

## INTRODUCTION

Individual homework is one of the forms of students' independent work.

In these methodical recommendations the typical exercises of "Medical chemistry" discipline is given.

The study of the chemical cycle and related disciplines by the first-year students of Medical institute is started with this discipline.

For the successful solution of problems it is appropriate to begin with a study of theoretical material by using textbooks, educational supplies, lecture notes or other sources. Then you'll see an example of the typical problem which is given in the methodical recommendations and only after that start to do it.

If you have any questions during the problem solution the tutor recommendations should be obtained.

If you make a report of individual tasks you should follow the rules:

- ✓ Each task will be started on the new page.
- ✓ A complete statement of the problem together with short statement (for countable problems) should be given.
- ✓ The detailed calculation, complete way of problem solution and an answer should be given.

On the title page the name of the discipline, a variant number of an individual task, a group number, student's name and surname are mandatory.

The report of individual tasks should be handed in time (before deadline).

The solution of some problems requires the use of reference data that is given for convenience in the statement of the proper problem.

Making the individual task by yourself, promotes formation of deep knowledge and skills, allows the student to be oriented in the level of his grounding and highlighted the questions that required further study.

## BIOGENIC ELEMENTS

According to the number of your variant:

- 1) name a chemical element;
- 2) write its electronic configuration;
- 3) determine if it belongs to the s-, p-, or d-block;
- 4) describe its role in the human organism;
- 5) give an example of drugs containing the given element (the formula of the active substance), describe its application;
- 6) describe the effects of excess or deficiency of this element in the human body. \*

Answer to questions denoted by asterisks (\*), are not mandatory for each element.

### Example

The symbol of the chemical element is Zn.

1. The name of the chemical element is zinc.
2. Electronic configuration is following:  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10}$ .
3. Zn is d-element.
4. Plants get zinc from the soil and water, animals-from food. The daily human need for Zn is 5 -20 mg (for newborn - 4-6 mg). Human receives Zn from bread, meat, milk, vegetables (newborn - from breast milk).

Zn plays a key role in many biological functions such as reproduction, diabetes control, stress level modulation, immune resistance, smell and taste reception, physical growth, appetite and digestion stimulation.

Zn is an essential component of more than 40 enzymes (e.g. carboanhydrase, aldolase, lactate dehydrogenase, malate dehydrogenase, carboxypeptidase, etc.) that helps in regulation of cell growth, protein synthesis, level of hormones, DNA regulating gene transcription, energy metabolism and other related functions. Zn is an antidote for Cd.

The salivary gland, the prostate and the pancreas are organs of the human body which secrete Zn.

5. Zinc sulfate has antibacterial action. It also reveals astringent and anti-inflammatory effect. Diluted solutions of zinc sulfate (0,1-0,25%) are used in ophthalmology. Zinc chloride has astringent and antiseptic effect and is used to heal ulcers, fistulas, etc. Zinc oxide is applied in dermatology in the form of ointments and powders as astringent and antibacterial agent.

6. The signs of Zn deficiency include: changes in appetite, including food cravings for salty or sweet foods; changes in ability to taste and smell; weight gain or loss; hair loss; digestive problems, including diarrhea; chronic fatigue syndrome; infertility; hormonal problems, including worsened PMS or menopause symptoms; low immunity; poor concentration and memory; slowed ability to heal wounds; skin infections or irritation; nerve dysfunction.

Number of task	Symbol of element	Number of task	Symbol of element
<b>1</b>	O	<b>11</b>	P
<b>2</b>	I	<b>12</b>	Co
<b>3</b>	Fe	<b>13</b>	S
<b>4</b>	C	<b>14</b>	Na
<b>5</b>	Ag	<b>15</b>	Sr
<b>6</b>	Ca	<b>16</b>	Ba
<b>7</b>	Br	<b>17</b>	F
<b>8</b>	N	<b>18</b>	Mg
<b>9</b>	H	<b>19</b>	Cl
<b>10</b>	Cu	<b>20</b>	Zn

## COORDINATION COMPOUNDS

According to the task number of your variant

1. Indicate the central metal atom, its oxidation and coordination number, ligands.

2. Indicate complex ion and its charge.
3. Name the coordination compound.
4. Indicate the class of coordination compound: a) according to the ion charge of complex ion; b) according to the type of ligands.
5. Write down the equation of the coordination compound dissociation by the first stage.
6. Write down the equation of the coordination compound dissociation by the second stage.
7. Write down the equation for dissociation constant of complex ion.

### Example

The formula of coordination compound is  $[\text{Pt}(\text{NH}_3)_3\text{Cl}]\text{Cl}$

1. Central metal ion is Pt, its oxidation number is +2, its coordination number is 4, ligands are  $\text{NH}_3$  and  $\text{Cl}^-$ .
2. Complex ion is  $[\text{Pt}(\text{NH}_3)_3\text{Cl}]^+$  ;
3. Triamminechloroplatinum (II) chloride;
4. a) according to the charge of the complex ion it is an anionic complex, b) according to the ligands type it is mixed complex;
5. The equation of the coordination compound dissociation by the first stage is following:



6. The equation of the coordination compound dissociation by the second stage is following:



7. The equation for dissociation constant of complex ion is following:

$$K_{([\text{Pt}(\text{NH}_3)_3\text{Cl}]^+)} \leftrightarrow \frac{[\text{Pt}^{2+}] \cdot [\text{NH}_3]^3 \cdot [\text{Cl}^-]}{[[\text{Pt}(\text{NH}_3)_3\text{Cl}]^+]}$$

Task number	Formula of the coordination compound	Task number	Formula of the coordination compound
21	$K_4[Fe(CN)_6]$	31	$[Pt(NH_3)_6]Cl_4$
22	$[Al(H_2O)_6]Cl_3$	32	$K_2[Cd(CN)_4]$
23	$K[BF_4]$	33	$Na_3[Fe(CN)_5NH_3]$
24	$Na[AlCl_4]$	34	$[Ag(NH_3)_2]Cl$
25	$[Ni(H_2O)_6]SO_4$	35	$K_2[HgI_4]$
26	$K_3[Cr(OH)_6]$	36	$[PtNO_2(NH_3)_3]NO_3$
27	$[Cu(NH_3)_4]SO_4$	37	$[PdCl(NH_3)_2H_2O]Cl$
28	$K_2[CuCl_4]$	38	$K_3[Fe(CN)_6]$
29	$Na_3[AlF_6]$	39	$[Zn(NH_3)_4](OH)_2$
30	$K[Ag(CN)_2]$	40	$K_2[SiF_6]$

## QUANTITATIVE COMPOSITION OF SOLUTIONS

According to the number of your variant:

- 1) calculate and fill in the omitted data;
- 2) describe the application of the given solution in the medical practice.

