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General Information

Instructions

- You have three hours to solve the problems.
- Write all calculations and everything else legibly.
- Clearly state which assumptions you are making, if you do.
- Put your pages into the provided envelope at the end of the exam. Do not seal the envelope.
- Finish your work immediately when the **STOP** signal is given.
- Leave your seat only when you have been given permission to do so.
- Only legible answers written **on the question sheets** can be considered. You may use the back page if you require more space. Indicate this in the respective answer box.
- This exam has **10** problems.

Viel Erfolg!

Bonne chance!

Buona fortuna!

Good luck!

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Physical Constants and Formulae

Constants

Planck constant	$h = 6.626\,070\,15 \times 10^{-34}\,\mathrm{J\,s}$
Boltzmann constant	$k_B = 1.380\,649 \times 10^{-23}\,\mathrm{J\,K^{-1}}$
Speed of light	$c = 2.997\,924\,58 \times 10^{8}\,\mathrm{m\,s^{-1}}$
Elementary charge	$e = 1.602\,176\,634 \times 10^{-19}\,\mathrm{C}$
Avogadro constant	$N_A = 6.022\,140\,76 \times 10^{23}\,\mathrm{mol^{-1}}$
Universal gas constant	$R = 8.314\,462\,\mathrm{J\,mol^{-1}\,K^{-1}}$
Atomic mass unit	$u = 1.660\,539\,066\,60 \times 10^{-27}\,\mathrm{kg}$
Proton mass	$m_{p^+} = 1.672\,621\,923\,69 \times 10^{-27}\,\mathrm{kg}$
Neutron mass	$m_{n^0} = 1.674\,927\,498\,04 \times 10^{-27}\,\mathrm{kg}$
Electron mass	$m_{e^-} = 9.109 \times 10^{-31}\,\mathrm{kg}$
Faraday constant	$F = 9.6485 \times 10^{4}\,\mathrm{C\,mol^{-1}}$
Standard pressure	$p_0 = 1.00 \times 10^{5}\,\mathrm{Pa}$
Electronvolt	$1\,\mathrm{eV} = 1.602\,176\,634 \times 10^{-19}\,\mathrm{J}$
Absolute zero	$0\,\mathrm{K} = -273.15\,^{\circ}\mathrm{C}$
Ångstrom	$1\,\text{Å} = 1 \times 10^{-10}\,\mathrm{m}$
Pi (π)	$\pi \approx 3.141592$
Euler's number	$e \approx 2.718281$
Vacuum permittivity	$\epsilon_0 = 8.854\,188 \times 10^{-12}\,\mathrm{C^2\,N^{-1}\,m^{-2}}$

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Formulae and Equations

Ideal gas law	$pV = nRT = Nk_BT$
Coulomb's law	$F_c = \frac{1}{4\pi\epsilon_0} \cdot \frac{q_1 q_2}{r^2}$
Gibbs free energy	$\Delta G = \Delta H - T\Delta S$
Relation between ΔG and K	$\Delta G = -RT \ln(K)$
Reaction quotient Q for reaction aA+bB $\rightleftharpoons$ cC+dD	$Q = \frac{[\mathrm{C}]^c[\mathrm{D}]^d}{[\mathrm{A}]^a[\mathrm{B}]^b}$
Relationship between ΔG and ΔE_{cell}	$\Delta_r G^\circ = -nF\Delta E_{\text{cell}}{}^\circ$
Nonstandard ΔG	$\Delta_r G = \Delta_r G^\circ + RT \ln(Q)$
Clausius–Clapeyron equation	$\ln(\frac{p_2}{p_1}) = -\frac{\Delta_{\alpha\to\beta}H}{R}(\frac{1}{T_1} - \frac{1}{T_2})$ where α and β represent the aggregate state of a phase transition
Nernst equation	$E = E^\circ - \frac{RT}{zF} \ln(Q)$
Electric current	$I = \frac{q}{t}$
Arrhenius law	$k = Ae^{-\frac{E_a}{RT}}$
Lambert-Beer law	$A = \epsilon Lc = \log\left(\frac{I_0}{I}\right)$
Buffer equation	$\mathrm{pH} = \mathrm{pK_a} + \log\left(\frac{[\mathrm{A}^-]}{[\mathrm{HA}]}\right)$
Energy of a photon	$E = h\nu = \frac{hc}{\lambda}$
Half life for a first-order reaction	$t_{\frac{1}{2}} = \frac{\ln(2)}{k}$
Activity of a radioactive sample	$A = kN$
Surface area of a sphere	$A = 4\pi R^2$
Volume of a sphere	$V = \frac{4\pi}{3}R^3$

For calculations of equilibrium constants and all concentrations, refer to the standard concentration $1\,\mathrm{mol\,dm^{-3}} = 1\,\mathrm{mol\,L^{-1}}$. If not stated otherwise in the task, consider all gases ideal throughout this exam.

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Periodic Table of Elements

1																		2
H																		He
1.008																		4.003
3	4												5	6	7	8	9	10
Li	Be												B	C	N	O	F	Ne
6.94	9.01												10.81	12.01	14.01	16.00	19.00	20.18
11	12												13	14	15	16	17	18
Na	Mg												Al	Si	P	S	Cl	Ar
22.99	24.31												26.98	28.09	30.97	32.06	35.45	39.95
19	20	21	22	23	24	25	26	27	28	29	30		31	32	33	34	35	36
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn		Ga	Ge	As	Se	Br	Kr
39.10	40.08	44.96	47.87	50.94	52.00	54.94	55.85	58.93	58.69	63.55	65.38		69.72	72.63	74.92	78.97	79.90	83.80
37	38	39	40	41	42	43	44	45	46	47	48		49	50	51	52	53	54
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd		In	Sn	Sb	Te	I	Xe
85.47	87.62	88.91	91.22	92.91	95.95	[98]	101.07	102.91	106.42	107.87	112.41		114.82	118.71	121.76	127.60	126.90	131.29
55	56		72	73	74	75	76	77	78	79	80		81	82	83	84	85	86
Cs	Ba	57–71	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg		Tl	Pb	Bi	Po	At	Rn
132.91	137.33		178.49	180.95	183.84	186.21	190.23	192.22	195.08	196.97	200.59		204.38	207.2	208.98	[209]	[210]	[212]
87	88		104	105	106	107	108	109	110	111	112		113	114	115	116	117	118
Fr	Ra	89–103	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn		Nh	Fl	Mc	Lv	Ts	Og
[223]	[226]		[267]	[268]	[269]	[270]	[270]	[278]	[281]	[282]	[285]		[286]	[289]	[290]	[293]	[294]	[294]

57	58	59	60	61	62	63	64	65	66	67	68	69	70	71
La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
138.91	140.12	140.91	140.24	[145]	150.36	151.96	157.25	158.93	162.50	164.93	167.26	168.93	173.05	174.97
89	90	91	92	93	94	95	96	97	98	99	100	101	102	103
Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
[227]	232.04	231.04	238.03	[237]	[244]	[243]	[247]	[247]	[251]	[252]	[257]	[258]	[259]	[266]

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Score Sheet

Name of participant: _____

Problem	Title	Points	Weight
Q1	Peptide Synthesis in the Lab	11.5 pt	8 %
Q2	Nonlinear Networks	19.0 pt	12 %
Q3	Total Synthesis of Acutumine	18.0 pt	10 %
Q4	Click Chemistry on Gold Nanoparticle	15.0 pt	11 %
Q5	Bohr Model and Energy Levels	16.5 pt	10 %
Q6	Lanthanum's Momentum in Hydrogen Retention	18.5 pt	9 %
Q7	Radically Important Complexes	17.0 pt	9 %
Q8	'Funky'-Block Elements	17.0 pt	11 %
Q9	Not Just Playing with Fire	16.5 pt	12 %
Q10	Fluorines Activate Acetate	11.0 pt	8 %
Total		160.0 pt	100 %

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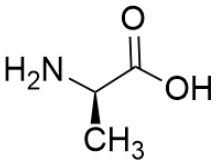
Peptide Synthesis in the Lab (11.5 pts, 8%)

The way nature and a lab chemist approach a synthesis is very different: nature is likely to have specific enzymes for the very specific synthesis it wants to carry out, while the humble chemist is typically forced to work with an array of glasswares, reagents and other gizmos, only to then produce a few grams of the desired product (we're being optimistic).

Peptides are polymers formed by amino acids, so called due to the presence of an amino group and a carboxylic acid.

Most amino acids we know of are chiral, and nature seems to have picked a favourite enantiomeric configuration: the L configuration. Although nowadays we're used to absolute configuration labels such as *R* and *S*, some compounds are still commonly referred to using their L or D label, like amino acids and carbohydrates. Most L-amino acids would be labelled as *S* using Cahn-Ingold-Prelog rules, with one exception being L-cysteine.

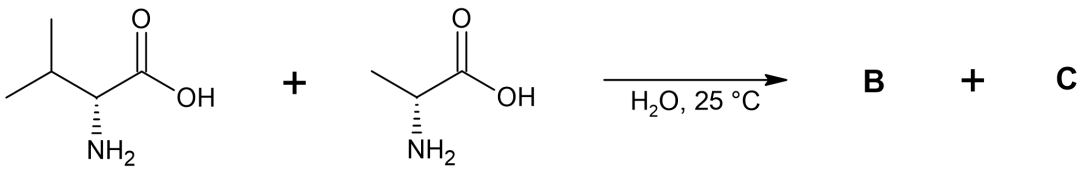


A

1.1	**Determine** the absolute configuration of the amino acid **A** and **label** it as either *R* or *S*.	0.5 pt

In the lab, things immediately become trickier when we try coupling two amino acids. Jotting it down on a piece of paper it may seem like the amine group would readily add to the carboxylic acid via addition, as other good nucleophiles could, but this doesn't happen. In fact, an unwanted reaction occurs instead, yielding no desired peptide product.

