Q1)

(a)(i)

1. Diprotic refers to an acid that donates a **<u>maximum</u>** of two of its protons to other atoms [0.5]
2. Organic acid refers to an acid that is largely made of **carbon, hydrogen and oxygen** atoms [0.5]

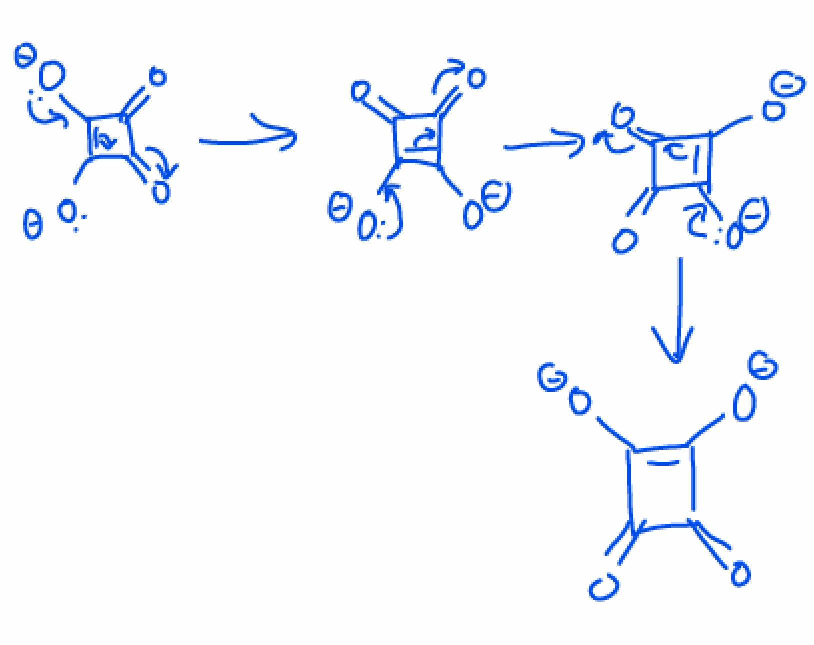
(ii)

1. Bond angle is 90 degrees [1]
2. Due to **ring strain** which forces the bonds to be 90 degrees rather than 120 degrees [1]

(b)(i)

1. Single bonds and double bonds have **different lengths** - single bonds are longer while double bonds are shorter [0.5]
2. **Increased electron density** in a bond means **stronger EFOA** with nucleus, hence bond length decreases [0.5]

(ii)



Any 3 arrows correct - [0.5]

Any 6 arrows correct - [1]

(iii)

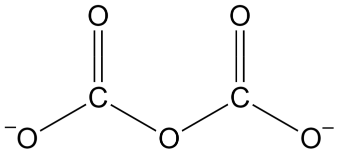
1. Electrons can be delocalised into pi electron cloud system across the entire molecule [0.5]
2. Hence all the C - C bonds are partial double bonds and have a partial double bond length [0.5]

(c)

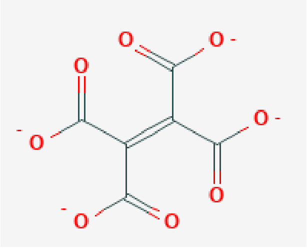
1. Squaric acid has a higher pH
2. Reason 1: Squaric acid is diprotic while ethanoic acid is monoprotic - twice as many H+ ions can be donated per molecule of squaric acid than ethanoic acid
3. Reason 2: Squaric acid has more highly EN oxygen atoms that disperse the negative charge on the conjugate base, increasing its stability and hence increasing its acid strength. Ethanoic acid however, involves electron donating alkyl groups that intensifies the negative charge on the conjugate base and destabilises it.
4. Reason 3: Negative charge can be dispersed to a greater extent in conjugate base of squaric acid because the pi electron cloud system is spread across the whole molecule, while that of ethanoic acid is only spread across COO-

Point 1 + 1 correct reason - 1m
Point 1 + 2 correct reasons - 2m

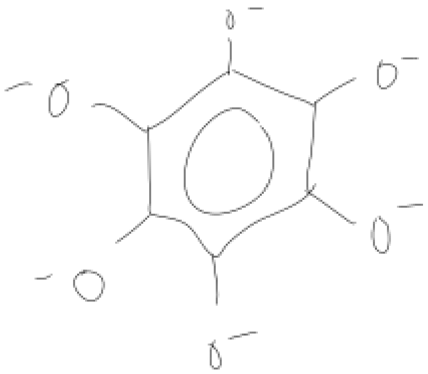
(d) (i)
Dicarbonate:



Ethylenetetracarboxylate:



Benzenehexolate:



1 correct structure - 0.5m

2 correct structures - 1m
3 correct structures - 2m
Penalise 0.5m once, maximum twice, if candidate gave the protonated form instead of the deprotonated form

(ii)

1. Oxidisation [0.5]
2. as species loses electrons in order to neutralise the negative charge [0.5]
3. More unstable as **oxygen atoms** [0.5]
4. Do not have a fully filled valence shell [0.5]

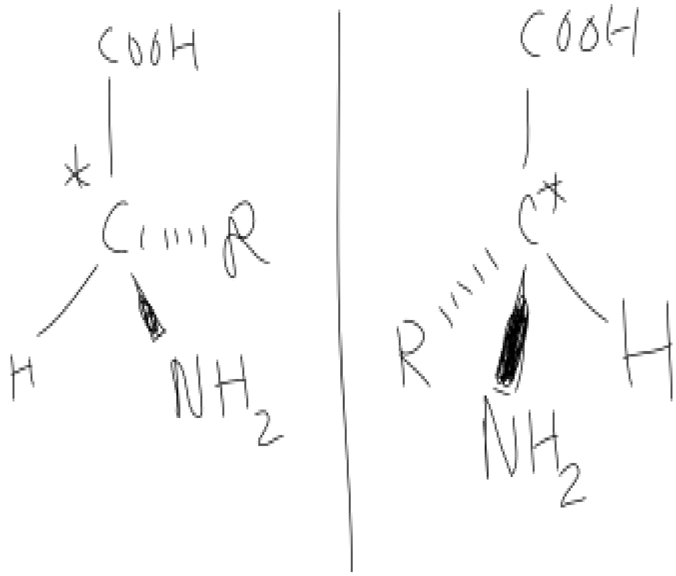
(iii) Let z be ave. oxidation no.
+k +xz -2y = -m
z= (2y-m-k)/x [1]
[0.5] if working is correct but algebraic manipulation is wrong

Q2)
(i)

1. Species (keto and enol)
2. with the same molecular formula
3. of C_3H_6O,
4. but different structural formula -
5. as keto has C=O
6. but enol has HO-C=C

4-5 points: 0.5m
6 points: 1m

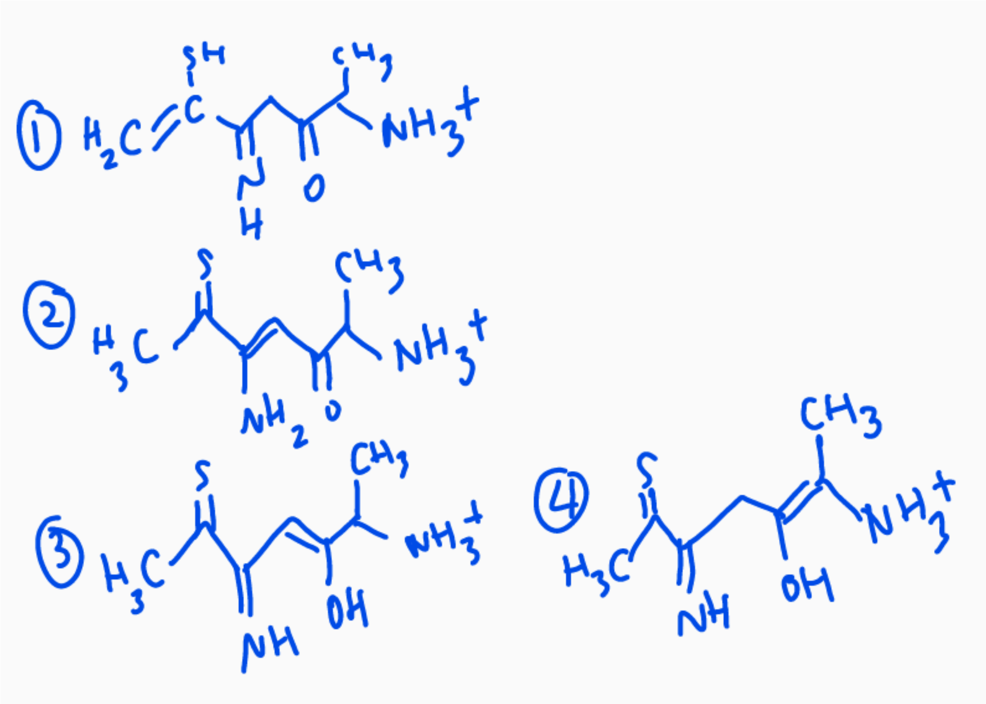
(ii)