### Example

Formula of solute	$m_{solute}$	$V_{solution}$	$\rho$	w	$C_M$	$C_N$
$Na_2S_2O_3$	79	?	1,27	?	2,4	?

### Solution:

1.

$$M(\text{Na}_2\text{S}_2\text{O}_3) = 2 \cdot 23 + 2 \cdot 32 + 3 \cdot 16 = 158 \text{ g/mol.}$$

$$n(\text{Na}_2\text{S}_2\text{O}_3) = \frac{m}{M} = \frac{79 \text{ g}}{158 \text{ g/mol}} = 0.5 \text{ mol.}$$

$$V_{\text{solution}} = \frac{n}{C_M} = \frac{0.5 \text{ mol}}{2.4 \text{ mol/L}} = 0.208 \text{ l} = 208 \text{ ml.}$$

$$m_{\text{solution}} = V_{\text{solution}} \cdot \rho = 208 \text{ ml} \cdot 1.27 \text{ g/ml} = 264.2 \text{ g}$$

$$w(\text{Na}_2\text{S}_2\text{O}_3) = \frac{m_{\text{solute}}}{m_{\text{solution}}} = \frac{79 \text{ g}}{264.2 \text{ g}} = 0.299; 29.9\%.$$

$$M_{\text{eq.}}(\text{Na}_2\text{S}_2\text{O}_3) = \frac{M}{2} = 79 \text{ g/mol - eq.}$$

$$n_{\text{eq.}} = \frac{m_{\text{solute}}}{M_{\text{eq}}} = \frac{79 \text{ g}}{79 \text{ g/mol}} = 1 \text{ mol.}$$

$$C_N = \frac{n_{\text{eq}}(\text{Na}_2\text{S}_2\text{O}_3)}{V_{\text{solution}}} = \frac{1 \text{ mol}}{0.208 \text{ L}} = 4.8 \text{ mol/L.}$$

Answer:  $V_{\text{solution}} = 0,208 \text{ L}$ ,  $w = 29,9\%$ ,  $C_N = 4.8 \text{ mol/L}$ .

2. Sodium thiosulfate has colorless crystals, odorless, bitter-salty taste. It is very easily soluble in water (1:1) and practically insoluble in alcohol.

30% solution of sodium thiosulfate for injections is used for detoxication, as anti-inflammatory, antiallergic and antiparasitic agents. Sodium thiosulfate is also administered as antidote in poisonings with heavy metals, hydrocyanic acid, halogens, arsenic, and mercury. With these substances it forms harmless or less poisonous compounds which are excreted from the organism. When sodium thiosulfate reacts with HCl (Demynovich method) sulfur

dioxide and free sulfur are formed which are known to have antiparasitic action.

Number of task	Formula of solute	$m_{solute}$	$V_{solution}$	$\rho$	w	$C_M$	$C_N$
1	2	3	4	5	6	7	8
<b>41</b>	MgSO <sub>4</sub>	60	?	1.22	20	?	?
<b>42</b>	NaNO <sub>2</sub>	?	20	1.011	2	?	?
<b>43</b>	NaCl	?	50	1.07	10	?	?
<b>44</b>	HCl	71	?	1.04	8	?	?
<b>45</b>	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	316	829.4	?	30	?	?
<b>46</b>	H <sub>2</sub> O <sub>2</sub>	?	100	1.013	?	0.06	?
<b>47</b>	CaCl <sub>2</sub>	21,6	?	1.08	5	?	?
<b>48</b>	MgSO <sub>4</sub>	?	200	1.22	?	2.03	?
<b>49</b>	KMnO <sub>4</sub>	79	?	1.013	?	0.128	?
<b>50</b>	NaHCO <sub>3</sub>	?	400	1.013	2	?	?
<b>51</b>	KI	?	160	1.028	4	?	?
<b>52</b>	NH <sub>4</sub> Cl	101.4	2000		5	?	?
<b>53</b>	NaBr	15.33	500		3	?	?
<b>54</b>	NaCl	234	?	1.07	?	1.83	?
<b>55</b>	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	79	?	1.27	?	2.4	?
<b>56</b>	CaCl <sub>2</sub>	?	300	1.084	10	?	?
<b>57</b>	KI	49.8	?	1.028	4	?	?
<b>58</b>	NaI		432	1.08	?	0.721	?
<b>59</b>	NaHCO <sub>3</sub>	?	150	1.035	?	0.62	?
<b>60</b>	HCl	14.6	?	1.04	?	2.4	?

Conventional signs:

$m_{solute}$  - mass of solute, g;

$V_{solution}$  - volume of the solution, ml;

$\rho$  - density of the solution. g / ml;

w - mass percent (percent concentration by mass), %;

$C_M$  - molar concentration (molarity), mol / L;

$C_N$  - molar concentration of the equivalent (normality), mol / L;

n – number of moles, mol;

$n_{eq}$  – number of equivalent, mol;

M – molar mass, g/mol;

$M_{eq}$  – molar mass of equivalent, g/mol.

## COLLIGATIVE PROPERTIES OF SOLUTIONS

Solve the problem according to your task number:

**Example** 1.2 L of solution contains 20.5 ml of sucrose ( $C_{12}H_{22}O_{11}$ ). Calculate the osmotic pressure of the solution at 22°C.

