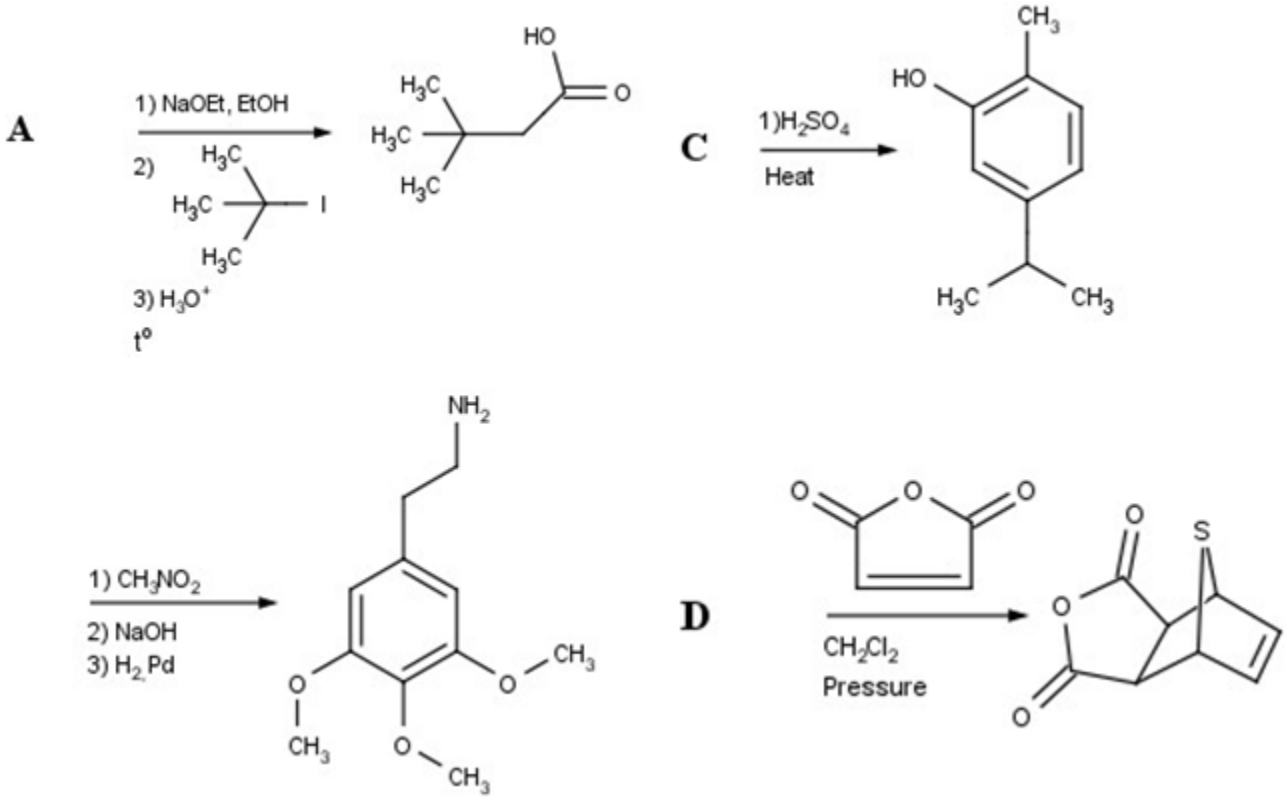
PART II.d – Organic chemistry

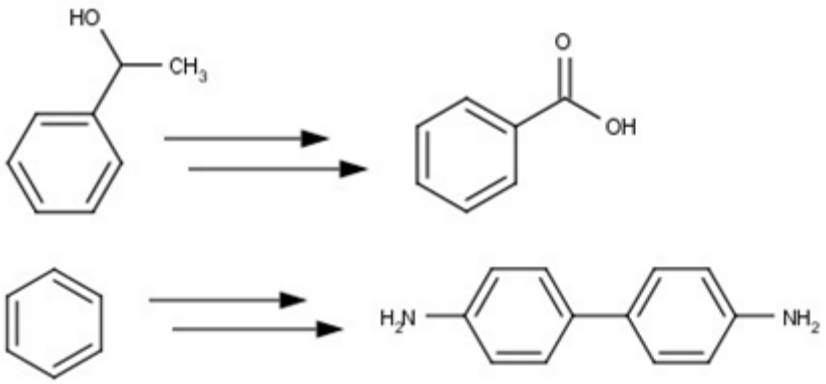
Problem 1

A little bit of organic chemistry

1. Determine and write the structure of **A**, **B**, **C**, **D** starting compounds. Write reaction mechanisms with **A** and **B** compounds.

