



58th International
Chemistry Olympiad
Uzbekistan 2026

Preparatory Problems

FOR THE 58th INTERNATIONAL
CHEMISTRY OLYMPIAD

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Tashkent, Uzbekistan



The Ministry of
Preschool and School
Education



AGENCY
FOR SPECIALIZED
EDUCATIONAL INSTITUTIONS



Preface

Dear future participants of the International Chemistry Olympiad, dear friends!

Only six months remain until the annual meeting of the best young chemists from around the world. Today, we are announcing this year's fields of advanced difficulty and publishing a collection of preparatory problems. The Scientific Committee of the 58th International Chemistry Olympiad has brought together the most outstanding Uzbek scientists, recent Olympiad medal winners, and experienced international experts. We are all working hard to present interesting ideas and facts about modern chemistry as the centre of the upcoming competition.

We hope you enjoy the preparatory problems, find them challenging, and spark further interest in chemistry and related sciences. Most of the problems are interdisciplinary, highlighting current trends in human development.

For the first time in history, in 2026, the International Chemistry Olympiad will be held in Central Asia. Uzbekistan is a historical land with deep traditions in science and culture. It is also renowned for its exquisite and diverse cuisine. We have done our utmost to highlight specific features of Uzbekistan in both the theoretical and practical problems, so that you are well prepared to see these in action in July 2026.

We wish you every success in your preparations and selection for your national teams. We look forward to seeing you all in Uzbekistan!

Sincerely,
Members of the 58th IChO Science Committee

Acknowledgements

We would like to express our sincere gratitude to the authors who contributed with interesting and novel ideas for the preparatory and competition problems of the 58th International Chemistry Olympiad (IChO). We greatly appreciate the immense efforts of the international experts who worked hard to bring the tasks up to the highest IChO standards. We thank the organizers of the Abu Rayhan Biruni International Chemistry Olympiad for adapting the format of this competition to that of IChO, giving the Science Committee a unique opportunity to begin real work well in advance. After months of dedicated effort, we have produced a collection of challenging puzzles that cover all major areas of contemporary chemistry. Additionally, we thank the members of the IChO Steering Committee for their invaluable contribution in reviewing and improving the preparatory problems.

List of Contributors

Co-Chairs of Scientific Committee:

Prof. Shamansur Sagdullaev, *Yunusov Institute of the Chemistry of Plant Substances, Uzbekistan*

Prof. Alexander Gladilin, *Moscow State University, Russia*

Authors and Reviewers:

Dr. Khamidulla Tukhtaev, *King Abdullah University of Science and Technology, Saudi Arabia*

Bekhzodbek Boltaev, *National Medical Center, Uzbekistan*

Prof. Burkhon Elmurodov, *Yunusov Institute of the Chemistry of Plant Substances, Uzbekistan*

Prof. Khamid Khodjaniyozov, *Sadikov Institute of Bioorganic Chemistry, Uzbekistan*

Prof. Vadim Eremin, *Moscow State University, Russia*

Azimjon Jamolov, *Nanyang Technological University, Singapore*

Dr. Aleksandr Koronotov, *Technion – Israel Institute of Technology, Israel & Stratingh Institute for Chemistry, University of Groningen, The Netherlands*

Mirumid Mirakbarov, *Higher School of Economics, Russia*

Dr. Bulat Garifullin, *Hospital No. 13 in Ufa, Russia*

Dr. Andrei Shved, *Lucerne International School, Switzerland*

Prof. Yunus Turkmen, *Middle East Technical University, Turkey*

Prof. Ben Pilgrim, *University of Nottingham, UK*

Prof. Petra Menova, *University of Chemistry and Technology, Czech Republic*

Zhihan Nan, *Harvard University, USA*

Dr. Filip Ilievski, *Yale University, USA*

Boburbek Boltaev, *Cardiovascular Surgery Center “American Hospital”, Uzbekistan*

Islomjon Karimov, *Center for Advanced Technologies, Uzbekistan*

Maftuna Badalova, *Nanyang Technological University, Singapore*

Ibrohim Temurov, *Science Olympiad Center, Uzbekistan*

Mirjahon Muhammadov, *Science Olympiad Center, Uzbekistan*

Elyorbek Adkhamov, *Pirogov Russian National Research Medical University, Russia*

Azizbek Nazarov, *Tashkent State Medical University, Uzbekistan*

Sherzod Shaymatov, *Tashkent State Medical University, Uzbekistan*

Ahrorbek Bahodirov, *Moscow Institute of Physics and Technology, Russia*

Biloliddin Zukhriddinov, *Central Asia University, Uzbekistan*

Saida Abdullaeva, *Tashkent State Medical University, Uzbekistan*

Kirill Kozlov, *N. D. Zelinsky Institute of Organic Chemistry, Russia*

Dr. Abdurakhim Nabiev, *Tashkent Institute of Chemical Technology, Uzbekistan*

Dr. Asqar Abdurazakov, *Yunusov Institute of the Chemistry of Plant Substances, Uzbekistan*

Ikromiddin Boymahammadov, *New Uzbekistan University, Uzbekistan*

Firdavs Sobirov, *Science Olympiad Center, Uzbekistan*

Abdulloh Mahmudov, *Massachusetts Institute of Technology, USA*

Daler Rahimov, *Science Olympiad Center, Uzbekistan*

Durdona Mukhtorkhodjaeva, *D. Mendeleev University of Chemical Technology of Russia in Tashkent, Uzbekistan*

Fields of advanced difficulty

Theoretical

1. **Mass Spectrometry:** molecular ions, mass-to-charge ratio, isotope distribution.
2. **Kinetics:** steady-state and quasi-equilibrium approximations, enzymatic kinetics, interpretation of phase portraits.
3. **Thermodynamics:** heat capacity, temperature dependence of equilibrium constant, entropy and enthalpy change.
4. **Transition metal catalysis:** elementary steps in the catalytic cycles with transition metal complexes; single electron transfer (SET) and hydrogen atom transfer (HAT); cross-coupling reactions.
5. **Photochemistry:** Jablonski and Förster diagrams, fluorescence and phosphorescence, quenching, lifetimes, quantum yield.
6. **Carbohydrate chemistry:** represent chair conformations, carbohydrate reactions and protecting groups, repeating units.

The students are not expected to be specifically trained on the hereunder topics:

- ❖ Fragmentation in mass spectrometry.
- ❖ Advanced calculations (differentiation, iteration).
- ❖ Graph theory.
- ❖ 2nd and 3rd order kinetics.
- ❖ Cycloaddition reaction mechanisms.
- ❖ Memorising the structures of canonical amino acids.
- ❖ Archaea metabolism.
- ❖ Carothers equation.
- ❖ Memorising specific values of bond lengths.
- ❖ Memorising mechanisms of transition metal-catalysed coupling reactions.
- ❖ Details behind the techniques of STM and AFM.

Practical

1. Using micropipettes and 96-well plates.
2. Vacuum filtration.
3. Titration using pH meter.

The students are not expected to be specifically trained on the hereunder topics:

- ❖ Recrystallisation.
- ❖ Using spectrophotometer.

Physical constants, units, formulae

Constants

Avogadro constant	N_A	$6.022 \times 10^{23} \text{ mol}^{-1}$
Universal gas constant	R	$8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$
Faraday constant	F	$96485 \text{ C} \cdot \text{mol}^{-1}$
Planck constant	h	$6.626 \times 10^{-34} \text{ J} \cdot \text{s}$
Speed of light in vacuum	c	$2.998 \times 10^8 \text{ m} \cdot \text{s}^{-1}$
Mass of electron	m_e	$9.109 \times 10^{-31} \text{ kg}$
Charge of electron	e	$1.602 \times 10^{-19} \text{ C}$
Standard pressure	P°	$1 \text{ bar} = 10^5 \text{ Pa}$
Ionic product of water at 25 °C	K_w	1.00×10^{-14}

Units

Zero of the Celsius scale	$0^\circ \text{C} = 273.15 \text{ K}$
Electronvolt	$1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$
Watt	$1 \text{ W} = 1 \text{ J} \cdot \text{s}^{-1}$
Coulomb	$1 \text{ C} = 1 \text{ A} \cdot \text{s}$
Nanometre	$1 \text{ nm} = 1 \times 10^{-9} \text{ m}$

Formulae

Ideal gas law	$PV = nRT$
Dalton law	$P_i = x_i P$
Faraday law	$n(e^-) = \frac{It}{F}$
Lambert–Beer law	$A = \log_{10} \frac{I_0}{I} = \varepsilon cl$
Energy of a photon	$E = h\nu = \frac{hc}{\lambda}$
Heat and temperature change	$Q = nC_m \Delta T$
Gibbs energy definition	$G = H - TS$
Gibbs energy and equilibrium constant	$\Delta_r G^\circ = -RT \ln K$
Enthalpy change dependence on temperature (at $\Delta C_p = \text{const}$)	$\Delta_r H_{T_2} = \Delta_r H_{T_1} + \Delta_r C_p (T_2 - T_1)$
Entropy change dependence on temperature (at $\Delta C_p = \text{const}$)	$\Delta_r S_{T_2} = \Delta_r S_{T_1} + \Delta_r C_p \ln \frac{T_2}{T_1}$
Henderson–Hasselbalch equation	$\text{pH} = \text{p}K_a + \log_{10} \frac{[\text{A}^-]}{[\text{HA}]}$
Average reaction rate	$r = \frac{\Delta c}{\Delta t}$
The rate law	$r = k[\text{A}]^x [\text{B}]^y$
Arrhenius law	$k = A \exp\left(-\frac{E_a}{RT}\right)$
Integrated rate law for a 1 st order reaction	$c = c_0 e^{-kt}$ $kt = \ln \frac{c_0}{c}$

Lifetime of a reagent in a 1 st order reaction	$\tau = \frac{1}{k}$
Integrated rate law for n^{th} order reaction ($n \neq 1$)	$kt = \frac{1}{n-1} (c^{1-n} - c_0^{1-n})$ for $n \neq 1$
Concentration of an intermediate in a consecutive reaction: $A \xrightarrow{k_1} B \xrightarrow{k_2} D$	$[B] = \frac{k_1[A]_0}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t})$
The ratio of products in the competitive reactions: $A \xrightarrow{k_1} B, A \xrightarrow{k_2} C$	$\frac{[B]}{[C]} = \frac{k_1}{k_2}$
Michaelis–Menten equation	$r_0 = r_{\max} \frac{[S]_0}{K_M + [S]_0}$
Enantiomeric excess (L – D)	$ee = \frac{[L] - [D]}{[L] + [D]}$
Specific surface area	$s = \frac{S}{m}$

Math

Progressions: arithmetic geometric	$a_n = a_1 + d(n - 1)$ $a_n = a_1 q^{n-1}$
Sum of geometric progression	$\sum_{k=0}^n a_1 q^k = a_1 \frac{q^{n+1} - 1}{q - 1}$
The degree sum for a graph (v – vertices, E – edges)	$\sum_{v \in V} \deg v = 2 E $
Volume of cube with edge length a	$V = a^3$
Surface area of a cube with edge length a	$S = 6a^2$

Volume of a sphere with radius r	$V = \frac{4}{3}\pi r^3$
Surface area of sphere with radius r	$S = 4\pi r^2$
Volume of a cone with base radius r and height h	$V = \frac{1}{3}\pi r^2 h$
Volume of a rectangular wedge with base S and height h	$V = \frac{1}{2}Sh$
Volume of a cylinder with base radius r and height h	$V = \pi r^2 h$

Consider all gases ideal.

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

Periodic table

1 H 1.008	2											13	14	15	16	17	18 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	3	4	5	6	7	8	9	10	11	12	13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.06	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 72.63	33 As 74.92	34 Se 78.97	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 101.1	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	57-71	72 Hf 178.5	73 Ta 180.9	74 W 183.8	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 -	85 At -	86 Rn -
87 Fr -	88 Ra -	89-103	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 -

57 La 138.9	58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm -	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
89 Ac -	90 Th 232.0	91 Pa 231.0	92 U 238.0	93 Np -	94 Pu -	95 Am -	96 Cm -	97 Bk -	98 Cf -	99 Es -	100 Fm -	101 Md -	102 No -	103 Lr -

**Preparatory Problems for
the 58th International Chemistry Olympiad 2026
Tashkent, Uzbekistan**

Theoretical Problems

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Fields of advanced difficulty

Theoretical

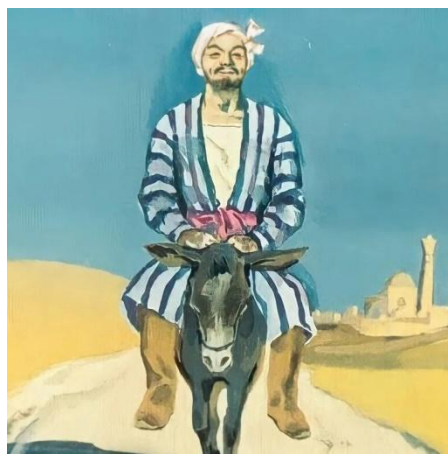
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- ❖ Details behind the techniques of STM and AFM.

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.

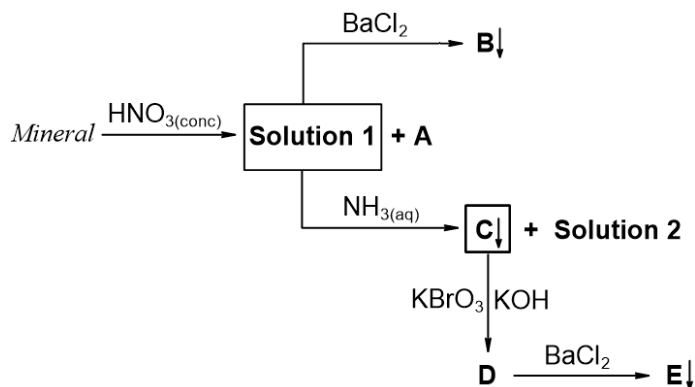
To determine the amount of gas **F** required for the synthesis of 1.000 g of **D**, he passed as much **F** as necessary through 100 mL of potassium iodide solution (**Reaction 3**). For titration of a 10.00 mL aliquot of the resulting brown solution, 16.30 mL of sodium thiosulfate solution (**Reaction 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**.

Problem 2. Avicenna

The philosopher Avicenna took a vial with a strange brownish-bronze mineral inside. Avicenna performed many reactions with this mineral and created a scheme to help to clearly identify the composition of the mineral.

Avicenna dissolved 1.00 g of the mineral in an excess of concentrated nitric acid and observed a release of a brown gas **A** with a volume of 1.65 L under standard conditions (0 °C, 1 atm). The solution formed (**Solution 1**) was divided into two equal parts for further analysis. To the first half of **Solution 1**, he added an excess of BaCl_2 , which led to 0.929 g of white precipitate **B**. He added excess aqueous ammonia solution to the second half of **Solution 1**, causing the formation of brown precipitate **C** and deep-blue **Solution 2**. **C** was filtered off, dissolved in an alkaline solution of KBrO_3 , giving a purple solution of compound **D**. **D** reacted with BaCl_2 to form 0.256 g of the red precipitate **E**.



1. **Determine** the possible elemental composition of the mineral.
2. **Determine** the molecular formula of the mineral and compounds **A–E**. **Show** your calculations where necessary.
3. **Write** all the reaction equations described in the scheme.

Problem 3. Unusual inorganic synthesis

Until 1968, it was believed that anion **A1** and its salts were unstable. However, in 1968, Evan H. Appelman performed an unusual synthesis of **A1**. A 90% enriched isotope of element **X** was first irradiated with thermal neutrons, then dissolved in nitric acid and oxidised by ozone in alkaline solution, giving anion **B**, which within a few minutes spontaneously turned into **A1** without absorbing or releasing any chemical substances. 1.613 g of anion **B** was obtained from 1.000 g of **X**.

After the first unusual but successful attempt, scientists managed to oxidise anion **A2** to **A1** using electrolysis. For this purpose, Pt electrodes were immersed into 3.0 mL of the solution containing **A2** (solution **S0**) and into HClO₄ solution. Electrolysis was carried out with a current strength of 10 A/cm² for 1 hour. The work surface of each Pt electrode was 0.785 mm², the current yield for **A1** was 11.5%.

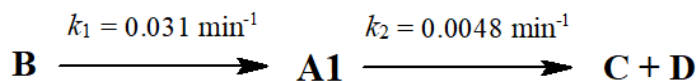
1. **Write** the equation of the half-reaction occurring at the cathode and **calculate** the total volume (in mL at 0 °C, 1 atm) of the gas released at the cathode during electrolysis.

After electrolysis, the analyte contained a mixture of anions **A1** and **A2** (colourless solution **S1**). The Pt electrode was removed from the analyte, an excess of diluted (~1 M) acidic solution containing anion **A3** was added, and a yellow solution **S2** (containing elemental substance **A4**) was obtained. **A4** was removed by bubbling argon through **S2**, and a colourless solution **S3** was obtained. An excess of saturated (~10 M) acidic solution containing **A3** was added to solution **S3**, and a yellow solution **S4** (also containing elemental substance **A4**) was obtained. The whole volume of **S4** was diluted to 100.0 mL, and thus solution **S5** was obtained. An excess of acidified KI solution was added to a 10.0 mL aliquot of solution **S5**, and the I₂ formed was titrated with 0.100 M Na₂S₂O₃ solution. A titre of 1.35 mL of Na₂S₂O₃ solution was obtained.

Another 3.0 mL sample of solution **S0** was not subjected to electrolysis. Instead, it was diluted to 500.0 mL giving solution **S6**. An excess of acidified KI solution was added to a 10.0 mL aliquot of **S6**, and the I₂ formed was titrated with 0.100 M Na₂S₂O₃ solution. A titre of 10.10 mL of Na₂S₂O₃ solution was obtained.

2. **Write** the equation of the reaction occurring during titration between I₂ and Na₂S₂O₃.
3. **Determine** the chemical composition of **A1–A4**, **B**, and **X** (with atomic mass of enriched isotope). *Note: A1–A4 contain the same element.*
4. **Calculate** the molar concentration (in M) of **A2** in solution **S0**.

A1, formed within a few minutes from anion **B**, spontaneously decomposes within a few hours into gaseous elemental substances **C** and **D** in a molar ratio 1:2. The reaction scheme shows the formation and decay of **A1** with the corresponding rate constants



5. **Determine** the detailed chemical composition of **C** and **D**. Both reactions shown in the scheme above are first order with respect to the corresponding reactants.
6. **Calculate** the time (t , in min) after the start of the decomposition of **B**, which corresponds to the maximum concentration of **A1**.

It was subsequently discovered that XeF_2 also oxidises **A2** to **A1**. Interestingly, another binary compound, **E**, of xenon (which does not contain fluoride) was also obtained by exactly the same unusual method (like $\mathbf{B} \rightarrow \mathbf{A1}$) from a potassium-containing salt **F** with a mass fraction of potassium of 12.62%.

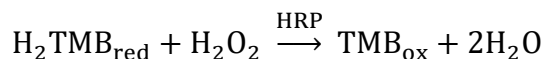
7. **Determine** the detailed chemical composition of compounds **E** and **F**.

Problem 4. Nanozymes

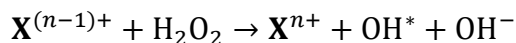
Nanozymes are nanoparticles (NPs) that exhibit enzymatic activities under different physiological conditions, offering advantages such as high stability, low cost, and tunable activity compared to natural enzymes. Nanozyme X_nO_m NPs can be obtained by co-precipitation of salts **S1** and **S2**, both containing element **X**, in alkaline media. 2.7025 g of **S1** and 1.3901 g of **S2** were dissolved in an acidic solvent and treated with tetramethylammonium hydroxide, and 1.1578 g of X_nO_m NPs were formed as a result as the only substance containing **X**. The electrospray ionisation mass spectrometry of **S1** revealed positive ion $[XHal_2(H_2O)_4]^+$ with m/z 198 and negative ion $[XHal_4]^-$ with m/z 196 being the most intense peaks. **S2** lost 45.36% of the total of the original mass and changed colour from green to white above 300 °C. Elemental analysis revealed a mass fraction of 20.09% of element **X** in **S2**.

1. **Find** element **X**, and salts **S1** and **S2**.
2. **Determine** the values of n and m for X_nO_m NPs.
3. **Write** the equation of the co-precipitation reaction of X_nO_m NPs in ionic form.

Peroxidases are enzymes that catalyse the oxidation of substrates with H_2O_2 as an electron acceptor. Horseradish Peroxidase (HRP) catalyses a typical colourimetric reaction involving H_2O_2 and a chromogenic substrate (H_2TMB_{red}):



X_nO_m NPs behave like peroxidase due to their ability to participate in the following reaction:



4. The peroxidase activity of X_nO_m NPs is short-lived. After a certain time, X_nO_m NPs are converted into another oxide NPs of element **X** and lose their catalytic activity. **Determine** the chemical formula of the latter, if the mass fraction of **X** in them is smaller than that in X_nO_m .
5. Which of the following reagents can be used to sustain the catalytic activity of X_nO_m NPs? **Choose** the correct answer(s).

a) $NaIO_4$ b) $NaBH_4$ c) $Na_3C_6H_5O_7$ (sodium citrate) d) Na_3PO_4

In contrast, another Y_p -based nanozyme can act not only as a peroxidase or catalase (converts hydrogen peroxide into water and oxygen) but also can exhibit hydrolase and phosphomonoesterase-like activities without being consumed during the reaction. Y_p has a spherical structure, in which the **Y** atoms are linked together by covalent bonds. The covalent spherical framework Y_p has a volume of $1.128 \times 10^{-4} \text{ m}^3 \cdot \text{mol}^{-1}$ and a surface area of $1.324 \times 10^6 \text{ m}^2 \cdot \text{kg}^{-1}$.

6. **Identify** element **Y** and number p .

The catalytic activity of Y_p -based nanozymes fits Michaelis-Menten kinetics.

The effect of functionalised Y_p -nanozyme was tested with *para*-nitrophenyl phosphate at $\text{pH} = 7.4$ and $T = 37\text{ }^\circ\text{C}$. The analysis showed $K_M = 1.03\text{ mM}$ and $r_{\text{max}} = 3.73\text{ nM}\cdot\text{s}^{-1}$.

7. The substrate's concentration should be high enough to saturate catalytic sites in nanozymes. If the recorded rate was $0.001\text{ }\mu\text{M}\cdot\text{min}^{-1}$, **calculate** the corresponding substrate concentration (in μM).
8. If the reaction mixture contained 0.025 mM substrate, **calculate** the time (in min) needed to produce $0.025\text{ }\mu\text{M}$ product.

Problem 5. 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.

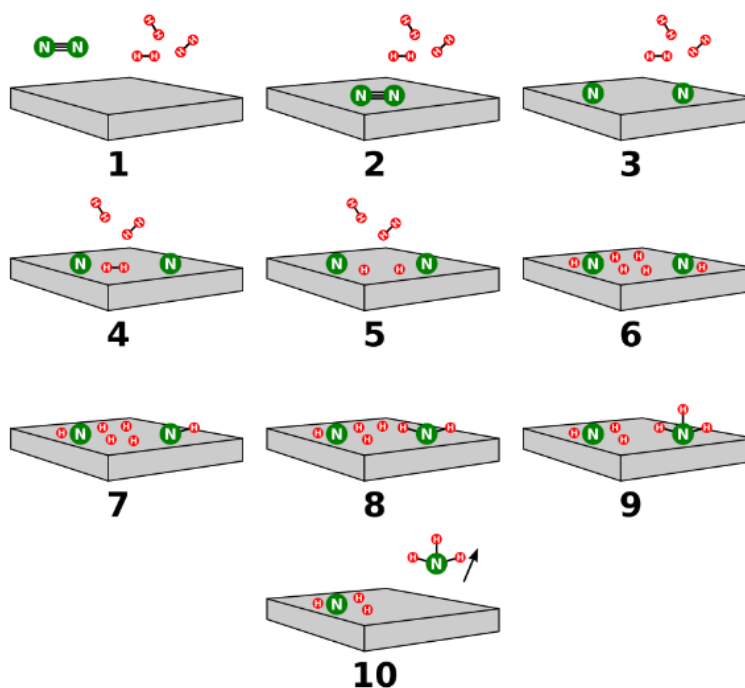
In reality, $\Delta_r H^\circ$ and $\Delta_r S^\circ$ depend on temperature.

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.

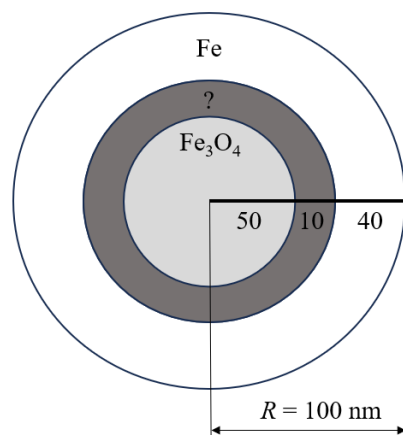
Ammonia formation proceeds via adsorption of gases on the catalyst surface, as shown in the diagram:



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, $R = 100$ nm, as shown in the diagram on the right.



7. **Choose** the composition of the “?” layer in the nanoparticle:
a) Fe_2O_3 b) FeO c) FeOOH d) $\text{Fe}(\text{OH})_3$
8. **Calculate** the total surface area of the catalyst, assuming all nanoparticles are spherical and uniform in size and composition.
9. **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

Problem 6. Hydrogen fuel

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

Hydrogen is an environmentally clean fuel which is, in principle, ideal for powering the millions of vehicles on our roads.

1. **Write** the combustion reaction equations and **calculate** $\Delta_c H^\circ$ at $T = 298\text{ K}$, $P = 1\text{ bar}$ for:
 - a) Hydrogen
 - b) Methane
 - c) Isooctane
2. **Determine** the energy density ($\text{MJ}\cdot\text{kg}^{-1}$) for these fuels at $T = 298\text{ K}$ and $P = 1\text{ bar}$. **Choose** the substance that is the best fuel, considering the energy-to-mass ratio?

For the rest of this problem, assume that air consists of 20% O_2 and 80% N_2 by mole fraction.

3. **Determine** the volume of air at $T = 298\text{ K}$ and $P = 1\text{ bar}$ required for an internal combustion engine (ICE) operating on hydrogen fuel ($\eta = 36\%$) with a power of 1 kW to work for 1 hour.

Hydrogen-fuelled cars do not release CO_2 , in contrast to both gasoline and methane engines, which emit CO_2 as a direct product of fuel combustion. Uzbekistan maintains a national fleet of approximately 3.75 million cars. 65% of them operate on methane, while 35% run on gasoline (assume that isooctane is used). An average vehicle in the country travels 22 000 km per year.

Note:

- Gasoline engines consume 9 dm^3 of fuel per 100 km ($\rho_{\text{gasoline}} = 0.72\text{ kg}\cdot\text{dm}^{-3}$).
 - Methane engines consume 5 m^3 of fuel per 100 km ($T = 298\text{ K}$ and $P = 1\text{ bar}$).
4. **Estimate** the amount of CO_2 emissions (in million tons) from cars that would be avoided annually, if every vehicle in Uzbekistan operated solely on hydrogen.
 5. **Calculate** the amount (in moles) of nitrogen contained in an isolated system with initial temperature, $T_{\text{initial}} = 298\text{ K}$, and constant pressure ($P = 1\text{ bar}$), containing 1 mol of H_2 and excess air, if after combustion, the temperature of the system reached $T = 800\text{ K}$.

When stoichiometric mixtures undergo combustion, the system temperature increases to such a high level that the combustion reaction begins to proceed in the reverse direction. As a result, a situation arises in which both the composition of the mixture and the final temperature after combustion are unknown.

6. In another isolated reactor, the process takes place under a constant pressure ($P = 1\text{ bar}$) and an initial temperature, $T_{\text{initial}} = 298\text{ K}$, with the assumption that only the combustion reaction takes place.

- a) **Determine** the final temperature for combustion of a stoichiometric mixture of hydrogen and oxygen, assuming that the reaction proceeds quantitatively.
- b) **Determine** the mole fractions of gases in the mixture using K_p at the temperature from question 6-a).
- c) **Determine** the final temperature for the system using an energy balance, if after combustion the mixture composition corresponds to the mixture from question 6-b). **Compare** the final temperature with the temperature in 6-a).
- d) **Determine** the real final temperature (T_f , with an accuracy of ~ 20 K) for the combustion of a stoichiometric H_2 and O_2 mixture. **Choose** the nearest temperature value for T_f :
i) 3900 K ii) 3850 K iii) 3800 K iv) 3750 K v) 3700 K vi) 3650 K

Combustion in air at high temperatures may lead to side reactions, such as NO formation.

7. **Calculate** the mole fraction of NO after the stoichiometric combustion of H_2 in air at equilibrium ($T = 3200$ K, $P_{\text{total}} = 1$ bar). Assume that only two reactions that reach equilibrium occur, and use reasonable assumptions where necessary.
8. **Choose** the option(s) which help to decrease NO formation in ICE operating on H_2 and air:
 - a) Lower the combustion temperature.
 - b) Increase the excess air ratio significantly.
 - c) Raise the compression ratio in the engine.
 - d) Increase the fuel flow speed.

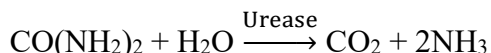
For this problem, assume that C_p does not depend on temperature, while enthalpy and entropy do depend.

Thermodynamic data ($T = 298$ K, $p = 1$ bar):

Substance	$\Delta_f H^\circ / \text{kJ} \cdot \text{mol}^{-1}$	$S^\circ / \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$	$C_p / \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$
$H_2(g)$	0	130.7	28.8
$O_2(g)$	0	205.2	29.4
$N_2(g)$	0	191.6	29.1
$H_2O(g)$	-241.8	188.7	37.4
$H_2O(l)$	-285.8	70.0	75.4
$CH_4(g)$	-74.8	186.3	35.3
$C_8H_{18}(l)$	-260.2	361.2	254.7
$CO_2(g)$	-393.5	213.8	37.1
$NO(g)$	90.3	210.8	29.9

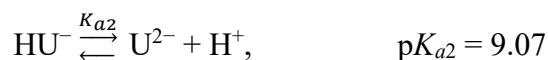
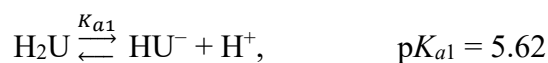
Problem 7. 150 Years of Urease

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 :

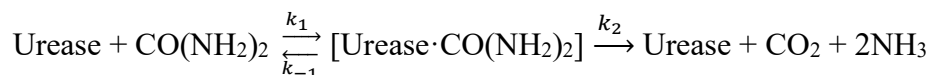


Urease activity as a soluble enzyme was first identified in 1876 by Frédéric Alphonse Musculus. Urease was the first enzyme crystallised in 1926 by James Batcheller Sumner. For his discovery that enzymes could be crystallised, Sumner was awarded the Nobel Prize in Chemistry in 1946.

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.

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 °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 °C.

Problem 8. Step-by-step

Uzbekistan's polymer industry is a growing sector, driven by domestic demand in construction, packaging, and agriculture. Polycondensation, also known as condensation polymerisation, leads to multiple important polymeric products and is known to proceed by a stepwise mechanism.

Let's consider a polymer produced by polycondensation of HO–A–OH and HOOC–B–COOH monomers. Such polymers, obtained via esterification reactions, are called polyesters. It is generally assumed that the reactivity of functional groups is independent of the length of the corresponding molecular chain.



$$-\frac{d[\text{OH}]}{dt} = -\frac{d[\text{COOH}]}{dt} = k[\text{OH}]^x[\text{COOH}]^y$$

The Initial Rate Method was used to determine the kinetic order of the reaction.

Initial Rate / $\text{M}\cdot\text{s}^{-1}$	$[\text{OH}]_0 / \text{M}$	$[\text{COOH}]_0 / \text{M}$
2.70×10^{-4}	0.100	0.100
1.08×10^{-3}	0.200	0.200
1.62×10^{-3}	0.300	0.200

- Using the information above, **calculate** the values of k , x and y .

It is reasonable to consider that the concentrations of the functional groups are equal, that is $[\text{OH}] = [\text{COOH}] = C$. Thus, the kinetic equation can be further simplified as:

$$-\frac{dC}{dt} = kC^z$$

- Give** the value of z in this case. **Write** the integrated kinetic equation.

The Carothers equation relates the average degree of polymerisation (DP) of polymers with the degree of conversion, p , where C is the concentration of functional groups at a particular time and C_0 is the initial concentration of those groups in monomers.

$$DP = \frac{C_0}{C}$$

- Derive** the Carothers equation $DP = f(p)$.
- Find** the dependence of DP on time, $DP = f(t)$.
- Using the functions $DP = f(t)$ and $DP = f(p)$, **present** the relationship between p and t in a linear form.

Polycondensation reactions typically have an overall reaction order of 2. However, this can be different in particular cases. Thus, aryl halide–bisphenol A polycondensation systems are unusual because they show different kinetic behaviours depending on whether the halide is chlorine or fluorine. The following mechanism of polycondensation kinetics was found for DCDPS (dichlorodiphenylsulfone, 2-body pathway) and for DFDPS (difluorodiphenylsulfone, 3-body pathway):

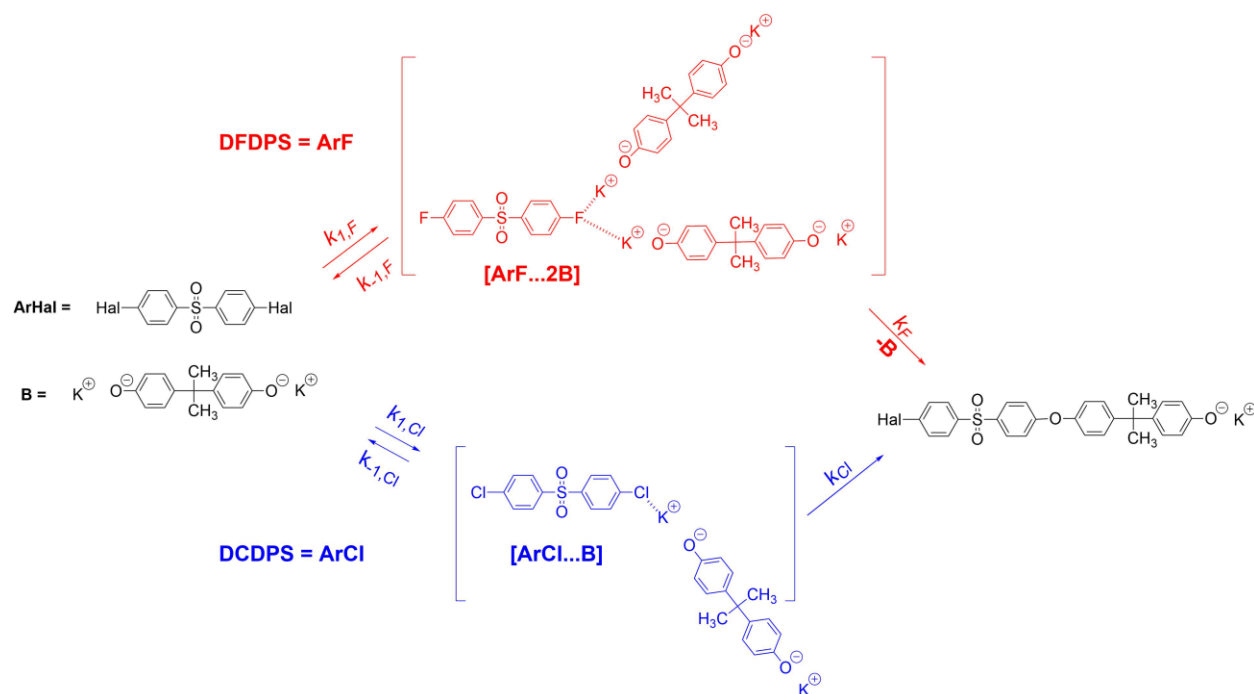


Figure 1. Substrate-dependent mechanisms of reaction for DFDPS (ArF) and DCDPS (ArCl)

- Based on the above mechanisms, **find** the expressions for the equilibrium constants K_F and K_{Cl} of the formation of intermediates $[\text{ArF}\dots 2\text{B}]$ and $[\text{ArCl}\dots \text{B}]$, respectively.
- Assuming that equilibrium is established very quickly in the first step, **find** the overall reaction rate law $r = k_{\text{obs}}[\text{ArHal}]^m[\text{B}]^n$ for both halides, using K_F and K_{Cl} , respectively.

Polymerisation of DFDPS can be schematically shown as follows:



Assume that $[\text{ArF}]_0 = [\text{B}]_0$ and $[\text{ArF}] = [\text{B}]$ at any time.

- Deduce** the relationship between the degree of polymerisation and time for DFDPS polymerisation. **Calculate** the average degree of polymerisation after 1 hour, if the initial concentration $[\text{ArF}]_0 = [\text{B}]_0 = 0.1633 \text{ M}$ and $k_{\text{obs}} = 7023 \text{ L}^2\cdot\text{mol}^{-2}\cdot\text{h}^{-1}$.

So far, we've considered a model in which the rate constant is independent of the degree of polymerisation (DP). However, reactions are known that don't conform to this model. Consider the more complicated model where every propagation step of the step-growth reaction accelerates by a factor ξ .

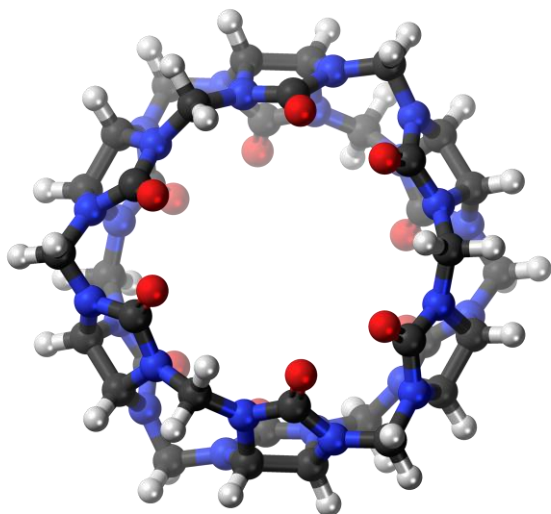
9. **Sketch** qualitatively $DP = f(t)$ curves for $\xi = 1$ (common case, already done in question 4) and $\xi > 1$ in one graph.
10. **Derive** the relationship $DP = f(t)$ for $\xi > 1$.

Problem 9. Host-guest chemistry of cucurbiturils as Uzbek hospitality

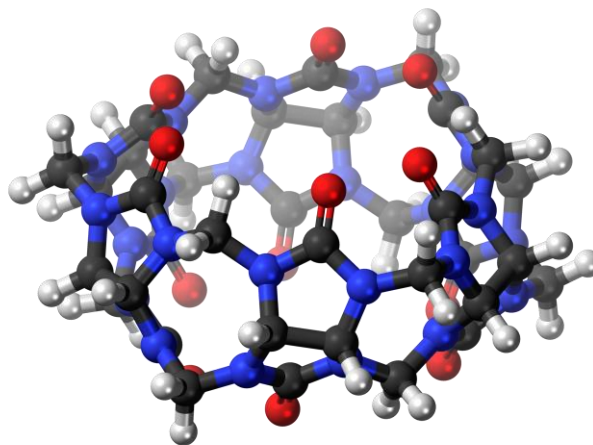
The cucurbiturils are a family of macrocyclic compounds, which, incidentally, resemble pumpkins. They are doughnut-shaped molecules with functional groups within their voids that can bind small guest molecules.

Fortunately, the synthesis of cucurbiturils is extremely simple. The scheme below shows the synthesis of cucurbit[6]uril (**X**), the [6] indicating a macrocycle with six repeating units.

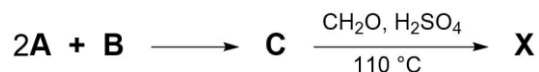
Cucurbit[6]uril (**X**)



Top view



Side view

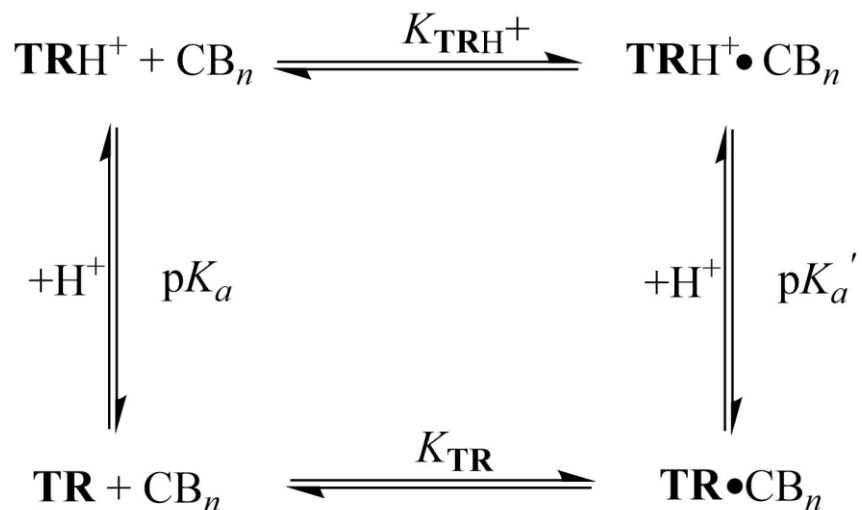


Hints:

- *A* is obtained by heating an inorganic salt of **Y**, which happens without mass loss;
- In the mass spectrum, **B** has peaks at m/z 58 and 29. **B** gives a positive Tollens reaction and has only one type of hydrogen atoms and one type of carbon atoms;
- Compound **C** is not polymeric, and **C** is the main building block for constructing cucurbiturils.

1. **Draw** structures **A–C** and the repeating unit of **X**. **Determine Y**.

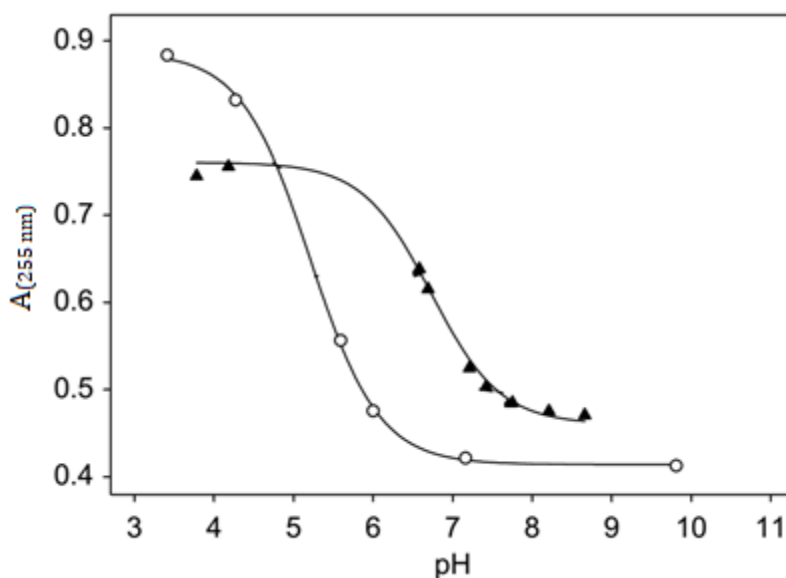
Cucurbiturils form host-guest type complexes. For example, the host cucurbit[*n*]uril (CB_n) can stabilise the ocular drug tropicamide ($\text{TR} - \text{C}_{17}\text{H}_{20}\text{N}_2\text{O}_2$). The four-state complexation model of neutral and protonated TR with CB_n is shown below:



The $[\text{TR} \cdot \text{CB}_8]$ complex was studied using mass spectra. Peaks at m/z 285, 665, and 807 were detected in the spectrum.

2. **Determine** the species to which these peaks correspond.

For the $[\text{TR} \cdot \text{CB}_8]$ complex, the formation constant, $K_{\text{TR}} = 1.4 \times 10^4$. pH titrations monitored by UV-spectrophotometry of pure TR (○), and of TR with CB_8 (▲) are shown below. The concentration of the host was sufficient to ensure virtually quantitative complexation of TR over the investigated pH range.

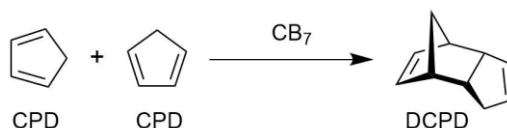


3. **Determine** the approximate values of pK_a , pK_a' and K_{TRH^+} .

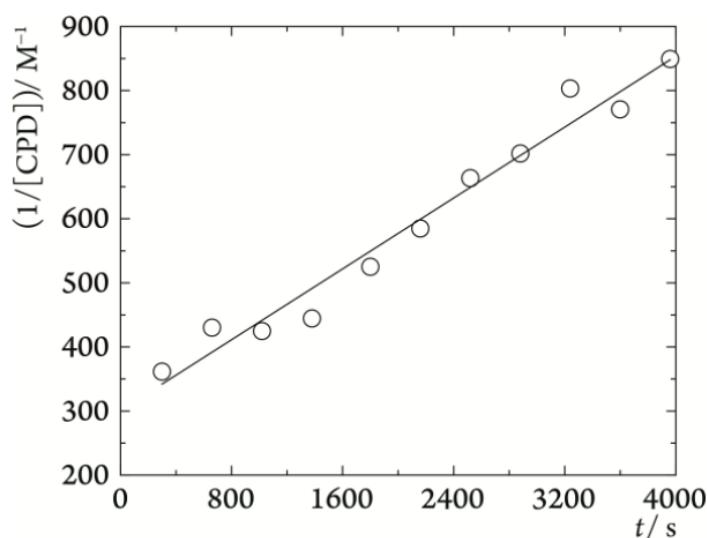
Tropicamide is an anticholinergic drug commonly used as eye drops for mydriatic effect (pupil dilation) in preparation for ophthalmological examinations and surgical procedures. The drug is available as an aqueous solution with $pH = 4.0$. Since this value is significantly lower than the physiological pH of the eye ($pH = 7.0$), topical application of the drug causes significant, albeit temporary, discomfort in patients. Using tropicamide with the CB_8 complex allows the drug to be used at physiological pH .

4. **Indicate** whether TR or TRH^+ is the biologically active form of tropicamide.
 5. **Calculate** how many times the molar fraction of the biologically active form of tropicamide increases at $pH = 7.0$ if its complex with the CB_8 is used.

Cucurbiturils are also used as supramolecular catalysts. For example, cucurbit[7]uril (CB_7) catalyses the dimerisation reaction of cyclopentadiene (CPD) to dicyclopentadiene (DCPD):

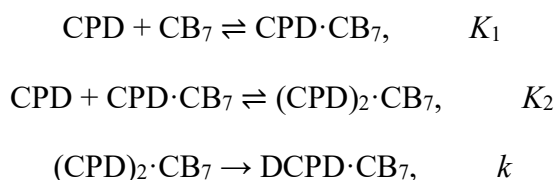


The plot of $1/[CPD]$ (M^{-1}) versus reaction time (s), monitored in the presence of CB_7 , is as follows:



6. **Determine** the reaction order for CPD and the observed rate constant.

The following equations describe the kinetics based on the binding equilibria:



7. **Derive** the dependence of the rate of the dimerisation reaction on the equilibrium concentrations of CPD and CB₇, which agrees with the experimental data from question 6.

The following table shows the observed rate constants for cucurbiturils with the same initial concentrations and different cavity volumes:

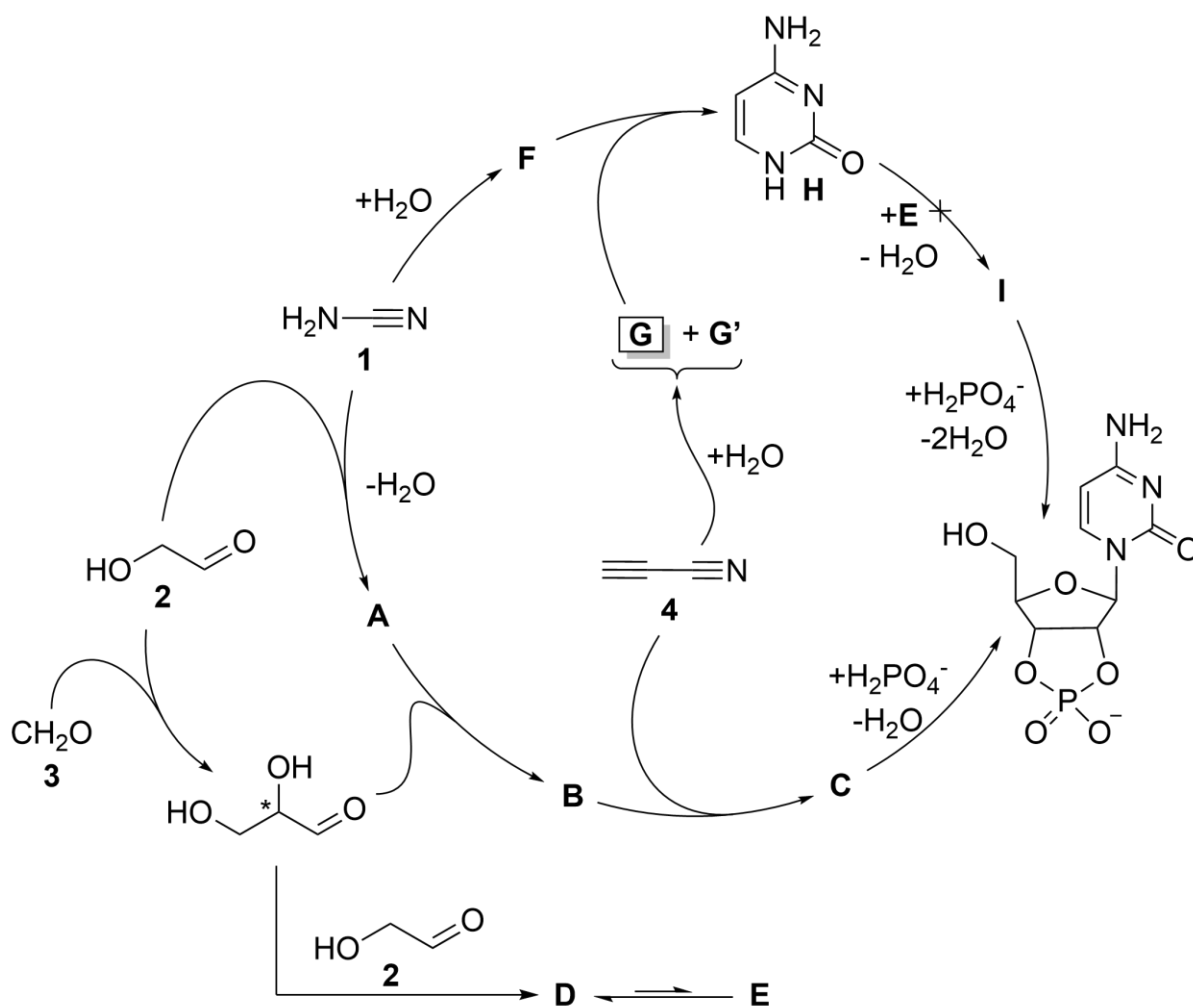
Cucurbit[n]uril	CB ₅	CB ₆	CB ₇	CB ₈
$k_{obs} / \text{M}^{-1} \cdot \text{s}^{-1}$	9.4×10^{-6}	5.0×10^{-6}	?	9.0×10^{-6}

8. **Explain** why CB₆ has the lowest observed rate constant.

Problem 10. Prebiotic life

What makes Earth unique is that it has life. As far as we know, it is the only place in the universe where complex forms of life exist. The impact of life has been so great that it has changed the planet's air, water, and climate. Therefore, a central goal of science is to understand what life is, how it works, and ultimately, how it emerged from non-living matter. This leads to the core mysteries of prebiotic chemistry: what conditions and processes on the early Earth transformed simple chemicals into the first self-replicating systems that kickstarted biological evolution?

One of the possible routes of how complex molecules like RNA and ribonucleotides formed from simple molecules cyanamide **1**, glycoaldehyde **2**, formaldehyde **3**, and cyanoacetylene **4** in prebiotic Earth was suggested by Powner *et al.*:



In this scheme, direct reaction between sugar **E** and cytosine **H** (which is formed via reaction of **G**) yields no product **I**, presumably because of the low nucleophilicity of **H**. Therefore, the $1 + 2 \rightarrow A \rightarrow B \rightarrow C$ prebiotic route was suggested by researchers, where in each step the number of rings in the product increases by one.

1. **Draw** molecular structures of compounds **A–G**, **G'** and **I**.
2. What is the reason behind the low nucleophilicity of **H**? **Choose** the correct answer(s):
 - a) electron delocalisation due to the aromaticity of pyrimidine ring;
 - b) extreme ring strain in cytosine that interrupts the reaction;
 - c) the positive charge due to the formation of ammonium salts that repels other molecules.

The fact that life relies almost exclusively on single molecular handedness (homochirality) is still not fully understood. It is well established that, in biological systems, most amino acids in proteins occur in the so-called L-configuration, while most sugars adopt the D-configuration.

3. In the scheme above, glycoaldehyde **2** and formaldehyde **3** react to form glyceraldehyde – the simplest sugar molecule that contains a stereocentre. **Depict** the structural formulae of L- and D-glyceraldehyde with the shown absolute configuration of the stereocentre.

There are several hypotheses about the origin of such a unique property as homochirality. A plausible early Earth scenario involves shallow lakes with magnetite deposits. UV light (200–300 nm) shining on magnetite can generate spin-polarised electrons – special electrons with aligned spins – that act as reducing agents. These electrons interact differently with left- and right-handed molecules due to the chiral-induced spin selectivity (CISS) effect, changing reaction rates selectively. This spin-based interaction could break chiral symmetry in prebiotic chemistry, favouring one enantiomer and possibly leading to life's homochirality.

In this case, it is useful to present the term of electron helicity, which is a physical property describing the direction of the electron's spin relative to its direction of motion. For example, if helicity is right-handed, then the electron's spin is parallel to its momentum, and vice versa.

Consider a process that occurs in a prebiotic lake of reactants:



The L-/D- isomer of **X** reacts with a right-handed electron donor De^- and produces the L-/D- isomer of compound **Y**. The spin-chirality coupling hypothesis states that the interaction of the L-isomer with the D-electron is more kinetically favoured. The amount of this preference can be expressed via the rate constant formula:

$$k_{(\text{L})} = A \cdot \exp\left(-\frac{(E_a - H_{\text{SO}})}{k_{\text{B}}T}\right),$$

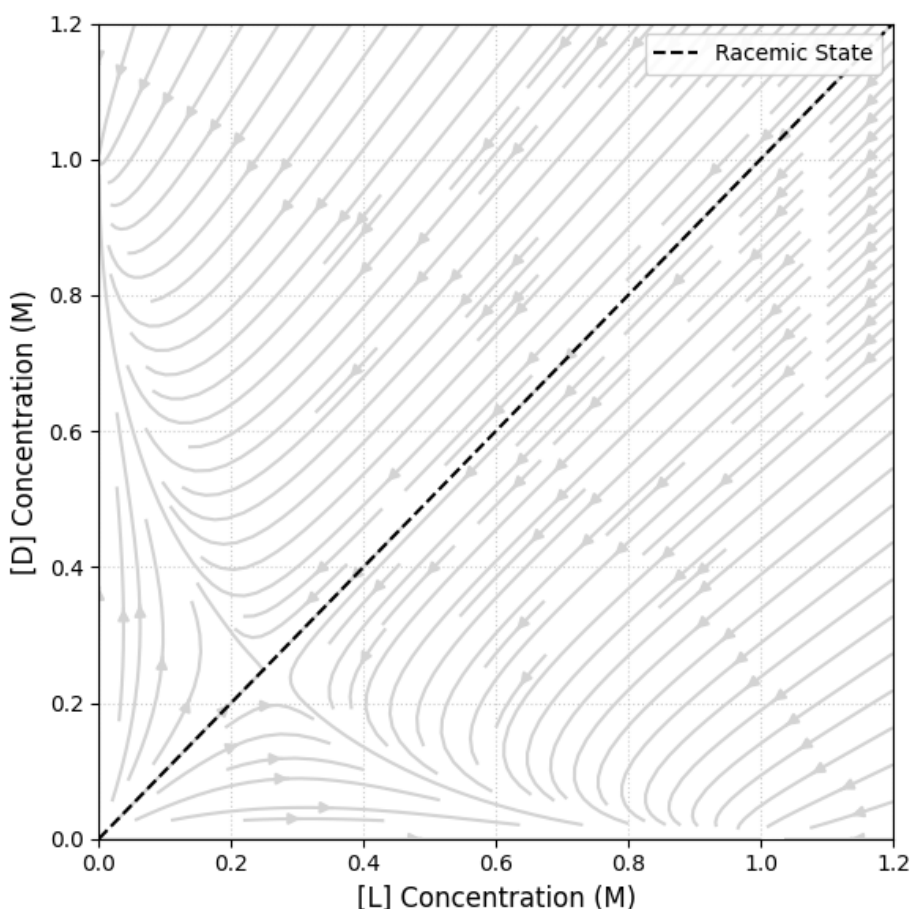
$$k_{(\text{D})} = A \cdot \exp\left(-\frac{(E_a + H_{\text{SO}})}{k_{\text{B}}T}\right),$$

where $k_{L/D}$ is the rate constant of the reaction, E_a is the activation energy of the process, and H_{SO} is the spin-orbit energy.

The enantiomeric excess, ee , is a measure of the purity of a chiral substance in terms of the predominance of one enantiomer over the other in a mixture:

$$ee = \frac{[LY] - [DY]}{[LY] + [DY]}$$

- Given $H_{SO} = 0.5$ meV, considering that the A factor is equal for L- and D-isomers and the substrate is a racemic mixture ($[LX] = [DX]$), **determine** the ee of the reaction product **Y** at $T = 313$ K (~ 40 °C), which is a good assumption for the average surface temperature of water bodies during the prebiotic era.
- Consider some racemic solution of L-/D-isomers in water with a total concentration of 1 M, where symmetry breaking (i.e. conversion of one isomer into another) occurs, resulting in overall chiral amplification of the system. **Depict** possible symmetry-breaking trajectories in a phase portrait of the system.



This example of kinetic resolution has demonstrated the chiral amplification of single monomeric units. However, the origin of life requires processes for the ligation of monomers into the homochiral polymeric molecules that constitute proteins and enzymes and the genetic polymers of RNA. Can a pool of partially enantioenriched monomers successfully produce homochiral polymers?

Let's consider two amino acids in their L- and D- forms. The possible reactions between them are listed below:



where k_{homo} and k_{hetero} denote the homochiral and heterochiral dimer formation rate constants, respectively.

6. Considering that $k_{\text{homo}} = k_{\text{hetero}}$ and thus neglecting kinetic control, **derive** that:

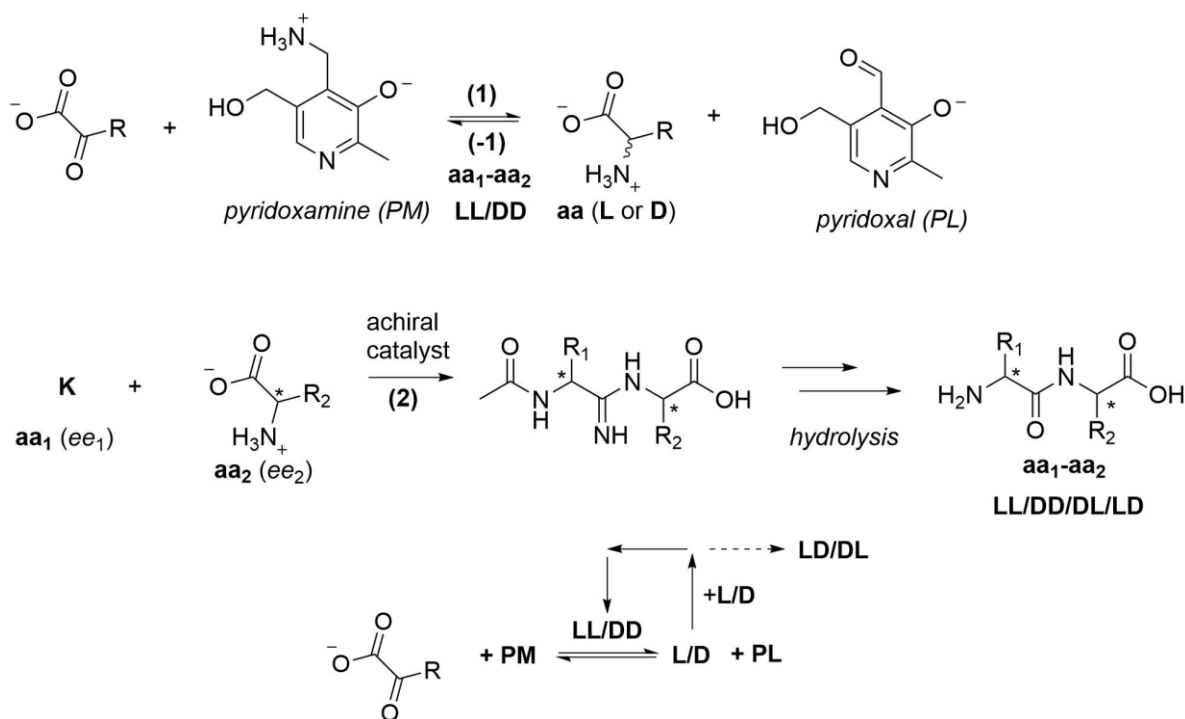
$$ee_{\text{homochiral}} = \frac{[L_1L_2] - [D_1D_2]}{[L_1L_2] + [D_1D_2]} = \frac{ee_1 + ee_2}{1 + ee_1ee_2}$$

where ee_1 and ee_2 stand for:

$$ee_1 = \frac{[L_1] - [D_1]}{[L_1] + [D_1]}, \quad ee_2 = \frac{[L_2] - [D_2]}{[L_2] + [D_2]}$$

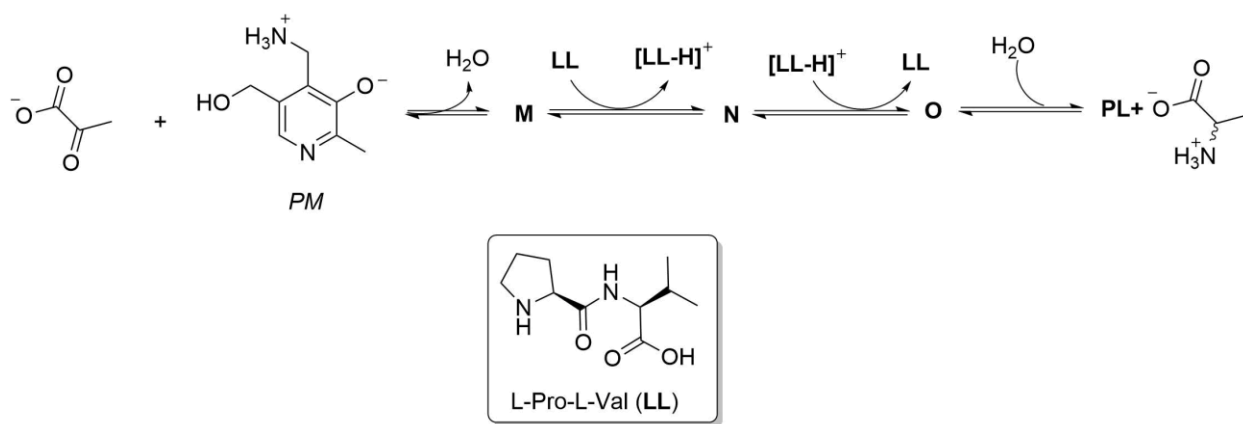
7. **Calculate** $ee_{\text{homochiral}}$ for the prebiotic lake system from question 4 with $ee_1 = ee_2 = ee_{q4}$.
Note: If you could not solve question 4, consider $ee_{q4} = 0.05$ (5%).
8. Now, considering that only homochiral oligomers are responsible for chain propagation, **find** the smallest number of amino acid residues needed for a resulting polymeric chain to have $ee_{\text{homochiral}} > 0.99$. For initial amino acids, **assume** each amino acid has an $ee = 0.05$.

The mathematical model above was found valid for a real biochemical system, where the initial transamination reaction with pyridoxamine catalysed by a strictly homochiral dipeptide molecule **aa1-aa2** yields a racemic amino acid molecule **aa** and pyridoxal. The amino acid molecules formed react with another amino acid's derivative molecule **K**, which results in a dipeptide derivative. The latter yields the dipeptide **aa1-aa2**, thus looping the cycle:



9. **Draw** the structure of **K**.

The role of the dipeptide catalyst in reaction (1) is based on promoting a hydrogen atom transfer (HAT) reaction. For instance, Yu *et al.* proposed the mechanism below for the L-prolinyl-L-valine-catalysed alanine synthesis reaction from pyruvate:



10. **Mark** the functional group(s) in the **LL** molecule involved in the hydrogen atom transfer process.

11. **Draw** the structures of compounds **M–O**.

Yu *et al.* also discovered that in the reverse reaction (–1), which leads to pyruvate from alanine, D-alanine reacts faster than L-alanine, thus enriching the prebiotic system with the L-enantiomer.

12. Which intermolecular forces (or their absence) between alanine and **PL-LL** in the corresponding transition state could be behind the faster reaction of D-Ala compared to that of L-Ala? **Choose** the correct statement(s):
- Hydrogen bonds
 - π -stacking
 - Steric repulsion
 - Alignment of stereocentres

Constructive and destructive mechanisms, where the corresponding amino acid was formed or destroyed, respectively, were investigated in open systems with a flow rate, ϕ , of corresponding reactants in each case.

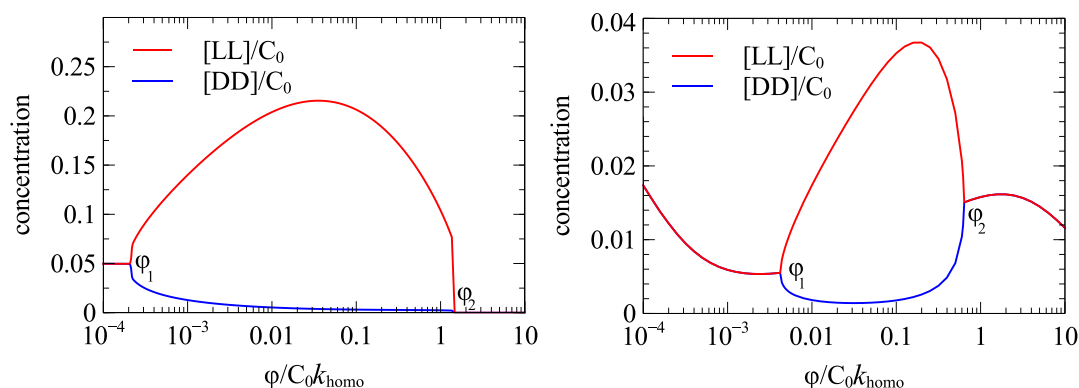


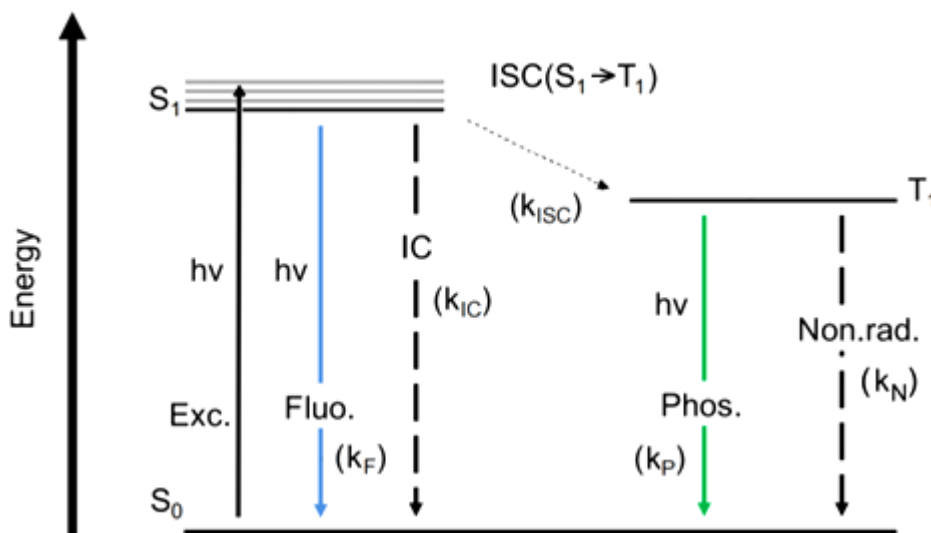
Figure 2. Concentration of homochiral dipeptides vs flow rate of a) ketoacid (left, constructive mechanism); b) amino acid (right, destructive mechanism)

13. **Deduce** the value of ϕ , at which the maximum chiral asymmetry is observed.
14. **Explain** the concentration behaviour of [LL] and [DD] when:
- $\phi < \phi_1$;
 - $\phi_1 < \phi < \phi_2$;
 - $\phi > \phi_2$.

Problem 11. 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.

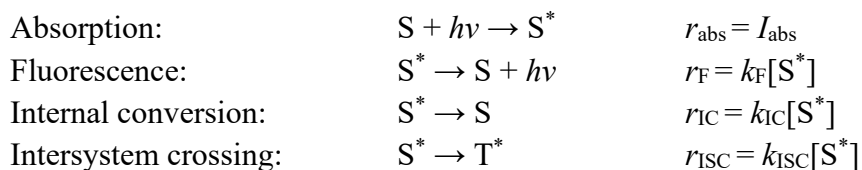


1. **Choose** the correct option: “For electron excitation, the wavelength of the absorbed photon must be ...”:
 - a) higher than that of the fluorescence wavelength
 - b) equal to that of the fluorescence wavelength
 - c) lower than that of the fluorescence wavelength

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 ...”:
- higher
 - lower

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



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.

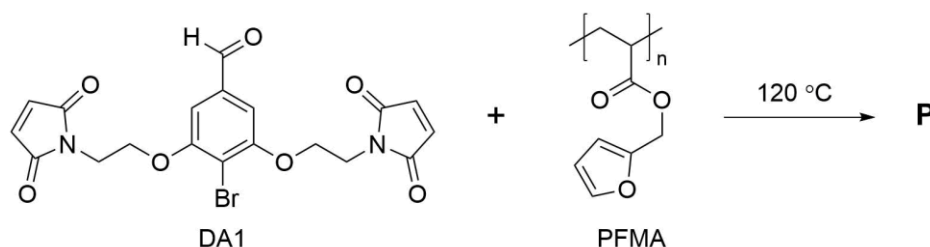
In one experiment, quenching of tryptophan fluorescence in a solution by dissolved O_2 gas was monitored by measuring emission lifetimes at 348 nm in aqueous solutions.

$[O_2] / M$	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}

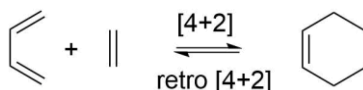
7. **Determine** the quenching rate constant (k_Q) for this process.
8. **Calculate** the concentration of O_2 at which half of the excited tryptophan molecules are quenched.

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.



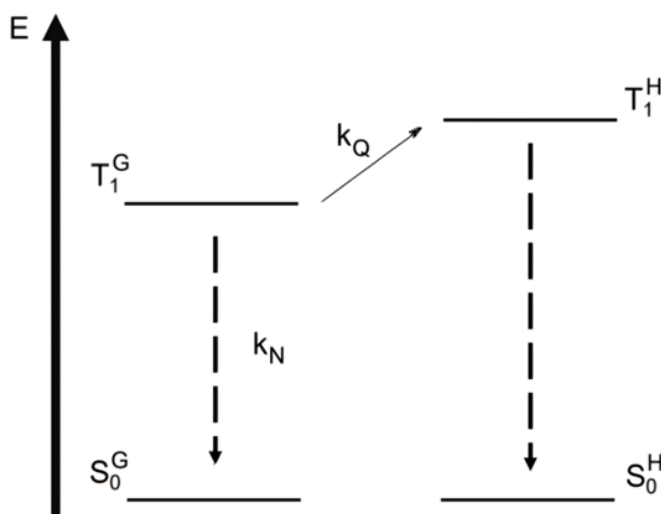
9. **Draw** the structure of **P**, which is an adduct of the following [4+2] cycloaddition reaction:



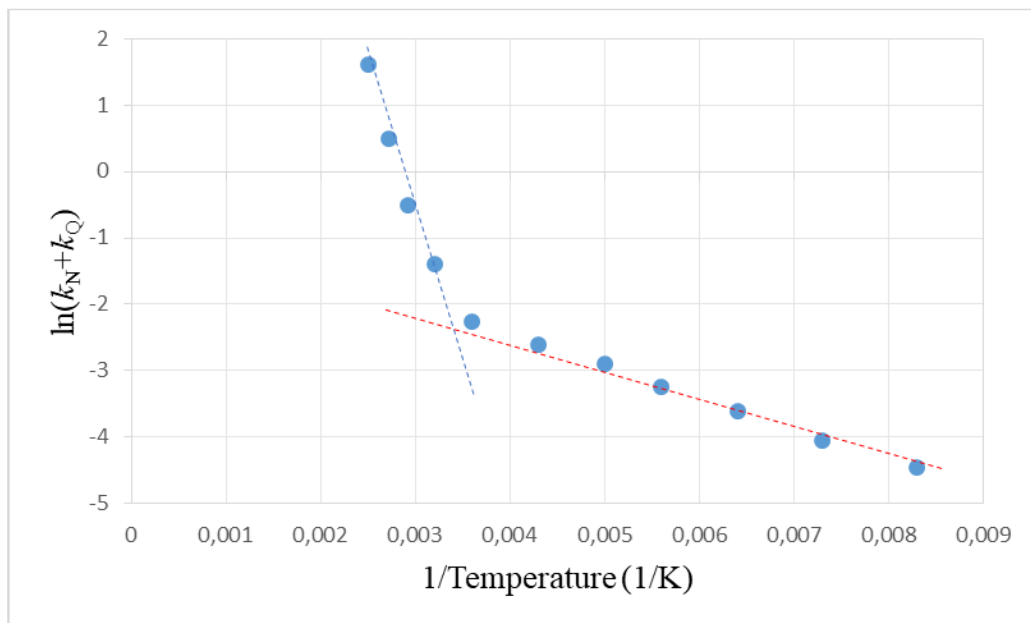
At low temperatures, the process of quenching is limited by an energy barrier:

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

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:



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



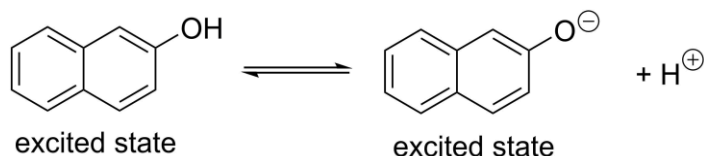
k_N – rate constant of the non-radiative decay of the triplet state.

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.

Problem 12. Photoacids

Photoacids form a unique class of molecules that undergo a major change in their pK_a values between their ground and excited states. The loss of a proton is facilitated by light excitation. This phenomenon is also called excited state proton transfer (ESPT).

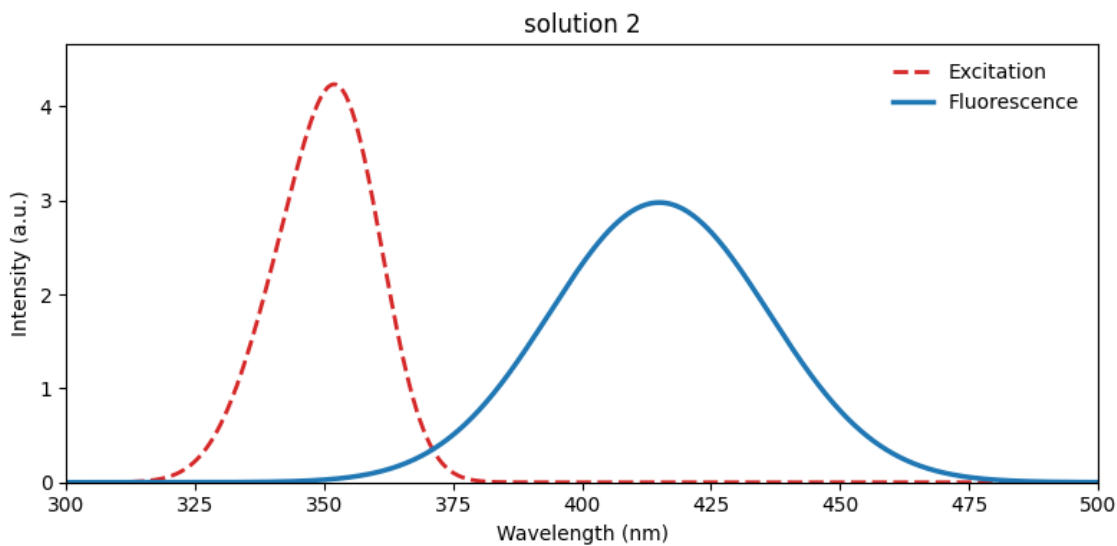
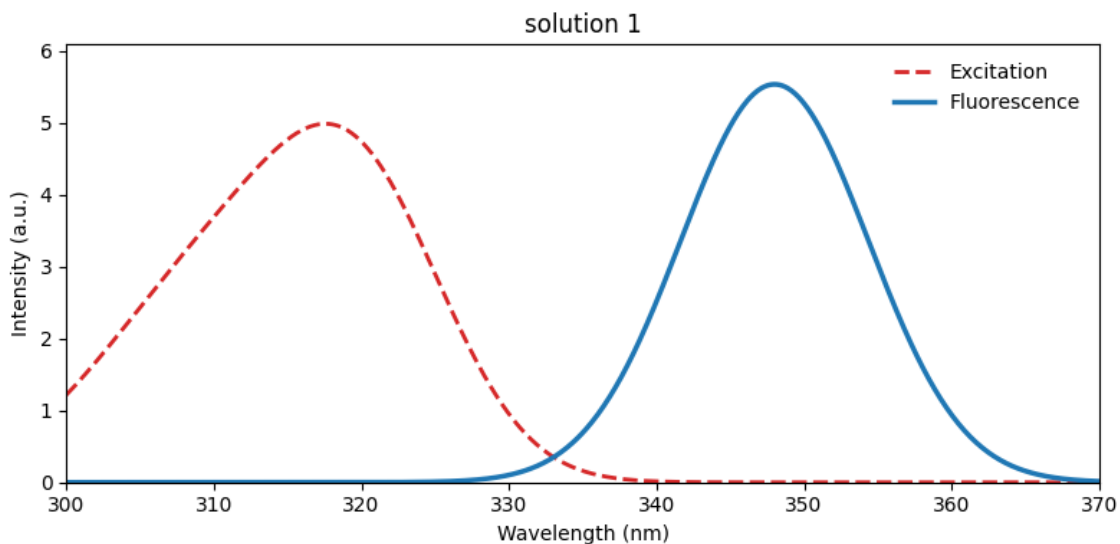


Once, Khoja Nasreddin, who was bored with his usual routine, decided to investigate 2-naphthol, a simple molecule that exhibits the ESPT phenomenon. He prepared five 2-naphthol solutions (each of 25 mL) in different pH media, using a 2.1 mM 2-naphthol solution (**solution Z**) and measured light absorbance ($l = 1.0$ cm) at 344 nm:

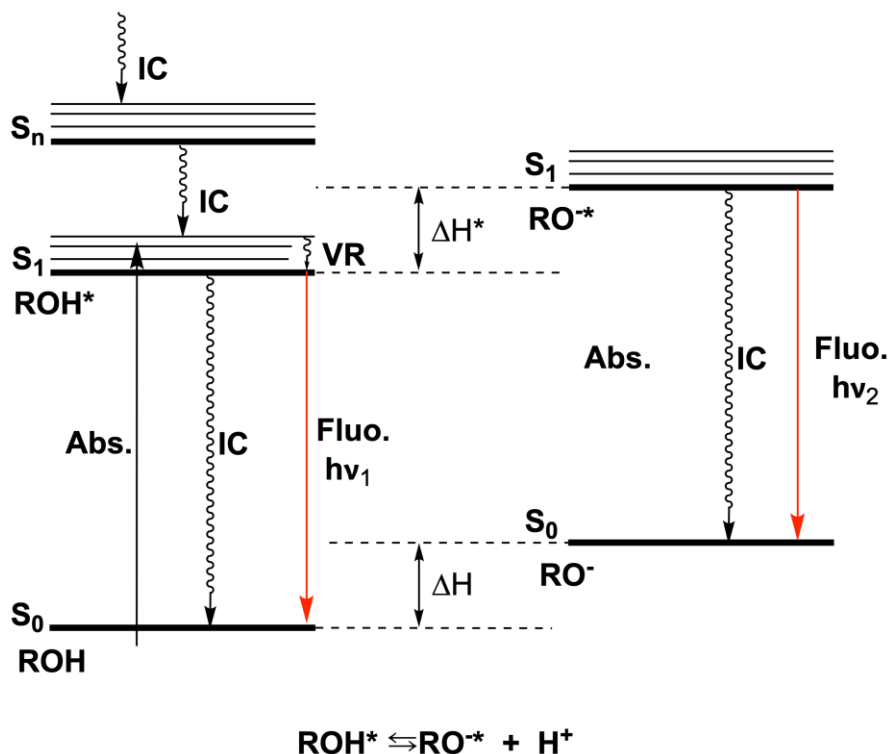
Solution	1	2	3	4	5
Composition	5 mL Z + 20 mL 0.02 M HCl	5 mL Z + 20 mL 0.02 M NaOH	5 mL Z + 20 mL NH ₄ Cl/NH ₃ (3:1 buffer)	5 mL Z + 20 mL NH ₄ Cl/NH ₃ (2:1 buffer)	5 mL Z + 20 mL NH ₄ Cl/NH ₃ (1:1 buffer)
Absorbance	0.219	0.440	0.256	0.273	0.300

- Find** the final concentration ($\text{mol} \cdot \text{L}^{-1}$) of 2-naphthol in solutions **1–5**.
- Calculate** the molar extinction coefficients, ϵ_{ArO^-} and ϵ_{ArOH} at this wavelength.
- Plot** the graph pH vs $\log \frac{[\text{ArO}^-]}{[\text{ArOH}]}$. **Estimate** the pK_a of 2-naphthol if $pK_b(\text{NH}_3) = 4.75$.

To check the ESPT phenomenon in 2-naphthol, Khoja Nasreddin recorded the fluorescence spectra of solutions **1** and **2**:



Dissociation of a photoacid in the ground and excited states can be described with a combined Förster and Jablonski diagram:

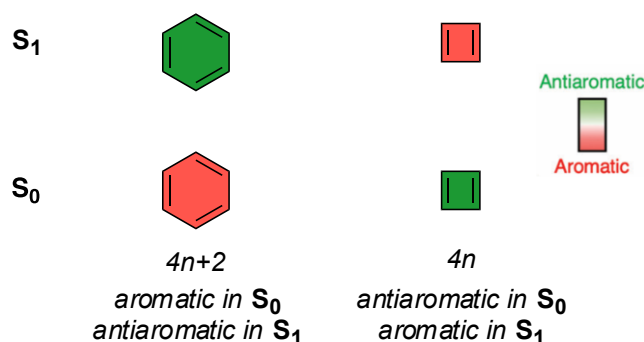


$S_0, S_1, \dots, S_n$ stand for different electronic states, each of them having multiple vibrational levels. ΔH and ΔH^* indicate changes in the enthalpy of dissociation in the ground and excited states, respectively. ν_1 and ν_2 are the frequencies of S_1 to S_0 (0–0) transitions for the photoacid and its deprotonated form, respectively. Internal conversion (IC) is a spin-allowed non-radiative transition from a higher to a lower electronic state and does not show any peak in the spectra. Fluorescence, on the other hand, is the emission of a photon during a transition between the states with the same spin quantum number (for example, $S_1 \rightarrow S_0$). Vibrational relaxation (VR) is a non-radiative transition from a higher vibrational level to a lower one in the same electronic state of the molecule. VR is very fast, so it occurs right after light absorption and precedes other radiative processes like fluorescence.

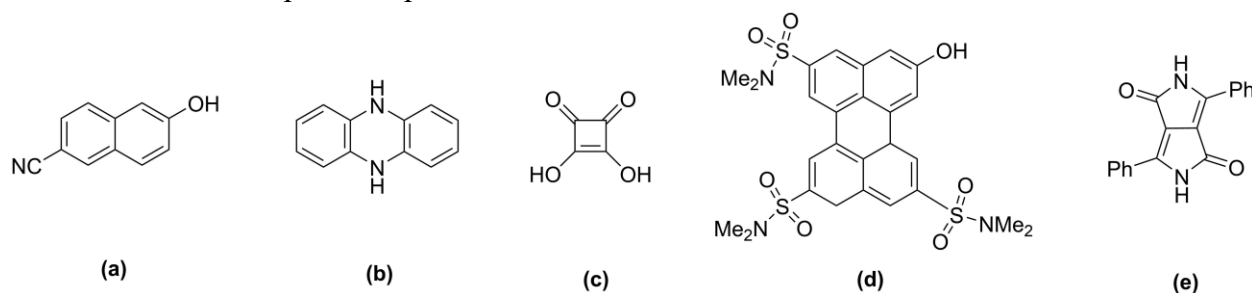
In practice, transition wavelengths λ_1 and λ_2 are commonly used instead of corresponding frequencies.

- Assuming $\Delta H^{\circ*} - \Delta H^{\circ} = \Delta G^{\circ*} - \Delta G^{\circ}$, **derive** the relationship between ΔpK_a , λ_1 , λ_2 , and temperature. $\Delta pK_a = pK_a - pK_a^*$.
- Determine** the pK_a^* of the excited state (ES) of 2-naphthol at 298 K. **Calculate** $[\text{ArOH}^*]/[\text{ArO}^{*-}]$ at pH = 5.

Khoja Nasreddin wondered whether every acid decreases its pK_a in its excited state. After consulting with Prof. Beruni, Khoja found out that this might relate to Baird's rules – the analogue of Hückel's aromaticity rules for excited states. According to Baird's rules, in the excited state, planar conjugated structures with $4n$ π -electrons are considered aromatic, and $(4n + 2)$ π -electrons are considered antiaromatic. In this terminology, photoacidity is the result of Baird-antiaromatic molecules "relieving stress" through deprotonation. This is made possible because of the excess charge redistribution from the anionic centre to the ring.

