SOLUTIONS OF THE THEORETICAL PROBLEMS

Problem 1. ON THE BORDERS OF THE PERIODIC SYSTEM

1. In 1875 the French chemist Paul-Emile Lecoq de Boisbaudran studied the spectra of zinc ore and discovered the traces of a new element, which he called “gallium” from the Latin word "*Gallia*" meaning "*France*" and perhaps also from the Latin word "*gallus*" (the cock, a translation of Lecoq). In the same year Lecoq de Boisbaudran obtained the free metal by electrolysis of a solution of the hydroxide $Ga(OH)_3$ in KOH. When Mendeleev knew about this discovery he understood that the properties of gallium resemble those of ekaaluminum. Moreover, he wrote to Boisbaudran that he obtained the wrong value for the density of gallium (4.7 g/cm^3 whereas Mendeleev predicted the density to be 5.9-6.0 g/cm^3). Indeed, more accurate measurements gave the correct value 5.904 g/cm^3.

Scandium (from the Latin word "*Scandia*" meaning "*Scandinavia*") was discovered by Swedish chemist Lars Frederick Nilson in 1876 in the minerals euxenite and gadolinite, which had not yet been found anywhere except in Scandinavia. He and his coworkers were actually looking for rare earth metals. By processing 10 kg of euxenite and other residues of rare-earth minerals, Nilson was able to prepare about 2 g of scandium oxide (scandia, Sc_2O_3) of high purity. Per Theodor Cleve found scandium oxide at about the same time. He noted that the new element was the element ekaboron predicted by Mendeleev in 1871.

Germanium (from the Latin word "*Germania*" meaning "*Germany*") was discovered in a mineral called argyrodite by Clemens Alexander Winkler in 1886. The properties of germanium became remarkably close to those predicted by Mendeleev.

2. Nuclear synthesis of the 118th element led to formation of three neutrons:

$$^{249}_{98}\mathrm{Cf} + ^{48}_{20}\mathrm{Ca} \rightarrow ^{294}_{118}118 + 3\,^{1}_{0}n\,.$$

The α-decay of the obtained nuclide gave the nuclei of the 116th element:

$$^{294}_{118}118 \rightarrow ^{290}_{116}116 + ^{4}_{2}\mathrm{He}$$

3. The 118-th element completes the 7-th period. It belongs to the inert gases (group 18). Its electron configuration is [Rn] $5f^{14}\ 6d^{10}\ 7s^2\ 7p^6$.

4. For the extrapolation we will consider inert gases of the periods 3-6 because helium and neon differ significantly in their properties from other inert gases.

i) Melting points:

Z	T_m, K
18	84
36	116
54	161
86	202

The dependence of boiling point on atomic number is almost linear. Linear extrapolation gives $T_m(118)$ = 263 K = –10 °C.

ii) Boiling points:

Z	T_b, K
18	87
36	120
54	165
86	211

On average, boiling points are 4 degrees higher than the corresponding melting points, hence we predict that $T_b(118)$ = 267 K = –6 °C.

iii) Covalent atomic radii:

Z	r, nm
18	0.097
36	0.110
54	0.130
86	0.145

Linear extrapolation gives: $r(118)$ = 0.171 nm.

iv) Ionization energies:

Z	IE, eV
18	15.8
36	14.0
54	12.1
86	10.7

Ionization energy is a non-linear function of atomic number. Linearization in logarithmic coordinates ln Z – IE gives for Z = 118 the ionization energy IE = 9.7 eV.

Compare these data with the values predicted for the 118th element by American chemists 40 years ago: t_m = –15 °C, t_b = –10 °C, r = 0.23 nm, I = 9.8 eV.

Of course, these results obtained by extrapolation are approximate. Moreover, bulk properties such as melting and boiling points can be measured only for significant amounts of an element, whereas only three atoms of the 118-th element were obtained and they decayed during milliseconds. For this reason, our predictions may hardly be confirmed in future.

v) The highest oxidation state for the 118-th element is +8, and the corresponding oxide should be RO_4 as for xenon (for radon neither oxide, nor any other compounds have been obtained).

Problem 2. SCHRÖDINGER CAT AND CHEMISTRY

1. (i) All orbitals make equal contribution, hence $|c_1|^2 = |c_2|^2 = |c_3|^2 = |c_4|^2 = 1/4$, because the sum of squares of all modulus is unity. Therefore, $|c_1| = |c_2| = |c_3| = |c_4| = 1/2$.

(ii) For the sp^2-orbital $|c_1|^2 = |c_2|^2 = |c_3|^2 = 1/3$, hence $|c_1| = |c_2| = |c_3| = 1/\sqrt{3}$.

2. The probability of being found in a definite state is equal to the square of the modulus of the corresponding coefficient:

$$p_a = \left(\frac{1}{\sqrt{2}}\right)^2 = \frac{1}{2}.$$

This result is obvious because both hydrogen atoms are indistinguishable in H_2^+.

3. The probability of ionic state is 17%:

$$|c_{ion}|^2 = 0.17,$$

Whence $|c_{ion}| = \sqrt{0.17} \approx 0.41$. Similarly, $|c_{cov}| = \sqrt{0.83} \approx 0.91$.

4. The total contribution of two Kekule structures is equal to the sum of squares of the moduli of all the corresponding coefficients in the linear combination:

$$p_{\text{Kekule}} = \left(\sqrt{\frac{2}{5}}\right)^2 + \left(\sqrt{\frac{2}{5}}\right)^2 = \frac{4}{5}.$$

It means that in a given state 80% of benzene molecules have one of the Kekule structures, and 20% – one of the Dewar ones.

5.

$$\Psi(x,t) = c_1(t)\Psi_1(x) + c_2(t)\Psi_2(x)$$

$c_1(t)$, $c_2(t)$ – are periodic functions of time with the boundary conditions $c_1(0) = 1$, $c_1(\pi/\omega) = 0$, $c_2(0) = 0$, $c_2(\pi/\omega) = 1$. It is natural to express these coefficients via the sine and cosine trigonometric functions:

$$c_1(t) = \cos\left(\frac{\omega t}{2}\right), \quad c_2(t) = \sin\left(\frac{\omega t}{2}\right)$$

After a quarter of a period, at $t = \pi/(2\omega)$, the total wave function is a superposition of both states with equal weights:

$$\Psi\left(x, \frac{\pi}{2\omega}\right) = \cos\left(\frac{\omega}{2}\frac{\pi}{2\omega}\right)\Psi_1(x) + \sin\left(\frac{\omega}{2}\frac{\pi}{2\omega}\right)\Psi_2(x) = \frac{1}{\sqrt{2}}\Psi_1(x) + \frac{1}{\sqrt{2}}\Psi_2(x)$$

Problem 3. QUANTUM UNCERTAINTY

1. From uncertainty relation it follows:

$$\Delta V_{\min} = \frac{\hbar}{2m\Delta x}$$

Of all the particles listed above, a O_2 molecule, (e), has the largest mass and Δx and hence is characterized by smallest $\Delta V_{\min}$. In three other cases (b)-(d) the particles have a comparable mass – proton (b, c) and H_2 molecule, therefore uncertainty of velocity may be determined by localization length Δx. The uncertainty in position, Δx, is the largest for

nanotube (about 1 nm), smaller by an order of magnitude for H_2 and is very small for the carbon nucleus, so that ΔV_{min} increases in the following order: (d) < (b) < (c).

Consider now localization of an electron in a H_2 molecule. Electron mass is approximately 2000 smaller than that of proton, hence ΔV_{min} for the electron is larger than in cases (b) and (d). But the size of the carbon nucleus is by 100 thousand times (5 orders of magnitude) smaller than diameter of H_2, therefore ΔV_{min} for the proton in the carbon nucleus is larger than that for the electron in H_2.

The final sequence is as follows: (e) < (d) < (b) < (a) < (c).

2. For O_2 molecule in a room of 5 m width we get:

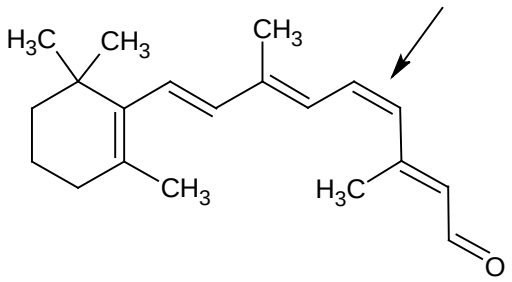
$$\Delta V_{\min} = \frac{1.05 \cdot 10^{-34}}{2 \cdot \frac{0.032}{6.0 \cdot 10^{23}} \cdot 5} = 2.0 \cdot 10^{-10} \text{ m/s} = 2.0 \text{ Å/s.}$$

In the carbon nucleus the size of the proton localization area is equal to the nucleus diameter – about $4 \cdot 10^{-15}$ m.

$$\Delta V_{\min} = \frac{1.05 \cdot 10^{-34}}{2 \cdot \frac{0.001}{6.0 \cdot 10^{23}} \cdot 4 \cdot 10^{-15}} = 7.9 \cdot 10^{6} \text{ m/s} \approx 8000 \text{ km/s.}$$

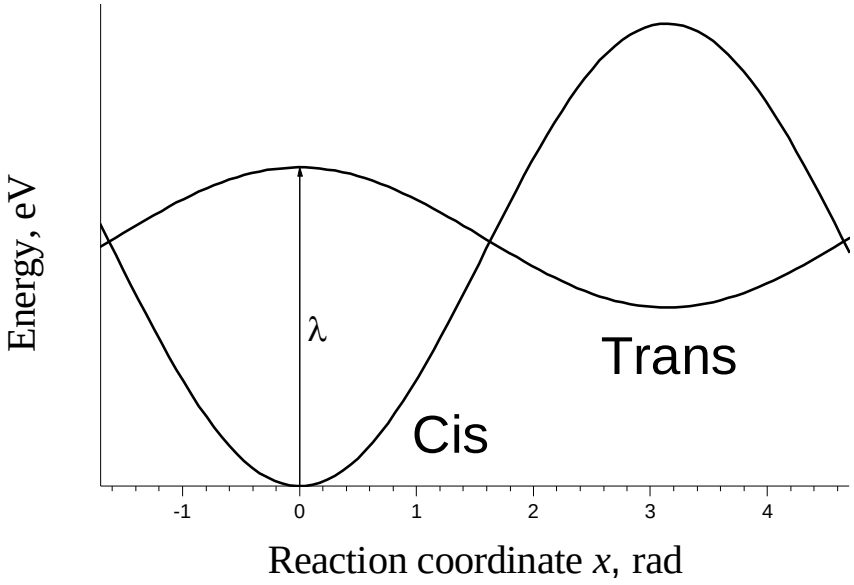
Problem 4. QUANTUM CHEMISTRY OF VISION

1. Reaction proceeds by rotation of a part of the molecule about the C_{11}–C_{12} bond:



The rotation angle is the reaction coordinate.

2.



The energy change is the difference between the lowest energies of the *trans*- and *cis*-isomers:

$$Q = E_{\text{trans}}(\pi) - E_{\text{cis}}(0) = 1.40 - 0 = 1.40 \text{ eV} = 135 \text{ kJ/mol}.$$

Transition state of reaction is near the region of curve-crossing:

$$1.79 \cdot \left(1 - \cos(x)\right) = 1.94 + 0.54 \cdot \cos(x),$$

$$x = 1.64 = 0.521\pi = 93.7°.$$

Activation energy (reaction barrier) is defined by the energy difference between the transition state and the reagent:

$$E_A = E_{\text{cis}}(1.64) - E_{\text{cis}}(0) = 1.91 \text{ eV} = 184 \text{ kJ/mol}.$$

This barrier is rather high to be overcome at ambient temperature.

3. Maximal wavelength is determined by the energy difference between *trans*- and *cis*-retinal at $x = 0$:

$$\frac{hc}{\lambda} = E_{\text{trans}}(0) - E_{\text{cis}}(0) = 2.48 - 0 = 2.48 \text{ eV} = 3.97\cdot10^{-19} \text{ J}.$$

$$\lambda = \frac{hc}{\Delta E} = \frac{6.63\cdot10^{-34}\cdot3.00\cdot10^{8}}{3.97\cdot10^{-19}} = 5.01\cdot10^{-7} \text{ m} = 501 \text{ nm}.$$

4. Conjugated electronic system of retinal contains 6 double bonds, that is, 12 π-electrons that occupy 6 lowest energy levels.

5. Absorption of light causes the transition from the highest occupied to the lowest unoccupied level:

$$E_7 - E_6 = \frac{h^2}{8ml^2}\left(7^2 - 6^2\right) = \frac{13h^2}{8ml^2},$$

where electron mass is $m = 9.11\cdot10^{-31}$ kg. Hence,

$$l = \sqrt{\frac{13h^2}{8m\Delta E}} = 6.63\cdot10^{-34}\cdot\sqrt{\frac{13}{8\cdot9.11\cdot10^{-31}\cdot3.97\cdot10^{-19}}} = 1.41\cdot10^{-9} \text{ m} = 1.41 \text{ nm}.$$

This value correlates well with the sum of bond lengths in the conjugated system – 6 double bonds and 5 ordinary bonds.

Problem 5. NANOPARTICLES AND NANOPHASES

1. From equations (1) and (3) one gets

$$2\sigma V/r = RT \ln(p^*/p)$$

$$p^* = p\exp\left(\frac{2\sigma V}{rRT}\right) \qquad (5)$$

Knowing p we get p^*.

For r = 1 μm: $$p^* = 3.15\cdot10^{-2}\exp\left(\frac{2\cdot0.072\cdot18\cdot10^{-6}}{10^{-6}\cdot8.314\cdot298}\right) = 3.15\cdot10^{-2} \text{ bar}$$

For r = 1 nm: $$p^* = 3.15\cdot10^{-2}\exp\left(\frac{2\cdot0.072\cdot18\cdot10^{-6}}{10^{-9}\cdot8.314\cdot298}\right) = 8.97\cdot10^{-2} \text{ bar}$$

The minimum size of the spherical sample that can still be considered as a bulk phase can be calculated from the inequality

$$\exp\left(\frac{2\sigma V}{rRT}\right) \le 1.01,$$

$$\exp\left(\frac{2\cdot 0.072\cdot 18\cdot 10^{-6}}{r\cdot 8.314\cdot 298}\right) \le 1.01$$

$$r \ge 1.05\cdot 10^{-7}\ \text{m} = 105\ \text{nm}.$$

r = 105 nm may be considered as the minimum radius.

The number of molecules N in the drop with r = 105 nm can be calculated from the formula

$$N = \frac{4\pi r^3}{3V} N_{\text{A}},$$

$V = 18\cdot 10^{-6}$ m^3 is the molar volume of water, $N_{\text{A}} = 6.02\cdot 10^{23}$ mol^{-1} is the Avogadro' number.

$$N = \frac{4\pi\cdot(1.05\cdot 10^{-7})^3}{3\cdot 18\cdot 10^{-6}}\cdot 6.02\cdot 10^{23} = 1.62\cdot 10^8$$

2. The maximum radius of the droplet is equal to the internal radius of the nanotube. The saturated pressure goes up while the radius of the droplet goes down. Therefore, the maximum radius corresponds to the minimum vapor pressure of mercury inside the tube. One has to calculate the saturated vapor pressure above the droplet with r = 0.75 nm (d = 1.5 nm). From eq.5 one gets:

$$p^* = 1.38\cdot 10^{-3}\exp\left(\frac{2\cdot 0.484\cdot\frac{200.5}{13.5}\cdot 10^{-6}}{0.75\cdot 10^{-9}\cdot 8.314\cdot 400}\right) = 0.440\ \text{bar}.$$

This pressure is approximately three hundred times higher than the one of the bulk liquid mercury.

Comment. The droplets of mercury are so small, that the whole basis of calculation is suspect. There is an experimental evidence of a validity of the equation at least for $r \ge 3$ nm.

For smaller values it is believed that the orders of the magnitude of the vapor pressures are approximately correct.

3. The boiling temperature of the dispersed benzene is T^*. At this temperature the saturated vapor pressure p^* is equal to the atmospheric pressure 1 bar. So,

$$\ln p^*(T^*) = \ln \frac{p^*(T^*)}{p(T^*)} + \ln p(T^*) = 0$$

From equations (4) and (5)

$$\frac{2\sigma V}{rRT^*} - \frac{\Delta H_{\text{vap}}}{RT^*} + const = 0$$

The *const* can be calculated from the boiling point of bulk benzene:

$$\ln p(T_{\text{b}}) = -\frac{\Delta H_{\text{vap}}}{RT_{\text{b}}} + const = 0;$$

$$const = \frac{\Delta H_{\text{vap}}}{RT_{\text{b}}}$$

So

$$\frac{2\sigma V}{rRT^*} - \frac{\Delta H_{\text{vap}}}{RT^*} + \frac{\Delta H_{\text{vap}}}{RT_{\text{b}}} = 0;$$

$$T^* = T_{\text{b}}\left(1 - \frac{2\sigma V}{\Delta H_{\text{vap}} r}\right) = 353.3 \cdot \left(1 - \frac{2 \cdot 0.021 \cdot \frac{78}{0.814} \cdot 10^{-6}}{30720 \cdot 5 \cdot 10^{-8}}\right) = 352.4 \text{ K}$$

4. The molar Gibbs energy of liquid A increases when passing from the bulk phase to the small droplet (see equation 2).

Increase of the molar Gibbs energy leads to the decrease of the boiling temperature at atmospheric pressure and the equilibrium constant of the chemical reaction (A is a product).

The decrease of the boiling temperature was demonstrated above.

The equilibrium constant *K* can be calculated from the standard reaction Gibbs energy, $\Delta_r G^\circ$:

$$RT \ln K = -\Delta_r G^\circ = -\left(G^\circ_{\text{prod}} - G^\circ_{\text{react}}\right)$$

G°_{prod}, G°_{react} are molar Gibbs energies for products and reactants, respectively. If G°_{prod} increases, the equilibrium constant *K* goes down.

Problem 6. IN WHICH DIRECTION DOES A CHEMICAL REACTION PROCEED?

1. The standard Gibbs energy of the reaction (1) is equal to the Gibbs energy of formation of NiO, multiplied by two:

$$\Delta G^\circ_{1900} = 2\cdot(-72.1) = -144.2 \text{ kJ/mol}$$

The equilibrium constant and the equilibrium partial pressure of oxygen at 1900 K are:

$$K = \frac{1}{p(\text{O}_2)} = \exp\left(-\frac{\Delta G^\circ}{RT}\right) = \exp\left(-\frac{144200}{8.314\cdot 1900}\right) = 9215,$$

$$p(\text{O}_2) = \frac{1}{K} = 1.085\cdot 10^{-4} \text{ atm} = 0.0825 \text{ Torr}.$$

If the oxygen pressure is above the equilibrium value, the reaction will proceed from the left to the right to reach the equilibrium state. So the answer is

$$0.0825 \text{ Torr} < p(\text{O}_2) < 1.00 \text{ Torr}.$$

2. The reaction proceeds forward as long as ΔG, not ΔG° is negative! The following equation is valid for the reaction (2):

$$\Delta G = \Delta G^\circ + RT \ln p(\text{CO})^2$$

(solid reactants and products are considered to be pure substances, they do not contribute to this equation). The reaction proceeds from the left to the right if $\Delta G < 0$:

$$\Delta G^\circ > -RT \ln p(\text{CO})^2,$$

$$p(\mathrm{CO}) < \exp\left(-\frac{\Delta G^\circ}{2RT}\right)$$

Using the data from Table 1 we obtain:

$$\Delta G^\circ = -162.6 + 2\cdot(-200.2) - (-757.8) = 194.8 \text{ kJ/mol.}$$

$$p(\mathrm{CO}) < \exp\left(-\frac{194800}{2\cdot 8.314\cdot 1000}\right) = 8.17\cdot 10^{-6} \text{ atm.}$$

So if the partial pressure of CO in the system is below $8.17\cdot 10^{-6}$ atm, the reaction can predominantly proceed from the left to the right.

3. Using the data from Table 1, the following expression for ΔG of the reaction (3) is derived

$$\Delta G = \Delta G^\circ + RT\ln\frac{p(\mathrm{NH_3})^2}{p(\mathrm{H_2})^3\,p(\mathrm{N_2})} = 2\cdot(-16260) + 8.314\cdot 300\cdot\ln\frac{1.0^2}{0.50^3\cdot 3.0} =$$

$$= -30100 \text{ J/mol} = -30.1 \text{ kJ/mol.}$$

At 300 K the reaction (3) is allowed to proceed from the left to the right only. However, formation of ammonia is extremely slow under these conditions due to the kinetic restrictions.

Problem 7. LE CHATELIER'S PRINCIPLE

1. $$\Delta G^\circ = -RT\ln K_p = -RT\ln\frac{p(\mathrm{NH_3})^2}{p(\mathrm{H_2})^3\,p(\mathrm{N_2})} \qquad (2)$$

$$\Delta G^\circ = -8.314\cdot 400\cdot\ln\frac{0.499^2}{0.376^3\cdot 0.125} = -12100 \text{ J/mol} = -12.1 \text{ kJ/mol.}$$

2. After perturbation, the Gibbs energy of the reaction is:

$$\Delta G = \Delta G^\circ + RT\ln\frac{p'(\mathrm{NH_3})^2}{p'(\mathrm{H_2})^3\,p'(\mathrm{N_2})} \qquad (3)$$

The apostrophe ‘ denotes the partial pressures at the non-equilibrium state. The sign of ΔG (positive or negative) determines the direction in which the equilibrium shifts after perturbation.

3., 4. Let us determine the sign of ΔG in all the considered cases. From equations (2) and (3), we get:

$$\frac{\Delta G}{RT} = 2\ln\frac{p'(\mathrm{NH_3})}{p(\mathrm{NH_3})} - 3\ln\frac{p'(\mathrm{H_2})}{p(\mathrm{H_2})} - \ln\frac{p'(\mathrm{N_2})}{p(\mathrm{N_2})} \qquad (4)$$

Reactants and product are ideal gases, so we can use the Dalton law. Molar fractions x can be calculated from the partial pressures:

$$\begin{aligned} &p(\mathrm{NH_3}) = x_{\mathrm{NH_3}}P,\ p(\mathrm{H_2}) = x_{\mathrm{H_2}}P,\ p(\mathrm{N_2}) = x_{\mathrm{N_2}}P \\ &x_{\mathrm{NH_3}} + x_{\mathrm{H_2}} + x_{\mathrm{N_2}} = 1 \end{aligned} \qquad (5)$$

P is the total pressure in the system. Taking into account (5), equation (4) can be written in a form:

$$\frac{\Delta G}{RT} = 2\ln\frac{x'_{\mathrm{NH_3}}}{x_{\mathrm{NH_3}}} - 3\ln\frac{x'_{\mathrm{H_2}}}{x_{\mathrm{H_2}}} - \ln\frac{x'_{N_2}}{x_{N_2}} - 2\ln\frac{P'}{P} \qquad (6)$$

In the case (a), only the last term in the right hand side of the equation (6) is non-zero. Since the total pressure is increased $P' > P$, the right side of equation (6) is negative, $\Delta G < 0$. The increase of the total pressure will push the reaction towards formation of additional amounts of ammonia. The reaction will proceed predominantly in the forward direction (a product-favored reaction).

In the case (b), only the last term on the right side of (6) is equal to zero. Molar fraction of ammonia increases, whereas molar fractions of hydrogen and nitrogen decrease:

$$\ln\frac{x'_{\mathrm{NH_3}}}{x_{\mathrm{NH_3}}} > 0, \quad \ln\frac{x'_{\mathrm{H_2}}}{x_{\mathrm{H_2}}} < 0, \quad \ln\frac{x'_{N_2}}{x_{N_2}} < 0.$$

The right side of (6) is positive and $\Delta G > 0$. In the case b), the reaction will proceed predominantly in the reverse direction towards formation of additional amounts of reactants.

c) As in the case (b), all the molar fractions change after the addition of hydrogen to the system. After simple rearrangements of the equation (6) one gets

$$\frac{\Delta G}{RT} = -3\ln\frac{n'_{H_2}}{n_{H_2}} - 2\ln\frac{n_{H_2}+n_{N_2}+n_{NH_3}}{n'_{H_2}+n_{N_2}+n_{NH_3}}, \qquad (7)$$

where n is the number of moles of reactants or product. The first term in the right side of (7) is negative ($n'_{H_2} > n_{H_2}$) while the second one is positive.

Let us solve the inequality $\Delta G < 0$:

$$-2\ln\frac{n_{H_2}+n_{N_2}+n_{NH_3}}{n'_{H_2}+n_{N_2}+n_{NH_3}} < 3\ln\frac{n'_{H_2}}{n_{H_2}} \qquad (8)$$

Let $n'_{H_2} = n_{H_2} + \Delta_{H_2}$, where Δ_{H_2} is the number of moles of hydrogen added to the system. Since Δ_{H_2} is small, $\Delta_{H_2} \ll n_{H_2}$. The inequality (8) can be written in the form:

$$\left(1+\frac{\Delta_{H_2}}{n_{NH_3}+n_{N_2}+n_{H_2}}\right)^2 < \left(1+\frac{\Delta_{H_2}}{n_{H_2}}\right)^3.$$

Terms with the second and third powers of Δ_{H_2} can be neglected, then:

$$\frac{2\Delta_{H_2}}{n_{NH_3}+n_{N_2}+n_{H_2}} < \frac{3\Delta_{H_2}}{n_{H_2}},$$

or

$$x_{H_2} < \frac{3}{2}$$

This inequality is always valid, since molar fractions are less than one. It means that in the case (c) $\Delta G < 0$, no matter what the initial composition of the mixture was. After addition of a small amount of hydrogen to the system the reaction will proceed predominantly in the direction of ammonia synthesis.

d) Both hydrogen and nitrogen are reactants. Their roles in the reaction (1) are similar. It is reasonable to expect that in cases (c) and (d) the answer to the problem will be the same. However, let us look at equation (9) which is similar to equation (8):

$$\frac{\Delta G}{RT} = -\ln\frac{n'_{N_2}}{n_{N_2}} - 2\ln\frac{n_{H_2}+n_{N_2}+n_{NH_3}}{n_{H_2}+n'_{N_2}+n_{NH_3}}. \qquad (9)$$

In the right side of (9) the first term is negative ($n'_{N_2} > n_{N_2}$), while the second is positive.

Let us solve the inequality $\Delta G < 0$:

$$-2\ln\frac{n_{H_2}+n_{N_2}+n_{NH_3}}{n_{H_2}+n'_{N_2}+n_{NH_3}} < \ln\frac{n'_{N_2}}{n_{N_2}}. \qquad (10)$$

Denote $n'_{N_2} = n_{N_2} + \Delta_{N_2}$, then

$$\left(1+\frac{\Delta_{N_2}}{n_{NH_3}+n_{N_2}+n_{H_2}}\right)^2 < 1+\frac{\Delta_{N_2}}{n_{N_2}}.$$

Again, term with the second power of Δ_{N_2} can be neglected, so:

$$\frac{2\Delta_{N_2}}{n_{NH_3}+n_{N_2}+n_{H_2}} < \frac{\Delta_{N_2}}{n_{N_2}},$$

so

$$x_{N_2} < \frac{1}{2}$$

If the molar fraction of nitrogen in the initial equilibrium mixture is less than 0.5 (question 3), the small increase of the amount of nitrogen will push the reaction towards the formation of ammonia. But if

$$x_{N_2} > \frac{1}{2}$$

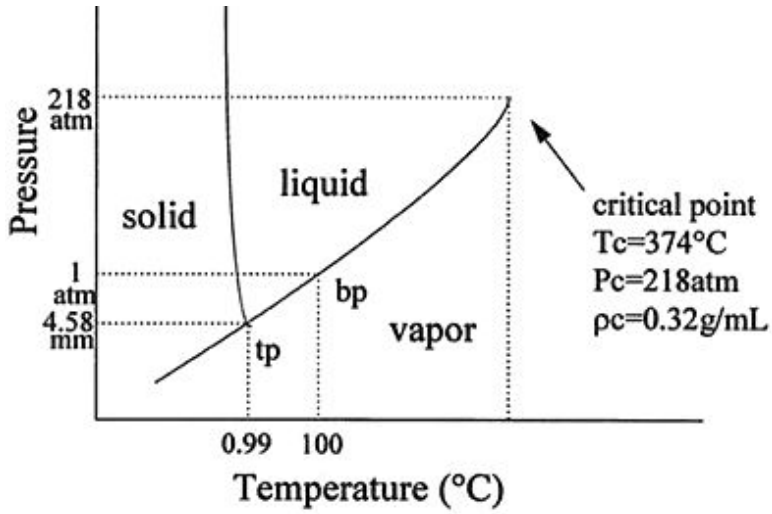
(question 4) after the addition of nitrogen the reaction will proceed predominantly in the reverse direction towards formation of the reactants.

Thus, in some cases addition of the reactant can lead to the opposite results. This “strange conclusion” is in full accord with the Le Chatelier’s principle!

Problem 8. DMITRY IVANOVICH MENDELEEV: WHAT BESIDES THE PERIODIC TABLE?

1. a) At present temperature of the absolute boiling is called critical temperature. D. Mendeleev introduced the «temperature of the absolute boiling» in 1860. T. Andrews introduced his concepts of the critical temperature and the critical point in 1869.

b) On the phase diagram of water the line of phase equilibrium between liquid and vapor terminates at the critical point. The corresponding temperature is “the temperature of the absolute boiling” (see figure).



c) Critical temperature T_c can be calculated from the parameters *a* and *b* of the Van-der-Waals equation of state:

$$T_c = \frac{8a}{27Rb}$$

For H_2O this equation gives

$$T_c(\mathrm{H_2O}) = \frac{8 \cdot 5.464 \cdot 101.3}{27 \cdot 8.314 \cdot 0.03049} = 647\ \mathrm{K} = 374\ ^\circ\mathrm{C}$$

One can see that Mendeleev overestimated the temperature of absolute boiling of water significantly. His value was 170 degrees above the real one.

2. From weight percent we calculate molar ratio:

$$\frac{n(\mathrm{C_2H_5OH})}{n(\mathrm{H_2O})} = \frac{\dfrac{W(\%)}{46}}{\dfrac{100 - W(\%)}{18}} = \frac{18W}{46(100 - W)}$$

There are three break points in the figure, namely at W = 17.5, 46 and 88%. They correspond to the molar ratios $\frac{n(\mathrm{C_2H_5OH})}{n(\mathrm{H_2O})} = 1{:}12; 1{:}3; 3{:}1$. According to Mendeleev the bi-

nary solution consists of the weakly bonded associates of ethanol with water. The compositions of these “hydrates of ethanol” are given by the molar ratios mentioned above.

However, the special compositions found by Mendeleev have nothing in common with the recipe of vodka. The volume percent $V\%$ of the ethanol in vodka is 40. The corresponding weight percent is:

$$W\% = \frac{40 \cdot 0.794}{40 \cdot 0.794 + 60 \cdot 1.000} \cdot 100 = 34.6\%$$

There is nothing special in this part of the graph! From the point of view of physical chemistry there is nothing special in the recipe of vodka.

Problem 9. KINETICS OF A FREE RADICAL REACTION

1.

$$\frac{d[2]}{dt} = 0 = k_1[\mathrm{S}] - k_2[\mathrm{S}][2]$$

$$r = k_2[\mathrm{S}][2] = k_1[\mathrm{S}]$$

2.

$$\frac{d[1]}{dt} = 0 = k_1[\mathrm{S}] - k_3[\mathrm{S}][1] + k_4[3]$$

$$\frac{d[3]}{dt} = 0 = k_2[\mathrm{S}][2] + k_3[\mathrm{S}][1] - k_4[3] = k_1[\mathrm{S}] + k_3[\mathrm{S}][1] - k_4[3]$$

The first step is the slowest, therefore $k_1[\mathrm{S}] << k_3[\mathrm{S}][1]$, by neglecting $k_1[\mathrm{S}]$ term, we get:

$$k_3[\mathrm{S}][1] = k_4[3]$$

$$\frac{[1]}{[3]} = \frac{k_4}{k_3[\mathrm{S}]}$$

3. Since the rate of radicals generation is small, the concentrations of radicals is low, and the rate of chain propagation which is proportional to the radical concentration is much higher than the rate of recombination which is proportional to the square of the radical

concentration. This approximation is known as the long-chain approximation (many chain propagation steps occur before the radical recombinates).

4. The correct answer is (b).

5. The rate of free radicals generation must be equal to their recombination rate. Since the concentration of $PhCH_2\bullet$ is much higher than those of other radicals, only the rate of two benzyl radicals recombination should be taken into account:

$$\frac{d[R]}{dt} = 0 = 2k_1[\mathrm{S}] - 2k_R[1]^2$$

$$[1] = \sqrt{\frac{k_1[\mathrm{S}]}{k_R}}$$

$$r = k_3[1][\mathrm{S}] = \frac{k_1^{1/2}k_3[\mathrm{S}]^{3/2}}{k_R^{1/2}}$$

The total order is 1.5.

The effective rate constant:

$$k = \frac{k_1^{1/2}k_3}{k_R^{1/2}}$$

The activation energy is:

$$E = \frac{E_1}{2} + E_3 - \frac{E_R}{2} \approx \frac{E_1}{2} + E_3,$$

because activation energy of free radical recombination is close to zero.

Problem 10. ASYMMETRIC AUTOCATALYSIS – AMPLIFICATION OF CHIRAL ASYMMETRY

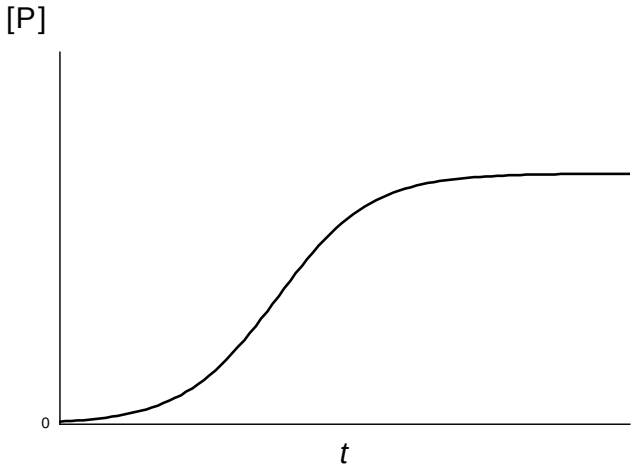
1. a) The closed system. The kinetic equation:

$$\frac{d[\mathrm{P}]}{dt} = k[\mathrm{A}][\mathrm{P}]$$

Taking into account the mass balance $[A] + [P] = [A]_0 + [P]_0$, we get:

$$\frac{d[\mathrm{P}]}{dt} = k\left([\mathrm{A}]_0 + [\mathrm{P}]_0 - [\mathrm{P}]\right)[\mathrm{P}]$$

At early stages the rate of P formation increases, but after some accumulation of the product reaction becomes more slow and finally its rate approaches zero.

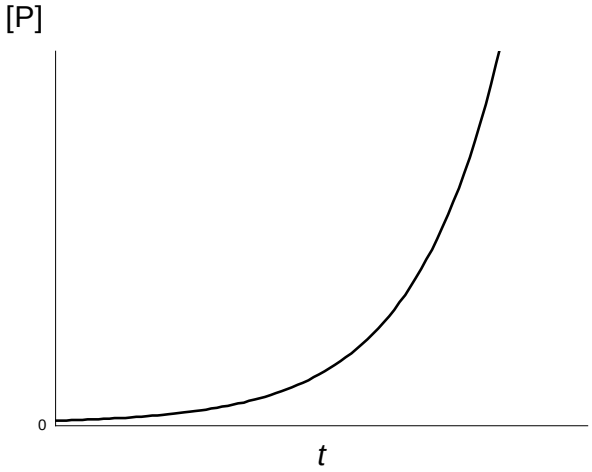


b) The open system. The kinetic equation:

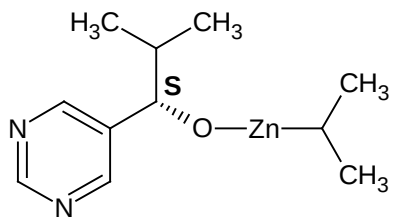
$$\frac{d[\mathrm{P}]}{dt} = k[\mathrm{A}]_0[\mathrm{P}]$$

Both the rate of reaction and concentration [P] increase with time:

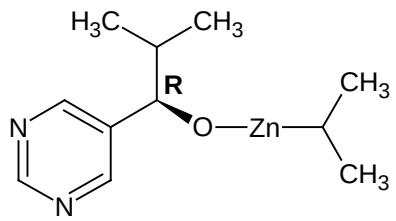
$$[\mathrm{P}] = [\mathrm{P}]_0 \exp\left(k[\mathrm{A}]_0 t\right)$$



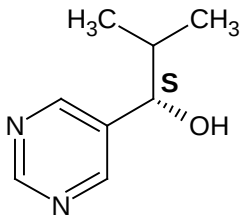
2. Diisopropylzinc is added across the C=O bond. Subsequent hydrolysis leads to a mixture of enantiomeric secondary alcohols:



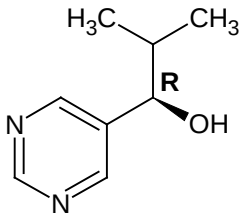
X1



X2



Y1



Y2

3. After the (n – 1)th addition the system will contain n mmol of mixture of alcohols. Let the fraction of (S)-isomer be a_n, and that of (R)-isomer – b_n. Let us add one more mmol of reagents. The yield of each alcohol is proportional to its fraction, hence additionally $\frac{a_n^2}{a_n^2+b_n^2}$ mmol of (S)- and $\frac{b_n^2}{a_n^2+b_n^2}$ mmol of (R)-isomer are formed. The new fraction of (S)-isomer is:

$$a_{n+1} = \frac{na_n + \frac{a_n^2}{a_n^2+b_n^2}}{n+1} = \frac{na_n + \frac{a_n^2}{a_n^2+(1-a_n)^2}}{n+1}$$

Now we need to solve the inequalities $a_{n+1} > 0.7$; 0.9; 0.99 with the initial condition $a_1 = 0.55$. It is easily done numerically. The iteration program can be written in any language. For example, the procedure in MathCad package has the form:

$$n := 436$$

$$r := \left| \begin{array}{l} a \leftarrow 0.55 \\ \text{for } x \in 1..n \\ \quad a \leftarrow \dfrac{a\cdot x + \dfrac{a^2}{a^2+(1-a)^2}}{x+1} \end{array} \right.$$

$$r = 0.99001$$

Applying recurrence formula, we obtain: $a_9 > 0.7$, $a_{40} > 0.9$, $a_{437} > 0.99$.

Answer. a) $n = 8$; b) $n = 39$; c) $n = 436$.

Problem 11. RADIOCARBON DATING

1.

$$^{14}_{7}\mathrm{N} + {}^{1}_{0}n \rightarrow {}^{14}_{6}\mathrm{C} + {}^{1}_{1}\mathrm{H}$$

$$^{14}_{6}\mathrm{C} \xrightarrow{\beta^-} {}^{14}_{7}\mathrm{N}$$

2. Dependence of the activity (a) on time:

$$a = a_0 e^{-\lambda t}$$

$$\ln\frac{a_0}{a} = \lambda t;$$

$$\lambda = \frac{\ln 2}{t'_{1/2}} = 1.245 \cdot 10^{-4}\ \text{years}^{-1}$$

$$t = \frac{\ln\dfrac{230}{480 \cdot 1000/3600}}{1.245 \cdot 10^{-4}} = 4380\ \text{years}$$

3. Activity 230 Bq/kg corresponds to the following $^{14}C/^{12}C$ ratio:

$$a = N_A k \frac{m}{M\left(^{12}\mathrm{C}\right)} w = N_A \frac{\ln 2}{t_{1/2}} \frac{m}{M\left(^{12}\mathrm{C}\right)} w$$

(neglecting ^{13}C content)

$$w = \frac{a t_{1/2} M\left(^{12}\mathrm{C}\right)}{N_A m \ln 2} = \frac{230 \cdot 5730 \cdot 365 \cdot 24 \cdot 3600 \cdot 12}{6.02 \cdot 10^{23} \cdot 1000 \cdot \ln 2} = 1.20 \cdot 10^{-12}$$

Since $6.0 \cdot 10^{-13} / 1.20 \cdot 10^{-12} = 1/2$, one half-life time elapsed (we use the value 5568 year for the age determination). The archaeologists thought that the powder was made approximately in 3560 BC.

4. In fact, the phenoxyacetyl group is formed from phenoxyacetic acid synthesized in industry from the products of petroleum and coal processing. It does not contain radiocarbon. Only 8 carbon atoms of 16 are natural (formed from living matter), so the ^{14}C content is twice that in a natural part, and $w = 1.2 \cdot 10^{-12}$, that is the powder is present-day.

Problem 12. IRON DETERMINATION

1. An oxidizing agent can convert Fe(II) to Fe(III) only if the corresponding redox potential is higher than that of the Fe(III)/Fe(II) couple. Therefore, all the oxidizing agents listed in Table with the exception of I_2 could be used:

$$3Fe^{2+} + NO_3^- + 4H^+ \rightarrow 3Fe^{3+} + NO + 2H_2O$$
$$2Fe^{2+} + H_2O_2 + 2H^+ \rightarrow 2Fe^{3+} + 2H_2O$$
$$2Fe^{2+} + Br_2 \rightarrow 2Fe^{3+} + 2Br^-$$

2. a) $Fe(OH_2)_6^{3+} \rightleftarrows Fe(OH_2)_5(OH)^{2+} + H^+$, $K_a = \dfrac{[Fe(OH_2)_5(OH)^{2+}][H^+]}{[Fe(OH_2)_6^{3+}]} = 6.3 \cdot 10^{-3}$

$[Fe(OH_2)_6^{3+}]$ (further referred to as $[Fe^{3+}]$) + $[Fe(OH_2)_5(OH)^{2+}]$ (further referred to as $[Fe(OH)^{2+}]$) = c(Fe) = 0.010 M, $[Fe(OH)^{2+}] = [H^+] = x$.

Therefore

$$6.3 \cdot 10^{-3} = \frac{x^2}{0.01 - x} \Rightarrow x = 5.4 \cdot 10^{-3} \text{ M} = [H^+] \Rightarrow \text{pH} = \mathbf{2.3}$$

Note. In this case a simplified approach to calculate $[H^+]$ as $\sqrt{K_a c}$ leading to the pH value of 2.1 is not acceptable since the dissociation constant of $[Fe(OH_2)_6^{3+}]$ is large and x in the denominator of the expression above should not be neglected compared to c.

b) $K_{sp} = [Fe^{3+}][OH^-]^3 = 6.3 \cdot 10^{-38}$;
$[Fe^{3+}] + [Fe(OH)^{2+}] = c(Fe) = 0.010$;

$K_a = \frac{[Fe(OH)^{2+}][H^+]}{[Fe^{3+}]} \Rightarrow [Fe(OH)^{2+}] = [Fe^{3+}]\frac{K_a}{[H^+]} = [Fe^{3+}][OH^-]\beta$, where $\beta = \frac{K_a}{K_w} =$ $6.3 \cdot 10^{11}$ and $K_w = [H^+][OH^-] = 1.0 \cdot 10^{-14}$.

A cubic equation relative to $[OH^-]$ can be obtained from the equations above, which may be solved iteratively as follows.

Denote $[Fe^{3+}] = x$, $[OH^-] = y$, then

$$x(1+\beta y) = c \Rightarrow x = \frac{c}{1+\beta y}$$

$$K_{sp} = xy^3 \Rightarrow y = \sqrt[3]{\frac{K_{sp}}{x}} \Rightarrow \text{pH} = -\log K_w + \log y.$$

Zeroth approximation: $y = 0 \Rightarrow x = \frac{c}{1+\beta y} = 0.010$ M $\Rightarrow y = \sqrt[3]{\frac{K_{sp}}{x}} = 1.85 \cdot 10^{-12}$ M $\Rightarrow$ pH = 2.27;

1st iteration: $y = 1.85 \cdot 10^{-12}$ M $\Rightarrow x = \frac{c}{1+\beta y} = 0.00462$ M $\Rightarrow y = \sqrt[3]{\frac{K_{sp}}{x}} = 2.39 \cdot 10^{-12}$ M $\Rightarrow$ pH = 2.38;

2nd iteration: $y = 2.39 \cdot 10^{-12}$ M $\Rightarrow x = \frac{c}{1+\beta y} = 0.00399$ M $\Rightarrow y = \sqrt[3]{\frac{K_{sp}}{x}} = 2.51 \cdot 10^{-12}$ M $\Rightarrow$ pH = 2.40 ~ **2.4**. Accuracy required obtained.

c) To be solved in a similar way with $c(Fe) = 1 \cdot 10^{-6}$ M. pH = **4.3** (after 4 iterations).

3. Determination of $KMnO_4$ concentration:

$$5\ As_2O_3 + 4\ MnO_4^- + 12\ H^+ + 9\ H_2O \rightarrow 10\ H_3AsO_4 + 4\ Mn^{2+};$$

M.W.(As_2O_3) = 197.8

$c(As_2O_3)$ = 0.2483 / 0.1000 / 197.8 = 0.01255 M

$c(KMnO_4)$ = 0.01255/5 · 10.00/12.79 · 4 = $7.850 \cdot 10^{-3}$ M

Determination of Fe(II):

$$5\ Fe^{2+} + MnO_4^- + 8\ H^+ \rightarrow 5\ Fe^{3+} + Mn^{2+} + 4\ H_2O;$$

A.W.(Fe) = 55.85

c(Fe(II)) = $7.850 \cdot 10^{-3} \cdot 11.80/15.00 \cdot 5 \cdot 55.85$ = 1.724 mg/mL = 1.724 g/L

ω(Fe(II)) = (1.724/2.505)·100% = **68.8%**

4. a) From Nernst equation (at 25 °C)

$$E = E^{\circ} + \frac{0.059}{1}\log\frac{[\mathrm{Fe(CN)}_6^{3-}]}{[\mathrm{Fe(CN)}_6^{4-}]};$$

E = 0.132 + 0.241 = 0.373 V; E° = 0.364 V $\Rightarrow \log\frac{[\mathrm{Fe(CN)}_6^{3-}]}{[\mathrm{Fe(CN)}_6^{4-}]} = \frac{E - E^{\circ}}{0.059} = 0.153 \Rightarrow$

$\frac{[\mathrm{Fe(CN)}_6^{3-}]}{[\mathrm{Fe(CN)}_6^{4-}]}$ = 1.42; ω(Fe(II)) = 1 / (1+1.42) · 100% = **41.3%**

b) Adding ammonia prevents formation of HCN in acidic medium:

$$CN^- + H^+ \rightarrow HCN$$

Adding tartaric acid leads to formation of stable Fe(III) and Fe(II) tartrate complexes and prevents:

(i) precipitation of $Fe(OH)_3$ and, possibly, $Fe(OH)_2$ with NH_3:

$$Fe^{3+} + 3\ H_2O + 3\ NH_3 \rightarrow Fe(OH)_3 + 3\ NH_4^+$$

$$Fe^{2+} + 2\ H_2O + 2\ NH_3 \rightarrow Fe(OH)_2 + 2\ NH_4^+$$

(ii) formation of insoluble mixed Fe(II)-Fe(III) cyanide (Berlin blue, Prussian blue, Turnbull's blue):

$$Fe^{3+} + Fe^{2+} + K^+ + 6\ CN^- \rightarrow KFe^{II}Fe^{III}(CN)_6$$

Problem 13. SULFUR DETERMINATION

1. a) $ZnCO_{3(s)} + S^{2-} \rightarrow ZnS_{(s)} + CO_3^{2-}$

$SO_3^{2-} + CH_2O + H^+ \rightarrow CH_2(OH)SO_3^-$

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

b) $S_2O_3^{2-}$

c) $n(S_2O_3^{2-}) = 2 \times 5.20 \times 0.01000 = 0.104$ mmol (in 20.00 mL of the filtrate)

$c(S_2O_3^{2-}) = 0.104 / 20.00 \times 50.00 / 20.00 = 0.0130$ mol/L (in the initial) = 0.01300×112.13 g/L = 1.46 g/L (**1460 ppm)**

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

$SO_3^{2-} + I_2 + H_2O \rightarrow SO_4^{2-} + 2\ H^+ + 2I^-$

b) SO_3^{2-}

c) $n(I_2)$ initial = $20.00 \times 0.01000 = 0.2000$ mmol

$n(I_2)$ excessive = $½ \times 6.43 \times 0.01000 = 0.0322$ mmol

$n(SO_3^{2-}) + ½\ n(S_2O_3^{2-}) = 0.2000 – 0.03215 = 0.1679$ mmol (in 15.00 mL of the filtrate)

$n(SO_3^{2-}) = 0.1679 – ½ \times 0.1040 / 20.00 \times 15.00 = 0.1289$ mmol (in 15.00 mL of the filtrate)

$c(SO_3^{2-}) = 0.1289 / 15.00 \times 50.00 / 20.00 = 0.02148$ mol/L (in the initial) = 0.02148×80.07 g/L = 1.720 g/L (**1720 ppm)**

3. a) $2\ S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^-$

$SO_3^{2-} + I_2 + H_2O \rightarrow SO_4^{2-} + 2\ H^+ + 2I^-$

$S^{2-} + I_2 \rightarrow S + 2\ I^-$

b) S^{2-}

c) $n(I_2)$ initial = $10.00 \times 0.05000 = 0.5000$ mmol

$n(I_2)$ excessive = $½ \times 4.12 \times 0.05000 = 0.103$ mmol

$n(S^{2-}) + n(SO_3^{2-}) + ½\ n(S_2O_3^{2-}) = 0.5000 – 0.1030 = 0.3970$ mmol (in 10.00 mL of the initial)

$n(S^{2-}) = 0.3970 – 10.00 \times 0.02148 – 10.00 \times ½ \times 0.01300 = 0.1172$ mmol (in 10.00 mL of the initial)

$c(S^{2-}) = 0.1172 / 10.00 = 0.01172$ mol/L = 0.01172×32.07 g/L = 0.376 g/L (**376 ppm)**

Problem 14. MAGNESIUM DETERMINATION

1. $Mg^{2+} + HPO_4^{2-} + NH_3 \rightarrow MgNH_4PO_{4\,(s)}$

2. $2\ MgNH_4PO_4 \rightarrow Mg_2P_2O_7 + 2\ NH_3 + H_2O$

3. $M_r(MgO) = 24.31 + 16.00 = 40.31$;

$M_r(Mg_2P_2O_7) = 2{\cdot}24.31 + 2{\cdot}30.97 + 7{\cdot}16.00 = 222.56$;

$$\omega(MgO) = \frac{2 \times 40.31}{222.56} \times \frac{0.1532}{1.8005} \times 100\% = \mathbf{3.08\%}$$

4. $2\ MgHPO_4 \rightarrow Mg_2P_2O_7 + H_2O$

$Mg(NH_4)_4(PO_4)_2 \rightarrow Mg(PO_3)_2 + 4\ NH_3 + 2\ H_2O$

($Mg_3(PO_4)_2 \rightarrow$ no changes)

$Mg(OH)_2 \rightarrow MgO + H_2O$

$(NH_4)_2HPO_4 \rightarrow HPO_3 + 2\ NH_3 + H_2O$

$NH_4Cl \rightarrow NH_3 + HCl$

5.

Impurity	Error
$MgHPO_4$	0
$Mg(NH_4)_4(PO_4)_2$	+
$Mg_3(PO_4)_2$	–
$Mg(OH)_2$	–
$(NH_4)_2HPO_4$	+
NH_4Cl	0

The error is positive if the percentage (by mass) of magnesium in the annealing product is *lower* than that in $Mg_2P_2O_7$, negative if *higher* and equal to zero if the same or if the impurity completely volatilizes during annealing.

6. $pH = -\lg[H^+] = -\lg K_w + \lg[OH^-]$

$$[OH^-] = \sqrt{\frac{K_{sp}(Mg(OH)_2)}{[Mg^{2+}]}};$$

$$[Mg^{2+}] = \frac{0.10\ \text{g}}{0.200\ \text{L} \times 24.31\ \text{g/mol}} \approx 2.1 \cdot 10^{-2}\ \text{mol/L}$$

$$[OH^-] = \sqrt{\frac{6.0 \cdot 10^{-10}}{2.1 \cdot 10^{-2}}} = 1.7 \cdot 10^{-4}\ \text{mol/L};\ \text{pH} = 14.00 - 3.8 = \mathbf{10.2}$$

7. At pH = 6.48 $[H^+] = 3.31 \cdot 10^{-7}$ M

$$[PO_4^{3-}] = c(PO_4) \cdot \frac{K_{a1}K_{a2}K_{a3}}{K_{a1}K_{a2}K_{a3} + K_{a1}K_{a2}[H^+] + K_{a1}[H^+]^2 + [H^+]^3} = 0.010 \times$$

$$\times \frac{7.1 \cdot 10^{-3} \cdot 6.2 \cdot 10^{-8} \cdot 5.0 \cdot 10^{-13}}{7.1 \cdot 10^{-3} \cdot 6.2 \cdot 10^{-8} \cdot \left(5.0 \cdot 10^{-13} + 3.31 \cdot 10^{-7}\right) + 7.1 \cdot 10^{-3} \cdot (3.31 \cdot 10^{-7})^2 + (3.31 \cdot 10^{-7})^3} =$$

$$= 2.4 \cdot 10^{-9}\ \text{M}$$

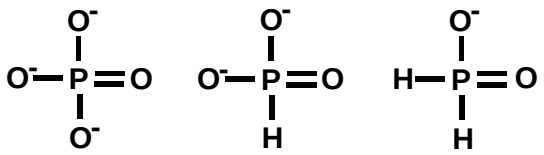
$[NH_4^+] \approx c(NH_4^+) = 0.010$ M (pH << $pK_a(NH_3) = pK_w - pK_b(NH_3) = 9.25$)

$[Mg^{2+}] = 0.010$ M

$$K_{sp} = [Mg^{2+}][NH_4^+][PO_4^{3-}] = \mathbf{2.4 \cdot 10^{-13}}$$

Problem 15. INORGANIC PHOSPHATES: FROM SOLUTION TO CRYSTALS

1. a)

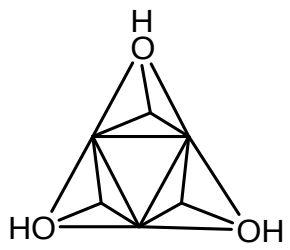


b) 1) Strength of the acids decreases from H_3PO_2 to H_3PO_4, i.e. pK_{a1} increases in this sequence. The explanation is based on the fact that one O-terminated side of each PO_n-tetrahedron with double bond P=O (shifting electron density from protons in P–OH groups due to inductive effect) acts on three P–OH groups in phosphoric acid and only on the sole P–OH group in the case of phosphinic (hypophosphorous) acid.

2) According to the Valence Shell Electron Pair Repulsion (VSEPR) theory O–P–O angle decreases in the same sequence. This is due to different polarity of P–O and P–H bonds

(it is apparent from the values of Pauling's electronegativity χ_P for these three atoms χ_P(H) = 2.20, χ_P(P) = 2.19 and χ_P(O) = 3.44). This fact stipulates partial negative charge δ– at oxygen atoms and almost δ = 0 in the case of hydrogen atoms. Thus, the P–O bonds endure higher repulsion from each other than from P–H bonds, and to a first approximation we can ignore the P–H bonds in our consideration. Then the following strong repulsive bonds for the above acids should be taken into account: one P=O and one P–OH for H_3PO_2, one P=O and two P–OH for H_3PO_3, and one P=O and three P–OH for H_3PO_4.

2. Three tetrahedra linked through the common vertices; protons are attached to one oxygen atoms in each tetrahedron so that $CN(O)_{OH} = 2$.



In a species with two phosphorus atoms two tetrahedra should share an edge which contradicts the initial assumption that each two adjacent tetrahedra have one shared oxygen atom. Thus, minimal amount of P-atoms is equal to three. It corresponds to *cyclo*-trimetaphosphoric acid.

3. a)

m	Q_m(P)
1	(–2/1)·3 + (–2/2)·1 + 5 = –2
2	(–2/1)·2 + (–2/2)·2 + 5 = –1
3	(–2/1)·1 + (–2/2)·3 + 5 = 0
4	(–2/1)·0 + (–2/2)·4 + 5 = +1

b) 1), 2)

m	Q_m(Si)	Q_m(S)
1	(–2/1)·3 + (–2/2)·1 + 4 = –3	(–2/1)·3 + (–2/2)·1 + 6 = –1
2	(–2/1)·2 + (–2/2)·2 + 4 = –2	(–2/1)·2 + (–2/2)·2 + 6 = 0
3	(–2/1)·1 + (–2/2)·3 + 4 = –1	(–2/1)·1 + (–2/2)·3 + 6 = +1
4	(–2/1)·0 + (–2/2)·4 + 4 = 0	(–2/1)·0 + (–2/2)·4 + 6 = +2

4. a) $m = 3$,

b) $m(\text{Si}) = 4$, $m(\text{S}) = 2$ according to the assumption.

5. a) Since the bonds between M and P are missing, the following equality is to be fulfilled: $CN_O \cdot b = (a+1)\cdot 4$, therefore $CN_O = (a+1)\cdot 4/b$.

The M to P ratio in an oxygen surrounding, $n(\text{M}) : n(\text{P})$, is $a : 1$, then, the number of atoms of M and P in the coordination sphere of O is:

$$n(\text{M}) = a/(a+1)\cdot CN_O = a/(a+1)\cdot(a+1)\cdot 4/b = 4a/b, \qquad n(\text{P}) = 4/b,$$

$$Q(\text{O}) = (5/4)\cdot(4/b) + (Z/4)\cdot(4a/b) + (-2) = (-2\cdot b + 5 + Z\cdot a)/b$$

where Z is the oxidation number of M.

The condition of the charge balance for M_aPO_b requires that $-2\cdot b + 5 + Z\cdot a = 0$. Therefore, $Q(\text{O}) = 0$.

b) According to the result above, $n(\text{P}) = 4/b$. Therefore, the number of phosphorus atoms in the oxygen coordination sphere, $n(\text{P})$, can be 1, 2 or 4 since b is an integer. Note that stoichiometry «M_aPO» and «M_aPO_2», b =1 and 2 respectively, is not possible for a phosphorus atom in the oxidation state +5. Hence, $b = 4$.

From the condition of the charge balance, $-8 + 5 + Z\cdot a = 0$. Solving this equation in integers gives $Z = +3$ ($a = 1$) or $Z = +1$ ($a = 3$). Indeed, the empirical formulas MPO_4 and M_3PO_4 correspond to known compounds such as $AlPO_4$ and Li_3PO_4. Note that the condition of oxygen atom equivalence is fulfilled here.

6. a) Since Ca^{2+} ions when combined with either NaF or Na_2HPO_4 solutions give precipitates, it is advisable to separate solutions containing calcium cations and phosphate/fluoride anions with the membrane.

	$Ca(NO_3)_2$	NaF	Na_2HPO_4			$Ca(NO_3)_2$	NaF	Na_2HPO_4
Soln. 1	v			or	Soln. 1		v	v
Soln. 2		v	v		Soln. 2	v		

b) $10Ca(NO_3)_2 + 2NaF + 6\,Na_2HPO_4 + 6NaOH \rightarrow Ca_{10}(PO_4)_6F_2 \downarrow + 20\,NaNO_3 + 6H_2O$,

if the pH values of the solutions were adjusted to alkaline range prior to the experiment. Or,

$$10Ca(NO_3)_2 + 2NaF + 6\ Na_2HPO_4 \rightarrow Ca_{10}(PO_4)_6F_2 \downarrow + 14\ NaNO_3 + 6\ HNO_3,$$

without the pH adjustment. The equation gives a clear evidence of acidification. Note that this is not favorable for fluorapatite formation, since it is rather soluble in acidic solutions.

c) Dissociation of $Ca(NO_3)_2$ and Na_2HPO_4 gives 3 ions for calcium- and phosphorous-containing salts, and two ions in the case of NaF. Then, the overall concentration of ions at the right and the left sides of the membrane is:

$$c = 5\cdot10^{-3}\cdot3 + 2\cdot10^{-3} + 3\cdot10^{-3}\cdot3 = (15 + 2 + 9)\cdot10^{-3} = 2.6\cdot10^{-2}\ \text{M} = 26\ \text{mol/m}^3.$$

$$p = cRT = 26\ \text{mol/m}^3\cdot8.31\cdot298 = 6.44\cdot10^4\ \text{Pa}.$$

Problem 16. FRUITS, VEGETABLES, ATOMS

1. a) Since tomatoes touch each other in layers **A** and **B**, regular *n*-polygons (where *n* is the number of the nearest neighbors) with touch points located in the middle of their sides define the square relevant to one tomato. Among *n*-polygons only squares and hexagons fill space without voids. Therefore, $\varphi = S_{tomat}/S_{polygon}$. *R* is the radius of vegetable or fruit (hereunder).

$$S_{square} = 4R^2,\ S_{hexagon} = 2\sqrt{3}R^2.\ S_{tomat} = \pi R^2.$$

$$\varphi_A = \frac{\pi}{4} \approx 0.7854;\quad \varphi_B = \frac{\pi}{2\sqrt{3}} \approx 0.9069$$

b) Type **B**.

2. a) The density of a packing can be estimated as the ratio of the volume of all tomatoes (*Z*) with the radius R filling the space inside of an arbitrarily chosen bulk polyhedron (P) of a certain volume V_P.

$$\varphi = \frac{4\pi ZR^3}{3\cdot V_P}$$

Type of packing	s.c.	b.c.c.	h.p.	h.c.p.
P	Cube, $a = 2R$	Cube, $a = \frac{4\sqrt{3}}{3}R$	Rhombic prism, $h = 2R$, $L = 2R$	Rhombic prism $h = \frac{4\sqrt{6}}{3}R$, $L = 2R$
V_P	$8R^3$	$\frac{64\sqrt{3}}{9}R^3$	$4\sqrt{3}R^3$	$8\sqrt{2}R^3$
Z	8·(1/8) = 1	1+ 8·(1/8) = 2	4·(1/12)+4·(1/6) = 1	1+4·(1/12)+4·(1/6) = 2
Φ	0.5236	0.6802	0.6046	0.7405

b) The case **(4)** (h.c.p.) corresponds to the most efficient way to fill space.

c) Calculation for f.c.c.: P is a cube $a = 2\sqrt{2}R$, $Z = 6\cdot(1/2) + 8\cdot(1/8) = 4$, $V_P = 16\sqrt{2}R^3$.

$$\varphi_{f.c.p.} = \frac{16\pi}{3\cdot 16\sqrt{2}} \approx 0.7405.$$

d) For c.p.s. φ does not depend on the type of the layer sequence.

3. a) In order to avoid peaches smashing the radius of a void should be less than the radius of a peach (r – radius of a peach, R – radius of a watermelon).

Type of packing	s.c.	b.c.c.	f.c.c.
The criterion of successful transportation	$2r < (a_{s.c.}\sqrt{3} - 2R)$	$2r < (a_{b.c.c.} - 2R)$	$2r < (a_{f.c.c.} - 2R)$
$r(\max)/R$	$(\sqrt{3} - 1) \approx 0.7321$	$(\frac{2\sqrt{3}}{3} - 1) \approx 0.1547$	$(\sqrt{2} - 1) \approx 0.4142$

b) The number of peaches cannot exceed that of corresponding voids:

Type of packing	s.c.	b.c.c.	h.c.p.	f.c.c.
Z_{peach}	1	6·1/2 +12·1/4 = 6	2	1 + 12·1/4 = 4
$Z_{peach}/Z_{watermelon}$	1	3	2	1

c) Let us calculate the maximal density according to the formula:

$$\varphi = \frac{4\pi R^3 Z_{\text{watermelon}}\left(1+\dfrac{Z_{\text{peach}} r^3(\max)}{Z_{\text{watermelon}} R^3}\right)}{3\cdot V_P}$$

Type of packing	s.c.	b.c.c.	f.c.c.
P	Cube, $a = 2R$	Cube, $a = \frac{4\sqrt{3}}{3}R$	Cube, $a = 2\sqrt{2}\,R$
V_P	$8R^3$	$\frac{64\sqrt{3}}{9}R^3$	$16\sqrt{2}\,R^3$
$Z_{\text{peach}}/Z_{\text{watermelon}}$	1	3	1
$1+\frac{Z_{\text{peach}} r^3(\max)}{Z_{\text{watermelon}} R^3}$	1.3924	1.0111	1.0711
φ	0.721	0.6878	0.7931

4. a) In the case of b.c.c. ventilation of voids can be achieved by filling ¼ of voids: the network composed of octahedra linked by common apexes with ¼ watermelons which have no neighboring peaches. Similar calculation for f.c.c. gives ¼ (the same algorithm for void filling, for details see Appendix).

b) For f.c.c. $Z_{\text{apple}} = 8$ accounting for 4 watermelons (forming f.c.c. unit cell),

$$Z_{\text{apple}} / Z_{\text{watermelon}} = 2.$$

5. a) The rigorous condition for a diffraction maximum is: the product of inverse coordinates of diffracted planes ($\frac{h}{a}\,\frac{k}{a}\,\frac{l}{a}$) and coordinates of each microsphere in a cubic unit cell with side a has to be integer. In the case of f.c.c. there are three independent translations ($\frac{a}{2}\,\frac{a}{2}\,0$), ($\frac{a}{2}\,0\,\frac{a}{2}$) and ($0\,\frac{a}{2}\,\frac{a}{2}$), then the condition of diffraction maximum is: $h + k = 2n$, $k + l = 2m$, $h + l = 2q$, where m, n, q – integers. Hence, the reflection with $h\,k\,l$ =(1 1 1) satisfies the condition above.

b) $a = 2\sqrt{2}r$, $d_{\mathbf{min}} = \dfrac{2\sqrt{2}r}{\sqrt{h^2+k^2+l^2}} = 2\sqrt{\dfrac{2}{3}}\cdot 450 \approx 734.85$ nm.

$$\lambda = d_{\min} \sin 30^{\circ} = 734.85 \cdot \frac{1}{2} \approx 367.42 \text{ nm.}$$

Appendix

How to achieve ventilation of partially filled b.c.c. and f.c.c. packings

b.c.c. Filling the void at the center of a face in b.c.c., one should consider (from a viewpoint of symmetry) that the opposite face of the b.c.c. cell is occupied either. Filling any remaining void in the cell immediately leads to joining of octahedra by edges. Apparently, such a cell cannot be stacked with the other ones through a face but can be stacked via edges. Thus, filled cells are arranged within 0*xy* (and similar) plane in checkerboard order. Moving from plane to plane along coordinate axis, filled and empty cells arise alternately (like Na and Cl in rock salt structure) or they form columns. In each case above, watermelon/peach ratio will be the same, since the ratio (filled cells)/(empty cells) = 1:1 remains the same. Then, $1_{cell} \cdot 1/2 \cdot 2 = 1$ peach is accounting for $2_{cell} \cdot 2 = 4$ watermelon, i.e. the optimal ratio peach/watermelon = 1/4. If all watermelons have 2 peach-neighbors in octahedral voids, then the ratio peach/watermelon = (the number of neighbors for a watermelon)/(the number of neighbors for a peach) = 2/6 = 1/3. However, this is impossible within the frame of b.c.c. type of packing.

Another glance on the transformation of c.p.s. layers during the filling of voids can be described as follows. Filling of octahedral voids immediately leads to the framework of octahedra joined by apexes like in ABX_3 perovskite structure. Here watermelons play roles of both A-cation and X-anion. From this consideration it is quite clear that further compaction of fruit-vegetable mixture is impossible without smashing. This means that we have reached the ultimate value of peach/watermelon ratio.

f.c.c. Placing a peach at the origin of f.c.c. cell, one can find out that it is impossible to fill more voids. Then, the ratio peach/watermelon is equal to $1/Z_{f.c.c.} = 1/4$. Moving the origin of f.c.c. cell into the filled void, it is easy to show up the ABX_3 perovskite structure again with the same consequences related to further compaction of fruit-vegetable mixture.

Problem 17. CHAMELEONIC COBALT

1. $CoCl_2{\cdot}6H_2O_{(cr)} \rightleftarrows CoCl_2{\cdot}4H_2O_{(cr)} + 2H_2O_{(g)}$

$\Delta_r H^\circ_{298}$ = 2·(–241.8) – 1538.6 – (– 2113) = 90.8 kJ

$\Delta_r S^\circ_{298}$ = 2·188.7 + 211.4 – 346 = 242.8 J K^{-1}

$\Delta_r G^\circ_{298}$ = 90800 – 298·242.8 = 18.45 kJ

$$-RT\ln K_p = \Delta_r G^\circ_T$$

$$-RT\ln p^2_{H_2O} = \Delta_r G^\circ_T$$

$$\lg p_{H_2O} = -\frac{\Delta_r G^\circ_{298}}{2\cdot 2.3\cdot 298\cdot R} = -\frac{18450}{2.3\cdot 2\cdot 298\cdot 8.31} = -1.62$$

p_{H_2O} = 0.024 atm

At 298 K, the pressure of saturated water vapor can be estimated from the equilibrium

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

$\Delta_r H^\circ_{298}$ = –241.8 – (– 285.8) = 44.0 kJ

$\Delta_r S^\circ_{298}$ = 188.7 – 70.1 = 118.6 J K^{-1}

$\Delta_r G^\circ_{298}$ = 44000 – 298·118.6 = 8.66 kJ

$$-RT\ln p^0_{H_2O} = \Delta_r G^\circ_T$$

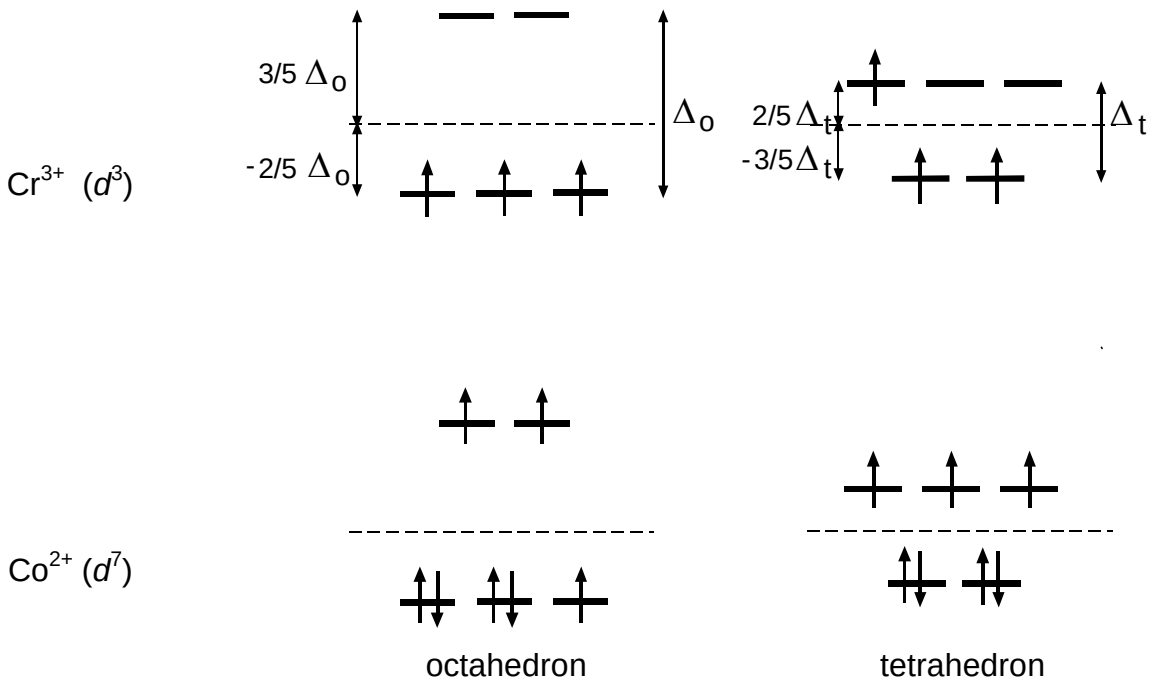
$$\lg p^0_{H_2O} = -\frac{\Delta_r G^\circ_{298}}{2.3\cdot 298\cdot R} = -\frac{8660}{2.3\cdot 298\cdot 8.31} = -1.52$$

$p^0_{H_2O}$ = 0.030 atm

The threshold of <u>relative humidity of air</u> specific to the hygrometer response is

$$\frac{p_{H_2O}}{p^0_{H_2O}} = 0.024 / 0.030 = 0.80 \text{ or } \mathbf{80\%}$$

2. In a weak Crystal Filed (ligands are water molecules)



a) CFSE ($[Cr(H_2O)_6]^{3+}$) = –6/5 Δ_o = **–1.2Δ_o**;
CFSE($[Cr(H_2O)_4]^{3+}$) = –4/5 Δ_t ≈ –16/45 Δ_o = **– 0.36 Δ_o** (assuming that Δ_t ≈ 4/9 Δ_o);

b) CFSE ($[Co(H_2O)_6]^{2+}$) = –4/5 Δ_o = **–0.8 Δ_o**;
CFSE ($[Co(H_2O)_4]^{2+}$) = –6/5 Δ_t ≈ –24/45 Δ_o = **–0.53 Δ_o** (assuming that Δ_t ≈ 4/9 Δ_o);

The value |CFSE(tetrahedron) – CFSE(octahedron)| becomes minimal just for the configuration d^7 (i.e. for Co^{2+}). The Crystal Field Theory assumes ionic bonding of ligand-central ion. That is true for the case of hard acid (a central ion) – hard base (a ligand) in terms of HSAB (see below). In the case of Co^{2+} ion (which is close to a soft acid) covalent contribution to chemical bonding of the central ion with a large polarizable ligand is an additional factor that stabilizes a tetrahedral complex.

3. a) We may expect that the entropy change for the reaction (1) $\Delta_r S^\circ_{298}$ > 0, since the reaction is accompanied by an increase of the number of species. At the same time $\Delta_r G^\circ_{298}$ is slightly above zero (otherwise the reaction (1) would proceed from left to right completely). Therefore, $\Delta_r H^\circ_{298} > T\Delta_r S^\circ_{298} > 0$. This conclusion agrees well with CFSE calculations (see above).

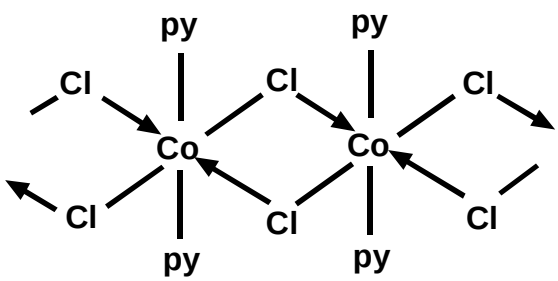
b) Heating shifts the equilibrium (1) to the right, since $\Delta_r H^{\circ}_{298} > 0$, and a pink solution turns its color to deep blue.

c) Since Co^{2+} is not a hard acid according to HSAB (rather it is an intermediate acid close to a soft one), it forms stable complexes with soft bases. Thiocyanate-ion SCN^- is a softer base compared to Cl^-, hence, <u>in the case of SCN^- the equilibrium (1) is largely shifted to the right</u>. This is used to discover Co^{2+} in solutions.

4. a) X = I^-. According to HSAB I^- is a softer base than Cl^-.

b) In both cases, i.e. for X = I^- and for X = Cl^-, the tetrahedral coordination compounds are stable. The reason lies in the fact that PH_3 is much softer base compared to pyridine. Then, softness of the secondary ligand is not the determining factor in stabilization of the tetrahedral complex.

c) Violet color of the compound corresponds to octahedral environment of Co ion. It is possible if the compound has a polymeric structure (bonding via Cl bridges):



5. $CoCl_2 + 2NaOH + 2H_2O \rightarrow 2NaCl + [Co(H_2O)_2(OH)_2]\downarrow$ – blue precipitate

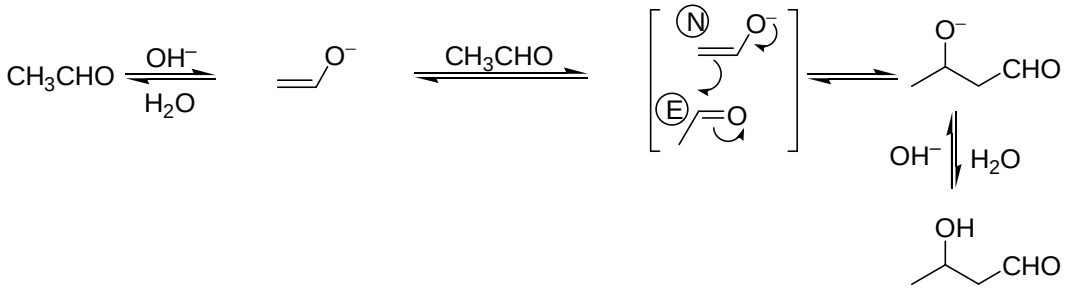
(in fact, the structure of hydroxides or basic salts of transition metals is quite complex, often polymeric in its nature, however, the color of the precipitate gives correct information concerning the coordination environment of Co ions having CN = 4)

$[Co(H_2O)_2(OH)_2]\downarrow + 2H_2O = [Co(H_2O)_4(OH)_2]\downarrow$ (pink precipitate)

$[Co(H_2O)_4(OH)_2]\downarrow + 2NaOH = Na_2[Co(OH)_4]$ (blue solution) $+ 4H_2O$

Problem 18. THE FORMOSE REACTION

The base-catalyzed aldol condensation involves a highly reactive nucleophilic enolate-ion, which directly attacks the electrophilic carbonyl carbon of another aldehyde molecule giving β-hydroxyaldehyde (aldol).

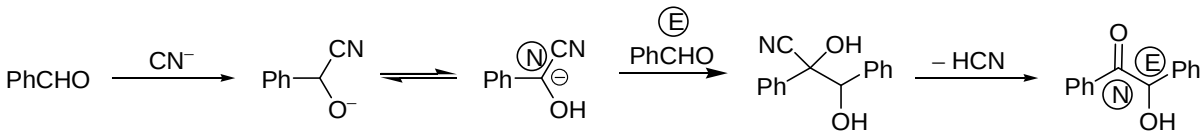


Non-enolizable are aldehydes lacking β-protons, that are those which cannot give enols or enolates. Among important non-enolizable aldehydes, besides formaldehyde are benzaldehyde PhCHO, trichloroacetic acid aldehyde (chloral) CCl_3CHO, glyoxal OHC–CHO, and many others.

Formaldehyde is produced by a 3-step process involving a) gasification of coal by the action of steam at high temperature to give the so-called *syngas*, which is used as feedstock for b) methanol synthesis using copper on zinc oxide catalyst at 250 °C and 100 atm pressure. Methanol is catalytically dehydrogenized into formaldehyde over silver mesh at 650°.

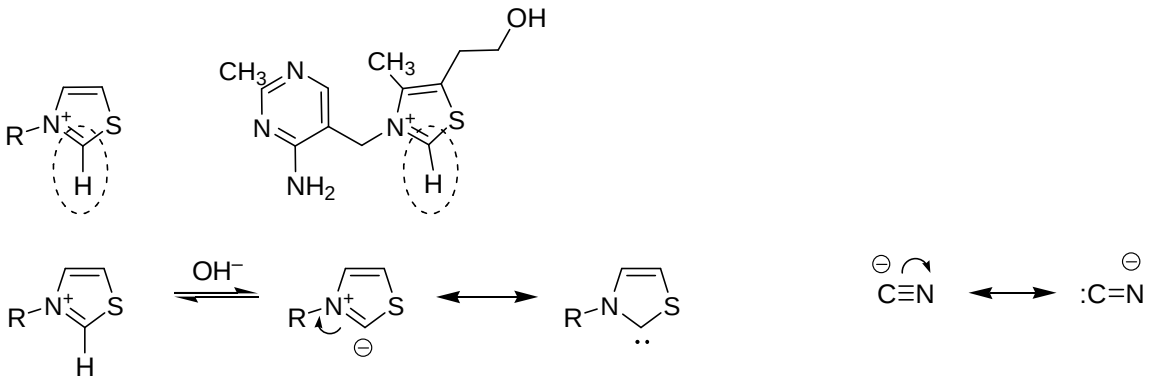
$$C + H_2O \longrightarrow CO + H_2 \longrightarrow CH_3OH \longrightarrow CH_2O$$

The main trick in the mechanism of benzoin condensation is the addition of nucleophilic catalyst to carbonyl group of a non-enolizable aldehyde. Central carbon of the adduct is no more sp^2-carbon, but rather sp^3-carbon bearing two substituents capable of delocalization of negative charge and thus rendering a reasonable CH-acidity. After deprotonation the resulting carbanion serves as a nucleophile attacking carbonyl group of the other aldehyde molecule. Elimination of nucleophilic catalyst (here, cyanide) regenerates carbonyl group. Thus, the net result is the transfer of PhCO (or generally RCO, acyl) residue from aldehyde.



Normally, acyl groups are transferred by electrophilic reagents (acid chlorides, anhydrides, and other carboxylic acid derivatives) to nucleophiles. The Umpolung principle shows the way how it can be done by using a pair of reagents of reverse reactivity.

The analogy between cyanide and thiazolium is profound and very interesting. Apparently, both HCN and thiazolium (with regard to C-2 atom) can be considered as derivatives of formic acid.

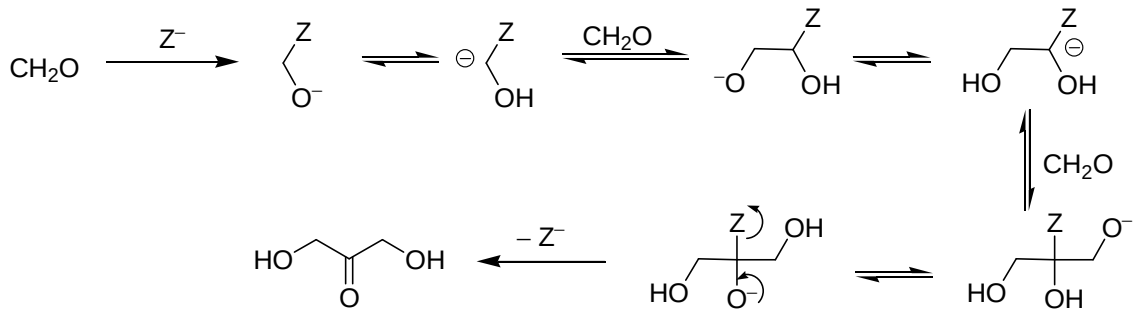


Resonance structures for thiazolium anion suggest that besides carbanionic form there is the only one other form, an electroneutral carbene! Indeed, this is a true carbene with 6-electron configuration of carbon atom, a lone pair and a vacant orbital. Recent research has shown that thiazolium anion and closely related anions of analogous heterocycles (e.g. imidazolium) are indeed stable (!) carbenes, which immediately found a lot of applications in organic chemistry and catalysis. These carbenes are nucleophilic due to two electron-rich heteroatoms connected to carbene center. Thus, it can be assumed that Nature employs a stable carbene in the transketolase catalysis.

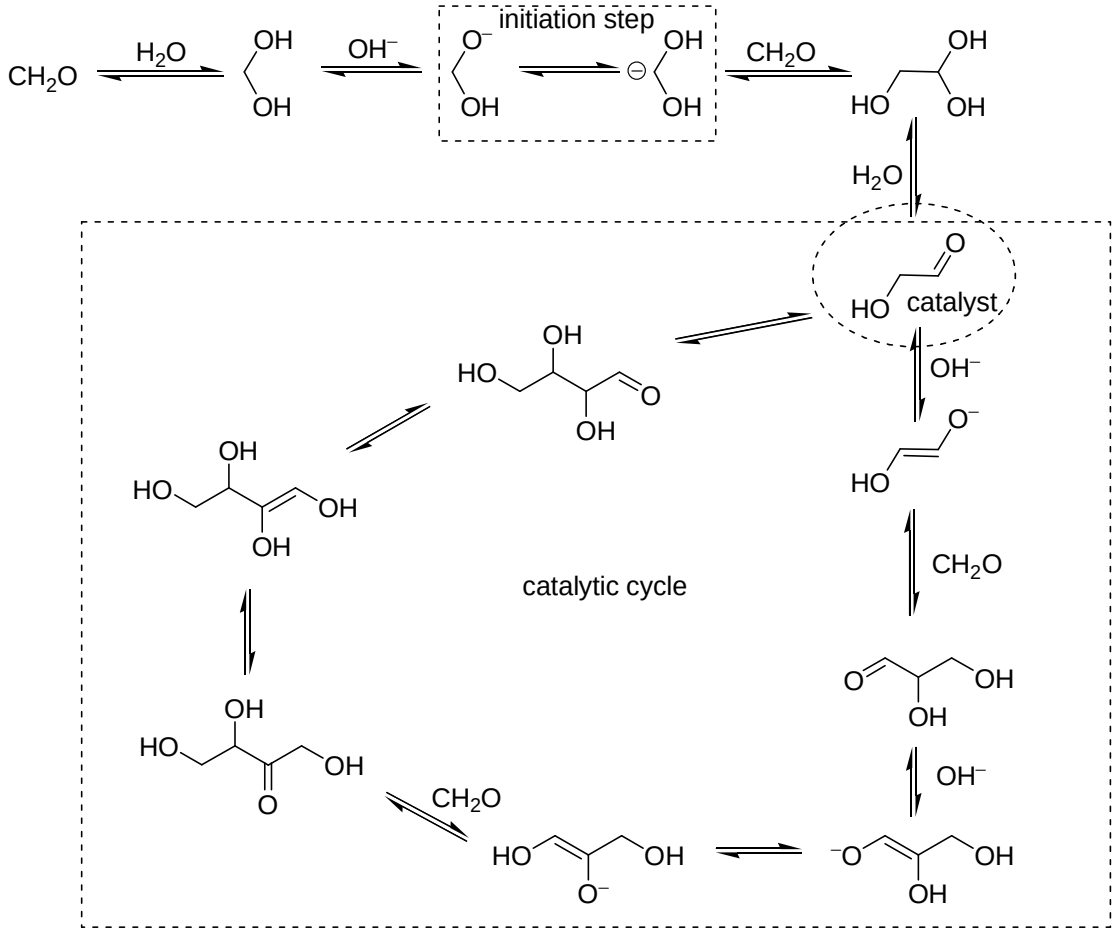
Coming back to the analogy with cyanide, we see that cyanide has a second resonance form, isocyanide with carbene-like divalent carbon.

As shown above thiamine pyrophosphate, as other thiazolim salts, is very reactive towards aldehydes. In the organisms of heavy drunkards there is a lot of alcohol dehydrogenation product, acetaldehyde. This reactive aldehyde binds to thiamine thiazolium residue, thus stealing the vitamin from vital biochemical processes.

Continuation is straightforward to employ the same chemistry as in the steps already shown. Catalyst (thiazolium anion or thiazolidene, if we choose the carbene form) is regenerated at the last stage exactly as in the benzoin condensation.

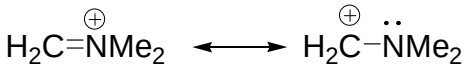


(also 9 and 10) The Umpolung in the true formose reaction is apparently furnished by CH-acidic properties of the hydrated form of formaldehyde. Due to the lack of good mesomeric stabilization CH-acidity is much lower, and the deprotonation leading to nucleophilic carbanion is much less efficient. Therefore, the reaction is very slow at the beginning. The induction period is accounted for by very low concentration of carbanion. But as soon as some glyoxal is accumulated, a highly effective catalytic cycle is switched on. Within the catalytic cycle formaldehyde behaves as a normal electrophile.



Problem 19. THE ANALOGY IN ORGANIC CHEMISTRY

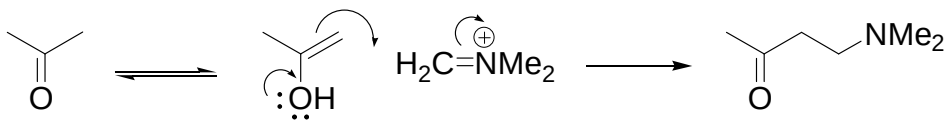
1. Echenmoser's salt is an iminium salt, which involves a heteroanalogue of carbonyl group. Thus, Echenmoser's salt is an electrophile with electrophilic carbon center similar to the carbonyl carbon. Formally, it should behave as a stabilized carbenium ion, as is well seen by considering the resonance forms



Due to very high π-donicity of dimethylamino group, the first form predominates, and thus nucleophilic properties, which may be attributed to the second form, are virtually missing. It can be considered a Lewis acid, as any C-electrophile is, due to apparent ability to combine with bases, e.g. hydroxide ion or water.

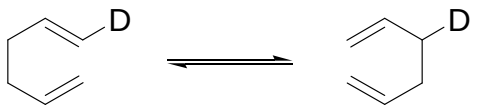
Thus, electrophile is the true answer, and Lewis acid and/or nucleophile can be regarded as valid additional answers.

2. No catalyst is required because iminium salt is already strongly polarized, and carbon atom is sufficiently electrophilic to attack carbonyl group without any additional activation by catalysts. In the reactions with aldehydes or ketones the iminium salt serves as a heteroanalogue of the *protonated carbonyl compound*, with the double carbon-nitrogen bond strongly polaryzed due to the positive charge at heteroatom. Therefore, the iminium salt is already reactive enough to take part in electrophilic attack at enol to form the so called Mannich base, which is itself a heteroanalogue of the aldols.



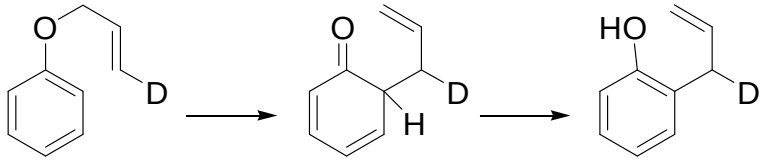
3. In the Cope rearrangement, it is highly important to realize that the reaction is an equilibrium, which is perfectly evident from the fact that the reactant and product are the same compound (or the same type of compound, if a substituted diene is used). Thus, the forward and the reverse transformations are the same reaction.

In the case of degenerate reaction (when reactant and product are the same, if isotope effects are neglected), it is evident that equilibrium constant is unity.



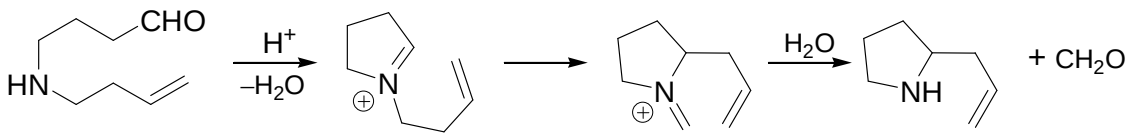
Thus, the result would be an equimolar mixture of 1- and 3-deuteriohexadiene-1,5.

4. Unlike the Cope rearrangement, oxo-Cope rearrangement involves two different compounds (belonging to different classes), thus the reversibility is not evident. In the case of allylic phenol ether hetero-hexadiene fragment is formed by allyloxy chain and one of the double bonds of benzene ring:



As the initial keto-form of phenol is immediately transformed into much more stable normal phenol (*enol*) form, the arrangement of double bonds for Cope-Claisen rearrangement disappears, and the whole reaction becomes irreversible.

5. The domino-reaction starts from the formation of a cyclic iminium salt similar to the Eschenmoser's salt, with triethyl-orthoformate serving as a dehydrating agent. In this salt there are two double bonds at a distance required for the Cope rearrangement, thus here we have the aza-Cope rearrangement. A new iminium salt is formed, which is readily hydrolyzed to liberate secondary amine and formaldehyde.

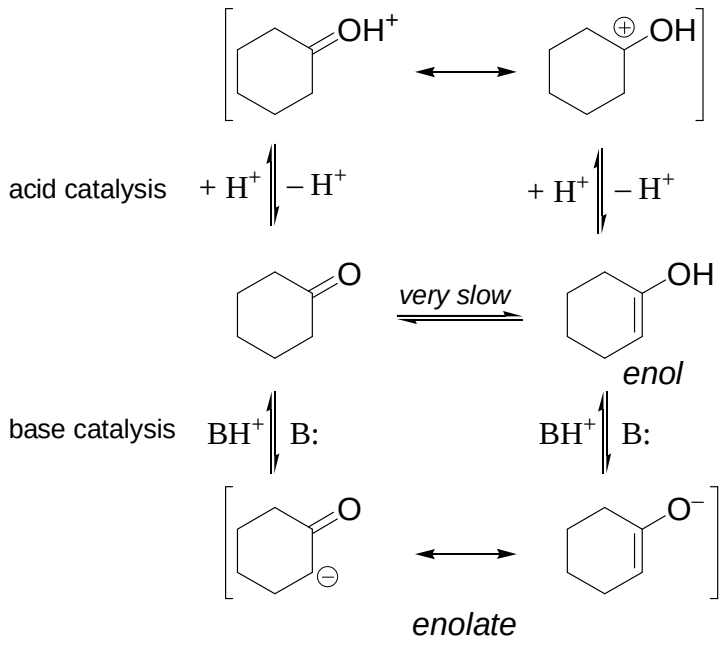


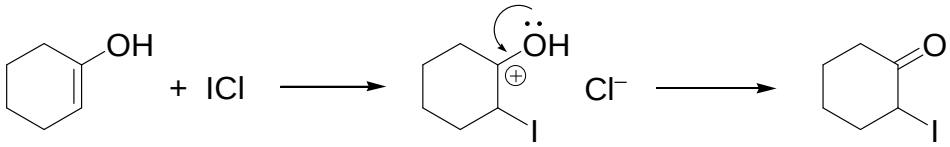
Problem 20. KETO-ENOL TAUTOMERISM

1-3. Ketones do not react directly with halogens. Enolizable ketones and aldehydes contain the respective enols, which are unsaturated electron-rich compounds very reactive towards electrophiles. The reactions are very fast and quantitative. The transformation of ketone to enol is normally rather slow, but is effectively catalyzed by acids and bases. Thus, if the reaction with halogen is performed fast, only enol is consumed. In order to

avoid catalyzed enolization the acid liberated during the addition should be neutralized by salt, which is not alkaline enough to switch on the base-catalyzed enolization.

Iodine chloride is more convenient as titration agent than bromine or iodine, as the former interhalide is more polar, and thus is more reactive towards the double bond.



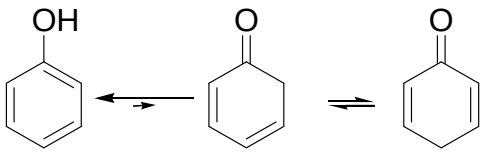


$ICl + I^- = I_2 + Cl^-$

$2S_2O_3^{2-} + I_2 = S_4O_6^{2-} + 2I^-$

Calculation of enol content should give the value of 1.18%. As has been shown by more accurate kinetic and spectroscopic investigations, this estimate is hugely overestimated. Real tautomerism constant for cyclohexanol is of the order p*K* = 5-6.

4-5. The content of enol in simple ketones is very low. However, there are some compounds for which the enol form is more stable, and even those with predominating enol form. One of the most important examples of such behavior are … phenols. Simple phenols practically do not show any properties characteristic of keto-form, because this form is not aromatic and thus very unstable in comparison with enol (phenol)

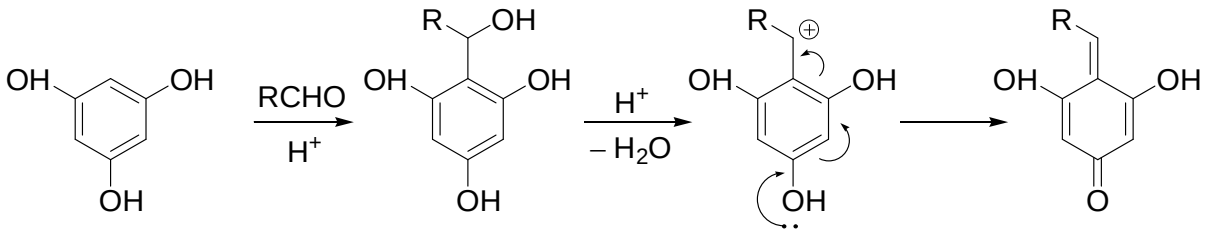


enol *keto-forms*

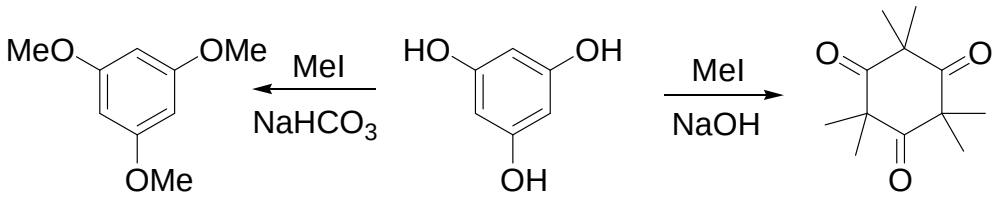
However, for some substituted phenols, as well as for polycyclic or heterocyclic phenols the presence of keto-form is well manifested. One of such examples is used in the second part of the task.

The transformations mentioned reveal the reactivity of carbonyl group (reactions with hydroxylamine, bisulfite, and condensation with aldehydes). From the empirical formula of bisulfite derivative it can be deduced that the compound has 6 carbon atoms, and all other empirical formulas are the results of factorization of divisible formulas. Thus, compound **A** is $C_6H_6O_3$ and is, according to ^{13}C NMR, a highly symmetrical compound. As it follows from apparent presence of keto-group this might be cyclohexatrione-1,3,5, or a fully enolized form of this compound 1,3,5-trihydroxybenzene, known as floroglucine.

Condensation with aldehydes gives normal aldols, which readily eliminate water to form quinoid structure, a well-known chromophore. Two or three aldehyde molecules can enter this reaction, and more complex structures can form if aldehyde bears some functional groups (such as e.g. carbohydrates or cinnamic aldehydes which are the building blocks of lignin).

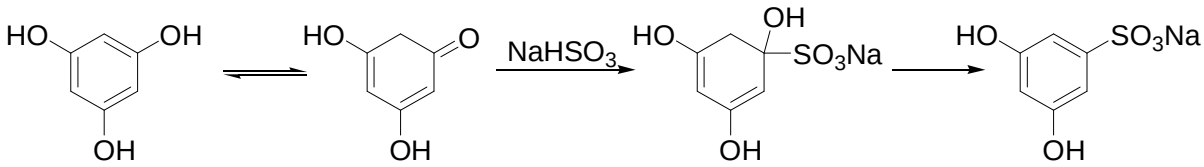


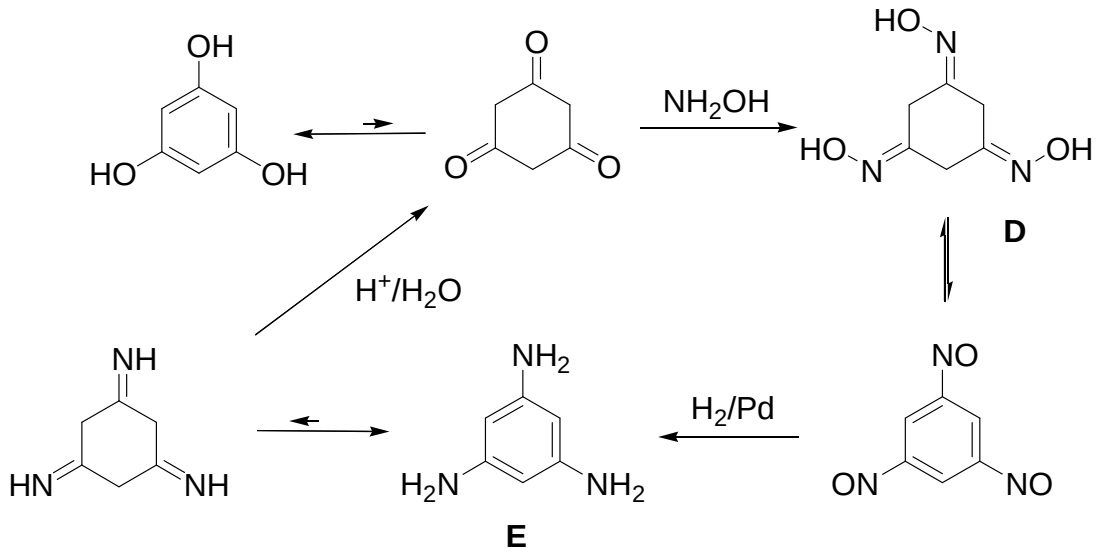
Methylation can give either permethylated enol or keto-forms, the former takes 3 methyls, the latter 6 methyls



C **A** **B**

Bisulfite derivative readily loses water to give 3,5-dihydroxybenzenesulfonic acid



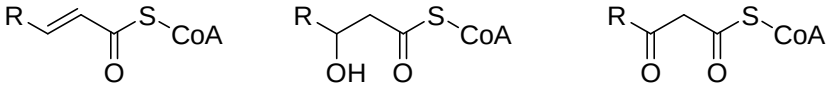


Problem 21. UNUSUAL PATHWAYS OF FATTY ACID OXIDATION: ALPHA-OXIDATION

1. According to IUB classification:
   1.3. – oxidoreductases acting on the CH–CH group of donors;
   4.2. – carbon-oxygen lyases (or hydrolases);
   1.1. – oxidoreductases acting on the CH–OH group of donors;

2.3. – acyltransferases.

The 1st enzyme catalyzes dehydrogenation resulting in β-unsaturated acyl derivative (all the rest carbon atoms but carbonyl belong to R, and thus are not modified). Addition of water to this unsaturated acyl CoA leads to 3-hydroxyacyl CoA (formation of 2-hydroxyacyl CoA is not consistent with the final products given in the task). This is also confirmed by the subclass of the 3rd enzyme, which catalyzes oxidative transformation of a hydroxyl group into carbonyl one. The 4th enzyme leads to the final products of the cycle as a result of thioclastic degradation (transfer of R-CO fragment on a new CoA-SH molecule).



X **Y** **Z**

2. According to the task data, **E1** catalyzes two successive reactions. Based on the list of reaction types given, two variants are possible for the first stage: either formation of an ester bond of ribonucleoside phosphate and carbonic acid or kinase reaction. Then thioester of carbonic acid (phytanoyl CoA) is formed at the second stage. Two-stage character of **E1** catalyzed reaction is due to a positive change of Gibbs free energy of phytanoyl CoA formation. This process is possible if only it is conjugated with cleavage of high energy bond in NTP.

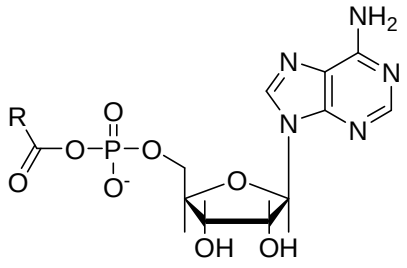
If the first stage is the kinase reaction, one product is possible: residue of phytanic acid linked with one phosphate. P:O ratio in this product would be 1:5. Thus, one can conclude that intermediate containing either NMP or NTP residue is formed. Note that NDP residue is not consistent with further phosphorus-containing products.

Finally, the reaction types are: **E1** – a), d); **E3** – f).

3. To decipher nucleotide in **E1** catalyzed reaction, a table with P:O molar ratios for all possible derivatives of ribonucleotide mono- and triphosphates is of help.

Intermediate contains	P:O molar ratio if the starting nucleotide contains as a base			
	Adenine	Guanine	Uracil	Cytosine
Monophosphate	1:8	1:9	1:10	1:9
Triphosphate	1:4.66	1:5	1:5.33	1:5

It is seen that the only possible variant is **E1**catalyzed transfer of adenosine monophosphate residue on phytanic acid molecule:

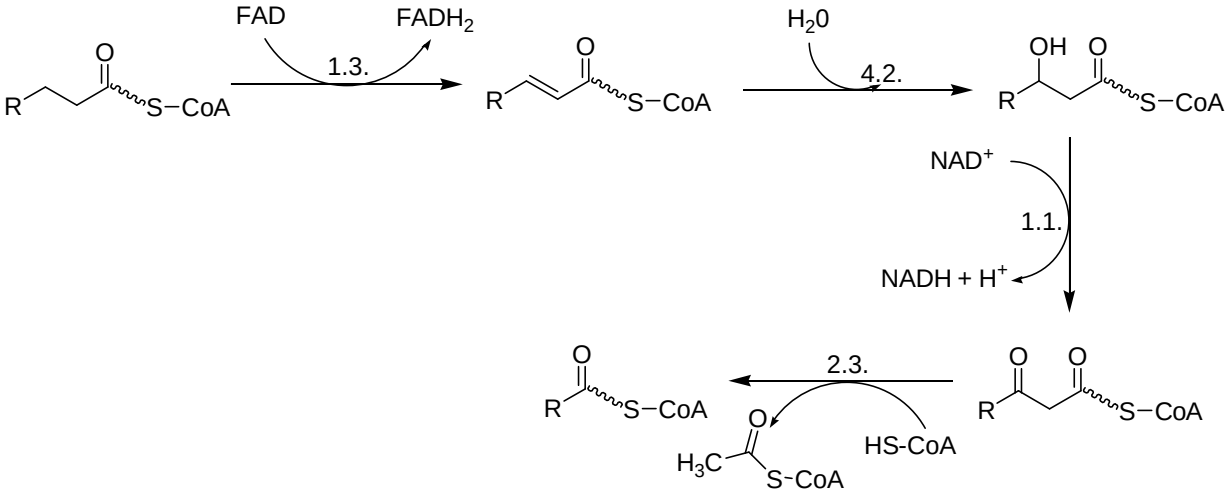


4. It is seen from the table in the task that the number of carbon atoms in prystanic acid is: 4·3 (propionyl CoA) + 3·2 (acetyl CoA) + 1 (formyl CoA) = 19.

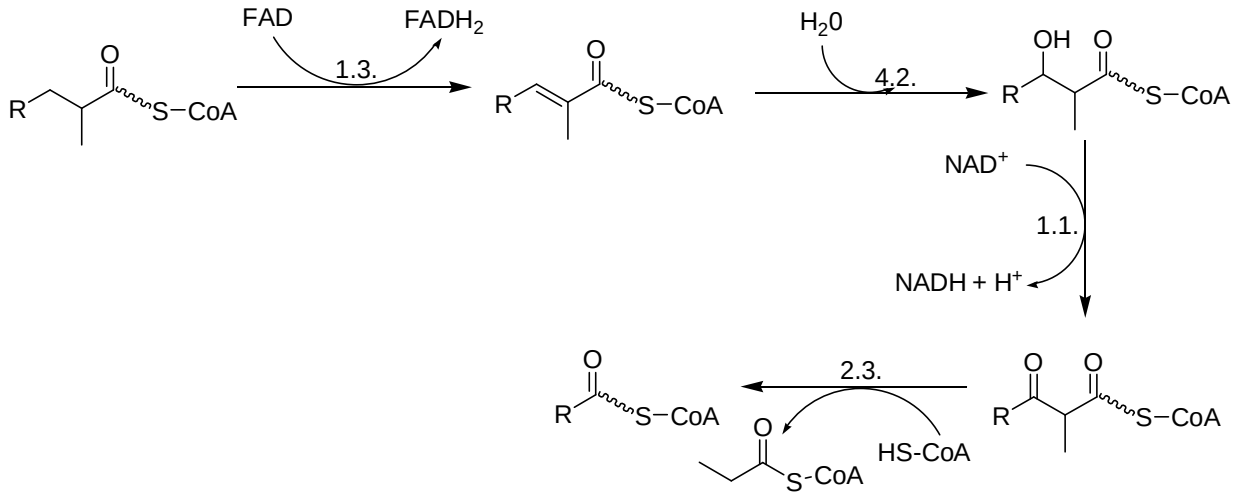
According to α-cycle reactions, **E3** catalyzed stage results in splitting off a monocarbon fragment attached to CoA. At the other stages including that catalyzed by **E2** no changes in the number of carbon atoms in phytanic acid metabolites is observed (note that reaction <u>equations</u> are given). Thus, **A** contains 19+1=20 carbon atoms.

For determination of the molecular formula of saturated phytanic acid: hydrogen – 20·2, oxygen – 2 (both in one carboxylic group). Finally, $C_{20}H_{40}O_2$. Note that it is given that phytanic acid can be represented as R–COOH, where R is hydrocarbon residue. Thus, R does not contain functional groups (including hydroxyl or carboxylic). Empirical formula: $C_{10}H_{20}O$.

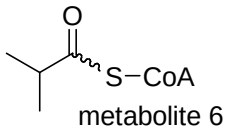
5. In the scheme of β–oxidation discussed in question 1, acetyl CoA is the product which is finally split off from a fatty acid:



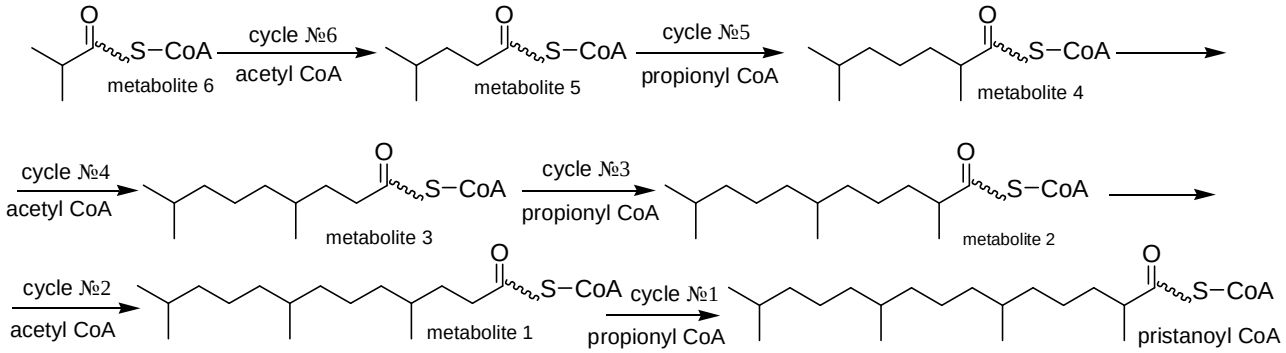
Another metabolite, propionyl CoA, is elaborated as a result of every second cycle when prystanic acid is degraded. Propionyl CoA would be formed if a methyl group is linked with α-carbon atom. In this case α-carbon atom must also be linked with hydrogen atom which is removed at the first stage of the cycle. Thus, presence of the methyl group in this position does not prevent the fatty acid from being involved into β-oxidation, which is illustrated at the scheme below:



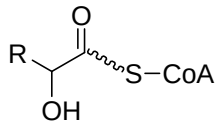
It is seen from the scheme that the final products of prystanic acid metabolism can be achieved if only R is substituted by H for the 7th β-oxidation cycle. Then, the product resulting from the 6th cycle would be:



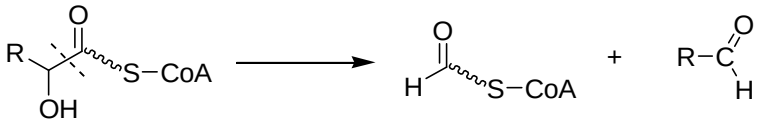
Similarly, moving in the direction opposite to oxidative degradation of prystanic acid we have:



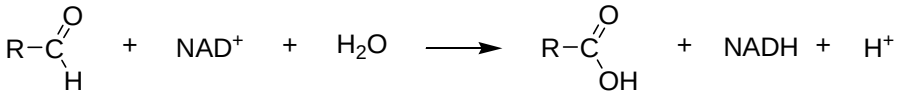
Once the structure of **B** is established, it is possible to clarify the scheme of α-oxidation and determine the structure of **A**. Transition from **A** to $\mathbf{A_1}$ corresponds to formation of phytanoyl CoA. According to the matter balance for the second reaction, only one oxygen atom is incorporated into $\mathbf{A_1}$ to form $\mathbf{A_2}$. It is obvious that this oxygen atom is linked with α-carbon atom. This is supported by the name of oxidation pathway, as well as by the fact that formyl CoA (and not acetyl CoA) is produced at the next stage. Thus, the general formula of $\mathbf{A_2}$ is:



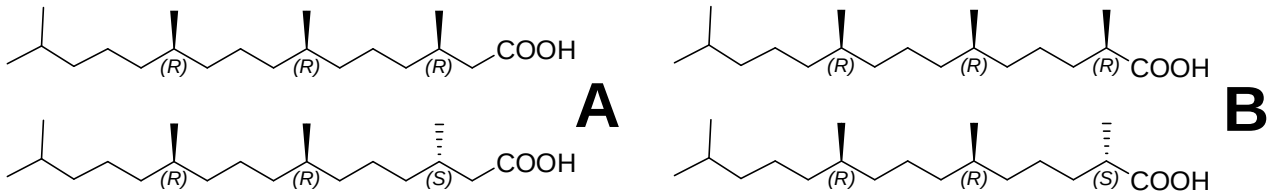
At the next step carbon-carbon bond is cleaved, which leads to formyl CoA and corresponding aldehyde $\mathbf{A_3}$:



Carbonyl group is further oxidized to carboxyl allowing formation of **B** from $\mathbf{A_3}$.

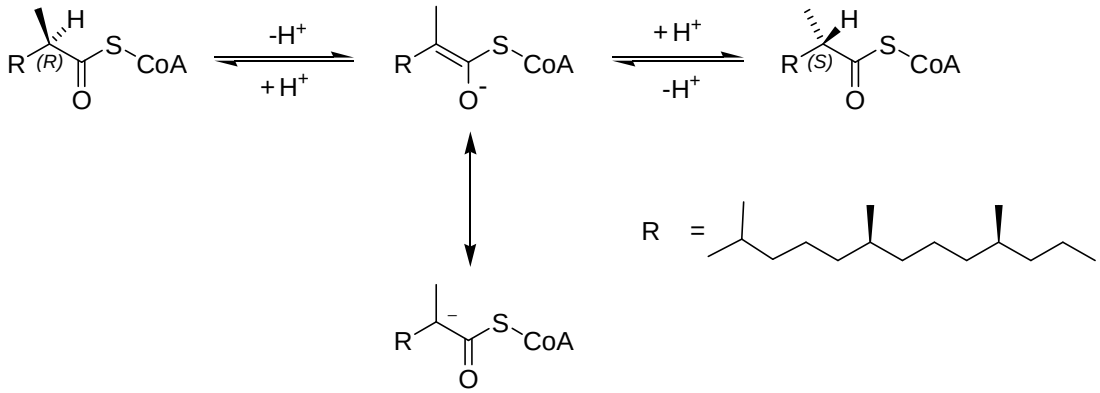


Taking into account configuration of chiral atoms in phytanic acid~~s~~, existence of two natural diastereomers of phytanic acid and retention of configuration of chiral atoms during α–oxidation, one can finally deduce structures of **A** and **B**:



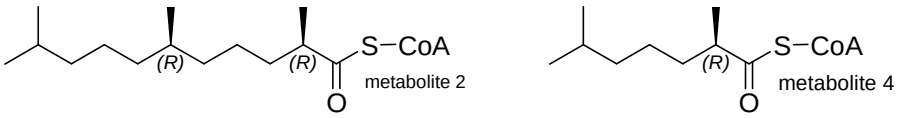
6. Phytanic acid is not oxidized according to β-scheme because of the methyl group in β–position, which makes impossible formation of keto-acyl derivative in the 3rd reaction of the cycle.

7.



Thioesterification of pristanic acid increases the acidity of the C-2 hydrogen, which is sufficient to allow deprotonation and reprotonation.

8. It is seen that racemization affects substituents at α-position. Thus, two intermediates of pristanic acid degradation (metabolites 2 and 4, see the scheme above) can be AMCAR (α-methylacyl-CoA racemase) substrates.



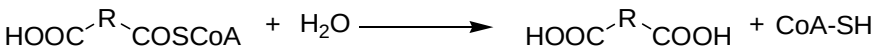
9. Since only two stereoisomers of four possible are formed, hydroxylation of C-2 is stereospecific. It occurs from the side opposite to the methyl group, because the carbon atom is characterized by higher sterical availability from this side.

Configurations of chiral centers in diastereomers: 11R,7R,3R,2S and 11R,7R,3S, 2R.

Problem 22. UNUSUAL PATHWAYS OF FATTY ACID OXIDATION: OMEGA- AND (OMEGA-1)-OXIDATION

1. Consideration of mechanisms of ω- and β-oxidation suggests that **F1** is an acyl CoA of a dicarbonic acid. Actually, the first carboxyl group was initially present in **D**, whereas the second one is formed as a result of the final β-oxidation cycle.

Taking into account the hydrolysis reaction:

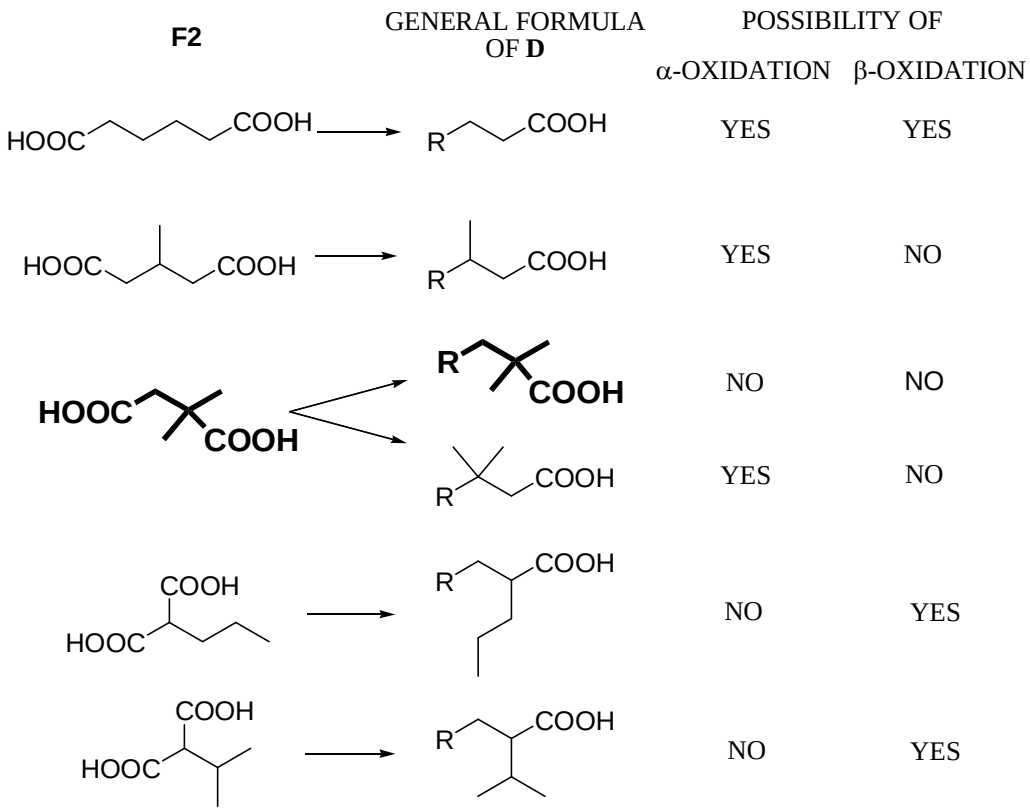


one can determine the formula of **F2** from the following calculations:

Formula of **F2** = Formula of anion **F1** + H_5 – Formula of non-ionized form of coenzyme A + H_2O = $C_{27}H_{39}N_7P_3SO_{19}$ + H_5 – $C_{21}H_{36}N_7P_3SO_{16}$ + H_2O = $C_6H_{10}O_4$.

Note that the second product of hydrolysis, coenzyme A, cannot be **F2** because it contains chiral carbon atoms.

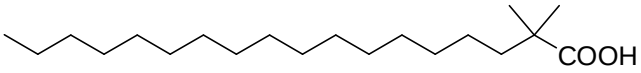
All possible structures of dicarbonic acids free of chiral carbon atoms and described by the formula $C_6H_{10}O_4$ are presented below, as well as fatty acids **D** corresponding to each variant of **F2**. Having in mind that **D** cannot be involved in either α- or β-oxidation, one can conclude that there is only one choice (highlighted in bold) meeting all above requirements.



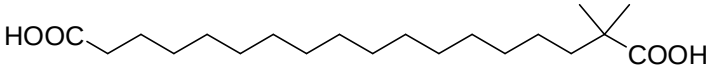
R - non-identical residues

Formulae of **D** and **E** are generated by addition of 14 carbon atoms (7 β-cycles) to the forth carbon atom in **F2**. There is no branching in the molecules except one at the α-carbon atom, since only acetyl CoA (and not propionyl CoA, *etc.*) molecules are released after every β-oxidation cycle.

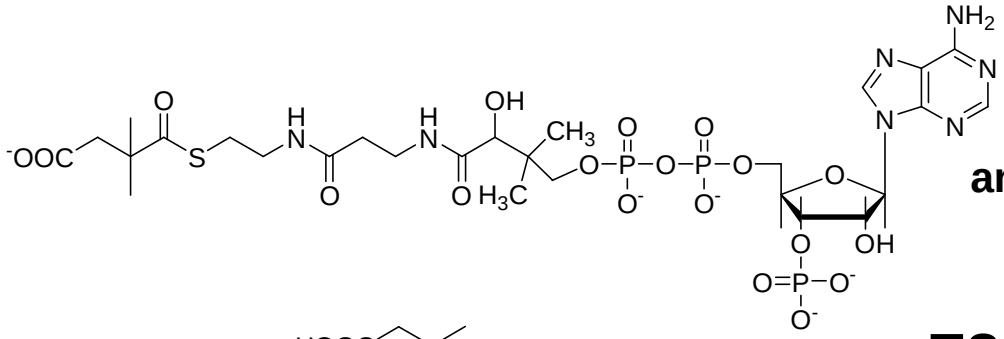
Thus,



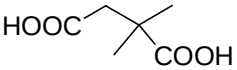
D



E



anion F1

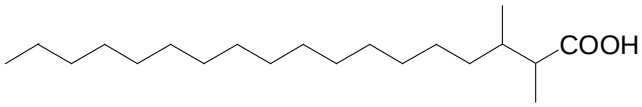


F2

2. **D** cannot be involved in α- or β-oxidation because it does not contain hydrogen atoms bound to α-carbon atom. This makes impossible formation of hydroxyl group and double bond, which are necessary for α- and β-pathways, respectively.

3. Fatty acid **D** and its isomer **G** contain 18 carbon atoms in their main chains. Thus, for **G** only two variants of branching are possible: either two methyl groups or one ethyl group. Possible structures of **G** with the ethyl group are equivalent with respect to oxidation pathways to phytanic and pristanic acids containing methyl substituents (see problem 22). We have found in question 1 of this problem that α- and β-oxidation pathways are restricted for fatty acids containing two substituents at the α-carbon atom. At the same time, α-pathway is possible if two substituents are bound to β-carbon atom (see solution of question 1). Thus, only a fatty acid containing methyl groups at both α- and β-carbon atoms is left in consideration. In this case β-oxidation is not possible for the same reason as for phytanic acid, whereas α-oxidation is restricted due to formation of ketone instead of aldehyde as an intermediate (a ketone group can not be oxidized to a carboxyl one *in vivo*).

Thus, the structure of **G** is:



G

4. Calculations to determine empirical formulae of compounds **H** and **I**:

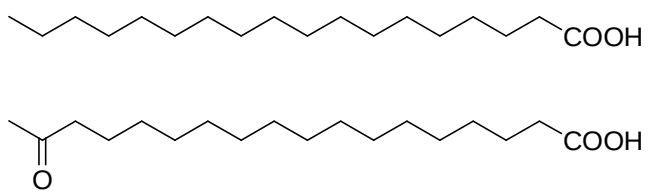
H: n(C): n(H) : n(O) = 75.97/12.01 : 12.78/1.01 : 11.25/16.00 = 9 : 18 : 1;

I: n(C) : n(H) : n(O) = 72.42/12.01 : 11.50/1.01 : 16.08/16.00 = 6: 11.33 : 1.

Empirical formula of **I** is $C_{18}H_{34}O_3$. Fatty acid **H** cannot contain less carbon atoms than its metabolite. It should also contain two oxygen atoms (monocarbonic acid). Thus, the molecular formula of **H** is $C_{18}H_{36}O_2$.

H is a saturated fatty acid. Formally, one oxygen atom substitutes two hydrogen atoms in **H** to give **I**. There are several options for such substitution, namely formation of: 1) carbonyl group; 2) epoxide; 3) unsaturated double bond and hydroxyl group at another carbon atom; 4) oxygen containing heterocycle. One of singlets corresponds to hydrogen atom of a carboxyl group (integral intensity is minimal). Thus, **I** is free of hydrogen atoms with the same intensity, and hydroxyl group, –CH–CH– fragment in epoxide cycle, and –CH– fragment in heterocycle are impossible. Carbonyl group is the only variant left, aldehyde group being impossible, since it produces a singlet with the same integral intensity as carboxyl group. Keto group is the final choice. This group should be located at [(ω)-1] carbon atom, because only in this case the methyl group would give a singlet with integral intensity three times higher than that of the carboxyl group. All multiplets give signals with integral intensity of 2 (higher than 1 and lower than 3). Thus, **H** is a linear fatty acid without branching (only nonequivalent CH_2 groups are present between terminal carbon atoms).

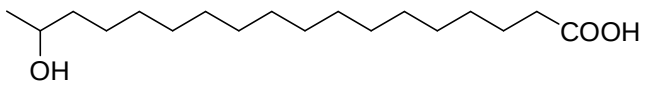
Finally,



H

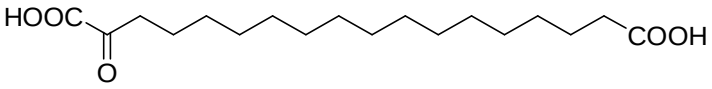
I

5. All reactions of (ω-1)-pathway are two-electron oxidations of a fatty acid. Reverse analysis shows that **I** is formed from the corresponding secondary alcohol.



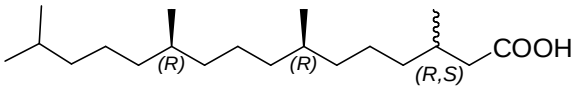
This alcohol is formed (do not forget two electrons) directly from stearic acid. (**H**) by oxygenase reaction Thus, **H** is converted into **I** in two steps.

6. Three steps are needed to metabolize **I** to the final product **J**, since (ω-1)-oxidation includes five consecutive steps. It is further needed to count the number of steps of ω-pathway, which allows formation of carboxyl group from the terminal methyl group. All steps of ω-pathway are also two-electron oxidations as it is a part of (ω-1)-pathway. At the first stage the fatty acid is transformed into primary alcohol by oxygenase reaction. The alcohol is then oxidized to aldehyde, and finally to carbonic acid (similar to (ω-1)-oxidation described above). Thus, ω-oxidation starts from **I** and includes the final product **J**. Finally,

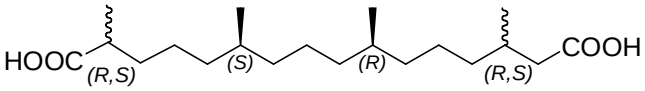


J

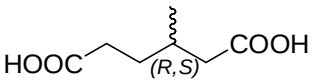
7. Structure of phytanic acid **A** (determined in problem 22):



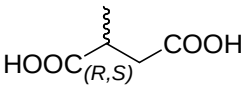
In organisms of patients with ARD, oxidation of this fatty acid from carboxyl terminus is impossible by any of known pathways. Therefore, degradation should start from ω-terminus. Presence of the methyl group at (ω-1) carbon atom does not allow (ω-1)-oxidation. So, the first step is ω-oxidation, which leads to the following intermediate:



Repetitive ω-oxidation of the intermediate would lead to tricarbonic acid. Subsequent β-oxidation of this acid would give malonyl CoA, which is in contradiction with the task conditions. Thus, β-oxidation is the only possible pathway of further metabolism of the above dicarbonic acid. The number of β-cycles can be found by analyzing data on compounds **A** and **C**. Being a mixture of two enantiomers, **C** contains one chiral carbon atom. Only two metabolites of β-oxidation pathway are in agreement with this condition:

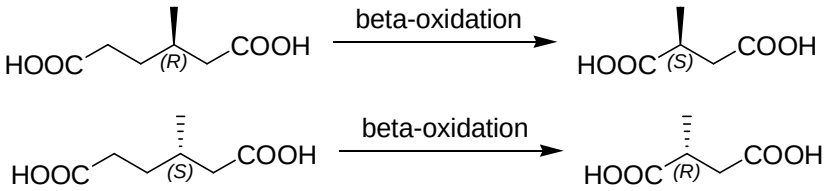


(1)



(2)

β-Oxidation of metabolite (1) leads to metabolite (2). This transformation is accompanied by inversion of the stereochemical configuration due to changes of the substituents priority.

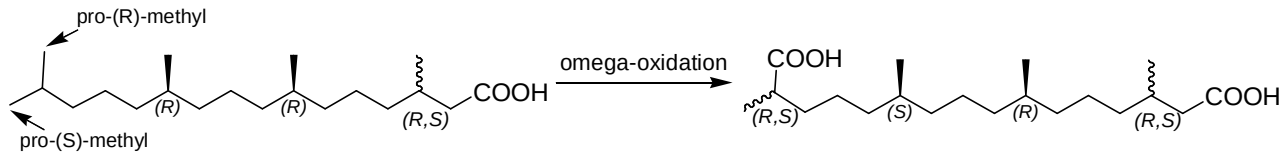


At the same time, five β-oxidation cycles of the dicarbonic acid (giving intermediate (1)) do not lead to inversion of the stereochemical configuration of the chiral carbon atom nearest to the initial carboxyl group. Since the R>S ratio is retained as a result of **A** metabolism to **C**, metabolite (1) is the final choice. Even an assumption that metabolite (2) is an AMCAR substrate will not allow treating this substance as appropriate (AMCAR will not alter the S>R ratio).

Thus, the number of steps needed on the way from **A** to **C**:

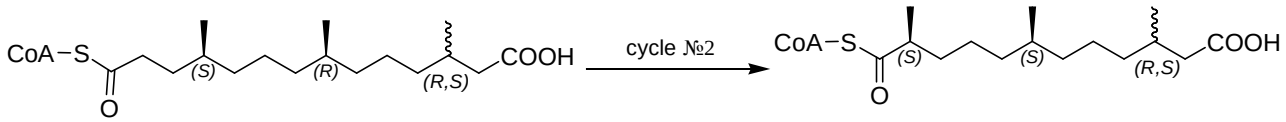
β-oxidation	five steps
ω-oxidation	one step
(ω-1)-oxidation	zero (the pathway impossible)

8. The enzyme catalyzing the first step of ω-oxidation is not stereospecific, thus a mixture of diastereomers will be obtained in the case of phytanic acid:

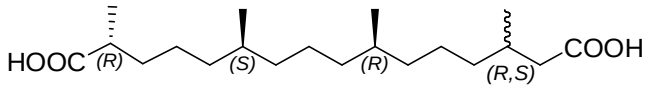


Therefore, acyl CoA formed by the product of ω-oxidation (15R-epimer) will be transformed by AMCAR into corresponding S-epimer.

As can be seen from the above scheme, ω-oxidation alters the absolute configuration of C-11 due to the changes in substituents priority, which makes AMCAR catalyzed reaction prior to the third β-oxidation cycle unnecessary. Similar considerations are true for C-7, the absolute configuration of which is changed after second β-oxidation cycle:

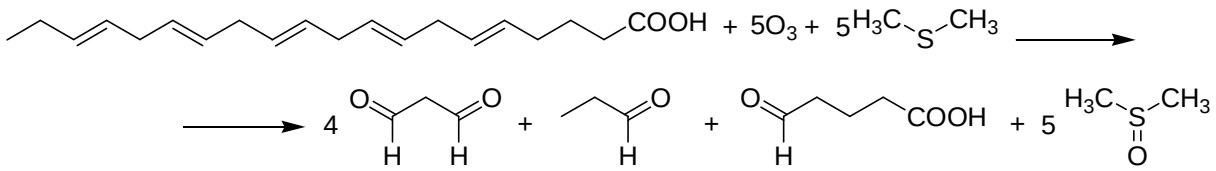


Thus, the only AMCAR substrate is:



Problem 23. UNUSUAL PATHWAYS OF FATTY ACID OXIDATION: PEROXIDATION

1.



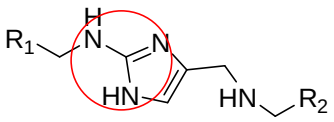
2. Since **X** is formed as a result of reductive ozonolysis of PUFA, it contains atoms of only three elements: carbon, hydrogen and oxygen. Hence, all four nitrogen atoms found in the linker originate from side groups of two amino acids (note that there is no way to insert peptide bond –NH–CO– into the linker).

There exist six canonical amino acids containing nitrogen in the side group: asparagine, glutamine, lysine, histidine, arginine and tryptophan.

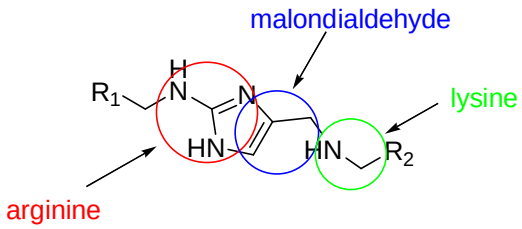
Tryptophan can not be inserted into the linker. Glutamine and asparagine should be rejected for the same reason as peptide bonds: the linker does not contain CO-groups connected with nitrogen atoms and R_1 and R_2 residues (amide reduction to amine as a result of non-enzymatic reaction with aldehyde is impossible).

There are two reasons allowing discrimination of histidine, though imidazole fragment can be easily seen in the linker. First, there is no space left for substance **X** which contains three or five carbon atoms. And second, origin of the rest two nitrogen atoms separated by imidazole group is absolutely unclear.

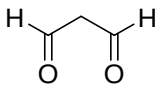
Lysine and arginine are only amino acids left for consideration. These amino acids provide for two combinations: Arg-Arg and Arg-Lys (Lys-Lys can be omitted since it would grant only two nitrogen atoms to the linker). Thus, arginine is definitely one of canonical amino acids. Guanidine group of arginine is found in the linker according to the following picture:



The remaining nitrogen atom can originate from lysine only, since it is connected with two CH_2-groups (if it were the second arginine, another guanidine group should at least be partially found in the linker). Finally:

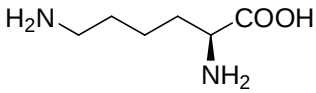


X unambiguously corresponds to malonic dialdehyde (see the above picture). The other product of timnodonic acid ozonolysis, propanal, also contains three carbon atoms. Still, it can not be **X**, since sole carbonyl group is insufficient for cross-linking. Also, propanal is not formed by peroxidation of most PUFA.

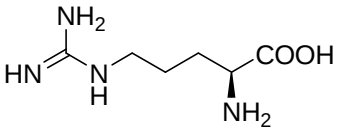


X

Structures of L-lysise and L-arginine (L isomers since amino acids found in proteins):

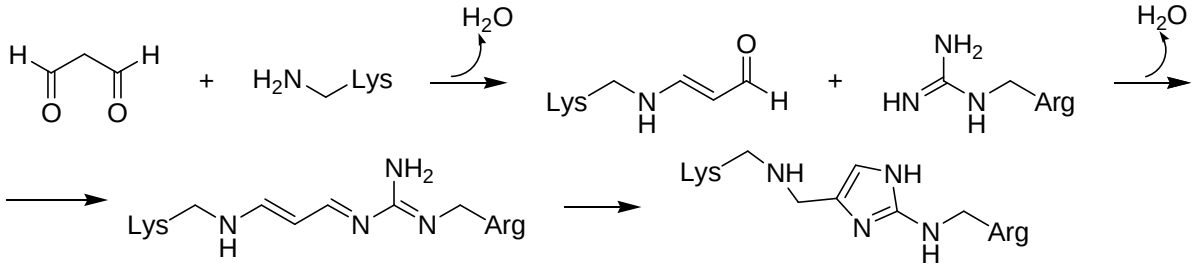


L-lysine



L-arginine

3. Mechanism of the linker formation (for easier representation R_1 is substituted by Arg, and R_2 by Lys):

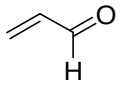


4. It is seen that the adduct of lysine with **Y** contains six extra carbon atoms as compared to the starting amino acid. **Y** contains three carbon atoms (as **X** does). Thus, attachment of two **Y** molecules to lysine is needed to form FDP-lysine.

Since equimolar amount of water is being released, the brutto-formula of **Y** is:

Y = (FDP-lysine – lysine + H_2O)/2 = ($C_{12}H_{20}O_3N_2$ – $C_6H_{14}O_2N_2$ + H_2O)/2 = C_3H_4O.

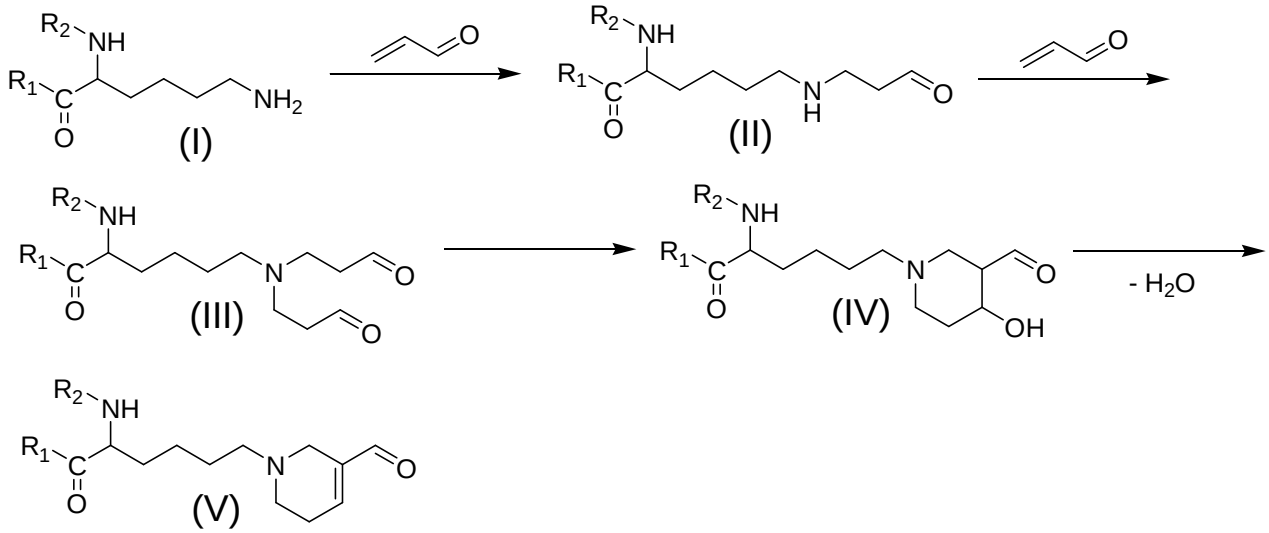
FDP-lysine contains carbonyl group, which strongly suggests that **Y** is an aldehyde (it was shown in question 1 that aldehydes are common products of peroxidation of lipids). Then **Y** is acrolein (only vinyl group can be the substituent C_2H_3 attached to carbonyl group).



Y

Methyl ketene CH_3–CH=C=O also meets the formula C_3H_4O. Still, this variant is hardly possible because of chemical properties of the substance. For instance, there are no methyl groups in the adduct, which would have inevitably been found in the case of methyl ketene.

5.



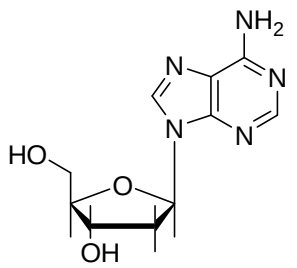
At the first stage, nucleophilic addition of free ε-amino group of lysine to the double bond (C-3) of acrolein leads to a derivative of secondary amine (**II**) with retention of carbonyl group. **II** interacts with the second acrolein molecule according to Michael reaction to give **III**, which transforms into **IV** as a result of aldol condensation. Subsequent dehydration (croton condensation) finally gives FDP-lysine residue (**V)**.

6. Both peaks in the mass spectrum of **Z1** correspond to monoprotonated fragments of it. Let us determine which fragment is missing in the species corresponding to the peak with lower *m/z* value. Difference in *m/z* values is: 307 – 191 = 116. Analysis of this data along with nucleoside structure strongly suggests deoxyribose residue, indicating that the most vulnerable N-glycoside bond is subjected to fragmentation (ribose residue as well as other conventional bases have different molecular masses). Thus, **Z** is a deoxyribonucleoside found in DNA.

Molecular mass of the other component of **Z1** is equal to 191. Since deoxyribose residue is intact (according to FAB-MS data), it is a conventional base modified by **Y**. The following table is of use for determination of the base (note that the reaction of **Z** with **Y** gives solely product **Z1**).

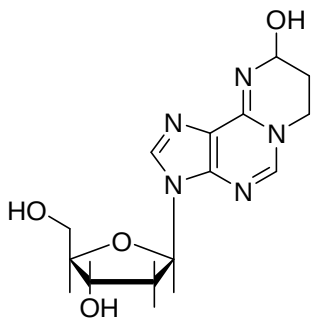
The number (*N*) of acrolein residues (molecular mass of 56) in the adduct	1	2	3
Molecular mass of the base in **Z** (191 – *N*·56)	135	79	23

Only adenine (*M* = 135, *N* = 1) is in agreement with the data in the table. Finally, **Z** is deoxyadenine:



Z

7. The fragment given in the task can be inserted into deoxyadenine molecule only as shown below:

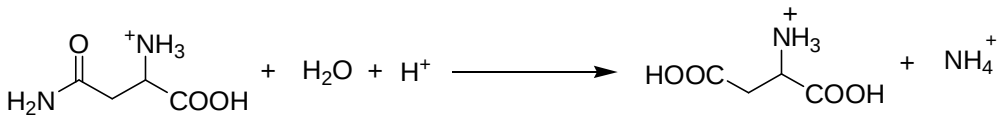


Z1

Since the substances react in equimolar quantities, there are no other modifications of the base but that given in the task.

Problem 24. BIOLOGICALLY ACTIVE PEPTIDES AND THEIR METABOLIC PATHWAYS

1.



2. **X** and **Z** are nonapeptides. To pass from Ang I to these substances one terminal amino acid should be cut off in each case. Ang I is an acyclic peptide having two ends, thus N- and C-terminal residues are affected in these reactions. Heptapeptide **Y** is formed from Ang II, which is definitely not a nonapeptide (only two nonapeptides are possible, and these are **X** and **Z**). Thus, Ang II is an octapeptide. Since ACE is a carboxypeptidase, **Y** can be either Ang (1-7) or Ang (2-8). The fact that **Y** is formed directly from Ang I through one step process allows attributing **Y** to Ang (1-7).

By the other reaction **Y** is formed directly from **X**. Thus, the latter comprises **Y** in its structure and has the same N-terminal amino acid as Ang I and **Y**. Then nonapeptide **X** is formed as a result of cleavage of C-terminal peptide bond in Ang I. The molecular mass of the leaving amino acid is: 1295 – 1182 + 18 = 131, which corresponds to either leucine or isoleucine.

Ang II is formed from Ang I as a result of cutting off two C-terminal amino acids. The molecular mass of 9th (from the N-terminus) amino acid in Ang I is: 1182 – 1045 + 18 = 155, which corresponds to histidine.

Finally, two dipeptides are possible as leaving fragments: His-Leu and His-Ile.

3. **X** – Ang (1-9)
   Y – Ang (1-7).

Z – Ang (2-10), since is being formed by cutting off N-terminal amino acid.

2 - Amino peptidase;

1 and 3 - Carboxypeptidase.

4. Gross amino acid content of Ang I can be determined from its molecular mass using the following calculations:

M(Ang I) – sum of molecular masses of amino acids formed as a result of hydrolysis + 9*M*(H_2O) = molecular mass of the repeating amino acid (this is correct only if Ang I does not contain Asn).

If Ang I contains Asn, the calculated above value of molecular mass will be different from the molecular mass of the repeating amino acid by 1 g/mol. This deviation is due to the difference of the molecular masses of Asn and Asp (132 and 133 g/mol, respectively).

Calculations:

M (repeating-amino acid) = 1295 – (155 + 2·131 + 133 + 174 + 117 + 181 + 115 + 165 – 18·9) = 155.

The value corresponds to histidine as the repeating amino acid and Asp. Thus, the gross amino acid content of Ang I is: 2His : 1Asp : 1Arg : 1Ile : 1Leu : 1Phe : 1Pro : 1Tyr.

5. **Z1** is formed in two ways: from Ang I in the trypsin catalyzed reaction and from nonapeptide Z (Ang (2-10)) in the AM-N (N-peptidase) catalyzed reaction. Thus, **Z1** is Ang (3-10), whereas Arg is the 2nd amino acid residue in Ang I.

Studying the transformation of Ang II to Ang IV, we come to the conclusion that Ang III is a heptapeptide (pay attention to the reactions catalyzed by enzymes 7, 8, 10). Since Ang IV is formed from heptapeptide Ang III and further hydrolyzed to pentapeptide Y3, it is a hexapeptide. Taking into account that Ang IV is formed from both Ang (3-10) and Ang (1-8), we finally attribute Ang IV to Ang (3-8). Thus, on the way from Ang II to Ang IV the 1st and 2nd amino acids residues are consecutively cut off. The 2nd residue was earlier found to be Arg. The first residue can be easily determined from the difference of molecular masses of Ang II and Ang IV: 1045 – 774 – 174 + 2·18 = 133, which corresponds to Asp.

6. PEP cuts off the 8th amino acid residue from Ang (3-8), revealing that proline is the 7th residue in Ang I. Molecular mass of the 8th eighth amino acid in Ang I is: 774 – 627 + 18 = 165, which corresponds to Phe.

Heptapeptide **Y** is Ang (1-7). ACE catalyzed hydrolysis can lead only to one pentapeptide, Ang (1-5). Molecular mass of the 6th amino acid, which is released from **Y** as a part of the dipeptide, is: 1045 – 664 – 165 – 115 + 3·18 = 155, which corresponds to His.

Thus, C-terminal amino acid of Ang II is Phe, and dipeptide released from **Y** is His-Pro.

7. Only two tetrapeptides are formed when octapeptide Ang II is treated with chymotrypsin. This means that one the following amino acids: Tyr, Phe or Leu is among the first 7 amino acids and occupies the 4th position. Phe was earlier established as the 8th amino acid, and can be thus omitted from subsequent considerations. If the 4th position is occupied by Leu, Tyr should be either the 3rd or 5th residue (the 10th position is already occupied by either Leu or Ile, see answer to question 2), which will result in a complicated mixture of products of chymotrypsin catalyzed hydrolysis. Thus, the 4th amino acid is Tyr. For similar reasons, Leu can be placed in the 3rd or 5th position. So, it is Leu that occupies the 10th position.

There are only two positions (the 3rd and 5th) and two amino acids (Val and Ile) left. Exact assignment can be done by calculating possible molecular masses of tetrapeptides formed as a result of Ang II treatment with NEP.

Variant 1. Val – 3, Ile – 5: M(angiotensin (1-4)) = 133 + 174 + 117 + 181 – 3·18 = 551;
M(angiotensin (5-8)) = 131 + 155 + 115 + 165 – 3·18 = 512;

Variant 2. Val – 5, Ile – 3: M(angiotensin (1-4)) = 133 + 174 + 131 + 181 – 3·18 = 565;
M(angiotensin (5-8)) = 117 + 155 + 115 + 165 – 3·18 = 498.

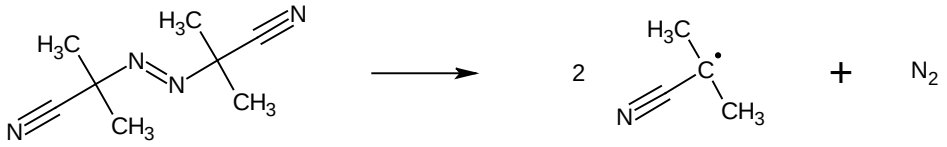
It is seen that Variant 1 is in agreement with the task conditions. Finally, Ang I structure:

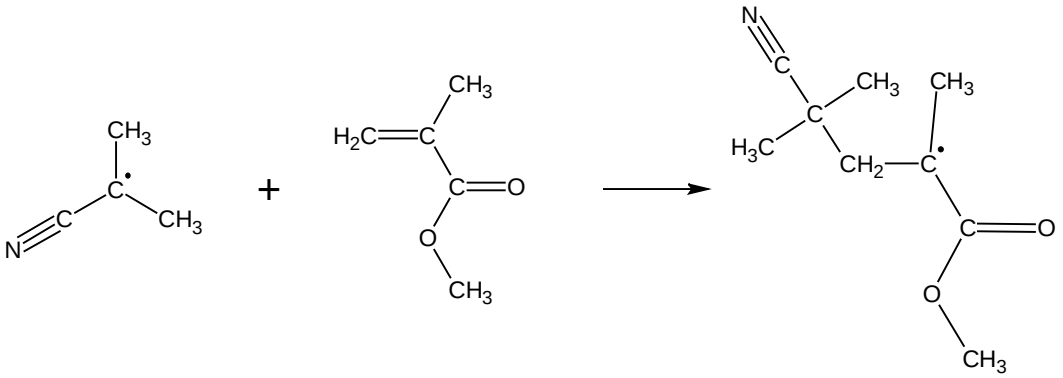
Asp-Arg-Val-Tyr-Ile-His-Pro-Phe-His-Leu

8. **X1** – Ang (5-8);
Y1 – Ang (2-7);
Z1 – Ang (3-10).

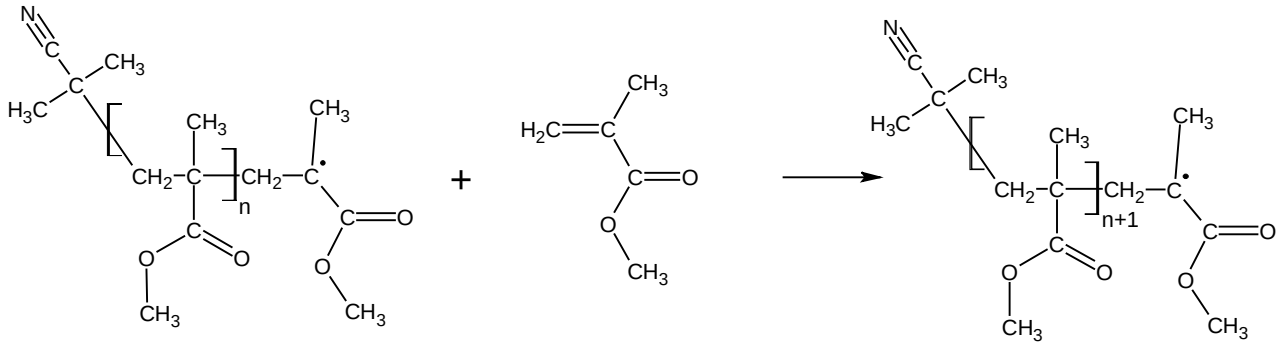
Problem 25. RADICAL POLYMERIZATION

1. Initiation:

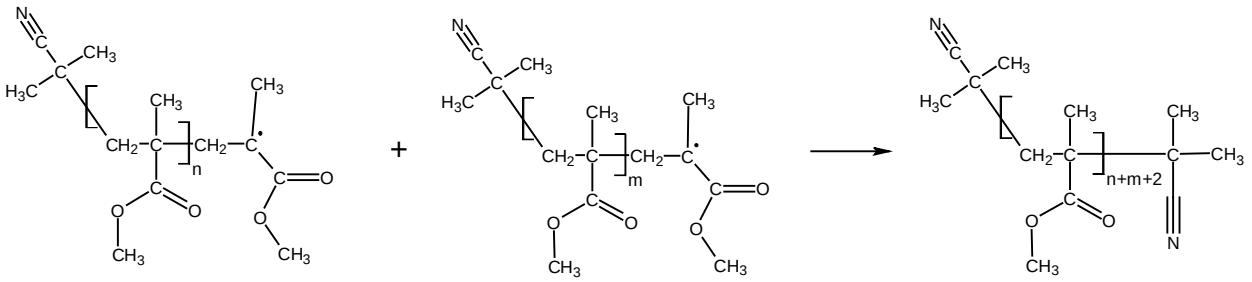




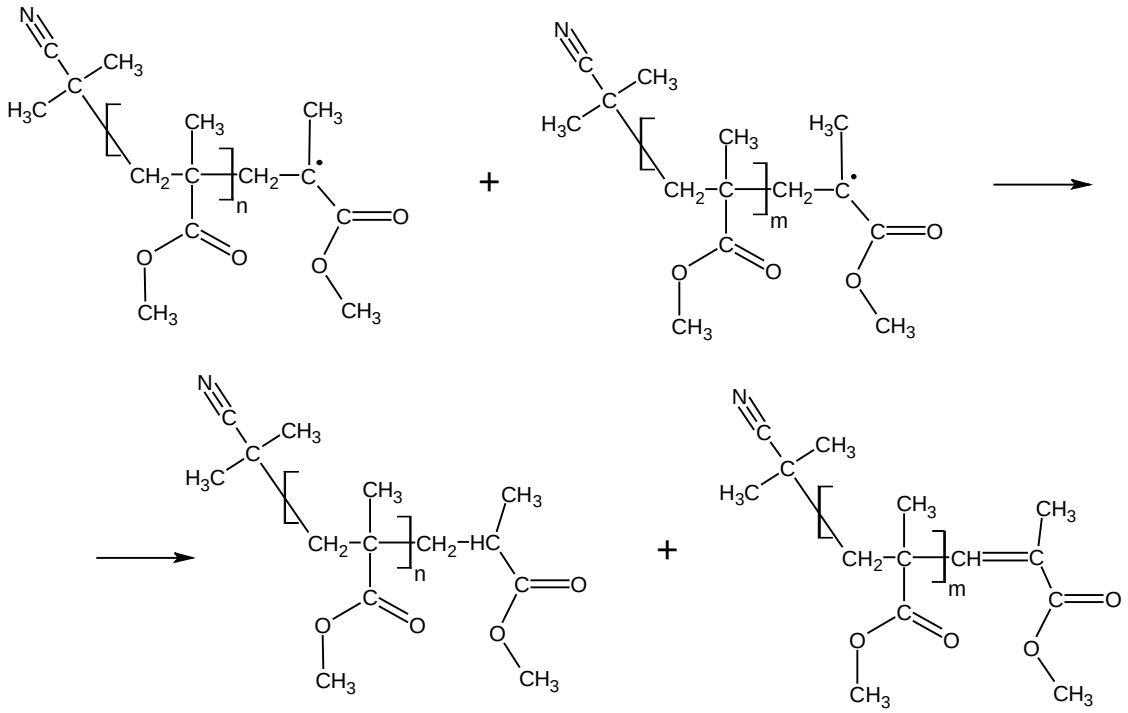
Chain propagation:



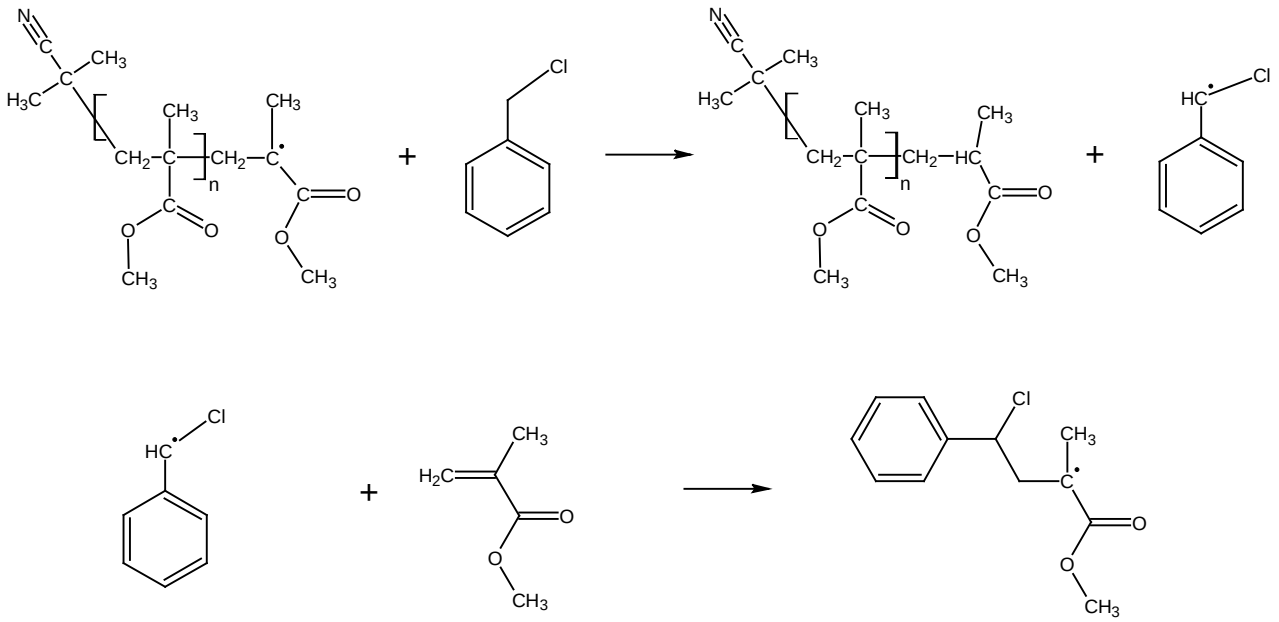
Chain termination via recombination:



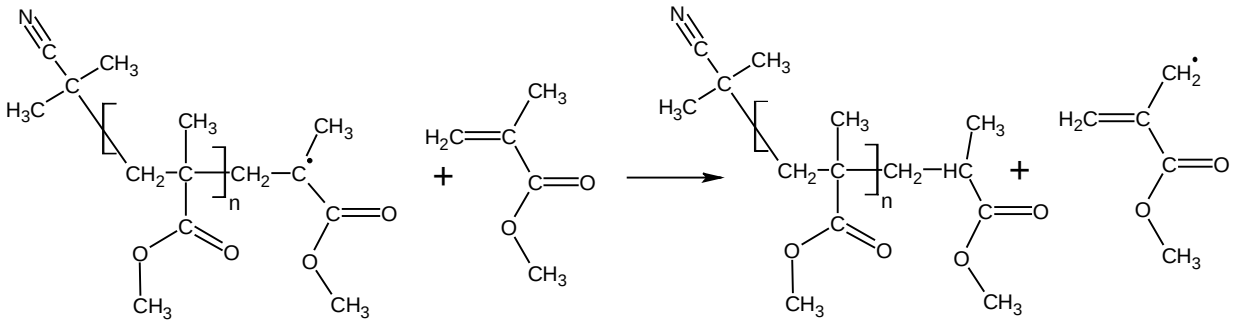
Chain termination via disproportionation:



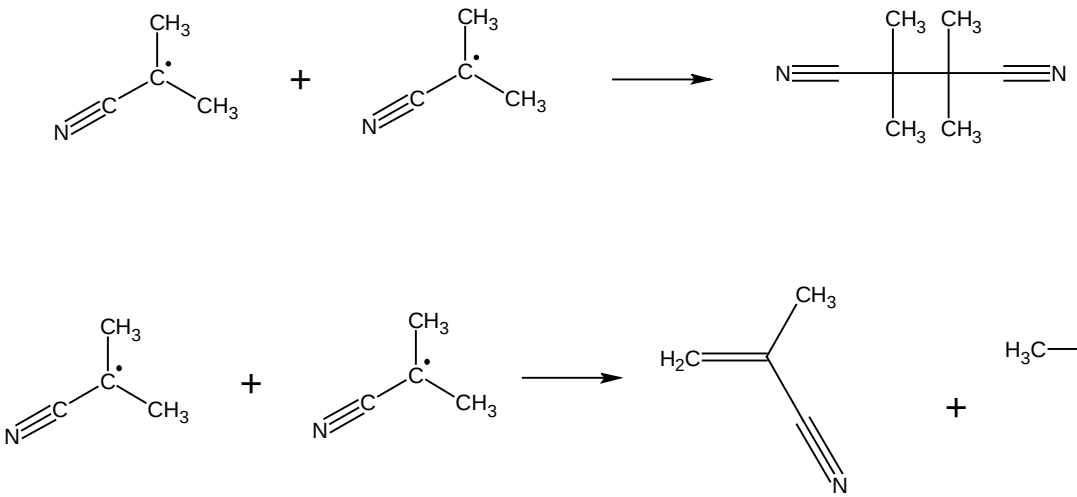
Chain transfer to α-chlorotoluene:



Chain transfer to the monomer:



2.



3. Generation of active radicals:

$$\frac{d[\mathrm{P}^{\cdot}]}{dt} = 2 \cdot k_{\mathrm{in}} \cdot f_{\mathrm{in}} \cdot [\mathrm{In}]$$

Monomer consumption:

$$\frac{d[\mathrm{M}]}{dt} = -k_{\mathrm{p}} \cdot [\mathrm{P}^{\cdot}] \cdot [\mathrm{M}] - k_{\mathrm{tr,M}} [\mathrm{P}^{\cdot}][\mathrm{M}]$$

Change of concentration of radicals:

$$\frac{d[\mathrm{P}^{\cdot}]}{dt} = 2 \cdot k_{\mathrm{in}} \cdot f_{\mathrm{in}} \cdot [\mathrm{In}] - 2k_{\mathrm{t}} \cdot [\mathrm{P}^{\cdot}]^2$$

4.

$$\frac{d[\mathrm{P}^{\cdot}]}{dt} = 2 \cdot k_{\mathrm{in}} \cdot f_{\mathrm{in}} \cdot [\mathrm{In}] - 2k_{\mathrm{t}} \cdot [\mathrm{P}^{\cdot}]^2 = 0$$

$$[\mathrm{P}^{\cdot}] = \left(\frac{k_{\mathrm{in}} \cdot f_{\mathrm{in}} \cdot [\mathrm{In}]}{k_{\mathrm{t}}} \right)^{1/2}$$

5. $$-\frac{d[\mathrm{M}]}{dt} = R_{\mathrm{p}} = k_{\mathrm{p}} \cdot [\mathrm{P}^{\cdot}] \cdot [\mathrm{M}] = k_{\mathrm{p}} \cdot \left(\frac{k_{\mathrm{in}} \cdot f_{\mathrm{in}} \cdot [\mathrm{In}]}{k_{\mathrm{t}}} \right)^{1/2} \cdot [\mathrm{M}]$$

Thus the order of the reaction is 1 on the monomer, ½ on the initiator.

6. Number-average degree of polymerization P_n can be expressed as a ratio of the number of polymerized monomer units to that of polymer chains appeared during the same time interval. The latter value is equal to ½ of the number of polymer end groups not involved in the polymerization process (inactive end groups of the polymer).

$$P_n = \frac{\Delta n(\mathrm{M})}{\frac{1}{2}\Delta n(\mathrm{tails})}$$

Different stages either increase or remain unchanged the number of end groups. Namely,

Initiation: + 1 end group per each radical formed,

Propagation: 0 end groups,

Chain transfer: + 2 end groups,

Disproportionation: + 1 end group,

Recombination: + 0 end groups.

So,

$$P_n = \frac{R_{\mathrm{p}} \cdot dt}{\frac{1}{2}\left(R_{\mathrm{i}} + R_{\mathrm{t,d}} + 2R_{\mathrm{tr}}\right) \cdot dt} = \frac{R_{\mathrm{p}}}{\frac{1}{2}\left(R_{\mathrm{i}} + R_{\mathrm{t,d}} + 2R_{\mathrm{tr}}\right)},$$

where R_{p}, R_{i}, $R_{\mathrm{t,d}}$, R_{tr} are rates of propagation, initiation, disproportionation and chain transfer, respectively.

$$R_{\mathrm{i}} = 2 f_{\mathrm{in}} \cdot k_{\mathrm{in}} \cdot [\mathrm{In}] = 2 \cdot \left(k_{\mathrm{t,d}} + k_{\mathrm{t,c}}\right) \cdot [\mathrm{P}^{\cdot}]^2$$

$$R_{\mathrm{t,d}} = 2k_{\mathrm{t,d}} \cdot [\mathrm{P}^{\cdot}]^2$$

$$R_{\mathrm{tr}} = k_{\mathrm{tr}}^{\mathrm{M}}[\mathrm{P}^{\cdot}][\mathrm{M}] + k_{\mathrm{tr}}^{\mathrm{A}}[\mathrm{P}^{\cdot}][\mathrm{A}] \ ,$$

where k_{tr}^{M} and k_{tr}^{A} are rate constants of chain transfer to monomer and compound A, respectively (in this task compound A is α-chlorotoluene). (According to transfer constant definition, $k_{tr}^{M} = C_M \cdot k_p$ and $k_{tr}^{A} = C_A \cdot k_p$.)

$$R_p = k_p \cdot [M][P^{\cdot}]$$

Using expressions for the corresponding rates in the equation for P_n and carrying out transformations, we come to:

$$\frac{1}{P_n} = \frac{\left(2k_{t,d} + k_{t,c}\right)}{k_p[M]}\left(\frac{k_{in} \cdot f_{in}[In]}{k_{t,d} + k_{t,c}}\right)^{1/2} + C_M + C_A \frac{[A]}{[M]}$$

with $k_{t,d}$ and $k_{t,c}$ denoting rate constants for termination via disproportionation and recombination, respectively.

Monomer concentration [M] = 9.4 g / (100.1 g/mol) / (10 g / 0.91 g/ml) = 8.5 mol/l.
Concentration of the initiator [In] = 0.1 g / (164.2 g/mol) / (10 g / 0.91 g/ml) = 0.055 mol/l.
Concentration of the chain transfer agent [A] = 0.5 g / (98.96 g/mol) / (10 g / 0.91 g/ml) = 0.46 mol/l.
Other values are given in task.

Substituting the 2nd and 3rd items with numerals, we get:

$$\frac{1}{P_n} = \frac{\left(2k_{t,d} + k_{t,c}\right)}{k_p[M]}\left(\frac{k_{in} \cdot f_{in}[In]}{k_{t,d} + k_{t,c}}\right)^{1/2} + 1.0 \cdot 10^{-5} + 2.26 \cdot 10^{-5}$$

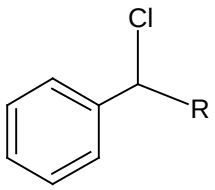
As disproportionation and recombination are described by similar kinetic equations (differing only in the values of rate constants), one can substitute the sum $k_{t,d} + k_{t,c}$ with the observed rate constant of chain termination k_t. Then,

$$\frac{1}{P_n} = \frac{\left(k_{t,d} + k_t\right)}{k_p[M]}\left(\frac{k_{in} \cdot f_{in}[In]}{k_{t,d} + k_{t,c}}\right)^{1/2} + 1.0 \cdot 10^{-5} + 2.26 \cdot 10^{-5} =$$
$$= \left(k_{t,d} + 2.6 \cdot 10^{7}\right) \cdot 1.8 \cdot 10^{-10} + 1.0 \cdot 10^{-5} + 2.26 \cdot 10^{-5}$$

Substituting P_n = 125, we get: $\boldsymbol{k_{t,d} = 1.8 \cdot 10^{7}\ l \cdot mol^{-1} \cdot s^{-1}}$**.**

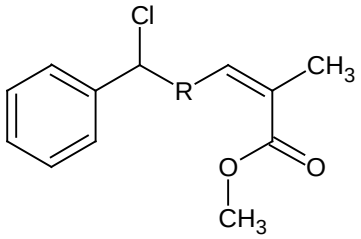
The first item makes the maximal contribution to the $1/P_n$ value, whereas those of the second and third items are comparable (the second item is slightly less than the third). So, contributions of the processes to the observed value of P_n decrease in the following order: **chain termination >> chain transfer to chlorotoluene> chain transfer to monomer.**

7. Signal ***a*** corresponds to protons of an aromatic ring. This suggests that benzene ring can be found at least at one end of the polymer, which is due to chain transfer to chlorotoluene. So, one or both ends have the following structure

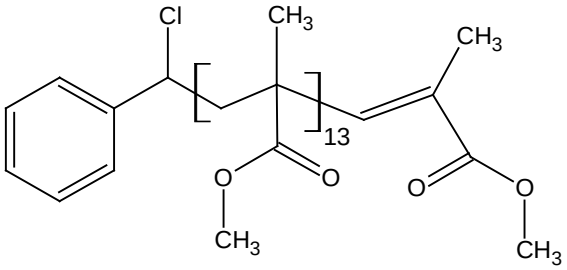


Then, either peak ***b*** or peak ***c*** should be assigned to the proton of the chloromethyl group (this is supported by the values of chemical shifts of ***b*** and ***c*** and by the ratios ***b/c*** and ***a/c*** both being equal to 1:5).

If chlorotoluene residues are found at both ends of the polymer, the molecular formula of the polymer may be written as follows: $(C_7H_6Cl)–(C_5H_8O_2)_n–(C_7H_6Cl)$. Ratio of the total integral intensities of peaks ***a*** and (***b*** or ***c***) to the total integral intensities of peaks (***c*** or ***b***) + ***d*** + ***e*** + ***f*** + ***g*** (peak of TMS ***h*** is omitted) is equal to 6:111. Thus, the total signal of $(C_5H_8O_2)_n$ corresponds to 111·12/6 = 222 protons. Dividing this value by the number of protons in one repeated unit (8), one obtains the polymerization degree of 27.75. Polymerization degree being an integer number, the deviation of 0.25 exceeds possible round-off error. So, the polymer has the chlorotoluene residue only at one of its ends. Moreover, there is only one proton in the weak field area (at 5 ppm), which is seen from the ratio of integral intensities ***a***:***b***:***c***. This chemical shift can hardly be ascribed to aromatic protons. It may rather correspond to the proton located near a double bond. Analysis of all possible variants of chain termination and transfer allows concluding that the structure fitting best of all to all ratios of peak intensities is formed as a result of disproportionation. Then, the polymer structure is:

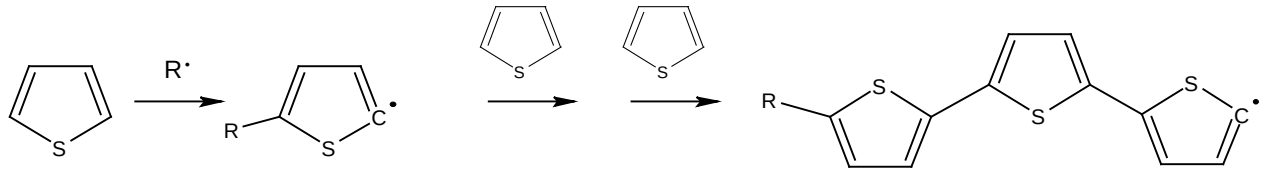


its brutto-formula being either $(C_7H_6Cl)–(C_5H_8O_2)_n–(C_5H_7O_2)$ or $(C_7H_6Cl)–(C_{5n+5}H_{8n+7}O_{2n+2})$. From the ratio of intensities of ***a*** + (***b*** or ***c***) to those of (***c*** or ***b***) + ***d*** + ***e*** + ***f*** + ***g*** = 6:111 one concludes that the peak of $(C_{5n+5}H_{8n+7}O_{2n+2})$ corresponds to 111·6/6 = 111 protons. So, 8*n* + 7 = 111, or *n* = 13. Finally, the polymer structure is:



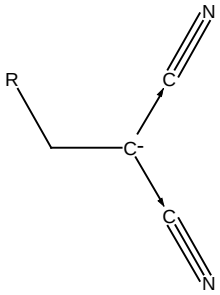
Problem 26. IONIC POLYMERIZATION

1. All compounds containing double bonds (including cyclic unsaturated compounds thiophene (***e***) and pyrrole (***l***)) can be polymerized according to radical mechanism. In case of aromatic heterocycles, the radical on a propagating chain is stabilized by interaction with the conjugated system of double bonds:

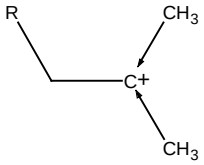


<u>Thus, radical polymerization is possible for compounds **a**-**f**, **h**, **j**-**l**</u>.

Electron acceptors, such as nitrile (***a***), carbonyl (***f***), or nitro (***k***) groups stabilize negatively charged macroions (see structure below). Compounds containing such groups can be polymerized according to anionic mechanism.



On the contrary, compounds containing electron donor substituents close to double bond (isobutylene (**j**)**)** form stable carbocations. Such compounds are polymerized according to cationic mechanism.

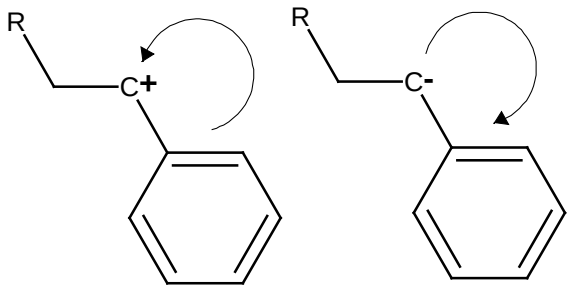


Vinyl ethers can also be involved in cationic polymerization. In this case alkoxyl group stabilizes the macrocation due to its positive mesomeric effect.

Highly strained epoxy cycle can be opened as a result of carbanion formation. Thus, (***g***) may be a monomer in anionic ring-opening polymerization. Interaction of epoxides with strong acids leads to ring-opening and carbocation formation, which allows polymerization of epoxides according to cationic mechanism.

Tetrahydrofuran (***i***) is not involved in anionic polymerization, since the cycle in its molecule is less strained and is not altered by bases. Still, strong acids can protonate ether oxygen in THF causing cleavage of C–O bond. As a result, carbocation is formed which initiates cationic ring-opening polymerization.

Mesomeric effect of phenyl substituent stabilizes both carbocation and carbanion, so styrene (***d***) can be polymerized according to both ionic mechanisms . The same is true for thiophene and furane (***e*** and ***l***).



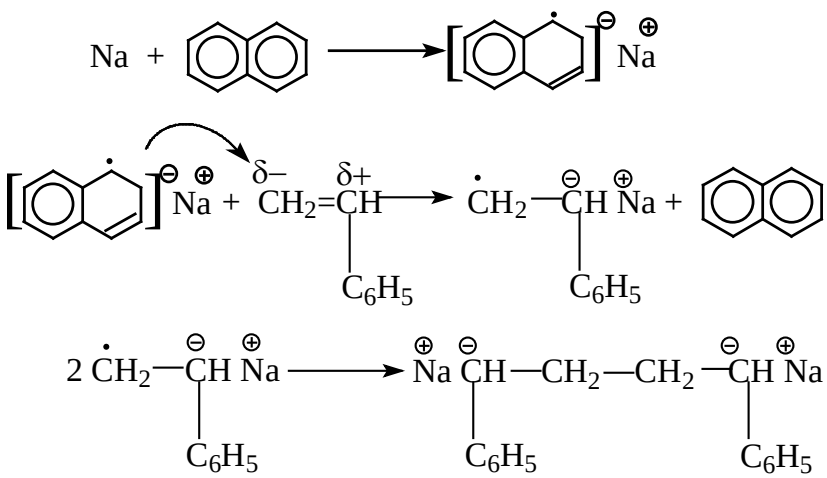
Thus, Anionic polymerization is possible for compounds **a**, **d**, **e**, **f**, **g**, **k**, **l**

Cationic polymerization is possible for compounds **d**, **e**, **h**, **j**, **l**.

2. a) $r_P = -\dfrac{d[\mathrm{M}]}{dt} = k_\mathrm{p} \cdot [\mathrm{M}^-] \cdot [\mathrm{M}]$

2. b) All chains of monodisperse polymer are of equal length, which is possible if all the chains are initiated at one and the same time and then propagate simultaneously. Thus, initiation must occur much faster than propagation, $k_{in} >> k_p$.

2. c) Interaction of naphthalene and sodium in dioxane gives rise to anion-radical of sodium naphthalenide, which further produces styrene anion-radical due to one-electron reduction of styrene:



The combination of two anion-radicals results in the formation of dianion, which is capable of propagating in two directions (sides). So, sodium in the presence of naphthalene initiates the anionic polymerization.

To find the relationship between the degree of polymerization (P_n) and the fraction of a monomer consumed (q), one needs to write the balance equation for the monomer (express the total monomer concentration via current concentrations of the monomer, macroanions and initiator):

$$[\mathrm{M}]_0 = [\mathrm{M}] + P_n([\mathrm{M}^-] + [\mathrm{In}])/2 = [\mathrm{M}] + P_n[\mathrm{In}]_0/2$$

$[\mathrm{In}]_0$ is the initial concentration of sodium naphthalenide.

Now one can express [M] as a function of q:

$$q = \frac{[\mathrm{M}]_0 - [\mathrm{M}]}{[\mathrm{M}]_0} = 1 - \frac{[\mathrm{M}]}{[\mathrm{M}]_0} \Rightarrow [\mathrm{M}] = [\mathrm{M}]_0(1-q) \Rightarrow [\mathrm{M}]_0 = [\mathrm{M}]_0(1-q) + P_n[\mathrm{In}]_0/2$$

And finally, $P_n = 2\frac{[\mathrm{M}]_0 q}{[\mathrm{In}]_0}$

Monomer concentration $[\mathrm{M}]_0 = \frac{100}{0.600 \cdot 104} = 1.60$ mol/l.

Initiator concentration $[\mathrm{In}]_0 = \frac{0.234}{0.600 \cdot 128} = \frac{0.042}{0.600 \cdot 22.99} = 3.04 \cdot 10^{-3}$ mol/l.

Substituting these values, one gets

$$P_n = 2\frac{q[M]_0}{[In]_0} = 2\frac{0.589 \cdot 1.60}{3.04 \cdot 10^{-3}} = 620,$$

Molecular mass of the synthesized polymer is $P_n \cdot 104$ = 64480 g/mol.

3. a)

Type of chain termination	Radical polymerization	Anionic polymerization
Disproportionation	+	Improbable for most monomers
Recombination	+	–
Chain transfer to solvent	+	Possible in some solvents, e.g. in liquid ammonia. Trace amounts of water and acids in the reaction mixture may also terminate chain propagation.
Chain transfer to monomer	+	–

3. b) In contrast to radical, anionic polymerization may proceed almost without chain termination. Thus, active centers at chain ends are retained until the process is completed. If initiation is faster that propagation, then all chains are of almost the same length, which stipulates the narrow molecular mass distribution.

3. c) Rate of anionic polymerization depends on the strength of interaction between propagating carbanion and counter ion. Lower ability of a solvent to interact with the counterion may result in diminished polymerization rate. Benzene is characterized by the lowest ability to solvate ions of alkaline metals. 1,4-Dioxane possesses a symmetrical structure and zero dipole moment. As a result it also solvates ions of alkaline metals marginally, its sol-

vating ability being slightly higher than that of benzene. Tetrahydrofuran having one oxygen atom is characterized by higher polarity, and thus solvates ions of alkaline metals with higher efficiency than dioxane. Dimethoxyethane molecule is flexible and possesses two ether functions, which allows formation of chelates with ions of alkaline metals.

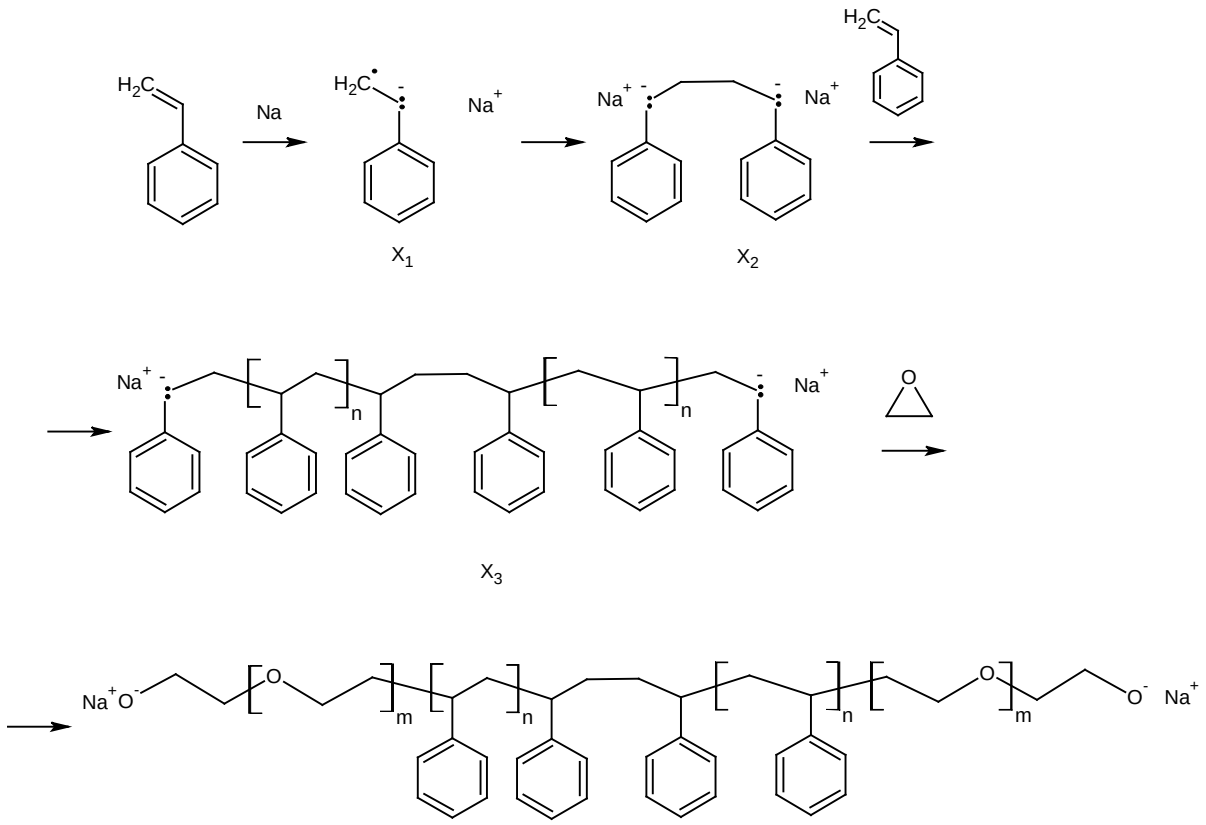
Thus, rate of anionic polymerization increases in the following order:

benzene < 1,4-dioxane < tetrahydrofuran < dimethoxyethane

3. d) Strong electrostatic interaction between cation of alkaline metal and macroanion diminishes propagation rate in the case of anionic polymerization. Value of the constant of this interaction depends on the size of a counter ion, cations with bigger radius being subjected to weaker interaction. Ionic radii increase in the order of $Na^+ < K^+ < Cs^+$. The rate of anionic polymerization changes in the same order.

Problem 27. CO-POLYMERIZATION

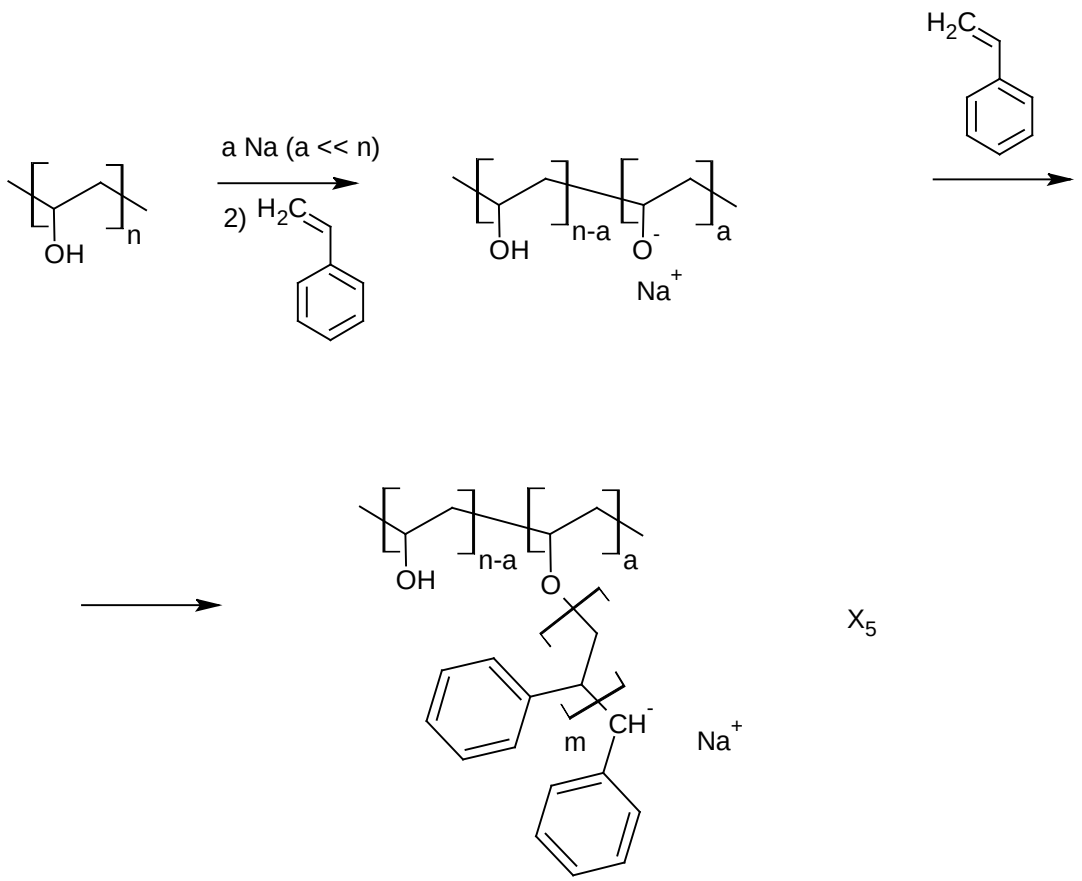
1. a)



X_4

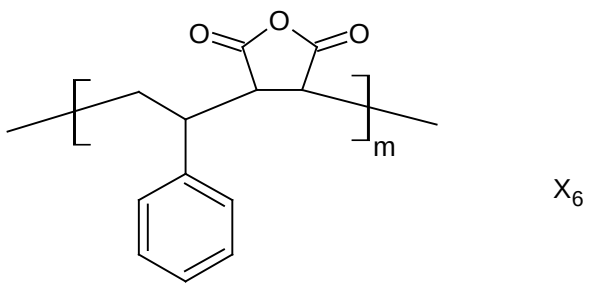
X_4 : poly(EO)-block-poly(St)-block-poly(EO)

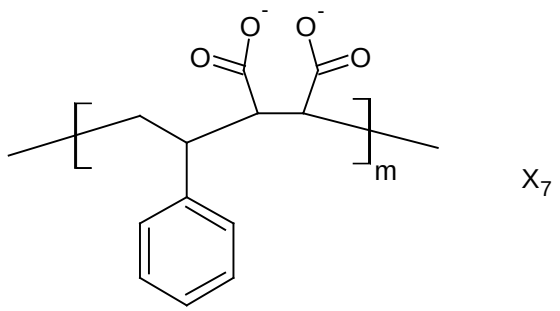
b)



X_5 : poly(VA)-graft-poly(St)

c)





X_6 : poly(St-alt-MA)

X_7 : poly(St-alt-Ma) (here Ma is used for maleate)

2. Monomers possess equal reactivity ($r_1 = r_2 = 1$). Thus, fraction of units A in the polymer is the same as that of monomers in the reaction mixture and is equal to ½. Besides, distribution of units along the chain is random. So we conclude that fractions of dyads AA, AB, BA and BB are equal (¼).

Solution 1.

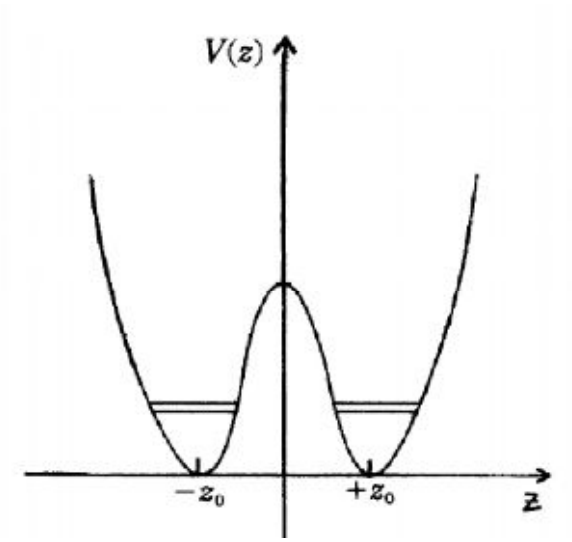
Let us consider a long polymeric chain of N units. It contains $N/2$ of units A (with accuracy to one unit). The total number of dyads AB and BA is $(N–1)/2$, as there are $N–1$ dyads in the whole chain. The number of blocks in the chain exceeds the total number of dyads AB and BA by 1, and is equal to $(N+1)/2$, half of the blocks being composed of A. Thus, there are $(N+1)/4$ blocks of A in the chain. Then the average number of A units per block is: $((N+1)/2) : ((N+1)/4) \approx (N/2) : (N/4) = 2$.

Solution 2.

Average lengths of blocks composed of A and B are equal due to symmetry of problem with respect to permutation (A, B). In the chain containing N units there are $(N+1)/2 \approx N/2$ blocks (see calculations in solution 1). Thus, the average length of block is $N:(N/2) = 2$.

Problem 28. TUNNELING IN CHEMISTRY

1. Energy profile is the symmetric double-well curve, where the minima correspond to stable pyramidal geometries of ammonia and the maximum – to the unstable planar geometry.



The reaction coordinate is the bond angle ∠HNH. In the planar geometry corresponding to the maximum of energy ∠HNH = 120°.

2. The wavelength for the tunneling transition is

$$\lambda = \frac{c}{\nu} = \frac{3.00 \cdot 10^{10}\ \text{cm/s}}{24 \cdot 10^{9}\ \text{s}^{-1}} = 1.25\ \text{cm}.$$

This wavelength corresponds to radiowaves.

3. The transition energy per 1 mol is:

$$E = h\nu N_{\text{A}} = 6.63 \cdot 10^{-34} \cdot 24 \cdot 10^{9} \cdot 6 \cdot 10^{23} = 10\ \text{J/mol},$$

which accounts for 10 / 25000 = 0.0004, or 0.040% of the energy barrier.

4. Tunneling of the heavier particles is less probable, hence the tunneling frequency for deuterated ammonia is smaller than that for NH_3.