

**CHEMISTRY.
OLYMPIAD.CH**

CHEMIE-OLYMPIADE
OLYMPIADES DE CHIMIE
OLIMPIADI DELLA CHIMICA

SwissChO 2021 - 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 stick down 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 test has 33 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

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 24.30															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																	
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.96	43 Tc –	44 Ru 101.07	45 Rh 102.91	46 Pd 106.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.76	52 Te 127.60	53 I 126.90	54 Xe 131.29											
55 Cs 132.91	56 Ba 137.33	57–71 –	72 Hf 178.49	73 Ta 180.95	74 W 183.84	75 Re 186.21	76 Os 190.23	77 Ir 192.22	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	84 Po –	85 At –	86 Rn –											
87 Fr –	88 Ra –	89–103 –	104 Rf –	105 Db –	106 Sg –	107 Bh –	108 Hs –	109 Mt –	110 Ds –	111 Rg –	112 Cn –																	
57 La 138.91	58 Ce 140.12	59 Pr 140.91	60 Nd 140.24	61 Pm –	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 –	90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np –	94 Pu –	95 Am –	96 Cm –	97 Bk –	98 Cf –	99 Es –	100 Fm –	101 Md –	102 No –	103 Lr –														

PROBLEM 1 - MULTIPLE CHOICE QUESTIONS

8.0 POINTS

For any question, choose exactly one answer:

SOLUTION:

0.5 points each, 8.0 points total

1.1 Why is the ionization enthalpy of nitrogen higher than that of oxygen?

a) Nitrogen is more stable than oxygen as its highest valence subshell is half-filled.

1.2 Which represents a correct electron configuration for a chlorine atom?

c) [Ne] 3s² 3p⁵

1.3 What is the explanation for the sequence of electronegativity F > O > Cl?

d) The smallest possible atomic core has more influence than the largest possible atomic core charge.

1.4 What is the mass in grams of 3.0×10^{23} molecules of CO₂?

a) 22 g

1.5 During the process of _____, a nucleus emits an energetic electron, called a _____, resulting from the spontaneous transformation of a neutron into a proton and an electron.

b) beta decay; beta particle

1.6 Which rule applies to oxo acids (H_nXO_n such as HNO₃, H₂SO₄, HBrO₄, ...)?

c) Acids with central atoms from uneven main groups have an uneven number of protons.

1.7 Which of the following reactions is an example of homogeneous catalysis?

a) Alkylation of benzene using hydrochloric acid as the catalyst

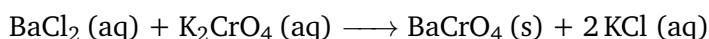
1.8 When calculating the average kinetic energy using the equation $KE_{avg} = 3/2 * k * T$, which of the following does k stand for?

b) Boltzmann constant

1.9 Which chemical equation shows a redox reaction?

c) $5 \text{Fe}^{2+} + \text{MnO}_4^- + 8 \text{H}_3\text{O}^+ \longrightarrow 6 \text{Fe}^{3+} + \text{Mn}^{2+} + 12 \text{H}_2\text{O}$

1.10 Which of the following correctly names the precipitate formed in the reaction below?



c) Barium chromate

1.11 Which of the following correctly defines buffering capacity?

c) The amount of protons or hydroxide ions a buffer can absorb with a minimal change in pH.

1.12 For the first order reaction with rate constant k , which expression will give the half-life with respect to its initial concentration a ?

d) $\ln(2)/k$

1.13 To predict the major product in the addition reaction of a hydrogen halide with an unsymmetrical alkene, which of the following conditions is used?

a) Markownikoff's rule

1.14 Which of the following reagents is used to carry out the oxidation of 2-butene to acetic acid?

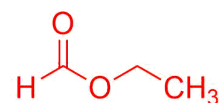
a) acidic KMnO_4

1.15 Which of the following organic compounds does NOT have a structural isomer?

b) ethene

1.16 Given the image shown on the right, what is the correct chemical name for a structural isomer of this compound, assuming that $\text{R} = \text{CH}_2\text{CH}_3$?

b) ethyl methanoate



PROBLEM 2 - BASALUMINITE

13.0 POINTS

Nanocrystalline basaluminite $[\text{Al}_4(\text{OH})_{10}(\text{SO}_4) \cdot (\text{H}_2\text{O})_5]$ ($M = 464.14 \text{ g/mol}$) usually occurs as a precipitate downstream of acid mine drainages and acid sulfate soils. In 2016 only, the first natural occurrence of basaluminite has been found in Switzerland. The cold alpine stream in question is called “Ova Lavirun” and is located in Maloja district. The pond, from which it springs, is acidic due to oxidation of the mineral pyrite $\text{Fe}(\text{II})\text{S}_2$ upstream of the pond. At the same time, the generated acid dissolves aluminum from potassium feldspar KAlSi_3O_8 . Downstream of the pond, Ova Lavirun is joined by three smaller tributaries assumed to be pure water here. A simplified scheme of the streams is shown in Fig. 1. The flow rate Q at each point is expressed in m^3/s .

The proton concentration of a strongly diluted solution of a monoprotic acid is calculated as:

$$[\text{H}^+] = \frac{[\text{HA}] + \sqrt{[\text{HA}]^2 + 4 * K_W}}{2}$$

The solubility product of basaluminite is $K_{sp} = 10^{-117.7} \text{ mol}^{15} \text{ L}^{-15}$. In cold water, the dissociation constant is $K_W = 10^{-14.9} \text{ mol}^2 \text{ L}^{-2}$.

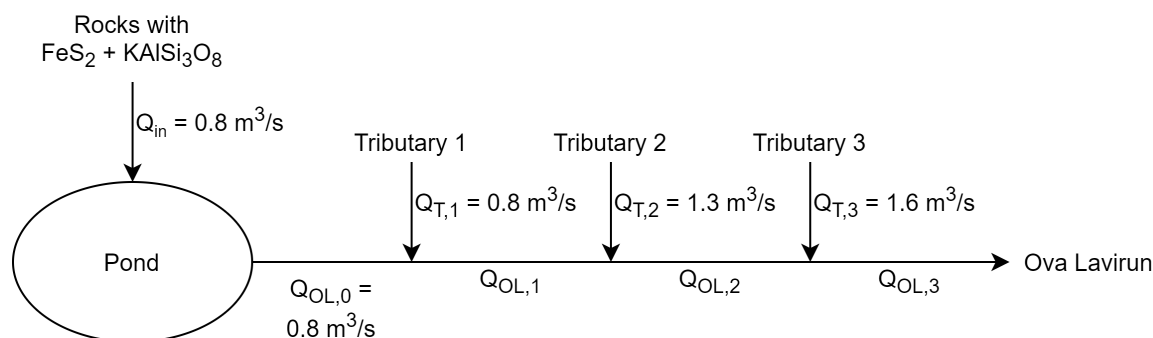
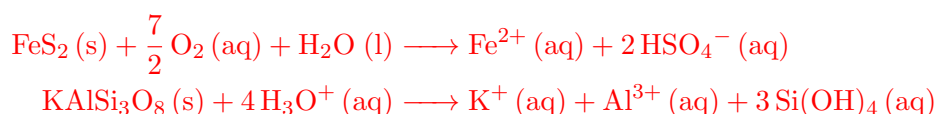


Figure 1: Simplified scheme of Ova Lavirun with joining tributary.

2.1 Write the chemical equations for 1) the oxidative dissolution of pyrite to Fe^{2+} and hydrogensulfate HSO_4^- by dissolved oxygen and 2) the acidic dissolution of feldspar by H_3O^+ generating $\text{Si}(\text{OH})_4$.

SOLUTION:

1.0 points total



0.5 points for each

2.2 The pond has a constant inflow and outflow of $0.8 \text{ m}^3/\text{s}$. The inflow provides $25.6 \text{ mmol HSO}_4^-$, $6.91 \text{ mmol Al}^{3+}$ and no other sulfur species per second. Calculate the pH of the pond.

