The 2nd Abu Rayhan al-Biruni International Chemistry Olympiad

May 28 – June 4, 2025

Tashkent, Uzbekistan

ABU RAYHAN BIRUNI
INTERNATIONAL
CHEMISTRY OLYMPIAD

Preparatory problems

Ministry of Preschool and School Education of the Republic of Uzbekistan

MAKTABGACHA VA MAKTAB TA´LIMI VAZIRLIGI

Science Olympiad Center

SCIENCE OLYMPIAD CENTER

Table of contents

Theoretical problems

Practical problems

Preface

Dear participants!

The first Abu Rayhan Biruni International Chemistry Olympiad (ARBIChO) was held in 2023. From the very beginning it turned out to be a huge success, since it offered the participants a unique combination of old national traditions and comprehensive science achievements as a solid background behind the tasks.

We are now very close to the completion of 2025. Since Uzbekistan will be hosting the International Chemistry Olympiad (IChO) in 2026, the decision was taken to mimic many IChO procedures at this year ARBIChO. Existence of the Olympiad Syllabus, Fields of Advanced Difficulty announced by the hosts and the set of Preparatory Problems (PP) are among the most important novelties of this year competition. The ARBIChO Science Committee has compiled a challenging set of PP, which appeared at previous Olympiads, mostly International Chemistry Olympiads and International Mendeleev Chemistry Olympiads. We strongly suggest you do not search for the solutions in the net (which is sometimes possible). Instead, you have a unique chance to practice in solving challenging tasks, which will help you to prepare efficiently for the competition.

Chemistry is an experimental science, but serious attention must be paid to safe operations that will not bring harm to either you or other competitors. Please take time to thoroughly study the lab safety instructions that must be followed at the ARBIChO.

We would like to thank all the colleagues who has already contributed to the ARBIChO and those who will do it in future!

We wish you good luck! Enjoy chemistry!

The members of the Scientific Committee in charge of the preparatory problems

Alexander Gladilin, *akgladilin@yahoo.com*
Khamidulla Tukhtaev, *chem.hamidullo@gmail.com*
Bekhzodbek Boltaev, *bekhzodbekboltaev1995@gmail.com*

Acknowledgments

We would like to thank the Ministry of Preschool and School Education of the Republic of Uzbekistan, which became the main initiator of the 2nd ARBICHO. We are also grateful to the Steering Committees of International Chemistry Olympiad and International Mendeleev Chemistry Olympiad for their assistance in preparing a set of Preparatory Problems. We would like to thank all members of the Science Committee for the work they have done.

Science Committee

Khamid Khodjaniyazov, *A.S.Sadykov Bioorganic Chemistry Institute, Tashkent*

Alexander Gladilin, *Moscow State University, Moscow*

Shamansur Sagdullaev, *Institute of Plant Chemistry, Tashkent*

Burkhon Elmuradov, *Institute of Plant Chemistry, Tashkent*

Abdujalol Sidikov, *Tashkent Institute of Chemical Technologies, Tashkent*

Vadim Eremin, *Moscow State University, Moscow*

Yunus Turkmen, *Bilkent University, Ankara*

Andrei Shved, *ETH Zurich, Switzerland*

Alex Koronatov, *Technion, Croatia*

Bulat Garifullin, *Hospital No.13, Ufa*

Khamidulla Tukhtaev, *KAUST, Saudi Arabia*

Bekhzodbek Boltaev, *National Medical Center, Tashkent*

Azimjon Jamolov, *Nanyang Technological University, Singapore*

Boburbek Boltaev, *Bekobod Central Hospital, Tashkent*

Azizbek Nazarov, *Tashkent Medical Academy, Tashkent*

Islomjon Karimov, *Bilkent University, Ankara*

Maftuna Badalova, *Nanyang Technological University, Singapore*

Mirumid Mirakbarov, *HSE University, Moscow*

Mokhira Boltaeva, *D.I.Mendeleev University of Chemical Technology, Tashkent branch*

Saida Abdullaeva, *Tashkent Medical Academy, Tashkent*

Ikromiddin Boymahammadov, *New Uzbekistan University, Tashkent*

Sherzod Shaymatov, *Tashkent Medical Academy, Tashkent*

Abdullokh Makhmudov, *Massachusetts Institute of Technology, USA*

Fields of advanced difficulty

Theoretical

1. Solid state structures, basic unit cells, cell parameters, solid sphere model, calculation of densities and atomic radii.
2. Crystal field theory.
3. Radioactivity and radioactive series.
4. Thermodynamic cycles, adiabatic processes, phase diagrams, the Clausius-Clapeyron equation.
5. Interpretation of ^{1}H NMR spectra (chemical shift, multiplicity, integrals) and ^{13}C NMR spectra in combination with mass spectroscopy data.
6. Calculations of thermodynamic data from electrochemical data and vice versa, Latimer and Pourbaix diagrams.

Practical

1. Use of a pH-meter.

The IChO and ARBIChO Syllabus

Knowledge expected to be known by all participants:

Awareness of experimental errors, use of significant figures;

Mathematics skills commonly encountered at secondary school level, including solving quadratic equations, use of logarithms and exponentials, solving simultaneous equations with 2 unknowns, the meaning of sine and cosine, elementary geometry such as Pythagoras' theorem, plotting graphs (more advanced math skills such as differentiation and integration, if required must be included as one of the advanced topics);

Nucleons, isotopes, radioactive decay and nuclear reactions (alpha, beta, gamma);

Quantum numbers (n, l, m) and orbitals (s, p, d) in hydrogen-like atoms;

Hund's rule, Pauli exclusion principle;

Electronic configuration of main group and the first-row transition metal atoms and their ions;

Periodic table and trends (electronegativity, electron affinity, ionization energy, atomic and ionic size, melting points, metallic character, reactivity);

Bond types (covalent, ionic, metallic, coordination), intermolecular forces and relation to properties;

Lewis theory;

Molecular structures and VSEPR theory;

Balancing equations, empirical formulae, mole concept and Avogadro constant, stoichiometric calculations, density, calculations with different concentration units;

Chemical equilibrium, Le Chatelier's principle, equilibrium constants in terms of concentrations, pressures and mole fractions;

Arrhenius and Bronsted acid-base theory, pH, self-ionization of water, equilibrium constants of acid-base reactions, pH of weak acid solutions, pH of very dilute solutions and simple buffer solutions, hydrolysis of salts;

Solubility constants and solubility;

Complexation reactions, definition of coordination number, complex formation constants;

Partition coefficients: definition and simple calculations;

Basics of electrochemistry: electromotive force, Nernst equation, electrolysis, Faraday's laws;

Rate of chemical reactions, elementary reactions, factors affecting the reaction rate, rate law for homogeneous and heterogeneous reactions, rate constant, reaction order;

Reaction energy profile, activation energy, Arrhenius-equation, catalysis, influence of a catalyst on thermodynamic and kinetic characteristics of a reaction;

Use of simple first-order and zeroth-order kinetic rate laws, exponential decay, half-lives;

Energy, heat and work, enthalpy and energy, heat capacity, Hess' law, Born-Haber cycle, standard formation enthalpies, solution, solvation and bond enthalpies;

Definition and concept of entropy and Gibbs' energy, second law of thermodynamics, direction of spontaneous change;

Calculation of equilibrium constants from standard enthalpy and entropy data;

Ideal gas law, partial pressures;

Principles of direct and indirect titration (back titration);

Acidi- and alkalimetry, acidimetric titration curves, choice and color of indicators for acidimetry;

Redox titrations (permanganometric and iodometric);

Simple complexometric and precipitation titrations;

Basic principles of inorganic qualitative analysis for ions specified in factual knowledge, flame tests;

Basic concepts of light and color, wavelength, frequency, wave numbers, photon energies, Lambert-Beer law;

Reactions of s-block elements with water, oxygen and halogens, their color in flame tests;

Stoichiometry, reactions and properties of binary non-metal hydrides;

Common reactions of carbon, nitrogen and sulfur oxides (CO, CO_2, NO, NO_2, N_2O_4, SO_2, SO_3);

Common oxidation states of p-block elements, stoichiometry of common halides and oxoacids (HNO_2, HNO_3, H_2CO_3, H_3PO_4, H_3PO_3, H_2SO_3, H_2SO_4, $HOCl$, $HClO_3$, $HClO_4$);

Reaction of halogens with water;

Common oxidation states of first row transition metals (Cr(III), Cr(VI), Mn(II), Mn(IV), Mn(VII), Fe(II), Fe(III), Co(II), Ni(II), Cu(I), Cu(II), Ag(I), Zn(II), Hg(I), and Hg(II)) and the color of these ions;

Dissolution of these metals and Al, amphoteric hydroxides ($Al(OH)_3$, $Cr(OH)_3$, $Zn(OH)_2$);

Permanganate, chromate, dichromate ions and their redox reactions;

Iodometry (reaction of thiosulfate and iodine);

Identification of Ag^+, Ba^{2+}, Fe^{3+}, Cu^{2+}, Cl^-, CO_3^{2-}, SO_4^{2-};

Organic structure-reactivity relations (polarity, electrophilicity, nucleophilicity, inductive effects, relative stability), structure-property relations (boiling point, acidity, basicity);

Simple organic nomenclature;

Hybridization and geometry at carbon and other centers;

Sigma and pi bonds, delocalization, aromaticity, resonance structures;

Isomerism (constitutional, configuration, conformation, tautomerism);

Stereochemistry (E/Z, cis/trans isomers, chirality, optical activity, Cahn-Ingold-Prelog system, Fisher projections, D/L);

Cyclohexane conformations;

Common electrophiles and nucleophiles;

Electrophilic addition: addition to double and triple bonds, regioselectivity (Markovnikoff/Kharasch rule), stereochemistry;

Electrophilic substitution: substitution on aromatic rings, influence of substituents on the reactivity and regioselectivity, electrophilic species;

Elimination: E1 and E2 reactions at sp^3 carbon centers, stereochemistry, acid-base catalysis, common leaving groups;

Nucleophilic substitution: S_N1 and S_N2 reactions at sp^3 carbon centers, stereochemistry;

Nucleophilic addition: addition to carbon-carbon and carbon-hetero atom double and triple bonds, addition-elimination reactions, acid-base catalysis;

Radical substitution: reaction of halogens with alkanes;

Oxidations and reductions: switching between the different oxidation levels of common functional groups (alkyne – alkene – alkane – alkyl halide, alcohol – aldehyde, ketone – carboxylic acid derivatives, nitriles – carbonates);

Grignard reaction, Fehling and Tollens reaction;

Simple polymers and their preparation (polystyrene, polyethylene, polyamides, polyesters);

Amino acids and their classification in groups, isoelectric point, peptide bond, peptides and proteins;

Carbohydrates: open chain and cyclic forms;

Structures of glucose and fructose;

Lipids: general formulae of di- and triacyl glycerides, saturated and unsaturated fatty acids;

General structure of DNA and RNA, hydrogen bonding between bases, the concept of replication and transcription;

Use of common protecting groups in organic synthesis;

Simple multistep organic synthesis;

Hydrophilic and hydrophobic groups, micelle and bilayer formation;

Polymers and monomers, chain polymerizations, polyaddition and polycondensation;

Laboratory skills expected to be known by all participants:

Heating in the laboratory, heating under reflux;

Mass and volume measurement (with electronic balance, measuring cylinder, pipette and burette, volumetric flask);

Reading temperature from a non-digital thermometer;

Preparation and dilution of solutions and standard solutions;

Operation of a magnetic stirrer;

Carrying out of test tube reactions (e.g. qualitative testing for organic functional groups using a given procedure);
Volumetric determination, titrations, use of a pipette bulb or filler;
Measurement of pH (by pH paper or calibrated pH meter);
Gravity filtration;
Drying of precipitates;
Operation of simple semi-automatic digital instruments using detailed instructions (not application specific);
Plotting experimental data on graphs, analysis of graphs.

Physical constants and equations

In this booklet, we assume the activities of all aqueous species to be well approximated by their respective concentration in mol L^{-1}. To further simplify formulae and expressions, the standard concentration $c° = 1$ mol L^{-1} is omitted.

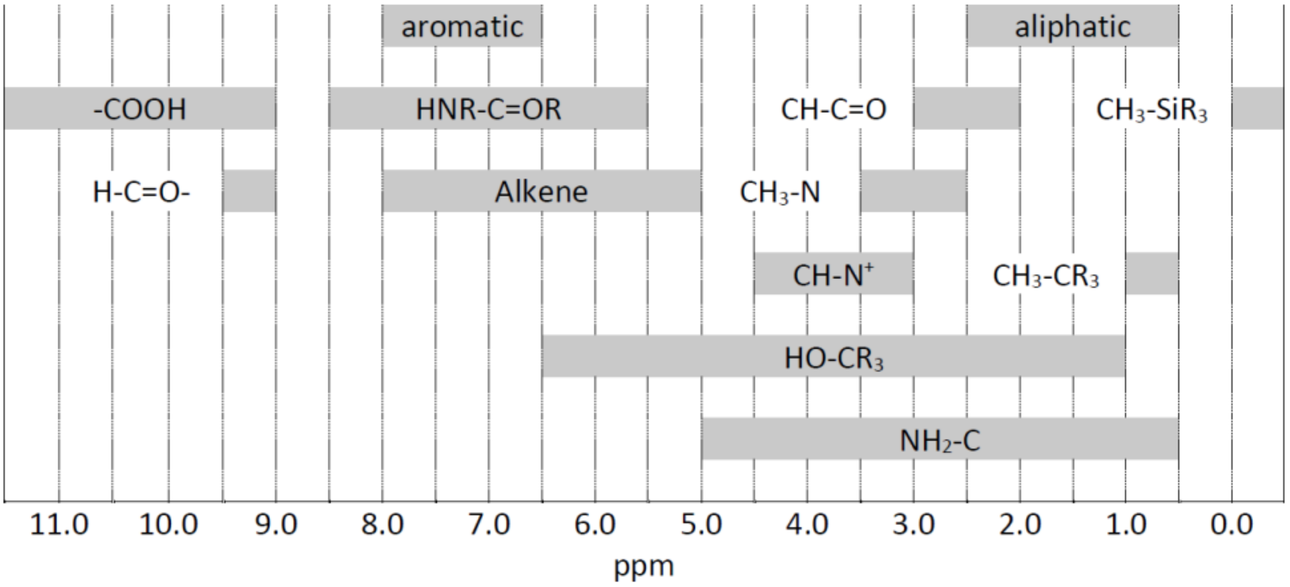
Avogadro's constant:	$N_A = 6.022\cdot 10^{23}$ mol^{-1}
Universal gas constant:	$R = 8.314$ J mol^{-1} K^{-1}
Standard pressure:	$p° = 1$ bar $= 10^5$ Pa
Atmospheric pressure:	Patm = 1 atm = 1.013 bar = $1.013\cdot 10^5$ Pa
Zero of the Celsius scale:	273.15 K
Faraday constant:	$F = 9.6485\cdot 10^4$ C mol^{-1}
Ideal gas equation:	$pV = nRT$
Gibbs free energy:	$G = H - TS$ $\Delta_r G° = -RT \ln K°$ $\Delta_r G° = -nFE_{\text{cell}}°$ $\Delta_r G = \Delta_r G° + RT \ln Q$
Reaction quotient Q for a reaction a A(aq) + b B(aq) = c C(aq) + d D(aq):	$Q = \frac{[C]^c[D]^d}{[A]^a[B]^b}$
Nernst–Peterson equation:	$E = E^0 - \frac{RT}{zF} lnQ$
where Q is the reaction quotient of the reduction half-reaction	at $T = 298$ K, $\frac{RT}{F} ln10 \approx 0.059$ V
Clausius-Clapeyron equation:	$ln\frac{P_2}{P_1} = -\frac{\Delta_{vap}H^0}{R}(\frac{1}{T_2} - \frac{1}{T_1})$
Arrhenius equation:	$k = A\, e^{-\frac{E_a}{RT}}$
Rate laws in integrated form:	
Zero order:	$[A] = [A]_0 - kt$
First order:	$\ln[A] = \ln[A]_0 - kt$
Second order:	$\frac{1}{[A]} = \frac{1}{[A]_0} + kt$
Half-life for a first order process:	$t_{1/2} = \frac{ln2}{k}$
The activity of radionuclide:	$A = kN$