[1]

Reject if stereoisomers drawn with chiral carbon being the one attached to OH group

(iii)



Compound 1: C=S changes
Compound 2: C=N changes

- BOD if there is 2 consecutive double bonds, i.e. S=C=C-NH or HS-C=C=NH

Compound 3: C=O changes
Compound 4: C=O changes but forms different double bond to different carbon
Accept variations, such as C=S and C=O changes in the same compound.

[1] per compound

(iv)

1. Alkenes involve C=C [idea of two same atoms]
2. Have equal electronegativity
3. will not be deprotonated easily

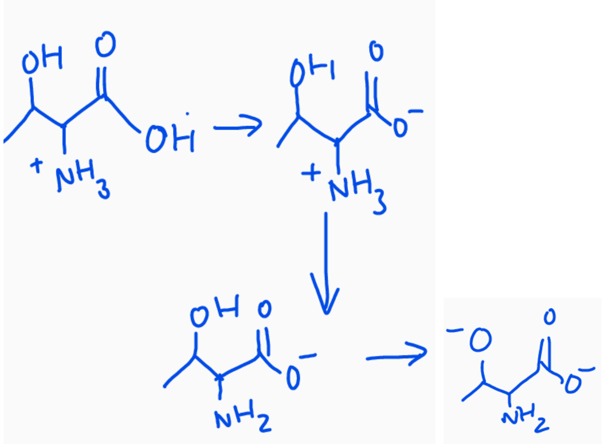
[0.5] per point

(v)

1. Lactam-lactim [0.5]
2. Amide-imidic acid [1]
3. Enol-ketone [0.5]

Penalise 0.5m for every additional wrong tautomer pair

(v)



[0.5] for any 2 structures correct
[1] for all 4 structures correct

1. At low pH, NH2 group is protonated due to high [H+] conc
2. As pH increases, carboxylic acid is deprotonated first as conjugate base highly stabilised by 2 highly EN O atoms
3. NH3+ is then deprotonated to remove the charge as pH exceeds 7 via neutralisation for stability
4. OH group is deprotonated the last because it has a very high pKa value as the alkoxide is destabilised by the electron donating alkyl groups

[0.5] for any 1 point
[1] for any 3 points

Q3)
(a)
Molar conc of Mg2+ = (1.25+1.5)/2 = 1.375 [0.5]
Molar conc of Cl- = 2x(1.25/2) = 1.25 [0.5]
Molar ionic strength = (½)(1.375)(2)^2 + (½)(1.25)(1)^2 = 3.375 OR 3.38 [0.5] mol dm^{-3} [0.5]

(b)(i)

1. Should not be AgCN or AgBr because Ksp is much lower than the other 2 compounds,
2. and they only dissociate to give 1 Ag+ and 1 CN- or Br- ions, so molar concentration is lower
3. PbCl2 dissociates to give 3 ions - 1 Pb2+ and 2 Cl-
4. MgC2O4 dissociates to give 2 ions - 1 Mg2+ and 1 C2O4 2-
5. Let x be [Pb2+], 2x = [Cl-]. Let y be [Mg2+] = [C2O4 2-]
6. Molar ionic strength of PbCl2 = (½)(x)(2)^2 + (½)(2x)(1)^2 = 3x
7. Molar ionic strength of MgC2O4 = (½)(y)(2)^2 + (½)(y)(2)^2 = 4y
8. Ksp of PbCl2 = 4x^3 = 1.7 x 10^{-5}
9. Ksp of MgC2O4 = y^2 = 8.6 x 10^{-5}
10. By direct comparison, y is larger
11. 4y>3x

