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4298 Collection of individual exercises to the course «Medical chemistry»

for students of specialty 222 «Medicine» full-time education

Усі цитати, цифровий та фактичний матеріал, бібліографічні відомості перевірені, запис одиниць відповідає стандартам

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Суми Сумський державний університет 2017

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Навчальне видання

Збірник індивідуальних завдань до курсу «Медична хімія»

для студентів спеціальності 222 «Медицина» денної форми навчання (Англійською мовою)

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

The typical exercises of "Medical chemistry" discipline are given in these methodological instructions.

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

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

 \checkmark Each task should be started on the new page.

- ✓ A complete statement of the problem together with a short statement (for countable problems) should be given.
- ✓ The detailed calculation, complete way of problem solution and an answer should be given.

The name of the discipline, a variant number of an individual task, a group number, student's name and surname are mandatory, and should be written on the title page.

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 highlights 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 the 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). A human receives Zn from bread, meat, milk, vegetables (a 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, prostate and 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 used 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. Table 1

Number of	Symbol of	Number of	Symbol of
task	element	task	element
1	0	11	Р
2	Ι	12	Со
3	Fe	13	S
4	С	14	Na
5	Ag	15	Sr
6	Ca	16	Ba
7	Br	17	F
8	Ν	18	Mg
9	Н	19	Cl
10	Cu	20	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 at the first stage.

- 6. Write down the equation of the coordination compound dissociation at the second stage.
- 7. Write down the equation for dissociation constant of complex ion.

Example

The formula of coordination compound is [Pt(NH₃)₃Cl]Cl

- 1. Central metal ion is Pt, its oxidation number is +2, its coordination number is 4, ligands are NH₃ and Cl⁻.
- 2. Complex ion is $[Pt(NH_3)_3Cl]^+$;
- 3. Triamminechloroplatinum (II) chloride
- 4.
 - a. according to the charge of the complex ion it is an kationic complex,
 - b. according to the ligands type it is mixed complex;
- 5. The equation of the coordination compound dissociation at the first stage is the following:

 $[Pt(NH_3)_3Cl]Cl \leftrightarrow [Pt(NH_3)_3Cl]^+ + Cl^-;$

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

 $[Pt(NH_3)_3Cl]Cl \leftrightarrow [Pt(NH_3)_3Cl]^+ + Cl^-;$

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

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

Table 2	2
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Task number	Formula of the coordination	Task number	Formula of the coordination
number	compound	number	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	$Na_3[Fe(CN)_5 NH_3]$
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) ₂ H ₂ O]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

Table 3

Formula of solute	<i>m_{solute}</i>	$V_{\scriptscriptstyle solution}$	ρ	W	C _M	C _N
$Na_2S_2O_3$	79	?	1,27	?	2,4	?

Solution:

1.
$$M(Na_2S_2O_3) = 2 \cdot 23 + 2 \cdot 32 + 3 \cdot 16 = 158 \text{ g/mol.}$$

 $n(Na_2S_2O_3) = \frac{m}{M} = \frac{79 \text{ g}}{158 \text{ g/mol}} = 0.5 \text{ mol.}$
 $V_{\text{solution}} = \frac{n}{C_M} = \frac{0.5 \text{mol}}{2.4 \text{ mol/L}} = 0.208 \text{ l} = 208 \text{ ml.}$
 $m_{\text{solution}} = V_{\text{solution}} \cdot \rho = 208 \text{ ml} \cdot 1.27 \text{ g/ml} = 264.2 \text{ g.}$
 $w(Na_2S_2O_3) = \frac{m_{\text{solute}}}{m_{\text{solution}}} = \frac{79 \text{ g}}{264.2 \text{ g}} = 0.299; 29.9 \%.$
 $M_{\text{eq.}}(Na_2S_2O_3) = \frac{M}{2} = 79 \text{ g/mol} - \text{eq.}$
 $n_{\text{eq.}} = \frac{m_{\text{solute}}}{M_{\text{eq}}} = \frac{79 \text{ g}}{79 \text{ g/mol}} = 1 \text{ mol.}$
 $C_N = \frac{n_{\text{eq}}(Na_2S_2O_3)}{V_{\text{solution}}} = \frac{1 \text{ mol}}{0.208 \text{ L}} = 4.8 \text{ mol/L.}$

Answer: $V_{solution} = 0,208$ L, w = 29,9 %, C_N = 4.8 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 (Demyanovich method), sulfur dioxide and free sulfur are formed which are known to have antiparasitic action.

