Face your challenge,
Be smart

THEORETICAL EXAMINATION

JULY 20, 2013
MOSCOW, RUSSIA

General Directions

- Write down your name and code number on each page.

- You have 5 h to fulfill the tasks. Failure to stop after the STOP command may result in zero points for the current task.

- Write down answers and calculations within the designated boxes. Give your work where required.

- Use only the pen and calculator provided.

- If you need draft paper use the back side of the paper. It will not be marked.

- There are **38** pages in the booklet including the answer boxes, Cover Sheet and Periodic Table.

- The official English version is available on demand for clarification only.

- Need to go to the restroom – raise your hand. You will be guided there.

- **After the STOP signal** put your booklet in the envelope (don’t seal), leave at your table. Do not leave the room without permission.

- You have additional 15 minutes to read the whole set.

Physical Constants, Units, Formulas and Equations

Avogadro's constant	$N_A = 6.0221 \times 10^{23}\ \text{mol}^{-1}$
Universal gas constant	$R = 8.3145\ \text{J·K}^{-1}\text{·mol}^{-1}$
Speed of light	$c = 2.9979 \times 10^{8}\ \text{m·s}^{-1}$
Planck's constant	$h = 6.6261 \times 10^{-34}\ \text{J·s}$
Faraday constant	$F = 96485\ \text{C·mol}^{-1}$
Gravity of Earth	$g = 9.81\ \text{m·s}^{-2}$
Standard pressure	$p° = 1\ \text{bar} = 10^5\ \text{Pa} = 750\ \text{mmHg}$
Atmospheric pressure	$1\ \text{atm} = 1.013 \times 10^5\ \text{Pa} = 760\ \text{mmHg}$
Zero of the Celsius scale	273.15 K

1 nanometer (nm) = 10^{-9} m
1 Da = 1 atomic mass unit
1 electron volt (eV) = $1.6022 \cdot 10^{-19}$ J = 96485 J·mol^{-1}

Energy of a light quantum with wavelength λ	$E = hc / \lambda$
Energy of one mole of photons	$E_m = hcN_A / \lambda$
Gibbs energy	$G = H - TS$
Relation between equilibrium constant and standard Gibbs energy	$K = \exp\left(-\frac{\Delta G°}{RT}\right)$
Relation between standard Gibbs energy and standard emf	$\Delta G° = -nFE°$
Clapeyron equation for phase transitions	$\frac{dp}{dT} = \frac{\Delta H}{T\Delta V}$
Integrated Clausius-Clapeyron equation for phase transitions involving vapor	$\ln\frac{p_2}{p_1} = \frac{\Delta H}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$
Dependence of Gibbs energy of reaction on concentration or pressure	$\Delta G = \Delta G° + RT\ln\frac{a_{\text{prod}}}{a_{\text{reag}}}$, $a = c$ / (1 mol/L) for the substances in solution, $a = p$ / (1 bar) for gases
Volume of a sphere of radius R	$V = \frac{4}{3}\pi R^3$
Surface area of a sphere of radius R	$S = 4\pi R^2$
Hydrostatic pressure	$p = \rho gh$

Problem 1. Clathrate gun (8 points)

Question	1	2	3	4	5	6	Total
Marks	2	1	3	5	6	2	19

The only gun that is able to kill all living people in one shot

On the floors of oceans and seas there are vast reserves of methane in the form of clathrate compounds called methane hydrates. These reserves can be mined and serve as a source of energy or raw materials for organic synthesis. However, scientists are seriously worried about the possibility of spontaneous decomposition of hydrates caused by the raising ocean temperature. It is believed that if a sufficient amount of methane is released into the atmosphere, the oceans will warm up quicker due to the greenhouse effect, further accelerating the decomposition of clathrates. Due to the explosion of the resulting methane-air mixture and/or changes in the composition of the atmosphere, all living creatures may become extinct. This apocalyptic scenario is called a clathrate gun.

Upon decomposition of 1.00 g of a methane hydrate with a fixed composition at 25 °C and atmospheric (101.3 kPa) pressure, 205 mL of methane is released.

1. Determine *n* (not necessarily integer) in the formula of methane hydrate, $CH_4 \cdot nH_2O$.

Calculations:

Answer:

Real methane hydrate has a non-stoichiometric composition close to $CH_4 \cdot 6H_2O$. At atmospheric pressure, methane hydrate decomposes at –81 °C. However, under high pressures (e.g. on the ocean floor) it is stable at much higher temperatures. Decomposition of methane hydrate produces gaseous methane and solid or liquid water depending on temperature.

2. Write down the equation of decomposition of 1 mole of $CH_4 \cdot 6H_2O$ producing solid water (ice) $H_2O(s)$.

The enthalpy of this process equals 17.47 kJ·mol^{-1}. Assume that the enthalpies do not depend on temperature and pressure, the volume change upon decomposition of hydrate is equal to the volume of released methane, and methane is an ideal gas.

3. At what external pressure does decomposition of methane hydrate into methane and ice take place at –5 °C?

Calculations:

Answer:

4. What is the minimum possible depth of pure liquid water at which methane hydrates can be stable?
To answer this question, you should first deduce at which minimum temperature methane hydrate can coexist with liquid water. Choose the correct answer.

☐ 272.9 K ☐ 273.15 K ☐ 273.4 K

Calculations:

Answer:

Large methane hydrate stocks on the floor of Baikal lake, the largest freshwater lake in Russia and in the world, have been discovered in July 2009 by the crew of a deep-submergence vehicle «Mir-2». During the ascent from the depth of 1400 m methane hydrate samples started to decompose at the depth of 372 m.

5. Determine the temperature in Baikal lake at the depth of 372 m. The enthalpy of fusion of ice is 6.01 kJ·mol^{-1}.

Calculations:

Answer:

Total amount of methane in hydrates on Earth is no less than $5\cdot10^{11}$ tons.

6. By how many degrees would the Earth atmosphere heat up, if such amount of methane is burned by reacting with atmospheric oxygen? The enthalpy of combustion of methane is –889 kJ·mol^{-1}, the total heat capacity of the Earth's atmosphere is about $4\cdot10^{21}$ J·K^{-1}.

Calculations:

Answer:

Problem 2. Break down photosynthesis – the Hill reaction (7 points)

Question	1	2	3			4		5	6	Total
			a	b	c	a	b			
Points	1	2	2	2	3.5	1	2	3	2.5	19

In the history of photosynthesis research, there were some breakthrough experiments which added much to our knowledge of this very complex process. One of such experiments was performed in 1930s by an English biochemist Robert Hill. In this problem, we consider some of his data together with the data of more recent experiments.

