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Problems prepared by Commission of Ministry of Education:

Mrs Svetlana V. Vasilenko (Ukrainian Ministry of Education)

Prof. Svetlana A. Volkova (Kherson Pedagogical University)

Mr Sergey V. Kolotilov (Taras Shevchenko Kiev University)

Prof. Igor' V. Komarov (Taras Shevchenko Kiev University)

Prof. Ivan I. Kocherga (Nezhin Pedagogical University)

Prof. Nelli T. Maleeva (Donetsk State University)

Prof. Pavel P. Popel' (Taras Shevchenko Kiev University)

Prof. George M. Rosantsev (Donetsk State University)

Prof . Yuriy V. Kholin (Kharkov State University)

Prof. Elena N. Shved (Donetsk State University)

Prof. Vitaliy K. Yatsimirsky (Taras Shevchenko Kiev University)

First Theoretical Tour

8 class (1st year of studying chemistry)

1. List characteristic manifestations of chemical reactions and give corresponding examples. Which of them take place also during physical transformations?

2. When adding Sodium hydroxide to the solution of Copper(II) sulfate, precipitate of $Cu_m(OH)_n(SO_4)_p$ is formed. For the complete precipitation of Copper ions which are contained in 25 ml of the Copper(II) sulfate solution with concentration 0.100 mol/dm^3, 18.75 ml of Sodium hydroxide solution with concentration 0.200 mol/dm^3 is needed.

- Determine molar ratio Cu^{2+} / OH^- in precipitate.
- Calculate elementary composition of $Cu_m(OH)_n(SO_4)_p$.
- Write down the equation of the chemical reaction.

3. The mineral water «Mirgorodska» has the following composition (mg/ml):

Cl^-	1300
HCO_3^-	400
SO_4^{2-}	300
Ca^{2+}	60
Mg^{2+}	25
(Na+K)	?

- Calculate the (Na+K) content in 1 L of water.
- Calculate the mass of dry residue after evaporation of 1 L of the mineral water and baking at 200-300^{o}C.
- Calculate the mass of the precipitate formed after addition of an excess of $BaCl_2$ solution to 1 L of this water with boiling.

4. Suggest different methods of isolation of each component from their dry mixture: $CuCl_2$, NH_4Cl, NaCl, AgCl. Propose reactions for qualitative analysis of each component of this mixture. Give examples of practical usage of these substances. Give the equations of corresponding reactions.

5. 49.03 g of the 29.78% solution of HCl was added to the jar containing 52.20 g of alkali metal. The solution obtained was cautiously evaporated in the absence of air to the solid residue. Determine the metal. Consider possibilities:

a) the solid residue is one substance, mass 67.40g
b) the solid residue is a mixture of two substances, total mass 99,92 g
c) the solid residue is a mixture of three substances, total mass 99,92 g.

6. Glass vessel with capacity 201.6 ml was filled in (0^oC, 1 atm) with three simple gaseous substances with volume ratio $V_1(A_2):V_2(B_2):V_3(C_2) = 1:3:5$. The mixture has been exploded at 60^oC and this temperature was hold for 2 hours. After that the vessel was opened and only 0.054 g of white wet substance D was found there.

- Determine gases. The ratio of densities for A_2, B_2 and C_2 is 16:19:1.
- Determine the pressure in the vessel after explosion in comparison with the initial conditions.
- Write down the equations of reactions.
- Determine substance D, if it contains elements A, C and E (the content of E by mass is equal to 35,9%).
- Explain the change of the mass of D in time. Calculate the maximal possible mass of D.
- What reactions will take place in the absence of gas A in initial mixture?

9 class (2nd year of studying chemistry)

1. The weighed sample of hydrazine (10.000 g) was placed into a vacuumed vessel (volume 2.000 L). The vessel was heated at 300 ^oC until complete decomposition of hydrazine. After that the pressure in the vessel was 1387.38 kPa. Calculate mass fractions of components in the obtained gaseous mixture.

2. Thermal decomposition of colorless crystalline substance X at 450 ^oC results in obtaining the mixture of three gaseous products (mixture <u>1</u>) with density by hydrogen 40.6. When mixture <u>1</u> was quickly cooled to 150 ^oC, the liquid product and gaseous mixture <u>2</u> with density by hydrogen 20.7 were obtained, and volume of this mixture is 2.279 times less then the volume of mixture <u>1</u>, measured at 450 ^oC. Mixture <u>2</u> after cooling to 30^oC was passed through the excess of the alkali base solution. Then colorless incombustible (but maintaining combustion) gas with density by hydrogen 16 remains in the gas phase, which volume is 4.188 times less then the volume of mixture <u>2</u> at 150^oC.

- Determine the formula of substance X.
- Write down the equations of reactions described above.
- Write down the equation of the reaction that occurs at heating X to 360-400 ^oC.

3. 6.2 g of phosphorous was placed in 300 ml–jar, the jar was filled with 5.0 g of gas A and heated to 350 ^oC. To fix gas B obtained in reaction, it is necessary to pass it through 40 ml of 0.1 mol/l solution of HI.

- Determine gases A (simple substance) and B (w_P=91.2%).
- Calculate content of B in gaseous mixture in per cent by volume.
- Calculate the equilibrium constant K_P and the yield of B.
- Estimate is it reasonable to obtain B using this reaction?
- Draw the structural formula of B. Is it possible to use HCl or HNO_3 instead of HI?

4. The dissolution of a simple substance (0.775 g) in nitric acid causes the formation of gaseous products (total mass 5.75 g). Also, the solution of two oxygen containing acids with maximum possible oxygen contents is produced. For neutralization of this solution 0.100 mol of Sodium hydroxide are needed.

- Determine the composition of gaseous mixture obtained at 90^o (in percent by volume) if its density by hydrogen is equal to 38.3.
- Determine the simple substance.
- Calculate molar ratio of the acids obtained.
- Give structural formulas of all substances. Specify the state of hybridization of central atoms.

5. Which couples of substances cannot co-exist in aqueous solutions? Confirm your decisions by equations of reactions.

1) $AgNO_3$, NaCl	2) $FeCl_3$, KI	3) $FeCl_3$, KBr
4) H_2S, I_2	5) KI, $HClO_3$	6) $Cr_2(SO_4)_3$, HCl
7) $Cr_2(SO_4)_3$, $NaHCO_3$	8) $Cr_2(SO_4)_3$, NH_3	9) $SnCl_4$, Na_2CO_3
10) $FeCl_3$, KCl	11) $FeCl_3$, KF	12) $K[Fe(CN)_4]$, $AgNO_3$
13) $CuCl_2$, $[Ag(NH_3)_2]Cl$	14) $CuCl_2$, $[Ag(NH_3)_2]Cl$	

6. Dmitriy Mendeleev have placed Uranium to VI group of the Periodic table of ele– ments. This decision was based on the properties of this metallic element: it readily shows the highest valence 6. However, the highest Uranium oxide is only «half-similar» to analogous Chromium oxide: it reacts with alkalis forming two types of salts, but it is also able to react with acids. The latter reactions give salts which are derivatives of corresponding dibasic hydroxide.

- For mentioned Uranium oxide give the equations of the reactions with a) aqueous ammonia solution and b) nitric acid.
- Among lower oxidation levels of Uranium +4 is fairly typical. Taking this into account characterize the chemical nature of U_3O_8 which is the main component of Uranium ores.

7. For the preparation of «Greek fire» one has to mix sulfur, tartar emetic (Potassium bitartrate), gum (plant glue), resin, saltpeter, petrolatum (oil) and ordinary oil (olive) and to leave the mixture for some time. Then boil the mixture, plunge there tow and ignite it... (from the book «About the fire for enemy ignition» by Mark Greek).

- Propose your ideas about the action mechanism of «Greek fire».
- Specify the significance of the each component of the mixture in the process of combustion.

10 class (3rd year of studying chemistry)

1. Substances A and B contain octahedral complex anions of the same elementary composition, but they have different magnetic moments ($\mu=[n(n+2)]^{1/2}$, where n is the number of unpaired electrons): $\mu_A = 0$, $\mu_B = 1.72$ D. When 20 ml of 0.1 mol/l solution of A reacts with 1.3240 g of $Pb(NO_3)_2$, 1.2520 g of white precipitate is formed, and only Potassium salt remains in solution. When 1.2700 g of $FeCl_3$ is added to excess of solution of A, 1.6200 g of white precipitate G (which contains 51.85% of Iron by mass) is obtained. When exposed to air, G becames blue and turns into D. Reacting with $FeCl_2$, the solution B gives immediately blue precipitate E with composition identical to D.

- Determine substances A–E. Calculate the value of n for substance B.
- Give the equations of the reactions.
- What is the difference between blue precipitates D and E?

