

56th IChO International
Chemistry Olympiad
Saudi Arabia 2024

Preparatory problems for the 56th International Chemistry Olympiad 2024

Riyadh, Saudi Arabia

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King Abdulaziz & his Compagnons Foundation for Giftedness & Creativity



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Preparatory problems for the 56th International Chemistry Olympiad

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Editor: Gábor Magyarfalvi



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56th International Chemistry Olympiad

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Preface

The scientific committee of the 56th International Chemistry Olympiad is excited to announce that the 56th International Chemistry Olympiad Preparatory Problems have been released. It is expected that these problems will assist the students in their preparation for the Olympiad. It is intended to align both the theoretical and practical problems with the core IChO syllabus (www.ichosc.org/regulations, Appendix C) while reducing topics that go beyond the core syllabus. However, advanced topics have been included in this year's preparatory problems, as shown in the listing later.

This scientific committee has provided 30 theoretical problems and 8 practical tasks to illustrate the depth of these fields. Our goal is to provide challenging and interesting problems, similar in style to those on the final exam, yet these problems are long and numerous. The committee is welcoming comments and questions from the mentors at the icho2024.science@mawhiba.org.sa email address.

Through this international scientific event, young people around the world can learn about chemistry and inspire one another. In addition to inspiring young people to pursue careers in the fundamental sciences, this competition influences public attitudes toward chemistry, an important branch of science. Moreover, you will learn about the culture and history of the host country as well as meet people from all over the world.

The scientific committee of the 56th International Chemistry Olympiad

Riyadh, Saudi Arabia, January 2024

Acknowledgments

Thank you to all the authors who prepared both preparatory and competition problems for the 56th International Chemistry Olympiad. During months of hard work, they created a booklet that would be of assistance to young chemists taking part in the Olympiad. The IChO Steering Committee members, scientific reviewers, and language proofreaders have helped us with a splendid job.

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Fields of advanced difficulty

Theoretical

- Solid state structures, unit cell types, cell parameters,
- Analysis of complex reactions using steady-state and quasi-equilibrium approximations, mechanisms of catalytic reactions (also as applied to kinetics of enzyme catalysis),
- Basic concepts of molecular orbital theory, electron configurations, bond orders, orbitals in homonuclear diatomics, interpretation of MO schemes provided for more complex systems,
- Interpretation of ^1H NMR spectra: chemical shift, multiplicity (including coupling to other nuclei with $I > 1/2$), integrals,
- Basics of polymer science, polymerization mechanisms, polydispersity, polymer functionalization, GPC chromatography,

Practical

- Synthesis techniques: thin layer chromatography

Familiarity with the following advanced topics will not be expected in the exams:

Calculation of kinetic isotope effects,

Crystal field theory and ligand field theory (beyond the fact that d orbitals can be split and can be part of molecular orbitals),

Mechanistic and stereochemical details of cycloadditions,

Pericyclic reactions other than Diels-Alder reactions,

Mechanistic details of metal catalyzed cross-coupling reactions,

No other cross-coupling reactions besides the examples presented in the preparatory are expected to be known without further explanation.

For NMR spectroscopy of nuclei other than ^1H , students only need to be able to determine the number of chemical environments present, and do not need to know information about chemical shifts or coupling.

Use of spreadsheet software,

Solving higher-order equations

Constants and formulae

Avogadro constant:	$N_A = 6.022 \cdot 10^{23} \text{ mol}^{-1}$	Zero of the Celsius scale:	273.15 K
Gas constant:	$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$	Faraday constant:	$F = 96485 \text{ C mol}^{-1}$
Ionic product of water at 298.15 K :	$K_w = 10^{-14}$	Planck-constant:	$h = 6.626 \cdot 10^{-34} \text{ J s}$
Ideal gas equation:	$pV = nRT$	Enthalpy	$H = U + pV$
Beer-Lambert law:	$A = \log \frac{I_0}{I} = \epsilon cl$	Gibbs energy:	$G = H - TS$
Arrhenius equation:	$k = A e^{\frac{-E_a}{RT}}$	Henderson-Hasselbalch equation:	$\text{pH} = \text{p}K_a + \log \frac{[A^-]}{[AH]}$
Speed of light:	$c = 3.000 \cdot 10^8 \text{ m s}^{-1}$	Integrated rate laws Zeroth order:	$[A] = [A]_0 - kt$
$\Delta_r G^\circ = -RT \ln K = -nFE_{cell}^\circ$		First order:	$\ln[A] = \ln[A]_0 - kt$
$\sum_{k=0}^{\infty} a r^k = \frac{a}{1-r} \quad \text{for } r < 1$		Second order:	$\frac{1}{[A]} = \frac{1}{[A]_0} + kt$

Consider all gases ideal throughout the exam.

In equilibrium constant calculations all concentrations are referenced to a standard concentration of one mol per dm³.

Periodic table with relative atomic masses

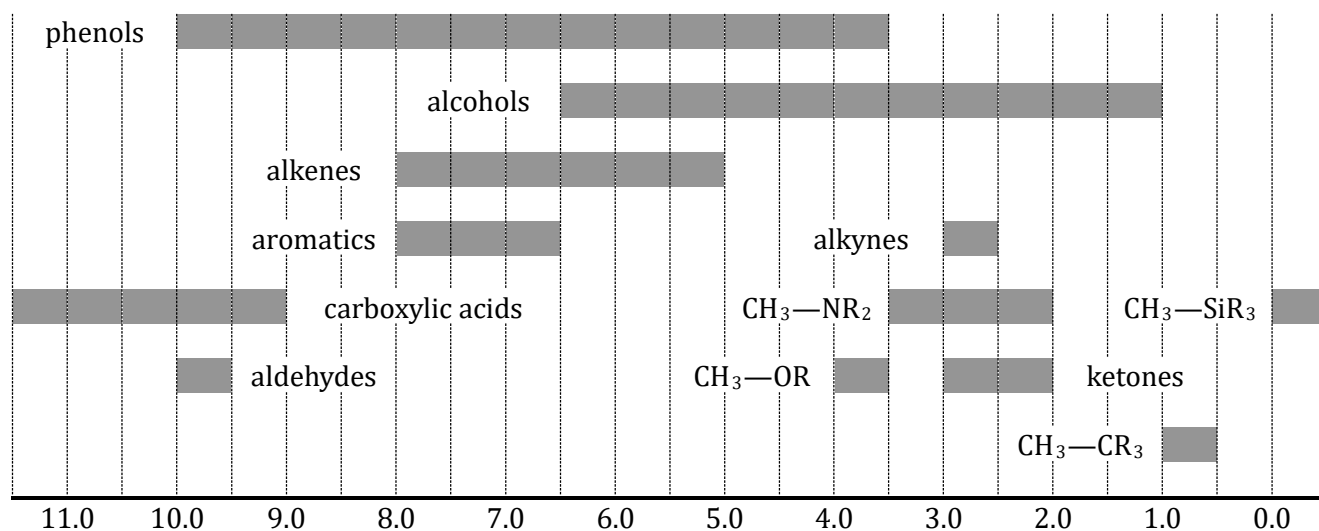
1 H 1.008																	18 He 4.003
3 Li 6.94	4 Be 9.01											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
11 Na 22.99	12 Mg 24.30	3	4	5	6	7	8	9	10	11	12	13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.06	17 Cl 35.45	18 Ar 39.95
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.87	23 V 50.94	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 -

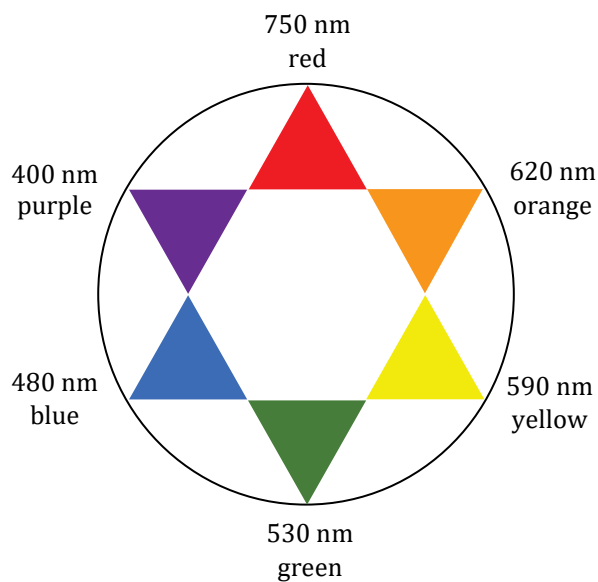
Spectroscopical data

^1H NMR

Chemical shifts of hydrogen (in ppm /TMS)



Visible light



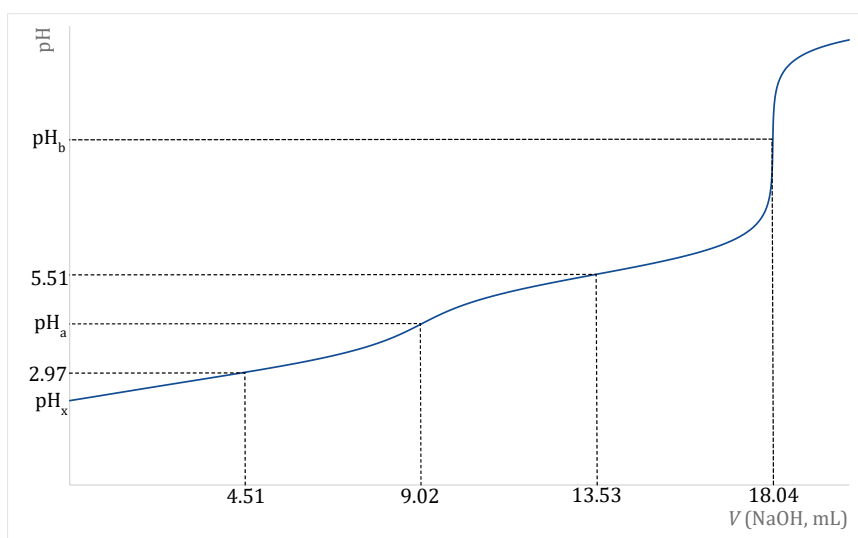
Theoretical Problems

1. Two acids

Ali received a lab project to investigate two diprotic carboxylic acids, **B** and **C**.

Part I.

According to his observation compound **B** is a white solid material that is slightly soluble in water. Ali made 200 cm³ of stock solution from 1.2000 g of compound **B**, and he titrated 25.00 cm³ of the stock solution with 0.1000 mol/dm³ NaOH solution. He has found a pH meter therefore he could monitor the pH change of the solution as a function of the volume of NaOH solution added. The graph below shows his experimental results.



Based on the graph Ali could determine many things about the dicarboxylic acid (**B**) and its solution. (In this concentration range, the volumes of the solutions are additive.) Let us follow his work.

- 1.1. **Calculate** the molar mass of compound **B**.
- 1.2. **Determine** $K_{a,1}(\mathbf{B})$ and $K_{a,2}(\mathbf{B})$, the acid dissociation constants of compound **B** based on the diagram.

Using the molar mass of compound **B**, he deduced its molecular formula. He then searched for K_a data and, with the aid of his initial findings, successfully identified the structure.

He realized that one of the dissociation constants obtained from the diagram is probably not very reliable. To improve accuracy, he decided to use the literature value of K , the cumulative acid dissociation constant for the $\text{H}_2\text{A} \rightleftharpoons 2 \text{H}^+ + \text{A}^{2-}$ reaction which in the case of **B** is $3.99 \cdot 10^{-9}$.

- 1.3. **Reproduce** his reasoning presented below by marking the correct alternatives in the sentence below and **reproduce** his estimate calculation. K_{ax} (x is 1 or 2) based on the graph is probably inaccurate due to the following two factors: the total concentration of the acid in the titrated solution was relatively too (high/low) while the K_{ax} value in question was relatively too (large/small).

1.4. **Calculate** the value that is marked as pH_a on the diagram (the first equivalence point). Use the most accurate data for calculation. Give your answer with two decimal places.

1.5. Using appropriate approximations, **calculate** the pH of the initial stock solution (pH_x on the graph) and the pH of the second equivalence point, pH_b . Give your answer with two decimal places.

Ali wants to set up a titration using **B** for his fellow students using acid-base indicator. He has found the following data of the indicators:

Name	pH range of color change
Thymolphthalein	9.3–10.5
Phenolphthalein	8.3–10.0
Cresol red	7.2–8.8
Bromothymol blue	6.0–7.6
Methyl red	4.4–6.2
Methyl orange	3.1–4.4
Thymol blue	1.2–2.8

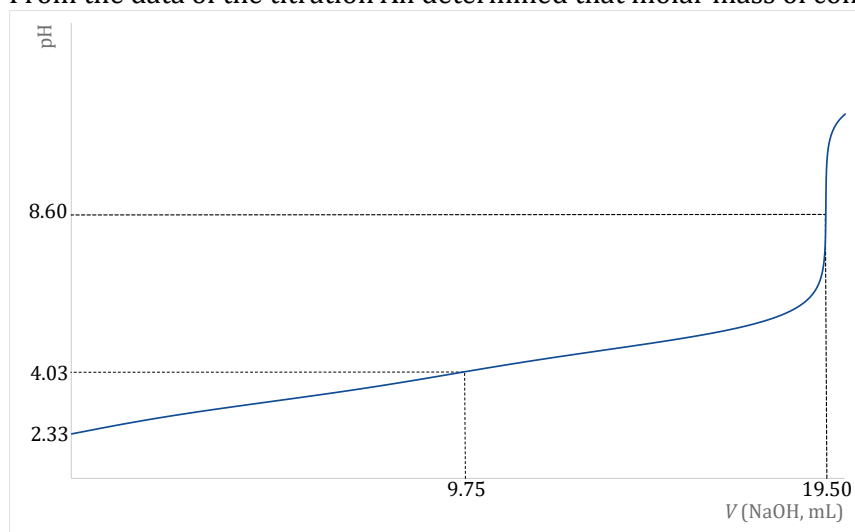
1.6. **Choose** the best indicator for the titration.

Part II.

Compound **C** is also white, but it has excellent solubility in water. Although the name was missing on the bottle, the acid dissociation constants were written on it:

$$K_{a,1}(\text{C}) = 6.03 \cdot 10^{-4}, K_{a,2}(\text{C}) = 1.41 \cdot 10^{-5}$$

Ali made 200 cm³ of solution from 1.1700 g of the dry, anhydrous compound **C** and 25.00 cm³ of the stock solution was titrated with the same NaOH solution as before while he monitored the pH by the pH meter. The following graph has been made according to his experimental values. From the data of the titration Ali determined that molar mass of compound **C** is 150 g mol⁻¹.



Ali wants to set up a titration of **C** as well using acid base indicator.

- 1.7. **Choose** a suitable indicator from the list above.
- 1.8. **Calculate** the concentration ratio of the three species originating from the acid at pH = 4.03. Give the result as $[H_2A] : [HA^-] : [A^{2-}] =:.....:1$
- 1.9. **Calculate** the percentage of the H^+ ions originating from the second deprotonation step of **C** in the initial solution (at pH = 2.33).

Part III.

It is known that both acids contain C, H and O atoms only. One of the two unknown compounds is optically inactive, but there are two chirality centers, and the other one is an aromatic compound.

- 1.10. **Draw** the possible structures of the two unknown acids (with stereochemistry and *R/S* notation for chiral centers where necessary).

Solution

1.1.

Titrated as a diprotic acid: $n(\text{NaOH}) = 0.100 \text{ mol dm}^{-3} \cdot 0.01804 \text{ dm}^3 = 1.804 \cdot 10^{-3} \text{ mol}$

$$n(\text{acid}) = n(\text{NaOH})/2 = 9.02 \cdot 10^{-4} \text{ mol}$$

$$\text{In the total stock solution: } \frac{200}{25} \cdot 9.02 \cdot 10^{-4} \text{ mol} = 7.216 \cdot 10^{-3} \text{ mol}$$

$$M(\text{acid}) = 1.200 \text{ g} / 7.216 \cdot 10^{-3} \text{ mol} = \mathbf{166 \text{ g mol}^{-1}}$$

1.2.

$$\text{At pH} = 5.51 \quad [\text{HA}^-] = [\text{A}^{2-}] \Rightarrow \text{pH} = \text{p}K_{a,2} \Rightarrow K_{a,2} = 10^{-5.51} = \mathbf{3.09 \cdot 10^{-6}}$$

$$\text{At pH} = 2.97 \quad \text{theoretically } [\text{HA}^-] = [\text{H}_2\text{A}] \Rightarrow K_{a,1} = 10^{-2.97} = \mathbf{1.07 \cdot 10^{-3}}$$

1.3.

K_{ax} (x is **1** or 2) based on the graph is probably inaccurate due to the following two factors: the total concentration of the acid in the titrated solution was relatively too (high/**low**) while the K_{ax} value in question was relatively too (**large**/small).

Better estimate calculation:

$$K_a = K_{a,1} \cdot K_{a,2} \rightarrow K_{a,1} = 3.99 \cdot 10^{-9} / 3.09 \cdot 10^{-6} = \mathbf{1.29 \cdot 10^{-3}}$$

1.4.

$$\text{p}K_{a,1} = -\log(1.29 \cdot 10^{-3}) = 2.89$$

$$\text{At pH}_a \text{ an ampholyte solution exists, where } \text{pH} = \frac{1}{2} (\text{p}K_{a,1} + \text{p}K_{a,2}) = \frac{1}{2} (2.89 + 5.51) = \mathbf{4.20}$$

1.5.

$$\text{Concentration of stock solution: } c_1 = 7.216 \cdot 10^{-3} \text{ mol} / 0.200 \text{ dm}^3 = 0.03608 \text{ mol dm}^{-3}$$

$$[\text{HA}^-] \approx [\text{H}^+] \quad (\text{because } K_{a,1} \text{ much larger than } K_{a,2})$$

$[\text{H}_2\text{A}] = c_1 - [\text{H}^+]$ ($[\text{H}^+]$ can't be neglected compared to the initial concentration, but the second deprotonation can be.)

$$K_{a,1} = [\text{H}^+]^2 / (c_1 - [\text{H}^+])$$

$$\frac{[\text{H}^+]^2}{0.03608 - [\text{H}^+]} = 1.29 \cdot 10^{-3}$$

From the equation: $[H^+] = 0.00621 \text{ mol dm}^{-3}$

$$\text{pH}_x = 2.21$$

At that point of the titration there is $9.02 \cdot 10^{-4} \text{ mol Na}_2\text{A}$ in the solution.

The volume of the solution is: $25.00 \text{ cm}^3 + 18.04 \text{ cm}^3 = 43.04 \text{ cm}^3$

$$c_2 = 9.02 \cdot 10^{-4} \text{ mol} / 0.04304 \text{ dm}^3 = 0.02096 \text{ mol dm}^{-3}$$



The 2nd step of the hydrolysis can be neglected ($K_{h,2} = 7.75 \cdot 10^{-12}$, that is too small.)

$$[\text{HA}^-] \approx [\text{OH}^-]$$

$$[\text{A}^{2-}] \approx c_2 - [\text{OH}^-] \approx c_2 \quad (K_h \text{ is too small.})$$

$$\frac{[\text{OH}^-]^2}{0.02096} = 3.24 \cdot 10^{-9}$$

$$[\text{OH}^-] = 8.24 \cdot 10^{-6} \text{ mol dm}^{-3}$$

$$\text{pOH} = 5.08 \quad \Rightarrow \quad \text{pH}_b = \mathbf{8.92}$$

1.6.

The acid can only be titrated as diprotic. Phenolphthalein has the right color change range.

1.7.

Phenolphthalein is again the best for the titration. Cresol red should also work with a slightly more acidic color change than the end point.

1.8.

$$\alpha_H = [\text{H}_2\text{A}] : [\text{HA}^-] : [\text{A}^{2-}] = \frac{[\text{H}^+]^2}{K_1 K_2} : \frac{[\text{H}^+]}{K_2} : 1.00 = \mathbf{1.024 : 6.62 : 1.00}$$

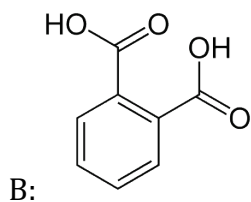
1.9.

$$[\text{HA}^-] : [\text{A}^{2-}] = \frac{[\text{H}^+]}{K_2} : 1.00 = 332 : 1$$

$$\frac{[\text{A}^{2-}]}{[\text{HA}^-] + 2[\text{A}^{2-}]} = \frac{1}{332 + 2} = 2.99 \cdot 10^{-3} \quad \approx \mathbf{0.3\%}$$

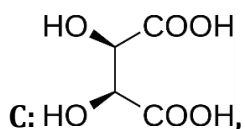
1.10.

Considering the molar masses and the two carboxylate groups, only **B** can be aromatic, and it is one of the benzenedicarboxylic acids, phthalic acid.



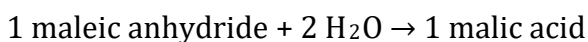
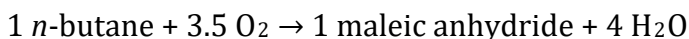
The *meta* and *para* isomers cannot be excluded by the students based on the limited data available. Actually, the first and second dissociation constants of the other two isomers are closer to each other than of the *ortho* isomer in which the interaction between the two carboxylic groups increases the first and decreases the second dissociation constant.

Based on the molar masses and two chirality centers with symmetry, **C** must be (2R,3S)-tartaric acid.



2. Malic acid

Malic acid is a diprotic organic acid found in apples and other fruits. It is also prepared in the chemical industry by the following two-step process, for which balanced chemical equations are given.



The ^1H NMR spectrum of maleic anhydride contains one singlet. The ^{13}C NMR spectrum of the compound contains two lines, a relatively intense one, and a less intense one downfield from the other.


2.1. Give the molecular and structural formulas of the three organic compounds.

2.2. Give the number of the lines in the ^{13}C NMR spectrum of malic acid.

Apple juice is a nice drink itself but is also used to make apple cider vinegar in a two-step process. In the first, fermentation produces ethanol from the sugars in apple juice. Interestingly, malic acid is also fermented in this step into ethanol. In the second, ambient oxygen oxidizes the ethanol to acetic acid in the presence of microbes. It can be assumed that all the sugars present in apple juice are simple hexoses that have the same formula as glucose and are fermented very similarly.

2.3. Give the balanced chemical equations of the reactions of the apple cider vinegar preparation process.

The structure of malic acid contains one asymmetric carbon atom, so the molecule is chiral. In apples, only the enantiomer called L-malic acid occurs, in which the asymmetric carbon atom has *S* configuration in the CIP convention. The other enantiomer, D-malic acid is the mirror image.

2.4. Give the stereostructures of the two enantiomers using wedge-dash notation ( ;).

Interestingly, chemical vendors sell three different kinds of malic acid: they are called L-(-)-Malic acid, D-(+)-Malic acid, and racemic DL-Malic acid .

2.5. Match the product to the properties given in the table.

product identifier (D, L, DL)	properties
	price: 0.50 euros/g; melting point range: 101 - 103 °C
	price: 0.10 euros/g; melting point range: 131 - 133 °C
	price: 30 euros/g; melting point/range: 98 – 102 °C

2.6. Identify the product produced directly by the industrial method shown above.

In a small family business producing apple cider vinegar from apple juice, one day the final product did not contain any alcohol but tasted sweet rather than sour. The chief chemist discovered that the same apple juice was used as in the previous day when everything went OK. There was a pH-meter in good working order in the small lab and some equipment for acid-base titrations. To discover what went wrong, a few experiments were carried out. The chief chemist also remembered some important facts that were established by earlier investigations when the business was started:

- The acidity of apple juice is practically only caused by malic acid.
- The acidity of proper apple cider vinegar is practically only caused by acetic acid.
- Neither apple juice, nor apple cider vinegar contains any metals in concentrations comparable to those of their major organic components (not even potassium and sodium).

First, the 2.00 cm³ of the proper apple cider vinegar produced on the previous day was titrated with 0.1000 mol/dm³ sodium hydroxide solution using phenolphthalein as an indicator. The end point was reached at 21.72 cm³. Then a sample was prepared by mixing 2.00 cm³ of the proper apple cider vinegar with 10.86 cm³ of 0.1000 mol/dm³ sodium hydroxide solution and enough water to bring the final volume to 25.00 cm³. The pH of this solution was measured as 4.76.

2.7. Calculate the acetic acid content of proper apple cider vinegar in g/dm³ units, and then **estimate** the pK_a of acetic acid.

Next, 10.00 cm³ of apple juice was titrated with 0.1000 mol/dm³ sodium hydroxide solution using phenolphthalein as an indicator. The end point was reached at 11.01 cm³. In this case, two samples were prepared for pH measurement. In the first, 10.00 cm³ of apple juice was mixed with 3.67 cm³ of 0.1000 mol/dm³ sodium hydroxide solution and the final volume was adjusted to 25.00 cm³: the pH was measured as 3.67. In the second, 10.00 cm³ of apple juice was mixed with 7.35 cm³ of 0.1000 mol/dm³ sodium hydroxide solution and the final volume was adjusted to 25.00 cm³: the pH was measured as 4.95.

2.8. Calculate the malic acid content of apple juice in g/dm³ units, and then **estimate** the two pK_a values of malic acid.

2.9. Based on the data already available, estimate the sugar content of apple juice in g/dm³ units assuming that the volume of the solution does not change significantly during fermentation. Assume 100% efficiency in all steps.


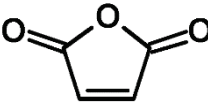
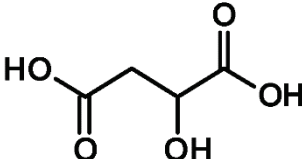
Then it was time to analyze the sweet batch obtained. 5.00 cm³ of this solution was diluted to 100.00 cm³, the pH of the resulting solution was 3.03. Then another 5.00 cm³ of the solution was mixed with 5.00 cm³ of 0.1000 mol/dm³ NaOH first and diluted to 100.00 cm³. The pH of the resulting solution was 4.52.

2.10. Calculate the concentrations of acetic and malic acids in the sweet batch in g/dm³ units.

2.11. Calculate the concentration of sugars in the in the sweet batch in g/dm³ units.

Solution

2.1.

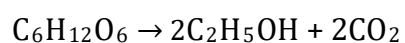
	molecular formula	structural formula
n-butane	C_4H_{10}	
maleic anhydride	$C_4H_2O_3$	
malic acid	$C_4H_6O_5$	

2.2.

4 lines as there are 4 different carbon atoms (all of them are singlets under proton decoupling)

2.3.

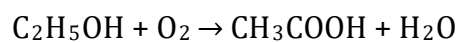
Fermentation of sugars:



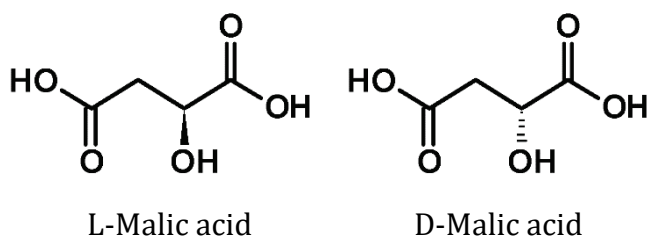
Fermentation of malic acid:



Oxidation of ethanol:



2.4.



2.5.

L-(-)-Malic acid 0.50 euros/g

DL-Malic acid 0.10 euros/g

D-(+)-Malic acid 30 euros/g

Note: the first and the third products have the same melting points, so they are enantiomers. Therefore, the second product is the racemic malic acid. The first product is a lot less expensive as it occurs in nature in an enantiomerically pure form, which is not true for the third one.

2.6.

Racemic DL-Malic acid

2.7.

1:1 acid-base reaction, $0.1000 \text{ mol/dm}^3 \cdot 21.72 \text{ cm}^3 / 2.00 \text{ cm}^3 = 1.086 \text{ mol/dm}^3$

$1.086 \text{ mol/dm}^3 \cdot 60.05 \text{ g/mol} = 65.21 \text{ g/dm}^3$

pK: equilibrium concentrations in the 25.00 cm^3 sample

$[\text{H}^+] = 10^{-4.76} \text{ mol/dm}^3 = 1.738 \cdot 10^{-5} \text{ mol/dm}^3$

$[\text{Na}^+] = 0.1000 \text{ mol/dm}^3 \cdot 10.86 \text{ cm}^3 / 25.00 \text{ cm}^3 = 0.04344 \text{ mol/dm}^3$

As the solution is acidic, the concentration of hydroxide ion is very low. From charge balance:

$[\text{CH}_3\text{COO}^-] = [\text{Na}^+] + [\text{H}^+] = 0.04346 \text{ mol/dm}^3$

$[\text{CH}_3\text{COOH}] = 1.086 \text{ mol/dm}^3 \cdot 2.00 \text{ cm}^3 / 25.00 \text{ cm}^3 - [\text{CH}_3\text{COO}^-] = 0.04342 \text{ mol/dm}^3$

$K_a = [\text{H}^+][\text{CH}_3\text{COO}^-] / [\text{CH}_3\text{COOH}] = 1.740 \cdot 10^{-5} \text{ mol/dm}^3$

$\text{p}K_a = 4.76$

Remark: In the present case a shorter solution is possible by noting that the added NaOH neutralizes exactly 50% of the acetic acid. If $[\text{Na}^+] \gg [\text{H}^+]$ then the equilibrium concentrations of acetate and acetic acid are practically equal, so $\text{p}K_a = \text{pH}$. However, the conditions of using the simplified formula (Henderson-Hasselbalch equation) need to be satisfied.

2.8.

1:2 acid-base reaction, $0.1000 \text{ mol/dm}^3 \cdot 11.01 \text{ cm}^3 / 10.00 \text{ cm}^3 / 2 = 0.05505 \text{ mol/dm}^3$

$0.05505 \text{ mol/dm}^3 \cdot 134.09 \text{ g/mol} = 7.382 \text{ g/dm}^3$

pK calculations:

In both measured samples, the analytical concentration of malic acid is:

$$[\text{C}_4\text{H}_6\text{O}_4] + [\text{C}_4\text{H}_5\text{O}_4^-] + [\text{C}_4\text{H}_4\text{O}_4^{2-}] = 0.05505 \text{ mol/dm}^3 \cdot 10.0 \text{ cm}^3 / 25.00 \text{ cm}^3 = 0.02202 \text{ mol/dm}^3$$

From the dissociation equilibria:

$$[\text{C}_4\text{H}_5\text{O}_4^-] = 0.02202 \text{ mol/dm}^3 \cdot K_{a1} [\text{H}^+] / ([\text{H}^+]^2 + K_{a1} [\text{H}^+] + K_{a1} K_{a2})$$

$$[\text{C}_4\text{H}_4\text{O}_4^{2-}] = 0.02202 \text{ mol/dm}^3 \cdot K_{a1} K_{a2} / ([\text{H}^+]^2 + K_{a1} [\text{H}^+] + K_{a1} K_{a2})$$

From the first pH measurement:

$$[\text{H}^+] = 10^{-3.67} \text{ mol/dm}^3 = 2.138 \cdot 10^{-4} \text{ mol/dm}^3$$

$$[\text{Na}^+] = 0.1000 \text{ mol/dm}^3 \cdot 3.67 \text{ cm}^3 / 25.00 \text{ cm}^3 = 0.01468 \text{ mol/dm}^3$$

As the solution is acidic, the concentration of hydroxide ion is very low. From charge balance:

$$[\text{C}_4\text{H}_5\text{O}_4^-] + 2[\text{C}_4\text{H}_4\text{O}_4^{2-}] = [\text{Na}^+] + [\text{H}^+] = 0.01489 \text{ mol/dm}^3$$

$$0.02202 \text{ mol/dm}^3 \cdot (K_{a1} [\text{H}^+] + 2K_{a1} K_{a2}) / ([\text{H}^+]^2 + K_{a1} [\text{H}^+] + K_{a1} K_{a2}) = 0.01489 \text{ mol/dm}^3$$

$$(K_{a1} \cdot 2.138 \cdot 10^{-4} \text{ mol/dm}^3 + 2K_{a1} K_{a2}) / ((2.138 \cdot 10^{-4} \text{ mol/dm}^3)^2 + K_{a1} \cdot 2.138 \cdot 10^{-4} \text{ mol/dm}^3 + K_{a1} K_{a2}) = 0.6762$$

$$3.091 \cdot 10^{-8} \text{ mol}^2/\text{dm}^6 - K_{a1} \cdot 6.923 \cdot 10^{-5} \text{ mol/dm}^3 - K_{a1} \cdot K_{a2} \cdot 1.3238 = 0 \text{ (Eq. 1)}$$

From the second pH measurement:

$$[\text{H}^+] = 10^{-4.95} \text{ mol/dm}^3 = 1.122 \cdot 10^{-5} \text{ mol/dm}^3$$

$$[\text{Na}^+] = 0.1000 \text{ mol/dm}^3 \cdot 7.35 \text{ cm}^3 / 25.00 \text{ cm}^3 = 0.02940 \text{ mol/dm}^3$$

As the solution is acidic, the concentration of hydroxide ion is very low. From charge balance:

$$[\text{C}_4\text{H}_5\text{O}_4^-] + 2[\text{C}_4\text{H}_4\text{O}_4^{2-}] = [\text{Na}^+] + [\text{H}^+] = 0.02941 \text{ mol/dm}^3$$

$$0.02202 \text{ mol/dm}^3 \cdot (K_{a1} [\text{H}^+] + 2K_{a1} K_{a2}) / ([\text{H}^+]^2 + K_{a1} [\text{H}^+] + K_{a1} K_{a2}) = 0.02941 \text{ mol/dm}^3$$

$$(K_{a1} \cdot 1.122 \cdot 10^{-5} \text{ mol/dm}^3 + 2K_{a1} K_{a2}) / ((1.122 \cdot 10^{-5} \text{ mol/dm}^3)^2 + K_{a1} \cdot 1.122 \cdot 10^{-5} \text{ mol/dm}^3 + K_{a1} K_{a2}) = 1.3356$$

$$1.681 \cdot 10^{-10} \text{ mol}^2/\text{dm}^6 + K_{a1} \cdot 3.765 \cdot 10^{-6} \text{ mol/dm}^3 - K_{a1} \cdot K_{a2} \cdot 0.6644 = 0 \text{ (Eq. 2)}$$

Eq.1 and Eq. 2 are two equations with two unknowns, which can be solved:

$$(1.681 \cdot 10^{-10} \text{ mol}^2/\text{dm}^6 + K_{a1} \cdot 3.765 \cdot 10^{-6} \text{ mol/dm}^3 - K_{a1} \cdot K_{a2} \cdot 0.6644) \cdot 1.3238 - (3.091 \cdot 10^{-8} \text{ mol}^2/\text{dm}^6 - K_{a1} \cdot 6.923 \cdot 10^{-5} \text{ mol/dm}^3 - K_{a1} \cdot K_{a2} \cdot 1.3238) \cdot 0.6644 = 0$$

$$-2.031 \cdot 10^{-8} \text{ mol}^2/\text{dm}^6 + K_{a1} \cdot 5.098 \cdot 10^{-5} \text{ mol/dm}^3 = 0$$

$$K_{a1} = 3.984 \cdot 10^{-4} \text{ mol/dm}^3 \text{ (p}K_{a1} = 3.40\text{)}$$

For K_{a2}

$$1.681 \cdot 10^{-10} \text{ mol}^2/\text{dm}^6 + 3.984 \cdot 10^{-4} \text{ mol}/\text{dm}^3 \cdot 3.765 \cdot 10^{-6} \text{ mol}/\text{dm}^3 - 3.984 \cdot 10^{-4} \text{ mol}/\text{dm}^3 \cdot K_{a2} \cdot 0.6644 = 0$$

$$K_{a2} = 6.302 \cdot 10^{-6} \text{ mol}/\text{dm}^3 \text{ (p}K_{a2} = 5.20\text{)}$$

Remark: Here a shorter line of thought is possible based on the observation that 1/3 and 2/3 equivalents of NaOH are added to malic acid. But this approach yields pK_a values that are slightly off because the two acid dissociation steps are not sufficiently separated.

2.9.

In apple cider vinegar, the concentration of acetic acid is $1.086 \text{ mol}/\text{dm}^3$, $0.05505 \text{ mol}/\text{dm}^3$ of which comes from the fermentation of malic acid. Therefore, the original sugar concentration is $(1.086 \text{ mol}/\text{dm}^3 - 0.05505 \text{ mol}/\text{dm}^3) / 2 = 0.5155 \text{ mol}/\text{dm}^3$. So, the mass concentration is $0.5155 \text{ mol}/\text{dm}^3 \cdot 180.16 \text{ g}/\text{mol} = 92.87 \text{ g}/\text{dm}^3$

2.10.

Denote the analytical concentration of acetic acid c_A , the analytical concentration of malic acid c_M . As we know the acid dissociation constants, the concentrations of the deprotonated forms can be given at a known pH:

$$[\text{CH}_3\text{COO}^-] = c_A \cdot K_a / ([\text{H}^+] + K_a)$$

$$[\text{C}_4\text{H}_5\text{O}_4^-] = c_M \cdot K_{a1} [\text{H}^+] / ([\text{H}^+]^2 + K_{a1} [\text{H}^+] + K_{a1} K_{a2})$$

$$[\text{C}_4\text{H}_4\text{O}_4^{2-}] = c_M \cdot K_{a1} K_{a2} / ([\text{H}^+]^2 + K_{a1} [\text{H}^+] + K_{a1} K_{a2})$$

$$\text{At pH } 3.03, [\text{H}^+] = 9.333 \cdot 10^{-4} \text{ mol}/\text{dm}^3$$

$$[\text{H}^+] = [\text{CH}_3\text{COO}^-] + [\text{C}_4\text{H}_5\text{O}_4^-] + 2[\text{C}_4\text{H}_4\text{O}_4^{2-}]$$

$$9.333 \cdot 10^{-4} \text{ mol}/\text{dm}^3 = c_A/20 \cdot 0.01830 + c_M/20 \cdot 0.2986 + c_M/20 \cdot 0.004032 \text{ (Eq. 3)}$$

$$\text{At pH } 4.52, [\text{H}^+] = 3.030 \cdot 10^{-5} \text{ mol}/\text{dm}^3 \text{ and } [\text{Na}^+] = 0.1000 \text{ mol}/\text{dm}^3 \cdot 5.00 \text{ cm}^3/100.00 \text{ cm}^3 = 0.005000 \text{ mol}/\text{dm}^3$$

$$[\text{H}^+] + [\text{Na}^+] = [\text{CH}_3\text{COO}^-] + [\text{C}_4\text{H}_5\text{O}_4^-] + 2[\text{C}_4\text{H}_4\text{O}_4^{2-}]$$

$$0.005030 \text{ mol}/\text{dm}^3 = c_A/20 \cdot 0.3648 + c_M/20 \cdot 0.7788 + c_M/20 \cdot 0.3240 \text{ (Eq. 4)}$$

Eq. 3 and Eq. 4 are two equations with two unknowns, they can be solved:

$$0.3648 \cdot 9.333 \cdot 10^{-4} \text{ mol}/\text{dm}^3 - 0.01830 \cdot 0.005030 \text{ mol}/\text{dm}^3 = 0.3648 \cdot (c_A/20 \cdot 0.01830 + c_M/20 \cdot 0.2986 + c_M/20 \cdot 0.004032) - 0.01830 \cdot (c_A/20 \cdot 0.3648 + c_M/20 \cdot 0.7788 + c_M/20 \cdot 0.3240)$$

$$2.484 \cdot 10^{-4} \text{ mol}/\text{dm}^3 = 0.004511 c_M$$

$$c_M = 0.05507 \text{ mol}/\text{dm}^3$$

From $0.005030 \text{ mol/dm}^3 = c_A/20 \cdot 0.3648 + 0.05507 \text{ mol/dm}^3/20 \cdot (0.7788 + 0.3240)$

$$c_A = 0.1093 \text{ mol/dm}^3$$

2.11.

Malic acid was not fermented at all, and only a small amount of the sugars was fermented. 0.1093 mol/dm^3 acetic acid formed from the fermentation of 0.05465 mol/dm^3 of sugar (roughly 10% of the normal value), so there is still $0.5155 \text{ mol/dm}^3 - 0.05465 \text{ mol/dm}^3 = 0.4608 \text{ mol/dm}^3$ of sugar in the product, which is 83.02 g/dm^3 .

3. Hydrazine salts

Hydrazine (N_2H_4) is a weak diprotic base ($K_{b1} = 8.5 \cdot 10^{-7}$; $K_{b2} = 8.9 \cdot 10^{-16}$). It can form various anhydrous salts with sulfuric acid. The second acid dissociation constant of sulfuric acid is $K_{a2} = 1.02 \cdot 10^{-2}$.

- 3.1. **Provide** the theoretically conceivable empirical formulas of anhydrous salts.
- 3.2. Starting from aqueous solutions, two of these salts can be expected to form. **Identify** these two salts? **Why** doesn't the aqueous procedure work for the other salts?
- 3.3. **Calculate** the pH of the 0.1 M solutions of these salts?

Solution

3.1.

In theory, salts with the following compositions, containing two types of ions, can exist:

$(\text{N}_2\text{H}_5)(\text{HSO}_4)$, empirical formula $\text{N}_2\text{H}_6\text{SO}_4$

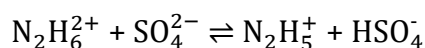
$(\text{N}_2\text{H}_5)_2(\text{SO}_4)$, empirical formula $\text{N}_4\text{H}_{10}\text{SO}_4$

$(\text{N}_2\text{H}_6)(\text{HSO}_4)_2$, empirical formula $\text{N}_2\text{H}_8\text{S}_2\text{O}_8$

$(\text{N}_2\text{H}_6)(\text{SO}_4)$, empirical formula $\text{N}_2\text{H}_6\text{SO}_4$

3.2.

The salt with the empirical formula $\text{N}_2\text{H}_6\text{SO}_4$ can be described as $(\text{N}_2\text{H}_5)(\text{HSO}_4)$ in solution. It is easily shown that the equilibrium:



is strongly shifted to the right due to the high equilibrium constant of the process.

$$K = \frac{K_w}{K_{a2} \cdot K_{b2}} = 1.1 \cdot 10^3$$

The preparation of $\text{N}_2\text{H}_6(\text{HSO}_4)_2$ would also be problematic because the concentration of $\text{N}_2\text{H}_6^{2+}$ ions is very low compared to N_2H_5^+ ions. Their concentration ratio is low even at pH 1.

$$\frac{[\text{N}_2\text{H}_6^{2+}]}{[\text{N}_2\text{H}_5^+]} = \frac{K_{b2}}{K_w} [\text{H}^+] = 8.9 \cdot 10^{-3}$$

That is because the diprotonated hydrazine is a rather strong acid.

$$K_a = \frac{K_w}{K_{b2}} = 11.2$$

We only expect $(\text{N}_2\text{H}_5)(\text{HSO}_4)$ and $(\text{N}_2\text{H}_5)_2(\text{SO}_4)$ as feasible in solution. [Actually, in the solid $(\text{N}_2\text{H}_6)(\text{SO}_4)$ was detected.]

3.3.

Let us first calculate the pH of the 0.1 mol/dm^3 $(\text{N}_2\text{H}_5)(\text{HSO}_4)$ solution. In the first approximation, neglect the hydrolysis of the N_2H_5^+ ion. This seems justified because it is very weak both as an acid and as a base. In this case, the pH is practically determined only by the hydrolysis of the HSO_4^- ion.

$$K_{a2} = \frac{[\text{H}^+]^2}{c - [\text{H}^+]}, \text{ giving } [\text{H}^+] = 2.72 \cdot 10^{-2}, \text{ and pH} = 1.56$$

If we consider the hydrolysis of the N_2H_5^+ ion, it suffices to account for the presence of $\text{N}_2\text{H}_6^{2+}$. The N_2H_4 concentration is still negligible, because $\frac{[\text{N}_2\text{H}_5^+]}{[\text{N}_2\text{H}_4]} = \frac{K_{b1}}{K_w} \cdot [\text{H}^+] = 2.3 \cdot 10^6$ at the estimated pH.

Writing down the usual system of equations (equilibrium constants, charge and mass balance), we arrive at the following third-order equation:

$$\frac{K_{b2}}{K_w \cdot K_{a2}} \cdot [\text{H}^+]^3 + \left(\frac{K_{b2}}{K_w} + \frac{K_{b2} \cdot c}{K_w \cdot K_{a2}} + \frac{1}{K_{a2}} \right) \cdot [\text{H}^+]^2 + [\text{H}^+] - c = 0$$

From this $[\text{H}^+] = 2.71 \cdot 10^{-2} \text{ mol/dm}^3$, and $\text{pH} = 1.57$. So, the neglect of the hydrolysis was justified.

Some simplifications can be made when calculating the pH of $0.1 \text{ mol/dm}^3 (\text{N}_2\text{H}_5)_2(\text{SO}_4)$ solution. The protonation of N_2H_5^+ is certainly negligible, because the $\frac{[\text{N}_2\text{H}_6^{2+}]}{[\text{N}_2\text{H}_5^+]}$ ratio was already very small at pH 1.

If we consider the low basicity of sulfate ions and disregard their protonation, then the system simplifies to the pH of a 0.2 mol/dm^3 weak acid. ($K_a = \frac{K_w}{K_{b1}} = 1.18 \cdot 10^{-8}$)

$$[\text{H}^+] = \sqrt{K_a \cdot c} = 4.86 \cdot 10^{-5}, \text{pH} = 4.3$$

If we do not neglect the protonation of sulfate and the deprotonation of N_2H_5^+ ions, then the system of equations gives another third-order equation.

$$\frac{K_{b1}}{K_w \cdot K_{a2}} \cdot [\text{H}^+]^3 + \left(\frac{K_{b1} \cdot c}{K_w \cdot K_{a2}} + \frac{1}{K_{a2}} + \frac{K_{b1}}{K_w} \right) \cdot [\text{H}^+]^2 + \left(1 - \frac{c}{K_{a2}} \right) [\text{H}^+] - 2c = 0$$

Here $[\text{H}^+] = 1.48 \cdot 10^{-5} \text{ mol/dm}^3$, and $\text{pH} = 4.83$. Here the simplifications caused a sizable difference. Although only a small portion of the sulfate ions gets protonated, the resulting shift in the hydrazonium deprotonation yields a noticeable pH shift.

4. CCM

Caustic calcined magnesita (CCM) is a valuable product from Saudi Arabia, primarily composed of magnesium oxide. CCM with lower purity finds use in industrial applications like wastewater treatment, while higher-purity CCM serves roles in pharmaceuticals, cattle feed supplements, fertilizers, adhesives, tires, and magnetic materials.

