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ACJC Chemistry Prelim Paper 3 Suggested Solution

1	(a)	(i)	$CH_2=CHCH_2OCOCH_3 + Br_2 \rightarrow CH_2BrCHBrCH_2OCOCH_3$
		(ii)	Compare Expt No. 1 and 2, $[Br_2]$ constant, when [propenyl ethanoate] increases by 1.5 times, rate increases by 1.5 times. Order of reaction with respect to propenyl ethanoate is 1 Compare Expt No. 1 and 3, [propenyl ethanoate] constant, when $[Br_2]$ doubles, rate increases by 4 times. Order of reaction with respect to bromine is 2 Rate = $k[Br_2]^2$[propenyl ethanoate]
		(iii)	1% of ester = $1/100 \times 4.0 \times 10^{-2} = 4.0 \times 10^{-4}$ mol dm^{-3} Time taken = $(4.0 \times 10^{-4}) / (5.16 \times 10^{-3})$ = 0.0775 s (assume constant rate)
		(iv)	Chlorine is electron-withdrawing; hence will lower the electron density on the carbon-carbon double bond, hence less susceptible to electrophiles. Rate is expected to be slower. OR Chlorine is electron-withdrawing, hence makes the carbocation intermediate less stable as positive charge on carbocation is more intensified. Thus rate is expected to be slower.
		(v)	$CH_2BrCHOHCH_2OCOCH_3$ / $CH_2OHCHBrCH_2OCOCH_3$
		(vi)	Rate of reaction would be faster. Water is more polar than ethanoic acid. It can form ion-dipole interaction with carbocation, hence stabilize it. Activation energy would be lowered. OR Rate of reaction would be slower. Water dilutes the concentration of Br_2. Since rate depends on concentration of Br_2 and concentration of Br_2 is decreased, rate is expected to be slower.
	(b)	(i)	From the graph, 20 cm^3 of NaOH reacted with $MgCl_2$. No. of moles of NaOH in 20 cm^3 = $1.00 \times 20/1000$ = 0.02 mol $MgCl_2 + 2NaOH \rightarrow 2NaCl + Mg(OH)_2$ No. of moles of $MgCl_2$ that reacted with NaOH = 0.02/2 = 0.01 mol Initial concentration of $MgCl_2$ = $0.01/(50/1000)$ = 0.200 mol dm^{-3}
		(ii)	pH = 9 $[H^+] = 10^{-9}$ mol dm^{-3} $[OH^-] = 10^{-5}$ mol dm^{-3} No. of moles of Mg^{2+} = 0.01/2 = 0.005 mol $[Mg^{2+}] = 0.00500/(60/1000) = 0.0833$ mol dm^{-3}

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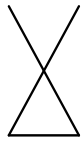
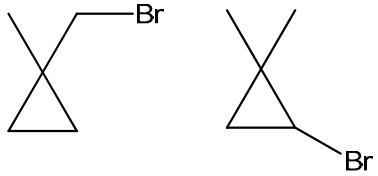
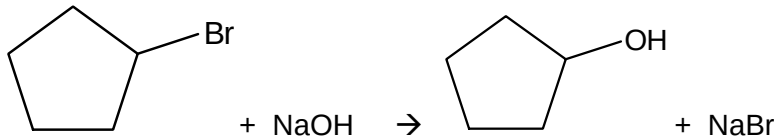
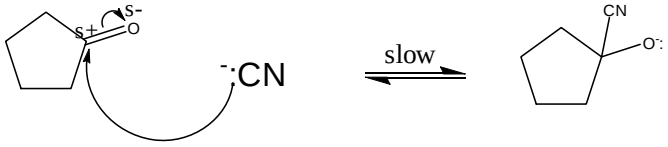
			K_{sp} of $Mg(OH)_2$ = $[Mg^{2+}]\,[OH^-]^2$ = (0.0833) $(10^{-5})^2$ **= <u>8.33 x 10^{-12} mol^3 dm^{-9}</u>**
		(iii)	**Solubility decreases with increasing temperature** **Less OH^- needed to reach K_{sp}.** **pH would be less than 9.**
		(iv)	**Mg^{2+} has <u>high charge density</u> and can polarize H_2O molecules slightly, <u>weakening the O-H bond in water</u>.** **$Mg(H_2O)_6^{2+}$ (aq) $\rightleftharpoons$ $Mg(H_2O)_5(OH)^+$ (aq) + H^+ (aq)**