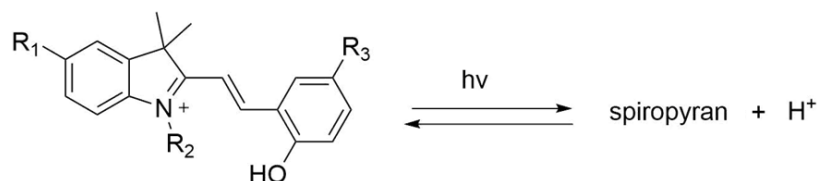


6. **Classify** the structures below as Baird-aromatic and Baird-antiaromatic. **Identify** those that could be used as potential photoacids.



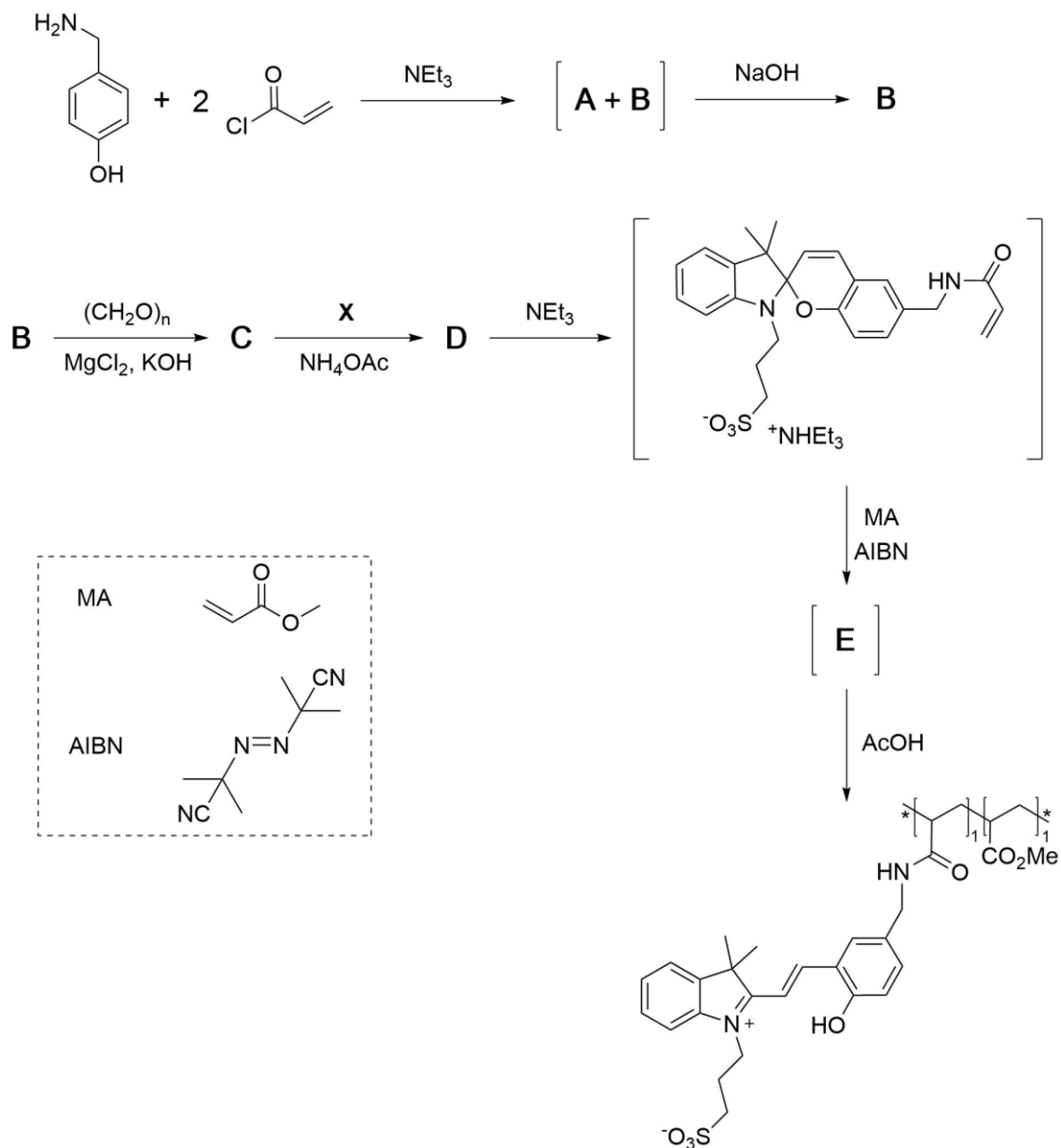
7. 2-Naphtalenecarboxylic acid behaves the opposite way when treated with light – its $\Delta pK_a = pK_a - pK_a^* < 0$. **Explain** this phenomenon.

Merocyanines are an excellent example of photoacidity, turning into spiropyrans under light irradiation.



8. **Draw** the structure of the spiropyran.

The synthesis of a merocyanine photoacid polymer is given below.



Hints:

- Hydrolysis of compound **A** results in compound **B**.
- C** can be converted into **C'** with a carboxylic acid moiety under NaClO_2 .

9. Draw the structures of **A–F** and **X**.

Problem 13. Interested in micelles?

Part 1. The forms of micelles

The form of a micelle can be described by the surfactant packing parameter, N_s . The packing parameter considers the volume and the length of the hydrophobic chain (V_C and L_C , respectively), and the equilibrium hydrophilic area per molecule at the aggregate interface, a_0 :

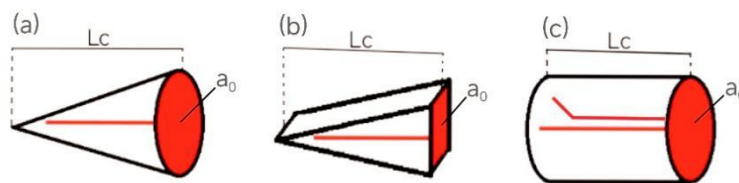
$$N_s = \frac{V_C}{a_0 \times L_C}$$

The table below shows the relationships between the surfactant packing parameter and the form of the structure:

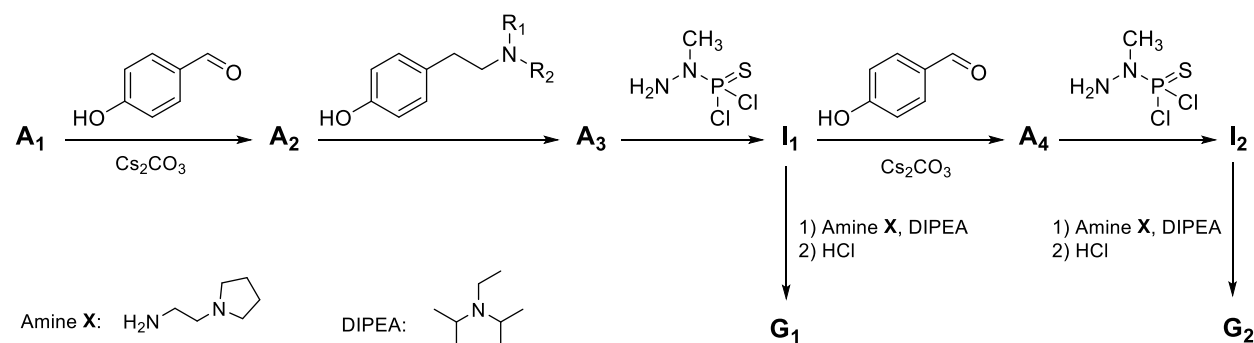
Form of micelle	Sphere	Cylinder	Bilayer
N_s	$\leq \frac{1}{3}$	$\frac{1}{3} < \dots \leq \frac{1}{2}$	$\frac{1}{2} < \dots \leq 1$

1. If there are cone (a), rectangular wedge (b) and cylinder-shaped (c) surfactants, **match** them with their appropriate form of structure. **Prove** your answers by calculation.

Note: It is only an assumption. In fact, surfactants themselves are more complicated structures and can have shapes which are different from these three below.

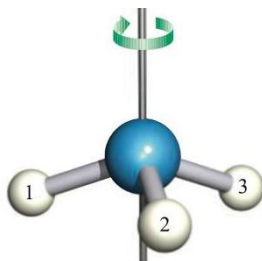


The phosphorus dendrons **G**₁ and **G**₂ act as charged surface active substances, although their structure differs from that of classical surfactants with a well-defined polar head and non-polar tail. They aggregate into clear structures and can be synthesised through the scheme below.



A₁ is a cyclic compound with a threefold symmetry axis, with mass fractions of P, N, and Cl of 26.73%, 12.09%, and 61.18%, respectively. With the addition of an appropriate number of equivalents of 4-hydroxybenzaldehyde to **A**₁, **A**₂ is produced as the main product with only one Cl atom.

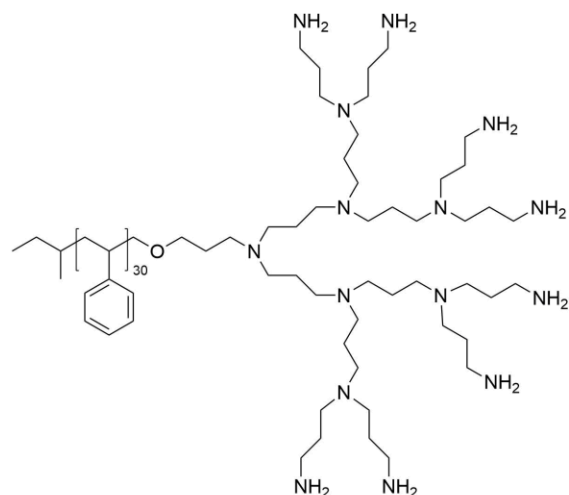
Note: A threefold symmetry axis is an imaginary line through an object around which it can be rotated by 120° and appear unchanged. For example, it is present in the molecule of ammonia.



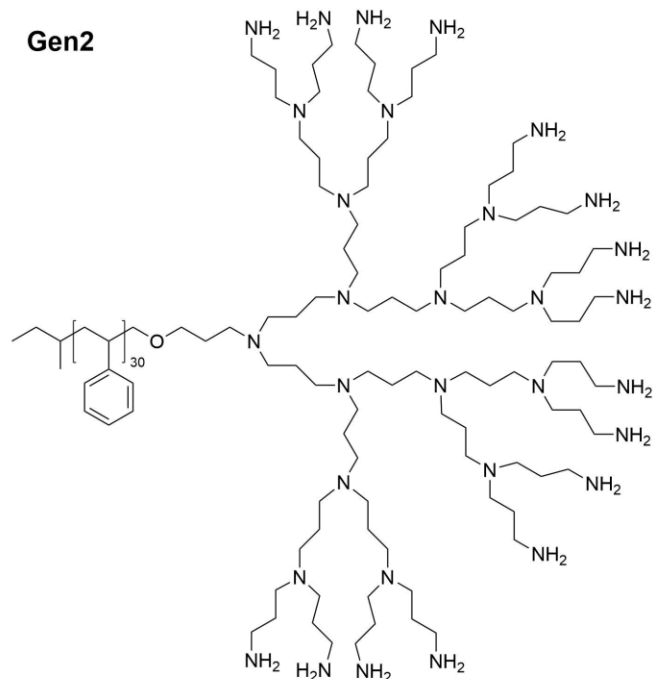
2. **Identify** structures **A**₁–**A**₄, **I**₁–**I**₂, and **G**₁–**G**₂.
3. Based on the synthesis pattern for **G**₁ and **G**₂ shown in the scheme, **calculate** how many cationic groups will be present in **G**₁₀ if the same reaction stages are repeated.
4. By analysing the structure, **determine** which type of surfactants the **G**₁ and **G**₂ molecules resemble. **Indicate** the type of assembly they most likely show. **Specify** without calculations.
5. **Choose** the main purpose of adding HCl at the end of the synthesis:
 - a) to hydrolyse unreacted P–Cl bonds for purification;
 - b) to make the fluorescent label brighter;
 - c) to create a water-soluble, positively charged form that will show biological activity;
 - d) to rigidify the dendron structure via cyclisation.

In contrast to **G**₁ and **G**₂, in a series of amphiphilic polystyrene (PS)-poly(propylene imine) dendrimer diblock copolymers **Gen1**–**Gen3**, varying in head group size, the form of micelles within a polar medium depends on the generation number.

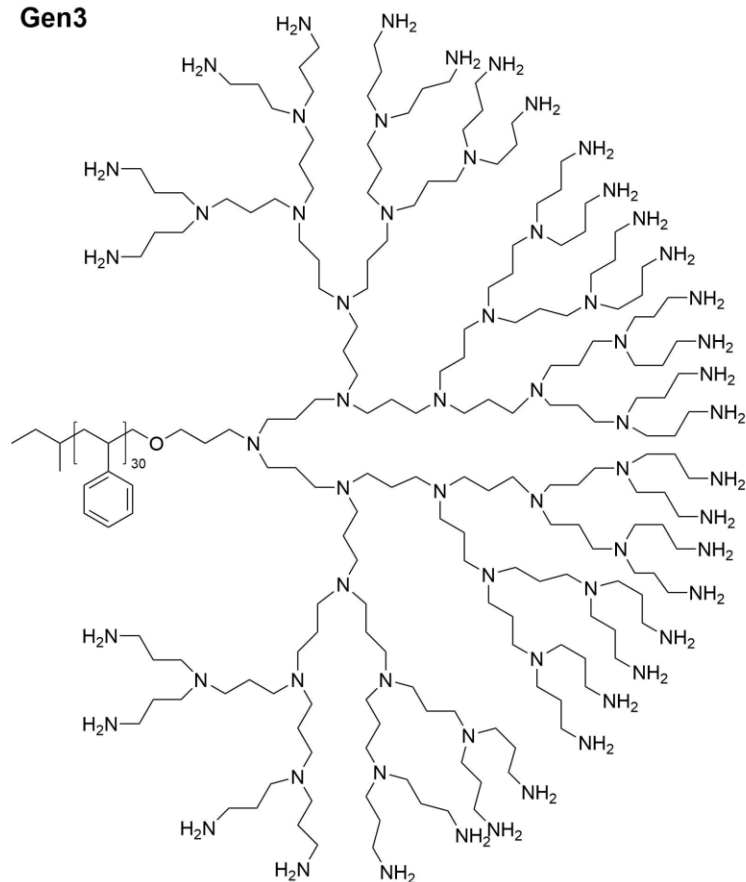
Gen1



Gen2



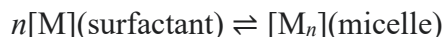
Gen3



6. Propose the forms of micelle in which **Gen1**, **Gen2** and **Gen3** are assembled in water, if each generation forms a distinct micelle type.

Part 2. Thermodynamics of micelle formation

The micelle formation process can be seen as an equilibrium between two states:



$$K_n = \frac{[\text{M}_n]}{[\text{M}]^n} = e^{\frac{-\Delta_r G^\circ_{\text{micelle}}}{RT}}$$

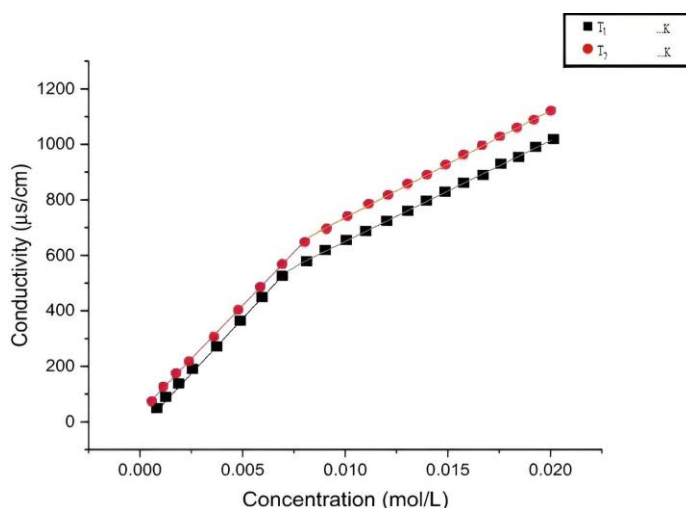
where n is the aggregation number, i.e. the number of surfactant molecules (further referred to as monomers) in the micelle; $[\text{M}]$, $[\text{M}_n]$ reflect the concentrations of monomers and micelles, respectively.

7. **Derive** the equation for the fraction of monomers present in micelles as a function of $[\text{M}]$, n and K_n .
8. **Choose** which of the suggested conditions would lead to the maximum number of monomers inside the micelles. **Assume** that in all conditions the equilibrium constants are the same and the monomer concentration is lower than $1 \text{ mol} \cdot \text{dm}^{-3}$.
 - (a) Low concentration of monomers with low aggregation number.
 - (b) Low concentration of monomers with high aggregation number.
 - (c) High concentration of monomers with low aggregation number.
 - (d) High concentration of monomers with high aggregation number.

At the critical point, the monomers inside the micelles start to account for the largest fraction. This is the so-called “critical micelle concentration (CMC)”, above which the monomers will mostly be within the micelles.

9. **Describe** CMC as a function of aggregation number.

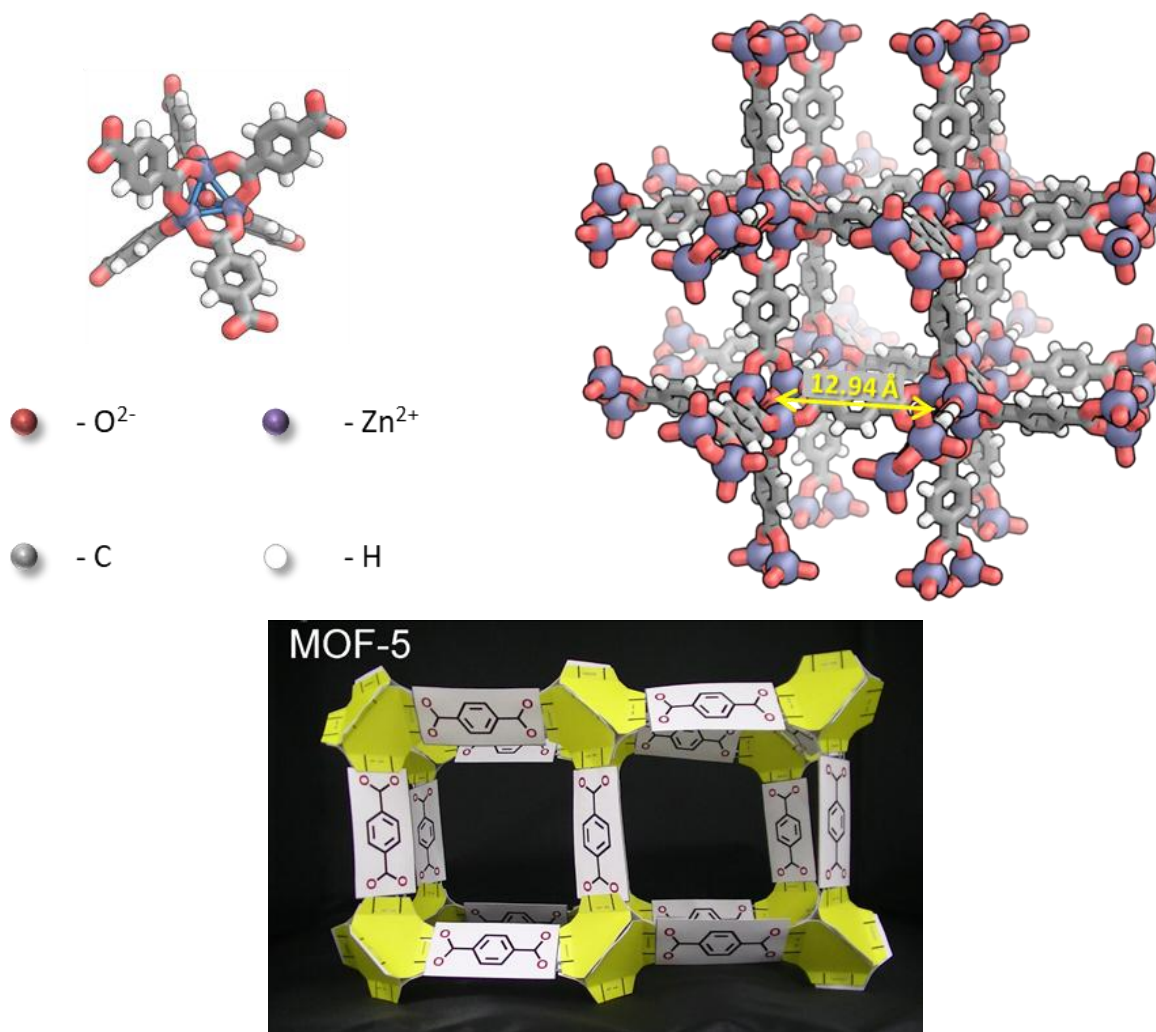
The dependence of specific conductivity on the concentration of surfactant monomers is shown in the picture below at temperatures T_1 and T_2 :



10. Assuming that the Gibbs energy of micelle formation, $\Delta_r G^\circ_{\text{micelle}}$, and the aggregation number remain constant, **compare** T_1 and T_2 .

Problem 14. The basics of Metal–Organic Frameworks

The 2025 Nobel Prize in Chemistry was awarded to Susumu Kitagawa, Richard Robson, and Omar M. Yaghi for the development of Metal–Organic Frameworks (MOFs). MOFs are crystalline, nanoporous coordination polymers formed by linking metal nodes (ions or metal oxide clusters – secondary building units) with multidentate organic ligands. Their hallmark is the combination of molecular-level tunability with permanent porosity, producing materials whose structural and functional diversity exceeds that of classical zeolites or activated carbons. MOFs are 3D frameworks with a complex structure. Thus, building models is useful to understand elementary units. For that, please follow the instructions from *J. Chem. Educ.* 2025, 102, 2, 877–881 (<https://doi.org/10.1021/acs.jchemed.4c01312>). Normal paper, glue, and tape can also be used as alternatives. One of the famous materials in this field is MOF-5 constructed from zinc oxo-clusters (Zn_4O) and 1,4-benzenedicarboxylate (BDC) ligands.



- From the figure above and/or constructed model, **write down** the empirical formula for the repeating unit.

The first synthesis of MOF-5 was carried out by mixing $\text{Zn}(\text{NO}_3)_2$, H_2BDC (benzene-1,4-dicarboxylic acid), and triethylamine in a *N,N*-dimethylformamide/chlorobenzene mixture. Small amounts of water were added to initiate oxo-anion formation. The crystals formed were filtered and activated (dried) in a vacuum oven.

2. **Write down** the chemical equation of MOF-5 formation.

Elemental analysis of the crystals before activation showed elemental content (by mass): C – 44.21%, H – 5.02%, N – 7.64%. In mass spectra of crystals during heating up to 350 °C, four m/z signals were detected: 73, 77, 112, and 114. The relative intensity of the latter two signals was 3:1.

3. **Write down** the empirical formula of the crystals before activation.

MOF-5 has a high surface area of $2900 \text{ m}^2 \cdot \text{g}^{-1}$. The distance between oxygen atoms in the cluster centres was found to be 12.94 Å.

4. **Find** the free volume (which is not occupied by framework atoms) and experimental surface area (m^2) of one cubic cell. **Account** only **for** Van der Waals radii of atoms (r), which are as follows:

Element	Zn	H	C	O
$r / \text{Å}$	1.5	1.2	1.7	1.5

5. To be correct, there are two pores with diameters of 11.0 Å and 15.1 Å. **Find** the elementary unit cell parameter a .
6. MOF-5 has been tested for hydrogen uptake. It was found that 10 g of the material can take up to 1 wt% of H_2 at 20 bar, 298 K. Assuming all the material is an ideal crystal, **calculate** excessive hydrogen uptake (how much excess hydrogen can be stored compared to pure hydrogen of the same volume without MOF-5 under the given conditions).
7. **Suggest** the ligands which might change the cubic cell volume down to 69.3%. The distance between the 1- and 4-carbons of a benzene ring is 2.69 Å.

Problem 15. Microscopy in chemistry

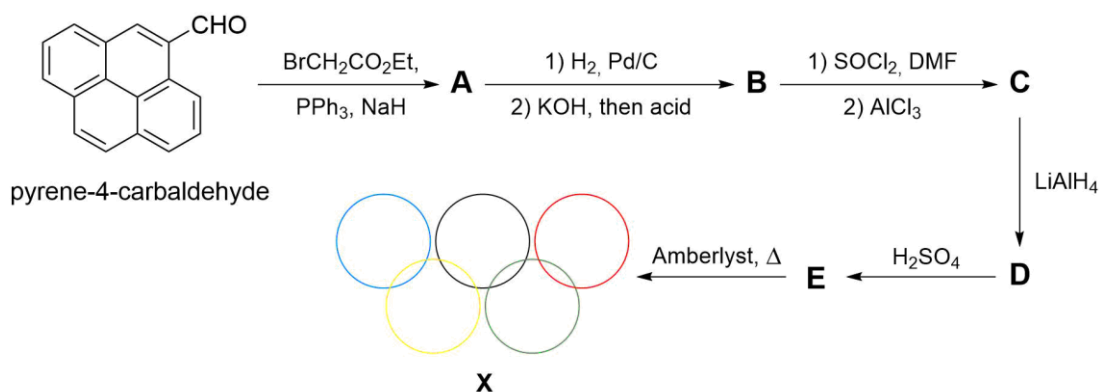
Scanning tunnelling microscopy (STM) is a microscopy method that lets us see individual atoms and molecules on the surface. It works by moving a sharp metal tip very close to the surface and applying a small voltage. In 1986, Binnig, Quate, and Gerber combined the principles of STM with a stylus profilometer to create Atomic Force Microscopy (AFM). While STM can only be used to image conductive samples, AFM does not require a current flow between the tip and the sample and can map a surface regardless of its conductivity.



Figure. 40 years ago, in 1986, Gerd Binnig and Heinrich Rohrer shared a Nobel Prize in Physics "for their design of the scanning tunneling microscope".

In 2012, an article was published reporting that British chemists from the University of Warwick, together with a group of scientists from IBM Research, had captured an AFM image of a hydrocarbon molecule called **X** (see the image below). This image was subsequently recognised as the smallest logo for the London 2012 Summer Olympics.

The synthesis of this hydrocarbon began with pyrene-4-carbaldehyde:



DMF – dimethylformamide, Amberlyst – protonic ion exchange resin. Initially obtained hydrocarbon molecule **E** easily isomerises to more symmetrical **X** under proton migration conditions.

1. **Draw** the structures of **A–E**, **X**. Note: Molecule **X** possesses a twofold symmetry axis.
2. Compound **X** was named as ...cene. **Suggest** its full name.

X-based units can be used as building blocks of 1D quantum magnet chains via the formation of stable radical centres:



3. **Draw** the structures of compounds **F–I**, based on the following information about compound **F**:

- A peak with m/z 411.89 was registered as the main peak in the mass spectrum;
- Only 4 types of protons exist in **F**;
- Compound **F** has a twofold symmetry axis.

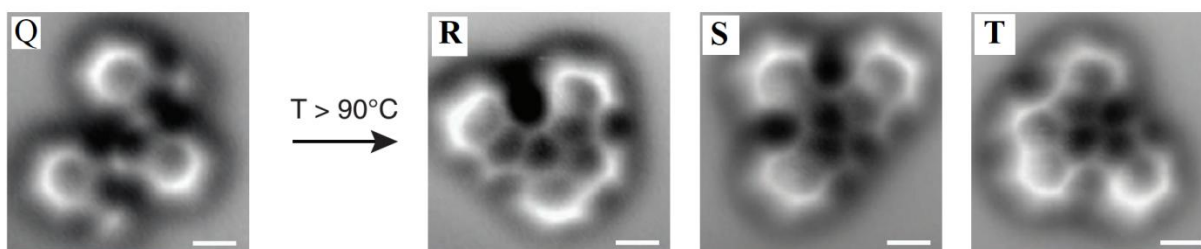
The beauty of such systems is that for finite chains like these, the lowest spin excitation energy, Δ_{LEE} , is inversely proportional to L :

$$\Delta_{\text{LEE}} \leq J \frac{2\pi^2 S^2}{L}$$

where J is an exchange coupling parameter between the nearest neighbours, S is a spin number, and L is the number of repeating units in the quantum chain. Therefore, for a considerably large L , we can design spin fluids with a very low excitation gap, which can be considered gapless.

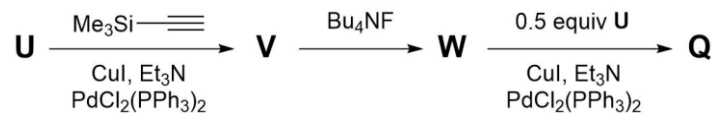
4. **Calculate** the value of L for which the quantum chain **H** becomes gapless at room temperature ($T = 298$ K), i.e. Δ_{LEE} becomes comparable with the average thermal energy $k_{\text{B}}T$. Use $J = 38$ meV and $S = 1$.

AFM can be used to study the transformation of individual molecules during complex transformations. AFM was performed for the products of the thermally induced isomerisation reaction of **Q**. It is known that compound **S** has a twofold symmetry axis, **R** and **T** contain only 5- and 6-membered fused rings.



5. **Draw** the structures of **R–T**.

The molecule **Q** itself is obtained from **U** according to the following scheme:



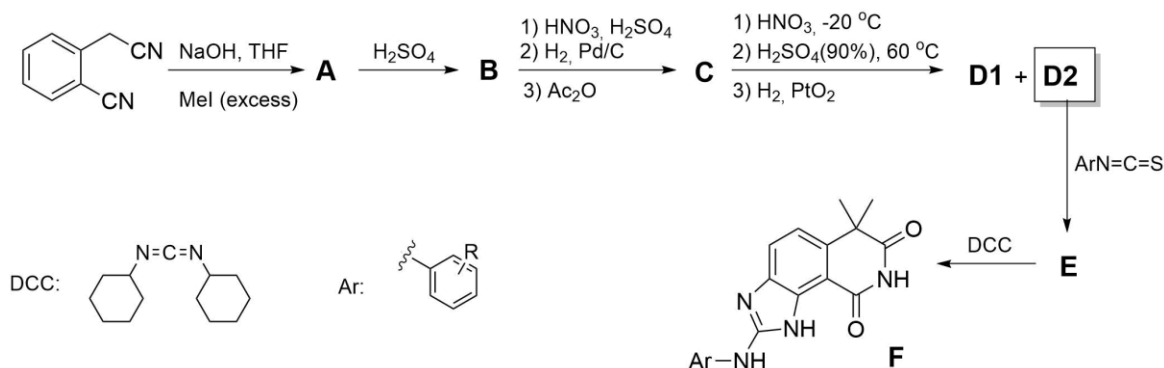
Additionally:

- In the mass spectrum, compound **U** has a molecular ion cluster of three peaks at m/z 234, 236, and 238 in an intensity ratio of 1:2:1;
 - **U** has 2 types of protons in the aromatic region.
6. Based on the given AFM image and additional hints, **draw** the structures of **Q** and **U–W**.

Problem 16. Kinase inhibitors

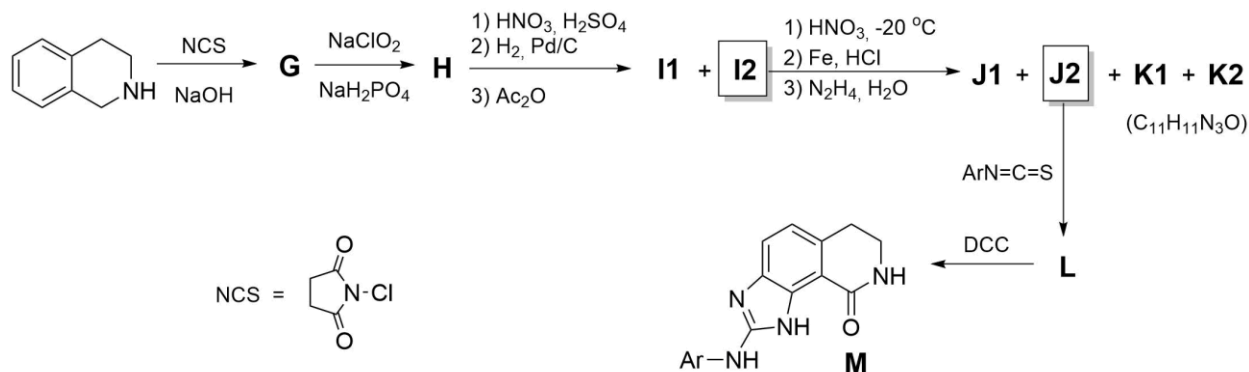
Kinases are enzymes controlling many processes in living things, including cell growth. Kinase inhibition has become an important direction for anticancer drug development. Two synthetic approaches to the class of *Lck*-kinase inhibitors are discussed.

A synthesis of promising inhibitor **F** is shown below:



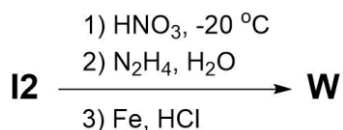
- Draw** the structures of compounds **A–E**. Note: Nitrogen content (by mass) in **B** is 7.40%. **D2** is separated from **D1**, and only **D2** is transformed into **F**.

Another promising molecule **M** was synthesised. Compound **M** has a similar core to **F** but has a molecular mass lower than that of **F** by 42 atomic mass units. The first two steps were a benzylic oxidation by *N*-chlorosuccinimide and oxidation by NaClO_2 . The transformation of **H** to **I1** and **I2** proceeds in the same manner as **B** to **C**, but with the formation of a mixture of isomers. The transformation of **I2** to the desired product **J2** is analogous to the conversion of **C** to **D2**. However, the order of the hydrolysis and reduction steps is switched. This change in order results in the formation of additional side products **K1** and **K2**.



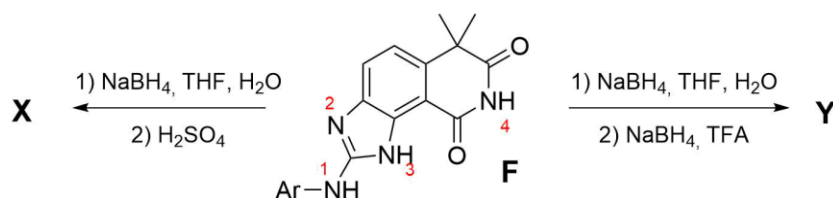
- Draw** the structures of **G–L**, including all isomers shown on the scheme.
- Explain** why only one product is formed during the reaction of **B**.

In the reaction of **I2** to **J2**, changing the order of the reduction and hydrolysis steps compared to the previous scheme was crucial to obtain **J**. The compound **W** could have formed following the sequence with the original order.



4. **Draw** the structure of product **W** (21.52% nitrogen by mass).

The molecules obtained showed high potency with a specific kinase enzyme. However, two transformations of **F** were also carried out to give molecules **X** and **Y**, the molecular formulae of which differ only by two hydrogen atoms.



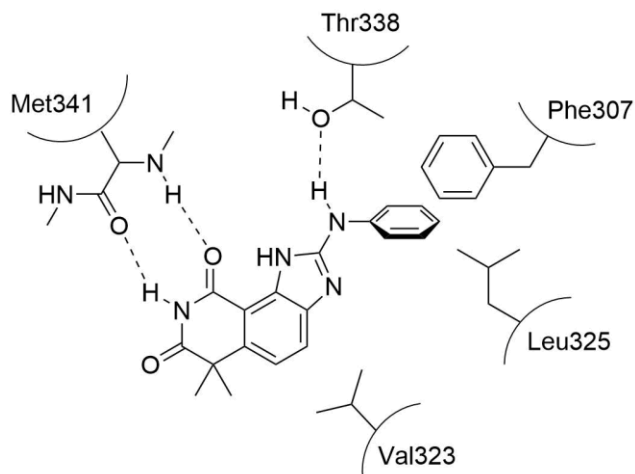
5. **Draw** the structures of **X** and **Y**. **Y** is a homologous compound to **M**. Note: The number of *sp*²-hybridised carbons in **X** increased by one.

The synthesised molecules were evaluated by IC₅₀ (half-maximum inhibitory concentration), which is a quantitative measure that indicates how much of a particular drug is needed to inhibit *in vitro* a given biological process or biological component by 50%. The results are shown in the table below:

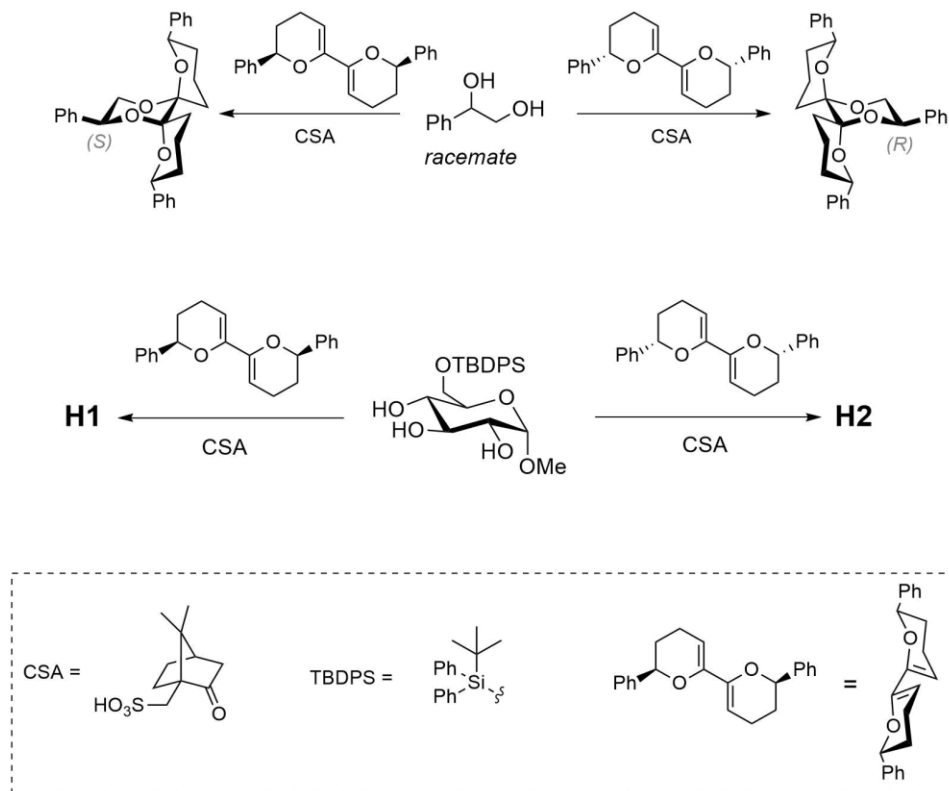
Compound	R	IC ₅₀ / μM
F	2,6-Cl ₂	0.46
F	2-Cl	>40
F	2,4-Cl ₂	>40
F	4-Cl	>40
F	2,6-Me ₂	0.46
F	2,6-Et ₂	>40

Compound	R	IC ₅₀ / μM
F (N3-Me)	2,6-Cl ₂	1.1
F (N1-Me)	2,6-Cl ₂	12.5
F (N4-Me)	2,6-Cl ₂	9.6
Y	2,6-Cl ₂	1.1
M	2,6-Cl ₂	0.38
X	2,6-Cl ₂	0.026

6. **Explain** the effect of the substituents in the aromatic ring if the coordination of **F** in a simplified enzyme pocket looks as follows:

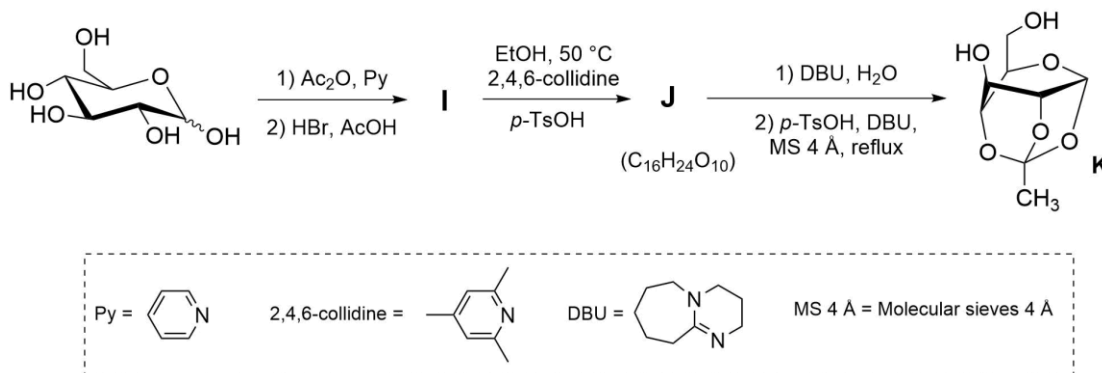


However, these transformations cannot differentiate neighbouring 2,3- and 3,4-diols, since in both cases the hydroxy groups are in a *trans*-configuration and occupy equatorial positions. A brilliant solution to this challenge was found by using the common tetrahydropyranyl protecting group in chiral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



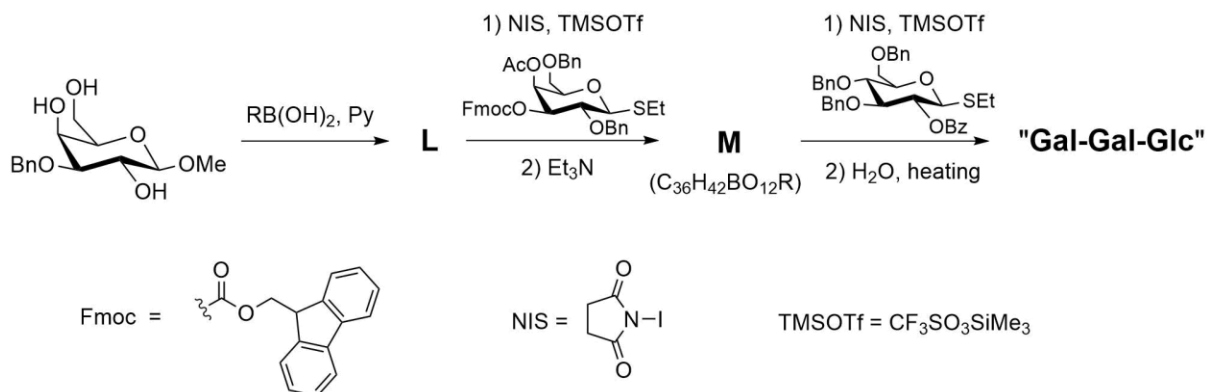
3. Based on the given example and considering that sterically bulky groups tend to occupy equatorial positions in chair conformations, **draw** the structures of **H1** and **H2**. For drawing **H1** you need to redraw the glucopyranose ring so that the 2,3-hydroxy groups are on the right side of the drawing. **Use** a chair conformation of the protecting group.

A very interesting example of a glucopyranose transformation led to adamantane-type cyclic compound **K** stepwise blocking three hydroxyl groups with only one protecting group:



4. **Draw** the structures of **I** and **J**.

Another class of reagents that can form cyclic acetal-type structures is boronic acids. Their chemistry was successfully used to synthesise the trisaccharide “Gal-Gal-Glc” derivative:



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

Problem 18. Inositol

In Uzbekistan, people greatly appreciate foods that are both rich in flavour and highly nutritious. Rice is one of the main ingredients in Uzbek cuisine and forms the basis of many traditional dishes, such as *pilaf* and *mastava*.

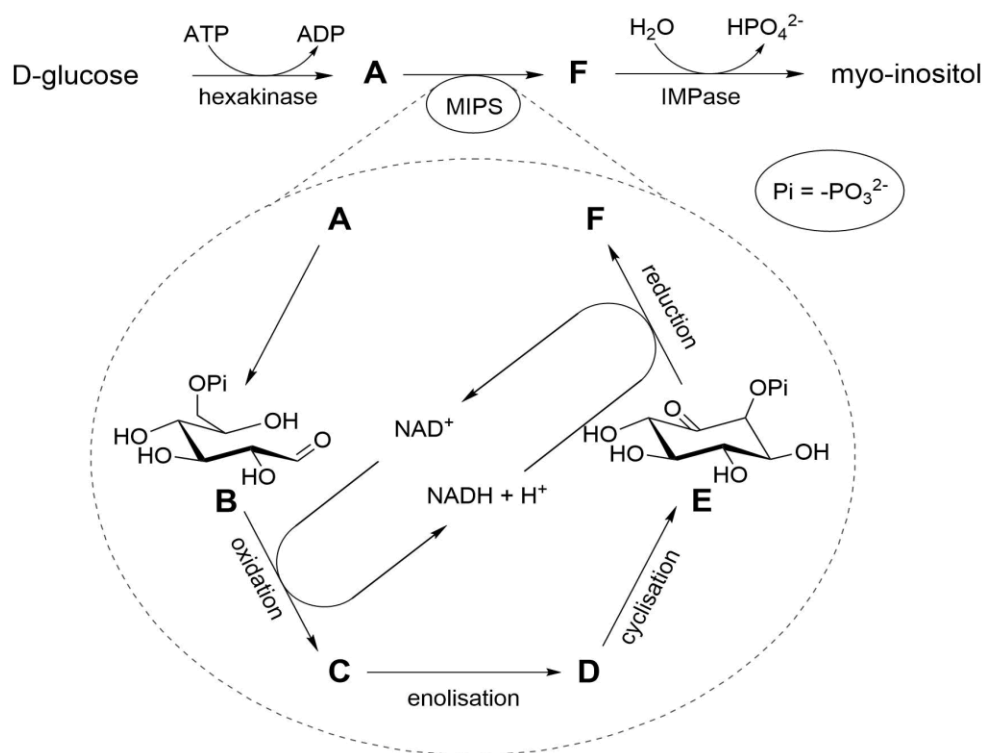


Cooked rice consists of approximately 29% carbohydrates by mass, primarily in the form of α -amylose, which is a polysaccharide composed of α -D-glucose units linked through $\alpha(1\rightarrow4)$ glycosidic bonds. Carbohydrates are the primary source of energy for humans and occur in nature in a wide variety of forms.

- Draw** the most stable chair conformation of D-glucose.
 - Draw** the structure of the repeating unit of α -amylose in Haworth projection.
- Calculate** the number of repeating units that one amylose chain with a molar mass of 243 kDa contains.

Glucose, which is a well-known representative of carbohydrates in living organisms, can be converted into many different biomolecules.

One such compound is **myo-inositol** (one of the isomers of inositol), whose biosynthesis pathway is shown below:



ATP = Adenosine Triphosphate, ADP = Adenosine Diphosphate

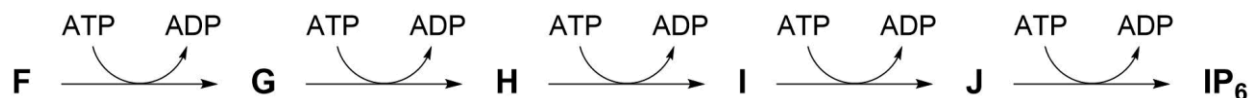
3. **Draw** one of the chair conformations for each of **A–F** and **myo-inositol**.

*Note: Molecules of **F** and **myo-inositol** contain a plane of symmetry.*

4. **Draw** the structures of all inositol stereoisomers and **indicate** which of them are chiral.

Many plants synthesise myo-inositol hexaphosphate (**IP6**) as a phosphorus storage compound. Studies of various plant species have revealed that the biosynthesis of **IP6** proceeds through stepwise phosphorylation of compound **F**.

Below is the biosynthesis pathway of **IP6** that occurs in *Dictyostelium*:



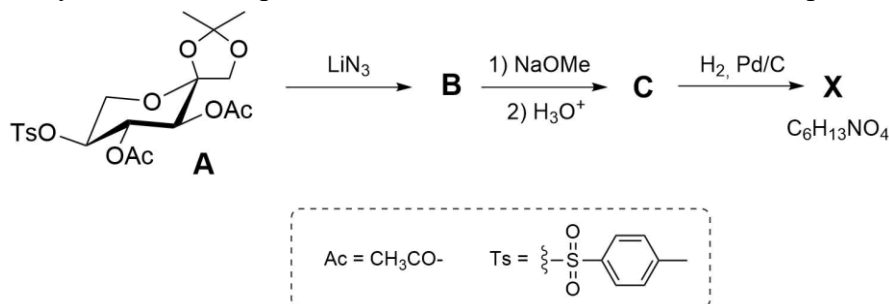
5. **Determine** the maximum number of **myo-inositol diphosphate (G)** isomers that can be formed in this pathway. **Draw** their structures and **indicate** which of them are chiral/achiral.
6. **Determine** the maximum theoretically possible number of isomers of **myo-inositol diphosphate** (that do not necessarily originate from **F**). **Draw** their structures and **indicate** which of them are chiral/achiral.

Phosphorylation of **myo-inositol** occurs according to the following rule: *the most distant accessible hydroxyl group relative to the previously phosphorylated hydroxyl group is phosphorylated.*

7. **Draw** the structures of **G–J** and **IP6**. **Indicate** the structures that contain a plane of symmetry.

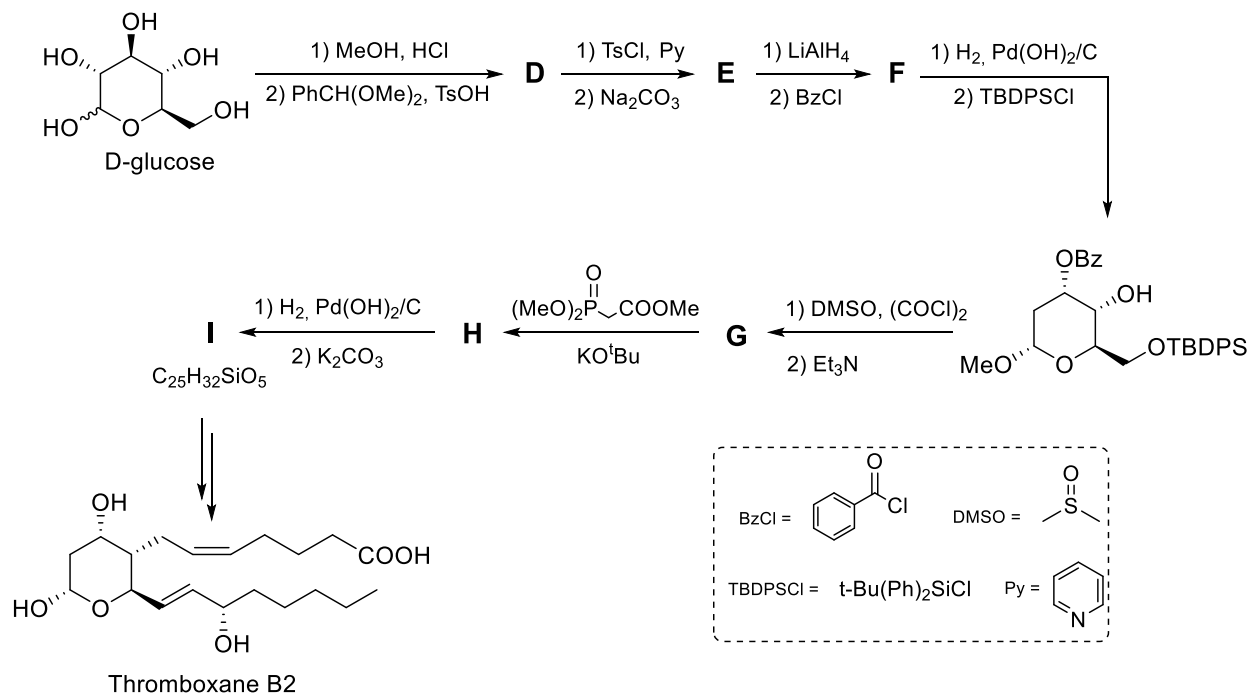
Problem 19. Carbohydrates as chiral pools

Asymmetric synthesis has attracted significant attention in recent years thanks to advances in asymmetric catalysis. However, using chiral auxiliary groups in the substrate structure remains an efficient approach for chiral total synthesis, especially when chiral substrates are readily available. Different monosaccharides are handy starting materials in natural product synthesis. For example, in 1985, the first synthesis of compound **X** from *L-sorbose* derivative **A** was published.



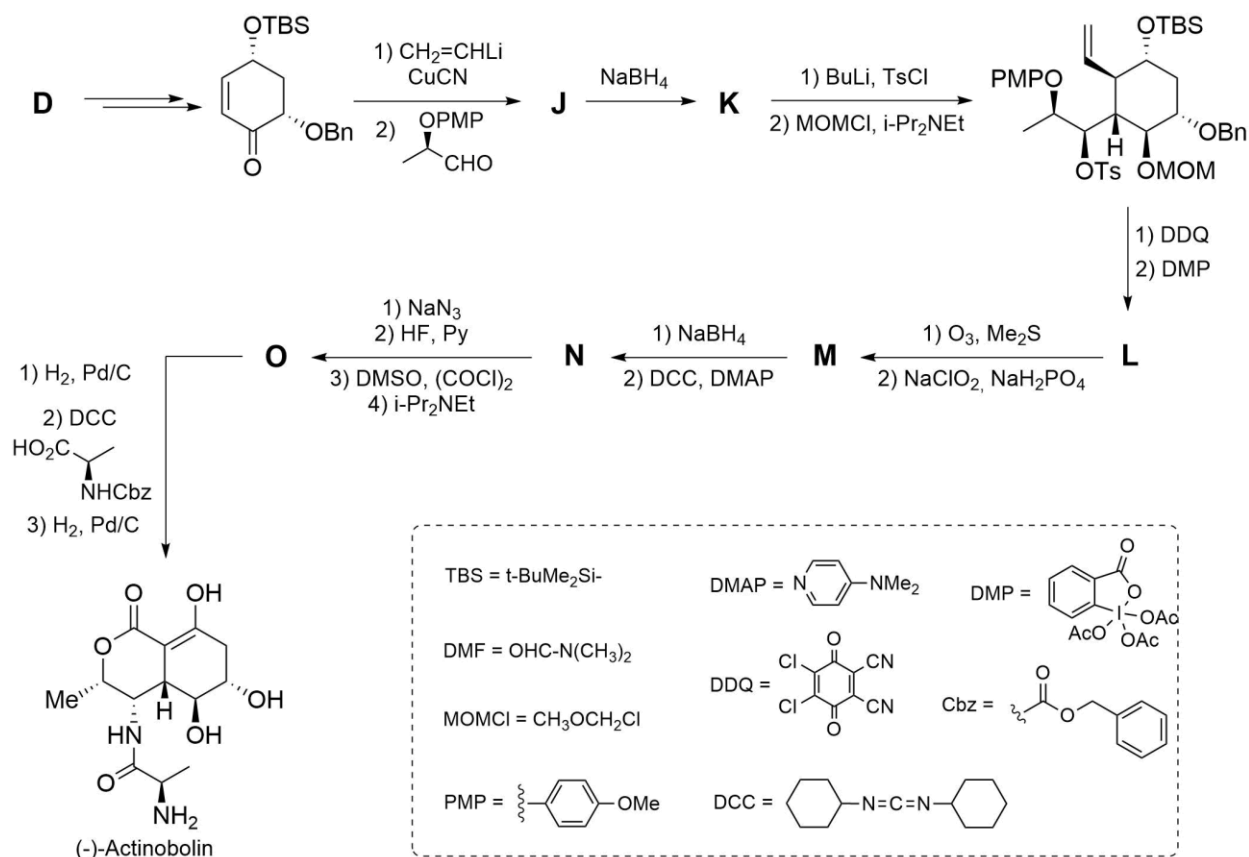
- Draw** the structures of compounds **B**, **C**, and the most stable diastereomer of **X**, including stereochemistry. *Note: X contains a five-membered heterocycle, and the formation of X proceeds through an imine intermediate.*

Thromboxane B2 (TxB2) is a stable, inactive breakdown product of *Thromboxane A2* (TxA2), a potent molecule that causes blood platelets to clump (aggregate) and blood vessels to constrict. It was synthesised from *D-glucose*. The following scheme shows the synthesis of key intermediate **I**.



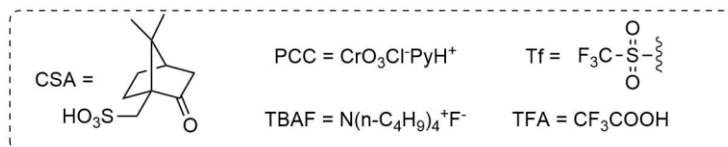
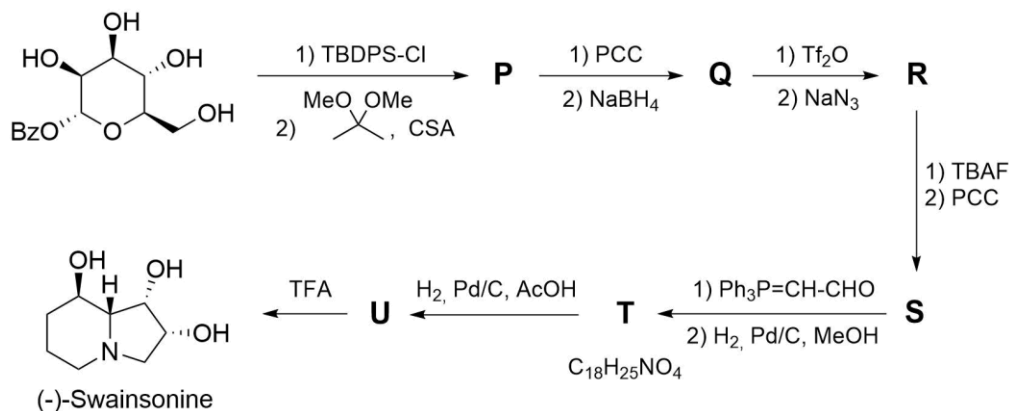
- Draw** the structures of **D–I** with stereochemistry. *Note: Acetal/ketal formation involves a primary alcohol when it is available.*
- Determine** in what order the following combinations of reagents (Z_1 – Z_4) must be used to obtain *Thromboxane B₂* from **I**:
 Z_1 – 1) PCC ($\text{PyH}^+\cdot\text{CrO}_3\text{Cl}^-$), 2) $\text{Ph}_3\text{P}^+\text{CH}^-\text{C}(\text{O})(\text{CH}_2)_4\text{CH}_3$;
 Z_2 – 1) BzCl , 2) BuN_4^+F^- ;
 Z_3 – 1) NaBH_4 , 2) K_2CO_3 , 3) HCl ;
 Z_4 – 1) $(i\text{-Bu})_2\text{AlH}$, 2) $\text{Ph}_3\text{P}^+\text{CH}^-(\text{CH}_2)_3\text{COOH}$, 3) CH_2N_2 .

Using compound **D**, it is possible to synthesise other chiral molecules. (+)-*Actinobolin*, isolated from the culture fluid of *Streptomyces*, has a broad antibacterial spectrum and moderate antitumor activity. In the synthesis of (+)-*Actinobolin*, overall, five new stereocentres were formed using the chiral auxiliary.



- Draw** the structures of **J–O**, including stereochemistry.

Swainsonine, an indolizidine alkaloid, was synthesised using benzyl- α -D-mannopyranoside. It is a potent inhibitor of Golgi apparatus α -mannosidase II, an immunomodulator, and a potential chemotherapeutic agent. The synthesis of (–)-*Swainsonine* is given below.



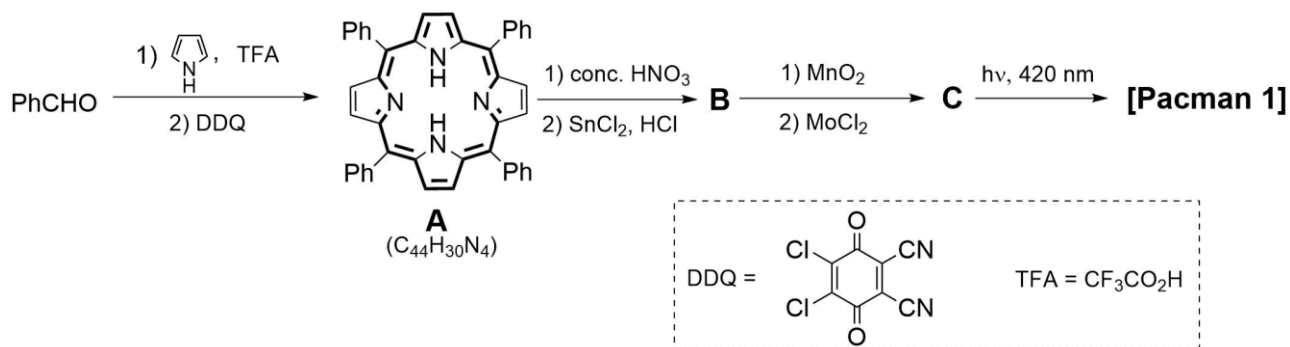
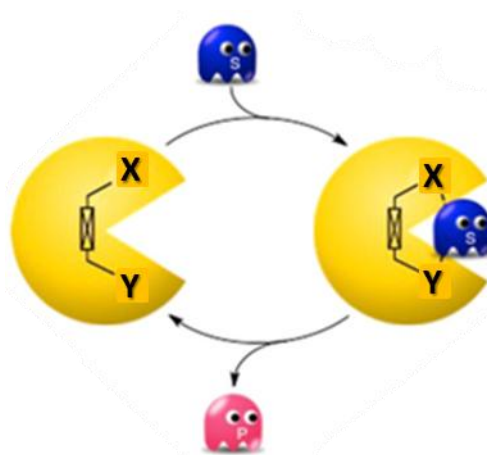
Hint: **P** and **Q** are epimers.

- Determine** the configurations of all stereocentres in (–)-*Swainsonine* and the starting material.
- Draw** the structures of **P–U**, including stereochemistry.
- Indicate** which stereocentres are preserved and which centres are newly formed.

Problem 20. Pacman, Hangman, Cageman

Scientists often look for analogies in culture to explain their discoveries. One example of such a comparison was the arcade video game *Pacman*, popular in the 1980s and 1990s, where the main task of the yellow ball (Pacman) is to eat all the dots on the map.

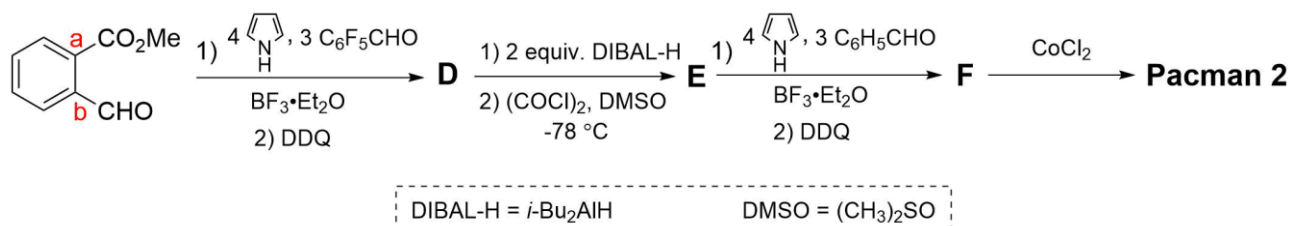
The same task must be performed by the molecules **Pacman 1** and **Pacman 2**, which must “eat” small molecules such as CO₂, N₂, or O₂, catalysing their transformations. Pacman molecules are two catalytically active structural fragments connected by a linker at a certain angle. Inspiration for such molecules comes from the active site of natural cytochrome P450, which contains a porphyrin macrocycle. Porphyrin is a macrocycle with an 18 π -electron Hückel aromatic system, which can coordinate metal ions in the middle. The synthesis of **Pacman 1** is shown below:



Note: C–H bonds of porphyrin rings are not involved in chemical transformations in this problem.

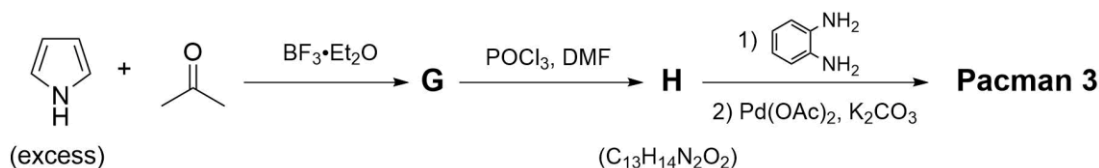
- Draw** the structures of compounds **B** and **C**, if it is known that neither of these compounds, nor **Pacman 1–2** contain oxygen. The nitrogen content (by mass) in compounds **B** and **C** is 11.12% and 9.70%, respectively.

Unfortunately, it was impossible to isolate **Pacman 1**. As a result, another approach to the stable **Pacman 2** with two different porphyrin rings was suggested. In the mass spectrum of this compound, the molecular ion peak was at m/z 1535.04.



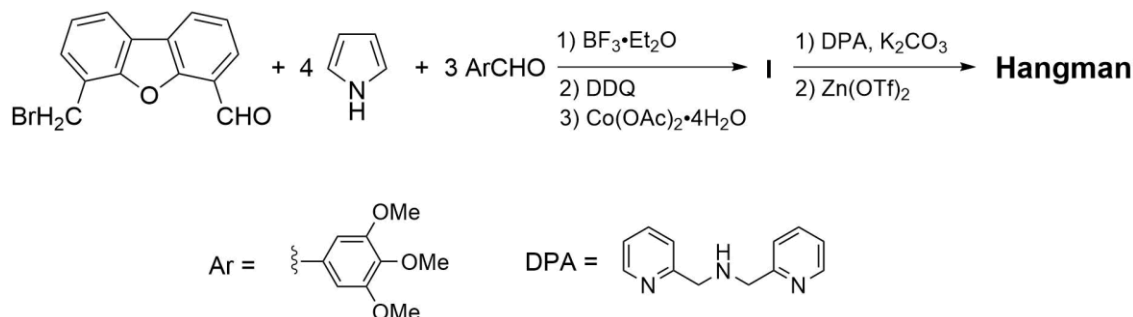
- Draw** the structures of compounds **D–F**, and **Pacman 1–2**. All molecules can be drawn flat. **Pacman 2** contains 7.678% of the metal by weight.
- Calculate** the distance between the two metals in **Pacman 2**, if the distance from carbon atoms a and b to the corresponding metals is the same and equals 4.7 Å. **Assume** that porphyrin and benzene rings are coplanar, and bond lengths and angles on benzene rings are ideal. *Note: The carbon–carbon bond distance in the benzene ring is 1.39 Å.*
- Draw** a 3D schematic structure of **Pacman 2** binding an oxygen molecule. *Note: You can simplify the macrocycle as a quadrilateral, only drawing out the linker and metals.*

Another version of a binuclear complex was synthesised as follows to yield **Pacman 3**:



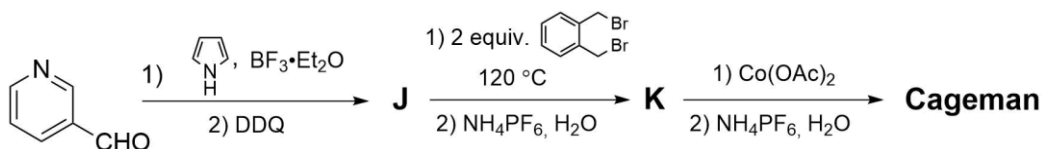
- Draw** the structures of compounds **G–H** and **Pacman 3**.

In the catalytic centre of cytochrome *c* oxidase, heme (a porphyrin-based iron-containing compound which forms the non-protein part of haemoglobin) and Cu atoms are placed in close proximity to ease the reduction of oxygen to water. Scientists attempted to mimic this pocket by synthesising a salt called **Hangman**, bearing two different metal ions:



- Draw** the structures of **I** and **Hangman**.

Another type of binuclear porphyrin complexes can be called **Cageman**. One of the examples of a **Cageman** synthesis is shown below. In the mass spectrum of the compound **K**, a series of signals at m/z 2667.0, 1261.0, 792.3, 558.0, and 417.4 were detected.

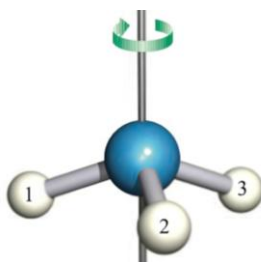


- Calculate** the molecular weight of **Cageman** (use integer values of atomic mass).

Problem 21. Catalyst C

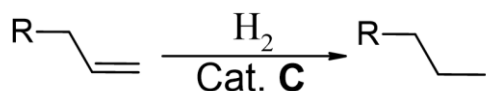
Compound **A** is a trihydrate which contains a metal of the 5th period, **M**, with a mass fraction of 39.09%. A 2.00 g sample of **A** was dissolved in ethanol. This ethanolic solution of **A** was added to an ethanolic solution of 7.96 g **B**. Compound **B** is a well-known ligand, which is composed of three elements: C, H, and P. It has 11.81% of P by mass and a threefold symmetry axis. The resulting mixture was refluxed for about two hours, yielding 6.18 g of a dark red compound **C** with 88% yield.

Note: A threefold symmetry axis is an imaginary line through an object around which it can be rotated by 120° and appear unchanged. For example, a threefold symmetry axis is present in the molecule of ammonia:



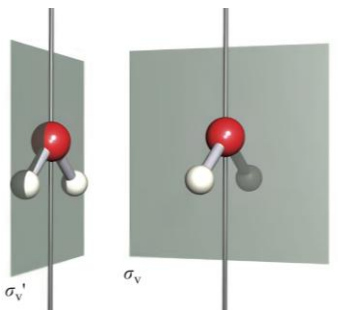
1. **Identify** the formulae of **A–C** and **M**, if each coefficient in the synthesis reaction is lower than 5.
2. **Write** the equation for the synthesis of compound **C**.

Compound **C** is a well-known catalyst in the hydrogenation of alkenes:

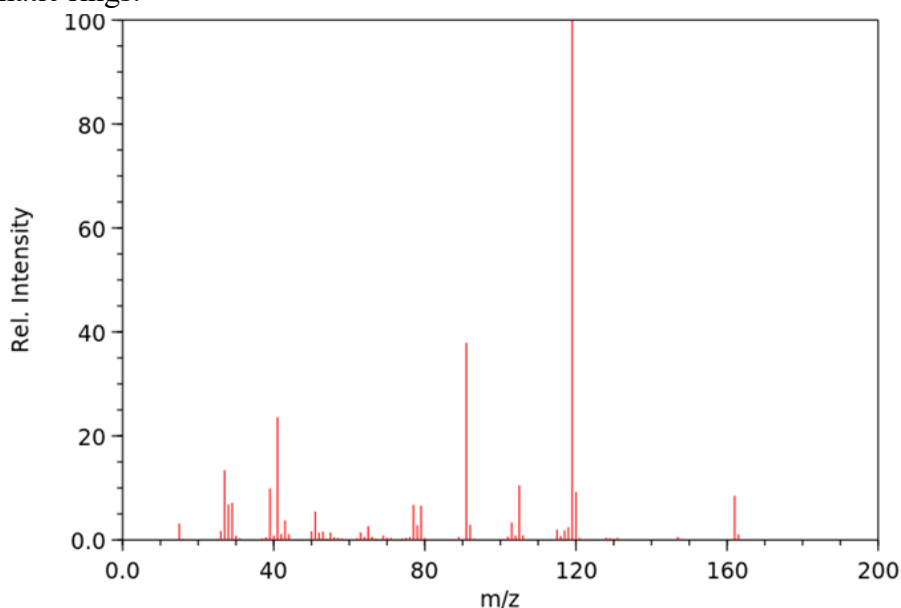


One example of the **product** ($\text{R}-\text{CH}_2-\text{CH}_3$) has a maximum of one plane of symmetry.

Note: A plane of symmetry is an imaginary plane that divides an object into two mirror-image halves. For example, the molecule of water has two planes of symmetry:

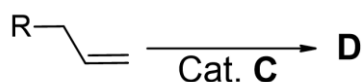


The mass spectrum of this **product** is shown below. The three peaks at m/z 41, 91, and 119 are noticeably more intense than the others, and two of them correspond to fragments containing different aromatic rings.



3. **Draw** the structures of the cations that correspond to those 3 peaks.
4. **Draw** the structure of the **product**.
5. **Find** the intensity ratio $[M]^+:[M+1]^+$ in the mass spectrum if the relative atomic mass of carbon is 12.011 and it consists of two stable isotopes.

In the catalytic system, a minor product **D** can be formed according to the reaction:

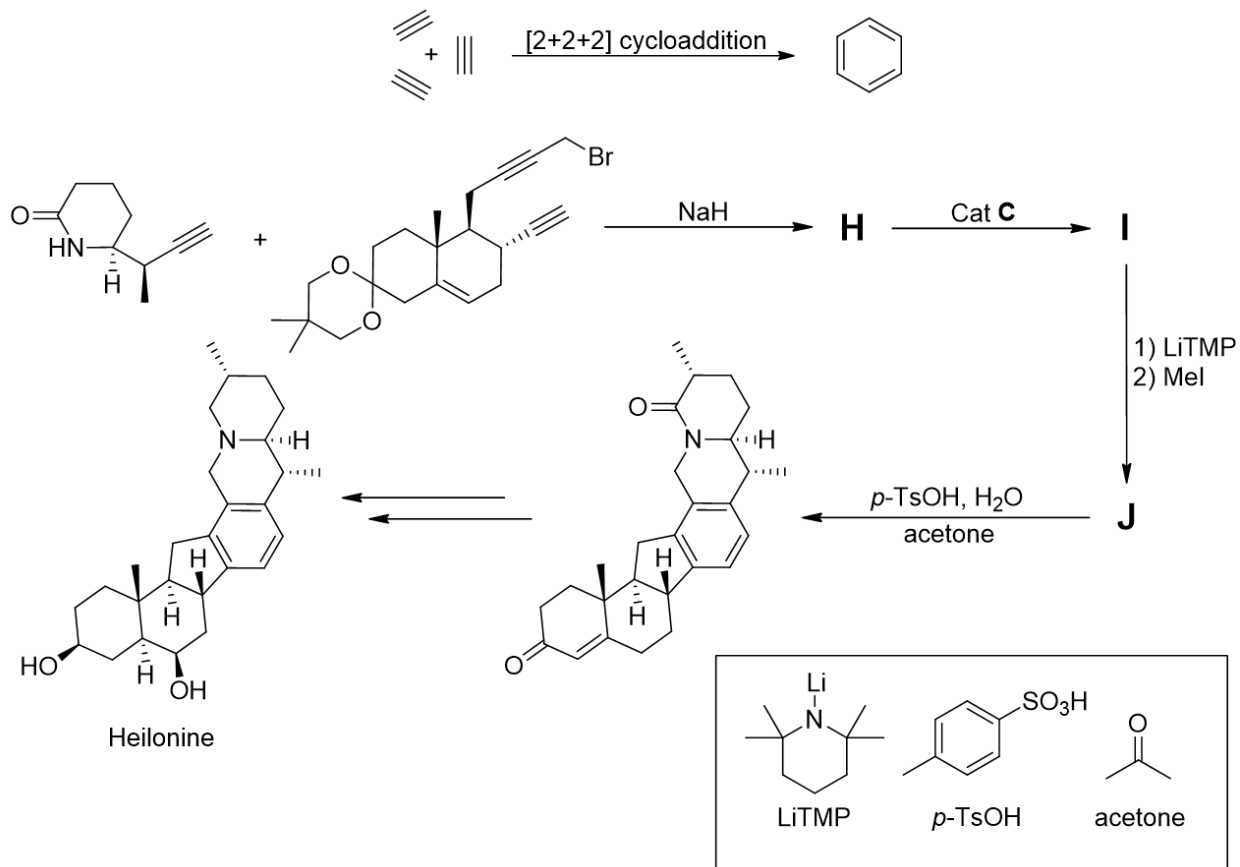


6. **Draw** the structure of **D** (you do not have to show stereochemistry).

After several catalytic cycles, the catalyst loses its activity due to the decomposition of **C**, forming products **F** and **M**. **F** is produced by the oxidation of **B** with atmospheric O_2 .

7. **Identify** the formulae of **F** and **write** the equation for the oxidation reaction of **B**.

Catalyst **C** can catalyse other types of reactions. For example, **C** was used to catalyse a [2+2+2] cycloaddition reaction in the synthesis of Heilonine:



8. **Draw** the structures of **H–J** (you do not have to show stereochemistry).

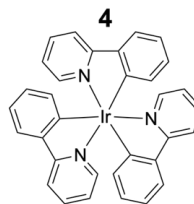
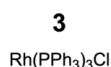
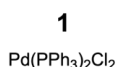
Problem 22. Transition metals in organometallic catalysis

Organometallic chemistry studies various aspects of compounds containing a metal–carbon bond. Many transition metal (TM) complexes are of fundamental importance due to their role in industrial catalytic processes.

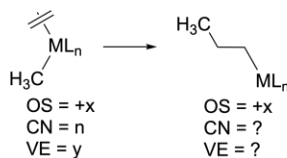
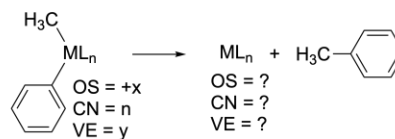
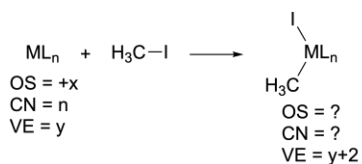
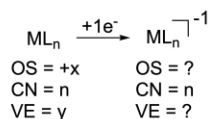
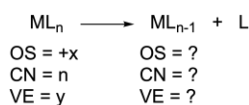
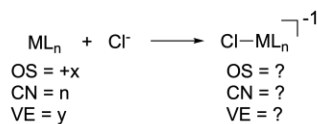
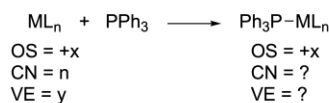
There are many parameters that should be considered when choosing a TM complex for a particular process, and four significant ones are:

- oxidation state (OS) of the metal in the complex,
- coordination number (CN),
- total number of valence electrons (VE), which is the sum of the number of the metal *d*-electrons and electrons provided by the ligands coordinated to the metal,
- overall net charge of the species that contains the transition metal.

1. For complexes 1–4, **calculate** OS, CN, and VE.

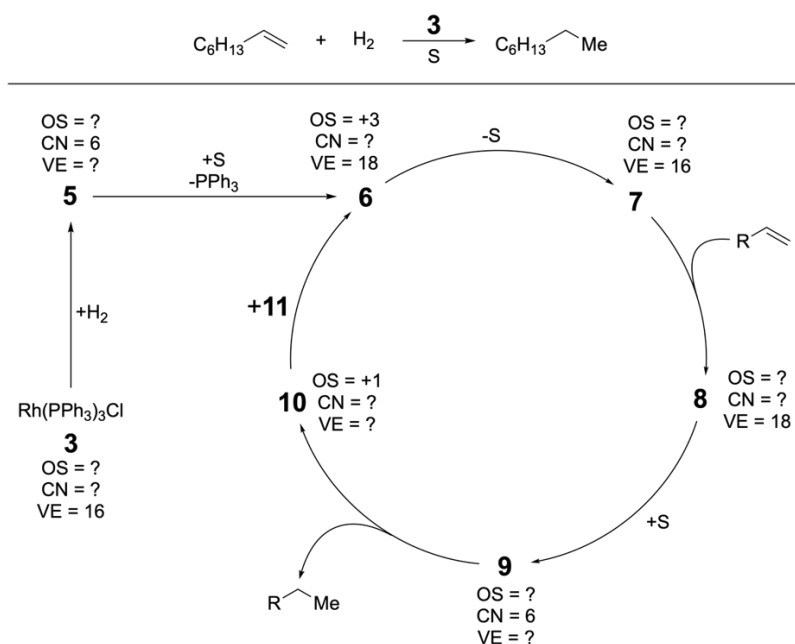


These parameters can change every time a TM complex undergoes different transformations. Below you can find the most important elementary steps that are essential for most TM-catalysed reactions.



2. **Find** the unknown parameters (OS, CN, VE) for complexes that underwent the mentioned elementary steps.

The parameters mentioned are quite important for catalytic transformations mediated by TM complexes. As such, **3** can catalyse the transformation of *n*-octene to *n*-octane via the catalytic cycle depicted below. S is a solvent that can coordinate to a metal with a pair of electrons.

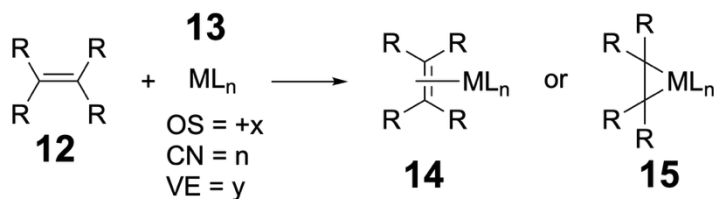


- Decipher** the structures **5–10** and **specify** the unknown parameters (OS, CN, VE) for them if the overall charge is zero for all the metal species.
- Determine** the structure of molecule **11**.

Oxidative addition of hydrogen can occur not only from complex **3**, but also from another complex. This complex is a neutral 14-electron species (which are generally more reactive), and it is obtained after one ligand leaves complex **3**. Thus, an alternative catalytic cycle can be proposed for the above transformation.

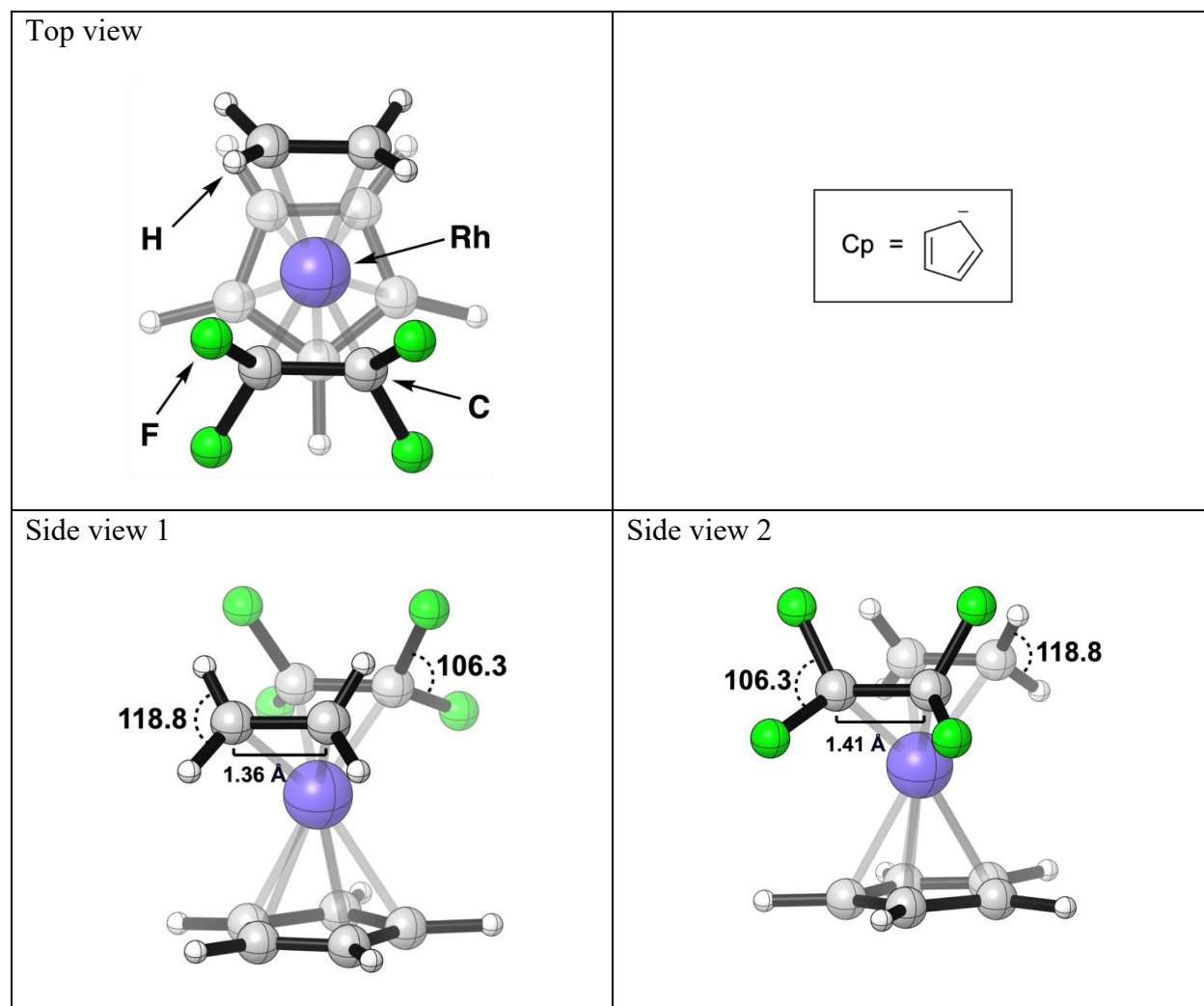
- Suggest** an alternative catalytic cycle that involves the aforementioned 14-electron complex. **Specify** the unknown parameters (OS, CN, VE) for the intermediates in your catalytic cycle (VE should be equal or greater than 14 for all the intermediates).

Some ligands can coordinate to metals in different ways. One example of such a case is the coordination of alkenes to a metal. Specifically, alkene **12** can coordinate to complex **13** without much disturbance of the C=C bond to produce **14** or via a metallacyclopropane mode to produce **15**.

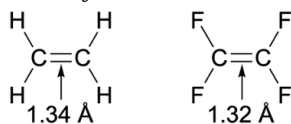


6. **Find** the unknown parameters (OS, CN, VE) for complexes **14** and **15** if the OS, CN, and VE are given for **13** in the scheme above.

The geometry of complex **16** $\text{RhCp}(\text{H}_2\text{CCH}_2)(\text{F}_2\text{CCF}_2)$ is shown below. The colour codes of the atoms are as follows: Rh – violet, C – grey, F – green, H – white.



