

**CHEMISTRY.
OLYMPIAD.CH**

CHEMIE-OLYMPIADE
OLYMPIADES DE CHIMIE
OLIMPIADI DELLA CHIMICA

SwissChO 2022 - Central Exam

SOLUTION KEY

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 32 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															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 [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 La 138.91	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 Ac [227]	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:

SOLUTION:

0.5 or 1.0 points each, 12.0 points total

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

SOLUTION:

0.5 points

c) Cl^-

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

SOLUTION:

1.0 points

b) 3-hydroxybutanoic acid

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

SOLUTION:

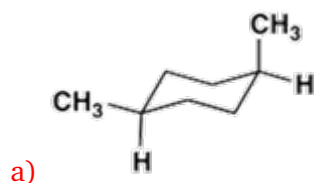
1.0 points total

d) all-staggered with Cl-Cl gauche, Cl-Br anti, and 2x H-Br gauche

1.4 Which structure is different from the following?

SOLUTION:

0.5 points total



1.5 Which of the following statements regarding cycloalkanes is wrong?

SOLUTION:

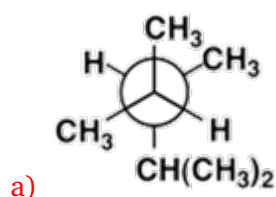
1.0 points total

c) Any disubstituted cycloalkane can have *cis* and *trans* isomers.

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

SOLUTION:

0.5 points total



1.7 Which of the following statements is false?

SOLUTION:

1.0 points total

b) Any orbital can accommodate up to two electrons, so buta-1,3-diene has eight π electrons.

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

SOLUTION:

0.5 points total

d) $\text{CH}_3 - \text{CH} = \text{C} = \text{CH} - \text{CH}_3$

1.9 Which carboxylic acid is most acidic?

SOLUTION:

0.5 points total

b) $\text{CH}_3\text{CH}_2\text{CH}(\text{Cl})\text{CO}_2\text{H}$

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

SOLUTION:

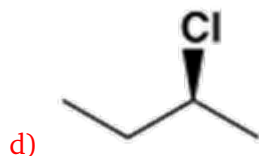
1.0 points total

c) $\text{H}_2\text{NCH}_2\text{CO}_2\text{H}$ and $\text{H}_3\text{N}^+\text{CH}_2\text{CO}_2^-$, these two molecules have the same sum formula and should therefore not be considered as a conjugate acid-base pair.

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

SOLUTION:

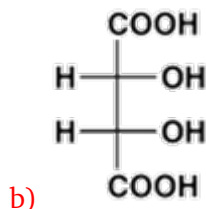
1.0 points total



1.12 Which of the following compounds is achiral?

SOLUTION:

1.0 points total



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

SOLUTION:

1.0 points total

c) Reaction C gives benzyl alcohol and ethanol, both of which are achiral. The other reactions give racemic alcohols (and EtOH in D).

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

SOLUTION:

1.0 points total

a) $\text{CH}_3\text{CH}=\text{CH}_2$. Draw Lewis structures for each compound and look for one with a double bond conjugated with an electron excess (negative charge or lone pair needed).

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

SOLUTION:

0.5 points total

b) 2*R*, 4*R*

PROBLEM 2 - SOLUBILITY: FLUORESCENCE & URANINE**9.0 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.

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

SOLUTION:**1.0 points total**

$$M(\text{C}_{20}\text{H}_{10}\text{Na}_2\text{O}_5) = 376.28 \text{ g mol}^{-1}$$

$$c = \frac{c(\text{m})}{M} = \frac{500 \text{ g L}^{-1}}{376.28 \text{ g mol}^{-1}} = 1.339 \text{ mol L}^{-1}$$

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

SOLUTION:**1.0 points total**

$$p = [\text{Na}^+]^2 \cdot [\text{C}_{20}\text{H}_{10}\text{O}_5^{2-}]$$

Because we have nothing else, we know that $\frac{1}{2} \cdot [\text{Na}^+] = [\text{C}_{20}\text{H}_{10}\text{O}_5^{2-}] = [\text{C}_{20}\text{H}_{10}\text{HNa}_2\text{O}_5] = c$, thus $[\text{Na}^+] = 2c$

So we get:

$$p = 4c^3 = 9.6 \frac{\text{mol}^3}{\text{L}^3}$$

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?

SOLUTION:**2.5 points total**

$$M(\text{NaCl}) = 58.433 \text{ g mol}^{-1}$$

$$n_{\text{NaCl}} = \frac{100 \text{ g}}{M(\text{NaCl})} = 1.711 \text{ mol}$$

$$n_{\text{Uranine}} = \frac{500 \text{ g}}{M(\text{C}_{20}\text{H}_{10}\text{Na}_2\text{O}_5)} = 1.329 \text{ mol}$$

$$[\text{Na}^+] = \frac{(n_{\text{NaCl}} + 2 \cdot n_{\text{Uranine}})}{V}$$

$$[\text{C}_{20}\text{H}_{10}\text{O}_5^{2-}] = \frac{n_{\text{Uranine}}}{V}$$

$$p = [\text{Na}^+]^2 \cdot [\text{C}_{20}\text{H}_{10}\text{O}_5^{2-}]$$

0.5 points each

When we plug the equations together, we get

$$p = \left(\frac{(n_{\text{NaCl}} + 2 \cdot n_{\text{Uranine}})}{V} \right)^2 \cdot \frac{n_{\text{Uranine}}}{V} \implies$$

$$V = \left(\frac{(n_{\text{NaCl}} + 2 \cdot n_{\text{Uranine}})}{p} \right)^{\frac{1}{3}} = 1.38 \text{ L}$$

1.0 points

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 indicate that Lake Zurich (Zürichsee) and Lake Constance (Bodensee) 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 in the small river next to your house?

