River Valley High School

2024 JC 2 H2 Chemistry 9729 Prelim Paper 3 Suggested Solutions

1 (a) (i) Dynamic equilibrium refers to a <u>reversible process</u> at equilibrium in a <u>closed system</u>, in which the <u>rate of forward reaction is equal to the rate</u> <u>of backward reaction</u>, where there is <u>no net change in concentration</u> <u>of reactants and products</u>.

(ii)
$$Kc = \frac{[H_2][I_2]}{[HI]^2}$$

(iii) Initial amount of HI = $\frac{15.4}{127.9}$ = 0.1204 mol [HI]_{initial} = $\frac{0.1204}{2.00}$ = 0.06020 mol dm⁻³

$$[HI]_{change} = 0.06020 \times 0.34 = 0.02047 \text{ mol dm}^{-3}$$

	2HI(g)	=	H ₂ (g)	+	I2(g)
[] _{initial} / mol dm ⁻³	0.06020		0		0
[] _{change} / mol dm ⁻³	- 0.02047		+ 0.010235		+ 0.010235
[] _{eqm} / mol dm ⁻³	0.03973		0.010235		0.010235

$$K_{c} = \frac{(0.010235)^{2}}{(0.03973)^{2}} = 0.0664 \text{ (to 3 s.f.)}$$



(iv) The K_C value will increase. [\checkmark] Position of equilibrium will shift right [\checkmark] to favour the forward endothermic reaction [\checkmark] to absorb the some of the heat. [\checkmark]. (Hence the concentration of hydrogen and iodine will increase while the concentration of hydrogen iodide will decrease.)

2



Benzylamine is the most basic because the <u>electron-donating benzyl group</u> ($-CH_2C_6H_5$) makes the <u>lone pair of electrons on the N atom the most</u> available for donation/protonation.

Phenylamine is the less basic than benzylamine because the lone pair of electrons on the N atom delocalised into the the benzene ring due to the overlap of the p-orbital of the N atom with the π -electron cloud of benzene.

3-aminobenzonitrile is the least basic because the presence of the additional electron withdrawing nitrile (CN) increases delocalisation of the lone pair of electrons on the N atom into the benzene ring. This causes the lone pair of electrons to be least available for donation/protonation.



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(c) (i)





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(ii) Electrophilic substitution

Fe + $3/_2$ Cl₂ \rightarrow FeCl₃ FeCl₃ + Cl₂ \rightarrow FeCl₄⁻ + Cl⁺ [\checkmark]





(d) (i)
$$\Delta H_c = -\frac{\text{mc}\Delta T}{n}$$

 $\Delta H_c = -\frac{(0.600 \times 1000)(4.18)(40.0 - 25.0)}{3.00/78.0}$
 $\Delta H_c = -978.12 = -978 \text{ kJ mol}^{-1} \text{ (to 3 s.f.)}$

(ii) Copper is a good conductor of heat and will

- maximise heat transfer to the water.

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- allow more efficient transfer of heat.

Any logical answer that points to maximising transfer of heat to water

Copper will allow the calorimeter to <u>withstand high pressure of the</u> <u>oxygen pump in.</u>

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(iii) The apparent value obtained is <u>less exothermic</u>. [✓]
 The layer of black solid is <u>soot/ carbon</u> [✓] which suggest that <u>incomplete combustion</u> [✓] of benzene took place.

5

2 (a) (i) Na₂O(s) <u>reacts vigorously</u> with water to give a strongly alkaline <u>solution of pH = 12 to 14</u>.

 $Na_2O(s) + H_2O(l) \rightarrow 2NaOH(aq)$

 $P_4O_{10}(s)$ <u>reacts vigorously</u> with water to give an acidic solution of pH = 2.

 $P_4O_{10}(s) + 6H_2O(I) \rightarrow 4H_3PO_4(aq)$

OR

 $P_4O_6(s)$ <u>reacts vigorously</u> with water to give an acidic solution of pH = 2.