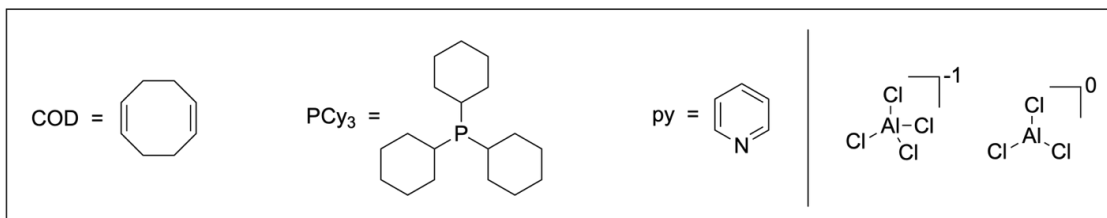
7. Based on this geometry, **find** the unknown parameters (OS and VE) for complex **16**.
Hint: the C–C bond lengths for free olefins are shown below.



8. **Specify** which mode of coordination is utilised by ethylene and tetrafluoroethylene in structure **16**. **Choose** from the following options:
- alkene coordination (similar to structure **14**);
 - metallocyclopropane coordination (similar to structure **15**);
 - no coordination.

Sometimes, the transition metal complex carries an overall charge (positive or negative).

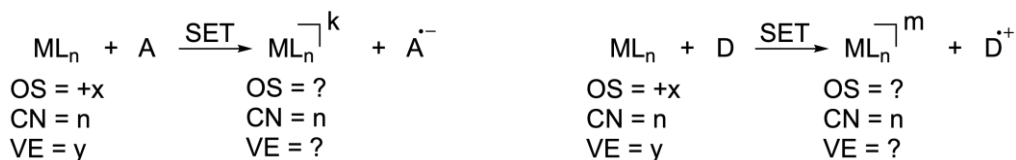
9. **Compare** the following two complexes: $\text{IrCl}(\text{PPh}_3)_3$ (**17**) and $\text{Ir}(\text{COD})(\text{py})(\text{PCy}_3)(\text{PF}_6)$ (**18**). **Calculate** the unknown parameters (OS, CN, VE) for **18** if OS, CN, and VE are the same for **17** and **18**. **Specify** the overall charge of the metal part with the charge as presented in the example below for AlCl_4^- and AlCl_3 .



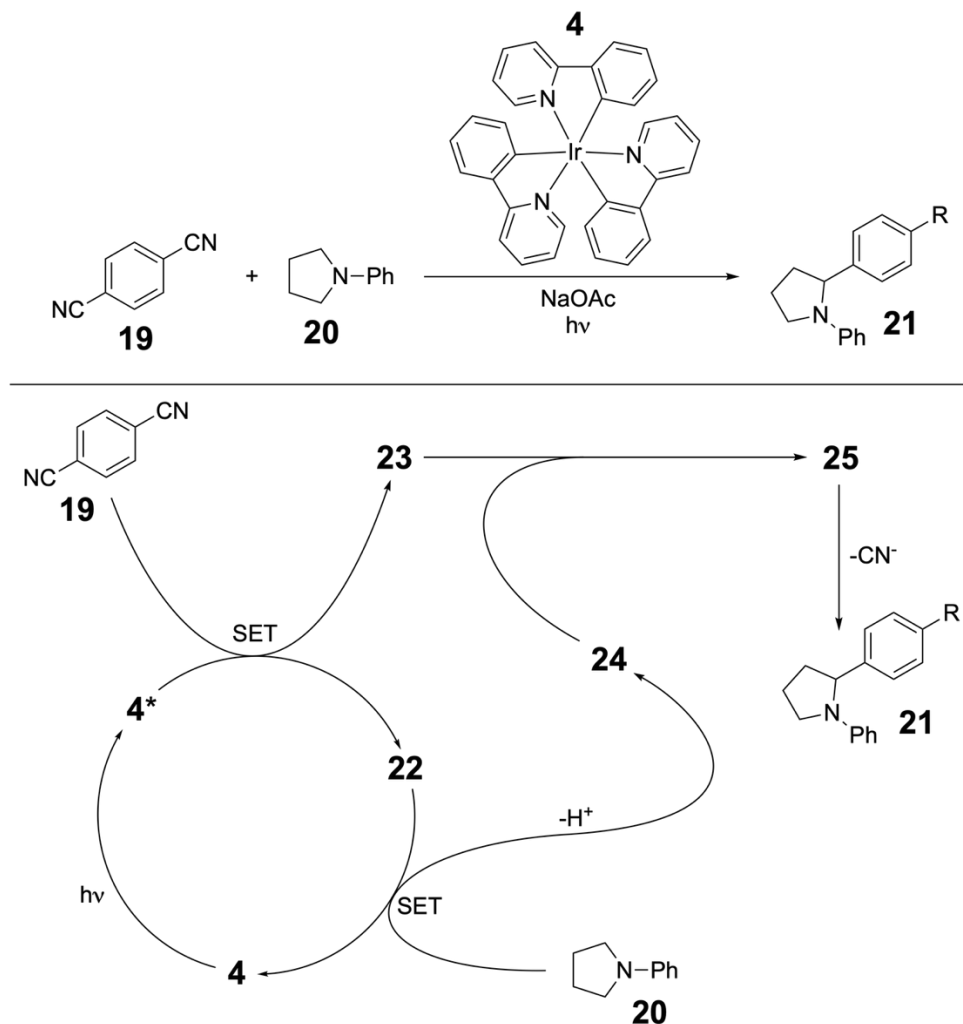
SET is a single electron transfer process and it is known that metal complexes can take part in it. An example of SET is shown below where donor D has a lone pair and during SET it gives one electron to acceptor A. This process produces a radical cation and a radical anion.



10. **Find** the unknown parameters (OS, CN, VE) for complexes below that underwent SET process. **Specify** overall charges k and m for the new complexes.



Some of metal complexes are useful photocatalysts. For instance, previously discussed complex **4** can be applied for C–H-functionalisation of tertiary amines such as **20** with electron poor arenes such as **19**. The catalytic cycle for the synthesis of **21** is shown below and it consists of two SET processes.

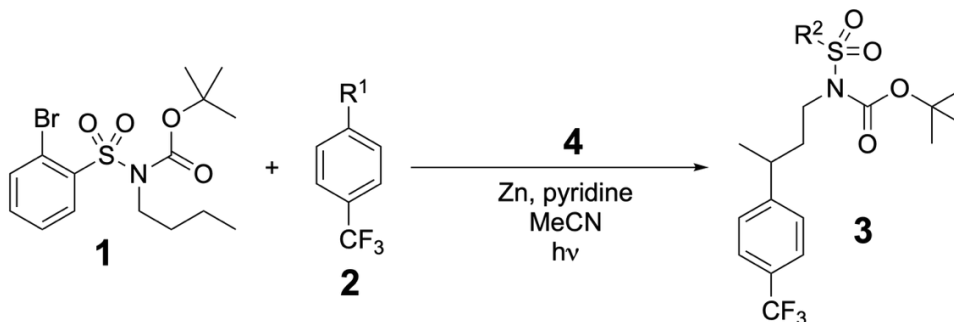


- 11. Indicate** which compound (**19** or **20**) is likely to be a donor in the SET process and which is likely to be an acceptor.
- 12. Determine** the unknown structures **22**–**25**. Intermediate **4*** is an excited state of complex **4**. **Calculate** OS, CN, and VE for **22**, and show the overall charge of **22**.
- 13. Identify** substituent R in product **21**.

Problem 23. HAT and XAT (HalAT)

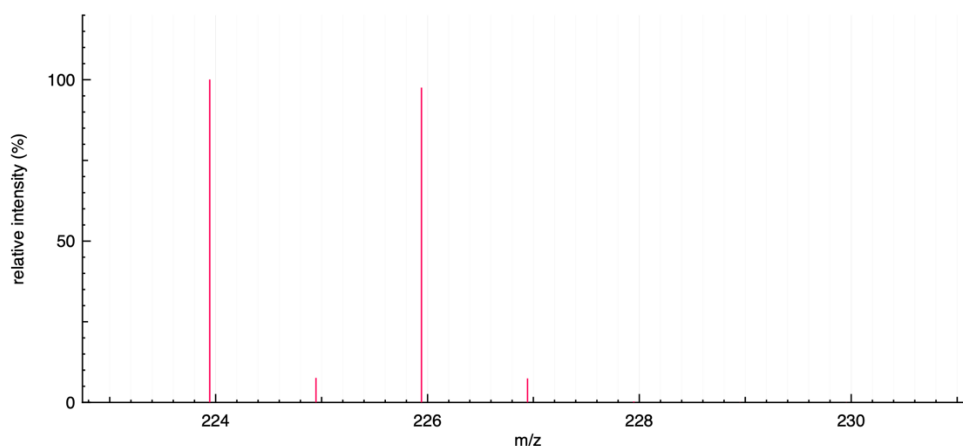
Note: Natural abundances of some isotopes are given at the end of the problem.

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.

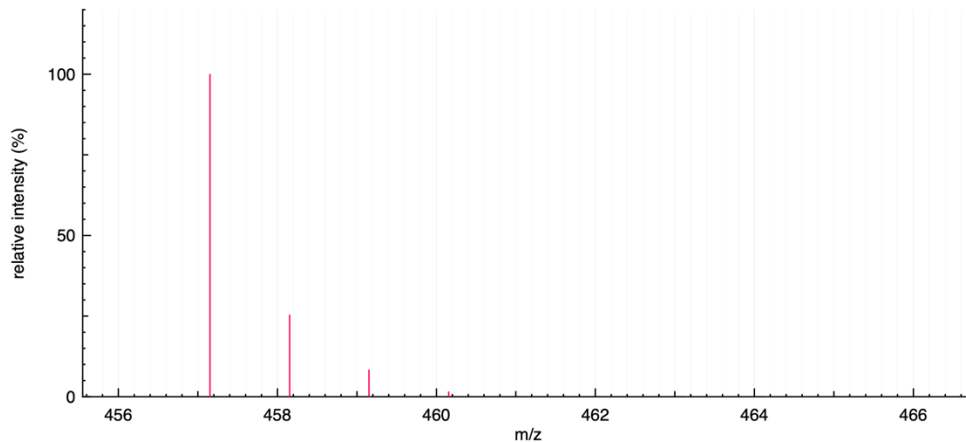


- The mass spectra (MS) of **2** and **3** are shown (electron impact ionisation method). **Determine** the structures of **2** and **3**.

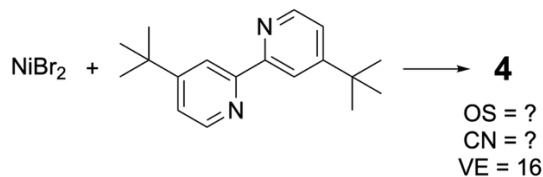
MS of **2**



MS of **3**

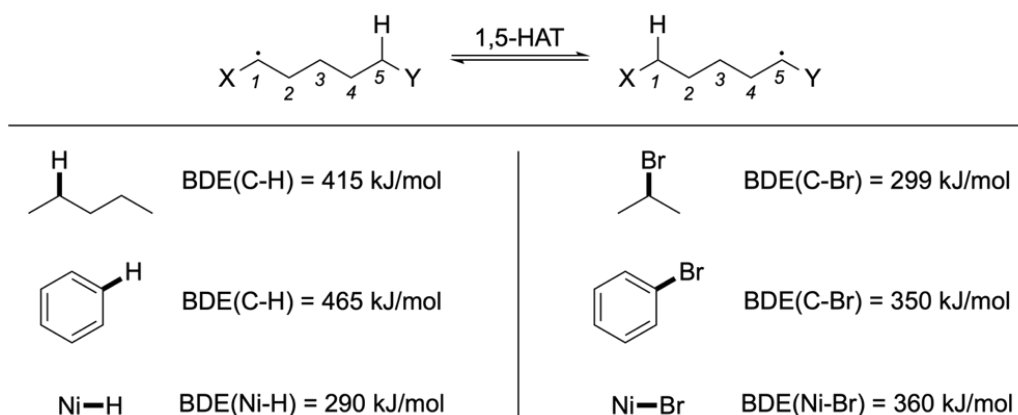


Complex **4** can be obtained via the following reaction. OS is the oxidation state of a metal in a complex; CN is the coordination number, and VE is the total number of valence electrons.

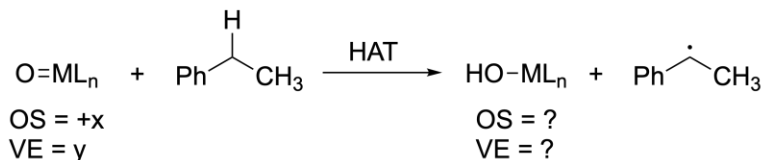


2. **Draw** the structure of **4** and **report** the OS and CN of the metal in it.

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.

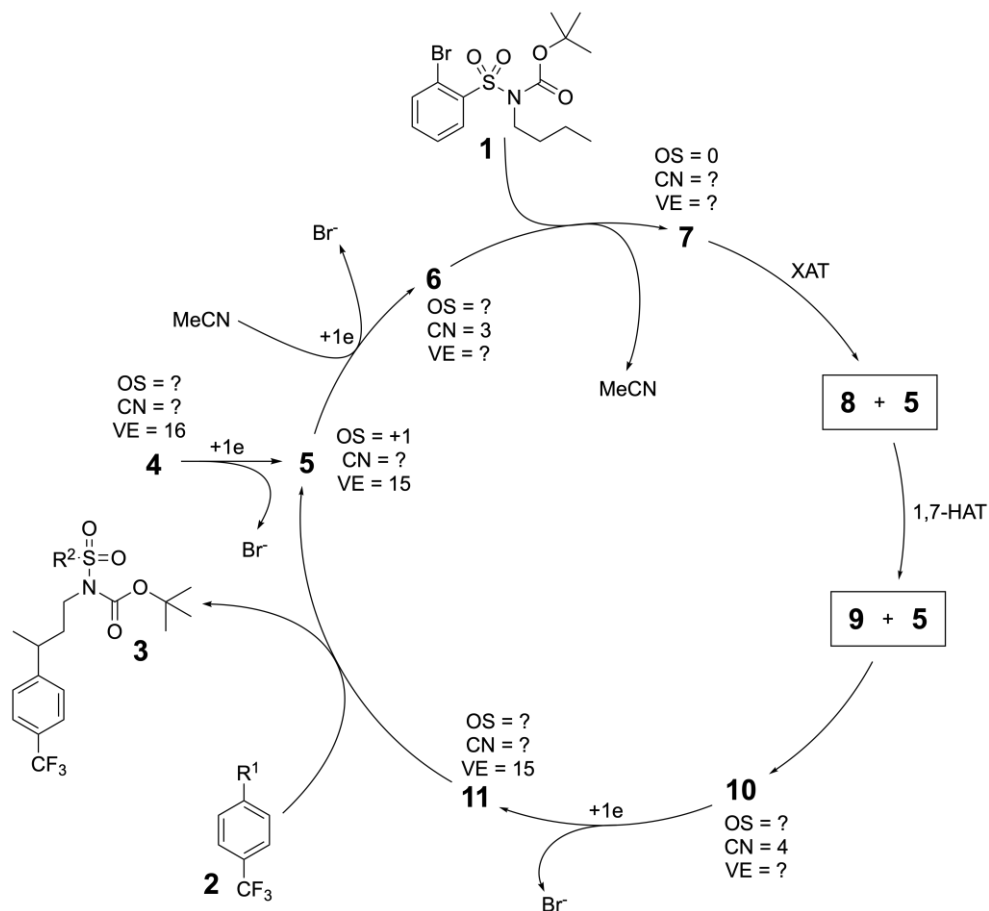


Metal complexes can participate in HAT and XAT processes. Two examples are given below:



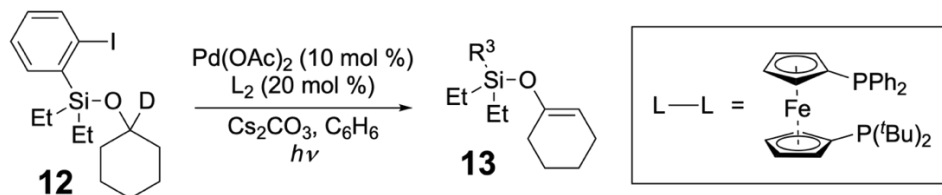
3. **Find** the missing parameters (OS, CN, and VE) for the complexes produced in HAT and XAT processes.

The catalytic cycle for the transformation of **1** and **2** to product **3** is described below:

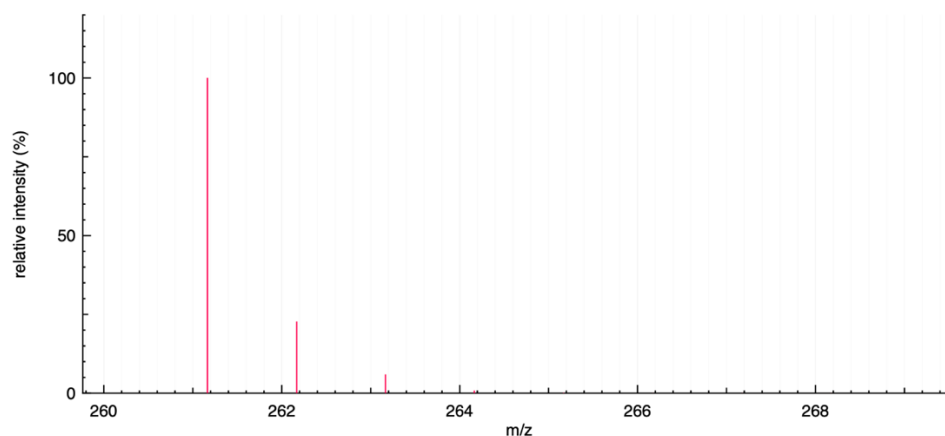


- Find** the structures of **5–11** in the cycle. For Ni-containing structures **5–7** and **10–11**, **find** the missing parameters (OS, CN, and VE).
- Analyse** the given reaction conditions for the synthesis of compound **3** and **determine** the electron donor in the above catalytic cycle.

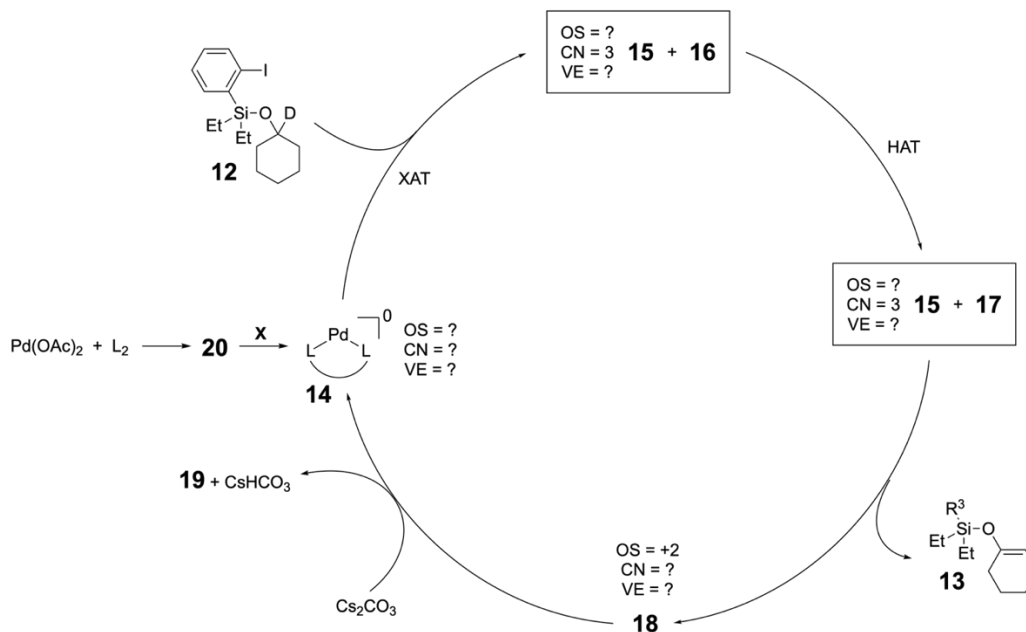
A conceptually similar catalytic reaction is a desaturation of silylated alcohols such as **12**. In the example below a deuterium label was installed for mechanistic studies.



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



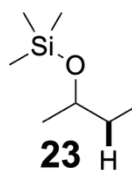
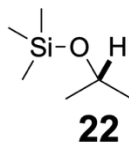
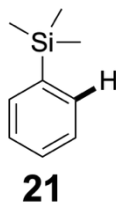
The catalytic cycle for the transformation of **12** into **13** is shown below:



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 / %
¹ H	99.9885
² H	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

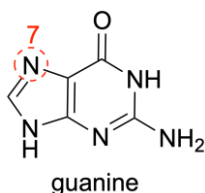
Problem 24. Anticancer complexes

The World Health Organisation reports that 20% of population will suffer from cancer in their lifetime. Today, cancer treatment is increasingly personalised being a combination of surgery, radiation, and chemotherapy with biomarker-guided targeted drugs and immunotherapies that can give long-lasting responses for some cancers. In this problem, we will consider some types of drugs used in cancer treatment.

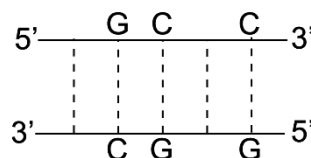
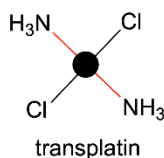
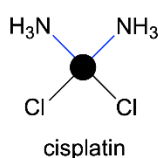
Part 1. Platinum complexes

Platinum complexes show antitumor activity by covalently binding to DNA, thus preventing its replication. The first-generation platinum drug, *cis*-diaminedichloroplatinum(II) (cisplatin), is efficient against cancer, whereas its *trans*-isomer (transplatin) is not. One reason for this difference is that cisplatin and transplatin form different types of crosslinks with DNA strands.

There are two possibilities for a complex to bind DNA: intrastrand and interstrand crosslinks through the N7 position of guanine. Intrastrand crosslinks form between two bases of the same DNA strand, while interstrand crosslinks connect one base from one strand to a base on the opposite strand.

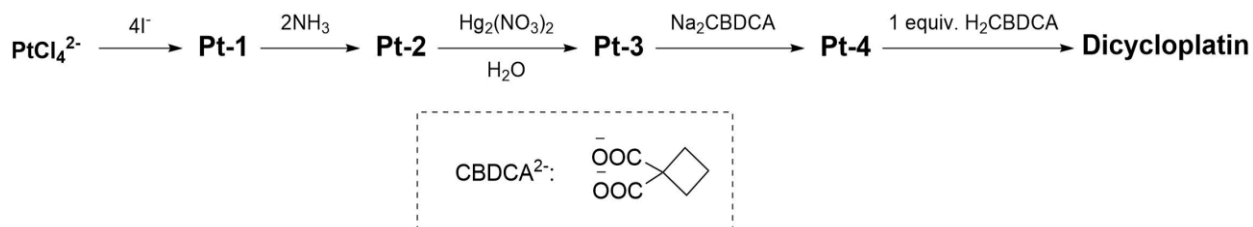


- Using the dot notation shown below, **draw** the intrastrand and interstrand crosslinks on the given DNA template. **State** the kind of crosslink that is formed by a) cisplatin; b) transplatin.



- Deduce** the effect of the formation of intrastrand and interstrand crosslinks on the melting temperature, T_m . T_m is the temperature at which half of DNA duplexes dissociate into single-stranded DNA.

Dicycloplatin, a third-generation platinum-based anticancer drug, was developed to reduce the dose-limiting toxicities that restrict the clinical use of cisplatin. Dicycloplatin crystals precipitate from a saturated aqueous solution containing **Pt-4** and 1,1-cyclobutanedicarboxylic acid (H_2CBDCA) in a 1:1 molar ratio. Dicycloplatin was found to have four hydrogen bonds in one structural unit.



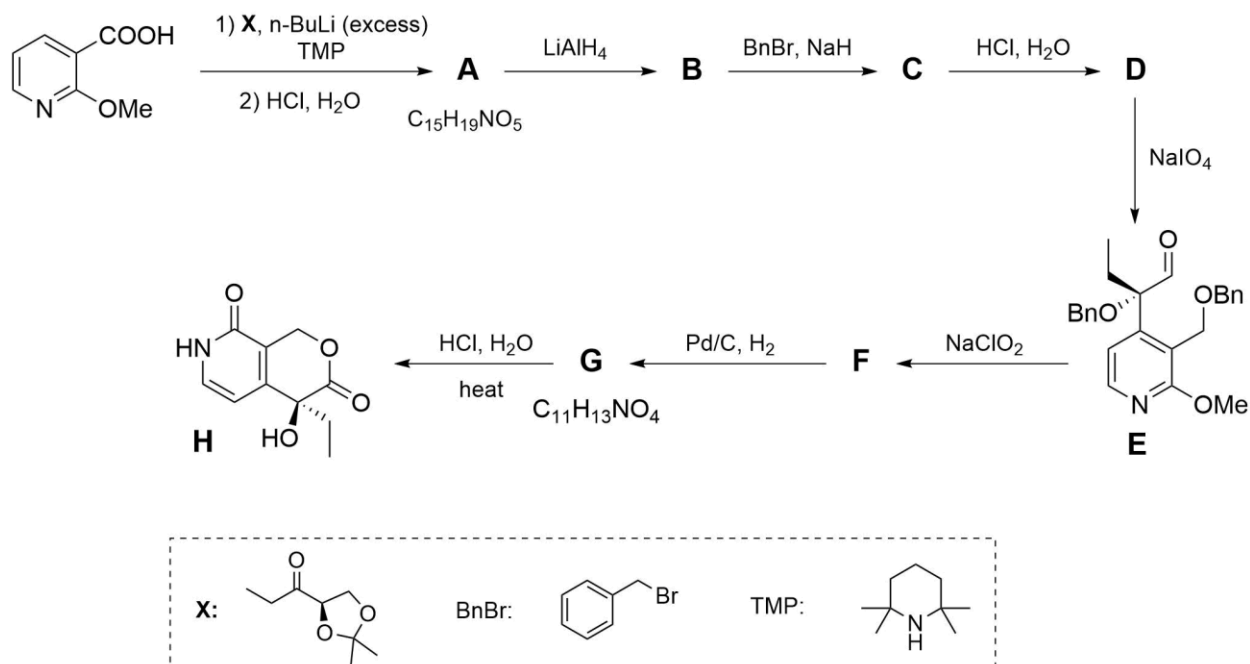
3. **Draw** the structural formulae of particles **Pt-1**, **Pt-2**, **Pt-3** and **Pt-4**. The mass percentage of platinum in PtCl_4^{2-} to **Pt-4** changes as 57.9% $\rightarrow$ 27.7% $\rightarrow$ 40.4% $\rightarrow$ 73.6% $\rightarrow$ 52.6%, respectively.
4. **Draw** the structural formula of dicycloplatin showing the hydrogen bonds.

Pt-4 (carboplatin) was introduced into clinical use in the late 1980s and has been widely used in cancer treatment. One practical challenge with platinum-based drugs is that, in aqueous solution, they can undergo hydrolysis, which may affect their stability and reactivity.

5. **Explain** which drug, **Pt-4** or dicycloplatin, is more resistant to hydrolysis in aqueous solution.

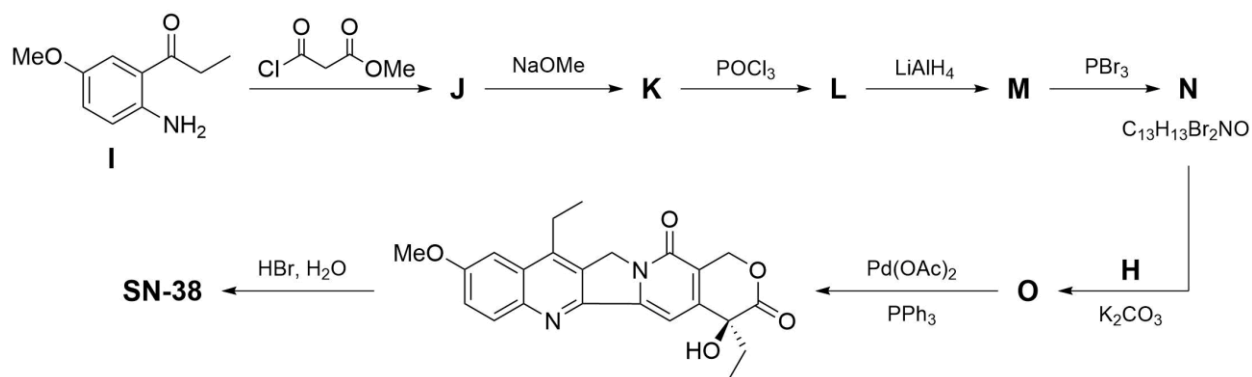
Part 2. Camptothecin and its derivatives

Alkaloid camptothecin and its derivatives form another group of drugs that show antitumor activity by inhibiting topoisomerase I, the enzyme that ‘untangles’ the DNA helix. Total synthesis of camptothecin derivative, **SN-38**, was carried out by coupling two building blocks **H** and **N**.



6. **Draw** the structural formulae of compounds **A–G** showing stereochemistry, if the step from **B** to **C** requires an excess of benzyl bromide.

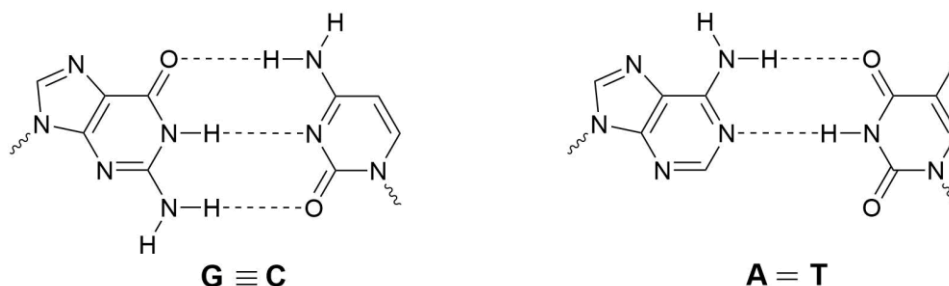
The second part of the synthesis is given below:



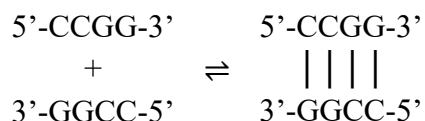
7. **Draw** the structural formulae of compounds **J–O** and **SN-38** showing stereochemistry where applicable.

Problem 25. The equilibria in DNA

A single-stranded DNA (ss-DNA) molecule can dimerise into a double-stranded one (ds-DNA) in the case that the ss-DNA is complementary to itself. Complementarity arises due to the ability of nitrogenous bases to form hydrogen bonds with each other. As shown below, guanine (G) forms three hydrogen bonds with cytosine (C), whereas adenine (A) forms two hydrogen bonds with thymine (T):



Tetranucleotide 5'-CCGG-3' can dimerise as follows:



1. **Deduce** how many tetranucleotides exist that are capable of dimerisation with pairing of all 4 nucleotides in the strands.

Dimerisation of tetranucleotide 5'-CCGG-3' was studied at different temperatures by measuring the absorbance, A , of solutions at 280 nm, with total initial concentration of single strands $[\text{ss-DNA}]_0 = 10 \mu\text{M}$. The results of the experiments were as follows: $A = 0.89$ at 10°C and $A = 1.17$ at 30°C .

2. **Calculate** $\Delta_r H^\circ$ and $\Delta_r S^\circ$ values for the dimerisation reaction of tetranucleotide 5'-CCGG-3', if they are independent of temperature and $\epsilon_{\text{ss-DNA}} = 2.44 \times 10^4 \text{ cm}^{-1} \cdot \text{M}^{-1}$, $\epsilon_{\text{ds-DNA}} = 2.93 \times 10^4 \text{ cm}^{-1} \cdot \text{M}^{-1}$ at 280 nm for tetranucleotide 5'-CCGG-3', $l = 5 \text{ cm}$.

The melting temperature of ds-DNA, T_m , is the temperature at which half of ds-DNA dissociates into ss-DNA.

3. **Calculate** T_m for the double strand of tetranucleotide 5'-CCGG-3' when the total concentration of single strands, $[\text{ss-DNA}]_0 = 10 \mu\text{M}$.

Another driving force for ds-DNA formation is the π - π -stacking between the nitrogenous bases in addition to hydrogen bonds. To estimate the contribution of the π - π -stacking to the stabilisation energy of ds-DNA, the dimerisation of oligonucleotides 5'-ACCGG-3', 5'-CCGGT-3', and 5'-ACCGGT-3' was investigated.

4. **Deduce** what dimers do oligonucleotides 5'-ACCGG-3', 5'-CCGGT-3', 5'-ACCGGT-3' form. **Draw** them schematically.

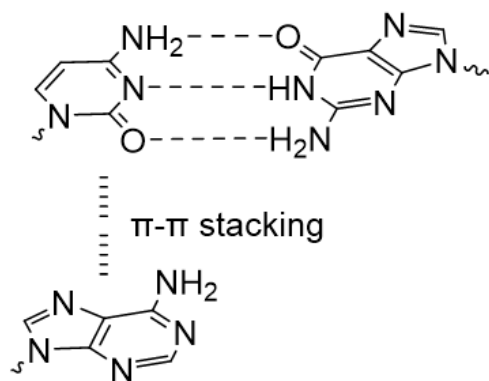
The T_m of these oligonucleotides has the following dependence on the total concentration of single strands:

$$\frac{1}{T_m} = k \times \ln[ss - \text{DNA}]_0 + b$$

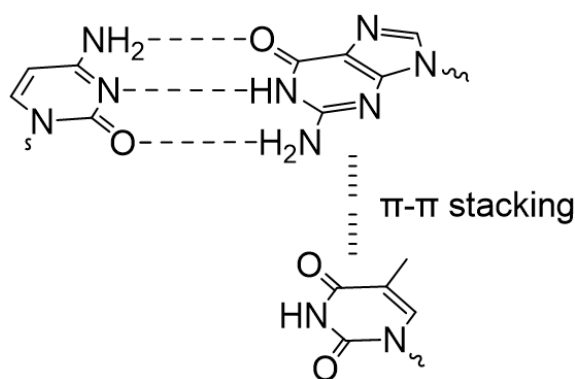
The following table shows k and b parameters for some oligonucleotides:

Oligonucleotide	k / K^{-1}	b / K^{-1}
5'-ACCGG-3'	-5.15×10^{-5}	2.76×10^{-3}
5'-CCGGT-3'	-4.80×10^{-5}	2.78×10^{-3}

5. **Calculate** the $\Delta_r H^\circ$ values for the dimerisation reactions of oligonucleotides 5'-ACCGG-3' and 5'-CCGGT-3', assuming they are independent of temperature.
6. **Determine** the π - π -stacking energies for A-CG and T-GC stackings (see figure below). **Assume** that there is no π - π stacking in ss-DNA.



A-CG π - π stacking

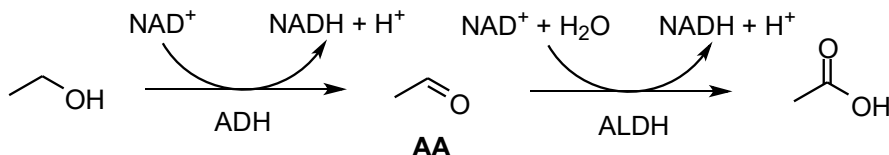


T-GC π - π stacking

7. **Predict** the $\Delta_r H^\circ$ value for the dimerisation reaction of oligonucleotide 5'-ACCGGT-3', if the total hydrogen bond energy in an A=T pair is $28842.0 \text{ J} \cdot \text{mol}^{-1}$.

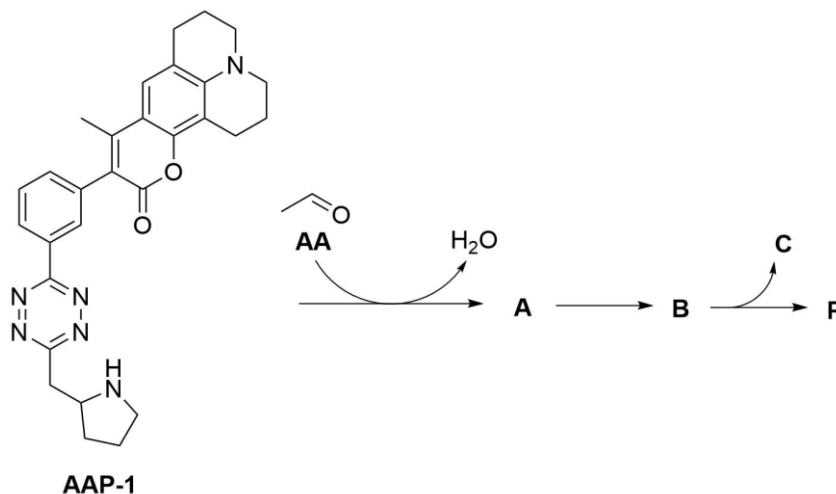
Problem 26. Sensing of acetaldehyde

Acetaldehyde (AA) is a reactive aldehyde primarily produced in cells as a metabolic intermediate during ethanol oxidation:

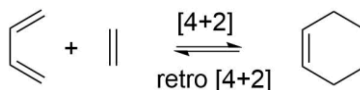


ADH – alcohol dehydrogenase, ALDH – aldehyde dehydrogenase.

Excess AA, often resulting from impaired AA detoxification, leads to aberrant DNA, protein, and/or lipid damage, and increases risk of diseases such as cancer, hepatitis, and cirrhosis. Recently, G. Li, C. Chang *et al.* reported the development of a highly selective method for the detection of AA in living cells. In this system, AAP-1 reacts with AA to form a fluorescent product **P** by the following mechanism:



A is an enamine, **C** is an inorganic byproduct, and **P** contains the same number of rings as AAP-1. The above mechanism includes [4+2] and retro [4+2] cycloaddition reactions:



- Draw** the structures of intermediates **A–B**, product **P**, and determine the inorganic byproduct **C**. Note: Molecular ions of AAP-1 and **P** in mass spectra have peaks with masses of 494 and 492, respectively.

Although biological fluids contain different types of aldehydes and ketones, **AAP-1** reacts only with **AA**.

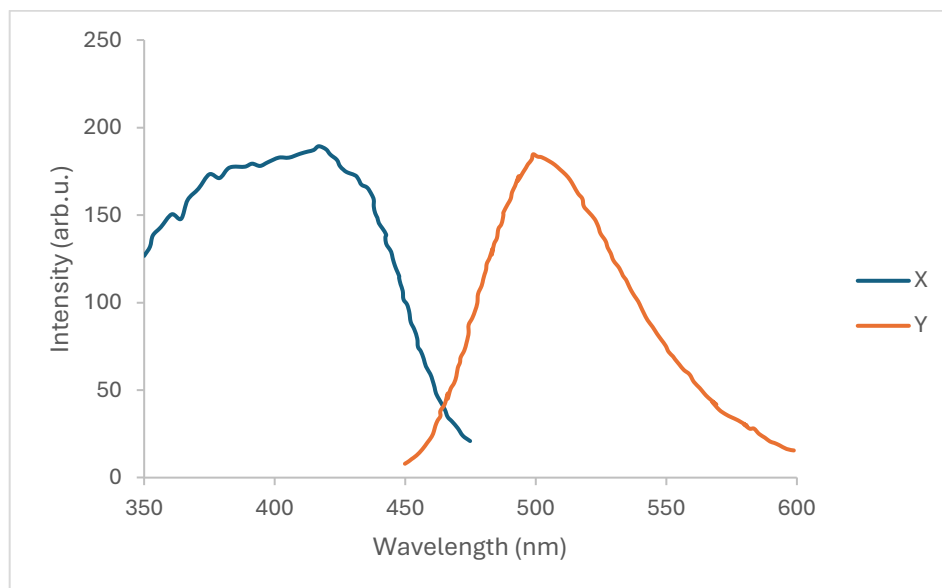
2. **Give** the reason why formaldehyde (methanal) and methylglyoxal (2-oxopropanal) do not react with **AAP-1**.

Aldehydes and ketones on relatively large molecules also do not react with **APP-1** due to the steric effects during transformation of enamine **A** to [4+2] cycloaddition product **B**. The following table shows the [4+2] cycloaddition reaction participants' Gibbs energies relative to reagents for **AA** (**A**, transition state #1 and **B**) and hexanal (**A'**, transition state #2 and **B'**):

Species	$\Delta G / \text{kJ}\cdot\text{mol}^{-1}$	Species	$\Delta G / \text{kJ}\cdot\text{mol}^{-1}$
enamine A	-8.36	enamine A'	-12.96
transition state #1	63.95	transition state #2	68.13
cycloaddition product B	-21.74	cycloaddition product B'	-19.23

3. **Calculate** the Gibbs energy changes ($\text{kJ}\cdot\text{mol}^{-1}$) for processes **A**→**B** and **A'**→**B'**. **Conclude** whether these reactions are spontaneous.
4. **Calculate** the ratio of the rate constants corresponding to the **A**→**B** and **A'**→**B'** transformations at 310 K. **Assume** that in both reactions pre-exponential constant is the same, and that activation energy is equal to activation Gibbs energy.

The excitation and emission spectra of product **P** are shown below:



5. **Match** the spectral lines **X** and **Y** with excitation and emission processes.

The fluorescence intensity, F , of **P** depends linearly on its concentration: $F = F_0 + k[\mathbf{P}]$. The following table shows the fluorescence intensities (in arbitrary units) of solutions with different concentrations of **P**:

$F / \text{arb.u.}$	92.50	97.50	102.50	107.50
$[\mathbf{P}] / \mu\text{M}$	10	20	30	40

6. **Calculate** the values of F_0 and k .

The lower detection limit of the fluorescence intensity of **P** is 90.65 arb.u. In the absence of ethanol, the concentration of **AA** can very quickly decrease due to enzyme ALDH ($r_{\max} = 4.1 \text{ mM} \cdot \text{min}^{-1}$, $K_M = 0.2 \mu\text{M}$).

7. **Calculate** the time needed (in seconds) for the fluorescence intensity of the product of **AA** with **AAP-1** to decrease from 137.50 arb.u. to 90.65 arb.u. in the absence of ethanol. *Note: ALDH obeys Michaelis–Menten kinetics.*

Adding inhibitors to cell cultures where the concentration of **AA** is determined using **AAP-1** affects the intensity of fluorescence:

Control (no inhibitor, no EtOH)	EtOH	EtOH + Fomepizole (ADH inhibitor)	EtOH + CVT-10216 (ALDH inhibitor)
F_1	F_2	F_3	F_4

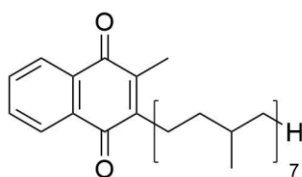
8. **Arrange** F_1 – F_4 in order of increasing fluorescence intensity.

Problem 27. Archaeal metabolism

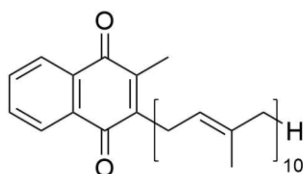
Archaea, along with bacteria and eukaryotes, constitute a distinct domain of living organisms. Archaea were previously grouped with bacteria, but this classification is now considered obsolete, as it has been established that archaea have their own independent evolutionary history and are characterised by many biochemical features that distinguish them from other life forms. Archaea appeared on Earth 3.5–4 billion years ago during the Archean Eon and have evolved continuously since then.

1. **Select** from the options provided a measurable, planetary-scale quantitative parameter that has not changed within reasonable accuracy throughout the entire evolution of archaea and to changes to which they can quickly adapt:
 - a) *Chemical parameters*: the concentration of a gaseous substance in the atmosphere (oxygen, nitrogen or carbon dioxide), the composition of the environment (reservoirs) as the ratio of various compounds (salinity, pH, buffer capacity), etc.
 - b) *Physical parameters*: temperature, atmospheric pressure, radioactivity, gravitational force, total luminosity of the Sun.

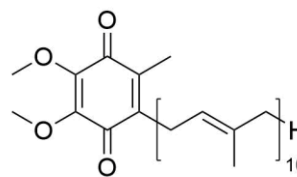
To demonstrate the differences between the three main domains of living organisms, one can cite as an example the quinone derivatives that play a role in oxidation-reduction processes in archaea (menaquinone MK-7), bacteria (menaquinone MK-10), and eukaryotes (ubiquinone, presented in the form of coenzyme Q₁₀, CoQ₁₀):



MK-7



MK-10

coenzyme Q₁₀

2. **Draw** the structure of the two-electron reduction product of MK-7.

The standard biochemical redox potentials, $E^{\circ'}$, of some redox pairs are given in the table below.

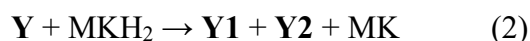
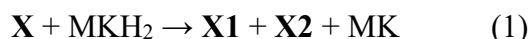
Redox pair	$E^{\circ'} / \text{V}$
$0.5 \text{ O}_2/\text{H}_2\text{O}$	0.82
cytochrome <i>c</i> (+3)/ cytochrome <i>c</i> (+2)	0.22
CoQ ₁₀ /CoQ ₁₀ H ₂	0.10
fumarate/succinate	0.03
MK-10/MKH ₂ -10	−0.07
acetaldehyde/ethanol	−0.20

3. Based on the information provided, qualitatively **explain** why menaquinone was displaced by ubiquinone in the ancestors of modern eukaryotes and is currently not found in eukaryotes, with a few exceptions.

Natural ubiquinol (reduced form of ubiquinone), obtained from eukaryotic cell culture, is a hydrophobic unsaturated compound that can be incorporated into the standard method for determining bromine value (strictly in the dark!).

4. **Suggest** at least two chemical structural features of natural samples of ubiquinol that distinguish it from, for example, the triacylglycerol of linoleic acid, often called linolein, and that should be considered when analysing the obtained results of interaction with molecular bromine.

The unique habitat of archaea, from their very inception, has led some species to possess an enzyme involved in the metabolism of extremely intriguing substrates – substances **X**, **Y**, and **Z**, which exhibit similar chemical properties. Thus, structural isomers **X** and **Y** react *in vitro* with menaquinol (MKH₂-7), catalysed by an enzyme commonly referred to as **Z**-reductase, according to the following reaction equations:



For the molar masses of unknown substances rounded to the nearest integer, three strict inequalities hold: $M(\text{X}) < 250 \text{ g/mol}$; $M(\text{X1}) > M(\text{X2})$; $M(\text{Y1}) > M(\text{Y2})$.

5. Using only the information above, **find** the upper limit of the range of possible integer molar masses of **X2**.

X1 and **X2** each contain 22% of element **E1** and 1.0% of element **E2** by mass, while **X** contains 23.4% oxygen by mass.

6. **Calculate** the percentage by mass of **E2** in **X** to the nearest whole number.
7. Without disclosing any elements other than **E2**, **narrow** the range of possible whole-number molecular masses of **X2** as much as possible, taking into account the mass fractions given above.
8. **Suggest** two potential explanations for the apparent logical inconsistency between the equal mass fractions of elements in two compounds despite different whole-number molecular masses; **discriminate** against one of them for the purposes of the problem.

Despite the lack of any direct information, the problem statement provides sufficient information to unambiguously determine the structures of **Y1** and **Y2**.

9. **Draw** the molecular formulae of **Y1** and **Y2**, and propose the structural formulae of substrates **X** and **Y**.

Compounds **X** and **Y**, unlike compound **Z**, are not found in nature.

10. Based on the principles of enzymatic catalysis, **propose** the molecular formula of **Z**.

Surprisingly, there is a substrate **W** that, when catalysed by the enzyme **Z**-reductase, yields two products with identical molecular masses when rounded to the nearest whole number.

11. **Suggest** two variants of the molecular formula of **W**, both containing **E1**.
12. **Describe** the metabolic characteristics and habitat of the archaea species whose metabolic fragment was discussed above.

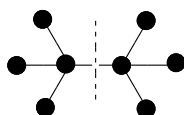
Most of the IChO 2026 problem authors are recent medalists of the International Chemistry Olympiads. Try testing your skills by creating an Olympiad problem based on the composition you've just solved. Your goal is to simplify this problem somewhat, guiding the participants' thinking toward the correct answers.

13. **Analyse** the reaction equations (1) and (2) and, based on the interesting coincidences/patterns you've identified, **offer** two hints to make the problem easier for the solvers without oversimplifying it.

Problem 28. Non-archea-typal form of life

Molecule **A**, with the formula $C_xH_yO_z$, where $x, y, z \in \mathbb{N}$, is found in some fossil deposits (such as oil), and serves as a biomarker for the presence of archaea in a particular region of the planet in the past.

Molecule **A** can be represented using a simplified version of knot notation: each covalent bond, regardless of the type of atoms forming it, is represented by a strand, with the atoms themselves being the knots at the ends of one or more strands. The ethane molecule, written in this notation, looks like this:



Using scissors, it takes 123 cuts to completely separate molecule **A** into individual nodes along the strands (the same operation with ethane requires 7 cuts). Note that two nodes are separated by the number of cuts equal to the number of strands between them (for example, a double bond requires two cuts). It is known that there is a single cut that bisects the molecule **A** into two identical fragments (similarly to ethane, as shown by the dashed line in the figure above).

1. Based on the data presented above, **decide** whether the indices x , y , and z are even or odd numbers or can be either of these. Is it possible to decide with $x \leq 60$ or not? For $x = 60$, **suggest** two fundamentally different theoretically possible structures that meet the conditions (ignore the reality of their existence; this is just a theoretical concept).

Hint: Using the method of incomplete mathematical induction, try to consider the dependence of the number of bonds on the molecular formula for the first members of the homologous series of alkanes or saturated alcohols, as well as the acetylene-ethylene-ethane series.

2. **Deduce** whether there exists a theoretical acyclic form of **A** that can be divided into two identical fragments: a) by two cuts; b) by three cuts. If you answered yes, **propose** a molecular formula supporting your choice.

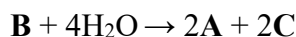
It is known that **A** has a molecular mass, rounded to the nearest whole number, of 595 g/mol.

3. Without guessing, uniquely **find** the molecular formula of **A**.

Molecule **A**, containing 8 stereocentres, can be cut along the strands into two types of fragments (fragments of the same type are defined as those that can be superimposed). Note that the cuts are made at equal distances from each other (the shortest number of strands between them, excluding branches), and one of the cuts coincides in location with the one that bisects **A** into two identical fragments as described above. Based on the experiment, **A** can be represented as a sequence of two fragments, c and d , as $dcccccccd$.

4. **State** whether the hydroxy groups in **A** can be: a) secondary; b) tertiary? If so, **draw** the corresponding structural formula(e) representing the cuts by dashed lines. Showing stereochemistry is not required.
5. **Draw** all possible structural formulae of **A** that form the *dcccccccd* pattern with cuts spaced apart by at least three intact strands.
6. Knowing the prevalence of certain structural biochemical motifs, **choose** the variant(s) of **A** (from those found in question 5) that best fit(s) to the metabolites of living things.

A is formed by the hydrolysis of compound **B** ($C_kH_lO_m$), which is involved in the formation of membranes in most archaeal species. The number of covalent bonds (n) in **B** is in the range $261 \leq n \leq 265$. The hydrolysis process is abiotic in nature and is a classic example of diagenesis (the long-term decomposition of organic material in geological deposits). The reaction equation for the decomposition of **B** can be written as follows:



Note:

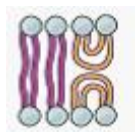
- *Optically inactive C has a symmetry axis passing through one of the carbon atoms;*
- *The molecular formula of both C residues in B is the same.*

7. **Prove**, without determining the formulae, that $l \leq 2k$.
8. **Find** all structural formulae of **C** that satisfy the above condition.

By combining pairwise the structures of **A** obtained in question 6 with the structures of **C** from question 8, we can see that one variant of **C** yields more structural isomers of **B** than all the other variants of **C** combined. This variant of **C** is found in archaeal lipids.

9. **Find** the final structure of **C** and determine the number of structural isomers of **B**. Draw the structural formulae of any two isomers of **B**.
10. **Explain** why the hydrolysis of **B** takes long and is not catalysed by enzymes of other microorganisms.

It is known that esterified derivatives of **B** are located in the membranes of some species of archaea in two fundamentally different ways (*O*- and *U*-conformations), shown below:



11. Of the **B** isomers proposed earlier, **select** those that can form similar membrane types. **Give** the advantage that such membranes have over those formed by bacterial and eukaryotic cells.
12. **Suggest** two explanations why the evolution chose **C** for the synthesis of **B**, rather than compounds from the same group with lower molecular weights.
13. Based on the information obtained in questions 11 and 12, **narrow down** as much as possible the range of isomers of **B** that meet the biological requirements of archaea.

Archaea of the phylum *Thaumarchaeota* adapt to rising environmental temperatures through a process virtually unique to them. It is known as homeoviscous adaptation, which involves modifying the structure of **B** by forming saturated cycles of either only five or only six carbon atoms (but not spirocycles) and, as a consequence, the biosynthesis of a separate family of lipids (**D**).

It is known that this modification of the structure of **B** is catalysed by two enzymes that are extremely similar in function and structure and exhibit strict positional specificity. Theoretically, based on the number of suitable loci, there could be up to four such enzymes, which would lead to an expansion of the **D** family (however, the third and fourth enzymes are not present in nature).

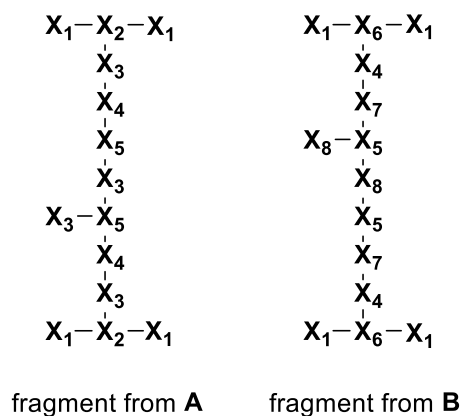
14. **Determine** the molecular formula of lipid **D1**, found in archaea, which withstands extreme temperature conditions better than other members of the family.

It is known that symmetrical molecule **D1** contains 26 stereocentres.

15. **How many** structural isomers that meet the condition can be proposed for **D1**? **Draw** any one of them. In this case, keep in mind that it is necessary to carefully analyse which carbon atoms can participate in the closure of the hydrocarbon ring, whether this option leads to an increase in the number of chiral centres and, if so, by what value.

Problem 29. Archaea-ology

Structural differences between biopolymers form one of fundamental criteria by which life forms are classified into separate domains. Biopolymers **A** (found in some archaea) and **B** (found in bacteria) have molecular weights over 100 kDa. The biopolymer fragments important for formation of spatial structures are shown below as I-shaped sequences of monomers (X_1 – X_8) linked by covalent bonds.



Each of the above fragments can be separated from the respective polymers (**A** or **B**) by cleaving four bonds.

- The molecular masses of all X_i were rounded to the nearest integer. **Determine** whether the difference between the molecular masses of the fragment from **A** and the fragment from **B** is an even or odd number or can be any of these.

The ratio of all monomers forming the biopolymer **B** is close to equimolar.

- Propose** the regular two-dimensional structures of biopolymers **A** and **B**. Note that **A** and **B** contain no monomers other than those shown in the figure.

Hint: It may be useful to redraw the I-shaped fragments with X_1 – X_8 depicted as dots of different colours.

A set of 6 molecular formulae is needed to be able to describe any X_i of X_1 – X_8 . *Note: the X_1 – X_8 monomers might be both D- and L-compounds.*

- Based only on the information given above, **choose** the theoretically correct statements from the given hereunder:
 - X_1 – X_8 can belong to different classes of biomolecules;
 - Some of X_1 – X_8 are isomers;
 - Some of X_1 – X_8 contain phosphorus;
 - Some of X_1 – X_8 are interclass isomers;
 - 50% of X_1 – X_8 are homologs.

In fact, only the first two statements are correct for X_1 – X_8 .

4. **State** whether it is now possible to determine unambiguously the nature of biopolymers **A** and **B**.

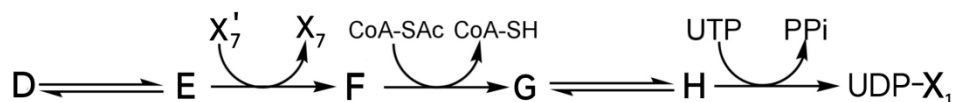
Any of the fragments (from **A** or **B**) can be divided into three pairs of smaller fragments containing at least two monomers linked together. The molecular mass of any of these resulting fragments (after rounding) belongs to the set: 217, 218, 275, 642 and 700. In **A** and **B**, monomers with identical molecular masses do not form covalent bonds with each other, and $M(X_6) > M(X_2)$.

5. **Determine** unambiguously the molecular formulae of as many monomers as possible. If you fail doing so, **determine** the molecular masses of the monomers without assigning them to specific X_i .

The sums of the molecular masses of all fragments formed from **A** and **B**, rounded to the nearest integer, are the same, 2270 g/mol.

6. **Explain** why these sums are equal. **Choose** the correct statement(s):
- occasionally;
 - because the fragments from **A** and **B** are isomers;
 - due to evolution reasons (only polymers with such molecular masses are functional).
7. **Determine** the molecular formulae of the yet unknown monomers.

Monomer X_1 is synthesised from the product of photosynthesis, substance **D**, via the following biochemical pathway:



where CoA is coenzyme A, UDP is uridine diphosphate, UTP is uridine triphosphate, and PPi is pyrophosphate.

It is known that:

- F** reacts with the Tollens reagent;
 - X_1 molecule is formed by atoms of four elements (C, H, N, and O);
 - X_1 contains 8 carbon atoms;
 - Only two carbon atoms are involved in transformations;
 - Three pairs can be arranged from compounds **D**, **E**, **F**, X_7 , and X_7' . The molecular masses of these pairs differ by 1.
8. **Draw** the structures of **D**–**H** and X_1 . **Explain** how you decided which isomer is encoded by **D** and which by **E**.

To finally identify the structures of polymers **A** and **B**, previously unidentified fragments **A-1** and **B-1** were isolated. They were methylated on alcoholic hydroxy groups, followed by exhaustive hydrolysis. In the case of **B**, this resulted in the formation of the 3,4,6-tri-*O*-methyl derivative of **X₁**, the 1,4,6-tri-*O*-methyl derivative of **X₁**, and the 6-mono-*O*-methyl derivative of **X₆**. For **A**, this resulted in the formation of the 1,4,6-tri-*O*-methyl derivative of **X₁**, the 3,4,6-tri-*O*-methyl derivative of **X₁**, and the 4-mono-*O*-methyl derivative of **X₂**.

9. **Draw** the structures of **A-1** and **B-1**, designating the unknown substituents as R_i .

Complete acidic hydrolysis of **A-1** and **B-1**, followed by oxidation with HIO_4 , leads to the formation of acetaldehyde in the amount equimolar to that of the starting fragment for only one of **A-1** and **B-1**.

10. **Propose** the complete structural formulae of **A-1** and **B-1**.

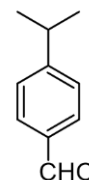
Problem 30. Pilaf ingredients

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:



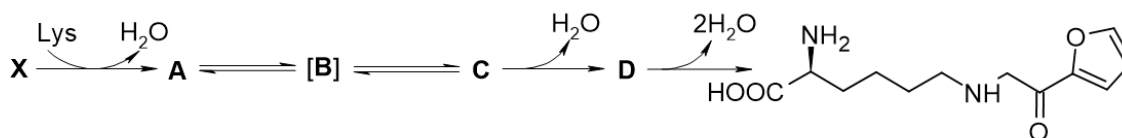
“Oil is first heated in a *kazan*. Chopped **onions** are fried until they reach a uniform golden-brown color. Pieces of **meat** are then added and cooked until they develop a caramelised surface. Afterwards, sliced **carrots** are introduced, and the mixture is seasoned with **black pepper** and **cumin**. 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.



1. **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.

2. **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:

- The indexes α , β , and γ are members of a geometric progression (not exactly in this order) and $\delta + \alpha = \epsilon$;
 - 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.

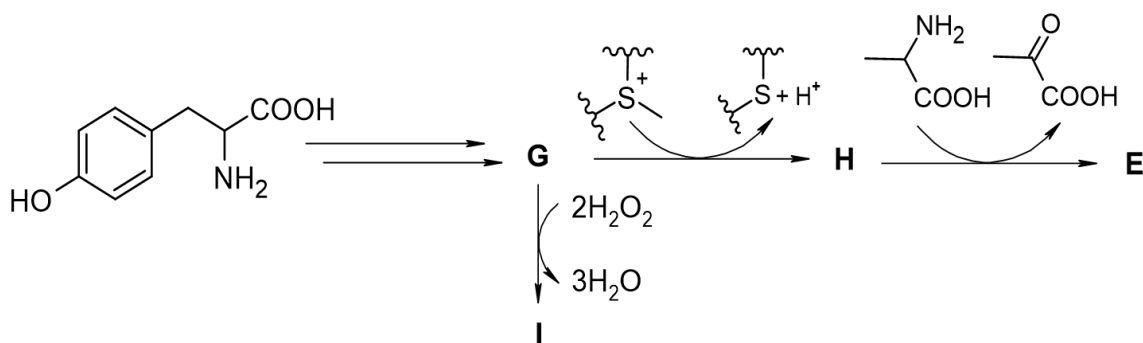
The **F**₁ and **F**₂ structures contain three types of hydrogen atoms and at least one plane of symmetry, while these compounds lack stereocentres and alcohol groups.

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:

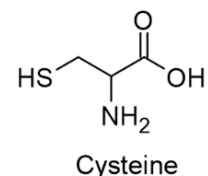
- **G** contains an aldehyde group.
- The initial hydroxy group in L-tyrosine is unchanged during the biosynthesis of **E**.
- **I** is an ortho-quinone derivative.

6. **Draw** the structures of compounds **G**, **H**, **I**, **E**, and **Z**.

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**.

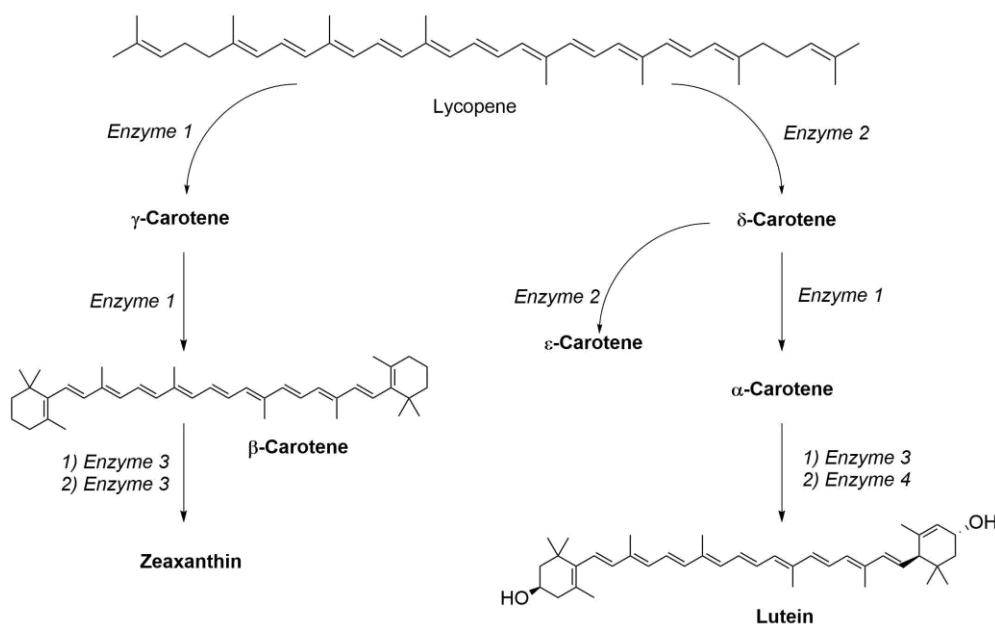


8. **Draw** the structures of compounds **M** and **N**.

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.
 - *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.

The chef in *Besh Qozon* did not mention the most important spice used in the preparation of pilaf.

13. **Identify** this unmentioned spice in Tashkent's pilaf.

**Preparatory Problems for
the 58th International Chemistry Olympiad 2026
Tashkent, Uzbekistan**

Practical Problems

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Fields of advanced difficulty

Practical

1. Using micropipettes and 96-well plates.
2. Vacuum filtration.
3. Titration using pH meter.

The students are not expected to be specifically trained on the hereunder topics:

- ❖ Recrystallisation.
- ❖ Using spectrophotometer.

List of GHS hazard statements and H codes

H221	Flammable gas
H225	Highly flammable liquid and vapour
H226	Flammable liquid and vapour
H272	May intensify fire; oxidiser
H290	May be corrosive to metals
H301	Toxic if swallowed
H302	Harmful if swallowed
H312	Harmful in contact with skin
H314	Causes severe skin burns and eye damage
H315	Causes skin irritation
H317	May cause an allergic skin reaction
H318	Causes serious eye damage
H319	Causes serious eye irritation
H331	Toxic if inhaled
H332	Harmful if inhaled
H334	May cause allergy or asthma symptoms or breathing difficulties if inhaled
H335	May cause respiratory irritation
H341	Suspected of causing genetic defects
H351	Suspected of causing cancer
H372	Causes damage to organs through prolonged or repeated exposure
H373	May cause damage to organs through prolonged or repeated exposure
H400	Very toxic to aquatic life
H410	Very toxic to aquatic life with long-lasting effects
H411	Toxic to aquatic life with long-lasting effects
H412	Harmful to aquatic life with long-lasting effects

Please note that the table of Globally Harmonised System (GHS) hazard codes provided for the chemicals used in these experiments is intended as a reference only. There is no guarantee that the information provided is perfect or complete. The list does not replace the need for professional attention to local regulations and the safety information provided by the actual suppliers of the chemicals.

Introduction to microplates (96-well plates) and micropipettes

Part A: What is a microplate?

This summer, you will visit the ancient city of Samarkand, a central part of the world's scientific heritage. Next to the Bibi-Khanym Mosque, you will notice the laughter of customers, the selling buzz of the traders and the colour of the most authentic products in the world – the Siyob Bazaar.

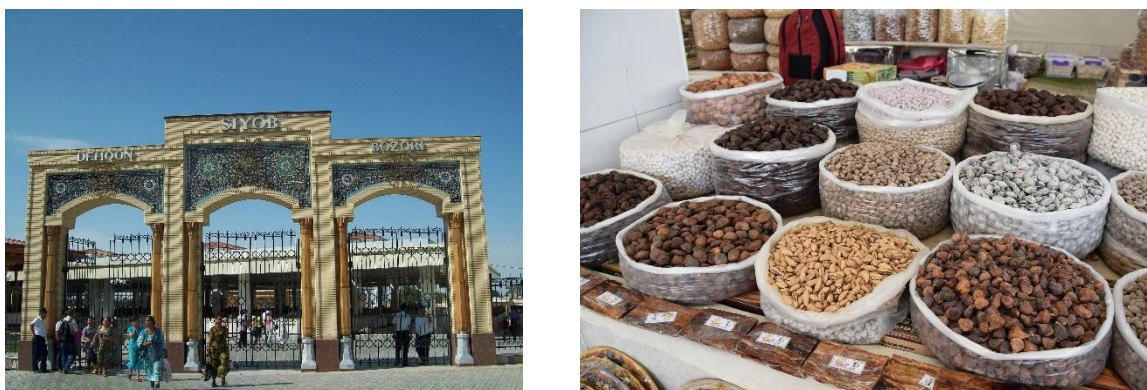


Figure 1. Entrance of the Siyob Bazaar and one of the delicious offerings hidden behind the gates. Maybe there are more? Images are reproduced from Wikipedia, under Wikimedia Commons, CC BY-SA 4.0.

In the Siyob Bazaar, your curiosity leads you to souvenirs, exotic food, and spices. So, you need a container of sufficient size for this. However, you don't want to select a lot, just enough so you can carry it all back home. For this, you are given a rectangular plastic tray, the size of your hand, with 96 tiny boxes in a grid of 8 rows and 12 columns. That's a 96-well plate – your access not only to the mystical culture of Uzbekistan, but to performing multiple, parallel microscale reactions for the practical problems in this set. There are, of course, trays with different box sizes, depending on how much candy you want to fill them with.

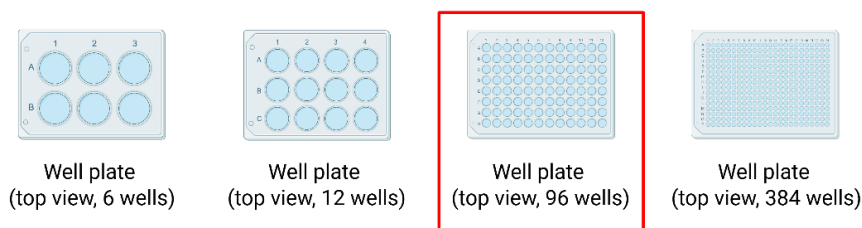


Figure 2. Types of multi-well plates. The 96-well plate is highlighted in red.

Each “box” is referred to as a “well”. It is nothing more than a small container that holds a micro-volume of up to 300 μL , depending on the vendor. A 96-well plate really is like a box of chocolates, just for chemical reactions. For practical purposes, we will use the terms “microplate” and “96-well plate” synonymously.

Why a microplate for microscale reactions?

Instead of running one reaction experimental condition at a time with such a small volume, we can run up to 96 experiments simultaneously. This is incredibly useful when we need to:

- Test multiple samples at the same time.
- Compare how different concentrations of reagents affect different reactions.
- Screen multiple reactions quickly.
- Save time, materials, and space in the laboratory.

Finding your way in a microplate

The microplate uses a simple coordinate system, like an Excel spreadsheet or the game of Battleships:

- The **rows** are labelled with letters A–H. There are 8 rows in total.
- The **columns** are numbered with numbers 1–12. There are 12 columns in total.

Every well has a unique identity. For example, the well in the top-left corner is **A1**, while the well in the bottom-right corner is **H12**. The well, three rows down and five columns across, would be **C5**. See Figure 3 for clarity. This naming system helps scientists keep track of exactly what's in each well and ensures experiments are organised and, hopefully, reproducible.

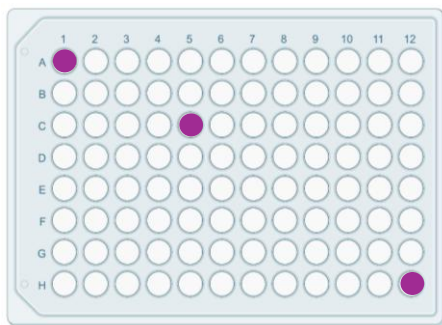


Figure 3. The classical organisation of a 96-well plate. The discussed wells in the text are marked with purple circles.

Basic terminology

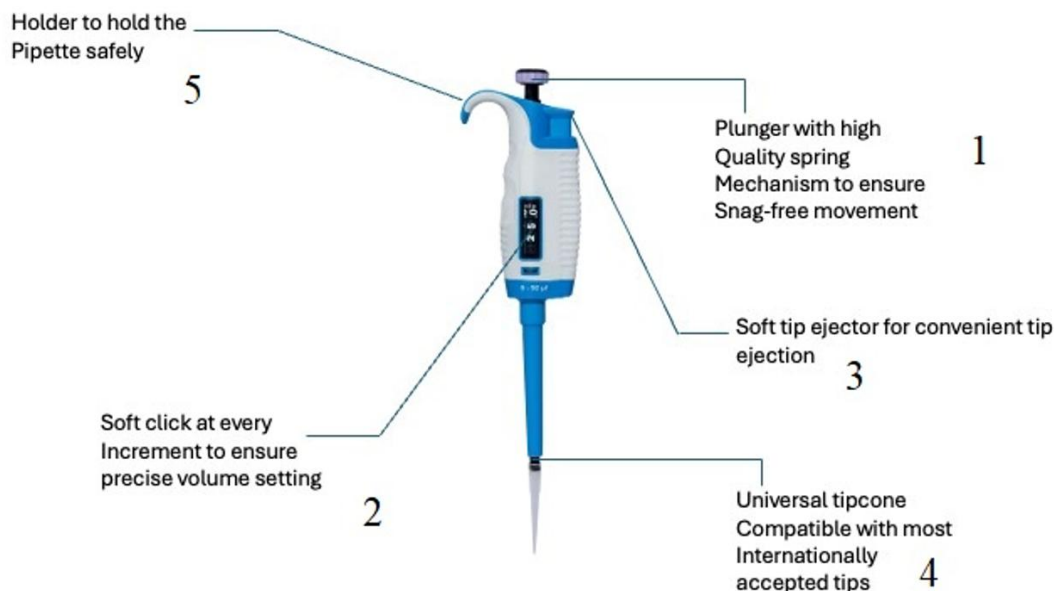
- **Well:** the individual container or “box” in the plate.
- **Micropipette:** A special tool that transfers liquid into a single well.

How to operate a microplate?

1. **Sketch out your plate layout on paper or use a template.** It is crucial to know exactly which chemical and which concentration goes in the corresponding well.
2. **Pay attention to the volumes used.** Follow the instructions of the experimental procedures where this is denoted.
3. **Beware of cross-contamination.** Be careful not to let your pipette tip touch the liquid of a well other than the one you are working with before moving to another well. On a microscale, this will contaminate your samples and ruin your experiment.

Part B: What is a micropipette?

The definition of the pipette (micropipette) is given above. Micropipettes are used to measure and transfer small amounts of liquids (from 1 μL and up to 5 mL). Note that there are different types of micropipettes, thus particular items has much narrower range. Be sure to check it before using.



Micropipette operation

1. Setting the delivery volume:

- Set** the delivery volume using the push button on the top of the micropipette (1). To increase the delivery volume, **turn** the push button counter-clockwise. To decrease the delivery volume, **turn** it clockwise.

Note: Micropipettes from other manufacturers can have a different design of the ring used to adjust volume. If you have trouble finding or using it, approach your lab assistant.

- Make sure** that the desired delivery volume clicks into place. **Check** the volume reading at window 2.
- Do not set** a volume that lies outside the micropipette's specified volume range. Using excessive force to turn the push button outside the range may jam the mechanism and eventually damage the micropipette.

2. Tip ejection:

In order to eject the tip, **point** the micropipette at a suitable waste receptacle and **press** the ejector button (3) with your thumb.

3. Doing pipetting:

- a) **Press** and **release** the push button (1) slowly. **Do not let** it snap.
- b) **Make sure** that the tip is firmly attached to the tip cone (4).
- c) Before you begin your actual work, **fill** and **empty** the tip 2–3 times with the reagent or solution that you will be pipetting.
- d) **Hold** the micropipette in an upright position while aspirating. The holder (5) must rest on your index finger.
- e) **Fill** a clean reagent/solution reservoir with the reagent/solution to be dispensed.
- f) **Press** the push button (1) till the first stop.
- g) **Dip** the tip under the upper surface of the reagent/solution in the reservoir, till a depth of about 1 cm.
- h) Slowly **release** the push button.
- i) **Withdraw** the tip from the reagent/solution.
- j) **Let** the tip touch against the edge of the reservoir to remove the excess reagent/solution.
- k) **Deliver** the reagent/solution by gently pressing the push button till the first stop. After a delay of about one second, **stop**. This action will empty the tip.
- l) **Release** the push button to let it retract to the ready position. If necessary, **change** the tip and **continue** pipetting. Always **use** a new clean tip when pipetting a new reagent/solution.
- m) Final instruction: **follow** the order of addition specified in the task, as it might be important to obtain the correct observations. Good luck!

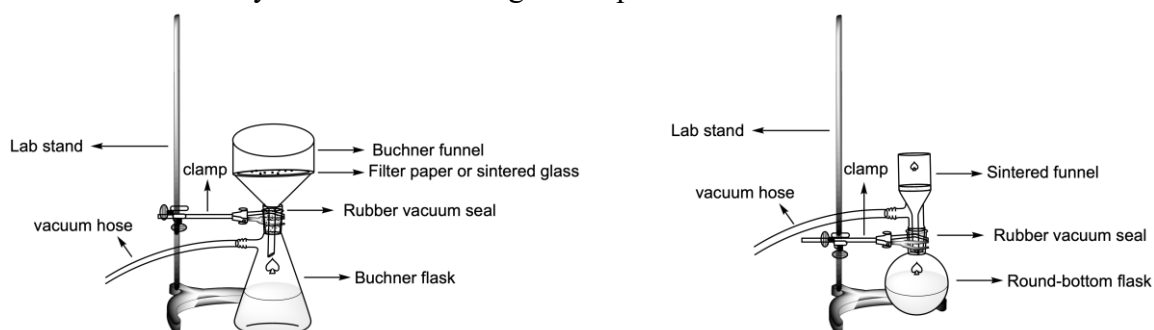
Introduction to vacuum filtration technique

Part A: What is vacuum filtration?

Filtration is a physical process used to separate the solid from the liquid by passing the mixture through a filter. Vacuum filtration applies suction to pull the solution, the mixture or suspension through the filter. For the filter, one can use a paper filter with a regular funnel or Büchner funnel, cotton with a regular funnel or sintered glass funnel.

Part B: Typical vacuum filtration set-up

The apparatus for vacuum filtration consists of a filter flask (Büchner flask or round-bottom flask with an appropriate connector), a filter that is sealed with a rubber vacuum seal or glass joint, and a vacuum hose connected to a vacuum pump. It is always recommended to mount the filter flask firmly to a lab stand using a clamp.



Part C: General instructions for vacuum filtration

1. **Clamp** the filter flask to a lab stand using an appropriate clamp.
2. **Connect** the filter using a rubber seal or a filter with the appropriate size of glass joint.
3. **Connect** one end to the vacuum valve on your bench and another end of the vacuum hose to the apparatus through the suction inlet.
4. **Turn** the vacuum **on**.
5. **Inspect** the suction by gently placing the palm of your hand on the top of the filter or passing some of the solvent through the filter.
6. **Pour** the mixture to be filtered from the reaction flask or beaker into the funnel using a glass rod, spatula or spout of the beaker if necessary. **Fill** a maximum of 3/4 of the funnel height and **do not let** it overflow.
7. Once the solution is fully transferred and the liquid is drained completely, **disconnect** the vacuum hose carefully and/or **turn off** the vacuum.
8. If it is necessary to wash the desired solid, **rinse** the reaction container, **pour** the washing liquid over the solid and **mix** thoroughly. **Turn** the vacuum back **on** to discard the washing liquid. **Repeat** the washing as many times as required.
9. **Turn** the vacuum **on** and **let** the air pass through to dry the solid. When the compound is dry enough (usually 5–15 min), **scrape** out the solid and **crush** it for more effective drying in air or on the filter. **Dry** the solid for a period of 5 min to 1 h as necessary.
10. **Turn** the vacuum **off** and **remove** the hose from the apparatus.
11. Using a spatula, **transfer** the solid to another container if required by the instructions.

Introduction to titration using a pH meter

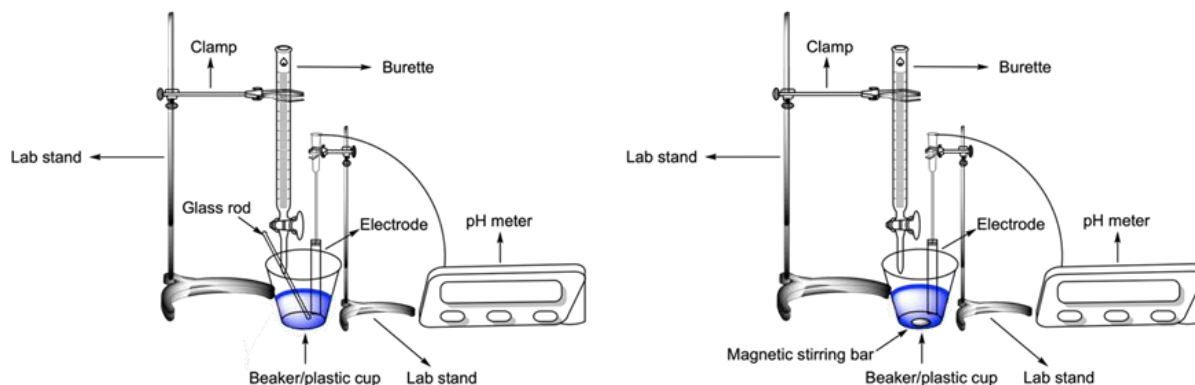
Part A: What is a pH meter?

A pH meter is a scientific instrument that measures the hydrogen-ion concentration in water-based solutions, indicating their acidity or alkalinity expressed as pH. The pH meter measures the difference in electrical potential between a pH electrode and a reference electrode, and so the pH meter is sometimes referred to as a “potentiometric pH meter”. The difference in electrical potential relates to the acidity or pH of the solution. Testing of pH via pH meters (pH-metry) is used in many applications, ranging from laboratory experimentation to quality control.

Potentiometric titration with a pH meter can be used to determine the concentration of an acid or a base. This is done by recording the pH change as a function of the titrant volume. Instead of relying on a colour-changing indicator, you use a pH meter with an electrode put into the titrated solution. As you add the titrant (for example, adding a base to an acid), at first, the pH changes gradually, but around the equivalence point, the pH increases or decreases sharply. If you plot the change in pH against the volume of the titrant, you’ll see a characteristic S-shaped curve. The steepest part of that curve marks the equivalence point.

Part B: Typical set-up for titration using a pH meter

It consists of a pH meter with its electrode, a fixed burette attached to the lab stand, a plastic beaker, a glass rod or a magnetic stirring bar. It is recommended that the electrode in the solution does not touch the wall and the bottom of the beaker, plastic beaker or magnetic stirring bar.



Part C: General instructions for titration using a pH meter

1. **Make sure** that the pH meter is calibrated and ready for use.
2. **Set up** the equipment as shown above.
3. **Keep** the electrode of the pH meter inside the storage solution. **Do not leave** the electrode dry for too long when it is not in use. Either **leave it** in the sample solution between measurements or in the storage solution if not in use for a long period of time.
4. **Rinse** the electrode with deionised water and **dry** it with tissue.

5. **Immerse** the pH meter electrode in the titrating solution, which contains a glass rod or magnetic stirring bar.
6. After each titrant probe addition, **stir** with a glass rod for 5 seconds (or **use** a magnetic stir bar), then **measure** the pH of the solution.
7. **Do not touch** the electrode with the glass rod or stir bar, as this may damage the electrode.
8. When you finish your titration, **rinse** the electrode with deionised water and **dry** it with tissue. Then, **put** the electrode back into the storage solution or **use** it in the next titration.

Problem 31. Blue pigment

Equipment

Item	Quantity
Part A	
Beaker, 250 mL	1
Stirring bar	1
Measuring cylinder, 25 mL	1
Hotplate with magnetic stirrer	1
Small spatula	1
Sintered funnel	1
Filtration flask	1
Vacuum pump	1
Part B	
Volumetric flask, 100 mL	1
Laboratory stand with burette clamp	1
Burette, 25 mL	1
Volumetric pipette, 10 mL	1
Conical flask, 100 mL	2
Aluminium foil	1
Pipette bulb	1
Small funnel	2
Small beaker under the burette	1
Part C	
96-well plate (or transparent Eppendorf tubes)	1 (or 30)
Pasteur pipettes	6+2 extra pieces
Microspatula	1
Black paper	1 piece
White paper	1 piece

Chemicals

Name	State	Concentration	Quantity	Placed in	Label
Part A					
A	Solid	–	1.87 g	Vial	A-synth
B	Solid	–	9.00 g	Vial	B-synth
Distilled water	Liquid	–	500 mL	Washing bottle	H ₂ O
Part B					
Pigment X	Solid	–	~1 g	Volumetric flask	Pigment X $m(\mathbf{X}) = \dots \text{ g}$

Sulfuric acid	Aqueous solution	10%	40 mL	Vial	H ₂ SO ₄ (10%)
Potassium iodide	Aqueous solution	1 M	20 mL	Vial	KI (1 M)
Sodium thiosulfate	Aqueous solution	0.1000 M	50 mL	Bottle	Na ₂ S ₂ O ₃ (0.1000 M)
Starch indicator	Aqueous solution	1%	1 mL	Eppendorf tube	Starch
Part C					
A	Aqueous solution	0.5 M	0.5 mL	Vial	A
B	Aqueous solution	0.5 M	0.5 mL	Vial	B
C	Solid	–	0.2 g	Vial	C
D	Aqueous solution	0.5 M	0.5 mL	Vial	D
E	Aqueous solution	0.5 M	0.5 mL	Vial	E
F	Aqueous solution	0.5 M	0.5 mL	Vial	F

GHS Codes

Chemical	GHS Code(s)
A	H302, H318, H410
B	no hazards
C	no hazards
D	H272, H314, H410
E	H302, H318
F	H319
X	H302, H319, H332, H410
Sulfuric acid (10%)	H290, H314, H335
Potassium iodide	H372
Sodium thiosulfate	no hazards
Starch indicator	no hazards



Uzbekistan is known worldwide for its architectural heritage and rich history. The cities of Samarkand, Bukhara, and Khiva are called the Pearls of the East for their ancient past and architectural masterpieces. Their madrasas, mosques, and mausoleums are renowned for intricate tilework and majestic blue domes that shimmer in the sunlight and have become one of the country's most iconic symbols. Blue pigment **X** is one of the components used in creating the blue domes.

In this task, you will explore different synthetic routes towards blue pigment **X** and analyse it.

Part A: Synthesis of pigment **X**

1. **Place** compound **A** (1.87 g) in a 250 mL beaker.
2. **Add** 25 mL of H₂O and a magnetic stirring bar.
3. **Clamp** the beaker on the stirring plate and start stirring. **Wait** until **A** is completely dissolved.
4. While stirring, **add** compound **B** (9.00 g) in small portions to the solution of **A**. Before adding a new portion, **wait** until the effervescence has subsided. The approximate total time of addition is 15–25 min.
5. After the addition is completed, **stir** the solution for 5 min.
6. While stirring, **add** 25 mL of H₂O to the solution (wash the beaker wall) and **stir** for an additional 20 min.
7. **Turn off** the stirring and check if the solution has become almost colourless. If not, **continue** stirring the solution until it becomes colourless.
8. **Add** 30 mL of H₂O and stir the reaction mixture for 5 min.
9. **Perform** the vacuum filtration of the mixture using the sintered funnel and **wash** the precipitate **X** on it with 10 mL of ice-cold H₂O.
10. **Dry** the product on the sintered funnel for 30 min. You **can perform** the subsequent parts of the tasks while drying.