2. The mixture of two nitrates $A(NO_3)_2$ and $B(NO_3)_2$ (A is an alkaline-earth metal, B is a d-metal), with mass 83.5 g, was calcinated until formation of oxides. The volume of obtained mixture of NO_2 and O_2 was 26.88 L (0 ^oC, 1 atm). After passing the gaseous mixture through the excess of NaOH solution, the gas decreases its volume 6 times.

- Determine metals A and B.
- Calculate the composition of the mixture of nitrates (mol %).
- Give the equations of the reactions.
- Which salts may be obtained at higher temperature of calcination?

3. In two consequent reactions of first order $A \xrightarrow{k_1} B \xrightarrow{k_2} C$ the concentration of substance B has the maximum, at the moment of time defined by equation

$$\tau = \frac{\ln(k_2/k_1)}{k_2 - k_1}.$$

- Write down differential kinetic equations for substances A, B, C.
- At what k_1/k_2 ratio τ will be equal to the half-period of conversion of substance A?

4.

Thermodynamical function (298 K)	H_3PO_4 (solution)	$H_2PO_4^-$ (solution)	HPO_4^{2-} (solution)	PO_4^{3-} (solution)	$H^+ + OH^- =$ $= H_2O$ (liquid)
Δ H°, kJ/mol	-1288	-1269	-1292	-1277	-56
S°, J/mol·K	158	90	-33	-220	81

- Calculate ΔH^o and ΔG^o for the reactions of the H_3PO_4 stepwise neutralization with alkali:

$$OH^- + H_nPO_4^{n-3} = H_{n-1}PO_4^{n-4} + H_2O$$

- Using data from the table determine the dissociation constants of H_3PO_4 at 25°C.
- Determine the volumes of 0.1 mol/l solutions of acid and alkali which, when mixed, give 25 ml of final solution and 90 J of heat.

5. When heated with P_2O_5, compound A transforms into substance B ($C_4H_4O_3$). Reactions of these substances (both A and B) with NaOH solution give substance X, which being electrochemically oxidized turns to compound C. This compound is able to decolorize solution of $KMnO_4$. When heated, X turns to compound G, which doesn't decolorize $KMnO_4$ solution. Both substances react with bromine: C gives dibromderivative and G gives monobromderivative.

- Determine the structure of all compounds.
- Write down corresponding equations of the reactions.
- Specify conditions of the bromation of C and G.
- Write down the mechanism of conversion of X into C.

6. Let us consider the addition reaction of Hal_2 to alkene C_nH_{2n}. Alkene is the donor of electrons and halogen is the electrophylic reagent.

- Propose the ionic mechanism of addition of bromine to propene .
- Write down the equations of the addition reactions of interhalides BrI, ICl, BrCl to propene.
- The rate of the addition reaction of Hal_2 to propene increases in the sequence $I_2 – Br_2 – Cl_2$. Add interhalides to this sequence.
- Write down the equation of the reaction of BrCl with
  a) 1-buthene,
  b) 2-pentene,
  c) propenic acid,
  d) bromethene.

  Arrange compounds a) – d) in the order of increasing the addition rate.

7. At 1912 Prof. Favorsky studied the possibility to insert triple bond into cycles with different numbers of atoms. He attempted to synthesize cyclopentyne by treating 1,2-dibromcyclopenten with metallic Na. Instead of the cyclopentyne, he has obtained hydrocarbon A. Studied with the aid of PMR-spectroscopy, it demonstrates two signals with ratio of integral intensities 2:1. This hydrocarbon can be oxidized to acid B. 60 ml of NaOH solution (1 mol/L) is needed for the neutralization of 3.42 g of B.

- Write down the formulas of substances A and B.
- Suggest the mechanism of formation of A.
- Explain the reasons of the instability of cycles with triple bonds.
- Which of synthesized cycles with triple bond is the smallest?

11 class (4th year of studying chemistry)

1. When 6.84 g of red crystals of oxychloride A was treated with hot water, the precipitate of one-aqueous crystallohydrate B was formed. By calcination of B 4.64 g of yellow substance G may be obtained. At 300^{o}C G reacts with CCl_4 forming 7.94 g of violet compound D, which being heated in atmosphere of dry HI forms brown, amorphous, diamagnetic powder E.

- Determine substances A-E, if only 1/3 of Iodine atoms in E gives the precipitate with Ag^+.
- Write down the equations of reactions.
- Give the structural formulas of A and D. What is the hybridization state of the central atom, which has bonds with chlorine of the same length.
- Suggest the structure of E in the solid state and explain the fact that only four, but not eight atoms of Iodine, can be involved into exchange reactions.

2. Specify which of the following diatomic molecules – N_2, C_2, O_2, CN, CO and NO

a) can attach one electron forming more stable molecular ions AB^-;
b) can lose one electron forming less stable molecular ions AB^+;
c) are more stable than corresponding ions AB^+ and AB^-.

3. Distribution constant for benzoic acid (HA) water/benzene system at 10^{o}C is $K=[HA]_W/[HA]_B=0.700$. Dissociation constant of HA is $K_a=6.20\cdot10^{-5}$. In benzene HA is partially dimerized. At equilibrium state 200 ml of aqueous layer contain 0.0429 g of HA and 200 ml of benzene layer contain 0.145 g of HA.

- Give the formula for calculation of equilibrium concentration $[H^+]$ in aqueous layer.
- Calculate concentrations of all species, including $[H^+]$, in the aqueous layer.
- Calculate concentrations of the molecules and the dimerization constant (K_D) in the benzene layer.
- Show how concentrations of all forms of HA change with increasing pH.
- Explain the reason of HA dimerization.

4. Two isomers of alkene I (Ia and Ib) were subjected to transformations:

$$\left.\begin{matrix}Ia\rightarrow \\ Ib\rightarrow\end{matrix}\right| \xrightarrow{HBr} II \xrightarrow{NH_3(excess)} III \xrightarrow{CH_3I(excess)} IV \xrightarrow{Ag_2O} V \begin{cases} \xrightarrow{t^{o+},\ ethanol} Ia \\ \xrightarrow{t^{o},\ ethanol\ +\ water\ (4:1)} Ib \end{cases}$$

- Determine compounds I-V, if substance II contains 53.0% of bromine by mass and the reducing ozonolysis of both compounds Ia and Ib gives the mixture of aldehyde and ketone.
- Propose the mechanisms of reactions V→Ia and V→Ib.
- Propose the equations of reactions described above.
- Draw the geometrical isomers.

5. Usually reactions of alkillithium reagents (RLi) with amides giving ketones is ineffective. Meanwhile, Weinreb's amides, N-methoxy-N-methylamides, are the exception of this rule. When these amides react with alkillithium reagents, ketones are formed with a high yield under soft conditions.

- Explain, why common amides react with alkillithium reagents practically without formation of ketones. What products are typical for these reactions?
- Why Weinreb's amides, reacting with RLi unlike common amides, form exceptionally ketones (after treating mixtures with water)?
- Suggest the scheme of N-methoxy-N-methylamides synthesis from carbonic acid.

6. Benzaldehyde (I) was transformed into compound II by cyanhydryne synthesis with subsequent hydrolysis. Substance II has optical isomers. It can be obtained from substance X (homolog of I) according to the following scheme:

$$X \xrightarrow{Br_2/P} A \xrightarrow{NaOH} B \xrightarrow{20\ ^\circ C} C \xrightarrow{HBr} D \xrightarrow{Br_2} E \xrightarrow{2\ NaOH} F \xrightarrow{NaOH} II$$

- Suggest the structural formulas of compounds mentioned in the scheme. Take into account that A and B have optical isomers; there are four multiplets (two doublets and two singlets) with ratio of intensities 1:1:5:1 in PMR spectrum of compound B; substance C has three multiplets with ratio 2:1:5.
- Write equations of the given reactions.
- Draw optical isomers of substance II and name them in terms of R,S-nomenclature.
- Suggest the mechanism of reaction F →II.

7. The mixture of hydrocarbons A and B having one or two types of bonds C-C of different order, has mass 2.70 g and volume 12.22 L at 0.1 atm and 298 K. The mixture can be completely bromized in the solution with 16.0 g of bromine and reacts with 1.26 g of water in the presence of catalyst.

- Give the homologous series of A and B.
- Determine the qualitative and quantitative composition (in % by volume) of the mixture, if it is known that the solution containing a complex cation G (w_N≈20%)

a) reacts with A and doesn't react with products of the reaction of the mixture with water;

b) doesn't react with both initial mixture and products of the reaction with water;

c) reacts both with A and products of reaction of A with water.

