Raffles Institution **2 Oct 2013**
H2 Chemistry Prelim Exam 2013 – Paper 3 (Suggested Answers)

Question 1

(a) The reaction involves autocatalysis where CH_3CH_2COOH (or H^+ from the dissociation of CH_3CH_2COOH) is the autocatalyst.

The rate of reaction gradually increases at first as the autocatalyst produced catalyses the reaction. However, the rate decreases subsequently as the $[CH_3CH_2COOCH_2CH_3]$ decreases.

(b) (i) Plotted the graph for Experiment 2.
- smooth curve with 6 correctly plotted points

(ii) **To find the order of reaction with respect to the ester.**
Consider the graph for experiment 1.
1^{st} $t_{1/2}$ = 31.0 min (with construction lines shown on the graph)
2^{nd} $t_{1/2}$ = 32.0 min (with construction lines shown on the graph)
Since $t_{1/2}$ is constant, order of reaction with respect to ethyl propanoate = 1

Alternative answer
Can also use the graph for experiment 2 to find two $t_{1/2}$ values.
1^{st} $t_{1/2}$ = 63.0 min (with construction lines shown on the graph)
2^{nd} $t_{1/2}$ = 63.0 min (with construction lines shown on the graph)
Since $t_{1/2}$ is constant, order of reaction with respect to ethyl propanoate = 1

To find the order of reaction with respect to NaOH.
For experiment 1, initial rate = 0.010/24.0 = 4.17×10^{-4} mol dm^{-3} min^{-1}
For experiment 2, initial rate = 0.010/48.0 = 2.08×10^{-4} mol dm^{-3} min^{-1}
When [NaOH] is doubled, initial rate is also doubled ($4.17 \times 10^{-4} / 2.08 \times 10^{-4} = 2$).
Hence order of reaction with respect to NaOH = 1

Alternative answer
Consider the graph for experiment 2.
$t_{1/2}$ = 63.0 min
$\Rightarrow$ $t_{1/2}$ for experiment 2 = (2)($t_{1/2}$ for experiment 1)
$\Rightarrow$ reaction rate is halved when [NaOH] is halved.
Hence order of reaction with respect to NaOH = 1

(iii) Rate = k $[CH_3CH_2CO_2CH_2CH_3]$ [NaOH]

(iv) For experiment 1,
initial rate = 0.010/24.0 = 4.17×10^{-4} mol dm^{-3} min^{-1}
initial [NaOH] = 2.0 mol dm^{-3}
initial $[CH_3CH_2CO_2CH_2CH_3]$ = 0.0200 mol dm^{-3}

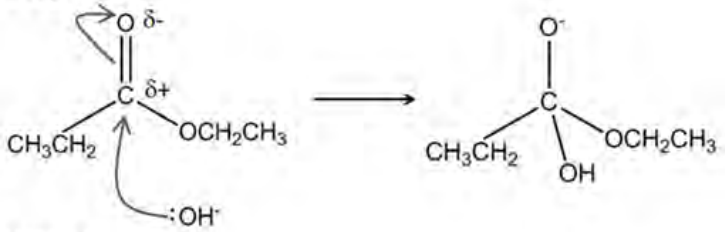
Hence k = $4.17 \times 10^{-4} / [(2.0)(0.0200)]$ = 0.0104 mol^{-1} dm^3 min^{-1}

(v) Refer to the graph.
Sketch with correct co-ordinates and 2 half-lives.
Half-life = 31 to 32 min

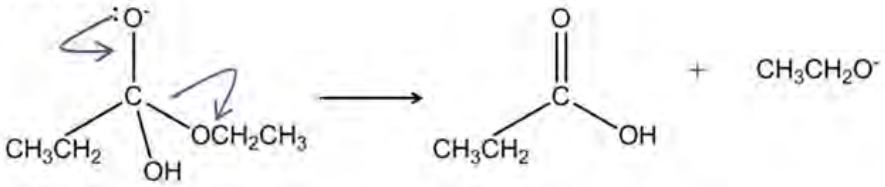
Question 1

(b) (vi)

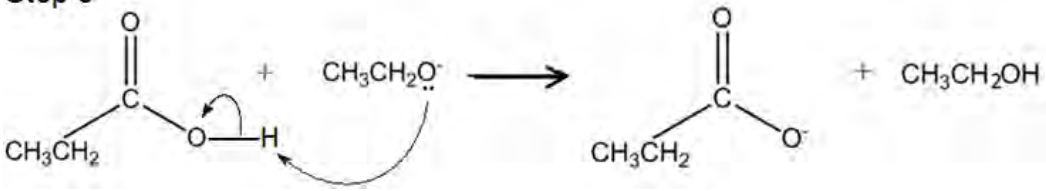
Step 1



Step 2



Step 3



(c) (i) The conjugate base of the ester is stabilised as the negative charge can be dispersed by delocalisation into the adjacent C=O group.

