CANADIAN CHEMISTRY OLYMPIAD 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 OF THE EXAMINATION.

2. IN QUESTIONS WHICH REQUIRE NUMERICAL CALCULATIONS, BE SURE TO SHOW YOUR REASONING AND YOUR WORK.

3. ONLY NON-PROGRAMMABLE CALCULATORS MAY BE USED ON THIS EXAMINATION.

4. 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.

Name _____ School _____

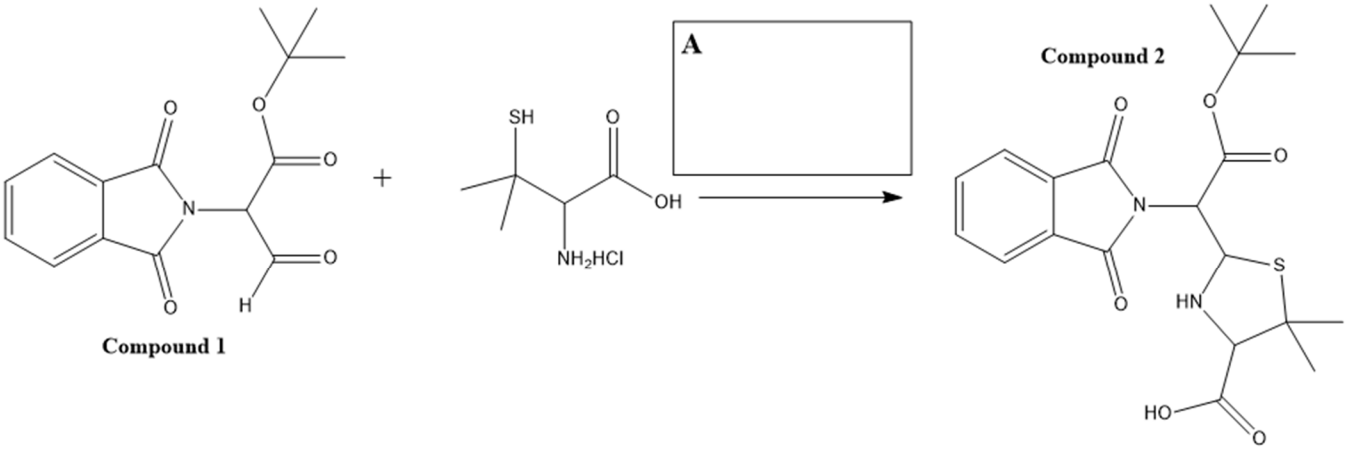
(LAST NAME, Given Name; Print Clearly)

