Pioneer Junior College
H2 Chemistry Preliminary Examination
Paper 3 Answer Scheme

1(a)(i) $FeBr_3(s) + 6H_2O \rightarrow [Fe(H_2O)_6]^{3+} + 3Br^-$

$[Fe(H_2O)_6]^{3+} + H_2O \rightleftharpoons [Fe(H_2O)_5OH]^{2+} + H_3O^+$

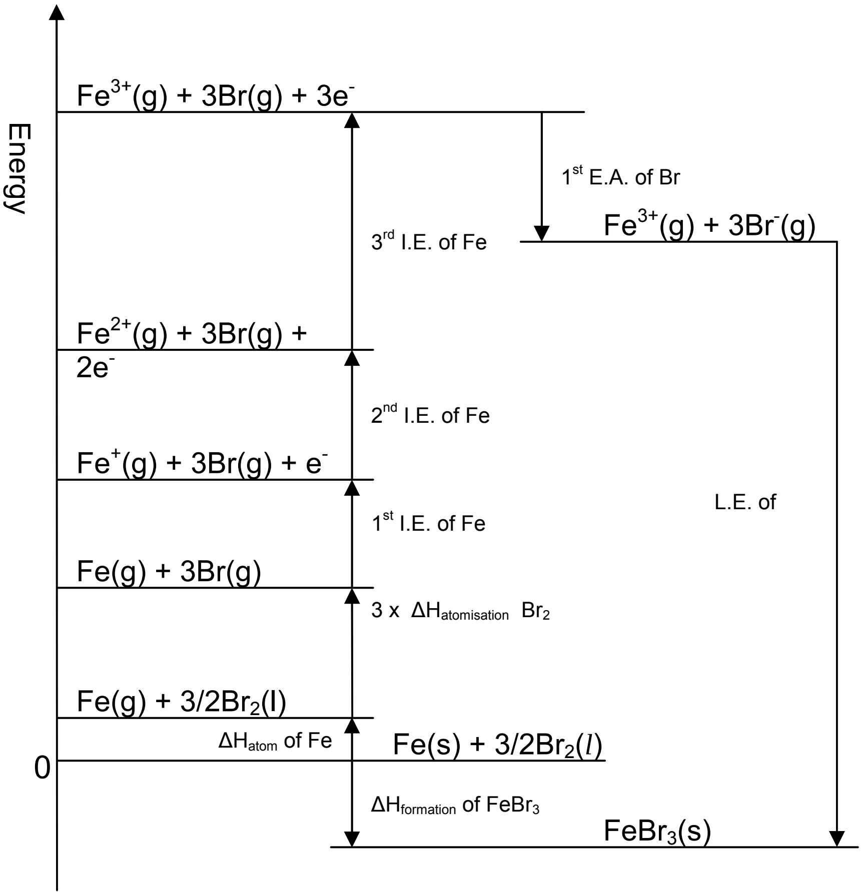
Due to high charge density of Fe^{3+} ion, it is able to polarize the water molecule weakening the O—H bond, releasing H^+ ion. Hence a solution of $FeBr_3$ has pH less than 7 at 298 K.

(ii) K_a (Fe^{3+} (aq)) = 6.34×10^{-6} mol dm^{-3}

(b) (i) $Fe(s) + 3/2Br_2(l) \rightarrow FeBr_3(s)$

The standard enthalpy of formation is the change in energy when 1 mole of $FeBr_3$, at its standard state, is formed from its constituent elements in their stand states at the conditions of 1 atm, 298 K.

(ii)



$\Delta H(LE) + [350+(3 \times 112)+762+1560+2960 + (3 \times -325)] = -320$

$\Delta H(LE) = -5313$ kJ mol^{-1}

(iii) When there is a large difference in electronegativity between the ions in a crystal, as in the case of the alkali metal halides then the ionic model is satisfactory. However as the difference in electronegativity gets smaller, as in the case of the silver halides, the bonding is stronger than the ionic model predicts.

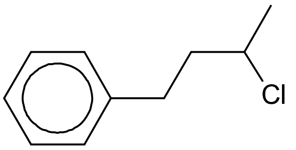
The bonding in this case is not purely ionic but intermediate in character between ionic and covalent. The ionic bonds have been polarised giving some covalent character.

(c)(i) Electrophilic substitution

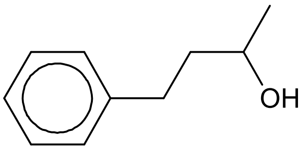
$FeBr_3$ has to be anhydrous as it has to be electron deficient to accept a lone pair from Br^- to form the electrophile $CH_3(CH_2)_3^+$ for Electrophilic substitution to take place.