SOLUTION:

1.0 points total

$$V = 0.05 \frac{\text{g}}{\text{m}^3} \cdot \frac{V_{\text{Lake}}}{500 \frac{\text{g}}{\text{L}}}$$

We only need the volume of Lake Constance, since we want to know where the water actually flows to.

$$V_{\text{in}} = 0.05 \frac{\text{g}}{\text{m}^3} \cdot \frac{48 \times 10^9 \text{ m}^3}{500,000 \frac{\text{g}}{\text{m}^3}} = 4800 \text{ m}^3 = 4.8 \times 10^6 \text{ L}$$

0.5 points each

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?

SOLUTION:

0.5 points total

Because it could be that the river flows in neither of the two expected lakes. Then the smaller lake wouldn't get coloured, and you'd assume it went into the larger one, what in this case still would not be true.

0.5 points

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

SOLUTION:

1.0 points total

The river would get a very strong greenish colour. Even though it would not be an environmental threat, it would sure cause people to freak out and you would get in trouble for doing that.

0.5 points

The river will overflow, since it is a small river, but you add enormous amounts of water in very little time.

0.5 points

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?

SOLUTION:

1.0 points total

You could try to execute the experiment at night, because then nobody would notice that the river had changed its colour.

0.5 points

Pouring just a little bit at a time is no good solution, because then it might just flow out of the lakes again and the desired concentration to make it visible would never be reached.

0.5 points

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.

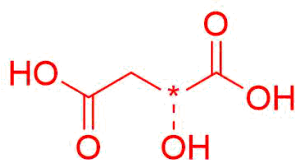
You can read the formula and acidity from the following table:

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 Is one of the two acids chiral? Which one? Draw the skeletal formula and mark the chiral center!

SOLUTION:

1.5 points total

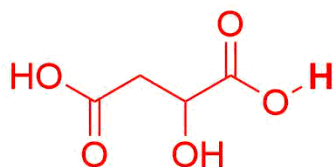


Malic acid with chiral center at C2.

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?

SOLUTION:

1.0 points total



Proton of the carboxylic acid group closer to the hydroxyl group (EWG) is more acidic. An alternative answer where a strong H-bond between the carboxylate anion and the hydroxy group is proposed, should also receive full marks.

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.

SOLUTION:

2.0 points total

pH of the solution of a weak acid: pH = 2.3, and the second deprotonation can be neglected if the pK_a values are sufficiently far apart (≥ 1 unit).

0.5 points

$$\text{pH} = \frac{1}{2} (\text{pK}_a - \log [\text{HA}]) \implies 10^{(\text{pK}_a - 2 \text{pH})} = [\text{HA}]$$

1.0 points

Calculation: $[\text{HA}] \approx 0.07 \text{ mol L}^{-1}$

0.5 points

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} ?

SOLUTION:

1.5 points total

$$c_{\text{Base}} \cdot V_{\text{Base}} \cdot 1 = c_{\text{Acid}} \cdot V_{\text{Acid}} \cdot 2$$

$$c_{\text{Acid}} = 1 \text{ mol L}^{-1} \cdot \frac{23 \text{ mL}}{100 \text{ mL} \cdot 2} = 0.115 \text{ mol L}^{-1}$$

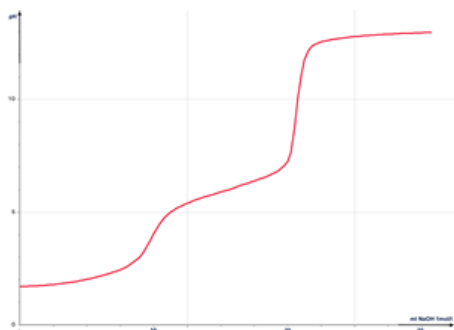
$$0.115 \text{ mol L}^{-1} \cdot 134.1 \text{ g mol}^{-1} = 15.4 \text{ g L}^{-1}$$

0.5 points each

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 $\text{pH} = 5.5$? You may use certain approximations.

