Problem 1

> *Each metal has a certain power, which is different from metal to metal,*
> *of setting the electricfluid in motion...*
> Alessandro Volta (1745–1827)

The first galvanic cell was invented in 1800 by A. Volta, which was based on the experiments of L. Galvani. Subsequently, galvanic elements have found wide application in science, technology and everyday life.

The left half-cell of the electrochemical element consists of an iron electrode (in excess) that is oxidized during the action and an aqueous solution of iron (III) nitrate with a concentration of 0.01 M. The right half-cell consists of graphite electrode and a mixture of iron (II) and (III) nitrates with concentrations of 0.05 M and 0.30 M, respectively. The volume of each half-cell is 1 L.

1. Indicate which of the electrodes is cathode and which is anode, and also indicate the kind of these two electrodes

2. Write schematically this cell as (–)… |…||…| …(+)

3. Write the half-reactions on each electrode and the total reaction

4. Using the information on ion mobility (μ°), select the most suitable ionic compound(s) for the salt bridge

Cation	μ°, $m^2V^{-1}s^{-1}\cdot10^9$, 25°C	Anion	μ°, $m^2V^{-1}s^{-1}\cdot10^9$, 25°C
Ca^{2+}(aq)	61.6	F^-(aq)	51.5
K^+(aq)	73.5	CO_3^{2-}(aq)	70.3
NH_4^+(aq)	76.1	NO_3^-(aq)	74.1
H^+(aq)	205	Br^-(aq)	81.8

From the thermodynamic data it is known that the standard entropies of Fe(s), Fe^{2+}(aq) and Fe^{3+}(aq) at 25°C are 27.3, –137.7 and –316.0 J/mol·K, respectively. An increase in temperature by 20°C leads to a 85-fold decrease of total reaction equilibrium constant K.

5. a) Indicate an ion whose standard entropy in an aqueous solution is conditionally assumed to be zero b) Indicate the reason why the entropy of the triple-charged ion is much lower than that of the doubly charged ion (choose a case in the answer sheet); c) Calculate the entropy, enthalpy and Gibbs energy (at 25°C) of full reaction. Consider that Δ_rH^0 and Δ_rS^0 are constant values in this temperature range. R = 8.314 J/mol·K and F = 96485 C/mol (Faraday constant).

6. Calculate (in volts, accurate to 3 decimal places) the initial EMF of the cell and the initial potentials of the cathode and anode at 25°C. It is known that $E°(Fe^{2+}/Fe) = –0.447$ V.

The cell was working for 3 hours and 20 minutes until it was completely used.

7. What was the average current in the circuit?

Problem 2

Acid **B** (pK_a = 0.77) can be conveniently prepared in the chemical laboratory by heating one of the acids **X** (pK_a = –1.74), **Y** (pK_a = –1) or **Z** (binary, pK_a = 11.65) with an elementary substance **A**, which exists as a solid at STP. Each of these reactions produces a gas, while the target compound, as very soluble substance, remains in the aqueous solution. After the reaction is complete, the aqueous solution is carefully evaporated to give the final product. When heating to 110°C, the final product melts with decomposition to give substance **C** which contains 74.69% (by mass) of the chemical element of which **A** consists. Heating **C** in an air flow at 220°C results in a loss of 1.77% of **C** by mass and produces solid **D**. When **D** is heated in air to 300°C, it decomposes completely without a solid residue.

Calcination of an anhydrous barium salt of acid **B** in air results in a mass loss and produces salt **E**, which cannot be obtained in aqueous solution.

When a 6.00 g of **B** is heated with excess of concentrated sulfuric acid, a certain compound **F** can be isolated from the reaction mixture. This reaction also produces 382 cm^3 (STP) of a gas with a relative density of just above 1 with respect to air. Compound **F** contains 66.46% (by mass) of the chemical element comprising **A**. When, after separation and drying, **F** is slowly rinsed with cold water on a glass filter, it turns into substance **G** which has the same qualitative composition as **D** but with 1.190 times less oxygen (by mass).