### Solution

1.  $M(C_{12}H_{22}O_{11}) = 342 \text{ g/mol}$

2. 
$$C_M = \frac{n(C_{12}H_{22}O_{11})}{V(\text{solution})} = \frac{m(C_{12}H_{22}O_{11})}{M(C_{12}H_{22}O_{11}) \cdot V(\text{solution})} =$$
$$= \frac{20.5 \cdot 10^{-2} \text{ g}}{342 \text{ g/mol} \cdot 1.2 \text{ L}} = 5.0 \cdot 10^{-5} \text{ mol/L}$$

3.  $P_{osmotic} = C_M RT = 5.0 \cdot 10^{-5} \text{ mol/L} \cdot 8.314 \text{ J/mol} \cdot \text{K} \cdot 295 \text{ K} =$   
 $= 0.123 \text{ kPa} = 123 \text{ Pa}.$

Answer:  $P_{osmotic} = 123 \text{ Pa}.$

**Example** A solution is prepared by dissolving 35.0 g of ethanol ( $C_2H_5OH$ ) in 65.0 g of water. What is the freezing point depression of the solvent? ( $K_f(H_2O) = 1.86 \text{ K} \cdot \text{kg/mol}$ ).

### Solution

1.  $M(C_2H_5OH) = 46 \text{ g/mol}$

$$2. \Delta T_f = K_f \cdot C_m \Rightarrow$$

$$\Delta T_f = 1.86\text{K} \cdot \text{kg/mol} \cdot \frac{35.0\text{g}(\text{C}_2\text{H}_5\text{OH}) \cdot 1000}{46\text{g/mol} \cdot 65.0\text{g}(\text{H}_2\text{O})} = 21.77\text{K}.$$

$$3. \text{Answer: } \Delta T_f = 21.77\text{K}.$$

**Example** Calculate the expected vapor pressure at  $25^\circ\text{C}$  for a solution prepared by dissolving 158.0 g of common table sugar (sucrose,  $M(\text{C}_{12}\text{H}_{22}\text{O}_{11})=342\text{ g/mol}$ ) in 643.5 ml of water. At  $25^\circ\text{C}$  the density of water is 0.9971 g/ml and the vapor pressure is 3168 Pa.

### Solution

$$1. \text{ We will use Raoult's law } \Delta p^0 = p^0 \cdot \chi(\text{C}_{12}\text{H}_{22}\text{O}_{11}).$$

$$2. n(\text{C}_{12}\text{H}_{22}\text{O}_{11}) = \frac{m(\text{C}_{12}\text{H}_{22}\text{O}_{11})}{M(\text{C}_{12}\text{H}_{22}\text{O}_{11})} = \frac{158.0\text{g}}{342\text{g/mol}} = 0.462\text{ mol}.$$

$$3. n(\text{H}_2\text{O}) = \frac{m(\text{H}_2\text{O})}{M(\text{H}_2\text{O})} = \frac{V(\text{H}_2\text{O}) \cdot d(\text{H}_2\text{O})}{M(\text{H}_2\text{O})} =$$

$$= \frac{643.5\text{ml} \cdot 0.9971\text{g/ml}}{18\text{g/mol}} = 35.65\text{mol}.$$

$$4. \chi(\text{C}_{12}\text{H}_{22}\text{O}_{11}) = \frac{n(\text{C}_{12}\text{H}_{22}\text{O}_{11})}{n(\text{C}_{12}\text{H}_{22}\text{O}_{11}) + n(\text{H}_2\text{O})} =$$

$$= \frac{0.462\text{mol}}{0.462\text{mol} + 35.65\text{mol}} = 0.0128.$$

$$5. \Delta p^0 = p^0 \cdot \chi(\text{C}_{12}\text{H}_{22}\text{O}_{11}) = 3168\text{ Pa} \cdot 0.0128 = 40.55\text{ Pa}.$$

$$\text{Answer: } \Delta p^0 = 40.55\text{ Pa}.$$

**61** A solution is prepared by mixing 50.0 g glucose ( $\text{C}_6\text{H}_{12}\text{O}_6$ ) with 600.0 g water. What is the vapor pressure of this solution at  $25^\circ\text{C}$ ? (at  $25^\circ\text{C}$  the vapor pressure of pure water is 3173 Pa. Glucose is a nonelectrolyte).

- 62** A solution is prepared by dissolving 4.9 g of sucrose ( $C_{12}H_{22}O_{11}$ ) in 175 g water. Calculate the boiling point of this solution. Sucrose is nonelectrolyte. ( $K_b(H_2O)=0.52\text{ K}\cdot\text{kg/mol}$ ).
- 63** What will be boiling point of an aqueous solution containing 55.0 g of glycerol ( $C_3H_8O_3$ ) and 250 g of water? ( $K_b(H_2O)=0.52\text{ K}\cdot\text{kg/mol}$ ).
- 64** A solution is made by dissolving 25.8 g urea ( $CH_4N_2O$ ), a nonelectrolyte, in 275 g water. Calculate vapor pressure of this solution at  $25^\circ\text{C}$  (at  $25^\circ\text{C}$  the vapor pressure of pure water is 3173 Pa).
- 65** A solution contains 3.75 g a nonvolatile hydrocarbon in 95 g of acetone. The boiling points of pure acetone ( $C_3H_6O$ ) and the solution are  $55.95^\circ\text{C}$  and  $56.50^\circ\text{C}$ , respectively. The molar boiling–point constant of acetone is  $1.71^\circ\text{C}\cdot\text{kg/mol}$ . Calculate molar mass of the hydrocarbon.
- 66** Calculate the molecular weight of an unknown substance if dissolving 7.39 g in 85.0 g of benzene ( $C_6H_6$ , a non-polar solvent) raises the boiling point from  $80.2^\circ\text{C}$  to  $82.6^\circ\text{C}$ . ( $K_b(C_6H_6) = 2.52^\circ\text{C}\cdot\text{kg/mol}$ ).
- 67** In order to find the molecular weight of hemoglobin 0.5 g was dissolved in enough water in a volumetric flask to give 100.0 ml of solution. The osmotic pressure of this solution was then measured at  $25^\circ\text{C}$  and found to be 0.18 kPa. Calculate the molecular weight.
- 68** A solution is made by dissolving 45.0 g urea ( $CH_4N_2O$ ), a nonelectrolyte, in 270 g of water. Calculate vapor pressure of this solution at  $45^\circ\text{C}$  (at  $45^\circ\text{C}$  the vapor pressure of pure water is 9586 Pa).
- 69** Calculate the concentration of urea ( $NH_2CONH_2$ ) that has an osmotic pressure of 3040 kPa at  $25^\circ\text{C}$ .