Periodic table

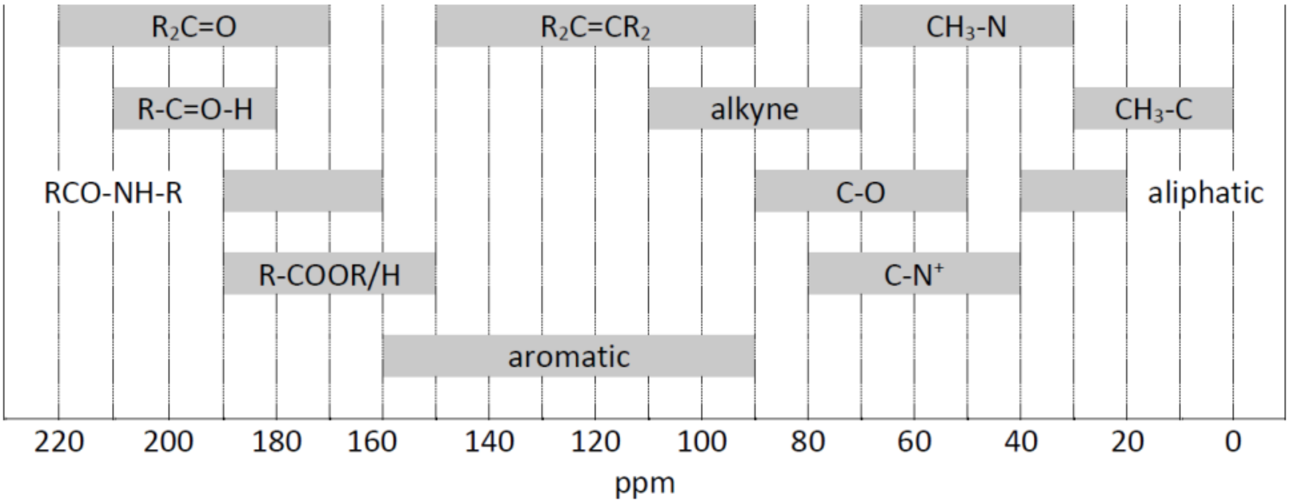
1																	18
1 H 1.008	2											13	14	15	16	17	2 He 4.003
3 Li 6.94	4 Be 9.01											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
11 Na 22.99	12 Mg 24.31	3	4	5	6	7	8	9	10	11	12	13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.06	17 Cl 35.45	18 Ar 39.95
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.87	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.38	31 Ga 69.72	32 Ge 72.63	33 As 74.92	34 Se 78.97	35 Br 79.90	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.95	43 Tc -	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
55 Cs 132.9	56 Ba 137.3	57-71	72 Hf 178.5	73 Ta 180.9	74 W 183.8	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po -	85 At -	86 Rn -
87 Fr -	88 Ra -	89- 103	104 Rf -	105 Db -	106 Sg -	107 Bh -	108 Hs -	109 Mt -	110 Ds -	111 Rg -	112 Cn -	113 Nh -	114 Fl -	115 Mc -	116 Lv -	117 Ts -	118 Og -

57 La 138.9	58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm -	62 Sm 150.4	63 Eu 152.0	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0	71 Lu 175.0
89 Ac -	90 Th 232.0	91 Pa 231.0	92 U 238.0	93 Np -	94 Pu -	95 Am -	96 Cm -	97 Bk -	98 Cf -	99 Es -	100 Fm -	101 Md -	102 No -	103 Lr -

^{1}H NMR chemical shifts



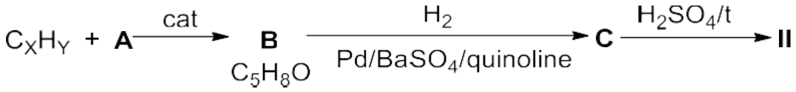
^{13}C NMR chemical shifts



Problem 1

(*International Mendeleev Chemistry Olympiad, 2024, the 1st exam, Problem 2*)

Crystals of an optically active terpene hydrocarbon further referred to as "cembrene" (**I**) were isolated from *Pinus albicaulis* (Whitebark Pine) in 1951. This hydrocarbon was the first natural compound, the molecule of which was found to contain a carbocycle of an unusual size. All terpenes are usually considered as polymerization products of the hydrocarbon **II**. Terpenes are subdivided into monoterpenes (n = 2), sesquiterpenes (n = 3), diterpenes (n = 4), triterpenes (n = 6) and polyterpenes depending on the number of units (n) of **II**. One of the industrial syntheses of **II** is given below:



$$C_XH_Y + \mathbf{A} \xrightarrow{\text{cat}} \underset{C_5H_8O}{\mathbf{B}} \xrightarrow[\text{Pd/BaSO}_4\text{/quinoline}]{H_2} \mathbf{C} \xrightarrow{H_2SO_4/t} \mathbf{II}$$

1. Determine the structures of C_XH_Y, **A**–**C,** and **II**, if C_XH_Y gives a precipitate with an ammonia solution of silver oxide, while the carbonyl compound **A** does not react with it.

2. Choose the catalyst for the first step from the list: a) Al_2O_3; b) H_2SO_4; c) $(C_2H_5)_3N$; d) $[(i\text{-}C_3H_7)_2N]Li$; e) KOH.

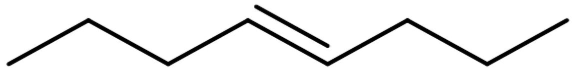
The structure of cembrene was elucidated in 1962. According to the mass spectrum data, the molecular weight of **I** is 272 a.m.u. 16.32 g of **I** can completely add 2764 mL of H_2 (50°C, 2.3 atm) in the presence of Pd/C.

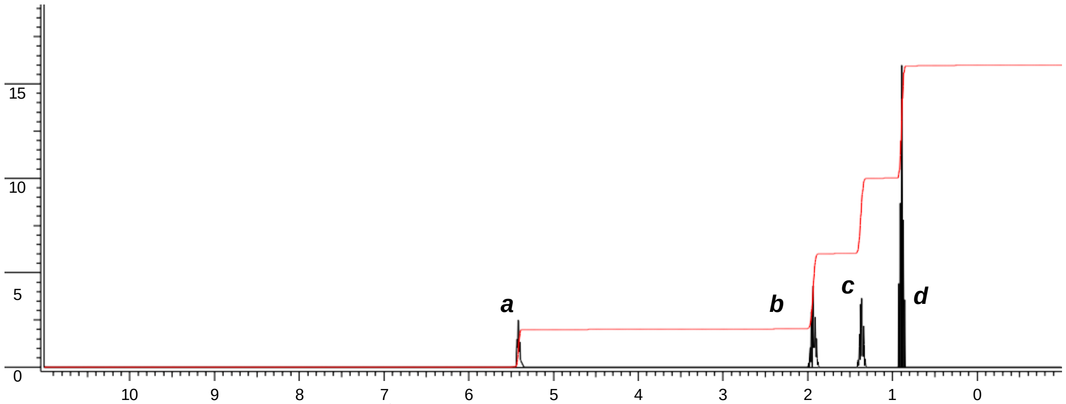
3. Determine the molecular formula of **I.** Which class of terpenes (monoterpene, sesquiterpene, diterpene, triterpene, polyterpene) does it belong to?

4. Calculate the number of rings (n_{ring}) and double bonds ($n_{C=C}$) in the molecule of **I**.

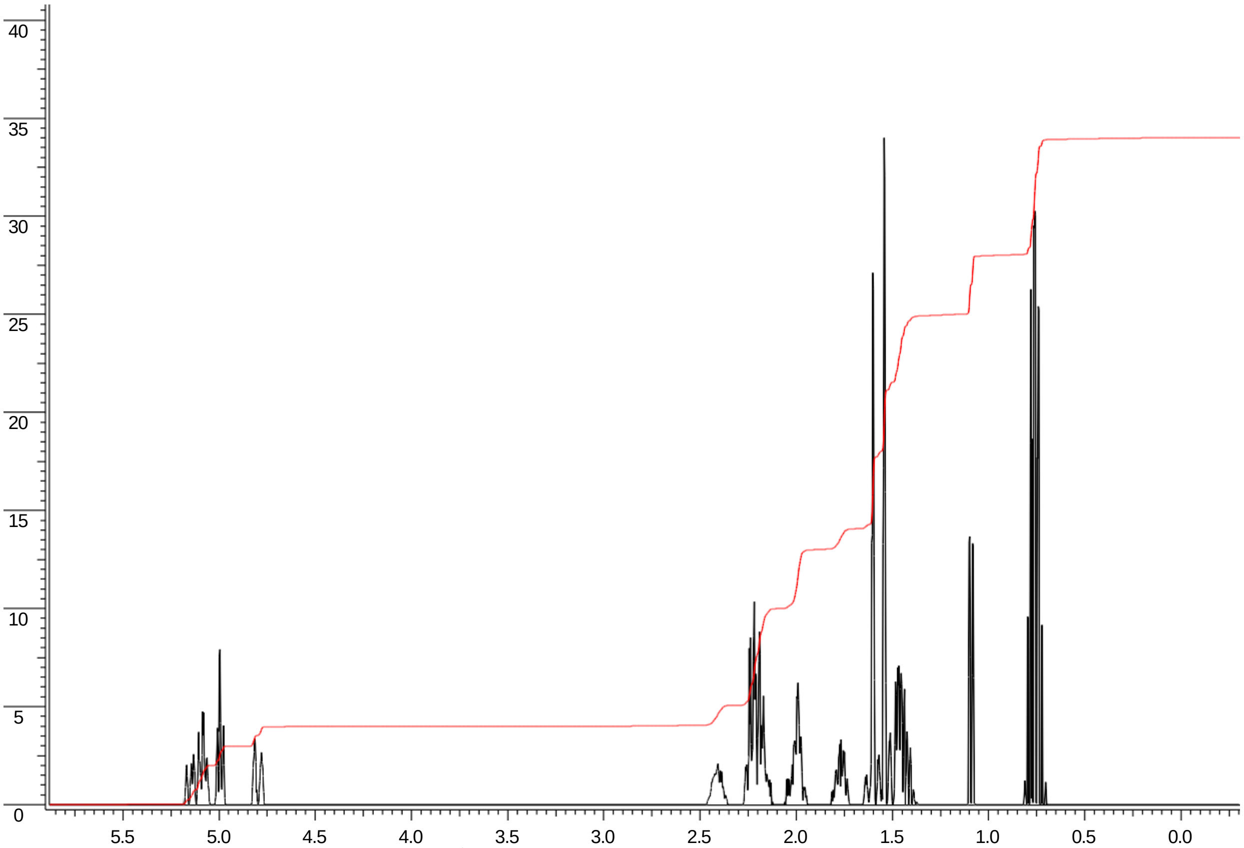
The reduction of **I** under the action of Li/NH_3 leads to the formation of dihydrocembrene (**III**). The ^{1}H NMR spectra of *trans*-4-octene and **III** are shown below.

5. In the *trans*-4-octene structure, label the groups ***a*** – ***d*** that give the corresponding signals in the spectrum. Calculate the total number of hydrogen atoms at the double (n_H-sp^2) and single (n_H-sp^3) C-C bonds in the molecule of **III**.





^{1}H NMR spectrum of *trans*-4-octene.



^{1}H NMR spectrum of **III**.

Ozonolysis of **III** with subsequent treatment with H_2O_2 gave an equimolar mixture of 2-isopropyl-5-oxohexanoic acid, 2-methylpentanedioic acid and a thermally stable bifunctional compound **X**; no other carbon-containing products were found.

6. Calculate the molecular formula of **X** and determine its structure.

7. Determine the ring size in cembrene.

Problem 2

(*International Mendeleev Chemistry Olympiad, 2006, the 2nd exam, Inorganic Chemistry, Problem 3*)

A popular method to synthesize organometallic compounds that play an important role in catalytic transformations is a reaction of salts of transition metals in alcohols with hydrocarbons in the presence of reductants. In 1964 G. Wilkinson synthesized neutral diamagnetic complexes **A** and **B**, in which coordination numbers (CN) of metal atoms differ by one, using the reactions in ethanol:

$$b\mathbf{X}Cl_3 + bC_nH_{2n\text{-}4} + b\mathbf{Y}Cl_2 \xrightarrow{\text{ethanol}} \mathbf{A} + b\mathbf{Y}Cl_{2b} \qquad (1)$$

$$bNa_2\mathbf{Z}Cl_6 + 2bC_nH_{2n\text{-}4} + 5\mathbf{Y}Cl_2 \xrightarrow{\text{ethanol}} b\mathbf{B} + 3\mathbf{Y}Cl_{2b} + 2bNaCl \qquad (2)$$

The hydrocarbon C_nH_{2n-4} is a thermodynamically controlled product of catalytic cyclization of alkadiene and has 2 peaks in its ^1H NMR spectrum (δ = 2.36 and 5.57 ppm) with the 2:1 intensity ratio, and 2 peaks in its ^{13}C NMR spectrum (128.7 and 28.2 ppm). In the pure hydrocarbon and in the complexes **A** and **B**, the ratio $\omega(C) : \omega(H) \approx n$; $\omega(\mathbf{X})$ = 41.73 mass% in complex **A**, $\omega(C) = \omega(\mathbf{Z}) = 1.619\ \omega(\mathbf{Y})$ in complex **B**.

1. Indicate the number of types of protons in the C_nH_{2n-4} hydrocarbon according to ^1H NMR data, their ratio; the number of protons of each type; the symmetry of the cycle. Find the structure of the hydrocarbon and suggest its two most stable structural conformations.

2. Find transition metals **X** and **Z** by calculating their atomic weights. In these calculations use four significant figures.

3. Find metal **Y** and describe the role of $\mathbf{Y}Cl_2$ in reactions (1) and (2) (oxidizing agent, reducing agent, ligand, outer sphere, central ion).

4. Write formulas **A** and **B**, indicate the oxidation numbers and CNs of transition metal atoms and the structure of the hydrocarbon in these compounds.

5. Indicate the hybridization of **X** and **Z** in initial compounds and complexes, determine the coordination polyhedron type around **X** and **Z** in **A** and **B**.

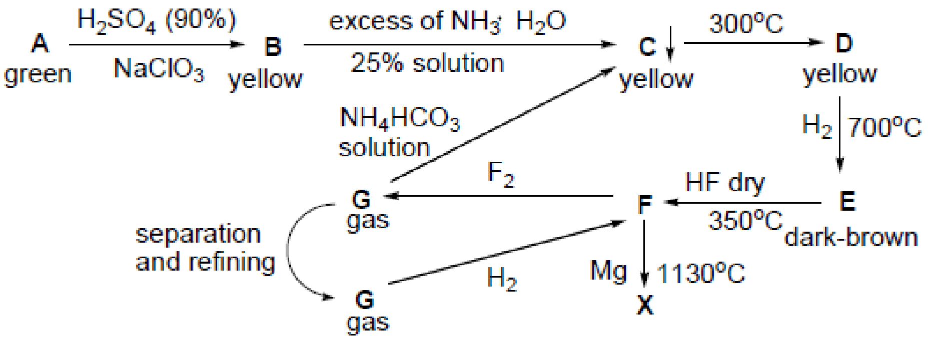
6. Describe the structure of **A** and **B** using crystal field theory. Write the desired letter (**A** or **B**) under the diagram and fill the orbitals with electrons:

—	b_1					—	b_1
—	b_2	— —	e_g	— — —	t_{2g}	—	a_1
—	a_1					—	b_2
— —	e	— — —	t_{2g}	— —	e_g	— —	e

Problem 3

(*International Mendeleev Chemistry Olympiad, 2008, the 2nd exam, Inorganic Chemistry, Problem 2*)

Uzbekistan has the widest deposits of metal **X** in CIS region. Following to one of the modern technological schemes, a raw material for its production is oxide **A (**84.8% **X**) containing **X** in two oxidation numbers (one of them is the maximal number for **X**). In industry, metal **X** is obtained according to the scheme below.



Four times charged complex anion of acid **B** contains only **X**, oxygen, and three sulfate ions. Neutral salt **C** contains nitrogen, oxygen, hydrogen and **X** (n(**X**) : n(N) = 1 : 1). Refined **G** in amount of 1.000 g can be converted to at least 0.891 g but less than 0.892 g of **F**. **D** – **G** are binary compounds. Variation of an oxidation number of **X** leads to a color change in the corresponding compound.

