HWA CHONG INSTITUTION
2025 C2 H2 CHEMISTRY PRELIMINARY EXAMINATION
MARK SCHEME

Paper 3

1 (a) (i) Let the solubility of $MgCO_3$ and $Mg(OH)_2$ be x and y respectively, in mol dm^{-3}.

For $MgCO_3$
$K_{sp} = [Mg^{2+}][CO_3^{2-}]$ **[0.5]**
$1.0 \times 10^{-5} = (x)(x)$
$x = 3.16 \times 10^{-3}$ **[0.5]** mol dm^{-3}

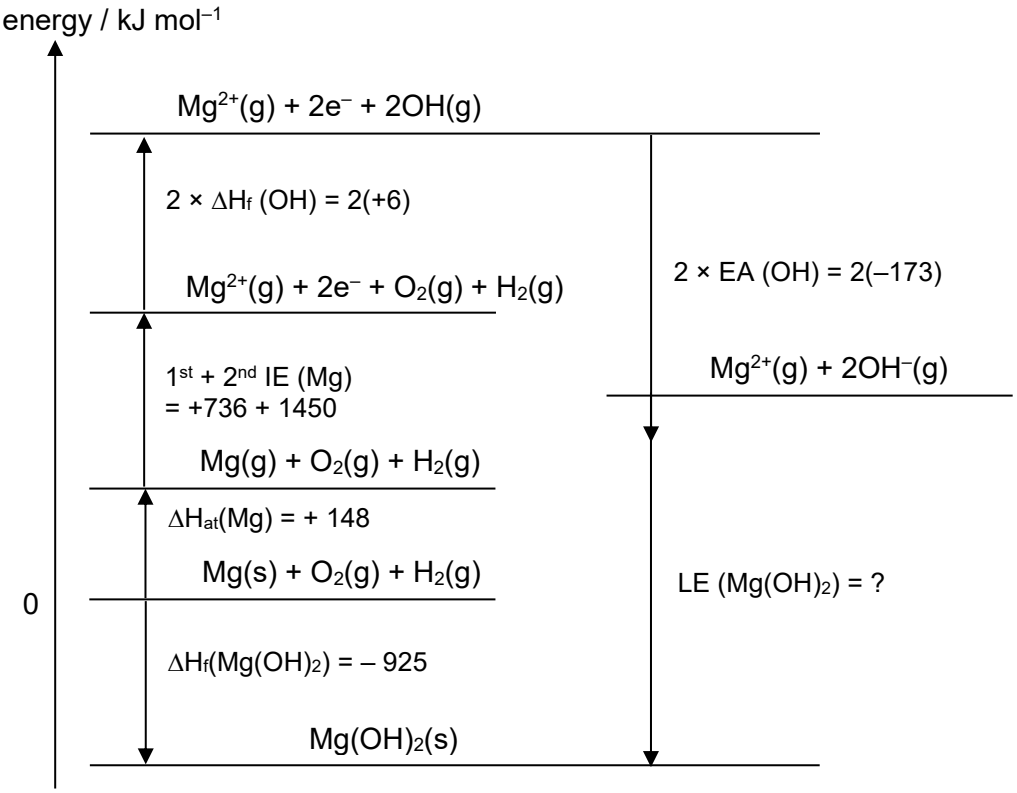
For Mg(OH)2
$K_{sp} = [Mg^{2+}][OH^-]^2$ **[0.5]**
$1.1 \times 10^{-11} = (y)(2y)^2$
$y = 1.40 \times 10^{-4}$ **[0.5]** mol dm^{-3}

(ii) $[Mg^{2+}][OH^-]^2 = 1.1 \times 10^{-11}$ **[0.5]**
$(3.0 \times 10^{-5})[OH^-]^2 = 1.1 \times 10^{-11}$
$[OH^-] = 6.06 \times 10^{-4}$ mol dm^{-3} **[0.5]**

(iii) **[0.5]** CO_3^{2-} ions are added first to <u>precipitate Ca^{2+}</u> as $CaCO_3$
[0.5] such that the <u>filtrate contains</u> <u>mainly Mg^{2+}</u> / <u>very little Ca^{2+}</u>.
[1] This must be controlled to <u>prevent precipitation of Mg^{2+}</u> as $MgCO_3$

(b) (i) Lattice energy is the heat evolved when 1 mole of solid ionic compound is formed from its constituent gaseous ions. **[1]**