Table 4

Number	Formula	<i>m</i> _{solute}	$V_{solution}$	ρ	W	См	C _N
of task	of solute	solute	solution			СM	- _N
1	2	3	4	5	6	7	8
41	$MgSO_4$	60	?	1.22	20	?	?
42	NaNO ₂	?	20	1.011	2	?	?
43	NaCl	?	50	1.07	10	?	?
44	HCl	71	?	1.04	8	?	?
45	$Na_2S_2O_3$	316	829.4	?	30	?	?
46	H_2O_2	?	100	1.013	?	0.06	?
47	CaCl ₂	21,6	?	1.08	5	?	?
48	$MgSO_4$?	200	1.22	?	2.03	?
49	KMnO ₄	79	?	1.013	?	0.128	?
50	NaHCO ₃	?	400	1.013	2	?	?
51	KI	?	160	1.028	4	?	?
52	NH ₄ Cl	101.4	2000		5	?	?
53	NaBr	15.33	500		3	?	?
54	NaCl	234	?	1.07	?	1.83	?
55	$Na_2S_2O_3$	79	?	1.27	?	2.4	?
56	CaCl ₂	?	300	1.084	10	?	?
57	KI	49.8	?	1.028	4	?	?
58	NaI		432	1.08	?	0.721	?
59	NaHCO ₃	?	150	1.035	?	0.62	?
60	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;

Meq - 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

$$M(C_{12}H_{12}O_{11})=342g/mol$$

 $C_{M} = \frac{n(C_{12}H_{22}O_{11})}{V(solution)} = \frac{m(C_{12}H_{22}O_{11})}{M(C_{12}H_{22}O_{11}) \cdot V(solution)} =$
 $= \frac{20.5 \cdot 10^{-2}g}{342g/mol \cdot 1.2L} = 5.0 \cdot 10^{-5} mol/L$
 $P_{osmotic} = C_{M}RT = 5.0 \cdot 10^{-5} mol/L \cdot 8.314 J/mol \cdot K \cdot 295 K$
 $= 0.123 \text{ kPa} = 123 \text{ Pa}.$
Answer: $P_{osmotic} = 123 \text{ Pa}.$

Example: A solution is prepared by dissolving 35.0 g of ethanol (C₂H₅OH) in 65.0 g of water. What is the freezing point depression of the solvent? (K_f (H₂O) = 1.86 K ·kg/mol).

Solution

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

2. $\Delta T_f = K_f \cdot C_m \Rightarrow$
 $\Delta T_f = 1.86K \cdot \text{kg/mol} \cdot \frac{35.0 \text{ g}(C_2H_5OH) \cdot 1000}{46 \text{ g/mol} \cdot 65.0 \text{ g}(H_2O)} = 21.77 \text{ K.}$

Answer: $\Delta T_f = 21.77$ K.

Example: Calculate the expected vapour pressure at 25 °C for a solution prepared by dissolving 158.0 g of common table sugar (sucrose, $M(C_{12}H_{22}O_{11}) = 342$ g/mol) in 643.5 ml of water. At 25 °C the density of water is 0.9971 g/ml and the vapour pressure is 3168 Pa.

Solution

1. We will use Raoult's law $\Delta p^0 = p^0 \cdot \chi(C_{12}H_{22}O_{11})$.

2.
$$n(C_{12}H_{22}O_{11}) = \frac{m(C_{12}H_{22}O_{11})}{M(C_{12}H_{22}O_{11})} = \frac{158.0g}{342g/mol} = 0.462 \text{ mol.}$$

3.
$$n(H_2O) = \frac{m(H_2O)}{M(H_2O)} = \frac{V(H_2O) \cdot d(H_2O)}{M(H_2O)} = \frac{643.5ml \cdot 0.9971g / ml}{18g / mol} = 35.65 mol.$$