1. Determine compositions of the compounds **A** – **X**. Write down the equations of the reactions presented in the scheme above.

2. What is the purpose of the stage of separation and refining of **G** in industry of **X**? Mark one correct answer.

-removal of the intermediate product of transformation of F;	-removal of hydrogen fluoride;
-filtration of suspended particles;	-separation of isotopes ^{235}U and ^{238}U;
-cleaning from vacuum grease	-removal of the products of decomposition of **G.**

3. Depict the structures of $XC_{20}H_{20}$ and $XC_{16}H_{16}$. Note that the oxidation number of **X** is the same for both compounds and coincides with one of those in oxide **A**; all carbon atoms are equivalent in each compound and belong to aromatic cycles.

Problem 4

(*The VI All-Russian Internet Olympiad "Nanotechnology - a breakthrough into the future", 2012*)

Interest in short peptide sequences is driven by their ability to self-assemble into stable supramolecular structures. In pathophysiology, an example of such peptide structures can be amyloid fibers, which are formed, in particular, in Alzheimer's disease and prion diseases (mad cow disease, which has received media coverage).

In 1993, American researchers documented the spontaneous formation of a membrane from a solution of oligopeptide **X-II**, which has a molecular weight of 1615.76 g/mol.

1. Determine the range of amino acid residues in **X-II**, based on the fact that this peptide contains only canonical amino acids.

In reality **X-II** is composed of 16 residues from three amino acids: alanine (Ala), glutamic acid (Glu), and lysine (Lys).

2. Determine the gross amino acid composition of **X-II** by suggesting a solution to this issue based not on a search of options, but on a logical approach. Use single–letter amino acid designations: alanine - A, glutamic acid – E, lysine – K.

Subsequently, two isomeric peptides with a similar **X-II** amino acid composition, **X-I** and **X-IV**, were synthesized. It is known that all three peptides lack peptide bonds formed simultaneously by glutamate and lysine, and separate treatment of the peptides with the enzyme trypsin, which hydrolyzes the peptide bonds formed by the carboxyl group of lysine, leads to the following results:

peptide	the number of peptides according to the treatment results			
	dipeptide	tetrapeptide	hexapeptide	decapeptide
X-I	-	4	-	-
X-II	2	-	2	-
X-IV	3	-	-	1

3. Determine structures of **X-I**, **X-II**, and **X-IV**.

Hydrophilic matrices based on hexadecapeptide **X** sequences have proved to be extremely interesting for such a rapidly developing field of biotechnology as the creation of body tissues from stem cells using nanomaterials.

4. Explain the principles of self-organization of peptides of the **X** family.

Problem 5

(*The VI All-Russian Internet Olympiad "Nanotechnology - a breakthrough into the future", 2012*)

Recently, there has been a growing interest in oligopeptides with the properties of surfactants as a promising area of nanomedicine. Acid hydrolysis of peptide **A** (M=572.67 g/mol) leads to the formation of a mixture of two canonical amino acids **X** and **Y** in a molar ratio of 1:6, respectively.

1. Determine the total number of amino acid residues contained in **A**.

2. Determine the amino acids **X** and **Y**, limiting the selection of options as much as possible.

Peptide **B** is an isomer of compound **A**, having a similar amino acid composition. It is known that peptide **B** does not hydrolyze under the action of trypsin or chymotrypsin, and peptide **A** contains the maximum possible number of peptide bonds linking the residues of amino acid **Y** to each other.

3. Determine the amino acid sequence of peptides **A** and **B**. The formation of micelles (aggregates of surfactants) in an aqueous solution of peptide **A** was studied at different pH values. The following results were obtained:

concentration of peptide **A**, mM	the average diameter of micelles, microns		
	pH 2	pH 7	pH 11
1	4,68	2,20	-
2	4,83	3,32	-
5	5,09	3,56	0,13

The critical concentrations of micelle formation for peptide **A** at pH values of 2.7 and 11 were 0.61, 0.94 and 3.63 mM, respectively.

4. Based on structure **A**, offer a reasoned explanation for the change in micelle formation parameters depending on the pH of the solution.

5. Peptide **B** differs sharply in surface-active properties from compound **A** and is significantly less suitable as a surfactant. Why?

6. Suggest possible application points and indicate the advantages of peptide **A** micelles in targeted drug delivery in the human body.

Problem 6

(*Russian IChO-2012 Selection Camp, Problem 3*)

The polypeptide **Z**, consisting of 44 amino acid residues, was sequenced using the three-step procedure described below.

At the first stage, the polypeptide was treated with the enzyme papain, which cleaves the peptide bonds between two amino acid residues following phenylalanine. The resulting peptide fragments were not separated. The mixture of peptides was analyzed on an automatic protein sequencer, which was used to determine the number of daughter sequences and the position of amino acid residues in them (in the direction from the *N*-terminus). No more than 10 amino acid residues were analyzed in each peptide. The results of this stage are summarized in Table 1.

Table 1

Phe-X-↓-Y	**The peptide number**	**The position of amino acids in daughter oligopeptides**									
		1	2	3	4	5	6	7	8	9	10
	1	Cys	Lys	Val	Cys	Met	Lys	Pro	Ser	Phe	Gln
	2	Val	Met	Pro	Glu	Asn	Gly	Leu	Pro	Thr	Ser
	3	Pro	His	Ala	Cys	Ile	Asp	Phe	Pro		
	4	Ile	Asn	Gly	Pro	Arg	Trp	Phe	Glu		
	5	Tyr	Asp	Arg	Pro	Phe	His				

In the second stage of sequencing, peptide **Z** was treated with sodium in ammonia. In this case, the peptide bonds formed by the amino group of proline (Pro) were cleaved. The resulting mixture of peptides was analyzed in the same way as at the first stage, while proline itself is cleaved off as a free amino acid during such processing, and thus its positions in daughter peptides cannot be shown by the sequencer. The results are shown in Table 2.

Table 2

X-↓-Pro	**The peptide number**	**The position of amino acids in daughter oligopeptides**									
		1	2	3	4	5	6	7	8	9	10
	6	Thr	Ser	Phe	Lys	Ile	Asn	Gly			
	7	Ser	Phe	Gln	Tyr	Asp	Arg				
	8	His	Ala	Cys	Ile	Asp	Phe				
	9	Cys	Lys	Val	Cys	Met	Lys				
	10	Phe	His	Val	Met						
	11	Arg	Trp	Phe	Glu						
	12	Glu	Asn	Gly	Leu						

The final stage is the treatment of the initial polypeptide *N*-bromosuccinimide, which cleaves the peptide bonds formed by the carboxyl groups of tryptophan (Trp) or tyrosine (Tyr). As a result, two new polypeptides of approximately equal length were obtained.

1. Derive the complete amino acid sequence of the initial polypeptide

Problem 7

(*International Mendeleev Chemistry Olympiad, 2007, the 1st exam, Problem 5*)

A way to measure the age of geological samples is based on radioactive decay of potassium-40. This isotope is converted in parallel into calcium-40 and argon-40 with half- life periods of $T_1 = 1.47 \cdot 10^9$ and $T_2 = 1.19 \cdot 10^{10}$ years, respectively.

1. Write the equations of both nuclear reactions.

To measure the age of a rock, it is melted in vacuum and the volume of the liberated argon is measured.

2. Why is argon rather than calcium used to measure the age?

When a substance decays on parallel routes, the dependence of its weight on time is described with the equation: $m(t) = m(0) \cdot e^{-(k_1 + k_2)t}$, where k_1 and k_2 are the decay rate constants, $e \approx 2.72$ is the base of the natural logarithms. The rate constant is related to the decay half-period: $k = (\ln 2)/T$.

3. Calculate the total half-life of potassium-40 for both reactions.

4. In parallel reactions, the fraction of a substance that decays in a certain direction in direction is inversely proportional to the corresponding half-life. How many and of each 100 decayed atoms of potassium-40 turns into argon?

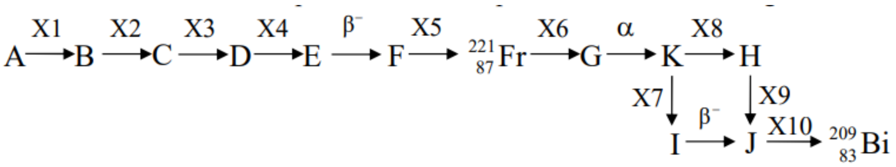
5. Assuming that the Earth's age is 5 billion years, determine the volume of argon (standard conditions) formed from potassium over the entire life of the Earth. Compare it with the volume of argon in the atmosphere, assuming that the concentration of argon in the air is 1%. Determine how much argon (%) has a radioactive origin. The current proportion of radioactive potassium-40 is 0.0119 at.% of the total amount of potassium. The weight fraction of potassium in the earth's crust is 1.5%, and the total mass of the earth's crust is $5 \cdot 10^{22}$ kg. The total volume of the Earth's atmosphere is 40 billion km^3.

6. In 1959, human remains were found in the Olduvai Gorge (Tanzania). It is believed that they belong to our oldest ancestor. A sample of the rock in which the remains were found, was melted. From 1000 g of rock containing 3.24% potassium by weight, $5.9 \cdot 10^{15}$ argon atoms were released. Determine the age of the remains.

Problem 8

(*International Mendeleev Chemistry Olympiad, 2013, the 1st exam, Problem 5*)

There are three natural radioactive series and an artificial one. After α- and β-radioactive transformations the series end up with stable isotopes. One of the series is given below:



In this series X4 = X1 (X – type of decay). Radioactive decay proceeds as a first-order reaction: $dN / dt = -\lambda N$, where λ is the decay constant, N is the number of radioactive nuclei at time t.

1. Determine the half-life time $T_{1/2}$ for **C**, if only one of $7.24 \cdot 10^{12}$ atoms of C undergoes the decay each second (on average). Determine **C** – **F**, if: a) in 500 years, $9.333 \cdot 10^{-6}$ moles of helium is released from 1 g of **C** as a result of α-decay; b) the molar mass of **C** is by factor 2.533 higher than the nuclear charge.

Only seven minerals of **I** are found in nature. Two of them are lorandite **I**AsS_x and vrbaite **I**$_4Hg_3Sb_xAs_8S_{20}$. The abundance of **I** in them is 60 and 28.6% (mass), respectively.

2. Determine the elements **I** and **J**, if the molar mass of **I** is by factor 2.580 higher than the nuclear charge.

3. A radioactive sample (3 g) consists of isotopes **A1** (35% mass, $T_{1/2}$ = 2.1 days) and **A2** (65% mass, $T_{1/2}$ = 4.4 days). The mass number of **A1** is by 1 a.m.u. higher than that of **A**, and the mass number of **A2** by 3 a.m.u. lower than that of **A**. Determine **A**, if 12 hours after preparation of the sample its activity was $4.61 \cdot 10^5$ Curie (1 Curie means $3.7 \cdot 10^{10}$ decays/s). Activity of the sample consisting of several isotopes is an additive quantity. The molar mass of **A** is by factor 2.548 higher than the nuclear charge.

4. Determine nuclides **B**, **G**, **H**, and **K**.

5. Write one equation of the nuclear reaction for each of alpha- and beta-decays in the most detailed form.

6. Calculate the binding energy (in MeV) per 1 nucleon for bismuth-209.

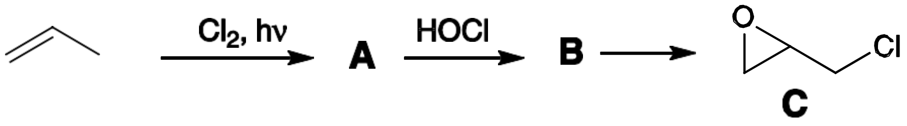
Precise mass of the particles (a.m.u.): atom – 208.980, proton – 1.0072747, neutron – 1.0086658, electron – $5.4857937 \cdot 10^{-4}$; 1 eV = $1.602 \cdot 10^{-19}$ J, the speed of light in vacuum $c = 2.99792458 \cdot 10^8$ m/s, 1 a.m.u. = $1.66054 \cdot 10^{-27}$ kg.

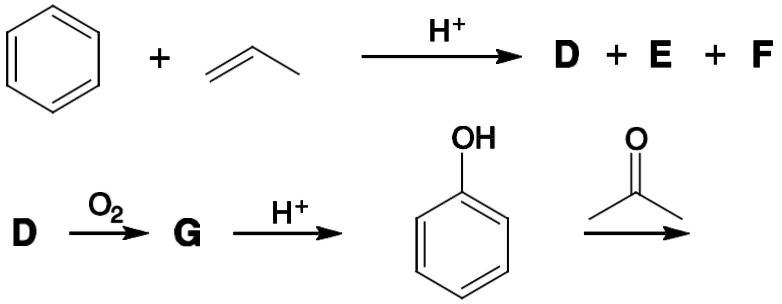
Problem 9

(*International Chemistry Olympiad, 2009, Problem 5*)

Epoxy resins

The synthesis of epoxy resins is a multi-billion dollar industry worldwide. Epoxy resins are high performance adhesives synthesized from the reaction of a bis-epoxide with a diamine. The bis-epoxide is made from **H** and epichlorohydrin, **C**. Compounds **C** and **H** can be synthesized according to the scheme below.





The synthesis of epichlorohydrin **C** begins with the reaction of propene with chlorine in the presence of light.

1. Draw the structures of **A** and **B**.

2. Give the formula f a suitable reagent for the conversion of **B** into epichlorohydrin **C.**

3. Draw the structures of **D**, **E**, and **F** from the following data:

D: Elemental composition: C 89.94%, H 10.06 %; 6 signals in the ^{13}C NMR spectrum.

E: Elemental composition: C 88.82%, H 11.18 %; 4 signals in the ^{13}C NMR spectrum.

F: Elemental composition: C 88.82%, H 11.18 %; 5 signals in the ^{13}C NMR spectrum.

Bubbling oxygen through a hot solution of **D** gives **G** which on exposure to acid gives phenol (hydroxylbenzene) and acetone (propanone). **G** turns starch iodide paper from white to dark blue. **G** has 6 signals in the ^{13}C NMR spectrum: δ 7.78 (1H, s), 7.45 – 7.22 (5H, m), 1.56 (6H, s); addition of D_2O results in the disappearance of the signal at $\delta = 7.78$.

4. Draw the structure of **G**.

Exposure of phenol and acetone to hydrochloric acid gives compound **H**. The ^{13}C NMR spectrum for **H** is shown in Fig. 1. The ^{1}H NMR spectrum is shown in Fig. 2 together with a four-fold expansion of the region 6.5 – 7.1 ppm. The ^{1}H NMR spectrum after the addition of a drop of D_2O, is shown in Fig. 3. Peaks due to the solvent are marked with an asterisl (*).

