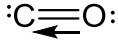
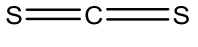
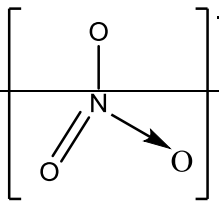
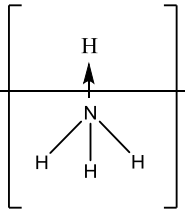
RIVER VALLEY HIGH SCHOOL
2023 JC 2 H2 Chemistry 9729
Preliminary Examination (Paper 1 - 3)
Suggested Solutions

Paper 1

		Worked solutions
1	D	Statement A: Incorrect. This statement would explain why the 3rd IE of aluminium is higher than that of magnesium. Statement B: Incorrect. Ionisation energy is dependent on nuclear charge and shielding effect, not octet configuration. Statement C: While it is a factual statement, it does not explain the significant difference in 3rd IE between the two species. Statement D: Al^{2+}: $1s^2\ 2s^2\ 2p^6\ 3s^1$ vs Mg^{2+}: 1s2 2s2 2p6 Electron to be removed from Mg^{2+} is from n = 2 principal quantum shell and is closer and more strongly attracted to the nucleus due to a significantly smaller shielding effect, while that to be removed from Al^{2+} is from n = 3 principal quantum shell.
2	C	$\frac{\text{charge}}{\text{mass}}$ ratio of proton ($^1H^+$) = $\frac{1}{1}$ = 1 $\frac{\text{charge}}{\text{mass}}$ ratio of particle to be deflected = $\frac{1}{12.0} \times 8.0 = \frac{2}{3}$ $\frac{\text{charge}}{\text{mass}}$ ratios of: $^{12}C^{3-}$: $\frac{3}{12} = \frac{1}{4}$ (incorrect) $^{10}B^{2-}$: $\frac{2}{10} = \frac{1}{5}$ (incorrect) $^{6}Li^{4-}$: $\frac{4}{6} = \frac{2}{3}$ (correct) $^{3}He^{-}$: $\frac{1}{3}$ (incorrect)
3	D	Tritium isotope: 1p, 1e, 2n Helium isotope: 2p, 2e, 1n Option 1 is incorrect. Option 2 is incorrect. Option 3 is incorrect (charged sub-atomic particles refer to protons and electrons).
4	B	   

		A	B	C	D
5	B	A is correct. Ice cannot conduct electricity. B is incorrect. Water has a simple covalent structure. When it is in the form of ice, hydrogen bonds are formed between the molecules of water. However, it is not a giant covalent structure. C is correct. Each O atom in water molecule has 4 bond pairs. So bond angle is 109.5° D is correct. Density of ice is lower due to its open structure.			
6	B	$\frac{p_1V_1}{T_1} = \frac{p_2V_2}{T_2}$ Let initial volume be $3V_2$ => final volume is V_2 $\frac{(4.50)(3V_2)}{298} = \frac{p_2(V_2)}{753}$ (Note: T needs to be converted to K) p_2 = 34.1 atm			
7	C	When temperature increases from 25 ^oC to 62 ^oC, K_w increases, signifiying that there is more dissociation of water (to form H^+ and OH^-). Since H_2O % H^+ % OH^-, $n(H^+) = n(OH^-)$ ➔ value of pH = value of pOH At 62 ^oC, $pK_w = -\lg(1.00 \times 10^{-13}) = 13$ ➔ pH = 6.5 and pOH = 6.5 (i.e., $[H^+] = [OH^-] = 3.162 \times 10^{-7}$ mol dm^{-3})			
8	A	$\Delta S < 0$ since amount of gaseous molecules decrease from 1.5 to 1. $\Delta H = -396 - (-297) = -99$ kJ mol^{-1} < 0			
9	B	Statement A: Incorrect. Energy level of products is <u>higher</u> than that of reactants. Statement B: Correct. $\Delta H_{soln} = -LE + \sum \Delta H_{hyd}$ Both LE and ΔH_{hyd} are negative values, so $-LE > 0$, $\sum \Delta H_{hyd} < 0$. For ΔH_{soln} to be > 0, magnitude of LE has to be > magnitude of $\sum \Delta H_{hyd}$. Statement C: Reaction is endothermic, heat is taken in. Statement D: Incorrect definition of ΔH_{soln}			
10	A	Statement 1: Correct. $\Delta H = -12/18 \times 44 = -29.3$ kJ mol^{-1} Statement 2: Incorrect. $\Delta G = 0$ during phase change. Statement 3: Correct. $\Delta G = \Delta H - T\Delta S$, $\Delta S = (-29.3)/(373) = -78.6$ J K^{-1}			
11	B	$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$ $HCHO + O_2 \rightarrow CO_2 + H_2O$ V_{CO_2} = 10 cm^3 = $V_{org\ total}$ V_{O_2} left = 18 – 10 = 8 cm^3 V_{O_2} used = 20 – 8 = 12 cm^3 Let V_{CH_4} = x, V_{HCHO} = 10 – x Since $CH_4 \equiv 2O_2$, $HCHO \equiv O_2$			

<table>
<tr><td></td><td></td><td>$2x + (10 – x) = 12$
$x = 2$
Ratio is 4:1</td></tr>
<tr><td>12</td><td>C</td><td>No of mole of Chlorine= (90/1000) / 24 = 0.00375 mol
Mass of NaClO = $0.00375 \times (23.0+ 35.5+ 16.0) = 0.27948$ g
Volume of solution = 0.2794 / 0.005 = 55.87 cm^3</td></tr>
<tr><td>13</td><td>D</td><td>rate = $k\,[O_2]\,[NO_2]^2$
rate = $k\,[O_2]\,[NO_2]^2 = k\,(0.1)\,(0.1)^2 = 0.1$
k =100
rate = $100\,[O_2]\,[NO_2]^2$</td></tr>
<tr><td>14</td><td>B</td><td>Half life = ln 2/ k = 1386s
(0.5)n = 0.4
n = 1.32
time = $1386 \times 1.32 = 1829$s = 30.5 min</td></tr>
<tr><td>15</td><td>C</td><td>At constant temperature, when pressure increase, % of product decreases. Eqm position shift to the left to reduce the pressure by reducing the no. of moles of particles. Hence left side of the eqm should have less no. of moles of gaseous particles.
At constant pressure, as T increase, % product decrease. This implies that forward reaction is endothermic reaction.</td></tr>
<tr><td>16</td><td>A</td><td>$s = 3.60 \times 10^{-5}$ mol dm^{-3}
$K_{sp} = 4s^3 = 4(3.60 \times 10^{-5})^3 = 1.866 \times 10^{-13}$ $mol^3\ dm^{-9}$
pOH = 2.0
$[OH^-] = 10^{-2}$ mol dm^{-3}
Let solubility of salt in buffer solution of pH 12.0 be a mol dm^{-3}
$(10^{-2} + 2a)^2(a) = 1.866 \times 10^{-13}$
Since a is small, $10^{-2} + 2a \approx 10^{-2}$
$(10^{-2})^2(a) = 1.866 \times 10^{-13}$
$a = 1.87 \times 10^{-9}$</td></tr>
<tr><td>17</td><td>B</td><td>
<table>
<tr><td></td><td>$CaCO_3$</td><td>CaF_2</td></tr>
<tr><td>K_{sp}</td><td>8.7×10^{-9}</td><td>4.0×10^{-11}</td></tr>
<tr><td>Solubility</td><td>$(8.7 \times 10^{-9})^{1/2} = 9.32 \times 10^{-10}$</td><td>$(4.0 \times 10^{-11}/4)^{1/3} = 4.00 \times 10^{-11}$</td></tr>
</table>
Option 1: Correct.
Option 2: Correct. Adding NaF will increase $[F^-]$. IP of CaF_2 increases.
Option 3: Incorrect. K_{sp} is affected only by T.
Option 4: Incorrect.
Let concentration of Ca^{2+} in solution be y mol dm^{-3}
IP of $CaCO_3$ = (y)(1) = y
IP of $CaF_2 = (y)(1)^2 = y$
Since CaF_2 has a lower K_{sp} value, CaF_2 will precipitate out 1^{st}.</td></tr>
</table>