If water is present, Fe^{3+} (aq) will be present and will not be able to do so.

(ii) **J**



K



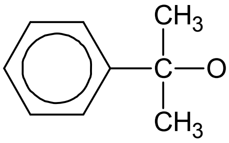
(iii) **II:** limited Cl_2, UV light

III: NaOH (aq), heat

IV: CH_3COOH (aq), concentrated H_2SO_4, heat

(iv) Reagent: $KMnO_4$, H_2SO_4, heat

Butylbenzene will undergo oxidation to give colourless/pale pink solution of Mn^{2+}.

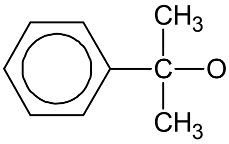


Compound **M** does not undergo oxidation. Solution remains purple

OR

Reagent: Sodium

Butylbenzene: No observable change.



Compound **M** reacts to produce H_2 gas, which gives a pop sound with a lighted splint.

2(a)(i) At the cathode,

Due to the high negative reduction potential of Na^+, H_2O is preferentially discharged, producing H_2 and NaOH which turns litmus blue at region **Y**.

At the anode,

Although the oxidation of water is more favourable based on the oxidation potential, Cl^- is discharged in preference due to its high concentration, thus liberating Cl_2 at the anode.

Region **X** becomes red initially due to formation of HCl and eventually becomes white due to the bleaching action of HOCl.

(ii) $3Cl_2 + 6NaOH \rightarrow NaClO_3 + 6NaCl + 3H_2O$

Chlorine is produced at the anode while the $[OH^-]$ in the electrolyte will increase as the electrolysis proceeds. As a result, Cl_2 will react with the OH^- in the electrolyte to produce $NaClO_3$.

(iii) Q= 1.8×10^5 C (hence amt of electrons = 1.865 mol)

Since $2Cl^- \rightarrow Cl_2 + 2e$ and

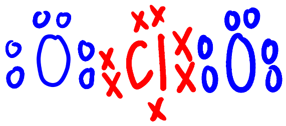
$3Cl_2 + 6NaOH \rightarrow NaClO_3 + 6NaCl + 3H_2O$

$n(e^-) \equiv \frac{1}{2}n(Cl_2) \equiv 1/3\ n(NaClO_3)$

Hence $n(NaClO_3)$ = 0.3109 mol

$[NaClO_3]$ = 0.3109 / 2 = **0.155 mol dm^{-3}**

(b) (i)



Chlorine dioxide has an unpaired electron thus it has a tendency to take in electrons to achieve a stable octet configuration.

(ii) Lone pair on oxygen in chlorine dioxide is able to form H-bonding with water molecules.

(iii) $2AgClO_3 + Cl_2 \rightarrow 2AgCl + O_2 + 2ClO_2$

AgCl is the white ppt while the effervescence is O_2.

(c) Oxidising power of halogens decrease down the group.

$F_2 + 2e \rightarrow F_2$ $E^\theta = +2.87$ V

$Cl_2 + 2e \rightarrow Cl_2$ $E^\theta = +1.36$ V

$I_2 + 2e \rightarrow I_2$ $E^\theta = +0.54$ V

Fluorine, being the strongest oxidising agent, can oxidise Cr to CrF_4 when oxidation state of chromium is $\underline{+4}$.

Chlorine, less oxidising, oxidises Cr to $CrCl_3$ when oxidation state of chromium is $\underline{+3}$.

Iodine, being the weakest oxidising agent, can only oxidise Cr to CrI_2 when oxidation state of chromium is $\underline{+2}$.

(d) **(i)** $I_xCl_y^- \rightarrow 0.5x\, I_2 + yCl^-$
$n(I_2) = 0.5\, n(S_2O_3^{2-}) = 6.39 \times 10^{-4}$ mol
$n(Cl^-) = n(Ag^+) = 6.4 \times 10^{-4}$ mol
Hence x=2, y=1

(ii) Molar mass = 0.27 / 6.39 x 10^{-4} = 422 g mol^{-1}
$ICl_2^- \rightarrow I_2 + Cl^-$ (thus n(salt) = $n(I_2) = n(Cl^-)$)
Molar mass of M = 133, hence M = Cs

3(a) **(i)** $K_a = 10^{-pKa} = 10^{-6.80} = 1.58 \times 10^{-7}$ $moldm^{-3}$
$K_a = [C_{10}H_{14}N]\,[H_3O^+] / [C_{10}H_{14}NH^+]$
$K_a = [H_3O^+]^2 / [C_{10}H_{14}NH^+]$
$[H_3O^+] = [(1.58 \times 10^{-7})(0.100)]^{1/2} = 1.26 \times 10^{-4}$ $moldm^{-3}$

$pH = -\log_{10}[H_3O^+] = 3.90$

(ii) When pH is decreased, $[H_3O^+]$ increases and position of equilibrium shift to the left, concentration of conjugate of nicotine increases.