4.
$$\chi(C_{12}H_{22}O_{11}) = \frac{n(C_{12}H_{22}O_{11})}{n(C_{12}H_{22}O_{11}) + n(H_2O)} =$$

= $\frac{0.462 \ mol}{0.0128} = 0.0128.$

5. $\Delta p^0 = p^0 \cdot \chi(C_{12}H_{22}O_{11}) = 3168 \text{ Pa} \cdot 0.0128 = 40.55 \text{ Pa}.$

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

61. A solution is prepared by mixing 50.0 g of glucose ($C_6H_{12}O_6$) with 600.0 g of water. What is the vapour pressure of this solution at 25 °C? (at 25 °C the vapour 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 of 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 the 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 of urea (CH₄N₂O), a nonelectrolyte, in 275 g of water. Calculate vapour pressure of this solution at 25 $^{\circ}$ C (at 25 $^{\circ}$ C the vapour pressure of pure water is 3173 Pa).

65. A solution contains 3.75 g of a nonvolatile hydrocarbon in 95 g of acetone. The boiling points of pure acetone (C_3H_6O) and the solution are 55.95 °C and 56.50 °C, respectively. The molar boiling

point constant of acetone is 1.71 °C '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 (C₆H₆, a non-polar solvent) raises the boiling point from 80.2 °C to 82.6 °C. (K_b(C₆H₆) = 2.52 °C · kg/mol).

67. In order to find the molecular weight of hemoglobin 0.5 g was dissolved in sufficient quantity of water in a volumetric flask to give 100.0 ml of solution. The osmotic pressure of this solution was then measured at 25 °C and found to be 0.18 kPa. Calculate the molecular weight.

68. A solution is made by dissolving 45.0 g of urea (CH₄N₂O), a nonelectrolyte, in 270 g of water. Calculate vapour pressure of this solution at 45 $^{\circ}$ C (at 45 $^{\circ}$ C the vapour 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 °C.

70. What mass of urea ((NH₂)₂CO), a nonelectrolyte, must be dissolved in 150.0 g of water to give a solution with a freezing point of - 3.00 °C? (K_f (H₂O) = 1.86 °C ·kg/mol).

71. A student needs to prepare an aqueous solution of sucrose at a temperature of 20 $^{\circ}$ C with a vapour pressure of 2000 Pa. How many grams of sucrose (C₁₂H₂₂O₁₁) does she need if she uses 375 g of H₂O? (The vapour pressure of water at 20 $^{\circ}$ C is 2333 Pa.)

72. A solution is made by dissolving 36 g of glucose ($C_6H_{12}O_6$), a nonelectrolyte, in 324 g of water. Calculate vapour pressure of this solution at 25^oC (at 25 °C the vapour pressure of pure water is 3173 Pa).

73. What is the vapour pressure of a solution of 16.0 g of glucose $(C_6H_{12}O_6)$ in 80.0 g of methanol (CH₃OH) at 27 °C? The vapour pressure of pure methanol at 27 °C is 18665 Pa.

74. A solution is made by dissolving 5.08 g iodine (I_2), a nonelectrolyte, in 5 mol of benzene (C_6H_6). Calculate vapour pressure of this solution at 25^oC (at 25^oC the vapour pressure of pure benzene is 12666 Pa).

75. How would you prepare 1 liter of an aqueous solution of sucrose $(C_{12}H_{22}O_{11})$ having an osmotic pressure of 1519.9 kPa at a temperature of 22 °C? Sucrose is a nonelectrolyte.

76. A solution prepared by dissolving 3.00 g of ascorbic acid (vitamin C, $C_6H_8O_6$) in 50.0 g of acetic acid has a freezing point that is depressed by $\Delta T = 1.33$ °C below that of pure acetic acid. What is the value of the molal freezingpointdepression constant for acetic acid?

77. At what temperature does the solution of 500 ml of glycerol (d = 1.26 g/ml) in 4l of water begin to freeze? $(K_f(H_2O) = 1.86 \text{ °C} \cdot \text{kg/mol}).$

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 vapour pressure of this solution at 25 °C (at 25 °C the vapour 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. $(K_b(C_2H_6O_2) = 0.51 \text{ °C} \cdot \text{kg/mol}).$

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

Equilibrium in Electrolyte Solutions

According to the number of your variant:

- 1) Make a dissociation equation of the salt and analyse its composition.
- 2) Make the molecular and ionic equations of the salt hydrolysis at the first stage;

3) Make short ionic equations of the salt hydrolysis at the second and third stages.

