32nd BALTIC
CHEMISTRY
OLYMPIAD
Riga, Latvia 2026

UNIVERSITY OF
LATVIA

FACULTY OF
MEDICINE AND
LIFE SCIENCES

THEORY
EXAM

CODE: EST___

May 12th, 2026
Riga, Latvia

General Instructions

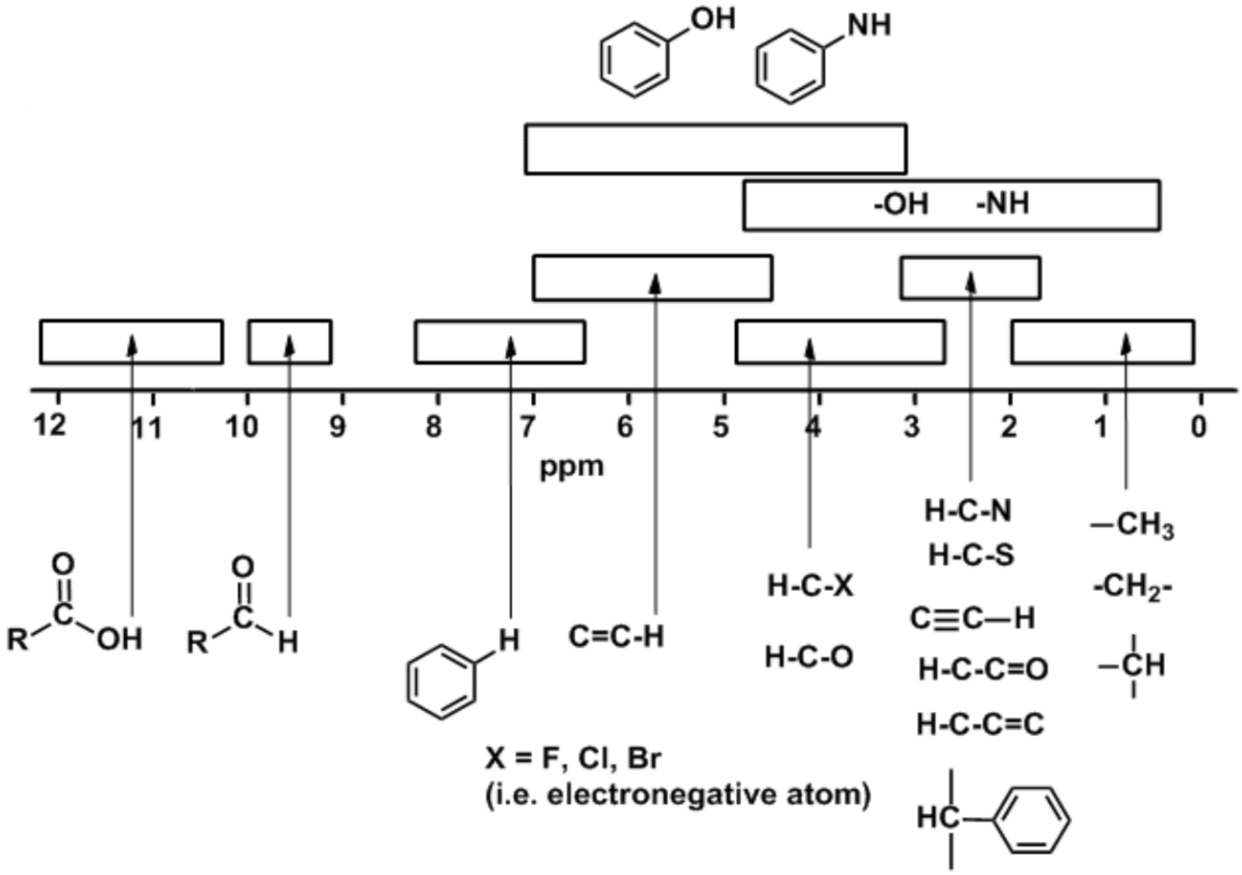
- You have 5 hours to complete the theoretical exam.
- All answers must be clearly written with a pen. Do not leave answers written with a pencil, they will not be graded!
- For drafts use the other sides of the exam paper or ask exam observers for additional draft sheet paper.
- Even if not directly required in the question, always include necessary calculations in your answer.
- Write your participant code on the top right corner of each page.
- Use of mobile phones or other electronic devices (laptops, smart watches etc) is strictly prohibited during exam.
- Talking between students is strictly prohibited during exam.
- If you have any questions, raise your hand and the exam observers will come to you.

Good luck!

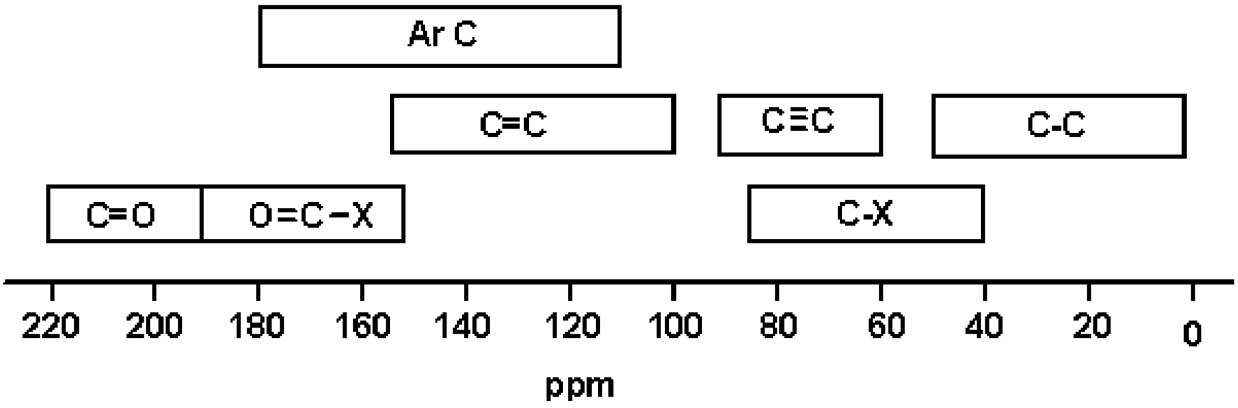
Formulas and Constants

Gas constant	$R = 8.3144\, J \cdot mol^{-1}\, K^{-1}$
Faraday constant	$F = 96485\, C \cdot mol^{-1}$
Avogadro constant	$N_A = 6.0221 \cdot 10^{23}\, mol^{-1}$
Normal pressure	$p^\circ = 1\, atm = 101325\, Pa$
STP temperature	$T = 273.15\, K$
Ideal-gas molar volume at STP	$V_m = 22.41\, L \cdot mol^{-1}$
Ionic product of water at 25 °C	$K_w = 1.0 \times 10^{-14}$, $pK_w = 14.00$
Henderson-Hasselbalch equation	$pH = pK_a + log\, \frac{[A^-]}{[HA]}$
Electric charge	$Q = It$
Current from current density	$I = jA$
Amount of electrons	$n(e^-) = \frac{Q}{F}$
Faraday's law of electrolysis	$m = \frac{MIt}{zF}$
Gibbs free energy relation	$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$
Gibbs free energy and equilibrium	$\Delta G^\circ = -RTlnK$
Van 't Hoff equation	$ln\ K = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}$

Chemical Shifts in ^1H NMR



Chemical Shifts in ^{13}C NMR



Periodic Table

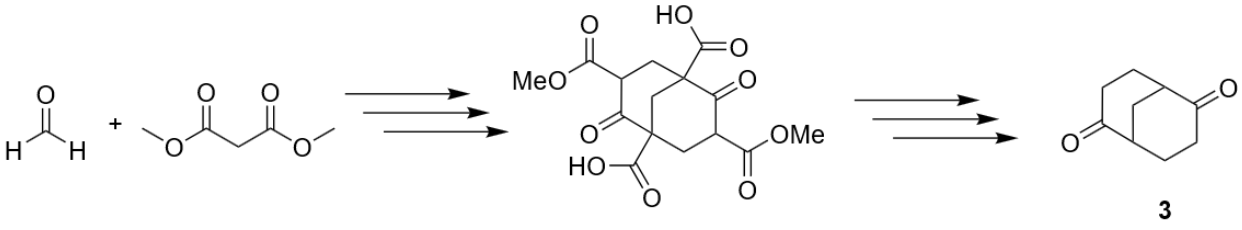
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 H 1.008																	2 He 4.003
3 Li 6.94	4 Be 9.01											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
11 Na 22.99	12 Mg 24.31											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.06	17 Cl 35.45	18 Ar 39.95
19 K 39.10	20 Ca 40.08	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 -

Problem 1. 80 Points. 10% of Total Score.

Building Blocks for Supramolecules

Bicyclo[3.3.1]nonane-2,6-dione (**3**) is perhaps the most useful and easily available starting material for the synthesis of many of bicyclo[3.3.1]nonane (**BCN**) derivatives, which are used as building blocks in supramolecular chemistry. The diketone molecule is C_2 –symmetric and thus chiral.