SOLUTION:

1.5 points total

$$[\text{HSO}_4^-]_0 = \frac{n_{in}}{Q_{in}} = \frac{25.6 \times 10^{-3} \text{ mol/s}}{800 \text{ L/s}} = 3.2 \times 10^{-5} \text{ M}$$

$$[\text{H}^+]_0 = \frac{3.2 \times 10^{-5} \text{ M} + \sqrt{(3.2 \times 10^{-5} \text{ M})^2 + 4 * 10^{-14.9} \text{ M}^2}}{2} = 3.2 \times 10^{-5} \text{ M}$$

$$\text{pH}_0 = -\log[\text{H}^+] = 4.49$$

0.5 points for each

2.3 Calculate flow rates $Q_{OL,i}$ at each point.

SOLUTION:

1.5 points total

$$Q_{OL,1} = Q_{OL,0} + Q_{T,1} = 0.8 \text{ m}^3/\text{s} + 0.8 \text{ m}^3/\text{s} = 1.6 \text{ m}^3/\text{s}$$

$$Q_{OL,2} = Q_{OL,1} + Q_{T,2} = 1.6 \text{ m}^3/\text{s} + 1.3 \text{ m}^3/\text{s} = 2.9 \text{ m}^3/\text{s}$$

$$Q_{OL,3} = Q_{OL,2} + Q_{T,3} = 2.9 \text{ m}^3/\text{s} + 1.6 \text{ m}^3/\text{s} = 4.5 \text{ m}^3/\text{s}$$

0.5 points for each

2.4 What is the pH after each tributary inflow?

SOLUTION:

3.0 points total

$$[\text{HSO}_4^-]_1 = [\text{HSO}_4^-]_0 * \frac{Q_{OL,0}}{Q_{OL,1}} = 3.2 \times 10^{-5} \text{ M} * \frac{0.8 \text{ m}^3/\text{s}}{1.6 \text{ m}^3/\text{s}} = 1.6 \times 10^{-5} \text{ M}$$

$$[\text{HSO}_4^-]_2 = [\text{HSO}_4^-]_1 * \frac{Q_{OL,1}}{Q_{OL,2}} = 1.6 \times 10^{-5} \text{ M} * \frac{1.6 \text{ m}^3/\text{s}}{2.9 \text{ m}^3/\text{s}} = 8.8 \times 10^{-6} \text{ M}$$

$$[\text{HSO}_4^-]_3 = [\text{HSO}_4^-]_2 * \frac{Q_{OL,2}}{Q_{OL,3}} = 8.8 \times 10^{-6} \text{ M} * \frac{2.9 \text{ m}^3/\text{s}}{4.5 \text{ m}^3/\text{s}} = 5.7 \times 10^{-6} \text{ M}$$

$$\text{pH}_1 = -\log \left(\frac{1.6 \times 10^{-5} \text{ M} + \sqrt{(1.6 \times 10^{-5} \text{ M})^2 + 4 * 10^{-14.9} \text{ M}^2}}{2} \right) = 4.80$$

$$\text{pH}_2 = -\log \left(\frac{8.8 \times 10^{-6} \text{ M} + \sqrt{(8.8 \times 10^{-6} \text{ M})^2 + 4 * 10^{-14.9} \text{ M}^2}}{2} \right) = 5.05$$

$$\text{pH}_3 = -\log \left(\frac{5.7 \times 10^{-6} \text{ M} + \sqrt{(5.7 \times 10^{-6} \text{ M})^2 + 4 * 10^{-14.9} \text{ M}^2}}{2} \right) = 5.25$$

0.5 points for each

2.5 The ion product Q_{sp} can be used to determine whether a precipitate will form for a given concentration of ions. State the ion product for basaluminite and re-write it in terms of the concentration of SO_4^- and the pH only.

SOLUTION:

2.0 points total

$$Q_{sp} = [\text{Al}^{3+}]^4 * [\text{OH}^-]^{10} * [\text{SO}_4^-]$$

$$\text{pH} = \log[\text{H}^+] = -\log \left(\frac{K_W}{[\text{OH}^-]} \right)$$

$$[\text{OH}^-] = K_W * 10^{\text{pH}} = 10^{\text{pH}-14.9}$$

$$Q_{sp} = (0.27 * [\text{SO}_4^-])^4 * 10^{\text{pH}-14.9} * [\text{SO}_4^-]$$

0.5 points for each

2.6 After which tributary inflow does precipitation occur?

SOLUTION:

1.5 points total

$$Q_{sp,1}/K_{sp} = \frac{5.1 \times 10^{-119} \text{ M}^{15}}{10^{-117.7} \text{ M}^{15}} = 0.25$$

$$Q_{sp,2}/K_{sp} = \frac{9.9 \times 10^{-118} \text{ M}^{15}}{10^{-117.7} \text{ M}^{15}} = 4.97$$

$$Q_{sp,3}/K_{sp} = \frac{8.9 \times 10^{-117} \text{ M}^{15}}{10^{-117.7} \text{ M}^{15}} = 44.7$$

0.5 points for realization $Q_{sp} > K_{sp}$ means precipitation favored
 1.0 points for precipitation after inflow of T_2 WITH calculation(s)

2.7 Given that nanocrystalline basaluminite is formed, we can assume that the precipitation is instantaneous and runs to completion once it has started. Under the present conditions, $21.8 \mu\text{g}$ basaluminite can be precipitated per liter and second. Over which distance of Ova Lavirun could you find basaluminite if the stream is on average 2.7 m wide and 17 cm deep after this point? If you could not solve 2.6, assume that precipitation occurs after tributary 2.

SOLUTION:

2.5 points total

$$v = \frac{Q}{A} = \frac{2.9 \text{ m}^3/\text{s}}{2.7 \text{ m} * 0.17 \text{ m}} = 6.32 \text{ m/s}$$

$$\Delta c = k * \Delta t$$

$$\frac{\Delta x}{\Delta t} = \Delta c \Rightarrow \Delta c = k * \Delta x / v / M$$

$$\Delta x = \Delta c * v * M / k$$

$$\Delta x = \frac{8.8 \times 10^{-6} \text{ mol/L} * 6.32 \text{ m/s} * 464.14 \text{ g/mol}}{21.8 \times 10^{-6} \text{ g/Ls}} = 1.2 \text{ km}$$

0.5 points for each

PROBLEM 3 - TITRATION OF TARTARIC ACID

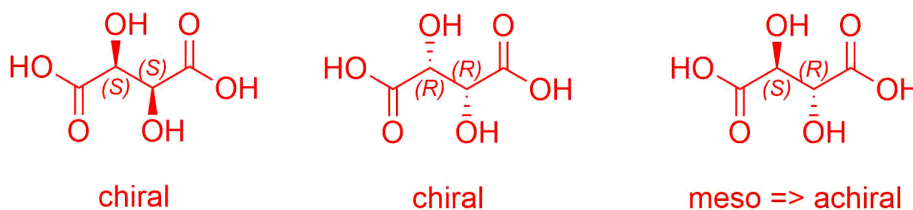
10.0 POINTS

2,3-Dihydroxybutanedioic acid, commonly known as “tartaric acid”, is an organic substance with two carboxyl groups. Tartaric acid is used for acidifying gelatine products such as gummy bears and sour gummy rings. The pK_a values of tartaric acid are $pK_{a,1} = 2.98$ and $pK_{a,2} = 4.34$.

3.1 Tartaric acid has two stereogenic centers in its molecule. Draw all diastereomers! Determine the absolute configurations (R/S) of all stereogenic centers. Which diastereomers are chiral?

SOLUTION:

2.0 points total



3 x 0.25 points for unique structures

3 x 0.25 points for correct R/S

0.5 points for all chiral & meso (achiral)

3.2 Tartaric acid is very soluble in water. The literature value is 1394 g L^{-1} at 20°C . What is the molarity of a saturated solution? Explain with one or two keywords why the solubility is so high.

SOLUTION:

1.0 points total

$$c(\text{C}_4\text{H}_6\text{O}_6) = \frac{m}{V * M} = \frac{1394 \text{ g/L}}{150.1 \text{ g/mol}} = 9.29 \text{ mol/L}$$

Tartaric acid is highly soluble in water since it 1) partially forms IONIC SPECIES and 2) has multiple FGs which can engage in H BONDS.

0.5 points for calculation

2 x 0.25 points for keywords

3.3 What pH value do you expect for a tartaric acid solution with a total concentration of 0.5 M? What simplifying assumption can be made? Give a rule when this simplifying assumption can be made in case of a diprotic acid?

SOLUTION:

1.5 points total

$$[\text{H}^+] = -\frac{K_{a,1}}{2} + \sqrt{\frac{K_{a,1}^2}{4} + K_{a,1} * c_0} = 0.0224 \text{ M}$$

$$\text{pH} = -\log[\text{H}^+] = 1.65$$

0.5 points for calculation

Simplifying assumption: the second deprotonation can be neglected (0.5 points) if the pK_a values are sufficiently far apart (≥ 1 unit) (0.5 points)

3.4 In said 0.5 M solution of tartaric acid which ions or molecules are to be found in this solution? At which concentrations? Note also the second deprotonated stage! You can use the following laws which say that the degree of protolysis α_i depends on the (initial) concentration c_0 and the pH through

$$\alpha_0 = \frac{[\text{H}_2\text{A}]}{c_0} = \frac{[\text{H}^+]^2}{D} \quad \alpha_1 = \frac{[\text{HA}^-]}{c_0} = \frac{[\text{H}^+]K_{a,1}}{D} \quad \alpha_2 = \frac{[\text{A}^{2-}]}{c_0} = \frac{K_{a,1}K_{a,2}}{D}$$

$$D = [\text{H}^+]^2 + K_{a,1} * [\text{H}^+] + K_{a,1} * K_{a,2}$$

SOLUTION:

2.0 points total

$$[\text{H}^+] = 0.0224 \text{ M}$$

$$[\text{H}_2\text{A}] = \frac{[\text{H}^+]^2 * c_0}{D} = \frac{0.0224 \text{ M} * 0.0224 \text{ M} * 0.5 \text{ M}}{5.25 \times 10^{-4} \text{ M}^2} = 0.478 \text{ M}$$

$$[\text{HA}^-] = \frac{[\text{H}^+] * K_{a,1} * c_0}{D} = \frac{0.0224 \text{ M} * 10^{-2.98} \text{ M} * 0.5 \text{ M}}{5.25 \times 10^{-4} \text{ M}^2} = 0.223 \text{ M} \simeq [\text{H}^+]$$

$$[\text{A}^{2-}] = \frac{K_{a,1} * K_{a,2} * c_0}{D} = \frac{10^{-2.98} \text{ M} * 10^{-4.34} \text{ M} * 0.5 \text{ M}}{5.25 \times 10^{-4} \text{ M}^2} = 4.56 \times 10^{-5} \text{ M}$$

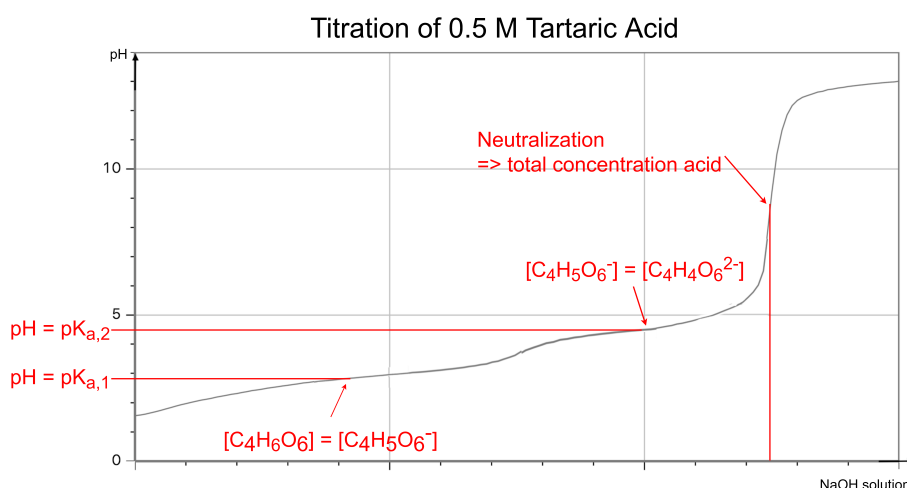
$$[\text{OH}^-] = \frac{[\text{H}^+]}{K_W} = \frac{10^{-14.0} \text{ M}^2}{0.0224 \text{ M}} = 4.46 \times 10^{-13} \text{ M}$$

3 x 0.5 points for calculation regarding $\text{C}_4\text{H}_6\text{O}_6$
2 x 0.25 points for calculation regarding H^+ and OH^-

3.5 Write down the two neutralization equations for the titration of tartaric acid solution by sodium hydroxide solution (NaOH solution). Copy the titration curve of tartaric acid below to your answer sheet. Mark all points where you can extract useful information.

SOLUTION:

2.0 points total



2 x 0.25 points for equations
3 x 0.5 points for points in curve

3.6 A 12.34 g gummy bear is dissolved and diluted to a total volume of 100.0 mL in H₂O. 25.0 mL of this solution are titrated with a 0.100 M sodium hydroxide solution (NaOH solution). 17.3 mL titer are consumed up to the end point of titration. What is the mass fraction in % of tartaric acid in the gummy assuming that no other acid is present?

SOLUTION:

1.5 points total

$$n(\text{NaOH}) = V(\text{NaOH}) * c(\text{NaOH}) = 1.73 \text{ mmol}$$

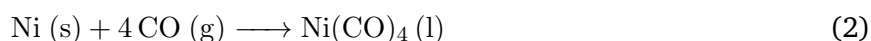
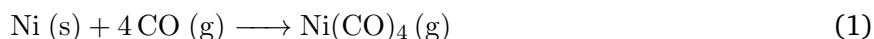
$$n_{\text{bear}}(\text{H}_2\text{A}) = 0.5 * n(\text{NaOH}) * \frac{100.0 \text{ mL}}{25.0 \text{ mL}} = 3.46 \text{ mmol}$$

$$wt\%_{\text{bear}}(\text{H}_2\text{A}) = \frac{m_{\text{bear}}(\text{H}_2\text{A})}{m_{\text{tot}}} = \frac{n_{\text{bear}}(\text{H}_2\text{A}) * M(\text{H}_2\text{A})}{m_{\text{tot}}} = \frac{3.45 \text{ mmol} * 150.1 \text{ g/mol}}{12.34 \text{ g}} = 4.21 \text{ wt}\%$$

0.5 points for $n(\text{NaOH})$, $n_{\text{bear}}(\text{H}_2\text{A})$ and $wt\%_{\text{bear}}(\text{H}_2\text{A})$

PROBLEM 4 - ISOLATION OF Ni(CO)₄**11.0 POINTS**

Most of the nickel in the world comes from a single mine in Canada where the impact of a comet many years ago brought a deeply buried deposit of NiS to the earth's surface. To obtain pure Ni, the ore is reduced to an impure metallic Ni and purified by reacting with carbon monoxide, CO, to form Ni(CO)₄, which is isolated and converted back to pure Ni. Depending on the temperature, the reaction is one or the other of these two reactions:



The desired product is Ni(CO)₄ (g) because it is easier to separate a gas from solid impurities than it is to remove a liquid from these same impurities.

4.1 Using the provided thermodynamic data, determine the enthalpy and entropy changes for both reactions.

SOLUTION:**2.0 points total**

$$\begin{aligned} \Delta_r H^\circ &= \Delta_f H^\circ(\text{Ni(CO)}_4, \text{g}) - \Delta_f H^\circ(\text{Ni, s}) - 4 * \Delta_f H^\circ(\text{CO, g}) \\ &= -602.8 \text{ kJ/mol} - 0.0 \text{ kJ/mol} - 4 * -110.5 \text{ kJ/mol} \\ &= -160.8 \text{ kJ/mol} \\ \Delta_r S^\circ &= \Delta_f S^\circ(\text{Ni(CO)}_4, \text{g}) - \Delta_f S^\circ(\text{Ni, s}) - 4 * \Delta_f S^\circ(\text{CO, g}) \\ &= 411.0 \text{ J/molK} - 29.90 \text{ J/molK} - 4 * 197.9 \text{ J/molK} \\ &= -410.5 \text{ J/molK} \\ \Delta_r H^\circ &= \Delta_f H^\circ(\text{Ni(CO)}_4, \text{l}) - \Delta_f H^\circ(\text{Ni, s}) - 4 * \Delta_f H^\circ(\text{CO, g}) \\ &= -632.9 \text{ kJ/mol} - 0.0 \text{ kJ/mol} - 4 * -110.5 \text{ kJ/mol} \\ &= -190.9 \text{ kJ/mol} \\ \Delta_r S^\circ &= \Delta_f S^\circ(\text{Ni(CO)}_4, \text{l}) - \Delta_f S^\circ(\text{Ni, s}) - 4 * \Delta_f S^\circ(\text{CO, g}) \\ &= 313.9 \text{ J/molK} - 29.90 \text{ J/molK} - 4 * 197.9 \text{ J/molK} \\ &= -507.6 \text{ J/molK} \end{aligned}$$

0.5 points for each

4.2 Explain why the entropy values were to be expected (consider absolute values in relation to each other and changes during the reactions)!

SOLUTION:**1.0 points total**

- (1): decreasing number of gas phase molecules => decrease in entropy
- (2): same as (1) plus "condensation" => stronger decrease in entropy
OR
(2): larger decreasing number of gas phase molecules => stronger decrease in entropy

0.5 points for each

4.3 Determine on which side the chemical equilibria of the two reactions are at room temperature!

SOLUTION:

2.0 points total

$$\begin{aligned}
 T &= 298 \text{ K} \\
 \Delta_{r1}G^\circ &= \Delta_{r1}H^\circ - T * \Delta_{r1}S^\circ \\
 &= -160.8 \text{ kJ/mol} - (298 \text{ K} * -410.5 \text{ J/molK}) \\
 &= -38.5 \text{ kJ/mol} \Rightarrow \text{spontaneous reaction, equilibrium on the product side} \\
 \Delta_{r2}G^\circ &= \Delta_{r2}H^\circ - T * \Delta_{r2}S^\circ \\
 &= -190.9 \text{ kJ/mol} - (298 \text{ K} * -507.6 \text{ J/molK}) \\
 &= -39.6 \text{ kJ/mol} \Rightarrow \text{spontaneous reaction, equilibrium on the product side}
 \end{aligned}$$

0.5 points for each

4.4 Starting from an excess of nickel, calculate the mole fraction of $\text{Ni}(\text{CO})_4$ in the gas phase in equilibrium with CO at 150°C and $p_{\text{tot}} = 1.00 \text{ bar}$. Assume a small degree of formation $\alpha \ll 1$ (i.e. fraction of molecules formed) and therefore $1 - 4\alpha \simeq 1 - 3\alpha$.