Table 5	1 1		
Number of		Number	
variant	Salt formula	of variant	Salt formula
81	Na ₂ CO ₃	91	$Pb(NO_3)_2$
82	CuSO ₄	92	NH ₄ F
83	$Zn(NO_3)_2$	93	ZnSO ₄
84	FeCl ₃	94	$Mn(NO_3)_2$
85	K ₂ SiO ₃	95	AlBr ₃
86	Na ₂ S	96	NH ₄ NO ₂
87	$Al(NO_3)_3$	97	$Cu(NO_3)_2$
88	Na ₃ PO ₄	98	CH ₃ COONa
89	$Fe(NO_3)_2$	99	Na ₂ SO ₃
90	K ₂ CO ₃	100	KCN

4) Indicate the pH of the salt aqueous solution.

Example. The formula of the salt is K_2SO_3

- 1. $K_2SO_3 \leftrightarrow 2K^+ + SO_3^{2-}$, salt is formed by the cation of a strong electrolyte $(K^+ \rightarrow KOH)$ and by the anion of weak electrolyte $(SO_3^{2-} \rightarrow H_2SO_3)$;
- 2. $SO_3^{2-} + H_2O \leftrightarrow HSO_3^- + OH^ 2K^+ + SO_3^{2-} + H_2O \leftrightarrow 2K^+ + HSO_3^- + OH^ K_2SO_3 + H_2O \leftrightarrow KOH + KHSO_3$.
- 3. $HSO_3^- + H_2O \leftrightarrow SO_3^{2-} + OH^-;$
- 4. 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 (OH⁻) and protons (H^+) in the solution with 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 (OH⁻) and protons (H^+) in the solution with pH=10.

105. Calculate the solution pH if the molar concentration of CH₃COOH 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 HCOOH is 0.025 mol/L. The acid dissociation constant is $K_a = 1.8 \cdot 10^{-4}$.

107. Calculate pOH of the solution if the molarity of NH₄OH is 0.0015 mol/L. The base dissociation constant is $K_b = 1.76 \cdot 10^{-5}$

108. Calculate the solution pH if the molar concentration of HF is 0.003 mol/L. The acid dissociation constant is $K_a = 6.6 \cdot 10^{-4}$

109. Calculate how solution pH will be changed if 0.001 mol of HCl is added to 1 litre of buffer solution containing 0.01 mol of acetic acid and 0.01 mol of sodium acetate ($pK_{(CH_3COOH)} = 4.76$)

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 mol of each component per litre. How pH will be changed if 0.01 mol of HCl is added to 1 l of buffer solution ($pK_a = 4.76$).

112. Calculate the pH of a buffer solution containing 0.3 mol of C_6H_5COOH and 0.2 mol of C_6H_5COONa per litre. Calculate pH changes if 0.02 mol of NaOH is added to 1 1 of buffer solution ($pK_{(C_6H_5COOH)} = 4.2$).

113. Calculate the pH of 20 mL buffer solution obtained by mixing 12 mL of 0.1 M acetic acid solution and 8 mL of 0.1 M sodium acetate solution ($pK_{(CH_2COOH)} = 4.76$).

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 50 mL of 0.5 M ammonia hydroxide solution and 200 mL of 0.1 M ammonia chloride solution ($pK_{(NH,OH)} = 4.75$)

116. Calculate the pH of a buffer solution containing 0.1 mol of each component per litre of HCOOH/HCOOK. How pH will be changed if the 0.01 mol of KOH solution is added to 1 1 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 ($pK_{(CH_2COOH)} = 4.76$).

118. Calculate the pH of a buffer solution containing 0.1 mol/L of ammonia hydroxide and 0.2 mol/L of ammonia chloride ($pK_{(NH4OH)} = 4.75$).

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 of acetic acid and 0.01 mol/L of 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 $\Delta H^0_{f,298}$ and standard entropy $S^0_{f,298}$ for substances listed in Table 6, calculate ΔH^0_{298} , ΔS^0_{298} , ΔG^0_{298} for chemical reaction;

2) make the conclusion in what direction the reaction proceeds under standard conditions.