12. Hence molar ionic strength of MgC_2O_4 is the highest

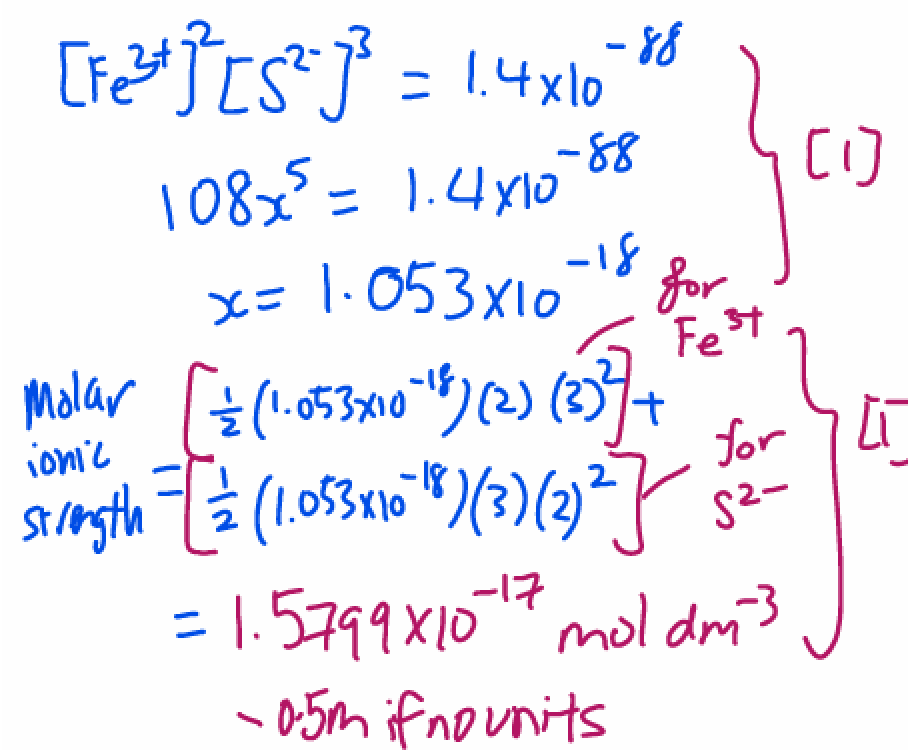
[1] for eliminating AgCN and AgBr
[0.5] for letting concentration of ions be unknowns
[1] for using molar ionic strength equation correctly
[0.5] comparing Ksp values
[1] correct deduction
Max 2m if specific calculations used

(ii)

1. Solutions are fully saturated [1], OR
2. Temperature of all solutions are equal (at 25 deg C) [1]

Reject equal volume of water as molar ionic strength involves concentration, i.e. mol PER vol

(iii)



$[Fe^{3+}]^2[S^{2-}]^3 = 1.4\times10^{-88}$

$108x^5 = 1.4\times10^{-88}$

$x = 1.053\times10^{-18}$

[1]

Molar ionic strength $= \left[\frac{1}{2}(1.053\times10^{-18})(2)(3)^2\right] + \left[\frac{1}{2}(1.053\times10^{-18})(3)(2)^2\right]$

for Fe^{3+}

for S^{2-}

$= 1.5799\times10^{-17}$ mol dm^{-3}

[1

−0.5m if no units

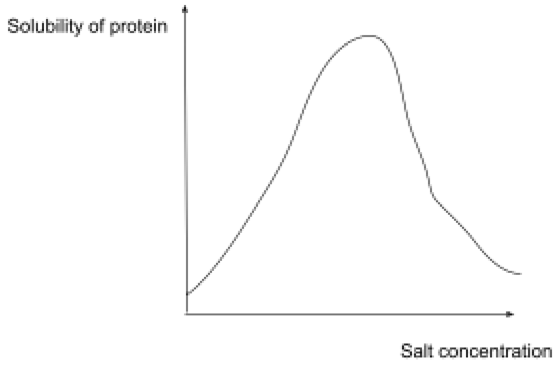
(iv)

1. Formation of soluble $PbCl_4^-$ decreases $[Pb^{2+}]$
2. $PbCl_2 \rightleftharpoons Pb^{2+} + 2Cl^-$
3. Poe shift right
4. More $PbCl_2$ dissolves to increase ionic strength
5. Although there is a decrease in number of ions due to complex formation,

6. This is negated by the much more significant increase in solubility of $PbCl_2$

1-2 points: 0.5m
3 points: 1m
4-5 points: 1.5m
6 points: 2m

(c)(i)



[1] for bell shaped curve

(ii)

<u>Salting in</u>

1. Ionic salt dissolves in water to form mobile charge carriers/ free ions
2. **Ionic bond** between the salt ions and the **<u>R groups</u>** of a.a. residues
3. Decreases **intramolecular** ionic bonds
4. Increases favourable interactions/ H-bonding of protein with water molecules
5. Energy released from these interactions is sufficient to overcome the already lowered energy used to break the intramolecular ionic bonds