SOLUTION:

3.5 points total

$$\begin{aligned}
 T &= 423 \text{ K} \\
 \Delta_{r1}G^\circ &= \Delta_{r1}H^\circ - T * \Delta_{r1}S^\circ \\
 &= -160.8 \text{ kJ/mol} - (423 \text{ K} * -410.5 \text{ J/molK}) \\
 &= 12.8 \text{ kJ/mol} \\
 K &= \exp\left(-\frac{\Delta_{r1}G^\circ}{RT}\right) = 0.026 \\
 K &= \frac{[p(\text{Ni}(\text{CO})_4)/p^\circ]}{[p(\text{CO})/p^\circ]^4} = \frac{x(\text{Ni}(\text{CO})_4)}{x(\text{CO})^4} \\
 x(\text{Ni}(\text{CO})_4) &= \alpha/(1 - 3\alpha) \\
 x(\text{CO}) &= (1 - 4\alpha)/(1 - 3\alpha) \\
 \alpha &= K/(1 + 4K) = 0.0236 \\
 x(\text{Ni}(\text{CO})_4) &= 2.54 \%
 \end{aligned}$$

0.5 points for each (T excluded)

4.5 Using the provided thermodynamic data, report the range of possible temperatures for which the formation of $\text{Ni}(\text{CO})_4$ (g) is both favorable and more favorable than the formation of $\text{Ni}(\text{CO})_4$ (l).

SOLUTION:

2.0 points total

Upper limit at $\Delta_{r1}G^\circ = 0$ (decomposition of gaseous $\text{Ni}(\text{CO})_4$):

$$T_{upper} = \frac{\Delta_{r1}H^\circ}{\Delta_{r1}S^\circ} = 392 \text{ K}$$

Lower limit at $\Delta_{r1-r2}G^\circ = 0$ (evaporation of liquid $\text{Ni}(\text{CO})_4$):

$$T_{lower} = \frac{\Delta_{r1-r2}H^\circ}{\Delta_{r1-r2}S^\circ} = 310 \text{ K}$$

0.5 points for each correctly identified limit
0.5 points for each correctly calculated limit

4.6 Suggest a sequence of steps to obtain pure metallic nickel from impure metallic nickel.

SOLUTION:

0.5 points total

1) Form (or distill) gaseous complex withing temperature range: $T = 310 - -392 \text{ K}$ 2) Decompose complex above upper temperature limit: $T > 392 \text{ K}$

0.25 points for each

Table 1: Thermodynamic data for standard pressure $p^\circ = 1.00 \text{ bar}$.

Compound	State	$\Delta_f H^\circ / \text{kJmol}^{-1}$	$\Delta_f S^\circ / \text{Jmol}^{-1}\text{K}^{-1}$
CO_2	(g)	-393.5	213.6
CO	(g)	-110.5	197.9
Ni	(g)	0.00	29.90
Ni	(l)	17.48	41.49
Ni	(g)	429.7	182.2
$\text{Ni}(\text{CO})_4$	(l)	-632.9	313.9
$\text{Ni}(\text{CO})_4$	(g)	-602.8	411.0
NiS	(s)	-131.38	71.96
S	(s)	0.00	31.90
S	(g)	279.0	167.7

PROBLEM 5 - DANGER UNDERGROUND

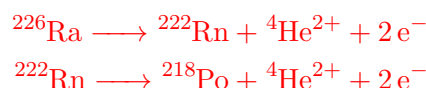
7.0 POINTS

Radon-222 is a radioactive noble gas with a rather short half-life. It occurs naturally in granite soil as decomposition product in the “uranium series”, the $4n+2$ decay chain of uranium-238. Being a gas, radon quickly diffuses upwards from the soil into the atmosphere, gets diluted and is no longer of much concern. However, if it accumulates in caves or cellars, it can pose a serious problem being the second most likely reason for lung cancer in Switzerland. In early 2018, the Swiss federal government has lowered the legal maximum concentration to 300 Bq/m^3 . You have been tasked to calculate the expected radioactivity due to radon-222 in a cellar and compare it to the new legal limit. The cellar has a length of 4.0 m, width of 3.0 m and height of 2.2 m. The half-lives of radium-226 and radon-222 are $t_{1/2,Ra} = 1602$ years and $t_{1/2,Rn} = 3.82$ days, respectively. On average, there are 1.0 g radium-226 near the surface in each 2.6 km^2 soil.

5.1 Write the chemical equations for the alpha decays producing and consuming radon-222.

SOLUTION:

1.0 points total



0.5 points for each

5.2 Write the rate laws for the amounts of Ra, Rn and Po in the cellar. Assume polonium-218 to be stable.

SOLUTION:

1.5 points total

$$\begin{aligned} \frac{dn_{Ra}}{dt} &= -k_{Ra} * n_{Ra} \\ \frac{dn_{Rn}}{dt} &= +k_{Ra} * n_{Ra} - k_{Rn} * n_{Rn} \\ \frac{dn_{Po}}{dt} &= +k_{Rn} * n_{Rn} \end{aligned}$$

0.5 points for each

The integrated form of n_{Ra} and n_{Rn} can be formulated as:

$$\begin{aligned} n_{Ra}(t) &= n_{Ra}(0) * \exp(-k_{Ra} * t) \\ n_{Rn}(t) &= n_{Rn}(0) * \frac{k_{Ra}}{k_{Ra} - k_{Rn}} * [\exp(-k_{Ra} * t) - \exp(-k_{Rn} * t)] \end{aligned}$$

where $n_{Ra}(0)$ and $n_{Rn}(0) = 0$ denotes the initial amounts of radium and radon at a point in time $t = 0$ at which the whole air in the cellar has been renewed.

5.3 Using the integrated rate laws, derive the expression for $n_{Po}(t)$.

SOLUTION:

1.0 points total

$$\begin{aligned} n_{Po}(t) &= n_{Ra}(0) - n_{Ra}(t) - n_{Rn}(t) \\ n_{Po}(t) &= n_{Ra}(0) * \left(1 - \exp(-k_{Ra} * t) - \frac{k_{Ra}}{k_{Ra} - k_{Rn}} [\exp(-k_{Ra} * t) - \exp(-k_{Rn} * t)] \right) \end{aligned}$$

0.5 points for each

5.4 Based on the provided data, the equations describe a steady state for n_{Rn} which is reached after one month ($t = 30$ d). What is the steady state concentration of radon-222 in the cellar in mol/m^3 ?

SOLUTION:

2.0 points total

$$\begin{aligned}
 V &= L * W * H = 4.0 \text{ m} * 3.0 \text{ m} * 2.2 \text{ m} = 26.4 \text{ m}^3 \\
 n_{Rn}(0) &= \frac{1.0 \text{ g}}{2.6 \times 10^6 \text{ m}^2} * 4.0 \text{ m} * 3.0 \text{ m} / 226 \text{ g/mol} = 2.04 \times 10^{-8} \text{ mol} \\
 n_{Rn}(t) &= n_{Rn}(0) * \frac{k_{Ra}}{k_{Ra} - k_{Rn}} * [\exp(-k_{Ra} * t) - \exp(-k_{Rn} * t)] \\
 &= 2.04 \times 10^{-8} \text{ mol} * \frac{\frac{\ln(2)}{584730 \text{ d}}}{\frac{\ln(2)}{584730 \text{ d}} - \frac{\ln(2)}{3.82 \text{ d}}} * \left[\exp\left(-\frac{\ln(2)}{584730 \text{ d}} * 30 \text{ d}\right) - \exp\left(-\frac{\ln(2)}{3.82 \text{ d}} * 30 \text{ d}\right) \right] \\
 &= 1.33 \times 10^{-13} \text{ mol} \\
 c_{Rn}(t) &= \frac{n_{Rn}(t)}{V} = \frac{1.33 \times 10^{-13} \text{ mol}}{26.4 \text{ m}^3} = 1.33 \times 10^{-13} \text{ mol}/\text{m}^3
 \end{aligned}$$

0.5 points for each

5.5 One becquerel ($1 \text{ Bq} = 1 \text{ s}^{-1}$) is defined as the radioactivity of a quantity of material in which one nucleus decays per second. The radioactivity of a species i can be calculated using: $A_i = n_i * k_i * N_A$. Is the steady state activity due to radon-222 above the legal maximum? If so by what factor?

SOLUTION:

1.0 points total

$$\begin{aligned}
 A_{Rn}(t) &= n_{Rn}(t) * k_{Rn} * N_A = 1.33 \times 10^{-13} \text{ mol} * \frac{\ln(2)}{3.3 \times 10^5 \text{ s}} * 6.022 \times 10^{23} \text{ mol}^{-1} \\
 &= 1.69 \times 10^5 \text{ Bq}
 \end{aligned}$$

0.5 points for $A_{Rn}(t)$

0.5 points for exceeded by factor 21

5.6 How could you lower the radioactive exposure in the cellar be lower? Give two possible measures.

SOLUTION:

0.5 points total

- Ventilate permanently (by leaving windows open)
- Ventilate frequently
- Fix fissures in floor and walls to lower radon influx
- Use a filter to trap radioactive dust (polonium-218 still decays!)
- ...