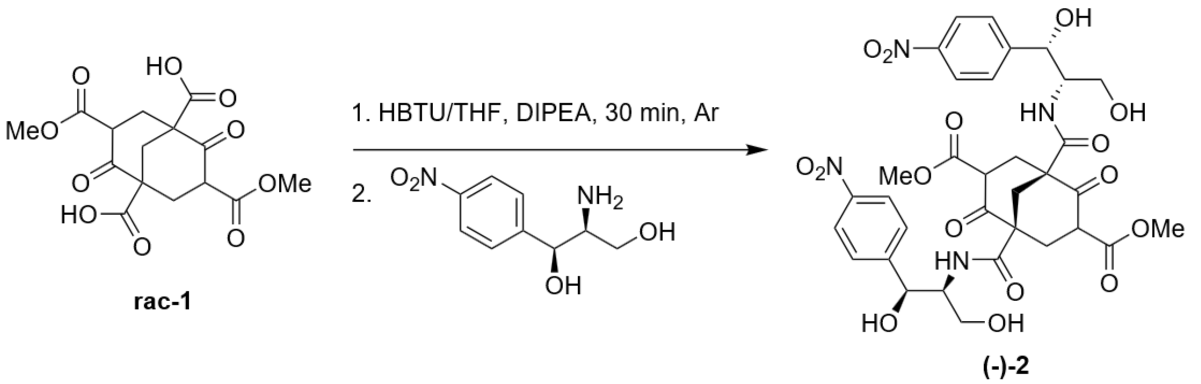
rac-1

3

Scheme 1. Synthesis of bicyclo[3.3.1]nonane-2,6-dione.

1. While preparing **1**, it was observed that over time it degrades iron spatulas. Draw a complex, which is formed when **1** reacts with Fe^{3+}. (10 points)

Since it is impossible to separate **rac-1** by traditional column chromatography, enantiomeric resolution must be performed. The idea is to produce a mixture of diastereomers, which can be purified more easily. To resolve **rac-1**, a chiral amine was used:

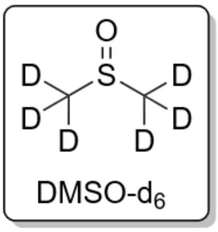


Scheme 2. Chiral resolution of **rac-1**.

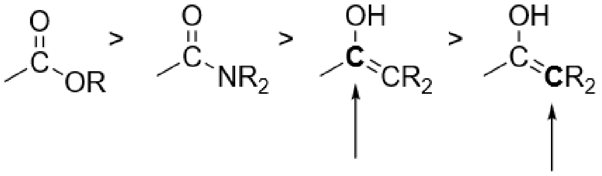
HSQC (*Heteronuclear Single Quantum Correlation*) is an experiment, used to determine proton-carbon single bond correlations, where proton shifts lie along the X axis and carbon along the Y axis, allowing to identify, which hydrogen atoms are connected to a specific carbon atom.

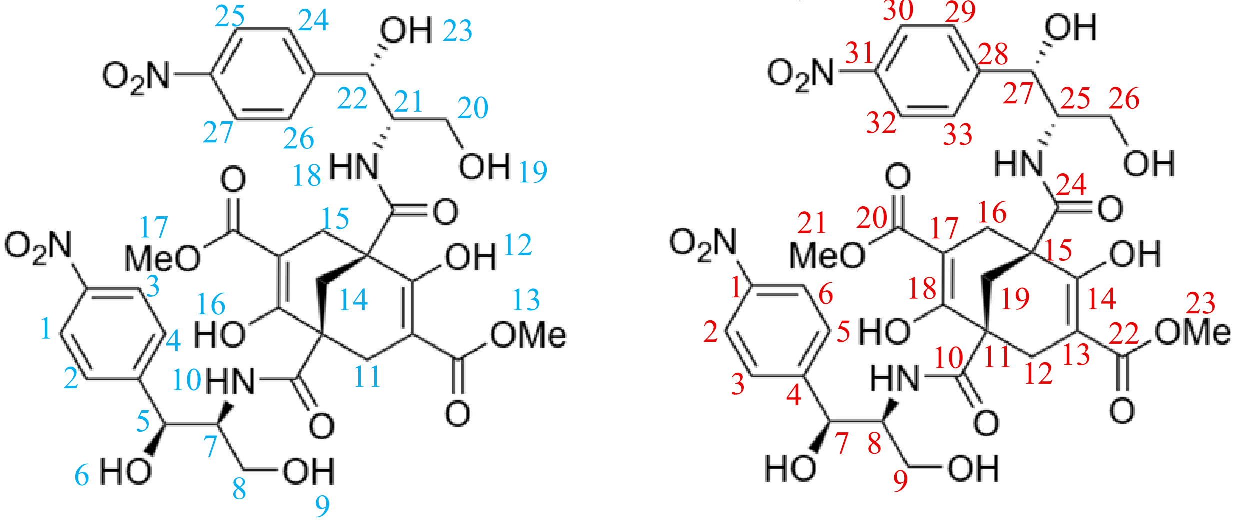
2. After purification of **(-)-2** by column chromatography, ^1H,^{13}C and HSQC NMR spectra in DMSO-d$_6$ were recorded. Assign H and C atoms to their corresponding signals. Differentiate between diastereotopic hydrogens with ‘. (25 points)

Hints:

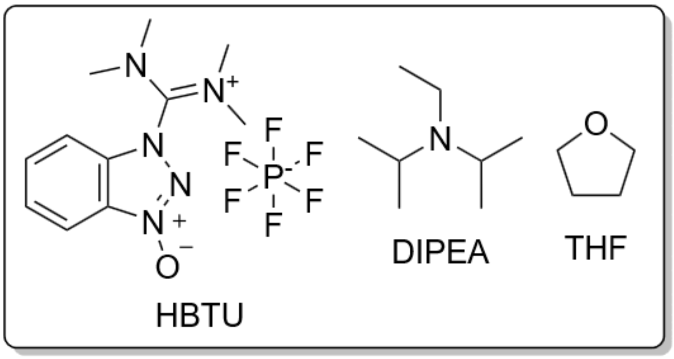

DMSO-d$_6$

- No C-H interactions are observed with carbons δ > 140 ppm
- There is only one impurity in the sample
- Some signals are already assigned to their corresponding atoms
- **^{13}C NMR (δ):**





δ, ppm	**H #**	**δ, ppm**	**C #**
11.92 (s, 2H)		172.6	
8.18 (d, *J* = 8.3 Hz, 4H)		170.3	
7.59 (d, *J* = 8.4 Hz, 4H)		169.5	
7.44 (d, *J* = 8.9 Hz, 2H)	10,18	165.1	Impurity
5.81 (d, *J* = 5.3 Hz, 2H)	6,23	152.5	
5.06 (br s, 2H)		146.8	
4.83 (t, *J* = 5.5 Hz 2H)	9,19	127.7	
4.09 (m, 2H)		123.3	
3.70 (s, 6H)		97.6	
3.62 – 3.56 (m, 2H)		69.9	
3.30 (m, 2H)		60.5	
2.69 (s)	Impurity	56.9	
2.55 (d, *J* = 16.3 Hz, 2H)		52.4	
2.40 (d, *J* = 16.4 Hz, 2H)		47.7	
2.06 (s, 2H)		38.7	Impurity
		35.7	
		30.6	12,16



To determine the impurity mentioned in **Task 2**, a sample was analysed using *Gas Chromatography - Mass Spectrometry* (GC-MS) with electrospray ionisation (EI), most intense peaks: m/z = 116, 72, 44. *High-Resolution Mass Spectrometry* (HRMS) analysis determined monoisotopic molar mass of the impurity to be 116.0950 g/mol.

3. Draw the molecular structure of the impurity mentioned in **Task 2**. (15 points)

Isotope	**Mass (Da)**	**Isotope**	**Mass (Da)**
^{1}H	1.007825	^{16}O	15.994915
^{12}C	12.000000	^{19}F	18.998403
^{14}N	14.003074	^{31}P	30.973762

Answer =

Compound **4** is often used to cross-link **BCN** derivatives. A 0.5000 g sample of **4** was burned, and combustion products were passed through designated columns: first, anhydrous $CaCl_2$, then NaOH solution. The first column mass increased by 0.2192 g and the second by 1.0722 g. In another experiment, 0.5000 g of **4** was decomposed in boiling H_2SO_4 and converted to ammonium salts, which, after purification, required 10.15 mL of 0.6000 M NaOH to neutralise.

