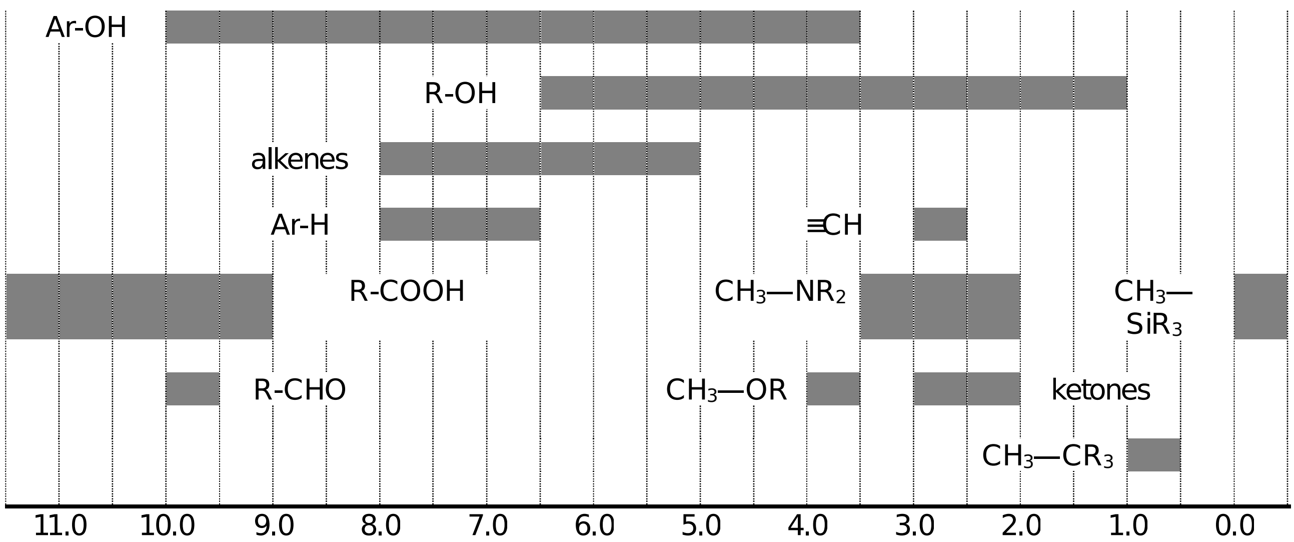
General Instructions

- This examination has **9 problems** delivered in two booklets. This question booklet has **29 pages** and contains the problems with numbered questions translated to the language of your choice. The answer booklet has **28 pages** and contains numbered boxes corresponding to the questions. Only language-independent symbols and formulas 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 scratch paper. **Do not** draw anything into or close to the QR codes.
- Write relevant calculations in the appropriate boxes when necessary. 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**, fill the tick box completely and then make 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!

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:	$A = \log(\frac{I_0}{I}) = \varepsilon \cdot l \cdot c$
Enthalpy:	$H = U + pV$	Gibbs energy:	$G = H - TS$
$\Delta_r G^o = -RT lnK = -nFE^o_{cell}$		Henderson-Hasselbalch equation:	$\text{pH} = \text{pK}_a + \log(\frac{[A^-]}{[HA]})$
Arrhenius equation:	$k = A \exp\left(\frac{-E_A}{RT}\right)$	Zeroth order integrated rate law:	$[A] = [A]_0 - kt$
Surface of a sphere:	$A = 4\pi R^2$	First order integrated rate law:	$\ln[A] = \ln[A]_0 - kt$
Volume of a sphere:	$V = \frac{4\pi}{3} R^3$	$\sum_{k=0}^{\infty} ar^k = \frac{a}{1-r}$ for $\lvert r \rvert < 1$	

^{1}H NMR chemical shifts (in ppm/TMS)



Translation for region names

Periodic table

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 H 1.008																	2 He 4.003
3 Li 6.94	4 Be 9.01											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
11 Na 22.99	12 Mg 24.30											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 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 in the reactor.

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.

	$N_2(g)$	$H_2(g)$	$NH_3(g)$
$\Delta_f H^\circ/(\text{kJ mol}^{-1})$	0	0	−45.9
$S^\circ/(\text{J mol}^{-1}\text{ K}^{-1})$	191.6	130.7	192.8

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

SOLUTION:

A balanced equation for the ammonia synthesis reaction: $N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$

Standard reaction enthalpy:

$$\Delta H^\circ = 2\Delta_f H^\circ(NH_3) - 3\Delta_f H^\circ(H_2) - \Delta_f H^\circ(N_2)$$

$$\Delta H^\circ = 2(-45.9\text{ kJ mol}^{-1}) = -91.8\text{ kJ mol}^{-1}$$

Standard reaction entropy:

$$\Delta S^\circ = 2S^\circ(NH_3) - 3S^\circ(H_2) - S^\circ(N_2)$$

$$\Delta S^\circ = [2(192.8) - 3(130.7) - (191.6)](\text{J mol}^{-1}\text{ K}^{-1}) = -198.1\text{ J mol}^{-1}\text{ K}^{-1}$$

The change in Gibbs free energy at 400 °C

$$\Delta G_{400^\circ C} = \Delta H^\circ - T\Delta S^\circ = (-91.8\text{ kJ mol}^{-1}) - (673.15\text{ K})(-198.1\text{ J mol}^{-1}\text{ K}^{-1})$$

$$\Delta G_{400^\circ C} = +41.6\text{ kJ/mol}$$

The equilibrium constant at 400 °C:

$$K_{400^\circ C} = \exp\left(-\frac{\Delta G}{RT}\right) = \exp\left(\frac{-41,600}{8.3145(673.15)}\right) = 5.92\cdot 10^{-4}$$

For a stoichiometric mixture ($N_2 : H_2 = 1 : 3$), at equilibrium, the governing equation is:

$$K = \left(\frac{p^\circ}{p_{total}}\right)^2 \frac{\left(y_{NH_3}\right)^2}{\left(y_{N_2}\right)\left(y_{H_2}\right)^3} = \left(\frac{p^\circ}{p_{total}}\right)^2 \frac{(2x)^2(4-2x)^2}{(1-x)(3-3x)^3}$$

$$\sqrt{27K(p_{total}/p^\circ)^2}(1-x)^2 = (2x)(4-2x)$$

Solving for $p_{total} = 100$ bar and $K = 5.92\cdot 10^{-4}$ gives $x = 0.51$ (51% N_2 conversion)

One of the reactants in the Haber–Bosch process is hydrogen, mainly produced by steam reforming of methane. The two-step process starts with CH_4 reacting with water to produce H_2 and CO. In a 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}). **SOLUTION:** The overall reaction: $CH_4 + 2\,H_2O \longrightarrow CO_2 + 4\,H_2$ For 1.0 kg of H_2 produced in this process, $44/8 = 5.5$ kg CO_2 is coproduced.	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 "gray" ammonia, the CO_2 is released in 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 the carbon dioxide ($m_{CO_2,\,\mathrm{blue}}$) that needs to be captured to produce 40,000 kg of "blue" ammonia. Assume that carbon dioxide only comes from a real steam reforming process. Assume further that the ammonia is produced at equilibrium from a stoichiometric mixture of nitrogen and hydrogen. **SOLUTION:** 40,000 kg of ammonia are $40 \times 10^6\mathrm{g}\ (\frac{1\mathrm{mol}}{17\mathrm{g}}) = 2.4 \times 10^6\mathrm{mol\ NH_3}$ The stoichiometric H_2 is $(\frac{3}{2})(2.4 \times 10^6\mathrm{mol}) = 3.5 \times 10^6\mathrm{mol\ H_2}$ The required H_2 needs to take into account the conversion of H_2 (calculated in part 1.1): $(\frac{1}{51\%})(3.5 \times 10^6\mathrm{mol}) = 6.9 \times 10^6\mathrm{mol\ H_2}$, which is 13,800 kg$H_2$ The CO_2 produced during steam reforming is $(\frac{7\mathrm{kg\ CO_2}}{1\mathrm{kg\ H_2}})(13{,}800\ \mathrm{kg\ H_2}) =$ 96,600 kg CO_2	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:

$$CO_2(g) + 3\,H_2(g) \rightleftharpoons CH_3OH\,(g) + H_2O\,(g)$$

$$CO_2(g) + H_2(g) \rightleftharpoons CO\,(g) + H_2O\,(g)$$

Into a reactor maintained at 250 °C and 50 bar, a mixture containing $CO_2 : H_2$ in a molar ratio of $1 : 4$ is fed. It has been found that the CO_2 conversion is 30% and the H_2 conversion is 18.5% when these two reactions are at equilibrium. No other processes need to be considered.

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

SOLUTION:

Let the reaction extent of the first reaction be ξ_1 and that of the second reaction be ξ_2 .

The CO_2 conversion gives the following equation: $\xi_1 + \xi_2 = 0.30$.

The H_2 conversion gives the following equation: $3\xi_1 + \xi_2 = 4(0.185) = 0.74$.

Solving the system of two equations gives $\xi_1 = 0.22$ and $\xi_2 = 0.08$.

The equilibrium constants are given by:

$$K_1(250^\circ\mathrm{C}) = \frac{n_{\mathrm{CH_3OH}} n_{\mathrm{H_2O}} (n_{total})^2}{n_{\mathrm{CO_2}} (n_{\mathrm{H_2}})^3} \left(\frac{p^\circ}{p_{total}} \right)^2$$

$$\Rightarrow K_1(250^\circ\mathrm{C}) = \frac{(\xi_1)(\xi_1 + \xi_2)(5 - 2\xi_1)^2}{(1 - \xi_1 - \xi_2)(4 - 3\xi_1 - \xi_2)^3} \left(\frac{1\ \mathrm{bar}}{50\ \mathrm{bar}} \right)^2 = 2.3 \times 10^{-5}$$

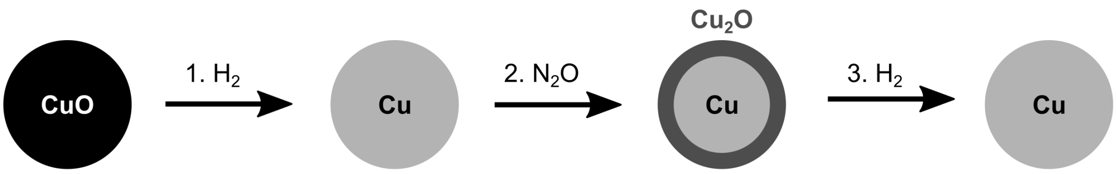
$$K_2(250^\circ\mathrm{C}) = \frac{n_{\mathrm{CO}} n_{\mathrm{H_2O}}}{n_{\mathrm{CO_2}} n_{\mathrm{H_2}}} = \frac{(\xi_2)(\xi_1 + \xi_2)}{(1 - \xi_1 - \xi_2)(4 - 3\xi_1 - \xi_2)} = 0.011$$

Heterogeneous copper-containing catalysts are commonly used for CO_2 hydrogenation. Two specific, Cu-containing catalysts (*A* and *B*) showed 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 CO_2 hydrogenation. Under this assumption, 1 mole of active sites corresponds to 1 mole of surface Cu. The efficiency of these active sites is shown by their turnover frequencies (*TOF*, moles of product formed per moles of active site in a given time).

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

1. At the start, all the copper in the catalysts (oxidized beforehand) is present as Cu(II); that was fully reduced to Cu(0) with hydrogen. No other species in the catalysts reacted with hydrogen besides copper oxides.
2. N_2O was introduced to the reduced samples at room temperature. At this temperature, N_2O only oxidizes 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 <u>**Find**</u> the methanol production rate per total mass of Cu (in $g_{MeOH}\ g_{Cu}^{-1}\ h^{-1}$) for catalysts *A* and *B*. 3 pt

SOLUTION:

Step 1 of N_2O titration: $CuO + H_2 \longrightarrow Cu + H_2O$, meaning 1 mol of H_2 corresponds to 1 mol of Cu.