Note: Accept all sensible answers

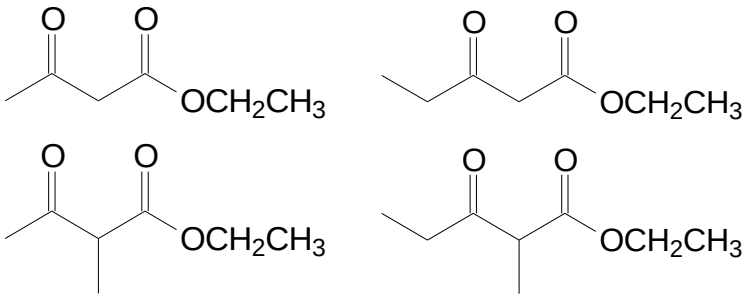
(ii) (1) The conjugate base of ethane is unstable as the electron-donating methyl group will intensify the negative charge.

Note: Accept all other sensible answers.

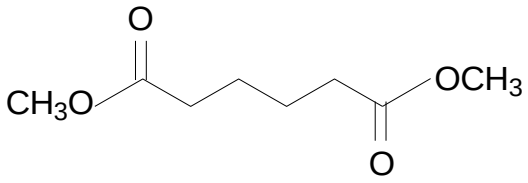
(ii) (2) The –COOH group of ethanoic acid is more acidic than the α-hydrogen atom.

Note: Accept all other sensible answers.

(iii)



(iv)

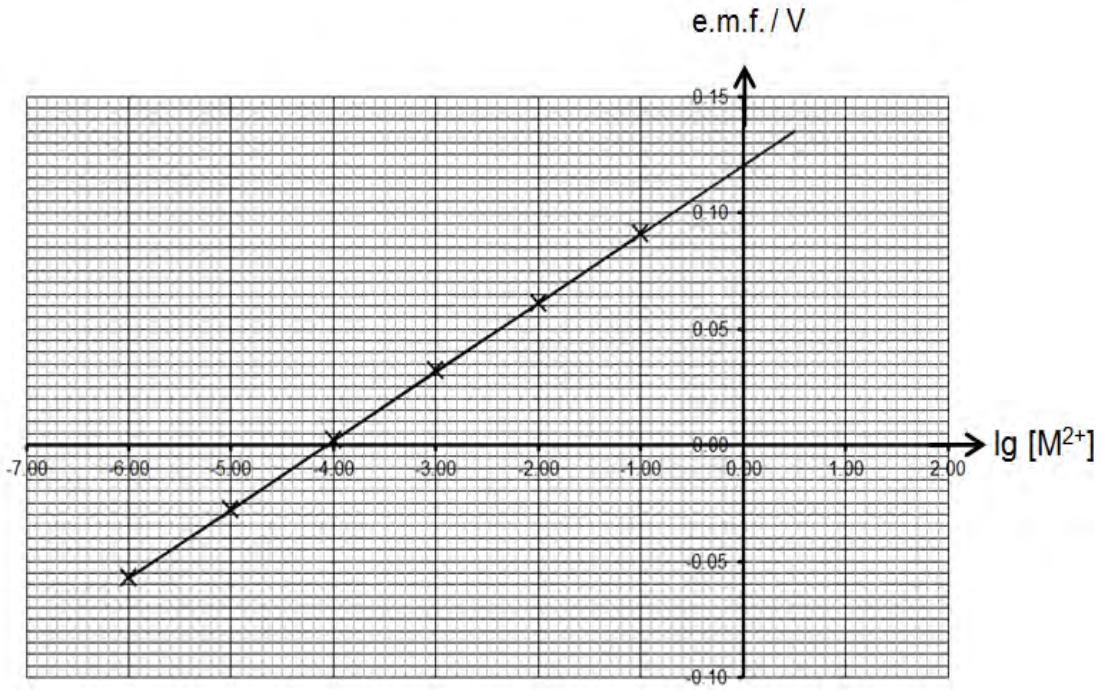


Question 2

(a) Nickel is regarded as a transition element because it is able to form at least <u>one stable ion</u> (e.g. Ni^{2+}) with a <u>partially filled d-subshell</u>.