(ii)



[3] total for correct Born-Haber cycle
ΔH_{at} (Mg) + 1st + 2nd IE (Mg) + ΔH_f (OH) + EA (OH) x 2 + LE ($Mg(OH)_2$) = ΔH_f ($Mg(OH)_2$)
148 + 736 + 1450 + (6 x 2) – (173 x 2) + LE ($Mg(OH)_2$) = –925
LE ($Mg(OH)_2$) = –2925 (or 2900 or 2930) kJ mol^{-1} **[1]**

(iii) **[1]** *correct trend:*
decreasing magnitude of LE: $MgO > Mg(OH)_2 > Ca(OH)_2$
or LE for MgO is larger than for $Mg(OH)_2$ + LE for $Mg(OH)_2$ is larger than for $Ca(OH)_2$

[1] *explain why LE of MgO > LE of $Mg(OH)_2$:*
The cation Mg^{2+} is the same for both compounds.
- O^{2-} anion has larger charge [0.5]
- but smaller ionic radius than OH^- [0.5]

[0.5] *explain why LE of $Mg(OH)_2$ > LE of $Ca(OH)_2$:*
The anion OH^- is the same for both compounds and Mg^{2+} cation has the same charge as Ca^{2+} but Mg^{2+} has smaller ionic radius than Ca^{2+}

[0.5] *link between ionic radius and charge with magnitude of LE* (e.g. quote LE eqn or link to strength of ionic bond / attraction bet. oppositely-charged ion *at least once*)

(c) **(i)** Al : $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^1$ **[0.5]**
Mg: $1s^2\ 2s^2\ 2p^6\ 3s^2$ **[0.5]**

[0.5] The 3p subshell of Al is further away from the nucleus than the 3s subshell (or at higher energy level).
[0.5] There is weaker attraction between the nucleus and the outermost electron of Al (or less energy is needed to remove the 3p electron) resulting in lower ionisation energy.

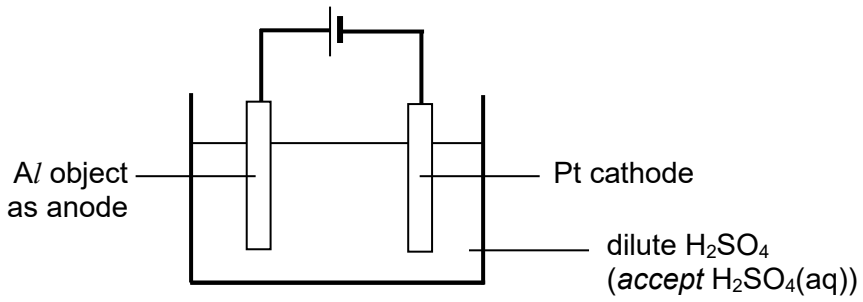
(ii) $MgCl_2$ dissolves in water to form aqueous ions.
$MgCl_2(s) + 6H_2O(l) \rightarrow [Mg(H_2O)_6]^{2+}(aq) + 2Cl^-(aq)$
or $MgCl_2(s) + aq \rightarrow Mg^{2+}(aq) + 2Cl^-(aq)$ **[1]**

Mg^{2+} has slightly high charge density. Slight hydrolysis occurs, forming a slightly acidic solution of pH 6.5.
$[Mg(H_2O)_6]^{2+}(aq) + H_2O(l) \rightleftharpoons [Mg(H_2O)_5(OH)]^+(aq) + H_3O^+(aq)$ **[1]**

$AlCl_3$ dissolves in water to form aqueous ions.
$AlCl_3(s) + 6H_2O(l) \rightarrow [Al(H_2O)_6]^{3+}(aq) + 3Cl^-(aq)$
or $AlCl_3(s) + aq \rightarrow Al^{3+}(aq) + 3Cl^-(aq)$ **[1]**

Al^{3+} having high charge density, undergoes hydrolysis **to a greater extent** to give an acidic solution with pH 3. (*must compare extent of hydrolysis with Mg^{2+}*)
$Al(H_2O)_6]^{3+}(aq) + H_2O(l) \rightleftharpoons [Al(H_2O)_5(OH)]^{2+}(aq) + H_3O^+(aq)$ **[1]**

(d)



[1] diagram
- label anode, cathode and electrolyte
- battery in correct orientation

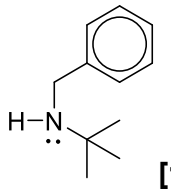
anode: $2Al\ (s) + 3H_2O\ (l) \rightarrow Al_2O_3\ (s) + 6H^+\ (aq) + 6e^-$ **[1]**
cathode: $2H^+\ (aq) + 2e^- \rightarrow H_2\ (g)$ **[1]**

2 (a) <u>The negative charge on O atom in phenoxide ion is delocalised into the benzene ring</u>, hence negative charge is dispersed, <u>stabilising the phenoxide ion</u> **[1]**. So phenol is a stronger acid than alcohol.

