

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	<p>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: $e^{\circ}_{SO_4^{2-}/SO_3^{2-}} = -0.93V$, $e^{\circ}_{MnO_4^-/MnO_2} = 0.6V$.</p> $Na_2SO_4 + MnO_2 + KOH \rightarrow Na_2SO_3 + KMnO_4 + H_2O$ <p>Solution: $S^{+6} + 2\bar{e} \rightarrow S^{+4} \quad \left \begin{array}{l} 6 \\ 3 \end{array} \right. \quad \text{Reduction, cathode, } e^{\circ} = -0.93 V$ $Mn^{+4} - 3\bar{e} \rightarrow Mn^{+7} \quad \left \begin{array}{l} 2 \\ 2 \end{array} \right. \quad \text{Oxidation, anode, } e^{\circ} = 0.6 V$</p> <p>Balance: $3Na_2SO_4 + 2MnO_2 + 2KOH \rightarrow 3Na_2SO_3 + 2KMnO_4 + H_2O$</p> <p>$E^{\circ} = e^{\circ}_{\text{cathode}} - e^{\circ}_{\text{anode}} = -0.93 - 0.6 = -1.53 V$</p> <p>$E^{\circ} < 0 \Rightarrow \Delta G > 0$</p> <p>The forward reaction is nonspontaneous. The backward reaction flows spontaneously.</p>
2	<p>Calculate the standard emf of the following cell at 25°C using standard electrode potentials.</p> $Al \mid Al^{3+} \parallel Fe^{2+} \mid Fe$ <p>What is the cell reaction?</p> <p>Solution: The half-cell reactions and standard electrode potentials are</p> $Al^{\circ} - 3\bar{e} \rightarrow Al^{+3} \quad \left \begin{array}{l} 6 \\ 2 \end{array} \right. \quad \text{Oxidation, anode, } e^{\circ} = -1,662 V$ $Fe^{+2} + 2\bar{e} \rightarrow Fe^{\circ} \quad \left \begin{array}{l} 3 \\ 3 \end{array} \right. \quad \text{Reduction, cathode, } e^{\circ} = -0.44 V$ <p>So, the addition of half-reactions is:</p> $2Al + 3Fe^{+2} \rightarrow 2Al^{+3} + 3Fe$ <p>The standard emf can be calculated from the formula:</p> <p>$E^{\circ} = e^{\circ}_{\text{cathode}} - e^{\circ}_{\text{anode}} = -0.44 - (-1.66) = 1.22 V$</p>
3	<p>Calculate the emf of the following cell at 25°C:</p> $Zn \mid Zn(NO_3)_2 (0.1 M) \parallel AgNO_3 (1 M) \mid Ag$ <p>Solution:</p> $Zn^{\circ} - 2\bar{e} \rightarrow Zn^{+2} \quad \left \begin{array}{l} 2 \\ 1 \end{array} \right. \quad \text{oxidation, anode, } e^{\circ} = -0.76 V$ $Ag^{+} + 1\bar{e} \rightarrow Ag^{\circ} \quad \left \begin{array}{l} 2 \\ 2 \end{array} \right. \quad \text{reduction, cathode, } e^{\circ} = +0.8 V$ <p>The overall cell reaction is:</p>

	<p style="text-align: center;">$Zn + 2Ag^+ \rightarrow Zn^{+2} + 2Ag$</p> <p>The number of electron transferred (least common multiple) is two: hence, $n = 2$</p> <p>According to the Nernst equation: $E = E^{\circ} - \frac{0,059}{n} \times \log Q$,</p> <p>where Q – an equilibrium constant, $Q = \frac{[Zn^{+2}]}{[Ag^+]^2}$</p> <p>So, $E = E^{\circ} - \frac{0,059}{2} \times \log \frac{[Zn^{+2}]}{[Ag^+]^2}$, where $E^{\circ} = e^{\circ}_{\text{cathode}} - e^{\circ}_{\text{anode}}$</p> <p>$E^{\circ} = 0.8 - (-0.76) = 1.56 \text{ V}$</p> <p>$E = 1.56 - 0.0295 \times \log \frac{0.1}{1^2}$</p> <p>$E = 1.56 - 0.0295 \times \log 0.1$</p> <p>$E = 1.56 + 0.0295 = 1.59 \text{ V}$</p>										
4	<p>Calculate the emf of the following cell at 25°C:</p> <p style="text-align: center;">$Cu \mid Cu(NO_3)_2 (0.1 \text{ M}) \parallel Cu (NO_3)_2 (1 \text{ M}) \mid Cu$</p> <p>Solution:</p> <table style="margin-left: 20px;"> <tr> <td>$Cu - 2e^- \rightarrow Cu^{+2}$</td> <td style="border-left: 1px solid black; padding-left: 5px;">2</td> <td style="border-left: 1px solid black; padding-left: 5px;">1</td> <td>$e^{\circ} = 0.34 \text{ V}$</td> <td>oxidation, anode</td> </tr> <tr> <td>$Cu^{+2} + 2e^- \rightarrow Cu$</td> <td style="border-left: 1px solid black; padding-left: 5px;">1</td> <td style="border-left: 1px solid black; padding-left: 5px;">1</td> <td>$e^{\circ} = 0.34 \text{ V}$</td> <td>reduction, cathode</td> </tr> </table> <p>The overall cell reaction is: $Cu + Cu^{+2} (1M) \rightarrow Cu^{+2} (0.1M) + Cu$</p> <p>According to the Nernst equation for the concentration cell: $E = E^{\circ} - \frac{0,059}{n} \cdot \log \frac{C_1}{C_2}$,</p> <p>where $E^{\circ} = e^{\circ}_{\text{cathode}} - e^{\circ}_{\text{anode}} = 0.34 - 0.34 = 0 \text{ V}$</p> <p>$E = \frac{0.059}{2} \cdot \log \frac{C_2}{C_1} = 0.0295 \times \log \frac{1}{0.1} \Rightarrow E = 0.0295 \times \log 10 = 0.0295 \text{ V}$</p>	$Cu - 2e^- \rightarrow Cu^{+2}$	2	1	$e^{\circ} = 0.34 \text{ V}$	oxidation, anode	$Cu^{+2} + 2e^- \rightarrow Cu$	1	1	$e^{\circ} = 0.34 \text{ V}$	reduction, cathode
$Cu - 2e^- \rightarrow Cu^{+2}$	2	1	$e^{\circ} = 0.34 \text{ V}$	oxidation, anode							
$Cu^{+2} + 2e^- \rightarrow Cu$	1	1	$e^{\circ} = 0.34 \text{ V}$	reduction, cathode							