<table>
<tr><td>18</td><td>C</td><td>$H_2PO_4^- + HBO_3^{2-} = HPO_4^{2-} + H_2BO_3^-$
Acid Base Acid Base
Since forward reaction is favoured, the acid and base on the LHS are stronger.</td></tr>
<tr><td>19</td><td>D</td><td>A: Incorrect. K_w, is the product of K_a of citric acid and K_b of citrate anion.
B: Incorrect. The pH of a buffer solution remains relatively unchanged when small amount of water is added to it OR the pH of a buffer solution reaches pH 7 when large amount of water is added to it.
C: Incorrect. The pH of a buffer solution remains <u>relatively</u> unchanged when small amount of acid or base is added to it.
D: Correct.</td></tr>
<tr><td>20</td><td>A</td><td>Red: $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$
Ox: $2Cl^- \rightarrow Cl_2 + 2e^-$
Amount of NaCl = (58.5 × 1000) / 58.5 = 1000 mol = Amount of Cl^-
Amount of Cl_2 = 1000 / 2 = 500 mol Mass of Cl_2 = 500 × 71 = 35.5 kg
Amount of H_2 = 1000 / 2 = 500 mol Mass of H_2 = 500 × 2 = 1 kg
Amount of NaOH = 1000 mol Mass of NaOH = 1000 × 40 = 40 kg</td></tr>
<tr><td>21</td><td>D</td><td>Ox: $M \rightarrow M^{n+} + ne^-$
Red: $ClO^- + H_2O + 2e^- \rightarrow Cl^- + 2OH^-$ $E^\ominus = 0.81$ V
Under standard conditions, lg [1 mol dm^{-3} M^{n+}] = 0
Let $E^\ominus(M^{n+}/M)$ be x
1.2 = 0.81 – x
x = –0.39 V</td></tr>
<tr><td>22</td><td>C</td><td>This question is about probable products from a single propagation step.
Options A and C: products attained through a single propagation step
Options B and D: products required multisteps

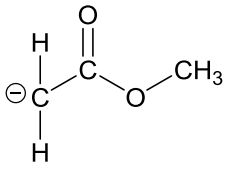
<table><tr><td></td><td>Bonds broken</td><td>Bonds formed</td><td>ΔH (bonds broken – bonds formed)</td></tr><tr><td>A</td><td>C–H</td><td>C–H</td><td>0</td></tr><tr><td>C</td><td>C–Cl</td><td>C–C</td><td>–10</td></tr></table></td></tr>
<tr><td>23</td><td>C</td><td>Refer to Kinetic notes Pg 35</td></tr>
</table>

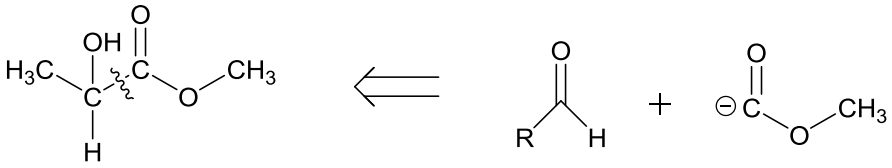
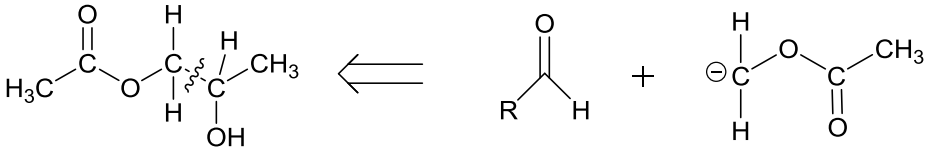
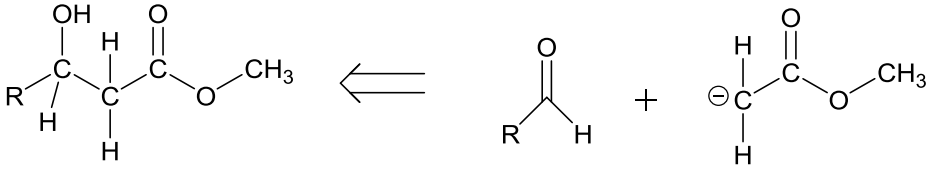
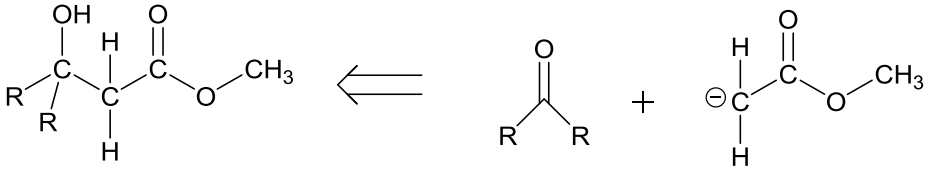
24 D

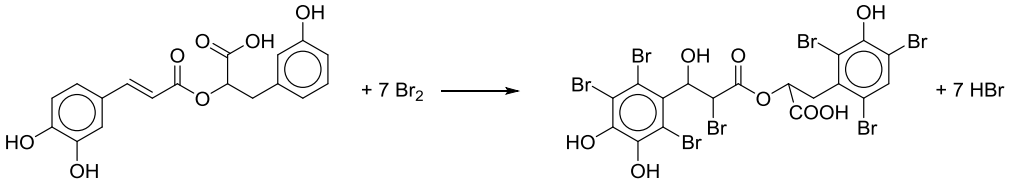
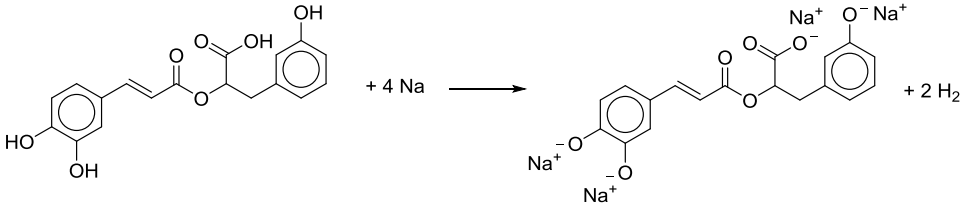
$2NaOH + H_2SO_4 \rightarrow H_2O + Na_2SO_4$

	n_{NaOH} reacted/ mol	n_{NaOH} remains/ mol	$n_{H_2SO_4}$ required/ mol	Remarks
W	$0.01 \times 2 = 0.02$	$0.05 - 0.02 = 0.03$	0.015	Rxn: Hydrolysis of amides product: $(COO^-)_2$
X	0.01	$0.05 - 0.01 = 0.04$	0.02	Rxn: Hydrolysis of nitrile product: CH_3COO^-
Y	0	0.05	0.025	Aryl halides do not undergo hydrolysis

25 C

The anion generated from $CH_3CO_2CH_3$ in the presence of a strong base is $^-CH_2CO_2CH_3$ which is  .