0.25 points for each

PROBLEM 6 - WATER SPLITTING

8.5 POINTS

Water splitting is the chemical reaction in which water is broken down into oxygen and hydrogen. Efficient and economical photochemical water splitting would be a technological breakthrough that could underpin a hydrogen economy. Electrolysis is a convenient way to split water.

6.1 Copy the scheme in Fig ?? to your answer sheet. Label the electrodes in your sketch. Write down which half-reactions can occur if a sufficiently large voltage is applied. Indicate which gas evolves at anode and cathode.

SOLUTION:

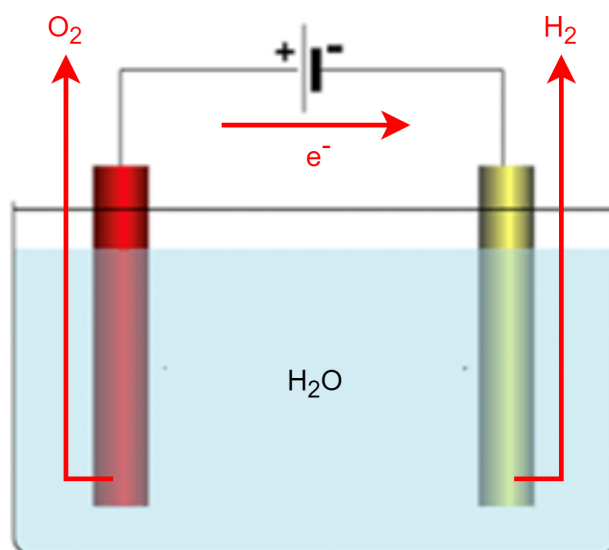
1.0 points total



OR



OR



2 x 0.25 points for equations
no points for equations with both H^+ and OH^-
0.5 points for gas evolution in figure

6.2 Calculate the voltage required for the splitting of water to occur at standard conditions ($pH = 0.0$).

SOLUTION:

0.5 points total

$$\Delta E^\circ = E_{red}^\circ + E_{ox}^\circ = 0.00\text{ V} + 1.23\text{ V} = 1.23\text{ V}$$

no points for 0.40 V or 0.83 V

6.3 Briefly explain what would happen if the electrodes were made of silver.

SOLUTION:

1.0 points total

A silver anode would be oxidized and Ag^+ would go into solution.
Nothing would happen to a silver cathode.

0.5 points for each

6.4 Experimentally, it is observed that a significant overpotential is necessary. What factors could determine the extent of overpotential?

SOLUTION:

1.5 points max

Temperature, electrolyte and their concentration (incl. pH), electrode material, surface condition of the electrodes, current density, ...

0.5 points for each

6.5 How does the voltage of water splitting depend on pH?

SOLUTION:

1.0 points

It does not since an equal number of H^+ ions are produced and consumed by both half-reactions respectively. The concentration dependency therefore cancels in the Nernst equation.

6.6 Because a student disposed of his chemicals improperly, a new water sample is contaminated with copper(I) iodide. The concentration of CuI is 0.05 mol/L . Calculate the potentials of the two newly added half-reactions and explain what overall reaction will initially take place.

SOLUTION:

2.0 points total

$$\begin{aligned}
 \text{Cu}^+ : E_{red} &= E_{red}^\circ + \frac{RT}{zF} \ln \left(\frac{c_{ox}}{c_{red}} \right) \\
 &= 0.52 \text{ V} + \frac{8.3145 \text{ J/molK} * 298 \text{ K}}{1 * 96485 \text{ C/mol}} \ln ([\text{Cu}^+]) \\
 &= 0.52 \text{ V} + 0.059 \text{ V} \log (0.05) \\
 &= 0.443 \text{ V} \\
 \text{I}^- : E_{ox} &= E_{ox}^\circ - \frac{RT}{zF} \ln \left(\frac{c_{ox}}{c_{red}} \right) \\
 &= -0.54 \text{ V} - \frac{8.3145 \text{ J/molK} * 298 \text{ K}}{2 * 96485 \text{ C/mol}} \ln \left(\frac{1}{[\text{I}^-]^2} \right) \\
 &= -0.54 \text{ V} - \frac{0.059 \text{ V}}{2} \log \left(\frac{1}{0.05^2} \right) \\
 &= -0.617 \text{ V} \\
 \text{overall : } E_{tot} &= E_{red} + E_{ox} = -0.174 \text{ V}
 \end{aligned}$$

0.5 points for each correct half-reaction
0.5 points for each correct potential thereof

6.7 For the sample in 6.6, water splitting occurs after 12.3 seconds. The volume of the water sample was 50.0 mL. Calculate the needed current assuming that it is constant. Explain what you expect if this current runs through a too thin wire.

SOLUTION:

1.5 points total

$$n(\text{CuI}) = c * V = 0.05 \text{ M} * 0.050 \text{ L} = 0.0025 \text{ mol}$$

$$I = \frac{Q}{t} = \frac{n * F}{t} = \frac{241 \text{ C}}{12.3 \text{ s}} = 19.6 \text{ A}$$

1.0 points for calculation

0.5 points for resistive heating => wire burning through

Table 2: Reduction potentials at standard conditions.

Reduced species	\rightleftharpoons	Oxidized species	$+z * e^-$	E° / V
Li (s)	\rightleftharpoons	$\text{Li}^+ \text{ (aq)}$	$+1 * e^-$	-3.04
Na (s)	\rightleftharpoons	$\text{Na}^+ \text{ (aq)}$	$+1 * e^-$	-2.71
Al (s)	\rightleftharpoons	$\text{Al}^{3+} \text{ (aq)}$	$+3 * e^-$	-1.66
Zn (s)	\rightleftharpoons	$\text{Zn}^{2+} \text{ (aq)}$	$+2 * e^-$	-0.76
$\text{S}^{2-} \text{ (aq)}$	\rightleftharpoons	S (s)	$+2 * e^-$	-0.51
Fe (s)	\rightleftharpoons	$\text{Fe}^{2+} \text{ (aq)}$	$+2 * e^-$	-0.41
Ni (s)	\rightleftharpoons	$\text{Ni}^{2+} \text{ (aq)}$	$+2 * e^-$	-0.23
Pb (s)	\rightleftharpoons	$\text{Pb}^{2+} \text{ (aq)}$	$+2 * e^-$	-0.13
$\text{H}_2 \text{ (g)} + 2 \text{ H}_2\text{O (l)}$	\rightleftharpoons	$2 \text{ H}_3\text{O}^+ \text{ (aq)}$	$+2 * e^-$	-0.00
Cu (s)	\rightleftharpoons	$\text{Cu}^{2+} \text{ (aq)}$	$+2 * e^-$	+0.35
$4 \text{ OH}^- \text{ (aq)}$	\rightleftharpoons	$\text{O}_2 \text{ (g)} + 2 \text{ H}_2\text{O (l)}$	$+4 * e^-$	+0.40
Cu (s)	\rightleftharpoons	$\text{Cu}^+ \text{ (aq)}$	$+1 * e^-$	+0.52
$2 \text{ I}^- \text{ (aq)}$	\rightleftharpoons	$\text{I}_2 \text{ (s)}$	$+2 * e^-$	+0.54
Ag (s)	\rightleftharpoons	$\text{Ag}^+ \text{ (aq)}$	$+1 * e^-$	+0.80
Hg (l)	\rightleftharpoons	$\text{Hg}^{2+} \text{ (aq)}$	$+2 * e^-$	+0.85
$2 \text{ Br}^- \text{ (aq)}$	\rightleftharpoons	$\text{Br}_2 \text{ (l)}$	$+2 * e^-$	+1.07
Pt (s)	\rightleftharpoons	$\text{Pt}^{2+} \text{ (aq)}$	$+2 * e^-$	+1.20
$6 \text{ H}_2\text{O (l)}$	\rightleftharpoons	$\text{O}_2 \text{ (g)} + 4 \text{ H}_3\text{O}^+$	$+4 * e^-$	+1.23
$2 \text{ Cl}^- \text{ (aq)}$	\rightleftharpoons	$\text{Cl}_2 \text{ (g)}$	$+2 * e^-$	+1.36
Au (s)	\rightleftharpoons	$\text{Au}^{3+} \text{ (aq)}$	$+3 * e^-$	+1.41
$2 \text{ F}^- \text{ (aq)}$	\rightleftharpoons	$\text{F}_2 \text{ (g)}$	$+2 * e^-$	+2.87

PROBLEM 7 - VSEPR AND SULFUR

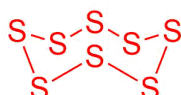
9.5 POINTS

Since the nineteenth century, almost all elemental sulfur is produced as a byproduct of removing sulfur-containing contaminants from natural gas and petroleum. The greatest commercial use of the element is the production of sulfuric acid for sulfate and phosphate fertilizers, and other chemical processes. Sulfur is also an essential element for all life, most often in the form of organosulfur compounds such as cysteine, methionine, biotin and thiamine.

