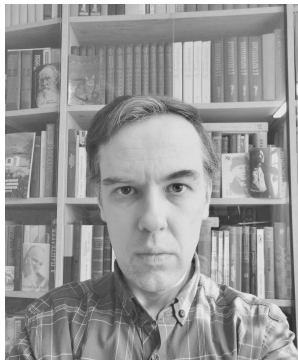


General and Inorganic Chemistry Department,
National Technical University “Kharkiv Polytechnic Institute”

REDOX REACTIONS



Responsible Lecturer:
Andrey V. Kramarenko

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OXIDATION STATE

- There are 2 groups of reactions based on changes in a formal parameter, the **oxidation state**
 - $2\text{HCl} + \text{K}_2\text{O} = 2\text{KCl} + \text{H}_2\text{O}$ – exchange reaction
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- Rules for determining the oxidation state (we use it in the given order):

1. The oxidation state of all atoms in a molecule is 0.

2. The oxidation state of an atom in a simple substance is 0.

3. The oxidation state of oxygen is -2.

4. The oxidation state of hydrogen is +1.

5. The oxidation state of fluorine is -1.

6. The oxidation state of chlorine is -1.

7. The oxidation state of bromine is -1.

8. The oxidation state of iodine is -1.

9. The oxidation state of potassium is +1.

10. The oxidation state of sodium is +1.

- Examples: $\overset{+1}{\text{K}}_2\overset{+6}{\text{C}}\overset{-2}{\text{r}}_2\overset{-2}{\text{O}}_7, \overset{+1}{\text{H}}_2\overset{+6}{\text{S}}\overset{-2}{\text{O}}_4, \overset{+3}{\text{F}}\overset{+3}{\text{e}}_2(\overset{-2}{\text{S}}\overset{-2}{\text{O}}_4)_3$



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Li, Na, K, Rb, Cs: +1

Ca, Sr, Ba, Mg, Be, Zn, Cd, Hg, Cu: +2

Ag: +1; Pt: +2, +4

Al: +3; Fe, Ni, Co: +2, +3

C, Si: +4; B, Pb: +2, +4

Sn, Pb: +2, +4; Bi: +3

Mn: +2, +4, +7; Cr: +2, +3, +6

V: +2, +3, +5; Mo, W: +2, +3, +6

U, Th: +3, +4; N: +3, +5

O: -2; F: -1; Cl, Br, I: -1, +1, +3, +5, +7

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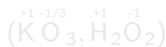


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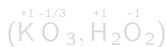


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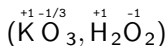


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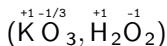


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REACTIONS WITH CHANGES IN OXIDATION STATE

- Oxidation is the **loss** of electrons
- Reduction is the gain electrons
- Electrons are taken by the oxidizing agent, and lost by the reducing agent
- The oxidizing agent is reduced, the reducing agent is oxidized



- Broad sense of the term "oxidizing agent":
particle KMnO_4 , ion MnO_4^- , atom Mn (+7)
- There are three Redox reactions groups:

- Cannizzaro reaction – disproportionation of aldehyde:



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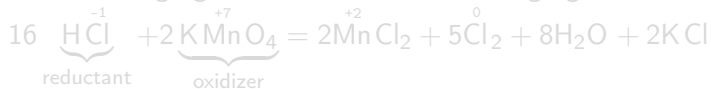
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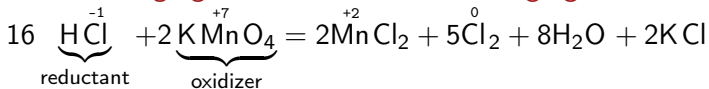
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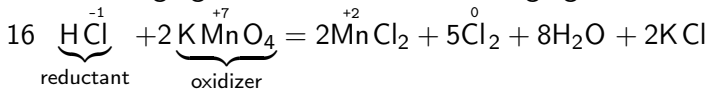
• **Disproportionation of aldehyde:**
 $2\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{H} + \text{OH}^- \rightarrow \text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}^- + \text{R}-\text{CH}_2\text{OH}$

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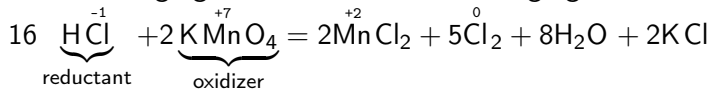