	Starting materials
A	 Starting materials include an aldehyde, but incorrect nucleophile.
B	 Starting materials include an aldehyde, but incorrect nucleophile.
C	 Starting materials include an aldehyde (R is $-CH_2CH_3$) and correct nucleophile.
D	 Starting materials include the correct nucleophile, but a ketone.

26	B	Statement 1: Incorrect. 1 mole of rosmarinic acid reacts with 7 moles of Br_2.  Statement 2: Correct.  Statement 3: Incorrect. No orange ppt due to absence of carbonyl C=O.
27	A	• **T** undergoes reduction with $NaBH_4$, only gains 2 H atoms, **T** contains only 1 C=O, either ketone or aldehyde. • **T** undergoes oxidation with alkaline iodine, ○ **T** contains $-COCH_3$ and $-CH(OH)CH_3$. ○ **T** gives $C_{x-1}H_{y-3}O_{z+2}{}^{2-}$, loss of C*I* ➔**T** undergoes alkaline hydrolysis (using <u>warm</u> alkali) ➔**T** contains acyl chloride, $-COCl$ instead of alkyl chloride, RCl (alkyl chloride requires strong heating. $-COCl$ reacts to give $-COOH$, deprotonates to give $-COO^-$. • T does not react with dry $SOCl_2$, T contains $-COCH_3$ instead of $-CH(OH)CH_3$. ○ With alkaline iodine, $-COCH_3$ gives an organic product $-COO^-$.
28	A	Statement B: Incorrect product. Dilute HNO_3 should give mono-substituted product. Statement C: Incorrect reaction. The reaction is known as elimination. Statement D: Incorrect conditions. With limited CH_3NH_2, the product will be poly-substituted. Other conditions required: ethanolic medium, heat.
29	D	A: Incorrect. L is a bidentate ligand, with lone pairs on #O^- and N atoms that are available for dative bonding to the central metal atom/ion. B: Incorrect & D: Correct. The peak on the colorimeter reading graph occurs at the intersection corresponding to 4 cm^3 of $Ni^{2+}(aq)$ and 6 cm^3 of L(aq). Amount of $Ni^{2+} = 0.004 \times 3 \times 10^{-3} = 1.2 \times 10^{-5}$ mol Amount of L = $0.006 \times 4 \times 10^{-3} = 2.4 \times 10^{-5}$ mol Hence, mole ratio of Ni^{2+} to L = 1 : 2 Thus, the complex formed is NiL_2, which is a neutral complex. C: Incorrect. The question mentions the complex to appear red, which means the wavelengths complementary to red light, i.e., mainly green/green-blue light, will be strongly absorbed.
30	B	A: Not relevant. The statement about electrical conductivity is correct, but it is

		not the explanation to the use of transition metals as catalysts. B: Correct. C: Not relevant. The statement about forming coloured ions is correct, but it is not the explanation to the use of transition metals as catalysts. D: Incorrect. The question mentions the use of transition **metals** as heterogeneous catalysts, not about transition metal ions which are used mainly for homogeneous catalysis.

Paper 2

RVHS JC 2 H2 CM Prelim Suggested Solutions

1 (a) (i) Chromium sheet

(ii) Total no. of Cr atoms

$= (\frac{0.1}{3.0\times10^{-12}})^2 \times 1000 \times 0.9$

$= 1.0 \times 10^{24}$ atoms

Amount of Cr atoms = $\frac{1.00 \times 10^{24}}{6.02\times10^{23}}$ = 1.661 mol

$Cr \rightarrow Cr^{3+} + 3e$

Amount of e = $1.661 \times 3 = 4.983$ mol

$Q=nF$

$= 4.983 \times 96500 = 4.809 \times 10^5$ C

$Q = It$

$= (4.803 \times 10^5) \div 4 = 1.202 \times 10^5$ s = 33.4 h

(iii) Anodising of aluminium occurs at the anode. Oxygen produced at the anode reacts the aluminium, forming a layer of Al_2O_3 on the electrode.

$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$

$2Al(s) + {}^3/_2O_2(g) \rightarrow Al_2O_3(s)$

(b) (i) The first ionisation energy is the energy required to remove 1 mole of electrons from 1 mole of gaseous atoms to form one mole of singly charged gaseous cations.

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

(ii) As electrons are removed one by one from a neutral atom, an ion of increasing positive charge will be formed. The remaining electrons will be more strongly attracted to the nucleus via electrostatic attraction, requiring more energy to remove.

When an electron is removed from the inner principal quantum shell, the electron experiences less shielding effect, hence requiring more energy to remove.

(iii) There is a significant increase from the 5^{th} to 6^{th} ionisation energies, implying that the 6^{th} electron is removed from an inner principal quantum shell which is closer to the nucleus and experiences a greater electrostatic force of attraction by the nucleus. Therefore, element **X** is in Group 15.

(iv) $1s^2 2s^2 2p^6 3s^2 3p^3$

2 (a) (i) With H_2O: Bronsted-Lowry base. Methylamine accepts a H^+ from H_2O. / Lewis base. Methylamine donates a lone pair of electrons to H^+.

With BF_3: Lewis base. Methylamine donates a lone pair of electrons to (the electron-deficient) B atom.

(ii)

	CH_3NH_2	+	H_2O	=	$CH_3NH_3^+$	+	OH^-
$[\ ]_I$	0.10				0		0
$[\ ]_C$	$-x$				$+x$		$+x$
$[\ ]_E$	$0.10 - x$				x		X

$$10^{-3.38} = \frac{(x)(x)}{0.10 - x}$$

Assume x is small such that $0.10 - x \approx 0.10$

$$10^{-3.38} = \frac{x^2}{0.10}$$

$[OH^-] = x = \underline{6.457 \times 10^{-3}\ mol\ dm^{-3}}$

$pOH = -\lg(6.457 \times 10^{-3}) = 2.19$

$pH = 14 - 2.19 = \underline{11.8}$

(b) (i) Hydrochloric acid

(ii) pOH = 14 – 11.1 = 2.9

$$pOH = pK_b + \lg \frac{[salt]}{[base]}$$

$$2.9 = 3.38 + \lg \frac{[salt]}{[base]}$$

$$\frac{[salt]}{[base]} = 0.33 \text{ (shown)}$$

(iii) $CH_3NH_2 + HCl \rightarrow CH_3NH_3^+ Cl^-$

Amount of CH_3NH_2 initially = $\frac{50}{1000} \times 0.10 = 0.00500$ mol

Let the amount of HC*l* to be added be y mol.

Amount of $CH_3NH_3^+ Cl^-$ formed = y mol

Amount of CH_3NH_2 remaining = (0.00500 – y) mol

$$\frac{y}{0.00500 - y} = 0.33$$

y = 0.00165 – 0.33y

y = 0.001241

Volume of HC*l* to be added = $\frac{0.001241}{0.10}$ = 0.01241 dm^3 = <u>12.4 cm^3</u>

(c) **<u>FA 1</u>** <u>is $MgCO_3$</u> and **<u>FA 2</u>** <u>is $BaCO_3$</u>. <u>Mg^{2+} is smaller</u> than Ba^{2+}, <u>charge density of Mg^{2+} is higher</u> than that of Ba^{2+}. <u>Polarising power of Mg^{2+} is higher</u>. The <u>C#O bonds</u> of CO_3^{2-} <u>in $MgCO_3$ are weakened to a larger extent</u>. and require less energy to break. $MgCO_3$ decomposes at a lower temperature to produce CO_2.

$MgCO_3 \rightarrow MgO + CO_2$

$BaCO_3 \rightarrow BaO + CO_2$

MgO reacts with water to form <u>$Mg(OH)_2$, which is sparingly soluble</u> in water to give a weakly alkaline solution.