7.1 Draw the structure of elemental sulfur under standard conditions.

SOLUTION:

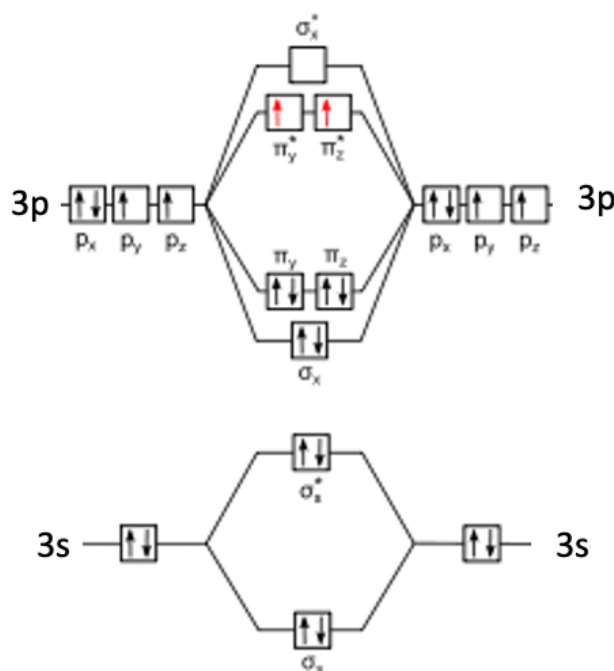
0.5 points total



7.2 Copy the molecular orbital diagram for S_2 to your answersheet and fill in the valence electrons. Is disulfur paramagnetic or diamagnetic?

SOLUTION:

1.0 points total



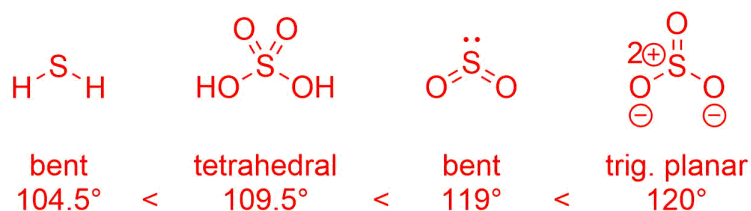
0.5 points for correct electron filling
0.5 points for paramagnetic

7.3 Draw and state the geometry of the following compounds according to the VSEPR model. Arrange the compounds in increasing order of their bond angles and state the value of the bond angles for II and IV.

I. SO_2 II. SO_3 III. H_2S IV. H_2SO_4

SOLUTION:

2.0 points total



0.25 points for each structures

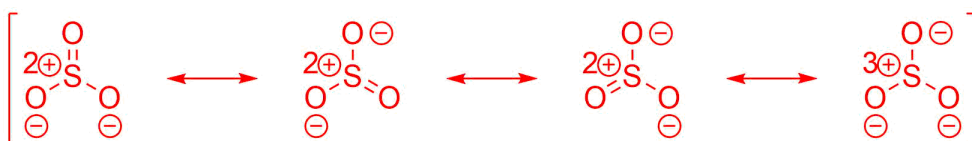
0.25 points for 109.5° and 120°

0.5 points for correct order with respect to bond angle

7.4 Draw the four resonance structures of SO_3 .

SOLUTION:

1.0 points total



0.25 points for each structure

-0.25 points for missing brackets

7.5 There are several methods for producing sulfur dioxide. Two of those methods are described by the reaction equations below. Complete these equations.

SOLUTION:

2.0 points total



OR



OR

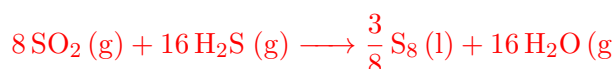


1.0 points for each

7.6 Sulfur dioxide can react with hydrogen sulfide in a comproportionation reaction at 250 °C. Write a balanced reaction equation for this reaction. Under atmospheric pressure, sulfur melts at 115 °C.

SOLUTION:

1.0 points total



OR



7.7 Hydrogen sulfide interacts explosively with fluorine gas being converted into hydrogen fluoride and sulfur hexafluoride. Draw the geometry of sulfur hexafluoride have according to the VSEPR model. How large are the bond angles? How could you separate sulfur hexafluoride from the resulting mixture?

SOLUTION:

1.0 points total



octahedral
90°

Separation by passing through a gas wash bottle with water

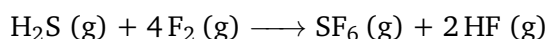
OR

Separation by gaseous diffusion (uranium enrichment)

0.5 for structure

0.5 for any feasible separation method

7.8 The reaction equation to this explosion is given below. State the oxidation numbers for all elements in all compounds.



SOLUTION:

1.0 points total

H_2S , H : + I

H_2S , S : - II

F_2 , F : + 0

SF_6 , S : + VI

SF_6 , F : - I

HF, H : + I

HF, F : - I

0.25 for each correct compound

PROBLEM 8 - IDEAL GAS LAWS AND VAN DER WAALS EQUATION**9.0 POINTS**

The ideal gas law was first stated by Benoît Paul Émile Clapeyron in 1834 as a combination of the empirical Boyle's law, Charles's law, Avogadro's law, and Gay-Lussac's law. It can also be derived for non-interacting point masses:

8.1 Suppose a gas consists of N particles in a cube of edge length a . Furthermore, suppose that a particle moves back and forth at the average speed v on the shortest distance between two opposite walls without collating with other particles. Specify the average change of momentum per time that this particle experiences upon colliding with a wall as a function of the mass m of the particle, its velocity v , and the side length a of the cube.

SOLUTION:**0.5 points total**

$$\frac{\Delta p}{\Delta t} = \frac{2mv}{2a/v} = m * v^2 / a$$

8.2 Provide a formula for the pressure exerted by all particles on the vessel wall, bearing in mind that, on average, one third of the particles ($N/3$) move in a certain direction.

SOLUTION:**0.5 points total**

$$P = \frac{F}{A} = \frac{N}{3} \frac{mv^2}{a^3}$$

8.3 Derive a relationship between the temperature of the gas and the kinetic energy of the particles by comparing the equation obtained in question 8.2 with the known form of the ideal gas.

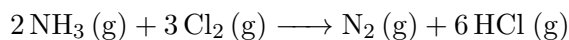
SOLUTION:**1.0 points total**

$$\begin{aligned} pV &= \frac{1}{3} N m v^2 \\ pV &= n \frac{2}{3} N_A E_{kin} \\ T &= \frac{2}{3} \frac{N_A}{R} E_{kin} \end{aligned}$$

1.0 point for the last line

In many cases, the ideal gas law is sufficiently accurate to describe a gaseous mixture:

8.4 In a cylinder with a piston, a mixture of 0.70 L NH₃ (g) and 0.85 L Cl₂ (g) are reacted at atmospheric pressure and 25 °C according to the irreversible reaction:



Calculate the amount of all substances present at the end of the reaction.

SOLUTION:

2.0 points total

$$n_f(\text{Cl}_2) = 0.0 \text{ mmol (limiting)}$$

$$n_f(\text{NH}_3) = \frac{p * (V_i(\text{NH}_3) - \frac{2}{3} * V_i(\text{Cl}_2))}{RT} = \frac{101\,325 \text{ Pa} * (0.70 \times 10^{-3} \text{ m}^3 - \frac{2}{3} * 0.85 \times 10^{-3} \text{ m}^3)}{8.3145 \text{ J/molK} \cdot 298 \text{ K}}$$

$$= 5.5 \text{ mmol}$$

$$n_f(\text{N}_2) = \frac{p * \frac{1}{3} * V_i(\text{Cl}_2)}{RT} = \frac{101\,325 \text{ Pa} * \frac{1}{3} * 0.85 \times 10^{-3} \text{ m}^3}{8.3145 \text{ J/molK} \cdot 298 \text{ K}}$$

$$= 11.6 \text{ mmol}$$

$$n_f(\text{HCl}) = \frac{p * 2 * V_i(\text{Cl}_2)}{RT} = \frac{101\,325 \text{ Pa} * 2 * 0.85 \times 10^{-3} \text{ m}^3}{8.3145 \text{ J/molK} \cdot 298 \text{ K}}$$

$$= 69.5 \text{ mmol}$$

0.5 point for each

8.5 After completion, the mixture is then heated to 351 K while the piston's position is fixed. Calculate the final total pressure of the gas.

