Oxidation - reduction reactions (ORR)

Lecture 3

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What will we study?

1. The concept of a conjugated redox pair and its oxidation-reduction (redox) potential

2. Mechanism of origin of electrode potentials

3. The value of ORR in biology and medicine

4. Methods of oxidimetry. Determination of oxidizing and reducing agents in solutions

Relevance

- Redox processes underlie the interconversion of different forms of energy.

Rusting of Iron   Browning of Fruits   Process of Respiration   Photosynthesis
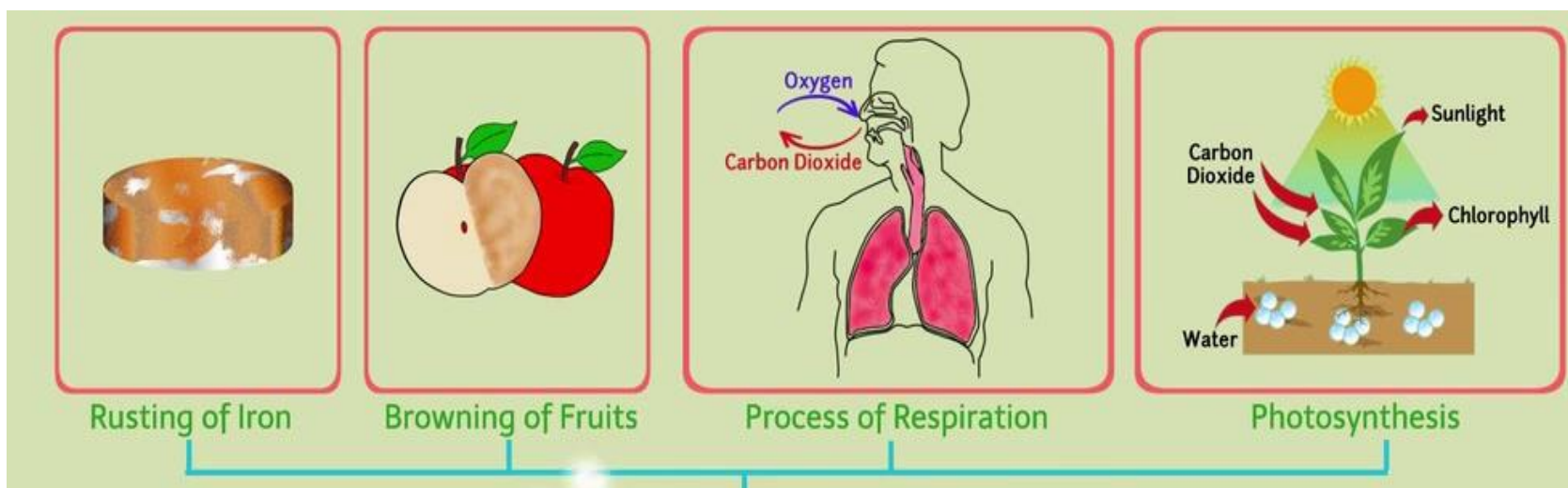
- Knowing the redox status of the cell helps to justify the use of antioxidants or the connection of emergency assistance in case of poisoning with oxidants or reducing agents.

Relevance

- Many oxidizing agents, such as potassium permanganate $KMnO_4$, hydrogen peroxide H_2O_2 (3% solution), iodine I_2 (5% alcohol solution), ozone O_3, are used as bactericidal agents in medical practice
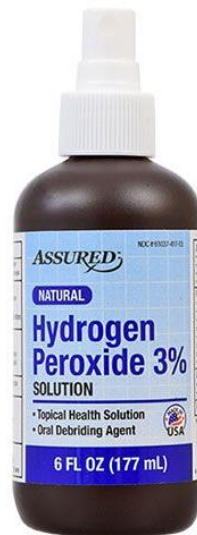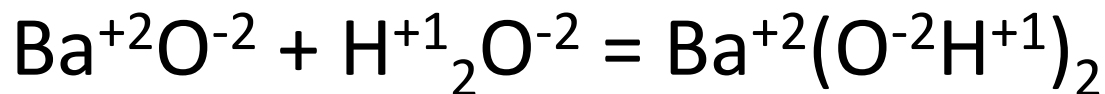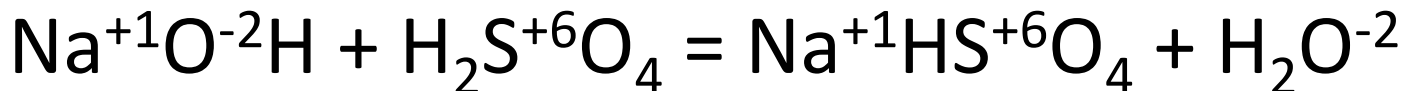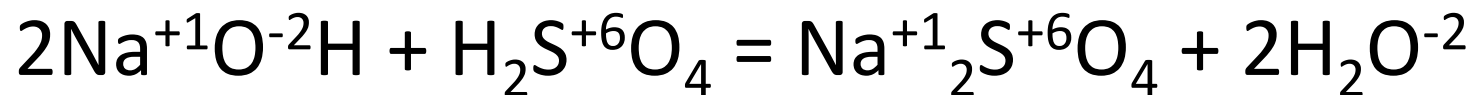
The aim of the lecture is

- to show the essence of redox reactions through the concepts of conjugated redox pair and its redox potential.
- to substantiate the use of oxidants, reducing agents and antioxidants in pharmacotherapy and consider methods for determining their quantitative content in solutions (concentration).

The concept of a conjugated redox pair

$$2Na^{+1}O^{-2}H + H_2S^{+6}O_4 = Na^{+1}{}_2S^{+6}O_4 + 2H_2O^{-2}$$

$$Na^{+1}O^{-2}H + H_2S^{+6}O_4 = Na^{+1}HS^{+6}O_4 + H_2O^{-2}$$

$$Ba^{+2}O^{-2} + H^{+1}{}_2O^{-2} = Ba^{+2}(O^{-2}H^{+1})_2$$

The concept of a conjugated redox pair

Oxidation-reduction reactions (ORR) are chemical reactions that occur with a change in the oxidation state of atoms due to the redistribution of electrons between them.

The oxidation state is the conditional charge that an atom gets as a result of the donation or attachment of electrons. The process of giving an atom of electrons is called **oxidation** and the acceptance of electrons is called a **reduction**. The starting material containing the atom to be oxidized is called **a reducing agent**. **An oxidizing agent** is a substance in which a reducing atom is present, that is the atom that takes away electrons from another atom.

An oxidizer (oxidizing agent, oxidant) is a substance that contains an atom which is capable of accepting electrons (electron acceptor). At the same time, its oxidation state decreases, and it transfers into the reduced form.

