

**CHEMISTRY.
OLYMPIAD.CH**

CHEMIE-OLYMPIADE
OLYMPIADES DE CHIMIE
OLIMPIADI DELLA CHIMICA

SwissChO 2022 - Central Exam

INSTRUCTIONS

- Write your name on each page and number these.
- You have three hours to solve the problems. Wait for the **START** signal before you begin.
- Use a new page for each problem.
- Write all necessary calculations legibly.
- 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 allowed to do so.
- Only **answers written on the answer sheets** can be considered.
- This exam has 20 pages.

Viel Erfolg!
Bonne chance!
Buona fortuna!
Good luck!

CONSTANTS AND FORMULAE

Avogadro constant	$N_A = 6.022 \cdot 10^{23} \text{ mol}^{-1}$	Ideal gas law	$pV = nRT$
Universal gas constant	$R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$	Gibbs energy	$G = H - TS$
Faraday constant	$F = 96\,485 \text{ C mol}^{-1}$	$\Delta_r G^0 = -RT \cdot \ln(K) = -nFE_{\text{Zelle}}^0$	
Planck constant	$h = 6.626 \cdot 10^{-34} \text{ J s}$	Nernst equation	$E = E^0 + \frac{R \cdot T}{z \cdot F} \cdot \ln\left(\frac{c_{\text{ox}}}{c_{\text{red}}}\right)$
Speed of light	$c = 2.998 \cdot 10^8 \text{ m s}^{-1}$	Energy of a photon	$E = \frac{h \cdot c}{\lambda}$
Temperature	$0^\circ\text{C} = 273.15 \text{ K}$	Lambert-Beer law	$A = \log\left(\frac{I_0}{I}\right) = \epsilon \cdot c \cdot L$

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

Periodic Table of Elements

1 H 1.008																	2 He 4.003
3 Li 6.94	4 Be 9.01																9 F 19.00
11 Na 22.99	12 Mg 24.31																17 Cl 35.45
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						35 Br 79.90
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 [98]	44 Ru 101.07	45 Rh 102.91	46 Pd 106.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.76	52 Te 127.60	53 I 126.90	54 Xe 131.29
55 Cs 132.91	56 Ba 137.33	57–71	72 Hf 178.49	73 Ta 180.95	74 W 183.84	75 Re 186.21	76 Os 190.23	77 Ir 192.22	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	84 Po [209]	85 At [210]	86 Rn [212]
87 Fr [223]	88 Ra [226]	89–103	104 Rf [267]	105 Db [268]	106 Sg [269]	107 Bh [270]	108 Hs [270]	109 Mt [278]	110 Ds [281]	111 Rg [282]	112 Cn [285]	113 Nh [286]	114 Fl [289]	115 Mc [290]	116 Lv [293]	117 Ts [294]	118 Og [294]
57 La 138.91	58 Ce 140.12	59 Pr 140.91	60 Nd 140.24	61 Pm [145]	62 Sm 150.36	63 Eu 151.96	64 Gd 157.25	65 Tb 158.93	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.05	71 Lu 174.97			
89 Ac [227]	90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np [237]	94 Pu [244]	95 Am [243]	96 Cm [247]	97 Bk [247]	98 Cf [251]	99 Es [252]	100 Fm [257]	101 Md [258]	102 No [259]	103 Lr [266]			

SCORE SHEET

NOT TO BE FILLED IN BY PARTICIPANTS

Name of participant: _____

Task	Title	Maximum Points	Achieved Points
1	Multiple Choice Questions	12.0	
2	Solubility: Fluorescence & Uranine	8.0	
3	Titration: Malic Acid and Maleic Acid	10.0	
4	Thermodynamics: Gas Heater of a House	11.5	
5	Kinetics: Radioactive Decay in an Apple Tree	14.0	
6	Redox and Electrochemistry: Unknown metal	9.0	
7	Lambert-Beer Law: Analysis of Traces of Copper Salts	8.5	
8	Ideal Gas Law: Start of a Roller Coaster	12.0	
9	Organic Chemistry: Standard Reactions	9.0	
10	Organic Chemistry II: Synthesis of Indigo	6.0	
Total		100.0	

PROBLEM 1 - MULTIPLE CHOICE QUESTIONS

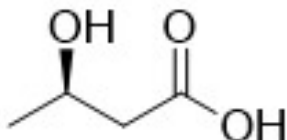
12.0 POINTS

For any question, choose exactly one answer:

1.1 Which of the following does **not** have the ground state configuration $1s^2 2s^2 2p^6$?

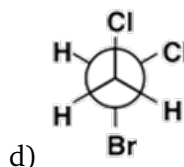
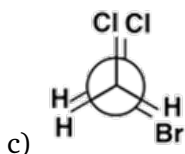
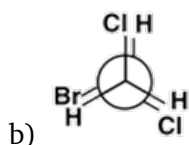
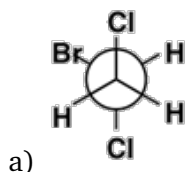
- a) Ne b) Na^+ c) Cl^- d) F^-