When solutions of two different amino acids are mixed together, no coupling occurs. Instead, the two amino acids will be found in forms **B** and **C** in the solution.

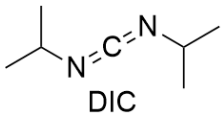


1.2 **Draw** the structures of forms **B** and **C**. 1.0 pt
Hint: **Think** about other properties than nucleophilicity/electrophilicity.

B:

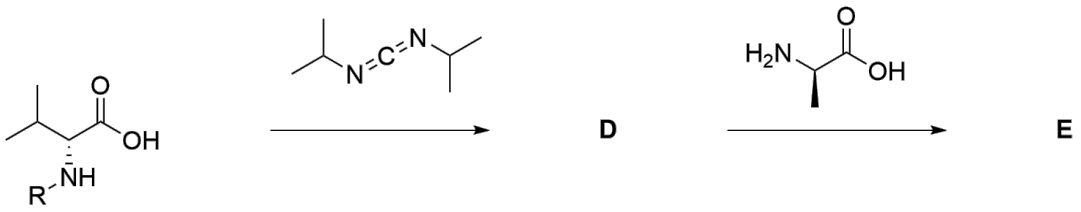
C:

It is for this reason that coupling reagent are used in peptide synthesis; without them, the amino acids would typically not couple in a desirable manner.



DIC

A commonly used coupling reagent is diisopropylcarbodiimide (DIC). The coupling takes place via an *O*-acylisourea intermediate.



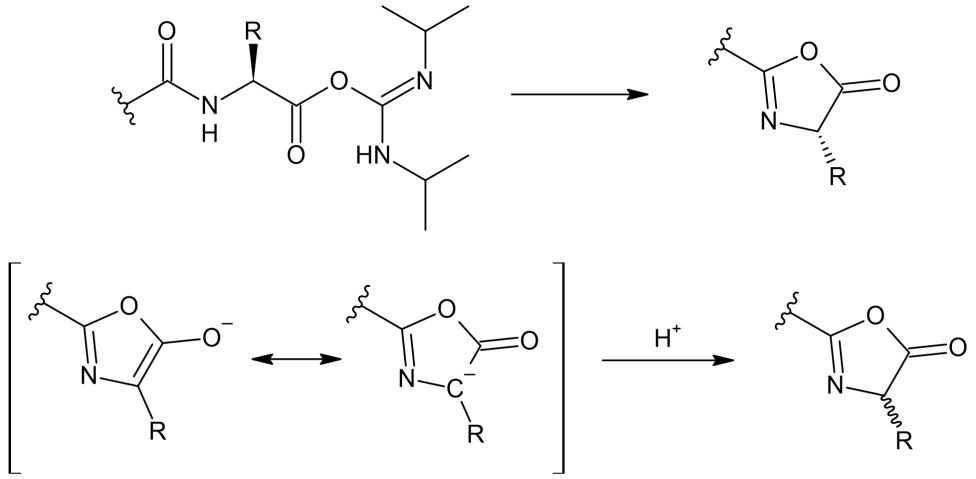
1.3 **Draw** the structure of the intermediate **D** and of the final coupling product **E**. 3.0 pt
Hint: diisopropylurea is produced as a byproduct alongside **E**.

D:

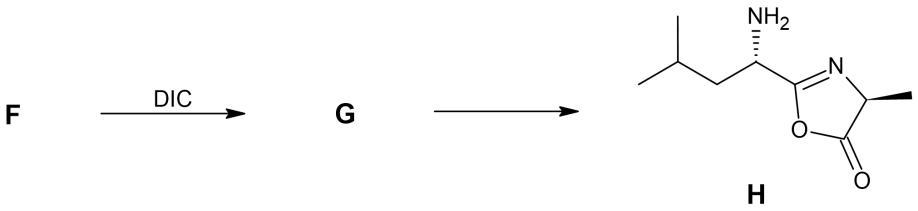
E:

Running the coupling reactions with only a coupling reagent poses a risk of racemization, which can be circumvented by using an additives. Racemization can be detrimental to a peptide's biological activity, as most physiological processes are highly specific to one stereoisomer.

The main culprit is a cyclic and planar oxazolone intermediate. This intermediate is produced via a reaction between the carbonyl oxygen of the penultimate amino acid and the carbonyl carbon of the last amino acid (see figure below).



1.4 **State** two reasons why the oxazolone precursor is so easily deprotonated. 1.0 pt



H

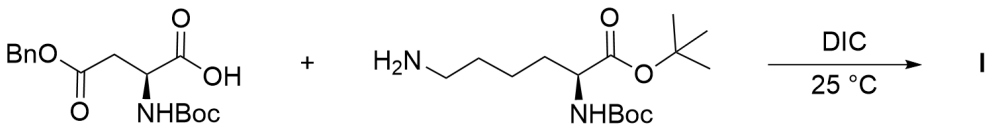
1.5 **Draw** the structures of dipeptide **F** and intermediate **G** working backwards from oxazolone **H**. 4.0 pt

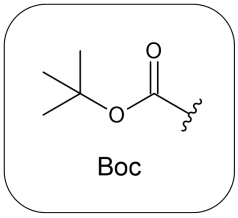
F:

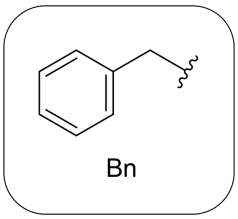
G:

Protecting groups are also commonly employed to prevent self-coupling and unwanted side chain reactivity.

In liquid-phase peptide synthesis, a commonly seen scheme uses *tert*-butyloxycarbonyl (Boc) as a temporary N-terminal protecting group, and benzyl (Bn) as a permanent side chain carboxyl protecting group. This means Boc protecting groups are periodically added and cleaved to prevent unwanted reactivity at the N-terminus, while Bn is used to protect the side chains permanently throughout the synthesis.







1.6 **Draw** the structure of product **I**. 2.0 pt

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Nonlinear Networks (19.0 pts, 12%)

Oscillating reactions are chemical reactions that show periodic changes in reaction rate and intermediate concentrations instead of progressing smoothly to equilibrium. This behavior arises from non-linear kinetics, where the rate of certain steps depends on the concentration of intermediates. Positive feedback (autocatalysis) accelerates the reaction, while negative feedback (inhibition) slows it down, producing repeating cycles.

Autocatalysis occurs when a reaction product catalyzes its own formation, leading to positive feedback.

Inhibition occurs when a species consumes or removes an autocatalytic reactant, preventing the autocatalytic cycle from starting.

The Belousov–Zhabotinsky (BZ) reaction is a classic example of a nonlinear chemical oscillator. It alternates between an inhibitory phase, characterized by a high concentration of bromide ions consuming bromous acid ($HBrO_2$), and an autocatalytic production of bromous acid that occurs once bromide levels fall below a critical treshold. The reaction is typically performed in an acidic medium, while using potassium bromate as the oxidant and malonic acid as the reductant, with cerium ions serving as a redox indicator. After an initial induction period, the solution undergoes periodic color changes between colorless (Ce^{3+}) and yellow (Ce^{4+}). When carried out in a Petri dish, these oscillations appear as expanding spirals as seen in the image below. The reaction continues until all reactants have been consumed.

There are multiple variations of the BZ reaction each characterised by its own set of colors.

Consider the following simplified reaction scheme focusing on the autocatalytic and inhibitory reactions. Assume all reaction steps to be elementary. The radical $BrO_2^\bullet$ is a short-lived intermediate.

Reaction	Rate Constant
$R_1:\ BrO_3^- + Br^- + 2\,H^+ \rightarrow HBrO_2 + HOBr$	$k_1 = 2.4\,L^3\,mol^{-3}\,s^{-1}$
$R_2:\ HBrO_2 + Br^- + H^+ \rightarrow 2\,HOBr$	$k_2 = 1 \times 10^6\,L^2\,mol^{-2}\,s^{-1}$
$R_3:\ HOBr + Br^- + H^+ \rightarrow Br_2 + H_2O$	$k_3 = 3.16 \times 10^8\,L^2\,mol^{-2}\,s^{-1}$
$R_4:\ BrO_3^- + HBrO_2 + H^+ \rightarrow 2\,BrO_2^\bullet + H_2O$	$k_4 = 10\,L^2\,mol^{-2}\,s^{-1}$
$R_5:\ BrO_2^\bullet + Ce^{3+} + H^+ \rightarrow HBrO_2 + Ce^{4+}$	$k_5 = 5 \times 10^5\,L^2\,mol^{-2}\,s^{-1}$

2.1 **Explain** why R_4 and R_5 are an autocatalytic system and **identify** the catalytic species. **Show** why we see an increase in the reaction rate as the reaction progresses. 2.5 pt

Catalytic species: _____

2.2 **Write** the differential rate law for R_1 and **indicate** the reaction order with respect to $HBrO_2$ and the overall reaction order. 3.0 pt

Rate law R_1:

Reaction order with respect to $HBrO_2$:

Overall reaction order:

For the following problems you may assume these concentrations:

$[BrO_3^-] = 0.3\,mol\,L^{-1}$ $[Ce^{3+}] = 0.005\,mol\,L^{-1}$ $[H^+] = 0.3\,mol\,L^{-1}$ $[HBrO_2] = 0.0001\,mol\,L^{-1}$

2.3 **Calculate** the concentration of $BrO_2^\bullet$ in $mol\,L^{-1}$ using the steady-state approximation. 3.5 pt

$[BrO_2^\bullet] =$ _____ $mol\,L^{-1}$

The oscillations in the BZ reaction depend on the bromide ion concentration. When the bromide concentration is high, the inhibitory reaction dominates. When the bromide concentration drops below a critical threshold $[Br^-]_{crit}$ the autocatalytic process takes over and the color change becomes visible.

2.4 **Show** that $[Br^-]_{crit}(T) \propto \frac{k_5(T)}{k_2(T)}$. 5.0 pt

Hint: You only need to consider one autocatalytic and one inhibitory reaction for this.