Example

$$3SO_{2(g)} + 2H_2O_{(g)} = S_{(S)} + 2H_2SO_{4(l)}$$

	$H_2SO_{4(g)}$	S _(S)	$H_2O_{(g)}$	SO _{2(g)}
ΔH_{f}^{0} , kJ/mol	-813.99	0	-241.81	-296.9
ΔS_{f}^{0} , J/mol	156.90	31.92	188.72	248.07

Solution

 $\Delta H_{298}^{0} = (2 \cdot \Delta H_{f}^{0}(H_{2}SO_{4(l)}) + \Delta H_{f}^{0}(S_{(s)})) - (2 \cdot \Delta H_{f}^{0}(H_{2}O_{(g)}) + 3 \cdot \Delta H_{f}^{0}(SO_{2(g)})) = (2 \cdot (-813.99 + 0) - (2 \cdot (-241.81) + 3 \cdot (-296.9)) = -253.66 \text{ kJ}.$ $\Delta S_{298}^{0} = (2 \cdot S_{f}^{0}(H_{2}SO_{4(l)}) + S_{f}^{0}(S_{(s)})) - (2 \cdot S_{f}^{0}(H_{2}O_{(g)}) + 3 \cdot S_{f}^{0}(SO_{2(g)})) = (2 \cdot 156.9 + 31.92) - (2 \cdot S_{f}^{0}(H_{2}O_{(g)}) + 3 \cdot S_{f}^{0}(SO_{2(g)})) = (2 \cdot 156.9 + 31.92) - (2 \cdot S_{f}^{0}(H_{2}O_{(g)}) + 3 \cdot S_{f}^{0}(SO_{2(g)})) = (2 \cdot 156.9 + 31.92) - (2 \cdot S_{f}^{0}(H_{2}O_{(g)}) + 3 \cdot S_{f}^{0}(SO_{2(g)})) = (2 \cdot 156.9 + 31.92) - (2 \cdot S_{f}^{0}(H_{2}O_{(g)}) + 3 \cdot S_{f}^{0}(SO_{2(g)})) = (2 \cdot 156.9 + 31.92) - (2 \cdot S_{f}^{0}(H_{2}O_{(g)}) + 3 \cdot S_{f}^{0}(SO_{2(g)})) = (2 \cdot 156.9 + 31.92) - (2 \cdot S_{f}^{0}(H_{2}O_{(g)}) + 3 \cdot S_{f}^{0}(SO_{2(g)})) = (2 \cdot 156.9 + 31.92) - (2 \cdot S_{f}^{0}(H_{2}O_{(g)}) + 3 \cdot S_{f}^{0}(SO_{2(g)})) = (2 \cdot 156.9 + 31.92) - (2 \cdot S_{f}^{0}(H_{2}O_{(g)}) + 3 \cdot S_{f}^{0}(SO_{2(g)})) = (2 \cdot 156.9 + 31.92) - (2 \cdot S_{f}^{0}(H_{2}O_{(g)}) + 3 \cdot S_{f}^{0}(SO_{2(g)})) = (2 \cdot 156.9 + 31.92) - (2 \cdot S_{f}^{0}(H_{2}O_{(g)}) + 3 \cdot S_{f}^{0}(SO_{2(g)})) = (2 \cdot 156.9 + 31.92) - (2 \cdot S_{f}^{0}(H_{2}O_{(g)}) + 3 \cdot S_{f}^{0}(SO_{2(g)})) = (2 \cdot 156.9 + 31.92) - (2 \cdot S_{f}^{0}(H_{2}O_{(g)}) + 3 \cdot S_{f}^{0}(SO_{2(g)})) = (2 \cdot 156.9 + 31.92) - (2 \cdot S_{f}^{0}(H_{2}O_{(g)}) + 3 \cdot S_{f}^{0}(SO_{2(g)})) = (2 \cdot 156.9 + 31.92) - (2 \cdot S_{f}^{0}(H_{2}O_{(g)}) + 3 \cdot S_{f}^{0}(SO_{2(g)})) = (2 \cdot 156.9 + 31.92) - (2 \cdot 156.9 + 31.92)$