<u>Alkyl group is electron-donating</u>, alkyl group intensifies the negative charge on the alkoxide ion through inductive effect, <u>destabilising the alkoxide ion</u> **[1]**.

(b) (i) step 1: electrophilic substitution **[1]**
step 2: nucleophilic substitution **[1]**

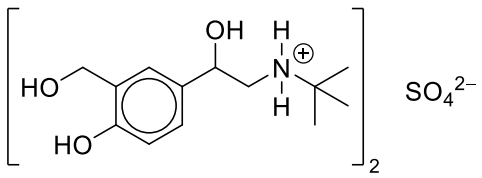
(ii)



[1]

(iii) Amine in **C** has **<u>one more</u>** <u>electron-donating</u> ($-CH_2C_6H_5$) <u>group</u> **[1]** that increases the electron density on N, making the <u>lone pair of electrons on N more available for donation</u> to form a dative bond with a Lewis acid **[1]**.

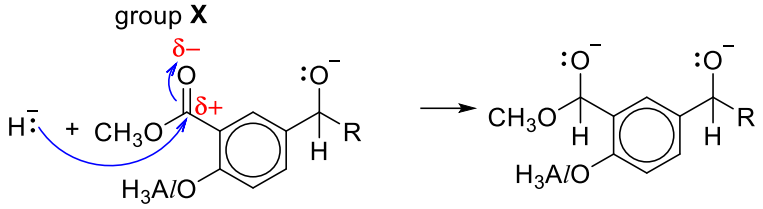
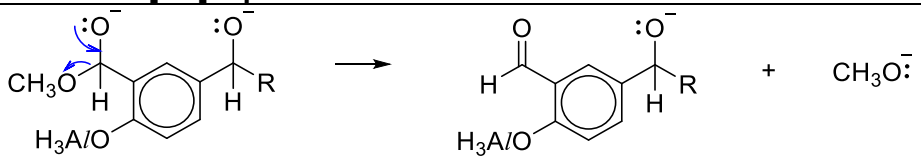
(c) (i)



[1] cation structure, minus 0.5 if structure of SO_4^{2-} was incorrect
[1] cation:anion ratio = 2:1

(ii) Salbutamol sulfate forms strong <u>ion-dipole</u> interactions **[1]** and <u>hydrogen bonding</u> **[1]** with water molecules.

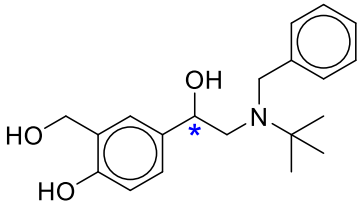
(d) (i)

stage	equation
2	 **[0.5] for two arrows [0.5] dipoles**
3	 **[1] for two arrows**

(ii) Lone pair on O of OCH_3 delocalises into C=O in group **X** (ester) making ester carbon of group **X** less electron-deficient **[1]** than aldehyde carbon of group **Y**, hence ester carbon attracts electron-rich hydride ion less well as compared to aldehyde carbon.

Ester carbon of group **X** is more sterically hindered than aldehyde carbon of group **Y** for the approach of the hydride ion as OCH_3 is larger than H atom **[1]**.

(iii)



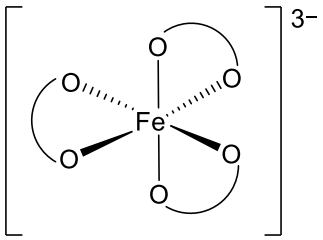
[1]

(iv) In stage 1, the ketone carbon is trigonal planar, there is equal probability for the hydride ion to attack the ketone carbon from the top and bottom **[1]** of the plane.

