2025 CCO Take Home Exam

CANADIAN
CHEMISTRY
OLYMPIAD

OLYMPIADE
DE CHIMIE
DU CANADA

Due Date: Friday, April 4th, 2025 (midnight)

Name:
School:

Physical constants and formulae

Avogadro constant	N_A	6.022×10^{23} mol^{-1}
molar gas constant	R	8.314 J K^{-1} mol^{-1}
Faraday constant	F	96485 C mol^{-1}
Planck constant	h	6.626×10^{-34} J s
speed of light in vacuum	c	2.998×10^{8} m s^{-1}
mass of electron	m_e	9.109×10^{-31} kg
charge of electron	e	1.602×10^{-19} C
atmospheric pressure	p_{atm}	101325 Pa
ionic product of water at 298 K	K_w	10^{-14}

1 nm = 1×10^{-9} m
1 Å = 1×10^{-10} m
1 pm = 1×10^{-12} m
0 °C = 273.15 K

area of triangle	$A = \frac{1}{2}ab \cdot sinC$
volume of cube	$V = a^3$
volume of sphere	$V = \frac{4}{3}\pi r^3$
surface area of sphere	$S = 4\pi r^2$
volume of cylinder	$V = \pi r^2 h$
ideal gas equation	$pV = nRT$
frequency of light	$\nu = \frac{c}{\lambda}$
energy of a photon	$\mathrm{E} = \frac{hc}{\lambda}$
Beer-Lambert law	$A = \log\frac{I_0}{I} = \varepsilon cl$
spin only magnetic moment	$\mu = \sqrt{n(n+2)}\,\mathrm{BM}$
Henderson–Hasselbalch equation	$\mathrm{pH} = \mathrm{p}K_\mathrm{a} + \log\frac{[\mathrm{A}^-]}{[\mathrm{HA}]}$
0th order integrated rate law	$[\mathrm{A}] = [\mathrm{A}]_0 - kt$
1st order integrated rate law	$\ln[\mathrm{A}] = \ln\,[\mathrm{A}]_0 - kt$
Arrhenius equation	$k = A \cdot e^{-\frac{E_a}{RT}}$
enthalpy	$H = U + pV$
Gibbs energy	$G = H - TS$
standard Gibbs energy change	$\Delta_r G^\circ = -RT\ln K = -nFE^\circ_{cell}$
Clausius-Clapeyron equation	$\ln\frac{P_1}{P_2} = \frac{\Delta H_{vap}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$
Raoult's law	$p_i = x_i p_i^*$
boiling point elevation	$\Delta T = iK_b m$
freezing point depression	$\Delta T = iK_f m$

Consider all gases ideal unless told otherwise.

In equilibrium constant calculations, all concentrations are referenced to a concentration of 1 mol dm^{-3}.

IR absorption data

Bond stretching frequencies

Bond type		**Wavenumber (cm^{-1})**
C-H	Alkane	3000-2850
	Alkene	3100-3000
	Aromatic	3150-3050
	Alkyne	~3300
	Aldehyde	2900-2700
C=C	Alkene	1680-1600
	Aromatic	1600-1400
C≡C	Alkyne	2250-2100
C=C	Aldehyde	1740-1720
	Ketone	1725-1705
	Carboxylic acid	1725-1700
	Ester	1750-1720
	Amide	1670-1640
	Anhydride	1810, 1760
C-C	Alcohol, ether, ester, carboxylic acid, anhydride	1300-800
O-H	Alcohol, phenol, free	3600-3200
	Hydrogen bonded	3500-3200
	Carboxylic acid	3400-2500
N-H	Primary and secondary amine and amide	3500-3100
C-N	Amine	1350-1000
C=N	Imine and oxime	1690-1640
C≡N	Nitrile	2260-2240
N=O	Nitro ($R-NO_2$)	1600-1500, 1400-1300
S=O	Sulfoxide	1050
	Sulfate, sulfoamide	1200-1140

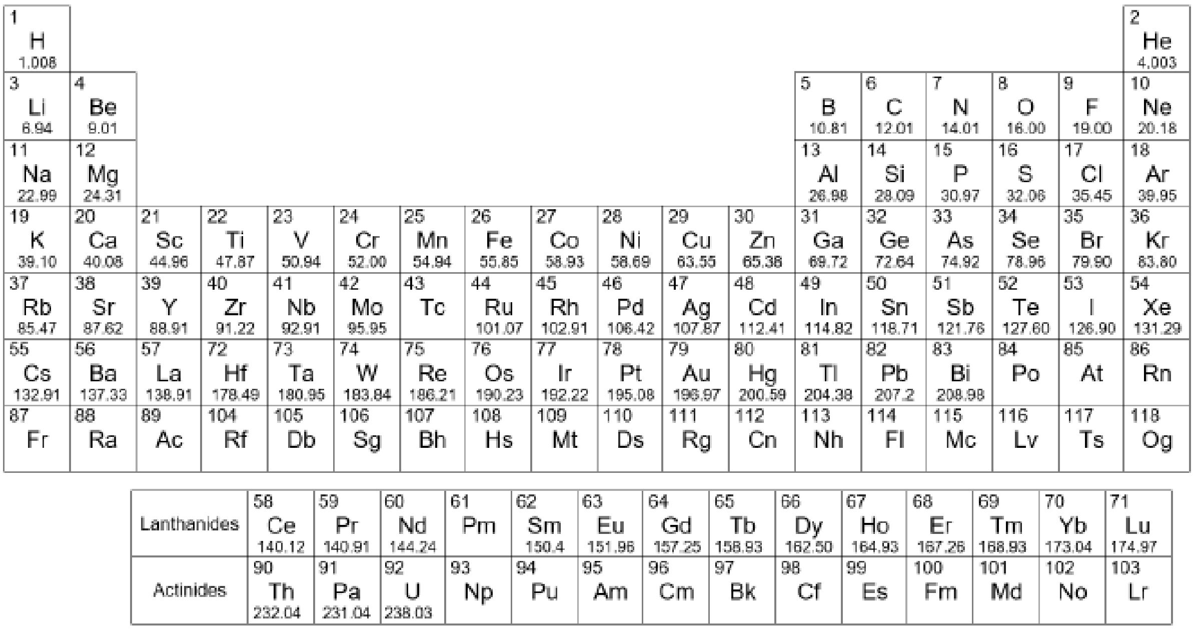
Characteristic bond stretching frequencies of anionic species

Anion	**Wavenumber (cm^{-1})**
SO_4^{2-}	1100-1200 (ν_{as})
ClO_4^-	1050-1170 (ν_{as})
NO_3^-	1370 (ν_{as})
CN^-	2089
SCN^-	2053 (νC-N), 748 (νC-S)
N_3^-	2042 (ν_{as}), 1343 (ν_s)
CNO^-	2052 (νC-N), 1057 (νN-O)

Number of CO stretching bands in the IR spectra of metal carbonyl complexes

Complex	Number of expected bands
$M(CO)_6$	1
$M(CO)_5X$	3
trans-$M(CO)_4X_2$	1
cis-$M(CO)_4X_2$	4
fac-$M(CO)_3X_3$	3
mer-$M(CO)_3X_3$	3
trans-$M(CO)_2X_4$	1
cis-$M(CO)_2X_4$	2

Periodic table



1 H 1.008																	2 He 4.003
3 Li 6.94	4 Be 9.01											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											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.06	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 72.64	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 95.95	43 Tc	44 Ru 101.07	45 Rh 102.91	46 Pd 106.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.76	52 Te 127.60	53 I 126.90	54 Xe 131.29
55 Cs 132.91	56 Ba 137.33	57 La 138.91	72 Hf 178.49	73 Ta 180.95	74 W 183.84	75 Re 186.21	76 Os 190.23	77 Ir 192.22	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Nh	114 Fl	115 Mc	116 Lv	117 Ts	118 Og

Lanthanides	58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm	62 Sm 150.4	63 Eu 151.96	64 Gd 157.25	65 Tb 158.93	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.04	71 Lu 174.97
Actinides	90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