Oxidizer + e = conjugate reductant

A reductant (reducing agent) is a substance that contains an atom which is capable of donating electrons (electron donor). At the same time, its oxidation state increases, and it transfers into an oxidized form.
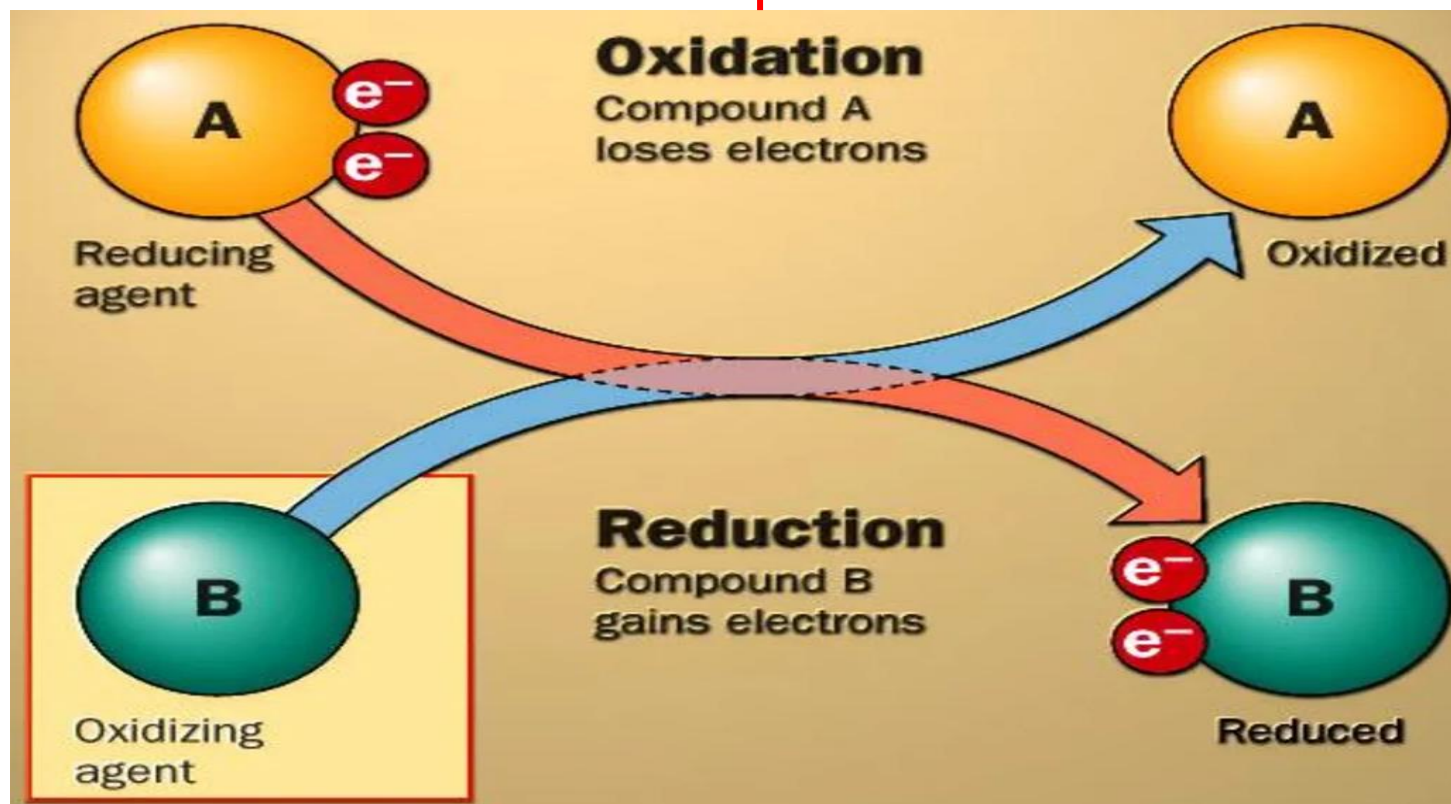
Reductant – e = conjugate oxidizer
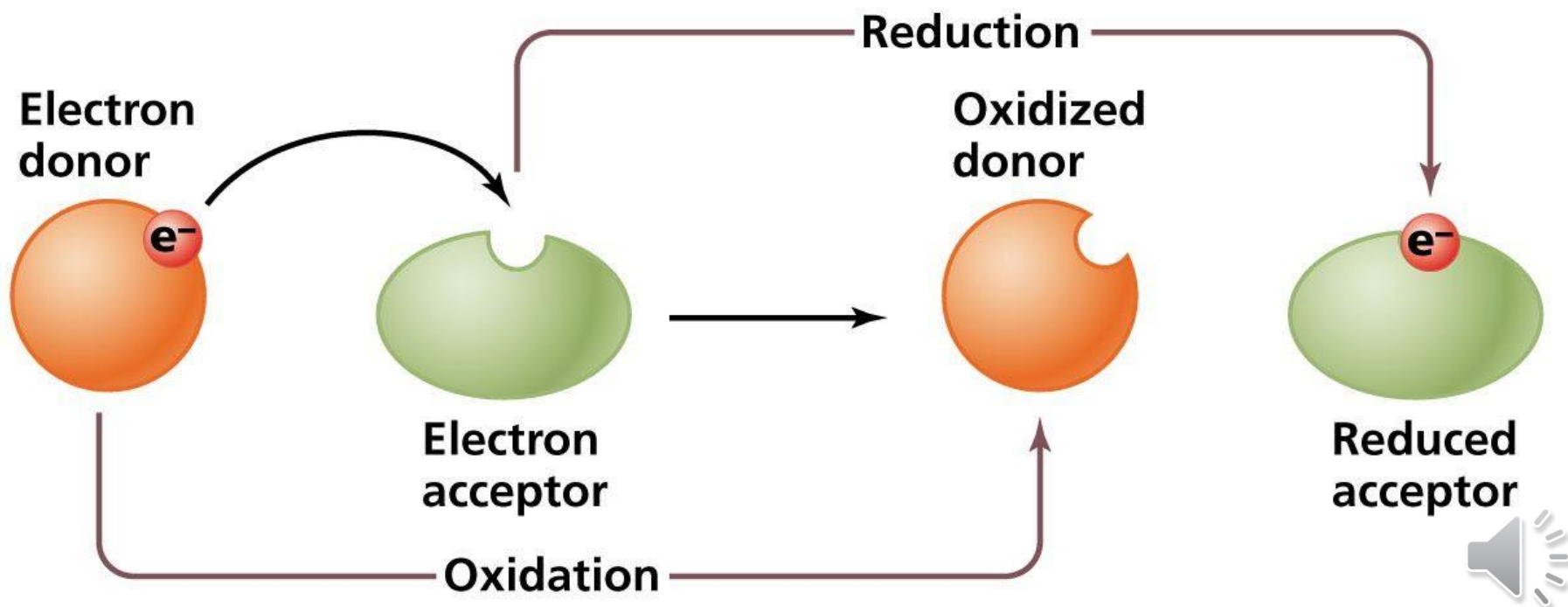
! Please, don't confuse

- the **oxidizing agent takes electrons** from the reducing agent **and** therefore it is **reduced**

- the **reducing agent gives electrons** to the oxidizing agent **and** therefore it is **oxidizes**