Fig. 1

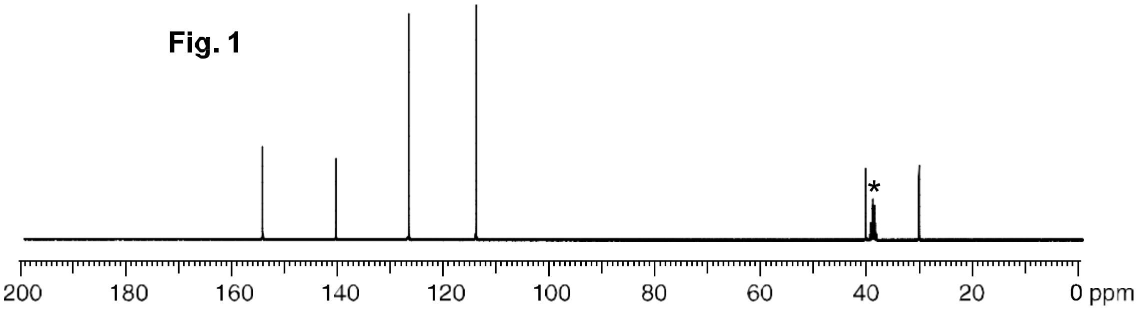


Fig. 2

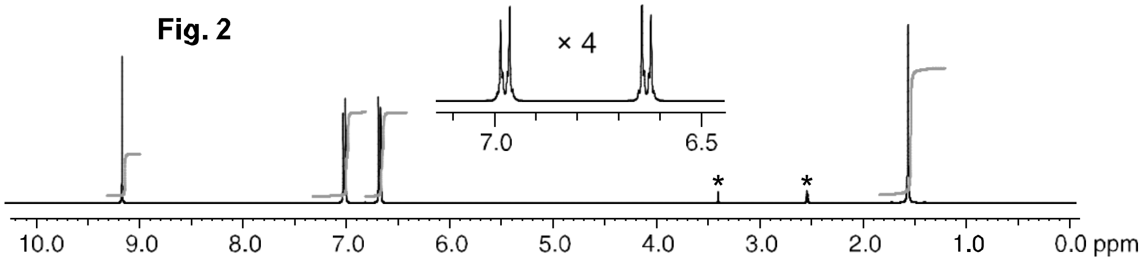
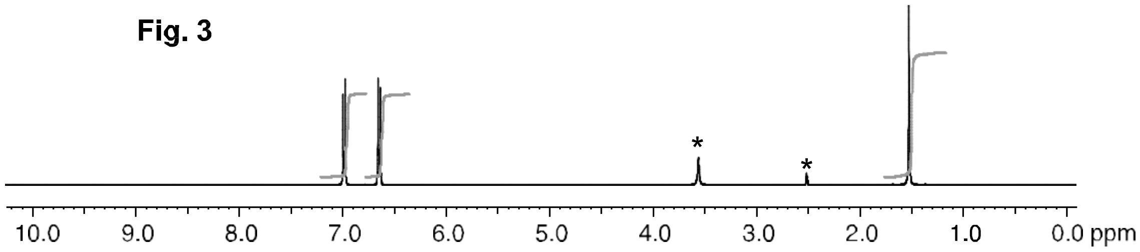


Fig. 3



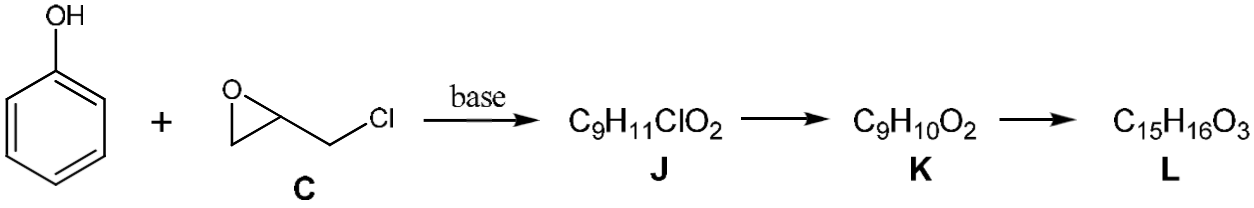
5. Draw the structure of **H**.

6. Draw one resonance structure of phenol which explains the regioselective formation of **H**.

A second compound, **I**, is also formed in the reaction of phenol with acetone. The ^{13}C NMR spectrum of **I** has 12 signals. The ^{1}H NMR spectrum has the following signals: δ 7.50 – 6.51 (8H, m), 5.19 (1H, s), 4.45 (1H, s), 1.67 (1H, s); addition of D_2O results in the disappearance of the signals at δ = 5.19 and 4.45.

7. Draw a structure for **I**.

Excess phenol reacts with epichlorohydrin **C** in the presence of base to give compound **L** which has 6 signals in the ^{13}C NMR spectrum. If the reaction is stopped before completion, compounds **J** fnd **K** can be also isolated. Compound **L** is formed from compound **K** and compound **K** is formed from compound **J**.



8. Draw the structures of **J**, **K**, and **L**.

Treatment of **H** with a large excess of epichlorohydrin **C** and base gives a monomeric bis-epoxide **M**. **M** contains no chlorine atoms or OH groups.

9. Draw the structure of **M**.

Treatment of **H** with a small excess of epichlorohydrin **C** and base gives **N**. **N** has the form: endgroup 1-[repeat unit]$_n$-endgroup 2 here *n* is approximately 10-15. **N** does not contain chlorine atoms and contain one OH group per repeat unit.

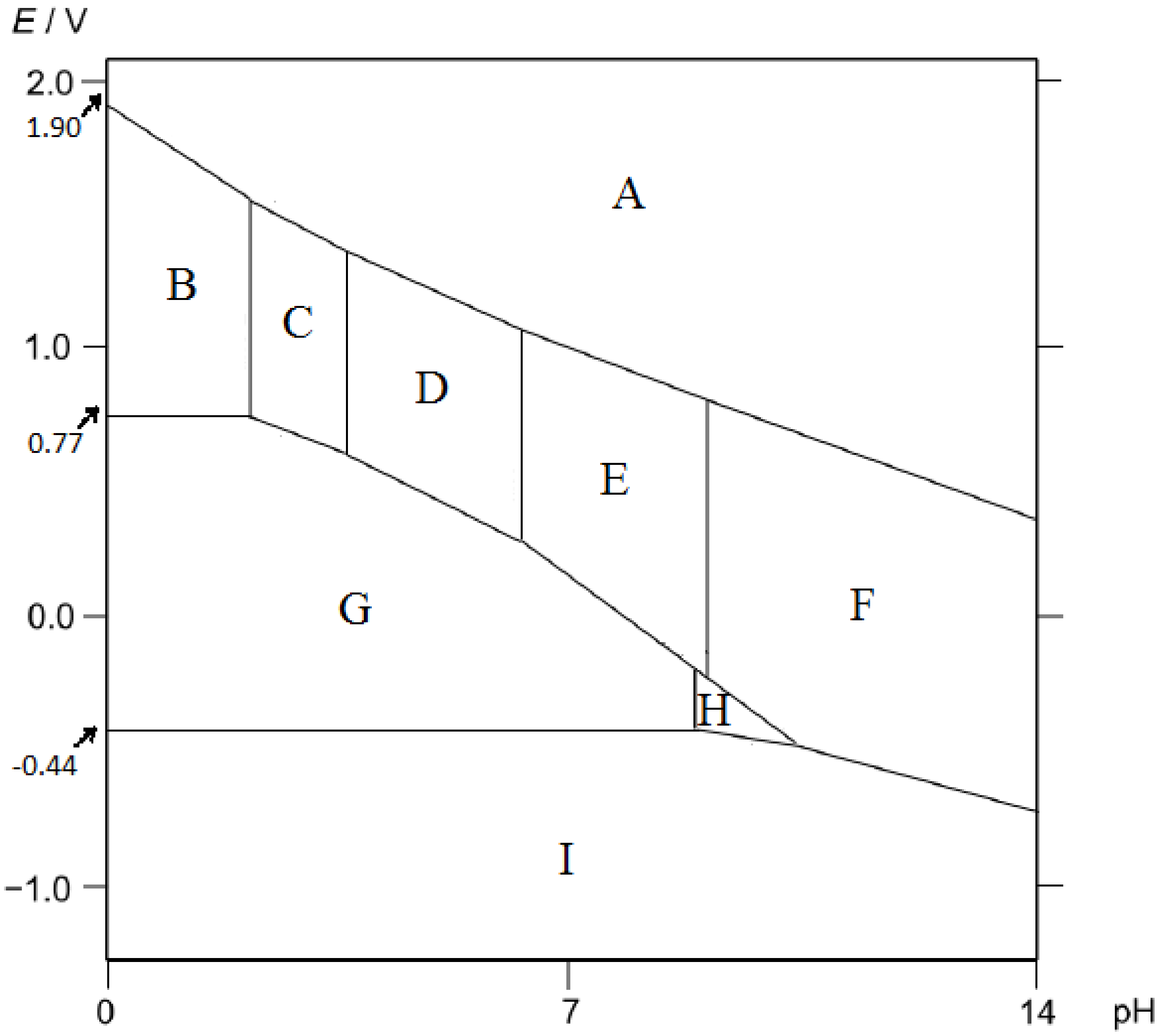
10. Draw the structure of **N** in the for indicated above: (endgroup 1-[repeat unit]$_n$-endgroup 2).

11. Draw the repeat unit of the polymeric epoxy resin **O** formed from the reaction of the bis-epoxide M with ethane-1,2-diamine.

Problem 10

(*Uzbekistan IChO-2022 Selection Camp*)

Below is a Pourbaix diagram (the dependence of the equilibrium value of *E* on the pH of the solution) for iron at standard conditions and 298 K. Note that each line in the diagram separates the stability zones of two different particles and along the line the concentrations of these particles are equal.



From the Pourbaix diagram, one can create the Latimer diagram for iron at pH = 14:

$$FeO_4^{2-} \xrightarrow[+0.374\ V]{+3e} [Fe(H_2O)_2(OH)_4]^- \xrightarrow[-0.726\ V]{+3e} Fe$$

1. Identify the unknown particles **A, B, C, D, E, F, G, H, I**.

2. Using the Latimer diagram for iron at pH = 14, calculate the standard electrode potential for the reduction of FeO_4^{2-} to Fe.

3. Using the data from the Pourbaix diagram, create a similar Latimer diagram for iron at pH = 0 as shown in the problem statement at pH = 14.

4. Why is the line separating particles **B** and **C** vertical? Choose correct answer.

A) because there is no exchange of protons during the B → C transformation.

B) because there is no exchange of electrons during the B → C transformation.

C) because in the process of transformation B → C an exchange of the same number of protons and electrons occurs.

D) because in the process of transformation B → C an exchange of unequal numbers of protons and electrons occurs.

5. Select the strongest acid from the following:

A) $[Fe(H_2O)_6]^{2+}$

B) $HFeO_4^-$

C) $[Fe(H_2O)_3(OH)_3]$

D) H_2FeO_4

6. The line separating particles **A** and **B** can be written as a function: $E = a + b \cdot pH$. Determine the values of a and b.

7. Calculate similar values of a and b for the line separating particles **A** and **F**. $K_w = 1 \cdot 10^{-14}$.

8. When water is oxidized, oxygen is released, and when water is reduced, hydrogen is released. Draw a similar Pourbaix diagram for water under standard conditions and 298 K in the pH range 0-14 if it is known that $E^0(O_2, 4H^+/2H_2O) = 1.23\ V, E^0(2H^+/H_2) = 0\ V$.

9. Which iron particles are stable under standard conditions and 298 K in water in a neutral solution?

Problem 11

(*International Mendeleev Chemistry Olympiad, 2013, the 2nd exam, Physical Chemistry, Problem 3*)

Latimer diagrams contain compact information about standard redox potentials for different forms of the element. The Latimer diagram for sulfur compounds at pH = 0 and 298K is given below.

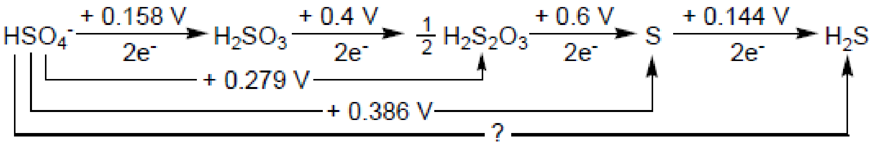
$$HSO_4^- \xrightarrow[2e^-]{+\,0.158\ V} H_2SO_3 \xrightarrow[2e^-]{+\,0.4\ V} \tfrac{1}{2}\,H_2S_2O_3 \xrightarrow[2e^-]{+\,0.6\ V} S \xrightarrow[2e^-]{+\,0.144\ V} H_2S$$

The diagram gives the standard potentials, e.g.

$$E^0_{HSO_4^-/H_2SO_3} = \quad +0.158\ \mathrm{V},$$

$$E^0_{H_2SO_3/\frac{1}{2}H_2S_2O_3} = \ = +0.4\ \mathrm{V},\ \text{etc.}$$

The potential for any couple can be calculated from the diagram.



1. Write down the equations of the half-reactions for HSO_4^- reduction to H_2SO_3, $H_2S_2O_3$, S, and H_2S in acidic medium.

2. Calculate $E^0_{HSO_4^-/H_2S}$ from the potentials $E^0_{HSO_4^-/S}$ and E^0_{S/H_2S}.

3. Can Cu $(E^0_{Cu^{2+}/Cu} = 0.337\ \mathrm{V})$ be dissolved in the H_2SO_4 solution at pH = 0 and 298K? What product of the H_2SO_4 reduction is formed predominantly?

4. Thiosulfuric acid ($H_2S_2O_3$) is unstable in acidic medium. To prove this, calculate the Gibbs energy for the disproportionation of $H_2S_2O_3$ yielding S and H_2SO_3.

Thiosulfates are much more stable in alkaline medium. pH influences the standard potentials significantly. The Latimer diagram at pH = 14 is:

$$SO_4^{2-} \xrightarrow[2e^-]{-\,0.936\ V} SO_3^{2-} \xrightarrow[2e^-]{-\,0.576\ V} \tfrac{1}{2}\,S_2O_3^{2-} \xrightarrow[2e^-]{?} S \xrightarrow[2e^-]{-\,0.476\ V} HS^-$$

5. Calculate the potential $E^0_{\frac{1}{2}S_2O_3^{2-}/S}$ at pH 14. $H_2S_2O_3$: $K_{a1} = 0.251$, $K_{a2} = 0.0191$.

In chemistry class of the Lyceum in Tashkent in April 2008, there was found a solution in tightly closed flask marked as “1 mM $Na_2S_2O_3$, 1 mM NaOH, 05.09.2007”. At pH = 11:

$$SO_3^{2-} \xrightarrow[2e^-]{-\,0.397\ V} \tfrac{1}{2}\,S_2O_3^{2-} \xrightarrow[2e^-]{-\,0.414\ V} S$$

6. Estimate the concentration of $S_2O_3^{2-}$ in this solution after complete disproportionation.

Problem 12

(*International Chemistry Olympiad, 1997, Problem 5*)

Iron metal melts at 1811 K. Between room temperature and its melting point, iron metal can exist in different allotropic or crystalline forms. From room temperature to 1185 K, the crystal structure of iron metal exists as a body-centred cubic (bcc) lattice known as α-iron. From 1185 K to 1667 K, the structure becomes face-centred cubic (fcc) and is called γ-iron. Above 1667 K, and up to its melting point, iron reverts to a bcc structure similar to that of α-iron. The latter phase is called δ-iron.

Given that the density of pure iron metal is 7.874 g cm^{-3} at 293 K:

1. Calculate the atomic radius of iron (expressed in cm).

2. Calculate its density (expressed in g cm^{-3}) at 1250 K.

Notes: Ignore the small effects due to the thermal expansion of the metal.

Clearly define any symbols which you use, e.g. r = atomic radius of Fe.

Steel is an alloy of iron and carbon in which some of the interstitial spaces ("holes") of the crystal lattice (iron) are occupied by small atoms (carbon). Its carbon content typically ranges from 0.1 % to 4.0 %. In a blast-furnace, the melting of iron is facilitated when it contains 4.3 % of carbon by mass. If this mixture is cooled too rapidly the carbon atoms remain dispersed within the α-iron phase. This new solid, called martensite, is extremely hard and brittle. Although is it slightly distorted, the size of the unit cell of this solid (martensite) is the same as that of α-iron (bcc).

Assuming that the carbon atoms are evenly distributed in the iron structure:

3. Calculate the average number of carbon atoms per unit cell of α-iron in martensite containing 4.3 % C by mass.

4. Calculate the density (expressed in g cm^{-3}) of this material.

Molar masses and constants:
$M(\mathrm{Fe}) = 55.847$ g mol^{-1}
$M(\mathrm{C}) = 12.011$ g mol^{-1}
$N_A = 6.02214\times10^{23}$ mol^{-1}.

Problem 13

(*International Chemistry Olympiad, 2000, Problem 2*)

Bridge between Denmark and Sweden

On July 1, 2000, the combined tunnel and bridge connecting Denmark and Sweden was officially opened. It consists of a tunnel from Copenhagen to an artificial island, and a bridge from the island to Malmö in Sweden. The major construction materials employed are concrete and steel. This problem deals with chemical reactions relating to production and degradation of such materials.