Ni^{2+} $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^8$

(b) **(i)**



(ii) Under standard conditions, $[M^{2+}] = 1.0$ mol dm^{-3}
$\Rightarrow$ lg $[M^{2+}]$ = lg 1.0 = 0
From the graph, when lg $[M^{2+}] = 0$, e.m.f. = $E^{\ominus}_{cell}$ = +0.12 V

$Ni(s) + M^{2+}(aq) \longrightarrow Ni^{2+}(aq) + M(s)$
$E^{\ominus}_{cell} = E^{\ominus}_{M2+/M} - E^{\ominus}_{Ni2+/Ni} = E^{\ominus}_{M2+/M} - (-0.25) = +0.12$ V
$E^{\ominus}_{M2+/M} = -0.13$ V

(iii) At equilibrium, $E_{cell} = 0$ V
From the graph, when $E_{cell} = 0$ V, lg $[M^{2+}] = -4.10$
$\Rightarrow [M^{2+}] = 10^{-4.10} = 7.943 \times 10^{-5}$ mol dm^{-3}

$[Ni^{2+}] = 1.0$ mol dm^{-3}
$K_c = \frac{[Ni^{2+}]}{[M^{2+}]} = \frac{1.0}{7.943 \times 10^{-5}} = 1.26 \times 10^4$

(iv) Reaction: $Cu^{2+}(aq) + M(s) \longrightarrow Cu(s) + M^{2+}(aq)$
$E^{\ominus}_{cell} = 0.34 - (-0.13) = +0.47$ V
Since $E^{\ominus}_{cell} > 0$, the reaction is feasible under standard conditions.

Any **<u>one</u>** of the following observations:
- blue solution of $CuSO_4$ fades
- pink deposit of Cu forms
- the rod of metal M dissolves

Assumption: $M^{2+}(aq)$ is colourless.

Question 2

(c) **(i)** In both cases, there are 4 electron pairs around the central O atom giving rise to a tetrahedral electron-pair geometry to minimize repulsion.

In the $[Ni(H_2O)_6]^{2+}$ ion, there are 3 bond pairs and 1 lone pair around the O atom. In the isolated H_2O molecule, there are 2 bond pairs and 2 lone pairs around the O atom.

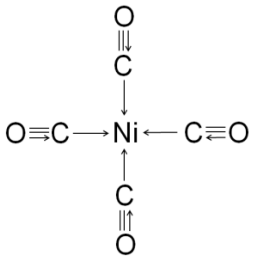
Since the isolated H_2O molecule has one more lone pair around the O atom and the strength of electron-pair repulsion decreases in the following order:
lone pair–lone pair > lone pair–bond pair > bond pair–bond pair,
the H-O-H bond angle is smaller in the isolated H_2O molecule.

(ii) The two solutions have different colours despite containing the same nickel(II) ion because of the presence of different ligands.

Both the H_2O and NH_3 ligands split the five 3d-orbitals of the Ni^{2+} ion into two sets of slightly different energy levels but to different extents.

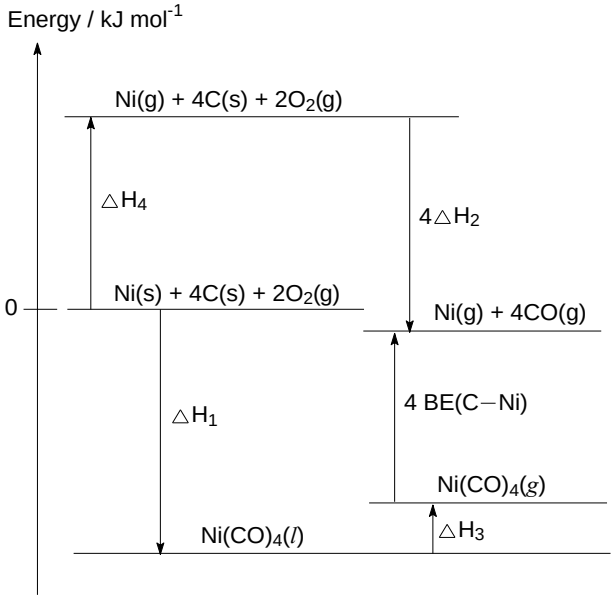
Hence $[Ni(H_2O)_6]^{2+}(aq)$ and $[Ni(NH_3)_6]^{2+}(aq)$ ions absorb different wavelengths of light from the visible spectrum for d-d transitions (i.e. the promotion of electrons from the lower energy d orbitals to the higher energy d orbitals). Consequently different colours, corresponding to the complements of the different colours absorbed, are observed for the two different complex ions.

