

ENG

english
version



THEORETICAL EXAMINATION SOLUTIONS

30th of April, 2006

Rīga

Problem 1

Chile saltpeter is sodium nitrate – it is mineral which deposits are found in South America (**Chile** deserts).

Element A is iodine (violet solution in xylene; blue compound with starch (p.2)). So B should be compound of I, perhaps with Na. If I in free state is obtained from B by reduction (NaHSO₃ is reducing agent), compound B cannot be NaI, it should be some compound of I in oxidized state. The most stable I compounds where I is in oxidized state are I(V), so compound B is possibly NaIO₃.

Reaction:



Exchange of substances between two non-miscible liquid phases moved by differences in solubility and diffusion.

Iodine tincture (5% iodine solution in ethanol) – for disinfection of small wounds

Lugol's solution (1% solution of I₂ and 2% KI in water) – for disinfection of abscesses etc.

Radioactive isotope Iodine-131 was one of the most important pollution agents due to its volatility. In humans iodine is concentrated in thyroid gland; radioactive iodine may cause cancer and malfunction of this gland. All people involved was treated with sodium iodide to make more rapid the elimination of radioactive isotope from organism: $^{131}\text{I}^-$ - absorbed + $^{127}\text{I}^- \rightarrow ^{127}\text{I}^-$ -absorbed + $^{131}\text{I}^-$ (eliminated)

Halogen lamps.

Lamps without iodine: W evaporates from the filament at 2200 °C and is sedimented on the glass bulb. Filament becomes less, bulb – grey.

Halogen lamp – W evaporates; $\text{W} + \text{I}_2 \rightarrow \text{WI}_x$ (in vapor state) – recycles to the filament: $\text{WI}_x \rightarrow \text{W} + \text{I}_2$
Tungsten is regenerated.

Moisture causes the hydrolysis of PI₃:



Gas C – hydrogen iodide; aqueous solution – hydroiodic acid

$$\text{pH} = -\log [\text{H}^+]$$

$$[\text{H}^+] = c(\text{HI}) = n / v \quad n = m / M = 12.79 / 127.9 = 0.10 \text{ mol} / \text{L} \quad v = 1 \text{ L}$$

$$\text{pH} = -\log 0.1 = 1$$

When using the same formula without additional thinking, we get:

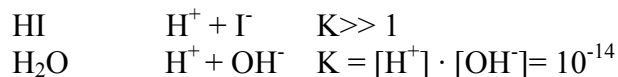
$$c'(\text{HI}) = n' / v' \quad n' = c \cdot v = 0.1 \cdot 0.001 \text{ L} = 1 \cdot 10^{-4} \text{ mol}$$

$$v' \approx v(\text{added}) = 10 \text{ m}^3 = 10^4 \text{ L}$$

$$c'(\text{HI}) = 10^{-4} / 10^4 = 10^{-8} \text{ mol/L}; \quad \text{pH} = 8$$

It makes no sense because pure water has pH = 7, and strong acid added should lower pH, so pH < 7 is expected.

As the $c'(\text{HI})$ is so low, autoprotolysis of water should be taken into account as the alternative source of H^+ ions. Then we have:



The amount of cations and anions should be equal: $[\text{H}^+] = [\text{I}^-] + [\text{OH}^-]$

$$[\text{I}^-] = c'(\text{HI}) \quad [\text{OH}^-] = 10^{-14} / [\text{H}^+] \quad , \text{ then}$$

$$[\text{H}^+] = c'(\text{HI}) + (10^{-14} / [\text{H}^+])$$

$$[\text{H}^+]^2 - 10^{-8} \cdot [\text{H}^+] + 10^{-14} = 0 \quad \text{solving square equation we get } [\text{H}^+] = 1.05 \cdot 10^{-7}$$