SOLUTION:

4.0 points total



Correct shape: 0.5 points
2 buffer areas: 0.5 points each

$$[\text{H}_3\text{O}^+] = 0.0000032 \text{ mol L}^{-1} = 3.2 \times 10^{-6} \text{ mol L}^{-1}$$

$$[\text{OH}^-] = 0.000000032 \text{ mol L}^{-1} = 3.2 \times 10^{-9} \text{ mol L}^{-1}$$

$$1 \text{ pH below } \text{pK}_{a,2} \Rightarrow \frac{[\text{C}_4\text{H}_3\text{O}_4^-]}{[\text{C}_4\text{H}_2\text{O}_4^{2-}]} = \frac{10}{1}$$

$$\Rightarrow [\text{C}_4\text{H}_3\text{O}_4^-] = 0.182 \text{ mol L}^{-1} \text{ and } [\text{C}_4\text{H}_2\text{O}_4^{2-}] = 0.018 \text{ mol L}^{-1}$$

$$\text{And } \frac{[\text{C}_4\text{H}_4\text{O}_4]}{[\text{C}_4\text{H}_3\text{O}_4^-]} = \frac{1}{32000} \Rightarrow [\text{C}_4\text{H}_4\text{O}_4] \approx 6 \times 10^{-7} \text{ mol L}^{-1}$$

0.5 points for each calculation and correct result

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

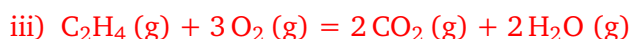
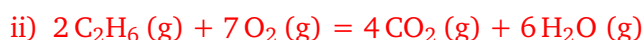
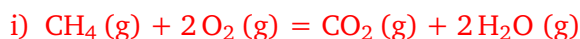
Today most houses use a gas heater to keep the temperature at a constant level during the cold winter times. In this exercise we want to take a look at the thermodynamics behind such devices and train the application by calculating the energetic properties of the gas.

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 (CH₄), 20 % ethane (C₂H₆) and 10 % ethylene (C₂H₄).

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

SOLUTION:

1.5 points total



0.5 points per correct equation, 0 points per equation with false coefficients, but do not give follow-up mistakes in calculations further down.

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 ₂ H ₆	- 83.75
C ₂ H ₄	+ 52.53
CO ₂	-393.47
H ₂ O	-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.

SOLUTION:

3.0 points total

i) $(-393.47 + 2 \times (-292.74)) - ((-74.53) + 2 \times 0) \text{ kJ mol}^{-1} = -904.42 \text{ kJ mol}^{-1}$

ii) $\frac{1}{2} \times (4 \times (-393.47) + 6 \times (-292.74) - 2 \times (-83.75) + 7 \times 0) \text{ kJ mol}^{-1} = -1581.41 \text{ kJ mol}^{-1}$

iii) $(2 \times (-393.47) + 2 \times (-292.74) - (52.53 + 3 \times 0)) \text{ kJ mol}^{-1} = -1424.95 \text{ kJ mol}^{-1}$

1.0 points per calculation

0.5 points if reactants and products are switched

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 m³ and will be assumed to be perfectly insulated and air-tight. The initial pressure in the house is 100'000 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.

SOLUTION:

2.0 points total

$$n = \frac{p \cdot V}{R \cdot T} = \frac{10^5 \text{ Pa} \cdot 500 \text{ m}^3}{8.3145 \text{ J mol}^{-1} \text{ K}^{-1} \cdot 273.15 \text{ K}} = 22015 \text{ mol}$$

$$m = n \cdot M = 22015 \text{ mol} \cdot 28.96 \text{ g mol}^{-1} = 637554.4 \text{ g} = 637.55 \text{ kg}$$

1.0 points per calculation

0.5 points if result is in g instead of kg

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.

SOLUTION:

1.0 points total

$$\Delta H = C_v \cdot \Delta T \cdot m = 0.718 \text{ kJ kg}^{-1} \text{ K}^{-1} \cdot 20 \text{ K} \cdot 637.55 \text{ kg} = 9155.2 \text{ kJ}$$

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

SOLUTION:

2.0 points total

$$M(\text{CH}_4) = 16.132 \text{ g mol}^{-1}, M(\text{C}_2\text{H}_6) = 30.248 \text{ g mol}^{-1}, M(\text{C}_2\text{H}_4) = 28.232 \text{ g mol}^{-1}$$

$$n(\text{CH}_4) = 1 \text{ kg} \cdot \frac{0.7}{M(\text{CH}_4)} = 43.3 \text{ mol}$$

$$n(\text{C}_2\text{H}_6) = 1 \text{ kg} \cdot \frac{0.2}{M(\text{C}_2\text{H}_6)} = 6.6 \text{ mol}$$

$$n(\text{C}_2\text{H}_4) = 1 \text{ kg} \cdot \frac{0.1}{M(\text{C}_2\text{H}_4)} = 3.5 \text{ mol}$$

0.5 points each

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

SOLUTION:

2.0 points total

First, we compute the heat provided by 1 kg gas:

$$\frac{\Delta H_{\text{gas}}}{\text{kg}} = -(\text{n}(\text{CH}_4) \cdot \Delta_{\text{R}}\text{H}(\text{CH}_4) + \text{n}(\text{C}_2\text{H}_6) \cdot \Delta_{\text{R}}\text{H}(\text{C}_2\text{H}_6) + \text{n}(\text{C}_2\text{H}_4) \cdot \Delta_{\text{R}}\text{H}(\text{C}_2\text{H}_4)) = 54586 \text{ kJ kg}^{-1}$$

Then we divide the required heat by that value:

$$\frac{\Delta H}{\Delta H_{\text{gas}}} = \frac{9155.22 \text{ kJ}}{54586 \text{ kJ kg}^{-1}} = 0.1677 \text{ kg} = 167.7 \text{ g}$$

So about 168 g of natural gas are needed to heat the house to the desired temperature.