1.2 Which of (a)-(d) is the correct IUPAC name of the following compound?

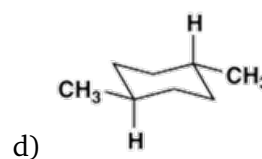
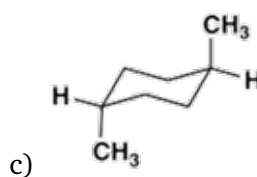
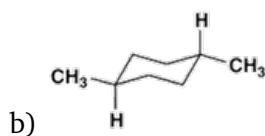
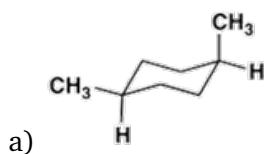
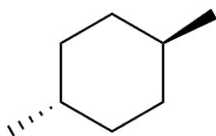


- a) 2-hydroxybutanoic acid
b) 3-hydroxybutanoic acid
c) 2-hydroxypropanoic acid
d) 1-carboxypropan-2-ol

1.3 Which of (a)-(d) is the most stable conformation?



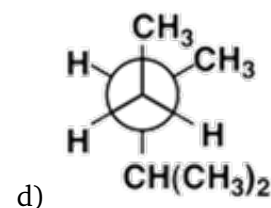
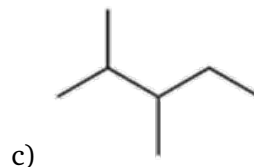
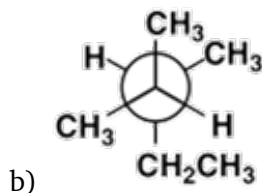
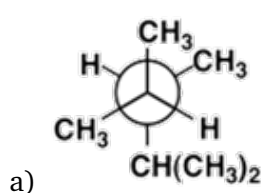
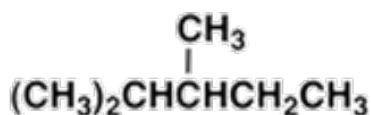
1.4 Which structure is different from the following?



1.5 Which of the following statements regarding cycloalkanes is wrong?

- a) The planar form of any cycloalkane with a ring larger than cyclopropane will not be the most stable conformation.
b) Cyclopentane is nonplanar to avoid the torsional strain between adjacent C-H bonds.
c) Any disubstituted cycloalkane can have *cis* and *trans* isomers.
d) The least strained form of any unsubstituted cycloalkane is the chair conformation of cyclohexane.

1.6 Which structure is of a compound different than the following?



1.7 Which of the following statements is false?

- a) The π molecular orbitals of buta-1,3-diene are derived from 2p atomic orbitals of carbon atoms, and there are four of them.
- b) Any orbital can accommodate up to two electrons, so buta-1,3-diene has eight π electrons.
- c) The complete set of molecular orbitals obtained by combining atomic orbitals includes an increased number of nodes.
- d) Some orbitals do not have any nodes.

1.8 Which compound does **not** have a conjugated system?

- a) $\text{CH}_2=\text{CH}-\text{C}\equiv\text{C}-\text{CH}_3$
- b) $\text{CH}_3-\text{CH}=\text{CH}-\text{OCH}_3$
- c) $\text{CH}_3-\text{CH}=\text{CH}-\text{CN}$
- d) $\text{CH}_3-\text{CH}=\text{C}=\text{CH}-\text{CH}_3$

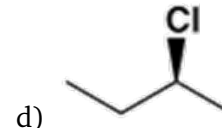
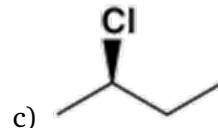
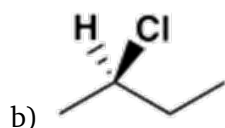
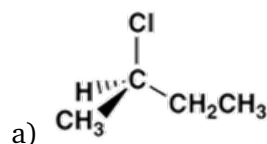
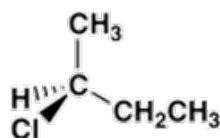
1.9 Which carboxylic acid is most acidic?

- a) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CO}_2\text{H}$
- b) $\text{CH}_3\text{CH}_2\text{CH}(\text{Cl})\text{CO}_2\text{H}$
- c) $\text{CH}_3\text{CH}(\text{Cl})\text{CH}_2\text{CO}_2\text{H}$
- d) $\text{ClCH}_2\text{CH}_2\text{CH}_2\text{CO}_2\text{H}$

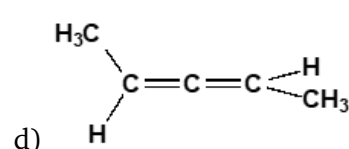
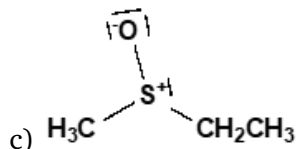
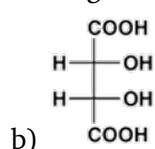
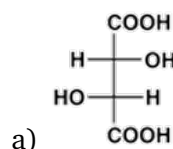
1.10 Which of the following pairs does **not** show an acid and its conjugate base?