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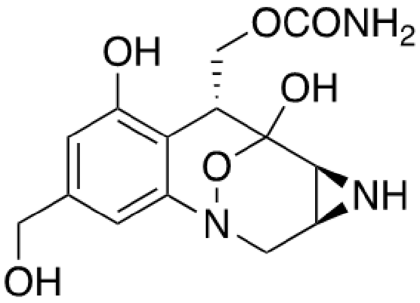
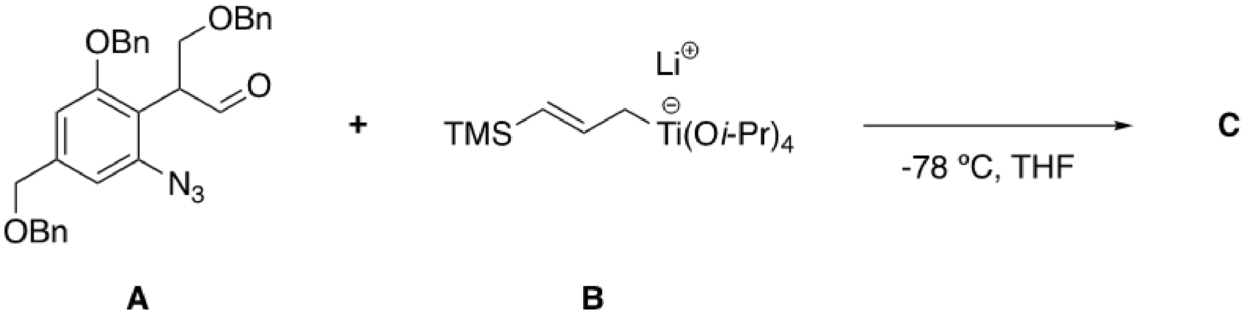
1. Stereocontrol in the synthesis of FR66979.



FR66979

FR66979 was isolated from the bacterium Streptomyces sandaensis in 1987. It was first identified as a promising antibiotic, but subsequently found to also possess potent antitumour activity by forming interstrand cross-links in duplex DNA. In this question, we will examine the total synthesis of **FR66979** completed in 2002 by Ciufolini and co-workers.

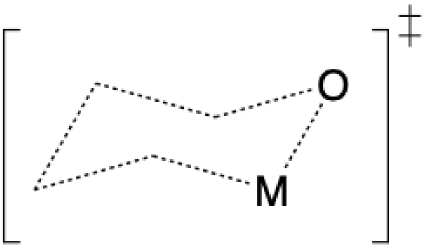


The first step in the synthesis involved the coupling of aldehyde **A** with organometallic species **B** to form **C**.

(a) Draw all the possible stereoisomers of **C**.

Consider the reaction between (*R*)-**A** and **B**.
(b) Draw a Newman projection showing the ideal approach of the nucleophile in this reaction. Use the labels =O, –H, –Ar, –CH_2OBn, and Nu.

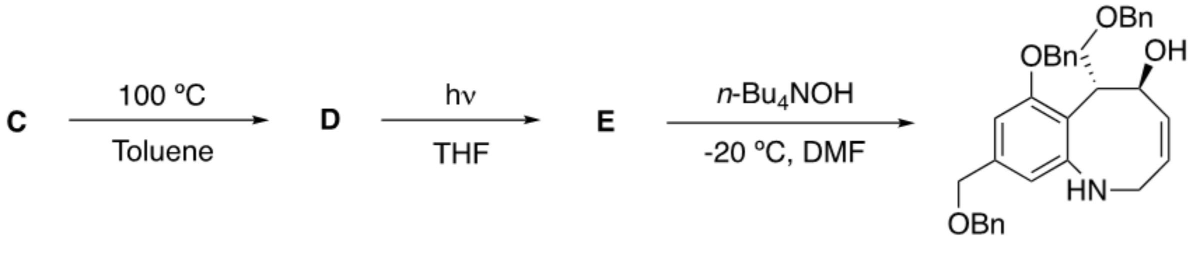
(c) Referencing your answer to part **(b)**, draw the arrangement of the reactants as they come together to form the six-membered ring transition state in the reaction to form **C** following the template below. Clearly show the orientation of the stereocentre, using the same labels as in part **(b)**. Edit the dotted lines to show the correct bond orders and add substituents as necessary.



(d) Draw the structure of compound **C** showing all stereochemistry.

Compound **C** was further transformed into compound **D** by heating in toluene. Brief photolysis of **D** yielded **E**, which can undergo fragmentation to form **F**.

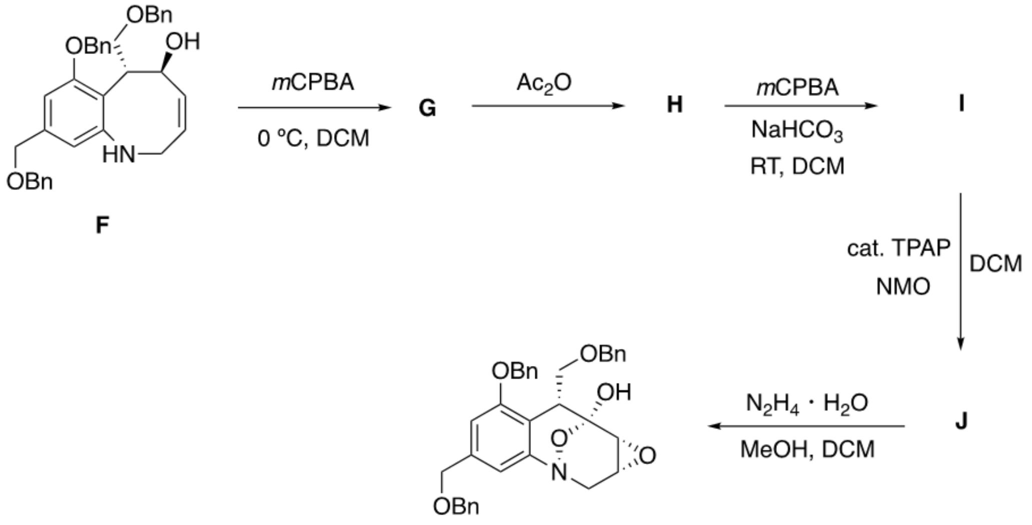
Hint: Nitrogen gas evolved during the photolysis of **D** to form **E**. **D** contained a five-membered ring while **E** contained a three-membered ring.

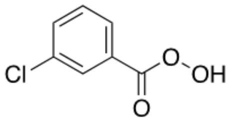


F

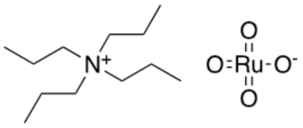
(e) Draw the structures of **D** and **E**. You do not need to indicate stereochemistry.

The next series of steps allowed the formation of the bridged bicyclic ring scaffold.

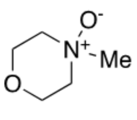




*m*CPBA



TPAP



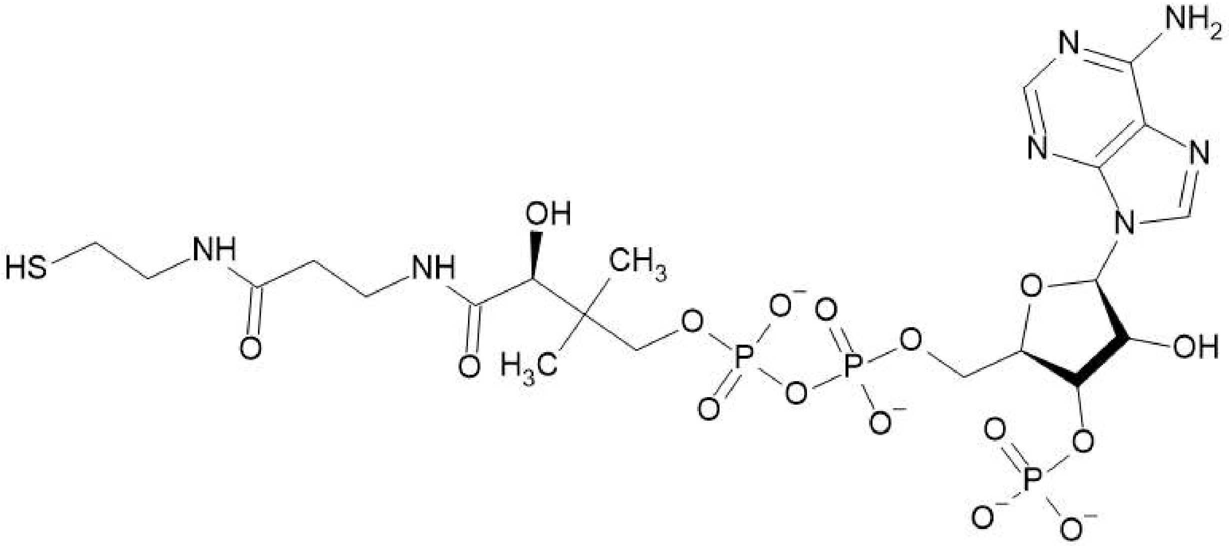
NMO

(f) Draw the structures of compounds **G**, **H**, **I**, and **J**. You do not need to indicate stereochemistry. *Hint*: cat. TPAP/NMO works similarly to pyridinium chlorochromate (PCC).