1.0 points per calculation

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 .

SOLUTION:

1.0 points total



-0.5 points per mistake, min. 0 points

5.2 Calculate the rate constant for the reaction above.

SOLUTION:

1.0 points total

$$k = \frac{\ln(2)}{t_{1/2}(^{137}\text{Cs})} = 7.28 \times 10^{-10} \text{ s}^{-1} = 0.0230 \text{ a}^{-1}$$

We assume that the sphere with a 10 km radius from the reactor was contaminated with 20kg of ^{137}Cs . The radiation that humans can cope with is measured by the activity of a probe. The activity A can be calculated with the rate constant k and the number of nuclei N using the following formula. The molar mass $M(^{137}\text{Cs})$ is given as 136.9 g mol^{-1} .

$$A = k \cdot N$$

Hint: the volume of a sphere of radius r is given by

$$V = \frac{4}{3} \cdot \pi \cdot r^3$$

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

SOLUTION:

2.0 points total

If full sphere instead of half-sphere was used, -0.5 points

$$V = \frac{1}{2} \cdot \frac{4}{3} \pi r^3 = 2.09 \times 10^{12} \text{ m}^3$$

$$A = k \cdot N = k \cdot \frac{m}{M(^{137}\text{Cs})} \cdot N_A = 6.401 \times 10^{16} \text{ Bq}$$

$$\frac{A}{V} = 30622 \text{ Bq m}^{-3} = A_V(t=0)$$

1.0 points each for second and third calculation

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?

SOLUTION:

2.5 points total

$$N(t) = N(t=0) \cdot 2^{-\frac{t}{t_{1/2}}} \quad (0.5 \text{ points})$$

$$A_V(t) = k \cdot \frac{N(t)}{V} = k \cdot \frac{m}{M(^{137}\text{Cs})} \cdot \frac{N_A}{V} \cdot 2^{-\frac{t}{t_{1/2}}} \quad (0.5 \text{ points})$$

$$t = \frac{\ln\left(\frac{V \cdot A_V(t) \cdot M(^{137}\text{Cs})}{k \cdot m \cdot N_A}\right)}{\ln(2)} \quad (0.5 \text{ points})$$

For $A_V(t) = 3000 \text{ Bq} \cdot \text{m}^{-3}$: Time until working is possible = 101.2 years later

0.5 points

For $A_V(t) = 1000 \text{ Bq} \cdot \text{m}^{-3}$: Time until living is possible: 149.0 years later

0.5 points

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?

SOLUTION:

4.0 points total

$$m_{1a} = m \cdot 2^{-\frac{t}{t_{1/2}}} = 19.546 \text{ kg}$$

$$m_{\text{Cs in tree}}(t) = m_{1a} \cdot 10^{-8} \cdot 2^{-\frac{t}{t_{1/2}}}$$

$$c_{\text{Apple}}(t) = \frac{m_{\text{Cs in tree}}(t)}{5000 \text{ kg}}$$

$$A_{\text{Apple}}(t) = c_{\text{Apple}}(t) \cdot \frac{k}{M(^{137}\text{Cs})} \cdot N_A$$

0.5 points per equation

Plugging all the equations together gives:

$$A_{\text{Apple}}(t) = m_{1a} \cdot 10^{-8} \cdot \frac{2^{-\frac{t}{t_{1/2}}}}{5000 \text{ kg}} \cdot \frac{k}{M(^{137}\text{Cs})} \cdot N_A$$

$$t = -t_{1/2} \cdot \frac{\ln\left(\frac{5000 \text{ kg} \cdot M(^{137}\text{Cs}) \cdot A_{\text{Apple}}(t)}{m_{1a} \cdot 10^{-8} \cdot k \cdot N_A}\right)}{\ln(2)} = 232 \text{ a}$$

1.0 points per calculation

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?

SOLUTION:

3.5 points total

$$A(t = 1a) = \frac{(5000 - 250) \text{ kg}}{5000 \text{ kg}} \times A(t = 0a) = 0.95 \times A(t = 0a) = A(t = 0a) \times e^{-k_{\text{biol}} \cdot 1a}$$

$$0.95 = e^{-k_{\text{biol}} \cdot 1a}$$

$$\ln(0.95) = -k_{\text{biol}} \times 1a$$

$$k_{\text{biol}} = -\frac{\ln(0.95)}{1a} = 1.627 \times 10^{-9} \text{ s}^{-1}$$

1.0 points

$$k_{\text{total}} = k_{\text{biol}} + k = 2.534 \times 10^{-9} \text{ s}^{-1}$$

$$t_{1/2, \text{total}} = \frac{\ln(2)}{k_{\text{total}}} = 9.34 \text{ a}$$

$$m_{\text{Cs in tree}}(t) = m_{1a} \cdot 10^{-8} \cdot 2^{-\frac{t}{t_{1/2, \text{total}}}}$$

0.5 points for each

$$t = t_{1/2, \text{total}} \cdot \frac{\ln\left(\frac{5000 \text{ kg} \cdot M(^{137}\text{Cs}) \cdot 600 \text{ Bq kg}^{-1}}{m_{1a} \cdot 10^{-8} \cdot k_{\text{total}} \cdot N_A}\right)}{\ln(2)} \approx 88 \text{ a}$$

So Dimitri would have to wait 88 years for his apples to be edible again.