- a) $\text{H}_3\text{N}^+\text{CH}_2\text{CO}_2\text{H}$ and $\text{H}_3\text{N}^+\text{CH}_2\text{CO}_2^-$
- b) $\text{H}_2\text{NCH}_2\text{CO}_2\text{H}$ and $\text{H}_2\text{NCH}_2\text{CO}_2^-$
- c) $\text{H}_2\text{NCH}_2\text{CO}_2\text{H}$ and $\text{H}_3\text{N}^+\text{CH}_2\text{CO}_2^-$
- d) $\text{H}_3\text{N}^+\text{CH}_2\text{CO}_2^-$ and $\text{H}_2\text{NCH}_2\text{CO}_2^-$

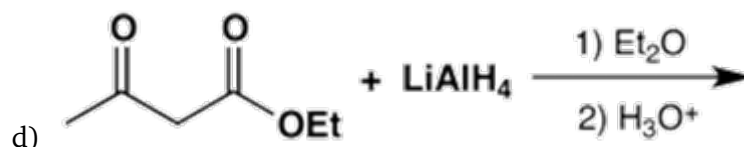
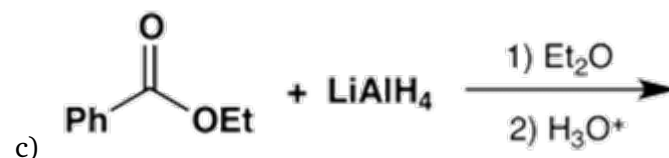
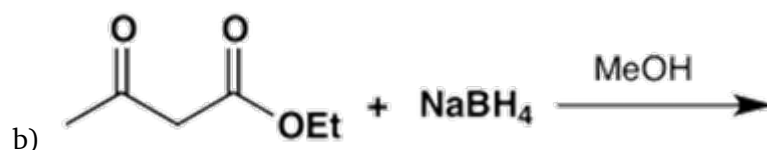
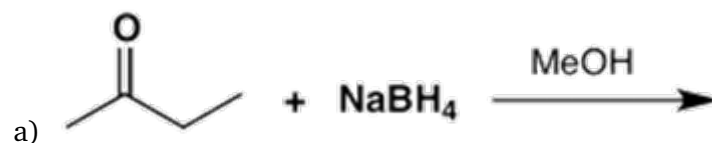
1.11 Which of (a)-(d) shows the same compound as the following?



1.12 Which of the following compounds is achiral?



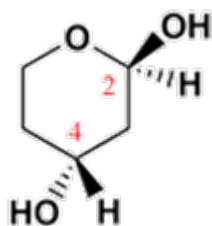
1.13 Which of the following reactions gives no product containing a stereocenter?



1.14 Which of the following is **not** an allyl anion analogue?

- a) $\text{CH}_3\text{CH}=\text{CH}_2$
- b) $^-\text{CH}_2\text{CO}_2\text{Et}$
- c) $^-\text{CH}_2\text{NO}_2$
- d) $\text{CH}_3\text{OCH}=\text{CH}_2$

1.15 Which is the correct assignment of chirality at C2 and C4 of the following molecule?



- a) 2*S*, 4*S*
- b) 2*R*, 4*R*
- c) 2*S*, 4*R*
- d) 2*R*, 4*S*

PROBLEM 2 - SOLUBILITY: FLUORESCENCE & URANINE**8.0 POINTS**

In this task, we will take a look at Fluorescein, or to be a bit more specific its sodium salt Uranine ($\text{C}_{20}\text{H}_{10}\text{Na}_2\text{O}_5$). Uranine is very well soluble in water, a saturated solution has a concentration of 500 g L^{-1} .

2.1 What is the concentration of a saturated Uranine solution in mol L^{-1}

2.2 What is the solubility product of the sodium salt Uranine (in $\text{mol}^3 \text{ L}^{-3}$)?

2.3 We have a bucket of water. We already dissolved 100 g of table salt (NaCl) in there. When we add uranine, we get to the saturated solution after adding 0.5 kg and then no more will dissolve. What is the final volume of the solution?

When Uranine is dissolved in water, a phenomenon called fluorescence can be seen. A solution of Uranine will appear with a green colour, because the light that shines on it is absorbed and only the green part of the light is emitted. In water, a concentration of about 0.05 g m^{-3} is required to see the coloration.

You live in Graubünden and you want to find out whether the river next to your house goes into Lake Zurich (Zürichsee) or into Lake Constance (Bodensee). You have read that Uranine does not cause any environmental damage, so you decide to make an experiment to find out where the river goes.

The values you found were that Lake Zurich and Lake Constance contain an approximate volume of 3.9 km^3 and 48 km^3 , respectively. You want to use a saturated solution of Uranine that you still have standing in your basement.