2. Coenzyme A and anaplerotic reactions.

Glycolysis is one of the most important catabolic transformations. It affords pyruvate, which is further subjected to oxidative decarboxylation under aerobic conditions entering the tricarboxylic acid (TCA) cycle in the form of acetyl-coenzyme A (CoA), which reacts with oxaloacetate to produce citrate.

CoA is composed of three blocks, which are residues of phosphorylated ADP, pantothenic acid (vitamin B$_5$), and thioethanolamine:



During CoA biosynthesis, vitamin B$_5$ is modified from both sides.

(a) Suggest the canonical amino acid **X1**, from which the thioethanolamine residue originates. Draw the structure of the L-isomer of **X1** with stereochemical details. What is the absolute configuration (*R* or *S*) of the stereocentre?

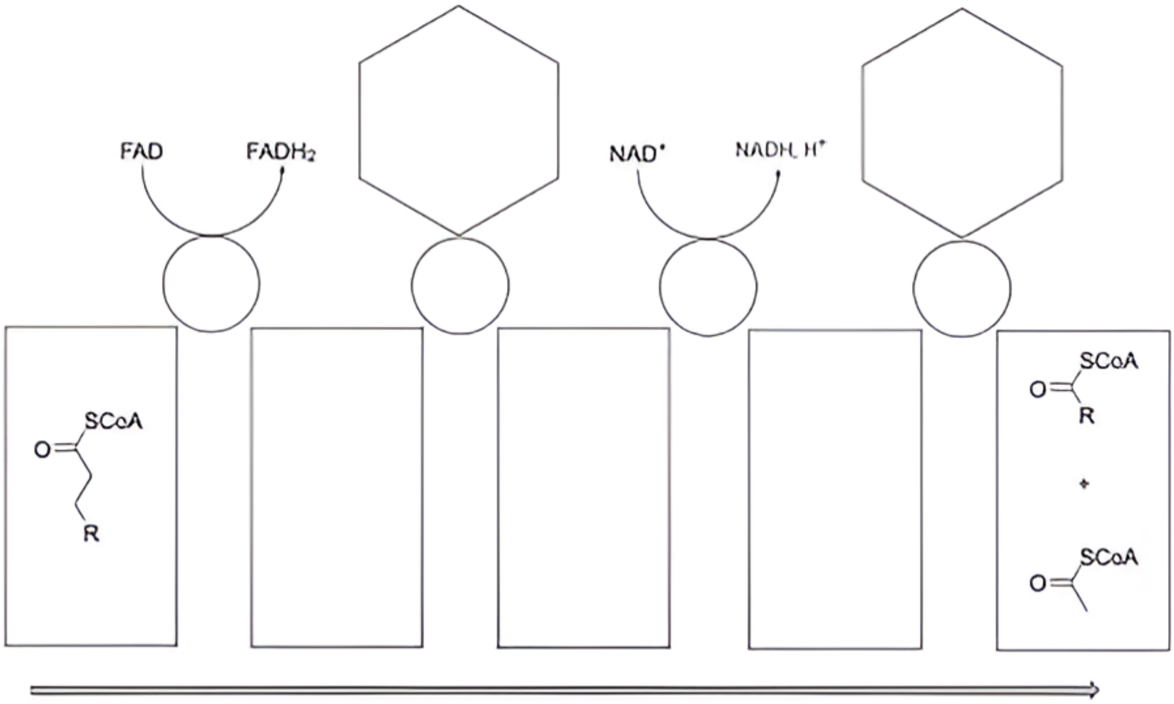
Vitamin B$_5$ is produced in most bacteria by a combination of pantoate and a noncanonical amino acid **X2**, which is a nearest homologue of the canonical amino acid **X3** and a structural isomer of the canonical amino acid **X4**.

(b) Draw the structures of **X2**-**X4** and pantoate.

CoA is a universal carrier of acyl groups in numerous metabolic processes including degradation and biosynthesis of fatty acids. The β-oxidation of fatty acids takes place in the mitochondrial matrix through a series of four reactions collectively referred to as β-oxidation. This process is named for the successive oxidations occurring at the β-carbon, which lead to the stepwise removal of two carbon atoms from the carboxyl end of the fatty acyl-CoA molecule.

Abbreviation	Name	Function
EH	Enoyl-CoA Hydratase	Forms a β-hydroxyl carbonyl (aldol) from an α, β-unsaturated carbonyl
KT	β-ketothiolase	Cleaves the bond between the α and β-carbons in a β-ketothioester
HD	3-L-hydroxyacyl-CoA Dehydrogenase	Oxidizes a hydroxyl group to a carbonyl group
AD	Acyl-CoA Dehydrogenase	Removes hydrogen atoms from the α and β positions of a carbonyl to form an α, β-unsaturated carbonyl

The process of the β-oxidation of fatty acids is shown underneath with blanks.



(c) Fill in the circles with the abbreviations of the enzymes needed. Each enzyme should be used once.

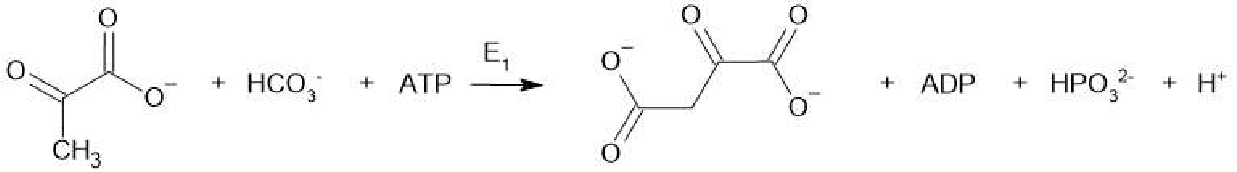
(d) Draw in the hexagons the structure(s) of the substrate(s) needed by the enzyme at each point.
(e) Complete the rectangles with the structures of the intermediates.

Recently CoA was found to play an important protective role in preserving a particular functional group in various enzymes from irreversible oxidation. This reaction is referred to as CoAlation.
(f) From the following functional groups, choose the most probable one that is being protected:
–OH   –C=O   –COOH $–C(O)NH_2$ $–NH_2$ $–NH\text{-}C(NH_2)_2^+$ –SH $\text{-S-}CH_3$

During the periods of rest, organisms synthesize various important molecules including storage compounds, mostly using TCA cycle intermediates as starting substrates, thus depleting the pool of cycle intermediates. As a result, glycolytic overproduction of pyruvate and phosphoenolpyruvate as well as that of acetyl-CoA is observed when energy is required again. This happens because of a diminished concentration of oxaloacetate, which slows down the initial reaction of the TCA cycle.
Most organisms can overcome this potentially dangerous situation due to four different reactions catalyzed by enzymes **E1**-**E4** belonging to three different classes.