Finally we would like to calculate the temperature dependence of this reaction. Assume the $[Br^-]_{crit}$ is found to be 6×10^{-6} mol L^{-1} at $T_1 = 298$ K. Assume the following activation energies:

$E_a^{autocatalytic} = 45$ kJ mol^{-1}

$E_a^{inhibitory} = 20$ kJ mol^{-1}

2.5 **Find** $[Br^-]_{crit}$ at $T_2 = 318$ K. 5.0 pt

$[Br^-]_{crit}(T_2) =$ _____ mol L^{-1}

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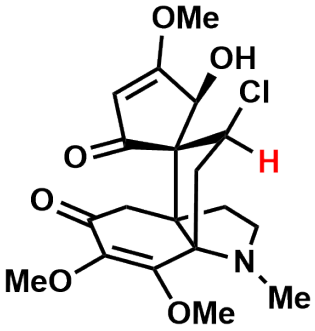
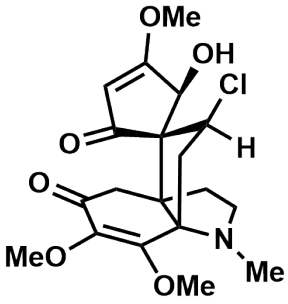
Total Synthesis of Acutumine (18.0 pts, 10%)

Acutumine belongs to a class of chlorinated aza-propellane tetracyclic alkaloids. It was first isolated in 1929 by Goto and Sudzuki from *Sinomenium acutum*. Later, Tomita obtained Acutumine from *Menispermum dauricum* and determined its structure by X-ray crystallography. The structure of Acutumine is shown below:

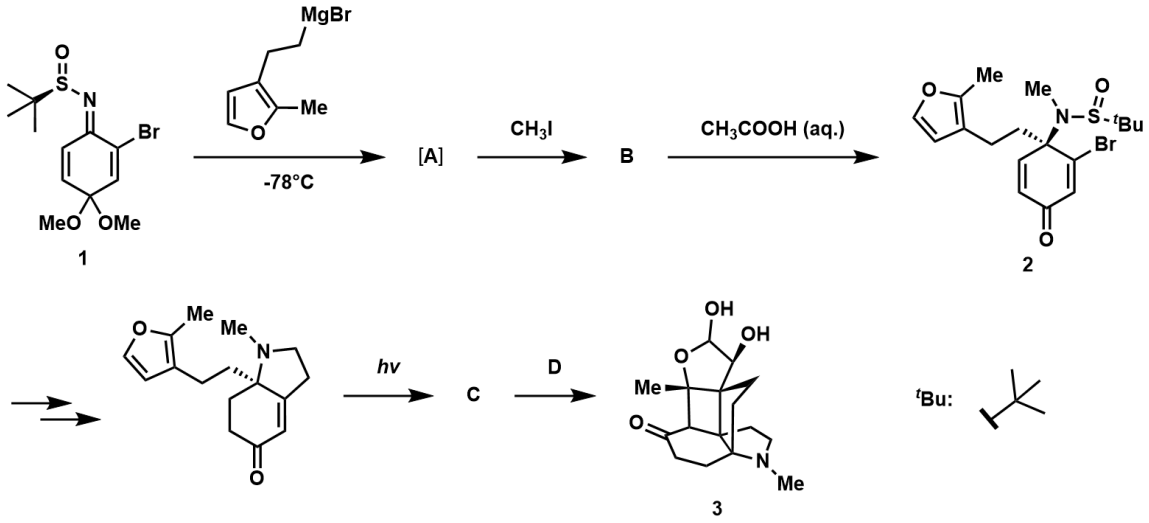


3.1 **Circle** all the stereogenic centers of Acutumine. 2.5 pt



3.2 **State** the expected splitting pattern of the highlighted hydrogen in ^{1}H NMR. 1.0 pt

The molecule is highly functionalized and exhibits several notable biological activities. Due to its densely packed functional groups and structural complexity, the total synthesis of Acutumine remains exceptionally challenging and has aroused significant interest within the synthetic chemistry community. During the development of synthetic strategies towards the core skeleton of Acutumine, the following studies were carried out by Reisman's group in 2012:



3.3 **Draw** the structure of **A** and **B**, including stereochemistry. 4.0 pt

A:

B:

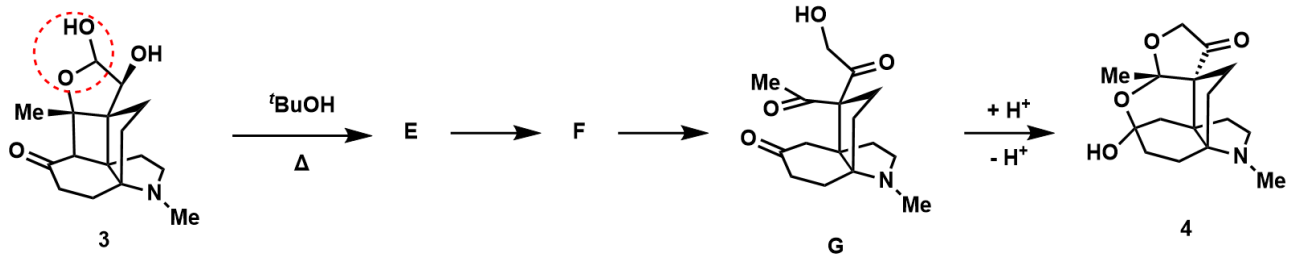
The structure of **C** is formed by photo-induced [2+2] cycloaddition (*hv* means light), which is a reaction very similar to Diels-Alder cyclization (also known as [4+2] cycloaddition).

3.4 Based on the structure of the product, **deduce** the structure of **C** and **provide** the reaction condition **D**. 3.0 pt

C:

D:

The synthesis goes on with the following consequences:



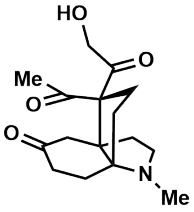
It is known that the highlighted part in **3** is prone to hydrolysis. The formation of **E** involves a retro-Aldol reaction (reverse of the Aldol reaction). **E** contains 3 carbonyl groups and **F** contains 2 carbonyl groups.

3.5 **Draw** the structure of **E** and **F**. 4.0 pt

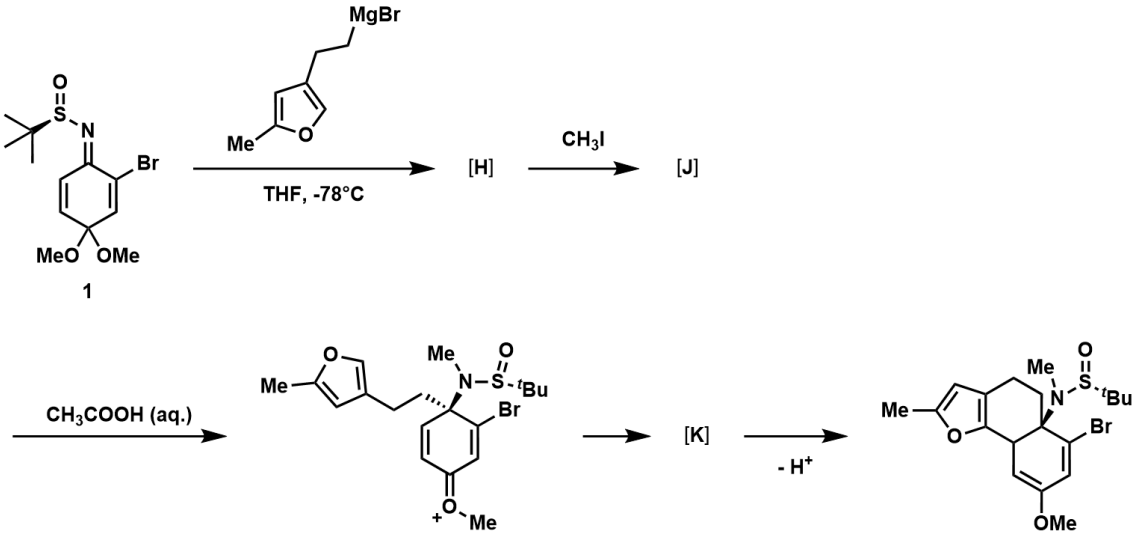
E:

F:

3.6 **Draw** the curly-arrow mechanism indicating the electron flow for the formation of **4** from **G** in the structure below. 1.5 pt



If we use different Grignard reagent to react with **1**, the product changes:



3.7 **Draw** the structure of the intermediate **K**. 2.0 pt

K:

Click Chemistry on Gold Nanoparticles (15.0 pts, 11%)

The nanoparticle ***nucleation rate*** (the rate at which stable particles of a new solid phase get formed in a given volume over time), J, can be expressed using the Arrhenius-style relationship:

$$J = A(S-1) \cdot \exp\left(-\frac{\Delta G_{\text{crit}}}{k_B T}\right) \tag{1}$$

$$\Delta G_{\text{crit}} = \frac{16\pi\gamma^3\nu^2}{3(k_B T \ln(S))^2} \tag{2}$$

The ***rate of particle growth*** (r) can be described as:

$$r = \frac{dR}{dt} = k_0 \cdot \exp\left(-\frac{\Delta G_g}{k_B T}\right) \cdot (S-1) \tag{3}$$

Where parameters are:

A – Arrhenius constant

γ – surface energy

ν – molecular (or atomic) volume of the phase being formed

S – supersaturation (***not entropy***), defined as $S = \frac{c_\infty}{c_0}$, where: c_∞ is actual concentration of the solute in the bulk solution and c_0 is the concentration of saturated solution

ΔG_g – activation energy for the growth process

R – radius of the particle

k_0 – constant

Consider all parameters (γ, ν, c_∞, c_0, k_0, ΔG_g) independent from each other and temperature.

To analyse how the temperature T affects the particle size, the ratio of the nucleation rate to the growth rate J/r needs to be analysed.

