THE CANADIAN CHEMISTRY CONTEST 2023
for high school and CEGEP students

PART C: CANADIAN CHEMISTRY OLYMPIAD
Final Selection Examination 2023

(120 minutes)

This segment has five (5) questions. While students are expected to attempt **all** questions for a complete examination in 2 hours, it is recognized that backgrounds will vary and **students will not be eliminated from further competition because they have missed parts of the paper.**

Your answers are to be written in the spaces provided on this paper. All of the paper, is to be returned **immediately** by upload.

— PLEASE READ —

1. BE SURE TO COMPLETE THE INFORMATION REQUESTED AT THE BOTTOM OF THIS PAGE BEFORE BEGINNING PART C OF THE EXAMINATION.
2. STUDENTS ARE EXPECTED TO ATTEMPT ALL QUESTIONS OF **PART A** AND **PART C**. CREDITABLE WORK ON A LIMITED NUMBER OF THE QUESTIONS MAY BE SUFFICIENT TO EARN AN INVITATION TO THE NEXT LEVEL OF THE SELECTION PROCESS.
3. IN QUESTIONS WHICH REQUIRE NUMERICAL CALCULATIONS, BE SURE TO SHOW YOUR REASONING AND YOUR WORK.
4. ONLY NON-PROGRAMMABLE CALCULATORS MAY BE USED ON THIS EXAMINATION.
5. NOTE THAT A PERIODIC TABLE AND A LIST OF SOME PHYSICAL CONSTANTS WHICH MAY BE USEFUL CAN BE FOUND ON A DATA SHEET PROVIDED AT THE END OF THIS EXAMINATION.

PART A ( )
Correct Answers

25 x 1.6 = .../040

PART C

1. ...../012
2. ...../012
3. ...../012
4. ...../012
5. ...../012

TOTAL ...../100

Name _____ School _____
(LAST NAME, Given Name; Print Clearly)

City & Province _____ Date of Birth _____

E-Mail _____ Home Telephone ( ) -_____

Years at a Canadian high school ___ No. of chemistry courses at a Québec CÉGEP ___

Male ☐ Canadian Citizen ☐ Landed Immigrant ☐ Visa Student ☐

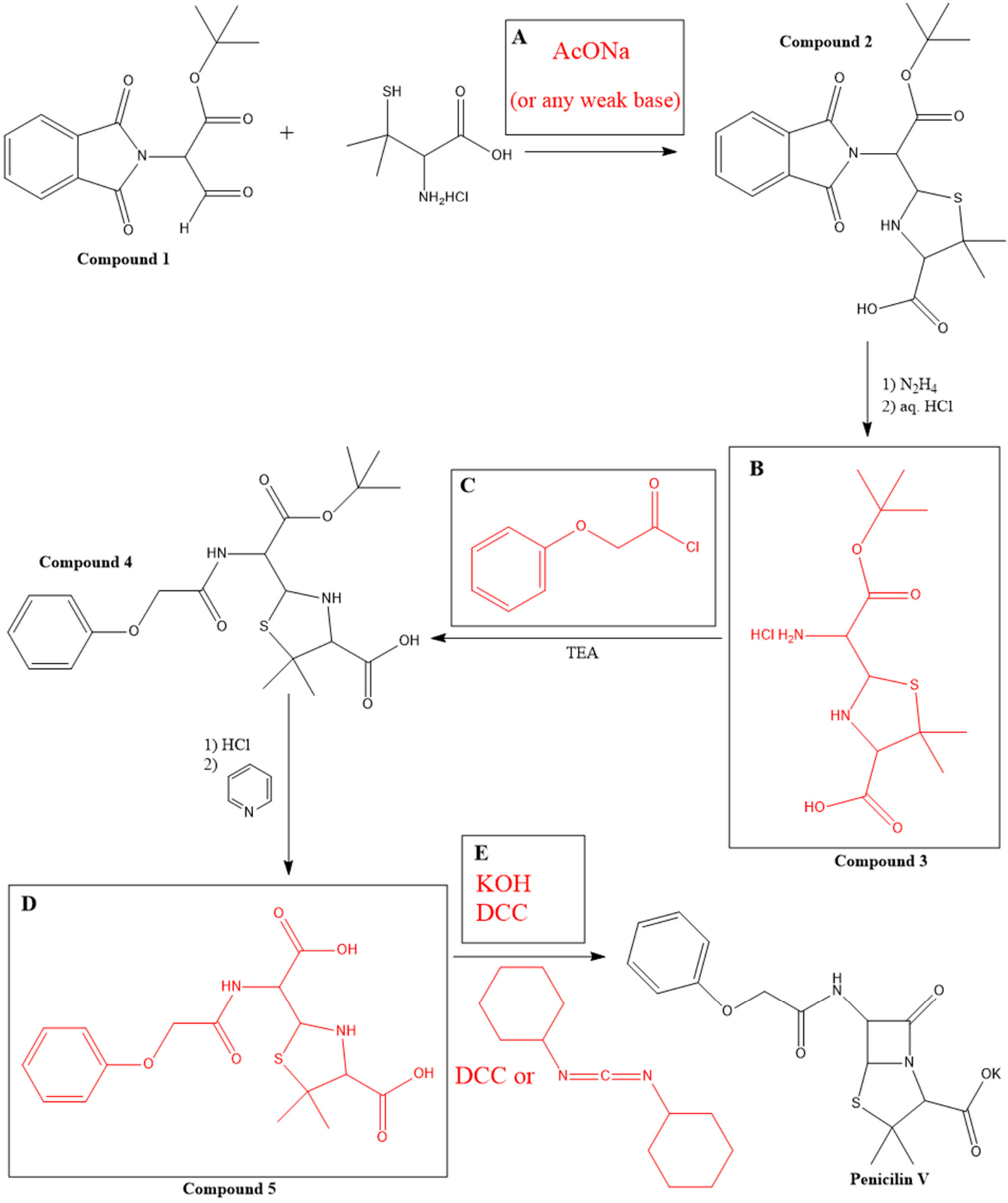
Female ☐ Passport valid until February 2024 ☐ Nationality of Passport _____

Teacher _____ Teacher E-Mail_____

1. ORGANIC CHEMISTRY

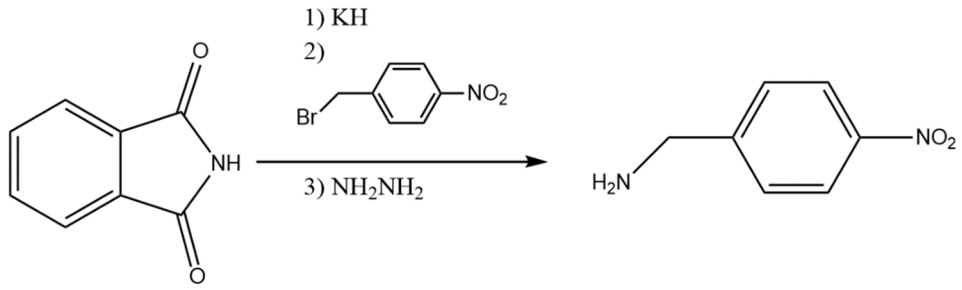
Penicillin is an antibiotic class first discovered by Alexander Fleming in 1928. Its total synthesis requires 7 steps.