1.0 points for calculation with result, 0.5 points if only formal

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

SOLUTION:

0.5 points total

Probably not, as he would have to reach an age beyond 100 years.

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 H_2O (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 Ag + 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 H_2O	$\text{O}_2 + 4 \text{H}_3\text{O}^+$ (pH = 0)	1.24
$\text{H}_2 + 2 \text{H}_2\text{O}$	2 H_3O^+	-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 H_3O^+	± 0	2 F^-	F_2	2.87

SOLUTION:

3.0 points total

- i) Metal is a stronger reducing agent than Hg: above "Hg line" in table 0.5 points
- ii) Metal is a weaker reducing agent than Sn: below "Sn line" in table 0.5 points
- iii) Metal is a stronger reducing agent than I: above "I₂ line" in table 0.5 points

The metal is Pb (lead/Blei/plomb/piombo), because colourless and in the area outlined by tests i)-iii). It's a weaker reducing agent than Fe. 1.0 points

0.5 points here if Cu (copper/Kupfer/cuivre/rame) is chosen, since Cu is reddish in colour.

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?

SOLUTION:

1.0 points total

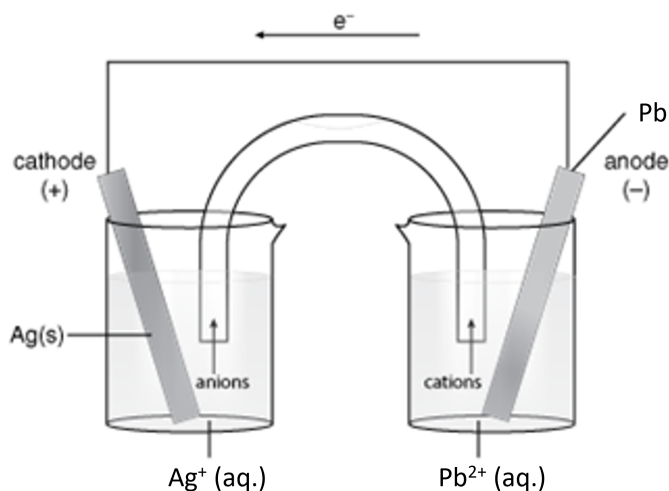
As we don't know whether we can find a corresponding salt of our unknown metal, it is probably wise to use it as reducing agent. 0.5 points

We have to look for a weaker reducing agent, a "more noble" metal. 0.5 points

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.

SOLUTION:

2.0 points total



Standard drawing with the metals in their corresponding solutions

Membrane or "salt bridge"

Positive pole at silver

Correct electron or at least ion transport

0.5 points each

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

SOLUTION:

3.0 points total

Anode (oxidation): $\text{Pb} = \text{Pb}^{2+} + 2 \text{e}^{-}$

1.0 points

Cathode (reduction): $\text{Ag}^{+} + \text{e}^{-} = \text{Ag} \downarrow$

1.0 points

 $-(-0.13 \text{ V} - 0.80 \text{ V}) = 0.93 \text{ V}$ if concentrations are 1 mol L^{-1} and $T = 25^{\circ}\text{C}$

1.0 points

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.

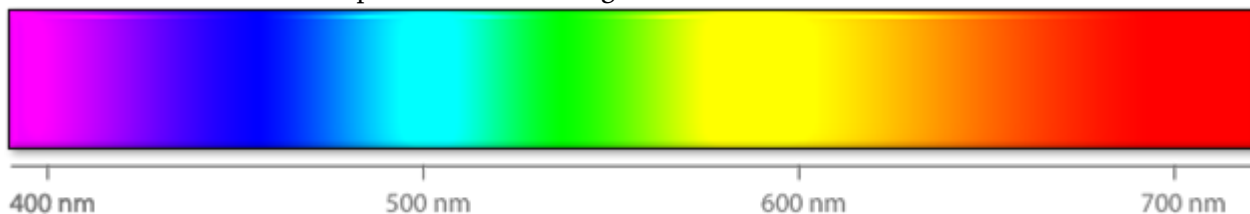
When a solution is being crossed by a light beam of intensity I_0 , the light intensity decreases and becomes $I < I_0$. For the measurements, the law first formulated in 1729 and supplemented by August Beer in 1852 applies, according to which the extinction, i.e. the absorbance of the material for light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

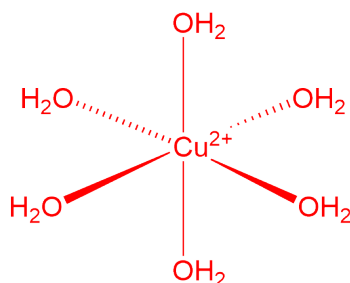
Just a reminder: relationship between wavelength and colour:



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?

