

General Instructions

- This examination has **9 problems** in two booklets. This question booklet has **29 pages** and contains the problems with numbered questions in English. The answer booklet has **28 pages** and contains numbered boxes corresponding to the questions. Only language-independent symbols and formulae are used in the answer booklet.
- You may begin working as soon as the **START** command is given. You will then have **5 hours** to complete the exam.
- All results must be written with pen in the appropriate answer boxes of the **answer booklet**. If you must write outside of the designated box, make a note in the box. Keep your answer on the same page.
- Only the answer booklet is collected. Do not separate the pages of the stapled answer booklet.
- Do not write on the back sides of the answer booklet! Markers will only see the printed sides of the answer booklet. Use the back sides of the question booklet if you need scrap paper. **Do not** draw anything into or close to the QR codes.
- Write relevant calculations in the appropriate boxes. Full marks will be given for correct answers only when your work is shown.
- For the multiple choice questions, **if you want to change your answer**, completely scribble out the box you have ticked and draw a **new box next to it**.
- Use only the pen and calculator provided.
- The "official" English version of this examination is available on request for clarification only.
- If you need a toilet break or any assistance, or want to review the "official" English version, raise your hand.
- The supervisors will announce a **30-minute** warning before the **STOP** command. You **must stop** working when the **STOP** command is given. Failure to stop writing can lead to the nullification of your examination.
- After the supervisor tells you to do so, put **only your answer booklet** back into the envelope. You can keep the question booklet. **Do not** seal the envelope.

GOOD LUCK!

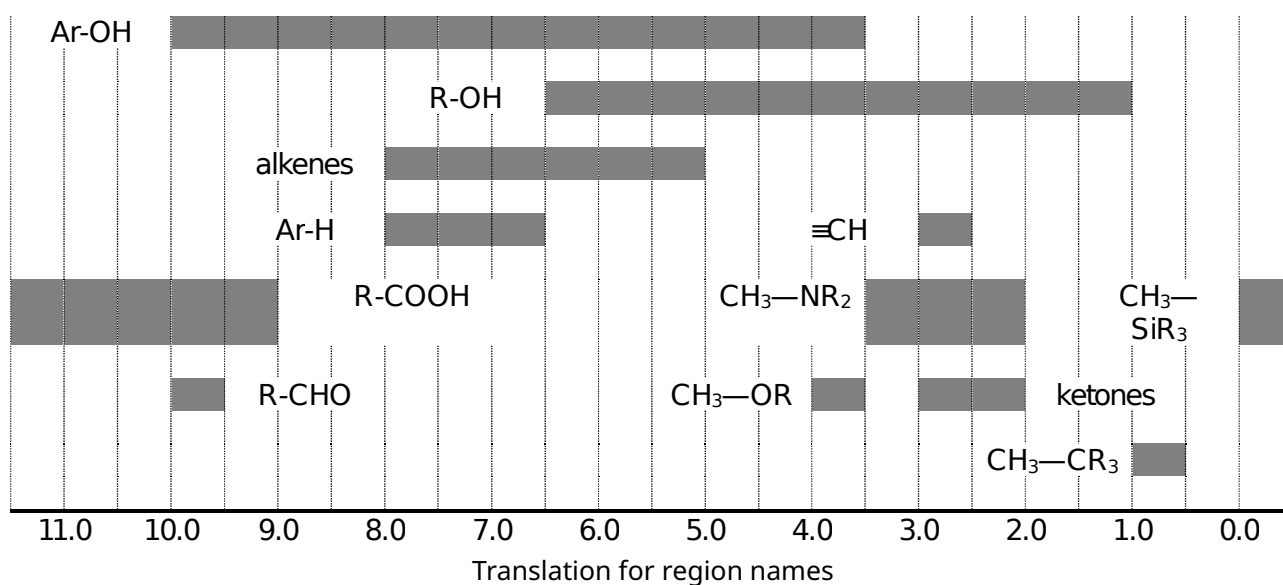
Theory

G0-2

Estonian English (Estonia)

Avogadro constant:	$N_A = 6.022 \cdot 10^{23} \text{ mol}^{-1}$	Gas constant:	$R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$
Ionic product of water at 298.15 K:	$K_w = 10^{-14}$	Zero of the Celsius scale:	$0^\circ \text{ C} = 273.15 \text{ K}$
Faraday constant:	$F = 96485 \text{ C mol}^{-1}$	Planck constant:	$h = 6.626 \cdot 10^{-34} \text{ J s}$
Speed of light:	$c = 2.998 \cdot 10^8 \text{ m s}^{-1}$	Standard pressure:	$p^\circ = 1 \cdot 10^5 \text{ Pa} = 1 \text{ bar}$
Ideal gas law:	$pV = nRT$	Beer-Lambert law:	$A = \log\left(\frac{I_0}{I}\right) = \varepsilon \cdot l \cdot c$
Enthalpy:	$H = U + pV$	Gibbs energy:	$G = H - TS$
$\Delta_r G^\circ = -RT \ln K = -nFE_{cell}^\circ$		Henderson-Hasselbalch equation:	$\text{pH} = \text{pK}_a + \log\left(\frac{[A^-]}{[HA]}\right)$
Arrhenius equation:	$k = A \exp\left(\frac{-E_A}{RT}\right)$	Zeroth order integrated rate law:	$[A] = [A]_0 - kt$
Surface area of a sphere:	$A = 4\pi R^2$	First order integrated rate law:	$\ln[A] = \ln[A]_0 - kt$
Volume of a sphere:	$V = \frac{4\pi}{3} R^3$	$\sum_{k=0}^{\infty} ar^k = \frac{a}{1-r} \quad \text{for } r < 1$	

¹H NMR chemical shifts (in ppm/TMS)



Theory

G0-3

Estonian English (Estonia)

Periodic table

1																		18					
1 H 1.008	2																2 He 4.003						
3 Li 6.94	4 Be 9.01											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18						
11 Na 22.99	12 Mg 24.30	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 -

Problems and Grading Information

	Title	Question pages	Answer pages	Total score	Percentage
1	Ammonia	3	5	24	7.5
2	Electronic nose	3	2	12	6
3	Tyrosinase	4	4	31	7.5
4	Potassium	2	3	21	6
5	Unknown	2	3	44	6
6	Penicillin	3	2	38	6
7	SABIC	5	3	23	7.5
8	Safflower	3	2	38	6
9	Porphyrin complexes	4	4	35	7.5
				Total	60

Problem 1 Ammonia

The Haber–Bosch process to produce ammonia from nitrogen and hydrogen is one of the most impactful industrial processes in history and is estimated to sustain around half of today's population. The process typically occurs at constant temperature and pressure, 400 °C and 100 bar, respectively. Equilibrium between the reactants and the product is established over Fe-based catalysts.

The standard gas phase thermochemistry data of N_2 , H_2 , and NH_3 are shown below. Assume the enthalpy and entropy of the reaction are temperature independent.

	$\text{N}_2(\text{g})$	$\text{H}_2(\text{g})$	$\text{NH}_3(\text{g})$
$\Delta_f H^\circ / (\text{kJ mol}^{-1})$	0	0	−45.9
$S^\circ / (\text{J mol}^{-1} \text{K}^{-1})$	191.6	130.7	192.8

- 1.1** **Find** the percentage of moles of nitrogen converted to ammonia under the production conditions from a stoichiometric mixture of nitrogen and hydrogen. 7 pt
Show your calculations for partial credit. *If you cannot find a result, use 66% in subsequent calculations.*

One of the reactants in the Haber–Bosch process is hydrogen which is mainly produced by steam reforming of methane. The two-step steam reforming process starts with CH_4 reacting with water to produce H_2 and CO . In the subsequent step, CO reacts with water to form CO_2 and additional hydrogen.