$$\text{pH} = 6.98$$

Problem 2

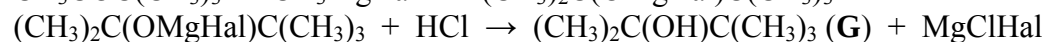
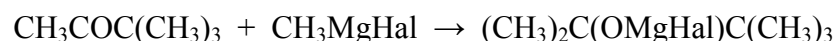
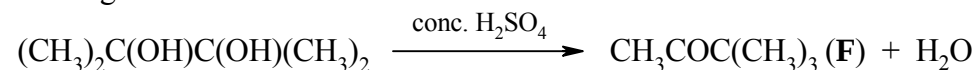
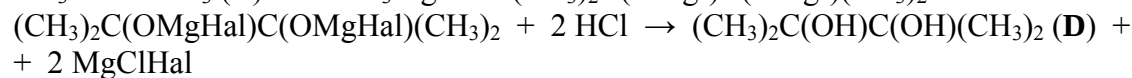
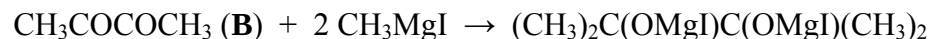
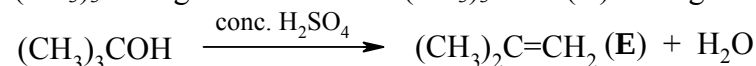
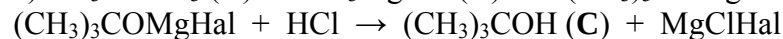
$$\text{a) } \rho_1 \approx \frac{578813 \cdot \frac{4}{3} \pi \cdot (0.5)^3}{75 \cdot 75 \cdot 75} = 0.72$$

$$\text{b) } \text{I} - \text{cF} - \text{fcc}, \text{II} - \text{cI} - \text{bcc}, \text{III} - \text{cP}.$$

$$\text{c) } N = (53^3 + 3 \cdot 52^2 \cdot 53 - 65^3 - 64^2) = 42044 \text{ (7.26\%)}$$

$$N = (65^3 + 64^2 - 75^3) = 114894 \text{ (19.85\%)}$$

Problem 3



Hal – Cl, Br, or I.

$$\text{b) } \text{B} > \text{A} > \text{C} \approx \text{D} > \text{X}$$

$$\text{c) } \text{CH}_3\text{OCOOCH}_3 \text{ and } \text{CH}_3\text{OCOCOOCH}_3 \text{ (dimethyl carbonate and dimethyl oxalate).}$$

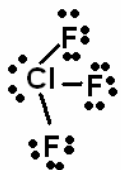
Problem 4

1.1.

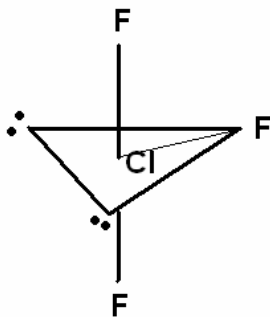
$$\mu = \left(\frac{127 \cdot 37}{127 + 37} \right) \cdot 1,66054 \cdot 10^{-27} \text{ kg} = 4,76 \cdot 10^{-26} \text{ kg}$$

$$R = \sqrt{\frac{h}{\mu 8 \pi^2 B}} = 2,31 \cdot 10^{-10} \text{ m} \approx 230 \text{ pm}$$

1.2.

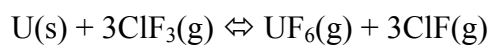


1.3.



Molecule is “T” shape. All angles is close to 90°C.

1.4.



$$T = 360 \text{ K}$$

Initial:

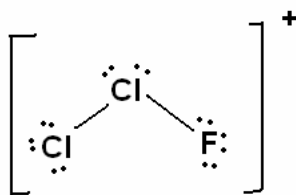
$$pV = nRT; \quad p = cRT = 0,0453 \text{ mol/L} \cdot 0,08206 \text{ L} \cdot \text{atm} / \text{mol K} \cdot 360 \text{ K} = 1,338 \text{ atm}$$

$$\text{Increase in pressure} = p_{\text{UF}_6} = 1,69 \text{ atm} - 1,338 \text{ atm} = 0,352 \text{ atm} \approx 0,35 \text{ atm}$$

$$P_{\text{ClF}} = 3 \times 0,352 = 1,056 \text{ atm} \approx 1,06 \text{ atm}$$

$$P_{\text{ClF}_3} = 1,338 \text{ atm} - 1,056 \text{ atm} = 0,282 \text{ atm} \approx 0,28 \text{ atm}$$

1.5.