 $-(2 \cdot 188.72 + 3 \cdot 248.07) = -775.93J / K.$ $\Delta G_{208}^{0} = \Delta H_{208}^{0} - T \cdot \Delta S_{208}^{0} = -253.66 - 298(-0.77593) =$

 $\Delta G_{298} = \Delta H_{298} - I \cdot \Delta S_{298} = -255.00 - 298(-0.77595) = -22.43 \text{ kJ}.$ $\Delta H_{209} = -253.66 \text{ kJ}. \Delta S_{209} = -775.93 \text{ J/K}.$

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.

121. $CO_{(g)} + H_2O_{(l)} = CO_{2(g)} + H_{2(g)}$ **122**. $Fe_3O_4 + CO = 3FeO + CO_2$. $123 \ 2C_2H_2 + 5O_2 = 4CO_2 + 2H_2O_{(g)}$ 124. $CO_2 + H_2 = CO + H_2O_{(g)}$ 125. $CO + 3H_2 = CH_4 + H_2O_{(g)}$ **126.** $C_2H_4 + 3O_2 = 2CO_2 + 2H_2O_{(g)}$. $127 \quad 4NH_3 + 5O_2 = 4NO + 6H_2O_{(l)}$ 128. $^{2H_2O_2} = ^{2H_2O_{(l)}} + O_2$ 129 $2C_2H_2 + 5O_2 = 4CO_2 + 2H_2O_{(g)}$. **130.** $Fe_2O_3 + 3H_2 = Fe + 3H_2O_{(g)}$. **131.** $SO_2 + 2H_2S = 3S + 2H_2O_{(l)}$ $132 \quad CS_{2(l)} + 3O_2 = CO_2 + 2SO_2$ **133.** $^{2H_2S+SO_2=3S+2H_2O_{(l)}}$ **134**. $2CH_3OH_{(l)} + 3O_2 = 4H_2O_{(g)} + 2CO_2$ **135.** $2PH_3 + 4O_2 = P_2O_5 + 3H_2O_{(l)}$ **136.** $2C_2H_6 + 7O_2 = 4CO_2 + 6H_2O_{(g)}$. $137 \quad 2SO_2 + O_2 = 2SO_{3(g)}$ **138.** $CH_4 + 2O_2 = CO_2 + 2H_2O_{(1)}$ **139.** $Fe_2O_3 + H_2 = 2FeO + H_2O_{(l)}$ **140**. $2NO + O_2 = 2NO_2$

Substance	$\Delta {H}_{f}^{0}$	S_f^0
Substance	kJ/mol	J/(mol · K)
1	2	3
CH ₃ OH (l)	-239.45	126.6
CH _{4 (g)}	-74.81	186.31
CO (g)	-110.52	197.54
CO _{2 (g)}	-393.51	213.67
C_2H_2 (g)	226.0	200.83
C_2H_4 (g)	52.5	219.3
C_2H_6 (g)	-84.7	229.5
$CS_{2(l)}$	88.70	151.04
$\operatorname{CaC}_{2(s)}$	-60	70.0
CaO (s)	-635.1	38.1
$Cl_{2(g)}$	0	222.98
HCl (g)	-92.31	186.79
Fe _(s)	0	27.15
FeO _(s)	-265	60.8
Fe ₂ O _{3 (s)}	-822	87
Fe ₃ O _{4 (s)}	-1117.13	146.19
H _{2 (g)}	0	130.52
N _{2 (g)}	0	191.5
NH _{3 (g)}	-46.2	192.6
NH ₄ Cl (s)	-314.2	95.81
NO (g)	90.2	210.6
NO _{2 (g)}	33.5	240.2
O _{2 (g)}	0	205.04
H ₂ O _(g)	-241.82	188.72
$H_2O_{(l)}$	-285.83	70.08
H_2O_2 (l)	-187.78	109.5
P_2O_5 (s)	-1507.2	140.3
PH _{3 (g)}	5.4	210.2
S (s)	0	31.9

Table 6 - Standard enthalpy change of formation, standard entropy of some common substances at 298,15K*

Contination of the Table 6

SO _{2 (g)}	-296.90	248.07
SO _{3 (g)}	-395.8	256.7
$H_2S_{(g)}$	-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 will the equilibrium of the reversible reaction be shifted:
 - a) when temperature increases (p = const); b) when pressure decreases (T = const)? Explain your answer.