Second Theoretical Tour

9 class

1. Kinetic equation for the reaction of synthesis of ammonia at iron catalyst is:

$$r = k \cdot p_{N2} \cdot \frac{p_{H2}^{1.5}}{P_{NH3}}$$

- Write down the kinetic equation for the inverse reaction of ammonia decomposing, if the reversible reaction of synthesis-decomposition of ammonia is considered to proceed under equilibrium conditions.

2. It happened in the Donetsk- Kharkov-Uzhgorod train. The post-graduate student of Kharkov University Asya Karpova headed the group of biochemistry students of Donetsk University who served as railway during their summer vacations. She noted that one of these students poured water on burning coal when some passengers were present in the tambour. Asya Karpova was horrified. During the next talk about safety precautions she emphasized the harmful influence of CO. In reply the student–conductor suggested Asya to solve the following problem:

$C(s) + H_2O = CO(g) + H_2(g)$

$$K_P = \frac{P_{CO} \cdot P_{H_2}}{P_{H_2O}}\text{ ; } \lg K_P = -6630/T + 1.57 \cdot \lg T + 2.57;$$

$m_C = 12$ kg ; $V(H_2O)_{liquid} = 1.8$ L; $t_{in\ stove} = 723\ ^oC$; p=1 atm;
$t_{in\ tambur} = 25\ ^oC$; $V_{of\ tambur} = 10\ m^3$.

Assume, that at equilibrium state there are no air in the stove, and 0.1% of gas gets into tambur from the stove.

- Calculate conversion fraction (α) and the composition of the equilibrium mixture (in % by volume).
- Calculate concentration of CO (g/cm^3) in tambour.
- Why the reaction of CO and H_2 with O_2 from air in the tambour can be neglected?
- Show the general reason of harmful influence of CO, basing on the equilibrium:
  O_2 + haemoglobin = oxyhaemoglobin.
- Who was right, the student or Asya Karpova, if maximal admitted concentration of CO is equal to 0.2 g/cm^3 during 15 minutes. Passengers spend 15 minutes in tambour.

3. Below you can see contents of the label of bottles of mineral waters:

Mirgorodska		Berezovskaya	
Chemical composition, mg/dm^3		Chemical composition, mg/dm^3	
		kations	
hydrocarbonates	300-450	Iron	0.003
sulfates	250-300	Potassium	0.0763
clorides	1000-1600	Calcium	0.074
Calcium	<50	Magnesium	0.207
Magnesium	<25	**anions**	
Sodium + Potassium	900-1200	chloride	0.0124
		sulfate	0. 037
Total mineralisation	2.5-3.5 g/dm^3	hydrocarbonates	0.4636
When standing, it becomes yellow and opalescencive.		Total mineralization	0.684 g/l
		Curative properties of this water were investigated by outstanding chemists N.N. Beketov, A.N. Butlerov, L. Lambla	

- Which components give different kinds of taste to this waters?
- What is the total mineralization of water? Ground your answer with calculations on «Berezovskaya»
- What causes of water hardness you know? Which water is harder?
- Whether concentrations of calcium and sulfate ions can both be maximum, if there is no precipitate in the water and the water is transparent? Solubility product of $CaSO_4$ is $9.1 \cdot 10^{-6}$.
- Is the above composition of «Berezovskaya» correct? Ground your answer with calculations based on the electroneutrality of water.

4.

	Chlorides (gaseous)				Chlorides (solid)				CO	C	O_2	Cl_2
	TiO_2	Ti(4+)	Fe(3+)	Al(3+)	Ti(4+) liquid	Fe(3+)	Fe(2+)	Al(3+)				
ΔH^0, kJ/mol	-938	-761	-253	-583	-805	-377	-342	-704	-110	0	0	0
S^0, J/mol·K	50	352	344	322	252	142	118	111	198	6	205	223

During industrial synthesis of $TiCl_4$, ore containing oxides of Ti(4+), Fe(3+) and Al(3+) is treated with chlorine at 2000 K. Formed gaseous mixture is carried out from the reaction zone and cooled to 500 K, and then to 298 K.

- Calculate sublimation/boiling points and show the aggregation state of chlorides at 2000 K.
- Prove with calculations that reaction $TiO_2 + Cl_2$ at 2000 K is impossible.
- Confirm with calculation a possibility of chlorination in the presence of carbon.
- Why was the gaseous mixture cooled to 500 and 298 K?
- Draw the structural formulas of chlorides in gaseous state.
- Write down the equations of reactions.

5. Draw the structural formulas of NH_4^+, $N_2H_5^+$, CO_3^{2-}, NO_3^-, RNO_2 (R - Cl, H, SbF_6^-) and answer the questions:

- Which of cations NH_4^+ or $N_2H_5^+$ is more strong oxidant?
- Why stability of anions CO_3^{2-}, NO_3^- and corresponding acids H_2CO_3, HNO_3^- differ?
- Explain the difference in oxidation-reducing properties of compounds RNO_2.

10–11 classes

1a. Borax ($Na_2B_4O_7{\cdot}10H_2O$) is frequently used for standardization of acids. Two portions of borax (m= 0.1910 g) were dissolved in 100 ml of water. First portion was titrated with 9.90 ml of hydrochloric acid, and other portion was titrated with 19.40 ml of tartaric acid solution in the presence of acid-base indicator (Methyl-red, pH of transition 4.4-6.2 or Methyl-violet, pH of transition 2.0-3.0)

- Calculate pH at equivalence point and choose indicator for titration of hydrochloric acid if $K_a = 5.75{\cdot}10^{-10}$ for $H_3BO_3{\cdot}H_2O$.
- Suggest indicator for titration by tartaric acid ($K_{a1}=1.3{\cdot}10^{-3}$, $K_{a2} = 3.0{\cdot}10^{-5}$) and explain your choice without calculations.
- Determine concentrations of acids, if they are approximately equal.

1b. Exchange reactions can be used for synthesis of sparingly soluble compounds, if yield is higher then 90%. Synthesis of Silver acetate by reaction $AgNO_3$ + NaAc is pointless Explain this the fact using the data listed below:

$AgOH = Ag^+ + OH^-$ ($K_b=5.10^{-3}$)
$AgOH(s) = Ag^+ + OH^-$ ($K_{s1} = 2{\cdot}10^{-4}$)
$HAc = H^+ + Ac^-$ ($K_a = 1.8{\cdot}10^{-5}$)
$AgAc(s) = Ag^+ + Ac^-$ ($K_{s2} = 4.4{\cdot}10^{-3}$)
$H_2O = H^+ + OH^-$ ($K_w = 10^{-14}$)
C° of salts = 0.1 mol/l

- Calculate pH interval for synthesis and show that pH of initial solutions gets to this interval.
- Give the formula for calculation of NaAc solution volume, required to obtain yield of 90%. (V°($AgNO_3$)=0.1 L).
- Estimate pH of the saturated solution of AgAc and the solubility of salt (S). Prove that the precipitate can't be washed by water, if 30 ml of water is spent for 1g of the precipitate.
- Estimate the possibility to use HAc for this synthesis with calculation of its required concentration.
- Suggest a method for synthesis of AgAc with the use of HAc.

2a. Three elements A, B, C form a number of compounds, structural characteristics of which are described in «Structural Inorganic Chemistry» by A. Wells.

Formula	Content, mass %			Bond length, A			Angle, degree			Hybridization of B
	A	B	C	A-A	B-C	B-A	A-B-A	A-B-C	C-B-C	
	18.60	X	X	-	1.56	1.41	-	107	93	
	X	25.81	X	-	1.54 1.58		-	____ 90	90 110 180	
	X	X	37.25	-	1.55		118	X	97	
B_2AC_{10}	5.93	23.70	70.37	-	1.56	1.59	-	90	90	
$B_2A_2C_{10}$	X	X	X	1.46			-		____ 180	sp^3d^2
$B_2A_5C_2$	X	X	X	-	1.56	1.42	115		-	sp^3
$B_2A_6C_2$	X	X	X			1.42 1.66		107	-	sp^3

- Determine the atomic weights of elements if A and B belong to the same group, A and C belong to the same period of the Mendeleev Periodic Table.
- Give completely filled table. Underline added figures and formulas.
- Give structural formulas of molecules.
- Suggest structural formulas of BA_3C_2 and BAC_6, if each of them contains one bond A–C

2b. Oxygen molecule (length of O-O bond 0.121 nm) can attach two atoms of fluorine almost without increasing the length of O-O bond (0.122 nm). If hydrogen is attached, the bond length is increased to a marked degree (0.148 nm). When dimer N_2O_2 is formed, the length of N-O bond remains almost constant and bond N-N is faint. Similar faint bond occurs in the dimer Cl_2O_2 molecule.

