

2026 CCO Take Home Exam

CANADIAN
CHEMISTRY
OLYMPIAD



OLYMPIADE
DE CHIMIE
DU CANADA

Due Date: Saturday, April 4th, 2026 (midnight)

Name:

School:



Periodic table

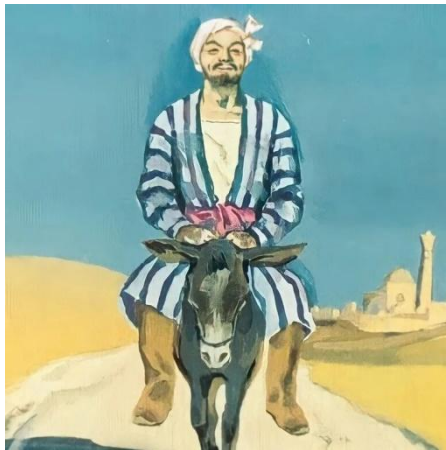
1	H	1.008																	2	He	4.003																																
3	Li	6.94	4	Be	9.01																	9	F	19.00	10	Ne	20.18																										
11	Na	22.99	12	Mg	24.31																	17	S	32.06	18	Ar	39.95																										
19	K	39.10	20	Ca	40.08	21	Sc	44.96	22	Ti	47.87	23	V	50.94	24	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	89	Ac	89	104	Rf	104	105	Db	105	Sg	106	107	Bh	107	108	Hs	108	109	Mt	109	110	Ds	110	Rg	111	Cn	112	Nh	113	Fl	114	Mc	115	Lv	116	Ts	117	Og	118									
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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Problem 1. Khoja Nasreddin is now a chemist

Khoja Nasreddin is a folklore character from the East, the hero of short humorous and satirical stories and anecdotes, and sometimes even everyday tales. In 2022, the tradition of retelling jokes about Khoja Nasreddin was inscribed on the Representative List of the Intangible Cultural Heritage of Humanity.



One day, Khoja Nasreddin decided to become a chemist. He began his journey in chemistry by studying the thermal decomposition of an unknown red salt **A**, even though such work was quite challenging for beginners.

Khoja Nasreddin carefully decomposed 1.00 g of **A** at $-70\text{ }^{\circ}\text{C}$ (**Reaction 1**) in a closed 1.00 L reactor initially filled with argon at a pressure of 100.0 kPa. After the decomposition, the pressure inside the reactor increased to 106.42 kPa, and the solid residue consisted of two compounds, one of which was identified as salt **B**.

Following the first stage of decomposition, he gradually heated the reactor to $200\text{ }^{\circ}\text{C}$. During heating, the solid residue first turned into a mixture of solid and liquid, then into a solely liquid phase, and finally, at $128\text{ }^{\circ}\text{C}$, a solid phase reappeared. At this temperature, the pressure in the reactor was 260.63 kPa.

Upon reaching $200\text{ }^{\circ}\text{C}$, **B** began to decompose (**Reaction 2**), and after complete decomposition, no solid residue remained in the reactor. The pressure at $200\text{ }^{\circ}\text{C}$ was 396.82 kPa. When he introduced a glowing splint into the reactor, it ignited vigorously.

Nasreddin then attempted to synthesise salt **C**, which differs from **A** only by its cation. The mass fraction of the metal in **C** is equal to 12.63%. However, according to various sources, **C** is difficult to obtain. Instead, he successfully synthesised salt **D** (containing a complex cation, the same metal as in **C**, and 9.83% hydrogen by mass) by treating compound **E** (mass fraction of one of the elements in **E** is 4.21%) with gas **F** in liquid ammonia. He noted that at very low temperatures, **F** exists as a dark blue liquid.

To determine the amount of gas **F** required for the synthesis of 1.000 g of **D**, he passed as much **F** as necessary through 100 mL of potassium iodide solution (**Reaction 3**). For titration of a 10.00 mL aliquot of the resulting brown solution, 16.30 mL of sodium thiosulfate solution (**Reaction 4**) with a concentration of 0.0998 M was used. He also noted that when he was passing gas **F** through the iodide solution, another colourless gas was produced in the same amount as gas **F**.

1. **Identify** substances **A–F**.
2. **Write** the balanced equations of **Reactions 1–4**.



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Problem 2. Haber–Bosch process

Note: Necessary thermodynamic data are at the end of the problem.

In the Haber–Bosch process, ammonia (NH_3) is synthesised directly from the corresponding elements using an iron-based catalyst.

1. **Write** the equation for ammonia synthesis.
2. **Determine** the temperature, T (K), of the ammonia synthesis reaction, at which $K_p = 1$, assuming $\Delta_r H^\circ$ and $\Delta_r S^\circ$ do not depend on temperature.

In reality, $\Delta_r H^\circ$ and $\Delta_r S^\circ$ depend on temperature.

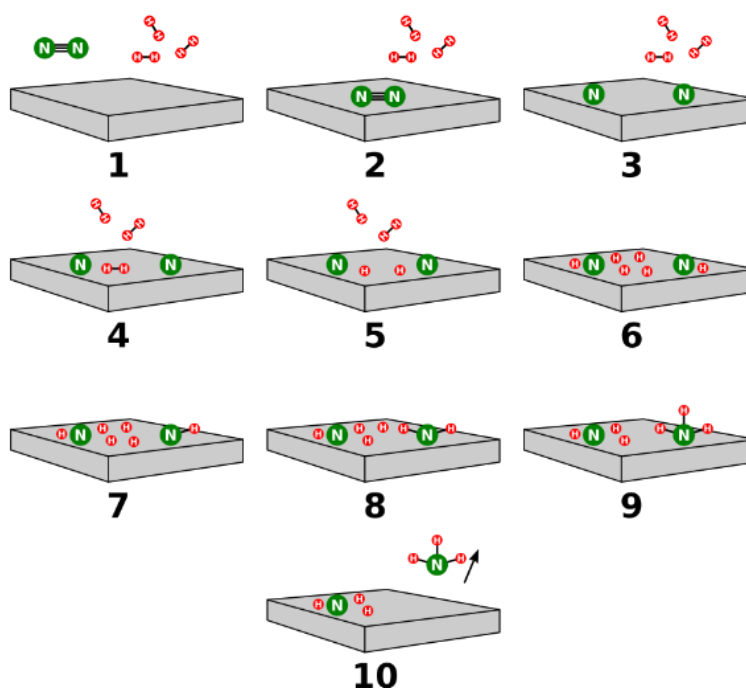
3. **Calculate** the value of K_p at 300 °C, assuming that heat capacities of the gases remain constant while enthalpy and entropy depend on temperature.
4. **Determine** the minimum amount (moles) of hydrogen required to achieve 90% conversion of 1 mol of nitrogen.

Ammonia synthesis is exothermic. Thus, low temperatures favour higher equilibrium yields, but the reaction rate decreases significantly. Industrially, the process is conducted at high temperatures and pressures to achieve optimal rate and conversion.

5. a) **Calculate** the equilibrium yield, η (%), of ammonia at 300 °C and a final total pressure of 150 bar from a stoichiometric mixture of reactants.
b) **Explain** qualitatively how the equilibrium yield would change if the total pressure were increased while keeping the temperature constant.