Exam Code _____

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**. **4 marks**

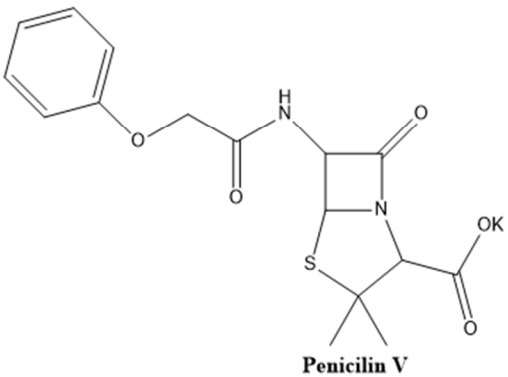


D

E

Compound 3

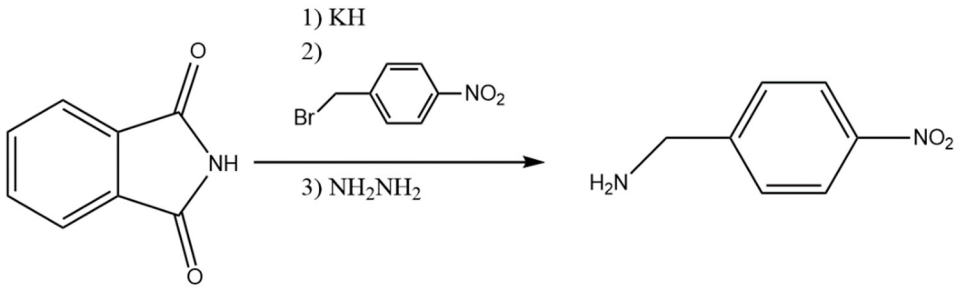
Compound 5



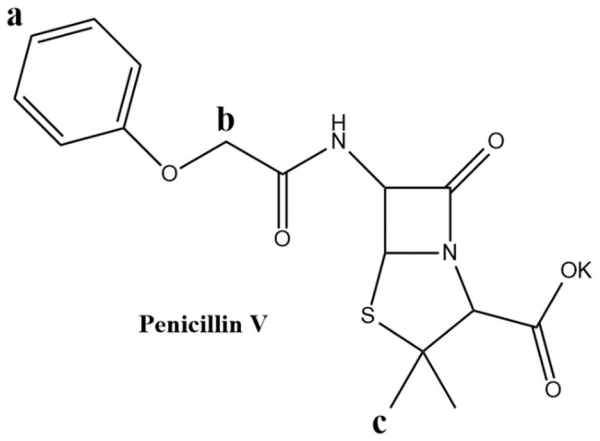
Penicilin V

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



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			
b			
c			

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 concentration nitric acid, pale yellow sulfur suspension was observed. When sulfur was removed from the solution, the remaining solution became **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

A: **B:** **C:**

D: **E:** **F:**

G: **H:**

b) Write the balanced chemical reaction equations for the following
3.2 marks

Reaction to produce **B:**

Reaction to produce **C:**

Reaction to produce **D:**

Reaction to produce **E:**

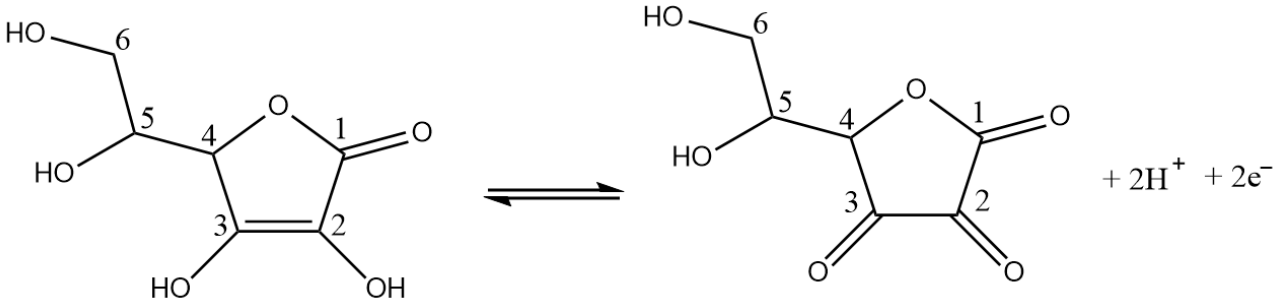
Reaction to produce **F:**

Reaction to produce **G:**

Reaction to produce **H:**

Reaction of **H** with HNO_3(aq) to produce sulfur and **A**:

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 $\mathbf{KIO_3}$ into water to make an exact volume of solution.
3) Preparation and standardization of sodium thiosulfate solution by dissolving a given amount of $\mathbf{Na_2S_2O_3}$ 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 $\mathbf{Na_2S_2O_3}$ 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

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

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

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 KIO_3 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 $Na_2S_2O_3$ solution. 2 mL of the indicator solution was then added at some point of the titration. At the end point, 12.14 mL of $Na_2S_2O_3$ solution was used. Calculate the purity of the sample.