- 70** What mass of urea ( $(\text{NH}_2)_2\text{CO}$ )? a nonelectrolyte, must be dissolved in 150.0 g water to give a solution with a freezing point of  $-3.00^\circ\text{C}$ ? ( $K_f(\text{H}_2\text{O})=1.86^\circ\text{C}\cdot\text{kg}/\text{mol}$ ).
- 71** A student needs to prepare an aqueous solution of sucrose at a temperature of  $20^\circ\text{C}$  with a vapor pressure of 2000 Pa. How many grams of sucrose ( $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ ) does she need if she uses 375 g  $\text{H}_2\text{O}$ ? (The vapor pressure of water at  $20^\circ\text{C}$  is 2333 Pa.)
- 72** A solution is made by dissolving 36 g glucose ( $\text{C}_6\text{H}_{12}\text{O}_6$ ), a nonelectrolyte, in 324 g of water. Calculate vapor pressure of this solution at  $25^\circ\text{C}$  (at  $25^\circ\text{C}$  the vapor pressure of pure water is 3173 Pa).
- 73** What is the vapor pressure of a solution of 16.0 g of glucose ( $\text{C}_6\text{H}_{12}\text{O}_6$ ) in 80.0 g of methanol ( $\text{CH}_3\text{OH}$ ) at  $27^\circ\text{C}$ ? The vapor pressure of pure methanol at  $27^\circ\text{C}$  is 18665 Pa.
- 74** A solution is made by dissolving 5.08 g iodine ( $\text{I}_2$ ), a nonelectrolyte, in 5 mol of benzene ( $\text{C}_6\text{H}_6$ ). Calculate vapor pressure of this solution at  $25^\circ\text{C}$  (at  $25^\circ\text{C}$  the vapor pressure of pure benzene is 12666 Pa).
- 75** How would you prepare 1.0 liter of an aqueous solution of sucrose ( $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ ) having an osmotic pressure of 1519.9 kPa at a temperature of  $22^\circ\text{C}$ ? Sucrose is a nonelectrolyte.
- 76** A solution prepared by dissolving 3.00 g of ascorbic acid (vitamin C,  $\text{C}_6\text{H}_8\text{O}_6$ ) in 50.0 g of acetic acid has a freezing point that is depressed by  $\Delta T = 1.33^\circ\text{C}$  below that of pure acetic acid. What is the value of the molal freezing-point-depression constant for acetic acid?
- 77** At what temperature does the solution of 500 ml of glycerol ( $d=1.26\text{ g}/\text{ml}$ ) in 4 l of water begin to freeze? ( $K_f(\text{H}_2\text{O})=1.86^\circ\text{C}\cdot\text{kg}/\text{mol}$ ).

**78** A solution is made by dissolving 2.54 g of iodine ( $I_2$ ), a nonelectrolyte, in 4 mol of toluene ( $C_7H_8$ ). Calculate vapor pressure of this solution at  $25^\circ C$  (at  $25^\circ C$  the vapor pressure of pure toluene is 3733 Pa).

**79** Calculate the molal concentration of ethylene glycol ( $C_2H_6O_2$ ) in the aqueous solution with mass concentration 30.2%. Calculate the increase of boiling point for this solution. ( $K_b(C_2H_6O_2)=0.51^\circ C \cdot kg/mol$ ).

**80** What the weight of methanol dissolved in 800 g of water if the solution begins to freeze at  $-9^\circ C$ ? ( $K_f(H_2O)=1.86^\circ C \cdot kg/mol$ ).

## EQUILIBRIUM IN ELECTROLYTE SOLUTIONS

According to the number of your variant:

- 1) Make a dissociation equation of the salt and analyze its composition.
- 2) Make the molecular and ionic equations of the salt hydrolysis by the first stage;
- 3) Make short ionic equations of the salt hydrolysis by the second and third stages.
- 4) Indicate the pH of the salt aqueous solution.

Number of variant	Salt formula	Number of variant	Salt formula
<b>81</b>	$Na_2CO_3$	<b>91</b>	$Pb(NO_3)_2$
<b>82</b>	$CuSO_4$	<b>92</b>	$NH_4F$
<b>83</b>	$Zn(NO_3)_2$	<b>93</b>	$ZnSO_4$
<b>84</b>	$FeCl_3$	<b>94</b>	$Mn(NO_3)_2$
<b>85</b>	$K_2SiO_3$	<b>95</b>	$AlBr_3$
<b>86</b>	$Na_2S$	<b>96</b>	$NH_4NO_2$

<b>87</b>	$\text{Al}(\text{NO}_3)_3$	<b>97</b>	$\text{Cu}(\text{NO}_3)_2$
<b>88</b>	$\text{Na}_3\text{PO}_4$	<b>98</b>	$\text{CH}_3\text{COONa}$
<b>89</b>	$\text{Fe}(\text{NO}_3)_2$	<b>99</b>	$\text{Na}_2\text{SO}_3$
<b>90</b>	$\text{K}_2\text{CO}_3$	<b>100</b>	$\text{KCN}$

**Example.** The formula of the salt is  $\text{K}_2\text{SO}_3$

1.  $\text{K}_2\text{SO}_3 \leftrightarrow 2\text{K}^+ + \text{SO}_3^{2-}$ , salt is formed by the cation of a strong electrolyte ( $\text{K}^+ \rightarrow \text{KOH}$ ) and by the anion of weak electrolyte ( $\text{SO}_3^{2-} \rightarrow \text{H}_2\text{SO}_3$ );

2  $\text{SO}_3^{2-} + \text{H}_2\text{O} \leftrightarrow \text{HSO}_3^- + \text{OH}^-$

$2\text{K}^+ + \text{SO}_3^{2-} + \text{H}_2\text{O} \leftrightarrow 2\text{K}^+ + \text{HSO}_3^- + \text{OH}^-$

$\text{K}_2\text{SO}_3 + \text{H}_2\text{O} \leftrightarrow \text{KOH} + \text{KHSO}_3$ ;

3  $\text{HSO}_3^- + \text{H}_2\text{O} \leftrightarrow \text{SO}_3^{2-} + \text{OH}^-$ ;

4  $\text{pH} > 7$

*In accordance to your variant number make necessary calculations.*

**101.** Calculate pH and pOH of the solution if the molar concentration of KOH is 0.00001 mol/L.

**102.** Calculate the concentrations of hydroxyl-ions ( $\text{OH}^-$ ) and protons ( $\text{H}^+$ ) in the solution with  $\text{pH}=9$ .

