Best tasks form BCC

Chemistry for year and bit more!!!

Baltic chemistry competition has been provided to school students for last four years, but seems that year 2013 was last year for this competition. There are two main reasons for this, first of all interest from students were small, especially from students coming from Baltic States – Latvia, Lithuania and Estonia. Second reason, people who initiated this project back in 2008 are now involved in other activities.

Problems which were most interesting and may be bit strange and hard for students are selected as best problems of this competition. Enjoy these tasks and grade yourself as solutions are available at the end of this file.

Organizers of BCC

List of problems:

Problem 1	**Searching for secrets of Superman**
Problem 2	**Everyone loves spectra**
Problem 3	**Unknown highly flammable gas**
Problem 4	**Sulfur containing gases**
Problem 5	**Bless you!**
Problem 6	**Quantum observations due to laser cooling**
Problem 7	**Chemical rebuss**
Problem 8	**Some organic mechanisms**
Problem 9	**Quite symmetric product**
Problem 10	**Chanel N°5**
Problem 11	**Balance equation!**
Problem 12	**Redox reactions**
Problem 13	**Bad smell**
Problem 14	**Complex compound**

Problem 1   *Searching for secrets of Superman*

We all know what term *kryptonite* is related to; there is no clear definition for that. This material is usually shown as having been created from the remains of Superman's native planet of Krypton, and generally has detrimental effects on Superman and other Kryptonians. The name "Kryptonite" covers a variety of forms of the substance, but usually refers to the most common "green" form.

In one of "Supermans" episodes it is given as " element 126" in periodic table, which in reality corresponds to unbihexium/ekaplutonium and is called Kryptonium. Kryptonium has a radioactive half-life of 250 000 years.

1. *Calculate radioactive decay rate constant of Kryptonium.*
2. *Calculate, after what time only 10% of starting kryptonium will remain.*

In other episode there is another idea for what kryptonite is:
The chemical composition for the Kryptonite according to "Superman III" is Plutonium: 15.08%, Tantalum: 18.06%, Xenon: 27.71%, Promethium: 24.02%, Dialium: 10.62%, Mercury: 3.94%, Unknown: 0.57%.

3. *Calculate the empirical formula of Kryptonite in "Superman III", assuming that Dialium is a particle that contains two aluminum atoms, and the unknown element is hydrogen. Is there is a possible mineral for this formula? Substantiate your answer.*

Another version of what is kryptonite is mentioned in "Superman Returns". There are some screenshots from this movie that shows chemical composition and appearance of this mineral:
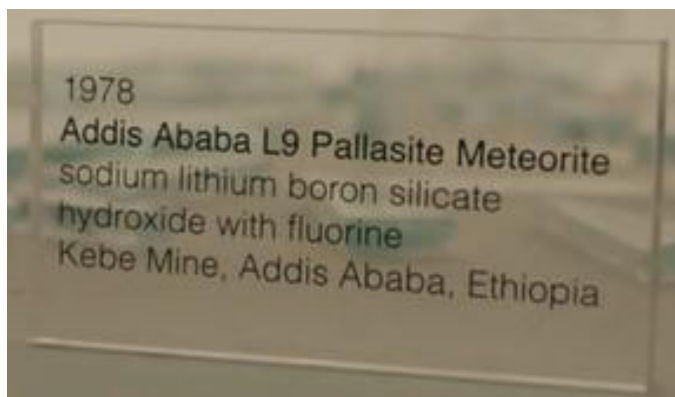
There was no mineral with such composition until the movie was presented, but after that, in November 2006, a mineral Jadarite was discovered in Serbia, Jadar Valley. Its chemical formula is *sodium lithium boron silicate hydroxide*: $LiNaSiB_3O_7(OH)$ or $Na_2OLi_2O(SiO_2)_2(B_2O_3)_3H_2O$. Although there is no fluorine in this mineral and it is white rather than green (see picture below), it made a small sensation due to its noticeable similarity with kryptonite. The jadarite fluoresces in a pinkish-orange color when exposed to UV light.

4. *Explain how fluorine can be bound in jadarite. In what other mineral same situation with fluorine is observed?*

Jadarite crystallizes in hard monoclinic crystals; space group is P2$_1$/c with lattice parameters a = 6.76421(7) Å, b = 13.8047(1) Å, c = 7.86951(9) Å, and β = 124.0895(5)° [1].

5. *Calculate the volume of jadarite unit cell and density of jadarite (in g/cm^3 if crystal structure [1] of it is shown on the right).*

The most intensive diffraction reflexes are shown in table (relative intensity, and d-spacing) [2].

d-spacing (Å)	Relative intensity
4.666	62
3.716	39
3.180	82
3.152	74
3.027	40
2.946	100
2.252	38
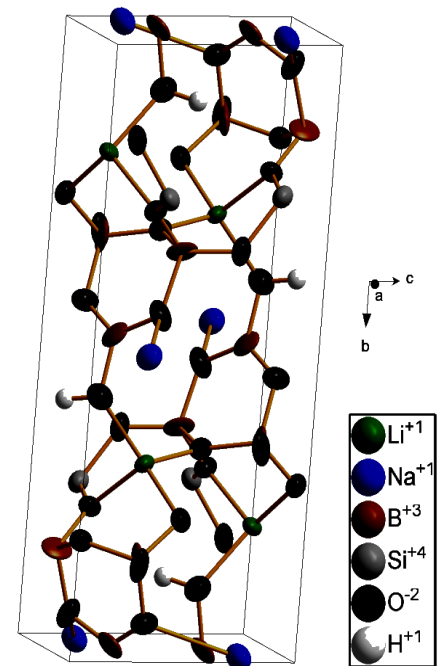
6. *Use Bragg's equation to calculate positions of 1st order diffraction reflexes in 2-Θ scale(^{o}) if Cu K$_\alpha$ radiation with the wavelength 0.15418 nm is used.*
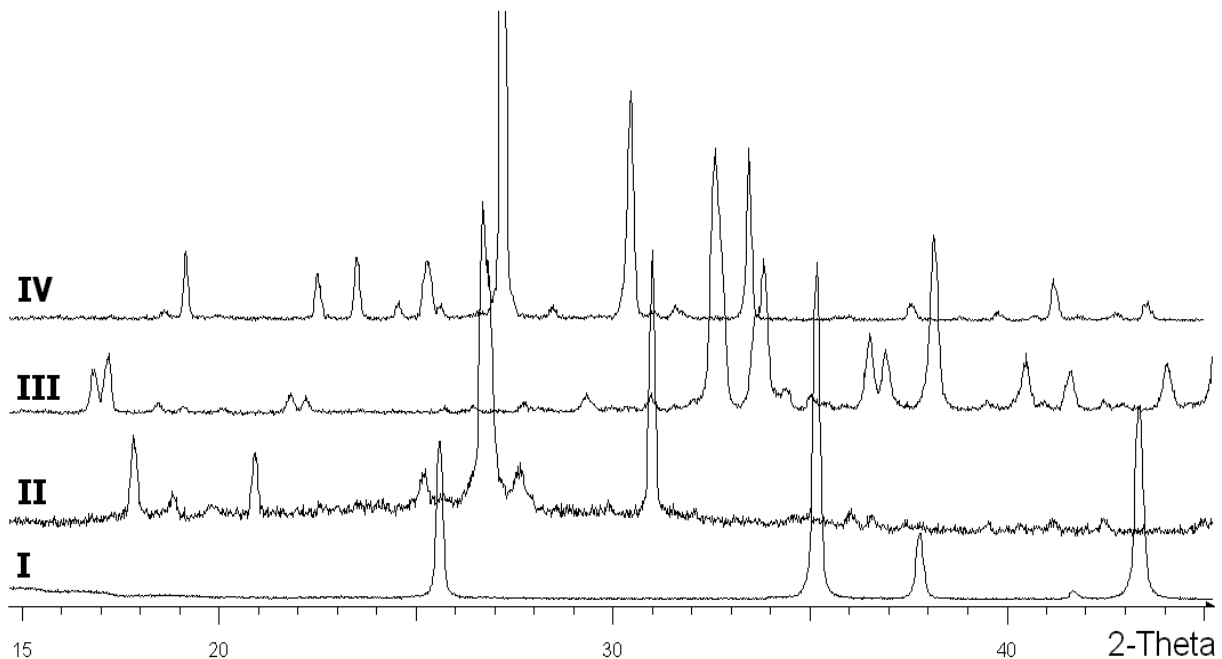
Possible jadarite PXRD patterns

3

7. *If it is possible from data given above, please, select the right powder diffraction (PXRD) pattern from figure in previous page which corresponds to jadarite. All patterns are done with Bruker D8 Advance diffractomter using Cu K_α radiation.*

Jadarite

Hydrated copper uranyl phosphate

There is a real mineral what is green and radioactive. Its chemical composition is: $Cu(UO_2)_2(PO_4)_2 \cdot (8-12)H_2O$ (hydrated copper uranyl phosphate).

On the right side of the page the decay chain of uranium-238 (main isotope of natural uranium) is shown. Assume, that process $^{238}U \rightarrow {}^{234}U$ is one step process with the rate constant the same as for $^{238}U \rightarrow {}^{234}Th$. In natural uranium nowadays the abundance of isotopes is $^{238}U - 99.2742\%$, $^{235}U - 0.7204\%$ and $^{234}U - 0.0054\%$.

8. *Write down all the reactions and classify them by the type of decay (alpha, beta or gamma).*

Alchemist Daniel Rebuss took 5.00 g of $Cu(UO_2)_2(PO_4)_2 \cdot (8-12)H_2O$ (hydrated copper uranyl phosphate) and determined that it loses 20.6% of mass by heating. Let's assign amount of uranium atoms in this ore with N_0.

9. Calculate N_0.

10. *Construct the graph to show how the amounts of ^{238}U, ^{234}U, ^{230}Th, ^{226}Ra and ^{222}Rn in this sample will change during the next million years.*

For your calculations you can use computer program "Kinet" from IChO 2007 (Moscow, Russia), program "Kinetics" (available in http://lu.lv/skoleniem/kim/konkurss/2009/, created by Mihails Arhangeļskis) or create your own calculation spreadsheet, for example, in *MS Excel*. Graphs can be saved as screenshots (use *Print Screen* button).
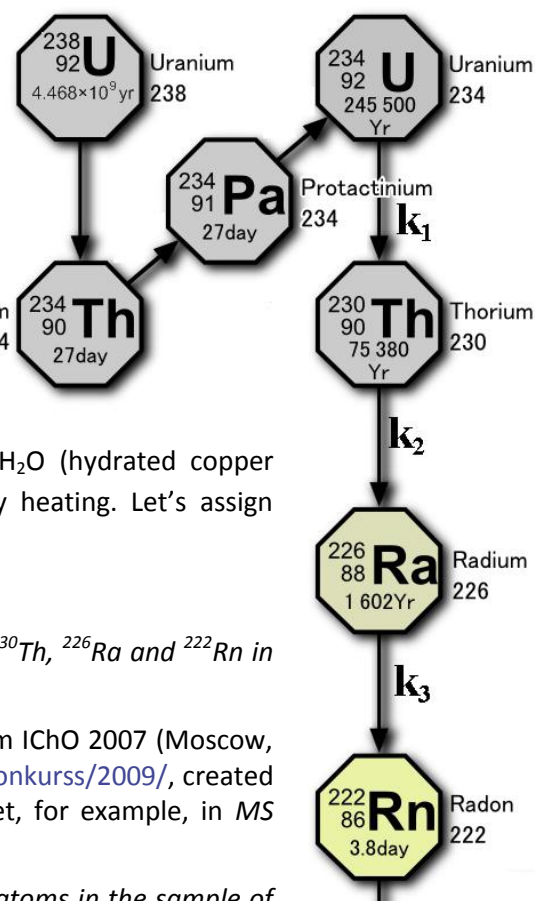
11. *Find the time t_{max1}, when there is maximum number of ^{230}Th atoms in the sample of Daniel Rebuss.*

Now, assume that you have pure ^{234}U isotope. In situations like this tone can use equations given below for calculation of the amount of particles in left (?) time:

$$N\left(^{230}Th\right) = N\left(^{234}U\right)_o \frac{k_1}{k_2 - k_1}\left(e^{-k_1 t} - e^{-k_2 t}\right)$$

And its derivative:

$$\frac{dN\left(^{230}Th\right)}{dt} = N\left(^{234}U\right)_o \frac{k_1}{k_2 - k_1}\left(-k_1 e^{-k_1 t} + k_2 e^{-k_2 t}\right)$$

4

12. Using formulas given above calculate the time t_{max2}, when there is the maximum number of ^{230}Th atoms in the sample.

13. Explain the differences between t_{max1} and t_{max2}!

Scientific references

1. **P. S. Whitfield, Y. Le Page, J. D. Grice, C. J. Stanley et.al.** LiNaSiB$_3$O$_7$(OH) - novel structure of the new borosilicate mineral jadarite determined from laboratory powder diffraction data, *Acta Cryst.* (2007). B**63**, 396-401

2. Web page: mindat.org - the mineral and locality database Available online: http://www.mindat.org/min-31570.html [07.07.2009.],Copyright Jolyon Ralph and Ida Chau 1993-2009

Problem 2   *Everyone loves spectra*

Colour of a firework or a flame in a flame test is an evidence of photon emission at frequency range 430–750 THz. Let's find out how emission happens in alkaline elements atoms.

When the electrons in the atom are excited (by heating for example), they jump to higher energy levels. As the electrons fall back down, energy is re-emitted, the wavelength of which refers to the discrete lines of the emission spectrum. The photon energy due to an electron transition between an exited atomic level k (of energy E_k) and a lower level i is $\Delta E = E_k - E_i = h\nu = hc/\lambda$, where ν is the frequency, and λ the wavelength. Since a photon carries energy and angular momentum (1 unit), any electronic transition from one allowed energy level to another must conserve energy and angular momentum for the atom-photon system. These restrictions are known as selection rules and they are, $\Delta S = 0$, $\Delta L = \pm 1$, and $\Delta J = 0, \pm 1$, with $J = 0$ to $J = 0$ forbidden. Allowed transition between electronic states in alkaline elements atoms obeys these selection rules.