(d) **(i)**

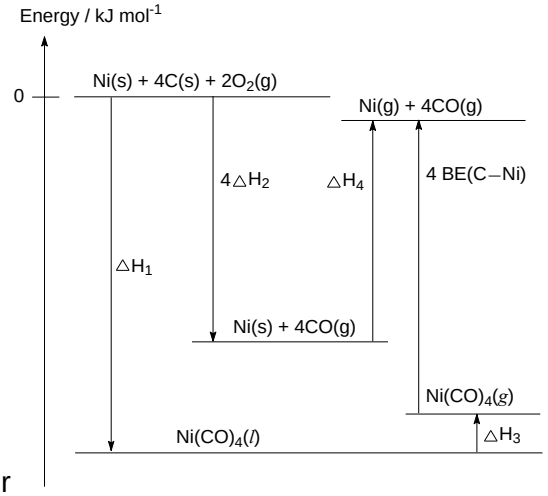


(ii) The bond energy of a X–Y bond is the average amount of energy required to break 1 mole of the X–Y bonds in the gaseous state to form X(g) and Y(g) atoms.

(iii)



or



(d) **(iii)** By Hess' law, $\Delta H_1 = \Delta H_4 + (4)(\Delta H_2) - 4\ BE(C–Ni) - \Delta H_3$

$-636 = +431 + (4)(-111) - 4\ BE(C–Ni) - 29$

$4\ BE(C–Ni) = 594$

$BE(C–Ni) = 594/4 = 148.5 = 149\ kJ\ mol^{-1}$

Question 3

(a) $Si > S_8 > P_4$ or Si, S_8, P_4

Si has a giant molecular structure. It has the highest melting point because a lot of heat energy is required to break the extensive network of relatively strong Si–Si covalent bonds.

Both P and S have simple molecular structures, with P existing as non-polar P_4 molecules and S existing as non-polar S_8 molecules.

S has a lower melting point than Si because less heat energy is needed to overcome the weaker instantaneous dipole-induced dipole attractive forces among the S_8 molecules than breaking the covalent bonds in Si.

P has the lowest melting point among the three elements because the instantaneous dipole-induced dipole forces present are even weaker than those in S since the P_4 molecule has fewer electrons and hence a smaller electron cloud size than that of the S_8 molecule.

(b) (i) **A**: Na_2O

pH = 13.70
pOH = 14 – 13.70 = 0.30
$[OH^-] = 10^{-0.30} = 0.501$ mol dm^{-3}
Amount of NaOH = (0.100)(0.501) = 0.0501 mol
$Na_2O(s) + H_2O(l) \longrightarrow 2NaOH(aq)$
Amount of Na_2O = (½)(0.0501) = 0.0251 mol

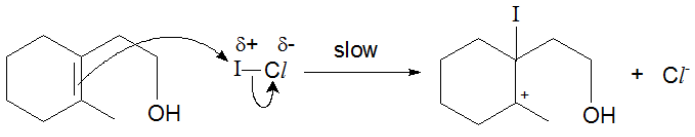
(ii) **B:** $SiCl_4$
$SiCl_4(l) + 2H_2O(l) \longrightarrow SiO_2(s) + 4HCl(aq)$
Or $SiCl_4(l) + 4H_2O(l) \longrightarrow SiO_2.2H_2O(s) + 4HCl(aq)$
Or $SiCl_4(l) + 4H_2O(l) \longrightarrow Si(OH)_4(s) + 4HCl(aq)$

(c) (i) $2\ IF_5 \rightleftharpoons IF_4^+ + IF_6^- \Rightarrow x = 4$ and $y = 6$

Consider the IF_4^+ ion.
Around the I atom, there are 5 electron pairs.
To minimise repulsion, the electron-pair geometry is trigonal bipyramidal.
Since there are 4 bond pairs and 1 lone pair, the shape of the IF_4^+ ion is distorted tetrahedral (or seesaw or sawhorse).