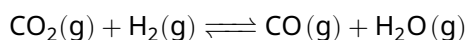
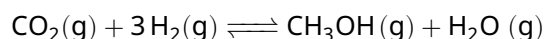
- 1.2** **Write** the overall reaction equation for the combined process. **Give** the mass of CO_2 produced in the reaction per 1.0 kg of H_2 (m_{CO_2}). 2 pt

In reality, 7.0 kg of carbon dioxide is produced for each 1.0 kg of hydrogen in steam reforming. The generated ammonia is classified based on CO_2 management. For "grey" ammonia, the CO_2 is released into the atmosphere; for "blue" ammonia, it is captured and stored. "Green" ammonia is made from hydrogen produced without carbon emissions.

- 1.3** **Calculate** the mass of carbon dioxide ($m_{\text{CO}_2, \text{blue}}$) that needs to be captured to produce 40000 kg of "blue" ammonia. Assume that the carbon dioxide only comes from the steam reforming process. Also assume that the ammonia is produced at equilibrium from a stoichiometric mixture of nitrogen and hydrogen. 3 pt

Using cheap renewable hydrogen, the prospect of converting it with captured CO_2 into methanol appears

promising. However, in this procedure, there is a competing reaction that produces CO:



A mixture containing $\text{CO}_2 : \text{H}_2$ in a molar ratio of 1 : 4 is added into a reactor kept at 250 °C and 50 bar. When these two reactions are at equilibrium, it has been found that the CO_2 conversion is 30% and the H_2 conversion is 18.5%. No other processes need to be considered.

1.4 **Calculate** the thermodynamic equilibrium constants (at 250 °C) of the two reactions. 5 pt

Heterogeneous copper-containing catalysts are commonly used for CO_2 hydrogenation. Two Cu-containing catalysts (*A* and *B*) show promise for converting CO_2 to methanol. These catalysts differ not only in their catalytic rates, but also in surface area, Cu content, and Cu dispersion (the ratio of surface Cu to the total Cu in the catalyst).

Cu dispersion is important because only Cu species at the surface are active in this CO_2 hydrogenation. Under this assumption, 1 mol active sites corresponds to 1 mol surface Cu. The efficiency of these active sites is shown by their turnover frequency (*TOF*). *TOF* is moles of product formed per moles of active site in a given time.

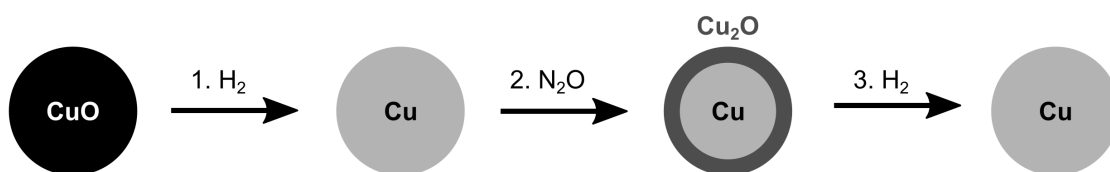
Theory

Q1-3

Estonian English (Estonia)

The **table** below shows the performance (given as mass of methanol produced per total catalyst mass in a given time) and the specific surface area of the two catalysts. The Cu content and dispersion of the catalysts were also measured and reported as follows:

1. At the start, all the copper in the catalysts (oxidised beforehand) was present as Cu(II); this was fully reduced to Cu(0) with hydrogen. No other species in the catalysts reacted with hydrogen besides copper oxides.
2. N₂O was introduced to the reduced samples at room temperature. At this temperature, N₂O only oxidises the active surface sites to Cu(I).
3. The Cu(I) active surface sites were reduced again to Cu(0) with hydrogen.



	Catalyst performance (g _{MeOH} g _{cat} ⁻¹ h ⁻¹)	Specific surface area (m ² g _{cat} ⁻¹)	H ₂ consumed in step 1 (mmol g _{cat} ⁻¹)	H ₂ consumed in step 3 (mmol g _{cat} ⁻¹)
Catalyst A	0.80	100	5.0	0.30
Catalyst B	0.90	120	4.0	0.70

1.5 **Find** the methanol production rate per total mass of Cu (in g_{MeOH} g_{Cu}⁻¹ h⁻¹) for catalysts A and B. 3 pt

1.6 **Find** the TOF (in h⁻¹) for catalysts A and B. 3 pt
If you cannot calculate them, use TOF_{Catalyst A} = 100 h⁻¹ and TOF_{Catalyst B} = 1 h⁻¹ in subsequent calculations.

1.7 **Indicate** the correct statement on the answer sheet. 1 pt

- a. The active sites of Catalyst A are more efficient.
- b. The active sites of Catalyst B are more efficient.
- c. The two catalysts have active sites with the same efficiency.

Problem 2 Electronic nose

Resistive gas sensors, especially those using semiconducting metal oxides (SMOX), are becoming increasingly popular. They are small, stable, easy to make and use, and can detect tiny amounts of impurities. These features make SMOX sensors stand out among gas sensors that work based on different physical and chemical principles.

The mixed oxide **X** that has the normal spinel crystal structure, $A^{2+}B^{3+}_2O^{2-}_4$, is an example of one of these SMOX materials. **X** can be obtained by decomposition of the crystalline hydrated metal oxalate $ZC_2O_4 \cdot kH_2O$ of metal **Z** in air. When heated to 140 °C, the crystalline hydrate loses 19.7% of its mass. Further heating in air leads to the formation of 2.407 g of black coloured **X** and 3.8 dm³ of carbon dioxide at 500 °C and 101325 Pa.

2.1 Determine the formula of **X** and the value of **k** in $ZC_2O_4 \cdot kH_2O$.

4 pt

In spinel structures, the oxygen atoms form a face-centered cubic (FCC) lattice. In normal spinels, A^{2+} cations occupy some of the tetrahedral sites; B^{3+} cations occupy some of the octahedral sites.

2.2 Calculate the percentage of tetrahedral sites that are occupied in a normal spinel $A^{2+}B^{3+}_2O^{2-}_4$.

2 pt

In addition to normal spinels, the MM'_2O_4 general formula describes inverse and mixed spinel structures. Here, M are the tetrahedrally coordinated cations, and M' are the octahedrally coordinated cations. Unlike in normal spinels, particular cations are not restricted to a single type of lattice site. A characteristic of inverse spinel structures is that the electron configuration of the M' site cations is d^0 , d^5 , or d^{10} .

2.3 Select on the answer sheet two of the given formulas which correspond to an inverse spinel structure: Fe_3O_4 , $NiFe_2O_4$, Mn_3O_4 , $FeCr_2O_4$.

1 pt

Semiconductors are materials whose orbitals contain a small excess or deficit of electrons, leading to negative charges or positive charges (holes), respectively. These charges can move through the semiconductor and allow it to conduct electricity. Chemical reactions can increase or decrease the charge on a semiconductor, altering its conductivity.

X is an example of a semiconductor where electricity is carried by positive charges (holes). For a resistive gas sensor based on **X**, the resistance *R* is measured over time *t*, while passing a gas over the sensor. This allows redox reactions to occur between the gas and the semiconductor surface. These redox reactions affect the resistance of the sensor; and how it changes depends on the donor or acceptor properties of the gas. **Figure 1** shows the two different types of signal obtained this way.

Figure 1: plot of resistance against time for two possible signal types, (a) and (b).

Grey bars = air; white bars = air + analyte gas.

2.4 **Match** the signal type (a or b) obtained from the **X** based sensor with the analyte gases (H_2S , O_3 , NO_2 , NH_3) during their detection at low concentrations. 2 pt

The dependence of the specific conductivity (σ) of **X** on temperature is described by the Arrhenius law: $\sigma(T) = \sigma_0 \exp(-E_a/(RT))$, where E_a is the activation energy of conductivity. Three types of conductivity can be distinguished in different temperature ranges:

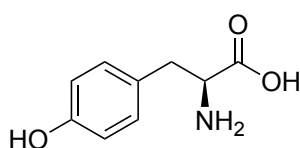
Ionisation (I): 444–570 K, Impurity (II): 585–765 K, and Intrinsic (III): 800–905 K.

The sketch below illustrates the conductivity-temperature relation for the three temperature ranges.

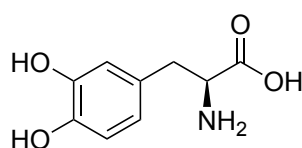
- 2.5** Based on the sketch above, **order** the activation energies for the different conductivity types, $E_a(I)$, $E_a(II)$, and $E_a(III)$, from largest to smallest. 3 pt

Problem 3 Tyrosinase

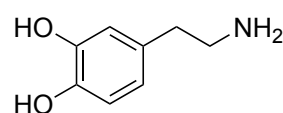
The enzyme tyrosine 3-monooxygenase has an important biological role because it catalyses the rate-limiting, initial step in the biosynthesis of the neurotransmitter dopamine. In this first step, L-DOPA is produced from the amino acid L-tyrosine (Tyr) in the presence of dissolved oxygen, tetrahydrofolic acid, and ferrous ions. In a subsequent step, another enzyme transforms L-DOPA into dopamine.



L-Tyrosine



L-DOPA



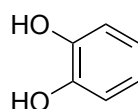
Dopamine

The activity of the tyrosine 3-monooxygenase enzyme is well described by the simplest model of enzyme action, the Michaelis-Menten equation. This gives the rate of formation (r) of L-DOPA as a function of the enzyme (E) and substrate Tyr (S) concentrations as follows:

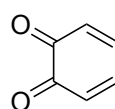
$$r = \frac{k[E][S]}{K_M + [S]}$$

The following values of enzymatic turnover frequency ($k = 250 \text{ min}^{-1}$) and Michaelis constant ($K_M = 0.49 \text{ mmol dm}^{-3}$) can be used in this task when needed.

Catechol (1,2-dihydroxybenzene) inactivates the enzyme tyrosine 3-monooxygenase irreversibly. When a carefully purified sample of catechol is mixed with the enzyme in the absence of any dissolved oxygen, no change is seen at all. So, the reaction of catechol with dissolved oxygen to produce *o*-quinone must be important.



Catechol



o-Quinone

This process can be studied in the absence of the enzyme. A test experiment in a reactor not in contact with ambient air at 37°C and at pH 7.5 gave the following kinetic data:

Theory

Q3-2

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time (min)	catechol concentration (mmol dm ⁻³)	oxygen concentration (mmol dm ⁻³)	<i>o</i> -quinone concentration (μmol dm ⁻³)
0	2.00	0.200	0
20.0	1.97	0.170	30
40.0	1.94	0.140	60
60.0	1.91	0.111	89
80.0	1.88	0.083	117
100.0	1.85	0.054	146

3.1 **Identify** the only by-product (which is not one of the molecules listed in the table above) and **write** the balanced equation of the process with molecular formulas based on the kinetic data. 5.0 pt

3.2 **Calculate** the initial rate (r_0) of *o*-quinone formation in this experiment, giving the appropriate unit. 2.0 pt

The rate law of this process was determined by varying the initial concentrations of the reactants. Changing the oxygen concentration did not influence the initial rate of this process. Using different catechol concentrations gave the following initial rates of *o*-quinone formation:

catechol concentration (mmol dm ⁻³)	initial rate of <i>o</i> -quinone formation (μmol dm ⁻³ min ⁻¹)
1.0	0.75
4.0	3.0
6.0	4.5
8.0	6.0
10.0	7.5

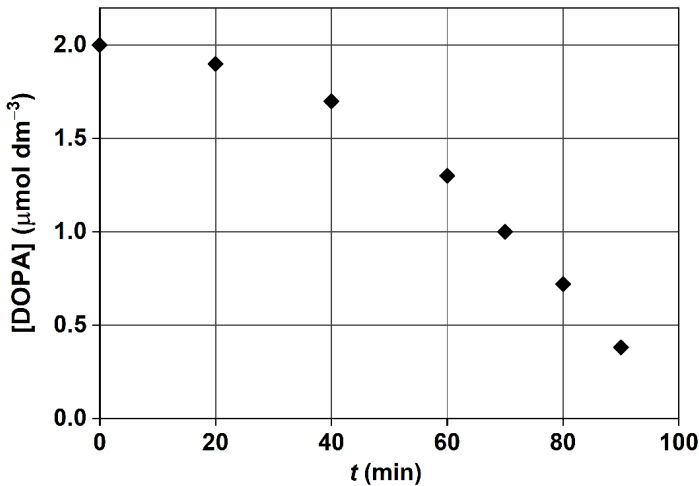
3.3 **Determine** the rate law of the reaction between catechol and oxygen to produce *o*-quinone. **Calculate** the rate constant of this process (k_{catechol}) with an appropriate unit. 5.0 pt

In separate experiments, it was confirmed that neither *o*-quinone, nor the by-product, inactivates the enzyme alone, nor even in combination.

However, an experiment in which the enzyme reacts with catechol in the presence of dissolved oxygen did show inactivation.

The experiment was done in an open container so that any oxygen consumed in the process could be continuously replenished from air. The initial concentration of the enzyme was 4.2 nmol dm^{-3} and the initial concentration of catechol was 2.00 mmol dm^{-3} at $37\text{ }^{\circ}\text{C}$ and at pH 7.5.

Samples were taken regularly from the enzyme-catechol reaction mixture, and the activity of the enzyme was analyzed by adding L-tyrosine, tetrahydrofolic acid, and ferrous ions. During the enzyme activity measurements, the concentration of added L-tyrosine was 10.0 mmol dm^{-3} and the concentration of L-DOPA in each assay sample was measured after 2.0 minutes. The following results were obtained:



inactivation reaction time <i>t</i> (min)	L-DOPA concentration after 2.0 minutes from the start of the assay [DOPA] ($\mu\text{mol dm}^{-3}$)
0	2.0
20.0	1.9
40.0	1.7
60.0	1.3
70.0	1.00
80.0	0.72
90.0	0.38

Theory

Q3-4

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- 3.4** Derive a formula that allows you to calculate the actual concentration of active enzyme ($[E]$) from the data of these experiments in terms of k ($= 250 \text{ min}^{-1}$), K_M ($= 0.49 \text{ mmol dm}^{-3}$), and/or reagent concentrations. 4.0 pt

The change in the active enzyme concentration as a function of time is well described by a parabola ($[E] = [E]_0 - k_{\text{obs}}t^2$), where k_{obs} is an observed rate constant (i.e. one that can be written later as a combination of elementary rate constants and initial concentrations), and $[E]_0$ is the initial concentration of the enzyme.

- 3.5** Give the value of k_{obs} with an appropriate unit. 3.0 pt

- 3.6** Determine the first half-life of the enzyme inactivation reaction. Derive a formula that gives the first half-life as a function of the initial enzyme concentration and of k_{obs} . 3.0 pt

The first half-lives for enzyme inactivation were determined for other initial catechol concentrations. The dependence of active enzyme concentration on time was well described by a parabola in these cases as well.

catechol concentration (mmol dm^{-3})	first half-life (min)
1.0	140
4.0	35
6.0	23
8.0	17.5
10.0	14

- 3.7** Derive a rate equation for the enzyme inactivation process consistent with all the experimental observations. 6.0 pt

3.8 What are the reactants of the rate determining step for the enzyme inactivation process? **Select** the ONLY correct option on the answer sheet. 3.0 pt

- A) catechol + $O_2 \rightarrow \dots$
- B) catechol + *o*-quinone $\rightarrow \dots$
- C) *o*-quinone + $O_2 \rightarrow \dots$
- D) enzyme + 2 catechol $\rightarrow \dots$
- E) enzyme + $O_2 \rightarrow \dots$
- F) 2 catechol + $O_2 \rightarrow \dots$
- G) enzyme + catechol $\rightarrow \dots$
- H) enzyme + by-product $\rightarrow \dots$

Problem 4 Potassium

In 1807, elementary potassium was the first metal to be synthesised by electrolysis. Humphry Davy used voltaic cells and electrodes immersed in molten KOH.

4.1 **Give** balanced equations for the processes taking place at the cathode (1) and the anode (2). 2 pt

Only a year after Davy, French chemists produced potassium in a chemical reduction. One of the methods involved a mixture of potassium carbonate and finely powdered carbon. This mixture was heated to very high temperatures in a gun barrel. Carbon monoxide and potassium vapours left the end of the barrel, where the metal condensed to a solid.

4.2 **Write** down the balanced equation for the reaction giving only these two products. 1 pt

The chemical production of potassium had a low yield. Depending on the circumstances, a considerable amount of reddish paste was left behind in the gun barrel. Gmelin isolated an interesting compound (**X**) from this residue in 1825 by recrystallisation in water. The exact structure of the by-product **X** was determined more than one and a half centuries later.

X is a hydrated salt (2 mol water : 1 mol of salt) forming golden yellow crystals. Its anion has an exceptionally symmetric and stable planar cyclic structure (shown by its vibrational spectrum).

The diprotic acid (**Y**) that can be formed from the salt **X** has surprisingly (at least to the superficial observer) low pK_a values: 0.8 and 2.2.

4.3 **Give** the pH where 95% of all dissolved acid **Y** is in the neutral acid form. 3 pt

4.4 **Calculate** the pH of a 0.01 mol dm^{-3} solution of the salt **X** in pure water. 4 pt

The key step in the structure identification of **X** was the treatment of the anhydrous salt with methyl iodide. The salt reacted with two equivalents of methyl iodide. The somewhat volatile compound that was obtained had a molar mass of 170.12 g/mol (measured in a mass spectrometer).

A number of analogous salts were also identified in the mixture in smaller quantities. The appropriate potassium salts when treated with two equivalent of MeI gave derivatives with molar masses of: 142.11 g/mol , 114.10 g/mol , 198.13 g/mol .

4.5 Give the empirical formula of Gmelin's compound **X**.

4 pt

4.6 Draw the structure of the free acid **Y**.

3 pt

The extraordinary stability of the series of anions in the salts analogous to **X** can be attributed to electron delocalisation.

4.7 Draw one resonance structure with a significant contribution to the anion for each of the four salts. 4 pt

Problem 5 Unknown

Metal containing salt **A** can be prepared in a simple exchange reaction when the cold, saturated aqueous solutions of the two distinctly coloured compounds, **B** and **C** are mixed in a stoichiometric ratio. 10.00 g **B** in solution mixed with 12.86 g **C** in solution and immediately cooled to 2 °C will give 4.90 g solid **A**. The yield of **A** is 32.6 %.

To determine the composition of **A**, iodometry is performed first. A known mass of **A** is added to a titration flask, acidified with sulfuric acid, then KI is added in excess leading to precipitation. After a few minutes, sodium citrate solution is added until the mixture is free of precipitate. The citrate ions form a strong complex with a metal ion present in the mixture, reversing completely the reaction leading to the precipitate. The resulting mixture is titrated with sodium thiosulfate solution (Titration I via reaction [1]). To the blue titrated solution, another portion of sulfuric acid (significantly more than the initial amount) is added to protonate the citrate. The previous solid precipitate is formed once again (reaction [2]). The mixture is titrated with the same thiosulfate solution (Titration II via reaction [1]).

The average volumes for 100.0 mg **A** with $5.000 \cdot 10^{-2} \text{ mol dm}^{-3}$ thiosulfate are 54.12 cm³ in Titration I and 5.41 cm³ in Titration II.

When the aqueous solution of **A** is heated, the light blue precipitate **D** can be observed (reaction [3]). Compound **E** can be crystallised from the solution above **D**. The low temperature during the synthesis of **A** is important to avoid contamination by **E**.

5.1 Write balanced equations for reactions [1] and [2].

4.0 pt

The thermal decomposition of **A** was studied in detail. When pure **A** is slowly heated it explodes at around 75 °C . When the compound is dispersed in aluminium oxide and the mixture is heated, then the matrix absorbs the excess heat, and the explosion can be avoided. Two decomposition steps can be observed. In the first step (at 65 °C), in addition to the 14.1% mass decrease, a two-component solid residue forms (reaction [4]). The components of this residue can be easily separated, as **F** is very soluble in water, while **G** does not dissolve at all. The **F**:**G** mass ratio is 1.00 : 2.97. On further heating, **F** decomposes without a solid residue (reaction [5]). That means pure **G** is the final solid decomposition product of **A**. **G** contains two other elements in addition to 27.0 wt% oxygen. One of the two components of the gas mixture forming in the first decomposition step can be easily quantified if it is absorbed into acidic solution.

Some hints

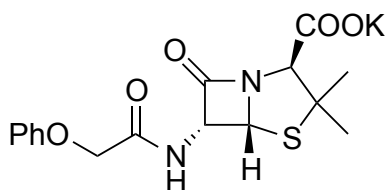
- Compound **A** decomposes without releasing oxygen.
- Compound **A** contains two different metals.
- Compounds **A** and **B** both contain a complex ion.
- Compound **C** is well-known to any chemistry student.
- Compound **F** does not contain any metal.

5.2	<u>Give chemical formulas</u> of A—G . You don't have to show your calculations, but if your compounds are incorrect you may gain partial marks from correct calculations.	28.0 pt
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5.3	<u>Write</u> balanced equations for reactions [3]—[5].	12.0 pt
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Problem 6 Penicillin

Penicillins are a group of antibiotics that have played a crucial role in medicine since their discovery.



Penicillin VK

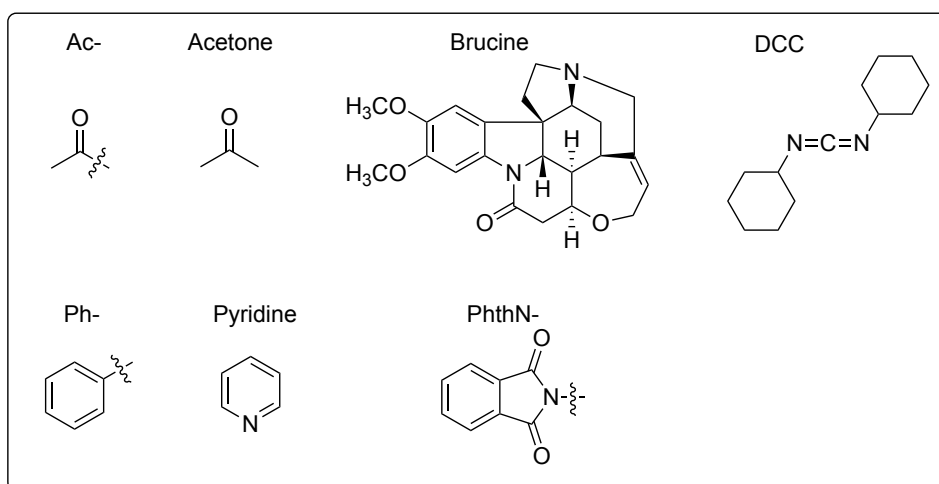
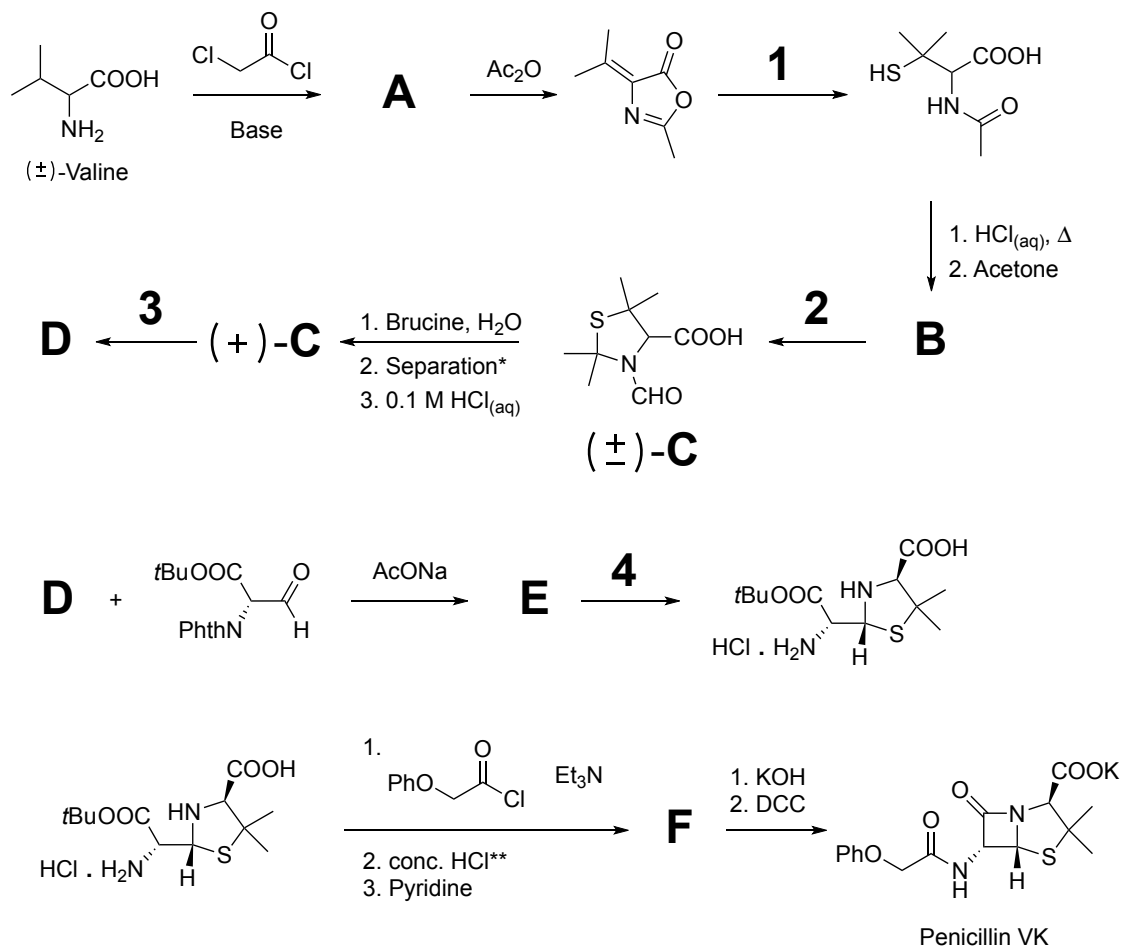
6.1. **Mark** the stereogenic carbon centers on the structure of Penicillin VK on the answer sheet. **Write** the corresponding *R/S* stereodescriptors next to the centers on the answer sheet. 6 pt

6.2. **Give** the total number of possible stereoisomers of Penicillin VK. 2 pt

One of the many synthetic methods to obtain Penicillin VK starts from the amino acid valine, as shown in the scheme on the next page of this problem.

Hints:

- Among other signals, the ^1H NMR spectrum of compound **A** contains two signals that each integrate to 3H. Both of these signals are doublets.
- Compounds **A** and **D** are open-chain compounds, while **B** and **E** each have a five membered ring (in addition to any rings in the PhthN-group).
- Brucine is used for chiral resolution.



*Asterisk(s) are to allow translation for non-English exams.

6.3. Choose the suitable reagent for the numbered steps (1–4) on the answer sheet. 8 pt

- a) 2 M $\text{HCl}_{(\text{aq})}$
- b) SO_3 , H_2SO_4
- c) $\text{NaOH}_{(\text{aq})}$
- d) HCO_2H , Ac_2O
- e) i) N_2H_4 ii) $\text{HCl}_{(\text{aq})}$, AcOH
- f) i) H_2S , Na , CH_3OH ii) H_2O

6.4. Draw the structures of **A**, **B**, **(+)-C**, **D**, **E** and **F** on the answer sheet. Show the stereostructure using wedge-dash notation (; |||.....) when relevant. 18 pt

6.5. Select the role of acetone in the step leading to **B** on the answer sheet. 2 pt

- a) solvent
- b) catalyst
- c) electrophile
- d) nucleophile

6.6. Select the role of DCC in the step leading from **F** to Penicillin VK on the answer sheet. 2 pt

- a) oxidizing reagent
- b) catalyst
- c) coupling reagent
- d) radical initiator

Problem 7 SABIC

The Saudi Basic Industries Corporation (SABIC) was established in the mid-1970s as part of Saudi Arabia's plan to diversify its economy. Today, SABIC is a global chemical giant, producing 69 million tons of products annually.

Part A

Oligomers are polymers with few monomer units. SABIC's ethene oligomerisation technology produces linear alpha olefins (1-alkenes), which are used in numerous industrial applications.

Linear alpha olefins are produced by catalytic oligomerisation of ethene, resulting in a distribution of chain lengths. Different catalysts can yield various distributions of products.

In the geometric or Schulz–Flory distribution, each oligomer fraction is related to the previous fraction by the equation, $T_{n+1} = \alpha T_n$, where T_n represents the molar amount of the oligomer with n ethene units, and α is a constant called the probability of chain propagation. The monomer ethene is not a member of the series ($n \geq 2$).

One catalytic oligomerisation process can be described by a relatively simple mechanism:

This mechanism is not a classical chain reaction because the final product is not produced within the cycle. However, the usual kinetic treatment of chain reactions can be applied to it. The three processes shown (**1–3**) are all chain propagation steps. R is lengthened by each cycle.

All three reactions are first order with respect to the chain carriers. For ethene, use an unknown order ρ , to be determined later.

- 7.1** **Write** the rate equations for reactions **1–3** using k_1 , k_2 , and k_3 as the corresponding rate constants, which are independent of the carbon chain length. 1 pt

The chain termination step, producing the oligomers, is a first order reaction competing with reaction **1**.

- 7.2** **Write** i) the chemical equation and ii) rate equation of termination. Use k_t as the corresponding rate constant. 2 pt

- 7.3** **Find** the value of ρ which ensures that the product mixture of olefins shows the required ratio of products in accordance with the Schulz–Flory distribution when the reaction is run in a closed system. **Derive** a formula for this case that gives α as the function of rate constants. 4 pt

Aluminium alkyls are used as co-catalysts in the ethene oligomerisation process. It was found that they also catalysed the Friedel–Crafts alkylation of the aromatic solvents used for the oligomerisation.

In a typical oligomerisation reaction, an alkylated aromatic compound **Q** was isolated from the complex reaction mixture of ethene oligomerisation using methylbenzene as solvent. The alkylated aromatic compound **Q** has the molecular formula $C_{11}H_{16}$ and its 1H NMR spectrum contains the following peaks.

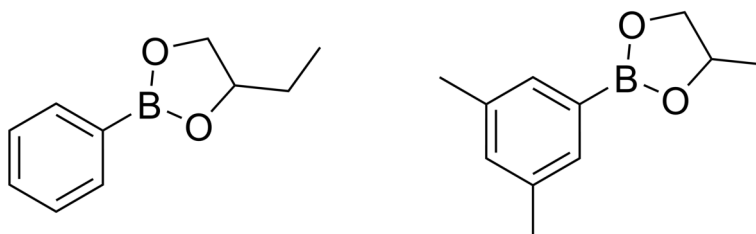
1H NMR of **Q**: δ 0.9 (*t*, 3H); 1.35 (*m*, 2H); 1.59 (*m*, 2H); 2.34 (*s*, 3H), 2.60 (*t*, 2H); 7.18 (*d*, 2H); 7.22 (*d*, 2H).

- 7.4** **Draw** the structure of **Q**. 3 pt

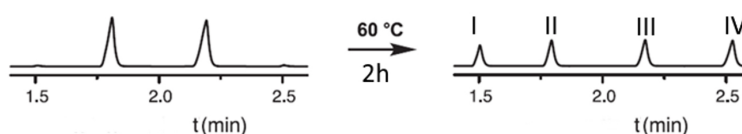
Part B

Vitrimers are adaptive polymers with "reversible" covalent bonds, allowing shape-changing and self-healing under specific conditions. This subtask explores the principles of vitrimer chemistry, a topic in SABIC's research.

A recently elucidated fast and reversible reaction involving dioxaborolanes can serve as the chemical background for this adaptable polymer network. The two dioxaborolanes below were prepared by the reaction of phenylboronic acid with 1,2-butanediol, and 3,5-dimethylphenylboronic acid with 1,2-propanediol, respectively.



They participate in a model metathesis (exchange) reaction. The two carefully purified compounds were mixed in the absence of solvent and the mixture was kept at 60 °C for two hours. Interestingly, the gas chromatograms of the mixture at the start and at the end of the incubation period showed only the peaks below, with equimolar quantities of the components. The peaks in this system separate in a way that correlates with molar mass; compounds with **lower** mass appear at **earlier** elution times.

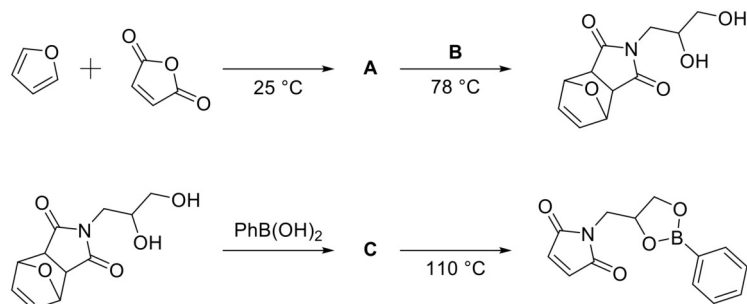


No catalyst, water, diol or acid was detectable in the mixture.

7.5 Draw the compounds associated with peaks I-IV in the chromatogram.

2 pt

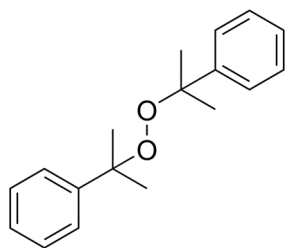
Linking functional units to a polymer chain is known as grafting. The functional units are referred to as grafting agents. In this case, the dioxaborolane units are linked to the polymer chains by maleimide groups via a radical process, in which one maleimide group is coupling to the polymer chain at a random carbon atom. The scheme below introduces a flexible synthesis route towards the dioxaborolane maleimide grafting agent used in the vitrimers.



7.6 **Draw** the structures of **A-C**.

3 pt

7.7 **Select** on the answer sheet which reagent(s) and/or condition(s) is/are appropriate for linking the dioxaborolane maleimide units to **polyethylene**. 1 pt



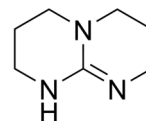
a)

Pt, H₂

b)

hν, 454 nm

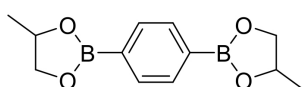
c)



d)

The vitrimer was prepared as follows:

- Polyethylene is grafted with dioxaborolane maleimide. Assume no side reactions occur between the dioxaborolane maleimide compounds.
- The reagents are removed from the macromolecules.
- Propanediol-functionalised bis-dioxaborolane is added to enable crosslinking.



- The mixture is carefully heated for the metathesis (exchange) reaction to take place.

Theory

Q7-5

Estonian English (Estonia)

To determine the extent of grafting and crosslinking in the vitrimer, infrared (IR) spectroscopy was used at room temperature where the metathesis reaction is extremely slow. Assume the vitrimer is homogeneous.

- All of the small molecules are removed from the polymer.
- The IR spectrum of a thin polymer film is measured.
- IR spectrum contains absorption peaks that correspond to specific functional groups.
- The Beer–Lambert law can be used to quantify the concentration of these functional groups.

The provided data table gives the following information about relevant bands for the specified functional groups: the wavenumber, the corresponding molar absorption coefficient, and the absorbance of the vitrimer sample.

Wavenumber, with the functional group indicated	Molar absorption coefficient, ϵ ($\text{dm}^3 \text{mol}^{-1} \mu\text{m}^{-1}$)	Sample absorbance at this wavenumber, A
Imide band at 1710 cm^{-1}	2.67	0.451
Monosubstituted benzene ring band at 1600 cm^{-1}	0.28	0.022
Disubstituted benzene ring band at 1520 cm^{-1}	0.68	0.042
Polyethylene CH_2 band at 1470 cm^{-1}	0.021	0.904

7.8 **Calculate** the grafting density (X_g) of polyethylene based on these measurements. This is the ratio of the grafted groups over the ethylene units. 3 pt

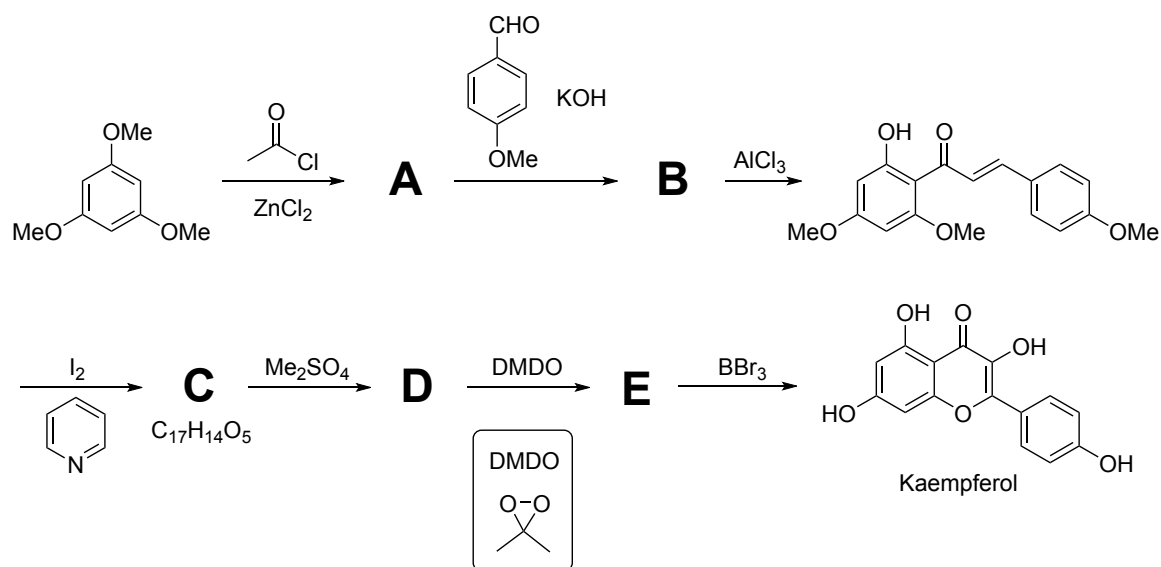
7.9 **Calculate** the percentage of the grafted groups that are not part of a crosslink (p_{nc}). 4 pt

Problem 8 Safflower

In Saudi culture, safflower drink is a traditional remedy used for its calming effects.



One ingredient with health benefits is kaempferol. The following scheme shows its total synthesis.



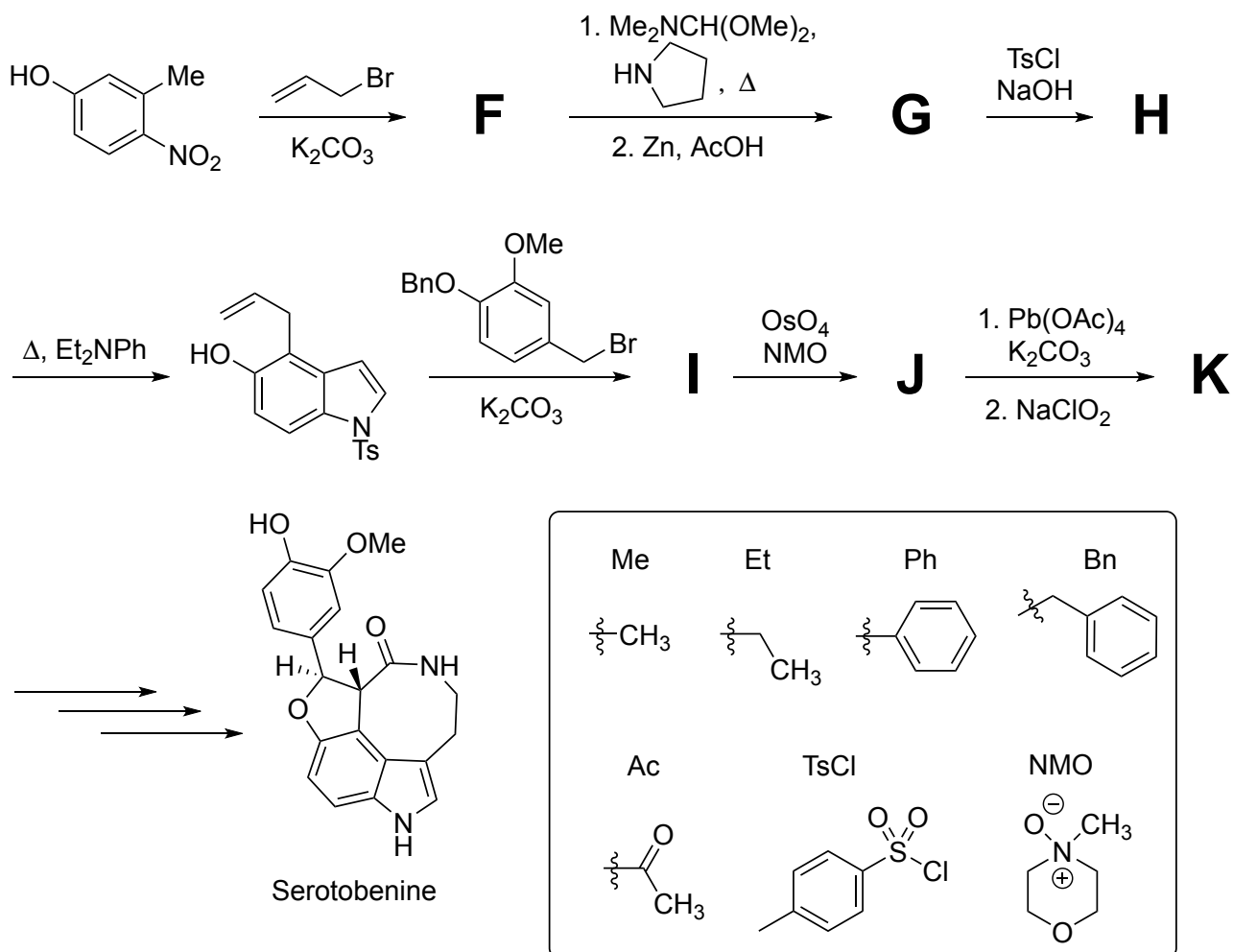
Hints:

- **C** has three rings and has the same number of hydroxyl groups as the compound it was made from.
- The step **C** to **D** is necessary to avoid any unwanted reactivity with DMDO.
- DMDO is a hydroxylating agent.

8.1. **Draw** the structures of compounds **A-E**.

15 pt

Serotobenine is a pentacyclic indole alkaloid with antimicrobial properties found in safflower. Its total synthesis is shown below:



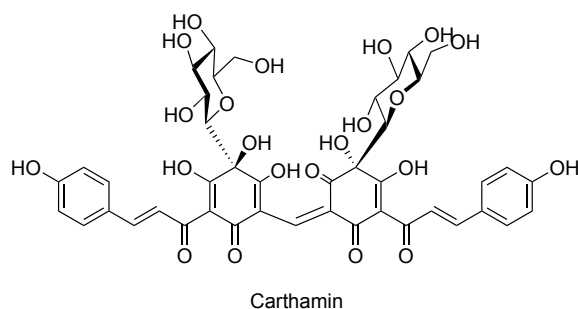
Hints:

- **G** is a bicyclic compound with one of the rings being a heterocycle.
- **H** isomerises upon heating in the presence of the amine base.
- **K** is a product of an oxidative cleavage of the newly formed functional group in **J**. **K** has a ^1H NMR signal at 12 ppm.

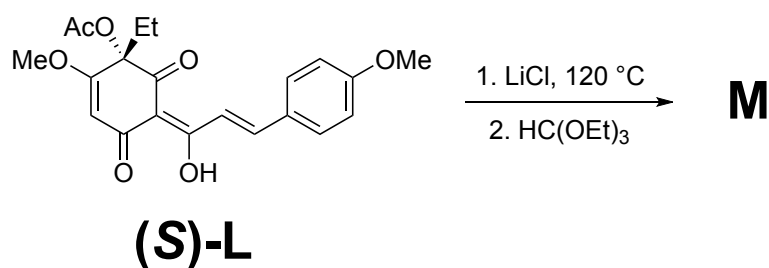
8.2. **Draw** the structures of compounds **F–K**.

18 pt

Carthamin gives safflower its red colour.



In the total synthesis of carthamin, the assembly was tested on a model substrate **L**. Note that **M** resembles carthamin's core structure.



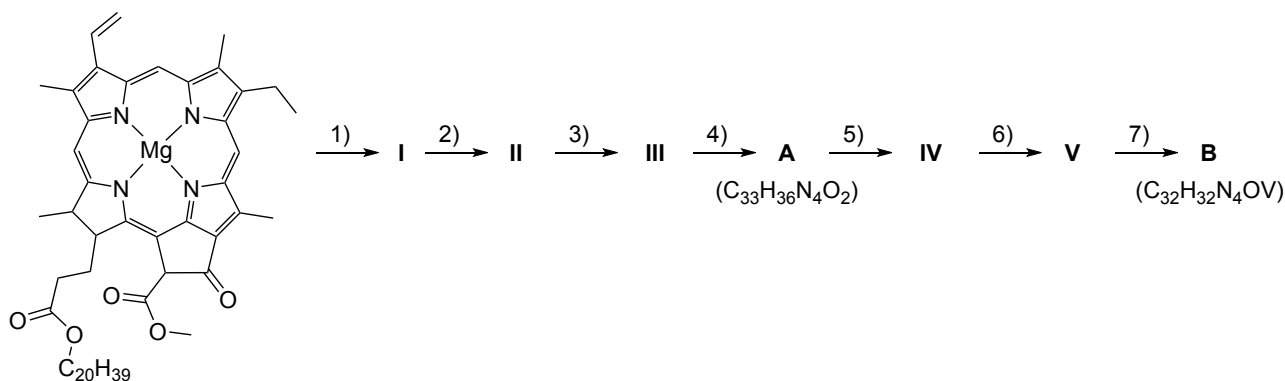
- 8.3. **Draw** the structure of compound **M** including its stereochemistry. (Hint: In methanol-*d*₄ **L** has 11 and **M** has 10 distinct proton signals in their ¹H NMR spectra). 5 pt

Problem 9 Porphyrin complexes

Part A. Metals in petroleum

Saudi Arabian petroleum is primarily hydrocarbons but also contains elements like vanadium in porphyrin complexes, hinting at its biological origins.

Vanadium complex **B** is presumably formed in petroleum from chlorophyll according to the following scheme:



Step	Name
1)	Demetallisation
2)	Hydrolysis
3)	Decarbomethoxylation
4)	Reduction
5)	Aromatisation
6)	Decarboxylation
7)	Metal chelation

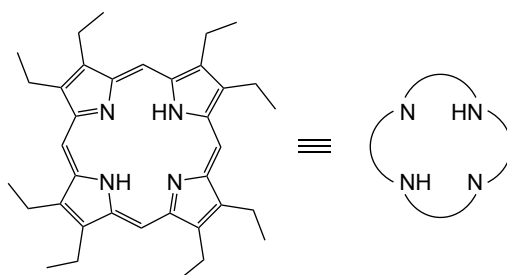
9.1 **Assign** the molecular formulae **a–e** (given in the answer sheet) to the intermediates **I–V**. 4.0 pt

9.2 **Draw** the structures of intermediate **A** and vanadium complex **B** using the pre-drawn framework of porphyrin. (If you need a new template to redraw your structure(s), please ask the supervisor.) 7.0 pt

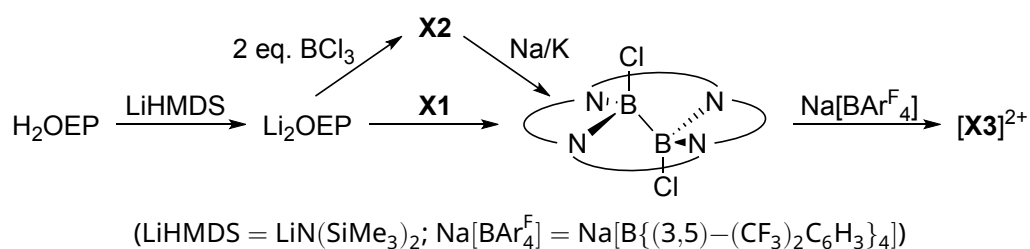
9.3 **Indicate** the oxidation state of vanadium in **B**. 1.0 pt

Part B. Porphyrin non-metal complexes

Porphyrins are known to form chelate-type complexes not only with metals but also with some non-metals, for example, with boron and phosphorus. Octaethylporphyrin (H_2OEP) is often used to model natural porphyrins and to study porphyrin complexes. It has the following structure and can be represented as:

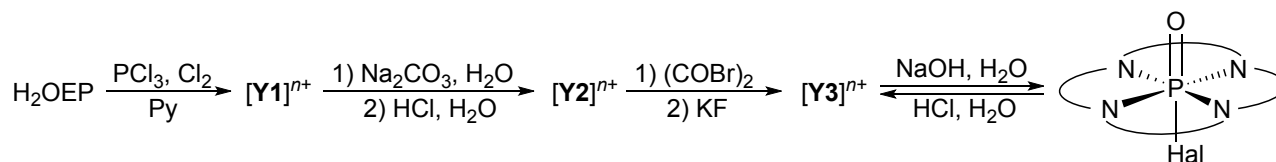


To produce the dicationic planar boron porphyrin complex $[\mathbf{X3}]^{2+}$, either BCl_3 or another binary compound $\mathbf{X1}$ can be used as a precursor:



9.4 Draw the structures of $\mathbf{X1}$, intermediate complex $\mathbf{X2}$, and the product $[\mathbf{X3}]^{2+}$. 3.0 pt

Phosphorus forms porphyrin cationic complexes $[\mathbf{Y1}]^{n+}$, $[\mathbf{Y2}]^{n+}$, and $[\mathbf{Y3}]^{n+}$. The complex $[\mathbf{Y3}]^{n+}$ has one less plane of symmetry compared to $[\mathbf{Y1}]^{n+}$ and $[\mathbf{Y2}]^{n+}$ (ignore ethyl substituents in OEP ligand when considering symmetry). Pyridine (Py) is used here as a basic solvent, "Hal" is one of the halogens: F, Cl, or Br:



9.5 **Indicate:** a) the charge " $n+$ " of phosphorus porphyrin complexes; b) the number of planes of symmetry $N(\sigma)$ that complex $[\text{Y1}]^{n+}$ has. 2.0 pt

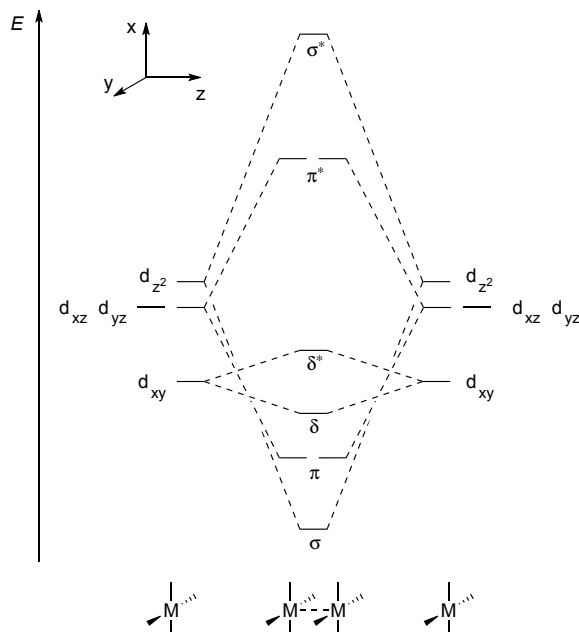
9.6 **Draw** the structures of $[\text{Y1}]^{n+}$, $[\text{Y2}]^{n+}$, and $[\text{Y3}]^{n+}$. 4.0 pt

Part C. Porphyrin sandwiches

Porphyrin sandwich-type complexes form when there are several porphyrin rings aligned relative to each other. Examples are $\text{Zr}(\text{OEP})_2$, $\text{Eu}_2(\text{OEP})_3$, $\text{Bi}_2(\text{OEP})_2\text{Cl}_2$ that have at least 3 planes of symmetry each. Note that the hole size in the OEP ligand is about 4.0 Å, and the average metal–N distances in these complexes are 2.4, 2.5, 2.3 Å, respectively.

9.7 **Suggest** the structures of $\text{Zr}(\text{OEP})_2$, $\text{Eu}_2(\text{OEP})_3$, and $\text{Bi}_2(\text{OEP})_2\text{Cl}_2$. Use the simplified representation of the OEP ligand. 3.0 pt

Another type of porphyrin sandwich-type complex is a metal–porphyrin dimer with single or multiple metal–metal bonds. For example, $[\text{Ru}(\text{OEP})]_2$ has a Ru–Ru double bond (considering only d-electrons). Below is the molecular orbital diagram for an eclipsed dimer of the type $[\text{M}(\text{porphyrin})]_2$ (interaction between $d_{x^2-y^2}$ is not considered as these orbitals lie high in energy):



9.8 **Draw** the $\sigma (d_{z^2} + d_{z^2})$, $\pi (d_{xz} + d_{xz})$, $\pi (d_{yz} + d_{yz})$, and $\delta (d_{xy} + d_{xy})$ bonding orbitals according to the specified coordinate system. 4.0 pt

9.9 **Calculate** the metal-metal bond order in the following complexes in eclipsed conformation: $[\text{Mo}(\text{OEP})]_2$, $[\text{Ir}(\text{OEP})]_2$, $[\text{Re}(\text{OEP})]_2^+$. 3.0 pt

The eclipsed conformation is generally preferred for metal-porphyrin dimers with 7, 8, and 9 d-electrons. Otherwise, these complexes are more stable in a staggered conformation, where the porphyrin rings are rotated relative to each other by 45° .

9.10 **Select** how the splitting (i.e., the energy between antibonding and bonding orbitals) changes for each type of orbital interaction during the conversion of eclipsed conformation into staggered:

- a) increases;
- b) remains unchanged;
- c) decreases (not to zero);
- d) decreases to zero.