Concrete is produced from a mixture of cement, water, sand and small stones. Cement consists primarily of calcium silicates and calcium aluminates formed by heating and grinding of clay and limestone. In the later steps of cement production a small amount of gypsum, $CaSO_4 \cdot 2\ H_2O$, is added to improve subsequent hardening of the concrete. The use of elevated temperatures during the final production may lead to formation of unwanted hemihydrate, $CaSO_4 \cdot \frac{1}{2}\ H_2O$. Consider the following reaction:

$$CaSO_4 \cdot 2\ H_2O(s) \rightarrow CaSO_4 \cdot \tfrac{1}{2}\ H_2O(s) + 1\tfrac{1}{2}\ H_2O(g)$$

The following thermodynamic data apply at 25 °C, standard pressure: 1.00 bar:

Compound	$\Delta_f H°$(kJ mol^{-1})	$S°$(J K^{-1} mol^{-1})
$CaSO_4 \cdot 2\ H_2O(s)$	–2021.0	194.0
$CaSO_4 \cdot \frac{1}{2}\ H_2O(s)$	–1575.0	130.5
$H_2O(g)$	–241.8	188.6

Gas constant: $R = 8.314$ J mol^{-1} K^{-1} = 0.08314 L bar mol^{-1} K^{-1}

0 °C = 273.15 K.

1. Calculate ΔH (in kJ) for transformation of 1.00 kg of $CaSO_4 \cdot 2\ H_2O(s)$ to hemihydrate $CaSO_4 . \frac{1}{2}\ H_2O(s)$. Is this reaction endothermic or is it exothermic?

2. Calculate the equilibrium pressure (in bar) of water vapour in a closed vessel containing $CaSO_4 \cdot 2\ H_2O(s)$, $CaSO_4 \cdot \frac{1}{2}\ H_2O(s)$ and $H_2O(g)$ at 25 °C.

3. Calculate the temperature at which the equilibrium water vapour pressure is 1.00 bar in the system described in problem 2-2. Assume that ΔH and ΔS are temperature independent.

Corrosion of metals is associated with electrochemical reactions. This also applies for the formation of rust on iron surfaces, where the initial electrode reactions usually are:

$Fe(s) \rightarrow Fe^{2+}(aq) + 2\ e^-$ (1)

$O_2(g) + 2\ H_2O(l) + 4\ e^- \rightarrow 4\ OH^-(aq)$ (2)

An electrochemical cell in which these electrode reactions take place is constructed. The temperature is 25 ºC. The cell is represented by the following cell diagram:

$Fe(s)\ |Fe^{2+}(aq)\ ||\ OH^-(aq), O_2(g)\ |\ Pt(s)$

Standard electrode potentials (at 25 ºC):

$Fe^{2+}(aq) + 2\ e^- \rightarrow Fe(s)$ $E^o = -0.44$ V

$O_2(g) + 2\ H_2O(l) + 4\ e^- \rightarrow 4\ OH^-(aq)$ $E^o = 0.40$ V

Nernst factor: $RT \ln 10 / F = 0.05916$ volt (at 25 ºC)

Faraday constant: $F = 96485$ C mol^{-1}

4. Calculate the standard electromotive force (the standard cell voltage), E^o, at 25 ºC.

5. Write down the overall reaction which takes place during discharge of the cell under standard conditions.

6. Calculate the equilibrium constant at 25 °C for the overall cell reaction.

7. The overall reaction referred to above is allowed to proceed for 24 hours under standard conditions and at a constant current of 0.12 A. Calculate the mass of Fe converted to Fe^{2+} after 24 hours. Oxygen and water may be assumed to be present in excess.

8. Calculate E for the cell at 25 °C for the following conditions :

$[Fe^{2+}] = 0.015$ M, $pH_{\text{right-hand half-cell}} = 9.00$, $p(O_2) = 0.700$ bar.

Problem 14

(*International Chemistry Olympiad, 2021, Preparatory problem 4*)

Synthesis of diamonds

Diamond, one of the allotropes of carbon, is used not only for jewelry, but also in various tools that take advantage of its extremely high hardness. Natural diamond is considered to be produced under high-pressure and high-temperature conditions in the bowels of the earth. Currently, several techniques to synthetically generate diamonds are available, and massive amounts of artificial diamonds are used industrially.

Let us examine the stability of diamonds at ambient pressure and temperature. The enthalpies of combustion (ΔH°) for 1 mole of graphite, diamond, and C_{60}, as well as the standard entropy changes (ΔS°) for the conversion of 1 mole of graphite to diamond or C_{60} under ambient conditions (1 bar, 298.15 K) are summarized in Table 1. For graphite and diamond, 1 mole represents 12.01 g.

Table 1. Thermodynamic data for carbon allotropes

	$\Delta_c H^\circ$ / kJ mol^{-1}	ΔS°/ J K^{-1} mol^{-1}
Graphite	−393.5	(0)
Diamond	−395.3	−3.25
C_{60}	−25965	1.54

1. Calculate the change in enthalpy, entropy, and Gibbs free energy for the transformation of 1 mole of graphite into diamond and into C_{60} under ambient conditions. Then, rank graphite, diamond, and C_{60} in order of decreasing stability in terms of Gibbs free energy.

2. Under ambient conditions, diamond does not transform into graphite, which is energetically more stable than diamond. Explain why this transformation does not occur.

The enthalpies of combustion for graphite and diamond are comparable, and therefore, it is difficult to determine the change in enthalpy from graphite to diamond precisely via the calculation method used in Q1. To overcome this difficulty, the temperature dependence of the electromotive force of the following battery was measured:

$$\text{Pt, C(graphite)} + CaC_2 + CaF_2 \parallel CaF_2 \parallel CaF_2 + CaC_2 + \text{C(diamond), Pt} \qquad (1)$$

This is a solid-state battery in which diamond is used as the cathode (positive electrode) and graphite is used as the anode (negative electrode). On the cathode, the diamond is reduced and CaC_2 is produced. On the anode, CaC_2 is oxidized and graphite is produced.

3. Write the half-reactions occurring on the cathode and the anode.

4. The electromotive force of this battery over the temperature range 940–1260 K can be expressed as a function of the absolute temperature T according to:

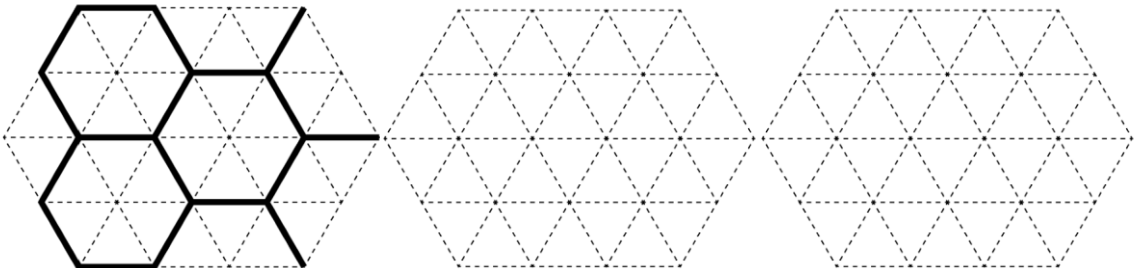
$$E = 11.4 + 0.0481T \ \text{[mV]} \tag{2}$$

Calculate the change in enthalpy and entropy for the conversion of 1 mole of graphite to diamond in this temperature range.

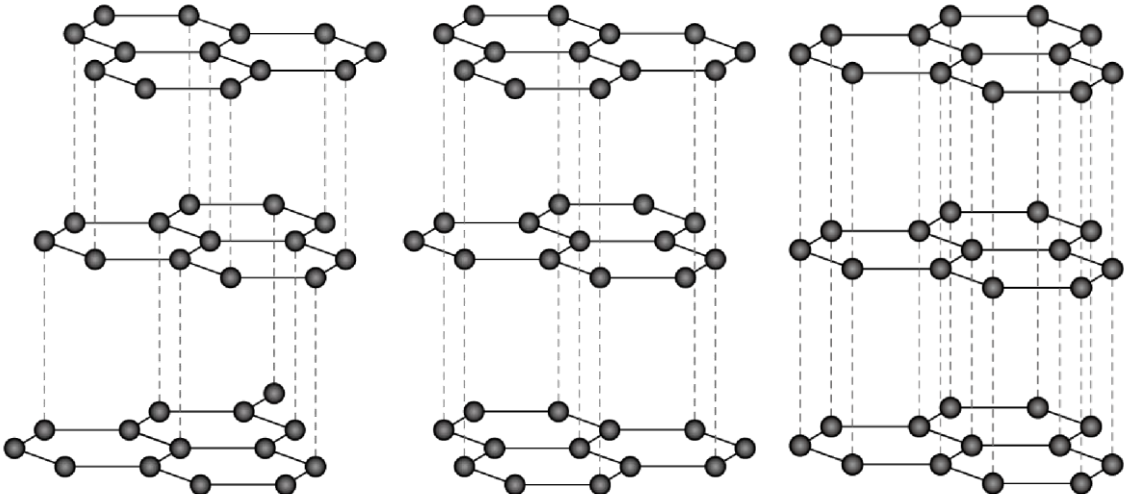
One of the techniques to synthesize diamond is the direct conversion of graphite into diamond by applying high pressure to graphite. The mechanism underlying this conversion is known as the puckering mechanism.

Graphite is composed of stacked layers of graphene. For each layer, there are three possible relative positionings in which the graphene layer can be placed. From here on, these geometries are referred to as A, B, and C. The crystal structures of graphite can exhibit one of three stacking patterns: AAAAAA… (1H where H stands for hexagonal), ABABAB… (2H), and ABCABC… (3R where R stands for rhombohedral). The most stable structure is 2H, and typical graphite also contains a small amount of the 3R structure.

5. One of the geometries of graphene is shown below (left, set as A). Draw the other two geometries (B and C, you do not have to distinguish these two).

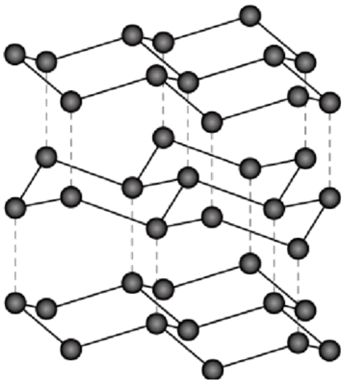


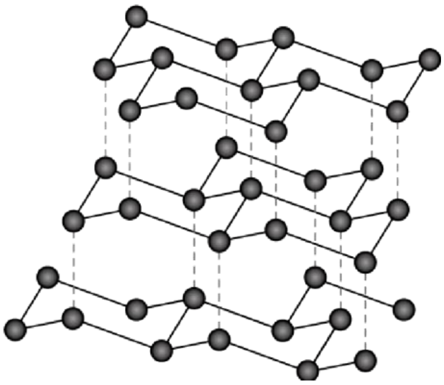
6. Assign the following three crystal structures as the 1H, 2H, and 3R structures.



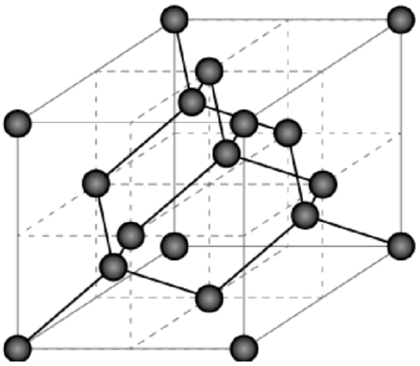
Diamond (cubic crystal) is generated from the 3R structure by displacing each carbon atom in a direction perpendicular to the plane. A crystal structure similar to that of diamond is obtained by displacing each carbon atom of the 1H structure in a direction perpendicular to the plane. The crystal structure generated from the 1H structure is called lonsdaleite, and is a hexagonal crystal. It has been theoretically predicted that pure lonsdaleite would be harder than diamond.

7. Assign the following crystal structures as diamond and lonsdaleite.





8. Under ambient conditions, the distance between covalently bonded carbon atoms in graphite is 1.42 Å, while the distance between the graphene layers of graphite is 3.35 Å; the distance between covalently bonded carbon atoms in diamond is 1.54 Å. Calculate the density of graphite and diamond under ambient conditions. The unit cell of diamond is shown below:



In the puckering mechanism, there are two energy barriers: The barrier for the transformation from the 2H structure to the 3R structure (Step 1), and the barrier for the transformation of the carbon atoms from a planar to a tetrahedral configuration via puckering (Step 2).

9. The activation energy in Step 2 will be small if there is no volume change between graphite and diamond. Calculate the distance between the graphene layers of graphite for which there would be no volume change. Assume that the distances between the covalently bonded carbon atoms in graphite and diamond do not change on account of the applied pressure.

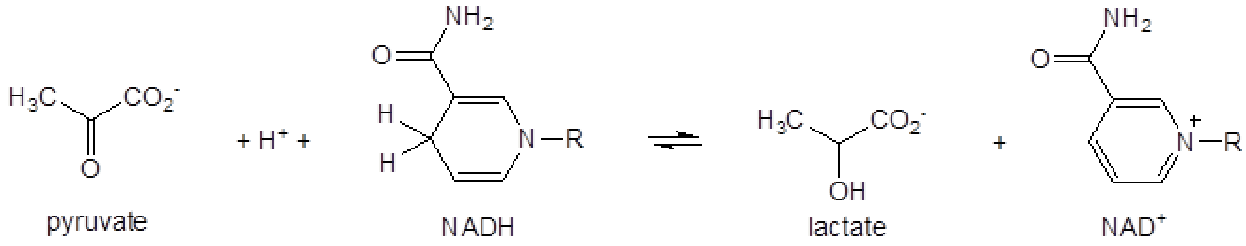
[Note] The direct conversion method described above requires high temperature (3000–4000 K) to increase the reaction rate in addition to high pressure (~ 10 GPa). A new conversion method, in which the graphite is first melted with metals to break the covalent bonds among the carbon atoms before new covalent bonds are generated under high-pressure conditions where diamond is thermodynamically stable, has been developed.

Problem 15. Mechanism of Catalysis by Lactate Dehydrogenase

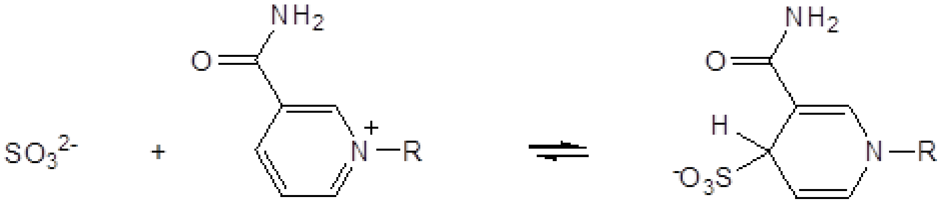
(*International Chemistry Olympiad, 2012, Preparatory problem 20*)

The structures of the 20 amino acids found in proteins are shown in the Figure at the end of this problem.

The enzyme lactate dehydrogenase (LDH) catalyzes the reversible reduction of pyruvate anion to lactate anion, with NADH as the reducing agent. The reaction is formally the transfer of hydride ion (H^-) from NADH to pyruvate:

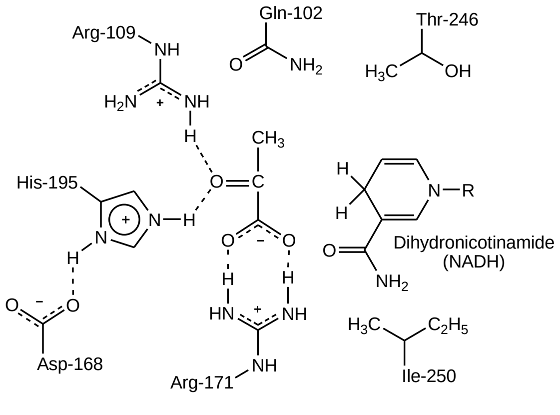


The enzyme also catalyzes a reaction of sulfite (SO_3^{2-}) and NAD^+:



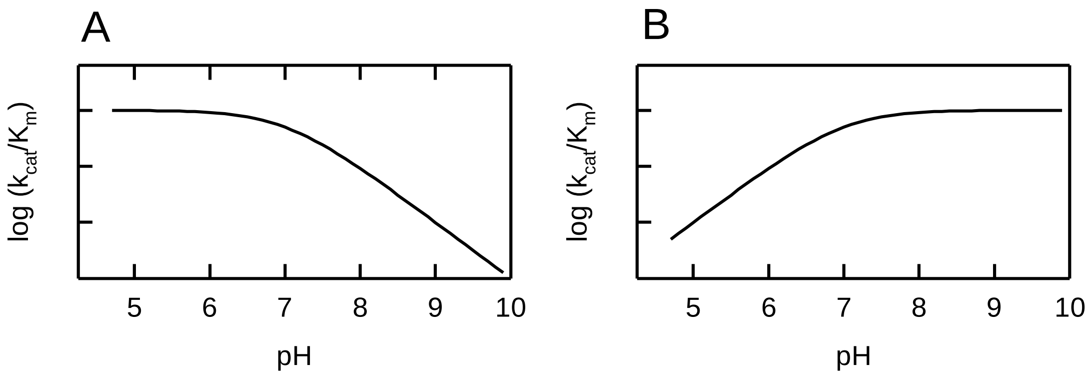
The structure of the substrates pyruvate and NADH bound in the active site of LDH is shown schematically in Scheme 1. Several key amino acid residues in the active site are indicated. The dotted lines between fragments of LDH indicate weak intermolecular interactions among groups in the active site.