Oxidation
Compound A
loses electrons

Reducing agent

A e⁻ e⁻

A Oxidized

Reduction
Compound B
gains electrons

Oxidizing agent

B

e⁻ e⁻ B Reduced

Stages of Digestion
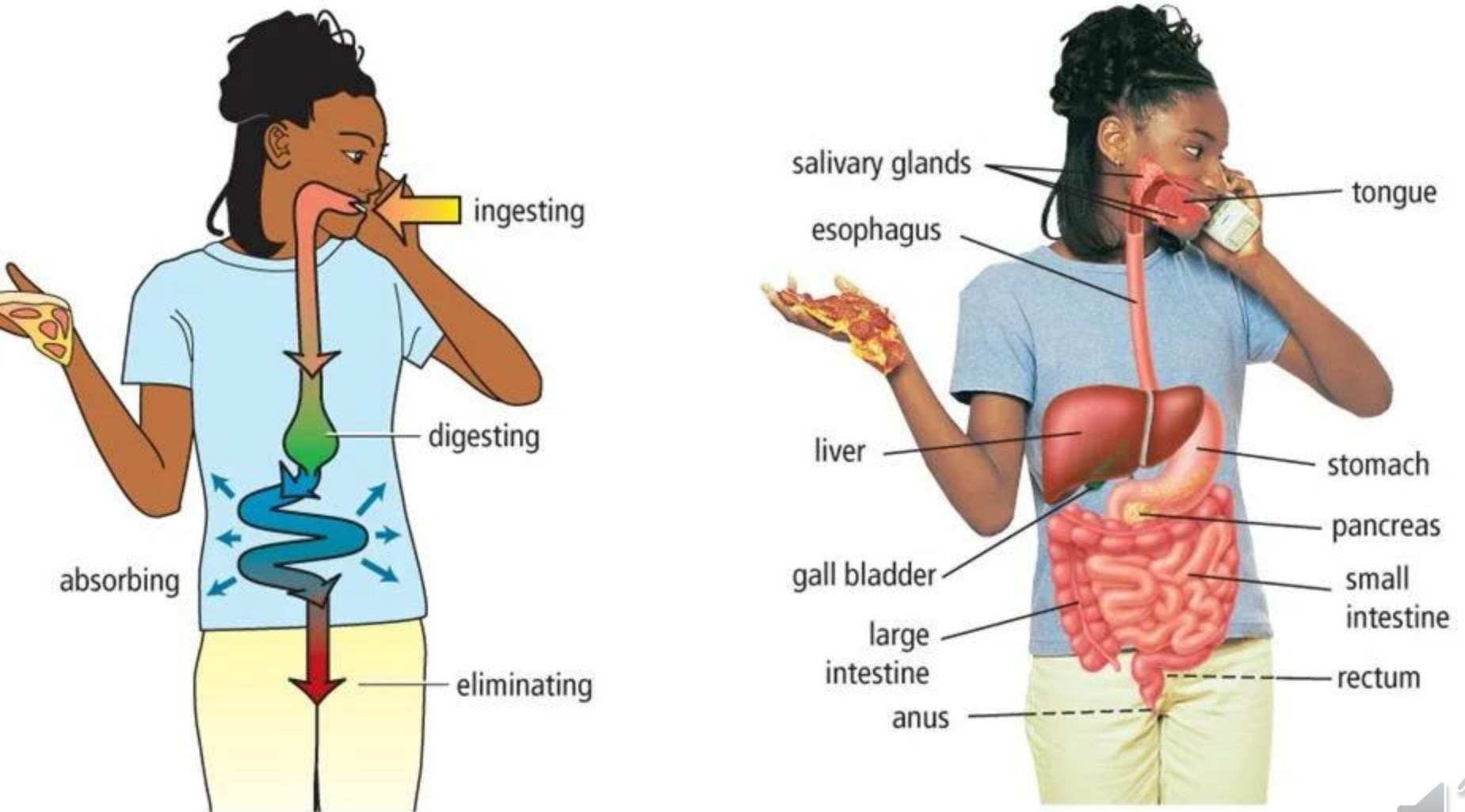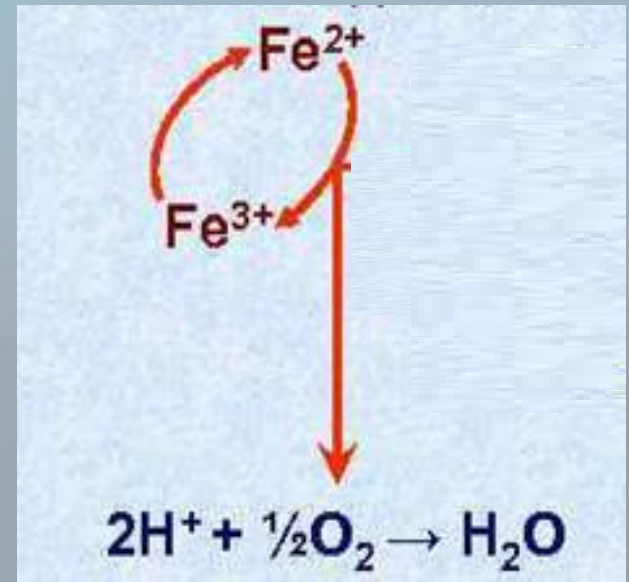

Figure 2.12 The four stages of digestion in the digestive system

Breathing air

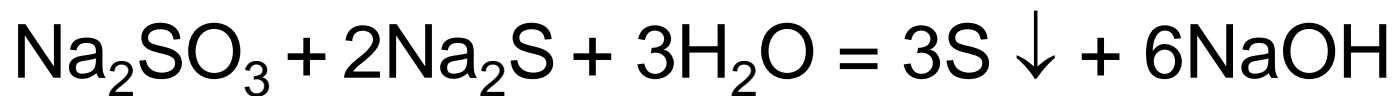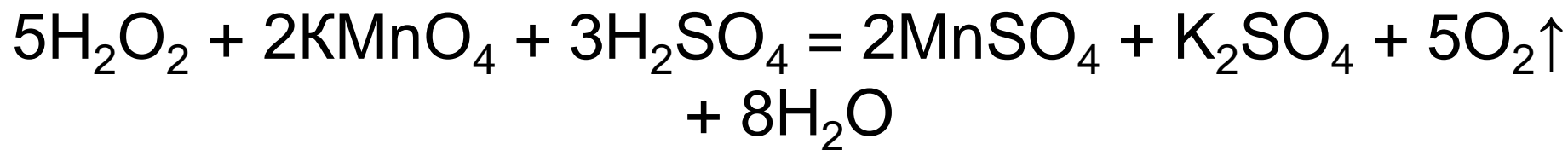$$2H^+ + \tfrac{1}{2}O_2 \rightarrow H_2O$$

The most important oxidizing and reducing agents

Reductants		Oxidants	
Metals	Na, Ca, Zn	Halogens	F_2; Cl_2; I_2; Br_2
Hydrogen, carbon	H_2; C	Permanganates, manganates	$KMnO_4$, K_2MnO_4
Carbon monoxide (II)	CO	Manganese oxide (IV)	MnO_2
Hydrogen sulfide	H_2S	Chromates, dichromates	K_2CrO_4, $K_2Cr_2O_7$
Sulfur oxide (IV)	SO_2	Nitric acid	HNO_3
Sulfurous acid, its salts	H_2SO_3; Na_2SO_3	Sulphuric acid	H_2SO_4 конц.
Hydrogen halides	HCl; HBr; HI	Lead oxide (IV)	PbO_2
Metal cations in lower OS	$SnCl_2$, $FeCl_2$, $MnSO_4$, $Cr_2(SO_4)_3$	Hydrogen peroxide	H_2O_2
		Monosulfuric acid	H_2SO_5
Nitrous acid	HNO_2	Disulfuric acid	$H_2S_2O_8$
Ammonia	NH_3	Metal cations in higher OS	$FeCl_3$; $TlCl_3$,
Hydrazine	NH_2NH_2	Potassium chlorate	$KClO_3$
Electrolysis cathode		Electrolysis anode	

The division of substances into oxidizing and reducing agents is often relative, because depending on the conditions, the same compounds exhibit both oxidizing and reducing properties

$$5H_2O_2 + 2KMnO_4 + 3H_2SO_4 = 2MnSO_4 + K_2SO_4 + 5O_2\uparrow + 8H_2O$$

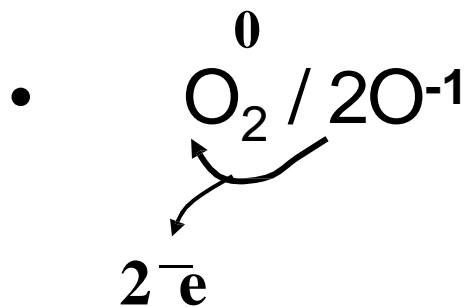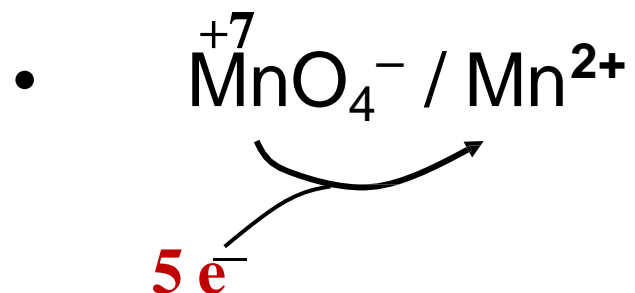$$Na_2SO_3 + 2Na_2S + 3H_2O = 3S\downarrow + 6NaOH$$

Remember

- Compounds containing atoms of elements with the maximum oxidation state (OS) can only be **oxidizing agents**, because they have already given all their valence electrons and are only able to accept other electrons **($Fe^{+3}Cl_3$, $KMn^{+7}O_4$ …)**

- Compounds containing atoms of elements with a minimum oxidation state can only serve as **reducing agents**, because they are only able to donate their electrons, because the external energy level of such atoms is completed by eight electrons **(H_2S^{-2}, KI^- …)**

- Compounds containing atoms of elements with an intermediate oxidation state can be both **oxidizing and reducing agents**, depending on the partner they interact with and on the reaction conditions **($H_2O_2^{-1}$, S^0, $Na_2S^{+4}O_3$…)**

The concept of a conjugated redox pair

Two forms of the same element which differ in the oxidation state and in dynamic equilibrium are called **a conjugated redox pair** (Ox / Red). Any redox reaction is a unity of two opposite transformations - oxidation and reduction.