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 $\text{emf} > 0, \Delta G > 0$
 - B $\text{emf} > 0, \Delta G < 0$
 - C $\text{emf} < 0, \Delta G > 0$
 - D $\text{emf} < 0, \Delta G < 0$
- 15 What is a direction of electron transfer in galvanic cell: $\text{Cd} | \text{Cd}^{2+} || \text{Cu}^{2+} | \text{Cu}$?
- 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 $\text{Al} | \text{Al}^{3+} || \text{Sn}^{2+} | \text{Sn}$
 - B $\text{Fe} | \text{Fe}^{2+} || \text{Cu}^{2+} | \text{Cu}$
 - C $\text{Al} | \text{Al}^{3+} || \text{Ag}^{+} | \text{Ag}$
- 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 $e = \frac{RT}{nF} \times \ln \frac{C_{\text{Ox}}}{C_{\text{Red}}}$
 - 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):

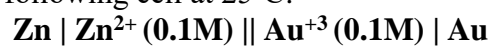
1. Determine the oxidation number (state) of N in each of the following compounds:



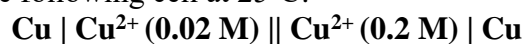
2. Balance the redox equation using the change in oxidation number method. Does the reaction go spontaneously in the direction indicated under standard conditions? The corresponding electrode potentials are: $e^0_{Br_2/Br^-} = 1.0652V$, $e^0_{MnO_4^-/MnO_2} = 0.6V$



3. Calculate the emf of the following cell at 25°C:



4. Calculate the emf of the following cell at 25°C:



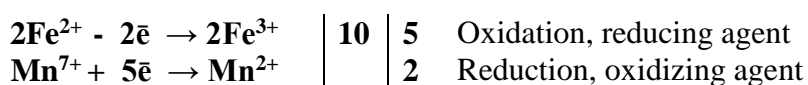
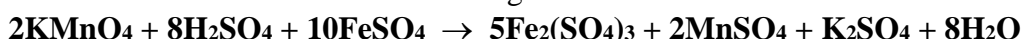
Laboratory work: «Determination of the molar concentration of equivalent (normality) of FeSO₄ solution by the redox titration (permanganometry)».

Permanganate ion (MnO₄⁻) can undergo several different reactions. The one that occurs in acid solution is the most commonly used:



Permanganate has the advantage of being its own indicator – the MnO₄⁻ ion is intensely purple, and the Mn²⁺ ion is almost colorless. As long as some reducing agent remains in the solution being titrated, the solution remains colorless, since the purple MnO₄⁻ ion being added is converted to the essentially colorless Mn²⁺ 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 KMnO₄ is often used as a titrant to determine the concentration of FeSO₄. The redox reaction in acidic solution is following:



Procedure:

1. Measure exactly 10 ml of FeSO₄ solution with pipette or graduated test-tube and pour this solution into a conical flask. Add 8 ml of H₂SO₄ to this flask.
2. Begin by preparing your burette. Your burette should be conditioned and filled with titrant (0.1 N KMnO₄ 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 FeSO₄ solution using the formula:

$$C_f(\text{FeSO}_4) = \frac{C_f(\text{KMnO}_4) \cdot V(\text{KMnO}_4)}{V(\text{FeSO}_4)}$$

Make a conclusion.

Standard electrode (reduction) potentials at 25 °C:

Electrode	Half-reaction	e⁰, V
Li ⁺ /Li	Li ⁺ + e ↔ Li	-3.045
K ⁺ /K	K ⁺ + e ↔ K	-2.925
Ba ⁺² /Ba	Ba ⁺² + 2e ↔ Ba	-2.906
Ca ⁺² /Ca	Ca ⁺² + 2e ↔ Ca	-2.866
Na ⁺ /Na	Na ⁺ + e ↔ Na	-2.714
Mg ⁺² /Mg	Mg ⁺² + 2e ↔ Mg	-2.363
Be ⁺² /Be	Be ⁺² + 2e ↔ Be	-1.847
Al ⁺³ /Al	Al ⁺³ + 3e ↔ Al	-1.662
V ⁺² /V	V ⁺² + 2e ↔ V	-1.186
Mn ⁺² /Mn	Mn ⁺² + 2e ↔ Mn	-1.180
WO ₄ ²⁻ /W	WO ₄ ²⁻ + 4H ₂ O + 6e ↔ W + 8OH ⁻	-1.105
OH ⁻ /H ₂ , Pt	H ₂ O + e ↔ ½ H ₂ + OH ⁻	-0.8279
Se ²⁻ /Se	Se + 2e ↔ Se ²⁻	-0.77
Zn ⁺² /Zn	Zn ⁺² + 2e ↔ Zn	-0.763
Cr ⁺³ /Cr	Cr ⁺³ + 3e ↔ Cr	-0.744
S ²⁻ /S	S + 2e ↔ S ²⁻	-0.51
Fe ⁺² /Fe	Fe ⁺² + 2e ↔ Fe	-0.440
Cr ⁺³ , Cr ⁺² /Pt	Cr ⁺³ + e ↔ Cr ⁺²	-0.408
Cd ⁺² /Cd	Cd ⁺² + 2e ↔ Cd	-0.403
Co ⁺² /Co	Co ⁺² + 2e ↔ Co	-0.277
Ni ⁺² /Ni	Ni ⁺² + 2e ↔ Ni	-0.250
Sn ⁺² /Sn	Sn ⁺² + 2e ↔ Sn	-0.136
Pb ⁺² /Pb	Pb ⁺² + 2e ↔ Pb	-0.126
H⁺/H₂, Pt	H⁺ + e ↔ ½ H₂	0.000
Ge ⁺² /Ge	Ge ⁺² + 2e ↔ Ge	+0.01
Sn ⁺⁴ , Sn ⁺² /Pt	Sn ⁺⁴ + 2e ↔ Sn ⁺²	+0.15
Cu ⁺² , Cu ⁺ /Pt	Cu ⁺² + e ↔ Cu ⁺	+0.153
Cl ⁻ /AgCl, Ag	AgCl + e ↔ Ag + Cl ⁻	+0.2224
Cl ⁻ /Hg ₂ Cl ₂ , Hg	Hg ₂ Cl ₂ + 2e ↔ 2Hg + 2Cl ⁻	+0.268
Cu ⁺² /Cu	Cu ⁺² + 2e ↔ Cu	+0.337
Cu ⁺ /Cu	Cu ⁺ + e ↔ Cu	+0.521
I ⁻ /I ₂ , Pt	I ₂ + 2e ↔ 2I ⁻	+0.5355
Fe ⁺³ , Fe ⁺² /Pt	Fe ⁺³ + e ↔ Fe ⁺²	+0.771
Hg ₂ ⁺² /Hg	Hg ₂ ⁺² + 2e ↔ 2Hg	+0.788
Ag ⁺ /Ag	Ag ⁺ + e ↔ Ag	+0.7991
Hg ⁺² /Hg	Hg ⁺² + 2e ↔ Hg	+0.854
Hg ⁺² , Hg ⁺ /Pt	Hg ⁺² + 2e ↔ Hg ⁺	+0.91
Pd ⁺² /Pd	Pd ⁺² + 2e ↔ Pd	+0.987
Br ⁻ /Br ₂ , Pt	Br ₂ + 2e ↔ 2Br ⁻	+1.0652
Pt ⁺² /Pt	Pt ⁺² + 2e ↔ Pt	+1.2
H ⁺ /O ₂ , Pt	2H ⁺ + ½ O ₂ + 2e ↔ H ₂ O	+1.2288
Cl ⁻ /Cl ₂ , Pt	Cl ₂ + 2e ↔ 2Cl ⁻	+1.3595
Pb ⁺² , H ⁺ /PbO ₂ , Pt	PbO ₂ + 4H ⁺ + 2e ↔ Pb ⁺² + 2H ₂ O	+1.455
Au ⁺³ /Au	Au ⁺³ + 3e ↔ Au	+1.498
MnO ₄ ⁻ , H ⁺ /MnO ₂ , Pt	MnO ₄ ⁻ + 4H ⁺ + 3e ↔ MnO ₂ + 2H ₂ O	+1.695
Au ⁺ /Au	Au ⁺ + e ↔ Au	+1.691
H ⁻ /H ₂ , Pt	H ₂ + 2e ↔ 2H ⁻	+2.2
F ⁻ /F ₂ , Pt	F ₂ + 2e ↔ 2F ⁻	+2.87