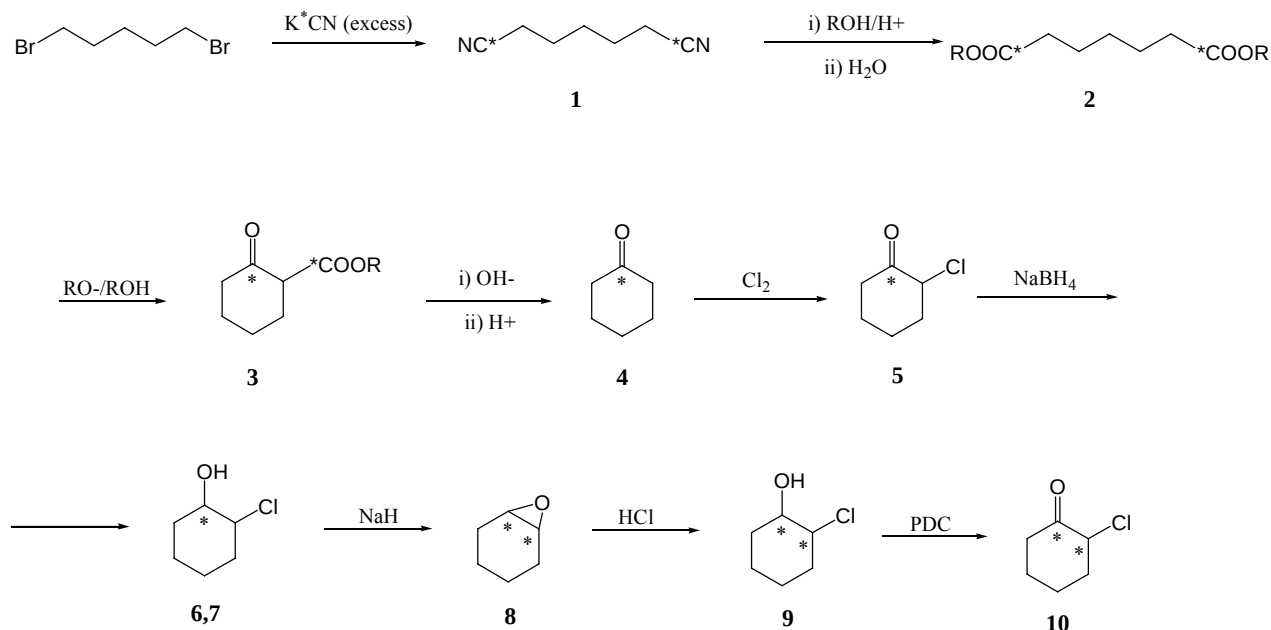


1.6. B

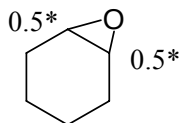
1.7. D

Problem 5

1.

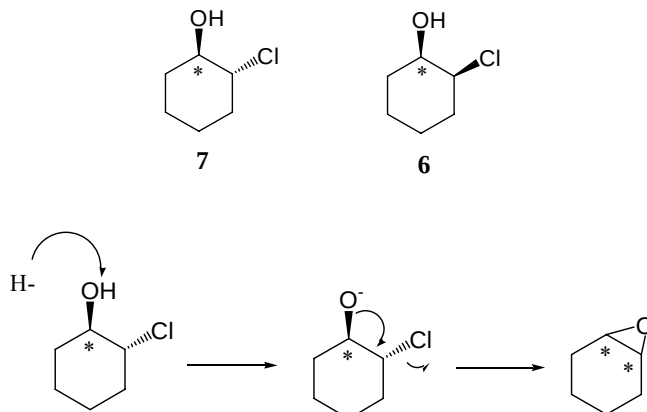


The compound **8** has a symmetry plane, therefore the radioactive label distributes between two carbons- there is an equal possibility to open the epoxide with HCl from both ends. We can also draw compound **8** as shown bellow

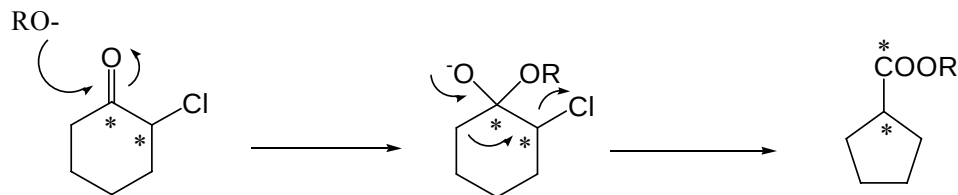


The symbol 0.5^* means that only half of starting radioactivity is on the labeled carbon. On the other hand, in this step we do not need to care about absolute radioactivity-only relative radioactivity does matter.

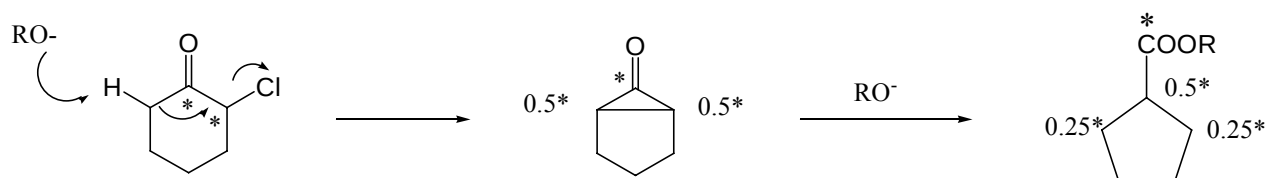
2. The reduction of compound **5** could lead to formation of two stereoisomers- trans and cis chloroalcohols. The next step is an intramolecular S_N2 nucleophilic substitution which requires the trans spatial orientation of nucleophile and leaving group. Therefore, the compound **6** is cis isomer and compound **7** is trans isomer:



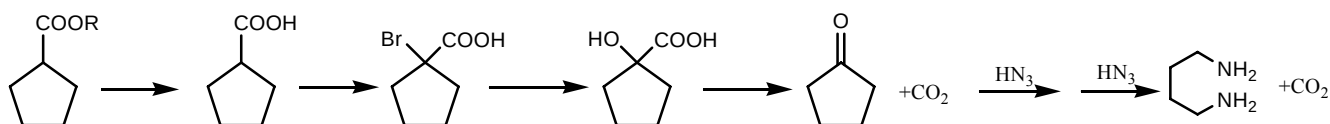
3. Mechanism A:



Mechanism B:

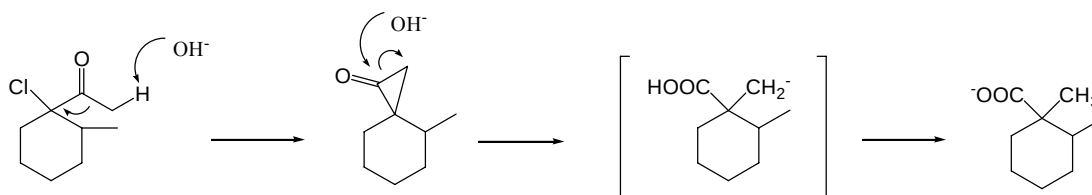


4.



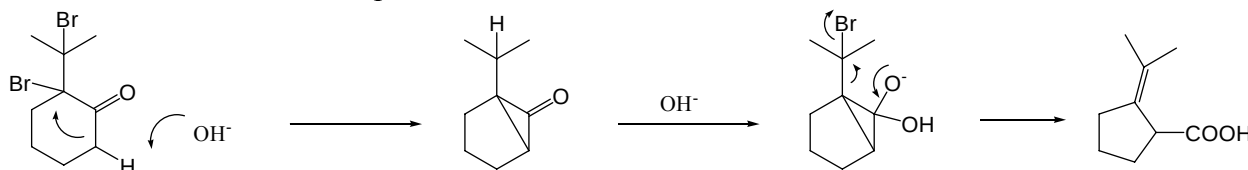
The only gaseous product of the sequence is CO_2 . One carbene dioxide molecule is formed from ester group and according to both mechanisms, this carbon atom has a half of the total radioactivity. Another carbon dioxide molecule originates from the keto group of cyclopentanone. In the case of mechanism **A**, we should have all the radioactivity of the starting material in CO_2 form. On the other hand, mechanism **B** predicts that radioactivity of CO_2 will be only 75% of the total radioactivity. It means that mechanism B is the correct one.

5. The first example is a typical Favorskii rearrangement:

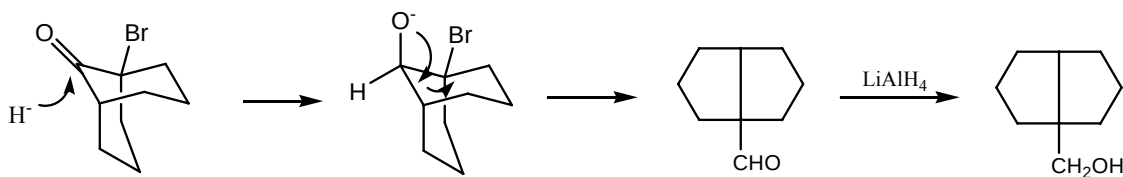


Note that the opening of cyclopropane ring forms more stable primary carbanion.

Second example combines two reactions- Favorskii rearrangement and elimination. In this case the less stable anion leads to the product formation.

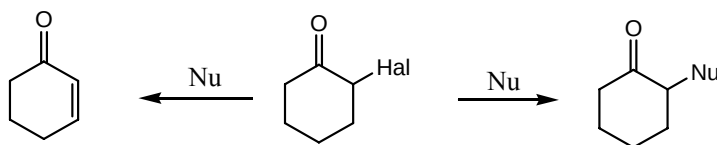


The last example is a Favorskii type reaction when hydride anion acts as nucleophile:



The α -proton of the starting ketone is not acidic, hence the reaction could not proceed via cyclopropane mechanism (mechanism B).

6. There are mainly two Favorskii reaction by-products that are formed either by nucleophilic substitution or elimination:



Problem 6

$$1. \Delta_r H_H = (-699,0 - (-393,5) - (-285,8)) = -19,7 \text{ kJ/mol}$$

$$\Delta_r S_H = (190,0 - 213,8 - 70,1) = -93,9 \text{ J/(mol}\cdot\text{K)}$$

$$\Delta_r G_H = -19700 + 296 \cdot 93,9 = 8094 \text{ J/mol,}$$

$$K_H = \exp(-8094/296/8.314) = 0,0373 \text{ M/bar.}$$

2. Давление на глубине h определяется формулой $p = \rho gh$. Предположим, что на глубине h находится пузырек воздуха, тогда давление углекислого газа равно $p(\text{CO}_{2(r)}) = (p_{\text{atm}} w + \rho gh w)$.

$$\text{Общая концентрация } \text{CO}_2 \text{ равна } c(\text{CO}_2)_0 = [\text{H}_2\text{CO}_{3(p-p)}] + [\text{HCO}_3^-(p-p)] + [\text{CO}_3^{2-}(p-p)].$$

Выразим ее через давление углекислого газа

$$c(\text{CO}_2)_0 = p(\text{CO}_{2(r)}) K_H^T \left(1 + K_1^T / [\text{H}^+] + K_1^T K_2^T / [\text{H}^+]^2 \right).$$

Общая формула для концентрации углекислого газа:

$$c(\text{CO}_2)_0 = (p_{\text{atm}} w + \rho gh w) \cdot K_H^T \cdot \left(1 + \frac{K_1^T}{[\text{H}^+]} + \frac{K_1^T K_2^T}{[\text{H}^+]^2} \right) \quad (0.1)$$

Теперь запишем массовый баланс:

$$[\text{Fe}_{(p-p)}^{2+}] = c(\text{CO}_2)_0 = [\text{H}_2\text{CO}_{3(p-p)}] + [\text{HCO}_3^-(p-p)] + [\text{CO}_3^{2-}(p-p)]$$

$$[\text{Fe}_{(p-p)}^{2+}] = [\text{CO}_3^{2-}(p-p)] \frac{[\text{H}^+]^2}{K_1^T K_2^T} \left(1 + \frac{K_1^T}{[\text{H}^+]} + \frac{K_1^T K_2^T}{[\text{H}^+]^2} \right)$$

Введем константу растворимости:

$$[\text{Fe}_{(p-p)}^{2+}] = \frac{K_{sp}^T}{[\text{Fe}_{(p-p)}^{2+}] K_1^T K_2^T} \left(1 + \frac{K_1^T}{[\text{H}^+]} + \frac{K_1^T K_2^T}{[\text{H}^+]^2} \right)$$

Отсюда

$$[\text{Fe}_{(p-p)}^{2+}] = c(\text{CO}_2)_0 = \sqrt{\frac{K_{sp}^T [\text{H}^+]^2}{K_1^T K_2^T} \left(1 + \frac{K_1^T}{[\text{H}^+]} + \frac{K_1^T K_2^T}{[\text{H}^+]^2} \right)} \quad (0.2)$$