3 marks

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

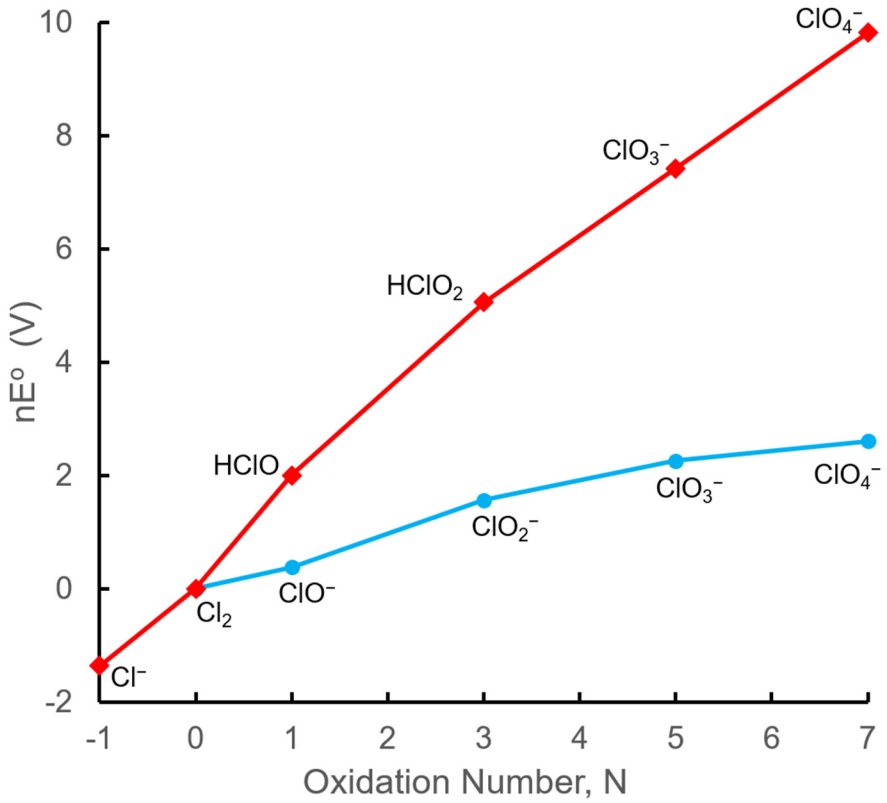
One of the best catalysts used in the Sonogashira coupling reaction is $Pd(PPh_3)_2Cl_2$

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

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

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

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

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

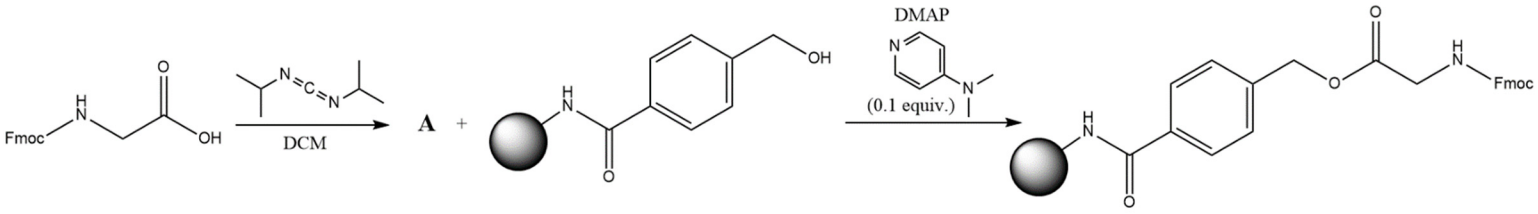
g) Which solution is formed when Cl_2 is dissolved in an aqueous base?
1 mark

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

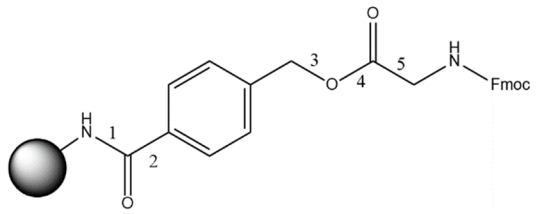
4. BIOCHEMISTRY

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.

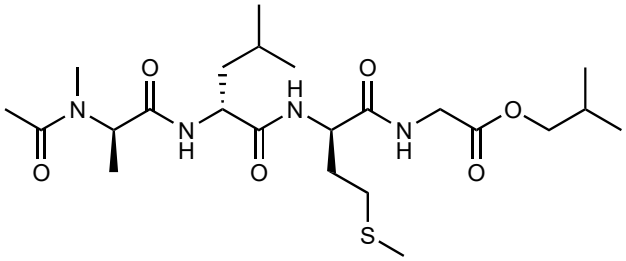
a) Fmoc-amino acids can be attached to the HMBA resin through the formation of a symmetrical anhydride. **Draw** the symmetric anhydride of Fmoc-glycine (shown below) and **draw** the mechanism for the resulting attachment to the HMBA resin. Note the DMAP (0.1 equivalent) acts as a base and the reaction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