a) Given the following compounds and reagents, determine reagents **A**, **C**, and **E**, as well as compounds **B** and **D**. **B, D & E 1 Mark each A & C 0.5 Mark each**
4 marks

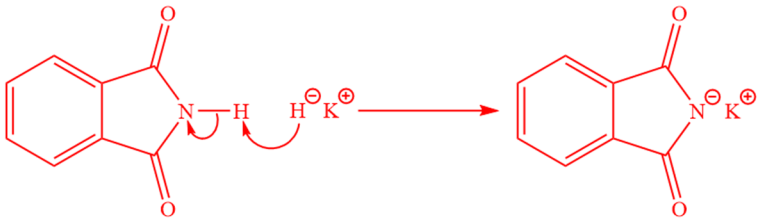


b) The synthesis of penicillin V features a phthalimide which is later deprotected to release a free amine, the full process of which is referred to as Gabriel synthesis. **Draw** the mechanism for the Gabriel synthesis shown below.

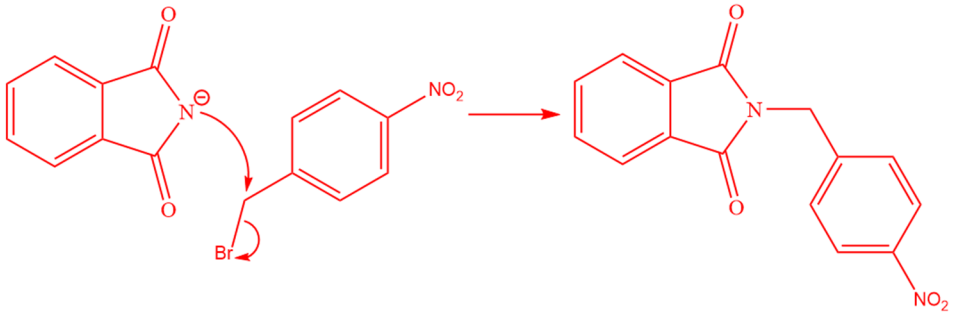
3.5 marks



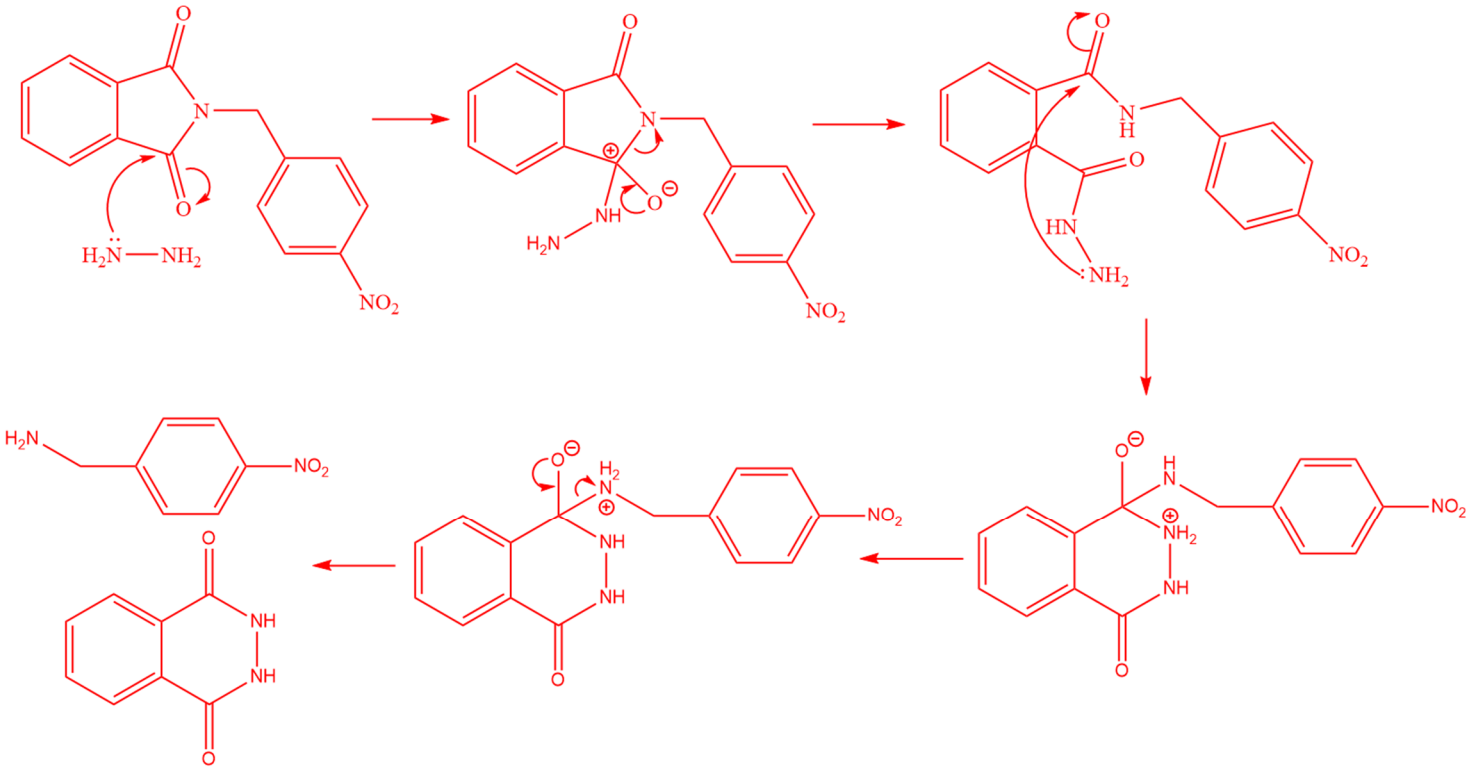
Step 1: Deprotonation



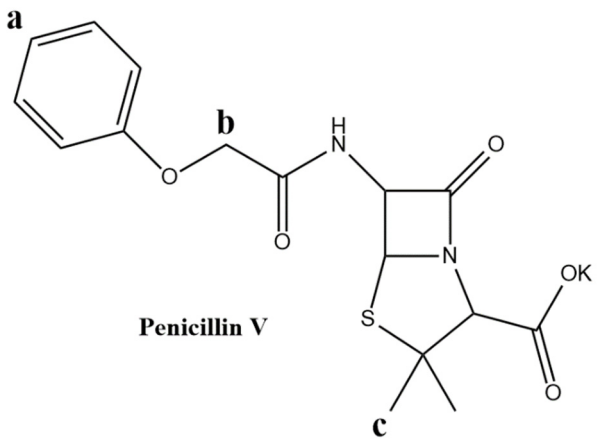
Step 2: S_N2 Reaction



Step 3: Amine liberation



c) Complete the table with the expected chemical shift, integration, and multiplicity of the labelled protons in penicillin V from ^{1}H NMR.
4.5 marks



Penicillin V

Protons	Chemical Shift (ppm)	Integration	Multiplicity Splitting pattern
a	6-8	1	tt
b	4-5	2	s
c	1-2	6	s

2. ANALYTICAL CHEMISTRY

A colorless solution **A** was added to a sodium chloride solution, a white precipitate **B** was formed, **B** will dissolve in ammonia to form solution of **C**. When NaBr was added to **C**, a pale-yellow solid **D** was formed. **D** will turn to black color under the sun light. **D** will dissolve in a $Na_2S_2O_3$ solution and form solution **E**. When NaI was added to solution **E**, a yellow solid **F** was formed. **F** will dissolve in a NaCN solution and form solution **G**. When Na_2S was added to solution **G**, a black precipitate **H** was formed. When **H** was separated from the solution and then **H** was boiled with concentrated nitric acid, a pale-yellow sulfur suspension was observed. When sulfur is removed from the solution, the remaining solution is **A**.