2.4 How many litres of your solution do you have to pour into the small river next to your house?

2.5 Why could you not only throw in a solution that would be just sufficient to be detected if all of it went into the smaller of the two lakes?

2.6 What will happen to the river after you poured in your solution?

2.7 To avoid the problem in 2.6, what would you do? Why is pouring just a little bit at a time not a solution?

PROBLEM 3 - TITRATION: MALIC ACID AND MALEIC ACID**10.0 POINTS**

In ripe fruits such as apples and pears, the majority of acids is malic acid, a diprotic acid, also synthetically produced and used in e.g. sour apple rings. When this acid is heated to a high temperature (around 250°C), maleic acid is formed.

You can read the formula and acidity from the following table:

Fruit Acid	Simplified Formula	pK _{a,1}	pK _{a,2}
Malic acid	HOOC-CHOH-CH ₂ -COOH	3.45	5.6
Maleic acid	HOOC-CH=CH-COOH	1.9	6.5

3.1 Which of the two acids is chiral? Draw its skeletal formula and mark the chiral center!

3.2 Consider only the first acid, malic acid: Can you determine whether a special H is given off first as H⁺? Why this one or why not?

3.3 A relatively sour-tasting fruit juice is being titrated. The initial pH is 2.3. With a short calculation, show which malic acid concentration this indicates! Assume malic acid to be the only acid present in the fruit juice.

3.4 To determine the amount of malic acid exactly, 100 ml of the fruit juice is being titrated with 1 mol L⁻¹ sodium hydroxide solution (NaOH) and 23 ml NaOH solution is needed until the acid is fully neutralised. What should be written on the fruit juice package as the content of malic acid in g L⁻¹?

3.5 Now imagine that you titrate 0.2 mol L⁻¹ maleic acid with 1 mol L⁻¹ sodium hydroxide solution. Sketch the titration curve you expect!

Which species should occur with which concentration exactly at pH = 5.5? You may use certain approximations.

PROBLEM 4 - THERMODYNAMICS: GAS HEATER OF A HOUSE**11.5 POINTS**

Today most houses use a gas heater to keep the temperature at a constant level during the cold winter times. In this exercise we want to take a look at the thermodynamics behind such devices and train the application by calculating the energetic properties of the gas. We are looking at a heater that uses natural gas as the energy source. We assume the gas does only consist of (mass percent) 70 % methane (CH_4), 20 % ethane (C_2H_6) and 10 % ethylene (C_2H_4).

4.1 Write down the reaction equation for the combustion of each constituent of the gas.

The standard enthalpy of formation of a compound is the change of enthalpy during the formation of the compound from its elements in their most stable states under standard conditions. In the scope of this task standard conditions can be assumed for all reactions.

Compound	Enthalpy of Formation (kJ mol^{-1})
CH_4	-74.53
C_2H_6	-83.75
C_2H_4	+52.53
CO_2	-393.47
H_2O	-292.74

A positive enthalpy of formation implies that heat is required to create a compound from its elements and a negative enthalpy means heat is released when it is created. The standard enthalpy of a reaction can be computed by subtracting the heat required to create the products from their elements by the heat required to create the reactants from their elements.

4.2 Calculate the standard enthalpy of reaction for each of the above combustion reactions per mol of the respective gas using the data given in the table above.

Now that we know how much heat is produced by the reactions, let's apply it in a realistic situation. Winter broke over Switzerland and the outside temperature dropped to 0°C . We bought a new house we want to move into. Our preferred temperature for a comfortable living is 20°C . The house contains a volume of 500 m^3 and will be assumed to be perfectly insulated and air-tight. The initial pressure in the house is $100'000\text{ Pa}$. The molar weight of the air is given as 28.96 g mol^{-1} .

4.3 Calculate the mass of air in kg in the house.

The heat it takes to alter the temperature of air can easily be calculated with the formula:

$$\Delta H = C_v \cdot \Delta T \cdot m$$

where $C_v = 0.718 \frac{\text{kJ}}{\text{kg}\cdot\text{K}}$ can be assumed as a constant value.

4.4 Calculate the enthalpy difference required to heat up our house from the outside temperature to the desired temperature.

4.5 For each constituent of the gas compute the molar amount in 1 kg natural gas.

4.6 Find the mass of gas required to heat up the house.

PROBLEM 5 - KINETICS: RADIOACTIVE DECAY IN AN APPLE TREE**14.0 POINTS**

During the nuclear catastrophe in Chernobyl, many environmental threats were released. In the scope of this problem, we want to take a look at the radioactivity of the isotope ^{137}Cs and assume that only this isotope was released. Caesium decays with β^- -decay and has a half-life of $t_{1/2}(^{137}\text{Cs}) = 30.19 \text{ a}$. This means it takes 30.19 years until half of it has decayed.