4. Determine the molecular formula of **4**. (18 points)

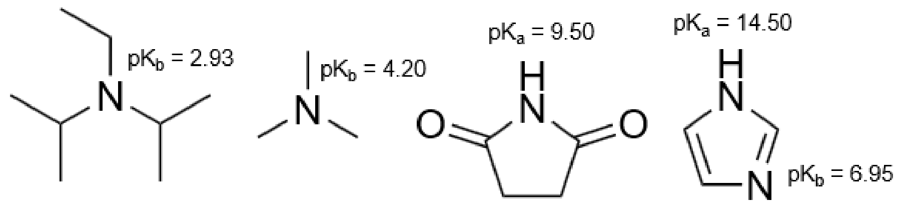
Hints:

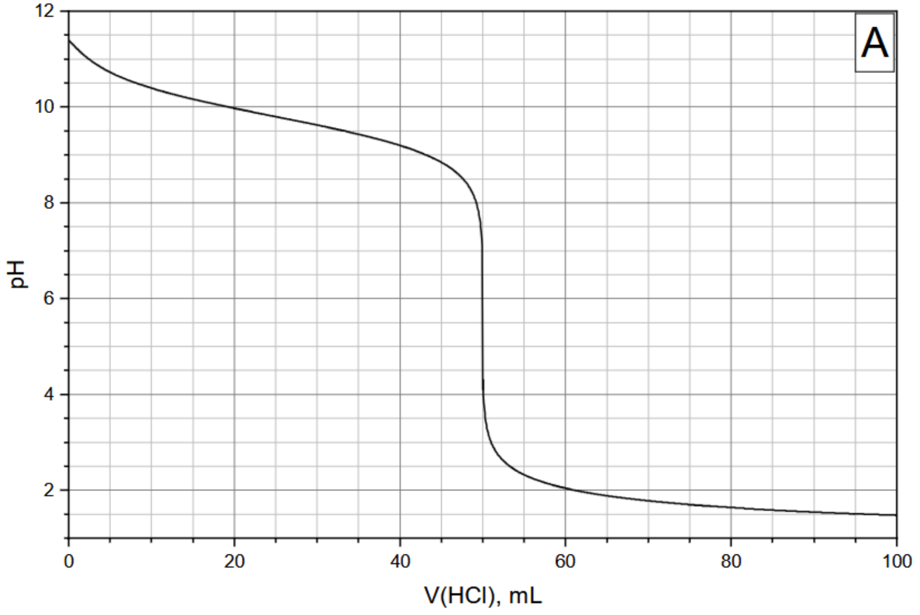
- Mass of **4** is less than 200 g/mol
- Assume that the only nitrogen combustion product was N_2

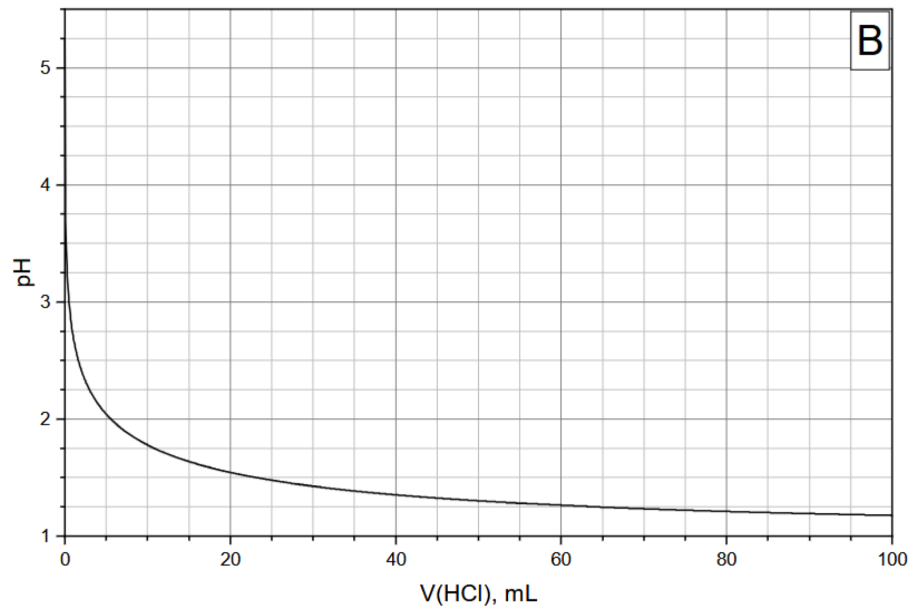
Answer = __________

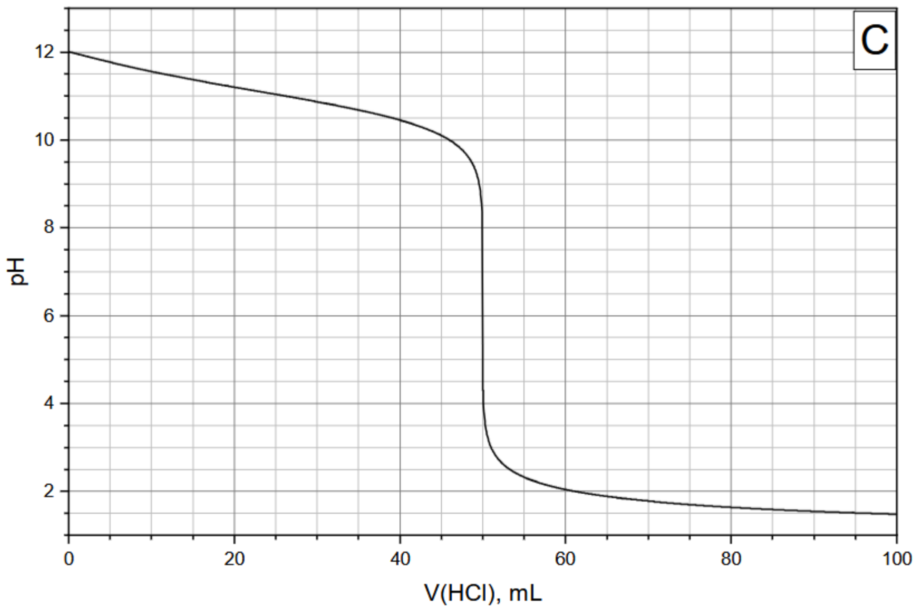
DIPEA, mentioned in **Scheme 2**, functions as a proton acceptor and, like most amines, can react with acids, forming salts in the process. This property of amines is exploited during acid-base extractions and titrations.

5. Assign each titration curve to a specific compound. (12 points)




A
12
10
8
6
4
2
pH
0
20
40
60
80
100
V(HCl), mL


B
5
4
3
2
1
pH
0
20
40
60
80
100
V(HCl), mL


C
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2
pH
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40
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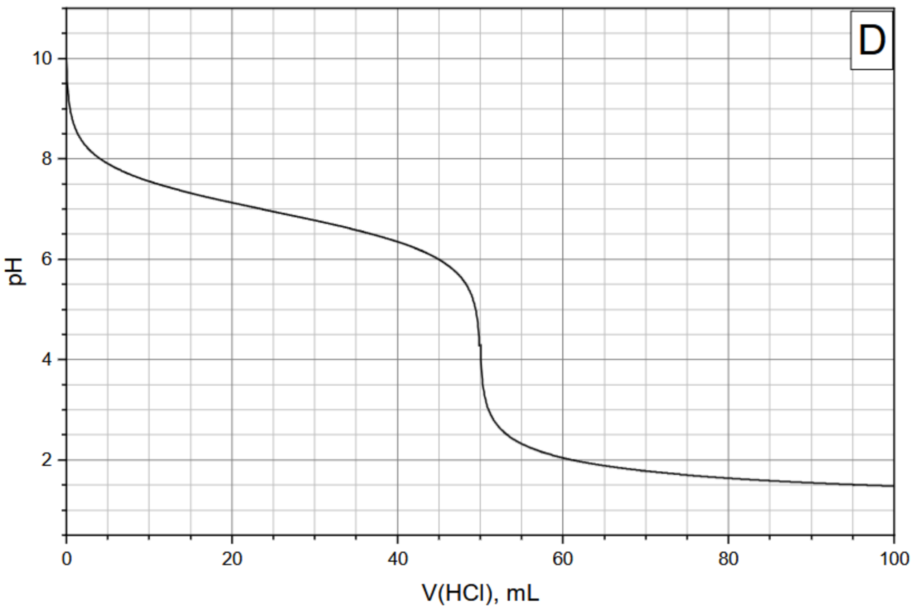
80
100
V(HCl), mL