Scheme 1



The *pH* dependence of the rate of the reactions catalyzed by LDH was determined with pyruvate and NADH as the substrates for the forward reaction, and with lactate and NAD^+ as the substrates for the reverse reaction. The data indicate the participation in catalysis of a group with $pK_a = 7$, which corresponds to His-195 of LDH.

The *pH* vs. reaction rate $[\log(k_{cat}/K_m)]$ curves were different depending on whether the rate of the forward (pyruvate + NADH) or reverse (lactate + NAD^+) reaction was measured, as shown in Figure below.



a) Which curve in the Figure above corresponds to the reaction with pyruvate and NADH? Which curve corresponds to the reaction with lactate and NAD^+?

As shown in Scheme 1, the side chains of Arg-109 and His-195 are very close to the carbonyl group of pyruvate.

b) What type of weak intermolecular interactions exists between Arg-109 and the carbonyl group of pyruvate, and between His-195 and the carbonyl group of pyruvate? What is the electronic basis of this interaction?

The side chain of Ile-250 lies directly below the plane of the dihydronicotinamide ring of NADH (Scheme 1).

c) What type of intermolecular interaction would the side chain of Ile-250 make with NADH?

The function of Arg-109 in catalysis by LDH was investigated by site-directed mutagenesis. Arg-109 was changed to glutamine, and the catalytic activity of the mutant enzyme was studied. The results were:

- The rate of the (pyruvate + NADH) reaction catalyzed by the mutant enzyme was 1400-fold less than the reaction catalyzed by the wild-type enzyme.
- The ability of the mutant enzyme to bind pyruvate in the active site was also reduced, but by only about 15-fold compared to the wild-type enzyme.
- The rate of the reaction of sulfite with NAD^+ was unaffected by the mutation.

d) Given the observations above, what is the function of Arg-109 in catalysis by LDH?

The side chain of Asp-168 is thought to interact non-covalently with the side chain of His-195 (see Scheme 1). Two hypotheses were proposed for the function of Asp-168 in catalysis by LDH:

1) The interaction between Asp-168 and His-195 might serve to hold the His-195 in the correct position to interact with pyruvate.

2) The interaction between Asp-168 and His-195 might serve to polarize His-195, which would make His-195 a stronger base.

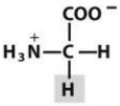
To test these possibilities Asp-168 was changed to Ala (Mutant 2), and to Asn (Mutant 1), and the catalytic properties of the mutant enzymes were compared to those of the wild-type enzyme.

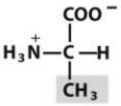
The results are summarized in the following table:

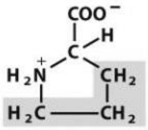
Constant	**Wild-type** (Asp-168)	**Mutant 1** (Asn-168)	**Ratio: Wild-type / Mutant 1**	**Mutant 2** (Ala-168)	**Ratio: Wild-type / Mutant 2**
Forward reaction:					
K_m (pyruvate), mM	0.06	10	0.006	3.3	0.018
k_{cat}, s^{-1}	250	20	12.5	5.5	45
k_{cat}/K_m, $M^{-1}\cdot s^{-1}$	$4.2\cdot10^6$	$2\cdot10^3$	2080	$1.7\cdot10^3$	2500
Reverse reaction:					
K_m (lactate), mM	40	120	0.33	80	0.5
k_{cat}, s^{-1}	9	0.12	75	0.09	100
k_{cat}/K_m, $M^{-1}\cdot s^{-1}$	$2.2\cdot10^2$	1	225	1.13	200

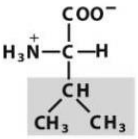
e) Given the facts above, which of the proposed functions, (1) or (2), of Asp-168 is better supported by the data?

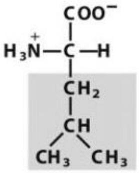
The 20 amino acids found in proteins (side chains are shaded in gray).

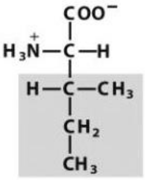

Glycine
Gly

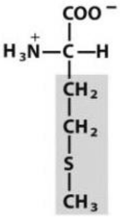

Alanine
Ala

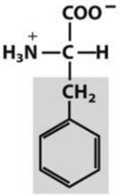

Proline
Pro

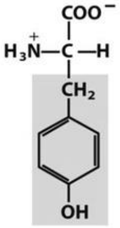

Valine
Val

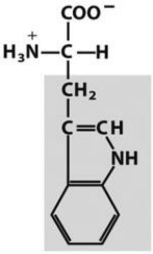

Leucine
Leu

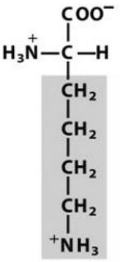

Isoleucine
Ile

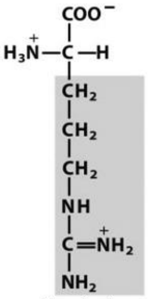

Methionine
Met

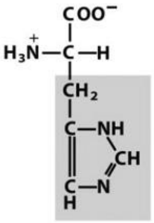

Phenylalanine
Phe

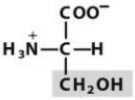

Tyrosine
Tyr

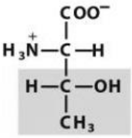

Tryptophan
Trp

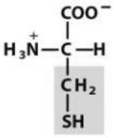

Lysine
Lys

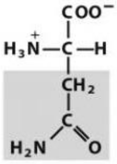

Arginine
Arg

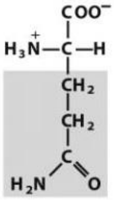

Histidine
His

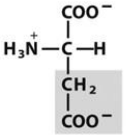

Serine
Ser

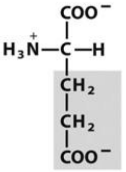

Threonine
Thr


Cysteine
Cys


Asparagine
Asn


Glutamine
Gln


Aspartate
Asp


Glutamate
Glu

Problem 16

(*International Chemistry Olympiad, 2015, Preparatory problem 1*)

Brayton cycle

Students have made a device capable to operate in a mode that is close to the ideal Brayton cycle. This thermodynamic cycle has once been proposed for development of internal combustion engines. The device consists of a cylinder with 1 mole of helium fitted with a computer-controlled movable piston. A Peltier element which can heat or cool the gas is mounted in the cylinder wall. The device can operate in the following modes: reversible adiabatic expansion or compression either reversible isobaric cooling or heating.

Through a number of cooling and compression steps, helium is going from the initial state with the pressure of 1 bar and the temperature of 298 K into the final state with the pressure of 8 bar and the temperature of 298 K. (The total number of cooling and compression stages can be from two up to infinity).

1. What is the minimum work that should be done on the gas for this? Compare this value to the work during a reversible isothermal compression.

2. What is the maximum work that can be done on the gas in this process?

3. Let the process be accomplished in three steps. At each step helium is first cooled and then compressed. At the end of each step the pressure increases twice and the temperature returns to the value of 298 K. What is the total heat removed from the gas by a Peltier element?

Once the gas is compressed, it is returned to the initial state (1 bar and 298 K) in two stages (heating and expansion).

4. What is the range of possible values of the formal efficiency η for the resulting cycle? η is the ratio of the useful work done by the gas to the amount of heat given to the gas during the heating stage.

5. In one of the experiments, the gas has been compressed from 1 bar and 298 K to 8 bar and 298 K in several steps (like in question 3). At the end of each step the pressure is increased by x times and the temperature returns to 298 K. Then helium has been returned to the initial state in two stages – heating and expansion. Theoretical value of η for this cycle is 0.379. How many steps were used?

In fact, Peltier elements also consume electric energy during the cooling stage. Assume that they consume as much energy as is removed from the gas.

6. What is the maximum possible efficiency of the considered cycle, taking into account energy consumption during cooling?

Hint: in reversible adiabatic process for helium $pV^{5/3} = const$. Isochoric molar heat capacity of helium is 3/2*R*.

Problem 17

(*International Chemistry Olympiad, 2020, Preparatory problem 20*)

Journey to Different Earth-Like Planets

In the future, humankind will most likely consume all resources that are necessary for life on earth and will have to relocate to an earth-like planet. Assume that you have started to live on a new planet where standard pressure condition is 2 bar, standard concentration is 1 mol dm^{-3}, and all types of gases behave as an ideal gas. On this planet, you are asked to determine equilibrium conditions for the reaction below:

$$XY_4(g) \rightleftharpoons X(s) + 2Y_2(g)$$

$$\Delta_r S° = 80\,JK^{-1}mol^{-1} \text{ at } 298\,K$$

1. Calculate the change in standard enthalpy of the reaction at 298 K by using the following information:

$$X_4Y_8(s) \rightarrow 4X(s) + 4Y_2(g) \qquad \Delta_r H_1^° = 123.34\,kJ\,mol^{-1}$$

$$Y_2(g) + X_4Y_6(l) \rightarrow X_4Y_8(s) \qquad \Delta_r H_2^° = -48.48\,kJ\,mol^{-1}$$

$$X_4Y_6(l) \rightarrow 2X_2Y_3(g) \qquad \Delta_r H_3^° = 32.84\,kJ\,mol^{-1}$$

$$X_2Y_3(g) + {}^1\!/_2\,Y_2(g) \rightarrow X(s) + XY_4(g) \qquad \Delta_r H_4^° = -53.84\,kJ\,mol^{-1}$$

2. Calculate $\Delta_r G°$ of the reaction at 298 K.

3. Calculate K° of the reaction at 298 K.

4. Assume that $\Delta_r H°$ of the reaction does not depend on temperature. Find K of the reaction at 50 °C.

5. Calculate the percent degree of dissociation for XY_4 at 298 K where total pressure is 0.2 bar.

6. In order to increase the amounts of products, which one do you choose to increase (if you choose both, put a cross next to both of them):

☐ pressure

☐ temperature of the reaction vessel

Moreover, in this future, the Earth will have a very unstable climate. The surface temperature could increase or decrease all of a sudden. Suppose that you travelled through time to the era in which the Earth's climate is extremely unstable. Your task in this era is to observe the thermodynamics of phase transitions of water, the most precious substance where all life has originated. Suppose that the temperature suddenly decreased to −20 °C.

One mole of water becomes supercooled liquid water at −20 °C and 1 bar pressure and then turns into ice at the same temperature (note that the temperature of the surroundings is constant at −20 °C).

By using the following data for water:

The heat of fusion ($\Delta_m H°$) of ice at 0 °C and 1 bar is 6020 J mol^{-1}

$C_{p,m}\big(H_2O(s)\big) = 37.7 J\ mol^{-1}K^{-1}$

$C_{p,m}\big(H_2O(l)\big) = 75.3\ J\ mol^{-1}K^{-1}$

During the conversion of supercooled liquid water to ice at −20 °C:

7. Calculate the total entropy change in the system.

8. Calculate the total entropy change in the surroundings.

9. Calculate the total entropy change in the universe.

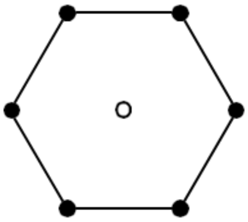
$\Delta S = C_p ln \frac{T_{final}}{T_{initial}}$ and $\Delta S = -\frac{q_{transition}}{T}$

Problem 18

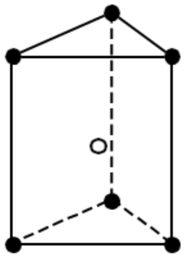
(*International Chemistry Olympiad, 2009, Problem 6*)

Transition metal complexes

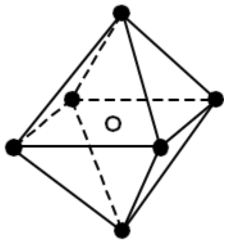
Alfred Werner used the technique of ‘isomer counting’ to deduce the structure of metal complexes with coordination number six. Three of the shapes he considered are shown below.



X



Y



Z

In each structure, the empty circle shows the location of the central metal atom and the filled circles show the location of the ligands. Structure **X** is hexagonal planar, structure **Y** is trigonal prismatic and structure **Z** is octahedral.

For each of the three shapes, there is only one structure when all of the ligands are the same, i.e. when the complex has the general formula MA_6 where A is the ligand. However, when achiral ligands A are substituted by one or more achiral ligands, it may be possible for each structure to form geometrical isomers. It might be also possible for one or more of the geometrical isomers to be optically active and exist as pairs of enantiomers.

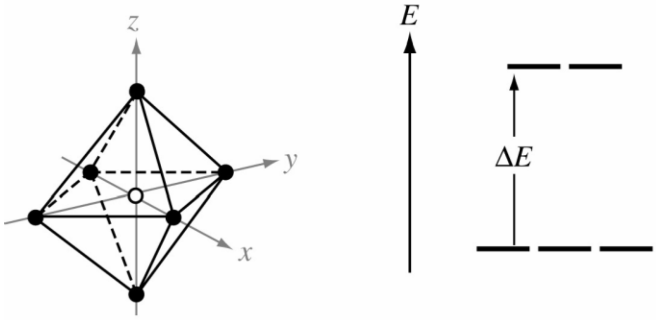
1. Fill in the table below to indicate how many geometrical isomers may be formed for each structure **X**, **Y**, and **Z** as the monodentate ligands A are substituted by monodentate ligands B or by symmetrical bidentate ligands denoted C-C. Bidentate ligands C-C can only link between two atoms on adjacent positions, i.e. those positions connected by a line in the structures **X**, **Y**, and **Z**.

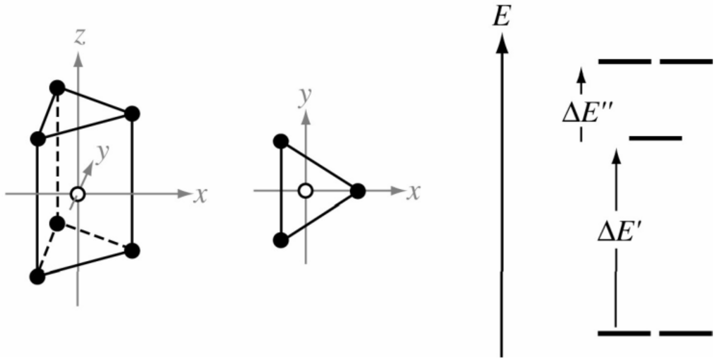
In each case write the number of the geometrical isomers in the space provided. If one of the isomers exists as a pair of enantiomers, include an asterisk, *, in the box. If two exist as two pairs of enantiomers, include two asterisks and so on. For example, if you think there are five geometrical isomers of a particular structure, three of which exist as a pair of enantiomers, write 5***.