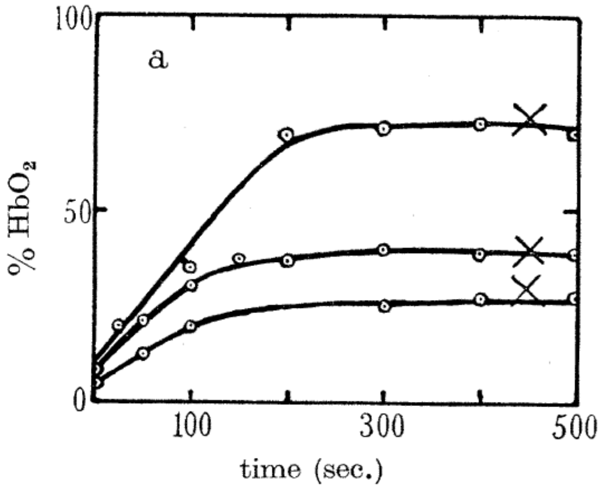
1. In plants, under illumination, carbon dioxide is reduced to carbohydrates (denote as $\{CH_2O\}$) and oxygen is produced. Write the overall equation of photosynthesis in plants.

Much of the photosynthesis takes place in chloroplasts – organelles found in plant cells and containing chlorophyll – the light-absorbing substance. Hill isolated chloroplasts from the cells by grinding the leaves in the sucrose solutions. The cell-free chloroplasts did not produce oxygen under illumination even in the presence of CO_2. However, upon adding potassium ferrioxalate $K_3[Fe(C_2O_4)_3]$ (with the excess of potassium oxalate) to the chloroplast suspension Hill observed oxygen liberation under illumination even without CO_2.

2. Hill's experiment enabled to determine the source of oxygen during photosynthesis. Write the formulas of the oxidant and the reducing agent in the photosynthesis inside the plant cells and in the cell-free chloroplasts (the Hill reaction).

Natural photosynthesis		Hill reaction	
Oxidant	Reducing agent	Oxidant	Reducing agent

Hill measured the amount of evolved oxygen using muscle haemoglobin (Hill denoted it Hb) which binds all molecular oxygen in a 1:1 ratio to form HbO_2. The initial concentration of Hb was $0.6 \cdot 10^{-4}$ M. Kinetic curves corresponding to different ferrioxalate concentrations are shown in the figure (the upper curve corresponds to $2.0 \cdot 10^{-4}$ M).



The fraction of bound haemoglobin HbO$_2$ (with respect to the initial amount of Hb) as function of time. Crosses denote the end of reaction

(Figure 2a from the original Hill's paper: *R. Hill. Oxygen produced by isolated chloroplasts. – Proc. R. Soc. B, 1939, v. 127, pp. 192-210*)

3. a. From the figure, estimate the Fe / O$_2$ mole ratio at the end of reaction. Do not take into account the iron from Hb.

b. Write the equation of Hill reaction assuming that it proceeds with a high yield.

c. Using the table of standard electrode potentials, determine the Gibbs energy of the Hill reaction at T = 298 K, oxygen pressure 1 mmHg, pH = 8 and standard concentrations of other species. Is this reaction spontaneous at such conditions?

Half-reaction	$E°$, V
$O_2 + 4H^+ + 4e \rightarrow 2H_2O$	+1.23
$CO_2 + 4H^+ + 8e \rightarrow \{CH_2O\} + H_2O$	–0.01
$Fe^{3+} + e \rightarrow Fe^{2+}$	+0.77
$Fe^{3+} + 3e \rightarrow Fe^0$	–0.04
$[Fe(C_2O_4)_3]^{3-} + e \rightarrow [Fe(C_2O_4)_3]^{4-}$	+0.05
$[Fe(C_2O_4)_3]^{4-} + 2e \rightarrow Fe + 3C_2O_4^{2-}$	–0.59

a. Calculations

n(Fe) / n(O$_2$) =

b.

Reaction equation:

c. Calculations

ΔG =

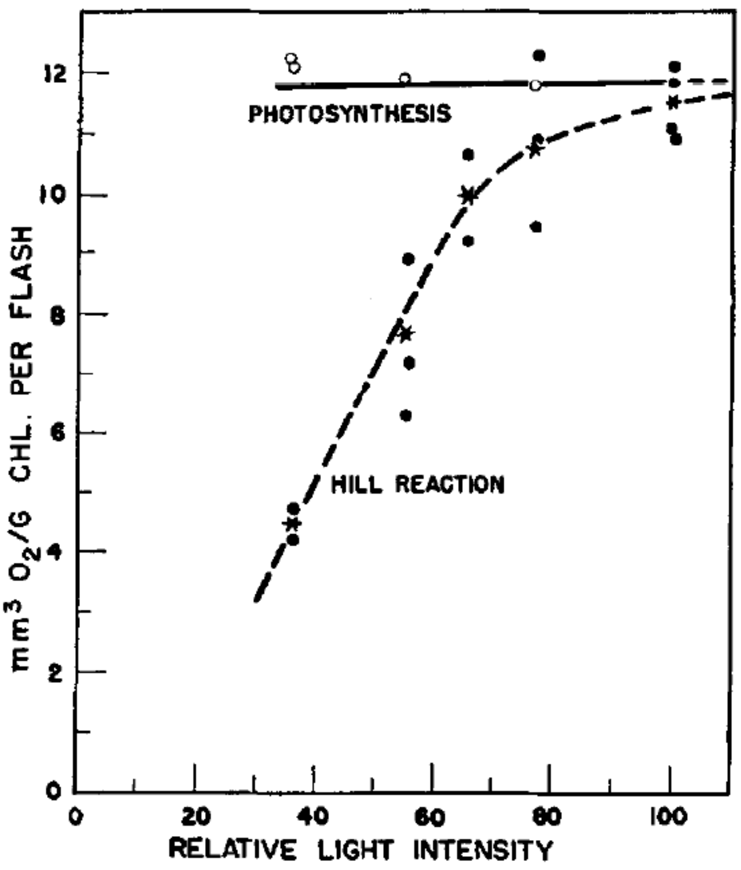
The reaction is

spontaneous ☐

not spontaneous ☐

Now, the name “Hill reaction” denotes photochemical oxidation of water by any oxidant other than carbon dioxide which is sensitized by plant cells or isolated chloroplasts.

In another experiment (1952), quinone in an acid solution was used as an oxidant in the Hill reaction initiated by light flashes in the *Chlorella* algae. Experimental data are shown in the figure. The volume of oxygen (in mm^3, at temperature 10 ^{o}C and pressure 740 mmHg) per one gram of chlorophyll per one flash was determined as a function of light intensity for natural photosynthesis and for isolated chloroplasts. It was found that the maximum yield of oxygen is the same for natural photosynthesis and the Hill reaction.



(Figure 1 from: *H. Ehrmantraut, E. Rabinovitch. Kinetics of Hill reaction. – Archives of Biochemistry and Biophysics, 1952, v. 38, pp. 67-84*)

4 a. Determine the reaction order of a photochemical Hill reaction with respect to light intensity at low and high intensity. For each case choose one of three values:

Reaction order:

Low intensity

0 ☐ 1 ☐ 2 ☐

High intensity

0 ☐ 1 ☐ 2 ☐

b. How many chlorophyll molecules participate in the formation of one oxygen molecule in the saturation limit of the Hill reaction? (The molecular mass of chlorophyll is about 900 Da).

Calculations:

$n(\text{Chl}) / n(O_2)$ =

The quantum requirement of the light redox reactions is defined as the average number of light photons (not necessarily integer) needed for the transfer of one electron from a reducing agent to an oxidant. The isolated chloroplasts were irradiated during 2 hours by a monochromatic light (wavelength 672 nm) with the energy input 0.503 mJ/s, and the total volume of oxygen formed was 47.6 mm^3 (under the same conditions as in question 4).