S   P   D

3d

3p

3s

2p

2s

Energy level diagram
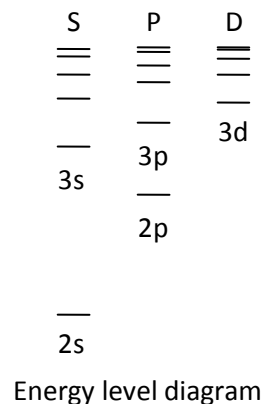
1. *Schematic presentation of energy levels – energy level diagram, is shown. Mark allowed transitions by arrows which lead to 2s and 2p configurations.*

All the allowed transitions may be easily calculated, if electronic configuration energies are known. Persistent lines in the visible spectrum of alkaline elements mainly due prior to transitions between np^1, $(n + 1)p^1$, and ns^1 configuration. The energy of corresponding levels of an upper electron may be obtained by: $E = -13.6 \cdot Z_{eff}^2 / n^2$, where Z_{eff} is the effective nuclear charge ($Z_{eff} < Z$), and n is the principal quantum number. Value of Li ionization energy (5.3917 eV) may be used to estimate $Z_{eff}(2s)$. Z_{eff} value for an electron on 2p and 3p levels in Li atom is 0.25 and 0.75 units lower than $Z_{eff}(2s)$, respectively. $Z_{eff}(ns)$ in other alkaline elements atoms increased by 0.485 in the transition to the next period. Similarly $Z_{eff}(np)$ and $Z_{eff}((n + 1)p)$ increased by 0.389 and 0.114.[1]

2. *Calculate photon wavelength due to an electron transition between np or (n + 1)p and ns levels of alkaline elements from Li to Cs.*

Calculated values may be now used to predict the colours of the alkali compounds in firework or flame. Assume, that calculated values are differ from experimental data by ±100 nm in average except for lithium.

3. *In visible spectra of Li is another persistent line (610 nm). Which transition does it belong to?*

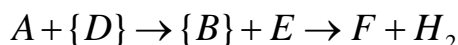[1] These simplified data were adjusted based on photon wavelength values from the experimental spectra.
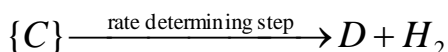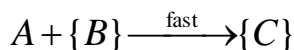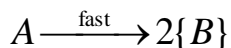
4. *Compounds of which alkali elements give colour to yellow, red and violet firework?*

More information about this problem: http://eko.olunet.org/2010/01/15/lost-in-translation/

Problem 3   Unknown highly flammable gas

Compound **A** is a colorless highly flammable gas containing 21.7% of Hydrogen by mass (use atomic masses with one decimal place). It undergoes pyrolysis at temperatures above $100^{o}C$. The process is very complicated, but the first steps can be described by the following equations:

$$A \xrightarrow{\text{fast}} 2\{B\}$$

$$A + \{B\} \xrightarrow{\text{fast}} \{C\}$$

$$\{C\} \xrightarrow{\text{rate determining step}} D + H_2$$

$$\{B\} + \{D\} \rightarrow E$$

$$A + \{D\} \rightarrow \{B\} + E \rightarrow F + H_2$$

Compounds in brackets {} are unstable intermediates.

1) What is compound **A**? Draw its structure and describe the bonding in its molecule.
2) Determine the formulae of compounds **B – F**.
3) At room temperature **B** dimerises into **A**. Why does not **B** exist in monomer form?

Problem 4   Sulfur containing gases

A 5.00 L closed container was filled with SO_2 (70% of total volume) and O_2 (30% of total volume) gases, the temperature inside the container was kept at 25°C.

$SO_2 + 0.5\ O_2 \rightleftharpoons SO_3$ reaction occurs at 25°C.

1. What will be the final volume of the O_2 in that container after the equilibrium is reached?

1.00 L of water was added into the same container keeping it still closed.

2. Write the reaction that occurs upon the addition of water? What is the pH of the resulting solution?
3. What would be the pH of the solution if the temperature inside the container (during the addition of the gases??) would be at 200°C? After adding water the solution is cooled to 25°C.
4. What would be the pH of the solution if the initial proportion of gases is 30 % (SO_2) and 70 % (O_2) of the total volume (at 25°C)?
5. Is it possible change concentration of hydrogen ions in solution to be two times higher or lower than in part 2 by changing temperature or initial proportion of gases? If so then how? Show the calculations.

	$\Delta_f H^{o}$/ (kJ mol^{-1})	S_m^{o}/ (J mol^{-1} K^{-1})
SO_2	-296.83	248.22
SO_3	-395.72	256.76
O_2	0	205.138

All required constants can be found online or in handbooks. References should be given to the source of information.
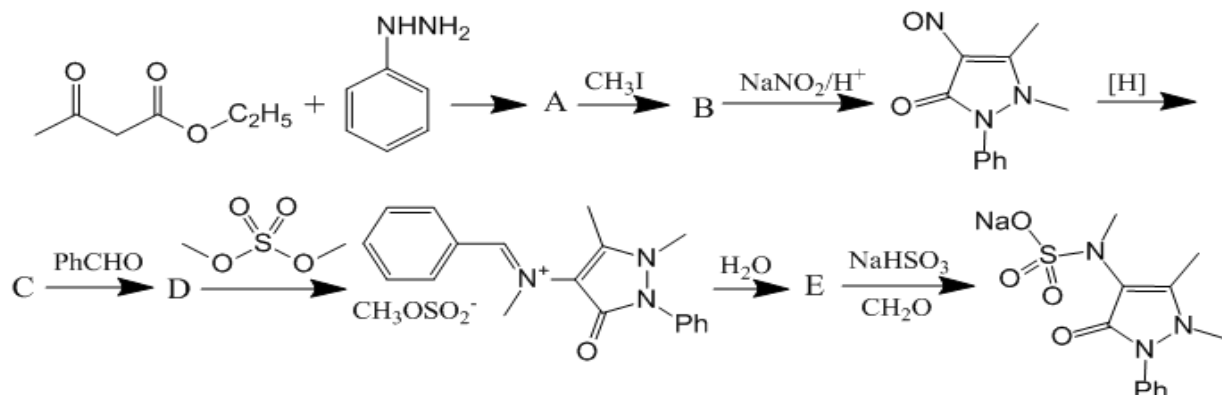
Problem 5   Bless you!

If too many drugs are provided against one illness, then it means that this illness cannot be healed.
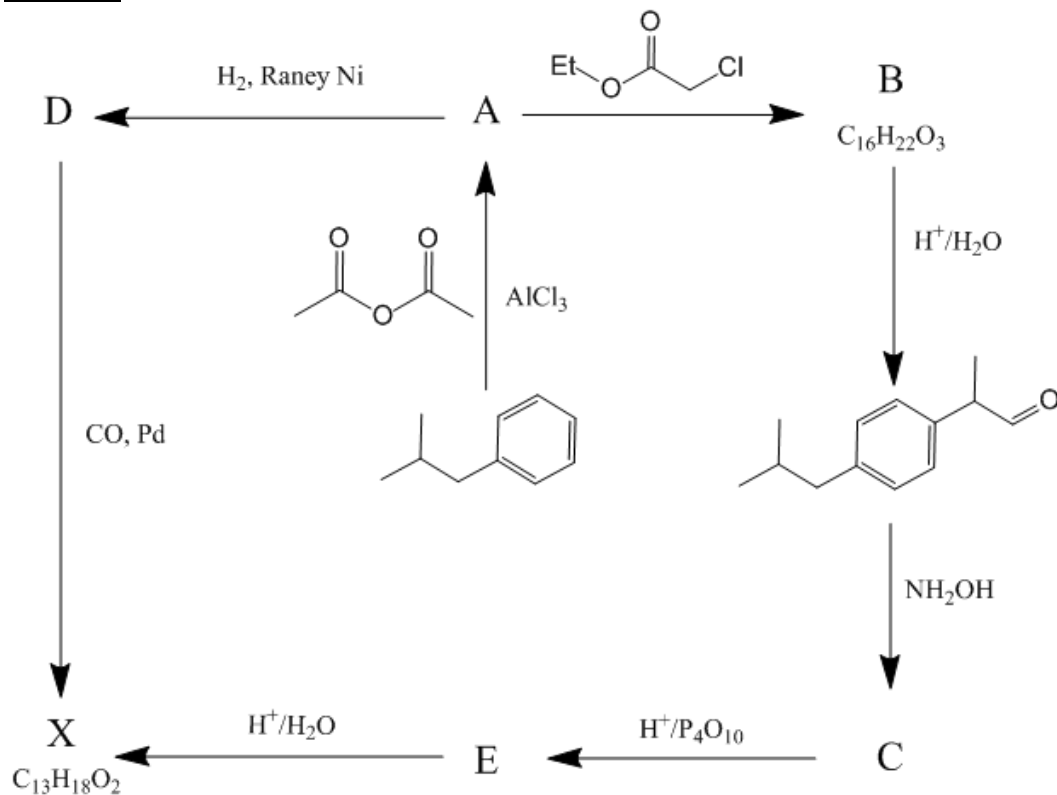
Anton Chekhov

Scheme 1

NHNH$_2$

ON

CH$_3$I

NaNO$_2$/H$^+$

[H]

A

B

Ph

C$_2$H$_5$

+

PhCHO

NaO

C

D

CH$_3$OSO$_2$$^-$

H$_2$O

E

NaHSO$_3$

CH$_2$O

Ph

Ph

Write the structures for compounds A-E.

Do you agree that in case when nitrogen atom carries three different substituents it is chiral, because of its lone electron pair that plays the role of the forth substituent? Why?

Scheme 2

H$_2$, Raney Ni

Et

O

Cl

B

C$_{16}$H$_{22}$O$_3$

D

A

H$^+$/H$_2$O

AlCl$_3$

CO, Pd

NH$_2$OH

X

H$^+$/H$_2$O

E

H$^+$/P$_4$O$_{10}$

C

C$_{13}$H$_{18}$O$_2$

Write the structures for compounds A-E, X.

Write down the structures for all of the compound B stereoisomers and assign configurations at their stereocenters.

Problem 6   *Quantum observations due to laser cooling*

All the elementary particles can be divided into two groups: bosons and fermions. The main difference between them is that several bosons can occupy the same quantum state, whereas fermions cannot due to Pauli exclusion principle. A decent chemist should already have understood (if he had not known it earlier) that electrons are fermions, because their spin is ½ just as the spin of neutrons and protons. The easiest way to determine whether composite particles, eg nuclei, atoms, are fermions or bosons, is to calculate the number of fermions in a particle. If it is even, then the particle is a boson, otherwise it is a fermion. Thus, the ^{4}He atom is a boson as well as the nucleus of ^{12}C.

In 2001, the Nobel Prize in Physics was given to Eric Cornell and Carl Wieman from University of Colorado at Boulder, and Wolfgang Ketterle from MIT for achieving the so-called Bose-Einstein condensate (BEC) - a state of matter, where quantum properties can be observed at macro scale. Currently, one of the many research trends in BEC is an effortto **observe** how the chemical reactions are happening in such state.

The first two scientists used the monatomic gas of ^{87}Rb atoms, the third - worked with monatomic gas of ^{23}Na atoms.

1. *Why ^{87}Rb and ^{23}Na atoms are bosons, despitetheir mass numbers beingcertainly odd (noteven)? Can you state the simplest method fortelling if the atom is a boson?*

The main problem of getting BEC is that the atoms have to be cooled down to temperatures near the absolute zero, because then we can assume that all the particles collapse into the lowest energy state and become indistinguishable.

Nowadays scientists usually use laser cooling. To understand how it works, first we have to remember that light is also made of matter (photons), which can hit an atom similarly as tennis balls can hit a bowling ball going in an opposite direction and eventually stop it. Suppose that we have confined atoms, which we want to cool down, in one dimension. Then, we need two lasers in total: one that hits the atoms going forward and the other thathits the atoms going back.

2. *How many lasers do we need to cool atoms in three dimensions?*

3. *Calculate the average translational kinetic energy of a monoatomic ideal gas atom of ^{87}Rb and ^{23}Na at 25.00℃.*

While cooling ^{87}Rb, scientists managed to achieve an impressive temperature of **170.0nK**. Due to the very weak interaction in BEC, the kinetic theory of gases still works pretty well at such temperatures.

4. *What is the root mean square speed of rubidium atoms at such temperature?*

To cool the atoms, the wavelength of the laser light is adjusted to correspond to the difference between the most possible excitation and the ground states. The commonly used wavelength of the laser beam used for cooling ^{87}Rb is 780.0nm at 25°C.

5. *Calculate the corresponding energy of a laser beam of 780.0nm.*
6. *Which electron excitation does it correspond to?*

In real laboratory laser cooling, the Doppler Effect has to be taken into account as well. Usually the frequency of the laser is lowered and then only the atoms going in opposite direction of the laser beam are slowed down.

7. *Show how the formula for calculating the Doppler Shift in frequency used for laser cooling is derived:*

$$f_{laser} = \frac{f_{atom}}{\left(1+\frac{v_{atom}}{c}\right)}$$

8. *What is the change in frequency of the laser due to the Doppler Effect in this transition? This change is also called detuning.*
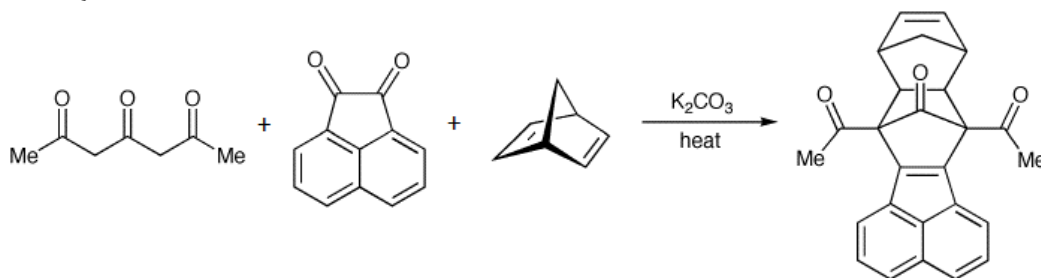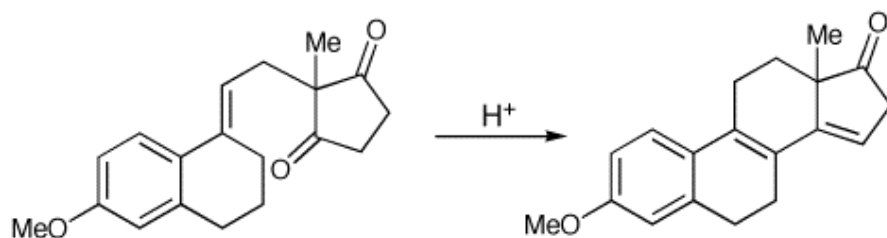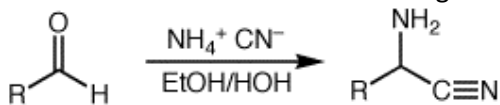
Problem 7 — Chemical rebuss

A yellow and very poisonous chemical substance **A** is sometimes said to belong to the same group of binary polyatomic compounds as substances **L** and **M**. It can be prepared by reacting two concentrated acids **B** and **C**. Yellow gas **E** and water are produced as a byproduct. Although the mixture of these two acids has been known for quite some time, there reaction product **A** was described only in 1831. Alternative production method for **A** would be a reaction between gasses **E** and **D**, which doesnot produce any byproducts. However, this reaction is reversible at high temperatures. Gas **D** is produced by reacting a reddish transitional metal **I** with diluted acid **C**. If you use concentrated acid in this reaction you would get brown gas **N** instead of **D**. A blue salt **J** is produced in both cases. Gas **N** reacts with water to produce acids **C** and **F** simultaneously. Acid **F** upon reacting with acid **G** produces compound **H,** which in turn reacts with acid **B** to give compound **A** and acid **G**. Compound **H** canbe considered as an anhydride of both acids. Gas **E** is made in small quantities by reacting **B** with potassium permanganate. This gas can also be used to produce **L** in a reaction with a sodium salt of a weak acid **K**, which has a faint almond smell. Compound **M** is produced by thermal decomposition of a mercury (II) salt of acid **K** and it is symmetrical. Acid **G** upon reacting with barium chloride solution gives white precipitate. In air, gas **D** is oxidized to **N.**

1. Identify compounds **A-N**
2. A 2.0 L container was filled with 1molof gas **A** at 400K temperature. Calculate the concentrations of **A**, **D**, and **E** at the equilibrium point.
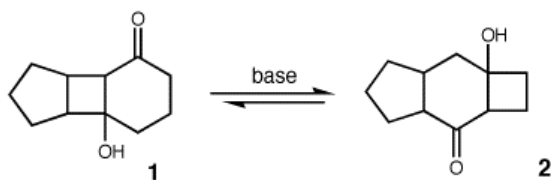3. At which temperature the molar fraction of**A** equals to 0.01?

Problem 8 — Some organic mechanisms

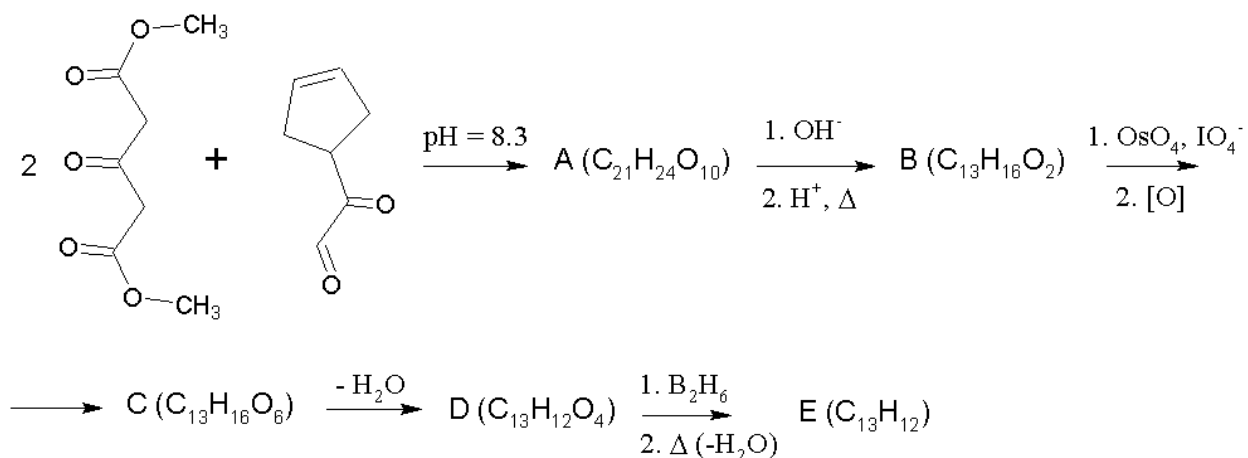Wright plausible mechanisms for the following reactions:

Ketones **1** and **2** are readily interconverted upon treatment with base. Write mechanism which explains following transformation.

Problem 9 *Quite symmetric product*

Compounds **A**-**C** possess a mirror symmetry while substances **D** and **E** are even more symmetrical.

Write the structures of compounds **A-E**.

Problem 10 *Chanel №5 (not the same problem as in BChO)*

In 1937 proposed theory about how the smell works proposes that nose reacts to vibrations of different frequencies, just like our eyes or ears do.

1) *How does the nose react to frequences and is able to identify so many different fragrances?*

Since you already know how materials create the sense of smell,

2) Why some volatile substances does not have smell?

This theory makes parfumers work quite easy. Once the mechanism is understood, any fragrance and smell can be made synthetically to such accurate that human nose is unable to distinct original smell from artificial one. Now I suggest you would try on beign parfumer.

3) Identify spectra and the compound. Offer three more compounds that would have essentialy the same smell as the given. Also provide its synthesis pathways using alkanes as starting materials.
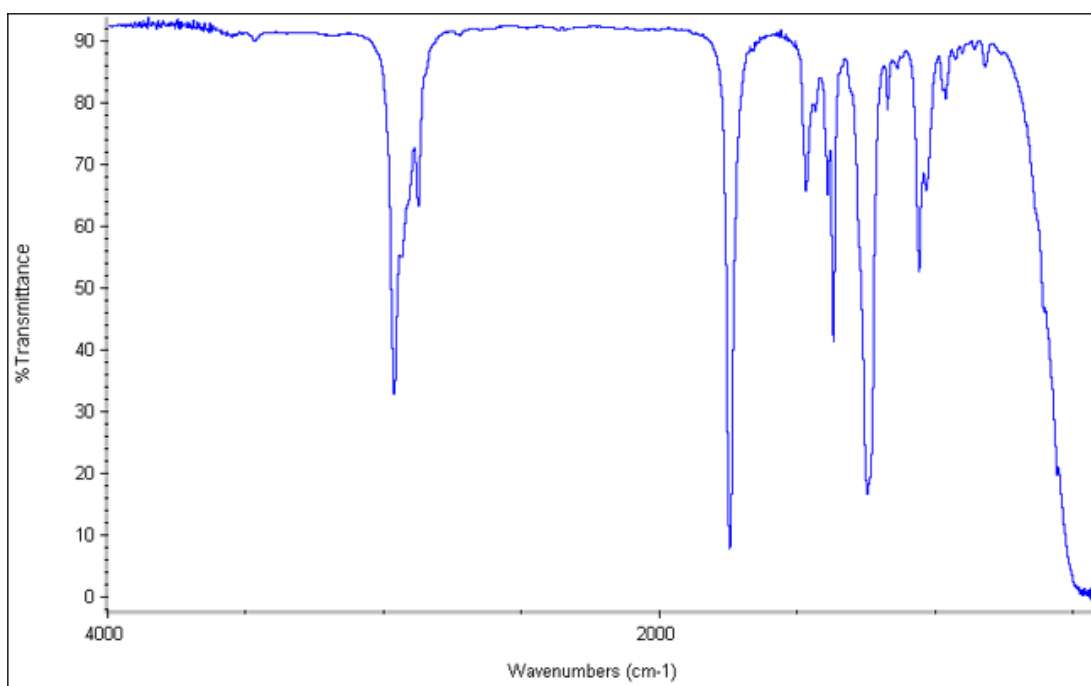

Even if this sounds very simple it gets more complicated when we are creating perfumes. They ussually have complex smells with different notes and different strenght of particular notes. Thus to make a good perfume, one must take into account the strenght of smell.

4) *Why particular molecules (for example, vanilline, indole, thiols, etc.) smell very strongly while other do not?*

Unfortunately, our nose is not the best tool in indentifying unknown materials, which we make in laboratory, thus, we need to be able use other, greater tools which are H NMR and C NMR for example. These two techniques make possible to indentify almost any organic structure. Therefore, it is crucial that every chemist would know how to use this powerful tool.

5) You are given the starting material and a chain of reaction and spectra of every intermediate product. Identify X's and assign spectra.

X₁

X₂

X₃

X₄

X₅

X₆

Problem 11   Balance equation!

Given the imbalanced chemical equation summarizing the experimentally observed facts for the production of perchloric acid:

$NH_4ClO_4 + HNO_3 + HCl \rightarrow HClO_4 \cdot 2H_2O + N_2O + NO + NO_2 + Cl_2 + H_2O$

a) Balance the equation in such a way, that the sum of positive, integer coefficients would be minimal, i.e. with smallest possible whole number (including zero) coefficients.

b) Balance the equation in such a way, that it would satisfy experimentally estimated $HClO_4 \cdot 2H_2O$ to Cl_2 ratio of 9:1.

Problem 12   Redox reactions

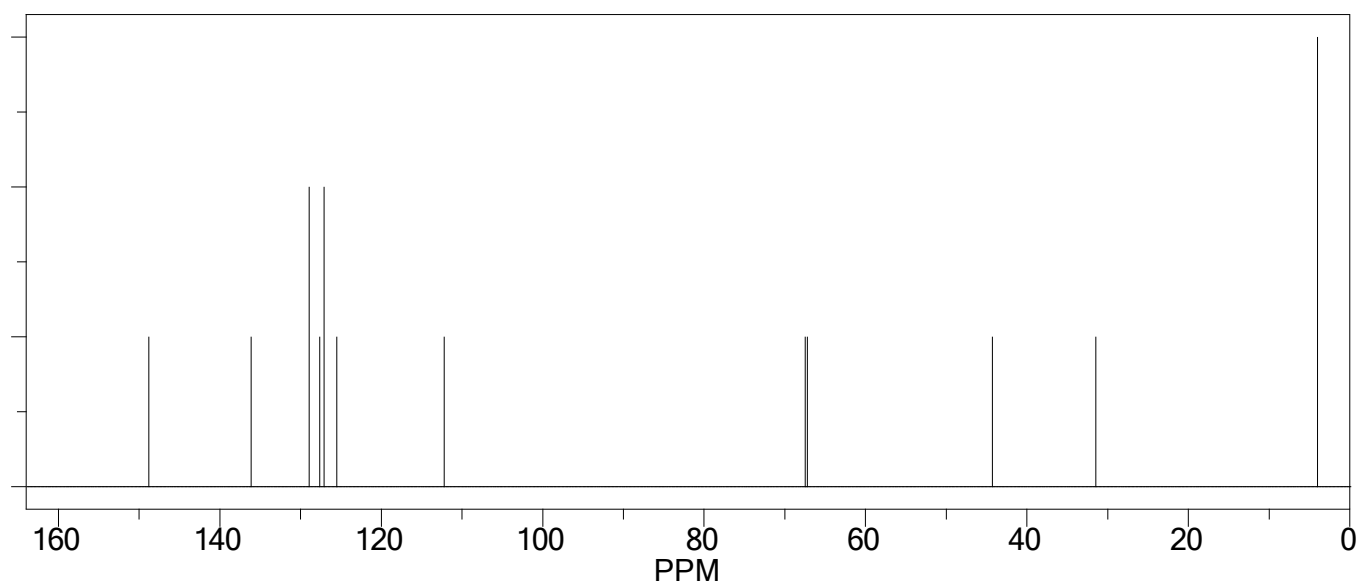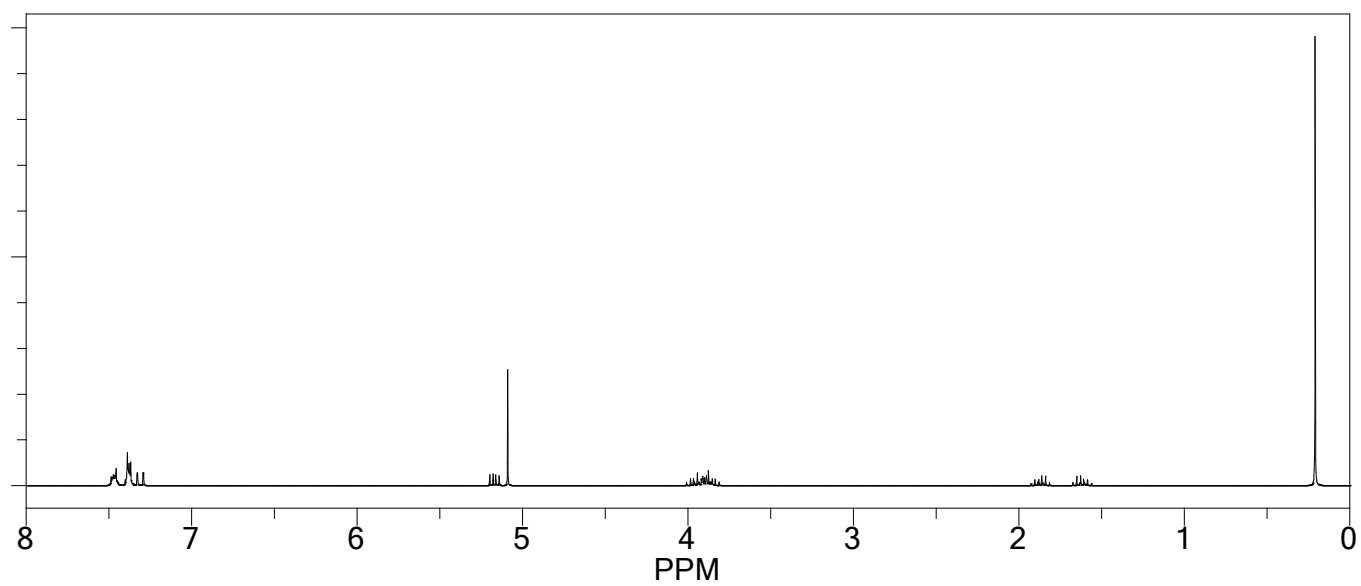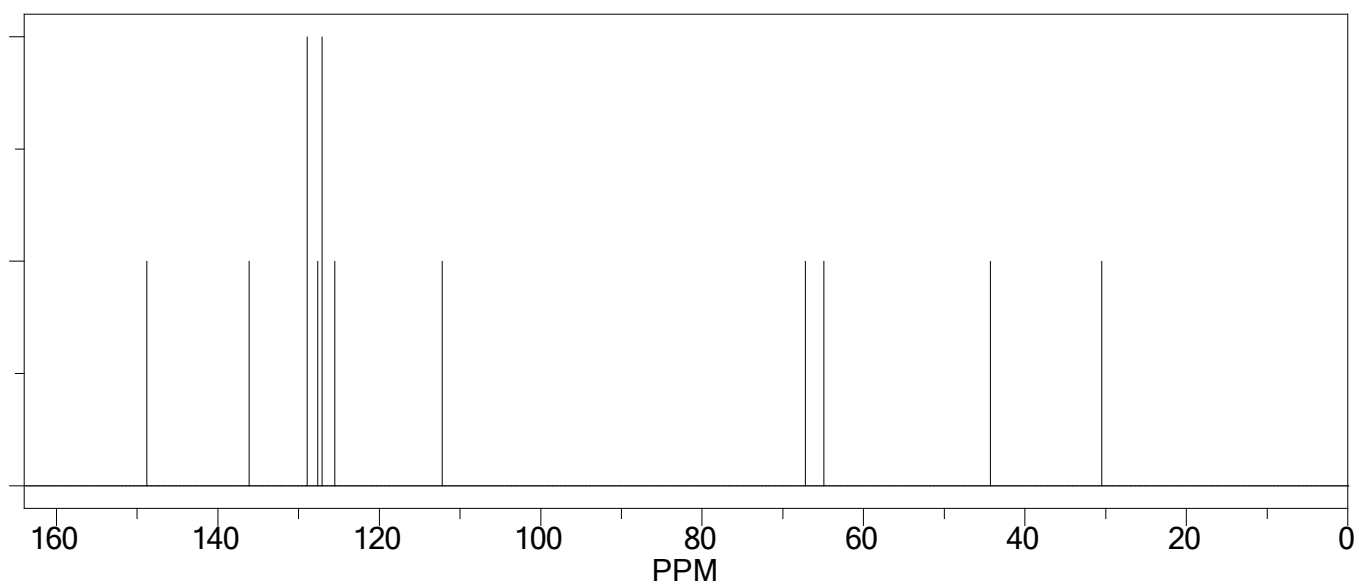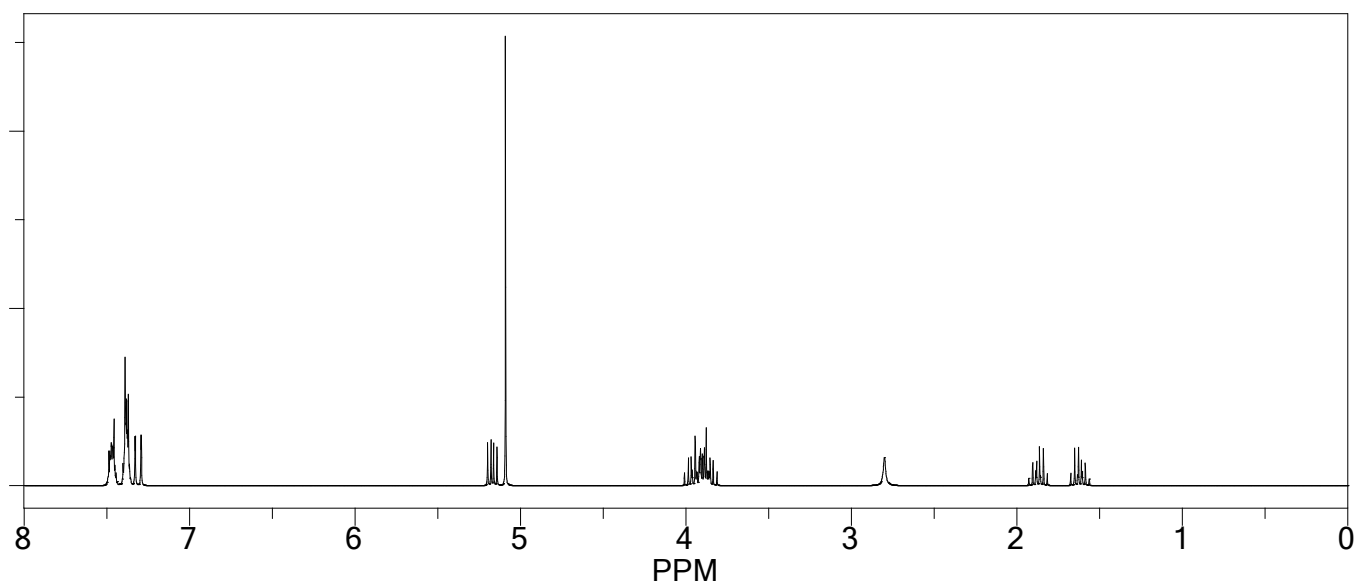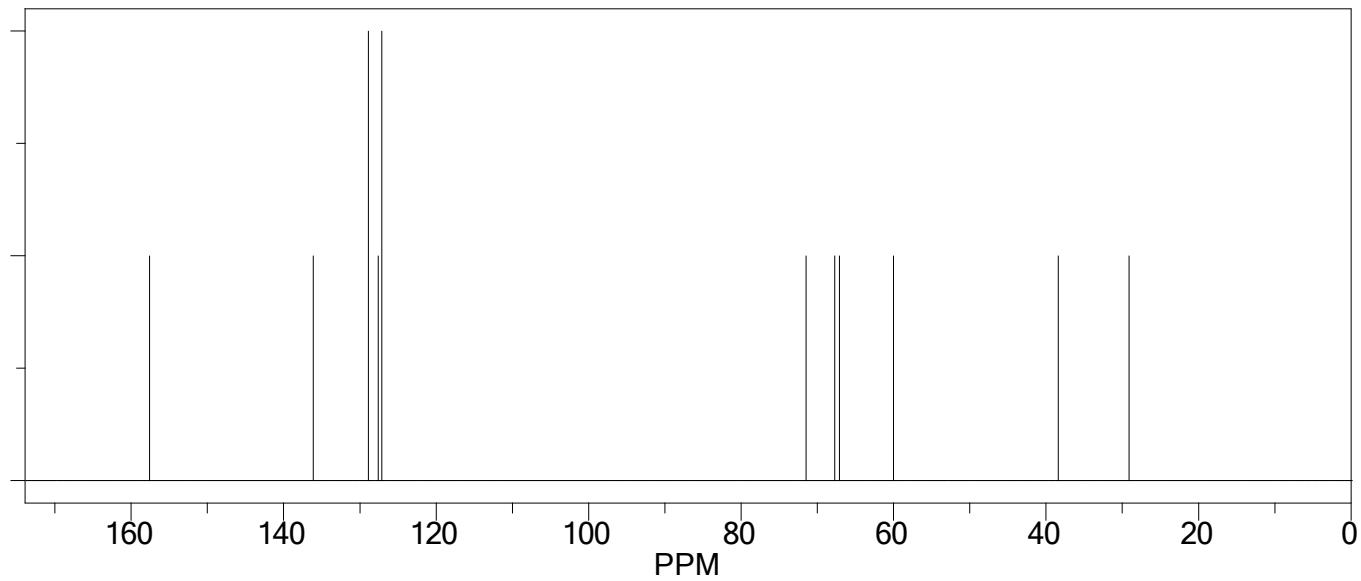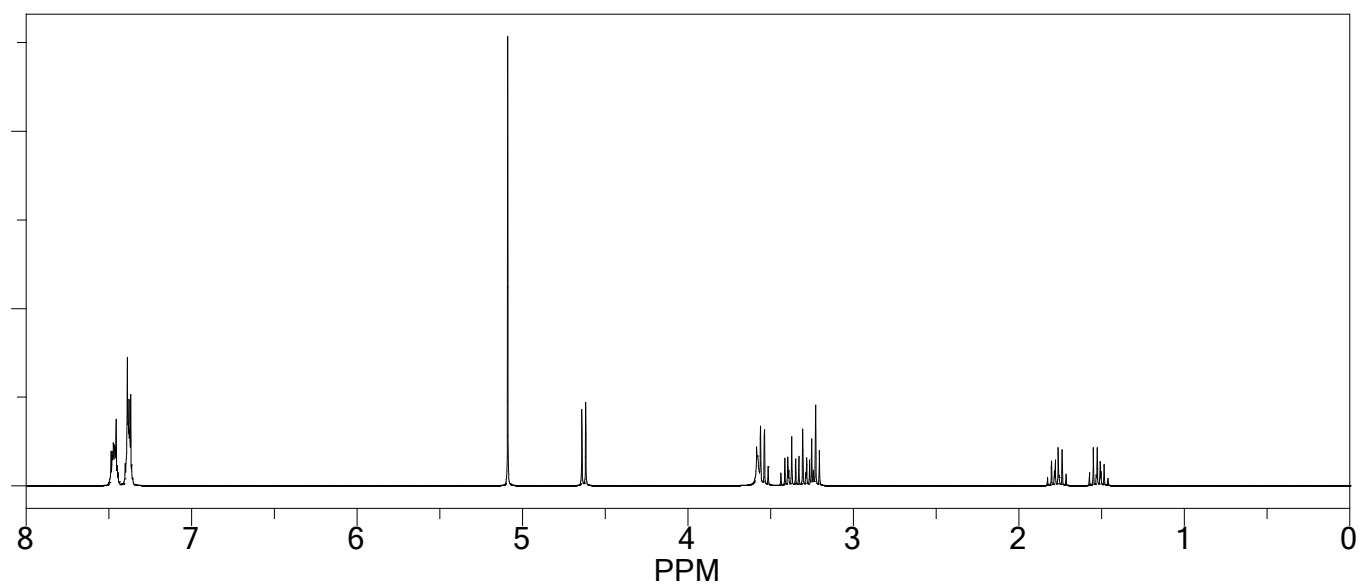The explanation of redox reaction is often based on standard electrode potentials. In most cases this concept results in correct conclusions, but it is important to know that the electrode potential depends on other circumstances as well.

a) Consider the following galvanic cells. What redox reactions take place? Why?
   i.   Standard Ni^{2+}/Ni and standard Cd^{2+}/Cd half-cells
   ii.   Standard Ni^{2+}/Ni half-cell, and Cd^{2+}/Cd half-cell at pH=11
   iii. Ni^{2+}/Ni half-cell at pH=11, and standard Cd^{2+}/Cd half-cell
   iv.   Following half-cells at 25°C:
        1) Cd(s) in 1.00 L solution containing 5.814 g of $CdSO_4$
        2) Ni(s) in 1.00 L solution containing 158.0 mg of $NiSO_4$ and 200.0 mg of NaCN.
b) Consider the following half-cells at 25°C:
        1) Cd(s) in a solution that has 25.02 mg of $CdSO_4$ dissolved in 100.0 mL of distilled water and 20.00 mL of KI solution (c = 0,2100 mol/L) was added.
        2) Ni(s) in 0.1000 L solution that has a $1.00 \cdot 10^{-4}$ mol/L concentration of Ni^{2+}.
   Calculate the mass of NaOH *added to* Ni^{2+} *electrolyte, if there is no potential difference between the two half-cells.*
The volume contraction is negligible.

$\varepsilon^0(Ni^{2+}/Ni) = -0{,}23$ V, $\varepsilon^0(Cd^{2+}/Cd) = -0{,}40$ V; $pL[Cd(OH)_2] = 13{,}5$; $pL[Ni(OH)_2] = 17{,}19$;

$lg\beta_4([Ni(CN)_4]^{2-}) = 31{,}11$; $lg\beta_1([CdI_4]^{2-}) = 2{,}48$; $lg\beta_2([CdI_4]^{2-}) = 3{,}92$; $lg\beta_3([CdI_4]^{2-}) = 5{,}00$; $lg\beta_4([CdI_4]^{2-}) = 6{,}10$.

Problem 13   Bad smell

Aqueous hydrogen sulfide is a common reagent, but it has an unpleasant smell. Its first acidic dissociation constant is generally accepted to be $K_{a1} = 10^{-6{,}9}$. The second dissociation constant is at least three orders of magnitude smaller. The solubility of hydrogen sulfide in water is 4 g/dm^3.
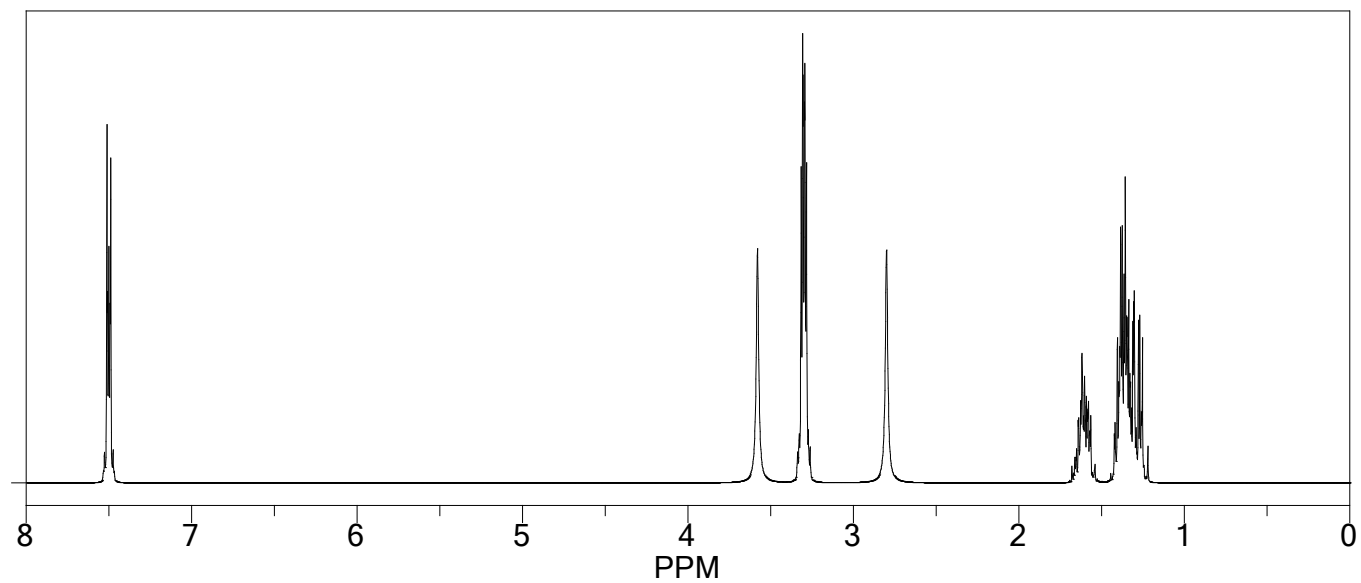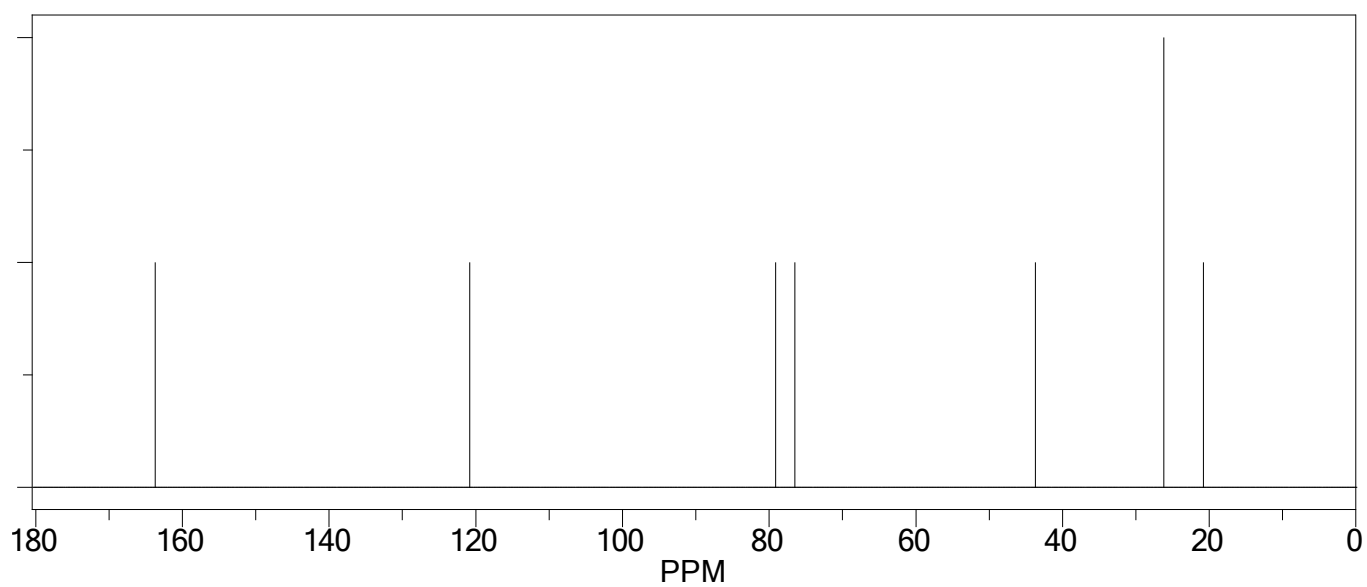
1. *What is the pH of a saturated* H_2S *solution? When increasing the pH of the saturated solution, what will be the pH when 99% of the hydrogen sulfide is in HS$^-$ form?*
The second dissociation constant has a much more contested value. Older textbooks contain $K_{a2} = 10^{-13}$-10^{-14}.

2. *Using 10^{-14} as the constant, what percentage of the hydrogen sulfide would be in sulfide ion form in solutions containing 5 mol/dm³ OH⁻?*

Practical considerations show that these constant values are probably inaccurate. Spectroscopical measurements showed that while making H_2S solutions more basic, the HS⁻-ion concentration does not significantly decrease until a 5 mol/dm³ OH⁻ concentration is reached. (Oxygen was carefully removed from the samples.)

3. *Supposing that a 1% concentration decrease could be detected, give an estimate for the second dissociation constant based on this experiment.*

Strongly basic solutions are not really practical for dissociation constant determinations.

4. *Why?*

The precipitation of metal sulfides is a phenomenon that can be more helpful in the estimation. Qualitative analysis says that a sulfide precipitate forms on adding saturated H_2S solution to tin(II) solution acidified with a few drops of reagent acid, but no precipitation is observed with zinc solutions.

5. *Estimate the second dissociation constant supposing that*
    i) the metal concentration in the original solution is 0.01 mol/dm³
    ii) acidification is carried out with nitric acid giving c(HNO_3)= 0.2 mol/dm³ in the original metal soln
    iii) identical volumes are mixed from the original metal and the H_2S solution
    iv) pL(ZnS)=22,9 pL(SnS)=26,0.

It is interesting that without acidification ZnS precipitates in the same experiment.

6. *What will be the pH of the resulting solution?*

Problem 14   *Complex compound*

Organometallic compounds act as catalysts in many important industrial processes. In this task you will determine the identity of one such compound, using various spectroscopic data, and then investigate its derivative, which is thought to be even better suited for industrial applications, due to its thermal stability.

Metal **M** makes an organometallic complex **A**, which, when added to a popular organic solvent **B** gives a yellow solution.
When a well-known compound **C** is dissolved in the solvent **B**, it gives a purple solution. This solution of **C** is added to compound **A**, to produce an emerald green solution of **D**, which has **C** as one of its ligands. A neutral molecule **E** is also produced in this reaction.

1. Metal **M** was examined using X-ray diffraction. The first diffraction peak at is due to a {111} reflection at $2\theta =$ 41.11°. The X-ray wavelength is 1.542 Å.
    a. Write down the Bragg's law and calculate the {111} plane spacing. Based on your result, calculate the lattice parameter.
    b. Given that **M** has an fcc structure and a density of 12.43 g cm⁻³, identify the metal.
2. ¹³C-NMR spectra were obtained for compounds **C** and **B.** The following peaks were obtained for **B**: 137.8; 129.2; 128.4; 125.5; 21.4 ppm.
    The spectrum of **C** only showed one signal at 143.5 ppm.
    a. Given that **C** contains one element only, deduce **C**'s identity.

     b. Give the structure of the common organic solvent **B** and assign as many signals as you can. What is the trivial name for **B**?

3. Compound **A** was examined using ^{1}H NMR. The following signals were obtained:

- 9.50 ppm (minus 9.50) (quartet, ^{2}J (P-H, 14 Hz), 1H); three signals from 7.08 to 7.88 ppm (multiplets, total 45H).

An IR spectrum of **A** has a sharp absorption at 1920 cm^{-1}.

     a. Using the information provided, deduce the structure of **A**, and explain your reasoning.

     b. Hence deduce the structure of **D** and **E**.

     c. Given that both the complexes are coloured, propose a method for determining concentrations of their solutions. What additional information do you need for that?

Best tasks form BCC - SOLUTIONS

SOLUTION – Problem 1

1. Radioactive decays are 1st order reactions, so:

   $$\ln \frac{C_0}{C} = kt$$

   If t = t(half-life) = 250 000 years, then C = 0,5 C_0.

   $$\ln 2 = k \cdot 250000$$

   $$k = \frac{\ln 2}{t_{1/2}} = 2.77 \cdot 10^{-6}\, years^{-1}$$

2. If C = 0,1 C_0, then:

   $$\ln \frac{C_0}{0,1 C_0} = 2.77 \cdot 10^{-6} \cdot t \quad \Rightarrow \quad t = \frac{\ln 10}{2.77 \cdot 10^{-6}} = 830482 = 8,3 \cdot 10^5\, years$$

3. $n_{Pu} : n_{Ta} : n_{Xe} : n_{Pm} : n_{Dialium} : n_{Hg} : n_H = \dfrac{15.08}{244.06} : \dfrac{18.06}{180.95} : \dfrac{27.71}{131.29} : \dfrac{24.02}{144.91} : \dfrac{10.62}{2 \cdot 26.98} : \dfrac{3.94}{200.59} : \dfrac{0.57}{1.01} =$

   $$= 0.0618 : 0.0998 : 0.211 : 0.166 : 0.197 : 0.0196 : 0.564 =$$

   $$= 3.15 : 5.09 : 10.77 : 8.45 : 10.05 : 1 : 28.8 =$$

   $$\approx 3 : 5 : 11 : 8.5 : 10 : 1 : 29$$

   $Pu_6Ta_{10}Xe_{22}Pm_{17}(Al_2)_{20}Hg_2H_{58}$

   Sum = 15.08 + 18.06 + 27.71 + 24.02 + 10.62 + 3.94 + 0.57 = 100

   It is not possible mineral formula because it does not contain proper amount of anions (such as oxygen which is not in this mineral).

4. Fluoride ions can replace hydroxide ions in $LiNaSiB_3O_7(OH)$. Similar compounds in nature are apatite and fluoroapatite. [http://en.wikipedia.org/wiki/Apatite]

5. Volume of monoclinic cell is equal to area of face between **a** and **b** powers height of cell.

V = a * b * c * sin β = 6.76421 * 13.8047 * 7.86951 * sin 124.0895 = 608.566 Å^3

Or you can use freeware *Winplotr* to calculate cell volumes (it also works for triclinic cells) and many other data:

608.566 Å^3 = 608.566 * 10^{-30} m^3 = 608.566 * 10^{-30} * 10^6 cm^3 = 6.0856 * 10^{-22} cm^3

If we count correctly green colored lithium atoms and blue colored sodium atoms, then we can find that Z (number of molecules in unit cell) is 4.

M[LiNaSiB$_3$O$_7$(OH)] = 6.94 + 22.99 + 28.09 + 3 * 10.81 + 8 * 16.00 + 1.01 = 219.46 g/mol

Mass of one "molecule":

$$m_0 = \frac{M}{N_A} = \frac{219.46}{6.02 \cdot 10^{23}} = 3.6455 \cdot 10^{-22} g$$

$$density = \frac{m}{V} = \frac{4 \cdot m_0}{V} = \frac{4 \cdot 3.6455 \cdot 10^{-22}}{6.0856 \cdot 10^{-22}} = 2.396 \, g \cdot cm^{-3}$$

6. Bragg equation:

$$n\lambda = 2d \cdot \sin\theta,$$

where:

- n is an integer determined by the order given (in this problem it is 1),
- λ is the wavelength of X-rays, and moving electrons, protons and neutrons (λ = 0.15418 nm = 1.5418 Å),
- d is the spacing between the planes in the atomic lattice, and
- θ is the angle between the incident ray and the scattering planes.

So from this equation:

$$\sin\frac{2\theta}{2} = \frac{\lambda}{2d}$$

$$2\theta = 2 \cdot \arcsin\left(\frac{\lambda}{2d}\right)$$

d-spacing (Å)	Relative intensity	2-theta, °
4.666	62	19,02
3.716	39	23,95
3.180	82	28,06
3.152	74	28,31
3.027	40	29,51
2.946	100	30,34
2.252	38	40,04

Jadarite PXRD pattern (found somewhere in literature; Bruker AXS presentation, Riga, 2009) and it corresponds to results calculated. In all calculated positions we can find diffraction signals.

7. None of those diffraction patterns refers to jadarite.

$$^{238}_{92}U \rightarrow \ ^{234}_{90}Th + \ ^{4}_{2}He \qquad\qquad \alpha \text{ decay}$$

$$^{234}_{90}Th \rightarrow \ ^{234}_{91}Pa + \ ^{0}_{-1}e \qquad\qquad \beta \text{ decay}$$

$$^{234}_{91}Pa \rightarrow \ ^{234}_{92}U + \ ^{0}_{-1}e \qquad\qquad \beta \text{ decay}$$

$$^{234}_{92}U \rightarrow \ ^{230}_{90}Th + \ ^{4}_{2}He \qquad\qquad \alpha \text{ decay}$$

$$^{230}_{90}Th \rightarrow \ ^{226}_{88}Ra + \ ^{4}_{2}He \qquad\qquad \alpha \text{ decay}$$

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

8. Firstly we have to calculate amount of water in given hydrate. $Cu(UO_2)_2(PO_4)_2 \cdot (8\text{-}12)H_2O$

$$w(H_2O) = 0.206 = \frac{M(H_2O) \cdot x}{M(anhydrous\ compound) + M(H_2O)}$$

$$18x = 0.206 \cdot (793.55 + 18x)$$

Molar mass calculations:

M_r	n	$M_r * n$
63.55	1	63.55
238.03	2	476.06
16	12	192
30.97	2	61.94
	sum	793.55

$18x = 163.47 + 3.708x$

$14.292x = 163.47$

$x = 11.4$

So molar mass of hydrated compound $Cu(UO_2)_2(PO_4)_2 \cdot (11.4)H_2O$ is:

M = 793.55 + 11.4 * 18 = 999 g/mol

n[$Cu(UO_2)_2(PO_4)_2 \cdot (11.4)H_2O$] = $\dfrac{m}{M} = \dfrac{5.00}{999.4} = 0.005003$ mol ≈ 0.005 mol

$N_0 = N_A * n = 6.02 * 10^{23} * 0.005$ *** 2**= **6.0 * 10²¹ atoms**

9. Formation of 234-Th and 234-Pa can be assigned as negligible and it can be assumed that 238-U decays to form 234-U with half life of $4.468 * 10^9$ years.

$$\frac{\Delta N(^{238}U)}{\Delta t} \approx \frac{dN(^{238}U)}{dt} = -k_0 \cdot N_{238U}$$

$$\frac{\Delta N(^{234}U)}{\Delta t} \approx \frac{d(^{234}U)}{dt} = k_0 \cdot N_{238U} - k_1 \cdot N_{234U}$$

$$\frac{\Delta N(^{230}Th)}{\Delta t} \approx \frac{d(^{230}Th)}{dt} = k_1 \cdot N_{234U} - k_2 \cdot N_{230Th}$$

$$\frac{\Delta N(^{226}Ra)}{\Delta t} \approx \frac{d(^{226}Ra)}{dt} = k_2 \cdot N_{230Th} - k_3 \cdot N_{226Ra}$$

$$\frac{\Delta N(^{222}Rn)}{\Delta t} \approx \frac{d(^{222}Rn)}{dt} = k_3 \cdot N_{226Ra}$$

At the beginning: $N_0(^{238}U) = 0.992742 * 3.0 * 10^{21} = 2.99 * 10^{21}$ atoms

$N_0(^{234}U) = 0.000054 * 3.0 * 10^{21} = 1.63 * 10^{17}$ atoms

$N_0(^{230}Th) = 0$

$N_0(^{226}Ra) = 0$

$N_0(^{222}Rn) = 0$

$$k_0 = \frac{\ln 2}{4.468 \cdot 10^9} = 1.55 \cdot 10^{-11} \, years^{-1}$$

$$k_1 = \frac{\ln 2}{245500} = 2.82 \cdot 10^{-6} \, years^{-1}$$

$$k_2 = \frac{\ln 2}{75380} = 9.19 \cdot 10^{-6} \, years^{-1}$$

$$k_3 = \frac{\ln 2}{1602} = 0.0004327 \cdot 10^{-6} \, years^{-1}$$

$$\Delta N(^{238}U) = -k_0 \cdot N_{238U} \cdot \Delta t$$

where Δt is as small as possible.

$$N(^{238}U)_{at \, t+\Delta t} = N(^{238}U)_{at \, t} + \Delta N(^{238}U)$$

for rest particles similar equations can be obtained.

Inputting them into *MS Excel* worksheet we can obtain results that are shown below. *MS Excel* function =max(..) is used to find maximum value of 230-Th in 1 million years. It has been found that after one million years it is 5.03895 * 10^{16} atoms (maximum value for that time) and value of 1.00855*10^{17} atoms in 1.974 million years.

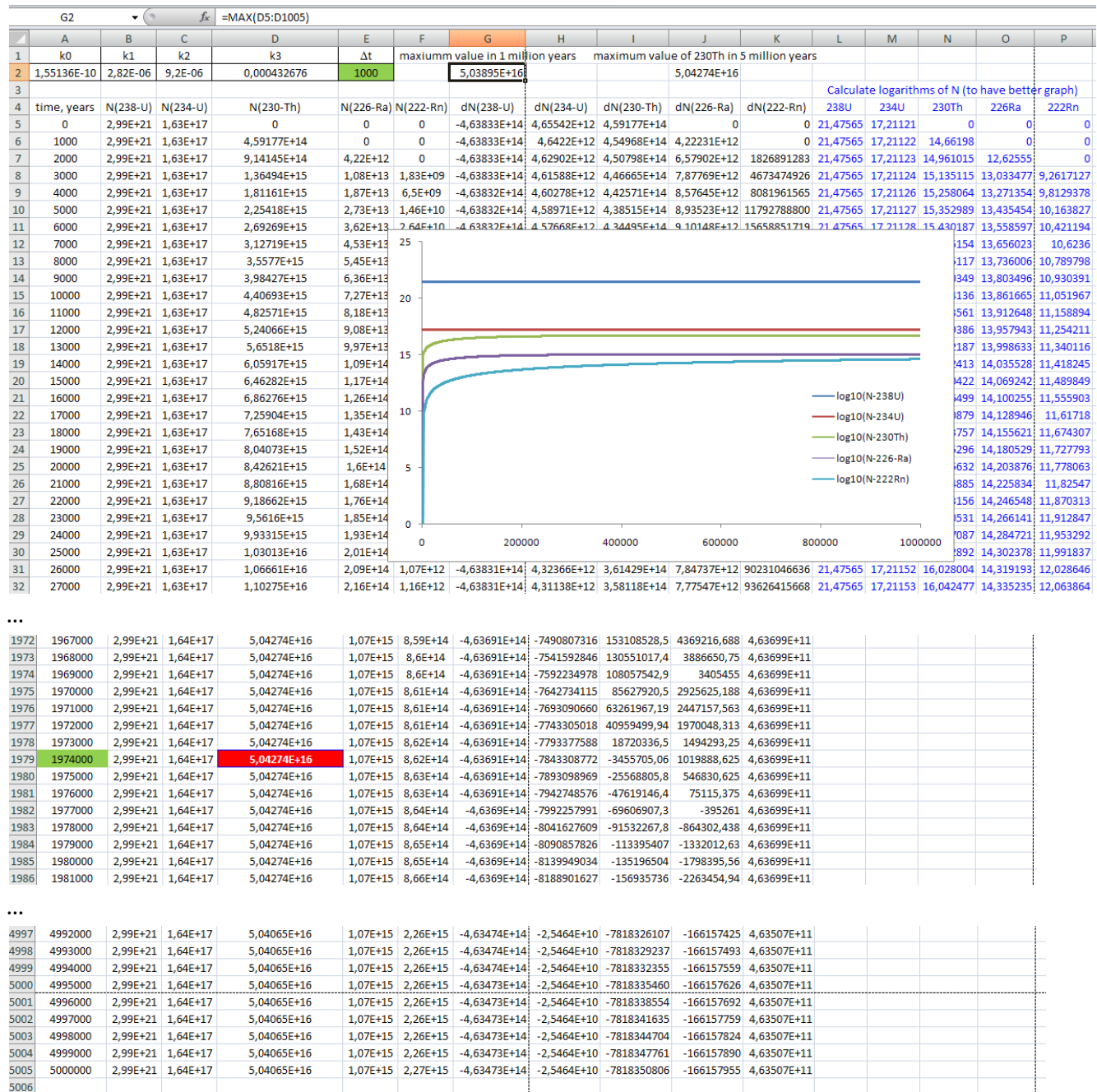|	G2		f_x	=MAX(D5:D1005)												
	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P
1	k0	k1	k2	k3	Δt	maxiumm value in 1 million years			maximum value of 230Th in 5 million years							
2	1,55136E-10	2,82E-06	9,2E-06	0,000432676	1000		5,03895E+16			5,04274E+16						
3												Calculate logarithms of N (to have better graph)				
4	time, years	N(238-U)	N(234-U)	N(230-Th)	N(226-Ra)	N(222-Rn)	dN(238-U)	dN(234-U)	dN(230-Th)	dN(226-Ra)	dN(222-Rn)	238U	234U	230Th	226Ra	222Rn
5	0	2,99E+21	1,63E+17	0	0	0	-4,63833E+14	4,65542E+12	4,59177E+14	0	0	21,47565	17,21121	0	0	0
6	1000	2,99E+21	1,63E+17	4,59177E+14	0	0	-4,63833E+14	4,6422E+12	4,54968E+14	4,22231E+12	0	21,47565	17,21122	14,66198	0	0
7	2000	2,99E+21	1,63E+17	9,14145E+14	4,22E+12	0	-4,63833E+14	4,62902E+12	4,50798E+14	6,57902E+12	1826891283	21,47565	17,21123	14,961015	12,62555	0
8	3000	2,99E+21	1,63E+17	1,36494E+15	1,08E+13	1,83E+09	-4,63833E+14	4,61588E+12	4,46665E+14	7,87769E+12	4673474926	21,47565	17,21124	15,135115	13,033477	9,2617127
9	4000	2,99E+21	1,63E+17	1,81161E+15	1,87E+13	6,5E+09	-4,63832E+14	4,60278E+12	4,42571E+14	8,57645E+12	8081961565	21,47565	17,21126	15,258064	13,271354	9,8129378
10	5000	2,99E+21	1,63E+17	2,25418E+15	2,73E+13	1,46E+10	-4,63832E+14	4,58971E+12	4,38515E+14	8,93523E+12	11792788800	21,47565	17,21127	15,352989	13,435454	10,163827
11	6000	2,99E+21	1,63E+17	2,69269E+15	3,62E+13	2,64E+10	-4,63832E+14	4,57668E+12	4,34495E+14	9,10148E+12	15658851719	21,47565	17,21128	15,430187	13,558597	10,421194
12	7000	2,99E+21	1,63E+17	3,12719E+15	4,53E+13							…154	13,656023			10,6236
13	8000	2,99E+21	1,63E+17	3,5577E+15	5,45E+13							…117	13,736006			10,789798
14	9000	2,99E+21	1,63E+17	3,98427E+15	6,36E+13							…349	13,803496			10,930391
15	10000	2,99E+21	1,63E+17	4,40693E+15	7,27E+13							…136	13,861665			11,051967
16	11000	2,99E+21	1,63E+17	4,82571E+15	8,18E+13							…561	13,912648			11,158894
17	12000	2,99E+21	1,63E+17	5,24066E+15	9,08E+13							…386	13,957943			11,254211
18	13000	2,99E+21	1,63E+17	5,6518E+15	9,97E+13							…187	13,998633			11,340116
19	14000	2,99E+21	1,63E+17	6,05917E+15	1,09E+14							…413	14,035528			11,418245
20	15000	2,99E+21	1,63E+17	6,46282E+15	1,17E+14							…422	14,069242			11,489849
21	16000	2,99E+21	1,63E+17	6,86276E+15	1,26E+14							…499	14,100255			11,555903
22	17000	2,99E+21	1,63E+17	7,25904E+15	1,35E+14							…879	14,128946			11,61718
23	18000	2,99E+21	1,63E+17	7,65168E+15	1,43E+14							…757	14,155621			11,674307
24	19000	2,99E+21	1,63E+17	8,04073E+15	1,52E+14							…296	14,180529			11,727793
25	20000	2,99E+21	1,63E+17	8,42621E+15	1,6E+14							…632	14,203876			11,778063
26	21000	2,99E+21	1,63E+17	8,80816E+15	1,68E+14							…885	14,225834			11,82547
27	22000	2,99E+21	1,63E+17	9,18662E+15	1,76E+14							…156	14,246548			11,870313
28	23000	2,99E+21	1,63E+17	9,5616E+15	1,85E+14							…531	14,266141			11,912847
29	24000	2,99E+21	1,63E+17	9,93315E+15	1,93E+14							…087	14,284721			11,953292
30	25000	2,99E+21	1,63E+17	1,03013E+16	2,01E+14							…892	14,302503			11,991837
31	26000	2,99E+21	1,63E+17	1,06661E+16	2,09E+14	1,07E+12	-4,63831E+14	4,32366E+12	3,61429E+14	7,84737E+12	90231046636	21,47565	17,21152	16,028004	14,319193	12,028646
32	27000	2,99E+21	1,63E+17	1,10275E+16	2,16E+14	1,16E+12	-4,63831E+14	4,31118E+12	3,58118E+14	7,77547E+12	93626415668	21,47565	17,21153	16,042477	14,335235	12,063864

...

1972	1967000	2,99E+21	1,64E+17	5,04274E+16	1,07E+15	8,59E+14	-4,63691E+14	-7490807316	153108528,5	4369216,688	4,63699E+11					
1973	1968000	2,99E+21	1,64E+17	5,04274E+16	1,07E+15	8,6E+14	-4,63691E+14	-7541592846	130551017,4	3886650,75	4,63699E+11					
1974	1969000	2,99E+21	1,64E+17	5,04274E+16	1,07E+15	8,6E+14	-4,63691E+14	-7592234978	108057542,9	3405455	4,63699E+11					
1975	1970000	2,99E+21	1,64E+17	5,04274E+16	1,07E+15	8,61E+14	-4,63691E+14	-7642734115	85627920,5	2925625,188	4,63699E+11					
1976	1971000	2,99E+21	1,64E+17	5,04274E+16	1,07E+15	8,61E+14	-4,63691E+14	-7693090660	63261967,19	2447157,563	4,63699E+11					
1977	1972000	2,99E+21	1,64E+17	5,04274E+16	1,07E+15	8,61E+14	-4,63691E+14	-7743305018	40959499,94	1970048,313	4,63699E+11					
1978	1973000	2,99E+21	1,64E+17	5,04274E+16	1,07E+15	8,62E+14	-4,63691E+14	-7793377588	18720336,5	1494293,25	4,63699E+11					
1979	1974000	2,99E+21	1,64E+17	5,04274E+16	1,07E+15	8,62E+14	-4,63691E+14	-7843308772	-3455705,06	1019888,625	4,63699E+11					
1980	1975000	2,99E+21	1,64E+17	5,04274E+16	1,07E+15	8,63E+14	-4,63691E+14	-7893098969	-25568805,8	546830,625	4,63699E+11					
1981	1976000	2,99E+21	1,64E+17	5,04274E+16	1,07E+15	8,63E+14	-4,63691E+14	-7942748576	-47619146,4	75115,375	4,63699E+11					
1982	1977000	2,99E+21	1,64E+17	5,04274E+16	1,07E+15	8,64E+14	-4,6369E+14	-7992257991	-69606907,3	-395261	4,63699E+11					
1983	1978000	2,99E+21	1,64E+17	5,04274E+16	1,07E+15	8,64E+14	-4,6369E+14	-8041627609	-91532267,8	-864302,438	4,63699E+11					
1984	1979000	2,99E+21	1,64E+17	5,04274E+16	1,07E+15	8,65E+14	-4,6369E+14	-8090857826	-113395407	-1332012,63	4,63699E+11					
1985	1980000	2,99E+21	1,64E+17	5,04274E+16	1,07E+15	8,65E+14	-4,6369E+14	-8139949034	-135196504	-1798395,56	4,63699E+11					
1986	1981000	2,99E+21	1,64E+17	5,04274E+16	1,07E+15	8,66E+14	-4,6369E+14	-8188901627	-156935736	-2263454,94	4,63699E+11					

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4997	4992000	2,99E+21	1,64E+17	5,04065E+16	1,07E+15	2,26E+15	-4,63474E+14	-2,5464E+10	-7818326107	-166157425	4,63507E+11					
4998	4993000	2,99E+21	1,64E+17	5,04065E+16	1,07E+15	2,26E+15	-4,63474E+14	-2,5464E+10	-7818329237	-166157493	4,63507E+11					
4999	4994000	2,99E+21	1,64E+17	5,04065E+16	1,07E+15	2,26E+15	-4,63474E+14	-2,5464E+10	-7818332355	-166157559	4,63507E+11					
5000	4995000	2,99E+21	1,64E+17	5,04065E+16	1,07E+15	2,26E+15	-4,63473E+14	-2,5464E+10	-7818335460	-166157626	4,63507E+11					
5001	4996000	2,99E+21	1,64E+17	5,04065E+16	1,07E+15	2,26E+15	-4,63473E+14	-2,5464E+10	-7818338554	-166157692	4,63507E+11					
5002	4997000	2,99E+21	1,64E+17	5,04065E+16	1,07E+15	2,26E+15	-4,63473E+14	-2,5464E+10	-7818341635	-166157759	4,63507E+11					
5003	4998000	2,99E+21	1,64E+17	5,04065E+16	1,07E+15	2,26E+15	-4,63473E+14	-2,5464E+10	-7818344704	-166157824	4,63507E+11					
5004	4999000	2,99E+21	1,64E+17	5,04065E+16	1,07E+15	2,26E+15	-4,63473E+14	-2,5464E+10	-7818347761	-166157890	4,63507E+11					
5005	5000000	2,99E+21	1,64E+17	5,04065E+16	1,07E+15	2,27E+15	-4,63473E+14	-2,5464E+10	-7818350806	-166157955	4,63507E+11					
5006																

The embedded chart legend shows: log10(N-238U), log10(N-234U), log10(N-230Th), log10(N-226-Ra), log10(N-222Rn), with x-axis values 0, 200000, 400000, 600000, 800000, 1000000 and y-axis 0, 5, 10, 15, 20, 25.

10. See answer between graph.

11. Function extremes such as maximum points can be determined from function derivative. It must be equal to zero.

$$N(^{230}U)_o \frac{k_1}{k_2 - k_1}(-k_1 \cdot e^{-k_1 t} + k_2 \cdot e^{-k_2 t}) = 0$$

$$N(^{230}U)_o \frac{k_1}{k_2 - k_1} \neq 0$$

so

$$-k_1 \cdot e^{-k_1 t} + k_2 \cdot e^{-k_2 t} = 0$$

$$k_1 \cdot e^{-k_1 t} = k_2 \cdot e^{-k_2 t} \qquad \Rightarrow \qquad \frac{k_1 \cdot e^{-k_1 t}}{k_2 \cdot e^{-k_2 t}} = 1$$

$$\frac{k_1}{k_2} \cdot e^{t \cdot (k_2 - k_1)} = 1 \qquad \frac{2.82 \cdot 10^{-6}}{9.19 \cdot 10^{-6}} \cdot e^{t \cdot (9.19 \cdot 10^{-6} - 2.82 \cdot 10^{-6})} = 1$$

$$0.3069 \cdot e^{t \cdot (6.37 \cdot 10^{-6})} = 1$$

$$e^{t \cdot (6.37 \cdot 10^{-6})} = \frac{1}{0.3069} = 3.26$$

$$\ln e^{t \cdot (6.37 \cdot 10^{-6})} = \ln 3.26$$

$$t \cdot (6.37 \cdot 10^{-6}) = 1.18$$

$$t = \frac{1.18}{6.37 \cdot 10^{-6}} = 185459 \ years$$

12. This big difference can be explained by fact that in calculation of t_{max2} formation of ^{234}U (from ^{238}U) has not taken into account, but in Excel file it is included. If we exclude this from Excel file (simply set constant $k_0 = 0$), then we obtain same result, see figure bellow.