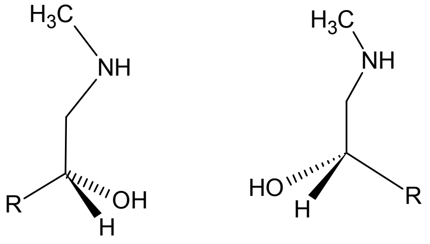
(iii) $pH = pK_a(C_{10}H_{14}NH^+) + \log_{10} [C_{10}H_{14}N]/[C_{10}H_{14}NH^+] = 6.50$

(iv) $[C_{10}H_{14}N]_{new} = (5 \times 0.100 - 0.200v) / (5.00 + v)$
$[C_{10}H_{14}NH^+]_{new} = (5 \times 0.200 + 0.200v) / (5.00 + v)$

$pH = pK_a(C_{10}H_{14}NH^+) + \log_{10} [C_{10}H_{14}N]/[C_{10}H_{14}NH^+]$

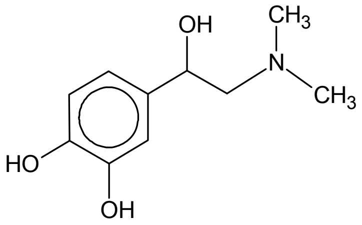
$$6.40 = 6.80 + \log_{10}\frac{(5 \times 0.100 - 0.200v)/(5.00 + v)}{(5 \times 0.200 + 0.200v)/(5.00 + v)}$$ solving, v = **0.364 dm^3**

(b) **(i)** Optical isomerism



(ii) Epinephrine is a stronger base
Epinephrine has an electron donating CH_3 group bonded to the nitrogen atom. It enhances the availability of lone pair of electrons on the N atom for protonation.

(c) **(i)**



React Dopamine and chloromethane in a 1:2 mole ratio in ethanol in sealed tube, high temperature.

(ii)

Reagents and conditions	Observations		
	Dopamine	Ephinephrine	Acetylcholine
$K_2Cr_2O_7$(aq), H_2SO_4(aq), heat	Orange solution remains orange	Orange solution turns green	Orange solution turns green
CH_3COC/	White misty fumes of HC/ gas seen	White misty fumes of HC/ gas seen	No white misty fumes of HC/ gas seen

4(a) **(i)** Empirical formula = $C_5H_{10}O_3$
Molecular formula = $C_5H_{10}O_3$

(ii) **P** and **Q** have at least one chiral carbon each
P undergoes <u>acid-base/ neutralisation</u> with NaOH(aq).
Q undergoes <u>alkaline hydrolysis</u> with NaOH(aq), heat.
P has tertiary alcohol group
Q undergoes hydrolysis and its products undergo oxidation.
S and **T** each have two $CH_3CH(OH)$- group or CH_3CO- group.

P is $CH_3CH_2CH(CH3)(OH)C_2OH$
Q is $HCO_2CH(CH_3)CH(OH)CH_3$
R is $HCO_2^-Na^+$. (reject HCO_2^-)
S is $CH_3CH(OH)CH(OH)CH_3$
T is $CH_3COCOCH_3$

(b)
$CH_3CH_2CH(OH)CH_3 \rightarrow CH_3CH_2COCH_3 \rightarrow CH_3CH_2C(OH)(CN)CH_3 \rightarrow CH_3CH_2C(OH)(CO_2H)CH_3$
Step 1: $KMnO_4$, H_2SO_4, heat
Step 2: HCN(aq), trace amount of NaOH(aq) / NaCN(aq), cold (10 to 20 ^oC)
Step 3: HC*l*(aq) / H_2SO_4(aq), heat

(c)(i) less steric hindrance by the two methyl groups on opposite side
(ii) increase in number of mole of gaseous compounds.