5. Calculate the quantum requirement for the Hill reaction.

Calculations:

Quantum requirement:

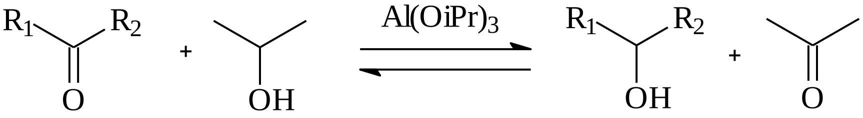
6. Try to make conclusions from the above experiments (questions 2-5). For each of the following statements **<u>choose either “Yes” or “No”</u>**.

	Yes	**No**
In natural photosynthesis, water oxidation and CO_2 reduction are separated in space.		
In chloroplasts, O_2 is produced from CO_2.		
Oxidation of water in chloroplasts requires light illumination.		
Most of chlorophylls in chloroplasts participate directly in the photochemical O_2 production.		
In isolated chloroplasts, every absorbed photon causes transfer of one electron.		

Problem 3. Meerwein-Schmidt-Ponndorf-Verley reaction (8 points)

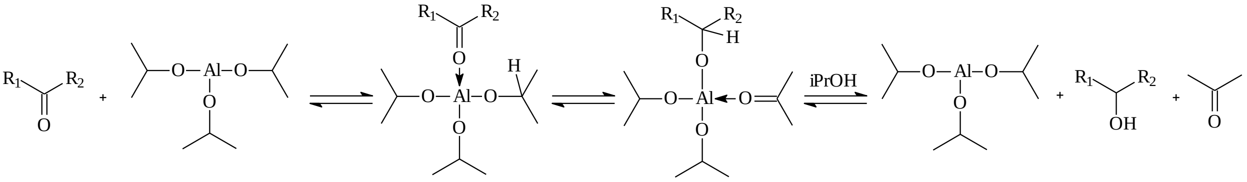
Question	1		2	3	4	Total
	a	b				
Marks	7	3	8.5	6	8	32.5

Meerwein-Schmidt-Ponndorf-Verley (MSPV) reaction is a useful tool for reduction of carbonyl compounds to alcohols. The reaction is the reduction of carbonyl compounds by low molecular weight alcohols in the presence of alkoxides of aluminium or other metals:



(1)

The mechanism of the reaction includes coordination of carbonyl compound by aluminium alkoxide, hydride transfer in the inner sphere of the complex and subsequent transalkoxylation. It can be schematically represented as follows (transalkoxylation is shown as a one-step process for brevity):



(2)

The reaction is reversible and shifting the equilibrium to the desired product requires some excess of the reductant. In some cases (e.g. in the case of reduction of aromatic aldehydes and ketones) the equilibrium constant is so large that the reverse reaction can be neglected.

The table below contains standard entropies and standard enthalpies of formation of liquid substances at 298 K. The boiling points of the substances at 1 bar are also given.

Substance	$\Delta_f H^o_{298}$, kJ/mol	S^o_{298}, J/(mol·K)	t_{vap}, ^oC
Acetone	–248.4	200.4	56
Isopropanol	–318.1	180.6	82
Cyclohexanone	–271.2	229.0	156
Cyclohexanol	–348.2	203.4	161

1a. Calculate the minimum isopropanol:cyclohexanone mass ratio which is required to reach a 99% yield of reaction at 298 K. Assume that a) the reaction mixture eventually gets at equilibrium and b) no products are initially present.

Calculations:

Answer:
$m(C_3H_8O) : m(C_6H_{10}O) =$

1b. Choose the appropriate way(s) to increase the cyclohexanol yield.
Warning: erroneously ticked boxes will result in penalty points

Increase the temperature up to 50°C using a reflux	
Increase the temperature up to 60°C, evaporating (distilling) the acetone	
Add some ethanol to the reaction mixture	
Add some ethanal to the reaction mixture	

2. Often the rate-limiting step in the MSPV reaction is the hydride transfer or the alcoholysis of the alkoxide after hydride transfer. For these two cases, using the above mechanism (2), derive an expression for the rate of reaction as a function of current concentrations of a carbonyl compound, isopropanol and a catalyst. In both cases determine the rate orders in the reactants and the catalyst. Assume that all reaction steps before the limiting step are fast and reversible. Use equilibrium approximation, if necessary. For brevity use the following

notation: **A** for carbonyl compound, **B** for isopropanol, **C** for catalyst. Denote intermediates as you wish.

Rate-limiting step is the hydride transfer

Derivation:

r **=**

Answer

Order in carbonyl compound: ________

Order in isopropanol: ________

Order in the catalyst: ________

Rate-limiting step is the transalkoxylation of the alcoholate by isopropanol

Derivation:

r **=**

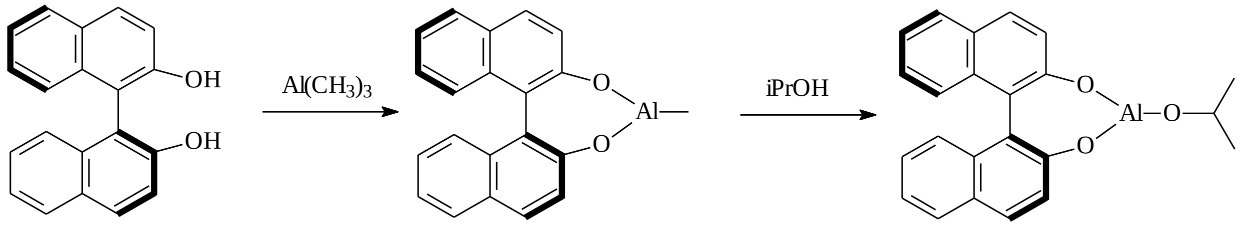
<u>Answer</u>

Order in carbonyl compound: ________

Order in isopropanol: ________

Order in the catalyst: ________

MSPV reaction can be used to obtain chiral alcohols, if the chiral catalyst is employed. For instance, Campbell et al. used the catalyst based on the chiral 2,2’-dihydroxy-1,1’-binaphtyl (BINOL), which is synthesized *in situ* from binaphtol and trimethylaluminium:



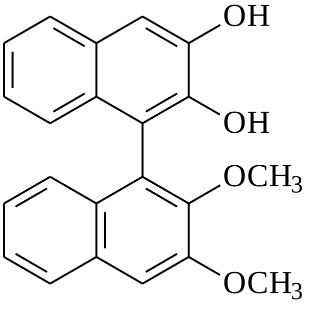
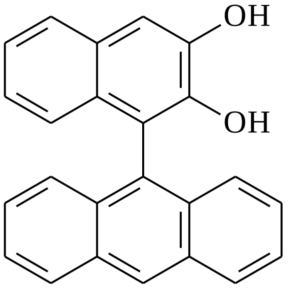
(BINOL)Al(OiPr)

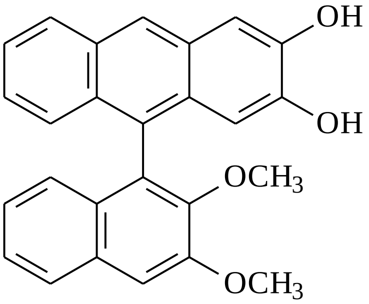
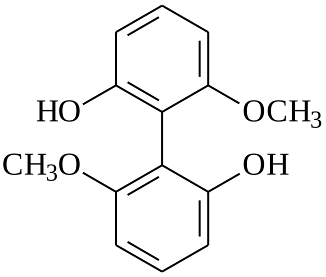
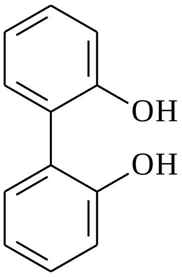
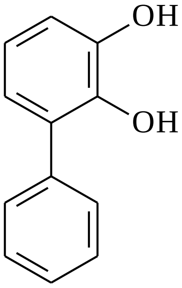
(3)

The chirality of BINOL is due to the sterically hindered rotation around the C-C bond. Though perfectly stable at room temperature, BINOL may racemize when heated.