SOLUTION:

1.5 points total



Hexaaquacopper(II) complex

1.0 points

The complementary colour of turquoise is reddish/orange-ish.

0.5 points

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?

SOLUTION:

2.0 points total

$$\epsilon = \frac{A}{c \cdot d} = \frac{0.473}{0.0002 \text{ mol m}^{-3} \cdot 0.04 \text{ m}} = 59.125 \text{ L mol}^{-1} \text{ m}^{-1}$$

1.0 points

With all three values: $\bar{\epsilon} = \frac{59.125 + 59.000 + 58.500}{3} \text{ L mol}^{-1} \text{ m}^{-1} = 58.875 \text{ L mol}^{-1} \text{ m}^{-1}$

1.0 points

(If results are given in m² mol⁻¹ and values are 1000x larger than written above: full marks
If results are given in m² mol⁻¹ but numbers are as written above: -0.5 points each time)

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?

SOLUTION:

1.5 points total

Linear law

0.5 points

$$\frac{0.0017}{0.473} \cdot 0.2 \text{ mol L}^{-1} = 7.2 \times 10^{-4} \text{ mol L}^{-1}$$

0.5 points

$$7.2 \times 10^{-4} \text{ mol L}^{-1} \cdot 159.6 \text{ g mol}^{-1} = 0.115 \text{ g L}^{-1} \text{ CuSO}_4 \text{ solution}$$

$$0.115 \text{ g L}^{-1} \cdot 0.2 \text{ L} = 0.023 \text{ g CuSO}_4 \text{ on 100 g grapes}$$

0.5 points

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 Cu²⁺ directly?

SOLUTION:

2.0 points total

Green is absorbed; the complementary colour is red.

0.5 points for each statement

The Cu²⁺-phenanthroline complex has a much higher extinction coefficient; the analysis is more precise

0.5 points for each statement

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?

SOLUTION:

1.0 points total

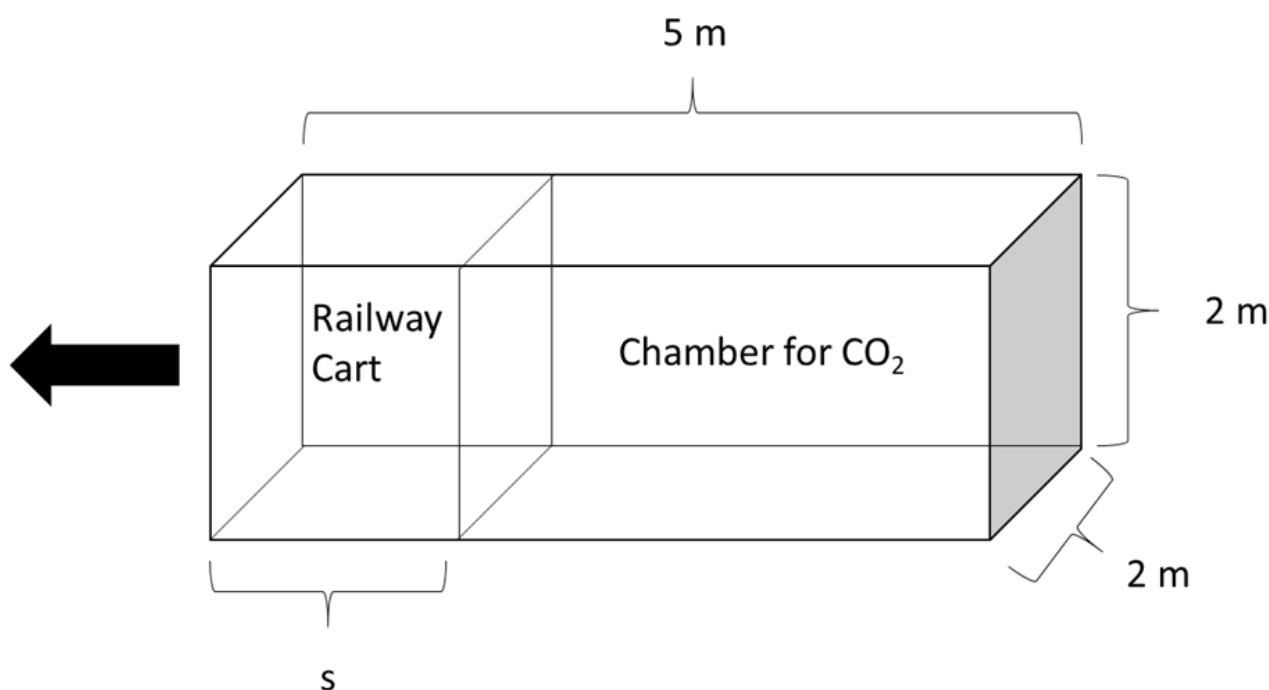
I.; logarithmic function of intensity of transmitted light, so this excludes option III which shows a linear function. The graph of a function log(1/x) (corresponding to the function log(I₀/I) looks like displayed in I.