**103.** Calculate the solution pH and pOH if the molar concentration of NaOH is 0.000001 mol/L.

**104.** Calculate the concentrations of hydroxyl-ions ( $\text{OH}^-$ ) and protons ( $\text{H}^+$ ) in the solution with  $\text{pH}=10$ .

- 105.** Calculate the solution pH if the molar concentration of  $\text{CH}_3\text{COOH}$  is 0.01 mol/L. The acid dissociation constant is  $1.8 \cdot 10^{-5}$  ( $K_a = 1.8 \cdot 10^{-5}$ ).
- 106.** Calculate the solution pH if the molar concentration of  $\text{HCOOH}$  is 0.025 mol/L. The acid dissociation constant is following  $K_a = 1.8 \cdot 10^{-4}$ .
- 107.** Calculate pOH of the solution if the molarity of  $\text{NH}_4\text{OH}$  is 0.0015 mol/L. The base dissociation constant is following  $K_b = 1.76 \cdot 10^{-5}$ .
- 108.** Calculate the solution pH if the molar concentration of  $\text{HF}$  is 0.003 mol/L. The acid dissociation constant is following  $K_a = 6.6 \cdot 10^{-4}$ .
- 109.** Calculate how solution pH will be changed if 0.001 mol of  $\text{HCl}$  is added to the 1 liter of buffer solution containing 0.01 mol of acetic acid and 0.01 mole of sodium acetate ( $pK_{(\text{CH}_3\text{COOH})} = 4.76$ ).
- 110.** Calculate the pH of a buffer solution obtained by mixing 15 mL of 0.5 M acetic acid solution and 25 mL of 0.5 M sodium acetate solution ( $pK_a = 4.76$ ).
- 111.** Calculate the pH of acetic buffer solution containing 0.2 mole of each component per liter. How pH will be changed if 0.01 mole of  $\text{HCl}$  is added to the 1 L of buffer solution ( $pK_a = 4.76$ ).
- 112.** Calculate the pH of a buffer solution containing 0.3 mole of  $\text{C}_6\text{H}_5\text{COOH}$  and 0.2 mole of  $\text{C}_6\text{H}_5\text{COONa}$  per liter. Calculate pH changes if 0.02 mole of  $\text{NaOH}$  is added to the 1 L of buffer solution ( $pK_{(\text{C}_6\text{H}_5\text{COOH})} = 4.2$ ).

- 113.** Calculate the pH of 20 mL buffer solution made by mixing of 12 mL 0.1 M acetic acid solution and 8 mL 0.1 M sodium acetate solution ( $pK_{(CH_3COOH)} = 4.76$ )
- 114.** Calculate the pH of a buffer solution containing 0.2 mol/L of formic acid and 0.15 mol/L of sodium formate ( $pK_{(HCOOH)} = 3.74$ ).
- 115.** Calculate the pH of a buffer solution prepared by mixing of 50 mL 0.5 M ammonia hydroxide solution and 200 mL 0.1 M ammonia chloride solution ( $pK_{(NH_4OH)} = 4.75$ ).
- 116.** Calculate the pH of a buffer solution containing 0.1 mole of each component per liter HCOOH/HCOOK. How pH will be changed if the 0.01 mole of KOH solution is added to the 1 L of this mixture? ( $pK_{(HCOOH)} = 3.74$ ).
- 117.** Calculate the concentration relation of sodium acetate and acetic acid in a buffer solution with pH=5.8 ( $pK_{(CH_3COOH)} = 4.76$ ).
- 118.** Calculate the pH of a buffer solution containing 0.1 mol/L of ammonia hydroxide and 0.2 mol/L of ammonia chloride ( $pK_{(NH_4OH)} = 4.75$ ).
- 119.** Calculate which mass of sodium acetate will be added to 200 ml of acetic acid solution with concentration 2 mol/L to obtain buffer solution with pH=3.44 ( $pK_{(CH_3COOH)} = 4.76$ ).
- 120.** Calculate the pH of a buffer solution containing 0.1 mol/L acetic acid and 0.01 mol/L sodium acetate ( $pK_{(CH_3COOH)} = 4.76$ ).

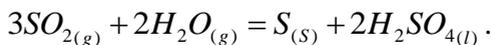
## CHEMICAL THERMODYNAMICS

For the reaction scheme according to your variant number:

1) using the values of standard enthalpy change of formation  $\Delta H_{f,298}^0$  and standard entropy  $S_{f,298}^0$  for substances listed in Table 1, calculate  $\Delta H_{298}^0$ ,  $\Delta S_{298}^0$ ,  $\Delta G_{298}^0$  for chemical reaction;

2) make the conclusion, in what direction does the reaction proceed under standard conditions.

### Example



### Solution

	H <sub>2</sub> SO <sub>4(g)</sub>	S <sub>(s)</sub>	H <sub>2</sub> O <sub>(g)</sub>	SO <sub>2(g)</sub>
$\Delta H_f^0$ , kJ/mol	-813.99	0	-241.81	-296.9
$\Delta S_f^0$ , J/mol	156.90	31.92	188.72	248.07

1.

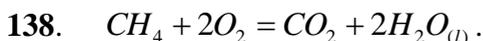
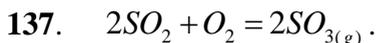
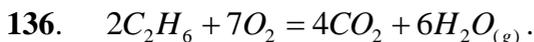
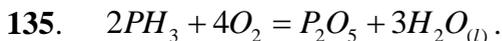
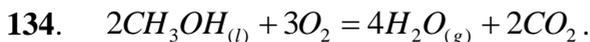
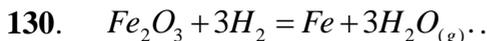
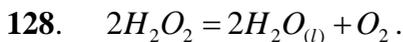
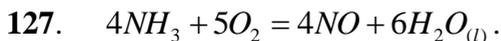
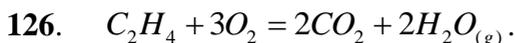
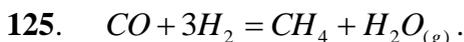
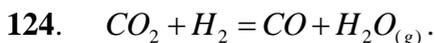
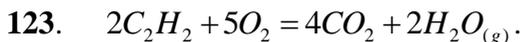
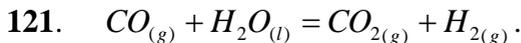
$$\begin{aligned} \Delta H_{298}^0 &= (2 \cdot \Delta H_f^0(H_2SO_{4(l)}) + \Delta H_f^0(S_{(s)})) - \\ &\quad - (2 \cdot \Delta H_f^0(H_2O_{(g)}) + 3 \cdot \Delta H_f^0(SO_{2(g)})) = (2 \cdot (-813.99) + 0) - \\ &\quad - (2 \cdot (-241.81) + 3 \cdot (-296.9)) = -253.66 \text{ kJ.} \end{aligned}$$

$$\begin{aligned} \Delta S_{298}^0 &= (2 \cdot S_f^0(H_2SO_{4(l)}) + S_f^0(S_{(s)})) - \\ &\quad - (2 \cdot S_f^0(H_2O_{(g)}) + 3 \cdot S_f^0(SO_{2(g)})) = (2 \cdot 156.9 + 31.92) - \\ &\quad - (2 \cdot 188.72 + 3 \cdot 248.07) = -775.93 \text{ J / K.} \end{aligned}$$

$$\Delta G_{298}^0 = \Delta H_{298}^0 - T \cdot \Delta S_{298}^0 = -253.66 - 298(-0.77593) = -22.43 \text{ kJ.}$$

Answer:  $\Delta H_{298} = -253.66 \text{ kJ}$ ,  $\Delta S_{298} = -775.93 \text{ J/K}$ ,  
 $\Delta G_{298} = -22.43 \text{ kJ}$ .

2. The negative value of free energy change ( $\Delta G_{298}^0 < 0$ ) indicates a spontaneous forward reaction under standard conditions.



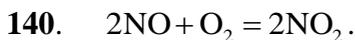
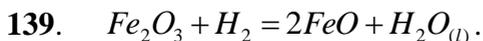


Table 1 - Standard enthalpy change of formation  $\Delta H_f^0$ , standard entropy  $S^0$  of some common substances at 298,15K\*

Substance	$\Delta H_f^0$ kJ/mole	$S_f^0$ , J/(mole·K)
1	2	3
CH <sub>3</sub> OH (l)	-239.45	126.6
CH <sub>4</sub> (g)	-74.81	186.31
CO (g)	-110.52	197.54
CO <sub>2</sub> (g)	-393.51	213.67
C <sub>2</sub> H <sub>2</sub> (g)	226.0	200.83
C <sub>2</sub> H <sub>4</sub> (g)	52.5	219.3
C <sub>2</sub> H <sub>6</sub> (g)	-84.7	229.5
CS <sub>2</sub> (l)	88.70	151.04
CaC <sub>2</sub> (s)	-60	70.0
CaO (s)	-635.1	38.1
Cl <sub>2</sub> (g)	0	222.98
HCl (g)	-92.31	186.79
Fe (s)	0	27.15
FeO (s)	-265	60.8
Fe <sub>2</sub> O <sub>3</sub> (s)	-822	87
Fe <sub>3</sub> O <sub>4</sub> (s)	-1117.13	146.19
H <sub>2</sub> (g)	0	130.52
N <sub>2</sub> (g)	0	191.5
NH <sub>3</sub> (g)	-46.2	192.6
NH <sub>4</sub> Cl (s)	-314.2	95.81
NO (g)	90.2	210.6
NO <sub>2</sub> (g)	33.5	240.2
O <sub>2</sub> (g)	0	205.04
H <sub>2</sub> O (g)	-241.82	188.72

H <sub>2</sub> O (l)	-285.83	70.08
H <sub>2</sub> O <sub>2</sub> (l)	-187.78	109.5
P <sub>2</sub> O <sub>5</sub> (s)	-1507.2	140.3
PH <sub>3</sub> (g)	5.4	210.2
S (s)	0	31.9
SO <sub>2</sub> (g)	-296.90	248.07
SO <sub>3</sub> (g)	-395.8	256.7
H <sub>2</sub> S (g)	-20.9	205.69

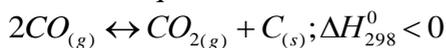
## CHEMICAL KINETICS

In accordance with your variant number:

1. Write the equilibrium expression of the reversible reaction
2. In what direction the equilibrium of the reversible reaction will be shifted:
  - a) When temperature increases (p=const); b) when pressure decreases (T = const)? Explain your answer.

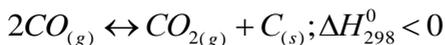
### Example

Chemical equation:



$$K_{eq} = \frac{[CO_2]}{[CO]^2}$$

- a) In the equilibrium system



The forward reaction is exothermic, so when temperature increases the equilibrium will shift to the reverse reaction which is endothermic (to the left).

- b) When pressure decreases the equilibrium will shift to the reverse reaction which is accompanied by an increase the volume of gases (to the left).