3. Which of the phenols below can form stable (at room temperature) enantiomers so that they can be used in the same fashion to produce a chiral catalyst?

Warning: erroneously ticked boxes will result in penalty points

Substance	Can be used	Substance	Can be used
			

4. *Enantiomeric excess*, *ee*, is used to characterize the enantiomeric purity of the substance. This quantity equals ratio of the difference of concentrations of enantiomers *R* and *S* to their sum:

$$ee = \frac{[R]-[S]}{[R]+[S]}$$

Enantiomeric excess of the pure *R* isomer is unity, *ee* of the racemic mixture is zero.

When using the enantiomerically pure (BINOL)Al(OiPr) as a catalyst for reduction of α-bromoacetophenone, the *ee* of the product equals 81%. What is the *ee* of the product if the catalyst *ee* equals 50%? Provide your calculation with an illustration or derivation of the final formula.

Derivation:

$ee =$

Problem 4. A simple inorganic experiment (6 points)

Question	1	2	3	Total
Marks	5	12	7	24

Compound **A** which contains metal **X** is a colorless crystalline solid and highly soluble in water. It is used as a reagent in analysis and gives in alkali media a binary compound **B** containing 6.9 % (mass) of oxygen. Under heating **A** decomposes with a mass loss of 36.5%.

1. Determine the metal **X** and compounds **A**, **B**.

Your work:

X =______ **A** = ______ **B** = ______

2. Upon adding some amount of sodium thiosulphate to the solution of **A** the color immediately becomes red, then changes to reddish-brown, and after some minutes a dark-brown precipitate **C** forms (reaction 1). The solution over it is colorless. Being heated on air at 600ºC, **C** gives a grey powder **X** (reaction 2), so as 0.90 g of residue can be obtained from 1.10 g of **C**. A gas evolved by heating **C** in vacuum (reaction 3) can be absorbed by calcium hydroxide suspension (reaction 4). Being stored for a long time under saturated solution of barium perchlorate in 0.1 M $HClO_4$, the color of the precipitate becomes lighter, while the use of magnesium perchlorate doesn't give such effect. What is **C**? Write the equations of the reactions (1 – 4).

Your work:

C = _______

Reaction equations:

3. The compound **C** being stored under the mother liquor (containing an excess of **A**) its color changes to yellow due to the transformation into **D**. If barium ions are added to the suspension of **C** in the mother liquor, a mixture of **D** and of a white precipitate forms. Propose the formula of **D**, taking into account that it contains 77.5% (mass) of **X**. Give the equation of **D** formation.

Your work:

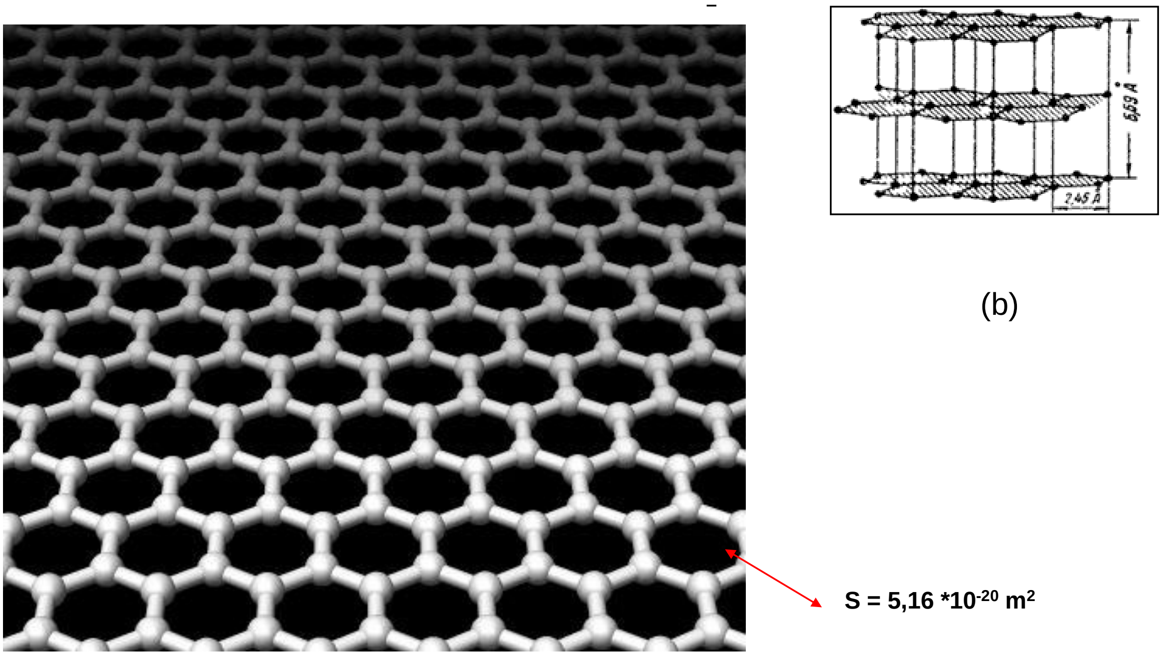
D = _______

Reaction equation:

Problem 5. Simple estimates of graphene properties (7 points)

Question	1		2	3	Total
	a	b			
Marks	2	2.5	4	5.5	14

Graphene is a two-dimensional, one atom thick carbon material (Fig.1 a). Many layers of graphene stack together to form graphite (Fig. 1b).



(b)

(a)

Fig. 1. (a) The structure of graphene. Spheres are carbon atoms. They are arranged in hexagons. The area of one carbon hexagon is $5.16 \cdot 10^{-20}$ m^2 (b) Crystal lattice of graphite. Three graphene layers are shown

Such atomic structure was long considered to be unstable. However, in 2004 Andrey Geim and Konstantin Novoselov have reported production of the first samples of this unusual material. This groundbreaking invention was awarded by Nobel prize in 2010.

Experimental studies of graphene are still restricted. Production of massive portions of the new substance still is a challenging synthetic problem. Many properties of graphene were *estimated*. Usually, there is not enough information for rigorous calculations, so we have to make assumptions and neglect unimportant factors. In this problem, you will estimate the adsorption properties of graphene.

1a. Estimate the specific surface of graphene open for adsorption in units m^2 /g. Consider that graphene plane is separated from any other solid or liquid substance.