186	181000	2,99E+21	9,75E+16	2,96594E+16	6,3E+14	3,49E+13	0	-2,7525E+14	2,5202E+12	93979944307	2,72635E+11	21,47565	16,98895	16,472162 14,799418 13,542259
187	182000	2,99E+21	9,72E+16	2,96619E+16	6,3E+14	3,51E+13	0	-2,7447E+14	1,71988E+12	76491230004	2,72676E+11	21,47565	16,98772	16,472199 14,799483 13,545643
188	183000	2,99E+21	9,69E+16	2,96636E+16	6,3E+14	3,54E+13	0	-2,737E+14	9,29122E+11	59210268820	2,72709E+11	21,47565	16,9865	16,472224 14,799536 13,549001
189	184000	2,99E+21	9,67E+16	2,96645E+16	6,3E+14	3,57E+13	0	-2,7292E+14	1,47819E+11	42135017863	2,72734E+11	21,47565	16,98527	16,472237 14,799577 13,552334
190	185000	2,99E+21	9,64E+16	2,96647E+16	6,3E+14	3,59E+13	0	-2,7215E+14	-6,2412E+11	25263453401	2,72753E+11	21,47565	16,98404	16,47224 14,799606 13,555642
191	186000	2,99E+21	9,61E+16	2,96641E+16	6,3E+14	3,62E+13	0	-2,7139E+14	-1,3868E+12	8593570682	2,72763E+11	21,47565	16,98281	16,472231 14,799623 13,558925
192	187000	2,99E+21	9,58E+16	2,96627E+16	6,3E+14	3,65E+13	0	-2,7062E+14	-2,1403E+12	-7876616238	2,72767E+11	21,47565	16,98158	16,47221 14,799629 13,562183
193	188000	2,99E+21	9,56E+16	2,96605E+16	6,3E+14	3,68E+13	0	-2,6985E+14	-2,8846E+12	-2,4149E+10	2,72764E+11	21,47565	16,98036	16,472179 14,799624 13,565418

SOLUTION – Problem 2

a)

Energy level diagram

b) $IE = E' - E = -13.6 \cdot \left(\dfrac{2Z_{eff,1s}^2}{1^2} \right) + 13.6 \cdot \left(\dfrac{2Z_{eff,1s}^2}{1^2} + \dfrac{Z_{eff,2s}^2}{2^2} \right) = 13.6 \cdot \dfrac{Z_{eff,2s}^2}{2^2} = 5.3917 \text{ eV}$

Li: $\quad Z_{eff,2s} = 2 \cdot \sqrt{\dfrac{5.3917}{13.6}} = 1.259$

Li: $\quad Z_{eff,2p} = 1.259 - 0.25 = 1.009$

$$\lambda = 6.626 \cdot 10^{-34} \cdot 3.00 \cdot 10^8 \Big/ 1.602 \cdot 10^{-19} \cdot 13.6 \left(\dfrac{Z_{eff,2s}^2}{2^2} - \dfrac{Z_{eff,2p}^2}{2^2} \right) =$$

$$= 91.2 \text{ nm} \Big/ \left(\dfrac{1.259^2}{2^2} - \dfrac{1.009^2}{2^2} \right) = 643 \text{ nm}$$

Li: $\quad Z_{eff,3p} = 1.259 - 0.75 = 0.509 \qquad \lambda = 248 \text{ nm}$

Na: $\quad Z_{eff,3s} = 1.259 + 0.485 = 1.744$

Na: $\quad Z_{eff,3p} = 1.009 + 0.389 = 1.398 \; \lambda = 755 \text{ nm}$

Na: $\quad Z_{eff,4p} = 0.509 + 0.114 = 0.623 \qquad \lambda = 291 \text{ nm}$

K: $\quad Z_{eff,4s} = 1.744 + 0.485 = 2.229$

K: $\quad Z_{eff,4p} = 1.398 + 0.389 = 1.787 \; \lambda = 822 \text{ nm}$

K: $\quad Z_{eff,5p} = 0.623 + 0.114 = 0.737 \qquad \lambda = 316 \text{ nm}$

Rb: $\quad Z_{eff,5s} = 2.229 + 0.485 = 2.714$

Rb: $Z_{\text{eff, 5p}} = 1.787 + 0.389 = 2.176$ λ = 867 nm

Rb: $Z_{\text{eff, 6p}} = 0.737 + 0.114 = 0.851$ λ = 332 nm

Cs: $Z_{\text{eff, 6s}} = 2.714 + 0.485 = 3.199$

Cs: $Z_{\text{eff, 6p}} = 2.176 + 0.389 = 2.565$ λ = 898 nm

Cs: $Z_{\text{eff, 7p}} = 0.851 + 0.114 = 0.965$ λ = 344 nm

c) 3d→2p

d) Li has also orange and red lines. Li_2CO_3 is used for colouring fireworks in red. $(n+1)s \rightarrow np$ transition appear in violet–blue part of visible spectrum starting from K. KNO_3 and $RbNO_3$ are used for colouring fireworks in violet and violet-red. $np \rightarrow ns$ transition is shifted to red (K, 722 nm) down the group, thus we may guess, that Na should give yellow colouring, (<655 nm). $NaNO_3$ is used in fireworks.

SOLUTION – Problem 3

1) Assuming that **A** has a formula EH_x molar mass of element E can be determined.

x	M_E / g mol^{-1}	element E
1	3,6	-
2	7,2	-
3	10,8	Boron
4	14,4	-
5	18,0	-
6	21,6	-

Compound **A** may have the formula BH_3. However, the first reaction equation suggests that **A** is a dimer. Therfore, **A** is diborane B_2H_6. It has the following structure:

Boron atoms are tetrahedral. The interesting feature of this molecule is bonding of the bridging Hydrogens. The B-H-B bond is an example of a 2-electron-3-centre bond.

2)

Letter	Formula
B	BH_3
C	B_3H_9
D	B_3H_7
E	B_4H_{10}
F	B_5H_{11}

3) In monomeric BH_3 Boron atom has got an empty 2p orbital and six electrons (two from each B-H bond). Formation of a dimer allows to fulfil the octet rule as the electrons of the bridging Hydrogens become equally shared between both Boron atoms.

SOLUTION – Problem 4

PART 1

At 25°C temperature SO_3 is a liquid.

Two reactions occur:

SO_2 (g) + 0.5 O_2 (g) $\leftrightarrow$ SO_3 (l)

SO_3 (l) $\leftrightarrow$ 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)
$\Delta_f H^o$, kJ mol^{-1}	-296.83	0	-441.0	-395.7	-285.83	-909.27
S^o, 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) $\leftrightarrow$ SO_3 (l)

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

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

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

$K_1 = e^{\frac{-\Delta G}{RT}} = e^{\frac{73550}{8.314 \cdot 298.15}} = 7.693 \cdot 10^{12}$ ➔ [reagents]<<[products]
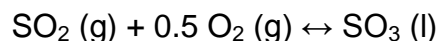
SO_3 (l) $\leftrightarrow$ SO_3 (g)

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

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

$\Delta_{r2}G = 2.698$ 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

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

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

$0.208 < 1$

Therefore, the final volume of O_2 equals 0 L.

PART 2

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

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

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

$\Delta_{r3}G = -133.7$ 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)

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

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

$\Delta_{r4}G = -136.4$ 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) $\qquad K_5 = 1.25 \cdot 10^{-2}$ (B)

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

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

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

$$n(SO_3, l \text{ and } g) = n(SO_3) = 2 \cdot n(O_2) = \frac{2p(O_2)V}{RT} = \frac{2 \cdot 0.3p(total)V}{RT} = \frac{2 \cdot 0.3 \cdot 101325 \cdot 5 \cdot 10^{-3} mol}{8.314 \cdot 298.15} =$$

$0.1226 \, mol$ 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^+]$_0$ = (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^+]$_0$+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^+]$_0$ + 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)

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

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

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

$K_7 = e^{\frac{-\Delta G}{RT}} = e^{\frac{40114}{8.314 \cdot 473.15}} = 2.68 \cdot 10^4$ ➜ [reagents]<<[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 (g) + 0.5 O_2 (g) ↔ SO_3 (l)

$n(SO_3, l \text{ and } g) = n(SO_3) = n(SO_2) = \frac{p(SO_2)V}{RT} = \frac{0.3p(total)V}{RT} = \frac{0.3 \cdot 101325 \cdot 5 \cdot 10^{-3} mol}{8.314 \cdot 298.15} = 0.0613 \text{ mol}$ 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, $[H^+]_o = (SO_3)$ = 0.0605 mol

	HSO_4^- (aq) ↔	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

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

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) ↔ SO_3 (l) occur, and:

$$n(SO_3, l \ and \ g) = n(SO_3) = n(SO_2) = \frac{p(SO_2)V}{RT} = \frac{0.667p(total)V}{RT} = \frac{0.3 \cdot 101325 \cdot 5 \cdot 10^{-3} mol}{8.314 \cdot 298.15} = 0.1345 \ mol$$ 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

$$HSO_4^- \text{ (aq)} \leftrightarrow SO_3^{2-} \text{ (aq)} + H^+ \text{ (aq)} \qquad\qquad \text{(B)}$$

	HSO_4^-	SO_3^{2-}	H^+
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) ↔ 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).

SOLUTION – Problem 5

Scheme 1

A   B   C

D   E   X

Scheme 2

A   B   C

D   E

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.

SOLUTION – Problem 6

1. ^{87}Rb atom has 87 nucleons and 37 electrons, hence: $87 + 37 = 124$ subatomic particles in total, and 124 is even. ^{23}Na has 23 nucleons and 11 electrons- 34 subatomic particles. The number of electrons is equal to the number of protons in an atom, so it actually only depends on the number of neutrons- if it is even, then the atom is a boson.

2. Two lasers in every possible dimension, therefore 6 lasers in 3D.

3. The general equation is: $E_k = \frac{f}{2}kT$, where f is the number of degrees of freedom and for monatomic gas it is 3. As we can see, the kinetic energy only depends on the type of the gas. Because both sodium and rubidium gasses are monatomic their average kinetic energies are equal: $E_k = \frac{3}{2}kT = 1.5 * 1.380 * 10^{-23}J/K * (25.00 + 273.15)K = 6.172 * 10^{-21}J$

4. $v = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3*8.314\frac{J}{mol*K}*170.0*10^{\wedge}(-9)K}{87.00*10^{\wedge}(-3)\frac{kg}{mol}}} = 6.981 \times 10^{-3}\frac{m}{s} = 6.981\frac{mm}{s}$

5. $E = \frac{hc}{\lambda} = \frac{6.626*10^{-34}\,Js\,*2.99\,8*10^{8}\frac{m}{s}}{780.0*10^{-9}m} = 2.54676 * 10^{-19}\,J$

6. This energy corresponds to the energy needed for the electron of rubidium to go from the s orbital of the fifth layer to the p orbital of the same layer: $5s^1 \rightarrow 5p^1$

7. The general Doppler effect is expressed in the following way for the moving detector (atom) and stationary source (laser):

$$f' = f\frac{v \pm v_d}{v}$$

Where f' is the frequency observed by the detector and f is the frequency of the source. If we put f'=f(atom), f= f(laser), v= c, v(d)= v(atom) then:

$$f_{atom} = f_{laser}\frac{c \pm v_{atom}}{c} = f_{laser}(1 \pm \frac{v_{atom}}{c})$$

Because we want for the atoms to slow down when they are moving towards the laser, so the frequency detected by the atom increases. So we take v/c positive. If we then divide by $\left(1 + \frac{v_{atom}}{c}\right)$ we obtain the desired equation

$$f_{laser} = \frac{f_{atom}}{\left(1 + \frac{v_{atom}}{c}\right)}$$

Due to the fact that the speed of the atoms is really small, compared to the speed of light, we do not have to take the relativity into account.

8. $\Delta f_{atom} = \frac{v_{atom}}{c}f_{laser} = \frac{v_{atom}*c}{c*\lambda} = \frac{\sqrt{\frac{3RT}{M}}}{\lambda} = \frac{\sqrt{\frac{3*8.314*(25.00+273.15)}{87*10^{-3}}}}{780.0*10^{-9}} = 3.748 \times 10^8\,Hz$

Compared to the 3.846×10^{14} Hz frequency of the laser it is not a lot, so during the experiments the scientists usually detune the lasers using the trial and error method.

SOLUTION – Problem 7

1.A – NOCl

   B – HCl

   C – HNO$_3$

   D – NO

   E – Cl$_2$

   F – HNO$_2$

   G – H$_2$SO$_4$

   H – NOHSO$_4$

   I – Cu

   J - Cu(NO$_3$)$_2$

   K – HCN

   L – CNCl

   M – (CN)$_2$

   N – NO$_2$

2.

$$\Delta H_f^0(NOCl_{(g)}) = 51.71 kJ/mol$$

$$\Delta H_f^0(NO_{(g)}) = 90.25 kJ/mol$$

$$S^0(NOCl_{(g)}) = 261.69 J/(mol \cdot K)$$

$$S^0(NO_{(g)}) = 210.761 J/(mol \cdot K)$$

$$S^0(Cl_{2(g)}) = 223.066 J/(mol \cdot K)$$

$$2NOCl_{(g)} \leftrightarrow 2NO_{(g)} + Cl_{2(g)} \quad \Delta H_r^0 = 77.08 kJ/mol \quad \Delta S_r^0 = 121.21 J/(mol \cdot K)$$

$$K = e^{-\frac{\Delta H_r - T\Delta S_r}{RT}} = e^{-\frac{77080 J/mol - 400K \cdot 121.21 J/(mol \cdot K)}{8.314 J/(mol \cdot K) \cdot 400K}} = 1.84 \times 10^{-4}$$

$$K_C = \frac{K_p}{(RT)^{\Delta n}} = \frac{1.84 \times 10^{-4}}{0.008314 \cdot 400} = 5.53 \times 10^{-5}$$

$$[NOCl]_0 = 0.50M$$

$$[Cl_2]_0 = [NO]_0 = 0.00M$$

$$K = \frac{[NO]^2[Cl_2]}{[NOCl]^2} = \frac{4x^3}{(0.50 - 2x)^2} = 5.53 \times 10^{-5}$$

$$4x^3 - 0.0002212x^2 + 0.0001106x - 0.000013825 = 0$$

$$x \approx 0.0145$$

$$[NOCl] = 0.5 - 2 \cdot 0.0145 \approx 0.471M$$

$$[NO] = 2 \cdot 0.0145 \approx 0.029M$$

$$[Cl_2] \approx 0.0145M$$

3.

$$\chi(NOCl) = \frac{n(NOCl)}{n(NOCl)+n(NO)+n(Cl_2)} = \frac{n(NOCl)}{1.5n(NOCl)_0 - 0.5n(NOCl)} = \frac{p(NOCl)}{1.5p(NOCl)_0 - 0.5p(NOCl)}$$

For example $p(NOCl)_0 = 1bar$, then:

$p(NOCl) = 0.0149 bar$

$p(NO) = 0.985 bar$

$p(Cl_2) = 0.493 bar$

$$K = K_p = \frac{0.985^2 \cdot 0.493}{(0.0149)^2} = 2.15 \times 10^3$$

$$T = \frac{\Delta H}{\Delta S - R \ln K} = \frac{77080 J/mol}{121.21 J/(molK) - 8.314 J/(molK) \cdot \ln(2.15 \times 10^3)} = 1343K$$

SOLUTION – Problem 8

H+

Me

O

O

MeO

⊕

H

Me

O

O

MeO

−H⁺

Me

O

MeO

O⊕H

Me

O

MeO

⊕

O—H

Me

O

MeO

O⊕H

H

−H₂O

Product

Me

O

O

O⊖

Me

O

O

O

K_2CO_3

aldol

⊖O

Me

O

O

OH

Me

K_2CO_3

aldol

O

O

Me

HO

OH

Me

K_2CO_3

⊖O

Me

HO

O

O

OH

Me

O

O

Me

OH

Me

repeat dehydration
steps

O

O

O

Me

Me

Diels-Alder step

O

O

Me

Me

O

OH

·B

O

O⊖

O⁻

O

H⁺ transfer

O

O⁻

O

ḢB

O

OH

O

SOLUTION – Problem 9

P.S. Stereochemistry of the products was not expected to be shown by the students. All given structures are obtained after structure optimization.

SOLUTION – Problem 10

1)   According to Luca Turin' theory, nose works like vibrational spectrometer. Receptor has an emtpy cavity which is being occupyied by a fragrance molecule and usual eletron tunelling pathway is being disturbed. In an inclusion complex tunelling is still possible if a molecule or part of it can vibrate in a particular frequencie, thus sending signal to our brains and perceiving the sense of smell. This theory is based on a fact that totally different compounds but having the same IR spectra smells identically. Another theory is based on molecules size and shape, but falls under mentioned above facts. Kadangi jau aišku, ką ir kaip žmogaus nosis atpažįsta, dabar sudėtingesnis klausimas.

2) There are six features, why particular molecules does not trigger our smell sensors. If any of mentioned is present, molecule has little or no odour:

1. If molecules do not have dipole, electron tunelling is impossible.

2. If molecules are big (heavier than 400 g/mol) electron tunneling is also becomes impossible because electron tunneling is possible only in small range (1-2 nm), but heavy molecules are bigger that that.

3. There exist blind spots. For example, our nose do not react to molecules present in air, or to any other frequent vibrations, such as C-H.

4. Also, there exists a vibration frequency limit to which receptors are being triggered. If below, spectra comes in mix with rotational spectra, thus giving n actual information to our receptor.

5. Electron scattering must be greater than yet undetermined limit, otherwise, to change between original and subsequential electon tunnelling pathway is observed.

6. Inadequate space orientation of a molecule. Particular fragrance molecule enters the receptor in a defined orientation and only one part of a receptor identifies vibrations. Thus if a most intensily vibrating group is situated on another side of a molecul, smell would be mild if any.

3)

ZGiven compound: Isoamylacetate or 3-methyl-1-butyl acetate.

It does not matter what three compunds are offered by students. The crucial thing is that their IR spectra would have chracteristical peaks. And of course the synthesis method would be justified.

41

4) According to previous mentioned theory, zinc is involved in smell receptors. Thus, all molecules which are able to get to the receptor (i.e. fits the cavity, is volatile, binds to the receptor) smells very strong if has a structural ability to bind the zinc cation. If it does not smell is comperatively less strong.

5)

Spectra of these compunds are attached in a zip file. ChemDraw is required to open compressed files.

SOLUTION – Problem 11

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

SOLUTION – Problem 12

a) Solution of the first three tasks is based on the Nernst equation. The general formula is the following: $\varepsilon = \varepsilon_0 + \frac{RT}{zF} \ln\left(\frac{[ox]}{[red]}\right)$ where ε_0 is the standard, ε is the actual potential; R is ideal gas constant; T is the temperature in Kelvins; z is the stoichiometric number of electrons; F is the Faraday constant; [ox] and [red] are the concentration of oxidized and reduced species – for approaching the chemical activity.

i) The half-cells are standard, $\varepsilon = \varepsilon_0$, therefore the following reaction will take place: $Cd + Ni^{2+} = Cd^{2+} + Ni$, because the Cd^{2+}/Cd half-cell has lower potential.

ii) At pH=11 precipitation should be considered. $[Cd^{2+}]$ can be determined by using the solubility constant:

$L = [Cd^{2+}][OH^-]^2 \qquad x = [Cd^{2+}]$
$10^{-13.5} = x \times (10^{-3})^2 , \qquad x = 10^{-7.5} = 3.162 \times 10^{-8}$ mol/L.
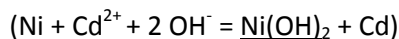Using the Nernst equation the actual potential of Cd^{2+}/Cd half-cell:
$$\varepsilon(Cd^{2+}/Cd) = -0.40 + \frac{8.3145 \times 298.15}{2 \times 96485} \ln\left(\frac{10^{-7.5}}{1}\right) = -0.62\ \text{V}$$
Therefore the reaction is the same as in the previous subtask.

Another reasoning: precipitation means that the $[Cd^{2+}]$ will decrease. According to the properties of logarithms this means that the actual potential of Cd^{2+}/Cd half-cell will be lower than $\varepsilon(Cd^{2+}/Cd)$ so the $Cd + Ni^{2+} = Cd^{2+} + Ni$ redox reaction will take place as well.
(Because of the precipitation: $Cd + Ni^{2+} + 2\ OH^- = \underline{Cd(OH)_2} + Ni$)

iii) This case is quite similar to the previous one. Using the same method: $\varepsilon(Ni^{2+}/Ni)$ = -0.56 V so the direction of the redox reaction will be different: $Ni + Cd^{2+} = Ni^{2+} + Cd$
($Ni + Cd^{2+} + 2\ OH^- = \underline{Ni(OH)_2} + Cd$)

iv) The actual potential of half-cell 1) can be determined similarly, the concentration is known from the masses: $\varepsilon(Cd^{2+}/Cd)$ = -0.45 V.
$[Ni^{2+}]$ will be lower because of formation of $Ni(CN)_4^{2-}$. The initial amounts are stoichiometric and the equilibrium constant is a large number, so $[Ni(CN)_4^{2-}]$ could be approached by $[Ni^{2+}]$.
$$10^{31.11} = \frac{1.021 \times 10^{-3}}{x \times (4x)^4}$$
where $x = [Ni^{2+}] = 4.991 \times 10^{-8}$mol/L
Using the Nernst equation: $\varepsilon(Ni^{2+}/Ni) = -0,45$ V. $\varepsilon(Ni^{2+}/Ni) \cong \varepsilon(Cd^{2+}/Cd)$ therefore no redox reaction will be expected.

43

b) The main difficulty of this task is that none of the complexes are negligible. The equilibrium constants are given for each complex: $\beta_n = \frac{[CdI^{(n-2)-}]}{[Cd^{2+}][I^-]^n}$ $[CdI^{(n-2)-}] = \beta_n[Cd^{2+}][I^-]^n$

Using these correspondences $[Cd^{2+}]$ and $[I^-]$ could be written by the linear combination of concentrations of species. This results a system of equations for $[Cd^{2+}]$ and $[I^-]$:

$$[Cd^{2+}]' = [Cd^{2+}]\left(\sum_{n=0}^{4}\beta_n[I^-]^n\right) \qquad \beta_0 = 1 \qquad\qquad (1)$$

$$[I^-]' = [I^-] + [Cd^{2+}]\left(\sum_{n=1}^{4}\beta_n n[I^-]^n\right) \qquad\qquad (2)$$

This could be solved by computer or an iterative method.

Considering the $[I^-]$ it must be between 0.031 and 0.035 mol/L. Let us suppose that $[I^-] = 0{,}031$ mol/L. Using equation (1): $[Cd^{2+}] = 4.445 \times 10^{-5}$ mol/dm^3. Substituting these for equation (2) $[I^-] = 0.03327$ mol/L. Repeating this method until $[I^-]$ will not change during the cycle the solutions are $[I^-] = 0.03321$ mol/L and $[Cd^{2+}] = 3.937 \times 10^{-5}$ mol/L. The actual potential of this half-cell: $\varepsilon(Cd^{2+}/Cd) = -0{,}53$ V. If there is no difference between these half-cells $\varepsilon(Ni^{2+}/Ni)$ must be -0.53 V.

$$\varepsilon(Ni^{2+}/Ni) = -0.53 \text{ V} = -0.23 + \frac{8.3145 \times 298.15}{2 \times 96485}\ln\left(\frac{[Ni^{2+}]}{1}\right)$$

so $[Ni^{2+}] = 7.050 \times 10^{-11}$ mol/L.

In basic solution of $[Ni^{2+}]$ there must be equilibrium between precipitate and free $[Ni^{2+}]$, therefore:

$$[OH^-] = \sqrt{\frac{L}{[Ni^{2+}]}} = \sqrt{\frac{10^{-17,19}}{7{,}050 \times 10^{-11}}} = 3{,}026 \times 10^{-4}\,\frac{mol}{dm^3}$$

Almost the entire amount of Ni^{2+} is in precipitate so $2 \times 0{,}1 \times 1 \times 10^{-4}$ mol NaOH is necessary for it. Besides this additional $0{,}1 \times 3{,}026 \times 10^{-4}$ mol NaOH is needed to set the pH value of the solution. As result **2,011 mg** NaOH must be added.

SOLUTION – Problem 13

1. The sulfur containing species have a total concentration of 0.117 mol/dm^3. Hydrogen ions coming from the second dissociation step can be neglected. The first dissociation of a weak acid in this concentration gives pH = 3.92. (3 points)
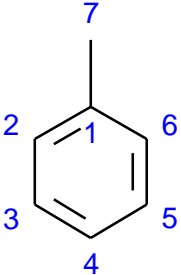
The same first dissociation step gives pH = 8.90 as the answer for the second question. (2 points)
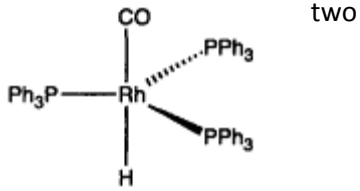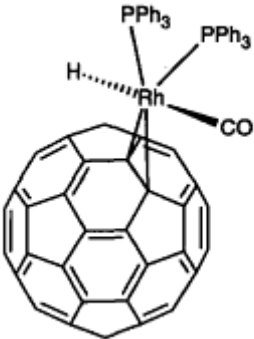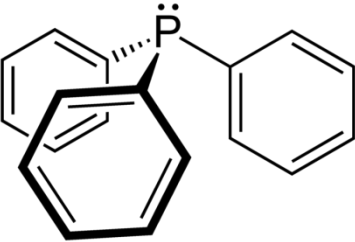
2. Using the second dissociation constant given, the ratio $[HS^-]/[S^{2-}] = 5$ results. This means that 83% of hydrogen sulfide would be in sulfide ion form in this solution. (2 points)

3. In moderately basic solutions HS^- ion will be the dominant species, present in 100%. The detectable 1% decrease in 5 mol/dm^3 hydroxide ion solutions will mean 99% of hydrogen sulfide as HS^- ion. So $[HS^-]/[S^{2-}] > 99$, and $K_2 < 2 \cdot 10^{-17}$. (3 points)

4. In concentrated solutions activity coefficients can significantly deviate from unity. (2 points)

5. From the concentrations and the appearances of the precipitates two limits can be estimated: based on no ZnS precipitate: $K_2 < 3.41 \cdot 10^{-15}$, based on SnS: $K_2 > 2.71 \cdot 10^{-18}$. (4+4 points)

6) If we take the precipitation of ZnS complete, then the pH of the solution is determined by the hydrogen ions formed in the $Zn^{2+} + H_2S \rightarrow ZnS + 2\,H^+$ process, as the hydrogen sulfide dissociation is suppressed. Final pH = 2 in this case. However the complete precipitation is not obvious and depends on the true value of the second dissociation constant. If $K_2 = 10^{-17}$ then pH = 2.39 and only 40% of the zinc is precipitated. (2+2 points)

SOLUTION – Problem 14

1 a	**Important note! Points are taken for an incorrect number of significant figures in numerical calculations.** $\lambda = 2d \sin \Theta$ $d = \dfrac{\lambda}{2 \sin \theta} = \dfrac{1.542}{2 \sin \frac{41.11°}{2}} = 2.196 \text{Å} \ [2]$ $\dfrac{1}{d^2} = \dfrac{h^2 + k^2 + l^2}{a^2}$ $\therefore a^2 = 2.196\sqrt{3} \approx 3.803 \text{ Å} \equiv 3.803 \times 10^{-8} \ cm \ [3]$
1 b	In an fcc structure there are four formula units (here – atoms) per unit cell. Given the density and the lattice parameter, calculated above, the atomic mass of **M** can be derived: $\rho = \dfrac{m}{V} = \dfrac{4M}{N_A a^3} \ \therefore M = \dfrac{N_A \rho a^3}{4} = 102.9 \ g \ mol^{-1} \ [2]$ **M = Rh (rhodium)**
2 a	Since **C** contains one element only and gives a signal in ^{13}C-NMR, it must be some allotrope of carbon. In addition, it must contain carbon in sp^2 hybridization state. Given the colour of the toluene solution, **C** can only be the buckminsterfullerene **C$_{60}$**, which is aromatic and highly symmetric, as seen from the spectrum. **C = C$_{60}$**
2 b	 Note: no points should be taken for incorrect assignment of signals at 123.1, 125.4, 128.3 ppm. **B = C$_7$H$_8$, toluene**

Table in 2 b:

Signal (ppm)	Carbon number
21.4	7
123.1	
125.4	2-6
128.3	
137.8	1

3 a	The signal at – 9.50 ppm is most probably due to a hydrogen, directly attached to the metal. It shows coupling over two bonds (as hinted in the problem) to phosphorus, which has a spin of ½, just like ^{1}H. This means, that if the hydrogen signal is split into a quartet there must be three phosphorus atoms two bonds away from it (i.e. attached directly to the metal). The other signals in the NMR spectrum must be due to the hydrogens of the other ligands. The signals are characteristic to aromatic compounds, and bearing in mind the presence of phosphorus, we can predict, that there are going to be **three triphenylphosphine** ligands attached to rhodium in this complex (this correlates nicely with the chemical shifts and the total intensity: 5*3*3 = 45) From the IR spectrum we can infer, that there is also one or two C≡O ligands attached to the rhodium atom. $RhH(CO)(PPh_3)_3$, a yellow solid, fits the description very well. **A** = $RhH(CO)(PPh_3)_3$
3 b	**D** = $RhH(CO)(PPh_3)_2C_{60}$ (a dark green solid) **E** = PPh_3 (triphenylphosphine)
3 c	Since both the complexes are coloured, they absorb in the near UV/ visible light region of the electromagnetic spectrum. Thus, UV-Vis spectroscopy can be used. To carry out the spectroscopic analysis the maximum absorption wavelengths for both compounds are required, as well as the molar extinction coefficient at the desired wavelengths. A = εlC – Lambert-Beer law, where A is the absorption, ε is the extinction coefficient, l is the sample thickness and C is the concentration
Notes	The material for this task was taken from the following paper: *Claridge, J.B., Douthwaite, R.E., Green, M.L.H., Lago, R.M., Tsang, S.C., York, A.P.E. 1993. Studies on a new catalyst for the hydroformylation of alkenes using C_{60} as a ligands. Journal of Molecular Catalysis 89:113–120* Molecular structure for the coordination complex compounds were taken from *Hirsch, A 1994. The Chemistry of the Fullerenes. New York: Thieme*

Enjoy chemistry! ☺