Ammonia formation proceeds via adsorption of gases on the catalyst surface, as shown in the diagram:

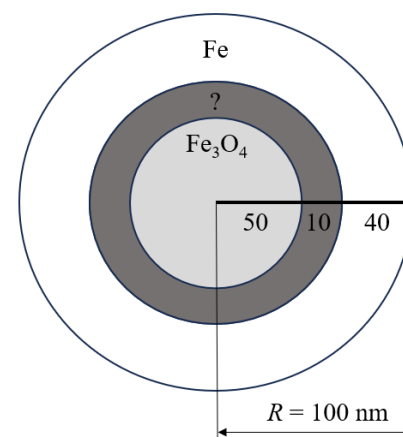


6. **Suggest** the possible rate-determining step of the mechanism.

The iron catalyst is produced from finely ground iron powder, which is usually obtained by reduction of high-purity magnetite (Fe_3O_4). The pulverised iron is oxidised to give magnetite particles of a specific size. The magnetite particles are then reduced. The catalyst maintains most of its bulk volume during the reduction, resulting in a highly porous high-surface-area material, which increases its catalytic efficiency.

The catalyst synthesised from 10 g of iron consists of nanoparticles with a radius, $R = 100 \text{ nm}$, as shown in the diagram on the right.

- Choose** the composition of the “?” layer in the nanoparticle:
a) Fe_2O_3 b) FeO c) FeOOH d) $\text{Fe}(\text{OH})_3$
- Calculate** the total surface area of the catalyst, assuming all nanoparticles are spherical and uniform in size and composition.
- Calculate** how many times faster the ammonia synthesis reaction proceeds on the synthesised catalyst compared to a 10 g iron cube if the rate is directly proportional to the surface area.



Thermodynamic data ($T = 298 \text{ K}$, $p = 1 \text{ bar}$):

Substance	$\Delta_f H^\circ / \text{kJ}\cdot\text{mol}^{-1}$	$S^\circ / \text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	$C_p / \text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$
$\text{H}_2(\text{g})$	0	130.7	28.8
$\text{N}_2(\text{g})$	0	191.6	29.1
$\text{NH}_3(\text{g})$	-46.2	192.7	35.1

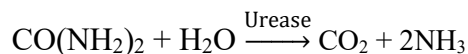
Substance	Fe	FeO	Fe_3O_4	Fe_2O_3	FeOOH	$\text{Fe}(\text{OH})_3$
$\rho / \text{g}\cdot\text{cm}^{-3}$	7.9	5.7	5.0	5.3	4.3	3.9



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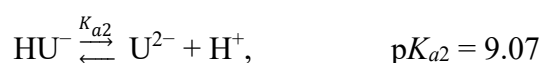
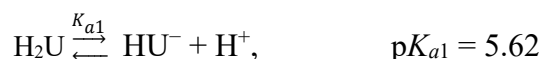
Problem 3. 150 Years of Urease

Urease is an important enzyme because of its role in the nitrogen cycle as a key catalyst in the reaction converting urea to NH_3 and CO_2 :



Urease activity as a soluble enzyme was first identified in 1876 by Frédéric Alphonse Musculus. Urease was the first enzyme crystallised in 1926 by James Batcheller Sumner. For his discovery that enzymes could be crystallised, Sumner was awarded the Nobel Prize in Chemistry in 1946.

The active centre of Urease behaves as a diprotic acid both in the free state and the substrate-bound state, with the following equilibrium constants at 25 °C:



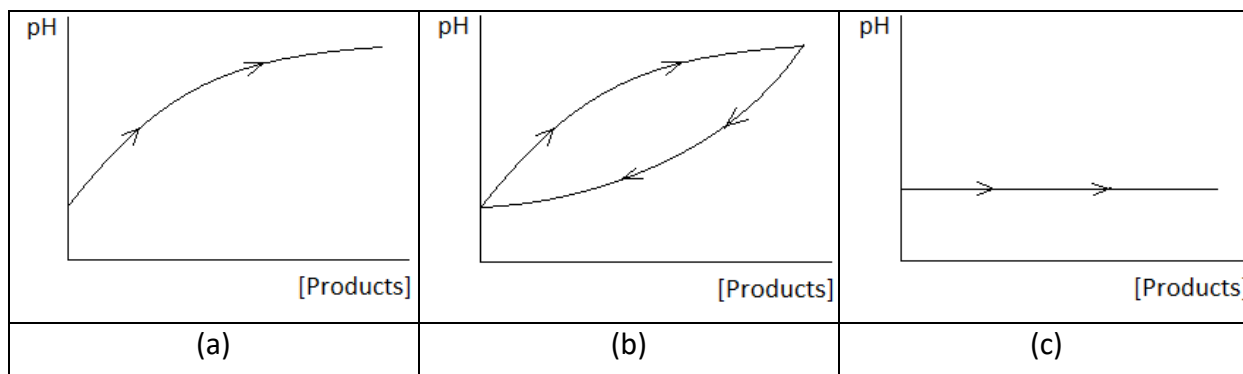
Only the HU^- form exhibits enzymatic activity, which obeys Michaelis–Menten kinetics as shown below:



- Using the steady-state approximation, **derive** the dependence of the rate of the above enzymatic reaction on the total concentrations of Urease, $\text{CO}(\text{NH}_2)_2$ and H^+ . *Note:* $[\text{CO}(\text{NH}_2)_2]_{\text{total}} \gg [\text{Urease}]_{\text{total}}$.
- Determine** the reaction orders with respect to Urease and $\text{CO}(\text{NH}_2)_2$ in the buffer solutions when:
 - $\frac{k_{-1}+k_2}{k_1} \gg [\text{CO}(\text{NH}_2)_2]_{\text{total}}$
 - $\frac{k_{-1}+k_2}{k_1} \ll [\text{CO}(\text{NH}_2)_2]_{\text{total}}$
- The dependence of the rate of these enzymatic reactions on pH forms bell-shaped graphs with the maximum rate when the total concentrations of Urease and $\text{CO}(\text{NH}_2)_2$ are unchanged. **Calculate** the pH value when Urease demonstrates the maximum rate.
- In the absence of any buffer, the decomposition products of $\text{CO}(\text{NH}_2)_2$ change the pH of the solution, thereby reducing the activity of Urease. **Calculate:**
 - The pH of the solution after decomposition of 0.005 M $\text{CO}(\text{NH}_2)_2$. Neglect the contribution of Urease to the acid-base equilibrium and the dissolution of atmospheric CO_2 .
 $\text{p}K_b(\text{NH}_3) = 4.75$; $\text{p}K_{a1}(\text{H}_2\text{CO}_3) = 3.75$; $\text{p}K_{a2}(\text{HCO}_3^-) = 10.33$ at 25 °C.
 - The factor by which the rate of the enzymatic reaction decreases when the pH of the solution changes from neutral to the value obtained in question 4-a), if the total concentrations of Urease and $\text{CO}(\text{NH}_2)_2$ are the same in both conditions.
- Match** the following conditions (1)–(3) with the phase portraits (a)–(c):
 - Urease in buffer solution with $\text{CO}(\text{NH}_2)_2$;
 - Urease in neutral solution with $\text{CO}(\text{NH}_2)_2$ without any buffer;
 - Urease in liposomes with a permeable membrane with $\text{CO}(\text{NH}_2)_2$ and without any buffer inside. Assume that Urease doesn't leave the liposome, while $\text{CO}(\text{NH}_2)_2$ and products can pass through the membrane.