Ali was tasked with quickly determining the mass percentage composition of a CCM sample. His measuring equipment (a balance and a thermometer) and chemicals were very limited, so he was thinking about a thermochemical method for this analysis. He was informed that the CCM sample had detectable quantities of calcium oxide and silicon dioxide alongside magnesium oxide. He also located the necessary data.

	$\Delta_f H^\circ$ (kJ mol ⁻¹)		$\Delta_f H^\circ$ (kJ mol ⁻¹)		c_p (kJ kg ⁻¹ K ⁻¹)
CaO(s)	-636	H ⁺ (aq)	0.0	H ₂ O(l)*	4.178
MgO(s)	-602	Cl ⁻ (aq)	-168	CaO(s)	0.918
SiO ₂ (s)	-854	Ca ²⁺ (aq)	-543	MgO(s)	0.877
HCl(g)	-92.5	Mg ²⁺ (aq)	-462	SiO ₂ (s)	0.736
H ₂ O(l)	-286				
CaCl ₂ (s)	-796				
MgCl ₂ (s)	-641				

	$\Delta_r H^\circ$ (kJ mol ⁻¹)
H ⁺ (aq) + OH ⁻ (aq) = H ₂ O(l)	-56.0

* He assumed that all aqueous solutions have the same specific heat capacity as the water.

To begin, he set up a calorimeter with improvised isolation and proceeded to measure its heat capacity the following way. He introduced 200 cm³ of 0.500 M HCl solution (density: 1.007 g cm⁻³) into the calorimeter and 300 cm³ of 0.400 M NaOH solution (density: 1.016 g cm⁻³) into a separate beaker. Both solutions were initially at 24.2 °C. After pouring the alkaline solution into the calorimeter, he observed the highest temperature reached after the reaction, which was recorded as 26.3 °C.

4.1. Calculate the heat capacity of the calorimeter Ali improvised.

Subsequently, Ali carefully weighed out a 12.81 g sample of the CCM. Following a thorough cleaning of the calorimeter, he introduced 500 cm³ of 2.000 M hydrochloric acid (density: 1.033 g cm⁻³) into it and waited for the temperature to stabilize at 24.4 °C (consistent with the lab temperature). He then added the CCM sample into the hydrochloric acid, stirring the solution until it reached its peak temperature of 40.5 °C. Following this reaction, Ali filtered the contents of the calorimeter. After washing and drying, he isolated a solid insoluble material with a mass of 0.51 g.

4.2. Write balanced ionic equations for the relevant processes happening during the dissolution of CCM in hydrochloric acid. **Calculate** their standard enthalpy change.

Ali started to analyze his result and the various factors determining it.

-
- 4.3. Based on Ali's experimental data, **calculate** the mass percentage MgO content of the CCM sample.
- 4.4. **Identify** the factor with the smallest effect on the value of MgO content if neglected in the calculation?
- ☐ Heat capacity of the calorimeter
 - ☐ Warming of the undissolved solid
 - ☐ Warming of the aqueous solution
 - ☐ Reaction of CaO with hydrochloric acid
- 4.5. **Calculate** the final observed temperature if his CCM sample in the same experiment was pure magnesia?

Ali became quite suspicious after carrying out the same calculations. He was happy to locate some phenolphthalein solution. He managed to devise a method using the very same tools and chemicals as in the thermochemical experiment and measure the MgO content more accurately.

- 4.6. **Write** down such a procedure.

Solution

4.1.

200 cm³ 0.500 M HCl solution contains 0.100 mol H⁺,

300 cm³ 0.400 M NaOH solution contains 0.120 mol OH⁻,

0.100 mol H⁺ is the limiting agent, therefore: $Q = 0.100 \text{ mol} \cdot (56 \text{ kJ mol}^{-1}) = 5.60 \text{ kJ}$

200 cm³ of hydrochloric acid: $m_1 = 200 \text{ cm}^3 \cdot 1.007 \text{ g cm}^{-3} = 201.4 \text{ g}$

300 cm³ of NaOH solution: $m_2 = 300 \text{ cm}^3 \cdot 1.016 \text{ g cm}^{-3} = 304.8 \text{ g}$

Total mass of the final solution: $m_1 + m_2 = 506.2 \text{ g}$.

Temperature change: $\Delta T = 26.3 \text{ }^\circ\text{C} - 24.2 \text{ }^\circ\text{C} = 2.1 \text{ }^\circ\text{C} = 2.1 \text{ K}$

$5600 \text{ J} = 4.178 \text{ J g}^{-1} \text{ K}^{-1} \cdot 506.2 \text{ g} \cdot 2.1 \text{ K} + C(\text{calorimeter}) \cdot 2.1 \text{ K}$

$C(\text{calorimeter}) = 552 \text{ J K}^{-1}$

4.2.

$\text{MgO}(s) + 2 \text{H}^+(aq) = \text{Mg}^{2+}(aq) + \text{H}_2\text{O}(l)$

$$\Delta_r H_1 = -462 + (-286) - (-602) = \mathbf{-146 \text{ kJ mol}^{-1}}$$

$\text{CaO}(s) + 2 \text{H}^+(aq) = \text{Ca}^{2+}(aq) + \text{H}_2\text{O}(l)$

$$\Delta_r H_2 = -543 + (-286) - (-636) = \mathbf{-193 \text{ kJ mol}^{-1}}$$

4.3.

There was 0.51 g SiO₂ in the CCM sample. The mass of MgO–CaO was:

$$12.81 \text{ g} - 0.51 \text{ g} = 12.30 \text{ g}.$$

The mass of the final solution: $500 \text{ cm}^3 \cdot 1.033 \text{ g cm}^{-3} + 12.30 \text{ g} = 528.8 \text{ g}$.

Temperature change: $\Delta T = 40.5 \text{ }^\circ\text{C} - 24.4 \text{ }^\circ\text{C} = 16.1 \text{ }^\circ\text{C} = 16.1 \text{ K}$

$$Q = 4.178 \text{ J g}^{-1} \text{ K}^{-1} \cdot 528.8 \text{ g} \cdot 16.1 \text{ K} + 552 \text{ J K}^{-1} \cdot 16.1 \text{ K} + 0.736 \text{ J g}^{-1} \text{ K}^{-1} \cdot 0.51 \text{ g} \cdot 16.1 \text{ K}$$

$$Q = 35\,570 \text{ J} + 8887 \text{ J} + 6.04 \text{ J} = 44\,463 \text{ J} = 44.463 \text{ kJ}$$

If there are x mol of MgO and y mol of CaO in the mixture:

$$40.3x + 56.1y = 12.3$$

$$146x + 193y = 44.463$$

From these equations: $x = 0.2919$

$$m(\text{MgO}) = 0.2919 \text{ mol} \cdot 40.3 \text{ g mol}^{-1} = 11.76 \text{ g}$$

$$w(\text{MgO}) = 11.76 \text{ g} : 12.81 \text{ g} = 0.92 \rightarrow \quad \mathbf{92 \text{ w\% MgO}}$$

4.4.

Warming of the undissolved solid

4.5.

12.81 g of pure MgO dissolution would result in 46.408 kJ released.

Taking the heat capacity of the whole system into account, this means a temperature increase of 16.8 °C and a peak temperature of 41.2 °C

Since the temperature is reported to one decimal, the procedure is very sensitive to the accuracy of the temperature change measured. The calculated MgO content is not very reliable unless the thermal measurements were much more accurate.

4.6.

With the help of the phenolphthalein solution the excess of the HCl solution used to dissolve the sample could be determined:

Using a balance and knowing the density of the acid and base solution, one can measure out an excess of acid solution (measuring the mass of the container with and without the acid) and the mass of the added CCM sample.

If one uses the solutions used for the heat capacity measurement and starts adding NaOH solution dropwise after the dissolution of CCM, one can observe when the excess acid is neutralized, and the mixture turns basic (pink with phenolphthalein).

The mass of the added NaOH solution at that point will allow the calculation of the acid amount needed to dissolve the CCM. Since the balance can reliably measure 0.01 g, the results are much more reliable.

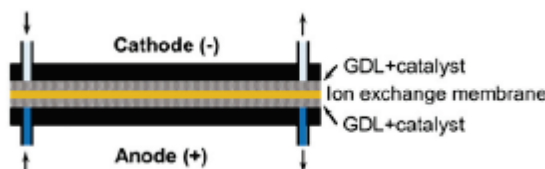
E.g.:

Measuring out 12.81 g from the sample with 92% MgO or from pure MgO and dissolving either of them in 400 cm³ of 2.000 M HCl solution will result in mixtures that require different amounts from the 0.400 M NaOH solution for neutralization. The difference between the masses of these solutions (cca. 80 g) can be measured quite accurately.

5. Carbon capture

Carbon capture, storage and utilization is an important area of technological research. A few years ago, a water-fed electrolyzer was reported to achieve a current density of 420 mA/cm^2 for CO generation without difficulty. The cell design is as follows:

The key is the central ion exchange membrane, in which certain ions are mobile. On either side of this membrane is a GDL - a gas diffusion layer. This is a partially wettable porous material on whose surface a catalyst is deposited. Optimally, both the gas and the electrolyte enter and leave the pores and electricity is conducted through the layer.



5.1. What could be this cheap, modifiable, inert, porous, and conductive layer on the cathode side?

This carrier is activated on the cathode side by a silver nanoparticle catalyst. On the anode side, the gas diffusion layer is a porous Ti-film with an IrOx nanoparticle catalyst on its surface.

Humidified carbon dioxide is passed through the cathode space wetted with a neutral solution, while a more concentrated (1 M) KOH solution is usually passed through the anode space.

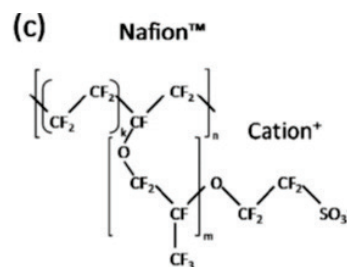
5.2. Give the expected cathode and anode electrode reactions (in a form appropriate for the pH of solutions). **Give** is the net reaction of electrolysis?

The material of the ion exchange membrane is indeed crucial. Commonly used porous polymers in electrochemistry, such as Nafion or SPEEK (structures are on the figure on the right) present practical challenges in this system.

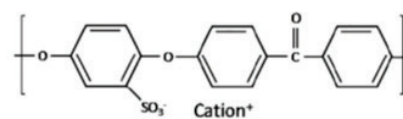
If these membrane materials were employed, two ions could permeate them, leading to undesirable outcomes. One ion can alter the pH at the cathode, influencing product composition through an alternative electrode reaction. On the other hand, if the other ion flows through the membrane, the cathode space would maintain a near-neutral pH, but the solid filling the pores would hinder extended electrolysis.

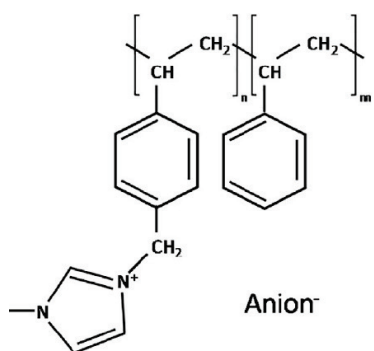
5.3. Identify these two ions and the direction in which they could flow across the membranes.

Write down the side reaction mentioned for one of them and the formula of the solid that would form in the pores due to the flow of the other ion.



SPEEK: sulfonated poly(ether ketone)





If the ion-exchange membrane is made of the polymer on the left, the situation improves. Additional chemical reactions are still likely to happen in the cathode space due to the high concentration of carbon dioxide.

5.4. **Name** the ions and the direction in which they can flow through this separation membrane.

In the case of continuous operation (after one hour), steady-state operation of the system is established and the two-component gas leaving the anode space will have only 1/3 as the oxygen mole fraction.

- 5.5. **Name** the other component in the gas. **Determine**, based on the stoichiometry of the chemical and electrochemical processes involved, which of the various ions capable of passing through the membrane serves as the primary charge carrier.
- 5.6. In the case of ideal electrochemical selectivity, **calculate** the fraction of the CO₂ input that is converted to CO in this steady state?
- 5.7. **Calculate** the minimum CO₂ volume flow rate with a 100 cm² electrode and a steady current density of 420 mA/cm². The temperature of the gas at atmospheric pressure is 60°C.

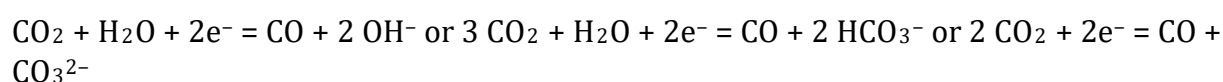
Solution

5.1.

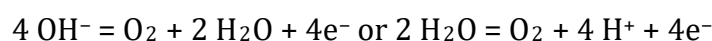
graphite

5.2.

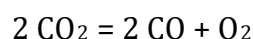
cathode:



anode:



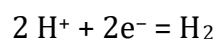
net:



5.3.

Protons or potassium ions would be able to permeate the membrane from the anode to the cathode.

If protons decreased the pH at the cathode, then hydrogen evolution could start more easily:



The precipitation of solid KHCO_3 in the pores of the cathode could be the other challenge.

5.4.

Anions in the system, i.e.: OH^- , HCO_3^- , CO_3^{2-} could get through this membrane from the cathode to the anode.

5.5.

The other component must be CO_2 from the anions diffusing through the membrane. Thus, hydroxide cannot be the primary charge carrier.

If one mol of oxygen is produced on the anode, then 4 moles of acid are also produced. That would produce 4 moles of CO_2 if hydrocarbonate anions or 2 moles if carbonate ions were the main carriers of charge. Thus, carbonate ions are the main carriers of charge through the membrane:



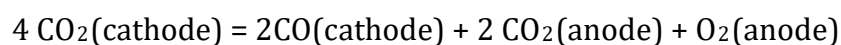
5.6.

Half of the CO_2 will get reduced, the other half will be transported through the membrane as carbonate.

5.7.

The current flowing through the 100 cm^2 electrode is 42 A.

That is 0.435 mmol of electrons in a second and the same amount of CO_2 reacting:



Under these conditions 0.435 mmol of ideal gas is 11.9 cm^3 . that means a $42.8 \text{ dm}^3/\text{hour}$ flow of the gas.

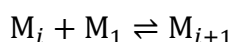
Reference:

Endrődi, B., Samu, A., Kecsenovity, E. *et al.* Operando cathode activation with alkali metal cations for high current density operation of water-fed zero-gap carbon dioxide electrolyzers. *Nat Energy* 6, 439–448 (2021). <https://doi.org/10.1038/s41560-021-00813-w>

6. Nanoparticles

Nanoparticles have attracted growing scientific interest in recent decades. Physical, optical and electronic properties of nanoparticles in comparison with bulk phases of similar chemical composition are fundamentally determined by their size. However, this size is never uniform, as particles of varying sizes are present in any real sample. As a result, the size cannot be characterized by a simple number, not even by an average. Typically, the size distribution of nanoparticles needs to be determined experimentally.

A simplified model of nanoparticle size distribution is the following. Monomer unit M_1 is assumed to be engaged in a series of equilibrium reactions in which growing nanoparticles are produced. M_i denotes the particle with exactly i monomeric units in it. The equilibria are described by the following general reaction:



As a first approach, the equilibrium constants (K) of all such processes are assumed to be equal, so independent of the value of i .

$$\frac{[M_{i+1}]}{[M_i][M_1]} = K$$

Imagine an experiment in which initial concentration of M_1 (before the formation of any nanoparticles) was T , and the molar mass M_1 is W .

6.1. Derive a formula that gives the average molar mass of the nanoparticles formed as a function of T , W , and K .

Hint: you might need the formula to sum an infinite geometric series:

$$\sum_{k=0}^{\infty} a r^k = \frac{a}{1-r} \quad \text{for } |r| < 1$$

The size of the individual nanoparticles is not proportional to their mass. If the particle shape is assumed to be approximately spherical, then the size of a particle (d_i) is proportional to the cube root of the molar mass, which is directly proportional to i , the number of monomeric units in it. So overall:

$$r_i = r_0 \sqrt[3]{i}$$

Here, r_0 is a constant representing the hypothetical size of the 'nanoparticle' containing a single monomeric unit.

Distributions are frequently illustrated using histograms, which are bar diagrams. The x-axis of the histogram displays ranges of the property of interest, while the height of the bars is proportionate to the probability of finding the property within the specified range.

-
- 6.2.** Utilizing spreadsheet software, **create** two histograms based on the outlined system. Set $T = 1 \text{ mol dm}^{-3}$ and $K = 10^6 \text{ mol}^{-1} \text{ dm}^3$ for the calculations. The first histogram should depict the distribution of molar masses of the nanoparticles, with a range width of $100W$. This implies the first column represents the molar mass range $0\text{--}100W$, the second $100W\text{--}200W$, and so forth. The second histogram should display the distribution of nanoparticle sizes, with r_0 as the width of the range.

Solution

6.1.

From the equilibrium constant:

$$[M_{i+1}] = K[M_i][M_1]$$

So generally,

$$[M_{i+1}] = [M_1](K[M_1])^i$$

The total concentration of nanoparticles is (a known formula for the sum of the geometric series is used):

$$\sum_{i=0}^{\infty} [M_{i+1}] = [M_1] \sum_{i=0}^{\infty} (K[M_1])^i = \frac{[M_1]}{1-K[M_1]}$$

In equilibrium, $K[M_1] < 1$ is always true (i.e. the decrease in concentration of M_1 cannot stop before this condition becomes true).

Mass conservation for the nanoparticles is stated as follows:

$$T = \sum_{i=0}^{\infty} (i+1)[M_{i+1}] = [M_1] \sum_{i=0}^{\infty} (i+1)(K[M_1])^i$$

We have already used the formula for the sum of a geometric series, which is:

$$\sum_{i=0}^{\infty} (K[M_1])^i = \frac{1}{1-K[M_1]}$$

There is a clever re-arrangement of the sum that needs to be calculated:

$$\begin{aligned} \sum_{i=0}^{\infty} (i+1)(K[M_1])^i &= (K[M_1])^0 + 2(K[M_1])^1 + 3(K[M_1])^2 + 4(K[M_1])^3 + \dots = ((K[M_1])^0 + \\ &(K[M_1])^1 + \dots) + ((K[M_1])^1 + (K[M_1])^2 + \dots) + ((K[M_1])^2 + (K[M_1])^3 + \dots) + \dots = \\ \sum_{i=0}^{\infty} (K[M_1])^i &+ K[M_1] \sum_{i=0}^{\infty} (K[M_1])^i + (K[M_1])^2 \sum_{i=0}^{\infty} (K[M_1])^i + \dots = \\ (\sum_{i=0}^{\infty} (K[M_1])^i) &(\sum_{i=0}^{\infty} (K[M_1])^i) = \left(\frac{1}{1-K[M_1]}\right)^2 \end{aligned}$$

Therefore:

$$T = \frac{[M_1]}{(1-K[M_1])^2}$$

Rearranging:

$$K^2[M_1]^2 - \left(2K + \frac{1}{T}\right)[M_1] + 1 = 0$$

The physically meaningful root is:

$$[M_1] = \frac{2K + \frac{1}{T} - \sqrt{\left(2K + \frac{1}{T}\right)^2 - 4K^2}}{2K^2} = \frac{1}{K} + \frac{1}{2K^2T} - \frac{1}{K} \sqrt{\frac{1}{KT} + \frac{1}{K^2T^2}}$$

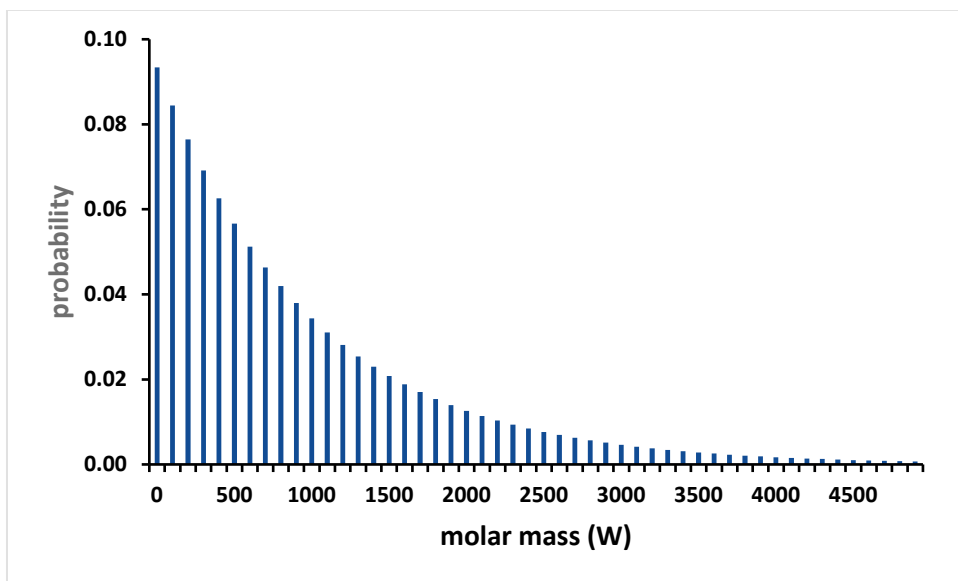
The average molar weight of the nanoparticles is their total mass divided by the total amount of substance:

$$W_{\text{ave}} = \frac{TW}{\frac{[M_1]}{1-K[M_1]}} = WT \frac{1 - \frac{K}{K} - \frac{K}{2K^2T} + \frac{K}{K} \sqrt{\frac{1}{KT} + \frac{1}{K^2T^2}}}{\frac{1}{K} + \frac{1}{2K^2T} - \frac{1}{K} \sqrt{\frac{1}{KT} + \frac{1}{K^2T^2}}} = W \frac{2KT\sqrt{KT+1} - KT}{2KT+1 - 2\sqrt{KT+1}}$$

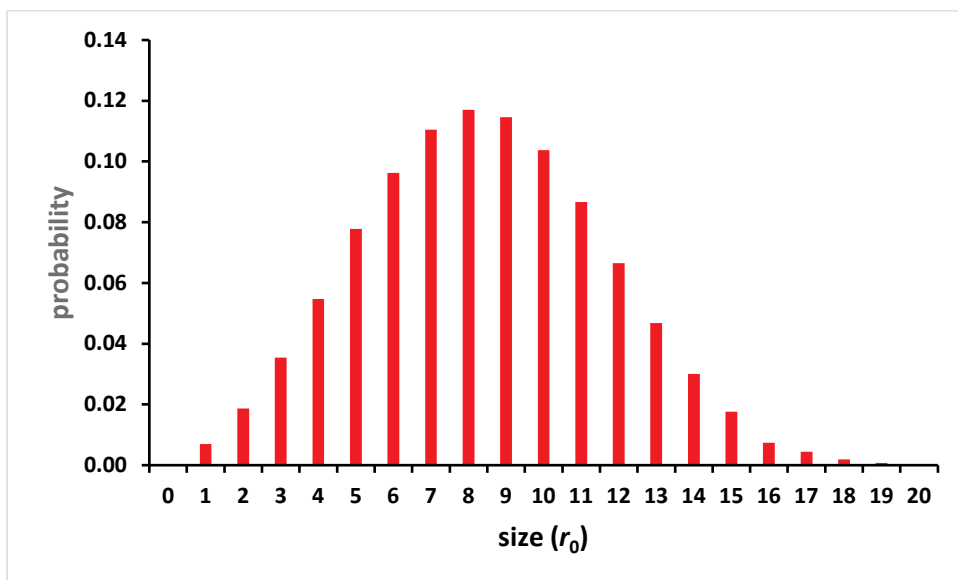
6.2.

A sample Google sheet is available at <http://bit.ly/icho56nano>.

The first histogram:



The second histogram:



7. Adiabatic reactor

A constant-volume adiabatic reactor is primarily a theoretical construct that helps in understanding the concepts of thermodynamics. In a reactor like this no heat exchange is possible with the environment, and the overall volume is constant, so if chemical reactions occur, other parameters like temperature and pressure change in response. This reactor also helps to some extent imagine what happens during gas explosions.

Imagine the burning of carbon monoxide in a constant-volume adiabatic reactor. The fixed volume is 1.00 m^3 , 50.0 mol carbon monoxide and 50.0 mol oxygen is fed into the reactor at the beginning, the initial temperature is 298 K .

You can assume that all gases and their mixture follow the ideal gas law. Note, that the molar entropy of an ideal gas has the following temperature and pressure dependence:

$$S_m(p, T) = S_m(p_0, T_0) + C_p \ln \frac{T}{T_0} - R \ln \frac{p}{p_0}$$

Use the following data:

	$C_p \text{ (Jmol}^{-1}\text{K}^{-1}\text{)}$	$S_{298}^0 \text{ (Jmol}^{-1}\text{K}^{-1}\text{)}$	$\Delta_f H_{298}^0 \text{ (kJ mol}^{-1}\text{)}$
$\text{O}_2(\text{g})$	29.4	205.2	
$\text{CO}(\text{g})$	29.1	197.7	-110.5
$\text{CO}_2(\text{g})$	37.1	213.8	-393.5

The constant pressure molar heat capacities are independent of temperature above 298 K .

7.1. Give the balanced chemical equation of the reaction and its standard enthalpy ($\Delta_r H^\circ$).

The amount of carbon dioxide formed in the reaction is $n_{\text{CO}_2} \text{ mol}$.

7.2. Give the stoichiometrically possible maximum value of n_{CO_2} ?

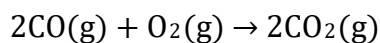
7.3. Using n_{CO_2} as an independent variable **derive** expressions that give certain thermodynamic properties of the system. Where it is not possible to give an expression for the property itself, **give** the expression for the change in the property relative to the initial conditions.

- the internal energy (U) of the system
- the temperature (T) of the system
- the pressure (p) of the system
- the reaction quotient (Q)
- the enthalpy of the system (H)
- the entropy of the system (S)
- the Gibbs free energy of the system (G)
- the equilibrium constant of the reaction (K) at the given temperature (already obtained as T)

-
- 7.4. **Use** spreadsheet software to calculate each property for $n_{\text{CO}_2} = 1 \text{ mol}$, 2 mol , 3 mol ,
On the spreadsheet, **find** the n_{CO_2} value at which the system is in equilibrium
Which of the previously listed properties has an extremum in the equilibrium?

Solution

7.1.



$$\Delta H^\circ_{298} = 2 \cdot (-393.5) - 2 \cdot (-110.5) = -566.0 \text{ kJ/mol}$$

7.2.

50 mol

7.3.

a) Only the change in the internal energy can be calculated. This is zero at any point as the system is isolated (first law of thermodynamics).

$$\text{b) } \Delta U^\circ_{298} = \Delta H^\circ_{298\text{K}} - p^\circ \Delta V^\circ_{298} = -566.0 \text{ kJ/mol} - \Delta n R \cdot 298 \text{ K}$$

$$\Delta n = -1 \text{ mol, so } \Delta U^\circ = -563.5 \text{ kJ/mol}$$

$$n_{\text{CO}} = 50 \text{ mol} - n_{\text{CO}_2}$$

$$n_{\text{O}_2} = 50 \text{ mol} - 0.5 n_{\text{CO}_2}$$

For each gas, $C_V = C_p - R$

From the constant internal energy:

$$0 = -563500 \frac{\text{J}}{\text{mol}} \cdot 0.5 n_{\text{CO}_2} + C_{V,\text{CO}_2} \cdot n_{\text{CO}_2} \cdot \Delta T + C_{V,\text{CO}} \cdot n_{\text{CO}} \cdot \Delta T + C_{V,\text{O}_2} \cdot n_{\text{O}_2} \cdot \Delta T$$
$$\Delta T = \frac{563.5 \frac{\text{kJ}}{\text{mol}} \cdot 0.5 n_{\text{CO}_2}}{(C_{p,\text{CO}_2} - R)n_{\text{CO}_2} + (C_{p,\text{CO}} - R)(50 \text{ mol} - n_{\text{CO}_2}) + (C_{p,\text{O}_2} - R)(50 \text{ mol} - 0.5 n_{\text{CO}_2})}$$

$$\Delta T = \frac{281750 \frac{\text{J}}{\text{mol}} \cdot n_{\text{CO}_2}}{2095 \frac{\text{J}}{\text{K}} - 2.55 \frac{\text{J}}{\text{mol K}} \cdot n_{\text{CO}_2}}$$

$$T = 298 \text{ K} + \Delta T$$

c)

$$p = (50 \text{ mol} - 0.5 n_{\text{CO}_2}) \frac{RT}{V}$$

d)

$$Q = \frac{\left(\frac{p_{\text{CO}_2}}{p^\circ}\right)^2}{\left(\frac{p_{\text{CO}}}{p^\circ}\right)^2 \left(\frac{p_{\text{O}_2}}{p^\circ}\right)} = \frac{(n_{\text{CO}_2})^2 V p^\circ}{(n_{\text{CO}})^2 (n_{\text{O}_2}) R T} = \frac{(n_{\text{CO}_2})^2 \cdot 1.203 \cdot 10^4 \text{ mol K}}{(50 - n_{\text{CO}_2})^2 (50 - 0.5 n_{\text{CO}_2}) T}$$

e) Only the change can be calculated from the initial conditions

$$\Delta H = \Delta U + \Delta(pV)$$

ΔU is already known to be zero, therefore:

$$\Delta H = (p - p_{298}) \cdot 1.00 \text{ m}^3$$

p_{298} is the initial pressure, can be obtained from the ideal gas law (248 kPa)

f) The absolute entropy can be calculated (3rd law of thermodynamics)

$$\begin{aligned} S = & n_{\text{CO}_2} \left(S^\circ_{\text{CO}_2, 298} + C_{p, \text{CO}_2} \cdot \ln \frac{T}{298 \text{ K}} + R \cdot \ln \frac{(100 \text{ mol} - 0.5 n_{\text{CO}_2}) 100 \text{ kPa}}{n_{\text{CO}_2} \cdot p} \right) + \\ & + (50 \text{ mol} - n_{\text{CO}_2}) \left(S^\circ_{\text{CO}, 298} + C_{p, \text{CO}} \cdot \ln \frac{T}{298 \text{ K}} + R \cdot \ln \frac{(100 \text{ mol} - 0.5 n_{\text{CO}_2}) 100 \text{ kPa}}{(50 \text{ mol} - n_{\text{CO}_2}) p} \right) + \\ & + (50 \text{ mol} - 0.5 n_{\text{CO}_2}) \left(S^\circ_{\text{O}_2, 298} + C_{p, \text{O}_2} \cdot \ln \frac{T}{298 \text{ K}} + R \cdot \ln \frac{(100 - 0.5 n_{\text{CO}_2}) 100 \text{ kPa}}{(50 \text{ mol} - 0.5 n_{\text{CO}_2}) p} \right) \end{aligned}$$

g) Only the change can be calculated:

$$\Delta G = \Delta H - \Delta(TS) = (p - p_{298}) \cdot 1.00 \text{ m}^3 + 298 \text{ K} \cdot S_{298} - T \cdot S$$

h) The equilibrium constant of the reaction can be calculated from the standard molar Gibbs energy change of the process. This is not the same as the one calculated in the previous point (i.e. it cannot be dependent on amounts of substances).

$$\Delta G^\circ = \Delta H^\circ - T \Delta(S^\circ)$$

$$\Delta G^\circ = \Delta H^\circ_{298} + \Delta C_p (T - 298 \text{ K}) + T \Delta S^\circ_{298} + T \Delta C_p \cdot \ln \frac{T}{298 \text{ K}}$$

Here ΔS°_{298} is the standard entropy change of the reaction at 298 K, it can be calculated directly from the given standard entropy values as $-173.0 \text{ J}/(\text{mol K})$. ΔC_p is the molar heat capacity change of the reaction, $-13.4 \text{ J}/(\text{mol K})$. Then the equilibrium constant is:

$$K = \exp \left(-\frac{\Delta G^\circ}{RT} \right)$$

7.4.

n_{CO_2} (mol)	T (K)	p (kPa)	Q	$H - H_{298}$ (kJ)	S (kJ/K)	$G - G_{298}$ (MJ)	K
0	298	248	0	0	19.97	0.00	$1.50 \cdot 10^{90}$
1	433	358	$2.34 \cdot 10^{-4}$	110	20.71	-2.90	$1.86 \cdot 10^{59}$
2	567	467	$7.51 \cdot 10^{-4}$	219	21.22	-5.87	$9.15 \cdot 10^{42}$
3	702	575	$1.44 \cdot 10^{-3}$	327	21.60	-8.89	$7.43 \cdot 10^{32}$
4	837	682	$2.26 \cdot 10^{-3}$	434	21.91	-12.0	$1.01 \cdot 10^{26}$
5	972	788	$3.22 \cdot 10^{-3}$	541	22.16	-15.1	$1.05 \cdot 10^{21}$
6	1108	893	$4.30 \cdot 10^{-3}$	646	22.36	-18.2	$1.75 \cdot 10^{17}$
7	1243	998	$5.51 \cdot 10^{-3}$	750	22.53	-21.3	$1.87 \cdot 10^{14}$
8	1379	1101	$6.88 \cdot 10^{-3}$	853	22.67	-24.5	$7.53 \cdot 10^{11}$
9	1515	1203	$8.41 \cdot 10^{-2}$	955	22.80	-27.6	$7.98 \cdot 10^9$
10	1651	1304	$1.01 \cdot 10^{-2}$	1056	22.90	-30.8	$1.76 \cdot 10^8$
11	1787	1404	$1.20 \cdot 10^{-2}$	1156	22.99	-34.0	$6.83 \cdot 10^6$
12	1924	1503	$1.42 \cdot 10^{-2}$	1256	23.06	-37.2	$4.15 \cdot 10^5$
13	2060	1602	$1.66 \cdot 10^{-2}$	1354	23.13	-40.3	$3.62 \cdot 10^4$
14	2197	1699	$1.93 \cdot 10^{-2}$	1451	23.18	-43.5	$4.24 \cdot 10^3$
15	2334	1795	$2.23 \cdot 10^{-2}$	1547	23.22	-46.7	$6.33 \cdot 10^2$
16	2471	1890	$2.57 \cdot 10^{-2}$	1642	23.26	-49.9	$1.16 \cdot 10^2$
17	2608	1984	$2.95 \cdot 10^{-2}$	1736	23.29	-53.1	$2.51 \cdot 10^1$
18	2746	2077	$3.38 \cdot 10^{-2}$	1829	23.31	-56.2	6.33
19	2883	2169	$3.87 \cdot 10^{-2}$	1922	23.33	-59.4	1.81
20	3021	2260	$4.42 \cdot 10^{-2}$	2013	23.340	-62.5	$5.75 \cdot 10^{-1}$
21	3159	2350	$5.06 \cdot 10^{-2}$	2103	23.346	-65.7	$2.02 \cdot 10^{-1}$
22	3297	2440	$5.78 \cdot 10^{-2}$	2192	23.347	-68.8	$7.68 \cdot 10^{-2}$
23	3435	2528	$6.60 \cdot 10^{-2}$	2280	23.343	-72.0	$3.15 \cdot 10^{-2}$
24	3574	2615	$7.55 \cdot 10^{-2}$	2367	23.336	-75.1	$1.38 \cdot 10^{-2}$
25	3712	2700	$8.64 \cdot 10^{-2}$	2453	23.32	-78.2	$6.40 \cdot 10^{-3}$
26	3851	2785	$9.91 \cdot 10^{-2}$	2538	23.31	-81.3	$3.13 \cdot 10^{-3}$
27	3990	2869	$1.14 \cdot 10^{-1}$	2622	23.29	-84.4	$1.60 \cdot 10^{-3}$
28	4129	2952	$1.31 \cdot 10^{-1}$	2704	23.27	-87.4	$8.57 \cdot 10^{-4}$
29	4268	3034	$1.51 \cdot 10^{-1}$	2786	23.24	-90.5	$4.76 \cdot 10^{-4}$
30	4408	3115	$1.75 \cdot 10^{-1}$	2867	23.22	-93.5	$2.74 \cdot 10^{-4}$
31	4547	3195	$2.04 \cdot 10^{-1}$	2947	23.19	-96.5	$1.63 \cdot 10^{-4}$
32	4687	3273	$2.39 \cdot 10^{-1}$	3026	23.15	-99.5	$9.95 \cdot 10^{-5}$
33	4827	3351	$2.80 \cdot 10^{-1}$	3103	23.12	-103	$6.25 \cdot 10^{-5}$
34	4967	3428	$3.31 \cdot 10^{-1}$	3180	23.08	-106	$4.02 \cdot 10^{-5}$
35	5107	3503	$3.95 \cdot 10^{-1}$	3255	23.04	-108	$2.64 \cdot 10^{-5}$
36	5248	3578	$4.74 \cdot 10^{-1}$	3330	22.99	-111	$1.78 \cdot 10^{-5}$
37	5389	3651	$5.74 \cdot 10^{-1}$	3404	22.95	-114	$1.22 \cdot 10^{-5}$
38	5529	3724	$7.04 \cdot 10^{-1}$	3476	22.90	-117	$8.47 \cdot 10^{-6}$
39	5671	3795	$8.74 \cdot 10^{-1}$	3547	22.85	-120	$6.00 \cdot 10^{-6}$
40	5812	3865	1.10	3618	22.79	-123	$4.32 \cdot 10^{-6}$
41	5953	3935	1.42	3687	22.74	-126	$3.15 \cdot 10^{-6}$
42	6095	4003	1.88	3755	22.68	-129	$2.33 \cdot 10^{-6}$
43	6236	4070	2.55	3822	22.62	-131	$1.75 \cdot 10^{-6}$
44	6378	4136	3.62	3888	22.56	-134	$1.32 \cdot 10^{-6}$
45	6520	4201	5.43	3954	22.49	-137	$1.01 \cdot 10^{-6}$
46	6663	4265	8.84	4017	22.42	-139	$7.84 \cdot 10^{-7}$
47	6805	4328	16.4	4080	22.35	-142	$6.13 \cdot 10^{-7}$

48	6948	4390	38.4	4142	22.28	-145	$4.83 \cdot 10^{-7}$
49	7090	4451	160	4203	22.20	-147	$3.85 \cdot 10^{-7}$
50	7233	4510	--	4263	22.10	-150	$3.08 \cdot 10^{-7}$

The equilibrium lies where the entropy has a maximum (second law of thermodynamics), this is close to $n_{\text{CO}_2} = 22$ mol. The $Q = K$ condition is also satisfied close to this point. It is notable that the Gibbs free energy of the system would keep decreasing even at higher conversions. This is a reminder of the fact that the minimum of G characterizes equilibrium conditions at constant temperature and pressure, while the present reactor is adiabatic.

8. Nitrogen oxides

The nitrogen oxides stand out among non-metal oxides, as there is at least one binary molecular oxide corresponding to each oxidation state between +1 and +5.

8.1. Give a molecular formula and a Lewis structure (one resonance structure is sufficient) of the simplest oxide for each oxidation state.

For some oxidation states, multiple oxides are possible. For example, when brown gas **A** is cooled down, a colorless liquid of compound **B** is formed, which is a dimer of **A**. For practical calculations, the volume of the liquid is negligible as compared to the volume of the gas.

8.2. Determine A and B. Give the molecular formula and a Lewis structure of **B**.

Let us consider the chemical equilibrium $2 \text{A(g)} \rightleftharpoons \text{B(g)}$ (reaction **1**) and the following data (assume them to be independent of temperature):

	$\Delta_f H^\circ / \text{kJ/mol}$	$S^\circ / \text{J/(mol}\cdot\text{K)}$
B(g)	9.16	304.29
A(g)	33.18	219.85

8.3. Calculate the equilibrium constant of reaction **1** at 25 °C.

1 mol of **A** is put into an empty container, it is closed with a fixed volume of 25 dm³ and thermostated at 25 °C.

8.4. Calculate the equilibrium pressure of the system.

The standard atmospheric boiling point of **B** is at 21.69 °C. $\Delta H_{\text{vap}} = 22.96 \text{ kJ/mol}$, $\Delta S_{\text{vap}} = 77.9 \frac{\text{J}}{\text{mol}\cdot\text{K}}$ for the evaporation of **B**. Assume them to be independent of temperature.

8.5. Calculate the enthalpy of formation of **B(l)**.

8.6. Calculate the entropy change of the reaction $2 \text{A(g)} = \text{B(l)}$ (reaction **2**).

We can assume that the entropy change of reaction **2** is independent of temperature between -10 and 22 °C.

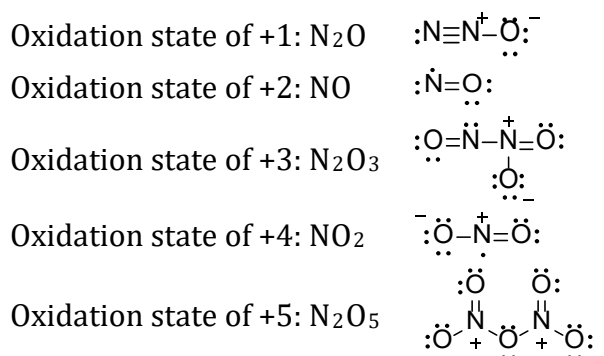
8.7. Calculate the equilibrium constant of reaction **2** at 0 °C.

1 mol of **A** is put into an empty container, it is closed with a fixed volume of 25 dm³ and thermostated at 0 °C.

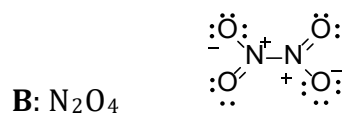
8.8. Calculate the equilibrium pressure of the cooled system.

Solution

8.1.



8.2.



8.3.

$$\Delta H_{\text{reaction}}^{\circ} = \Delta_f H(\mathbf{B}) - 2\Delta_f H(\mathbf{A}) = (9.16) - 2(33.18) = -57.2 \frac{\text{kJ}}{\text{mol}}$$

$$\Delta S_{\text{reaction}}^{\circ} = S(\mathbf{B}) - 2S(\mathbf{A}) = (304.29) - 2(219.85) = -135.41 \frac{\text{J}}{\text{mol}\cdot\text{K}}$$

$$\Delta G_{\text{reaction}}^{\circ} = \Delta H_{\text{reaction}}^{\circ} - T\Delta S_{\text{reaction}}^{\circ} = (-57.2) - (298.15)(-0.13541) = -16.83 \frac{\text{kJ}}{\text{mol}}$$

$$K = \exp\left(-\frac{\Delta G_{\text{reaction}}^{\circ}}{RT}\right) = \exp\left(\frac{16830}{(8.3145)(298.15)}\right) = 887$$

8.4.

$$K = \frac{p_B p^{\circ}}{(p_A)^2} = \frac{y_B}{(y_A)^2} \left(\frac{p^{\circ}}{p_{\text{total}}}\right) = \frac{n_B n_{\text{total}}}{(n_A)^2} \left(\frac{p^{\circ} V}{n_{\text{total}} RT}\right) = \frac{n_B}{(n_A)^2} \left(\frac{p^{\circ} V}{RT}\right) = 887$$

$$K = \frac{x}{(1-2x)^2} \left(\frac{(1)(25)}{(0.08314)(298.15)}\right) = 887$$

Solving for x gives 0.488. Therefore, $n_{\text{total}} = 1-x = 0.512 \text{ mol}$

$$p_{total} = \frac{n_{total}RT}{V} = \frac{(0.512)(8.3145)(298.15)}{(0.025)} (10^{-5}) = 0.508 \text{ bar} = 50.8 \text{ kPa}$$

8.5.

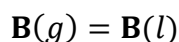
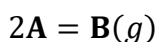
Consider the following reaction $\mathbf{B(l)} \rightarrow \mathbf{B(g)}$:

$$\Delta H_{reaction} = \Delta_f H(\mathbf{B(g)}) - \Delta_f H(\mathbf{B(l)}) = (9.16 \text{ kJ/mol}) - \Delta_f H(\mathbf{B(l)}) = 22.96 \text{ kJ/mol}$$

$$\therefore \Delta_f H(\mathbf{B(l)}) = -13.8 \text{ kJ/mol}$$

8.6.

The provided reaction is the sum of the two reactions:



$$\therefore \Delta S_{reaction} = -135.4 \frac{\text{J}}{\text{mol} \cdot \text{K}} - 77.9 \frac{\text{J}}{\text{mol} \cdot \text{K}} = -213.3 \frac{\text{J}}{\text{mol} \cdot \text{K}}$$

8.7.

$$\Delta H_{reaction} = \Delta_f H(\mathbf{B(l)}) - 2\Delta_f H(\mathbf{A(g)}) = -13.8 - 2(33.18) = -80.16 \frac{\text{kJ}}{\text{mol}}$$

$$\Delta G_{reaction} = \Delta H_{reaction} - T\Delta S_{reaction} = (-80.16) - (273.15)(-0.2133) = -21.9 \frac{\text{kJ}}{\text{mol}}$$

$$K = \exp\left(-\frac{\Delta G_{reaction}}{RT}\right) = \exp\left(\frac{21.9 \cdot 10^3}{(8.3145)(273.15)}\right) = 15400$$

8.8.

With such a Gibbs energy change, the reaction is also expected to go to completion. The equilibrium vapor pressure of $\mathbf{B(l)}$ at 0 °C can be obtained by considering $\mathbf{B(l)} = \mathbf{B(g)}$:

$$\ln\left(\frac{p}{101.325 \text{ kPa}}\right) = \frac{-(22960)}{8.3145} \left(\frac{1}{273.15} - \frac{1}{21.69 + 273.15}\right)$$

$$\Delta G = \Delta H - T\Delta S = (22.96) - (273.15)(0.0779) = 1.68 \text{ kJ/mol}$$

$$K = \exp(-\Delta G/(RT)) = \exp(-1.68 \cdot 1000/(8.3145 \cdot 273.15)) = 0.477$$

$$p_B = K \cdot p^\circ = 0.477 \text{ bar} = 47.7 \text{ kPa}$$

However, even if the entire system is only composed of $\text{N}_2\text{O}_4(\text{g})$ at 273.15 K in 25 dm³, the pressure is still only 45.4 kPa, so there is no condensed phase, and the pressure is 45.4 kPa.

9. Statin drugs

Statins are the drugs of first choice for management of many lipid disorders. All statins interfere with the conversion of 3-hydroxi-3-methyl-glutaryl coenzyme A (HMG-CoA) to the cholesterol precursor mevalonate by HMG-CoA reductase, an early and rate-limiting step in cholesterol synthesis. Statins competitively inhibit HMG-CoA reductase by binding to the enzyme and sterically inhibiting substrate binding.

The family of statins contains some very effective pharmaceutical compounds, a few of which are shown in the drawing below.