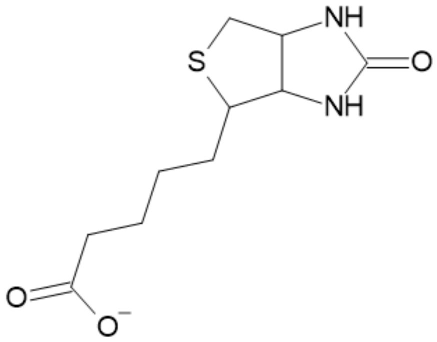
Enzymes catalyze diverse reactions and can be grouped into six classes:
i) Oxidoreductases – Oxidation/reduction reactions.
ii) Transferases – Transfer of a methyl-, acyl-, amino- or phosphate group from one substance to another; kinases forming a subclass catalyze the transfer of phosphate group(s) from high-energy phosphorylated species to accepting substrate(s).
iii) Hydrolases – Hydrolytic formation of two products from a substrate.
iv) Lyases – Non-hydrolytic addition or removal of groups from substrates, with C-C, C-N, C-O, or C-S bonds cleavage in the latter case.
v) Isomerases – Intramolecular rearrangement.
vi) Ligases – Joining together two molecules by formation of new C-O, C-S, C-N, or CC bonds with simultaneous breakdown of ATP.
Hint: enzymes catalyze both forward and reverse reactions.

A very important reaction occurring in mammalian livers and kidneys is catalyzed by **E1**:

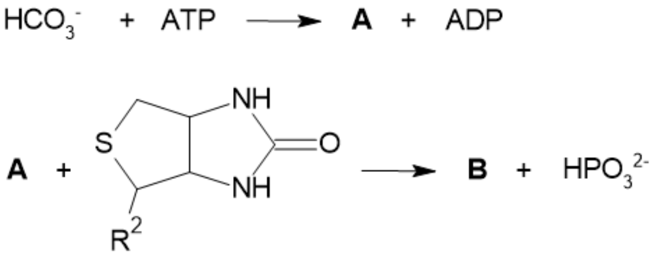


(g) What class does **E1** belong to?

Biotin (see below) covalently bound to a lysine (Lys) residue is the co-factor found in the active site of **E1**. The reaction develops in two subsites, one being responsible for the biotin carboxylation (Scheme 1) and the other for CO_2 attachment to pyruvate.



Biotin

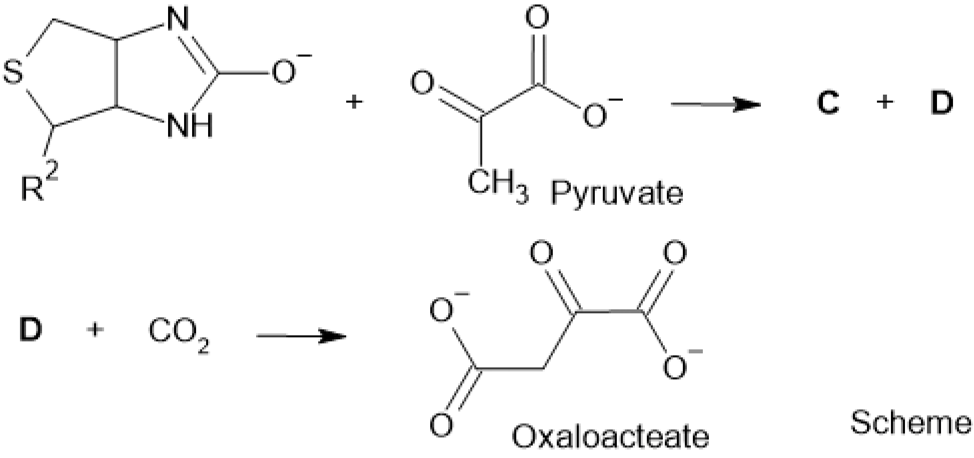


Scheme 1

(h) Write the reaction between biotin and the Lys residue (show the latter as R^1-$(CH_2)_4$-NH_3^+).

(i) Draw the activated intermediate **A** and the product of addition of carbon dioxide **B**. Show the biotin residue as in Scheme 1.

After being transferred to the second subunit, CO2 leaves the biotin residue, the enol form of which further activates pyruvate by removing one of its protons to facilitate its reaction with CO_2 (Scheme 2):



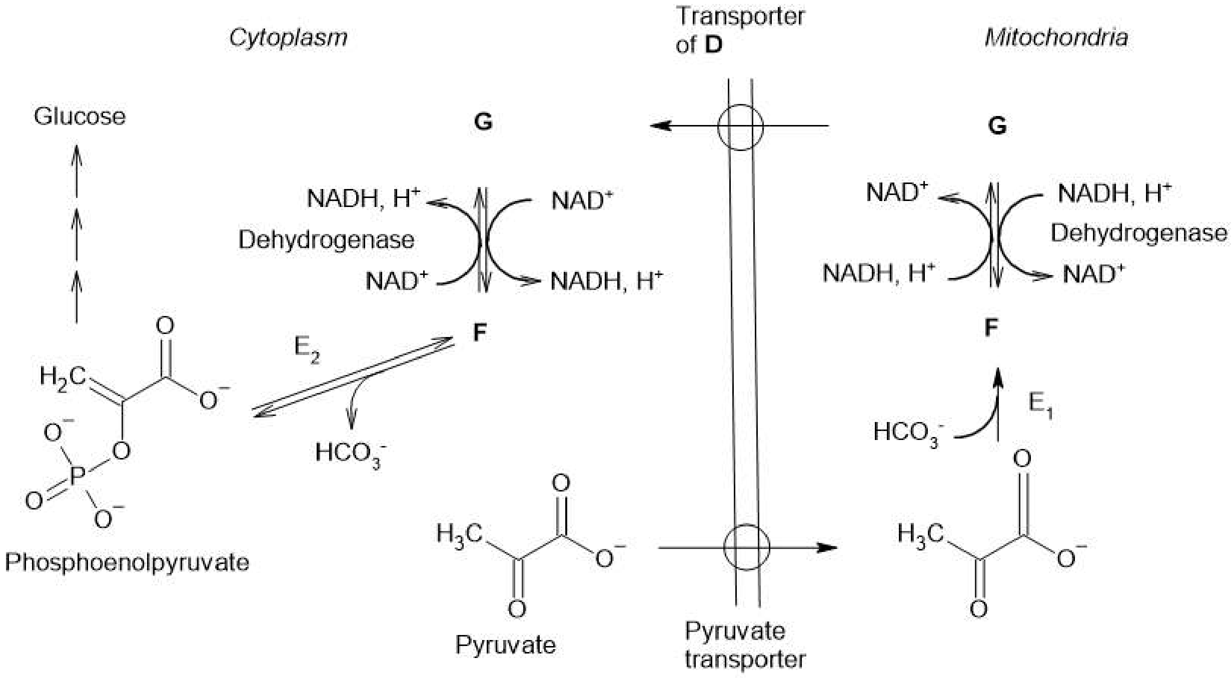
Scheme 2

(j) Draw the structures of **C** and **D**.

E2 catalyses a reversible reaction which involves (along with other reaction participants) GTP, oxaloacetate, and phosphoenolpyruvate, the latter containing nearly twice as much energy as in ATP.

(k) Write down the **E2** catalysed reaction.
(l) What class does **E2** belong to?

E2 plays an important role in the process of gluconeogenesis where it catalyses one of the bypass steps given in Scheme 3 (phosphorylated nucleosides and inorganic phosphate are not shown).



Scheme 3

(m) Draw the structures of **F** and **G**.

CO_2 (in the form of the hydrocarbonate anion) is attached to pyruvate in mitochondria and is released as a result of decomposition of **F** in the cytoplasm. Studies show that this is the same species. Thus, one should not expect any label in newly formed glucose if $^{14}CO_2$ enters the carboxylation reaction instead of $^{12}CO_2$.
However, a trace amount of labelled glucose is detected in actual experiments with $^{14}CO_2$.
(n) Explain the reason for this.
Hint: Some substances are intermediates of several metabolic pathways.