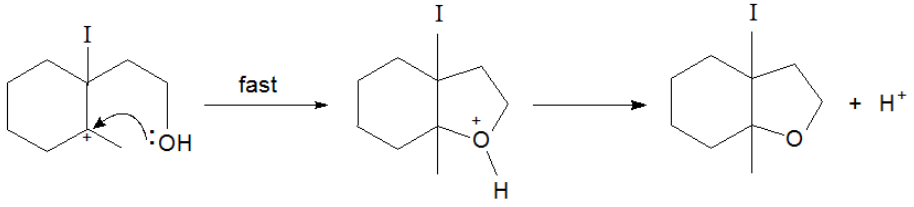
(ii) The mechanism involved in the reaction is electrophilic addition.

Step 1



a carbocation

Step 2



Question 3

(d) Initially, the solution of Br_2 in hexane is red-brown in colour.

When KI(aq) is added and the mixture shaken, Br_2 goes to the aqueous layer and the following redox reaction occurs:

$$Br_2(aq) + 2I^-(aq) \rightarrow 2Br^-(aq) + I_2(aq)$$

The I_2 formed in the aqueous layer dissolves in the hexane layer. Consequently, a violet/purple hexane layer above a colourless/pale yellow/yellow aqueous layer can be observed in the test-tube.

(e) **(i)** Molar ratio of Ag : C*l* : N : C : H $= \frac{52.6}{108} : \frac{17.3}{35.5} : \frac{13.6}{14.0} : \frac{11.7}{12.0} : \frac{4.8}{1.0}$

$= 0.487 : 0.487 : 0.971 : 0.975 : 4.8$

$= 1 : 1 : 2 : 2 : 10$

Hence the empirical formula of **F** is $AgClN_2C_2H_{10}$.
F is $[Ag(CH_3NH_2)_2]Cl$.

(ii) When dilute nitric acid is added to **F**, a white precipitate of AgC*l* forms and is insoluble in excess dilute nitric acid.

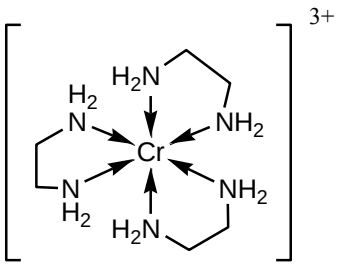
$[Ag(CH_3NH_2)_2]Cl(aq) + 2HNO_3(aq) \longrightarrow AgCl(s) + 2CH_3NH_3^+(aq) + 2NO_3^-(aq)$
Or
$Ag(CH_3NH_2)_2]^+ + Cl^- + 2H^+(aq) \longrightarrow AgCl(s) + 2CH_3NH_3^+(aq)$

Question 4a

(a) **(i)** $2Cr_2O_3(s) + 3O_2(g) + 8OH^-(aq) \longrightarrow 4CrO_4^{2-}(aq) + 4H_2O(l)$

(ii) $[Cr(H_2O)_6]^{3+}$

(iii)



- diagram should indicate the octahedral shape

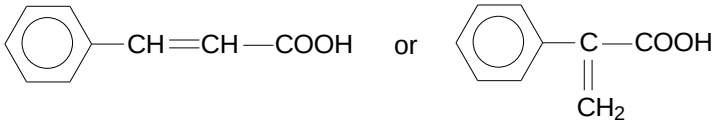
(iv) From yellow to orange to green.

(v) Test: Add NaOH(aq) dropwise till excess to each sample in a test-tube.

For the cation in **A**, a grey-green precipitate forms which is soluble in excess NaOH(aq) to form a dark green solution.
For the cation in **C**, a red-brown precipitate forms which is insoluble in excess NaOH(aq).