 $P_4O_6(s) + 6H_2O(l) \rightarrow 4H_3PO_3(aq)$

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(ii) Divide the powder into two portions. To one portion, <u>add H₂SO₄(aq)</u>.
 To the other portion, <u>add (concentrated) NaOH(aq)</u>.

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If the powder <u>reacts with acid only</u>, it is MgO.

 $MgO(s) + 2H^{+}(aq) \rightarrow Mg^{2+}(aq) + H_2O(I)$

If the powder <u>reacts with both acid and alkali</u>, it is Al_2O_3 . $Al_2O_3(s) + 6H^+(aq) \rightarrow 2Al^{3+}(aq) + 3H_2O(I)$ $Al_2O_3(s) + 2OH^-(aq) + 3H_2O(I) \rightarrow 2[Al(OH)_4]^-(aq)$

If the powder reacts with alkali only, it is SiO2.

 $SiO_2(s) + 2OH^-(aq) \rightarrow SiO_3^{2-}(aq) + H_2O(I)$

Marker's comments:

- Many candidates tried to distinguish the oxides by dissolving them in water, not realising that it would be ineffective since MgO is sparingly soluble while Al₂O₃ and SiO₂ are insoluble.
- Some candidates tried to use litmus or universal indicator to distinguish the oxides.
- A significant number of candidates wrongly assumed that the oxides would dissociate into aqueous ions and a cation test could be performed with dropwise/excess NaOH(aq).
- (b) (i) Lattice energy is the <u>enthalpy change</u> when <u>one mole of MgSiF₆ solid</u> is formed from gaseous Mg^{2+} and SiF_6^{2-} ions under <u>standard</u> <u>conditions</u>.

OR

 $Mg^{2+}(g) + SiF_{6}^{2-}(g) \rightarrow MgSiF_{6}(s) \quad \Delta H^{\ominus} = lattice energy of MgSiF_{6}$

Marker's comments:

- A significant number of candidates failed to define lattice energy in the context of magnesium silicofluoride.
- The phrase "under standard conditions" was commonly missing.

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By Hess' Law,

 $-2580 = +148 + 456 + 2(+158) + 736 + 1450 - 4(+565) + (-639) + LE(MgSiF_6(s))$

 $LE(MgSiF_6) = -2787$ = -2790 kJ mol⁻¹

Marker's comments:

- Common errors include reversing the enthalpy change for bond energy, and wrong multiplying factors for enthalpy changes.
- Some candidates left out or gave wrong state symbols for chemical species.

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(c) (i) Between 300 K and 400 K,

 $\frac{1/_2\text{Ti}(s) + Cl_2(g) \rightarrow \frac{1}{_2\text{Ti}Cl_4(I)}}{1 + Cl_2(g) \rightarrow \frac{1}{_2\text{Ti}Cl_4(I)}}$

 $\Delta S < 0$ due to a decrease in disorder as the <u>amount of gaseous</u> <u>molecules decreases from 1 to 0 mol</u>. Since ΔH and ΔS are both negative, <u> $-T\Delta S$ becomes more positive with increasing temperature</u>. Hence the graph for reaction 1 becomes more positive between 300 K and 400 K.

Between 400 K and 2000 K,

 $\frac{1/_2\text{Ti}(s) + Cl_2(g) \rightarrow \frac{1}{_2\text{Ti}Cl_4(g)}{}$

 $\Delta S \approx 0$ / is less negative/ has a smaller magnitude as the amount of gaseous molecules decreases from 1 to $\frac{1}{2}$ mol, so $-T\Delta S$ remains relatively constant with increasing temperature. Hence the graph for reaction 1 becomes almost independent of temperature from 400 K to 2000 K.

Marker's comments:

- This part proved to be a challenge.
- Most candidates did not appreciate how ∆S varied when TiCl₄ underwent a phase change, and did not further explain in terms of amount of gaseous molecules.
- Most candidates could not relate $-T\Delta S$ to the shape of graph.
- Common misconception: Entropy of TiCl₄ increased as it boiled, and remained constant beyond boiling point.
- (ii) To prevent the hot titanium extracted from oxidising back to TiO₂.