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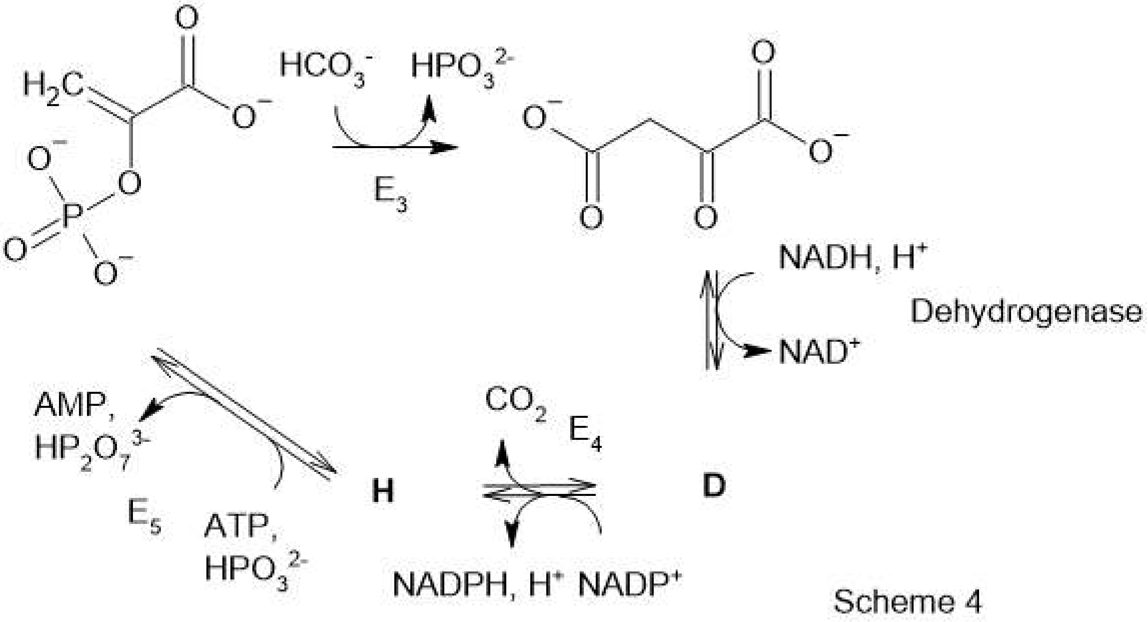
E3 and **E4** are involved in the metabolic cycle found in some plants (Scheme 4).



Scheme 4

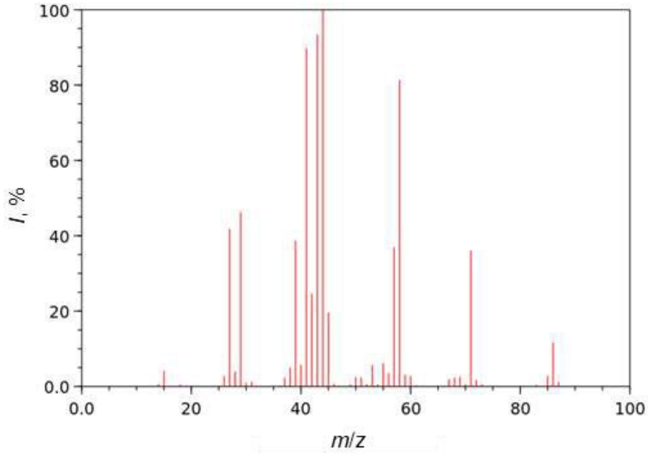
(o) Draw the structure of **H**.
(p) What class(es) do **E3** and **E4** belong to?
(q) Identify the kinase(s) in Scheme 4 (if any) and suggest the name of the enzyme(s).

3. In search of an oasis in the desert.

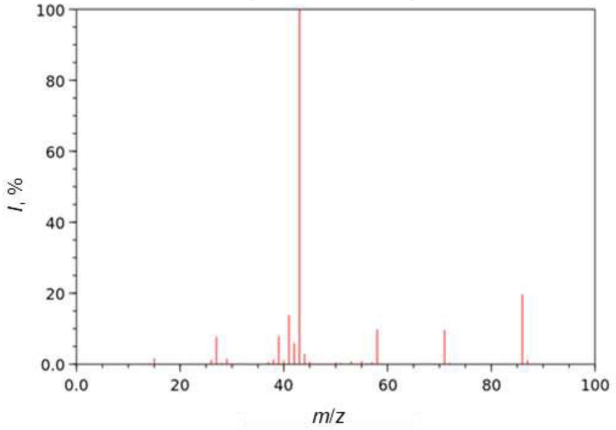
The United Arab Emirates University is located in the city of Al Ain, which is known for its rich history and lush greenery thanks to the largest oasis in the country. Just like searching for an oasis in a desert, in this problem, you will be challenged to find the structures of eight isomers from the large number of peaks in their infrared (IR) and mass spectra shown.

Compounds **A**–**H** are all isomers of $C_5H_{10}O$. The mass spectra (electron impact ionisation, I, % – relative intensity) of these compounds and the wavenumber of the strongest band in their IR spectra are given:

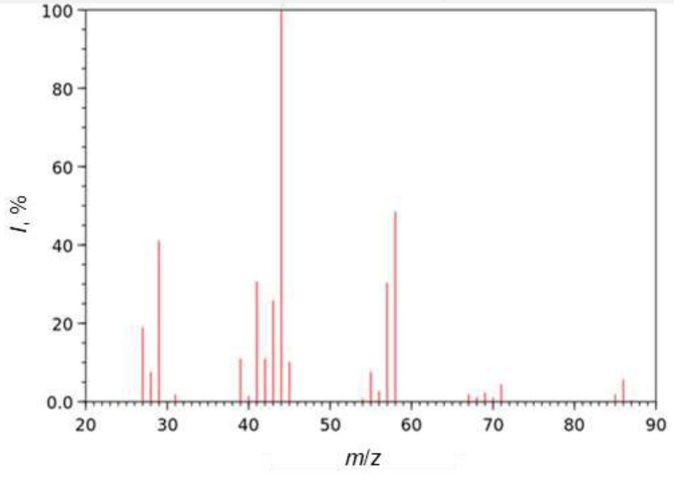
A (1728 cm^{-1})



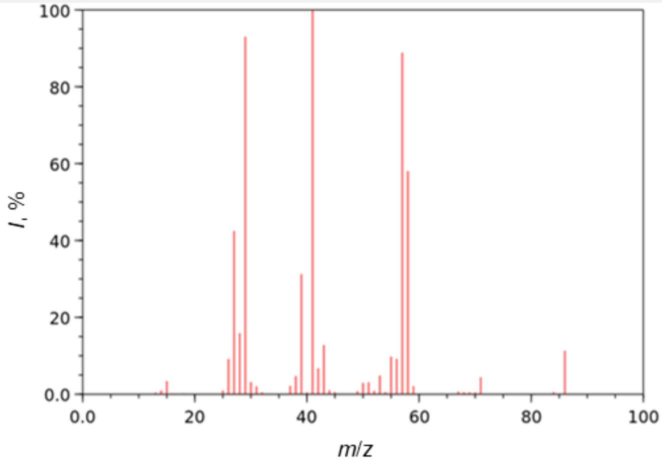
B (1717 cm^{-1})



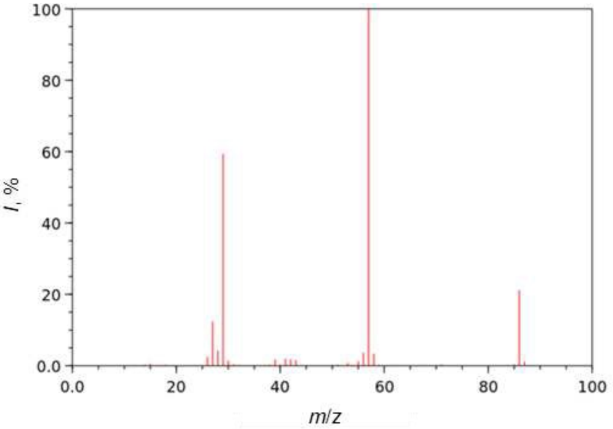
C (1727 cm^{-1})