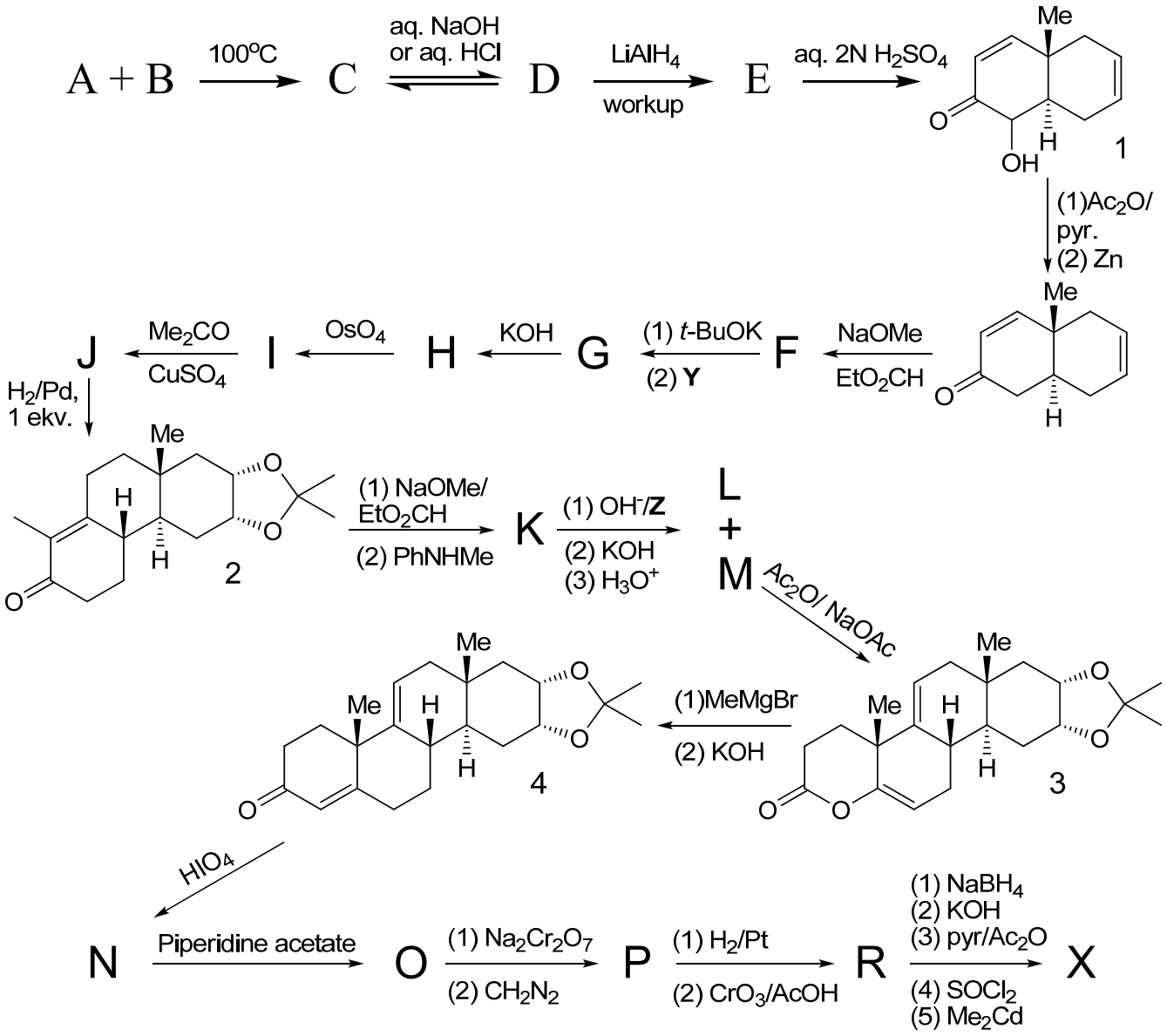


2. Provide plausible synthesis plans whit reagents and intermediate compounds.



Problem 2

Lord of the rings



A: $C_8H_8O_3$

^{1}HNMR (600 MHz, $CDCl_3$) δ 2.26 (d, *J*=0.8 Hz, 3H), 3.7 (s, 3H), 5.98 (s, 1H), 6.84 (d, *J*=0.8 Hz, 1H)