Number of variant	The equation of chemical reaction	$\Delta H_{cr}, kJ$
1	2	3
141	$CO_2 + 2H_2 \leftrightarrow CH_3OH_{(g)}$	193.3
142	$2N_2O \leftrightarrow 2N_2 + O_2$	-163.1
143	$2NO + Cl_2 \leftrightarrow 2NOCl$	-73.6
144	$3O_2 \leftrightarrow 2O_3$	184,6
145	$2H_2 + O_2 \leftrightarrow 2H_2O_{(g)}$	-483.7
146	$2CO + O_2 \leftrightarrow 2CO_2$	-566
147	$N_2O_4 \leftrightarrow 2NO_2$	58
148	$2NO + O_2 \leftrightarrow 2NO_2$	-113
149	$2SO_3 \leftrightarrow 2SO_2 + O_2$	196.6
150	$3H_2 + N_2 \leftrightarrow 2NH_3$	-92.5
151	$4HCl + O_2 \leftrightarrow 2H_2O_{(g)} + 2Cl_2$	-114.5
152	$C + H_2O_{(g)} \leftrightarrow CO + H_2$	131
153	$2NOCl \leftrightarrow 2NO + Cl_2$	73.6
154	$2NH_3 \leftrightarrow N_2 + 3H_2$	92.5
155	$2H_2S + 3O_2 \leftrightarrow 2H_2O_{(g)} + 2SO_2$	-561.1
156	$2H_2O_{(g)} + 2Cl_2 \leftrightarrow 4HCl + O_2$	114.5
157	$Cl_2 + CO \leftrightarrow COCl_2$	-112.5
158	$2O_3 \leftrightarrow 3O_2$	-184.6
159	$H_2 + CO_2 \leftrightarrow CO + H_2O_{(g)}$	41.2
160	$2SO_2 + O_2 \leftrightarrow 2SO_3$	-196.6

According to your variant number calculate the changes of forward and reverse reaction rates, if pressure is changed in  $n$  times.

### Example

Calculate the change of forward and reverse reaction rates,  $2SO_{2(r)} + O_{2(r)} \leftrightarrow 2SO_{3(r)}$  if pressure is increased in 4 times.

### Solution

$\mathcal{G}_{forward} = \kappa_1 \cdot p^2_{SO_2} \cdot p_{O_2}$  After pressure increasing:

$$\bar{\mathcal{G}}_{forward} = \kappa_1 \cdot (4p_{SO_2})^2 \cdot 4p_{O_2} = 64 \cdot \kappa_1 \cdot p^2_{SO_2} \cdot p_{O_2}$$

$$\frac{\bar{g}_{forward}}{g_{forward}} = \frac{64 \cdot k_1 \cdot p^2_{SO_2} \cdot p_{O_2}}{k_1 \cdot p^2_{SO_2} \cdot p_{O_2}} = 64$$

Forward reaction rate will increase in 64 times.

$$g_{reverse} = \kappa_2 \cdot p^2_{SO_3}$$

After pressure increasing:

$$\bar{g}_{reverse} = \kappa_2 \cdot (4p_{SO_3})^2 = 16 \cdot \kappa_2 \cdot p^2_{SO_3}; \quad \frac{\bar{g}_{reverse}}{g_{reverse}} = \frac{16 \cdot \kappa_2 \cdot p^2_{SO_3}}{\kappa_2 \cdot p^2_{SO_3}} = 16$$

Reverse reaction rate will increase in 16 times.

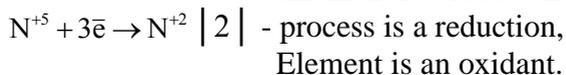
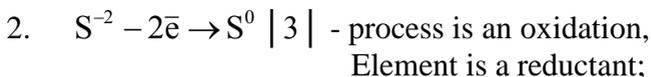
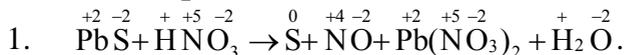
Number of variant	The equation of chemical reaction	Pressure change of gasses mix
1	2	3
161	$2SO_2 + O_2 \leftrightarrow 2SO_3$	Will increase in 2 times
162	$2NO + O_2 \leftrightarrow 2NO_2$	Will increase in 3 times
163	$3H_2 + N_2 \leftrightarrow 2NH_3$	Will increase in 3 times
164	$2NO + Cl_2 \leftrightarrow 2NOCl$	Will increase in 4 times
165	$CO + H_2O \leftrightarrow CO_2 + H_2$	Will decrease in 3 times
166	$N_2 + O_2 \leftrightarrow 2NO$	Will increase in 3 times
167	$4NH_3 + 5O_2 \leftrightarrow 4NO + 6H_2O$	Will decrease in 2 times
168	$4NH_3 + 3O_2 \leftrightarrow 2N_2 + 6H_2O$	Will decrease in 2 times
169	$N_2O_4 \leftrightarrow 2NO_2$	Will increase in 4 times
170	$4HCl + O_2 \leftrightarrow 2H_2O + 2Cl_2$	Will increase in 2 times
171	$2H_2S + 3O_2 \leftrightarrow 2H_2O + 2SO_2$	Will increase in 2 times
172	$3O_2 \leftrightarrow 2O_3$	Will increase in 3 times
173	$Cl_2 + CO \leftrightarrow COCl_2$	Will increase in 2 times
174	$2NO + Cl_2 \leftrightarrow 2NOCl$	Will increase in 2 times
175	$3H_2 + N_2 \leftrightarrow 2NH_3$	Will increase in 2 times
176	$2H_2S + 3O_2 \leftrightarrow 2H_2O + 2SO_2$	Will increase in 2 times
177	$2NO_2 \leftrightarrow 2NO + O_2$	Will decrease in 2 times
178	$2SO_3 \leftrightarrow 2SO_2 + O_2$	Will decrease in 2 times
179	$2NH_3 \leftrightarrow 3H_2 + N_2$	Will increase in 3 times
180	$2NOCl \leftrightarrow 2NO + Cl_2$	Will decrease in 4 times

## OXIDATION-REDUCTION REACTIONS

According to the number of your homework variant:

1. determine the elements oxidation numbers in the substances of the given scheme of chemical reaction, indicate the elements whose oxidation numbers were changed;
2. make an electron balance equations, point out the oxidant and reductant, processes of oxidation and reduction. Find the ratio of the number of electrons gained in reduction to that lost in oxidation;
3. make a balancing scheme of chemical reaction;
4. indicate the type of oxidation-reduction reaction.

