Baltic Chemistry Competition

BioSan
Medical - Biological Research and Technologies
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2011
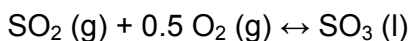## 1ST ROUND, SOLUTIONS

Problem 1 (Lithuania)

Sulfur containing gases (8 points)

PART 1

At 25°C temperature SO_3 is a liquid.
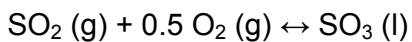
Two reactions occur:

SO_2 (g) + 0.5 O_2 (g) ↔ SO_3 (l)

SO_3 (l) ↔ SO_3 (g)

$$\Delta_r G = \Delta_r H - T\Delta_r S$$

T = 298.15 K

$$K = e^{\frac{-\Delta G}{RT}}$$

	SO_2 (g)	O_2 (g)	SO_3(l)	SO_3(g)	H_2O (l)	H_2SO_4 (aq)
$\Delta_f H$, kJ mol^{-1}	-296.83	0	-441.0	-395.7	-285.83	-909.27
S , J K^{-1} mol^{-1}	248.22	205.138	113.8	256.76	69.91	20.1

SO_2 (g) + 0.5 O_2 (g) ↔ SO_3 (l)

$$\Delta_{r1}H^o = \Delta_f H^o(SO_3, l) - \Delta_f H^o(SO_2, g) - 0.5\Delta_f H^o(O_2, g) = -144.2 kJ/mol$$

$$\Delta_{r1}S^o = S^o(SO_3, l) - S^o(SO_2, g) - 0.5S^o(O_2, g) = -237.0 JK^{-1}mol^{-1}$$

$$\Delta_{r1}G = -73.55 \text{ kJ/mol} = -73550 \text{ J/mol}$$

$$K_1 = e^{\frac{-\Delta G}{RT}} = e^{\frac{73550}{8.314 \cdot 298.15}} = 7.693 \cdot 10^{12}$$ ➔ [reagents]<<[products]

SO_3 (l) ↔ SO_3 (g)

$$\Delta_{r2}H^o = \Delta_f H^o(SO_3, g) - \Delta_f H^o(SO_3, l) = 45.3 kJ/mol$$

$$\Delta_{r2}S^o = S^o(SO_3, g) - S^o(SO_3, l) = 143.0 \text{ } JK^{-1}mol^{-1}$$

$\Delta_{r2}G = 2.698 \text{ kJ/mol}$

$$K_2 = e^{\frac{-\Delta G}{RT}} = e^{\frac{2698}{8.314 \cdot 298.15}} = 2.9693885$$

$$K_1 = \frac{a(SO_3, l)}{a(SO_2, g) \cdot a(O_2, g)} = \frac{1}{p_{SO_2,g} p_{O_2,g}^{0.5}}$$

There is an excess of SO_2 in a container, after reaction there is unreacted SO_2 :

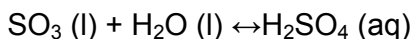$(70 - 30 \cdot 2)\% = 10\%$ of initial pressure/volume

$$p_{O_2,g} = \frac{1}{\left(K_1 p_{SO_2,g}\right)^2} = \frac{1}{(7.693 \cdot 10^{12} \cdot 0.1)^2} = 1.690 \cdot 10^{-24} \text{atm}$$

$$N(O_2, g) = nN_A = \frac{pVN_A}{RT} = \frac{1.690 \cdot 10^{-24} \cdot 101325 \cdot 5 \cdot 10^{-3} \cdot 6.022 \cdot 10^{23}}{8.314 \cdot 298.15} = 0.208 \text{ molecules}$$

0.208 < 1

Therefore, the final volume of O_2 equals 0 L.