D
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8
6
4
2
pH
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20
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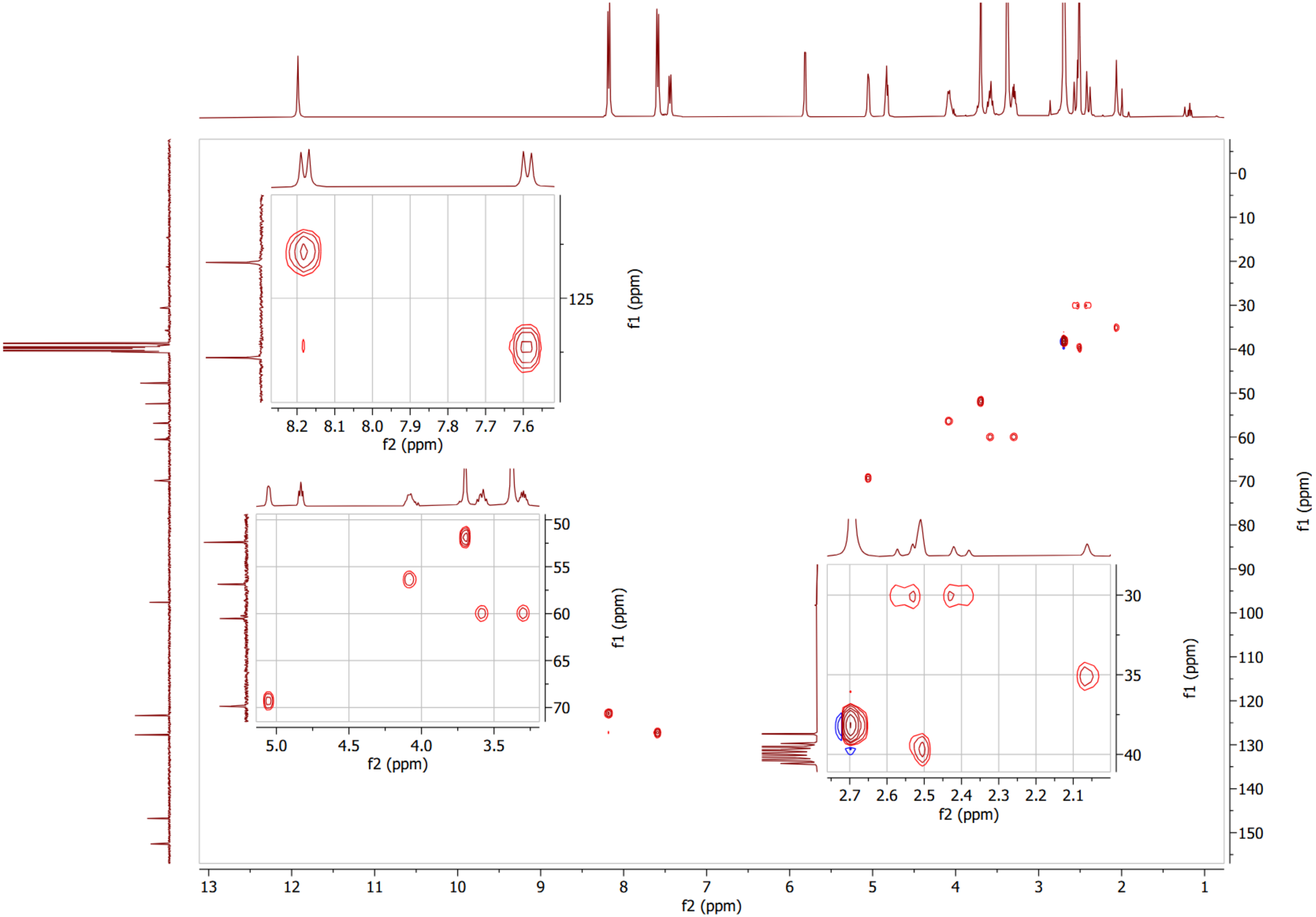
60
80
100
V(HCl), mL



f2 (ppm)
13
12
11
10
9
8
7
6
5
4
3
2
1
f1 (ppm)
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
f2 (ppm)
8.2
8.1
8.0
7.9
7.8
7.7
7.6
f1 (ppm)
125
f2 (ppm)
5.0
4.5
4.0
3.5
f1 (ppm)
50
55
60
65
70
f2 (ppm)
2.7
2.6
2.5
2.4
2.3
2.2
2.1
f1 (ppm)
30
35
40

Problem 2. 20 Points. 10% of Total Score.

Estonian Magnet Puzzle

In 2025, the largest neo magnet production plant in Europe was opened in Estonia. Its products are based on a magnetic alloy whose main component contains three elements **A**, **B**, and **C** in mass proportions **A** : **B** : **C** = 1.00 : 72.32 : 26.68. The most common oxides of all three elements have the same general formula, X_2O_3. **Reaction 1:** When the oxides of **A** and **B** are co-reduced with carbon to form 1.0 kg of binary compound **AB,** this also releases 1.0 m^3 of carbon monoxide at STP (1 atm and 0 °C). **Reaction 2:** The alloy is then produced by fusing **AB** with **C** and additional **B**. **Reaction 3:** The main challenge is obtaining pure metal **C**; a novel way to produce **C** is by electrolysis of a molten **C** chloride. **Reactions 4–6:** The chloride of **C** is obtained from the mineral bastnäsite (**C**CO_3F) by sequential treatment with sulfuric acid, sodium hydroxide, and hydrochloric acid. Electrodeposition of **C** within 1,0 hours on a 1,0 m^2 electrode at 1$\underline{0}$ A/cm^2 should give 179 kg of metal **C**.

1. Determine elements **A**, **B**, and **C**. Show your calculations. (6 points)

2. Write the chemical equations of all the mentioned **reactions 1–6**. If you failed to determine element **A**–**C**, use labels **A**–**C**. (6 points)

Natural bastnäsite does not contain only element **C**. Significant amounts of four other “light” elements **D**, **E**, **F**, and **G** are also present in this carbonate fluoride (**X**CO_3F). In the periodic table, elements **C**–**G** are close neighbours. Metal **D** can remain in the desired alloy together with metal **C**, while elements **E**, **F**, and **G** must be removed. After dissolution of bastnäsite in sulfuric acid, ions of **G** can be selectively oxidized and precipitated as hydroxide by increasing the pH to ~5. Ions of **E** can then be efficiently separated by solvent extraction due to its smaller ionic radius and different coordination ability. By further increasing the pH, hydroxides of **C** and **D** can be precipitated, while ions of **F** remain in solution. Ionic radii of ions **C**–**G** (in coordination of 9) and K_{sp} values are given in the table.

	C	**D**	**E**	**F**	**G**
r(ion), nm	0.116	0.118	0.102	0.122	0.120
$-\log(K_s(E(OH)_3))$	23.34	22.33	24.07	20.06	21.84

3. Determine elements **D**, **E**, **F**, and **G**. (4 points)

4. At some pH, precipitation of **C** and **D** is complete at least by *x*% each, while the concentration of **F** ions in solution remains at least *x*% of its initial value. Find the maximal *x* value and estimate the corresponding pH. Assume equal initial concentrations of 1.0 M. (4 points)

Problem 3. 28 Points. 12% of Total Score.

Insight to the self-assembly

Suppose the average number of monomers forming a micelle is n. Then the chemical equilibrium between micelles M_n and their constituent surfactant molecules is described by equation

$$n\, M \rightleftarrows M_n$$

The change in standard Gibbs free energy for micellization per mole of neutral monomer can be approximated as

$$\Delta G^{o}_{M,mic} \approx RTln\, [M]_{CMC} \#(1)$$

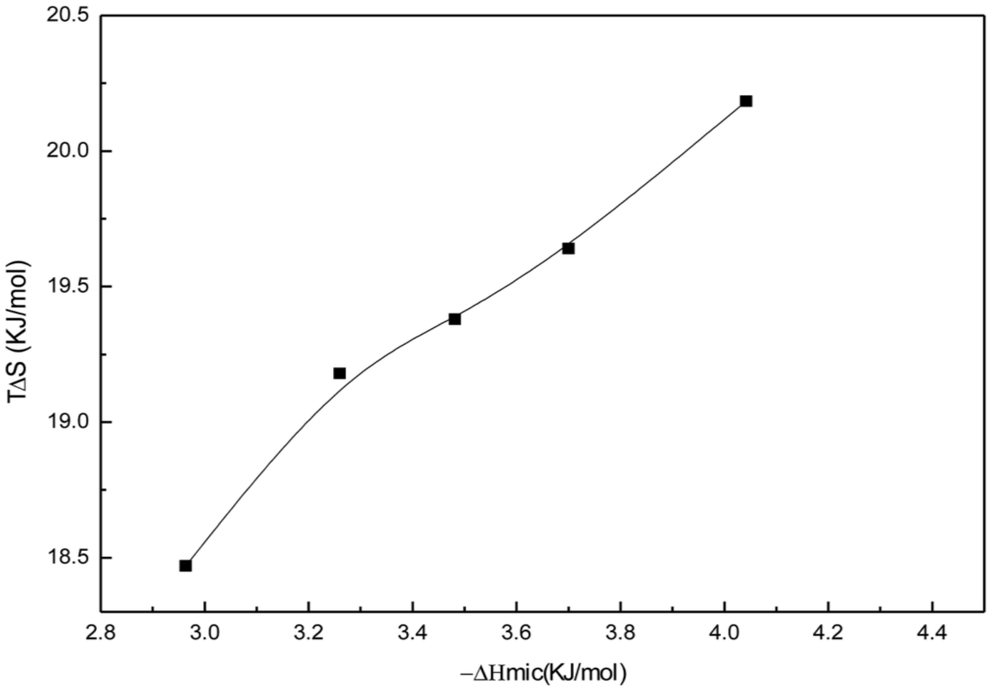
where $[M]_{CMC}$ is critical micelle concentration, above which all additional monomers added to the system will form micelles.

1. Show that n must be sufficiently large for this approximation to be valid. (3 points)

2. If surfactants are added to aqueous solution of with high ionic strength, not only spherical M_n but cylindrical $M_{c=4n}$ micelles might also form. In the solution, an equilibrium between monomer and two types of micelles is established. Find the expression for the fraction of monomers that are present in the solution as M_c micelles using $[M]$, K_n, K_c. (2 points)

3. The effect of alkyl chain length on surfactant solubility in water was explored. It was found that each additional $–CH_2–$ group contributes about +9.5 J/(mol·K) to the standard entropy of dissolution. Assuming that standard enthalpy of dissolution and activity coefficient does not vary significantly with the chain length, calculate the ratio of *n*-heptyl~X and *n*-nonyl~X solubility (polar head is denoted as X). (4 points)

Graphical variation of ΔS_{mic} with $-\Delta H_{mic}$ in aqueous solutions for a generic fatty acid ester is given below.