$MgO + H_2O \rightarrow Mg(OH)_2$

$Mg(OH)_2 = Mg^{2+} + 2OH^-$

BaO reacts with water to form <u>$Ba(OH)_2$, which dissociates completely</u> in water to give a strongly alkaline solution.

$BaO + H_2O \rightarrow Ba(OH)_2$

$Ba(OH)_2 \rightarrow Ba^{2+} + 2OH^-$

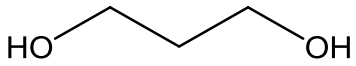
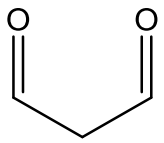
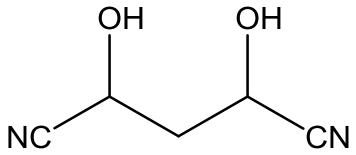
3 **(a)** **(i)** 2,4-dihydroxypentane-1,5-dioic acid

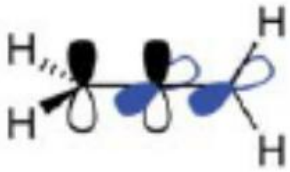
Accept 2,4-dihydroxypentadioic acid

(ii)

Reaction	Reagents and conditions
1	NaOH (aq), heat (under reflux)
2	$K_2Cr_2O_7/H_2SO_4$ (aq), heat with immediate distillation
3	HCN, trace amount of NaCN or NaOH

(iii)

Compound	Structure
E	
F	
G	

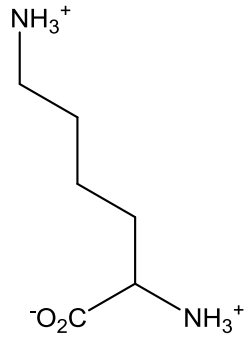
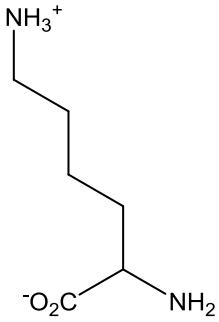
(iv) 

(v) $H_3C-C\equiv C-H$

(b) **(i)** Large amount of energy is required to overcome the strong electrostatic forces of attraction that exist between the charged $-NH_3^+$ and $\#CO_2^-$ groups of different zwitterions. Hence, high mpt and solid under rtp.

The energy released from formation of (favourable) ion–dipole interactions between zwitterions and polar water molecules is sufficient to overcome the electrostatic attraction between zwitterions and hydrogen bonds between water.

(ii)

	
pH 6.0	pH 9.5

4 (a) (i) A mixture containing equal amounts of both enantiomers will show no net optical activity as their effects on plane-polarised light cancel each other out.

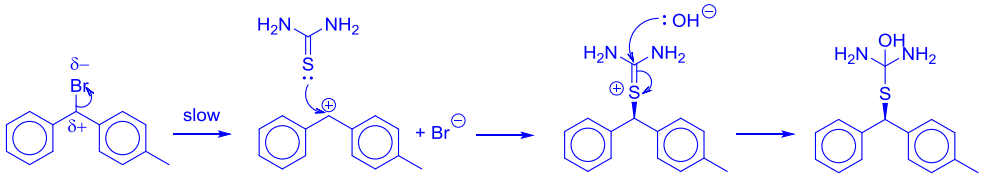
(ii) The nucleophilic substitution takes place via S_N1 mechanism, which involves the formation of a trigonal planar carbocation. There is an equal probability of the nucleophile attacking from either side of the plane, giving rise to equimolar mixture of two stereoisomers.

(iii) Sulfur is less electronegative than nitrogen, hence, the lone pair of electrons on S is more available for donation/ to act as nucleophile.

Or

The lone pair of electrons on N is delocalised over the C=S bond, hence unavailable for donation to electron-deficient carbon, unlike the lone pair of electrons on S atom, which is available for donation.

(iv)



(b) C–C*l* bond is stronger than C–Br, more energy is needed to break the C–C*l* bond, the rate of reaction with benzhydryl chloride is slower.

5 **(a)** **(i)** The acid is a catalyst and is <u>regenerated</u> eventually. Hence, its concentration remains <u>largely unchanged</u> and is <u>independent</u> to the reaction rate.

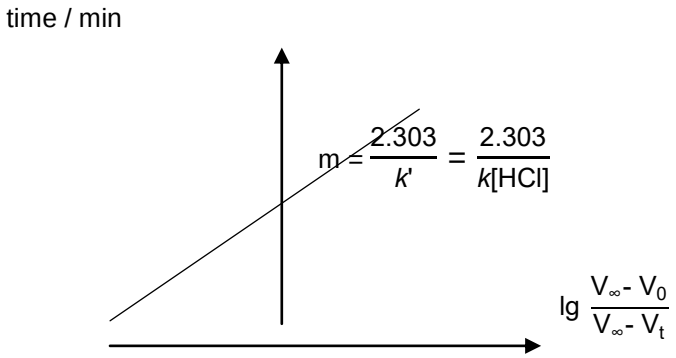
(ii) As <u>more CH_3COOH is being produced</u>, V_t is expected to increase.

(iii) $V_\infty - V_t \propto$ amount/ concentration of methyl acetate left unhydrolysed at time t.

(iv) Plot a straight line graph of time vs lg $\frac{V_\infty - V_0}{V_\infty - V_t}$