Example

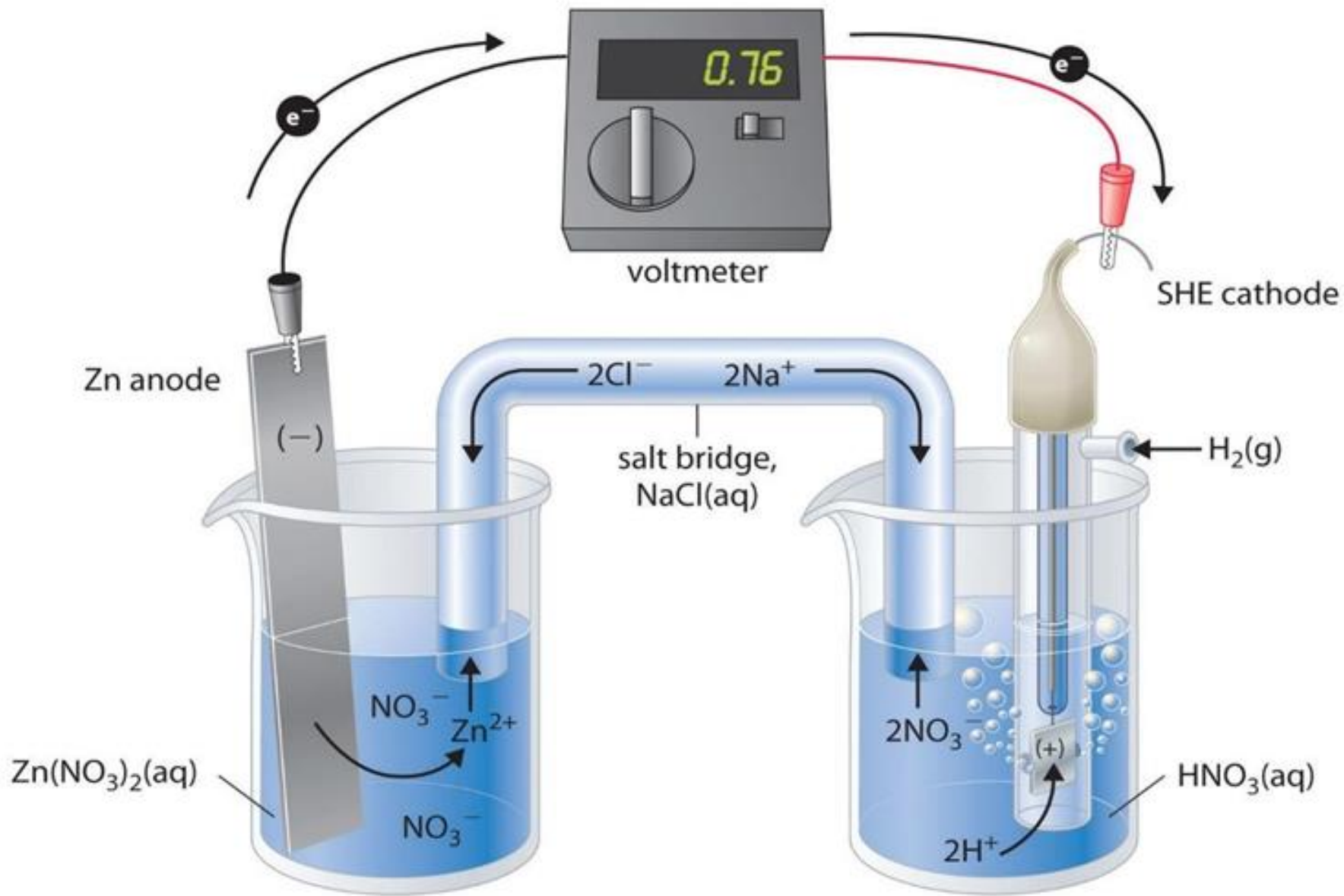- $\overset{+7}{Mn}O_4^- \,/\, Mn^{2+}$

  $5\ e^-$

$5H_2O_2 + 2KMnO_4 + 3H_2SO_4 = 2MnSO_4 + K_2SO_4 + 5O_2 + 8H_2O$

- $\overset{0}{O_2} \,/\, 2O^{-1}$

  $2\ \overline{e}$

Redox potential

conjugated redox pair	pH	Z	$^1/_Z$ MnO_4^-	φ^o, B
$^{+7}\quad\quad\quad^{+2}$ MnO_4^- / Mn^{2+} $5\bar{e}$	$\ll 7$	5	1/5	1,52
$^{+7}\quad\quad\quad^{+4}$ MnO_4^- / MnO_2 $3\bar{e}$	≈ 7	3	1/3	0,60
$^{+7}\quad\quad\quad^{+6}$ MnO_4^- / MnO_4^{2-} $\bar{e}$	> 7	1	1	0,58

Redox potential

Oxidation-reduction potential (standard electrode potential, redox potential) is the voltage (tension) that causes one redox pair in a galvanic cell in relation to another, the potential of which is taken as zero.

$$\varphi^o\ 2H^+/\ H_2 = 0$$

The standard electrode potential is measured in Volts (φ^o, V) using a galvanic cell under standard conditions ($t^o c = 25$, [ox] = [red] = 1 mol /l, pH = 0 and pressure P = 1 atm).

voltmeter

SHE cathode

Zn anode

$2Cl^-$ $2Na^+$

salt bridge, NaCl(aq)

$H_2(g)$

$(-)$

NO_3^- Zn^{2+}

$2NO_3^-$

$(+)$

$Zn(NO_3)_2(aq)$

NO_3^-

$2H^+$

$HNO_3(aq)$

oxidation half-reaction:
$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$

reduction half-reaction:
$2H^+(aq) + 2e^- \rightarrow H_2(g)$

overall reaction: $Zn(s) + 2H^+(aq) \rightarrow Zn^{2+}(aq) + H_2(g)$

Scale of redox potentials for the conditional assessment of the strength of an oxidizing agent and a reducing agent" (according to Puzakov)
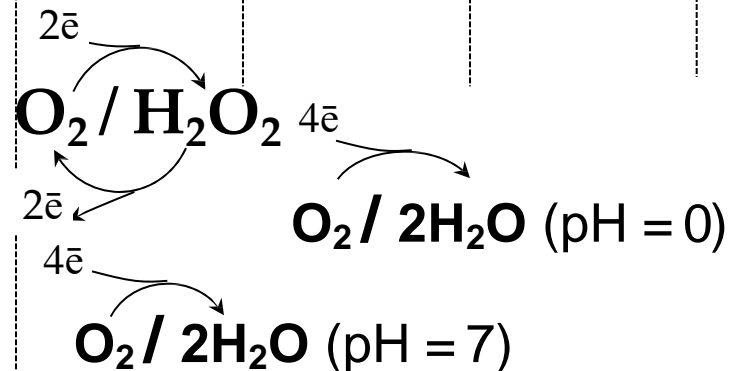
$I_2 / 2\,I^-$

$Cl_2 / 2\,Cl^-$

$F_2 / 2\,F^-$

Oxidizing Properties are increasing

$H_2O_2 / 2\,H_2O$

$2\bar{e}$

ϕ^o, в

-1,0   -0,5   0   0,5   1,0   1,5   2,0
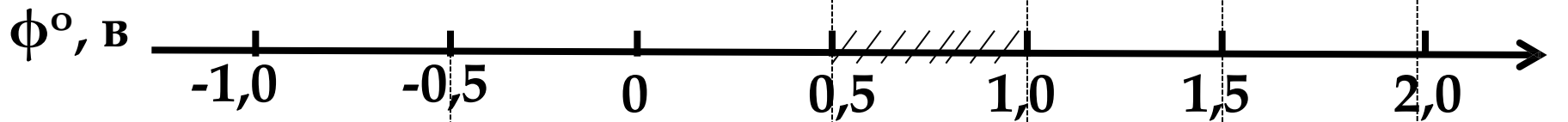
Reducing properties weaken

Most of the body's molecules => biomolecules are strong reducing agents

$2\bar{e}$

O_2 / H_2O_2 $4\bar{e}$

$2\bar{e}$

$O_2 / 2H_2O$ (pH = 0)