Q1. Weigh the product and **record** its mass.

Note: The product will be dried in air overnight and re-weighed by the lab staff.

Part B: Analysis of pigment X

You are provided with a sample of the pigment. In this part, we will analyse it and deduce its structural formula.

1. **Note** the exact mass of sample **X** in the volumetric flask.
2. **Add** 15 mL of 10% H₂SO₄ portion-wise to **X** in the volumetric flask while swirling.

Q2. Note your observations.

3. After dissolving is complete, **dilute** the solution with distilled water to the mark.
4. **Transfer** a 10.0 mL aliquot of this solution into a conical flask.
5. **Add** 5 mL of 10% H₂SO₄ and 5 mL of 1 M KI.
6. **Cover** the flask with aluminium foil and **leave** it for about 5 min in a dark place.
7. **Titrate** the formed iodine with the standard 0.1000 M solution of Na₂S₂O₃ until the colour turns pale yellow. Then **add** 2–3 drops of the starch solution and **continue** titration until the blue colour disappears.
8. **Repeat** steps 2–3 as necessary.

Q3. Record your results.

Q4. Write the reaction equations for steps 5 and 7.

Q5. Calculate the mass percentage of the heaviest atom in the sample of **X**.

Part C: The way to identify A, B and X

There are various procedures to synthesise this pigment. Besides compounds **A** and **B**, one can use three chemicals out of the four salts **C–F**. You will perform pairwise reactions with them to identify compounds **A–F**.

It is known that:

- The set **A–F** contains three different cations.
- Na⁺ is one of the cations.
- Two unknown metal cations are in the same period of the Periodic table.
- Each cation is present twice in the set **A–F**.
- The set **A–F** contains four different anions.
- NO₃[–] is one of the anions.
- Two anions are present once, while the other two are present twice in the set **A–F**.
- Two anions are formed from the same acid.

Using the pairwise reaction method, **identify** the salts **A–F**. **Perform** the pairwise reactions as follows:

1. **Take** the well plate or Eppendorf tubes.
2. **Add** 2–3 drops or 1 microspatula of the first reagent to a well.
3. **Add** 2–3 drops or 1 microspatula of the second reagent to the same well.
4. **Write down** the observations, if any. In case of no reaction, **write** “NR”.
5. **Wait** for approximately 5 min and **note** additional observations, if any.

Note: For your convenience, you can use black or white paper as a background to see the reaction results more clearly.

Q6. Write the observations from the performed pairwise reactions in the following table.

	A	B	C	D	E	F
A						
B						
C						
D						
E						
F						

Different indicators can help to identify the metal ions in solution. One reagent that can be used is dithizone. The colours of metal complexes formed by several metals in aqueous solution with dithizone (in acetone) are shown below.

green	pink	red brick	brown	yellow	pale yellow
					
no metal	Zn ²⁺	Pb ²⁺	Cu ²⁺	Hg ²⁺	Cd ²⁺

Q7. Assuming solution **D** gives a brown colour with dithizone, **suggest** the colour of solution **A** after reaction with dithizone.

Q8. Identify the formulae of compounds A–F based on your observations and provided information.

Q9. Suggest additional tests that can help you to identify the unknown compounds. You **may** use only the chemicals present in this task.

Q10. Choose the compound from A–F which cannot be used to obtain pigment X through pairwise reaction.

Q11. State whether solid C is soluble in H₂O.

Problem 32. Synthesis and characterisation of metal complexes with a hydrazone-based ligand

Equipment

Item	Quantity
Shared	
Analytical balance	1
For each student	
Hotplate with magnetic stirrer	1
Stirring bar	1
Vacuum filtration set-up	1
Beaker, 100 mL	3
Beaker, 50 mL	1
Spatula	2
Pasteur pipette, 1.5 mL	1
Vial, 30 mL	2
Measuring cylinder, 50 mL	1
Measuring cylinder, 10 mL	2
Measuring cylinder, 1.5 mL	1
Conical flask, 100 mL	1
Ice-water bath	1

Chemicals

Name	State	Conc.	Quantity	Placed in	Label
Deionised water	Liquid	–	500 mL	Wash bottle, 500 mL	H ₂ O dist.
Ethanol	Liquid	–	100 mL	Bottle, 500 mL	Ethanol
Benzhydrazide	Solid	–	1.5 g	Vial	Benzhydrazide
Salicylaldehyde	Liquid	–	2 mL	Vial	Salicylaldehyde
Copper (II) chloride dihydrate	Solid	–	1 g	Vial	CuCl ₂

GHS Codes

Chemical	GHS Code(s)
Deionised water	no hazards
Ethanol	H225
Benzhydrazide	H301, H315, H319, H335, H351
Salicylaldehyde	H302, H312, H315, H319, H341
Salicylaldehyde benzoyl hydrazone	no hazards
Copper(II) chloride dihydrate	no hazards

Hydrazones are a common class of condensation products that are widely studied in organic and coordination chemistry. In this problem, you will synthesise salicylaldehyde benzoyl hydrazone (SBH) and its metal complex.

Part A: Synthesis of SBH

Note: This part of this synthesis should be performed under the fume hood.

1. **Weigh** 1.0 g benzhydrazide into a 100 mL beaker, **place** the beaker on the magnetic stirrer, **put** the stirring bar and **dissolve** the solid in 40 mL of distilled water while stirring.
2. To the second 100 mL beaker, **add** 1.5 mL salicylaldehyde ($\rho = 1.17 \text{ g}\cdot\text{cm}^{-3}$) using the Pasteur pipette, and **dissolve** in 15 mL ethanol. **Use** the same Pasteur pipette and **add** this solution dropwise to the benzhydrazide solution with stirring.
3. **Continue** to stir the resulting mixture at a lower speed for 10 min.
4. **Filter off** the product using vacuum filtration and **wash** the solid twice with 7 mL of ice-cold ethanol.
5. **Transfer** the solid to the 100 mL beaker and **put** the stirring bar in it.
6. **Add** 20 mL of ethanol and **heat** this solution on the hotplate with stirring until the solid completely dissolves.
7. **Remove** the beaker from the hotplate and **put** it in the ice-water bath to complete the crystallisation.
8. **Collect** your pure product using vacuum filtration, **wash** twice with 7 mL ice-cold ethanol.
9. **Dry** the solid in air with the operating vacuum pump for 30 min.
10. **Weigh** the vial and **record** the balance reading. **Transfer** the solid to the pre-weighed vial.

Q1. Write the reaction equation showing the structural formulae of the reagents and the product.

Q2. Calculate the reaction yield.

Part B: Synthesis of a copper complex

1. **Weigh** 0.51 g of $\text{CuCl}_2\cdot 2\text{H}_2\text{O}$ into the 50 mL beaker and **dissolve** it in 5 mL of ethanol.
2. **Weigh** 0.72 g of the SBH you prepared in **Part A** into a 100 mL conical flask, **add** 10 mL of ethanol using the measuring cylinder and **put** the stirring bar in the flask.
Note: If you did not get the desired product in Part A or its quantity is less than required, use the SBH given by your lab assistant.
3. **Turn on** the stirring.
4. **Heat** this mixture on the hotplate to facilitate dissolution of SBH.
5. When the SBH has completely dissolved, **remove** the conical flask from the hotplate, quickly **add** the metal salt solution and **swirl** to mix.

6. Once precipitation begins, **place** your flask in an ice-water bath, and **leave** it there for 10 min.
7. **Filter off** the solid using vacuum filtration, **wash** twice with 10 mL ice-cold water.
8. **Dry** the solid in air with the operating vacuum pump for 30 min.
9. **Weigh** the vial and **record** the balance reading.
10. **Transfer** the solid to the pre-weighed vial.
11. **Record** the mass of the product.

Q3. Indicate the stoichiometric ratio of Cu:SBH you expect in the complex based on the experimental procedure.

This kind of Metal-SBH complex can be studied by spectrophotometry to determine the Metal:SBH ratio. A synthesis similar to that in **Part B** can be used to obtain a Fe-SBH complex with the formula $[\text{Fe}_x(\text{SBH})_y]^{n+}$.

1 mM solution of Fe(III) and SBH in methanol were prepared for spectrophotometric experiments. The table below shows the prepared solutions and obtained absorbance (A) values.

$V(\text{Fe(III)}) / \text{mL}$	$V(\text{SBH}) / \text{mL}$	$V(\text{methanol}) / \text{mL}$	A
0.00	1.20	1.80	0.031
0.15	1.05	1.80	0.091
0.30	0.90	1.80	0.152
0.45	0.75	1.80	0.183
0.60	0.60	1.80	0.150
0.70	0.50	1.80	0.128
0.80	0.40	1.80	0.105
0.90	0.30	1.80	0.084
1.00	0.20	1.80	0.061
1.10	0.10	1.80	0.039
1.20	0.00	1.80	0.017

Job's plot can be used to analyse spectrophotometric data. It is based on the dependence of absorbance on the mole fraction of one component of the complex (metal or ligand). The absorbance reaches its maximum at the mole fraction corresponding to the stoichiometric composition of the complex.

Q4. Calculate the Fe:SBH ratio in the complex using the Job's plot.

Q5. Draw the structural formula of the complex.

Q6. Draw the structural formula of Cu-SBH complex if it is known that the coordination number of copper in the complex is 4 and it is a neutral complex.

Q7. Calculate the yield of the reaction in **Part B**.

Problem 33. Titration of apple juice

Equipment

Item	Quantity
Volumetric pipette, 10.0 mL	3
3-valve pipette bulb	1
Plastic beaker	4
Calibrated pH meter	1
Stand with burette clamp	1
Burette, 25 mL	3
Funnel	4
Glass rod	1
Erlenmeyer flask, 100 mL	2
Pasteur pipette	2
Volumetric flask with stopper, 100.0 mL	1
Measuring cylinder, 10 mL	3
Measuring cylinder, 50 mL	1
Aluminium foil, 20 × 20 cm	3
Hotplate	1
Glass boiling stones (chips)	20–40
Finger adapters for handling hot glassware	1 pair
Container for liquid waste, 1 L	1

Chemicals

Name	State	Concentration	Quantity	Placed in	Label
Distilled water	Liquid	-	500 mL	Wash bottle, 500 mL	H ₂ O dist.
Apple juice	Aqueous solution	to be determined	200 mL	Glass bottle with a screw cap, 250 mL	Apple juice
Sodium hydroxide	Aqueous solution	0.1000 M	100 mL	Glass bottle with a screw cap, 250 mL	NaOH, 0.1000 M
Copper sulfate	Aqueous solution	to be determined	100 mL	Glass bottle with a screw cap, 250 mL	CuSO ₄
Sulfuric acid	Aqueous solution	1 M	40 mL	Glass bottle with a screw cap, 50 mL	H ₂ SO ₄ , 1 M
Potassium iodide	Aqueous solution	20%	40 mL	Glass bottle with a screw cap, 50 mL	KI, 20%

Sodium thiosulfate	Aqueous solution	0.1000 M	100 mL	Glass bottle with a screw cap, 250 mL	Na ₂ S ₂ O ₃ , 0.1000 M
Starch	Aqueous solution	1%	4 mL	Eppendorf tube, 5 mL	Starch, 1%
Potassium sodium tartrate	Aqueous alkaline solution	350.0 g KNaC ₄ H ₄ O ₆ ·5H ₂ O and 100.0 g NaOH per 1 L	40 mL	Glass bottle with a screw cap, 50 mL	Alkaline tartrate
Methylene blue	Aqueous solution	1%	4 mL	Eppendorf tube, 5 mL	Methylene blue, 1%

GHS Codes

Chemical	GHS Code(s)
Sodium hydroxide	H314
Copper sulfate	H302, H315, H319, H400, H410
Sulfuric acid	H314
Potassium iodide	H302, H315, H317, H319, H334, H372, H373, H411
Sodium thiosulfate	no hazards
Starch	no hazards
Potassium sodium tartrate	no hazards
Methylene blue	H302, H318, H412

A distinctive feature of fruits grown in Uzbekistan is their taste, which is determined mainly by the content of carbohydrates and organic acids. In this task, you will need to determine the concentration of reducing sugars and organic acids in the apple juice using the titrimetric method.



Part A: Potentiometric titration of malic acid

In apple juice, organic acids are mainly represented by malic (2-hydroxybutanedioic) acid. You will determine the concentration of malic acid by potentiometric titration.

1. **Add** a 10.0 mL aliquot of apple juice and 50 mL of distilled H₂O to a 250 mL plastic beaker.
2. **Perform** potentiometric titration of the resulting mixture with 0.1000 M NaOH solution using a pH meter by adding 0.5 mL portions of NaOH until pH reaches 11.
3. **Record** your measurements in the following table:

V_{NaOH}	0.0	0.5	1.0	1.5	2.0	2.5	3.0	3.5	4.0	4.5
pH										
V_{NaOH}	5.0	5.5	6.0	6.5	7.0	7.5	8.0	8.5	9.0	9.5
pH										

Q1. Determine the range of NaOH volume (mL) corresponding to the equivalence point.

*Hint: It is the range with the greatest change in pH. **Tick** the correct box:*

V_{NaOH}	0.0	☐	0.5	☐	1.0	☐	1.5	☐	2.0	☐	2.5	☐	3.0
V_{NaOH}	3.0	☐	3.5	☐	4.0	☐	4.5	☐	5.0	☐	5.5	☐	6.0
V_{NaOH}	6.0	☐	6.5	☐	7.0	☐	7.5	☐	8.0	☐	8.5	☐	9.0

4. For a more precise titration, **repeat** the potentiometry for the range from **Q1** by adding 0.1 mL portions of 0.1000 M NaOH solution.

5. **Record** your measurements in the following table:

V_{NaOH}						
pH						

Q2. Determine the more accurate range of NaOH volume (mL) corresponding to the equivalence point. *Hint: It is the range with the greatest change in pH.*

Q3. Write the reaction equation for the titration of the apple juice with NaOH. **Assume** that malic acid is the only acid in the apple juice.

Q4. Calculate the concentration ($\text{mg} \cdot \text{mL}^{-1}$) of malic acid in the apple juice sample.

Part B: Standardisation of Cu(II) solution

You will determine the amount of reducing sugars in apple juice by Fehling's method using Cu(II). To do this, you must first standardise the Cu(II) solution iodometrically.

1. **Transfer** a 10.0 mL aliquot of Cu(II) solution to a 100.0 mL volumetric flask and dilute to the mark with distilled water (**Solution 1**).
2. **Transfer** a 10.0 mL aliquot of **Solution 1** to a conical flask. **Add** 5 mL of 1 M H_2SO_4 and 10 mL of 20% KI. **Cover** the flask and **leave** it for about 15 minutes in a dark place.
3. **Titrate** the formed iodine with a standard solution of $\text{Na}_2\text{S}_2\text{O}_3$ until the colour turns pale yellow. Then **add** 2–3 drops of starch solution, **continue** titration until the blue colour of the titrated solution disappears.
4. **Repeat** steps 2 and 3 as necessary.

Q5. Write the equations of the reactions that occurred during the standardisation of Cu(II).

Q6. Calculate the concentration (M) of Cu(II) in the initial solution.

Part C: Titration of reducing sugars

Note: Perform steps 1–2 in a fume hood.

1. **Add** 10.0 mL of Cu(II) solution to an Erlenmeyer flask, and 10 mL of alkaline tartrate solution. **Put** 5–10 glass boiling stones (chips) in the flask. **Heat** the mixture to boiling. **Add** 2–3 drops of methylene blue indicator.
2. **Take** the Erlenmeyer flask from the heater to the table and **immediately titrate** the boiling solution with apple juice until the blue colour of the solution fully disappears against the background of a brick-red precipitate.
3. **Repeat** steps 1 and 2 as necessary.

Q7. Write the reaction equation for the titration with Cu(II) in alkaline media, assuming that glucose is the only reducing sugar in apple juice. **Use** the molecular formula of glucose.

Q8. Calculate the concentration ($\text{mg} \cdot \text{mL}^{-1}$) of glucose in the apple juice.

Problem 34. Cottonseed oil

Equipment

Item	Quantity
Analytical balance (to 4 significant figures)	1
Burette, 25 mL	2
Stand with burette clamp	1
Erlenmeyer flask, 250 mL with glass stopper	2
Brown glass bottle, 50 mL	1
Volumetric pipette, 10.0 mL	1
Volumetric pipette, 25.0 mL	1
3-valve pipette bulb	1
Measuring cylinder, 10 mL	1
Measuring cylinder, 25 mL	1
Measuring cylinder, 100 mL	1
Erlenmeyer flask, 250 mL	2
Water bath	1
Reflux condenser	2
Boiling stones	20–40
Funnel	2
Pasteur pipette	3
Finger adapters for handling hot glassware	1 pair
Spatula	2
Container for liquid waste, 1 L	1

Chemicals

Name	State	Concentration	Quantity	Placed in	Label
Distilled water	Liquid	–	500 mL	Wash bottle, 500 mL	H ₂ O dist.
Cottonseed oil	Liquid	to be determined	10 mL	Glass bottle with a screw cap, 50 mL	Cottonseed oil
Sodium thiosulfate	Aqueous solution	0.1000 M	200 mL	Glass bottle with a screw cap, 250 mL	Na ₂ S ₂ O ₃ , 0.1000 M
Iodine trichloride	Solid	–	0.45 g	Brown glass vial with a screw cap, 1.5 mL	ICl ₃
Iodine	Solid	–	0.50 g	Brown glass vial with a screw cap, 1.5 mL	I ₂

Glacial acetic acid	Liquid	–	50 mL	Brown glass bottle with a ground stopper, 100 mL	CH ₃ COOH glacial
Dichloromethane	Liquid	–	50 mL	Glass bottle with a ground stopper, 100 mL	CH ₂ Cl ₂
Potassium iodide	Aqueous solution	20%	100 mL	Glass bottle with a screw cap, 250 mL	KI, 20%
Hydrochloric acid	Aqueous solution	0.5000 M	100 mL	Glass bottle with a screw cap, 250 mL	HCl, 0.5000 M
Potassium hydroxide	Freshly prepared ethanolic solution	~0.5 M	100 mL	Glass bottle with a screw cap, 250 mL	KOH/ C ₂ H ₅ OH, 0.5 M
Starch	Aqueous solution	1%	4 mL	Eppendorf tube, 5 mL	Starch, 1%
Alkali Blue 6B	Ethanolic solution	0.75%	4 mL	Eppendorf tube, 5 mL	Alkali Blue, 0.75%

GHS Codes

Name	GHS Code(s)
Cottonseed oil	no hazards
Sodium thiosulfate	no hazards
Iodine trichloride	H272, H314
Iodine	H312, H332, H400
Glacial acetic acid	H226, H314
Dichloromethane	H351
Potassium iodide	H302, H315, H317, H319, H334, H372, H373, H411
Hydrochloric acid	H314, H331
Potassium hydroxide	H302, H314
Starch	no hazards
Alkali Blue 6B	H315, H319, H335

Cotton is one of Uzbekistan's most important agricultural products and has long been known as the country's "white gold". It plays a major role in the national economy, providing export revenue and employment, though recent reforms have aimed to improve labour conditions and reduce reliance on forced labour in its production.



Cottonseed oil, which is extracted from the seeds of the cotton plant, is tested using key parameters such as saponification value and iodine value to determine its overall quality.

Part A: Determination of the saponification value

In this part, you will identify the saponification value of cottonseed oil volumetrically. The saponification value is the number of mg of KOH required to hydrolyse 1 g of a fat or oil.

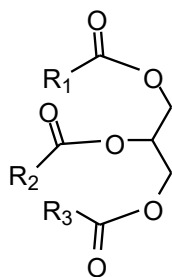
Testing the sample:

1. **Fill** the burette with 0.5000 M HCl solution.
2. **Weigh** approximately 2.0 g of cottonseed oil in the Erlenmeyer flask. **Record** the weight.
3. To the flask with the cottonseed oil sample, **add** 25.0 mL of ~0.5 M KOH/C₂H₅OH solution. **Put** 5–10 boiling stones (chips) in the reaction flask.
4. **Attach** the reflux condenser with floating water onto the reaction flask.
5. **Reflux** the content by intensive boiling of the water bath until all the oil disappears.
Note: This step usually takes ca. 60 minutes.
6. **Disconnect** the reflux condenser and **remove** the flask from the water bath.
7. **Add** 0.25 mL Alkali Blue solution to the hot flask.
8. **Titrate** the hot solution with 0.5000 M HCl until the red solution becomes blue. **Record** your answer.

Reference experiment:

9. **Skip** step 2 and **repeat** steps 1, 3–8 from the above procedure without cottonseed oil. **Record** your answer.

Q1. Write the reaction equations for the saponification of triglyceride and neutralisation of KOH during the titration. **Use** the following simplified structure for triglyceride:



Q2. Determine the exact concentration (M) of the alcoholic KOH solution.

Q3. Calculate the saponification value ($\text{mg} \cdot \text{g}^{-1}$) of the sample.

Part B: Determination of the iodine value

In this part, you will determine the iodine value of cottonseed oil through the volumetric method. Iodine value is a measure of the total number of double bonds present in fats and oils. It is expressed as the number of grams of iodine that will react with the double bonds in 100 grams of fats or oils. Firstly, you need to prepare the Wijs solution and then use it to determine the iodine value of cottonseed oil.

Note: Perform steps 1–9 in the fume hood.

1. **Weigh** and **dissolve** 0.45 g of ICl_3 in 50 mL glacial CH_3COOH in a brown glass bottle with a ground stopper.
2. **Add** 0.50 g I_2 to the ICl_3 solution in glacial acetic acid. **Mix** the contents of the bottle thoroughly until I_2 is completely dissolved. The resulting solution predominantly contains interhalogen **X** and is called Wijs solution.

Testing the sample:

3. **Fill** the burette with $\text{Na}_2\text{S}_2\text{O}_3$ solution.
4. **Weigh** approximately 0.1 g of cottonseed oil in the iodine flask. **Record** the mass.
5. To the iodine flask with the cottonseed oil sample, **add** 10 mL of CH_2Cl_2 , followed by 10.0 mL of Wijs solution.
6. **Immediately close** the flask with a stopper soaked in KI solution and **keep** it in a dark place for 60 minutes.
7. After 60 minutes, **add** 15 mL of 20% KI solution and 100 mL of distilled H_2O into the flask.
8. **Titrate** the mixture with $\text{Na}_2\text{S}_2\text{O}_3$ solution until it turns pale yellow, then **add** 2–3 drops of starch solution and **continue** titrating until the dark blue colour of the solution disappears. **Record** your answer.

Reference experiment:

9. **Skip** step 4 and **repeat** steps 3, 5–8 from the above procedure without cottonseed oil. **Record** your answer.

Q4. Determine the interhalogen **X**.

Q5. Write equations of the reactions occurring during the determination of the iodine number of cottonseed oil. **Use** the following simplified structure for unsaturated fatty acid residues:



Q6. Determine the concentration (M) of **X** in the Wijs solution.

Q7. Calculate the iodine value ($\text{g} \cdot (100 \text{ g})^{-1}$) of the sample.

The following table shows the saponification and iodine values of different oils:

Oil	Saponification value / $\text{mg} \cdot \text{g}^{-1}$	Iodine value / $\text{g} \cdot (100 \text{ g})^{-1}$
Sunflower	188–194	118–145
Fish	180–192	142–176
Palm	190–209	50–55
Butter	210–232	26–40

Q8. Identify the oil from the table above that contains the highest number of:

- short-chain fatty acids;
- unsaturated fatty acids.

Problem 35. An unknown salt

Equipment

Item	Quantity
Analytical balance (to 4 significant figures)	1
Spatula	1
Beaker, 250 mL	1
Funnel	3
Volumetric flask, 250 mL	1
Microplate (transparent 96-well plate)	1
Micropipette 10–100 μL	1
Micropipette tips	6
Rack for micropipette tips	1
Plastic beakers, 250 mL	2
Volumetric pipette, 50 mL	1
3-valve pipette bulb	1
Glass rod	1
Burette, 25 mL	1
Stand with burette clamp	1
Calibrated pH meter	1
Container for liquid waste, 1 L	1

Chemicals

Name	State	Concentration	Quantity	Placed in	Label
Distilled water	Liquid	–	500 mL	Wash bottle, 500 mL	H ₂ O
Unknown salt	Solid	–	1 g	Vial, 5 mL	Salt X
Barium chloride	Aqueous solution	5%	1 mL	Eppendorf tube, 2 mL	BaCl ₂ , 5%
Silver nitrate	Aqueous solution	5%	1 mL	Eppendorf tube, 2 mL	AgNO ₃ , 5%
Sodium nitrite	Aqueous solution	5%	1 mL	Eppendorf tube, 2 mL	NaNO ₂ , 5%
Hydrochloric acid	Aqueous solution	5%	1 mL	Eppendorf tube, 2 mL	HCl, 5%
Ammonia solution	Aqueous solution	10%	1 mL	Eppendorf tube, 2 mL	NH ₃ , 10%
Sodium hydroxide	Aqueous solution	0.2000 M	200 mL	Glass bottle with a screw cap, 250 mL	NaOH, 0.2000 M

GHS Codes

Chemical	GHS Code(s)
Unknown salt	H315, H319, H335
Barium chloride	H301, H332
Silver nitrate	H272, H314, H400, H410
Sodium nitrite	H272, H301, H400
Hydrochloric acid	H314, H331
Ammonia solution	H221, H314, H331, H400
Sodium hydroxide	H314

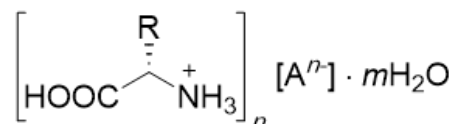
A very famous story of Khodja Nasreddin is about his encounter with **Salt X**. One sunny day in old Samarkand, Nasreddin met his neighbour:

“Do you know, dear neighbour, that this **Salt X** that I bought from Samarkand makes a loud noise when I throw it outside the window?”

“Impossible, respected Khodja, that is impossible! It’s only a very small amount!”

“Yes, but if I put it on the vial on the back of my donkey and throw it outside the window, it definitely makes a lot of noise!” the respected Nasreddin replied.

You are given a salt of an unknown canonical amino acid with the following molecular formula:



m is a non-zero integer number, whereas the anion A^{n-} can be any of the following anions: Cl^- , Br^- , I^- , NO_3^- , SO_4^{2-} .

Note: The list of 20 canonical amino acids with their molecular formulae, molecular weight and pK_a values is given at the end of the problem.

1. **Weigh** ca. 1 g of **Salt X**. **Write down** the exact mass that you will use for further calculations.
2. **Dissolve** **Salt X** in 50 mL of distilled water in a beaker.
3. **Transfer** the solution of **Salt X** quantitatively to a 250 mL volumetric flask.
4. **Fill** the flask with distilled water up to the mark to obtain **solution 1**.

Part A: Qualitative analysis

In this part of the problem, you need to determine the anion A^{n-} by using qualitative reactions in a 96-well plate. You are provided with the following reagents: BaCl_2 , AgNO_3 , NaNO_2 , HCl , NH_3 .

Q1. Fill in the table below with the observations you would expect for each reaction pair. **Indicate** all colour changes and if any precipitate or gas is formed.

	BaCl_2	AgNO_3	$\text{NaNO}_2 + \text{HCl}$
Cl^-			
Br^-			
I^-			
NO_3^-			
SO_4^{2-}			

Q2. Write the corresponding ionic reaction equations.

The solubility of silver halides **AgHal** (Hal = Cl⁻, Br⁻, I⁻) in an aqueous ammonia solution depends, in addition to other factors, on the solubility product (K_{sp}) of **AgHal** in water and the stability constant β of $[\text{Ag}(\text{NH}_3)_2]^+$:

$K_{sp}(\text{AgCl})$	$K_{sp}(\text{AgBr})$	$K_{sp}(\text{AgI})$	$\beta(\text{Ag}(\text{NH}_3)_2^+)$
1.77×10^{-10}	5.35×10^{-13}	8.52×10^{-17}	2.5×10^7

Q3. Calculate the solubility (M) of **AgHal** for each halogen anion (Cl⁻, Br⁻, I⁻) in 1.00 L of 10% NH₃ solution ($\rho = 0.958 \text{ g}\cdot\text{cm}^{-3}$). *Note: Assume that the activity of the species equals its concentration.*

Q4. Mix solution 1 with the provided reagents in the microplate according to the table below. If **AgHal** precipitate forms in reaction 2, **add** 70 μL of NH₃ to the reaction mixture. **Record** your observations.

Reaction number	Reaction mixture	Precipitate formed	Colour of the precipitate	Solubility of the precipitate in NH ₃	Colour of the resulting solution
1	70 μL solution 1 + 70 μL BaCl ₂	☐ Yes ☐ No		-	
2	70 μL solution 1 + 70 μL AgNO ₃	☐ Yes ☐ No		☐ Yes ☐ No	
3	70 μL solution 1 + 70 μL HCl + 70 μL NaNO ₂	—	—	—	

Q5. Determine the anion Aⁿ⁻. **Assume** that out of AgHal, only AgCl dissolves in ammonia solution at the given conditions.

Part B: Quantitative analysis

In this part of the problem, you need to determine the number of acidic protons and the molecular mass of **Salt X** by potentiometric titration.

- Transfer** 50.0 mL of **solution 1** into a 250 mL plastic beaker using a volumetric pipette.
- Perform** potentiometric titration of the resulting mixture with 0.2000 M NaOH solution using a pH meter by adding 0.5 mL portions of NaOH until pH reaches 11.

3. **Record** your measurements in the following table:

V_{NaOH}	0.0	0.5	1.0	1.5	2.0	2.5	3.0	3.5	4.0	4.5
pH										
V_{NaOH}	5.0	5.5	6.0	6.5	7.0	7.5	8.0	8.5	9.0	9.5
pH										
V_{NaOH}	10.0	10.5	11.0	11.5	12.0	12.5	13.0	13.5	14.0	14.5
pH										
V_{NaOH}	15.0	15.5	16.0	16.5	17.0	17.5	18.0	18.5	19.0	19.5
pH										

Q6. Determine the range(s) of NaOH volume (mL) corresponding to the equivalence point(s). *Hint: These are the ranges with the greatest change in pH.* **Tick** the correct box(es):

V_{NaOH}	0.0	☐	0.5	☐	1.0	☐	1.5	☐	2.0	☐	2.5	☐	3.0
V_{NaOH}	3.0	☐	3.5	☐	4.0	☐	4.5	☐	5.0	☐	5.5	☐	6.0
V_{NaOH}	6.0	☐	6.5	☐	7.0	☐	7.5	☐	8.0	☐	8.5	☐	9.0
V_{NaOH}	9.0	☐	9.5	☐	10.0	☐	10.5	☐	11.0	☐	11.5	☐	12.0
V_{NaOH}	12.0	☐	12.5	☐	13.0	☐	13.5	☐	14.0	☐	14.5	☐	15.0
V_{NaOH}	15.0	☐	15.5	☐	16.0	☐	16.5	☐	17.0	☐	17.5	☐	18.0

4. For a more precise titration, **repeat** the potentiometry for the range from **Q6** by adding 0.1 mL portions of 0.2000 M NaOH solution. *Hint: If you found two or more equivalence points, choose the one with the greatest change in pH.*

5. **Record** your measurements in the following table:

V_{NaOH}						
pH						

Q7. Determine the more accurate range of NaOH volume (mL) corresponding to the equivalence point(s). *Hint: It is the range with the greatest change in pH.*

Q8. Determine the number of acidic protons in **Salt X**.

Q9. Calculate the molecular mass (M) of **Salt X**.

Q10. Determine the molecular formula of **Salt X**.

Table. 20 canonical amino acids

Name	Molecular Weight	Molecular Formula	$pK_a(-COOH)$	$pK_a(-NH_3^+)$	$pK_a(-R)$
Alanine	89.10	$C_3H_7NO_2$	2.34	9.69	–
Arginine	174.20	$C_6H_{14}N_4O_2$	2.17	9.04	12.48
Asparagine	132.12	$C_4H_8N_2O_3$	2.02	8.80	–
Aspartic acid	133.11	$C_4H_7NO_4$	1.88	9.60	3.65
Cysteine	121.16	$C_3H_7NO_2S$	1.96	10.28	8.18
Glutamic acid	147.13	$C_5H_9NO_4$	2.19	9.67	4.25
Glutamine	146.15	$C_5H_{10}N_2O_3$	2.17	9.13	–
Glycine	75.07	$C_2H_5NO_2$	2.34	9.60	–
Histidine	155.16	$C_6H_9N_3O_2$	1.82	9.17	6.00
Isoleucine	131.18	$C_6H_{13}NO_2$	2.36	9.60	–
Leucine	131.18	$C_6H_{13}NO_2$	2.36	9.60	–
Lysine	146.19	$C_6H_{14}N_2O_2$	2.18	8.95	10.53
Methionine	149.21	$C_5H_{11}NO_2S$	2.28	9.21	–
Phenylalanine	165.19	$C_9H_{11}NO_2$	1.83	9.13	–
Proline	115.13	$C_5H_9NO_2$	1.99	10.60	–
Serine	105.09	$C_3H_7NO_3$	2.21	9.15	–
Threonine	119.12	$C_4H_9NO_3$	2.09	9.10	–
Tryptophan	204.23	$C_{11}H_{12}N_2O_2$	2.83	9.39	–
Tyrosine	181.19	$C_9H_{11}NO_3$	2.20	9.11	10.07
Valine	117.15	$C_5H_{11}NO_2$	2.32	9.62	–

Problem 36. Khodja Nasreddin's secret message

Equipment

Item	Quantity
Microplate with 96 wells (transparent)	1
Micropipette, 10–100 μL	1
Tips for the micropipette of the appropriate size	11
Rack for micropipette tips	1
Rack for Eppendorf tubes	1
Container for liquid waste, 1 L	1

Chemicals

Name	State	Concentration	Quantity	Placed in	Label
Distilled water	Liquid	–	500 mL	Wash bottle, 500 mL	H ₂ O dist.
Methyl orange	Aqueous solution	0.1%	5 mL	Centrifuge tube, 15 mL	MO, 0.1%
Hydrochloric acid	Aqueous solution	0.0500 M	15 mL	Centrifuge tube, 15 mL	HCl, 0.05 M
Sodium hydroxide	Aqueous solution	0.0500 M	15 mL	Centrifuge tube, 15 mL	NaOH, 0.05 M
HCl solutions I–III	Aqueous solutions	To be determined	5 mL	Centrifuge tube, 15 mL	I–VIII
NaOH solutions IV–VIII	Aqueous solutions	To be determined	5 mL	Centrifuge tube, 15 mL	

GHS Codes

Chemical	GHS Code(s)
Methyl orange	H301
Hydrochloric acid	H314, H331
Sodium hydroxide	H314

Closer to the end of this **Preparatory Problems set**, Khodja Nasreddin wants to inform you about an important event happening this year. Khodja Nasreddin loves chemistry and he is very good at hiding secrets. Thus, he encrypted the information in solutions **I–VIII**. The solutions **I–III** contain HCl and the solutions **IV–VIII** contain NaOH in different concentrations. Khodja Nasreddin believes that the talented chemists around the world can read his message.

To decipher the information, he proposes the following experiment:

1. **Fill** all the wells of the microplate with 10 μL of methyl orange (MO) solution.
2. **Add** 100 μL of solution **I** to the A1 well. Then **add** 20 μL of 0.05 M NaOH solution. **Record** the colour of the obtained solution.
3. **Add** 100 μL of solution **I** to the B1 well. Then **add** 40 μL of 0.05 M NaOH solution. **Record** the colour of the solution.
4. **Continue** the procedure as described in steps 2 and 3 by keeping the volume of solution **I** constant. **Increase** the volume of the 0.05 M NaOH by 20 μL in each new well until the colour of the solution changes.
5. Once you **observe** the colour change, **repeat** the addition as in steps 2 and 3 with the next solution.
Note: Each new solution is added to the wells column-wise (A1–H1, A2–H2, ..., A12–H12).
6. **Continue** the addition of the solutions until the 96-well plate is filled. The order of adding the solutions is given in **Table 1**.

We strongly recommend:

- **Follow** the instructions and **follow** the specific order given in the task.
- Solutions **I–III** are to be basified with 0.05 M NaOH solution, while solutions **IV–VIII** are to be acidified with 0.05 M HCl solution.
- **Keep** a specific tip for a specific solution.
- **See Figures 1–6** on the next pages for visual guidance on performing the experiment.

Table 1. Order of addition of the solutions

Order of addition	Solution	Order of addition	Solution	Order of addition	Solution
1	I	10	VIII	19	VIII
2	IV	11	I	20	II
3	II	12	IV	21	IV
4	VII	13	III	22	I
5	I	14	IV	23	III
6	VI	15	VII	24	VI
7	IV	16	II	25	II
8	V	17	IV	26	IV
9	III	18	II	27	II

As can be seen from **Table 1**, some solutions will need to be added multiple times. Continuing to “titrate” according to the order in **Table 1** and **Figures 1–6**, you should reach the well H12 and complete the “titration” with solution **II**.

Hint: In this task, “titrate” means “acidify” or “basify”, depending on which solution is added.

Q1. Decipher Khodja Nasreddin’s cryptogram.

Q2. Determine the concentration ranges of solutions **I–VIII**.

Q3. Give the number(s) of solution(s) (out of **I–VIII**) that can be used to replace solution **II** at the end of the sequence, so that the cryptogram pattern remains unchanged.

For arbitrary concentrations of “titrated” solutions, the working scheme is as follows:

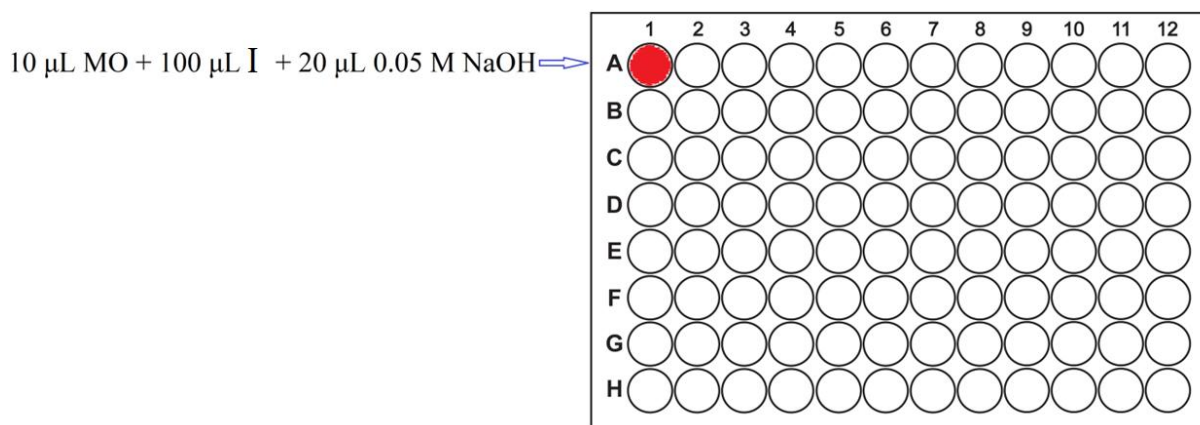


Figure 1. Step 1 – 100 μL of solution **I** is basified with 20 μL of NaOH.

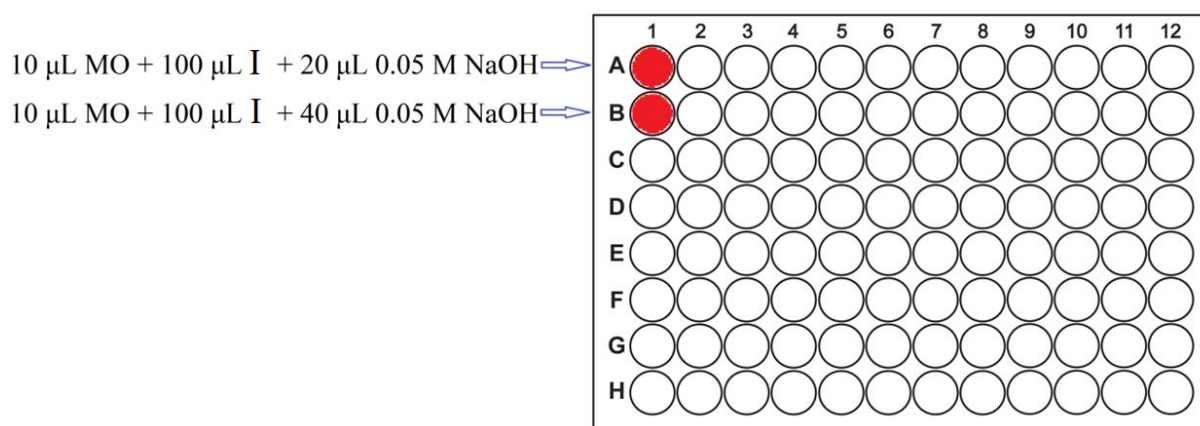


Figure 2. Step 2 – 100 μL of solution **I** is basified with 40 μL of NaOH.

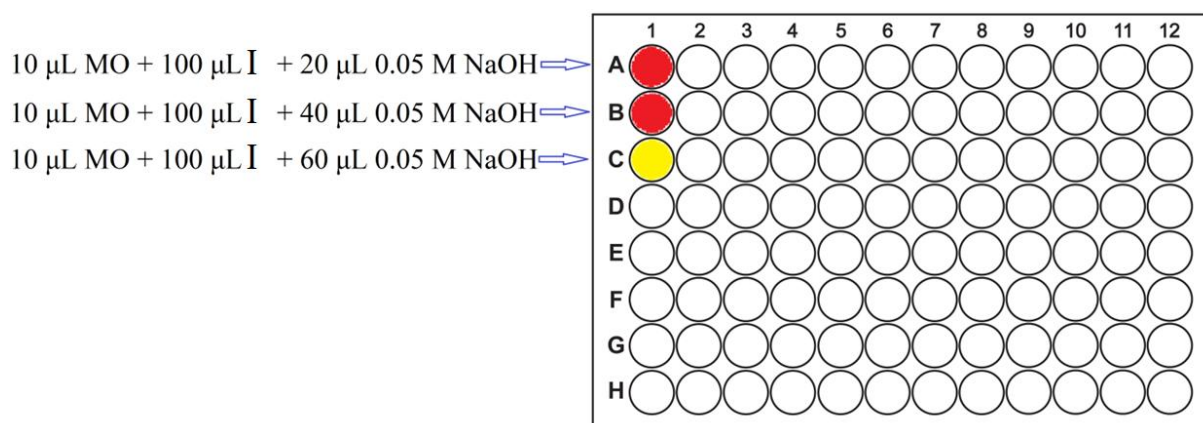


Figure 3. Step 3 – 100 μ L of solution I is basified with 60 μ L of NaOH. A colour change is recorded, which indicates the end of the “titration” of solution I.

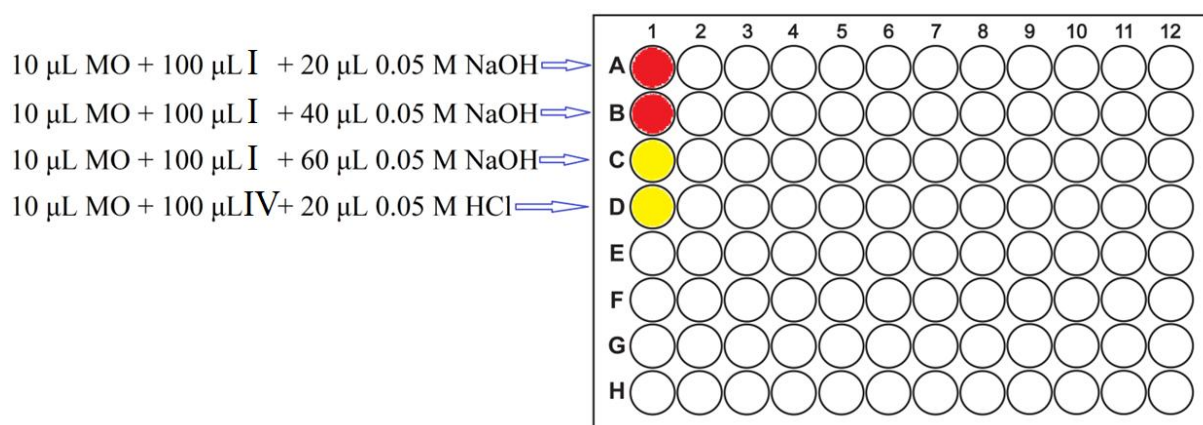


Figure 4. Step 4 – 100 μ L of solution IV is acidified with 20 μ L of HCl.

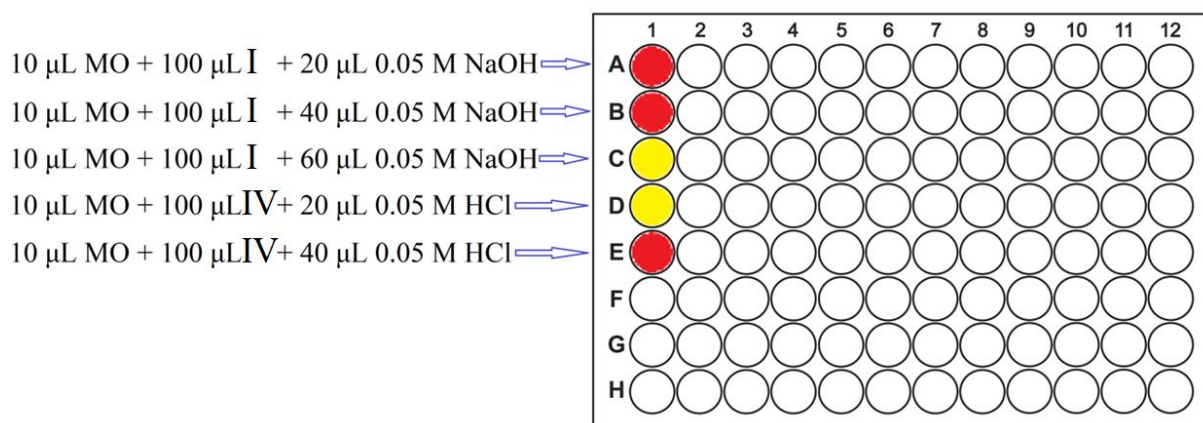


Figure 5. Step 5 – 100 μ L of solution IV is acidified with 40 μ L of HCl. A colour change is recorded, which indicates the end of the “titration” of solution IV.

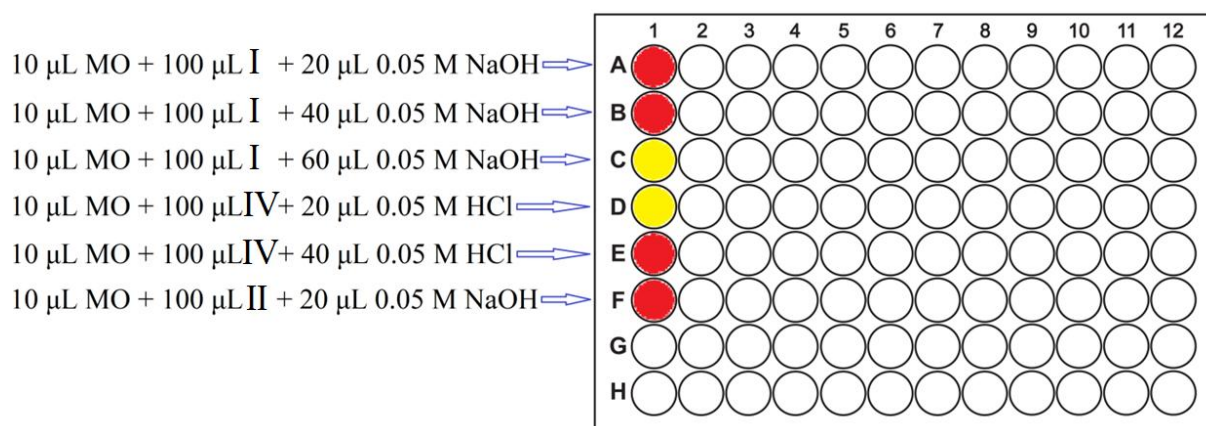
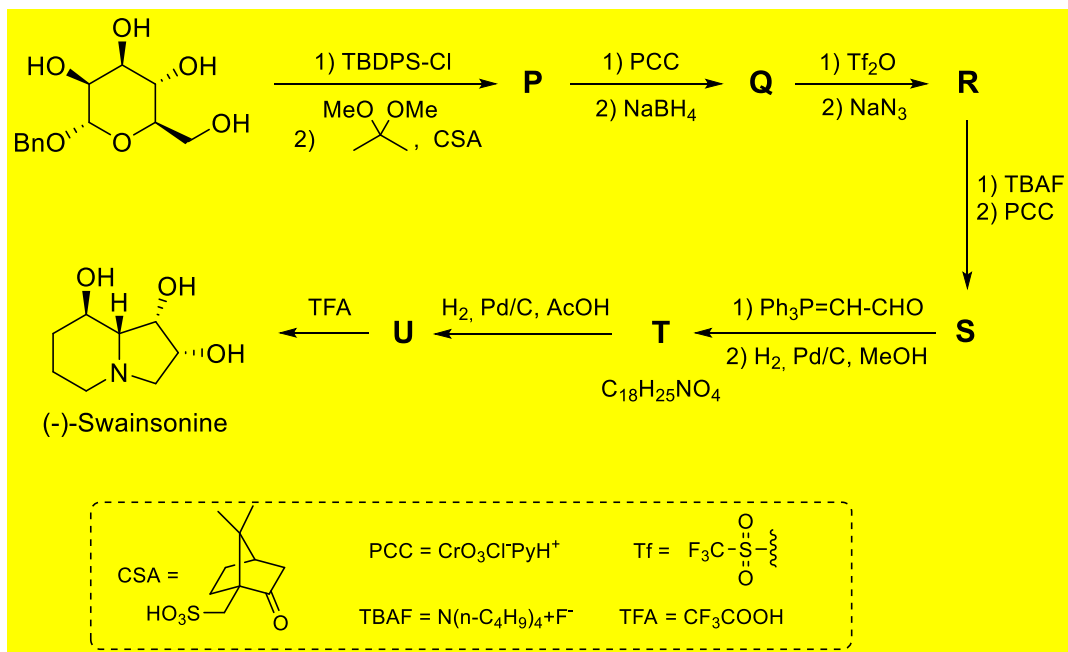


Figure 6. Step 6 – 100 μ L of solution **II** is basified with 20 μ L of NaOH.

**Corrections to Preparatory Problems for
the 58th International Chemistry Olympiad 2026
Tashkent, Uzbekistan**

Theoretical Problems

The synthesis of (–)-Swainsonine is given below.



Problem 30. Pilaf ingredients

Upon oxidative ozonolysis, acyclic compound **F**, without any triple bond, having one oxygen-containing group, yields an equimolar mixture of $\text{C}_\alpha\text{H}_\beta\text{O}_\gamma$ (**F**₁) and $\text{C}_\delta\text{H}_\epsilon\text{O}_\alpha$ (**F**₂), where $\alpha \neq \beta \neq \gamma \neq \delta \neq \epsilon$.

**Solutions to Preparatory problems for
the 58th International Chemistry Olympiad 2026
Tashkent, Uzbekistan**

Theoretical Problems

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Problem 1. Khoja Nasreddin is now a chemist

1. **F** is dark blue liquid at low temperatures. One well-known substance with this property is ozone. This identification is consistent with the observation that when **F** is passed through a potassium iodide solution, the solution turns brown due to the formation of iodine, while an equal amount of a colourless gas (O_2) is released — a behaviour characteristic of ozone reactions. O_2 and N_2O_3 does not fit these conditions since they cannot oxidise iodide solution with producing another colourless gas with the same amount.

F – O_3 .

D has a complex cation, which is obtained by treating **E** with ozone in liquid ammonia. The ligands could be ammonia since the reaction occurs in ammonia. This can be verified. We find the moles of ozone for the synthesis of 1 g of **D**: $\frac{16.3 \cdot 10^{-3} \cdot 0.0998}{2} \cdot 10 = 8.1337 \cdot 10^{-3} \text{ mol}$

$M(\mathbf{D}) = \frac{1}{8.1337 \cdot 10^{-3}} \cdot x = 122.945x \frac{\text{g}}{\text{mol}}$; $N(\text{H}) = 122.945x \cdot \frac{0.0983}{1.008} = 12x$ which is divisible by 3 without a remainder, which indirectly means that the ligands in it are ammonia molecules.

When assumed that $x = 1$ (which means the ratio of **D** to ozone is 1), then $M(\mathbf{D}) = 122.945 \frac{\text{g}}{\text{mol}}$;

$N(\text{NH}_3) = 12 : 3 = 4$

$122.945 - 17 \cdot 4 - 48 = 6.945$; this equals the atomic mass of lithium. This is consistent with the fact that the coordination number of lithium is always 4. The salt is an ozonide. **D** – $[\text{Li}(\text{NH}_3)_4]\text{O}_3$.

4.21% is a very small mass fraction. It may be hydrogen since its atomic mass is the smallest. Let's check this, $M(\mathbf{E}) = \frac{1.008x}{0.0421} = 23.94x \frac{\text{g}}{\text{mol}}$. It suits lithium hydroxide. **E** – LiOH .

In **C** there is the same metal as in **D**, that is, lithium. $M(\mathbf{C}) = \frac{6.94}{0.1263} = 54.95 \frac{\text{g}}{\text{mol}}$; which corresponds to **C** – LiO_3 .

In **A**, the anion is also an ozonide. There are no solids left after all the reactions have completed, which suggests NH_4^+ as the cation.

The increase in pressure at the first stage indicates that gas is formed.

Let's find its quantity, $n_1 = \frac{(106.42 - 100) \cdot 1}{8.314 \cdot (-70 + 273.15)} = 3.8 \cdot 10^{-3} \text{ mol}$

At a temperature of 128 °C the pressure should be,

$$P = 106.42 \cdot \frac{128 + 273.15}{-70 + 273.15} = 210.14 \text{ kPa} < 260.63 \text{ kPa}$$

indicating that more gas is formed. Finding its quantity,

$$n_2 = \frac{(260.63 - 210.14) * 1}{8.314 * (128 + 273.15)} = 0.01514 \text{ mol}$$

An increase in moles of gases at 128 °C without any reaction indicates that evaporation has occurred. This temperature indicates that it was water evaporation.

$$N = \frac{0.01514}{3.8 * 10^{-3}} = 4; \text{ the ratio of water to the first gas is 4.}$$

The combustion of a smoldering splinter indicates that there is oxygen in the gas mixture.

Oxygen is formed during the decomposition of ozonide, which is logical, since there are not many reactions where oxygen is formed during decomposition.

Then the first gas is oxygen, and during the decomposition of **A**, mixture of H₂O, O₂ and **B** was formed.

$$m(\mathbf{B}) = 1 - 3.8 * 10^{-3} * 32 - 0.01514 * 18 = 0.606 \text{ g}$$

One can find the amount of gases formed during the decomposition of **B**:

$$n_3 = \left\{ 396.82 - \left[260.63 * \frac{200 + 273.15}{128 + 273.15} \right] \right\} * \frac{1}{8.314 * (200 + 273.15)} = 0.02273 \text{ mol}$$

$$\text{In reaction: } 1\mathbf{B} \rightarrow y * \text{gases}; M(\mathbf{B}) = \frac{0.606y}{0.02273} = 26.66y \frac{\text{g}}{\text{mol}}; \text{ when } y = 3, M(\mathbf{B}) = 80 \frac{\text{g}}{\text{mol}}$$

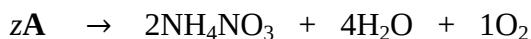
This molar mass is suitable for NH₄NO₃, which decomposes to form 3 moles of gases.

B – NH₄NO₃

$$n(\text{NH}_4\text{NO}_3) = \frac{0.606}{80} = 7.575 * 10^{-3} \text{ mol}$$

NH ₄ NO ₃	:	H ₂ O	:	O ₂
7.575 * 10 ⁻³		0.01514		3.8 * 10 ⁻³
2	:	4	:	1

$$1\text{g} \quad 3.8 * 10^{-3} \text{ mol}$$



$$M(\mathbf{A}) * z \quad 1$$

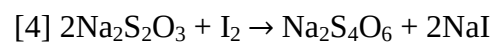
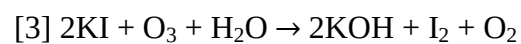
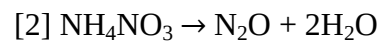
$M(\mathbf{A}) \cdot z = 263.16 \text{ g}$, when $z = 4$, $M(\mathbf{A}) = 65.8 \approx 66 \frac{\text{g}}{\text{mol}}$, which corresponds to NH_4O_3 .

$\mathbf{A} - \text{NH}_4\text{O}_3$

Another way to find $\mathbf{A}$ is to sum atoms in the products, so for $z\mathbf{A}$ we have $\text{N}_4\text{H}_{16}\text{O}_{12} = (\text{NH}_4\text{O}_3)_4$, and it becomes easier to find $\mathbf{A}$.

A	B	C	D	E	F
NH_4O_3	NH_4NO_3	LiO_3	$[\text{Li}(\text{NH}_3)_4]\text{O}_3$	LiOH	O_3

2.



Problem 2. Avicenna

1. Addition of BaCl_2 to **Solution 1** leads to the formation of the white precipitate BaSO_4 , meaning that the mineral should contain a sulfur atom(s), and probably an oxygen atom(s). The formation of deep-blue **Solution 2** when ammonia solution is added to **Solution 1**, is the qualitative reaction for copper (Cu^{2+}) ions, while the brown precipitate indicates the formation of iron hydroxide under basic conditions ($\text{Fe}(\text{OH})_3$). There are no more qualitative reactions for any other ions, so the possible elemental composition would be:

Fe-Cu-S; Fe-Cu-S-O.

Both combinations are considered correct.

2. Brown gas **A**, after dissolution of the mineral in concentrated nitric acid, is NO_2 :

$$n(\text{NO}_2) = \frac{1.65}{22.4} = 0.0737 \text{ mol}$$

White precipitate **B** when Solution 1 reacts with BaCl_2 , as mentioned above is BaSO_4 .

$$n(\text{BaSO}_4) = \frac{0.929}{233} = 3.99 \cdot 10^{-3} \text{ mol}$$

As **Solution 1** was divided into two parts:

$$n(\text{BaSO}_4) = 3.99 \cdot 10^{-3} \cdot 2 = 7.98 \cdot 10^{-3} \text{ mol}$$

$$n(\text{NO}_2) = \frac{1.65}{22.4} = 0.0737 \text{ mol}$$

We can make calculations for both combinations of the *mineral*:

Combination Fe-Cu-S:

$$m(\text{S}) = 7.98 \cdot 10^{-3} \cdot 32 = 0.255 \text{ g}$$

$$m(\text{residual}) = 1.0 - 0.255 = 0.745 \text{ g}$$

We don't exactly know the oxidation states of all atoms in the mineral, so let's consider them as 0.

Then,

$$n(\text{NO}_2)_{\text{metals}} = 0.0737 - 7.98 \cdot 10^{-3} \cdot 6 = 2.58 \cdot 10^{-2} \text{ mol}$$

Then, average equivalent mass of the metals:

$$\frac{0.745}{2.58 \cdot 10^{-2}} = 28.9 \text{ g/mol}$$

As we know that one of the metals is copper, the equivalent mass of the second atom should be lower than 28.9 g/mol and it should form a brown precipitate when reacted with an excess of ammonia. The only option here is iron – Fe.

The brown precipitate formed after reaction of Solution 1 with ammonia is $\text{Fe}(\text{OH})_3$ as mentioned above.

Then, $\text{Fe}(\text{OH})_3$ gets oxidised by KBrO_3 under alkaline conditions to FeO_4^{2-} (**D**). The red precipitate that forms when **D** reacts with BaCl_2 is BaFeO_4 .

$$n(\text{BaFeO}_4) = \frac{0.256}{256.8} = 1.0 \times 10^{-3} \text{ mol}$$

Remembering that **Solution 1** was divided into two parts:

$$n(\text{BaFeO}_4) = 1.0 \times 10^{-3} \times 2 = 2.0 \times 10^{-3} \text{ mol}$$

$$m(\text{Fe}) = 2.0 \times 10^{-3} \times 55.8 = 0.112 \text{ g}$$

$$\text{Then, } m(\text{Cu}) = 1 - 0.112 - 0.255 = 0.633 \text{ g}$$

$$n(\text{Cu}) = \frac{0.633}{63.5} = 0.01 \text{ mol}$$

Then, $n(\text{Cu}) : n(\text{Fe}) : n(\text{S}) = 5 : 1 : 4$; with the molecular formula of the mineral as Cu_5FeS_4 . This can be further confirmed by NO_2 formation.

Combination Fe-Cu-S-O

$$m(\text{Fe} + \text{Cu} + \text{O}) = 0.745 \text{ g}$$

$$m(\text{Fe}) = 0.112 \text{ g}$$

$$m(\text{Cu} + \text{O}) = 0.745 - 0.112 = 0.633 \text{ g}$$

$$n(\text{S}) : n(\text{Fe}) = 7.98 \times 10^{-3} : 2.0 \times 10^{-3} = 4 : 1$$

Considering *mineral* has only one iron atom:

$$M_r(\text{mineral}) = \frac{1.00}{2 \times 10^{-3}} = 500 \text{ g/mol}$$

Then,

$$m(\text{Cu} + \text{O}) = 500 - 56 - 32 \times 4 = 316 \text{ g/mol}$$

The only possible combination of copper and oxygen atoms for this relation is:

$$n(\text{Cu}) = 3 \quad n(\text{O}) = 7.84 \approx 8$$

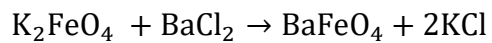
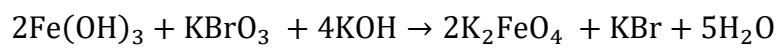
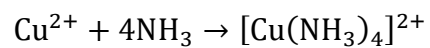
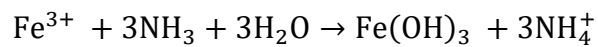
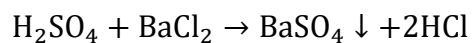
$$n(\text{Cu}) = 4 \quad n(\text{O}) = 3.88 \approx 4$$

However, these combinations can't be further confirmed by NO_2 formation, so these compositions of the mineral are incorrect.

Then,

$$\text{Mineral} - \text{Cu}_5\text{FeS}_4; \text{A} - \text{NO}_2; \text{B} - \text{BaSO}_4; \text{C} - \text{Fe}(\text{OH})_3; \text{D} - \text{K}_2\text{FeO}_4; \text{E} - \text{BaFeO}_4$$

3.



Problem 3. Unusual inorganic synthesis

1. Cathode: $2\text{H}^+ + 2e^- \rightarrow \text{H}_2$.

$$Q = 10 \cdot 0.785 \cdot 0.1^2 \cdot 3600 = 282.6 \text{ C}$$

$$V_{\text{H}_2} = \frac{282.6 \cdot 22.4 \cdot 10^3}{96485 \cdot 2} = 32.8 \text{ mL}$$

2. $\text{I}_2 + 2\text{S}_2\text{O}_3^{2-} \rightarrow 2\text{I}^- + \text{S}_4\text{O}_6^{2-}$

3. From the text of the problem it can be understood that **A1-A4** contain the same unknown element in different oxidation states, the oxidation state of the element increases in the series: **A3 < A4 < A2 < A1**.

Let's compare the oxidation potential of **S0** and **S1**:

$$\frac{0.100 \cdot 10.10 \cdot 10^{-3} \cdot 500}{10} = 0.0505 \text{ mol of electrons for } \mathbf{S0}$$

$$\frac{0.100 \cdot 1.35 \cdot 10^{-3} \cdot 100}{10} = 1.35 \cdot 10^{-3} \text{ mol of electrons for } \mathbf{S1}$$

During electrolysis, the following amount of electrons are removed from the anion **A2**:

$$\frac{282.6 \cdot 11.5 \cdot 10^{-2}}{96485} = 3.37 \cdot 10^{-4} \text{ mol of electrons}$$

If simplify the ratio $0.0505 : 1.35 \cdot 10^{-3} : 3.37 \cdot 10^{-4}$, we obtain the ratio 150 : 4 : 1. That means that the first titration determines the concentration of anion **A1** formed in solution **S1**, and the second titration determines the initial concentration of anion **A2** in solution **S0**. So, in the first titration anion **A2** was reduced and removed from solution **S2** in the form **A4**.

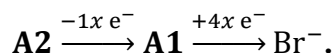
Element **A4** is a product of following conproportionation reactions:

Step **S1** → **S2**: **A2** + **A3** → **A4** (yellow),

Step **S3** → **S4**: **A1** + **A3** → **A4** (yellow).

Volatile, yellow element **A4** is Br_2 (this is further confirmed by calculating the atomic mass of the enriched isotope of **X**). So, anion **A3** has an oxidation state less than 0, this is Br^- .

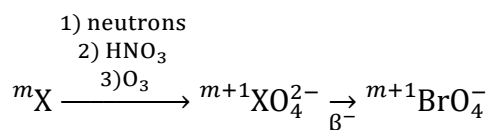
The following diagram shows the redox properties of anion **A1** according to our calculations:



In case $x = 1$, **A1** is BrO_2^- and **A2** is BrO . This is incorrect because **A2** must be an anion.

In case $x = 2$, **A1** is BrO_4^- and **A2** is BrO_3^- . This is correct.

The spontaneous transformation of anion **B** into anion **A1** without the absorption or release of any chemical substances indicates that one of the elements in its composition is undergoing radioactive decay (the possible radioactive process is also indicated by the irradiation of the enriched **X** isotope with thermal neutrons). If we assume that the element emits positively charged particles and the anion **A1** has a charge of “-1” (BrO_4^-), anion **B** must have “0” or “+” charge. It’s incorrect. So, the element in anion **B** emits negatively charged particles – electrons. Let’s summarize our findings:



So, **X** is Se.

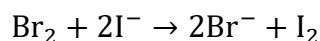
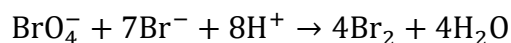
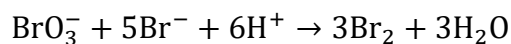
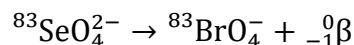
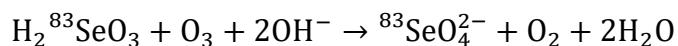
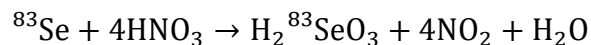
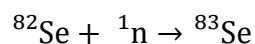
$$\frac{0.9 \cdot 1.000}{m} = \frac{1.613}{m + 1 + 16 \cdot 4} \rightarrow m = 82 \text{ (atomic mass of enriched isotope X)}.$$

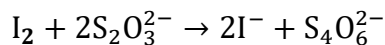
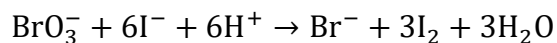
The atomic mass of the enriched isotope **X** is close to the relative atomic mass of bromine (79.916), which once again confirms our conclusions that substances **A1-A4** contain bromine.

Anion **B** is ${}^{83}\text{SeO}_4^{2-}$.

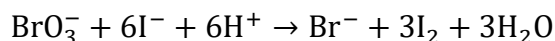
A1	A2	A3	A4	X	B
BrO_4^-	BrO_3^-	Br^-	Br_2	${}^{82}\text{Se}$	${}^{83}\text{SeO}_4^{2-}$

Reaction equations:





4. In the second titration the following reaction occurs:



$$C_0 = \frac{0.0505}{6 \cdot 3 \cdot 10^{-3}} = 2.8 \text{ M}$$

5. In this case, too, only the β^- decay of the anion $^{83}\text{BrO}_4^-$ will lead to the formation of two neutral gaseous elements **C** and **D**. The stoichiometric ratio (1:2) allows us to conclude that **C** is ^{83}Kr and **D** is O_2 .

6. The maximum concentration of anion **A1** will occur when the following condition is met:

$$\frac{d[\text{A1}]}{dt} = k_1[\text{B}] - k_2[\text{A1}] = 0$$

Let's express the concentrations of **B** and **A1** through the initial concentration of **B** and time:

$$\frac{d[\text{A1}]}{dt} = k_1[\text{B}]_0 e^{-k_1 t} - \frac{k_2 k_1 [\text{B}]_0}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t}) = 0$$

$$k_1[\text{B}]_0 e^{-k_1 t} = \frac{k_2 k_1 [\text{B}]_0}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t})$$

$$e^{-k_1 t} = \frac{k_2}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t})$$

$$\frac{k_2 - k_1}{k_2} = 1 - e^{(k_1 - k_2)t}$$

$$\frac{k_1}{k_2} = e^{(k_1 - k_2)t}$$

$$t = \frac{\ln\left(\frac{k_1}{k_2}\right)}{k_1 - k_2} = \frac{\ln\left(\frac{0.031}{0.0048}\right)}{0.031 - 0.0048} = 71.2 \text{ min}$$

An alternative solution method is using the derivative:

$$\left(\frac{k_1[\text{B}]_0}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t}) \right)' = 0$$

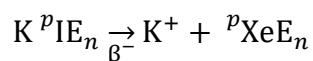
$$-\frac{k_1^2[\mathbf{B}]_0}{k_2 - k_1}e^{-k_1t} + \frac{k_1k_2[\mathbf{B}]_0}{k_2 - k_1}e^{-k_2t} = 0$$

$$k_2e^{-k_2t} = k_1e^{-k_1t}$$

$$e^{(k_1-k_2)t} = \frac{k_1}{k_2}$$

$$t = \frac{\ln \frac{k_1}{k_2}}{k_1 - k_2} = \frac{\ln \left(\frac{0.031}{0.0048} \right)}{0.031 - 0.0048} = 71.2 \text{ min}$$

7. For Xe to form because of β^- decay, salt **F** must contain an isotope of iodine:



$$0.1262 = \frac{39.1}{39.1 + p + nA_E} \rightarrow A_E = \frac{270.7 - p}{n}$$

If we temporarily assume that $p = 126.9$, we obtain the following:

n	1	2	3	4	5	6	7	8
A_E	143.8	71.9	47.9	35.9 ~ Cl	28.8	23.9	20.5 ~ F	17.9 ~ O or F

Fluorine is excluded as an element in the problem, and oxygen does not match in valence, which means that element E is chlorine and $n = 4$.

$$p = 270.7 - 35.45 \cdot 4 = 129.$$

So, **E** is ${}^{129}\text{XeCl}_4$ and **F** is $\text{K}^{129}\text{ICl}_4$.

Problem 4. Nanozymes

- From the co-precipitation method, **X** has multiple oxidation states and is a transition metal. We can start with the fact that the cation and the anion from **S1** have a common halogen. We can also see that the charge of metal **X** is 3+ in **S1**. By using m/z numbers of the cation and the anion we form the following equations:

$$\begin{cases} x + \text{Hal} \times 2 + 18 \times 4 = 198 \\ x + \text{Hal} \times 4 = 196 \end{cases}$$

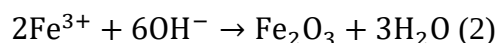
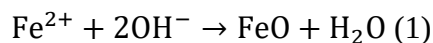
From here **Hal** = 35 and **x** = 56, which are most abundant isotopes for **Cl** and **Fe**. So, **X** is **Fe**, **S1** is the hydrated crystal of **FeCl₃**.

For **S2**, the mass losses to turn from green to white indicates the loss of all water from it. If **S2** contains only one atom of **X**, its molar mass and number of hydrated water molecules are as follows:

$$M_{\text{S2}} = \frac{55.85}{0.2009} = 278 \frac{\text{g}}{\text{mol}} \rightarrow N_{\text{H}_2\text{O}} = \frac{278 \times 0.4536}{18.016} = 7.$$

The residual molar mass for the anion of **S2** is $278 - 55.85 - 7 \times 18.016 = 96.038$, which corresponds to the SO_4^{2-} anion. So, **S2** is **FeSO₄ · 7H₂O**.

Finally, we need to determine the amount of water molecules of hydration in **S1**. We can assume that the co-precipitation reaction is the following two parallel reactions:



Salts **S1** and **S2** precipitate through reactions (1) and (2) respectively. The mass of FeO formed through reaction (1) is as follows:

$$m_{\text{FeO}} = \frac{1.3901}{278} \times (55.85 + 16.00) = 0.3593 \text{ g}$$

Through the mass of Fe_2O_3 , we can calculate the number of water molecules in **S1**:

$$N_{\text{H}_2\text{O}} \times 18.016 = \frac{2.7025}{2 \times \frac{1.1578 - 0.3593}{(2 \times 55.85 + 3 \times 16.00)}} - (55.85 + 3 \times 35.46) \rightarrow N_{\text{H}_2\text{O}} = 6$$

So, **S1** is **FeCl₃ · 6H₂O**.

- The molar ratio of Fe^{II} to Fe^{III} shows the stoichiometric relationship for **Fe₃O₄**. The values for n and m are 3 and 4 respectively.
- $\text{Fe}^{2+} + 2\text{Fe}^{3+} + 8\text{OH}^- \rightarrow \text{Fe}_3\text{O}_4 + 4\text{H}_2\text{O}$.
- So, $n = 3$ and $\text{X}^{(n-1)+}$ is Fe^{2+} , X^{n+} is Fe^{3+} . The absence of catalytic activity means that there is no Fe^{2+} ion. So, that oxide is **Fe₂O₃**, in which the mass fraction of Fe is smaller than in Fe_3O_4 .

5. To prolong the catalytic activity, we must reduce Fe^{3+} to Fe^{2+} :

NaIO_4 is incorrect, because it is an oxidant;

Sodium citrate is not a correct option as it forms a chelate complex with Fe^{2+} hindering the activity;

As Na_3PO_4 can interfere with Fe^{3+} ions, forming the insoluble FePO_4 salt, which has a reported solubility product constant around 1×10^{-22} , the catalytic performance is consequently reduced due to slower reduction of Fe^{3+} to Fe^{2+} ;

NaBH_4 is the only **correct option** without negative effects on the system. It reduces back oxidised Fe_2O_3 NPs to Fe_3O_4 NPs.

6. Firstly from the volume we can get $r = \sqrt[3]{\frac{3 \times V_{\max}}{4\pi N_A}} = 0.355 \text{ nm}$. Using that value, the surface for one mole of $\mathbf{Y}_p$ is $S = 4\pi r^2 N_A = 9.532 \times 10^5 \text{ m}^2 \text{ mol}^{-1}$. We can calculate the molar mass of $\mathbf{Y}_p$:

$$M_{\mathbf{Y}_p} = \frac{9.532 \times 10^5 \text{ m}^2 \text{ mol}^{-1}}{1.324 \times 10^6 \text{ m}^2 \text{ kg}^{-1}} = 0.720 \text{ kg mol}^{-1}$$

The only logical solution is C_{60} . So, $\mathbf{Y}$ is C, “p” is 60.

7. We have, $\frac{0.001 \times 10^{-6}}{60} = \frac{3.73 \times 10^{-9} [\text{S}]}{1.03 \times 10^{-3} + [\text{S}]}$, that gives $[\text{S}] = 4.62 \text{ }\mu\text{M}$.

8. First, we need to calculate: $r = \frac{3.73 \times 10^{-9} \cdot 0.025 \times 10^{-3}}{1.03 \times 10^{-3} + 0.025 \times 10^{-3}} = 8.84 \times 10^{-11} \text{ M} \cdot \text{s}^{-1}$, and from here we calculate $t = \frac{\Delta[\text{P}]}{r} = \frac{0.025 \times 10^{-6}}{8.84 \times 10^{-11}} = 283 \text{ s} = 4.72 \text{ min}$

Problem 5. Haber–Bosch process



2. $\Delta_r H^\circ = -46.2 \times 2 = -92.4 \left(\frac{\text{kJ}}{\text{mol}} \right)$

$$\Delta_r S^\circ = 192.7 \times 2 - 191.6 - 130.7 \times 3 = -198.3 \left(\frac{\text{J}}{\text{mol} \cdot \text{K}} \right)$$

$$K_p = 1 \rightarrow \Delta_r G^\circ = 0 \rightarrow T = \frac{92400}{198.3} = \mathbf{466 \text{ K}}$$

3. $\Delta_r C_p = 35.1 \times 2 - 29.1 - 28.8 \times 3 = -45.3 \left(\frac{\text{J}}{\text{mol} \cdot \text{K}} \right)$

$$T = 300 + 273 = 573 \text{ K}$$

$$\Delta_r H_{573}^\circ = -92400 - 45.3(573 - 298) = -104857.5 \left(\frac{\text{J}}{\text{mol}} \right)$$

$$\Delta_r S_{573}^\circ = -198.3 - 45.3 \ln \left(\frac{573}{298} \right) = -227.9 \left(\frac{\text{J}}{\text{mol} \cdot \text{K}} \right)$$

$$\Delta_r G_{573}^\circ = -104857.5 - 573 \times (-227.9) = 25729.2 \left(\frac{\text{J}}{\text{mol}} \right)$$

$$K_p = e^{-\frac{25729.2}{573 \times 8.314}} = \mathbf{4.5 \times 10^{-3}}$$

4. $n(\text{H}_2) = 0.9 \times 3 = \mathbf{2.7 \text{ mol.}}$

5. a)

	N_2	+	3H_2	$\rightarrow$	2NH_3
Initially	1		3		0
Reacted	$-x$		$-3x$		$+2x$
Equilibrium	$1-x$		$3-3x$		$2x$

$$K_p = \frac{\left(\frac{P_{\text{NH}_3}}{P^\circ} \right)^2}{\left(\frac{P_{\text{H}_2}}{P^\circ} \right)^3 \times \frac{P_{\text{N}_2}}{P^\circ}} = \frac{\left(\frac{2x}{4-2x} \times \frac{P}{P^\circ} \right)^2}{\left(\frac{3-3x}{4-2x} \times \frac{P}{P^\circ} \right)^3 \times \frac{1-x}{4-2x} \times \frac{P}{P^\circ}} ; P^\circ = 1 \text{ bar}; P = 150 \text{ bar}$$

$$K_p = 4.5 \times 10^{-3} = \frac{(2x)^2 \times (4-2x)^2}{(3-3x)^3 \times (1-x) \times 150^2}$$

$$x = 0.733; \text{ yield} = \mathbf{73.3\%}$$

b) The total pressure will be higher on the reactant side and vice versa. As the total pressure increases at a constant temperature, the equilibrium will shift toward the product according to Le Chatelier's principle, which in turn increases the equilibrium yield.

6. **Stage 2→3** is limiting because the triple bond of nitrogen is breaking, which requires the largest activation energy. In addition, **stage 5→6** also has a large activation energy, because two hydrogen molecules dissociate at a time, so, this answer is also accepted.

Note: In this problem, the simple kinetic model was considered to understand the mechanism. In real experiments, the rate determining step is the dissociative chemisorption of nitrogen, where absorption and dissociation are the intrinsically coupled parts of a single event.

7. The catalyst is produced by reducing Fe_3O_4 . However, the reducing agent cannot reduce the entire volume of Fe_3O_4 , since its concentration decreases as it penetrates the catalyst and does not reach its entire interior. Thus, the catalyst remains unreduced inside. According to this logic, there should be two layers, but an additional layer forms, an under-reduced form of Fe_3O_4 . It is known for certain that the oxidation state of Fe in this layer must be lower than that of Fe_3O_4 and greater than 0. Only **FeO** is suitable for this option.

8. $n(\text{Fe}) = \frac{10}{55.85} = 0.1791 \text{ mol}$

$$n(\text{Fe})_{\text{in Fe}_3\text{O}_4} = \frac{4}{3} \times 3.141 \times (50 \times 10^{-7})^3 \times \frac{5 \times 3}{231.55} = 3.3913 \times 10^{-17} \text{ mol}$$

$$\begin{aligned} n(\text{Fe})_{\text{in FeO}} &= \frac{4}{3} \times 3.141 \times (60 \times 10^{-7 \times 3} - 50 \times 10^{-7 \times 3}) \times \frac{5.7}{71.85} = \\ &= 3.0234 \times 10^{-17} \text{ mol} \end{aligned}$$

$$\begin{aligned} n(\text{Fe})_{\text{in Fe}} &= \frac{4}{3} \times 3.141 \times (100 \times 10^{-7 \times 3} - 60 \times 10^{-7 \times 3}) \times \frac{7.9}{55.85} = \\ &= 4.6444 \times 10^{-16} \text{ mol} \end{aligned}$$

$$\begin{aligned} \sum n(\text{Fe})_{\text{in nanoparticle}} &= 3.3913 \times 10^{-17} + 3.0234 \times 10^{-17} + 4.6444 \times 10^{-16} \\ &= 5.2859 \times 10^{-16} \text{ mol} \end{aligned}$$

$$N(\text{nanoparticle}) = \frac{0.1791}{5.2859 \times 10^{-16}} = 3.3883 \times 10^{14}$$

$$S(\text{nanoparticle}) = 4 \times 3.141 \times (100 \times 10^{-9})^2 = 1.2564 \times 10^{-13} \text{ m}^2$$

$$S_{\text{total}} = 1.2564 \times 10^{-13} \times 3.3883 \times 10^{14} = \mathbf{42.57 \text{ m}^2}$$

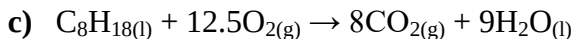
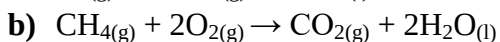
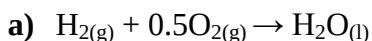
9. $V_{\text{cube}} = \frac{10}{7.9} = 1.266 \text{ cm}^3$

$$S_{\text{cube}} = 1.266^{\frac{2}{3}} \times 6 = 7.02 \text{ cm}^2 = 7.02 \times 10^{-4} \text{ m}^2$$

$$\frac{42.57}{7.02 \times 10^{-4}} = \mathbf{60640 \text{ times faster}}$$

Problem 6. Hydrogen fuel

1.



$$\Delta_r H^\circ = \sum \Delta_f H^\circ_{\text{products}} - \sum \Delta_f H^\circ_{\text{reagents}}$$

$$\Delta_c H^\circ(\text{H}_2) = -285.8 \text{ kJ/mol}$$

$$\Delta_c H^\circ(\text{CH}_4) = (-393.5 + (-285.8) \times 2) - (-74.8) = -890.3 \text{ kJ/mol}$$

$$\Delta_c H^\circ(\text{C}_8\text{H}_{18}) = (-393.5 \times 8 + (-285.8) \times 9) - (-260.2) = -5460 \text{ kJ/mol}$$

2. Energy density (H_2) = $285.8 \times \frac{1000}{2} \times \frac{1}{1000} = 142.9 \text{ MJ/kg}$

Energy density (CH_4) = $890.3 \times \frac{1000}{16} \times \frac{1}{1000} = 55.6 \text{ MJ/kg}$

Energy density (C_8H_{18}) = $5460 \times \frac{1000}{114} \times \frac{1}{1000} = 47.9 \text{ MJ/kg}$

Hydrogen is the best fuel, considering energy density.

