Proba-baraj de selectare a echipei pentru participarea la
Olimpiada Internaționala de Chimie "D.I. MENDELEEV"
TEORIE, 5 aprilie, 2019

PROBLEM 1 Determination of chlorides in biological materials (Inorganic and Analytical Chemistry **13 p.**

One of the methods often used for determination of chlorides in biological materials is a mercurimetric titration. The standard solution of mercury(II) nitrate is used as a titrant. In the course of the titration Hg^{2+} cations react with chloride anions under formation of a soluble but only to a small degree ionized mercury(II) chloride. Ethanol solution of 1,5-diphenylcarbazone is used as an indicator that forms with the excess of Hg^{2+} ions a violet complex in which the ratio of amounts of substances Hg^{2+} to 1,5-diphenylcarbazone is 1:2.

1.1. Write down the chemical equation in ionic form for the reaction in which Hg(II) nitrate reacts with sodium chloride in aqueous solution.

1.2. Summary formula of 1,5-diphenylcarbazone is $C_{13}H_{12}N_4O$.

a) Write the structural formula of 1,5-diphenylcarbazone. **Note:** The compound is nearly symmetric.

b) Sketch the structure of the chelate non-electrolyte complex that is formed by the reaction of Hg(II) cations with 1,5-diphenylcarbazone. You need not to show the position of free electron pairs and formal charges.

c) Give the scheme for the splitting of the d-orbitals in the crystal field of this ligand; calculate the crystal field stabilization energy; determine the geometry of the complex and the type of hybridization of the central ion; determine whether the substance is para- or diamagnetic.

A standard solution of mercury(II) nitrate with a concentration of exactly 0.01 $mol \cdot dm^{-3}$ should be prepared by dissolving a calculated amount of mercury(II) nitrate monohydrate in water acidified with 3 cm^3 of concentrated nitric acid. The solution prepared is then transferred into a 500 cm^3 volumetric flask and filled with water up to the mark. The hydrate used was in a reagent bottle which was already opened before the mentioned experiment and was equipped with a label "mercury(II) nitrate monohydrate p. a.".

1.3. When preparing aqueous solution of mercury(II) nitrate the resulting solution must be acidified. Explain the reason. Support your explanation by an appropriate chemical equation.

1.4. Calculate the mass of $Hg(NO_3)_2 \cdot H_2O$ that should be weighted for the preparation of the aqueous mercury(II) nitrate solution with the above exact concentration ($M_r(Hg(NO_3)_2 \cdot H_2O) = 342,61$).

To be sure about the correctness of the determined concentration of chloride anions in the blood serum, we cannot rely on the data given on the label of the reagent bottle (in particular when we know that the bottle has already been opened before our use). That is the reason why the concentration of Hg(II) cations in the prepared standard solution must be additionally determined. The following procedure was applied: A volume of 20.00 cm^3 of a standard solution of sodium chloride with a concentration of exactly 0.01 $mol \cdot dm^{-3}$ was measured into a titration flask. The solution was then acidified with 1 cm^3 of 5% nitric acid and 5 drops of 1,5-diphenylcarbazone indicator was added. The solution was then titrated with the prepared mercury(II) nitrate solution to a violet coloration of the solution.

1.5. Calculate the concentration of mercury(II) nitrate in the solution if its mean consumption at the titration was 10.2 cm^3.

1.6. The results of the titration support the conclusion that Hg(II) nitrate used was not exactly a monohydrate and thus, its formula can be written in the form $Hg(NO_3)_2 \cdot x\ H_2O$. Using the above results calculate the value of coefficient *x* in the formula.

Microanalytical determination of chlorides in the blood serum

Into a small flask, 2 cm^3 of water were measured and it was acidified with 4 drops of 5% nitric acid. Then 0.50 cm^3 of an analysed blood serum and 3 drops of indicator diphenylcarbazone were added. The solution was titrated with the standard solution of mercury(II) nitrate (prepared as given above) to a red coloration of the solution. The mean consumption was 1.53 cm^3.

Finally a blank experiment was performed. The determination was repeated but instead of blood serum an equal volume of water was used. In regard to the colour intensity of the indicator the final consumption could only be guessed and it was in the range 0.07 to 0.10 cm^3. In order to judge the colour change of the solution more precisely, the procedure has been changed and instead of blood serum a tenfold volume of water was used. The consumption in this case was 0.8 cm^3.