^{13}CNMR (150 MHz, $CDCl_3$) δ 14.3, 57.1, 106.7, 132.6, 143.7, 159.9, 182.0, 185.8

B: C_4H_6

^{1}HNMR (600 MHz, $CDCl_3$) δ 5.06 (dd, *J*=9.2 Hz, 2.3 Hz, 2H), 5.16 (dd, *J*=14.8 Hz, 2.3 Hz, 2H), 6.25 (dd, *J*=14.8 Hz, 9.2 Hz, 2H)

^{13}CNMR (150 MHz, $CDCl_3$) δ 115.2, 135.4

Y: C_5H_8O

^{1}HNMR (600 MHz, $CDCl_3$) δ 1.21 (t, *J* = 6.7 Hz, 3H), 3.04 (q, *J* = 6.7 Hz, 2H), 6.23 (dd, *J* = 16.8, 9.3 Hz, 1H), 6.10 (dd, *J* = 9.3, 2.8 Hz, 1H), 6.28 (dd, *J* = 16.8, 2.8 Hz, 2H)

^{13}CNMR (150 MHz, $CDCl_3$) δ 8.4, 34.3, 124.9, 133.2, 200

Z: C_3H_3N

^{1}HNMR (600 MHz, $CDCl_3$) δ 5.52 (dd, *J* = 15.3 Hz, 10.0 Hz, 1H), 5.88 (dd, *J* = 10.0, 2.1 Hz, 1H), 6.01 (dd, *J* = 15.3, 2.1 Hz, 1H)

Notes:

1. L and M compounds have identical molecular formulas, weigh and produce very similar HRMS spectra.
2. Me_2Cd converts acid chloranhydrides into corresponding methyl ketones.
3. Some of the reactions are stereospecific or highly stereoselective, don't forget that. You are required to provide formulae with correct absolute configuration.

Tasks:

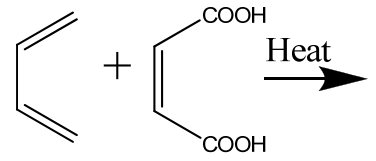
1. Determine the structures of compounds A – R and X.
2. Provide reasonable mechanisms for the given conversions: E → 1, G → H, 2 → K, 3 → 4
3. Determine the number of stereogenic centers in compound 4, assign absolute configurations to each of them.
4. Assign chemical shifts and coupling constants to each hydrogen of the compounds A and Y. Which signals do you expect to disappear after exposure to excess of D_2O/NaOD solution?
5. How are the compounds L and M called in relation to each other?
6. Many biologically active compounds share the ring system of compound X. Name the group of those compounds.

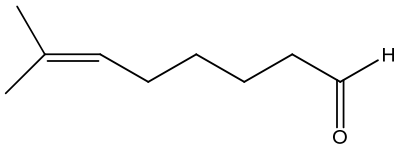
Problem 3

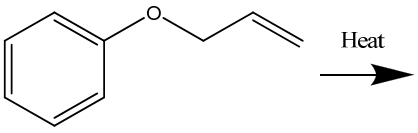
Pericyclic reactions

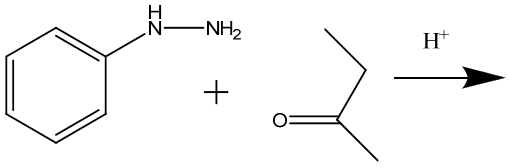
Diels –Alder, Alder ene,Claisen, Wittig, Fisher indole

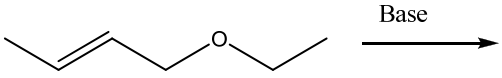
1. What's the main difference between pericyclic reactions and substitution/elimination reactions?
2. Name three main types of pericyclic reactions?
3. Here you have 5 examples of named pericyclic reactions. Write the products and give names to these reactions.