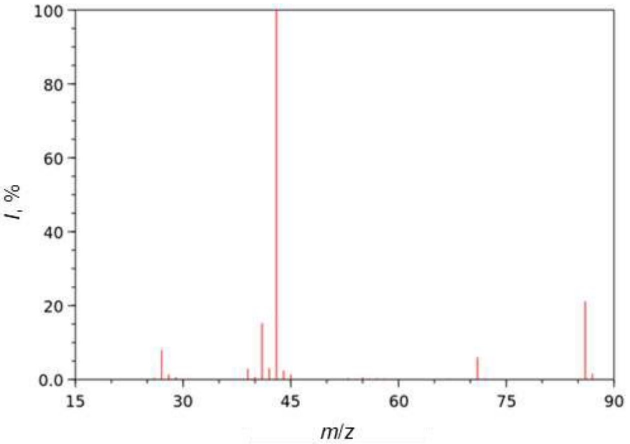
D (1728 cm^{-1})



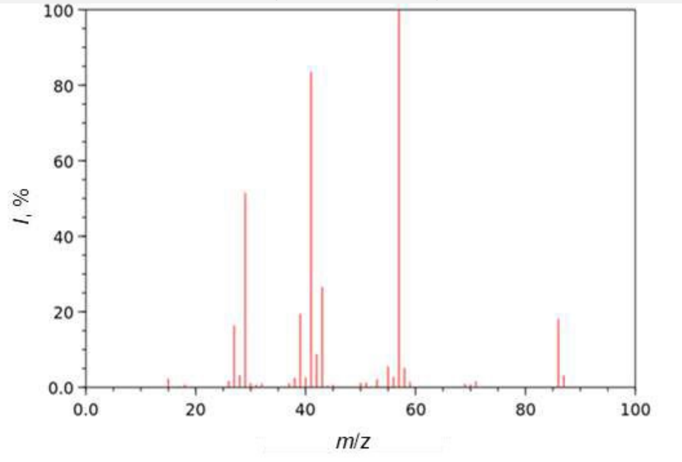
E (1720 cm^{-1})



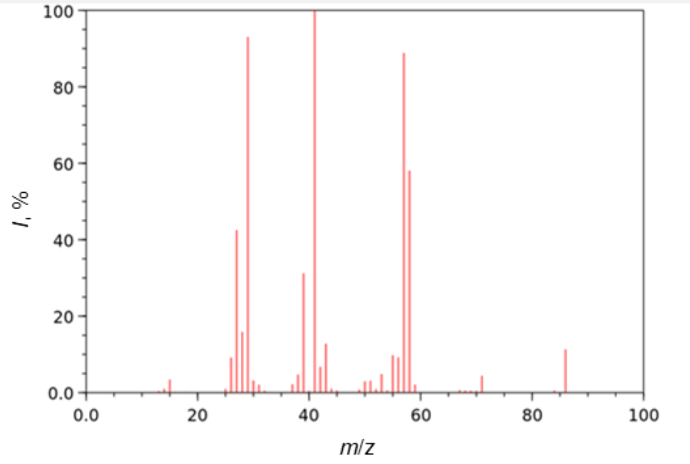
F (1718 cm^{-1})



G (1728 cm^{-1})

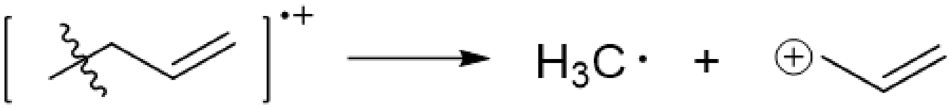


H (1728 cm^{-1})

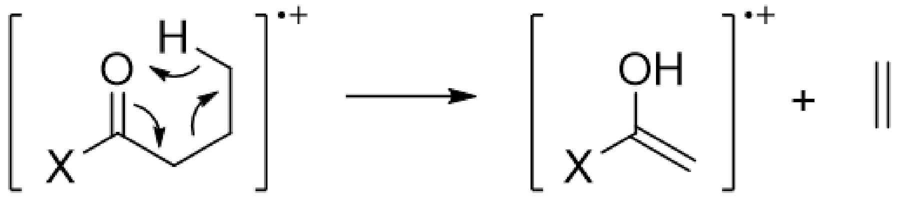


(a) State all the possible functional groups (or combinations of functional groups) that molecules with the molecular formula $C_5H_{10}O$ can have.

Molecular ions formed during electron impact ionization in a mass spectrometer are often in a high energy state and undergo dissociation into fragments. A typical fragmentation pathway is the cleavage of one of the bonds producing one charged and one neutral fragment. According to Stevenson's rule, the fragment with the lowest ionization energy will possess a charge after the fragmentation, for example:



Another typical fragmentation pathway is some kind of rearrangement. For example, the McLafferty rearrangement is normally observed for carbonyl compounds but also alkenes, imines, etc:



$X = H, R, OH, OR, NR_2$

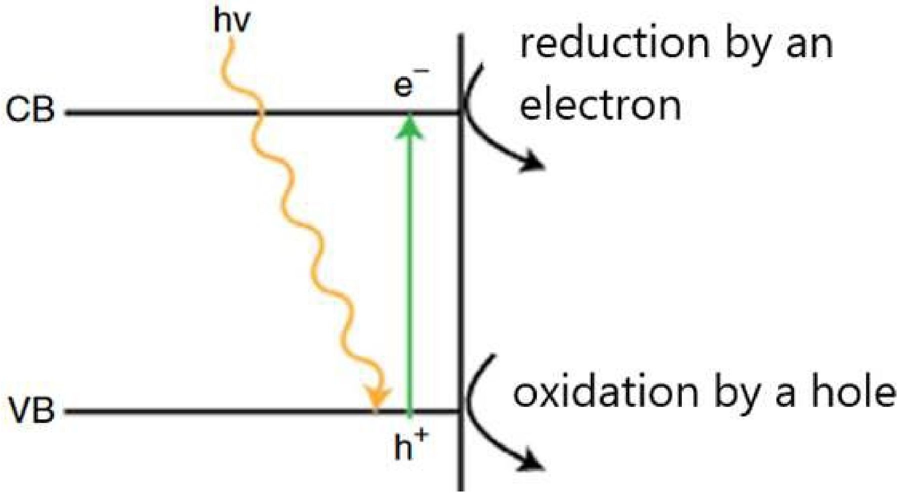
(b) Determine the structures of isomers **A**-**H** using the data. If you are not able to assign a specific structure to the unknown isomer, list all your options. The peak of the highest intensity in the mass spectrum is called a base peak. It is assigned 100% intensity, and the intensities of other peaks are calculated relative to the base peak.

(c) For each structure **A**-**H**, suggest a fragmentation pathway leading from the molecular ion to the species that gives the base peak in the mass spectrum.

4. Photocatalysis.

Photocatalysis is a way to utilize solar energy and carry out various useful but energetically unfavourable redox reactions, such as water splitting ($\Delta_rG°_{298}$ = +237 kJ / mol of H_2O), carbon dioxide methanation ($\Delta_rG°_{298}$ = +818 kJ / mol of CO_2), and others.

Common photocatalysts belong to one of the three classes of materials: transition metal complexes, organic dyes, and semiconductors. Let's consider the latter class. When a semiconductor absorbs a photon with energy equal to or greater than the material's band gap, an electron is excited from the valence band (VB) to the conduction band (CB), generating an electron hole, h^+, in the valence band. The excited electron can reduce a compound, while the positive hole can take up an electron from a compound and produce oxidised products. The overall process is a redox reaction at the surface of the semiconductor irradiated with light.



Not every semiconductor is suitable for a particular redox process. Both half-reactions – reduction by an electron and oxidation by a hole must be thermodynamically favourable, that is, the redox potential of a hole must be positive enough, while that of an electron – negative enough.