3 (a) Iron is a *d*-block element that forms one or more stable ions (or forms a stable Fe^{3+} ion) with partially filled *d* subshells. **[1]**

(b) (i) The phenoxide groups in Cat^{2-} donate their lone pair of electrons on O to the partially-filled 3d orbitals of Fe^{3+} ion, forming coordinate/dative bonds. **[1]**

(ii)



[2]

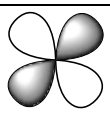
(iv) ligand exchange **[1]**

$[Fe(H_2O)_6]^{3+} + 3Cat^{2-} \rightarrow [Fe(Cat)_3]^{3-} + 6H_2O$ **[1]**

(c) $Fe(OH)_3\ (s) \rightleftharpoons Fe^{3+}(aq) + 3OH^-(aq)$ ---------- (1) **[0.5]**

The catechin in tea leaves could form a complex with Fe^{3+} ions, hence concentration of $Fe^{3+}(aq)$ decreases **[0.5]** and shifts the position of equilibrium (1) to the right **[0.5]** and increases its solubility into the mixture **[0.5]** to be discarded.

(d) (i) **[0.5]** for each correct shape (no need for axes or labels of orbitals)

	
d_{z^2} *orbital*	$d_{x^2-y^2}$, d_{xy}, d_{xz}, d_{yz} *orbitals*

In an octahedral complex, the ligands approach the central metal ion along the x, y and z axes. Hence the electrons in the d_z^2 and $d_{x^2-y^2}$ orbitals experience stronger repulsion from the direct approach of the ligands, causing the energies of d_z^2 and $d_{x^2-y^2}$ orbitals to be at a higher level than the d_{xy}, d_{xz} and d_{yz} orbitals. This results in d orbital splitting, where the originally degenerate five d orbitals are split into two groups with a small energy gap ΔE between them.

The lobes of the d_z^2 and $d_{x^2-y^2}$ orbitals lie along the axes, while those of d_{xy}, d_{xz} and d_{yz} orbitals lie in between the axes.

[1] states the 2 different orientations of lobes for the 2 groups of d orbitals

[0.5] states how the ligands approach in an octahedral complex
[0.5] recognizes 1 group experiences stronger repulsion due to direct approach of ligands

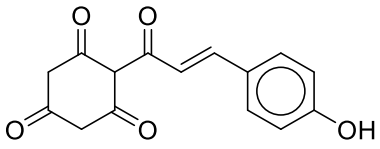
[1] states correct group of orbitals in each level

(ii) When white light shines on the complex, an electron from the lower energy *d* orbitals absorbs energy DE and is promoted to vacancies in the higher energy *d* orbitals. The energy absorbed in this *d-d* transition corresponds to wavelength of the visible region of the

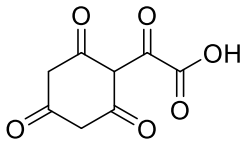
electromagnetic spectrum. Hence, we <u>observe colours complementary to the colours absorbed</u>.

[0.5] electron in lower E level absorb energy ΔE to promote to higher level
[0.5] vacancies in higher level
[0.5] energy absorbed/ΔE corresponds to visible region
[0.5] color observed is complementary of that absorbed

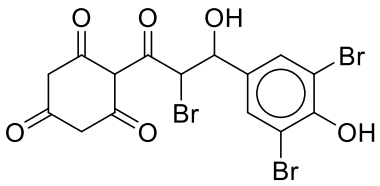
(e) **P** undergoes <u>oxidative cleavage</u> of alkene/C=C with acidified $KMnO_4$.
P undergoes <u>electrophilic addition</u> of alkene and <u>electrophilic substitution</u> of phenol group to give **R**.
P undergoes <u>reduction</u> of alkene/C=C and ketone groups with H_2



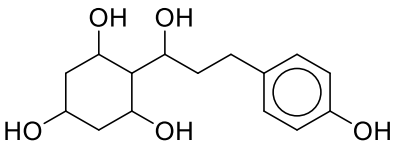
P



Q



R (accept if OH and Br swapped)



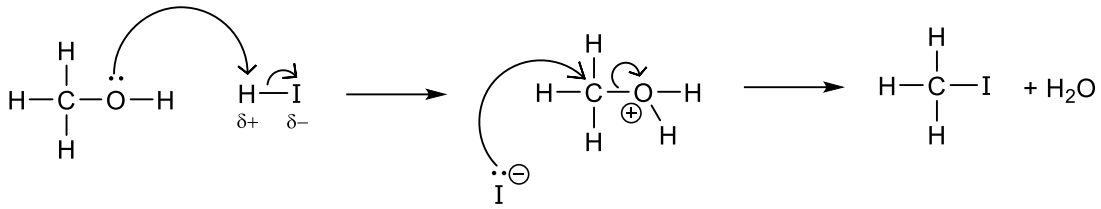
S

[1] for each correct compound
[1] for each correct type of reaction
Total **[8]**, award max **[7]**

