

# CHEMISTRY. OLYMPIAD.CH 

CHEMIE-OLYMPIADE

OLYMPIADES DE CHIMIE
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Theoretical Final Exam SwissChO 2021<br>SOLUTION KEY

## CONSTANTS AND Formulae

| Avogadro constant | $N_{A}=6.022 \cdot 10^{23} \mathrm{~mol}^{-1}$ | Ideal gas law | $p V=n R T$ |
| :--- | :--- | :--- | :--- |
| Universal gas constant | $R=8.314 \mathrm{~J} \mathrm{~mol}^{-1} \mathrm{~K}^{-1}$ | Gibbs energy | $G=H-T S$ |
| Faraday constant | $F=96485 \mathrm{C} \mathrm{mol}^{-1}$ | $\Delta_{r} G^{0}=-R T \cdot \ln (K)=-n F E_{\text {Zelle }}^{0}$ |  |
| Planck constant | $h=6.626 \cdot 10^{-34} \mathrm{~J} \mathrm{~s}$ | 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 | $c=2.998 \cdot 10^{8} \mathrm{~m} \mathrm{~s}^{-1}$ | Energy of a photon | $E=\frac{h \cdot c}{\lambda}$ |
| Temperature | $0^{\circ} \mathrm{C}=273.15 \mathrm{~K}$ | 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 $1 \mathrm{~mol} \mathrm{dm}^{-3}=1 \mathrm{~mol} \mathrm{~L}^{-1}$. If not stated otherwise in a task, consider all gases ideal throughout this test.
Periodic Table of Elements


|  | $2 \cdot$ |
| :---: | :---: |
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## ${ }^{1}$ H Nuclear Magnetic Resonance Spectroscopy

## Chemical Shifts (in PPM / TMS)



## H-H Coupling Constatns (in Hz)

| Connectivity | Specification | $\left\|J_{a b}\right\|$ |
| :--- | :--- | :--- |
| $\mathrm{R}_{2} \mathrm{CH}_{a} \mathrm{H}_{b}$ | - | $4-20$ |
|  | freely rotating | $6-8$ |
| $\mathrm{R}_{2} \mathrm{CH}_{a}-\mathrm{CR}_{2} \mathrm{H}_{b}$ | ax-ax in $\mathrm{C}_{6} \mathrm{H}_{12}$ <br> ax-eq in $\mathrm{C}_{6} \mathrm{H}_{12}$ | $10-12$ |
|  | eq-eq in $\mathrm{C}_{6} \mathrm{H}_{12}$ | $3-5$ |
|  | freely rotating <br> rigid | $2-3$ |
| $\mathrm{R}_{2} \mathrm{CH}_{a}-\mathrm{CR}_{2}-\mathrm{CR}_{2} \mathrm{H}_{b}$ | cis | $<0.1$ |
| $\mathrm{RCH}_{a}=\mathrm{CRH}_{b}$ | trans | $1-8$ |
|  | - | $7-12$ |
| $\mathrm{H}_{a}(\mathrm{CO})-\mathrm{CR}_{2} \mathrm{H}_{b}$ | - | $12-18$ |
| $\mathrm{RH}_{a} \mathrm{C}=\mathrm{CR}^{2}-\mathrm{CR}_{2} \mathrm{H}_{b}$ | - | $0.5-3$ |

$\mathrm{ax}=\mathrm{axial}, \mathrm{eq}=$ equatorial

## IR Spectroscopy Table

| Vibrational Mode | $\boldsymbol{\sigma} / \mathbf{c m}^{-1}$ | Intensity |
| :--- | :--- | :--- |
| alcohol O-H (stretching) | $3600-3200$ | strong |
| carboxylic acid O-H (stretching) | $3600-2500$ | strong |
| amine; amide N-H (stretching) | $3500-3350$ | strong |
| alkyne 三C-H (stretching) | 3300 | strong |
| alkene =C-H (stretching) | $3100-3000$ | weak |
| alkane -C-H (stretching) | $2950-2840$ | weak |
| aldehyde - (CO)-H (stretching) | $2900-2800$ | weak |
| nitrile C $\equiv$ N (stretching) | 2250 | strong |
| alkyne C $\equiv \mathrm{C}$ (stretching) | $2260-2100$ | variable |
| aldehyde C=O (stretching) | $1740-1720$ | strong |
| anhydride C=O (stretching 1) | $1840-1800$ | weak |
| anhydride C=O (stretching 2) | $1780-1740$ | strong |
| ester C=O (stretching) | $1750-1720$ | strong |
| ketone C=O (stretching) | $1750-1710$ | strong |
| amide C=O (stretching) | $1700-1500$ | strong |
| alkene C=C (stretching) | $1680-1600$ | weak |
| aromatic C=C (stretching) | $1600-1400$ | weak |
| amine $\mathrm{N}-\mathrm{H}$ (bending) | $1800-1600$ | medium |
| aliphatic CH2 (bending) | $1480-1440$ | medium |
| aliphatic CH (bending 1) | $1470-1440$ | medium |
| aliphatic CH3 (bending 2) | $1390-1360$ | medium |
| ester; ether C-O-C (stretching) | $1250-1050$ | strong |
| alcohol C-OH (stretching) | $1200-1020$ | strong |
| nitro $\mathrm{NO}_{2}$ (stretching 1) | $1600-1500$ | strong |
| nitro $\mathrm{NO}_{2}$ (stretching 2) | $1400-1300$ | strong |
| sulfonate S=O (stretching 1) | $1400-1200$ | strong |
| sulfonate S=O (stretching 2) | $1100-1000$ | strong |
| halide C-F (stretching) | $1400-1000$ | strong |
| halide C-Cl (stretching) | $800-600$ | strong |
| halide C-Br (stretching) | $600-500$ | strong |
| halide C-I (stretching) | 500 | strong |
|  |  |  |

Metallic iron and iron carbide nanoparticles, so called "nanomagnets", are rather unique materials. During their production in a sooty reductive flame, a few layers of graphite-like carbon get deposited on the magnetic core. After functionalization of the carbon coating such as the immobilization of an active catalyst or an antibody, the resulting nanopowders can be used for catalysis in lab-scale reactions or medical application. In any application, the advantage of the nanoparticles is their ease of separation due to their magnetism. In this task, you will produce and analyze nanomagnets theoretically.

Flame spray synthesis of iron and iron carbide nanoparticles is a scalable one-step process to obtain nanomagnets from a suitable iron precursor, Fe (2-ethylhexanoate) $)_{3}\left(\mathrm{C}_{24} \mathrm{H}_{45} \mathrm{FeO}_{6}, \mathrm{MW}=485.46 \mathrm{~g} / \mathrm{mol}\right)$. A precursor solution is dispersed by a nozzle and the spray is ignited by a secondary flame of premixed $\mathrm{CH}_{4}$ and $\mathrm{O}_{2}$. To obtain reducing conditions, the combustion of the spray thereby takes place in a $\mathrm{N}_{2}$ atmosphere. A scheme of the process in shown in Fig. 1. Assume gases to be ideal and to be at $1 \times 10^{5} \mathrm{~Pa}$ and 298 K throughout the problem.


Figure 1: Scheme of reducing flame spray pyrolysis.
a) Draw the structure of the precursor complex. Assume it to be mononuclear.

## SOLUTION:


0.25 points for ligands, 0.25 points for $\mathrm{O}_{\mathrm{h}}$
b) Write the combustion equation of $\mathrm{Fe}(2 \text {-ethylhexanoate) })_{3}$, of tetrahydrofuran (THF, $\mathrm{C}_{4} \mathrm{H}_{8} \mathrm{O}, \mathrm{MW}=$ $72.11 \mathrm{~g} / \mathrm{mol}$ ) and of methane separately. Assume the conditions to be reducing, resulting in the formation of metallic iron.

SOLUTION:
2.0 points

$$
\begin{aligned}
2 \mathrm{C}_{24} \mathrm{H}_{45} \mathrm{FeO}_{6}(\mathrm{l})+64.5 \mathrm{O}_{2}(\mathrm{~g}) & \longrightarrow 48 \mathrm{CO}_{2}(\mathrm{~g})+45 \mathrm{H}_{2} \mathrm{O}(\mathrm{~g})+2 \mathrm{Fe}(\mathrm{~s}) \\
\mathrm{C}_{4} \mathrm{H}_{8} \mathrm{O}(\mathrm{l})+5.5 \mathrm{O}_{2}(\mathrm{~g}) & \longrightarrow 4 \mathrm{CO}_{2}(\mathrm{~g})+4 \mathrm{H}_{2} \mathrm{O}(\mathrm{~g}) \\
\mathrm{CH}_{4}(\mathrm{~g})+2 \mathrm{O}_{2}(\mathrm{~g}) & \longrightarrow \mathrm{CO}_{2}(\mathrm{~g})+2 \mathrm{H}_{2} \mathrm{O}(\mathrm{~g})
\end{aligned}
$$

1.0 point first, 0.5 points each other equation
c) The equivalence ratio $\phi$ of a combustion is defined by the ratio of moles of $\mathrm{O}_{2}$ required for complete combustion to moles of $\mathrm{O}_{2}$ actually available. From this definition, it can be seen that for fuel-rich mixtures $\phi>1$. Calculate $\phi$ for the conditions shown in Fig. 1 .

## SOLUTION:

3.0 points

$$
\begin{aligned}
\phi & =\frac{n_{O_{2}, \text { required }}}{n_{O_{2}, \text { available }}} \\
& =\frac{32.25 * n_{\text {precursor }}+5.5 * n_{\text {THF }}+2 * n_{C H_{4}, \text { premix }}}{\left(V_{O_{2}, \text { dispersion }}+V_{O_{2}, \text { premix }}\right) * p^{0} / R T} \\
& =\frac{32.25 * 0.05 * m / M_{\text {precursor }}+5.5 * 0.95 * m / M_{T H F}+2 * V_{C H_{4}, \text { premix }} * p^{0} / R T}{\left(V_{O_{2}, \text { dispersion }}+V_{O_{2}, \text { premix }}\right) * p^{0} / R T} \\
& =\frac{32.25 * 0.05 * \frac{6 \mathrm{~g} / \mathrm{min}}{485.46 \mathrm{~g} / \mathrm{mol}}+5.5 * 0.95 * \frac{6 \mathrm{~g} / \mathrm{min}}{72.11 \mathrm{~g} / \mathrm{mol}}+2 * 0.0012 \mathrm{~m}^{3} / \mathrm{min} * \frac{100000 \mathrm{~Pa}}{8.3145 \mathrm{~J} / \mathrm{mol} / \mathrm{K} * 298 \mathrm{~K}}}{\left(0.0050 \mathrm{~m}^{3} / \mathrm{min}+0.0022 \mathrm{~m}^{3} / \mathrm{min}\right) * \frac{100000 \mathrm{~Pa}}{8.3145 \mathrm{~J} / \mathrm{mol} / \mathrm{K} * 298 \mathrm{~K}}} \\
& =\frac{0.0199 \mathrm{~mol}+0.4348 \mathrm{~mol}+0.0969 \mathrm{~mol}}{0.2018 \mathrm{~mol}+0.0888 \mathrm{~mol}}=\frac{0.5515}{0.2906}=1.90
\end{aligned}
$$

0.5 for each amount (bottom row, left equation terms), 0.5 final result
d) The following reaction summarizes the overall combustion process and is assumed to have the same oxygen equivalence ratio as calculated in c):

$$
\mathrm{C}_{4} \mathrm{H}_{8} \mathrm{OFe}_{0.07}(\mathrm{l})+n \mathrm{O}_{2}(\mathrm{~g}) \longrightarrow m \mathrm{CO}_{2}(\mathrm{~g})+4 \mathrm{H}_{2} \mathrm{O}(\mathrm{~g})+0.07 \mathrm{FeC}_{x}(\mathrm{~s})+c \mathrm{C}(\mathrm{~s})
$$

What is the mass fraction of carbon in the particles? Which phase(s) constitute(s) the produced particles if they are cooled down quickly? The binary phase diagram of iron and carbon is depicted in Fig. 2 below. You can assume that, first, all hydrogen gets converted to water and that, second, only $0.5 \%$ of elemental carbon gets incorporated in nanomagnets whereas the rest becomes soot. If you could no solve c), assume $\phi=2.00$ instead.


Figure 2: Left: Binary phase diagram of iron and carbon. Right: Simplified model for carbon-coated iron carbide nanoparticles.

## SOLUTION:

$$
\begin{aligned}
n_{\text {theo }} & =\frac{2 * m_{\text {theo }}+c_{\mathrm{H}_{2} \mathrm{O}}-c_{\text {prec }}}{2}=5.5 \\
n_{\text {real }} & =\frac{n_{\text {theo }}}{\phi}=2.89(\text { hint }: 2.25) \\
m_{\text {real }} & =\frac{2 *\left(n_{\text {real }}+0.5\right)-c_{H_{2} \mathrm{O}}}{2}=1.39(\text { hint }: 1.56) \\
x & =\frac{\left(4-m_{\text {real }}\right) * 0.005}{c_{F e C_{x}}}=0.186(\text { hint }: 0.196) \\
w t \%_{C} & =\frac{x * M(C)}{M(F e)+x * M(C)}=3.84 \%(\text { hint }: 4.05 \%) \\
& \rightarrow \gamma-\mathrm{Fe}+\mathrm{Fe}_{3} \mathrm{C}
\end{aligned}
$$

e) Even stronger sooty conditions can be achieved by co-feeding acetylene $\left(\mathrm{C}_{2} \mathrm{H}_{2}\right)$ to the combustion. Using $5 \mathrm{~L} / \mathrm{min}$ acetylene, you produced nanomagnets with a carbon mass fraction of $w t \% C=9.4 \%$ according to elemental microanalysis. Assuming monodisperse particles with a core radius of 30.00 nm , how many graphene layers were deposited on the nanoparticles on average? The density of $\mathrm{Fe}_{3} \mathrm{C}$ and C are 7.79 and $2.23 \mathrm{~g} \mathrm{~cm}^{-3}$ respectively. In bulk graphite, the interplane distance is 0.335 nm .

## SOLUTION:

$$
\begin{aligned}
V_{\text {core }} & =\frac{4}{3} * \pi * r_{\text {core }}^{3}=113100 \mathrm{~nm}^{3} \\
w t \%_{C, \text { particle }} & =\frac{w t \%_{C, \text { core }} * \rho_{\text {core }} * V_{\text {core }}+w t \%_{C, \text { graphite }} * \rho_{\text {graphite }} * V_{\text {graphite }}}{\rho_{\text {core }} * V_{\text {core }}+\rho_{\text {graphite }} * V_{\text {graphite }}} \\
V_{\text {graphite }} & =\frac{\rho_{\text {core }}}{\rho_{\text {graphite }}} \frac{w t \%_{C, \text { particle }}-w t \%_{C, F e C}}{w t \%_{C, \text { graphite }}-w t \%_{C, \text { particle }}} * V_{\text {core }} \\
& =\frac{7.79 \mathrm{~g} / \mathrm{cm}^{3}}{2.23 \mathrm{~g} / \mathrm{cm}^{3}} \frac{0.094-0.067}{1.000-0.094} * 113100 \mathrm{~nm}^{3}=11774 \mathrm{~nm}^{3} \\
d & =r_{\text {tot }}-r_{\text {core }}=\sqrt[3]{\frac{V_{\text {core }}+V_{\text {graphite }}}{4 / 3 * \pi}}-r_{\text {core }}=31.01 \mathrm{~nm}-30.00 \mathrm{~nm}=1.01 \mathrm{~nm} \\
n_{\text {layer }} & =\frac{d}{d_{\text {bulk }}}=1.01 \mathrm{~nm} \rightarrow 3 \text { layers }
\end{aligned}
$$

f) The produced particles were functionalized in three separate reactions to carry amine, nitro or sulfonic acid groups respectively. Unfortunately, the labels of the three vials got mixed up. The IR spectra of all samples are shown below in Fig. 3. Assign structures A - C to spectra I - III.

## SOLUTION:

A - III.
B - II.
C-I.
g) Suggest two other methods which you could assign the particles with.

## SOLUTION:

1.0 points

Elemental analysis, chemical reactivity, pH when suspended in $\mathrm{H}_{2} \mathrm{O}, \ldots$
0.5 for each, maximal 1.0 points
h) The amine particles are finally reacted with stearoyl chloride, $\mathrm{CH}_{3}\left(\mathrm{CH}_{2}\right)_{16} \mathrm{COCl}$, to demonstrate their surface reactivity. Calculate the yield for this test reaction given elemental analysis before and after the reaction. Assume the mass change during the reaction to be negligible.

## SOLUTION:

$$
\begin{aligned}
\bar{n}_{i, N H_{2}} & =\frac{w t \psi_{0_{i, N}}}{M(N)}=\frac{1.6 \mathrm{mg} / \mathrm{g}}{14.01 \mathrm{~g} / \mathrm{mol}}=0.11 \mathrm{mmol} / \mathrm{g} \\
\bar{n}_{i, H} & =\frac{w t \%_{0, H}}{M(H)}=\frac{0.2 \mathrm{mg} / \mathrm{g}}{1.008 \mathrm{~g} / \mathrm{mol}}=0.20 \mathrm{mmol} / \mathrm{g} \\
\bar{n}_{f, H} & =\frac{w t \%_{0_{f, H}}}{M(H)}=\frac{3.1 \mathrm{mg} / \mathrm{g}}{1.008 \mathrm{~g} / \mathrm{mol}}=3.08 \mathrm{mmol} / \mathrm{g} \\
\text { yield } & =\frac{\bar{n}_{f, N H C O R}}{\bar{n}_{i, N H_{2}}}=\frac{\left(\bar{n}_{f, H}-\bar{n}_{i, H}\right) / 34}{\bar{n}_{i, N H_{2}}}=(3.08-0.20) / 340.11=77 \%
\end{aligned}
$$

Alternative approach: At $100 \%$ yield we have 36 H for one N , with this $\mathrm{n}(\mathrm{H})=0.11 \times 36=$ $3.96 \mathrm{mmol} / \mathrm{g}$ Based on this we can then use: $\mathrm{x} * 3.96+\mathrm{y} * 0.2=3.08$, with $\mathrm{x}+\mathrm{y}=1$, we obtain the same result.


Figure 3: Left: Recorded IR spectra of particles A - C. Right: Structure of said functionalized particles.

Table 1: Elemental composition (by mass fraction) of amine functionalized nanomagnets before and after reaction.

| Element $i$ | $w t \%_{i, \text { before }}$ | $w t \%_{i, a f t e r}$ |
| :--- | :--- | :--- |
| C | 9.38 | 11.05 |
| H | 0.02 | 0.31 |
| N | 0.16 | 0.15 |

## Problem 2 - Exciting Photons and Electrons

If a metal plate is irradiated with light, emission of electrons can be detected. The energy needed for an electron to be emitted by a metal is called the work function. In the following exercise we will look at such metal plates and the events taking place as they are irradiated with light.
a) Assume that the energy from the light source is distributed equally on the atoms at the surface of the plate. The light source has an output $P=1.3 \mu \mathrm{~W}$. The surface of the metal plate is $1.0 \mathrm{~m}^{2}$ and the ionisation energy of a single metal atom is 1.0 eV . Further, only the atoms on the surface are relevant and an electron per atom takes up a space of $1.3 \AA^{2}$.

- Calculate the number of electrons at the surface of the plate.
- Calculate the time it would take until the first emission of an electron can be expected. Assume that the energy taken up by the electrons is saved over time.

SOLUTION:

$$
\begin{aligned}
n_{\text {electrons }} & =\frac{1.0 \mathrm{~m}^{2}}{1.3 \times 10^{-20} \mathrm{~m}^{2}}=7.69 \times 10^{19} \text { atoms }=7.69 \times 10^{19} \text { electrons } \\
t & =\frac{1.0 \mathrm{eV} * 7.69 \times 10^{19} \text { atoms }}{1.3 \times 10^{-6} \mathrm{~W}}=9480473 \mathrm{~s}=109.7 \mathrm{~d}
\end{aligned}
$$

b) This does not represent what is really observed. Actually, emission of an electron can be observed immediately below a certain wavelength of the light and no emission is observed above this wavelength, regardless of how long the plate is irradiated. Explain this phenomenon briefly (keywords).

## SOLUTION:

This phenomenon is called the photoelectric effect. Light consists of photons, which are particles "carrying" the energy of the light. The photon hits only one electron, thus it needs to have enough energy to transfer, such that the electron can be emitted. The energy of one photon is not "stored" by the electron. Either it is enough or not. The wavelength of the light is proportional to the energy of the photon: $E=\frac{h c}{\lambda}$
c) The work function of zinc, potassium and platinum are $4.34 \mathrm{eV}, 2.25 \mathrm{eV}$ and 5.60 eV . From which wavelength on can emission of an electron be expected for each of these metals, such that they could be used as active material for a photodetector?

## SOLUTION:

1.5 points

$$
\begin{aligned}
& \text { Zinc }: \frac{h c}{4.34 \mathrm{eV} * 1.6022 \times 10^{-19} \mathrm{~J} / \mathrm{eV}}=2.8567 \times 10^{-7} \mathrm{~m}=286 \mathrm{~nm} \\
& \text { Potassium }: 551 \mathrm{~nm} \quad \text { Platinum : } 221 \mathrm{~nm}
\end{aligned}
$$

d) Calculate the velocity of an electron emitted from aluminium (work function of 4.20 eV ) which has absorbed a photon of wavelength of I) 250 nm and II) 310 nm ?

## SOLUTION:

$$
\begin{aligned}
250 \mathrm{~nm}: E_{k i n} & =\frac{h c}{250 \times 10^{-9} \mathrm{~m}}-4.2 \mathrm{eV} * 1.6022 \times 10^{-19} \mathrm{~J} / \mathrm{eV}=1.22 \times 10^{-19} \mathrm{~J} \\
v_{k i n} & =\sqrt{\frac{2 * 1.22 \times 10^{-19} \mathrm{~J}}{m_{e}}}=516814 \mathrm{~m} / \mathrm{s} \\
310 \mathrm{~nm}: E_{k i n} & =\frac{h c}{310 \times 10^{-9} \mathrm{~m}}-4.2 \mathrm{eV} * 1.6022 \times 10^{-19} \mathrm{~J} / \mathrm{eV}<0 \mathrm{~J} \\
& \rightarrow \text { no emission occuring }
\end{aligned}
$$

0.5 for each line

An experiment was conducted to determine the work function of tungsten. A tungsten plate was placed into a vacuum tube and irradiated with light of different wavelengths. As an electron was emitted, an electric potential was applied inside the vacuum tube such that the electron was halted completely. This potential is called the stopping voltage.

Table 2: Experimentally determined stopping voltage for different irradiation wavelengths on a tungsten surface.

$$
\begin{array}{rllllll}
\lambda_{x} / \mathrm{nm} & 134 & 181 & 192 & 223 & 236 & 261 \\
\hline V_{\text {stopping }} / \mathrm{eV} & 4.7 & 2.3 & 1.9 & 1.0 & 0.7 & 0.2
\end{array}
$$

e) Now the scientists need your help. They have done six measurements at six different wavelengths. Help them determine the work function of tungsten with the six measurements given in the table above.

## SOLUTION: <br> 3.0 points


f) An electron was emitted from a metal plate with a kinetic energy of 3.4 eV . How high of an electrical potential would need to be applied in order to halt the electron completely?

SOLUTION: 0.5 points
3.4 eV

Electrolysis has found application in manufacturing of many useful chemical compounds and revealed new interesting transformations. Sometimes it allows to perform reactions, which normally occur in a reverse way. For example, sodium ( Na ) reacts with chlorine $\left(\mathrm{Cl}_{2}\right)$ to form sodium chloride ( NaCl ), but the electrolysis of molten NaCl reverses this reaction:

$$
2 \mathrm{NaCl}(\mathrm{l}) \xrightarrow{\Delta \mathrm{V}} 2 \mathrm{Na}(\mathrm{l})+\mathrm{Cl}_{2}(\mathrm{~g}) \uparrow
$$

If the electrolysis of an aqueous solution of NaCl is performed, gases are released both on cathode and anode.
a) Write down the reaction of electrolysis of a solution of NaCl , providing the reactions taking place on cathode and anode.

## SOLUTION:

1.5 points

During the electrolysis oxidation or reduction processes occur on the electrodes. The cathode, which is negatively charged, attracts cations formed by dissociation of the salt in solution. If the cation is formed by an active metal (e.g., $\mathrm{Na}+$ ) according to electrochemical series, then H 2 O will be reduced according to half reaction: $2 \mathrm{H}_{2} \mathrm{O}+2 \mathrm{e}^{-} \longrightarrow \mathrm{H}_{2} \uparrow+2 \mathrm{OH}^{-}$. If the cation is formed by inactive metal (e.g., $\mathrm{Cu}^{2+}$ ), then it will be reduced: $\mathrm{Cu}^{2+}+2 \mathrm{e}^{-} \longrightarrow \mathrm{Cu}$. If the metal is of mid activity, then both processes conquer.

The anode, which is positively charged, attracts anions from the salt. Chloride, bromide and iodide ions are oxidized on anode to a free halogen, e.g., $2 \mathrm{Cl}^{-}-2 \mathrm{e}^{-} \longrightarrow \mathrm{Cl}_{2} \uparrow$. If the anion can't be easily oxidized (e.g., $\mathrm{F}^{-}, \mathrm{NO}_{3}{ }^{-}, \mathrm{SO}_{4}{ }^{2-}, \mathrm{PO}_{4}{ }^{3-}, \mathrm{CO}_{3}{ }^{2-}$ ), then $\mathrm{H}_{2} \mathrm{O}$ is oxidized: $2 \mathrm{H}_{2} \mathrm{O}-4 \mathrm{e}^{-} \longrightarrow \mathrm{O}_{2} \uparrow+$ $4 \mathrm{H}^{+}$. In this problem some more complicated cases, which depend on the anion and conditions of the electrolysis, are also presented.

The net reaction for NaCl :

$$
\begin{gathered}
\text { Cathode : } 2 \mathrm{H}_{2} \mathrm{O}+2 \mathrm{e}^{-} \longrightarrow \mathrm{H}_{2} \uparrow+2 \mathrm{OH}^{-} \\
\text {Anode }: 2 \mathrm{Cl}^{-}-2 \mathrm{e}^{-} \longrightarrow \mathrm{Cl}_{2} \uparrow \\
\text { Overall: } 2 \mathrm{NaCl}+2 \mathrm{H}_{2} \mathrm{O} \xrightarrow{\Delta \mathrm{~V}} 2 \mathrm{NaOH}+\mathrm{H}_{2} \uparrow+\mathrm{Cl}_{2} \uparrow
\end{gathered}
$$

Imagine we conduct the electrolysis of cold and hot solutions of NaCl constantly mixing the reaction mixture. In both cases you will see that the gas evolution on one of the electrodes will stop.
b) Rationalize the observation by corresponding chemical reactions (for cold and hot solutions, respectively).

## SOLUTION:

When the reaction mentioned in a previous question is performed in industry, for example to produce chlorine gas, a diaphragm to separate cathodic and anodic space is used. If this diaphragm is missing and the solution is vigorously mixed, then $\mathrm{Cl}_{2}$, which is formed on the anode is able to react with NaOH formed on the cathode. This reaction is classified as disproportionation reaction and the products depend on the temperature:

$$
\begin{aligned}
& \text { cold solution: } \mathrm{Cl}_{2}+2 \mathrm{NaOH} \xrightarrow{0-5^{\circ} \mathrm{C}} \mathrm{NaClO}+\mathrm{NaCl}+\mathrm{H}_{2} \mathrm{O} \\
& \text { hot solution: } 3 \mathrm{Cl}_{2}+6 \mathrm{NaOH} \xrightarrow{\Delta \mathrm{~T}} \mathrm{NaClO}_{3}+5 \mathrm{NaCl}+3 \mathrm{H}_{2} \mathrm{O}
\end{aligned}
$$

Now we can combine these reactions with the electrolysis of NaCl and get:

$$
\begin{aligned}
& \text { cold solution : } \mathrm{NaCl}+\mathrm{H}_{2} \mathrm{O} \xrightarrow{0-5^{\circ} \mathrm{C}, \Delta \mathrm{~V}} \mathrm{NaClO}+\mathrm{H}_{2} \uparrow \\
& \text { hot solution }: \mathrm{NaCl}+3 \mathrm{H}_{2} \mathrm{O} \xrightarrow{\Delta \mathrm{~T}, \Delta \mathrm{~V}} \mathrm{NaClO}_{3}+3 \mathrm{H}_{2} \uparrow
\end{aligned}
$$

c) Propose a salt whose aqueous solution does not give any gaseous products when electrolysed. Write down the corresponding reaction of electrolysis.

## SOLUTION:

1.0 points

The possible solution can be found among bromides or iodides of inactive metals (see solution to the question a). As this salt must exist and be soluble in water, the simplest answer is copper(II) bromide, $\mathrm{CuBr}_{2}$ :

$$
\mathrm{CuBr}_{2}(\mathrm{aq}) \xrightarrow{\Delta \mathrm{V}} \mathrm{Cu} \downarrow+\mathrm{Br}_{2}(\mathrm{aq})
$$

6.04 g of some hydrate of copper(II) nitrate A were dissolved in 100 mL of distilled water and the solution formed was subjected to electrolysis. The electric current of 1.96 A was applied for 82 min to get equal amounts of gases on the cathode and anode. Note that none of the gases contains nitrogen.
d) Determine the formula of hydrate A and write down all the chemical reactions taking place during the experiment.

## SOLUTION:

During the electrolysis of $\mathrm{Cu}\left(\mathrm{NO}_{3}\right)_{2}$, copper is deposited on the cathode and oxygen is released on the anode:

$$
2 \mathrm{Cu}\left(\mathrm{NO}_{3}\right)_{2}+2 \mathrm{H}_{2} \mathrm{O} \xrightarrow{\Delta \mathrm{~V}} 2 \mathrm{Cu} \downarrow \text { (cathode) }+4 \mathrm{HNO}_{3}+\mathrm{O}_{2} \uparrow \text { (anode) }
$$

As according to the task, some gas was also released on the cathode, this is not the only reaction, which took place during the experiment. The other one is the electrolysis of water, which occurred in the presence of $\mathrm{HNO}_{3}$ after the complete consumption of $\mathrm{Cu}\left(\mathrm{NO}_{3}\right)_{2}$ :

$$
2 \mathrm{H}_{2} \mathrm{O} \xrightarrow{\Delta \mathrm{~V}, \mathrm{HNO}_{3}} 2 \mathrm{H}_{2} \uparrow \text { (cathode) }+\mathrm{O}_{2} \uparrow \text { (anode) }
$$

It should be noted here, that water does not undergo electrolysis without presence of electrolytes in the solution as it has very low conductivity itself. We know the electric current used and the time of electrolysis, hence we can use Faraday equation to calculate the number of moles of electrons, that took part in the processes of oxidation on anode and reduction on cathode:

$$
n\left(e^{-}\right)=\frac{I t}{F}=\frac{1.96 \mathrm{~A} * 4920 \mathrm{~s}}{96485 \mathrm{C} \mathrm{~mol}^{-1}}=0.100 \mathrm{~mol}
$$

The processes of reduction on cathode:

$$
\begin{gathered}
\mathrm{Cu}^{2+}+2 \mathrm{e}^{-} \longrightarrow \mathrm{Cu} \\
2 \mathrm{H}^{+}+2 \mathrm{e}^{-} \longrightarrow \mathrm{H}_{2} \uparrow
\end{gathered}
$$

The process of oxidation on anode:

$$
2 \mathrm{H}_{2} \mathrm{O}-4 \mathrm{e}^{-} \longrightarrow \mathrm{O}_{2} \uparrow+4 \mathrm{H}^{+}
$$

With these equations we can see, that $n\left(O_{2}\right)=1 / 4 * n\left(e^{-}\right)=1 / 4 * 0.100 \mathrm{~mol}=0.025 \mathrm{~mol}$. According to the task, the amounts of gases are equal, thus $n\left(H_{2}\right)=n\left(O_{2}\right)=0.025 \mathrm{~mol}$. And now we can figure out the amount of copper ions:

$$
n\left(C u^{2+}\right)=\frac{n\left(e^{-}\right)-2 * n\left(H_{2}\right)}{2}=\frac{0.100-2 * 0.025}{2}=0.025 \mathrm{~mol}
$$

The molar mass of $A$, which can be written as $\mathrm{Cu}\left(\mathrm{NO}_{3}\right)_{2}\left(\mathrm{H}_{2} \mathrm{O}\right)_{n}$ :

$$
M(A)=\frac{m(A)}{n\left(C u^{2+}\right)}=\frac{6.04 \mathrm{~g}}{0.025 \mathrm{~mol}}=241.6 \mathrm{~g} \mathrm{~mol}^{-1}
$$

And the number of waters of crystallization:

$$
n=\frac{\left(M(A)-M\left(\mathrm{Cu}\left(\mathrm{NO}_{3}\right)_{2}\right)\right.}{M(H 2 O)}=\frac{241.6-187.6}{18}=3
$$

The formula of hydrate $\mathbf{A}$ is $\mathrm{Cu}\left(\mathrm{NO}_{3}\right)_{2}\left(\mathrm{H}_{2} \mathrm{O}\right)_{3}$.
Thermal decomposition of coppe(II) nitrate hydrates occurs in 3 steps. On the first step, the blue copper hydroxy nitrate $\mathbf{B}$ is formed, which then decomposes to a black solid C. In both steps, the mixture of two gases is formed along with the formation of water vapours. If hexahydrate of copper(II) nitrate is decomposed, then the amount of gaseous mixture, including water vapours, on the first step is $57 / 11$ times higher than on the second. On the third step compound C loses $10.06 \%$ of its mass and forms a red solid D.
e) Determine the formulas of compounds B-D and write down all the reactions corresponding to the three steps of decomposition.

## SOLUTION:

4.5 points

Generally, decomposition of nitrates depends on the metal. If the metal is alkaline (except lithium) then the nitrite is formed along with the release of oxygen. Nitrates of calcium, strontium and barium firstly also decompose to nitrites, but at higher temperatures the decomposition goes further to oxides. Most of the other metal nitrates, including copper, directly decompose to their oxides along with evolution of nitrogen dioxide and oxygen. And if the metal forms thermally unstable oxides (e.g., Ag, Hg ) then the decomposition of their nitrates will give metal instead.

In the case of copper(II) nitrate hexahydrate, i.e., $\mathrm{Cu}\left(\mathrm{NO}_{3}\right)_{2}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}$ the decomposition goes via the formation of copper(II) hydroxy nitrate (B), which can be written as $\mathrm{Cu}(\mathrm{OH})_{x}\left(\mathrm{NO}_{3}\right)_{2-x}$. The next step is probably the formation of copper(II) oxide - CuO , which is exactly a black solid. According to the task $\mathbf{C}$ loses $10.06 \%$ of its mass to form $\mathbf{D}$, so if $\mathbf{C}$ is CuO then it loses $\mathrm{M}(\mathrm{CuO}) * 0.1006=$ $79.55 \mathrm{~g} \mathrm{~mol}^{-1} * 0.1006=8.00 \mathrm{~g} \mathrm{~mol}^{-1}$ of its molar mass. This can correspond to a half of oxygen atom. Hence the formula of $\mathbf{D}$ will be $\mathrm{CuO}_{0.5}$ or $\mathrm{Cu}_{2} \mathrm{O}-\operatorname{copper}(\mathrm{I})$ oxide, which is red and C is confirmed to be CuO. The equations of three steps of decomposition can be written then:

$$
\begin{gathered}
\mathrm{Cu}\left(\mathrm{NO}_{3}\right)_{2}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6} \xrightarrow{\Delta \mathrm{~T}} \mathrm{Cu}(\mathrm{OH})_{x}\left(\mathrm{NO}_{3}\right)_{2-x}+x \mathrm{NO}_{2} \uparrow+\mathrm{x} / 4 \mathrm{O}_{2} \uparrow+(12-\mathrm{x}) / 2 \mathrm{H}_{2} \mathrm{O} \uparrow \\
\mathrm{Cu}(\mathrm{OH})_{x}\left(\mathrm{NO}_{3}\right)_{2-x} \xrightarrow{\Delta \mathrm{~T}} \mathrm{CuO}+(2-\mathrm{x}) \mathrm{NO}_{2} \uparrow+(2-\mathrm{x}) / 4 \mathrm{O}_{2} \uparrow+\mathrm{x} / 2 \mathrm{H}_{2} \mathrm{O} \uparrow \\
4 \mathrm{CuO} \xrightarrow{\Delta \mathrm{~T}} 2 \mathrm{Cu}_{2} \mathrm{O}+\mathrm{O}_{2} \uparrow
\end{gathered}
$$

If the amount of gaseous mixture, including water vapours, on the first step is $57 / 11$ times higher than on the second, then:

$$
\frac{x+0.25 * x+0.5 *(12-x)}{(2-x)+0.25 *(2-x)+0.5 x}=\frac{6+0.75 x}{2.5-0.75 x}=57 / 11
$$

By solving this equation, we get $x=1.5$. The formula of $\mathbf{B}$ is then $\mathrm{Cu}(\mathrm{OH})_{1.5}\left(\mathrm{NO}_{3}\right)_{0.5}$ or $\mathrm{Cu}_{2}(\mathrm{OH})_{3}\left(\mathrm{NO}_{3}\right)$. The equations of first two steps with right coefficients (can be left fractional or multiplied to become integer):

$$
\begin{gathered}
\mathrm{Cu}\left(\mathrm{NO}_{3}\right)_{2}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6} \xrightarrow{\Delta \mathrm{~T}} \frac{1}{2} \mathrm{Cu}_{2}(\mathrm{OH})_{3}\left(\mathrm{NO}_{3}\right)+\frac{3}{2} \mathrm{NO}_{2} \uparrow+\frac{3}{8} \mathrm{O}_{2} \uparrow+\frac{21}{4} \mathrm{H}_{2} \mathrm{O} \uparrow \\
\frac{1}{2} \mathrm{Cu}_{2}(\mathrm{OH})_{3}\left(\mathrm{NO}_{3}\right) \xrightarrow{\Delta \mathrm{T}} \mathrm{CuO}+\frac{1}{2} \mathrm{NO}_{2} \uparrow+\frac{1}{8} \mathrm{O}_{2} \uparrow+\frac{3}{4} \mathrm{H}_{2} \mathrm{O} \uparrow
\end{gathered}
$$

Electrolysis allows obtaining different peroxy compounds, which can act as strong oxidants. For instance, electrolysis of ammonium hydrosulfate $\left(\mathrm{NH}_{4} \mathrm{HSO}_{4}\right)$ gives compound E with the same ratio of sulfur and oxygen in it as in $\mathrm{NH}_{4} \mathrm{HSO}_{4}$. The other example is compound $\mathbf{F}$, which is formed by electrolysis of borax $\left(\mathrm{Na}_{2} \mathrm{~B}_{4} \mathrm{O}_{7}\right)$ in alkaline solution. The mass percentages (in $\left.w t \%\right)$ of Na and B atoms in $\mathbf{F}$ are just near to their atomic masses rounded to integer values. The salt $\mathbf{F}$ has a doubly charged cyclic anion containing two peroxy groups. And the last example is a highly unstable salt $\mathbf{G}$, formed by 2 -electron oxidation of the carbonate ion during the electrolysis of lithium carbonate ( $\mathrm{Li}_{2} \mathrm{CO}_{3}$ ).
f) Provide the structural formulas of the anions present in compounds E-G.

SOLUTION:
During the electrolysis of $\mathrm{NH}_{4} \mathrm{HSO}_{4}$, the hydrosulfate anion is being oxidized. As the ratio of sulfur and oxygen remains the same, the following reaction of formation of peroxydisulfate ion can be proposed:

$$
2 \mathrm{HSO}_{4}^{-} \xrightarrow{\Delta \mathrm{V}} \mathrm{~S}_{2} \mathrm{O}_{8}{ }^{2-}+\mathrm{H}_{2} \uparrow
$$

Here each $\mathrm{HSO}_{4}{ }^{-}$performs 1-electron oxidation on the anode to form $\mathrm{HSO}_{4}$. radicals, which can combine and form peroxy group. On the cathode $\mathrm{H}^{+}$are reduced to $\mathrm{H}_{2}$.

The salt $\mathbf{F}$ consists of $\mathrm{Na}, \mathrm{B}, \mathrm{O}$ and maybe H. It is doubly charged and that is why contains probably 2 Na ions. If the mass percentages ( $\mathrm{wt} \%$ ) of Na and B are just near to their atomic masses in this salt, then the molar mass of $\mathbf{F}$ is close to $23 * 2 / 0.23=200$ and it contains $200 * 0.11 / 11=$ 2 atoms of B . With this and the fact that we have 2 peroxy ( $\mathrm{O}-\mathrm{O}$ ) groups in the anion, the rest is $200-2 * 23-2 * 11-2 * 16 * 2=68$, which can correspond to 4 hydroxy (OH) groups: $4 *(16+1)=68$. Combining all the pieces of information, the formula of $F$ is $\mathrm{Na}_{2}\left[\mathrm{~B}_{2}\left(\mathrm{O}_{2}\right)_{2}(\mathrm{OH})_{4}\right]$.

The last is 2-electron oxidation of carbonate ion to produce peroxy compound $\mathbf{G}$. This can be achieved by the following reaction:

$$
\mathrm{CO}_{3}{ }^{2-}+\mathrm{H}_{2} \mathrm{O} \xrightarrow{\Delta \mathrm{~V}} \mathrm{CO}_{2}\left(\mathrm{O}_{2}\right)^{2-}+\mathrm{H}_{2} \uparrow
$$

The structure of anions $\mathbf{E}, \mathrm{F}$ and G are therefore:


E


F


G
g) Determine compounds I-IX and give their molecular formulas or if the compound is ionic - the formulas of its cation and anion separately (coefficients are already given):

$$
\begin{gathered}
\mathrm{HCOONa}+\mathrm{H}_{2} \mathrm{O} \xrightarrow{\Delta \mathrm{~V}} \mathbf{I} \uparrow+\mathbf{I I} \uparrow+\mathrm{NaOH} \\
2 \mathrm{Au}+8 \mathrm{HCl} \xrightarrow{\Delta \mathrm{~V}} 3 \mathbf{I} \uparrow+2 \mathbf{I I I} \uparrow \\
2 \mathrm{CuF}_{2}+2 \mathrm{H}_{2} \mathrm{O} \xrightarrow{\Delta \mathrm{~V}} 2 \mathbf{I V} \downarrow+4 \mathbf{V}+\mathbf{V I} \uparrow \\
2 \mathrm{HNO}_{3}+2 \mathrm{HCl}+2 \mathrm{H}_{2} \mathrm{O} \xrightarrow{\Delta \mathrm{~V}} 3 \mathbf{V I} \uparrow+2 \mathbf{V I I} \downarrow \\
\mathrm{NH}_{4} \mathrm{~F}+2 \mathrm{HF} \xrightarrow{\Delta \mathrm{~V}} 3 \mathbf{I} \uparrow+\mathbf{V I I I} \uparrow \\
2 \mathrm{Na}_{2} \mathrm{~S}+2 \mathrm{H}_{2} \mathrm{O} \xrightarrow{\Delta \mathrm{~V}} \mathbf{I} \uparrow+\mathbf{I X}+2 \mathrm{NaOH}
\end{gathered}
$$

SOLUTION:
4.5 points

This question can be solved either by knowing the reactions and assuming reasonable oxidation and reduction processes, or by looking at it as a mathematical riddle. Here we will show both approaches.

In the first reaction, if we mathematically subtract " NaOH " from the left part " $\mathrm{HCOONa}+\mathrm{H}_{2} \mathrm{O}$ ", we get $\mathrm{CO}_{2} \mathrm{H}_{2}$, which corresponds to gases $\mathrm{CO}_{2}$ and $\mathrm{H}_{2}$. As I can be found in other reactions (2, 5 , 6) where there are no carbon atoms involved, then I is $\mathrm{H}_{2}$ and II is $\mathrm{CO}_{2}$. Indeed, this is an analogue of well-known Kolbe reaction from organic chemistry. Formate ion is oxidized on the anode to form HCOO - radicals, which then give $\mathrm{CO}_{2}$ and H • radicals. The last recombine with each other and produce $\mathrm{H}_{2}$. Also, on the cathode water is reduced to $\mathrm{H}_{2}$ as $\mathrm{Na}^{+}$can not be reduced in aqueous solution.

In the second reaction, "subtracting" we get the formula of III as $\left(2 \mathrm{Au}+8 \mathrm{HCl} 8 \mathrm{HCl} \longrightarrow \mathrm{AuHCl}_{4}\right.$. This corresponds to tetrachloroauric acid $\mathrm{H}^{+}\left[\mathrm{AuCl}_{4}\right]^{-}$- III. From chemical point of view we can consider this reaction as reduction of $\mathrm{H}^{+}$ions to $\mathrm{H}_{2}$ on the cathode and oxidation of $\mathrm{Cl}^{-}$ions to $\mathrm{Cl}_{2}$ on the anode. The chlorine formed oxidizes $\mathrm{Au}^{\text {to }} \mathrm{AuCl}_{3}$, which in the presence of HCl forms $\mathrm{H}\left[\mathrm{AuCl}_{4}\right]$.

In the third reaction, on the left we have $\mathrm{Cu}_{2} \mathrm{~F}_{4} \mathrm{H}_{4} \mathrm{O}_{2}$. Taking into account the coefficients on the right and states of matter, we can assign the formulas: IV - $\mathrm{Cu}, \mathrm{V}-\mathrm{HF}, \mathrm{VI}-\mathrm{O}_{2}$. This reaction is also can be easily explained: on the cathode we have a reduction of $\mathrm{Cu}^{2+}$ ions to Cu like in the previous questions and on the anode water is oxidized to $\mathrm{O}_{2}$ as it is easier to oxidize than fluoride ions. $\mathrm{F}_{2}$ is a stronger oxidant than $\mathrm{O}_{2}$ and even if it's formed it will readily react with water to go back to $\mathrm{F}^{-}$and form $\mathrm{O}_{2}$.

In the fourth reaction, the formula of VII is $\left(2 \mathrm{HNO}_{3}+2 \mathrm{HCl}+2 \mathrm{H}_{2} \mathrm{O} 2 \mathrm{H}_{2} \mathrm{O} \longrightarrow \mathrm{NH}_{4} \mathrm{OCl}\right.$. The oxidation state of nitrogen in this compound is -1 , which correspond to hydroxylamine derivatives. For this reason, VII is hydroxylamine hydrochloride (or hydroxylammonium chloride) $\left[\mathrm{NH}_{3} \mathrm{OH}\right]^{+} \mathrm{Cl}^{-}$. What happens here is 6-electron reduction of nitric acid - we can understand that because of formation of 3 molecules of $\mathbf{O} 2$ (means $12 \mathrm{e}^{-}$for oxidation in total and the same for reduction of 2 nitrate ions). Hydrochloric acid is used to form a sparingly soluble salt in concentrated solutions of nitric acid.

In the fifth reaction, VIII is $\mathrm{NH}_{4} \mathrm{~F}+2 \mathrm{HF} 2 \mathrm{HF} \longrightarrow \mathrm{NF}_{3}$ - nitrogen trifluoride. Knowing the fact that here we form 3 molecules of $\mathrm{H}_{2}, 6$ electrons are transferred in this reaction. For this reason, it is clear why nitrogen is oxidized from oxidation state -3 to +3 and forms $\mathrm{NF}_{3}$.

Finally, in the sixth reaction "mathematically" we have the formula of IX: $2 \mathrm{Na}_{2} \mathrm{~S}+2 \mathrm{H}_{2} \mathrm{O} 2 \mathrm{H}_{2} \mathrm{O} \longrightarrow$ $\mathrm{Na}_{2} \mathrm{~S}_{2}$ - it is sodium disulfide, an analogue to peroxides. Its formation can be explained if we imagine the partial reduction of $S_{2}{ }^{-}$to $S$ and the following reaction of $S$ with the residual $S_{2}{ }^{-}$to form $S_{2}{ }^{2-}$ or just as 1-electron oxidation of sulfur from oxidation state -2 to -1 , which is presented in disulfide anions. Considering the ionic structure of the compound, IX is $\left(\mathrm{Na}^{+}\right)_{2}\left[\mathrm{~S}_{2}\right]^{2-}$.

Latimer diagrams are the oldest and most compact way to represent the electrochemical stability of substances with several oxidation states. In the following Latimer diagram, the given values in V are the standard reduction potentials $E^{\circ}$ at standard conditions of $1.0 \mathrm{~atm}, 25^{\circ} \mathrm{C}$ and all concentrations are 1.0 M .


Figure 4: Latimer diagram for chromium at standard conditions.
a) Complete the Latimer diagram for chromium from above.

## SOLUTION:

$$
\begin{aligned}
\mathrm{Cr}(\mathrm{VI}) \longrightarrow \operatorname{Cr}(\mathrm{IV}): E^{\circ}=\frac{0.55 \mathrm{~V}+1.34 \mathrm{~V}}{2}=0.945 \mathrm{~V} \\
\mathrm{Cr}(\mathrm{VI}) \longrightarrow \operatorname{Cr}(\mathrm{III}): E^{\circ}=\frac{0.55 \mathrm{~V}+1.34 \mathrm{~V}+2.1 \mathrm{~V}}{3}=1.33 \mathrm{~V} \\
\mathrm{Cr}(\mathrm{II}) \longrightarrow \operatorname{Cr}(0): E^{\circ}=\frac{-3 * 0.74 \mathrm{~V}+0.424 \mathrm{~V}}{2}=-0.898 \mathrm{~V}
\end{aligned}
$$

Another way to represent the electrochemical stability of a substance is the Frost diagram. For this diagram, the oxidation number is plotted against $-\Delta G / F$. Frost diagrams can be drawn for different standard conditions such as $\mathrm{pH}=0$ or $\mathrm{pH}=14$ and combined into one single diagram as can be seen down below for chromium. As the oxidation number increases from left to right, this corresponds to the oxidation of the substance. The opposite direction, right to left, accordingly corresponds to the reduction. The "valleys and hills" of the diagram give a hint which species are thermodynamically stable or not. (The Frost diagram below is based on the standard reduction potentials of Chromium at standard conditions and the red curve has the exception that $\left[\mathrm{H}^{+}\right]=1 \times 10^{-14} \mathrm{M}$ whereas everything else conforms to the same standard conditions as the Latimer diagram above.)

Frost diagram for chromium


Figure 5: Frost diagram for chromium at standard conditions and at $\mathrm{pH}=14$.
b) Complete the two missing species in the Frost diagram: the one with oxidation number +6 at $\mathrm{pH}=14$, given that:

$$
\mathrm{Cr}+8 \mathrm{OH}^{-} \longrightarrow \mathrm{CrO}_{4}{ }^{2-}+4 \mathrm{H}_{2} \mathrm{O}+6 \mathrm{e}^{-}
$$

at $\mathrm{pH}=14$ has $E=-0.73 \mathrm{~V}$, and the one with oxidation number +3 at $\mathrm{pH}=0$.

## SOLUTION:

$$
\begin{gathered}
\mathrm{Cr}^{3+} \text { at } p H=0: E^{\circ}=2 *(-0.898 \mathrm{~V})-0.42 \mathrm{~V}=-2.216 \mathrm{~V} \\
\mathrm{CrO}_{4}{ }^{2-} \text { at } p H=14: E_{14}=6 *(-0.73 \mathrm{~V})=-4.38 \mathrm{~V}
\end{gathered}
$$

0.5 points for each calculation, 1.0 point for completing diagram/sketch
c) Which are the most stable and instable species for each pH ?
SOLUTION:
2.0 points

> most stable at $\mathrm{pH}=0: \mathrm{Cr}^{3+}$
> least stable at $\mathrm{pH}=0: \mathrm{Cr}_{2} \mathrm{O}_{7}{ }^{2-}$
> most stable at $\mathrm{pH}=14: \mathrm{CrO}_{4}{ }^{2-}$
> least stable at $\mathrm{pH}=14: \mathrm{Cr}(0)$
0.5 points for each
d) Even though standard reduction potentials are defined at $\mathrm{pH}=0$, they are not very realistic to consider for a biological system. Where in the Frost diagram would the species $\mathrm{Cr}_{2} \mathrm{O}_{7}{ }^{2-}$ be situated at $\mathrm{pH}=7$ ? Hints: Use $E^{\circ}$ from the Latimer diagram above and the reaction equation:

$$
\mathrm{Cr}_{2} \mathrm{O}_{7}{ }^{2-}+14 \mathrm{H}^{+}+12 \mathrm{e}^{-} \longrightarrow 2 \mathrm{Cr}(0)+7 \mathrm{H}_{2} \mathrm{O}
$$

SOLUTION:
2.0 points

$$
\text { from Latimer above : } \begin{aligned}
E^{\circ} & =0.294 \mathrm{~V} \\
E & =E^{\circ}-\frac{R T}{z F} \\
& =0.294 \mathrm{~V}-\frac{0.059 \mathrm{~V}}{12} * \log \left(\left(10^{-7}\right)^{-14}\right)=-0.019 \mathrm{~V} \\
E_{7} & =6 *(-0.19 \mathrm{~V})=-1.127 \mathrm{~V}
\end{aligned}
$$

e) Write down the balanced equation for one comproportionation and one disproportionation from the Frost diagram above. (Take a look at the "hills and valleys" of the diagram.)

## SOLUTION:

1.0 points

$$
\begin{aligned}
\text { com : } \mathrm{Cr}^{2+}+\mathrm{Cr}^{4+} & \longrightarrow 2 \mathrm{Cr}^{3+} \\
\text { dis : } 2 \mathrm{Cr}^{4+} & \longrightarrow \mathrm{Cr}^{3+}+\mathrm{Cr}^{5+} \\
\text { dis }: 4 \mathrm{Cr}^{5+}+7 \mathrm{H}_{2} \mathrm{O} & \longrightarrow 2 \mathrm{Cr}^{4+}+\mathrm{Cr}_{2} \mathrm{O}_{7}^{2-}+14 \mathrm{H}^{+}
\end{aligned}
$$

0.5 points for a com, 0.5 points for a dis, maximal 1.0 points

In Fig. 6t the electrochemical properties from Ca to Cu are combined into one single Frost diagram.
f) If we take a closer look at the diagram, we can see that the only lines that ever cross are the ones of Cr and Mn at the oxidation number +2 . Suggest a reason for this. (Hint: Take into account their $d$-electron configuration.)

SOLUTION:
$\mathrm{Mn}^{2+}$ has a $d^{5}$ configurations, which means a half-filled subshell, which is energetically favoured and makes it more stable than the $d^{4} \mathrm{Cr}^{2+}$ ion.
0.5 points for electron counts, 0.5 points for reasoning


Figure 6: Combined Frost diagrams for $3 s$ and $3 d$ metals at standard conditions.

## Problem 5 - Enzyme Kinetics

Enzymes are perhaps the most important biological molecules that maintain all the cellular cycles. They represent highly selective catalysts for almost every reaction in the human body, starting from digestion to synthesis of DNA.

To describe the mechanism of enzyme catalysis, the Michaelis-Menten mechanism (MM) was introduced in 1913. This mechanism describes the reaction of enzyme $\mathbf{E}$ with the substrate $\mathbf{S}$. It gives the dependence of the maximal reaction rate $v_{\max }$ as a function of the substrate concentration $[\mathrm{S}]_{0}$. In a nutshell, the mechanism suggests that before the irreversible formation of the final product $\mathbf{P}$, a reversible step involves the formation of an enzyme-substrate complex ES:

$$
\mathrm{E}+\mathrm{S} \underset{\mathrm{k}_{2}}{\stackrel{\mathrm{k}_{1}}{\rightleftarrows}} \mathrm{ES} \xrightarrow{\mathrm{k}_{3}} \mathrm{E}+\mathrm{P}
$$

a) To describe an enzyme reaction using only easily measurable quantities such as the initial enzyme concentration $[E]_{0}$ and the substrate concentration $S$ the following expression was derived:

$$
v=\frac{k_{3}[E]_{0}}{1+K_{M} /[S]_{0}}
$$

, where $K_{M}$ is defined as $\left(k_{2}+k_{3}\right) / k_{1}$ and is the so-called Michaelis-constant. You are supposed to show this by following the outlined sub-questions:

- Write down the rate equation for the formation of product $\mathbf{P}$.
- Do likewise for the formation of ES.
- Use the steady state approximation for ES.
- Use $[E]_{0}=[E]+[E S]$


## SOLUTION:

Using the steady-state approximation we obtain the equation:

$$
\frac{d[\mathrm{ES}]}{d t}=k_{1}[\mathrm{E}][\mathrm{S}]-k_{2}[\mathrm{ES}]-k_{3}[\mathrm{ES}]=0
$$

By rearrangement and solving for [ES] which is the intermediate we get:

$$
[\mathrm{ES}]=\frac{k_{1}}{k_{2}+k_{3}}[\mathrm{E}][\mathrm{S}]
$$

For the next step, precaution and critical thinking is necessary. In the MM equation, [E] and [S] are the free concentrations of the appropriate species. The term is the so called Michaelis constant $K_{M}$, which is unique for each enzyme. In such case we need to take into account the following equalities for the total concentrations of E and $\mathrm{S}:[\mathrm{E}]_{0}=[\mathrm{E}]+[\mathrm{ES}]$ and $[\mathrm{S}] \simeq[S]_{0}$. By substituting the following equalities in the equation for [ES] we get:

$$
[\mathrm{ES}]=\frac{\left.[E]_{0}\right)}{1+K_{M} /[\mathrm{S}]_{0}}
$$

Substituting this into the expression $n=k_{3}[\mathrm{ES}]$, we finally get the appropriate equation for the rate:

$$
v=\frac{k_{3}[E]_{0}}{1+K_{M} /[S]_{0}}
$$

1.0 point for [ES] as function of [E] and [S] 1.0 point for $[\mathrm{ES}]$ as function of $[\mathrm{E}]_{0}$ and $[\mathrm{S}]_{0}$ 1.0 point for final substitution
b) Write the equation for $v_{\max }$ and sketch the graph of $v$ as a function of $[\mathrm{S}]_{0}$.

## SOLUTION:

In the case of $v_{\max }$, one can easily conclude that by asking the following question, "what is the condition for which the function $v=f\left([S]_{0}\right)$ has the largest value?" This condition is satisfied when $[\mathrm{S}]_{0} \gg K_{M}$, and the function is reduced to $v_{\max }=k_{3}[\mathrm{E}]_{0}$.

Furthermore, we can incorporate $v_{\max }$ into our initial rate equation and obtain the necessary simplification and derive the equation of linearization for later:

$$
v=\frac{v_{\max }}{1+K_{M} /[\mathrm{S}]_{0}}
$$

$v_{\max }$ as a function of $[\mathrm{S}]_{0}$ is a hyperbolic function that ends with a "plate" which indicates that the enzyme is fully saturated on each catalytic site.
0.5 point for final equation
1.0 point for proper plot (plateau with denoted value)
c) The MM equation is more useful after linearization when assessing enzymatic activity. The so called Lineweaver-Burk plot is obtained by plotting $1 / v$ vs. $1 /[\mathrm{S}]_{0}$. Linearize the MM equation derived in a). Sketch the obtained Lineweaver-Burk plot, denoting the slope and the intercept.

## SOLUTION:

2.0 points

By a rearrangement of the MM equation with simple substitutions, we get:

$$
\frac{1}{v}=\frac{K_{M}}{v_{\max }} \frac{1}{[S]_{0}}+\frac{1}{v_{\max }}
$$

The obtained plot is known as Lineweaver-Burk plot. The graph can be sketched as a simple straight line, plotting $1 / v$ on the y-axis, $1 /[S]_{0}$ on the x-axis, the slope being $K_{M} / v_{\max }$ and the y-intercept $1 / v_{\max }$.
1.0 point for final equation
1.0 point for proper plot (axis and intercepts)

The catalytic efficiency $\epsilon$ of an enzyme, is defined as $\epsilon=k_{3} / K_{M}$ and describes how fast an enzyme can overall convert its substrate to product.
d) In which case does $\epsilon$ reach its maximum value? (Hint: consider the chemical problem at hand, not only the equation).

## SOLUTION:

1.0 points

The maximal value for $\epsilon$ is achieved when $k_{3} \gg k 2$ according to the expression for $K_{M}$, which means that essentially every encounter of the $\mathbf{E}$ with $S$ leads to turnover. In that case the equation for $\epsilon$ reduces to $k_{1}$, meaning that the maximal catalytic efficiency is then governed by how fast the substrate even binds to the enzyme.
1.0 point for inequality

Carbonic anhydrase is an enzyme that catalyses the hydration of $\mathrm{CO}_{2}$ in the red blood cells to give the bicarbonate ion and the reverse reaction in the lungs. Without this reaction, the bicarbonate buffer of the blood couldn't be sustained, leading to systematic acidosis and shut down of the respiratory system. For a reaction at $\mathrm{pH}=7.1, \mathrm{~T}=273.5 \mathrm{~K}$ and $[\mathrm{E}]_{0}=2.3 \mathrm{nM}$ the following data is obtained:

Table 3: Measured reaction rates $v$ for given $\mathrm{CO}_{2}$ concentrations.

$$
\begin{array}{rllll}
{\left[\mathrm{CO}_{2}\right] / \mathrm{mM}} & 1.25 & 2.50 & 5.00 & 20.0 \\
\hline v / \mathrm{mM} / \mathrm{s} & 0.0278 & 0.0500 & 0.0833 & 0.167
\end{array}
$$

e) Determine the catalytic efficiency and the value of $K_{M}$ (either arithmetically or graphically) using the principles in the previous points, bearing in mind that the reaction was monitored according to MM.

SOLUTION:

To solve this part, one needs to draw the graph and work out the regression line. First of all, let us construct the table for $x=1 /[\mathrm{S}]_{0}$ and $y=1 / v$ values. $1 / v_{\max }$ is y intercept and $K_{M} / v_{\max }$ is the slope.

The regression analysis is very simple: one need to find the equation $y^{\prime}=b x^{\prime}+a$, where y' and $x^{\prime}$ are the appropriate arithmetic values. Thus, one can obtain the following formulas for finding the equation of linear regression by simple partial integration of the mean error value SE by both a(the slope) and b(the intercept):

$$
b=\frac{x * y-n * x^{\prime} * y^{\prime}}{x^{2}-n * x^{\prime 2}}
$$

getting $\mathrm{x}^{\prime}=0.3625$ and $\mathrm{y}^{\prime}=32, \mathrm{n}=4, \mathrm{~b}=40$ and $\mathrm{a}=4$.
1.0 point for complete plot or calculating regression,
1.0 point for $K_{M}=10 \mathrm{mmol} / \mathrm{L}$,
1.0 point for $\epsilon=1.1 \times 10^{7} \mathrm{~L} \mathrm{~mol}^{-1} \mathrm{~s}^{-1}$

Technetium is a very rarely encountered element of the periodic table and was the first element to be produced artificially. Several complexes of technetium have found their use in medicine, where they are employed as radioactive tracers (radiopharmaceuticals) for the diagnosis of various diseases.

The diagnostically relevant isotope of Tc is the so-called ${ }^{99 m} \mathrm{Tc}$, a metastable $\gamma$-emitter nucleus. It is obtained from radioactive ${ }^{99} \mathrm{Mo}$ (itself being a fission product of ${ }^{235} \mathrm{U}$ ) and ultimately decays to the stable isotope ${ }^{99} \mathrm{Ru}$.
a) Complete the equations below and indicate what type of radiation is accompanying these nuclear decay processes.

$$
\begin{array}{r}
{ }^{99} \mathrm{Mo} \longrightarrow \ldots+\ldots \\
{ }^{99 m} \mathrm{Tc} \longrightarrow \mathrm{M}+\ldots \\
\mathrm{M} \longrightarrow \ldots+\ldots
\end{array}
$$

SOLUTION:

$$
\begin{aligned}
&{ }^{99} \mathrm{Mo} \longrightarrow{ }^{99 m} \mathrm{Tc}^{+}+\mathrm{e}^{-}+\bar{v}_{e}\left(\beta^{-}\right) \\
&{ }^{99 m} \mathrm{Tc} \longrightarrow{ }^{99} \mathrm{Tc}+\mathrm{h} \nu(\gamma) \\
&{ }^{99} \mathrm{Tc} \longrightarrow{ }^{99} \mathrm{Ru}^{+}+\mathrm{e}^{-}+\bar{v}_{e}\left(\beta^{-}\right)
\end{aligned}
$$

The particular form the ${ }^{99 m} \mathrm{Tc}$ is typically obtained as, is $\mathrm{TcO}_{4}{ }^{-}$(the so-called pertechnetate ion A ), which itself has found application as a radiopharmaceutical (in e.g. thyroid diagnostics). More typically however, the $\mathrm{TcO}_{4}^{-}$is being reduced with $\mathrm{SnCl}_{2}$ and complexated by different ligands to give a variety of radiopharmaceuticals. One important example is $\left[\mathrm{Tc}(\mathrm{MIBI})_{6}\right]^{+} \mathbf{B}$, a complex containing isonitrile ligands whose structure is shown in figure 7 .


A


CNR
B

Figure 7: Structure of the pertechnetate anion $\mathbf{A}$ as well as the $\left[\mathrm{Tc}(\mathrm{MIBI})_{6}\right]^{+}$complex $\mathbf{B}$.
b) Based on this information, what Mo-precursor is used for the synthesis of A and what would be a suitable way to separate remaining starting material from the product $\mathrm{TcO}_{4}{ }^{-}$?

## SOLUTION:

The precursor used is $\mathrm{MoO}_{4}{ }^{2-}$. Separation of the two differently charged ions may be achieved by ion chromatography (ion-exchanger) or potentially by precipitation.
c) Determine the oxidation numbers of the Tc -atoms in $\mathbf{A}$ and $\mathbf{B}$ and write a balanced redoxequation for the production of $\left[\mathrm{Tc}(\mathrm{MIBI})_{6}\right]^{+}$from $\mathrm{TcO}_{4}{ }^{-}$.

SOLUTION:

$$
\begin{aligned}
& \mathrm{TcO}_{4}{ }^{-}:+7 \\
& {\left[\mathrm{Tc}(\mathrm{MIBI})_{6}\right]^{+} }:+1 \\
& \text { Ox }: \mathrm{SnCl}_{2} \longrightarrow \mathrm{Sn}^{4+}+2 \mathrm{e}^{-}+2 \mathrm{Cl}^{-} \\
& \text {Red }: \mathrm{TcO}_{4}^{-}+6 \mathrm{MIBI}+6 \mathrm{e}^{-} \longrightarrow\left[\mathrm{Tc}(\mathrm{MIBI})_{6}\right]^{+}+4 \mathrm{O}^{2-} \\
& \text { Overall }: \mathrm{TcO}_{4}^{-}+6 \mathrm{MIBI}+3 \mathrm{SnCl}_{2} \longrightarrow\left[\mathrm{Tc}(\mathrm{MIBI})_{6}\right]^{+}+2 \mathrm{SnO}_{2}+\mathrm{SnCl}_{4}+2 \mathrm{Cl}^{-} \\
& \text {OR }(p H<1): \mathrm{TcO}_{4}{ }^{-}+6 \mathrm{MIBI}+3 \mathrm{SnCl}_{2}+8 \mathrm{H}^{+} \longrightarrow\left[\mathrm{Tc}(\mathrm{MIBI})_{6}\right]^{+}+3 \mathrm{Sn}_{4}^{+}+6 \mathrm{Cl}^{-}+4 \mathrm{H}_{2} \mathrm{O}
\end{aligned}
$$

0.5 points for each oxidation state, 1.0 point for overall equation
d) Based on the oxidation numbers of the two complexes, determine the $d$-electron count and draw ligand-field diagrams for the two complexes. Would you expect the complexes to be diamagnetic or paramagnetic? Justify why!

SOLUTION: 3.0 points

$$
\begin{array}{r}
\mathrm{TcO}_{4}{ }^{-}:+7->d^{0} \\
{\left[\mathrm{Tc}(\mathrm{MIBI})_{6}\right]^{+}:+1->d^{6}}
\end{array}
$$

After drawing the correct crystal field diagrams and filling in the electrons we find that both complexes

do not contain any unpaired electrons and are therefore diamagnetic.
0.5 points for each electron configuration, 0.5 points for each filled diagram, 0.5 points for each magnetism

## Energy levels of the d-orbitals in common stereochemistries



Figure 8: Crystal field splitting of different coordination geometries.

Radiopharmaceuticals are highly potent imaging agents and therefore only need to be administered in very low doses. ${ }^{99 m} \mathrm{Tc}$ has a physical half-life of 6.0 h and a typical dose of $\left[\mathrm{Tc}(\mathrm{MIBI})_{6}\right]^{+}$has an initial activity of $500 \mathrm{MBq}\left(1 \mathrm{~Bq}=1 \mathrm{~s}^{-1}=1\right.$ decay per second).
e) Calculate how many ${ }^{99 m} \mathrm{Tc}$ nuclei are required to achieve this activity and the mass of $\left[\mathrm{Tc}(\mathrm{MIBI})_{6}\right]^{+}$ that needs to be administered.

SOLUTION:

$$
\begin{aligned}
k & =\frac{\ln (2)}{T_{1 / 2}}=\frac{0.693}{6 * 3600 \mathrm{~s}}=3.21 \times 10^{-5} \mathrm{~s}^{-1} \\
N & =\frac{A}{k}=\frac{500 \mathrm{MBq}}{3.21 \times 10^{-5} \mathrm{~s}^{-1}}=1.56 \times 10^{13} \text { nuclei } \\
n & =\frac{N}{N_{A}}=1.56 \times 10^{13} \mathrm{~N}_{\mathrm{A}}=2.56 \times 10^{-11} \mathrm{~mol} \\
m & =n * M=2.56 \times 10^{-11} \mathrm{~mol} * 777 \mathrm{~g} / \mathrm{mol}=1.99 \times 10^{-8} \mathrm{~g}=20 \mathrm{ng}
\end{aligned}
$$

0.5 points for each

Another very important Tc-Radiopharmaceutical is ${ }^{99 m} \mathrm{Tc}$-HMPAO shown as two stereoisomers in figure 9.
f) Determine the overall charge $x$ of this Tc-complex, given that the oxidation state on Tc is +5 .

The complex is overall not charged, so neutral, $\mathrm{x}=0$.


Figure 9: Two stereoisomers of $[\mathrm{Tc}(\mathrm{HMPAO})]^{x+}$.
g) Based on the crystal-field splitting of an octahedral geometry, how would the crystal field splitting look like for such a complex?

## SOLUTION:

Similar to the case of square-planar, however the $d_{z^{2}}$ orbital is likely not getting lowered as much (i.e. below the $d_{x y}$ orbital) as only one axial ligand is being removed.
h) Which of the two shown stereoisomers shown C and D are chiral? Justify your answer.

## SOLUTION:

1.0 points

Only stereoisomer C is chiral. The stereoisomer D contains an internal plane of symmetry and is therefore non-chiral (meso).
0.5 points for each, with justification only

Aromatic molecules have fascinated chemists ever since they were originally discovered. They are widespread in nature and have found a plethora of uses to mankind. In this task we will try to have look at the underlying principles of aromaticity of molecules based on their molecular-orbital (MO) diagrams.


B

C

D

Figure 10: Stuctures of potentially aromatic compounds A - D.
a) For the shown molecules A-D, denote whether these are considered aromatic, anti-aromatic or non-aromatic according to Hückel's rule.

## SOLUTION:

2.0 points
A - aromatic B-anti-aromatic
C - non-aromatic (not fully conjugated)
D - non-aromatic (nonplanar due to steric repulsion)

In the following we will look deeper at the following series of molecules:


E


G


H

Figure 11: Structures from left to right: ethylene E, cyclobutadiene F, benzene G, cyclooctatetraene H.

Frost-Musulin diagrams are a useful aid for the construction of MO-diagrams of such cyclic $\pi$-systems and can easily be constructed as follows: Draw a circle with the arbitrary radius $2 \beta$. Draw the shape of an equilateral polygon into the circle with one corner of the polygon facing straight down. Note that $\beta$ is typically considered as a negative factor by convention and the lowest point of the circle has therefore an energy of $\alpha+2 \beta$.
To construct a Frost-Musulin diagram, everywhere the polygon touches the circle, draw a horizontal line which corresponds to the energy level of a MO. Above, the Frost-Musulin diagrams of cyclobutadiene $\mathbf{F}$ and benzene $\mathbf{G}$ are shown as an example.


Figure 12: Left: Frost-Musulin diagram for cyclobutadiene. Middle: Frost-Musulin diagram for benzene. Right: Molecular orbitals for benzene.
b) Draw the Frost-Musulin diagram of cyclooctatetraene $\mathbf{H}$ and fill in the $\pi$-electrons. Estimate the energy levels (in terms of the factor $\beta$ ) based on your sketch.

## SOLUTION:

2.0 points

cyclooctatetraene

Energy levels in rising order: $\alpha+2 \beta, \alpha+1.4 \beta, \alpha, \alpha-1.4 \beta, \alpha-2 \beta$ (also fine if they use the opposite sign for $\beta$ ).
0.5 points for diagram without electrons,
0.5 points for electron filling (Hund's rule),
1.0 points for energy estimates
c) In analogy to the shown MO-diagram of benzene draw all the molecular orbitals of flat cyclobutadiene $\mathbf{F}$ and flat cyclooctatetraene $\mathbf{H}$. Hint: It is enough to show a projection of the molecule from the top to save time while drawing.

## SOLUTION:

cyclobutadiene




cyclohexatriene






cyclooctatetraene

0.25 points for each MO in F and H

The factor $\beta$ used to draw the Frost-Musulin diagrams is related to the binding energy of ethylene. Given the MO-diagram of ethylene below, summation over all occupied orbitals for each filled-in electron yields an electronic energy of $2 \alpha+2 \beta$ for ethylene.


Figure 13: MO-diagram for ethylene.
d) Calculate the electronic energies of cyclobutadiene F, benzene G and cyclooctatetraene Hbased on their MO diagrams.

## SOLUTION:

$$
\begin{aligned}
& \mathbf{F}: 4 \alpha+4 \beta \\
& \mathbf{G}: 6 \alpha+8 \beta \\
& \mathbf{H}: 8 \alpha+9.6 \beta
\end{aligned}
$$

e) Compare the obtained values with the energy of the corresponding "localized structures", i.e. treating e.g. benzene as if it was a system of three non-interacting ethylene units (cyclohexatriene) and thereby effectively neglecting the effect of electron delocalization in the ring. Is this simple argument enough to explain why cyclobutadiene and cyclooctatetraene are antiaromatic?

```
Localized F : \(2 *(2 \alpha+2 \beta)=4 \alpha+4 \beta\)
Localized \(\mathbf{G}: 3 *(2 \alpha+2 \beta)=6 \alpha+6 \beta\)
Localized \(\mathbf{H}: 4 *(2 \alpha+2 \beta)=8 \alpha+8 \beta\)
```

For benzene $\mathbf{G}$, it is visible that the delocalization stabilizes the molecule by $2 \beta$. For cyclobutadiene F, the delocalization doesn't lead to any stabilization which is somewhat in accord with the antiaromatic (unstable) character. For cyclooctatetraene $\mathbf{H}$, the model predicts an actual stabilization by the delocalization by $1.4 \beta$ and therefore this crude approach/model cannot sufficiently explain the instability of cyclooctatetraene.
0.5 points for each calculation, 0.5 points for each conclusion

Both, cyclobutadiene $\mathbf{F}$ and cyclooctatetraene $\mathbf{H}$ in the previously shown flat geometry are antiaromatic. They try to avoid this property in two different ways: Cyclooctatetraene is flexible enough to distort out of planarity, while cyclobutadiene undergoes an in-plane distortion and gets from a square to a more rectangular shape.
f) Draw the geometry of non-planar cyclooctatetraene $\mathbf{H}$ (keep in mind that all double-bonds in the ring still need to have cis-configuration).