### Example



We put the coefficients before formulas of substances containing atoms of elements that have changed their oxidation number. It will be taken to account that among the products of the reaction are atoms  $\text{N}^{+4}$  and  $\text{N}^{+5}$  thus, not all the N atoms (in the left side of the equation  $\text{N}^{+5}$ ) change their oxidation numbers. Therefore, the obtained by the balance coefficient for N is 2, it should be written just before the formula NO.:



Then calculate the total number of N atoms in the formulae of nitrogen-containing substances in the right side of the equation (because in this part of the equation, the coefficients before the formulae of the N containing substances are already defined): 2NO, 3Pb(NO<sub>3</sub>)<sub>2</sub>. The total number of N atoms is 8. We should write this (8) as the coefficient before the formula of nitric acid (HNO<sub>3</sub>):

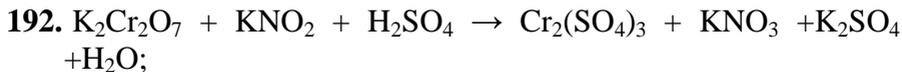
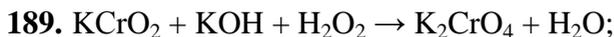
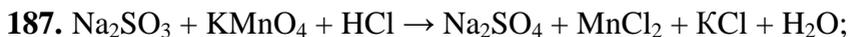
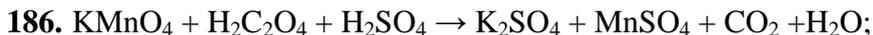
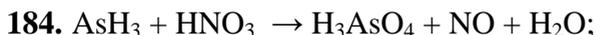
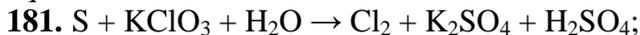


It is seen that the number of H atoms in the left side of the equation is 8 (before the formula  $\text{HNO}_3$ ). Therefore, before the formula  $\text{H}_2\text{O}$  we should write coefficient 4:



The total number of O atoms should be checked: the left and right sides of the equations are the same and there are 24. So the coefficients in the chemical equation are placed correctly.

4. The type of the reaction is the intermolecular oxidation-reduction equation.



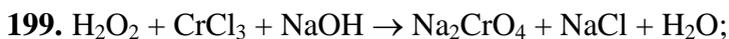
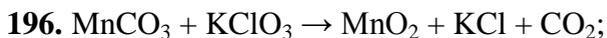
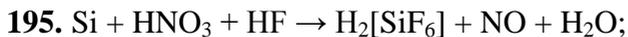
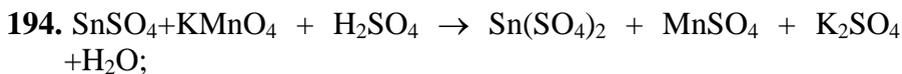


Table 2 – Table of individual tasks

Number of variant	Number of task
1.	1, 21, 41, 61, 81, 101, 121, 141, 161, 181
2.	2, 22, 42, 62, 82, 102, 122, 142, 162, 182
3.	3, 23, 43, 63, 83, 103, 123, 143, 163, 183
4.	4, 24, 44, 64, 84, 104, 124, 144, 164, 184
5.	5, 25, 45, 65, 85, 105, 125, 145, 165, 185
6.	6, 26, 46, 66, 86, 106, 126, 146, 166, 186
7.	7, 27, 47, 67, 87, 107, 127, 147, 167, 187
8.	8, 28, 48, 68, 88, 108, 128, 148, 168, 188
9.	9, 29, 49, 69, 89, 109, 129, 149, 169, 189
10.	10, 30, 50, 70, 90, 110, 130, 150, 170, 190
11.	11, 31, 51, 71, 91, 111, 131, 151, 171, 191
12.	12, 32, 52, 72, 92, 112, 132, 152, 172, 192
13.	13, 33, 53, 73, 93, 113, 133, 153, 173, 193
14.	14, 34, 54, 74, 94, 114, 134, 154, 174, 194
15.	15, 35, 55, 75, 95, 115, 135, 155, 175, 195
16.	16, 36, 56, 76, 96, 116, 136, 156, 176, 196
17.	17, 37, 57, 77, 97, 117, 137, 157, 177, 197
18.	18, 38, 58, 78, 98, 118, 138, 158, 178, 198
19.	19, 39, 59, 79, 99, 119, 139, 159, 179, 199
20.	20, 40, 60, 80, 100, 120, 140, 160, 180, 200
21.	1, 21, 42, 63, 84, 105, 126, 147, 168, 189
22.	2, 23, 44, 65, 86, 107, 128, 149, 170, 191
23.	3, 24, 45, 66, 87, 108, 129, 150, 171, 192
24.	4, 25, 46, 67, 88, 109, 130, 151, 172, 193
25.	5, 26, 47, 68, 89, 110, 131, 152, 173, 194

26.	6, 27, 48, 69, 90, 111, 132, 153, 174, 195
27.	7, 28, 49, 70, 91, 112, 133, 154, 175, 196
28.	8, 29, 50, 71, 92, 113, 134, 155, 176, 197
29.	9, 30, 51, 72, 93, 114, 135, 156, 177, 198
30.	10, 31, 52, 73, 94, 115, 136, 157, 178, 199
31.	11, 32, 53, 74, 95, 116, 137, 158, 179, 200
32.	12, 33, 54, 75, 96, 117, 138, 159, 180, 181
33.	13, 34, 55, 76, 97, 118, 139, 160, 161, 182
34.	14, 35, 56, 77, 98, 119, 140, 141, 162, 183
35.	15, 36, 57, 78, 99, 120, 121, 142, 163, 184
36.	16, 37, 58, 79, 100, 101, 122, 143, 164, 185
37.	17, 38, 59, 80, 81, 102, 123, 144, 165, 186
38.	18, 39, 60, 61, 82, 103, 124, 145, 166, 187
39.	19, 40, 41, 62, 83, 104, 125, 146, 167, 188
40.	20, 22, 40, 60, 80, 100, 120, 140, 160, 180