Ca^{2+} / Ca

$4\bar{e}$

$O_2 / 2H_2O$ (pH = 7)

$2\bar{e}$
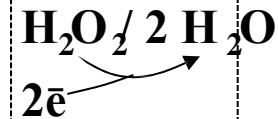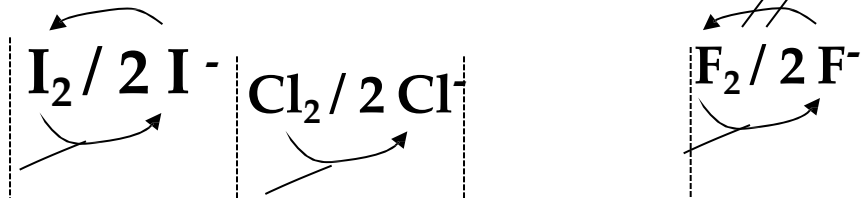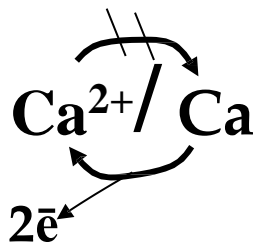
Oxygen O_2 is a harsh (strong) oxidant. Chlorine Cl_2, peroxide H_2O_2, sodium hypochlorite $NaClO$, potassium permanganate $KMnO_4$ and especially fluorine F_2 are also harsh (strong) oxidants.

Thus, it is clear why these compounds have an antiseptic effect (for example, a 3% sodium hypochlorite solution 3% $NaClO$ is used in surgery for intravenous infusion during the development of postoperative sepsis).

It is also obvious that harsh oxidants are toxic to our body at certain (increased) concentrations.

What is an indicator of spontaneous ORR?

Electromotive Reaction Force ($\mathcal{E}$) is the difference between the standard electrode potentials of a redox pair of an oxidizing agent and a redox pair of a reducing agent. Since the redox potential of the oxidizing agent is higher, the ERF of the reaction has a positive value.

$$\mathcal{E}^o = \Delta\varphi^o = \varphi^o\,(ox_1\,/\,red_1) - \varphi^o\,(ox_2\,/\,red_2) > 0$$

This is the condition for the spontaneous course of the reaction

Example

The reaction mixture contains two conjugated redox pairs:

1) I_2/I^-, $\varphi^o(I_2/I^-) = 0,54$ В.
2) S/H_2S, $\varphi^o(S/H_2S) = 0,17$ В.

Iodine has a range of oxidation states from -1 to +7, i.e. can be both an oxidizing agent and a reducing agent. Sulfur has a range of oxidation states from -2 to +6, i.e. can also be both an oxidizing agent and a reducing agent. BUT, **pair 1** (I_2) contains a stronger oxidant, judging by the value of the redox potential, than **pair 2** (S). Under standard conditions we have a reaction in which iodine I_2 is the oxidizing agent, and hydrogen sulfide acid is the reducing agent H_2S:

$$H_2S + I_2 \rightarrow 2HI + S$$

Nernst formula

- **Under non-standard conditions**, the potentials of redox pairs are calculated using the Nernst formula**:**

$$\phi_{ox/red} = \phi^o_{ox/red} + \frac{RT}{ZF} \ln \frac{[\,ox\,]^a}{[\,red\,]^b}\,[\,H^+]^c$$

R = 8.31 J / mol · K
T = 273 + t⁰C = 273 +25 = 298⁰
F = 96500 C / mol
Z is the number of electrons carried by this conjugated redox pair.

Nernst formula

- If we replace the natural logarithm with the decimal **ln → lg** (coefficient 2,3), we get the formula:

$$\varphi = \varphi^o + \frac{0,059}{Z} \lg \frac{[\text{ox}]^a}{[\text{red}]^b} \ [\text{H}^+]^c$$

- a, b, c - stoichiometric reaction coefficients

- This formula shows that the redox potential depends not only on the nature of the substance, but also on temperature, on the ratio of ox and red concentrations, and on the pH of the condition.

The lower the pH (> [H +]), the bigger the φ

Drawing up equations for redox reactions

• electronic balance method (scheme method),

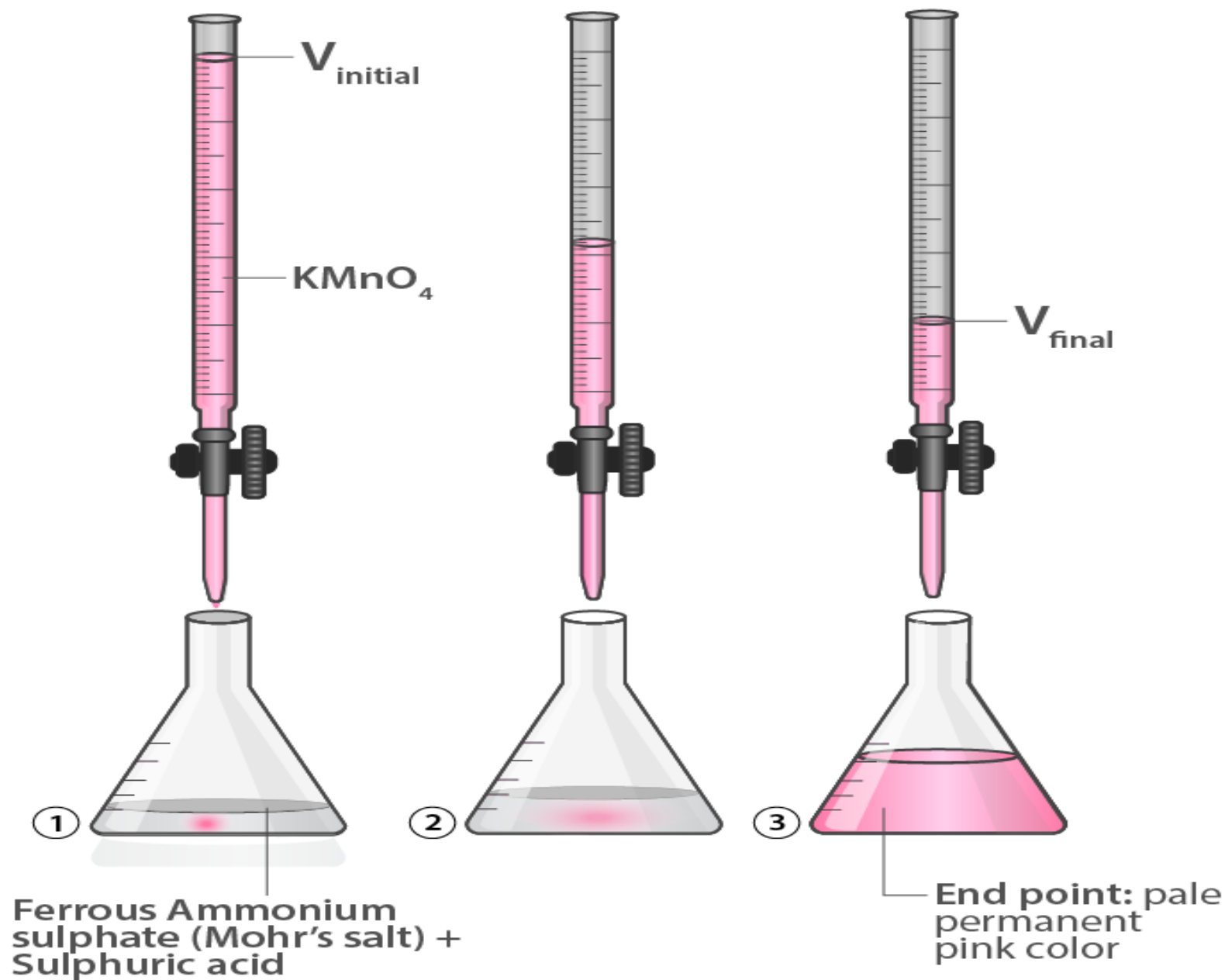• method of electron-ion balance (method of half-reactions).