Or

To prevent the hot magnesium from getting oxidised to MgO.

Marker's comments:

• Many candidates gave an ambiguous answer, pointing out that argon was an inert gas due to its stable octet configuration and would not interfere in the reaction.

(iii) $\frac{1}{2}$ TiC l_4 + Mg $\rightarrow \frac{1}{2}$ Ti + MgC l_2

Marker's comments:

• Some candidates failed to deduce that they should combine the equations for reaction 1 and 2. These candidates often included irrelevant species like Cl₂ and TiCl₂.

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 $\Delta G = -460 - (-350)$

= -110 kJ mol⁻¹

Note: ΔG will be doubled if the stoichiometric coefficient in previous part is doubled.

Marker's comments:

- Some candidates failed to deduce that they should combine the equations for reaction 1 and 2.
- Some candidates misread ΔG values from the graph.
- Among the candidates who managed to read off the values correctly, it was common for them to forget to double ∆G for the reaction when their stoichiometric coefficients in (c)(iii) were doubled.
- (v) 1870 K

(when T > 1870 K, $\Delta G > 0$)

Marker's comments:

• Some candidates either left this part blank or misread the value from the graph axis.





(d) (i)



[✓] correctly labelled anode

[✓] correctly labelled cathode

[✓] correct electrolyte

[<] complete circuit with battery

Marker's comments:

- Common errors include reversed polarity of battery and using a titanium salt for the electrolyte.
- Some candidates confused the electrolytic cell with galvanic cell, showing a voltmeter and salt bridge.
- A handful of candidates confused the setup for anodising with that of purification.

(ii) Anode: $2H_2O(I) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$

Cathode: $2H^+(aq) + 2e^- \rightarrow H_2(g)$

Marker's comments:

- Common errors include showing the reduction of H₂O instead of H⁺ at the cathode, or giving equations related to Ti.
- A handful of candidates omitted state symbols despite it being a question requirement.

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(iii) <u>Pink/ red-brown Cu solid</u> will be deposited on the <u>cathode</u>, and the <u>blue CuSO₄ solution will fade</u>.

Note: accept brown

Since <u> $E \ominus (Cu^{2+}/Cu)$ is more positive than $E \ominus (H^{+}/H_{2})$, Cu^{2+} will be preferentially reduced at the cathode.</u>

Marker's comments:

- Many candidates did not identify the colour of Cu(s) or address the colour change of CuSO₄(aq).
- Many candidates did not provide a complete explanation by comparing the E^{\ominus} values.

3 (a) (i) Mass of gas = 52.248 - 51.083 = 1.165 g

pV = nRT

 $(101300)(1000 \times 10^{-6}) = n(8.31)(20 + 273)$

n = 0.04160 mol

The gas could be N_2 or CO.

Marker's comments:

- Most candidates left out the units.
 - Note: while molar mass has the same numerical value as relative molecular mass (*M_r*), *M_r* has no units as it is a ratio whereas molar mass refers to the mass of one mole of substance.
- CO proved to be a challenge to list for many candidates, with them listing O₂(g) instead. This is incorrect as O₂(g) has a molar mass of 32.0 g mol⁻¹.
 - Note: diatomic means that the molecule has 2 atoms, and they need not necessarily be the same type of atoms.
- A handful of candidates did not do the units conversion correctly.





(ii) <u>N₂ behaves more ideally</u>. The <u>instantaneous dipole-induced dipole</u> <u>interactions between N₂ molecules</u> are <u>less significant/ weaker</u> than the <u>permanent dipole-permanent dipole interactions between CO</u> <u>molecules</u>.

12

Marker's comments:

- This part was fairly well done, with the exception of a handful of candidates who compared the size of the particles even though the more significant difference here was the strength of the intermolecular forces.
- Some candidates also did not specify the types of intermolecular forces between N₂ molecules and between CO molecules.

