Class №4 The theme: «Redox reactions. Galvanic cells. Redox potential».

1. Questions:

1. Oxidation number (oxidation state). Oxidation number rules.
2. Redox reactions (oxidation-reduction reactions). Classification of redox reactions. Oxidation, reduction, oxidizing and reducing agents.
3. Balancing oxidation-reduction equations using the electron-transfer method (change in oxidation number method).
4. Standard electrode potential. Anode. Cathode. Types of electrodes.
5. Galvanic cells. Electromotive force (emf). The Nernst equation.
6. Electrochemical (galvanic) cells. Types of electrochemical (galvanic) cells.
7. Spontaneity of redox reactions. Relationship between emf and ΔG.
8. Types of biological potentials (diffusion potential, membrane potential (rest and demarcation [injury] potentials), stream function (streaming potential), redox potential.
9. Application of redox titration: permanganatometry and iodimetry.

2. Familiarize with teaching tasks:

№	Content of the task:
1	Balance the redox equation using the change in oxidation number method. Does the reaction go spontaneously in the direction indicated under standard conditions? The corresponding electrode potentials are: $e^0_{SO_4^{2-}/SO_3^{2-}} = -0.93V$, $e^0_{MnO_4^-/MnO_2} = 0.6V$. $$\mathbf{Na_2SO_4 + MnO_2 + KOH \rightarrow Na_2SO_3 + KMnO_4 + H_2O}$$
	Solution: $\mathbf{S^{+6} + 2\bar{e} \rightarrow S^{+4}}$ | **6** | **3** **Reduction, cathode, eº = -0.93 V** $\mathbf{Mn^{+4} - 3\bar{e} \rightarrow Mn^{+7}}$ | | **2** **Oxidation, anode, eº = 0.6 V** Balance: $\mathbf{3Na_2SO_4 + 2MnO_2 + 2KOH \rightarrow 3Na_2SO_3 + 2KMnO_4 + H_2O}$ $E^o = e^o_{cathode} - e^o_{anode} = -0.93 - 0.6 = -1.53$ V $E^o < 0 \Rightarrow \Delta G > 0$ The forward reaction is nonspontaneous. The backward reaction flows spontaneously.
2	Calculate the standard emf of the following cell at 25ºC using standard electrode potentials. $$\mathbf{Al \mid Al^{3+} \parallel Fe^{2+} \mid Fe}$$ What is the cell reaction?
	Solution: The half-cell reactions and standard electrode potentials are $\mathbf{Al^o - 3\bar{e} \rightarrow Al^{+3}}$ | **6** | **2** **Oxidation, anode, eº = -1,662 V** $\mathbf{Fe^{+2} + 2\bar{e} \rightarrow Fe^o}$ | | **3** **Reduction, cathode, eº = -0.44 V** So, the addition of half-reactions is: $$\mathbf{2Al + 3Fe^{+2} \rightarrow 2Al^{+3} + 3Fe}$$ The standard emf can be calculated from the formula: $E^o = e^o_{cathode} - e^o_{anode} = -0.44 - (-1.66) = 1.22$ V
3	Calculate the emf of the following cell at 25ºC: $$Zn \mid Zn(NO_3)_2\ (0.1\ M) \parallel AgNO_3\ (1\ M) \mid Ag$$
	Solution: $\mathbf{Zn^o - 2\bar{e} \rightarrow Zn^{+2}}$ | **2** | **1** **oxidation, anode, eº = -0.76 V** $\mathbf{Ag^+ + 1\bar{e} \rightarrow Ag^o}$ | | **2** **reduction, cathode, eº = +0.8 V** The overall cell reaction is:

	$Zn + 2Ag^{+} \rightarrow Zn^{+2} + 2Ag$ The number of electron transferred (least common multiple) is two: hence, n = 2 According to the Nernst equation: $E = E^{o} - \frac{0,059}{n} \times \log Q$, where Q – an equilibrium constant, $Q = \frac{[Zn^{+2}]}{[Ag^{+}]^{2}}$ So, $E = E^{o} - \frac{0,059}{2} \times \log \frac{[Zn^{+2}]}{[Ag^{+}]^{2}}$, where $E^{o} = e^{o}_{cathode} - e^{o}_{anode}$ $E^{o} = 0.8 - (-0.76) = 1.56$ V $E = 1.56 - 0.0295 \times \log \frac{0.1}{1^{2}}$ $E = 1.56 - 0.0295 \times \log 0.1$ $E = 1.56 + 0.0295 = 1.59$ V
4	Calculate the emf of the following cell at 25ºC: $Cu \mid Cu(NO_3)_2\ (0.1\ M) \parallel Cu(NO_3)_2\ (1\ M) \mid Cu$
	Solution: $\mathbf{Cu - 2\bar{e} \rightarrow Cu^{+2}}$ | **2** | **1** **e^{o} = 0.34 V oxidation, anode** $\mathbf{Cu^{+2} + 2\bar{e} \rightarrow Cu}$ | | **1** **e^{o} = 0.34 V reduction, cathode** The overall cell reaction is: **$Cu + Cu^{+2}(1M) \rightarrow Cu^{+2}(0.1M) + Cu$** According to the Nernst equation for the concentration cell: $E = E^{o} - \frac{0,059}{n} \cdot \log \frac{C_1}{C_2}$, where $E^{o} = e^{o}_{cathode} - e^{o}_{anode} = 0.34 - 0.34 = 0$ V $E = \frac{0.059}{2} \cdot \log \frac{C_2}{C_1} = 0.0295 \times \log \frac{1}{0.1}$ $\Rightarrow$ $E = 0.0295 \times \log 10 = 0.0295$ V