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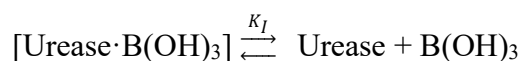
Biocatalytic calcification by Urease shows potential in innovative engineering applications, such as preparation of advanced carbonate materials, cleaning wastewaters/groundwaters of Ca^{2+} and $^{90}\text{Sr}^{2+}$, and most excitingly, sealing cracks and fissures in buildings and other historical stone monuments of cultural heritage during their restoration.

6. **Calculate** the minimum concentration of Ca^{2+} , at which CaCO_3 begins to precipitate from solution in question 4-a)? **Ignore** the dissolution of atmospheric CO_2 .

$$K_{\text{sp}}(\text{CaCO}_3) = 3.36 \times 10^{-9} \text{ at } 25 \text{ }^\circ\text{C}.$$

In agriculture, Urease in soil plays a crucial role in nitrogen uptake by plants in the form of NH_3 produced from the hydrolysis of the fertiliser $\text{CO}(\text{NH}_2)_2$. However, if too rapid, the hydrolysis may lead to overproduction of NH_3 resulting in detrimental effects, such as losses of nitrogen by ammonia volatilisation, and ammonia- and alkaline-induced plant damage. One way to counteract this is to suppress the ureolytic activity of soil with the use of Urease inhibitors. Urease inhibition can also be exploited as an analytical technique in Urease-based biosensors for the analysis of substances that act as inhibitors of the enzyme.

Boric acid is a competitive inhibitor of Urease and their complex, $[\text{Urease} \cdot \text{B}(\text{OH})_3]$, also behaves as a diprotic acid with the same acidity constants:



7. **Rederive** the dependence of the rate of the enzymatic reaction on the total concentrations of Urease, $\text{CO}(\text{NH}_2)_2$, $\text{B}(\text{OH})_3$, and H^+ . *Note: $[\text{CO}(\text{NH}_2)_2]_{\text{total}}$ and $[\text{B}(\text{OH})_3]_{\text{total}} \gg [\text{Urease}]_{\text{total}}$.* **Ignore** the acid-base properties of $\text{B}(\text{OH})_3$.

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8. According to the kinetic equation obtained in question 7, the function $\frac{1}{r} = f\left(\frac{1}{[\text{CO}(\text{NH}_2)_2]_{\text{total}}}\right)$ is linear. **Calculate** K_1 if the slope of this function with $[\text{B}(\text{OH})_3]_{\text{total}} = 0.300 \text{ mM}$ is 2.48 times greater than the slope with $[\text{B}(\text{OH})_3]_{\text{total}} = 0.075 \text{ mM}$ at $25 \text{ }^\circ\text{C}$. The total concentration of Urease and pH values are equal in both cases.
9. **Calculate** $\Delta_r H^\circ$ and $\Delta_r S^\circ$ values for the binding of boric acid with Urease, if they are independent of temperature and $K_1 = 1.57 \times 10^{-4}$ at $35 \text{ }^\circ\text{C}$.

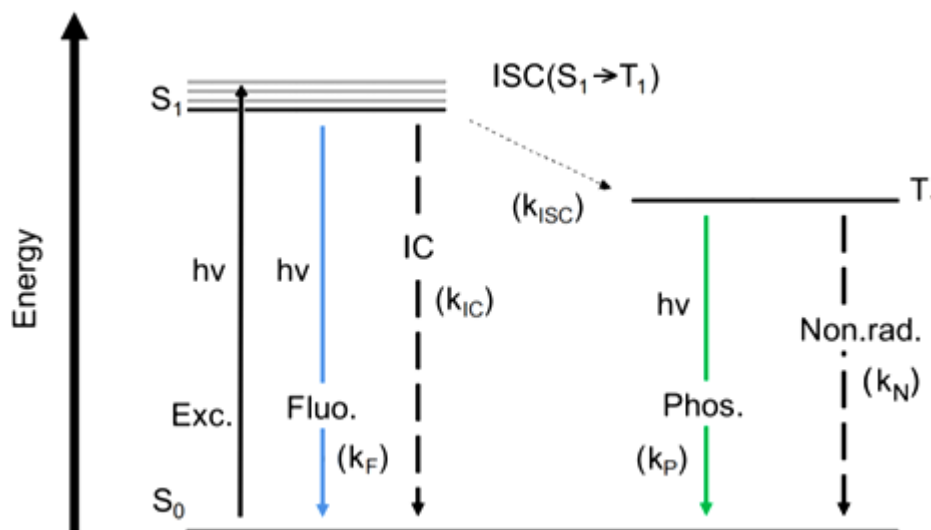


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Problem 4. Fluorescence, phosphorescence and quenching

Molecules can exist in different electronic spin states known as singlet and triplet states. A singlet state has all electron spins paired (total spin, $S = 0$), while a triplet state has two unpaired electrons with parallel spins ($S = 1$). Transitions between these states govern important luminescence processes such as fluorescence (singlet \rightarrow singlet) and phosphorescence (triplet \rightarrow singlet). Understanding the decay kinetics of these excited states is essential for interpreting emission lifetimes, nonradiative losses, and designing efficient photonic materials.

When a molecule absorbs a photon ($h\nu$), an electron is promoted to a higher energy level, called an excited state (S_1). This process is called **excitation** (Exc. with rate I_{abs}). From this excited state (S_1), the molecule can lose energy in different ways. It can undergo **internal conversion** (IC with rate constant k_{IC}), where energy is lost non-radiatively as heat through changes in vibrational states. Alternatively, it can return to the ground state (S_0) by emitting a photon ($h\nu$); this process is called **fluorescence** (Fluo. with rate constant k_{F}). The excited singlet state (S_1) can also convert to an excited triplet state (T_1) through **intersystem crossing** (ISC with rate constant k_{ISC}). The triplet state has a longer lifetime, and the molecule may return to the ground state (S_0) by emitting a photon ($h\nu$), known as **phosphorescence** (Phos. with rate constant k_{P}), or by losing energy as heat through **non-radiative decay** (Non.rad. with rate constant k_{N}). If a quencher is present, it can accept the excitation energy, causing the molecule to return to its ground singlet state (S_0) without emitting light.

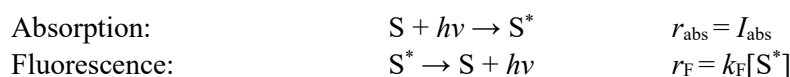


1. **Choose** the correct option: “For electron excitation, the wavelength of the absorbed photon must be ...”:
 - a) higher than that of the fluorescence wavelength
 - b) equal to that of the fluorescence wavelength
 - c) lower than that of the fluorescence wavelength

Internal Conversion (IC) is usually more common than Intersystem Crossing (ISC) because it is the spin allowed process (singlet \rightarrow singlet).

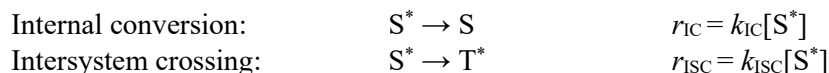
2. **Choose** the correct option: “To increase k_{ISC} the energy gap between S_1 and T_1 states should be ...”:
 - a) higher
 - b) lower

To predict light emission (e.g., fluorescence) quantum yield, it is necessary to know the decay mechanism of the excited singlet state:





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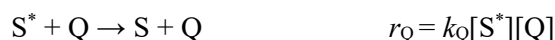


3. **Find** the order of $[S^*]$ and the observed rate constant (k_{obs}) for the rate of decay of the excited singlet state, and the emission lifetime (τ_0) after the incident light is turned off. *Note: Emission lifetime (τ_0) is the time required to reduce $[S^*]$ by e (≈ 2.72) times.*

Fluorescence quantum yield (ϕ_0) is the fraction of the excited singlet state molecules that **emit a photon** (fluoresce).