(b) (i)
$$A_r \text{ of iron} = (\frac{5.85}{5.85 + 91.75} \times 53.9396) + (\frac{91.75}{5.85 + 91.75} \times 55.9349)$$

= $\underline{55.82}$

Marker's comments:

- First common mistake: using the relative masses and relative abundances of all 4 atoms for the calculations.
- Note: the question asked for A_r of iron in this sample, and only atoms A and B are atoms of iron (since their relative masses are close to the Periodic Table A_r of iron). Atoms C and D are atoms of copper, and should not be considered at all.
- Second common mistake: using 100 as the denominator for the relative abundance.
- Note: the data given here is not percentage abundance, and the relative abundances of atoms A and B do not add up to 100. Hence, the denominator should be the sum of the relative abundance of the atoms present.
- (ii) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^9$
- (c) (i) Solubility of a substance is the <u>maximum amount (or mass)</u> of the substance that will dissolve in a <u>given volume of solvent</u> at a <u>specified</u> <u>temperature</u>.

(Accept: "in 1 dm³/ per unit volume of solvent")

Marker's comments: this part was poorly done, most candidates did not give the correct/ complete definition. A handful of candidates confused "solute" with "solvent".



13

 $7.9 \times 10^{-30} \ mol \ dm^{-3}$ < [S^2-] < $4.9 \times 10^{-21} \ mol \ dm^{-3}$

Let x be the maximum [H⁺] required.

$$(x)^{2}(7.9 \times 10^{-30}) = 1.0 \times 10^{-30}$$
$$x = [H^{+}] = \sqrt{\frac{1.0 \times 10^{-30}}{7.9 \times 10^{-30}}} = 0.3558 \text{ mol } dm^{-3}$$

Minimum pH = -lg(0.3558) = 0.449

Let y be the minimum [H⁺] required.

$$\begin{aligned} (y)^2 (4.9 \times 10^{-21}) &= 1.0 \times 10^{-30} \\ y &= [H^+] = \sqrt{\frac{1.0 \times 10^{-30}}{4.9 \times 10^{-21}}} = 1.429 \times 10^{-5} \text{ mol } dm^{-3} \end{aligned}$$

Maximum pH = $-lg(1.429 \times 10-5) = 4.85$ Hence, pH range is 0.449 to 4.85.

Markers' comments:

- Many candidates used $\sqrt{K_{sp}}$ of CuS or FeS to find the [S²⁻] required. This was incorrect as the solution was not a saturated solution of each salt; the concentrations of [Cu²⁺] and [Fe²⁺] were given to be 1 mol dm⁻³ and that value should be used together with the K_{sp} to find the required [S²⁻] for precipitation.
- A handful of candidates also did not give a pH range, choosing to calculate either the maximum or the minimum pH value.

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(d) (i)

	Со	N	Н	0	Cl
mass ratio	22.0	26.0	6.3	6.0	39.7
mole ratio	$\frac{22.0}{58.9} = 0.3735$	$\frac{26.0}{14.0} = 1.857$	$\frac{6.3}{1.0} = 6.30$	$\frac{6.0}{16.0} = 0.375$	$\frac{39.7}{35.5} =$ 1.118
simplest ratio	$ \begin{array}{r} 0.3735 \\ \overline{0.3735} \\ = 1.00 \end{array} $	$\frac{1.857}{0.3735} = 4.972$	$\frac{6.30}{0.3735} = 16.87$	$ \frac{0.375}{0.3735} \\ = 1.004 $	$\frac{1.118}{0.3735} = 2.993$
	1	5	17	1	3

Empirical formula of E is CoN₅H₁₇OC l_3 .