5.1 Write down the complete decay reaction of ^{137}Cs .

5.2 Calculate the rate constant for the reaction above.

We assume that the above-ground half-sphere with a 10 km radius from the reactor was contaminated with 20 kg of ^{137}Cs . The radiation that humans can cope with is measured by the activity of a probe. The activity A is given by $A = k \cdot N$ with the rate constant k and the number of nuclei N . The molar mass $M(^{137}\text{Cs})$ is given as 136.9 g mol^{-1} . The volume of a sphere of radius r is given by $V = \frac{4}{3}\pi r^3$.

5.3 Calculate the activity in Bq m^{-3} ($\text{s}^{-1} \text{ m}^{-3}$) in the 10 km radius area around the reactor.

According to Switzerland's radiation protection law from 1994, the maximum allowed activity for a housing can be 1000 Bq m^{-3} and the maximum allowed activity for workrooms is 3000 Bq m^{-3} .

5.4 According to the law mentioned above, in which year would people be able to work in the area 10 km around the reactor? And when would they be able to live there again?

A fictional character, Dimitri has been out of the country when the catastrophe happened. Despite all the warnings from his family members he went in there a year after the catastrophe to see whether his beloved apple tree survived. Because the tree has been such a long time in the contaminated area it established an equilibrium and accumulated 0.01 ppm (ppm = parts per million = 10^{-6}) of the currently existing amount of all ^{137}Cs in the entire contaminated area. It will be assumed that the contamination is spread evenly over the whole tree.

Dimitri took the tree with himself into a safe country far away. Because Dimitri cares about his health, he found out, that the maximum activity of food must be below 600 Bq kg^{-1} . So, he weighed his apple tree and got a mass of 5000 kg. It is already an adult tree, so its growth is negligible and the mass can be assumed constant. He also knows that his tree produced apples that sum up to 250 kg every year and that the radioactive material is distributed evenly over the whole tree at all time.

5.5 How long will Dimitri think it takes until he can enjoy his apples again if he only takes the half-life of ^{137}Cs into account?

Dimitri was really sad to see it would take so long. So, he did some more research and found out, that the decay actually goes faster than just with the given half-life. Because the tree loses contaminated apples every year and refreshes with new mass, the amount of ^{137}Cs decreases faster than just with the given half-life.

5.6 How long will Dimitri have to wait now until his apples will be edible without hazard?

5.7 Dimitri is now 20 years old, do you think he will still be able to eat one of his beloved apples?

PROBLEM 6 - REDOX AND ELECTROCHEMISTRY: UNKNOWN METAL**9.0 POINTS**

While cleaning up in the laboratory, a colourless block of an unknown metal is found. Because enough of this metal has been found, a galvanic element is to be built with it.

6.1 A few tests are made. Formulate your conclusions in each case (for test i) to iii))!

- i) If a mercury ion solution (Hg^{2+}) is dripped on it, a dark layer of mercury is deposited.
- ii) If the metal is dipped into a tin ion solution (Sn^{2+}), no reaction takes place!
- iii) The metal reacts with iodine (I_2) and forms a salt.

The metal is listed on the following redox table! Which metal is it? Is it a stronger or weaker reducing agent than iron?

Standard electrode potentials					
Ion concentrations: 1 mol L ⁻¹ in water, 25°C, values in volts					
Li	Li^+	-3.05	Sn^{2+}	Sn^{4+}	0.15
K	K^+	-2.93	Cu	Cu^{2+}	0.35
Ca	Ca^{2+}	-2.87	4 OH^-	$\text{O}_2 + 2 \text{ H}_2\text{O}$ (pH = 14)	0.40
Na	Na^+	-2.71	2 I^-	I_2	0.54
Mg	Mg^{2+}	-2.37	Fe^{2+}	Fe^{3+}	0.75
Al	Al^{3+}	-1.66	Ag	Ag^+	0.80
$\text{H}_2 + 2 \text{ OH}^-$	$2 \text{ H}_2\text{O}$ (pH = 14)	-0.83	$\text{NO}_2 + 2 \text{ H}_2\text{O}$	$\text{HNO}_3 + \text{H}_3\text{O}^+$	0.81
Zn	Zn^{2+}	-0.76	4 OH^-	$\text{O}_2 + 2 \text{ H}_2\text{O}$ (pH = 7)	0.83
Cr	Cr^{3+}	-0.74	Hg	Hg^{2+}	0.85
$2 \text{ Ag} + \text{S}^{2-}$	Ag_2S	-0.71	2 Br^-	Br_2	1.07
S^{2-}	S	-0.51	Pt	Pt^{2+}	1.20
Fe	Fe^{2+}	-0.44	$6 \text{ H}_2\text{O}$	$\text{O}_2 + 4 \text{ H}_3\text{O}^+$ (pH = 0)	1.24
$\text{H}_2 + 2 \text{ H}_2\text{O}$	$2 \text{ H}_3\text{O}^+$	-0.42	$2 \text{ Cr}^{3+} + 21 \text{ H}_2\text{O}$	$\text{Cr}_2\text{O}_7^{2-} + 14 \text{ H}_3\text{O}^+$	1.35
$\text{Pb} + \text{HSO}_4^- + \text{H}_2\text{O}$	$\text{PbSO}_4 + \text{H}_3\text{O}^+$	-0.36	2 Cl^-	Cl_2	1.36
Ni	Ni^{2+}	-0.25	Au	Au^{3+}	1.42
Sn	Sn^{2+}	-0.14	$\text{Mn}^{2+} + 12 \text{ H}_2\text{O}$	$\text{MnO}_4^- + 8 \text{ H}_3\text{O}^+$ (pH = 0)	1.51
Pb	Pb^{2+}	-0.13	$\text{PbSO}_4 + 5 \text{ H}_2\text{O}$	$\text{PbO}_2 + \text{HSO}_4^- + 3 \text{ H}_3\text{O}^+$	1.68
$\text{H}_2 + 2 \text{ H}_2\text{O}$	$2 \text{ H}_3\text{O}^+$	± 0	2 F^-	F_2	2.87

6.2 A galvanic element is to be built with the metal. What should be the successful strategy for this: to find a weaker reducing agent or a stronger one than the metal? Why?

6.3 Assume that some silver and the corresponding salts are also found in the same laboratory. Draw a galvanic element that works with the unknown metal against silver, with the poles correctly indicated.

6.4 What are the anode and cathode reactions in your galvanic element? What is the expected voltage? Under what conditions?

PROBLEM 7 - LAMBERT-BEER LAW: ANALYSIS OF TRACES OF COPPER SALTS**8.5 POINTS**

Copper salts are often used to spray grapes during the ripening period. For this, there are certain regulations as to when spraying is allowed for the last time in order to prevent excessive copper content in wines. Nevertheless, traces of copper can be detected in certain red wines.

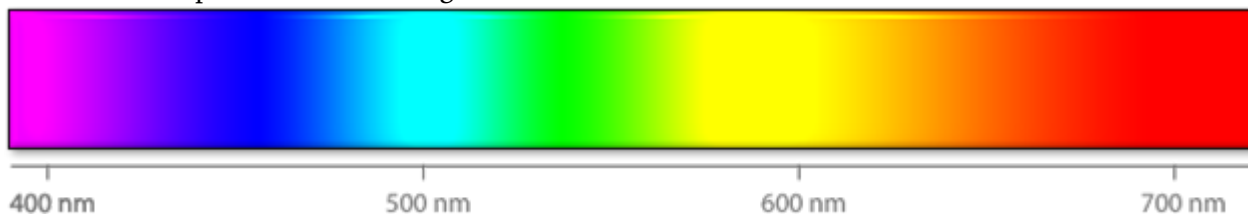
When a solution is being crossed by a light beam of intensity I_0 , the light intensity decreases and becomes $I < I_0$. For the measurements, the law first formulated in 1729 and supplemented by August Beer in 1852 applies, according to which the extinction, i.e. the absorbance of the material for light of the wavelength, is given by an extinction coefficient times the concentration times the layer thickness:

$$A = \log \left(\frac{I_0}{I} \right) = \log \left(\frac{1}{\tau} \right) = \epsilon(\lambda) \cdot c \cdot d$$

According to SI, the values are to be given as follows:

- c : concentration of the absorbing substance in the liquid (unit: $[\text{mol m}^{-3}]$).
- $\epsilon(\lambda)$: molar extinction coefficient at the wavelength λ . This is a quantity specific to the absorbing substance and has the unit $[\text{m}^3 \text{mol}^{-1} \text{m}^{-1}]$ (older non-SI-form: $[\text{L mol}^{-1} \text{m}^{-1}]$).
- d : path length of the light in the material, unit: $[\text{m}]$.
- τ defined as transmission

The relationship between wavelength and colour can be seen in this illustration:



7.1 When measuring a solution of copper sulfate in the laboratory, the first thing you notice is the light blue colour of the copper solution, which shows a very slight tinge of turquoise. A copper nitrate solution has the same colour. Which species are responsible for this colour? What colour does the absorbed light have?

7.2 When measuring copper sulfate solutions, the following values are measured in a cell of 4 cm thickness at 635 nm:

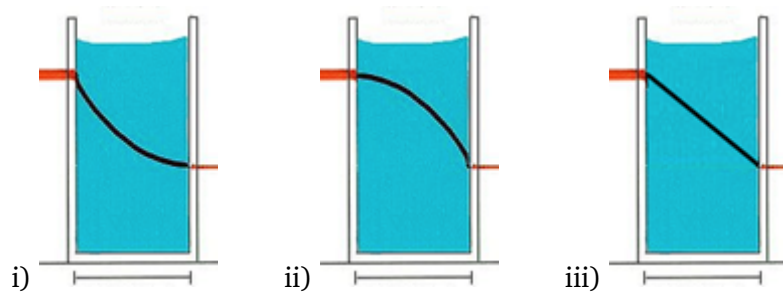
Concentration	Absorption
0.1 mol L ⁻¹	0.236
0.2 mol L ⁻¹	0.473
0.4 mol L ⁻¹	0.936

Determine the extinction coefficient! How do you get a more precise result?