(iii) $\Delta H^\theta = -2660 - (-2710) = +50$ kJ mol^{-1}
$\Delta G^\theta = \Delta H^\theta - T\Delta S^\theta = +50 - 298(+154/1000) = +4.11$ kJ mol^{-1}

(iv) The reaction is not <u>energetically/ thermodynamically</u> feasible at 25 ^oC / 298 K because $\Delta G^\theta > 0$.
A higher temperature is needed so that $\Delta G^\theta < 0$ since $\Delta H^\theta > 0$ and $\Delta S^\theta > 0$.

5(a) (i) A transition element is defined as a d-block element which forms at least one stable ion with a partially filled d-subshell of electrons.

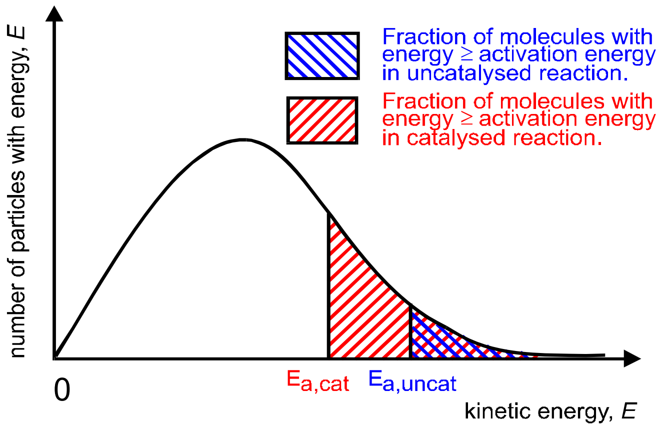
Iron, Fe

(ii) When the ligands approach the transition complex, the 3d orbitals experience different extent of electrostatic repulsion by the electron pair of the ligands, causing the 3d orbitals to be split into two groups of different energy levels. This is known as d-orbital splitting.

The transition complex absorbs light energy from the visible spectrum (with the equivalent energy of ΔE), an electron from the lower energy d-orbital is promoted to a vacant (half-filled) higher energy d-orbital. Such transitions are called d-d transitions.

The colour observed is the complementary colour of the colours absorbed. Hence, blood is red since red colour is reflected and its complementary colours are absorbed.

(b)(i) It is acting as a homogeneous catalyst.



The catalyst provides an alternative pathway with a lower E_a. More reactant molecules have energy greater than E_a. Hence, there is an increase in the number of effective collisions per unit time / increase in the frequency of effective collisions, resulting in an increase in reaction rate.

(ii) *Step 1: Formation of intermediate (VO_2^+ colliding with I^-)*

$VO_2^+ + 2H^+ + e^- \rightleftharpoons VO^{2+} + H_2O$ $\quad E^{\ominus}_{red} = +1.00\ V$

$2I^- \rightleftharpoons I_2 + 2e^-$ $\quad E^{\ominus}_{oxd} = -0.54\ V$

$2VO_2^+ + 4H^+ + 2I^- \rightarrow 2VO^{2+} + 2H_2O + I_2$

$E^{\ominus}_{cell} = E^{\ominus}_{oxd} + E^{\ominus}_{red}$

$= (-0.54) + (+1.00) = +0.46V$ (>0, hence energetically feasible)

Step 2: Regeneration of catalyst (VO^{2+}colliding with $S_2O_8^{2-}$)

$S_2O_8^{2-} + 2e^- \rightleftharpoons 2SO_4^{2-}$ $\quad E^{\ominus}_{red} = +2.01\ V$

$VO^{2+} + H_2O \rightleftharpoons VO_2^+ + 2H^+ + e^-$ $\quad E^{\ominus}_{oxd} = -1.00\ V$