3. $E = 1 \times \frac{3600}{0.36} = 10,000 \text{ kJ}$

$$n(\text{O}_2) = \frac{10000}{285.8} \times 0.5 = 17.5 \text{ mol}$$

$$V(\text{air}) = \frac{17.5}{0.2} \times \frac{RT}{P} = 87.5 \times \frac{8.314 \times 298}{100} = 2170 \text{ L}$$

4. Total distance = $3.75 \times 10^6 \times 22000 = 8.25 \times 10^{10} \text{ km}$

Methane used for : $8.25 \times 10^{10} \times 0.65 = 5.3625 \times 10^{10} \text{ km}$

Gasoline used for : $8.25 \times 10^{10} \times 0.35 = 2.8875 \times 10^{10} \text{ km}$

$$V(\text{CH}_4) = \frac{5.3625 \times 10^{10} \times 5}{100} = 2.68125 \times 10^9 \text{ m}^3$$

$$n(\text{CO}_2)_{\text{from methane}} = \frac{2.68125 \times 10^9 \times 10^5}{8.314 \times 298} = 1.08221 \times 10^{11} \text{ mol}$$

$$V(\text{isooctane}) = \frac{2.8875 \times 10^{10} \times 9}{100} = 2.5988 \times 10^9 \text{ dm}^3$$

$$n(\text{CO}_2)_{\text{from isooctane}} = \frac{2.5988 \times 10^9 \times 1000 \times 0.72 \times 8}{114} = 1.31305 \times 10^{11} \text{ mol}$$

$$n(\text{CO}_2)_{\text{total}} = 1.08221 \times 10^{11} + 1.31305 \times 10^{11} = 2.39526 \times 10^{11} \text{ mol}$$

$$m(\text{CO}_2) = \frac{2.39526 \times 10^{11} \times 44}{10^{12}} = \mathbf{10.539 \text{ million tons per year}}$$

This is approximately 7-8% of the total annual CO_2 emissions in Uzbekistan.

$$5. \quad 285800 = 75.4 \times (373 - 298) + (44000 + (-38) \times (373 - 298)) + 37.4 \times (800 - 373) +$$

$$+ (29.1 \times n(\text{N}_2) + 29.4 \times \left(\frac{n(\text{N}_2)}{4} - 0.5 \right)) \times (800 - 298)$$

$$n(\text{N}_2) = 12.6 \text{ mol}$$

For simplicity, the reaction: $\text{H}_{2(\text{g})} + 0.5\text{O}_{2(\text{g})} \rightarrow \text{H}_2\text{O}_{(\text{g})}$ ($T = 298 \text{ K}$, $P = 1 \text{ bar}$) can be used for the calculations. Considering the reaction with liquid water would introduce an additional term in the energy balance, but it does not affect the final result. $\Delta_r H^\circ = -241800 \text{ J/mol}$

$$241800 = \left(37.4 \times 1 + n(\text{N}_2) \times 29.1 + \left(\frac{n(\text{N}_2)}{4} - 0.5 \right) \times 29.4 \right) \times (800 - 298)$$

$$n(\text{N}_2) = 12.6 \text{ mol}$$

6.

a) $241800 = 37.4 \times 1 \times (T_f - 298)$

$$T_f = 6763.24 \text{ K}$$

b) $\Delta_r H^\circ$ and $\Delta_r S^\circ$ as functions of temperature:

- $\Delta_r H^\circ = -241800 - 6.1(T - 298)$

- $\Delta_r S^\circ = -44.6 - 6.1 \ln \left(\frac{T}{298} \right)$

K_p for the reaction:

$$K_p = \exp \left\{ - \frac{[(-241800 - 6.1(T - 298)) + T(44.6 + 6.1 \ln \left(\frac{T}{298} \right))]}{RT} \right\} \quad (1)$$

	$\text{H}_{2(\text{g})}$	+	$0.5\text{O}_{2(\text{g})}$	$\rightarrow$	$\text{H}_2\text{O}_{(\text{g})}$
Initially	-		-		1
Reacted	x		$0.5x$		$-x$
Equilibrium	x		0.5		$1-x$

$$\sum n = 1 + 0.5x$$

Since the equilibrium constant K_p is “large”, for simplification, it is assumed that the reaction initially proceeds to completion and then slightly reverses to reach equilibrium.

$$K_p = \frac{\frac{P_{\text{H}_2\text{O}}}{P^\circ}}{\frac{P_{\text{H}_2}}{P^\circ} \times \sqrt{\frac{P_{\text{O}_2}}{P^\circ}}} = \frac{\frac{1-x}{1+0.5x} \times \frac{P}{P^\circ}}{\frac{x}{1+0.5x} \times \frac{P}{P^\circ} \times \sqrt{\frac{0.5x}{1+0.5x} \times \frac{P}{P^\circ}}}; P = P^\circ = 1 \text{ bar}$$

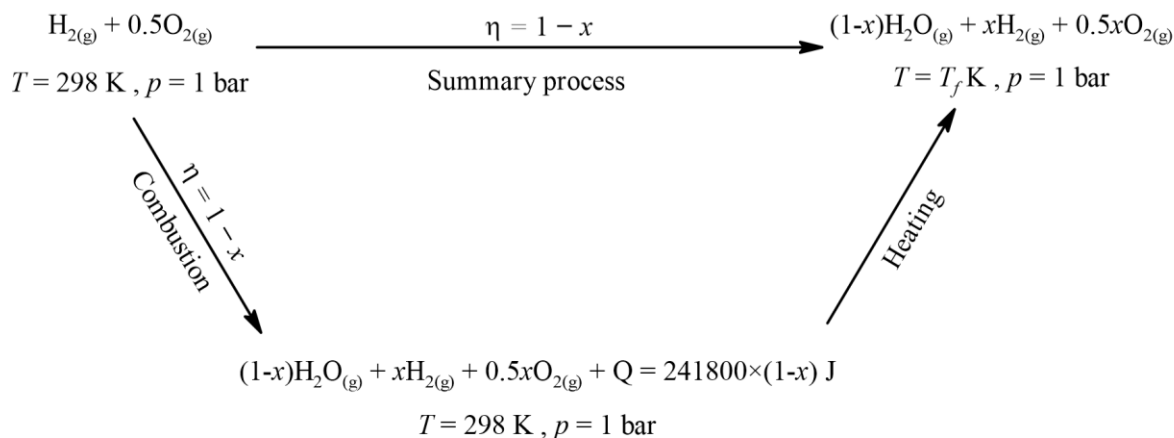
$$K_p = \frac{(1-x) \times \sqrt{1+0.5x}}{x \times \sqrt{0.5x}} \quad (2)$$

Using equations (1) and (2) with $T = 6763.24 \text{ K} \rightarrow x = 0.9614$.

Composition of mixture: $0.9614 \text{ H}_2 : 0.0386 \text{ H}_2\text{O} : 0.4807 \text{ O}_2$, that corresponds to

$$\chi(\text{H}_2) = 0.6493; \chi(\text{H}_2\text{O}) = 0.0261; \chi(\text{O}_2) = 0.3246.$$

c) One can construct a simple thermodynamic cycle for the combustion process:



$$241800 \times (1 - x) = \left[(1 - x) \times 37.4 + x \times 28.8 + x \times \frac{29.4}{2} \right] (T_f - 298)$$

$$T_f = \frac{241800 \times (1 - x)}{\left((1 - x) \times 37.4 + x \times 28.8 + x \times \frac{29.4}{2} \right)} + 298 \quad (3)$$

For $x = 0.9614$, $T_f = 513.73 \text{ K}$. This value is not even near to 6763.24 K because the composition of the mixtures is very different.

d) The composition of the gas mixture at the final temperature is initially unknown, which is required to determine the final temperature, while simultaneously, the final temperature is unknown for calculating the mixture composition. Therefore, an iterative procedure is necessary, adjusting the temperature until it is consistent with all other parameters. The iteration can be performed as follows:

1. Determine the composition of the gas mixture at a given temperature
2. Calculate the final temperature using the energy balance based on the determined composition.
3. Compare the calculated temperature with the given temperature: if the given temperature is lower than the calculated value, increase it; if it is higher, decrease it.
4. Repeat steps 1–3 until the given and calculated temperatures converge.

The iterative procedure using equations (1), (2) and (3):

First iteration step:

Assume $T = 3900$ K. Then, $K_p = 2.42$, $x = 0.4836$, and the calculated temperature, $T_f = 3392.6$ K < 3900 K, indicating that the temperature should be decreased.

Second iteration step:

Assume $T = 3850$ K. Then, the calculated temperature $T_f = 3533.2$ K < 3850 K, indicating that the temperature should be decreased.

The following table summarises the calculated values:

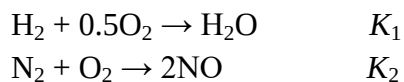
T	K_p	x	T_f
3900	2.42	0.4836	3392.6
3850	2.6893	0.4619	3533.2
3800	2.9967	0.4400	3676.1
3750	3.3485	0.4180	3820.6
3770	3.202	0.4268	3762.7
3768	3.2163	0.4259	3768.6

$$T_f = 3768.6 \text{ K}$$

☐ 3900 K ☐ 3850 K ☐ 3800 K ☒ 3750 K ☐ 3700 K ☐ 3650 K

In reality T_f is about 2400 K. The significantly higher temperatures obtained in calculations arise from the assumptions that the heat capacities (C_p) are independent from temperature and that the system consists only of H_2 , O_2 and H_2O . In practice, C_p also depends on temperature, and additional species such as H, OH, and O are present, which affect the energy balance and reduce the final temperature.

7.



K_p values for these reactions at 3200 K :

$$K_1 = \exp \left\{ - \frac{(-241800 - 6.1(3200 - 298)) + 3200 \left(44.6 + 6.1 \ln \left(\frac{3200}{298} \right) \right)}{R \times 3200} \right\} = 14.12$$

$$K_2 = \exp \left\{ - \frac{(180600 + 1.3(3200 - 298)) - 3200 \left(24.8 + 1.3 \ln \left(\frac{3200}{298} \right) \right)}{R \times 3200} \right\} = 0.028$$

If 1 mol of hydrogen is used for combustion, $n(\text{O}_2)_{\text{initial}} = 0.5 \text{ mol}$ and $n(\text{N}_2)_{\text{initial}} = 2 \text{ mol}$

	$\text{H}_{2(\text{g})}$	+	$0.5\text{O}_{2(\text{g})}$	→	$\text{H}_2\text{O}_{(\text{g})}$
Initially	1		0.5		-
Reacted	$-x$		$-0.5x-y$		x
Equilibrium	$1-x$		$0.5-0.5x-y$		x

	$\text{N}_{2(\text{g})}$	+	$\text{O}_{2(\text{g})}$	→	$2\text{NO}_{(\text{g})}$
Initially	2		0.5		-
Reacted	$-y$		$-0.5x-y$		$2y$
Equilibrium	$2-y$		$0.5-0.5x-y$		$2y$

It can be seen that $K_1 \gg K_2$, so it can be assumed that most of the oxygen is lost as a result of reaction 1.

	$\text{H}_{2(\text{g})}$	+	$0.5\text{O}_{2(\text{g})}$	→	$\text{H}_2\text{O}_{(\text{g})}$
Initially	1		0.5		-
Reacted	$-x$		$-0.5x$		x
Equilibrium	$1-x$		$0.5-0.5x$		x

$$\sum n = 1 + 0.5 + 2 - 0.5x = 3.5 - 0.5x$$

$$K_p = \frac{\frac{P_{\text{H}_2\text{O}}}{P^\circ}}{\frac{P_{\text{H}_2}}{P^\circ} \times \sqrt{\frac{P_{\text{O}_2}}{P^\circ}}} = \frac{\frac{x}{3.5 - 0.5x} \times \frac{P}{P^\circ}}{\frac{1-x}{3.5 - 0.5x} \times \frac{P}{P^\circ} \times \sqrt{\frac{0.5 - 0.5x}{3.5 - 0.5x} \times \frac{P}{P^\circ}}}; \quad P = P^\circ = 1 \text{ bar}$$

$$K_p = \frac{x \times \sqrt{3.5 - 0.5x}}{(1-x) \times \sqrt{0.5 - 0.5x}} = 14.12$$

$$x = 0.742 \text{ mol}$$

(without $K_1 \gg K_2$ assumption, $x = 0.719 \text{ mol}$)

$$0.028 = \frac{(2y)^2}{(2 - y) \times (0.5 - 0.5 \times 0.742 - y)}$$

$$y = 0.036 \text{ mol}$$

(without $K_1 \gg K_2$ assumption, $y = 0.038 \text{ mol}$)

$$\text{Mole fraction(NO)} = \frac{2 \times 0.036}{3.5 - 0.5 \times 0.742} = 0.023$$

(without $K_1 \gg K_2$ assumption, mole fraction (NO) = 0.024)

8.

- ☒ Lower the combustion temperature.
- ☐ Decrease the excess air ratio significantly.
- ☐ Raise the compression ratio in the engine.
- ☐ Increase the fuel flow speed.

Problem 7. 150 Years of Urease

1. The rate of product formation is as follows:

$$\frac{d[P]}{dt} = k_2[\text{Urease} * \text{CO}(\text{NH}_2)_2]$$

Use the steady-state approximation for $[\text{Urease} * \text{CO}(\text{NH}_2)_2]$:

$$\begin{aligned} \frac{d[\text{Urease} * \text{CO}(\text{NH}_2)_2]}{dt} &= \\ &= k_1[\text{Urease}][\text{CO}(\text{NH}_2)_2] - k_{-1}[\text{Urease} * \text{CO}(\text{NH}_2)_2] \\ &\quad - k_2[\text{Urease} * \text{CO}(\text{NH}_2)_2] = 0 \end{aligned}$$

Derive an equation for $[\text{Urease} * \text{CO}(\text{NH}_2)_2]$:

$$[\text{Urease} * \text{CO}(\text{NH}_2)_2] = \frac{k_1}{k_{-1} + k_2} [\text{Urease}][\text{CO}(\text{NH}_2)_2]$$

Express the rate of product formation in terms of the equilibrium concentrations: $[\text{Urease}]$ and $[\text{CO}(\text{NH}_2)_2]$:

$$\frac{d[P]}{dt} = \frac{k_1 k_2}{k_{-1} + k_2} [\text{Urease}][\text{CO}(\text{NH}_2)_2]$$

Use mass balance for $[\text{CO}(\text{NH}_2)_2]_{\text{total}}$ considering $[\text{CO}(\text{NH}_2)_2]_{\text{total}} \gg [\text{Urease}]_{\text{total}}$:

$$[\text{CO}(\text{NH}_2)_2]_{\text{total}} = [\text{CO}(\text{NH}_2)_2] + [\text{Urease} * \text{CO}(\text{NH}_2)_2] \approx [\text{CO}(\text{NH}_2)_2]$$

Use mass balance for $[\text{Urease}]_{\text{total}}$ considering acid-base equilibrium:

$$[\text{Urease}]_{\text{total}} = \frac{[\text{Urease}]}{\alpha_{\text{HU}^-}} + \frac{[\text{Urease} * \text{CO}(\text{NH}_2)_2]}{\alpha_{\text{HU}^-}} = \frac{[\text{Urease}] + \frac{k_1}{k_{-1} + k_2} [\text{Urease}][\text{CO}(\text{NH}_2)_2]}{\alpha_{\text{HU}^-}},$$

$$[\text{Urease}] = \frac{[\text{Urease}]_{\text{total}} \alpha_{\text{HU}^-}}{1 + \frac{k_1}{k_{-1} + k_2} [\text{CO}(\text{NH}_2)_2]}$$

Determine α_{HU^-} :

$$\alpha_{\text{HU}^-} = \frac{[\text{HU}^-]}{[\text{H}_2\text{U}] + [\text{HU}^-] + [\text{U}^{2-}]} = \frac{[\text{HU}^-]}{\frac{[\text{H}^+][\text{HU}^-]}{K_{a1}} + [\text{HU}^-] + \frac{K_{a2}[\text{HU}^-]}{[\text{H}^+]}} = \frac{1}{\frac{[\text{H}^+]}{K_{a1}} + 1 + \frac{K_{a2}}{[\text{H}^+]}}.$$

Express the rate of product formation in terms of the total concentrations of Urease, $\text{CO}(\text{NH}_2)_2$ and H^+ :

$$\begin{aligned} \frac{d[P]}{dt} &= \frac{k_1 k_2}{k_{-1} + k_2} \cdot \frac{[\text{Urease}]_{\text{total}}}{1 + \frac{k_1}{k_{-1} + k_2} [\text{CO}(\text{NH}_2)_2]_{\text{total}}} \cdot \frac{1}{\frac{[\text{H}^+]}{K_{a1}} + 1 + \frac{K_{a2}}{[\text{H}^+]}} [\text{CO}(\text{NH}_2)_2]_{\text{total}} = \\ &= \frac{k_2 [\text{Urease}]_{\text{total}} [\text{CO}(\text{NH}_2)_2]_{\text{total}}}{\left(\frac{k_{-1} + k_2}{k_1} + [\text{CO}(\text{NH}_2)_2]_{\text{total}} \right) \left(1 + \frac{[\text{H}^+]}{K_{a1}} + \frac{K_{a2}}{[\text{H}^+]} \right)} \end{aligned}$$

2.

$$a) \frac{d[P]}{dt} = \frac{k_2[\text{Urease}]_{\text{total}}[\text{CO}(\text{NH}_2)_2]_{\text{total}}}{\left(\frac{k_{-1}+k_2}{k_1}\right)\left(1+\frac{[\text{H}^+]}{K_{a1}}+\frac{K_{a2}}{[\text{H}^+]}\right)}. \text{ So } n(\text{Urease}) = 1 \text{ and } n(\text{CO}(\text{NH}_2)_2) = 1.$$

$$b) \frac{d[P]}{dt} = \frac{k_2[\text{Urease}]_{\text{total}}[\text{CO}(\text{NH}_2)_2]_{\text{total}}}{[\text{CO}(\text{NH}_2)_2]_{\text{total}}\left(1+\frac{[\text{H}^+]}{K_{a1}}+\frac{K_{a2}}{[\text{H}^+]}\right)} = \frac{k_2[\text{Urease}]_{\text{total}}}{\left(1+\frac{[\text{H}^+]}{K_{a1}}+\frac{K_{a2}}{[\text{H}^+]}\right)}. \text{ So } n(\text{Urease}) = 1 \text{ and } n(\text{CO}(\text{NH}_2)_2) = 0.$$

3.

$$r = \frac{d[P]}{dt} = \frac{k_2[\text{Urease}]_{\text{total}}[\text{CO}(\text{NH}_2)_2]_{\text{total}}}{\left(\frac{k_{-1}+k_2}{k_1}+[\text{CO}(\text{NH}_2)_2]_{\text{total}}\right)\left(1+\frac{[\text{H}^+]}{K_{a1}}+\frac{K_{a2}}{[\text{H}^+]}\right)} = \frac{\text{const}}{\left(1+\frac{[\text{H}^+]}{K_{a1}}+\frac{K_{a2}}{[\text{H}^+]}\right)}.$$

$$\text{At } r_{\text{max}} \rightarrow \frac{dr}{d[\text{H}^+]} = 0 \rightarrow r' = \frac{-\text{const} \cdot \left(1+\frac{[\text{H}^+]}{K_{a1}}+\frac{K_{a2}}{[\text{H}^+]}\right)'}{\left(1+\frac{[\text{H}^+]}{K_{a1}}+\frac{K_{a2}}{[\text{H}^+]}\right)^2} = 0 \rightarrow \frac{1}{K_{a1}} - \frac{K_{a2}}{[\text{H}^+]^2} = 0$$

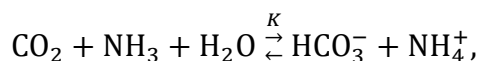
Or we can just differentiate the denominator (it should have minimum):

$$\frac{d\left(1+\frac{[\text{H}^+]}{K_{a1}}+\frac{K_{a2}}{[\text{H}^+]}\right)}{d[\text{H}^+]} = 0 \rightarrow \frac{1}{K_{a1}} - \frac{K_{a2}}{[\text{H}^+]^2} = 0$$

$$[\text{H}^+] = \sqrt{K_{a1}K_{a2}} \rightarrow \text{pH} = \frac{\text{p}K_{a1}+\text{p}K_{a2}}{2} = \frac{5.62+9.07}{2} = 7.35$$

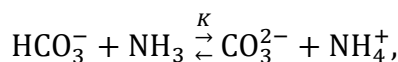
4.

- a) Products of decomposition of 0.005 M $\text{CO}(\text{NH}_2)_2$ are 0.005 M CO_2 and 0.010 M NH_3 . Firstly, ammonium bicarbonate is formed, because the equilibrium constant for this reaction is sufficiently large:



$$K = \frac{K_b K_{a1}}{K_w} = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} \cdot \frac{[\text{HCO}_3^-][\text{H}^+]}{[\text{CO}_2]} \cdot \frac{1}{[\text{H}^+][\text{OH}^-]} = \frac{[\text{NH}_4^+][\text{HCO}_3^-]}{[\text{NH}_3][\text{CO}_2]} = \frac{10^{-4.75} \cdot 10^{-3.75}}{10^{-14}} = 3.16 \cdot 10^5.$$

After this reaction, we can assume that the solution contains 0.005 M HCO_3^- , 0.005 M NH_4^+ and 0.005 M NH_3 . Residual ammonia can react with bicarbonate to form carbonate as follows:



$$K = \frac{K_b K_{a2}}{K_w} = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} \cdot \frac{[\text{CO}_3^{2-}][\text{H}^+]}{[\text{HCO}_3^-]} \cdot \frac{1}{[\text{H}^+][\text{OH}^-]} = \frac{[\text{NH}_4^+][\text{CO}_3^{2-}]}{[\text{NH}_3][\text{HCO}_3^-]} = \frac{10^{-4.75} \cdot 10^{-10.33}}{10^{-14}} = 8.32 \cdot 10^{-2}.$$

If x M carbonate is formed:

$$8.32 \cdot 10^{-2} = \frac{x \cdot (x+0.005)}{(0.005-x) \cdot (0.005-x)} \rightarrow x = 3.39 \cdot 10^{-4}$$

$$\text{So } [\text{H}^+] = \frac{K_{a2}[\text{HCO}_3^-]}{[\text{CO}_3^{2-}]} = \frac{10^{-10.33} \cdot (0.005 - 3.39 \cdot 10^{-4})}{3.39 \cdot 10^{-4}} = 6.43 \cdot 10^{-10} \text{ or}$$

$$[\text{H}^+] = \frac{K_w[\text{NH}_4^+]}{K_b[\text{NH}_3]} = \frac{10^{-14} \cdot (0.005 + 3.39 \cdot 10^{-4})}{10^{-4.75} \cdot (0.005 - 3.39 \cdot 10^{-4})} = 6.44 \cdot 10^{-10} \rightarrow \text{pH} = 9.19.$$

b) Let's simplify the kinetic equation as follows:

$$r = \frac{d[\text{P}]}{dt} = \frac{k_2[\text{Urease}]_{\text{total}}[\text{CO}(\text{NH}_2)_2]_{\text{total}}}{\left(\frac{k_{-1}+k_2}{k_1} + [\text{CO}(\text{NH}_2)_2]_{\text{total}}\right) \left(1 + \frac{[\text{H}^+]}{K_{a1}} + \frac{K_{a2}}{[\text{H}^+]}\right)} = \frac{\text{const}}{\left(1 + \frac{[\text{H}^+]}{K_{a1}} + \frac{K_{a2}}{[\text{H}^+]}\right)}$$

$$\text{At pH} = 7.00: \quad r(7.00) = \frac{\text{const}}{\left(1 + \frac{10^{-7.00}}{10^{-5.62}} + \frac{10^{-9.07}}{10^{-7.00}}\right)} = 0.9522 \cdot \text{const.}$$

$$\text{At pH} = 9.19: \quad r(9.19) = \frac{\text{const}}{\left(1 + \frac{10^{-9.19}}{10^{-5.62}} + \frac{10^{-9.07}}{10^{-9.19}}\right)} = 0.4313 \cdot \text{const.}$$

$$\text{So, } \frac{r(7.00)}{r(9.19)} = \frac{0.9522 \cdot \text{const}}{0.4313 \cdot \text{const}} = 2.21.$$

5. (1) – (c); (2) – (a); (3) – (b).

(1) When Urease is in the buffer solution with $\text{CO}(\text{NH}_2)_2$ the concentration of the product will increase at a constant pH until $\text{CO}(\text{NH}_2)_2$ runs out. This corresponds to option (c).

(2) When Urease is in the neutral solution with $\text{CO}(\text{NH}_2)_2$ and without any buffer, as the concentration of the product increases, the pH of the solution will shift towards an alkaline environment, which will inhibit Urease and slow down the enzymatic reaction. This corresponds to option (a).

(3) When Urease is in the liposomes with permeable membranes with $\text{CO}(\text{NH}_2)_2$ and without any buffer inside, first, in the liposome $\text{CO}(\text{NH}_2)_2$ decomposes under the action of Urease, thereby increasing the pH of the liposome and inhibiting Urease, but then the products leave the liposome (Urease remains in the liposome!), returning the pH and Urease activity to their original state. This corresponds to option (b).

6. The solution in question 4a contains $[\text{CO}_3^{2-}] = 3.39 \cdot 10^{-4} \text{ M}$.

$$\text{So, } [\text{Ca}^{2+}] \cdot 3.39 \cdot 10^{-4} > 3.36 \cdot 10^{-9} \rightarrow [\text{Ca}^{2+}] > 9.91 \cdot 10^{-6} \text{ M}$$

7. The rate of product formation from equilibrium concentrations of [Urease] and $[\text{CO}(\text{NH}_2)_2]$ remains as:

$$\frac{d[\text{P}]}{dt} = \frac{k_1 k_2}{k_{-1} + k_2} [\text{Urease}][\text{CO}(\text{NH}_2)_2]$$

For $[\text{CO}(\text{NH}_2)_2]_{\text{total}}$, the mass balance equation doesn't change:

$$[\text{CO}(\text{NH}_2)_2]_{\text{total}} = [\text{CO}(\text{NH}_2)_2] + [\text{Urease} * \text{CO}(\text{NH}_2)_2] \approx [\text{CO}(\text{NH}_2)_2]$$

Use mass balance for $[\text{B}(\text{OH})_3]_{\text{total}}$ considering $[\text{B}(\text{OH})_3]_{\text{total}} \gg [\text{Urease}]_{\text{total}}$:

$$[\text{B}(\text{OH})_3]_{\text{total}} = [\text{B}(\text{OH})_3] + [\text{Urease} * \text{B}(\text{OH})_3] \approx [\text{B}(\text{OH})_3]$$

Use mass balance for $[\text{Urease}]_{\text{total}}$:

$$[\text{Urease}]_{\text{total}} = \frac{[\text{Urease}]}{\alpha_{\text{HU}^-}} + \frac{[\text{Urease} \cdot \text{CO}(\text{NH}_2)_2]}{\alpha_{\text{HU}^-}} + \frac{[\text{Urease} \cdot \text{B}(\text{OH})_3]}{\alpha_{\text{HU}^-}} =$$

$$= \frac{[\text{Urease}] + \frac{k_1}{k_{-1}+k_2} [\text{Urease}] [\text{CO}(\text{NH}_2)_2] + \frac{[\text{Urease}] [\text{B}(\text{OH})_3]}{K_I}}{\alpha_{\text{HU}^-}},$$

$$[\text{Urease}] = \frac{[\text{Urease}]_{\text{total}} \alpha_{\text{HU}^-}}{1 + \frac{k_1}{k_{-1}+k_2} [\text{CO}(\text{NH}_2)_2] + \frac{[\text{B}(\text{OH})_3]}{K_I}},$$

$$\alpha_{\text{HU}^-} = \frac{[\text{HU}^-]}{[\text{H}_2\text{U}] + [\text{HU}^-] + [\text{U}^{2-}]} = \frac{[\text{HU}^-]}{\frac{[\text{H}^+][\text{HU}^-]}{K_{a1}} + [\text{HU}^-] + \frac{K_{a2}[\text{HU}^-]}{[\text{H}^+]}} = \frac{1}{\frac{[\text{H}^+]}{K_{a1}} + 1 + \frac{K_{a2}}{[\text{H}^+]}}.$$

Express the rate of product formation in terms of the total concentrations of Urease, $\text{CO}(\text{NH}_2)_2$, $\text{B}(\text{OH})_3$, and H^+ :

$$\frac{d[\text{P}]}{dt} = \frac{k_1 k_2}{k_{-1} + k_2} \cdot \frac{[\text{Urease}]_{\text{total}}}{1 + \frac{k_1}{k_{-1}+k_2} [\text{CO}(\text{NH}_2)_2]_{\text{total}} + \frac{[\text{B}(\text{OH})_3]_{\text{total}}}{K_I}} \cdot \frac{1}{\frac{[\text{H}^+]}{K_{a1}} + 1 + \frac{K_{a2}}{[\text{H}^+]}} \cdot [\text{CO}(\text{NH}_2)_2]_{\text{total}} =$$

$$= \frac{k_2 [\text{Urease}]_{\text{total}} [\text{CO}(\text{NH}_2)_2]_{\text{total}}}{\left(\frac{k_{-1}+k_2}{k_1} \left(1 + \frac{[\text{B}(\text{OH})_3]_{\text{total}}}{K_I} \right) + [\text{CO}(\text{NH}_2)_2]_{\text{total}} \right) \left(1 + \frac{[\text{H}^+]}{K_{a1}} + \frac{K_{a2}}{[\text{H}^+]} \right)}.$$

8. Make the linear function as follows:

$$r = \frac{k_2 [\text{Urease}]_{\text{total}} [\text{CO}(\text{NH}_2)_2]_{\text{total}}}{\left(\frac{k_{-1}+k_2}{k_1} \left(1 + \frac{[\text{B}(\text{OH})_3]_{\text{total}}}{K_I} \right) + [\text{CO}(\text{NH}_2)_2]_{\text{total}} \right) \left(1 + \frac{[\text{H}^+]}{K_{a1}} + \frac{K_{a2}}{[\text{H}^+]} \right)} = \frac{r_{\text{max}} [\text{CO}(\text{NH}_2)_2]_{\text{total}}}{K_M \left(1 + \frac{[\text{B}(\text{OH})_3]_{\text{total}}}{K_I} \right) + [\text{CO}(\text{NH}_2)_2]_{\text{total}}},$$

$$\frac{1}{r} = \frac{K_M \left(1 + \frac{[\text{B}(\text{OH})_3]_{\text{total}}}{K_I} \right)}{r_{\text{max}}} \cdot \frac{1}{[\text{CO}(\text{NH}_2)_2]_{\text{total}}} + \frac{1}{r_{\text{max}}} \rightarrow \text{slope} = \frac{K_M \left(1 + \frac{[\text{B}(\text{OH})_3]_{\text{total}}}{K_I} \right)}{r_{\text{max}}}.$$

Using the ratio of the slopes we find the value of K_I :

$$2.48 = \frac{1 + \frac{3.0 \cdot 10^{-4}}{K_I}}{1 + \frac{7.5 \cdot 10^{-5}}{K_I}} \rightarrow K_I = 7.7 \cdot 10^{-5}.$$

9. It is necessary to solve the following system of equations:

$$\begin{cases} \Delta_r H^\circ - 298.15 \cdot \Delta_r S^\circ = -R \cdot 298.15 \cdot \ln \left(\frac{1}{7.7 \cdot 10^{-5}} \right) \\ \Delta_r H^\circ - 308.15 \cdot \Delta_r S^\circ = -R \cdot 308.15 \cdot \ln \left(\frac{1}{1.57 \cdot 10^{-4}} \right) \end{cases} \rightarrow \begin{cases} \Delta_r H^\circ = -54.42 \text{ kJ mol}^{-1} \\ \Delta_r S^\circ = -103.8 \text{ J mol}^{-1} \text{K}^{-1} \end{cases}$$

Problem 8. Step-by-step

1. The overall kinetic equation is:

$$r = k[\text{OH}]^x[\text{COOH}]^y$$

We will use the values from the table to evaluate the values for k , x , and y .

$$\frac{k[0.2]^y}{k[0.2]^x[0.2]^y} = \frac{6}{4}, \text{ so, we have } \left(\frac{0.3}{0.2}\right)^x = \frac{6}{4}, \text{ so } x = 1.$$

We do the same for y ,

$$\frac{k[0.2][0.2]^y}{k[0.1][0.1]^y} = 4, \text{ or } 2 \cdot \frac{[0.2]^y}{[0.1]^y} = 4, \text{ so } y = 1.$$

Now we need to find the value of k by simply substituting the values of x and y .

$$2.7 \cdot 10^{-4} = k[0.1]^1[0.1]^1$$

$$k = 0.027 \text{ M}^{-1}\text{s}^{-1}$$

2. $z = x + y = 2$.

For a second order reaction with the equal initial concentrations:

$$\frac{1}{C} - \frac{1}{C_0} = kt$$

3. The degree of conversion is as follows:

$$p = 1 - \frac{C}{C_0}$$

$$DP = \frac{1}{1-p} \text{ (Carothers equation).}$$

4. Degree of polymerisation is as follows:

$$DP = \frac{C_0}{C}$$

$$\frac{C_0}{C} - 1 = C_0kt, \text{ so } DP(t) = C_0kt + 1, \text{ thus a linear equation.}$$

5. Therefore, $\frac{1}{1-p(t)} = C_0kt + 1$ – a linear relationship between $\frac{1}{1-p}$ and t .

6. Equilibrium constants for these reactions are expressed as the ratio between forward and reverse rate constants:

$$K_F = \frac{[\text{ArF} \cdots 2\text{B}]}{[\text{ArF}][\text{B}]^2} = \frac{k_{1,F}}{k_{-1,F}}$$

$$K_{\text{Cl}} = \frac{[\text{ArCl} \cdots \text{B}]}{[\text{ArCl}][\text{B}]} = \frac{k_{1,\text{Cl}}}{k_{-1,\text{Cl}}}$$

7. Rate of reaction is determined by the final step,

$$r = \frac{d[P]}{dt} = k_{\text{F}}[\text{ArF} \cdots 2\text{B}] \text{ for DFDPS,}$$

using the equilibrium constant, we can express the intermediate concentration,

$$[\text{ArF} \cdots 2\text{B}] = K_{\text{F}}[\text{ArF}][\text{B}]^2$$

So, the rate law is:

$$r = \frac{d[P]}{dt} = k_{\text{F}}K_{\text{F}}[\text{ArF}][\text{B}]^2$$

with $k_{\text{obs}} = k_{\text{F}}K_{\text{F}}$.

Similarly, for DCDPS:

$$r = \frac{d[P]}{dt} = k_{\text{Cl}}K_{\text{Cl}}[\text{ArCl}][\text{B}]$$

with $k_{\text{obs}} = k_{\text{Cl}}K_{\text{Cl}}$.

8. In the case of DFPDS (order of the reaction $n = 3$) $[\text{ArF}] = [\text{B}] = [\text{M}]$:

$$\frac{1}{[\text{M}]^2} - \frac{1}{[\text{M}]_0^2} = 2k_{\text{F}}K_{\text{F}}t$$

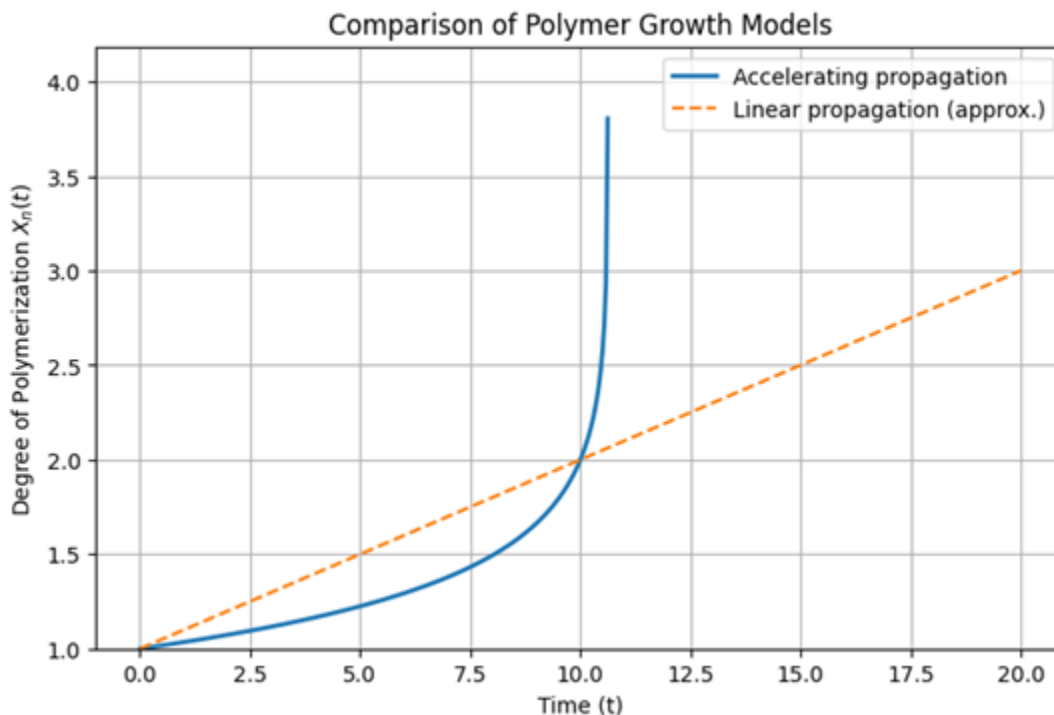
Degree of polymerisation: $DP = \frac{[\text{M}]_0}{[\text{M}]}$

$$\frac{[\text{M}]_0^2 - [\text{M}]^2}{[\text{M}]^2} = [\text{M}]_0^2 2k_{\text{F}}K_{\text{F}}t$$

According to the rate equation, $k_{\text{obs}} = k_{\text{F}}K_{\text{F}}$, then

$$DP^2 - 1 = [\text{M}]_0^2 2k_{\text{F}}K_{\text{F}}t = 0.1633^2 \times 2 \times 7023 \times 1 \Rightarrow DP = 19.4.$$

9. If we want to sketch qualitatively, then we start from DP = 1 in both cases:



In the second case ($\xi > 1$, blue line), propagation step accelerates by rate ratio ξ after every step of propagation, so eventually reaction proceeds so fast that it obtains exponential character.

10. So, for normal Carothers equation we have:

$$DP = \frac{1}{1-p}$$

How much time is needed to form a chain of length n ? Let's find it:

$$T_n = \frac{1}{kc_0} + \frac{1}{k\xi c_0} + \frac{1}{k\xi^2 c_0} + \dots = \sum_{i=1}^{n-1} \frac{1}{k\xi^{i-1} c_0} = \frac{1}{kc_0} \sum_{i=1}^{n-1} \frac{1}{\xi^{i-1}} = \frac{1}{kc_0} \sum_{i=0}^{n-2} \frac{1}{\xi^i}$$

So we came up with the sum of geometric progression:

$$T_n = \frac{1 - \xi^{-(n-1)}}{kc_0(1 - \xi^{-1})} = \frac{\xi - \xi^{-n+2}}{kc_0(\xi - 1)}$$

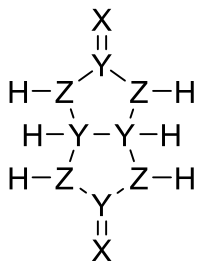
$$\xi^{-n+2} = \xi - kc_0(\xi - 1)T_n$$

$$(-n + 2) \ln \xi = \ln(\xi - kc_0(\xi - 1)T_n)$$

$$DP = n = 2 - \frac{\ln(\xi - kc_0(\xi - 1)T_n)}{\ln \xi} = 2 - \frac{\ln(\xi - kc_0(\xi - 1)t)}{\ln \xi}$$

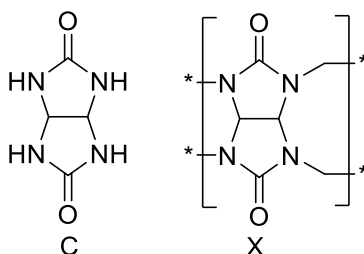
Problem 9. Host-guest chemistry of cucurbiturils as Uzbek hospitality

1. Mass spectra, one type of carbon and hydrogen and positive Tollens reaction of **B** correspond to the aldehyde group - CHO. This means **B** is glyoxal. From the figure, you can see that cucurbit[6]uril has six rotating links. Formaldehyde connects these fragments. Then **C** has the structure:



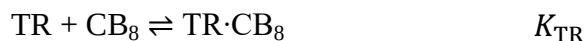
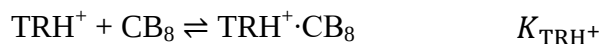
where most likely X is oxygen, Y is carbon and Z is nitrogen. In the synthesis of **C**, 1 mol of glyoxal and 2 mol of **A** are used. If we take this from the structure of **C**, then **A** should contain eight atoms, of which one atom is most likely oxygen and one carbon atom bound to it, and two are nitrogen, which condenses with the aldehyde. Then four atoms remain for hydrogen. Thus, the formula of **A** should be NH_2CONH_2 . This corresponds to urea, meaning salt **Y** will be NH_4OCN .

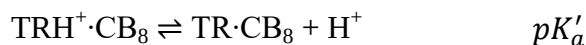
Y: NH_4OCN , **A:** $\text{CO}(\text{NH}_2)_2$, **B:** $(\text{CHO})_2$.



2. The molar mass of tropicamide is 284 g/mol, and for CB_8 1328 g/mol. 285 corresponds to $[\text{TRH}]^+$ ($m/z = (284+1)/1$). The peak with 665 with $z = 1$ does not have a suitable answer, then with $z = 2$ $m = 1330$ which corresponds to $[\text{CB}_8+2\text{H}]^{2+}$. Similarly, for peak 807 with $z = 1$ there is no answer, and for $z = 2$, $m = 1614$. This corresponds to $[\text{TR}\cdot\text{CB}_8+2\text{H}]^{2+}$.

3. The equilibria that occur:





Let's start with a pure TR solution. At $\text{pH} \approx 3$, the TRH^+ form predominates, and at $\text{pH} \approx 7$, the TR form predominates, and accordingly, the absorbances A_{max} and A_{min} depend only on their concentrations respectively. At the point $(A_{\text{max}} + A_{\text{min}})/2$, $[\text{TRH}^+] = [\text{TR}]$, therefore $K_a = [\text{H}^+]$, and from the graph, $pK_a \approx 5.2$.

Similarly, for the complex, $pK'_a \approx 6.7$

From the thermodynamic cycle we find $K_{\text{TRH}^+} = K_{\text{TR}} \cdot \frac{K_a}{K'_a} = 4.42 \cdot 10^5$.

4. At $\text{pH} = 4.0$ the molar fraction of protonated form of tropicamide is higher:

$$\alpha_{\text{TRH}^+} = \frac{[\text{TRH}^+]}{[\text{TRH}^+] + [\text{TRH}]} = \frac{[\text{H}^+]}{[\text{H}^+] + K_a} = \frac{10^{-4.0}}{10^{-4.0} + 10^{-5.2}} = 0.941$$

So, biologically active form is TRH^+ .

5. Without CB_8 :

$$\alpha_{\text{TRH}^+} = \frac{[\text{TRH}^+]}{[\text{TRH}^+] + [\text{TRH}]} = \frac{[\text{H}^+]}{[\text{H}^+] + K_a} = \frac{10^{-7.0}}{10^{-7.0} + 10^{-5.2}} = 0.0156$$

With CB_8 :

$$\alpha_{[\text{TRH}^+ \cdot \text{CB}_8]} = \frac{[\text{TRH}^+ \cdot \text{CB}_8]}{[\text{TRH}^+ \cdot \text{CB}_8] + [\text{TR} \cdot \text{CB}_8]} = \frac{[\text{H}^+]}{[\text{H}^+] + K'_a} = \frac{10^{-7.0}}{10^{-7.0} + 10^{-6.7}} = 0.334$$

The molar fraction of the protonated form of tropicamide increases by $\frac{0.334}{0.0156} = 21.4$ times in the presence of CB_8 .

6. Reaction order for CPD is 2 due to the linear dependence of $1/[\text{CPD}]$ on reaction time. This dependence is as follows:

$$\frac{1}{[\text{CPD}]} = \frac{1}{[\text{CPD}]_0} + k_{\text{obs}}t \rightarrow \text{slope} = k_{\text{obs}} = \frac{850 - 300}{4000 - 0} = 0.14 \text{ M}^{-1} \text{ s}^{-1}$$

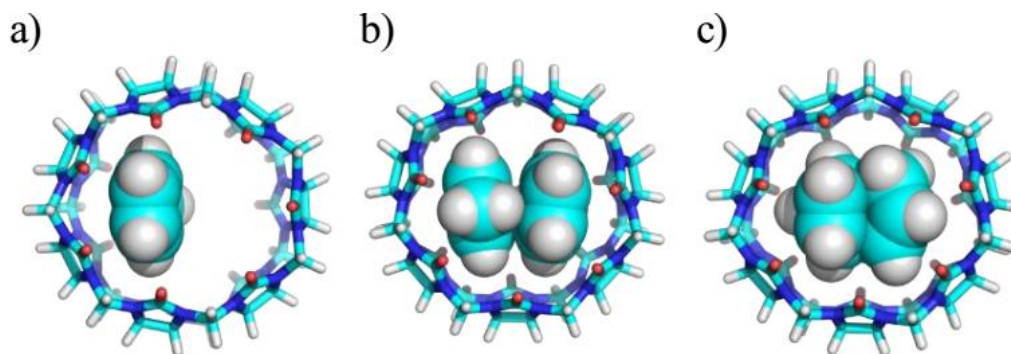
7. The rate of the dimerisation reaction is as follows:

$$r = \frac{d[\text{DCPD} \cdot \text{CB}_7]}{dt} = k[(\text{CPD})_2 \cdot \text{CB}_7] = kK_2[\text{CPD}][\text{CPD} \cdot \text{CB}_7] = kK_1K_2[\text{CPD}]^2[\text{CB}_7].$$

8. The rate of CPD dimerisation in the presence of CB₅, which is too small to encapsulate CPD, remains similar to that in water. There is neither complexation with CPD nor DCPD.

CB₆ is sufficiently large to encapsulate an individual CPD molecule. A CB₆-isolated CPD substrate is inaccessible to dimerisation and, unsurprisingly, addition of CB₆ markedly inhibits the reaction.

The intermediary-sized CB₇ accelerates the reaction by *ca.* five orders of magnitude. The dimerisation inside CB₇ proceeds in the tight-packing regime. This allows for transition-state stabilisation to occur.

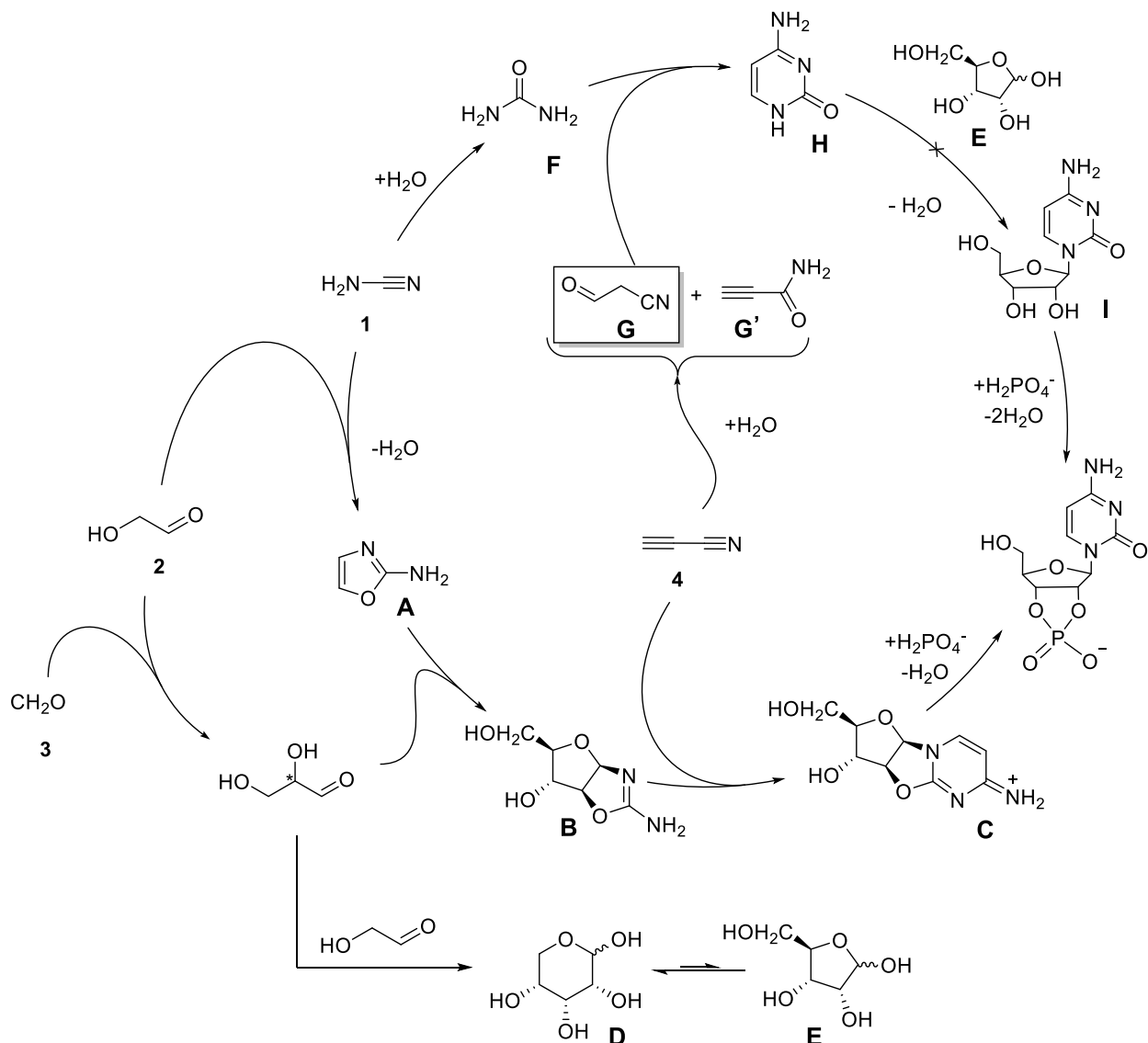


a) one CPD unit, b) two CPD units, and c) DCPD inside CB₇

For CB₈, the reaction proceeds in the loose-packing regime. In this case, a further contraction in the guest volume along the reaction coordinate would decrease rather than increase the overall complex stability, and no rate acceleration occurs for this homologue.

Problem 10. Prebiotic life

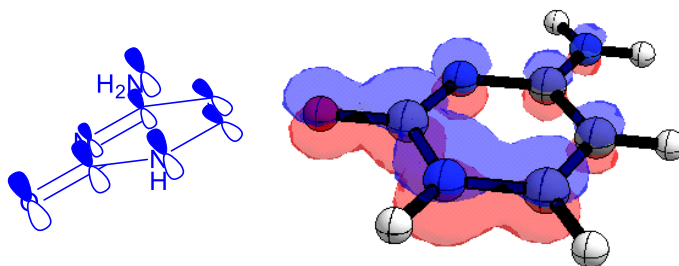
1. This is the Powner scheme:



The acyclic form of compound **D** is also considered as the correct answer.

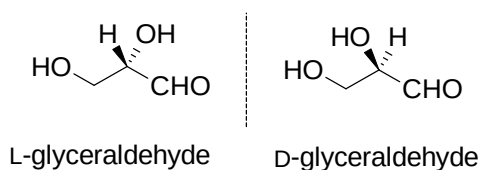
2.

- ☐ **electron delocalisation due to the aromaticity of pyrimidine ring**
- ☐ extreme ring strain in cytosine that interrupts the reaction
- ☐ the positive charge due to formation of ammonium salts that repels other molecules.



π -conjugation hinders nucleophilic activity of nitrogen atom

3.



4.

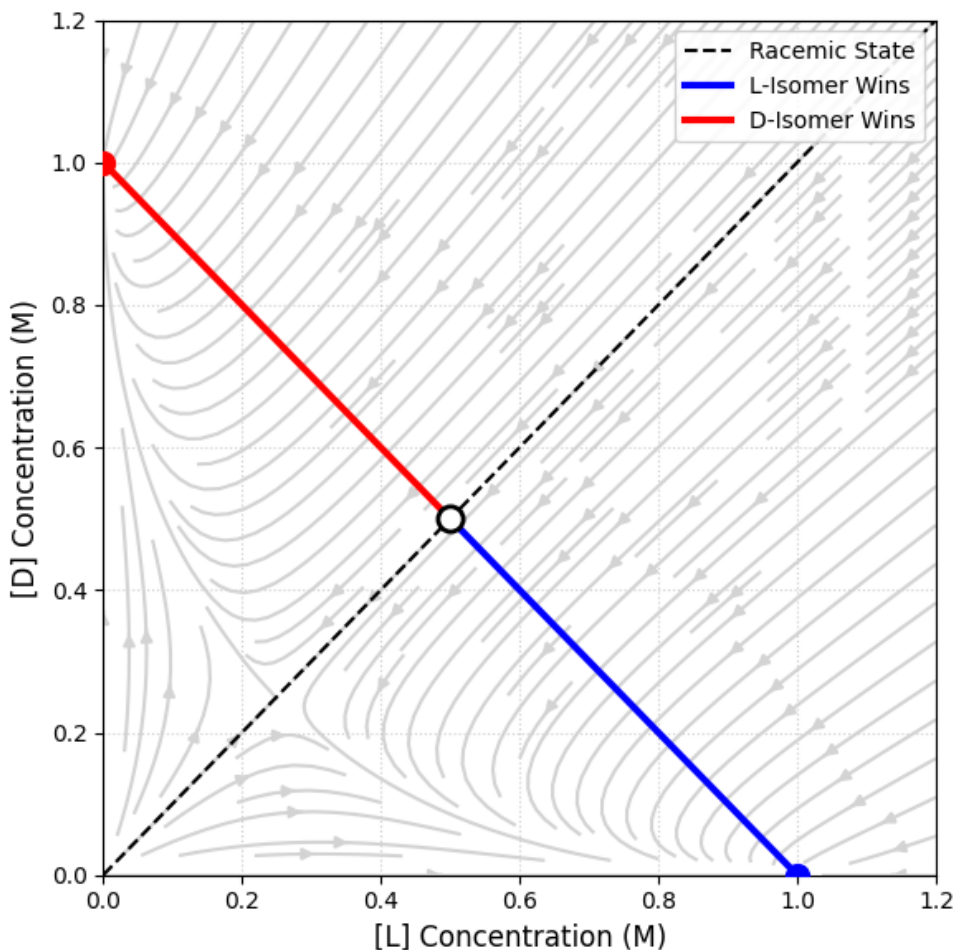
$$\frac{k_L}{k_D} = \exp\left(\frac{2H_{SO}}{k_B T}\right) \Rightarrow ee = \frac{[LY] - [DY]}{[LY] + [DY]} = \frac{(k_L - k_D)}{(k_L + k_D)} = \frac{\exp\left(\frac{2H_{SO}}{k_B T}\right) - 1}{\exp\left(\frac{2H_{SO}}{k_B T}\right) + 1}$$

$$\frac{k_L}{k_D} = \exp\left(2 \times 5 \times 10^{-4} \times 1.602 \times \frac{10^{-19}}{313 \times 1.38 \times 10^{-23}}\right) = 1.038$$

$$ee = \frac{1.038 - 1}{1.038 + 1} = 0.0185 = 1.85\% \approx 2\%$$

Very low magnitudes of spin-orbit coupling can lead to symmetry breaking in a racemic system.

5. So a trajectory that should be depicted needs to fit such criteria as starting from (0.5;0.5) point and ending in (1;0) and (0;1) points:



$$6. ee_1 = \frac{[L_1] - [D_1]}{[L_1] + [D_1]}, ee_2 = \frac{[L_2] - [D_2]}{[L_2] + [D_2]}$$

The total concentration of initial AA is defined as:

$$\begin{aligned} [1] &= [L_1] + [D_1], [2] = [L_2] + [D_2] \Rightarrow \text{for instance } [L_1] = \frac{1 + ee_1}{2} [1] \\ ee_{\text{homo}} &= \frac{[LL] - [DD]}{[LL] + [DD]} = \frac{[L_1][L_2] - [D_1][D_2]}{[L_1][L_2] + [D_1][D_2]} \\ &= \frac{\frac{1 + ee_1}{2} \times \frac{1 + ee_2}{2} \times [1][2] - \frac{1 - ee_1}{2} \times \frac{1 - ee_2}{2} \times [1][2]}{\frac{1 + ee_1}{2} \times \frac{1 + ee_2}{2} \times [1][2] + \frac{1 - ee_1}{2} \times \frac{1 - ee_2}{2} \times [1][2]} \\ &= \frac{(1 + ee_1)(1 + ee_2) - (1 - ee_1)(1 - ee_2)}{(1 + ee_1)(1 + ee_2) + (1 - ee_1)(1 - ee_2)} = \frac{ee_1 + ee_2}{1 + ee_1 ee_2} \end{aligned}$$

7.

$$ee_{\text{homochiral}} = \frac{0.02 + 0.02}{0.02^2 + 1} = 0.04$$

So, the ee of the system rises. For more significant initial conditions, ee will drastically converge to 1 when chain length is increased.

For ee taken as 5%, the answer is $9.98\% \approx 10\%$.

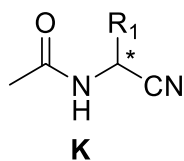
8. For final $ee_{\text{homo}} = \frac{[L_n] - [D_n]}{[L_n] + [D_n]} > 99\% \Rightarrow \chi_{L_n} > 99.5\%, \chi_{D_n} < 0.5\%$

$$\left(\frac{0.525}{0.475}\right)^n > \frac{99.5}{0.5}$$

$$n > 52.89$$

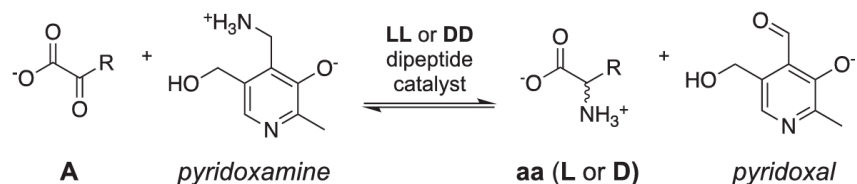
So, $n_{\text{min}} = 53$

9.

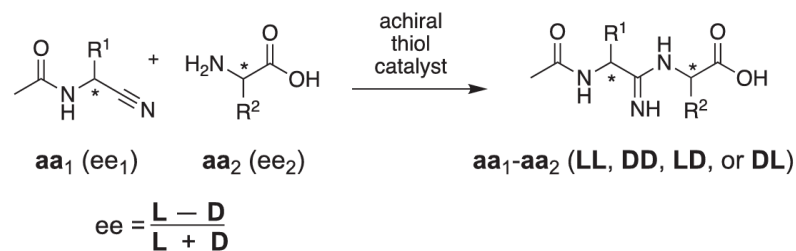


So, the full scheme of the model looks like this:

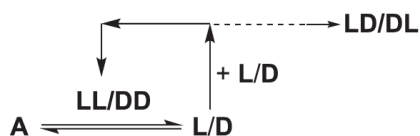
1A transamination



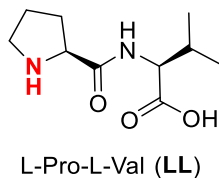
1B catalytic peptide ligation



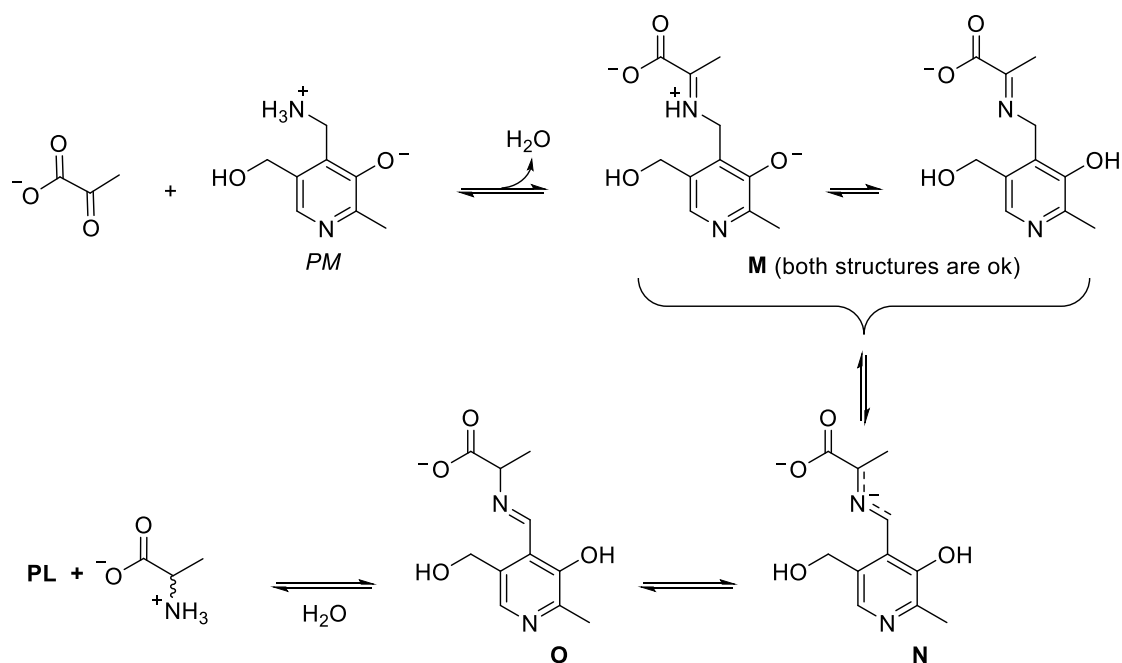
1C combined autocatalytic network



10. Proline imino groups, as they can be involved in acid-base interactions.



11.



12.

- ☐ Hydrogen bonds
- ☐ π -stacking
- ☐ Steric repulsion
- ☐ Alignment of stereocentres

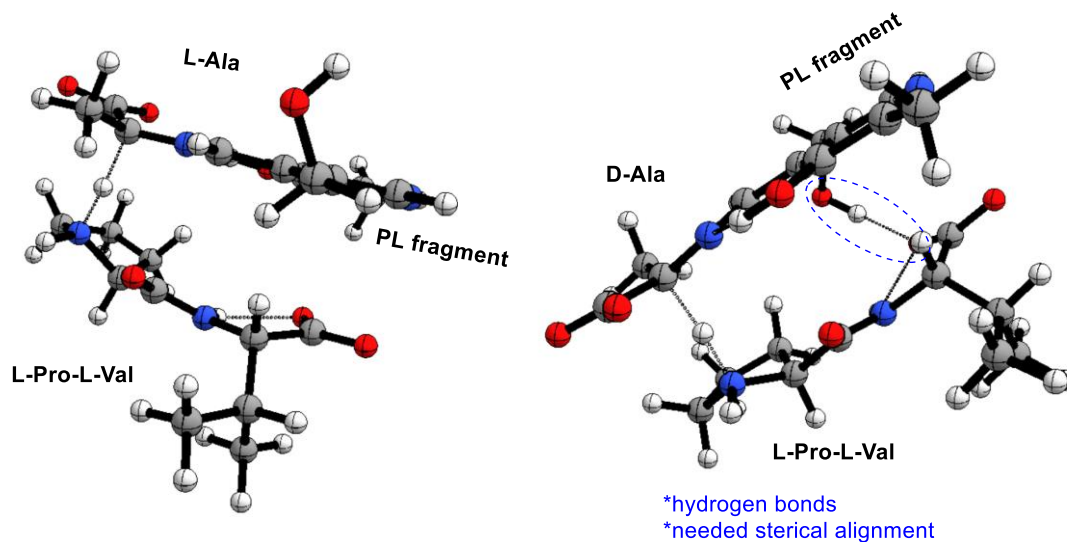
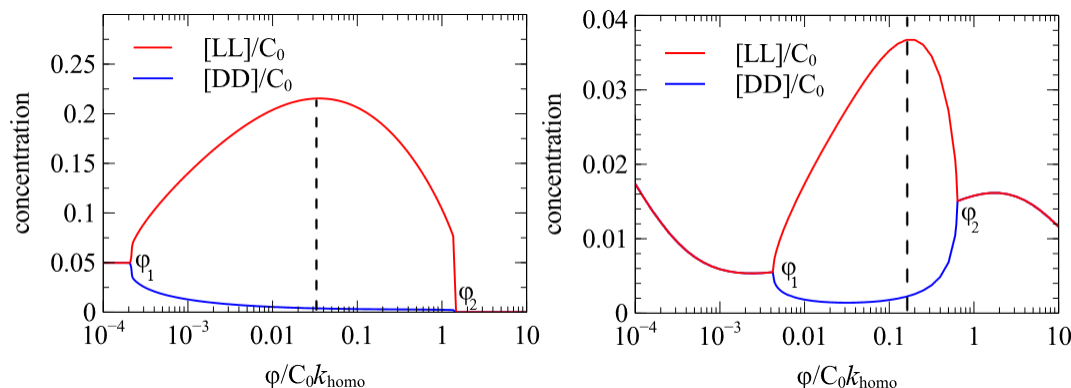


Figure 1. TS of deprotonation of α -hydrogen atom by L-Pro-L-Val for L- and D-Ala.

13. The maximum chiral asymmetry means the maximal difference between [LL] and [DD] values. On the given graphs, approximate lines corresponding to the maxima can be drawn at $\varphi/C_0k_{\text{homo}} = 0.04$ for the constructive mechanism and $\varphi/C_0k_{\text{homo}} = 0.2$ for the destructive mechanism:



14.

- When φ is small, the system is in equilibrium and it's predominantly racemic with little noise.
- Here we see symmetry breaking. The LL concentration rockets while the DD concentration falls. For the destructive mechanism, we feed the system with amino acids in the L- and D-form, but we've seen that generally D-amino acids get destroyed faster and amplify the ee , so at some flow rate the difference becomes significant. For the constructive mechanism, we feed the system with ketoacids and expect synthesis of amino acids. The symmetry breaking here is based on the same fact of D-amino acids being destroyed faster and that from insignificant ee_{monomer} of the initial amino acids we get a larger ee of the dipeptides (See Q6).
- If the flow rate becomes too high, the monomers can be washed out from the system, and the dimer concentrations drop to zero. In case of the destructive mechanism, there is a significant excess of L- and D-monomers, so it prevents the appearance of any ee .

Problem 11. Fluorescence, phosphorescence and quenching

1. The absorbed photon excites the electron from the ground state (S_0) to an excited state (S_1). During this process, the molecule absorbs high-energy (short-wavelength) light. Before fluorescence occurs, the excited molecule loses some energy non-radiatively (as heat or vibration). The correct answer is lower than that of fluorescence.

2. ISC efficiency increases when the energy gap between S_1 and T_1 is small, because the smaller the gap, the easier the spin-orbit coupling is, hence the more probable transition between the two states. The correct answer is lower.

3. The rate of decay: $-\frac{d[S^*]}{dt} = k_F \times [S^*] + k_{IC} \times [S^*] + k_{ISC} \times [S^*]$
 $= (k_F + k_{IC} + k_{ISC}) \times [S^*]$

So, $n([S^*]) = 1$ and $k_{obs} = (k_F + k_{IC} + k_{ISC})$

According to the first order kinetic equation:

$$\frac{[S^*]}{e} = [S^*] \times e^{-k_{obs}t} = [S^*] \times e^{-t/\tau_0} \rightarrow \tau_0 = \frac{1}{k_{obs}} = \frac{1}{k_F + k_{IC} + k_{ISC}}$$

4. $\varphi_0 = \frac{r_F}{r_F + r_{IC} + r_{ISC}} = \frac{k_F \times [S^*]}{(k_F + k_{IC} + k_{ISC}) \times [S^*]} = \frac{k_F}{k_F + k_{IC} + k_{ISC}}$

5. $\varphi = \frac{r_F}{r_F + r_{IC} + r_{ISC} + r_Q} = \frac{k_F \times [S^*]}{(k_F + k_{IC} + k_{ISC} + k_Q[Q]) \times [S^*]} = \frac{k_F}{k_F + k_{IC} + k_{ISC} + k_Q[Q]}$

6. $\frac{\varphi_0}{\varphi} = \frac{k_F + k_{IC} + k_{ISC} + k_Q[Q]}{k_F + k_{IC} + k_{ISC}} = 1 + \frac{k_Q}{k_F + k_{IC} + k_{ISC}} [Q]$

7. The emission lifetime (τ) depends on the concentration of Q as follows:

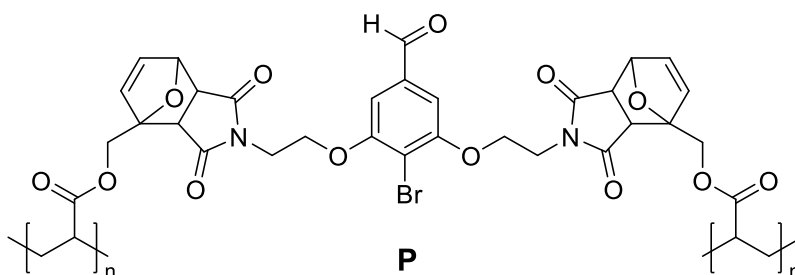
$$\tau = \frac{1}{k_{obs}} = \frac{1}{k_F + k_{IC} + k_{ISC} + k_Q[Q]} \rightarrow \frac{1}{\tau} = (k_F + k_{IC} + k_{ISC}) + k_Q[Q]$$

Using the obtained linear dependence:

$$k_F + k_{IC} + k_{ISC} = 3.85 \times 10^8 \text{ s}^{-1}, k_Q = 1.26 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$$

8. $0.5 = \frac{k_Q[Q]}{k_F + k_{IC} + k_{ISC} + k_Q[Q]} = \frac{1.26 \times 10^{10} \times [Q]}{3.85 \times 10^8 + 1.26 \times 10^{10} \times [Q]} \rightarrow [Q] = 0.0306 \text{ M}$

9.



10. At high temperatures (the blue dashed line), the total decay process of the T_1^G state is dominated by T-T energy transfer to the polymer matrix (rate constant k_Q), while at low temperatures (the red dashed line) non-radiative decay to the singlet state (rate constant k_N) prevails.

at low temperature (red dashed line): $\ln(k_N + k_Q) \approx \ln k_N = \ln A_N - \frac{E_N}{R} \cdot \frac{1}{T}$.

at high temperature (blue dashed line): $\ln(k_N + k_Q) \approx \ln k_Q = \ln A_Q - \frac{E_Q}{R} \cdot \frac{1}{T}$.

We find the slope of the blue dashed line, which equals to $-\frac{E_Q}{R}$:

$$\text{slope} = -\frac{E_Q}{R} = -4800 \rightarrow \Delta E = E_Q = 40 \text{ kJ / mol.}$$

Problem 12. Photoacids

1. $2.1 \times 10^{-3} \times \frac{5}{25} = 4.2 \times 10^{-4} \text{ mol / L}$

2. $A = \varepsilon lc \Rightarrow \varepsilon = \frac{A}{lc}$

$$\varepsilon_{\text{ArOH}} = \frac{0.219}{1 \cdot 4.2 \cdot 10^{-4}} = 521 \text{ cm}^{-1} \text{ M}^{-1}$$

$$\varepsilon_{\text{ArO}^-} = \frac{0.44}{1 \cdot 4.2 \cdot 10^{-4}} = 1048 \text{ cm}^{-1} \text{ M}^{-1}$$

3. Let's determine the pH of solutions 3-5:

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} \Rightarrow [\text{H}^+] = \frac{K_w}{K_b} \times \frac{[\text{NH}_3]}{[\text{NH}_4^+]}$$

$$\text{pH} = 14 - \text{p}K_b + \log \frac{[\text{NH}_3]}{[\text{NH}_4^+]}$$

$$\text{pH}_3 = 14 - 4.75 + \log \frac{1}{3} = 8.77$$

$$\text{pH}_4 = 14 - 4.75 + \log \frac{1}{2} = 8.95$$

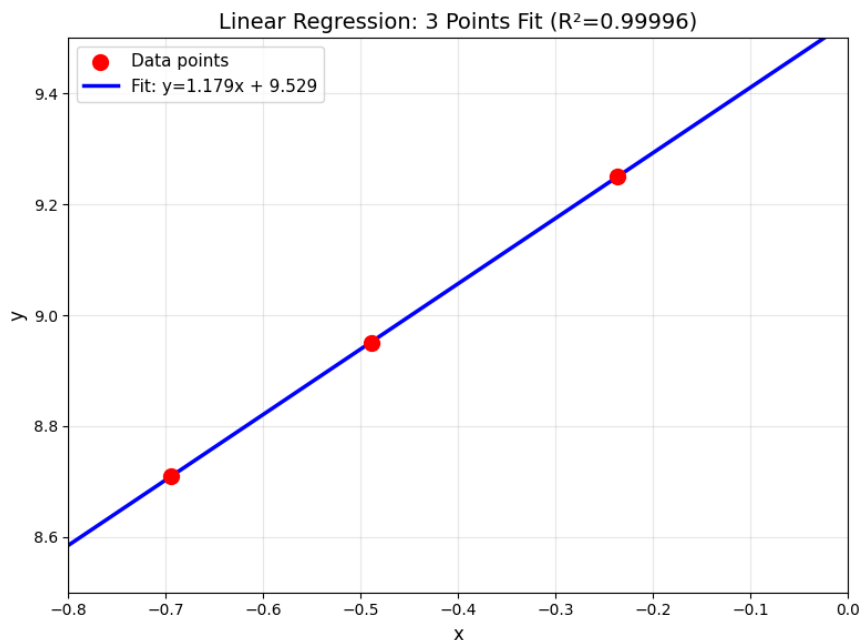
$$\text{pH}_5 = 14 - 4.75 = 9.25$$

The $\log[\text{ArO}^-]/[\text{ArOH}]$ values for solutions 3-5 can be found from three systems of linear equations:

$$\begin{cases} \varepsilon_{\text{ArOH}} c_{n,\text{ArOH}} + \varepsilon_{\text{ArO}^-} c_{n,\text{ArO}^-} = A_n \\ c_{n,\text{ArOH}} + c_{n,\text{ArO}^-} = c_{\text{total}} \end{cases}$$

Then:

Solution	[ArOH]	[ArO ⁻]	[ArO ⁻]/[ArOH]	$\log \frac{[\text{ArO}^-]}{[\text{ArOH}]}$
3	3.49×10^{-4}	7.05×10^{-5}	0.202	-0.695
4	3.20×10^{-4}	1.00×10^{-4}	0.324	-0.489
5	2.66×10^{-4}	1.54×10^{-4}	0.579	-0.237



From the intercept we obtain the $\text{p}K_a = 9.53$ (9.50 in literature)

$$4. \Delta G^\circ = \Delta H - T\Delta S = -RT \ln K_a$$

$$\Delta G^{\circ*} = \Delta H^* - T\Delta S = -RT \ln K_a^*$$

$$N_A h\nu_1 + \Delta H^* = N_A h\nu_2 + \Delta H$$

$$-RT \ln K_a - (-RT \ln K_a^*) = \Delta H - \Delta H^*$$

$$RT(-\ln K_a + \ln K_a^*) = N_A h\nu_1 - N_A h\nu_2$$

$$\ln x = 2.303 \log x$$

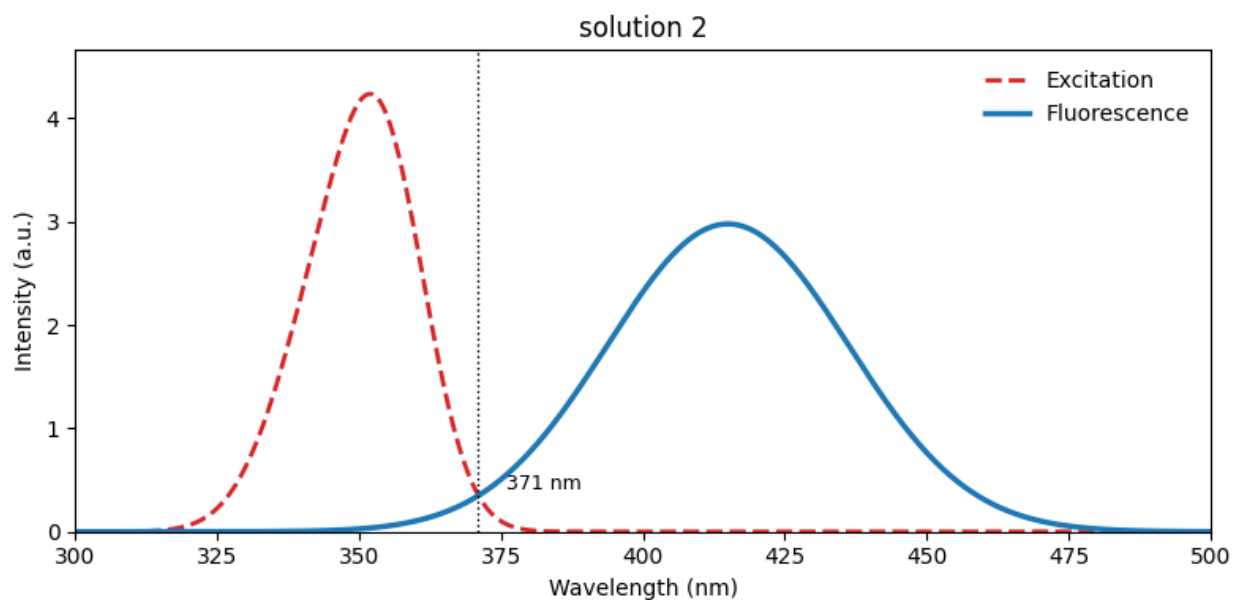
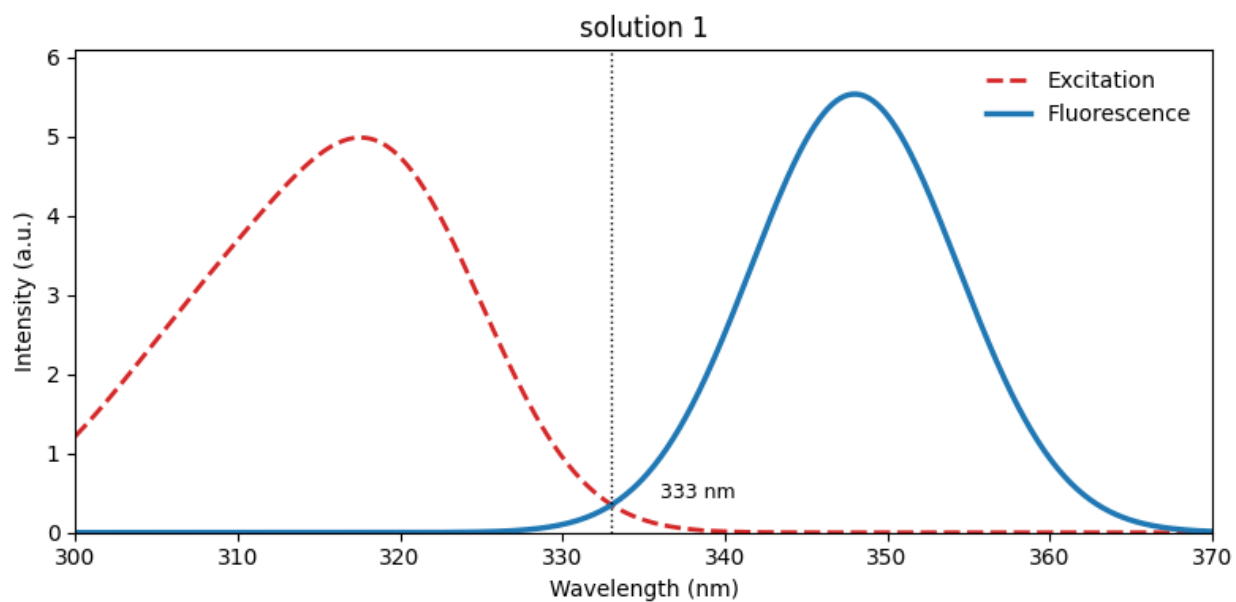
$$2.303RT(\text{p}K_a - \text{p}K_a^*) = N_A h(\nu_1 - \nu_2)$$

$$\text{p}K_a - \text{p}K_a^* = \Delta \text{p}K_a = \frac{N_A h}{2.303RT}(\nu_1 - \nu_2)$$

And finally, converting frequencies to wavelengths:

$$\Delta \text{p}K_a = \frac{N_A hc}{2.303RT} \left(\frac{1}{\lambda_1} - \frac{1}{\lambda_2} \right)$$

5. Based on the intersection of the two spectra we can find the minimal energy of excitation:



$$\Delta pK_a = \frac{N_A hc}{2.303 RT} \left(\frac{1}{333 \times 10^{-9}} - \frac{1}{371 \times 10^{-9}} \right)$$

$$\Delta pK_a = pK_a - pK_a^* = 6.45$$

$$pK_a^* = 9.53 - 6.45 = 3.08$$

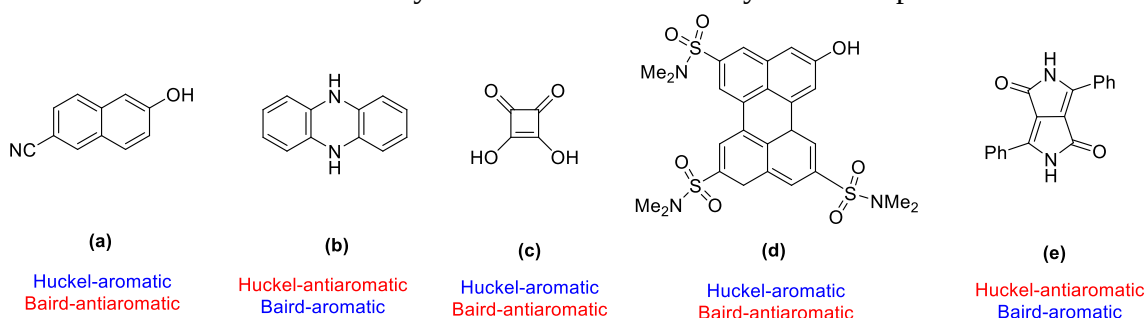
At pH 5:

$$5 = 3.08 + \log \frac{[\text{ArO}^{-*}]}{[\text{ArOH}^*]}$$

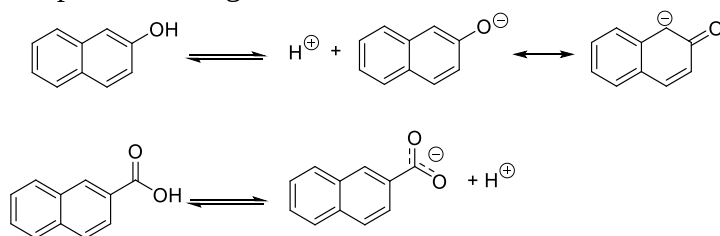
$$\frac{[\text{ArOH}^*]}{[\text{ArO}^{-*}]} = 0.012$$

Note: we can't use fluorescence maxima wavelengths λ_{max1} , λ_{max2} for the calculations of pK_a^* . The necessity of using intersection of absorption and fluorescence spectra is born because of vibrational relaxation (and this is why the wavelength shift occurs – this is also called the Stokes shift), that's why the intersection of the two spectra shows the minimum electronic energy difference needed for a molecule to reach its excited state.

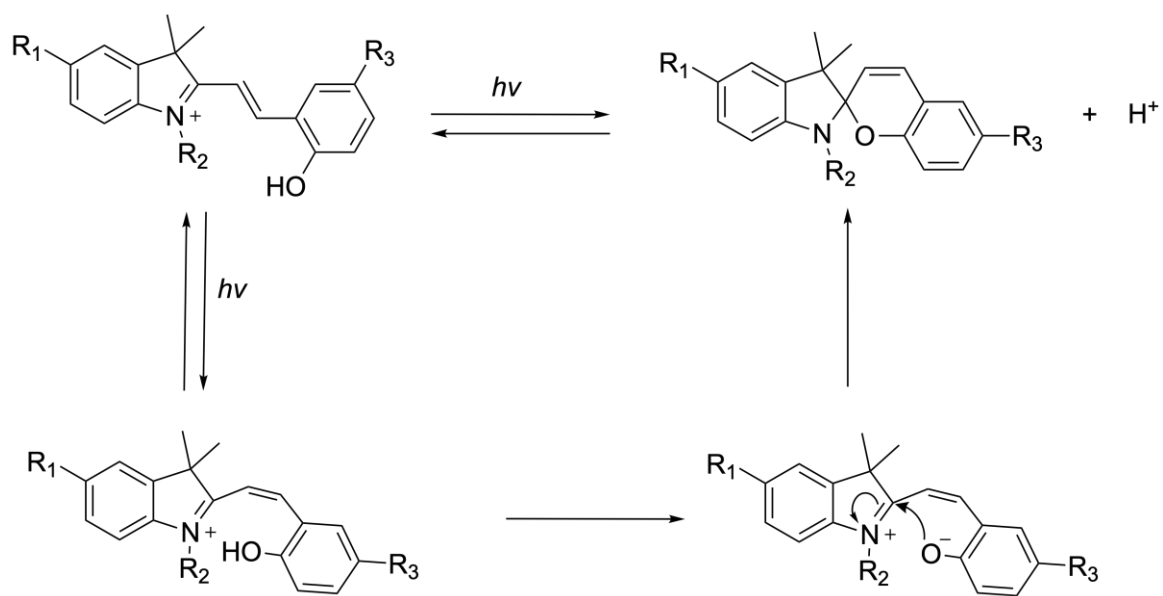
6. Based on the rule, we find out that **a**, **c**, and **d** are Baird-antiaromatic, and thus acidic forms of these molecules will try to relieve antiaromaticity and show photoacidic nature.



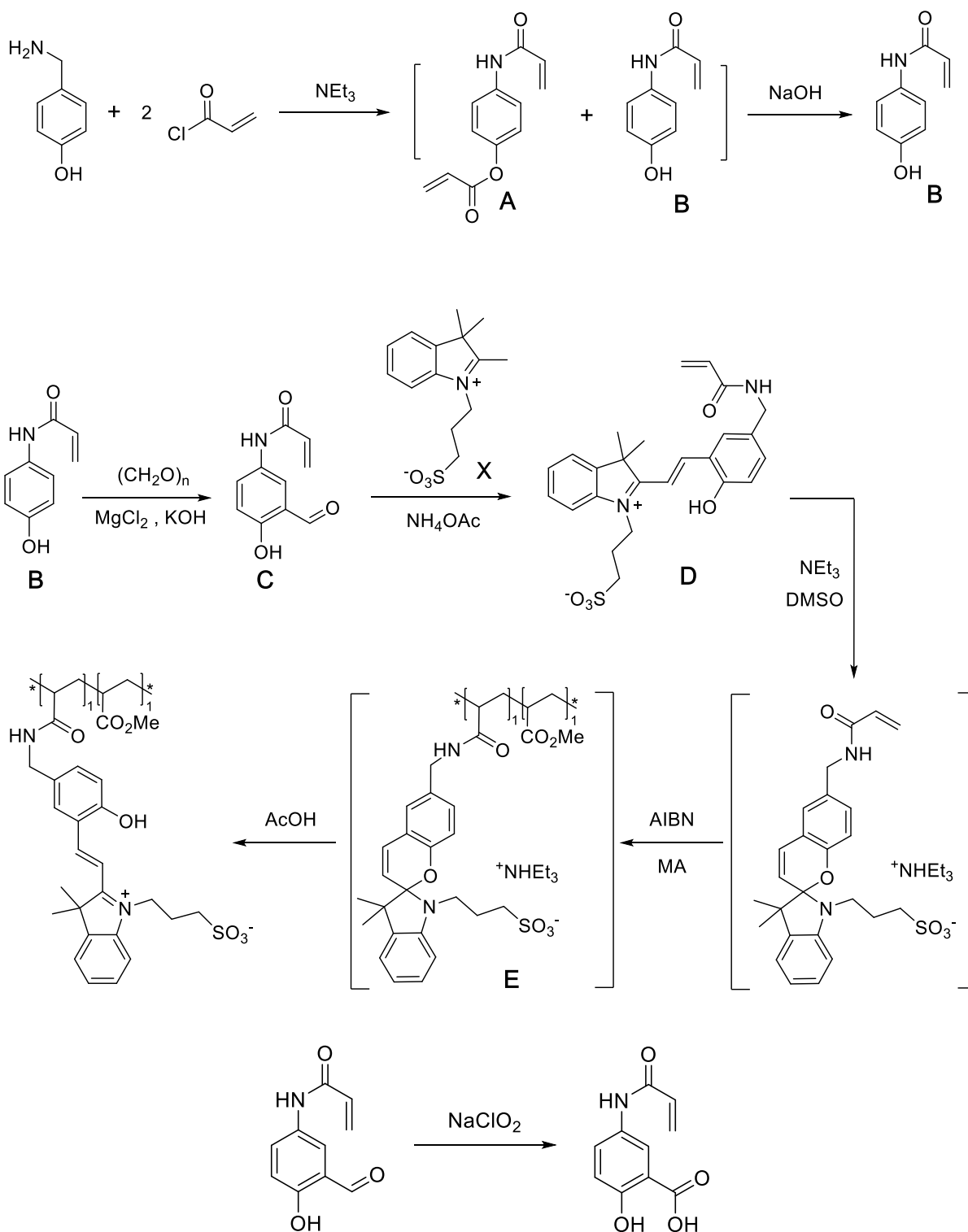
7. This is the result of the small charge redistribution on the ring. In the case of 2-naphthol, charge is partially redistributed to the aromatic core. But in the case of 2-naphthoate, the charge is mostly on the two oxygen atoms and that's why it doesn't help to lessen the antiaromaticity of naphthalene ring in the excited state.