1. Determine the chemical formulas of **A** – **D**, **X**, **Y** and **Z**.

2. Write down the chemical equations representing the three methods of preparation of acid **B**.

3. Identify salt **E** and write down the chemical equation representing its preparation.

4. Identify compound **F** and write down the equation representing its preparation.

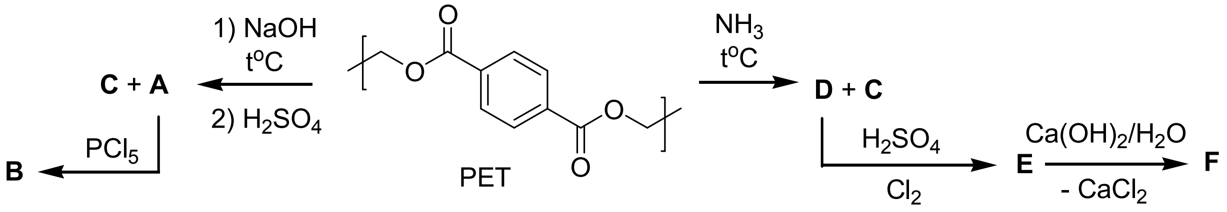
5. Identify substance **G** and write down the equations for the corresponding reactions.

6. In an aqueous solution under ambient conditions, acid **B** reacts with acid **H** to form two new acids. Write a chemical equation of this reaction.

Problem 3

In mid-1960ies, a high-strength fiber based on polymer **X** (prepared via polycondensation of equimolar mixture of monomers **B** and **F**) was developed at DuPont laboratories. Owing to the formation of intermolecular hydrogen bonds, the fiber is resistant to dynamic stresses (several times stronger than steel). The fiber is currently used for manufacturing of light-weight durable parts of sport equipment, body armors, ropes, and cables. The fiber retains its excellent mechanical properties at temperatures within the range of −196 to 420°C, allowing its applications in the development of fire-fighting and cryogenic equipment.

B and **F** can be obtained via recycling of plastic bottles made of polyethylene terephthalate (PET).



1. Identify the transformations involved in PET recycling.

2. a) Draw the structure of the repeating unit of **X**.

b) Determine the average polymerization degree *n* (number of the repeating units) in the polymer prepared from **B** and **F** under equilibrium conditions; the equilibrium constant of interaction between functional groups of **B** and **F** $K_{eq} = 10^6$.

3. How many bottles (20 g each) should be subjected to recycling to manufacture a body armor containing 2 kg of **X**, if each of the stages on the above scheme proceeds with a 90% yield (consider the PET → **A** transformation as a single stage)?

4. Depict the hydrogen bonds formed between polymer chains (draw at least two repeating units in each chain). Give the number of hydrogen bonds per one repeating unit.

X is stable when in contact with neutral and alkaline media, but is hydrolyzed in acidic medium.

5. Calculate the masses of 60·60 cm protective elements of body armors made of steel and of the fiber **X**, both capable of stopping a 4.7 g bullet with 5 mm diameter moving at the velocity of 247 m/s perpendicular to the armor. $\rho_{steel} = 7.7$ g/cm^3, $\rho_{\mathbf{X}} = 1.44$ g/cm^3. Depth of a bullet penetration is given by the formula: $L = \alpha \cdot m \cdot \left(\frac{V}{d}\right)^2$, where *d*, *V*, and *m* are the bullet diameter, velocity, and mass, respectively. The values of parameter α for steel and **X** are $5.84\cdot10^{-10}$ and $1.35\cdot10^{-9}$ m·s^2/kg, respectively.