Hint: The cation of A tends to form complexes of the form ML_2

a) Based on information given, please identify **A, B, C, D, E, F, G** and **H**.
2.8 marks **(0.35 each)**

A: $AgNO_3$

B: $AgCl$

C: $[Ag(NH_3)_2]Cl$ **or** $[Ag(NH_3)_2]^+$

D: $AgBr$

E: $Na_3[Ag(S_2O_3)_2]$ **or** $[Ag(S_2O_3)_2]^{3-}$

F: AgI

G: $Na[Ag(CN)_2]$ **or** $[Ag(CN)_2]^-$

H: Ag_2S

b) Write the balanced chemical reaction equations for the following
3.2 marks **(0.4 each)**

Reaction to produce **B:** **Net ion equations accepted**

$AgNO_3(aq) + NaCl(aq) \rightarrow AgCl(s) + NaNO_3(aq)$
or $Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$

Reaction to produce **C:** **Net ion equations accepted**

$AgCl(s) + 2NH_3(aq) \rightarrow [Ag(NH_3)_2]Cl(aq)$
or $AgCl(s) + 2NH_3(aq) \rightarrow [Ag(NH_3)_2]^+(aq) + Cl^-(aq)$

Reaction to produce **D:** **Net ion equations accepted**

$[Ag(NH_3)_2]Cl(aq) + NaBr(aq) \rightarrow AgBr(s) + NaCl(aq) + 2NH_3(aq)$
or $[Ag(NH_3)_2]^+(aq) + Br^-(aq) \rightarrow AgBr(s) + 2NH_3(aq)$

Reaction to produce **E:** **Net ion equations accepted**

$AgBr(s) + 2Na_2S_2O_3(aq) \rightarrow Na_3[Ag(S_2O_3)_2](aq) + NaBr(aq)$
or $AgBr(s) + 2S_2O_3^{2-}(aq) \rightarrow Ag(S_2O_3)_2]^{3-}(aq) + Br^-(aq)$

Reaction to produce **F:** **Net ion equations accepted**

$Na_3[Ag(S_2O_3)_2](aq) + NaI(aq) \rightarrow AgI(s) + 2Na_2S_2O_3(aq)$
or $[Ag(S_2O_3)_2]^{3-}(aq) + I^-(aq) \rightarrow AgI(s) + 2S_2O_3^{2-}(aq)$

Reaction to produce **G:** **Net ion equations accepted**

$AgI(s) + 2NaCN(aq) \rightarrow Na[Ag(CN)_2](aq) + NaI(aq)$
or $AgI(s) + 2CN^-(aq) \rightarrow [Ag(CN)_2]^-(aq) + I^-(aq)$

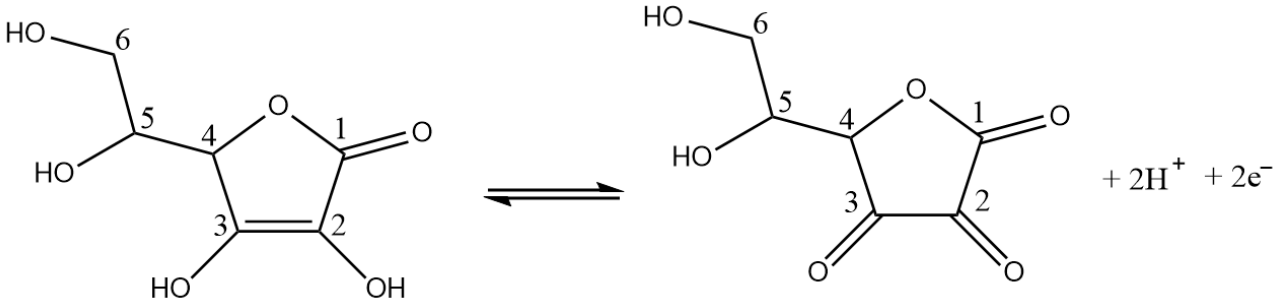
Reaction to produce **H:** **Net ion equations accepted**

$2Na[Ag(CN)_2](aq) + Na_2S(aq) \rightarrow Ag_2S(s) + 4NaCN(aq)$
or $2[Ag(CN)_2]^-(aq) + S^{2-}(aq) \rightarrow Ag_2S(s) + 4CN^-(aq)$

Reaction of **H** with $HNO_3(aq)$ to produce sulfur and **A**: **Net ion equations accepted**

$3Ag_2S(s) + 8HNO_3(con.\ aq) \rightarrow 3S(s)\ \left(or\ \frac{3}{8}S_8\right) + 6AgNO_3(aq) + 2NO(g) + 4H_2O(l)$
or $3Ag_2S(s) + 8H^+(aq) + 8NO_3^-(aq) \rightarrow S(s) + 6Ag^+(aq) + 8NO_3^-(aq) + 2NO(g) + 4H_2O(l)$

Vitamin C, known chemically as **ascorbic acid** ($C_6H_8O_6$), is an important component of a healthy diet. Many people take Vitamin C daily to boost their immune system especially during the last three years of COVID pandemic. To ensure the high quality for human consumption, the purity of vitamin C in an industrial product line was determined by a redox titration. In such redox titration, vitamin C (ascorbic acid) was first oxidized to dehydroascorbic acid as described by the following half reaction,



Ascorbic acid Dehydroascorbic acid

A typical titration process includes the following steps,

1) Preparation of **Vitamin C** solution by dissolving an exact amount sample into water to make an exact volume of solution.
2) Preparation of potassium iodate solution by dissolving an exact amount of **KIO_3** into water to make an exact volume of solution.
3) Preparation and standardization of sodium thiosulfate solution by dissolving a given amount of **$Na_2S_2O_3$** into water and then standardized by an acidified solution from **Step 2** with excess amount of **KI**.
4) A solution used as the **indicator** was freshly prepared by dissolving a given amount of a compound into nearly boiling water.
5) An exact volume of vitamin C solution from **Step 1** was treated with exact and excess amount (mole) of solution prepared from **Step 2** with excess amount of **KI** was added and the solution was acidified.
6) The solution from **Step 5** was then titrated by a **$Na_2S_2O_3$** solution from **Step 3**.
7) 2 mL of the indicator solution from **Step 4** was added to the solution being titrated.