1.7. Calculate the concentration of chloride anions in the analysed blood serum.

In biological laboratories it is used to express the concentration in g% or mg%, i. e. in a mass of a substance in grams or milligrams contained in 100 cm^3 of a solution.

1.8. Give the concentration of chlorides in the analysed blood serum in mg%.

1.9. Calculate the relative error of the above determination of the concentration of chlorides if it would be supposed that the mercury(II) nitrate is a monohydrate and the concentration of $Hg(NO_3)_2$ in the prepared standard solution is exactly 0.01 $mol \cdot dm^{-3}$.

PROBLEM 2. Industrial production of hydrogen (Physical Chemistry)

7 p.

In industry, hydrogen can be produced by heating hydrocarbons, like methane, with steam:

$$CH_4(g) + H_2O(g) \Leftrightarrow 3\,H_2(g) + CO(g)$$

2.1. Calculate the Gibbs change of energy $\Delta_r G^\circ$ of this reaction and, in doing so, the equilibrium constant K_p. Also indicate the unit of K_p. ***Use the data:***

$\Delta H^\circ(CH_{4(g)}) = -76\ kJ \cdot mol^{-1}$; $\Delta H^\circ(H_2O_{(g)}) = -242\ kJ \cdot mol^{-1}$; $\Delta H^\circ(CO_{(g)}) = -110\ kJ \cdot mol^{-1}$

$S^\circ(CH_{4(g)}) = 187\ J \cdot mol^{-1} K^{-1}$; $S^\circ(H_2O_{(g)}) = 189\ J \cdot mol^{-1} K^{-1}$; $S^\circ(CO_{(g)}) = 198\ J \cdot mol^{-1} K^{-1}$; $S^\circ(H_{2(g)}) = 131\ J \cdot mol^{-1} K^{-1}$

2.2. How does the value of equilibrium constant K_p change with temperature?

The industrial production can take place without a catalyst at atmospheric pressure and high temperature. At equilibrium, usually 0.20 volume% methane gas remains.

2.3. Calculate the value of K_p for this industrial process which gives 0.20 volume% methane gas at equilibrium. Assume that the reactions start with equal amounts of methane and steam.

Note: the conditions are far from standard.

2.4. Estimate, using the Van't Hoff-relation $\ln\frac{K_2}{K_1} = -\frac{\Delta_r H^\circ}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$ the temperature needed to produce hydrogen from methane in industry.

PROBLEM 3. Interstellar chemistry (Physical Chemistry)

10 p.

A possible ion-molecule reaction mechanism for the synthesis of ammonia in interstellar gas clouds is given below:

$N^+ + H_2 \rightarrow NH^+ + H$ k_1

$NH^+ + H_2 \rightarrow NH_2^+ + H$ k_2

$NH_2^+ + H_2 \rightarrow NH_3^+ + H$ k_3

$NH_3^+ + H_2 \rightarrow NH_4^+ + H$ k_4

$NH_4^+ + e^- \rightarrow NH_3 + H$ k_5

$NH_4^+ + e^- \rightarrow NH_2 + 2\,H$ k_6

3.1. Show the relations between the concentrations of the intermediates NH^+, NH_2^+, NH_3^+ and NH_4^+ and the concentrations of the reactants: $[N^+]$, $[H_2]$ and $[e^-]$. Use the steady state approximation.

3.2. Show that the overall production rate of NH_3 is given by: $\frac{d[NH_3]}{dt} = k_2e[N^+][H_2]$.

In this equation, k_2 is the 2^{nd} order reaction constant of the reaction. Express k_2e in the reaction rate equation by constants of the partial steps k_1, k_5 and k_6.

3.3. What is the cause of the activation energy in a chemical reaction?

The reaction rates of many ion-molecule reactions are almost independent of temperature.

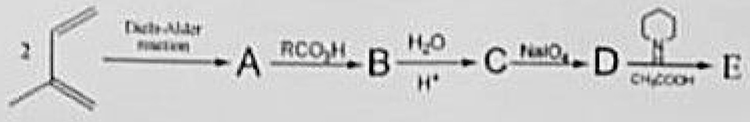
3.4. What can be concluded from this with regard to the activation energy?

Explain why this conclusion is important for reactions taking place in interstellar space.