7.3 If 100 g of grapes are washed with 200 mL distilled water in July and the rinsing water shows an absorbance value of 0.0017, what was the copper concentration in the solution and the amount of copper sulfate on the surface?

7.4 For the determination of copper in wine, e.g. in food control, the copper ions are complexated with phenanthroline. Measurements are being taken at 554 nm. What colour do you think the complex has? Why do they use a phenanthroline complex instead of measuring Cu^{2+} directly?

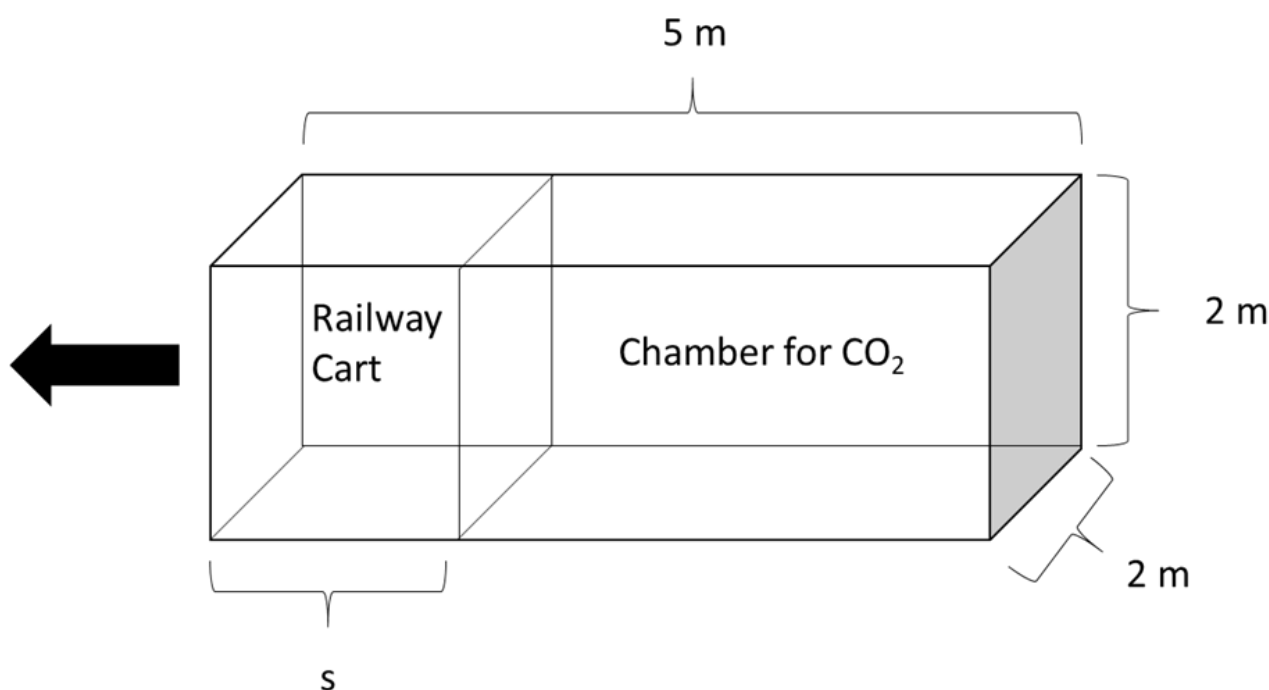
7.5 Which of the following pictures describes the intensity as a function of the light's way through the solution in the best possible way? Why?



PROBLEM 8 - IDEAL GAS LAW: START OF A ROLLER COASTER**12.0 POINTS**

The chemists at the University of Curiosity have started a new project. They want to have a little more fun on their campus, so they decided to build a roller coaster with what they have in the laboratory. Our lab is responsible for the starting box. The initial pressure over the whole campus is $1 \text{ atm} = 101\,325 \text{ Pa}$. The temperature can be assumed to be constant at 25°C .

The box which the railway car will be accelerated in is $L = 5 \text{ m}$ long, $H = 2 \text{ m}$ high, and $W = 2 \text{ m}$ wide and functions like a pneumatic cylinder. The roller coaster will be accelerated with solid CO_2 (dry ice) that is placed in the gas chamber behind the piston and will then be assumed to evaporate completely. Once all of it has evaporated, the brakes are loosened and the railway car will be accelerated through the built-up pressure until it is pushed out of the box, which constitutes a path length of 0.1 m , so the gas chamber behind will be $L' = 4.9 \text{ m}$ long. After that acceleration it should have reached a speed of $v = 100 \text{ km h}^{-1}$.