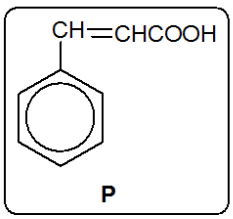
Note: Accept all sensible answers

Question 4b

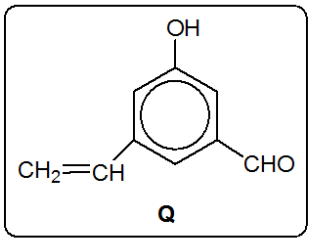
Observation	Deduction
P and **Q** have molecular formula $C_9H_8O_2$.	Both **P** and **Q** contain a benzene ring due to the relatively high C to H ratio.
P gives CO_2(g) upon reaction with $NaHCO_3$ but not **Q**.	**P** undergoes **acid-base reaction** with $NaHCO_3$ but not **Q**. $\Rightarrow$ **P** is a **carboxylic acid** but **Q** is not a carboxylic acid.
Q reacts with ammoniacal solution of $AgNO_3$ to give **R**.	**Q** undergoes **oxidation** with Tollens' reagent to give **a** grey precipitate of Ag and **R**, a carboxylate salt. $\Rightarrow$ **Q** is an **aldehyde.**
Upon oxidation with hot acidified $KMnO_4$, 1 mole of **P** gives 2 moles of CO_2 and 1 mole of benzoic acid	Oxidation of side-chain occurs. $\Rightarrow$ **P** contains **a benzene ring with only 1 side chain**. Hence **P** can either be 
Upon oxidation with hot acidified $KMnO_4$, 1 mole of **Q** gives 1 mole of CO_2 and 1 mole of a compound, $C_8H_6O_5$.	Oxidation of C=C in **Q** occurs. $\Rightarrow$ **Q** contains a $C=CH_2$ structural unit which is oxidised to give –COOH and CO_2. Oxidation of –CHO in **Q** also occurs. $\Rightarrow$ The oxidation product contains 2 –COOH groups. With a molecular formula of $C_8H_6O_5$, the oxidation product also has to contain a phenolic –OH group. Hence the oxidation product contains a benzene ring with 3 substituents: 2 –COOH groups and 1 –OH group. $\Rightarrow$ **Q** contains **a benzene ring with 3 substituents**: –CHO, $-CH=CH_2$ and –OH groups.
P decolourises Br_2(aq) in the dark to form **S**, $C_9H_9O_3Br$.	**P** undergoes **electrophilic addition**. $\Rightarrow$ **P** is an **alkene or contains a C=C bond.** And **S** is a bromohydrin.
Q reacts with Br_2(aq) to form a white precipitate **T**, $C_9H_6O_3Br_4$.	**Q** also undergoes **electrophilic substitution**. $\Rightarrow$ **Q** is a **phenol** and its two substituents are at positions 3 & 5. **Q** undergoes electrophilic addition $\Rightarrow$ **Q** is an alkene or contains a C=C bond.
P is reacted with a stoichiometric amount of KOH(aq).	**P** undergoes acid-base reaction to give a carboxylate salt as a nucleophile.
T reacts with the carboxylate salt to give **U**, $C_{18}H_{13}O_5Br_3$.	**T** undergoes **nucleophilic substitution** to give an **ester**, **U**.

Question 4b

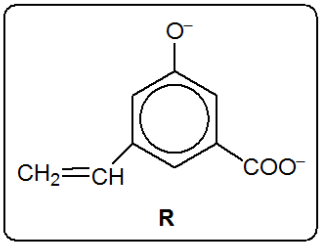
(b)



P



Q



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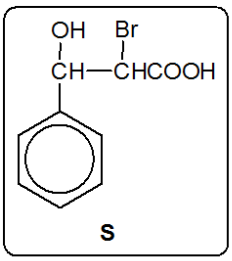
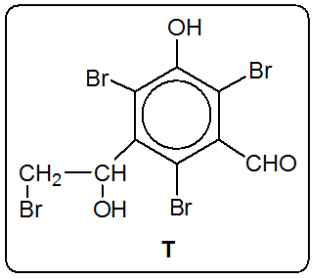
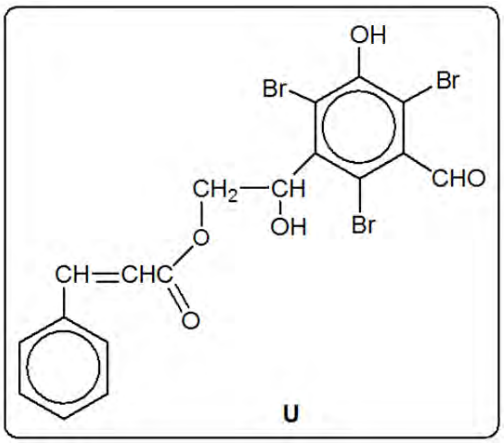


