Answer key to Paper 3

1 (a) (i) A buffer solution is one that can resist a change in pH when a small amount of acid or base is added to it.

(ii) **1.**

$pK_b = 5.93$

Let $[OH^-]$ be x

$x^2 \div (0.10 - x) = 10^{-5.93}$

Since x is small,

$x^2 \div 0.10 = 10^{-5.93}$

$x = 3.43 \times 10^{-4}$ mol dm^{-3}

pOH = 3.47

pH = 10.5

2.

At equivalence point, 12.5 cm^3 of HC*l* solution is required.

pK_a of conjugate acid = 8.07

Amt of $RNH_3^+ = (25/1000) \times 0.1 = 2.50 \times 10^{-3}$ mol dm^{-3}

$[RNH_3^+] = 2.50 \times 10^{-3} \div (37.5/1000)$

$= 6.67 \times 10^{-2}$ mol dm^{-3}

Let the concentration of $[H^+]$ be y

$y^2 \div (6.67 \times 10^{-2} - y) = 10^{-8.07}$

Since y is small,

$y = 2.38 \times 10^{-5}$ mol dm^{-3}

pH = 4.62

3.

Amt of HC*l* remaining = $(30/1000) \times 0.20 - 2.50 \times 10^{-3}$

$= 3.50 \times 10^{-3}$ mol

$[HCl] = 3.50 \times 10^{-3} \div (55/1000)$

$= 6.36 \times 10^{-2}$ mol dm^{-3}

pH = 1.20

(iii) Maximum buffering capacity occurs at 8.07, which is close to physiological pH of 7.4/ The buffering action occurs near physiological pH of 7.4/ Non-toxic **[6]**

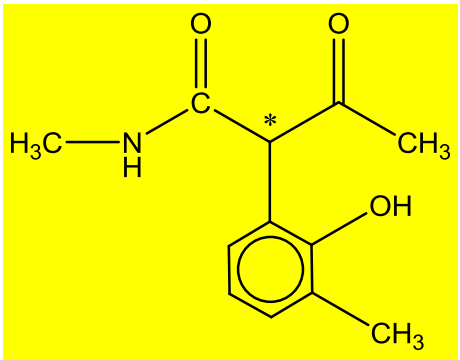
(b) **(i)** Rate = $k[HONO]^2[C_6H_5NH_2]^0$

(ii) Units for k ⇒ $mol^{-1}\ dm^3\ s^{-1}$ or $mol^{-1}\ dm^3\ min^{-1}$ **[2]**

(c)

Observations/Reactions	**Deduction**
G does not undergo (nucleophilic) <u>substitution</u> with PCl_5 to give white fumes	**G** does not contain carboxylic nor alcohol functional group.
G undergoes <u>alkaline hydrolysis</u> to give H and salt of **I**.	**G** is an amide **I** is a carboxylic acid
G has a fishy smell and does not react with HONO.	**G** is an alkyl amine
I rotates plane-polarised light	**I** is chiral
I undergoes <u>positive</u> iodoform test	**I** contains $–COCH_3$ or $–C(OH)CH_3$ groups
I undergoes <u>condensation</u> reaction with 2,4-DNPH	**I** does not have $-C(OH)CH_3$ groups / **I** must contain $–COCH_3$ functional group
I undergoes <u>electrophilic substitution</u> with $Br_2(aq)$	**I** undergoes **1** electrophilic substitution on benzene ring containing phenol functional group /other ortho & para positions are blocked from ES

G



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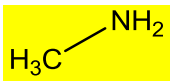

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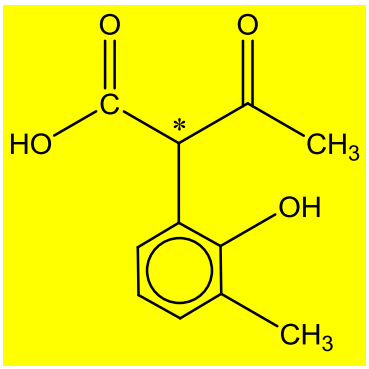

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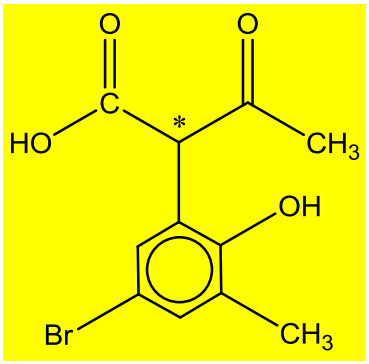


[9]

(d) $N_2 + 3H_2 \rightleftharpoons 2NH_3$

Heterogeneous catalyst: Fe

$S_2O_8^{2-} + 2I^- \rightarrow 2SO_4^{2-} + I_2$

Homogeneous catalyst: Fe^{2+} or Fe^{3+}

Or

$C_6H_6 + Br_2 \rightarrow C_6H_5Br + HBr$ (*or* $C_6H_6 + Cl_2 \rightarrow C_6H_5Cl + HCl$)

Homogeneous catalyst: $FeBr_3$ (*or* $FeCl_3$) **[3]**

[Total: 20]

2 **(a)** Nitrogen is inert and nitrogen compounds are hard to form.