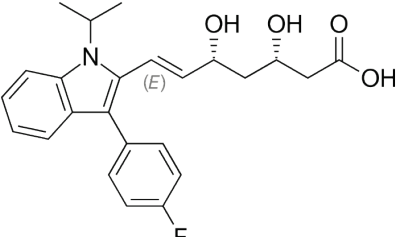
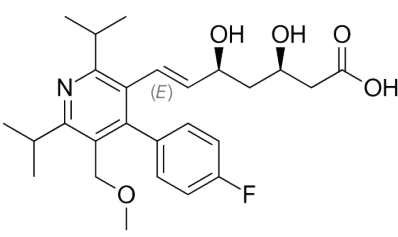
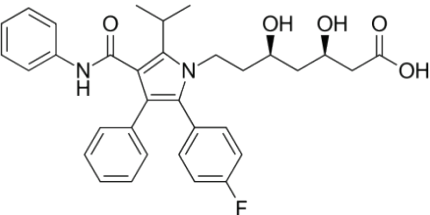
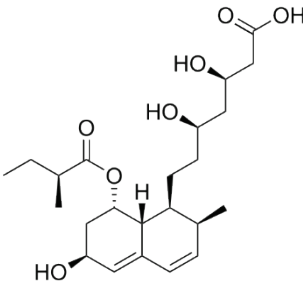
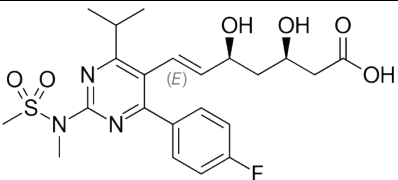
	
fluvastatin	cerivastatin
	
atorvastatin	pravastatin
	
rosuvastatin	

Table 1. Thermodynamic properties of the substrates at 37 °C.

	K_1 / nM	$\Delta_r H$ / kcal/mol	$\Delta_r H$ / kJ/mol
Atorvastatin	14	-4.3	-18.1
Cerivastatin	5.7	-3.3	-13.9
Fluvastatin	256	-	-
Pravastatin	103	-2.5	-10.5
Rosuvastatin	2.3	-9.3	-39.1

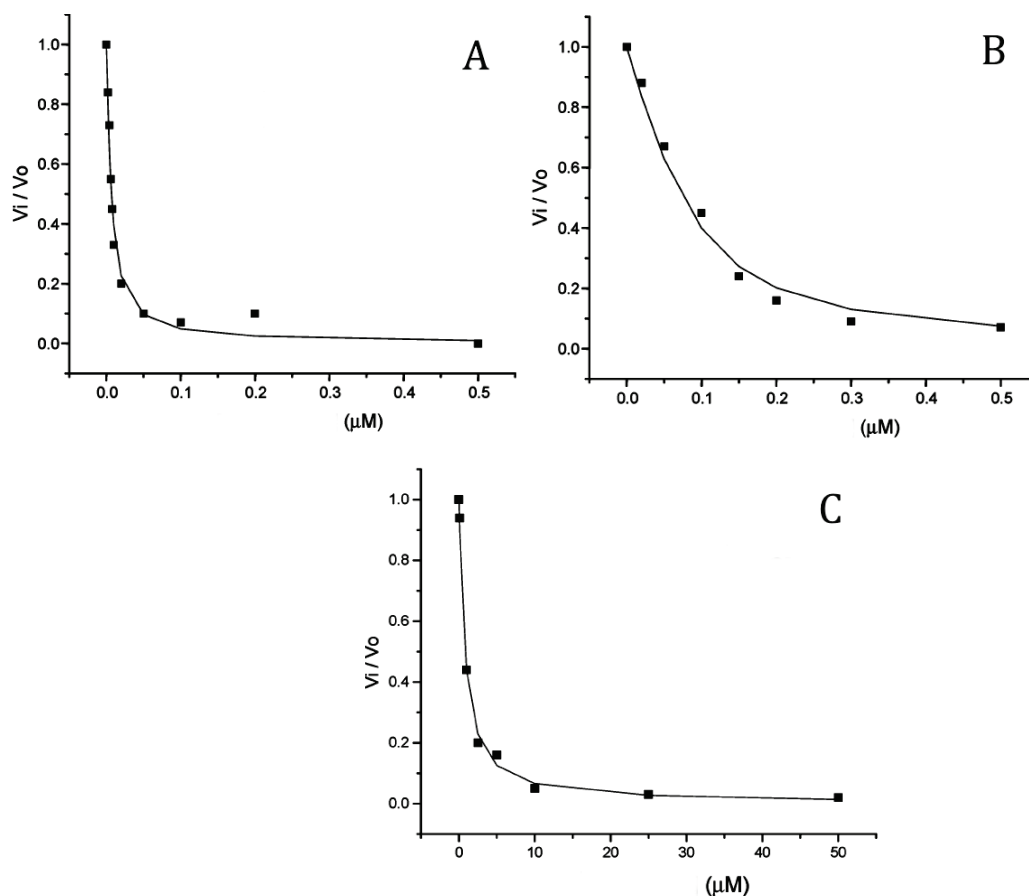
K_I is the equilibrium constant for the dissociation of the enzyme-inhibitor complex. $\Delta_r H$ is the binding enthalpy for the inhibitor and it can be assumed to be temperature independent.

Efficacy and selectivity of the drug substance depends on the strength of binding to the target enzyme. Thus, a binding study is usually carried out for larger active substance families. In a series of experiments the initial activity of the enzyme is measured by spectrophotometry at different substrate concentrations, and the results are evaluated using the formula of initial rate according to Michaelis-Menten kinetics (v_I is the initial rate of the reaction, K_M and v_{max} are coefficients depending on the reaction between the enzyme and substrate, c and $[I]_0$ are the initial concentrations of substrate and inhibitor, respectively):

$$v_I = v_{max} \cdot \frac{c}{K' + c} \quad \text{where } K' = K_M \left(1 + \frac{[I]}{K_I} \right)$$

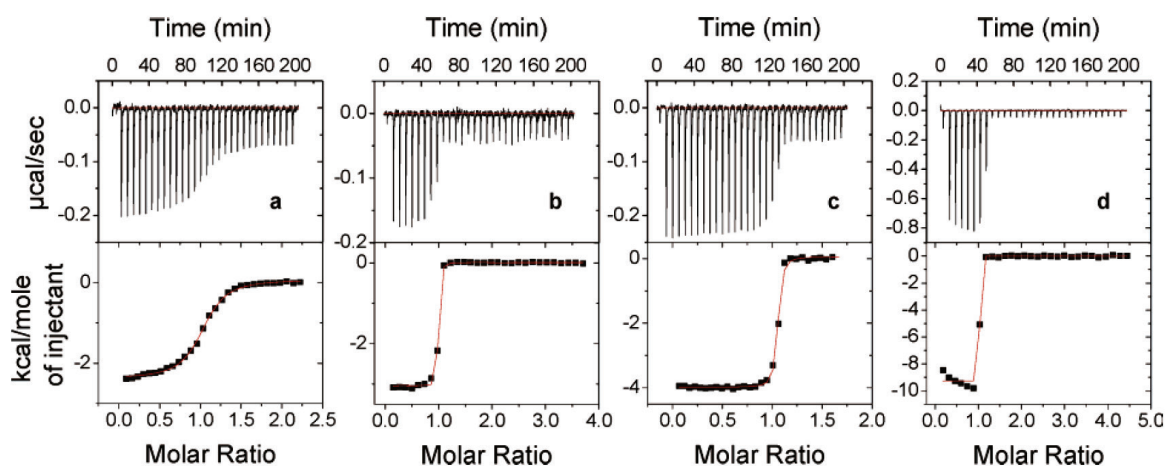
In the present study the binding of the drug molecule was characterized by the ratio v_I/v_0 , where v_0 is the initial rate in the absence of inhibitor at the given substrate (HMG-CoA) concentration. Under the experimental conditions of the study $K_M = 70 \mu\text{M}$ and all experiments were carried out at 37°C .

Results of the study were present on the diagrams A, B and C (v_I/v_0 vs. $[I]/\mu\text{M}$) but unfortunately the names of the active substances disappeared from the graphs.



- 9.1. **Match** the diagrams with the active substances taking into account that at this level of precision multiple drugs can belong to the same diagram.
- 9.2. **Estimate** the order of magnitude of substrate concentration in the spectrophotometry experiments.

Enthalpy change of the binding was determined by calorimetric titration. A solution with known concentration of the enzyme was titrated with the solution of the drug substance. In order to evaluate the results, the molar heat effect (with respect to substrate) versus molar ratio of substrate was shown on a diagram (bottom part of the next figure) but, unfortunately labelling was lost again. However, it was noted that in the case of Fluvastatin the enthalpy change was below the detection limit of the equipment (practically it is 0 kJ/mol).



- 9.3. **Match** diagrams with the drugs above (one molecule to each diagram)
- 9.4. **Determine** the equilibrium constant for the association of each pharmaceutical compound at 25 and at 37 °C.
- 9.5. **Estimate** the (overall) ratio of drug molecules necessary to obtain a solution at 37 °C where the concentration of free (unbound) drug molecules are equal if the enzyme is present
- in a catalytic amount.
 - in excess.

Solution

9.1.

$$\frac{v_I}{v_0} = \frac{\frac{v_{max}c}{K_M \left(1 + \frac{[I]}{K_I}\right) + c}}{\frac{v_{max}c}{K_M + c}} = \frac{K_M + c}{K_M \left(1 + \frac{[I]}{K_I}\right) + c} = \frac{\left(1 + \frac{c}{K_M}\right)}{\frac{[I]}{K_I} + \left(1 + \frac{c}{K_M}\right)} = \frac{K_I \left(1 + \frac{c}{K_M}\right)}{[I] + K_I \left(1 + \frac{c}{K_M}\right)}$$

Therefore, the higher K_I , the less steep the decay of v_I/v_0 .

A is the steepest decay. It should belong to Rosuvastatin and Cerivastatin (same order of magnitude).

C is the least steep decay. It should belong to Fluvastatin and Pravastatin (same order of magnitude).

B is in the middle. It should belong to Atorvastatin.

9.2.

Consider diagram B belonging to Atorvastatin:

$$\frac{v_I}{v_0} ([I] = 0.15 \mu\text{M}) = 0.2$$
$$\frac{K_I \left(1 + \frac{c}{K_M}\right)}{[I] + K_I \left(1 + \frac{c}{K_M}\right)} = \frac{(14 \text{ nM}) \left(1 + \frac{c}{70 \mu\text{M}}\right)}{(150 \text{ nM}) + (14 \text{ nM}) \left(1 + \frac{c}{70 \mu\text{M}}\right)} = 0.2$$

Solving for c gives $117.5 \mu\text{M}$ (magnitude of $100 \mu\text{M}$).

9.3.

a. Pravastatin b. Cerivastatin c. Atorvastatin d. Rosuvastatin

9.4.

$$K_{\text{association}}(T) = \frac{1}{K_{\text{dissociation}}(T)} = \frac{1}{K_I(T)}$$

$$K(T_2) = K(T_1) \exp\left(-\frac{\Delta_r H}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)\right)$$

	$K_i(37\text{ °C}) / \text{nM}$	$\Delta_r H / \text{kJ/mol}$	$K_{\text{assoc}}(37\text{ °C}) / \text{nM}^{-1}$	$K_{\text{assoc}}(25\text{ °C}) / \text{nM}^{-1}$
Atorvastatin	14	-18.1	0.0714	0.0947
Cerivastatin	5.7	-13.9	0.1754	0.2179
Fluvastatin	256	-	0.0039	0.0039
Pravastatin	103	-10.5	0.0097	0.0114
Rosuvastatin	2.3	-39.1	0.4348	0.8004

9.5.

- i. For a catalytic amount of the enzyme, the enzyme-inhibitor complex does not really change the amount of inhibitor, so a 1:1:1:1:1 mixture is needed.
- ii. For an excess of enzyme, the free inhibitor concentration is proportional to K_{ass} . So, the amounts used need to be inversely proportional to K_{ass} .

Reference:

Binding Thermodynamics of Statins to HMG-CoA Reductase, Teresa Carbonell and Ernesto Freire, *Biochemistry* **2005** *44* (35), 11741-11748, <https://doi.org/10.1021/bi050905v>

10. Minions and berries

Dr. Nefario after getting tired of doing evil, started a new project preparing his own brand of berry juice. Unfortunately, the product was a complete flop on the market, so he started a quality check on the process.

It turned out that the flavor compound berrine coming from the fruits is oxidized to diberrine during cooking by the moxone additive they used. Their research showed that when 75% of the berrine is used up, then the juice will become unpalatable due to the bitter taste of diberrine.

The reaction takes place according to the following overall reaction:



During their experiments they changed the quantity of the fruit and the added moxone. After starting cooking, they took samples from the mixture every minute and determined the initial rate of formation of diberrine. Every batch of juice was 100 dm³. The fruit contains 8.0 mass% berrine, and we can suppose that all of it is liberated at the start of cooking. Moxone was added as 1.0 mol/dm³ solution.

experiment	fruit (kg)	moxone (dm ³)	diberrine formation rate (10 ⁻⁵ mol dm ⁻³ min ⁻¹)
1	10.0	2.6	4.36
2	5.0	2.6	2.19
3	20.0	2.6	8.75
4	10.0	10.4	17.42
5	10.0	5.2	8.80

10.1. Determine the reaction order of the components and **give** the rate equation of the reaction, based on the initial rate data.

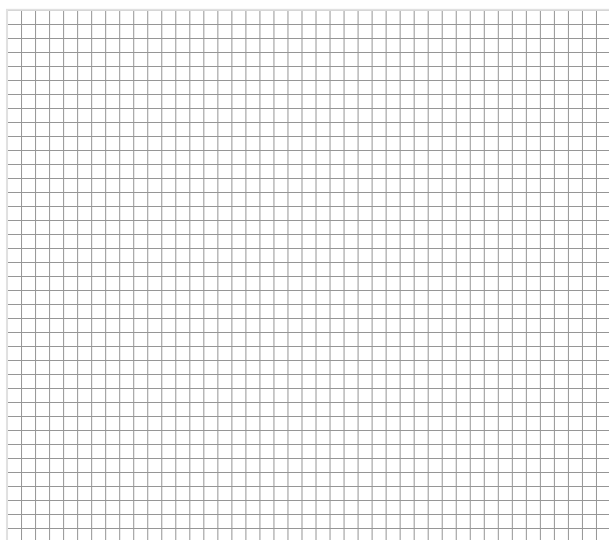
In a different series of experiments, a great excess of moxone was used when monitoring the formation of diberrine.

10.2. Identify the shapes of the detected kinetic curves?

The observed rate constants were the following in experiments with different oxidizer concentrations:

moxone (mol/dm ³)	k_{obs} (h ⁻¹)
0.040	0.180
0.100	0.460
0.160	0.747
0.220	1.020
0.280	1.320
0.340	1.560
0.400	1.838

Make a diagram to **determine** the rate constant of the reaction.



1 kg of berries and 11 dm³ of moxone stock solution were mixed in a 100 dm³ batch of juice. Berrine has a molar mass of 365 g/mol.

10.3. Calculate the berrine concentration in this experiment when 5 minutes have passed after the start of the cooking?

10.4. Calculate the duration of cooking before the juice becomes unpalatable when using a concentration of 0.100 mol/dm³ moxone (still in high excess).

Normally the cooking was run at 108 °C. In one experiment the minion responsible set the temperature to 120 °C. The activation energy of the reaction is 58.60 kJ/mol. Moxone was also in excess here in a concentration of 0.22 mol/dm³.

10.5. Determine if the juice remained tasty after 35 minutes of cooking?

Solution

10.1.

$$v = -\frac{1}{2} \frac{d[\text{berrine}]}{dt} = -\frac{d[\text{moxone}]}{dt} = \frac{d[\text{diberrine}]}{dt} = k \cdot [\text{berrine}] \cdot [\text{moxone}]$$

no.	fruit (kg)	moxone (dm ³)	diberrine formation rate (10 ⁻⁵ mol dm ⁻³ min ⁻¹)	berrine (M)	moxone (M)	k (M ⁻¹ min ⁻¹)	k (M ⁻¹ h ⁻¹)
1	10.0	2.6	4.36	0.0219	0.026	0.077	4.59
2	5.0	2.6	2.19	0.0110	0.026	0.077	4.59
3	20.0	2.6	8.75	0.0438	0.026	0.077	4.61
4	10.0	10.4	17.42	0.0219	0.104	0.076	4.59
5	10.0	5.2	8.80	0.0219	0.052	0.077	4.64

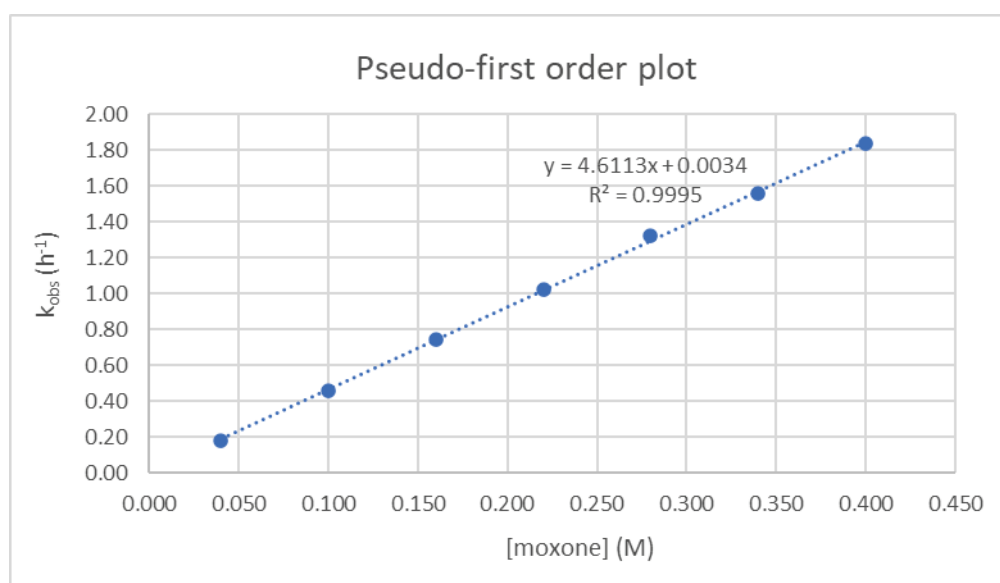
10.2.

pseudo-first order reaction → increasing exponential curves for the diberrine concentration

$$k = 4.61 \pm 0.07 \text{ M}^{-1} \text{ h}^{-1}$$

The second order rate constant can be determined as the slope of the k_{obs} vs [moxone] plot or numerically as the average of the $k_{\text{obs}}/[\text{moxone}]$ values in the table in question 10.2.

Obviously, manual plotting on a paper grid will result in a chart different than a computer-drawn version and certain level of scatter is expected between the students. However, maximum points can be given if the contestants follow the general rules of plotting and evaluate the data accordingly.



10.3.

This experiment is somewhat similar to exp.4 in Part 1, except that only 1/10 of berrine is used in order to ensure pseudo-first order conditions.

$$[\text{berrine}]_0 = \frac{1000 \cdot 0.08}{\frac{365}{100}} = 2.19 \cdot 10^{-3} M$$

$$[\text{moxone}]_0 = \frac{11 \cdot 1}{100} = 0.110 M$$

Moxone is present in a 50-fold excess \rightarrow pseudo-first order behavior is a valid assumption.

Estimated k_{obs} based on the data from Part 2:

$$k_{\text{obs}} = k \cdot [\text{moxone}] = 0.507 \text{ h}^{-1} = 8.45 \cdot 10^{-3} \text{ min}^{-1}$$

Stoichiometry has to be considered at this point, 2 moles of consumed berrine yields 1 mole of product. It is a key information that the product formation is monitored in the experiments.

Therefore:

$$v = -\frac{1}{2} \frac{d[\text{berrine}]}{dt} = \frac{d[\text{diberrine}]}{dt} = k \cdot [\text{berrine}] \cdot [\text{moxone}] = k_{\text{obs}}[\text{berrine}]$$

$$\frac{d[\text{berrine}]}{dt} = -2k_{\text{obs}}[\text{berrine}]$$

$$[\text{berrine}] = [\text{berrine}]_0 e^{-2k_{\text{obs}}t} = 2.19 \cdot 10^{-3} \cdot e^{-2 \cdot 8.45 \cdot 10^{-3} \cdot 5} = 2.01 \cdot 10^{-3} M$$

This represents 8% conversion.

An alternative possibility is to calculate the initial rate of diberrine formation in such a solution:

$$v_0 = -\frac{1}{2} \frac{d[\text{berrine}]}{dt} = \frac{d[\text{diberrine}]}{dt} = k \cdot [\text{berrine}]_0 \cdot [\text{moxone}]_0 = 1.85 \cdot 10^{-5} M \cdot \text{min}^{-1}$$

$$\text{At } t = 5 \text{ min} \quad \Delta[\text{diberrine}] = 9.25 \cdot 10^{-5} M$$

$$\Delta[\text{berrine}] = -2\Delta[\text{diberrine}] = -1.85 \cdot 10^{-4} M$$

$$[\text{berrine}]_{5\text{min}} = 2.00 \cdot 10^{-3} M$$

10.4.

$$v = -\frac{1}{2} \frac{d[\text{berrine}]}{dt} = k_{\text{obs}}[\text{berrine}]$$

$$\frac{d[\text{berrine}]}{dt} = -2k_{\text{obs}}[\text{berrine}]$$

$$[\text{berrine}] = [\text{berrine}]_0 e^{-2k_{\text{obs}}t} = 0.25[\text{berrine}]_0$$

$$e^{-2 \cdot 0.460 \cdot t} = 0.25$$

$$t = 1.51 \text{ h} \approx 90 \text{ min}$$

10.5.

	T (°C)	T (K)	k (M ⁻¹ h ⁻¹)
1	108	381.15	4.61
2	120	393.15	8.11

$$\ln k_1 = \ln A - \frac{E_a}{RT_1}$$

$$\ln k_2 = \ln A - \frac{E_a}{RT_2}$$

$$\ln \frac{k_2}{k_1} = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$k_2 = 8.11 \text{ M}^{-1}\text{h}^{-1}$$

$$k_{obs} = 1.784 \text{ h}^{-1}$$

for the consumption of berrine:

$$k_{obs}' = 3.568 \text{ h}^{-1}$$

$$t_{\frac{1}{2}}' = \frac{\ln 2}{k_{obs}'} = 0.194 \text{ h}$$

75% conversion takes 2 half-lives: $\Rightarrow t = 0.384 \text{ h} = 23 \text{ min}$

OR:

$$[\text{berrine}] = [\text{berrine}]_0 e^{-2k_{obs}t} = 0.25[\text{berrine}]_0$$

$$e^{-2 \cdot 1.784 \cdot t} = 0.25$$

$$t = 0.389 \text{ h} \approx 23.3 \text{ min}$$

\Rightarrow after 35 min, the juice is no longer consumable.

$$A = k e^{E_a/RT} = 5.0 \cdot 10^8 \text{ M}^{-1}\text{h}^{-1}$$

11. Clock reactions

Clock reactions show a sudden change in some property (typically color) after a period of induction. In iodine clock reactions iodide containing solutions are mixed with an oxidizer in the presence of thiosulfate and starch. After some time, the solution will suddenly turn blue due to the starch-iodine complex forming.

Measuring the time needed for this reaction gives an opportunity to study the iodide – oxidizer reactions, determining reaction orders and rate constants based on initial reaction rates.

The reaction between Fe(III) ions and iodide can be studied in this way. When the blue color appears that shows that the thiosulfate present was all used up. If a small quantity of thiosulfate is used, we can suppose that the concentration of other reagents will not change. Based on this and the stoichiometry of the reactions, we can use the following:

$$v_0 \approx -\frac{\Delta[\text{Fe}^{3+}]}{\Delta t} = -\frac{\Delta[\text{S}_2\text{O}_3^{2-}]}{\Delta t} = \frac{[\text{S}_2\text{O}_3^{2-}]_0}{\Delta t} \quad (1)$$

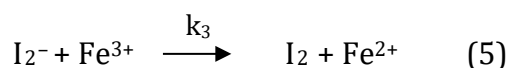
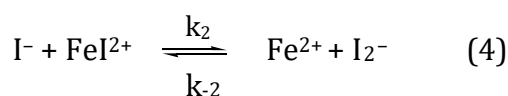
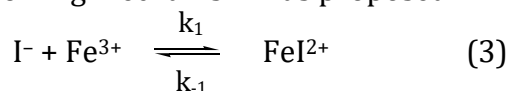
$$v_0 = k[\text{Fe}^{3+}]_0^n [\text{I}^-]_0^m = \frac{[\text{S}_2\text{O}_3^{2-}]_0}{\Delta t} \quad (2)$$

The following was found for the Δt period when the three concentrations were changed:

$[\text{S}_2\text{O}_3^{2-}]_0$ (mmol·dm ⁻³)	$[\text{KI}]_0$ (mmol·dm ⁻³)	$[\text{Fe}(\text{NO}_3)_3]_0$ (mmol·dm ⁻³)	Δt (s)
variable	20.0	6.5	$\Delta t = 2.32 \cdot 10^4 [\text{S}_2\text{O}_3^{2-}]_0$
0.2	variable	8.5	$\Delta t = 1.54 \cdot 10^{-3} ([\text{I}^-]_0)^{-1.98}$
0.25	13.0	variable	$\Delta t = 5.01 \cdot 10^{-2} ([\text{Fe}^{3+}]_0)^{-1.05}$

- 11.1. **Give** the balanced equation for the reaction of Fe(III) and I⁻.
- 11.2. **How** does the initial rate depend on the initial thiosulfate concentration?
- 11.3. **Give** the individual and the overall reaction orders? **Give** the rate equation.
- 11.4. **Give** the unit of the rate constant? **Calculate** the rate constant from the three sets of experiments. Considering that a 10% margin of error is often acceptable in reaction kinetics, **assess** the quality of these experiments.

The following mechanism was proposed:



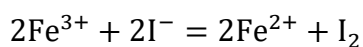
Supposing a steady state for the FeI^{2+} and I_2^- intermediates, the following rate equation was derived, but the result is not fully correct. One of the elements in the denominator is not necessary.

$$\frac{d[\text{I}_2]}{dt} = \frac{k_1 k_2 k_3 [\text{I}^-]^2 [\text{Fe}^{3+}]}{\frac{k_{-1} k_{-2} [\text{Fe}^{2+}]}{[\text{Fe}^{3+}]} + k_{-1} k_3 + \frac{k_2 k_{-2} [\text{Fe}^{2+}] [\text{I}^-]}{[\text{Fe}^{3+}]} + k_2 k_3 [\text{I}^-]} \quad (6)$$

11.5. Derive the right rate equation to identify the unnecessary element.

Solution

11.1.



11.2.

$$v_0 = \frac{[\text{S}_2\text{O}_3^{2-}]_0}{\Delta t} = 4.31 \cdot 10^{-8} \text{ mol} \cdot \text{dm}^{-3} \cdot \text{s}^{-1}$$

The ratio is constant. \Rightarrow The initial rate is independent from the concentration of thiosulfate.

11.3.

From the reaction time expressions:

$$n = 1.98 \approx 2, m = 1.05 \approx 1$$

The reaction is net third order:

$$v = k[\text{I}^{-}]^2[\text{Fe}^{3+}]$$

11.4.

$$\text{M} \cdot \text{s}^{-1} = \text{dimension}(k) \cdot \text{M}^3$$

$$\text{dimension}(k) = \text{M}^{-2} \cdot \text{s}^{-1}$$

1	$2.32 \cdot 10^4 = \frac{1}{k[\text{I}^{-}]_0^2[\text{Fe}^{3+}]_0}$	$k = 16.58 \text{ M}^{-2} \cdot \text{s}^{-1}$
2	$1.54 \cdot 10^{-3} = \frac{[\text{S}_2\text{O}_3^{2-}]}{k[\text{Fe}^{3+}]_0}$	$k = 15.28 \text{ M}^{-2} \cdot \text{s}^{-1}$
3	$5.01 \cdot 10^{-2} = \frac{[\text{S}_2\text{O}_3^{2-}]}{k[\text{I}^{-}]_0^2}$	$k = 29.53 \text{ M}^{-2} \cdot \text{s}^{-1}$

The spread of the k values around the mean is much higher than the 10% threshold \Rightarrow not acceptable.

11.5.

$$\frac{d[I^-]}{dt} = -k_1[I^-][Fe^{3+}] + k_{-1}[FeI^{2+}] - k_2[I^-][FeI^{2+}] + k_{-2}[Fe^{2+}][I_2^-]$$

$$\frac{d[Fe^{3+}]}{dt} = -k_1[I^-][Fe^{3+}] + k_{-1}[FeI^{2+}] - k_3[Fe^{3+}][I_2^-]$$

$$\frac{d[Fe^{2+}]}{dt} = k_2[I^-][FeI^{2+}] - k_{-2}[Fe^{2+}][I_2^-] + k_3[Fe^{3+}][I_2^-]$$

$$\frac{d[I_2]}{dt} = k_3[Fe^{3+}][I_2^-]$$

Steady-state intermediates: FeI^{2+} and $[I_2^-]$

$$\frac{d[FeI^{2+}]}{dt} = k_1[I^-][Fe^{3+}] - k_{-1}[FeI^{2+}] - k_2[I^-][FeI^{2+}] + k_{-2}[Fe^{2+}][I_2^-] = 0$$

$$\frac{d[I_2^-]}{dt} = k_2[I^-][FeI^{2+}] - k_{-2}[Fe^{2+}][I_2^-] - k_3[Fe^{3+}][I_2^-] = 0$$

Based on the steady-state conditions for the two species:

$$[FeI^{2+}]_{ss} = \frac{k_1[I^-][Fe^{3+}] + k_{-2}[Fe^{2+}][I_2^-]_{ss}}{k_{-1} + k_2[I^-]}$$

$$[I_2^-]_{ss} = \frac{k_2[I^-][FeI^{2+}]_{ss}}{k_{-2}[Fe^{2+}] + k_3[Fe^{3+}]}$$

These two equations can be combined and solved for $[I_2^-]_{ss}$:

$$[FeI^{2+}]_{ss} = \frac{[I_2^-]_{ss}(k_{-2}[Fe^{2+}] + k_3[Fe^{3+}])}{k_2[I^-]} = \frac{k_1[I^-][Fe^{3+}] + k_{-2}[Fe^{2+}][I_2^-]_{ss}}{k_{-1} + k_2[I^-]}$$

$$\frac{[I_2^-]_{ss}(k_{-2}[Fe^{2+}] + k_3[Fe^{3+}])}{k_2[I^-]} - \frac{k_{-2}[Fe^{2+}][I_2^-]_{ss}}{k_{-1} + k_2[I^-]} = \frac{k_1[I^-][Fe^{3+}]}{k_{-1} + k_2[I^-]}$$

$$[I_2^-]_{ss} \left(\frac{k_{-2}[Fe^{2+}] + k_3[Fe^{3+}]}{k_2[I^-]} - \frac{k_{-2}[Fe^{2+}]}{k_{-1} + k_2[I^-]} \right) = \frac{k_1[I^-][Fe^{3+}]}{k_{-1} + k_2[I^-]}$$

$$[I_2^-]_{ss} \left(\frac{k_{-2}[Fe^{2+}] + k_3[Fe^{3+}]}{k_2[I^-]} \cdot (k_{-1} + k_2[I^-]) - k_{-2}[Fe^{2+}] \right) = k_1[I^-][Fe^{3+}]$$

$$[I_2^-]_{ss} \frac{k_{-2}[Fe^{2+}]k_{-1} + k_{-2}[Fe^{2+}]k_2[I^-] + k_3[Fe^{3+}]k_{-1} + k_3[Fe^{3+}]k_2[I^-] - k_{-2}[Fe^{2+}]k_2[I^-]}{k_2[I^-]} = k_1[I^-][Fe^{3+}]$$

$$[I_2^-]_{ss}(k_{-1}k_{-2}[Fe^{2+}] + k_{-1}k_3[Fe^{3+}] + k_2k_3[Fe^{3+}][I^-]) = k_1k_2[I^-]^2[Fe^{3+}]$$

$$[I_2^-]_{ss} = \frac{k_1k_2[I^-]^2[Fe^{3+}]}{k_{-1}k_{-2}[Fe^{2+}] + k_{-1}k_3[Fe^{3+}] + k_2k_3[Fe^{3+}][I^-]}$$

The overall rate then:

$$\frac{d[I_2]}{dt} = k_3[Fe^{3+}][I_2^-]_{ss} = \frac{k_1 k_2 k_3 [I^-]^2 [Fe^{3+}]^2}{k_{-1} k_{-2} [Fe^{2+}] + k_{-1} k_3 [Fe^{3+}] + k_2 k_3 [Fe^{3+}] [I^-]}$$

$$\frac{d[I_2]}{dt} = \frac{k_1 k_2 k_3 [I^-]^2 [Fe^{3+}]}{k_{-1} k_{-2} \frac{[Fe^{2+}]}{[Fe^{3+}]} + k_{-1} k_3 + k_2 k_3 [I^-]}$$

compared to the given expression, the third term is extra in the denominator:

$$\frac{d[I_2]}{dt} = \frac{k_1 k_2 k_3 [I^-]^2 [Fe^{3+}]}{\frac{k_{-1} k_{-2} [Fe^{2+}]}{[Fe^{3+}]} + k_{-1} k_3 + \frac{k_2 k_{-2} [Fe^{2+}] [I^-]}{[Fe^{3+}]} + k_2 k_3 [I^-]}$$

Reference:

Kinetics and Mechanism of Iodide Oxidation by Iron(III): A Clock Reaction Approach, Petar B. A. Vrkljan, Jurica Bauer, and Vladislav Tomisic, *Journal of Chemical Education* **2008** 85 (8), 1123, <https://doi.org/10.1021/ed085p1123>

12. Crystal violet

Crystal violet (or gentian violet or methyl violet 10B), is known for its antiseptic and fungicide effects and is commonly used for staining Gram positive bacteria. In aqueous solution crystal violet (CV) dissociates into the cation shown in the

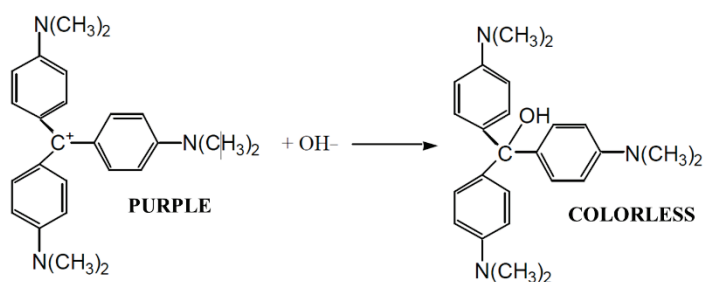
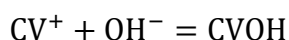


figure and chloride ions. The compound has a vivid violet color. In the presence of NaOH, crystal violet forms a colorless carbinol product.

The reaction is represented by the following simple equation:



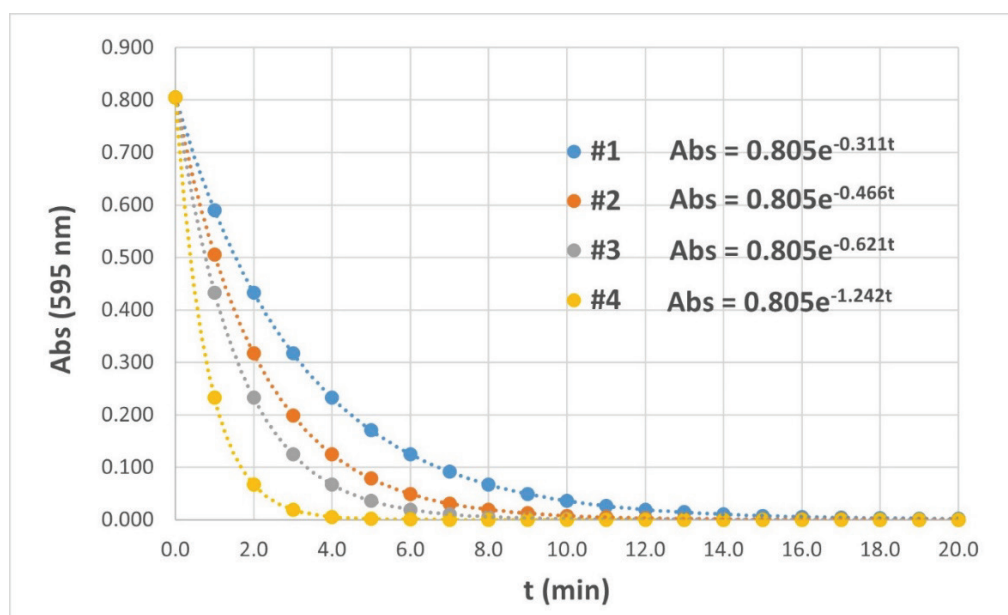
Due to the compound's intense color, the kinetic study of this reaction can be carried out by spectrophotometry at 595 nm. The rate law can be written:

$$v = k[\text{CV}]^a[\text{OH}^-]^b$$

A set of experiments was carried out at 30.0 °C using the following mixtures:

Exp. no.	$c(\text{CV})$, mol/dm ³	$V(\text{CV})$, cm ³	$c(\text{NaOH})$, mol/dm ³	$V(\text{NaOH})$, cm ³
#1	$1.82 \cdot 10^{-5}$	5	0.08	5
#2	$1.82 \cdot 10^{-5}$	5	0.12	5
#3	$1.82 \cdot 10^{-5}$	5	0.16	5
#4	$1.82 \cdot 10^{-5}$	5	0.32	5

Performing the measurements in a 1.000 cm pathlength cuvette, the following kinetic curves were recorded:



- 12.1. **Calculate** the initial concentrations of the reactants in each reaction mixture.
- 12.2. **Calculate** the molar absorption coefficient of CV at 595 nm (you can assume that the products do not absorb at this wavelength).
- 12.3. **Determine** a and b (the partial orders of the reactants) and **give** the rate law of the reaction. **Calculate** the rate constant (k), using the same units as the chart and the table.
- 12.4. **Calculate** the concentration of CV in experiment #3 at 6 minutes.

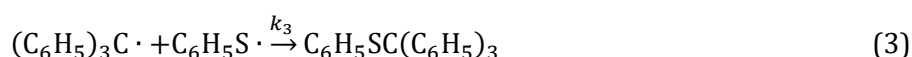
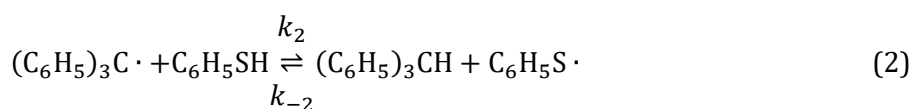
The k rate constant follows the Arrhenius law in this temperature range and its numeric value is 22.78 at 45 °C, in the same unit as calculated in Part 3.

- 12.5. **Calculate** the Arrhenius parameters (pre-exponential factor (A) and activation energy (E_a)).

6 cm³ of $2.75 \cdot 10^{-5}$ mol/dm³ crystal violet solution is mixed with 14 cm³ of $3.86 \cdot 10^{-4}$ mol/dm³ KMnO₄ solution. The optical pathlength of the cell is 0.6 cm, $\epsilon_{595}(\text{KMnO}_4) = 1875 \text{ M}^{-1}\text{cm}^{-1}$. Assume that the volumes are additive, no chemical reaction takes place in the cell and the solution is completely homogenized.

- 12.6. **Calculate** the absorbance of the mixture at 595 nm and the corresponding percentage light absorption.

Crystal violet belongs to the family of triphenyl-methyl dyes. A study revealed that triphenyl-methyl (trityl) radicals react with thiophenol producing triphenyl methane and phenyl trityl thioether according to the scheme below: ('I': hexaphenyl ethane)



Substitution of the thiol hydrogen with tritium (³T) in thiophenol leads to a significant decrease in the overall reaction rate.

- 12.7. **Which** elementary step is expected to be most affected by the described isotope exchange? **What** is expected to happen with the overall reaction rate when one of the carbon atoms in the aromatic ring of thiophenol is changed to ¹³C?

Solution

12.1.

	Mixture concentrations		excess (fold)
	[CV] (M)	[NaOH] (M)	
#1	$9.10 \cdot 10^{-6}$	0.04	4396
#2	$9.10 \cdot 10^{-6}$	0.06	6593
#3	$9.10 \cdot 10^{-6}$	0.08	8791
#4	$9.10 \cdot 10^{-6}$	0.16	17582

NaOH is in high excess \Rightarrow CV will determine the order

$$v = k[\text{CV}]^a[\text{OH}^-]^b = k_{\text{obs}}[\text{CV}]^a$$

$$k_{\text{obs}} = k[\text{OH}^-]^b$$

12.2.

$$A = A_0 e^{-k_{\text{obs}} t}$$

$$A_0 = 0.805$$

$$[\text{CV}]_0 = 9.1 \cdot 10^{-6} \text{ M}$$

$$\varepsilon_{595}(\text{CV}) = 88462 \text{ M}^{-1} \text{ cm}^{-1}$$

12.3.

$$a = 1 \quad \text{Exponential curves are observed.}$$

$$k_{\text{obs}} = k[\text{OH}^-]^b \quad k_{\text{obs}} \text{ is linearly proportional to } [\text{NaOH}]$$

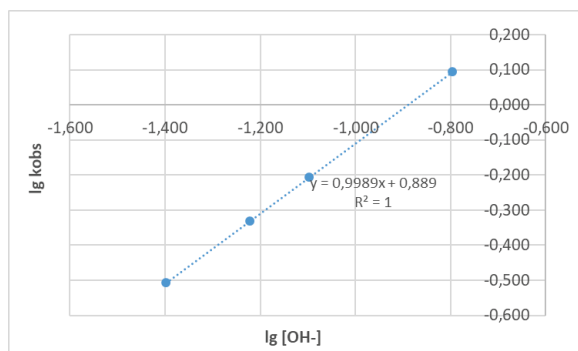
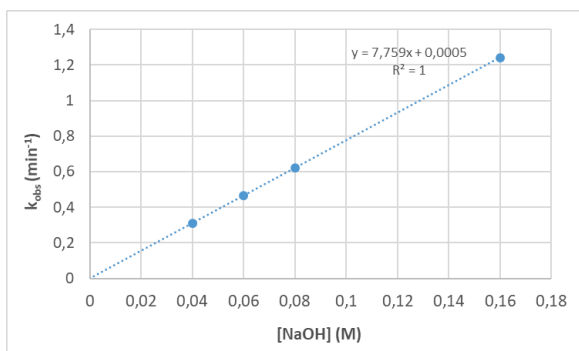
$$b = 1$$

$$v = k[\text{CV}][\text{OH}^-]$$

Potential plots (not required):

$$\lg k_{\text{obs}} = \lg k + b \lg [\text{OH}^-]$$

	[NaOH](M)	k_{obs} (min ⁻¹)	$\lg[\text{OH}^-]$	$\lg k_{\text{obs}}$
#1	0.04	0.311	-1.398	-0.507
#2	0.06	0.466	-1.222	-0.332
#3	0.08	0.621	-1.097	-0.207
#4	0.16	1.242	-0.796	0.094



	[NaOH](M)	k_{obs} (min ⁻¹)	k (M ⁻¹ min ⁻¹)
#1	0.04	0.311	7.78
#2	0.06	0.466	7.77
#3	0.08	0.621	7.76
#4	0.16	1.242	7.76

$$k_{avg} = 7.77 \text{ M}^{-1}\text{min}^{-1} = 0.130 \text{ M}^{-1}\text{s}^{-1}$$

12.4.

$$k_{obs} = 0.621 \text{ min}^{-1}$$

$$t = 6 \text{ min}$$

$$A = A_0 e^{-k_{obs}t}$$

$$A = 0.805 e^{-0.621 \cdot 6} = 0.0194$$

$$[CV] = \frac{A}{\epsilon l} = 2.19 \cdot 10^{-7} \text{ M}$$

OR:

$$[CV] = [CV]_0 e^{-k_{obs}t} = 9.1 \cdot 10^{-6} e^{-0.621 \cdot 6} = 2.19 \cdot 10^{-7} \text{ M}$$

12.5.

$T(^{\circ}\text{C})$	k (.....)	$T(\text{K})$
30	7.77	303.15
45	22.78	318.15

$$\ln \frac{k_{45}}{k_{30}} = -\frac{E_a}{R} \left(\frac{1}{318.15} - \frac{1}{303.15} \right)$$

$$-\frac{E_a}{R} = -6916.0$$

$$E_a = 57.5 \text{ kJ/mol}$$

$$\ln A = 24.9 \quad A = 6.52 \cdot 10^{10} \text{ M}^{-1} \text{ min}^{-1}$$

Arrhenius plot's equation:

$$\ln k = -6916.0 \frac{1}{T} + 24.9$$

12.6.

c_0 (M)	$2.75 \cdot 10^{-5}$	$3.86 \cdot 10^{-4}$		A_{total}	0.741
V (ml)	6	14		I/I_0	0.182
ε ($\text{M}^{-1} \text{cm}^{-1}$)	88273	1875		I/I_0 %	18.2
l (cm)	0.6	0.6		Absorption %	81.8
c (M)	$8.25 \cdot 10^{-6}$	$2.70 \cdot 10^{-4}$			
A	0.437	0.304			

12.7.

The forward reaction with k_2 will be affected most.

In the case of ^{13}C substitution, no significant effect is seen, because the aromatic ring does not participate in the reaction.

13. Aluminium in lattices

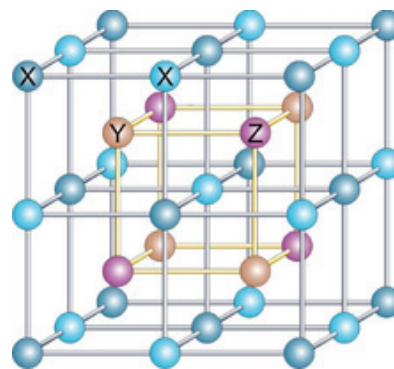
Metallic aluminium under standard conditions forms a face-centered cubic (FCC) crystal with a density of 2.710 g/cm^3 . Interestingly, it undergoes several structural changes under extreme pressures.

At a pressure of 213 GPa the FCC structure is still stable, but the unit cell dimension is changed to 324.6 pm. When the sample is further compressed between diamond anvils to above 310 GPa, a transformation to a body-centered cubic (BCC) structure with a unit cell size of 250.5 pm was detected.

