

## THEORETICAL PROBLEMS

### Problem 1

8 points

The stereoregular polymerization of unsaturated hydrocarbons is usually considered as one of the most important reactions in industrial organic chemistry. The salts of big nonlinear cations carrying a sufficiently high charge to attack the electron density distributed along the  $\pi$ -bonds of the olefin molecules are usually used as the catalysts in these processes. Chloroaluminate anions (like  $\text{AlCl}_4^-$ ) are normally used as they possess a highly delocalized negative charge. The need to develop new catalysts of this kind has urged chemists to study the interaction in the system **A** - **B**, where **A** = Te (cryst.) and **B** =  $(\text{TeCl}_4 + 4\text{AlCl}_3)$ . The second component **B** was considered as an analog of Te(IV)-chloroaluminate,  $\text{Te}[\text{AlCl}_4]_4$ , which, however, cannot be isolated as an individual compound. It was found out that the interaction of the components **A** and **B** can lead to the formation of three new compounds (**I**, **II** and **III**) in the systems containing initially 77.8, 87.5 and 91.7 mol.% of the component **A** respectively. It was also noticed that while in the case of compounds **II** and **III** no side products were formed, the formation of compound **I** was accompanied by the evolution of 1 mole of volatile  $\text{TeCl}_4$  per two moles of **I**.

Both compounds have a pinkish-purple color and both dissociate into three ions as the conductivity studies in molten  $\text{NaAlCl}_4$  showed. From cryoscopic measurements in molten  $\text{NaAlCl}_4$  the molecular weights of these compounds were calculated to be  $1126 \pm 43$  g/mole and  $867 \pm 48$  g/mole for **I** and **II** respectively. In the IR spectra of both compounds there is only one band observed which can be attributed to a vibration mode of a bond formed by a Te atom. This band lies at  $133 \text{ cm}^{-1}$  and is therefore so low in energy that this bond undoubtedly is a kind of Te—Te interaction. The  $^{27}\text{Al}$  NMR data for the complexes **I** and **II** show that in each compound there is only one type of tetrahedrally coordinated aluminum. However, the observed chemical shifts of aluminum for the compounds **I** and **II** are different, thus showing that the Al atoms are in different environments.

- Determine the minimum atomic ratio Te:Al:Cl for the complexes **I**, **II** and **III**.
- Write the molecular formulae of the compounds **I** and **II**.
- Write the formulae of the anions and cations in compounds **I** and **II**.
- Draw stereochemical formulae of cations and anions in the structures of **I** and **II** assuming that the cations in **I** and **II** are examples of inorganic aromatic systems.
- Which compound has the higher thermal stability, **I** or **II**, taking into account that  $\text{AlCl}_3$  is an extremely volatile compound.
- If one of the compounds **I** or **II** can be transformed into the other by heating, write the corresponding reaction equation.

### Problem 2

10 points

The detection limit is one of the basic parameters in quantitative analysis of trace amounts of elements. The detection limit is expressed as the least mass of an element which can be determined by a given method with a given accuracy. As an example, we shall consider two methods used for the determination of microscopic amounts of bismuth. In 1927, the German chemist Bergh suggested that bismuth could be precipitated as the insoluble salt: 8-hydroxyquinolinium tetraiodobismuthate  $[\text{C}_9\text{H}_6(\text{OH})\text{NH}][\text{BiI}_4]$ . (molar mass = 862.7 g/mol)

- Draw the structural formulae of the cation and anion of this salt.
  - What is the oxidation state of the Bi atom in this compound?
- Determine the smallest mass of bismuth (in *mg*), which can be reliably determined by the Bergh method, if the smallest mass of precipitate which can be reliably measured is 50.0 *mg*.

As an alternative method for the determination of trace amounts of bismuth, R. Belcher and coworkers from Birmingham developed a multiplicative method. According to this method, a chain of reactions followed by a titration of the final product is carried out. A detailed description follows.

**Step 1.** To a given small amount (about 2 mL) of cold acidified solution containing trace amounts of  $\text{Bi}^{3+}$ , 50 mg of potassium hexathiocyanatochromate(III),  $\text{K}_3[\text{Cr}(\text{SCN})_6]$ , is added in the cold, which leads to the quantitative precipitation of bismuth.

c) Write a balanced equation for this reaction. [Omit spectator ions]

**Step 2.** The precipitate is filtered off, washed by cold water, and treated with 5 mL of a 10% solution of sodium hydrogen carbonate. Upon this treatment the initial precipitate is transformed into another precipitate, oxobismuth carbonate,  $(\text{BiO})_2\text{CO}_3$ , with the liberation of hexathiocyanatochromate(III) ions into solution.