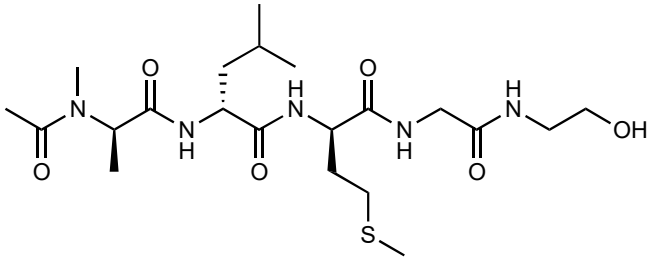


b) The final peptide can be cleaved from the resin under basic conditions with different nucleophiles. **Identify** the cleavage point for the HMBA linked-glycine below.
1 mark

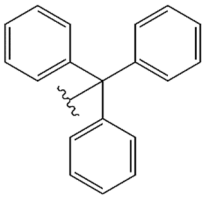


c) **Draw** the nucleophile used for the cleavage of each of the following peptides from HMBA resin.
1 mark



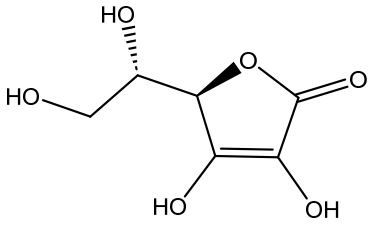


d) **Draw** the structure of the final cleaved peptide (H-Trp-Asp(Trt)-Ile-?) from MBHA resin using propane-1-thiol as the nucleophile and potassium tert-butoxide as the base. There is no need to draw the stereochemistry at each alpha-carbon.
2 marks

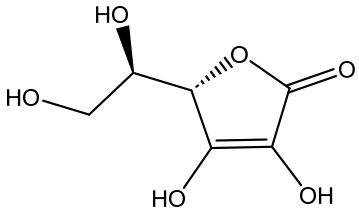


Trityl (Trt)

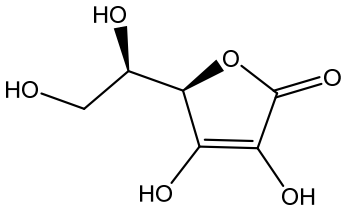
Isoascorbic acid (erythorbic acid) is an isomer of the compound L-ascorbic acid which is also known as Vitamin C. Like L-ascorbic acid, Isoascorbic acid has antioxidant properties. Vitamin C has another closely related stereoisomer, D-ascorbic acid. The structures of all three molecules is given below.



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

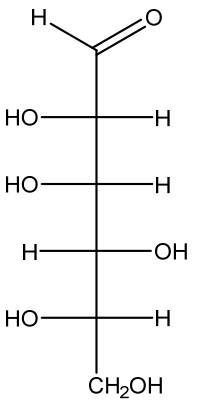
pH of the D-ascorbic acid solution will be

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

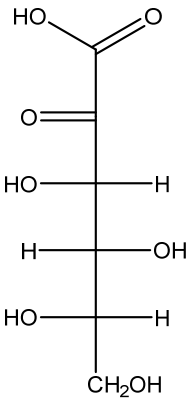
pH of the Isoascorbic acid solution will be

☐ 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.