Problem 4

Until the middle of the XIX century, kindling the fire was very tedious. Radical changes occurred with the discovery of substances that can ignite at fairly low temperatures. The first step to creating the prototypes of modern matches was made in 1805. The head of the first matches was covered with a mixture of substances **A**, **B**, **C**, powdered sugar and resin extracted from the acacia. However, they were ignited not from friction, but when the match was immersed in concentrated H_2SO_4. The matches made in 1826 become more convenient in use. The heads of these matches consisted of substances **A**, **D** and also acacia resin. The disadvantage of this option was the allocation of a large amount of gas **E** with an unpleasant odor. In order to eliminate this disadvantage, in 1830 matches were proposed that ignited with reaction **A** and poisonous substance **F**, which was initiated even by the slightest friction. To reduce the risk of autoignition, in 1836 substance **A** was replaced by **G**. To create "safe matches" **F** was replaced by a non-toxic substance **J**, formed by slow heating of **F** in a sealed vessel. By the beginning of the XX century, matches were being made, based on substances **A** and **H**, which was obtained by heating **F** and **B** above 100°C.

1. Determine the substances **A** – **J**, **L**. If it is known that:

1) gas **E** is formed by burning in a oxygen of **B**, **C**, **D**, **H** and **L**.

2) the mass fraction of **B** in the substance **H** is 43.6%.

3) at a reaction between **G** and 0.80 g of **B** 690 mL of gas **E** (400°C, 1 atm) are released and 2.99 g of a black solid **L** are formed ($\mathbf{G} + 2\mathbf{B} \rightarrow \mathbf{E} + \mathbf{L}$) which oxidizes in an oxygen flow at 1200°C and 1 atm pressure, also with an **E** release of 1.51 L ($2\mathbf{L} + 3O_2 \rightarrow 2\mathbf{E} + \ldots$).

4) **C** is reduced by iron to the metal which exists in the liquid aggregate state at the normal condition.

5) the unit cell of **D** has the following parameters: $a = 1.131$, $b = 0.3837$, $c = 1.123$ nm, $\alpha = \beta = \gamma = 90^\circ$, number of formula units $z = 4$. The calculated density of **D** is 4.63 g/cm^3.

6) substance **A** was first obtained in just 19 years before its application in the production of matches when passing chlorine through a hot KOH solution.

7) **F** has a high reactivity, burns in Br_2 and Cl_2, is easily oxidized by air oxygen. Directly does not interact with hydrogen, but hydride of **F** can be obtained by its interaction with a solution of alkali.

2. Write the reaction equations:

a) $\mathbf{A} + C_{12}H_{22}O_{11} \xrightarrow{H_2SO_4}$

b) $\mathbf{A} + \mathbf{D} \xrightarrow{friction}$

c) $\mathbf{A} + \mathbf{J} \xrightarrow{friction}$

d) $\mathbf{G} + \mathbf{J} \xrightarrow{friction}$

e) $\mathbf{A} + \mathbf{H} \xrightarrow{friction}$

Problem 5

On prolonged frying or storage, fats accumulate radical oxidation products. Oxidation of fats is studied by heating them in the presence of oxygen. One and the same vegetable fat was subjected to various treatments.

1. A weight of initial triglyceride (88 mg) was dissolved in a suitable solvent, acetic acid and 0.5 mL of a 5.0 M hydrogen peroxide solution were added (in this case, peracetic acid was formed, that transfers the C=C bond to the epoxide). The excess of peroxide remaining after the reaction liberated iodine from KI. The amount of iodine was equivalent to 8.8 mL of 0.50 M solution of thiosulfate. Considering epoxidation quantitative, estimate the number of double bonds in the sample. Write down the necessary reaction equations and the structure of the original fat, if all the fatty acid residues in it are the same.