<u>Salting out</u>

6. At high salt concentrations, the ion-dipole interactions between water molecules and ions become significantly stronger
7. Ions and water molecules are closer together
8. Ions no longer bind to ionisable groups of the amino acid residues
9. Increases strength of intramolecular ionic bonds between **<u>oppositely charged R groups</u>** of amino acid residues
10. Protein clumps/ become more compact
11. Decreases favourable interactions/ H-bonding of protein with water molecules
12. Energy released from these interactions is insufficient to overcome the increased energy required to break the intramolecular ionic bonds

Accept if any of the points are shown on a diagram

4-5 points: 0.5m
6 points: 1m
7 points: 1.5m
8 points: 2m
9 points: 2.5m
10> points: 3m

(d)(i)
Procedures:

1. Dissolve salt in a beaker containing specific volume of water [1]
2. Measured using a pipette [0.5]
3. Stir well until no further dissolution [0.5]
4. Can be seen by formation of cloudy suspension [0.5]
5. Filter the solution using a filter funnel lined with filter paper [0.5]
6. Discard residue [0.5]
7. Collect filtrate [0.5]
8. Add specific volume of specific concentration of NaOH(aq) into the filtrate [0.5]
9. Pour filtrate into the burette [0.5]
10. Pipette specific volume of specific concentration of HCl into a conical flask [0.5]
11. Indicator is methyl orange [0.5]
12. Dispense the titrant into the conical flask. At end point (red to orange), record the volume of hydroxide used. [1]

Max 3m

Results processing:

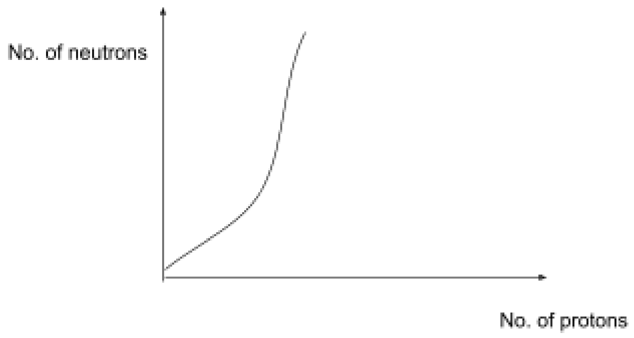
13. Find moles of OH- used [0.5]
14. Use a scale factor to determine number of moles in original solution (x) [0.5]
15. Find number of moles of OH- ions from NaOH (aq) (y) [0.5]
16. Find number of moles of OH- ions contributed by the salt (x-y) [0.5]
17. Find concentration of OH- ions in the initial solution [0.5]
18. Use Ksp formula (depending on the type of salt) to find the Ksp value [0.5]

Max 3m

Q4)
(a)(i)

1. Magic number is 184 [0.5]
2. Requires many protons in a nucleus, which is electrostatically unfavourable due to repelling of protons [0.5]

(ii)



[1] for correct axes + increase at increasing rate trend
Reject if the number of neutrons are on the x-axis. Number of neutrons is dependent on number of protons.

1. Neutrons have 0 charge [0.5]
2. Hence can stabilise the nucleus by preventing EFOA and hence repulsion of positively charged protons [0.5]

(b)
A is oxygen (oxygen-16) [0.5]
B is lead (lead-208) [0.5]

(c)(i)

1. Amount of time it takes for concentration of Roentgenium-282 sample to decrease to half the original sample (is 2.2 min) [1]

(ii)

1. Decays very quickly
2. Difficult to find the relative abundance of isotopes
3. Artificially synthesised element

0.5m per point

(iii)
(1.3)(0.5)^n = 0.1 [0.5]
n=3.70
(3.70)(2.2) = 8.14 min [0.5 - with units]

(d)
(i)

1. High temperatures
2. Protected from external environment
3. Requires high speed of nuclei for nuclear fission
4. Have highly sensitive sensors to detect atoms

5. AVP;;

0.5m per point

(ii)