1. 

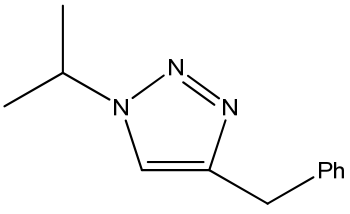
2. 

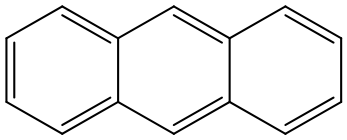
3. 

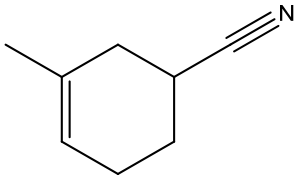
4. 

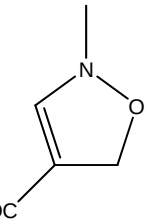
5. 

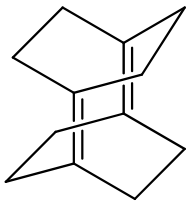
4. 5 different compounds are given, recognize which of them was made using pericyclic reactions. Give names of those reactions.

1. 

2. 

3. 

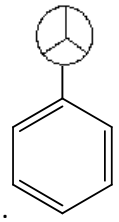
4. 

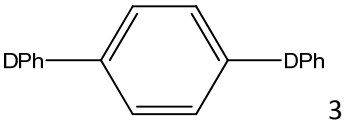
5. 

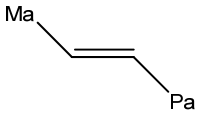
5. Butadiene reacts with itself when heated to yield compound A. Under presence of catalyst the rection gives product B. Draw structures of A and B an explain why A is formed instead of B when butadiene is heated.

6. Compound A gives this HNMR spectra: 2.90(2H, t), 6.40(2H, m), 6.50(2H, m). Salt of compound A(BF_4) is reduced to coumpound B. B also could be made from A using NaH in THF and I_2 with CuBr and Me_2S. B reacts with dimethyl but-2-ynedioate to yield products C and D.Then an in molecular reaction occurs in both C and D to give E and F respectively. Finaly E and F reacts with NaOH in water to give final products G and H.
   Draw the structural formulae for compounds A-H. Write mechanisms for reactions B-> C, C-> E .

7. And now the fun part :D. Just give the „systematic“ names to these compounds.

1. 

2. 

3. 

PROBLEM AUTHORS:

Donatas Ramaška (2nd year BSc student, Vilnius University, Department of Chemistry)
Vidmantas Bieliūnas (2nd year BSc student, Vilnius University, Department of Chemistry)
Karolis Goda (1st year BSc student, Vilnius University, Department of Chemistry)

PART II.b – Inorganic chemistry

Problem 1

a) $NH_4ClO_4 + HNO_3 = N_2O + HClO_4 \cdot 2H_2O$; sum = 4

b) $36NH_4ClO_4 + 38HNO_3 + 8HCl = 36HClO4 \cdot 2H_2O + 37N2O + 4Cl_2 + 5H_2O$; ratio = 4/36 = 1/9

$36NH_4ClO_4 + 44HNO_3 + 8HCl = 36HClO_4 \cdot 2H_2O + 36N_2O + 4Cl_2 + 8NO_2 + 8H_2O$; ratio = 4/36 = 1/9

Problem 2

Complex compounds

to be prepared

Problem 3

Crystal structure

PC:

$$a = 2r_X$$

$$\rho = \frac{M_X}{N_A \cdot a^3} = \frac{M_X}{N_A \cdot 8r_X^3} \Rightarrow M_X = \rho \cdot N_A \cdot 8r_X^3$$

$$M_X = 9.196 \cdot 10^6 \ \tfrac{g}{m^3} \cdot 6.02 \cdot 10^{23} \ \tfrac{1}{mol} \cdot 8 \cdot \left(1.68 \cdot 10^{-10}\right)^3 \ m^3 = 210 \ \tfrac{g}{mol}$$