4. **Derive** ϕ_0 as a function of the rate constants (k_F , k_{IC} , and k_{ISC}).

To control fluorescence efficiency in devices (e.g., LEDs, sensors), quenching is very helpful. Fluorescence quenching is the promotion of non-radiative decay of the excited state. In a collision quenching, an excited fluorophore collides with a quencher, and due to the energy loss, there is no light emission:



5. **Derive** the fluorescence quantum yield (ϕ) as a function of the quencher concentration.
6. In the Stern–Volmer equation, the relationship between ϕ_0/ϕ and $[Q]$ is linear. **Derive** this relationship.

In one experiment, quenching of tryptophan fluorescence in a solution by dissolved O_2 gas was monitored by measuring emission lifetimes at 348 nm in aqueous solutions.

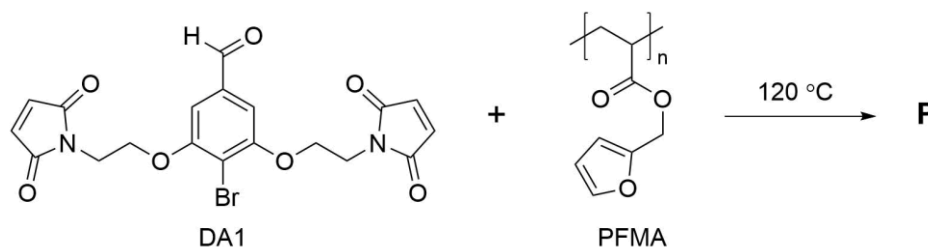
$[O_2] / M$	0	2.3×10^{-2}	5.5×10^{-2}	8×10^{-2}	10.8×10^{-2}
τ_0 / s	2.6×10^{-9}	1.5×10^{-9}	0.92×10^{-9}	0.71×10^{-9}	0.57×10^{-9}

7. **Determine** the quenching rate constant (k_Q) for this process.
8. **Calculate** the concentration of O_2 at which half of the excited tryptophan molecules are quenched.

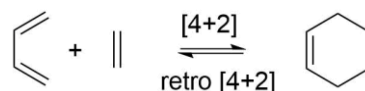
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Phosphorescence can also be influenced by singlet state quenchers. There are several approaches to reducing the likelihood of collisions between quencher and phosphorescent molecules. One effective method is to increase the rigidity of the molecule. This rigidity also reduces non-radiative decay by limiting additional vibrational modes and suppressing vibrational relaxation pathways.

Phosphorescence molecule DA1 was heated at 120 °C with PFMA and the product obtained suppressed the non-radiative decay (k_N) of the triplet state.



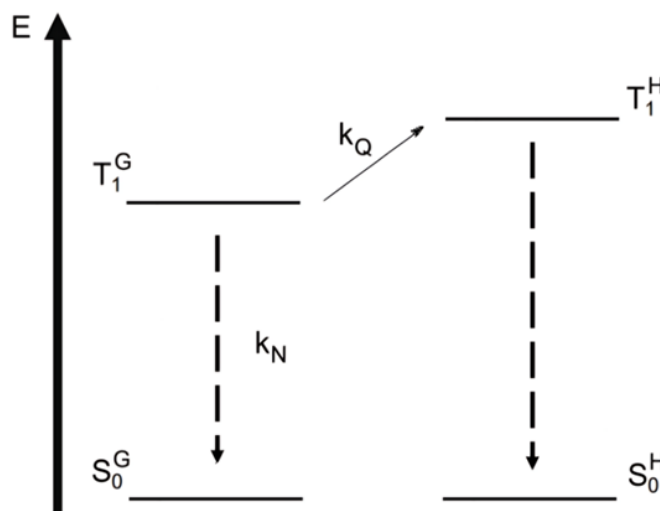
9. **Draw** the structure of P, which is an adduct of the following [4+2] cycloaddition reaction:



At low temperatures, the process of quenching is limited by an energy barrier:

$$\Delta E = E(T_1^{\text{Host}}) - E(T_1^{\text{Guest}})$$

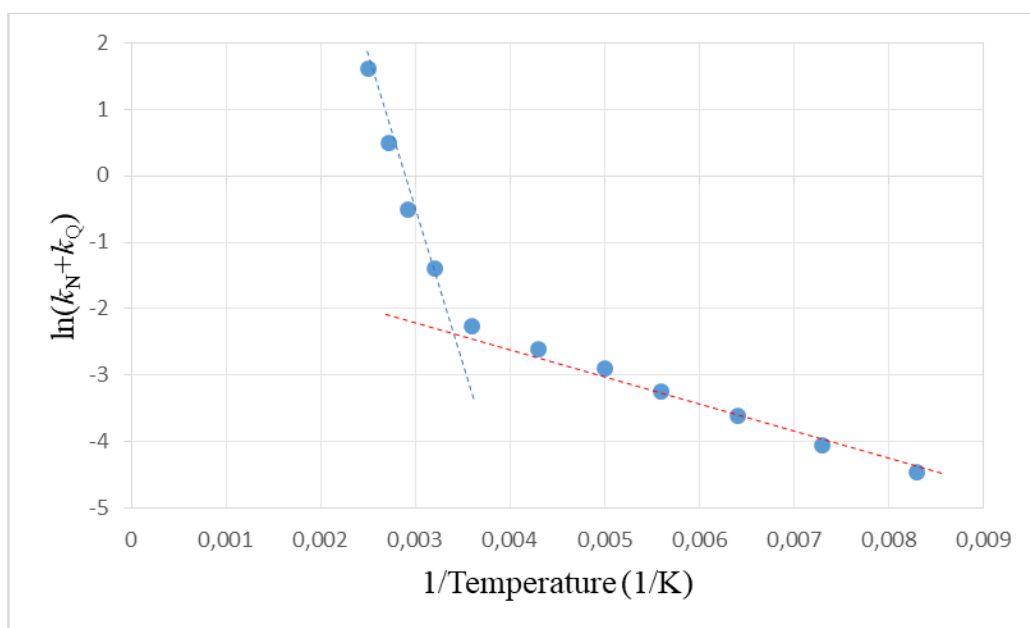
Therefore, non-radiative decay can be suppressed by maintaining rigidity with a polymer matrix under this condition. At higher temperatures, vibrations increase and triplet energy transfer from the triplet state of the phosphorescent guest molecule to the polymer matrix (host) becomes possible:





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$\ln(k_N+k_Q)$ as a function of $(1/\text{Temperature})$ is given below:



k_N – rate constant of the non-radiative decay of the triplet state.

