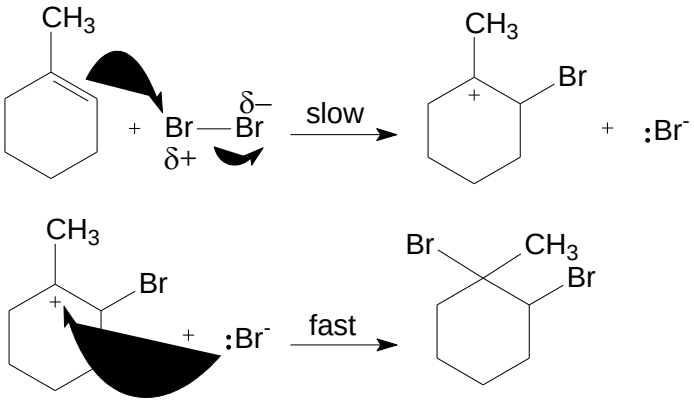


two $2sp^2$ hybrid orbitals overlapping head-on to form σ bond

[1]: correctly drawn diagram
[1]: correct labelling of orbitals

Comments:
The orbitals involved in the bonding must be clearly labelled. The types of bonds formed (σ or π) should also be indicated on the diagram.

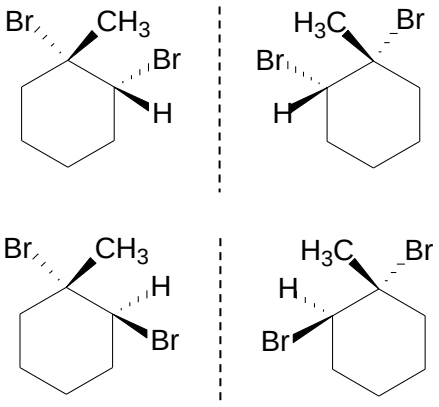
(b) (i) mechanism name: electrophilic addition [4]



[1]: name of mechanism
[1]: correct curly arrows and dipoles shown
[1]: correct carbocation generated
[1]: bromide with lone pair shown

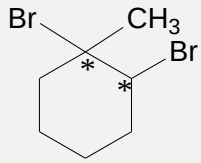
Comments:
Care must be taken to show clearly the start points (either from a bond or a lone pair) and end points of the curly arrows. The lone pair on the bromide ion must be shown.

(ii) [2]

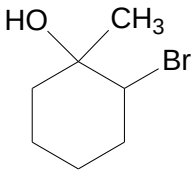


[1]: correct structures of each pair of enantiomers

Comments:
There are two chiral centres in the compound and hence there are 4 stereoisomers. (Recall number of stereoisomers = 2^n, where n = number of chiral carbons and number of double bonds that can exhibit cis–trans isomerism).



The use of 3–D bonds (using wedge/dotted bonds) will allow differentiation of the two stereoisomers about each chiral carbon.

(c) 

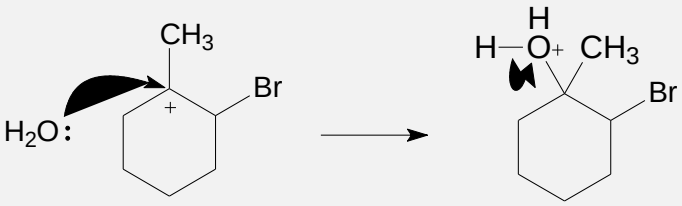
[2]

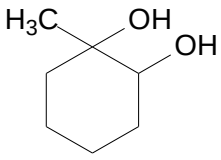
This organic compound is formed when the <u>oxygen atom in H_2O act as a nucleophile</u> and <u>reacts with the carbocation formed in the slow step</u>.

[1]: correct structure of organic compound
[1]: correctly identifies oxygen atom in H_2O as the nucleophile (either in words or as a diagram)

Comments:
H_2O can act as a nucleophile to compete with Br^- (formed in the slow step of the mechanism) for the carbocation.

Diagrammatically, H_2O acting as a nucleophile can be represented as follows:



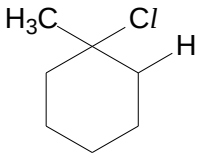
(d) **(i)** 

[3]

Step 1: <u>cold</u> $KMnO_4$, dilute H_2SO_4
Step 2: $K_2Cr_2O_7$, dilute H_2SO_4, heat under reflux

[1]: correct structure of intermediate organic compound
[1]: correct reagents and conditions for each step

Comments:
The cold condition to synthesize the diol must be clearly stated in the answer.

(ii) 

[3]

Step 1: HC*l*(g), room temperature and pressure
Step 2: excess conc. NH_3 in ethanol, heat in a sealed tube

[1]: correct structure of intermediate organic compound
[1]: correct reagents and conditions for each step