Ammonium salts and nitrates are soluble in water and thus would only accumulate in dry areas. **[2]**

(b) Low temperature and high pressure.

Ammonia gas has hydrogen bonding between its molecules and thus significant intermolecular forces are present at low temperatures.

At high pressure, the ammonia molecules would be very close to each other and the volume of the gas molecules would be significant when compared to the volume of the container / gas. **[3]**

(c) $pV = nRT$

$pV = mRT/M_r$

density $= m/V = pM_r/RT$

$= (1.01 \times 10^5 \times 17.0) / (8.31 \times 303)$

$= 682 \text{ g m}^{-3}$

$= 682 \text{ mg dm}^{-3}$

Concentration is below lethal value. **[3]**

(d) **(i)** Gradient

$= [(-5.44 - (-8.72)] / (3.33 \times 10^{-3} - 2.50 \times 10^{-3})$

$= 3.95 \times 10^3 \text{ K}$

$\Delta H = -3.95 \times 10^3 \times 8.31 = -32825 \text{ J mol}^{-1} = -32.8 \text{ kJ mol}^{-1}$

(ii) $\ln K_c = -\frac{\Delta H^\ominus}{RT} + \frac{\Delta S^\ominus}{R}$

$-5.44 = (3.95 \times 10^3)(3.33 \times 10^{-3}) + \Delta S/8.31$

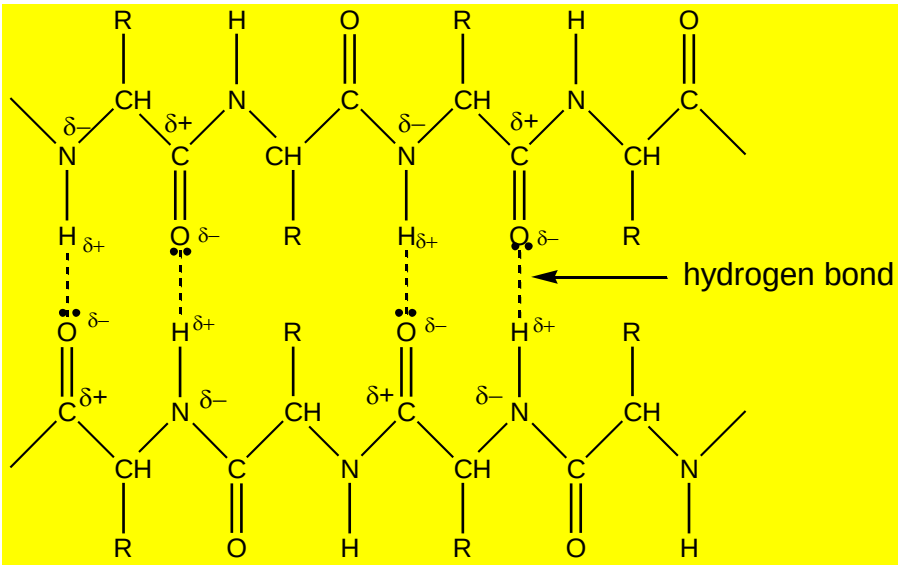
$\Delta S = -155 \text{ J mol}^{-1} \text{ K}^{-1}$

(iii) $\Delta G = \Delta H - T\Delta S$

$T = -32825/-155 = 212 \text{ K}$ **[6]**

(e) **(i)** Transport, structure, catalysts, defence, signalling / control (any 3)

(ii) *β*-pleated sheet consists of adjacent polypeptide strands stabilised by hydrogen bonds between the *backbone* C=O group of one strand and the *backbone* N-H group of the adjacent strand.