2	**(a)**	**(i)**	 **<u>Two mono-brominated products:</u>**  (ignore stereoisomers)
		(ii)	Ratio of the above products = 6:4 = **<u>3:2</u>**
	(b)	**(i)**	Step **I** is a first order reaction. Write a balanced equation for the reaction, stating suitable reagents and conditions required. Hence, state the rate equation of the reaction.  aq NaOH & heat under reflux or heat rate = $k[C_5H_9Br]$
		(ii)	**Step III**: HCN in the presence of traces of NaCN or NaOH & 10°C - 20°C Mechanism: **<u>Nucleophilic Addition</u>** 

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			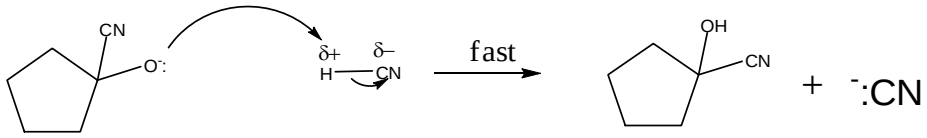

2	**(c)**	**(i)**	**Al_2O_3 (s) + 2NaOH (aq) + 3H_2O (l) → 2$NaAl(OH)_4$ (aq)** **Or** **Al_2O_3 (s) + 2OH^- (aq) + 3H_2O (l) → 2$Al(OH)_4^-$ (aq)**
		(ii)	**Aluminium hydroxide $Al(OH)_3$** **2$NaAl(OH)_4$ (aq) + CO_2 (g) → 2 $Al(OH)_3$ (s) + Na_2CO_3 (aq) + H_2O (l)** **Or** **2$Al(OH)_4^-$ (aq) + CO_2 (g) → 2 $Al(OH)_3$ (s) + CO_3^{2-} (aq) + H_2O (l)** **[Accept $Al(OH)_4^-$ (aq) + CO_2 (g) → $Al(OH)_3$ (s) + HCO_3^- (aq)]**
		(iii)	**Cathode: Al^{3+} + 3e → Al** **Anode: 2O^{2-} → O_2 + 4e**
		(iv)	**Water is reduced preferentially over Al^{3+}.** **Cryolite is added form a mixture which melts at a lower temperature.**
		(v)	**Mass of aluminium oxide in bauxite = 54/100 x 1.00 x 10^8** **= 5.40 x 10^7 kg** **Amount of aluminium = 2 x {5.40 x 10^{10} / [2(27) + 3(16)] }** **= 1.05 x 10^9 mol** **Mass of aluminium = 1.05 x 10^9 x 27 = 2.86 x 10^{10} g = <u>2.86 x 10^7 kg</u>** **Amount of electrons required = 1.05 x 10^9 x 3 = 3.15 x 10^9 mol** **Q = 3.15 x 10^9 x 96500 = <u>3.04 x 10^{14} C</u>**

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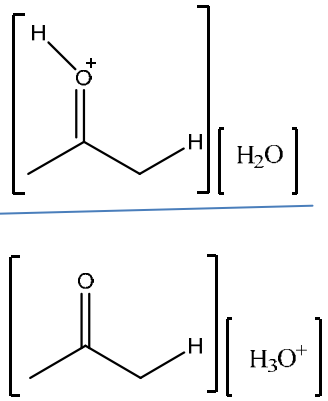
3	**(a)**		**Bonds broken = 740 + 410 +350 = +1500 kJ mol^{-1}** **Bonds formed = 460 + 610 + 360 = +1430 kJ mol^{-1}** **ΔHr = 1500 – 1430 = +70 kJ mol^{-1}**
	(b)	**(i)**	**K_a (H_3O^+) = [H^+] [H_2O] / [H_3O^+] and** **K_a ($(CH_3)_2C{=}OH^+$) = [H^+] [$(CH_3)_2C{=}O$] / [$(CH_3)_2C{=}OH^+$]**
		(ii)	• Kc = 
		(iii)	**K_c = ($10^{1.7}$ / $10^{7.2}$) = $10^{-5.5}$ = 3.16 x 10^{-6}**
		(iv)	**ΔG^o = - 8.31 x 298 x ln ($10^{-5.5}$) = + 31361 J mol^{-1} = + 31.4 kJ mol^{-1}**
		(v)	**K_c value is very small indicating that the keto form is predominant in the overall equilibrium** **Also ΔG^o is very positive indicating that the enol form is not energetically favourable.**
	(c)	**(i)**	**Enol form is stabilised by intra-molecular hydrogen bonding OR Conjugation of the C=O bond with the C=C bond also contributes to the stability.**
		(ii)	**No / less likely** **No conjugation between the C=O bond with the C=C bond.**
		(iii)	**Keto form participates in dipole-dipole interaction or hydrogen bond formation with polar solvents which suppresses intra-molecular hydrogen bonding** **In a non polar solvent, the enol form becomes more stable through intramolecular hydrogen bonding**
	(d)		• MF = $C_{10}H_{12}$ • P has no alkene functional group or C=C • Q has 2 –COOH groups • R is an acid derivative since it is neutral