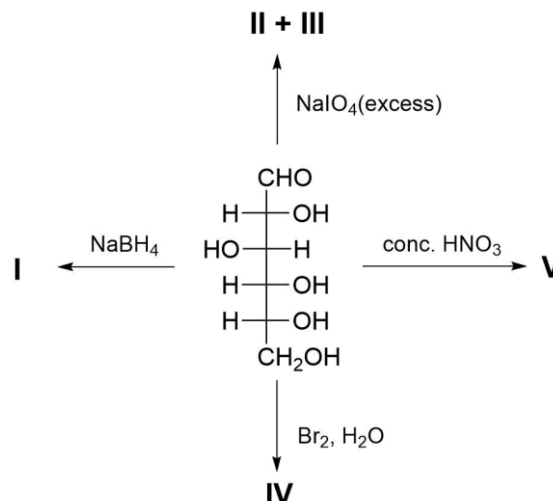
k_Q – quenching of the triplet state by T–T energy transfer from the guest to the host molecule.

10. Estimate the energy barrier ΔE of T–T energy transfer.

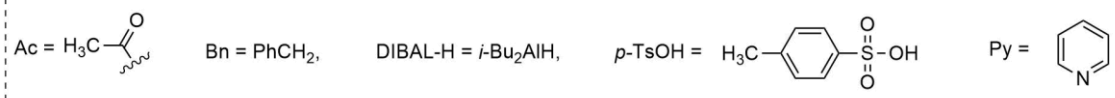
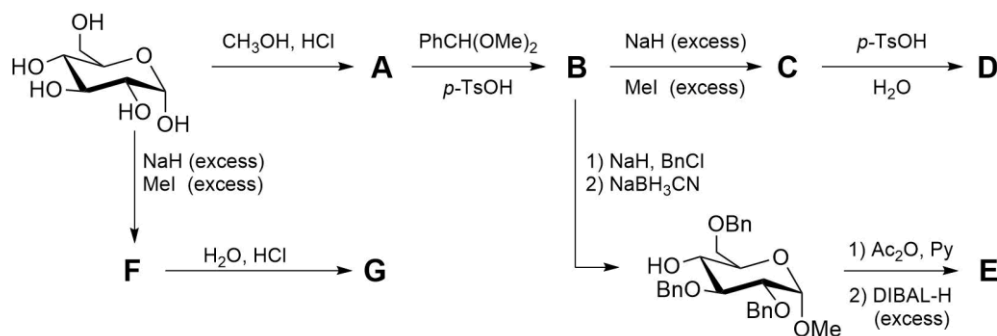
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Problem 5. Carbohydrate chemistry

Carbohydrates are an essential class of chemicals that fuel living organisms with energy. The common saccharide glucose (Glc) exists in either a linear or cyclic form. It can undergo some common chemical transformations:

1. **Identify** products I–V.

In its cyclic form, glucose contains five hydroxy groups. Regioselective transformation of each position represents a challenge for chemists. Some synthetic transformations of α -glucopyranose are shown below:

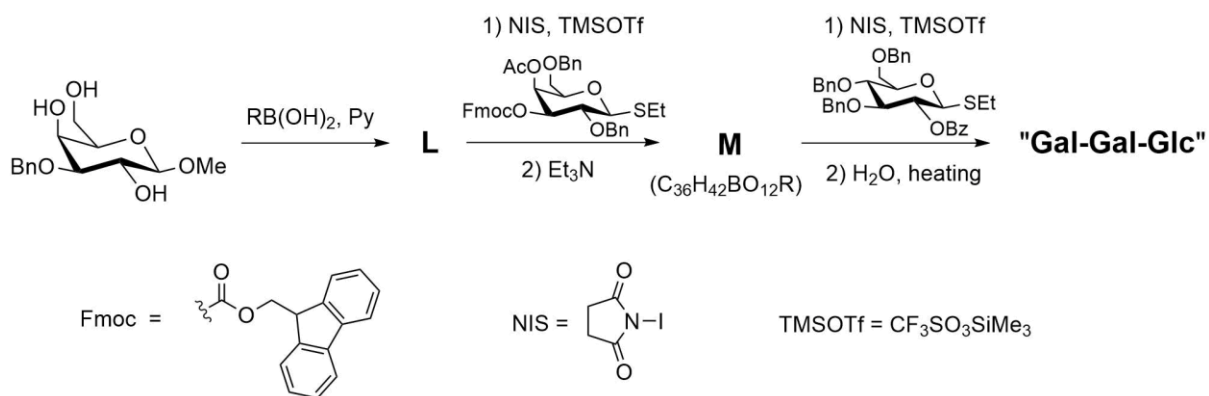


It is known that **A**, **G**, and **D** contain the same functional groups; **G** and **D** differ in formulae by CH_2 ; **B** and **C** contain three six-membered rings in their structures; there are two different CH_3 -groups in **E**.

2. **Draw** the structures of A–G.

However, these transformations cannot differentiate neighbouring 2,3- and 3,4-diols, since in both cases the hydroxy groups are in a *trans*-configuration and occupy equatorial positions. A brilliant solution to this challenge was found by using the common tetrahydropyranyl protecting group in chiral form:

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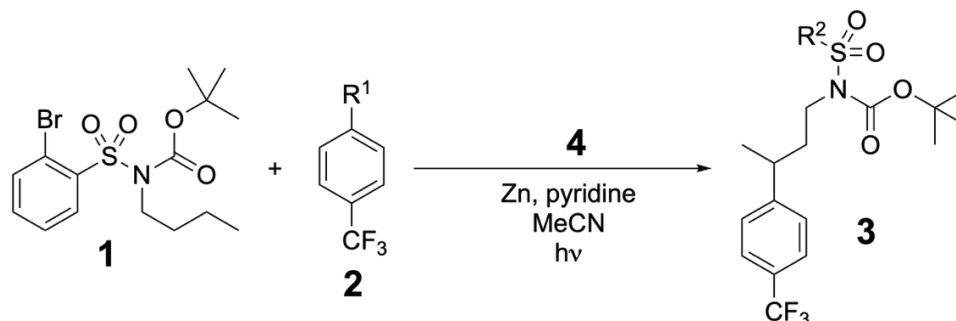
5. **Draw** the structures of **L**, **M**, and trisaccharide “**Gal-Gal-Glc**”. Do not specify the configuration of the newly formed anomeric centres.