8.

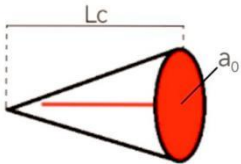
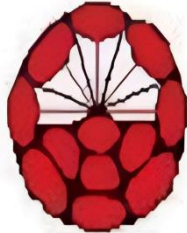
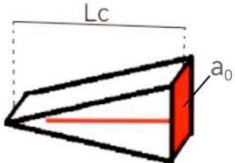
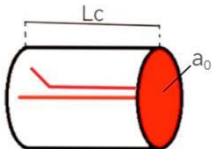
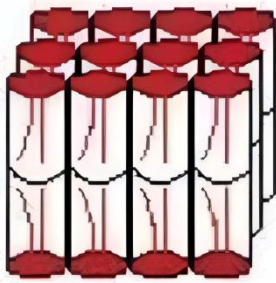


9.

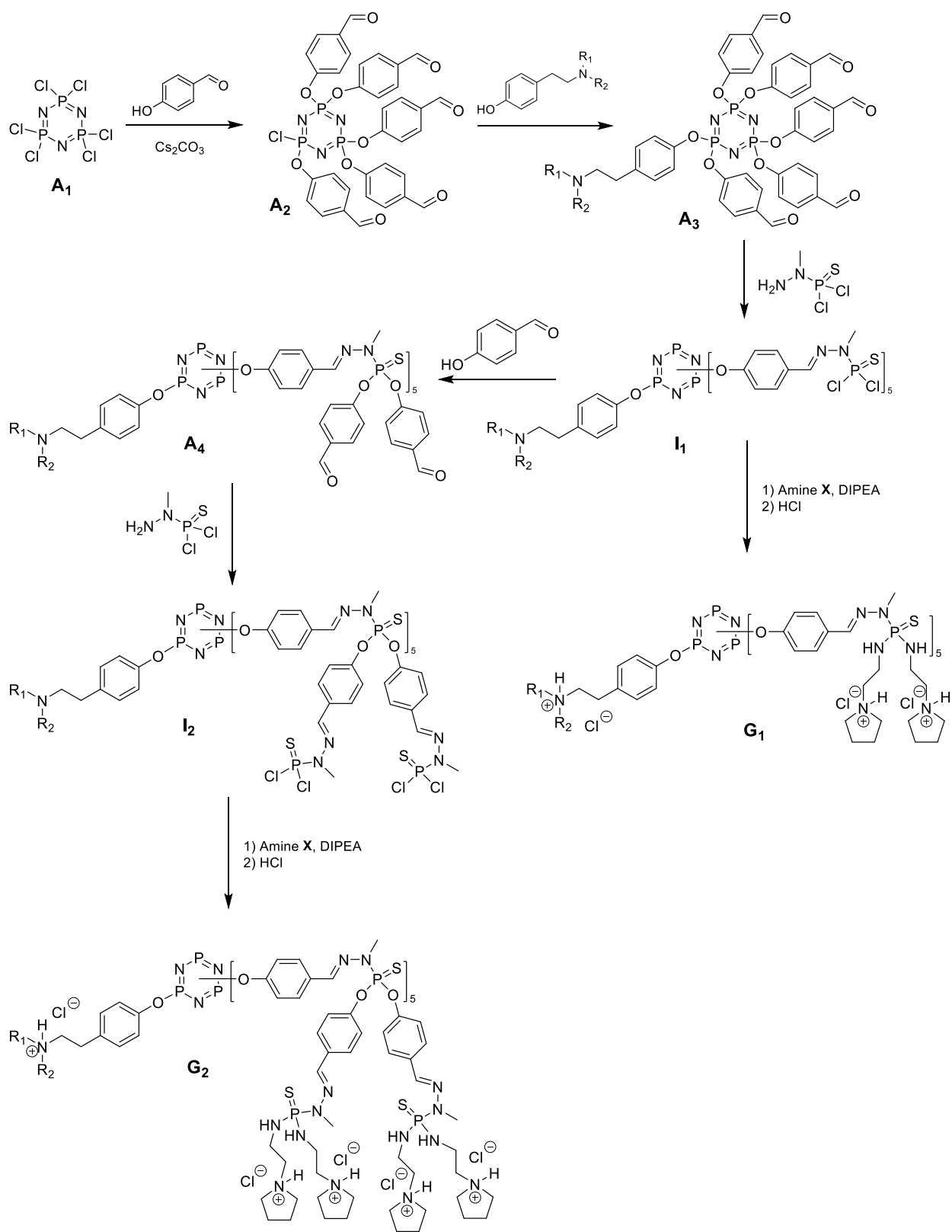


Problem 13. Interested in micelles?

1.

For cone-shaped molecules: 	$\frac{V_C}{L_C} = \frac{\frac{1}{3}\pi r^2 L_C}{L_C} = \frac{1}{3}a_0$ This will form a spherical micelle.	
For rectangular wedge-shaped surfactants: 	$\frac{V_C}{L_C} = \frac{\frac{1}{2}a_0 L_C}{L_C} = \frac{1}{2}a_0$ This will form a cylindrical micelle.	
For cylinder-shaped molecules: 	$\frac{V_C}{L_C} = \frac{\pi r^2 L_C}{L_C} = a_0$ This will form a bilayer structure.	

2. We can find the ratio of atoms in **A₁** – 26.73/31:12.09/14:61.18/35.45 = 1:1:2. So, the empirical formula of **A₁** is PNC_l₂. The structure N≡PCl₂ does not have a threefold symmetry axis, but the cyclic trimer of it demonstrates possesses such a symmetry axis. So, **A₁** is P₃N₃Cl₆.



3. In the final step, hydrochloric acid protonates the external amino group to form an ammonium salt. The amino groups inside are too densely packed to be protonated. The number of cationic groups we can find: $5 \times 2^{10} + 1 = 5121$.
4. As can be seen from the structures of **G₁** and **G₂**, they are likely to have cone shapes and assemble into spherical micelles.
5. The correct answer is: [c] to create a water-soluble, positively charged form that will show biological activity.

HCl protonates the amine groups, creating cationic dendrons (*e.g.*, P1G1·HCl). This is essential for water solubility (enabling micelle formation) and provides the positive surface charge needed for cellular uptake and anticancer activity.

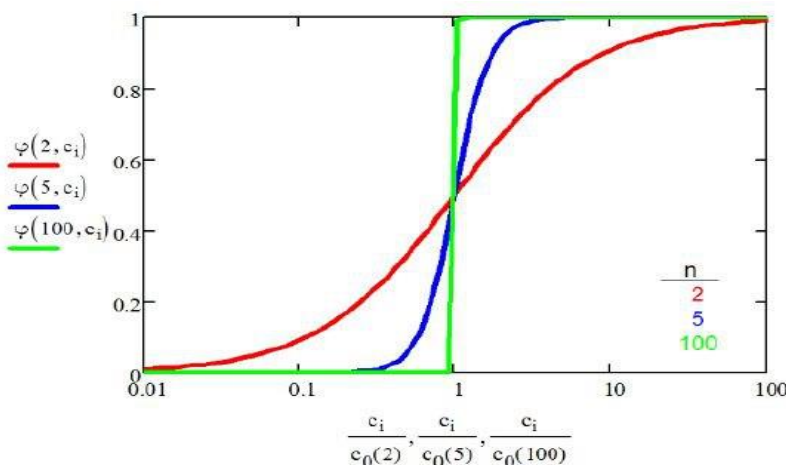
6. The form of micelle is dependent on the generation of the head groups. Since **Gen₃** has the largest hydrophilic surface area and smallest N_s , it forms a spherical micelle, whereas **Gen₂** and **Gen₁** with a moderate and smaller hydrophilic surface accumulate in cylindrical and bilayer structures respectively.
7. The initial concentration of monomers can be described as:

$$C_i = [M] + n \times [M_n]$$

So, the fraction of monomers present in micelles:

$$\varphi_{n \times [M_n]} = \frac{n \times [M_n]}{C_i} = \frac{K_n [M]^n \times n}{[M] + K_n [M]^n \times n} = \frac{K_n [M]^{n-1} \times n}{1 + K_n [M]^{n-1} \times n}$$

8. According to the equation derived in question 7, the maximum number monomers will be present inside the micelles when the concentration of monomers is high and the aggregation number is low, as the concentration of the monomers is lower than 1 mol/dm³. So the correct answer is [c].
9. The function in the solution of question 7 has an inflection point, c_0 , at the CMC, which steepens with increasing aggregation number:



At the point where $\varphi_{n \times [M_n]} = 0.5$ CMC is reached so:

$$1 = K_n \times [M]^{n-1} \times n \rightarrow \text{CMC} = [M] = (K_n \times n)^{\frac{1}{1-n}}$$

- 10.** As there are aggregates formed, the specific conductivity of the solution falls. This feature corresponds to the moment that monomer concentration is equal to the CMC (slope of line reduces). Using the CMC's dependence on the aggregation number, we can derive the equation for calculating the equilibrium constant and for the free energy of micelle formation:

$$K_n = \frac{1}{n} \times \text{CMC}^{1-n} = e^{\frac{-\Delta_r G^\circ_{\text{micelle}}}{RT}} \rightarrow \Delta_r G^\circ_{\text{micelle}} = RT \times \ln(n \times \text{CMC}^{n-1})$$

Here it can be seen that if the aggregation number and free energy remain constant, the temperature will increase with CMC which is under 1 mol/dm^3 . So the comparison is as follows:

$$T_1 < T_2$$

Problem 14. The basics of Metal–Organic Frameworks

- From the figure and model, it is clear that MOF-5 has a simple cubic (SC) unit cell (if we do not take into account linker geometry). The Zn_4O cluster forms corners and the linker forms edges. SC has 8 corners and 12 edges. Knowing that $Z = 1$ for SC we can calculate the empirical formula:



- $4\text{Zn}(\text{NO}_3)_2 + 3\text{H}_2\text{C}_8\text{H}_4\text{O}_4 + 8\text{Et}_3\text{N} + \text{H}_2\text{O} \rightarrow \text{Zn}_4\text{O}(\text{C}_8\text{H}_4\text{O}_4)_3 + 8\text{Et}_3\text{N} \cdot \text{HNO}_3$
- Elemental analysis of crystals before activation showed nitrogen content N 7.64%, which originates from DMF molecules. In the mass spectra, the signal at 73 m/z indicates its presence. The 112 and 114 signals with relative intensity 3:1 are characteristic of a chlorine containing molecule $\text{C}_6\text{H}_5\text{Cl}$. The 77 m/z signal indicates C_6H_5^+ ions. From the nitrogen content and knowing the empirical formula of activated MOF-5 we can calculate the unactivated material formula: $\text{C}_{24}\text{H}_{12}\text{O}_{13}\text{Zn}_4 \cdot x\text{C}_3\text{H}_7\text{NO} \cdot y\text{C}_6\text{H}_5\text{Cl}$

We have two proportions:

$14.01x \text{ ----- } 7.64$	$14.01x \text{ ----- } 7.64$
$1.008 \cdot (12+7x+5y) \text{ ----- } 5.02$	$12.01 \cdot (24+3x+6y) \text{ ----- } 44.2$

Solving this system of equations we get $x = 8$ and $y = 1$.

Empirical formula $\text{C}_{24}\text{H}_{12}\text{O}_{13}\text{Zn}_4 \cdot 8\text{C}_3\text{H}_7\text{NO} \cdot \text{C}_6\text{H}_5\text{Cl}$

- Volume of unit cell $V = a^3 = (12.94 \text{ \AA})^3 = 2166.72 \text{ \AA}^3$

Volume of the atom $v = 4/3\pi r^3$

$$v = 4/3\pi (1.5^3 \times 4 + 13 \times 1.5^3 + 24 \times 1.7^3 + 12 \times 1.2^3) = 820.68 \text{ \AA}^3$$

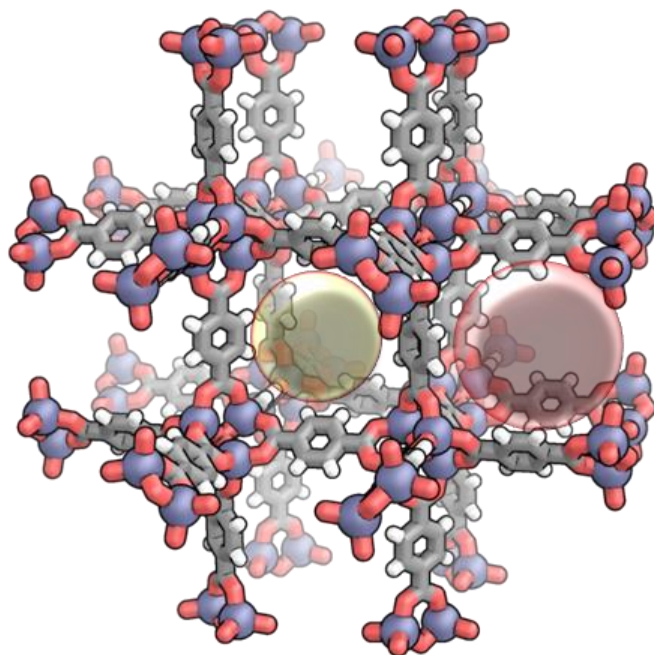
Free volume equals to $2166.72 \text{ \AA}^3 - 820.68 \text{ \AA}^3 = 1346.04 \text{ \AA}^3$ or 62.1%.

$$\text{The mass of one unit cell } m = \frac{M}{N_A} = \frac{769.856 \text{ g/mol}}{6.02 \times 10^{23} \text{ mol}^{-1}} = 1.28 \times 10^{-21} \text{ g}$$

Experimental surface area of one unit cell:

$$S_{\text{cell}} = S \times m = 2900 \text{ m}^2/\text{g} \times 1.28 \times 10^{-21} \text{ g} = 3.7 \times 10^{-18} \text{ m}^2 \text{ or } 370.86 \text{ \AA}^2$$

- As can be seen from the constructed model, the BDC units are placed at 45° to the cube faces. This along with not matching orientation of Zn_4O clusters in a row differentiates two neighbour cubes with different pore sizes. Therefore, we should increase the unit cell to eight cubes, doubling unit cell parameter to $25.88 \text{ \AA}$.



6. First, we should find the volume occupied by 10 g of material. This can be done by finding the density: $\rho = \frac{m}{V} = \frac{1.28 \times 10^{-21} \text{ g}}{2166.72 \times 10^{-24} \text{ cm}^3} = 0.59 \text{ g/cm}^3$, then 10.0 g would occupy $10/0.59 = 16.95 \text{ cm}^3$. The mass of hydrogen can be found through the ideal gas law

$$m = \frac{M \times P \times V}{R \times T} = \frac{2 \frac{\text{g}}{\text{mol}} \times 20 \times 10^5 \text{ Pa} \times 16.95 \times 10^{-6} \text{ m}^3}{8.314 \frac{\text{m}^3 \times \text{Pa}}{\text{K} \times \text{mol}} \times 298 \text{ K}} = 0.027 \text{ g}.$$

MOF-5 uptakes 0.1 g hydrogen. Excess uptake equals to $\frac{0.1 - 0.027}{0.027} * 100 = 270\%$

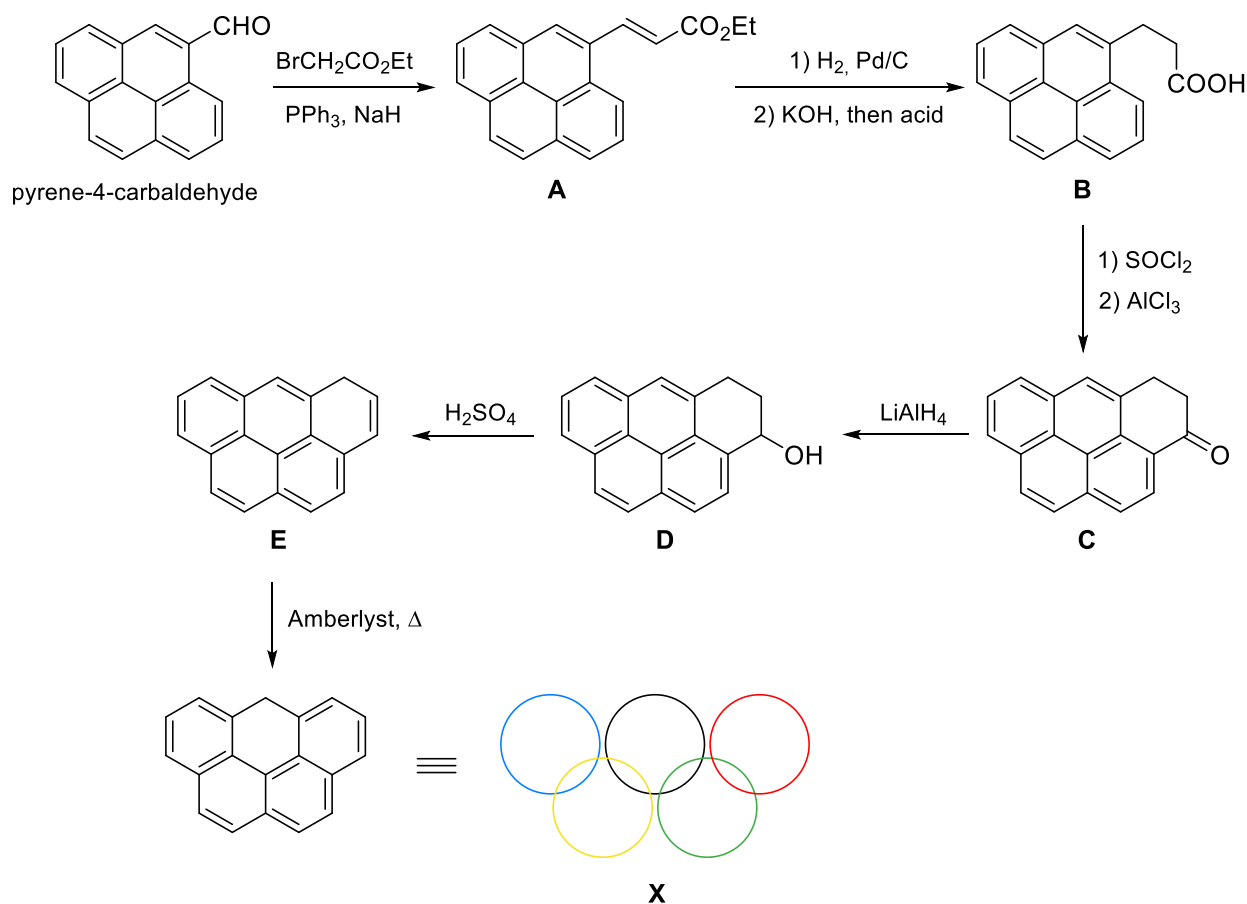
7. We know the distance $a = 12.94 \text{ \AA}$. Now we should find the length of the linker:

$$\frac{V_1}{V_0} = \left(\frac{12.94 - 2.69 + x}{12.94} \right)^3 = 0.693; \quad \frac{10.25 + x}{12.94} = \sqrt[3]{0.693}; \quad x = 1.20 \text{ \AA}.$$

The linker is acetylenedicarboxylic acid (*students are not expected to memorise bond lengths in exam*).

Problem 15. Microscopy in chemistry

1.



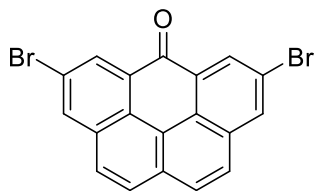
2. Because of its similarity to the Olympic flag, it was called *Olympicene*.

3. Let's find F first. It's similar to olympicene X and contains 2 bromine atoms. Moreover, we are given it's $m/z = 411.89 \approx 412$ in the mass spectrum. Considering that 2 hydrogen atoms of the original olympicene are substituted with bromine and subtracting $M(\text{X})$ and $2M(\text{Br})$ we get:

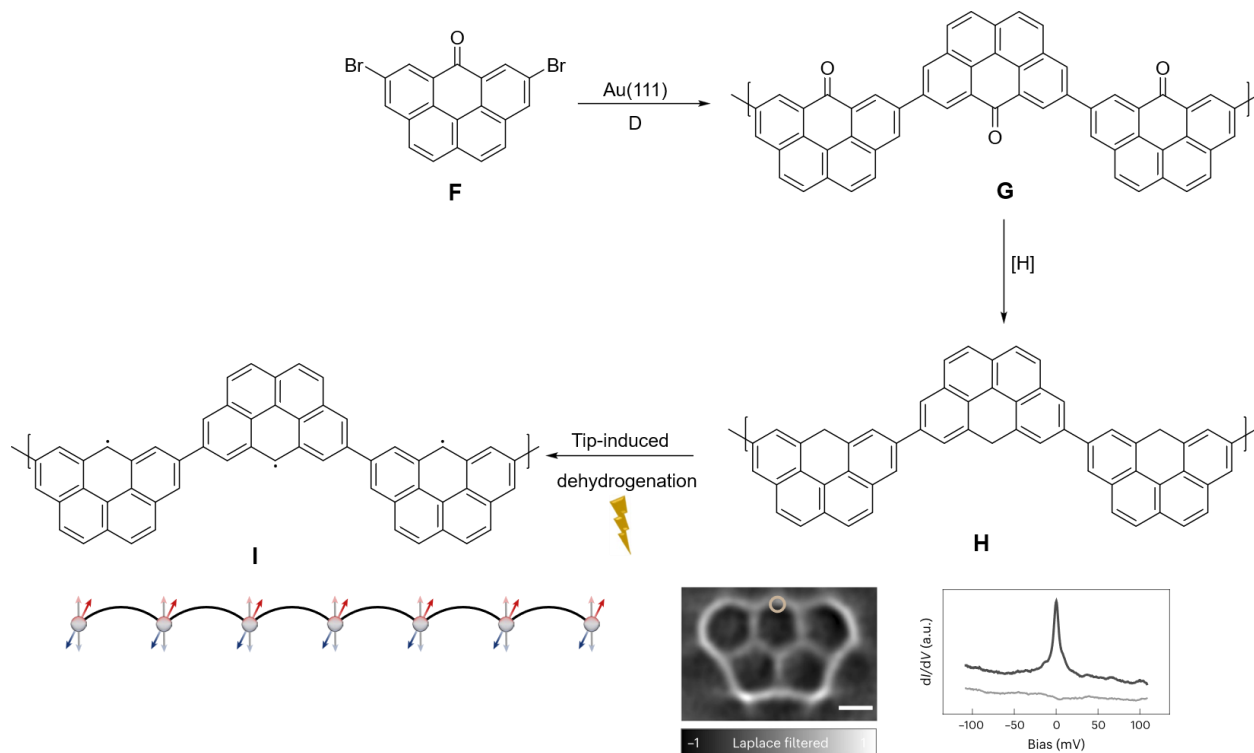
$$\Delta M = 412 - M(\text{X}) - 2M(\text{Br}) + 2M(\text{H}) = 412 - 240 - 160 + 2 = 14 \text{ g/mol}$$

As we know that the central carbon atom of olympicene is fully substituted (because there are only 4 types of protons according to problem), we thus can add 2 missing H to get:

$$\Delta M = M(\text{?}) = 14 + 2 = 16 \text{ g/mol} \Rightarrow \text{C} = \text{O} \text{ group}$$



Then proceed with the scheme:

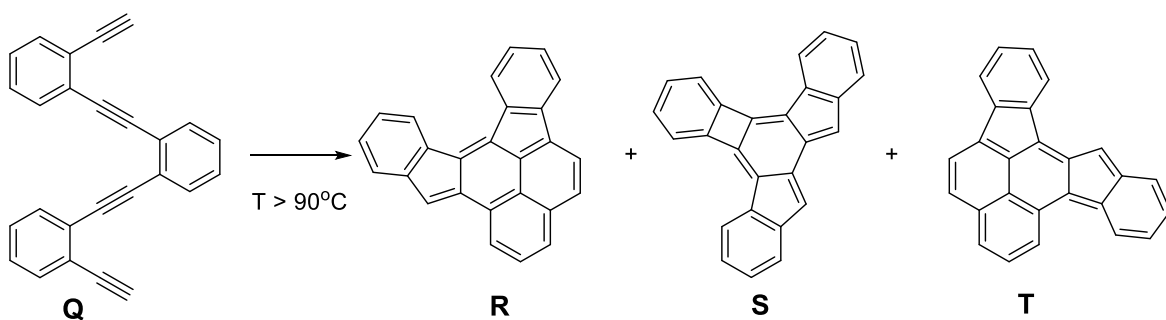


4.

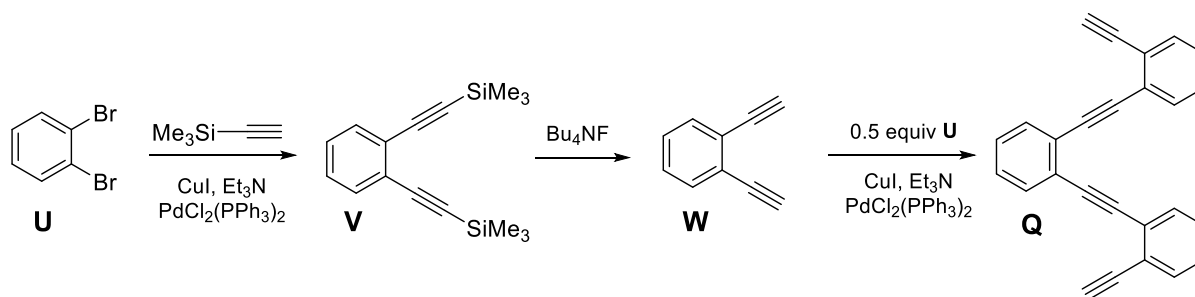
$$38 \cdot 10^{-3} \cdot \frac{2\pi^2}{L} \cdot 1.602 \cdot 10^{-19} = 1.38 \cdot 10^{-23} \cdot 298$$

So, the minimal $L = 29.22 \approx 30$

5.

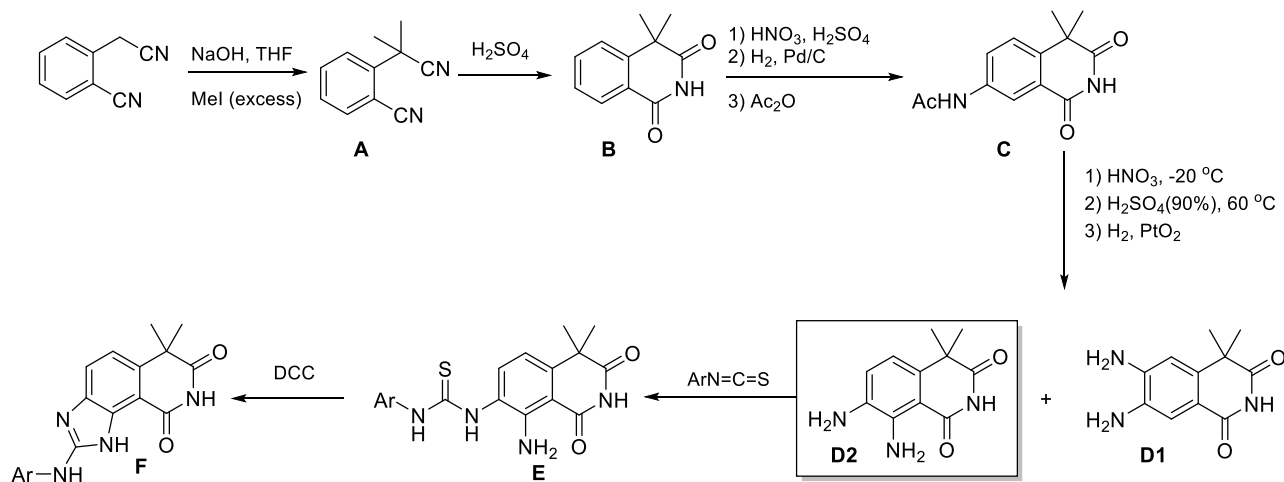


6.

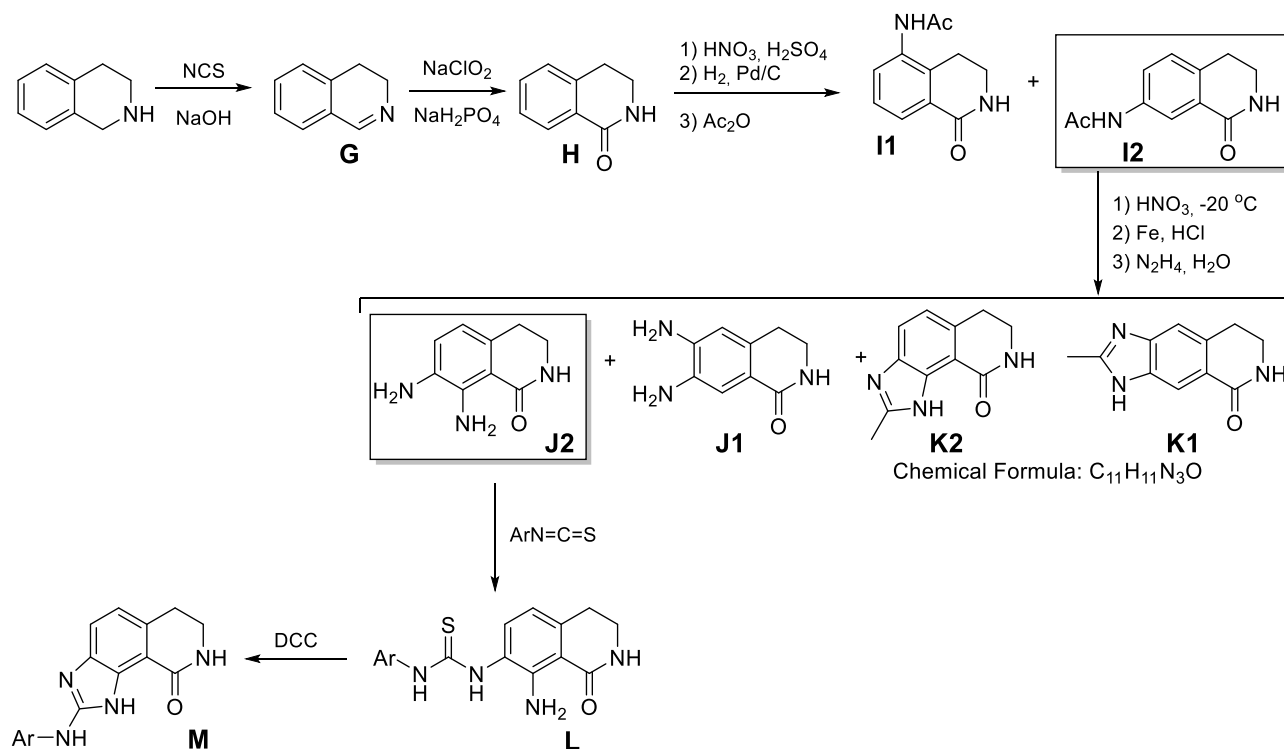


Problem 16. Kinase inhibitors

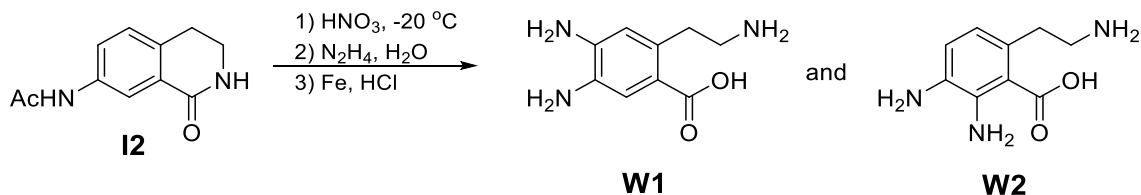
- The formation of the two isomers of compound **D** occurs because of non-selective nitration of **C**.



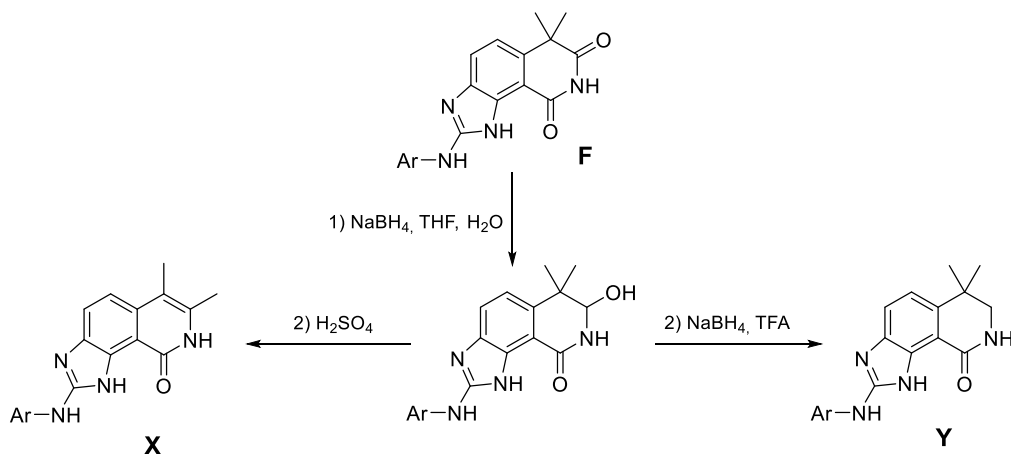
- During the hydrolysis of the amide bond in diamine **I2** the acyl group tends to form a conjugated benzimidazole ring.



- The *ortho*-position to the alkyl substituent in **B** is sterically hindered.
- The order was changed due to hydrolysis of the lactam. Reduction of the nitro group to the amino group increases the electron donating effect of the aromatic ring and reduces the electrophilicity of lactam. If the order is left unchanged, two isomeric structures can be proposed for **W**:



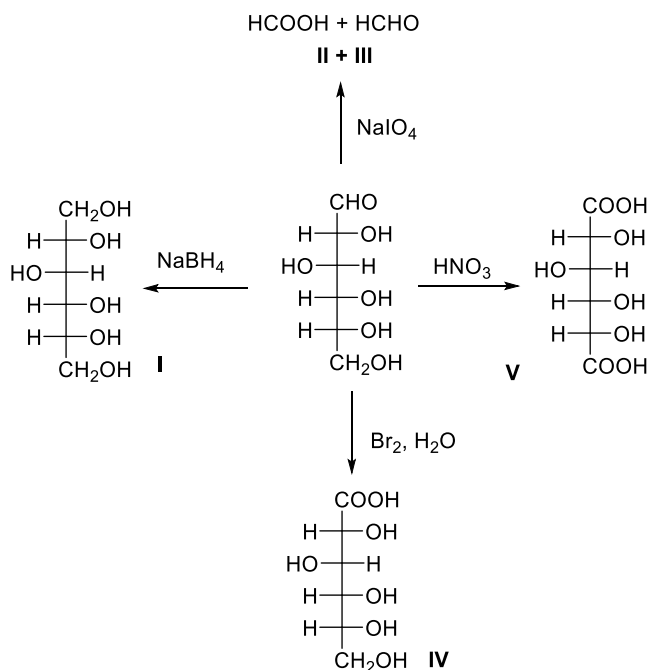
- The reduction of the imide with NaBH_4 as the first step leads to the hemi-aminal formation. Since **Y** is a homologous compound to **M**, subsequent elimination and then reduction leads to **Y**. If only acid is used as the second step, the 1,2-alkyl shift product **X** is formed via tertiary carbocation formation.



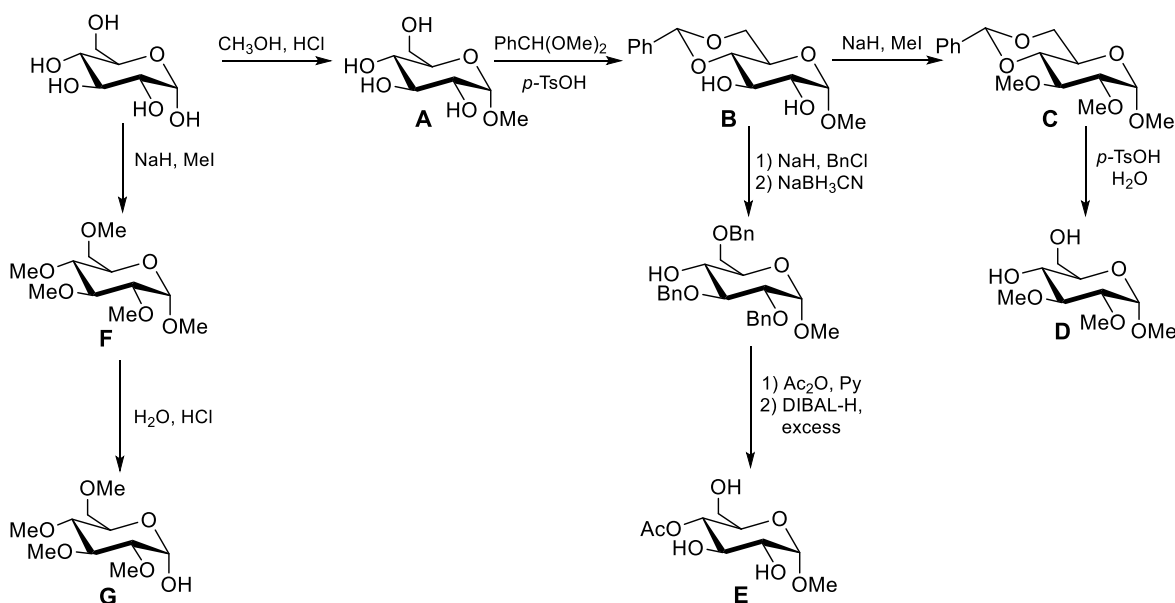
- The phenyl-substituent has a coplanar orientation with the core structure. The 2,6-dichlorophenyl-substituent, due to steric repulsion of the *ortho*-substituents, limits any rotation, which enhances packing in hydrophobic pocket of the enzyme binding site. If one of the substituents is replaced by smaller (H) or bigger group (Et), coordination becomes weaker.

Problem 17. Carbohydrate chemistry

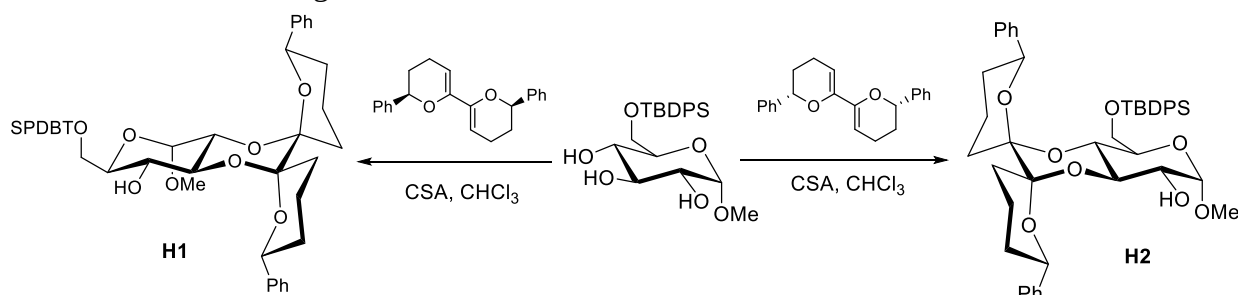
1.



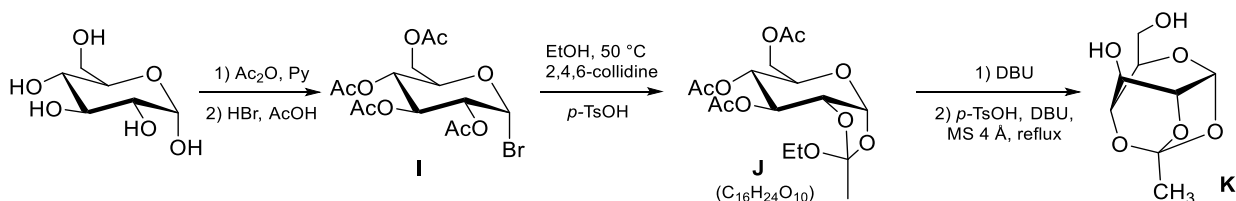
2. Acetal formation and hydrolysis occur under acidic conditions due to the reactivity of the anomeric positions (**A** and **G**). However, in the presence of TsOH, hydrolysis of the anomeric group can be avoided. According to the hint, **D** has fewer methylene groups than **G**. The formation of a second six-membered ring clearly indicates the position of acetal formation. The acetal group then is reduced to a benzyl group. DIBAL-H removes the benzylic protecting group.



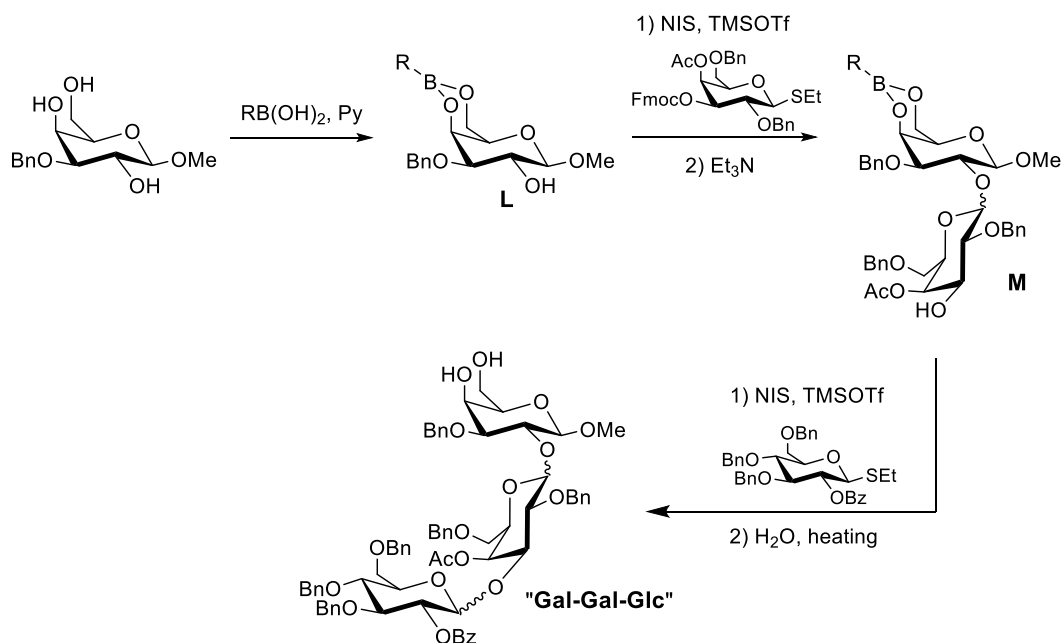
3. The phenyl groups in the THP rings sit in equatorial positions in chair conformations. This defines which of the two OH groups gets protected. For the correct stereochemical result in **H1**, the glucose derivative should be redrawn:



4. In the first step, all hydroxy groups are transformed to esters. Then the anomeric ester group is substituted by bromide. According to the structure of **K**, we can predict a bicyclic structure of **J**. **J** is further deprotected in basic conditions which do not affect the orthoester. Transorthoesterification in weak acidic conditions yields **K**.



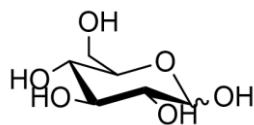
5. The reaction of a galactose derivative with the boronic acid derivative yields boronic ester **L**. NIS/TMSOTf-promoted glycosylation and following cleavage of the Fmoc group in basic conditions leads to formation of disaccharide **M** (which group leaves can be deduced from the chemical formula). Another glycosylation and hydrolysis of the boronic ester in hot water yields the Gal-Gal-Glc derivative.



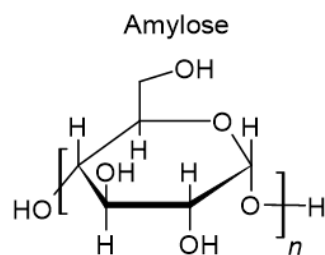
Problem 18. Inositol

1.

a)



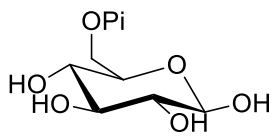
b)



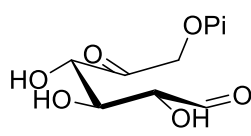
2. $243\,000 = 162 \times n$;

$n = 1500$

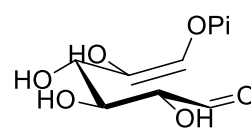
3.



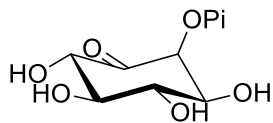
A



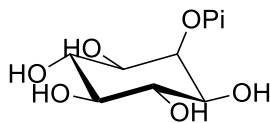
C



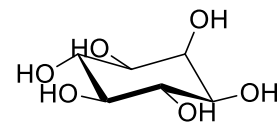
D



E



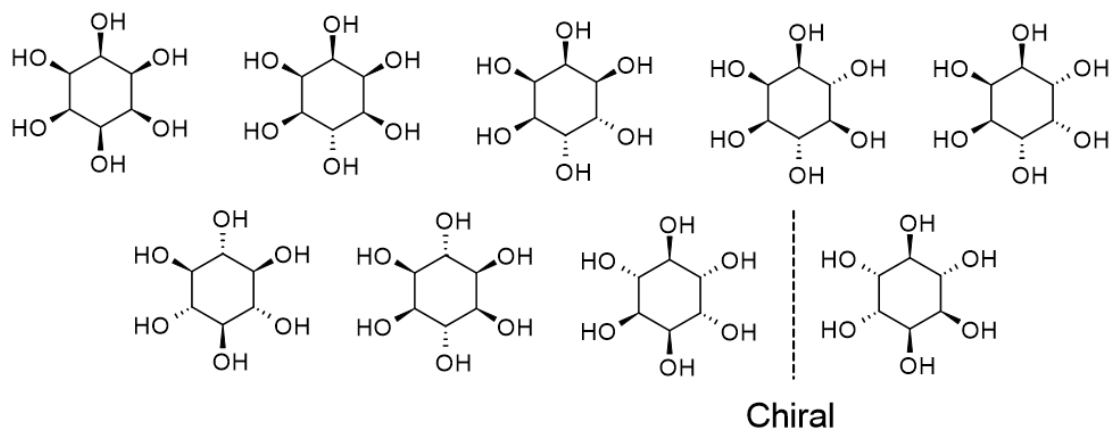
F



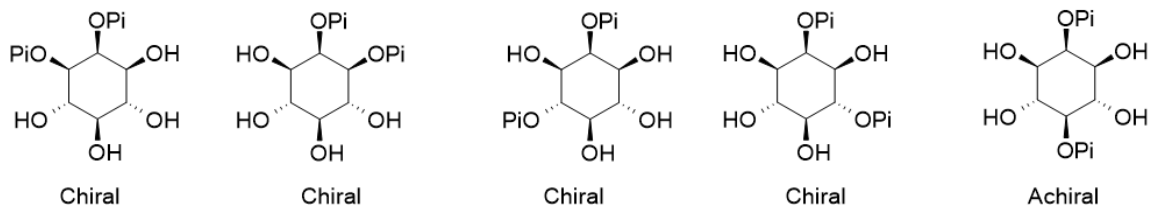
myo-inositol

Another geometric isomer of **D** is also correct.

4.

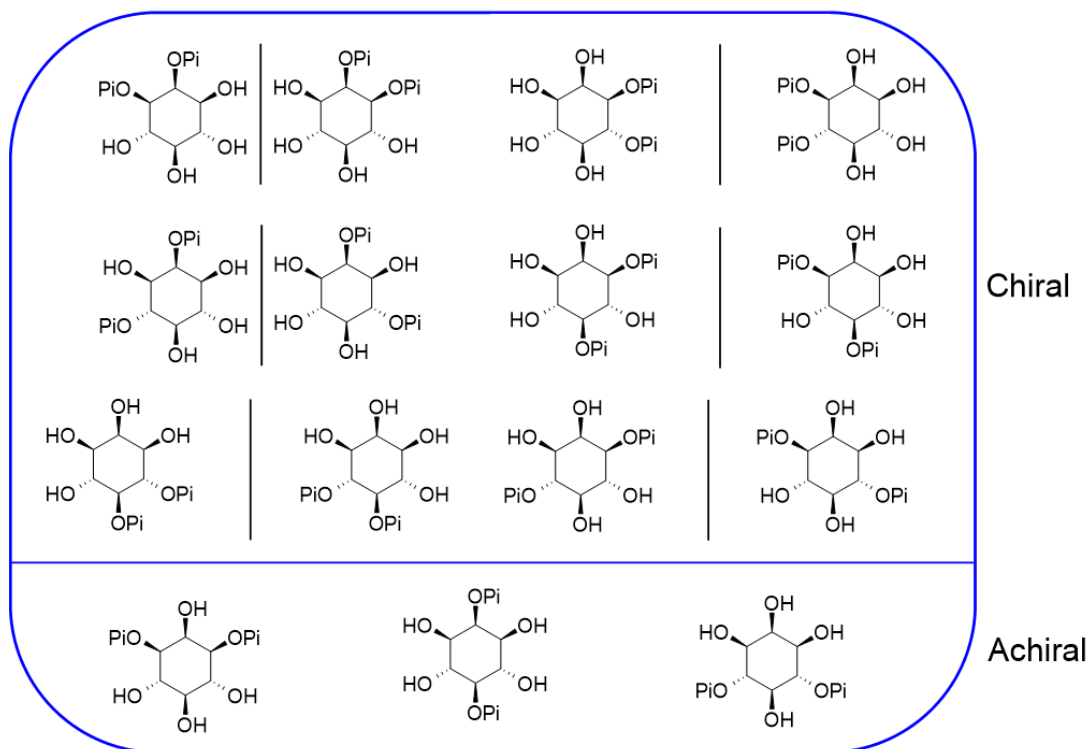


5.



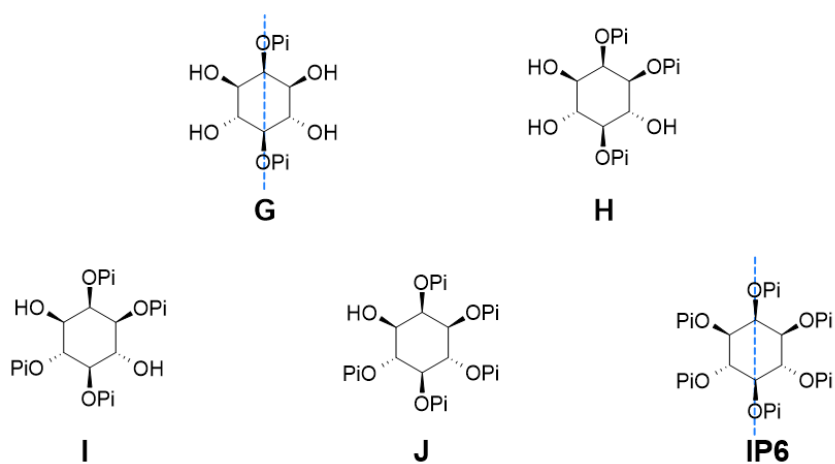
5 isomers of **G** can be formed in this pathway.

6.



15 isomers

7.

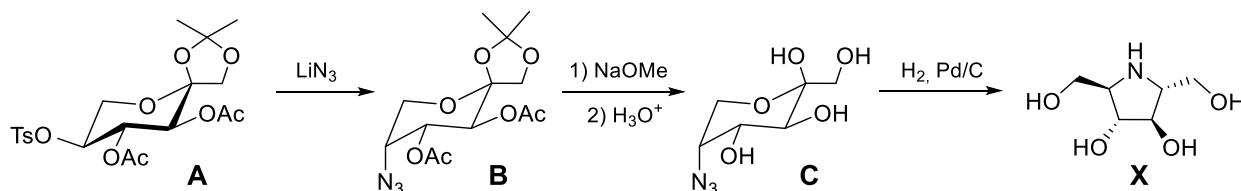


Enantiomers of **H**, **I** and **J** are also correct.

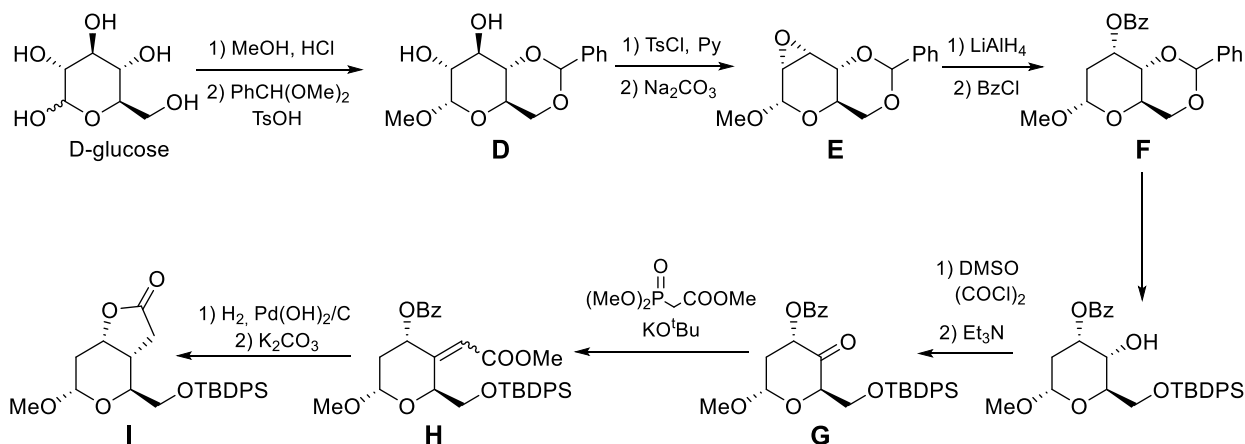
G and **IP6** contain a plane of symmetry.

Problem 19. Carbohydrates as chiral pools

1. When azide acts on **A**, a nucleophilic substitution reaction occurs with an inversion of configuration, and **B** is formed. When the protecting groups are removed, **C** is obtained, and then upon reduction, **X** is obtained.

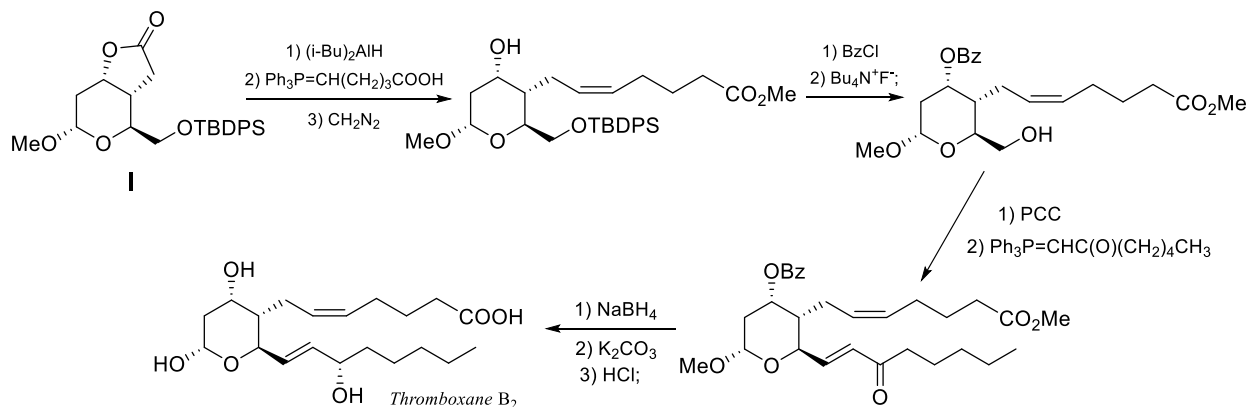


2. Reactions: MeOH, HCl with D-glucose leads to the formation of methyl glucoside, which then yields benzylidene acetal **D**. Reaction of **D** with TsCl: OH group (3-OH) reacts with TsCl and then in basic conditions, the other OH group (2-OH) attacks the tosylate and forms the epoxide **E**. Next, **E** is reduced with LiAlH₄, forming an OH, which upon benzylation leads to **F**. The reaction of **F** with H₂, Pd(OH)₂/C leads to hydrogenolysis of the benzylidene group, which is followed by protection of the OH with TBDPSCl. Further oxidation in the Swern reaction yields **G**, which through the Wittig reaction yields **H**. After reduction and hydrolysis, **H** yields **I**.

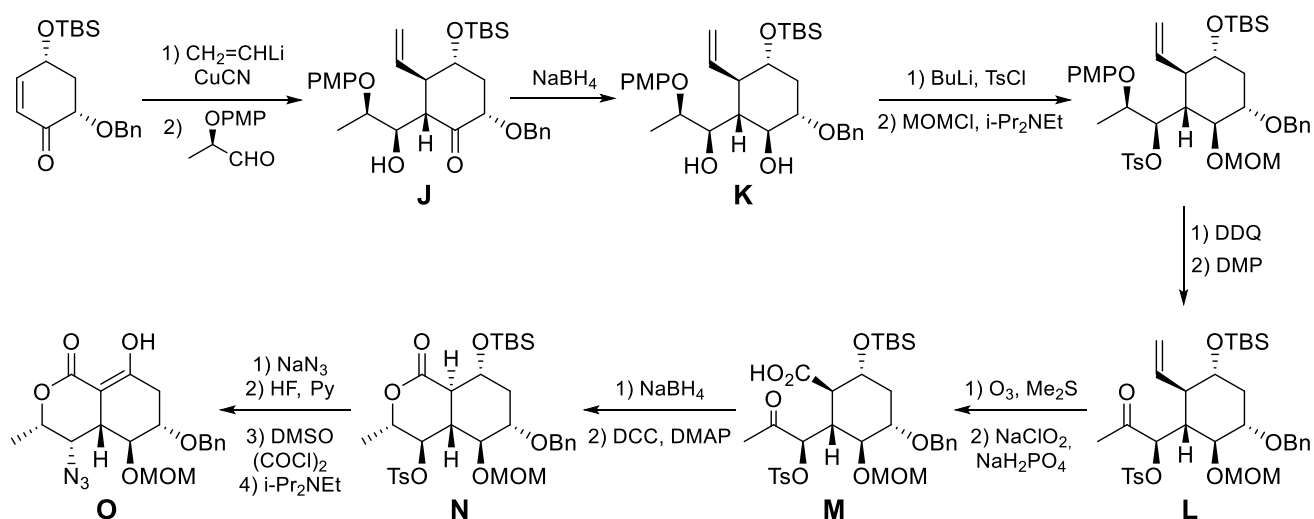


3. To obtain *Thromboxane B₂*, the reagents must be added in the following sequence:

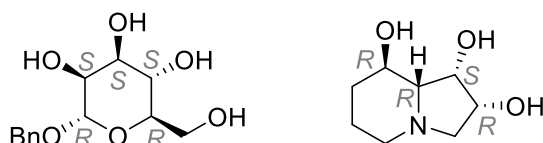
$Z_4 \rightarrow Z_2 \rightarrow Z_1 \rightarrow Z_3$ (the reduction of enone in conditions Z_3 is not diastereoselective)



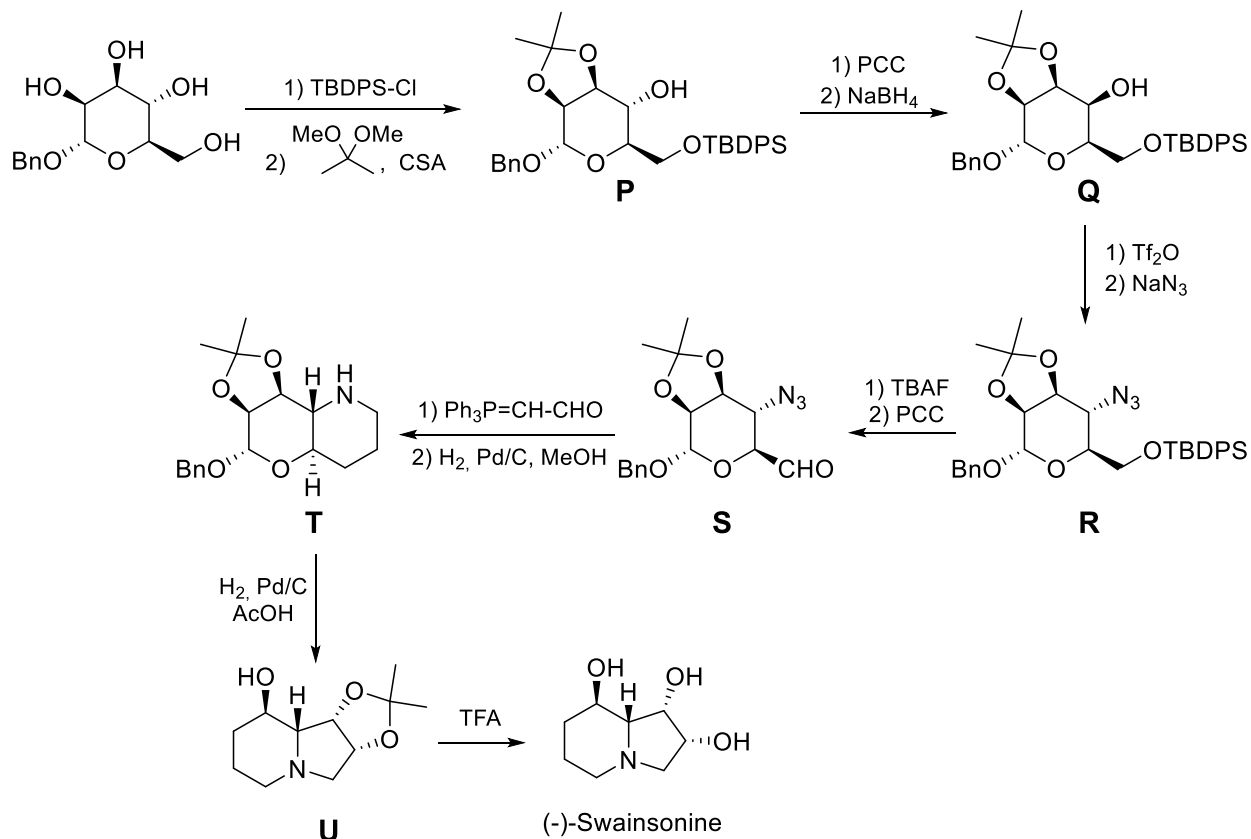
4. The 1,4-addition and coupling reactions yield **J** from the starting compound, which upon reduction yields **K**. The OH is then protected by the MOM group. During oxidation with DDQ, the PMPO group is removed, and the resulting OH is then oxidized to form **L**. Ozonolysis of **L** yields an aldehyde, which upon oxidation yields carboxylic acid **M**. Reduction and condensation yield lactone **N**. Nucleophilic substitution, removal of the TBS-protecting group, Swern oxidation followed by basic treatment yields **O**. Hydrogenation in the presence of HCl reduces azide function along with removal of two other protecting groups.



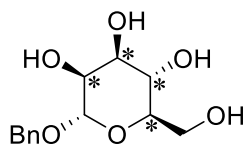
5.



6. The OH groups from the starting compound are subsequently protected, yielding **P**. Oxidation and reduction yield **Q**, which is the epimer of **P**. After the OH group is replaced by an azide, compound **R** is formed. After the protecting group is removed and the newly formed OH group is oxidised, aldehyde **S** is formed. After the Wittig reaction and reduction, **T** is obtained, which further upon reduction yields **U**. After the protecting group is removed, the final product is obtained.



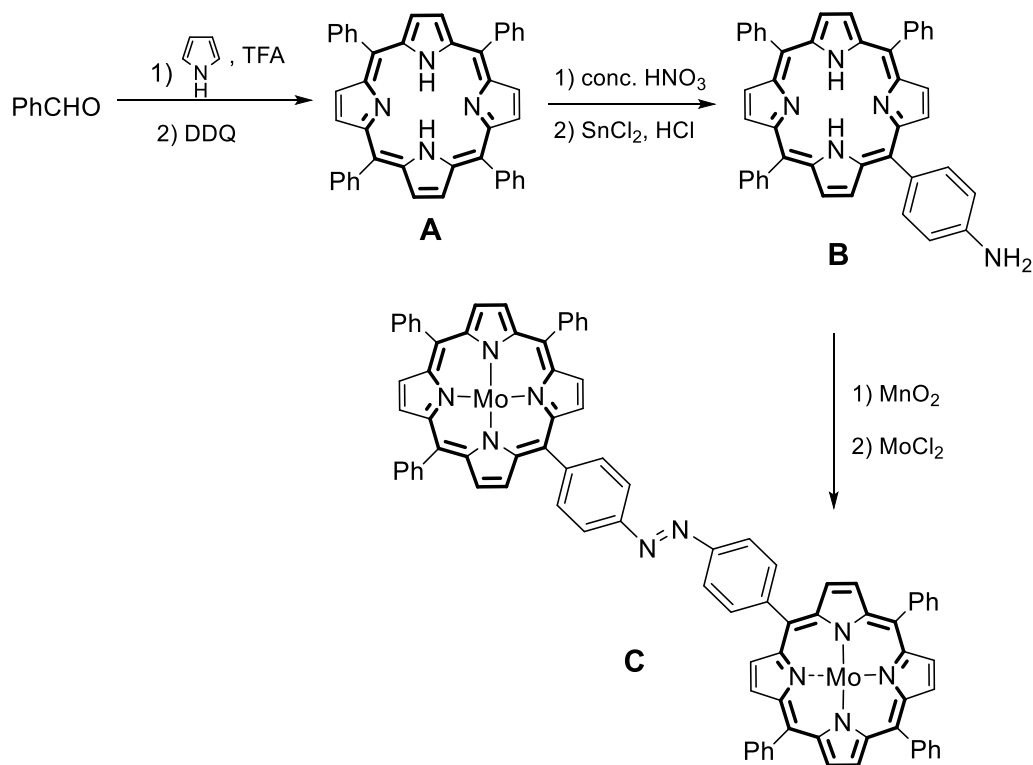
8. Preserved stereocentres:



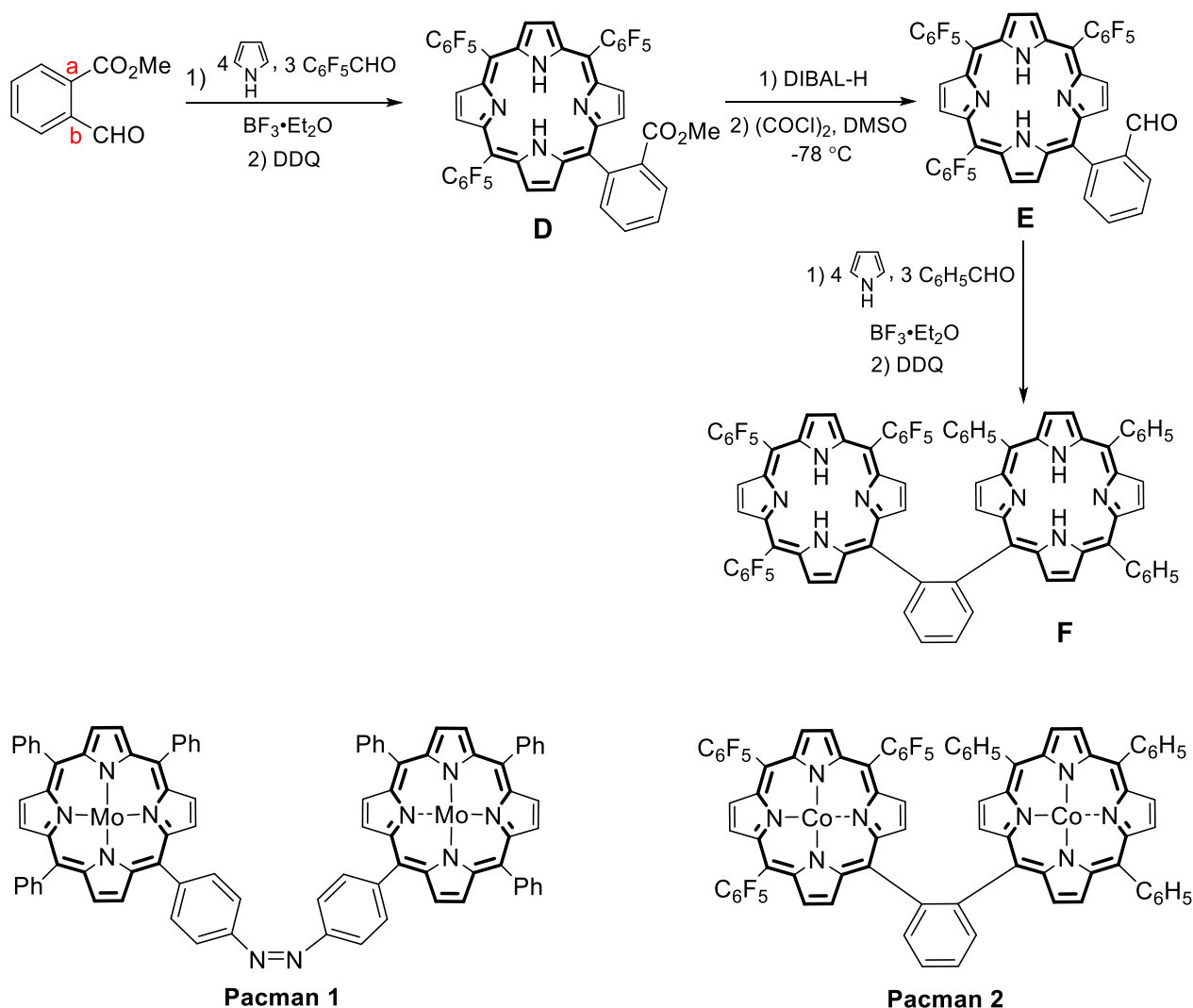
The newly formed stereocentre is absent in the final product.

Problem 20. Pacman, Hangman, Cageman

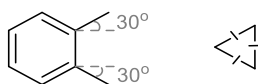
- According to the nitrogen content, only one nitro group was added to the structure of compound **B**. The next stage is dimerisation and formation of a diazaporphyrin with molybdenum insertion:



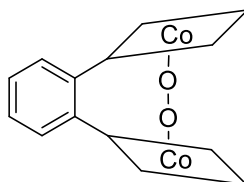
2. In this scheme stepwise formation of porphyrin rings was used.



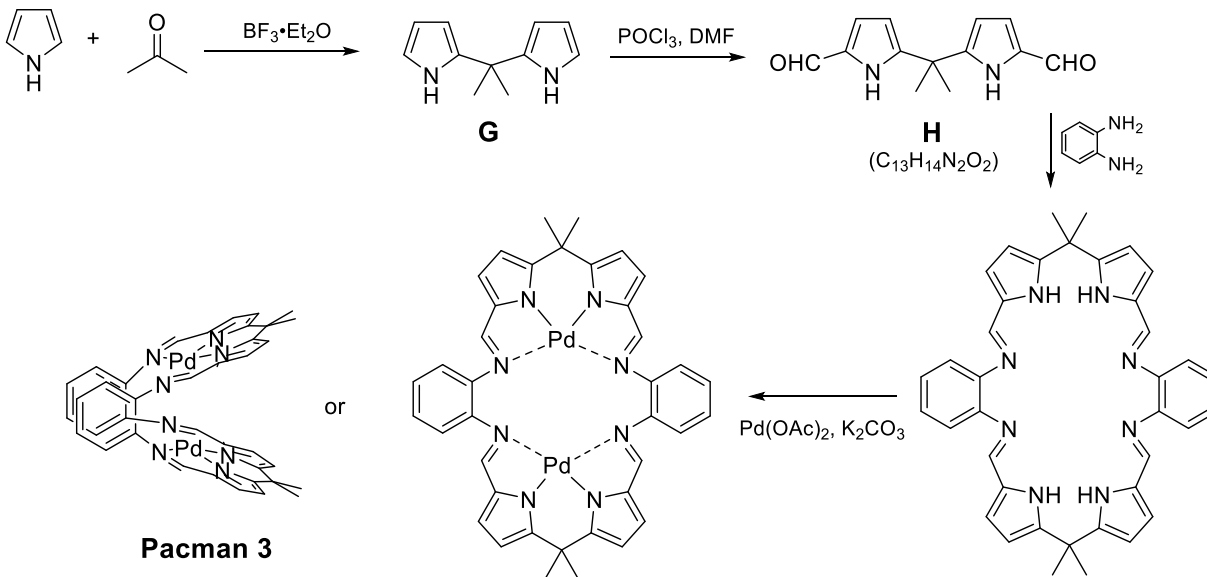
3. The porphyrin rings and metals form an equilateral triangle. Thus, the distance between metals will be equal to $4.7 + 1.39 = 6.09$ Å (*students are not expected to memorise bond lengths in exam*).



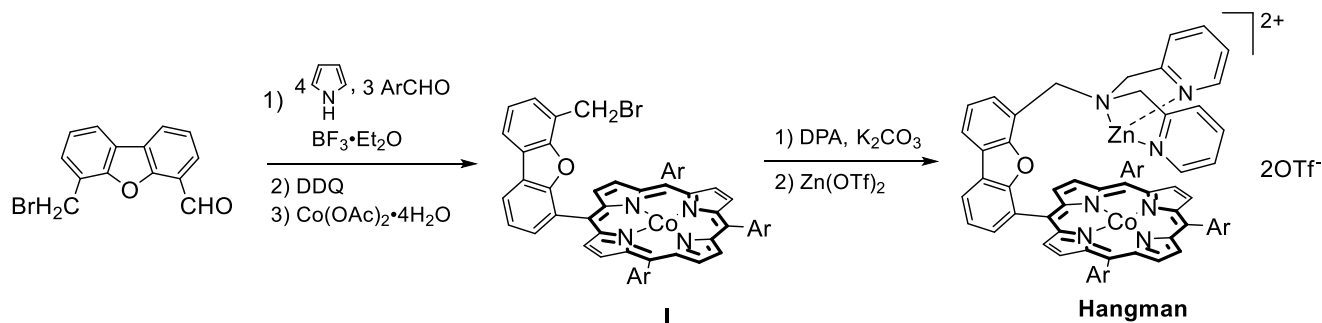
4.



5. In an excess of pyrrole, the reaction of acetone and pyrrole yields bispyrrolic compound **G** which is then formylated through the Vilsmeier–Haack reaction. Further macrocyclisation happens through imine condensation. Addition of the metal forces the macrocycle to the Pacman-type conformation.



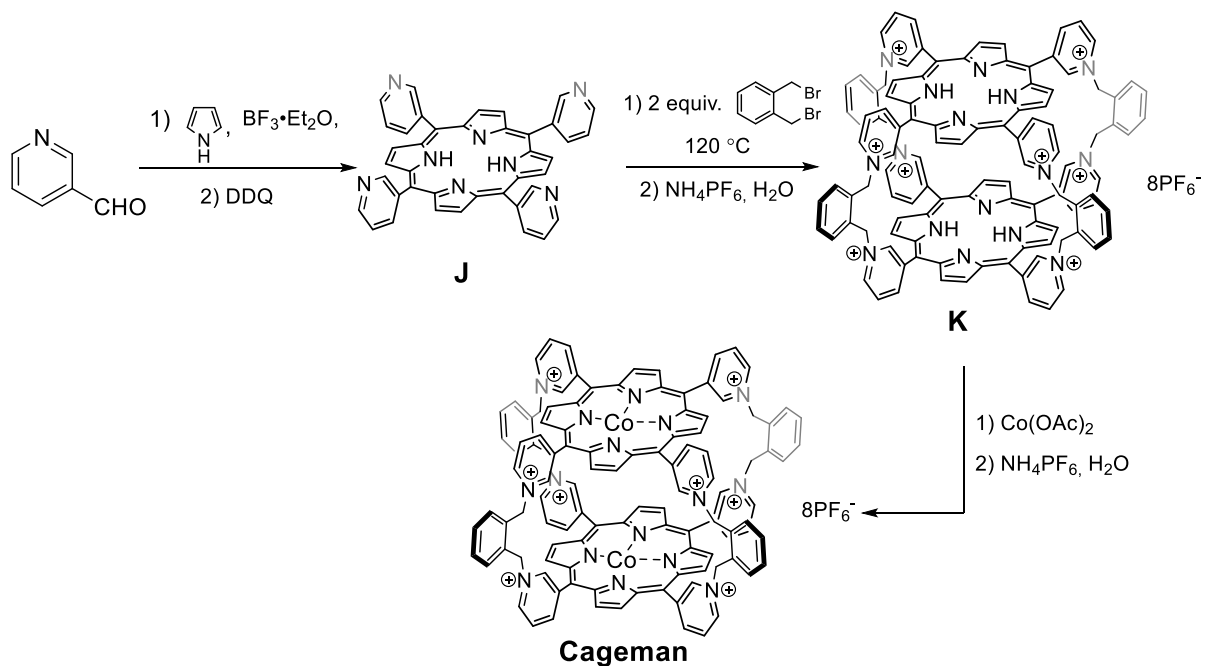
6.



7. In a molecule **J** there are 4 Py groups. In *o*-xylene dibromide, there are two benzylic bromides. These two compounds can react in 1+2, 2+4, 3+6, ... manner. From the molecular weight of **J** (618) and the dimethylenebenzene unit (104), it is easy to calculate molecular weight of **K**: $618 \cdot n + (104 \cdot 2n) + (4n \cdot 145) = 1406n$. From the name – **Cageman** and the mass spectra results (for $n = 2$: $1406 \cdot 2 - 145 = 2667$), it is clear that **K** forms in a 2+4 manner.

In the mass spectrum signal is assumed as mass to charge ratio, signals from ions of higher charge (and thus lower m/z) can be expected. The easiest way of ionisation in case of **K** is losing anions. Therefore, the following ion signals could be expected: $[\text{cage} \cdot 7\text{PF}_6]^+ - 2667.0$, $[\text{cage} \cdot 6\text{PF}_6]^{2+} - 1261.0$, $[\text{cage} \cdot 5\text{PF}_6]^{3+} - 792.3$, $[\text{cage} \cdot 4\text{PF}_6]^{4+} -$

558.0, $[\text{cage} \cdot 3\text{PF}_6]^{5+} - 417.4$, $[\text{cage} \cdot 2\text{PF}_6]^{6+} - 323.7$. Therefore, the molecular weight of **Cageman** is 2930 g/mol.



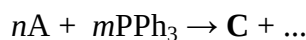
Problem 21. Catalyst C

1. Carbon and hydrogen in **B** indicate that it might be an organic compound. The threefold symmetry suggests that it has formulae PR_3 , in which R is an organic radical. Hence, $M(\text{R})$ equals:

$$M(\text{R}) = \left(\frac{30.97}{0.118} - 30.97 \right) \div 3 = 77 \text{ g/mol}$$

This corresponds to a phenyl group C_6H_5 , hence **B** = **PPh₃**, a well-known ligand for large transition metals.

The overall reaction equation of compound **A** can be written like:



By varying the values of m and n (which are less than 5), one can determine the molar mass of compound **A**, as well as the metal **M** contained in it:

$$M(\text{A}) = \frac{2.0 \cdot (77 \cdot 3 + 31) \cdot m}{7.96 \cdot n} \rightarrow A_r(\text{M}) = \frac{2.0 \cdot (77 \cdot 3 + 31) \cdot m}{7.96 \cdot n} \cdot 0.3909$$

$$A_r(\text{M}) = \frac{m}{n} \cdot 25.73$$

For metals in the 5th period, A_r is more than 85(Rb) and less than 120(Sn) (85-120).

$(m:n)=(1:1)$	$(m:n)=(2:1)$	$(m:n)=(3:1)$	$(m:n)=(4:1)$	$(m:n)=(5:1)$
25.73(<85)	51.46(<85)	77.2(<85)	102.93 (Rh)	128.66(>120)

(as we can see trying numbers more than 1 for n would lead to values less than 85)

From the table, when $(m:n) = (4:1)$, the mass corresponds to the molar mass of **Rh**, which fits the conditions in the task. Other values of $A_r(\text{M})$ don't fit any metal from the 5th period. Furthermore, the molar mass of **A** is 263.3 g/mol. By subtracting the mass of the metal **M** and three H_2O molecules, we get the mass of 106.4, which corresponds to three Cl atoms.

Hence, **A** = **RhCl₃·3H₂O**.

There are many ways to find **C**. One of them is with the molar mass of **C**, considering that **C** contains rhodium:

$$M(\text{C}) = \frac{6.18}{0.88 \times \frac{2.00}{263.3}} = 924.54 \text{ g/mol}$$

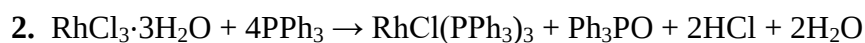
By subtracting the molar mass of Rh and $x\text{PPh}_3$ molecules, we can find other species in compound **C**.

When $x = 1$, the remainder is 559.61;

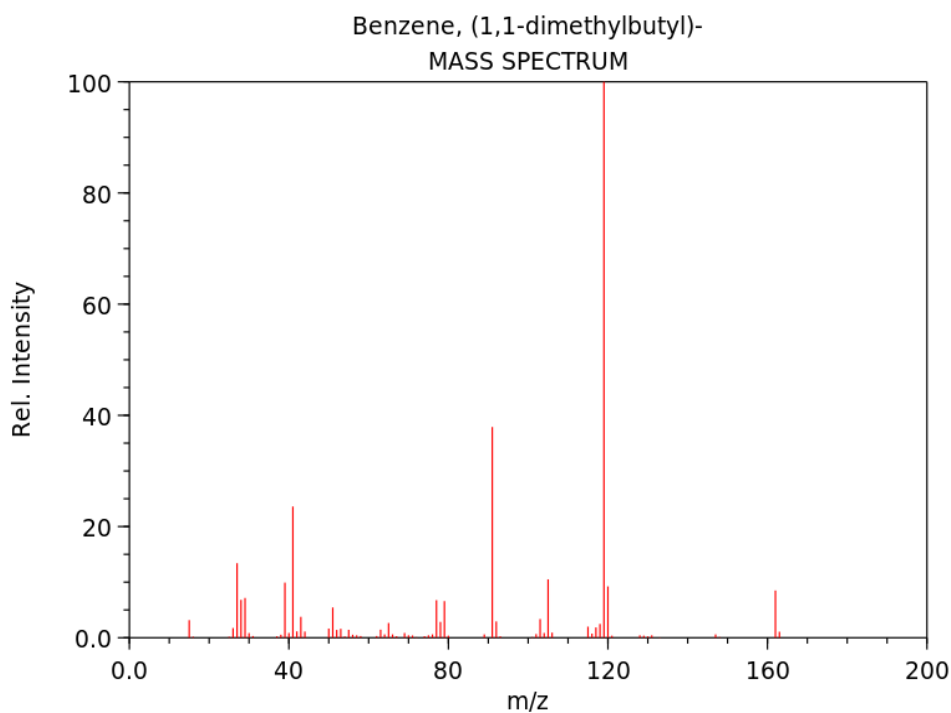
when $x = 2$, the remainder is 297.61;

when $x = 3$, the remainder is 35.6, which is approximately equal to one Cl atom.

M	A	B	C
Rh	$\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$	PPh_3	$\text{RhCl}(\text{PPh}_3)_3$



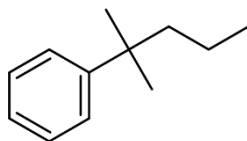
3. Mass spectrum below is copied from 'NIST' database.



NIST Chemistry WebBook (<https://webbook.nist.gov/chemistry>)

m/z	119	91	41
Structure			

4.



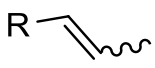
Product

5. Natural carbon consists of ^{12}C and ^{13}C isotopes:

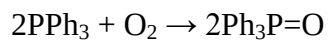
$$12.011 = 12 \cdot x + (1 - x) \cdot 13; x - \text{abundance of } ^{12}\text{C}$$

$$x = 0.989$$

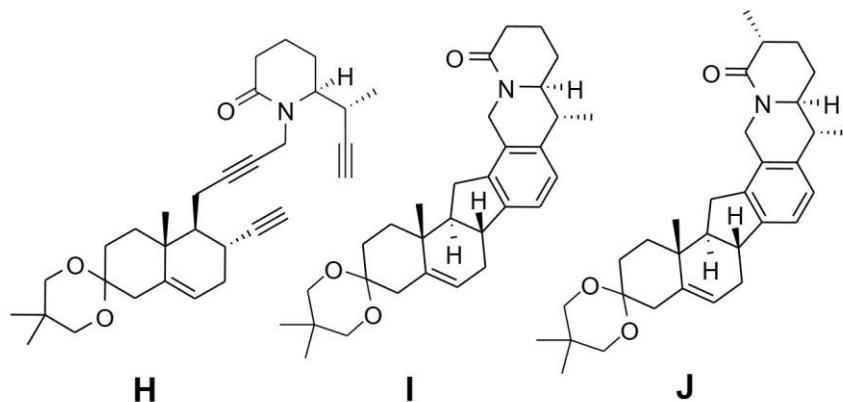
$$[M]^+ : [M + 1]^+ = \frac{0.989^{12}}{0.989^{11} \cdot (1 - 0.989) \cdot \frac{12!}{(12-1)!}} = \frac{0.989}{0.011 \times 12} = 7.5$$

6. **D** 

7. **F** is a product of oxidizing **B** with oxygen, triphenylphosphine oxide, $\text{Ph}_3\text{P}=\text{O}$.