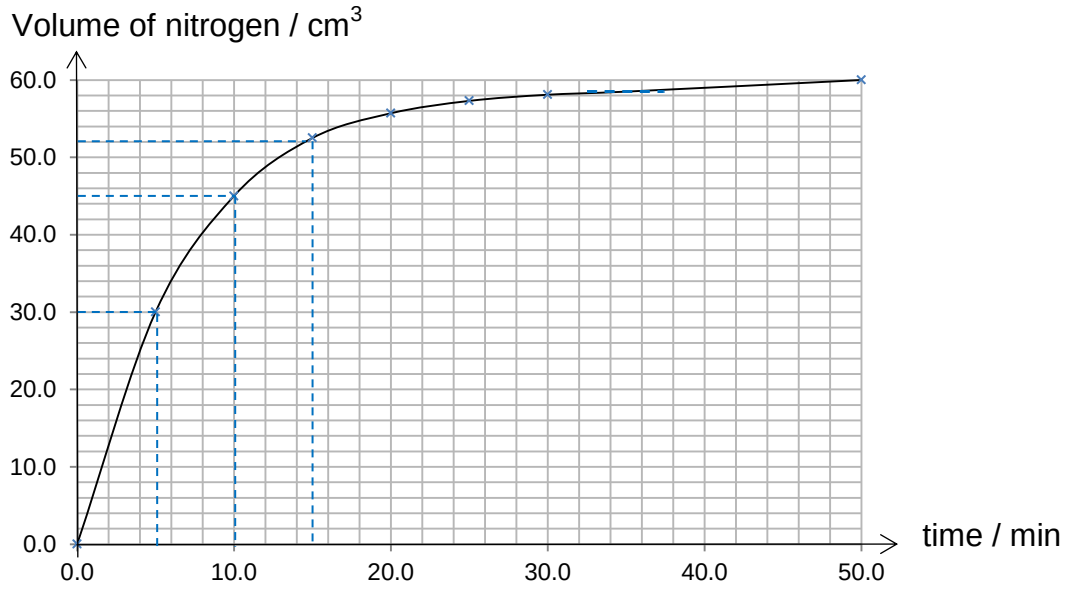


(iii) Charged and polar R groups / side chains of amino acid residues will form ion-dipole and hydrogen bonds with water molecules.

Addition of ammonium ions and sulfate ions can disrupt these interactions which will cause the proteins to precipitate out. **[6]**

[Total: 20]

3 **(a)** **(i)**



(ii) From the graph, $t_{1/2}$ is (approximately) constant at 5.0 min. (Since the reaction occurs in aqueous medium, the concentration of water (the other reactant) can be assumed to be constant.) Therefore the reaction is first order with respect to ethyl diazoethanoate.

(iii) Rate constant = $\frac{\ln 2}{t_{1/2}}$ = 0.139 (min^{-1})

[5]

(b) **(i)** Nucleophilic Addition

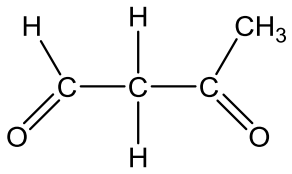
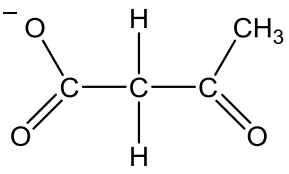
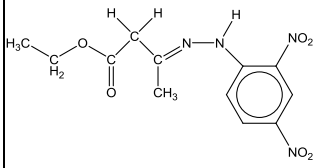
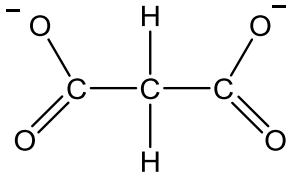
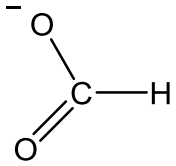
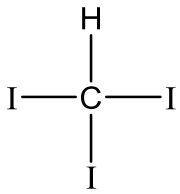
(ii) Formation of gaseous molecule results in an increase in entropy. **[2]**

(c) **(i)** Reduction

Oxidation

(ii) Dilute HCl/H_2SO_4(aq), heat under reflux

(iii)

C	**D**	**E**
		
F	**G**	**H**
		

[9]

(d) (i)

	B	+	Methanol	⇌	Ester	+	Water
Initial amount / mol	0.25		0.34		0		0
Change in amount / mol	– 0.13		– 0.13		+ 0.13		+ 0.13
Eqm amount / mol	0.12		0.21		0.13		0.13