PROBLEM 4. Cyclopentene derivative (Organic Chemistry)

10 p.

In 1959 professors of Purdue University Joseph Volinsky and Walter Barker performed the synthesis of one of cyclopentene derivative according to the following scheme:



It is known that compound **E** after treating with O_3/H_2O_2 system produces CO_2 and diketocarboxylic acid and that compound **D** has two intensive peaks in 1725 cm^{-1} and 1715 cm^{-1} region in its IR spectrum.

a) Draw the structures of all the unknown compounds.

b) Write the mechanism of the formation of compound **B** from **A**.

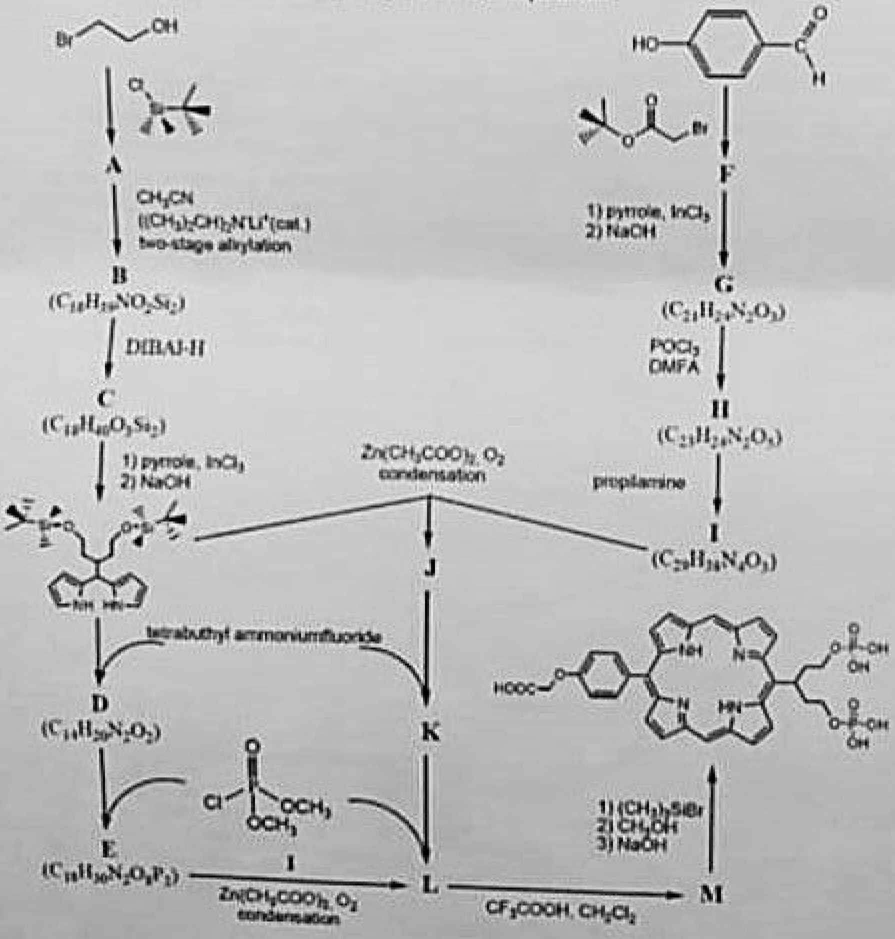
c) Write the mechanism of the formation of compound **E** from **D**.

Problem 5. Porphyrin synthesis (Organic Chemistry) **10 p.**

Porphyrins are aromatic compounds which over hundred years attracts the attention of scientists from various fields like chemistry, biochemistry, biology, technology and medicine. At least eight people have received Nobel Prize for their researches on tetra-pyrrole compounds (Willstetter, Fischer, Warburg, Calvin, Perutz and Kendrew, Crowfoot-Hodgkin, Woodward).

In the twenties century an immense advance in the chemistry of these compounds boosted their application for pharmaceutical purposes. Below it is represented the scheme of porphyrin synthesis performed by Lindsey in 2005 which is based on the reaction of 1,9-bis(imino)dipyrromethane and dipyrromethane in the presence of zinc acetate for getting trans-AB type porphyrins.

Write down the formulae of all the unknown compounds.



DIBAl-H = Diisobutylaluminium hydride =  ; Pyrrole =  ; DMFA =