Therefore, methanol production rate per mass of bulk Cu could be given by:
(space time yield)/[(H_2 consumption in step 1) × (atomic mass of Cu)]

For catalyst A:

$$\frac{0.80\,\frac{g_{MeOH}}{g_{Cat}\ h}}{\left(5.0\,\frac{\text{mmol Cu}}{g_{Cat}}\right)\left(63.546\,\frac{g_{Cu}}{\text{mol Cu}}\right)} = 2.5\,\frac{g_{MeOH}}{g_{Cu}\ h}$$

For catalyst B:

$$\frac{0.90\,\frac{g_{MeOH}}{g_{Cat}\ h}}{\left(4.0\,\frac{\text{mmol Cu}}{g_{Cat}}\right)\left(63.546\,\frac{g_{Cu}}{\text{mol Cu}}\right)} = 3.5\,\frac{g_{MeOH}}{g_{Cu}\ h}$$

1.6 **Find** the *TOF* (in h^{-1}) for catalysts *A* and *B*. 3 pt

If you cannot find results, use $TOF_{\text{Catalyst A}} = 100\ h^{-1}$ *and* $TOF_{\text{Catalyst B}} = 1\ h^{-1}$ *in subsequent calculations.*

SOLUTION:

The rates found in part (1.5) are normalized by the total mass of Cu. In order to normalize by only surface Cu, we need to find out how much of the Cu is on the surface. Step 3 of N_2O titration: $Cu_2O\ (\text{surface}) + H_2 \longrightarrow 2\ Cu\ (\text{surface}) + H_2O$, meaning 1 mol of H_2 corresponds to 2 mol of surface Cu. Therefore, the fraction of surface Cu is given by:

$$(2 \times (H_2 \text{ consumption in step 3}))/(H_2 \text{ consumption in step 1})$$

Finally, we need the ratio of molar masses to convert $g_{\text{MeOH}}/g_{\text{Cu}}$ to $\text{mol}_{\text{MeOH}}/\text{mol}_{\text{Cu}}$.

For catalyst A:

$$\frac{\left(2.5 \frac{g_{\text{MeOH}}}{g_{\text{Cu}}\ \text{h}}\right)}{\left(\frac{2(0.3)\ \text{mol Cu(surface)}}{5.0\ \text{mol Cu}}\right)} \left(\frac{1\ \text{mol MeOH}}{32.04\ \text{g MeOH}}\right) \left(\frac{63.546\ \text{g Cu}}{1\ \text{mol Cu}}\right) = 41\ \text{h}^{-1}$$

For catalyst B:

$$\frac{\left(3.5 \frac{g_{\text{MeOH}}}{g_{\text{Cu}}\ \text{h}}\right)}{\left(\frac{2(0.7)\ \text{mol Cu(surface)}}{4.0\ \text{mol Cu}}\right)} \left(\frac{1\ \text{mol MeOH}}{32.04\ \text{g MeOH}}\right) \left(\frac{63.546\ \text{g Cu}}{1\ \text{mol Cu}}\right) = 20\ \text{h}^{-1}$$

Alternative solution, the TOF can be calculated directly from the table as follows:

$$(\text{catalyst performance})/(2 \times (H_2 \text{ consumption in step 3}) \times M_{MeOH})$$

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

a. Catalyst *A* has more efficient active sites.
b. Catalyst *B* has more efficient active sites.
c. The two catalysts have active sites with the same efficiency.

SOLUTION:

a.

Problem 1 Ammonia

1.1 (7 pt)

%

1.2 (2 pt)

$m_{CO_2} =$ kg

1.3 (3 pt)

$m_{CO_2,\text{ blue}} =$ kg

1.4 (5 pt)

$K_1 =$ $K_2 =$

1.5 (3 pt)

A : $g_{MeOH}\ g_{Cu}^{-1}\ h^{-1}$ B : $g_{MeOH}\ g_{Cu}^{-1}\ h^{-1}$

1.6 (3 pt)

A : h^{-1} B : h^{-1}

1.7 (1.0 pt) ☐ a ☐ b ☐ c

Problem 2 Electronic nose

Resistive gas sensors, especially those using semiconducting metal oxides (SMOX), are becoming increasingly popular. They can detect tiny amounts of impurities, are small and stable, and are easy to make and use. These features make SMOX sensors stand out among the many types of gas sensors that work 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 $\mathbf{Z}C_2O_4 \cdot kH_2O$ of metal **Z** on 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 colored **X** at 500 °C and 3.8 dm^3 of carbon dioxide at 101325 Pa.

2.1	**Determine** the formula of **X** and the value of ***k*** in $\mathbf{Z}C_2O_4 \cdot kH_2O$. **SOLUTION:** The mass loss under heating to 140 °C is the loss of H_2O. Calculation the number of moles of CO_2 released: $\frac{pV}{RT} = \frac{101325 \cdot 3.8 \cdot 10^{-3}}{8.314 \cdot 773} = 0.060$ mol The general equation for the decomposition: $3\,ZC_2O_4 + 2\,O_2 \longrightarrow Z_3O_4 + 6\,CO_2\uparrow$ Then $M(Z_3O_4) = \frac{2.407\text{ g}}{0.010\text{ mol}} = 240.7\text{ g}\cdot\text{mol}^{-1}$. $M(Z) = \frac{(240.7-64)}{3}\text{ g}\cdot\text{mol}^{-1} = 58.9\text{ g}\cdot\text{mol}^{-1}$. Consequently, the semiconducting oxide **X** is Co_3O_4, $\mathbf{A^{n+}}-Co^{2+}$, $\mathbf{B^{m+}}-Co^{3+}$. Let's determine the composition of crystalline hydrate: $\frac{18k\text{ g/mol}}{(146.9+18k)\text{ g/mol}} = 0.197$. We obtain that k=2.	4 pt

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

2.2	**Calculate** the percentage of the tetrahedral sites that is occupied in the case of a normal spinel $A^{2+}B^{3+}{}_2O^{2-}{}_4$. **SOLUTION:** Number of tetrahedral voids per FCC unit cell is $2 \cdot 4 = 8$. According to the formula AB_2O_4 there is 1 A cation per FCC unit cell. Thus $(\frac{1}{8}) \cdot 100\% = 12.5\%$.	2 pt

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

2.3	<u>**Select**</u> on the answer sheet two of the given formulas, which correspond to the structure of inverse spinel: Fe_3O_4, $NiFe_2O_4$, Mn_3O_4, $FeCr_2O_4$. **SOLUTION:** Fe_3O_4 and $NiFe_2O_4$	1 pt

Semiconductors are materials whose orbitals contain a small excess or deficit of electrons, leading to negative 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, which will change the resistance of the sensor depending on the donor/acceptor properties of the gas. **Figure 1** shows the two different types of signal obtained this way.

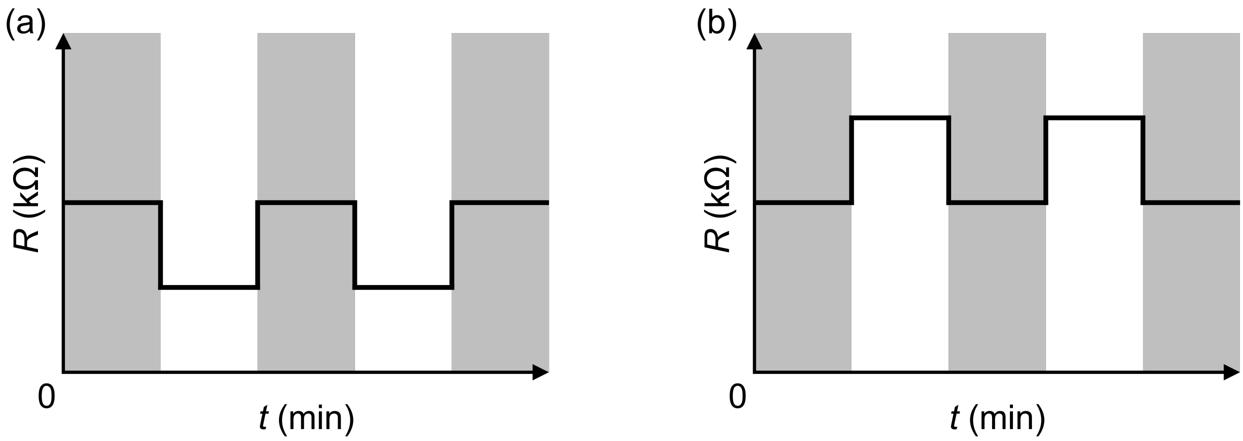


Figure 1: plot of resistance against time for two possible signal types, (a) and (b).

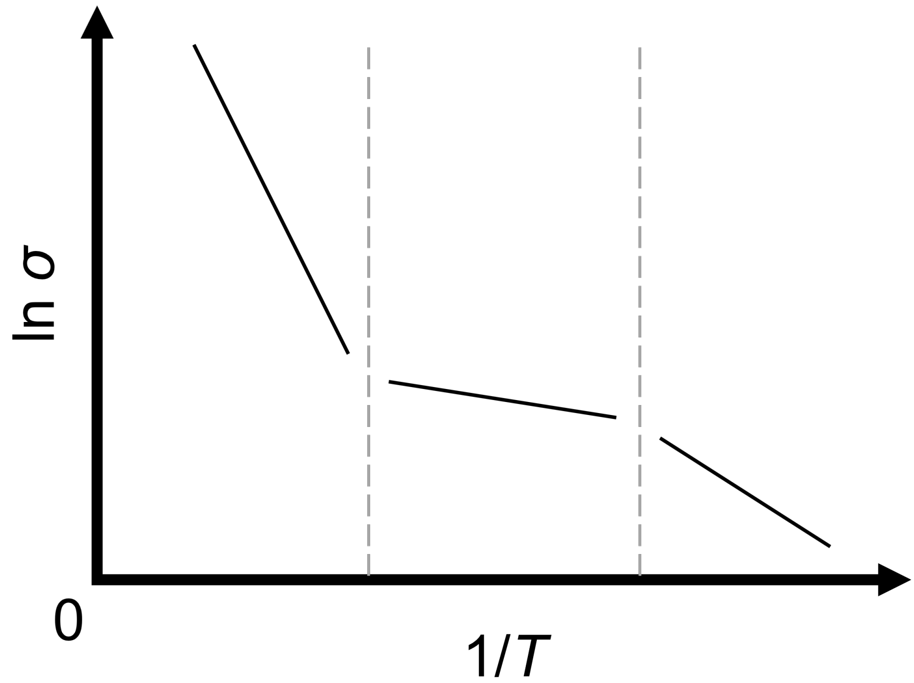
Grey bars = air, white bars = air + analyte gas.

2.4	<u>**Correlate**</u> 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. **SOLUTION:** Based on the p-type conductivity of Co_3O_4 and the electronic structures of gases, the resistance of the sensor will decrease when the oxide surface interacts with electron-acceptor NO_2 and O_3(a) and increase in the case of electron-donor H_2S and NH_3 (b).	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:

Ionization (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 associated with the different conductivity types, $E_a(I)$, $E_a(II)$, and $E_a(III)$, from largest to smallest. **SOLUTION:** $E_a(III) > E_a(I) > E_a(II)$	3 pt

Problem 2 Electronic nose

2.1 (4 pt)

Formula of **X**:

Value of *k*:

2.2 (2 pt)

%

2.3 (1 pt) ☐ Fe_3O_4 ☐ $NiFe_2O_4$ ☐ Mn_3O_4 ☐ $FeCr_2O_4$

2.4 (2 pt)

H_2S : ☐ a ☐ b

O_3 : ☐ a ☐ b

NO_2 : ☐ a ☐ b

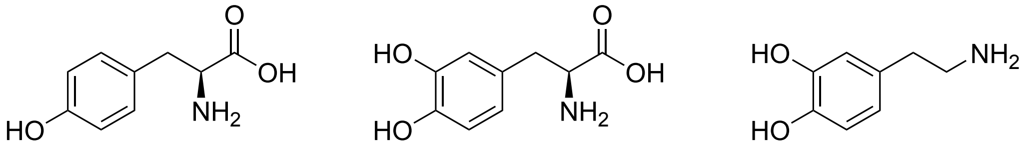
NH_3 : ☐ a ☐ b

2.5 (3 pt)

> >

Problem 3 Tyrosinase

The enzyme tyrosine 3-monooxygenase has an important biological role because it catalyzes the initial and rate-limiting 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.