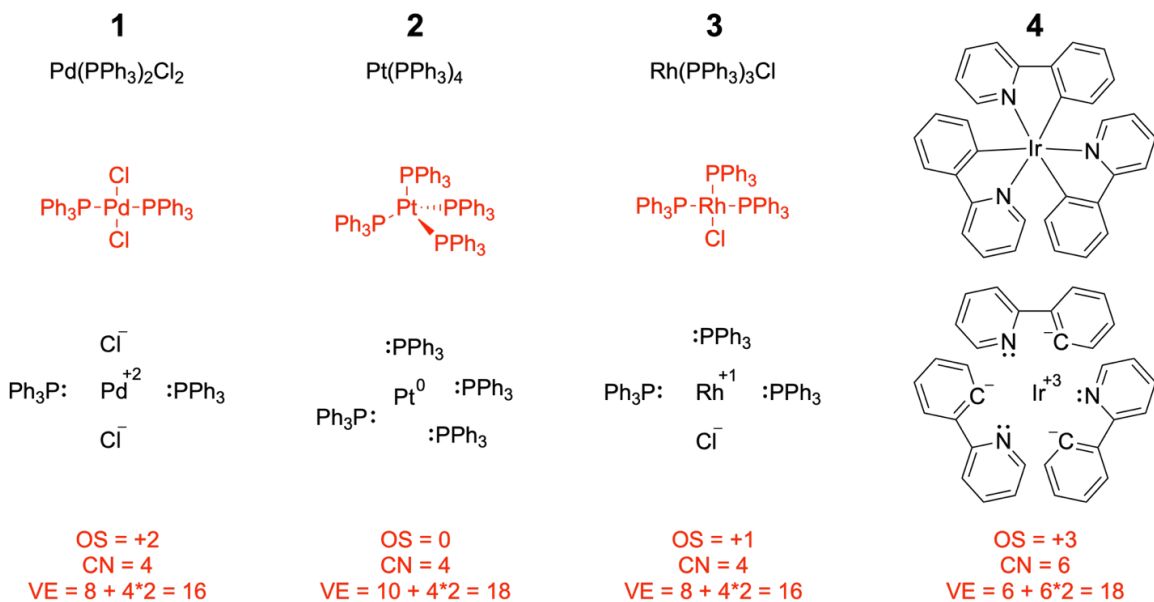


8.

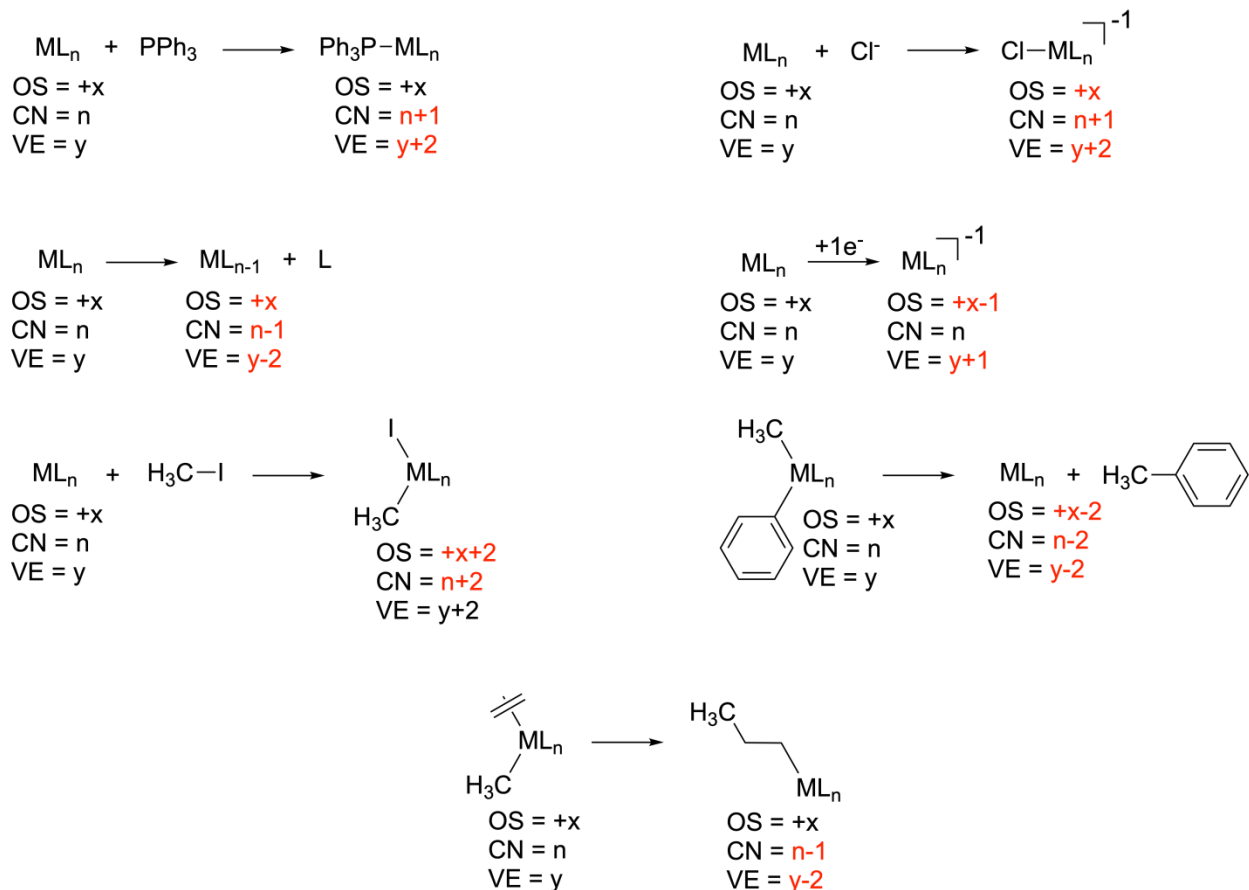


Problem 22. Transition metals in organometallic catalysis

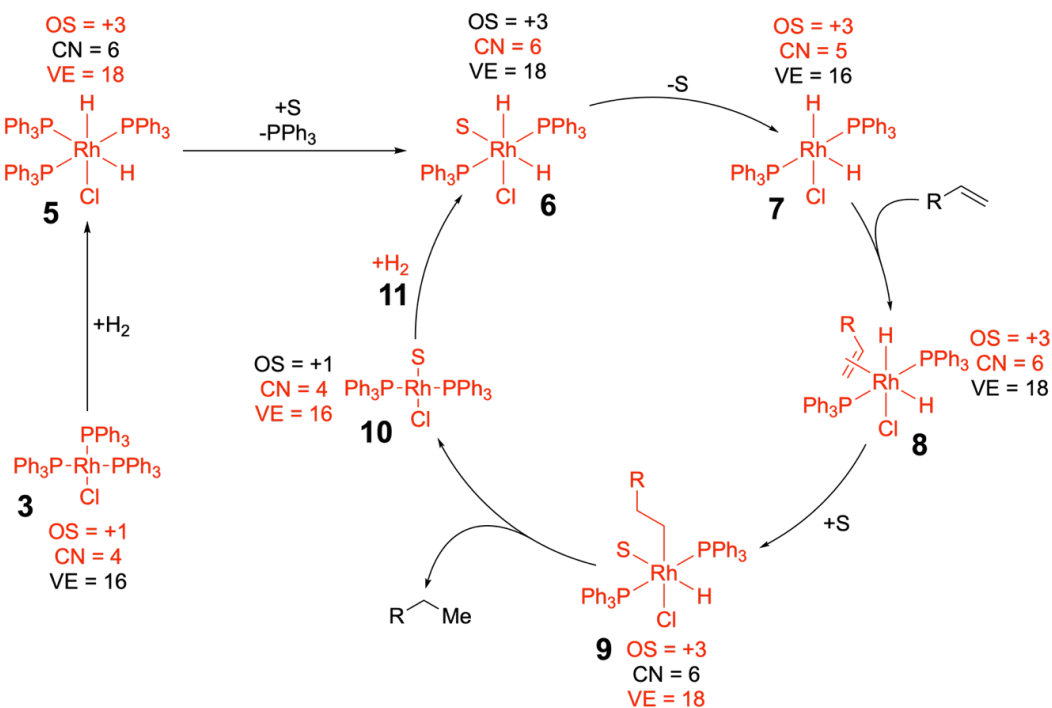
1.



2.

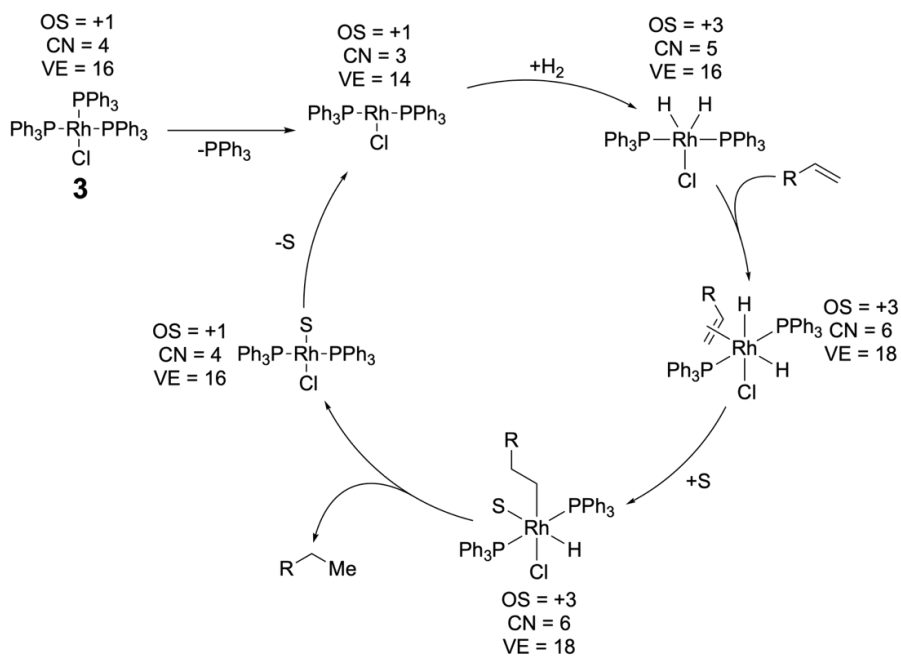


3. Any reasonable alternative stereoisomers of complexes are accepted as a correct answer since this is not a field of advanced difficulty, and it is beyond the purpose and scope of this task.

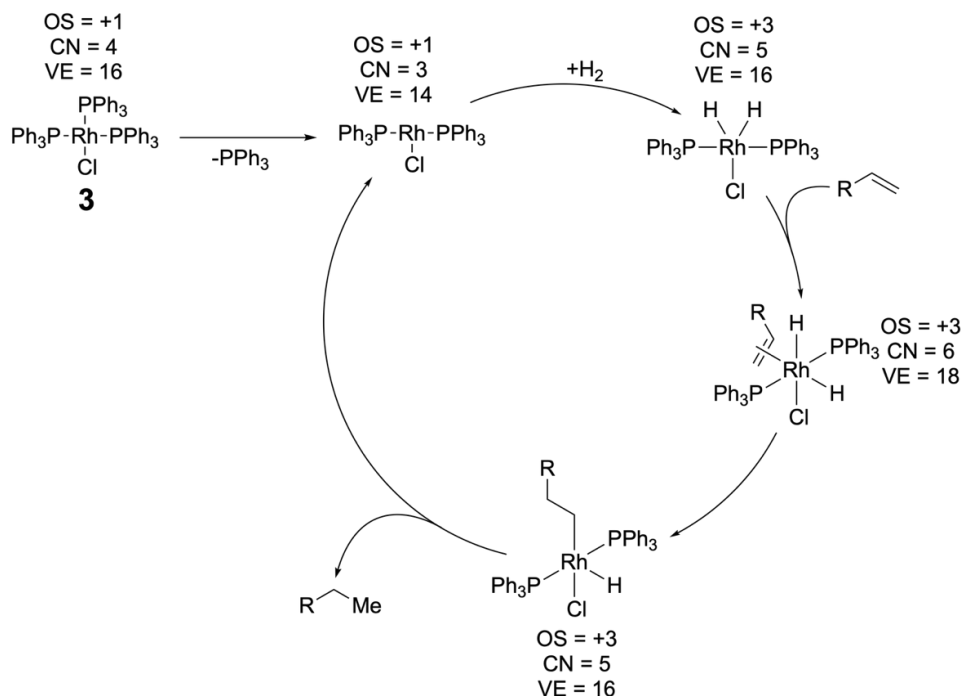


4. $11 = \text{H}_2$

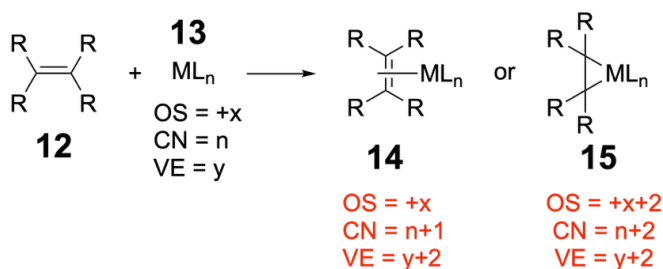
5. An alternative catalytic cycle is presented below.



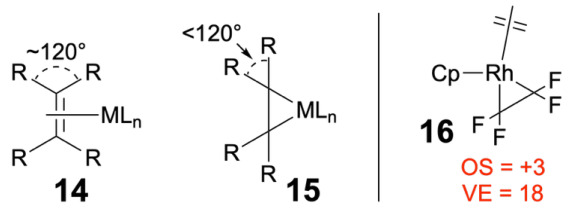
Any other reasonable catalytic cycles which fit the conditions in the task are graded fully. For instance, see an alternative option below.



6. When an alkene coordinates via dative bonding, the oxidation state of the metal is not changed, the coordination number increases (+1) and the total amount valence electrons is also increased (+2). If the metallocyclopropane mode takes place, all the parameters are increased (+2).



7. Ethylene did not significantly change its C–C bond length upon metal binding, whereas tetrafluoroethylene did. Moreover, metallocyclopropane coordination implies that substituents on the C=C bond will become non-coplanar with the C–C bond. This should decrease the angle R–C–R in the alkene upon binding (compare complex **14** where the R–C–R angle is about 120°, to an R–C–R angle of less than 120° for **15**). Therefore, ethylene has dative bond coordination, while tetrafluoroethylene has coordination closer to metallocyclopropane.

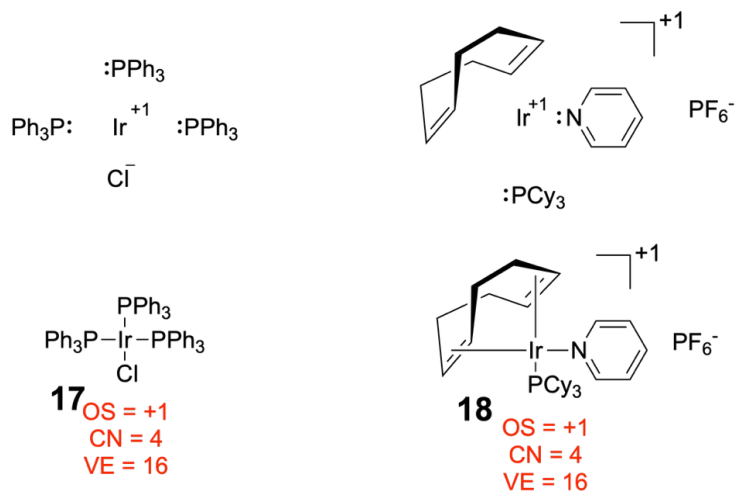


8. The geometry of complex **16** was discussed above.

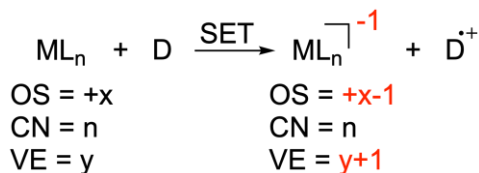
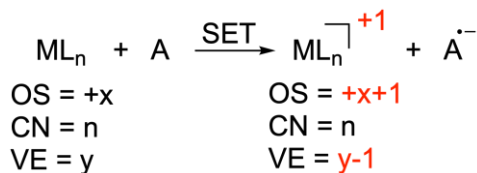
ethylene = a. alkene coordination

tetrafluoroethylene = b. metallocyclopropane coordination

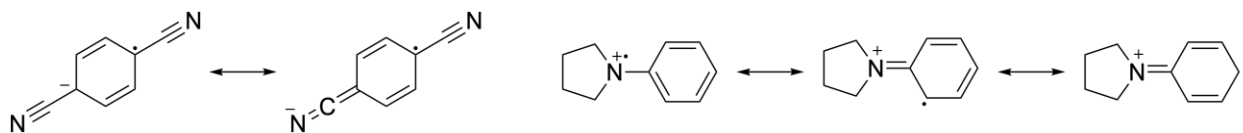
9. Complex **17** $\text{IrCl}(\text{PPh}_3)_3$ should be identical to that of rhodium ($\text{RhCl}(\text{PPh}_3)_3$), thus, it is reasonable to start with its parameters. After finding them, we know that **18** has exactly the same parameters, therefore, it should be a cationic complex (which is reasonable, since PF_6^- is a non-coordinating anion).



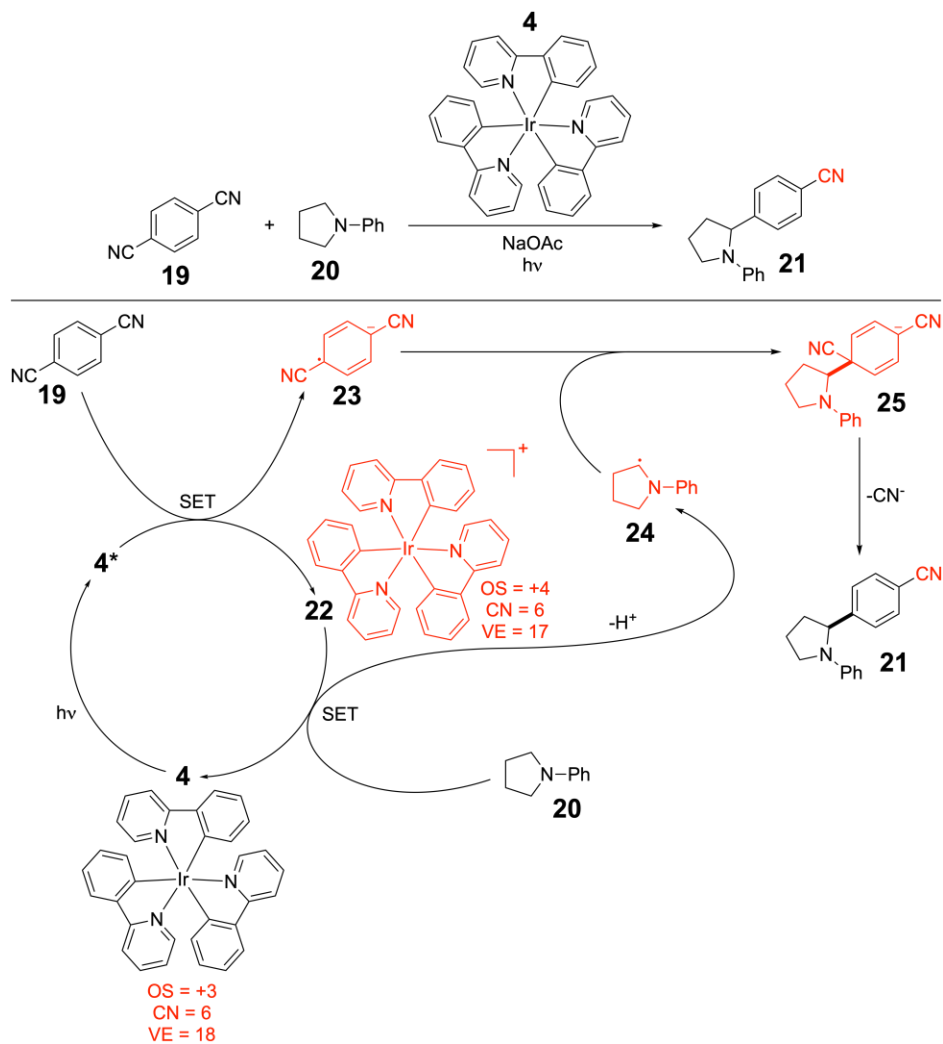
10.



11. Reasonably, electron poor arene **19** should be an electron acceptor, since it has two electron withdrawing groups to stabilize negative charge which can be demonstrated by the resonance structures shown below for the product of single electron reduction of **19**. Similarly, compound **20** will give away one electron more readily than **19**, because of the stabilization of radical cation obtained from it (see the resonance structures below).



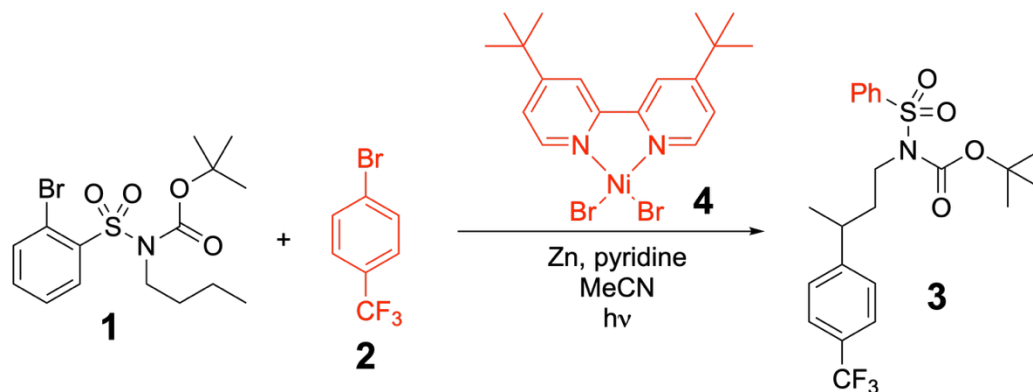
12. As discussed, **19** will be an electron acceptor, thus, excited complex **4*** should donate one electron during SET to **19**, providing cationic complex **22** and radical anion **23**. Complex **22** has iridium in a +4 oxidation state and it has only 17 VE, thus, during the SET it will be an electron acceptor to produce complex **4** again. Upon SET and deprotonation, radical **24** is generated which can be coupled with **23** creating the highlighted C–C bond in **25**.



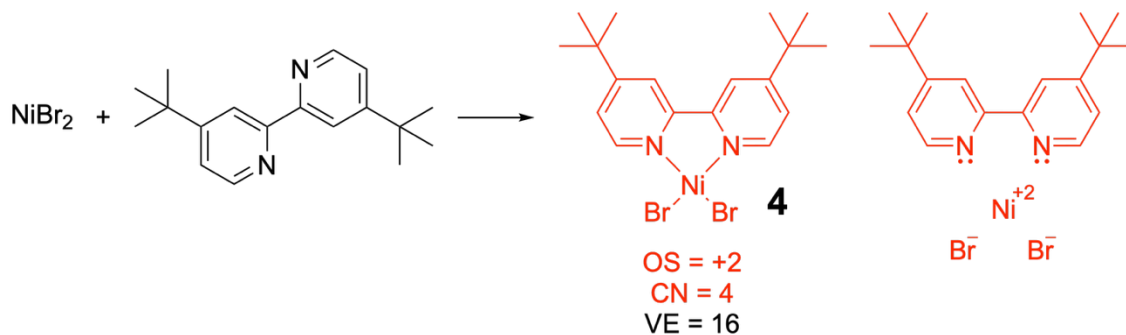
13. R = CN

Problem 23. HAT and XAT (HalAT)

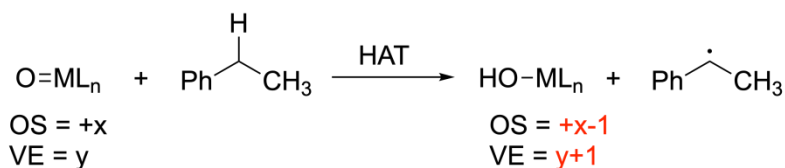
- According to MS of **2**, there is a bromine atom there, while in **3** there is no bromine and $R^2 = \text{Ph}$.



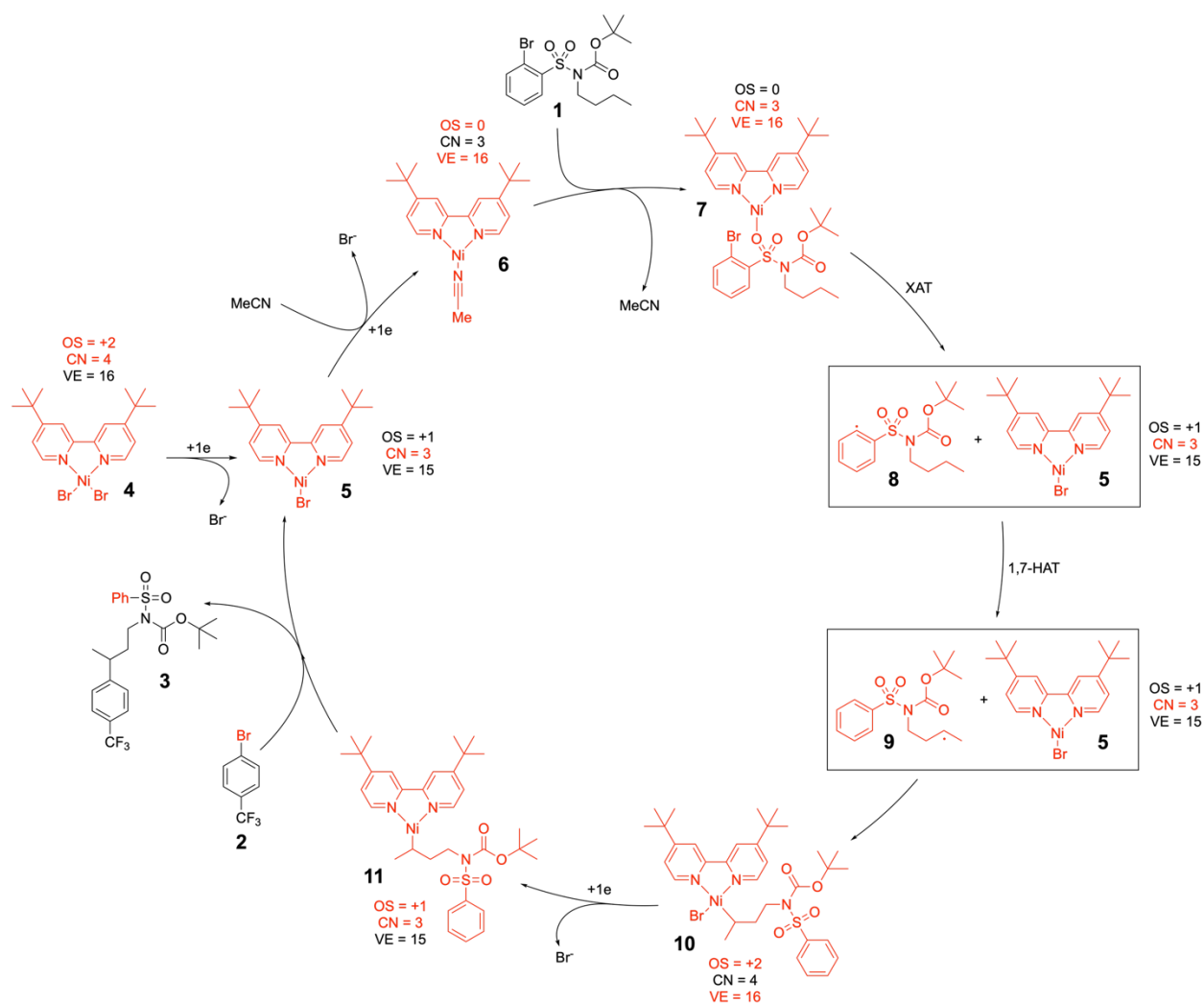
2.



3.

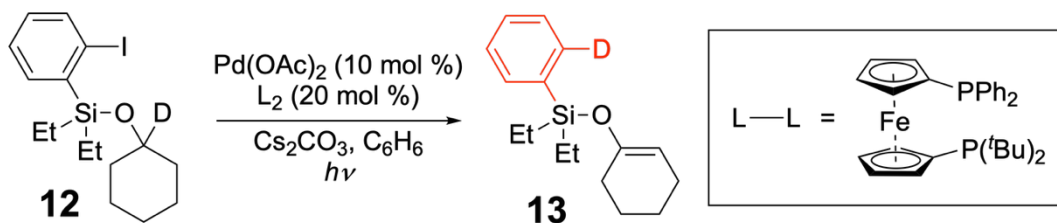


4. Two coordination modes are accepted for **7** (coordination via S=O or coordination via C=O; the latter is less favorable due to bulky ^tBu-group); coordination from a nitrogen atom or another oxygen (O-^tBu) are considered as incorrect answers for structure **7**.

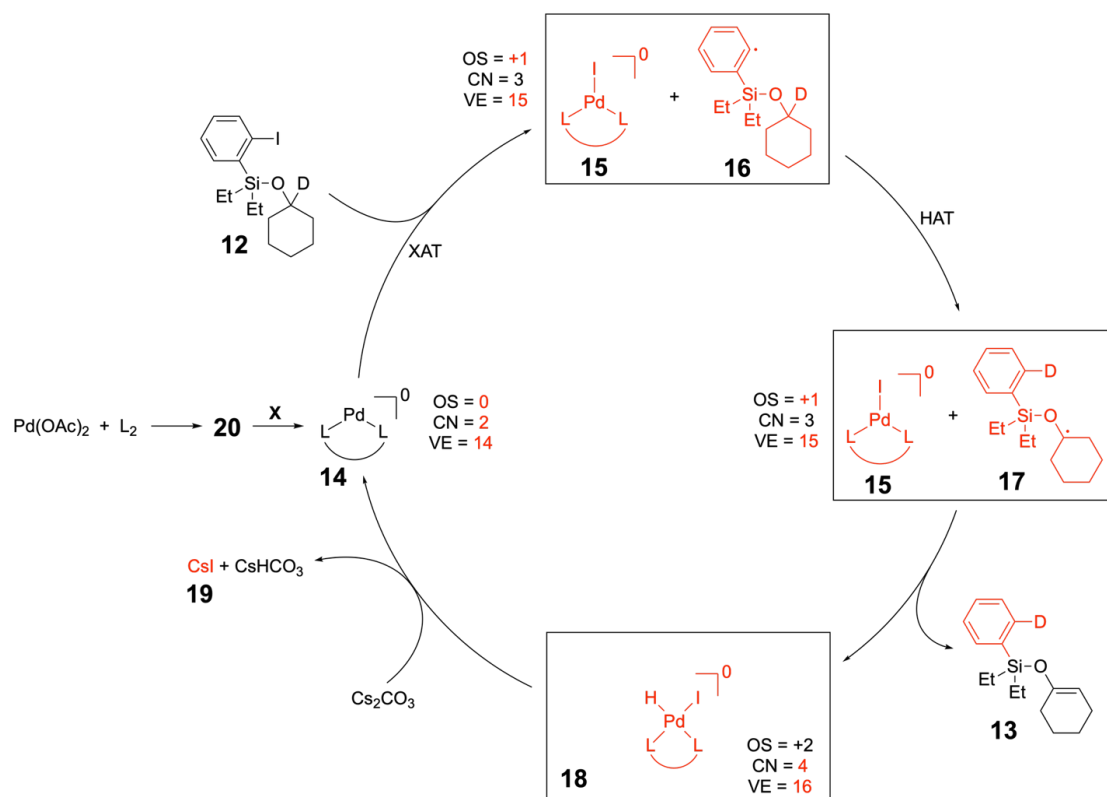


5. Zn

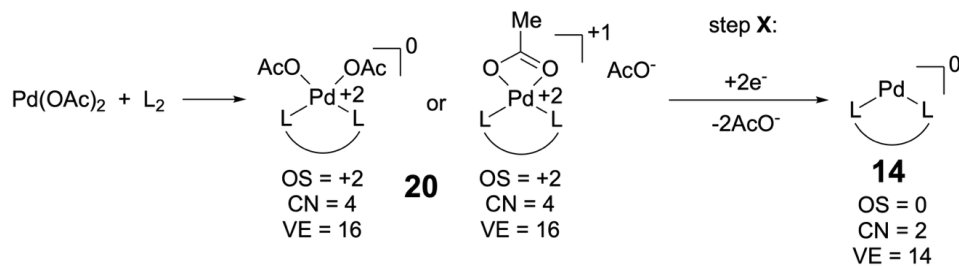
6. MS of **13** suggests that HI was eliminated from molecule **12**. Since there is a C=C bond in **13**, it is reasonable to suggest a deuterium transferred to the aromatic ring (it corresponds to the catalytic cycle of this transformation and it is conceptually similar with previous catalytic cycle).



7.



8. Evidently, a reduction should occur with acetate groups leaving the metal. In principle, excess of phosphine ligand L_2 can reduce the complex **20** to **14**.



9.

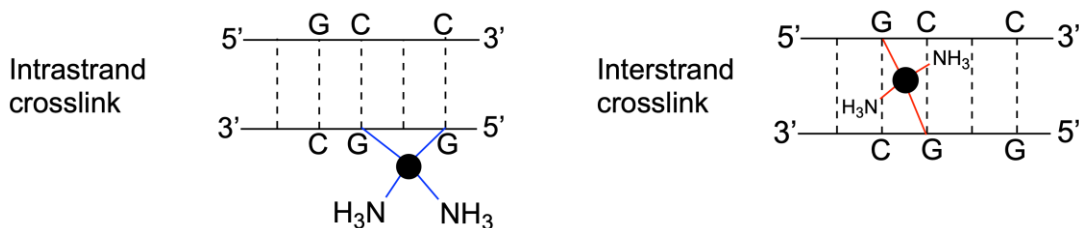
$$\text{BDE}(\text{C-H})_{21} > \text{BDE}(\text{C-H})_{22}$$

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

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

Problem 24. Anticancer complexes

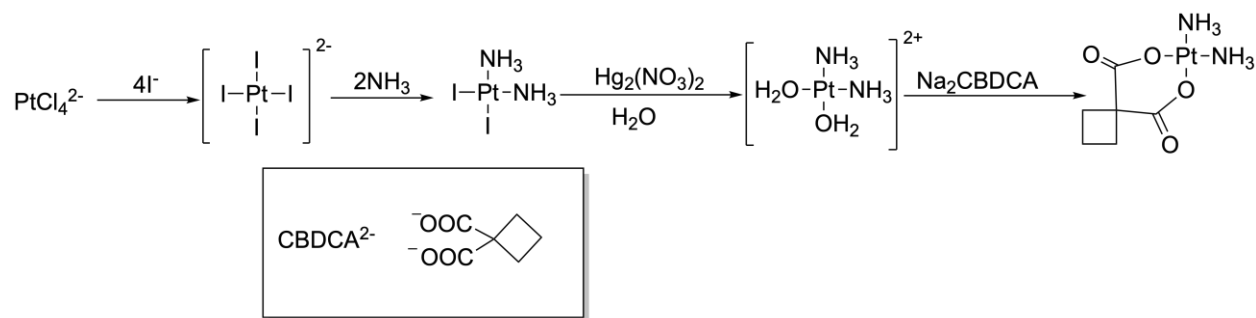
1. a)



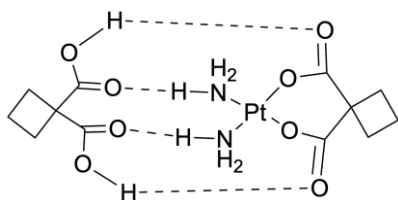
b) Cisplatin favours formation of intrastrand crosslinks, while transplatin, due to its geometry, forms a higher proportion of interstrand crosslinks.

2. Intrastrand crosslinks decrease the melting temperature as they destroy the helix structure of DNA. Interstrand crosslinks increase the duplex melting temperature as they physically tie the two strands together and prevent separation.

3.

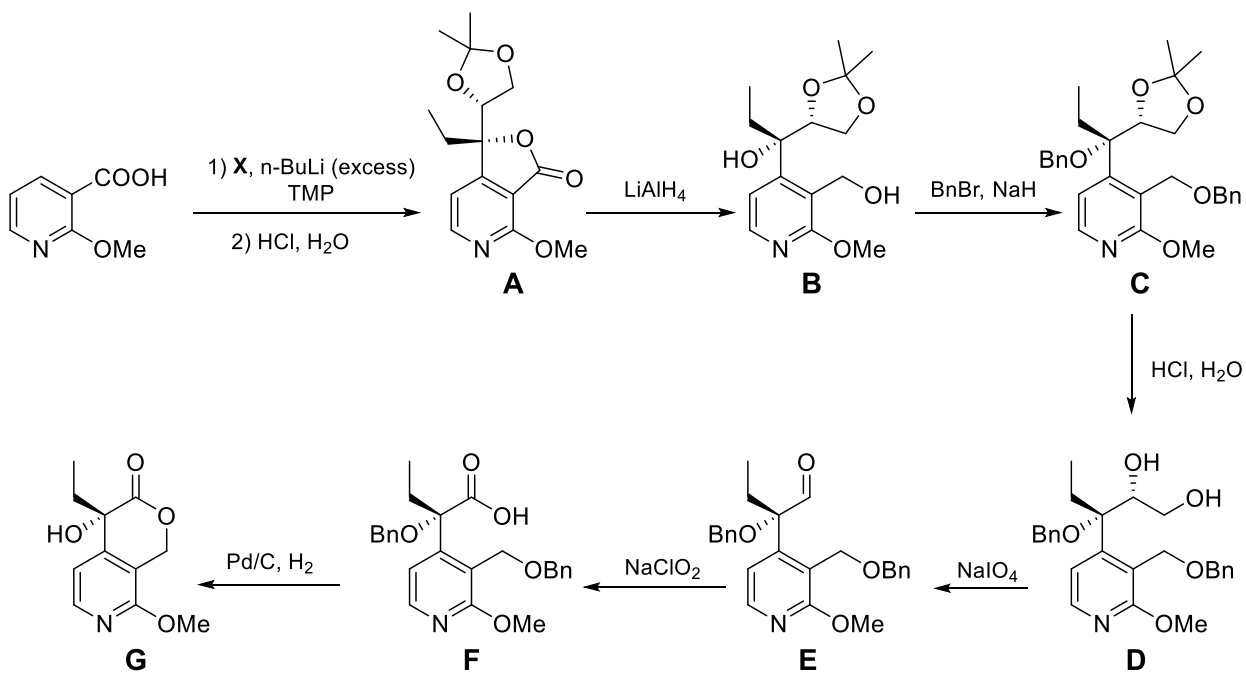


4.

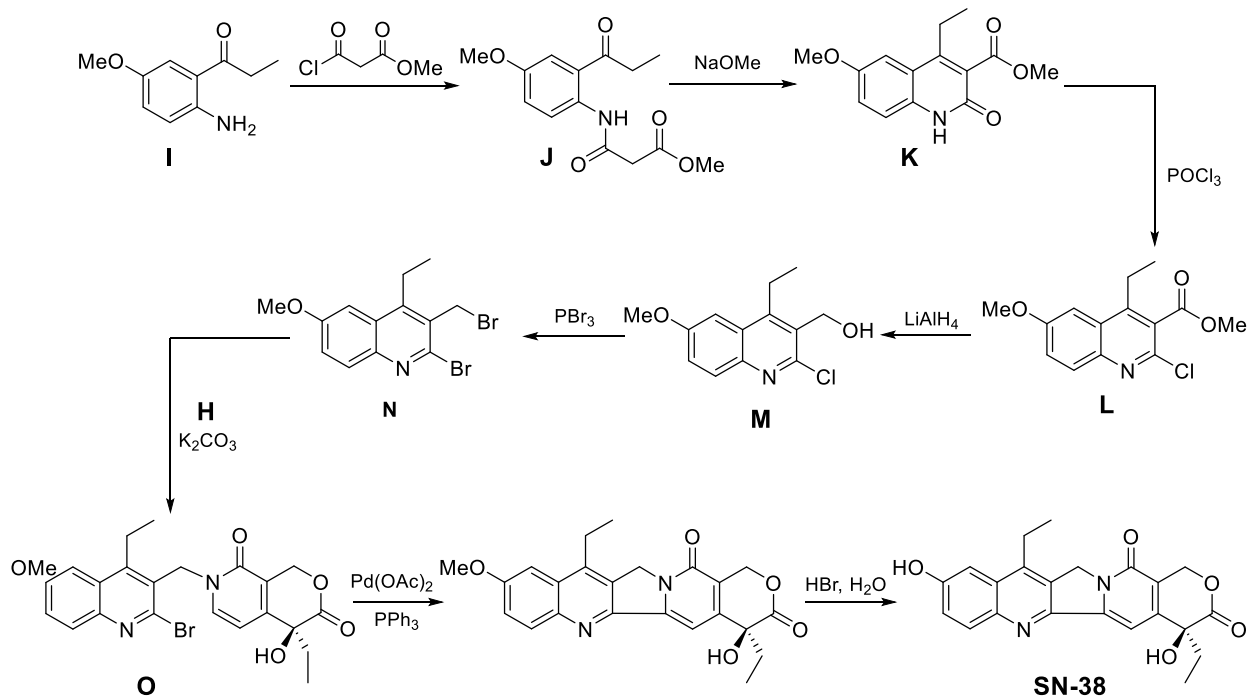


5. Dicycloplatin is more stable in aqueous solution than carboplatin because it forms a supramolecular complex with 1,1-cyclobutanedicarboxylic acid, which enhances stability through hydrogen-bonding interactions.

6.



7.



Problem 25. The equilibria in DNA

1. $n = 4 \cdot 4 \cdot 1 \cdot 1 = 16$. They are: 5'-AATT-3', 5'-TTAA-3', 5'-ATAT-3', 5'-TATA-3', 5'-GGCC-3', 5'-CCGG-3', 5'-GCGC-3', 5'-CGCG-3', 5'-AGCT-3', 5'-GATC-3', 5'-ACGT-3', 5'-CATG-3', 5'-GTAC-3', 5'-TGCA-3', 5'-CTAG-3', 5'-TCGA-3'.
2. At 10 °C:

$$\begin{cases} [\text{ss-DNA}] + 2[\text{ds-DNA}] = 1 \times 10^{-5} \text{ M} \\ 2.44 \times 10^4 \text{ cm}^{-1} \text{ M}^{-1} \times 5 \text{ cm} \times [\text{ss-DNA}] + 2.93 \times 10^4 \text{ cm}^{-1} \text{ M}^{-1} \times 5 \text{ cm} \times [\text{ds-DNA}] = 0.89 \end{cases} \rightarrow$$

$$\begin{cases} [\text{ss-DNA}] = 3.23 \times 10^{-6} \text{ M} \\ [\text{ds-DNA}] = 3.38 \times 10^{-6} \text{ M} \end{cases} \rightarrow K(10^\circ \text{C}) = \frac{3.38 \times 10^{-6}}{(3.23 \times 10^{-6})^2} = 3.24 \times 10^5$$

At 30°C:

$$\begin{cases} [\text{ss-DNA}] + 2[\text{ds-DNA}] = 1 \times 10^{-5} \\ 2.44 \times 10^4 \text{ cm}^{-1} \text{ M}^{-1} \times 5 \text{ cm} \times [\text{ss-DNA}] + 2.93 \times 10^4 \text{ cm}^{-1} \text{ M}^{-1} \times 5 \text{ cm} \times [\text{ds-DNA}] = 1.17 \end{cases} \rightarrow$$

$$\begin{cases} [\text{ss-DNA}] = 8.97 \times 10^{-6} \text{ M} \\ [\text{ds-DNA}] = 5.13 \times 10^{-7} \text{ M} \end{cases} \rightarrow K(30^\circ \text{C}) = \frac{5.13 \times 10^{-7}}{(8.97 \times 10^{-6})^2} = 6.38 \times 10^3$$

Combining the results at different temperatures we obtain the following:

$$\begin{cases} \Delta_r H^\circ - 283.15 \times \Delta_r S^\circ = -8.314 \times 283.15 \times \ln(3.24 \times 10^5) = -29870.1 \text{ J mol}^{-1} \\ \Delta_r H^\circ - 303.15 \times \Delta_r S^\circ = -8.314 \times 303.15 \times \ln(6.38 \times 10^3) = -22080.9 \text{ J mol}^{-1} \end{cases} \rightarrow$$

$$\begin{cases} \Delta_r H^\circ = -140157.0 \text{ J mol}^{-1} = -140.2 \text{ kJ mol}^{-1}, \\ \Delta_r S^\circ = -389.5 \text{ J mol}^{-1} \text{ K}^{-1}. \end{cases}$$

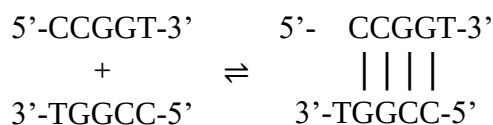
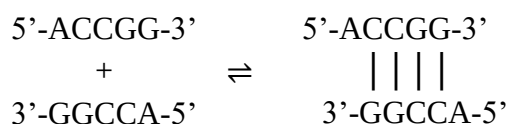
3. At T_m :

$$\begin{cases} [\text{ds-DNA}] = 2.5 \times 10^{-6} \text{ M} \\ [\text{ss-DNA}] = 5.0 \times 10^{-6} \text{ M} \end{cases} \rightarrow K(T_m) = \frac{2.5 \times 10^{-6}}{(5.0 \times 10^{-6})^2} = 1.0 \times 10^5$$

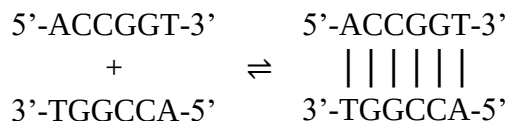
$$-140157.0 - T_m \times (-389.5) = -8.314 \times T_m \times \ln(1.0 \times 10^5)$$

$$T_m = 288.85 \text{ K} = 15.70^\circ \text{C}.$$

4. Dimerisation with pairing four pairs of complementary nucleotides:



Dimerisation with pairing six pairs of complementary nucleotides:



5. At T_m :

$$\begin{cases} [\text{ss} - \text{DNA}] = \frac{1}{2} [\text{ss} - \text{DNA}]_0 \\ [\text{ds} - \text{DNA}] = \frac{1}{4} [\text{ss} - \text{DNA}]_0 \end{cases} \rightarrow K(T_m) = \frac{\frac{1}{4} [\text{ss} - \text{DNA}]_0}{(\frac{1}{2} [\text{ss} - \text{DNA}]_0)^2} = \frac{1}{[\text{ss} - \text{DNA}]_0}$$

$$\Delta_r H^\circ - T_m \times \Delta_r S^\circ = -R \times T_m \times \ln \frac{1}{[\text{ss} - \text{DNA}]_0},$$

$$\frac{1}{T_m} - \frac{\Delta_r S^\circ}{\Delta_r H^\circ} = \frac{R}{\Delta_r H^\circ} \ln [\text{ss} - \text{DNA}]_0,$$

$$\frac{1}{T_m} = \frac{R}{\Delta_r H^\circ} \ln [\text{ss} - \text{DNA}]_0 + \frac{\Delta_r S^\circ}{\Delta_r H^\circ} \rightarrow k = \frac{R}{\Delta_r H^\circ}, b = \frac{\Delta_r S^\circ}{\Delta_r H^\circ}.$$

$$\Delta_r H^\circ(5'\text{-ACCGG-3'}) = 8.314 / (-5.15 \times 10^{-5}) = -161436.9 \text{ J mol}^{-1} = -161.4 \text{ kJ mol}^{-1}.$$

$$\Delta_r H^\circ(5'\text{-CCGGT-3'}) = 8.314 / (-4.80 \times 10^{-5}) = -173,208.3 \text{ J mol}^{-1} = -173.2 \text{ kJ mol}^{-1}.$$

$$6. E_{\text{A-CG}} = [-161436.9 - (-140157.0)] / 2 = -10639.9 \text{ J mol}^{-1} = -10.6 \text{ kJ mol}^{-1}.$$

$$E_{\text{T-GC}} = [-173208.3 - (-140157.0)] / 2 = -16525.6 \text{ J mol}^{-1} = -16.5 \text{ kJ mol}^{-1}.$$

$$\begin{aligned} 7. \Delta_r H^\circ(5'\text{-ACCGGT-3'}) &= \Delta_r H^\circ(5'\text{-CCGG-3'}) + 2E_{\text{A-CG}} + 2E_{\text{T-GC}} + 2E_{\text{A=T}} = \\ &= -140157.0 + 2 \times (-10639.9) + 2 \times (-16525.6) + 2 \times (-28842.0) = -252172.0 \text{ J mol}^{-1} = \\ &= -252.2 \text{ kJ mol}^{-1}. \end{aligned}$$

Problem 26. Sensing of acetaldehyde

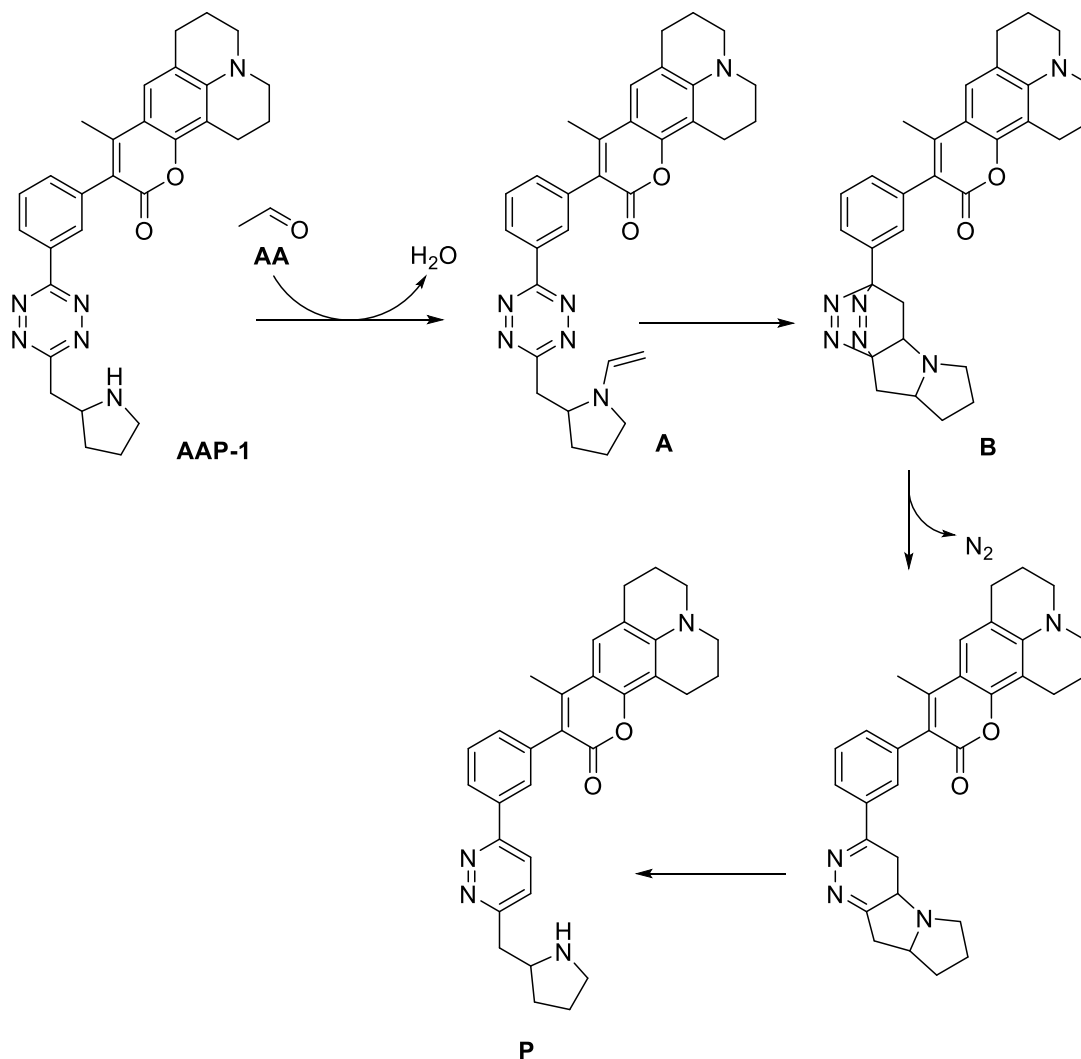
1.

$$M_{\text{AAP-1}} - M_{\text{P}} = 494 - 492 = M_{\text{AAP-1}} - (M_{\text{AAP-1}} + M_{\text{AA}} - M_{\text{H}_2\text{O}} - M_{\text{C}}) = M_{\text{C}} - 26$$

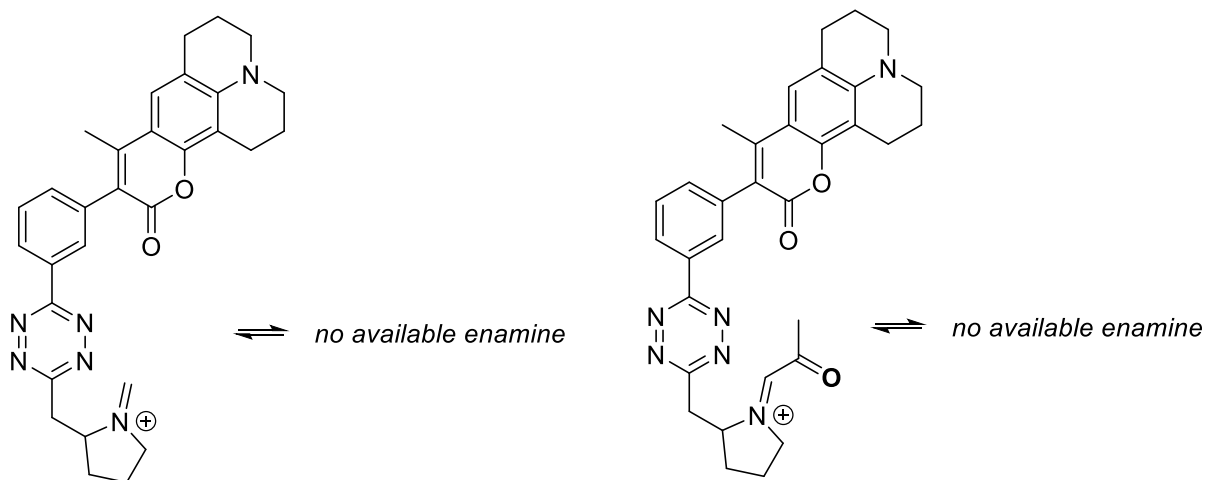
$$M_{\text{C}} = 28$$

Therefore this is nitrogen (N_2). This means that the tetrazine ring of **AAP-1** is involved in the reaction.

By analysing the mechanism, we can understand that **B** is a product of intramolecular [4+2] cycloaddition of **A**, and **P** is formed as a result of retro [4+2] cycloaddition followed by aromatisation. The intermediate product of the retro [4+2] cycloaddition of **B** does not count as **P** given that **P** contains the same number of rings as **AAP-1**. The complete deciphered mechanism looks like this:



2. In case of formaldehyde and methylglyoxal, iminium-enamine tautomerisation cannot occur:



In case of methylglyoxal, keton group will not be involved in the reaction due to less electrophilicity.

3. The Gibbs energy changes are as follows:

$$\Delta G (\mathbf{A} \rightarrow \mathbf{B}) = -21.74 - (-8.36) = -13.38 \text{ kJ}\cdot\text{mol}^{-1}.$$

$$\Delta G (\mathbf{A}' \rightarrow \mathbf{B}') = -19.23 - (-12.96) = -6.27 \text{ kJ}\cdot\text{mol}^{-1}.$$

Both processes are thermodynamically favorable.

4. By using an Arrhenius equation, we obtain the following ratio of rate constants:

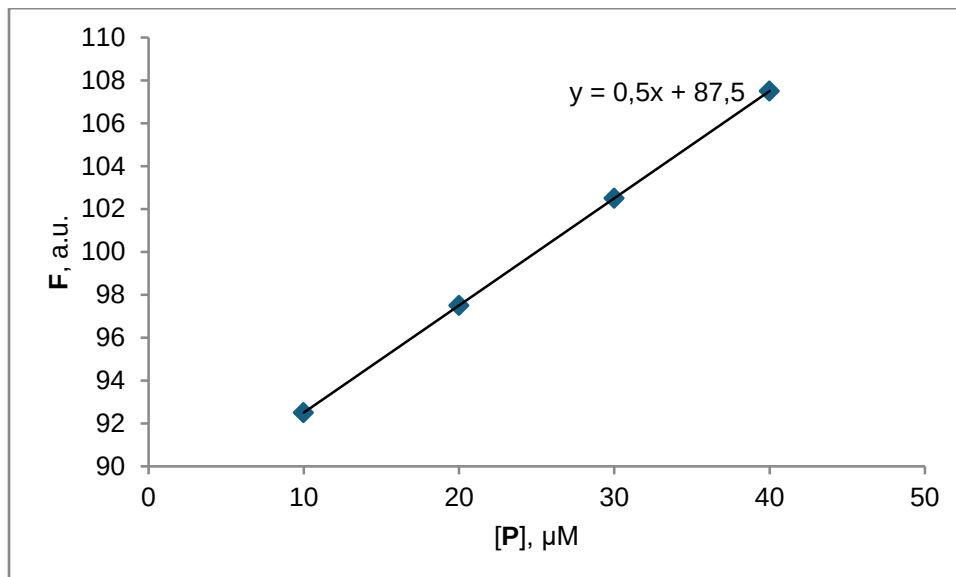
$$\frac{k_{\mathbf{A} \rightarrow \mathbf{B}}}{k_{\mathbf{A}' \rightarrow \mathbf{B}'}} = e^{\frac{(68.13 - (-12.96)) - (63.95 - (-8.36)) \cdot 10^3}{8.314 \cdot 310}} = 30$$

This means that hexanal, due to steric effects, will react very slowly with **AAP-1**.

5. Molecules of **P** must emit photons with lower energy than the photons they absorb during excitation. This means that wavelength of emitted photons must be higher than wavelength of absorbed photons. So, **X** – excitation, **Y** – emission.

6. From the data in the table in the condition, we construct the following graph and find the corresponding parameters of the linear function:

$$F = 87.5 + 0.5[P]$$



So, $F_0 = 87.50$ arb.u., $k = 0.5$ arb.u.·μM⁻¹.

7. Let's calculate the concentration of **AA** at the beginning and at the end of the enzymatic reaction:

$$[\text{AA}]_0 = \frac{137.50 - 87.50}{0.5} = 100.0 \text{ μM}; \quad [\text{AA}]_t = \frac{90.65 - 87.50}{0.5} = 6.3 \text{ μM}.$$

Due to $[S]_0 \gg K_M = 0.2 \text{ μM}$ during this enzymatic reaction, we simplify Michaelis-Menten kinetics as follows:

$$r = \frac{r_{\max}[S]_0}{K_M + [S]_0} \approx \frac{r_{\max}[S]_0}{[S]_0} = r_{\max} = 4.1 \text{ mM} \cdot \text{min}^{-1} = 6.83 \cdot 10^{-5} \text{ M} \cdot \text{s}^{-1}$$

$$t = \frac{(100.0 - 6.3) \cdot 10^{-6}}{6.83 \cdot 10^{-5}} = 1.37 \text{ s}$$

8. Co-treatment of the cell cultures with ethanol and Fomepizole, which inhibits ADH, markedly suppresses **AAP-1** activation, with fluorescence signals comparable to basal levels ($F_1 \approx F_3 < F_2$), because there is no conversion of ethanol to **AA**. Conversely, inhibition of ALDH with CVT-10216 in the presence of ethanol, which leads to the intracellular accumulation of **AA**, further enhances the fluorescence signal ($F_2 < F_4$). So, $F_1 \approx F_3 < F_2 < F_4$.

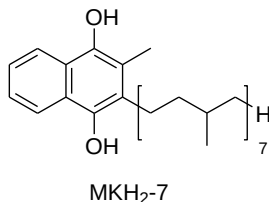
Problem 27. Archaeal metabolism

1. In the 3.5-4 billion years since the emergence of archaea, the Earth's appearance has changed dramatically. Moreover, a number of physical parameters, such as temperature, have fluctuated cyclically due to alternating glacial and interglacial periods. Radioactivity has gradually decreased over this time, as long-lived isotopes gradually decayed, reducing natural background radiation. According to the standard model of stellar evolution, the Sun's luminosity increases continuously throughout the main sequence.

The chemical composition of the environment has also undergone significant changes: initially, there was virtually no oxygen on Earth, the planet's early atmosphere was denser than it is today (and therefore had higher atmospheric pressure), the salt composition and pH of the water were largely determined by violent volcanic activity, etc. Thus, it is impossible to propose any chemical parameter that has been constant for as long as there is life on Earth.

In fact, the only physical parameter that has remained approximately constant throughout the entire era of life on Earth is gravitational force. Changes in gravity would only be possible as a result of catastrophic events, such as a collision between Earth and a large celestial body, ejecting a significant portion of the planet's mass into outer space, but archaea would not have survived such a catastrophe. It should be noted that studies in microgravity conditions have demonstrated the influence of gravity on the metabolic rate of archaea, including through changes in gene expression. Moreover, since gravitational forces have an indirect effect on archaea (changes in sedimentation, convection, and nutrient/waste distribution in aquatic environments), archaea can easily adapt to changes in these forces, unlike other factors: for example, a sharp increase in radiation is more likely to destroy the archaea population.

2. The two-electron reduction of menaquinone essentially corresponds to the conversion of the quinone to hydroquinone:



3. Menaquinone is found predominantly in anaerobic organisms (although it is not an obligate signature) because its low standard redox potential corresponds to the low standard potential terminal electron acceptors (*e.g.*, fumarate, $E^\circ = +0.03$ V) typical of anaerobic respiration. This ensures efficient electron transfer under energy-limited conditions. Ubiquinone is characteristic of aerobes (which include the vast majority of eukaryotes), in which oxygen ($E^\circ = +0.82$ V) serves as the terminal electron acceptor in the respiratory chain. Ubiquinone's higher potential allows for efficient electron transfer in the aerobic respiratory chain. Thus, menaquinone is suitable for the low-potential systems of anaerobes, while ubiquinone is suitable for the high-potential systems characteristic of aerobes.

4. The first thing to consider is a way of oxidation of ubiquinol (a hydroquinone derivative) with a bromine-containing reagent to ubiquinone. It should also be noted that the benzene ring in ubiquinol is completely devoid of hydrogen atoms, which prevents electrophilic substitution reactions. The reaction with Br_2 should be carried out strictly in the dark to avoid side processes, such as benzylic bromination.

Second, ubiquinol, which is predominantly found in the mitochondrial membrane of eukaryotes, is a mixture of several compounds differing in the number of isoprenyl groups (from 6 to 10). Note how carefully the formulae and names of the three coenzymes are reflected in the problem statement, with the number of C_5H_7 units always indicated as a subscript. Therefore, coenzyme Q_{10} , whose structure is given in the problem statement, is only one representative of the ubiquinol family. Therefore, the substance isolated from cell culture will behave experimentally as a mixture of compounds with varying numbers of unsaturated bonds.

5. Using mass balance for reaction equation (1), we write the mathematical equation:

$$M_r(\text{X}) = M_r(\text{X1}) + M_r(\text{X2}) - 2$$

Taking into account the inequality $M_r(\text{X}) < 250$, we obtain:

$$M_r(\text{X1}) + M_r(\text{X2}) < 252$$

Since the inequality $M_r(\text{X1}) > M_r(\text{X2})$ is valid, the upper estimate of $M_r(\text{X2})$ is $M_r(\text{X2}) \leq 125$, where $M_r(\text{X1}), M_r(\text{X2}) \in \mathbb{N}$.

6. In accordance with the answer to the previous question, the element **E2** in **X2** accounts for no more than 1.3 g/mol of the molar mass. Therefore, **E2** is hydrogen, and in the formula unit of both **X1** and **X2** it is represented by only one atom (since even in the limit, the inequality $250 \times 0.010 < 3$ is valid). Hence, **X** contains no hydrogen (0% by mass), since both hydrogens in the products of reaction (1) originate from ubiquinol.

7. Knowing the mass fraction of oxygen in **X**, we first find three possible values for the sum $M_r(\text{X1}) + M_r(\text{X2})$ with high precision: 70.35, 138.68, and 207.01. However, only for the third option is it possible to obtain the relative mass corresponding to two hydrogen atoms by multiplication. Based on the number of significant digits in the mass fraction of hydrogen, we note the closeness of the values of the terms in the expression $M_r(\text{X1}) + M_r(\text{X2})$. Accordingly, it is necessary to examine the sums $103 + 104$, $102 + 105$, $101 + 106$, etc., to determine whether the correctly rounded mass fraction of hydrogen for $M_r(\text{X1})$ exceeds the lower limit of the range, equal to 0.950%. In this case, $A_r(\text{H})$ should be taken as 1.008 in the calculations. At values of $M_r(\text{X1}) > 106$, the mass fraction of hydrogen becomes less than 0.95. Hence, the range of possible molar masses of **X1** is $\{104, 105, 106\}$, meaning for **X2** the range will be $\{101, 102, 103\}$.

8. The equality of the element mass fractions in two compounds despite the difference in their whole-number molecular masses can be explained in at least two ways.

First, the small number of significant digits in the element mass fractions.

Second, the composition of **X1** can be represented as multiple formulae (**X1**)₂ or (**X1**)₃. This is impossible due to the small mass fraction of **E2** and the small molar mass of **X** itself.

9. Let's try to determine element **E1**. Since **X1** and **X2** each contain one hydrogen atom, the atomic mass $A_r(\mathbf{E1})$ obeys the following equation: $A_r(\mathbf{E1}) \approx 22/n$, where n is the number of **E1** atoms in **X1** (or **X2**).

It is clear that **X** also contains approximately 22% of element **E1** (while not being oxygen, since 23.41% is too far from 22%). Then, by a quick search of four elements (Na, C, B, and Li), we find that **X** contains Na (**E2**) and O in a molar ratio of 2:3, respectively.

Let's rewrite reaction equation (1) taking into account the data obtained:



Note that the three oxygen atoms could be redistributed between **X1** and **X2** in only two ways: 3+0 or 2+1. Thus:



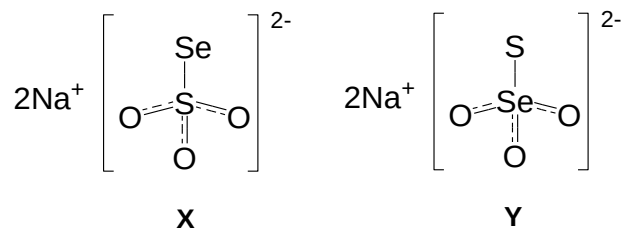
It's clear that we're dealing with neutral (reagents) and acidic salts (one subclass of chemical compounds) of oxygen-containing and (possibly) anoxic acids. For the NaH...O salt, we can't come up with an adequate solution, so reaction equation (4) is correct.

The molar mass of residue **X** (taking into account its constraint in the conditions) accounts for 111 g/mol. However, given the similarity of the molar masses of **X1** and **X2**, we can find the unknown elemental residue in the anoxic acid salt: $(111 - 48)/2 = 31.5$, which is close to the atomic mass of sulfur. Thus the sodium salt of the oxyacid contains selenium: the sum of 32 + 48 is, in turn, close to 79. From this, we can fully reconstruct the equation for reaction (1) involving sodium selenosulfate (**X**):



The molar masses of sodium hydrosulfite NaHSO₃ (**X1**) and sodium hydroselenide NaHS (**X2**), rounded to the nearest whole number, are close, amounting to 104 and 103 g/mol, respectively. This, given the low accuracy of the element mass fraction calculations, leads to the coincidence of the obtained values.

Now we can depict the structural formulae of both isomeric salts with tetrahedral anions of similar shape:



Based on the formula of **Y**, it is easy to determine the products of the reduction reaction: sodium hydroselenite NaHSeO₃ (**Y1**) and sodium hydrosulfide NaHS (**Y2**), simultaneously revealing reaction (2):



Note that all reactions must occur at a physiological pH close to 7.5, which clearly indicates the preferential formation of acidic salts of the corresponding acids.

10. Based on the condition, neither **X** nor **Y** are natural substrates for any enzymes. A group of compounds found in nature that are structurally similar to them is, of course, the thiosulfates (**Z**), for example, sodium thiosulfate Na₂S₂O₃. The active site of the enzyme thiosulfate reductase cannot fundamentally distinguish between metabolites that differ by the replacement of one sulfur atom with selenium, due to the similar geometric parameters of the anions. The sulfate ion also has a similar structure, but it exhibits chemical properties different from those of **X** and **Y**.

11. The known substrates **X**, **Y**, and **Z** must be modified in some way to satisfy the conditional criterion. The only possible option is to use isotopically labeled sodium salts to increase $M_r(\mathbf{X2})$ by one unit (NaH⁸⁰Se; ⁸⁰Se is the most common stable isotope of selenium; **W** is Na₂⁸⁰SeSO₃) or decrease $M_r(\mathbf{X1})$ by one unit (NaH³¹SO₃ or NaHS¹⁵OO₂; ³¹S and ¹⁵O are radioactive isotopes with short half-lives). The second option is obviously unsuitable, so the only other suitable candidate is a combined compound – Na₂⁸²Se³⁴SO₃ – where the ³⁴S isotope is stable, and the ⁸²Se isotope has a long half-life and extremely low radioactivity, which does not interfere with the biochemical experiment. The correct answer is: Na₂⁸⁰SeSO₃ and Na₂⁸²Se³⁴SO₃.

12. It is logical to assume that thiosulfate is integrated into the metabolism of sulfur-containing compounds in archaea. The interconversion of inorganic sulfur and nitrogen compounds is an example of energy metabolism, established at the initial stages of evolution, before the advent of photosynthesis and requiring no oxygen (the process of sulfate reduction with the simultaneous oxidation of organic compounds during anaerobic respiration). Therefore, these archaea, being anaerobes, inhabit bodies of water rich in sulfur compounds (*e.g.*, hydrothermal vents or hypersaline environments).

13. The first hint: indicate that all unknown products of the two reactions belong to the same subclass of chemical compounds (referring to acidic salts), preferably without directly naming the subclass itself in the problem.

The second clue is much more elegant: the structure of any of the six compounds with the letters **X** and **Y** contains at least two elements that are located in the same group of the Periodic Table.

Perhaps you could come up with other, equally creative clues.

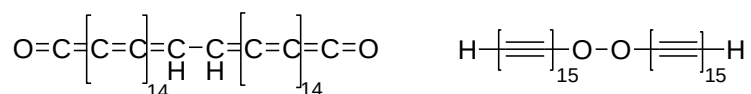
Problem 28. Non-Archea-typal form of life

1. Since cuts occur along the strands and not on the nodes, **A** can be represented as a dimer (**A'**)₂. In other words, the axis of symmetry in **A** passes through the middle of the central bond, not through any specific atom. This, in turn, means that the molecular formula of **A'** is C_{x/2}H_{y/2}O_{z/2}, and due to the integer nature of the indices, the values of *x*, *y*, and *z* must be divisible by two without a remainder.

Since each cut breaks exactly one bond, the total number of bonds in molecule **A** is equal to the total number of cuts (123). Note that carbon in organic compounds is tetravalent, while the valences of hydrogen and oxygen, in turn, are 1 and 2, respectively. Considering that two atoms are involved in the formation of each covalent bond, we can write the following equation:

$$4x + y + 2z = 246$$

To estimate the upper limit on the number of carbon atoms, we minimise the number of hydrogen and oxygen atoms to two each (remember the parity!), then *x* equals 60. Theoretically, symmetrical structures corresponding to the formula C₆₀H₂O₂ might be:



2. a) Let's try to prove the impossibility of such a molecule in general. It is clear that the number of multiple bonds in such molecule is odd (1, 3, 5, etc.). In fact, it does not matter how many of them are triple or double; the important thing is that they occur in pairs, and the only double bond without repetition is located in the centre of the molecule. Then we can re-write the expression as follows (*4k* is the number of hydrogens lost with the appearance of each pair of double bonds):

$$4x + 2x - 4k + 2z = 246, \text{ where } k \in \mathbb{Z}_{\geq 0}$$

Rearranging, we obtain:

$$3(x - 41) = 2k - z$$

According to the fundamental theorem of arithmetic, with the even number of oxygen atoms *z*, the left-hand side of the equation must be a multiple of two. However, for *x* : 2, both factors (3 and *x* - 41) are odd. Therefore, with an even number of carbon atoms, the equation has no integer solution.

This statement can be also proven by understanding that the removal of the two central bonds would lead to the identical fragments having 121 bonds in total, which is impossible due to the odd number.

b) In the case of a single central carbon-carbon triple bond, the equation transforms as follows:

$$4x + 2x + 2 - 4 + 2z = 246$$

and after rearrangement: $3x + z = 124$

For example, for $z = 4$, the value of x is even, and the formula is $C_{40}H_{78}O_4$.

At the crossroads of chemistry and math: In fact, the formulations in the problem are a veiled application of graph theory in chemistry. An alternative solution to the first two questions is as follows.

The molecule **A** is a connected graph $G = (V, E)$, where vertices are atoms and edges are covalent bonds. The graph has x vertices v_c , such that $\deg(v_c) = 4$, y vertices v_h $\deg(v_h) = 1$, and z vertices v_o $\deg(v_o) = 2$. E (the number of edges) is equal to 123 by assumption.

1a) An edge can be removed from graph G such that two identical connected graphs $G' = (V', E')$, remain. For G' , v'_c, v'_h, v'_o are called vertices that were inherited from v_c, v_h, v_o of graph G . x', y', z' are the numbers of vertices of the form v'_c, v'_h, v'_o , respectively.

$$2x' = x; 2y' = y; 2z' = z \text{ (by construction)} \Rightarrow x, y, z - \text{even}$$

1b) By the well-known handshaking lemma:

$$\sum \deg(v) = 2 \cdot E \Rightarrow 4x + 2z + y = 246.$$

Suppose the contrary. Let $x > 60$. Then, considering the parity, $x \geq 62$.

$$4x + 2z + y \geq 248 + 2z + y \geq 246$$

We arrive at a contradiction, since z and y are non-negative.

2a) We define the graph $G'' = (V'', E'')$ similarly to the graph G' , but obtained by deleting two edges. Then:

$$2 \cdot E'' = E + 2 \Rightarrow E'' = 60.5$$

E'' is a natural number. We arrive at a contradiction. Accordingly, this is impossible.

3. The odd molecular mass of a compound composed of carbon, oxygen, and hydrogen can be explained only in one way: the calculations used precise atomic masses of the elements, which have a small deviation from the whole number (0.01 for carbon and 0.008 for hydrogen). With a total number of these atoms close to 100, a surplus of one unit is added to the molecular mass of **A**, which is cleared of tenths and hundredths when rounding. Taking this into account, we can write a system of equations:

$$\begin{cases} 4x + y + 2z = 246 \\ 12x + y + 16z = 594 \end{cases}$$

Removing z , we obtain:

$$y = \frac{1374 - 20x}{7}$$

Chemical considerations (remember the alkanes!) yield the inequality:

$$y \leq 2x + 2$$

Substituting one into the other, we obtain $x \geq 40$.

Now we express x in terms of z from the system of equations:

$$x = \frac{348 - 14z}{8}$$

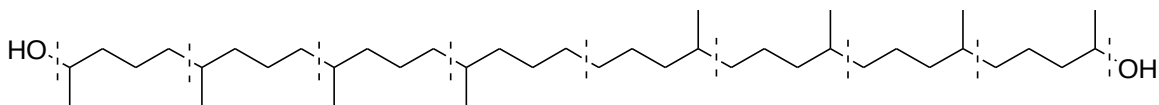
Substituting this into the inequality we just obtained, we find that $z \leq 2$. But, as we discovered earlier, z is an even natural number, so $z = 2$ is certain.

Now it is easy to find the values of x (40) and y (82), as well as the molecular formula of **A** as $C_{40}H_{82}O_2$.

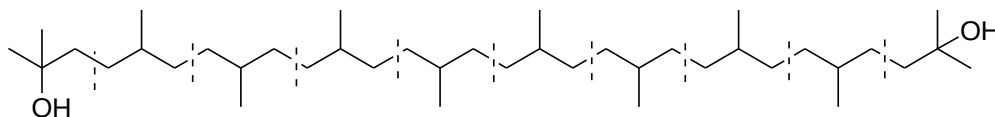
4. Note that each of the terminal d fragments must contain one hydroxyl group, since the number of d fragments coincides with that of oxygen atoms in **A**. Incidentally, the possibility that **A** is an ether is discriminated by the wording of the question and the small number of oxygen atoms in the molecule.

Since molecule **A** contains 8 stereocentres, there are 4 branching points of the hydrocarbon chain on each side of the symmetry axis, one for each c fragment.

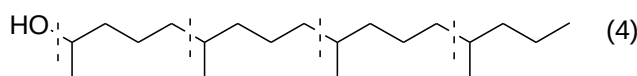
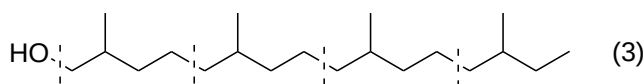
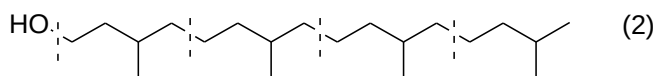
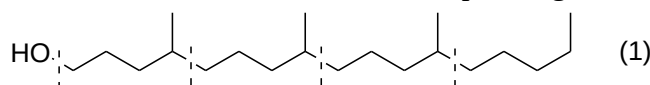
The hydroxyl group can be secondary only if the d fragment is represented by a hydroxyl group, and the stereocentre of the adjacent c fragment is represented by a carbon atom directly bonded to the hydroxy group (the C–O bond is cut):



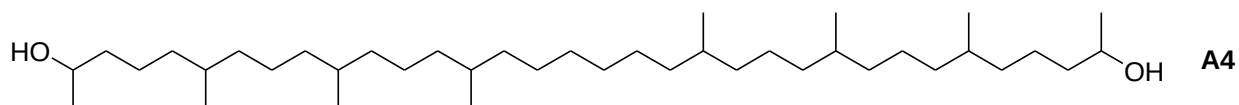
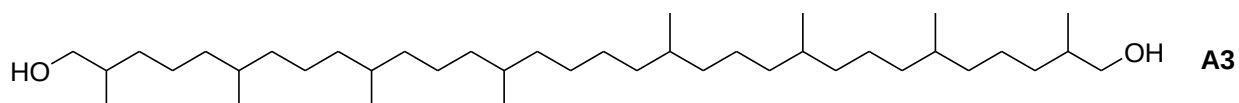
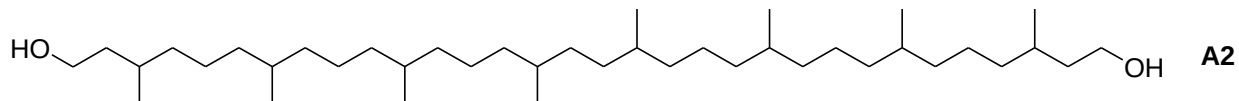
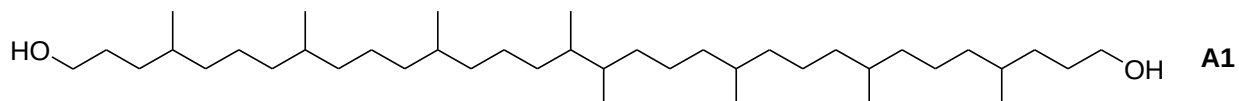
There are many more variants with a tertiary hydroxyl group, for example, one shown below (with two methyl groups bonded to the carbon atom to avoid the formation of an additional stereocentre):



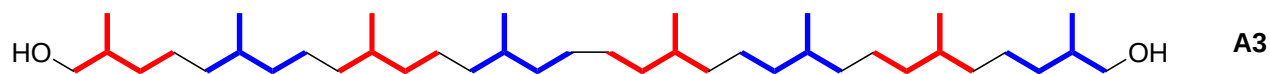
5. Since two symmetrical half-molecules with 20 carbon atoms each can be found in **A**, each *c* fragment have at least 5 carbon atoms (three C-C bonds formed by four atoms plus a methyl group as a branch), and *d* is a hydroxy group (a complete fragment consisting of two linked nodes). Clearly, the length of **A** is not sufficient to obtain eight *c* fragments containing six or more carbon atoms. 4 possible half-chains of **A** with corresponding cuts are:



All of these satisfy the condition. Therefore, 4 structures are possible for **A** (**A1-A4**) are:



6. Structures based on isoprenyl units (shown in colours) are extremely common in nature, so two intermediate variants remain for consideration. Note that structures **A2** and **A3** differ in the type of attachment of the two symmetrical fragments being head-to-head in the former case, and tail-to-tail in the latter case:



7. Note that the two **A** molecules contain four hydroxyl groups, and four water molecules reacted. Therefore, due to symmetry, **C** must contain at least two identical oxygen-containing functional groups, and **B** is a single large macrocycle, regardless the order in which the **A** and **C** residues are joined:



In any case, **B** will contain not more than $2k$ hydrogen atoms.

8. Since the hydrolysis reaction of **B** is not a redox reaction, we can apply the assumption that the total number of bonds in the reactants is equal to the total number of bonds in the products. It is easy to see that in this case, the number of bonds in **B** is an even natural number (262 or 264), since all the remaining substances in the reaction equation have even coefficients. It is also important to understand that the elemental composition of **C** is similar to that of **B**.

Let's consider both options (x_1 , y_1 , and z_1 are the numbers of carbon, hydrogen, and oxygen atoms, respectively).

First:

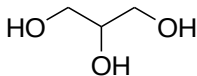
$$264 + 4 * 2 = 2 * 123 + 2x, \text{ where } x \text{ is the number of bonds in C}$$

Hence, $x = 13$. Then, the following equation is valid:

$$4x_1 + y_1 + 2z_1 = 26, \text{ where } z_1 \geq 2$$

The presence of an axis of symmetry implies that the number of carbon atoms is odd, while chemical considerations imply the inequality: $1 < x_1 < 7$. Then $x_1 \in \{3, 5\}$.

If **C** is a dicarboxylic acid (**B**, in turn, is a diester), then $C_3H_6O_4$ is the only formula for it, which is impossible. If **C** contains hydroxyl groups (**B** is an ether), then for C_5 molecular formulae, the hydroxyl groups must be located at unsaturated bonds, so $C_3H_8O_3$ is the only formula left for consideration. It corresponds to glycerol.

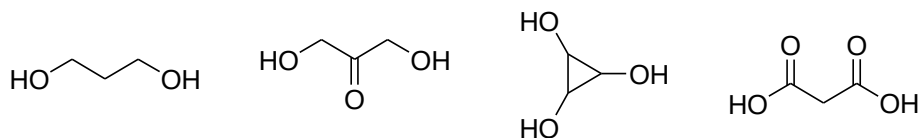


Second:

$$262 + 4 * 2 = 2 * 123 + 2x, \text{ where } x \text{ is the number of bonds in C}$$

$$4x_1 + y_1 + 2z_1 = 24, \text{ where } z_1 \geq 2$$

It is clear that $x_1 = 3$, so three options are possible: $C_3H_8O_2$, $C_3H_6O_3$ and $C_3H_4O_4$. One structure can be proposed for each of the molecular formulae $C_3H_8O_2$ and $C_3H_4O_4$, while two structures can be proposed for $C_3H_6O_3$:

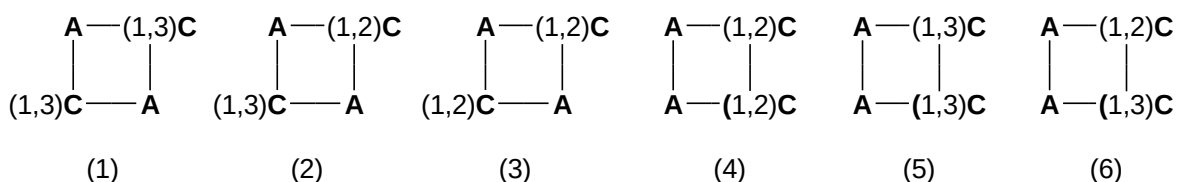


However, cyclopropane-1,2,3-triol is an extremely unstable compound. It should also be noted that the cyclic dimer of dihydroxyacetone does not correspond to the material balance of the equation of the hydrolysis of **B**.

All other symmetrical substances (glycerol, 1,3-propanediol, dihydroxyacetone, and malonic acid) are widely found in nature.

9. The presence of three hydroxy groups in glycerol greatly increases the range of possible variants of **B**, while for each of the rest three molecules the number of isomers equals 2, according to the schematic diagram in q7.

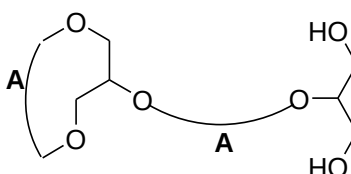
The six structural isomers of **B**, as a combination of glycerol and diphytanyl diol, can be represented schematically:



Each of the variants **B1**, **B2**, and **B5** corresponds to one isomer. The remaining three will yield a greater number of isomers due to the order of formation of ester bonds by the hydroxy groups of glycerol (the numbers indicate their positions):

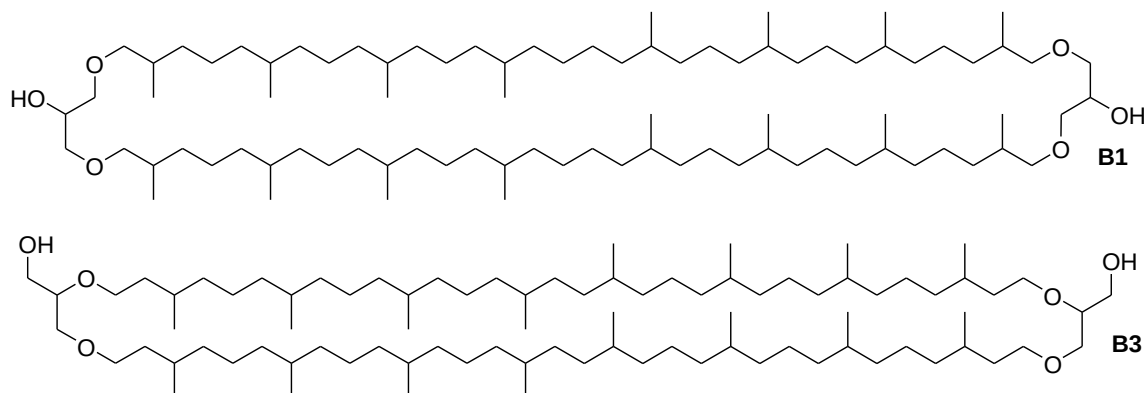
Option	Order of formation of ether bonds by glycerol residues
B3	-A-1-2-A-1-2-; -A-1-2-A-2-1-
B4	-A-1-2-2-1-A-; -A-2-1-1-2-A-; -A-2-1-2-1-A-
B6	-A-1-2-1-3-A-; -A-2-1-1-3-A-

The indication of identical molecular formulae for the glycerol residues excludes the following variants from consideration:



Thus, the total number of isomers satisfying the condition for each type of **A** is 10, and the total number of isomers is 20.