$$K_c = \frac{[CH_3COCH_2CO_2CH_3][H_2O]}{[CH_3COCH_2CO_2H][CH_3OH]}$$

$$= \frac{(0.13/V)(0.13/V)}{(0.12/V)(0.21/V)}$$

$$= 0.671$$

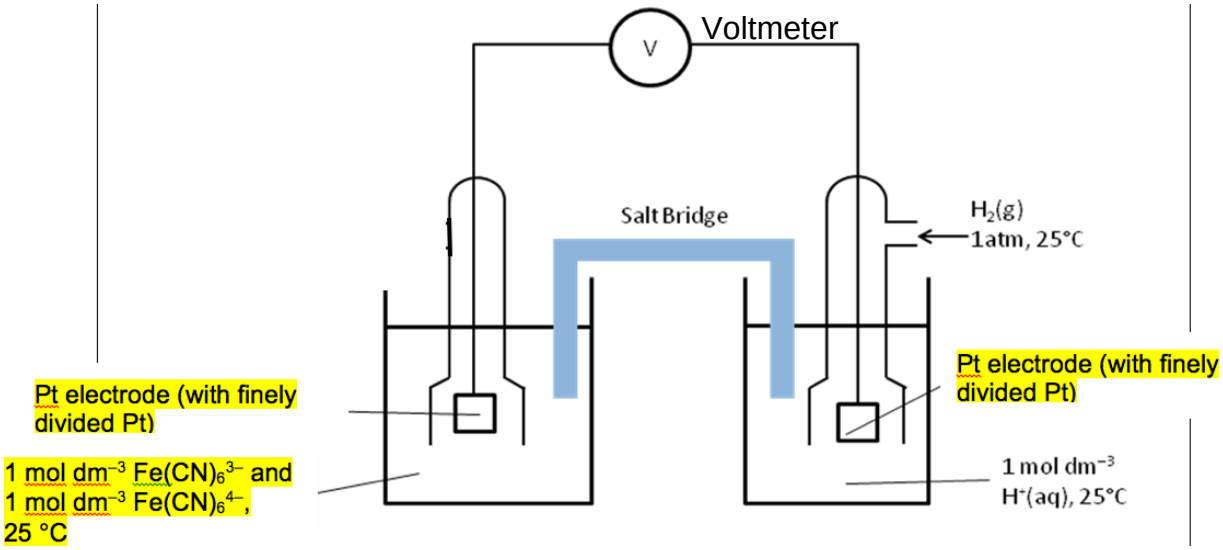
(ii) Concentrated sulfuric acid removes the water formed / is a dehydrating agent, causing the equilibrium position to shift to the right to produce more water.

Or concentrated sulfuric acid acts as a catalyst and does not change the equilibrium position.

Increasing the temperature favours the endothermic reaction to absorb some of the added heat. Since the forward reaction is exothermic, the equilibrium position shifts to the left to favour the backward endothermic reaction. **[4]**

[Total: 20]

4 (a) (i)



(ii)

	$E^{\ominus}$ / V
$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$	+ 0.77
$[Fe(CN)_6]^{3-} + e^- \rightleftharpoons [Fe(CN)_6]^{4-}$	+ 0.36

Since $E^{\ominus}(Fe^{3+}/Fe^{2+})$ is **more positive** than $E^{\ominus}([Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-})$, $Fe^{3+}/[Fe(H_2O)_6]^{3+}$ is **more easily reduced** than $[Fe(CN)_6]^{3-}$.

Hence, $[Fe(H_2O)_6]^{3+}$ is a stronger oxidising agent.

(iii) There will be repulsion between the negatively charged $[Fe(CN)_6]^{3-}$ and the electron to be added. / CN^- is a stronger ligand than H_2O, hence it stabilises the complex ion to a greater extent.

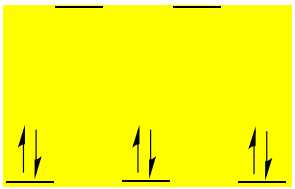
Hence, $[Fe(CN)_6]^{3-}$ is less easily reduced and a weaker oxidising agent. **[6]**

(b) (i) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^6$

(ii) The energy gap between the two sets of d-orbitals is greater than the repulsion energy, favouring the pairing of electrons.

(iii) $[Fe(CN)_6]^{4-}$ will adopt a low spin state. since CN^- ligands will result in a large ΔE so electrons will pair up in the lower energy orbital.