S

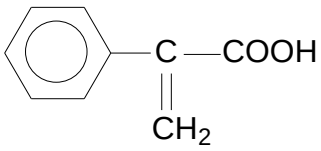


T

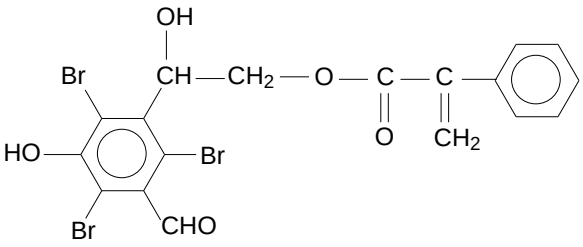


U

Alternative answer for **P**:

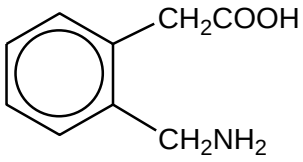


Corresponding answer for **U**



Question 4c

(c) **(i)**



L

(ii) If hot, acidified potassium manganate(VII) is used, side chain oxidation occurs, resulting in formation of **benzene-1,2-dicarboxylic acid** and the loss of the N atom**.** Hence the cyclic amide cannot be formed.

Suitable alternative: I_2(aq) and NaOH(aq), heat

Question 5

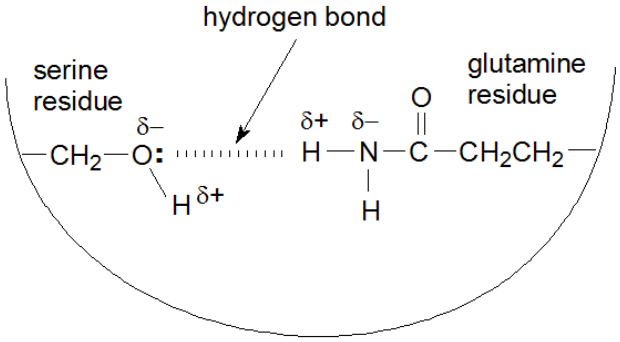
(a) val-ala-val-ser-gly-arg-asn-leu-gly-val

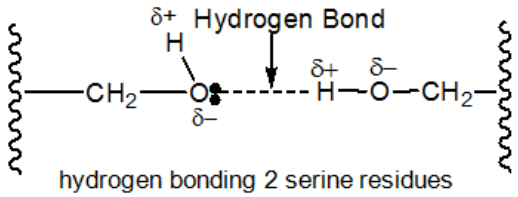
or leu-gly-val-ala-val-ser-gly-arg-asn-leu

or arg-asn-leu-gly-val-ala-val-ser-gly-arg

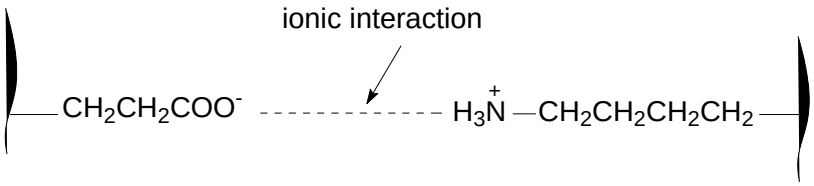
(b) Any **two** of the following:

1. Hydrogen bonding between the side chains of serine and glutamine amino acid residues.

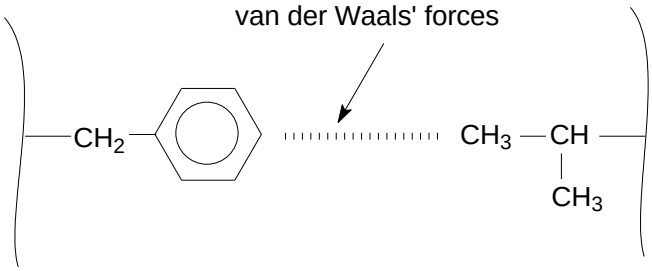




2. Ionic interaction (or electrostatic forces of attraction between positively and negatively charged groups) between the side chains of glutamic acid and lysine amino acid residues.



3. Van der Waals' forces between non-polar side chains of valine and phenylalanine amino acid residues.



Question 5

(c) **(i)** Entropy change is negative. This is because the protein chain folds into a tertiary structure which is less disordered (or more ordered).