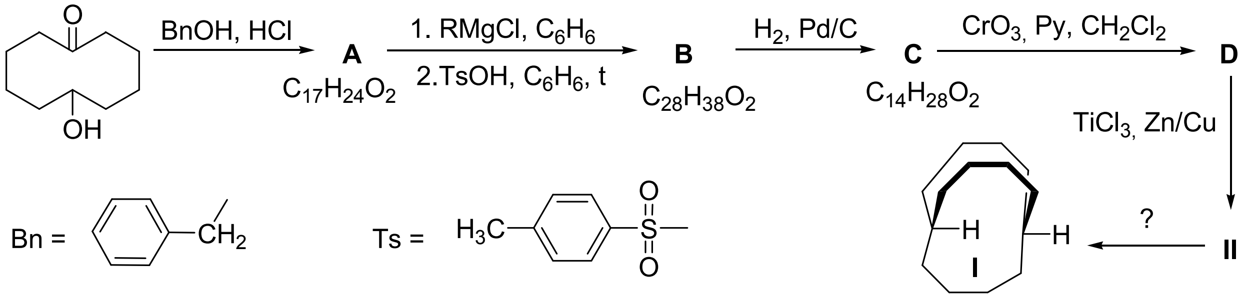
2. Another portion of the same fat weighed 10 g was heated for a long time in air at 50°C. As a result, hydroperoxides containing C–O–O–H fragment were formed. An excess of KI was added to the fat and the liberated iodine was titrated with 2.2 mL of 0.100 M thiosulphate. Draw the structure of one of the monohydroperoxides (if only one of the fatty acid residues reacts) and write down the reactions of its formation and interaction with KI in an acidic medium. Calculate the peroxide number of fat PN (mmol of absorbed O_2 / kg fat).

3. a) The same fat in the amount of 88 mg (if you did not determine the structure of fat in paragraph 1, take its molar mass equal to 700 g/mol) was emulsified in a surfactant solution and oxidized with permanganate in an acidic medium with heating, which required 0.48 mmol of $KMnO_4$. How many electrons does a fat molecule lose in this reaction? Write down the formulas of the products formed upon the oxidation of fat with $KMnO_4$.

b) A similar procedure conducted with 88 mg of fat containing hydroperoxides required 0.54 mmol of $KMnO_4$. Write down the reaction equation of the thermal degradation product with permanganate if the peroxy group is transformed into keto group. Calculate the number of hydroperoxide groups per fat molecule.

Problem 6

In 1984, the research group led by John McMurry (an American chemist, the author of the well-known textbook "Organic Chemistry", which has already undergone the 9th edition) synthesized interesting bridged polycyclic compounds **I** and **II** according to the scheme:



1. In the synthesis of **I**, the conversion of **D** into **II** is so-called McMurry reaction. If C_3H_6O (**III**) is used in this reaction (instead of **D**), then a compound C_6H_{12} (**IV**) will be obtained. Determine the structures of **III** and **IV** if IR spectrum of **III** exhibits an intense absorption band at 1715 cm^{-1}, and only one singlet is detected in the ^1H NMR spectrum of **IV**.

Compounds **I** and **II** are characterized by an unusual type of stereoisomerism – the so-called in/out-isomerism.

2. Draw the structural formulas of **Ia** and **Ib** (in,in- and out,out-stereoisomers of **I**, respectively).

3. Determine the structures of **A** – **D**, RMgCl, **II** and suggest the reagents for the stage **II** → **I** if the ^1H NMR spectrum of the Grignard reagent RMgCl ($w_C = 59.24\%$, $w_{Mg} = 10.90\%$) includes a singlet, triplet, triplet, quintet, quintet and multiplet ($\delta = 7.5$ ppm) with an integral intensity ratio of 2:2:2:2:2:5, and **B** contains an endocyclic double bond. Specify the **B** configuration (*Z*/*E*).