BCC:

$$a = 4r_X / \sqrt{3}$$

$$\rho = \frac{2M_X}{N_A \cdot a^3} = \frac{2M_X}{N_A \cdot \left(\frac{4}{\sqrt{3}}\right)^3 \cdot r_X^3} \Rightarrow M_X = \tfrac{1}{2}\rho \cdot N_A \cdot \left(\tfrac{4}{\sqrt{3}}\right)^3 \cdot r_X^3$$

$$M_X = \tfrac{1}{2} \cdot 9.196 \cdot 10^6 \ \tfrac{g}{m^3} \cdot 6.02 \cdot 10^{23} \ \tfrac{1}{mol} \cdot \left(\tfrac{4}{\sqrt{3}}\right)^3 \cdot \left(1.68 \cdot 10^{-10}\right)^3 \ m^3 = 162 \ \tfrac{g}{mol}$$

FCC:

$$a = 4r_X \Big/ \sqrt{2}$$

$$\rho = \frac{4M_{\mathrm{X}}}{N_{\mathrm{A}} \cdot a^3} = \frac{2M_{\mathrm{X}}}{N_{\mathrm{A}} \cdot \left(\frac{4}{\sqrt{2}}\right)^3 \cdot r_{\mathrm{X}}^3} \Rightarrow M_{\mathrm{X}} = \tfrac{1}{4}\rho \cdot N_{\mathrm{A}} \cdot \left(\tfrac{4}{\sqrt{2}}\right)^3 \cdot r_{\mathrm{X}}^3$$

$$M_{\mathrm{X}} = \tfrac{1}{4} \cdot 9.196 \cdot 10^6 \ \tfrac{\mathrm{g}}{\mathrm{m}^3} \cdot 6.02 \cdot 10^{23} \ \tfrac{1}{\mathrm{mol}} \cdot \left(\tfrac{4}{\sqrt{2}}\right)^3 \cdot \left(1.68 \cdot 10^{-10}\right)^3 \ \mathrm{m}^3 = 148 \ \tfrac{\mathrm{g}}{\mathrm{mol}}$$

XO:

$$\left(d_{hkl}\right)_{\max} = a \Big/ \sqrt{1^2 + 0^2 + 0^2} = a$$

$$a = d_{hkl} = \frac{\lambda}{2\sin\theta_{hkl}} = \frac{154 \text{ pm}}{2 \cdot 0.2365} = 326 \text{ pm}$$

$$\rho = \frac{M_{\mathrm{XO}}}{N_{\mathrm{A}} \cdot a^3} \Rightarrow M_{\mathrm{XO}} = \rho \cdot N_{\mathrm{A}} \cdot a^3$$

$$M_{\mathrm{X}} = 8.96 \cdot 10^6 \ \tfrac{\mathrm{g}}{\mathrm{m}^3} \cdot 6.02 \cdot 10^{23} \ \tfrac{1}{\mathrm{mol}} \cdot \left(326 \cdot 10^{-12}\right)^3 \ \mathrm{m}^3 - 16 \ \tfrac{\mathrm{g}}{\mathrm{mol}} = 171 \ \tfrac{\mathrm{g}}{\mathrm{mol}}$$

XO_2:

$$\left(d_{hkl}\right)_{\max} = a \Big/ \sqrt{1^2 + 1^2 + 1^2} = a \Big/ \sqrt{3}$$

$$a = \sqrt{3} \cdot d_{hkl} = \frac{\sqrt{3} \cdot \lambda}{2\sin\theta_{hkl}} = \frac{\sqrt{3} \cdot 154 \text{ pm}}{2 \cdot 0.2365} = 564 \text{ pm}$$

$$\rho = \frac{4M_{\mathrm{XO_2}}}{N_{\mathrm{A}} \cdot a^3} \Rightarrow M_{\mathrm{XO_2}} = \tfrac{1}{4}\rho \cdot N_{\mathrm{A}} \cdot a^3$$

$$M_{\mathrm{X}} = \tfrac{1}{4} \cdot 8.96 \cdot 10^6 \ \tfrac{\mathrm{g}}{\mathrm{m}^3} \cdot 6.02 \cdot 10^{23} \ \tfrac{1}{\mathrm{mol}} \cdot \left(564 \cdot 10^{-12}\right)^3 \ \mathrm{m}^3 - 2 \cdot 16 \ \tfrac{\mathrm{g}}{\mathrm{mol}} = 210 \ \tfrac{\mathrm{g}}{\mathrm{mol}}$$