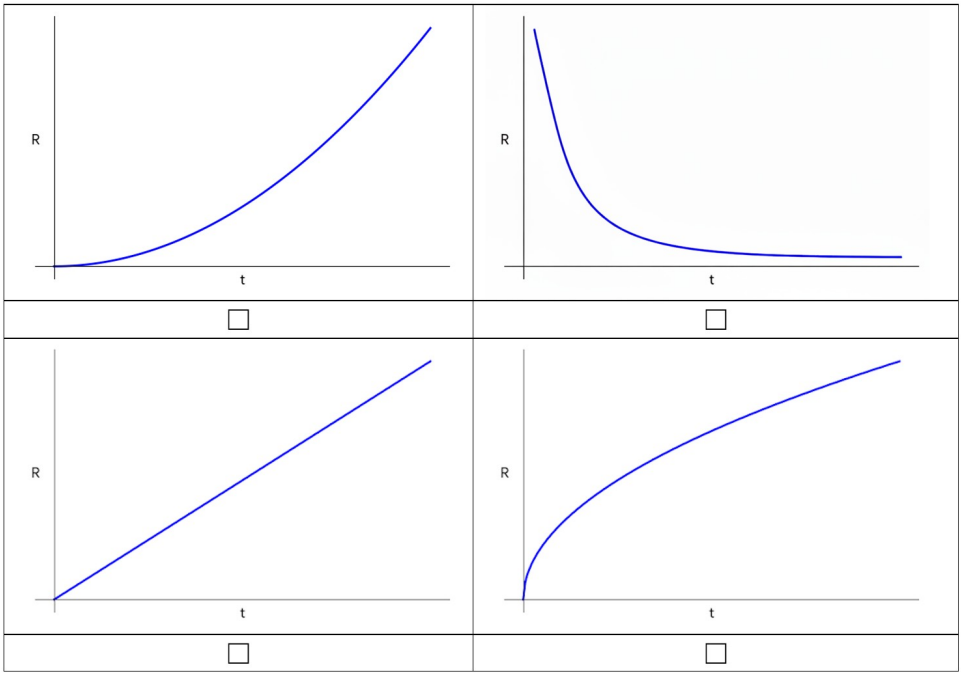
4.1 **Analyse** how the ratio J/r depends on T and **simplify** the obtained equation, assuming $T \longrightarrow +\infty$. Based on this, **identify** whether bigger or smaller particles are formed at higher T. **Note:** S remains constant and $S > 1$. 3.0 pt

Particle size ☐ increases with T ☐ decreases with T

4.2 Among the four parameters J, c_∞, r and γ, **select** two that, when increased, lead to a larger final particle size. **Note:** **Assume** all other parameters remain constant in each case. 1.0 pt

☐ J ☐ c_∞ ☐ r ☐ γ

4.3 Assuming $S > 1$ remains constant over time, **select** the graph correctly representing the change in particle radius (R) as a function of time (t). 1.0 pt

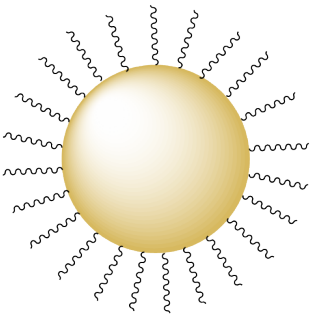


☐ ☐

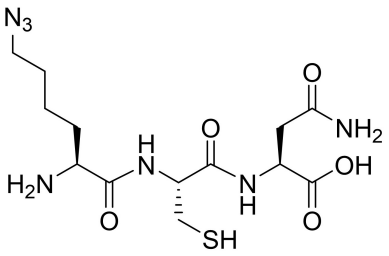
☐ ☐

4.4 **Suggest** the likely outcome of a nanoparticle synthesis attempt in the regime where $S < 1$. 1.0 pt

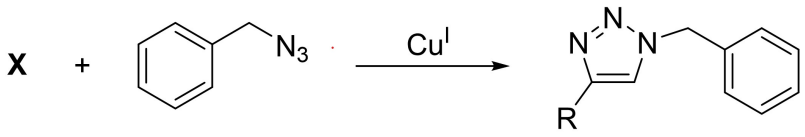
To obtain particles of a desired size, the reaction is typically quenched after a certain amount of time to stop further growth. Following quenching, the nanoparticles are capped with a ligand to stabilize them and prevent aggregation. An obtained gold nanoparticle capped with the ligand can be represented schematically as follows:



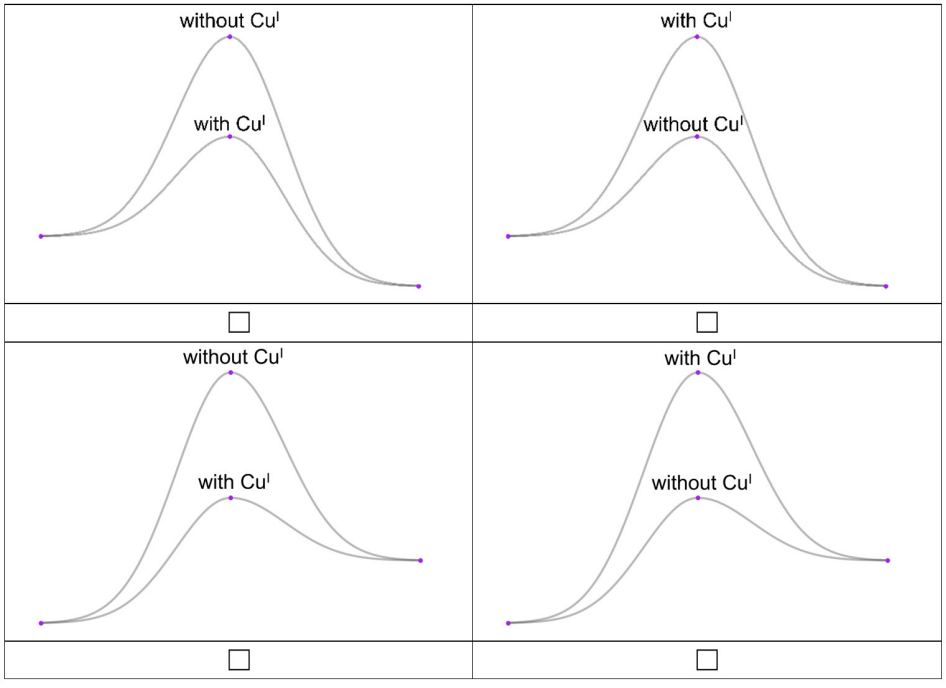
4.5 **Circle** the functional group in the following ligand structure that binds most strongly to the gold surface during the capping of gold nanoparticles. **Note:** The ligand is monodentate. 1.0 pt



Capped gold nanoparticles can be further functionalized or labeled using CuAAC, a classic copper-catalyzed click chemistry reaction. This classic reaction is characterized by high efficiency and 100% atom economy, as all atoms of the reactants are incorporated into the final product:



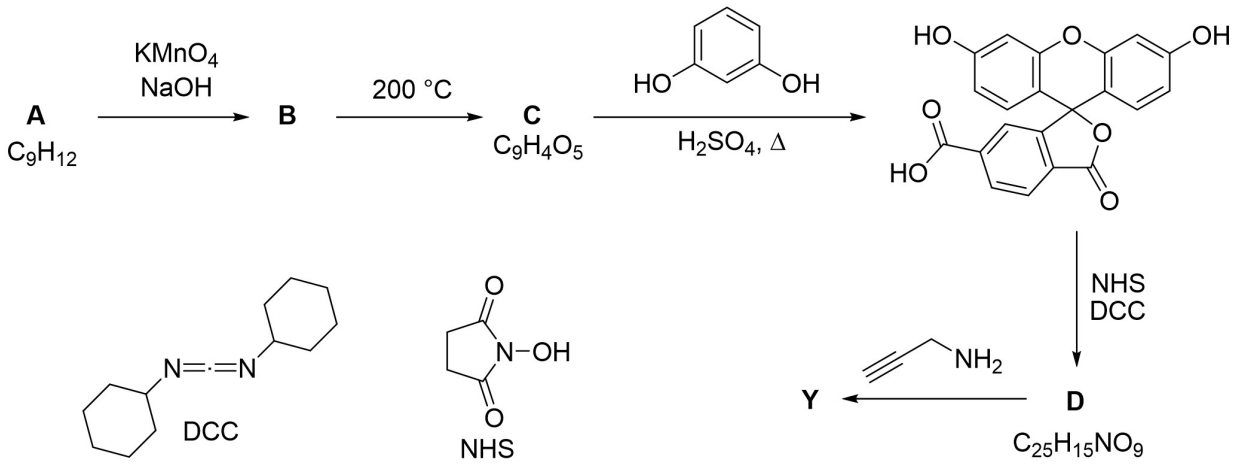
4.6 **Choose** the Gibbs free energy diagram that corresponds to the catalyzed and uncatalyzed labeling reaction (CuAAC). For simplicity, **assume** all intermediate states are omitted and the highest transition states in each case are shown. **Note:** Starting materials are located on the left side of the diagram, while the product on the right side. 1.0 pt



4.7 **Identify** compound **X**, if: 2.0 pt

- its chemical formular is C_9H_8O
- its ^{1}H NMR: 7.27 (t, 2H), 6.97 (d, 2H), 6.93 (t, 1H), 4.68 (s, 2H), 2.50 (s, 1H)
- **assume** that coupling in ^{1}H NMR is only observed for hydrogens separated by at most three bonds

Fluorescein derivative **Y** was used for the labeling of capped gold nanoparticles via CuAAC. It was synthesized according to the following scheme:



4.8 **Identify** compounds **A**–**D** and **Y** if **A** has 3 signals in aromatic region (each integrates to 1H) and 3 signals in aliphatic region (each integrates to 3H). 5.0 pt

A	B	C

D	Y

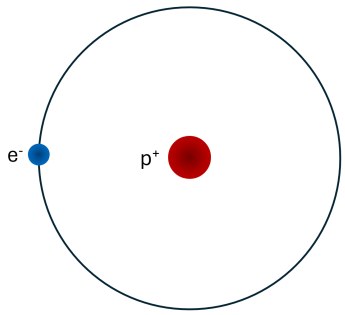
CHEMISTRY.
OLYMPIAD.CH
CHEMIE-OLYMPIADE
OLYMPIADES DE CHIMIE
OLIMPIADI DELLA CHIMICA

Q5-1

English (Official)

Bohr Model and Energy Levels (16.5 pts, 10%)

Hydrogen-like atoms can be well approximated using the Bohr model. In this model, the electron is assumed to move in a circular orbit around the nucleus (see figure below). Apart from hydrogen, all atoms with just one electron are also considered hydrogen-like, e.g. He^+.