Calculations:

S = _________ m^2/g

The single layer of nitrogen molecules adsorbed on the outer surface of graphite is shown in Fig. 2. Assume that the same arrangement of nitrogen molecules is formed on a graphene surface.

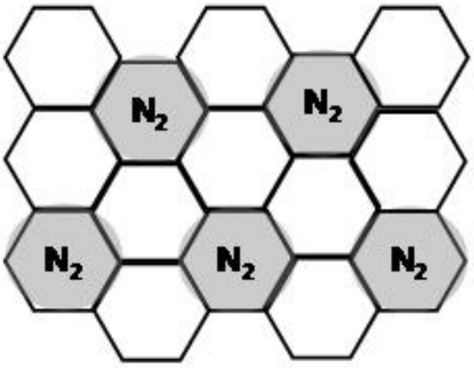


Fig. 2. Nitrogen molecules N_2 (grey circles) on the outer surface of graphite

1b. How many grams of nitrogen can be adsorbed on 1 gram of graphene assuming that the graphene layer is placed onto the surface of a solid support? Estimate the volume occupied by these nitrogen molecules after the complete desorption from 1 g of graphene (pressure 1 bar, temperature 298 K).

Calculations:

m_{N_2} = _______ g

V_{N_2} = _______ .

Let us consider adsorption as a common chemical equilibrium

$$A_{gas} \rightleftarrows A_{ads}\,, \qquad (1)$$

(A_{gas} are molecules A in the gaseous state, A_{ads} are the same molecules on the surface) with the equilibrium constant K:

$$K = \frac{n_{A_{ads}}(\text{mol/m}^2)}{p_{A_{gas}}(\text{bar})}$$

(such assumption holds if a small number of molecules is adsorbed on the surface)

Adsorption properties of graphene can be estimated from the data for adsorption on a regular three-dimensional graphite. The enthalpy of adsorption (ΔH^o of reaction (1)) of any molecule A on graphene is on average by 10% less negative compared to that on graphite. On graphite, the adsorbed molecule is bound more strongly due to the interaction with the lower graphene layers in the lattice (Fig. 1b) and hence the enthalpy of adsorption is more negative. The standard entropies of adsorption on graphene and graphite are assumed to be the same.

2. How many moles, n, of CCl_4 are adsorbed on 1 g of graphene at $p(CCl_4) = 10^{-4}$ bar if $2.0\cdot10^{-7}$ mol of CCl_4 are adsorbed on 1 m^2 of graphite at $p(CCl_4) = 6.6\cdot10^{-5}$ bar? Assume that graphene is placed onto the surface of a solid support and the interaction of CCl_4 with the support does not change the enthalpy of adsorption of CCl_4 on graphene. The temperature in both cases is 293 K. ΔH^o of adsorption of CCl_4 on graphite is –35.1 kJ/mol.

Calculations:

$n(CCl_4)$ = _______

The graphene films are expected to be sensitive gas detectors. If 10^9 particles of a gas are adsorbed on 1 cm^2 of a graphene surface this is enough to measure an electrical resistivity change of the graphene layer and to detect the presence of a gas in the environment.

3. Determine the minimal content of ethane, C_2H_6, in the air (in mol.%) at atmospheric pressure (T = 293K) at which a graphene sensor will detect this gas. The known data for the adsorption of alkanes on graphite are shown in Fig 3. Assume that air doesn't affect the adsorption properties of ethane.

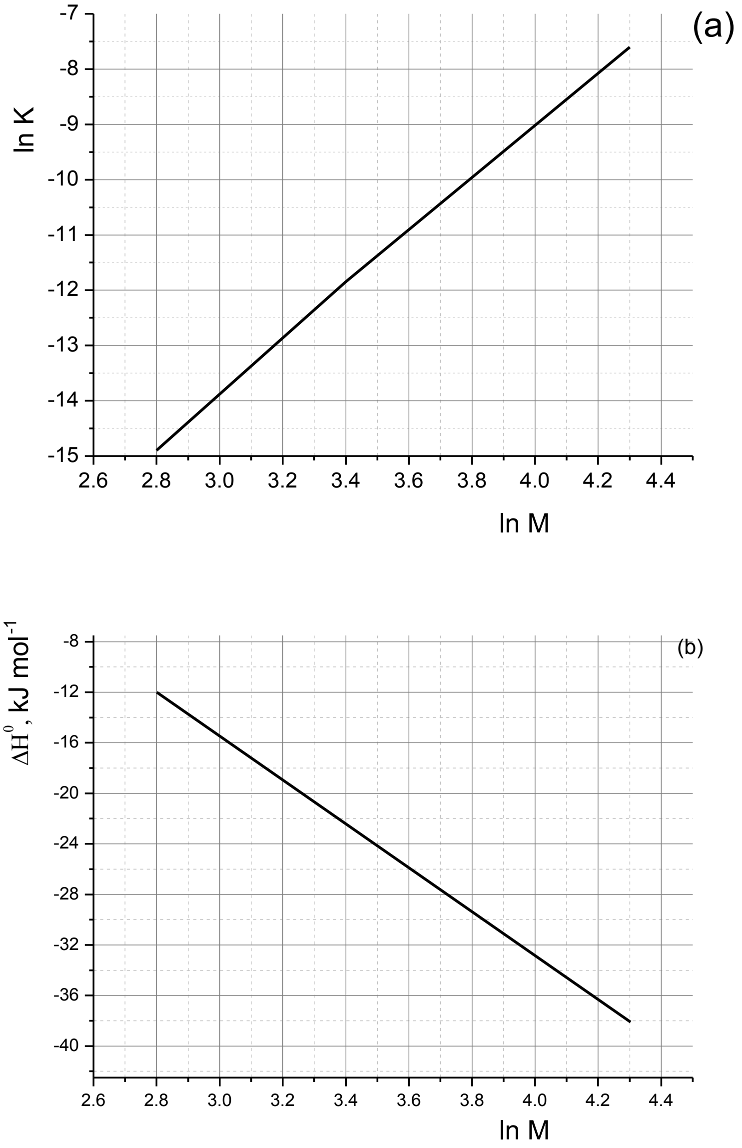


Fig. 3. Thermodynamic properties for adsorption of alkanes on a graphite surface. (a) ln K {mol/m^2/bar} as a function of ln M (M – molecular mass of alkane in g/mol); (b) ΔH^o of adsorption as a function of ln M. Linear dependences are assumed in both cases

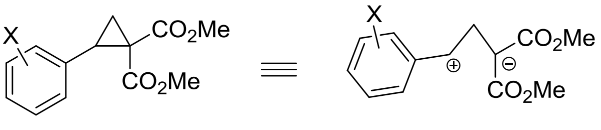
Calculations:

Content of C_2H_6 = _________ mol.%

Problem 6. Cyclopropanes. So simple. So fancy… (8 points)

Question	1	2	3	Total
Marks	8	22	70	100

Cyclopropanes bearing donor and acceptor substituents at the neighboring C-atoms, for example, **A**, demonstrate high reactivity behaving similar to 1,3-zwitterion **B**.