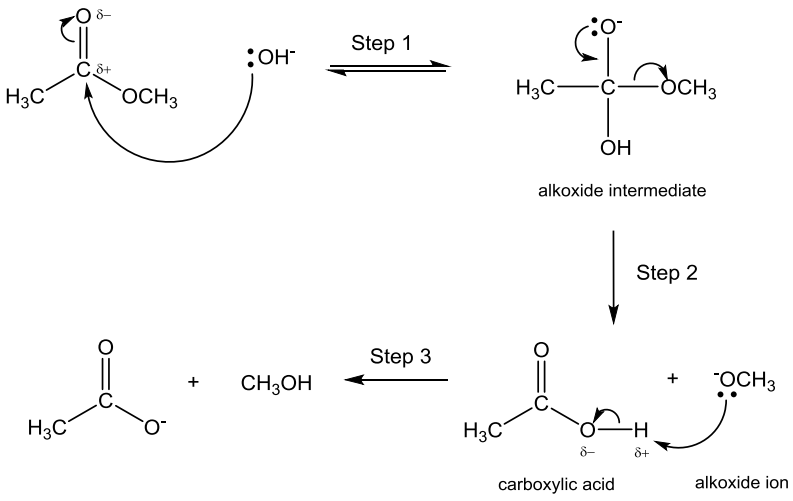
Gradient will be $\frac{2.303}{k'}$

or

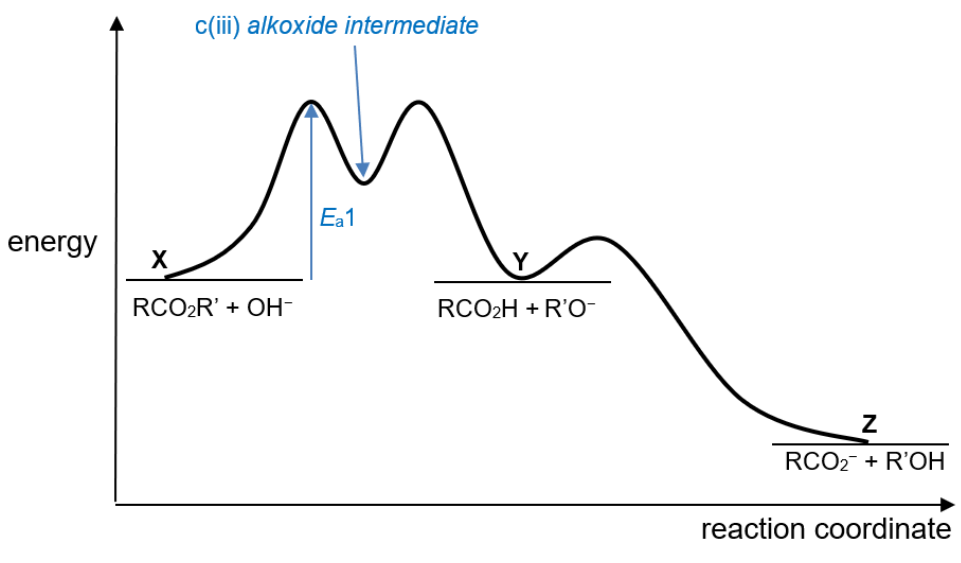


Hence, $k' = \frac{2.303}{\text{gradient}} \rightarrow k = \frac{2.303}{\text{gradient}[HCl]}$

(b)



(c) **(i)**
(iii)



Step 1 is the rate-determining step. Activation energy for Step 1 is the highest among the 3 steps, as indicated on the energy profile diagram.

(ii) Rate = k $[RCO_2R']$ $[OH^-]$

(iv) In Step 1, a C#O bond is formed and a C#O π bond is broken.

In Step 2, a C#O π bond is formed and a C#O bond is broken.

Or A C-O bond is broken and a C-O bond is formed.

Hence the net enthalpy change is zero.

(v) The negative charge on the RCO_2^- ion is delocalised over the $\#COO^-$, allowing the RCO_2^- ion to be stabilised by resonance. (The negative charges on OH^- and $R'O^-$ are localised on the O atom respectively). Thus, the RCO_2^- is much more stable than either OH^- or $R'O^-$.

6 **(a)** A transition element is a d-block element which forms at least one stable ion with a partially filled d subshell.

(b) $K_s = \dfrac{[Co(NH_3)_6^{2+}]}{[Co(H_2O)_6^{2+}][NH_3]^6}$

(c) Initial $[NH_3] = (\dfrac{50.0}{1000} \times 0.200) \div \dfrac{100.0}{1000} = 0.100 \text{ mol dm}^{-3}$

Initial $[Co(H_2O)_6^{2+}] = (\dfrac{50.0}{1000} \times 0.200) \div \dfrac{100.0}{1000} = 0.100 \text{ mol dm}^{-3}$

	$[Co(H_2O)_6]^{2+}(aq)$	+ $NH_3(aq)$ ⇌	$[Co(H_2O)_5(NH_3)]^{2+}(aq)$	+ $H_2O(l)$
$[\ ]_I$	0.100		0.100	0
$[\ ]_C$	–x		–x	+x
$[\ ]_E$	0.100 – x		0.100 – x	x

$K_c = 10^{1.30} = \dfrac{x}{(0.100 - x)^2}$

x = 0.2002 (rejected) or 0.04995

$[Co(H_2O)_6]^{2+} = 0.100 - 0.04995 = 0.05005 = \underline{0.0501 \text{ mol dm}^{-3}}$

$[Co(H_2O)_5(NH_3)]^{2+} = x = \underline{0.0500 \text{ mol dm}^{-3}}$

(d) **(i)** (1) $[Co(H_2O)_6]^{2+} + 6NH_3 \rightleftharpoons [Co(NH_3)_6]^{2+} + 6H_2O$ $\quad K_{s1} = 10^{5.11}$

$$10^{5.11} = \frac{[Co(NH_3)_6^{2+}]}{[Co(H_2O)_6^{2+}][NH_3]^6}$$

(2) $[Co(H_2O)_6]^{2+} + 4SCN^- \rightleftharpoons [Co(SCN)_4]^{2-} + 6H_2O$ $\quad K_{s2} = 10^{3.00}$

$$10^{3.00} = \frac{[Co(SCN)_4^{2-}]}{[Co(H_2O)_6^{2+}][SCN^-]^4}$$

Combining (1) and (2)

For $[Co(SCN)_4]^{2-} + 6NH_3 = [Co(NH_3)_6]^{2+} + 4SCN^-$:

$$K_c = \frac{[Co(NH_3)_6^{2+}][SCN^-]^4}{[Co(SCN)_4^{2-}][NH_3]^6}$$

$$= \frac{[Co(NH_3)_6^{2+}]}{\cancel{[Co(H_2O)_6^{2+}]}[NH_3]^6} \times \frac{\cancel{[Co(H_2O)_6^{2+}]}[SCN^-]^4}{[Co(SCN)_4^{2-}]}$$

$$= K_{s1} \times \frac{1}{K_{s2}}$$

$= \frac{10^{5.11}}{10^{3.00}}$

= 129 (shown)

(ii) $[Co(SCN)_4]^{2-}(aq) + 6NH_3(aq) = [Co(NH_3)_6]^{2+}(aq) + 4SCN^-(aq)$

bright blue light brown

An increase in temperature favours the endothermic reaction to consume some heat. When temperature increases, the position of equilibrium shifts right to produce more $[Co(NH_3)_6]^{2+}(aq)$ and turns the solution light brown. The forward reaction is endothermic.

(iii) A hexadentate ligand is able to hold onto the Co^{2+} ion more tightly compared to 6 monodentate ligand/ a hexadentate ligand provides chelating effect, hence $[Co(edta)]^{2-}$ is more stable.

$[Co(H_2O)_6]^{2+}(aq) + edta^{4-}(aq) \rightleftharpoons [Co(edta)]^{2-}(aq) + 6H_2O(l)$

Or

As the amount of particles increases from 2 mol to 7 mol, the ligand exchange reaction is entropically-driven / the disorder of the system increases.

(d) (iv) The presence of NH_3 ligands causes the 3d orbitals to split into two sets of non-degenerate orbitals with different energies. The energy gaps, ΔE, for the two complexes are different from each other as the cobalt ions are in different oxidation states. The ΔE falls within the energy range of the visible spectrum of the electromagnetic spectrum. Thus, radiation in the visible region is absorbed when an electron from a lower energy d orbital is promoted to a partially filled/ empty d orbital of higher energy. The colours observed are complement of the colours absorbed.

(e) (i) In an octahedral complex, the ligands are modelled as six-point negative charges that surround the positively-charged metal ion/ approach the central metal atom/ion along the (cartesian) axes, the d_{z^2} and $d_{x^2-y^2}$ orbitals have lobes that are in the region of the negative charges, while the d_{xy}, d_{yz} and d_{xz} orbitals have lobes that project between the charges. Hence, the orbitals on the ligands repel the d_{z^2} and $d_{x^2-y^2}$ orbitals more than the other d orbitals.

(ii) (I) LFSE $= [(0.4 \times 4) - (0.6 \times 2)] \times \alpha =$ 0.4α kJ mol^{-1}

(II) LFSE $= [(0.4 \times 6) - (0.6 \times 3)] \times \beta =$ 0.6β kJ mol^{-1}

(f) **(i)** Across the period, ionic radius of M^{2+} decreases, hence charge density of M^{2+} increases. Stronger electrostatic attractions/ ion-dipole interactions are formed between the M^{2+} ion and H_2O molecules, hence ΔH_{hyd} becomes more negative.