When **II** is treated with CF_3COOH at 40°C, it is quantitatively converted to [**V**], which has an increased stability for this class of intermediates. Alternatively, [**V**] can be synthesized from **I** by the action of trifluoromethanesulfonic acid, which is accompanied by the release of gas **X**. The structure of [**V**] contains a bridged two-electron three-center bond and is more symmetric in comparison with **I**, as evidenced by the ^1H NMR spectrum (in particular, the molecule of [**V**] has one more symmetry plane than **I**). The described regularities and increased stability of [**V**] are due to the fact that two resonance structures can be represented for it:

$$[\mathbf{V}] = [\mathbf{Va} \longleftrightarrow \mathbf{Vb}]$$

4. Write the structural formulas of [**V**], **Va**, **Vb**, **X**. Suppose which of the in/out-stereoisomers of **I** (**Ia** or **Ib**) can exhibit similar reactivity.

Problem 7

Some irreversible chemical conversion of a substance **X** to a substance **W** that takes place in a solution and includes only successive steps was studied by means of UV-vis spectroscopy at the wavelength $\lambda_1 = 320$ nm in a cuvette with optical path length 0.5 cm. Before all, solution 0.00131 M of pure substance **X** was taken. Obtained dependence of absorbance (A) on time is in the table below.

t, min	0	2	4	6	10	20	50	100	∞
A	0.982	2.073	2.538	2.727	2.883	2.713	2.369	1.919	0.681

1. What is minimum number of the successive stages in the conversion of **X** to **W**?

2. Calculate molar extinction coefficient (indicate its dimension) of substance **X** at the mentioned wavelength.

3. A series of standard solutions of final product (**W**) was investigated by means of UV-vis spectroscopy at 320 nm in a cuvette with optical path length 1 cm. Calculate the molar extinction coefficient for **W** using the data below.

c(**W**), M	0.00100	0.00200	0.00300	0.00500
A	0.56	1.08	1.60	2.64

4. Accept the number of stages that you suggested (1st order) and write down a scheme of the conversion of **X** (use the results of point 3).

5. Estimate molar extinction coefficient at 320 nm for every intermediate in the scheme you proposed.

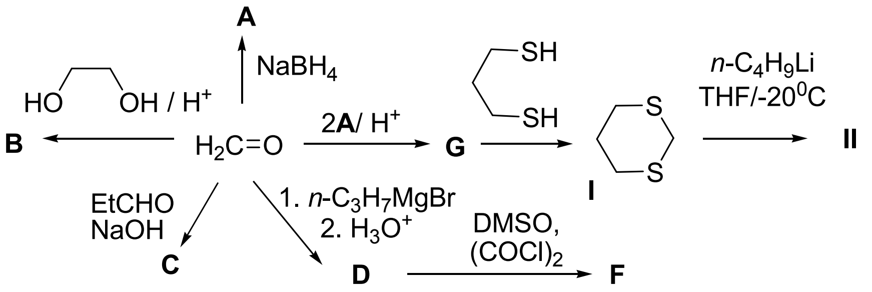
6. Estimate every rate constant in the scheme you proposed.

7. Initial and final substances have an isosbestic point at the wavelength $\lambda_2 = 710$ nm, and none of the intermediate substances absorbs light. Schematically depict the dependence of the optical density on time if the solution is monitored at this wavelength (include point $t = \infty$). Indicate characteristic properties of the dependence if any.

Additional information: Beer – Lambert – Bouguer law: $A = \varepsilon lc$, for a 1st order reaction: $c(t) = c_0 \cdot \exp(-kt)$. Isosbestic point of a couple of substances is the wavelength where molar extinction coefficients of both substances are equal.