The titration will continue until the equivalence point as indicated by the change of color of the indicator.

Relevant reactions and standard reduction potentials are as follows (unless otherwise specified, all species are in aqueous solution):

$I_3^- + 2e^- \rightarrow 3I^-$	0.536V
$IO_3^- + 6H^+ + 5e^- \rightarrow \frac{1}{2} I_2(s) + 3H_2O(l)$	1.195V
$S_4O_6^{2-} + 2e^- \rightarrow 2S_2O_3^{2-}$	0.080V
$I_{2(s)} + I^- \rightarrow I_3^-$	

c) Write the reduction half reaction for the redox reaction involving Ascorbic Acid.
0.5 marks

$I_3^-(aq) + 2e^- \rightarrow 3I^-(aq)$ or $I_2(aq) + 2e^- \rightarrow 2I^-(aq)$

d) Write the balanced overall redox equation for the redox reaction involving Ascorbic Acid.
0.5 marks

$C_6H_8O_6(aq) + I_3^-(aq) \rightarrow 3I^-(aq) + C_6H_6O_6(aq) + 2H^+(aq)$ or
$C_6H_8O_6(aq) + I_2(aq) \rightarrow 2I^-(aq) + C_6H_6O_6(aq) + 2H^+(aq)$

e) What was used as the indicator? (circle one)
0.5 marks

1) Phenolphthalein
2) Potassium Chromate
3) Starch
4) Phenol Red
5) Eriochrome Black T

f) What was the color change at the equivalence point? (circle one)
0.5 marks

1) Colorless to pink
2) Blue to milky white
3) Orange to colorless
4) White to purple
5) Red to green

g) The titration is a (circle one)
0.5 marks

1) Gravimetric titration
2) Neutralization titration
3) Direct titration
4) Back titration
5) Complex titration

h) Write the balanced overall redox reaction equation for the titration.
0.5 marks

$2S_2O_3^{2-}(aq) + I_3^-(aq) \rightarrow 3I^-(aq) + S_4O_6^{2-}(aq)$

i) A vitamin C sample with a mass of 1.048g was dissolved into water to make an exact 100 mL of solution. 10.00mL of 1.082M of KI was added to 5.00mL of 0.235M of KIO3 solution, the solution was acidified, then 10.00ml of the Vitamin C solution was added to this solution. After the reaction was completed, the resulting solution was then titrated by a 0.485M of a standardized Na2S2O3 solution. 2 mL of the indicator solution was then added at some point of the titration. At the end point, 12.14 mL of Na2S2O3 solution was used. Calculate the purity of the sample.

3 marks

[Reaction equations (not required)]

$C_6H_8O_6 + I_3^- \rightarrow C_6H_6O_6 + 3I^- + 2H^+$

$IO_3^- + 8I^- \rightarrow 3I_3^- + 3H_2O$

$I_3^- + 2S_2O_3^{2-} \rightarrow 3I^- + S_4O_6^{2-}$

Moles of $Na_2S_2O_3$ (0.5 points)

12.14 mL * 0.485 M = 5.888 mMoles or $5.888 * 10^{-3}$ Moles

Mole of KOI_3 (0.5 points)

5.00 mL * 0.235 M = 1.175 mMoles or $1.175 * 10^{-3}$ Moles

Moles of I_2 produced (0.5 points)

1.175 mMoles * 3 = 3.525 mMoles or $3.525 * 10^{-3}$ Moles

Moles of I_2 being titrated (0.5 points)

5.888 mMoles / 2 = 2.944 mMoles or $2.944 * 10^{-3}$ Moles

Moles of I_2 used to reduce ascorbic acid (0.5 points)

3.525 mMoles - 2.944 mMoles = 0.581 mMoles or $5.81 * 10^{-4}$ Moles

Moles of Ascorbic Acid in 10.00 mL solution (0.25 points)

0.581 mMoles or $5.81 * 10^{-4}$ Moles

Purity of Vitamin C sample (0.25 points)

($5.81 * 10^{-4}$ Moles) *10 *176 g/Mole / 1.048g = 97.6%

2.5 points will be given for any answers between 97.0% & and 98.0% without detailed procedures.

3. INORGANIC CHEMISTRY

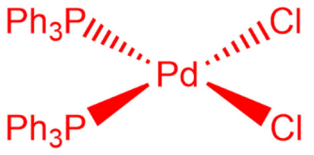
Palladium catalysts are an effective heterogeneous catalyst for carbon–carbon (C–C) coupling reactions. They are used in a variety of organometallic reactions such as Stille reaction, Suzuki reaction, Sonogashira coupling, Heck reaction and Negishi coupling to name a few.

a) What is the full electronic configuration of Pd?
1 mark

Pd: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^0 4d^{10}$

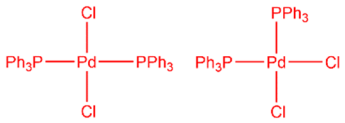
One of the best catalysts used in the Sonogashira coupling reaction is $Pd(PPh_3)_2Cl_2$

b) **Draw** and **name** two possible isomers of this compound.
2 marks 0.5 marks each drawing





trans cis



Also accepted

cis-dichlorobis(triphenylphosphine)palladium(II) (0.5 marks)

trans-dichlorobis(triphenylphosphine)palladium(II) (0.5 marks)

c) For the coordination complex, what is the oxidation state and electron count for this metal complex?
1 mark

covalent method

Pd (group 10) → 10 e^-
2 x PPh_3 → 4 e^-
2 x Cl → 2 e^-
16 e^-

or

ionic method

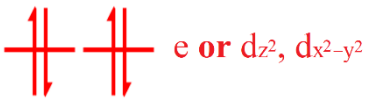
Pd(II) d^8 → 8 e^-
2 x PPh_3 → 4 e^-
2 x Cl^- → 4 e^-
16 e^-

d) $Pd(PPh_3)_2Cl_2$ is diamagnetic, but the nickel analogue, $Ni(PPh_3)_2Cl_2$, can be either diamagnetic (red solid) or paramagnetic (dark blue). **Draw** the crystal field splitting, fill with electrons and use geometries to explain how this occurs in the nickel species.
4 marks