4. Circle the correct statement(s). (2 points)

- micellization is enthalpically driven process;
- micellization is entropically driven process;
- micellization becomes less spontaneous at higher temperatures;
- micellization becomes less spontaneous at lower temperatures;
- micellization is exothermic process;
- micellization is endothermic process.

Consider this situation: two different surfactants S and T are mixed in the solution. After enough time passes, their monomers pack together to form ST_2 and S_2T_3 aggregates.

$$S + 2T \rightleftarrows ST_2\#\left(lg\ K_{ST_2}\ = 5.72\right)$$
$$2S + 3T \rightleftarrows S_2T_3\#\left(lg\ K_{S_2T_3}\ = 7.95\right)$$

5. 1.62 g of S (M = 288.38 g/mol) and 0.18 g of T (M = 364.45 g/mol) were dissolved in 500 mL of water. Calculate molar concentrations of all particles present in the solution. (8 points)

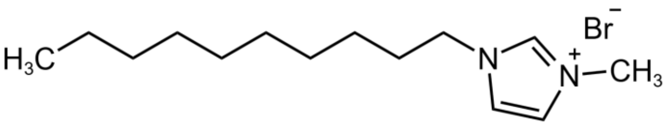


Fig. 1. C$_{10}$mimBr.

Surfactants can also be ionic – besides being ionic liquid 1-Decyl-3-methylimidazolium bromide (abbreviated as C$_{10}$mimBr) is also a common cationic surfactant. In reality, eq. (1) must be corrected for ionic surfactants due to counter-ion binding to the micelle's surface and has the following form:

$$\Delta G^{o}_{mic} \approx (1+\beta)RTln\,[M]_{CMC}\,\#(2)$$

where β is degree of counter-ion binding.

CMC of aqueous C$_{10}$mimBr solutions at different temperatures was determined using conductivity measurements. Data is given in the table below.

Table 1. Thermodynamic data of aqueous C$_{10}$mimBr solutions.

T, K	298.15	308.15	318.15	328.15	338.15	348.15	358.15
β	0.321	0.417	0.481	0.504	0.511	0.515	0.518
$[C_{10}mimBr]_{CMC}, mM$	0.91	1.49	2.03	2.28	2.40	2.50	2.58

6. Assuming that aggregation number is temperature-independent, calculate standard micellization enthalpy and entropy of C$_{10}$mimBr. **Provide the graph.** (8 points)

7. Which of the following conditions result in increased CMC of ionic surfactants in aqueous solutions? Circle the correct answer(s). (2 points)

- Increase in nonpolar chain length of surfactant;
- Increase in charge density of hydrophilic head group;
- Increase in ionic strength of the solution;
- Increase in isovalent counter-ion radius;
- Increase in valency of the counter-ion;
- Increase in nonpolar chain branching.

The type of aggregate structure formed depends on many different factors, though can be predicted by parameter N_S, referred as the packing ratio:

$$N_S = \frac{V_C}{L_C \cdot \sigma_A} \#(3)$$

where V_C is the volume of the hydrophobic part of the surfactant, L_C is the length of the hydrocarbon chain, and σ_A is the effective area per head group.

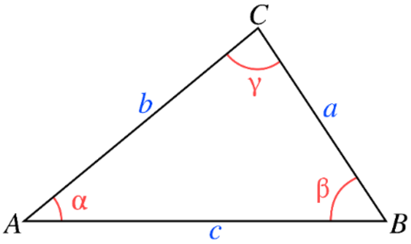
Table 2. Expected aggregate characteristics in relation to surfactant packing ratio.

N_S	**Expected aggregate structure**
<0.33	Spherical or elipsoidal micelles
0.33-0.5	Cylindrical micelles
0.5-1.0	Vesicles
1.0	Planar bilayers
>1.0	Inverted micelles

8. By calculating the packing ratio of C_{10}mimBr, show which structural type of micelles does it form. C_{10}mimBr has an effective head group area in water of 0.57 nm^2. **Note:** bond, connecting the last atom of hydrophobic tail to the first atom of hydrophilic head, is not included in the L_C. (7 points)

You may use this data:

- M(n-C_6H_{14}) = 86.178 g/mol, ρ(n-C_6H_{14}) = 0.661 g/cm^3;
- M(n-$C_{12}H_{26}$) = 170.340 g/mol, ρ(n-$C_{12}H_{26}$) = 0.749 g/cm^3;
- Van der Waals radius of terminal methyl group is 150 pm;
- C–C bond length is 154 pm.



$$c^2 = a^2 + b^2 - 2abcos\,\gamma$$

Problem 4. 28 Points. 12% of Total Score.

Kinetics of formic acid electrooxidation

Electrooxidation of formic acid is a promising reaction for fuel cell applications. Depending on the catalyst materials, the electrooxidation proceeds by different mechanisms. Notably, the most common problem of CO poisoning is not observed on palladium catalysts. In this task we will explore the kinetics of formic acid electrooxidation on a palladium catalyst.

Before beginning the task, let us provide a brief background on kinetic analysis of electrochemical reactions on heterogenous catalysts. In general, we can distinguish between oxidation, reduction and non-electrochemical reactions:

$A + * \xrightarrow{k_1} A*$ (non-electrochemical)

$A* \xrightarrow{k_2} A^+ + e^- + *$ (oxidation)

$A* + e^- \xrightarrow{k_3} A^- + *$ (reduction),

where * denotes empty surface site of the catalyst, and $A*$ denotes particle A adsorbed on surface site of the catalyst.

The rate equations for those elementary reactions accordingly are:

$r_1 = k_1[A](1-\theta_A)$,

$r_2 = k_2\theta_A e^{\alpha f E}$,

$r_3 = k_3\theta_A e^{-(1-\alpha)fE}$,

where $1-\theta_A$ is the surface coverage of empty sites, θ_A is the surface coverage of $A*$ species, α is the reaction symmetry factor (usually considered to be 0.5), $f = \frac{F}{RT}$, and E is the applied potential.

The current density dependence on applied potential $j(E)$ for an electrooxidation reaction can be expressed in terms of elementary rate equations as follows:

$j(E) = F\sum r_{i,\mathrm{ox}} - F\sum r_{i,\mathrm{red}}$, where r_i are rates of oxidation and reduction steps.

The steps for the proposed mechanism for formic acid oxidation on palladium catalyst are as follows:

$HCOOH + \mathbf{2}* \xrightarrow{k_1} HCOO* + H*$ (1)

$H* \xrightarrow{k_2} H^+ + e^- + *$ (2)

$HCOO* \xrightarrow{k_3} CO_2 + H^+ + e^- + *$ (3)

$HCOO* \xrightarrow{k_4} CO_2 + H*$ (4)

$H_2O + * \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} OH* + H^+ + e^-$ (5)

1. Write the reaction rate equations for each of the elementary steps. (5 points)

$r_1 =$

$r_2 =$

$r_3 =$

$r_4 =$

$r_5 =$

2. Assuming steady state for all adsorbed species, obtain equations relating the rate equations. (3 points)

3. Write the expression for current density dependence on potential $j(E)$ in terms of reaction rate constants and surface coverages of adsorbates. (2 points)

4. Obtain expression for θ_H in terms of θ_{HCOO}. (3 points)

$\theta_H =$

5. Obtain implicit equation of the variation of θ_{HCOO} with potential. (9 points)

(Hint: The implicit equation should have a form of $\alpha\theta_{HCOO} + \beta\theta_{HCOOH}^{\frac{1}{2}} + \gamma = 0$, *where* α, β, γ *are coefficients to be determined dependant on concentrations, reaction rate constants, applied potential etc.)*

6. Briefly explain how obtained equations can be used to obtain plots relating surface coverage with applied potential. (2 points)

Problem 5. 25 Points. 10% of Total Score.