- Suggest structural formulas of O_2, F_2O_2, H_2O_2, N_2O_2 and Cl_2O_2.
- Specify orders of O-O and O-X bond in this molecules.

3. Analysis of Arsenic in the presence of Antimony is made by March reaction:

$$As_2O_3 + 12\ H^+ + 6\ Me \rightarrow 2\ AsH_3 + 6\ Me^{2+} + 3\ H_2O, \qquad (1)$$

$$2\ AsH_3 \xrightarrow{t} 2\ As + 3\ H_2, \qquad (2)$$

where Me is a metal.

The following data were obtained for the decomposition of arsine at 310°C:

t, hours	0	5.5	6.5	8.0
P total, mm m. col.	1833.30	1905.76	1918.09	1935.32

- Is this reaction reversible, if the standard Gibbs energy of arsine formation is $\Delta G°(AsH_3) = +68.9$ kJ/mol?
- Using the standard electrode potentials
  $\varphi° As_2O_3/AsH_3 = -0.11V$, $\varphi° Sn^{2+}/Sn = -0.14V$,
  $\varphi° Sb_2O_3 = -0.37V$, $\varphi° Zn^{2+}/Zn = -0.76V$,

find partial pressure of AsH_3 for the initial mixture, if 1.5-fold surplus of metal and H^+ were used in reaction (1).

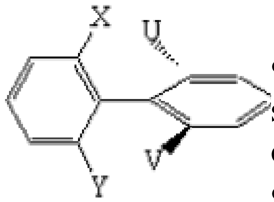
- Determine order of reaction (2) and calculate rate constant at 310 °C.
- Assuming activation energy of reaction (2) E = 118.4 kJ/mol, estimate at which temperature 99% of AsH_3 are decomposed within 1 hour.

4a. The compound A ($C_7H_6O_2$) can be synthesized from phenol in one stage. It reacts with acetic anhydride in the presence of Sodium acetate forming bicyclic product B ($C_9H_6O_2$). If B is successively treated with bromine and with excess of KOH aqueous solution, and then the formed mixture is acidified with HCl, the colorless crystals of compound C are precipitated from solution. When heated, substance C forms a substance D and a colorless gas E. Compound A reacts with chloracetic acid in the presence of bases giving, with a low yield, a mixture of C and D and also gas E. The compound A is present among the products of reducing ozonolysis of D.

- Determine the structures of all compounds. Give the equations of the reactions.
- Suggest the mechanism of the transformation of B into C.
- Propose a way to obtain A from phenol in one stage.

4b. Atropoisomerism is a special kind of stereoisomerism. Biaryls shown in the picture are the classical examples of compounds demonstrating atropoisomerism.

- What can you say about X,Y,U and V if atropoisomerism is observed in biaryls? Choose the correct answer: a) X=Y=U≠V; b) X≠Y and U≠V; c) X≠V and Y≠U.



- The condition (a, b or c) chosen is necessary but it is not sufficient. In what cases biaryl is achiral, even when this condition is satisfied?
- What is the minimal number of the ortho-substituents at which atropoisomerism in the substituted biaryls is observed?
- Give an example of substituted biphenyl with all identical orto-substituents which can display atropoisomerism.

• Suggest the scheme of synthesis of biphenyl which demonstrates atropoisomerism.

5. The mixture containing aniline, glycerol and nitrobenzene was heated in the presence of ferric sulfate and sulfuric acid. In the course of the reaction the formation of the intermediate compounds A ($C_9H_{11}ON$), B ($C_9H_{11}ON$), C (C_9H_9N) and, filially, the product of the reaction D (C_9H_7N) and one of the starting materials were observed. Being heated with Potassium permanganate in alkali medium, substance D transforms into compound E ($C_6H_5O_2N$). As a result of decarboxylation, E produces substance F. Treating compound F with ammonia at heating produces compound G which is a well known vitamin. This substance is a co-factor (non-protein part) of the ferment Succinatedehydrohenaza as the cofactor (non-protein part of the ferment).

- Determine the structures of substances A-G.
- Write down the corresponding equations of the reactions.
- What is the role of nitrobenzene in this process?
- What is the structure of the co-factor containing G? Write down its full and short names.
- What is the substrate of the reaction catalyzed with ferment (succinic or malonic acid)? What are the reasons for your choice?
- What is the product of the dehydrohenization reaction of this substrate?
- Write down the general scheme of action of the ferment which causes the reaction.
- Does this reaction accumulate the energy? Explain your answer.

Examples of laboratory problems (experimental tour) 11 class

Demands for carrying out the experiment and making an account

1. You may begin the experiment after you have taken a permission and also methodical instructions for its execution given by teacher.
2. To take a permission for carrying out the experiment it's necessary to work out the plan of the synthesis which contains such parts as: a) equations of general and side reactions; b) scheme of the device; c) short description of the method of the synthesis; d) execution of rules of safety precautions.
3. Making an account you have a) to describe shortly the effects observed during the synthesis; b) to calculate the experimental and theoretical yields of the product; c) to propose a method of the purification of obtained product.

Synthesis of β-naphthylacetate

Reagents:		Equipment
• β-naphthol	5 g	• 250 ml round flask
• acetic anhydride	5.3 ml	• air reflux condenser
• Sodium hydroxide	2.8 g	• graduated cylinder-2
• distilled water	25 ml	• stand
• pounded ice	63 g	• 2 clamps (for flask and reflux condenser)
• ethanol for recrystallization		• Shot filter
		• glass rod
		• filter flask
		• beaker
		• filter paper
		• devise for indication of malting point

Dissolve 2.8 g of Sodium hydroxide in 25 ml of water in a 250 ml-round flask, add 5 g of recrystallized β-naphthol and mix until complete dissolving. Then add 63 g of pounded ice and acetic anhydride (5.3 ml).

Warning! Acetic anhydride irritates skin.

Close flask with a cork with air reflux condenser, vigorously mix the mixture, wash at a filter with water and dry on air. Purify the product by recrystallization from diluted ethanol. The yield of β-naphthilacetate is 6.5 g. β-naphthilacetate is colorless crystal substance, which crystallizes from ethanol as needle crystals. It is soluble in ethanol, ester, chloroform and insoluble in water.

Identification of substances

There are substances in five test tubes without inscriptions on them.

- solution of phenol
- solution of hydroquinone
- $FeCl_3$ solution
- C_2H_5OH
- Sodium acetate solution

Using no other reagents determine content of each test tube. Write down the equations of relevant reactions.

Answers

First Theoretical Tour

8 class

2. Ideal case: $CuSO_4 + 2\ NaOH \rightarrow Cu(OH)_2 + Na_2SO_4$

$n(Cu^{2+}) = 0{,}025\ L\cdot 0{,}100\ mol\cdot L^{-1} = 2{,}5\cdot 10^{-3}$ mol

$n(OH^-) = 0{,}01875\ L\cdot 0{,}200\ mol\cdot L^{-1} = 3{,}75\cdot 10^{-3}$ mol

$n(Cu^{2+})/n(OH^-) = 2{,}5\cdot 10^{-3}/3{,}75\cdot 10^{-3} = 0{,}67$

Elementary composition is $Cu_m(OH)_n(SO_4)_p$:

$p = m-n/2$; for $n=1$ $m=0{,}67$ and $p=0{,}17$

$Cu_{0,67}(OH)(SO_4)_{0,17}$ or $Cu_4(OH)_6(SO_4)$ or $3Cu(OH)_2\cdot CuSO_4$

Equations:

General: $mCuSO_4 + n\ NaOH \rightarrow Cu_m(OH)_n(SO_4)_{m-n/2} + n/2Na_2SO_4$

In this case: $4CuSO_4 + 6NaOH \rightarrow Cu_4(OH)_6(SO_4)\downarrow + 3Na_2SO_4$

3. 1) In 1 L: $n(Cl^-) = (1{,}3\ g) / (35{,}5\ g/mol) = 3{,}66\cdot 10^{-2}$ mol

$n(HCO_3^-) = (0{,}4\ g) / (61\ g/mol) = 6{,}6\cdot 10^{-3}$ mol

$n(SO_4^{2-}) = (0{,}3\ g) / (96\ g/mol) = 3{,}1\cdot 10^{-3}$ mol

$n(Ca^{2+}) = (0{,}05\ g) / (40\ g/mol) = 1{,}5\cdot 10^{-3}$ mol

$n(Mg^{2+}) = (0{,}025\ g) / (24\ g/mol) = 1{,}0\cdot 10^{-3}$ mol

2) $n(Na+K) = 3{,}66\cdot 10^{-2} + 6{,}6\cdot 10^{-3} + 2\cdot 3{,}1\cdot 10^{-3} - 2\cdot 1{,}5\cdot 10^{-3} - 2\cdot 1{,}0\cdot 10^{-3} = 4{,}44\cdot 10^{-2}$ mol

If there is only Na^+ in water, than $m(Na^+) = 23\cdot 4{,}44\cdot 10^{-2} = 1{,}02$ g (in 1 L)

If there is only K^+ in water, than $m(K^+) = 39\cdot 4{,}44\cdot 10^{-2} = 1{,}73$ g (in 1 L)

Hence, the total mass 1020 mg/L < m(Na+K) < 1730 mg/L

3) Mass of residue after evaporation:

$2\ HCO_3 \rightarrow CO_3^{2-} + H_2O + CO_2$

$n(HCO_3^-)_{in\ 1\ L} = 6{,}6\cdot 10^{-3}$ mol; $n(CO_3^{2-})$=n(residue) $= 3{,}3\cdot 10^{-3}$ mol

$m(CO_3^{2-}) = 60\ g/mol\cdot 3{,}3\cdot 10^{-3}\ mol = 0{,}198$ g

Loss of weight at evaporation of 1 L: $\Delta m = 0{,}400\ g - 0{,}198\ g = 0{,}202$ g

m(residue) = (2898 — 3618) mg/L .