13.1. Calculate and compare the densities (g/cm^3) of the different modifications under extreme pressures.

13.2. Calculate the metallic radius of Al in the three structures.

The unit cell for a family of magnetic alloys is shown on the figure. If the alloys contain Al, then the Al atoms usually take up the positions labeled with Z. The other two metals in the alloy are usually transition metals.



Interesting variations arise from the possibility that in some cases all (dark and light) blue positions are taken by X atoms, and in other cases only the dark blue positions.

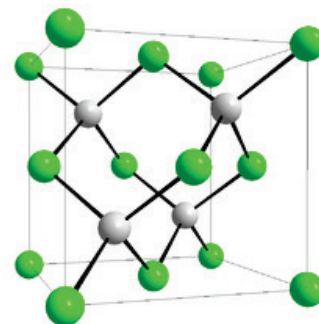
13.3. Identify the lattice (primitive cubic, FCC, BCC, something else) formed by the Z atoms only. **Identify** the lattice formed by the blue (both dark and light) atoms only.

13.4. Determine the empirical formula of the alloy if all blue positions contain X as shown on the figure. Consider the Z atoms: **How many X, how many Y and how many Z** atoms are nearest neighbors with a Z atom?

13.5. Identify the lattice formed by the dark blue atoms. **Determine** the empirical formula of the alloy if the X atoms are only present in the dark blue positions.

An aluminium containing semiconductor has the following unit cell. The lattice constant is 613.5 pm, the density of the material is 4.277 g/cm^3 .

13.6. Determine the empirical formula of this semiconductor. **Identify** the other element.



Solution

13.1.

FCC has 4 Al atoms/cell, BCC 2 atoms /cell.

Using the cell sizes and the contents, the densities of the high-pressure modifications are 5.240 and 5.700 g/cm³. Density increases with pressure, not surprisingly.

13.2.

In FCC, the face diagonal of the unit cell corresponds to 4 atomic radii. In BCC, the body diagonal is equal to 4 radii.

For the two high-pressure forms the radii are thus 114.8 and 108.5 pm.

One can calculate the unit cell dimensions of Al under standard conditions: 404.4 pm. Atomic radius is thus 143.0 pm.

13.3.

Z – FCC

X – Primitive cubic

13.4.

X₂YZ

8 X, 6 Y, 12 Z

13.5.

FCC

XYZ

13.6.

1 mol of unit cells weigh 594.7 g. There are 4-4 atoms in a cell. Subtracting the Al atoms, the other atom has a molar mass of 121.7 g/mol. The empirical formula is AlSb.

14. Sulfide minerals

Element substitutions and crystal defects are common in most complex sulfide minerals, resulting in variable compositions in natural samples. However, specimens with relatively pure compositions identifiable as compounds do exist. While not mined in large quantities, many complex sulfide minerals are present in copper ores and are reasonably well-documented due to the significance of copper. These minerals will be discussed in this task.

In minerals of the chalcopyrite group, which are structurally equivalent to chalcopyrite (CuFeS_2), iron atom substitution is most prevalent. Some variants with a pure composition in such substitution structures have only been identified in microscopic samples.

Two of these minerals/compounds, which can be derived by complete substitution of iron, have a sulfur content of 32.5 % (**A**) and 26.5 % (**B**) by weight.

14.1. Give the empirical formula of **A** and **B**.

Mineral **C** can be derived from mineral **B** by an additional element substitution and has a sulfur content of 22.4%.

14.2. Give the formula of **C**.

Significant copper ore minerals include enargite (**D**) with a theoretical composition of Cu_3AsS_4 and bornite (**E**) with a composition of Cu_5FeS_4 . Neither structure has an S-S bond, there are no S atoms close to each other in the lattice. Each crystal has chemically equivalent atoms of the same kind (e.g., all Cu atoms in **E** are identical).

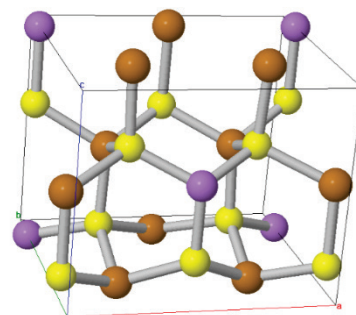
14.3. Give the conventional oxidation numbers of the elements in **D** and **E**.

14.4. Write balanced equations for the reactions of the two minerals if

- they undergo roasting in air with excess oxygen (resulting in black metal oxides, including magnetite)
- react with an excess of bleach solution.

The figure shows the structure of the elementary cell of enargite.

14.5. Find the coordination number of Cu (brown), As (purple) and S (yellow) atoms. **Find** the number of formula units per elementary cell.



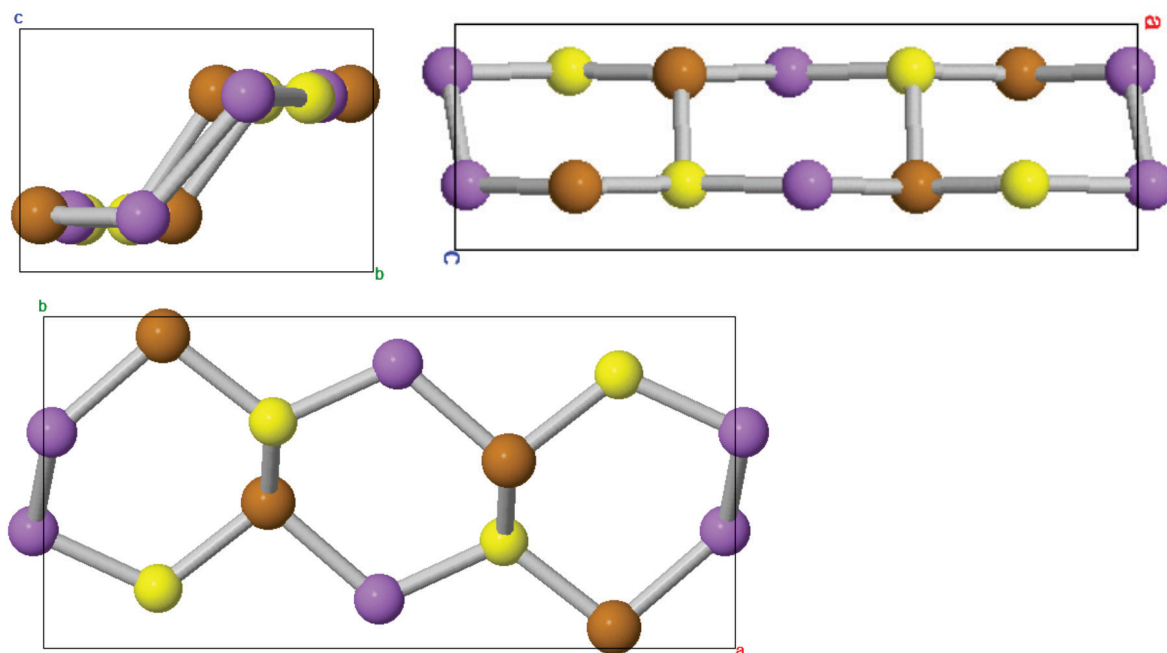
Two additional minerals, **F** and **G**, are derived from the same elements as enargite. Mineral **F** has an ideal composition with a sulfur content of 18.8%, featuring a relatively simple composition. On the other hand, mineral **G** presents challenges in determining the ideal composition due to wide substitution possibilities and a relatively complex structure (its empirical formula mass is close to 1500 g/mol). Its ideal sulfur content is 28.18%. The World Mineralogical Association last fine-tuned the data and classification of this mineral in 2019.

14.6. Identify the ideal empirical formulas of **F** and **G**.

In the crystal structure of **G**, Cu(I), Cu(II), thioarsenite (AsS_3^{3-}) and sulfide ions can be identified.

14.7. Give the proportions of these ions in **G**.

Lautite is a rare copper arsenosulfide. In it, the coordination number of all atoms is 4. Three projections of the elementary cell:



14.8. Give the empirical formula of the mineral. **Identify** the homonuclear bonds found in the crystal. **How many** of these homonuclear bonds are there in an elementary cell?

Solution

14.1.

32.5 % sulfur in CuXS_2 means that $M(\text{CuXS}_2) = 2 M(\text{S})/0.325 = 197.3 \text{ g/mol}$.

$M(\text{X}) = 69.7 \text{ g/mol}$. So, **A** is CuGaS_2 .

The analogous calculation for **B** leads to the CuInS_2 formula.

14.2.

A substitution in CuInS_2 will lead to XInS_2 . The molar mass calculated from the sulfur content, 286.3 g/mol points to AgInS_2 . **C** is expected to be AgInS_2 . Interestingly there is a formula with CuTbS_2 that fits the same molar mass. Quite often one finds multiple elements fitting such puzzles numerically, but usually the chemistry is questionable in those cases. CuTbS_2 is actually reported in the literature, however.

14.3.

Sulfur is expected to be sulfide, oxidation number -2 in both minerals.

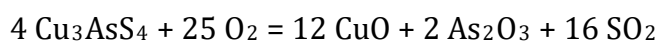
Equivalence of the atoms limits the oxidation numbers in bornite to Cu: $+1$, Fe: $+3$.

In enargite the possibilities are Cu: $+1$ and As: $+5$ (in line with conventional oxidation numbers). Cu: $+2$ would mean As: $+2$, which would be unusual for an element in group 15.

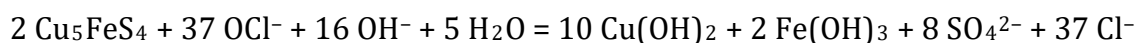
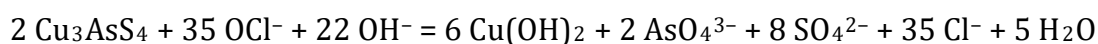
14.4.

Black oxides would be CuO and Fe_3O_4 .

Roasting:



Reaction with bleach:



The net equations are naturally also acceptable.

14.5.

Coordination numbers: $4 - 4 - 4$

2 formula / cell: 6 Cu, 2 As and 8 S atoms

14.6.

18.8 % S content for **F** implies a molar mass of 170.5 g/mol for a composition with one S atom. That fits nicely to CuAsS.

For **G**, the molar mass per one S atom is 113.8 g/mol based on the sulfur content. With 13 S atoms this gets close to the specified value (1478.4 g/mol) and fits the Cu₁₂As₄S₁₃ empirical formula.

14.7.

Thioarsenite (AsS₃³⁻) and sulfide ions must be in 4:1 ratio to reproduce the empirical formula.

If the number of Cu²⁺ ions in the empirical formula is x , then charge balance gives:

$$2x + (12 - x) = 14$$

Thus $x = 2$, and there are 2 Cu(II) and 10 Cu(I) ions in the empirical formula.

14.8.

Formula: CuAsS

As-As bonds are found, 4 in each unit cell.

There are 12 tetrahedral atoms in each cell, and thus $12 \times 4 / 2 = 24$ bonds.

Of these there are 4-4-4 of each As-As, As-S and As-Cu bonds and 12 Cu-S bonds.

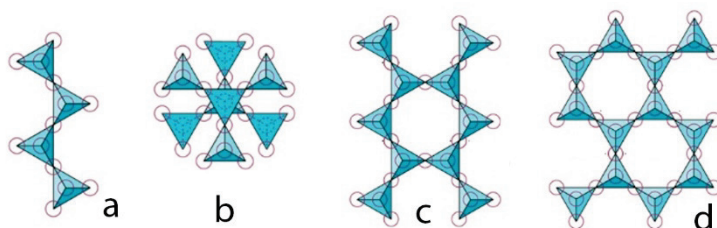
15. Beauty and Infinity

Part I

The largest sand desert on Earth, the Rub' al Khali (الرُّبْعُ الْخَالِي) covers the southeastern part of Saudi Arabia. The most common constituents of sand grains are silica (SiO_2) and various silicates. Indeed, silicon and oxygen are the two main elements of Earth's crust in various minerals. Olivine, $(\text{Mg,Fe})_2\text{SiO}_4$ and garnet, $(\text{Mg,Fe,Mn})_3\text{Al}_2\text{Si}_3\text{O}_{12}$ or $\text{Ca}_3(\text{Al,Cr,Fe})_2\text{Si}_3\text{O}_{12}$ are only two examples of the many silicate minerals. The bracketed elements signify a variable composition crystal structure with different atoms taking a certain crystal position. For olivine, this means that specimens with any $x = 0-1$ exist for $(\text{Mg}_{1-x}\text{Fe}_x)_2\text{SiO}_4$.

15.1. Express the formula of the garnet variant with the lowest silica content as a combination of oxides.

Several skeletal structures of polysilicate ions are represented on the figure, showing SiO_4 tetrahedra.



15.2. Find the corresponding charge for each of the four structures in the Figure. Structures **a** and **c** can be extended to a 1D, structure **d** to a 2D polymeric ion. Find the empirical formula for the polymeric ions.

Some silicates are beautiful gemstones, displaying a spectrum of colors. Recent findings in the southwest of Saudi Arabia, in the Bisha area include beryls, belonging to the mineral family of emeralds and aquamarines.



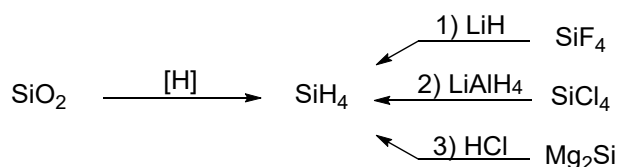
Emerald and aquamarine share the same beryl structure and have specific green and blue colors. Pure beryl is colorless and consists of Si, O, Al and Be. 0.2024 g of beryl contains 0.0635 g of Si and 0.0102 g Be. Another mineral, sky blue bazzite has the same stoichiometry as beryl, but the Al is replaced by another metal. The Si mass fraction in bazzite differs by 6.25% when compared to the Si mass fraction in beryl.

15.3. Find the formula of these two minerals: beryl and bazzite.

15.4. Identify the color of light absorbed by emerald: a) No absorption in the visible spectrum, b) Green color light, c) Red color light, d) Emerald color light.

Part II

In industrial processes, pure silicon, a primary semiconductor in the electronics industry, is derived from silane (SiH_4), itself obtained through the reduction of SiO_2 . Additionally, on a smaller scale, silane can be produced from certain silicon derivatives such as silicon halides (SiF_4 , SiCl_4) or metal silicides like Mg_2Si .



15.5. Write balanced equations for the three numbered reactions of silane formation.

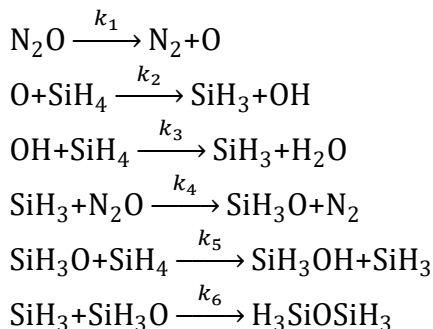
These reactions can yield Si containing byproducts. From the byproducts, let us consider **A**, **B**, and **C**, each unique for one of the three reactions. Their molecular mass increases in order: **B**, **C**, **A**. Compound **A** contains 93.3 % Si by mass. The mass spectrum of compound **B** can be used to obtain an average molar mass of 101 g/mol. Also, **B** possesses two planes of symmetry. Finally, **C** contains 73.1% halogen by mass.

15.6. Identify the unknown compounds **A**, **B** and **C** and assign them to their respective reactions.

15.7. Among the SiX₄ molecules (SiH₄, SiF₄, SiCl₄), determine a) the one with the lowest melting point, and b) the one with the highest Lewis acidity.

Part III

SiH₄ is highly flammable in O₂ containing atmospheres. The final product is SiO₂, however, in a less oxidative atmosphere like N₂O gas, partial oxidation of silane can yield valuable products. Significant elementary reactions of the radical mechanism of this gas-phase reaction are below. The 1st and the 6th steps are very slow.



15.8. Categorize steps 1, 4 and 6 with respect to their role in the chain reaction mechanism.

15.9. Write the net chemical reaction.

15.10. Find the kinetic law and reaction orders for the net reaction when N₂O is in excess. Use the steady-state approximation for the intermediates.

15.11. Identify the coordinate system that would result in a linear graph:

a) ln [SiH₄] vs. t, b) log[SiH₄] vs. t, c) 1/[SiH₄] vs. t, d) 1/[SiH₄]² vs. t, e) none of these

Solution

15.1.

$\text{Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ or $\text{Ca}_3\text{Fe}_2\text{Si}_3\text{O}_{12}$ have the heaviest variable substituents, and the latter has the highest molar mass, and thus the lowest silica content. $3\text{CaO} \cdot \text{Fe}_2\text{O}_3 \cdot 3\text{SiO}_2$ is the oxide decomposition.

15.2.

From the picture we see that each Si atom is surrounded by 4 oxygen atoms. If an O atom is connected only to 1 Si atom thus it will have charge -1. In order we will have charges: -10, -18, -20, -22

Structure a) is a chain silicate fragment: $(\text{SiO}_3^{2-})_x$

Structure c) is a double chain silicate fragment: $(\text{Si}_4\text{O}_{11}^{6-})_x$

Structure d) is a sheet silicate fragment: $(\text{Si}_2\text{O}_5^{2-})_x$

15.3.

In this sample of beryl, the total mass of O and Al is 0.1287g. The ratio between these 4 atoms is the next:

$$n_{\text{Be}}:n_{\text{Si}}:n_{\text{O}}:n_{\text{Al}} = \frac{0,0102}{9} : \frac{0,0635}{28} : \frac{x}{16} : \frac{0,1287-x}{27}$$

Using electroneutrality:

$$n_{\text{Be}} \cdot (+2) + n_{\text{Si}} \cdot (+4) + n_{\text{O}} \cdot (-2) + n_{\text{Al}} \cdot (+3) = 0$$

$$\frac{0,0102}{9} \cdot 2 + \frac{0,0635}{28} \cdot 4 + \frac{x}{16} \cdot (-2) + \left(\frac{0,1287-x}{27} \right) \cdot 3 = 0 \Rightarrow x = 0.1086$$

$$n_{\text{Be}}:n_{\text{Si}}:n_{\text{O}}:n_{\text{Al}} = \frac{0,0102}{9} : \frac{0,0635}{28} : \frac{0,1086}{16} : \frac{0,0201}{27} = 3:6:18:2$$

Thus, beryl is $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$

Bazzite is $\text{Be}_3\text{X}_2\text{Si}_6\text{O}_{18}$ and we don't know if element **X** is lighter or heavier than Al.

The Si mass fraction is $\omega = \frac{m(\text{Si})}{m(\text{beryl})} = \frac{0.0635}{0.2024} = \frac{6 \cdot 28.09}{537.5} = 0.3136$. If we replace Al by **X**, the bazzite molar mass will change by $2a$ g/mol where a is the molar mass difference between **X** and Al.

If the mass fraction of Si decreases and increases:

$$\frac{6 \cdot 28.09}{537.5 + 2a} = 0.3136 \cdot (1 - 0.0627) \Rightarrow a = 17.94 \Rightarrow M(\text{X}) = 44.95 \Rightarrow \text{Sc}$$

$$\frac{6 \cdot 28.09}{537.5 + 2a} = 0.3136 \cdot (1 + 0.0627) \Rightarrow a = -15.88 \Rightarrow M(\mathbf{X}) = 11.11 \Rightarrow \text{almost B}$$

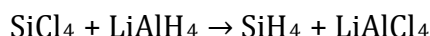
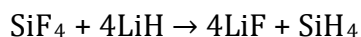
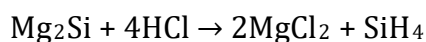
Boron is different in size and chemistry (e.g., not a metal) from Al, but scandium is rather similar and can substitute Al in a lattice easily.

Thus, bazzite is $\text{Be}_3\text{Sc}_2\text{Si}_6\text{O}_{18}$

15.4.

The mineral absorbs the light, thus we should search for the complementary color of green. That is red: green and emerald are very close thus emerald cannot be a complementary color to green.

15.5.



15.6.

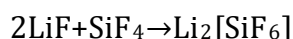
A contains more than 90% of Si indicating that the remaining element could only be hydrogen. SiH_2 corresponds to the composition, but the high molar mass (the highest of all) means that it is an oligomer or polymer cyclic compound $(\text{SiH}_2)_x$ where x is 6 or more. A polymer could only be formed from Mg_2Si where Si-Si bonds can be present already.

Molecule **B** has two planes of symmetry, so it can be SiH_2X_2 (SiH_4 or SiY_4 are not byproducts). X as Cl gives the right molar mass, thus **B** is SiH_2Cl_2 , a byproduct of the second reaction.

Molecule **C** has $\omega_{\text{Hal}} = 73.1\%$ and the halogen must be fluorine as the remaining reaction starts from SiF_4 . The molar mass of the compound is also higher than 101 g/mol and can be calculated as

$$M = \frac{19n}{0.731} = 26n,$$

where n is the number of F atoms. Very curiously $n = 1$ is close LiF, but its molar mass is smaller than 101 g/mol, and it does not contain Si atoms. At the same time $n = 4$ is close to SiF_4 , one of the reactants. The combination of the two could also be a byproduct:



So **C** is $\text{Li}_2[\text{SiF}_6]$

15.7.

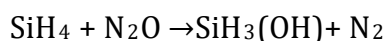
The lowest melting point belongs to SiH_4 as a very light molecule with only weak intermolecular interactions (Si and H have a similar electronegativity). The strongest Lewis acid is SiF_4 due to the inductive effect of F.

15.8.

Step 1 is chain initiation.

Steps 4 is chain propagation.

Step 6 is chain termination.

15.9.**15.10.**

For unbranched chain reactions, there are two useful rules of thumb that accelerate the kinetic derivations:

i. The rate of the initiation and termination steps are equal (as the chain carriers must be in steady state). In this case:

$$k_1[\text{N}_2\text{O}] = k_6[\text{SiH}_3][\text{SiH}_3\text{O}]$$

ii. The rates of all propagation steps are equal to the rate of product formation (as the stoichiometry of the overall reaction must be shown by the chain):

$$v = k_4[\text{SiH}_3][\text{N}_2\text{O}] = k_5[\text{SiH}_3\text{O}][\text{SiH}_4]$$

From the second condition:

$$[\text{SiH}_3] = \frac{k_5[\text{SiH}_3\text{O}][\text{SiH}_4]}{k_4[\text{N}_2\text{O}]}$$

Substituting this into the first condition:

$$[\text{SiH}_3\text{O}] = [\text{N}_2\text{O}] \sqrt{\frac{k_1 k_4}{k_5 k_6 [\text{SiH}_4]}}$$

The rate of product formation:

$$v = k_5[\text{SiH}_3\text{O}][\text{SiH}_4] = \sqrt{\frac{k_1 k_4 k_5}{k_6}} [\text{SiH}_4]^{0.5} [\text{N}_2\text{O}]$$

$$v = k[\text{N}_2\text{O}][\text{SiH}_4]^{0.5} = k'[\text{SiH}_4]^{0.5}$$

15.11.

The reaction order with respect to silane is 0.5, so none of the proposed coordinates gives a linear dependence.

16. Boron clusters

The chemistry of boron-based cluster anions is undergoing a revival thanks to their high stability, kinetic inertness, and easy functionalization.

A synthesis starts by heating NaBH_4 with equimolar amount of B_2H_6 to produce compound **A**. A reaction was accompanied by the evolution of a combustible gas equimolar with **A**. After that, compound **A** was heated up to $165\text{ }^\circ\text{C}$ in diglyme (bis(2-methoxyethyl) ether) with 1.5 equivalent of B_2H_6 in a sealed air-free reactor to produce a salt **B** containing a doubly charged cluster anion and the same combustible gas. Compound **B** has 1:1 B:H ratio and a 24.5% by weight Na content.

16.1. Give the formulas of **A** and **B** and the balanced reactions of their formation.

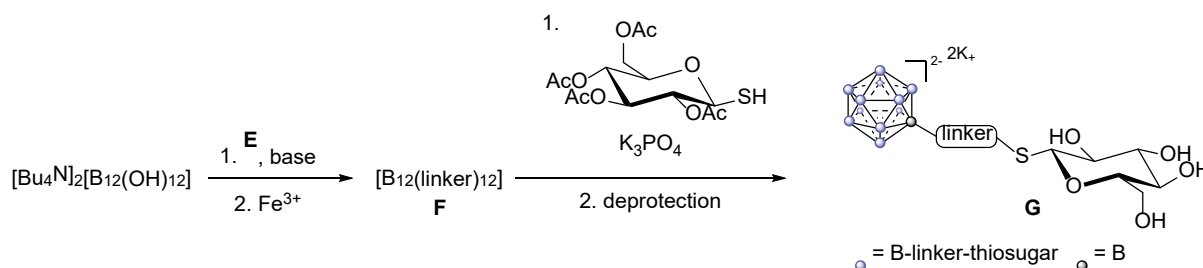
Functionalizing boron clusters can be done using a wide range of reagents. One of the functionalization reactions is halogenation, forming weakly coordinating anions that activate their counter cations.

The cesium salt prepared by ion exchange from compound **B** was suspended in 1:1 water-methanol solvent mixture. Then the suspension was cooled down using an ice bath and halogen **C** was added slowly. After that, the reaction mixture was heated up to $90\text{ }^\circ\text{C}$ under reflux. After quenching the small excess of halogen using sodium sulfite, the solvent was removed using rotary evaporator and product **D** was recrystallized using hot water, which is another cesium salt with a doubly charged anion. It has 19.6% by weight cesium and 9.6% by weight boron besides halogen.

16.2. Give the formulas of **C** and **D** and the balanced reactions of the formation of **D** and the quenching of excess **C**.

These clusters can serve as scaffolds for multifunctional nanomolecules with a well-defined structure. Using varied linkers and functional groups, the size and functionality of the nanomolecules can be tuned. A recent work showed great promise with covalently attached saccharides as functional groups that can bind with proteins.

The synthesis was pursued according to the synthesis scheme below:



The synthesis starts by reacting the tetrabutylammonium salt of the perhydroxylated clusters in the presence of a base with compound **E** ($\text{C}_{13}\text{H}_6\text{BrF}_5$) in a polar solvent. Compound **E** shows two doublets around 7.5 ppm and a singlet around 4.5 ppm in its ^1H -NMR spectrum and 3 different signals in ^{19}F -NMR. The attachment reaction of linker **E** is reasonably fast and complete on all cluster atoms. Subsequent functionalization is carried out on the neutral molecule **F** produced by reaction with Fe(III)-chloride.

16.3. Give the structure of **E** and **F**. Use \otimes to symbolize the cluster and only draw out one of the attached groups.

F was reacted with 1-thio- β -D-glucose tetraacetate (and other thiols) in the presence of K_3PO_4 to introduce biologically relevant functionality. The rapid and complete functionalization reaction was monitored by ^{19}F -NMR because the pure product only has 2 different fluorine environments. The final product obtained after deprotecting the glucose is a dipotassium salt of the decorated cluster, **G**.

Thiols were always used in excess, because they serve in another role besides the attachment of functionality to the cluster.

16.4. Determine the minimum amount of thiol needed by 1 mol of **F**. What is an appropriate reagent to deprotect the glucose residue?

16.5. Draw the structure of a linker in **G** indicating only the B and S atoms from the rest of the molecule.

The glucose-coated nanomolecules show a much higher affinity towards lectin (a carbohydrate binding protein) than individual glucose molecules. Gold nanoparticles coordinated with 1-thio- β -D-glucose molecules also strongly bind to lectin.

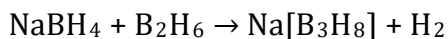
16.6. What molecules potentially present in biological samples could affect the stability of the coordinated gold nanoparticles, but not the functionalized borate clusters?

Solution

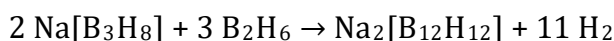
16.1.

Hydrogen gas is the byproduct.

A: Na[B₃H₈]



B: Na₂[B₁₂H₁₂],



Calculations: Since the compound is a salt with anion that has -2 charge, it has two sodium cations per formula. Assuming that the compound has the formula Na₂B_xH_x, since 24.5% by weight is Na, one can make the following equation:

$$\frac{22.99 \cdot 2}{22.99 \cdot 2 + x \cdot (10.81 + 1.008)} \cdot 100\% = 24.5\%$$

$x = 12$.

16.2.

C is Br₂, **D** is Cs₂[B₁₂Br₁₂].

Since the compound contains Cs, B, and halogen with -2 anion, the general formula is Cs₂[B_xHal_y],

If halogen % by weight is 70.8%, one can solve for x using the relationship between the number of moles of Cs and B (assuming that we have 100 g of the compound):

$$\frac{19.6}{132.9} = \frac{2}{x} \cdot \frac{9.6}{10.811}$$

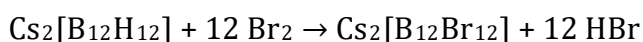
$x = 12$.

For the halogen, one can use the same reasoning giving:

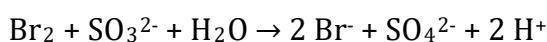
$$\frac{19.6}{132.9} = \frac{2}{y} \cdot \frac{70.8}{M} \Rightarrow M = \frac{960.13}{y}$$

using $y = 12$ gives 80 g mol⁻¹, which corresponds to bromine (Br).

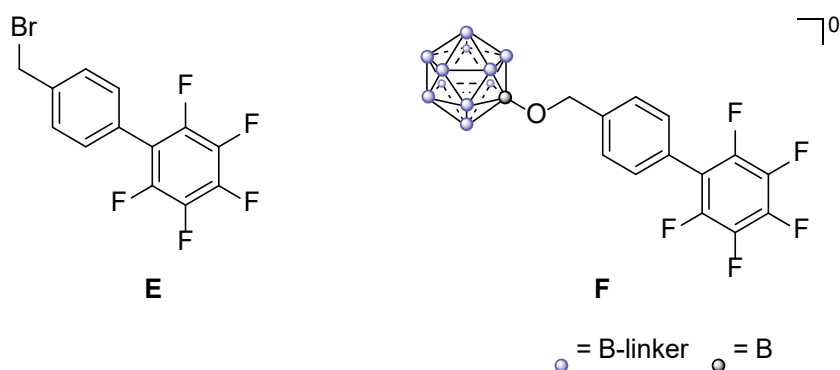
Formation of **D**:



Quenching reaction:



16.3.



$\otimes(-\text{CH}_2-p\text{-C}_6\text{H}_4\text{-C}_6\text{F}_5)_{12}$ is another representation of **F**.

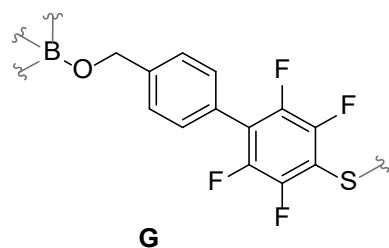
16.4.

12 equivalents of thiol are needed for functionalization.

The thiol also reduces the neutral boron cluster into the dianion ($2 e^-$ needed). As 1 thiol furnishes $1 e^-$, at least 14 eq. of the thiol are needed.

MeONa in MeOH is a possible deprotecting agent.

16.5.



16.6.

Thiols, e.g. cysteine can also bind to the gold and crowd out the sulfur-coordinated functional parts of the nanoparticle. The covalent bonds in the boron-based nanoparticle keep the nanoparticle intact.

Reference: Qian, E., Wixtrom, A., Axtell, J. *et al.* Atomically precise organomimetic cluster nanomolecules assembled via perfluoroaryl-thiol $\text{S}_{\text{N}}\text{Ar}$ chemistry. *Nature Chem* **9**, 333–340 (2017). <https://doi.org/10.1038/nchem.2686>

17. MOFs: The Ultimate Coordination Network

Metal Organic Frameworks (MOFs) are coordination polymers typically built up from a transition metal and an organic linker featuring multiple coordinating functional groups. They play a significant role in hydrogen or ammonia storage and catalysis due to their large cavities and high porosity. The wide range of linker variations in size, shape, and coordinating functional group, coupled with the diverse metals available, results in numerous MOFs with distinct properties and applications. Their cavities make them excellent for storing various gases (hydrogen, ammonia, carbon dioxide, etc.).

The copper-based **MOF-a** holds promise in ammonia storage. The synthesis of the structure starts by combining copper(II) salt **A** with an equimolar amount of the double linker **B** in DMF (*N,N*-dimethylformamide), resulting in a blue solution. This solution is stirred for 16 hours at 90°C, leading to the formation of a green-blue precipitate. After filtration, the precipitate was washed three times with DMF, followed by soaking in methanol for 24 hours. This soaking process is repeated with fresh methanol before final storage in a separate portion of methanol.

To analyze **A**, slow heating was applied under a flow of inert gas, and the weight loss was monitored. Around 120 °C, a 19.4% weight loss was observed, attributed to water loss. After reaching 250 °C, a black material **C** remained, and a reddish gas mixture evolved. The total mass loss up to this point, including water, amounted to 65.8% by weight. Switching the gas flow to hydrogen, and continuing heating, the black material lost 20.1% weight and copper was left behind.

17.1. Give the formula of **A** and **C**. **Support** your result by calculations.

Linker **B** is a symmetrical molecule containing only 3 elements and has a molar mass of 172 g/mol. It has an inversion center, and it does not decolorize bromine water. Titrating the distinctly acidic solution of 0.500 g of **B** needed 11.6 mL of 0.500 M NaOH solution. **B** has 3 different signals in ¹³C-NMR.

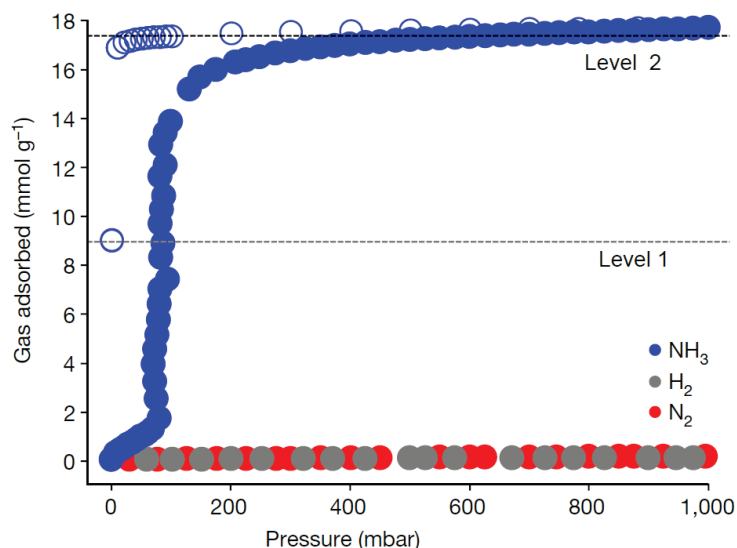
17.2. Draw the structure of **B**. Does it have any stereoisomers?

One method to estimate the surface area of a porous material consists of flooding nitrogen gas on the evacuated sample and monitoring pressure and adsorption. For **MOF-a**, the nitrogen uptake flattened out around $5.0 \cdot 10^{-3}$ mol/g before further increase. This region is interpreted to correspond to the formation of a monolayer on the surface.

17.3. Calculate the specific surface area of **MOF-a** in m²/g if we know that the cross-sectional surface area of a nitrogen molecule is 0.162 nm².

MOF-a has a unique metal coordination environment resulting in a 3D framework. Each copper atom is linked to 4 oxygen atoms from 4 different linkers in an approximately square planar way. That places two Cu atoms in each other's vicinity, and an oxygen atom from a 5th linker is attached to each copper.

When ammonia, nitrogen, and hydrogen adsorptions were tested at room temperature, **MOF-a** adsorbed significant amounts of ammonia compared to nitrogen and hydrogen as summarized on the graph below. The green solid becomes blue on exposure to ammonia (solid circles), and on desorption (empty circles) it turns purple. Two levels are marked on the graph for their importance. Level 2 corresponds to saturation with ammonia and Level 1 is the endpoint of desorption at 1 mbar pressure at room temperature. Careful heating resulted in the reconstruction of the original **MOF-a**.



- 17.4. Calculate** the number of ammonia molecules coordinating to each Cu atom in the structure corresponding to Level 1 and 2. **MOF-a** has 27.2% by weight of copper.

X-ray measurements established that both structures are one-dimensional (i.e. have a straight linear arrangement of linked Cu atoms) and the copper atoms in both structures have two oxygen atoms from two ligands coordinated.

- 17.5. What** are the primary coordination environments of the copper atoms in the two structures?

Solution

17.1.

Answer: **A** is $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$, **C** is CuO .

Calculations: Since **C** has 79.9% by weight of copper, one can calculate the molar mass of the leftover by calculating the molar mass per mol of copper giving us the following relationship for the rest of the molar mass: $\frac{63.5}{0.799} - 63.5 = 16 \text{ g/mol}$ (oxygen).

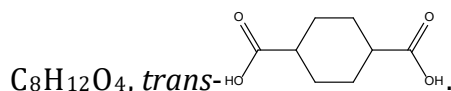
As for **A**, since we know the % by weight for water loss and the overall loss, we can find the loss of the other elements, which is 55.2% by weight, since we know that copper forms 79.9% of what is left from **A** (34.2%), Cu forms 27.3% of the overall % by weight of **A**.

Using this information with the 19.4% of water, the rest of the elements forms 53.3% by weight. Using all these data points, the molar mass of the anion is: $\frac{63.5}{0.273} \cdot 53.3\% \cdot \frac{1}{2} = 62 \text{ g mol}^{-1}$, which implies the existence of nitrate since reddish gas (NO_2) is formed from the TGA.

The amount of water can be calculated from the molar ratio between the water and copper nitrate: $\frac{19.4 \text{ g} / 18 \text{ g mol}^{-1}}{80.6 \text{ g} / 187.5 \text{ g mol}^{-1}} = 2.5$.

A is $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$

17.2.



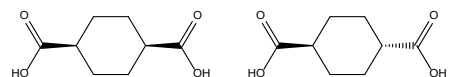
Acidity and neutralization by NaOH mean that the linker has carboxylic acid groups (2 of them since it is a double linker).

Using the titration calculations: $\frac{0.5 \text{ M} \cdot 0.0116 \text{ dm}^3}{0.5 \text{ g} / 172 \text{ g/mol}} = 2$.

This implies that what is left of the molar mass is: $172 - 90$ ($2 \text{ CO}_2\text{H}$) = 82 g mol^{-1} . Since it is an organic linker with C, H, and O, the rest of the molar mass can be attributed to C_6H_{10} . Therefore, the chemical formula is $\text{C}_8\text{H}_{12}\text{O}_4$.

Since the molecule does not decolorize bromine water, it does not have any double bonds and is symmetric with 3 carbon environments, it has to be a cyclohexane with 2 carboxylic acid groups *trans* to each other in positions 1 and 4.

A *cis*-stereoisomer exists.



17.3.

After converting everything to the correct units,

$$SA = 0.0050 \text{ mol g}^{-1} \cdot 6.02 \cdot 10^{23} \text{ mol}^{-1} \cdot 0.162 \cdot 10^{-18} \text{ m}^2 = 490 \text{ m}^2 \text{ g}^{-1}.$$

17.4.

Level 2 is around 17 mmol of adsorbed ammonia per 1 g of **MOF-a**. So, by converting units of the uptake: $\frac{0.017 \text{ mol NH}_3}{1 \text{ g MOF-a}} \cdot \frac{100 \text{ g MOF-a}}{27.2 \text{ g Cu}} \cdot \frac{63.5 \text{ g Cu}}{1 \text{ mol Cu}} = 4 \frac{\text{mol NH}_3}{\text{mol Cu}}.$

Therefore, 4 molecules of NH₃ are there per Cu center in the structure corresponding to Level 2. Level 1 has approximately half as much ammonia absorbed, and thus 2 ammonia molecules per Cu center.

17.5.

The Cu atoms will have 2 O atoms opposite each other in both structures to allow for the 1D structures. The level 1 structure has a square planar coordination sphere with 2 ammonia molecules and 2 linker O atoms in trans positions.

The structure corresponding to Level 2 has octahedral coordination with 4 square planar ammonia molecules and two axial oxygens from the linker.

Reference:

Snyder, B.E.R., Turkiewicz, A.B., Furukawa, H. *et al.* A ligand insertion mechanism for cooperative NH₃ capture in metal-organic frameworks. *Nature* **613**, 287–291 (2023). <https://doi.org/10.1038/s41586-022-05409-2>

18. Black gold

"Black gold" has nothing to do with the actual element Au or its compounds. It is a name which refers to oil, also known as petroleum: "black" due to the color of crude oil and "gold" as it is a very valuable resource nowadays.

Saudi Arabia has the second-largest proven petroleum reserves in the world. The country actively produces, exports, and refines petroleum crude oil. Gasoline and diesel are the products of petroleum that are used as fuels for vehicles. Due to the nature of engine combustion phenomena, burning these fuels in automotive engines contributes to the emission of air pollutants. Among them are unburned hydrocarbons (UHC), particulate carbon (C), carbon monoxide (CO), and nitrogen oxides (NO_x).

18.1. Choose the major products of gasoline combustion when the air supply is 10 kg per 1 dm³ of fuel. Use octane C₈H₁₈ (density $\rho = 0.703$ g/cm³) as the model compound for gasoline.

☐ UHC ☐ C ☐ CO ☐ CO₂ ☐ H₂ ☐ H₂O ☐ H₂O₂

The formula NO_x represents two nitrogen oxides: NO and NO₂. These gases are formed in engines from atmospheric nitrogen and oxygen due to high temperatures achieved during the combustion of fuels. Although NO and NO₂ are relatively simple compounds, they have rather complicated structures and bonding. First of all, both compounds are radical species, for which the commonly used octet rule doesn't apply.

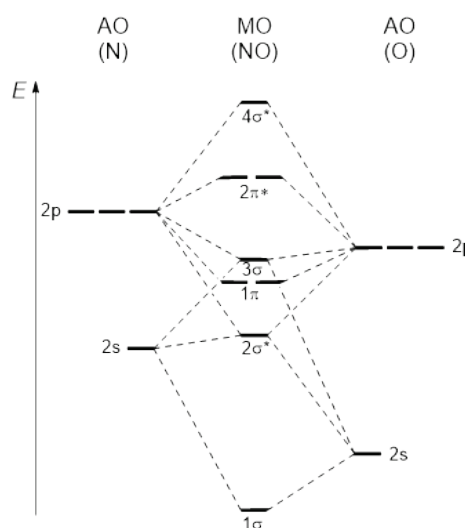
18.2. For the NO₂ molecule:

- Draw** the Lewis structures of two resonance forms,
- Indicate** the N–O bond order,
- Indicate** the hybridization of N atom,
- Indicate** the geometry of the molecule.

The correct N–O bond order in NO molecule can't be determined using Lewis structures with the typical two-center two-electron bonds. Instead, the molecular orbital (MO) diagram can provide the answer.

18.3. For the NO molecule:

- Fill in** the atomic (AO) and molecular (MO) orbitals in the provided MO diagram with the electrons.
- Calculate** the N–O bond order.
- Compare** the dissociation energies of NO, NO⁺ and NO[−].



It is mandatory now in most countries that all the vehicles sold are equipped with a special device that converts harmful exhaust gases from the engine into less harmful ones. This device is called a catalytic converter as it has a heterogeneous redox catalyst, which is usually a mixture of precious metals.

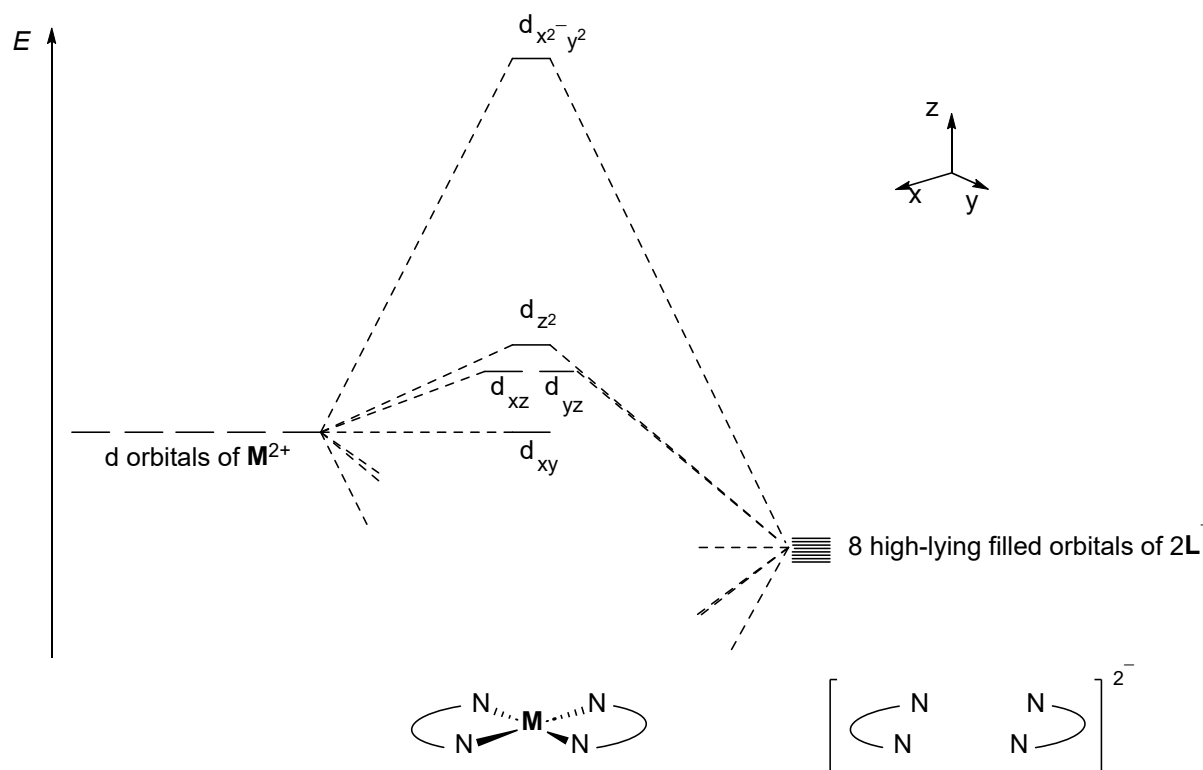
18.4. Give the formulas for the target products of catalytic conversion of UHC, C, CO and NO_x .

More than half of metal **M** mined is used by the automotive industry to produce catalytic converters. This has a drastic influence on the price of this metal: although there are rarer elements than metal **M**, some of them actually cost less because of the lower demand.

Organic compound **HL** is used to precipitate metal **M** from solutions in the form of a ML_2 complex for recovery, purification, and gravimetric purposes. The content of metal **M** in ML_2 is 31.61% by mass (wt.%, mass fraction, ω) and 3.23% by number of atoms (at.%, atomic percent, χ). The **HL** molecule consists of 2 nitrogen atoms, 2 oxygen atoms and 2 other elements, and has a degree of unsaturation (also known as “double bond equivalent”) of 2.