A Basket Case

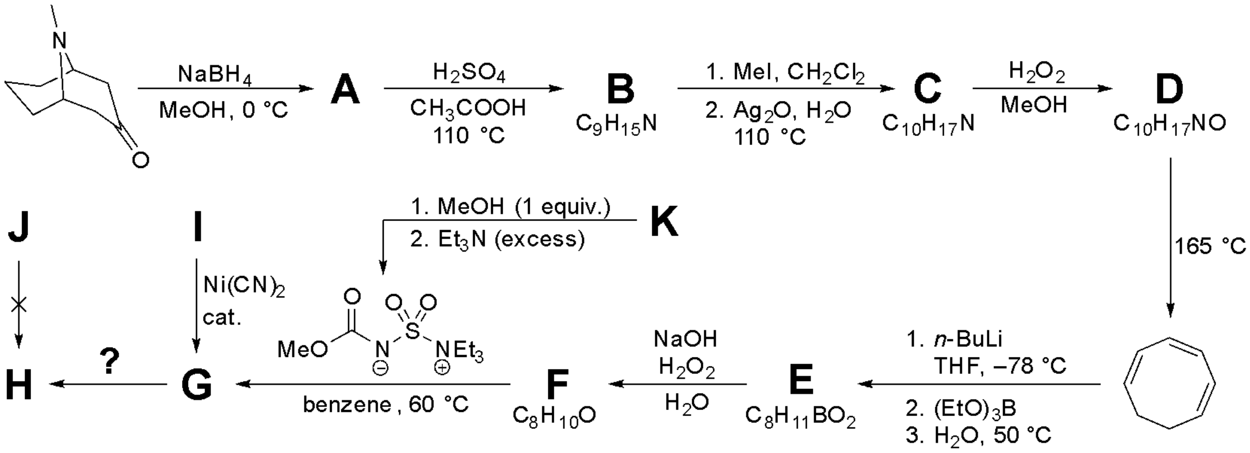
Basketane is a hydrocarbon which – as can be inferred from its name – structurally resembles a basket. This “wannabe cubane” was originally synthesized by Masamune, Cuts and Hogben in 1965 from the another no less curious hydrocarbon, **G**.

In turn, compound **G** was first prepared from pseudopelletierine by the German chemist Richard Wilstätter exactly 60 years earlier. However, his original 7-step synthetic route was too long and complicated – so much so that American chemists were unable to reproduce it and even suggested that Wilstätter had in fact obtained not **G**, but its isomer **J**, a hydrocarbon widely used in polymer production.

Nevertheless, Wilstätter dispelled doubts about the structure of **G** by converting it into **H**, a hydrocarbon already known in the literature and not obtainable from **J** in this way.

The synthesis of **G** remained highly challenging until 1948, when another German chemist, Walter Reppe, reported that compound **G** can be readily obtained from the common industrial gas **I** using a nickel(II) catalyst.

A slightly modified version of Wilstätter’s synthetic protocol is provided below.



1. The reagent used in the step from **F** to **G** is called *Burgess reagent*. It can be prepared *in situ* from **K** by consecutive addition of methanol and triethylamine. Compound **K** contains chlorine and oxygen (25.05% and 33.91% by mass, respectively), and one of its atoms is *sp*-hybridized. Propose the structure of **K**. (2 points)

2. Identify the reaction conditions which Wilstätter applied to prove the structure of **G**. (1 point)

● $(CH_2OH)_2$, cat. Me_3SiCl	● MeOH, cat. HCl	● *t*-BuOK, toluene
● PhMgBr, THF; then H_2O	● Pd/C, H_2, MeOH	● O_3, CH_2Cl_2; then H_2O_2

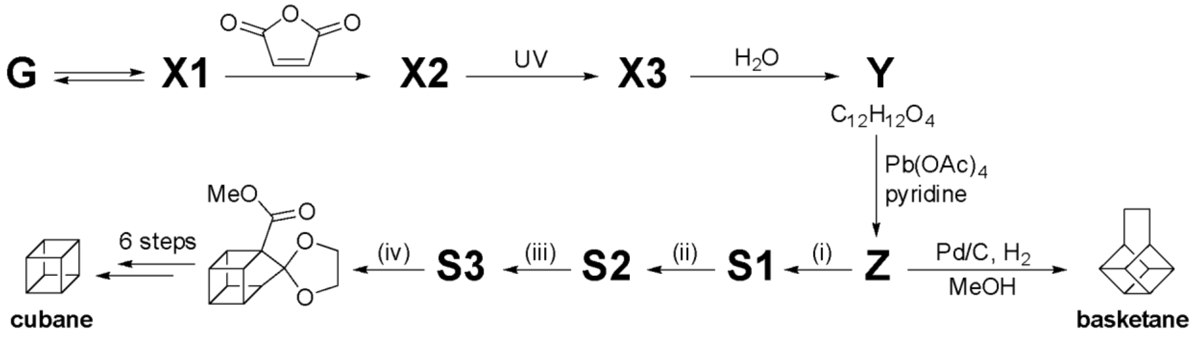
3. Draw the structures of compounds **A**–**J**. (10 points)

Hints: ***B*** *is bicyclic and* ***D*** *is zwitterionic.*

A	**B**
C	**D**
E	**F**
G	**H**

I	**J**

Basketane can be obtained from **G** in 4 steps. First, a mixture of **G** and maleic anhydride is irradiated with UV light, triggering a reaction cascade. Initially, bicyclic **X1** is formed, followed by tetracyclic **X2** and, subsequently, hexacyclic **X3**. The latter undergoes hydrolysis to afford **Y**, which then reacts with $Pb(OAc)_4$ to give multiple products: hydrocarbon **Z** (having the same empirical formula as **G**), acetic acid and two additional compounds – one (gaseous) making water acidic, the other (solid) making water sweet. Hydrogenation of **Z** affords basketane. **Z** can also serve as a cubane precursor, although the corresponding synthesis requires 10 steps.



4. Draw the structures of compounds **X**–**Z**. (5 points)

X1	**X2**

X3	**Y**
Z	*corrections*

5. Propose the appropriate reaction conditions (i)–(iv) for the initial steps in the synthesis of cubane from **Z**. (4 points)

Hint: all necessary conditions are provided in Subtask 2.

(i)
(ii)
(iii)
(iv)

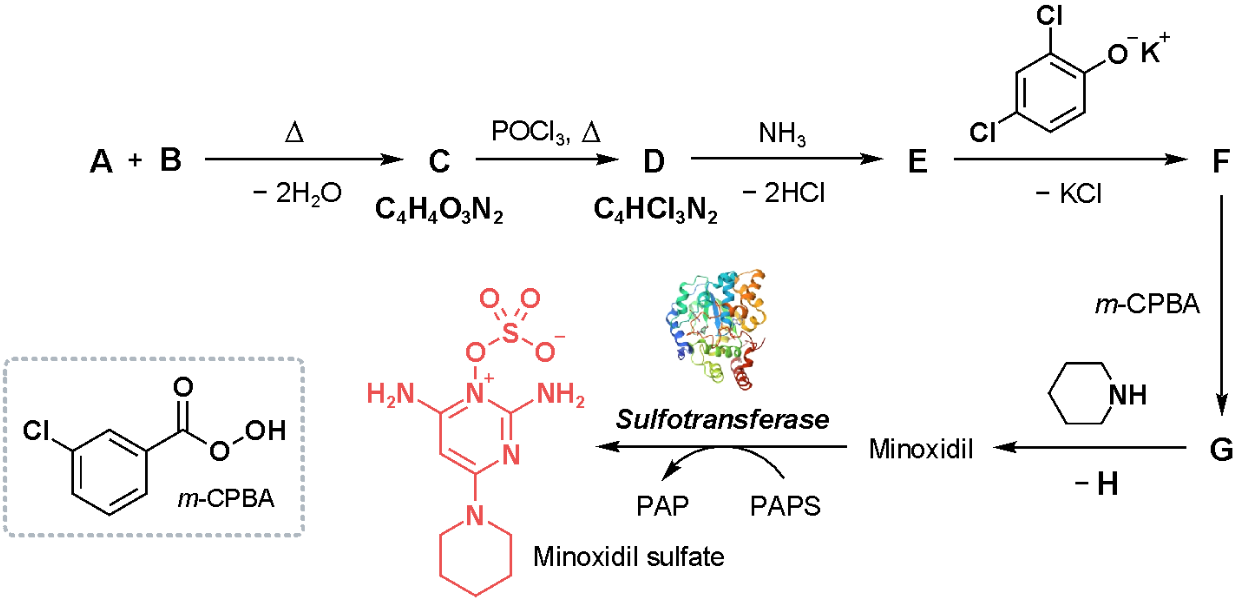
6. Draw the structures of intermediates **S1**–**S3**. (3 points)

S1	**S2**
S3	*corrections*

Problem 6. 32 Points. 10% of Total Score.