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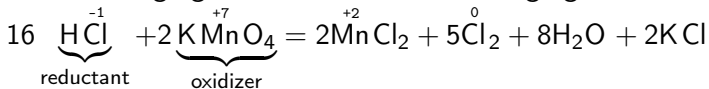


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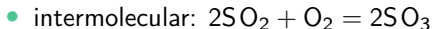


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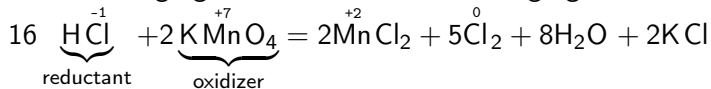


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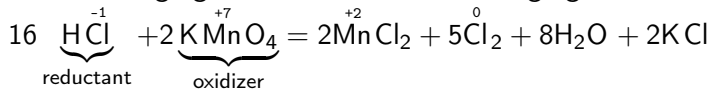


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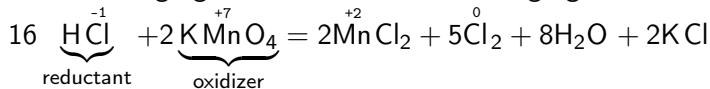


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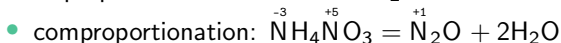
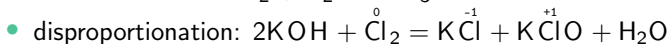
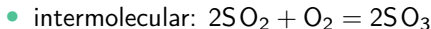


REACTIONS WITH CHANGES IN OXIDATION STATE

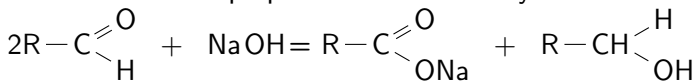
- Oxidation is the loss of electrons
- Reduction is the gain electrons
- Electrons are taken by the oxidizing agent, and lost by the reducing agent
- The oxidizing agent is reduced, the reducing agent is oxidized



- Broad sense of the term “oxidizing agent”:
particle KMnO_4 , ion MnO_4^- , atom $\text{Mn} (+7)$
- There are three Redox reactions groups:



- **Cannizzaro reaction** – disproportionation of aldehyde:



OXIDIZING AGENTS AND REDUCING AGENTS

- Oxidation corresponds to an increase in the oxidation state of a certain atom, and reduction corresponds to a decrease
- An atom in the highest oxidation state can only be an oxidizing agent, and in a lower state - only a reducing agent
- The highest oxidation state of an element is the same as total number of valence electrons

Examples: S^{+6} (SO_3 , H_2SO_4 , H_2SO_5), Mn^{+7} (KMnO_4), Cr^{+6} ($\text{K}_2\text{Cr}_2\text{O}_7$), Cl^{+7} (Cl_2O_7), N^{+5} (HNO_3), P^{+5} (H_3PO_4)

- Lowest oxidation state:

Examples: S^{-2} (H_2S , FeS , ZnS), Mn^{+2} (MnCl_2), Cr^{+3} (CrCl_3), Cl^{-1} (HCl), N^{-3} (NH_3), P^{-3} (PH_3)

- We are talking only about the possibility of manifesting certain properties: P (+5) can only be an oxidizing agent, but almost does not exhibit these properties



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 - * examples: S($3s^23p^4$) : +6, P($3s^23p^3$) : +5, Mn($3d^54s^2$) : +7
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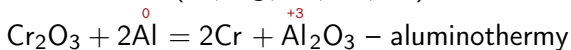
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IMPORTANT REDUCING AGENTS

Commonly used reducing agents include:

- active metals (Al, Mg, Ca, Na, Zn)



- compounds of some metals in low oxidation states (FeSO_4 , SnCl_2 , CrSO_4)



- series of nonmetals (H_2 , C) and their compounds (CO , Na_2SO_3)



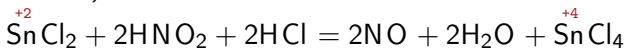
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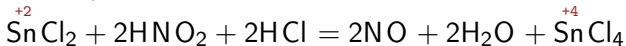
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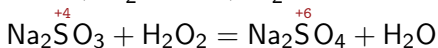
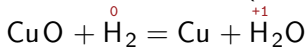
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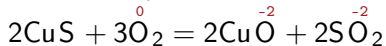
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- compounds of some metals in higher oxidation states ($KMnO_4$, $K_2Cr_2O_7$, PbO_2)