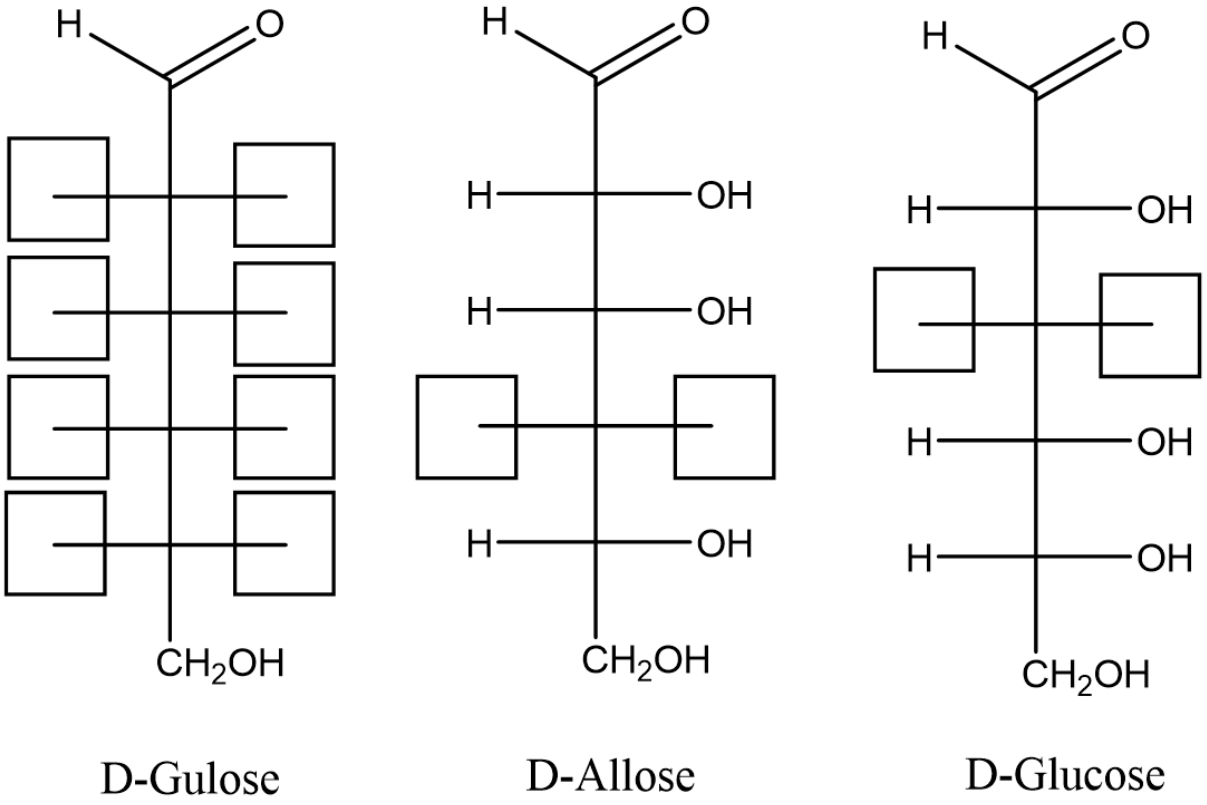
L-Gulose



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



D-Gulose D-Allose D-Glucose

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	
Cathode	
Total Cell	

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

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.

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 initial enzyme concentration $[E]_0$ which is usually known and constant. $[E]_0$ is defined by the following equation:

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

The initial 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 initial 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 you must use.

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

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 initial enzyme concentration $[E]_0$. Remember that [E] and [ES] ***cannot*** be in the rate law.
3 marks

The mechanism can be written in 3 steps:

1) $E + S \overset{k_1}{\rightarrow} ES$ *with* $v_1 = k_1[E][S]$

2) $ES \overset{k_{-1}}{\longrightarrow} E + S$ *with* $v_{-1} = k_{-1}[ES]$

3) $ES \overset{k_2}{\rightarrow} E + P$ *with* $v_2 = k_2[ES]$

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

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

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

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

END OF PAPER

Preparatory Problems (Theory)

55TH INTERNATIONAL CHEMISTRY OLYMPIAD SWITZERLAND 2023

G0-11

English (Official)