4 **(a)** $CH_3OH + CO \rightarrow CH_3CO_2H$ **[1]**

(b) **(i)** (nucleophilic) substitution **[1]**

(ii)



[1] for each step

(c) **(i)** When temperature increased, the <u>position of equilibrium shifts to the left</u>. As the system will try to <u>absorb the additional heat</u> / <u>by favouring the backward endothermic reaction</u> **[1]**.

When a catalyst is added, the <u>position of equilibrium is unaffected</u>. As the catalyst just <u>shortens the time taken to reach equilibrium</u> / <u>increases the rates of both forward and backward reactions</u> **<u>by the same extent</u>**. **[1]**

(ii) $K_c = \frac{[CH_3COI]}{[CH_3I][CO]}$ **[1]**

	$CH_3I(aq)$	+	$CO(aq)$	⇌	$CH_3COI(aq)$
I / mol	0.400		0.300		–
C / mol	–0.105		–0.105		+0.105
E / mol	**0.295**		**0.195**		**0.15 × 0.7 = 0.105 [1]**

$K_c = \frac{(\frac{0.105}{0.7})}{(\frac{0.295}{0.7})(\frac{0.195}{0.7})}$ **[1]**

$= 1.28\ mol^{-1}\ dm^3$ **[1] ecf**

(d) **(i)** <u>Homogeneous</u> catalyst acts in the <u>same phase as the reactants</u>, while heterogeneous catalyst acts in a <u>different phase from the reactants.</u> **[1]**
Homogeneous catalyst forms an <u>intermediate with one of the reactants</u>, providing an alternative pathway with lower activation energy. Heterogeneous catalyst has <u>active sites on its surface for reactants to adsorb on</u>, <u>weakening the bonds in the reactants</u>, hence lowering the activation energy. **[1]**

(ii) In the rhodium(I) complex, the Rh^+ is coordinated by two CO ligands and two I^- ligands and is still able to <u>accomodate two more ligands</u> to form an intermediate. **[1]**
OR
vacant *d* orbitals to accept up to 6 electron pairs / coordination number can vary from 4 to 6
OR
C−I bond breaks, forming CH_3^+ and I^- ligands which can dative bond to rhodium

Rhodium being a transition element can have <u>variable oxidation states</u>. Its oxidation state can increase (*accept* changes) from <u>+1 to +3</u> (then regenerated back to +1). **[1]**

(e) (i) $CH_3CO_2H + OH^- \rightarrow CH_3CO_2^- + H_2O$ **[1]**

(ii)

	CH_3CO_2H	$+ OH^-$	$\rightarrow CH_3CO_2^-$	$+ H_2O$
amt after adding NaOH / mol	0.4 – 0.15 = 0.25	−	0.15	
conc after reaction / mol dm^{-3}	$\frac{0.25}{0.8}$ = 0.313 **[0.5]**		$\frac{0.15}{0.8}$ = 0.188 **[0.5]**	

$CH_3CO_2H + H_2O \rightleftharpoons CH_3CO_2^- + H_3O^+$

$K_a = \frac{(0.1875)[H^+]}{(0.3125)} = 1.8 \times 10^{-5}$ **[1]**

$[H^+] = 3 \times 10^{-5}$ mol dm^{-3}

$pH = -\lg (3 \times 10^{-5}) = 4.52$ **[1] ecf**

(iii) In the buffer: $CH_3CO_2H + H_2O \rightleftharpoons CH_3CO_2^- + H_3O^+$ ----- (1) When H^+ is added, the <u>position of equilibrium (1) shifts to the left</u> to form more CH_3CO_2H. **[1]**