XO_3:

$$\left(d_{hkl}\right)_{\max} = a \Big/ \sqrt{1^2 + 1^2 + 0^2} = a \Big/ \sqrt{2}$$

$$a = \sqrt{2} \cdot d_{hkl} = \frac{\sqrt{2} \cdot \lambda}{2\sin\theta_{hkl}} = \frac{\sqrt{2} \cdot 154 \text{ pm}}{2 \cdot 0.2365} = 460 \text{ pm}$$

$$\rho = \frac{M_{\mathrm{XO_3}}}{N_{\mathrm{A}} \cdot a^3} \Rightarrow M_{\mathrm{XO_3}} = \rho \cdot N_{\mathrm{A}} \cdot a^3$$

$$M_{\mathrm{X}} = 8.96 \cdot 10^{6}\ \tfrac{\mathrm{g}}{\mathrm{m}^3} \cdot 6.02 \cdot 10^{23}\ \tfrac{1}{\mathrm{mol}} \cdot \left(460 \cdot 10^{-12}\right)^3\ \mathrm{m}^3 - 3 \cdot 16\ \tfrac{\mathrm{g}}{\mathrm{mol}} = 477\ \tfrac{\mathrm{g}}{\mathrm{mol}}$$

X – $^{210}\mathrm{Po}$

PART II.c – Analytical chemistry

Problem 1

to be prepared

Problem 2

to be prepared

Problem 3

A – $(NH_4)_3AsS_4$

B – $(NH_4)_3SbS_3$

C – $PbSO_4$

D – $(BiO)_2SO_4$

E – $Bi(OH)_3$

F – Bi_2S_3

G – PoS

$S(PbS) = K_{sp}(PbS)/[S^{2-}]$

$S(CuS) = K_{sp}(CuS)/[S^{2-}]$

$S(PoS) = K_{sp}(PoS)/[S^{2-}]$

$S(Bi_2S_3) = \{K_{sp}(Bi_2S_3)\}^{1/2}/[S^{2-}]^{3/2}$

Järjekord: Bi^{3+}, Cu^{2+}, Po^{2+}, Pb^{2+}

$$[OH^-]_{low} = \sqrt[3]{K_{sp}/[Bi^{3+}]} = \sqrt[3]{10^{-39.5}/0.01} = 3.16\cdot10^{-13} \Rightarrow pH = 1.5$$

$$[OH^-]_{up} = \sqrt[3]{K_{sp}/[Bi^{3+}]} = \sqrt[3]{10^{-39.5}/(0.01\cdot0.0001)} = 6.81\cdot10^{-12} \Rightarrow pH = 2.8$$

http://profbeckman.narod.ru/Radium.files/Radium.pdf

PART II.a – Physical chemistry

Problem 1

1)-dN/dt=k*N, where N is initial number of radioactive isotope and k is a decay constant $k=\ln 2/t_{1/2}$
-dN/dt=k*N can be rearranged and integrated to give $N=N_0*e^{(-k*t)}$, where N is number of remaining atoms and N_0 is the initial number of atoms. Since $N_0=N+D$, where D is number of daughter atoms produced, we can say that $N_0=N+D=N*e^{(k*t)}$ and $D=N*(e^{(k*t)}-1)$.
^{87}Rb is our N and ^{87}Sr is our D. Therefore we can write $^{87}Sr=^{87}Rb*(e^{(k*t)}-1)$, however, rock initially contains some ^{87}Sr as well. So the equation we will use is
$^{87}Sr=^{87}Rb*(e^{(k*t)}-1)+ ^{87}Sr_0$. Than we normalize the equation with respect to ^{86}Sr and we get $^{87}Sr/^{87}Sr=^{87}Rb/^{87}Sr*(e^{(k*t)}-1)+ ^{87}Sr_0/^{87}Sr$ which can be used to plot a graph. $(e^{(k*t)}-1)$ will be the slope and can be used to calculate age t, and $^{87}Sr_0/^{87}Sr$ will be the intercept.
2)age is 3665Ma and initial $^{87}Sr_0/^{87}Sr$ is 0.7007
3)Because it would mean that all calculations and measurements have to be done in number of atoms or concentrations, however, it is very hard to measure these things practically with high precision. It is relatively very easy to measure ratios precisely.
4)The half life of this decay is too large and it would be impossible to obtain a decent accuracy. Rocks are usually dated with precision of 1-0.5Ma.