PART 2
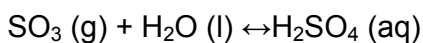
SO_3 (l) + H_2O (l) $\leftrightarrow$ H_2SO_4 (aq)

$\Delta_{r3}H^o = -182.4 \text{kJ/mol}$

$\Delta_{r3}S^o = -163.6 \text{ JK}^{-1}\text{mol}^{-1}$

$\Delta_{r3}G = -133.7 \text{ kJ/mol}$

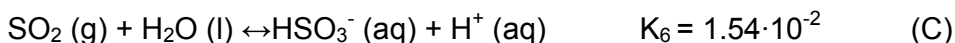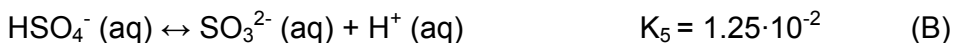$$K_3 = e^{\frac{-\Delta G}{RT}} = e^{\frac{133700}{8.314 \cdot 298.15}} = 2.705 \cdot 10^{23}$$

SO_3 (g) + H_2O (l) $\leftrightarrow$ H_2SO_4 (aq)

$\Delta_{r4}H^o = -227.7 \text{kJ/mol}$

$\Delta_{r4}S^o = -306.6 \text{ JK}^{-1}\text{mol}^{-1}$

$\Delta_{r4}G = -136.4 \text{ kJ/mol}$

$$K_4 = e^{\frac{-\Delta G}{RT}} = e^{\frac{136400}{8.314 \cdot 298.15}} = 8.036 \cdot 10^{23}$$

$K_3 \gg 1$, $K_4 \gg 1$. So, all SO_3 dissolves into H_2SO_4 (aq).

H_2SO_4 (aq) + H_2O (l) $\rightarrow$ HSO_4^- (aq) + H_3O^+ (aq)　　　　　　　　　(A)

HSO_4^- (aq) $\leftrightarrow$ SO_3^{2-} (aq) + H^+ (aq)　　　　　　$K_5 = 1.25 \cdot 10^{-2}$　　(B)

SO_2 (g) + H_2O (l) $\leftrightarrow$ HSO_3^- (aq) + H^+ (aq)　　　$K_6 = 1.54 \cdot 10^{-2}$　　(C)

HSO_3^- (aq) $\leftrightarrow$ SO_3^{2-} (aq) + H^+ (aq)　　　　$K_5 = 6.3 \cdot 10^{-8}$ constant is too small, so reaction is not significant

2
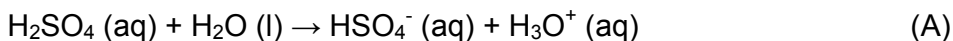
The major protons are formed from A, B and C reactions

$$n(SO_3, l \text{ and } g) = n(SO_3) = 2 \cdot n(O_2) = \frac{2p(O_2)V}{RT} = \frac{2 \cdot 0.3 p(total)V}{RT} =$$

$$\frac{2 \cdot 0.3 \cdot 101325 \cdot 5 \cdot 10^{-3} mol}{8.314 \cdot 298.15} = 0.1226 \ mol \text{ if pressure is 1 atm;}$$

If pressure (Standard) is 1 bar = 100kPa n(SO_3) = 0.1210 mol

All SO_3 dissolves in 1.00 L of water, so [H_2SO_4] = 0.1210 M

According to the reaction A, [H^+]$_o$ = (SO_3) = 0.1210 mol

After the addition of water

$$p(SO_2) = \frac{n(SO_2)RT}{V} = \frac{0.1n(g, initial)RT}{V} = \frac{\frac{p(initial)V(initial)}{RT} 0.1RT}{V} =$$

$$\frac{0.1p(initial)V(initial)}{V} = \frac{0.1 \cdot 100kPa \cdot 5.00L}{4.00L} = 12.5kPa = 0.125 \ bar$$
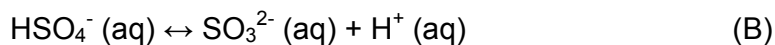
	HSO_4^- (aq)	↔ SO_3^{2-} (aq)	+ H^+ (aq)	(B)
Initial	0.1210	0	0.1210	
Change	-x	+x	+x	
Final	0.1210-x	x	0.1210+x	
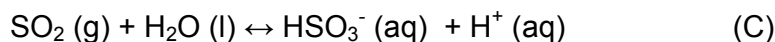
	SO_2 (g)	+ H_2O (l) ↔ HSO_3^- (aq)	+ H^+ (aq)	(C)
Initial	0.125	0	0.1210	
Change	-yRT/V	+y	+y	
Final	0.125-yRT/V	y	0.1210+y	