	Number of geometrical isomers		
	Hexagonal planar **X**	Ttrigonal prismatic **Y**	Octahedral **Z**
MA_6	1	1	1
MA_5B			

MA_4B_2			
MA_3B_3			
$MA_4(C\text{-}C)$			
$MA_2(C\text{-}C)_2$			
$M(C\text{-}C)_3$			

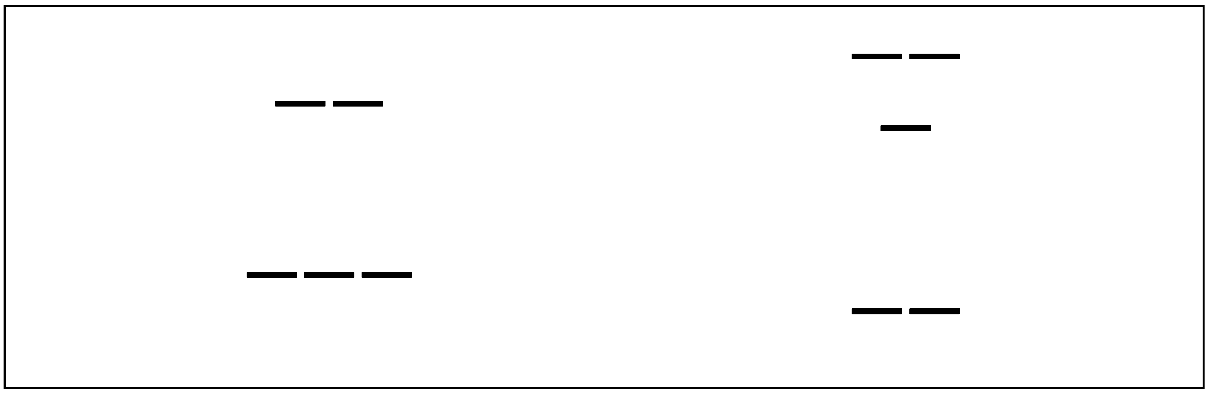
There are no known complexes that adopt the hexagonal planar geometry **X**, but structures are known for both the trigonal prismatic geometry **Y** the octahedral geometry **Z**. In these complexes, the orbitals derived from the metal d orbitals have different energies depending on the geometry of the complex. The splitting patterns for the trigonal prismatic geometry and for the octahedral geometry are given below.





The separations in energy, ΔE, $\Delta E'$ and $\Delta E''$ depend on the particular complex.

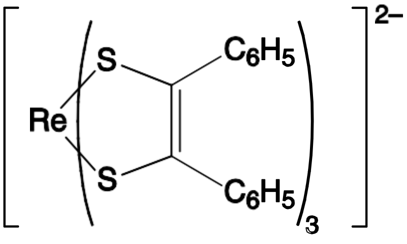
2. For each of the splitting patterns shown below label which d orbitals are which.



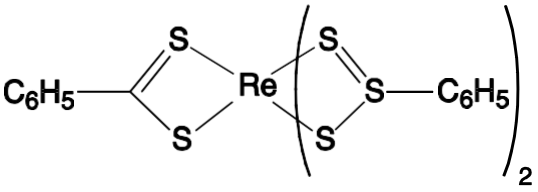
The two complexes $[Mn(H_2O)_6]^{2+}$ and $[Mn(CN)_6]^{2-}$ are octahedral. One has a magnetic moment of 5.9 BM, the other has a magnetic moment of 3.8 BM but must decide which is which.

3. On the diagram below, draw the electronic arrangements for each of the complexes.

The magnetic moments of complexes **A** and **B** shown below have been measured and found to be 1.9 and 2.7 BM but must decide which is which.



A



B

4. Draw the orbital splitting diagrams for the two complexes, including the arrangements of the electrons.

Octahedral complexes are far more common than trigonal prismatic. Werner isolated three compounds **C** – **G** containing Co(III), Cl, and NH_3 only, each of which contained one octahedral complex. (There is actually a sixth compound but Werner could not isolate it). Werner's five compounds had the molar conductivities shown below. The conductivities are extrapolated to infinite dilution an are expressed in arbitrary units. Compound **G** does not react with aqueous $AgNO_3$; compounds **C**, **D**, and **E** react with different stoichiometric ratios of aqueous $AgNO_3$; **E** and **F** react with the same stoichiometric ratio of aqueous $AgNO_3$;

	C	**D**	**E**	**F**	**G**

molar conductivity	510	372	249	249	~0

5. As far as you are able, suggest a structure for each **C** – **G**.

Werner was also the first person to separate the enantiomers of an octahedral compound, **H**, which contained no carbon atoms. The compound, **H**, is composed of only cobalt, ammonia, chloride and an oxygen species which could be either H_2O, or HO or O^{2-}. The compound contains octahedrally coordinated cobalt ions. All of the chloride is easily removed from the compound by titration with aqueous silver nitrate. A 0.2872 g sample of **H** (containing no water of crystallization) required 22.8 cm^3 of silver nitrate solution (c = 0.100 mol dm^{-3}) to exchange all the chloride.

6. Calculate the percentage, by mass, of chloride in **H**.

H is stable to acids, but is hydrolyzed in alkali. A 0.7934 g sample of **H** (containing no water of crystallization) was heated with excess aqueous sodium hydroxide. Cobalt(III) oxide was formed and ammonia gas given off. The ammonia produced was distilled off and absorbed into 50.0 cm^3 of aqueous HCl (c_{HCl} = 0.500 mol dm^{-3}). The residual HCl required 24.8 cm^3 of aqueous KOH solution (c_{KOH} = 0.500 mol dm^{-3}) to be neutralized.

The remaining suspension of cobalt(III) oxide was allowed to cool, approximately 1 g of potassium iodide was added, and then the mixture was acidified with aqueous HCl. The liberated iodine was then titrated with aqueous solution of sodium thiosulfate (c = 0.200 mol dm^{-3}) and required 21.0 cm^3 for complete reaction.

7. Calculate the percentage, by mass, of ammonia in **H**.

8. Give the equation for the reaction of cobalt(III) oxide with potassium iodide in aqueous acid.

9. Calculate the percentage, by mass, of cobalt in **H**.

10. Calculate the identity of the oxygen species contained in **H**. Show your working.

11. Give the empirical formula of **H**.

12. Suggest a structure for the chiral compound **H**.

Problem 19

(*International Chemistry Olympiad, 2019, Preparatory problem 5*)

Hydrogen storage

Dihydrogen is a promising fuel for the future, notably for power production or mobility purposes. It is an attractive alternative to the use of fossil fuels (hydrocarbons), which release carbon dioxide during their combustion, thus contributing to global warming. Unfortunately, storing efficiently large amounts of H2 is not easy. Dihydrogen has a low energy per unit volume at room temperature, is highly flammable and requires several technological advances to be competitive with fossil fuels. In this problem, we investigate the advantages and disadvantages of some hydrogen storing methods.

Storing H_2 as a gas

Compressing dihydrogen is one of the methods commonly used to store it. The gas is stored in containers at a pressure kept between 350 and 700 bars.

1. Calculate the density of an ideal dihydrogen gas at a pressure of 500 bar and at room temperature (293 K).

Storing H_2 as a liquid

Dihydrogen gas is liquefied and kept in a Dewar flask (a thermally insulated container) usually under a relatively low pressure (1 to 4 bar). However, the system needs to be kept at very low temperatures, because the melting point of H_2 at a pressure P = 1 atm is T_m = –259.2 °C and its boiling point under the same pressure is T_V = –252.78 °C. Its critical point is located at: P_C = 13.0 bar, T_C = −240.01 °C.

2. At which temperatures can liquid hydrogen be observed?

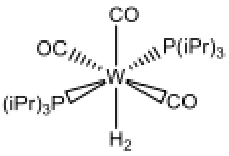
☐ 16 K
☐ 25 K
☐ 77 K
☐ 293 K

3. Using the Clausius-Clapeyron relation, calculate the pressure needed to liquefy ideal gaseous dihydrogen at 27.15 K.

Storing dihydrogen as a complex

In 1984, using measurements obtained from neutron diffraction, G. J. Kubas and his collaborators (G. J. Kubas *et al.*, J. Am. Chem. Soc., 1984) identified a tungsten complex $[W(CO)_3(P(iPr)_3)_2(\eta^2\text{-}H_2)]$ that possesses a H—H bond with a length of 0.82 Å, close to that of an isolated H_2 molecule (0.74 Å). ((*i*Pr)

= iso-propyl). This complex easily dissociates under partial vacuum or under argon atmosphere, and it can be regenerated in the presence of dihydrogen.



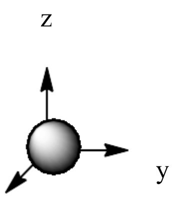
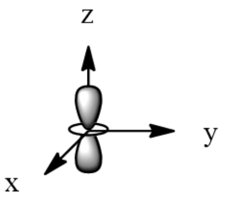
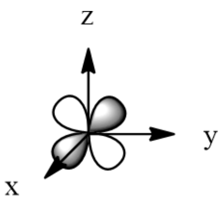
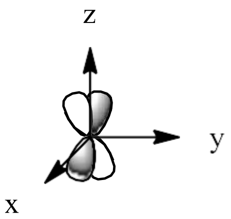
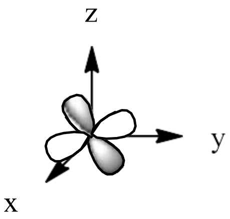
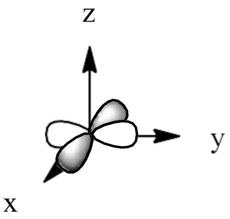
4. Calculate the mass of the dehydrogenated complex needed to store 1 kg of dihydrogen. Calculate ρH (the density of hydrogen in the complex, defined as the mass of hydrogen atoms per volume unit of complex).

The next section will study the binding of a H_2 molecule to the dehydrogenated complex within the field of other ligands. The dehydrogenated complex is assumed to be a square-based pyramid, which the dihydrogen molecule is added to.

Metallic central atom

5. Give the electronic configuration of atomic tungsten. Specify the number of valence electrons.

6. Fill in the table with the name of each depicted atomic orbital (s, d_{yz}, d_{z^2}, $d_{(x^2-y^2)}$, d_{xz}, d_{xy}).

Dihydrogen as a ligand

7. Draw and fill the molecular orbital diagram of dihydrogen.

Kubas complex

Since the complex is considered as a square-based pyramid to which the H_2 molecule is added, we have to take into account the influence of other ligands. The splitting thus obtained is given in the diagram below.

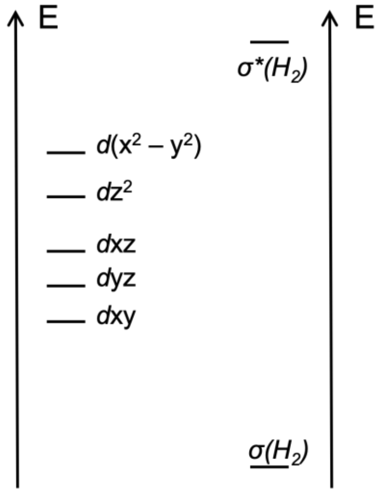


Figure 1: Simplified diagram of molecular orbitals of the Kubas complex

In order to build the molecular orbital diagram of the Kubas complex, we can study the interaction of the molecular orbitals of the complex ([$W(CO)_3(P(i\text{Pr})_3)_2$]) —which will be merely considered as the *d* orbitals of the metallic central atom— with the H_2 molecule orbitals.

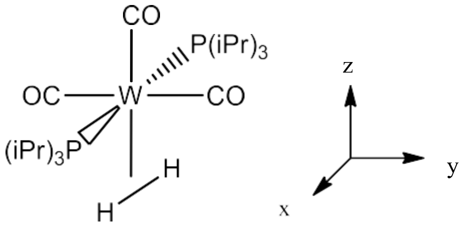
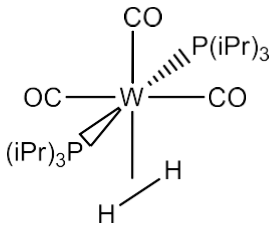


Figure 2: Kubas complex and reference axes

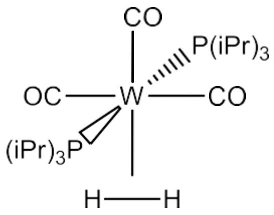
8. Give the two planes of symmetry of the Kubas complex (using the axes of figure 2).

9. Indicate for each orbital *d* of the metallic central atom if they are symmetric or antisymmetric with respect to each of the symmetry planes (using the axes of figure 2).

Two conformations have been proposed: (1) where H_2 is parallel to the phosphine ligands P(*i*Pr)$_3$, and (2) where H_2 is parallel to the CO ligands. Even if steric effects favor conformation (2), conformation (1) is actually more stable.



(1)



(2)

10. Fill in the diagram in figure 1 with electrons.

11. Knowing that only orbitals with the same symmetry interact, enumerate the possible interactions for each conformation. Which conformation is the most stable one?

Storing hydrogen in form of formic acid

In 2006, a research team of EPFL (Switzerland) (C. Fellay *et al.*, Angew. Chem. Int. Ed., 2008) proposed to store H2 in form of formic acid. The main idea is to use formic acid as fuel that can be decomposed on a catalyst made of ruthenium to produce dihydrogen and carbon dioxide according to the following reaction:

$$HCOOH(l) \rightarrow CO_2(g) + H_2(g) \qquad (R1)$$

12. Calculate ρ_H (the density of hydrogen at 25 °C defined as the mass of hydrogen atoms per volume unit of formic acid). Compare this value to those obtained for gaseous dihydrogen at 500 bar and for liquid dihydrogen.

13. Calculate the standard enthalpy and entropy of reaction at 20 °C for reaction (R1).

14. Using the Ellingham approximation (that supposes enthalpy and entropy independent of temperature), calculate the equilibrium constant at 20 °C for reaction (R1).

Formic acid (2.3 g) is added to a 1 L container with 0.1 g of ruthenium catalyst, under constant atmospheric pressure and at an initial temperature of 25 °C. The container initially contains dinitrogen.

15. Determine the final composition of the mixture.

Storing hydrogen in metal hydrides

Metal hydrides have also been proposed to store dihydrogen. Compounds with a $X_xY_yH_n$ formula can store large amounts of hydrogen in a compact way. Moreover, the adsorption- desorption properties of hydrogen can be tailored by choosing an element X from light elements (Li, Mg, B,…) or other electropositive elements (lanthanides) that have a good affinity with hydride ligands, and an element Y from transition metals that have a low affinity with hydride ligands. Among the numerous existing metal hydrides, two of them will be studied in their operating conditions: $LaNi_5H_6$ (300 K, 2 bar) and

Mg_2NiH_4 (550 K, 4 bar).

16. Determine ρH at 25 °C (the density of hydrogen, which is defined as the mass of hydrogen atoms per volume for these two compounds in their operating conditions).

Safety rules for students in the laboratory

All students of chemistry must recognize that hazardous materials cannot be completely avoided. Chemists must learn to handle all materials in an appropriate fashion. While it is not expected that all students participating in the International Chemistry Olympiad know the hazards of every chemical, the organizers of the competition will assume that all participating students know the basic safety procedures. For example, the organizers will assume that students know that eating, drinking, or smoking in the laboratory or tasting a chemical is strictly forbidden.

In addition to the commonsense safety considerations to which students should have been previously exposed, some specific rules, listed below, must also be followed during the Olympiad. If any question arises concerning safety procedures during the practical exam, the student should not hesitate to ask the nearest supervisor for directions.

Rules regarding personal protection

1. Eye protection must be worn in the laboratories at all times. If the student wears contact lenses, full protection goggles must also be worn. Eye protection will be provided by the host country.

2. A laboratory coat is required. Each student will supply this item for himself/herself.

3. Long pants and closedtoed shoes are recommended for individual safety. Long hair and loose clothing should be confined.

4. Pipetting by mouth is strictly forbidden. Each student must be provided with a pipette bulb or pipette filler.

Rules for Handling Materials

1. Specific instructions for handling hazardous materials will be included by the host country in the procedures of the practical exam. All potentially dangerous materials will be labeled using the GHS symbols. Each student is responsible for recognizing these symbols and knowing their meaning.

2. Do not indiscriminately dispose chemicals in the sink. Follow all disposal rules provided by the host country.

The GHS hazard statements (H-phrases):

H225 Highly Flammable liquid and vapour.

H301 Toxic if swallowed.

H302 Harmful if swallowed.

H311 Toxic in contact with skin

H314 Causes severe skin burns and eye damage.

H315 Causes skin irritation.

H317 May cause an allergic skin reaction.

H318 Causes serious eye damage.

H319 Causes serious eye irritation.

H320 Causes eye irritation.

H330 Fatal if inhaled.

H331 Toxic if inhaled.

H332 Harmful if inhaled.

H334 May cause allergy or asthma symptoms or breathing difficulties if inhaled.