4) $BaCl_2 + 2NaHCO_3 \xrightarrow{100^\circ C} BaCO_3\downarrow + 2NaCl + CO_2 + H_2O$

$BaCl_2 + Na_2SO_4 \rightarrow BaSO_4\downarrow + 2NaCl$

$n(BaCO_3) = n(CO_3^{2-}) = 3{,}3\cdot 10^{-3}$ mol

$m(BaCO_3) = 197\ g/mol \cdot 3{,}3\cdot 10^{-3} = 0{,}650$ g

$n(BaSO_4) = n(SO_4^{2-}) = 3{,}1\cdot 10^{-3}$ mol

$m(BaSO_4) = 233\ g/mol\cdot 3{,}1\cdot 10^{-3}\ mol = 0{,}722$ g

m(precipitate) = 0,650 + 0,722 = 1,372 g

5. $2M + 2HCl \rightarrow 2MCl + H_2$ (in excess of acid)

53,2/a mol 67,4/(A+35,5 mol)

53,2/A = 67,4/(A+35,5); A = 133g/mol - Cs.

2) $2M + 2HCl \rightarrow 2MCl + H_2$;

0,4 0,4 0,4 0,2

$\nu_{HCl} = 49{,}03\cdot 29{,}78/(100\cdot 36{,}5) = 4{,}4$ mol

$2M + 2H_2O \rightarrow 2MOH + H_2$

53,2/A-0,4 1,913 1,913

$\nu_{H2O} = (49{,}03 - 36{,}5\cdot 0{,}4)/18 = 1{,}913$ mol

53,2/A - 0,4 = 1,913; A = 23 g/mol - Na

3) $2M + 2HCl \rightarrow 2MCl + H_2$ (M is in excess)
0,4 0,4 0,4
$2M + 2H_2O \rightarrow 2MCl + H_2$
1,913 1,913 1,913
53,2>2,313A; A<23 g/mol - Li.

6. 1) $\rho_{A2} : \rho_{B2} : \rho_{C2} = M_{A2} : M_{B2} : M_{C2} = 16:19:1 = 32:38:2$
$A_2 \rightarrow O_2$; $B_2 \rightarrow F_2$; $C_2 \rightarrow H_2$

2) $2H_2 + O_2 \rightarrow 2H_2O(l)$ | $H_2 + F_2 \rightarrow 2\,HF$

H_2	O_2	H_2O	H_2	F_2	HF
5	1	0	3	3	0
2	1	2	3	3	6
3	0	2	0	0	6

$I_{nitial}/V_{final} = P_{intail}/P_{final} = 9/6 = 1{,}5$.
Starting temperature was 273 K and after explosion it increased to 273+69 = 333 K. Allowing for the change of pressure:
$P_{initial} / 273 = P_{final} / 333$; $P_{final} = 1{,}2P_{starting}$
So, the pressure changes in 1,5/1,2=1,25 times (decreases).

3) $H_2 + F_2 \rightarrow 2HF$; $2H_2 + O_2 \rightarrow 2H_2O$;
$4HF + SiO_2\text{(from glass)} \xrightarrow{H_2O} SiF_4 + 2H_2O$;
$SiF_4 + 3H_2O \rightarrow H_2SiO_3 + 4HF$;
(general equation: $ySiF_4 + (x+2y)H_2O \rightarrow xH_2O\cdot ySiO_2 + 4yHF$).

4) $xH_2O\cdot ySiO_2$
$E \rightarrow Si$
39,5%=28y/(18x+60y); 6,462x+21,54y=28y;
when x=1, y=1 H_2SiO_3.

5) Mass of D will decrease until water presents:
$SiO_2 + H_2O \rightarrow H_2SiO_3$ $\nu_{H2O} = 2\nu_{O2} = 2\cdot 201{,}6\cdot 10^{-3}/(9\cdot 22{,}4) = 2\cdot 10^{-3}$ mol
$\nu_{H2SiO3} = 2\cdot 10^{-3}$; $m_{H2SiO3} = 0{,}156$ g.

6) In the absence of gas A after reaction $H_2 + F_2 \rightarrow 2HF$ all processes will stop as dissolving SiO_2 in HF is possible only in the presence of water.

9 class

1. The decomposition can pass by two reaction
1)$N_2H_4 = N_2 + 2H_2$,
$\nu(N_2H_4) = 10{,}000$ g/32,06 g/mol = 0,3119 mol = $\nu(N_2) = 1/2\nu(H_2)$,
$\nu\Sigma = \nu(N_2) + \nu(H_2) = 0{,}9357$ mol
$P = \nu\Sigma RT/V = 2229384$ Pa = 2229,4 kPa.
2) $N_2H_4 \rightarrow 4/3NH_3 + 1/3N_2$,
$\nu(N_2) = 1/3\nu(N_2H_4) = 0{,}1040$ mol;
$\nu(NH_3) = 0{,}4159$ mol, $\nu\Sigma = 0{,}5199$ mol,
P = 1238,7 kPa
So, decomposition of N_2H_4 is passed by both reactions 1) and 2).
Summary amount of gases after reaction is:
$\nu\Sigma = PV/RT = 0{,}5823$ mol.
If x mol of 1 mol of N_2H_4 are decomposed by reaction 1) and (1-x) mol – by reaction 2), then:
$0{,}5823 = x\cdot 0{,}9357 + (1-x)\cdot 0{,}5198$, x=0,1501.
$\nu(N_2) = 0{,}1501\cdot 0{,}3119 + 0{,}8499\cdot 0{,}1040 = 0{,}1352$ mol (3,786 g)
$\nu(H_2) = 0{,}0936$ mol (0,187 g)
$m(NH_3) = 10{,}000 - 3{,}786 - 0{,}187 = 6{,}027$ g;
$\omega(N_2) = 37{,}68\%$; $\omega(H_2) = 1{,}87\%$; $\omega(NH_3) = 60{,}27\%$.

2. Colorless gas with M=32 g/mol is O_2, $X \rightarrow A + B + O_2$.
Mixture 2 at 150 °C contains B and O_2, $V_2 = V(B) + V(O_2)$. At 150 °C $V(O_2)$ exceeds the volume of the same amount of O_2 at 30 °C in 423K/303K=1,396 times, so
$(V(B) + V(O_2))/V(O_2) = 4{,}188/1{,}396 = 3$, $V(B):V(O_2)=2:1$, in mixture 2.
$\varphi(B)=2/3$, $\varphi(O_2)=1/3$. The average molar mass of the mixture is
$2\cdot D_{H2}=41{,}4$ g/mol, $2/3\mu(B)+1/3\cdot 32=41{,}4$;
$\mu(B)=46$ g/mol
$B \rightarrow NO_2$; X - nitrate;
At 459 °C the volume of mixture 2 exceeds the volume of the same mixture at 150 °C in 723K/423K=1,709 times. So, at 450 °C
$(V(A) + V(N)_2) + V(O_2))/(V(NO_2) + V(O_2)) = 1{,}333$
$V(A):V(NO_2):V(O_2)=1:2:1$, $\varphi(A)=\varphi(O_2)=1/4$; $\varphi(NO_2)=1/2$.
The average molar mass of mixture 1 is equal to 81,2 g/mol,
$1/4\mu(A)=1/2\cdot 46+1/4\cdot 32=81{,}2$; $\mu(A)=201$ g/mol,
A – Hg, X – $Hg(NO_2)_2$.

$$Hg(NO_3) \xrightarrow{450^\circ C} Hg + 2NO_2 + O_2;$$

$$Hg(NO_3)_2 \xrightarrow{360^\circ\text{-}400^\circ C} HgO + 2NO_2 + 1/2O_2.$$

$$2\,NO_2 + 2\,NaOH \rightarrow NaNO_3 + NaNO_2 + H_2O$$

3. 1) B – PX_n; $91{,}2=31\cdot 100/(31+nM_x)$; $M_x=2{,}99/n$, when n=3 $M_x=1$
X – H; A – H_2; B – PH_3.
2) $\nu_{PH3}=\nu_{HI}=0{,}04\cdot 0{,}1=0{,}004$ mol; $\nu°_P=6{,}2/31= 0{,}2$ mol; $\nu°_{H2}=5/2=2{,}5$ mol;

$2P$	+ $3H_2$	= $2PH_3$.	
0,2	2,5	0	
0,004	0,006	0,004	$\varphi_{PH3}=0{,}004\cdot 100/(0{,}004+2{,}494)=0{,}16\%$
0,196	2,494	0,004	

3) $P=\nu RT/V=2{,}498\cdot 8{,}314\cdot 623/0{,}300=43129$ Pa
$P_{PH3} = 0{,}0016\cdot 43129=69$; $P_{H2}=43060$ Pa;
$K_P=69^2/43060^3=5{,}96\cdot 10^{-11}$ Pa^{-1}; $\alpha=0{,}004\cdot 100/0{,}2=2\%$.
4) Even at high pressure yield is small. There is no reason to use this reaction.
5)
```
  H
  |
  P:
 / \
H   H
```
$PH_3 + HCl \neq$; $PH_3 + HNO_3$ = (mixture of products of oxidation).

4. 1) $M_{average}=38{,}2\cdot 2=76{,}6$ g/mol. The mixture contains NO_2 and N_2O_4.
$76{,}6=\varphi_{NO2}\cdot 46+(1-\varphi_{NO2})\cdot 92$; $\varphi_{NO2}=0{,}335$ (33,5%).
$\varphi_{N2O4} = 1-0{,}335 = 0{,}665$(66,5%).
2) $x \rightarrow$ in NO_2; $\nu_x=0{,}775/A_x$; $\nu_{NO2}=5{,}75/46=0{,}125$ mol;
$0{,}775b/A_x=0{,}125$; $A_x=6{,}2b$ when b=5 $A_x=31$ — P.
3) $\nu_{H3PO4}=\nu_P$ $0{,}125/5=0{,}025$ mol
$\nu_{HNO3} = 0{,}1\cdot 1-0.025\cdot 3=0{,}025$ mol; $\nu_{H3PO4} : \nu_{HNO3} = 1:1$.

5. 1) $Ag^+ + Cl^- = AgCl\downarrow$, $Ag^+ + 2Cl^- = AgCl_2^-$;
2) $2Fe^{3+} + 2I^- = 2\,Fe^{2+} + I_2$;
4) $H_2S + I_2 = S\downarrow + 2HI$;
5) $I^- + HClO_3 = IO_3^- + H^+ + Cl^-$;
7) hydrolysis:

$$Cr^{3+} \xrightarrow{H_2O,\ -H^+} CrOH^{2+} \xrightarrow{H_2O,\ -H^+} Cr(OH)_2^+ \xrightarrow{H_2O,\ -H^+} Cr(OH)_3$$

$$HCO_3^- \xrightarrow[-OH^-]{H_2O} H_2CO_3$$

8) $Cr^{3+} + 3NH_3 + 3H_2O = 3NH_4^+ + Cr(OH)_3\downarrow$;

9) $SnCl_4 + 4CO_3^{2-} + (2+x)H_2O = SnO_2 \cdot xH_2O + 4Cl^- + 4HCO_3^-$;

11) $Fe^{3+} + 6F^- = FeF_6^{3-}$;

12) Addition of $AgNO_3$ results in decomposition of complex $[Fe(SCN)_4]^-$;

$[Fe(SCN)_4]^- = [Fe(SCN)_3] + SCN^-$ $\quad$ $[Fe(SCN)_3] = [Fe(SCN)_2]^+ + SCN^-$

$[Fe(SCN)_2]^+ = [Fe(SCN)]^{2+} + SCN^-$ $\quad$ $[Fe(SCN)]^{2+} = Fe^{3+} + SCN^-$,

$Ag^+ + SCN^- = AgSCN\downarrow$, $\quad$ $AgSCN + SCN^- = [Ag(SCN)_2]^-$;

13) Precipitate of AgCl and ammonia complexes of Cu(II) are formed:

$[Ag(NH_3)_2]^+ \leftrightarrow Ag^+ + 2NH_3$, $Ag^+ + Cl^- = AgCl\downarrow$,

$Cu^{2+} + iNH_3 = [Cu(NH_3)_i]^{2+}$, i=1,2,3,4;

14) $HSO_3^- + H_2O = H_2SO_3 + OH^-$, $\quad$ $H_2SO_3 = H_2O + SO_2$;

$$Al^{3+} \xrightarrow{H_2O,\ -H^+} AlOH^{2+} \xrightarrow{H_2O,\ -H^+} Al(OH)_2^+ \xrightarrow{H_2O,\ -H^+} Al(OH)_3$$

6. $UO_3 + 2NH_3 + H_2O = (NH_4)_2UO_4$;

$2UO_3 + 2NH_3 + H_2O = (NH_4)_2U_2O_7$;

$UO_3 + 2HNO_3 = UO_2(NO_3)_2 + H_2O$.

$U_3O_8 \equiv UO_2 \cdot 2UO_3$, or UOU_2O_7.

Two interpretations of this compound are possible:

a) double or combined oxide (uranium oxide (IV,VI));

b) salt: uranium uranate, oxyuranium(IV) diuranate.

7. Total composition of «Greek fire» and the mechanism of its action are not completely known. Its action in some respects resembles the action of napalm. «Greek fire» couldn't be extinguished with any methods known that time. It contains such groups of substances as combustible substances; connective substances, which have high viscosity even at high temperatures; substances, which have high adhesion properties; sources of oxygen (in absence of air); catalysts.

10 class

1. 1) $\nu_{Pb(NO3)2}:\nu_A = 1,3240/331:0,1 \cdot 0,02 = 2:1$ (anion in A is X^{4-}).

$2Pb^{2+} + X^{4-} \rightarrow Pb_2X\downarrow$

$4 \cdot 10^{-3}$ $\quad$ $2 \cdot 10^{-3}$ $\quad$ $2 \cdot 10^{-3}$

$M_{Pb2X} = 1,252/2 \cdot 10^{-3} = 626$; $\quad$ $M_X = 212$.

$2Fe^{2+} + X^{4-} \rightarrow Fe_2X\downarrow$

0,01 $\quad$ 0,005

$\nu_{FeCl2} = 1,2700/127 = 0,01$; $M_{FeX2} = 1,62/0,005 = 324$; $\nu_{Fe} = 324 \cdot 0,5185/56 = 3$;

C – $Fe_2[FeY_6]$; $M_Y = (324-3 \cdot 56)/6 = 26$; $\quad$ $1,72=\sqrt{n(n+2)}$; $n\approx1$, Fe^{2+}; $\quad$ $\mu=0$, Fe^{3+}.

Y – CN

A – $K_4[Fe(CN)_6]$; B – $K_3[Fe(CN)_6]$; C – $Fe_2[Fe(CN)_6]$;

D, E – $KFe[Fe(CN)_6]$.

2) $K_4[Fe(CN)_6] + 2Pb(NO_3)_2 \rightarrow Pb_2[Fe(CN)_6]\downarrow + 4KNO_3$

$K_4[Fe(CN)_6] + 2FeCl_2 \rightarrow Fe_2[Fe(CN)_6]\downarrow + 4KCl$

$2Fe_2[Fe(CN)_6] + 2K_4[Fe(CN)_6] + O_2 + H_2O \rightarrow 4KOH + 4KFe[Fe(CN)_6]\downarrow$

$K_3[Fe(CN)_6] + FeCl_2 \rightarrow KFe[Fe(CN)_6]\downarrow + 2KCl$

3) $KFe^{2+}[Fe^{3+}(CN)_6]$ and $KFe^{3+}[Fe^{2+}(CN)_6]$ are one and the same compound.

2. 1) $\nu_{NO2+O2} = 26,88/1,2 = 1,2$; $\nu_{O2} = 1,2/6 = 0,2$; $\nu_{NO2} = 1$ mol

$\varphi_{NO2} = 100/1,2 = 83,3\%$; $\varphi_{O2} = 0,2\cdot100/1,2 = 16,7\%$; $\nu_{NO2} : \nu_{O2} = 5:1$;

$2Me(NO_3)_2 = 2MeO + 4NO_2 + O_2$; $\nu_{NO2} : \nu_{O2} = 4:1$,

O_2 oxidize BO to B_2O_x.