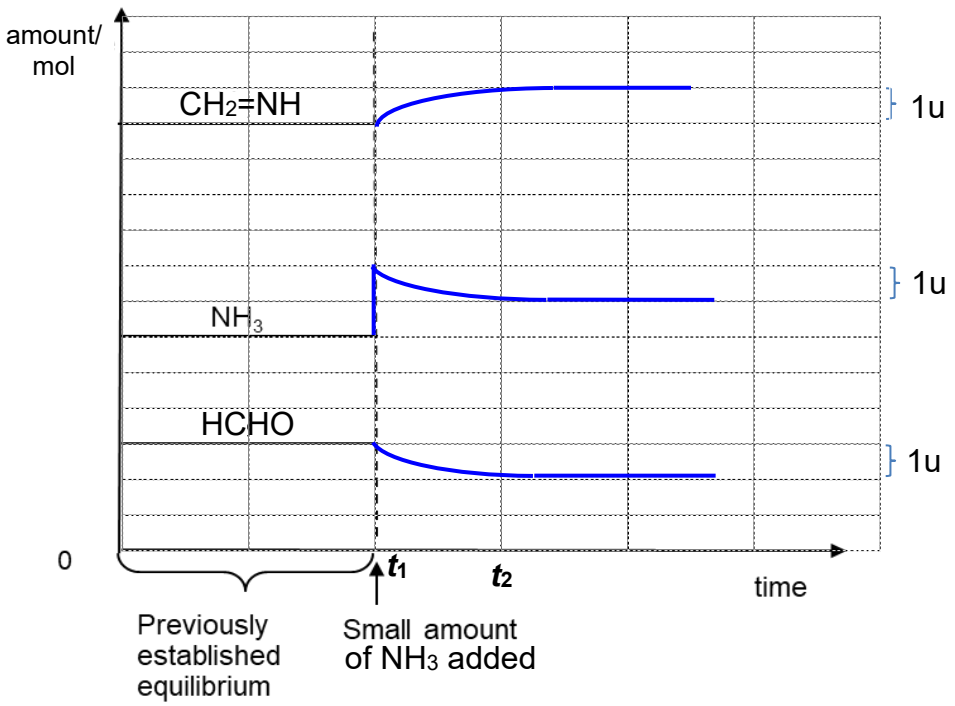
As the <u>original amounts of CH_3CO_2H and $CH_3CO_2^-$ are **large**</u> (or large reservoir of both species) compared to the **small** amount of H^+ ions added, the <u>ratio $[CH_3CO_2^-] / [CH_3CO_2H]$ remains **almost** constant</u>. Since $K_a = [H^+][CH_3CO_2^-] / [CH_3CO_2H]$, and <u>$K_a$ is a constant</u>, so $[H^+]$ and <u>pH remains **almost** constant</u>. **[1]**

5 (a) (i) Le Chatelier's Principle states that if the conditions of a system at equilibrium are changed, the position of equilibrium shifts so as to reduce that change. **[1]**

(ii) When temperature is increased, the system will try to <u>absorb the additional heat</u> by favouring the <u>backward endothermic reaction</u>, hence the <u>position of equilibrium shifts to the left</u>. **[1]**

The <u>number of moles of gas on both sides</u> of the equation are <u>the same</u>. Hence when pressure is increased, the <u>position of equilibrium is unaffected</u>. **[1]**

(b) (i)



[1] correct shapes of CH_2=NH and HCHO graphs (increase for CH_2=NH and decrease for HCHO)
[1] correct shape of NH_3 graph (sharp increase at t_1, followed by decrease)
[1] correct relative amounts of increase/decrease according to 1:1:1 mole ratio + new equilibrium established at $\mathbf{t_2}$.

(ii) $K_p = \frac{(P_{CH_2=NH})(P_{H_2O})}{(P_{NH_3})(P_{HCHO})}$ **[0.5]** no unit **[0.5]**

(iii)

	NH_3(g)	+	HCHO(g)	⇌	CH_2=NH(g)	+	H_2O(g)
initial amount/mol	5		5		0		0
change/mol	-(1-0.09)(5) =-4.55		-4.55		+4.55		+4.55
final amount/mol	0.45		0.45		4.55		4.55

Total amount present at equilibrium = 0.9 + 0.9 + 4.1 + 4.1 = 10.0 mol

$K_p = \frac{(P_{CH_2=NH})(P_{H_2O})}{(P_{NH_3})(P_{HCHO})} = \frac{(4.55/10\times P_T)(4.55/10\times P_T)}{((0.45/10\times P_T))((0.45/10\times P_T))}$ = **102** (to 3 s.f.)

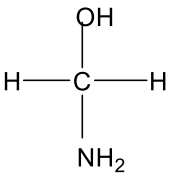
where P_T is the total pressure of the system.