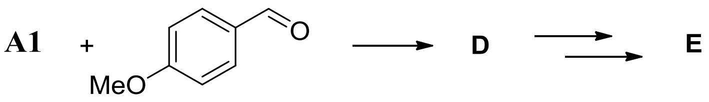
A **B**

Thus, **A1** (X = 4-OMe) undergoes the three-membered ring opening in the Lewis acid-catalyzed reaction with 1,3-dimethoxybenzene as a nucleophile giving the product **C**.

1. Write down structural formula of **C**.

Structural formula of **C:**

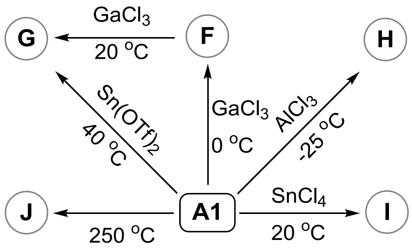
A1 participates in cycloadditions, annulations, oligomerizations, and other processes. Thus, formal [3+2]-cycloaddition between **A1** and 4-methoxybenzaldehyde leads to a five-membered ring in **D**. Decarboxylation of all carboxylic groups in **D** produces **E** ($C_{18}H_{20}O_3$), the molecule of the latter having a plane of symmetry.



2. Write down structural formulae of **D** and **E** indicating their stereochemistry.

D	**E**

Also, **A** can undergo various transformations in the absence of any reaction partners except catalysts. Some transformations typical of **A1** are shown in the Scheme below.



OTf = OSO_2CF_3

To determine the structures of **F-J**, a set of physico-chemical data was obtained (see Table 1 for some results). It was found that:

a) **F** and **G** have the same molecular formula as **A1**;

b) **G** is formed as the most stable stereoisomer;

c) **H** and **I** are structural isomers;

d) **H** is formed as a single diastereomer with C_2 axis of symmetry (the molecule looks the same after rotation through the angle of 180°);

e) **I** is formed as a mixture of two diastereomers;

f) **J** is naphthalene derivative.

In the process leading to **I**, one molecule of **A1** demonstrates the described above common reactivity (analogous to that of **B**). The other molecule of **A1** behaves differently. Also, the latter behavior is demonstrated by cyclopropane **A2** (dimethyl 2-(3,4,5-trimethoxyphenyl)cylopropane-1,1-dicarboxylate; X in **A** = 3,4,5-$(MeO)_3$) when treated with $SnCl_4$ affording **K** as a mixture of two diastereomers. The major isomer has the center of symmetry. Similar reactivity is shown by **A2** in $Sn(OTf)_2$-catalyzed reaction with **G** furnishing **L**.

$$\mathbf{K} \xleftarrow{SnCl_4} \mathbf{A2} \xrightarrow[Sn(OTf)_2]{\mathbf{G}} \mathbf{L}$$

Table 1. Information about the compounds.

	Ratio of the number of hydrogen-containing groups					Empirical formula
	Non-aromatic				Aromatic CH	
	CH	CH_2	CH_3	OH		
A1	1	1	1+1+1	0	2+2	$(C_{14}H_{16}O_5)_n$
F	1	1	1+1+1	0	2+2	$(C_{14}H_{16}O_5)_n$
G	1+1+1	0	2+1	0	2+2	$(C_{14}H_{16}O_5)_n$
H	1	1	1+1+1	0	2+2	$(C_{14}H_{16}O_5)_n$
I	1+1+1	1+1	2+1+1+1+1	0	2+2+1+1+1	$(C_{14}H_{16}O_5)_n$
J	0	0	1+1	1	1+1+1+1+1	$(C_{13}H_{12}O_4)_n$
K	1+1	1	2+1+1+1	0	1	$(C_{16}H_{20}O_7)_n$
L	1+1+1+1+1	1	2+2+1+1+1+1	0	2+2+1	$(C_5H_6O_2)_n$

3. Write down the structural formulae of **F-J, L** and the major isomer of **K**.

F	**G**
H	**I**
J	**K** (major isomer)
L	

Problem 7. Diverse permanganatometry (8 points)

Quest.	1	2	3				4	5		Total
			a	b	c	d		a	b	
Marks	2	2	4	2	2	6	7	7	2	34

The amount of many reducing agents can be determined by permanganatometric titration in alkaline medium allowing permanganate ion reduction to manganate.

1. Write down the ionic equation of the reaction for formate titration with permanganate in an aqueous solution containing ~0.5 M NaOH.

Titration with permanganate in alkaline medium is often supplemented by addition of a barium salt, which leads to precipitation of manganate as $BaMnO_4$.

2. Which side redox processes involving manganate is suppressed by the barium salt? Write down an example of equation of the corresponding reaction.

10.00 mL (V_{Mn}) of 0.0400 M (c_{Mn}) $KMnO_4$ solution was placed in each of flasks **A**, **B**, and **C** and different reactions were conducted in each flask.

3. To flask **A**, a sample solution containing unknown amount of crotonic acid (CA) CH_3–CH=CH–COOH (m_{CA}), an alkali and barium nitrate (both in an excess) were added, and the reaction mixture was incubated for 45 min. It is known that each molecule of crotonic acid loses 10 electrons under the experiment conditions. The molar mass of CA is 86.09 g/mol.

a) Write down the total ionic equation of the reaction.

8.00 mL (V_{CN}) of 0.0100 M (c_{CN}) potassium cyanide solution was further added to the incubated mixture. This resulted in completion of the following reaction:

$$2Ba^{2+} + 2MnO_4^- + CN^- + 2OH^- = 2BaMnO_4 + CNO^- + H_2O$$

$BaMnO_4$ precipitate was then filtered off, and the excess of cyanide in the filtrate was titrated with 0.0050 M (c_{Ag}) $AgNO_3$ solution till detectable precipitation was observed. Note that both CN^- and CNO^- are analogs of halide ions, but CNO^- affords soluble silver salt.

b) Give the formula for the complex formed when Ag^+ ions were initially added to the cyanide solution (until the precipitate was formed).

c) Give the formula of the precipitate formed.

d) Calculate the mass of crotonic acid (in mg) if 5.40 mL (V_{Ag}) of the silver salt solution was consumed for the titration to the endpoint.

4. Another sample with different concentration of crotonic acid and alkali (in an excess) were added to flask **B**, this mixture lacking barium salt. An excess of KI (instead of cyanide) was added as a reducing agent. The mixture was further acidified, and the iodine evolved was titrated with 0.1000 M (c_S) thiosulfate solution. 4.90 mL (V_{S1}) of the titrant was used to reach the endpoint.

Calculate the mass of crotonic acid (in mg).

5. A sample containing tin(II) was added to flask **C**, and the medium was adjusted to weak alkaline. Tin(II) was quantitatively oxidized to $Sn(OH)_6^{2-}$, whereas a precipitate formed as a result of permanganate reduction. The precipitate was isolated, washed off, dried at 250°C, weighed (the mass of the water-free precipitate (m_{prec}), representing a binary compound Mn_xO_y, was of 28.6 mg), and dissolved in H_2SO_4 in the presence of an excess of potassium iodide. The evolved iodine was titrated with 0.1000 M thiosulfate solution. 2.50 mL (V_{S2}) of the latter was consumed to attain the endpoint.

a) Determine x and y. Write down the reaction of precipitation.