(iv)



electron arrangement in $[Fe(CN)_6]^{4-}$

The 6 d-electrons are all paired up in the lower energy orbitals/There are no unpaired electrons in $[Fe(CN)_6]^{4-}$. Hence $[Fe(CN)_6]^{4-}$ will not be paramagnetic. **[7]**

(c) Amount of Fe^{2+} reacted = $(30/1000) \times 0.200 = 6.00 \times 10^{-3}$ mol

Amount of FeO_x^{2-} reacted = $(10/1000) \times 0.200 = 2.00 \times 10^{-3}$ mol

Since $Fe^{2+} \equiv e^-$

Amount of e^- gained by 1 mol of FeO_x^{2-}

$= 6.00 \times 10^{-3} / 2.00 \times 10^{-3} = 3$ mol

Oxidation state of Fe in FeO_x^{2-} = +3 + 3 = +6

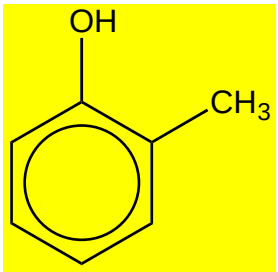
$+6 + (-2)x = -2$

$x = 4$ **[3]**

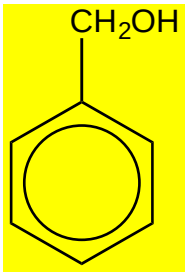
(d) **(i)** NH_4SCN gives a blood/deep red colouration with iron(III) chloride but NH_4NO_3 does not give blood/deep red colouration.

(ii) A violet colouration/solution will be formed.

(iii) Positive test:



Negative test:



[4]

[Total: 20]

5 **(a)** **(i)** White fumes : HC*l*

Purple fumes : I_2

(ii) $NaI(s) + H_2SO_4(l) \rightarrow NaHSO_4(s) + HI(g)$

$8HI(g) + H_2SO_4(l) \rightarrow H_2S(g) + 4I_2(g) + 4H_2O(l)$

(iii) I^- is a stronger reducing agent/undergoes oxidation more readily. Hence, HI will be further oxidised by H_2SO_4 which is an oxidising agent to I_2. **[4]**

(b) **(i)** The oxidising power of the halogens decreases down the group.

Oxidising power of halogens decreases down the group due to increasing radius of halogen atoms from F_2 to I_2.

Hence, the attractive force by the nucleus for electrons decreases and the tendency for the halogen atom to gain electrons decreases.

(ii) The thermal stabilities decreases down the group.

The size of the halogen atoms increases from F to I and their valence orbitals become more diffuse. This results in less effective overlap of the orbitals between the H atom and halogen atom and less energy is required to break the weaker H–X bond. **[5]**

(c) **(i)** The methyl group has an electron-donating effect, intensifying the negative charge on oxygen atom, making the $HO_2CCH(CH_3)COO^-$ ion less stable than $HO_2CCH_2COO^-$. Hence methylmalonic acid is a weaker acid/has a lower K_1 with a higher pK_1.

(ii) Both $HO_2CCH(CH_3)COO^-$ and $HO_2CCH_2COO^-$ can be stabilised by intramolecular hydrogen bonding. / It is difficult to remove the H^+ from both anions.

(iii) 1. pOH = 14 – 8 = 6

Concentration of OH^- = 10^{-6}

= 1.00×10^{-6} mol dm^{-3}

2. $X^{2-}(aq) + H_2O(l) \rightleftharpoons HX^-(aq) + OH^-(aq)$

Initial [ ] / mol dm^{-3}	y	0	0
Change in [ ] / mol dm^{-3}	-1.00×10^{-6}	$+1.00\times10^{-6}$	$+1.00\times10^{-6}$
Equilibrium [ ] / mol dm^{-3}	$y - 1.00\times10^{-6}$	1.00×10^{-6}	1.00×10^{-6}

$K_{a2} = 10^{-5.70}$

$K_{a2} = 2.00 \times 10^{-6}$ mol dm^{-3}

$$K_b\ (X^{2-}) = \frac{1.00\times10^{-14}}{2.00\times10^{-6}} = 5.01 \times 10^{-9} \text{ mol dm}^{-3}$$

$$K_b = \frac{[HX^-][OH^-]}{[X^{2-}]}$$

$$5.01 \times 10^{-9} = \frac{(1.00\times10^{-6})^2}{[y - 1.00\times10^{-6}]}$$

$y - 1.00 \times10^{-6} = 2.00 \times 10^{-4}$ mol dm^{-3}

Initial concentration of malonate = y = 2.01×10^{-4} mol dm^{-3} **[7]**

(d) Ethanoic acid is the most acidic, followed by phenol then propan-1-ol.

Ethanoic acid is the most acidic due to delocalisation of the negative charge over the COO^- group, making the ethanoate anion the most stable anion.

Comparing phenol and propan-1-ol, phenoxide anion is more stable than the propanoxide anion as the negative charge on the oxygen is delocalised into the benzene ring.

On the other hand, the electron-donating propyl group intensifies the negative charge on oxygen of propanoxide anion, making the anion less stable. **[4]**

[Total: 20]