Problem 8

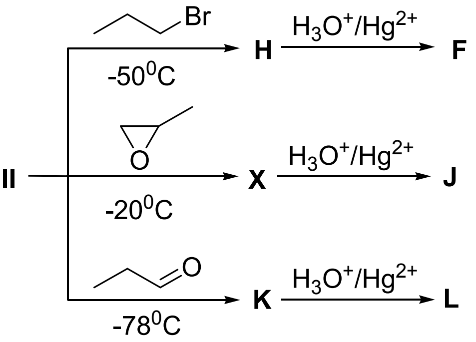
Synthons for Vermiculin. The term “synthon” was coined in 1967 by E.J. Corey. Its term means a real or idealized structural unit of a molecule that can be introduced into chemical synthesis by known techniques. Synthon does not exist as a specific reagent; it is a formal particle (ion, radical or carbene). Each synthon can be associated with one or more real reagents, and conversely, one reagent could be a synthetic equivalent for a few synthons. The prominent example of such dual reagents in formaldehyde, which can act as a C_1-electrophile, but upon transformation into 1,3-dithiane **I** undergoes a retrosynthetic umpolung to C_1-nucleophile. The real nucleophilic reagent in the case is organolithium compound **II.**



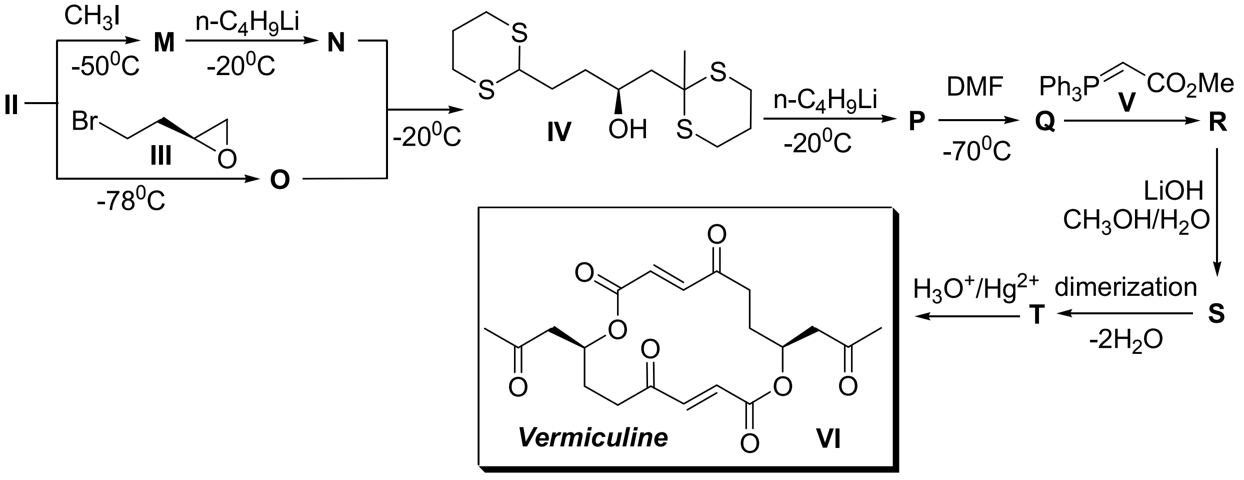
1. Decipher the substances **A**, **B**, **C**, **D**, **F**, **G**, **II**.

Compound **II** is successfully applied for the selective synthesis of homo- and polyfunctional compounds (see scheme at right)

2. Decipher the substances **H**, **X**, **J**, **K**, **L**, if **J**, **L** and **C** are isomers, which NMR ^{1}H spectra possess signals at ~ 10 ppm: doublet (for **L** and **C**) or triplet (for **J**).



The using of dithiane **I** leads to development of effective "short" synthesis of polyfunctional natural compounds, for example, an antibiotic, *vermiculin* (**IV**), isolated from *Talaromyces vermiculatus*:



3. Decipher the substances **M**, **N**, **O**, **P**, **Q**, **R**, **S**, **T** from Scheme, if known that MW (**IV**) less than the molar mass of Q by 8.64%. Structures **T** and **III** – isocyclic; the molecule **T** have the number of hydrogen atoms is twice as large, and the oxygen atoms are half as much as in comparison with **VI**, and the number of carbon atoms in **T** is 60% larger than in **VI**.