

## PART II.a – Physical chemistry

### Problem 1

#### Radiometric dating of rocks

When a rock is formed it incorporates a small amount of radioactive elements that decay over time. A rock forming shows different preference for different elements but not isotopes. However, when a radioactive element decays the new formed element cannot leave the rock even if the rock shows no preference for it during formation. Elements that are not normally incorporated in a rock are named incompatible. Due to radioactive decay the rock becomes depleted in radioactive elements and enriched in incompatible elements over time. This effect can be used in dating rocks. To complicate things a bit all elements are present in the rock in small but significant amounts.

Rocks can be dated by measuring the ratio (ratio 1) between radioactive isotope and stable isotope of its decay product and ratio (ratio 2) between the decay product and a stable isotope of the same element.  $X \rightarrow A$  ratio 1:  $X/B$  ratio 2:  $A/B$ , where  $X$  is a radioactive isotope,  $A$  is its daughter element,  $B$  is a stable isotope of the same element as  $A$ . Quite commonly used system to date rocks is rubidium/strontium system.  $^{87}\text{Rb}$  decays to  $^{87}\text{Sr}$  via beta decay. Half life of this decay is  $4.92 \times 10^{10}$  yr. Decay is first order reaction.

Following ratios were measured in a rock from Greenland:

$^{87}\text{Rb}/^{86}\text{Sr}$	$^{87}\text{Sr}/^{86}\text{Sr}$
0.34	0.719
0.61	0.733
0.90	0.749
0.98	0.753

- 1) Develop a method for dating rocks by using rubidium/strontium system.  
[Hint: Start with 1<sup>st</sup> order rate equation. Normalization relative to  $^{86}\text{Sr}$  is the last step]
- 2) Use the method of question 1 to plot a graph and calculate the age of the rock and initial  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio.
- 3) Why is the normalization step relative to  $^{86}\text{Sr}$  necessary?
- 4) Why is this method useful for dating rocks but not as useful to date archeological findings from ancient civilizations?

Feldspars are very common group of aluminosilicate minerals with similar structures. Albite ( $\text{NaAlSi}_3\text{O}_8$ ) and Anorthite ( $\text{CaAl}_2\text{Si}_2\text{O}_8$ ) are sodium rich endmember and calcium rich endmember respectively of feldspar group. Orthoclase ( $\text{KAlSi}_3\text{O}_8$ ) is potassium rich feldspar. In Albite-Anorthite series sodium can be freely substituted with calcium in any amount and the resulting crystal structure is thermodynamically stable. In Orthoclase-Albite and Orthoclase-Anorthite series, however, potassium cannot be substituted with neither sodium or calcium because the resulting crystal structure is thermodynamically unstable.

5) Give explanation to this fact.

## Problem 2

### Random walk model

On a one dimensional grid (1D) random walk is following: imagine that you are standing in the beginning of coordinate axis and toss a coin – if you get tails you make a unit step forward and if you get heads you make a unit step backwards and so on.

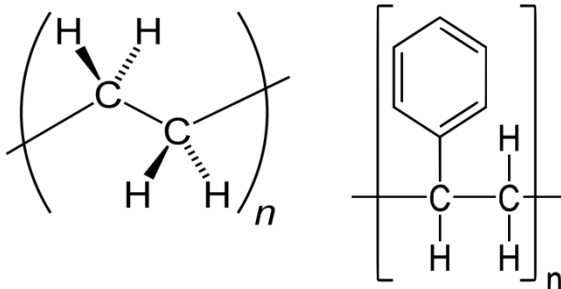
a) Show that in 1D after  $N$  tosses you will be at an average distance  $\sqrt{N}$  from the origin.

On a three dimensional grid (3D) step along any of coordinate axes is equally probable.

b) Show that in 3D after  $N$  tosses you will also end up at an average distance  $\sqrt{N}$  from the origin.

We can use random walk model to estimate sizes of polymer molecules, since we know the number of steps (number of monomers in a macromolecule) and step size (length of a monomer unit).

c) Find end-to-end distance in a polyethylene molecule containing 10000 monomers (C-C bond length is 0.154 nm in alkanes).



Applying random walk model to polymers is, of course, silly, because we assume that every next monomer can take any position, whereas in real molecules its position is constrained due to repulsion between side chains. However, we may introduce a concept of Kuhn length. The Kuhn length is a length below which the chain does not bend. For polyethylene the Kuhn length is 3.5 lengths of C-C bond and for polystyrene it is 5 C-C bond lengths.

d) Explain differences between Kuhn lengths for polyethylene and polystyrene and find end-to-end distance for both if each macromolecule has 10000 monomers in it.

### Problem 3

**In the quantum world** all systems are described with discrete energy states and no continuous energy spectrum can be obtained. If we want to describe motion of particle it can be described either as free particle, particle in one-, two- and three- dimensional box depending on the dimensions in which particle is allowed to move. If particle (like electron) can be described as moving in one dimensional box (like in conjugated dienes) the energy of this particle can be described with equation:

$$E_n = \frac{n^2 h^2}{8mL^2}$$

Where  $n$  is the quantum number for the energy state and is an integer between 1 and  $\infty$ ,  $h$  is the Planck's constant in J·s,  $m$  is the mass of the particle in kilograms and  $L$  is the length of the box in meters.

If we want to describe particle in the closed space, then particle in three-dimensional box equation should be used:

$$E_n = \frac{h^2}{8m} \left( \frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2} \right)$$

Where  $n_x$ ,  $n_y$  and  $n_z$  are quantum numbers in corresponding directions and  $a$ ,  $b$  and  $c$  is length of the box in each direction.

#### Part I

In this problem we will explore molecule in three dimensional box. We will look on hydrogen molecule.

Case A. Hydrogen atom is inserted in cubic box with volume  $0.500 \text{ m}^3$ .

Case B. Hydrogen atom is inserted in pore of zeolite structure which can be described as cubic box with edge length  $1 \text{ nm}$ .

1. Calculate the edge length of the box in Case A.
2. Calculate the energy of first level with quantum numbers  $n_x = n_y = n_z = 1$  for both cases.
3. Calculate the energy difference between first two energy levels for each case.
4. Calculate the energy difference between energy level for  $n_x = n_y = n_z = 10$  and the next energy level for each case.
5. Calculate the wavelength which corresponds to each of transition calculated in 4.? To which part of the spectrum can be classified this wave?

As stated above, quantum chemical approach is described with discrete energy spectrum while classical approach is described with continuous energy spectrum. We can analyse which approach can be used by using approximate Boltzmann distribution:

$$\frac{n_i}{n_j} = e^{-[E_i - E_j]/kT}$$

Where  $n_i/n_j$  is ratio between particles in states  $i$  and  $j$ ,  $E_i$  and  $E_j$  is corresponding energy values,  $k$  is Boltzmann constant and  $T$  is temperature in Kelvins. If  $\Delta E \gg kT$  then quantum approach is used. However, if  $\Delta E \approx kT$  then classical approach can be used.

6. Calculate ratio  $n_i/n_j$  for energy level spacing calculated in 4. for both cases if temperature is 298 K.
7. Which approach can be used in each system?

## **Part II**

Electrons in benzene can be described with two approaches. First and simpler approach describes electrons with "particle on a ring model". In this case energy of each state are defined by equation:

$$E_n = \frac{n^2 h^2}{8\pi^2 m_e R^2}$$

where  $R$  is the radius of the ring in meters, and quantum number  $n$  equals  $0, \pm 1, \pm 2, \dots, \pm\infty$ . Assume that the benzene ring radius is 139 pm.

8. Calculate the energy of all occupied and the lowest unoccupied states of benzene. Are there any states with equal energy values?
9. Draw diagram showing all occupied and lowest unoccupied levels. Filling the energy levels, keep in mind the Pauli exclusion principle.
10. Calculate the energy difference between highest occupied and lowest unoccupied states. In which diapason of spectrum lies the radiation corresponding to this transition.

A more accurate approach is based on molecular orbital theory. For monocyclic conjugated polyenes energy level diagram can be obtained in the following way:

Inscribe a regular polygon with the shape of the polyene in a circle of radius  $2\beta$  with one vertex of the polygon pointing directly downward. Draw a horizontal line at each point for which a polygon is tangent to the circle. These lines correspond to the energy levels, with the centre of the circle corresponding to the energy  $\alpha$ . It is known that  $\beta = -65$  kcal/mol.

11. Draw the diagram showing all possible energy states in benzene. Show the electrons in your diagram.
12. Calculate the energy difference between highest occupied and lowest unoccupied states. In which diapason of spectrum lies the radiation corresponding to this transition.
13. Which one of these approaches is more correct? Provide explanations.

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