5.1 **Give** the force that keeps the electron bound to the proton. **Show** that the kinetic energy of an electron in a hydrogen atom is given by $E_{\text{kin}} = -\frac{1}{8\pi\epsilon_0}\frac{q_1 q_2}{r}$. 1.5 pt

Hint: The centripetal force is given by $F_z = -\frac{mv^2}{r}$.

The Bohr model assumes that the angular momentum L of the electron is quantized:

$$L = m_e v r = \frac{nh}{2\pi} \text{ with } n = 1, 2, 3, \ldots \quad (1)$$

5.2 **Show** that this condition leads to discrete energy levels for the electron given by $E(n) = -\frac{q_1^2 q_2^2 m_e}{8\epsilon_0^2 n^2 h^2}$. 2.0 pt

5.3 Schematically **draw** a diagram of the electron energy levels $E(n)$. Is there a limit to how much energy a bound electron can absorb? **Explain** what happens when this value is exceeded. 2.0 pt

In 1888, Johannes Rydberg empirically found the formula now known as the Rydberg formula. It is given as follows, where λ is the wavelength of light emitted by a transition from the energy level of n_1 to the energy level n_2. R_∞ is a constant.

$$\frac{1}{\lambda} = R_\infty \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \tag{2}$$

5.4 Based on the Bohr model, **show** that it holds $R_\infty = \frac{q_1^2 q_2^2 m_e}{8\epsilon_0 h^3 c}$. 2.0 pt

The Bohr model can also be applied to larger atoms. We now look at this in more detail.

5.5 **Give** the full electron configuration of caesium. 1.0 pt

Experimentally, it is observed that when a metal surface is irradiated with light, electrons are emitted only if the frequency of the incident light exceeds a well-defined threshold value. Increasing the light intensity below this threshold has no effect on electron emission, regardless of how intense the radiation is. This behavior is known as the photoelectric effect.

The minimum energy required to liberate an electron from the metal is called the work function Φ. It is given as follows, where h is Planck constant and $\nu_{\text{threshold}}$ is the threshold frequency.

$$\Phi = h\nu_{\text{threshold}} \tag{3}$$

5.6 **Calculate** the work function Φ_{Cs} of Cs in eV. **Assume** you can apply the Bohr model. 3.0 pt
Hint: **Consider** only the outermost electron and **treat** the remaining electrons as part of the atomic core.

$\Phi_{Cs} =$ _____ eV

Experimentally, the work function Φ_{Cs} of Cs is measured to be 2.1 eV.

5.7 **Give** one possible reason for the difference between the theoretical estimate and the experimental value. **Specify** the exact reason what the difference is between our model and what we measure in reality. 2.0 pt
Note: If you could not solve **5.6**, **assume** that the theoretical value is $\Phi_{Cs} = 0.832$ eV.

A hydrogen laser can be built using the $n = 4$ to $n = 2$ transition.

5.8 If we irradiate Cs with this laser, **calculate** the speed of the emitted electrons. For the work function Φ_{Cs} of Cs, **use** the experimental measured value of 2.1 eV. 3.0 pt

$v_{\text{electron}} =$ _____ m s^{-1}

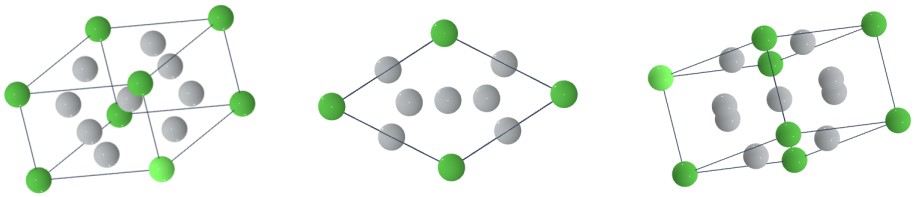
Lanthanum's Momentum in Hydrogen Retention (18.5 pts, 9%)

Hydrogen is a promising energy carrier due to its high energy density and the fact that it produces water upon combustion, making it a potential sustainable fuel. However, further research is still needed to enable efficient and truly sustainable hydrogen production, since most of hydrogen is currently produced from hydrocarbons, which releases typically significant amounts of CO_2.

Additionally, hydrogen storage remains challenging because hydrogen has a very low density and is difficult to store as a gas or liquid, partly due to its low molar mass and tendency to escape from containment systems.

A possible hydrogen storage is lanthanum pentanickel $LaNi_5$. But just like all other hydrogen storage solutions it comes with a specific set of properties and challenges, which you decide to investigate.

6.1 **Assign** nickel and lanthanum to their respective coloured atom in the crystal structure. 1.0 pt



Grey _____ Green _____

During your research you find that the unit cell (uc) contains one lanthanum atom and five nickel atoms. You also discover that one unit cell can store up to 6 hydrogen atoms.

	r/pm	V/pm^3
uc_{LaNi_5}		9.0×10^7
$uc_{LaNi_5H_6}$		1.1×10^8
La	195	3.1×10^7
Ni	135	1.0×10^7
H	53	

6.2 **Calculate** the available volume for hydrogen in the unit cell (V_a) in pm^3 and the volume hydrogen requires (V_H) in pm^3. 2.0 pt

$V_a =$ _____ pm^3 $V_H =$ _____ pm^3

6.3 **Calculate** the mass percentage of hydrogen (%wt.) in the saturated unit cell. 1.0 pt

%wt.= _____ %

You decide to compare the hydrogen storage capacity of Lanthanum pentanickel to just liquid dihydrogen. You find that the density of liquid hydrogen is $\rho_{H_2(l)} = 70.85\,\text{kg m}^{-3}$.

6.4 **Calculate** the density of hydrogen ($\rho_{H,LaNi_5}$ in kg m^{-3}) when stored in lanthanum pentanickel. 3.0 pt

$\rho_{H,LaNi_5} =$ _____ kg m^{-3}

6.5 **Comment** on the difference of hydrogen density between pure liquid hydrogen and hydrogen in $LaNi_5H_6$. **Propose** a reason for the difference. **Hint**: You may assume that $LaNi_5$ stores more hydrogen per volume. 2.0 pt

Besides storage capacity an important hydrogen storage factor is the efficient adsorption (**Ad**) and desorption (**De**) of hydrogen. You look up the enthaply values of both processes in the literature.

	$\Delta_r H\,(\mathrm{kJ\,mol^{-1}})$
Ad	-40 ± 7
De	29 ± 1

When running a test experiment in your reactor, you observe slow adsorption and desorption.

6.6 **Propose** two things you could change to increase adsorption efficiency and two ways to increase desorption efficiency. **Explain** your choice. 4.0 pt

Another important consideration for hydrogen storage is efficient longevity, meaning little degradation over many cycles.

Repeated adsorption/desorption cycles cause several signs of wear in lanthanum pentanickel such as decrepitation (pulverisation), H trapping, amorphisation and disproportionation. All of which decrease hydrogen storage capacity over time.

Pulverisation means that the crystalline material cracks, eventually forming a powder. This changes the kinetics of adsorption/desorption. During the first few cycles, pulverisation accelerates adsorption until it reaches a maximum, after which pulverisation progressively slows down adsorption.

6.7 **Explain** how cycling-induced pulverisation leads to the changes in the rate of hydrogen adsorption. **Note**: Desorption follows the same trend. 2.0 pt

6.8 **Draw** an example of the atomic structure of amorphous $LaNi_5$. **Reason** how amorphisation has a negative effect on the hydrogen storage capacity of $LaNi_5$. 2.0 pt

One possibility to reduce degration effects and increase the life time of $LaNi_5$ is doping it with aluminum, creating $LaNi_{4.5}Al_{0.5}$. The added aluminum reduces strain during adsorption/desorption and slightly changes the electronics of the compound.

During your experiments you are able to store 60 mol H_2 in 10 kg $LaNi_{4.5}Al_{0.5}$.

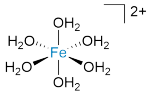
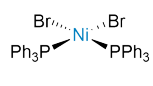
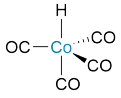
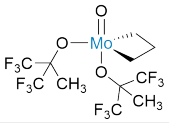
6.9 **Complete** the sum formula of hydrogen saturated $LaNi_{4.5}Al_{0.5}$. 1.5 pt

$LaNi_{4.5}Al_{0.5}H$_____

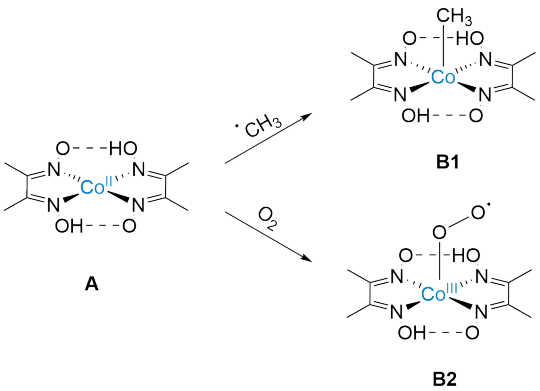
Radically Important Complexes (17.0 pts, 9%)

Transition metal complexes are some of the most important catalysts—both in the laboratory and in your body. Most transition metals strive to fulfil the so-called 18-electron rule, which is similar to the octet rule for non-transition metals. However, opposed to the octet rule, the 18-electron rule is more flexible, and complexes with lower and higher valence electron counts can exist.