Problem 2

Random walk model

a) Пой той же логике, если после N шагов вы находитесь на расстояинии $s^2= x^2+ y^2+ z^2$, то сделав ещё шаг вы окажетесь расстоянии $s'^2= (x\pm 1)^2+ y^2+ z^2$ или

$s'^2= x^2+ (y\pm 1)^2+ z^2$ или $s'^2= x^2+ y^2+ (z\pm 1)^2$, что в среднем даёт $s'^2= x^2+ y^2+ x^2+ 1$ или, что то же $s'^2= s^2+ 1$. Следовательно $s^2= N$

Возможно решение с помощью векторов: если после N шагов ваше положение задано вектором **R**, то расстояние до начала координат равно **|R*R|** и сделав ещё один шаг, ваше новое положение будет задано вектором **R+r**, где **r** – случайный единичный вектор, тогда

|R'*R'|=(R+r)*(R+r)=|R*R|+2|R|*|r|*cos(θ)**+|r*r|**, где θ – угол между векторами **R** и **r**, чей косинус в среднем равен нулю, так что |R'*R'|=|R*R|+|r*r|=|R*R|+1 – опять среднее расстояние получается $s= \sqrt{(N)}$.

b) Если взять размер шага за l, то $s= \sqrt{(N)}l$. $s= \sqrt{(10000)}\cdot 0.154\ нм= 15.4\ нм$.

c) Полистирол содержит более объёмные боковые группы, которые сильнее препятствуют случайному направлению звеньев, чем в полиэтилене.

$$s(полиэтилен) = \sqrt{\frac{10000}{3.5}} \cdot (3.5 \cdot 0.154\ нм) = 28.8\ нм$$

$$s(полистирол) = \sqrt{\frac{N}{5}} \cdot (5 \cdot 0.154\ нм) = 34.4\ нм$$

Problem 3

In the quantum world

to be prepared

1 .	D
2 .	C
3 .	B
4 .	D
5 .	B
6 .	E
7 .	C
8 .	D
9 .	A
10 .	D
11 .	C
12 .	E
13 .	B
14 .	B
15 .	C
16 .	A
17 .	b
18 .	b
19 .	d
20 .	a
21 .	e
22 .	d
23 .	e
24 .	d
25 .	d
26 .	e
27 .	f
28 .	a
29 .	d
30 .	a
31 .	e
32 .	b
33 .	d
34 .	d
35 .	d
36 .	deleted
37 .	e
38 .	d
39 .	e
40 .	a
41 .	e
42 .	e
43 .	b
44 .	b
45 .	d
46 .	a
47 .	d
48 .	a
49 .	a
50 .	c
51 .	e
52 .	b
53 .	b
54 .	E
55 .	E
56 .	B
57 .	E
58 .	d
59 .	D
60 .	D
61 .	D
62 .	D
63 .	C
64 .	C
65 .	B
66 .	D
67 .	c
68 .	A

Instructions:

Write only one letter in each blue cell.

Fill personal information!

Part I

General chemistry

Information about participant:
(all fields are obligate)

Name:	Surname:	School year:	School:	City:

69 .	E
70 .	B
71 .	E
72 .	A
73 .	B
74 .	B
75 .	F
76 .	B
77 .	D
78 .	a
79 .	a
80 .	a
81 .	a
82 .	d
83 .	a
84 .	c
85 .	d
86 .	c
87 .	d
88 .	e
89 .	d
90 .	a
91 .	d
92 .	deleted
93 .	c
94 .	b
95 .	a
96 .	b
97 .	b
98 .	a
99 .	f
100 .	e