(0.5 mark labelled orbitals





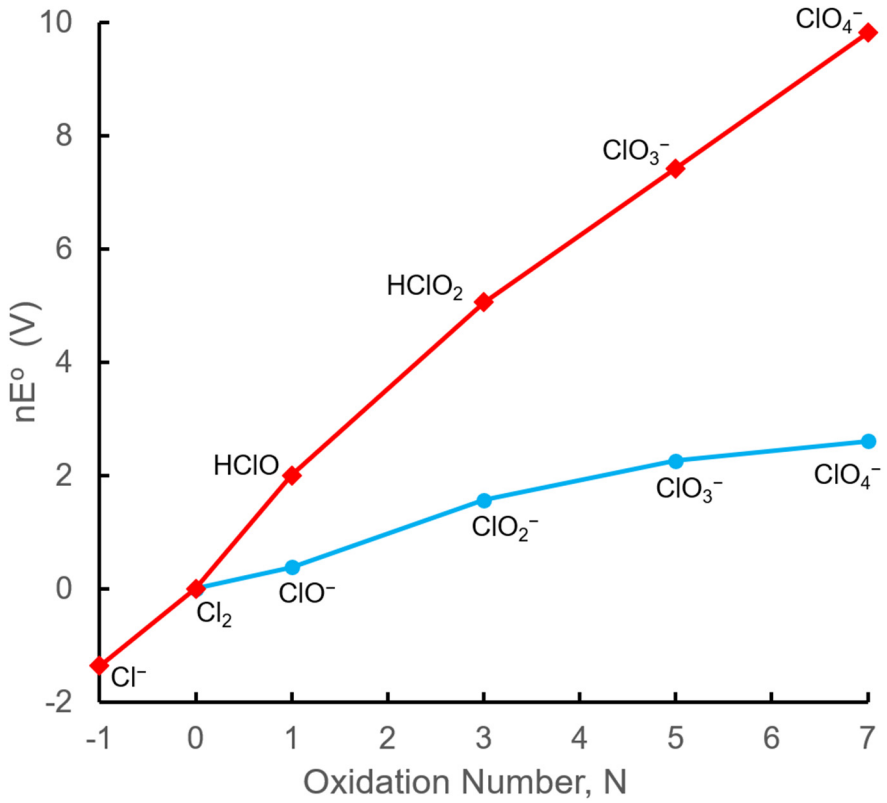
Paramagnetic (blue) is tetrahedral (1 marks)

Correct # of electrons filling the orbitals (1 mark)



(0.5 mark labelled orbitals)
Diamagnetic (red) is square planar (1 marks)

Answer the following questions using the Frost diagram below:



Frost diagram for chlorine.
The red line refers to acidic conditions (pH=0) and the blue line refers to basic conditions (pH=14)

e) When Cl_2 is dissolved in a basic aqueous solution disproportionation to Cl^- and ClO_4^- is not observed, is this a kinetic or thermodynamic phenomenon?
1 mark
Kinetic

f) When Cl_2 is dissolved in an acidic aqueous solution disproportionation to Cl^- and HClO is not observed, is this a kinetic or thermodynamic phenomenon?
1 mark
Thermodynamic

g) Which solution is formed when Cl_2 is dissolved in an aqueous base?
1 mark

An aqueous solution of Cl^- and ClO^- is formed when Cl_2 is dissolved into a base

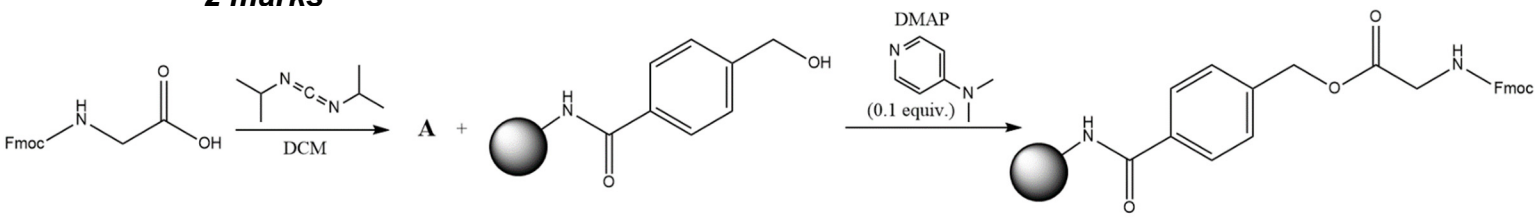
h) How can the Frost diagram above be used to explain your answer in g)?
1 mark

If a straight line is drawn between Cl^- and ClO^-, Cl_2 lies above the line. This means that Cl_2 is less stable than Cl^- and ClO^- in a basic solution.

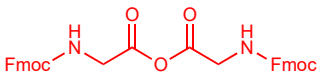
4. BIOCHEMISTRY

4-hydroxymethylbenzamide (HMBA) is a common linker in solid-phase peptide synthesis which allows for C-terminal functionalization of peptides when cleaved with different nucleophiles under basic conditions.

a) Fmoc-amino acids can be attached to the HMBA resin through the formation of a symmetrical anhydride. **Draw** the symmetric anhydride of Fmoc-glycine (shown below) and **draw** the mechanism for the resulting attachment to the HMBA resin. Note the DMAP (0.1 equiv.) acts as a base and the reaction proceeds through an acetylpyridinium intermediate.
2 marks



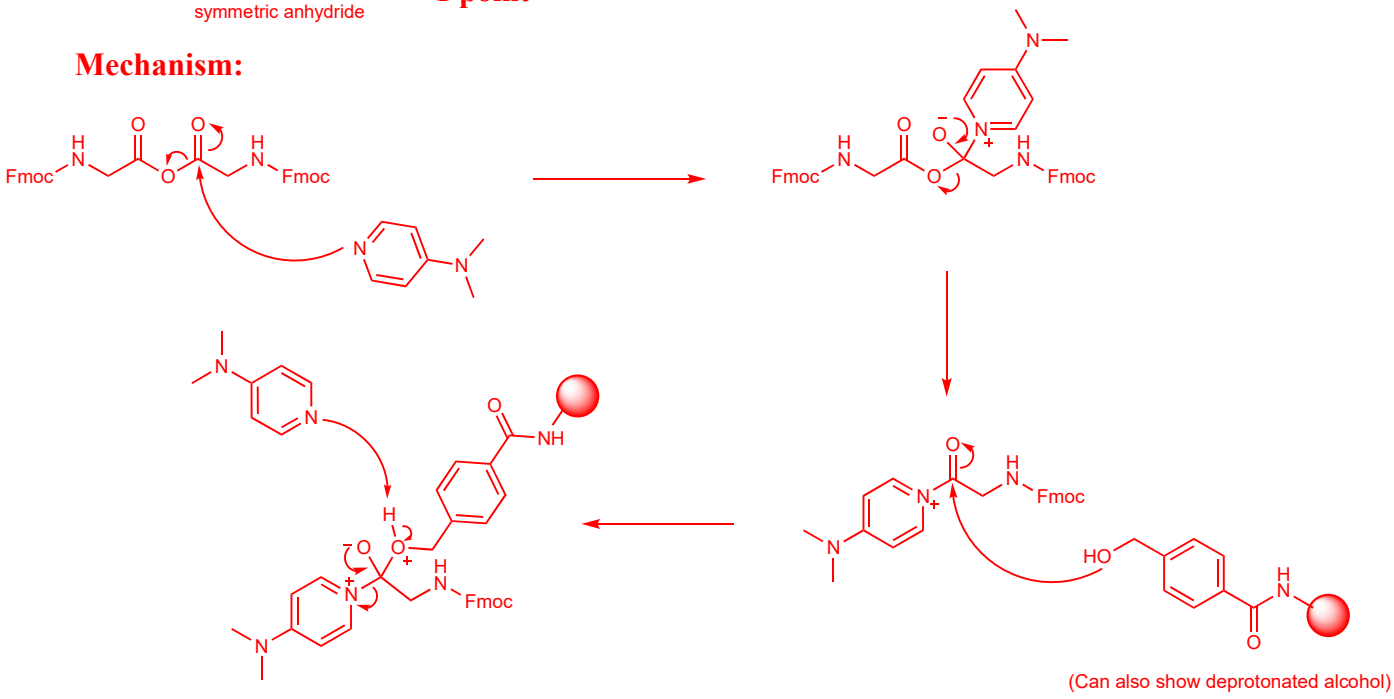
A



symmetric anhydride

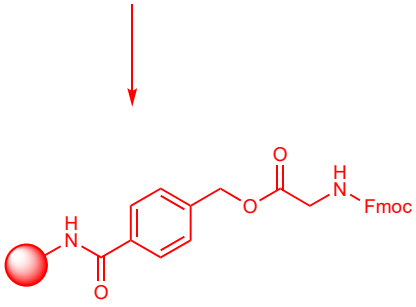
1 point

Mechanism:



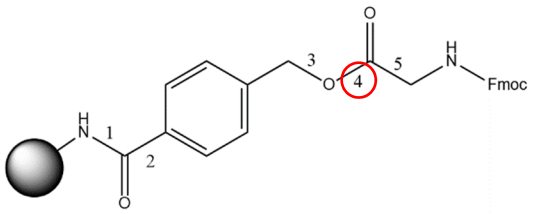
(Can also show as two separate steps)

(Can also show deprotonated alcohol)



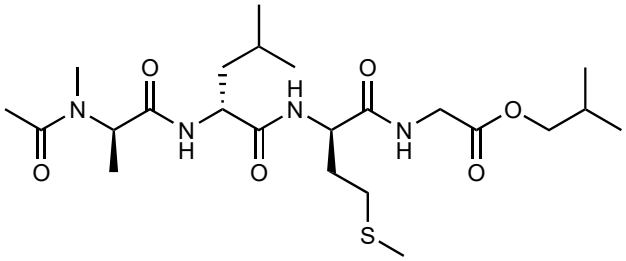
0.5 points for DMAP addition to anhydride
0.5 points for addition of resin

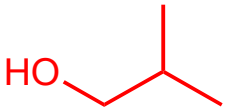
b) The final peptide can be cleaved from the resin under basic conditions with different nucleophiles. **Identify** the cleavage point for the HMBA linked-glycine below.
1 mark



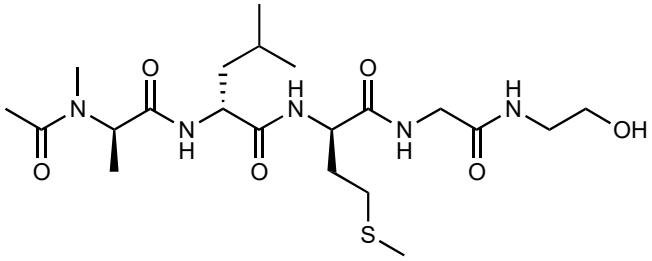
Position 4

c) **Draw** the nucleophile used for the cleavage of each of the following peptides from HMBA resin.
1 mark



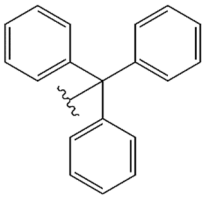


(0.5 marks each)

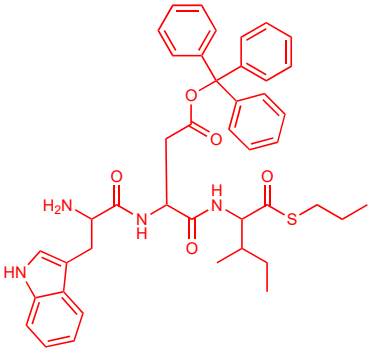




d) **Draw** the structure of the final cleaved peptide (H-Trp-Asp(Trt)-Ile-?) from MBHA resin using propane-1-thiol as the nucleophile and potassium tert-butoxide as the base. There is no need to draw the stereochemistry at each alpha-carbon.
2 marks

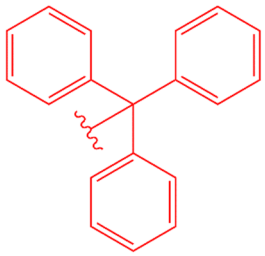


Trityl (Trt)

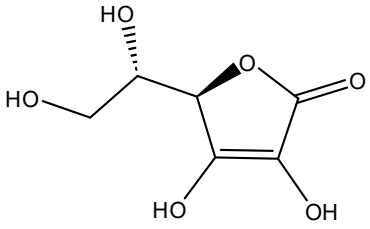


(0.5 marks for trityl protecting group,
1 mark for correct amino acid structures
and sequence, 0.5 marks for the thiol addition)

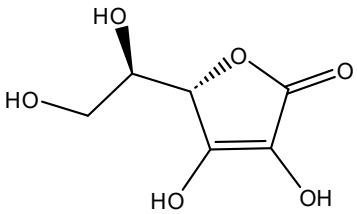
trityl protecting group:



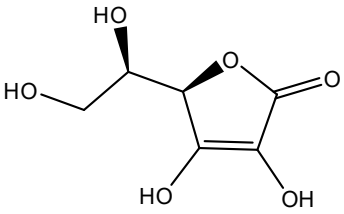
Isoascorbic acid (erythorbic acid) is an isomer of the compound L-ascorbic acid which is also known as Vitamin C. Like L-ascorbic acid, Isoascorbic acid a naturally occurring molecule and it has similar antioxidant properties. Vitamin C has another closely related stereoisomer, D-ascorbic acid. The structures of all three molecules is given below.



L-Ascorbic acid



D-Ascorbic acid



Isoascorbic acid

e) Determine the relationship between these molecules.
1.5 marks

L-Ascorbic acid and D-Ascorbic acid are ☑ enantiomer, ☐ diastereomer.
L-Ascorbic acid and Isoascorbic acid are ☐ enantiomer, ☑ diastereomer.
D-Ascorbic acid and Isoascorbic acid are ☐ enantiomer, ☑ diastereomer.

f) L-ascorbic acid is called an acid because the aqueous solution of its pure form has an acidic pH. If the pH of a solution derived from dissolving X g of pure L-ascorbic acid in a litre of water has a pH of 5, what can we say about the pH of X g of pure D-ascorbic acid and Iso-ascorbic acid in the same amount of water?
1 mark

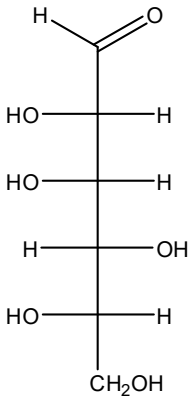
pH of the D-ascorbic acid solution will be

☐ higher ☐ lower ☑ exactly the same ☐ not enough information.

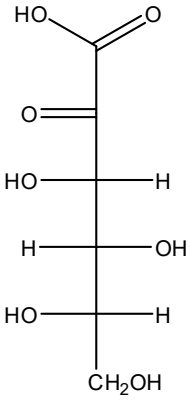
pH of the Isoascorbic acid solution will be

☐ higher ☐ lower ☐ exactly the same ☑ not enough information.