H335 May cause respiratory irritation.

H336 May cause drowsiness or dizziness.

H340 May cause genetic defects.

H341 Suspected of causing genetic defects.

H350i May cause cancer by inhalation.

H351 Suspected of causing cancer.

H370 Causes damage to organs.

H372 Causes damage to organs through prolonged or repeated exposure.

H373 Causes damage to organs through prolonged or repeated exposure.

H400 Very toxic to aquatic life.

H402 Harmful to aquatic life.

H410 Very toxic to aquatic life with long lasting effects.

Problem 20 (Practical)

(*International Chemistry Olympiad, 2001, Problem 3*)

Determination of the rate constant for the redox reaction between ethanol and chromium (VI)

At the work bench

Burette, 50 mL	2 pcs
Conical flasks, 100 mL	4 pcs
Funnels	2 pcs
Measuring cylinder, 10 mL	2 pcs
Stop watch	1 pc

Reagent bottles containing:

- $K_2Cr_2O_7$ solution (0.0xxx M) in HCl (3.6M), 100 mL
- $Na_2S_2O_3$ (0.0xx M), 100 mL
- KI solution (3 % w/v), 30 mL
- Starch indicator, 15 mL
- Vial containing ethanol, 1 mL

The oxidation of alcohols by chromium (VI) forms the basis for analysis of breath samples for measuring alcohol content. A dilute solution of $K_2Cr_2O_7$ in the presence of a strong acid (3.6 M HCl here) is a source of $HCrO_4^-$ which is the oxidant involved in the reaction.

In this experiment, the rate of the reaction between $HCrO_4^-$ and CH_3CH_2OH is determined titrimetrically. Under the given experimental conditions, the rate law reduces to

$$\text{rate} = k[HCrO_4^-]^x$$

where x is the order of the reaction.

At any given time, $[HCrO_4^-]$ is obtained by iodometric titration.

Table of Chemicals

Compound	Name	State	GHS codes
$K_2Cr_2O_7$	Potassium dichromate	Aqueous solution	H315, H317, H319, H335, H340, H350i, H410
$Na_2S_2O_3$	Sodium thiosulfate	Aqueous solution	H315, H319, H335
KI	Potassium iodide	Aqueous solution	H302, H315, H319

HCl	Hydrochloric acid	Aqueous solution	H301, H314, H318, H330, H331, H334, H370, H372, H400
$(C_6H_{10}O_5)_n$	starch	Aqueous solution	-
CH_3CH_2OH	ethanol	liquid	H225, H319

Procedure

You are given 100 mL of standard $K_2Cr_2O_7$ solution in HCl in a bottle. Transfer all the absolute ethanol given in a vial into this bottle and stopper it. Mix the contents thoroughly, start the stopwatch immediately and regard this as time t = 0. Fill the burette with this solution.

After every 10 minutes, start to draw 10 mL of this solution to a clean conical flask containing 4 mL of the given KI solution. The solution will turn brown. Titrate this solution with the given standard $Na_2S_2O_3$ solution until the colour changes to pale greenish yellow. Add 2 mL of starch indicator and continue the titration until the colour changes from blue to pale green. Record the burette reading in the answer sheet. Repeat this procedure at 10 minutes intervals to obtain four readings.

Concentration of standard $Na_2S_2O_3$: _______________

Concentration of $HCrO_4^-$ at t = 0: ______________

	Titration 1 [10 min]	Titration 2 [20 min]	Titration 3 [30 min]	Titration 4 [40 min]
Initial burette reading (mL)				
Final burette reading (mL)				
Volume of $Na_2S_2O_3$ solution (mL)				

1. Write down the possible oxidation products in the reaction of $HCrO_4^-$ and CH_3CH_2OH.

2. Write down the balanced chemical equation for the reaction between $HCrO_4^-$ and KI.

3. Write down the balanced chemical equation involved in the titration.

4. Give the main steps for the calculation of $HCrO_4^-$ concentration (M) for any one titration reading.

5. Concentration (M) of $HCrO_4^-$ at different times:

Time (min)	$[HCrO_4^-]$	ln $[HCrO_4^-]$
0		
10		
20		
30		
40		

6. Plot the graph of log $[HCrO_4^-]$ vs time.

7. From the nature of the graph, determine the order (**x**) of the reaction with respect to $HCrO_4^-$.

8. Determine the rate constant for the reaction.

Problem 21 (Practical)

(*International Chemistry Olympiad, 2021, Preparatory problem 2*)

Simultaneous acid–base titration

Introduction

Sodium carbonate, which is a raw material for glass, is produced by absorbing ammonia into an aqueous solution of sodium chloride and subsequent thermal decomposition of the sodium hydrogen carbonate obtained after passing carbon dioxide. Sodium carbonate can also be obtained by reacting carbon dioxide with an aqueous solution of sodium hydroxide, which is an important chemical for the production of soap, paper, and fibers.

In this experiment, a differential titration (Warder method) is used to simultaneously determine the concentrations of two electrolytes with different basicity. Specifically, the mass of the electrolytes in a mixed aqueous solution containing sodium hydroxide ($pK_a > 13$) and sodium carbonate ($pK_{a1} = 6.35$, $pK_{a2} = 10.33$) will be determined using two pH indicators.

Chemicals

Substance	Name	State	GHS Codes
HCl	Hydrochloric acid	Aqueous solution	H301, H314, H318, H330, H331, H334, H370, H372, H400
$C_{20}H_{14}O_4$	Phenolphthalein	Ethanol solution	H225, H320, H335, H336, H341, H351, H372, H373
$C_{14}H_{14}N_3NaO_3S$	Methyl orange	Aqueous solution	-
NaOH	Sodium hydroxide	Aqueous solution	H314, H318, H370, H402
Na_2CO_3	Sodium carbonate	Aqueous solution	H332, H318, H335, H336

Glassware and Equipment

- 1 Volumetric pipette, 20 mL with pipette filler
- 1 Burette, 25 mL
- 2 Erlenmeyer flasks with stopper (HCl standard solution, unknown alkali solution), 300 mL
- 1 Plastic container (for solution-state chemical waste), 1 L
- 2 Pipettes and pipetting bulbs (for indicators ***a*** and ***b***)
- 5 Titration flasks, 100 mL
- 1 Erlenmeyer flask (for transferring the HCl standard solution to the burette), 50 mL
- 1 Transfer funnel
- 1 Laboratory stand with burette clamp

Chemicals

- $0.1\ \mathrm{mol\ L^{-1}}$ HCl standard aqueous solution
- Unknown alkali solution containing NaOH and Na_2CO_3
- Indicator *a*: Phenolphthalein ethanolic solution
- Indicator *b*: Methyl orange aqueous solution
- Deionized water

Procedure

(1) Transfer 20.00 mL of the unknown alkali aqueous solution into a 100 mL titration flask using a 20 mL volumetric pipette. Add indicator *a*, which will turn the solution reddish purple. Titrate the unknown alkali solution by adding the HCl standard solution in the burette. When the alkali solution turns pale pink, you have reached the first equivalence point. Record the volume (V_a) in your notebook.

(2) Add indicator *b* to the now pale-pink aqueous solution. The color of the solution will turn yellow. Continue the titration using the HCl standard solution until the aqueous solution turns light orange, where you have reached the second equivalence point. Record the volume (V_b; volume from the first equivalence point to the second equivalence point).

Repeat procedures (1) and (2) if necessary.

Results

Titration Step (1)

No.	Vfinal (mL)	Vinitial (mL)	V (mL)
1			
2			
3			
4			
5			
Accepted volume V_a			

Titration Step (2)

No.	Vfinal (mL)	Vinitial (mL)	V (mL)
1			
2			
3			
4			

5			
Accepted volume *Vb*			

Questions

1. Write the two chemical equations for the neutralization reactions during titration step (1).

2. Write the chemical equation for the neutralization reaction during titration step (2).

3. From the results of the above titration operation, calculate the weights (g) of NaOH and Na_2CO_3 contained in 1 L of the unknown alkali aqueous solution.

4. Sketch the pH titration curve expected for the unknown alkali solution.

Problem 22 (Practical)

(*International Chemistry Olympiad, 2013, Preparatory problem 30*)

Analysis of fire retardants by potentiometric titration

The purpose of the experiment is to determine the composition of a mixture simulating a fire retardant containing $(NH_4)_2HPO_4$ and NH_4Cl. First, the sample is dissolved in HCl and titrated with NaOH to determine the amount of phosphoric acid, the best precision being achieved if potentiometric titration (pH values recorded with a pH meter) is used. Generally, titration of a mixture of hydrochloric and phosphoric acids with an alkali results in two end points (inflexio ns in the titration curve). The first end point indicates the total amount of hydrochloric and phosphoric acids, while the second one corresponds to the completion of the second stage neutralization of phosphoric acid. In this experiment, the second end point cannot be observed due to the formation of ammonium buffer.

To determine the concentration of the ammonium salt, the formaldehyde method is used. The reaction between formaldehyde and ammonium produces the hexamethylene tetrammonium cation $(CH_2)_6(NH^+)_4$, which is more acidic than the NH_4^+cation. Another potentiometric titration is necessary to find the total amount of $(CH_2)_6(NH^+)_4$, and thus calculate the total amount of diammonium phosphate and ammonium chloride in the sample.

The acidity constants of phosphoric acid:$K_{a1}= 7.1\times10^{-3}$, $K_{a2} = 6.2\times10^{-8}$, $K_{a3} = 5.0\times10^{-13}$.

Chemicals and Reagents

- Mixture of $(NH_4)_2HPO_4$ and NH_4Cl, about 1:1 by weight
- Sodium hydroxide, 0.1 M NaOH (aq)
- Hydrochloric acid, 0.1 M HCl (aq)
- Formaldehyde, 20 % CH_2O (aq)

Table of Chemicals

Compound	Name	State	GHS codes
$(NH_4)_2HPO_4$	Diammonium hydrogen phosphate	Solid	H319, H335, H315
NH_4Cl	Ammonium chloride	Solid	H302, H319
HCl	Hydrochloric acid	Aqueous solution	H301, H314, H318, H330, H331, H334, H370, H372, H400
NaOH	Sodium hydroxide	Aqueous solution	H314, H318, H370, H402
CH_2O	Formaldehyde	Aqueous solution	H331, H311, H301, H314, H351,

			H317

Equipment and Glassware

- Analytical balance (± 0.0001 g)
- Volumetric pipette, 10 mL
- Pipette pump
- Burette, 25 mL
- Beaker, 100 mL
- Volumetric flask, 100 mL
- Magnetic stirrer
- Stirring bar
- pH meter

A. Determination of phosphate amount as phosphoric acid

a) Weigh about 0.6 g of the test mixture and place it in a 100 mL volumetric flask. Fill with water up to the mark.

b) Transfer 10 mL of the prepared solution into a 100 mL beaker using a 10 mL volumetric pipette. Add 10 mL of 0.1 M hydrochloric acid (concentration known exactly) using a 10 mL volumetric pipette, and dilute it with 20 mL of distilled water. Place the beaker onto a magnetic stirrer and put in the stirring bar.

Titrate the sample with 0.1 M sodium hydroxide adding it by 0.5 mL portions until the pH starts increasing. Continue adding the titrant in drop portions. When the change of pH with each added portion significantly decreases, continue titration with larger portions of sodium hydroxide. Record the volume of sodium hydroxide added and each pH value measured.

c) Repeat the titration with new aliquots of the sample solution as needed to obtain consistent results.

B. Determination of the total amount of ammonium salts

e) Prepare a 20% aqueous solution of formaldehyde free of formic acid. Neutralize the solution with sodium hydroxide, if needed. Use titration in the presence of phenolphthalein to determine the necessary amount of NaOH for the neutralization.

f) Transfer 10 mL of the sample solution into a 100 mL beaker using a 10 mL volumetric pipette. Add 5 mL of the formaldehyde solution and wait for 2 min.

g) Place the beaker onto the magnetic stirrer and put in the stirring bar. Titrate the sample with 0.1 M sodium hydroxide with constant stirring as described in part **A**.

h) Repeat the titration with new aliquots of the sample solution as needed to obtain consistent results.

Questions and Data Analysis

1. How many end points are expected during the titration of a mixture of H_3PO_4 and HCl?

2. Can color indicators be used in the determination of concentrations of hydrochloric and phosphoric acids in their mixture?

3. Write down the equations of all the reactions occurred.

4. Plot the graphs of pH, $\Delta pH/\Delta V$, and $\Delta^2 pH/\Delta V^2$ *vs*. volume of the titrant added. Find the end points from the curves analysis. Why is there only one end point in the titration curve of hydrochloric and phosphoric acids in the presence of ammonium ion?

5. Calculate the content (in weight %) of (a) diammonium phosphate and (b) ammonium chloride in the test sample.

Problem 23 (Practical)

(*International Mendeleev Chemistry Olympiad, 2018, Problem 2*)

Determination of neutralizing capacity of an antacid drug

Hydrotalcite, aluminum magnesium hydroxycarbonate $Mg_nAl_m(CO_3)_x(OH)_y{\cdot}4H_2O$, is an efficient antacid. The so-called neutralizing capacity is used to check an antacid quality. You will have to determine this value modeling the antacid effect of the preparation in stomach. In this part you will study the time dependence of neutralization of hydrochloric acid with hydrotalcite.

Equipment and reagents

Hydrochloric acid, 0.10 M
Sodium hydroxide, 0.033 M
Dropper with Methyl Orange, 0.1%
Burette
Cylinder, 50 mL
Beaker, 150 mL
Conical flasks, 2 pcs
Pipette
Wall-mounted clock

Table of Chemicals

Compound	Name	State	GHS codes
$C_{14}H_{14}N_3NaO_3S$	Methyl Orange	Aqueous solution	H301
HCl	Hydrochloric acid	Aqueous solution	H301, H314, H318, H330, H331, H334, H370, H372, H400
NaOH	Sodium hydroxide	Aqueous solution	H314, H318, H370, H402

Procedure

Before you start working, note the mass of the sample 2 (see the 150 mL beaker labeled «Sample 2»). Place 30 mL of distilled water into the 50 mL cylinder. Wet the weighed amount of the antacid (Sample 2) with 2-3 drops of water and paste up with the glass rod. Keep adding water from the measuring cylinder dropwise, grinding the mixture into paste with the glass rod every time a new droplet is added. You are expected to finally get a yogurt-like mixture. *Only after this,* pour out the rest of the water from the cylinder into the beaker. Using the glass rod, carefully break down all the preparation lumps, if any. Then, measure by burette 80.0 mL of 0.10 M HCl and transfer into the beaker, write down the time with an accuracy of 10 s into the table below. A stable opalescent suspension is expected to be formed.

Two minutes after the addition of hydrochloric acid, transfer by pipette 10.00 mL of the suspension into the titration flask, and add 1 drop of the methyl orange solution. (Note that the solution to be titrated must be light-pink. An excess of the indicator complicates observation of the color change!). Titrate with 0.033 M NaOH solution until pure yellow color appears. It is recommended to prepare the reference solution in the other conical flask. To do so, add 1 drop of each of the alkali and indicator solutions to the corresponding volume of water. Denote the moment when the titration is completed as the experiment time. Record the time with an accuracy of 10 s.

To study time dependence of the acid neutralization by the anticide, perform 3 other titrations described in i. 2 making 5-7 min breaks between the titrations. Record the results in the table.

Time on the clock when HCl added					
Time on the clock when the titration completed					
Time since the experiment start, min					
The initial burette reading, mL					
The final burette reading, mL					
V(NaOH), mL					
The amount of the reacted HCl, mmol					
Neutralizing capacity, mmol/g					

1. Calculate the neutralizing capacity of the antacid as the amount (in mmol) of hydrochloric acid reacted with it. Refer the results to the sample mass. Write down the results into the table.

2. Plot the hydrochloric acid neutralization in the coordinates: *time, min – neutralizing capacity, mmol HCl/g of the drug preparation*. Clearly show all the experimental points in the plot.

3. You are given 4 different pH values at which titration of the acid excess is completed. Circle the pH value corresponding to the maximum neutralizing capacity of the drug preparation.

a) 1; b) 2; c) 3; d) 4.

4. Write down the reaction equation explaining that the neutralizing capacity of the drug preparation depends on the acidity of the medium.