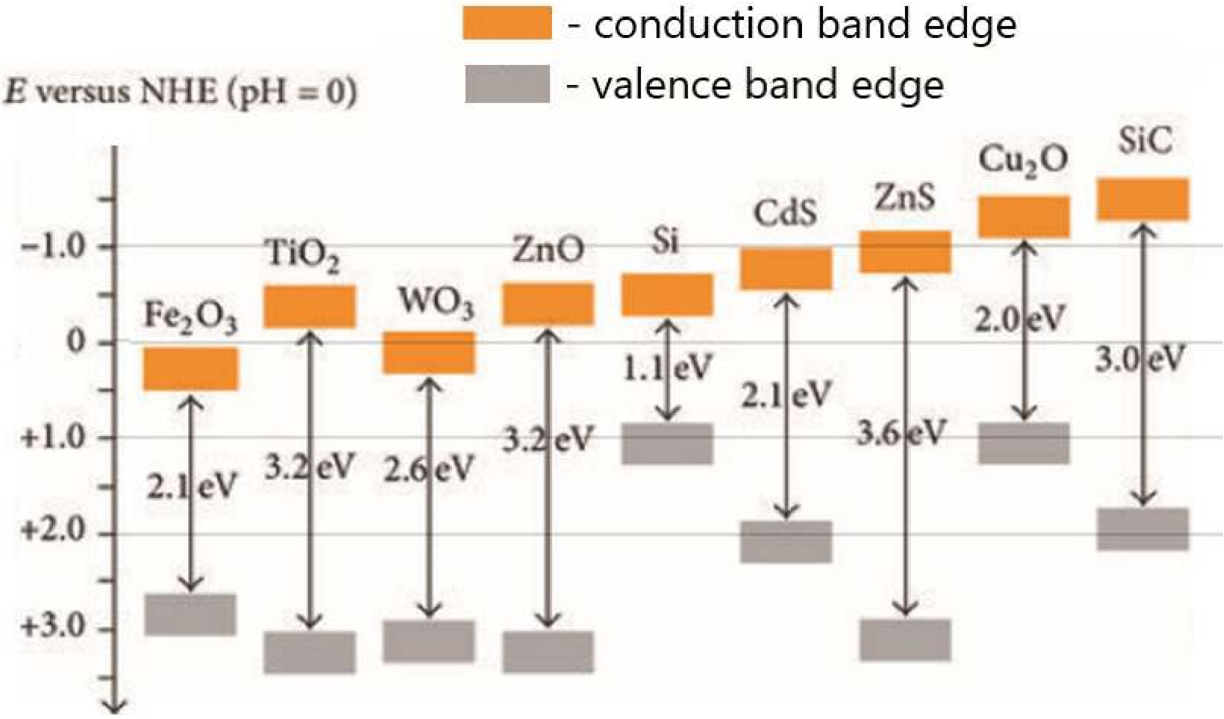
Consider two photochemical reactions: water splitting and carbon dioxide methanation by water. In both reactions, consider an acidic medium.

(a) Write down the half-reactions occurring at the photocathode and photoanode, and the overall reactions.

(b) If the acidic medium is replaced by a basic one, which of the following electrochemical properties for water splitting will change and which will not? Mark the correct cells.

Electrochemical property	**will change**	**will not change**
Overall reaction		
Cathode potential		
Emf		

The band energy diagrams of selected semiconductors and the table of standard reduction potentials for selected half-reactions are shown below.



Half-reaction	E°, V (pH 0)
$O_2 \rightarrow H_2O$	1.23
$CO_2 \rightarrow CH_4$	0.17
$H^+ \rightarrow H_2$	0

(c) Using these data, determine which of the listed semiconductors upon irradiation at pH = 0 are able to:

i) oxidize water to O_2;

ii) reduce water to H_2;

iii) reduce carbon dioxide to methane

iv) both oxidize and reduce water.

The catalytic activity of photocatalysts is evaluated by the normalized reaction rates measured, e.g., in mol·h^{-1}·g^{-1}. However, to estimate the efficiency of light energy conversion, other quantities are used. In homogeneous photochemistry, the quantum yield (QY) is defined as the number of product molecules to the number of absorbed photons ratio:

$$QY = \frac{number\ of\ product\ molecules}{number\ of\ absorbed\ photons} \times 100\%$$

However, in non-homogeneous photocatalytic systems, the actual number of photons absorbed is difficult to determine due to scattering and reflection of light. Therefore, the absorbed photon number is replaced by the incident photon number. In addition, the number of product molecules is replaced by the number of electrons transferred. The quantity calculated in this manner is referred to as the "apparent quantum yield" (AQY):

$$AQY = \frac{number\ of\ electrons\ transferred}{number\ of\ incident\ photons} \times 100\%$$

In a recent photocatalytic experiment, the catalyst (0.1 g) was dispersed in an aqueous solution of lactic acid and the solution was irradiated by a laser at 532 nm with a power of 200 mW. Hydrogen evolved from the solution at a normalized rate of 160 mol·h^{-1}·g^{-1}.

(d) Calculate the apparent quantum yield of water reduction.

5. New drug formulation.

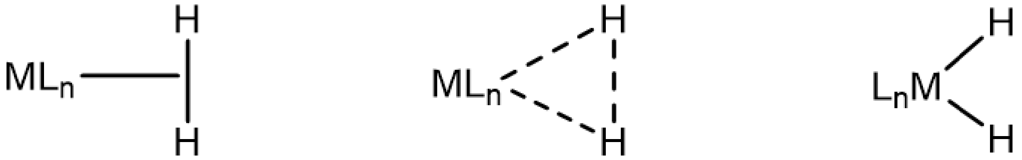
In the UAE, researchers at a pharmaceutical company are developing a new drug formulation that needs to remain stable at sub-zero temperatures, especially when transported through cold desert nights or to mountainous areas such as Jebel Hafeet. A sample of 15 g of this drug is dissolved in 250 g of a solvent, which has the following properties:

- Freezing point of the pure solvent: −15°C
- Freezing point depression constant (K_f) for the solvent: 4.5 K kg mol^{-1}
- Standard enthalpy of vaporization of the solvent: 25.0 kJ mol^{-1}
- Vapour pressure of the pure solvent at −15°C : 0.0075 atm
- The freezing point of the solution containing the drug: −16.5°C

(a) Calculate the molality of the drug in the solution.
(b) Determine the molecular weight of the drug.
(c) Estimate the vapour pressure of the solvent at a new freezing point after dissolving the drug, using the Clausius-Clapeyron equation and Raoult's law.
(d) Discuss how the freezing point depression and the vapour pressure changes affect the stability and transport of the drug in UAE’s variable climate conditions.

6. Coordination chemistry of dihydrogen.

Molecular hydrogen (H_2) can act as a ligand in certain transition metal complexes. In these complexes, the hydrogen atoms can have a different character depending on the metal as well as the nature of other ligands coordinated to the metal atom. They can range from a dihydrogen complex where the H2 molecule keeps its bond, to dihydrido complexes when the bond between the two H atoms is completely broken. There are intermediate states as well, of course.



(a) Draw an MO energy diagram for the interaction between the metal d orbitals and the molecular orbitals of H_2. Indicate which orbitals on the metal are of correct symmetry to interact with each molecular orbital of H_2. Indicate how the energy levels of the orbitals change, and draw cartoon representations of these orbitals. Assume the H_2 bond/axis lies along the x-axis and the M-H_2 bond/axis lies along the z-axis.

Consider the two complexes below. One of them can be classified as a dihydrogen complex, whereas the other can be classified as a dihydrido complex.

$W(CO)_5H_2$ $\qquad$ $Ir(PPh_3)_2H_2$

(b) Determine which complex belongs to which class. Provide a reason based on the MO diagrams you have drawn.

(c) Arrange the following complexes in order of decreasing H-H bond distance:

$W(CO)_5H_2$ $\qquad$ $W(CO)_4(PPh_3)H_2$ $\qquad$ $W(CO)_4(Cl)H_2$

(d) Draw the interactions of the ligand π-orbitals with the metal d-orbitals in M-X where X is a halide.