3. Answer the multiple-choice test questions (in written form):

1 What is the oxidation number of chromium in potassium chromate (K_2CrO_4)?

A +6
B +7
C +3
D +4

2 What is the oxidation state of nitrogen in ammonium ion $(NH_4)^{+}$?

A +3
B -3
C +4
D -4

3 What species (atoms or ions) are losing electrons (or increasing the oxidation state) during the redox reaction?

A Oxidizing agent
B Disproportionate agent
C Reducing agent
D All answers correct

4 Identify the oxidizing agent: $H_2S + 4Cl_2 + 4H_2O \rightarrow H_2SO_4 + 8HCl$

A H_2S
B Cl_2
C H_2O

D HCl

5 Identify the type of reaction: $S^{-2} \rightarrow S^{+6}$. How many electrons transfer in this reaction?

A Reduction – 8e

B Oxidation – $6e^-$

C Oxidation - $8e^-$

6 In what substance nitrogen can **only** be an oxidizing agent:

A HNO_3

B NO_2

C HNO_2

D NH_3

7 Indicate the reduction half-reaction:

A $N_2 \rightarrow (NH_4)^+$

B $MnO_2 \rightarrow (MnO_4)^-$

C $Cl_2 \rightarrow (ClO_3)^-$

D $(SO_3)^{2-} \rightarrow (SO_4)^{2-}$

8 What is the equivalent mass of $KMnO_4$, if it reduces to MnO_2?

A 58

B 52.7

C 31.61

D 79

9 What process occurs on cathode of galvanic cell?

A Reduction

B Oxidation

C Neutralization

D Adsorption

10 Indicate the strongest reducing agent:

A Cu

B Fe

C Zn

D Ag

11 What is a concentration of Cu^{2+} ions in solution if electrode potential of Cu-electrode in this solution is equal to standard.

A 0.1 mol/L

B 0.5 mol/L

C 1 mol/L

D 2 mol/L

12 What is the standard electrode from the following:

A Hydrogen electrode

B Carbon electrode

C Glass electrode

D Enzyme electrode

13 A Galvanic cell is an electrochemical device that:

A Converts the thermal energy into work

B Derives the electrical energy from chemical reactions

C Derives the thermal energy from electrical energy

D Determines conductivity of solutions of electrolytes

14 A redox reaction is spontaneous if:

A emf > 0, ΔG > 0

B emf > 0, ΔG < 0

C emf < 0, ΔG > 0

D emf < 0, ΔG < 0

15 What is a direction of electron transfer in galvanic cell: $Cd|Cd^{2+}||Cu^{2+}|Cu$?

A From Cd-electrode to Cu-electrode

B From Cu-electrode to Cd-electrode

C No electrons transfer

16 For which electrode the emf value is the biggest (answer without calculations)?

A $Al|Al^{3+}||Sn^{2+}|Sn$

B $Fe|Fe^{2+}||Cu^{2+}|Cu$

C $Al|Al^{3+}||Ag^{+}|Ag$

17 What changes in mass of zinc electrode occur as a result of work of the Daniell cell (Zn-Cu cell):

A Increase

B Decrease

C Do not change

18 What is the formula of a membrane potential?

A $e = \frac{RT}{n} \times \ln \frac{C_1}{C_o}$

B $e = \frac{RT}{nF} \times \ln \frac{C_2}{C_1}$

C $e = \frac{RT}{nF} \times \ln \frac{C_{Ox}}{C_{Red}}$

D $e = \frac{0{,}059}{nF} \times \log \frac{C_1}{C_2}$

19 What is a name of biopotential that appears between the interior and exterior of a cell?

A Electrode potential

B Diffusion potential

C Membrane potential

D Streaming potential

20 What potential arises as a result of different rates of diffusion of ions at the interface of two dissimilar fluids?

A Redox potential

B Membrane potential

C Streaming potential

D Diffusion potential

4. Tasks for an independent work (in written form):

1. Determine the oxidation number (state) of **N** in each of the following compounds:

$\mathbf{NH_4F}$, $\mathbf{NO}$, $\mathbf{HNO_3}$, $\mathbf{Ca(NO_2)_2}$, $\mathbf{N_2}$