Reaction:

b) Calculate the mass of tin in the sample (in mg).

Problem 8. Unique life of archaea (8 points)

Question	1	2	3	4	5	6	7	8	9		Total
									a	b	
Marks	2	7	3	8	4	4	5	4	3	5	45

Archaea (or archaebacteria) are single-celled microorganisms significantly differing from bacteria and eukaryotes at the molecular level.

Enzymatic reaction of methylamine with water is the major energy source for some archaea. In a particular experiment, an archaea strain was cultivated at pH 7 under anaerobic (oxygen free) conditions with the nutrient medium containing $^{13}CH_3NH_2$ as the only energy source. After a certain incubation period, the gas over the archaea culture was sampled and analyzed. It was found that the gas contains two substances **A** and **B** in the molar ratio of 1.00:3.00 correspondingly. The sample density rel. H_2 is of 12.0.

1. Calculate the volume fractions (in %) of **A** and **B** in the mixture.

2. Determine **A** and **B** if there is no N atoms in gas collected.

Your work:

A	**B**

3. Write down the equation of enzymatic reaction of methylamine with water described in the above experiment using predominant form of each species.

Enzymes containing the residue of α-amino acid **X** are found in many archaea. It is known that **X**:

- is composed of atoms of 4 elements;
- is 18.8 % oxygen by mass;
- possesses the single individual tRNA and is incorporated into proteins during translation.

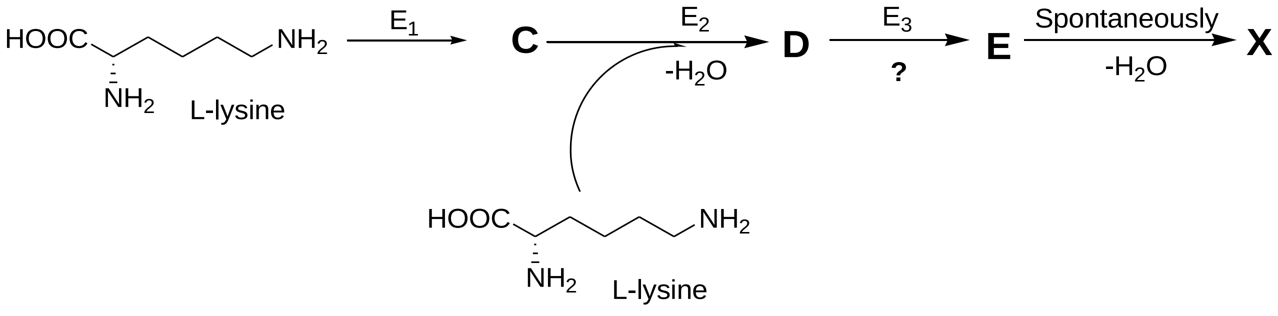
Amino acid *L*-lysine (see the structure in scheme below) was identified as the **X** precursor in archaea. All C and N atoms found in **X** originate from two starting lysine molecules. Different isotope-labeled *L*-lysines were introduced into a model system to clarify the biosynthetic pathways of **X**. The results are summarized in the table.

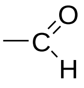
Isotope composition of *L*-lysine	Molecular mass (rounded to integer) of the **X** residue [RCH(NH_2)CO], bound to tRNA, g/mol
Normal	238
All carbons ^{13}C, all nitrogens ^{15}N	253
ε-Amino group with ^{15}N	239

4. Determine the molecular formula of **X**.

Calculations:
X:

X is biosynthesized in archaea according to the following scheme (E_1–E_3 – enzymes):

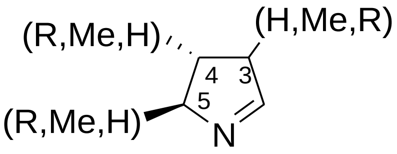


At the first step, lysine is transformed into its structural isomer (α–amino acid, **C**), whereas **D** contains a peptide bond, and **E** a formyl group [ $-\mathrm{C}(=\mathrm{O})\mathrm{H}$]. All reaction coefficients in the above scheme equal 1.

5. Give the chemical formula of **C**, **D** and **E**. From the reaction types given hereunder, choose (tick) **only one** corresponding to the E_3 catalyzed reaction.

<table>
<tr><td colspan="3">Calculations:</td></tr>
<tr><td>C</td><td>D</td><td>E</td></tr>
<tr><td colspan="3">☐ Oxidative deamination;
☐ Decarboxylation;
☐ Intermolecular deamination;
☐ Hydroxylation;
☐ Peptide bond hydrolysis.</td></tr>
</table>

X contains the fragment:



R is a massive substituent (M>100 g/mol). The 3rd C atom is non-asymmetric, 4th and 5th C atoms are stereogenic centers. All C atoms in the cycle are bound with at least one H atom. Each substituent (H, Me and R) is found only once.

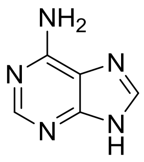
6. Determine the positions of substituents H, Me, and R.

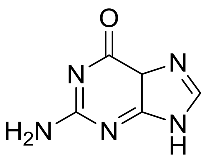
Your work:

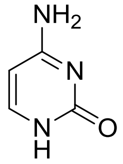
7. Draw structural formulae of **C** and **X** with stereochemical details. There are no stereo centers affected on the way from **C** to **X**. Mark every stereocenter of **X** with either *R* or *S*.

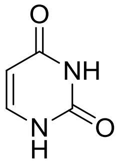
C	**X**

Only one codon is responsible for incorporation of **X** residues into proteins in archaea. The nitrogen bases forming this codon contain two exocyclic amino groups and three exocyclic oxygen atoms in total.


adenine


guanine


cytosine


uracyl

8. Fill in the hereunder table to determine the nucleotide composition of the codon encoding **X**. **Tick only one box in each line**.

Your work:

Nitrogen base	The number of bases in the codon				
	1	2	3	0 or 1	1 or 2
A					
C					
G					
U					

The fragment of mRNA coding sequence given below contains the codons encoding **X** residue incorporation into an archaea enzyme:

5'…AAUAGAAUUAGCGGAACAGAGGGUGAC…3'

9a. Using the table of the genetic code, decide how many amino acid residues are incorporated into the enzyme chain due to this fragment translation.

Your work:

Number of amino acids = ___

9b. Write down the amino acid sequence translated from this fragment. Note that more than one **X** residue is found in the fragment.

Fill in the boxes with the amino acid abbreviations (from N- to C-terminus).

Note that the number of boxes is excessive. If there is more than one possibility, write all separated by “/”. If the translation is stopped in a particular position, write “STOP” and leave all the boxes to the right empty.