(ii) Amount of
$$\mathbf{E} = \frac{0.845}{58.9 + (5 \times 14.0) + (17 \times 1.0) + 16.0 + (3 \times 35.5)}$$

= 0.003148 mol
Amount of $Cl^{-} = \frac{1.354}{107.9 + 35.5} = 0.009442$ mol
Amount of Cl^{-} per mole of $\mathbf{E} = \frac{0.009442}{0.003148} = 3.00$ mol
Complex ion: $[Co(NH_3)_5(H_2O)]^{3+}$

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- (e) F does not rotate plane-polarised light \Rightarrow F <u>does not contain chiral</u> <u>carbon/ has an internal plane of symmetry/ achiral</u>.
 - 1 mole of F undergoes <u>acid-base</u> reaction with Na₂CO₃ to give 1 mole of CO₂ ⇒ F has <u>2 -COOH</u> groups/ is a <u>dicarboxylic acid</u>.
 - 1 mole of F undergoes <u>nucleophilic substitution</u> with 2 moles of ethanolic CH₃Br to give quaternary ammonium salt ⇒ F is a <u>secondary amine</u>.
 - **F** undergoes <u>nucleophilic substitution</u> with CH₂(OH)CH(OH)C*l*.
 - **G** undergoes (intramolecular) <u>condensation</u> to form **H** ⇒ **H** is a (cyclic) <u>ester</u>.





Section B

> Shape: Square planar Bond angle: 90°

(b) (i) Br-

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(ii)

Amount of Br⁻ in 25.0 cm³ of solution $\mathbf{Q} = \frac{1.942}{79.9+107.9} = 0.01034$ mol Amount of Br₂ in 250.0 cm³ of solution $\mathbf{Q} = \frac{9.909}{2 \times 79.9} = 0.06201$ mol Amount of **Y** in 250.0 cm³ of solution **Q**

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$$= (2)(0.06201) - \left(\frac{250}{25.0}\right)(0.01034)$$

= 0.02062 mol

Amount of \boldsymbol{Y} in 25.0 cm^3 of solution \boldsymbol{Q}

$$=\left(\frac{25.0}{250}\right)(0.02062) = 0.002062 \approx 0.00206 \text{ mol (shown)}$$



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(iii) Y reacts with KI to form Br-

Amount of S₂O₃^{2–} reacted = $\left(\frac{24.80}{1000}\right)(0.500) = 0.01240$ mol

 $2S_2O_3{}^{2-}\ \%\ I_2\ \%\ 2I^-$

Amount of KI reacted with \mathbf{Y} in step 3 = 0.01240 mol

 $\frac{\text{amount of KI}}{\text{amount of }\mathbf{Y}} = \frac{0.01240}{0.002062} \approx \frac{6}{1}$

 $I^-\,\%\,\,\text{e}^-$

i.e. Each mol of Y gained 6 mol of electrons to form Br-

Original oxidation state of Br in Y = -1 + 6 = +5

(iv) Y is BrO₃⁻, 5Br⁻% BrO₃⁻

 $3Br_2 + 6OH^- \rightarrow 5Br^- + BrO_3^- + 3H_2O$

Allow ECF from incorrect answer from (ii) and (iii), but only if the balance is correct. E.g. $Br_2 + 2OH^- \rightarrow Br^- + BrO^- + H_2O$

(c) (i) It is the <u>minimum amount of (kinetic) energy</u> that reacting particles require <u>for reaction to take place</u>.



(ii) Let the rate equation be: Rate = $k[BrO_3^-]^p[Br^-]^q[H^+]^r$

Comparing experiment 1 and 2:

When $[BrO_3^-]$ is doubled, and $[Br^-]$ and $[H^+]$ are kept constant, rate of reaction doubles. Hence, reaction is 1^{st} order with respect to BrO_3^- .

Comparing experiment 2 and 3:

 $\frac{(0.24)^{1}(0.1)^{q}(0.15)^{r}}{(0.18)^{1}(0.2)^{q}(0.15)^{r}} = \frac{2.00 \times 10^{-5}}{3.00 \times 10^{-5}}$ $\frac{(0.1)^{q}}{(0.2)^{q}} = \left(\frac{3}{4}\right) \frac{2.00 \times 10^{-5}}{3.00 \times 10^{-5}}$ q = 1

Hence, reaction is 1st order with respect to Br-.

(iii) From experiment 1:

 $1.00\times 10^{-5}\,\text{=}\,k(0.120)(0.100)(0.150)^2$

k = 0.03704

Substituting to experiment 4:

 $3.00\times 10^{-4} = (0.03704)(0.300)(0.300)a^2$

$$a = 0.300 \text{ (mol dm}^{-3}\text{)}$$

OR

Using experiment 3 and 4:

$$\frac{k(0.18)(0.20)(0.15)^2}{k(0.30)(0.30)(a)^2} = \frac{3.00 \times 10^{-5}}{3.00 \times 10^{-4}}$$
$$a^2 = 0.0900$$
$$a = 0.300$$



(iv)

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- Set up an experiment where known concentration and volumes of BrO₃⁻, Br⁻ and H⁺ are prepared separately.
 - 2) Mix these solutions and immediately start a stopwatch.
 - 3) Place the mixture inside a spectrometer, and stop the timer when a fixed absorbance value is reached
 - Repeat steps 1 to 3 using different [H⁺] while keeping [BrO₃⁻], [Br⁻] constant.
 - 5) Plot a graph of 1/t against [H⁺]²





(d) Bond energy of $H#Cl = +432 \text{ kJ mol}^{-1}$

Bond energy of H#Br = +366 kJ mol⁻¹

Less energy is needed to overcome the weaker H#Br bond, resulting in a decomposition reaction and production of red-brown Br₂(g).

Stronger H#Cl bond is thermally stable/ does not break easily when heated.

- **5 (a) (i)** Enthalpy change of reaction is the enthalpy change when <u>molar</u> <u>quantities of reactants</u>, <u>as specified by the balanced chemical</u> <u>equation</u> react to form products.
 - (ii) $\Delta H_r = +590 + 1150 = +1740 \text{ kJ mol}^{\#1}$

 $\Delta H_r = +502 + 966 = +1468 \text{ kJ mol}^{\#1}$

(iii) ΔH_r for Ba is <u>less endothermic/ positive</u> as less energy is required to remove the 1st and 2nd electrons from the larger principal quantum shell of Ba <u>which is less attracted to the nucleus/ further away from the nucleus/ experience lower (effective) nuclear charge.</u>



OR

The *E* values takes into account the <u>enthalpy change of hydration</u> and entropy factor.

- (c) (i) <u>Bulky ions/irregular shaped ions</u> that prevent <u>good packing of ions/</u> <u>uniform lattice structure from forming</u>, leading to lower melting point.
 - (ii) $(CH_3CH_2)_2(CH_3)_2P^+$ and $PF_6^{\#}$

Diethyldimethylphosphonium cation and hexafluorophosphate anion

have the <u>larger ionic radius</u>. As $|LE| \propto \left| \frac{Z^+ \times Z^-}{r^+ + r^-} \right|$, less energy will be

required to overcome the electrostatic forces of attraction between the oppositely charged ions. The <u>lattice energy will have the lowest</u> <u>magnitude</u> and will have the lowest melting point.

- (iii) VSEPR Theory is used to predict the shapes of molecules and or polyatomic ions and applies to the outer shell of the central atom. <u>The</u> <u>electron pairs around the central atoms are arranged as far apart as</u> <u>possible to minimise inter-electron repulsions</u>. <u>Lone pair-lone pair (lplp) repulsions are greater than bond pair-lone pair repulsions (bp-lp),</u> <u>which are greater than bond pair-bond pair (bp-bp) repulsions.</u> <u>Triple/Double bonds are treated as an electron pair.</u>
- (iv)



Tetrahedral. 4 bp and no lp around B atom arranged at 109.5° to minimise repulsion.

(d) (i) Add Br₂(aq)

D will <u>not</u> decolourise orange Br₂(aq).

E will <u>decolourise orange $Br_2(aq)$ </u> to form a white precipitate.

- Aromatic halide is not expected to undergo nucleophilic substitution due to partial double bond character in C-X
 - reduced polarity of C-X bond



- Hinders nucleophilic attack (electronic repulsion between electrons in ring with approaching electron rich nucleophile)
- C-F bonds are quite <u>strong</u> and stable and are <u>not expected</u> to be broken in nucleophilic substitution
- Phenylamine is a poor/weak nucleophile as the lone pair of electrons on N atom can delocalised into the benzene ring



(iii)

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