0.5 points for correct solution, 0.5 points for justification

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 where the railway car will be accelerated 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 is a way of $s = 0.1 \text{ m}$, 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 by an acceleration a over a time t is given by $s = \frac{1}{2} \cdot a \cdot t^2$.

SOLUTION:**6.0 points total**

If everything is correct but not all equations were used, full marks. There are several different ways to solve the problem.

$$V = W \times H \times L \quad (1)$$

$$A = W \times H \quad (2)$$

$$p = \frac{n \cdot R \cdot T}{V} \quad (3)$$

$$F = p \cdot A \quad (4)$$

$$F = m \cdot a \quad (5)$$

$$v = a \cdot t \quad (6)$$

$$s = \frac{1}{2} \cdot a \cdot t^2 \implies t = \sqrt{\frac{2s}{a}} \quad (7)$$

(5), (6), and (7) will give

$$v = \frac{F}{m} \cdot \sqrt{\frac{2 \cdot s \cdot m}{F}} \implies F = \frac{v^2 \cdot m}{2s} \quad (8)$$

(1), (2), (3), and (4) will give

$$F = \frac{n \cdot R \cdot T}{L} \quad (9)$$

(8) and (9) then give

$$n = \frac{v^2 \cdot m \cdot L}{2s \cdot R \cdot T} = 9153 \text{ mol}$$

0.5 points for each correct calculation

From this, the mass can be easily computed:

$$m_{\text{CO}_2} = n \cdot M(\text{CO}_2) = 4.03 \times 10^5 \text{ g} = 403 \text{ kg}$$

1.0 points

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, the chemists 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 path 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 task 8.1, assume a mass of 400 kg dry ice loaded into the chamber.)

SOLUTION:

2.0 points total

Again, there are several ways to solve the problem. Full marks if the approach is different, but the results are correct.

From 8.1 we get, with new values $s = 4 \text{ m}$ and $L' = 4 \text{ m}$:

$$F = \frac{n \cdot R \cdot T}{L'}$$

1.0 points

And plug in the formula for the velocity:

$$v = \frac{F}{m} \cdot \sqrt{\frac{2s \cdot m}{F}} \Rightarrow v = \sqrt{\frac{2s \cdot F}{m}} = \sqrt{\frac{2s \cdot \frac{n \cdot R \cdot T}{L'}}{m}} = 388.9 \text{ m s}^{-1}$$

1.0 points

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

SOLUTION:

1.0 points total

$$E_{\text{kin}} = \frac{1}{2} \cdot m \cdot v^2 = 9.07 \times 10^7 \text{ J}$$

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.

SOLUTION:

1.0 points total

$$E_{\text{pot}} = (p - p_0) \cdot V = (n \cdot R \cdot T) - (V \cdot p_0) = (n \cdot R \cdot T) - (W \cdot H \cdot L' \cdot p_0) = 2.23 \times 10^7 \text{ J}$$

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?

SOLUTION:

1.0 points total

Because in 8.3 the approximation that the pressure is at a constant level does not fit anymore, since the difference of the Volume of the chamber from the pressurised gas is way larger when the railway car exits than it was when the initial pressure was calculated in 8.1. (Compare the percentage volume change between 19.6 m^3 to 20 m^3 vs. 4 m^3 to 20 m^3 .)

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

Option 1: You could take the average of the initial pressure and the pressure when the railway car exits the chamber as the source of the force that accelerates the railway car. That would yield a quite good approximation.

Option 2 (They don't have to know that, but if they do it should count): You create the differential equation and solve the integral for either the kinetic energy the railway car will obtain and get the speed from there or solve it for the position and get its derivative at the time it exits the box.

1.0 points per option, max. 1.0 points

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

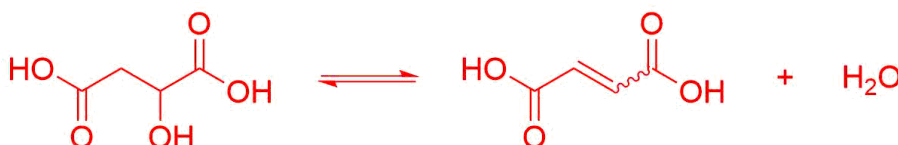
Maleic acid: $\text{HOOC}-\text{CH}=\text{CH}-\text{COOH}$

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

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

SOLUTION:

2.5 points total



Maleic acid is the *cis* isomer
Fumaric acid is the *trans* isomer

1.0 points

Elimination of water

0.5 points

Usually catalysed by strong acid

0.5 points

In this case ($T = 250^\circ\text{C}$), catalysed by own protons

0.5 points

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

SOLUTION:

1.0 points total

Malic acid: 2-Hydroxybutane-1,4-dioic acid; Maleic acid: (2Z)-But-2-enedioic acid