2) $2A(NO_3)_2 = 2AO + 4NO_2 + O_2$; $2B(NO_3)_2 = 2BO + 4NO_2 + O_2$;

a a 2a 0,5a b b 2b 0,5b

$2BO_2 + (x\text{-}2)/2O_2 = B_2O_x$; $\Delta\nu_{O2} = 1\cdot1/4 - 0,2 = 0,05$ mol;

b b(x-2)/4

$b(x\text{-}2)/4 = 0,05$; $b = 0,2/(x\text{-}2)$; $Me(NO_3)_2 \rightarrow 2NO_2$;

$M_{average} = 83,5/0,5 = 167$ g/mol; $M_{average,\ Me} = 167-124 = 43$ g/mol;

A – Ca (M_A=40 g/mol).

$M_{average} = (40a+b\cdot M_B)/0,5$; $2a+2b=1$, $a=(1-2b)/2= 0,5-0,2/(x-2)=(0,5x-1,2)/(x-2)$;

$43= (40(0,5x-1,2)+0,2M_B)/((x-2)\cdot0,5)$;

$x = 4$; $M_B = 55$ g/mol – Mn.

3) a=0,4; b=0,1. $X_{Ca(NO3)2} = 0,4\cdot100/0,5 = 80\%$; $X_{Mn(NO3)2} = 20\%$.

4) $2Ca(NO_3)_2 = 2CaO + 4NO_2 + O_2$; $Mn(NO_3)_2 + 2NO_2$;

$2NO_2 + 2NaOH = NaNO_3 + H_2O$.

5) $xCaO + MnO_2 = Ca_xO_{x-1}MnO_3$ ($4 \geq x \geq 1$), basic manganates.

3. 1) $dC_A/d\tau = -k_1C_A$; $dC_B/d\tau = k_1C_A - k_2C_B$; $dC_C/d\tau = k_2C_B$.

$2\tau_{1/2} = \ln2/k_1$; $\tau_{1/2} = \tau$.

$$\frac{\ln(k_1/k_2)}{k_2 - k_1} = \ln2/k_1; \quad k_1/k_2 = x, \ \ln x/(x-1) = \ln2; \quad x=2.$$

4. 1) $\Delta H°$ and $S°$ for H^+ are equal to 0: $\Delta H°_{H2O} - \Delta H°_{OH-} = -56$ kJ/mol

$\Delta H_n° = \Delta H_{3-n}° - \Delta H_{3-n+1}° - 56$; $\Delta S_n° = S_{3-n}° - S_{4-n}° + 81$; $\Delta G° = \Delta H° - T\Delta S°$

$\Delta H_1° = -1296+1288-56 = -64$ kJ/mol; $\Delta S_1° = 90-158+81 = 13$ J/mol·K; $\Delta G_1° = -68$ kJ/mol

$\Delta H_2° = -1296 + 1292 - 56 = -52$ kJ/mol; $\Delta S_2° = -33-90+81 = -42$ J/mol·K; $\Delta G_2° = -39,5$ kJ/mol

$\Delta H_3° = -1277+1292-56 = -41$ kJ/mol; $\Delta S_3° = -220+33+81 = -106$ J/mol·K; $\Delta G_3° = -9,5$ kJ/mol.

2) $\Delta G°_{H2O} = -56-0,081\cdot298\cdot(-80)$; $\ln K = -\Delta G_x°/RT$; $K = e^{-\Delta Gx°/RT}$

$H_3PO_4 = H^+ + H_2PO_4^-$; $\Delta G_a° = \Delta G_1° - \Delta G°_{H2O} = -68+80 = 12$ kJ/mol; $K_1 = 7,9\cdot10^{-3}$

$H_3PO_4 = 2H^+ + HPO_4^{2-}$; $\Delta G_b° = -39,5+80 = 40,5$ kJ/mol; $K_2 = 8,0\cdot10^{-8}$

$H_3PO_4 = 3H^+ + PO_4^{3-}$; $\Delta Gc° = -9,5+80 = 70,5$ kJ/mol; $K_3 = 4,4\cdot10^{-13}$

3) a) The mixture of two acidic salts ($\nu_{OH-} = 0,1\cdot V_2$; $\nu_{H3PO4} = 0,1\cdot V_1$)

$64\cdot0,1V_1+(0,1V_2-0,1V_1)\cdot52=0,09$; $1,2V_1+5,2V_2=0,09$; $V_1+V_2=0,025$.

$4V_2=0,06$; $V_2=0,015$ L; $V_1=0,025-0,015=0,01$ L.

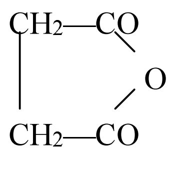
b) The mixture of acidic and normal salts:

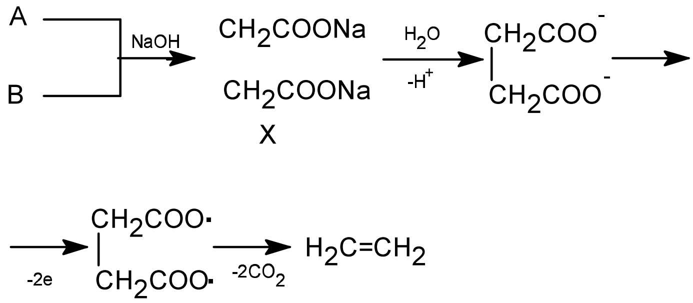
$V_1=0,0071$ L; $V_2=0,0175$ L.

5.

A — HOOC–(CH2)2–COOH

B —





$X + NaOH \xrightarrow{t^o,\ -Na_2CO_3} CH_3—CH_3$ (D)

(C)+$Br_2 \rightarrow CH_2Br—CH_2Br$ mechanism A_E

(D)+$Br_2 \xrightarrow{h\nu} CH_3CH_2Br$ mechanism A_R

(C)+$KMnO_4 \rightarrow CH_2(OH)$-$CH_2(OH)+MnO_2+KOH$.

6. 3) The rate of addition is increased according to the raw: I_2, IBr, Br_2, ICl, BrCl, Cl_2 .

4)

a) $CH_3CH_2\overset{+\delta}{C}H=\overset{-\delta}{C}H_2 + \overset{+\delta}{Br}Cl \rightarrow CH_3CH_2CHCl—CH_2Br$

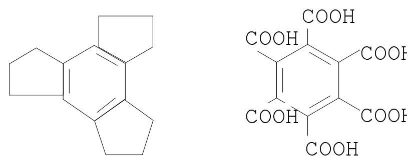
b) $CH_3CH_2\overset{+\delta}{C}H=\overset{-\delta}{C}HCH_3 + BrCl \rightarrow CH_3CH_2CHCl—CHBr—CH_3$

c) $\overset{+\delta}{C}H_2=\overset{-\delta}{C}H—COOH + BrCl \rightarrow ClCH_2—CHBr—COOH$

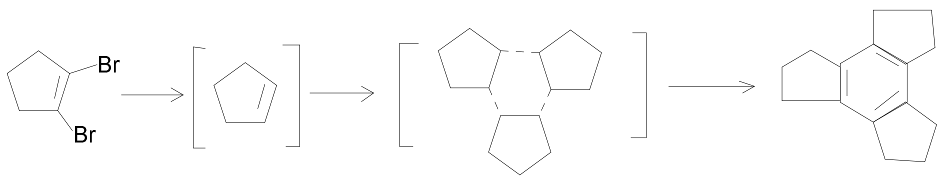
d) $:Br—\overset{+\delta}{C}H=\overset{-\delta}{C}H_2 + BrCl \rightarrow BrCHCl—CH_2Br$

5) $CH_3CH=CH_2 + Br_2 + H_2O \rightarrow CH_3CH(OH)—CH_2Br$

7. Compound B is mellitic acid $C_6(COOH)_6$.



As compound B contains benzene ring, the trimerization takes place:



11 class

1. 1) $2MO_xCl_{n-2x} \rightarrow M_2O_n$ $68{,}4/(A+35{,}5n-55x)=4{,}64/(2A-16n)$;
$A=50n-116x$

$M_2O_n \rightarrow 2MCl_2$ $4{,}64\cdot2/(2A+16n)=7{,}94/(A+35{,}5n)$; $A=30{,}67n$.