(ii) $\Delta G = -585 - (298)(-1740 \times 10^{-3}) = -66.5$ kJ mol^{-1}

(iii) For the unfolding process, $\Delta H = +585$ kJ mol^{-1}

$\Delta S = +1740/1000 = 1.74$ kJ mol^{-1} K^{-1}

For the unfolding process to be feasible, $\Delta G(\text{unfolding}) < 0$

$\Delta G(\text{unfolding}) = \Delta H - T\Delta S < 0$

$T > \Delta H/\Delta S$

$T > 585/1.74$

$T > 336$ K

Hence the temperature at which unfolding <u>begins</u> is **336 K**.

Note: At T = 336 K, the reaction is at equilibrium and unfolding has begun.

Reaction: folding of protein chain $\rightleftharpoons$ unfolding of protein chain

Assumptions: ΔS and ΔH do not change with temperature.

(d) **(i)** Nucleophilic addition.

(ii) The shape with respect to the carbonyl carbon (of the aldehyde) is trigonal planar. Hence the carbonyl carbon atom can be attacked from either side of the plane by the lone pair on the O atom of the alcohol group, forming both the α-glucose and β-glucose units.

(e) **(i)** Let the mole fraction of β-glucose be x.

Hence the mole fraction of α-glucose is (1 – x).

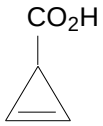
$(19.0)(x) + (113.4)(1-x) = 52.2$

$94.4x = 61.2$

$x = 0.648$

(ii) $K_c = \dfrac{[\alpha\text{-glucose}]}{[\beta\text{-glucose}]} = \dfrac{(1-0.648)(1.0)}{(0.648)(1.0)} = 0.543$

(f) **(i)** **T**:

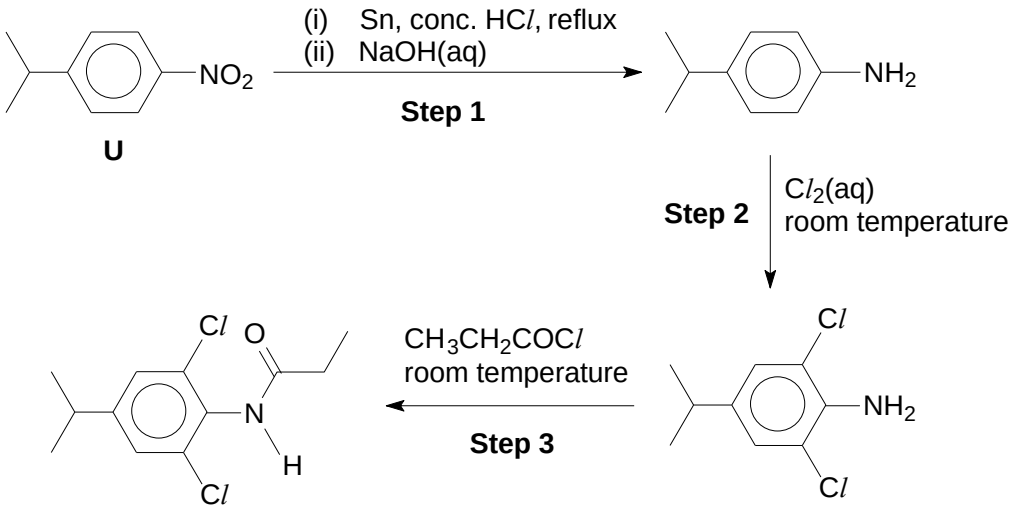


(ii) Ethanolic KOH, heat (or reflux)

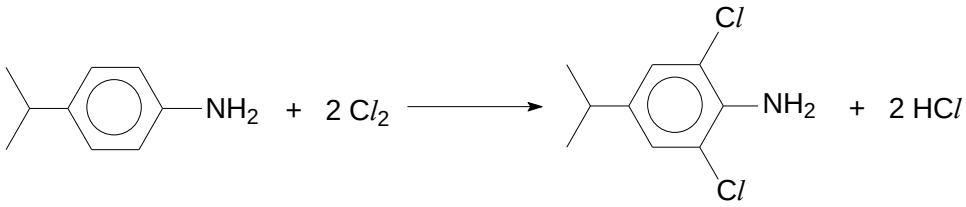
Or alcoholic KOH, heat

Question 5

(g) (i)



(ii)



(iii) Compound V is not basic because the lone pair of electrons on the nitrogen atom interacts with the pi-electron cloud of the adjacent C=O bond and is delocalised, and hence not available for co-ordination to a proton.

In addition, this lone pair of electrons also delocalises into the pi-electron cloud of the benzene ring.

(iv) **W**: