2021 H2 Chemistry Preliminary Exam Paper 3 Suggested Solutions

C1 **(a)(i)** Cl_2(aq) is added to solution of KI, followed by hexane. The mixture is shaken and the hexane layer turns purple, indicating the presence of I_2.

$Cl_2 + 2I^- \longrightarrow I_2 + 2Cl^-$

(a)(ii)

$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$ $E^\ominus = 1.36$ V

$I_2 + 2e^- \rightleftharpoons 2I^-$ $E^\ominus = 0.54$ V

$E^\ominus_{cell} = 1.36 - 0.54 = +0.82$ V

Since the $E^\ominus_{cell}$ value is positive, the reaction is spontaneous.

OR

Since the $E^\ominus$ value for Cl_2 is higher than that of I_2, chlorine has a higher tendency for reduction and is hence, a stronger oxidising agent.

(a)(iii) Half-equation for iodine: $I_2(aq) + 2e^- \rightleftharpoons 2I^-(aq)$

Hence, ascorbic acid and iodine react in a 1:1 mole ratio.

Amount of iodine titrated = $0.005 \times 0.02205 = 1.1025 \times 10^{-4}$ mol

Amount of ascorbic acid present in 10.0 cm^3 = 1.1025×10^{-4} mol

Amount of ascorbic acid present in 100 cm^3 = $10 \times 1.1025 \times 10^{-4}$

= 1.1025×10^{-3} mol

Mass of ascorbic acid present = $1.1025 \times 10^{-3} \times 176.0 = 0.194$ g

Mass of ascorbic acid present in 100.0 g of candy = 0.194 g

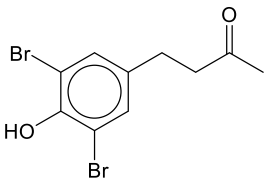
% by mass of ascorbic acid = $\frac{0.194}{100.0} \times 100\% = 0.194\%$

(b) Add equal amounts of bromopropane, chloropropane and iodopropane in separate test tubes and warm the test tubes in a water bath maintained at 50 °C.

Then add 5.0 cm^3 of silver nitrate solution in ethanol to each compound and note the time taken for the precipitates to first appear.

The mixture containing iodopropane will form a yellow ppt of AgI first, followed by the mixture containing bromopropane with a pale cream ppt of AgBr and in the mixture containing chloropropane with a white ppt of AgCl.

(c)(i)



(c)(ii) $NaBH_4$ / H_2, Ni, heat / $LiAlH_4$ in dry ether

Reduction reaction

(c)(iii) There are two functional groups on rhododendrol: phenol and aliphatic alcohol.

When added to sodium hydroxide, only phenol will react to form phenoxide.

This is because phenol is a stronger acid than the aliphatic alcohol. In the phenoxide ion, the p–orbital of the O atom overlaps with the π–electron cloud of the benzene ring and the negative charge/lone pair on the O atom is delocalised into the ring. Hence, the phenoxide ion is resonance-stabilised and more stable than the alkoxide ion.

Or

This is because the aliphatic alcohol is a weaker acid than phenol. The O atom on the alkoxide ion is bonded to two electron donating alkyl groups which intensifies the negative charge on the O atom. The alkoxide ion is less stable than the phenoxide ion.

(c)(iv) Add 2,4-dinitrophenylhydrazine/2,4-DNPH to each compound in a test tube.
- For RK, orange ppt is formed
- For rhododendrol, no ppt is formed

OR

Add $K_2Cr_2O_7$(aq), H_2SO_4(aq) to each compound in a test tube and heat in a hot water bath.
- For rhododendrol, orange acidified $K_2Cr_2O_7$(aq) turns green
- For RK, the solution remains orange

(d)(i) The reaction is acidic hydrolysis.

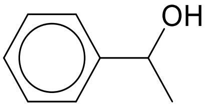
- Gardenol is an ester
- **B** is a carboxylic acid
- **C** is an alcohol/phenol

(d)(ii)

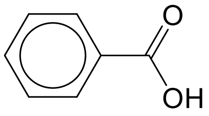
Gardenol has formula $C_{10}H_{12}O_2$	C:H ratio ≈ 1:1 ⇒ benzene ring present
Gardenol reacts with acidified $KMnO_4$ to give **B** and **D**	Gardenol undergoes oxidation and acidic hydrolysis. • **C** undergoes oxidation to form **D** • **C** is not phenol OR **C** is an alcohol • **D** is a ketone / carboxylic acid
C reacts with acidified $KMnO_4$ to give **D**	**C** undergoes side-chain oxidation • **D** is benzoic acid

CH_3COOH

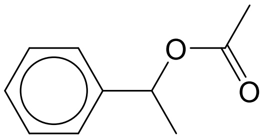
B



C

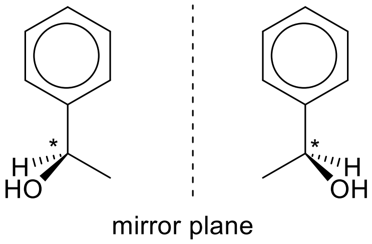


D

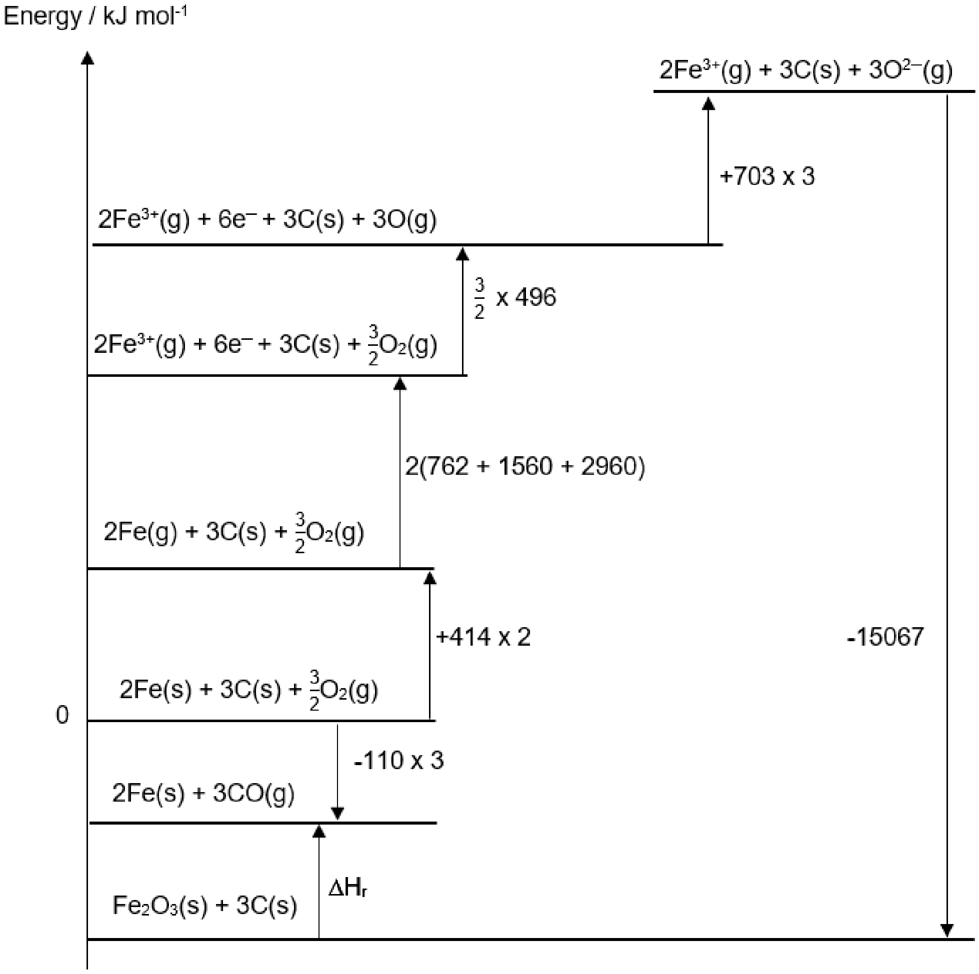


gardenol

(d)(iii) The carbon bonded to the -OH group is chiral because it is bonded to four different groups.



C2 **(a)**



$\Delta H_r = -(-15067) - (+703 \times 3) - (\frac{3}{2} \times 496) - 2(762 + 1560 + 2960) - (+414 \times 2)$
$+ (-110 \times 3) = \underline{+492 \text{ kJ mol}^{-1}}$

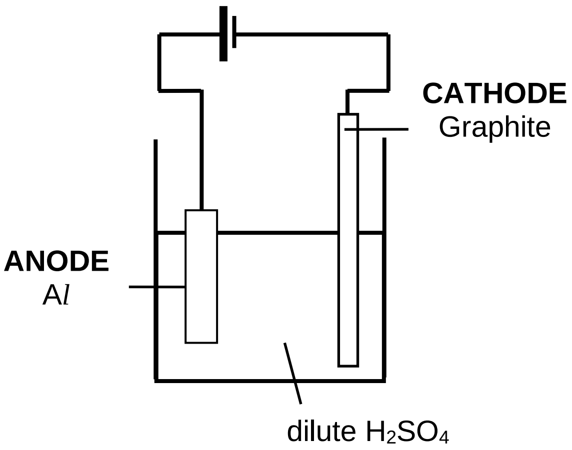
(b)(i) Nanoparticles have relatively large surface area (when compared to the same volume of material made up of bigger particles) resulting in more / faster adsorption of the SeO_3^{2-} ions.

(b)(ii) At high alkaline pH, the OH^- ions will compete with SeO_3^{2-} to be adsorbed on the surfaces of the nanoparticles. OR
$Fe(OH)_2$ gets oxidised to $Fe(OH)_3$ in an alkaline medium. As such, there are less $Fe(OH)_2$ available for adsorption/ SeO_3^{2-} adsorbs less effectively on the surfaces of $Fe(OH)_3$ nanoparticles.

(b)(iii) $SeO_3^{2-} + 3H_2O + 4e^- \rightarrow Se + 6OH^-$

(b)(iv) $Fe(OH)_2$ gets <u>oxidised</u> by air/O_2/SeO_3^{2-} to form red-brown $\underline{Fe(OH)_3}$.

(c)



Reactions at anode:
$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$
$4Al + 3O_2 \rightarrow 2Al_2O_3$

(d)(i) Number of moles of HF in solution **E** = $2 \times \frac{19.90}{1000} \times 0.40 = \underline{0.0159 \text{ mol}}$

$Q = It = n_eF$
$n_e = \frac{0.40 \times (32 \times 60)}{96500} = 0.0079585$ mol

$Ni^{2+} + 2e \rightarrow Ni$
Number of moles of $Ni^{2+} = \frac{0.0079585}{2} = 0.0039793$ mol
Number of moles of NiF_2 in solution **E** = 2×0.0039793
$= \underline{0.00796 \text{ mol}}$

(d)(ii) Number of moles of $O_2 : HF : NiF_2 = 0.004 : 0.0159 : 0.00796$
$= 1 : 4 : 2$

$2K_xNiF_6 + 2H_2O \rightarrow 2x\ KF + 4HF + 2NiF_2 + O_2$

Considering the number of F, $12 = 2x + 4 + 4 \Rightarrow x = 2$

(e)(i) $pV = nRT$
$(100 \times 10^3)\ V = (\frac{300}{170.7} \times 4) \times 8.31 \times (170+273)$
$V = 0.259\ m^3$

(e)(ii) The sign of $\Delta S_r^\ominus$ is positive because the reaction leads to an increase in the number of gaseous particles in the system such that the system becomes more disordered than before.

(e)(iii) At 70 °C, $Ni(CO)_4$ is formed as a gas and can be separated from the solid impurities. It also ensures rate of reaction is sufficiently high to make it practical on an industrial scale.

(e)(iv) For the reaction in step 2 to be spontaneous,
$\Delta G_r^\ominus < 0$
$\Delta H_r^\ominus - T\Delta S_r^\ominus < 0$
$+160.9 - T\,(+410/1000) < 0$
$T > 392$ K (or 119 °C)

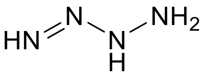
<u>Alternatively,</u>
At 170 °C,
$\Delta G_r^\ominus = \Delta H_r^\ominus - T\Delta S_r^\ominus$
$= +160.9 - (170+273)\,(+410/1000)$
$= -20.7 \text{ kJ mol}^{-1} < 0$

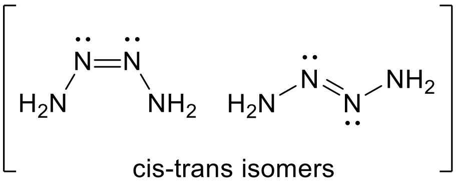
At 70 °C,

$$\begin{aligned}\Delta G_r^{\ominus} &= \Delta H_r^{\ominus} - T\Delta S_r^{\ominus} \\ &= +160.9 - (70+273)(+410/1000) \\ &= +20.3 \text{ kJ mol}^{-1} > 0\end{aligned}$$

Increasing the temperature from 70 °C to 170 °C (which is > 119 °C) ensures that the reaction is spontaneous.

C3 **(a)**

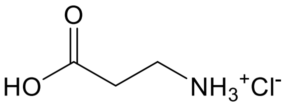




(b)(i) NH_3 is a nucleophile and is repelled by the electron-rich C=C bond in ethene / there are no electron deficient sites in ethene.

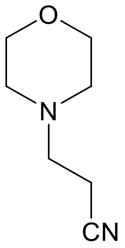
Due to presence of electronegative N / electron-withdrawing -CN group, electron density is withdrawn away from the C=C bond. This causes the carbon of the terminal alkene to be more electron deficient, hence more susceptible to nucleophilic attack by NH_3.

(b)(ii)



(b)(iii) Morpholine has reacted.

There are 2 electron-donating alkyl groups bonded to N of morpholine which increases the electron density on N making the lone pair of electrons on N more available for nucleophilic attack. OR
The lone pair of electrons on N of phenylamine delocalises into the π electron cloud of benzene, making it less available for nucleophilic attack.

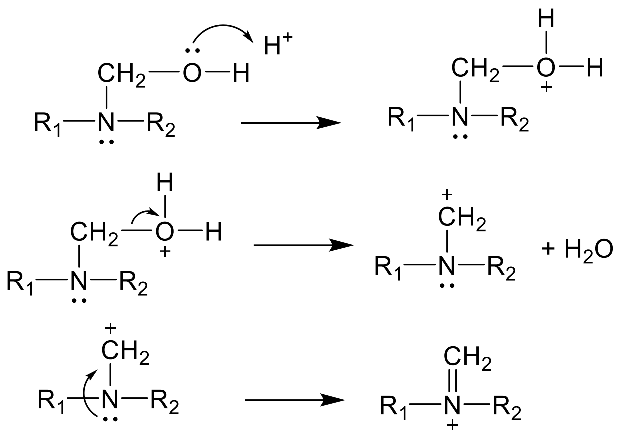


(c)(i) $R_1R_2(CH_3)N$ is more basic than R_1R_2NH.
$R_1R_2(CH_3)N$ has an additional electron donating methyl / alkyl group bonded to N, making the lone pair of electrons on N more available for forming a dative bond to a proton.

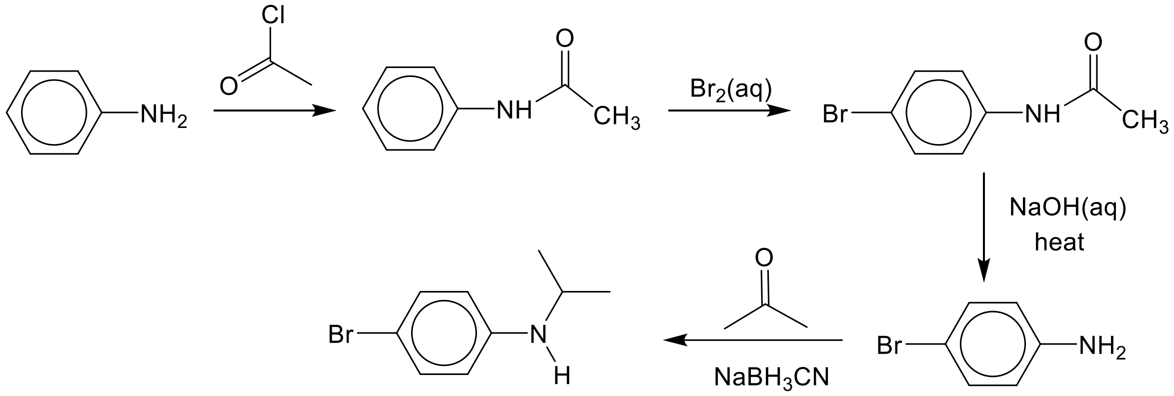
(c)(ii) ① $NaBH_3CN$ is a weaker reducing agent. –CN is an electron-withdrawing group / N is electronegative, making the H less electron rich / less δ^- in $NaBH_3CN$.

② If $NaBH_4$ is used, methanal would also be reduced.

(c)(iii)



(c)(iv)



C4 **(a)(i)** The order of reaction with respect to a given reactant is the power to which the concentration of that reactant is raised in the rate equation.

(a)(ii) $(V_\infty - V_t)$ refers to the volume of N_2 yet to be evolved OR
$(V_\infty - V_t)$ is proportional to the amount / concentration of $C_6H_5N_2Cl$ remaining.

(a)(iii) As $(V_\infty - V_t)$ decreased from 190 cm^3 to 95 cm^3 , half-life was 17 min.
As $(V_\infty - V_t)$ decreased from 180 cm^3 to 90 cm^3, half-life was 17 min.
Since $(V_\infty - V_t) \propto [C_6H_5N_2Cl]$, reaction is 1st order with respect to $C_6H_5N_2Cl$.

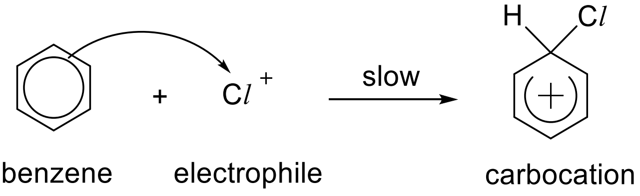
(a)(iv) H_2O is a solvent and is in excess. The concentration of H_2O does not change during the reaction.

rate = $k[C_6H_5N_2Cl]$

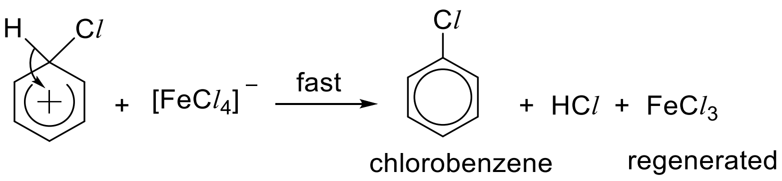
(b)(i) A suitable catalyst is $\underline{FeCl_3 / AlCl_3}$.

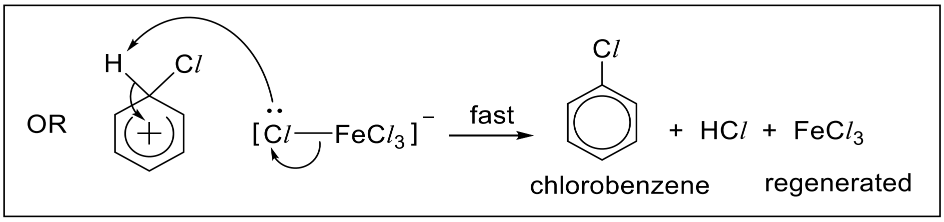
<u>Electrophilic substitution</u>
$Cl_2 + FeCl_3 \rightleftharpoons Cl^+ + [FeCl_4]^-$

Step 1:



Step 2:





(b)(ii) ΔH_{rxn} for iodination of benzene
= BE(I–I) + BE(C–H) – BE(C–I) – BE(H–I)
= + 151 + 410 – 240 – 299 = +22.0 kJ mol^{-1}

Since ΔH_{rxn} is positive and ΔS_{rxn} is approximately 0, ΔG_{rxn} will be positive. Therefore, iodination of benzene is not spontaneous.

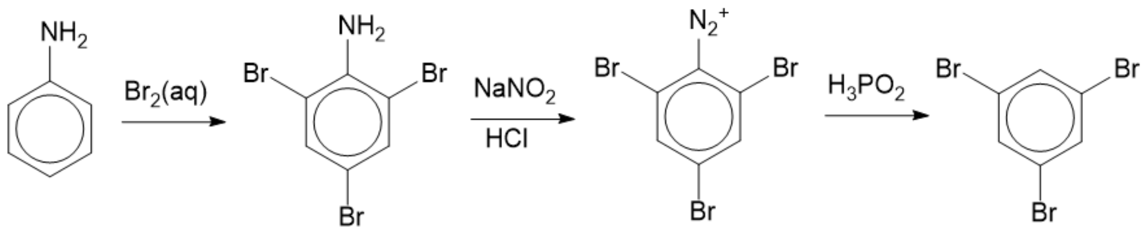
(b)(iii) $I_2 + 2HNO_3 + 2H^+ \rightarrow 2I^+ + 2NO_2 + 2H_2O$
OR
$I_2 + 2NO_3^- + 4H^+ \rightarrow 2I^+ + 2NO_2 + 2H_2O$

(c)(i)

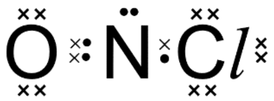
P	**Q**
	

Reagents and conditions:
Step 1: conc HNO_3, conc H_2SO_4, heat
Step 2: Sn, conc. HC*l*, heat, followed by aq. NaOH
Step 4: CuCN
Step 5: H_2SO_4(aq), heat

(c)(ii)



C5 **(a)(i)**



(a)(ii) bent, 110º

(a)(iii) There are four electrons in the N=O bond as compared to only two electrons in the N–C*l* bond and hence there is greater electrostatic attraction between the bonding electrons and the N and O nuclei, which causes these nuclei to be closer together in the N=O bond. The nitrogen-oxygen bond length would be shorter.

(a)(iv) NOC*l* is polar and the <u>permanent dipole-permanent dipole interactions</u> (and instantaneous dipole-induced dipole interactions) between NOC*l* molecules are <u>stronger than the instantaneous dipole-induced dipole interactions</u> between non-polar Cl_2 molecules.

More energy is required to overcome the attraction between NOC*l* molecules and hence NOC*l* has a higher boiling point.

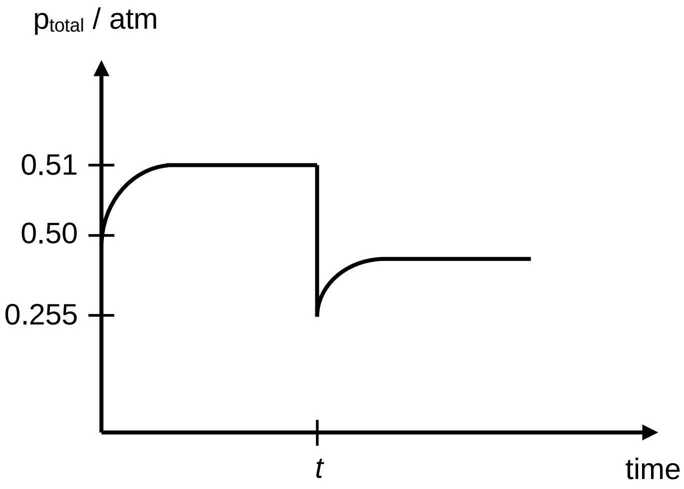
(b)(i) $K_p = p_{NO}^2\ p_{Cl2}\ /\ p_{NOCl}^2$

(b)(ii)

	$2NOCl(g) \rightleftharpoons$	$2NO(g)$ +	$Cl_2(g)$	
$p_{initial}$ / atm	0.50	-	-	
p_{change} / atm	–0.02	+0.02	+0.01	
p_{final} / atm	0.48	0.02	0.01	p_{total} = 0.51 atm

$$K_p = (0.02)^2\ (0.01)\ /\ (0.48)^2 = 1.74 \times 10^{-5} \text{ atm}$$

(b)(iii)



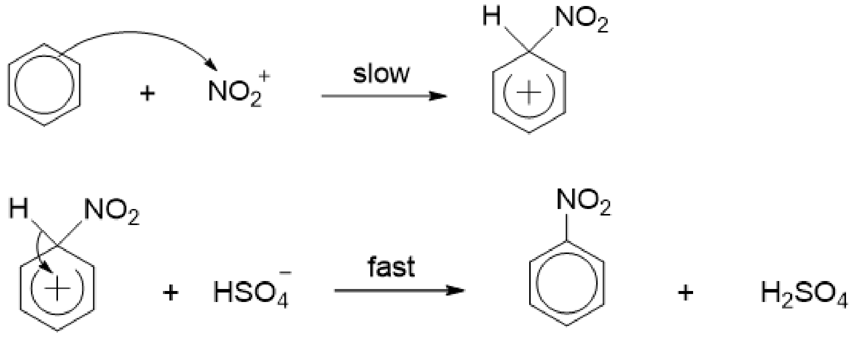
(b)(iv) When the volume was doubled, the total pressure was decreased (halved). The partial pressures of the 3 gases would also be halved initially/decrease.

To increase the total pressure / increase the total number of gaseous particles in the system, by Le Chatelier's Principle, the position of equilibrium would shift to the right.

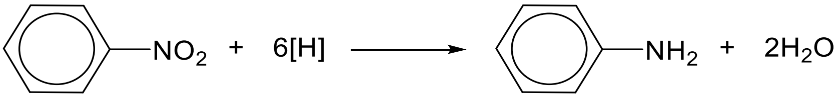
The partial pressure of NOC*l* would then decrease further while that of NO and Cl_2 would increase until equilibrium is re-established.

(c) Electrophilic substitution

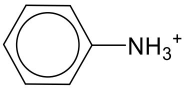
$2H_2SO_4 + HNO_3 \rightleftharpoons NO_2^+ + 2HSO_4^- + H_3O^+$



(d)(i)



(d)(ii) Under acidic conditions, phenylamine undergoes acid-base reaction to produce a high proportion of



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The $-NH_3^+$ is 3-directing and hence a large proportion of the 3-isomer is produced.

(d)(iii)