$50n-116x=30{,}67n$; $n=6x$ $(n=6, x=1)$ A=184 g/mol

A – $WOCl_4$; B – $WO_3\cdot H_2O$; G – WO_3; D – WCl_6; E – $[W_6I_8]I_4$

2) $WOCl_4 + 3H_2O = WO_3\cdot H_2O\downarrow + 4HCl$;

$WO_3\cdot H_2O=WO_3 + H_2O\uparrow$; $2WO_3 + 3CCl_4 = 2WCl_6 + 3CO_2$;

$6WCl_6 + 36HI=[W_6I_8]I_4 + 36HCl + 12I_2$; $[W_6I_8]I_4 + 4AgX = 4AgI + [W_6I_8]X_4$.

3) The central ion (W) is in the following hybridization states: $dsp^3(WOCl_4)$, d^2sp^3 (WCl_6)

2. Basing on MO energy diagram it's possible to find orders (***P***) of bonds for each molecule:

P = (number of e^- at bonding orbitals - number of e^- atnibonding orbitals) /2.

Calculated values of ***P*** are as follows:

	N_2	C_2	O_2	CN	CO	NO
AB	3	2	2	2,5	3	2,5
AB^-	2,5	2,5	1,5	3	2,5	2
AB^+	2,5	1,5	2,5	2	2,5	3

a) C_2^-, CN^-; b) C_2^+, NO^+; c) N_2, CO.

3. 1) $[A^-] + [OH^-] = [H^+]$; $K_aC_w°/(K_a+[H^+])+K_w/[H^+] = [H^+]$;

$[H^+]^3 + K_a[H^+]^2 - (K_aC_w° + K_w)\cdot[H^+]\cdot K_wK_a=0$;

2) $C_w°=0{,}0429/(122\cdot 0{,}2)= 1{,}76\cdot 10^{-3}$ mol/l;

$C_b°=0{,}145/(122\cdot 0{,}2)=5{,}94\cdot 10^{-3}$ mol/l;

$[H^+]^2 + K_a[H^+] - K_aC_w°=0$; $[H^+]^2 + 6{,}2\cdot 10^{-5}[H^+]-1{,}09\cdot 10^{-7}=0$;

$[H^+]=3{,}00\cdot 10^{-4}$; pH=3,52;

$[A^-]=3{,}01/10^{-4}$; $[HA]=1{,}46\cdot 10^{-3}$;

$[OH]=3{,}33\cdot 10^{-11}$;

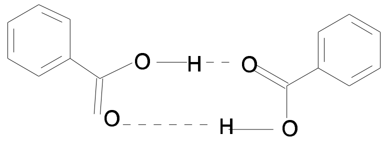
3) $[HA]_b=[HA]_w/K=1{,}46\cdot 10^{-3}/0{,}700=2{,}09\cdot 10^{-3}$;

$[(HA)_2]_b=(C_b°-[HA]_b)\cdot 0{,}5=1{,}93\cdot 10^{-3}$;

$K_D=[(HA)_2]/[HA]^2 = 442$.

4) Aqueous layer: $[A^-]$ increases; benzene layer: [HA], $[(HA)_2]$ decreases.

5)



→ hydrogen bond

4. 1) C_nH_{2n} (I); $C_nH_{2n+1}Br$ (II); W_{Br} = 53,0%; $53.0=80\cdot 100/(14_n+81)$; n=5;

C_5H_{10}; Taking into account ozonolysis:

$CH_2=C(CH_3)CH_2CH_3$ (Ib); $CH_3CH=C(CH_3)CH_3$ (Ia);

$$\text{Ia or Ib} \xrightarrow{HBr} \underset{(II)}{CH_3CBr(CH_3)CH_2CH_3} \xrightarrow{NH_3} \underset{(III)}{CH_3CNH_2(CH_3)CH_2CH_3} \rightarrow$$

$$\xrightarrow{CH_3I} [CH_3CH_2C(NH_3)_2N(CH_3)_3]^+I^- \xrightarrow{Ag_2O} [CH_3CH_2C(NH_3)_2N(CH_3)_3]^+(OH^-) \rightarrow$$ Ia (in ethanol) or Ib (in ethanol-water mixture)

2) I_a is formed in ethanol by mechanism E1

I_b is formed in ethanol+water mixture by mechanism E2.

3) $\text{Ib} \xrightarrow[2)H_2O/Zn]{1)O_3} H_2C=O + O=C(CH_3)C_2H_5$; $\text{Ia} \xrightarrow[2)H_2O/Zn]{1)O_3} CH_3CHO + O=C(CH_3)_2$;

4) (I) has cis- and trans-isomers;

6.

1) $PhCHO\ (I) \xrightarrow[2)\ H_3O^+]{1)\ HCN} PhCH(OH)CHO\ (II)$

2) $Ph(CH_2)_nCHO \xrightarrow{Br_2/P} Ph(CH_2)_{n-1}CH(Br)CHO \xrightarrow{NaOH} Ph(CH_2)_{n-1}CH(OH)CHO\ (B) \rightarrow$

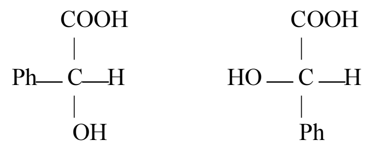
$\xrightarrow{20°C} Ph(CH_2)_{n-1}COCH_2OH\ (C) \xrightarrow{HBr} Ph(CH_2)_{n-1}COCH_2Br\ (D) \rightarrow$

$\xrightarrow{Br_2} Ph(CH_2)_{n-1}COCHBr_2\ (E) \xrightarrow{2NaOH} Ph(CH_2)_{n-1}COCHO\ (F) \xrightarrow{NaOH} Ph(CH_2)_{n-1}C(OH)COOH$ (III)

n = 1

In PMR spectrum compound B shows 4 multyplets (1:1:5:1) and compound C demonstrates 3 singlets (2:1:5).

3)



S-mandelic acid R-mandelic acid

4) E→ II hydride transfer reaction.

7. 1) C_xH_{2n-2} (alkyne or alkadiene) ; C_xH_{2x} (alkene).

2) ν_{sum} = 0,1·12,22/(0,082·298)=0,05 mol;

$M_{average}$ =2,70/0,05=54 g/mol

ν_{Br2}=16/160=0,1; ν_{H2O}=1,26/18=0,07 mol;

$RC{\equiv}CR' + 2Br_2 \rightarrow RCBr_2\text{-}CBr_2R'$;

$R_2C{=}C{=}CR_2 + 2Br_2 \rightarrow R_2CBr\text{-}CBr_2\text{-}CBrR_2$;

$R_2C{=}CH\text{-}CH{=}CR_2 + 2Br_2 \rightarrow R_2CBr\text{-}CHBr\text{-}CHBr\text{-}CBrR_2$;

$R_2C{=}CR_2 + Br_2 \rightarrow R_2BrC\text{-}CBrR_2$;

$RC{\equiv}CR \xrightarrow{Hg(II)+H^+} R\text{—}CO\text{—}CH_2R$;

$R_2C{=}C{=}CR_2 \xrightarrow{H^+} R_2CH\text{–}CO\text{—}CHR_2$;

$R_2C{=}CH\text{—}CH{=}CR_2 \xrightarrow{H^+} R_2C(OH)\text{—}CH_2\text{—}CH(OH)\text{—}CHR_2$;

$R_2C{=}CR_2 \xrightarrow{H^+} R_2C(OH)\text{—}CHR_2$;

A – a mol; B – b mol; in reaction with Br_2

2a+2b=0,1; a+b=0,05 (possibly);

2a+b=0,1 ; a+0,5b=0,05 (impossibly, as there is no alkene in the mixture);

In reaction with water: a+2b=0,07.

a+2b=0,07 a=0,03 (φ_A=60%, φ_B =40%)

a+b=0,05 b=0,02

φ_N = 28/142=19,7%; G-$[Ag(NH_3)_2]^+$.

3) a) A – C_nH_{2n-2}; B – C_mH_{2m-2};

0,6·(14n-2)+0,4(14m-2)=54; m=10-1,5n;

when n = 2 then m=7; <u>when n = 4 then m = 4.</u>

A – $CH{\equiv}C\text{—}CH_2\text{—}CH_3$; B – $CH_2{=}CH\text{—}CH{=}CH_2$;

b) n = 4, m = 4 A – $CH_3\text{—}C{\equiv}C\text{—}CH_3$; B – $CH_2{=}CH\text{—}CH{=}CH_2$

$CH_2{=}C{=}CH\text{—}CH_3$; $CH_2{=}CH\text{—}CH{=}CH_2$

c) n = 2, m = 7 A – $HC{\equiv}CH$; B – $CH_2{=}CH\text{—}(CH_2)_3\text{—}CH{=}CH_2$;

or isomers of B without cumulated bonds.