7.1 For the following compounds, **give** the oxidation state (OS), d-electron count (d^n), coordination number (CN) and total valence electron count (VEC) of the metal. 4.0 pt

Complex				
OS			+I	
d^n				d^0
CN		4		
VEC	18			

Let us now consider the following reactions where a Co(II) complex **A** encounters a methyl radical and reacts with it to form **B1** or where it encounters O_2, and forms **B2**.
Note: The CH_3 ligand in **B1** is formally a CH_3^- anion.



7.2 **Determine** d^n for **A** and the OS of Co for **B1**. 1.0 pt

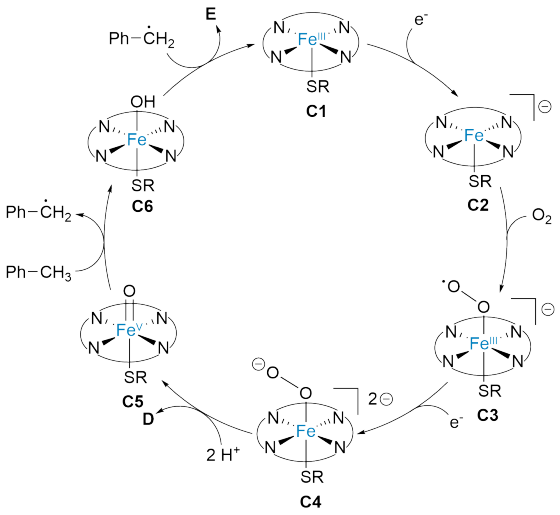
$d^n(\mathbf{A}) =$ _____ OS(**B1**) = _____

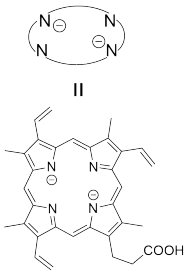
7.3 **Select** the correct electronic nature of the dioxygen ligand in **B2**. 0.5 pt

☐ O_2^{2-} ☐ $O_2^{\bullet-}$ ☐ O_2 ☐ $O_2^{\bullet+}$ ☐ O_2^{2+}

Knowing this, let us look at two enzymes that involve both transition metals and radicals: Cytochrome P450 and Methyl CoM Reductase.

Cytochrome P450 is an enzyme that catalyses the mono-oxygenation (introduction of a single oxygen atom) of various compounds within your body, making them more water-soluble and more easy to excrete. A simplified catalytic cycle is shown below, where toluene ($H_3C{-}Ph$) functions as the substrate. The structure of the doubly negatively charged porphyrin ligand is given next to the catalytic cycle. The axial $R{-}S^-$ ligand is a thiolate. Neither of these ligands undergo any changes throughout the course of the catalytic cycle.





7.4 **Determine** the OS of Fe in the following catalytic intermediates. 3.0 pt

Intermediate	**C2**	**C4**	**C6**
OS of Fe			

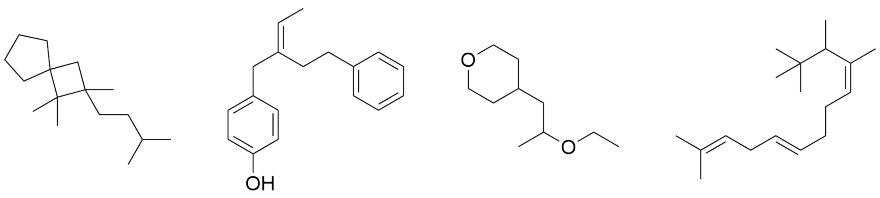
7.5 **Choose** the appropriate processes for **C3**→**C4** and **C5**→**C6**. 2.0 pt

Step	Single-electron transfer (SET)	Hydrogen-atom transfer (HAT)	Halogen-atom transfer (XAT)	Proton transfer (PT)	None of these options
C3→**C4**	☐	☐	☐	☐	☐
C5→**C6**	☐	☐	☐	☐	☐

7.6 **Draw** the structure of **D** and **E**. 1.5 pt

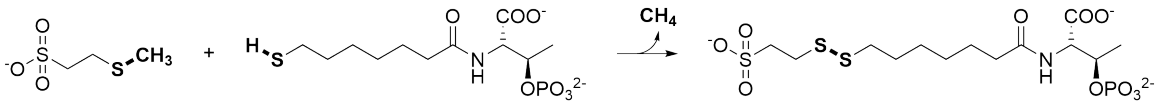
D	**E**

7.7 For each of the following molecules, **circle** the carbon atom whose C–H bond is most readily oxidised by Cytochrome P450. 2.0 pt



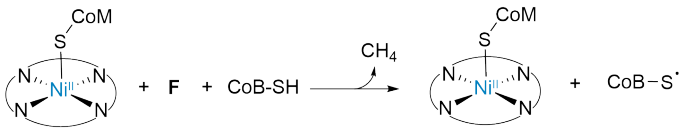
Another enzyme that deals with radicals is Methyl CoM Reductase (MCR), the enzyme involved in the last step of methanogenesis in bacteria. MCR is responsible for the biological production of around 1 billion tonnes of methane per year.

The reaction involves a methyl donor ($H_3C{-}S{-}CoM$) and a hydrogen donor ($H{-}S{-}CoB$) that are formally coupled together like so, resulting in a disulfide bond between the two sulfurs:

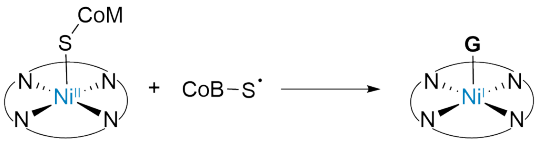


The reaction is mediated using a Ni-containing active site. The ring structure containing four N is similar to the one in P450, however, it only carries a single negative charge. Let us now examine the catalytic steps one-by-one.

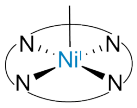
7.8 **Draw** the structure of **F**. 0.5 pt

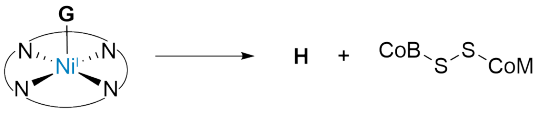


7.9 **Name** the type of elementary step that is occurring in this reaction. 0.5 pt



7.10 Given the OS of the nickel centre, **draw** the ligand **G** that is missing below. 1.0 pt





7.11 **Draw** **H**, **indicating** the correct OS on Ni. 1.0 pt

'Funky'-Block Elements (17.0 pts, 11%)

The f-block elements are rarely discussed in detail in high-school chemistry courses, yet they play important roles in redox chemistry, catalysis and material science. Among the lanthanides, the $+\mathrm{III}$ oxidation state is by far the most common because of formation of lanthanide ions.

Cerium is a notable exception: the oxidation of Ce^{3+} to Ce^{4+} is possible. Ce^{4+} is a strong oxidising agent that reacts vigorously with water (hydrolysis) under neutral and basic conditions. However, under highly acidic conditions, free Ce^{4+} can exist in solution.

8.1 **Explain** why Ce^{4+} exists, whereas other lanthanide ions usually occur only in their $+\mathrm{III}$ form. 1.0 pt

The cumulative formation constant β_n^{L} of a complex ML_n is given as the equilibrium constant for the formation of the complex from the free metal centre M with n ligands L.

Ce^{4+} is most well-known as its nitrate complex hexanitrocerate(IV) $[Ce(NO_3)_6]^{2-}$. Which is formed like so:

$$Ce^{4+} \overset{+NO_3^-}{\rightleftharpoons} [Ce(NO_3)]^{3+} \overset{+NO_3^-}{\rightleftharpoons} [Ce(NO_3)_2]^{2+} \overset{+NO_3^-}{\rightleftharpoons} [Ce(NO_3)_3]^{+} \overset{+NO_3^-}{\rightleftharpoons} \ldots$$

8.2 **Give** $\beta_3^{NO_3^-}$ and $\beta_6^{NO_3^-}$ of the complex forming reaction between Ce^{4+} with NO_3^-. 2.0 pt

$\beta_3^{NO_3^-} =$

$\beta_6^{NO_3^-} =$

The aforementioned hydrolysis $Ce^{4+} + 4\,H_2O \longrightarrow Ce(OH)_4 + 4\,H^+$ has $\beta_1^{H_2O}$ through $\beta_4^{H_2O}$.

$$\beta_1^{H_2O} = \frac{[Ce(OH)^{3+}]\cdot[H^+]}{[Ce^{4+}]\cdot[H_2O]} \qquad \beta_2^{H_2O} = \frac{[Ce(OH)_2{}^{2+}]\cdot[H^+]^2}{[Ce^{4+}]\cdot[H_2O]^2} \qquad \beta_3^{H_2O} = \frac{[Ce(OH)_3{}^{+}]\cdot[H^+]^3}{[Ce^{4+}]\cdot[H_2O]^3} \qquad \beta_4^{H_2O} = \frac{[Ce(OH)_4]\cdot[H^+]^4}{[Ce^{4+}]\cdot[H_2O]^4}$$

For $\beta_n^{H_2O}$ of the hydrolysis products, the following values were obtained.

n	1	2	3	4
$\ln\left(\beta_n^{H_2O}\right)$	33.99	64.56	93.32	119.41

The standard molar Gibbs free energy of formation of some relevant substances, $\Delta_f G^\ominus(298.15\ K)$ is listed in the table below.