(e) Arrange the following complexes in order of decreasing H-H bond distance:

$Ir(CO)_3(F)H_2$ $\qquad$ $Ir(CO)_3(Cl)H_2$ $\qquad$ $Ir(CO)_3(I)H_2$

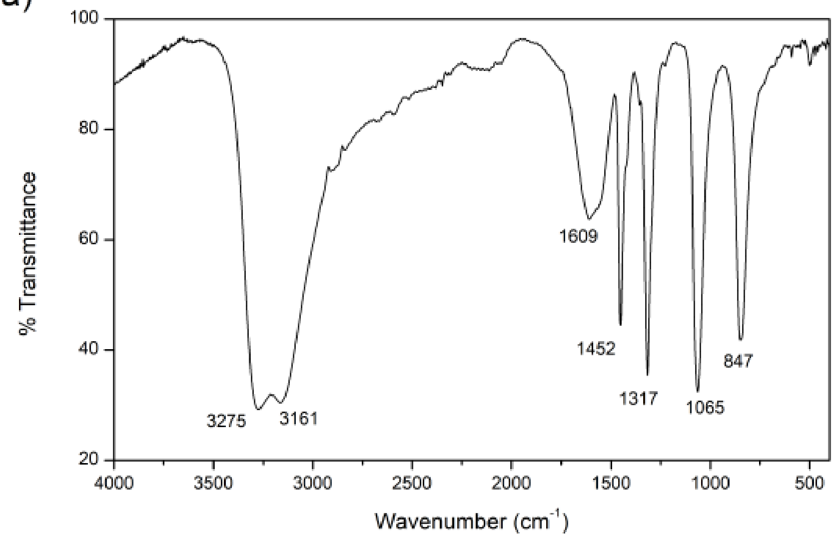
7. Applications of infrared spectroscopy to coordination chemistry.

Part A

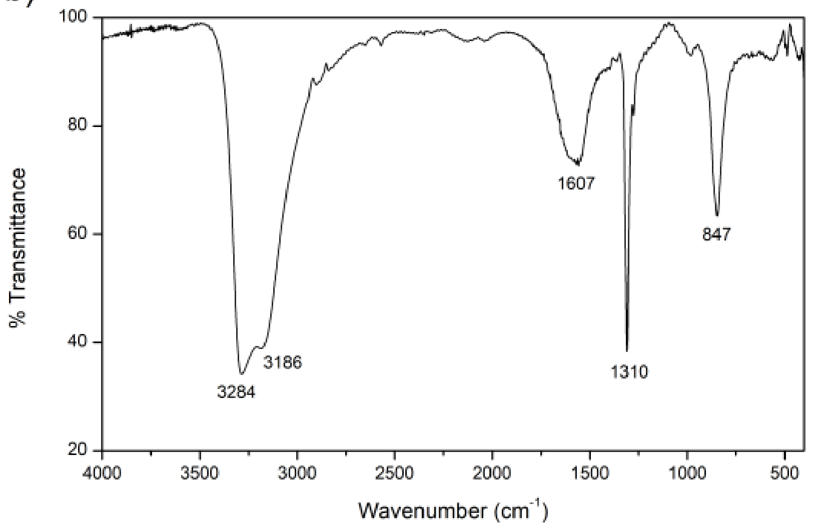
Linkage isomerism is a form of isomerism in which coordination compounds have the same composition but differ in the ligand connectivity to a metal. It can be observed in complexes in which the ligands have more than one donor atom, such as pseudohalogens or NO_2^-.

Reaction of $[Co(NH_3)_5Cl]Cl_2$ with $NaNO_2$ yields two complexes of general formula $[Co(NO_2)(NH_3)_5]Cl_2$. These two complexes differ in the mode of coordination of the NO_2^- anion (nitro: -NO_2 and nitrito: -ONO). The FTIR spectra of the starting material and two products are shown in figures a-c.

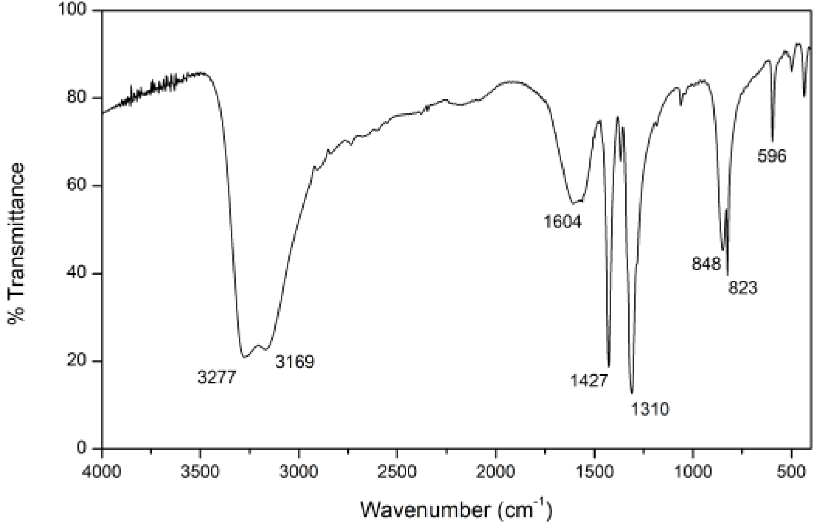
a)



b)



c)



(a) How many bands are expected for the NO_2^- ion and how are they affected by coordination? Consider both nitro and nitrito isomers.

(b) Which spectrum corresponds to which of the cobalt complexes mentioned above?

Part B

Metal carbonyls are coordination complexes of transition metals with CO as a ligand. Their properties have been extensively studied as they are useful in organic synthesis and as catalyst precursors, and more recently, because of their potential in cancer therapy.

Several octahedral complexes, $[M(CO)_6]^{x+}$, are known, in which the total charge depends on the metal. These can be used as precursors in the synthesis of heteroleptic complexes for different applications. IR spectroscopy enables analysis of the final product and can determine if the second ligand is bound to the metal.

(c) How many stretching bands are expected in the FTIR spectrum of CO and $[M(CO)_6]^{x+}$?

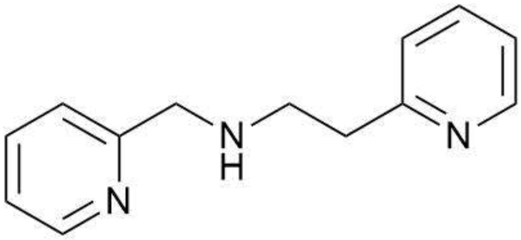
Partial ligand substitution can lead to the formation of complexes such as $[M(CO)_4L_2]^{x+}$, where L is monodentate ligand.

(d) State the type and number of possible isomers in complexes of type $[M(CO)_4L_2]^{x+}$.

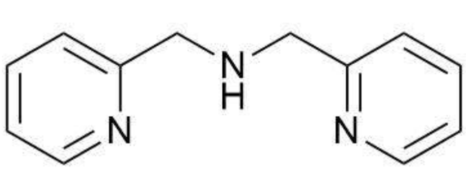
(e) The FTIR spectra of $[M(CO)_4L_2]^{x+}$ isomers show different numbers of bands in the region close to 2100 cm^{-1}. How would you explain this observation?

Part C

Pyridylalkyl-amine complexes became relevant as versatile platforms for several catalytic transformations, for instance, serving as models of O_2 activating metalloproteins. By treatment of a solution of $Co(ClO_4)_2$ in acetonitrile with two equivalents of pyridylalkyl-amine ligands, mononuclear complexes can be obtained rapidly in good yield. For the ligand pepma the product is a pink solid (**A**) and for bpma, a purple solid (**B**) is formed.



pepma



bpma

Infrared spectra of both compounds show very strong absorption bands around 1100 cm^{-1}. Furthermore, a medium intensity band at 3292 cm^{-1} and 3185 cm^{-1} was observed for **A** and **B** respectively. Their magnetic properties were studied, with both complexes having a value of $\mu \approx 4.0$ BM.

(f) What are the molecular formulae of compounds **A** and **B**? Draw all possible isomers of compound **A**, ignore the enantiomers of chiral structures.
(g) Draw the corresponding d-orbital splitting diagram and write down the electron configuration of the metal ion in these complexes.
(h) Assign the infrared bands at 1100 cm^{-1}, 3292 cm^{-1}, and 3185 cm^{-1}.

Both complexes are quite sensitive to air. Complex **A** shows reactivity to oxygen even in the solid state, as it gradually converts to an orange solid **C**. Complex **B** reacts only in solution, changing its colour to pale yellow due to the formation of compound **D**. The nature of **C** and **D** was studied through elemental analysis, infrared spectroscopy, and magnetic studies. Both the elemental analysis and magnetic moment of complex **C** are almost the same as those of compound **A**. In the infrared spectrum of **C** an additional band at 1643 cm^{-1} was observed. The elemental analysis of **D** is significantly different from that of **B**. Compound **D** is diamagnetic.
(i) Based on this additional information, propose the molecular structures of compounds **C** and **D**.