Industrial synthesis of Vitamin C can be achieved via a compound called 2-keto-L-Gulonic acid, depicted below. This compound itself can be made by oxidation of the monosaccharide L-Gulose, also shown below.



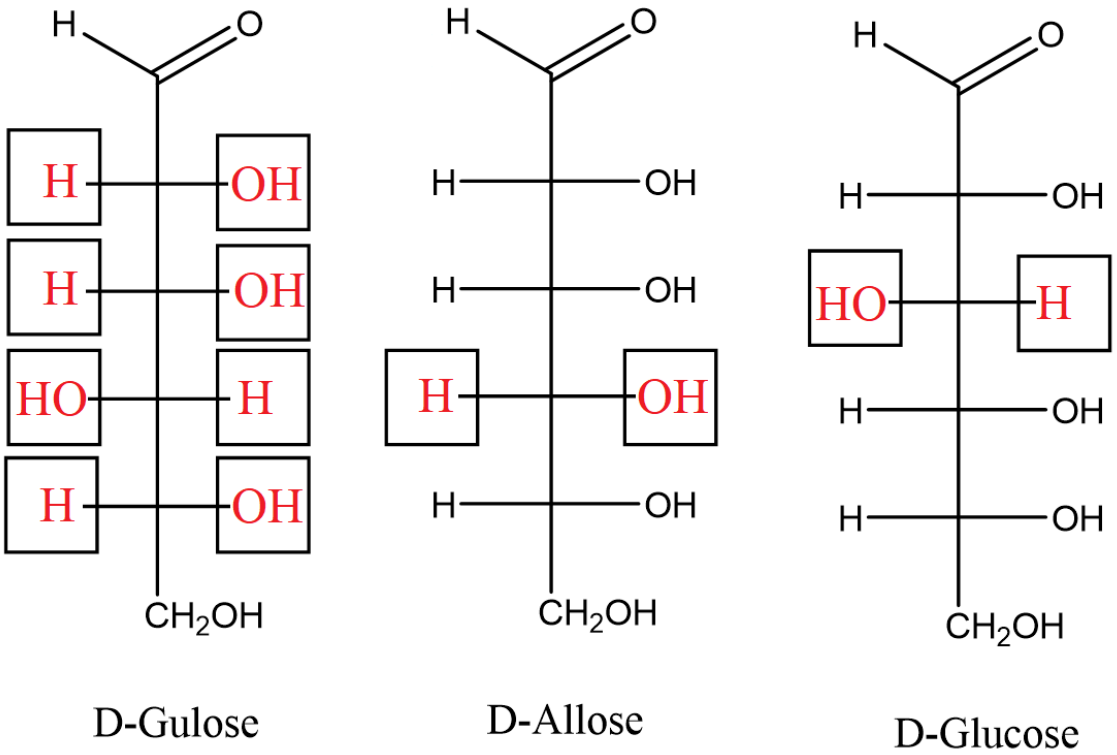
L-Gulose



2-keto-L-Gulonic acid

L-Gulose is one of the 12 possible isomers of the monosaccharides called aldohexoses, carbohydrates that have 6 carbons and an aldehyde group. Carbohydrates, as the name suggests have the general formula of hydrates of Carbon: $C_n(H_2O)_n$ and the formula of L-Gulose, like that of all the rest of aldohexoses is $C_6H_{12}O_6$.

g) Complete the fisher projections of the aldohexoses shown below. Note that D-Gulose is the enantiomer of L-Gulose and that these three molecules are different from one another.
1.5 marks



h) Suppose we want to synthesize D-ascorbic acid and Isoascorbic acid using the same industrial synthesis that is used for making Vitamin C. Which one of the hexoses shown above can be utilized for making each of them?
2 marks

D-Ascorbic acid can be made using:

☑ D-Gulose ☐ D-Allose ☐ D-Glucose

Isoascorbic acid can be made using:

☐ D-Gulose ☐ D-Allose ☑ D-Glucose

5. PHYSICAL CHEMISTRY

Two half-cells in a galvanic cell consist of one iron electrode, Fe(s), in a solution of iron(II) sulphate and a silver electrode, Ag(s) in a silver nitrate solution. We know the following standard reduction potentials, at 25 °C:

$$Fe^{2+}(aq) + 2e^- \rightarrow Fe(s) \qquad E^o = -0.447V$$
$$Ag^+(aq) + e^- \rightarrow Ag(s) \qquad E^o = 0.800V$$

a) In the empty boxes below, write the overall cell reaction in the direction of spontaneous change and write out the reactions occurring at the electrodes.
1.5 marks

Anode	$Fe(s) \rightarrow Fe^{2+} + 2e^-$
Cathode	$Ag^+ + e^- \rightarrow Ag(s)$
Total Cell	$Fe(s) + 2Ag^+ \rightarrow Fe^{2+} + 2Ag(s)$

b) Calculate E° and ΔG° for the total cell reaction.
1 mark

$E^o = 0.800 + 0.447 = 1.247V$

$\Delta G = -nFE = -2 \times 96485 \times 1.247 = -240634J \; or \; -240.6 \; kJ$

Remove 0.5 mark for missing or wrong units

c) What is the iron concentration, [Fe^{2+}], that would give a potential of 1.200 V at 25°C for the cell in the previous question?
3 marks
Assume that initially all solutes are present at 1 M, all gases at 1 bar.

$$E = E° - \frac{RT}{nF} lnQ$$

$$1.2 = 1.247 - \frac{8.3145(298.15)}{2(96485)} lnQ$$

$$-0.047 = -0.012846 lnQ$$

$$lnQ = 3.6586$$

$$Q = 38.8$$

	$[Ag^+]$	$[Fe^{2+}]$
I	1	1
C	$-2x$	$+x$
E	$1-2x$	$1+x$

$$Q = \frac{[Fe^{2+}]}{[Ag^+]^2} = \frac{1+x}{(1-2x)^2} = 38.8$$

$$38.8(1-2x)^2 = 1+x$$
$$38.8(1-4x+4x^2) = 1+x$$
$$38.8 - 155.2x + 155.2x^2 = 1+x$$
$$37.8 - 156.2x + 155.2x^2 = 0$$

$$a = 155.2, \quad b = -156.2, \quad c = 37.8 \quad \Delta = b^2 - 4ac = 932.2 \ and \ \sqrt{\Delta} = 30.53$$

$$x = \frac{-b \pm \sqrt{\Delta}}{2a} = \frac{156.2 - 30.53}{310.4} = 0.405 \quad or \quad = \frac{156.2 + 30.53}{310.4} = 0.602$$

With $x = 0.602, [Ag^+] = 1 - 2x < 0$ therefore 0.602 is not a good solution

$$x = 0.405 \quad and \quad [Fe^{2+}] = 1.405 \ M$$

Any answer reasonably close to 1.4 M is worth 3 marks
Remove 0.5 mark for missing or wrong units

Catalysis of biochemical reactions in the cell is vital since many metabolically essential reactions have very low rates when uncatalyzed. Enzymes are biological molecules (mostly proteins) that catalyze the reactions necessary to life.