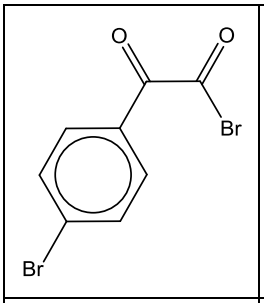
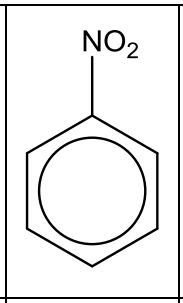
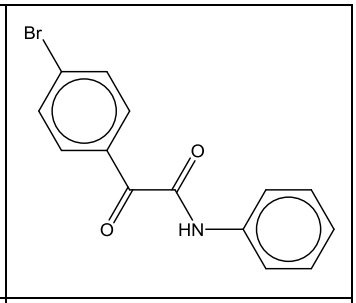
(ii) The LFSE for these 2 ions is zero, hence there is no deviation./

They correspond to Mn^{2+} with d^5 (high spin) configuration and Zn^{2+} with d^{10} configuration respectively./

The 3d orbitals of these ions are half-filled (in high spin configuration) and fully-filled respectively.

Paper 3

1 (a) (i)

		
A	**B**	**C**

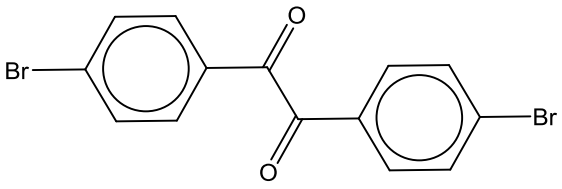
[3]

(ii)

Steps	Reagents and conditions
2	Conc HNO_3, conc H_2SO_4, maintained at 55°C
4	Sn, concentrated HC*l*, heat Followed by NaOH(aq)
6	LiA/H_4 in dry ether

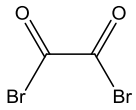
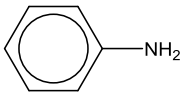
[3]

(iii)



[1]

(iv)

		C_6H_5Br	
Test 1: $AgNO_3(aq)$	Cream ppt	No ppt	No ppt
Test 2: Add $Br_2(aq)$	Orange $Br_2(aq)$ remains	Orange $Br_2(aq)$ remains	Orange $Br_2(aq)$ turns colourless

[4]

(b)

Equations	pH
$PCl_5(s) + 4H_2O(l) \rightarrow H_3PO_4(aq) + 5HCl(aq)$	2
$MgCl_2(s) + 6H_2O(l) \rightarrow [Mg(H_2O)_6]^{2+}(aq) + 2Cl^-(aq)$ $[Mg(H_2O)_6]^{2+}(aq) + H_2O(l) \rightleftharpoons [Mg(H_2O)_5(OH)]^+(aq) + H_3O^+(aq)$	6.5

[4]

(c) **(i)** $\Delta H_r^\ominus = 2(-393.5) + 4(-241.8) - 83.3 - 2(9.1)$

$= -1855.7$

$= -1860 \text{ kJ mol}^{-1}$ [1]

(ii) There is an <u>increase in gaseous particles from 0 to 9</u>. [1]

(iii) $\Delta S_r^\ominus = = 2(213.8) + 4(188.8) + 3(191.6) - (304.7) - 2(304.4)$

$= +844.1 \text{ J mol}^{-1} \text{ K}^{-1}$

$= +0.844 \text{ kJ mol}^{-1} \text{ K}^{-1}$

$\Delta G_r^\ominus = -1856 - (298 \times 0.8441)$

$= -2108$

$= -2110 \text{ kJ mol}^{-1}$ [2]

2 (a) (i) $2Ag^+(aq) + Ni(s) \rightarrow 2Ag(s) + Ni^{2+}(aq)$ [1]

(ii) $\Delta G = -nFE = -(2)(96500)(0.924) = -178 \text{ kJ mol}^{-1}$ [1]

(iii) $K_{sp} = [Ag^+]^2[Cr_2O_7^{2-}]$ [1]

(iv) $E_{cell} = E_{red} - E_{ox}$

$+0.924 = E_{electrode} - (-0.25)$

$E_{electrode} = +0.674 \text{ V}$ [1]

(v) $+0.674 = 0.80 + 0.0592 \log [Ag^+]$

$[Ag^+] = 7.441 \times 10^{-3} = 7.441 \times 10^{-3} \text{ mol dm}^{-3}$

$K_{sp} = (7.441 \times 10^{-3})^2 \times ½ \times 7.441 \times 10^{-3}$

$= 2.06 \times 10^{-7} \text{ mol}^3 \text{ dm}^{-9}$ [2]

(vi) Let s' be the reduced solubility of $Ag_2Cr_2O_7$,

assume that s' << 0.5,

$[Ag^+]^2 \times 0.5 = 2.06 \times 10^{-7}$

$[Ag^+] = 6.42 \times 10^{-4} \text{ mol dm}^{-3}$ [1]

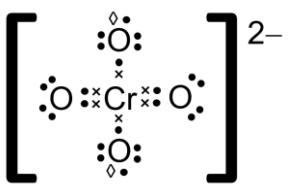
(vii) $NiCO_3$ will be precipitated, $[Ni^{2+}]$ decreases, position of equilibrium of $Ni^{2+} + 2e = Ni$ shifts left to replenish some of the Ni^{2+}, $E(Ni^{2+}/Ni)$ becomes less positive. E_{cell} becomes more positive. [2]

(b) (i) The energy released when 1 mole of solid $Na_2Cr_2O_7$ is formed from its constituent gaseous ions, $Na^+(g)$ and $Cr_2O_7^{2-}(g)$. [1]

(ii) $|\text{L.E.}| \ \alpha \ \left|\frac{q^+q^-}{r^+ + r^-}\right|$

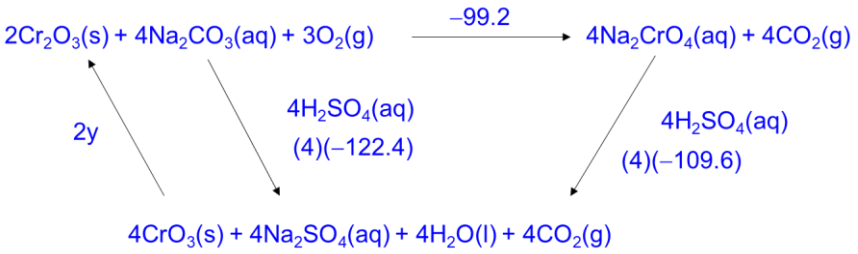
The lattice energy of $Na_2Cr_2O_7$ is less exothermic than that of Na_2CrO_4. Size of $Cr_2O_7^{2-}$ is bigger than that of CrO_4^{2-}. [2]

(c) (i)



[1]

(ii)



$-99.2 = (4)(-122.4) - (2y) - (4)(-109.6)$

$y = +24.0$ [3]

(d) **(i)** Amount of $(NH_4)_2Cr_2O_7 = \frac{20}{252} = 7.937 \times 10^{-2}$ mol

Pressure = $\frac{5 \times 7.937 \times 10^{-2} \times 8.31 \times (273 + 225)}{5 \times 10^{-3}} = 3.28 \times 10^{5}$ Pa [1]

(ii) Under high temperature and low pressure.