Protons are formed from two reactions, so the final [H^+]=[H^+]$_o$+x+y

$$\begin{cases} K_5 = \dfrac{(0.1210 + x + y)x}{0.1210 - x} = 0.0125 \\ K_6 = \dfrac{(0.1210 + x + y)y}{0.125 - y \cdot 6.197} = 0.0154 \end{cases}$$

x = 0.00997; y = 0.00821

[H^+] = [H^+]$_o$ + x + y = (0.1210 + 0.00997 + 0.00821)M = 0.13918 M

pH = − lg[H^+] = 0.08564

PART 3

When T = 200 C, only one significant reaction occur:

SO_2 (g) + 0.5 O_2 (g) ↔ SO_3 (g)

$$\Delta_{r7}H^o = \Delta_f H^o(SO_3, g) - \Delta_f H^o(SO_2, g) - 0.5\Delta_f H^o(O_2, g) = -98.7kJ/mol$$

3
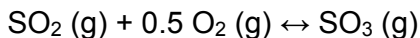
$$\Delta_{r7}S^\circ = S^\circ(SO_3,g) - S^\circ(SO_2,g) - 0.5S^\circ(O_2,g) = -196.598 JK^{-1}mol^{-1}$$

$$\Delta_{r7}G = -73.55 \text{ kJ/mol} = -40114 \text{ J/mol}$$

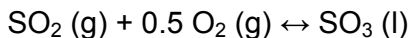$$K_7 = e^{\frac{-\Delta G}{RT}} = e^{\frac{40114}{8.314 \cdot 473.15}} = 2.68 \cdot 10^4 \;\rightarrow\; [\text{reagents}] << [\text{products}]$$

There is an excess of SO_2, so all O_2 is converted into SO_3, and all SO_3 dissolves in water (as in part 2), so pH is the same; **pH = 0.08564**

PART 4

There is an excess of O2, so all SO2 is reacted

$$SO_2 \text{ (g)} + 0.5\, O_2 \text{ (g)} \leftrightarrow SO_3 \text{ (l)}$$

$$n(SO_3, l \text{ and } g) = n(SO_3) = n(SO_2) = \frac{p(SO_2)V}{RT} = \frac{0.3p(total)V}{RT} = \frac{0.3 \cdot 101325 \cdot 5 \cdot 10^{-3} mol}{8.314 \cdot 298.15} =$$
$0.0613 \; mol$ if pressure is 1 atm;

If pressure (Standard) is 1 bar = 100kPa n(SO_3) = 0.0605 mol

All SO_3 dissolves in 1.00 L of water, so [H_2SO_4] = 0.0605 M

According to the reaction A, $[H^+]_0$ = (SO_3) = 0.0605 mol

	HSO_4^- (aq) $\leftrightarrow$	SO_3^{2-} (aq) +	H^+ (aq)	(B)
Initial	0.0605	0	0.0605	
Change	-x	+x	+x	
Final	0.0605 -x	x	0.0605+x	

$$K_5 = \frac{(0.0605 + x)x}{0.0605 - x} = 0.0125$$

x = 0.00920

$[H^+]$ = $[H^+]_0$ + x = (0.0605 + 0.00920)M = 0.0697 M

pH = 1.157

PART 5

H^+ concentration two times lower: $[H^+]$ = 0.13918M / 2 = 0.06959 M (similar to part 4).

By changing initial proportion of gases (the increase of O_2, the decrease of SO_2) the two times lower concentration of H+ can be reached.

H^+ concentration two times higher: $[H^+]$ = 2·0.13918 M = 0.2784 M
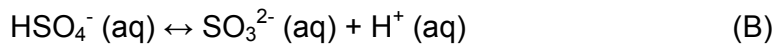
For the most acidic final solution, the iniatial proportion of gases should be 66.7 % SO2 and 33.3 % O2, then reaction SO_2 (g) + 0.5 O_2 (g) $\leftrightarrow$ SO_3 (l) occur, and:

$$n(SO_3, l \text{ and } g) = n(SO_3) = n(SO_2) = \frac{p(SO_2)V}{RT} = \frac{0.667p(total)V}{RT} = \frac{0.3 \cdot 101325 \cdot 5 \cdot 10^{-3} mol}{8.314 \cdot 298.15} =$$

$0.1345\ mol$ if pressure is 1 bar;

According to the reaction A, $[H^+]_o = (SO_3) = 0.1345$ mol

All SO_3 dissolves in 1.00 L of water, so $[H_2SO_4] = 0.1345$ M

$$\text{HSO}_4^- \text{ (aq)} \leftrightarrow \text{SO}_3^{2-} \text{ (aq)} + \text{H}^+ \text{ (aq)} \hspace{4cm} \text{(B)}$$