SOLUTION:

0.5 points total

$$p_f = \frac{T_f}{T_i} * p_i = \frac{351 \text{ K}}{298 \text{ K}} * 1.013 \text{ bar} = 1.194 \text{ bar}$$

The van der Waals (vdW) equation is a modification of the ideal gas equation. It is often stated as:

$$\left(p + \frac{n^2 a}{V^2}\right) * (V - nb) = nRT$$

where a and b are gas-specific constants. Solve the following tasks using the vdW equation:

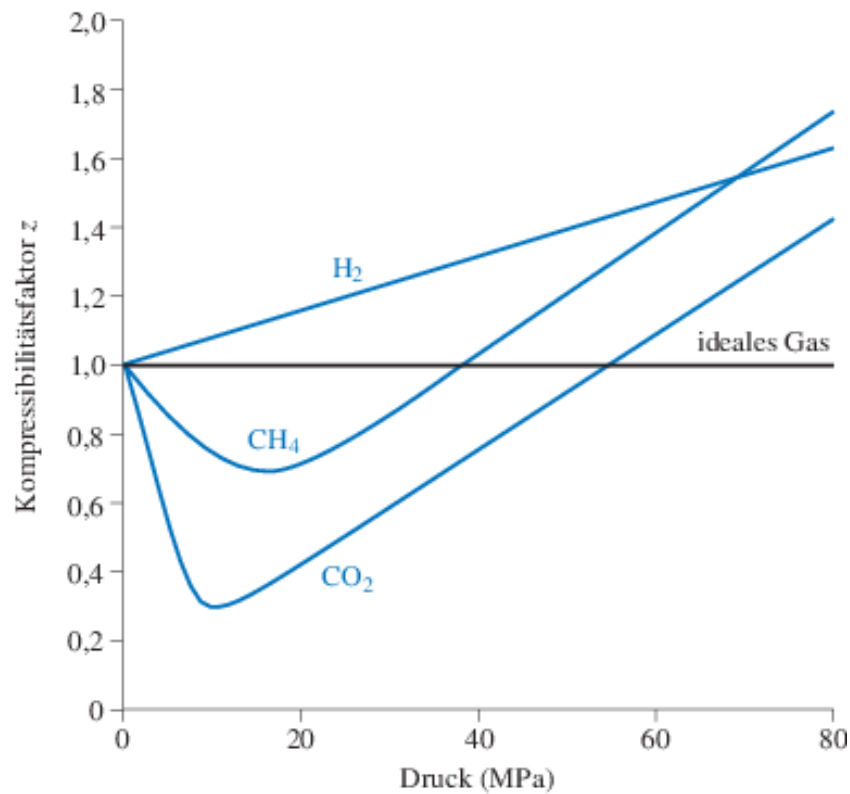
8.6 Provide a physical interpretation of the gas-specific correction terms of the vdW equation.

SOLUTION:

1.0 points total

- $\frac{n^2 a}{V^2}$: average intermolecular interaction
- nb : total volume of all particles

0.5 point for each



8.7 Use your explanations from question 8.7 to explain the following figure. The compressibility factor z is defined by the ratio of pV to RT .

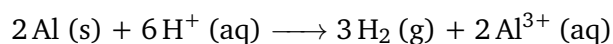
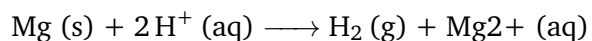
SOLUTION:

1.0 points total

- $\frac{n^2 a}{V^2}$ causes an increase in z
- $\frac{n^2 a}{V^2}$ dominates at high pressure
- nb has the opposite effect
- nb dominates at low pressure

0.25 point for each

8.8 Most metals can be oxidized by acids, for example:



12.17 g of an Mg/Al alloy reacts with an excess of hydrochloric acid to form 13.68 L H_2 gas at standard conditions. For H_2 , $a = 24.7 \text{ kPa L}^2 \text{ mol}^{-2}$ and b is negligible. How much aluminum does the alloy contain?

SOLUTION:

2.5 points total

$$pV + \frac{n^2 a}{V} = nRT$$

$$n = \frac{-RT + \sqrt{(RT)^2 - 4ap}}{2a/V} = 0.56 \text{ mol}$$

0.056 mol H_2 from 1.00 g Al

0.041 mol H_2 from 1.00 g Mg

$$0.56 \text{ mol} = x * 0.056 \text{ mol} + (12.17 \text{ g} - x) * 0.041 \text{ mol}$$

$$x = 4.1 \text{ g}$$

0.5 point for each
Except 0.25 point for equivalence H_2 evolution

PROBLEM 9 - ORGANIC SUBSTITUTION

14.0 POINTS

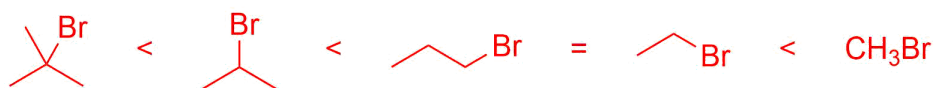
Substitution reactions are of prime importance in organic chemistry since they allow for easy interconversion of functional groups and elaborate synthesis strategies when involved with protecting groups.

9.1 Draw and order the following halogen alkanes in terms of increasing reaction rate when reacted in a S_N2 reaction:

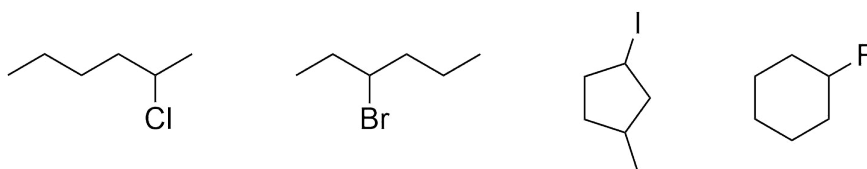
1-bromopropane, 2-bromopropane, bromomethane, 2-bromo-2-methylpropane, bromoethane

SOLUTION:

1.0 points total

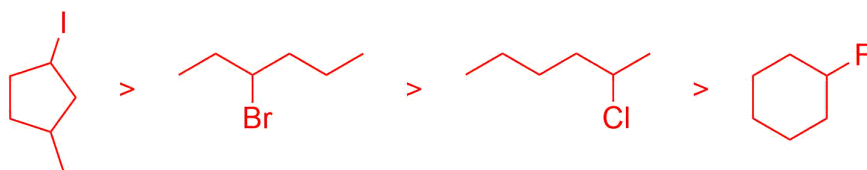


9.2 Order the following halogen alkanes in terms of decreasing reactivity in S_N2 reactions:

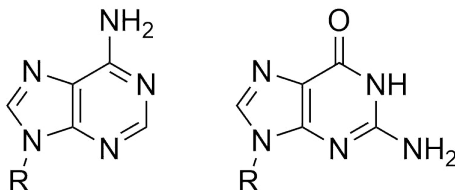


SOLUTION:

1.0 points total

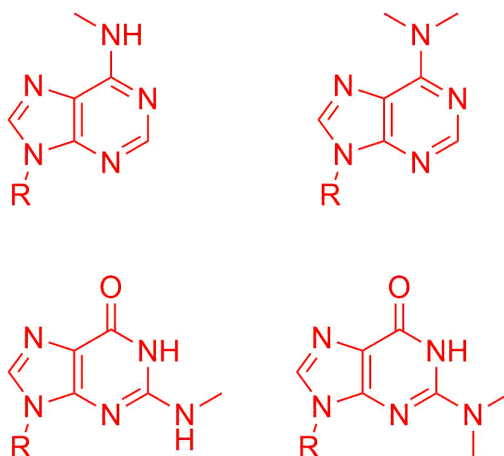


9.3 DNA-methylation is the most common biological process used by cells to change the activity of DNA. Below, you are given the structure of both purine DNA bases. Draw the two most likely methylation products for both bases.



SOLUTION:

1.0 points total

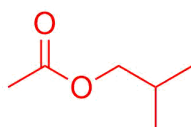


0.25 point for each

9.4 Draw the product of the reaction of $(\text{CH}_3)_3\text{CCH}_2\text{Cl}$ with acetic acid. The reaction could also be carried out with trifluoroacetic acid instead of acetic acid. Explain which reaction is faster.

SOLUTION:

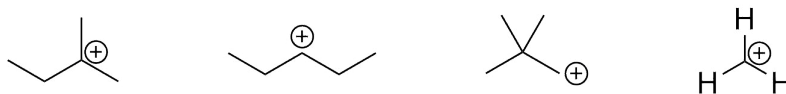
2.0 points total



TFA reacts slower due to the inductive effect of fluorine (oxygen atoms are less nucleophilic)

1.0 point for structure
1.0 point for explanation

9.5 Order the following carbocations in terms of increasing stability.

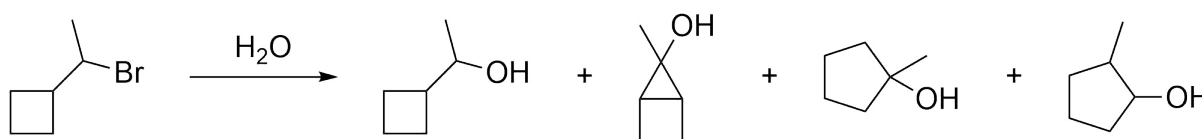


SOLUTION:

1.0 points total



9.6 Choose the main product of the following S_N1 reaction and explain your choice.



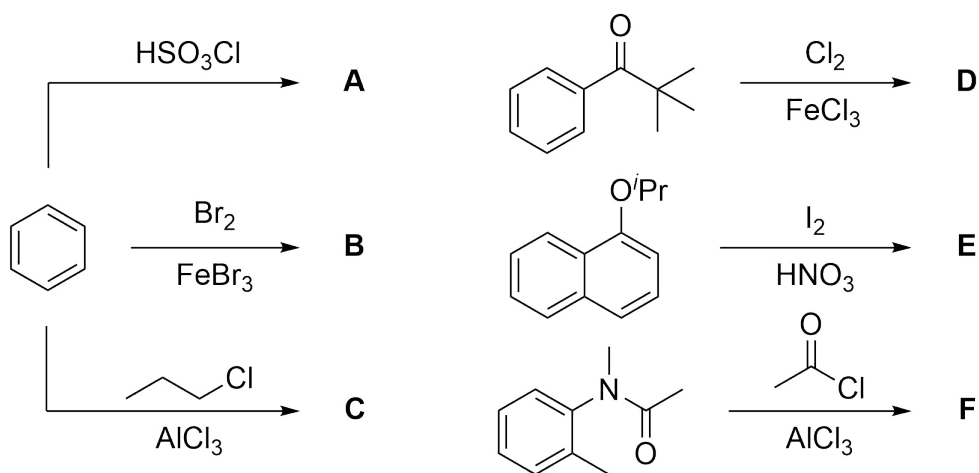
SOLUTION:

2.0 points total

1-Methylcyclopentanol. Ring expansion due to strain release and relative stability of carbocations.