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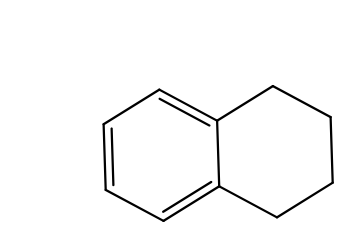
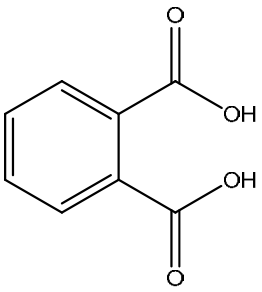


P



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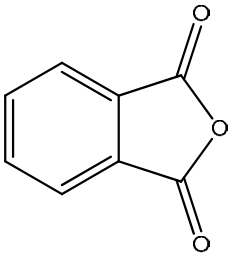
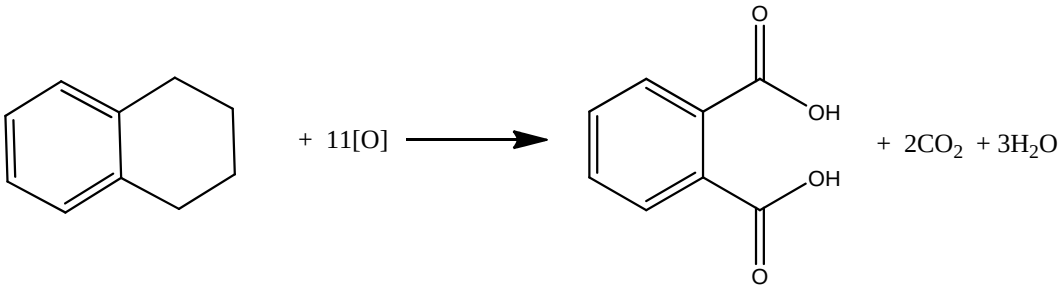
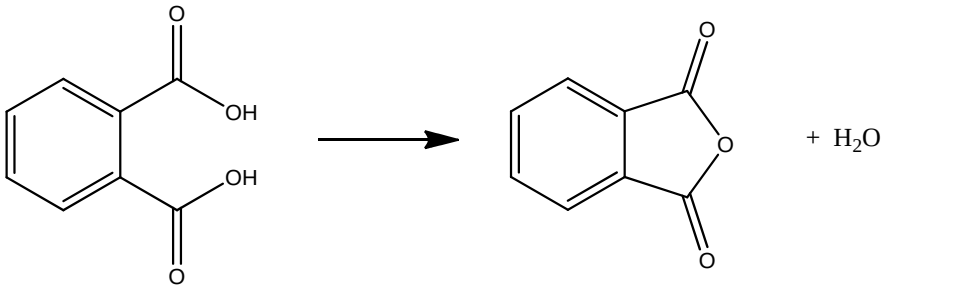
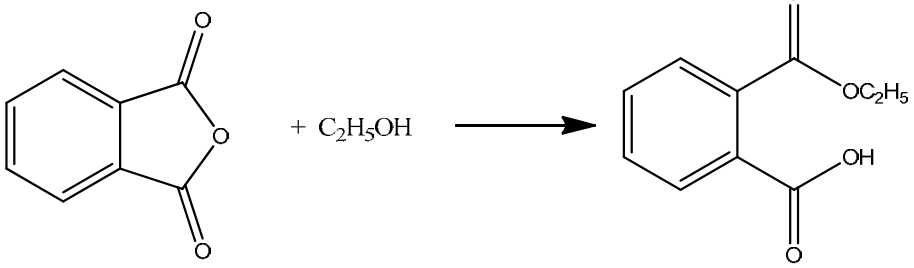