d) Write a balanced equation for this reaction. [Omit spectator ions]

**Step 3.** The filtrate is slightly acidified and transferred to a separatory funnel, after which 0.5 mL of saturated iodine solution in chloroform is added and the mixture is vigorously shaken. Iodine undergoes an oxidation-reduction reaction with the ligand of the complex ion to form products including cyanogen iodide [ICN] and the sulfate ion.

e) Write a balanced equation for this reaction. [Omit spectator ions]

**Step 4.** After 5 minutes, 4 mL of 2 M  $\text{H}_2\text{SO}_4$  solution are added to the mixture. This acidification leads to an oxidation-reduction reaction with the evolution of molecular iodine.

f) Write a balanced equation for this reaction. [Omit spectator ions]

**Step 5.** Iodine is quantitatively extracted by 4 portions of chloroform. The aqueous layer is transferred to a flask, to which 1 mL of bromine water is added, and the mixture is shaken for 5 minutes.

g) Write the balanced equations for the reactions which occurred upon the addition of bromine water [omit spectator ions]. Note that an excess of bromine can react with hydrogen cyanide to give cyanogen bromide,  $\text{BrCN}$ , and with iodide to form  $\text{IO}_3^-$ .

**Step 6.** To eliminate an excess of molecular bromine, 3 mL of 90% methanoic (formic) acid is added to the mixture.

h) Write a balanced equation for this reaction. [Omit spectator ions]

**Step 7.** To this slightly acidic solution, an excess (1.5 g) of potassium iodide is added.

i) Write the balanced equations for the reactions which occurred upon the addition of KI, taking into consideration that iodide reacts with  $\text{BrCN}$  in a similar manner as with ICN to form molecular iodine.

**Step 8.** The resulting solution is titrated by a standard 0.00200 M  $\text{Na}_2\text{S}_2\text{O}_3$  solution. The results thus obtained are used to calculate the content of bismuth in the sample taken for analysis.

j) i) How many moles of thiosulfate are equivalent to 1 mole of bismuth in the initial sample?

ii) What is the least amount of bismuth which can be determined by Belcher's method? Assume that this determination is reliable if no less than 1 mL of standard 0.00200 M  $\text{Na}_2\text{S}_2\text{O}_3$  solution is used.

k) By how many times is this multiplicative method of Belcher more sensitive than Bergh's gravimetric method?

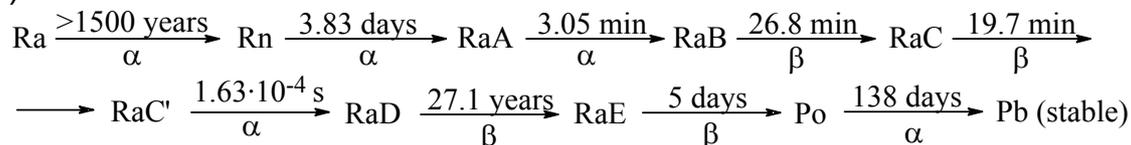
### Problem 3

10 points

In 1908 Rutherford, together with H. Geiger, measured the rate of emission of  $\alpha$ -particles ( $x$ ) by radium (in nature this element is represented by a single nuclide  $^{226}\text{Ra}$ ) and found that 1.00 g of radium emits  $x = 3.42 \cdot 10^{10}$   $\alpha$ -particles per second.

In 1911 Rutherford and the physical chemist B. Boltwood measured the rate of formation of helium from radium. This experiment permitted them to obtain the most accurate value of Avogadro's number available at that time, given that the value of the molar volume of ideal gas was well established. To achieve this goal a sample of radium salt, purified from decay products and containing  $m = 192 \text{ mg}$  of Ra, was put into a device and the volume of the evolved helium was measured. After 83 days ( $t = 83.0 \text{ days}$ ) of the experiment  $6.58 \text{ mm}^3$  of He was collected ( $V_{\text{He}} = 6.58 \text{ mm}^3$  corrected to  $0^\circ\text{C}$  and  $1 \text{ atm}$ ).

To understand the results of this experiment we shall need the kinetic scheme of radioactive decay of Ra which is given below (half-lives are over the arrows, the type of decay is below the arrows).



(RaA -RaE are intermediate products of radon decay).

**a)** Write the first five radioactive decays using a modern notation showing atomic and mass numbers of all nuclei involved.

As a rough first approximation, the half-lives of all radium decay products, except those of RaD and Po, may be assumed to be negligible compared to the time of measurement  $t$ . Using this approximation perform the following calculations.