List of Amino Acids

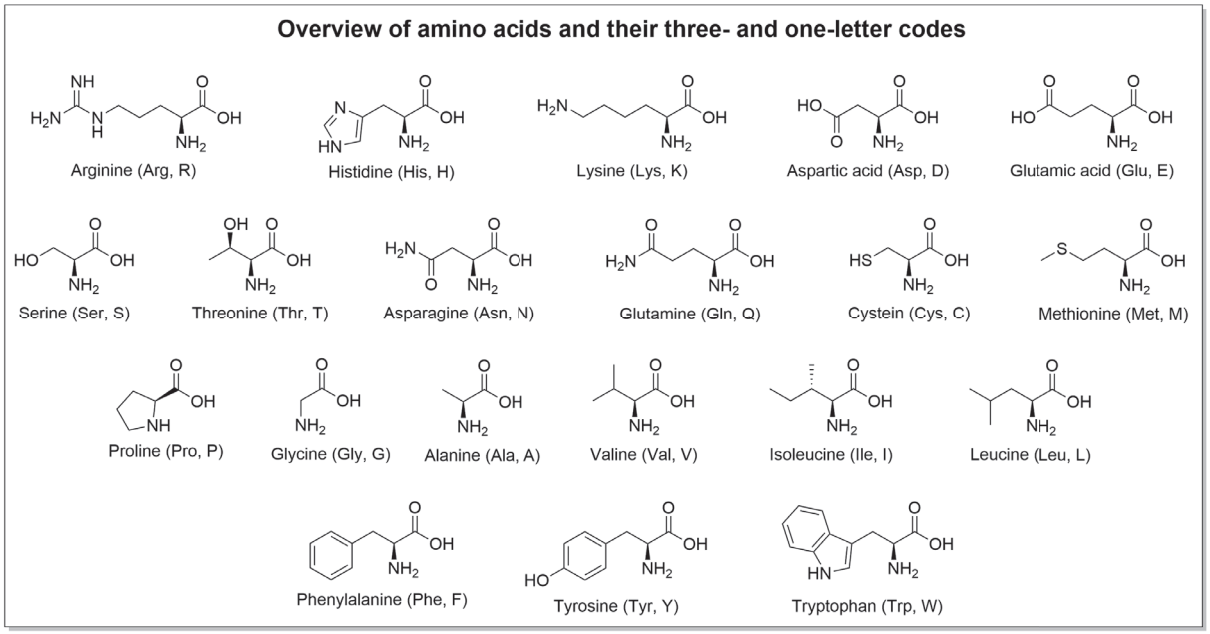
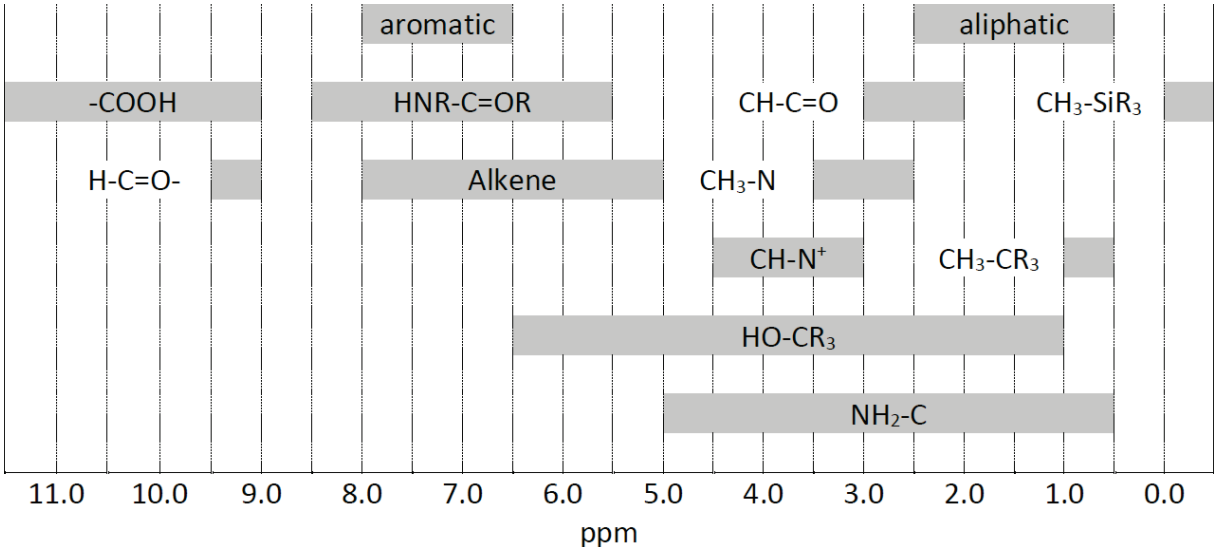
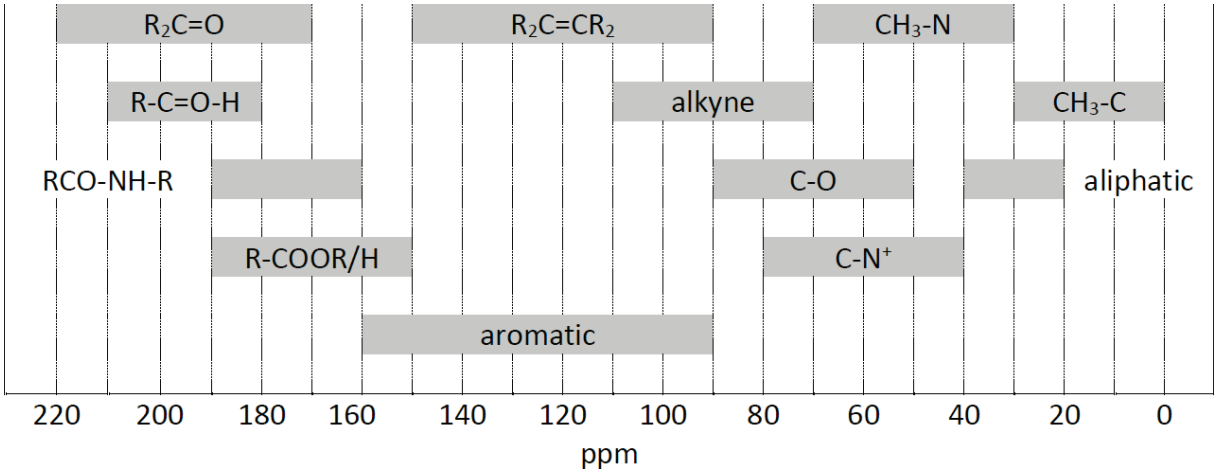