Apfelsäure: 2-Hydroxybutan-1,4-disäure; Maleinsäure: (2Z)-But-2-endisäure

Acide malique: acide 2-hydroxybutanedioïque; acide maléique: acide (Z)-but-2-èn-1,4-dioïque

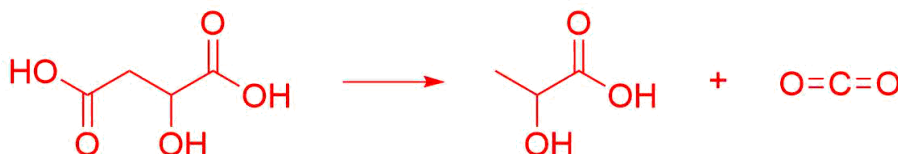
Acido malico: acido 2S-idrossi-1,4-butandioico; acido maleico: acido Z-butendioico

0.5 points each

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.

SOLUTION:

1.5 points total



1.0 points

Decarboxylation

0.5 points

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

SOLUTION:

2.0 points total

Starting material and product are both chiral

1.0 points

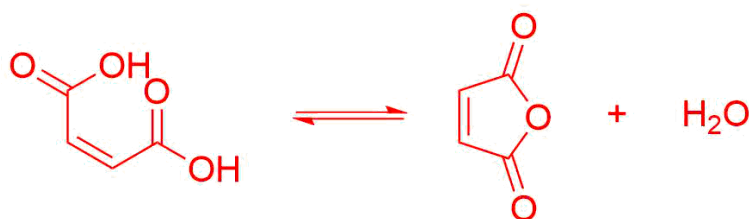
Stereochemistry does not change due to same order in CIP nomenclature

1.0 points

9.5 The maleic acid mentioned at the beginning reacts at increased temperatures to a cyclic form with 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?

SOLUTION:

2.0 points total



1.0 points

(Cyclo-) Condensation

0.5 points

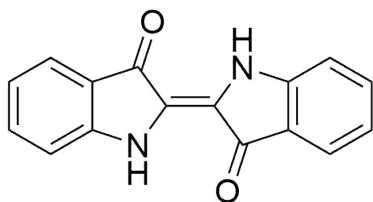
Reverse: Hydrolysis

0.5 points

PROBLEM 10 - ORGANIC SYNTHESIS: SYNTHESIS OF INDIGO

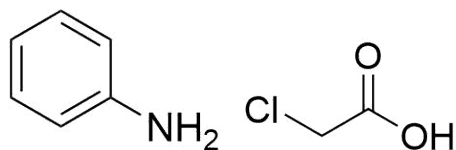
6.0 POINTS

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.

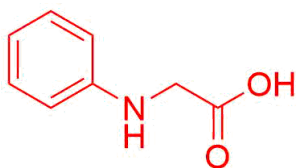
For the first way we start with the following two reactants:



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

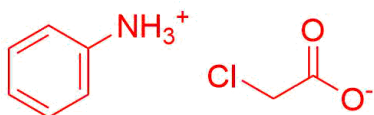
SOLUTION:

1.5 points total



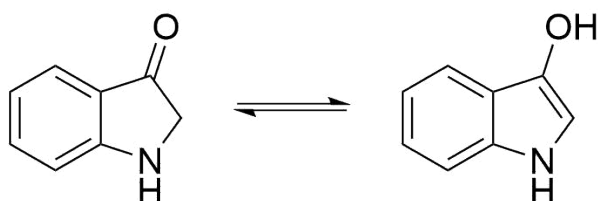
the second product of this reaction is HCl

1.0 points
+0.5 points



0.5 points only if this product is drawn

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

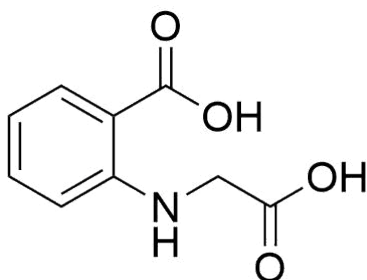


SOLUTION:

1.0 points total

Several answers should be considered correct here: 1) High temperatures to drive the evaporation of water as byproduct. 2) A dehydrating agent to bind the formed water (e.g. molecular sieves, P_2O_5 , etc.) - In fact the classical synthesis uses $NaNH_2$ for this purpose. 3) Conversion of the acid to an acid chloride (e.g. with $SOCl_2$) followed by a Friedel-Crafts Acylation (using e.g. $AlCl_3$ as activating Lewis acid).

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?



SOLUTION:

1.0 points total

The byproducts will be water and carbon dioxide.

0.5 points

For the oxidation of the acid to carbon dioxide a higher temperature is required.

0.5 points

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?

SOLUTION:

1.0 points total

Oxygen will be needed for the reaction (since it's an oxidation).

0.5 points

Water will be the byproduct.

0.5 points

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

SOLUTION:

1.5 points total

Indigo has a large system of conjugated double bonds.

0.5 points

The large conjugated π -system is able to absorb light at a wavelength in the visible area of the electromagnetic spectrum, while small π -systems can only absorb photons with higher energy.

1.0 points