Solutions to Preparatory problems

Problem 1. Graphite oxide

1) In GO the interplane spacing is larger. This facilitates exfoliation of GO. Graphite is hydrophobic, whereas GO is hydrophilic due to the formation of the functional groups. This makes GO soluble in water, which is very important for chemical exfoliation. The grave disadvantage of GO as a precursor of graphene is the necessity of reduction of single sheets after exfoliation. Graphene produced from GO is always defective.

2) 25% of carbon atoms retain the sp^2 hybridization, which means that they are not bonded to oxygen atoms. 75% of carbon atoms form chemical bonds with oxygen. Each oxygen atom is bonded to the pair of carbon atoms. The net formula is $CO_{0.375}$. Maximum X in the Hoffman model is 0.5. The net formula is $CO_{0.5}$.

3) The four groups are the phenol (OH sp^2), hydroxyl (OH sp^3), and epoxide groups in the basal plane, and the carboxylic acid groups at the edges.

4) Each hydrogen atom corresponds to one oxidized carbon atom. 22% of carbon atoms are bonded to the hydroxyl or phenol group, or are in the carboxylic acid group. Let all the hydrogen atoms be in the carboxylic acid groups. Then 44% of oxygen atoms are in the carboxylic acid groups and 2% are in the epoxy groups. In this case 22% + 2·2% = 26% of all the carbon atoms are oxidized. 74% of the total amount of carbon atoms do not form chemical bonds with oxygen. This is the upper limit. Let all the hydrogen atoms be in the hydroxyl or phenol groups. This means that there are no carboxylic acid groups in the particular GO sample! Then 24% of oxygen atoms are in the epoxy groups. In this case 22% + 2·24% =70% of all the carbon atoms are bonded to oxygen. 30% of carbon atoms are not oxidized. This is the lower limit.

5) Acid groups do not participate in the hydrogen bonding network (Fig. 3). It means that maximum degree of water absorption will be reached in case of the absence of such groups in GO. Then each pair of hydrogen atoms holds one molecule of H_2O (0.11), and each pair of epoxy groups also holds one molecule of H_2O (0.46–0.22) / 2 = 0.12. Altogether there are 0.23 molecules of water per one carbon atom. The chemical formula of GO hydrate is $CH_{0.22}O_{0.46}{\cdot}0.23H_2O$.

Problem 2. Efficiency of photosynthesis

1. $H_2O + CO_2 \rightarrow CH_2O + O_2$.

The process is reverse to combustion of 1/6(glucose), hence:

$$\Delta_r H^\circ_{298} = -\frac{1}{6}\Delta_c H^\circ_{298}(C_6H_{12}O_6) = \mathbf{467.5\ kJ{\cdot}mol^{-1}}.$$

Standard entropy change in the reaction:

$$\Delta_r S^\circ_{298} = \frac{1}{6}S^\circ_{298}(C_6H_{12}O_6) + S^\circ_{298}(O_2) - S^\circ_{298}(H_2O) - S^\circ_{298}(CO_2) = -43.7\ \text{J}{\cdot}\text{K}^{-1}{\cdot}\text{mol}^{-1}.$$

Standard Gibbs energy change:

$$\Delta_r G^\circ_{298} = \Delta_r H^\circ_{298} - 298\Delta_r S^\circ_{298} = 467.5 - 298\cdot(-43.7\cdot10^{-3}) = \mathbf{480.5\ kJ{\cdot}mol^{-1}}.$$

Energy of 1 mol of photons with wavelength of 680 nm:

$$E_m = \frac{hcN_A}{\lambda} = \frac{6.63\cdot10^{-34}\cdot3.00\cdot10^{8}\cdot6.02\cdot10^{23}}{680\cdot10^{-9}}\cdot10^{-3} = 176\ \text{kJ}{\cdot}\text{mol}^{-1}.$$

The minimum number of photons necessary to supply more energy than E = 480.5 kJ·mol^{-1} is **3**.

(Instead of $E = \Delta_r G^\circ_{298}$, one can use $E = \Delta_r H^\circ_{298} = \Delta_r U^\circ_{298}$ – the result is the same: 3 photons.)

2. $$\Delta_r G_{298} = \Delta_r G^\circ_{298} + RT\ln\frac{p_{O_2}}{p_{CO_2}} = 480.5 + 8.314\cdot298\cdot10^{-3}\cdot\ln\frac{0.21}{3\cdot10^{-4}} = \mathbf{496.7\ kJ{\cdot}mol^{-1}}.$$

The correction from non-standard pressures is not large – about 1/30 of the standard Gibbs energy.

3. Energy of 10 mol of photons absorbed by green plants is 176·10 = 1760 kJ. Of this amount 480.5 kJ is converted to Gibbs energy. The efficiency of the solar energy conversion by green plants can be estimated as 480.5 / 1760 · 100% = **27%**.

4. Total solar energy absorbed:

a) Moscow area: $E = 1070\cdot10^6\ \text{m}^2 \cdot 150\ \text{J}{\cdot}\text{s}^{-1}{\cdot}\text{m}^{-2} \cdot (10\cdot86400)\ \text{s} = 1.4\cdot10^{17}\ \text{J}$.

b) MSU campus: $E = 1.7\cdot10^6\ \text{m}^2 \cdot 150\ \text{J}{\cdot}\text{s}^{-1}{\cdot}\text{m}^{-2} \cdot (5\cdot3600)\ \text{s} = 4.6\cdot10^{12}\ \text{J}$.

Number of photons $N = (E / E_m)\cdot N_A$:

a) Moscow area: $N = \mathbf{4.8\cdot10^{35}}$.

b) MSU campus: $N = \mathbf{1.6\cdot10^{31}}$.

Solar energy utilized by green plants and converted to chemical energy:

a) Moscow area: $E_{util} = 1.4\cdot10^{17} \cdot (18\%/100\%) \cdot (10\%/100\%) \cdot (27\%/100\%) = 6.8\cdot10^{14}\ \text{J}$

b) MSU campus: $E_{util} = 4.6\cdot10^{12} \cdot (54\%/100\%) \cdot (10\%/100\%) \cdot (27\%/100\%) = 6.7\cdot10^{10}\ \text{J}$

Quantity of photosynthesis products $n(CH_2O) = E_{util} / \Delta_r G^\circ_{298}$

a) Moscow area: $n(CH_2O) = n(O_2) = 1.4 \cdot 10^9$ mol

$m(CH_2O) = n \cdot M = 1.4 \cdot 10^9$ mol $\cdot$ 0.03 kg/mol = **$4.2 \cdot 10^7$ kg**

$V(O_2) = n \cdot V_m = 1.4 \cdot 10^9$ mol $\cdot$ 0.0244 m^3/mol = **$3.4 \cdot 10^7$ m^3**

b) MSU campus: $n(CH_2O) = n(O_2) = 1.4 \cdot 10^5$ mol

$m(CH_2O) = n \cdot M = 1.4 \cdot 10^5$ mol $\cdot$ 0.03 kg/mol = **4200 kg**

$V(O_2) = n \cdot V_m = 1.4 \cdot 10^5$ mol $\cdot$ 0.0244 m^3/mol = **3400 m^3**

5. Percent of solar energy converted to chemical energy:

a) Moscow area: (18%/100%) $\cdot$ (10%/100%) $\cdot$ (27%/100%) = 0.005 = **0.5%**

b) MSU campus: (54%/100%) $\cdot$ (10%/100%) $\cdot$ (27%/100%) = 0.015 = **1.5%**

Problem 3. Ammine complexes of transition metals

1. Chrome is dissolved in a diluted sulfuric or hydrochloric acid:

$$Cr + 2HCl = CrCl_2 + H_2$$

The experiment is conducted under inert atmosphere.

2. $4[Cr(NH_3)_6]Cl_2 + 4NH_4Cl + O_2 = 4[Cr(NH_3)_5Cl]Cl_2\downarrow + 4NH_3 + 2H_2O$

The formula of the precipitate is $CrCl_3N_5H_{15}$.

3. H_2O_2. The compound $[Cr(NH_3)_5Cl]Cl_2$ is formed because the oxidation takes place via the η_2-bridging peroxocomplex, followed by the hydrolysis when the leaving peroxo-group is replaced by the chloride-ion from the solution.

4. $2[Cr(NH_3)_6]Cl_2 + 2NH_4Cl = 2[Cr(NH_3)_6]Cl_3 + H_2 + 2NH_3$

5. The chromium(3+) complexes are inert, thus the substitution process occurs slowly. This is due to the d^3 configuration.

6. $Fe(NH_3)_6^{2+} < Ru(NH_3)_6^{2+} < Cr(NH_3)_6^{2+}$

The coordinated ammonia has no vacant electron pair and therefore cannot interact with a proton. The iron(2+) complex is labile, that is, ammonia ligands can be easily substituted by water molecules, which have a free electron pair even when linked to a metal atom. The ruthenium(2+) complex is inert, but due to high atomic radius of ruthenium has a possibility to

form an intermediate complex with an enhanced coordination number. The chromium(3+) complex is inert and has no possibility to bind a proton. Therefore it is the most stable complex in the acidic media.

7. $[Ru(NH_3)_6]^{2+} + H_2O + H^+ \rightarrow [Ru(H_2O)(NH_3)_5]^{2+} + NH_4^+$

$[Ru(NH_3)_6]^{2+} + H^+ \rightarrow [RuH(NH_3)_6]^{3+}$ rate r_1

$[RuH(NH_3)_6]^{3+} + H_2O + H^+ \rightarrow [RuH(NH_3)_5(H_2O)]^{3+} + NH_4^+$ (fast, rate r_2)

$[RuH(NH_3)_5(H_2O)]^{3+} \rightarrow [Ru(NH_3)_5(H_2O)]^{2+} + H^+$ rate r_3

$r = r_3 = r_2 = r_1$ (steady state) $= k[H^+][Ru(NH_3)_6^{2+}]$

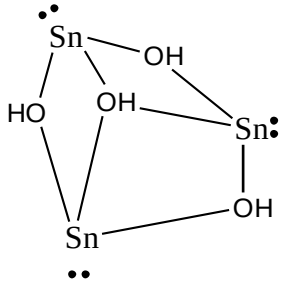
See J.D. Atwood, Inorganic and organometallic reaction mechanisms, 2nd edition, Wiley-VCH, pp.85-86 and P.C. Ford et al, Inorg. Chem., 1968, 7, 1976.

Problem 4. Preparation of inorganic compound

1. The common mineral of tin is cassiterite, SnO_2. Thus, 1.05 g of X after decomposition give 0.8664 g of SnO_2 that contains 5.738 mmol of tin. Under decomposition 0.069 g (3.833 mmol) of water form. As the ratio n(Sn) : $n(H_2O)$ is equal to 1.5 (or 3 : 2), the brutto formula of X contains 3 equivalents of SnO_2, 4 of H and 2 of O (from 2 water molecules). In addition, it also contains nitrogen and probably more oxygen. Their mass is 1.05 – 0.8664 – 0.069 = 0.1146 g and the average molar mass is M = 0.1146 / (0.00383/2) = 60 g/mol, which corresponds to N_2O_2. Thus, the formula of X is $Sn_3O_{10}N_2H_4$, or $Sn_3O_2(NO_3)_2(H_2O)_2$.

2. All the operations should be performed in an inert atmosphere, because tin(II) hydroxide is oxidized in air.

3. If all the metal atoms in the cation are equivalent they have the same coordination sphere. So, we may suppose the formula $[Sn_3(OH)_4]^{2+}$, that is a combination of three pyramids linked by joint edges in a cycle (See J.D. Donaldson et al, JCS Dalton Trans, 1995, 2273.):



The pyramidal nonplanar geometry is due to the electron pair on each tin atom.

4. In the acidic solution the hydrated tin(2+) ions are formed, in the basic media – the anions $[Sn(OH)_3]^-$, $[Sn(OH)_6]^{4-}$ and oligonuclear species such as $[Sn_2O(OH)_4]^{2-}$, $[Sn_4O(OH)_{10}]^{4-}$.

5. $2BiCl_3 + 3SnCl_2 + 6HCl = 2Bi + 3H_2SnCl_6$

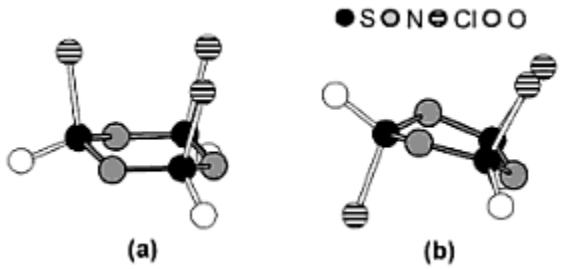
$E° = 0.317 - 0.15 = 0.167$ V,

$$K = \exp\left(\frac{nFE^\circ}{RT}\right) = \exp\left(\frac{6 \cdot 96500 \cdot 0.167}{8.314 \cdot 298}\right) = 8.90 \cdot 10^{16}$$

Problem 5. Inorganic chains and rings

1. $3SOCl_2 + 3NaN_3 = [NS(O)Cl]_3 + 3NaCl + N_2$

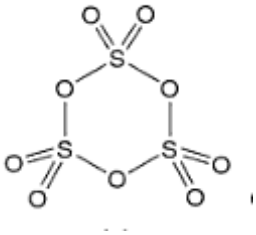
X – $[NS(O)Cl]_3$

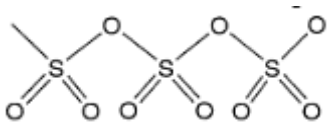
2. 

3. Y – $[NS(O)F]_3$

$2[NS(O)F]_3 + 9Ba(CH_3COO)_2 + 18H_2O = 3BaF_2\downarrow + 6BaSO_4\downarrow + 12CH_3COOH + 6CH_3COONH_4$

4. $[NS(O)(NHCH_3)]_3$

5.  $[N_3S_3O_6]^{3-}$ and  $(SO_3)_3$

6.  Z = $(SO_3)_n$

Problem 6. Transition metal compounds

1. Anhydrous salt **D** is the main constituent of compound **B**. We may suppose that **B** is a hydrate of **D**. The Na : **X** molar ratio in **D** is 3:1. **D** is not a binary compound Na_3X as in this case M_X = (29.3·69/70.7) = 28.6. There is no such element. So, **D** contains some other element(s) too. Oxygen is the most probable element, *i.e.*, **D** is Na_3XO_n (salt **D** cannot have formulae of $Na_3H_mXO_n$ type as all volatiles should be removed under reaction conditions used for synthesis of **D** (heating at 800ºC)). High content of **X** in compound **C** allows one to suppose that **C** is a binary compound, *i.e.*, it is an oxide of **X**. Now we can determine **X**.

Oxide	X_2O	XO	X_2O_3	XO_2	X_2O_5	XO_3	X_2O_7	XO_4
M_X	13.74	27.48	41.22	54.96	68.70	82.43	96.17	109.91

Therefore, **X** is Mn and **C** is MnO_2. From the content of Mn in **D** we derive its formula, Na_3MnO_4. The manganese oxidation state in this compound is +5. Under heating or cooling, the alkaline solution of **D** disproportionates, giving solid MnO_2 and a green solution. Solutions of manganese(VII) derivatives are usually purple but not green. Therefore, the solution contains a salt of manganese (VI). The analogous green solution is formed in the last procedure. We may conclude that this procedure leads to manganate, K_2MnO_4. Indeed, the content of Mn in K_2MnO_4 (compound **E**) is 27.9%.

Compound **B** (a Mn(V) derivative)is obtained by the reaction of **A** with sodium sulfite which is a well-known reducing agent. Heating of the alkaline solution of **A** affords K_2MnO_4. It is possible only if **A** is a Mn(VII) derivative. Indeed, the Mn content in **A** corresponds to the formula of $KMnO_4$. The remaining unknown compound is **B**. Above we supposed that **B** is a hydrate of **D**. Calculations using the formula of $Na_3MnO_4 \cdot nH_2O$ lead to M_B = 413.5. It corresponds to n = 12.5. However, M_B = 381.2 from the Na content. In other words, Na : Mn ratio in **B** is not 3 : 1 but 3.25 : 1. This additional sodium appears due to the presence of some other Na compound(s) in the solvate. To determine this compound, the analysis of the synthetic procedure is required. During the synthesis of **B** solvate is washed with NaOH solution. So, the possible formula of **B** is $Na_3MnO_4 \cdot 0.25NaOH \cdot nH_2O$. From Na and Mn content we conclude that n = 12. Finally, **B** is $[4Na_3MnO_4 \cdot NaOH \cdot 48H_2O]$.

2. Four reactions are discussed in the text. They are:

1) $4\ KMnO_4 + 4\ Na_2SO_3 \cdot 7H_2O + 13\ NaOH + 16\ H_2O = [4Na_3MnO_4 \cdot NaOH \cdot 48H_2O]\downarrow +$
$+ 4\ Na_2SO_4 + 4\ KOH$

$(4KMnO_4 + 4Na_2SO_3 + 13NaOH + 44H_2O = [4Na_3MnO_4 \cdot NaOH \cdot 48H_2O]\downarrow + 4Na_2SO_4 + 4KOH)$

2) $2\ Na_3MnO_4 + 2\ H_2O = Na_2MnO_4 + MnO_2 + 4\ NaOH$

3) $12\ NaOH + 4\ MnO_2 + O_2 = 4\ Na_3MnO_4 + 6\ H_2O$

4) $4\ KMnO_4 + 4\ KOH = 4\ K_2MnO_4 + O_2 + 2\ H_2O$

Problem 7. Simple equilibrium

1. The initial ratio $A_2 : B_2 = 2 : 1$

$$\begin{array}{ccccc} & 2 & & 1 & \\ & A_2 & + & B_2 & = 2AB \\ & x & & x & 2x \\ 2-x & & & 1-x & 2x \end{array}$$

$n(AB) = 2x = n(A_2) + n(B_2) = (2–x) + (1–x)$,

$x = 0.75$

$$K_1 = \frac{n(AB)^2}{n(A_2)n(B_2)} = \frac{1.5^2}{1.25 \cdot 0.25} = 7.2$$

2. The initial ratio $A_2 : B_2 = 1 : 1$

$$\begin{array}{ccccc} & 1 & & 1 & \\ & A_2 & + & B_2 & = 2AB \\ & y & & y & 2y \\ 1-y & & & 1-y & 2y \end{array}$$

$$K_1 = \frac{n(AB)^2}{n(A_2)n(B_2)} = \frac{(2y)^2}{(1-y) \cdot (1-y)}$$

The ratio of heteronuclear to homonuclear molecules:

$$\frac{n(AB)}{n(A_2) + n(B_2)} = \frac{2y}{(1-y) + (1-y)} = \frac{y}{1-y} = \sqrt{\frac{K_1}{4}} = 1.34$$

3. New equilibrium constant: $K_2 = K_1 / 2 = 3.6$.

Equilibrium amounts: $n(AB) = 1.5$ mol, $n(A_2) = 1.25$ mol, $n(B_2) = 0.25+x$ mol,

$$K_2 = \frac{1.5^2}{1.25 \cdot (0.25 + x)} = 3.6,$$

$x = 0.25$ mol = 25% of initial amount of B_2 should be added.

4. Consider two initial mixtures: $A_2 : B_2 = x : 1$ and $A_2 : B_2 = 1/x : 1 = 1 : x$. It is clear that in both cases the equilibrium yield is the same, hence $\eta(x) = \eta(1/x)$. The value $x = 1$ for such functions is the extremum point. We can prove it in the following way. Consider the identity:

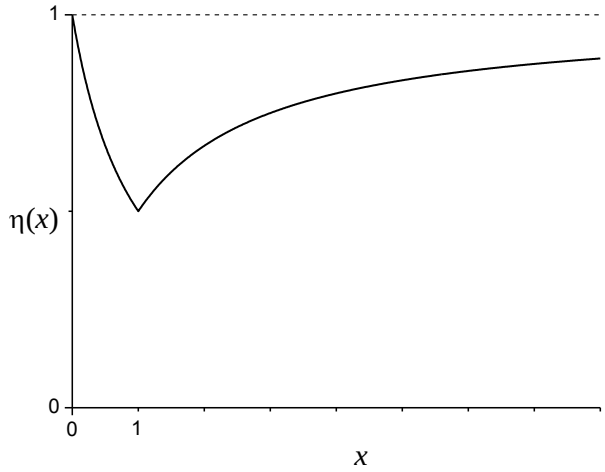
$$\eta(1) - \eta(x) = \eta(1) - \eta\left(\frac{1}{x}\right)$$

near the point $x = 1$. If $\eta(x)$ is an increasing or decreasing function at $x = 1$, then near this point both sides of the identity will have opposite signs. Hence, either $\eta(x) = \text{const}$ (which is chemical nonsense), or $x = 1$ is the point of extremum.

5. a) At $x \to \infty$ the very large amount of A_2 will almost completely shift the equilibrium $A_2 + B_2 = 2AB$ to the right, and almost all B_2 will be converted to AB, the yield will tend to 1, $\eta(x \to \infty) \to 1$.

b) At $x \to 0$ ($1/x \to \infty$) the situation is the same as in (a) if we interchange A_2 and B_2, that is $\eta(x \to 0) \to 1$.

6. From question 5 it follows that at $x = 1$ the function $\eta(x)$ has a minimum, because at $x = 0$ or $x = \infty$ it approaches the maximum possible value of 1. Qualitatively, the graph is as follows:



7. Suppose we have in total 1 mol of A_2 and B_2, and the molar ratio $A_2 : B_2 = x : 1$. Then, the initial amounts of reagents are: $n(A_2) = x/(x+1)$, $n(B_2) = 1/(x+1)$. It follows from the symmetry between A_2 and B_2 that the equilibrium amount of AB will be the same for the molar ratios x and $1/x$, hence $x = 1$ corresponds to the maximum or minimum $n_{eq}(AB)$.

If x is very large (small), then the initial amount of B_2 (A_2) will be small and so will be $n_{eq}(AB)$. Therefore, the maximum amount of AB will be obtained at $A_2 : B_2 = 1 : 1$. The equilibrium calculation for this case is as follows.

$$\begin{array}{ccccc} & 0.5 & 0.5 & & \\ & A_2 & + B_2 & = & 2AB \\ & y & y & & 2y \\ & 0.5-y & 0.5-y & & 2y \end{array}$$

$$K = \frac{n(\mathrm{AB})^2}{n(\mathrm{A_2})n(\mathrm{B_2})} = \frac{(2y)^2}{(0.5-y)^2}$$

$$y = \frac{\sqrt{K}}{4+2\sqrt{K}}$$

$$n_{\mathrm{eq}}(\mathrm{AB}) = \frac{\sqrt{K}}{2+\sqrt{K}}$$

Problem 8. Copper sulfate and its hydrates

1. $CuSO_4 \cdot 5H_2O$.

2. The Clausius-Clapeyron equation for the decomposition of a solid hydrate:

$$CuSO_4 \cdot 5H_2O_{(s)} = CuSO_4 \cdot 3H_2O_{(s)} + 2H_2O_{(g)}$$

has the form:

$$\frac{dp_h}{dT} = \frac{\Delta H_d}{T\Delta V} \approx \frac{p_h \Delta H_d}{2RT^2},$$

where p_h is the vapor pressure of water over the hydrate, ΔH_d is the enthalpy of decomposition. The solution of this equation is:

$$p_h = p_{h0} \exp\left(\frac{\Delta H_d}{2R}\left(\frac{1}{T_0} - \frac{1}{T}\right)\right),$$

where p_{h0} = 1047 Pa is the saturated vapor pressure over $CuSO_4 \cdot 5H_2O$ and T_0 = 298K. Enthalpy of decomposition of $CuSO_4 \cdot 5H_2O$ is: $\Delta H_d = 2 \cdot (-241.83) - 1688.7 + 2277.4 = 105.04$ kJ·mol^{-1}.

The similar equation describes the temperature dependence of the vapor pressure of water p_w:

$$p_w = p_{w0} \exp\left(\frac{\Delta H_{\mathrm{vap}}}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right)\right).$$

The enthalpy of vaporization of water is: $\Delta H_{\mathrm{vap}} = -241.83 + 285.83 = 44.0$ kJ·mol^{-1}. The humidity is the ratio of two vapor pressures:

$$\frac{p_h}{p_w} = \frac{p_{h0}}{p_{w0}} \exp\left(\frac{\Delta H_d / 2 - \Delta H_{\mathrm{vap}}}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right)\right) = 0.35.$$

From this equation we find the required temperature:

$$\frac{1}{T} = \frac{1}{T_0} - \frac{R}{\Delta H_d / 2 - \Delta H_{\text{vap}}} \ln \frac{0.35 p_{w0}}{p_{h0}} = \frac{1}{298} - \frac{8.314}{(105.04/2 - 44)\cdot 10^3} \ln \frac{0.35 \cdot 3200}{1047} = 0.00329$$

$$T_0 = \frac{1}{0.00329} = 304 \text{ K} \text{ or } 31 \text{ °C.}$$

3. b)

4. After several repetitions of the procedure, the equilibrium is established between the anhydrous copper sulfate and its monohydrate: $CuSO_4 \cdot H_2O = CuSO_4 + H_2O$. In this case the saturated vapor pressure of water over its solution in ethanol is equal to the saturated vapor pressure of water over $CuSO_4 \cdot H_2O$. Thus, $p_h = p_w \gamma x$, $x = \frac{p_h}{p_w \gamma} = 0.0136$, the mass fraction of water is:

$$w(\text{H}_2\text{O}) = \frac{xM(\text{H}_2\text{O})}{xM(\text{H}_2\text{O}) + (1-x)M(\text{C}_2\text{H}_5\text{OH})} = 0.0054, \text{ or } 0.54\%.$$

5. Enthalpy of decomposition of $CuSO_4 \cdot H_2O$ is: $\Delta H_d = -241.83 - 770.4 + 1084.4 = 72.17$ kJ·mol^{-1}. From the equations above it follows that:

$$x = \frac{p_h}{p_w \gamma} = \frac{p_{h0}}{\gamma p_{w0}} \exp\left(\frac{\Delta H_d - \Delta H_{\text{vap}}}{R} \left(\frac{1}{T_0} - \frac{1}{T} \right) \right).$$

At T = 273 K, x = 0.0048, w = 0.19 %; at T = 313 K x = 0.0235, w = 0.93 %.

Problem 9. TOF and TON

1. The *TOF* unit is {time^{-1}}. SI unit for *TOF* is {s^{-1}}.

TOF relates to *TON* by the equation

$$TOF \times t = TON,$$

where t is the time till the moment of inactivation of a catalyst. The formula gives the upper limit for *TON*. It assumes that the catalyst works with its best efficiency (*TOF*) all the time and becomes inactivated suddenly, in a moment. It is more realistic to assume that *TOF* goes down gradually. Then the following relation is valid:

$$TOF \times t \geq TON.$$

2. a) *TOF* is a maximum value of

$$\frac{\Delta N_{\mathrm{B}}}{\Delta t \cdot 10^{15}} \qquad (1)$$

Maximum of $\Delta N_{\mathrm{B}}/\Delta t$ corresponds to the initial linear part of the curve in Fig. 1a and is equal to

$$\frac{\Delta N_{\mathrm{B}}}{\Delta t} = \tan\alpha = \left(\frac{7}{2}\right)\cdot 10^{-8}\ \ \frac{\mathrm{mol}}{\mathrm{cm}^2\cdot\mathrm{s}} = 21\cdot 10^{15}\ \ \frac{\mathrm{molec}}{\mathrm{cm}^2\cdot\mathrm{s}}$$

TOF is equal to

$$TOF = \frac{\Delta N_{\mathrm{B}}}{\Delta t \cdot 10^{15}} = 21$$

b) There are several curves in Fig. 1b. It is obvious that the value of $\Delta N_{\mathrm{B}}/\Delta t$ for the initial linear parts of the curves goes up with the increase of the initial pressures of the reagent A. However for curves (10) and (11) the initial slopes $\Delta N_{\mathrm{B}}/\Delta t$ are the same. It means that the maximum efficiency of the catalyst is achieved. Now $\Delta N_{\mathrm{B}}/\Delta t$ is independent of the reagent pressure and no more A can be converted into products per unit of time per catalytic site. The initial slopes of the curves (10) and (11) should be used to calculate *TOF* and *TON*

$$\frac{\Delta N_{\mathrm{B}}}{\Delta t \cdot 10^{15}} = 210\ \mathrm{s}^{-1}; \qquad TON \le TOF \times t = 210\cdot 40\cdot 60 = 5\cdot 10^{5}$$

3. a) The slope of the linear dependence in Fig. 2a should be used to calculate *TOF*:

$$TOF = \tan\alpha = 6\mathrm{s}^{-1}$$

It is assumed that every single atom of the metal forms a catalytic site and works independently. *TOF* is independent of the amount of atoms deposited.

b) In this case a group of *n* atoms, rather than a single atom, forms a catalytic site. The number of catalytic sites is

$$k = \frac{N_{\mathrm{B}}}{TOF} = \frac{18\cdot 6.02\cdot 10^{23}\cdot 10^{-11}}{35} = 3.1\cdot 10^{12}\ \mathrm{molec/cm}^2,$$

and the number of atoms *n* in one catalytic site is equal to:

$$n = \frac{N_{\mathrm{Cat}}}{k} = \frac{N_{\mathrm{Cat}}}{N_{\mathrm{B}}} TOF = \frac{7\cdot 10^{12}}{3.1\cdot 10^{12}} = 2.2 \approx 2$$

4) The authors of this study considered every single Au atom to be a catalytic site. One has to calculate the number of Au atoms involved in the catalytic process in Fig. 3a and 3b. In the case (b), all yellow spheres are taking part in the reaction. In the case (a), 1/3 of the yellow spheres from the lower monolayer are involved together with all red spheres. 2/3 of the yellow

spheres are blocked by the red spheres from the top and do not participate in the catalytic reaction.

Let N_{Au} be the number of the yellow spheres in Fig. 3b. The number of the red spheres in Fig. 3a is equal to 1/3 N_{Au}. The total number of Au atoms involved in catalytic reaction in Fig. 3a is 1/3 N_{Au}(red) + 1/3 N_{Au} (yellow). The rate of the reaction in case (a) is:

$$r_2 = 4r_1 = r_2(\text{red}) + \frac{1}{3}r_1,$$

where r_2(red) and $1/3r_1$ are partial rates for the red and yellow spheres, respectively.

Finally, $$\frac{TOF(\text{a})}{TOF(\text{b})} = \frac{4r_1 - \frac{1}{3}r_1}{\frac{1}{3}N_{Au}} : \frac{r_1}{N_{Au}} = \frac{3(11/3r_1)}{r_1} = 11$$

Problem 10. Kinetic puzzles

Below are given the mechanisms of these reactions, established by various experimental methods. However, the limited data given in the text of a problem allow multiple mechanisms. Therefore the only two criteria for the correct solutions are: 1) the consistency of the mechanism with the rate law; 2) the chemical sense.

1. The schematic mechanism is:

$2H^+ + Br^- + MnO_4^- \leftrightarrow H_2MnO_4Br$	K	fast
$H_2MnO_4Br + H^+ + Br^- \rightarrow H_3MnO_4 + Br_2$	k	limiting
$H_3MnO_4 \rightarrow$ products		fast

At low concentrations of proton and bromide the equilibrium of the first reaction is shifted to the left, hence the concentration of the complex H_2MnO_4Br is

$$[H_2MnO_4Br] = K[MnO_4^-][Br^-][H^+]^2 \approx Kc(MnO_4^-)c(Br^-)c^2(H^+)$$

At high concentrations of proton and bromide the equilibrium of the first reaction is shifted to the right, hence the concentration of complex H_2MnO_4Br equals the total concentration of permanganate:

$$[H_2MnO_4Br] \approx c(MnO_4^-)$$

The rate of the reaction

$$2MnO_4^- + 10Br^- + 16H^+ = 2Mn^{2+} + 5Br_2 + 8H_2O$$

is half of that of the rate-determining step:

$$r = ½\ k[H_2MnO_4Br][H^+][Br^-]$$

in the case (a)

$$r = ½\ k[H_2MnO_4Br][H^+][Br^-] \approx k_{eff}c(MnO_4^-)c^2(Br^-)c^3(H^+)$$

where $k_{eff} = ½\ kK$.

In the case (b)

$$r = ½\ k[H_2MnO_4Br][H^+][Br^-] \approx k_{eff}c(MnO_4^-)c(Br^-)c(H^+)$$

where $k_{eff} = ½\ k$.

2. The catalytic effect of silver is due to formation of silver(II) ions and sulfate ion radicals upon reaction of Ag^+ with persulfate. The mechanism is:

$Ag^+ + S_2O_8^{2-} \rightarrow \cdot SO_4^- + SO_4^{2-} + Ag^{2+}$	slow, rate-determining
$\cdot SO_4^- + PhCONH_2 \rightarrow$ products	fast
$Ag^{2+} + PhCONH_2 \rightarrow$ products	fast

The first reaction is the rate-determining step; therefore the overall oxidation reaction has the same order as the rate-determining step:

$$r = k[Ag^+][S_2O_8^{2-}]$$

3. The minimal mechanism includes the following steps:

$S_2O_8^{2-} \rightarrow 2\cdot SO_4^-$	k_1	very slow
$HCOO^- + \cdot SO_4^- \rightarrow H^+ + \cdot CO_2^- + SO_4^{2-}$	k_2	fast
$\cdot CO_2^- + S_2O_8^{2-} \rightarrow \cdot SO_4^- + CO_2 + SO_4^{2-}$	k_3	fast
$\cdot CO_2^- + \cdot SO_4^- \rightarrow SO_4^{2-} + CO_2$	k_4	fast

The second and the third reaction make a chain process involving consumption of peroxydisulfate and formate. The first reaction is very slow, so most of peroxydisulfate is consumed in the third reaction. Applying the steady-state approximation to $\cdot SO_4^-$ and $\cdot CO_2^-$ we get:

$$2r_1 - r_2 + r_3 - r_4 = 0$$

$$r_2 - r_3 - r_4 = 0$$

Hence

$$r_1 = r_4$$

$$r_2 - r_3 = r_1$$

Since the rate of the first reaction is very low, then

$$r_1 = r_4$$

$$r_2 = r_3$$

Applying the rate laws we get:

$$k_1[S_2O_8^{2-}] = k_4[\cdot CO_2^-][\cdot SO_4^-]$$

$$k_2[HCOO^-][\cdot SO_4^-] = k_3[\cdot CO_2^-][S_2O_8^{2-}]$$

Hence

$$[\cdot CO_2^-] = (k_1k_2)^{1/2}(k_3k_4)^{-1/2}[HCOO^-]^{1/2}$$

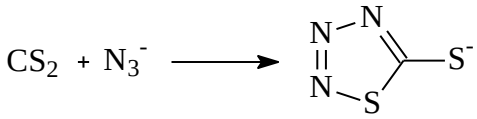
$$[\cdot SO_4^-] = (k_1k_3)^{1/2}(k_2k_4)^{-1/2}[S_2O_8^{2-}][HCOO^-]^{-1/2}$$

The rate of the reaction is equal to the rate of formate consumption:

$r = r_2 = k_2[HCOO^-][\cdot SO_4^-] = (k_1k_2k_3)^{1/2}k_4^{-1/2}[HCOO^-]^{1/2}[S_2O_8^{2-}] = k_{eff}[HCOO^-]^{1/2}[S_2O_8^{2-}]$

A more complex mechanism includes the formation of OH radicals and several chain termination reactions. That's why the given rate law is valid only for a limited range of reactant concentrations.

4. The rate-determining step is the addition of azide ion to the solvent, carbon disulfide:



The oxidation of this ion by iodine is a series of fast reactions. The overall rate of the reaction

$$I_2 + 2N_3^- = 3N_2 + 2I^-$$

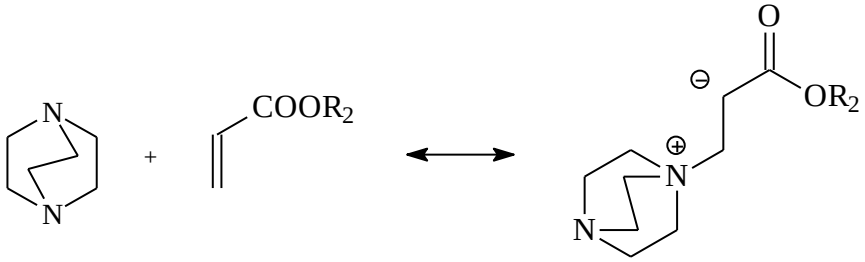
is half of that of the azide-CS_2 reaction:

$$r = ½\ k[N_3^-][CS_2].$$

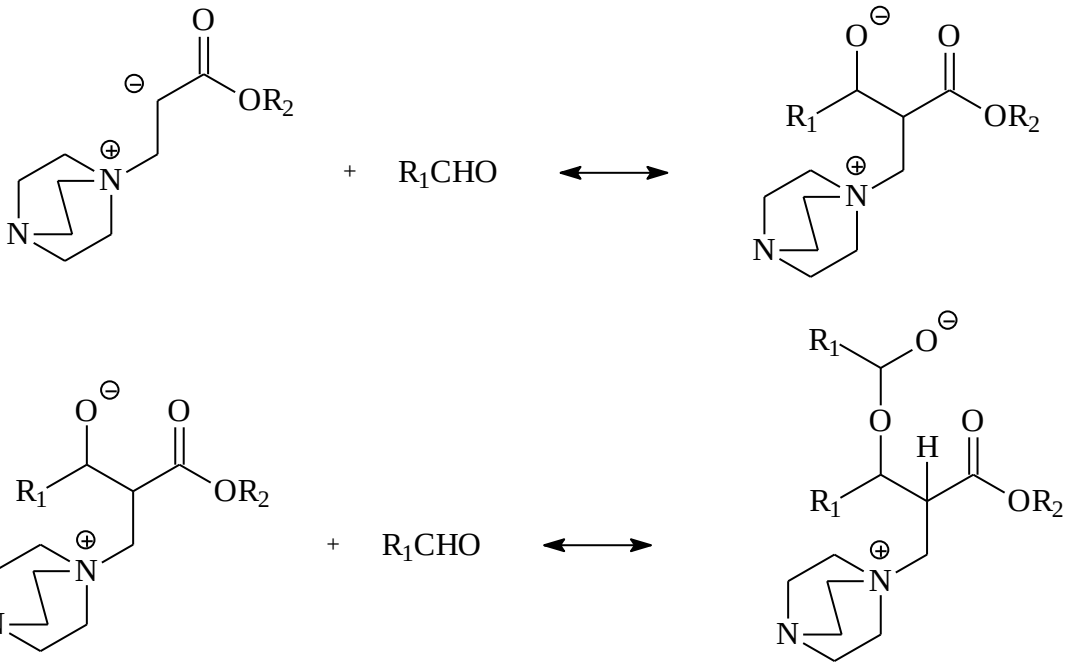
Introducing the effective constant $k_{eff} = ½\ k[CS_2]$ we get:

$$r = k_{eff}[N_3^-].$$

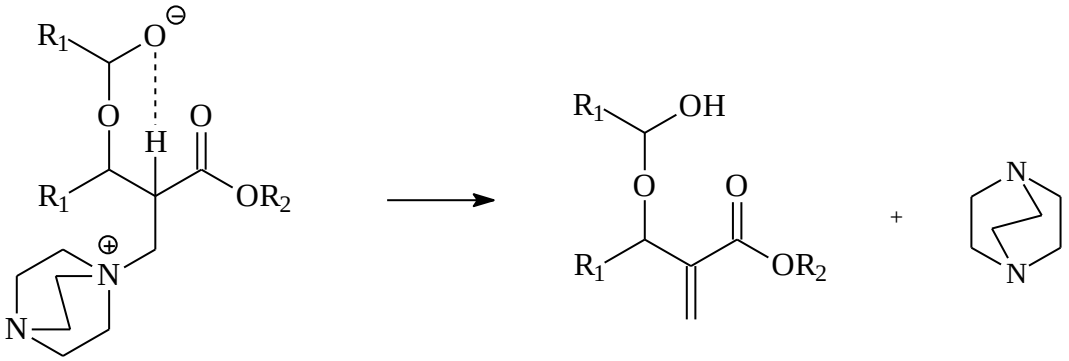
5. The reaction mechanism includes several steps. The first step is the reversible addition of DABCO to ester:



The next two steps are the reversible additions of two molecules of aldehyde to the zwitter ion formed in the previous step:



The rate-determining step is an intramolecular proton transfer followed by the elimination of DABCO:

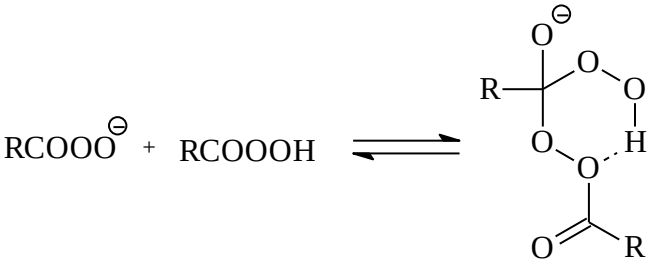


After that, the product rapidly eliminates one molecule of aldehyde. Applying quasi-equilibrium conditions to the first three steps, we get:

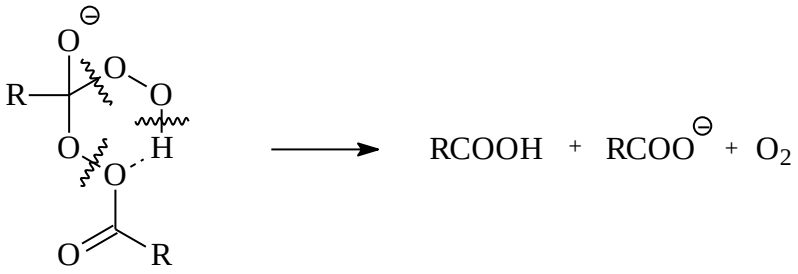
$$r = k_{RDS}K_1K_2K_3[\text{aldehyde}]^2[\text{ester}][\text{DABCO}] = k_{eff}[\text{aldehyde}]^2[\text{ester}][\text{DABCO}]$$

It is worth mentioning that in protic solvents the rate-determining step is the solvent-assisted proton transfer in DABCO-ester-aldehyde adduct, hence the reaction order is one with respect to either aldehyde, or ester or base.

6. The first step of the reaction is the reversible addition of peroxyacid anion to the carboxylic group of peroxyacid:



The next, rate-determining step is a decomposition of the addition product:



Applying a quasi-equilibrium approximation, we get:

$$r = k_{\text{eff}}[\text{RCO}_3\text{H}]\,[\text{RCO}_3^-]$$

The concentrations of peroxyacid and its anion are related to the total concentration of peroxy compound $c(\text{RCO}_3\text{H})$ and proton concentration $[\text{H}^+]$ as follows:

$$\left[\text{RCO}_3\text{H}\right] = \frac{\left[\text{H}^+\right]}{K_a + \left[\text{H}^+\right]} c\left(\text{RCO}_3\text{H}\right) \qquad \left[\text{RCO}_3^-\right] = \frac{K_a}{K_a + \left[\text{H}^+\right]} c\left(\text{RCO}_3\text{H}\right),$$

where K_a is the acidity constant of peroxyacid. Substituting these concentrations to the rate law we obtain:

$$r = c^2\left(\text{RCO}_3\text{H}\right)\frac{k_{eff} K_a \left[\text{H}^+\right]}{\left(K_a + \left[\text{H}^+\right]\right)^2} = c^2\left(\text{RCO}_3\text{H}\right)\frac{k_1\left[\text{H}^+\right]}{\left(k_2 + \left[\text{H}^+\right]\right)^2}$$

Note that at given $c(\text{RCO}_3\text{H})$ the reaction rate is maximum if $[\text{RCO}_3\text{H}] = [\text{RCO}_3^-]$ (and $[\text{H}^+] = K_a$).

Problem 11. Black box

Since this is a reactor with ideal stirring, the concentrations of substances in the output flow are equal to the concentrations inside the reactor. In a stationary state, the concentrations and quantities of substances in the reactor are constant. Consider the material balance with respect to X, Y and P.

Stationary conditions are:

$$\frac{\Delta \nu_{X,R}}{\Delta t} = 0 \qquad \frac{\Delta \nu_{Y,R}}{\Delta t} = 0 \qquad \frac{\Delta \nu_{P,R}}{\Delta t} = 0, \tag{1}$$

where $\Delta\nu_{X,R}$, $\Delta\nu_{Y,R}$, $\Delta\nu_{P,R}$ are the changes of the quantities for the substances X, Y and P in the reactor during time Δt. The quantity of the substance in the reactor may change due to input flow, chemical reaction, and output flow:

$$\frac{\Delta \nu_{X,R}}{\Delta t} = \left(\frac{\Delta \nu_{X,R}}{\Delta t}\right)_{input} + \left(\frac{\Delta \nu_{X,R}}{\Delta t}\right)_{reaction} + \left(\frac{\Delta \nu_{X,R}}{\Delta t}\right)_{output} \tag{2}$$

The same is true for Y and P.

Input flow rates of the substances are

$$\left(\frac{\Delta \nu_{X,R}}{\Delta t}\right)_{input} = f_X c_{X,I} \quad \left(\frac{\Delta \nu_{Y,R}}{\Delta t}\right)_{input} = f_Y c_{Y,I} \quad \left(\frac{\Delta \nu_{P,R}}{\Delta t}\right)_{input} = 0, \tag{3}$$

where f_X and f_Y are the input volumetric flows of the solutions of X and Y, $c_{X,I}$ and $c_{Y,I}$ – concentrations of X and Y in the respective solutions.

Let the balanced reaction equation be

$$n_X\,X + n_Y\,Y = n_P\,P$$

where n_X, n_Y and n_P are the stoichiometric coefficients for the corresponding substances. Due to a chemical reaction the quantities of the substances in the reactor change with the rates

$$\left(\frac{\Delta \nu_{X,R}}{\Delta t}\right)_{reaction} = -n_X r V_R \qquad \left(\frac{\Delta \nu_{Y,R}}{dt}\right)_{reaction} = -n_Y r V_R \qquad \left(\frac{\Delta \nu_{P,R}}{\Delta t}\right)_{reaction} = n_P r V_R, \tag{4}$$

where r – the reaction rate, V_R – the reactor volume.

The output flows of the substances are:

$$\left(\frac{\Delta \nu_{X,R}}{\Delta t}\right)_{output} = f_O c_{X,R} \quad \left(\frac{\Delta \nu_{Y,R}}{\Delta t}\right)_{output} = f_O c_{Y,R} \quad \left(\frac{\Delta \nu_{P,R}}{\Delta t}\right)_{output} = f_O c_{P,R}, \tag{5}$$

where f_O is the volumetric output flow, $c_{X,R}$, $c_{Y,R}$ and $c_{P,R}$ – the concentrations of substances X, Y and P in the reactor. Since the process is stationary and the reaction proceeds in the liquid phase, the output volumetric flow equals the sum of input volumetric flows:

$$f_O = f_X + f_Y \tag{6}$$

Thus the material balance equations (2) considering expressions (1) and (3)-(6) are

$$\frac{\Delta \nu_{X,R}}{\Delta t} = f_X c_{X,I} - n_X r V_R - c_{X,R}\left(f_X + f_Y\right) = 0$$

$$\frac{\Delta \nu_{Y,R}}{\Delta t} = f_Y c_{Y,I} - n_Y r V_R - c_{Y,R}\left(f_X + f_Y\right) = 0$$

$$\frac{\Delta \nu_{P,R}}{\Delta t} = n_P r V_R - c_{P,R}\left(f_X + f_Y\right) = 0$$

Hence

$$n_X r V_R = f_X c_{X,I} - c_{X,R}\left(f_X + f_Y\right)$$

$$n_Y r V_R = f_Y c_{Y,I} - c_{Y,R}\left(f_X + f_Y\right)$$

$$n_P r V_R = c_{P,R}\left(f_X + f_Y\right)$$

Exp. no.	$n_X r V_R$, mol/s	$n_Y r V_R$, mol/s	$n_P r V_R$, mol/s	n_X:n_Y:n_P
1	10.02	20.04	10.02	1:2:1
2	10.04	20.07	10.05	1:2:1
3	15.73	31.47	15.72	1:2:1
4	19.68	39.34	19.68	1:2:1

Hence the balanced reaction equation is

$$X + 2Y = P$$

Now consider the rate dependence on concentrations

Exp. no.	$c_{X,R}$, mol/m^3	$c_{Y,R}$, mol/m^3	$c_{P,R}$, mol/m^3	$r V_R$, mol/s
1	299	48.2	501	10.02
2	732	30.9	335	10.04
3	8.87	351	524	15.73
4	308	66.6	492	19.68

The rate law is

$$r = k c_{X,R}^x c_{Y,R}^y c_{P,R}^p$$

or, after multiplying by reactor volume,

$$r V_R = k V_R c_{X,R}^x c_{Y,R}^y c_{P,R}^p$$

Take the logarithm of both parts of the equation

$$\ln\left(r V_R\right) = \ln\left(k V_R\right) + x \ln c_{X,R} + y \ln c_{Y,R} + p \ln c_{P,R} \qquad (7)$$

The coefficients in this equation are given in the table below:

Exp. no.	$\ln c_{X,R}$	$\ln c_{Y,R}$	$\ln c_{P,R}$	$\ln(r V_R)$
1	5.70	3.88	6.22	2.30
2	6.60	3.43	5.81	2.31
3	2.18	5.86	6.26	2.76
4	5.73	4.20	6.20	2.98

Solving the system of equations (7) we get:

$x = 1.00$ $y = 2.00$ $p = 0.01$ $\ln(kV_R) = -11.20$

Hence the orders of the reaction are one in X, two in Y, and zero in P. The product kV_R is:

$$kV_R = \exp(-11.20) = 1.37 \cdot 10^{-5}\ \mathrm{m^9 mol^{-2} s^{-1}}.$$

One of the possible mechanisms that match the obtained rate law is:

$X + Y \leftrightarrow I$	fast
$I + Y \rightarrow P$	slow, rate-determining

Summarizing, the obtained results are:

- the reaction equation: X + 2Y = P;
- the reaction orders: 1, 2, and 0 with respect to X, Y, and P respectively;
- the product of the rate constant and reactor volume: $kV_R = 1.37 \cdot 10^{-5}\ \mathrm{m^9 \cdot mol^{-2} \cdot s^{-1}}$.

Problem 12. Chlorination of styrenes

1. Since all reaction pathways obey the same rate law, the quantity of the product is proportional to the respective rate constant. The overall constant equals the sum of constants for different pathways. Hence

for 1,2-dichloro:

$$k = 1.45 \cdot 10^4 \frac{61\%}{100\%} = 8.8 \cdot 10^3\ \mathrm{M^{-1} s^{-1}}$$

for 1-acetoxy-2-dichloro:

$$k = 1.45 \cdot 10^4 \frac{30\%}{100\%} = 4.4 \cdot 10^3\ \mathrm{M^{-1} s^{-1}}$$

for 2-chlorostyrene:

$$k = 1.45 \cdot 10^4 \frac{9\%}{100\%} = 1.3 \cdot 10^3\ \mathrm{M^{-1} s^{-1}}$$

2. This reaction is not stereospecific and leads to the formation of diastereomeric addition products in comparable amounts. The following products are obtained (approximate ratios of product quantities at 25°C are given as an illustration):

1,2-dichloro:

enantiomers ~1:3 enantiomers

1-acetoxy-2-chloro:

enantiomers ~1:1 enantiomers

2-chlorostyrene:

~1:3

The achiral sorbent is unable to separate enantiomers, so only 6 different fractions can be obtained. The chiral sorbent allows full separation, so in this case the determined number of products is 10.

Problem 13. The dense and hot ice

1. The boiling point of water and the melting point of ice V increase, and the melting point of ordinary ice decreases with the increasing pressure. This can be easily explained using the Le Chatelier principle. In the phase transitions

$$H_2O_{(l)} \rightleftarrows H_2O_{(g)}$$

and

$$H_2O_{(ice,V)} \rightleftarrows H_2O_{(l)}$$

the volume increases and heat is absorbed ($\Delta V > 0$, $\Delta H > 0$). Hence, with the increasing pressure both equilibria are shifted to the left; consequently, temperature should be increased to keep the equilibria.

In the phase transition

$$H_2O_{(ice,I)} \rightleftarrows H_2O_{(l)}$$

the volume decreases and heat is absorbed ($\Delta V < 0$, $\Delta H > 0$). Hence, with the increasing pressure the phase equilibrium is shifted to the right, and temperature should be decreased to keep the equilibrium.

2. a) 250 K: vapor → ice I → ice III → ice V → ice VI

b) 400 K: vapor → liquid → ice VII

c) 700 K: only vapor (at high pressure it may be called "supercritical fluid"), no phase transitions occur.

3. Phase transitions between condensed phases are described by the Clapeyron equation:

$$\frac{dp}{dT} = \frac{\Delta H}{T\Delta V},$$

or, in approximate form:

$$\frac{\Delta p}{\Delta T} = \frac{\Delta H}{T\Delta V}.$$

We calculate the right side of this equation for the ice I $\rightleftarrows$ water transition. The volume change is determined from the densities:

$$\Delta V = V(\text{water}) - V(\text{ice}) = \frac{M(H_2O)}{\rho(\text{water})} - \frac{M(H_2O)}{\rho(\text{ice})} = \frac{18}{1.000} - \frac{18}{0.917} = -1.63 \text{ cm}^3/\text{mol}$$

$$\frac{\Delta p}{\Delta T} = \frac{\Delta H}{T\Delta V} = \frac{6010 \text{ J/mol}}{273 \text{ K} \cdot (-1.63 \cdot 10^{-6} \text{ m}^3/\text{mol})} = -1.35 \cdot 10^7 \text{ Pa/K} = -13.5 \text{ MPa/K}.$$

If this slope does not depend on pressure and temperature then at the pressure of 210 MPa the temperature of liquid water in equilibrium with ice I and Ice III is approximately:

$$T = 273 + \Delta T = 273 + \frac{210 - 0.1}{-13.5} = -257.5 \text{ K} = -15.5 \text{ °C}.$$

This is an estimate; the real value is –22 °C. The difference between the estimated and real values is due to the fact that the enthalpy of fusion and densities vary with pressure. For example, at 210 MPa the enthalpy of fusion of ice I is 4230 J/mol (instead of 6010 at normal pressure), and the volume change is ΔV = –2.43 cm^3/mol (instead of –1.63 cm^3/mol at normal pressure).

4. From the Clapeyron equation it follows that the slope of the $p(T)$ dependencies for the melting points of ice III to ice VII is determined by ΔH, T, and ΔV. The first quantity is assumed to be the same for all transitions, the temperature is comparable in all cases, hence the main contribution to the slope comes from ΔV. For ice VII, the slope is the smallest, hence, the $\Delta V = V(\text{water}) - V(\text{ice})$ is the largest, whereas V(ice) is the smallest. It means that ice VII is the densest form of ice (among those forms that are shown on the phase diagram).

From the phase diagram we see that the melting point of ice VII at a pressure of 10 GPa is about 630 K. This is, indeed, a very "hot" ice.

5. Determine the molar volume of ice VII. One mole contains $N_A/2$ cubic unit cells:

$$V_m = \frac{N_A}{2} d^3 = 3.01 \cdot 10^{23} \cdot (0.335 \cdot 10^{-7})^3 = 11.3 \text{ cm}^3/\text{mol}.$$

The density of ice VII is:

$$\rho = M / V_m = 18 / 11.3 = 1.59 \text{ g/cm}^3.$$

6. Knowing the density of ice VII, we use the Clapeyron equation to estimate its enthalpy of fusion. Comparing the triple point "water – ice VI – ice VII" and the melting point of ice VII at pressure 10 GPa we estimate the slope: $\Delta p / \Delta T = (10^4 - 2200) / (630 - 355) = 28$ MPa / K. The volume change during melting is: $\Delta V = (18/1.00) - 11.3 = 6.7$ cm^3/mol. Substituting these data into the Clapeyron equation, we get:

$$\Delta H = T \Delta V \frac{\Delta p}{\Delta T} = 355 \text{ K} \cdot (6.7 \cdot 10^{-6} \text{ m}^3/\text{mol}) \cdot (28 \cdot 10^6 \text{ Pa/K}) = 66000 \text{ J/mol}.$$

This value is by an order of magnitude larger than the exact value 6400 J/mol. The reason is probably due to a low resolution of the phase diagram at high pressures, which leads to a rough estimate of the slope. This result also shows that the approximations used are not valid at high pressures and temperatures.

Problem 14. Redox reactions in photosynthesis

1. Applying the Nernst equation for a half-reaction

$$\text{Ox} + m\text{H}^+ + ne \rightarrow \text{R}$$

and putting $[\text{H}^+] = 10^{-7}$, we get a standard biochemical redox potential:

$$E^{\circ\prime} = E^\circ + \frac{0.0591}{n} \lg\left(10^{-7}\right)^m = E^\circ - 0.414 \frac{m}{n}$$

Half-reaction	$E°$ (V)	$E°'$ (V)
$O_2 + 4H^+ + 4e \rightarrow 2H_2O$	1.23	0.82
$S + 2H^+ + 2e \rightarrow H_2S$	0.14	–0.27
Plastoquinone $+ 2H^+ + 2e \rightarrow$ Plastoquinone·H_2	0.52	0.11
Cytochrome f(Fe^{3+}) $+ e \rightarrow$ Cytochrome f(Fe^{2+})	0.365	0.365
$NADP^+ + H^+ + 2e \rightarrow$ NADP·H	–0.11	–0.32
$P680^+ + e \rightarrow P680$	1.10	1.10
Chlorophyll$^+ + e \rightarrow$ Chlorophyll	0.78	0.78

2. The standard electromotive force for the reaction

$$H_2O + CO_2 \rightarrow CH_2O + O_2$$

is the difference between standard redox potentials for oxidant and reductant.

$CO_2 + 4H^+ + 4e \rightarrow CH_2O + H_2O$ $\qquad E_1^\circ$

$O_2 + 4H^+ + 4e \rightarrow 2H_2O$ $\qquad E_2^\circ = 1.23$ V

For this reaction, the standard Gibbs energy is 480.5 kJ/mol, and 4 electrons are transferred from H_2O to CO_2. Hence, the standard emf is:

$$E^\circ = -\frac{\Delta G^\circ}{nF} = -\frac{480500}{4 \cdot 96500} = -1.24 \text{ V} = E_1^\circ - 1.23 \text{ V}$$

For CO_2 reduction to carbohydrates the standard redox potential is $E_1^\circ = -0.01$ V. The standard biochemical potential is: $E_1^{\circ\prime} = -0.01 - 0.414\frac{4}{4} = -0.42$ V.

3. The overall reaction: $CO_2 + 2H_2S \rightarrow CH_2O + 2S + H_2O$

Oxidation: $H_2S - 2e \rightarrow S + 2H^+$

Reduction: $CO_2 + 4H^+ + 4e \rightarrow CH_2O + H_2O$

Standard emf: $E° = –0.01 – 0.14 = –0.15$ V

Standard Gibbs energy: $\Delta G^\circ = -nFE^\circ = -4 \cdot 96500 \cdot (-0.15) \cdot 10^{-3} = 57.9$ kJ/mol.

Energy of light with wavelength 840 nm:

$$E_m = \frac{hcN_A}{\lambda} = \frac{6.63 \cdot 10^{-34} \cdot 3.00 \cdot 10^8 \cdot 6.02 \cdot 10^{23}}{840 \cdot 10^{-9}} \cdot 10^{-3} = 143 \text{ kJ/mol.}$$

One quantum gives enough energy to oxidize two molecules of H_2S.

4. Both $NADP^+$ reduction and ATP formation require one proton, and during H_2O oxidation two protons are released. Hence, the overall reaction equation of light stages is:

$$NADP^+ + ADP + P_i + h\nu \rightarrow ½\ O_2 + NADP{\cdot}H + ATP$$

(water is not present in this reaction, because the number of H_2O molecules oxidized to O_2 is equal to the number of H_2O molecules formed during ADP phosporylation).

5. The overall reaction is the sum of two reactions:

$$H_2O + NADP^+ + h\nu \rightarrow ½\ O_2 + NADP{\cdot}H + H^+$$

and

$$ADP + P_i + H^+ \rightarrow ATP + H_2O.$$

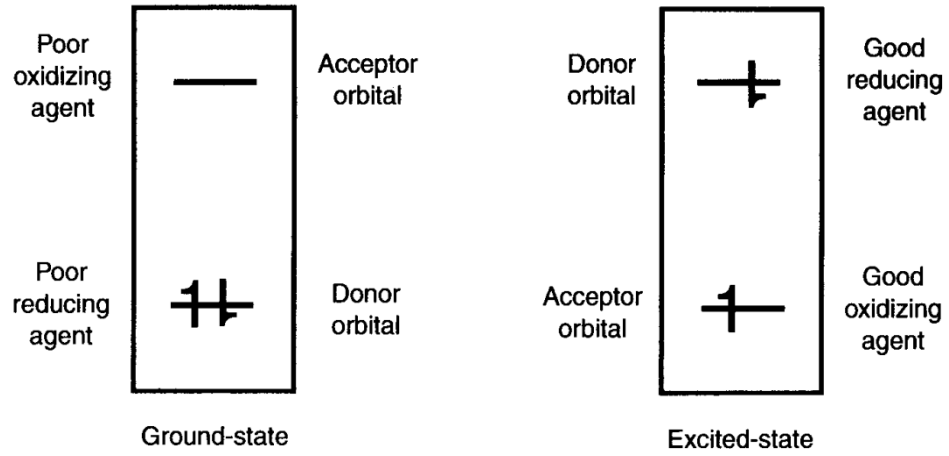
For the latter, the standard biochemical Gibbs energy is known (30.5 kJ/mol) and for the former it can be determined from the standard biochemical redox potentials.

$$\Delta G^{\circ\prime} = -nFE^{\circ\prime} = -2\cdot 96500\cdot(0.82-(-0.32))\cdot 10^{-3} = 220\ \text{kJ/mol}.$$

The overall light stages reaction contains no protons, hence the standard Gibbs energy is the same as the standard biochemical Gibbs energy:

$$\Delta G^{\circ} = \Delta G^{\circ\prime} = 220 + 30.5 = 250.5\ \text{kJ/mol}$$

6. This effect is easily understood using a simple orbital diagram (see Appendix in "Molecular Mechanisms of Photosynthesis" by R.E.Blankenship). In the ground state, a lost electron comes from the low-energy HOMO, while an acquired electron enters the high-energy LUMO. As a result, the molecule is neither a strong oxidant nor a good reductant. In the excited state, the situation is different: a lost electron leaves the high-energy LUMO, and the acquired electron comes to low-energy HOMO: both processes are energetically favorable, and the molecule can act both as a strong oxidant and a powerful reductant.



7. Consider two half-reactions:

$\mathrm{Ox} + \mathrm{e} \rightarrow \mathrm{R}$ (standard redox potential $E^{\circ}_{\mathrm{Ox/R}}$)

and $\mathrm{Ox} + \mathrm{e} \rightarrow \mathrm{R}^*$ (standard redox potential $E^{\circ}_{\mathrm{Ox/R^*}}$).

The difference in their Gibbs energies is equal to the excitation energy:

$$F\left(E^{\circ}_{\mathrm{Ox/R}} - E^{\circ}_{\mathrm{Ox/R^*}}\right) = E_{\mathrm{ex}} = \frac{hcN_{\mathrm{A}}}{\lambda},$$

whence it follows:

$$E^{\circ}_{\mathrm{Ox/R^*}} = E^{\circ}_{\mathrm{Ox/R}} - \frac{hcN_{\mathrm{A}}}{\lambda F}.$$

For $P680^+$: $E^{\circ}_{\mathrm{P680^+/P680^*}} = 1.10 - \dfrac{6.63\cdot10^{-34}\cdot3.00\cdot10^{8}\cdot6.02\cdot10^{23}}{680\cdot10^{-9}\cdot96500} = -0.72\ \mathrm{V}$

For $\mathrm{Chlorophyll}^+$: $E^{\circ}_{\mathrm{Chl^+/Chl^*}} = 0.78 - \dfrac{6.63\cdot10^{-34}\cdot3.00\cdot10^{8}\cdot6.02\cdot10^{23}}{680\cdot10^{-9}\cdot96500} = -1.04\ \mathrm{V}$

Problem 15. Complexation reactions in the determination of inorganic ions

1. After the endpoint, the excessive Al^{3+} ions undergo hydrolysis, which makes the medium acidic, and the indicator turns red:

$$Al(H_2O)_6^{3+} = Al(OH)(H_2O)_5^{2+} + H^+$$

2. On heating, the hydrolysis equilibrium shifts rightwards.

3. Cryolite Na_3AlF_6 being formed upon the titration is only slightly soluble in water. Hence, NaCl was added to further decrease its solubility and shift the equilibrium of complex formation rightwards.

4. Neutralization of the sample solution before titration is missing. This operation is mandatory if an acid–base indicator is used to observe the endpoint and the sample is suspected to contain acids. Heating makes the endpoint sharper but is not as critical.

5. In this case a reverse titration was applied. Fluoride precipitates calcium:

$$Ca^{2+} + 2F^- = CaF_2\downarrow,$$

and the excess of fluoride is titrated with $AlCl_3$:

$$6F^- + Al^{3+} = AlF_6^{3-}$$

6. 10.25 mL of 0.1000 M $AlCl_3$ gives 1.025 mmol of Al^{3+}, corresponding to 6.15 mmol of F^-. The initial amount of NaF was 0.500 g, or 11.91 mmol, i.e. 5.76 mmol of F^- was spent for the precipitation of calcium. The amount of calcium is $2.88 \cdot 10^{-3}$ mol.

7. $Si(OH)_4 + 6KF + 4HCl = K_2SiF_6 + 4KCl + 2H_2O$

As can be seen from the equation, HCl is spent in this process, and its excess is titrated with NaOH in the presence of an acid-base indicator. (To be more precise, the excess of HCl reacts with KF yielding a weak acid HF, which is then titrated with NaOH.)

8. The solution of free silicic acid (a weak acid with pK_a of about 10) will be slightly acidic; hence, the indicator used in the neutralization of the sample should change its color in a weakly acidic medium (methyl red, p$K_a \approx 5$). In weakly alkaline media (color change range of two other indicators), a considerable part of the silicic acid will be present in the form of a silicate ion, the buffer solution of which will consume a certain amount of the reacting HCl.

9. The amount of NaOH and the excess of HCl are the same and equal to 0.550 mmol. Hence, the amount of HCl spent for the reaction with silicic acid is 0.994 – 0.550 = 0.444 mmol, and the amount of silicic acid is 0.111 mmol.

Problem 16. Malaprade reaction

1. With glycerol: HCOOH + 2 HCHO, with butane-1,2-diol: C_2H_5CHO + HCHO

2. $HCHO - 2e^- \rightarrow HCOOH$; $HCOOH - 2e^- \rightarrow CO_2$;

$C_2H_5CHO - 2e^- \rightarrow C_2H_5COOH$; $Mn^{+7} + 5e^- \rightarrow Mn^{2+}$;

The complete reactions are:

$$5HCHO + 4MnO_4^- + 12H^+ = 5CO_2 + 4Mn^{2+} + 11H_2O$$

$$5HCOOH + 2MnO_4^- + 6H^+ = 5CO_2 + 2Mn^{2+} + 8H_2O$$

$$5C_2H_5CHO + 2MnO_4^- + 6H^+ = 5C_2H_5COOH + 2Mn^{2+} + 3H_2O$$

The total mass of the mixture: $m_A = n_{gly}M_{gly} + n_{but}M_{but}$.

The number of mols of 1/5 $KMnO_4$ spent for the oxidation of aldehyde groups:

$n_{ald} = 4 \cdot 2n_{gly}$ (2 moles of CH_2O from glycerol, $4e^-$ each) + $2n_{gly}$ (HCOOH from glycerol, $2e^-$) + $2n_{but}$ (C_2H_5CHO from butylene glycol, $2e^-$) + $4n_{but}$ (1 mol of CH_2O from butylene glycol, $4e^-$) = $10n_{gly} + 6n_{but}$.

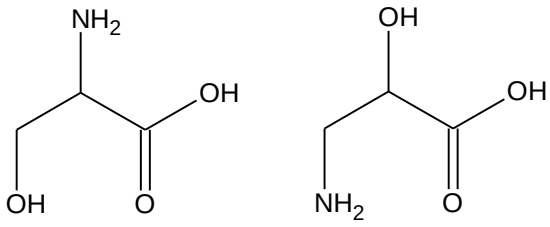
Solving these two simultaneous equations (with $M_{gly} = 92$ and $M_{but} = 90$) one gets:

$n_{but} = 0.0101$ mol, $n_{gly} = 0.0079$ mol.

3. The carboxylic group could either exist in the original compound **B** (a) or be formed during the oxidation (b).

(a). Let us suppose a minimum amount of oxygen-containing groups in **B**: 0.001 mol of –COOH (45 mg) and two hydroxyl groups (≡C–OH 29 g/mol · 0.002 mol = 58 mg); then, 0.001 mol of nitrogen should be also present (14 mg); this gives the total mass of 117 mg, which is even higher than the mass of **B** (105 mg). Therefore, part of oxygen originates from the oxidant or water as a result of the substitution of amine nitrogen atom (which has transformed into the ammonium ion) with oxygen (so, amino groups in Malaprade reaction behave as hydroxyl ones). In case **B** contains one oxygen atom less, we will get: 1 mmol of ≡C–OH groups (29 mg) + 1 mmol of $CHNH_2$ (29 mg) + 1 mmol of COOH (45 mg) = 103 mg. To attain the required 105 mg, the following groups can be suggested: CHOH (30 mg), CH_2NH_2 (30 mg) and COOH (45 mg), which brings us to the empirical formula of **B**: $C_3H_7NO_3$. Remembering that nitrogen must be in the form of an amino group, no ether oxygens are permitted and an acid is formed as the result of

oxidation (this can only be HCOOH, and to obtain that, a –CH(OH)– or –CH(NH_2)– group must be present), we can make up a list of possible structures of **B**. In case the carboxylic group was present in the original compound (a), that will be 2-amino-3-hydroxypropionic acid or 3-amino-2-hydroxypropionic acid:

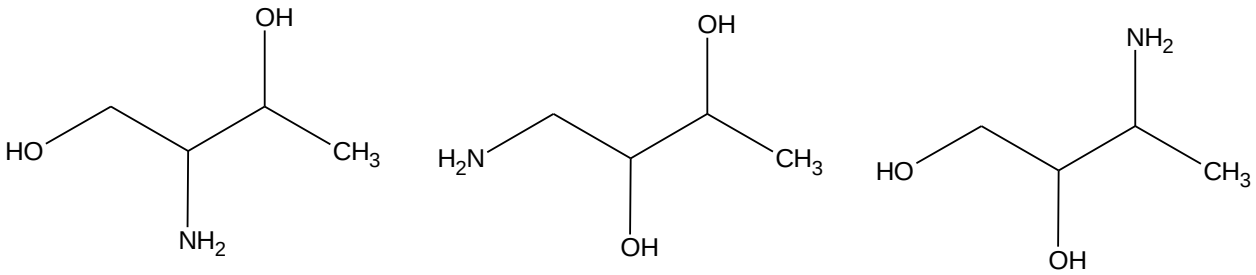


Scheme of their oxidation with periodate:

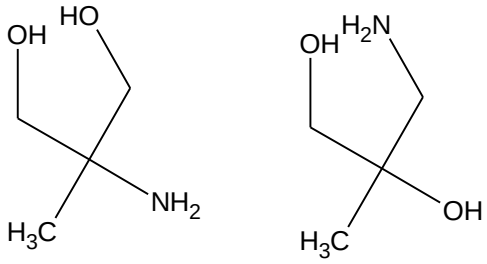
$$HOCH_2–CH(NH_2)–COOH \rightarrow CH_2O + HOOC–CHO + NH_4^+.$$

Glyoxylic acid HOOC–CHO is oxidized by $KMnO_4$ to oxalic acid and then to CO_2 (4 mmol equivalents of $KMnO_4$); together with formaldehyde (4 mmol eq.) it makes up the required 8 mmol eq. to be spent for the titration.

(b). In case compound **B** is originally lacking carboxylic group, the molecular weight of 105 corresponds to compounds containing 1 oxygen atom less and 1 extra carbon atom ($C_4H_{11}NO_2$), i.e. *butane* derivatives containing 1 amino and 2 hydroxyl groups. (*Propanes* with 3 hydroxyl groups and 1 amino group will give molecular weights of 107.) If the butane moiety is unbranched and all three groups (two OH and the NH_2) are vicinal:



then periodate oxidation yields HCHO, HCOOH and CH_3CHO; the two isobutane derivatives



both result in 1 mol of CH_3COOH and 2 moles of HCHO, while all these butanes meet the task requirements, as they require 8 mmol equivalents of $KMnO_4$ for their oxidation. Compound $HC(CH_2OH)_2CH_2NH_2$ is not oxidized with periodate. If OH and NH_2 groups are not vicinal, formaldehyde and an aldehyde are formed, but no necessary carboxylic acid is produced. If **B** contains a C=O group (for instance, O=CH–CH(OH)–CH(NH_2)–CH_3), its formula is $C_4H_9NO_2$ (molecular weight 103), which is not consistent with the problem conditions.

Scheme of periodate oxidation for the linear butane derivatives:

$$CH_2NH_2–CH(OH)–CH(OH)–CH_3 \rightarrow CH_2O + HCOOH + CH_3CHO$$

For the branched butanes:

$$HOCH_2–C(CH_3)NH_2–CH_2OH \rightarrow CH_2O + CH_3COOH + CH_2O$$

Problem 17. Analysis of Chrome Green

1. $PbCrO_4 + 4Na_2CO_3 + 4H_2O \rightarrow Na_2Pb(OH)_4 + Na_2CrO_4 + 4NaHCO_3$

$2Fe_3[Fe(CN)_6]_2 + 12Na_2CO_3 + 12H_2O \rightarrow 6Fe(OH)_2\downarrow + 4Na_3[Fe(CN)_6] + 12NaHCO_3$

and then

$6Fe(OH)_2\downarrow + 4Na_3[Fe(CN)_6] + ½O_2 + 4Na_2CO_3 + 5H_2O \rightarrow 6Fe(OH)_3\downarrow + 4Na_4[Fe(CN)_6] + 4NaHCO_3$

Totally:

$2Fe_3[Fe(CN)_6]_2 + ½O_2 + 16Na_2CO_3 + 17H_2O \rightarrow 6Fe(OH)_3\downarrow + 4Na_4[Fe(CN)_6] + 16NaHCO_3$

Ferric hydroxide is left on the filter.

2. Direct oxidation of thiosulfate with dichromate is not stoichiometric. The reactions normally used are:

$$Cr_2O_7^{2-} + 6\ I^- + 14H^+ \rightarrow 2Cr^{3+} + 3I_2 + 7H_2O$$

$$I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$$

3. If reaction B is induced by reaction A, it implies that reaction A produces some intermediates active with the components of reaction B. In our case, the reduction of Cr(VI) occurs via the formation of intermediate oxidation states of chromium, predominantly Cr(V) species. (At the same time, the oxidation of I^- to I^0 may not require any iodine-containing intermediates.) A reasonable reaction scheme is as follows:

$$H_2Cr_2O_7 + I^- \rightarrow Cr(V) + I;\ Cr(V) + O_2 \rightarrow Cr_2O_7^{2-}, \text{ etc.}$$

As a result of oxygen involvement, a higher amount of free iodine is obtained, which results in a greater amount of $Na_2S_2O_3$ titrant spent and lower apparent concentration determined.

4. The amount of chromium is found as follows: $3n_{Cr} = n_{thios} = 0.0485\ M \cdot 5.01\ mL = 0.2430$ mmol ($n_{Cr} = 0.081$ mmol). This corresponds to 26.2 mg of $PbCrO_4$ (M = 323.2 g/mol) in the aliquot, or 131 mg totally.

5. Owing to the fast redox equilibrium:

$$[Fe(CN)_6]^{4-} + Fe^{3+} \rightarrow [Fe(CN)_6]^{3-} + Fe^{2+},$$

a certain amount of $[Fe(CN)_6]^{4-}$ will be present in the system. The side reaction

$$CrO_4^{2-} + 3[Fe(CN)_6]^{4-} + 8H^+ \rightarrow Cr^{3+} + 3[Fe(CN)_6]^{3-} + 4H_2O$$

produces an amount of $[Fe(CN)_6]^{3-}$ equivalent to CrO_4^{2-} reacted. At the titration stage that hexacyanoferrate(III) would also liberate free iodine; hence, the side process can be neglected.

6. Acidification of the sample: $CrO_4^{2-} + 3[Fe(CN)_6]^{4-} + 8H^+ \rightarrow Cr^{3+} + 3[Fe(CN)_6]^{3-} + 4H_2O$
Titration: $MnO_4^- + 5[Fe(CN)_6]^{4-} + 8H^+ \rightarrow Mn^{2+} + 5[Fe(CN)_6]^{3-} + 4H_2O$
Hexacyanoferrates may be partially precipitated in the form of Pb^{2+} salts but this does not preclude them from the redox reactions.

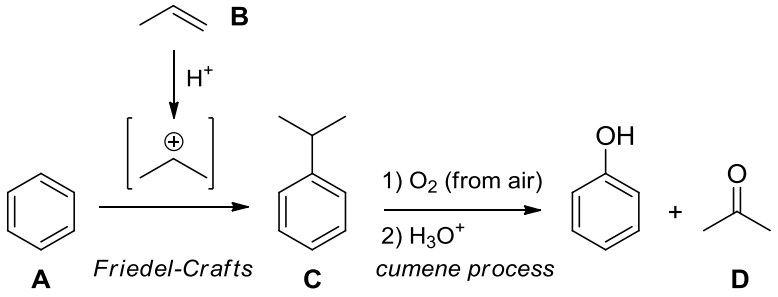
7. On acidification of the 2nd aliquot, chromium is reduced by $[Fe(CN)_6]^{4-}$ (see i. 5). Then permanganate is spent for the oxidation of $[Fe(CN)_6]^{4-}$, namely, the amount of $[Fe(CN)_6]^{4-}$ added plus the amount contained initially in the sample less the amount spent for the reduction of Cr(VI): $5n_{MnO_4} = n_{Fe\ added} + n_{Fe\ from\ sample} - 3n_{Cr}$. From this equation we can find $n_{Fe\ from\ sample} = 5n_{MnO_4} - n_{Fe\ added} + 3n_{Cr} = 5 \cdot 0.00500 \cdot 2.85 - 10 \cdot 0.0300 + 0.2430 = 0.07125 - 0.3000 + 0.2430 = 0.0142$ mmol $[Fe(CN)_6]^{4-}$. One mol of $[Fe(CN)_6]^{4-}$ results from 0.5 mol of $Fe_3[Fe(CN)_6]_2$ (see solution to question 1), therefore, the answer is 4.21 mg of $Fe_{3/2}[Fe(CN)_6]$ (M = 295.6 g/mol) in the aliquot, or the total amount of 21.1 mg.

Problem 18. Chemistry of phenol

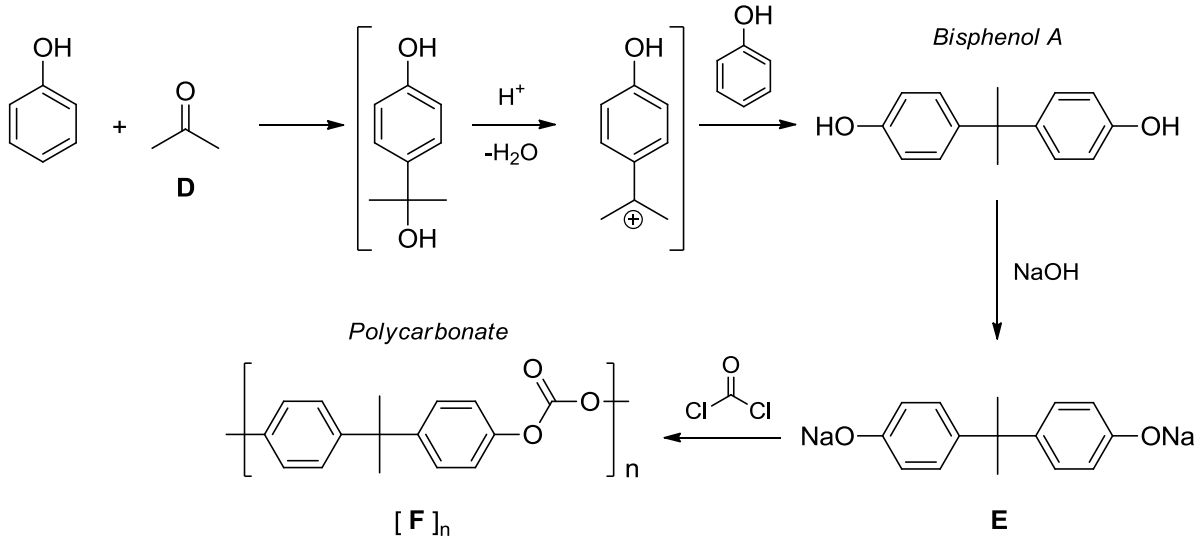
1-2. Structures of benzene **A** and propene **B** are commonly known.

The interaction between **A** and **B** under acidic condition proceeds as Friedel-Crafts alkylation of the aromatic ring with the thermodynamically more stable secondary propyl carbocation as an electrophile. Being a product of the interaction of equal amounts of **A** and **B**, **C** turns out to be

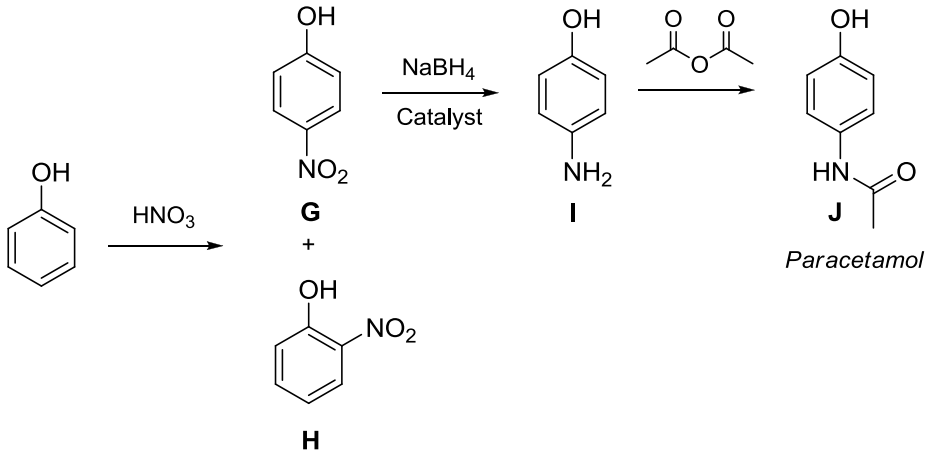
isopropylbenzene, i.e. cumene. Oxidation of **C** with subsequent acidification leads to phenol and acetone **D**. This classical industrial procedure is known as *cumene process*.



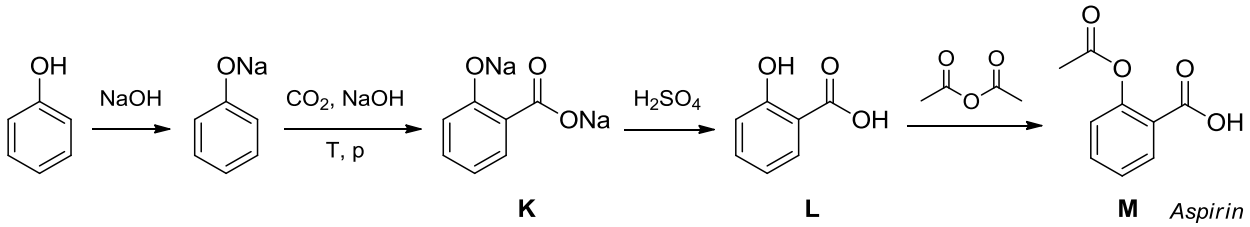
The structure of **D** can also be easily determined from that of *bisphenol A*, which is formed as a result of two consecutive Friedel-Crafts alkylations of phenol. Treatment of *bisphenol A* with NaOH leads to disodium bis-phenolate **E**, which gives *polycarbonate* with the monomeric unit **F** as a result of the reaction with phosgene.



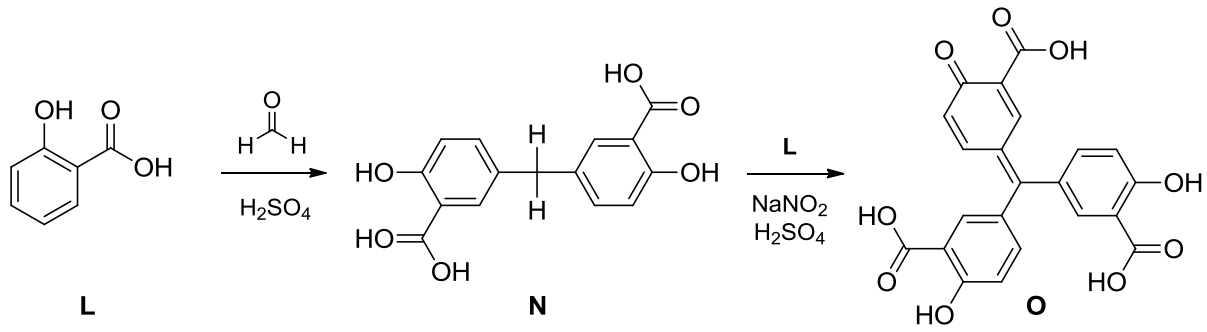
The reaction of phenol with diluted nitric acid proceeds as a mononitration resulting in isomeric nitrophenols **G** and **H**. Due to the activation effect of OH-group in phenol, electrophilic substitution can occur in *ortho*- and *para*-positions of phenol. **G** is *para*-nitrophenol (two planes of symmetry), whereas **H** is *ortho*-nitrophenol (only one plane of symmetry). Further reduction of NO_2-group in *para*-nitrophenol **G** results in *para*-aminophenol **I**. Due to its higher nucleophilicity, NH_2-group (rather than OH-group) in **I** is acetylated with acetic anhydride giving *paracetamol* **J**.



The reaction of phenol with CO_2 in the presence of NaOH proceeds through intermediate formation of sodium phenolate, which interacts with CO_2 under heating and high pressure (Kolbe-Schmitt reaction) to give disodium salicylate **K**. Acidification of **K** with two equivalents of an acid results in salicylic acid **L**, which provides *aspirin* **M** when acetylated with acetic anhydride.



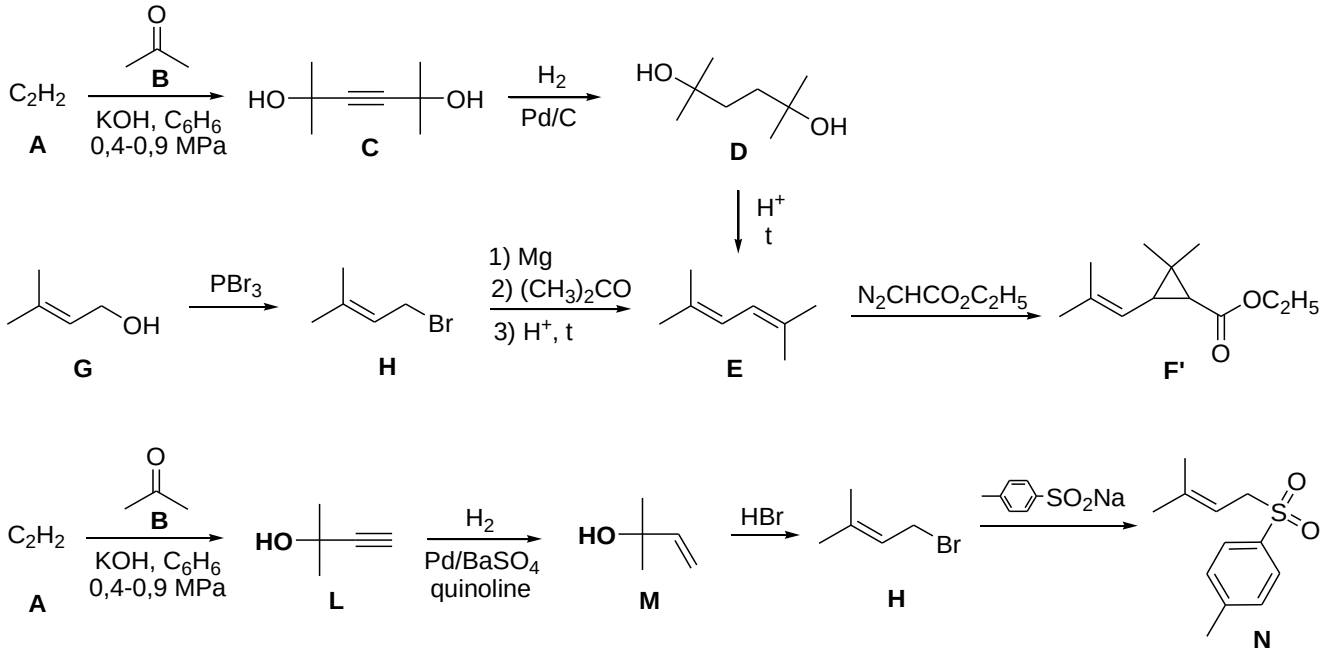
Aluminon synthesis is based on the same approach as previously considered for *bisphenol A*. The reaction of salicylic acid **L** with formaldehyde under acidic conditions affords **N**, which is an analogue of *bisphenol A*. Addition of another equivalent of salicylic acid **L** under oxidative conditions ($NaNO_2/H_2SO_4$) gives the tri-acid **O**, which is a direct precursor of *Aluminon*. Thus, the structure of **O** can be derived from that of *Aluminon*.



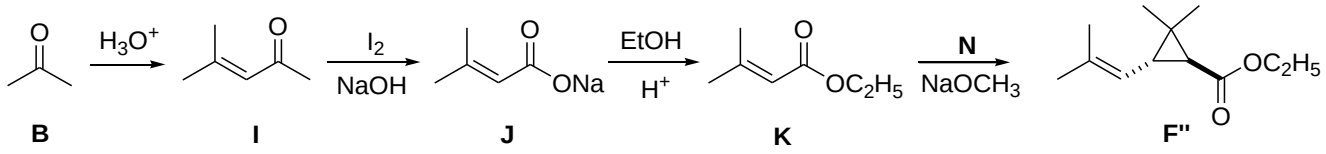
Problem 19. Chrysanthemic acid

1. Chrysanthemic acid is formed as a result of hydrolysis of its ethyl ester, **F**, which, in turn, is obtained by cyclopropanation of **E** with diazoacetic ester. Therefore, **E** is 2,5-dimethylhex-2,4-diene with molecular formula C_8H_{14}. This conclusion is supported by the molecular formula of **D**. Evidently, transformation of **D** to **E** is elimination of two water molecules.

Eight carbon atoms of **D** originate from **A** and **B**. The other reaction between these compounds affords **L** containing 5 carbon atoms (**N** is formed from **H** and $C_7H_7O_2SNa$; the number of carbon atoms in **H** and **L** is the same). The provided information strongly suggests that **A** is acetylene (C_2H_2). Hence, **A** is composed of 2, and **B** should be composed of 3 carbon atoms. Reaction between **A** and **B** was disclosed by Favorskii in 1905 as that between acetylenes and carbonyl compounds. It means that **B** is either propionic aldehyde (C_2H_5CHO) or acetone (CH_3COCH_3). Accounting for the structure of **E**, **B** is acetone. **E** is also formed through the Grignard reaction of acetone with the corresponding RMgBr followed by elimination of water. The structure of **H** can be unambiguously deduced from that of **E** – it is prenyl bromide. So, the natural alcohol is prenol (3-methylbut-2-en-1-ol). **L** is formed from **A** and **B** under the same reaction conditions but when **A** to **B** ratio is of 1:1. Therefore, **L** is 2-methylbut-3-yn-2-ol. Its hydrogenation in the presence of Lindlar catalyst leads to the corresponding alkene **M**. Subsequent reaction with HBr affords prenyl bromide **H** *via* nucleophilic substitution with double bond migration. The reaction of **H** with sodium 4-toluenesulfinate results in the corresponding sulfone **N**.



Finally, acid-catalyzed self-condensation of acetone yields 4-methylpent-3-en-2-one (mesityl oxide, **I**). Iodoformic reaction of **I** produces the salt of the corresponding acid **J** which is further transformed into ethyl ester **K**. The reaction of **K** with deprotonated sulfone **N** results in chrysanthemic acid ester F".



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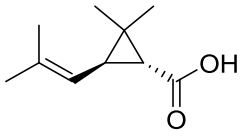
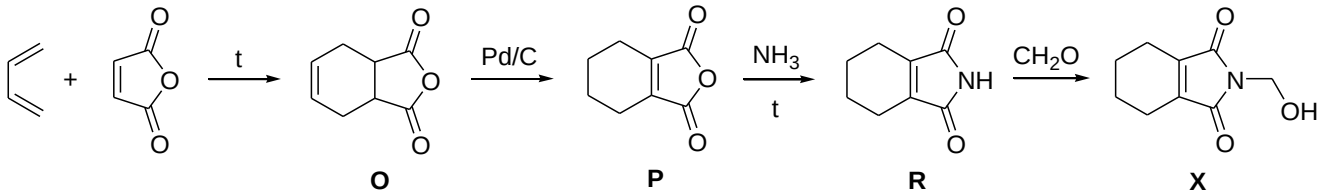


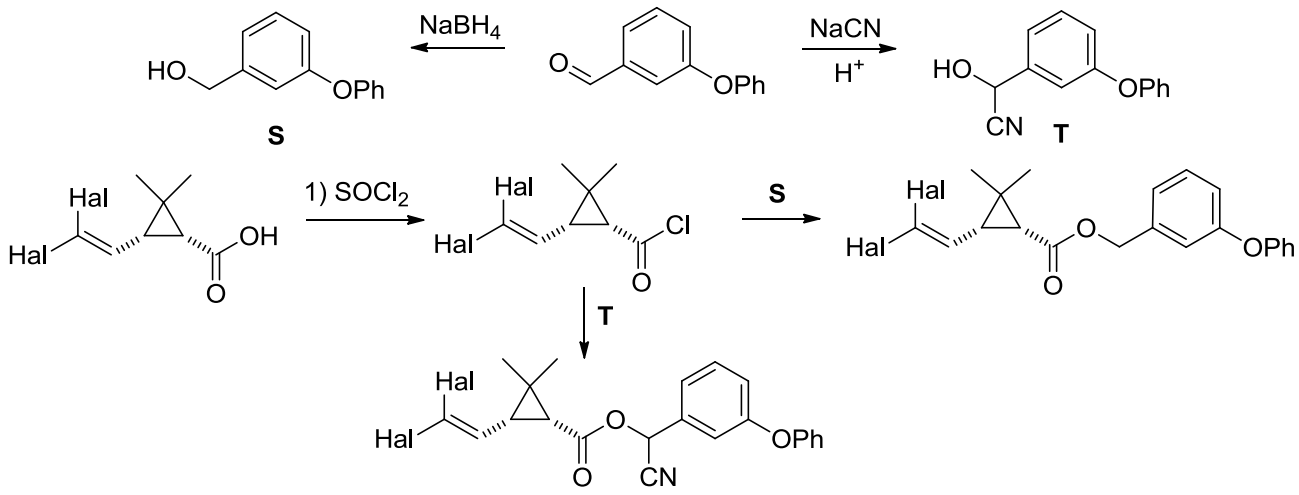
(1*R*,3*R*)-chrysanthemic acid

3. The first step is the Diels-Alder reaction. Compound **P** with tetrasubstituted double bond is the most stable isomer of **O** with the same carbocyclic skeleton. Heating of **P** with ammonia leads to imide **R**, which further reacts with CH_2O giving the target alcohol **X**.



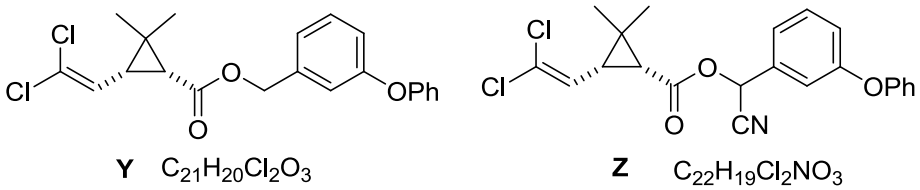
4. Amides and hydrazides do not easily form esters in reaction with alcohols. Oppositely, anhydrides are appropriate reagents for the ester synthesis. Moreover, re-esterification of methyl or ethyl esters with high-boiling alcohols is well-known. These reactions are efficient due to methanol (ethanol) removal from the reaction mixture via distillation (Le Chatelier's principle).

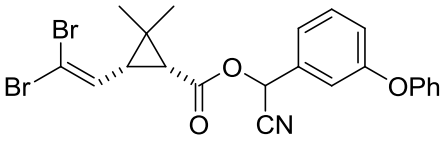
5. Reduction of 3-phenoxybenzaldehyde yields the corresponding benzyl alcohol **S**, while its reaction with NaCN produces cyanohydrin **T**. Reaction of **S** or **T** with 2,2-(dihalovinyl)-3,3-dimethylcyclopropane-1-carbonyl chloride affords the target pyrethroids.



Molecular formulae of the esters formed from alcohol **S** and **T** are $C_{21}H_{20}Hal_2O_3$ and $C_{22}H_{19}Hal_2NO_3$, respectively. Halide content in the esters is $2M_{Hal}/(2M_{Hal} + 320)$ and $2M_{Hal}/(2M_{Hal} + 345)$, respectively. Calculation of halide content in these compounds allows unambiguously deciding on the structures of the pyrethroids.

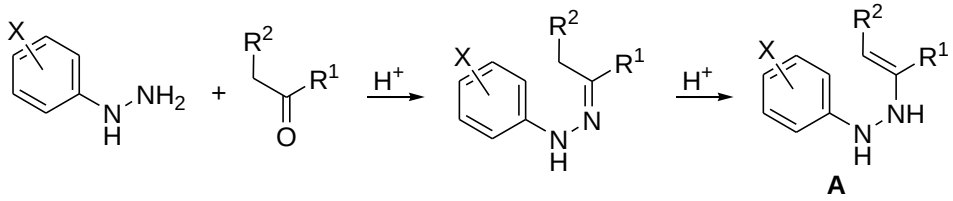
Content of Hal, %	Using exact atomic mass				Using approximate atomic mass			
	F	Cl	Br	I	F	Cl	Br	I
Ester of **S**	10.60	**18.12**	33.28	44.20	10.61	**18.16**	33.33	44.25
Ester of **T**	9.91	**17.03**	**31.63**	42.36	9.92	**17.07**	**31.68**	42.40





Problem 20. Heterocycles

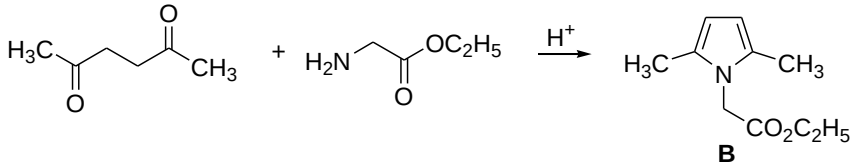
1. Interaction of ketone with arylhydrazine affords hydrazone, which isomerizes into enhydrazine under acidic conditions.



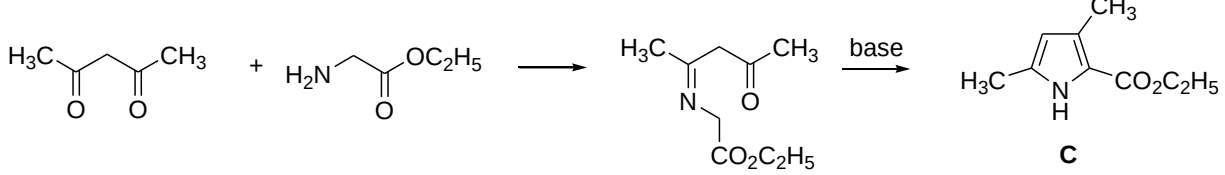
A

2. Mechanism ***a*** includes the electrophilic attack of aminoalkyl cation at the aromatic moiety. This attack is very susceptible to electron properties of the aryl group (attack on the electron-enriched aryl ring is much more efficient than that on the electron-depleted arene). The same is expected for mechanism ***c***. Only the sigmatropic shift has no significant dependence on substituents in both arenes. Therefore, I. Grandberg proved that the Fischer indole synthesis proceeds via mechanism ***b***.

3. Reactions are started by interaction of amine with the carbonyl group furnishing imine. To complete pyrrole moiety formation, monoimine of hexane-2,5-dione should isomerize into the enamine followed by an attack of the amine group on the second C=O group. Formally, imine of pentane-2,4-dione can form the pyrrole ring in two ways. First, it is the interaction of the nitrogen atom with the methyl group. However, the methyl group itself is unreactive towards nucleophiles. Keto-enol equilibrium with involvement of the methyl group in this compound is less probable than that with CH_2-fragment. Even if the equilibrium was true, enol is a nucleophile and cannot react with nucleophilic nitrogen atom. Therefore, the second possibility should be considered, namely, the reaction of the second carbonyl with CH_2 bound to N atom. This reaction is quite probable as CH_2-group is also connected with the electron-withdrawing ester group and can be deprotonated by a base as shown below.

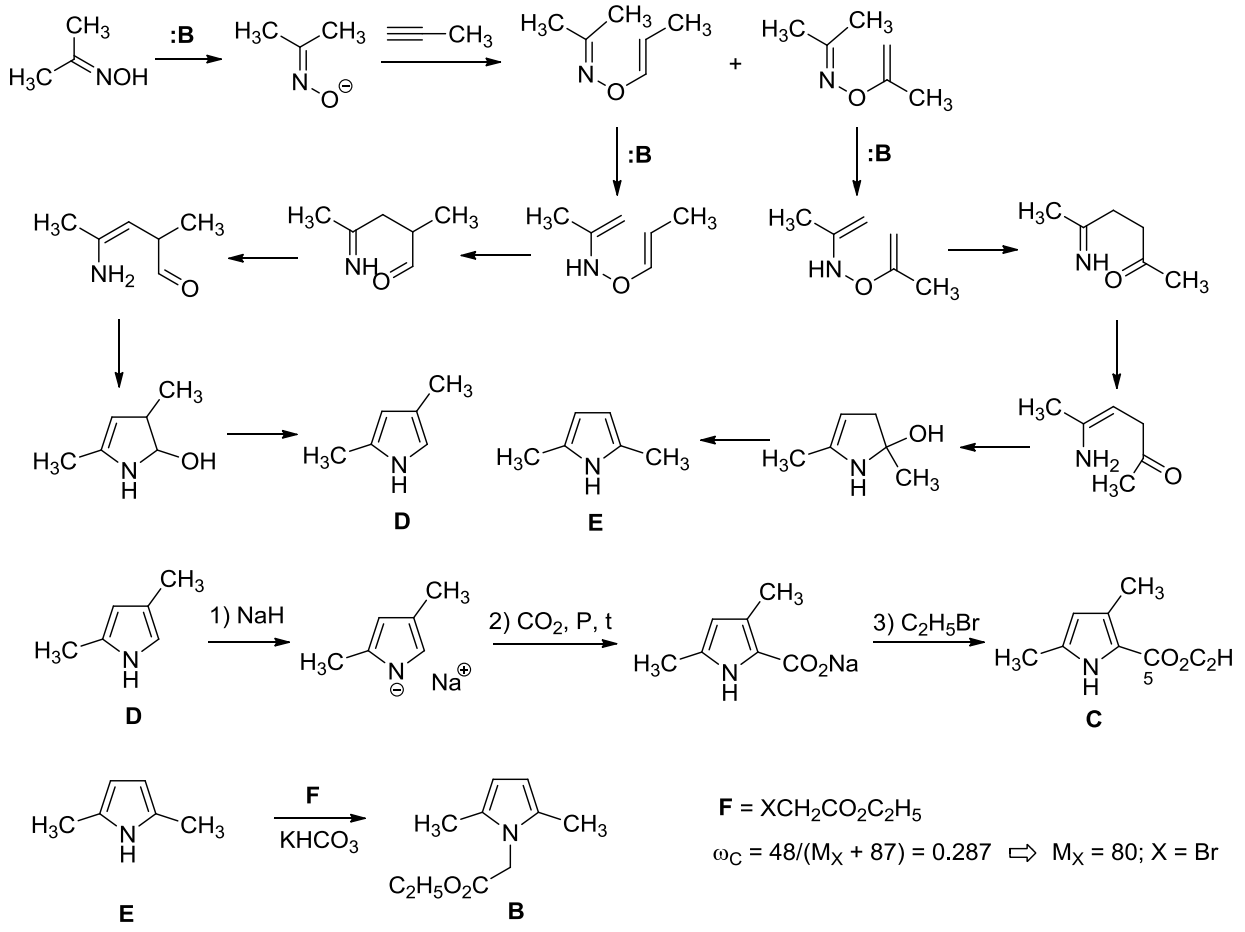


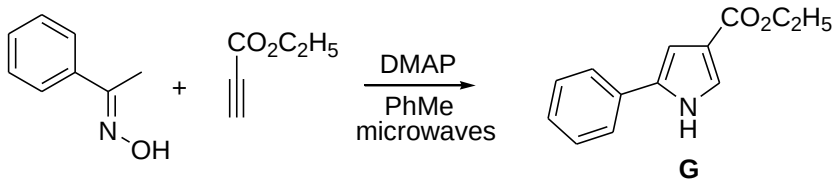
B



C

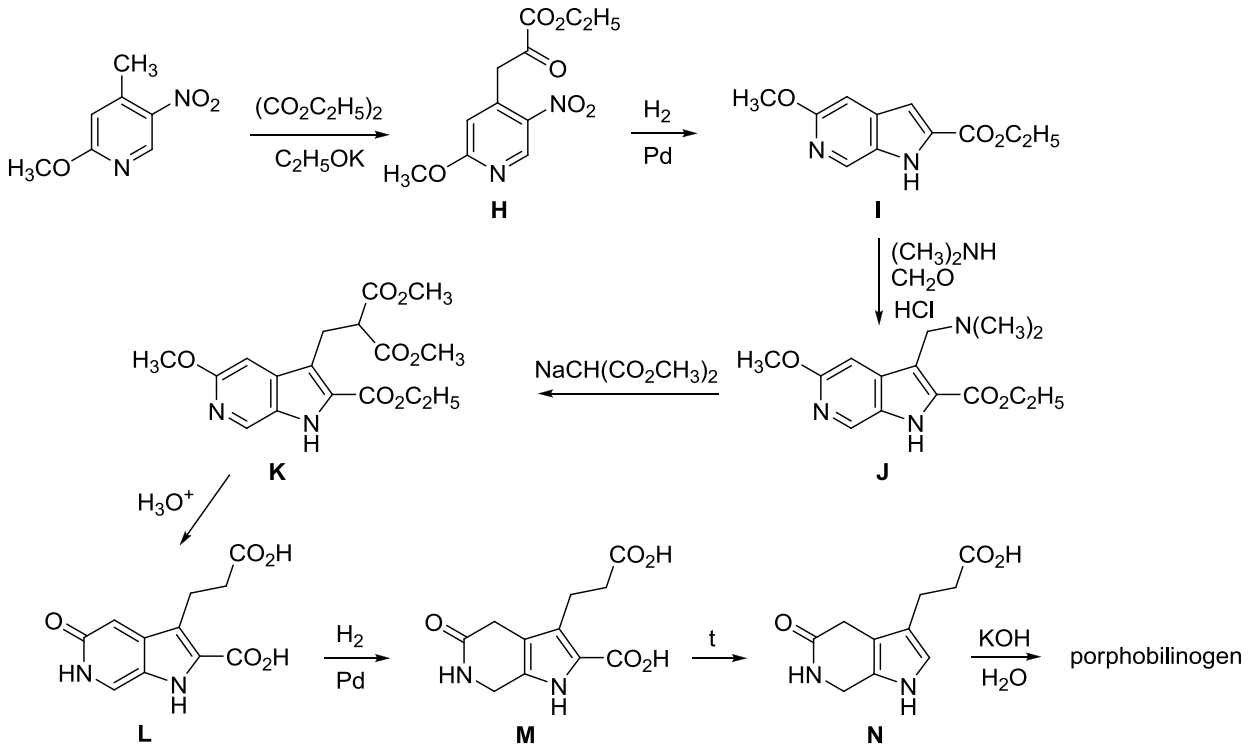
4-5. Two products are formed in the reaction of propyne, and only one product in the case of the alkyne bearing an electron-withdrawing ester group. This allows supposing a nucleophilic attack of a certain intermediate on the alkyne moiety. A base generates a nucleophilic agent from acetone oxime. Again, two ways of deprotonation are possible: *O*-deprotonation and *C*-deprotonation. However, oxime enolate, if formed, should add to alkyne with the formation of hex-4-en-2-one oxime. There is no possibility for the transformation of this oxime into pyrrole ring. The alternative possibility is *O*-deprotonation and nucleophilic addition of the oximate ion to alkyne furnishing *O*-alkenyl acetone oxime. Formation of the C-C bond between the methyl group of acetone and the β-carbon atom of the alkenyl group is needed to complete the pyrrole ring synthesis. At the first glance, such transformation is impossible. However, this system is very similar to the *N*-aryl-*N'*-alkenyl moiety which undergoes the 3,3-sigmatropic rearrangement in the Fischer indole synthesis. Indeed, isomerization of *O*-alkenyl acetone oxime into *O*-alkenyl-*N*-alkenyl derivative creates the fragment required for the 3,3-sigmatropic shift. So, formation of the pyrrole ring giving 2,4-dimethylpyrrole and 2,5-dimethylpyrrole is analogous to that of indole in the Fischer synthesis. The former compound is transformed into **C** via *N*-deprotonation followed by the Kolbe-Schmitt carboxylation and ester formation. To provide **B**, **E** should be *N*-alkylated with ethyl haloacetate. Halogen can be determined from the carbon content in the alkylation reagent.





G

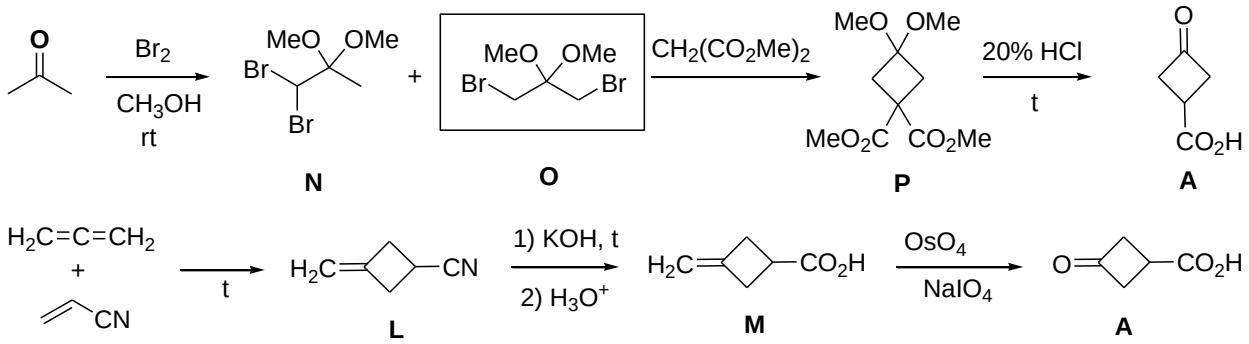
6. Methyl group in the starting compound is very acidic due to activation by both *ortho*-nitro group and *para*-nitrogen atom of pyridine. So, it can be easily deprotonated to further react with diethyl oxalate providing the corresponding ketoester **H**. Reduction of the nitro group gives aniline. Condensation of the amino group with the appropriately located ketone moiety affords the 6-azaindole derivative **I** ($C_{11}H_{12}N_2O_3$). Aminomethylation of this indole furnishes the gramine derivative **J** which undergoes nucleophilic substitution with sodium dimethylmalonate producing **K**. Its hydrolysis results in a compound with the molecular formula of $C_{11}H_{10}N_2O_5$. It means that: a) hydrolysis of the malonate fragment is accompanied by decarboxylation; b) the ester moiety at the C2 position of the indole is hydrolyzed too. However, even if so, the molecular formula should be $C_{12}H_{14}N_2O_5$. The difference equals to CH_2. Hydrolysis of OCH_3-group in *ortho*-position to pyridine nitrogen is the only possibility. Indeed, hydrogenation of this pyrrolopyridone yields **M**. Its decarboxylation and hydrolysis of the amide function finally leads to porphobilinogen.



H **I** **J** **K** **L** **M** **N**

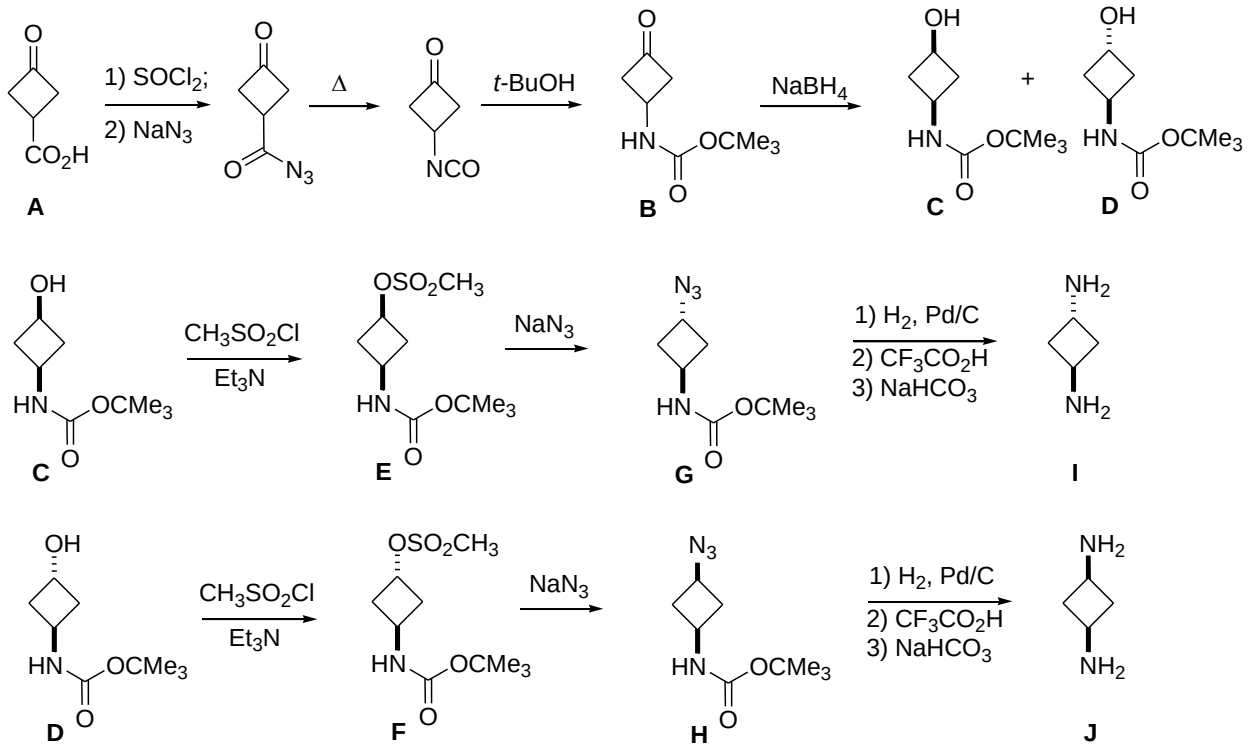
Problem 21. Cyclobutanes

1. Hydrocarbon **K** consists of 90% C and 10% H. Its simplest formula is $(C_3H_4)_n$, and it has a single type of H atoms. So, it is allene, $H_2C=C=CH_2$. **A** has 5 carbon atoms. Therefore, allene reacted with $CH_2=CHCN$ in a ratio of 1:1 and lost one carbon atom during the following steps. Various products can be supposed for this reaction, however, it is known that allene is prone to undergo cycloaddition as 2π-component. Acrylonitrile undergoes cycloaddition as 2π-component too. So, the product should be a cyclobutane derivative, which is consistent with the next scheme. The C and H content in **N** and **O** provides for their molecular formula ($C_5H_{10}Br_2O_2$). In this respect, two sub-processes should proceed: a) acetone is doubly brominated; b) ketone is transformed into ketal in the reaction with methanol catalyzed by HBr evolved in the bromination step. Two dibromoacetones (1,1- and 1,3-) can be formed. Reaction of the latter with dimethyl malonate affords the corresponding cyclobutane derivative. Its treatment with hydrochloric acid leads to the hydrolysis of ketal into ketone and esters into an acid. So, the product should be 3-oxocyclobutane-1,1-dicarboxylic acid. However, its formula is $C_6H_6O_5$. Therefore, hydrolysis is also accompanied by decarboxylation of the malonic acid moiety. So, **A** is 3-oxocyclobutanecarboxylic acid. Accounting for it, **L** is the product of [2+2] cycloaddition, *i.e.*, 1-cyano-3-methylenecyclobutane. Its hydrolysis followed by oxidation of C=C double bond produces **A.** Finally, the schemes for preparation of **A** are as follows:

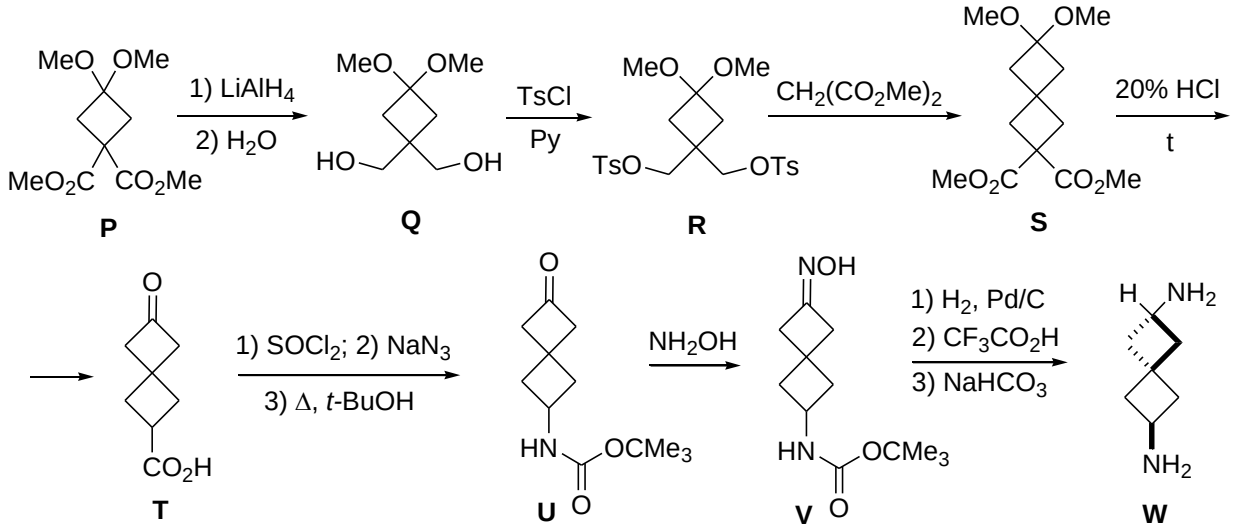


Reaction of **A** with $SOCl_2$ furnishes acyl chloride, which reacts with NaN_3 affording acyl azide. Heating of $RCON_3$ produces isocyanate R-N=C=O, which immediately reacts with *t*-BuOH giving rise to *N*-Boc-protected 3-aminocyclobutanone **B**. Reduction of keto group with $NaBH_4$ leads to *cis*- and *trans*-isomers of the corresponding aminocyclobutanol. Further reaction with CH_3SO_2Cl produces mesylates, which undergo S_N2 displacement with NaN_3 affording aminoazides. Reduction of azido group and deprotection of amine furnishes *cis*-and *trans*-isomers of 1,3-diaminocyclobutane. Therefore, **J** is *cis*-1,3-diaminocyclobutane (two planes of symmetry), and **I** is *trans*-isomer (one plane of symmetry). Similarly, **G** is *trans*-, and **H** is *cis*-

isomer. As the S_N2 reaction proceeds with inversion of the configuration, compound **E** (leading to **G**) is *cis*-, and **F** is *trans*-isomer.



2-3. Reduction of **P** with $LiAlH_4$ gives the corresponding diol **Q**, which is transformed into ditosylate **R**. Reaction of **R** with dimethyl malonate leads to formation of the second cyclobutane ring (**S**). Hydrolysis of **S** proceeds similarly to that of **P**, *i.e.*, it produces ketoacid **T**. Further transformations are also similar to those in the first scheme and produce spiro[3.3]heptane-2,6-diamine **W**. This compound has no plane or center of symmetry. It is chiral due to axial chirality (similarly to 1,3-disubstituted allenes), thus, it can be resolved into two enantiomers.



Problem 22. Introduction to translation

1. There are 4^3=64 different three-nucleotide combinations of 4 nucleotides. Only 61 codons encode amino acids added to the growing polypeptide chain. 3 remaining combinations are STOP codons determining termination of the translation process.

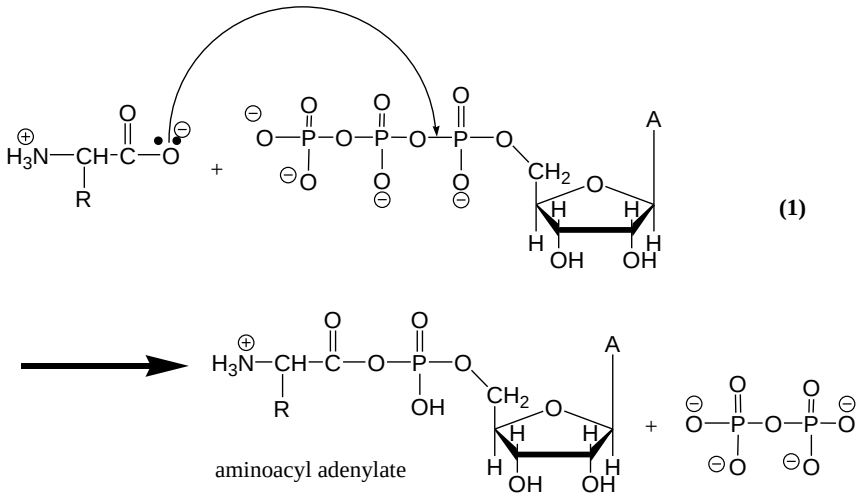
2. No, because of redundancy of the genetic code: most amino acids are encoded by several codons.

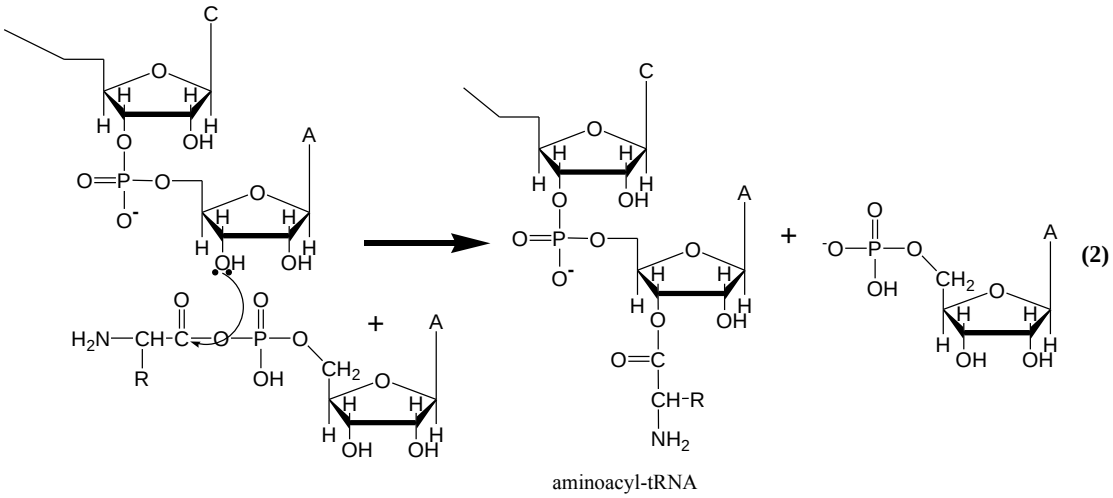
3. Leucine is encoded by 6 different codons, thus it is delivered to a ribosome by 6 different tRNAs. Being encoded by only 1 codon, methionine is transported by a sole tRNA. In some organisms the latter codon is also responsible for the translation start, encoding the N-terminal amino acid N-formylmethionine. Still, methionine and N-formylmethionine are transported by different tRNAs.

4. The equations of consecutive reactions are:

amino acid + ATP = aminoacyl adenylate + PPi (inorganic pyrophosphate) (1)

aminoacyl adenylate + tRNA = aminoacyl tRNA + AMP (2)





(2)

Thus, the carboxylic group of the amino acid reacts with 3'-OH group of its tRNA.

5. a) Met-Asp-His-Ala-Ile-Asn-Val-Val-Gly-Trp-Ser-Val-Asp-Thr-Leu-Asp-Asp-Gly-Thr-Glu-Ala or fMet-Asp-His-Ala-Ile-Asn-Val-Val-Gly-Trp-Ser-Val-Asp-Thr-Leu-Asp-Asp-Gly-Thr-Glu-Ala, depending on the biosynthesizing species (Eukaryotes, Prokaryotes, or Archaea).
b) The third amino acid is tyrosine, and the last one is valine. All the rest positions are the same.
c) The N-terminal amino acid is leucine. All the rest positions are the same. It should be noted that the translation in bacteria would not start without the START codon.
d) The last but one codon is changed into STOP codon, which will result in the oligopeptide shorter by 2 amino acid residues than that in i. 5a.

6. AUG-GA**U/C**-GU**N**-AA**U/C**-CA**U/C**-CC**N**-GA**A/G**-UA**U/C**-GG**N**-AA**A/G**

7. The protein consists of 51000/110≈464 amino acid residues.
Hence, it is encoded by the mRNA containing 464*3+3=1395 nucleotide residues including the STOP codon.
The length of mRNA is 1395*0.34=474.3≈474 nm.
The time needed for biosynthesis of the protein is:
1395/20=69.7≈70 s, that is a bit more than one minute.

8. Taking into account that the A:C ratio is 1:5, the probability of finding A and C at any position is 1/6 and 5/6, respectively. Thus, the probability of finding certain codons is:

AAA $=(1/6)^3=1/216$ CCC $=(5/6)^3=125/216$

AAC $=(1/6)^2*5/6=5/216$ CCA $=(5/6)^2*1/6=25/216$

ACA $=1/6*5/6*1/6=5/216$ CAC $=5/6*1/6*5/6=25/216$

ACC $=1/6*(5/6)^2=25/216$ CAA $=5/6*(1/6)^2=5/216$

Using the table of genetic code one gets: Lys:Asn:Thr:Pro:His:Gln=1:5:30:150:25:5

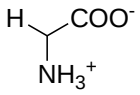
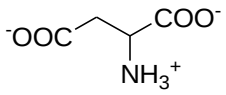
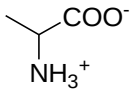
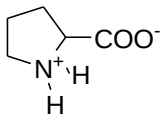
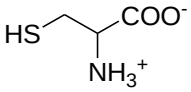
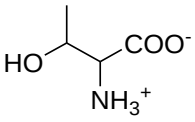
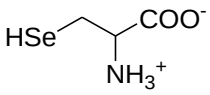
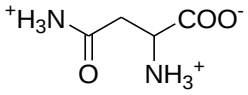
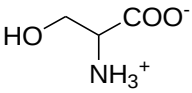
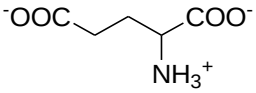
9. Anticodon has no influence on the CCA3' terminus. Thus, the mutant tRNA will add tyrosine to the positions where serine was initially expected with respect to mRNA sequence. This may lead to improper folding of the protein and total or partial loss of its functional activity.

10. Glu is encoded by GAA and GAG, and His by CAU and CAC. Two substitutions (of the 1st and 3rd residues) are needed to make this mutation true, which is quite improbable. Single residue mutations occur much more frequently, and Glu to Gln mutation can serve as an example (together with many other mutations of this type).

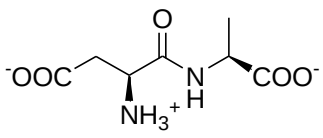
Problem 23. Intriguing translation

1. If **X** is an acyclic dipeptide, **A** and **B** should be composed of 28 atoms in total (25+3 for H_2O). In the case of an acyclic tripeptide similar calculations lead to 31 atoms in total (25+6 for $2H_2O$), this being true for any of two combinations of residues in the tripeptide (**A**+2**B** or 2**A**+**B)**. Analysis of the structures of all proteinogenic amino acids given in Wikipedia suggests glycine as one with the minimal number of atoms (10) followed by alanine formed by 13 atoms. Thus, the tripeptide with the minimal number of atoms is composed of 2 glycines and 1 alanine. The total number of atoms (33) in the amino acids forming this tripeptide exceeds 31, which makes any tripeptide as well as large peptides impossible. Therefore, **X** is a dipeptide.

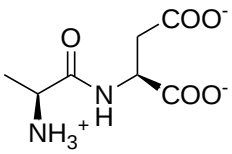
2. Both α-carboxylic and α-amino groups exist mostly in the ionic forms at pH 4.7. Ionization state of the side groups at the given pH value should be determined individually based on their pKa values as reported in Wikipedia. One should leave into consideration only amino acids with the number of atoms less than 19 (28-10=18; this is maximal possible value in case one of two amino acids is glycine). Surprisingly, the data found on different Wikipedia pages lead to contradictory results. According to the former weblink (http://en.wikipedia.org/wiki/Proteinogenic_amino_acid), only ten amino acids can be further considered. These are:

Amino acid	Prevailing form at pH 4.7 (according to Wikipedia)	Number of atoms	Amino acid	Prevailing form at pH 4.7 (according to Wikipedia)	Number of atoms
Gly		10	Asp		15
Ala		13	Pro		17
Cys		14	Thr		17
Sec		14	Asn		18
Ser		14	Glu		18

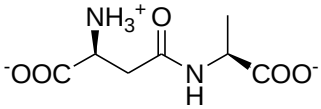
The listed amino acids provide for the following dipeptides (without regard to N- and C-termini): Ser-Cys, Ser-Sec, Cys-Sec, Gly-Asn, Gly-Glu и Asp-Ala. Taking into account the residue positioning (N- or C-terminal), one gets two different dipeptides for each of 4 former pairs, and 3 dipeptides for each 2 latter pairs (note that β-carboxyl group of Asp and γ-carboxyl group of Glu can be also involved in peptide bond formation; see an example below).



(1)



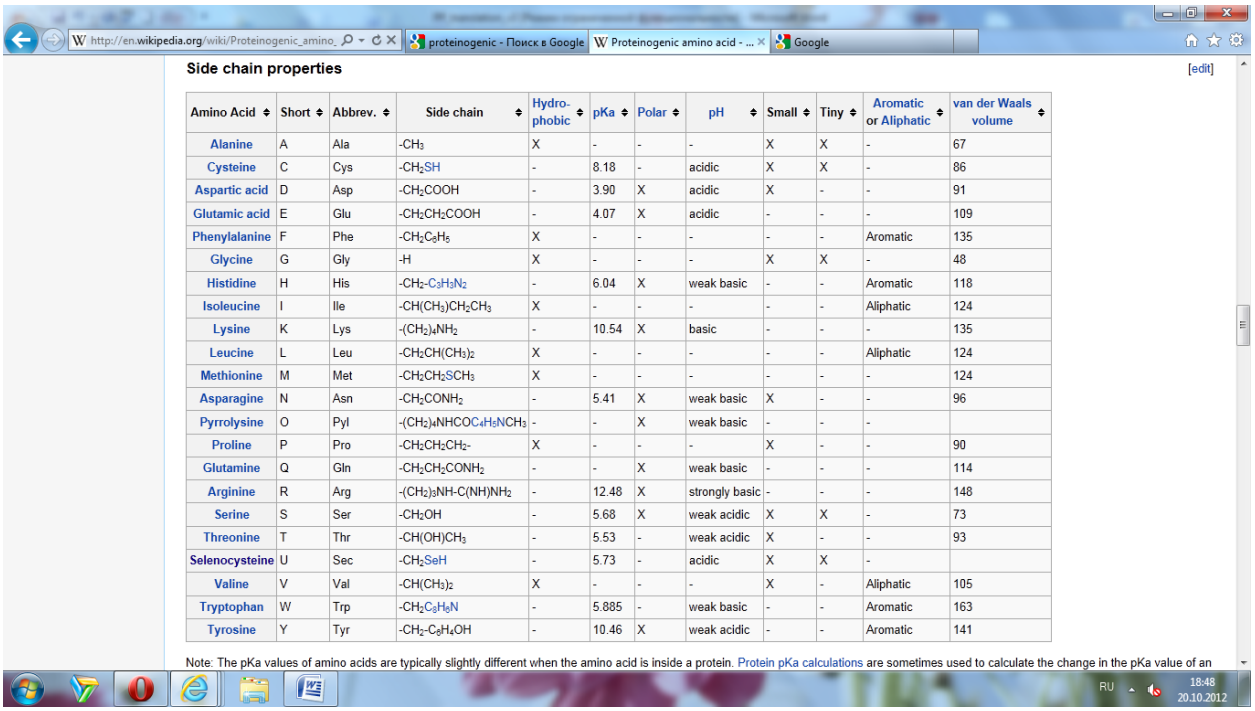
(2)



(3)

Thus, the total number of dipeptides equals to 14. However, serious caution is needed when using Wikipedia, since it is a collection of the user-generated content. Note that pKa values of some groups are absolutely incorrect (section “Side Chain Properties”). In particular, the side group of Asn is absolutely non-protonated at pH 4.7. Finally, the correct number of individual peptides is 12 (excluding Gly-Asn and Asn-Gly).

Screenshot of the webpage http://en.wikipedia.org/wiki/Proteinogenic_amino_acid dated 20.10.2012 is given below. Being irresponsible of these mistakes, authors of the problem promise to correct the data after publishing the Solutions to Preparatory problems.



Side chain properties [edit]

Amino Acid	Short	Abbrev.	Side chain	Hydrophobic	pKa	Polar	pH	Small	Tiny	Aromatic or Aliphatic	van der Waals volume
Alanine	A	Ala	$-CH_3$	X	-	-	-	X	X	-	67
Cysteine	C	Cys	$-CH_2SH$	-	8.18	-	acidic	X	X	-	86
Aspartic acid	D	Asp	$-CH_2COOH$	-	3.90	X	acidic	X	-	-	91
Glutamic acid	E	Glu	$-CH_2CH_2COOH$	-	4.07	X	acidic	-	-	-	109
Phenylalanine	F	Phe	$-CH_2C_6H_5$	X	-	-	-	-	-	Aromatic	135
Glycine	G	Gly	-H	X	-	-	-	X	X	-	48
Histidine	H	His	$-CH_2-C_3H_3N_2$	-	6.04	X	weak basic	-	-	Aromatic	118
Isoleucine	I	Ile	$-CH(CH_3)CH_2CH_3$	X	-	-	-	-	-	Aliphatic	124
Lysine	K	Lys	$-(CH_2)_4NH_2$	-	10.54	X	basic	-	-	-	135
Leucine	L	Leu	$-CH_2CH(CH_3)_2$	X	-	-	-	-	-	Aliphatic	124
Methionine	M	Met	$-CH_2CH_2SCH_3$	X	-	-	-	-	-	-	124
Asparagine	N	Asn	$-CH_2CONH_2$	-	5.41	X	weak basic	X	-	-	96
Pyrrolysine	O	Pyl	$-(CH_2)_4NHCOC_4H_5NCH_3$	-	-	X	weak basic	-	-	-	
Proline	P	Pro	$-CH_2CH_2CH_2-$	X	-	-	-	X	-	-	90
Glutamine	Q	Gln	$-CH_2CH_2CONH_2$	-	-	X	weak basic	-	-	-	114
Arginine	R	Arg	$-(CH_2)_3NH-C(NH)NH_2$	-	12.48	X	strongly basic	-	-	-	148
Serine	S	Ser	$-CH_2OH$	-	5.68	X	weak acidic	X	X	-	73
Threonine	T	Thr	$-CH(OH)CH_3$	-	5.53	-	weak acidic	X	-	-	93
Selenocysteine	U	Sec	$-CH_2SeH$	-	5.73	-	acidic	X	X	-	
Valine	V	Val	$-CH(CH_3)_2$	X	-	-	-	X	-	Aliphatic	105
Tryptophan	W	Trp	$-CH_2C_8H_6N$	-	5.885	-	weak basic	-	-	Aromatic	163
Tyrosine	Y	Tyr	$-CH_2-C_6H_4OH$	-	10.46	X	weak acidic	-	-	Aromatic	141

Note: The pKa values of amino acids are typically slightly different when the amino acid is inside a protein. Protein pKa calculations are sometimes used to calculate the change in the pKa value of an

At the same time, the pK_a values found at the other webpage (http://en.wikipedia.org/wiki/Amino_acid) are correct.

3. One should analyze all five variants of dipeptides (with no regard to N- and C-termini) from i. 2 by calculating masses of corresponding precipitates. Typical procedure is given below for the correct answer (Cys-Sec):

$$C_6H_{12}N_2O_3SSe + 9.5O_2 \rightarrow 6CO_2 + SO_2 + SeO_2 + N_2 + 6H_2O \ (1);$$

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3\downarrow + H_2O \ (2);$$

$$Ca(OH)_2 + SO_2 \rightarrow CaSO_3\downarrow + H_2O \ (3);$$

$$Ca(OH)_2 + SeO_2 \rightarrow CaSeO_3\downarrow + H_2O \ (4).$$

Number of moles of dipeptide: $1.000\,\mathrm{g}/271.19\,\mathrm{g/mol} = 3.687 \cdot 10^{-3}\mathrm{mol}$. Thus, the mass of precipitate is:

$$\mathrm{m(precipitate)} = 3.687 \cdot 10^{-3}\mathrm{mol} * (6 * 100.09 + 120.14 + 167.04)\mathrm{g/mol} = 3.273\ \mathrm{g}$$

However, further calculations according to the equations of chemical reactions of precipitate dissolution in hydrochloric acid

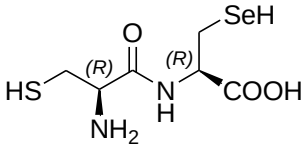
$$CaCO_3 + 2HCl \rightarrow CaCl_2 + CO_2\uparrow + H_2O \ (5);$$

$$CaSO_3 + 2HCl \rightarrow CaCl_2 + SO_2\uparrow + H_2O \ (6),$$

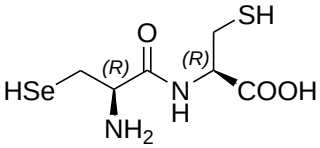
provide for contradictory results. Gas volume given in the task is by approx. 15% less than that obtained from the calculations. The only reason behind the difference is the deficiency of

hydrochloric acid with respect to the precipitate amount (Note that by contrast to the rest of the task, there is no indication of an excess or deficiency in the case of hydrochloric acid!).

Since the available data is insufficient to decide on the sequence of amino acid residues, both Cys-Sec and Sec-Cys are accepted as correct answers for **X**.



(1)



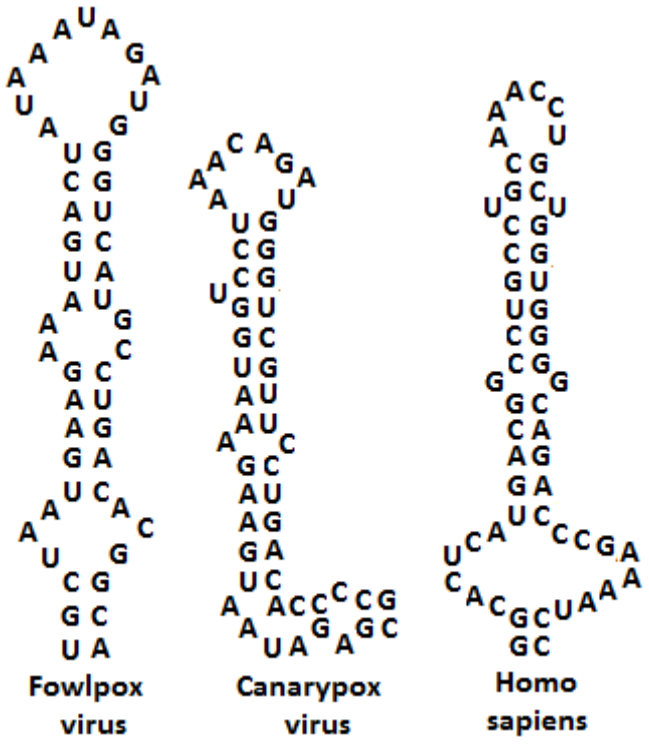
(2)

4. The –SeH group is a much stronger reducing agent than the –SH group. Thus, Sec is very readily oxidized, which makes its presence as free selenocysteine inside a cell impossible.

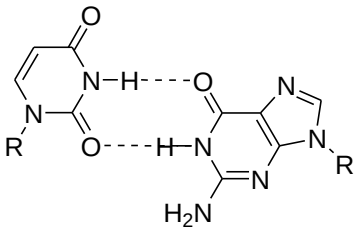
5. Searching for a correlation between the given images and sequences is much easier than can be expected. There could be many ways to reach the correct answer. A sample strategy is given below. First, one should decide which of the fragments refers to human RNA. Genomes of the viruses belonging to the same family should be phylogenetically close, with a slight divergence form the common ancestor. Indeed, sequences 1 and 3 reveal high similarity, both dramatically differing from sequence 2, the latter thus being attributed to human cell. Next step is the search for nucleotides corresponding to the black boxes in the image of human RNA. Note that there are colorless and grey boxes to the ends from black ones. These include 9 nucleotides at the 5'- and 11 nucleotides at the 3'-end. These forbidden areas are highlighted red in the hereunder sequence. Nucleotides corresponding to the black boxes are located between the red fragments, and should be twice two consecutive purine nucleotides AG, AA or GG (all options highlighted yellow). Furthermore, there should be exactly 30 nucleotides between the yellow fragments, which allows the final assignment (highlighted yellow and underlined).

AGGCACUCAUGACGGCCUGCCUGCAAACCUGCUGGUGGGGCAGACCCGAAAAUCCCAC

Thus, the encircled codon is UGA, which can be also found in fragments 1 and 3. Using the above strategy, one can fill in the rest two images and find the correlation between the images and fragments (fragments 1, 2, and 3 refer to the images of the fowlpox virus, homo sapiens, and canarypox virus, respectively).



6. Guanine-uracil is the so-called Wobble Base Pair.



7. UGA, according to the table of genetic code, is known as the STOP codon terminating translation. However, it is stated in the problem that the chain elongation proceeds after UGA (variants 2 and 3 invalid). UGA is similarly located in sequences of very dissimilar organisms (a mammal and viruses), which underlines its importance for translation and makes variant 5 hardly possible. Variant 4 can be also discriminated, since translation is an uninterruptible process.

Thus, variant 1 is the correct answer. Indeed, UGA in a certain motive (referred to as **SECIS element**, **Se**leno**c**ysteine **I**nsertion **S**equence) is read as the codon determining selenocysteine inclusion into polypeptides. In viruses, SECIS element is located in the translated region of RNA. In eukaryotes, this hairpin-like structure is found in the unreadable part of mRNA (in 3'-untranslated region, 3'-UTR), and Sec is not found in human proteins.

8. Knowledge of the UGA position allows setting the reading frame. In principle, there could be various mutations meeting the requirements. Examples are given below.

Choosing a mutation, one should keep in mind that the wild type and mutant codons must encode the same amino acid. Also, nucleotides of this codon should not be involved in maintaining the secondary structure of SECIS element (no hydrogen bonding to opposite nucleotides). Thus, one can suggest U-23→C-23 mutation for the fowlpox virus (both are tyrosine codons), and A-28→G-28 mutation for the canarypox virus (both are lysine codons).

Problem 24. Unusual amino acids: search for new properties

1. Calculation of molar ratios of carbon, hydrogen and oxygen in **A**-**C** allows determining their minimal molecular weights corresponding to the net formulae (note that isotopic ratios of C, H, N and O are native):

Compound	Calculation of ratios	Calculation of minimal molecular weights, g/mole
A	$n(\mathrm{C}) : n(\mathrm{H}) : n(\mathrm{O}) = \frac{31.09}{12.01} : \frac{5.74}{1.008} : \frac{16.57}{16.00} = 5 : 11 : 2$	$M = \frac{60.05 \cdot 100}{31.09} = 193.1$
B	$n(\mathrm{C}) : n(\mathrm{H}) : n(\mathrm{O}) = \frac{26.67}{12.01} : \frac{5.04}{1.008} : \frac{17.77}{16.00} = 4 : 9 : 2$	$M = \frac{48.04 \cdot 100}{26.67} = 180.1$
C	$n(\mathrm{C}) : n(\mathrm{H}) = \frac{9.24}{12.01} : \frac{3.10}{1.008} = 1 : 2.25 = 1 : 4$	$M = \frac{12.01 \cdot 100}{9.24} = 130.0$

With provision of the upper bound (M<250 g/mole), true and minimal molecular weights coincide. The residual molecular weights available for the other two elements (besides C, H, and O) in **A** and **B** are of 90.0 and 91.0 g/mole, respectively. There are two possible reasons behind the difference in the residual molecular weights for **A** and **B** (91.0-90.0=1 g/mole). These are dissimilarity of atomic weights of the fifth elements in **A** and **B** and/or different number of nitrogen atoms in these compounds. All possible variants of the number of nitrogen atoms (cannot exceed 6) in **A** are considered in the hereunder table:

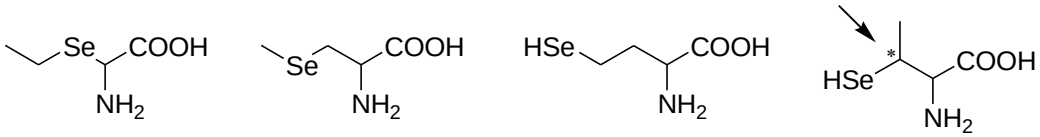
Number of N atoms in **A**	Residual molecular weight left for the 5th element in **A**	Variants of the 5th element	Biochemical sense
1	76	-	-
2	62	2P	To be considered
3	48	1 Ti?	Impossible
		2 Mg?	Impossible
		3 O?	Impossible
		4 C?	Impossible
4	34	-	-
5	20	1 Ne?	Impossible
6	6	6 H?	Impossible

With provision of the inequality given in the problem text, the variant of 2 nitrogen atoms in **A** corresponds to 1 or 2 nitrogen atoms in **B**, and 75 or 63 g/mole left for the 5th element in the latter compound, respectively. No reasonable variants are in agreement with the above values. Therefore, we seem to have come up against a brick wall.

2. Difference by 1 g/mole in the molecular weights of the 5th element in **A** and **B** is left as the only reason. This can be true in case of isotopes (note that native isotope ratios are mentioned only for four elements!). If so, isotopes should be stable (stability of all initial compounds) and most likely of one and the same element (**A**, **B**, and **C** are precursors of the same compound **X**). With account of the equal number of nitrogen atoms in **A** and **B**, the following set of isotope combinations is available: 20-21, 34-35, 48-49, 62-63, 76-77. Furthermore, the difference of 1 g/mole unambiguously suggests only one atom of the 5th element in each of **A** and **B**.

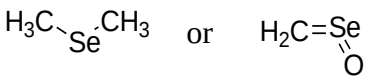
Two sets of stable isotopes (^{48}Ti-^{49}Ti and ^{76}Se-^{77}Se) formally fit well. Since there are no native titanium-containing amino acids, the elemental composition of **A** and **B** is finally found as: C, H, N, O, and Se.

3. As determined above, the molecular formula of **B** is $C_4H_9SeNO_2$. Four structures can be proposed for this α-amino acid. The rightmost structure contains two chiral atoms, thus being invalid, whereas the leftmost one is unstable. So, two central structures are left as the correct answer.



4. Both *R*- and *S*-amino acids are found in nature. Since it is not mentioned in the problem text which exactly of **A** and **B** is found in proteins, it is impossible to unambiguously assign configurations of α-carbon atoms without additional information.

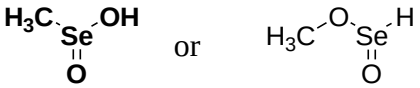
5. Gases **A1**, **B1**, and **C1** have molecular weights of 106, 107 and 112 g/mole, respectively. It is seen that the difference in the molecular weights of **A** and **B** (1 g/mole) is retained for their metabolites. Thus, **A1** and **B1** are likely to be isotopologues. Besides selenium, **A1** and **B1** contain elements with a total residual molecular weight of 106 – 76 = 30 g/mole. Since gaseous metabolites contain hydrogen, there are two possible variants of their molecular formula: C_2H_6Se or CH_2SeO. With provision of identity of hydrogen atoms in **A1**, the following structures are possible:



Of these two, only dimethylselenide does not contain π-bonds. Finally, **A1** is $(CH_3)_2{}^{76}Se$, and **B1** is $(CH_3)_2{}^{77}Se$.

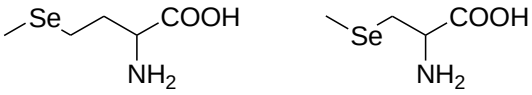
6. The atomic weight of selenium isotope in **C1** is 76 + (112-106) = 82 a.u. (Note that the final metabolite is the same for all three initial original compounds!). Residual molecular weight left for the 4th element in **C** (it consists of only four elements) is 130 – 16 – 82 = 32 g/mole, which corresponds to two atoms of oxygen. Thus, the molecular formula of **C** is $CH_4O_2{}^{82}Se$.

Presence of methyl groups in **C1** as well as lack of C–O bonds in the structure allow the final ascertainment of the structural formula of **C** (the leftmost of the hereunder ones with ^{82}Se):



Then, **X** is methyleselenide CH_3SeH, and **C1** is $(CH_3)_2Se$ produced as result of **X** methylation (transferase reaction).

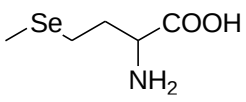
7. As determined in i. 6, methylation is the second step of the processes under consideration. With respect to extremely high specificity of enzymes, all substrates subjected to methylation should be very similar. Thus, the isotopologues of **X** ($CH_3{}^{76}SeH$ and $CH_3{}^{77}SeH$) are the only reasonable intermediates on the way from **A** and **B** to **A1** and **B1**, respectively. These intermediates can directly originate only from compounds containing CH_3-Se- residue. Thus, selenomethionine and methylselenocysteine can be attributed to **A** and **B**:



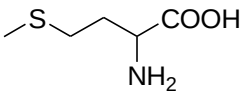
A **B**

8. Since the experiment under discussion is aimed at revealing pathways of selenium metabolism, it is reasonable to check masses of selenium in each of the administered compounds. Calculations involving the molecular weights of **A**, **B**, and **C** and masses of these compounds in the mixture provide for a wonderful result: the mixture contains 25 μg of each of selenium isotopes.

9. Variant 2 is the correct choice. Selenomethionine is structurally similar to methionine (compare the structures hereunder), which sometimes leads to mistakes in translation and false insertion of selenium-containing amino acid instead of sulfur-containing one.



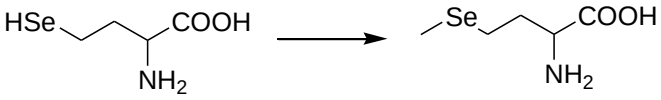
Selenomethionine



Methionine

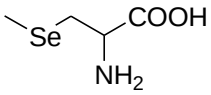
Isotope ^{76}Se is found in nature (~1% of the total selenium pool), so the residue of selenomethionine with ^{76}Se can be found (though rarely) in proteins.

Variant 1 is impossible, since posttranslational modification leading to **A** should involve methylation of selenohomocysteine residue, the latter amino acid also lacking its own tRNA:

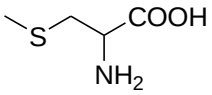


Variants 3 and 5 are impossible, since protein biosynthesis admits the only way of polypeptide chain elongation, which involves an amino acid residue transfer from aminoacyl-tRNA.

Variant 4 is impossible for the same reasons as Variant 2. Methylselenocysteine is structurally similar to S-methylcysteine (compare the hereunder structures), which is not a canonical amino acid, thus lacking its own tRNA:



Methylselenocystein



Methylcysteine

Problem 25. Specific features of *Clostridium* metabolism

1. Glucose consists of carbon, oxygen and hydrogen. As a result of its fermentation in H_2O the following gaseous (at STP) products could be theoretically formed:

    1) Molecular hydrogen,
    2) Various hydrocarbons,
    3) Formaldehyde,
    4) CO and CO_2.

Absence of C-H bonds in **C** and **D** allows excluding variants 2 and 3 from further consideration.

Molecular mass of the gas mixture is 10.55*2 g/mol = 21.1 g/mol. It is obvious that hydrogen is one of the two gases, whereas either CO or CO_2 is the other one. CO seems to be an improbable variant; still all the options should be checked by applying the hereunder formula for *n*:

$$M(\boldsymbol{C}) \cdot \frac{n}{n+10} + M(\boldsymbol{D}) \cdot \frac{10}{n+10} = 21.1$$

$$n = \frac{211 - 10 \cdot m(\boldsymbol{D})}{M(\boldsymbol{C}) - 21.1}$$

C	**D**	***Coefficient n***
H_2	CO_2	12.0
CO_2	H_2	8.3
H_2	CO	9.6
CO	H_2	27.7

Since *n* is integer in only one case, **C** and **D** are attributed to H_2 and CO_2, respectively.

Note that bacterial cultures exist in specific, sometimes solid, nutritious media. Thus, conventional data of gases (in particular, of CO_2) solubility in water may be inapplicable.

2. With respect to the results in i. 1, the updated reaction (1) is rewritten as:

$$5C_6H_{12}O_6 + kH_2O \rightarrow l\mathbf{A} + m\mathbf{B} + 12H_2 + 10CO_2$$

a) In the case when each of **A** and **B** is a saturated monocarboxylic acids, the equation transforms into:

$$5C_6H_{12}O_6 + kH_2O \rightarrow lC_xH_{2x}O_2 + mC_yH_{2y}O_2 + 12H_2 + 10CO_2,$$

where *x* and *y* are the numbers of carbon and hydrogen atoms in **C** and **D**, respectively.

With account of the balance of the elements numbers, one gets the hereunder system of equations:

Element	**Balance equation**
C	$l \cdot x + m \cdot y = 20$
H	$18 + k = l \cdot x + m \cdot y$
O	$k = 2l + 2m - 10$

It is seen from the first two equations that $k = 2$. Thus, the equation for oxygen can be rewritten as $l + m = 6$

b) In the case when **A** is a saturated monocarboxylic and **B** a saturated dicarboxylic acids (reverse variant is equivalent), the equation transforms into:

$$5C_6H_{12}O_6 + kH_2O \rightarrow lC_xH_{2x}O_2 + mC_yH_{2y-2}O_4 + 12H_2 + 10CO_2,$$

where *x* and *y* are the numbers of carbon and hydrogen atoms in **C** and **D**, respectively.

Further analysis provides an analogous system of equations:

Element	**Balance equation**
C	$l \cdot x + m \cdot y = 20$
H	$18 + k = l \cdot x + m \cdot y - m$
O	$k = 2l + 4m - 10$

There is only one set of integer values corresponding to $m = k = 1$. Still, then l=3.5, which is in contradiction with the conditions of the problem.

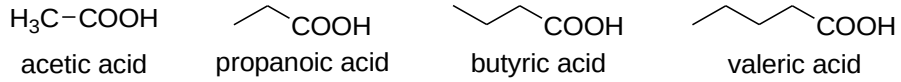
A and **B** with higher number of carboxylic groups (for example, two dicarboxylic acids) are impossible, as this results in negative k, l, or m.

3. l and m are integers, and $l + m = 6$. This suggests the following possible ratios: 1:1 (3:3), 1:2 (2:4) and 1:5. Still, $l \cdot x + m \cdot y = 20$, which makes the ratio of 1:1 impossible (both x and y non-integer, 20/3 = 6.67). Ratios of 2:1 and 5:1 are theoretically possible. Thus, the correct variants are b, e and f.

4. The next step is a search for integer solutions of the equation $l \cdot x + m \cdot y = 20$ for the ratios established in i. 3.

l = 2; m = 4		l = 1; m = 5	
x	**y**	**x**	**y**
8	1	15	1
6	2	10	2
4	**3**	**5**	**3**
2	**4**		

Since the number of carbon atoms decreases as a result of fermentation (x<6 and y<6), only the variants **underlined** in the above table are left for consideration. These correspond to four unbranched monocarboxylic acids:



acetic acid | propanoic acid | butyric acid | valeric acid

Further discrimination of the variants based on the available data is impossible.

For your information: **A** and **B** are acetic and butyric acids, respectively.

5. Since $\mathbf{Z}_{\mathbf{start}}$ and $\mathbf{Z}_{\mathbf{finish}}$ contain the same number of nitrogen atoms, a system of equations (2) and (3) can be set up:

$$\frac{a}{b} = 0.12727\ (2);\ \frac{a}{b+n} = 0.12069\ (3)$$

$$b = 18.34 \cdot n$$

where a is the number of N atoms, whereas b and b+n are the total numbers of atoms in $\mathbf{Z}_{\mathbf{finish}}$ and $\mathbf{Z}_{\mathbf{start}}$, respectively.

The given limitation of less than 100 atoms in each of $\mathbf{Z}_{\mathbf{start}}$ and $\mathbf{Z}_{\mathbf{finish}}$ can be written as n<6. Variable b is necessarily integer, thus leading to the solely possible combination of b=55 and n=3. So, $\mathbf{Z}_{\mathbf{start}}$ and $\mathbf{Z}_{\mathbf{finish}}$ are composed of 58 and 55 atoms, respectively. This means that $\mathbf{Z}_{\mathbf{start}}$ loses 3 atoms in acetyl-CoA formation.

6. The difference in the number of hydrogen atoms in $\mathbf{Z_{start}}$ and $\mathbf{Z_{finish}}$ is:

$$\Delta N_H = N_H(\boldsymbol{Z}_{\mathbf{start}}) - N_H(\boldsymbol{Z}_{\mathbf{finish}}) = 58 \cdot 0.43103 - 55 \cdot 0.41818 = 2$$

Thereby, two of three atoms appearing in acetyl-CoA from $\mathbf{Z_{start}}$ are hydrogen atoms. Oxygen or carbon can be the third atom lost by $\mathbf{Z_{start}}$. In the former case, $\mathbf{Z_{start}}$ loses H_2O, and in the latter case CH_2-group, which is formally equivalent to substituting a CH_3-group with 1 hydrogen atom.

Both variants can be rewritten in a form of equations (4) and (5):

$$\mathbf{Z}\text{-}CH_3 + CoA\text{-}SH + \mathbf{E} \rightarrow \mathbf{Z}\text{-}H + CH_3\text{-}CO\text{-}SCoA \quad (4);$$

$$H\text{-}\mathbf{Z}\text{-}OH + CoA\text{-}SH + \mathbf{E} \rightarrow \mathbf{Z} + CH_3\text{-}CO\text{-}SCoA \quad (5).$$

Equation (5) is invalid with any **E**, whereas equation (4) is correct, if **E** is carbon monoxide CO formed via enzymatic reduction of CO_2.

Since bacteria cultivation proceeds in the presence of isotope-labeled CO_2, the number and isotope distribution of nitrogen atoms in acetyl CoA are not influenced. Thus, the molecular mass of acetyl-CoA isotopologues is:

$$M(labeled\ AcCoA) = \frac{100 \cdot 14.01 \cdot 7}{12.08} = 811.8\ g/mol$$

Molecular mass of unlabeled acetyl-CoA is 809.5. With account of rounding of nitrogen mass fractions, the difference is of 2 g/mol. Two hereunder variants are possible:

1) CO_2 labeled with ^{13}C enters the reaction, thus giving acetyl residue with two ^{13}C atoms;
2) CO_2 labeled with two ^{18}O enters the reaction, thus giving acetyl residue with ^{18}O atom.

It is impossible to distinguish between **D1** and **D2** basing on the available data:

D1 – $^{13}CO_2$ or $C^{18}O_2$; **D2** – $^{13}CO_2$ or $C^{18}O_2$.

The above considered acetyl-CoA biosynthesis is referred to as the Wood-Ljungdahl pathway.

For your information. Exact attributing of **D1** and **D2** is possible using physico-chemical methods of analysis. Both isotopes are stable, which makes the radioactivity based methods useless. The suitable methods include mass-spectrometry (different patterns are formed for molecular fragments) and ^{13}C-NMR spectroscopy (^{18}O isotope is not used in NMR spectroscopy).

7. The initial nucleotide ratio is 1:1, thus the probability of finding G or C at any position equals ½. Hence, the probability of any of eight possible codons is of 1/2*1/2*1/2=1/8. Four amino acids are each encoded by two codons composed of only G and/or C. Thus, the ratio

between Pro, Arg, Gly, and Ala is 1:1:1:1. However, with account of the limited length of the oligopeptide (about 33 amino acid residues), there could be significant deviations from the above ratio. So, variant 6 is the most correct choice.

8. Using the table of genetic code, one can write down the nucleotide sequences of the initial and mutant mRNA fragments (see designations of N and N1/N2 in Problem 22, i. 6):

UGG-CA**U/C**-AUG-GA**A/G**-UA**U/C** (initial);

UGG-AC**N**-UA**U/C**-GG**N**-GU**N** (mutant).

Comparison of two sequences suggests that the mutation (insertion of A) occurred right after the first codon. Mutations influencing polypeptide biosynthesis are classified into two groups: the substitution of base pairs and the frameshift. The latter happens upon deletion or insertion of nucleotides in a number not multiple of three. Then, the initial sequence can be rewritten as:

UGGCAUAUGGAGUA**U/C**

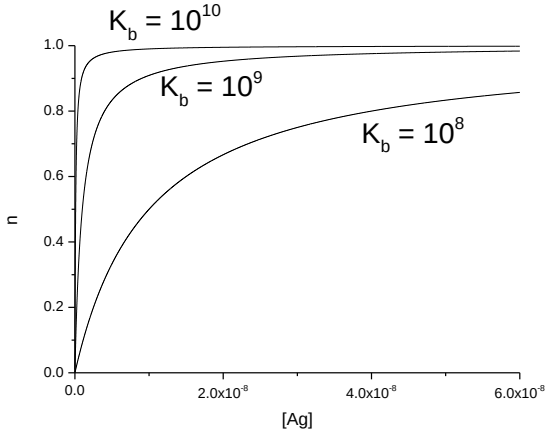
If the mutant protein ends up with the 234rd amino acid residue, the biosynthesis is terminated by a STOP codon present next. Since STOP codons always start with U, the completely deciphered sequence of nucleotides is:

UGGCAUAUGGAGUAU

Problem 26. Analysis of complex formation

1. $\mathrm{K}_b = \frac{[\mathbf{Ab}*\mathbf{Ag}]}{[\mathbf{Ab}]\cdot[\mathbf{Ag}]}$

2. $\bar{n} = \frac{[\mathbf{Ab}*\mathbf{Ag}]}{[\mathbf{Ab}*\mathbf{Ag}]+[\mathbf{Ab}]} = \frac{\mathrm{K}_b[\mathbf{Ab}]\cdot[\mathbf{Ag}]}{\mathrm{K}_b[\mathbf{Ab}]\cdot[\mathbf{Ag}]+[\mathbf{Ab}]} = \frac{\mathrm{K}_b[\mathbf{Ag}]}{\mathrm{K}_b[\mathbf{Ag}]+1}$

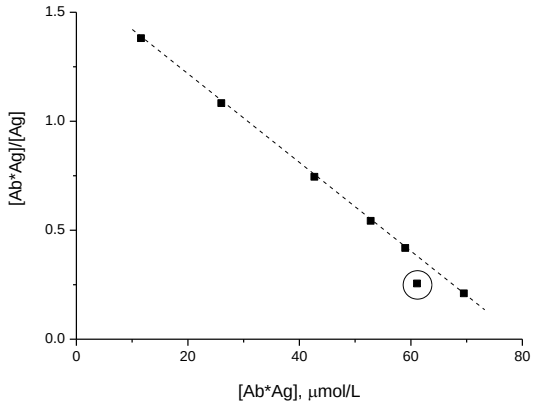


As seen, the titration curves are strongly non-linear, which makes their analysis complicated.

3. $$K_b = \frac{[\mathbf{Ab}*\mathbf{Ag}]}{[\mathbf{Ab}]\cdot[\mathbf{Ag}]} \Rightarrow \frac{[\mathbf{Ab}*\mathbf{Ag}]}{[\mathbf{Ag}]} = K_b(C_{\mathbf{Ab}} - [\mathbf{Ab}*\mathbf{Ag}])$$

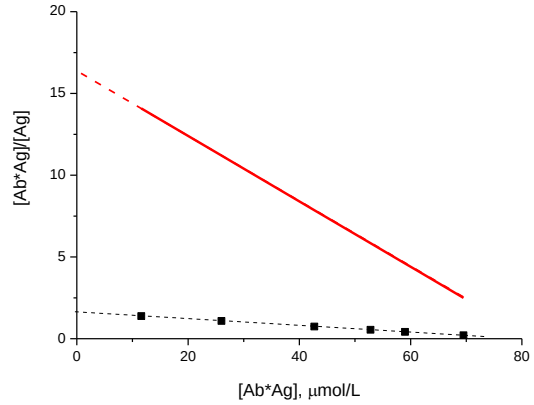
Thus, a plot in such coordinates (referred to as the Scatchard ones) should be a straight line with the slope of $-K_b$ and the intercept of $C_{\mathbf{Ab}}K_b$ ($C_{\mathbf{Ab}}$ is the total **Ab** concentration).

This is proved by plotting Set A data, point #6 is seemingly an outlier:



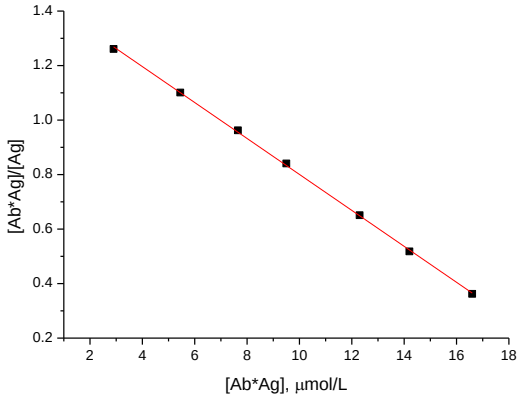
From the experimental data, $K_b = 2\cdot10^4$ L/mol.

According to the above equation, with a 10 times higher K_b, values for both the intercept (1.64 from the original data) and the slope should be 10 times higher:



4. If all the binding sites are independent, and K_b does not depend on the fraction of occupied binding sites, mathematically there is no difference between x molecules of antibody with valence N and N·x molecules of antibody with valence 1. Thus, the above mentioned Scatchard equation is only slightly modified to account for several binding sites per antibody:

$$\frac{[\mathbf{Ab}*\mathbf{Ag}]}{[\mathbf{Ag}]} = K_b(N \cdot C_{\mathbf{Ab}} - [\mathbf{Ab}*\mathbf{Ag}]).$$



The experimental data fit a straight line with a slope of -0.0660 (corresponding to K_b = 6.6·10^4 L/mol) and an intercept of 1.46. Thus, $1.46 = \mathrm{K}_b \cdot \mathrm{N} \cdot \mathrm{C}_{\mathbf{Ab}} = 6.6 \cdot 10^4 \cdot N \cdot 1.1 \cdot 10^{-5} \Rightarrow N = 2$.

5. A clear way to determine $\mathrm{C}_{\mathbf{Ab}}$ follows from the fact that the K_b value influences both the slope and the intercept of the plot in Scatchard coordinates. As soon as K_b is determined from the slope of the curve, $\mathrm{C}_{\mathbf{Ab}}$ can be immediately calculated, provided the antibody valence N is known. For instance, for the set A, N=1, K_b = 2·10^4 L/mol; $\mathrm{C}_{\mathbf{Ab}}$ = 1.64 / 2·10^4 ≈ 82 μmol/L, which reasonably corresponds to the given value of 80 μM. It can be concluded, thus, that the ADP protein does not contain any functionally inactive antibodies or other impurities.

The same analysis for the set B is impossible, because the real enzyme valence is not known *a priori*. (Value N = 2 determined above has been obtained under assumption of 100% enzyme purity.)

Problem 27. Inorganic polymers: polyphosphates and polysilicones

1. Well known examples are: C (acethylenic carbon), S (various forms of polymeric sulfur), Se (grey selenium), P (red phosphorus), As (black arsenic), Sb (black antimony). Not all of these substances consist of perfectly linear chain molecules, but for sure these elements are capable of forming quite long polymers.

2. $2\mathrm{HPO}_4^{2-} \rightleftarrows \mathrm{P_2O_7^{4-}} + \mathrm{H_2O}$ (ionization state of the phosphate precursor depends on pH).

3. With $\mathrm{P_i}$ standing for a polyphosphate with the degree of polymerization of *i*, for the reaction

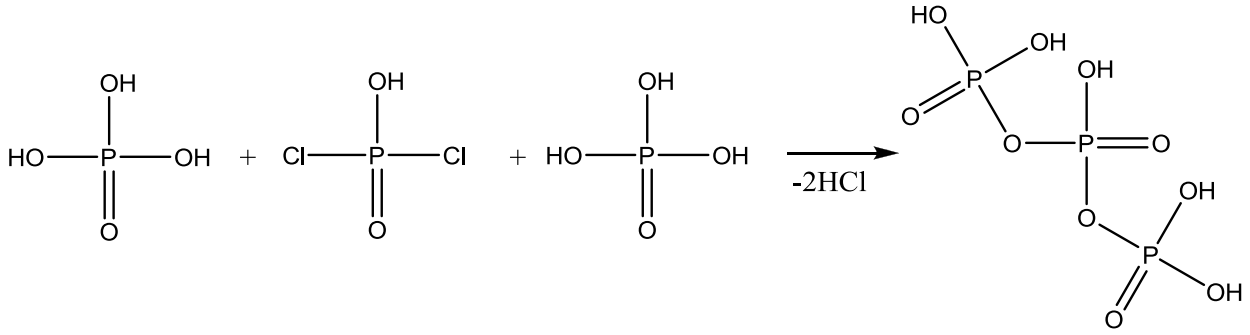
$$\mathrm{P_mOH} + \mathrm{P_nOH} \rightleftarrows \mathrm{P_mOP_n} + \mathrm{H_2O}$$

$$K = \frac{[\mathrm{P_{m+n}}][\mathrm{H_2O}]}{[\mathrm{P_m OH}][\mathrm{P_n OH}]}.$$

As polyphosphates of various degrees of polymerization are not distinguishable, each of concentrations $[P_m]$, $[P_n]$, $[P_{m+n}]$ can be substituted with the total concentration of all phosphate species, thus,

$$K = \frac{[\mathrm{P_{m+n}}][\mathrm{H_2O}]}{[\mathrm{P_m OH}][\mathrm{P_n OH}]} = \frac{[\mathrm{H_2O}]}{[\mathrm{P_i}]}$$

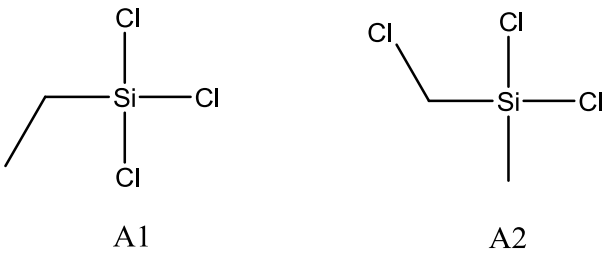
4. The following reasons should be taken into account. First, the free energy of hydrolysis is strongly negative, which means that the free energy of condensation (the reverse reaction) is positive. Thus, the equilibrium constant of an elementary condensation stage is low (less than 1), which is not consistent with the high-polymeric phosphate species. In general, lower equilibrium concentration of (poly)phosphate molecules means that more individual condensations have taken place, which is equivalent to the higher average degree of polymerization of the product. This is true for process ii): lower water concentration (at a certain equilibrium constant value) corresponds to lower equilibrium concentration of phosphate molecules (from the expression derived in i. 3). Thus, process ii) is more favorable than i). However, process iii) is the most favorable. According to the equation



a highly volatile HCl is formed, which is efficiently removed from the reaction mixture by heating. As a result, the equilibrium is shifted rightwards.

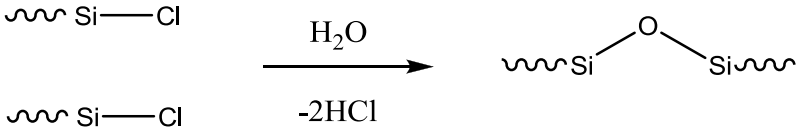
Indeed, only route iii) can be applied in practice for the preparation of polyphosphoric acids. Condensation in concentrated solutions (process ii)) is quite slow, and yields significant amounts of polyphosphoric acids only upon heating (molten H_3PO_4, 230-250°C). Direct condensation in dilute solution (process i)) is so unfavorable that may come true only when coupled with a certain exoergic reaction (for instance, substrate phosphorylation in various biochemical processes) with the actual mechanism much more complicated than direct condensation.

5.

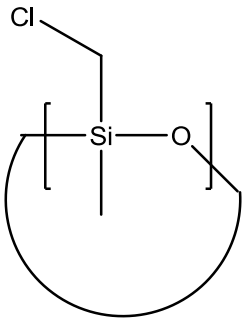


A1 A2

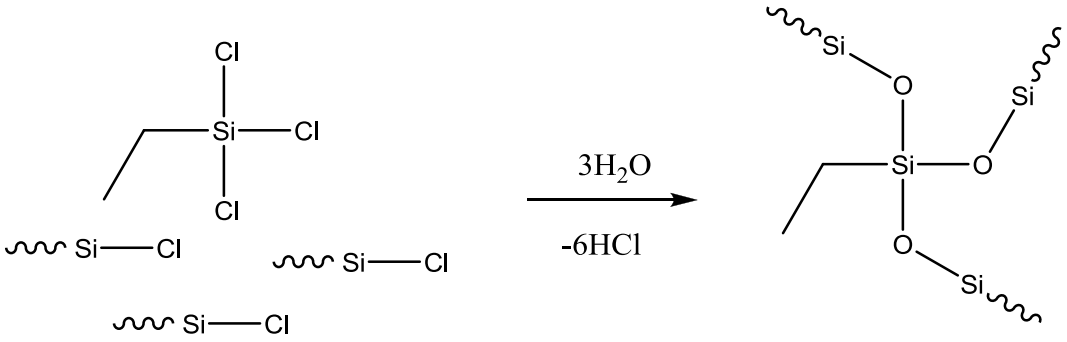
The main chain of the polymer molecule is composed of Si and O atoms:



6, 7. The Si–Cl bond is much more reactive than the C–Cl one in hydrolysis and condensation reactions. Thus, **A2** can be considered bifunctional in polycondensation reaction, giving a non-branched polymer with the cyclic giant macromolecule of poly(chlorodimethylsiloxane) as the final product when absolutely all Si-Cl bonds are reacted:



A1 is trifunctional, thus giving rise to a branched polymer:



If hydrolysis of Si-Cl bonds is incomplete, some Cl residues are present in the polymeric product. Incomplete condensation retains a number of OH–groups in the product.

Problem 28. Determination of copper and zinc by complexometric titration

1. $Cu + 4HNO_{3\,(conc.)} = Cu(NO_3)_2 + 2NO_2 + 2H_2O$

$Zn + 4HNO_{3\,(conc.)} = Zn(NO_3)_2 + 2NO_2 + 2H_2O$

$Cu^{2+} + Na_2H_2EDTA = CuH_2EDTA + 2Na^+$

$Zn^{2+} + Na_2H_2EDTA = ZnH_2EDTA + 2Na^+$

2. Cu^{2+} ions present in the aqueous solution are reduced to Cu^+ by thiosulfate. Moreover, the latter forms with Cu^+ a soluble complex $[Cu(S_2O_3)_3]^{5-}$, which is more stable than Cu_2H_2EDTA:

$$2Cu^{2+} + 8S_2O_3^{2-} = 2[Cu(S_2O_3)_3]^{5-} + S_4O_6^{2-}$$

3. Metal ions can be titrated with EDTA if the conditional stability constants β' of the metal – EDTA complexes are not less than 10^8–10^9. The β' values are connected with the real constants β as

$$\beta' = \alpha_{EDTA}\,\alpha_M\,\beta,$$

where α_{EDTA} and α_M are molar fractions of H_2EDTA^{2-} and free metal ion, respectively. As the values of α_{EDTA} and α_M significantly depend on pH of the solution, there is an optimal pH range for the titration of metals. In the case of Cu^{2+} and Zn^{2+}, the pH value within 5 to 6 is optimal. In such slightly acidic medium both metals do not form hydroxy complexes (α_M is high), whilst H_2EDTA^{2-} is not further protonated (α_{EDTA} is high).

4. $\alpha(H_2EDTA^{2-}) = K_1K_2[H^+]^2 / (K_1K_2K_3K_4 + K_1K_2K_3[H^+] + K_1K_2[H^+]^2 + K_1[H^+]^3 + [H^+]^4)$

$[H^+] = 10^{-6}$ M, $K_1 = 1.0\cdot10^{-2}$, $K_2 = 2.1\cdot10^{-3}$, $K_3 = 6.9\cdot10^{-7}$, $K_4 = 5.5\cdot10^{-11}$

$$\alpha(H_2EDTA^{2-}) = 0{,}59$$

5. The first titration (**B**) gives the volume of titrant V_{Cu+Zn}, whilst the second one (**C**) gives V_{Zn}. Zn^{2+} concentration is calculated as follows:

$$c(Zn^{2+}) = (V_{Zn}\,mL/1000\,mL\,L^{-1}) \cdot c_{EDTA}\,mol\,L^{-1} \cdot 100\,mL/10.00\,mL \cdot 65.39\,g\,mol^{-1} / 0.1000\,L$$

$$c(Zn^{2+})\,g\,L^{-1} = V_{Zn}\,mL \cdot c_{EDTA}\,mol\,L^{-1} \cdot 65.39\,g\,mol^{-1} \cdot 0.1\,mL^{-1}$$

$$c(Cu^{2+}) = ((V_{Cu+Zn} - V_{Zn})\,mL/1000\,mL\,L^{-1}) \cdot c_{EDTA}\,mol\,L^{-1} \cdot 100\,mL/10.00\,mL \cdot 63.55\,g\,mol^{-1} / 0.1000\,L$$

$$c(Cu^{2+})\,g\,L^{-1} = (V_{Cu+Zn} - V_{Zn})\,mL \cdot c_{EDTA}\,mol\,L^{-1} \cdot 63.55\,g\,mol^{-1} \cdot 0.1\,mL^{-1}$$

The mass ratio of the metals in alloy is calculated from $c(Cu^{2+})$ and $c(Zn^{2+})$ values in g L^{-1}:

$$m(Cu)/m(Zn) = c(Cu^{2+})/c(Zn^{2+})$$

Problem 29. Conductometric determination of ammonium nitrate and nitric acid

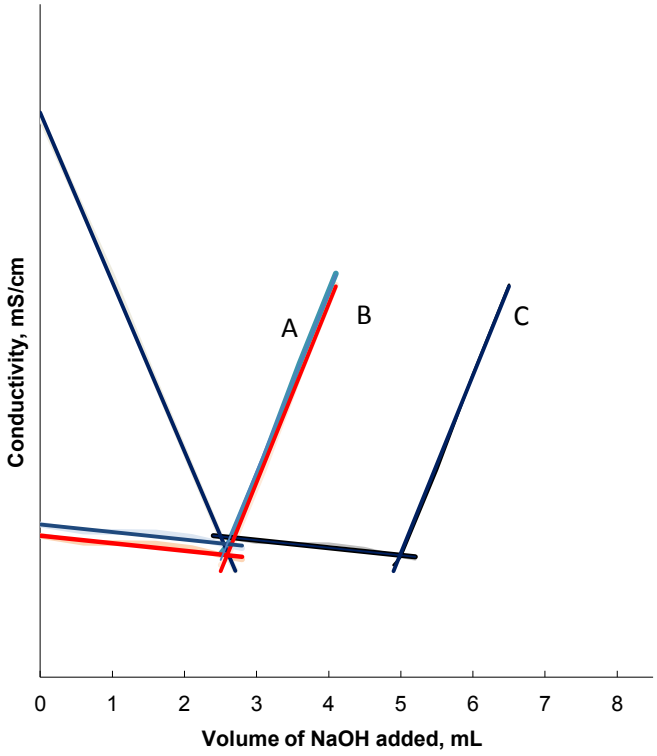
1. Equilibria in the system can be described by the following equations:

$$H^+ + OH^- \leftrightarrows H_2O \quad (1)$$

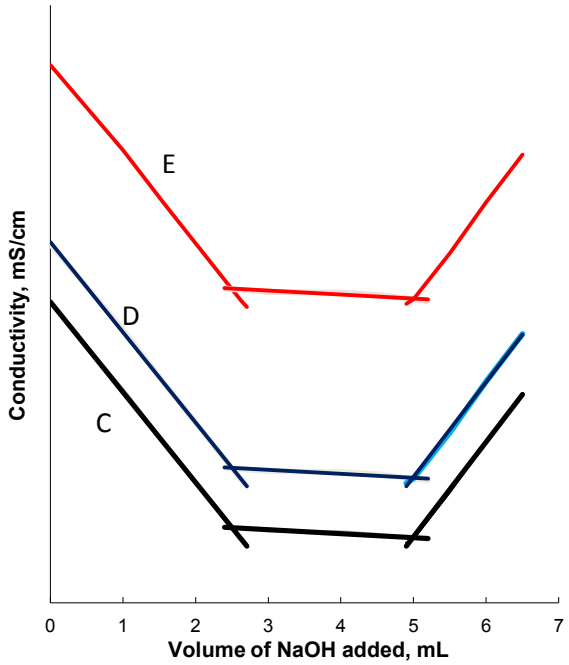
$$NH_4^+ + OH^- \leftrightarrows NH_3 + H_2O \quad (2)$$

2, 3. Conductivity of a solution is primarily dependent on the concentration of H^+ and OH^- ions (species with the highest mobility) as well as on that of salts. Solutions **A** and **B** contain the same amount of NH_4NO_3 (solution **A** with an excess of ammonia reveals a bit higher conductivity). On the titration curves, there are monotonously descending portions reflecting the displacement of the weak base (NH_3) from its salt (reaction 2). Minimum conductivity is reached when the concentration of protons appearing from NH_4^+ hydrolysis is minimal (reaction 2 completed). This is further changed by a sharp rise corresponding to the increasing excess of alkali.

In the case of solution **C,** the first descending portion is steeper (than those for **A** and **B**) and is associated with diminishing concentration of free protons coming from HNO_3. The first equivalence point causes a sharp break of the curve (reaction 1 completed). The second descending portion characterized by a lower slope reflects the displacement of the weak base from its salt (reaction 2). Minimum conductivity is also reached when reaction 2 is completed, which is followed by a sharp rise of conductivity due to the alkali excess.



Titration of NH_4NO_3 (**A),** of NH_4NO_3 in the presence of an excess of NH_3 (**B**), and of HNO_3 followed by that of NH_4NO_3 (**C**).



Titration of solutions of HNO_3 and NH_4NO_3 diluted with deionized water (**C**), distilled water (**D**), and deionized water containing NaCl (**E**).

The difference between cases **C, D,** and **E** is due to various levels of conductivity caused by the salts that are not titrated with NaOH.

4. Calculations can be done in the same way as for a regular acid-base titration, using titrant volumes in inflection points $V_{NaOH(1)}$, $V_{NaOH(2)}$:

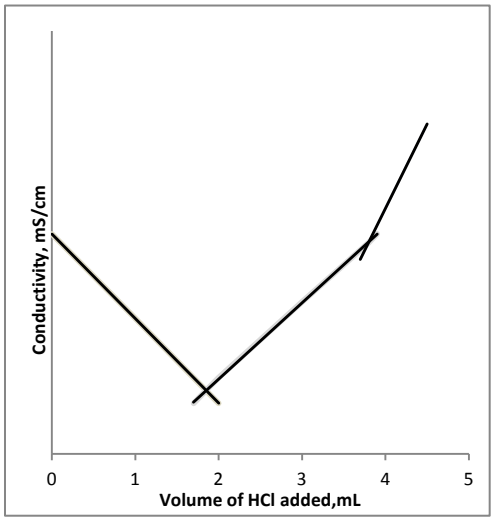
$$c_{H^+}V_{sample} = c_{NaOH}V_{NaOH(1)}, \qquad c_{NH4^+}V_{sample} = c_{NaOH}\cdot(V_{NaOH(2)} - V_{NaOH(1)})$$

Examples.

A and **B**: if 2.45 mL of 0.9987 M NaOH spent until the inflection point, then c_{NH4+} is: 0.9987 × 2,45 = c_{NH4+} × 25; c_{NH4+} = 0.0979 M.

C - E: if 2.40 mL of 0.9987 M NaOH spent until the first inflection point (neutralization of HNO_3) in a 25.0 mL sample aliquot, then c_{HNO3} = 0.0895 M. If the second inflection point reached at 4.85 mL, then c_{NH4+} is: 0.9987 × (4.85 – 2.40) = c_{NH4+} × 25; c_{NH4+} = 0.0979 M.

5. HCl first neutralizes the strong base, which is followed by neutralization of the weak one. So, the titration curve of a mixture of two bases reveals two breaks. NaOH neutralization is accompanied by a linear decrease of conductivity due to lowering concentration of highly mobile hydroxyl ions. After the first equivalence point, conductivity starts increasing due to the formation of a well dissociating salt (a strong electrolyte) as a result of ammonia (a weak electrolyte) neutralization. After the second equivalence point, conductivity of the solution sharply increases due to the excess of hydrogen ions.



Problem 30. Analysis of fire retardants by potentiometric titration

1. Titration curves for a polyprotic acid (such as phosphoric acid) or a mixture of acids are characterized by more than one endpoint if K_{a1}:$K_{a2} \geq 10^4$ and the equilibrium constant of acidity of the weak acid is more than $n \times 10^{-9}$. The equilibrium constants of acidity of phosphoric acid are: $K_{a1} = 7.1 \times 10^{-3}$, $K_{a2} = 6.2 \times 10^{-8}$, $K_{a3} = 5.0 \times 10^{-13}$. Thus, there are two breaks on the titration curve of phosphoric acid (Fig. 1). The third break is not observed due to very low value of K_{a3}.

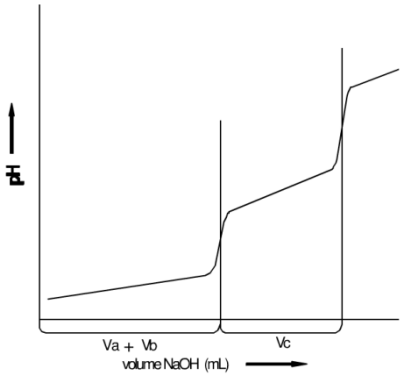


Fig. 1. Titration of a mixture of hydrochloric and phosphoric acids with sodium hydroxide.

During titration of a *mixture* of hydrochloric and phosphoric acids, the proton of hydrochloric acid and the first proton of phosphoric acid react with sodium hydroxide simultaneously. By the second endpoint $H_2PO_4^-$ is converted into HPO_4^{2-}.

2. The first and second equivalence points of H_3PO_4 are observed at pH of about 4.7 and 9.6, respectively. For determination of hydrochloric and phosphoric acids in their mixture, one can use indicators with color change around these pH values (for example, bromocresol green and thymol phthalein for the first and second titrations, respectively).

3. The following reaction takes place on addition of HCl to the sample:

$$(NH_4)_2HPO_4 + 2HCl = 2NH_4Cl + H_3PO_4$$

Formaldehyde reacts with ammonium salts to form hexamethylene tetrammonium cation:

$$4NH_4^+ + 6H_2CO = (CH_2)_6(NH^+)_4 + 6H_2O$$

The equations describing the titration of hexamethylene tetrammonium salt, hydrochloric and phosphoric acids with sodium hydroxide:

$$(CH_2)_6(NH^+)_4 + 4OH^- = (CH_2)_6N_4 + 4H_2O$$

$$HCl + NaOH = NaCl + H_2O$$

$$H_3PO_4 + NaOH = NaH_2PO_4 + H_2O$$

$$NaH_2PO_4 + NaOH = Na_2HPO_4 + H_2O$$

4. A typical analysis of potentiometric titration data is shown in Fig. 2. The most steeply rising portion on the curve (a) corresponds to the endpoint, which can be found more precisely by studying dependences of the first (maximum on curve (b)) or second (zero value on curve (c)) derivatives. In the presence of ammonium salts, the reaction corresponding to the second end point in H_3PO_4 titration

$$H_2PO_4^- + OH^- = HPO_4^{2-} + H_2O$$

is overlaid by the process

$$NH_4^+ + OH^- = NH_3 + H_2O,$$

which makes the potential rise gradually rather than sharply (ammonium buffer).

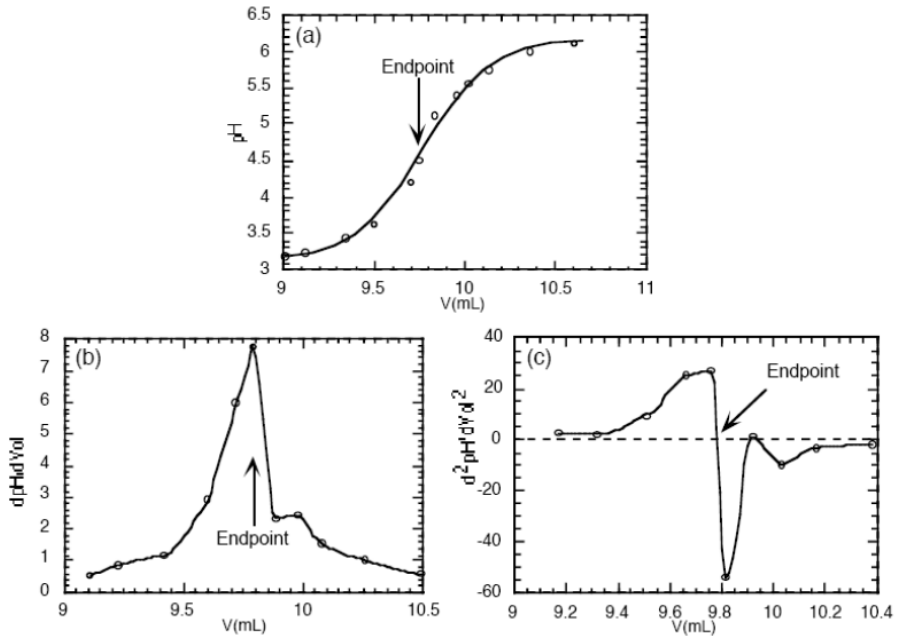


Fig. 2. Typical plots of potentiometric titration:
(a) titration curve of an acid with a base;
(b) curve of the first derivative;
(c) curve of the second derivative.

5. *(a) Calculation of phosphate amount*

With $V_{NaOH,1}$ designating the volume of sodium hydroxide used in titration **A,** the amount needed to neutralize hydrochloric acid and the first proton of phosphoric acid is:

$$n_{PO4} + n_{HCl}\,(\text{titrated}) = c_{NaOH} \times V_{NaOH,1}$$

At the same time,

$$c_{HCl} \times V_{HCl}\,(\text{added}) = n_{HCl}\,(\text{titrated}) + 2n_{PO4}\,(\text{HCl spent for the reaction with } (NH_4)_2HPO_4)$$

Then,

$$n_{PO4} = c_{HCl} \times V_{HCl}\,(\text{added}) - c_{NaOH} \times V_{NaOH,1}$$

Since $n_{(NH4)2HPO4} = n_{PO4}$, one finally gets:

$$\omega_{(NH4)2HPO4} = 10 \times n_{PO4} \times M_{(NH4)2HPO4} / m_{mixture}$$

(b) Calculation of the total amount of diammonium hydrophosphate and ammonium chloride

With $V_{NaOH,2}$ designating the volume of sodium hydroxide used in titration **B** (that is, spent for the neutralization of hexamethylene tetrammonium cation $(CH_2)_6(NH^+)_4$ obtained from the ammonium salts), one gets:

$$n_{NH4Cl} + 2n_{PO4} = c_{NaOH} \times V_{NaOH,2}$$

The amount of phosphate $n_{(NH4)2H3PO4}$ was determined in experiment **A**, which allows calculating the amount of NH_4Cl

$$n_{NH4Cl} = c_{NaOH} \times V_{NaOH,2} - 2\cdot(c_{HCl} \times V_{HCl} - c_{NaOH} \times V_{NaOH,1})$$

and its content in the mixture:

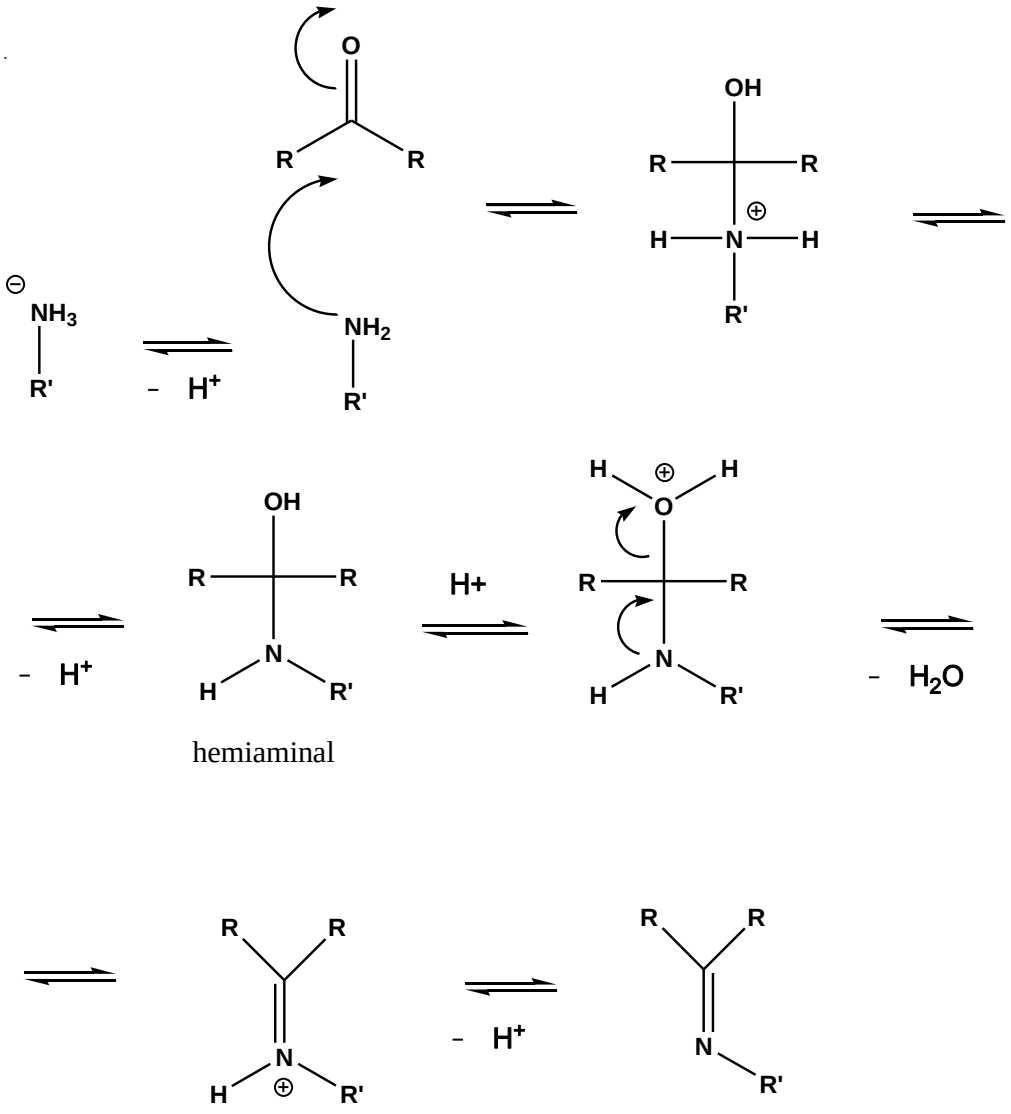
$$\omega_{NH4Cl} = 10 \times n_{NH4Cl} \times M_{NH4Cl} / m_{mixture}$$

Problems 31-33. Melting points and yields of the products

Problem #	Product	Melting point, °C	Yield, %
31	*N*-[(*E*)-Phenylmethylene]aniline	51-53	85
32	Osazone of *D*-glucose	205-207	62
33	Acetone derivative of mannose	118-120	79
33	Acetone derivative of cysteine	148-150	68

Problem 31. Formation of double carbon-nitrogen bond

1. Hemiaminal.



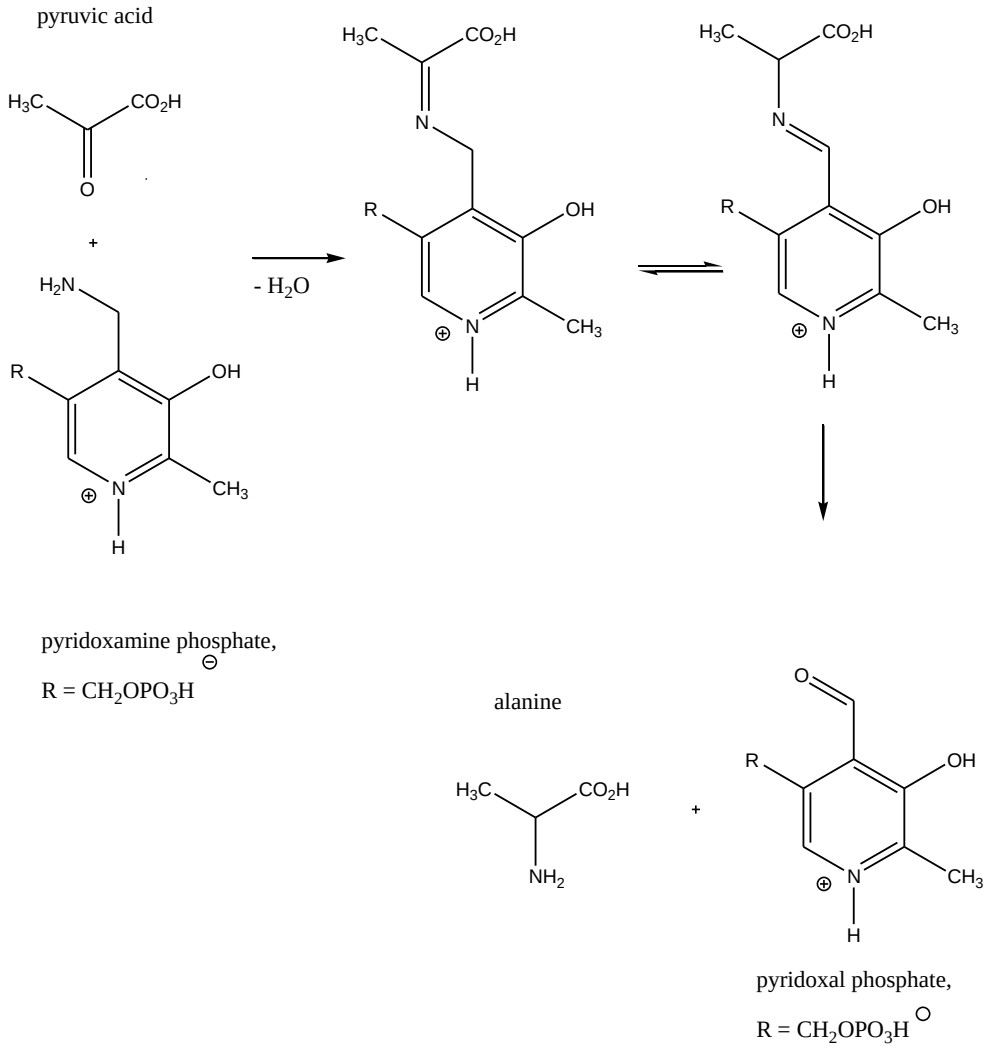
hemiaminal

The rate-determining steps are:

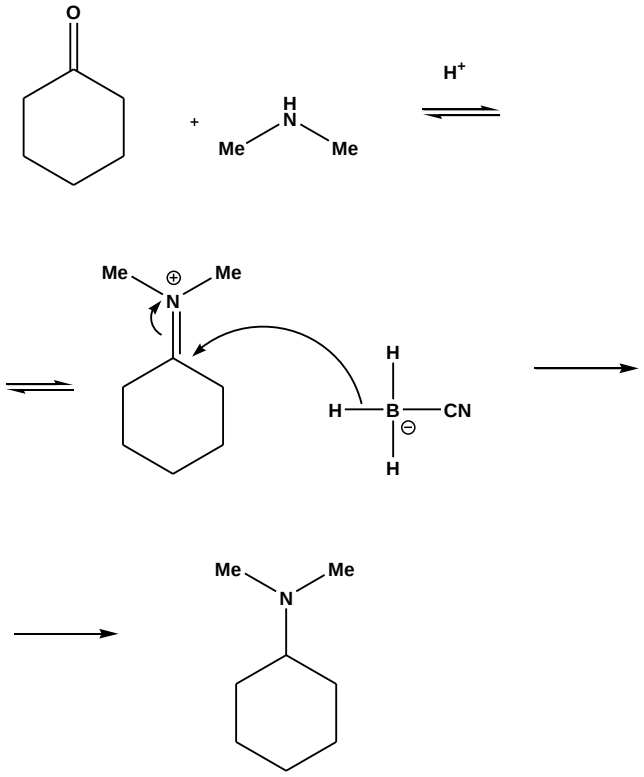
The amine attack at the carbonyl carbon atom at low pH, since most of the amine molecules are protonated;
Dehydration of the tetrahedral hemiaminal intermediate at high pH, since this requires protons.

2. Both reactions proceed through the positively charged intermediates, iminium and oxonium ions, respectively. While the former just loses the proton to form the final product, the later acts as an electrophile adding another molecule of alcohol to become the full acetal.

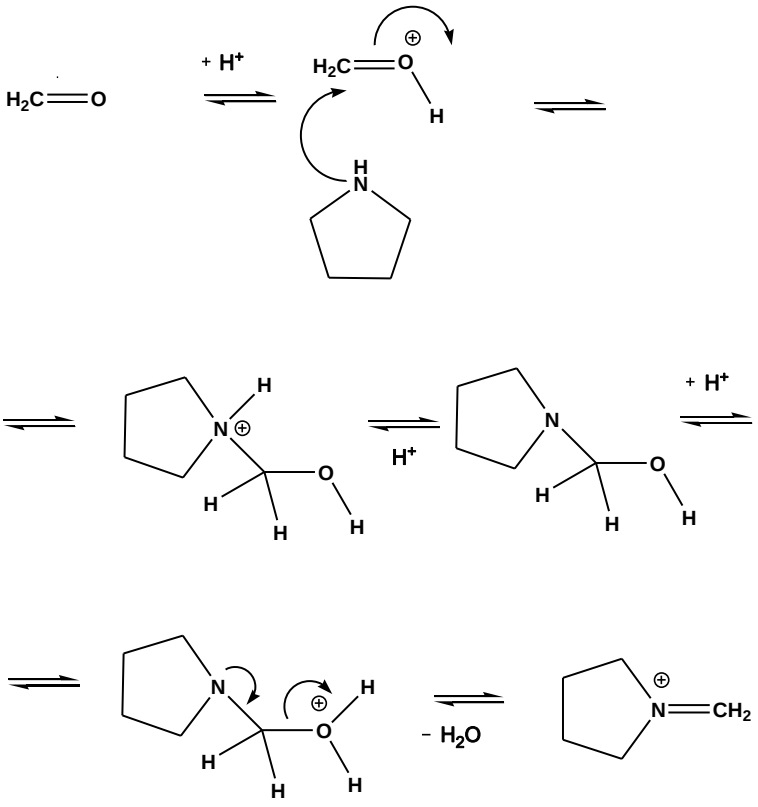
3.

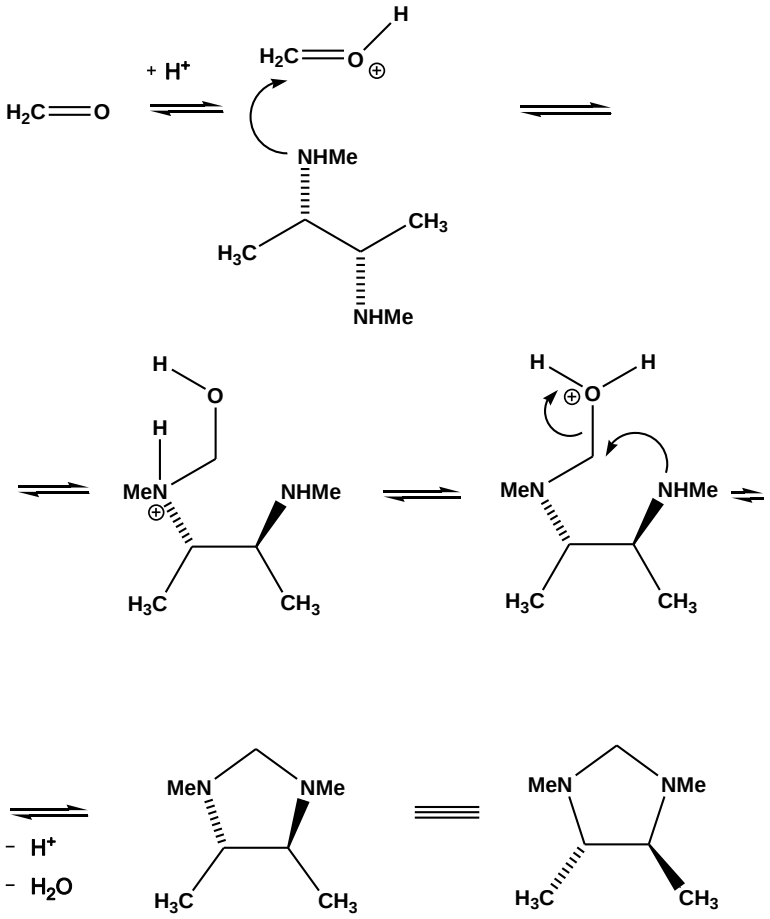


4.


O
H+
H
N
Me
Me
Me
N
Me
H
H
B
CN
H
Me
N
Me

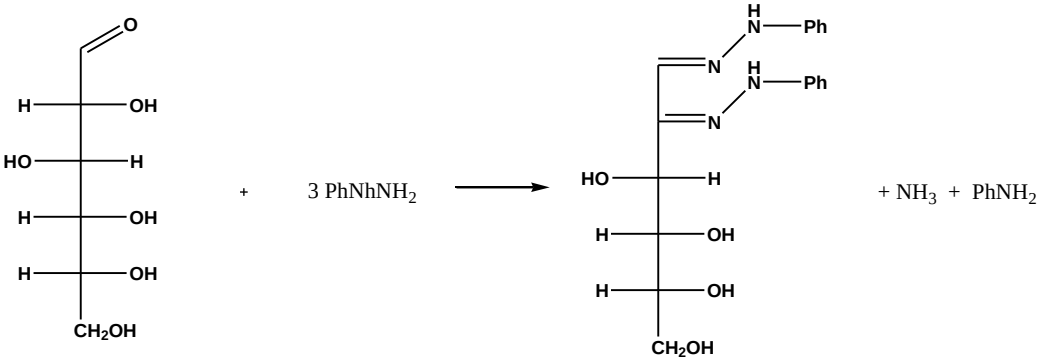
5.


H2C
O
+ H+
H2C
O
H
H
N
H
N
H
O
H
H
H
H+
N
O
H
H
H
+ H+
N
H
O
H
H
H
N
CH2
- H2O



Problem 32. Osazone of glucose

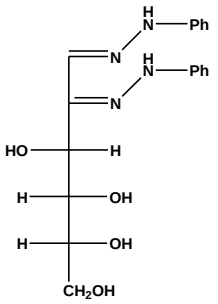
1.



2. *D*-Glucose, since phenylhydrazine is taken in an excess.

3. The appropriate phenyhydrazone of aldehyde.

4.



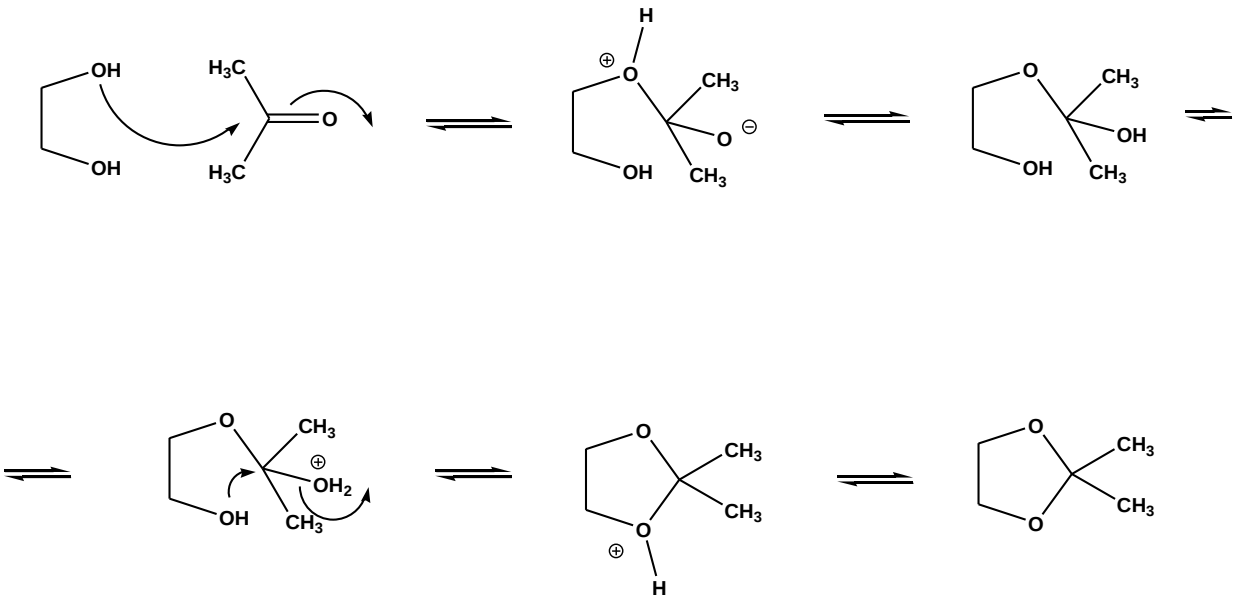
It is one and the same product for all the starting substances. These means the stereochemistry of C3, C4 and C5 of the starting sugars is the same. The initial difference in nature and/or stereochemistry at 1st and 2nd carbon atoms of the monosaccharides is equalizes by hydrazone formation.

5. a), b), d) are different; c) are the same.

Problem 33. Acetone as a protecting agent

Ninhydrine test. The spot with the product will show no color change, whilst that with the starting amino acid will become colored (blue-violet to brown-violet).

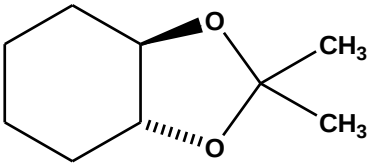
1.



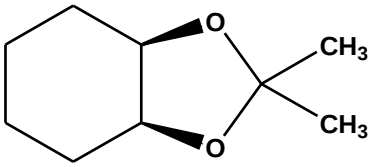
Transformation of hemiketal into full ketal needs the acid catalysis to protonate hydroxyl group, which is further removed in the form of water molecule. The resulting positively charged carbocation-type intermediate is stabilized by electron donation from oxygen lone pair.

2.

trans



cis

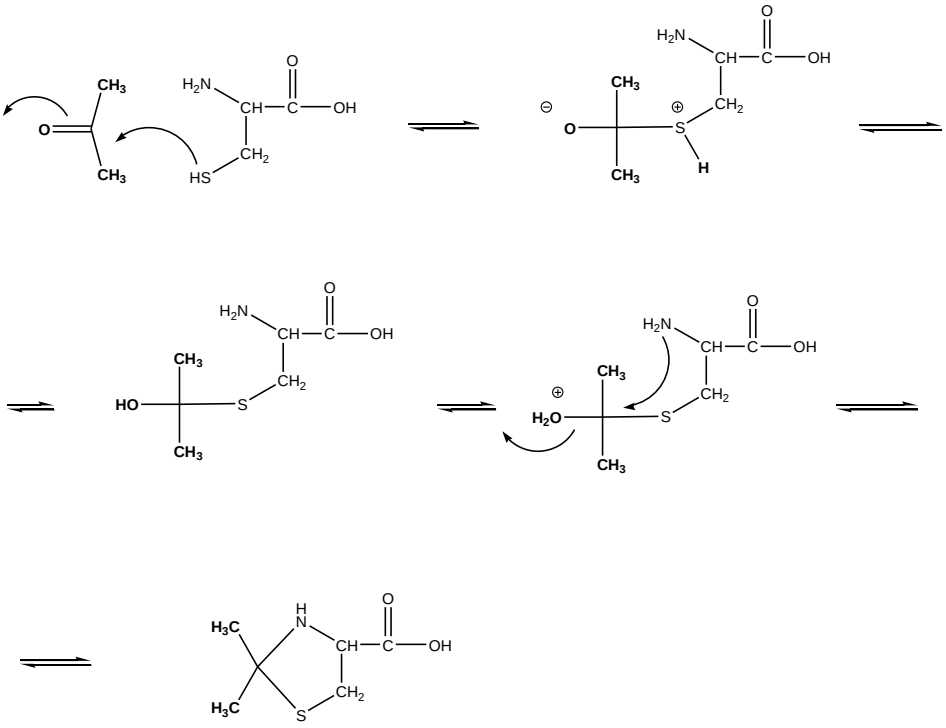


cis-Fused six- and five-membered rings in the resulting product of *cis*-cyclohexane-1,2-diol are more stable than *trans*-fused rings. The reason is the higher bond and angles distortion in *trans*-fused bicycles.

3. In the furanose form of *D*-mannose, there is a possibility to form two rather than one (in the pyranose from) 1,3-dioxolane rings, which is more thermodynamically favorable. Pyranose – furanose transformation proceeds via the open aldehyde form of the carbohydrate.

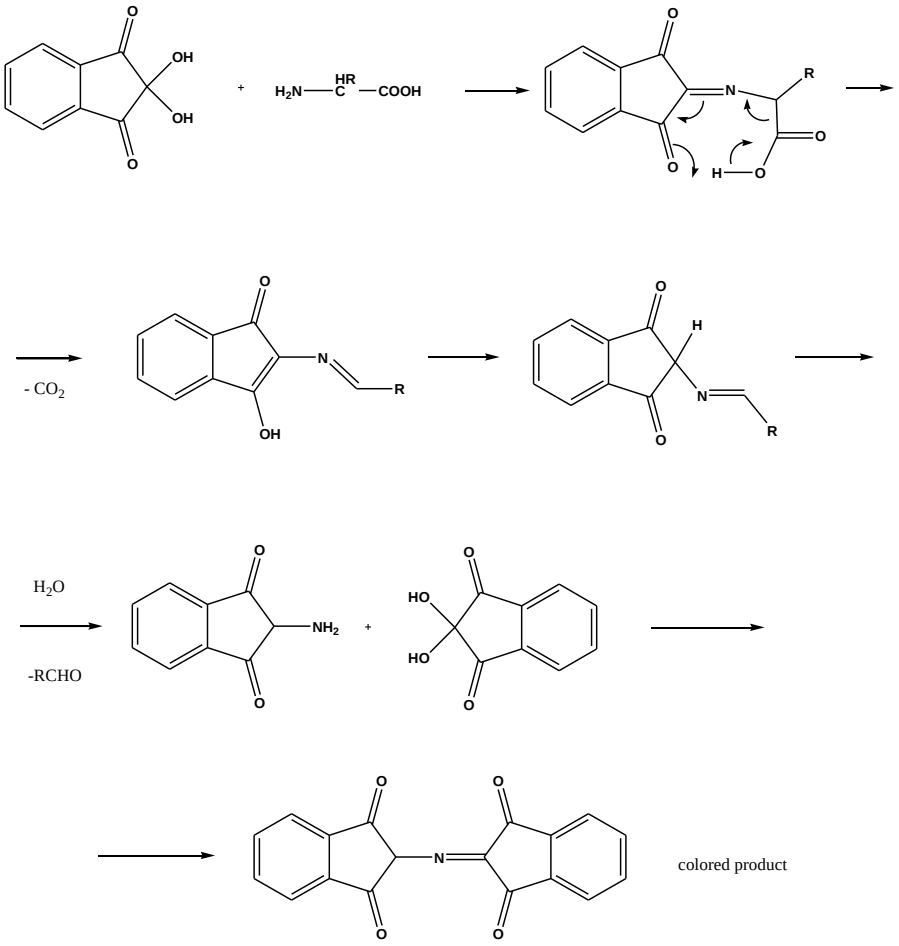
4. Aqueous hydrochloric acid.

5.



Acid catalysis enhances the electrophilicity of carbonyl carbon atom (enhancing carbonyl activity). Thiol group reacts first due to higher nucleophilicity compared to that of amino group.

6.



Problem 34. Determination of molecular mass parameters (characteristics) by viscometry

1. The viscosity values calculated from the flow times of polystyrene solutions (2 to 10 g/L) determined with the Ubbelohde viscometer at 25 °C are given in the hereunder tables. Each flow time value is an average of three measurements. Note that your experimental values may significantly differ from those in the tables, since the flow times depend on the molecular properties (mainly molecular weight distribution) of a particular polystyrene sample.

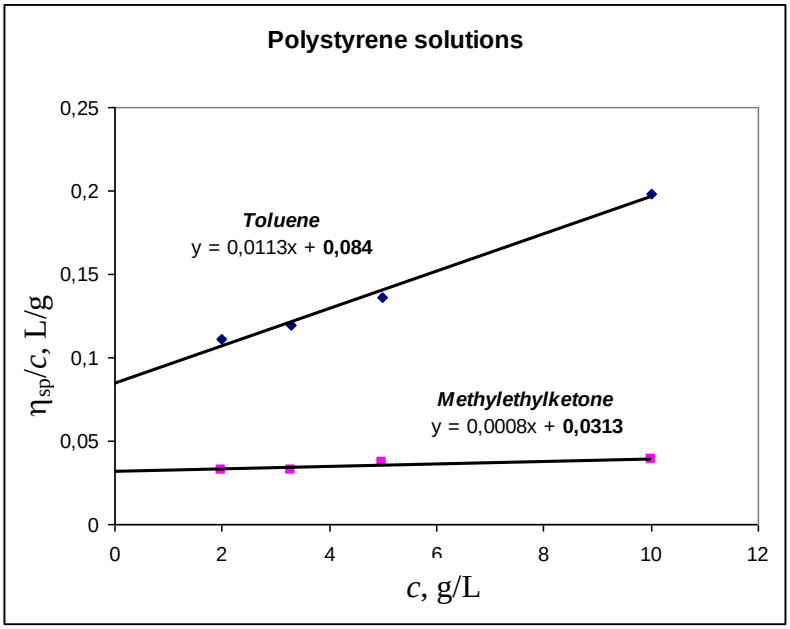
Polystyrene/toluene, the solvent flow time t_0 = 24.4 s

Concentration of the polymer *c*, g/L	Flow time *t*, s	$\eta_{rel} = \frac{t}{t_0}$	$\eta_{sp} = \frac{t - t_0}{t_0}$	$\frac{\eta_{sp}}{c}$, L/g
10	72.8	2.98	1.98	0.198
5	41.0	1.68	0.68	0.136
3.3	34.0	1.39	0.39	0.119
2	29.8	1.22	0.22	0.111

Polystyrene/methyl ethyl ketone, the solvent flow time t_0 = 26.0 s

Concentration of the polymer c, g/L	Flow time t, s	$\eta_{rel} = \frac{t}{t_0}$	$\eta_{sp} = \frac{t - t_0}{t_0}$	$\frac{\eta_{sp}}{c}$, L/g
10	36.0	1.38	0.38	0.0385
5	30.8	1.18	0.18	0.0369
3.3	28.8	1.11	0.11	0.0326
2	27.7	1.07	0.07	0.0327

2,3,4. The intrinsic viscosity [η] can be found by either graphical extrapolation to 0 concentration (as the Y-intercept), or by linear fitting (as an absolute term) of the reduced viscosity data.



Analysis of the data given in i. 1) leads to [η] equal to 0.0840 and 0.0313 L/g for the toluene and methyl ethyl ketone solutions, respectively. (Three significant digits are left in both cases based on the typical amplitude of the measured flow times).

5. The viscosity-average molecular weights as calculated from the Mark-Kuhn-Houwink equation are of 226000 and 125000 g/mol for the toluene and methyl ethyl ketone solutions, respectively.

6. The polydispersity index equals 226000/125000 = 1.81.

Problem 35. Cooperative interactions in polymer solutions

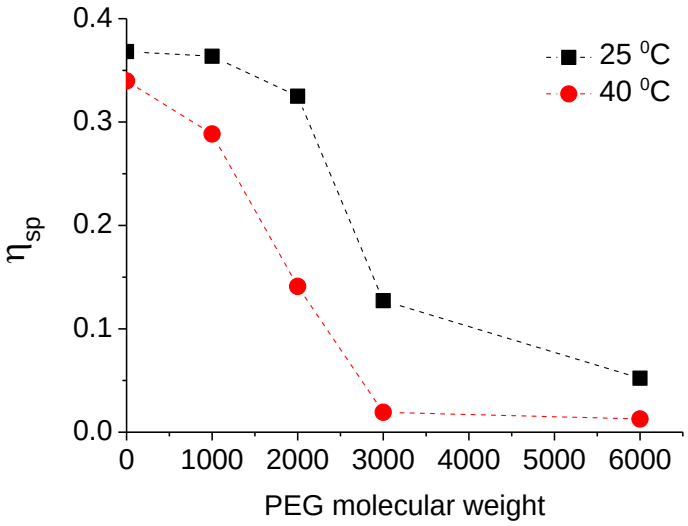
1. Experimental flow times and the calculated specific viscosities are given in the hereunder table.

Note 1. The molecular weights of the repeating units of PMMA and PEG are of 86.06 and 44.05 g/mol, respectively. Mixing of equal volumes of a 2 g/L PMMA and a 1 g/L PEG (of any molecular weight) solutions results in a reaction mixture with the molar ratio of the PMMA and PEG units of approximately 1:1.

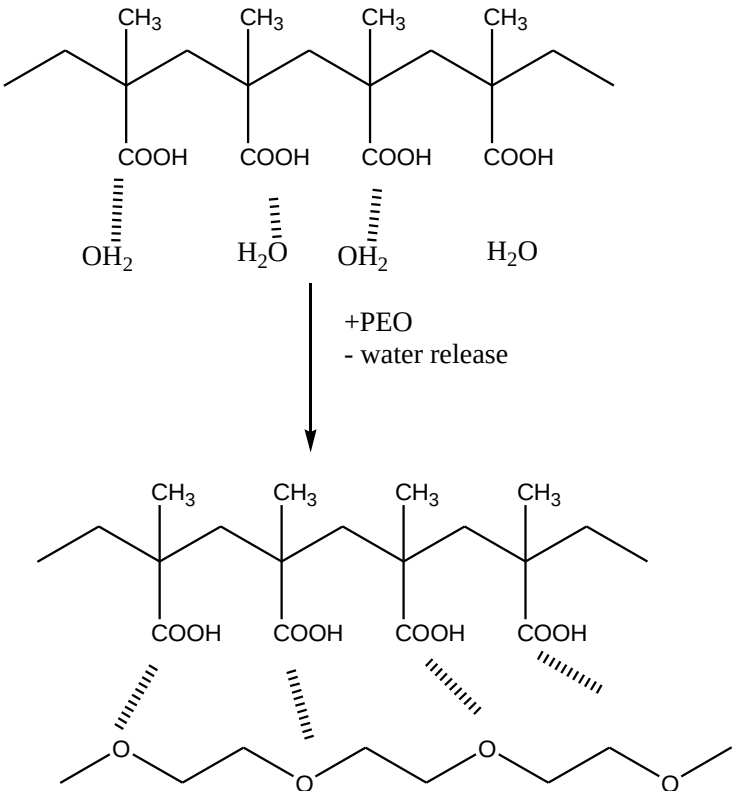
Note 2. The final concentration of PMMA in the resulting mixtures and its aqueous solutions is of 1 g/L.

Composition	Temperature, °C	Flow time *t*, s	Specific viscosity of the solution η_{sp}
Water	25	44.0	-
PMAA, 1 g/L	25	60.2	0.368
PMAA+PEG-1000	25	60.0	0.364
PMAA+PEG-2000	25	58.3	0.325
PMAA+PEG-3000	25	49.6	0.127
PMAA+PEG-6000	25	46.3	0.052
Water	40	31.2	-
PMAA, 1 g/L	40	41.8	0.340
PMAA+PEG-1000	40	40.2	0.288
PMAA+PEG-2000	40	35.6	0.141
PMAA+PEG-3000	40	31.8	0.019
PMAA+PEG-6000	40	31.6	0.013

2.



3. The reaction scheme of the complex formation is given below. A decrease of the specific viscosity of the PMAA solution upon addition of the equimolar amount of PEG is observed, which reflects that that polymer coils in the interpolymer complex are more compact than those in the initial solution. The compaction is due to hydrophobization of the PMAA chain with PEG.



Dramatic changes in the density of the complexes are observed within a rather narrow range of PEG molecular weights (of about 1500 g/mol at 40°C and 2500 g/mol at 25 °C). Such processes are often referred to as cooperative.

The enthalpy change in PMAA-PEG complex formation being negligible, the entropy gain due to the release of water molecules is the driving force of the reaction.

As positions of the repeating units in a polymer chains are constrained, the total entropy of the polymer coil is less than that of the same number of unbound monomer units. For longer polymer chains such entropy loss is more significant. Consequently, the entropy gain as a result of PMAA-PEG complex formation (ΔS = S(complex) + S(water) – S(PMAA) – S(PEG)) is increasing with an increase of the PEG chain length (total entropies of released water molecules, the complex, and the initial PMAA molecules are nearly the same). This is why the PMAA-PEG interaction proceeds efficiently only starting with a certain molecular weight of PEG (<1000 g/mol at 40°C and of about 1000-2000 g/mol at 25 °C).

Higher efficiency of the complex formation at elevated temperatures (PEG with a lower molecular weight is needed to provide for a noticeable viscosity drop) contributes to the consideration that the entropy gain is behind the process.