R







4	**(a)**	**(i)**	Cu^+ $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}$ 302 Cu^{2+} $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^9$ **7**
		(ii)	For $Cu^{2+}(aq)$, the **d-orbitals are not completely filled with electrons**. An electron from a lower energy level can be excited to higher energy level when light is absorbed **(d-d* electron transition)**. Light not absorbed is seen as colour of complex ion. For $Cu^+(aq)$, the **d-orbitals are completely filled with electrons**. **Hence d-d* electron transition is not possible**. Complex ion appears colourless.
		(iii)	$NH_3(aq) + H_2O(l) \rightarrow NH_4^+(aq) + OH^-(aq)$ $[Cu(H_2O)_6]^{2+}(aq) + 2OH^-(aq) \rightarrow Cu(OH)_2(s) + 6H_2O(l)$ When $NH_3(aq)$ is added slowly, **blue ppt** of $Cu(OH)_2$ is formed. $Cu(OH)_2(s) + 4NH_3(aq) + 2H_2O(l) \rightleftharpoons [Cu(NH_3)_4(H_2O)_2]^{2+}(aq) + 2OH^-(aq)$ or $Cu(OH)_2(s) + 4NH_3(aq) \rightleftharpoons [Cu(NH_3)_4]^{2+}(aq) + 2OH^-(aq)$ or $Cu^{2+}(s) + 4NH_3(aq) \rightleftharpoons [Cu(NH_3)_4]^{2+}(aq)$ When $NH_3(aq)$ is added in excess, blue **ppt dissolves** and a **deep blue solution** is formed.
		(iv)	$[Cu(H_2O)_6]^{2+}(aq) + 4Cl^-(aq) \rightleftharpoons [CuCl_4]^{2-}(aq) + 6H_2O(l)$ or $Cu^{2+}(aq) + 4Cl^-(aq) \rightleftharpoons [CuCl_4]^{2-}(aq)$ When HCl(aq) is added, an **intermediate green** colour is observed because blue $[Cu(H_2O)_6]^{2+}(aq)$ is mixed with yellow $[CuCl_4]^{2-}(aq)$. Final colour of solution is **greenish-yellow**.
		(v)	$2Cu^{2+}(aq) + 4I^-(aq) \rightarrow 2CuI(s) + I_2(s)$. When KI(aq) is added, CuI **white ppt** is formed in I_2 **brown solution**.
		(vi)	$Cu^+ + e \rightleftharpoons Cu$ +0.52V $Cu^{2+} + e \rightleftharpoons Cu^+$ +0.15V Overall: $2Cu^+ \rightarrow Cu^{2+} + Cu$ $E^\theta cell = +0.52 - (+0.15) =$ **+0.37V** Since $E^\theta cell > 0$ Volt, the reaction is thermodynamically feasible. Equation: $Cu_2O(s) + H_2SO_4(aq) \rightarrow Cu(s) + CuSO_4(aq) + H_2O(l)$ Acid-Base and Disproportionation
	(b)	$V^{2+} + Ce^{4+} \rightarrow V^{3+} + Ce^{3+}$ $E^\theta cell = +1.61 + (+0.26) = +1.87V$ Since $E^\theta cell > 0$ Volt, the reaction is thermodynamically feasible. Violet $V^{2+}(aq)$ solution becomes **green $V^{3+}(aq)$ solution**. $V^{3+} + Ce^{4+} + H_2O \rightarrow VO^{2+} + Ce^{3+} + 2H^+$ $E^\theta cell = +1.61 + (-0.34) = +1.27V$ Since $E^\theta cell > 0$ Volt, the reaction is thermodynamically feasible. Green $V^{3+}(aq)$ solution becomes **blue $VO^{2+}(aq)$ solution**. $VO^{2+} + Ce^{4+} + H_2O \rightarrow VO_2^+ + Ce^{3+} + 2H^+$ $E^\theta cell = +1.61 + (-1.00) = +0.61V$ Since $E^\theta cell > 0$ Volt, the reaction is thermodynamically feasible. Blue $VO^{2+}(aq)$ solution becomes **yellow $VO_2^+(aq)$ solution**.	