Substance	$H_2O\,(l)$	$OH^-(aq)$	$H^+(aq)$	$Ce^{4+}(aq)$
$\Delta_f G^\ominus(298.15\ K)$/kJ mol^{-1}	-237.10	-157.20	0	-503.80

8.3 **Calculate** the $\Delta_f G^\ominus$ of $Ce(OH)^{3+}$ and $Ce(OH)_3{}^+$ in kJ mol^{-1}. 6.0 pt

$\Delta_f G^\ominus\left(Ce(OH)^{3+}\right) =$ _____ kJ mol^{-1}

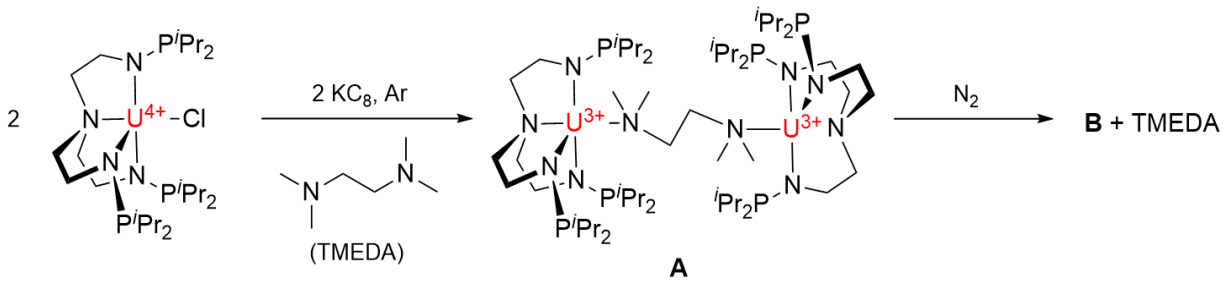
$\Delta_f G^\ominus\left(Ce(OH)_3{}^+\right) =$ _____ kJ mol^{-1}

Let us assume that only the non-complexed Ce^{4+} is redox-active and can be reduced to Ce^{3+}. In this case, the observed reduction potential of the $Ce^{4+}|Ce^{3+}$ redox couple ($E^{red}_{Ce^{4+}|Ce^{3+}}$) is pH-dependent.

8.4 **Explain** in both words and formulae why $E^{red}_{Ce^{4+}|Ce^{3+}}$ is pH-dependent. 4.0 pt
Determine whether $E^{red}_{Ce^{4+}|Ce^{3+}}$ increases or decreases, when the solution is acidified.

When acidified: ☐ $E^{red}_{Ce^{4+}|Ce^{3+}}$ increases ☐ $E^{red}_{Ce^{4+}|Ce^{3+}}$ decreases

The redox chemistry of cerium illustrates how the stability of different oxidation states and their interactions with ligands influence chemical behavior in aqueous solution. Similar principles apply more broadly in f-block chemistry, where metal–ligand interactions can significantly modify electronic structure and reactivity. In addition to simple hydrolysis equilibria, f-block elements are also capable of forming complexes that activate small, and inert molecules. One important example is the coordination of dinitrogen (N_2) by uranium complexes, which weakens the strong N ≡ N bond and enables its chemical transformation.
Consider the following reaction:



You are now working in a radioactive laboratory. The reaction was performed in a glovebox with argon atmosphere with water and oxygen level lower than 0.1 ppm. KC_8 is a super strong reducing agent that can reduce the metal by removing a chloride to form KCl and graphite as by-products.

The structure of product **B** could not be easily predicted from our knowledge. However, after single-crystal X-ray analysis (a technique used to determine how atoms are connected) and theoretical calculations, it was found that one molecule of N_2 reacts with complex **A**, and the strong N≡N triple bond is completely broken. The product **B** still contains two uranium atoms, but their oxidation states return to +IV. Each uranium atom is bonded to six nitrogen atoms and has an octahedral geometry. In addition, some phosphorus atoms in the ligands are oxidized, and the structure of **B** contains three four-membered rings.

8.5 Based on the information above, **predict** the structure of **B**. 3.0 pt

Complex **B** undergoes hydrolysis readily in the presence of water to form two small molecules **X** with molar mass smaller than 20 g mol^{-1}.

8.6 **Predict** the chemical formula of **X**. 1.0 pt

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Q9-1

English (Official)

Not Just Playing with Fire (16.5 pts, 12%)

Uzbekistan has large natural gas reserves. Natural gas mainly consists of methane, ethane, propane, and butane, as well as non-hydrocarbon impurities. The individual components are separated using cryogenic distillation, so that they can, for example, be used in a lighter.

The following table contains the standard enthalpy of formation $\Delta_f H^0$, standard enthalpy of vaporization $\Delta_{vap} H^0$, and the vapor pressure p (at the temperature T_{max} you will calculate in **9.5**) for several hydrocarbons and other molecules.

Molecule	$\Delta_f H^0$ / kJ mol^{-1}	$\Delta_{vap} H^0$ / kJ mol^{-1}	p / bar
Propane (g)	-104	18.8	24
Butane (g)	-126	23.2	6.5
H_2O (g)	-242		
CO_2 (g)	-394		

The following quantities may also prove useful for the task.

Density of propane (l)	0.58 g cm^{-3}
Density of butane (l)	0.60 g cm^{-3}

We have a lighter filled with 90 vol.% butane and 10 vol.% propane. Assume the lighter has a volume of 4 mL and that all the fuel is in the liquid phase due to the high pressure inside the lighter.

9.1 **Write** the combustion reactions and **calculate** the standard enthalpy of combustion $\Delta_{\text{comb}}H^0$ in kJ mol^{-1} for the complete fuel mixture, assuming that all of the fuel in the lighter is fully burned. 2.5 pt

Note: You do not need to take the vaporization of propane and butane into account.

combustion reaction propane:

combustion reaction butane:

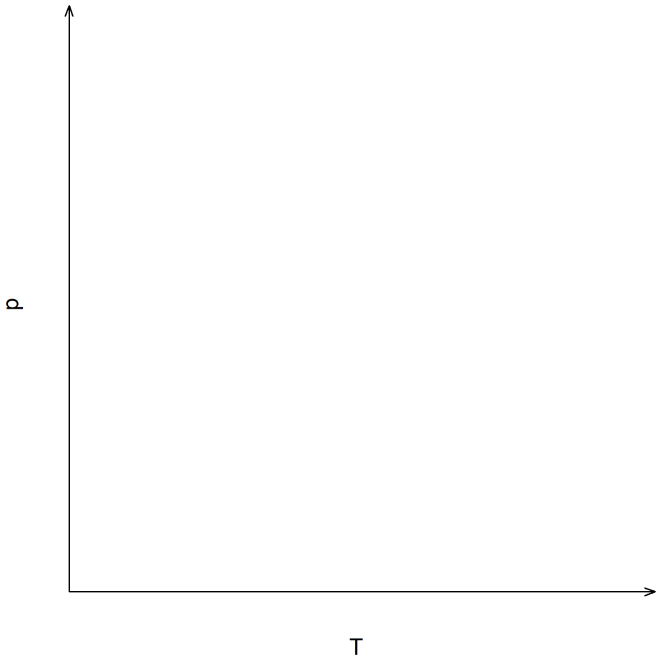
$\Delta_{\text{comb}}H^0 =$ _____ kJ mol^{-1}

9.2 **Draw** a qualitative phase diagram of butane in the grid below. **Label** all phases and **provide** a qualitative explanation of the slopes of the phase boundaries. 3.0 pt

Hint: The Clausius–Clapeyron equation can be rearranged as follows:

$$\frac{dp}{dT} = \frac{\Delta S_{\alpha \rightarrow \beta}}{\Delta V_{\alpha \rightarrow \beta}}$$

where $\frac{dp}{dT}$ is the slope of the coexistence line, $\Delta S_{\alpha \longrightarrow \beta}$ is the entropy change from phase α to phase β (for example liquid to solid), $\Delta V_{\alpha \longrightarrow \beta}$ is the volume change associated with the phase transition from phase α to β.



qualitative explanation of the slopes:

Now we add a small amount of ethanol.

9.3	**Draw** the coexistence curve of the butane-ethanol mixture into the phase diagram above. If the triple point shifts, **state** at which direction it shifts. **Note**: **Assume** that ethanol has a much higher boiling point than butane. Further **assume** that the mixture freezes fast, so the ethanol gets trapped inside the butane crystal lattice.	2.5 pt

Butane and propane originate from natural gas. To obtain the pure substances for use in a lighter, cryogenic distillation is carried out. For this purpose, the natural gas is cooled and compressed until it liquefies. The individual fractions are then separated.

Now all components of the natural gas except butane and propane were separated and another distillation is performed. For illustration, we consider a mole fraction versus pressure diagram (see **9.4**).

The dew line indicates the pressure at which the substance begins to condense. The bubble line describes the pressure at which the substance begins to boil. It can be derived that the following relations hold at the dew line and the bubble line.

The dew line is a function of Y_B and it holds:

$$p = \frac{p_A^* p_B^*}{p_B^* - Y_B(p_B^* - p_A^*)} \tag{1}$$

The bubble line is a linear function of x_B and it holds:

$$p = p_A^* + x_B(p_B^* - p_A^*) \tag{2}$$

where p is the pressure, p_i^* is the vapor pressure of substance i, $Y_B = \frac{p_B}{p}$ is the mole fraction of substance B in the vapor phase, and $x_B = \frac{p_B}{p_B^*}$ is the mole fraction of substance B in the liquid phase.