Enzymaxxing: From Midcursor to S-tier Alpha

Minoxidil is used to treat pattern hair loss. It is a prodrug that must be converted to its active sulfate form via a reaction catalyzed by the enzyme sulfotransferase. The coenzyme PAPS (3'-phosphoadenosine 5'-phosphosulfate) serves as the universal sulfuryl group ($-SO_3^-$) donor in eukaryotes and is essential for sulfation reactions. Minoxidil can be synthesized according to the following scheme:



Hints:

- *Compound **A** is produced as part of the nitrogen cycle and excreted in urine.*
- *Compound **B** is a dicarboxylic acid.*

1. Draw the structural formulas of the compounds **A**−**H**. (8 points)

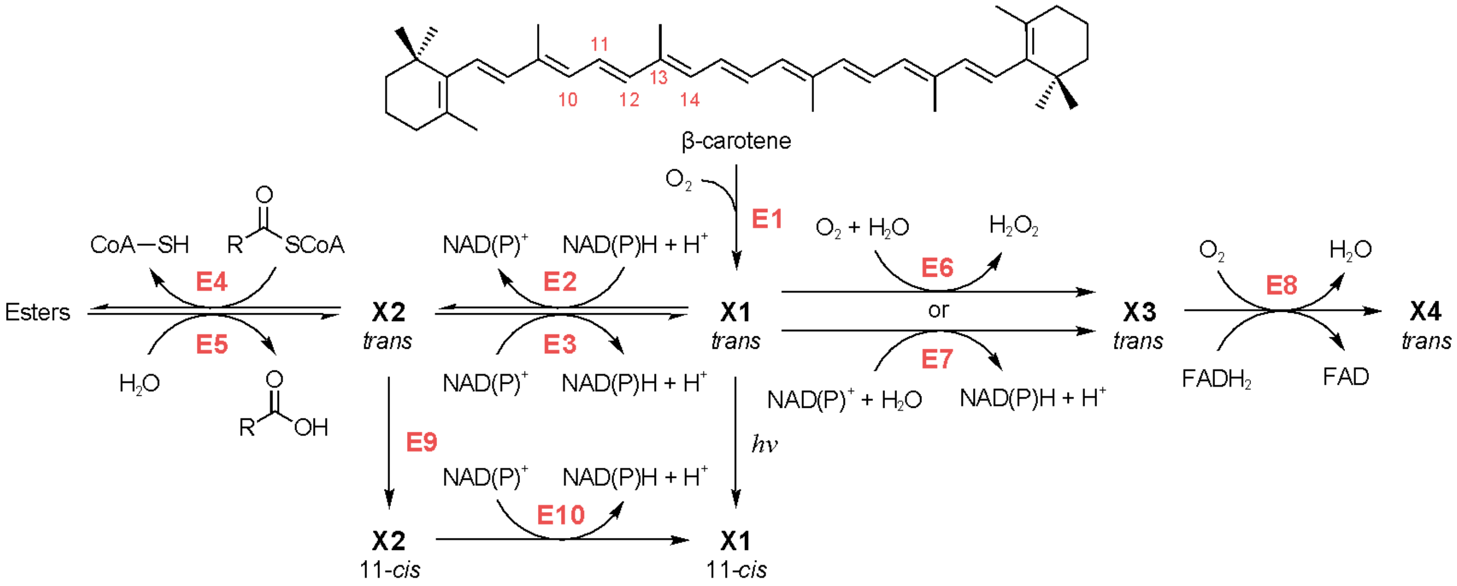
A	**B**

C	**D**
E	**F**
G	**H**

2. Draw **i)** the tautomeric form of compound **C** that is aromatic, and **ii)** a tautomeric form of Minoxidil in which no atoms carry a formal charge. (1 point)

i)	**ii)**

Tretinoin is used to treat acne, and its active ingredient is produced in the body from β-carotene, among other sources. The following scheme shows the various biosynthetic pathways leading to metabolites originating from β-carotene. Upon cleavage of β-carotene by enzyme **E1**, two equivalents of all-*trans* **X1** are formed. NAD(P)H is a redox coenzyme involved in biosynthetic reactions, where it acts as a hydride carrier. Donation of the hydride ion converts the coenzyme to its oxidized form, $NAD(P)^+$. $FADH_2$ similarly donates reducing equivalents as hydrogen atoms.



Coenzyme A (CoA or CoASH) functions as a carrier of acyl groups.

Hint:

- ***X4*** *($C_{20}H_{26}O_3$) contains 14 π-electrons in its conjugated system.*

3. **i)** Draw the structural formulas of **X1**−**X4** and 11-*cis*-**X1**. (2.5 points)

X1

X2

X3

X4

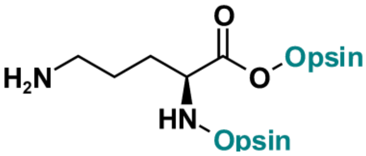
11-*cis*-**X1**

ii) Draw the structural formula of 11,13-di-*cis*-**X1**. (0.5 points)

11,13-di-*cis*-**X1**

4. Tick (✓) the enzymes (**E1**–**E10**) that catalyze the corresponding reactions. Some of the enzymes provided may not be involved in these reactions. (5 points)

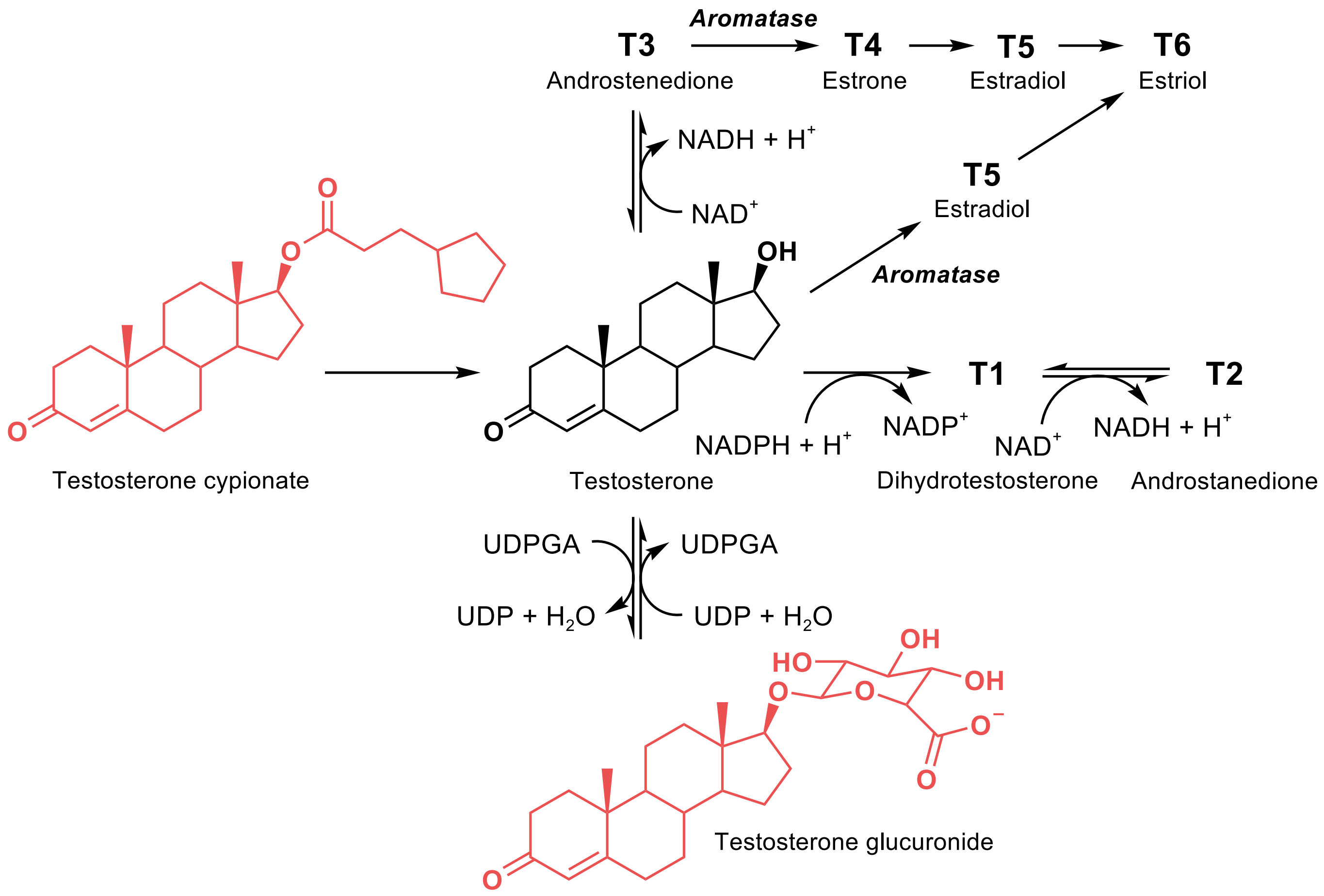
Enzyme	**E1**	**E2**	**E3**	**E4**	**E5**	**E6**	**E7**	**E8**	**E9**	**E10**
Dehydrogenase										
Deoxygenase										
Oxygenase										
Hydrolase										
Reductase										
Oxidase										
Isomerase										
Acyl transferase										



11-*cis*-**X1** initiates vision. When light enters the eye and reaches the retina, 11-*cis*-**X1** is converted into *trans*-**X1**. The *trans*-**X1** then binds to the protein opsin, which contains a lysine residue. The resulting light-sensitive pigment, formed through a protonated Schiff base linkage between *trans*-**X1** and the lysine, is called rhodopsin.

5. Draw the structural formula of the protonated Schiff base described above. (1 point)

Testosterone shots use testosterone cypionate to increase testosterone levels. They are often intended to promote muscle growth, reduce body fat, and create a more angular facial structure. While it can improve physical aesthetics, it also causes severe side effects, including acne and hair loss. Testosterone glucuronide is formed through glucuronidation, in which glucuronic acid conjugates to testosterone, increasing the molecule's water solubility.