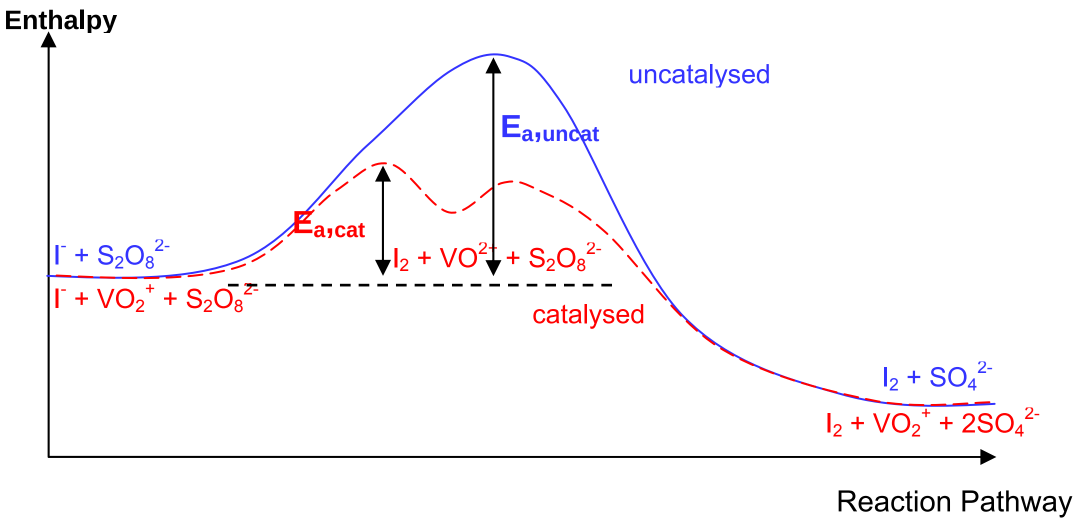
$S_2O_8^{2-} + 2VO^{2+} + 2H_2O \rightarrow 2SO_4^{2-} + 2VO_2^+ + 4H^+$

$E^{\ominus}_{cell} = E^{\ominus}_{oxd} + E^{\ominus}_{red}$

$= (-1.00) + (+2.01) = +1.01$ (>0, hence energetically feasible)

Overall Equation: $S_2O_8^{2-}(aq) + 2\ I^-(aq) \rightarrow 2SO_4^{2-}(aq) + I_2(aq)$

(iii)

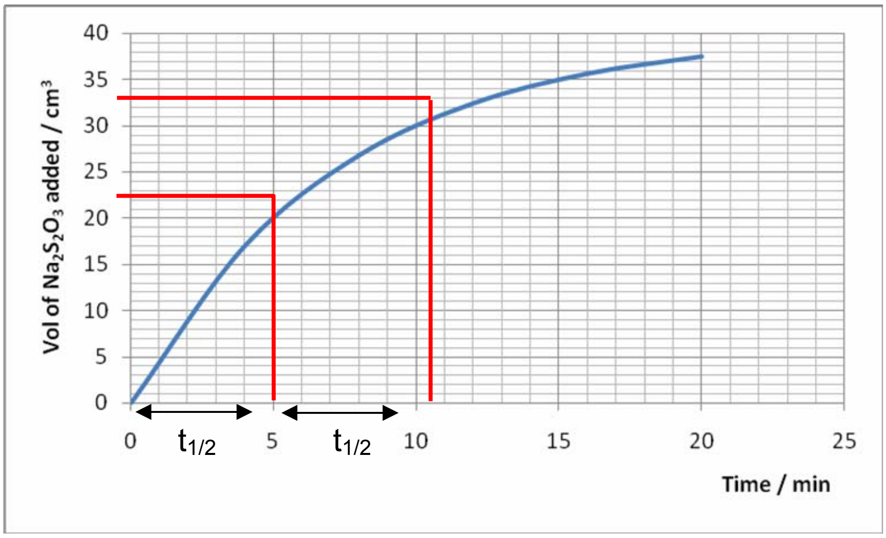


(d) **(i)** This is to make $[S_2O_8^{2-}]$ relatively constant throughout the experiment.

Hence, rate = $k\,[S_2O_8^{2-}]^a\,[I^-]^b \approx k'\,[I^-]^b$ (where $k' = k\,[S_2O_8^{2-}]^a$)

The order of reaction w.r.t I^- can then be determined by by plotting the volume of $Na_2S_2O_3$(aq) against time.

(ii)



$$0 \longrightarrow \tfrac{1}{2}[S_2O_3^{2-}]_o \longrightarrow \tfrac{3}{4}\,[S_2O_3^{2-}]_o$$

From the graph, $[S_2O_3^{2-}]_o \approx 40\ cm^3$

Hence, $\tfrac{1}{2}[S_2O_3^{2-}]_o \approx 20\ cm^3$

$\tfrac{3}{4}[S_2O_3^{2-}]_o \approx 30\ cm^3$

From the graph, $t_{1/2}$ = 5 minutes = constant

Hence, order of reaction with respect to iodide ions is 1.

(iii) Repeat the entire experiment with double the concentration of $K_2S_2O_8$(aq).

Plot a graph of the volume of aqueous $Na_2S_2O_3$ against time, then compare the **initial rates** of the new graph and the old graph.Since the order is one, the initial rate of the new graph should be doubled that of the first graph, since $[S_2O_8]^{2-}$ doubles.