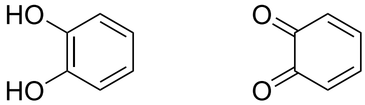
L-Tyrosine **L-DOPA** **Dopamine**

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

$$r = \frac{k[\mathrm{E}][\mathrm{S}]}{K_\mathrm{M} + [\mathrm{S}]}$$

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

Catechol (1,2-dihydroxybenzene) inactivates the enzyme tyrosine 3-monooxygenase irreversibly by turning it into an inactive form. When a carefully purified sample of catechol is mixed with the enzyme with the exclusion of dissolved oxygen, no change is seen at all. So the reaction of catechol with dissolved oxygen, which produces *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:

time (min)	catechol concentration (mmol dm^{-3})	oxygen concentration (mmol dm^{-3})	*o*-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 shown in the table above) and **write** the balanced equation of the process with molecular formulas based on the kinetic data. 5.0 pt

SOLUTION:

From the data, it is seen that the stoichiometry is catechol:oxygen:quinone -1:-1:1. The molecular formula of catechol is $C_6H_6O_2$, that of *o*-quinone is $C_6H_4O_2$. So the stoichiometry with the formation of hydrogen peroxide is:

$1\ C_6H_6O_2 + 1\ O_2 \rightarrow 1\ C_6H_4O_2 + 1\ H_2O_2$

(1 point for the -1:-1:1 stoichiometry, 2 ponts for recognizing H_2O_2/1 point for a not very unreasonable but incorrect by-product, 1 point for stating a chemical equation with the correct reactants, 1 point for balancing the equation)

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

SOLUTION:

In both the first and second 20 minutes of the reaction, the *o*-quinone concentration increases by 30 μmol dm^{-3}. So, the intial rate is:

$r_0 = \frac{30\ \mu\text{mol dm}^{-3}}{20\ \text{min}} = 1.5\ \mu\text{mol dm}^{-3}\ \text{min}^{-1}$

(1 point for calculation, 1 point for unit)

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

catechol concentration (mmol dm^{-3})	initial rate of *o*-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 producing *o*-quinone. **Calculate** the rate constant of this process ($k_{catechol}$) with an appropriate unit. 5.0 pt

SOLUTION:

The text stated that the rate is independent of the concentration of dissolved oxygen, so the rate law is zeroth order with respect to oxygen. The data in the table show that the initial rate is directly proportional to the catechol concentration, so the order of reaction is 1.

The rate law is: $r = k_{catechol}[\text{catechol}]$

$k_{catechol}$ can be calculated from any point in the table above:

$k_{catechol} = \frac{7.5\ \mu\text{mol dm}^{-3}\ \text{min}^{-1}}{10\ \text{mmol}} = 7.5 \times 10^{-4}\ \text{min}^{-1}$

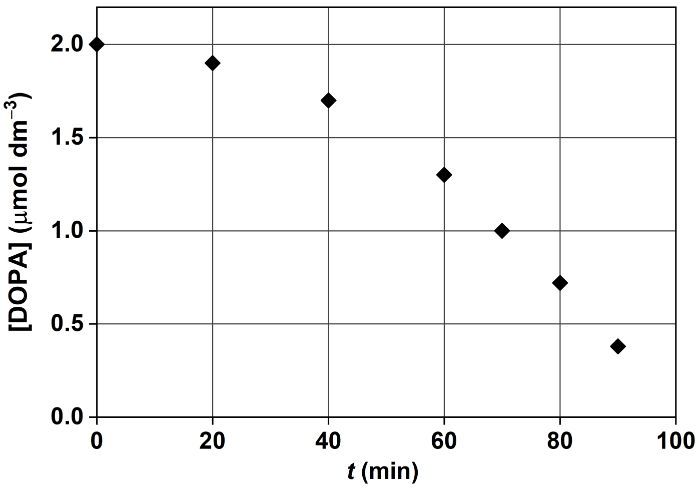
(1 point for each of the two orders of reaction, 1 point for stating the rate law, 1 point for calculation, 1 point for unit)

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

An experiment in which the enzyme is reacted with catechol in the presence of dissolved oxygen did show inactivation, though.

The experiment was done in an open vessel 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}, the initial concentration of catechol was 2.00 mmol dm^{-3} at 37 $^{\circ}$C and at pH 7.5.

Samples were taken regularly from the enzyme-catechol reaction mixture, and the activity of the enzyme was assayed by adding L-tyrosine, tetrahydrofolic acid and ferrous ion. 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 t (min)	L-DOPA concentration after 2.0 minutes from the start of the assay [DOPA] (μmol 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

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 min^{-1}), K_M (= 0.49 mmol dm^{-3}), and/or reagent concentrations. 4.0 pt

SOLUTION:

We already saw: $r = \frac{k[S][E]}{K_M + [S]}$

The rate is calculated from the concentration of DOPA formed: $r = \frac{[DOPA]}{2.0 \text{ min}}$

Therefore $\frac{[DOPA]}{2.0 \text{ min}} = \frac{k[S][E]}{K_M + [S]} \Rightarrow [E] = \frac{K_M + [S]}{k[S]} \frac{[DOPA]}{2.0 \text{ min}}$

Using $k = 250$ min^{-1}, $K_M = 0.49$ mmol dm^{-3} and $[S] = 10.0$ mmol dm^{-3} gives:
$[E] = 0.0021[DOPA]$

(Correct formula without substituting the constants is still maximum points.)

The change in the active enzyme concentration as a function of time is well described by a parabola ($[E] = [E]_0 - k_{obs}t^2$), 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 $[\text{E}]_0$ is the initial concentration of the enzyme.

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

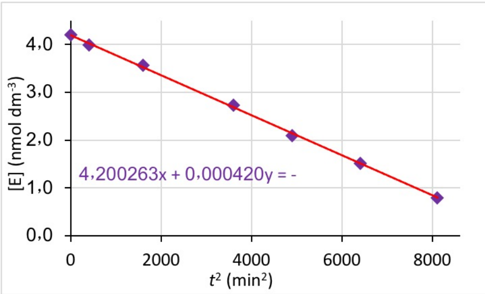
SOLUTION:

1. $k_{\text{obs}} = \frac{1}{t^2}([\text{E}]_0 - [\text{E}])$

Any one of the data points can be used except t = 0.

$k_{\text{obs}} = 4.2 \times 10^{-4}$ nmol dm^{-3} min^{-2} (Note the very unusual unit!!!)

2. The active enzyme concentrations can be plotted as a function of squared time:



(1 point for the calculation method, 1 point for the calculation, 1 point for the unit.)

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

SOLUTION:

$0.5[\text{E}]_0 = [\text{E}]_0 - k_{\text{obs}} t_{1/2}{}^2$

$k_{\text{obs}} t_{1/2}{}^2 = 0.5[\text{E}]_0$

Thus: $t_{1/2} = \sqrt{[\text{E}]_0 / 2k_{\text{obs}}} = 71$ min

Also, the first half-life can be directly read from the data as the concentration at 70 min is exactly one half that of the initial one.

(2 points for the formula, 1 point for the calculation including the unit)

The first half-lives for enzyme inactivation were determined using other initial catechol concentrations. The dependences of active enzyme concentrations on time were very well described by parabolas 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 of the enzyme inactivation process consistent with all the experimental observations. 6.0 pt

SOLUTION:

It is seen that the first half-lives are inversely proportional to the catechol concentration:

$t_{1/2} = \sqrt{\frac{[\mathrm{E}]_0}{2k_{\mathrm{obs}}}} = \frac{1}{k_{\mathrm{cat}}[\mathrm{catechol}]_0}$

From this equation, k_{cat} is calculated as 7.1 $\mathrm{mol^{-1}\ dm^3\ min^{-1}}$. The change in enzyme concentration is given as a function of time:

$[\mathrm{E}](t) = [\mathrm{E}]_0 - \frac{[\mathrm{E}]_0}{2}(k_{\mathrm{cat}}[\mathrm{catechol}]_0)^2 t^2$

The rate of enzyme inactivation is:

$r_{\mathrm{inact}}(t) = -[\mathrm{E}]_0(k_{\mathrm{cat}}[\mathrm{catechol}]_0)^2 t$

One way to calculate this is based on the definition of reaction rate, *i.e.* change in concentration divided by change in time:

$r_{\mathrm{inact}}(\frac{t_1+t_2}{2}) = -\frac{[\mathrm{E}]_{t_2}-[\mathrm{E}]_{t_1}}{t_2-t_1} = -\frac{[\mathrm{E}]_0}{2}(k_{\mathrm{cat}}[\mathrm{catechol}]_0)^2\frac{t_1^2-t_2^2}{t_2-t_1} = \frac{[\mathrm{E}]_0}{2}(k_{\mathrm{cat}}[\mathrm{catechol}]_0)^2(t_1+t_2)$

Re-labeling with $t = \frac{t_1+t_2}{2}$ gives as a function of t.

This cannot be a rate equation, as it contains time explicitly. However, from the independent experiments, it is known that the catechol reacts with the oxygen present to give *o*-quinone. As the initial enzyme concentration is much smaller than the catechol concentration, the latter can be considered constant within the time frame of the experiment ($[\mathrm{catechol}]=[\mathrm{catechol}]_0$ at any time instant). If this is true, the time dependence of the *o*-quinone formation can be described with a linear function:

$[o\text{-quinone}] = k_{\mathrm{catechol}}[\mathrm{catechol}]_0 t$

As the first half-lives are inversely proportional to the catechol concentration the rate law can be written containing both the catechol and the *o*-quinone concentration without the appearance of time:

$r_{\mathrm{inact}} = [\mathrm{E}]_0\frac{(k_{\mathrm{cat}})^2}{k_{\mathrm{catechol}}}[\mathrm{catechol}][o\text{-quinone}] = k_{\mathrm{2nd}}[\mathrm{catechol}][o\text{-quinone}]$

Important elements in marking:

Connection between catechol concentration and k_{obs} (1 point)

Calculating the rate from the parabolic concentration-time kinetic curve (1 point)

Recognizing that $[\mathrm{catechol}]^2$ is not a good option because it would imply deactivation without the presence of oxygen. (1 point)

Recognizing the role of *o*-quinone. (1 point)

Maximum points if the correct rate law is given without any derivation shown.

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

SOLUTION:

B

Problem 3 Tyrosinase

3.1 (5.0 pt)

3.2 (2.0 pt)

r_0 =

3.3 (5.0 pt)

r =

$k_{catechol}$ =

3.4 (4.0 pt)

[E] =

3.5 (3.0 pt)

k_{obs} =

3.6 (3.0 pt)

$t_{1/2}$ =

3.7 (6.0 pt)

3.8 (3.0 pt) ☐ A ☐ B ☐ C ☐ D ☐ E ☐ F ☐ G ☐ H

Problem 4 Potassium

Elementary potassium was the first metal synthesized by electrolysis (1807). Humphry Davy used voltaic cells and electrodes immersed into molten KOH.

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

SOLUTION:

$K^+ + e^- = K$ (1)

$4\,OH^- = O_2 + 2H_2O + 4e^-$ (2)

It is little known that only a year after Davy, French chemists have 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 vapors were leaving the end of the barrel, where the metal could be condensed to a solid.

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

SOLUTION:

$K_2CO_3 + 2\,C = 2\,K + 3\,CO$

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 recrystallization in water. The exact structure of the byproduct **X** was determined more than one and a half century later.

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

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. **SOLUTION:** **Solution 1** One can suppose that the second dissociation is negligible in such an acidic medium.$K_{a1} = 10^{-0.8} = [H^+][HA^-]/[H_2A] = [H^+]\frac{5}{95}$ $[H^+] = 10^{0.5}$,pH =−0.5 At this pH, the second dissociation is indeed almost completely shifted to the left. **Solution 2** Without neglecting the second dissociation: $\frac{100}{95} = c/[H_2A] = 1 + K_1/[H^+] + K_1K_2/[H^+]^2$ Solving the second order equation gives $[H^+] = 10^{0.5}$ and pH = -0.5.	3 pt

4.4	**Calculate** the pH of a 0.01 mol dm^{-3} solution of the salt **X** in pure water. **SOLUTION:** The hydrolysis constant of the anions is so low (11.8) that the dissociation of water also must be taken in account. Also, only the first step of the hydrolysis is important. Equations: 1. $K_w=[H^+][OH^-]$ 2. $K_{a2} = 10^{-2.2}=[H^+][A^{2-}]/[HA^-]$ 3. $[HA^-] + [A^{2-}] = c = 0.01M$ 4. $[K^+] + [H^+] = [OH^-] + [HA^-] + 2[A^{2-}]$ From eq. 2: $c/[A^{2-}] = 1^+ [HA^-]/[A^{2-}] = 1^+ [H^+]/K_{a2}$, which, between pH 6 and 8 is equal to 1. From eqs. 3-4 (and $[K^+] = 2c$): $2([HA^-] + [A^{2-}]) + [H^+] = [OH^-] + [HA^-] + 2[A^{2-}]$ thus $[OH^-] = [HA^-] + [H^+]$ Substituting all the equilibrium constants, neglecting the fully protonated acid concentration in the sum and rearranging gives: $K_w/(c/K_2 + 1) = [H^+]^2$ Solving the equations gives that pH is 7.21.	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

SOLUTION:

The mass series has differences of 28 units, which in a system of C, O and K could only be CO. The methyl derivatives are probably an ester of an oxoacid. Based on the mass values:

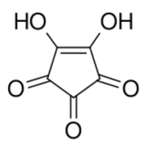
114.10 — $(CH_3)_2(CO)_3$
142.11 — $(CH_3)_2(CO)_4$
170.12 — $(CH_3)_2(CO)_5$
198.13 — $(CH_3)_2(CO)_6$

So the anions have the composition of $[(CO)_n]^{2-}$
Gmelin's salt was $K_2(CO)_5 \cdot 2\,H_2O$

4.6	**Draw** the structure of the free acid **Y**.	3 pt

SOLUTION:

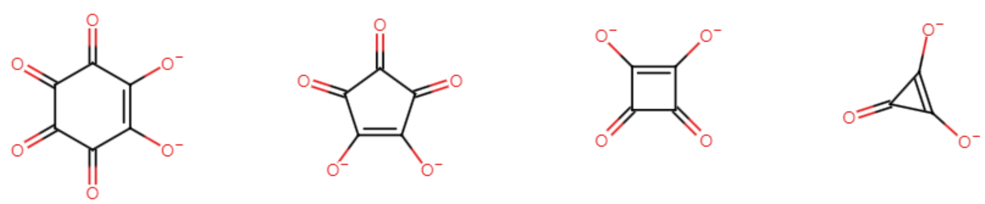
The anions being cyclic and very symmetric are the oxocarbon anions. When protonated, two adjacent oxygens will get protonated.



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

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

SOLUTION:



Problem 4 Potassium

4.1 (2 pt) 1:

2:

4.2 (1.0 pt)

4.3 (3.0 pt) pH :

4.4 (4 pt) pH :

4.5 (4 pt) X :

4.6 (3 pt)

4.7 (4.0 pt)

114.10 g/mol	142.11 g/mol
170.12 g/mol	198.13 g/mol

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 colored compounds, **B** and **C** are mixed in stoichiometric ratio. 10.00 g **B** in solution mixed with the solution of 12.86 g **C**, and immediately cooled to $2\,^{\circ}$C will give 4.90 g solid **A**. The yield of **A** is 32.6 %.

To determine the composition of **A**, first iodometry is performed. A known mass of **A** is added to a titration flask, acidified with sulfuric acid, then KI is added in excess and there is a precipitate formation. After a few minutes, sodium citrate solution is added until the solution 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 $5.000 \cdot 10^{-2}$ mol dm^{-3} thiosulfate are 54.12 cm^3 in Titration I and 5.41 cm^3 in Titration II.

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

5.1	<u>**Write**</u> balanced equations for reactions [1] and [2]. **SOLUTION:** [1]: $2\,S_2O_3^{2-} + I_2 \longrightarrow S_4O_6^{2-} + 2\,I^-$ The blue precipitate and the iodometric titration suggests the presence of copper (II) so the precipitation reaction is: [2]: $2\,Cu^{2+} + 4\,I^- \longrightarrow 2\,CuI + I_2$ 2 points for each equation (1 point equation and 1 point for the coefficients)	4.0 pt

The thermal decomposition of **A** was studied in detail. When pure **A** is slowly heated, already at around $75\,^{\circ}$C it explodes. 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 $65\,^{\circ}$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 well 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 quantitated if it is absorbed in acid solution.

<u>Some hints</u>

- Compound **A** decomposes without releasing oxygen.

- Compound **A** contains two different metals.
- Compounds **A** and **B** both contain a complex ion.
- **C** is a well-known compound for any chemistry student.
- Compound **F** does not contain any metal.

5.2 <u>**Give chemical formulae of**</u> **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

SOLUTION:

The blue precipitate and the iodometric titration suggests the presence of copper as it was mentioned in the previous question. In the first titration copper(II) precipitates iodine and copper(I)-iodide in acidic medium, but upon adding citrate the $2\,Cu^{2+} + 4\,I^- \rightleftharpoons 2\,CuI + I_2$ equilibrium is shifted to the left, as citrate forms a complex with copper(II) ions.

In the second titration the citrate complex decomposes, so the iodine equivalent to copper is formed again. So, another oxidizing material is present that will form 10 times as much iodine. In the first titration, this oxidizer, in the second Cu(II) is measured.

In $100\,mg$ **A** there is $2.705 \cdot 10^{-4}$ mol $(17,19\,mg)$ Cu^{2+}.

(1 point)

In the decomposition of $100\,mg$ **A** $100\,mg \cdot 0,859 \cdot \frac{2,97}{3,97} = 64.26\,mg$ **G** forms containing $17.19\,mg$ copper, $64.26\,mg \cdot 0.270 = 17.35\,mg$ O and a third element.

$n(Cu) : n(O) = 1 : 4$

(1 point)

The unknown element will give a reasonable atomic mass if n(**X**)=2n(Cu). Then M(**X**) = $54.94\,g\,mol^{-1}$ and manganese. **G** is $CuMn_2O_4$. The 10 electron oxidation [$2\,MnO_4^-$ so $Cu(MnO_4)_2$] supports this.

(1 point to find manganese and 1 point to give a correct molecular formula of **G.**)

From the 10 electron oxidation we can assume **A** contains MnO_4^-.

(1 point)

In $100\,mg$ **A** there is $2.705 \cdot 10^{-4}$ mol Cu^{2+} and $2 \cdot 2.705 \cdot 10^{-4}$ mol MnO_4^- giving a total mass of $81.54\,mg$. The mass of **A** containing 1 mol Cu^{2+} is $369.7\,g$ **A.**

(1 point)

$369.7\,g$ of **A** contains $301.4\,g$ of copper and permanganate. The difference is $68.3\,g$.

(1 point)

That is equivalent to 4 mol NH_3. (In accordance with a gas forming in the thermal decomposition and reacting with acid.)

(1 point)

The formula of **A** is: $[Cu(NH_3)_4](MnO_4)_2$.

During thermal decomposition, permanganate is reduced to Mn(III) in **G**, needing 8 electrons. Thus 1 NH_3 is oxidized to nitrate, so the **F** decomposition product is NH_4NO_3.

(1 point to conclude that it is an ammonium salt, 2 points to conclude that the anion is nitrate.)

This is also supported by the fact that starting from 1 mol of **A** the mass of the **F** produced is: $369.7\,g \cdot 0.859 \cdot \frac{1,00}{3,97} = 80.0\,g$

(1 point)

SOLUTION:

$Cu^{2+} + 2\,MnO_4^- + NH_3 \longrightarrow CuMn_2O_4 + NO_3^- + H_2O + H^+$ The remaining 2 NH_3leaves with water. The mass loss gives the same result: from 1 mol (369.5 g) of starting **A** two component gas mixture is lost. This could be 2 mol $NH_3$and 1 mol H_2O.
The full reaction:
$[Cu(NH_3)_4](MnO_4)_2 \longrightarrow CuMn_2O_4 + NH_4NO_3 + 2\,NH_3 + H_2O$
(This is the first known permanganate salt that decomposes without releasing oxygen.)
The starting materials are: a copper tetraammine salt and a permanganate. If the yield is 100% 3.75 g (0.01 mol) **A** forms containing 0.01 mol (0.635 g) Cu^{2+}, i.e. 1.32 g $[Cu(NH_3)_4]^{2+}$, and 0.02 mol (2, 38 g) MnO_4^-. Supposing that **C** is the permanganate salt, 0.82 g is the mass of the cation, which agrees with potassium. **C** is $KMnO_4$.
(3 points to find that **C** has permanganate anion and 1 point that the cation is potassium.)
In **B** there is 1.18 g of another component. that agrees well with $[Cu(NH_3)_4]SO_4 \cdot H_2O$.
(2 points to find that there is a molecule of water in **B.** If **B** is given as $[Cu(NH_3)_4]SO_4$ 2 points are attributed. 1 point is given for $CuSO_4$.)
In the aqueous solution of $[Cu(NH_3)_4](MnO_4)_2$ the protolysis of ammonia causes the formation of $Cu(OH)_2$. So an ammonium salts forms in the solution. $[Cu(NH_3)_4](MnO_4)_2 + 2\,H_2O \longrightarrow Cu(OH)_2 + 2\,NH_4MnO_4 + 2\,NH_3$
The unknown compounds are the following:

A: $[Cu(NH_3)_4](MnO_4)_2$	**B**: $[Cu(NH_3)_4]SO_4 \cdot H_2O$
C: $KMnO_4$	**D**: $Cu(OH)_2$
E: NH_4MnO_4	**F**: NH_4NO_3
G: $CuMn_2O_4$	

4 points for each compound. No partial points awarded for $Cu(OH)_2$ and NH_4MnO_4.
Summary of the marking scheme:
4 points are given for each correct compound. It is not necessary to provide calculations if the correct formula is provided. Calculations are only important to obtain partial points in case of incorrect formulae.
28 points in total.
Partial points are given as follows:
A: 1 point for the molar mass of compound, 1 point for the compound containing MnO_4^-, 1 point to find a molar mass of ligands and 1 point for conclusion about 4 mol NH_3
B: 2 points for$[Cu(NH_3)_4]SO_4$, 2 points for $CuSO_4 \cdot 5\,H_2O$ or 1 point for $CuSO_4$. Also, 1 point for the correct molar mass of **B**.
C: 3 points are awarded for MnO_4^- salts other than $KMnO_4$.
D and **E**: No partial markings awarded.
F: 1 point for the molar mass of the salt, 1 point for concluding the presence of NH_4^+ions, 2 points for conclusion about nitrate anions.
G: 1 point for the calculation of the mass or the mass fraction of copper, 1 point for the Cu to O ratio as 1:4 . Then 1 point for discovering manganese and 1 point for the correct ratio between the three correct elements.

5.3 **Write** balanced equations for reactions [3]—[5]. 12.0 pt

SOLUTION:

[3]: $[Cu(NH_3)_4](MnO_4)_2 + 2\,H_2O \longrightarrow Cu(OH)_2 + 2\,NH_4MnO_4 + 2\,NH_3$

[4]: $[Cu(NH_3)_4](MnO_4)_2 \longrightarrow CuMn_2O_4 + NH_4NO_3 + 2\,NH_3 + H_2O$

[5]: $NH_4NO_3 \longrightarrow N_2O + 2\,H_2O$ (or $NH_4NO_3 \longrightarrow N_2 + \frac{1}{2}\,O_2 + 2\,H_2O$)

4 points each reaction (2 points for the reaction and 2 points for the coefficients)

Problem 5 Unknown

5.1 (4.0 pt)

[1]:

[2]:

5.2 (28.0 pt)

5.2 (cont.)

A:	**B**:
C:	**D**:
E:	**F**:
G:	--

5.3 (12.0 pt)

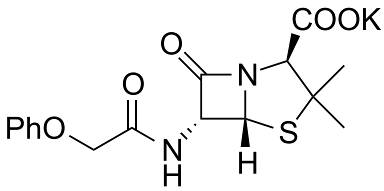
[3]:

[4]:

[5]:

Problem 6 Penicillin

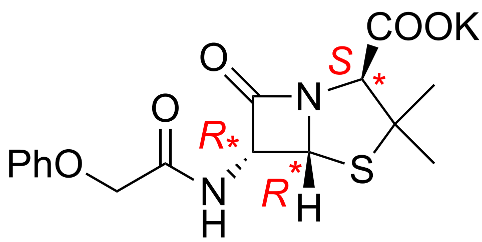
Penicillins are a group of antibiotics that have played a crucial role in medicine since their discovery.



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

SOLUTION:



Penicillin VK

1 point for clearly identifying each stereocenter.
1 point for each correct stereodescriptor.

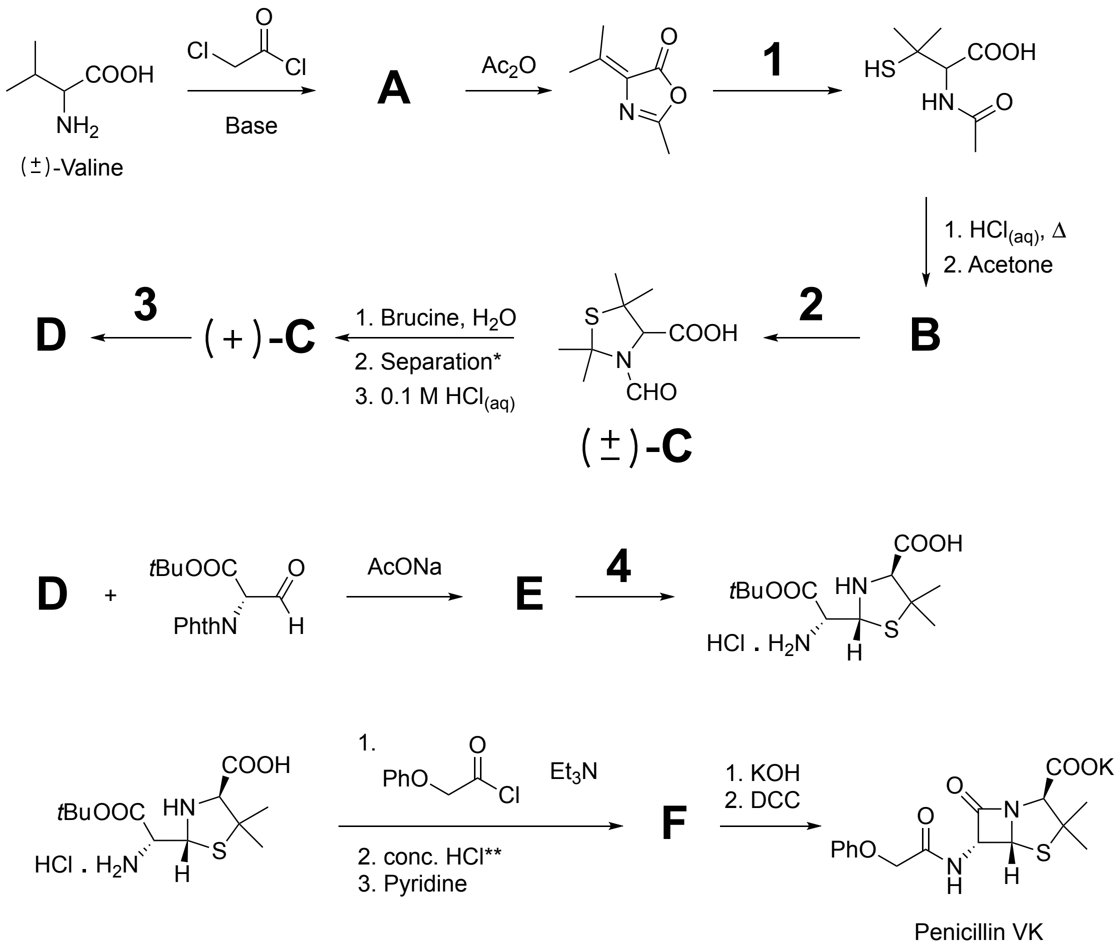
6.2.	**Give** the total number of possible stereoisomers of Penicillin VK.	2 pt

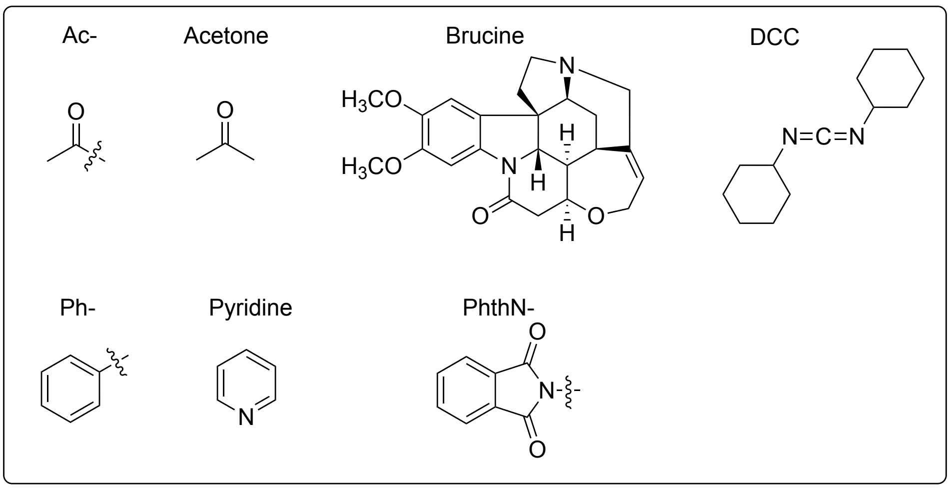
SOLUTION:
$2^3 = 8$
2 *points* for the correct number of possible stereoisomers.

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 ^{1}H 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.





*Please note that in the formation of **(+)-C**, the word "Separation" means **separation**.

Conc. HCl means **concentrated HCl.

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

a) 2 M $HCl_{(aq)}$

b) SO_3, H_2SO_4

c) $NaOH_{(aq)}$

d) HCO_2H, Ac_2O

e) i) N_2H_4 ii) $HCl_{(aq)}$, AcOH

f) i) H_2S, Na, CH_3OH ii) H_2O

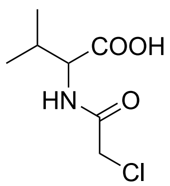
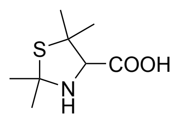
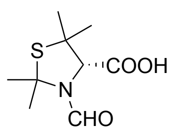
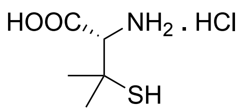
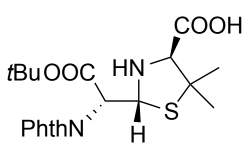
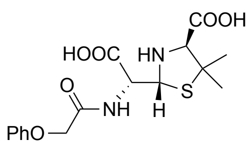
SOLUTION:
1 - f
2 - d
3 - a
4 - e

2 points for each correct answer.
0 points awarded if multiple answers are selected.

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

SOLUTION:

- Charge-neutral molecules as well as sensible zwitterions are accepted for all structures.
- 0 points are awarded for A and D, if the structures contain a ring.
- 0 points are awarded for B and E, if the structures do not contain a 5 membered ring (not taking the PhthN- group into account).
- 1 point will be deducted for each missing atom or group (i.e. -CH3).

A:  3 points for the correct structure. 2 points for the anhydride. 0 points for *N*-alkylation or *O*-alkylation. 0 points for structure not fitting the ^{1}H NMR data.	B:  3 points for the correct structure. 1 point for the structure containing an amide.
C:  3 points for the correct structure 1 points for the structure with a defined stereo-center that is incorrect. 0 points if stereochemistry is not indicated	D:  3 points for the correct structure. 1 point for structure with an amide.
E:  3 points for the correct structure	F:  3 points for the correct structure. 1 point for structure with amide formation, but no tert-butyl ester deprotection.

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

SOLUTION:
c
2 points

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

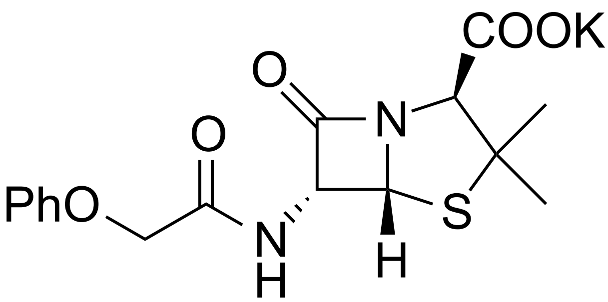
c) coupling reagent

d) radical initiator

SOLUTION:
c
2 points

Problem 6. Penicillin Answer Sheet

6.1. (6 pt)



Penicillin VK

6.2. (2 pt)

6.3. (8 pt)

1: ☐ a ☐ b ☐ c ☐ d ☐ e ☐ f

2: ☐ a ☐ b ☐ c ☐ d ☐ e ☐ f

3: ☐ a ☐ b ☐ c ☐ d ☐ e ☐ f

4: ☐ a ☐ b ☐ c ☐ d ☐ e ☐ f

6.4 (18 pt)

A:	**B:**
(+)-C:	**D:**
E:	**F:**

6.5. (2 pt)

☐ a ☐ b ☐ c ☐ d

6.6. (2 pt)

☐ a ☐ b ☐ c ☐ d

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.

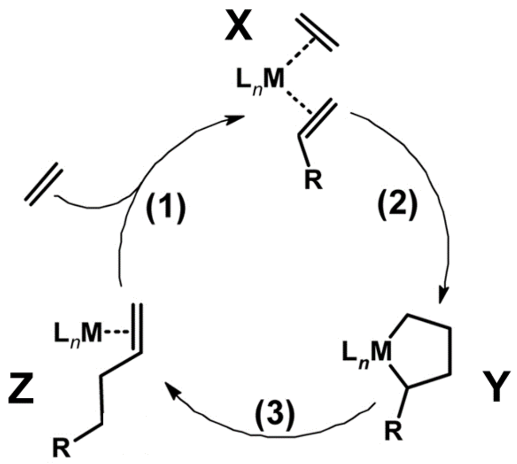
Part A

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

Linear alpha olefins are produced by catalytic oligomerization of ethene, resulting in a range of chain lengths with a distribution. 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. Ethene, the monomer is not a member of the series $(n \geq 2)$.

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



Although this mechanism is not a classical chain reaction because the final product is not produced within the cycle, 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. **SOLUTION:** (1) $r_1 = k_1[Z][=]^{\rho}$ 0.5 pt (2) $r_2 = k_2[X]$ 0.25 pt (3) $r_3 = k_3[Y]$ 0.25 pt	1 pt

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. **SOLUTION:** $Z \rightarrow L_nM + R - CH_2 - CH_2 - CH = CH_2$ 1 pt $r_t = k_t[Z]$ 1 pt	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. **SOLUTION:** The final product alkene is produced in the termination step. In each cycle, Z can either participate in the chain carrier step (1), or the termination step (t). The probability that a product molecule is formed from Z is the ratio of the rate of termination and the sum of the rates of carrier step (1) and termination step (t): $p = \frac{k_t[Z]}{k_t[Z]+k_1[Z][=]^{\rho}} = \frac{k_t}{k_t+k_1[=]^{\rho}}$ In able to obtain the Flory distribution from the mechanism, this probability needs to be independent of the concentrations. This requires $\rho = 0$, so zeroth order dependence in chain carrying step (1) on the concentration of free ethene. 2 pt with explanation; only the final value is 0.5 p If this is the case, the Flory parameter α is the same as the probability of propagation. $\alpha = \frac{k_1}{k_t+k_1}$ 2 p	4 pt

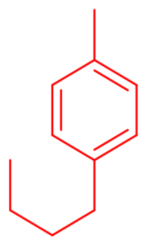
Aluminum alkyls are used as co-catalysts in the ethene oligomerization process. It was found that they also catalyzed the Friedel–Crafts alkylation of the aromatic solvents used for the oligomerization.

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

^{1}H 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

SOLUTION:



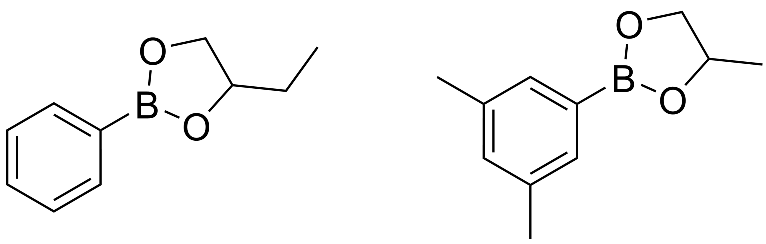
-1 pt if the multiplicity is not correct OR the alkyl chain length is not correct

-1 pt if the substitution ring positions are not correct

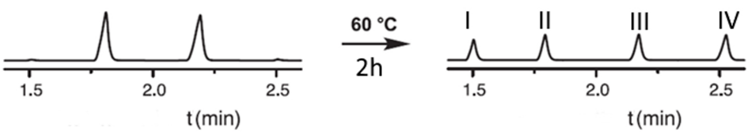
Part B

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, an important topic in SABIC's polymer research.

A recently elucidated fast and reversible reaction involving dioxaborolanes can serve as the chemical background for such an 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.



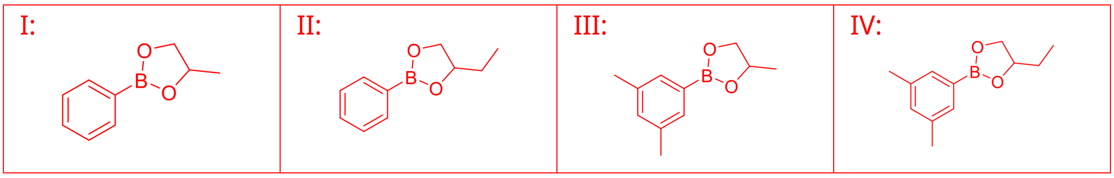
They participate in a model metathesis (exchange) reaction. The two carefully purified compounds were mixed in the absence of solvent and the mixture was kept at 60 °C for two hours. Interestingly, the gas chromatograms of the mixture at the start and at the end of the incubation period showed only the 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.

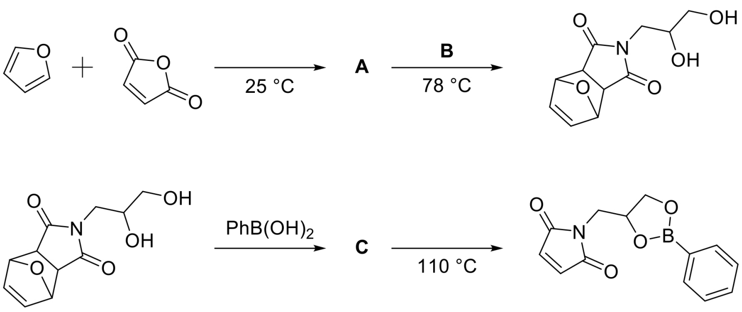
7.5 **Draw** the compounds associated with peaks I–IV in the chromatogram. 2 pt

SOLUTION:



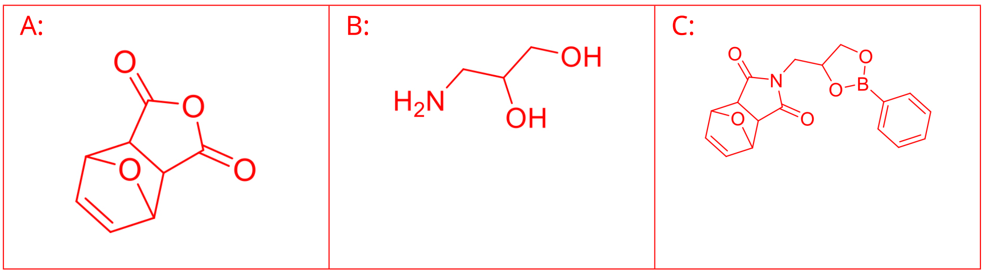
0.5 pt each

Linking functional units to a polymer chain is known as grafting, and 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.



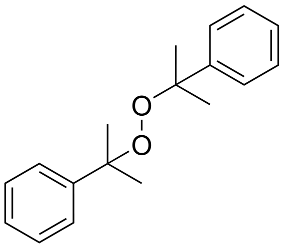
7.6 **Draw** the structures of **A–C**. 3 pt

SOLUTION:



1 pt each

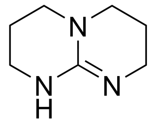
7.7 **Select** on the answer sheet which reagent(s) and/or condition is/are appropriate for linking the dioxaborolane maleimide units to **polyethylene**. 1 pt



a)

b) Pt, H_2

c) hv, 454 nm

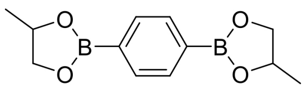


d)

SOLUTION:
(a) 1 pt for correct answer

The vitrimer was prepared as follows:

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



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

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 a homogeneous vitrimer.

- 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 wavelengths, corresponding molar (related to the specified functional groups) absorption coefficients for relevant characteristic peaks together with the absorbances of the vitrimer sample.

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

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

SOLUTION:

Given the absorption coefficient for the unique vibrating bonds, the Beer-Lambert law can be used to calculate the concentration as follow:

$$X_g = \frac{n_{grafted}}{n_{ethylene}} = \frac{\frac{A_{1710}}{\epsilon_{1710}}}{0.5 \cdot \frac{A_{1470}}{\epsilon_{1470}}} = 0.0078$$

1 pt for correct application of the Beer-Lambert Law 1 pt for correct ratio of imide over ethylene. 1 pt for number of -CH_2- halved The number of grafted methylene groups and the methylenes in the grafted groups can be neglected, but if it isn't, it will also be accepted, of course.

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

SOLUTION:

Given the absorption coefficient for the unique vibrating bonds, the Beer-Lambert law can be used to calculate the concentration as follow:

From the infrared data we can conclude that the number of all boronic acid moieties is proportional to:

$$n_{boronic} \sim \frac{A_{1600}}{\varepsilon_{1600}} + 2\frac{A_{1520}}{\varepsilon_{1520}}$$

The number of maleimide groups:

$$n_{maleimide} = n_{grafted} \sim \frac{A_{1710}}{\varepsilon_{1710}}$$

So the number of bifunctional grafting agents grafting via only 1 group: $n_{bif,nc} = n_{boronic} - n_{maleimide}$.

The non-crosslinking grafted groups are the monofunctional grafting agents and the bifunctional grafting agents grafting via only 1 group.

Their ratio is:

$$p_{nc} = \frac{n_{mono}+n_{bif,nc}}{n_{grafted}} = \frac{\frac{A_{1600}}{\epsilon_{1600}} + \frac{A_{1600}}{\epsilon_{1600}} + 2\cdot\frac{A_{1520}}{\epsilon_{1520}} - \frac{A_{1710}}{\epsilon_{1710}}}{\frac{A_{1710}}{\epsilon_{1710}}} = \frac{2\cdot\frac{0.022}{0.28} + 2\cdot\frac{0.042}{0.68} - \frac{0.451}{2.67}}{\frac{0.451}{2.67}} = 0.66$$

0.5 pt for correct application of the Beer-Lambert Law 0.5 pt denominator is correctly considered. 1 pt monofunctional grafting agents are considered. 2 pt bifunctional grafting agents with 1 connection are considered.

Problem 7 SABIC

7.1 (1 pt)

$r_1 =$

$r_2 =$

$r_3 =$

7.2 (2 pt)

i)

ii) $r_t =$

7.3 (4 pt)

$\rho =$ $\alpha =$

7.4 (3 pt)

Q:

7.5 (2 pt)

I:	II:	III:	IV:

7.6 (3 pt)

A:	B:	C:

7.7 (1 pt) ☐a ☐b ☐c ☐d

7.8 (3 pt)

$X_g =$

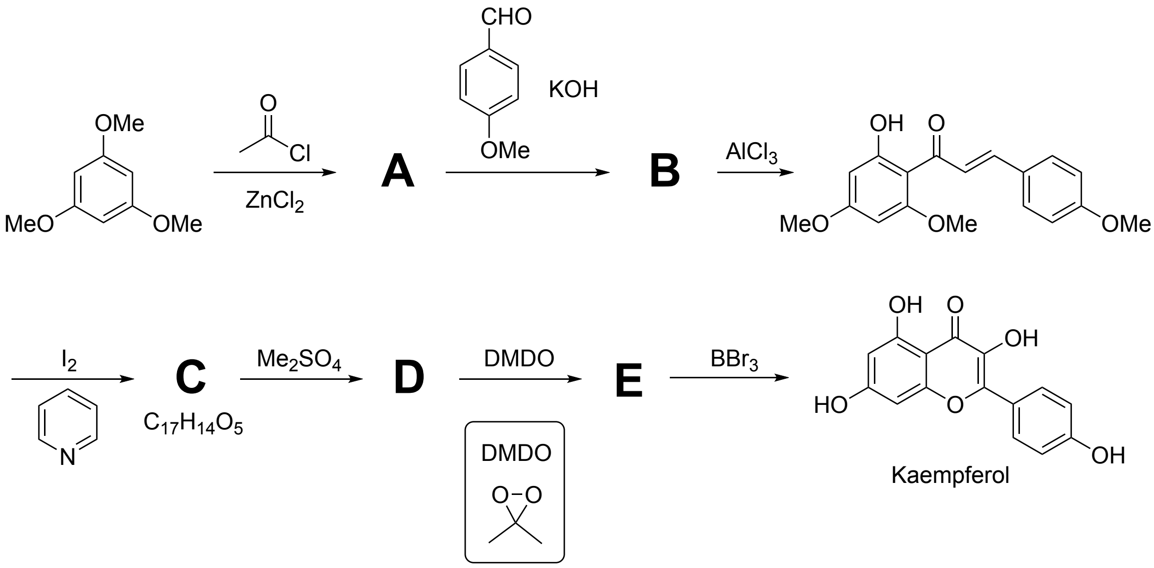
7.9 (4 pt)

$p_{nc} =$

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.

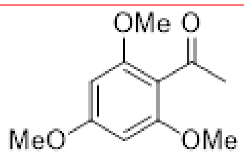
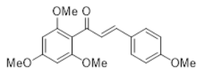
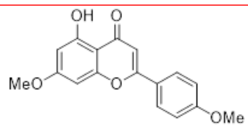
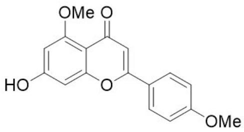
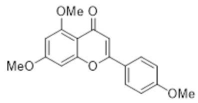
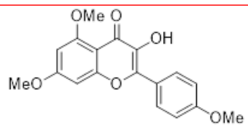


Hints:

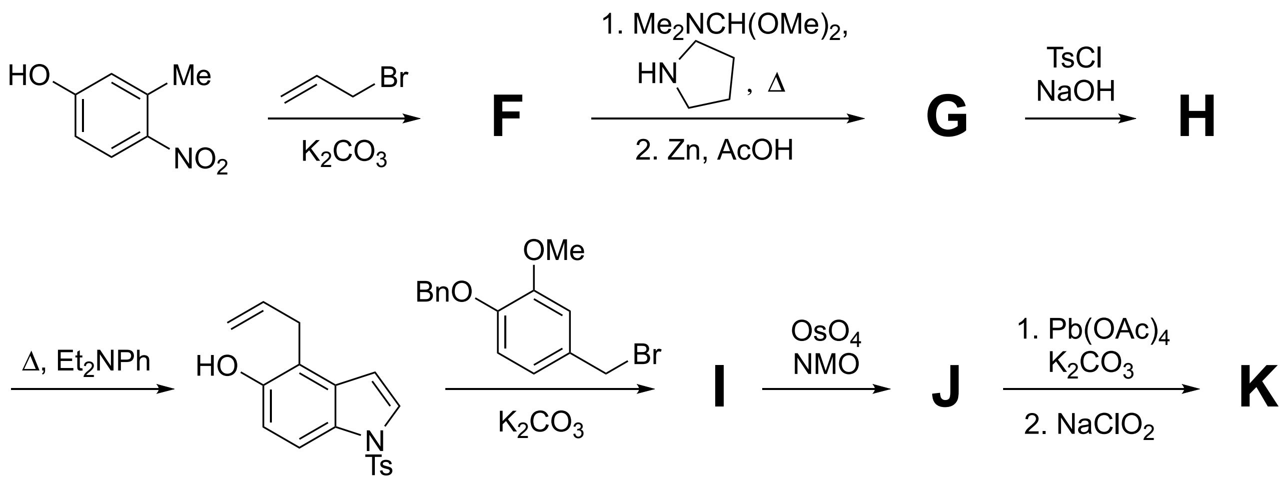
- **C** has a tricyclic system. Also, it has the same number of hydroxyl groups as the compound preceding it.
- The step **C** to **D** is necessary to avoid any unwanted reactivity with DMDO.
- DMDO is a hydroxylating agent.

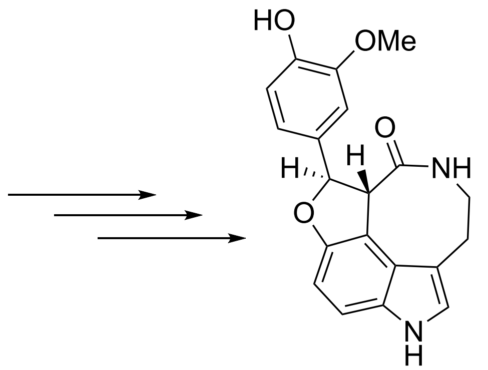
8.1. **Draw** the structures of compounds **A–E**. 15 pt

SOLUTION:

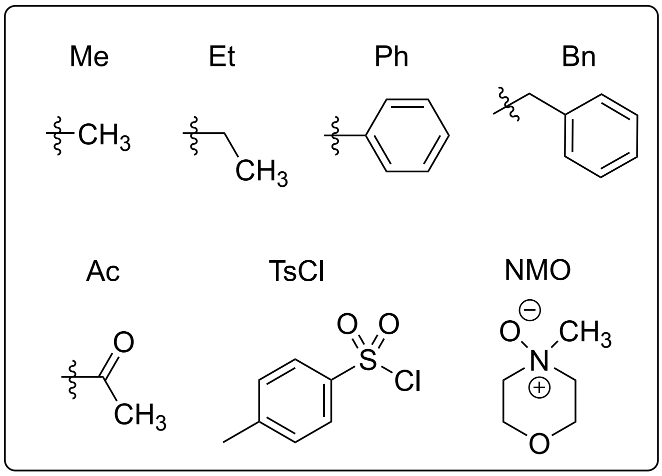
A  3 points for the correct structure	B  3 points for the correct structure
C  3 points for the correct structure (demethylation in any position is accepted)  0 point if -OH is not equal to 1 (as Hint is provided)	D  3 points for the correct structure
E  3 points for the correct structure	

A unique pentacyclic indole alkaloid, serotobenine found in safflower has antimicrobial properties. Its total synthesis is shown below:





Serotobenine

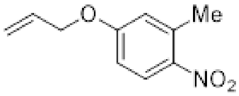
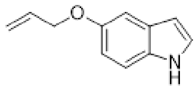
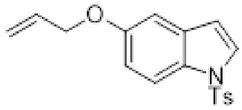
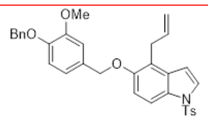
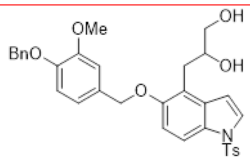
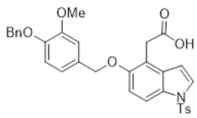


Hints:

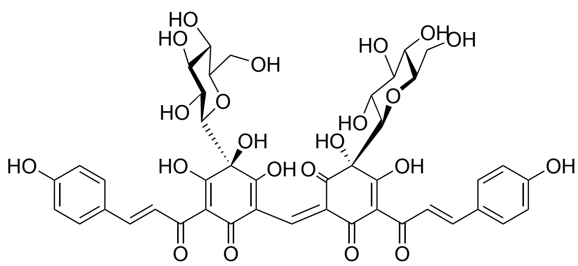
- **G** is a bicyclic compound with one of the rings being a heterocycle.
- **H** isomerizes upon heating in the presence of the amine base.
- **K** is a product of an oxidative cleavage of the newly formed functional group in **J**. **K** has a ^{1}H NMR signal at 12 ppm.

8.2. <u>**Draw**</u> the structures of compounds **F–K**. 18 pt

SOLUTION:

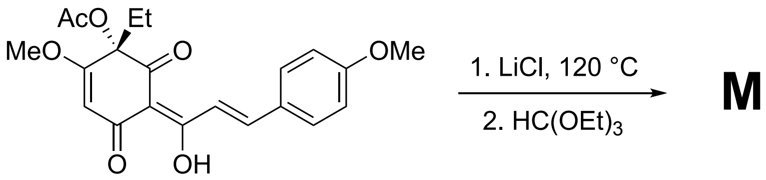
F  3 points for the correct structure	G  3 points for the correct structure
H  3 points for the correct structure	I  3 points for the correct structure
J  3 points for the correct structure	K  3 points for the correct structure -1 for missing Ts group

Carthamin gives safflower its red color.



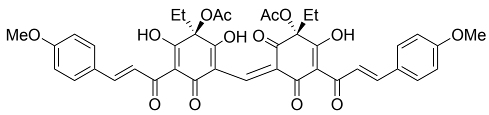
Carthamin

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



(*S*)-L

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 ^{1}H NMR spectra). **SOLUTION:**	5 pt



4 points for the correct structure (any form of resonance would be accepted) and 1 point for correct stereochemistry

Problem 8 Safflower

8.1. (15 pt)

A:	**B**:
C:	**D**:
E:	

8.2. (18 pt)

F:	**G**:
H:	**I**:
J:	**K**:

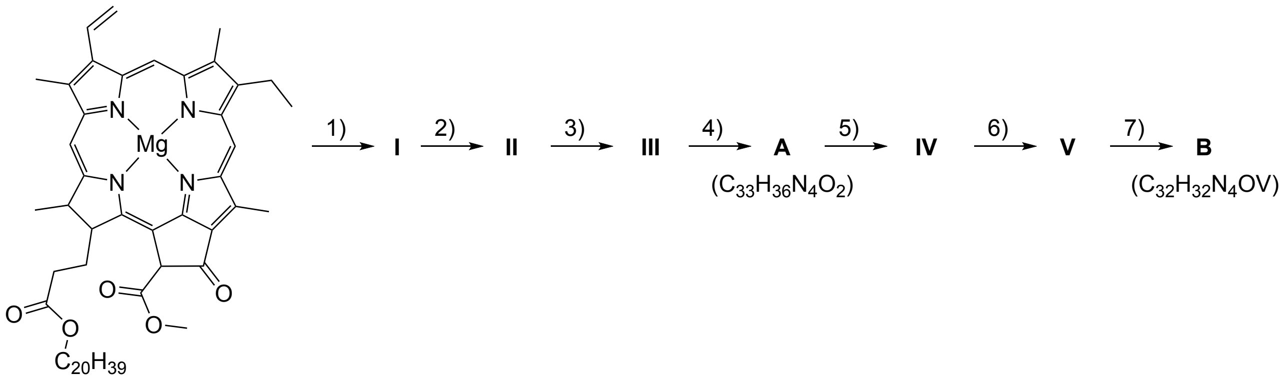
8.3. (5 pt)

Problem 9 Porphyrin complexes

Part A. Metals in petroleum

Saudi Arabian petroleum, primarily hydrocarbons, 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)	Demetallization
2)	Hydrolysis
3)	Decarbomethoxylation
4)	Reduction
5)	Aromatization
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

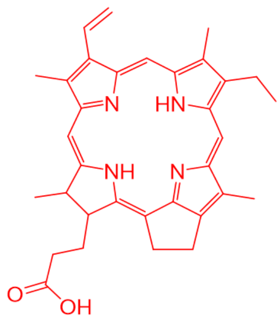
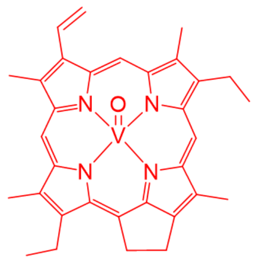
SOLUTION:

a	b	c	d	e
$C_{32}H_{34}N_4$	$C_{55}H_{74}N_4O_5$	$C_{33}H_{34}N_4O_3$	$C_{33}H_{34}N_4O_2$	$C_{35}H_{36}N_4O_5$
V	I	III	IV	II

All correct – 4 pt, 3 correct – 3 pt, 2 correct – 2 pt, 1 correct – 1 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

SOLUTION:

	
A ($C_{33}H_{36}N_4O_2$)	**B** ($C_{32}H_{32}N_4OV$)

A: N_4Mg to N_4H_2 – 1 pt, $COOC_{20}H_{39}$ to COOH – 1 pt, COOMe to H – 1 pt, C=O to CH_2 – 1 pt.
B: aromatization – 1 pt, COOH to H – 1 pt, N_4H_2 to N_4VO – 1 pt.
1 pt penalty for other modification(s) of the structure(s).

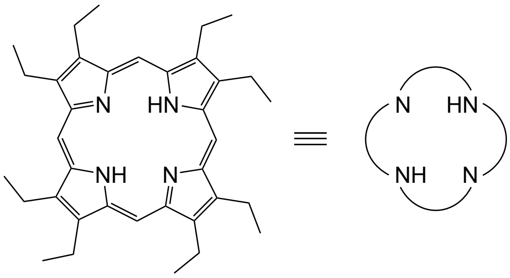
9.3 **Indicate** the oxidation state of vanadium in **B**. 1.0 pt

SOLUTION:

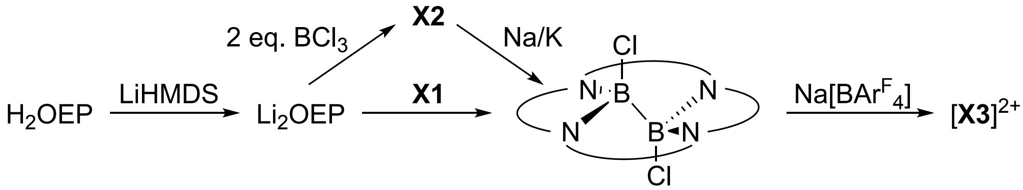
If **B** is correct or not provided: +4. Otherwise, the answer must be consistent with the provided structure of **B**. (1 pt)

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:



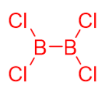
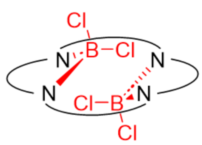
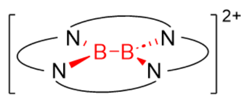
To produce dicationic planar boron porphyrin complex $[\mathbf{X3}]^{2+}$, either BCl_3 or another binary compound **X1** can be used as a precursor:



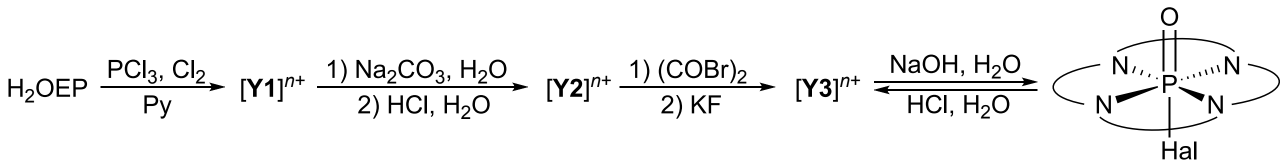
(LiHMDS = $LiN(SiMe_3)_2$; $Na[BAr^F_4]$ = $Na[B\{(3,5)-(CF_3)_2C_6H_3\}_4]$)

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

SOLUTION:

		
X1 (1 pt)	**X2** (1 pt)	**$[\mathbf{X3}]^{2+}$** (1 pt)

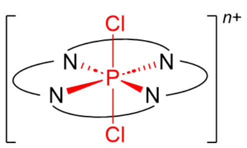
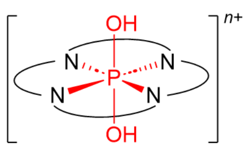
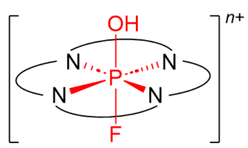
Phosphorus forms porphyrin cationic complexes $[\mathbf{Y1}]^{n+}$, $[\mathbf{Y2}]^{n+}$, and $[\mathbf{Y3}]^{n+}$. The complex $[\mathbf{Y3}]^{n+}$ has one less plane of symmetry compared to $[\mathbf{Y1}]^{n+}$ and $[\mathbf{Y2}]^{n+}$ (ignore ethyl substituents in OEP ligand when considering symmetry).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



9.5	**<u>Indicate</u>**: a) the charge "$n+$" of phosphorus porphyrin complexes; b) the number of planes of symmetry $N(\sigma)$ that complex $[\mathbf{Y1}]^{n+}$ has. **SOLUTION:** a) $n+$ = 1+ (1 pt) b) $N(\sigma)$ = 5 (1 pt)	2.0 pt

9.6 **<u>Draw</u>** the structures of $[\mathbf{Y1}]^{n+}$, $[\mathbf{Y2}]^{n+}$, and $[\mathbf{Y3}]^{n+}$. 4.0 pt

SOLUTION:

		
[Y1]$^{n+}$ (1 pt)	**[Y2]**$^{n+}$ (1 pt)	**[Y3]**$^{n+}$ (2 pt, 1 pt if Br instead of F)

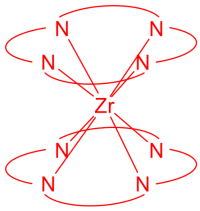
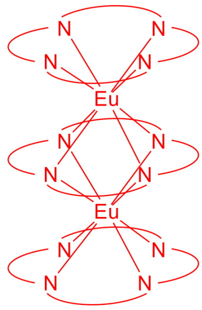
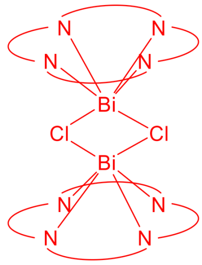
If all are incorrect: +1 pt bonus for correct symmetry and/or the same charge of all structures.

Part C. Porphyrin sandwiches

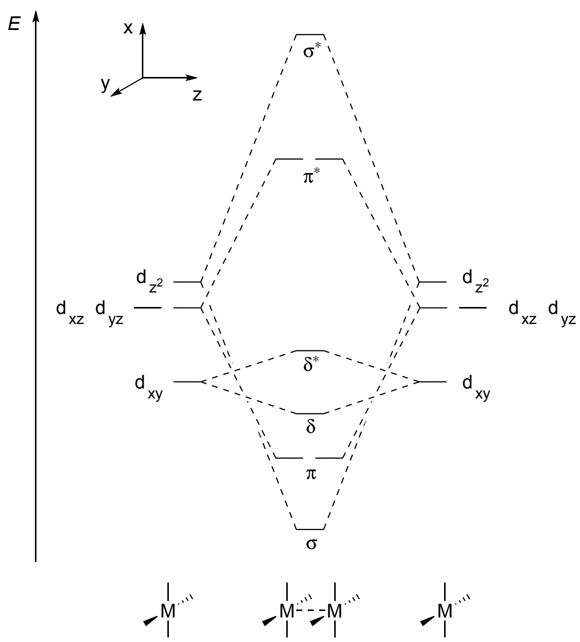
Porphyrin sandwich-type complexes form when there are several porphyrin rings aligned relative to each other. Examples are Zr(OEP)$_2$, Eu$_2$(OEP)$_3$, Bi$_2$(OEP)$_2$Cl$_2$ that have at least 3 planes of symmetry each. Note that the hole size in the OEP ligand is ca. 4.0 Å, and the average metal–N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

9.7 **Suggest** the structures of $Zr(OEP)_2$, $Eu_2(OEP)_3$, and $Bi_2(OEP)_2Cl_2$. You may use a simplified representation of the OEP ligand. 3.0 pt

SOLUTION:

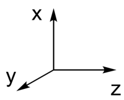
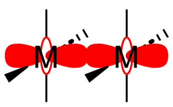
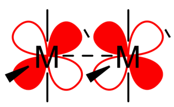
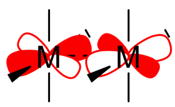
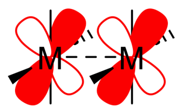
		
$Zr(OEP)_2$ (1 pt)	$Eu_2(OEP)_3$ (1 pt)	$Bi_2(OEP)_2Cl_2$ (1 pt)

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



9.8 **Draw** the σ (d_{z^2}+d_{z^2}), π (d_{xz}+d_{xz}), π (d_{yz}+d_{yz}), and δ (d_{xy}+d_{xy}) bonding orbitals according to the specified coordinate system. 4.0 pt

SOLUTION:

 	 	 	 	
	σ (d_{z^2} + d_{z^2}) (1 pt)	π (d_{xz} + d_{xz}) (1 pt)	π (d_{yz} + d_{yz}) (1 pt)	δ (d_{xy} + d_{xy}) (1 pt)

If orbital phases are not indicated: 1 pt penalty (1–2 orbitals) or 2 pt penalty (3–4 orbitals).

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

SOLUTION:

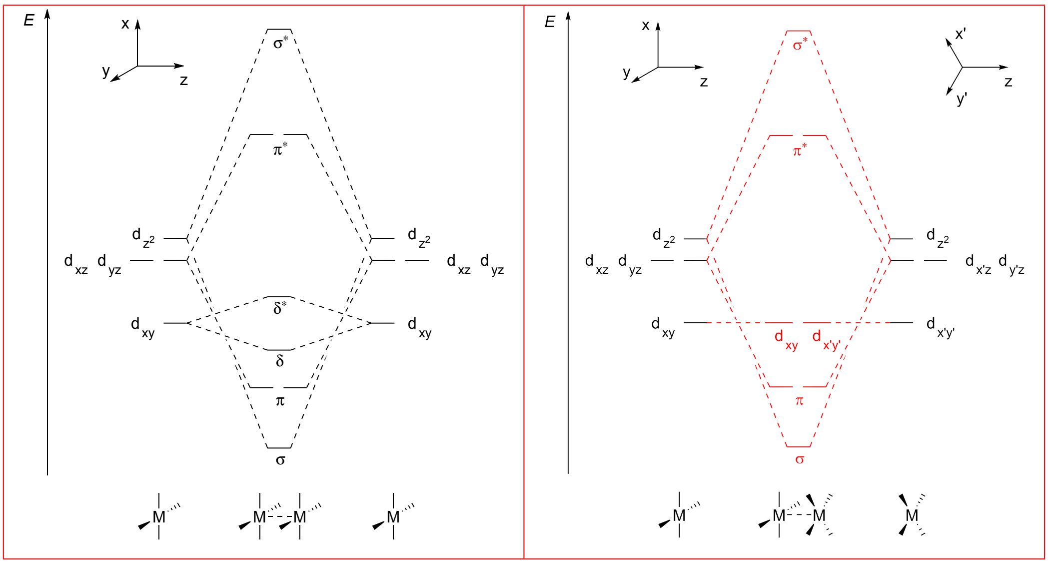
$[Mo(OEP)]_2$	$[Ir(OEP)]_2$	$[Re(OEP)]_2^+$
4 (1 pt)	1 (1 pt)	3.5 (1 pt)

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: 4.0 pt

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

SOLUTION:



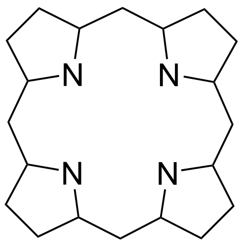
σ/σ^*: b (remains unchanged) – 1 pt.
π/π^*: b (remains unchanged) – 2 pt.
δ/δ^*: d (decreases to zero, i.e., d_{xy} and $d_{x'y'}$ are non-bonding) – 1 pt.

Problem 9 Porphyrin complexes

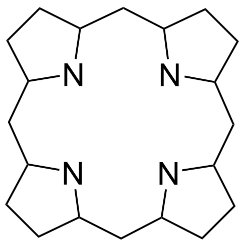
9.1 (4.0 pt)

a	b	c	d	e
$C_{32}H_{34}N_4$	$C_{55}H_{74}N_4O_5$	$C_{33}H_{34}N_4O_3$	$C_{33}H_{34}N_4O_2$	$C_{35}H_{36}N_4O_5$

9.2 (7.0 pt)



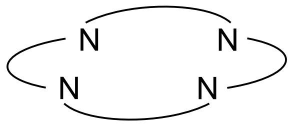
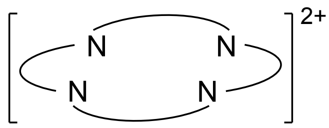
A ($C_{33}H_{36}N_4O_2$)



B ($C_{32}H_{32}N_4OV$)

9.3 (1.0 pt)

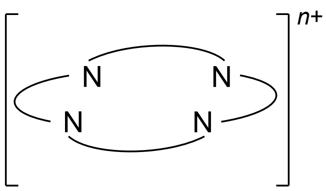
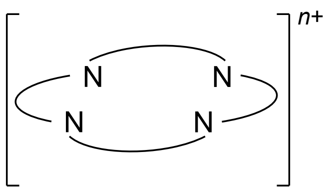
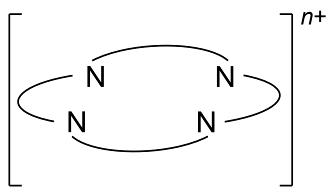
9.4 (3.0 pt)

		
X1	**X2**	$[\mathbf{X3}]^{2+}$

9.5 (2.0 pt)

a) $n+$ =	b) $N(\sigma)$ =

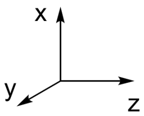
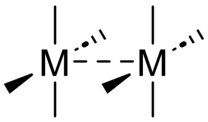
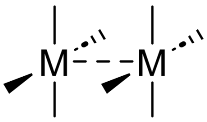
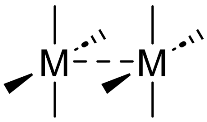
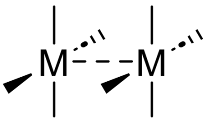
9.6 (4.0 pt)

		
$[\mathbf{Y1}]^{n+}$	$[\mathbf{Y2}]^{n+}$	$[\mathbf{Y3}]^{n+}$

9.7 (3.0 pt)

$Zr(OEP)_2$	$Eu_2(OEP)_3$	$Bi_2(OEP)_2Cl_2$

9.8 (4.0 pt)

				
	σ $(d_{z^2} + d_{z^2})$	π $(d_{xz} + d_{xz})$	π $(d_{yz} + d_{yz})$	δ $(d_{xy} + d_{xy})$

9.9 (3.0 pt)

$[Mo(OEP)]_2$	$[Ir(OEP)]_2$	$[Re(OEP)]_2^+$

9.10 (4.0 pt)

σ/σ^*				π/π^*				δ/δ^*			
☐ a	☐ b	☐ c	☐ d	☐ a	☐ b	☐ c	☐ d	☐ a	☐ b	☐ c	☐ d