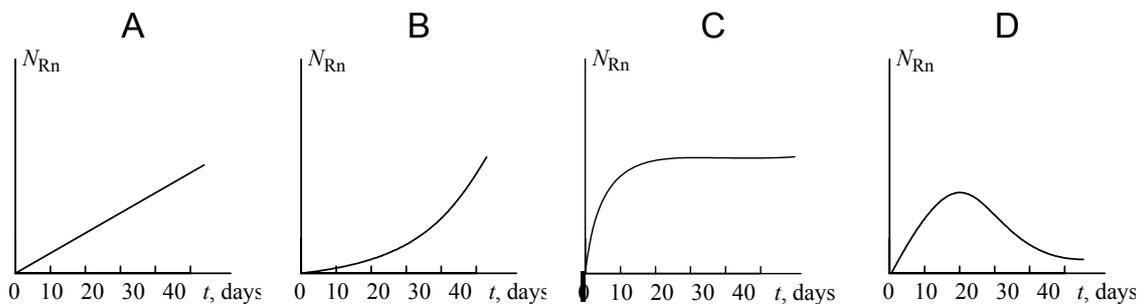
**b) i)** How many helium atoms were formed from each decayed radium atom after 83 days?

ii) How many helium atoms were formed in total during the experiment?

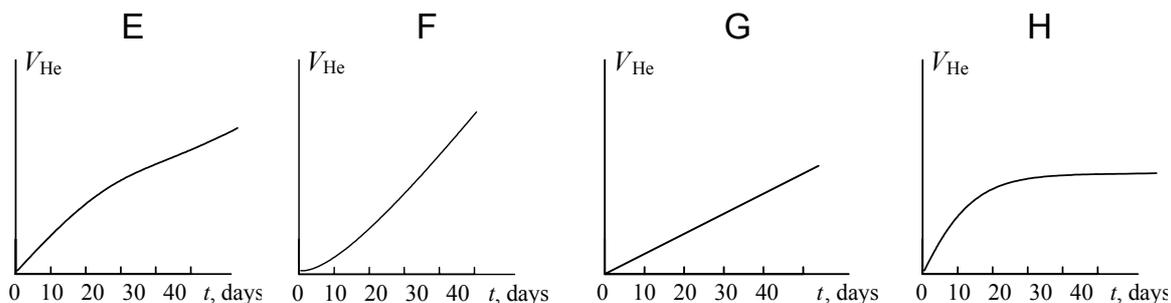
**c)** Calculate an approximate value of Avogadro's number from the above data. Molar volume is  $22.4 \text{ L}$  at  $0^\circ\text{C}$  and  $1 \text{ atm}$ .

For a more accurate computation of Avogadro's number, the half-life of radon ( $t_{1/2}(\text{Rn}) = 3.83 \text{ days}$ ) cannot be neglected, as it is comparable with the duration of experiment  $t$ ; i.e. not all of the radon atoms decayed by the end of the experiment.

**d)** Choose which of the plots given below displays the time dependence of the number  $N_{\text{Rn}}$  of radon atoms in the course of the experiment.



**e)** Choose which of the plots given below shows the time dependence of the volume of helium in the course of the experiment.



**f)** Choose the relation between the decay rate  $k$  of any given nuclide and its half-life  $t_{1/2}$ .

**g)** Using a short kinetic scheme  $\text{Ra} \xrightarrow{k_1} \text{Rn} \xrightarrow{k_2} \text{RaA}$

(where  $k_1$  and  $k_2$  are the rate constants of the corresponding reactions) and the plot which you have selected in question 4, write a relation between the number of radon atoms at the end of experiment  $N'_{Rn}$  and the number of radium atoms  $N_{Ra}$ . b) Evaluate  $N'_{Rn}$  using the rate of radium decay given above ( $x = 3.42 \times 10^{10}$   $\alpha$ -particles per gram of radium per second).

**h)** How many helium atoms could be formed from radon atoms remaining at the end of experiment  $N'_{Rn}$ , if all these atoms had decayed to RaD?

**i)** Using the solutions of the above questions calculate a better approximation to a) the number of helium atoms formed; b) Avogadro's number.

#### Problem 4

##### 8 points

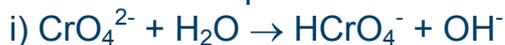
Potassium dichromate is one of the most widely used precipitating reagents. The following equilibria are established in aqueous solutions of Cr(VI).



All other equilibria involving chromium should be ignored. All the activity coefficients are assumed to be 1.