Mechanisms of enzyme catalysis vary, but are all similar in principle to other types of chemical catalysis in that the crucial factor is a reduction of the energy barrier separating the reactants from the products. In enzyme catalyzed reactions the reactant is called substrate (noted S), and an enzyme catalyzed reaction can be written as follows:

$$E + S \rightleftharpoons ES \rightarrow E + P$$

In this chemical equation, E denotes the free enzyme, ES the enzyme-substrate-complex and P denotes the product. A crucial step in enzyme catalysis is that the enzyme must bind the substrate before products are made. It is the enzyme-substrate-complex that forms the product.

The concentration of free enzyme [E] and enzyme-substrate-complex [ES] are usually not know and therefore are not useful in a rate equation (or rate law). To write down a useful rate law it is necessary to define the total enzyme concentration $[E]_0$ which is usually known and constant (remains unchanged, before, during and after the reaction). $[E]_0$ is defined by the following equation:

$$[E]_0 = [E] + [ES]$$

The total enzyme concentration, $[E]_0$, is equal to the concentration of free enzyme [E] plus the concentration of the bound enzyme in [ES] complex.

d) One method to find a rate equation for enzyme kinetics is called pre-equilibrium (or rapid equilibrium approximation). Using this method, one assumes that the equilibrium between E and S is much faster than the formation of products. Use the information above and below to write a rate law for enzyme kinetics. Your rate law must use the two constants defined below, the concentration of substrate [S] and the total enzyme concentration $[E]_0$. Remember that [E] and [ES] ***cannot*** be in the rate law.
2 marks

$$E + S \rightleftharpoons ES \overset{k_2}{\rightarrow} E + P$$

k_2 is a rate constant and $v = k_2[ES]$ is the rate law used to complete this proof.

It is also useful to define the [ES] dissociation constant: $K_s = \frac{[E][S]}{[ES]}$

$[E] = [E]_0 - [ES]$

$K_s = \frac{([E]_0 - [ES])[S]}{[ES]} = \frac{[E]_0[S]}{[ES]} - [S]$ *1 mark for the elimination of* $[E]$ *or* $[ES]$

$K_S + [S] = \frac{[E]_0[S]}{[ES]}$

$[ES] = \frac{[E]_0[S]}{K_S + [S]}$

$v = \frac{k_2[E]_0[S]}{K_S + [S]}$
2 marks

e) The steady state approximation can be used to find a rate law of the same form as found in d). In the steady state approximation, the [ES] complex is treated as an intermediate and its concentration change is set to zero: $d[ES]/dt = 0$. Use the steady state approximation to find a rate law for enzyme catalysis. Your rate law must use K_M and k_2 constants defined below, the concentration of substrate [S] and the total enzyme concentration $[E]_0$. Some useful starting information is given below. Remember that [E] and [ES] ***cannot*** be in the rate law.
3 marks

The mechanism can be written in 3 steps:

1) $E + S \xrightarrow{k_1} ES$ *with* $v_1 = k_1[E][S]$
2) $ES \xrightarrow{k_{-1}} E + S$ *with* $v_{-1} = k_{-1}[ES]$
3) $ES \xrightarrow{k_2} E + P$ *with* $v_2 = k_2[ES]$

$$K_M = \frac{k_{-1} + k_2}{k_1}, \quad K_M \text{ is the Michaelis Constant}$$

$$\frac{d[ES]}{dt} = k_1[E][S] - k_{-1}[ES] - k_2[ES] = 0 \qquad 0.5\ Mark$$

$$[E] = [E]_0 - [ES]$$

$$k_1([E]_0 - [ES])[S] - k_{-1}[ES] - k_2[ES] = 0$$

$$k_1[E]_0[S] - k_1[ES][S] - k_{-1}[ES] - k_2[ES] = 0$$

$$k_1[E]_0[S] = k_1[ES][S] + k_{-1}[ES] + k_2[ES]$$

$$k_1[E]_0[S] = [ES](k_1[S] + k_{-1} + k_2)$$

$$[ES] = \frac{k_1[E]_0[S]}{k_1[S] + k_{-1} + k_2} \qquad 1\ mark$$

Dividing both numerator and denominator by k_1 we get:

$$[ES] = \frac{[E]_0[S]}{[S] + \frac{k_{-1} + k_2}{k_1}} = \frac{[E]_0[S]}{[S] + K_M} \qquad 1\ mark$$

$$v = k_2[ES] = \frac{k_2[E]_0[S]}{K_M + [S]} \qquad 0.5\ mark$$

If the rate equation given is $v = \frac{k_2 k_1[E]_0[S]}{k_1[S] + k_{-1} + k_2}$ *with work, 2 marks are attributed*

If the a rate equation is given as $v = \frac{k_2 k_1[E]_0[S]}{k_1[S] + k_{-1} + k_2}$ *or* $v = \frac{k_2[E]_0[S]}{K_M + [S]}$ *with no work, 0.5 marks*

f) In the equation obtained in d) or e) we can define v_{max} which is the maximum rate for the enzyme catalyzed reaction. If v_{max} is used, the rate law is often called the Michaelis-Menten equation. Rewrite your equation obtained in d) or e) using v_{max}.
0.5 mark

$v_{max} = k_2[E]_0$

$$v = \frac{v_{max}[S]}{K_M + [S]} \quad or \quad v = \frac{v_{max}[S]}{K_S + [S]} \qquad 0.5\ mark$$

g) The decomposition of H_2O_2 by the enzyme catalase follows Michaelis-Menten kinetics. For a solution containing 2 mg of catalase per litre, the following rates of decomposition, v, were measured as a function of the H_2O_2 concentration. Calculate the values of v_{max} and K_M or K_S.
1 mark

$[H_2O_2]\ (molL^{-1})$	0.002	0.003	0.02	0.03	0.2	0.3	2.0	3.0
$v\ (10^{-3}\ molL^{-1}s^{-1})$	0.074	0.11	0.45	0.55	0.89	0.92	0.99	0.99

$when\ [S] \gg K_M \quad or \quad [S] \gg K_s \quad then:$

$$v = \frac{v_{max}[S]}{[S]} = v_{max} = 0.99 \times 10^{-3}\ molL^{-1}s^{-1} \qquad 0.5\ mark$$

$when\ [S] = K_M \quad or \quad [S] = K_s \quad then:$

$$v = \frac{v_{max}[S]}{2[S]} = \frac{v_{max}}{2} \approx 0.5 \times 10^{-3}\ molL^{-1}s^{-1}$$

$[H_2O_2] = K_M\ or\ K_S \approx 0.025\ molL^{-1} \quad when\ v \approx 0.5 \times 10^{-3}\ molL^{-1}s^{-1} \quad 0.5\ mark$

OR

Using the rate equation for $[H_2O_2]$ between 0.002 and 0.3 $molL^{-1}$

$$K_M + [S] = \frac{v_{max}[S]}{v}$$

$$K_M = \frac{v_{max}[S]}{v} - [S]$$

$K_M\ or\ K_S = 0.022\ to\ 0.025\ molL^{-1} \qquad 0.5\ mark$

Remove 0.25 for incorrect or missing units

-END OF PART C-