Initial	0.1345	0	0.1345
Change	-x	+x	+x
Final	0.1345 -x	x	0.1345+x

$$K_5 = \frac{(0.1345 + x)x}{0.1345 - x} = 0.0125$$

x = 0.01066

$[H^+] = [\,H^+]_o + x = (0.1345 + 0.01066)M = 0.1452\ M < 0.2784\ M$

If temperature is bigger than 45 C, reaction SO_2 (g) + 0.5 O_2 (g) $\leftrightarrow$ SO_3 (g) occur (like in part 3). The bigger temperature is, the smaller is K_5, therefore can't be reached the bigger amount of H^+ ions.

Thus, the hydrogen ions concentration two times bigger than in part 2 can be reached, but lower – can be (by changing initial proportion of gases).

Problem 2 (Estonia)

Bless you! (10 points)

Scheme 1

A   B   C

D   E   X
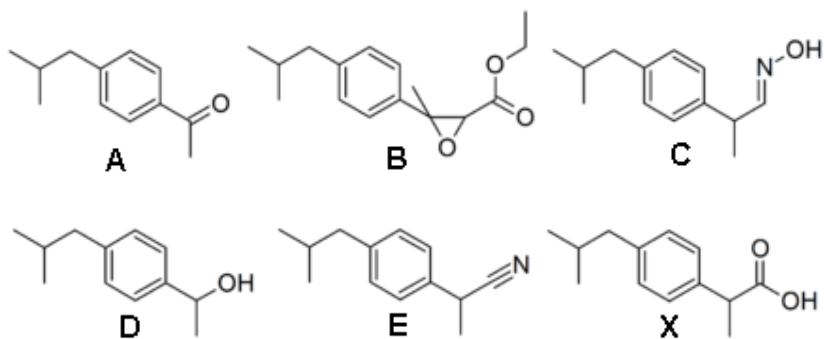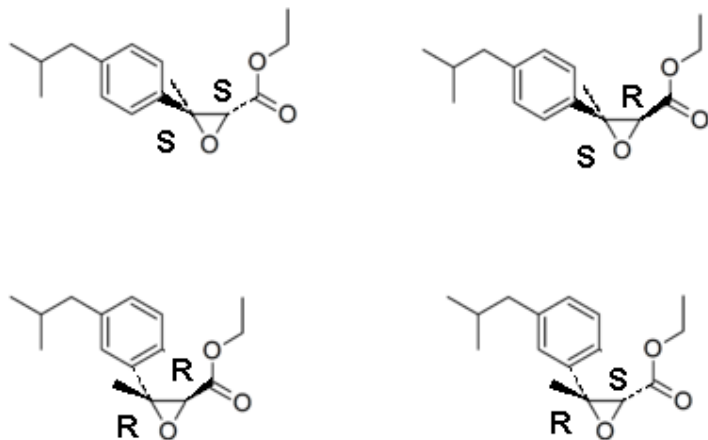
Scheme 2
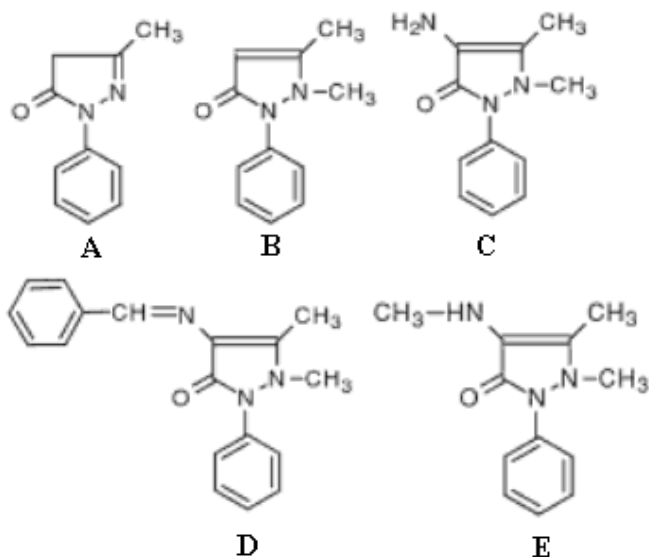
The question can be answered "no" as well as "yes". On the one hand, at room temperature, compounds such as the one mentioned in the question interconvert fast enough, so that two different isomers are not observed. On the other hand, two different isomers will exist at low temperatures. Both answers are correct, but no points should be allocated for the answer without proper explanation.

Problem 3 (Latvia)

Quantum organic chemistry (4 points)

Carotene has 22 π electrons . It has 11 HOMO orbitales and 12 LUMO orbitales.

Energy can be calculated from $E=n^2h^2/8mL^2$, where n number of electrons, h –Planc constant 6.63×10^{-34} Jxs, m – mass of electron 9.1×10^{-31} kg, L – electron distance in one dimensional box 3.17 nm.

Energy diference from LUMO to HOMO can be calculate $\Delta E=(12^2-11^2) h^2/8mL^2=1.38 \times 10^{-19}$ J.

Wavelength can be calculated from equation $\lambda=hc/\Delta E=1.44 \times 10^{-6}$ m.

Problem 4 (Estonia)

Chemistry of radioactive particles (8 points)

Unfotunaltely solution is provided in Russian. You may use google translate to understand it.

1.

$$^{1}_{0}n \rightarrow ^{1}_{0}p + ^{0}_{-1}e$$

$$^{99}_{43}Tc \rightarrow ^{99}_{44}Ru + ^{0}_{-1}e$$

$$^{204}_{82}Pb \rightarrow ^{200}_{80}Hg + ^{4}_{2}He$$

$$^{8}_{4}Be \rightarrow ^{4}_{2}He + ^{4}_{2}He$$

$$^{113}_{48}Cd \rightarrow ^{113}_{49}In + ^{0}_{-1}e$$

$$^{206}_{81}Tl \rightarrow ^{206}_{82}Pb + ^{0}_{-1}e$$

$$^{14}_{6}C \rightarrow ^{14}_{7}N + ^{0}_{-1}e$$

$$^{109}_{53}I \rightarrow ^{109}_{54}Sn + ^{0}_{-1}e$$

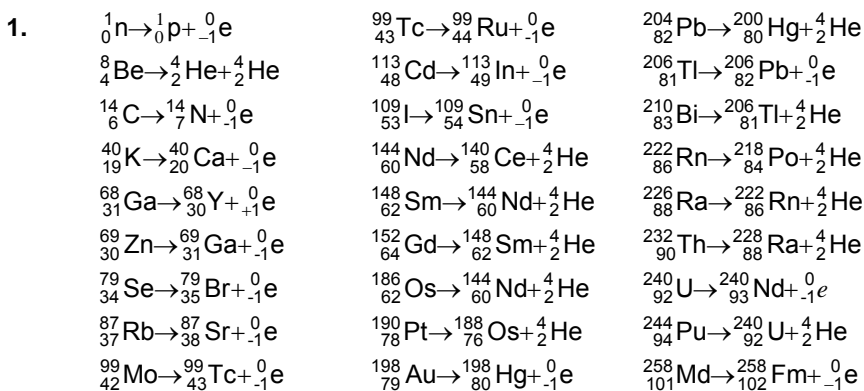$$^{210}_{83}Bi \rightarrow ^{206}_{81}Tl + ^{4}_{2}He$$

$$^{40}_{19}K \rightarrow ^{40}_{20}Ca + ^{0}_{-1}e$$

$$^{144}_{60}Nd \rightarrow ^{140}_{58}Ce + ^{4}_{2}He$$

$$^{222}_{86}Rn \rightarrow ^{218}_{84}Po + ^{4}_{2}He$$

$$^{68}_{31}Ga \rightarrow ^{68}_{30}Y + ^{0}_{+1}e$$

$$^{148}_{62}Sm \rightarrow ^{144}_{60}Nd + ^{4}_{2}He$$

$$^{226}_{88}Ra \rightarrow ^{222}_{86}Rn + ^{4}_{2}He$$

$$^{69}_{30}Zn \rightarrow ^{69}_{31}Ga + ^{0}_{-1}e$$

$$^{152}_{64}Gd \rightarrow ^{148}_{62}Sm + ^{4}_{2}He$$

$$^{232}_{90}Th \rightarrow ^{228}_{88}Ra + ^{4}_{2}He$$

$$^{79}_{34}Se \rightarrow ^{79}_{35}Br + ^{0}_{-1}e$$

$$^{186}_{62}Os \rightarrow ^{144}_{60}Nd + ^{4}_{2}He$$

$$^{240}_{92}U \rightarrow ^{240}_{93}Nd + ^{0}_{-1}e$$

$$^{87}_{37}Rb \rightarrow ^{87}_{38}Sr + ^{0}_{-1}e$$

$$^{190}_{78}Pt \rightarrow ^{188}_{76}Os + ^{4}_{2}He$$

$$^{244}_{94}Pu \rightarrow ^{240}_{92}U + ^{4}_{2}He$$

$$^{99}_{42}Mo \rightarrow ^{99}_{43}Tc + ^{0}_{-1}e$$

$$^{198}_{79}Au \rightarrow ^{198}_{80}Hg + ^{0}_{-1}e$$

$$^{258}_{101}Md \rightarrow ^{258}_{102}Fm + ^{0}_{-1}e$$

1.   **i)**   Формула для нахождения константы распада:

$$a = -\frac{dN}{dt} = \lambda N \Rightarrow \lambda = \frac{a}{N} = \frac{a}{N_A \cdot n} = \frac{a \cdot M}{N_A \cdot m} = \frac{3,70 \cdot 10^{10} \text{ Бк} \cdot 226 \text{ г/моль}}{6,02 \cdot 10^{23} \cdot 1,00 \text{ г}},$$

откуда, значение константы распада равно: <u>1,389·10⁻¹¹ с⁻¹</u>.

Период полураспада равен:

$$T_{1/2} = \frac{\ln 2}{\lambda} = \frac{0,693}{1,39 \cdot 10^{-11} c^{-1}} = 4,99 \cdot 10^{10} c = \underline{1580 \text{ лет}},$$

В справочнике можем найти значение: $T_{1/2}(^{226}_{88}Ra) = 1620$ лет.

ii) $$\lambda = \frac{\ln 2}{T_{1/2}} = 1,357 \cdot 10^{11} \text{ s}^{-1}$$

$$N = \frac{3,70 \cdot 10^{10} \text{ s}^{-1}}{1,357 \cdot 10^{11} \text{ s}^{-1}} = 2,727 \cdot 10^{21} \Rightarrow m = 1,024 \text{ g}$$

iii)   Формула хлорида радия $RaCl_2$. Его молярная масса равна 297 г/моль. Не трудно сосчитать:

$$a = \lambda N = \lambda \frac{m}{M} \cdot N_A =$$

$$= 1,357 \cdot 10^{-11} \text{ c}^{-1} \cdot \frac{1,00 \text{ г}}{297 \text{ г/моль}} \cdot 6,02 \cdot 10^{23} \cdot \frac{1000}{1 \text{ кг}} = \underline{2,75 \cdot 10^{10} \text{ Бк}}$$

Или 2,75·10¹³ Бк/кг.

iv)   Количество радия в начальный момент времени (1907 год):

$$n = \frac{m}{M} = \frac{1,00 \text{ г}}{226 \text{г} 26 \text{г/м}} = 0,00442 \text{ моль},$$

По закону радиоактивного распада:

$$n_t = n_0 e^{-\lambda tt} = 0{,}00442 \cdot e^{-1{,}39 \cdot 10^{-11} c^{-1} \cdot [(2010-1907) \cdot 365 \cdot 24 \cdot 3600 \, c]} = \underline{0{,}00423 \text{ моль}}.$$

v) масса распавшегося радия равна:
$$\Delta m = \Delta n \cdot M = (0{,}00442 - 0{,}00423) \text{ моль} \cdot 226 \text{ г/моль} = \underline{0{,}043 \text{ г}}$$

vi) Произведем следующие математические преобразования:
$$P_t = P_0 e^{-\lambda t} \Rightarrow \frac{P_t}{P_0} = e^{-\lambda t} \Rightarrow \text{логарифмируем} \Rightarrow \ln\frac{P_t}{P_0} = -\lambda t \Rightarrow \ln\frac{P_0}{P_t} = \lambda t,$$

откуда можно выражать λ и t, в нашем случае время:

$$t = \ln\frac{P_0}{P_t} \cdot \frac{1}{\lambda} = \ln\frac{100\%}{(100-99{,}99)\%} \cdot \frac{1}{1{,}39 \cdot 10^{-11} c^{-1}} = 6{,}63 \cdot 10^{11} c = \underline{2{,}10 \cdot 10^4 \text{ лет}},$$

Считается, что нуклид распадается полностью через время, равное 12 периодам полураспадов. Радай практически распадется в 23426 году.