**a)** The ionic product of water  $K_W = 1.0 \times 10^{-14}$ .

Evaluate the equilibrium constants for the following reactions:



**b)** The solubility product of  $\text{BaCrO}_4$   $K_s = 1.2 \times 10^{-10}$ .  $\text{BaCr}_2\text{O}_7$  is very soluble in water.

In what direction will the equilibrium (1b) shift upon the addition of the following reagents to a moderately concentrated aqueous solution of potassium dichromate?

i) KOH

ii)  $\text{BaCl}_2$

iii) HCl

iv)  $\text{H}_2\text{O}$  (consider all the above equilibria)

**c)** Dissociation constant of acetic acid  $K_a = 1.8 \times 10^{-5}$ . Calculate the pH value of the following solutions

i) 0.010 M  $\text{K}_2\text{CrO}_4$

ii) 0.010 M  $\text{K}_2\text{Cr}_2\text{O}_7$

iii) 0.010 M  $\text{K}_2\text{Cr}_2\text{O}_7 + 0.100$  M  $\text{CH}_3\text{COO}$

**d)** Calculate the equilibrium concentrations of the following ions in a solution of 0.010 M  $\text{K}_2\text{Cr}_2\text{O}_7 + 0.100$  M  $\text{CH}_3\text{COOH}$

ii)  $\text{CrO}_4^{2-}$

ii)  $\text{Cr}_2\text{O}_7^{2-}$

#### Problem 5

##### 7 points

Potentiometric and spectrophotometric methods are widely used for the determination of equilibrium concentrations and equilibrium constants in solution. Both methods are frequently used in combination to achieve simultaneous determination of several species.

Acidified aqueous solution I contains a mixture of  $\text{FeSO}_4$  and  $\text{Fe}_2(\text{SO}_4)_3$ , and aqueous solution II contains a mixture of  $\text{K}_4[\text{Fe}(\text{CN})_6]$  and  $\text{K}_3[\text{Fe}(\text{CN})_6]$ . The concentrations of iron-containing species satisfy the relations  $[\text{Fe}^{2+}]_I = [\text{Fe}(\text{CN})_6^{4-}]_{II}$  and  $[\text{Fe}^{3+}]_I = [\text{Fe}(\text{CN})_6^{3-}]_{II}$ . The potential of a platinum electrode immersed into the solution I is 0.652 V (relative to the standard hydrogen electrode), while the potential of a platinum electrode immersed into solution II is 0.242 V (relative to the standard hydrogen electrode). The % transmittance of the solution II measured relative to solution I at 420 nm is 10.7% (optical pathlength  $l = 5.02$  mm). Assume that the complexes  $\text{Fe}(\text{CN})_6^{4-}$ ,  $\text{Fe}^{3+}$  (aq),  $\text{Fe}^{2+}$  (aq), do not absorb light at 420 nm. Molar absorptivity  $\epsilon(\text{Fe}(\text{CN})_6^{3-}) = 1100$  L/mol·cm at this wavelength. The standard reduction potential for  $\text{Fe}^{3+}/\text{Fe}^{2+}$  is 0.771 V. The factor before the decimal logarithm in the Nernst equation is

0.0590 (and before natural logarithm is 0.0256). Assume that all the activity coefficients are equal to 1.

**a)** Write Nernst equations for redox systems of

i) solution I

ii) solution II (in the solution the presence of any forms except cyano-complexes should be ignored)

**b)** What is the unit of the pre-logarithm factor in the Nernst equation?

**c)** Calculate the ratio of the stability constants  $\beta\{\text{Fe}(\text{CN})_6^{3-}\}/\beta\{\text{Fe}(\text{CN})_6^{4-}\}$

**d)** What is the absolute range of variation in the magnitude of the following phys. parameters

i) transmittance  $T$ , %

ii) absorbance  $A$ ?

**f)** Draw a view of plots of concentration dependencies satisfying Lambert-Beer law for

i) absorbance  $A$

ii) transmittance  $T$ , %

iii) molar absorptivity  $\varepsilon$

**g)** Calculate the concentrations of

i)  $\text{Fe}^{3+}$  in solution I

ii)  $\text{Fe}^{2+}$  in solution I

### Problem 6

8 points

Two isomeric hydrocarbons **A** and **B** contain 85.7 % of carbon by mass.

**a)** Write a general formula (not an empirical formula) which satisfies this condition.

Hydrocarbons **A** and **B** possess the following properties: Reaction of each of the compounds with ozone and subsequent treatment of the product with zinc dust in the presence of acid gives a single organic product **C**. The oxidation of compound **C** gives a single product, the carboxylic acid **D**. According to its spectral data all hydrogen atoms in compound **D** except the hydrogen on the carboxyl group are contained in methyl groups. The density of vapors of **D** corrected to normal conditions is 9.1 g/L;  $V_M = 22.4$  L at  $0^\circ\text{C}$ , 1 atm).