18.5. Determine the molecular formula of **HL** and metal **M**.

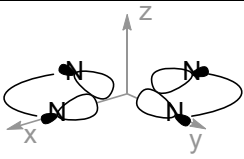
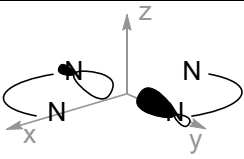
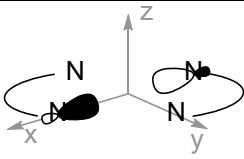
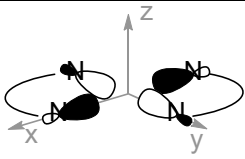
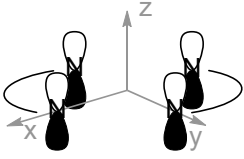
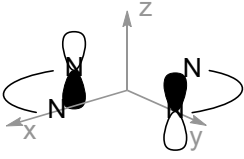
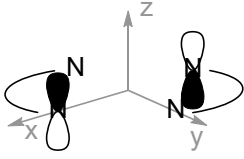
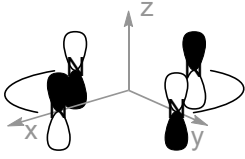
Below is the simplified MO diagram for ML_2 with the most important interactions shown. The interaction between d orbitals of metal cation M^{2+} and high-lying filled orbitals of the ligands L^- leads to the splitting of d orbitals.



18.6. Fill in the MO diagram with electrons of M^{2+} .

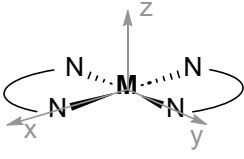
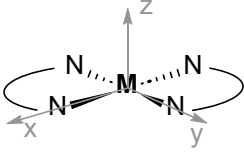
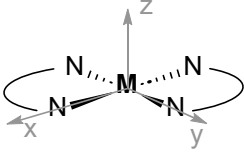
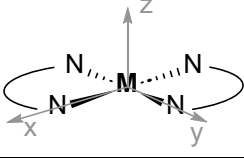
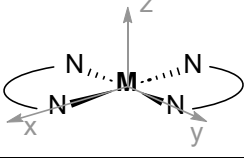
*Note: If you haven't found metal **M** in the previous question, take any platinum group metal and **note it** on the diagram.*

ML₂ is a square planar complex, where **M²⁺** is coordinated to all 4 sp²-hybridized N atoms. Therefore, 8 high lying filled ligand orbitals considered here are the following:

Combinations of sp ² -hybrid orbitals:			
			
ϕ_1	ϕ_2	ϕ_3	ϕ_4
Combinations of p orbitals:			
			
ϕ_5	ϕ_6	ϕ_7	ϕ_8

18.7. In the table below:

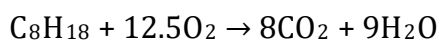
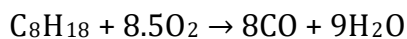
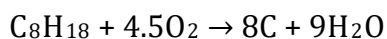
- Draw** each d orbital of the metal (note the coordinate system),
- Indicate** the interacting orbital(s) ϕ_i of appropriate symmetry and the type of overlap between these orbitals (σ , π , or δ).

d orbital	Drawing	Interacting orbital(s) ϕ_i	Overlap
d_{xy}			
d_{xz}			
d_{yz}			
d_{z^2}			
$d_{x^2-y^2}$			

Solution

18.1.

Combustion reactions of octane producing C, CO and CO₂:



Mole ratio between the supplied O₂ (mole fraction in air $\chi(\text{O}_2) = 21\%$) and C₈H₁₈:

$$\frac{n(\text{O}_2)}{n(\text{C}_8\text{H}_{18})} = \frac{m(\text{air})}{V(\text{C}_8\text{H}_{18})} \cdot \frac{\chi(\text{O}_2)M(\text{C}_8\text{H}_{18})}{M(\text{air})\rho(\text{C}_8\text{H}_{18})} = \frac{10000 \text{ g}}{1000 \text{ cm}^3} \cdot \frac{0.21 \cdot 114 \text{ g mol}^{-1}}{29 \text{ g mol}^{-1} \cdot 0.703 \text{ g cm}^{-3}} = 11.7$$

As $8.5 < 11.7 < 12.5$, the products of combustion are CO, CO₂ and H₂O.

18.2.

a) Lewis structures:



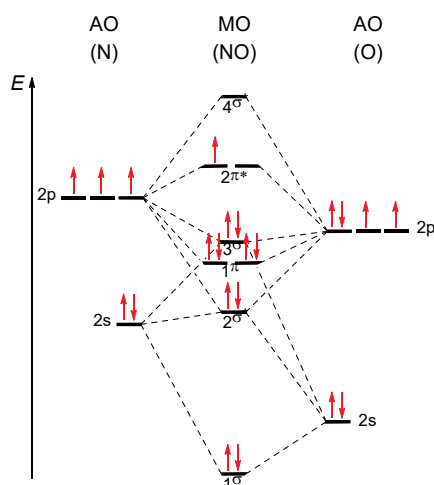
b) N–O bond order: 1.5

c) Hybridization of N: sp²

d) Geometry: bent (V-shaped)

18.3.

a) MO diagram:



b) N-O bond order: $\frac{N_{e^-}(\text{bonding}) - N_{e^-}(\text{antibonding})}{2} = \frac{8-3}{2} = 2.5$

c) The values of the bond orders in NO, NO⁺ and NO⁻ are equal to 2.5, 3 and 2, respectively. Thus, dissociation energy increases in the row: NO⁻ < NO < NO⁺.

18.4.

CO₂, H₂O, N₂

18.5.

There are 4 nitrogen and 4 oxygen atoms in complex **ML**₂, as well as carbon and hydrogen. Therefore, the composition of **ML**₂ is **MC**_{2x}**H**_{2y}**N**₄**O**₄, and **HL** should be C_xH_{y+1}N₂O₂.

From the atomic percent of metal **M**:

$$\chi(\mathbf{M}) = \frac{1}{1 + 2x + 2y + 4 + 4} = \frac{1}{2x + 2y + 9} = 0.0323$$
$$x + y = 11$$

From the degree of unsaturation of **HL**:

$$\text{DU} = \text{DBE} = \frac{2N(\text{C}) + 2 - N(\text{H}) + N(\text{N})}{2} = \frac{2x + 2 - (y + 1) + 2}{2} = 2$$
$$2x - y = 1$$

Solving the system of equations:

$$x = 4, y = 7$$

The molecular formula of **HL** is C₄H₈N₂O₂ (dimethylglyoxime).

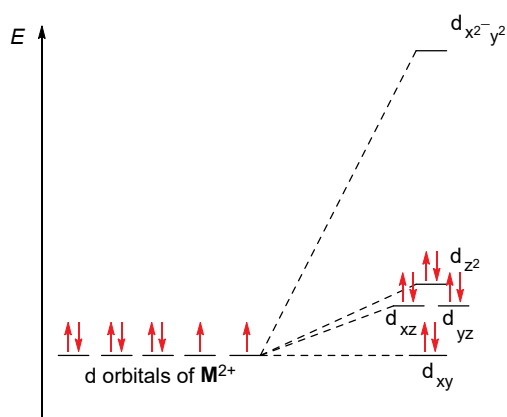
From the mass fraction of metal in **ML**₂:

$$\omega(\mathbf{M}) = \frac{M}{M + 12.01 \cdot 2x + 1.008 \cdot 2y + 14.01 \cdot 4 + 16.00 \cdot 4} = 0.3161$$
$$M + 230.2 = 3.164M$$
$$M = 106.4 \Rightarrow \mathbf{M} = \text{Pd}$$

Molecular formula of **HL**: C₄H₈N₂O₂

Metal **M**: Pd

18.6.



Note: This is an MO diagram, as opposed to more commonly taught CFT diagrams. Students are only expected to interpret these diagrams, not to build them from scratch.

18.7.

d orbital	Drawing	Interacting orbital(s) φ_i	Overlap
d_{xy}		none	none
d_{xz}		φ_7	π
d_{yz}		φ_6	π
d_{z^2}		φ_1	σ
$d_{x^2-y^2}$		φ_4	σ

19. Nitrogen fixation

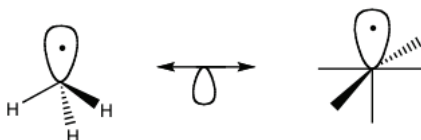
Dissociating the N_2 molecule requires 945 kJ/mol. The high bond energy results in nitrogen being inert and not very reactive. In the early 20th century, Haber and Bosch pioneered a method involving N_2 reacting with H_2 to produce NH_3 . However, their process requires high pressure and temperature to break the strong $\text{N}\equiv\text{N}$ bond. Overcoming this challenge is crucial as it would mark a significant advancement in artificial nitrogen fixation.

To understand this reaction, it's important to grasp the basics of nitrogen orbitals and bonding.

19.1. Draw the MO diagram of N_2 . Indicate the HOMO and LUMO of the molecule.

One approach to break the $\text{N}\equiv\text{N}$ bond is to connect nitrogen atoms with an organometallic species that's similar in terms of electronic structure. This concept predicting interactions between metals and main group elements is called the isolobal analogy.

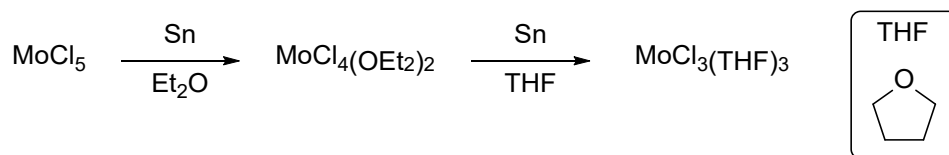
For instance, the CH_3 fragment and $\text{Mn}(\text{CO})_5$ are isolobal because they both possess a single unpaired electron. They are also one electron away from a closed shell: 8 electrons for carbon and 18 electrons for manganese.



The looped arrow is used to denote two species that are isolobal.

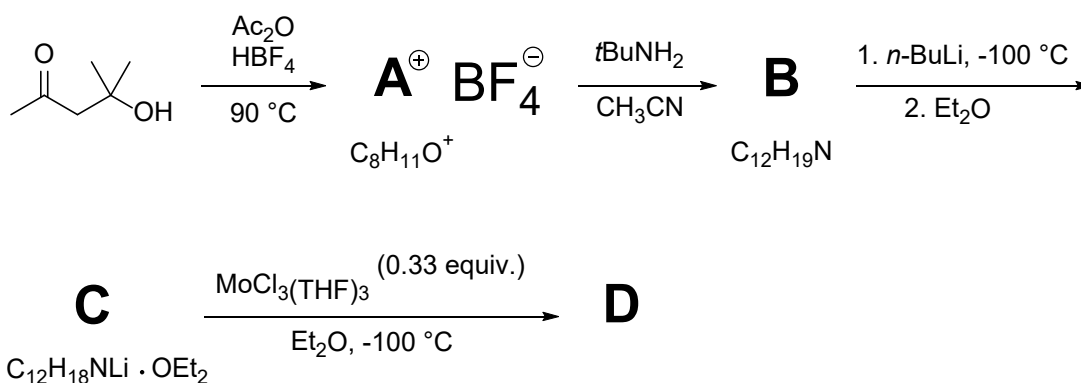
In the nitrogen fixation context, we will employ a molybdenum complex **D** that is isolobal to the nitrogen atom in N_2 .

To synthesize this complex, we start with MoCl_5 based on the scheme below:



19.2. Give the oxidation state of Mo and the d-electron count in each of the three compounds.

The next schemes show the steps to synthesize the ligand for the complex and the combination of the ligand and the metal.

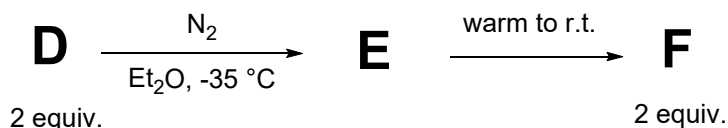


- Compound **A** ^1H NMR: 7.69 ppm (s, 2H), 2.80 ppm (s, 6H), 2.65 ppm (s, 3H).

- Compound **B** ^1H NMR: 6.36 ppm (s, 2H), 6.32 ppm (s, 1H), 3.89 ppm (br s, 1H), 2.17 ppm (s, 6H), 1.29 ppm (s, 9H).

19.3. Give the structures of compounds **A**, **B**, **C** and **D**. Hint: **A** is aromatic.

Finally, when exposed to nitrogen gas, 2 equivalents of **D** will cleave the $\text{N}\equiv\text{N}$ to produce the complex **F**, through the intermediate **E**. (r.t. = room temperature)

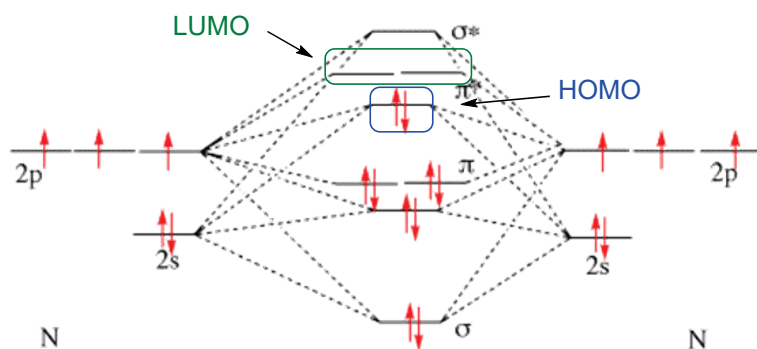


19.4. Provide the constitution (connectivity) of intermediate **E** and the structure of complex **F**. Use 'L' instead of drawing the entire ligand.

19.5. Show the isolobal analogy of the **D** complex synthesized with the N atom, considering the d-electron count and the number of ligands in the complex.

Solution

19.1.



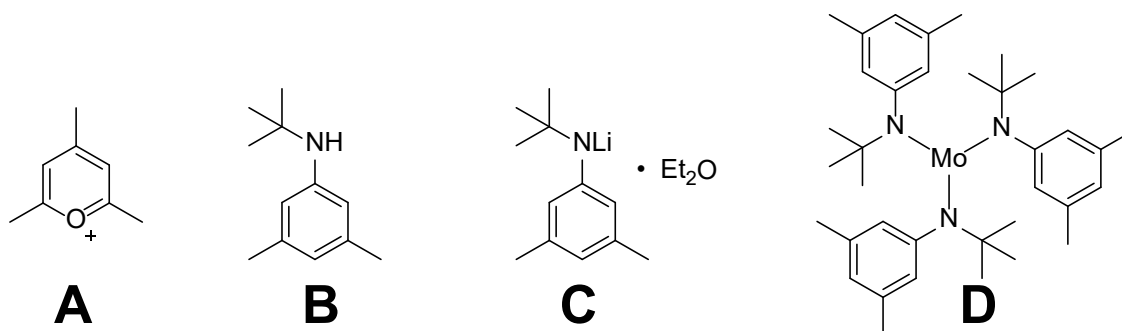
19.2.

$MoCl_5$ – oxidation state: +5, d^1

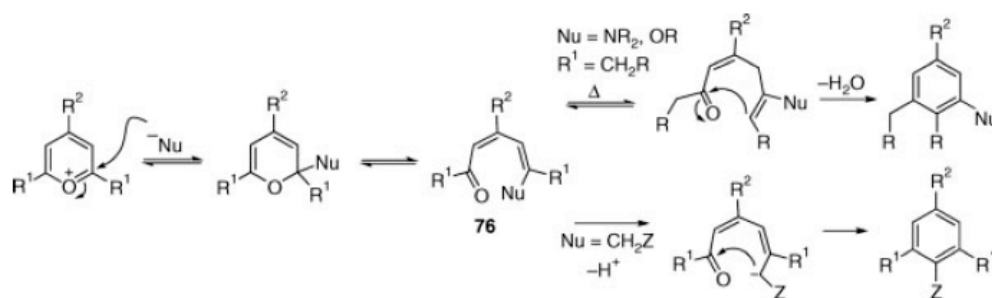
$MoCl_4(OEt_2)_2$ – oxidation state: +4, d^2

$MoCl_3(THF)_3$ – oxidation state: +3, d^3

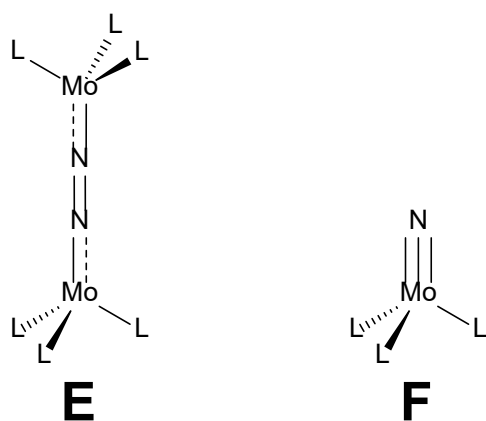
19.3.



Note: mechanism of transformation of **A** to **B** (not required, for illustration only).



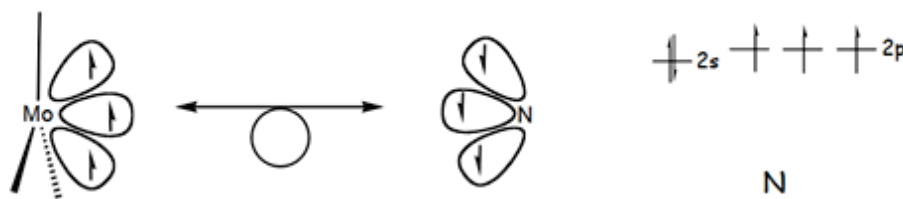
19.4.



E is an intermediate. The constitution is showing the connectivity. Bonding was not requested.

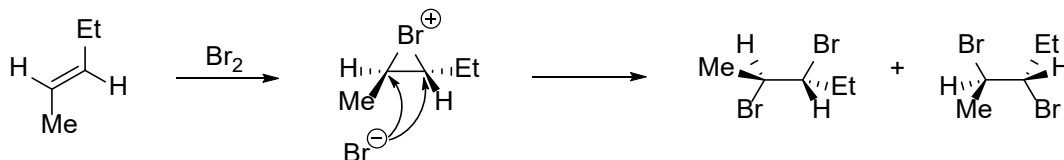
19.5.

D contains Mo(III) with three ligands. That implies a d^3 electron configuration on the metal with three unpaired electrons, just as the N atom has three unpaired electrons.



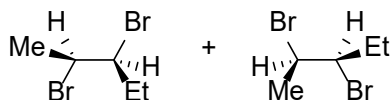
20. Bromination

The addition of bromine to alkenes occurs through a so-called bromonium ion intermediate:



The positively charged bromine atom occupies one side of the intermediate, so the bromide ion can only attack from the other side. This means that the process is stereospecific, i.e., not all stereoisomers that are theoretically possible are formed. For example, in the case of (*E*)-pent-2-ene, only molecules with the stereostructures shown above are formed.

If the bromine atoms could not only enter from the opposite side (so-called *anti*-position), the other two possible stereoisomers shown below could also be formed during the bromination of (*E*)-pent-2-ene:



In the following question, the bromine addition to hydrocarbon molecules with **eight** carbon atoms and **only one** double bond is investigated.



20.1. Give the structure of one alkene molecule that doesn't contain a ring and one alkene molecule that does contain a ring for which the particular statement is true if such a molecule exists. If no such molecule exists, write an X.

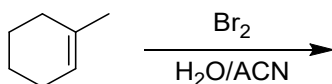
	Does not contain ring	Contains ring
a) During bromine addition, only one of the three possible stereoisomers is formed.		
b) During bromine addition, two of the three possible stereoisomers are formed, and they are enantiomers.		
c) During bromine addition, both of the two possible stereoisomers are formed, and they are enantiomers.		

d) During bromine addition, both of the two possible stereoisomers are formed, and they are diastereomers.		
e) The product of bromine addition has no stereoisomers.		

However, other products can also result from the bromination process. If the reaction takes place in an aqueous medium, the bromonium ion produced in the first step may be attacked by a water molecule instead of the bromide ion. The resulting cation is deprotonated, and overall, a hydroxy group is incorporated into the molecule. In aqueous solution, this so-called bromohydrin is the main product, in which a bromine atom and a hydroxy group are present at the 1,2 positions.

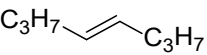

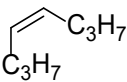
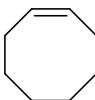
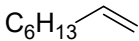
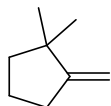
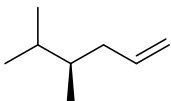
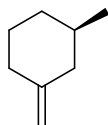
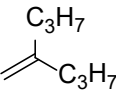
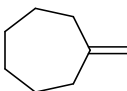
During the formation of bromohydrin, regioselectivity plays a role in addition to stereospecificity. The water molecule is more likely to attack the higher order (more substituted) carbon atom of the bromonium ion.

20.2. Which main product(s) do you expect to be formed during the bromination of 1-methylcyclohex-1-ene in an aqueous solution? **Show** the stereostructure using wedge-dash notation ( ; ).



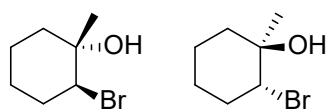
Solution

20.1.

	Does not contain ring	Contains ring
a) During bromine addition, only one of the three possible stereoisomers is formed.		
b) During bromine addition, two of the three possible stereoisomers are formed, and they are enantiomers.		
c) During bromine addition, both of the two possible stereoisomers are formed, and they are enantiomers.		
d) During bromine addition, both of the two possible stereoisomers are formed, and they are diastereomers.		
e) The product of bromine addition has no stereoisomers.		

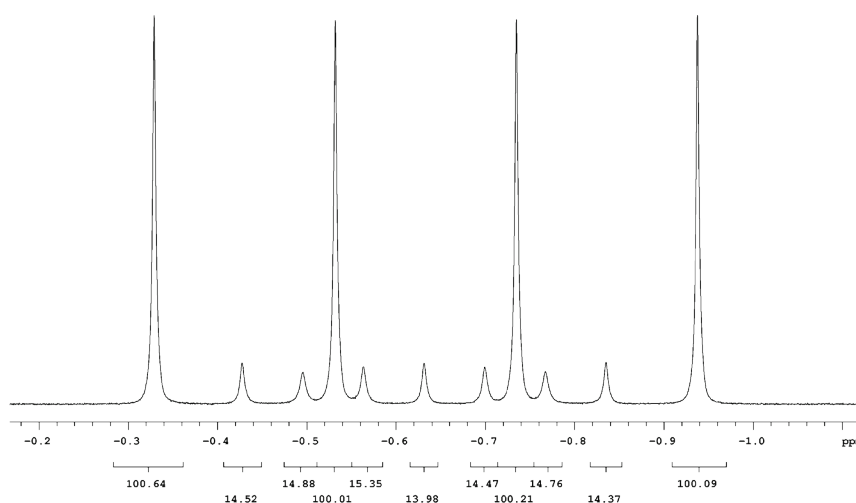
Other structures that fulfill the statements are acceptable.

20.2.



21. NMR puzzle

One day Dr. Preping found a sealed container in his lab, filled with a white powder. The label only said has disappeared. He did not want to dispose of it, so he tried to figure out what it was. Upon dissolving the powder in water, he experienced intensive bubbling and the solution turned slightly basic afterwards. When he dissolved the powder in alcohol, he experienced gas evolution again, but less intensive than before. He could not observe melting in the range of his apparatus (up to 300 °C). The compound could not be dissolved in ether and was only slightly soluble in THF. He asked for the help of Prof. Speclock, who examined the filtrate of the THF suspension, and found an interesting group of signals in the ^1H NMR spectrum. See the figure. (The numbers at the bottom are integrals of the respective signals.)

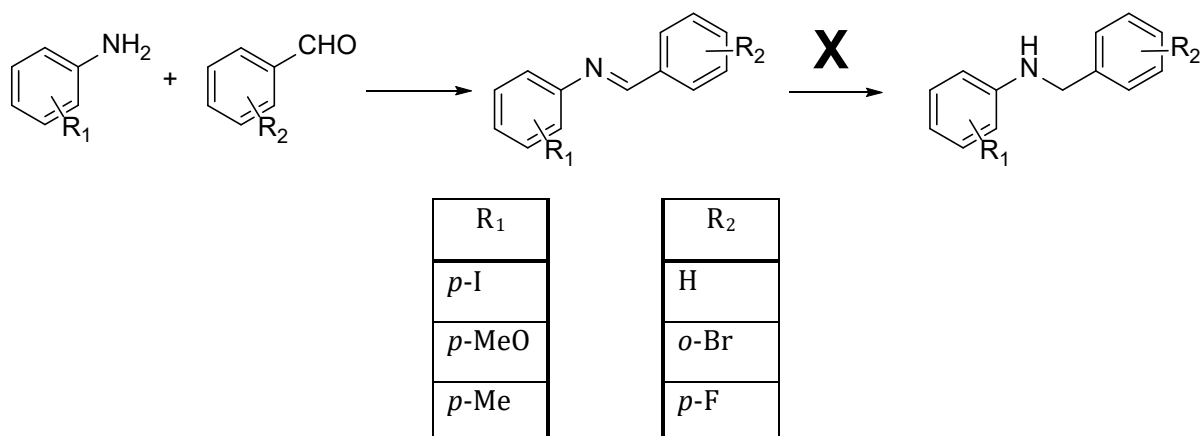


She immediately knew what the unknown compound could be. She showed Dr. Preping the following table.

Isotope	Spin quantum number	Natural abundance (%)	Isotope	Spin quantum number	Natural abundance (%)
^1H	$\frac{1}{2}$	99.99	^{29}Si	$-\frac{1}{2}$	4.69
^2H	1	0.0115	^{31}P	$\frac{1}{2}$	100
^6Li	1	7.42	^{32}S	0	99.24
^7Li	$\frac{3}{2}$	92.58	^{33}S	$\frac{3}{2}$	0.76
^{10}B	3	19.9	^{35}Cl	$\frac{3}{2}$	75.53
^{11}B	$\frac{3}{2}$	80.1	^{37}Cl	$\frac{3}{2}$	24.47
^{12}C	0	98.93	^{47}Ti	$\frac{5}{2}$	7.28
^{13}C	$\frac{1}{2}$	1.07	^{49}Ti	$\frac{7}{2}$	5.51
^{14}N	1	99.64	^{117}Sn	$\frac{1}{2}$	7.61
^{15}N	$-\frac{1}{2}$	0.36	^{119}Sn	$\frac{1}{2}$	8.58
^{16}O	0	99.96	^{121}Sb	$\frac{5}{2}$	57.21
^{17}O	$-\frac{5}{2}$	0.04	^{123}Sb	$\frac{7}{2}$	42.79
^{19}F	$\frac{1}{2}$	100	^{203}Tl	$\frac{1}{2}$	29.5
^{27}Al	$\frac{5}{2}$	100	^{205}Tl	$\frac{1}{2}$	70.5

21.1. Suggest a formula for the unknown compound **X**. (Give your explanation!)

Dr. Preping was very happy because he wanted to perform the following reactions and he had been looking for the necessary reagent in his lab for a long time. Now he understood that he hadn't been able to find it because it was labelled 'compound **X**' the whole time. When carrying out the reactions, he was again absentminded a bit and could not remember which reactants he used for which flask. He knew only that he used all the amines and aldehydes once (see table). Prof. Speclock helped again. Based on the ^1H NMR spectra of the amine products (**A**, **B**, **C**) it was obvious which flask contained which compound.



A: ^1H NMR δ 2.19 (3H, s), 3.7 (1H, br. s), 4.32 (2H, s), 6.86 (2H, d), 6.92 (1H, t), 7.05 (2H, d), 7.23 (1H, d), 7.28 (1H, t), 7.45 (1H, d) ppm.

B: ^1H NMR δ 3.6 (1H, br. s), 3.71 (3H, s), 4.25 (2H, s), 6.59 (2H, d), 6.74 (2H, d), 7.32 (5H, m) ppm.

C: ^1H NMR δ 4.31 (2H, s), 4.8 (1H, br. s), 6.41 (2H, d), 7.02 (2H, t), 7.29 (2H, dd), 7.52 (2H, d) ppm.

21.2. Give the structures for **A**, **B**, **C**.

The next week he attempted the same synthesis using a new combination of his amines and aldehydes listed above. He obtained a colored compound **D** with totally different characteristics. It gave the ^1H NMR spectrum listed below.

D: ^1H NMR δ 2.35 (3H, s), 7.14 (2H, d), 7.23 (2H, d), 7.45 (3H, m), 7.88 (2H, d), 8.44 (1H, s) ppm.

21.3. Identify compound **D** and **consider** the possible reasons for its formation.

Solution

21.1.

NaBH_4

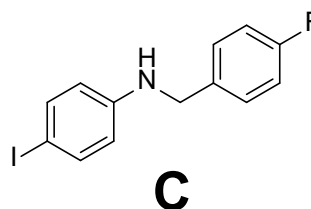
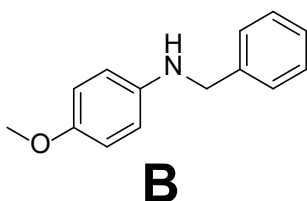
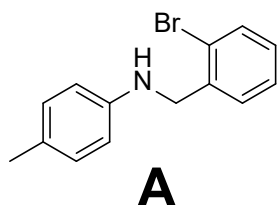
2 isotopes of the atom attached to H in intensity ratio $(4 \times 100):(7 \times 15)=400:105=80:20$

The spin numbers: $I_1 = (4-1)/2 = 3/2$, $I_2 = (7-1)/2 = 3$. Only nucleus B fits.

The reaction that uses this reagent is a reduction.

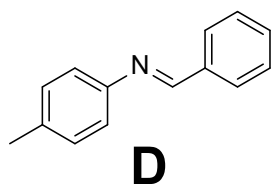
We cannot identify the cation, but sodium is a common borohydride.

21.2.



21.3.

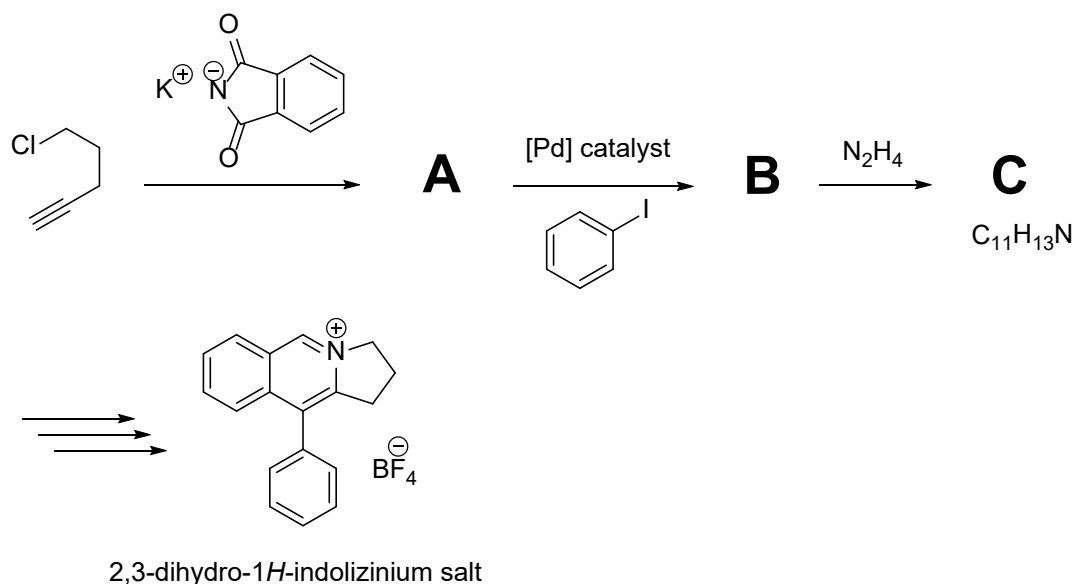
The reduction step did not take place due to e.g., the presence of water in the reaction mixture or Dr. Preping just forgot to add the reducing agent.



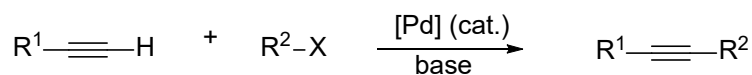
22. Organonitrogen Compounds: The Compounds of Life

Nitrogen-containing compounds, such as amino acids, proteins, dyes, and medicines play a crucial role in different aspects of our everyday lives. We shall explore some of their classes in this task.

Amines are used as organic bases, for example in polymer and drug synthesis. Historically, amines were made using the Gabriel synthesis, which was developed by Siegmund Gabriel in 1887. In this reaction, a primary alkyl halide reacts with potassium phthalimide in an S_N2 reaction, which is followed by reaction with hydrazine. Gabriel synthesis is a key step in the synthesis of the 2,3-dihydro-1*H*-indolizinium salt as shown below.



Palladium-catalyzed cross-coupling reaction
(Sonogashira coupling)



Note: More commonly, the reaction employs a palladium catalyst as well as copper co-catalyst.

22.1. Draw the structures of compounds A–C.

22.2. Determine the number of signals in the ^1H NMR spectrum of the final compound (indolizinium salt)?

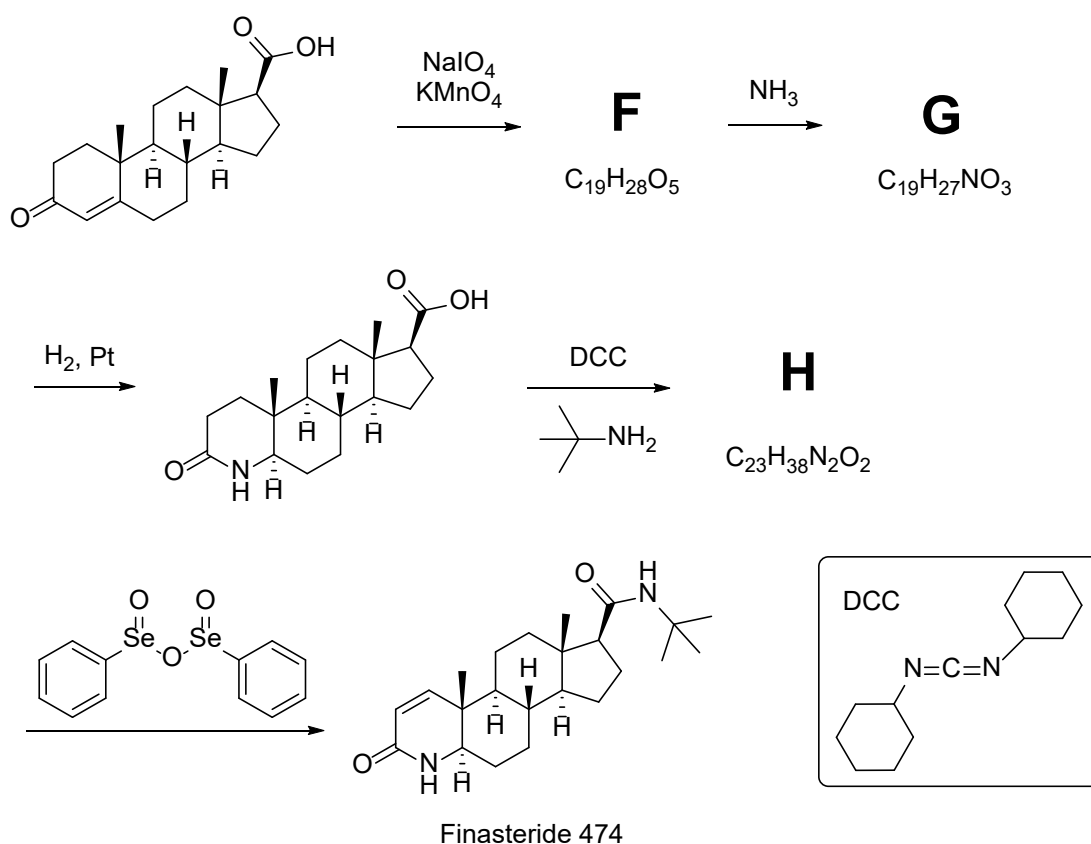
Amino acids are the building blocks of proteins. They can be synthesized from 2-oxoacids as shown below in the synthesis of amino acid **E**. The synthesis yields racemic **E**.



22.3. **Draw** the structures of compounds **D** and **E**.

22.4. **Draw** the two enantiomers of **E** and **assign** the *R/S* configuration of the chirality center(s).

Many commercial medicines contain nitrogen atoms. Finasteride 474 is a medicine used to treat hair loss in men. Its synthesis is shown below.



22.5. **Draw** the structures of compounds **F**, **G**, and **H**.

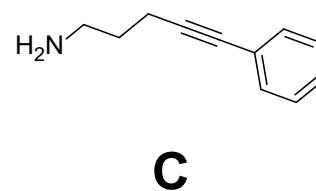
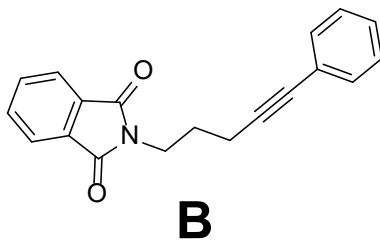
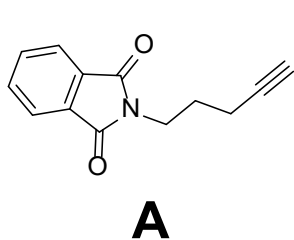
22.6. **Name** the two functional groups containing nitrogen in Finasteride 474.

22.7. **Label** all the stereogenic centers in Finasteride 474 with an asterisk and assign their *R/S* configuration.

22.8. **Identify** the role of DCC in the reaction leading to **H**.

Solution

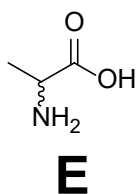
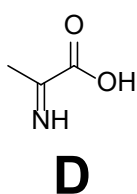
22.1.



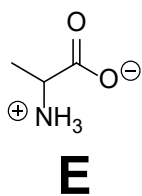
22.2.

11 NMR signals

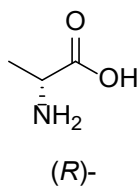
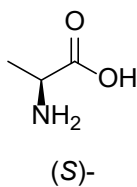
22.3.



Note: **E** can also be drawn as zwitterion



22.4.





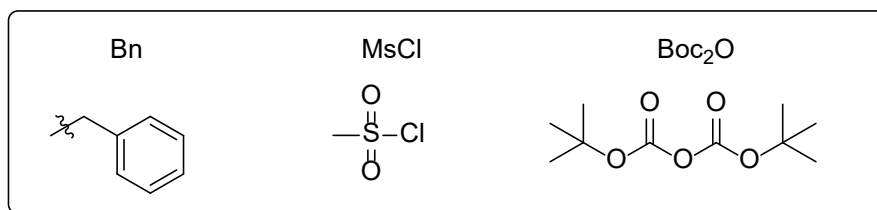
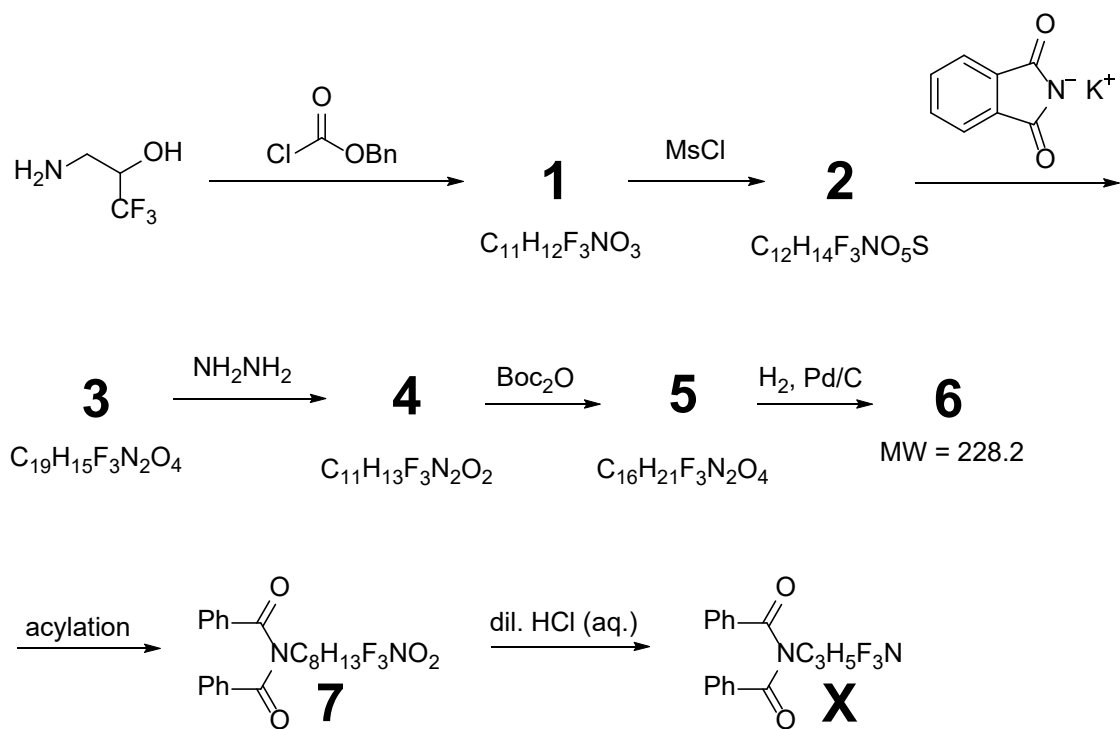
Lactam and amide. Note: A lactam is also an amide, so the answer amide is sufficient.

$$\text{O}=\text{N}-\text{N}=\text{O}$$


Amide coupling reagent / dehydrating agent / activator of the carboxylic acid

23. NMR clue

In the following reactions all the steps are routinely used basic transformations, so only the end product **X** was isolated, and the intermediates were not. Unfortunately, the ^1H NMR spectrum of **X** proved to be too complicated, so compound **7** was also investigated. This spectrum was also too crowded but contained a characteristic signal corresponding to an amide-type NH showing triplet multiplicity.



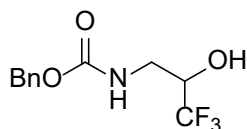
23.1. Determine the structures of compounds **1-7** and **X**.

Y, a constitutional isomer of **X** has also been prepared. The aliphatic part of its ^1H NMR is listed: 2.02 (2H, d), 3.65 (1H, m), 4.11 (1H, dd), 4.18 (1H, dd) ppm.

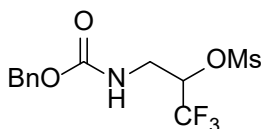
23.2. What is the structure of **Y**? **How** can we explain that only **X** and not **Y** is formed in the first synthesis?

Solution

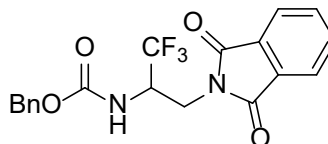
23.1.



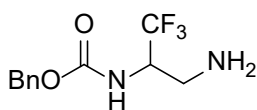
1



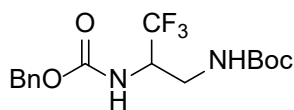
2



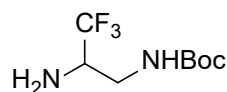
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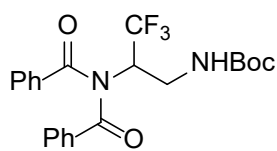
4



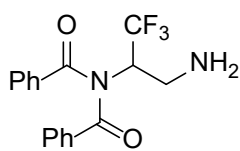
5



6

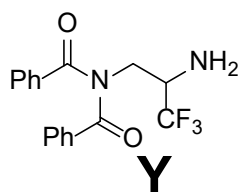


7



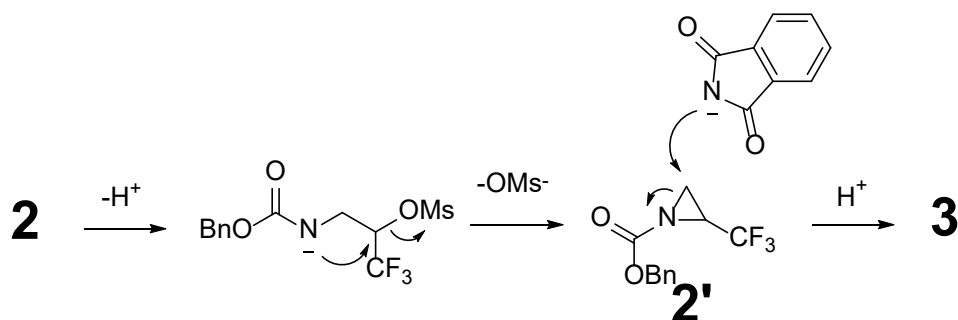
X

23.2.



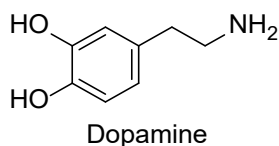
Y

In the conversion of **2** to **3** the strong base caused an intramolecular attack and resulted in an intermediate product containing a 3-membered ring (**2'**). The ring opening occurred from a different position.

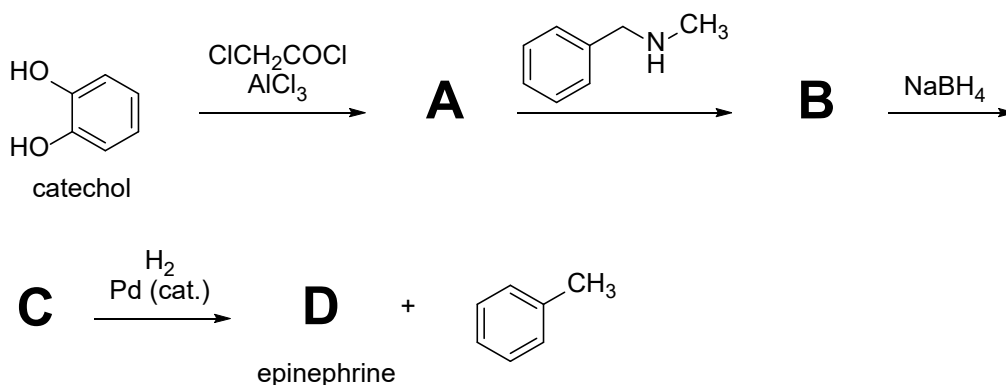


24. Neurotransmitters

Information is transmitted between neurons using neurotransmitters, chemicals that carry messages from one nerve cell across space to the next nerve. Catecholamines are neurotransmitters released by neurons and the adrenal gland. Dopamine, for example, induces feelings of pleasure, satisfaction and motivation.