Example

Chemical equation:

$$2CO_{(g)} \leftrightarrow CO_{2(g)} + C_{(s)}; \ \Delta H^0_{298} < 0$$
$$Keq_{.} = \frac{[CO_2]^2}{[CO]^2};$$

a) in the equilibrium system:

$$2CO_{(g)} \leftrightarrow CO_{2(g)} + C_{(s)}; \ \Delta H^0_{298} < 0.$$

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 the increase of volume of gases (to the left).

Table 7

Number of variant	The equation of chemical reaction	$\Delta Hc.r,kJ$
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	$2NO + CI_2 \iff 2NOCI$	-73.6
144	$3O_2 \Leftrightarrow 2O_3$	184,6
145	$2H_2 + O_2 \iff 2H_2O_{(g)}$	-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	$4\text{HCI} + \text{O}_2 \iff 2\text{H}_2\text{O}_{(g)} + 2\text{Cl}_2$	-114.5
152	$C + H_2O_{(g)} \Leftrightarrow CO + H_2$	131
153	$2NOCI \Leftrightarrow 2NO+CI_2$	73.6
154	$2NH_3 \iff N_2 + 3H_2$	92.5
155	$2H_2S + 3O_2 \iff 2H_2O_{(g)} + 2SO_2$	-561.1
156	$2H_2O_{(g)} + 2CI_2 \Leftrightarrow 4HCI + O_2$	114.5
157	$CI_2 + CO \Leftrightarrow COCI_2$	-112.5
158	$2O_3 \Leftrightarrow 3O_2$	-184.6
159	$H_2 + CO_2 \iff CO + H_2O_{(g)}$	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

$$\mathcal{G}_{\text{forward}} = \kappa_1 \cdot p^2 s_{O_2} \cdot p_{O_2}$$

After pressure increasing:

$$\overline{\mathcal{G}}_{forward} = \kappa_1 \cdot (4p \ so_2)^2 \cdot 4p_{O_2} = 64 \cdot \kappa_1 \cdot p^2 so_2 \cdot p_{O_2}$$

$$\frac{\overline{9}_{forward}}{9_{forward}} = \frac{64 \cdot k_1 \cdot p^2 s_{O_2} \cdot p_{O_2}}{k_1 \cdot p^2 s_{O_2} \cdot p_{O_2}} = 64$$

Forward reaction rate will increase in 64 times.

$$\mathcal{G}_{reverse} = \kappa_2 \cdot p^2 so_3$$

After pressure increasing:

$$\bar{\vartheta}_{reverse} = \kappa_2 \cdot (4p_{SO_3})^2 = 16 \cdot \kappa_2 \cdot p^2 SO_3; \quad \frac{\bar{\vartheta}_{reverse}}{\vartheta_{reverse}} = \frac{16 \cdot k_2 \cdot p^2 SO_3}{k_2 \cdot p^2 SO_3} = 16$$

reverse reaction rate will increase in 16 times.

Table	8
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Number of	The equation of chemical	Pressure change of
variant	reaction	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	$3H_2 + N_2 \iff 2NH_3$	Will increase in 3 times
164	$2NO + CI_2 \Leftrightarrow 2NOCI$	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	$4HCI+O_2 \Leftrightarrow 2H_2O+2CI_2$	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	$Cl_2 + CO \iff COCI_2$	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	$2NOCI \Leftrightarrow 2NO + CI_2$	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 the oxidation numbers of which 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

1. $PbS + HNO_3 \rightarrow S + NO + Pb(NO_3)_2 + H_2O_2$

2. $S^{-2} - 2\overline{e} \rightarrow S^{0} | 3 |$ - the process is an oxidation,

the element is a reductant;

 $N^{+5} + 3\overline{e} \rightarrow N^{+2} |2|$ – the process is a reduction,

the element is an oxidant.