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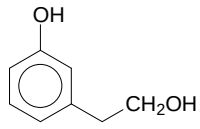
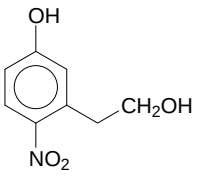
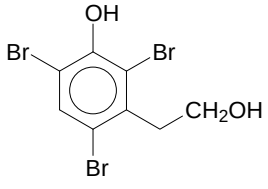
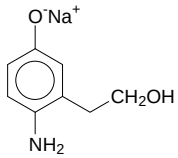
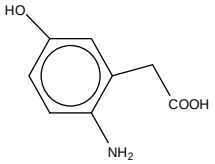
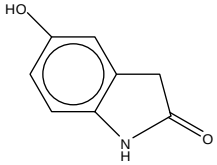
	(c)	$[Fe(CN)_6]^{3-}$(aq) will not be a catalyst because it is **thermodynamically not feasible** (E^0cell = +0.36 – 0.54 = **–0.18V**). Or This is because $[Fe(CN)_6]^{3-}$(aq) is **negatively charged** just like I^-. Hence it will be **repelled** by $S_2O_8^{2-}$(aq) as well. It is **kinetically not quite feasible**.

5	**(a)**	**(i)**	Primary amine, tertiary amine, phenol, primary amide
		(ii)	Disulfide
		(iii)	Arginine forms hydrogen bonds or ionic bonds Phenylalanine forms van der waals
		(iv)	**I.** Leucine has a much higher melting point than 1,7-Heptanediamine because the **electrostatic attractions (ionic bond)** in the crystal lattice of the zwitterionic form is stronger than the **intermolecular hydrogen bonding** between 1,7-Heptanediamine molecules. **II.** 1,7-Heptanediamine has a higher melting point than Heptanoic acid . **Both have hydrogen bonds between their molecules** and similar Mr (similar strength of VDW). **However, 1,7-Heptanediamine can form more extensive hydrogen bonds than Heptanoic acid**
	(b)	**(i)**	**I**: Lactic acid dissociates to give H ions, thus lowering the pH, The H^+ ions protonate the negatively charged $–COO^-$ R groups, thus disrupts the **ionic bonds** in the protein **II** Ethanol forms hydrogen bonds with the –OH groups in the R groups, hence disrupts the intermolecular hydrogen bonds.
	(c)		A:  B:  C:  D:  E:  F:  1 mark for each correct structure Accept also, -amine group at position 2 for structures B, D, E , F

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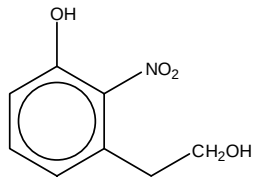
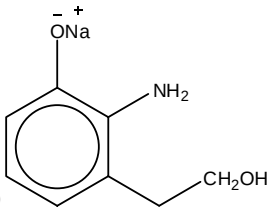
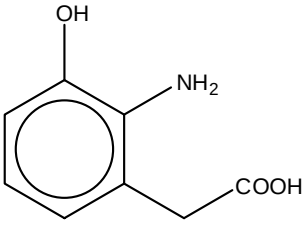
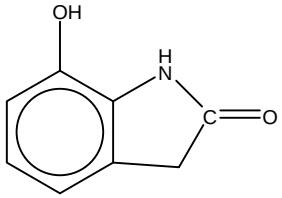
B: 

D 

E 

F: 

Deductions

- **A**, reacts with dilute nitric acid to give **B**,⇒ **A** contains phenol or A undergoes mononitration to give **B** by the dilute HNO_3
- **A** reacts with aqueoues bromine to form **C**, ⇒ **C is 2,4,6- trisubstituted or A is 1,3 disubstituted or A contains phenol**
- **B** is reduced by Sn/conc HC*l* to **D**⇒ $–NO_2$ group in **B** is reduced to $–NH_2$ and phenol in **B** is coverted to sodium phenoxide in **D**
- **D** undergoes oxidation with acidified dichromate to form carboxylic acid, ⇒primary alcohol present in **D,** or D is oxidised to form carboxylic acid in **E,** and phenoxide in **D** is acidified to phenol in **E.**
- Compound **E** reacts with 2 moles of sodium hydroxide.⇒presence of 2 acidic groups in **E** or (both phenol and carboxylic acid)
- **E**, C8H9NO3, is converted to **G**, ⇒The carboxyl group, $–CO_2H$, in **E** is converted into an **acyl chloride**, –COC*l*,by PCl_5.
- The amine then undergoes **internal nucleophilic substitution)**,with loss of C*l*–, to yield the **cyclic amide F** ⇒ Hence, the carboxymethyl group, $–CH_2CO_2H$, must be adjacent to amine – NH_2 group in **A** to enable ring formation