Table of NMR Chemical Shifts

^{1}H NMR Chemical Shifts



^{13}C NMR Chemical Shifts



Chemical Institute of Canada | *For Our Future*
Institut de chimie du Canada | *Pour notre avenir*

Data Sheet
Fiche de données

CHEMISTRY Olympiads
CANADA
Olympiades CHIMIE

1																	18
1 H 1.008	2											13	14	15	16	17	2 He 4.003
3 Li 6.941	4 Be 9.012											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
11 Na 22.99	12 Mg 24.31	3	4	5	6	7	8	9	10	11	12	13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.07	17 Cl 35.45	18 Ar 39.95
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.87	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.38	31 Ga 69.72	32 Ge 72.61	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.96	43 Tc (98)	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
55 Cs 132.9	56 Ba 137.3	57 La 138.9	72 Hf 178.5	73 Ta 180.9	74 W 183.9	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra (226)	89 Ac (227)	104 Rf (261)	105 Db (262)	106 Sg (266)	107 Bh (264)	108 Hs (277)	109 Mt (268)	110 Ds (269)	111 Rg (272)	112 Cn (285)	113 Nh (284)	114 Fl (289)	115 Mc (288)	116 Lv (292)	117 Ts (294)	118 Og (294)

Relative Atomic Masses (2012, IUPAC)
***For the radioactive elements the atomic mass of an important isotope is given**

Masses Atomiques Relatives (UICPA, 2012)
***Dans le cas des éléments radioactifs, la masse atomique fournie est celle d'un isotope important**

58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm (145)	62 Sm 150.4	63 Eu 152.0	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0	71 Lu 175.0
90 Th 232.0	91 Pa (231.0	92 U (238.0)	93 Np (237)	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (262)

	Symbol **Symbole**	**Value** **Quantité numérique**	
Atomic mass unit	*amu*	1.66054×10^{-27} kg	Unité de masse atomique
Avogadro's number	N_A	6.022×10^{23}	Nombre d'Avogadro
Charge of an electron	*e*	1.60218×10^{-19} C	Charge d'un électron
Dissociation constant (H_2O)	K_w	1.00×10^{-14} (25°C)	Constante de dissociation de l'eau (H_2O)
Faraday's constant	*F*	96 485 C mol^{-1}	Constante de Faraday
Gas constant	*R*	8.31451 J K^{-1} mol^{-1} 0.08206 L atm K^{-1} mol^{-1}	Constante des gaz
Mass of an electron	m_e	9.10939×10^{-31} kg	Masse d'un électron
Mass of a neutron	m_n	1.67493×10^{-27} kg	Masse d'un neutron
Mass of a proton	m_p	1.67262×10^{-27} kg	Masse d'un proton
Planck's constant	*h*	6.62608×10^{-34} J s	Constante de Planck
Speed of light	*c*	2.997925×10^{8} m s^{-1}	Vitesse de la lumière
Rydberg constant	R_H	1.096×10^{7} m^{-1}	Constante de Rydberg

1 Å	$= 1 \times 10^{-10}$ m
1 atm	= 101.325 kPa
1 bar	$= 1 \times 10^{5}$ Pa

STP/TPN	**SATP/TPAN**
273.15 K	298 K
100 kPa	100 kPa