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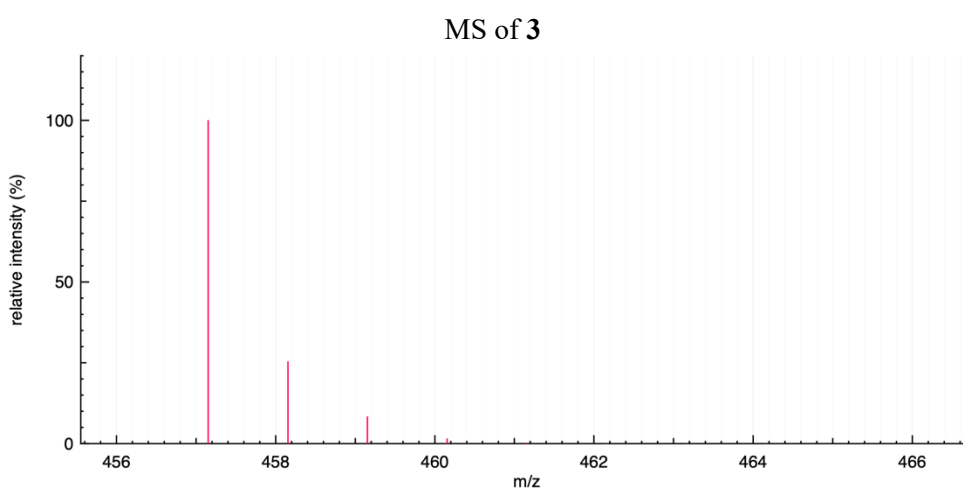
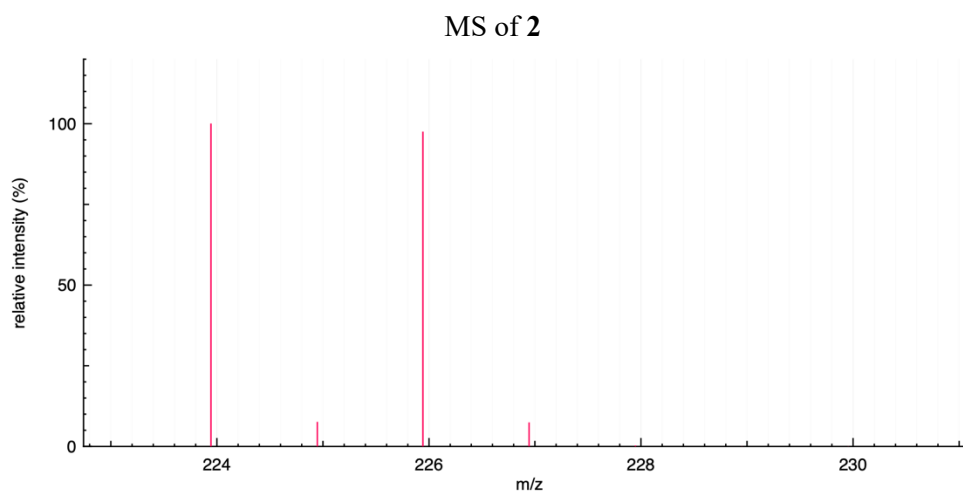
Problem 6. HAT and XAT (HalAT)

Note: Natural abundances of some isotopes are given at the end of the problem.

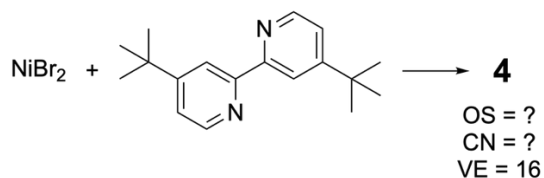
Transition metal-catalysed reactions can be versatile and unique. As such, nickel complex **4** can catalyse the transformation of compounds **1** and **2** into product **3** as described below.



1. The mass spectra (MS) of **2** and **3** are shown (electron impact ionisation method). **Determine** the structures of **2** and **3**.

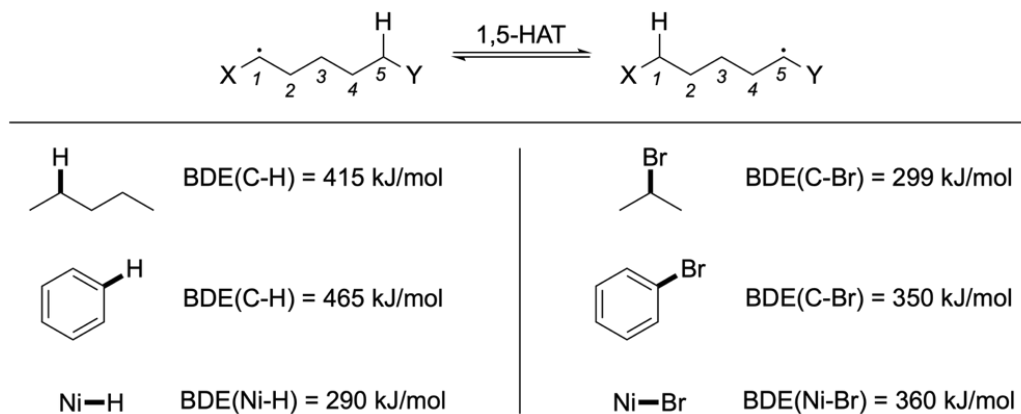


Complex **4** can be obtained via the following reaction. OS is the oxidation state of a metal in a complex; CN is the coordination number, and VE is the total number of valence electrons.

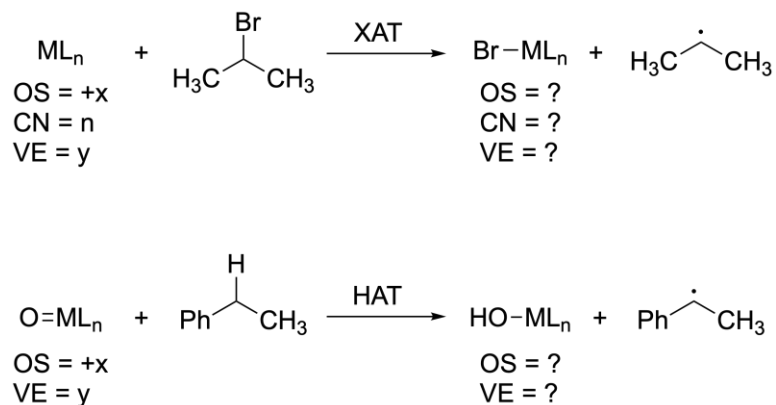


2. **Draw** the structure of **4** and **report** the OS and CN of the metal in it.

HAT is Hydrogen Atom Transfer, while XAT is Halogen Atom Transfer. If atom transfer is intramolecular, it is called 1,n-AT. An example of 1,5-HAT is presented on the scheme below along with some Bond Dissociation Energies (BDE) useful for this task.



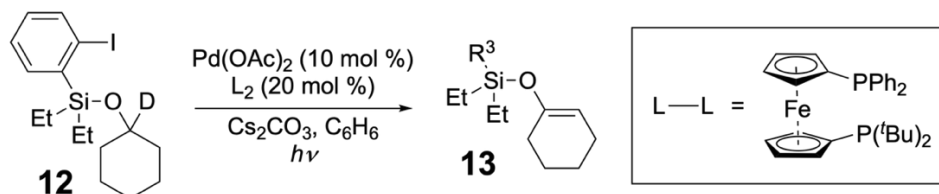
Metal complexes can participate in HAT and XAT processes. Two examples are given below:



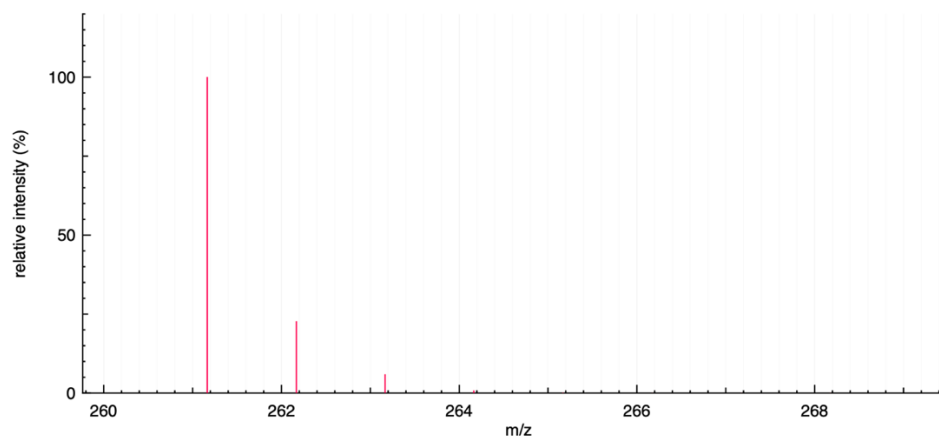
3. **Find** the missing parameters (OS, CN, and VE) for the complexes produced in HAT and XAT processes.

