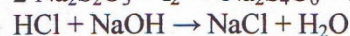
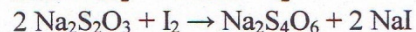
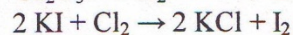
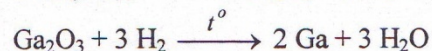
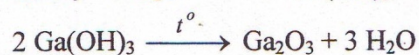
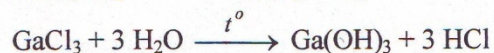
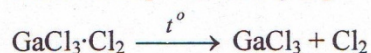
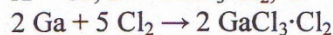


X BALTIC CHEMISTRY OLYMPIAD**Palanga, April 20-22, 2002****Solutions****Problem 1****A** – Ga, **B** – GaCl₃·Cl₂, **C** – GaCl₃, **D** – Ga(OH)₃, **E** – aqueous solution of HCl, **F** – Ga₂O₃.

71.5 ml of thiosulfate solution were needed for titration.

17.2 ml of sodium hydroxide solution were needed for titration.

Nitrogen is carrier gas – it carries chlorine into the solution of sodium iodide. The gas should be inert towards all components of the system.

Problem 2

1)

$$\Delta H_r^0 = 2 \cdot \Delta H_{f,298}^0(\text{CO}) = 182,5 \text{ kJ}$$

$$\Delta G_r^0 = 2 \cdot \Delta G_{f,298}^0(\text{CO}) = 175,6 \text{ kJ}$$

$$\Delta S_{r,298}^0 = \frac{1}{T} \cdot (\Delta H_{r,298}^0 - \Delta G_{r,298}^0)$$

$$\Delta S_{r,298}^0 = 24,62 \text{ J/K}$$

Reaction is impossible because $\Delta G_{r,298}^0$ possesses high and positive value.

2)

$$\Delta G_r^0 = \Delta H_r^0 - T \cdot \Delta S_r^0$$

$$\Delta G_r^0 = 182500 - 24.62 \cdot T \text{ (J)}$$

3)

$$K = \frac{p^2(\text{NO})}{p(\text{O}_2) \cdot p(\text{N}_2)}$$

$$K = \frac{(10^{-3})^2}{0.78 \cdot 0.21} = 6.1 \cdot 10^{-6}$$

$$\Delta G_r^0 = -RT \ln K$$

$$\Delta G_r^0 = -8.31 \cdot T \cdot \ln(6.1 \cdot 10^{-6}) = 99.72 \cdot T$$

$$182500 - 24.62 \cdot T = 99.72 \cdot T$$

$$T = 1468 \text{ K}$$

4)

$$v = \frac{d[\text{NOBr}]}{dt} = k_2 \cdot [\text{NO}] \cdot [\text{NOBr}_2]$$

$$\frac{v_1}{v_{-1}} = \frac{k_1 [\text{NO}] \cdot [\text{Br}_2]}{k_{-1} [\text{NOBr}_2]}$$

$$v = k_2 \cdot \frac{v_1}{v_{-1}} \cdot [\text{NO}] \cdot [\text{NOBr}]$$

$$v = k_2 \frac{k_1}{k_{-1}} [\text{NO}]^2 \cdot [\text{Br}_2] = k' [\text{NO}]^2 \cdot [\text{Br}_2]$$

Problem 3

a) It can be concluded that the increase of the concentration of substrate in experiments 1 and 2 does not change the rate of reaction substantially.

That means the $V_{\max}$ is achieved. Consequently $V_{\max} = 75 \mu\text{M}/\text{min}$.

K_m could be calculated from the Michaelis-Menten equation using data from the experiments 1 and 3 (the rate difference between experiments 1 and 2 is too small for calculation).

$$v_0 = \frac{V_{\max} [S]}{K_m + [S]} \Leftrightarrow 60 = \frac{75 \cdot 10^{-4}}{K_m + 10^{-4}} \Rightarrow K_m = 2.5 \cdot 10^{-5} \text{ M}$$

Experiments 1 and 4 as well as 1 and 5 are also giving the same results of K_m .

b) $[S] = 2.5 \times 10^{-5} \text{ M}$, this is also the K_m value. Then the initial rate is half of the maximal rate:
 $v_0 = V_{\max}/2 = 75/2 = 37.5 \mu\text{M}/\text{min}$.

$$[S] = 5 \times 10^{-5} \text{ M}$$

$$v_0 = \frac{V_{\max} [S]}{K_m + [S]} \Leftrightarrow v_0 = \frac{75 \cdot (5 \cdot 10^{-5})}{2.5 \cdot 10^{-5} + 5 \cdot 10^{-5}} \Rightarrow v_0 = 50 \mu\text{M} / \text{min}$$

c) $[S] = 0.02 \text{ M}$ ($K_m = 2.5 \times 10^{-5}$)

$$[S] = 800 K_m, [S] \gg K_m, v_0 = V_{\max} = 75 \mu\text{M}/\text{min}.$$

d) $V_{\max} = k_{\text{cat}}[E]_0$. Increasing the concentration of enzyme x 2 value of $V_{\max}$ will also increase x 2. The rate will increase x 2:

$$[S] = 10^{-4} \text{ M}, v_0 = 60 \mu\text{M}/\text{min}, v_0(\text{new}) = 120 \mu\text{M}/\text{min}.$$

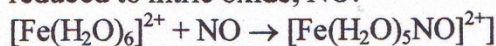
e) $[S] = 0.04 \text{ M}$. $[S] \gg K_m$, it means that the reaction order is 0.

$$V = P/\text{time}, [P] = V_{\max} \times \text{time}, [P] = (75 \mu\text{M}/\text{min}) \times 3 \text{ min} = 225 \mu\text{M} = 2.25 \times 10^{-4} \text{ M}.$$

Problem 4

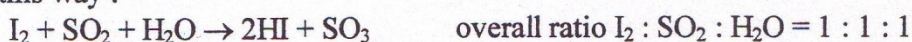
- a) color change in the case of thiocyanate ions indicates that the solution contains Fe^{3+} ions
 $\text{Fe}^{3+} + \text{CNS}^- \rightarrow [\text{Fe}(\text{CNS})]^{2+} - \text{red}$

A brown ring formed at the interface between the two liquids in another qualitative reaction indicates that the solution of sample X contains nitrate ions. The brown ring consists of a complex cation - pentaquanitroso iron(II) - which is formed when a nitrate is reduced to nitric oxide, NO:



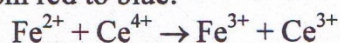
- b) i) Standardization of titrant A: $2\text{Ce}^{4+} + \text{C}_2\text{O}_4^{2-} \rightarrow 2\text{Ce}^{3+} + 2\text{CO}_2$

In 1935 Karl Fischer worked out a method for determination of water content in samples. For the simplification we can assume that equimolar mixture of $\text{I}_2 + \text{SO}_2$ reacts with H_2O in a this way :



ii) Standardization of titrant B: $\text{I}_2 + \text{SO}_2 + \text{H}_2\text{O} \rightarrow 2\text{HI} + \text{SO}_3$

- c) i) Before titration with titrant A the sample was allowed to react with TiCl_3 , this led to reduction of ferric ions: $\text{Fe}^{3+} + \text{Ti}^{3+} \rightarrow \text{Fe}^{2+} + \text{Ti}^{4+}$
 The obtained ferrous ions were titrated with Ce^{4+} solution, ferroin indicator changes color from red to blue.



ii) $\text{I}_2 + \text{SO}_2 + \text{H}_2\text{O} \rightarrow 2\text{HI} + \text{SO}_3$ (check b))

- d) $c(\text{Ce}^{4+}) = (0.189 \text{ g} / 126 \text{ g/mol}) \cdot 2 / 28 \text{ ml} = 0.107 \text{ M}$

$$n(\text{Fe}^{3+} \text{ in sample}) = 23 \text{ ml} \cdot 0.107 \text{ M} = 2.46 \text{ mmol}$$

$$c(\text{I}_2 = \text{SO}_2) = (0.1 \text{ g} / 294.1 \text{ g/mol}) \cdot 4 \cdot (1 / 0.0034 \text{ l}) = 0.4 \text{ M}$$

$$n(\text{H}_2\text{O} \text{ in sample}) = 8.5 \text{ ml} \cdot 0.4 \text{ M} = 3.4 \text{ mmol}$$

$$\Rightarrow 1 \text{ g of X contains } 3.4 / 0.15 = 22.67 \text{ mmol of water}$$

$$\Rightarrow \text{ratio } n(\text{Fe}^{3+}) : n(\text{H}_2\text{O}) = 2.46 : 22.67 \approx 1 : 9.2$$

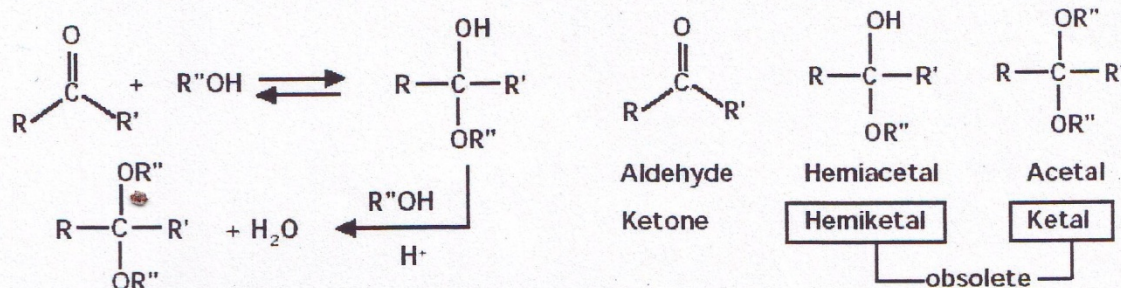
Using mass of the sample for cerimetric titration we can calculate the molar mass of X.

$$M(\text{X}) = 1 \text{ g} / 2.46 \cdot 10^{-3} \text{ mol} \approx 406 \text{ g/mol}$$

Collecting of all the obtained data results in determination of the composition of X.

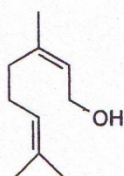


- e) No, because carbonyl group $-\text{C}=\text{O}$ of aldehydes or ketones can react with methanol in solution to give acetals or ketals producing water at the same time.



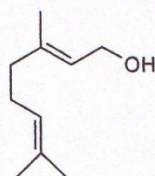
Problem 5

a)



nerol

(Z)-3,7-dimethylocta-2,6-dien-1-ol

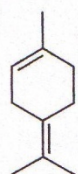


geraniol

(E)-3,7-dimethylocta-2,6-dien-1-ol

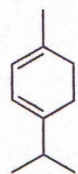
Nerol has Z configuration around the double bond at position 2, so the reacting atoms are closer together and the reaction is faster.

b)



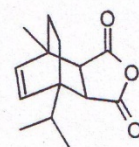
terpinolene

c)

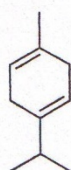
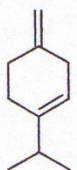
 α -terpinene

1-methyl-4-(1-methylethyl)cyclohexa-1,3-diene

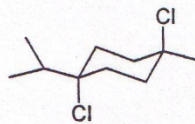
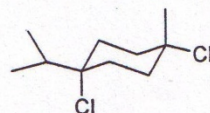
d)



e)

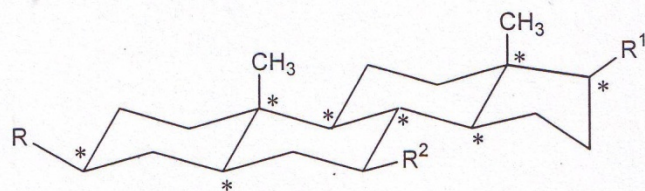


f)

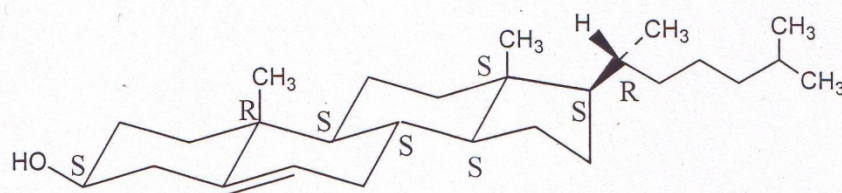
*trans*-1,4-dichloro-1-methyl-4-(1-methylethyl)cyclohexane*cis*-1,4-dichloro-1-methyl-4-(1-methylethyl)cyclohexane

Problem 6

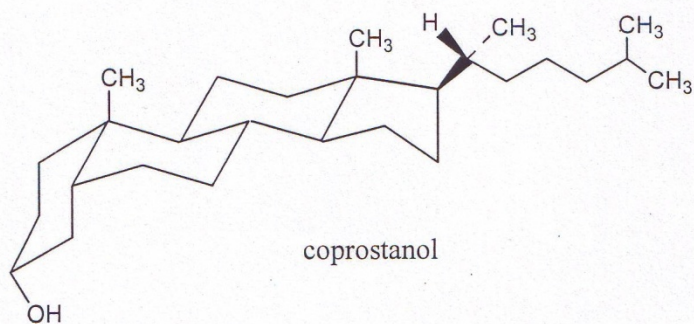
Conformational formula of the steroid nucleus:



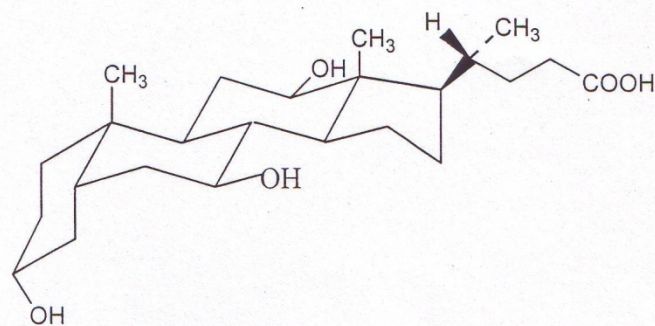
Chiral atoms are indicated by an asteric. Number of diastereomers is $2^8=256$



cholesterol

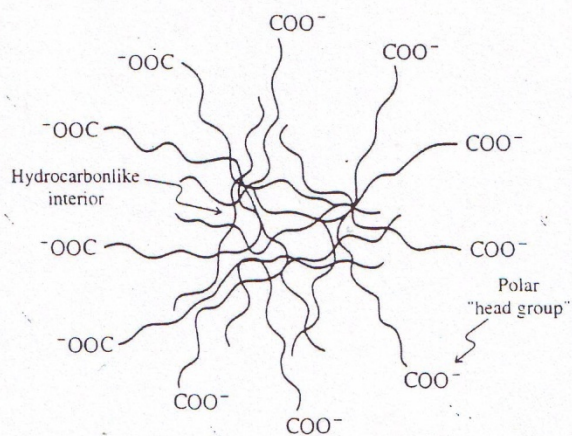


coprostanol

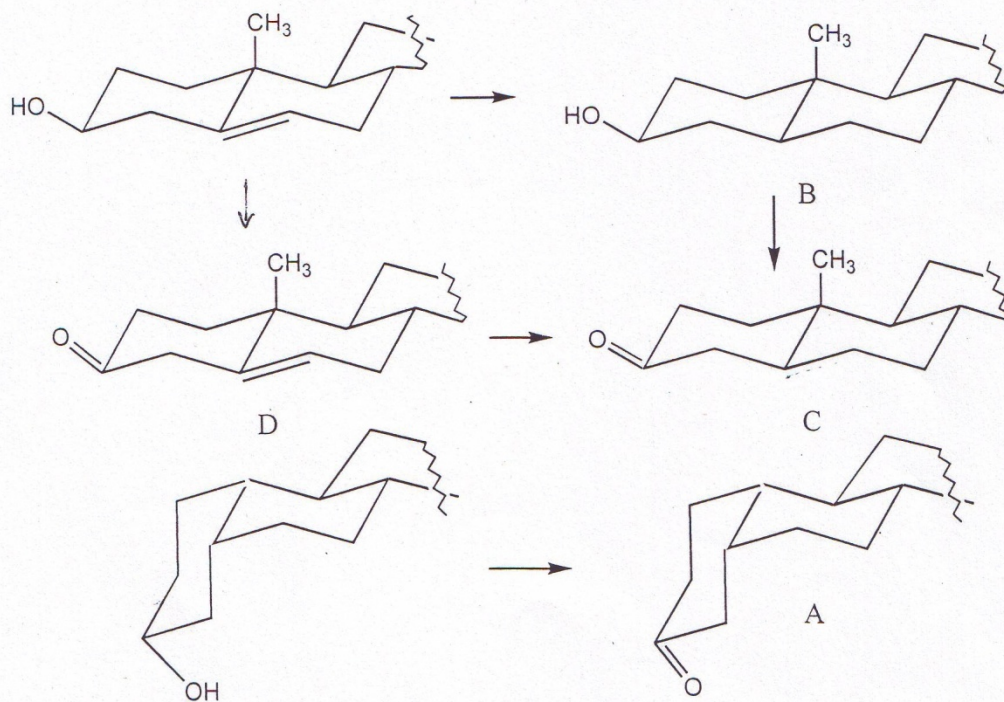


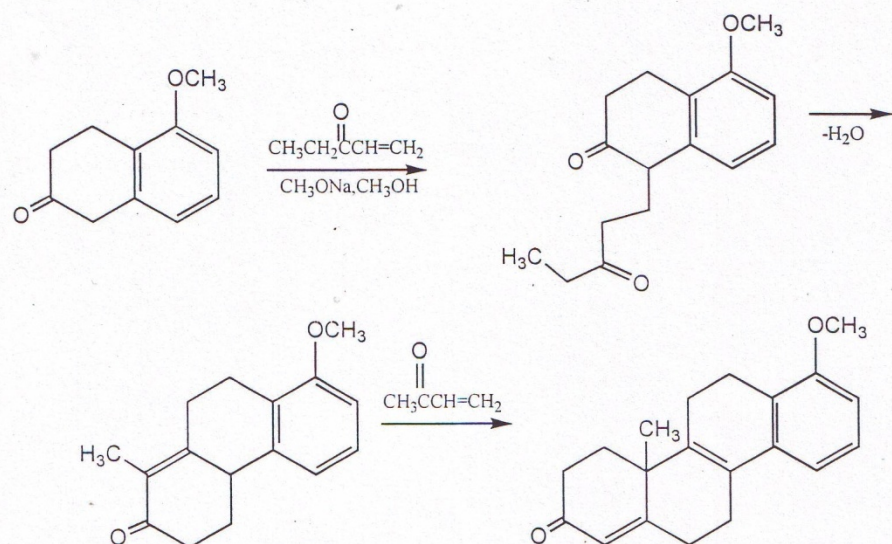
Cholic acid

Cholic acid can act as emulsifying agent forming micelles as shown below:



The transformations described are as follows:





The mechanism of the first step of Michael addition followed by an intramolecular aldol condensation:

