

Problem 1 (author D.V. Kandaskalov)

1. Linear Y-X-Y bonds are located only in the middle layer (m) on the pentagon faces. Totally, there are 9 bonds. These bonds are horizontal respecting side view picture. Also there are 2 vertical linear Y-X-Y bonds formed by atoms in the center of pentagons of each layer. Thus we have 11 bonds (1 point).

2. Elementary cell must contain the integer number of structural X_{13}Y_4 units to respect the stoichiometry. This means that the number of atoms in a given unit cell is multiple of 17. The molecular formula of **A** cluster is $\text{X}_{31}\text{Y}_{12}$ (43 atoms). Thus, two clusters contain 86 atoms. The total number of atoms in the unit cell could be from 87 to 116 atoms taking into account the fact that unit cell could contain up to 30 “glue” atoms. Only one number from this range, multiple of 17, is 102. Thus, the number of atoms in one unit cell is 102 (2 points).

3. By this means unit cell is $(\text{X}_{13}\text{Y}_4)_6 = 2$ clusters $(\text{X}_{31}\text{Y}_{12})_2 + 16$ “glue” atoms **X**. We have all necessary data to calculate the molecular mass of the unit cell:

$$\left. \begin{aligned} \rho &= \frac{m}{V} = \frac{m}{abc} \\ n &= \frac{m}{M} = \frac{N}{N_A} \Rightarrow m = \frac{MN}{N_A} \end{aligned} \right\} \rho = \frac{MN}{N_A abc} \Rightarrow M = \frac{\rho N_A abc}{N}$$

$$M = \frac{\rho N_A abc}{N} = \frac{4018 \cdot 10^3 \cdot 6.02 \cdot 10^{23} \cdot (8.16 \cdot 12.34 \cdot 14.45) \cdot 10^{-30}}{1} = 3519.5 \text{ g/mol}$$

The elementary cell contains 78 **X** atoms and 24 **Y** atoms. Also, we know that the mass of “glue” atoms (16 **X** atoms) is 12.27% of the total mass. Let the atomic mass of metals be x and y for metals **X** and **Y**. We have:

$$\begin{cases} 78x + 24y = 3519.5 \\ 16x/3519.5 = 0.1227 \end{cases} \Rightarrow \begin{cases} x = 26.99 \\ y = 58.93 \end{cases}$$

So, **X** – Al, **Y** – Co and $\text{X}_{13}\text{Y}_4 - \text{Al}_{13}\text{Co}_4$ (1 point for the number of “glue” atoms, 1.5 points for molecular mass of elementary cell, 1 point for each **X** and **Y**, 3.5 points in total).

4.
$$\left. \begin{aligned} k_1 &= A \exp\left(-\frac{E_A(1)}{RT}\right) \\ k_2 &= A \exp\left(-\frac{E_A(2)}{RT}\right) \end{aligned} \right\} \Rightarrow \ln \frac{k_1}{k_2} = -\frac{E_1 - E_2}{RT} \Rightarrow E_1 - E_2 = -RT \ln \frac{k_1}{k_2}$$

The difference of activation energies is

$$E_1 - E_2 = -8.314 \cdot 300 \cdot \ln(5 \cdot 10^7) = -44216 \text{ J/mol}$$

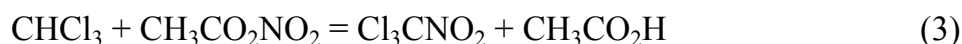
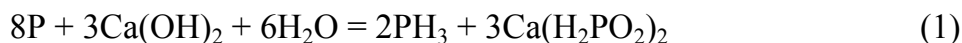
Also we know that $E_1 = 0.55E_2$, thus $E_2 = 98.257 \text{ kJ/mol}$, $E_1 = 54.041 \text{ kJ/mol}$ (1.5 points for ΔE , 0.75 points for each E_1 and E_2 , 3 points in total).

5. $k_1 = 10^5 \cdot \exp\left(-\frac{54041}{8.314 \cdot 350}\right) = 8.60 \cdot 10^{-4} \text{ mol/L}\cdot\text{s}$ (0.5 points).

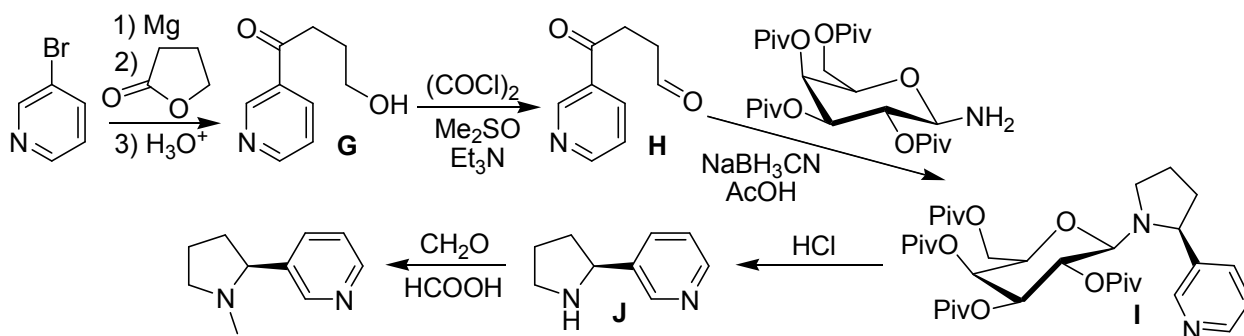
Problem 2 (author I.V. Trushkov)

1. Compound **B** is cyanide of some metal $M(CN)_x$. From the content of nitrogen we can calculate the atomic weight of metal as $20x$. This is calcium ($x = 2$), **B** is calcium cyanide, $Ca(CN)_2$. Therefore, **A** is HCN, **C** is calcium hydroxide, $Ca(OH)_2$ (1 point for **B**, 0.5 points for each **A** and **C**, 2 points in total).

2. Chloropicrin is synthesized by chlorination of the one widely used organic solvent and by nitration of another one. It is possible to suppose that molecular formula of this compound is $CCl_y(NO_2)_{4-y}$. Only trichloronitromethane, Cl_3CNO_2 has the chlorine content, which satisfies the condition of problem. This compound can be obtained by chlorination of nitromethane (**F**) or nitration of chloroform (**E**) (1 point for **D**, 0.5 points for each **E** and **F**, 4 equations 0.5 points for each, 4 points in total).



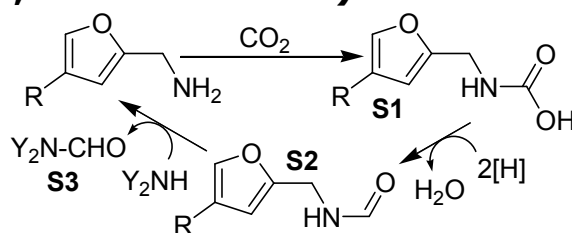
3. From molecular formula of **G**, we can deduce that this is the product of the attack of the Grignard reagent, obtained from 3-bromopyridine, onto the carbonyl group of lactone. One equiv of Grignard reagent participates in this reaction. Transformation of **G** into **H** proceeds with elimination of two hydrogen atoms. It is possible if this is oxidation of the alcohol function into aldehyde. Accounting for the structure of nicotine and molecular formulae of **I** and **J** it is possible to conclude that both aldehyde and ketone function of **H** participate in the reductive condensation with galactosamine producing *N*-substituted 2-(3-pyridyl)pyrrolidine **I**. Elimination of the galactose moiety leads to *NH*-2-(3-pyridyl)pyrrolidine **J**. The last step is the reductive methylation of NH-group (structural formulae of **G** – **J**, 1 point for each, 4 points in total).



Problem 3 (authors Yu.S. Golovko, B.N. Garifullin)

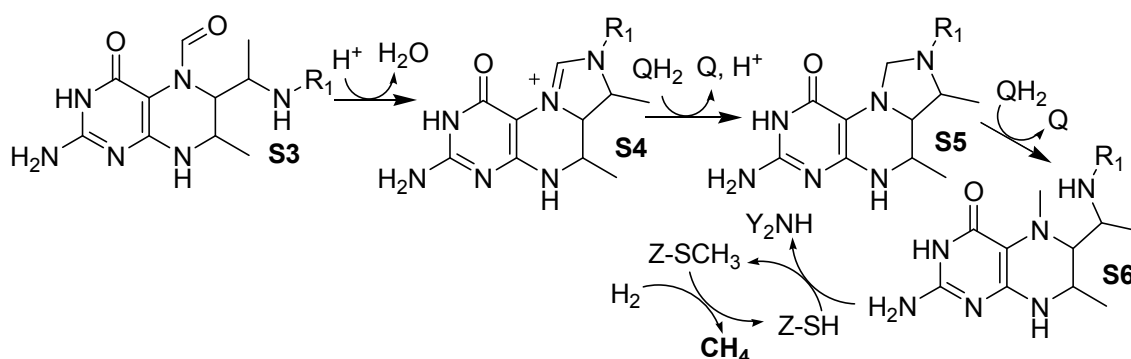
1. $\text{CO}_2 + 4\text{H}_2 = \text{CH}_4 + 2\text{H}_2\text{O}$ (1 point).

2. Analysis of the upper part of the cycle suggests that the carbamic acid derivative is formed at the first stage. It is further reduced to the



formamide derivative, which is followed by the transamination step. It is not necessary to disclose the structures of all intermediates to answer the next question. All of the stages $\text{S4} \rightarrow \text{S5}$, $\text{S5} \rightarrow \text{S6}$ and $\text{Z-SCH}_3 \rightarrow \text{Z-SH}$ are two-electron reductions. Thus, the oxidation states of the carbon atom originating from CO_2 are: +2 in S3 and S4 , 0 in S5 , and -2 in S6 (0.5 points for each structure, 0.5 points for each oxidation state, 3 points in total).

3. Release of a water molecule at the stage $\text{S3} \rightarrow \text{S4}$ suggests condensation of amino- and carboxylic groups. Only the secondary amino group linked to R_1 can be involved in such reaction due to the steric reasons. Then (1.5 point for S4):



4. $\frac{600 \cdot 10^{12}}{16.0} = 3.75 \cdot 10^{13}$ moles of methane replenish the atmosphere annually. It occupies the volume of $\frac{3.75 \cdot 10^{13} \cdot 8.314 \cdot (273 - 20)}{0.50 \cdot 10^5} = 1.6 \cdot 10^{12} \text{ m}^3$ under the given conditions. The height of the atmosphere is negligible if compared to the Earth radius, thus one can accept $dV = 4\pi R^2 dR$ for a tiny spherical layer of methane. The annual increase in the shell thickness is as low as $\frac{1.6 \cdot 10^{12}}{4 \cdot 3.14 \cdot (6370 \cdot 10^3)^2} = 3.1 \cdot 10^{-3} \text{ m}$ (about 3 mm) (2.5 points).

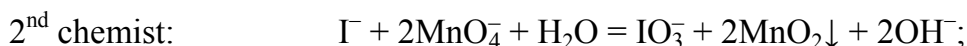
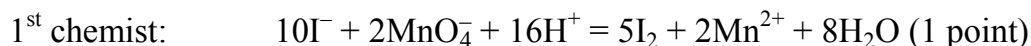
5. Carbon(IV) oxide is excluded from consideration due to the restriction on the density of the obtained gas. Only the equimolar mixture of H_2 and CO meets all the requirements. Then X is water (as vapor), whereas the equations are: $2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$ (1) and $\text{C} + \text{H}_2\text{O} \rightarrow \text{CO} + \text{H}_2$ (2) (1 point for X , 0.5 point for each equation, 2 points in total).

Problem 4 (author M.K. Beklemishev)

1. Let us calculate the amounts of permanganate required for the oxidation of 1 mol of iodide ($n(\text{Mn}^{\text{VII}}) : n(\text{I}^-)$, mol/mol), assuming that permanganate and iodide may pass into various oxidation states:

Permanganate reduction product	Iodide oxidation product			
	$\frac{1}{2}\text{I}_2 (-1e^-)$	$\text{IO}^- (-2e^-)$	$\text{IO}_3^- (-6e^-)$	$\text{IO}_4^- (-8e^-)$
$\text{MnO}_4^{2-} (+e^-)$	1	2	6	8
$\text{MnO}_2 (+3e^-)$	1/3	2/3	2	8/3
$\text{Mn}^{2+} (+5e^-)$	1/5	2/5	6/5	8/5

(We should note that periodate in solution actually exists as a salt of ortho-periodic acid H_5IO_6 .) As it can be seen from the Table, the amounts of permanganate differing by a factor of 10 (2.4 and 24 mL) may be spent for titration if $n(\text{Mn}^{\text{VII}}) : n(\text{I}^-) = 1/5$ and 2 (because $1/5 : 2 = 1 : 10$), i.e. in case of reactions $[\text{I}^- \rightarrow \text{I}_2; \text{MnO}_4^- \rightarrow \text{Mn}^{2+}]$ (1/5) and either $[\text{I}^- \rightarrow \text{IO}_3^-; \text{MnO}_4^- \rightarrow \text{MnO}_2]$, or $[\text{I}^- \rightarrow \text{IO}^-; \text{MnO}_4^- \rightarrow \text{MnO}_4^{2-}]$ (in fact, iodide is oxidized to give iodate, but the reaction with the formation of manganate and hypoiodite is also accepted). The amount of titrant (96 mL), 4 times higher than that of the third chemist, corresponds to $n(\text{Mn}^{\text{VII}}) : n(\text{I}^-) = 8$, i.e. the reaction $[\text{I}^- \rightarrow \text{IO}_4^-; \text{MnO}_4^- \rightarrow \text{MnO}_4^{2-}]$. Thus, we can write down the reactions that took place during titrations:



a theoretical variant: $\text{I}^- + 2\text{MnO}_4^- + 2\text{OH}^- = \text{IO}^- + 2\text{MnO}_4^{2-} + \text{H}_2\text{O}$ (2 points for either of the two equations)



Thus, 1st chemist titrated in an acidic medium, 2nd chemist titrated in a neutral or slightly alkaline medium, and the 3rd one titrated in an alkaline medium (precipitation of barium manganate accelerates the reduction of permanganate to manganate, helping to avoid the formation of MnO_2 that occurs slower) (5 points in total).

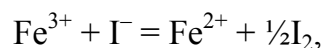
2. Concentration of KMnO_4 can be found from any titration, for example, from the first one: $5c_{\text{Mn}}V_{\text{Mn}} = n_{\text{iod}}$, hence $c_{\text{Mn}} = 0.100 \text{ g} / (166 \text{ g/mol KI} \cdot 5 \cdot 2.4 \text{ mL}) = 5.02 \cdot 10^{-2} \text{ M}$ (1 point).

3. The ratio of volumes of the titrant ($9.6 \text{ mL} \cdot 0.025 \text{ mol/L} = 0.24 \text{ mmol}$) and iodide ($0.1 \text{ g} = 0.60 \text{ mmol}$) will be equal to $24 : 60 = 2 : 5$ (1 point). In the acidic medium used, permanganate will be reduced to $\text{Mn}^{2+} (+5e^-)$, therefore, iodide will lose two electrons, being oxidized to I^+ . A stable compound of iodine(+) is iodine monochloride (1 point, 2 points in total):

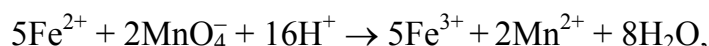


In the course of this titration, iodine is liberated and extracted into CCl_4 , that becomes pink-purple in color. Iodine monochloride present in the endpoint has practically invisible light yellow color.

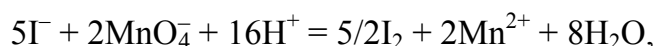
4. At first, Fe (III) releases free iodine (0.5 points):



but then Fe(II) enters the following reaction (0.5 points):



and totally we have:



which means that iron catalyzes the oxidation of iodine. In the endpoint iron will be oxidized into initial Fe(III) and thus will not affect the amount of the titrant spent.

Similarly, for copper we have (0.5 points for each reaction):



Thus, the result of the determination of permanganate will be correct independently of the presence of iron and copper salts (2 points totally).

Problem 5 (author R.V. Panin)

1. The gaseous SO_2 is formed on S combustion in oxygen: $\text{S} + \text{O}_2 = \text{SO}_2$, and could be oxidized in the presence of Pt catalyst to the solid SO_3 : $2\text{SO}_2 + \text{O}_2 = 2\text{SO}_3$. Thus, **E** = SO_2 , **F** = SO_3 . According to the density data, the molar mass of **G** equals to $4.42 \cdot 22.4 = 99$ g/mol. Taking into consideration the possible elements set (C, O, Cl), one may conclude the unique answer **G** = COCl_2 .

The white insoluble in acids precipitates **K** and **L** are BaSO_4 and AgCl respectively. IR-spectroscopy data proved the O–H bond to be only in the structure of **I**. Thus the **H** и **J** are built up from S, O, Cl, while **I** additionally contains hydrogen (the O–H bond).

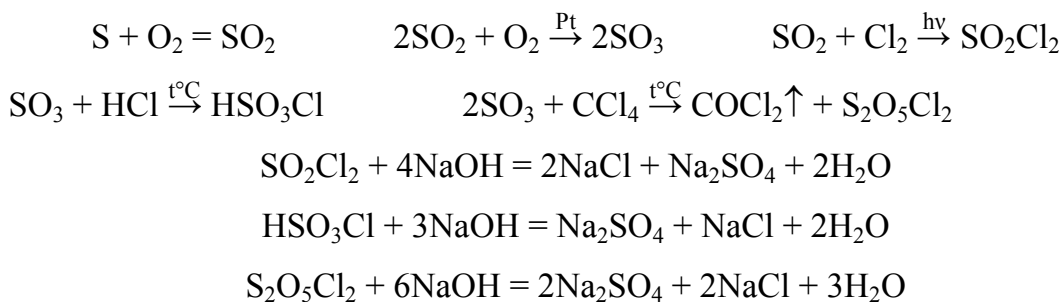
One may easily calculate the molar mass ratio $M(\text{BaSO}_4) / M(\text{AgCl}) = 1.628$, demonstrating that $\nu(\text{Cl}^-) = \nu(\text{SO}_4^{2-})$ for the **I** и **J** hydrolysis and $\nu(\text{Cl}^-) = 2\nu(\text{SO}_4^{2-})$ for the **H** hydrolysis products.

On the basis on these considerations one may draw the **H** formula as SCl_2O_m , next according to the electroneutrality principle $m = \frac{6-2}{2} = 2$, i.e. **H** = SO_2Cl_2 (the sulfuryl

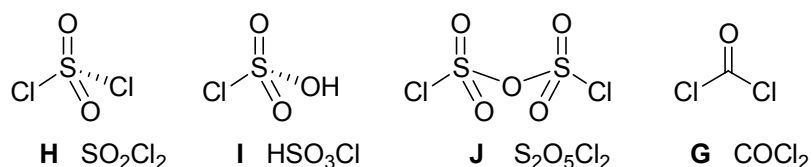
chloride), for **J** (the SClO_n formula), $n = \frac{6-1}{2} = 2.5$, i.e. $\text{SClO}_{2.5}$ or $\text{S}_2\text{Cl}_2\text{O}_5$ (the pyrosulfuryl chloride).

One may represent **I** as SClO_qH_r . The $r > 1$ (2, 3 and so on) values are hardly possible because of the strong tendency of such compounds to eliminate water molecule. For $r = 1$ $q = \frac{6-1+1}{2} = 3$, and **I** = $\text{SO}_2\text{Cl}(\text{OH})$ or HSO_3Cl (the chlorosulfonic acid) (0.5 points for each substance, 4 points in total).

2. One may write down the reactions equations as follows (0.5 points for each reaction equation, 4 points in total):



3. According to the valences of the elements, the next graphic formulae should be drawn (0.5 points for each formula, 2 points in total):



Problem 6 (author R.V. Panin)

1. One may assume that the salts given are built up from Na, N(or P) and O. If no other elements exist in formula, the remaining mass percentage corresponds to oxygen.

Consequently one may determine the formulae as follows:

A $\text{Na} : \text{N} : \text{O} = 46.9/23 : 9.5/14 : 43.6/16 = 2.039 : 0.678 : 2.725 = 3:1:4$ **A** = Na_3NO_4

B $\text{Na} : \text{N} : \text{O} = 27.1/23 : 16.5/14 : 56.4/16 = 1.178 : 1.178 : 3.525 = 1:1:3$ **B** = NaNO_3

C $\text{Na} : \text{N} : \text{O} = 33.3/23 : 20.3/14 : 46.4/16 = 1.448 : 1.45 : 2.9 = 1:1:2$ **C** = NaNO_2

D $\text{Na} : \text{N} : \text{O} = 43.4/23 : 26.4/14 : 30.2/16 = 1.887 : 1.886 : 1.888 = 1:1:1$ **D** = $(\text{NaNO})_n$,

that is, $\text{Na}_2\text{N}_2\text{O}_2$

E $\text{Na} : \text{P} : \text{O} = 42.1/23 : 18.9/31 : 39/16 = 1.83 : 0.61 : 2.44 = 3:1:4$ **E** = Na_3PO_4

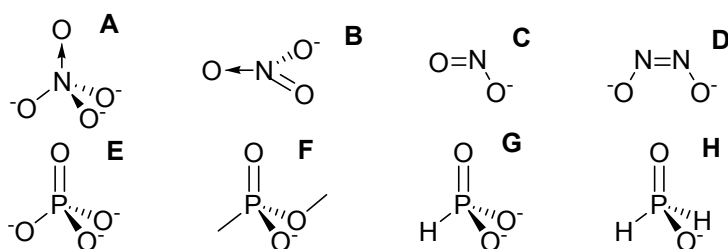
F $\text{Na} : \text{P} : \text{O} = 22.5/23 : 30.4/31 : 47.1/16 = 0.978 : 0.98 : 2.944 = 1:1:3$ **F** = NaPO_3

G $\text{Na} : \text{P} : \text{O} = 36.5/23 : 24.6/31 : 38.9/16 = 1.587 : 0.794 : 2.431 = 1.999:1:3.062$,

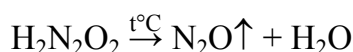
The calculated formula Na_2PO_3 correspond to oxidation state of P equal to +4, but not +3. One can propose that hydrogen atom is present in **G**. Therefore the formula of **G** = Na_2HPO_3 .

H $\text{Na} : \text{P} : \text{O} = 26.1/23 : 35.2/31 : 38.7/16 = 1.135 : 1.135 : 2.419 = 1:1:2$, the same argumentation gives rise to the formula of **H** = NaH_2PO_2 .

Taking into consideration the maximal covalence to be 4 for N and 5 for P, one may draw the graphic formulae of the salt anions given in the table as follows (0.25 points for each chemical formula **A – F**, 0.75 points for each chemical formula **G** and **H**, 0.5 points for each graphic formula, 7 points in total):



2. It is obviously that $\text{H}_2\text{N}_2\text{O}_2$ and H_3PO_2 are the acids corresponding to $\text{Na}_2\text{N}_2\text{O}_2$ and NaH_2PO_2 respectively. $\text{H}_2\text{N}_2\text{O}_2$ decomposes without solids:

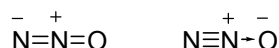


In case of H_3PO_2 decomposition the only gaseous product is phosphine. Consequently thermolysis of H_3PO_2 is disproportionation reaction:



Thus, **I** = $\text{H}_2\text{N}_2\text{O}_2$, **J** = H_3PO_2 , **K** = N_2O , **L** = H_3PO_3 , **M** = H_3PO_4 , **Q** = PH_3 (0.25 points for each chemical formula, 0.25 points for each reaction equation, 2.25 points in total).

3. One may draw the graphic formula of N_2O as follows (0.25 points)



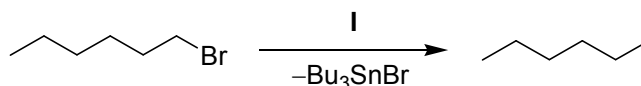
N_2O and H_2O are formed by an ammonium nitrate and nitramide thermal decomposition:



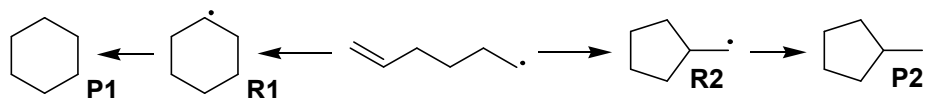
(0.25 points for the graphic formula of N_2O , 0.25 points for equation of its thermal decomposition reaction, 0.75 points in total).

Problem 7 (author S.G. Bakhtin)

1. From the mechanism given in the reaction condition, it is clear that RX is transformed into RH . Therefore, product is *n*-hexane (1 point).



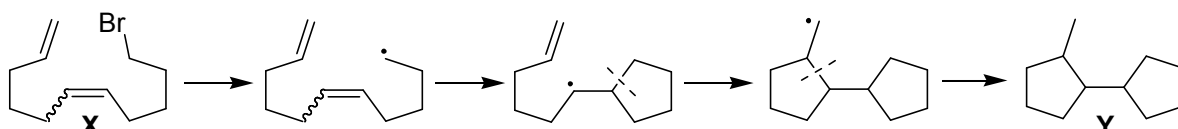
2. Radical R \cdot , which is formed from 6-bromohex-1-ene, can form a ring by two ways. The radical center can attack C(1) or C(2) atom producing 6-membered ring (cyclohexane, CH) and five-membered ring (methylcyclopentane, MCP), respectively (1 point for the structural formulae of each radical, 0.5 points for each product **P1** and **P2**, 3 points in total).



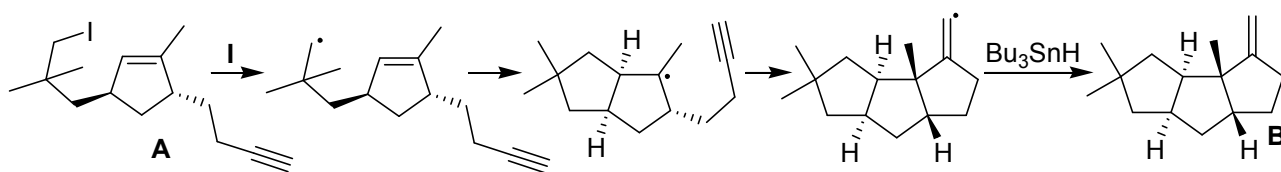
3. Let us determine the molar fraction of CH as X (in %). Then the molar fraction of MCP is $(100 - X)$. Therefore, the ratio of methylene and methyl protons in the obtained mixture is $\frac{12X + 8(100 - X)}{3(100 - X)} = 2.8$. So, $X = 3\%$. The molar fraction of MCP is 97%.

Cyclohexane is more stable than methylcyclopentane. Therefore, under thermodynamic control CH should predominate in the obtained mixture. However, our calculations demonstrate that the major product is MCP. It is possible if only reaction proceeds under kinetic control (transition state for the formation of five-membered ring has lower energy than transition state for the formation of six-membered ring) (1 point for the calculation of the mixture composition, 1 point for the determination of kinetic control, 2 points in total).

4. Accounting for answer on the question 3, **Y** is 2-methylbicyclopentyl. **Y** is formed by two consecutive cyclizations producing five-membered ring at both steps (1 point for each structural formulae, 2 points in total).

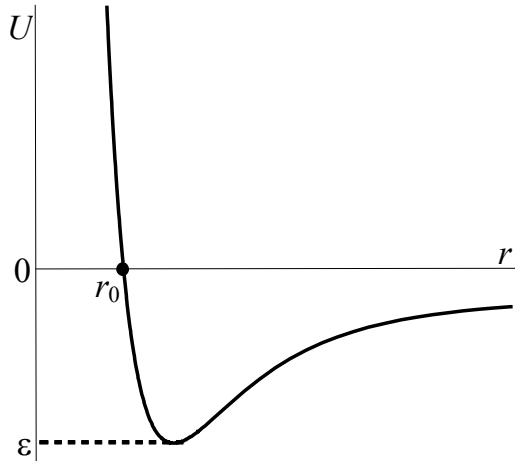


5. Molecule of **B** has three rings. It is possible to suppose that it is formed *via* two consecutive cyclizations. In the first one, radical attacks C=C bond; in the second step, the newly formed radical attacks C≡C bond. In both cases, 5-membered ring should be formed (see above). Due to steric restraints, two five-membered rings have *cis*-annulation. This allows for writing down structural formula of hirsutene (1 point for each structural formulae, 2 points in total).



Problem 8 (author D.G. Gulevich)

1. Considering the variable J as continuous, one should solve the equation $dN_J/dJ = 0$. Differentiation of by J leads to the equation $(2J+1)^2 = 4k_B T I / \hbar^2$, from where $J = (k_B T I)^{1/2} - 1/2 = 6.69$. Since the values of J can be only integer, rounding, we get $J = 7$ (differentiation of equation 1 point, the value of J 1 point, 2 points in total).



2. a) On the horizontal axis $r = r_0$. At this point $U = 0$. On the vertical axis $U = -\varepsilon$, i.e. ε – the depth of the potential well. b) The equilibrium value of r corresponds to the minimum energy U . Equating the dU/dr to zero, and solving the equation for r , we find $r_e = \sqrt[6]{2} r_0$ (0.25 points for each r_0 and ε , 0.5 points for r_e , 1 point in total).

3. For neighboring rotational levels $\Delta E_J = E_{J+1} - E_J = B_e(J+1)(J+2) - B_e J(J+1) = 2B_e(J+1)$. Therefore the spectrum is a series of lines spaced apart by the same distance $2B_e$. Thus, $\nu_1 = 2B_e/h = 2 \cdot 7.093 \cdot 10^{-24} / 6.63 \cdot 10^{-34} = 2.14 \cdot 10^{10}$ Hz; $\nu_2 = 2\nu_1 = 4.28 \cdot 10^{10}$ Гц (1.5 points for ΔE_J expression, 0.75 points for each ν_1 and ν_2 calculation, 3 points in total).

4. The energy difference between the levels $\Delta E = \Delta E_{Jn} = E_{00} - E_{11} = 2B_e + \hbar\omega = 2B_e + \hbar\sqrt{k/\mu}$

$$\Delta E = 2 \cdot 2.26 \cdot 10^{-23} + 1.055 \cdot 10^{-34} \sqrt{239 \frac{127+35}{(127+35) \cdot 1.66 \cdot 10^{-27}}} = 4.52 \cdot 10^{-23} + 7.64 \cdot 10^{-21}$$

$$\Delta E = 7.68 \cdot 10^{-21} \text{ J (1.5 points)}$$

Further $\lambda = hc / \Delta E = 6.63 \cdot 10^{-34} \cdot 3 \cdot 10^8 / 7.68 \cdot 10^{-21} = 2.59 \cdot 10^{-5}$ m (1 point, 2.5 points in total)

5. Using the expression $\omega = \sqrt{k/\mu}$, and the fact that k for both molecules is the same, we write (1.25 points):

$$\frac{\omega(^{81}\text{BrF})}{\omega(^{79}\text{BrF})} = \sqrt{\frac{\omega(^{79}\text{BrF})}{\omega(^{81}\text{BrF})}} = \sqrt{\frac{2.55 \cdot 10^{-26}}{2.56 \cdot 10^{-26}}} = 0.998$$

$\omega(^{81}\text{BrF}) = 0.998 \cdot 1326 = 1323 \text{ cm}^{-1}$ (0.25 points, 1.5 points in total).