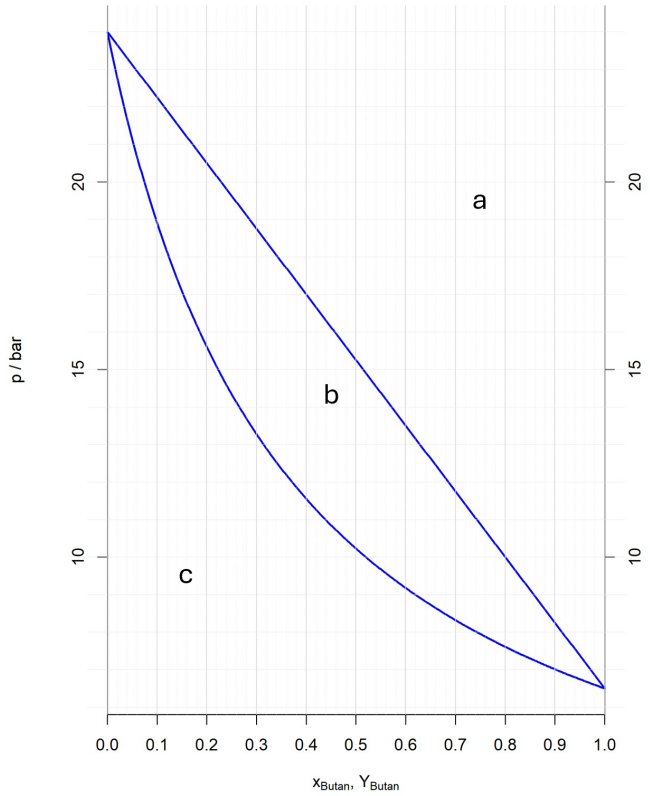
The mole fractions of a state (e.g. liquid) of all substances in a mixture add to 1. Mathematically speaking:

$$Y_A + Y_B + ... = 1 \tag{3}$$

$$x_A + x_B + ... = 1 \tag{4}$$

9.4 **Label** the dew line and the bubble line in the below figure. **Give** the states of matter of propane and butane found in the three regions bounded by the dew and bubble lines (i.e., in regions a, b, and c). 2.5 pt

Hint: **Think** about what happens when you lower the pressure of just a single substance. In which state is it at high pressure? In which state is it at low pressure? For region b, think about the mole fraction in the vapor phase and the mole fraction in the liquid phase.



pressure p against mole fractions of butane (x_{butane} and Y_{butane})

region a:

region b:

region c:

Industrially, distillation is carried out by varying both temperature and pressure. For simplicity, however, we separate our propane–butane mixture using changes in pressure only.

9.5 For a mole fraction $x_{\text{butane}} = 0.5$, **calculate** the maximum temperature T_{max} in °C at which both substances are just only in the liquid phase. **Note**: The vapour pressure of the mixture at 20 °C is 8.0 bar. 2.5 pt

$T_{\text{max}} =$ _____ °C

Now we lower the pressure isothermally until it lies slightly below the upper, linear line and wait until thermal equilibrium is reached. We then separate the gas phase.

9.6 **Read** the composition Y_{Butane} of the separated gas phase from the diagram and **state** the molar fractions in the gas phase of butane Y_{Butane} and propane Y_{Propane}. 0.5 pt

$Y_{\text{Butane}} =$ _____

$Y_{\text{Propane}} =$ _____

Now we perform another distillation with the obtained gas and again collect the gas phase.

9.7 **Find out** and **state** how many times we must repeat this procedure to obtain 95% pure propane. Include in your number also the first distillation starting at $x_{\text{Butane}} = 0.5$. **Give** the purity of propane after the last needed distillation. 2.0 pt

purity of propane = _____

Most lighters contain a mixture of butane and propane, with the relative proportions of each varying depending on how the lighter is used.

9.8 **Give** one reason why butane is used in lighters in addition to propane. **Give** one reason why butane is not used exlusively in lighters. 1.0 pt

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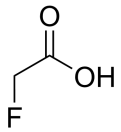
Q10-1

English (Official)

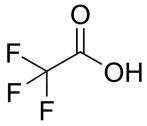
Fluorines Activate Acetate (11.0 pts, 8%)

While fluorine is rare in biological organic molecules, it is heavly used in synthetic chemistry. Its applications range from the deprotection of alcohols by cleaving Si—O bonds to the modification of metabolic stability of drugs and alteration of the reaction charateristics of chemicals.

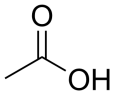
Trifluoroacetic acid (**TFA**) and monofluoroacetic acid (**MFA**) are fluorated derivatives of acetic acid (**AcOH**).



MFA



TFA



AcOH

10.1 **Order** acetic acid, **TFA** and **MFA** by their acid strength (pK_a). **Explain** your choice of strongest and weakest acid (using text and/or drawings). 2.0 pt

pK_a _____ < _____ < _____

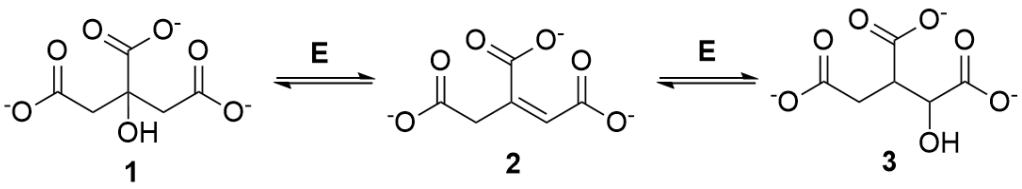
As a responsible chemist you check the safety data sheets of **TFA**, **MFA** and **AcOH** before doing any experiments. All three have warnings about severe skin burns and eye damage, which is typical for acids. **MFA** has the additional warning "fatal if swallowed" even at relatively low doses, which is absent in either **TFA** and **AcOH**. Surprised, you look into the mechanism of **MFA** toxicity.

You discover that intracellular **MFA** affects the citrate cycle, citrate transport in mitochondria and causes low bioavailability of calcium. The three mechanisms have various biological consequences such as ATP & metabolite depletion, heart failure and chaos in the nervous system.

After focusing on the chemical aspects, you discover that this is a case of lethal synthesis. This means not **MFA** (fluoroacetate in biological conditions) acts as the toxin, but rather a product, which is first synthesised via cell metabolism.

The responsible metabolic process is the citrate cycle, which is responsible for energy production and providing biosynthetic intermediates.

Under **MFA**-free conditions, the enzyme acetyl-CoA synthetase catalyses the formation of acetyl-CoA from acetate and cofactor A. Then acetyl-CoA is converted to citrate (**1**) via enzymatic reactions. The enzyme aconitase (**E**) converts citrate (**1**) to isocitrate (**3**) via the intermediate aconitate (**2**).



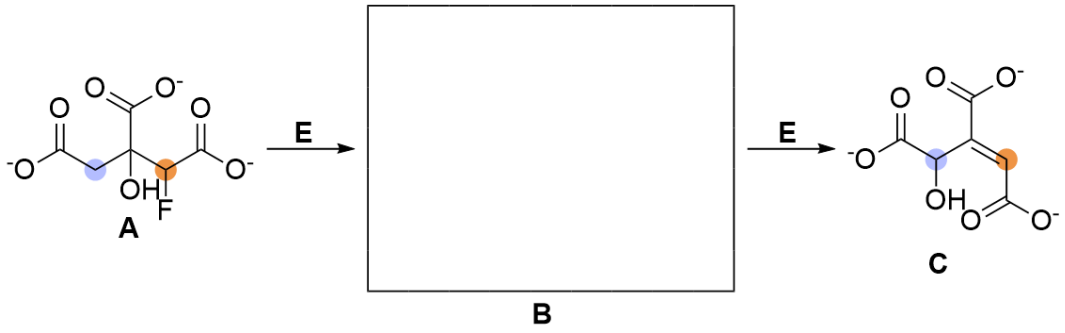
1 2 3

10.2 **Name** the two reactions catalysed by aconitase (**E**). 1.0 pt

Upon entering the cells, fluoroacetate (deprotonated **MFA**) is mistaken for acetate by acetyl-CoA synthetase and used to produce fluoroacetyl-CoA. Fluoroacetyl-CoA is used by the enzymes of the citrate cycle to produce 2-fluorocitrate (**A**).

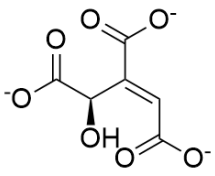
The enzyme aconitase (**E**) catalyses the reaction from **A** to 4-hydroxyaconitate (**C**). **C** binds the active site and fully inhibits enzymatic activity, halting the citrate cycle.

10.3 **Draw** intermediate **B** and the reaction mechanism from intermediate **B** to **C**. 2.0 pt



You read that only one of the four possible stereoisomers of 4-hydroxyaconitate is able to inhibit the enzyme.

10.4 **Assign** the two stereodescriptors of the inhibiting stereoisomer of 4-hydroxyaconitate. 1.0 pt



☐ *R*	☐ *Z*/*cis*
☐ *S*	☐ *E*/*trans*

When looking into the low calcium bioavailabilty (hypocalcaemia), you find the formation constant $K_{cit} = 2.76 \times 10^{-3}$ of this calcium citrate complex ($Ca(cit)^-$) under physiological conditions. Unfortunately you can not find any values for the calcium fluorocitrate complex ($Ca(Fcit)^-$). You decide to measure it yourself and get the following values.

	$mol\,dm^{-3}$
$[Ca^{2+}]$	2.083333×10^{-2}
$[Fcit^{3-}]_{total}$	6.000000×10^{-2}
$[Fcit^{3-}]$	5.999908×10^{-2}

10.5 **Calculate** the formation constant K_{Fcit} of calcium fluorocitrate ($Ca(Fcit)^-$). 1.0 pt

$K_{Fcit} =$ _____

10.6 Given that K_{Fcit} is lower than K_{cit}, **explain** how hypocalcaemia happens upon **MFA** exposure. 1.0 pt

When reading more about the toxicity of halogenated acetate derivatives, you find that many of them (iodoacetate, bromoacetate, dichloroacetate and others) are toxic to cell metabolism, all of them by inhibiting different enzymes.

Interestingly trifluoroacetate and difluoroacetate are not among them. The data suggests that both compounds enter the cell. While difluoroacetate can enter the citrate cycle, trifluoroacetate is not metabolised.

10.7 **Speculate** why trifluoroacetate can not be metabolised and is therefore not toxic via the same mechanism as monofluoroacetate. 1.0 pt

10.8 **Speculate** why difluoroacetate and its metabolites can not inhibit aconitase similarly to fluoroacetate and its metabolites. **State** the consequences. 2.0 pt