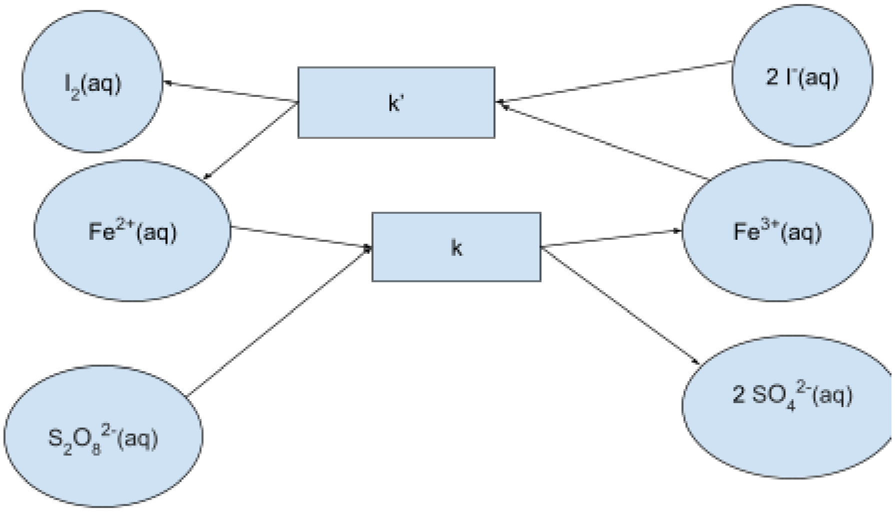
1. High nuclear charge
2. but even higher shielding effect
3. due to very high number of inner quantum electron shells
4. to ensure electrical neutrality of atom
5. Effective nuclear charge very low
6. Electrons are easily donated/ easily oxidised/ reduces other chemicals easily

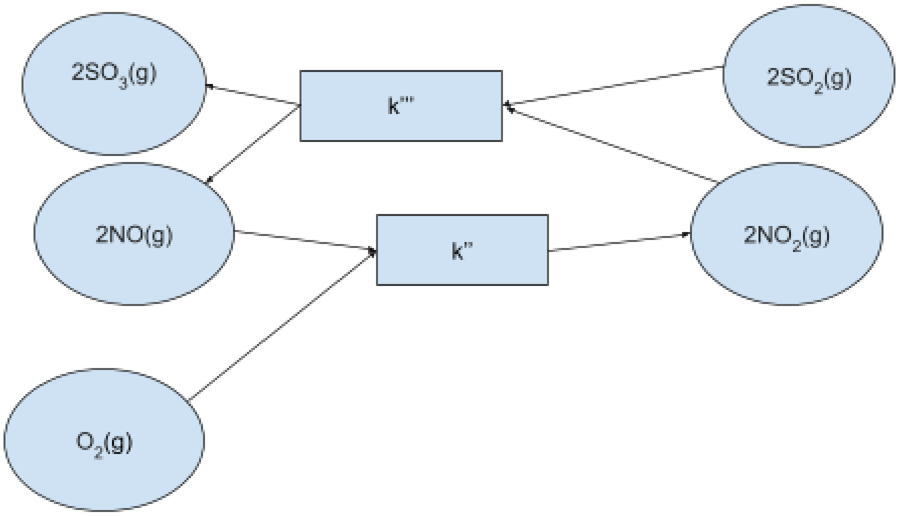
1-2 points: 0.5m
3 points: 1m
4 points: 1.5m
5 points: 2m

Q5)
(a) (i)
[1] for each correct network
Penalise 0.5m per mistake (max 1m for each network) for:

- Arrows pointing in wrong direction
- Wrong reactants/ products

Accept if no stoichiometric ratio is written
BOD if state symbols not written, or if balancing of equation was done wrongly
Penalise 0.5m once if rate constants *k* is repeated without use of k' etc





(ii)

1. Easier to see the relationship between different chemicals
2. Can see how different chemicals are linked/ used as reactants or products, especially for complex systems
3. AVP

[1] for any 1

(iii)

1. Homogenous [0.5] catalyst [0.5]
2. Provides alternative chemical pathway lower in activation energy/ increases ROR [0.5]
3. Regenerated [0.5]

(iv)

Time/ s	Final burette reading/ cm^3	Initial burette reading/ cm^3	Volume of $KMnO_4$/ cm^3	Concentration of **X** at specific time interval/ mol dm^{-3}	Concentration of [**A**]/ mol dm^{-3}
60	17.30	33.20	**15.90**	**1.33**	0.230

MnO4 – + 8H+ + 5e– → Mn2+ + 4H2O

5**X** (aq) → 5**Z** (aq) + $5e^-$

Overall equation: MnO4 – + 5X + 8H+ + 5e– → Mn2+ + 4H2O +5Z

No. of moles of KMnO4 used = 15.90/1000 x 0.250 = 0.003975 mol

Mole ratio of X to MnO4 - = 5/1

No. of moles of X = 0.003975 x 5 = 0.0200mol

[X] before quenching = 0.0200/ (15/1000) = 1.33 mol dm^{-3} (3sf)