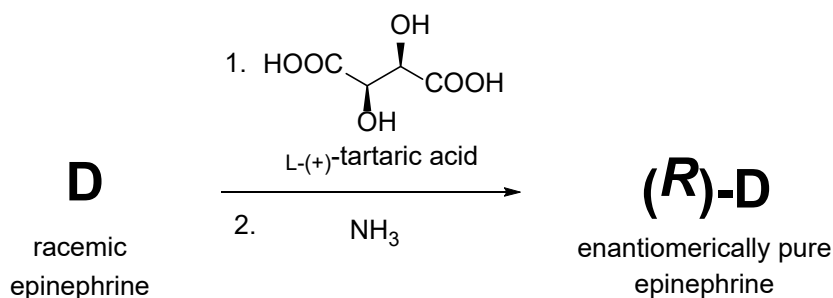


Other examples of catecholamines include epinephrine (**D**) and norepinephrine, derived from the amino acid phenylalanine. The following scheme shows a synthetic route to epinephrine (**D**), starting from catechol. **D** is stable under acid/alkaline hydrolysis conditions.



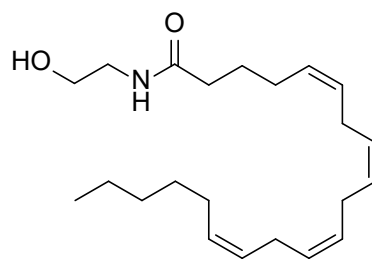
24.1. Draw the structures of compounds **A–D**.

The synthetic route above leads to a racemic epinephrine. However, our body produces it as a single enantiomer of (*R*)-configuration. Using chiral resolution, it is possible to isolate one enantiomer from a racemic mixture.



24.2. Explain how the chiral resolution works and **draw** the structure of (*R*)-**D**.

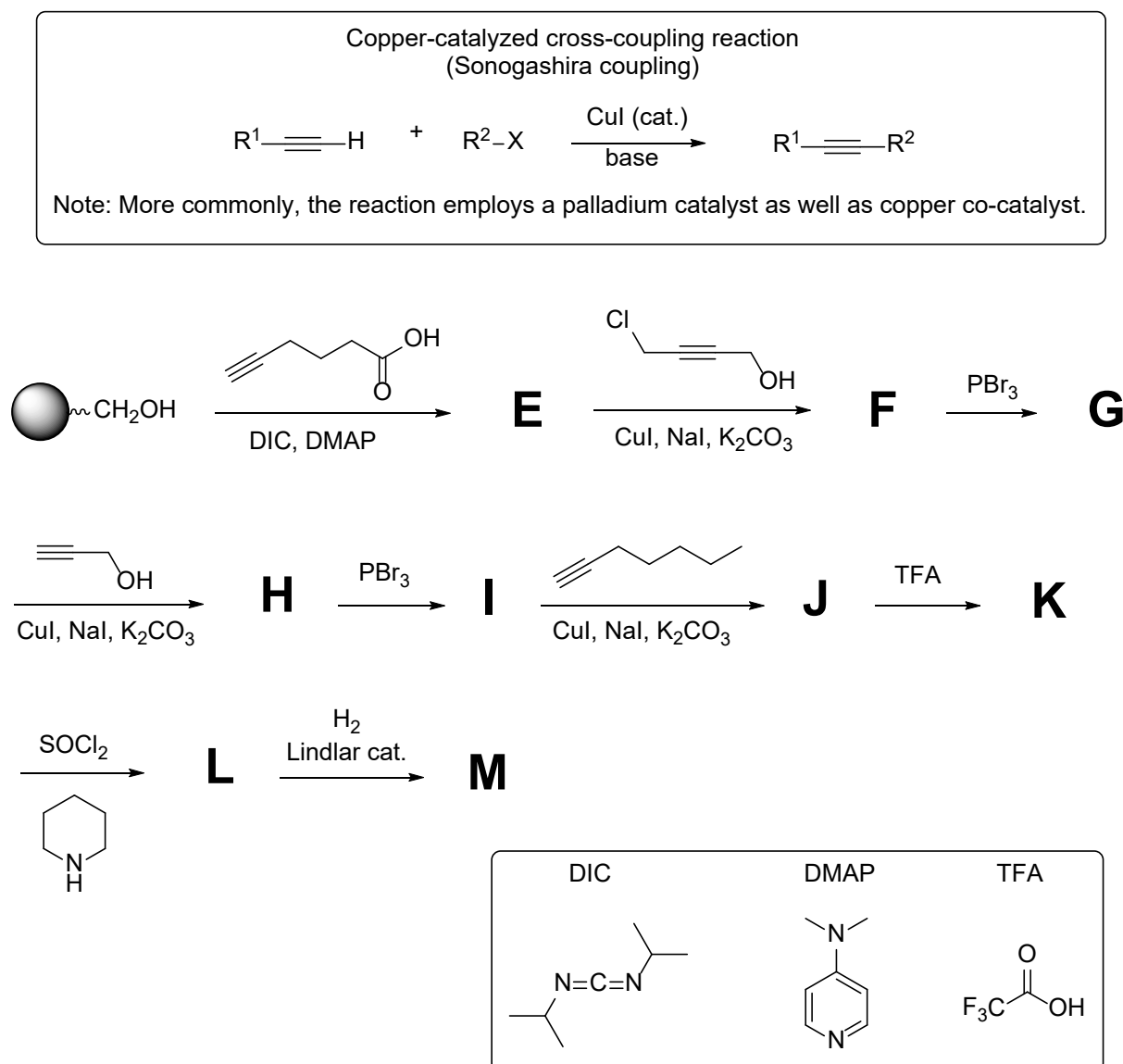
Another group of neurotransmitters is derived from lipids. Anandamide is a fatty acid-based neurotransmitter, first isolated and identified by William A. Devane in 1992. It is present in the brain and binds to cannabinoid receptors. The name anandamide is derived from the Sanskrit word ananda, which means joy, bliss, delight. It is responsible for calmness and dream states.



Anandamide

Anandamide has a short-duration neurological effect and has attracted scientists to use its structural variants as therapeutic agents to treat neuropathic pain. A series of anandamide analogues were synthesized by solid phase synthesis technique, in which the starting material is attached to a solid support. After a sequence of reactions building larger molecules, the product can be easily separated from the reaction mixture by a simple filtration. Then, the solid support is removed by an appropriate reagent.

The synthetic scheme below depicts the preparation of an analogue (**M**) of anandamide. Solid support is represented as a black ball. CuI and NaI serve as catalysts.



24.3. What is the role of DIC? Select all that apply.

- a) Base
- b) Acid
- c) Catalyst
- d) Coupling reagent
- e) Solvent

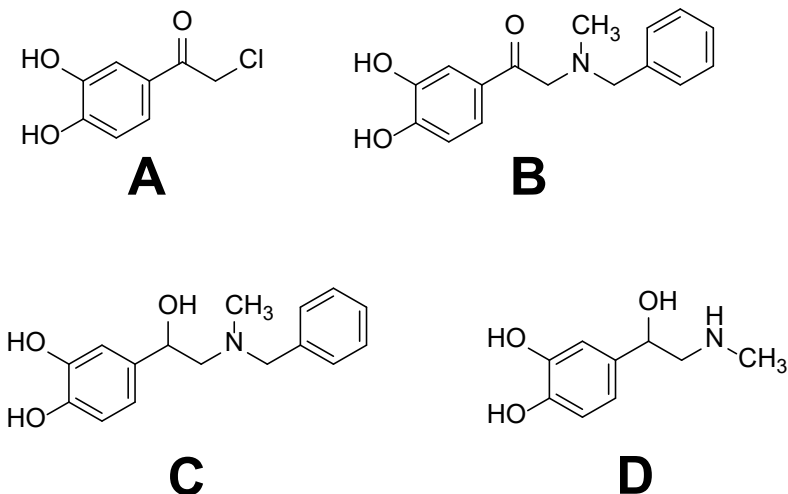
24.4. What is the role of DMAP? Select all that apply.

- a) Base
- b) Acid
- c) Catalyst
- d) Coupling reagent
- e) Solvent

24.5. Draw the structures of compounds **E–M**.

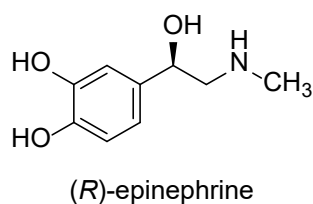
Solution

24.1.



24.2.

Chiral resolution is the process of separating the two enantiomers found in a racemic mixture. The process involves reacting the racemic mixture with an enantiomerically pure chiral molecule and thereby producing two different diastereomers. Since diastereomers differ from one another with respect to their physical properties, they can be separated using e.g. crystallization, distillation or column chromatography on silica. Finally, the title compound has to be liberated. Since epinephrine is a base, it reacts readily with an acid to form salt. Salts crystallize easily and therefore crystallization can be used to separate the two diastereomers. In the final step, (*R*)-epinephrine is obtained from its salt by the addition of a base.



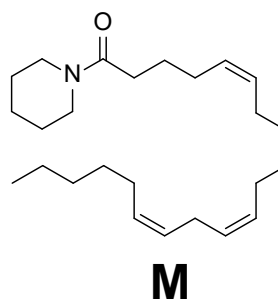
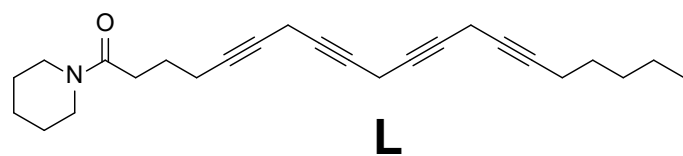
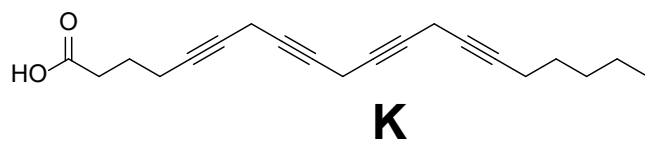
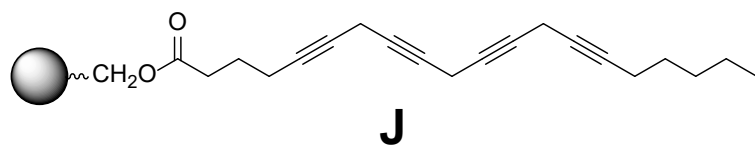
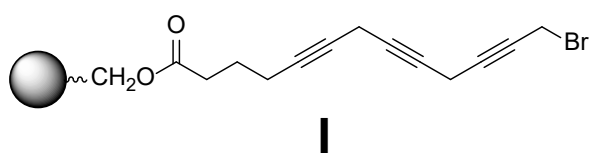
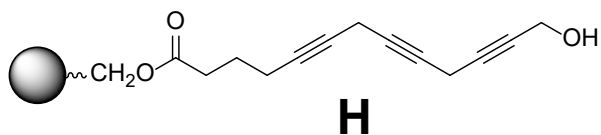
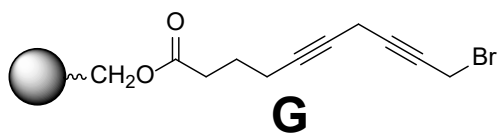
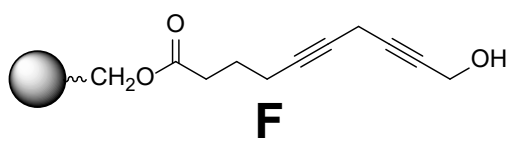
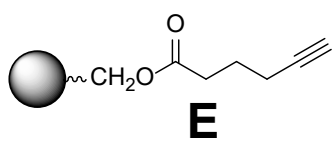
24.3.

d) Coupling reagent

24.4.

a) Base and c) Catalyst

24.5.

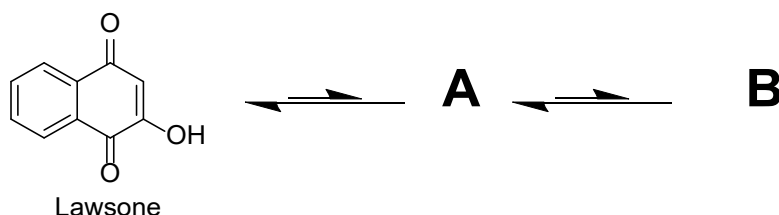


25. Henna

Henna is an essential product in the Saudi Arabian and Middle Eastern cultures. Traditionally, women use henna to make gorgeous ornaments on their hands, arms and feet for special occasions such as weddings and the two Eid holidays. Henna is a red or brown dye that is typically obtained from dried leaves of the henna tree (*Lawsonia inermis*). Henna leaves contain a dye molecule that is called lawsone. This molecule binds to the keratin in the skin and hair and the colour lasts for 2 to 6 weeks.



Lawsone exists in three tautomeric forms that are in equilibrium. The 1,4-naphthoquinone structure is the most stable form, followed by **A** and then **B**, which is the least stable.

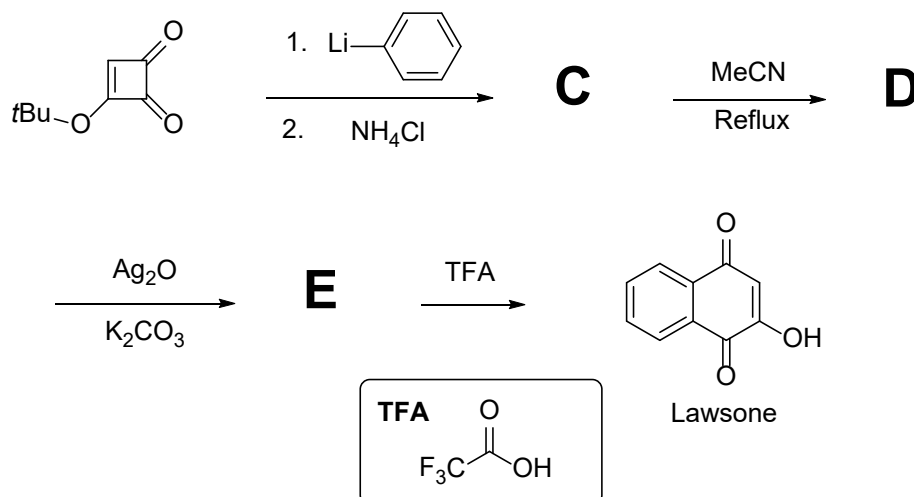


25.1. Draw the structures of lawsone tautomers **A** and **B**.

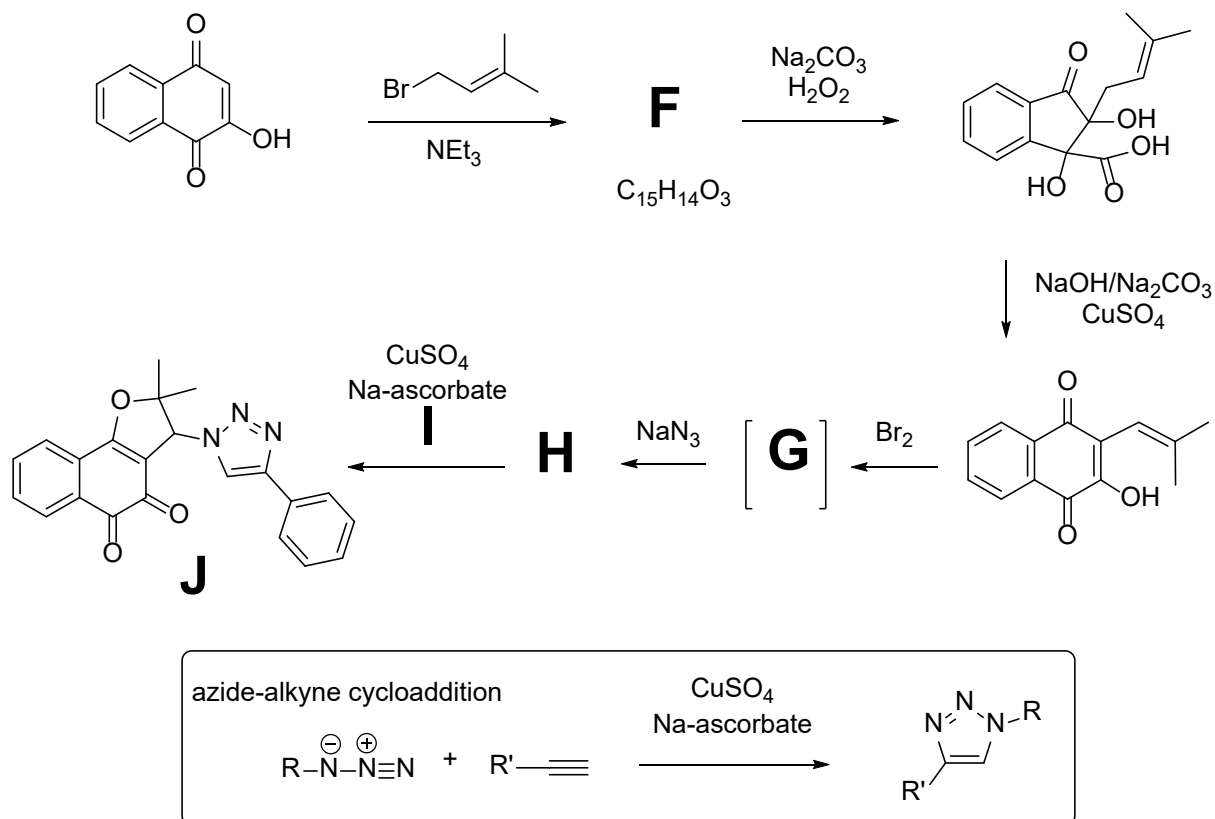
A short route to lawsone and other similar naphthoquinones was described by Heerding and Moore, proceeding *via* 4-aryl-3-*tert*-butoxy-4-hydroxycyclobutenones as illustrated below.

25.2. Draw the missing compounds **C**, **D**, and **E** in the total synthesis of lawsone.

Hint: **D** contains a hydroquinone motif.



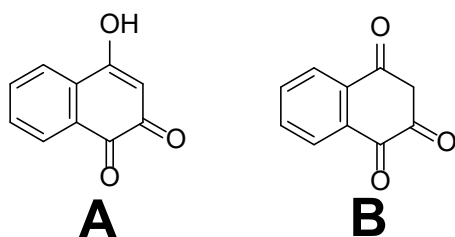
Naphthoquinone-based 1,2,3-triazole **J** was shown to have potent trypanocidal and antitumor activities. This compound can be synthesized starting from lawsone according to the scheme below. **E** contains two condensed six-membered rings. The final step is the azide-alkyne cycloaddition, which proceeds according to the scheme in the box.



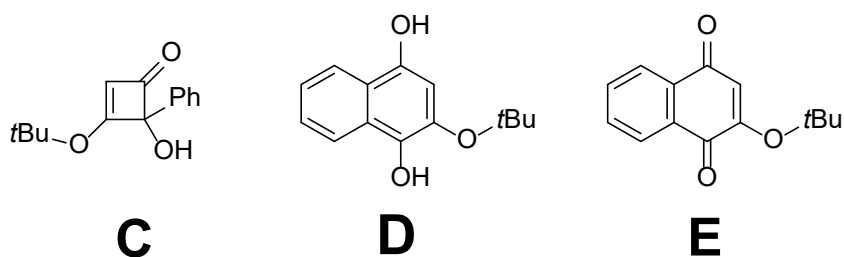
25.3. **Draw** the missing compounds **F–I** in the total synthesis of triazole **J**.

Solution

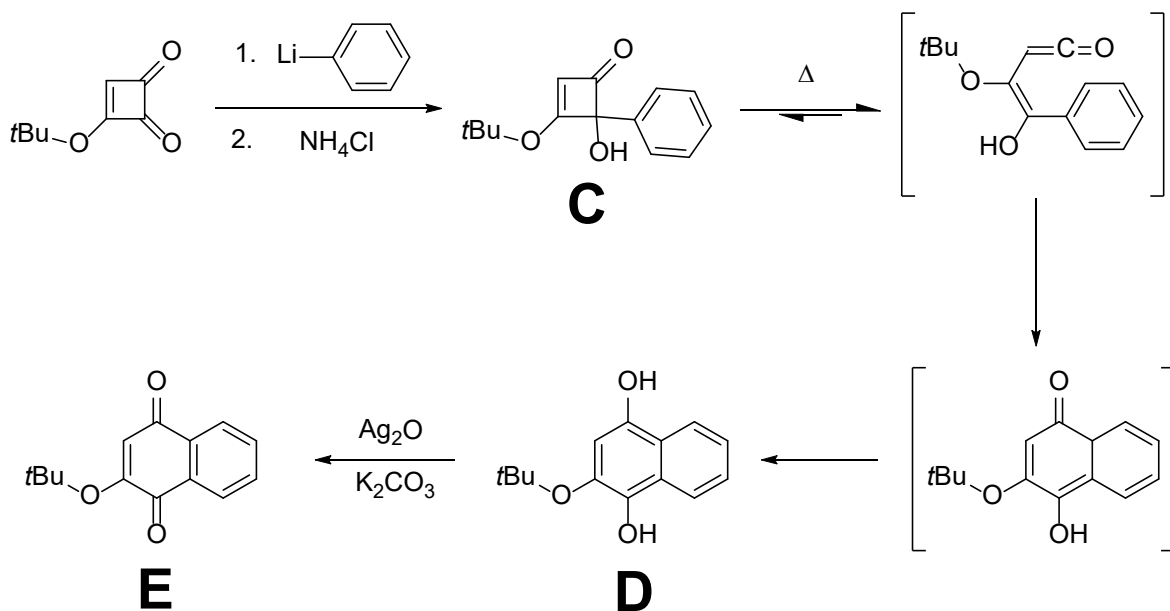
25.1.



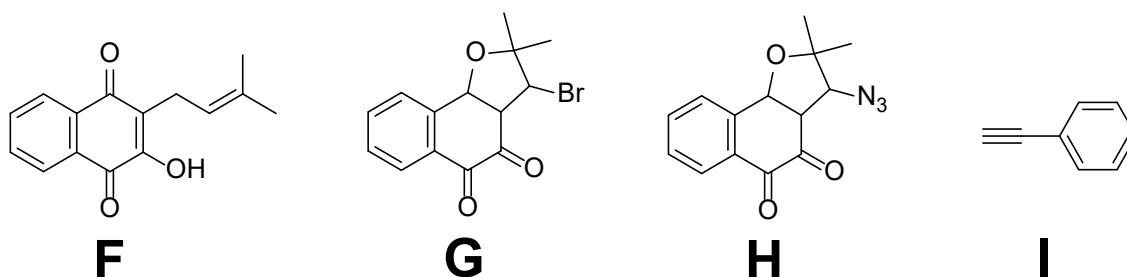
25.2.



Mechanism (not required, shown for deeper understanding):



25.3.



References:

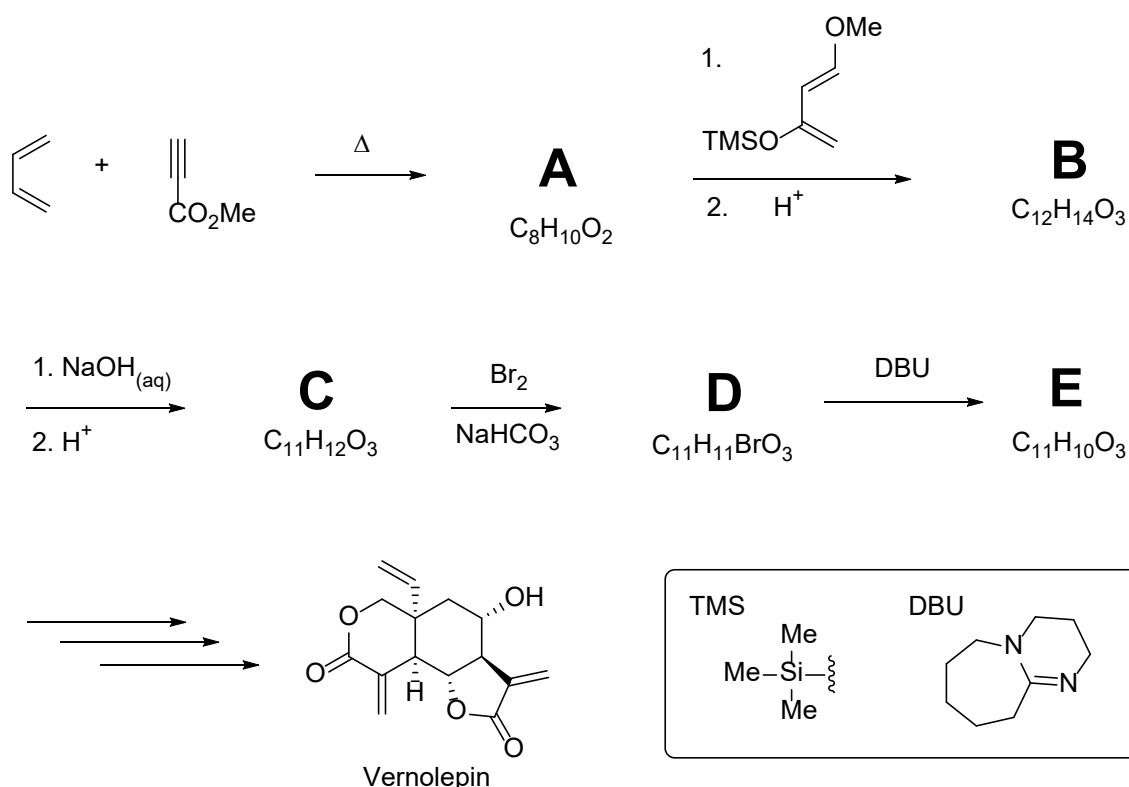
Regiospecific synthesis of hydroxyquinones and related compounds from 3-tert-butoxycyclobutene-1,2-dione, Julia M. Heerding and Harold W. Moore, *The Journal of Organic Chemistry* **1991** 56 (12), 4048-4050, <https://doi.org/10.1021/jo00012a046>

Molecular hybridization as a powerful tool towards multitarget quinoidal systems: synthesis, trypanocidal and antitumor activities of naphthoquinone-based 5-iodo-1,4-disubstituted-, 1,4- and 1,5-disubstituted-1,2,3-triazoles, S. B. B. Bahia, W. J. Reis, G. A. M. Jardim, F. T. Souto, C. A. de Simone, C. C. Gatto, R. F. S. Menna-Barreto, S. L. de Castro, B. C. Cavalcanti, C. Pessoa, M. H. Araujo and E. N. da Silva Júnior, *Med. Chem. Commun.*, 2016, **7**, 1555, <https://doi.org/10.1039/C6MD00216A>

26. Natural products syntheses

Part A

Vernolepin is a highly functionalized elemanolide dilactone isolated from sweet bitterleaf (*Vernonia hymenolepis*) that grows in tropical Africa. Thanks to its platelet anti-aggregating and irreversible DNA polymerase inhibiting properties, it may serve as antitumor agent. Compound **E** serves as a key intermediate in the total synthesis of vernolepin. It can be prepared in several steps, starting with a series of cycloaddition reactions as shown below.



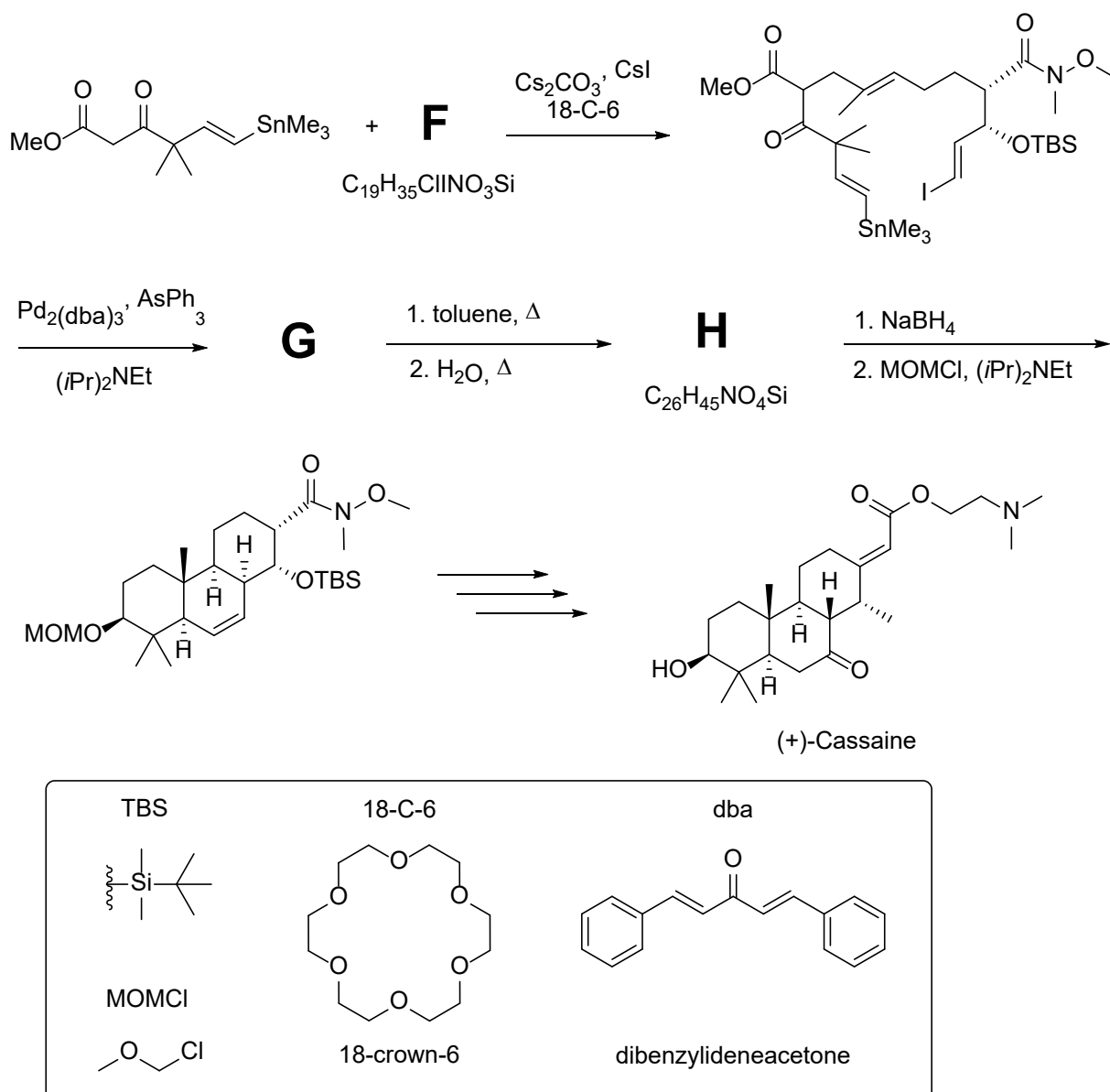
26.1. Draw the structures of compounds **A–E** (stereochemistry is not required).

Hints:

- B** contains two fused rings and two carbon–carbon double bonds.
- E** contains two carbon–carbon double bonds.

Part B

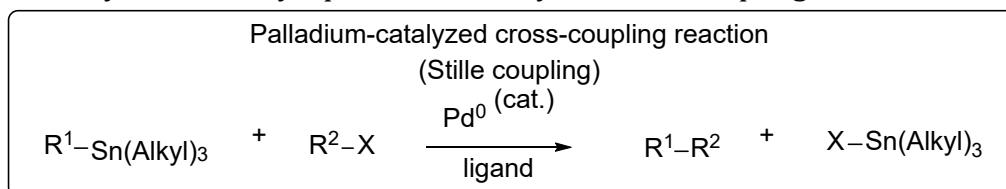
(+)-Cassaine is a toxic compound which is found in the tree genus *Erythrophleum*. Since ancient times, it has been used as an ordeal poison by African tribes and as an arrow poison by the Casamance people of Senegal. It inhibits Na^+ , K^+ -ATPase, thereby changing the force and energy of cardiac muscle contractions. One synthetic route to (+)-cassaine is depicted below.



26.2. Draw the structures of compounds **F–H**, including stereochemistry.

Hints:

- G** was synthesized by a palladium-catalyzed cross-coupling reaction.



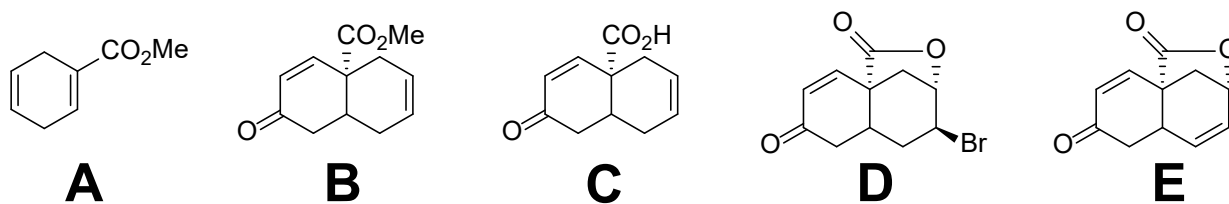
- The first reaction from **G** to **H** is a Diels–Alder reaction.

26.3. Explain the role of 18-C-6.

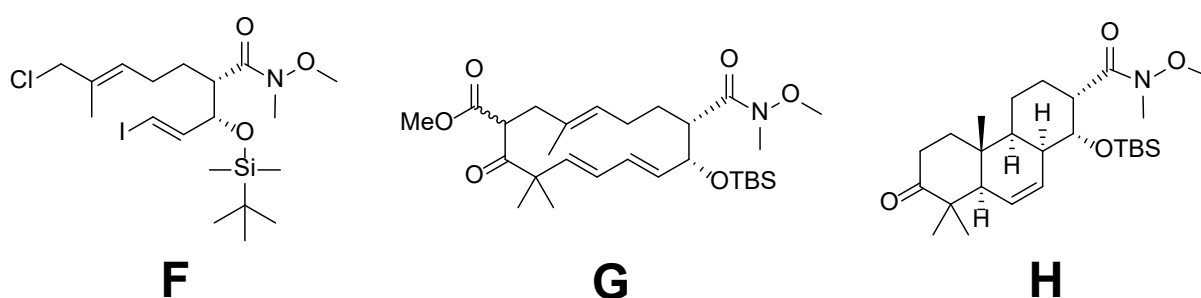
26.4. Identify all chirality centers in (+)-cassaine. **Label** them with an asterisk and assign *R/S* configuration to each of them.

Solution

26.1.



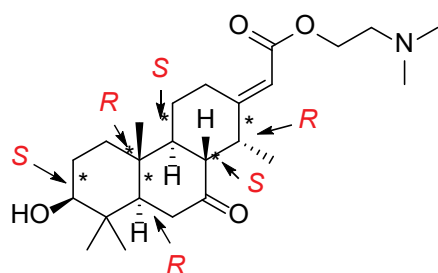
26.2.



26.3.

18-crown-6 functions as a ligand for cesium cations, making the naked anion more naked (nucleophilic).

26.4.

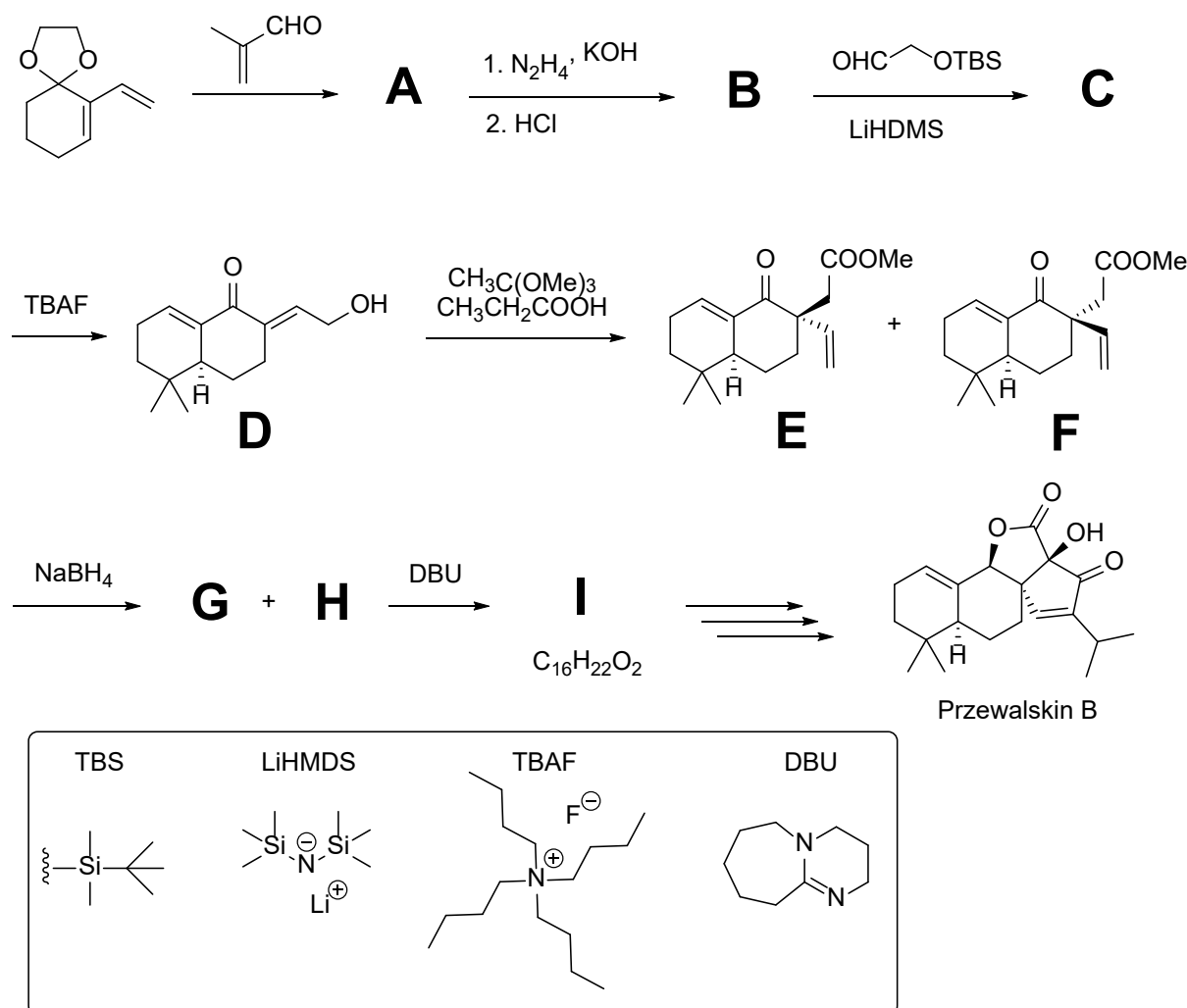


Reference:

Total Synthesis of (+)-Cassaine via Transannular Diels–Alder Reaction, Serge Phoenix, Maddi Sridhar Reddy, and Pierre Deslongchamps, *Journal of the American Chemical Society* **2008** 130 (42), 13989-13995, <https://doi.org/10.1021/ja805097s>

27. Przewalskin B: Medicine for the heart

(±)-Przewalskin is a diterpenoid found in a Chinese plant *Salvia przewalskii*, a member of the Labiatae plants family. Many species of this widely distributed genus have been used for centuries as folk medicine to treat a variety of illnesses. Przewalskin, first isolated in 2007, is used to treat cardiovascular diseases. Zhixiang Xie's group outlined the total synthesis shown below.



Compound **A** is made regioselectively *via* a Diels–Alder cycloaddition reaction. Then, **A** is reduced using Wolff–Kishner reduction and deprotected using HCl. Aldol condensation between **B** and protected aldehyde gave **C** which, after deprotection with TBAF, afforded a bicyclic intermediate **D**. The next step provided an inseparable mixture of stereoisomers **E** and **F**. The oxo group in both **E** and **F** can be reduced using NaBH_4 to yield stereoisomers **G** and **H**, respectively. This gives a new chirality center, which has the (*S*) configuration in both **G** and **H**.

27.1. **Draw** the structures of compounds **A**, **B**, **C**, **G**, and **H** (stereochemistry in **A**, **B**, and **C** is not required).

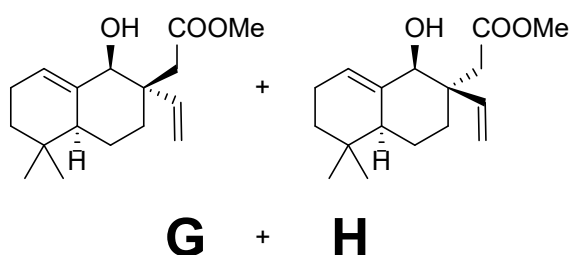
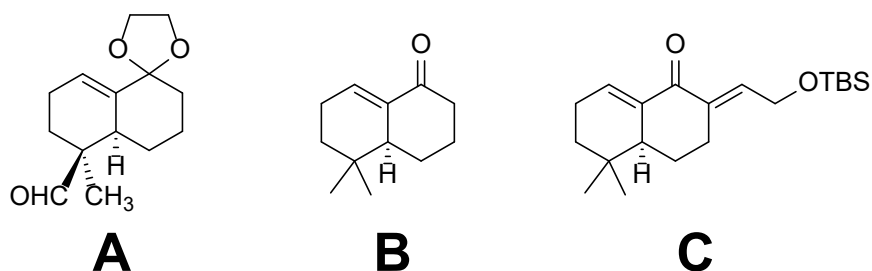
27.2. **What** is the stereochemical relation between compounds **E** and **F**?

When the reduced functional group in **G** and **H** is treated with the base DBU, it can form a cyclic ester if the other group is on the same face of the ring.

27.3. **Draw** the structure of **I**. **Identify** which compound(s) can form a cyclic ester: **G**, **H**, both, neither?

Solution

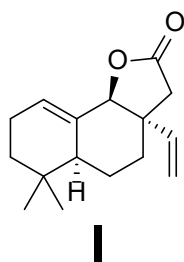
27.1.



27.2.

They are diastereomers.

27.3.



Cyclic ester **I** is formed from compound **G**.

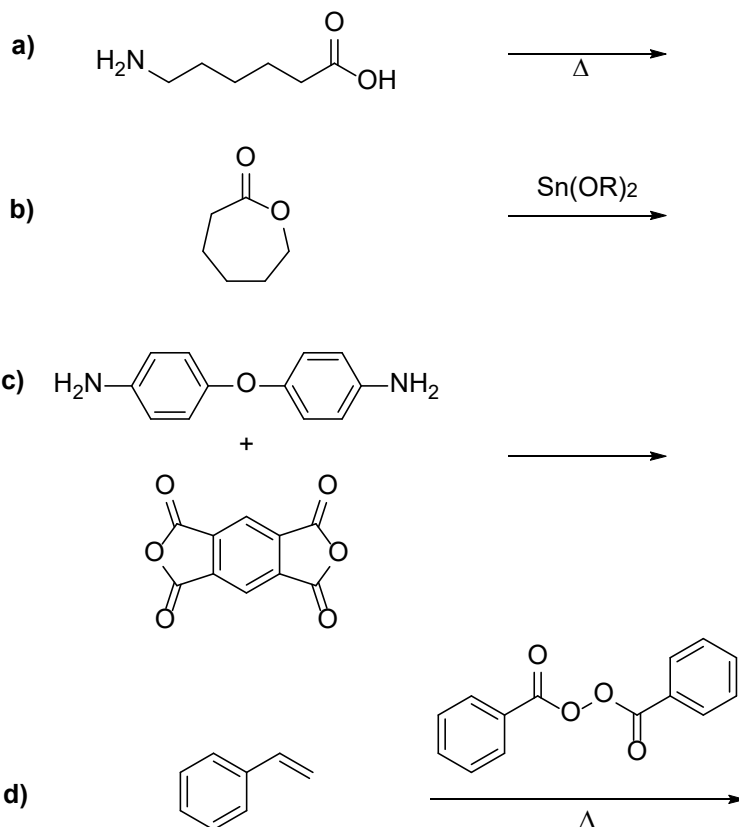
Reference:

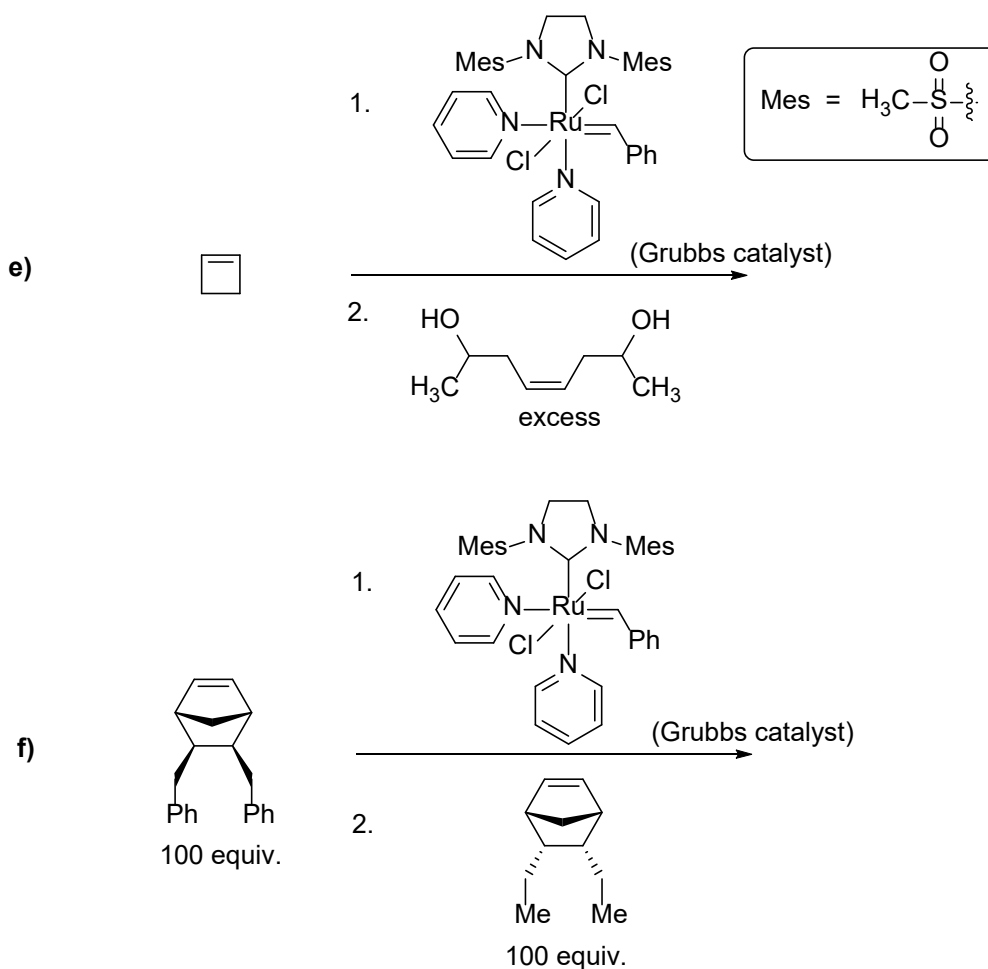
Total Synthesis of (±)-Przewalskin B, Mingxing Xiao, Lin Wei, Liqi Li, and Zhixiang Xie, *The Journal of Organic Chemistry* **2014** 79 (6), 2746-2750, <https://doi.org/10.1021/jo500047q>

28. Polymers

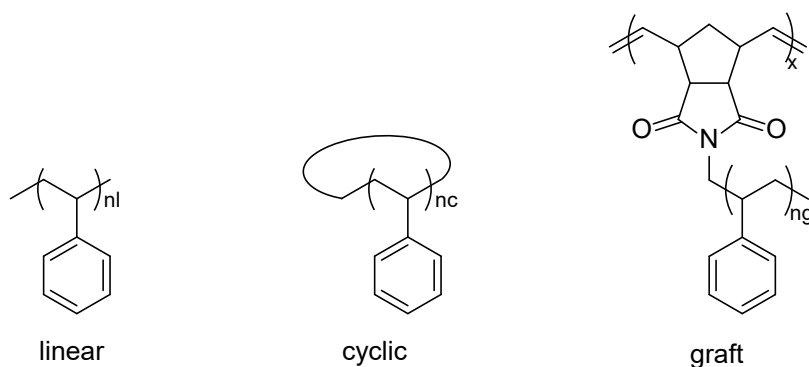
Polymerization processes play a crucial role in the petrochemical and manufacturing industries, allowing the creation of complex polymers that were previously inaccessible, thanks to techniques like olefin metathesis.