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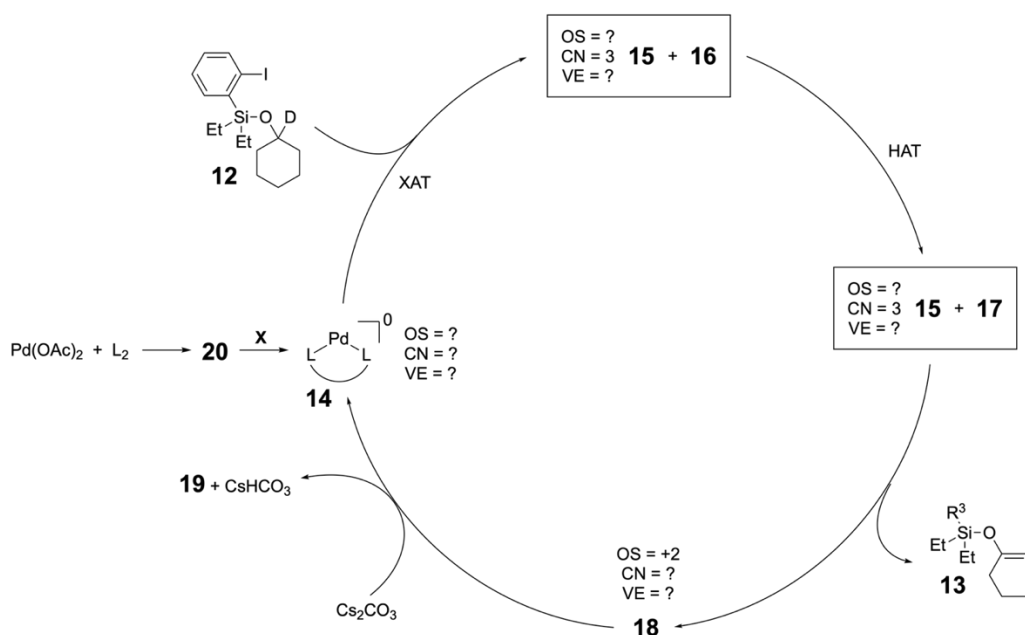
A conceptually similar catalytic reaction is a desaturation of silylated alcohols such as **12**. In the example below a deuterium label was installed for mechanistic studies.



6. The mass spectrum of **13** is presented below (electron impact ionisation method). **Determine** its structure.



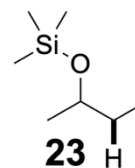
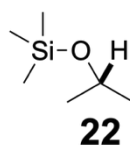
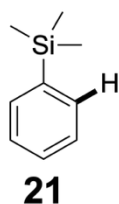
The catalytic cycle for the transformation of **12** into **13** is shown below:



7. **Determine** the structures of **15–19**. For Pd-containing intermediates **14**, **15**, and **18**, **find** the missing parameters (OS, CN, VE).

Active species **14** is not particularly stable, thus, it is practically easier to start the reaction with a bench-stable palladium complex Pd(OAc)₂. The first step towards **14** is reaction with the phosphine ligand.

8. **Draw** a possible structure for **20**. **Suggest** what type of process should occur in the second step marked as **X** on the scheme. **Analyse** the given reaction conditions for the synthesis of **13** and **suggest** what reagent can participate in the step **X**.



9. Based on the information in the task, **analyse** BDE(C–H) of highlighted bonds in compounds **21–23**. **Compare** the values in pairwise manner using symbols <, > or =:

$$\text{BDE}(\text{C-H})_{21} \text{ ______ } \text{BDE}(\text{C-H})_{22}$$

$$\text{BDE}(\text{C-H})_{21} \text{ ______ } \text{BDE}(\text{C-H})_{23}$$

$$\text{BDE}(\text{C-H})_{22} \text{ ______ } \text{BDE}(\text{C-H})_{23}$$

Table of Natural Abundances

Isotope	Natural Abundance / %
^1H	99.9885
^2H	0.0115
^{12}C	98.93
^{13}C	1.07
^{14}N	99.632
^{15}N	0.368
^{16}O	99.757
^{17}O	0.038
^{19}F	100

Isotope	Natural Abundance / %
^{32}S	94.93
^{33}S	0.76
^{34}S	4.29
^{36}S	0.02
^{35}Cl	75.78
^{37}Cl	24.22
^{79}Br	50.69
^{81}Br	49.31
^{127}I	100

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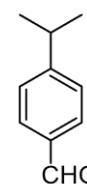
Problem 7. Pilaf ingredients



Pilaf is one of the most delicious, traditional meals in Uzbekistan. We asked a chef who works in *Besh Qozon*, a famous restaurant, how they make pilaf so delicious. The chef described the procedure as follows:

“Oil is first heated in a kazan. Chopped **onions** are fried until they reach a uniform golden-brown color. Pieces of **meat** are then added and cooked until they develop a caramelised surface. Afterwards, sliced **carrots** are introduced, and the mixture is seasoned with **black pepper** and **cumin**. Water is added, whole **garlic** bulbs are placed on top, and the mixture is simmered until the meat becomes tender. Subsequently, pre-washed **rice** is added in a separate upper layer without stirring. Additional water is poured carefully to cover the rice. The mixture is cooked until all the water is absorbed. Finally, the kazan is covered, and the pilaf is allowed to steam for approximately 30 minutes. After gentle mixing, the pilaf is ready to be served”.

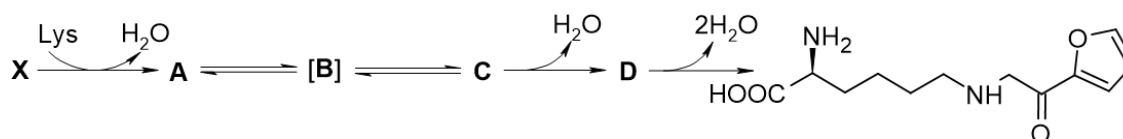
One of the key aromatic components of pilaf is **cumin**. Its characteristic flavour is largely due to the presence of the compound cuminaldehyde. This aldehyde can be obtained synthetically starting from benzene, isopropyl chloride, dimethylformamide, and appropriate inorganic reagents.



Cuminaldehyde

- Suggest** the synthesis scheme for cuminaldehyde using the reagents mentioned above.

The monomer **X** of the major polymeric compound present in **rice** undergoes several transformations during cooking. These reactions lead to the formation of volatile and non-volatile products that contribute to the characteristic aroma and flavour of the dish. The synthesis of one of these products is shown below:



Hints:

- Among **A–D** only compound **D** contains a ring.
- **D** does not have any acyclic tautomers.
- **A**, **B** and **C** are tautomers.

- Draw** the structures of compounds **A–D** and **X** without stereochemistry details.

The hydrolysis of the amide bond in the main component **Z** of **black pepper** produces compounds **E** and **F**. Upon oxidative ozonolysis, acyclic compound **F**, having one oxygen-containing group, yields an equimolar mixture of $C_\alpha H_\beta O_\gamma$ (**F**₁) and $C_\delta H_\epsilon O_\alpha$ (**F**₂), where $\alpha \neq \beta \neq \gamma \neq \delta \neq \epsilon$.