Your work:

(a) RNA Codons for the Twenty Amino Acids

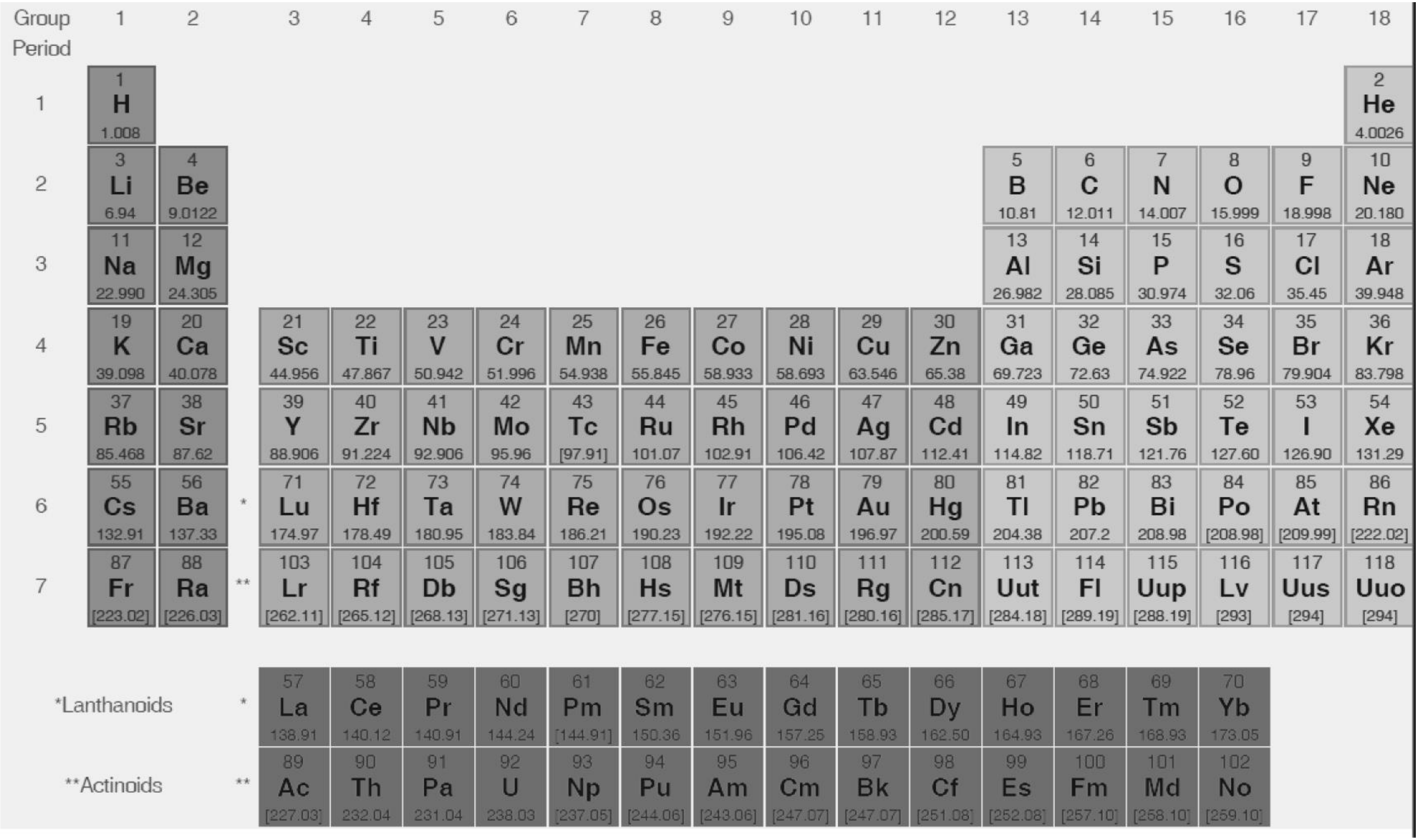
second base

	U	**C**	**A**	**G**	
U	Phe	Ser	Tyr	Cys	**U**
	Phe	Ser	Tyr	Cys	**C**
	Leu	Ser	STOP	STOP	**A**
	Leu	Ser	STOP	Trp	**G**
C	Leu	Pro	His	Arg	**U**
	Leu	Pro	His	Arg	**C**
	Leu	Pro	Gln	Arg	**A**
	Leu	Pro	Gln	Arg	**G**
A	Ile	Thr	Asn	Ser	**U**
	Ile	Thr	Asn	Ser	**C**
	Ile	Thr	Lys	Arg	**A**
	Met(start)	Thr	Lys	Arg	**G**
G	Val	Ala	Asp	Gly	**U**
	Val	Ala	Asp	Gly	**C**
	Val	Ala	Glu	Gly	**A**
	Val	Ala	Glu	Gly	**G**

Third base

Amino acid abbreviations:

Ala = Alanine
Arg = Arginine
Asn = Asparagine
Asp = Aspartic acid
Cys = Cysteine
Glu = Glutamic acid
Gln = Glutamine
Gly = Glycine
His = Histidine
Ile = Isoleucine
Leu = Leucine
Lys = Lysine
Met = Methionine
Phe = Phenylalanine
Pro = Proline
Ser = Serine
Thr = Threonine
Trp = Tryptophan
Tyr = Tyrosine
Val = Valine



Group Period	1	2		3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H 1.008																		2 He 4.0026
2	3 Li 6.94	4 Be 9.0122												5 B 10.81	6 C 12.011	7 N 14.007	8 O 15.999	9 F 18.998	10 Ne 20.180
3	11 Na 22.990	12 Mg 24.305												13 Al 26.982	14 Si 28.085	15 P 30.974	16 S 32.06	17 Cl 35.45	18 Ar 39.948
4	19 K 39.098	20 Ca 40.078		21 Sc 44.956	22 Ti 47.867	23 V 50.942	24 Cr 51.996	25 Mn 54.938	26 Fe 55.845	27 Co 58.933	28 Ni 58.693	29 Cu 63.546	30 Zn 65.38	31 Ga 69.723	32 Ge 72.63	33 As 74.922	34 Se 78.96	35 Br 79.904	36 Kr 83.798
5	37 Rb 85.468	38 Sr 87.62		39 Y 88.906	40 Zr 91.224	41 Nb 92.906	42 Mo 95.96	43 Tc [97.91]	44 Ru 101.07	45 Rh 102.91	46 Pd 106.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.76	52 Te 127.60	53 I 126.90	54 Xe 131.29
6	55 Cs 132.91	56 Ba 137.33	*	71 Lu 174.97	72 Hf 178.49	73 Ta 180.95	74 W 183.84	75 Re 186.21	76 Os 190.23	77 Ir 192.22	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	84 Po [208.98]	85 At [209.99]	86 Rn [222.02]
7	87 Fr [223.02]	88 Ra [226.03]	**	103 Lr [262.11]	104 Rf [265.12]	105 Db [268.13]	106 Sg [271.13]	107 Bh [270]	108 Hs [277.15]	109 Mt [276.15]	110 Ds [281.16]	111 Rg [280.16]	112 Cn [285.17]	113 Uut [284.18]	114 Fl [289.19]	115 Uup [288.19]	116 Lv [293]	117 Uus [294]	118 Uuo [294]
*Lanthanoids			*	57 La 138.91	58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm [144.91]	62 Sm 150.36	63 Eu 151.96	64 Gd 157.25	65 Tb 158.93	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.05		
**Actinoids			**	89 Ac [227.03]	90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np [237.05]	94 Pu [244.06]	95 Am [243.06]	96 Cm [247.07]	97 Bk [247.07]	98 Cf [251.08]	99 Es [252.08]	100 Fm [257.10]	101 Md [258.10]	102 No [259.10]		