When reacted with cold neutral aqueous potassium permanganate, compound **A** is more reactive than compound **B**. In this reaction, a single compound, **F**, is formed from **A** and a 1:1 mixture of isomers **G1** and **G2** is formed from **B**.

**All reactions must be written as a balanced equation. No mechanisms are required. Additional sheets of the report form are available from the supervisor if necessary.**

**b)** Draw the structural formulae of the compound **D** both in aqueous solution and in the vapor phase.

**c)** Write the structural formula of compound **C**.

**d)** Draw the structural formulae of isomers **A** and **B**.

**e)** i) write the reactions for the transformation of **A** or **B** into **C** and **D**.

ii) write the reactions for the transformation of **A** into **F**, and **B** into **G1** and **G2**.

**f)** compounds **G1** and **G2** readily react with acetone in the presence of acids and form compounds **H1** and **H2**. Draw the structures of **H1** and **H2**.

**g)** compounds **A** and **B** react with bromine. One of the products of these reactions is non-polar (the dipole moment of this molecule is almost zero) and optically inactive. Draw the stereochemical formula of this product, and write the equation for its formation. Determine the absolute configuration of chiral atoms in this molecule (if any) and mark them according to the R and S nomenclature rules by indicating the correct R or S designation at each stereocenter.

Alkenes react with peroxyacids resulting in the addition of an atom of oxygen to the double bond to form a three-membered oxygen-containing ring. This "epoxidation" reaction is highly stereospecific which results in the retention of the relative positions of the substituents on the double bond to which the oxygen atom is attached.

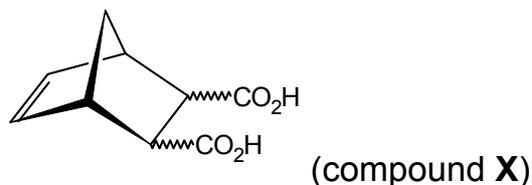
The epoxidation of compound **A** by peroxyacetic acid yields a single compound **K**. Under the same conditions **B** gives a mixture of isomers **L1** and **L2** (the ratio is 1:1).

**h)** Is the compound **K** optically active? Draw a stereochemical formula of **K** clearly indicating the stereochemistry. Are the individual compounds **L1** and **L2** optically active? Draw the stereochemical formulae of **L1** and **L2** clearly indicating the stereochemistry.

### Problem 7

10 points

The stereochemistry of organic compounds can sometimes be determined by studying their chemical behaviour. The structure of one of the isomers of 5-norbornene-2,3-dicarboxylic acid, compound **X** (no stereochemistry implied by the symbol  $\text{X}$ ) was established by the following experiments:



On heating, **X** melts and dehydrates to form a new compound **Y**. Compound **Y** slowly dissolves in excess aqueous NaOH to produce **X<sub>1</sub>**, the same product that **X** produces in an excess aqueous NaOH solution. The resulting solution of **X<sub>1</sub>** in aqueous NaOH was treated with iodine, to give compounds containing iodine. Acidification of the solution gives a mixture of two isomeric racemic compounds **A** and **B**, in a 3:1 ratio. The titration of 0.3913 g of compound **A** with 0.1000 M NaOH in the presence of phenolphthalein required 12.70 mL of base. The same volume of 0.1000 M NaOH was required for the titration of 0.3913 g of compound **B**. On heating, compound **A** was slowly transformed into a new compound **C**, which contained no iodine and was able to react with water. Under the same conditions compound **B** does not undergo this transformation, but on heating with hydrochloric acid slowly transforms into **A**.

**All reactions must be written as a balanced equation. You will find framework formulae for the bicycloheptane system on your answer sheet for parts 3 onward. No mechanisms are required. Additional sheets of the report form are available from the supervisor if necessary.**

- Mark by asterisks (\*) the asymmetric carbon atoms in 5-norbornene-2,3-dicarboxylic acids.
- Draw the stereochemical structures of each of the possible stereoisomers of compound **X**, and when they occur, the structures of their dehydration products.
- Write the reactions of any stereoisomer of **X**, and the corresponding compound **Y** with excess aqueous NaOH.
- Calculate the molar mass of compound **A**. Write the reactions from **X<sub>1</sub>** to **A**.
- Write the reaction of the formation of **C** from **A** and the reaction of **C** with water.
- Draw the stereochemical formula of compound **X** which satisfies all of the data.
- Write the reactions leading from **B** to **A**.
- Are compounds **A** and **B** diastereomers?