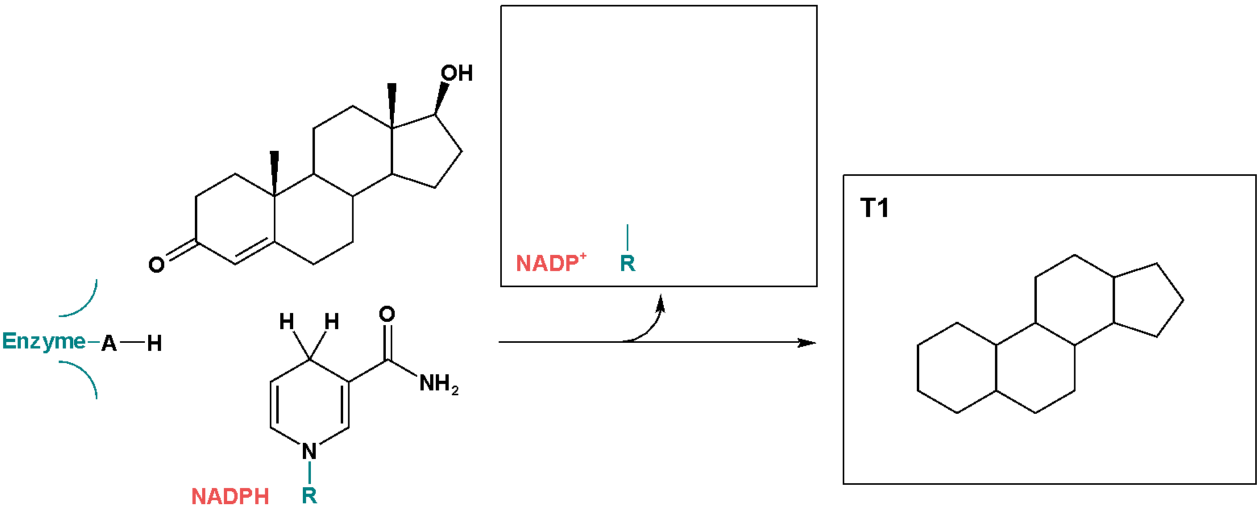
UDPGA (uridine diphosphate glucuronic acid) transfers the glucuronic acid moiety.

Hints:

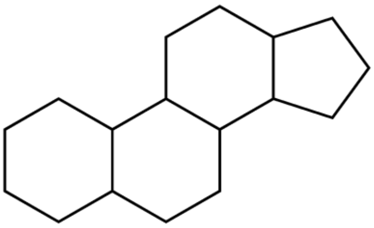
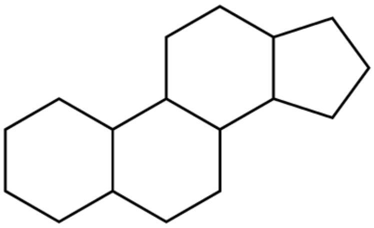
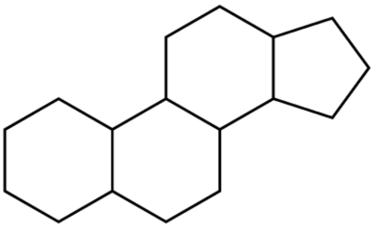
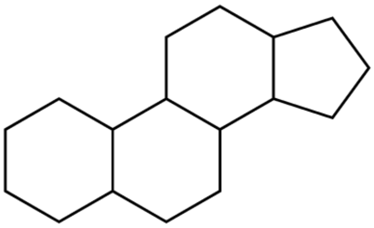
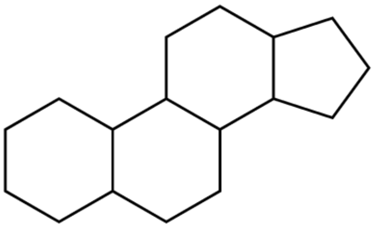
- ***T4**, **T5** ($C_{18}H_{24}O_2$) and **T6** are C18 steroids that contain a weakly acidic aromatic group.*
- ***T6** contains a vicinal diol group.*

6. **i)** Show, in a single mechanistic step with electron-pushing arrows, how testosterone is converted to dihydrotestosterone (**T1**) in the active site of an enzyme using NADPH. (0.5 points)

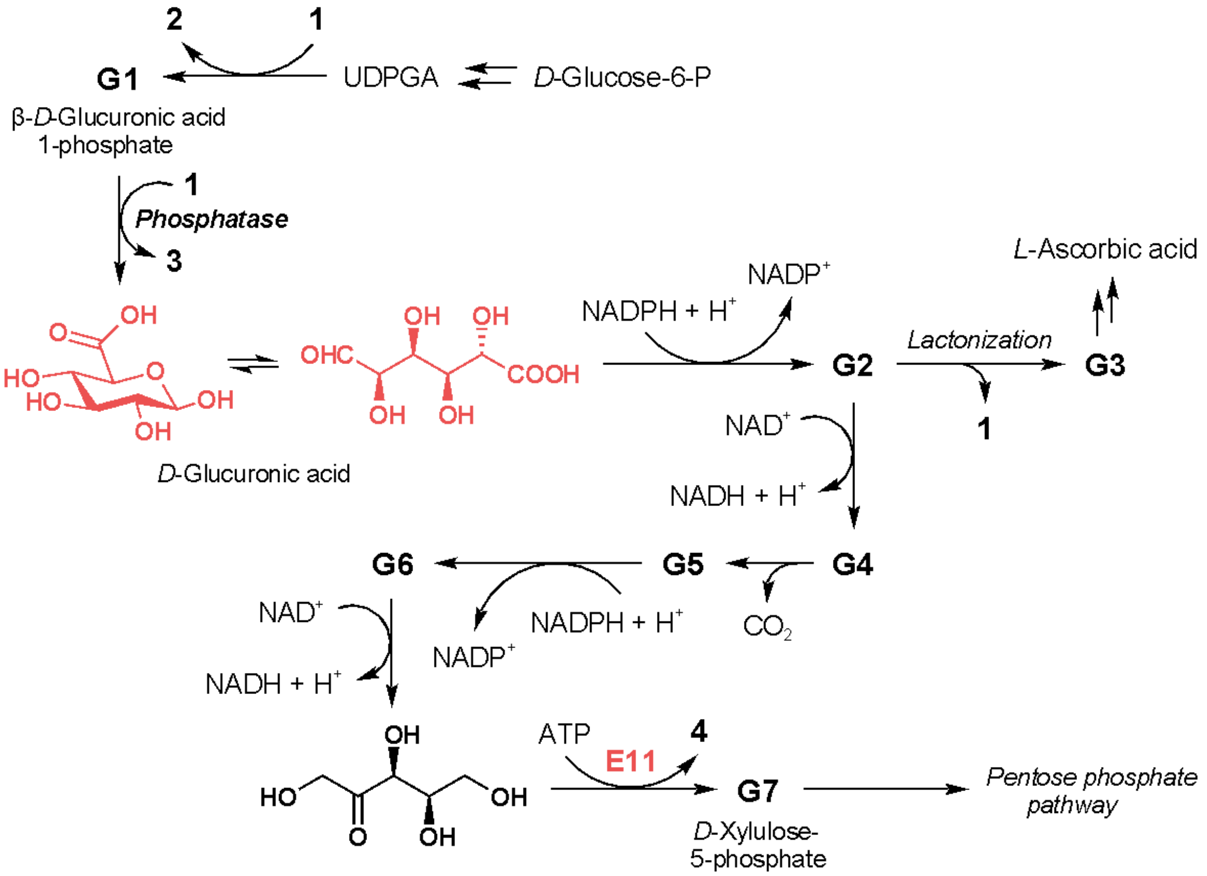
   ii) Complete the structural fragments of the niacinamide moiety in $NADP^+$ and **T1**. “Enzyme−A−H” represents an acidic side chain of an amino acid residue. (1 point)



7. Draw the structural formulas of **T2−T6** by completing the given structural fragments. (2.5 points)

T2 	**T3** 
T4 	**T5** 
T6 	

D-Glucuronic acid is a major component of many anti-inflammatory proteoglycans (glycosylated proteins). The glucuronic acid pathway is a route of glucose metabolism. Like the pentose phosphate pathway, it provides biosynthetic precursors and interconverts some less common sugars to ones that can be metabolized.



ATP (adenosine triphosphate) serves as a phosphoryl group donor.

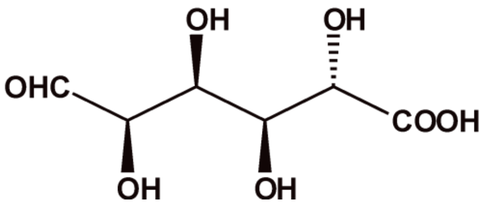
Hint:

- ***G3** is a γ-lactone.*

8. **i)** Tick the correct classification of the cyclic form of *D*-glucuronic acid. (0.5 points)

☐	Acetal	☐	Ketal
☐	Hemiacetal	☐	Hemiketal

ii) Determine the absolute configurations (*R*/*S*) of stereocenters in the open-chain form of *D*-glucuronic acid. (1 point)



iii) Determine the missing chemical species **1−4**. (1 points)

1		**2**	
3		**4**	

iv) Based on the scheme, classify the enzyme labeled **E11**, which catalyzes a phosphorylation involving ATP. (0.5 points)

v) Draw the structural formulas of **G1−G7**. (7 points)

G1	**G2**
G3	**G4**
G5	**G6**
G7	