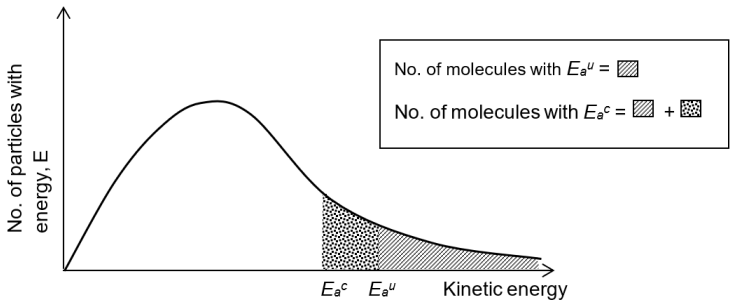
At high temperature, the gas particles are given sufficient energy to overcome the intermolecular forces of attraction between them, so the interactions between them become insignificant.

Under low pressure, the gas occupies a large volume, the size of the gas particles become insignificant compared to the size of the container. [3]

(e) Step 1: $NO_2(g) + SO_2(g) \rightarrow SO_3(g) + NO(g)$

Step 2: $NO(g) + \frac{1}{2}O_2(g) \rightarrow NO_2(g)$

NO_2 is a catalyst because it increases the rate of reaction by providing an alternative pathway with lower E_a (through NO intermediate). It is not consumed but regenerated (infer from equation).



More reactant particles possess the energy required for an effective collision and the frequency of effective collisions increases. The rate of reaction is thus increased. [4]

3 (a) In **A**, C:H ratio ≈ 1:1, **A** contains a benzene ring.

A undergoes electrophilic substitution and/ or electrophilic addition with Br_2(aq).

A contains a phenol and/ or alkene.

Based on molar mass, **B** contains 4 Br atoms and –OH OR 3 Br atoms with 1 halohydrin group.

A is 1, 3 disubstituted.

R_1/ R_3 are $-CH_3$ group

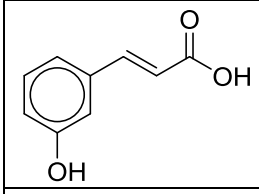
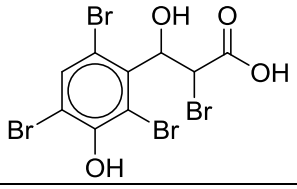
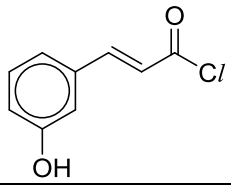
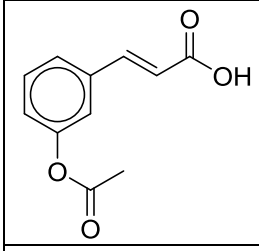
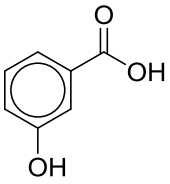
A undergoes nucleophilic substitution with PCl_5 to give **C**. **A** contains carboxylic acid, **C** contains acyl chloride

A gives violet colouration with neutral iron(III) chloride. **A** contains a phenol.

D undergoes acidic hydrolysis and oxidative cleavage/ oxidation of side chain.

E contains phenol and benzoic acid.

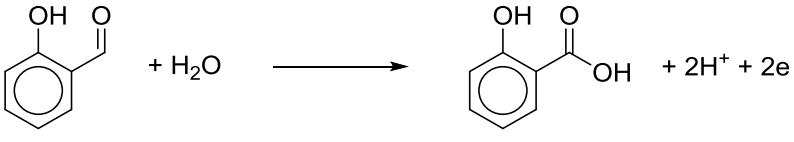
A/B/C/D/E has two substituents on benzene ring.

A	B	C
		
D	E	
		

[10]

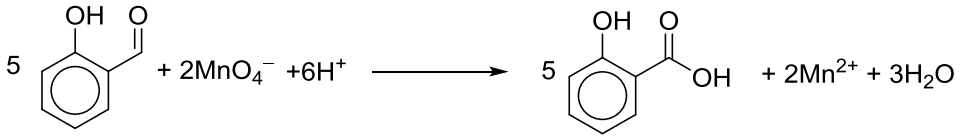
(b) (i)  [1]

(ii) +1 [1]

(iii) [O]: 

[R]: MnO_4^- + $8H^+$ + $5e^-$ → Mn^{2+} + $4H_2O$ [2]

Overall:



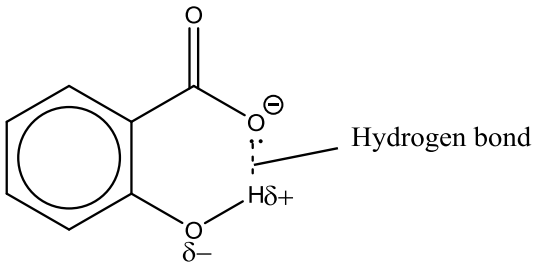
(c) Increasing acidity: benzoic acid < 3-hydroxybenzoic acid < salicylic acid

Anion stability: benzoate ion < 3-hydroxybenzoate ion < 2-hydroxybenzoate ion

Salicylic acid and 3-hydroxybenzoic acid are more acidic than benzoic acid due to the presence of extra hydroxy group on the benzoic acid. The electronegative oxygen increases the delocalisation of negative charge into the benzene ring/ has an inductive effect on the benzoate anion formed and thus stabilising the anion resulting in lower p*Ka* comparatively.

(Resonance effect of -OH opposes the release of H^+, not in line with the data provided)

Salicylic acid forms an anion which is capable of forming intramolecular hydrogen bond as the carboxylate anion is next to phenol group. Thus, enhancing the anion stability, resulting in much lower p*Ka.*



[3]

4 (a) (i) The volatility of the halogens decreases down the group (due to increasing boiling point).

F_2 is a pale-yellow gas, Cl_2 is a yellowish-green gas, Br_2 is a reddish-brown liquid and I_2 is a black solid. The colour intensifies/becomes darker down the group. [3]

(ii) Fluorine reacts explosively even in the dark.

Chlorine reacts explosively in sunlight but slowly in the dark.

Bromine reacts at above 200 °C over Pt catalyst [2]

(b) (i) $3(SCN)_2 + 4H_2O \rightarrow H_2SO_4 + HCN + 5HSCN$ [1]

(ii) M_r of $(SCN)_2$ = 116.2

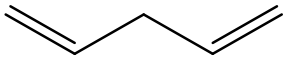
Difference in molecular mass = 300.4 – 68.0 = 232.4

Number of $(SCN)_2$ added = 232.4 / 116.2 = 2 [2]

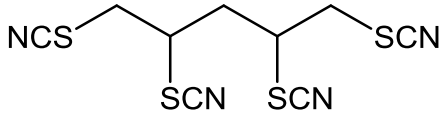
➔ There are 2 C∃C bonds present in the hydrocarbon.

Hence, with the molecular mass of 68.0, there should be 5 C and 8 H atoms in the hydrocarbon.

Structure of hydrocarbon:

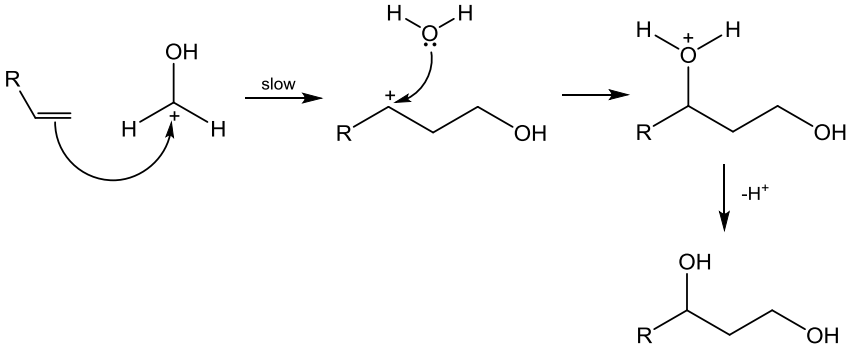


Structure of the achiral product:



(c) **(i)** Acid-base reaction [1]

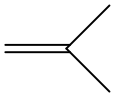
(ii) Electrophilic addition



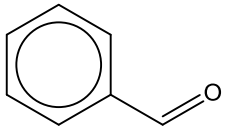
[3]

(iii)

Starting alkene: (2-methylpropene)



Starting aldehyde: (benzaldehyde)



[2]

(d) Since ΔH° is positive and ΔS° is also positive, $\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$ will only be negative at high temperatures when $|\Delta H^{\circ}| < |-T\Delta S^{\circ}|$. Therefore the reaction is spontaneous only at high temperatures.