In any case, both methods are based on the statement: ***"The number of electrons donated by the reducing agent is equal to the number of electrons donated by the oxidizing agent"***

Methods for the quantitative determination of oxidizing or reducing agents. Redox titration

- *permanganatometry* (measured using permanganate ion MnO_4^-)

- *chromatometry* (measured using dichromate ion $Cr_2O_7^-$)

- *iodometry* (measured using iodine I_2 formed or consumed during the reaction)

# Permanganatometry: $MnO_4^- + 8H^+ + 5\bar{e} = Mn^{2+} + 4H_2O$

$V_{initial}$

KMnO$_4$

V_{final}

① ② ③

Ferrous Ammonium
sulphate (Mohr's salt) +
Sulphuric acid

End point: pale
permanent
pink color

What is determined by using permanganometry and how does it happen?

- *Reducing agents* with a potential in the conjugated pair less 1.52 V (uric acid -0.36 V, lactic acid -0.19 V and many other) are determined by direct titration.

$$C_1 * V_1 = C_2 * V_2$$

Red - ?

$n\bar{e}$

MnO$_4^-$

Mn^{2+}

$5\bar{e}$
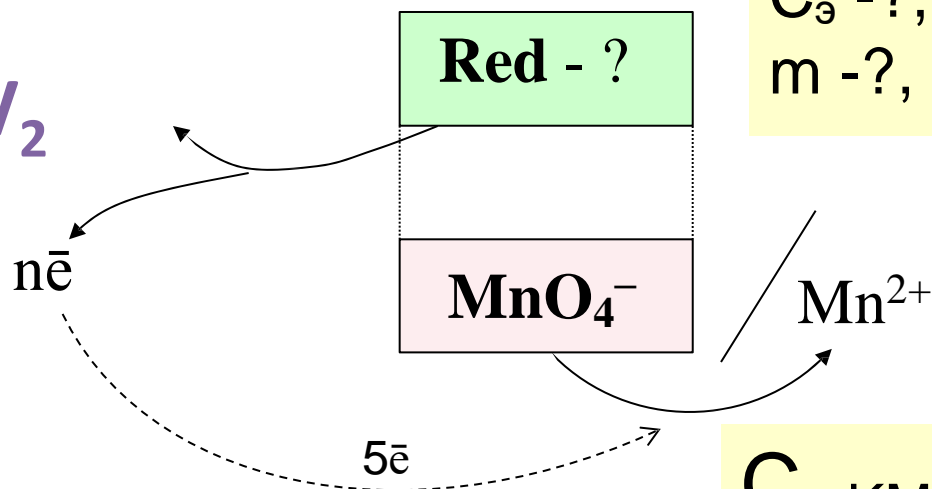
$C_э$ -?, $C_\%$ -?, m -?, $T_{KMnO_4 / red}$ - ?

$C_{э\ KMnO_4}$, V_{KMnO_4} - have

What is determined by using permanganometry and how does it happen?

- *Oxidizers* with a potential in the conjugate pair close to 1,52V are determined by reverse titration (or titration by excess).

- *Reverse titration* in permanganometry can determine such oxidants as bichromate ions $Cr_2O_7^{2-}$, chloric acid $HClO_4$ (reduced to Cl-, +1.49 B), chlorine Cl_2 (+1.36 B).

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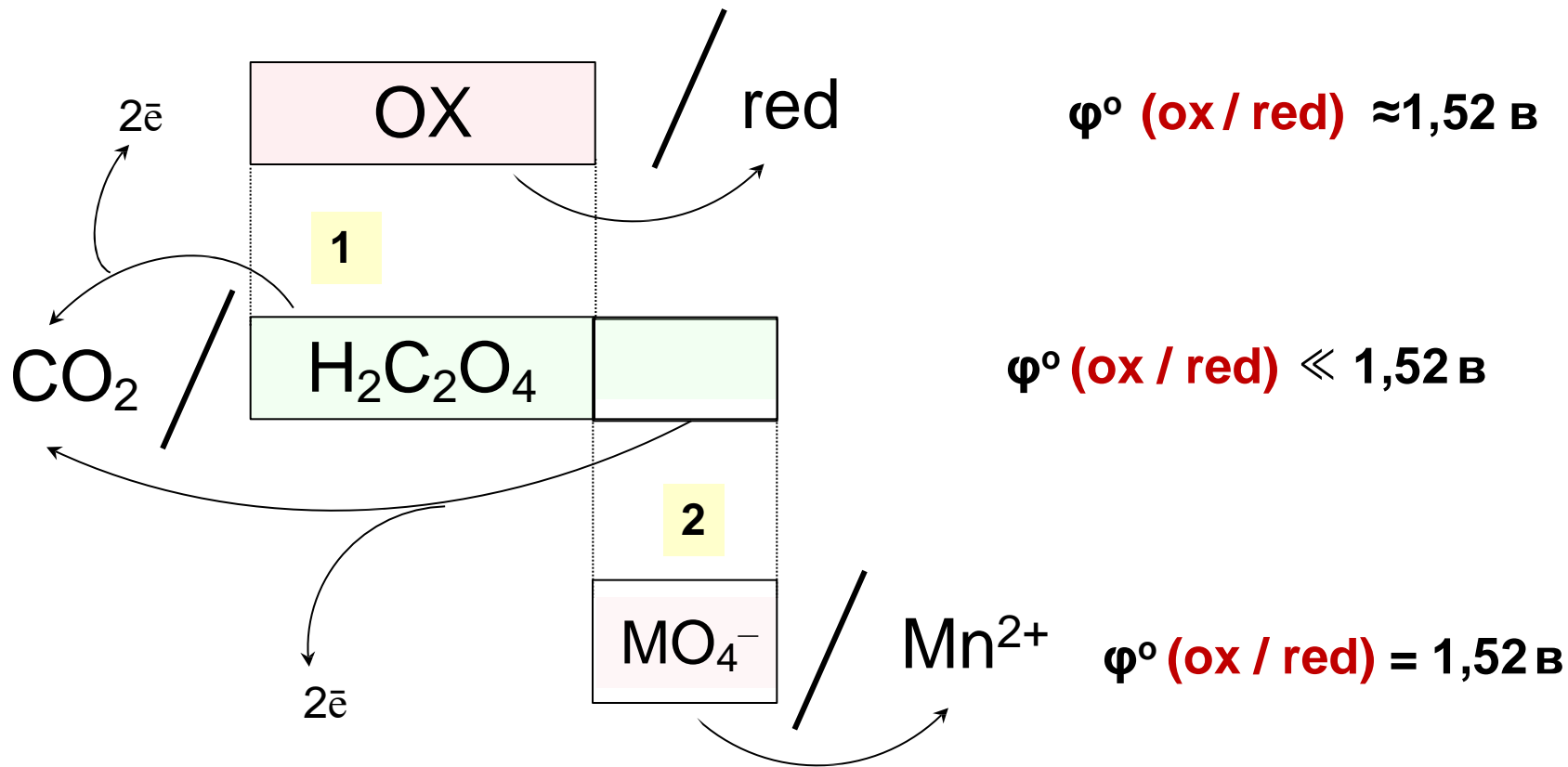
What is determined by using permanganometry and how does it happen?
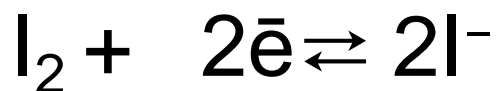
- Indirect titration (titration or substitution) can be used in permanganometry for substances with a potential in the conjugate pair more 1,52V.
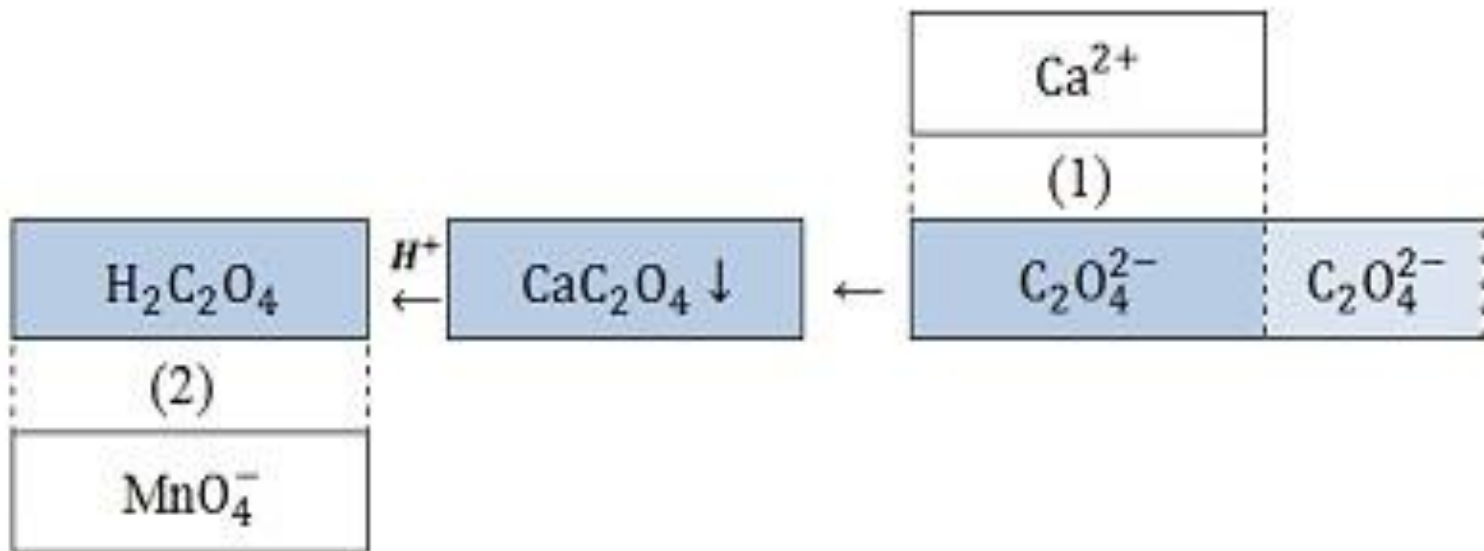
Iodometry