Tub-shaped $\left(D_{2 d}\right)$
g) Draw the Frost-Musulin diagram of a rectangular-distorted cyclobutadiene F. How do you expect the electron configuration to change?

SOLUTION: 1.0 points


Major observations they should make here: the degeneracy is broken and we get four non-degenerate energy levels. Filling in the electrons according to Hund's rule would yield a closed-shell (non-radical) system.
0.5 points for diagram with electrons,
0.5 points for conclusion

## Problem 8 - NMR Dynamics - Fast or Slow?

Chlorocyclohexane, $\mathrm{C}_{6} \mathrm{H}_{11} \mathrm{Cl}$, is a simple organic halide that finds limited application as a reagent in cross-coupling reactions or as a solvent slightly more polar than cyclohexane.
a) How many cyclic constitutional isomers of $\mathrm{C}_{6} \mathrm{H}_{11} \mathrm{Cl}$ could theoretically exist? (Start by drawing the different $\mathrm{C}-\mathrm{H}$ backbones and only then decide how many chloro regioisomers exist per backbone structure)

## SOLUTION:



1x

$5 x$

$4 x$

$4 x$

$5 x$

$5 x$

$3 x$

$6 x$

$3 x$


4x

$3 x$

$2 x$
1.0 point for finding all unique backbones, 1.0 point for weighing to get all regioisomers
b) How many peaks do you expect in the ${ }^{1} \mathrm{H}$ NMR spectra of the parent hydrocarbons?

SOLUTION:
Same number as weights for regioisomers: 1, 4, 5, 3, 3, 3, 5, 4, 5, 6, 4, 2
1.0 point for finding all number of peaks,

Below, you can find a simulated ${ }^{1} \mathrm{H}$ NMR spectrum of chlorocyclohexane in $\mathrm{CDCl}_{3}$ at 300 MHz at 298 K .
c) Assign all peaks to the protons in the structure.

## SOLUTION:

$$
\begin{aligned}
& 3.8 \mathrm{ppm} \longrightarrow \mathrm{C}_{1}-\mathrm{H} \\
& 1.9 \mathrm{ppm} \longrightarrow \mathrm{C}_{2}-\mathrm{H}_{2}, \mathrm{C}_{6}-\mathrm{H}_{2} \\
& 1.5 \mathrm{ppm} \longrightarrow \mathrm{C}_{3}-\mathrm{H}_{2}, \mathrm{C}_{4}-\mathrm{H}_{2} \\
& 1.4 \mathrm{ppm} \longrightarrow \mathrm{C}_{4}-\mathrm{H}
\end{aligned}
$$



Figure 14: Simulated ${ }^{1} \mathrm{H}$ NMR spectrum for chlorocyclohexane in $\mathrm{CDCl}_{3}$ at 300 MHz at 298 K .
d) What is the peak at 0.00 ppm ?

SOLUTION:
Reference for chemical shift: TMS, $\mathrm{Si}\left(\mathrm{CH}_{3}\right)_{4}$
Experimentally, you record a ${ }^{1} \mathrm{H}$ NMR spectrum for a chlorocyclohexane sample in $\mathrm{CDCl}_{3}$ at 300 MHz and both at 298 K and at 192 K . To your surprise, you now find two peaks near 4.00 ppm in the 192 K spectrum.


Figure 15: Recorded ${ }^{1} \mathrm{H}$ NMR spectrum for chlorocyclohexane in $\mathrm{CDCl}_{3}$ at 300 MHz at 192 K near 4.00 ppm .
e) Provide an explanation with structures for the observation of the splitting of the signal near 4.00 ppm .

## SOLUTION:



Going from fast to slow exchange, the ring flip of cyclohexane can be "frozen out". Axial and equatorial methine protons have different chemical shifts while no longer interconverting on the NMR timescale.
1.0 point for both structures,
1.0 point for explanation
f) What is the expected peak splitting for both peaks? Draw the splitting diagrams for both and label the type of expected patterns. Why is it experimentally only observed for one of the two peaks?

## SOLUTION:



Both protons are in a chemical environment leading to a $t t$ splitting. In the case of the equatorial position, coupling is weaker and poorly resolved.
1.0 point for each coupling tree, 0.5 points for each multiplicity, 0.5 points for resolution limited
g) Calculate the change in $\Delta \mathrm{G}$ for a chloride substituent at 192 K in $\mathrm{kcal} / \mathrm{mol}$.

$$
\begin{aligned}
K & =\frac{\left[H_{e q}\right]}{\left[H_{a x}\right]}=\frac{I_{e q}}{I_{a x}}=\frac{3.98}{1.00}=3.98 \\
\Delta G & =-R T \ln (K)=-8.3145 \mathrm{~J} / \mathrm{mol} / \mathrm{K} * 192 \mathrm{~K} * \ln (3.98)=-2.21 \mathrm{~kJ} / \mathrm{mol}=0.53 \mathrm{kcal} / \mathrm{mol}
\end{aligned}
$$

0.5 point for each
h) Finally, you record even more spectra at different temperatures and the obtained fitted interconversion rates as shown below. Calculate the activation energy in kcal/mol for the observed interconversion. You can assume the activation energy is constant over the whole temperature range.

## SOLUTION

$$
\begin{aligned}
k & =A * \exp \left(\frac{-E_{A}}{R T}\right) \\
\frac{k_{1}}{k_{2}} & =\exp \left(\frac{E_{A}}{R T_{2}}-\frac{E_{A}}{R T_{1}}\right) \\
E_{A} & =\frac{R * \ln \left(\frac{k_{1}}{k_{2}}\right)}{\frac{1}{T_{2}}-\frac{1}{T_{1}}}=\frac{8.3145 \mathrm{~J} / \mathrm{mol} / \mathrm{K} * \ln (2 / 400)}{\frac{1}{229 \mathrm{~K}}-\frac{1}{192 \mathrm{~K}}}=52.35 \mathrm{~kJ} / \mathrm{mol}=12.5 \mathrm{kcal} / \mathrm{mol}
\end{aligned}
$$



Figure 16: Series of ${ }^{1} \mathrm{H}$ NMR spectra for chlorocyclohexane in $\mathrm{CDCl}_{3}$ at 300 MHz near 4.00 ppm recorded at different temperatures. Fitted interconversion rates going from the axial to the equatorial conformer.



A









Figure 17: Scheme involving 2-tert-butylcyclopentanone.
a) For the scheme shown above fill in all the boxes. Provide stereoinformation where necessary.
1.0 point each, only 0.5 point if structure correct, but stereoinformation missing
b) Determine the absolute configuration of the following molecules A containing a plane and B containing an axis of chirality. Justify your answer.

## SOLUTION:

A: $R$ (looking through bridge from top and starting on the bridge O we go down to the $\mathrm{NH}_{2}$ as substituent with higher priority on the ring).
B: S (looking from $\mathrm{HOOC}-\mathrm{C}-\mathrm{Me}$ as carboxylic acid has highest priority.
1.0 point each


A


B

Figure 18: Two molecules showing planar or axial chirality.
c) For the two shown bis-helical systems $\mathbf{C}$ and $\mathbf{D}$, determine the helicality for all helical elements. Which of these stereoisomers are chiral? How do the two stereoisomers relate to each other?

## SOLUTION:

C: $P, M \longrightarrow$ achiral due to inversion center in the middle of the molecule
$\mathrm{D}: P, P \longrightarrow$ chiral
The two stereoisomers are diastereomers of each other.

> 0.5 point for correct helicity-descriptors per molecule,
> 0.5 point for chiral/achiral,
> 0.5 points for diastereomers


C


D

Figure 19: Two molecules C and D showing potential helical chirality.

## Problem 10 - Total Synthesis of Clavizepine

(-)-Clavizepine (1) is an alkaloid isolated in 1986 from Corydalis claviculata and first synthesized as a racemic mixture by the Japanese organic chemist Hiroyuki Ishibashi. One intriguing feature is the presence of a pharmacologically attractive 1-aryl-3-benzazepine moiety as highly selective central D-1 dopamine receptor antagonists. The key step is of this synthesis a Pummerer rearrangement to form elegantly the 7-membered ring.


1
Figure 20: Structure of clavizepine without stereoinformation.


Figure 21: First half of Ishibashi's route.
a) Draw the structures of compounds $\mathbf{A}-\mathbf{E}$ without stereochemistry.

## SOLUTION



A: $\mathrm{C}_{13} \mathrm{H}_{17} \mathrm{BrO}_{4} \mathrm{~S}$


B: $\mathrm{C}_{12} \mathrm{H}_{15} \mathrm{BrO}_{4}$


C: $\mathrm{C}_{25} \mathrm{H}_{26} \mathrm{O}_{6}$


D: $\mathrm{C}_{25} \mathrm{H}_{24} \mathrm{O}_{6}$


E: $\mathrm{C}_{24} \mathrm{H}_{23} \mathrm{NO}_{5}$
1.0 point for each


Figure 22: Second half of Ishibashi's route. $\mathrm{rt}=$ room temperature.
b) Suggest a suitable structure for reagent $\mathbf{F}$.

SOLUTION:
1.0 points

c) Draw the structures of compounds G-I without stereochemistry.

## SOLUTION



E: $\mathrm{C}_{27} \mathrm{H}_{27} \mathrm{NO}_{6} \mathrm{~S}$

$\mathrm{H}: \mathrm{C}_{26} \mathrm{H}_{25} \mathrm{NO}_{5}$


I: $\mathrm{C}_{26} \mathrm{H}_{27} \mathrm{NO}_{4}$
d) (-)-Clavizepine (1) has S-configuration. Draw the natural production with its proper stereochemistry.

SOLUTION:

(S)-1
e) How would you prepare (-)-clavizepine based on Ishibashi's route?

SOLUTION:
1.0 points

Have "3 steps" produce 4 enantioselectively, enantioselective fractional crystallization of 5, chiral column on any reasonable intermediate from 4 to 5
No separation at later stages, especially not natural product!

Hints:

- Reducing agents:
- Zn , selective for $\mathrm{C}-\mathrm{S}$ bonds
- $\mathrm{BH}_{3} \cdot \mathrm{THF}$
- Red-Al
- Raney Ni, for removal of benzyl protecting groups
- Oxidizing agents:
- $\mathrm{NaIO}_{4}$, for vicinal diols and sulfides

An alternative route to obtain enantiopure 1-aryl-3-benzazepines is based on the racemic separation by camphor-10-sulfonic acid.


Figure 23: Alternative route for clavizepine derivatives. dppf = bis(diphenylphosphino)ferrocene.
f) Draw structures $\mathbf{J}-\mathbf{N}$ including stereochemistry.

## SOLUTION:

5.0 points