28.1. For each polymerization reaction below, **draw** the draw the repeating units of the resulting polymers. In addition, **classify** each polymerization as step growth, chain growth, or living polymerization.

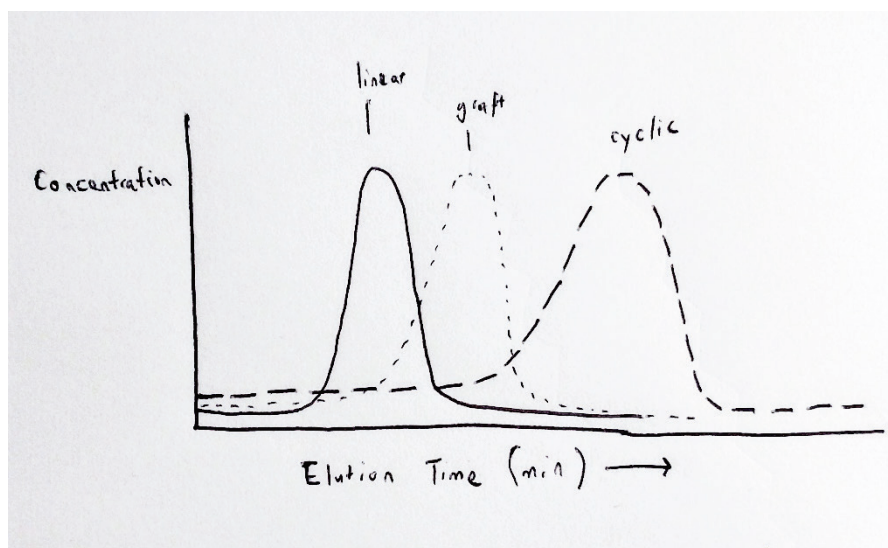




You have a mixture of polystyrenes with three different architectures (linear, cyclic, and graft). Suppose that, despite the different architectures, these polystyrenes have exactly the same overall number- and weight-average molecular weights.



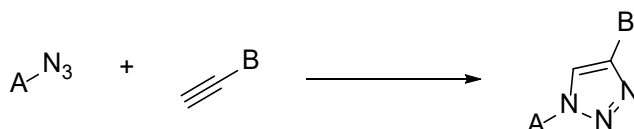
28.2. What do you expect the gel-permeation chromatography (GPC) data to look like? Draw the expected concentration signal and explain.

28.2.

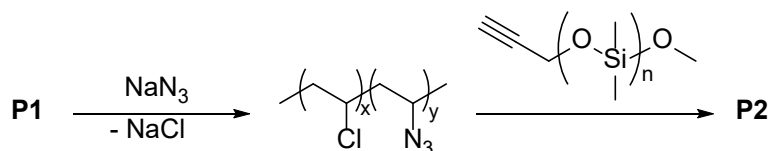
GPC (also called size-exclusion chromatography, SEC) separates objects based on their size (hydrodynamic radius). This trends with molecular weight, but also reflects the shape of the molecule. For these three polystyrenes, M_n and M_w are identical, but the architectures are different. We should expect the different polystyrenes to elute at different times. The cyclic polymer should have the most compact conformation in solution, so it experiences the most pore volume and elutes latest. The linear polymer should have a random coil conformation and elute first.

29. Polymer functionalization

The term "click chemistry" is a collective name for organic chemical reactions that allow the linking of two molecules with high specificity and efficiency under relatively mild reaction conditions. One of the most characteristic examples of this reaction family is the Cu(I)-catalyzed azide-alkyne cycloaddition. In this process, an azide group and a carbon-carbon triple bond form a 1,2,3-triazole ring, covalently linking species carrying two different functional groups.

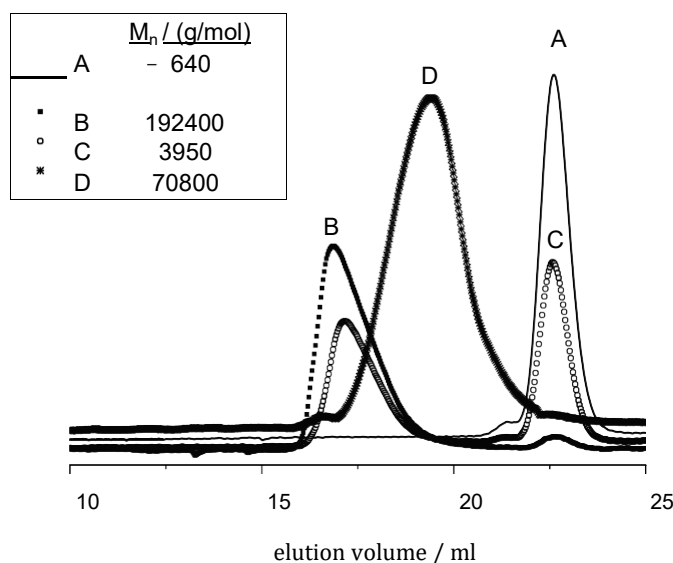


In the following, we utilize this reaction for the functionalization of poly(vinyl chloride) (PVC). This is achieved by replacing some of the Cl atoms with azide groups, followed by quantitatively introducing them into azide-alkyne cycloaddition with a slight excess of added propargyl-poly(dimethylsiloxane)-monomethyl ether. The reaction sequence is illustrated in the scheme below:



29.1. Draw the polymer structures P1 and P2 using the notations provided in the scheme.

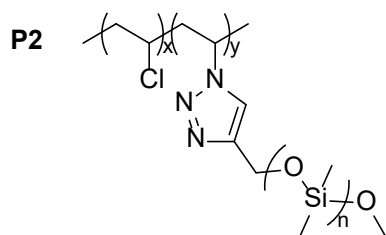
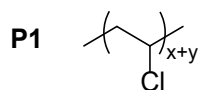
The propargyl-poly(dimethylsiloxane)-monomethyl ether, the substantially higher molecular weight partially azidated PVC, the cycloaddition reaction mixture at the end of the reaction, and the purified P2 product were all examined using gel permeation chromatography. The obtained chromatograms are presented below.



-
- 29.2. **Match** the measured samples with the obtained gel permeation chromatography curves.
- 29.3. **Estimate** the average number of poly(dimethylsiloxane) side chains per PVC molecule in the purified P2 product.
- 29.4. **Calculate** the excess (in mol%) of propargyl-poly(dimethylsiloxane)-monomethyl ether that was added to the azidated PVC in the functionalization reaction.

Solution

29.1.



29.2.

A: propargyl-poly(dimethylsiloxane)-monomethyl ether

B: purified P2

C: mixture at the end of the reaction

D: partially azidated PVC

29.3.

$$n = (192400 \text{ g/mol} - 70800 \text{ g/mol}) / 640 \text{ g/mol} = 190$$

29.4.

Let there be 1 P2 chain per x unreacted poly(dimethylsiloxane) chain

Then the average molar mass:

$$\langle M \rangle = ((1 \cdot 192400 \text{ g/mol}) + (x \cdot 640 \text{ g/mol})) / (1 + x) = 3950 \text{ g/mol}$$

$x = 56.9$, so $56.9/190 = 30\%$ was the excess of added propargyl poly(dimethylsiloxane)-monomethyl ether.

30. Polyurethane network

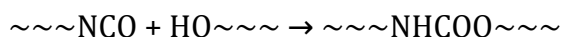
We aim to create a novel polyurethane network using hexamethylene diisocyanate (HDI, $\text{OCN}-(\text{CH}_2)_6-\text{NCO}$), poly(ethylene glycol) ($\text{HO}-(\text{CH}_2\text{CH}_2\text{O})_n-\text{H}$, $M_n = 500$ g/mol), and a "homemade" polyol crosslinker. Initially, we convert the hydroxyl groups of the cross-linking polyol into acetates using acetic anhydride. Subsequently, the obtained product, i.e., the acetylated polyol, along with the initial polyol, undergoes gel permeation chromatography. The results are as follows:

	M_n / g/mol	M_w / g/mol	I_p
Sample 1	1383	2531	1.83
Sample 2	1240	2232	1.80

For the polyurethane synthesis, we mix 1.6820 g of HDI, 4.0000 g of poly(ethylene glycol), and a sufficient amount of cross-linking polyol to ensure an equal number of hydroxyl and isocyanate groups.

- 30.1.** Determine the average number of hydroxyl groups per molecule in the cross-linking polyol.
- 30.2.** Calculate the mass of cross-linking polyol required for the polyurethane synthesis?

The reaction between isocyanate and hydroxyl groups is modeled by the following equation. Moving forward, we disregard changes in volume and temperature, and assume equal reactivity between identical groups in different chemical environments:



You can model the time evolution of the process using a simple kinetic law with an order of 1 for each reactant.

After 3 hours of the reaction, a sample was withdrawn, and the subsequent GPC result is as follows:

	M_n / g/mol	M_w / g/mol	I_p
Sample 3	1227	3288	2.68

- 30.3.** Calculate the conversion after 3 hours?

Crosslinking polymers leads to gelation, a sudden increase in viscosity. A simple model predicts that this gel point occurs when M_n becomes infinitely high.

- 30.4.** Identify the conversion corresponding to the gel point in this model.
- 30.5.** Determine the reaction time at which the reaction reaches the gel point.

Solution

30.1.

If one hydroxyl group is converted to an acetate ester, it results in a molecular weight increase of $\Delta M(\text{ac}) = 42.036 \text{ g/mol}$.

Therefore, on average, $(1383 \text{ g/mol} - 1240 \text{ g/mol}) / 42.036 \text{ g/mol} = 3.4$ hydroxyl groups are present in one polyol molecule.

30.2.

$$M(\text{HDI}) = 168.196 \text{ g/mol}$$

$$n(-\text{NCO}) = 0.02 \text{ mol}$$

$$n(-\text{OH, from PEG}) = 0.016 \text{ mol}$$

$$m(\text{polyol}) = (0.02 \text{ mol} - 0.016 \text{ mol}) / 3.4 * 1240 \text{ g/mol} = \underline{\underline{1.4588 \text{ g}}}$$

30.3.

The number-average molecular weight at time t is calculated using the formula:

$$M_n(t) = m_{\text{total}} / n_{\text{total},t}$$

Therefore, after 3 hours,

$$n_{\text{total},3\text{h}} = (1.6820 \text{ g} + 4.0000 \text{ g} + 1.4588 \text{ g}) / 1227 \text{ g/mol} = 0.00582 \text{ mol}$$

Initially, there were

$$(0.02 \text{ mol} / 2) + (0.016 \text{ mol} / 2) + ((0.02 \text{ mol} - 0.016 \text{ mol}) / 3.4) = 0.01918 \text{ moles}$$

Therefore, the number of molecules decreased by 0.01336 moles in 3 hours, indicating the amount of isocyanate groups (and hydroxyl groups) reacted.

$$\text{The conversion is } \chi(3\text{h}) = 0.01336 \text{ mol} / 0.02 \text{ mol} = \underline{\underline{66.8\%}}$$

30.4.

The gel point is reached when $M_n \rightarrow \infty$, implying that $n_{\text{total}} \rightarrow 0$.

$$\text{Therefore, } 0.01918 \text{ mol} - \chi_{\text{crit}} \times 0.02 \text{ mol} = 0.$$

Solving for the conversion at the gel point (χ_{crit}), we find $\chi_{\text{crit}} = 95.88\%$.

30.5. The rate equation, since $[-\text{NCO}] = [-\text{OH}]$:

$$-\frac{d[-\text{NCO}]}{dt} = k \cdot [-\text{NCO}] \cdot [-\text{OH}] = k \cdot [-\text{NCO}]^2$$

The integrated form:

$$\frac{1}{[-\text{NCO}]} = \frac{1}{(1 - \chi(3h)) \cdot [-\text{NCO}]_0} = \frac{1}{[-\text{NCO}]_0} + k \cdot t$$

From this, denoting the system volume as V : $[-\text{NCO}]_0 = 0.02 \text{ mol} / V$:

$$k/V = 33.5341 \text{ (1/(h mol))}$$

Time at the gel point ($t(\text{gel})$):

$$\begin{aligned} t(\text{gel}) &= \frac{1}{33.5341 \text{ (1/(h mol))}} \cdot \left(\frac{1}{(1 - 0.9588) \cdot 0.02 \text{ mol}} - \frac{1}{0.02 \text{ mol}} \right) = \\ &= 34.7 \text{ h} = 2082 \text{ min} \end{aligned}$$

Laboratory Procedures and Safety

Participants in the IChO must be prepared to work in a chemical laboratory and be aware of all relevant rules and safety procedures. The organizers will strictly enforce the safety rules during the event. See Appendix A and B of the IChO regulations for details.

The preparatory problems were created with students in mind who have limited experience in the laboratory. Detailed instructions on certain procedures are provided in the problem set for the benefit of these students. However, it's important to note that these step-by-step instructions or detailed instructions for the procedures in the practical part of the IChO syllabus will not be part of the actual exams.

Nonetheless, all experiments demand competent supervision and appropriately equipped laboratories. Students should, under no circumstances, attempt these experiments on their own.

Detailed safety and disposal instructions going beyond the GHS hazard codes of the chemicals used are not provided as regulations can significantly differ among countries. Mentors should adapt the instructions with great care according to local regulations. Hints for the setup of the experiments are included in the solutions that are shared only with the mentors in the preparation period.

Students will be provided with eye protection by the organisers. These must be worn during the laboratory exam. Contact lenses are prohibited. The goggles can be worn with prescription glasses. The dress code in the labs requires covered legs and closed shoes.

Students are welcome to bring and use their own lab coats. Organizers will also hand out lab coats. IChO experience in similar cases shows that a good fit cannot be guaranteed due to sizing inconsistencies between countries.

31. Identification with a battery

You find on your desk:

- 1 test tube stand
- 9 numbered test tubes with unknowns
- 10 empty test tubes
- 3 small crystallization dishes
- a simple circuit: a 9 V battery with a LED light and steel wires
- universal indicator solution
- 1 color scale for the indicator
- 3 filter papers
- tissues

You can only use these in addition to calculator and pen. Wash all equipment very carefully before reuse.

The following materials are in the nine numbered test tubes:

- distilled water
- boric acid (B(OH)_3), 0.1 mol/dm³ aqueous solution
- mannitol (hexane-1,2,3,4,5,6-hexol), 0.1 mol/dm³ aqueous solution
- KNO_3 , 0.1 mol/dm³ aqueous solution
- KI , 0.1 mol/dm³ aqueous solution
- H_3PO_4 , 1 mol/dm³ aqueous solution
- KH_2PO_4 , 0.1 mol/dm³ aqueous solution
- K_2HPO_4 , 0.1 mol/dm³ aqueous solution
- Na_3PO_4 , 0.1 mol/dm³ aqueous solution

Answer the following questions and identify the content of the test tubes.

The conductivity of solutions arises from the movement of ions in an electric field. As ion concentrations increase, conductivity also increases. In aqueous solutions, oxonium and hydroxide ions exhibit the highest conductivity.

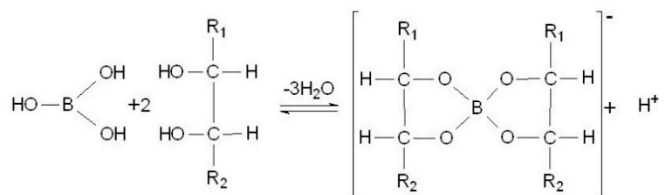
Boric acid is a weak acid, and surprisingly only B(OH)_4^- ions can be found in its aqueous solution besides the ions of water.

31.1. Give a balanced ionic equation of the reaction between boric acid and water.
Draw the structure of the product anion.

In a 0.1 mol/dm³ aqueous boric acid solution, the concentration of B(OH)_4^- ions was measured. The results indicate that the quantity of B(OH)_4^- ions in the solution is equivalent to 0.0085% of the dissolved boric acid.

31.2. Calculate the pH of 0.1 mol/dm³ boric acid.

The addition of mannitol to boric acid solution results in the formation of a monovalent complex acid, which exhibits a strength similar to acetic acid.



- 31.3. **Calculate** the pH of 0.1 mol/dm³ acetic acid. $K_a = 1.8 \cdot 10^{-5}$.
- 31.4. **Provide** the anode and cathode reactions occurring during the electrolysis of KI solution and phosphoric acid solution between steel electrodes.
- 31.5. **Identify** the positive wire (red or black) without disassembling the equipment. **Which** experiment and observation helped you to decide?
- 31.6. **Carry** out experiments and **assign** the test tube number to the solutions. **Give** the observation(s) that helped you to identify the solutions.

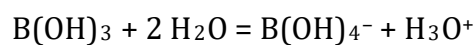
GHS codes

Please note that the table of Globally Harmonized 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.

Chemical	GHS Hazard code
H ₃ BO ₃ aqueous solution	H360FD
mannitol aqueous solution	No hazard
KNO ₃ aqueous solution	H272
KI aqueous solution	H372
H ₃ PO ₄ , aqueous solution	H314
KH ₂ PO ₄ aqueous solution	No hazard
K ₂ HPO ₄ aqueous solution	No hazard
Na ₃ PO ₄ aqueous solution	H315, H319

Solution

31.1.



B(OH)_4^- is tetrahedral.

31.2.

$$[\text{H}^+] = 0.0085 \cdot 0.01 \cdot 0.1 \text{ mol/dm}^3 = 8.5 \cdot 10^{-6} \text{ mol/dm}^3$$

$$\text{pH} = 5.1$$

31.3.

$$[\text{H}^+]^2 = 1.8 \cdot 10^{-5} \cdot 0.1 \text{ (mol/dm}^3)^2$$

$$\text{pH} = 2.9$$

31.4.

	Cathode	Anode
H_3PO_4	$2 \text{H}^+ + 2 \text{e}^- = \text{H}_2$	$\text{H}_2\text{O} = \frac{1}{2} \text{O}_2 + 2 \text{H}^+ + 2 \text{e}^-$
KI	$\text{H}_2\text{O} + 2 \text{e}^- = \text{H}_2 + 2 \text{OH}^-$	$3 \text{I}^- = \text{I}_3^- + 2 \text{e}^-$

31.5.

When electrolyzing the KI solution, a brown discoloration is observed at the positive electrode.

31.6.

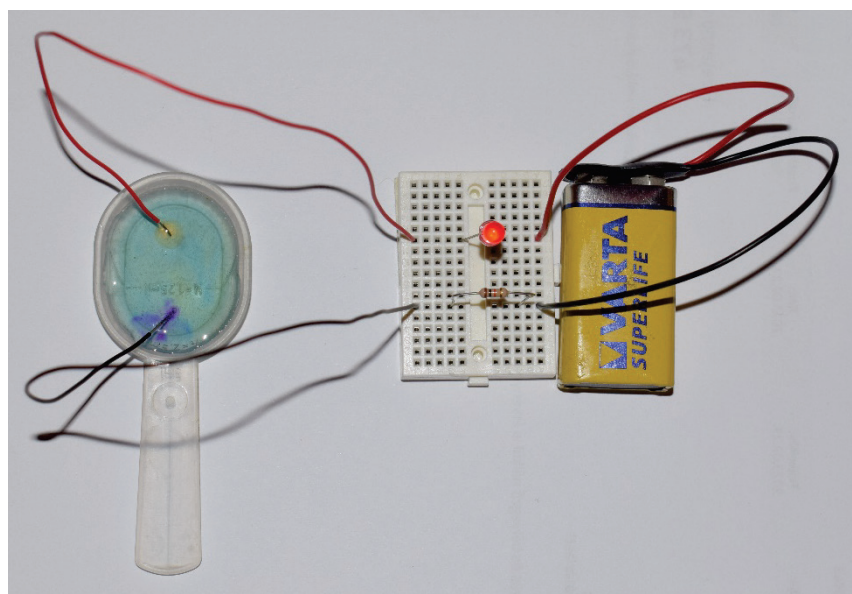
Test tube	Observation(s) necessary for unambiguous identification
Water	pH \approx 6-7, does not conduct added to boric acid, the pH does not change
Boric acid	pH \approx 5 shows weak conductivity, faint light mixed with mannitol turns more acidic
Mannitol	pH \approx 6-7 does not conduct mixed with boric acid, it makes it turn more acidic

KNO ₃	pH \approx 6-7 conducts no browning at anode
KI	pH \approx 6-7 conducts browning at anode
H ₃ PO ₄	pH \approx 2-3
KH ₂ PO ₄	pH \approx 4-5 conducts no change in pH with mannitol
K ₂ HPO ₄	pH \approx 9-10
Na ₃ PO ₄	pH \approx 12-13

Hints for the preparations:

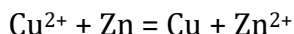
When preparing the experiment, mannitol can be substituted with any available sugar alcohol or appropriate polyol.

The photo below shows a simple setup for the circuit without the cover around the battery that hides the battery polarity. The components in this setup are a diffused 5mm red LED and a 10 kOhm resistor.



32. Direction of redox processes

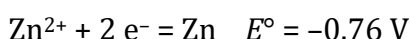
Redox reactions can always be broken down into two half reactions: oxidation and reduction. E.g. for the reaction



the two half reactions are:



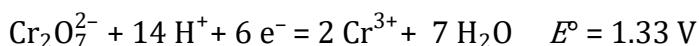
Each half reaction can be assigned a standard electrode potential value. By comparing these values, it is possible to predict the likely redox processes. The fundamental rule is that the oxidized form of the system with a higher standard potential oxidizes the reduced form of the system with a lower potential.



(By convention, half reactions are written in the direction of reduction.)

Here, then, Cu^{2+} can oxidize Zn.

It is crucial to note that the standard potential is associated with standard conditions aligned with the balanced equation of the half reaction, and therefore, it corresponds to the unit concentration of each indicated substance. The electrode potential is influenced by the concentration of other species, including hydrogen ions. For example, reduction of the dichromate ion to the chromium(III) ion:



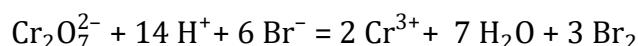
In this case, the concentration of hydrogen ions also affects the electrode potential. The standard electrode potential given above is valid for $[\text{H}^+] = 1 \text{ mol/dm}^3$, i.e., for strongly acidic media. If the hydrogen ion concentration is lower, then the electrode potential will also be smaller.

What does that mean? Let's see an example.

The standard electrode potential of the $\text{Br}_2 + 2 \text{e}^- = 2 \text{Br}^-$ half reaction $E^\circ = +1.09 \text{ V}$.

Does dichromate oxidize bromide? Based on standard electrode potentials, yes. This prediction works well in strongly acidic conditions, where the standard electrode potential is around 1.33 V. However, if the pH increases, the potential for the dichromate/chromium(III) reaction decreases. Generally, reducing the concentration of species on the left side of the reduction equation leads to a decrease in the electrode potential.

Indeed, the following reaction takes place in a strongly acidic medium, but not at a pH close to neutral:



To put it simply, we could say that for the reaction to take place as the equation shows, an acidic medium is needed.

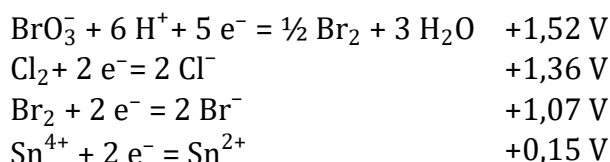
When solving this task, you will need to apply these principles.

Part A What do potentials say about reactions?

You find on your desk some aqueous reagent solutions in test tubes. Predict what reaction you expect to occur for each of the two half reactions specified in tasks 1 and 3. Then show experimentally that you have drawn the right conclusion. Carefully describe what and how you did the reaction and what your observations were.

The available reagents are the following substances in aqueous solution: bromine water, potassium bromate, potassium bromide, potassium chloride, chlorine water, hydrochloric acid, tin(II) chloride, tin(IV) chloride.

The standard electrode potentials (E°):



- 32.1. **Identify** the reactants that you think will undergo a redox reaction for the bromine/bromide and tin(IV)/tin(II) couples. **Perform** the reaction and **provide** details of your experiment along with your observations.
- 32.2. **Write** down the balanced equation of the reaction taking place.
- 32.3. **Identify** the reactants that you think will undergo a redox reaction for the chlorine/chloride and bromate/bromine couples. If allowed (some chemicals are classified in many jurisdictions as forbidden for students), **perform** the reaction and **provide** details of your experiment along with your observations.
- 32.4. **Write** down the balanced equation of the reaction taking place.

Part B What do reactions say about potentials?

You will study the following half reactions and find the order of their standard electrode potentials.

- 32.5. **Balance** the half reactions. **Fill in** the table with the expected observations.

No	Half reaction	Is there a visible change when reduction takes place? If yes, what?
1	$\text{IO}_3^- + \text{e}^- = \text{I}_2$	

2	$\text{I}_2 + \text{e}^- = \text{I}^-$	
3	$\text{Co}^{2+} + \text{e}^- = \text{Co(s)}$	
4	$\text{Cl}_2 + \text{e}^- = \text{Cl}^-$	
5	$\text{Fe}^{3+} + \text{e}^- = \text{Fe}^{2+}$	
6	$\text{C}_6\text{H}_6\text{O}_6 + \text{e}^- = \text{C}_6\text{H}_8\text{O}_6$	
7	$\text{MnO}_4^- + \text{e}^- = \text{Mn}^{2+}$	

The $\text{C}_6\text{H}_8\text{O}_6$ in the table denotes ascorbic acid, and $\text{C}_6\text{H}_6\text{O}_6$ dehydroascorbic acid.

In test tubes you will find the following solutions.

32.6. Fill the second column.

No		Are these oxidized or reduced forms of the above pairs?
1	acidified KIO_3 solution	
2	KI solution	
3	CoSO_4 solution	
4	acidified MnSO_4 solution	
5	acidified ascorbic acid solution	
6	chlorine water	
7	FeCl_3 solution	

Conduct experiments on the seven provided solutions to establish the order of redox pairs (1-7) based on their standard electrode potential. All anticipated reactions, based on standard potentials, indeed occur in these systems without any significantly slow reactions. You do not need to consider the possibility of other redox processes when solving the task.

32.7. Report your work using the template below. **Indicate** which solutions you have mixed (*with formulae*) and **report** your observations (even if there was no visible change). Be sure to **indicate** for each experiment the relation between standard potentials that it proves.

Solutions mixed:		Observation:
Did a reaction take place? +/-	(Reaction)	The relation of potentials this experiment proves: >

32.8. **Put** the numbered redox pairs (1-7) in increasing order according to their standard potential.

Equipment and material list

test tube stand

test tubes with a dropper containing the following solutions:

bromine water, 0.25 mol/dm³ KBrO₃, 0.1 mol/dm³ KBr, 0.1 mol/dm³ KCl, chlorine water, 0.1 mol/dm³ HCl, 0.25 mol/dm³ SnCl₂ (with HCl added to stop hydrolysis), 0.25 mol/dm³ SnCl₄ (with HCl added to stop hydrolysis), 1:1 mixture of 0.25 mol/dm³ KIO₃ and 0.1 mol/dm³ HCl, 0.1 mol/dm³ KI, 0.5 mol/dm³ CoSO₄, 1:1 mixture of 0.25 mol/dm³ MnSO₄ and 0.1 mol/dm³ HCl, 1:1 mixture of 0.1 mol/dm³ ascorbic acid and 0.1 mol/dm³ HCl, chlorine water, 0.5 mol/dm³ FeCl₃ (with HCl added to stop hydrolysis)

15 empty test tubes

GHS codes

Please note that the table of Globally Harmonized 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.

Chemical	GHS Hazard code
bromine water	H302, H314, H400, H410
0.25 mol/dm ³ KBrO ₃	H272, H302, H315, H319, H335, H350, H410
0.1 mol/dm ³ KBr	No hazard
0.1 mol/dm ³ KCl	No hazard
chlorine water	H290, H314, H400
0.1 mol/dm ³ HCl	H290, H314, H335
0.25 mol/dm ³ SnCl ₂	H290, H302, H314, H317, H335, H373, H412

0.25 mol/dm ³ SnCl ₄	H314, H412
1:1 mixture of 0.25 mol/dm ³ KIO ₃ and 0.1 mol/dm ³ HCl	H272, H302, H319
0.1 mol/dm ³ KI	H372
0.5 mol/dm ³ CoSO ₄	H302, H317, H334, H341, H350i, H360F, H372, H400
1:1 mixture of 0.25 mol/dm ³ MnSO ₄ and 0.1 mol/dm ³ HCl	H373, H411
1:1 mixture of 0.1 mol/dm ³ ascorbic acid and 0.1 mol/dm ³ HCl	No hazard
chlorine water	H302, H315, H319, H331, H335, H400
0.5 mol/dm ³ FeCl ₃	H290, H302, H314

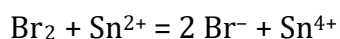
Solution

32.1.

Elemental bromine oxidizes tin(II) according to the standard potentials.

When dropping bromine water into Sn(II) chloride solution, the color disappears.

32.2.

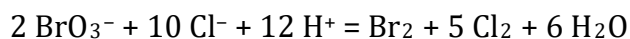


32.3.

Bromate can oxidize chloride in acidic media (has a higher standard potential).

When potassium bromate is added to hydrochloric acid, the solution slowly turns yellow. Instead of hydrochloric acid, other chloride-containing solutions (KCl, SnCl₄) do the same if acidified, but in the case of SnCl₂, tin(II) is oxidized, not chloride.

32.4.



32.5.

No	Half reaction	Is there a visible change when reduction takes place? If yes, what?
1	$\text{IO}_3^- + 5 \text{e}^- + 6 \text{H}^+ = 0,5 \text{I}_2 + 3 \text{H}_2\text{O}$	Turns yellow or brown, or even a solid (iodine) can precipitate (any of these is an acceptable answer)
2	$\text{I}_2 + 2 \text{e}^- = 2 \text{I}^-$	Loses color.
3	$\text{Co}^{2+} + 2 \text{e}^- = \text{Co(s)}$	A solid forms or the solution loses color (either is acceptable)
4	$\text{Cl}_2 + 2 \text{e}^- = 2 \text{Cl}^-$	Loses color, loses smell, or no apparent change (either of the three is acceptable)
5	$\text{Fe}^{3+} + \text{e}^- = \text{Fe}^{2+}$	Turns very faint green from yellow

6	$\text{C}_6\text{H}_6\text{O}_6 + 2 \text{e}^- + 2 \text{H}^+ = \text{C}_6\text{H}_8\text{O}_6$	nothing
7	$\text{MnO}_4^- + 5 \text{e}^- + 8 \text{H}^+ = \text{Mn}^{2+} + 4 \text{H}_2\text{O}$	Loses color.

32.6.

	Are these oxidized or reduced forms of the above pairs?
acidified KIO_3 solution	oxidized
KI solution	reduced
CoSO_4 solution	oxidized
acidified MnSO_4 solution	reduced
acidified ascorbic acid solution	reduced
chlorine water	oxidized
FeCl_3 solution	oxidized

32.7.

There could be other ways to find the right order. It needs to be checked whether all relations are established. Experiments that have no observable change are necessary for a complete solution.

Solutions mixed: $\text{Cl}_2 + \text{MnSO}_4$		Observation: NO purple color
Did a reaction take place? -	(Reaction)	The relation of potentials this experiment proves: $7 > 4$
Solutions mixed: $\text{Cl}_2 + \text{I}_2$ or excess $\text{Cl}_2 + \text{KI}$		Observation: The color of (produced) iodine disappears (with an excess of chlorine)

Did a reaction take place? +	(Reaction) $5 \text{Cl}_2 + 2 \text{I}_2 + 6 \text{H}_2\text{O} = 2 \text{IO}_3^- + 10 \text{Cl}^- + 12 \text{H}^+$	The relation of potentials this experiment proves: $4 > 1$
Solutions mixed: $\text{FeCl}_3 + \text{I}_2$ or FeCl_3 excess + KI		Observation: The color of (produced) iodine does not disappear (with an excess of reagent)
Did a reaction take place? -	(Reaction)	The relation of potentials this experiment proves: $1 > 5$
Solutions mixed: $\text{FeCl}_3 + \text{KI}$		Observation: Iodine is produced (and no further reaction)
Did a reaction take place? +	(Reaction) $2 \text{Fe}^{3+} + 2 \text{I}^- = \text{I}_2 + 2 \text{Fe}^{2+}$	The relation of potentials this experiment proves: $5 > 2$
Solutions mixed: $\text{IO}_3^- + \text{C}_6\text{H}_8\text{O}_6$ in excess or $\text{I}_2 + \text{C}_6\text{H}_8\text{O}_6$		Observation: The color of (produced) iodine disappears (with an excess of reagent)
Did a reaction take place? +	(Reaction) $\text{I}_2 + 2 \text{C}_6\text{H}_8\text{O}_6 = 2 \text{I}^- + \text{C}_6\text{H}_6\text{O}_6 + 2 \text{H}^+$	The relation of potentials this experiment proves: $2 > 6$
Solutions mixed: $\text{CoSO}_4 + \text{C}_6\text{H}_8\text{O}_6$		Observation: NO change
Did a reaction take place? -	(Reaction)	The relation of potentials this experiment proves: $6 > 3$

32.8.

3 < 6 < 2 < 5 < 1 < 4 < 7

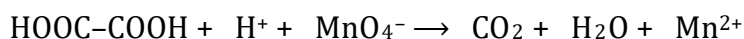
Hints for the preparations:

Bromate is classified in many jurisdictions as forbidden for students, while other countries use bromates rather freely. Based on your location, 32.3 should be a practical or theoretical question.

33. Oxalic acid content of turmeric

Turmeric is a characteristic spice used in Arabic cuisine in large amounts. Recent research indicates that care must be exercised with the overuse of spices, because some of them might naturally contain toxic compounds in addition to beneficial components. Turmeric, for instance, contains large amounts of oxalic acid. Oxalic acid is excreted by urine and may combine with Ca^{2+} -ions to form a Ca-oxalate precipitate, that in serious cases can block the kidneys. You will determine oxalic acid in turmeric in this experiment.

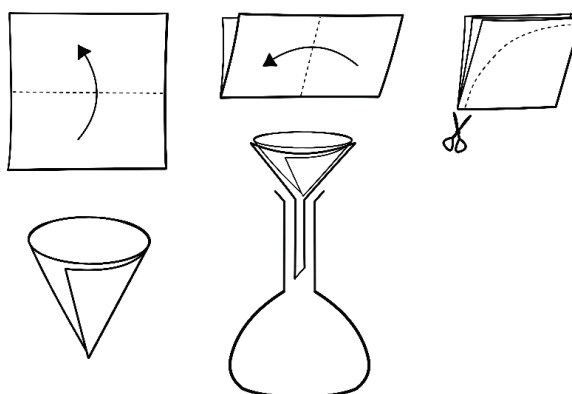
Oxalic acid is determined by permanganate using the following reaction (the equation is not balanced):



The reaction between oxalate ions and permanganate ions is slow at the beginning, but Mn^{2+} ions have a catalytic effect. The titration is thus made in hot solution and Mn^{2+} is added at the beginning. Turmeric of course contains several other compounds that may react with permanganate, so a separation needs to be done before titration to selectively dissolve oxalic acid from turmeric.

In the first step of the separation, we mix turmeric with water to dissolve the highly water-soluble oxalic acid. Many other components are not soluble (fats, oils, aromatic compounds, etc.). The solid parts are removed by filtration. The filtrate contains oxalic acid together with other compounds. In the next step, we selectively precipitate oxalic acid with CaCl_2 solution. The majority of the interfering compounds will remain in solution. We separate the calcium oxalate by filtration. Finally, we dissolve the precipitate in 20% H_2SO_4 and titrate it with permanganate.

For the filtrations, we will use a small plastic funnel placed directly into an Erlenmeyer flask. The solution is collected into the flask. We put a filter paper cone we made of a square sheet of filter paper into the funnel. For this, we fold the paper into halves twice, and cut it in a quarter-circle line with scissors. Finally, we open the paper to get a closed cone.



Pour the mixture into the funnel. Wash all the solid material onto the filter. To remove all soluble compounds, wash the solids with the recommended amount of solvent.

Sample preparation steps

1. Weigh 1-1.5 g of turmeric into an Erlenmeyer flask with the precision of **0.001 g**.
2. Pour 10 cm³ of distilled water over the turmeric. Mix it with occasional swirling. Let it stand for at least **15 minutes**.

-
3. Transfer the mixture onto a filter that is placed over a clean Erlenmeyer flask.
 4. After about 3 minutes add 5 cm³ of water to the original Erlenmeyer flask and wash any remaining solids onto the filter. This will also be washing the solids that were already on the filter.
 5. Repeat this washing after an additional 3 minutes with a fresh 5-cm³ aliquot of water.
 6. Wait until no more water drips down from the filter. You can speed up the process by folding and slightly pressing the filter paper with your gloved fingers. Be careful not to tear the filter paper. Try to gain as much solution from the solids as possible.
 7. Dispose of the filter paper and remove the funnel.
 8. Add **1 cm³ of 1 mol/dm³ CaCl₂** solution to the liquid. After a few seconds clearly visible crystals of Ca-oxalate are formed. Wait an additional minute to let the crystals grow for easier filtration.
 9. Make a second filter paper cone. In this step we will use the crystals on the filter paper, so we can use the first "dirty" flask to collect the "mother liquor" (the liquid phase).
 10. Pour the liquid with the precipitate onto the filter.
 11. As in step 4, wash the precipitate **two times** with 5 cm³ of water. Use washing water to transfer all the crystals onto the filter.
 12. Once there is no more liquid remaining on the filter, put the funnel in a **clean** Erlenmeyer flask that will be used for the titration.
 13. We will use 20% sulfuric acid to dissolve Ca-oxalate. Use a disposable plastic dropper for this. Use the graduation on the dropper to measure the volume. Use **three times** 3 cm³ of sulfuric acid. The next portion should be added only after the previous portion has already run down. Use your dropper to mix the liquid in the funnel to achieve fast and complete dissolution. **Be cautious not to puncture the filter paper. Sulfuric acid is corrosive!**
 14. When finished with the filtration, use your tweezers and a beaker to transfer the filter paper to the waste basket. **Sulfuric acid drops on your clothes result in unavoidable holes!**

Titration

In this task we will use weight measurement instead of burettes. Pour the permanganate solution into a beaker and put a plastic dropper into it. Weigh the mass of the beaker (with the solution and the dropper) with 0.001 g precision. You will use the dropper to titrate the sample solution. Be cautious not to pour out or waste drops of your permanganate solution. During the titration always mix the contents of the Erlenmeyer flask well. The permanganate ions have a very strong color that will indicate the endpoint of the titration: at the equivalence point the solution is faint pink (**the color should be constant for at least 10 seconds**).

When equivalence is reached, the beaker, dropper and the remaining permanganate solution are weighed again. The difference in masses gives the consumed mass.

The composition of the KMnO_4 solution is cca 0.32 wt. %; the exact value is on the flask.

Before starting the titration add 1 cm^3 of 1 mol/dm^3 MnSO_4 solution to catalyze the oxidation process and heat the contents of the flask (e.g., with a heat gun) to approx. 50°C .

Plan your work! Perform as many titrations as you feel necessary. We suggest preparing several samples at the same time as the sample preparation is a long process.

33.1. Report your results in the table.

Mass of turmeric (g)	Beaker + dropper + permanganate solution	
	mass before titration (g)	mass after titration (g)

Report your accepted result: g titrant / 1 g turmeric

33.2. Calculate the oxalic acid content in turmeric in mass percent.

33.3. Consider your findings. Is a high spice intake of 10 g per portion potentially risky for kidney health? The recommended daily oxalic acid consumption is under 50 mg.

Usually in permanganometric titrations sulfuric acid is added to the sample just before titration.

33.4. Why not in this procedure?

Imperfect washing of the calcium oxalate can cause errors if chloride ions remain in the sample.

33.5. Give the balanced equation of the reaction responsible for the error. **Will** this error cause higher or lower oxalic acid content?

Cinnamon, like turmeric, has a high oxalic acid content, but due to the high calcium content of this spice, a significant part of oxalic acid occurs in the form of calcium oxalate.

33.6. Select the necessary modification of the procedure to measure the total oxalic acid content of cinnamon?

☐ No changes to the procedure are required.

☐ In the first dissolution step, 20% sulfuric acid should be used, the rest is unchanged.

- ☐ In the first dissolution step, 2 mol/dm³ hydrochloric acid should be used, the rest is unchanged.
- ☐ In the first dissolution step, 2 mol/dm³ NaOH solution is used, the rest is unchanged.
- ☐ In the first dissolution step, 20% sulfuric acid is used. The sample is neutralized before adding 1 cm³ of CaCl₂ solution.
- ☐ In the first dissolution step, 2 mol/dm³ hydrochloric acid is used. The sample is neutralized before adding 1 cm³ of CaCl₂ solution.

Lactic acid (CH₃-CHOH-COOH), a harmless alternative, can be used to dissolve calcium oxalate instead of the corrosive sulfuric acid solution.

33.7. Can we replace sulfuric acid with lactic acid in this procedure? **Give** reasons for your answer.

A key part of this measurement is the separation of oxalic acid from the thousands of other compounds in turmeric. The number of components is decreased by dissolving only water-soluble compounds from turmeric, filtering only compounds giving precipitates with calcium ions, dissolving only calcium compounds soluble in sulfuric acid, and then measuring compounds reacting with permanganate.

33.8. Will the following compounds from turmeric be present during the titration? Will they influence the results? **Complete** the table with your answers.

Component	Is it present during the titration?	Does it influence results?	Explanation if no influence
alanine	<input type="checkbox"/>	<input type="checkbox"/>	The Ca salt of alanine dissolves in water.
sulfate ion	<input type="checkbox"/>	<input type="checkbox"/>	
glycerol tristearate ("fat")	<input type="checkbox"/>	<input type="checkbox"/>	
glycerol	<input type="checkbox"/>	<input type="checkbox"/>	
stearic acid (saturated)*	<input type="checkbox"/>	<input type="checkbox"/>	
oleic acid* (monounsaturated)*	<input type="checkbox"/>	<input type="checkbox"/>	
curcumin**	<input type="checkbox"/>	<input type="checkbox"/>	

* The water solubility of fatty acids varies between 0.3 and 0.6 g/dm³.

** Curcumin is the yellow dye found in turmeric used as a natural food coloring. Even at a concentration of 0.1 µg/cm³ it shows an intense yellow color.

Equipment and material list

All solutions and the water used must be thermally equilibrated with the room, so they have to be prepared and diluted in advance.

On each desk:

2 g turmeric
filter paper
100 cm³ of cca. 0.32 wt. % KMnO₄ solution, exact composition on the flask
10 cm³ of 1 mol/dm³ CaCl₂ solution
50 cm³ of 20% sulfuric acid solution
6 Erlenmeyer flasks (100 cm³)
3 plastic funnels
distilled water
2 graduated plastic Pasteur pipettes (1 cm³)
5 graduated plastic Pasteur pipettes (3 cm³)
2 beakers (100 cm³)
25 cm³ volumetric cylinder
Tweezers
goggles
paper tissue

Shared:

mg accuracy balances (1 for 5 students)
scissors
filter paper
gloves

GHS codes

Please note that the table of Globally Harmonized 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.

Chemical	GHS Hazard code
KMnO ₄ solution	H272, H302, H400
1 mol/dm ³ CaCl ₂ solution	No hazard
20% H ₂ SO ₄	H290, H314, H315, H318, H319

Solution

33.1.

Let the obtained consumption be m g permanganate solution for 1 g turmeric.

33.2.

In m g permanganate solution, we get $0.3161 \cdot 10^{-2} \cdot m$ g KMnO_4 .

$n(\text{permanganate}) : n(\text{oxalic acid}) = 2:5$

1 g turmeric contains:

$$\frac{0.3161 \cdot 10^{-2} \cdot m}{M(\text{KMnO}_4)} \cdot \frac{5}{2} \cdot M[(\text{COOH})_2]$$

oxalic acid.

The oxalic acid content of turmeric is $0.450m$ wt. % oxalic acid.

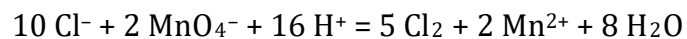
33.3.

Typical results in our samples were 1.3 wt. % oxalic acid. For 10 g of turmeric that is 130 mg of oxalic acid, way above the recommended amount.

33.4.

The calcium oxalate was already dissolved in sulfuric acid.

33.5.



This error would result in oxalic acid content being higher than the real value.

33.6.

In the first dissolution step, 2 mol/dm³ hydrochloric acid is used. The sample is neutralized before adding 1 cm³ of CaCl_2 solution.

33.7.

No, because permanganate would also oxidize excess lactic acid.

33.8.

Component	Is it present during the titration?	Does it influence results?	Explanation if no influence
alanine	<input type="checkbox"/>	<input type="checkbox"/>	The Ca salt of alanine dissolves in water.
sulfate ion	<input checked="" type="checkbox"/>	<input type="checkbox"/>	Permanganate does not oxidize it.
glycerol tristearate („fat")	<input type="checkbox"/>	<input type="checkbox"/>	Insoluble in water.
glycerol	<input type="checkbox"/>	<input type="checkbox"/>	Does not precipitate with Ca^{2+} .
stearic acid	<input checked="" type="checkbox"/>	<input type="checkbox"/>	Permanganate does not oxidize it.
oleic acid	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	
curcumin	<input type="checkbox"/>	<input type="checkbox"/>	Poorly soluble in water as observed.