The structural formulae of **B1** based on **A3** and **B3** based on **A2** are given below as examples:

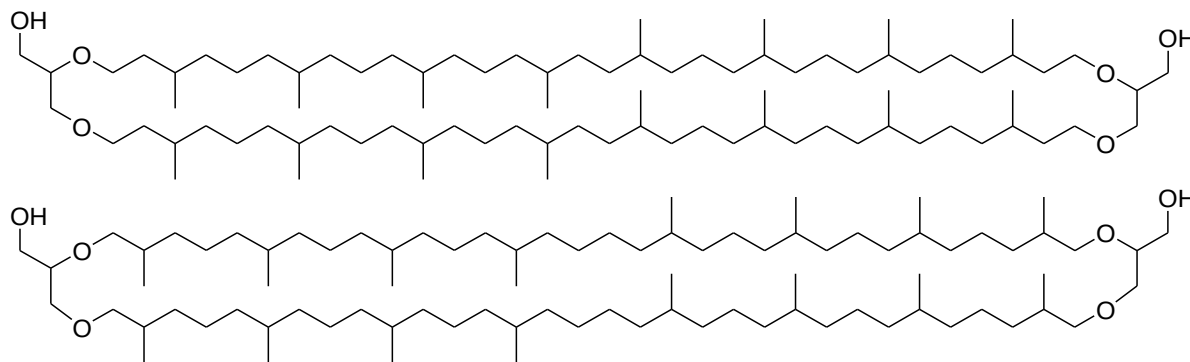


10. The properties of **B** described in the condition correspond to ethers, the hydrolysis of which requires fairly harsh conditions or long time if the conditions are close to standard ones. Enzymes that hydrolyse ester bonds (esterases) are widespread in nature, whereas enzymes that accelerate the hydrolysis of ethers are absent, which is an evolutionary advantage for archaea in competition with bacteria. Furthermore, archaea often live at temperatures that are extremely high for life, which also explains why ethers have an evolutionary advantage over complex membranes that are in direct contact with the aggressive (temperature, pH) aqueous environment of a hydrothermal vent.

11. We will continue to consider derivatives of isomers **B1**, **B2**, and **B3**, as the other ten will behave like classic phospholipids with a hydrophilic head and a lipophilic tail. The presence of two hydrophilic ends, which can be exposed on opposite sides of the membrane (*O*-conformation) or on the same side (*U*-conformation) is a distinctive feature of phospholipids based on dialkylglycerol tetraethers. The monolipid layer that forms the membrane of some archaea has lower fluidity than its bilayer counterpart, which is another factor in archaea's resistance to high ambient temperatures.

12. Polyhydric alcohols with a molecular weight lower than glycerol are either the simplest diol, ethylene glycol, or isomeric propanediols. When creating a phospholipid based on these compounds, one hydroxyl group will participate in the formation of an ester bond with a fatty acid (the lipophilic tail), while the second hydroxyl will be converted to a hydrophilic head after esterification. However, the presence of only one fatty acid residue (the tail) per lipid molecule geometrically leads to the formation of micelles rather than the required liposome bilayer (**the first reason**). Glycerol derivatives (in particular, glycerol-3-phosphate) are integrated into key metabolic pathways (for example, glycolysis), while ethylene glycol and propanediol derivatives are not actually used for living purposes (**the second reason**). Of course, since we are not privy to the evolution's plans, other answers to this question are possible.

13. Continuing our considerations of the correct arrangement of lipids in the archaeal membrane, we can see that the 1,3-arrangement of diphytanyl diol residues would be unfavourable in terms of the dense packing of isoprenyl units into the hydrophobic layer (carefully examine the width of the structures obtained in q9). Therefore, the structure (A-(1,2)C)₂ remains under consideration, which corresponds to two isomers due to the variability of the structure of **A**:



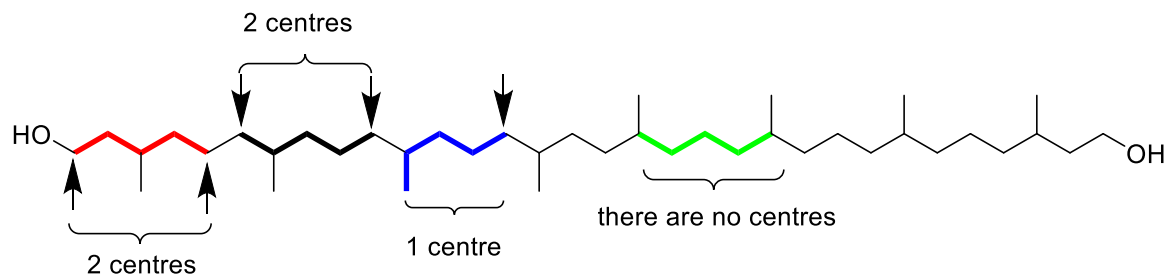
14. Note that any position of the residue **A** in molecule **B** occurs four times due to the symmetry and duplication of **A**. Thus, two enzymes specific to two different positions should form, in the limit, eight rings (in the limit, since **D1** withstands high temperatures best of all in the family). Therefore, the molecular formula of **D1** is calculated as $C_{86}H_{172}O_6 - 8H_2 = C_{86}H_{156}O_6$.

For future reference, we note that theoretically even more rings can be accommodated in molecule **B** (based on the premise of the third and fourth enzymes).

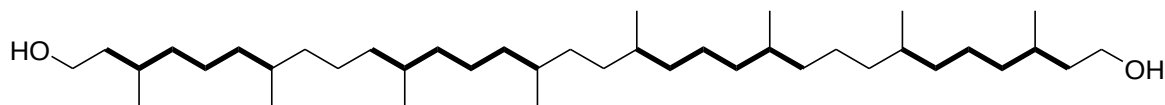
15. **B** contains 18 stereocentres. Thus, with the formation of eight rings in the **D1** molecule, additional eight stereocentres are formed. In other words, the formation of each ring adds one stereocentre; other variants (e.g., 0+2+0+2+0+2+0+2) can be excluded based on the similarity of the enzymes and the loci they act on. This consideration greatly limits the possibilities for hydrocarbon ring formation from parent isoprenyl units.

Let's consider variants with cyclopentane and cyclohexane fragments separately.

In the case of the formation of cyclopentane residues, 4 possible arrangements of the five carbon atoms relative to the isoprenyl chain are possible. Two of these result in two stereocentres per ring, one variant results in no increase in the number of stereocentres, and only one satisfies the condition:



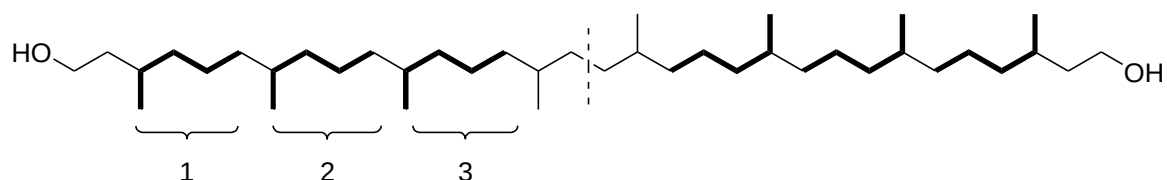
For cyclohexane, several possible arrangements of the six carbon atoms relative to the isoprenyl residues can be proposed, and only one satisfies the "one ring – one stereocentre" condition. However, it is not possible to place more than four such rings in a single **A** molecule:



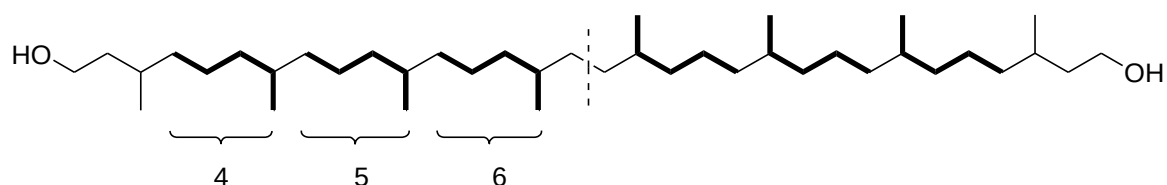
However, cyclohexane rings are found in some archaeal lipids, such as Crenarchaeola.

It should be noted that using **A3** instead of **A2** does not fundamentally change the picture.

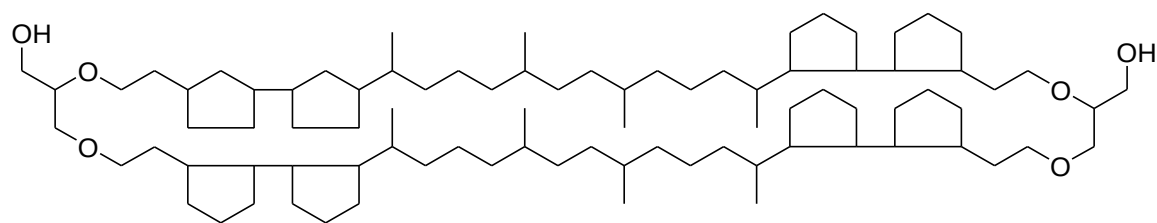
If the rings are formed in a left-to-right direction, the prototype of the future tetracyclopentane derivative looks as follows:



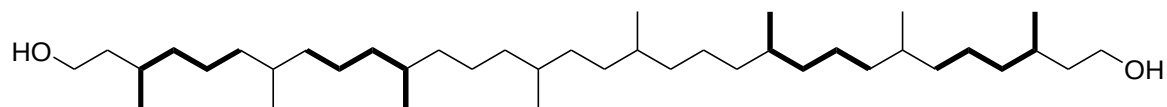
However, nothing prohibits the reverse direction of ring formation; the only difference is that position 1 is lost, but an additional position appears in the center of **A**:



It is clear that for each direction, three binary combinations are possible: 1+2, 1+3, 2+3, and 4+5, 4+6, 5+6. Then, the two different diols in **D1** correspond to 12 isomers. The structure of one that actually occurs in nature is shown below:



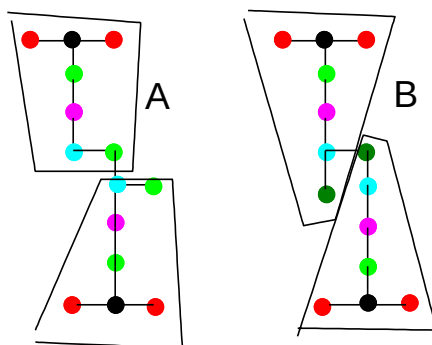
Structures that are opposite in the direction of ring formation (an example is given below) should be excluded from consideration given the extreme similarity of the functions of the two enzymes that cyclise the molecule. However, considering these **D1** isomers would not be a significant error.



This problem examines members of the glycerol dialkyl glycerol tetraester (GDGT) family, a class of membrane lipids.

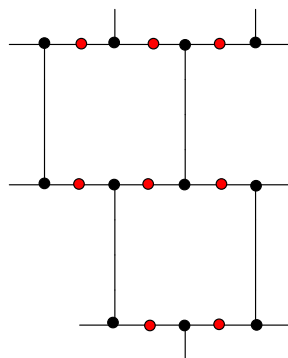
Problem 29. Archaea-ology

1. The formulae for sequences **A** and **B** can be represented as follows: $(X_1)_4(X_2)_2(X_3)_4(X_4)_2(X_5)_2$ and $(X_1)_4(X_4)_2(X_5)_2(X_6)_2(X_7)_2(X_8)_2$. It is clear that each monomer is present in the biopolymer fragments an even number of times (any index can be represented as $2n$), so the contribution of each to the total molecular mass is also an even number. Moreover, the difference between two even numbers is always an even number.
2. To construct the secondary structure of polymers, it is first necessary to correctly schematically depict the I-shaped structure:



The figure shows that the four terminal atoms for each structure are represented by the same monomer (red, X_1); matches in other colours in **A** and **B** are random.

Each I-shaped sequence can be divided into two oppositely oriented T-fragments (as shown above inside the frames). Then, it is necessary to replicate the I-shaped fragments to construct a two-dimensional network. The only feasible way is to match (partially superimpose) the upper and lower crossbars of the “letters I” with the corresponding crossbars of the neighboring ones. Only alteration of X_1 and X_6 in the polymer backbone can provide the ratio of the monomers in **B** close to equimolar. So, the biopolymers **A** and **B** are the networks built of chains of red (X_1) and black (X_2 , X_6) monomers linked by palindromic bridges, according to the following diagram:



In other words, to form a uniform two-dimensional network, adjacent I-shaped fragments must face opposite directions.

3. a) Let's note several key features of the sequences presented in the problem statement:

- there are branching points (X_2 , X_5 , and X_6) present, where a monomer forms covalent bonds with three other ones;
- the sequence composition is quite diverse (8 monomer types at 28 positions), with the primary structure at several positions coinciding between **A** and **B**;
- there is an indication of the key importance of short oligomeric fragments, which apparently repeat multiple times, forming a fairly large polymer (note the estimation of the molecular weights).

Most of the criteria are met by non-ribosomal peptides (without the participation of ribosomes, as the translation process implies the formation of a linear polymer) or proteins subjected to post-translational modification. Polysaccharides do not typically exhibit a wide variety of monomer units, although the structure of monosaccharides implies ample branch points. Therefore, the condition does not exclude heteropolysaccharides.

b) Since the number of monomers is greater than that of molecular formulae describing them, some monomers in fragments **A** and **B** are isomers of each other. This can occur for amino acids (recall the leucine-isoleucine pair) and, to an even greater extent, for monosaccharides (for example, the isomerism of aldohexoses).

c) Some amino acids may be present in proteins in a phosphorylated form (such as phosphoserine), which is quite common in both proteins and glycoproteins. Thus, this option is possible.

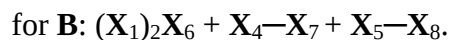
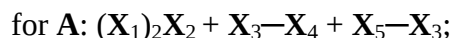
d) Aldohexoses and ketohexoses, which can be present in the long main chains of **A** and **B** can be considered as an example of interclass isomerism of monomers forming biopolymers.

e) Since the biopolymers can contain peptide fragments, theoretically, four homologous amino acids (glycine, alanine, valine, and leucine) can be present in the sequences.

Thus, theoretically, none of the five options can be excluded from consideration.

4. Based on the structures of polymers **A** and **B**, we can assume that these are heteropolymers containing heteropolysaccharides (alternation of two monosaccharide residues within long chains) and short peptides linkers. Such structural format is impossible for any other biological homopolymers: even fibrillar proteins with a poor amino acid composition form their 3D structures mostly through regular system of non-covalent bonds rather than regular bridges between chains.

5. The partitioning according to the criterion of fragment pairing is as follows:



The trisaccharide fragments $(\text{X}_1)_2\text{X}_2$ and $(\text{X}_1)_2\text{X}_6$ have the molecular masses of 642 and 700, respectively ($M_r(\text{X}_6) > M_r(\text{X}_2)$). X_1 is not an isomer of either X_2 or X_6 , since monomers with identical molecular masses do not form covalent bonds with each other. So, $M_r(\text{X}_1) \neq M_r(\text{X}_2) \neq M_r(\text{X}_6)$.

Note that three molecular masses correspond to four dipeptide fragments. This means that two dipeptides have the same molecular mass, and they are isomers (if not, four molecular masses would be needed in the case of two similar peptides). Thus, there are four dipeptides built of five amino acids. Moreover, the set includes two pairs or trios of structural isomers (interclass isomerism between monosaccharides and amino acids is impossible!). Given that no dipeptide contains amino acid residues that are isomeric to each other, a system of three equations can be proposed:

$$\begin{cases} M(\text{AA1}) + M(\text{AA2}) = 235 \\ M(\text{AA1}) + M(\text{AA3}) = 236 \\ M(\text{AA2}) + M(\text{AA3}) = 293 \end{cases}$$

The solution leads to the molecular masses of the amino acids of 89, 146, and 147 g/mol.

The molecular mass of 89 g/mol can only correspond to alanine, which naturally occurs in two stereoisomers (D and L) as well as in a structural isomer, β -alanine. Alanine cannot be found at branch points; these positions can be occupied by amino acids with an additional carboxyl group or amino group residues: $M(\text{lysine}) = 146$ g/mol and $M(\text{glutamic acid}) = 147$ g/mol. For these amino acids, possible presence of their stereoisomers in **A** and **B** can also be assumed. Thus, we cannot identify at least some of the monomers at this stage, since there may be both lysine and glutamate at the branching points.

6. Options a) and b) may be correct, since four elements (C, H, N, and O) can easily be combined into various combinations with matching molecular masses (for example, CH_4 and O. As to option c), evolution has no design, purpose, or predetermined plan from the scientific biological perspective.

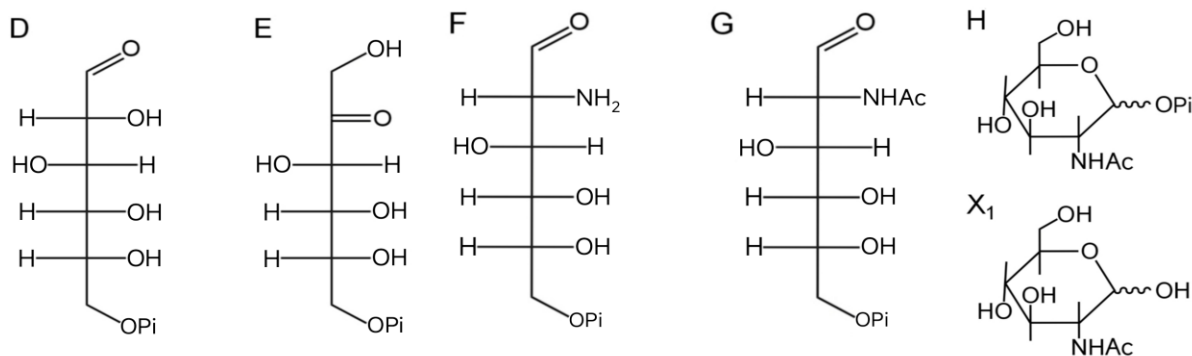
7. Since each sequence is split into three pairs of fragments, the sum of the molecular masses of the three different fragments can be found as $2270/2 = 1135$ g/mol. Note that the identical masses of the sums of the fragments can only be explained by the presence of the Glu+Lys pair in **A**. This leaves 860 g/mol of molecular mass for the two remaining pairs, which can be represented as the sum of 218 (Ala+Glu) and 642 $[(\text{X}_1)_2\text{X}_2]$.

Amino acid **X**₃, repeated four times in **A**, is glutamic acid. **X**₃ is not present at branch points, meaning **X**₅ is lysine. The remaining amino acid, **X**₄, is alanine.

Similar calculations can be performed for the fragment **B** with the composition of Ala + Glu, Ala + Lys + (**X**₁)₂**X**₆. Based on the positions of **X**₄ and **X**₅, we can determine that **X**₈ is alanine, and **X**₇ is glutamic acid. We were only able to determine the molecular formulae of the amino acid monomers; choosing between D- and L-alanine (β-alanine), D- and L-glutamic acids (as well as the variant of L-isoglutamic acid) is not possible.

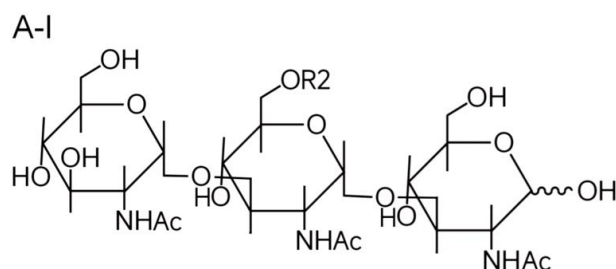
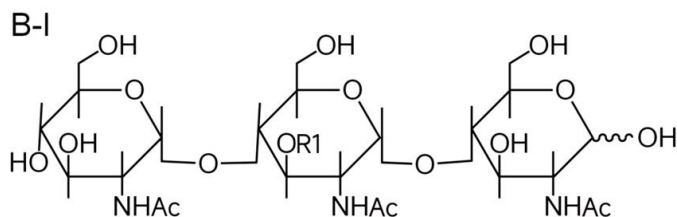
X ₃	X ₄	X ₅	X ₇	X ₈
C ₅ H ₉ NO ₄ (Glu)	C ₃ H ₇ NO ₂ (Ala)	C ₆ H ₁₄ N ₂ O ₂ (Lys)	C ₅ H ₉ NO ₄ (Glu)	C ₃ H ₇ NO ₂ (Ala)

8. Since **X**₁ does not contain phosphorus, there must definitely be one phosphoric acid residue in **D** in order to maintain the balance of phosphate groups. The number of carbon atoms changes only at the stage **F**→**G** (acetyl group transfer), thus **D** contains six carbon atoms. Taking into account the reference to photosynthesis, **D** and **E** are glucose-6-phosphate and fructose-6-phosphate, only their correlation with a specific letter is required. We can conclude that the transferase transfers an amino group (the molecular masses of glutamine and glutamate differ by 1), while **F** must have a free aldehyde group in order to react with the Tollens reagent:

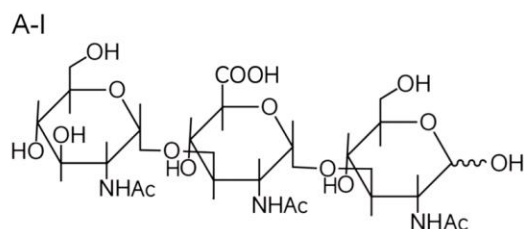
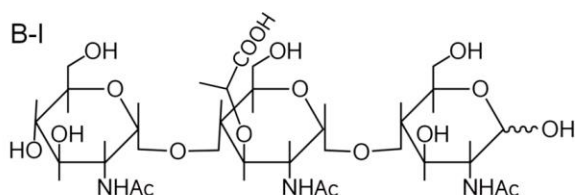


Note that the molecular weights also differ by one in the **D-F** and **E-F** pairs.

9. It is possible to determine which hydroxy groups are free, as well as the order of the monosaccharide residues as they are connected to each other. It is impossible to determine the stereochemistry of glycoside bonds (α or β):

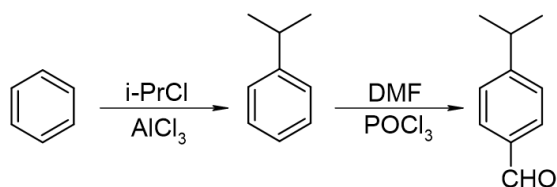


10. Since X_2 and X_6 bind to the peptides, they most likely contain a carboxyl or amino group in the non-methylated fragments. Using the molecular mass of the trisaccharide fragment for **A** (642 g/mol after rounding!), we obtain that the carboxyl group occupies the sixth position in X_2 . Acetaldehyde (CH_3CHO) is formed from the fragment $-\text{CH}(\text{OH})-\text{CH}_3$ upon oxidation with HIO_4 . Such a fragment is present only in lactate ($-\text{O}-\text{C}(\text{O})-\text{CH}(\text{OH})-\text{CH}_3$):

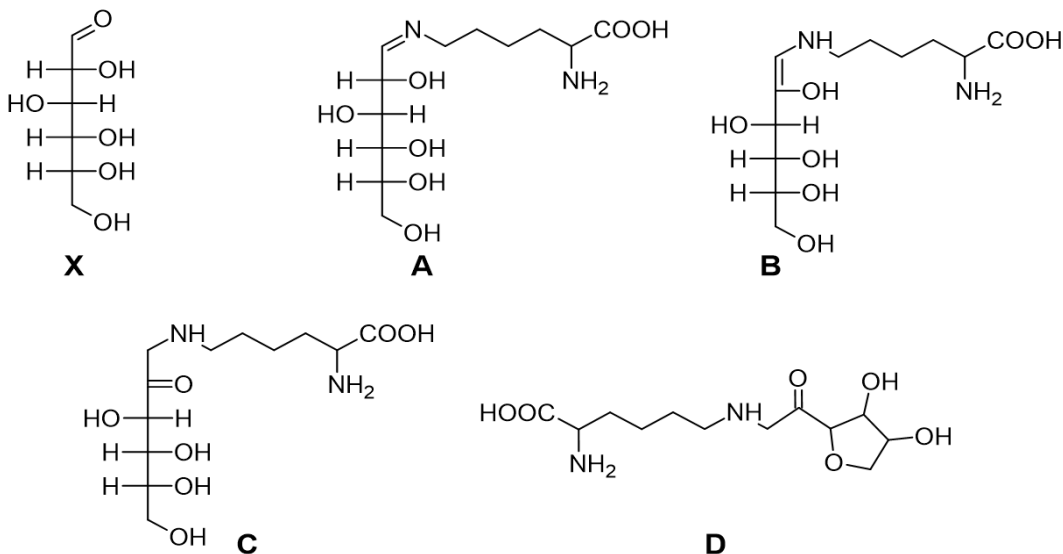


Problem 30. Pilaf ingredients

1.



2.



3. a) Note that the total number of atoms in the $\mathbf{F}_2$ molecule can be represented as 2ε . However, from the condition that $N = 2k$, where $k \in \mathbb{N}$, we can write the following expression:

$$\alpha + \beta + \gamma + 2\varepsilon = 2k$$

From this equation, it follows that the sum of the atoms in compound $\mathbf{F}_1$ is an even number.

From the valences of the elements that form $\mathbf{F}_1$ and $\mathbf{F}_2$, it follows that the coefficients β and ε , corresponding to the hydrogen atoms, are always even.

Let's look at the arithmetic progression formed by α , β , and γ (the order of the terms is naturally unknown). Since the sum of these coefficients, as we just found out, is an even number, two options are possible:

- a) α and γ are both odd numbers;
- b) α and γ are both even numbers.

If option a) is correct, then there must exist a geometric progression containing two odd numbers and one even number. However, this is impossible, since there are geometric progressions constructed entirely from odd numbers, and geometric progressions constructed from one odd number and the rest even.

Therefore, α and γ are both even numbers. The parity of the sum of the atoms in the compound $\mathbf{F}_2$ (2ε) leads to the conclusion that the last unrecognized coefficient ε is also an even number. Therefore this proves the statement completely.

b) Note that oxidative ozonolysis of the acyclic compound $\mathbf{F}$ yielded only two products in an equimolar ratio. This means that $\mathbf{F}$ contains one unsaturated bond, which, depending on its structure, can cleave to form either a ketone or a carboxylic acid.

However, the keto group contains an odd number of oxygen atoms (one), which contradicts the conclusions made previously regarding the coefficients α and γ . Therefore, ozonolysis can only form carboxylic acids. It should also be remembered that hydrolysis of the amide bond in $\mathbf{F}$ releases a carboxyl group, which is inherited by one of the ozonolysis products (there are no other oxygen-containing groups).

The simplest geometric progression consists entirely of even numbers: 2, 4, and 8. The next progression is 2, 6, and 18. However, for this progression, the sum of the coefficients in $\mathbf{F}_1$ will be 26, and the set of coefficients for $\mathbf{F}_2$ will yield a minimum sum of $4 + 6 + 10 = 20$, which together equals 46, exceeding the limit set by the condition.

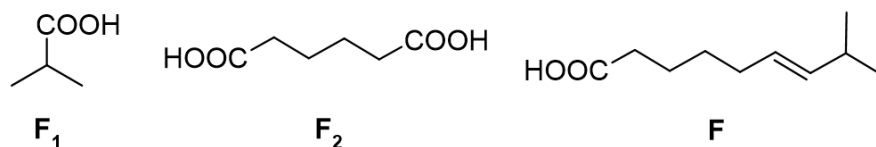
It remains to relate the coefficients α , β , and γ to the values 2, 4, and 8. Note that ozonolysis breaks all unsaturated bonds, and $\mathbf{F}_1$ (the derivative of $\mathbf{F}$) contains no rings. Therefore, only one chemical combination is possible: the formula for compound $\mathbf{F}_1$ is $\text{C}_4\text{H}_8\text{O}_2$.

Compound $\mathbf{F}_2$ contains four oxygen atoms. Similar to $\mathbf{F}_1$, we calculate the number of carbon atoms in it (δ):

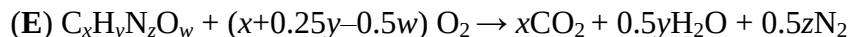
$$2\delta - 2 = \delta + 4$$

Solving, we find that $\delta = 6$. Thus the molecular formula of $\mathbf{F}_2$ is $\text{C}_6\text{H}_{10}\text{O}_4$.

4. The only possible structures for $\mathbf{F}_1$ and $\mathbf{F}_2$ given the information in the question is as follows:



5. According to the general combustion equation for $\mathbf{E}$:



we find that the rounded molecular weight of $\mathbf{E}$ can be expressed in terms of the number of nitrogen atoms it contains:

$$n(\text{N}_2) = \frac{0.0915}{28.02} = 3.267 \times 10^{-3} \text{ mol}$$

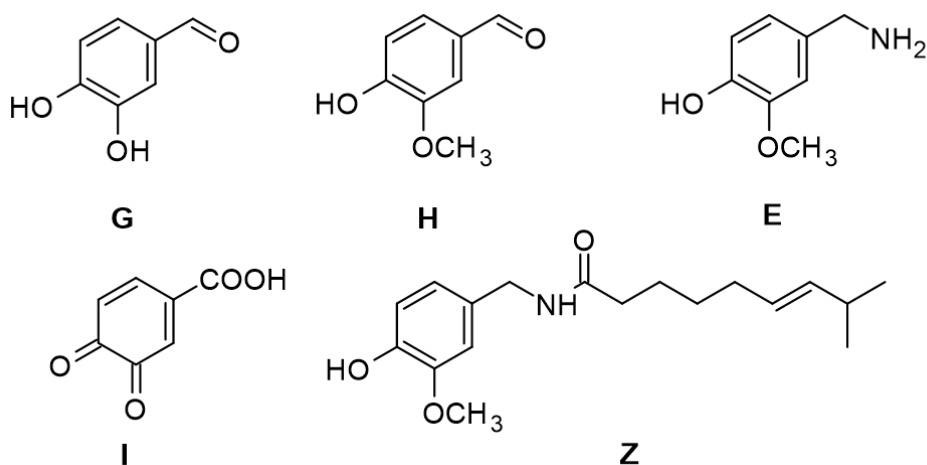
$$M(\mathbf{E}) = \frac{1 \times 0.5z}{3.267 \times 10^{-3}} = 153z$$

Note this means that the dependence of the molecular weight per oxygen on the number of nitrogen atoms is as follows:

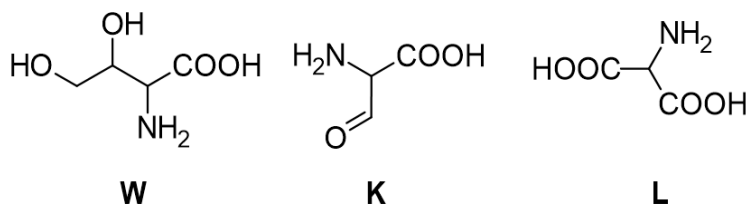
$$M(\mathbf{O}) = 153z \cdot 0.2092 = 32z$$

This means that the empirical formula **E** contains nitrogen and oxygen in a molar ratio of 1:2 and looks like NO₂. Carbon and hydrogen then account for the remainder of the molecular weight, which is equal to 107. This can only correspond to the C₈H₁₁ group (9 carbon atoms weigh 108, and for seven carbon atoms we get chemical nonsense in the form of C₇H₂₃). Hence, the empirical formula of **E** is C₈H₁₁NO₂.

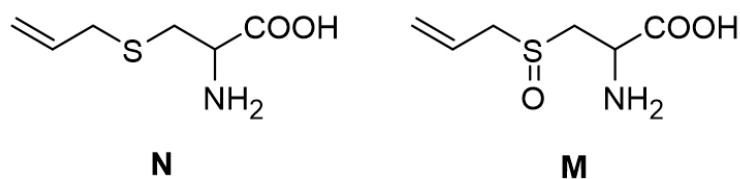
6.



7.



8.



9. General formula for arithmetic progressions:

$$a_n = a_1 + d(n - 1)$$

where d is common difference

Formula for given progression with molar masses:

$$M_n = M_1 + d(n - 1)$$

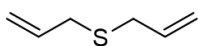
$$\begin{cases} M_2 = M_1 + d = 146 \text{ g mol}^{-1} \\ M_3 = M_1 + 2d = 178 \text{ g mol}^{-1} \end{cases}$$

Hence, $d = 32$

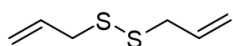
$$M_1 = M_1 + 32(1 - 1) = 114 \text{ g mol}^{-1}$$

$$M_4 = M_1 + 32(4 - 1) = 210 \text{ g mol}^{-1}$$

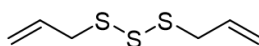
If P_1 is synthesised from alliin, then it should contain a sulfur atom and an allyl substituent. If we check it with molar mass, $114 - 32 - 41 = 41$, it indicates that there are two allyl groups attached to the sulfur atom. So, with respect to planes of symmetry, we can propose the following structures:



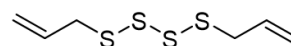
P₁



P₂

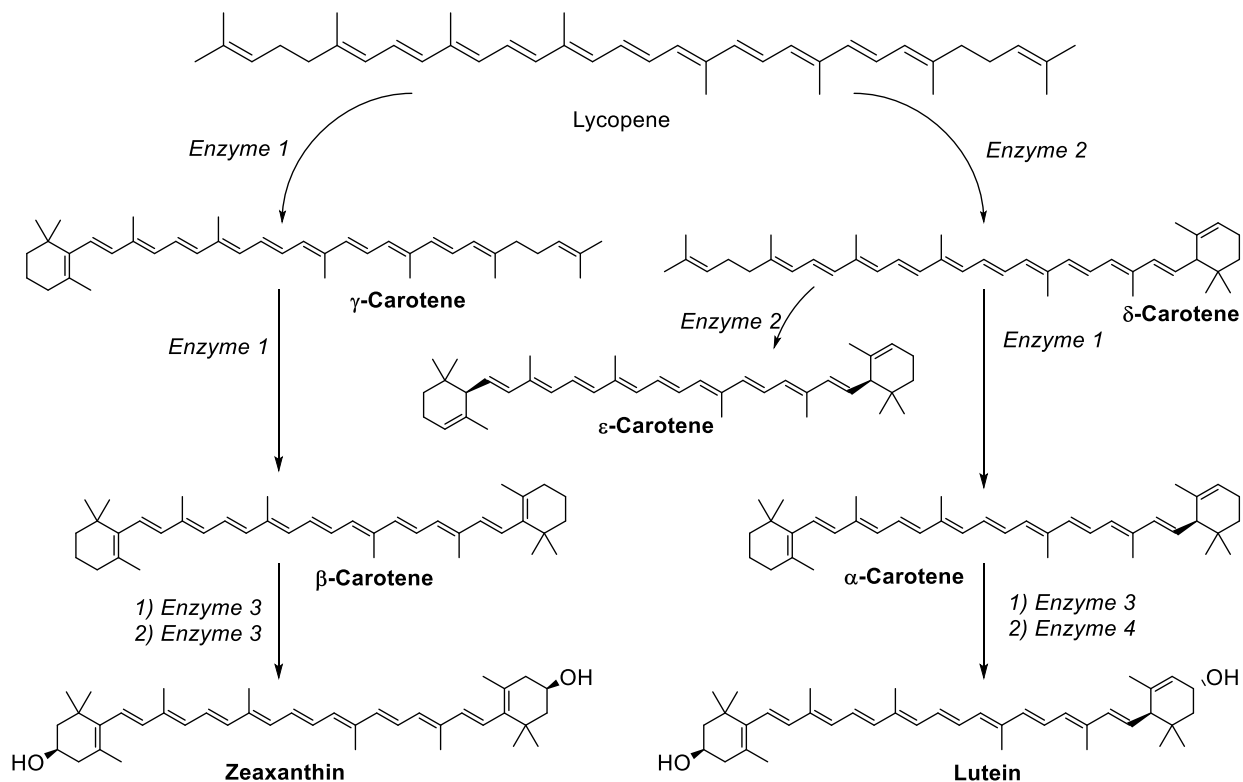


P₃



P₄

10. Since *Enzyme 1* acts two times to produce β -carotene from lycopene we can conclude that this enzyme catalyzes cyclisation. In the lutein core one double bond is shifted. Therefore *Enzyme 2* catalyses formation of second cycle type with an isomerised double bond. The difference between α -carotene and lutein is in hydroxyl groups, which have different configurations. *Enzymes 3* and *4* are hydroxylases.



11. Since only one type of enzyme is used to obtain zeaxanthin, it formed as either the *R,R*- or *S,S*- form. *R,S*- and *S,R*- are *meso*-forms. Zeaxanthin in this scheme is therefore optically active.

12. *Enzymes 1,2* – **Isomerases** , *Enzymes 3,4* – **Oxidoreductases**

13. Ask the chef in *Besh Qozon* during IChO 2026. (:

**Solutions to Preparatory Problems for
the 58th International Chemistry Olympiad 2026
Tashkent, Uzbekistan**

Practical Problems

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Problem 31. Blue pigment

Part A

Q1. $m \sim 2.7 \text{ g}$

The composition, mass and color of **X** depends on the reaction conditions and workup such as temperature and washing. The general formula of **X** is $\text{Cu}_x(\text{OH})_y(\text{CO}_3)_z \cdot w\text{H}_2\text{O}$.

Part B

Q2. Upon addition of sulfuric acid, the intense gas release and formation of blue solution can be observed, indicating the possible presence of carbonate anion and copper cation in **X**.

Q3. $V = 2.7 \text{ mL}$

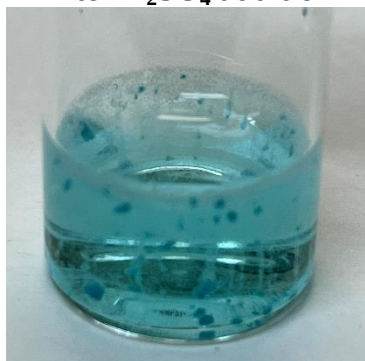
Note: the volumes of the $\text{Na}_2\text{S}_2\text{O}_3$ depends on the composition of the pigment **X**.

Q4. $2\text{Cu}^{2+} + 4\text{I}^- \rightarrow 2\text{CuI} + \text{I}_2$

$\text{I}_2 + 2\text{S}_2\text{O}_3^{2-} \rightarrow 2\text{I}^- + \text{S}_4\text{O}_6^{2-}$

Q5. $\omega(\text{Cu}) \sim 18\%$

After H_2SO_4 addition



After 1 min

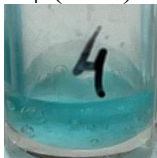
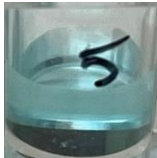


After 2 min – clear solution



Part C

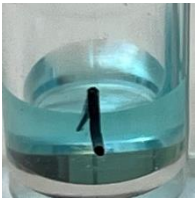
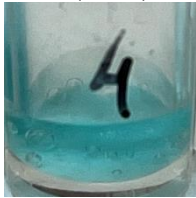
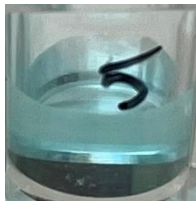
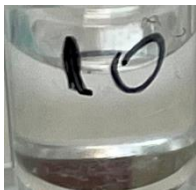
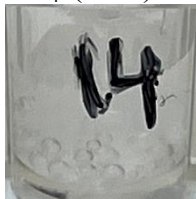
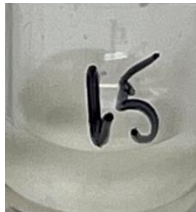
Q6. Pairwise reactions results (if performed properly; NR = no reaction):

	B	C	D	E	F
A	↓ blue ↑ gas 	NR or ↑ (very slow: after 15 min) 	NR 	↓ white (slow and maybe need stir) 	↓ blue ↑ gas (slow) 
B		NR 	↓ blue ↑ gas 	↓ white ↑ gas (slow) 	NR 
C			↑ (slow) 	NR 	NR 
D				NR 	↓ blue ↑ (slow) 
E					↓ white 

Q7. Appearance of brown color when solution of **D** reacts with dithizone indicates the presence of copper (II) ions, which can be confirmed by the color of the solution. Then, as solution of **A** is also blue, indicating the presence of copper (II) ions, it will give brown color when reacted with dithizone.

Q8. Cations: Cu^{2+} , Na^+ , Ca^{2+} . Anions: NO_3^- , SO_4^{2-} , CO_3^{2-} , HCO_3^-

Compound Code	A	B	C	D	E	F
Salt	CuSO_4	NaHCO_3	CaCO_3	$\text{Cu}(\text{NO}_3)_2$	$\text{Ca}(\text{NO}_3)_2$	Na_2CO_3

	CuSO_4 A	Na_2CO_3 F	NaHCO_3 B	CaCO_3 C	$\text{Ca}(\text{NO}_3)_2$ E
$\text{Cu}(\text{NO}_3)_2$ D	1 NR 	2 ↓ blue ↑ (slow) 	3 ↓ blue ↑ gas 	4 ↑ (slow) 	5 NR 
CuSO_4 A		6 ↓ blue ↑ (slow) 	7 ↓ blue ↑ gas 	8 NR or ↑ (very slow: after 15 min) 	9 ↓ white (slow and need stir) 
Na_2CO_3 F			10 NR 	11 NR 	12 ↓ white 
NaHCO_3 B				13 NR 	14 ↓ white ↑ (slow) 
CaCO_3 C					15 NR 

Q9. Additional tests that can be facilitate the compounds identification:

- Add H_2SO_4 from the **Part B** to compounds **A-F**:

Compound Code	A	B	C	D	E	F
Salt	NR	↑ gas	↑ gas ↓ white	NR	NR	↑ gas

- Add KI from the **Part B** to compounds **A-F**:

Compound Code	A	B	C	D	E	F
Salt	Brown solution + white precipitate	NR	NR	Brown solution + white precipitate	NR	NR

- Add H_2O to compound **C** (it is insoluble in water)

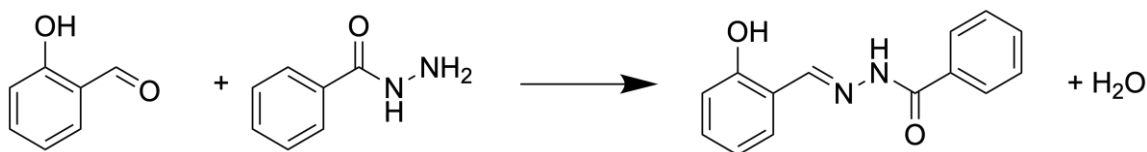
Q10. From $\text{Ca}(\text{NO}_3)_2$ (**E**) it is impossible to obtain the pigment.

Q11. Compound **C** (CaCO_3) is insoluble in water.

The reactions were tested in 10 well plates (well volume 0.4 ml, observations are visible nicely; 2-3 drops of liquid reagent or 1 microspatula tips of solid).

Problem 32. Synthesis and characterisation of metal complexes with a hydrazone-based ligand

Q1.



Q2. $m(\text{theoretical}) = 1.76 \text{ g}$

$m(\text{experimental}) \sim 1.15 \text{ g}$

Yields ranged from 13 to 97%, with an average of 65%. The greatest sources of yield loss arose from insufficient rinsing of crude product into the funnel.

Q3. $n(\text{Cu(II)}) = \frac{0.51}{170.5} = 0.003 \text{ mol}$

$n(\text{SBH}) = \frac{0.72}{240} = 0.003 \text{ mol}$

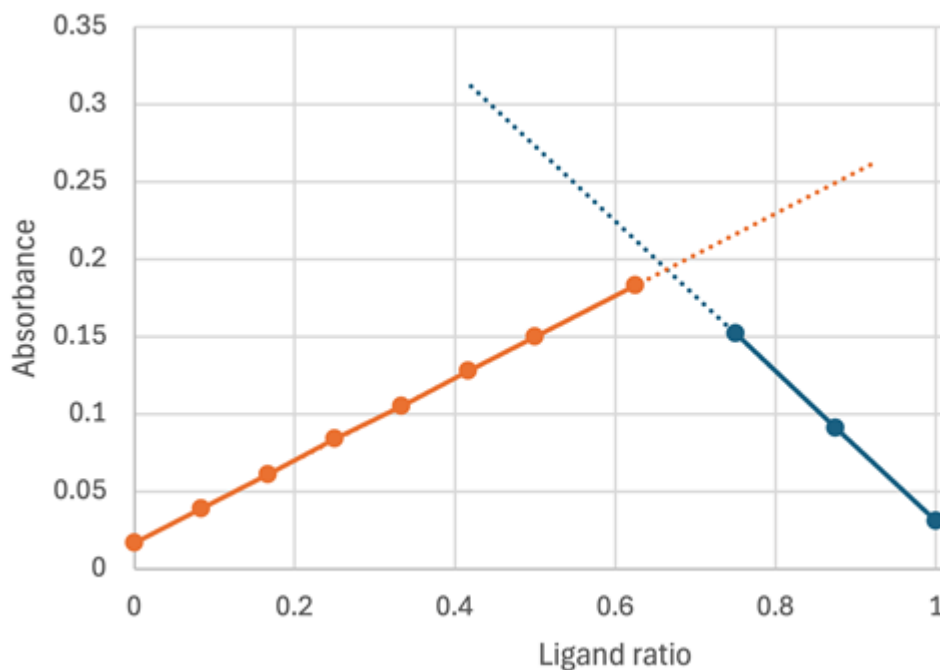
1:1 ratio of the reagents indicates the complex is expected to be in 1:1 form.

Cu-SBH ratio is 1:1.

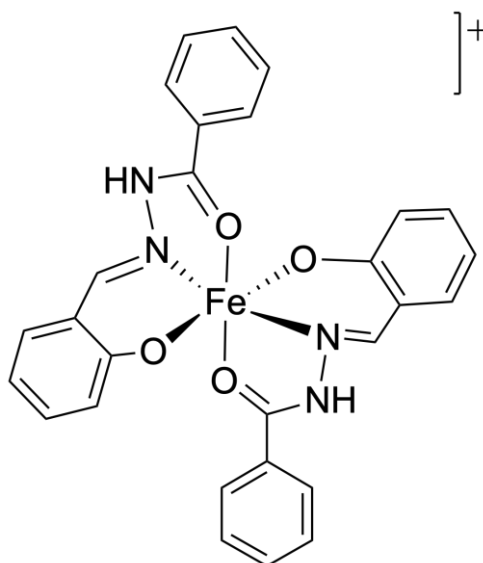
Q4. Plotting the Ligand mole fraction vs Absorbance results in 2 functions that cross each other at Ligand mole fraction = 0.66, meaning the stoichiometry of Fe-SBH is 1:2.

$$y_1 = 0.266 * x + 0.017$$

$$y_2 = -0.482 * x + 0.513$$

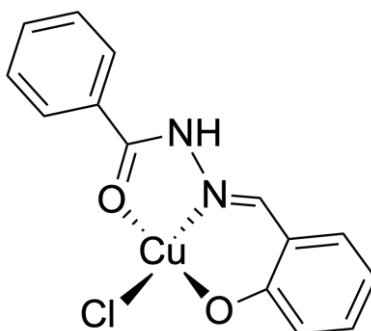


Q5.



Any structure that has correct molecular formula and complies to the chemical logic is considered correct.

Q6.



Q7. $m(\text{theoretical}) = 0.003 \cdot 338 = 1.01 \text{ g}$

$m(\text{experimental}) \sim 0.57 \text{ g}$

$\text{Yield} = 0.57/1.01 \cdot 100\% = 56\%$

The copper complex was collected as dark green crystals or powder with yields 30–89%, and average of 56%.

Problem 33. Titration of apple juice

Typical experimental results are given below.

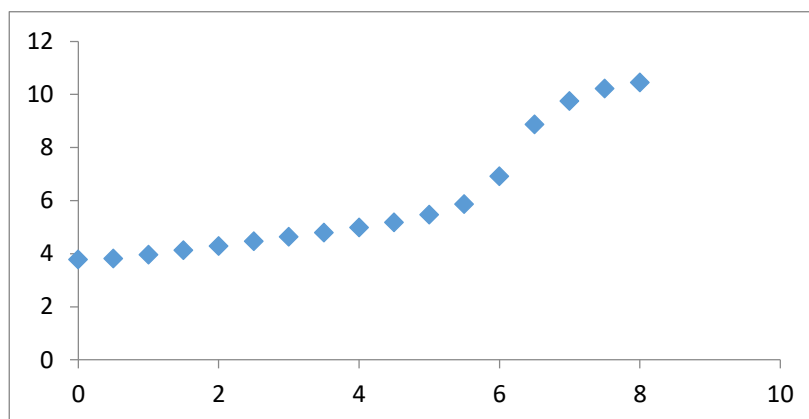
Q1. Result of potentiometric titration with 0.1000 M NaOH solution by adding 0.5 mL probes of the titrant:

V _{NaOH}	0.0	0.5	1.0	1.5	2.0	2.5	3.0	3.5	4.0	4.5
pH	3.78	3.81	3.96	4.12	4.28	4.46	4.63	4.79	4.98	5.17
V _{NaOH}	5.0	5.5	6.0	6.5	7.0	7.5	8.0	8.5	9.0	9.5
pH	5.46	5.86	6.91	8.87	9.75	10.21	10.45	-	-	-

The maximum value of ΔpH corresponds to the equivalence point, which is in 6.0-6.5 mL range here:

V _{NaOH}	0.0	☐	0.5	☐	1.0	☐	1.5	☐	2.0	☐	2.5	☐	3.0	☐	3.5	☐	4.0	☐	4.5
V _{NaOH}	4.5	☐	5.0	☐	5.5	☐	6.0	X	6.5	☐	7.0	☐	7.5	☐	8.0	☐	8.5	☐	9.0

We can draw the graph of $\text{pH} = f(V_{\text{NaOH}})$ function to clearly demonstrate the equivalence point:



Q2. For a more precise titration, we need repeat the potentiometry for the 6.0-6.5 mL range by adding 0.1 mL probes of the titrant:

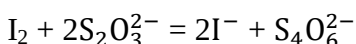
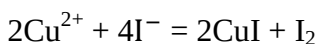
V _{NaOH}	6.0	6.1	6.2	6.3	6.4	6.5
pH	7.14	7.56	8.09	8.57	8.93	9.14

The maximum value of ΔpH we find at **6.1-6.2 mL** range. This is a more precise equivalent volume range of 0.1000 M NaOH solution.

Q3. $\text{HOOC-CH}_2\text{-CH(OH)-COOH} + 2\text{NaOH} \rightarrow \text{NaOOC-CH}_2\text{-CH(OH)-COONa} + 2\text{H}_2\text{O}$

Q4. For $V_{\text{NaOH}} = 6.2 \text{ mL}$, $C_{\text{malic acid}} = \frac{0.1 \cdot 6.2 \cdot 134}{2 \cdot 10} = 4.15 \text{ mg/mL}$.

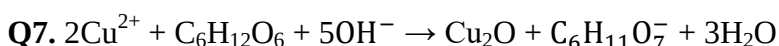
Q5. The reaction equations is as follows:



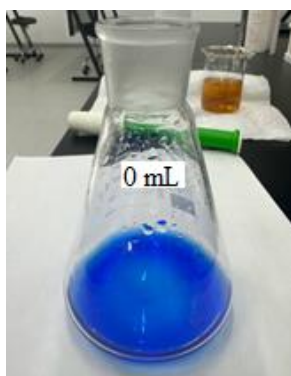
Q6. Formula for calculation of Cu(II) concentration:

$$C_{\text{Cu(II)}} = \frac{C_{\text{S}_2\text{O}_3^{2-}} \cdot V_{\text{S}_2\text{O}_3^{2-}} - \frac{V_{\text{volumetric flask}}}{V_{\text{aliquot of solution 1}}}}{V_{\text{aliquot of initial solution of Cu(II)}}}.$$

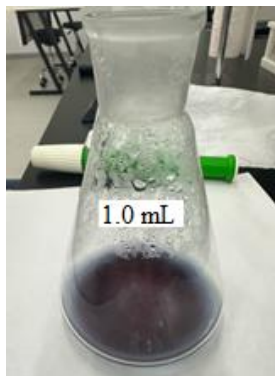
$$\text{for } V_{\text{S}_2\text{O}_3^{2-}} = 2.0 \text{ mL} \rightarrow C_{\text{Cu(II)}} = \frac{0.1000 \cdot 2.0 \cdot \frac{100}{10}}{10} = 0.2000 \text{ M}.$$



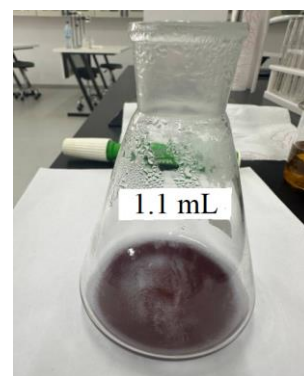
Q8. Color of the solution at the beginning ($V_{\text{apple juice}} = 0 \text{ mL}$), before the equivalent point ($V_{\text{apple juice}} = (V_{\text{eq}} - 0.1) \text{ mL}$) and at the equivalence point ($V_{\text{apple juice}} = V_{\text{eq}} \text{ mL}$) are shown below:



$V_{\text{apple juice}} = 0 \text{ mL}$



$V_{\text{apple juice}} = (V_{\text{eq}} - 0.1) \text{ mL}$



$V_{\text{apple juice}} = V_{\text{eq}} \text{ mL}$

$$C_{\text{glucose}} = \frac{C_{\text{Cu(II)}} V_{\text{Cu(II)}} \cdot 180}{2 \cdot V_{\text{apple juice}}}.$$

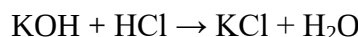
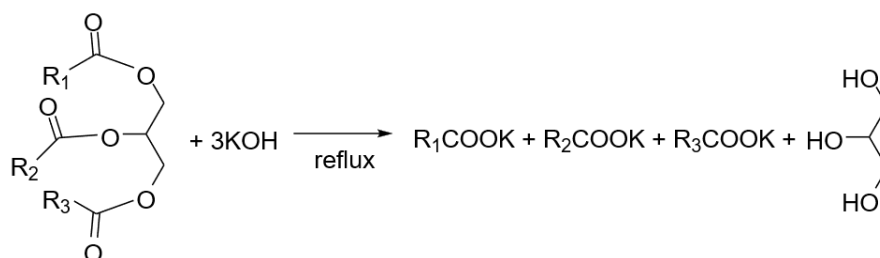
$$\text{For } C_{\text{Cu(II)}} = 0.2000 \text{ M and } V_{\text{apple juice}} = 1.1 \text{ mL} \rightarrow C_{\text{glucose}} = \frac{0.2000 \cdot 10 \cdot 180}{2 \cdot 1.1} = 163.6 \text{ mg/mL}.$$

Problem 34. Cottonseed oil

Notes:

- If cottonseed oil is not available, you may use other plant oil (sunflower, olive, corn, soy bean etc).
- It is important to use freshly prepare KOH solution for hydrolysis step.
- Instead of “Alkali Blue 6B” indicator, you can use Phenolphthalein or Thymolphthalein, if they are allowed in your countries.

Q1.



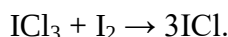
Q2. $C_{\text{KOH}} (\text{M}) = \frac{0.5000 \times V_0(\text{HCl})}{25.0}$

Q3. Saponification value (mg/g) = $\frac{0.5000 \times [V_0(\text{HCl}) - V(\text{HCl})]}{m_1(\text{cottonseed oil})} \times 56.1$

Q4. Let determine the mole ratio of ICl_3 and I_2 :

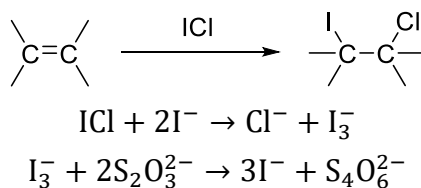
$$\frac{n_{\text{ICl}_3}}{n_{\text{I}_2}} = \frac{\frac{0.45}{233.29}}{\frac{0.50}{253.84}} \approx \frac{1}{1}$$

The product of the reaction between 1 mole of ICl_3 and 1 mole of I_2 is ICl :



So, **X** is ICl (iodine monochloride).

Q5.



Q6. $C_X (\text{M}) = \frac{0.1000 \times V_0(\text{Na}_2\text{S}_2\text{O}_3)}{2 \times 10.0}$

Q7. Iodine value (g/100 g) = $\frac{0.1000 \times [V_0(\text{Na}_2\text{S}_2\text{O}_3) - V(\text{Na}_2\text{S}_2\text{O}_3)]}{2 \times m_2(\text{cottonseed oil})} \times 253.84 \times \frac{100}{10000}$

Q8. a) Triglycerides of short chain fatty acids require more KOH for saponification per unit mass. Therefore, **butter** oil with the highest saponification value (210–232) contains the highest number of short-chain fatty acids.

b) Triglycerides, which contain more unsaturated fatty acids, have higher iodine value. Therefore, it is **fish** oil (142–176). It has the lowest melting point and it easily spoils when heated.

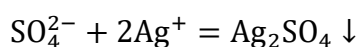
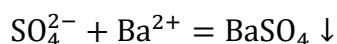
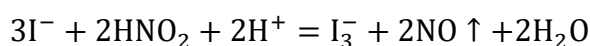
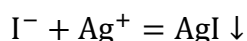
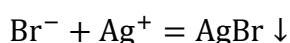
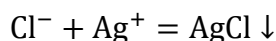
Problem 35. An unknown salt

The results and calculations in this solution are based on $m_{\text{exact}} = 1.0040 \text{ g}$.

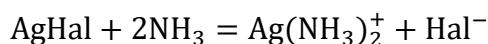
Q1. Table 1 looks as follows:

	BaCl₂	AgNO₃	NaNO₂ + HCl
Cl⁻	no changes	formation of white precipitate (AgCl↓)	no changes
Br⁻	no changes	formation of yellowish precipitate (AgBr↓)	no changes
I⁻	no changes	formation of bright yellow precipitate (AgI↓)	coloring the solution brown (I ₃ ⁻)
NO₃⁻	no changes	no changes	no changes
SO₄²⁻	formation of white precipitate (BaSO ₄ ↓)	formation of white precipitate (Ag ₂ SO ₄ ↓)	no changes

Q2. Ionic reaction equations as follows:



Q3. During dissolution of **AgHal** in the ammonia solution following reaction takes place:



Equilibrium constant of the above reaction can be determined as follows:

$$K = \frac{[\text{Ag}(\text{NH}_3)_2^+][\text{Hal}^-]}{[\text{NH}_3]^2} = \frac{[\text{Ag}(\text{NH}_3)_2^+]}{[\text{Ag}^+][\text{NH}_3]^2} \cdot \frac{[\text{Ag}^+][\text{Hal}^-]}{1} = \beta \cdot K_{sp}.$$

Total concentration of NH₃ in the solution can be calculated as follows:

$$c_0(\text{NH}_3) = \frac{\rho \cdot \omega \cdot 1000}{M \cdot 100} = \frac{0.958 \cdot 10 \cdot 1000}{17 \cdot 100} = 5.64 \text{ M}.$$

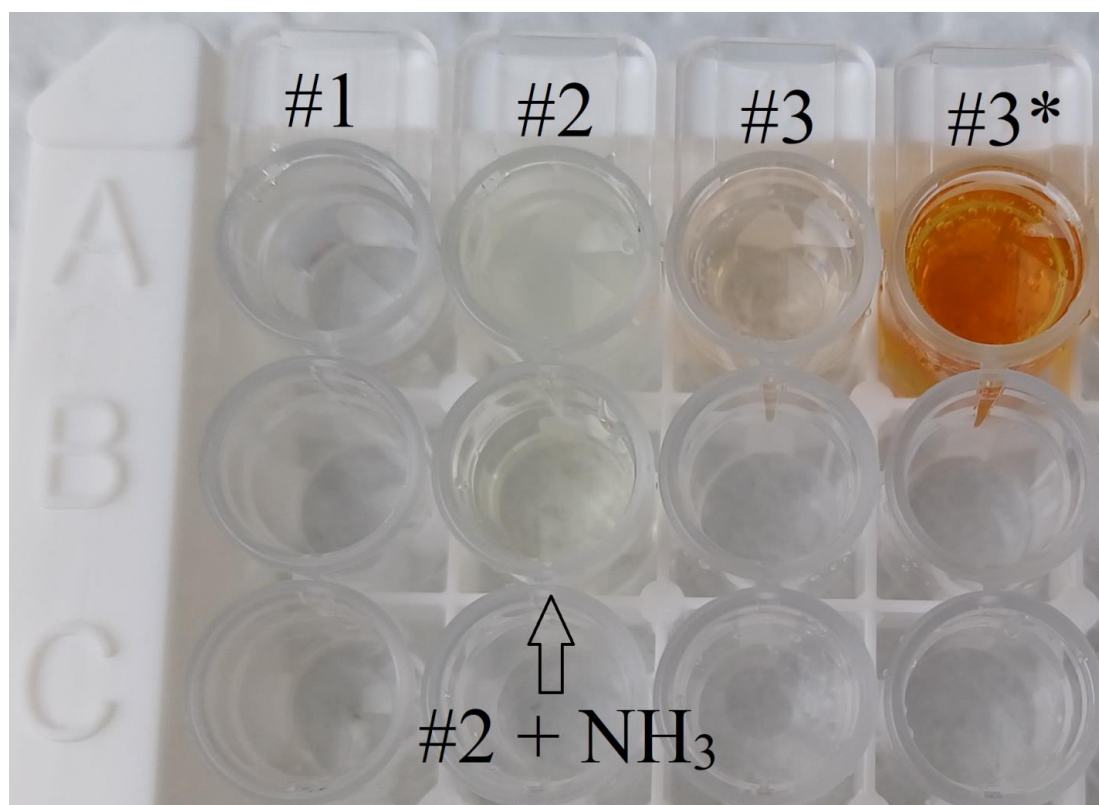
If s moles of **AgHal** are dissolved, molar concentration of other substances as follows at the equilibrium: $\text{NH}_3 - (5.64 - 2s) \text{ M}$, $\text{Ag}(\text{NH}_3)_2^+ - s \text{ M}$, $\text{Hal}^- - s \text{ M}$. We can calculate s by using equilibrium constant as follows:

$$K = \beta \cdot K_{sp} = \frac{s^2}{(5.64 - 2s)^2}$$

Solving quadratic equation for each **Hal** gives us the following results:

	Cl	Br	I
$\beta \cdot K_{sp}$	$4.43 \cdot 10^{-3}$	$1.34 \cdot 10^{-5}$	$2.13 \cdot 10^{-9}$
$s, \text{ M}$	0.331	0.0205	$2.60 \cdot 10^{-4}$

Q4. Results of qualitative reactions are as follows:



#	Mixture content	Observations
1	70 μL of solution A + 70 μL of BaCl_2	no changes
2	70 μL of solution A + 70 μL of AgNO_3	white precipitate is formed, which is soluble in NH_3 solution (#2 + NH_3)
3	70 μL of solution A + 70 μL of NaNO_2 + 70 μL of HCl	coloring the solution yellowish (due to nitrosylation of amino acid)
3*	70 μL of solution KI + 70 μL of NaNO_2 + 70 μL of HCl	coloring the solution brown (it is provided for distinguish from #3)

A correctly filled table looks as follows:

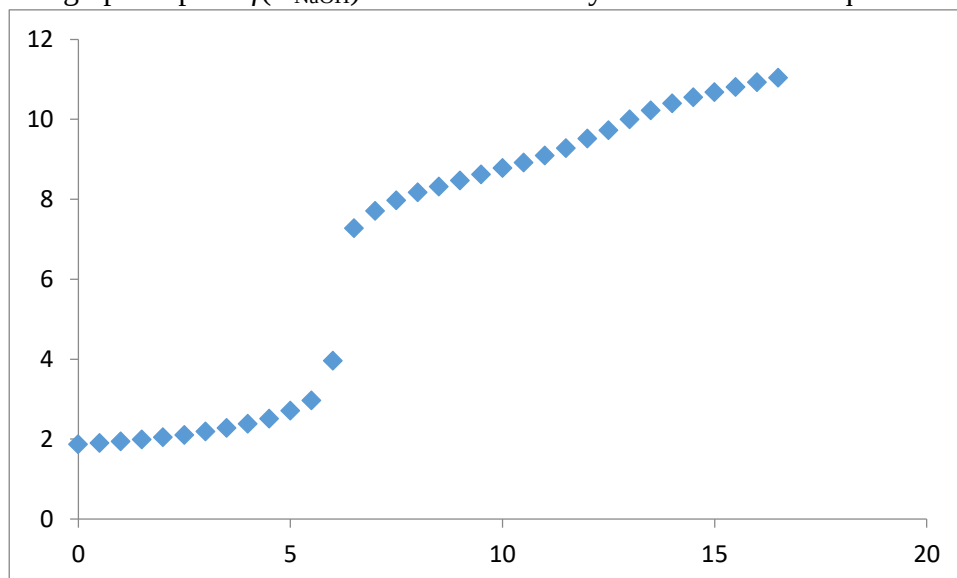
Reaction number	Reaction mixture	Precipitate formed	Colour of precipitate	Precipitate solubility in NH_3	Colour of resulting solution
1	70 μL of solution 1 + 70 μL of BaCl_2	☐ Yes ☒ No	-	-	colorless
2	70 μL of solution 1 + 70 μL of AgNO_3	☒ Yes ☐ No	white	☒ Yes ☐ No	colorless
3	70 μL of solution 1 + 70 μL of HCl + 70 μL of NaNO_2	-	-	-	yellowish

Q5. From qualitative reactions we can conclude that, X^{n-} is Cl^- .

Q6. Result of potentiometric titration of solution **A** with 0.182 M NaOH solution by adding 0.5 mL probes of the titrant:

V_{NaOH}	0.0	0.5	1.0	1.5	2.0	2.5	3.0	3.5	4.0	4.5
pH	1.87	1.90	1.94	1.99	2.05	2.10	2.19	2.28	2.38	2.51
V_{NaOH}	5.0	5.5	6.0	6.5	7.0	7.5	8.0	8.5	9.0	9.5
pH	2.71	2.97	3.96	7.28	7.71	7.97	8.17	8.32	8.47	8.62
V_{NaOH}	10.0	10.5	11.0	11.5	12.0	12.5	13.0	13.5	14.0	14.5
pH	8.78	8.92	9.09	9.28	9.52	9.73	10.00	10.22	10.40	10.55
V_{NaOH}	15.0	15.5	16.0	16.5	17.0	17.5	18.0	18.5	19.0	19.5
pH	10.68	10.81	10.93	11.04	-	-	-	-	-	-

We can draw the graph of $\text{pH} = f(V_{\text{NaOH}})$ function to clearly demonstrate the equivalence points:



There are two pH jumps: the first one is big at 6.0-6.5 mL range, the second is smoother at 12.5-13.0 mL range.

V_{NaOH}	0.0	☐	0.5	☐	1.0	☐	1.5	☐	2.0	☐	2.5	☐	3.0	☐	3.5	☐	4.0	☐	4.5
V_{NaOH}	4.5	☐	5.0	☐	5.5	☐	6.0	X	6.5	☐	7.0	☐	7.5	☐	8.0	☐	8.5	☐	9.0
V_{NaOH}	9.0	☐	9.5	☐	10.0	☐	10.5	☐	11.0	☐	11.5	☐	12.0	☐	12.5	X	13.0	☐	13.5
V_{NaOH}	13.5	☐	14.0	☐	14.5	☐	15.0	☐	15.5	☐	16.0	☐	16.5	☐	17.0	☐	17.5	☐	18.0
V_{NaOH}	18.0	☐	18.5	☐	19.0	☐	19.5	☐	20.0	☐	20.5	☐	21.0	☐	21.5	☐	22.0	☐	22.5

Q7. For a more precise titration, it is convenient to select the first jump, as it's more precise than the 2nd one. Potentiometry results for the 6.0-6.5 mL range of NaOH by adding 0.1 mL probes of the titrant are shown below:

V_{NaOH}	6.0	6.1	6.2	6.3	6.4	6.5
pH	4.36	6.42	6.91	7.15	7.32	7.45

So, the 1st equivalence point is at **6.0-6.1 mL** range due to it shows the highest pH change.

Q8. The salt contains **2 acidic protons**.

Q9-10. Using 6.1 mL volume for the 1st equivalence point, we calculate the molar mass of the salt as follows:

$$M = \frac{1.0040}{0.182 \cdot 6.1 \cdot 10^{-3} \cdot \frac{250}{50}} \approx 181 \text{ g/mole.}$$

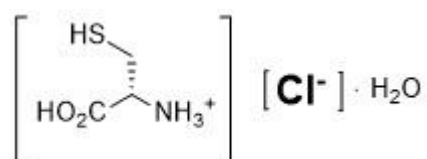
This value is sum of different parts of the salt:

$$181 = M_{\text{R}} + 110.5 + 18m \rightarrow M_{\text{R}} + 18m = 70.5.$$

During potentiometry the pH jump of neutralization of group $-\text{NH}_3^+$ is not observed in an aqueous solution due to the fact that it is a very weak acid ($\text{p}K_a > 10$). So, side chain ($-\text{R}$) contains another acidic group, which has higher $\text{p}K_a$ value than $-\text{COOH}$ group. The only possible variant that occurs in canonical amino acids is $-\text{SH}$ group [Histidine is not suitable due to the high molar mass of the side group ($M_R \approx 81 > 70.5$), low $\text{p}K_a$ value (the graph of $\text{pH} = f(V_{\text{NaOH}})$ shows it need to be higher than 8) and the cation in his case will have a charge of “2+”]. So, amino acid is **cysteine**, $-\text{R}$ is $-\text{CH}_2\text{SH}$. Than we calculate integer m :

$$m = \frac{70.5 - 47}{18} = 1.30 \approx 1.$$

So, the unknown salt is **cysteine hydrochloride monohydrate**:



Problem 36. Khodja Nasreddin's secret message

Q1. The final image in a 96-well plate after completion of titration according to the method given in the text of the problem as Figure 6.1:

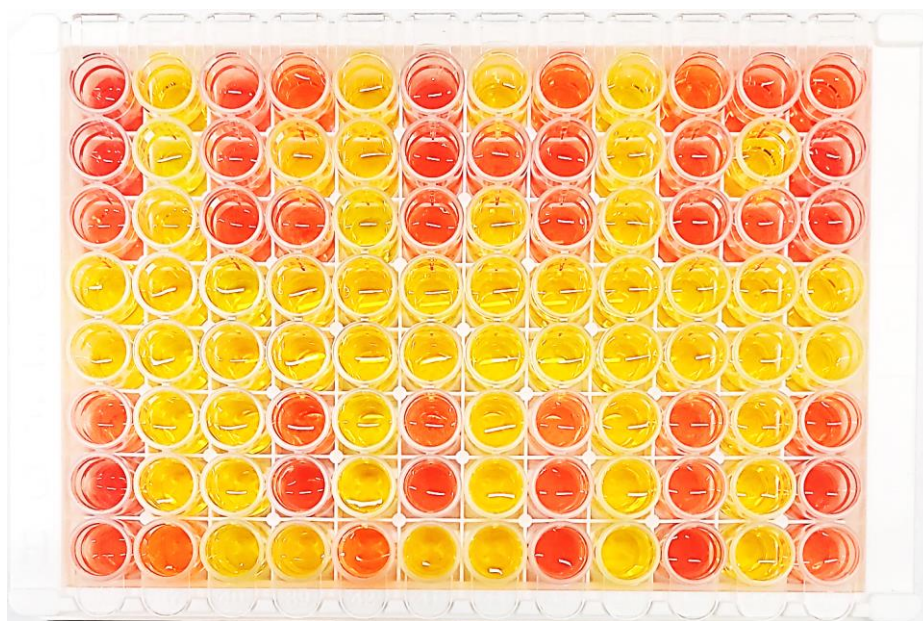


Figure 6.1.

The pattern looks as “IChO LVIII” (LVIII stands for 58 in Roman numerals), which means “The 58th International Chemistry Olympiad”. It is important to consider that incorrect titration of even one solution will lead to damage to the entire drawing.

There is an alternative approach. To do this, you first “titrate” each solution **I–VIII**, then determine how many wells there are and what color each will be during the “titration”. Results of “titrations” of 100 μL of solutions **I–VIII** with 0.05 M NaOH or 0.05 M HCl by increasing the volume of the titrant solution by 20 μL and moving to the next well until color of the solution changes as Figure 6.2:

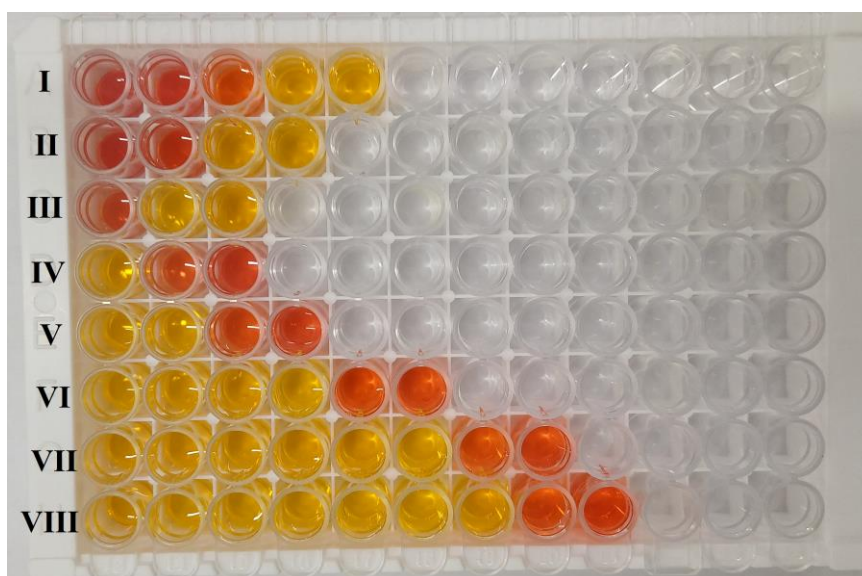


Figure 6.2.

From the results it can be understood that in the case of solution **I**, the equivalent point occurs in the 4th well and from the 5th well it will be necessary to begin “titrating” solution **IV** as indicated in the “titration” sequence in the problem condition etc. For each solution **I-VIII** it looks as Figure 6.3:

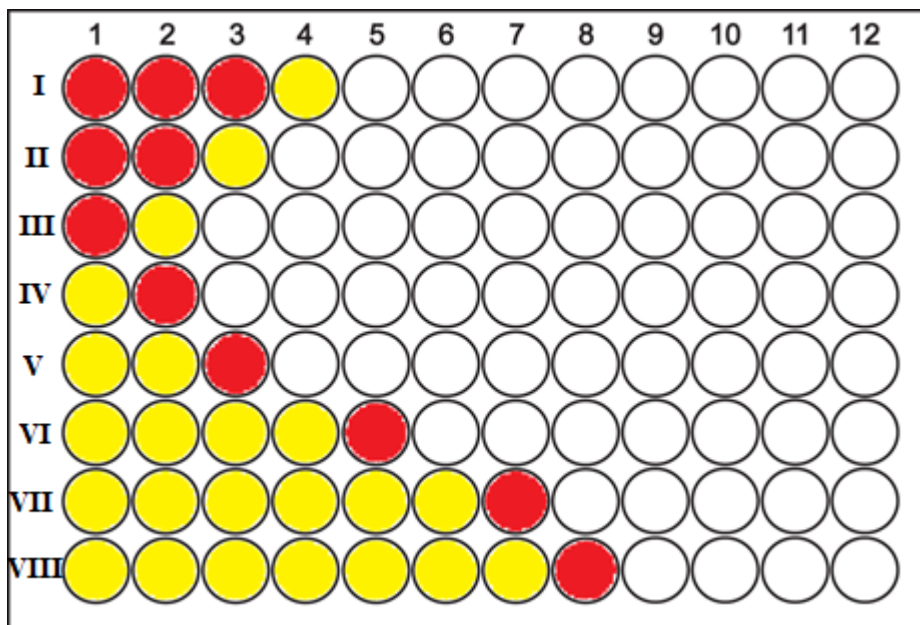


Figure 6.3.

According to **Table 1**, “titration” of the first 2 solutions (**I** and **IV**) recreates Figure 6.4:

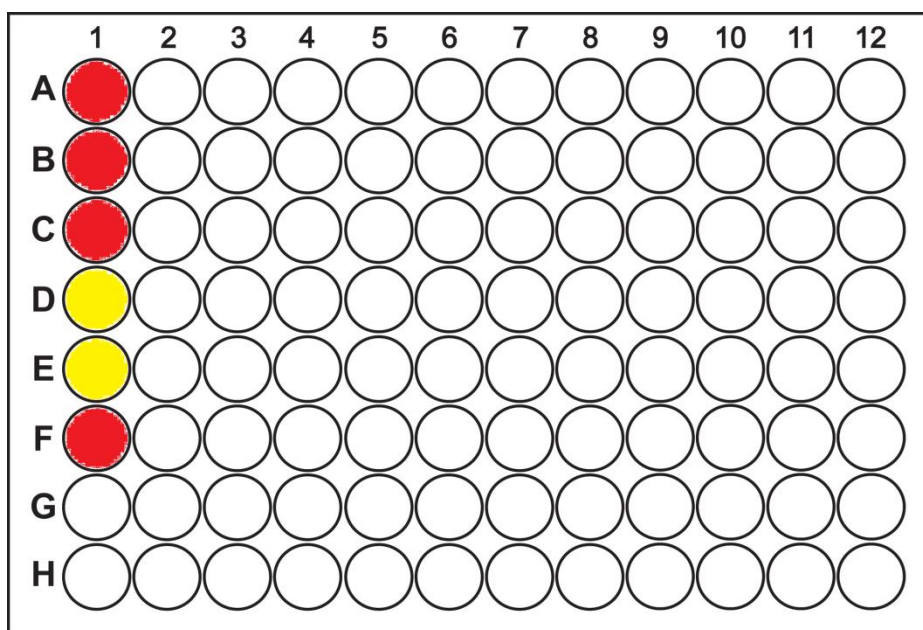


Figure 6.4.

When we continue “titration” with the third solution (**II**), we get Figure 6.5:

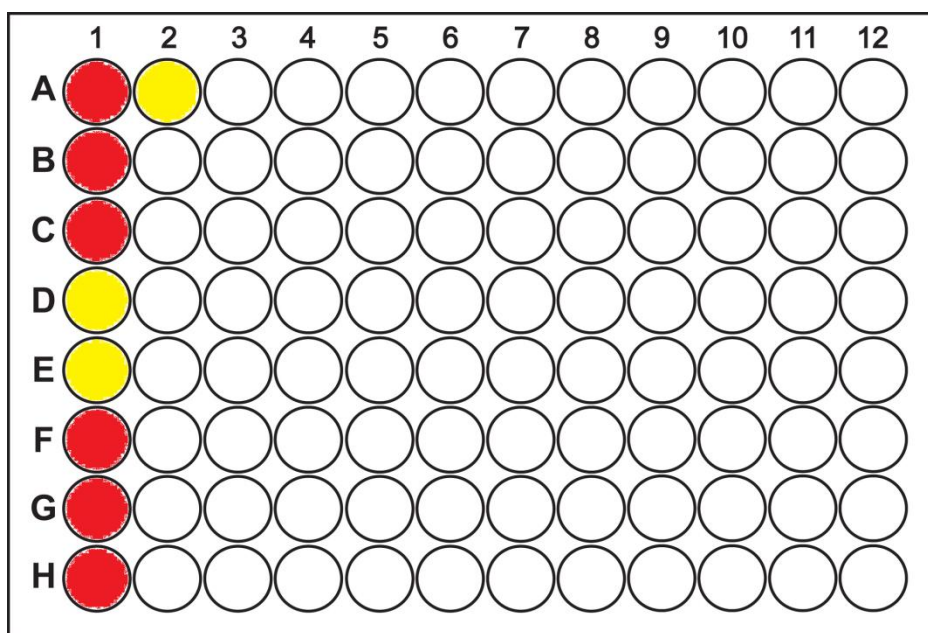


Figure 6.5.

Finally, after complete “titration” according to **Table 1**, we obtain the Figure 6.6:

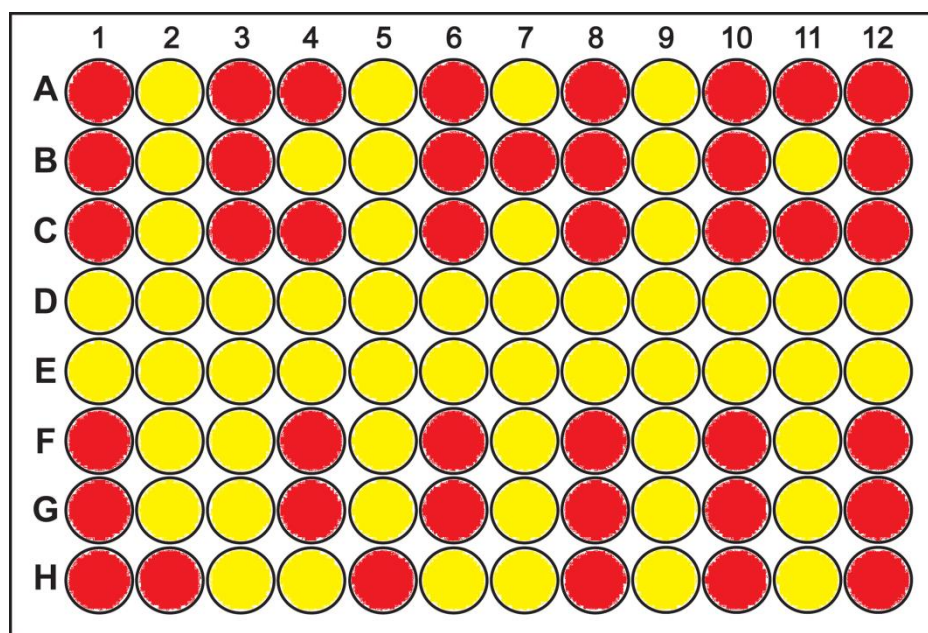
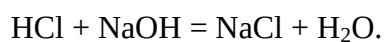


Figure 6.6.

Q2. During “titration” the following reaction occurs:



The concentration of solutions can be calculated using the following equation:

$$c_{\text{HCl}} V_{\text{HCl}} = c_{\text{NaOH}} V_{\text{NaOH}}.$$

Calculated concentration of solutions **I–VIII** by using the above formula as follows:

Solution	I	II	III	IV	V	VI	VII	VIII
Substance	HCl	HCl	HCl	NaOH	NaOH	NaOH	NaOH	NaOH
Calculated concentration ranges, M	0.03-0.04	0.02-0.03	0.01-0.02	0.01-0.02	0.02-0.03	0.04-0.05	0.06-0.07	0.07-0.08
Prepared concentration, M	0.035	0.025	0.015	0.015	0.025	0.045	0.065	0.075

Note: Lab assistants should normalize concentrations of solutions **I–VIII** as in Figure 6.3.

Q3. Towards the end of the “titration”, in well F12 (indicated by the red arrow), the “titration” of solution **IV** ends and in well G12 (indicated by the green arrow), the “titration” of solution **II** begins:

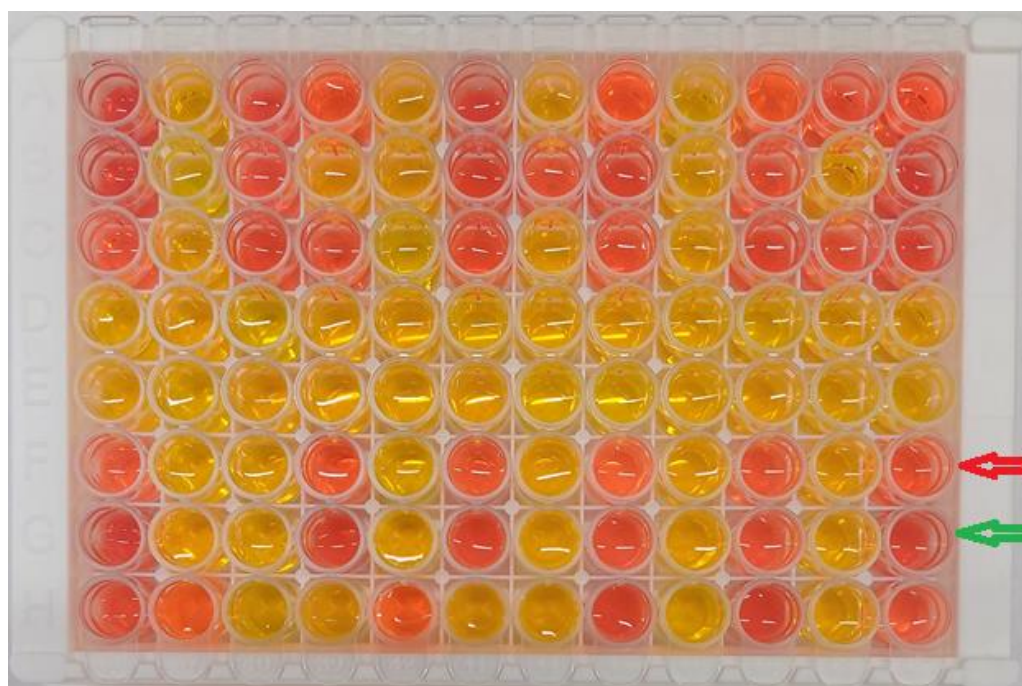


Figure 6.7.

As can be seen from the Figure 6.7, the last two wells (G12 and H12) need to be red. This will only be possible if solution **II** is replaced with solution **I**.