 $3PbS + 8HNO_3 \rightarrow 3S + 2NO + 3Pb(NO_3)_2 + 4 H_2O.$

We put the coefficients before formulas of substances containing atoms of elements that have changed their oxidation number. It will be taken into account that there are atoms N^{+4} and N^{+5} among the products of the reaction, thus, not all N atoms (in the left side of the equation 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:

3. $3PbS + HNO_3 \rightarrow 3S + 2NO + 3Pb(NO_3)_2 + H_2O$.

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): <u>2NO</u>, <u>3Pb(NO₃)₂</u>. The total number of N atoms is 8. We should write this (8) as the coefficient before the formula of nitric acid (HNO₃):

 $3PbS + 8 HNO_3 \rightarrow 3S + 2NO + 3Pb(NO_3)_2 + H_2O.$

One can see that the number of H atoms in the left side of the equation is 8 (before the formula HNO_3 . Therefore, before the formula H_2O we should write coefficient 4:

 $3PbS + 8HNO_3 \rightarrow 3S + 2NO + 3Pb(NO_3)_2 + 4 H_2O.$

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

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

181. $S + KClO3 + H2O \rightarrow Cl2 + K2SO4 + H2SO4.$

182. $FeSO_4 + KMnO_4 + H_2SO_4 \rightarrow Fe_2(SO_4)_3 + MnSO_4 + K_2SO_4 + H_2O.$

183. $Zn + KNO_3 + KOH + H_2O \rightarrow K_2[Zn(OH)_4] + NH_3.$

184. $AsH_3 + HNO_3 \rightarrow H_3AsO_4 + NO + H_2O.$

185. $K_2MnO_4 + H_2O \rightarrow KMnO_4 + MnO_2 + KOH.$

186. $KMnO_4 + H_2C_2O_4 + H_2SO_4 \rightarrow K_2SO_4 + MnSO_4 + CO_2 + H_2O.$

187. $Na_2SO_3 + KMnO_4 + HCl \rightarrow Na_2SO_4 + MnCl_2 + KCl + H_2O.$

188. $KClO_3 + KCl + H_2SO_4 \rightarrow Cl_2 + K_2SO_4 + H_2O.$

189. $KCrO_2 + KOH + H_2O_2 \rightarrow K_2CrO_4 + H_2O.$

190. $\operatorname{Zn} + \operatorname{HNO}_3 \rightarrow \operatorname{Zn}(\operatorname{NO}_3)_2 + \operatorname{NH}_4\operatorname{NO}_3 + \operatorname{H}_2\operatorname{O}.$

- 191. $\operatorname{Zn} + \operatorname{K_2Cr_2O_7} + \operatorname{H_2SO_4} \rightarrow \operatorname{ZnSO_4} + \operatorname{Cr_2(SO_4)_3} + \operatorname{K_2SO_4} + \operatorname{H_2O}.$
- 192. $K_2Cr_2O_7 + KNO_2 + H_2SO_4 \rightarrow Cr_2(SO_4)_3 + KNO_3 + K_2SO_4 + H_2O.$
- 193. $Br_2 + K_3[Cr(OH)_6] + KOH \rightarrow KBr + K_2CrO_4 + H_2O.$

194. $SnSO_4 + KMnO_4 + H_2SO_4 \rightarrow Sn(SO_4)_2 + MnSO_4 + K_2SO_4 + H_2O.$

195. $Si + HNO_3 + HF \rightarrow H_2[SiF_6] + NO + H_2O.$

196. $MnCO_3 + KClO_3 \rightarrow MnO_2 + KCl + CO_2$.

- 197. $\text{KClO}_3 + \text{FeSO}_4 + \text{H}_2\text{SO}_4 \rightarrow \text{KCl} + \text{Fe}_2(\text{SO}_4)_3 + \text{H}_2\text{O}.$
- 198. $Ti + HNO_3 + HF \rightarrow H_2[TiF_6] + NO + H_2O.$
- 199. $H_2O_2 + CrCl_3 + NaOH \rightarrow Na_2CrO_4 + NaCl + H_2O.$
- 200. $Zn + KClO_3 + KOH + H_2O \rightarrow K_2[Zn(OH)_4] + KCl.$

Number	Number of task
of variant	
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

Table 9 – Table of individual tasks

Continuation of the Table 9

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