It is also known that:



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- The indexes α , β , and γ are members of a geometric progression (not exactly in this order) and $\delta + \alpha = \varepsilon$;
 - The total number (N) of all atoms in molecules F_1 and F_2 is an even number less than 45.
3. a) Using mathematical logic and chemical considerations, rigorously **prove** that the coefficients in compounds F_1 and F_2 (α , β , γ , δ and ε) are even numbers.
b) **Find** the molecular formulae of F_1 and F_2 .

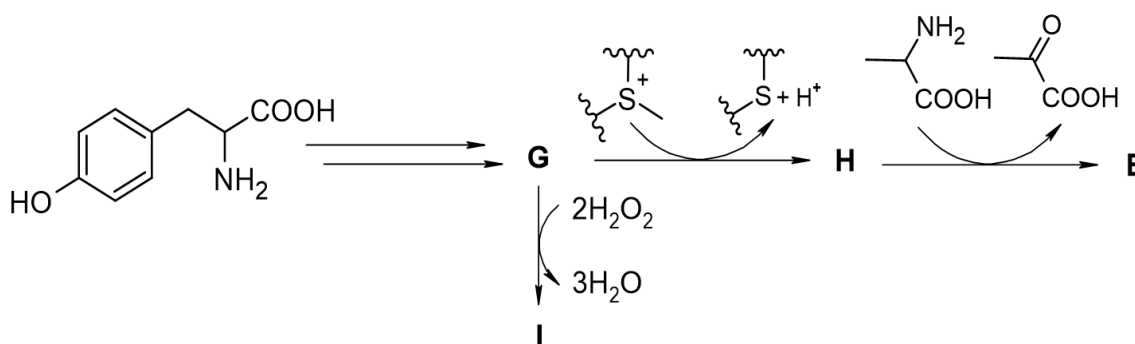
The F_1 and F_2 structures contain three types of hydrogen atoms and at least one plane of symmetry, while these compounds lack stereocentres and alcohol groups.

4. **Draw** the structures of compounds F_1 , F_2 , and F .

Combustion of 1.000 g of E at high temperature gives 3.0385 g of a gaseous mixture. Passing this mixture through solid sodium hydroxide increases the mass of the solid by 2.9470 g. E ($w(O) = 20.92\%$) has a trisubstituted aromatic ring.

5. **Determine** the empirical formula of E .

The biosynthesis of E from L-tyrosine is shown below:



Hints:

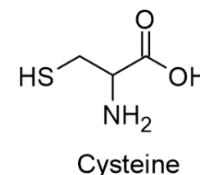
- G contains an aldehyde group.
 - The initial hydroxy group in L-tyrosine is unchanged during the biosynthesis of E .
 - I is an ortho-quinone derivative.
6. **Draw** the structures of compounds G , H , I , E , and Z .

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Numerous peptides and amino acids are contained in *meat*. A non-canonical α -amino acid **W** is one of these. The reaction of **W** with NaIO_4 yields a mixture of formaldehyde (CH_2O) and **K**. The oxidation of **K** with Fehling's reagent, gives the anion of acid **L**. Acid **L** is achiral and has three different hydrogen atom environments.

7. **Draw** the structures of compounds **J**, **K**, **L**, and **W**.

Another notable non-canonical amino acid is alliin, **M**, found in *garlic*, which serves as the precursor of the compounds responsible for its characteristic odour. Alliin, which contains a stereogenic sulfur atom, can be synthesised from cysteine in two steps. Firstly, cysteine reacts with allyl bromide under mildly basic conditions. The resulting intermediate, **N**, is then subjected to oxidation of the sulfur atom with H_2O_2 , yielding **M**.

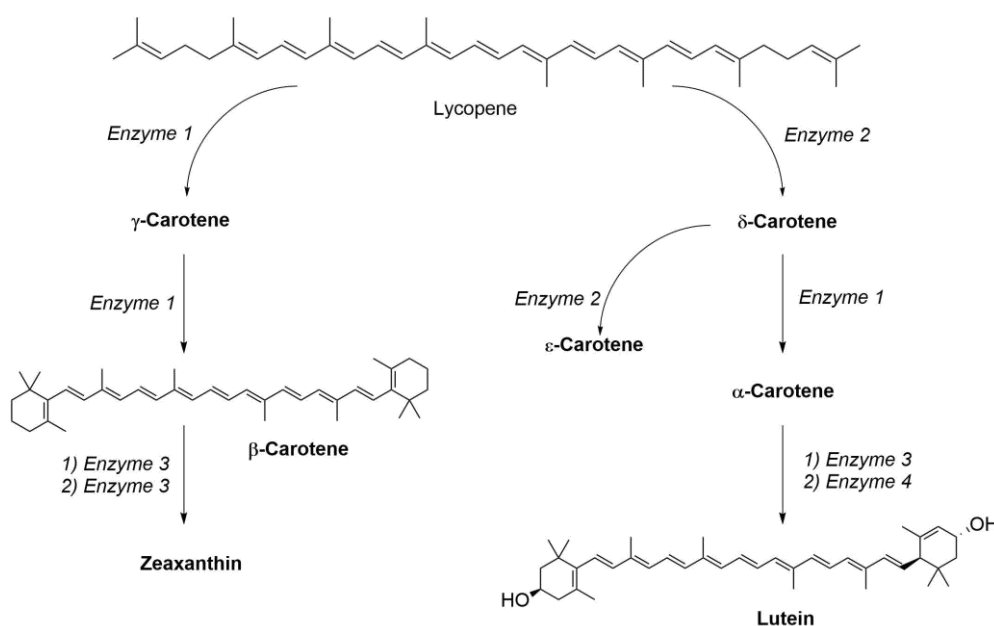


8. **Draw** the structures of compounds **M** and **N**.

Garlic also contains several other interesting molecules, e.g. four compounds **P**₁–**P**₄, which exhibit structural similarity. Their molar masses are members of an arithmetic progression, in which the first member is **P**₁. Molar masses of the second and third molecules are $146 \text{ g}\cdot\text{mol}^{-1}$ and $178 \text{ g}\cdot\text{mol}^{-1}$ respectively. Each of them contains at least one terminal $\text{C}=\text{C}$ bond and possesses two planes of symmetry.

9. **Draw** the structures of compounds **P**₁–**P**₄, if it is known that **P**₁ is biosynthesised from alliin.

There are a lot of dishes in the world using the combination of meat, rice, and carrots. However, Pilaf is the only one which utilises yellow *carrot*. The reason behind the different colour of these carrots is the presence of two pigments – β -carotene and lutein. In plants, they are synthesised from the tetraterpene, lycopene.



10. **Draw** the structures of α -, γ -, δ -, ϵ -carotenes and zeaxanthin.

11. **Determine** whether **zeaxanthin** is optically active or not, **justify** your answer.

12. **Classify** Enzymes 1–4 according to the main enzyme classes below:

- *Oxidoreductases* – Oxidation/reduction reactions.
- *Transferases* – Transfer of a methyl-, acyl-, amino-, or phosphate group from one substance to another; kinases forming a subclass catalyse the transfer of phosphate group(s) from high-energy phosphorylated species to accepting substrate(s).
- *Hydrolases* – Hydrolytic formation of two products from a substrate.



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- *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.
- *Isomerases* – Intramolecular rearrangement.
- *Ligases* – Joining together two molecules by formation of new C–O, C–S, C–N, or C–C bonds with simultaneous breakdown of ATP.