Hints for the preparation:

The permanganate solution can be the often used 0.02 M solution.

The graduated plastic Pasteur pipettes are quite useful and reasonably accurate tools, but students might not notice the graduations and their marks.

34. Titration with a pH meter

In chemistry competitions, we are familiar with using the color change of dye indicators to determine the endpoint during acid-base titrations. Nowadays, digital pH meters have become more affordable, and simple handheld devices are readily available in supermarkets and often cheaper than a roll of indicator paper. In this experiment, we explore how acid-base reactions can be monitored using a pH meter.

These simple devices are similar, but their operation and shape can be variable. All have a fragile measuring sensor, a glass electrode at the bottom. This goes into the solution studied.

Use the manual or description of the device you have. These manuals will write about the operation of the pH meters, buttons, immersion levels, cleaning of the sensor, and the protection of the device. Your instructors should have calibrated the device before the experiment to make sure you get accurate results.

Affix the pH meter to a stand enabling easy, continuous readout of a 150 cm³ volume of solution.

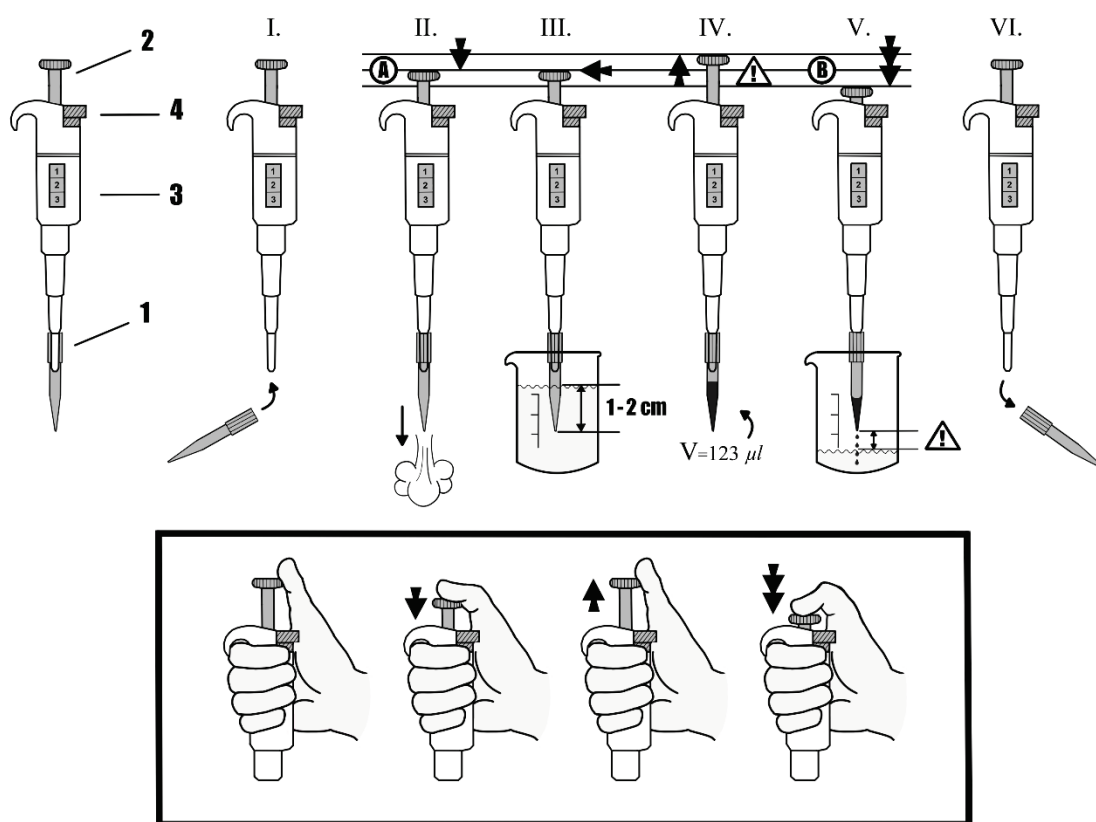
Using a micropipette

To deliver solutions, you will employ a micropipette instead of pipettes and burettes. This device enables the precise and rapid measurement of small volumes (0.200-1.000 cm³).

Instructions for using the micropipette:

1. **Attachment of pipette tip:** The liquid is not drawn directly into the pipette but into a single-use plastic pipette tip fitted at the end of the apparatus (**1** in the figure). The liquid should only touch the pipette tip. Ensure a tight, well-closing contact to prevent dripping (**I**). Use a pipette tip for measuring only one type of solution.
2. **Volume adjustment:** Adjust the volume to be measured by turning the push knob (**2**). The current value can be read on the display (**3**) on the side of the pipette in microliters (e.g., 750 means 0.75 cm³).
3. **Air displacement:** Depress the piston (**II**) until the first impact (**A**) to displace air from the pipette.
4. **Drawing the solution:** Immerse the tip in the liquid (**III**) and slowly release the knob to draw up the set volume into the pipette tip. Draw the solution slowly (about 1-2 seconds) to prevent splattering. Ensure that the tip is below the level of the solution throughout the withdrawal. The solution should never touch the pipette body (**IV**).

5. **Dispensing the liquid:** Introduce the liquid into the target vessel by pressing down on the plunger (V). If the piston is pushed further until the final impact (B) after the first impact, the entire amount of liquid is removed from the tip. Ensure that the tip does not touch the solution in the beaker during emptying to avoid contamination. Hold the tip above the solution during emptying, spraying the liquid forcefully into the beaker to mix quickly.
6. **Changing solutions:** If you switch to a new solution during pipetting, replace the tip with a clean one. Use a separate button to detach the tip from the pipette (4, VI). For feeding the same solution again, you can reuse the same tip. Be cautious not to accidentally draw solution inside the pipette. If this happens, seek assistance.



Measurement of hydrochloric acid and acetic acid solutions

Use the micropipette to measure 1.000 cm^3 of hydrochloric acid into the 250 cm^3 beaker. Add distilled water to the beaker until it reaches the 150 cm^3 mark. Place a glass rod in the beaker, stir, and position the pH meter in the stand to the appropriate height.

Add 3 drops of phenolphthalein indicator to the contents of the beaker and turn on the pH meter.

Add 0.3 cm³ portions of 0.500 mol/dm³ NaOH solution to the contents of the beaker until the pH reaches 11. It is essential to mix the contents of the beaker with the glass rod after each addition. Read the pH when the value no longer significantly changes on the display. The final stabilization of the last digit by 1-2 units practically does not affect the results, so do not wait for the value to stabilize for more than a few seconds.

After each addition, record the volume and the measured pH value in a table on a separate sheet. Observe and note the color changes of the indicator. Once finished with the measurements, wash the beaker with distilled water, rinse the pH meter and the glass rod, then repeat the measurements with 1.000 cm³ of acetic acid solution.

Graph the results of the two measurements (measured pH vs. added volume of NaOH solution) on the same chart (use graph paper) and mark the indicator's color change range. Identify and mark the equivalence point on the plotted graphs, and read the corresponding volume, which may not precisely align with any of the added volumes).

- 34.1. Calculate the concentration of the two solutions.
- 34.2. Hydrochloric acid is a strong, acetic acid is a weak acid. How does this manifest on the diagrams? What indicates that the strengths of the two acids are different?
- 34.3. Estimate the pK_a of acetic acid using the diagram.

Measurement of a mixture containing a strong and a weak acid

In the second part of the task, you will determine the composition of a mixture consisting of hydrochloric acid and *para*-nitrophenol (PNP). Pipette 1.000 cm³ of the unknown solution into the beaker. Add distilled water until the liquid level reaches the 150 cm³ mark. Add 3 drops of phenolphthalein indicator to the solution. Examine the solution by incrementally adding 0.3 cm³ portions of 0.5000 mol/dm³ NaOH solution, recording the pH until it reaches 11.

After each addition, record the volume and the measured pH value in a table on a separate sheet. Graph the results of the measurements on a chart (use graph paper). Record the volumes corresponding to the equivalence points.

- 34.4. Which step ('pH jump') corresponds to *para*-nitrophenol?
- ☐ The first.
 - ☐ The second.
 - ☐ Both.
 - ☐ It is impossible to decide.
- 34.5. Calculate the HCl and PNP concentrations in the sample.
- 34.6. PNP is a weak acid. How does this manifest on the diagram?
- The shade of the solution in alkaline medium is different compared to previous measurements.
- 34.7. Explain this change? Hint: Conduct an experiment in a small beaker without using indicators and pH measurement.

34.8. If solely relying on the indicator, which concentration could have been precisely determined?

- ☐ None.
- ☐ Only the concentration of HCl.
- ☐ Only the concentration of PNP.
- ☐ Only the sum of the two concentrations.
- ☐ Both concentrations.

When measuring acid mixtures, a mixture of two indicators is often used.

34.9. Identify which indicator pair from the table below could substitute for a pH meter in the conventional titration of HCl-PNP mixtures. If not, provide the reason.

Indicator 1.	Indicator 2.	Verdict, explanation
Methyl orange (red–yellow, 3.1–4.1)	Curcumin (yellow–burgundy, 7.8–9.2)	
Methyl red (red–yellow, 4.4–6.2)	Phenolphthalein (colorless–pink, 8.3–9.8)	
Bromophenol blue (yellow–blue, 3.5–4.6)	Thymolphthalein (colorless–blue, 9.3–10.5)	
Congo red (blue–red, 3.0–5.2)	4-nitrophenol (colorless–yellow, 5.4–7.5)	

List of equipment and materials

On each desk:

150 cm³ approx. 0,5 mol/dm³ standard sodium hydroxide solution (with exact concentration)

10 cm³ HCl solution, labelled HCl

10 cm³ CH₃COOH solution, labelled acetic acid

10 cm³ HCl+ *para*-nitrophenol solution, label: unknown

pH meter with stand and holder

micropipette with 6 pipette tips

beaker 250 cm³

2 beakers of 100 cm³

2 glass rods

distilled water
goggles
plastic Pasteur pipette
paper towels
graph paper

Shared:

phenolphthalein indicator solution with dropper
gloves

GHS codes

Please note that the table of Globally Harmonized 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.

Chemical	GHS Hazard code
0.5 mol/dm ³ NaOH	H290, H314, H315
HCl solution	H290, H314, H335
Acetic acid solution	H315, H319
<i>para</i> -nitrophenol solution	H302, H312, H332, H373
phenolphthalein indicator solution	H315, H341, H350, H361f
isopropanol	H225, H336, H319

Solution

34.1.

The concentrations are $0.5V \text{ mol/dm}^3$ if the volume consumed is $V \text{ cm}^3$.

34.2.

In the case of a weak acid, at approximately the same concentration, the initial pH is higher, and it rises more rapidly at the beginning of titration. The pH change near the equivalence point is smaller and more prolonged. The equivalence point falls into the basic range.

34.3.

If the solution is not very dilute, then at 50 % titration $K_a = [\text{H}^+]$.

$K_a = 10^{-\text{pH}}$, $\text{p}K_a = \text{pH}$ (50%).

34.4.

The second step.

34.5.

If the volumes for the equivalence points are $V_1 \text{ cm}^3$ and $V_2 \text{ cm}^3$ then the HCl concentration is $0.5V_1 \text{ mol/dm}^3$ and the PNP concentration is $0.5(V_2 - V_1) \text{ mol/dm}^3$.

34.6.

We observe a distinct pH jump in the basic region that is well separated from the hydrochloric acid equivalence. (The pH jump is also smaller and more prolonged compared to the case of hydrochloric acid.)

34.7.

Para-nitrophenol itself acts as an indicator: it is yellow in an alkaline environment. Therefore, one can observe a change in the pink hue of phenolphthalein.

34.8.

Only the sum of the two concentrations.

34.9.

Indicator 1.	Indicator 2.	Verdict, explanation
Methyl orange (red–yellow, 3.1–4.1)	Curcumin (yellow–burgundy, 7.8–9.2)	Suitable
Methyl red (red–yellow, 4.4–6.2)	Phenolphthalein (colorless–pink, 8.3–9.8)	Not suitable. The measurement of hydrochloric acid is inaccurate: it is overestimated
Bromophenol blue (yellow–blue, 3.5–4.6)	Thymolphthalein (colorless–blue, 9.3–10.5)	Not suitable. The color change of thymolphthalein is not seen next to the bromophenol blue color. The range of thymolphthalein is inadequate (it is at a higher pH).
Congo red (blue–red, 3.0–5.2)	4-nitrophenol (colorless–yellow, 5.4–7.5)	Not suitable. The transition of Congo red is too broad, and PNP is the measured material itself, and we wouldn't even see the color change against the red background.

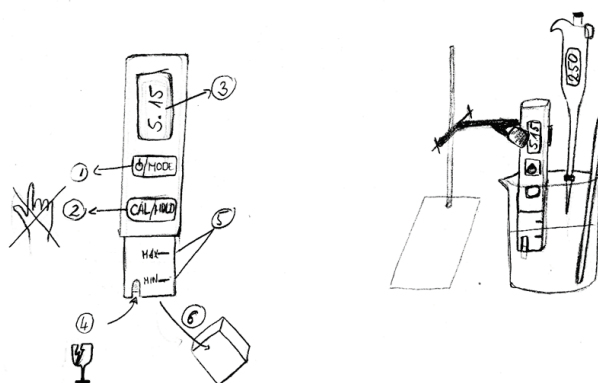
Hints for the preparations:

The HCl and acetic acid solutions were around 2 mol/dm³.

The HCl + PNP sample was prepared by dissolving 15–25 g of PNP in 80–100 cm³ of isopropanol and adding 15–25 cm³ of cc. HCl solution.

Inexpensive, but usable stick pH meters can be obtained from aquarium or pool supply stores or from global online retailers (available at around 20 USD on AliExpress and Temu). Micropipettes are in the same price range at global online retailers. Calibration of the pH meters is still necessary and can be tedious for dozens of units.

We include a sketch for the setup with our pH meters.



35. Analysis of a copper alloy

Brass and cupronickel are widely used copper alloys, e.g., in door handles and coins. You will analyze a nitric acid solution of an alloy sample. First you will determine the copper content using iodometry. Later you will measure the two metal ions together using complexometry.

The iodometric determination of copper(II) is based on the low solubility of CuI. During the titration the concentration of Cu(I) ions remains very low due to the low solubility of CuI. Thus the Cu(II)/Cu(I) redox system can quantitatively oxidize iodide ions, despite the small difference in standard redox potentials. The iodine formed can be titrated with sodium thiosulphate.

35.1. Give a balanced ionic equation for the reaction between copper(II) ions and iodide ions and the reaction between iodine and thiosulfate ions.

Your unknown sample solution is in a 100.00 cm³ volumetric flask. Your instructor will let you know if it was made from brass shavings or from a coin. Dilute it to the mark. Pipette a 10.00 cm³ aliquot to a stoppered 200 cm³ Erlenmeyer flask and dilute to 50 cm³ with distilled water. Acidify with 3 cm³ of 10% acetic acid and add about 2 g (a large spatula) of potassium iodide. Stopper the flask and wait 15 minutes before you titrate the iodine formed with 0.01 mol/dm³ sodium thiosulphate. Use 10 drops of the starch indicator towards the endpoint when the solution becomes faint yellow. Do not overtitrate, because the excess thiosulfate can interfere with the second titration.

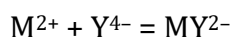
Repeat as necessary and report your accepted average consumption.

35.2. Describe the color of the solution both before the titration and after adding the indicator. **Explain** the source of the colors.

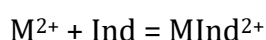
35.3. What happens if you leave the flask open after the titration is complete? **Why?**

Copper(I) is easily oxidized to copper(II). Atmospheric oxygen can complete the oxidation instantaneously after making the solution basic with ammonia.

Divalent and trivalent metal ions form stable 1:1 complexes with EDTA, making their determination convenient.



The reaction can be followed with indicators that form complexes with the metal ion participating in the reaction. The indicator works well if the Ind and MInd²⁺ forms have a different color and if the metal ion forms a more stable complex with ethylenediaminetetraacetate than with the indicator.



At the beginning of the titration, the metal-indicator complex is present, and at the end of the titration, the free color of the indicator appears.

Add 3 cm³ of conc. ammonia solution to the samples titrated with thiosulfate and dilute to 100 cm³. Titrate with 0.02 M EDTA solution using murexide indicator until the color change from yellow to purple is complete.

Repeat with your other samples and report your accepted average consumption.

35.4. What do you see after the addition of ammonia and why? What causes the color of the solution?

35.5. Why do you have to titrate until the color change is complete?

35.6. Calculate the mass percent composition of the alloy.

Equipment and material list

On each desk:

150 cm³ of 0.01 mol/dm³ thiosulfate solution with accurate concentration

150 cm³ of 0.02 mol/dm³ EDTA solution with accurate concentration

a 100 cm³ volumetric flask with the unknown sample

10 cm³ pipette

pipette bulb

burette (12 cm³)

distilled water

dropper

3 titrating flasks (200 cm³, with stopper)

2 beakers (100 cm³)

goggles

tissue paper

Shared between several students:

gloves

10% acetic acid solution with graduated plastic dropper (3 cm³)

concentrated ammonia solution under the hood, with graduated plastic dropper (3 cm³)

pH paper

starch solution with graduated plastic dropper

solid KI with a spatula (large end will deliver approximately 2 g of KI)

murexide indicator 0.2 m/m% in NaCl with a spatula

GHS codes

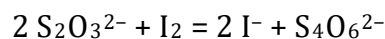
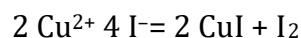
Please note that the table of Globally Harmonized System (GHS) hazard codes provided for the chemicals used in these experiments is intended as a reference only. There is no guarantee that the information provided is perfect or complete. The list does not replace the need for professional attention to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

Chemical	GHS Hazard code
0.02 mol/dm ³ Na ₂ EDTA solution	H332, H373
0.01 mol/dm ³ Na ₂ S ₂ O ₃	No hazard
10% acetic acid solution	H315, H319

conc. ammonia	H314, H318, H335, H400
KI	H372
starch solution	No hazard
murexide	No hazard
CuSO ₄ solution	H319, H412
ZnSO ₄ solution (optional)	H319, H411
NiSO ₄ solution (optional)	H317, H334, H341, H350, H360, H372

Solution

35.1.



35.2.

Before the titration the sample solution is turquoise blue due to the copper ions. After adding the indicator, the solution is blue due to the iodine-starch complex.

35.3.

The solution will turn blue again because air slowly oxidizes iodide to iodine in acidic media and the blue color of the starch-iodine complex appears.

35.4.

The precipitate dissolves, and the solution turns intensely blue. All the metals form ammonia complexes, and the Cu(II)-ammonia complex is blue.

35.5.

The endpoint of the titration is when all metal ions are in EDTA complex and there is no more metal bound to the indicator. The color of the metal indicator complex must disappear completely to reach the endpoint.

35.6.

If the volumes consumed are V_1 and V_2 for the two titrations, then the copper mass percentage:

$$w = \frac{M_{\text{Cu}} c_{\text{thio}} V_1}{M_{\text{Cu}} c_{\text{thio}} V_1 + M_{\text{M2}} (c_{\text{EDTA}} V_2 - c_{\text{thio}} V_1)}$$

Hints for the preparation:

The text does not strongly emphasize that the titrated samples from the first titration are used in the second part. This is intentional to stress that students need to plan their work in advance and prepare enough samples and finish the first titration before changing the solution in the burette.

Due to safety guidelines in some countries and in the IChO regulations, solutions containing nickel are not permitted in student laboratories. The procedure can utilize brass in place of cupronickel in the unknowns.

Samples can be created by combining 0.1 mol/dm^3 metal sulfate solutions. For a typical 63:37 brass composition, mix $12\text{-}13 \text{ cm}^3$ of CuSO_4 with $7\text{-}8 \text{ cm}^3$ of ZnSO_4 solution. For a 75:25 cupronickel composition, use about 15 cm^3 of 0.1 M CuSO_4 and about 5 cm^3 of 0.1 M NiSO_4 solution.

Instructors can also prepare the sample solutions by dissolving brass shavings or coins in concentrated nitric acid (in a hood), followed by neutralization with sodium carbonate and dilution. In Saudi Arabia, pre 2016 silver-colored common coins were made from cupronickel.

36. Titrations with hypochlorite

The hypochlorite ion is a strong oxidant, and reactions involving hypochlorite proceed rapidly with a well-defined stoichiometry. Despite these characteristics, direct titrations using hypochlorite are not common. In the first part of this task, you will determine the hypochlorite concentration by measuring the iodine it generates in acidic conditions. In the second part you will explore the reaction between hypochlorite and iodide in alkaline conditions, monitoring the temperature changes.

Use gloves when working with hypochlorite solutions!

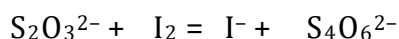
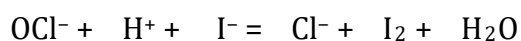
A. Precise determination of the concentration of a hypochlorite solution

Dilute 20.00 cm³ of the hypochlorite solution to 100.00 cm³ to get a stock solution. Take a 10.00 cm³ aliquot of the stock solution and add 25 cm³ 0.10 mol/dm³ KI solution that you mixed with 5 cm³ of 1 mol/dm³ sulfuric acid.

36.1. The sulfuric acid is added to the hypochlorite sample together with the KI solution, and not before. Explain the reason for this order.

The iodine formed must be titrated immediately with the ~0.1 mol/dm³ sodium thiosulfate solution. The exact concentration of the solutions can be found on the label. When the color of the iodine starts to fade, add 1 cm³ of starch solution and finish the titration dropwise. Record the consumed volume of the thiosulfate solution and repeat the titration as necessary.

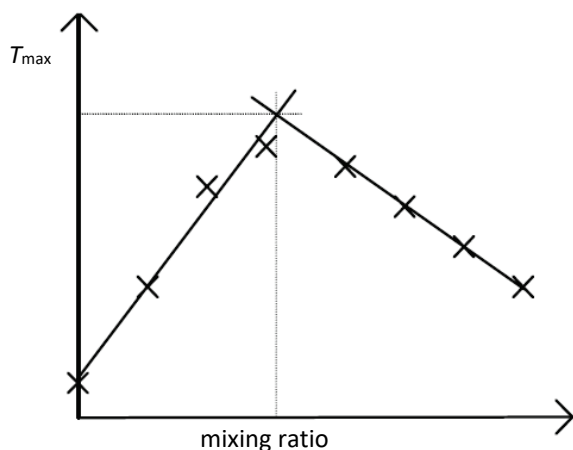
36.2. Balance the reaction equations. Calculate the hypochlorite concentration in the original bleach solution.



Investigating the reaction of hypochlorite and iodide in alkaline media

It is hard to keep track of the reactions of hypochlorite visually if the products are colorless. However, there are many instrumental methods to detect the equivalence point. One of the easiest procedures is the measurement of the temperature change during the reaction. If the reaction is conducted in a thermally well-isolated vessel (in this case a foam cup) the evolved heat is assumed to warm only the solution itself.

For practical reasons it makes sense to keep the volume of the reaction mixture constant. We can achieve this by mixing the two solutions in different ratios. A graph like the following can be obtained for an exothermic reaction when plotting the maximum temperature of the mixture as the function of the mixing ratio.



Measure the temperature before mixing the solutions. Mix 36 cm^3 of the two solutions (hypochlorite solution and the $0.10\text{ mol/dm}^3\text{ KI}$) in different ratios using the two burettes in the polystyrene cup. The solution with the higher volume needs to be the first one measured. Stir the mixture with the thermometer while keeping track of the temperature. The thermometer bulb (or sensing element) needs to be entirely below the surface of the solution. Record the highest temperatures of every mixture and draw a graph. Repeat the experiment a few times at different ratios until the ratio of the highest temperature can be read off the graph precisely.

36.3. Determine the volume ratio at the equivalence point using the graph. Determine the molar ratio of the hypochlorite and iodide ions at this point?

Change of color in the reaction mixture can be caused by contaminants in small concentrations, so ignore the color when thinking about the possible products.

36.4. Give a balanced reaction equation for the reaction of hypochlorite and iodide in alkaline media based on your results. Possible products are Cl_2 , Cl^- , I_2 , OI^- , IO_3^- , IO_4^- .

36.5. The density (1.0 g/cm^3) and heat capacity ($4.18\text{ J}\cdot\text{g}^{-1}\cdot\text{K}^{-1}$) of the solution are similar to water. Calculate the reaction enthalpy based on your measurements.

Equipment and material list

All solutions and the water used must be thermally equilibrated with the room, so they have to be prepared and diluted in advance.

On each desk:

250 cm^3 diluted bleach in plastic bottle
 250 cm^3 of $0.10\text{ mol/dm}^3\text{ KI}$ solution
 60 cm^3 of 0.1 mol/dm^3 thiosulfate with accurate concentration
 thermometer capable of measuring with an accuracy of 0.1 degree
 100 cm^3 volumetric flask
 10 cm^3 pipette
 20 cm^3 pipette
 pipette bulb

2 burettes (25 cm³)
distilled water
dropper
3 titrating flasks
3 beakers (100 cm³)
25 cm³ volumetric cylinder
2 polystyrene foam cups (200 cm³, coffee cups)
goggles
tissue

Shared in groups:

gloves
starch solution with graduated plastic dropper
1 mol/dm³ sulfuric acid solution with a 10 cm³ volumetric cylinder

GHS codes

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Chemical	GHS Hazard code
bleach	H315, H319, H400
0.1 mol/dm ³ KI	H372
0.1 mol/dm ³ Na ₂ S ₂ O ₃	No hazard
1 mol/dm ³ H ₂ SO ₄	H290, H314, H315, H318, H319
starch solution	No hazard

Hints for the preparations:

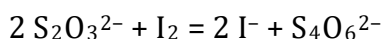
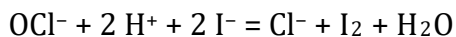
The bleach used was commercially available bleach containing 40 g/dm³ active chlorine diluted to 2.5 times its original volume.

Solution

36.1.

The hypochlorous acid formed in acidic media will decompose.

36.2.



If the titration volume is V_1

$$n(\text{S}_2\text{O}_3^{2-}) = 0.001V_1 \cdot c \quad (c \text{ is the thiosulfate concentration})$$

$$n(\text{I}_2) = n(\text{OCl}^-) = 0.0005V_1 \cdot c \quad (\text{in } 10.00 \text{ cm}^3 \text{ stock solution})$$

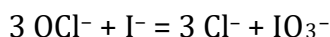
$$\text{In the original solution } [\text{OCl}^-] = 0.25V_1 \cdot c$$

36.3.

It makes sense to carry out experiments in the linear regime, away from the equivalence point in order to get a reliable ratio. The equivalence point can be obtained as the intersection of the two straight lines. Attempting to find the highest temperature amplifies the inaccuracy of the temperature measurements.

The expected mole ratio is $n(\text{OCl}^-) : n(\text{I}^-) \approx 3:1$.

36.4.



36.5.

The temperature change in the equivalence point is ΔT .

The mass of the solution is 36 g.

$$\text{The heat released: } Q = 4.18 \text{ J} \cdot \text{g}^{-1} \cdot \text{K}^{-1} \cdot 36 \text{ g} \cdot \Delta T$$

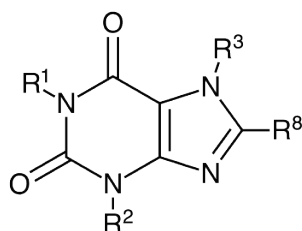
If the volume and concentration of hypochlorite at the equivalence is V_2 and c , then $V_2 \cdot c$ mol of hypochlorite reacts.

The reaction enthalpy for the $3 \text{OCl}^- + \text{I}^- = 3 \text{Cl}^- + \text{IO}_3^-$ reaction:

$$\Delta_r H = -3 \frac{150.5 \text{ J} \cdot \text{K}^{-1} \cdot \Delta T}{V_2 \cdot c}$$

37. TLC experiments with xanthine alkaloids

In this task, you will explore food items containing biologically active compounds known as xanthine alkaloids. Cocoa, chocolate, coffee, cola nuts, and tea all contain similar compounds that may have stimulant or mood-enhancing effects.



caffeine: $R^1 = R^2 = R^3 = \text{CH}_3$, $R^8 = \text{H}$ theobromine: $R^1, R^8 = \text{H}$, $R^2 = R^3 = \text{CH}_3$

In analytical chemistry, separating compounds with closely related structures is a challenge. Thin-layer chromatography (TLC) is a highly effective method in these situations, using adsorption equilibria on a solid surface for the separation of mixtures.

In Figure 1, the interaction of two substances with a solid surface (adsorbent) is illustrated. The substance denoted by solid circles (●) exhibits stronger binding to the surface, whereas the substance marked with empty circles (○) has weaker binding. As a solvent flows along the surface, it carries these two components at different rates, resulting in spatial separation. The component with stronger adsorption (●) lags behind the weakly bound component (○).

The technique employed is known as chromatography, where the solid surface is referred to as the stationary phase, and the solvent is called the mobile phase or eluent.

To become acquainted with the technique, an initial TLC analysis is conducted using samples of theobromine and caffeine.

The stationary phase you use consists of a uniform layer of fine silica particles attached to a thick aluminum foil. Handling of this composite sheet is similar to thicker paper, allowing tasks like cutting with scissors and marking with a pencil. The separation takes place on the white side of the sheet.

As the separation occurs on the surface, it is crucial to avoid touching the silica layer. Finger grease can significantly alter the binding affinity of the surface. Therefore, always handle the sheet by the edges or with tweezers.

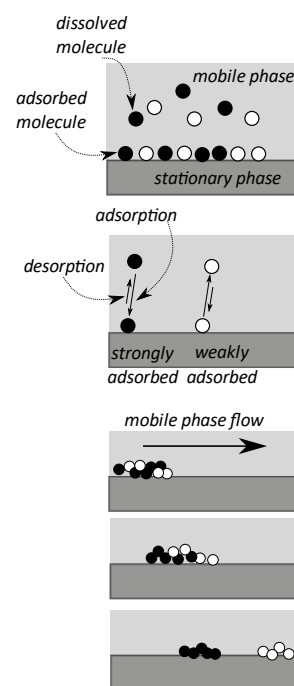


Figure 1

i. Prepare a solution with the theobromine and caffeine samples you find in two Eppendorf tubes. Dissolve them individually, adding 0.5-0.5 cm³ of 80% ethanol to each. Note that theobromine is challenging to dissolve in any solvent. If there is any material remaining undissolved in the tubes, use the clear portion of the solution.

ii. Draw a line approximately 1 cm from the short edge of the sheet using a pencil (Figure 2). This line, called the start line, is where we will place the materials to be separated. Always draw a thin line with a blunt, soft pencil to minimize damage to the surface.

iii. To apply the samples, place a capillary into the solution you wish to spot. A small amount of the solution will rise into the tube due to capillary action. Touch the tip of the capillary to the plate, depositing the sample along the start line. **Be cautious when handling glass capillaries, as they can cause injuries.** Keep them organized in a beaker or next to the samples. Ideally, use one capillary per sample. Dispose of used capillaries in the designated collection bin, not in the trash, to avoid potential injuries.

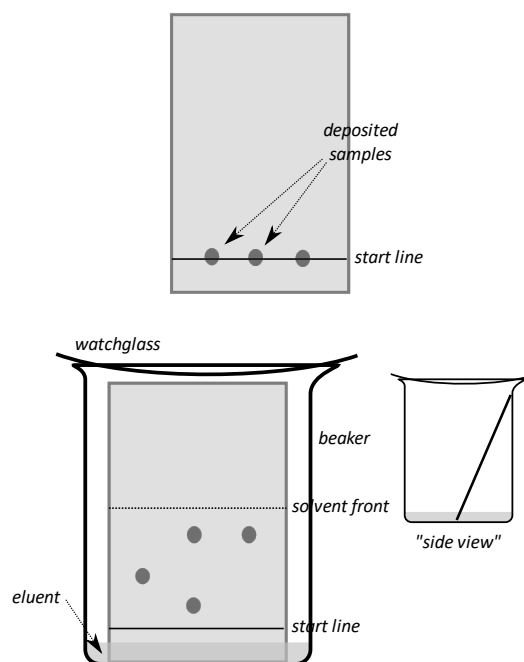


Figure 2

Mark the spots for the samples with a pencil. The spots should be evenly spaced from each other and from the edge of the plate. Write the symbols for each component below the start line using a pencil.

37.1. Why should you write below and not above the line? **Why** are you using a pencil, and not a pen?

Apply a small amount from each sample, ensuring that the spot is as small as possible. It's enough to briefly touch the capillary to the silica layer.

iv. Wait for the spots to dry completely (this may take 1-2 minutes). This is crucial because otherwise the separation will have problems. It is advisable to wait an additional minute after the spots disappear.

v. The eluent has already been prepared: we will use a mixture of chloroform, dichloromethane, and isopropyl alcohol in a 4:2:1 volume ratio. Pour enough eluent into a 100 ml beaker so that the solvent layer is about 0.75 cm deep. Add a filter paper strip as a wick to assist evaporation. Cover the beaker with a watch glass.

vi. With tweezers, place the TLC plate into the beaker so that the start line is at the bottom, and the plate leans against the wall of the container. It is important that the solvent level in the beaker does not reach the start line (see Figure 2). Do not shake or move the beaker from this point. Cover the beaker. **It is essential that the beaker is fully covered while the plate is inside.**

vii. The eluent begins to absorb into the TLC plate due to capillarity (i.e., capillary forces 'move' the mobile phase). **Ensure that the solvent forms a uniform front moving up the plate parallel to the liquid level.** If the solvent front is tilted sideways due to the plate's position or eluent disturbance, start with a new plate.

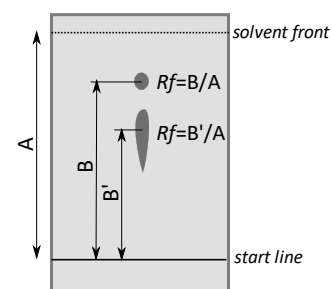
viii. Wait for the solvent front to approach about 1 cm from the top edge of the plate, then remove the plate from the beaker using tweezers. Lay it flat on the table, mark the position of the solvent front with a pencil, and let the plate dry.

In this task, you are examining colorless substances, so do not be surprised that even after the separation, the result is just a white plate. Fortunately, xanthine alkaloids absorb ultraviolet (UV) light, so their position on the TLC plate can be determined based on this. The silica gel on the TLC plate has been mixed with a substance that glows green under UV light. When we illuminate the plate with UV light, areas with xanthine alkaloids on the silica gel's surface will not let the light through. In other places, the silica will glow green, so we will see the samples as dark spots against a green background.

ix. Place the dried TLC plate under the UV lamp and outline the spots with a pencil.

If you feel that the separation was not successful, make and run a new plate.

The so-called retention factor, or R_f value, is used to characterize individual components. This can be determined by measuring the distance from the center of a component's spot to the starting line and dividing it by the distance between the starting line and the final solvent front (see Figure 3). The R_f value is thus a number between 0 and 1, typically given to two decimal places. In the case of oval or elongated spots, measure the distance from the center of the spot (the darkest part).



37.2. Determine the R_f value of the two alkaloids. **Can** caffeine and theobromine be clearly distinguished using this method based on the R_f values?

In your first real experiment, you will attempt to detect xanthine alkaloids in plant samples (cocoa bean, coffee bean, green tea leaves).

Grind an equal-sized piece of the provided three plant samples (e.g., a single coffee bean) in a mortar, then continue grinding with 2-3 ml of 80% ethanol. Transfer the mixture (paste) into a test tube and heat it with a heat gun until boiling begins. Let the solid parts settle, and from the clear solution, apply a sample to the TLC plate.

You can clean the mortar with dishwashing detergent. Wipe it dry before each new use.

Caution! The heat gun – actually a high-power hairdryer - blows very hot air, which can easily cause burns. The airstream should never be directed towards yourself or another person, and never blow onto flammable material! There should be no flammable material near the heat gun! When placing the heat gun down, be careful as the metal nozzle becomes very hot: avoid contact with tables, people, especially the power cable. The teacher will demonstrate the use of the heat gun at the beginning of the practice.

As before, mark the start line on the TLC plate. Apply the three samples and the previously prepared samples of the two compounds. Develop the TLC using the same eluent and mark the components under a UV lamp. If you feel the separation was unsuccessful, repeat the process.

37.3. Which alkaloids were you able to identify in the plant samples? Estimate which sample contains more of a particular alkaloid and which one contains less.

If you observe carefully, in the case of the tea sample, there are three faint, distinctive-colored spots visible even without UV light, which are not observed in the other two samples.

37.4. What color are these spots, and what is their R_f value? Where could these colored substances come from?

In the third part of the task, investigate the presence of alkaloids in processed products (chocolates). Utilize the given samples (dark chocolate, white chocolate, and milk chocolate) to prepare extracts, similar to the plant samples, and examine their alkaloid content.

37.5. Which chocolates contain which alkaloids? Compare the alkaloid content of each product!

37.6. Based on your experimental results, which statement(s) is/are true?

- ☐ White chocolate does not contain xanthine alkaloids.
- ☐ White chocolate does not contain xanthine alkaloids in amounts detectable by this method.
- ☐ White chocolate does not contain significant amounts of cocoa.
- ☐ All chocolates contain caffeine detectable by TLC.

At the end of the work, write your name on the three TLC plates corresponding to the three subtasks and place them in the ziploc bag found on your desk. Write your name on the bag. If you repeated experiments, submit only the plates you consider most successful.

List of equipment and materials

On each desk:

3 mg theobromine in Eppendorf tube
3 mg caffeine in Eppendorf tube
5 short test tubes
20 cm³ 80% ethanol
10 cm³ eluent, 4:2:1 chloroform: dichloromethane: isopropanol mixture
mortar and pestle
TLC chamber (beaker with watchglass cover and filter paper wick)
3 TLC plates (silica on Al) in ziploc bag
8 TLC capillaries
3 graduated plastic Pasteur pipettes (1 cm³)

tweezers
pencil and ruler
paper towels
goggles

Shared:

coffee beans, cocoa beans, green tea leaves, chocolate (dark, milk, white) samples
heat guns
UV lamp
dishwashing detergent and sponge
container for used capillaries
gloves

GHS codes

Please note that the table of Globally Harmonized 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.

Chemical	GHS Hazard code
theobromine	H302, H319
caffeine	H302
80% ethanol	H225, H319
dichloromethane	H351
chloroform	H302, H315, H319, H331, H336, H351, H361d, H372
isopropanol	H225, H336, H319

Solution

37.1.

Because if the writing is above the start line, then during the separation, the substances have to pass through the graphite-contaminated layer, which can alter their binding.

Because the components of the ink would be smeared/separated by the eluent.

37.2.

In a particular test the values were 0.49 for theobromine and 0.74 for caffeine. So they can be distinguished from each other.

37.3.

Cocoa beans contain a significant amount of theobromine and a visible quantity of caffeine, but much less compared to tea and coffee. Both tea and coffee contain caffeine and do not show detectable amounts of theobromine. The caffeine content in the two plants is approximately similar.

The size of the spots, and the intensity of the color (darkness) is reflects the quantity of the substance making up the spot.

37.4.

yellow: 0.82

green: 0.92

green: 0.93

Tea comes from a leaf where photosynthesis takes place. These spots correspond to photosynthetic pigments.

Specifically, these three are lutein, a type of carotenoid, and chlorophyll a and b, but you are not supposed to know that.

37.5.

Dark chocolate contains a significant amount of theobromine and a detectable quantity of caffeine. Milk chocolate has much less theobromine and no detectable caffeine. White chocolate does not contain either.

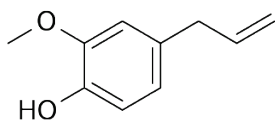
37.6.

☒ White chocolate does not contain xanthine alkaloids in amounts detectable by this method.

☒ White chocolate does not contain significant amounts of cocoa.

38. Determination of the eugenol content of cloves

Clove, a popular spice in Eastern cuisine and a common fragrance ingredient, derives its exotic scent from eugenol. In this task, we aim to determine the approximate eugenol content in cloves through thin-layer chromatography (TLC).



Eugenol

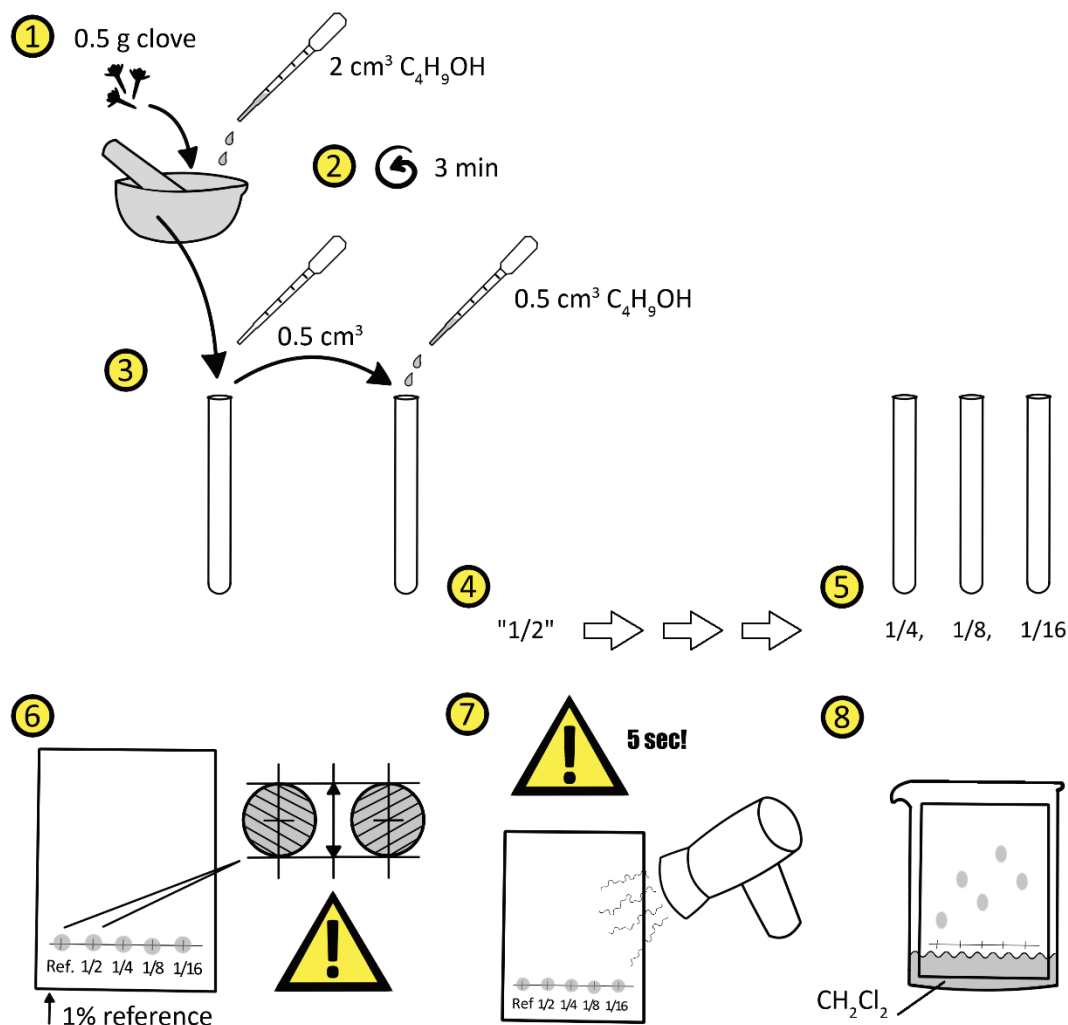
1. Weigh approx. 0.50 g of clove buds.
2. Add 2.0 cm³ of *n*-butanol and grind it in a porcelain mortar for at least 3 minutes.
3. Allow insoluble parts to settle and decant the clean portion of the solution into a small test tube using a Pasteur pipette.
4. Transfer 0.5 cm³ of this solution into a clean test-tube, and add 0.5 cm³ of butanol, creating a twofold dilution of the original extract. Label this sample as 1/2.
5. Repeat this dilution, creating a series of 1/4, 1/8 and 1/16 dilutions of the sample.
6. Apply equal volumes (in practice: equal size spots) of the standard eugenol solution (with 1 wt% concentration) and the dilution series of the unknown (1/2, 1/4, 1/8, 1/16) to the "start line" of a clean silica TLC plate.
7. Dry the plate with a heat gun. Be cautious! The heating should not be longer than 5 seconds!
8. Develop the plate with dichloromethane as the eluent.
9. Mark the spots with a pencil under a UV lamp.

The following figure helps in your work. If necessary, you can ask for a replacement plate.

Hand in your plate. It will be graded.

The density of *n*-butanol is $d = 0.810 \text{ g/cm}^3$.

- 38.1. **Calculate** the approximate eugenol content of clove buds in wt%.
- 38.2. **Determine** the R_f value of eugenol.
- 38.3. **Why** is it a problem if you use the heat gun for a longer time to dry the plate?



List of equipment and materials

On each desk:

test tube stand
 5 short test tubes
 8 cm³ *n*-butanol
 10 cm³ dichloromethane eluent
 mortar and pestle
 TLC chamber (beaker with Al foil cover and filter paper wick)
 2 TLC plates (silica on Al)
 6 TLC capillaries
 6 graduated plastic Pasteur pipettes (1 cm³)
 tweezers
 pencil and ruler
 paper towels
 goggles

Shared:

balances
heat guns
clove
1 wt. % eugenol solution in *n*-butanol
UV lamp
container for used capillaries
gloves

GHS codes

Please note that the table of Globally Harmonized 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.

Chemical	GHS Hazard code
<i>n</i> -butanol	H226, H302, H335, H336, H315, H318
dichloromethane	H351
eugenol	H317, H319

Solution

Marking of the plate: missing marks, line or circles, slanting, spots missing, spots too big result in a penalty.

38.1.

One of the dilutions spots will be matching the 1% solution in intensity. If that is the $\frac{1}{4}$ dilution, then the original solution contained $w = 4\%$ eugenol.

Taking the density of the first extract identical to butanol, that means 4% of 1.62 g = 64.8 mg of eugenol, 12.9% of the clove mass.

38.2.

The R_f value can be graded. Typical values are around 0.78 for eugenol in this setup.

38.3.

Eugenol, as a scent component, is also volatile.