The main reaction of the method:

$$I_2 + 2\bar{e} \rightleftarrows 2I^-$$

$$\varphi^o (I_2/ 2I^-) = + 0{,}54V$$

\# I_2 poorly soluble in water, but good in KI due to the complexation reaction with I^-:

$$I_2 + I^- \rightleftarrows I_3^- \text{ (complex ion)}$$

$$I_2 + KI \rightleftarrows KI_3 \text{ (molecular reaction)}$$

Taking complexation into account, the main reaction of the method can be written:

$$I_3^- + 2\bar{e} \rightleftarrows 3I^-$$

*The indicator for I_2 (I_3^-) is usually starch, which turns **blue** in the presence of iodine*

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Iodometry

Working solutions of the method are a solution of iodine 0.1e I_2 (used as a titrant and as an auxiliary reagent), a solution of potassium iodide 0.1e KI (used as a solvent for and as an auxiliary reagent), a solution of sodium thiosulfate $Na_2S_2O_3$ 0.1e (used as a titrant), it also specifies the titer of I_2.
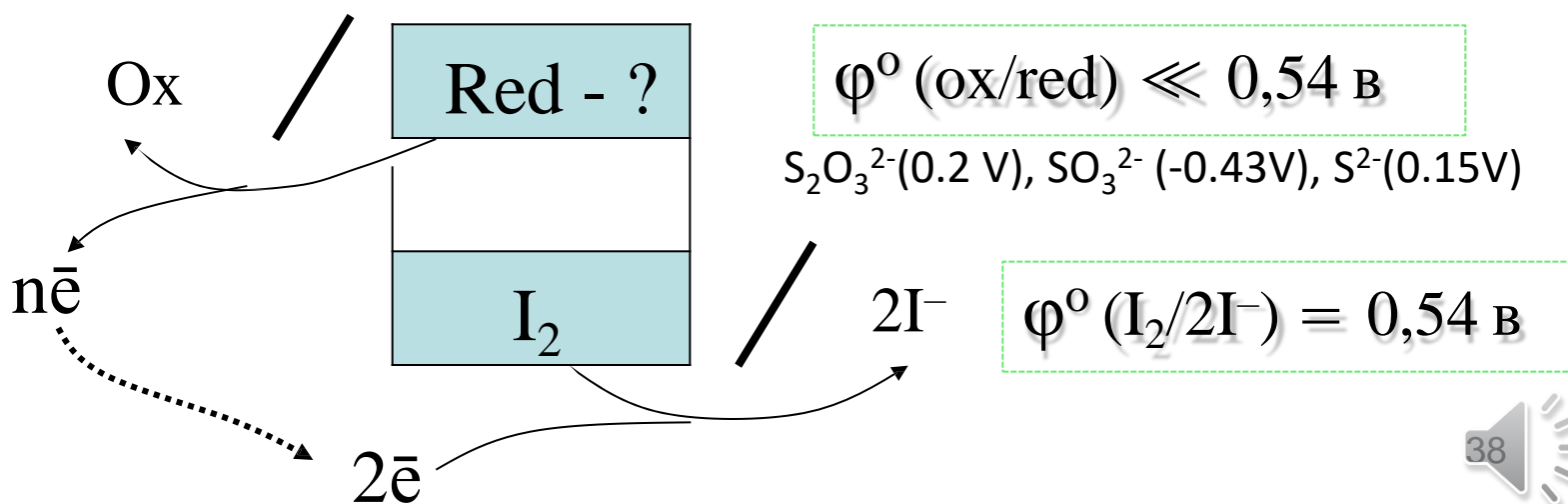
Starch is used as an **indicator** in iodometry, which is colored blue in the presence of iodine.

In iodometry all three types of titration are used: direct, reverse (for excess) and indirect (for substitution). 35

Direct titration

- reducing agents with φ^o (ox/red) $\ll$ 0,54 в

    nē

    To the reducing agent (in the presence of starch), a titrated I_2 solution is added directly from the burette drop by drop until blue staining appears. Diagram and calculations are the same as in permanganometry (see above, direct titration).

Ox — Red - ? φ^o (ox/red) $\ll$ 0,54 в

$S_2O_3^{2-}$(0.2 V), SO_3^{2-} (-0.43V), S^{2-}(0.15V)

nē I_2 $2I^-$ φ^o (I_2/$2I^-$) = 0,54 в

2ē

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By reverse titration

- Reducing agents with a potential in their conjugated ox/red pair close to **φ⁰ ~0,54 V**
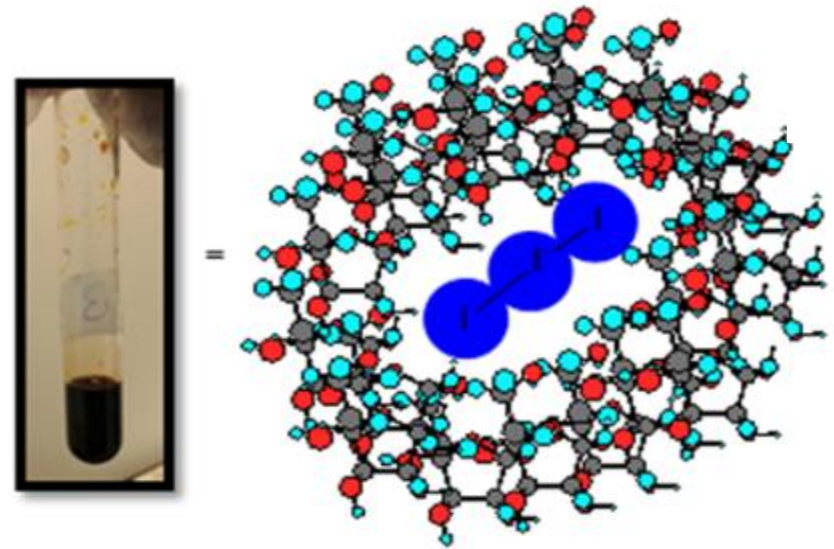
Starch-Iodine-Complex

- A fixed excess of I_2 is added to this reducing agent, which is then titrated with $Na_2S_2O_3$ in the presence of starch (adding it in the titration interval) until the blue color disappears.

Reverse titration scheme in iodometry

arsenic oxide (III) As2O3 (+0.56V), nitrite ions NO_2^- (+0.42V)

ox / **red**

$\phi \sim 0{,}54$ V

m - ?

$C_Э$ -?