2. Balance the redox equation using the change in oxidation number method. Does the reaction go spontaneously in the direction indicated under standard conditions? The corresponding electrode potentials are: $e^0_{Br_2/Br^-} = 1.0652V$, $e^0_{MnO_4^-/MnO_2} = 0.6V$

$$\mathbf{NaBr + KMnO_4 + H_2O \rightarrow NaOH + Br_2 + MnO_2 + KOH}$$

3. Calculate the emf of the following cell at 25ºC:

$$\mathbf{Zn \mid Zn^{2+}\,(0.1M) \parallel Au^{+3}\,(0.1M) \mid Au}$$

4. Calculate the emf of the following cell at 25ºC:

$$\mathbf{Cu \mid Cu^{2+}\,(0.02\ M) \parallel Cu^{2+}\,(0.2\ M) \mid Cu}$$

Laboratory work: «Determination of the molar concentration of equivalent (normality) of $FeSO_4$ solution by the redox titration (permanganatometry)».

Permanganate ion (MnO_4^-) can undergo several different reactions. The one that occurs in acid solution is the most commonly used:

$$MnO_4^- + 8H^+ + 5\bar{e} \rightarrow Mn^{2+} + H_2O$$

Permanganate has the advantage of being its own indicator – the MnO_4^- ion is intensely purple, and the Mn^{2+} ion is almost colorless. As long as some reducing agent remains in the solution being titrated, the solution remains colorless, since the purple MnO_4^- ion being added is converted to the essentially colorless Mn^{2+} ion. However, when the reducing agent has been consumed completely, the next drop of permanganate titrant will turn the solution into light purple (pink).

The solution of $KMnO_4$ is often used as a titrant to determine the concentration of $FeSO_4$. The redox reaction in acidic solution is following:

$$\mathbf{2KMnO_4 + 8H_2SO_4 + 10FeSO_4 \rightarrow 5Fe_2(SO_4)_3 + 2MnSO_4 + K_2SO_4 + 8H_2O}$$

$\mathbf{2Fe^{2+} - 2\bar{e} \rightarrow 2Fe^{3+}}$	**10**	**5**	Oxidation, reducing agent
$\mathbf{Mn^{7+} + 5\bar{e} \rightarrow Mn^{2+}}$		**2**	Reduction, oxidizing agent

Procedure:

1. Measure exactly 10 ml of $FeSO_4$ solution with pipette or graduated test-tube and pour this solution into a conical flask. Add 8 ml of H_2SO_4 to this flask.
2. Begin by preparing your burette. Your burette should be conditioned and filled with titrant (0.1 N $KMnO_4$ solution). You should check for air bubbles and leaks, before proceeding with the titration.
3. Slowly (drop-by-drop) add titrant from the burette to the flask until the solution just changes from colorless to pink.
4. Repeat titration procedure 2 – 3 times and fill in your table.

№	V($FeSO_4$), ml	V($KMnO_4$), ml	C_f($KMnO_4$), N	Average V($KMnO_4$), ml
1	10 ml		0.1	
2	10 ml		0.1	
3	10 ml		0.1	

5. Calculate the molar concentration of the equivalent (normality) of the $FeSO_4$ solution using the formula:

$$C_f(FeSO_4) = \frac{C_f(KMnO_4) \cdot V(KMnO_4)}{V(FeSO_4)}$$

Make a conclusion.

Standard electrode (reduction) potentials at 25 °C:

Electrode	Half-reaction	e^o, V
Li^+/Li	$Li^+ + e \leftrightarrow Li$	-3.045
K^+/K	$K^+ + e \leftrightarrow K$	-2.925
Ba^{+2}/Ba	$Ba^{+2} + 2e \leftrightarrow Ba$	-2.906
Ca^{+2}/Ca	$Ca^{+2} + 2e \leftrightarrow Ca$	-2.866
Na^+/Na	$Na^+ + e \leftrightarrow Na$	-2.714
Mg^{+2}/Mg	$Mg^{+2} + 2e \leftrightarrow Mg$	-2.363
Be^{+2}/Be	$Be^{+2} + 2e \leftrightarrow Be$	-1.847
Al^{+3}/Al	$Al^{+3} + 3e \leftrightarrow Al$	-1.662
V^{+2}/V	$V^{+2} + 2e \leftrightarrow V$	-1.186
Mn^{+2}/Mn	$Mn^{+2} + 2e \leftrightarrow Mn$	-1.180
WO_4^{2-}/W	$WO_4^{-2} + 4H_2O + 6e \leftrightarrow W + 8OH^-$	-1.105
OH^-/H_2, Pt	$H_2O + e \leftrightarrow ½ H_2 + OH^-$	-0.8279
Se^{2-}/Se	$Se + 2e \leftrightarrow Se^{-2}$	-0.77
Zn^{+2}/Zn	$Zn^{+2} + 2e \leftrightarrow Zn$	-0.763
Cr^{+3}/Cr	$Cr^{+3} + 3e \leftrightarrow Cr$	-0.744
S^{2-}/S	$S + 2e \leftrightarrow S^{-2}$	-0.51
Fe^{+2}/Fe	$Fe^{+2} + 2e \leftrightarrow Fe$	-0.440
$Cr^{+3},Cr^{+2}/Pt$	$Cr^{+3} + e \leftrightarrow Cr^{+2}$	-0.408
Cd^{+2}/Cd	$Cd^{+2} + 2e \leftrightarrow Cd$	-0.403
Co^{+2}/Co	$Co^{+2} + 2e \leftrightarrow Co$	-0.277
Ni^{+2}/Ni	$Ni^{+2} + 2e \leftrightarrow Ni$	-0.250
Sn^{+2}/Sn	$Sn^{+2} + 2e \leftrightarrow Sn$	-0.136
Pb^{+2}/Pb	$Pb^{+2} + 2e \leftrightarrow Pb$	-0.126
H^+/H_2, Pt	**$H^+ + e \leftrightarrow ½ H_2$**	**0.000**
Ge^{+2}/Ge	$Ge^{+2} + 2e \leftrightarrow Ge$	+0.01
$Sn^{+4},Sn^{+2}/Pt$	$Sn^{+4} + 2e \leftrightarrow Sn^{+2}$	+0.15
$Cu^{+2},Cu^+/Pt$	$Cu^{+2} + e \leftrightarrow Cu^+$	+0.153
$Cl^-/AgCl$, Ag	$AgCl + e \leftrightarrow Ag + Cl^-$	+0.2224
Cl^-/Hg_2Cl_2, Hg	$Hg_2Cl_2 + 2e \leftrightarrow 2Hg + 2Cl^-$	+0.268
Cu^{+2}/Cu	$Cu^{+2} + 2e \leftrightarrow Cu$	+0.337
Cu^+/Cu	$Cu^+ + e \leftrightarrow Cu$	+0.521
I^-/I_2, Pt	$I_2 + 2e \leftrightarrow 2I^-$	+0.5355
Fe^{+3}, Fe^{+2}/ Pt	$Fe^{+3} + e \leftrightarrow Fe^{+2}$	+0.771
Hg_2^{+2}/Hg	$Hg_2^{+2} + 2e \leftrightarrow 2Hg$	+0.788
Ag^+/Ag	$Ag^+ + e \leftrightarrow Ag$	+0.7991
Hg^{+2}/Hg	$Hg^{+2} + 2e \leftrightarrow Hg$	+0.854
Hg^{+2}, Hg^+/Pt	$Hg^{+2} + 2e \leftrightarrow Hg^+$	+0.91
Pd^{+2}/Pd	$Pd^{+2} + 2e \leftrightarrow Pd$	+0.987
Br^-/Br_2, Pt	$Br_2 + 2e \leftrightarrow 2Br^-$	+1.0652
Pt^{+2}/Pt	$Pt^{+2} + 2e \leftrightarrow Pt$	+1.2
H^+/O_2, Pt	$2H^+ + ½ O_2 + 2e \leftrightarrow H_2O$	+1.2288
Cl^-/Cl_2, Pt	$Cl_2 + 2e \leftrightarrow 2Cl^-$	+1.3595
Pb^{+2}, H^+/PbO_2, Pt	$PbO_2 + 4H^+ + 2e \leftrightarrow Pb^{+2} + 2H_2O$	+1.455
Au^{+3}/Au	$Au^{+3} + 3e \leftrightarrow Au$	+1.498
MnO_4^-, H^+ /MnO_2, Pt	$MnO_4^- + 4H^+ + 3e \leftrightarrow MnO_2 + 2H_2O$	+1.695
Au^+/Au	$Au^+ + e \leftrightarrow Au$	+1.691
H^-/H_2, Pt	$H_2 + 2e \leftrightarrow 2H^-$	+2.2
F/F_2, Pt	$F_2 + 2e \leftrightarrow 2F^-$	+2.87