[1] calculate the equilibrium amount of each species
[1] correct substitution into the K_p expression
[1] calculates K_p correctly

(iv) K_p >> 1, which means that at equilibrium, there are much more products than reactants. Hence, the sign for the Gibbs free energy of the forward reaction is <u>negative</u> and the <u>position of equilibrium lies to the right</u>. **[1]**

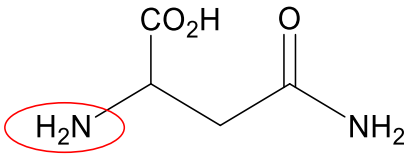
(c) (i) condensation **[1]**

(ii)



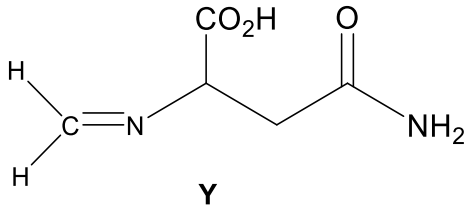
X is . **[1]**

(iii)



asparagine **[1]**

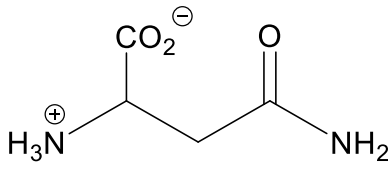
(iv)



Y

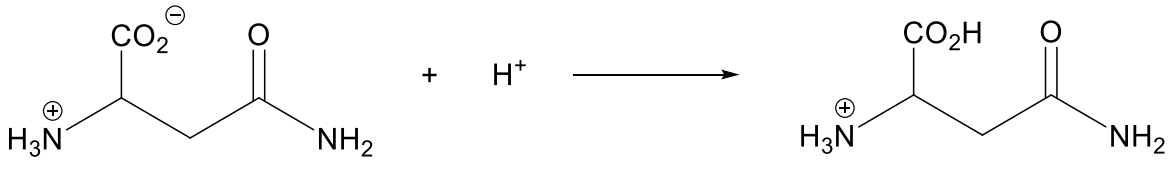
(v) In acidic medium, the -NH_2 group gets <u>protonated</u> to -NH_3^+ **[0.5]**, <u>reducing its nucleophilicity</u> **[0.5]** and reactivity in the formation of acrylamide. *no ecf*

(d) (i)

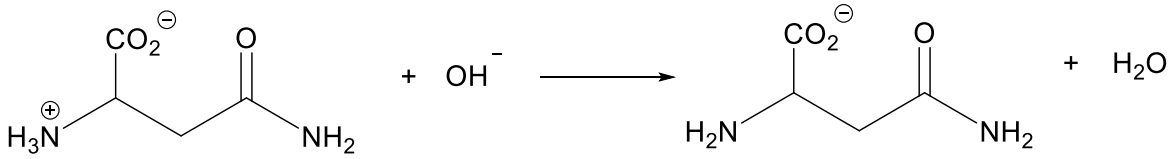


[1]

(ii) When a small amount of acid is added:

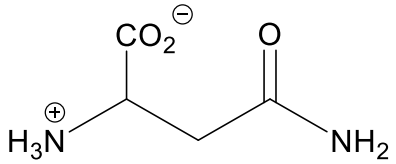


When a small amount of base is added:



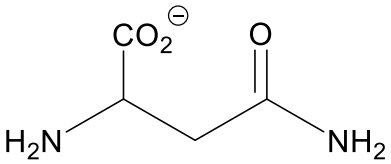
[1] for each equation

(iii) At pH 8, the predominant species of asparagine present are its zwitterionic form and its deprotonated conjugate base.



A

and



B

A and B are conjugate acid-base pairs

$K_a = \frac{[\mathrm{H^+}][\mathrm{B}]}{[\mathrm{A}]}$

$\frac{[\mathrm{B}]}{[\mathrm{A}]} = \frac{K_a}{[\mathrm{H^+}]}$

$\frac{[\mathrm{B}]}{[\mathrm{A}]} = \frac{10^{-8.8}}{10^{-8}}$

$\frac{[B]}{[A]} =$ **0.158** (to 3 s.f.) **[1]**

Also accept

$\frac{[\mathrm{A}]}{[\mathrm{B}]} = \frac{[\mathrm{H^+}]}{[K_a]} = \frac{10^{-8}}{10^{-8.8}}$ = **6.31** (to 3 s.f.)