Since units for rate constant is $mol^{-2}dm^{6}\ s^{-1}$, and order of reaction wrt [X] is 1, we can conclude that the order of reaction wrt [A] is 2.
Rate of reaction = 0.0230 x 1.3333 x 0.230^2 = 0.00162 mol $dm^{-3}\ s^{-1}$

[0.5] for correct vol of KMnO4
[0.5] for correct overall equation of redox
[0.5] for correct concentration of X
[0.5] Recognising that order of reaction wrt A is 2
[0.5] Correct substitution into rate equation and getting correct rate
[0.5] Correct units

(v)

1. Possible to find initial ROR [0.5]*
2. Rate = k [X][A]^2, and we know k, and [A] (using the sensor) [0.5]
3. ROR of C + Y to form D + X is much higher than that of A + X → Y + B [0.5]
4. We know the initial conc of X via the titration. Almost all of the X used up to form Y will immediately be converted back to X [0.5]
5. So [X] remains relatively constant, i.e. remains fixed at its ini conc [0.5]
6. Not possible to find ROR at t = 60s [0.5]*
7. Conc of X remains constant and a titration cannot be carried out to find its actual conc when t = 60s (which occurs without the contamination) [0.5]

Max 3m, points with * are compulsory

(b)(i)
All correct/ 1 or 2 errors: [1]
3 - 4 errors: [0.5]
Accept if positive signs are not written
BOD if R1, R2 etc. are not written
No marks if the minus signs are not written
No marks if chemical is not specified

$$\begin{array}{c|cccc}
 & R1 & R2 & R3 & R4 \\
\hline
[Co(NH_3)_5H_2O]^{3+} & -1 & 0 & 0 & 0 \\
H_2O & -1 & +1 & 0 & 0 \\
[Co(NH_3)_5OH]^{2+} & +1 & 0 & -1 & 0 \\
H_3O^+ & +1 & 0 & 0 & 0 \\
HNO_2 & 0 & -2 & 0 & +1 \\
N_2O_3 & 0 & +1 & -1 & 0 \\
[(NH_3)_5Co{-}O{-}H \cdots O{-}N{-}NO_2]^{2+} & 0 & 0 & +1 & -1 \\
[(NH_3)_5Co{-}ONO]^{2+} & 0 & 0 & 0 & +1
\end{array}$$

$$Rate = k\,[N_2O_3][[Co(NH_3)_5OH]^{2+}]$$

$$K_c = \frac{[N_2O_3]}{[HNO_2]^2}$$

$$K_c' = \frac{[H_3O^+][[Co(NH_3)_5OH]^{2+}]}{[[Co(NH_3)_5H_2O]^{3+}]}$$

A or B [0.5]

$$Rate = k\,\frac{[HNO_2]^2[[Co(NH_3)_5H_2O]^{3+}]}{[H_3O^+]}$$

[0.5]

(ii)

1. Co has high charge density/ high charge of +3 and low atomic radius [1]
2. Can polarise the O-H bond in the water ligand to liberate a H^+ (H_3O^+) ion [1]

(c)(i)

$2e^- + 2H^+ + HBrO_3 \rightarrow HBrO_2 + H_2O$

$Ce^{3+} \rightarrow Ce^{4+} + e^-$

Full equation: $2H^+ + HBrO_3 + 2Ce^{3+} \rightarrow HBrO_2 + H_2O + 2Ce^{4+}$ [1]

$Ce^{4+} + e^- \rightarrow Ce^{3+}$

$2H_2O + BrCH(COOH)_2 \rightarrow Br^- + 3CO_2 + 7H^+ + 6e^-$

Full equation: $6Ce^{4+} + 2H_2O + BrCH(COOH)_2 \rightarrow Br^- + 3CO_2 + 7H^+ + 6Ce^{3+}$ [1]

(ii)

1. When [Ce^{4+}] is very high, solution is yellow [0.5]
2. Ce^{4+} catalyses the oxidation of Ce^{3+} to form Ce^{4+}, which further intensifies the yellow colouration [0.5]
3. Ce^{4+} reduced by BMA to form Ce^{3+} and Br^-, so [Ce^{4+}] decreases and [Ce^{3+}] increases. [0.5]
4. Br^- inhibits the oxidation of Ce^{3+} to Ce^{4+} so [Ce^{3+}] is now very high [0.5]
5. Solution further decolourises from yellow to colourless [0.5]
6. As there is decreased [Ce^{4+}], no more Br^- is produced [0.5]
7. The inhibitory effect wears off and Ce^{3+} can be oxidised to Ce^{4+} again [0.5]
8. The cycle repeats [0.5]

Max 3m.