①

I_2 | I_2 / $2I^-$

0,54 V

$C_Э$, V

②

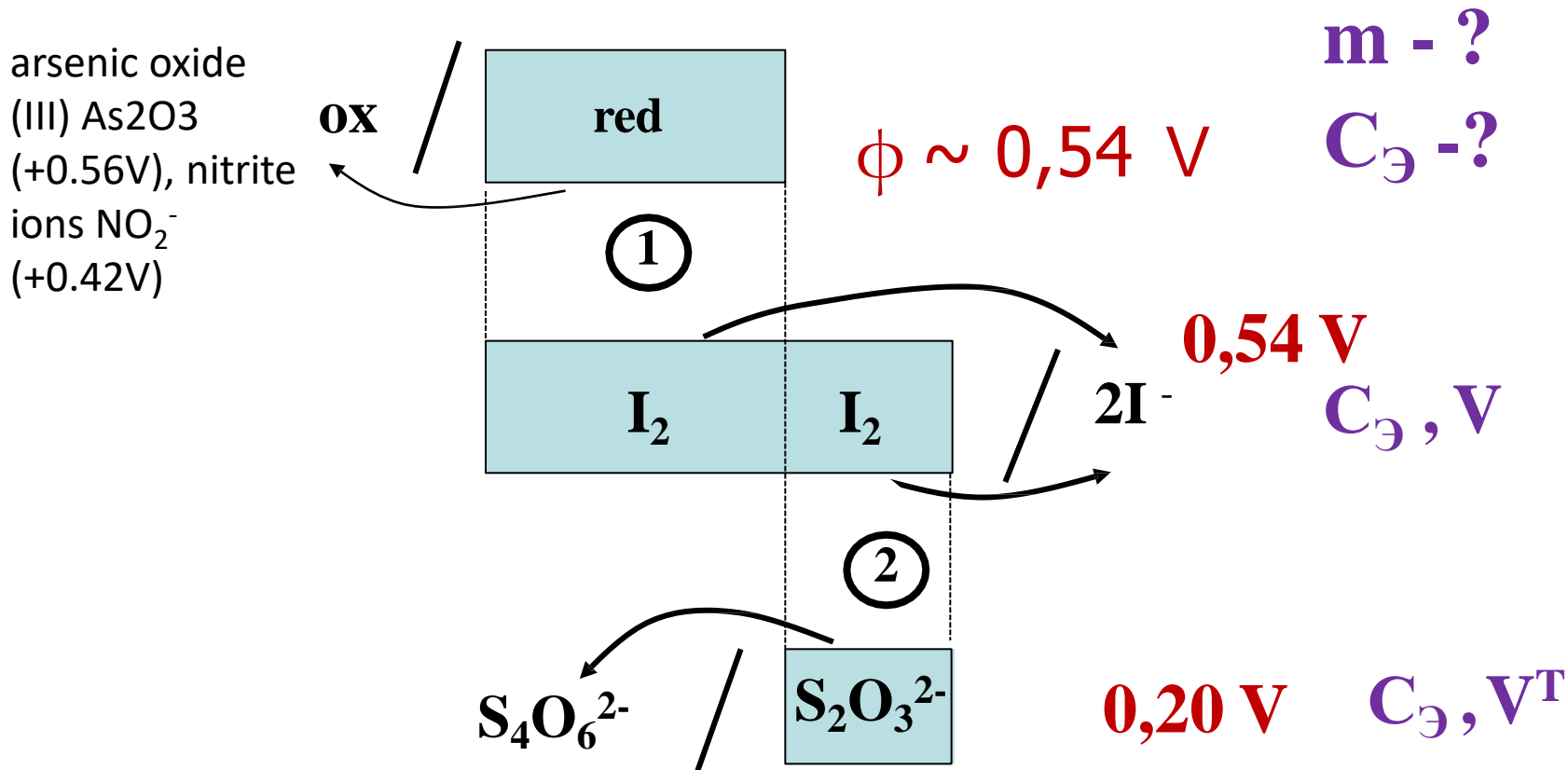$S_4O_6^{2-}$ / $S_2O_3^{2-}$

0,20 V $C_Э$, V^T

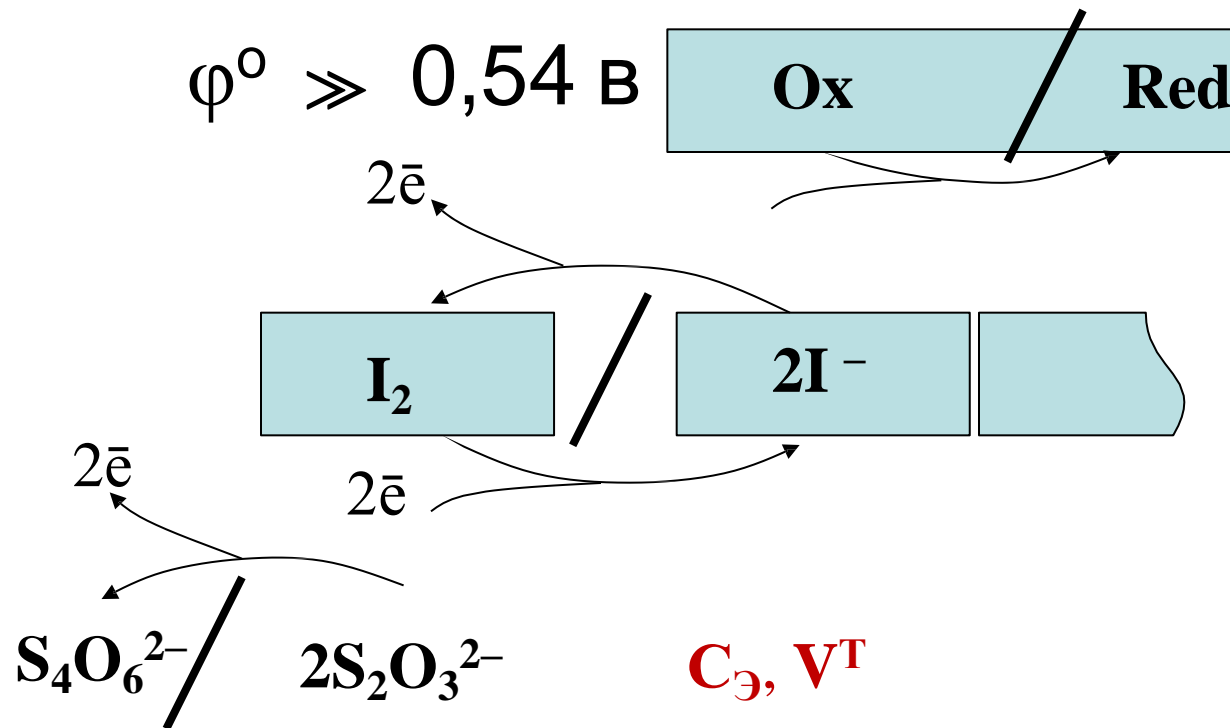Diagram and calculations are the same as in permanganometry (see above reverse titration).

Indirect (substitution) titration

determines oxidants with a potential in their conjugated ox / red pair more 0.54 V

$$\varphi° \gg 0,54V$$

chlorine Cl_2 (+1.36 V), hypochlorite-anions OCl^- (reduced to Cl^-, +1.49 V), Iodate-anions IO_3^- (reduced to I_2, +1.19V)

Indirect titration scheme in iodometry

$\varphi^o \gg 0{,}54$ в

Ox / **Red**

$2\bar{e}$

I$_2$ / **2I$^-$**

$2\bar{e}$

$2\bar{e}$

$2\bar{e}$

$S_4O_6^{2-}$ / $2S_2O_3^{2-}$ **C$_Э$, V^T**

$$n\,(1/z\ ox) = n\,(1/z\ I^-) = n\,(1/z\ I_2) = n\,(1/z\ S_2O_3^{2-})$$

Conclusion

1. The processes of respiration and metabolism, putrefaction and fermentation, photosynthesis and nervous activity of living organisms are associated with redox reactions.

2. Knowledge of redox processes makes it possible to justify the use of oxidants, reducing agents and antioxidants in pharmacotherapy. It also helps us to understand redox reactions in clinical biochemistry for the diagnosis of certain diseases.

3. The methods of permanganometry and iodometry help us to determine the oxidizing and reducing agents in different biological objects.