Приравняем выражения 1.1 и 1.2

$$\sqrt{\frac{K_{sp}^T [H^+]^2}{K_1^T K_2^T} \left(1 + \frac{K_1^T}{[H^+]} + \frac{K_1^T K_2^T}{[H^+]^2}\right)} = (p_{\text{atm}} w + \rho g h w) \cdot K_H^T \cdot \left(1 + \frac{K_1^T}{[H^+]} + \frac{K_1^T K_2^T}{[H^+]^2}\right)$$

упростив получим

$$\frac{K_{sp}^T [H^+]^2}{K_1^T K_2^T} = \left((p_{\text{atm}} w + \rho g h w) \cdot K_H^T\right)^2 \cdot \left(1 + \frac{K_1^T}{[H^+]} + \frac{K_1^T K_2^T}{[H^+]^2}\right)$$

Если $[H^+] > K_1 \gg K_2$,

$$[H^+] = \left((p_{\text{atm}} w + \rho g h w) \cdot K_H^T\right) \sqrt{\frac{K_1^T K_2^T}{K_{sp}^T}}$$

На глубине 50 метров:

$$[H^+] = \left(\frac{(100000 \cdot 1 + 1000 \cdot 9.81 \cdot 50 \cdot 1)}{100000} \cdot 0.0373\right) \sqrt{\frac{3.57 \cdot 10^{-7} \cdot 4.40 \cdot 10^{-11}}{5.91 \cdot 10^{-11}}} = 0,000113 \text{ М, pH} =$$

3,94

На глубине 180 метров:

$$[H^+] = \left(\frac{(100000 \cdot 1 + 1000 \cdot 9.81 \cdot 180 \cdot 1)}{100000} \cdot 0.0373\right) \sqrt{\frac{3.57 \cdot 10^{-7} \cdot 4.40 \cdot 10^{-11}}{5.91 \cdot 10^{-11}}} = 0.000359 \text{ М, pH} =$$

3,45

3. На глубине 50 метров:

$$c(\text{CO}_2)_0 = \frac{(100000 \cdot 1 + 1000 \cdot 9.81 \cdot 50 \cdot 1)}{100000} \cdot 0.0373 \cdot \left(1 + \frac{3.57 \cdot 10^{-7}}{10^{-3.94}} + \frac{1.57 \cdot 10^{-17}}{10^{-7.88}}\right)$$

$$c(\text{CO}_2)_0 = 0.221 \text{ М}$$

На глубине 180 метров:

$$c(\text{CO}_2)_0 = \frac{(100000 \cdot 1 + 1000 \cdot 9.81 \cdot 180 \cdot 1)}{100000} \cdot 0,0373 \cdot \left(1 + \frac{3,57 \cdot 10^{-7}}{10^{-3.45}} + \frac{1,57 \cdot 10^{-17}}{10^{-6.89}}\right)$$

$$c(\text{CO}_2)_0 = 0.697 \text{ М}$$

3. уравнение зависимости: $c(\text{CO}_2)_0 = (3.79 \cdot 10^{-2} + h \cdot 3.66 \cdot 10^{-3}) \text{ М}$.

Общее количество CO_2 в объеме от 50 до 180 метров равно:

$$\begin{aligned} N(\text{CO}_2)_{50-180} &= \int_{50}^{180} (3,79 \cdot 10^{-2} + h \cdot 3,66 \cdot 10^{-3}) \cdot 1200000 dh = \\ &= \left(h \cdot 45480 + h^2 \cdot \frac{1}{2} \cdot 4392\right) \Big|_{50}^{180} = \\ &= (180 \cdot 45480 + 180^2 \cdot 2196) - (50 \cdot 45480 + 50^2 \cdot 2196) = \\ &= 79336800 - 7764000 = 7,16 \cdot 10^7 \text{ mol} \end{aligned}$$

Масса CO_2 в объеме от 50 до 180 метров равна:

$$m(\text{CO}_2)_{50-180} = 7.17 \cdot 10^7 \text{ моль} \cdot 44.0 \text{ г/моль} = 3.15 \cdot 10^9 \text{ г} = 3150 \text{ тонн}$$

Оценим объем углекислого газа при 30°C:

$$V(\text{CO}_2)_{50-180} = 7.16 \cdot 10^7 \text{ mol} \cdot \frac{8.314 \text{ J/(K} \cdot \text{mol)} \cdot (30 + 273) \text{ К}}{100000 \text{ Па}} = 1.74 \cdot 10^6 \text{ м}^3$$