3. **i)** Через двести дней активность будет равна:

$$a_t = a_0 e^{-\lambda t} = a_0 e^{\frac{-\ln 2 \cdot t}{T_{1/2}}} = 0{,}0100 \cdot 10^{-6} \cdot 3{,}7 \cdot 10^{10} \text{ Бк} \cdot e^{\frac{-0{,}693 \cdot 200 \cdot 24 \cdot 3600}{87{,}9 \cdot 24 \cdot 3600}} = \underline{76{,}5 \text{ Бк}}$$ **ii)** Следует обратить внимание, что активность установленная прибором измеряется в расп./мин.

Чувствительность прибора равна:

$$\%(\Pi) = \frac{2600 \text{ dpm}}{76{,}5 \cdot 60 \text{ dpm}} \cdot 100\% = \underline{56{,}6\%}$$

iii) По закону радиоактивного распада, масса оставшегося в образце $^{51}_{24}Cr$ будет равна:

$$m_t = m_0 e^{-\lambda t} = 100 \text{м}0 \cdot e^{\frac{-0{,}693 \cdot 7 \cdot 24 \cdot 3600}{27{,}8 \cdot 24 \cdot 3600}} = 84{,}0 \text{ мг}$$

активность $^{51}_{24}Cr$ массой 84,0 мг будет равна:

$$a = \lambda N = \lambda\frac{m}{M} \cdot N_A = \frac{\ln 2}{T_{1/2}}\frac{m}{M} \cdot N_A = \frac{0{,}693}{27{,}8 \cdot 24 \cdot 3600 \, c} \cdot \frac{0{,}0840 \text{ г}}{51{,}0 \text{ г/моль}} \cdot 6{,}02 \cdot 10^{23} =$$
$$= 2{,}86 \cdot 10^{14} \text{ Бк}$$

Счетчик пакажет активность, равную:

$$a_\Pi = a \cdot \%(\Pi) = 2{,}86 \cdot 10^{14} \text{ Бк} \cdot 0{,}566 = \underline{1{,}62 \cdot 10^{14} \text{ Бк}}.$$

iv) Распадаясь, хром испускает бета-частицы – электроны, масса которых принибрежительно мала, поэтому будем считать, что масса образца остается равной 100 мг. Масса оставшего хрома – 84,0 г.

$$\omega = \frac{84{,}0\text{м}4}{100\text{м}0} \cdot 100\% = \underline{84{,}0\%},$$

процентное содержание хрома равно 84,0%.

3. **i)** Количество радиоактивного калия-40 в 20 г калия, равно:

$$N = \frac{m(\text{калия}) \cdot \omega}{M} \cdot N_A = \frac{20 \text{ г} \cdot 0{,}000117}{40{,}0 \text{ г/моль}} \cdot 6{,}02 \cdot 10^{23} = 3{,}52 \cdot 10^{19} \text{ атомов},$$

Активность такого количества калия-40 равна:

$$a = \lambda N = \frac{1}{\tau} \cdot N = 3{,}52 \cdot 10^{19} \cdot \frac{1}{1{,}843 \cdot 10^{9} \cdot 365 \cdot 24 \cdot 3600 \text{ с}} = \underline{606 \text{ Бк}}.$$

ii) **Students answer: there is about 140 g of potassium in human body of an average weight, 98% in cells, where the radioactive potassium potassium-40 decomposes and release harmful particles, but cells have adaptations to prevent the damage of DNA or to repair it, so that mutations wouldn't occur. The amount of potassium in a body is 7 times higher than that is given in the problem. It is also isolated in oil and put in glass, so that released beta-particles are consumed by the environment. Also abundance of potassium-40 is low and it's half-life is long giving us very low radioactivity overall.**

iii) **Strontium-90 is a radioactive isotope that emits harmful beta particles with hight energy. Due to the similarity with calcium in chemical behaviour, ^{90}Sr replaces calcium in teeth, bone surface and marrow. This may cause cancer of bone and nearby tissues, as well as leukemia.**

iii) $t = 5{,}04$ years.