When $\Delta G^{\circ} = 0$, $T = \Delta H^{\circ} / \Delta S^{\circ}$

$= 177 / 0.285$

$= 621$ K (348 ^{o}C)

The minimum temperature at which the reaction will take place is [2]

621 K.

(e) The #^{b}NH# group is a weaker base than the #^{c}NH$_2$ group.

The lone pair of electrons on the nitrogen atom in the #^{b}NH# group is delocalised into the π electron cloud of the benzene ring. Hence, the lone pair on the N atom in the #^{b}NH# group is less available for protonation than that in the #^{c}NH$_2$ group.

The #^{c}NH$_2$ group will be a stronger base than the ∃^{a}N# group.

The lone pair of electrons on the nitrogen atom in the ∃^{a}N# group resides in a sp^2 orbital [✓]and that in the #^{c}NH$_2$ group resides in a sp^3 orbital.

Since there is less s character/ more p character in a sp^3 orbital, as compared to a sp^2 orbital, the lone pair on the N atom in the #^{c}NH$_2$ group is further/ less tightly bound to the nucleus, and it is more available for protonation. [4]

5 (a) Electrical conductivities are high for Na, Mg and A*l* due to the presence of delocalised valence electrons which are able to act as mobile charge carriers. Electrical conductivity increases from Na to A*l* due to an increasing number of delocalised valence electrons.

Electrical conductivity drops sharply at Si as it is a semi-conductor.

Electrical conductivities drop to (almost) zero from P to Ar due to an absence of mobile charge carriers to conduct electricity. [3]

(b) **(i)**

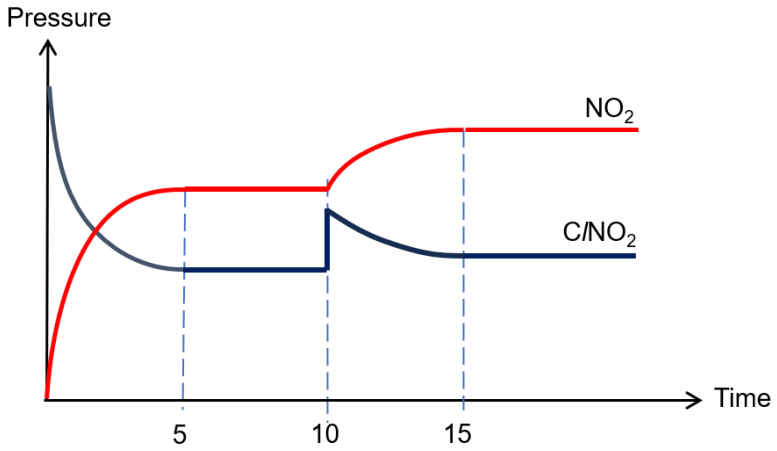
	$ClNO_2(g)$	+	$NO(g)$	=	$2NO_2(g)$	$ClNO(g)$
Initial pressure/ atm	1.5		1.5		0	0
Change in pressure/ atm	–0.62(1.5)		–0.62(1.5)		+0.62(1.5)	+0.62(1.5)
Equilibrium pressure/ atm	(0.38)(1.5) = 0.57		(0.38)(1.5) = 0.57		+0.62(1.5) =0.93	+0.62(1.5) =0.93

$$K_p = \frac{p_{ClNO}p_{NO_2}}{p_{ClNO_2}p_{NO}}$$

$$= \frac{(0.93)^2}{(0.57)^2} = 2.66$$

[2]

(ii)



- equilibrium is attained at the 5th minute
- addition of $ClNO_2$ and equilibrium is attained at the 15th minute
- addition of helium

[3]

(c) **(i)** Carbon nanotube has giant covalent structure. The carbon atoms are covalently bonded to three other carbon atoms. [1]

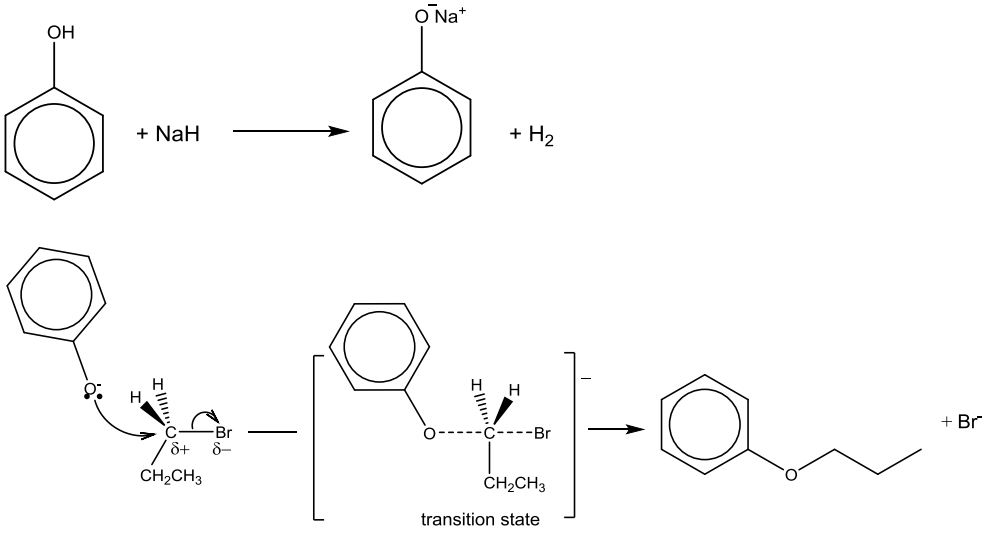
(ii) Multi–walled carbon nanotube has higher tensile strength as it has more covalent bonds that need to be broken due to the multiple walls [1]

of cylindrical graphene.

(iii) The <u>unhybridised p orbitals</u> on the carbon atoms in carbon nanotube can <u>overlap sideways</u> allowing <u>delocalisation of π electrons</u>, where the <u>electrons act as mobile charge carriers</u>. Hence carbon nanotube graphene can conduct electricity. [2]

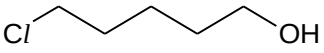
(d) **(i)** Sodium hydride reacts with alcohol to form a <u>stronger nucleophile, RO^-</u> [1]

(ii) Generation of nucleophile



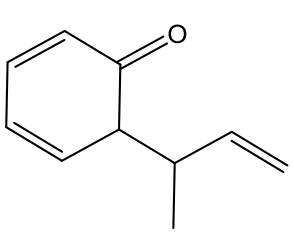
[3]

(iii) CH_3CH_2OH (in the presence of NaH) and CH_3CH_2Cl

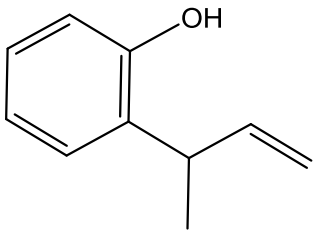


(in the presence of NaH) [2]

(e)



Intermediate



final product [2]