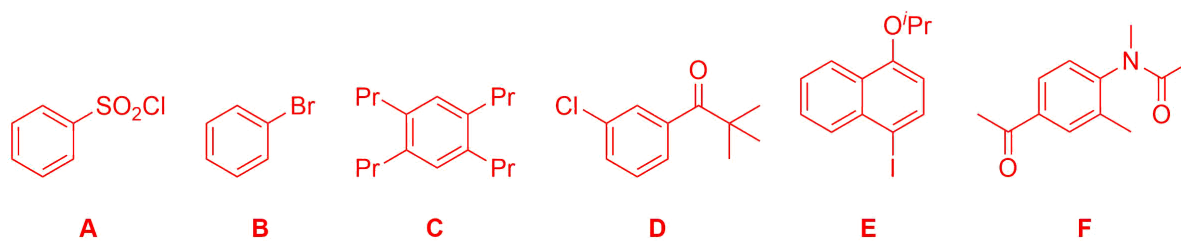
1.0 point for structure
1.0 point for explanation

9.7 Give the main products A – F.



SOLUTION:

6.0 points total



1.0 point for each

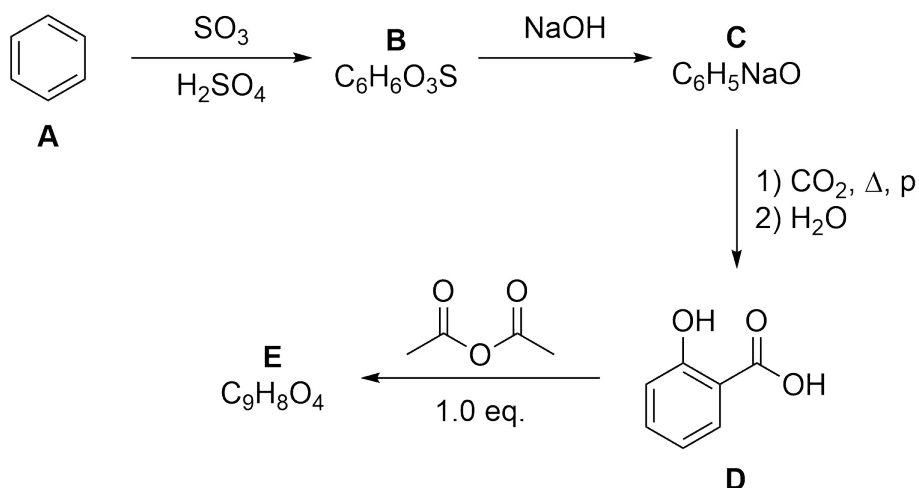
PROBLEM 10 - RELIEVE THE PAIN

9.0 POINTS

Aspirin and paracetamol are among the most commonly used medications to reduce pain and fever. The natural precursor to aspirin, salicylic acid, has been known for over 2400 years but widespread use of aspirin was only possible after the development of its industrial chemical synthesis in 1897. Paracetamol has no natural precursor and was first synthesized in 1877. Still today, their mechanisms of action have not been completely elucidated but they most likely act by inhibiting COX-1 and COX-2 enzymes in the brain.

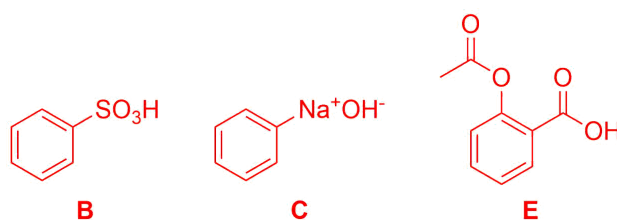
All industrial syntheses for both molecules start from benzene. In the synthesis of aspirin, benzene **A** is sulfonated by SO_3 and H_2SO_4 . Benzenesulfonic acid **B** is then converted to sodium phenolate **C** by NaOH . In a Kolbe-Schmitt reaction at high temperature and high pressure, **C** is reacted with CO_2 yielding salicylic acid **D**. In the final step, **D** is acylated by acetic anhydride to give aspirin **E**.

10.1 Draw the structure of molecules **B**, **C** and **E**.



SOLUTION:

3.0 points total



1.0 point for each

10.2 Assign the reaction conditions 1. – 7. to steps I. – VII.

SOLUTION:
See below.

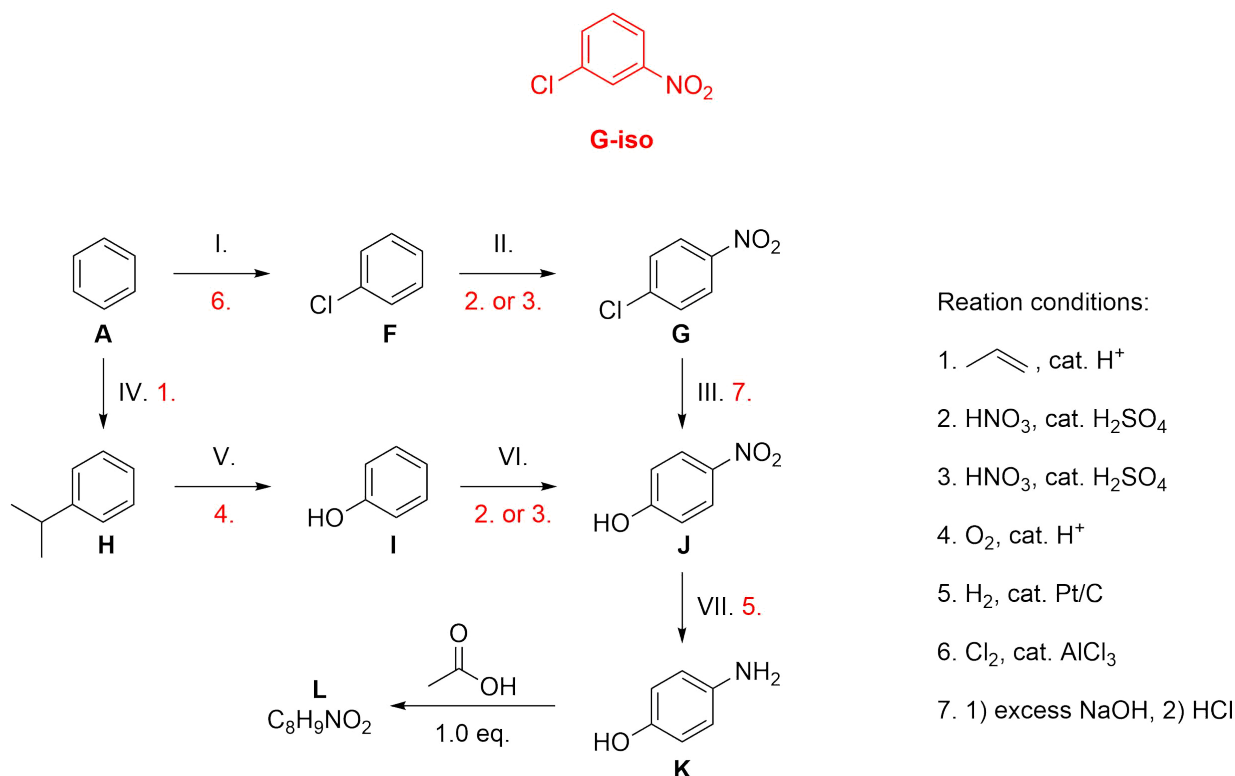
3.5 points total

0.5 point for each

10.3 Which product is formed if you change the order of steps I. and II.? Draw the structure of the new isomer **G-iso**.

SOLUTION:

1.0 points total



10.4 Draw the structure of product **L**. Which product is more acidic, **E** or **L**?

SOLUTION:

1.5 points total



1.0 point for structure
0.5 points for E begin more acidic