(ii)

1. Ce is a transition metal
2. Partially filled d orbitals
3. In the presence of water ligands
4. d orbitals split
5. Electrons from lower energy d orbitals absorb light
6. With a wavelength corresponding to the energy gap between the 2 orbitals
7. And are promoted to a higher energy level / d → d transition
8. The complementary colour is observed

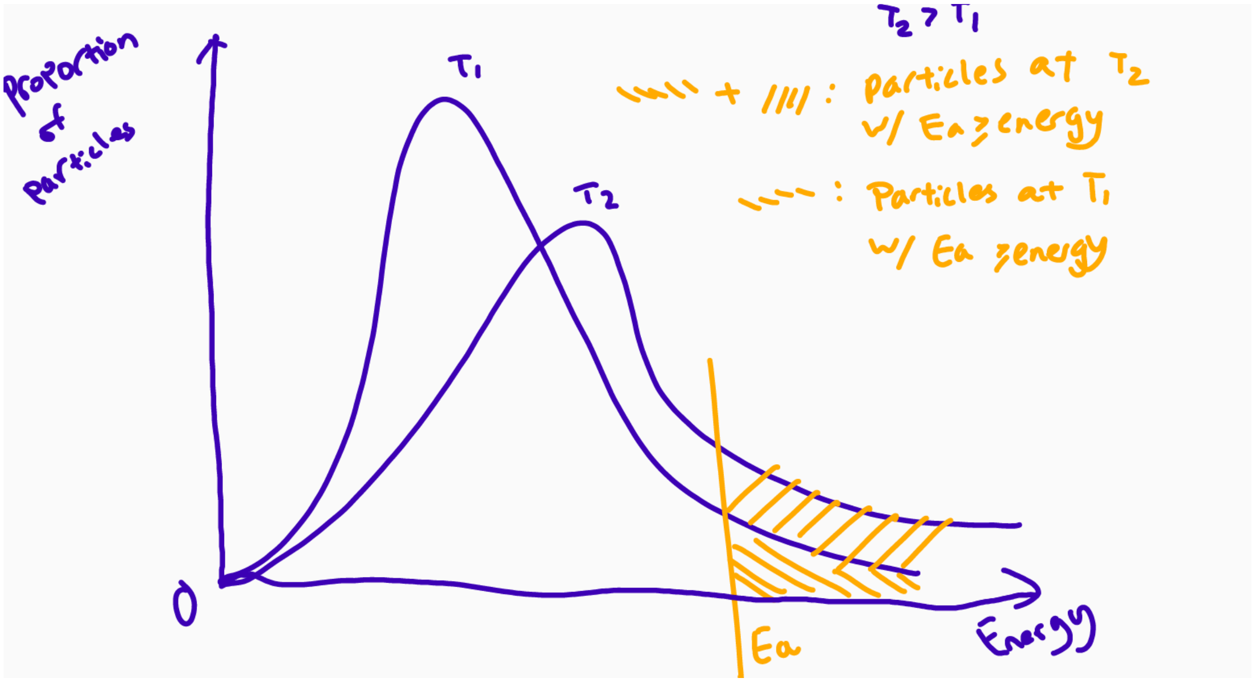
3-4 points: 0.5m

5 points: 1m

6-7 points: 1.5m

8 points: 2m

(iii)



[1] for correct diagram. Penalise 0.5m, max 1m, for every minor mistake, including **ONLY**:

- Not writing 0 at origin
- Not labelling axes

No marks if any of the following are wrong:

- Peaks (T2 should be lower than T1)
- Not labelling T2>T1
- Not labelleing Ea line

1. Increase temperature increases average KE of particles
2. Increased frequency of effective collisions between reactant particles
3. Higher proportion of particles have energies higher than activation energy
4. Hence can collide with sufficient energy
5. Any relevant link to the idea of oscillation - e.g. faster oxidation of Ce3+ and reduction of Ce4+

[0.5] for any 3 from points 1-4

[0.5] for compulsory point 5