

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

1 nanometer (nm) =  $10^{-9}$  m

1 Da = 1 atomic mass unit

1 electron volt (eV) =  $1.6022 \cdot 10^{-19}$  J =  $96485 \text{ J}\cdot\text{mol}^{-1}$

Energy of a light quantum with wavelength $\lambda$	$E = hc / \lambda$
Energy of one mole of photons	$E_m = hcN_A / \lambda$
Gibbs energy	$G = H - TS$
Relation between equilibrium constant and standard Gibbs energy	$K = \exp\left(-\frac{\Delta G^\circ}{RT}\right)$
Relation between standard Gibbs energy and standard emf	$\Delta G^\circ = -nFE^\circ$
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	$\Delta G = \Delta G^\circ + RT \ln \frac{a_{\text{prod}}}{a_{\text{reag}}}$ , $a = c / (1 \text{ mol/L})$ for the substances in solution, $a = p / (1 \text{ bar})$ 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,  $\text{CH}_4 \cdot n\text{H}_2\text{O}$ .

Calculations:

Answer:

Real methane hydrate has a non-stoichiometric composition close to  $\text{CH}_4 \cdot 6\text{H}_2\text{O}$ . 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  $\text{CH}_4 \cdot 6\text{H}_2\text{O}$  producing solid water (ice)  $\text{H}_2\text{O}(\text{s})$ .

The enthalpy of this process equals  $17.47 \text{ kJ}\cdot\text{mol}^{-1}$ . 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  $-5 \text{ }^\circ\text{C}$ ?

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  $6.01 \text{ kJ}\cdot\text{mol}^{-1}$ .

Calculations:

Answer:

Total amount of methane in hydrates on Earth is no less than  $5\cdot 10^{11}$  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  $-889 \text{ kJ}\cdot\text{mol}^{-1}$ , the total heat capacity of the Earth's atmosphere is about  $4\cdot 10^{21} \text{ J}\cdot\text{K}^{-1}$ .

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.

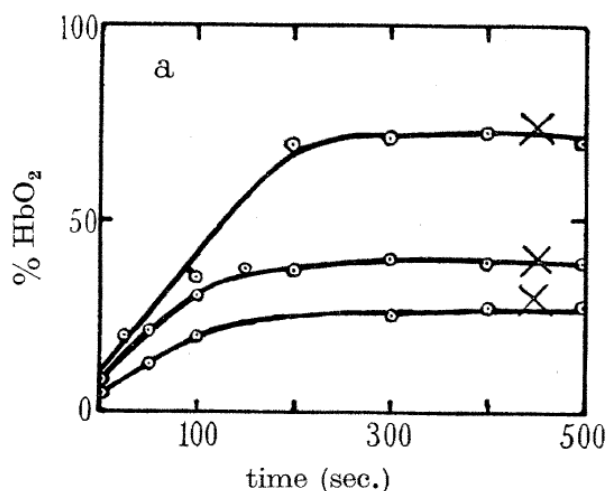
1. In plants, under illumination, carbon dioxide is reduced to carbohydrates (denote as  $\{CH_2O\}$ ) and oxygen is produced. Write the overall equation of photosynthesis in plants.

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<sub>2</sub> (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<sub>2</sub> 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	$E^\circ$ , 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

$\Delta G =$

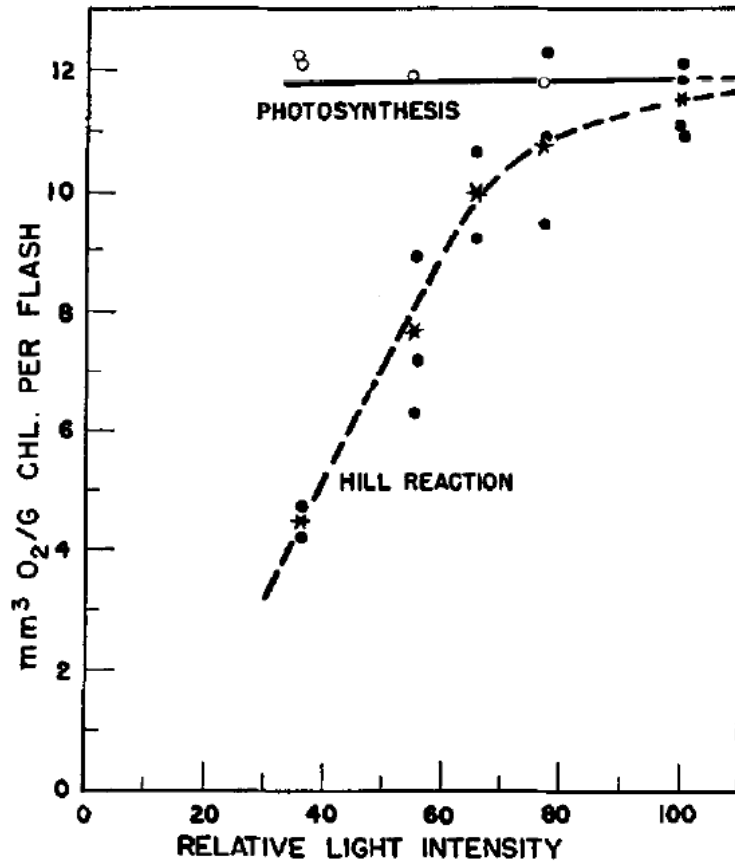
The reaction is

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<sup>3</sup>, at temperature 10 °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			High intensity		
0	<input type="checkbox"/>	1	<input type="checkbox"/>	2	<input type="checkbox"/>
0	<input type="checkbox"/>	1	<input type="checkbox"/>	2	<input type="checkbox"/>

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:

$$n(\text{Chl}) / n(\text{O}_2) =$$

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<sup>3</sup> (under the same conditions as in question 4).

5. Calculate the quantum requirement for the Hill reaction.

Calculations:

Quantum requirement:

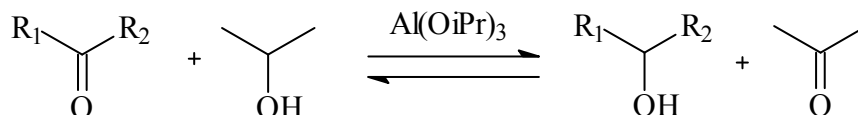
6. Try to make conclusions from the above experiments (questions 2-5). For each of the following statements **choose either “Yes” or “No”**.

	Yes	No
In natural photosynthesis, water oxidation and CO <sub>2</sub> reduction are separated in space.		
In chloroplasts, O <sub>2</sub> is produced from CO <sub>2</sub> .		
Oxidation of water in chloroplasts requires light illumination.		
Most of chlorophylls in chloroplasts participate directly in the photochemical O <sub>2</sub> production.		
In isolated chloroplasts, every absorbed photon causes transfer of one electron.		

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

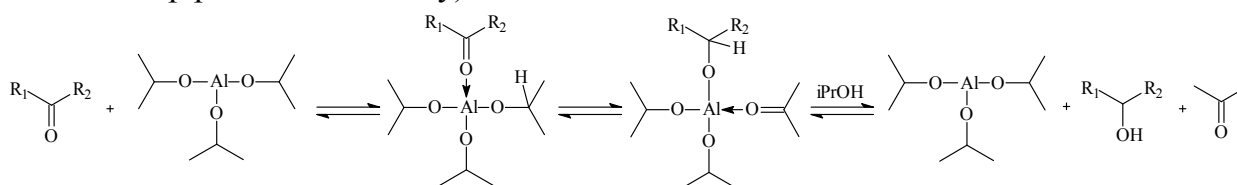
Question	1		2	3	4	Total
	a	b				
Marks	7	3	8.5	6	8	32.5

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	$\Delta_f H^\circ_{298}$ , kJ/mol	$S^\circ_{298}$ , J/(mol·K)	$t_{\text{vap}}$ , °C
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:

$$m(\text{C}_3\text{H}_8\text{O}) : m(\text{C}_6\text{H}_{10}\text{O}) =$$

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:

$r =$

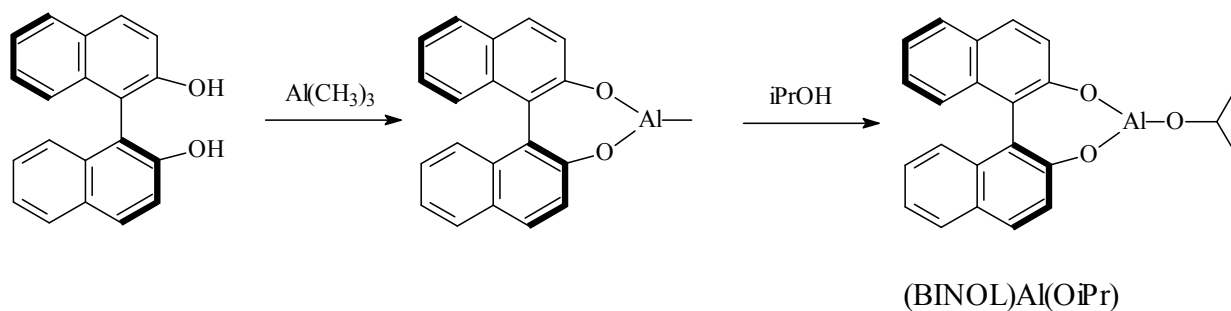
Answer

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'-binaphthyl (BINOL), which is synthesized *in situ* from binaphtol and trimethylaluminium:

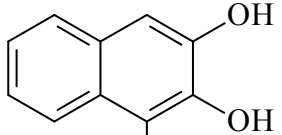
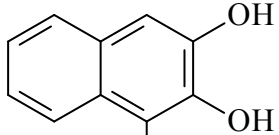
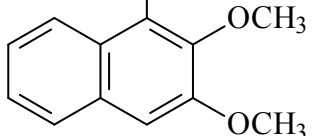
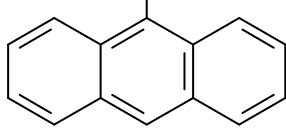


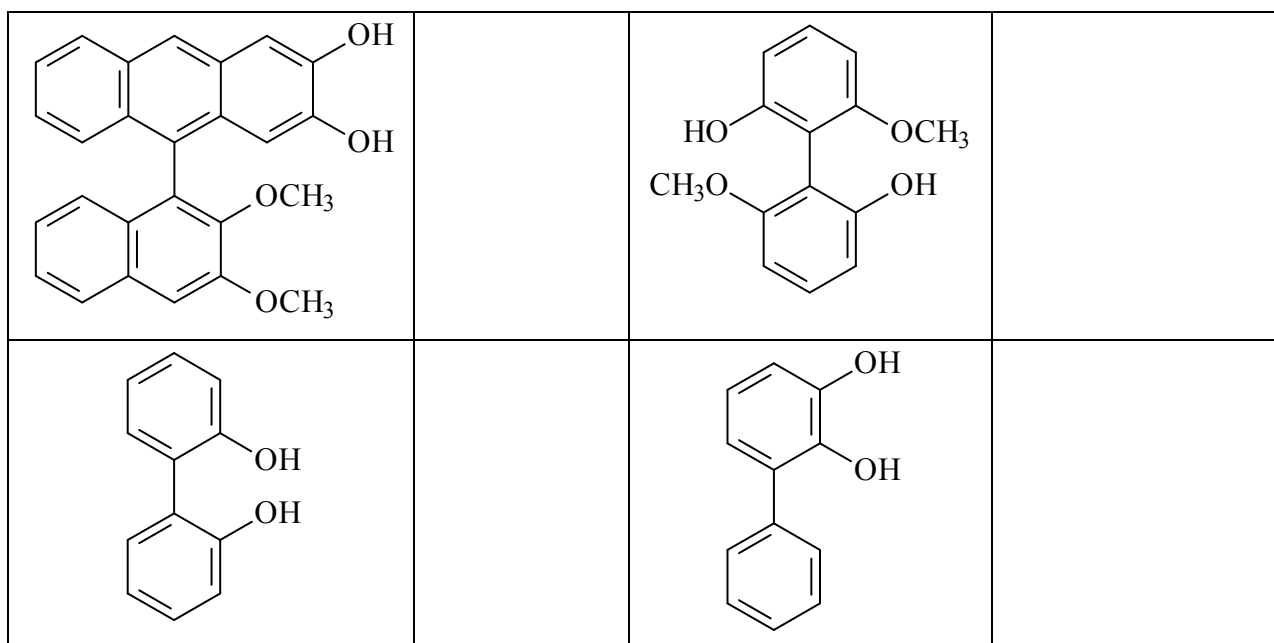
(3)

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  $\alpha$ -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 600°C, **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<sub>4</sub>, 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).

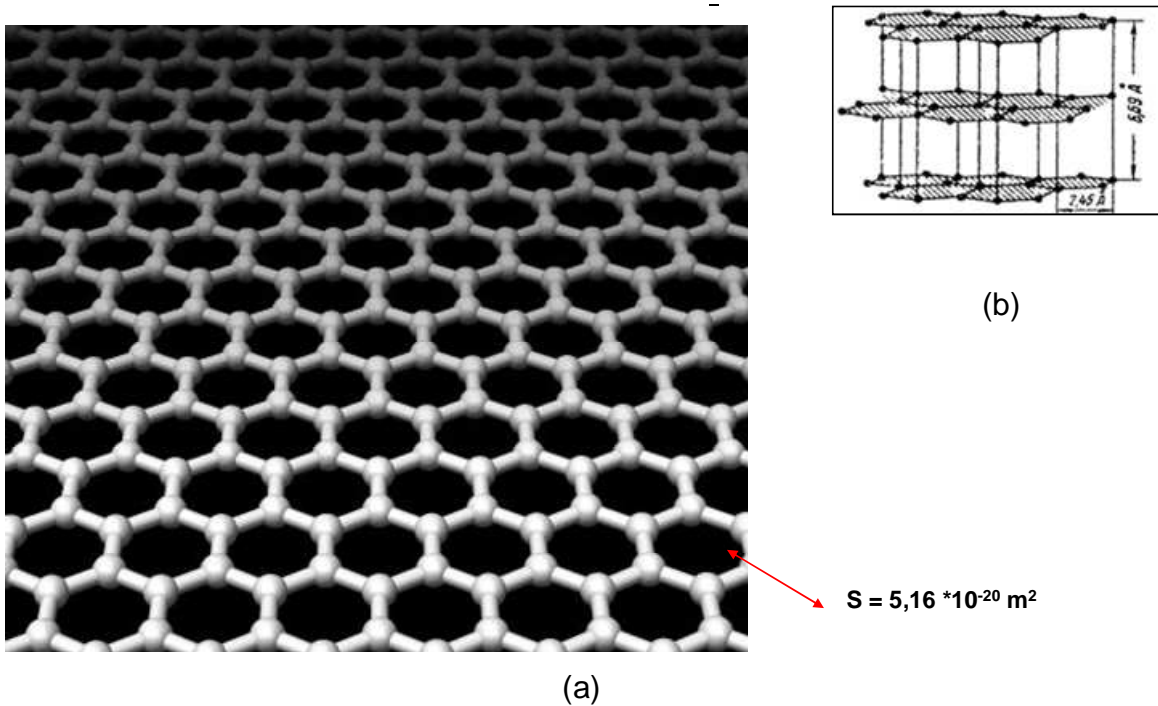


Fig. 1. (a) The structure of graphene. Spheres are carbon atoms. They are arranged in hexagons. The area of one carbon hexagon is  $5.16 \cdot 10^{-20} \text{ m}^2$  (b) Crystal lattice of graphite. Three graphene layers are shown

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  $\text{m}^2 / \text{g}$ . Consider that graphene plane is separated from any other solid or liquid substance.

Calculations:

$$S = \text{_____ m}^2/\text{g}$$

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.

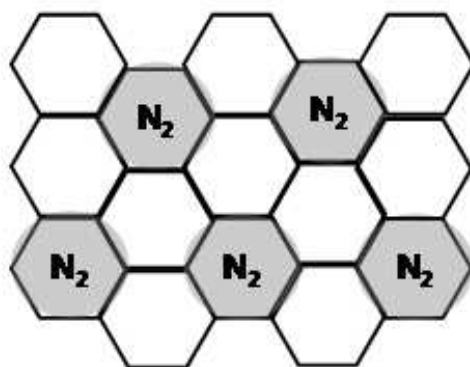


Fig. 2. Nitrogen molecules  $N_2$  (grey circles) on the outer surface of graphite

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:

$$m_{N_2} = \text{_____ g}$$

$$V_{N_2} = \text{_____ .}$$

Let us consider adsorption as a common chemical equilibrium



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

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

(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 ( $\Delta H^0$  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  $\text{CCl}_4$  are adsorbed on 1 g of graphene at  $p(\text{CCl}_4) = 10^{-4}$  bar if  $2.0 \cdot 10^{-7}$  mol of  $\text{CCl}_4$  are adsorbed on 1  $\text{m}^2$  of graphite at  $p(\text{CCl}_4) = 6.6 \cdot 10^{-5}$  bar? Assume that graphene is placed onto the surface of a solid support and the interaction of  $\text{CCl}_4$  with the support does not change the enthalpy of adsorption of  $\text{CCl}_4$  on graphene. The temperature in both cases is 293 K.  $\Delta H^0$  of adsorption of  $\text{CCl}_4$  on graphite is  $-35.1$  kJ/mol.

Calculations:

$$n(\text{CCl}_4) = \underline{\hspace{2cm}}$$

The graphene films are expected to be sensitive gas detectors. If  $10^9$  particles of a gas are adsorbed on 1  $\text{cm}^2$  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,  $\text{C}_2\text{H}_6$ , in the air (in mol.%) at atmospheric pressure ( $T = 293\text{K}$ ) 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.

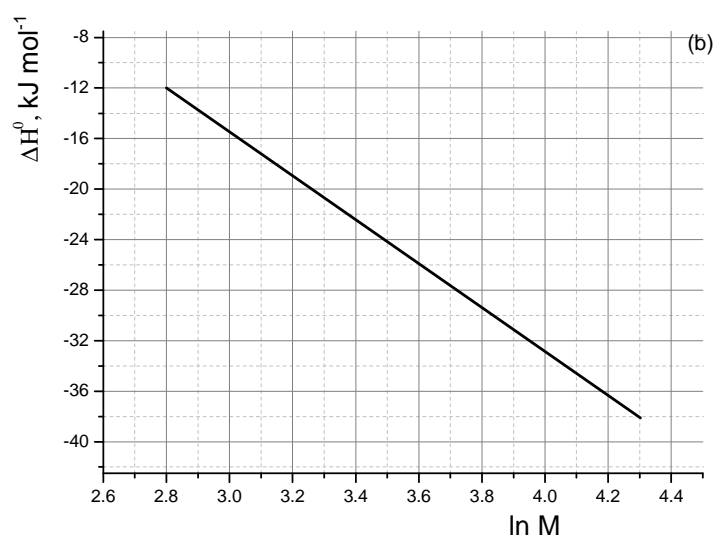
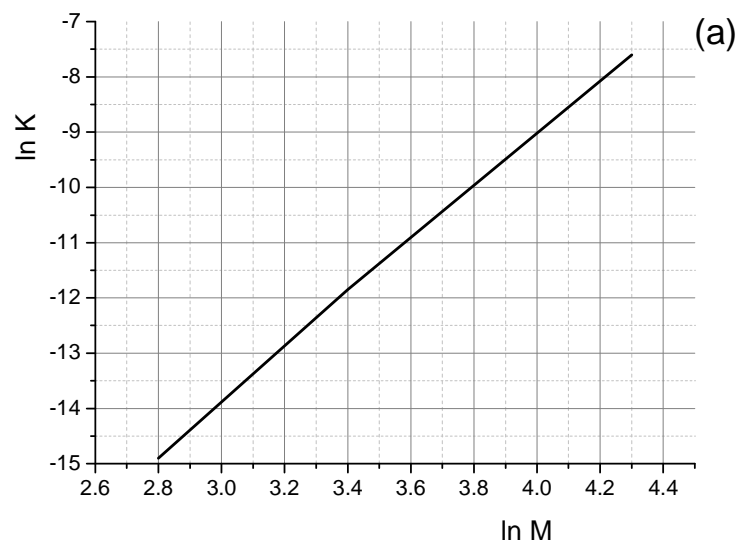


Fig. 3. Thermodynamic properties for adsorption of alkanes on a graphite surface. (a)  $\ln K$  {mol/m<sup>2</sup>/bar} as a function of  $\ln M$  ( $M$  – molecular mass of alkane in g/mol); (b)  $\Delta H^\circ$  of adsorption as a function of  $\ln M$ . Linear dependences are assumed in both cases

Calculations:

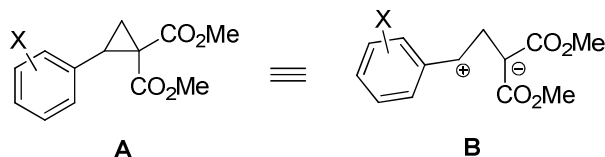
Content of  $C_2H_6$  = \_\_\_\_\_ mol.%



**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**.

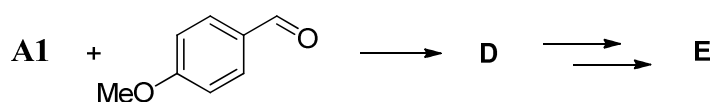


Thus, **A1** (X = 4-OMe) undergoes the three-membered ring opening in the Lewis acid-catalyzed reaction with 1,3-dimethoxybenzene as a nucleophile giving the product **C**.

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

Structural formula of **C**:

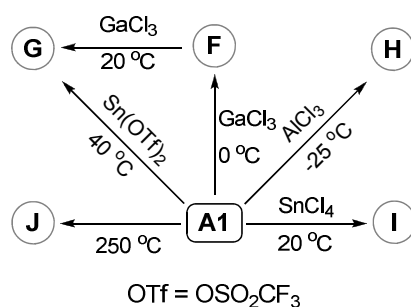
**A1** participates in cycloadditions, annulations, oligomerizations, and other processes. Thus, formal [3+2]-cycloaddition between **A1** and 4-methoxybenzaldehyde leads to a five-membered ring in **D**. Decarboxylation of all carboxylic groups in **D** produces **E** (C<sub>18</sub>H<sub>20</sub>O<sub>3</sub>), the molecule of the latter having a plane of symmetry.



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

<b>D</b>	<b>E</b>

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.



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:

- F** and **G** have the same molecular formula as **A1**;
- G** is formed as the most stable stereoisomer;
- H** and **I** are structural isomers;
- H** is formed as a single diastereomer with C<sub>2</sub> axis of symmetry (the molecule looks the same after rotation through the angle of 180°);
- I** is formed as a mixture of two diastereomers;
- 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)cyclopropane-1,1-dicarboxylate; X in **A** = 3,4,5-(MeO)<sub>3</sub>) when treated with SnCl<sub>4</sub> 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)<sub>2</sub>-catalyzed reaction with **G** furnishing **L**.



Table 1. Information about the compounds.

	Ratio of the number of hydrogen-containing groups					Empirical formula
	Non-aromatic				Aromatic	
	CH	CH <sub>2</sub>	CH <sub>3</sub>	OH	CH	
<b>A1</b>	1	1	1+1+1	0	2+2	(C <sub>14</sub> H <sub>16</sub> O <sub>5</sub> ) <sub>n</sub>
<b>F</b>	1	1	1+1+1	0	2+2	(C <sub>14</sub> H <sub>16</sub> O <sub>5</sub> ) <sub>n</sub>
<b>G</b>	1+1+1	0	2+1	0	2+2	(C <sub>14</sub> H <sub>16</sub> O <sub>5</sub> ) <sub>n</sub>
<b>H</b>	1	1	1+1+1	0	2+2	(C <sub>14</sub> H <sub>16</sub> O <sub>5</sub> ) <sub>n</sub>
<b>I</b>	1+1+1	1+1	2+1+1+1+1	0	2+2+1+1+1	(C <sub>14</sub> H <sub>16</sub> O <sub>5</sub> ) <sub>n</sub>
<b>J</b>	0	0	1+1	1	1+1+1+1+1	(C <sub>13</sub> H <sub>12</sub> O <sub>4</sub> ) <sub>n</sub>
<b>K</b>	1+1	1	2+1+1+1	0	1	(C <sub>16</sub> H <sub>20</sub> O <sub>7</sub> ) <sub>n</sub>
<b>L</b>	1+1+1+1+1	1	2+2+1+1+1+1	0	2+2+1	(C <sub>5</sub> H <sub>6</sub> O <sub>2</sub> ) <sub>n</sub>

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

<b>F</b>	<b>G</b>
<b>H</b>	<b>I</b>
<b>J</b>	<b>K (major isomer)</b>
<b>L</b>	

### 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  $\sim 0.5$  M NaOH.

Titration with permanganate in alkaline medium is often supplemented by addition of a barium salt, which leads to precipitation of manganate as  $\text{BaMnO}_4$ .

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 ( $V_{\text{Mn}}$ ) of 0.0400 M ( $c_{\text{Mn}}$ )  $\text{KMnO}_4$  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)  $\text{CH}_3\text{-CH=CH-COOH}$  ( $m_{\text{CA}}$ ), 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 ( $V_{\text{CN}}$ ) of 0.0100 M ( $c_{\text{CN}}$ ) potassium cyanide solution was further added to the incubated mixture. This resulted in completion of the following reaction:



$\text{BaMnO}_4$  precipitate was then filtered off, and the excess of cyanide in the filtrate was titrated with 0.0050 M ( $c_{\text{Ag}}$ )  $\text{AgNO}_3$  solution till detectable precipitation was observed. Note that both  $\text{CN}^-$  and  $\text{CNO}^-$  are analogs of halide ions, but  $\text{CNO}^-$  affords soluble silver salt.

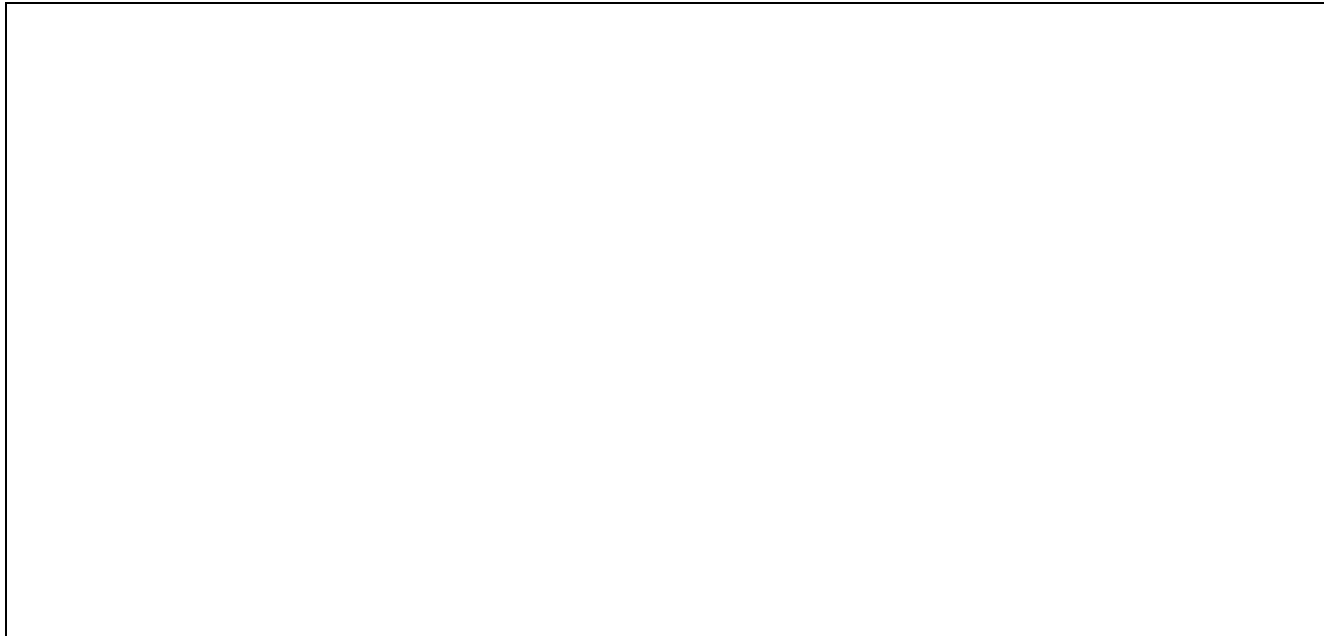
b) Give the formula for the complex formed when  $\text{Ag}^+$  ions were initially added to the cyanide solution (until the precipitate was formed).

c) Give the formula of the precipitate formed.

d) Calculate the mass of crotonic acid (in mg) if 5.40 mL ( $V_{\text{Ag}}$ ) 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 ( $c_{\text{S}}$ ) thiosulfate solution. 4.90 mL ( $V_{\text{S1}}$ ) 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  $\text{Sn(OH)}_6^{2-}$ , whereas a precipitate formed as a result of permanganate reduction. The precipitate was isolated, washed off, dried at  $250^\circ\text{C}$ , weighed (the mass of the water-free precipitate ( $m_{\text{prec}}$ ), representing a binary compound  $\text{Mn}_x\text{O}_y$ , was of 28.6 mg), and dissolved in  $\text{H}_2\text{SO}_4$  in the presence of an excess of potassium iodide. The evolved iodine was titrated with 0.1000 M thiosulfate solution. 2.50 mL ( $V_{\text{S}_2}$ ) 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).

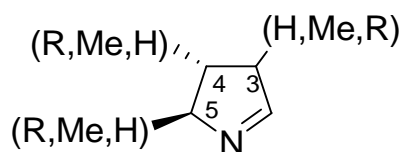






Calculations:		
C	D	E
<input type="checkbox"/> Oxidative deamination; <input type="checkbox"/> Decarboxylation; <input type="checkbox"/> Intermolecular deamination; <input type="checkbox"/> Hydroxylation; <input type="checkbox"/> Peptide bond hydrolysis.		

**X** contains the fragment:



R is a massive substituent ( $M > 100$  g/mol). The 3<sup>rd</sup> C atom is non-asymmetric, 4<sup>th</sup> and 5<sup>th</sup> 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.

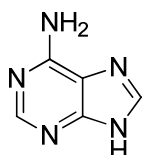
6. Determine the positions of substituents H, Me, and R.

Your work:
------------

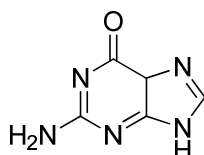
7. Draw structural formulae of **C** and **X** with stereochemical details. There are no stereocenters affected on the way from **C** to **X**. Mark every stereocenter of **X** with either *R* or *S*.

<b>C</b>	<b>X</b>
----------	----------

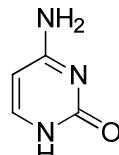
Only one codon is responsible for incorporation of **X** residues into proteins in archaea. The nitrogen bases forming this codon contain two exocyclic amino groups and three exocyclic oxygen atoms in total.



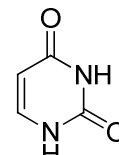
adenine



guanine



cytosine



uracil

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:



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

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

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

**Face your challenge,  
Be smart**



**PRACTICAL  
EXAMINATION**

**JULY 18, 2013  
MOSCOW, RUSSIA**

## General Directions

- **safety rules** follow ones given in the Preparatory problems booklet, no eating or drinking in the lab.
- **violating safety rules** you get one warning only; offend again: you are disqualified.
- **problems and answers booklet** 24 pages (incl. cover sheet and Periodic table of elements) with 3 problems. Start with problem 1.
- **time** 5 h; 15 min for reading before start. 30 min warning before the end.
- **your student code** write this on **every page**.
- **answers** only in the answer boxes in the booklet, nothing else will be graded. Relevant calculations have to be shown.
- **use only the pen, pencil and calculator provided.**
- **burette** read it as accurately as possible.
- **more chemicals** needed? Ask your lab assistant. No penalty for this with an exception of the hereunder.
- **each extra aldehyde, 2,4-dinitrophenylhydrazine, 50 mL of HCl, EDTA titrant or portion of a polymer solution:** a penalty of 1 point out of 40.
- **Be very careful! No replacement if you break your viscometer!**
- **questions** concerning safety, apparatus, chemicals, toilet break: **ask your lab assistant.**
- **chemical waste** put it only in the designated 800 mL beaker labeled "WASTE".
- **official English version available** on request **for clarification only.** Ask your lab assistant.
- **after the stop signal** put your booklet and all graph paper in the envelope (don't seal), leave at your table.
- **You must stop your work immediately after the stop signal has been given. A 5 min delay will result in zero points for the current task.**
- **During the Practical exam** some of the glassware and plastics are expected to be used several times. Clean it carefully.



## List of Chemicals

Reagent	Quantity	Placed in	Labeled	Safety
<b>Problem 1</b>				
2,4-Dinitrophenylhydrazine	200 mg each, 2 vials	small screw neck vial	2,4-dinitrophenylhydrazine	H228, H302
Sulfuric acid, concentrated	1 mL each, 2 tubes	Plastic tube with screw neck	H <sub>2</sub> SO <sub>4</sub> concentrated	H314
Aldehyde solution 1 mmol in ethanol	4 mL each, 2 bottles	30 mL small glass-stoppered bottle	Aldehyde 1 and Aldehyde2	H319 and H302
Ethanol	30 mL	glass-stoppered bottle	Ethanol	H225
NaOH solution (used in problems 1 and 2)	27 mL	60 mL glass-stoppered bottle	NaOH 2M	H314
Acetone	30 mL	amber glass screw neck vial	Acetone	H225, H319, H336
<b>Problem 2</b>				
EDTA, 0.0443M* standard solution	70 mL	125 mL glass-stoppered bottle	EDTA 0.05M	H319
HCl, 0.0535M* standard solution	70 mL	125 mL glass-stoppered bottle	HCl	H314, H335
Methyl orange, 0.1% in water	25 mL	dropping bottle	Methyl orange	H301
Murexide indicator, solid mix with NaCl (1:250 by mass)	in 10 mL bottle	small screw neck vial	Murexide	
Sample of water	500 mL	0.5 L plastic can	Water sample	
<b>Problem 3</b>				
Poly(vinyl) alcohol	40 mL each, 5 vials	amber glass screw neck vial	P1, P2, P3, P4 and X	
<b>To be used in all problems</b>				
Distilled water	500 mL	Plastic wash bottle	H <sub>2</sub> O	
<b>To be shared by students, on the common table</b>				
Sodium hydrocarbonate	800 mL	800 mL beaker	NaHCO <sub>3</sub>	

\*The concentration indicated on the label is approximate. The exact values are indicated in the table.

## Labware and equipment

Item	Quantity
<b>On every working place</b>	
5 mL Plastic tube with screw neck labeled “1” with your student code	1
5 mL Plastic tube with screw neck labeled “2” with your student code	1
Lab stand	1
50 mL beaker	2
25 mL beaker	2
25 or 50 mL beaker	1
Magnetic stirrer	1
Stirring bar	2
Glass filter	2
Adapter	1
50 mL round bottom flask	1
Water-jet pump	1
2 mL pipette	2
5 mL pipette	2
Pipette filler	1
Spatula	2
500 mL plastic washer bottle	1
800 mL beaker for waste	1
10 mL measuring cylinder	1
Filter paper, round	2
Scissors	1
Filter paper	2
Glass rod	1
pH indicator papers (in a zipper-bag)	3
Viscometer	1
Stop-watch	1
30 mL rubber bulb	1
Ruler	1
Marker	1
25 mL burette	1
25 mL pipette	1
Plastic funnel	1
Erlenmeyer flask	2
Test strips for determining total dissolved solids content in zipper bag	1
Paper tissues (on the corner of each table, to be shared between 3 students)	1 package
Plastic basket	1
Graph paper	4 sheets
pH scale (in zipper bag)	1
<b>On the tables for the common use</b>	
Filter paper, round	
Filter paper	
Gloves	
Balances	
Bottle labeled “H <sub>2</sub> O dist.”	
Thermometer immersed in H <sub>2</sub> O	
Measuring cylinder 100 mL	
pH-meter	

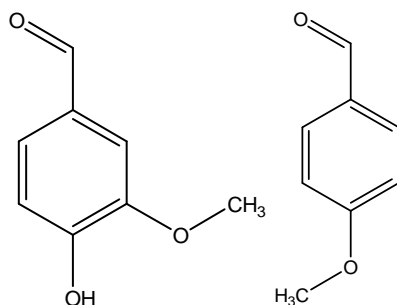
\*If you need more filter paper, you can find it at the table of common use.

<b>Problem 1</b>	Student code _____	Quest.	1	2	3	4	5	Total
		Marks	3.5	1.5	1	3	35	44

### Problem 1. Synthesis of 2,4-dinitrophenylhydrazones (13 points)

**Hydrazones** belong to the class of *imines*, which contain a nitrogen-nitrogen single bond adjacent to a carbon-nitrogen double bond. Hydrazones are formed when  $\text{NH}_2$ -containing hydrazine reacts with aldehydes or ketones under appropriate conditions. Because the hydrazone derivatives of the carbonyl compounds are often stable, crystalline, highly colored solids, they are used to confirm the identity of aldehydes and ketones.

In this task you will have to identify two substituted benzaldehydes (shown below) by studying the products of their reactions with 2,4-dinitrophenylhydrazine.



#### Procedure

##### Preparation of 2,4-dinitrophenylhydrazones

**Attention! Do not carry out two syntheses simultaneously, otherwise a beaker can fall from the magnetic stirrer, and you will lose your reaction mixture.**

Equip one 50 mL beaker with a magnetic bar. Fix the beaker on the stirrer using the metal ring attached to the stand. Place the content of vial (200 mg of 2,4-dinitrophenylhydrazine) into the beaker and start stirring carefully. **Only in the presence of your lab assistant**, carefully pour one sample of concentrated sulfuric acid (1 mL) onto the solid. Using pipettes add 1.6 mL of water and 4 mL of ethanol to the reaction mixture. Then using a pipette add dropwise the content of the aldehyde solution bottle (either “**aldehyde 1**” or “**aldehyde 2**”, each contains 1.00 mmol of the aldehyde). Bright precipitate starts forming at once. Continue stirring for 10 min, then add 10 mL of water and stir for another 3 min.

##### Separation and purification of the product

Using scissors carefully cut out a filter paper circle, *ca.* 1 cm bigger in diameter than that of the glass filter. Wet the filter circle with water, and carefully put it on the filtering surface. The paper filter should fit evenly and tightly. **If you fail to cut out an even circle, take a new filter from the table of common use and repeat cutting out.** Assemble the filtering apparatus. Remove the stirring bar from the beaker using the spatula and transfer the reaction product onto the filter. Turn on the water-jet pump (seek for help from your lab assistant if you experience difficulties) and filter out the precipitate. Put a little amount of water in the beaker and transfer the leftover product onto the filter. Wash the solid on the filter with water until the pH of the drops coming out the funnel are neutral. (Use the **WASTE** beaker to pour the round-bottom flask). Then wash the solid twice with ethanol

<b>Problem 1</b>	Student code _____	Quest.	1	2	3	4	5	Total
		Marks	3.5	1.5	1	3	35	44

using no more than 3 mL each time (**Note: Hydrazone is slightly soluble in ethanol**). Dry out the solid on the filter with working water-jet pump, loosening and squeezing the product with a glass rod from time to time. After *ca.* 20-30 min carefully transfer the dried powder into the self-made filter paper box for the final drying in the air. Put the box with the product in a safe place (e.g. on the shelf). **Turn off the water-jet pump when you do not use it!** As soon as your products seem dry, we advise you weigh them to avoid queuing at the balances. To collect the products, use the plastic tubes with your student code. Fill in the answer box below. **Note:** The products you synthesized will be further re-examined by lab staff.

**Repeat the above procedures with the other aldehyde.**

Plastic tube 1	Plastic tube 2
Mass of empty tube _____ mg	Mass of empty tube _____ mg
Mass of tube with product _____ mg	Mass of tube with product _____ mg
Mass of product _____ mg	Mass of product _____ mg

Lab assistant's signature \_\_\_\_\_

**1.1.** Write down the structures of 2,4-dinitrophenylhydrazine and both products.

<b>Problem 1</b>	Student code _____	Quest.	1	2	3	4	5	Total
		Marks	3.5	1.5	1	3	35	44

**1.2.** What kind of stereoisomerism (if any) is possible for these hydrazones? Tick the appropriate box

<input type="checkbox"/> R/S	<input type="checkbox"/> E/Z	<input type="checkbox"/> threo/erythro	<input type="checkbox"/> manno/gluco	<input type="checkbox"/> D/L
------------------------------	------------------------------	--	--------------------------------------	------------------------------

**2.1.** What is the role of sulfuric acid in 2,4-dinitrophenylhydrazone formation? Tick the appropriate box.

<input type="checkbox"/> stoichiometric reagent	<input type="checkbox"/> catalyst	<input type="checkbox"/> reducing agent	<input type="checkbox"/> oxidizing agent
---	-----------------------------------	---	--

**2.2.** How would the rate of the reaction change, if the synthesis is carried out in neutral medium? Tick the appropriate box.

<input type="checkbox"/> highly increase	<input type="checkbox"/> slightly increase
<input type="checkbox"/> not change	<input type="checkbox"/> the reaction would proceed very slow

**2.3.** How would the rate of the reaction change, if it is carried out in alkaline medium? Tick the appropriate box.

<input type="checkbox"/> highly increase	<input type="checkbox"/> slightly increase
<input type="checkbox"/> not change	<input type="checkbox"/> the reaction would not proceed

### Characterization

Place **small** amount (“on the tip of a spatula”) of each product in an individual 25 mL beaker. Add 10 mL of acetone to each beaker. **The best result will be obtained if the color and color intensity in each beaker are similarly yellow.** Pour 5 mL of NaHCO<sub>3</sub> solution into each beaker. Stir the resulting mixtures with the glass rod using different ends.

**3.1.** Record your observations of the solutions color change in the box.

<input type="checkbox"/> The color does not change in either beaker
<input type="checkbox"/> Color changes significantly in both beakers
<input type="checkbox"/> Color changes significantly only in one beaker

Add 2 mL of NaOH solution to each of the resultant mixtures from the question **3.1**. Stir the reaction mixtures with the glass rod.

**3.2.** Record your observations of the solutions color change in the box.

<input type="checkbox"/> The color does not change in either beaker
<input type="checkbox"/> Color changes significantly in both beakers
<input type="checkbox"/> Color changes significantly only in one beaker

<b>Problem 1</b>	Student code _____	Quest.	1	2	3	4	5	Total
		Marks	3.5	1.5	1	3	35	44

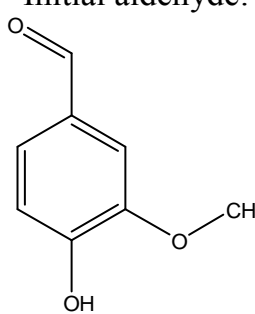
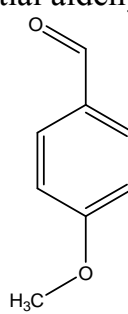
**4.1.** What structural features of your products explain the color change in the reaction with  $\text{NaHCO}_3$ ? Tick the appropriate box.

- presence of MeO group at position 4 in the benzene ring;  
 presence of MeO group at position 3 in the benzene ring;  
 presence of the OH group at position 4 in the benzene ring;  
 presence of both MeO and OH groups.

**4.2.** Which of the listed processes is responsible for the color change observed in the reaction of 2,4-dinitrophenylhydrazones with aqueous  $\text{NaOH}$ ? Tick the appropriate box.

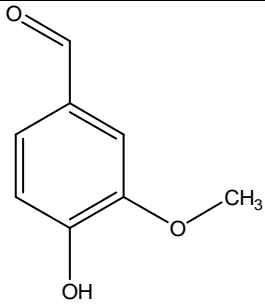
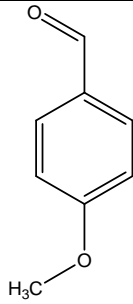
- alkaline hydrolysis       dehydration       hydration  
 deprotonation       dehydrogenation

**4.3.** Draw the structures of the main organic species present in each test reaction medium in the answer box below.

<p>Initial aldehyde:</p> 	<p>Initial aldehyde:</p> 
Solution of $\text{NaHCO}_3$	Solution of $\text{NaHCO}_3$
Solution of $\text{NaOH}$	Solution of $\text{NaOH}$

<b>Problem 1</b>	Student code _____	Quest.	1	2	3	4	5	Total
		Marks	3.5	1.5	1	3	35	44

5. Put the numbers 1 or 2 under each structure. Calculate the percent yields of both hydrazones

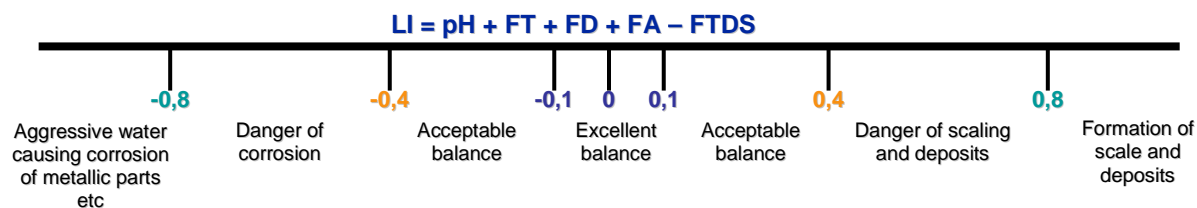
 <p>Number: _____</p> <p>Yield calculation:</p>	 <p>Number: _____</p> <p>Yield calculation:</p>
<p>Yields:</p> <p>Number 1 _____ %</p> <p>Number 2 _____ %</p>	

Replacement or extra chemicals	Lab assistant signature	Penalty
_____	_____	_____
_____	_____	_____
_____	_____	_____

<b>Problem 2</b>	Student code _____	Quest.	1	2	3	4	5	6	7	8	9	Total
		Marks	27	0	5	25	0	4	8	1	9	79

### Problem 2. Determination of the Langelier Saturation Index of a pool water (12 points)

The Langelier Saturation Index (LI) is a measure of a swimming pool water corrosivity as well as its ability to dissolve or deposit calcium carbonate. If LI is approximately zero, the water is considered “balanced”. If the LI is a positive number, the water tends to deposit calcium carbonate and is scale-forming. If the LI is a negative number, the water is corrosive and dissolves calcium carbonate. The LI is a combination of the physical values factors taken from Table 1 and can be calculated by the formula:



- pH :** pH value
- FT :** Temperature factor
- FD :** Calcium hardness (CH) factor
- FA :** Total alkalinity (TA) factor
- FTDS :** Total dissolved solids (TDS) factor

Table 1. Values and corresponding factors

Temperature, °C	FT	Calcium hardness (CH), mg/L CaCO <sub>3</sub>	FD	Total alkalinity (TA), mg/L CaCO <sub>3</sub>	FA	Total dissolved solids (TDS), mg/L NaCl	FTDS
0	0.0	5	0.3	5	0.7	0	12.0
3	0.1	25	1.0	25	1.4	-	-
8	0.2	50	1.3	50	1.7	1000	12.1
12	0.3	75	1.5	75	1.9	-	-
16	0.4	100	1.6	100	2.0	2000	12.2
19	0.5	150	1.8	125	2.1	-	-
24	0.6	200	1.9	150	2.2	3000	12.25
29	0.7	250	2.0	200	2.3	-	-
34	0.8	300	2.1	300	2.5	4000	12.3
41	0.9	400	2.2	400	2.6	-	-
53	1.0	600	2.35	800	2.9	5000	12.35
-	-	800	2.5	1000	3.0	-	-
-	-	1000	2.6	-	-	6000	12.4



<b>Problem 2</b>	Student code _____	Quest.	1	2	3	4	5	6	7	8	9	Total
		Marks	27	0	5	25	0	4	8	1	9	79

In this task you will have to determine the LI value of the given water sample. Note that hardness is expressed as the equivalent to the concentration of  $\text{CaCO}_3$  (expressed in mg/L). Total alkalinity being the acid equivalent to the total amount of carbonate and hydrocarbonate, also expressed in mg/L of  $\text{CaCO}_3$ , whereas TDS is recalculated as NaCl concentration (mg/L).

## Procedures

**Calcium hardness** is determined by complexometric titration with EDTA ( $\text{Na}_2\text{H}_2\text{Y}$ ). This is performed in a strongly alkaline medium to mask magnesium (large amounts of  $\text{Mg}^{2+}$  interfere due to the co-precipitation of calcium with  $\text{Mg}(\text{OH})_2$ ; moreover, the complexometric indicator is also adsorbed on  $\text{Mg}(\text{OH})_2$ , which impairs the observation of its color change). When the alkali is added, titration should be carried out immediately to avoid the deposition of  $\text{CaCO}_3$ .

**1.1.** Write down equation of the reaction occurring during titration with  $\text{Na}_2\text{H}_2\text{Y}$ :

### Procedure for calcium determination

- Put the standard solution of **EDTA** (exact concentration of 0.0443 M) in the burette.
- Pipette a 20 mL aliquot of the **Water sample** into an Erlenmeyer flask.
- Add 3 mL of 2M NaOH solution with the 10-mL measuring cylinder.
- Add murexide indicator with spatula to obtain noticeably pink solution.
- Within few minutes titrate the mixture with EDTA until the indicator color changes from pink to purple.

**1.2.** Fill in the table 2.

Table 2

<i>Calcium titration</i>	Titration No			
Initial reading of the burette, mL				
Final reading of the burette, mL				
Consumed volume, mL				

Accepted volume, mL \_\_\_\_\_

**2.** Calculate the hardness of the water sample in mg/L  $\text{CaCO}_3$ . Write down the result in Table 4 (see question 7).

Your work:

<b>Problem 2</b>	Student code _____	Quest.	1	2	3	4	5	6	7	8	9	Total
		Marks	27	0	5	25	0	4	8	1	9	79

**Measurement of pH.** Locate a pH meter in the lab (or ask your lab assistant).

- Place about 70-90 mL of the water sample into a clean Erlenmeyer flask.
- Remove the protective cap from the pH-meter (keep the cap standing, since there is solution in it).
- Rinse the electrode with distilled water using a plastic wash bottle.
- Turn the meter on by sliding the ON/OFF switch.
- Immerse the meter in the solution to be tested and stir gently by swirling the flask.
- Place the flask on the table and wait until the reading stabilizes (not more than 1 min).
- Read and record the pH value.
- Switch the meter off, rinse the electrode with distilled water and place the protective cap back (in case of queuing, pass over the meter to the next student).

**3.1.** Write down the pH value in Table 4 (see question 7).

**3.2.** Which form of carbonic acid predominates in your water sample?

Confirm your choice with calculation and tick one box.

*Note.* The dissociation constants of carbonic acid are:  $K_1 = 4.5 \cdot 10^{-7}$ ;  $K_2 = 4.8 \cdot 10^{-11}$ .

Your work:

Carbonate     Hydrogen carbonate     Carbonic acid

**3.3.** Write down the ionic equation of the predominant reaction of titration of the water sample with HCl.

**Determination of total alkalinity.** To obtain the value of the total alkalinity the water sample should be titrated to  $H_2CO_3$ . An acid-base indicator used is methyl orange, which starts changing its color from yellow to orange at pH of about 4.5.

<b>Problem 2</b>	Student code _____	Quest.	1	2	3	4	5	6	7	8	9	Total
		Marks	27	0	5	25	0	4	8	1	9	79

- Rinse the burette with distilled water and fill it with the standard HCl solution (exact concentration of 0.0535 M).
- Pipette a 50.0 mL aliquot of water sample into an Erlenmeyer flask and add 3 drops of methyl orange solution.
- If the sample is orange prior to addition of the acid the total alkalinity is zero. If the solution is yellow titrate it with the standard acid solution until the first noticeable color change towards orange is observed. Record the volume of the titrant used.

4.1. Fill in the Table 3.

Table 3

<i>Alkalinity determination</i>	Titration No			
Initial reading of the burette, mL				
Final reading of the burette, mL				
Consumed volume, mL				

Accepted volume, mL \_\_\_\_\_

4.2. Calculate the total alkalinity (in mg/L CaCO<sub>3</sub>). Write down the result in Table 4 (see question 7).

Your work:

5. **Temperature measurement.** Read the thermometer located at the table of common use and write down the value into Table 4 (see question 7).

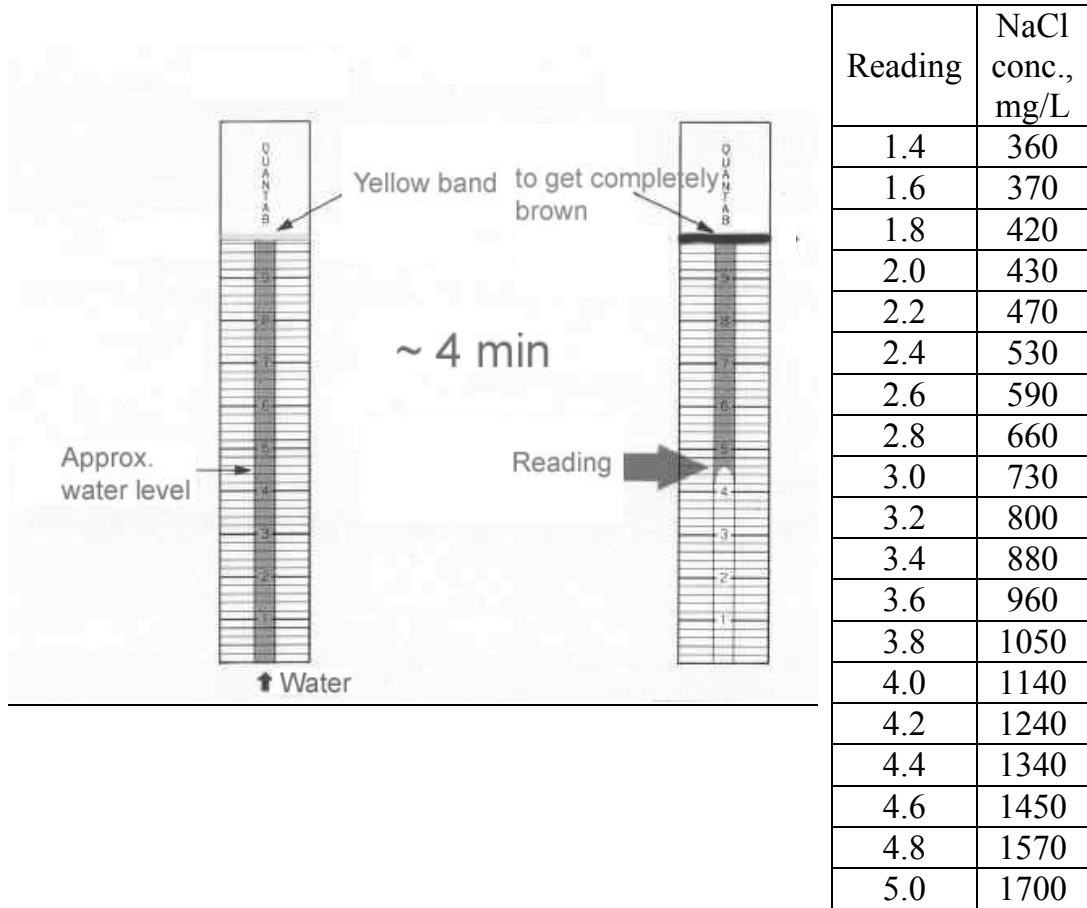
6. **TDS determination** in the water sample with the test strip.

- Fill a beaker with the water sample to a level of about 3 cm of height. Immerse the strip into water; be sure that the yellow band on the top of the strip does not touch the liquid.
- Wait for 3–4 min until the yellow band turns completely brown. Take the reading as shown in the picture hereunder, reading result to one decimal digit.
- Report the reading:

--

<b>Problem 2</b>	Student code _____	Quest.	1	2	3	4	5	6	7	8	9	Total
		Marks	27	0	5	25	0	4	8	1	9	79

- d) Find your TDS concentration as that of NaCl, mg/L in the table to the right of the picture.  
e) Write down the concentration of NaCl in Table 4 (see question 7).



7. Fill in all the blank boxes in the Table 4. Calculate LI and write down the result in Table 4. Take the values of the factors to the accuracy of two decimal digits.

Your work:

<b>Problem 2</b>	Student code _____	Quest.	1	2	3	4	5	6	7	8	9	Total
		Marks	27	0	5	25	0	4	8	1	9	79

Table 4. Calculation of LI of the water sample

<b>Water sample Number</b> _____					
CH, mg/L CaCO <sub>3</sub>	TA, mg/L CaCO <sub>3</sub>	<i>t</i> , °C	pH	TDS, mg/L NaCl	<b>LI</b>
FD	FA	FT		FTDS	

**Theoretical questions. Water balance correction.**

If LI significantly deviates from zero, it is needed to be adjusted to zero.

Imagine you are given a sample of pool water analyzed as you have done above. The results of the analysis are: CH = 550 mg/L, FD = 2.31, TA = 180 mg/L, FA=2.26, *t*° = 24°C, FT = 0.6; TDS = 1000 mg/L , FTDS = 12.1, pH = 7.9, LI = 0.97.

The pool serviceman added 10 mL of 0.0100 M solutions of reagents (NaHCO<sub>3</sub>, NaOH, NaHSO<sub>4</sub>, CaCl<sub>2</sub>, EDTA (disodium salt dihydrate) and HCl) to different pool water samples 200 mL each (one reagent for one sample).

8. Decide whether CaSO<sub>4</sub> is deposited upon addition of NaHSO<sub>4</sub>.

**Note:** CaSO<sub>4</sub> solubility product is  $5 \cdot 10^{-5}$ . Assume no precipitate of CaCO<sub>3</sub> is formed upon addition of any of the above reagents.

Your work:

Your answer (tick one) Yes  No

<b>Problem 2</b>	Student code _____	Quest.	1	2	3	4	5	6	7	8	9	Total
		Marks	27	0	5	25	0	4	8	1	9	79

9. Fill in the hereunder table by showing the trends of changes resulting from addition of each reagent to this particular water sample (use “+” if the factor increases, “-“ if it decreases, and “0” if it does not change).

Table 5

Reagent	pH	FA	FD	FTDS	LI
NaHCO <sub>3</sub>					
NaOH					
NaHSO <sub>4</sub>					
CaCl <sub>2</sub>					
Na <sub>2</sub> H <sub>2</sub> Y					
HCl					

Replacement or extra chemicals	Lab assistant signature	Penalty
_____	_____	_____
_____	_____	_____
_____	_____	_____

<b>Problem 3</b>	Name _____	Quest.	1	2	3	4	5	6	7	8	9	Total
	Student code _____	Marks	3	2	0	27.5	5	0	19.5	4	1	64

### Problem 3. Determination of molecular mass by viscometry (15 points)

Viscosity coefficient is a measure of fluid resistance to flow. It can be determined by measuring the rate of liquid flow through a thin capillary. Polymer solution viscosity grows with increasing concentration. At constant concentration, stronger solvent-polymer interactions result in more expanded polymer coils, and therefore, in higher viscosity.

Provided the density of the diluted solution of a polymer is equal to that of the solvent, the reduced viscosity  $\eta_{red}$  of the polymer solution with concentration  $c$  (g/mL) is defined as follows:

$$\eta_{red} = \frac{t - t_0}{t_0 c} \quad [mL/g],$$

where  $t$  and  $t_0$  are the flow times of the solution and pure solvent, respectively.

Reduced viscosity for dilute polymer solutions depends on concentration as follows:

$$\eta_{red}(c) = [\eta] + kc,$$

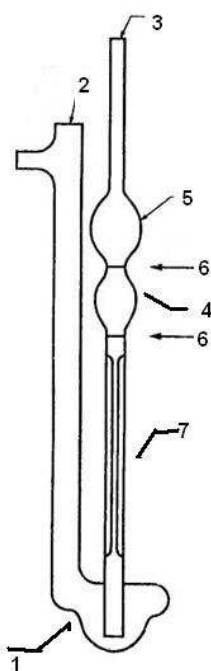
with  $k$ , a parameter ( $mL^2/g^2$ ) and  $[\eta]$ , intrinsic viscosity ( $mL/g$ ). The intrinsic viscosity  $[\eta]$  is determined by extrapolation of the reduced viscosity to zero polymer concentration. In general, the intrinsic viscosity is related to the molecular mass  $M$  of the polymer according to the Mark-Kuhn-Houwink equation:

$$[\eta] = KM^\alpha,$$

where  $K$  and  $\alpha$  are the constants for a particular solvent-polymer pair at a certain temperature.

Thus,  $M$  can be derived from the Mark-Kuhn-Houwink equation using experimentally determined  $[\eta]$  and reference data for  $K$  and  $\alpha$ .

#### How to work with viscometer



- |   |
|---|
| 1 – Collection vessel<br>2, 3 – Supplementary tubing<br>4 – Measurement vessel<br>5 – Collection vessel<br>6 – The match marks<br>7 - Capillary |
|---|

<b>Problem 3</b>	Name _____	Quest.	1	2	3	4	5	6	7	8	9	Total
	Student code _____	Marks	3	2	0	27.5	5	0	19.5	4	1	64

- a) Mount the viscometer so that its tubing (3) is vertical, and the collection vessel (1) stands on the lab stand basement. Adjust the fixing clamp as low as possible.
- b) Put 10 mL of the liquid to be analyzed into the collection vessel (1) through the tubing (2) using a pipette.
- c) Place the pipette filler or rubber bulb on top of the tubing (3) and suck the liquid into the measurement vessel (4) so that the liquid is drawn into the collection vessel (5). When sucking the liquid, avoid the air bubbles in the capillary (7) and the vessels (4, 5), as these can cause significant experimental errors. The liquid meniscus should be about 10 mm above the upper mark (6).
- d) Zero the stopwatch, and remove the pipette filler or bulb out of the tube (3). The liquid starts flowing down to the collection vessel (1).
- e) Measure the **flow time**: start the stopwatch when the liquid meniscus passes the upper match mark (6) and stop the stopwatch when the liquid meniscus passes the lower match mark (6).

**ATTENTION: Handle the viscometer with great care!**  
**There will be no replacement if you have broken your viscometer!**  
**If you do break your viscometer tell the lab assistant. You may then attempt to do the experiment using the 25 mL pipette and beaker in place of viscometer.**

Clean the viscometer three times with tap water and once with distilled water before you pass over to a new polymer sample. To do this, first wash it with tap water, and then rinse with distilled water. There is no need to wash it with the polymer solution, the error can occur but it is negligible.

You are NOT requested to fill in all table cells in the Answer Boxes. Perform as many measurements as you prefer for accurate averaging.

### Procedure

You are provided with a set of aqueous solutions of polymers (0.01 g/mL, stock solutions). Three of P1-P4 are solutions of poly(vinyl alcohol), whereas the fourth one is that of a partially hydrolyzed poly(vinyl acetate) containing *ca.* 10% of non-hydrolyzed units. It is unknown which of the P1-P4 solutions is partially hydrolyzed poly(vinyl acetate). Molecular masses of the polymers P1-P4 are given in the Table.

Approximate molecular mass	Sample code
26650	P2
50850	P1
65300	P4
91900	P3

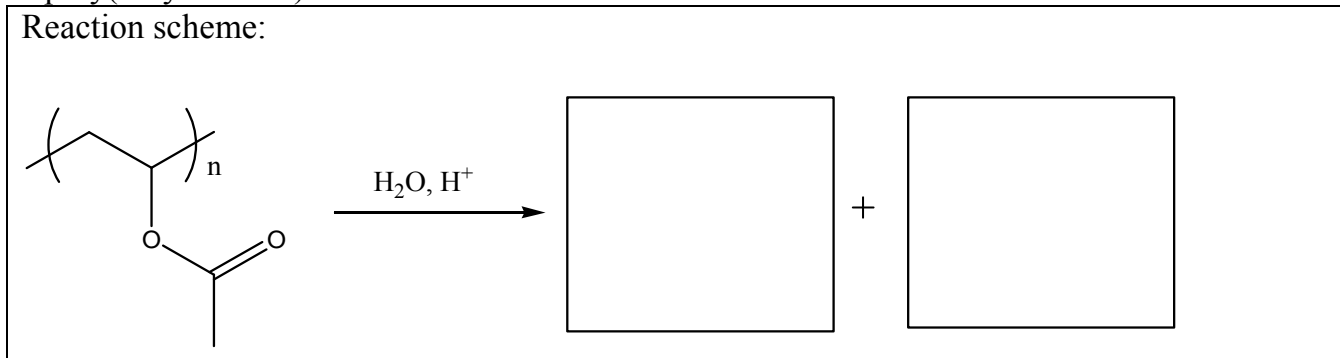


<b>Problem 3</b>	Name _____	Quest.	1	2	3	4	5	6	7	8	9	Total
	Student code _____	Marks	3	2	0	27.5	5	0	19.5	4	1	64

Sample X is poly(vinyl alcohol) of an unknown molecular mass.

In this task you will have to identify which of P1-P4 is the solution of partially hydrolyzed poly(vinyl acetate) and determine the molecular mass of polymer X.

1. Write down the reaction scheme of poly(vinyl alcohol) preparation by hydrolysis of poly(vinyl acetate).



2. Choose (tick appropriate box) which polymer shows the stronger interaction with water and compare the viscosities of aqueous solutions of fully and partially hydrolyzed poly(vinyl acetates). Assume that the concentration of the solutions and the molecular masses of the polymers are the same.

Poly(vinyl alcohol)	<input type="checkbox"/>
Partially hydrolyzed poly(vinyl acetate)	<input type="checkbox"/>

Compare the viscosities:

$\eta$  poly(vinyl alcohol) \_\_\_\_\_  $\eta$  partially hydrolyzed poly(vinyl acetate) (put either <, >, or  $\approx$ )

3. Measure the flow time of the pure solvent (distilled water). You are not requested to fill all the boxes below


Accepted value: \_\_\_\_\_ s

4. Measure the flow times of the stock solutions of P1-P4, and that of X. Calculate the reduced viscosities. You are NOT requested to fill in all table cells in the Answer Boxes. Perform as many measurements as you prefer for accurate averaging.

<b>Problem 3</b>	Name _____	Quest.	1	2	3	4	5	6	7	8	9	Total
	Student code _____	Marks	3	2	0	27.5	5	0	19.5	4	1	64

Sample→	P2 (26650)	P1 (50850)	P4 (65300)	P3 (91900)	X
Flow time, s					
Accepted flow time:	_____ s	_____ s	_____ s	_____ s	_____ s

Calculations:

Sample→	P2 (26650)	P1 (50850)	P4 (65300)	P3 (91900)	X
Reduced viscosity of the stock solutions, mL/g					

5. Encircle the solution out of P1-P2-P3-P4 which is the sample of partially hydrolyzed poly(vinyl acetate). **Hint:** Take into account the given molecular masses of the polymers P1-P4.

P1	P2	P3	P4
----	----	----	----

**DO NOT USE THIS POLYMER IN THE NEXT PART OF THE EXPERIMENT.**

6. To determine the parameters of the Mark-Kuhn-Houwink equation and calculate the unknown molecular mass of X choose and encircle two most appropriate solutions of poly(vinyl alcohol) with different molecular masses. Assume that the absolute error of intrinsic viscosity determination does not depend on the sample molecular mass.

P1	P2	P3	P4
----	----	----	----

7. Using appropriate measuring glassware to prepare the solutions, measure the flow time of a number of diluted solutions of three poly(vinyl alcohol) samples: that of unknown molecular mass (X), and the pair of poly(vinyl alcohols) chosen in i. 6, and calculate the corresponding reduced viscosities. When calculating the diluted solutions concentration, assume density of the polymer solutions is equal to that of water. Determine the intrinsic viscosities for each of the

<b>Problem 3</b>	Name _____	Quest.	1	2	3	4	5	6	7	8	9	Total
	Student code _____	Marks	3	2	0	27.5	5	0	19.5	4	1	64

examined samples. Submit the graph paper with your plots together with the booklet. **Note:** if you would like to plot the data referring to different samples on the same plot, make sure you use clearly distinguishable symbols for each dataset. You are NOT requested to fill in all table cells in the Answer Boxes.

Sample: ____					
Concentration, g/mL:					
Stock solution, mL					
Water, mL					
Flow time, s:					
Accepted flow time, s					
Reduced viscosity, mL/g					
Intrinsic viscosity $[\eta]$ , mL/g					

Sample: ____					
Concentration, g/mL:					
Stock solution, mL					
Water, mL					
Flow time, s:					
Accepted flow time, s					
Reduced viscosity, mL/g					
Intrinsic viscosity $[\eta]$ , mL/g					

<b>Problem 3</b>	Name _____	Quest.	1	2	3	4	5	6	7	8	9	Total
	Student code _____	Marks	3	2	0	27.5	5	0	19.5	4	1	64

Sample: ____					
Concentration , g/mL:					
Stock solution, mL					
Water, mL					
Flow time, s:					
Accepted flow time, s					
Reduced viscosity, mL/g					
Intrinsic viscosity $[\eta]$ , mL/g					

Summary of experimental results (only fill in the measured values)

Sample→	P__	P__	X
Concentration (c), g/mL:	0.01	0.01	0.01
Reduced viscosity ( $\eta_{red}$ ), mL/g			
c (1st dilution), g/mL:			
$\eta_{red}$ , mL/g			
c (2nd dilution), g/mL:			
$\eta_{red}$ , mL/g			
c (3rd dilution), g/mL:			
$\eta_{red}$ , mL/g			
c (4th dilution), g/mL:			
$\eta_{red}$ , mL/g			
c (5th dilution), g/mL:			
$\eta_{red}$ , mL/g			

<b>Problem 3</b>	Name _____	Quest.	1	2	3	4	5	6	7	8	9	Total
	Student code _____	Marks	3	2	0	27.5	5	0	19.5	4	1	64

8. Write down the form of equation you would use to determine  $K$  and  $\alpha$ .

Derive the  $K$  and  $\alpha$  values for the aqueous solution of poly(vinyl alcohol).

$K =$ _____ mL/g	$\alpha =$ _____
------------------	------------------

9. By using the obtained  $K$  and  $\alpha$  values, as well as the intrinsic viscosity of the X solution, calculate the molecular mass of the polymer X. If you have failed to determine  $K$  and  $\alpha$ , use  $K = 0.1$  mL/g and  $\alpha = 0.5$ .

Your work.

M (X) = \_\_\_\_\_

Replacement or extra chemicals	Lab assistant signature	Penalty
<u>Broken viscometer</u> _____ _____	_____ _____ _____	<u>0</u> _____ _____

# IUPAC Periodic Table of the Elements

1 <b>H</b> hydrogen [1.007; 1.009]																	18 <b>He</b> helium 4.003																		
3 <b>Li</b> lithium [6.938; 6.997]	4 <b>Be</b> beryllium 9.012																	13 <b>B</b> boron [10.80; 10.83]	14 <b>C</b> carbon [12.00; 12.02]	15 <b>N</b> nitrogen [14.00; 14.01]	16 <b>O</b> oxygen [15.99; 16.00]	17 <b>F</b> fluorine 19.00	10 <b>Ne</b> neon 20.18												
11 <b>Na</b> sodium 22.99	12 <b>Mg</b> magnesium 24.31																	13 <b>Al</b> aluminium 26.98	14 <b>Si</b> silicon [28.08; 28.09]	15 <b>P</b> phosphorus 30.97	16 <b>S</b> sulfur [32.05; 32.08]	17 <b>Cl</b> chlorine [35.44; 35.46]	18 <b>Ar</b> argon 39.95												
19 <b>K</b> potassium 39.10	20 <b>Ca</b> calcium 40.08	21 <b>Sc</b> scandium 44.96	22 <b>Ti</b> titanium 47.87	23 <b>V</b> vanadium 50.94	24 <b>Cr</b> chromium 52.00	25 <b>Mn</b> manganese 54.94	26 <b>Fe</b> iron 55.85	27 <b>Co</b> cobalt 58.93	28 <b>Ni</b> nickel 58.69	29 <b>Cu</b> copper 63.55	30 <b>Zn</b> zinc 65.38(2)	31 <b>Ga</b> gallium 69.72	32 <b>Ge</b> germanium 72.63	33 <b>As</b> arsenic 74.92	34 <b>Se</b> selenium 78.96(3)	35 <b>Br</b> bromine 79.90	36 <b>Kr</b> krypton 83.80																		
37 <b>Rb</b> rubidium 85.47	38 <b>Sr</b> strontium 87.62	39 <b>Y</b> yttrium 88.91	40 <b>Zr</b> zirconium 91.22	41 <b>Nb</b> niobium 92.91	42 <b>Mo</b> molybdenum 95.96(2)	43 <b>Tc</b> technetium	44 <b>Ru</b> ruthenium 101.1	45 <b>Rh</b> rhodium 102.9	46 <b>Pd</b> palladium 106.4	47 <b>Ag</b> silver 107.9	48 <b>Cd</b> cadmium 112.4	49 <b>In</b> indium 114.8	50 <b>Sn</b> tin 118.7	51 <b>Sb</b> antimony 121.8	52 <b>Te</b> tellurium 127.6	53 <b>I</b> iodine 126.9	54 <b>Xe</b> xenon 131.3																		
55 <b>Cs</b> caesium 132.9	56 <b>Ba</b> barium 137.3	57-71 lanthanoids	72 <b>Hf</b> hafnium 178.5	73 <b>Ta</b> tantalum 180.9	74 <b>W</b> tungsten 183.8	75 <b>Re</b> rhenium 186.2	76 <b>Os</b> osmium 190.2	77 <b>Ir</b> iridium 192.2	78 <b>Pt</b> platinum 195.1	79 <b>Au</b> gold 197.0	80 <b>Hg</b> mercury 200.6	81 <b>Tl</b> thallium [204.3; 204.4]	82 <b>Pb</b> lead 207.2	83 <b>Bi</b> bismuth 209.0	84 <b>Po</b> polonium	85 <b>At</b> astatine	86 <b>Rn</b> radon																		
87 <b>Fr</b> francium	88 <b>Ra</b> radium	89-103 actinoids	104 <b>Rf</b> rutherfordium	105 <b>Db</b> dubnium	106 <b>Sg</b> seaborgium	107 <b>Bh</b> bohrium	108 <b>Hs</b> hassium	109 <b>Mt</b> meitnerium	110 <b>Ds</b> darmstadtium	111 <b>Rg</b> roentgenium	112 <b>Cn</b> copernicium		114 <b>Fl</b> flerovium		116 <b>Lv</b> livermorium																				
																		57 <b>La</b> lanthanum 138.9	58 <b>Ce</b> cerium 140.1	59 <b>Pr</b> praseodymium 140.9	60 <b>Nd</b> neodymium 144.2	61 <b>Pm</b> promethium	62 <b>Sm</b> samarium 150.4	63 <b>Eu</b> europium 152.0	64 <b>Gd</b> gadolinium 157.3	65 <b>Tb</b> terbium 158.9	66 <b>Dy</b> dysprosium 162.5	67 <b>Ho</b> holmium 164.9	68 <b>Er</b> erbium 167.3	69 <b>Tm</b> thulium 168.9	70 <b>Yb</b> ytterbium 173.1	71 <b>Lu</b> lutetium 175.0			
																		89 <b>Ac</b> actinium	90 <b>Th</b> thorium 232.0	91 <b>Pa</b> protactinium 231.0	92 <b>U</b> uranium 238.0	93 <b>Np</b> neptunium	94 <b>Pu</b> plutonium	95 <b>Am</b> americium	96 <b>Cm</b> curium	97 <b>Bk</b> berkelium	98 <b>Cf</b> californium	99 <b>Es</b> einsteinium	100 <b>Fm</b> fermium	101 <b>Md</b> mendelevium	102 <b>No</b> nobelium	103 <b>Lr</b> lawrencium			

Key:  
atomic number  
**Symbol**  
name  
standard atomic weight



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## Notes

- IUPAC 2009 Standard atomic weights abridged to four significant digits (Table 4 published in *Pure Appl. Chem.* 83, 359-396 (2011); doi:10.1351/PAC-REP-10-09-14). The uncertainty in the last digit of the standard atomic weight value is listed in parentheses following the value. In the absence of parentheses, the uncertainty is one in that last digit. An interval in square brackets provides the lower and upper bounds of the standard atomic weight for that element. No values are listed for elements which lack isotopes with a characteristic isotopic abundance in natural terrestrial samples. See PAC for more details.

- "Aluminum" and "caesium" are commonly used alternative spellings for "aluminium" and "caesium."

- Claims for the discovery of all the remaining elements in the last row of the Table, namely elements with atomic numbers 113, 115, 117 and 118, and for which no assignments have yet been made, are being considered by a IUPAC and IUPAP Joint Working Party.

For updates to this table, see [iupac.org/reports/periodic\\_table/](http://iupac.org/reports/periodic_table/). This version is dated 1 June 2012.

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