8.1 In a test run, nobody sits in the railway car for safety reasons, thus its weight is only $1\,200 \text{ kg}$. Find the mass of solid CO_2 that would be needed to reach the desired speed of 100 km h^{-1} . You can use the assumption that the pressure will be constant from when the acceleration starts until the railway car leaves the box.

Hint: The distance covered by an object accelerated with an acceleration a over time t is given as $s = \frac{1}{2} \cdot a \cdot t^2$.

8.2 Noticing how much dry ice was going to be required and given the fact that the cart will also be heavier if filled with people, they decided to try to make their system more efficient. Therefore, they compressed the CO_2 further, by pushing the piston more into the start box. Now the way of acceleration is $s = 4 \text{ m}$ and the length of the gas chamber is $L' = 1 \text{ m}$. Compute the speed of the railway car when it gets out as in task 8.1. (If you were unable to solve 8.1 assume a mass of 400 kg dry ice loaded into the chamber.)

8.3 Calculate the kinetic energy the railway car from 8.2 will have obtained.

8.4 That energy seems a bit too much. Find the amount of energy that could be extracted from the pressurised gas in the room as in 8.2.

8.5 It is impossible, that the railway car gained more kinetic energy, than there was energy stored in the pressurised gas. Where is the conceptual error in the calculation in 8.2 and 8.3?

8.6 What could you do to get rid of that error/reduce it so that the approximation has a good fit again?

PROBLEM 9 - ORGANIC REACTIONS: STANDARD REACTIONS**9.0 POINTS**

In problem 3, it has been mentioned, how malic acid is able to form maleic acid, if it has been heated up to about 250°C. In a simple structural formula, the mentioned acids are:

Malic acid: $\text{HOOC}-\text{CHOH}-\text{CH}_2-\text{COOH}$

Maleic acid: $\text{HOOC}-\text{CH}=\text{CH}-\text{COOH}$

9.1 Write down the reaction equation with the skeletal formulae and name the byproduct of the reaction described above.

How is this kind of reaction called? And how is it usually catalyzed – and especially in this case?

9.2 Give the correct names of the two acids according to the IUPAC rules.

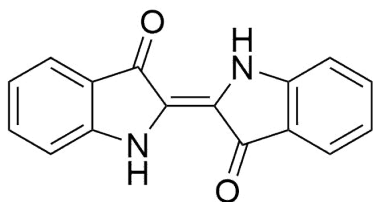
9.3 A reaction that is often called second fermentation in young wine is the reaction of malic acid to lactic acid. In the process, the less acidic group is lost as carbon dioxide. Sketch the reaction with the skeletal formulae and name this type of reaction.

9.4 What is special about a possible stereochemistry during this reaction?

9.5 The maleic acid mentioned at the beginning reacts at increased temperatures to a cyclic form with trans/cis-isomerization followed by elimination of water. Draw the skeletal formula of the product and give a name for this type of reaction! How do you call the type of reverse reaction?

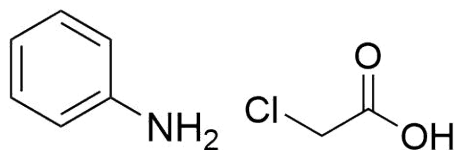
PROBLEM 10 - ORGANIC SYNTHESIS: SYNTHESIS OF INDIGO**6.0 POINTS**

The industrial chemist Heumann described two different syntheses for the blueish dye indigo. The difference is in the creation of one of the reactants for the final reaction.



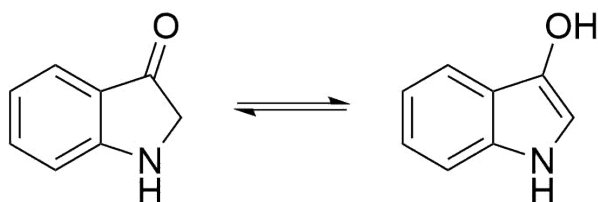
This is the molecule indigo, that shall be obtained by both reaction sequences.

For the first way we start with the following two reactants:

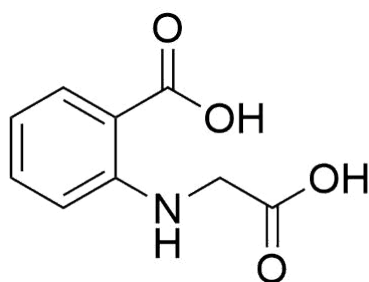


10.1 What will be the products, when the two molecules above react?

10.2 What do you need to get the product (indoxyl) of this first reaction sequence? How do you call such a species?



10.3 The other possible reactant is shown below. What will be the byproducts be when it reacts to the same product (indoxyl) of the first reaction sequence? Would you rather cool or heat the system?



10.4 What reactant will be needed to combine two of the indoxyl units of the first sequence to obtain indigo? What will be the corresponding byproduct?

10.5 What characteristics of a dye does Indigo have? How does that make it appear blue to the human eye?