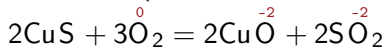
- the so-called non-oxidizing acids are oxidizers due to H^+ , and oxidizing acids due to the acid residue



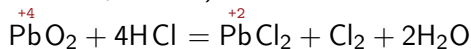
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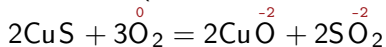
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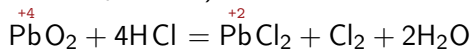
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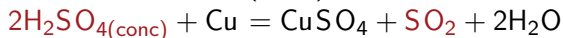
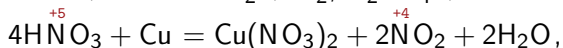
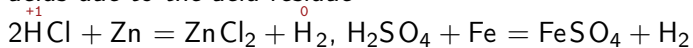
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COMBUSTION

- **Combustion** – a special type of Redox reaction:
 - a lot of heat is released in the reaction;
 - with intense combustion a flame is observed
- Up to 90% of energy humanity receives from burning various fuels
- Combustion requires both fuel and oxidizer

Combustion of natural gas in a burner:

1, 2 - lack of oxidizing agent (O_2)

3 - best ratio of components

4 - excess oxidizing agent

If the oxidizer is mixed with fuel in advance and then set on fire, an explosion is possible!

- To start combustion, the mixture must be heated to a certain temperature, the so-called autoignition temperature



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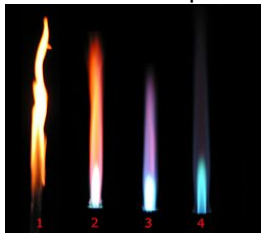
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REDOX BALANCING: GENERAL IDEAS

- Determining coefficients in Redox can be a difficult task
- The general idea is simple: the numbers of electrons donated by the reducing agent and accepted by the oxidizing agent are the same
- To assign coefficients in the Redox equation, 2 methods are used
 - The first method is based on the fact that the number of electrons in the reactants and products are known
 - The second method (half-reaction) method is suitable for any reaction in solution
- The first method is easy to learn, the second is more effective to apply



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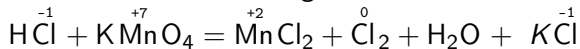
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OXIDATION NUMBER CHANGE METHOD

- Find elements that change the oxidation state



- Write down diagrams of oxidation and reduction processes



- Set the balance by the number of electrons
- The resulting factors are transferred to the equation
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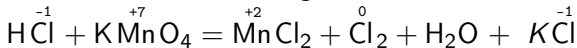


- $16\text{HCl} + 2\text{KMnO}_4 = 2\text{MnCl}_2 + 5\text{Cl}_2 + 8\text{H}_2\text{O} + 2\text{KCl}$

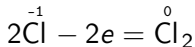
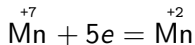


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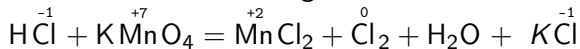


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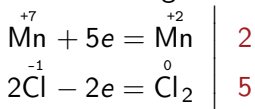


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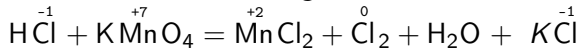


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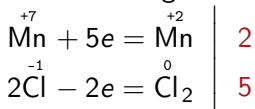


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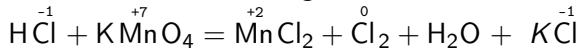
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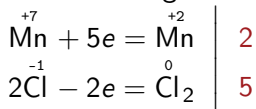


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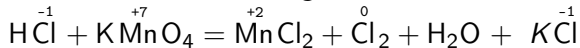
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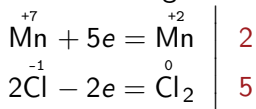


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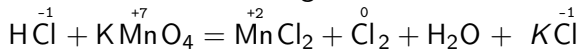
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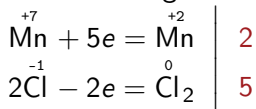


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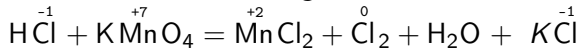
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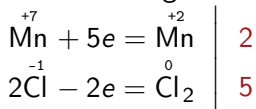


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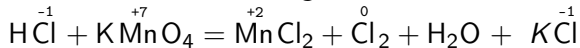


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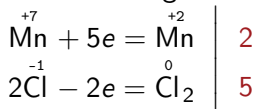


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- The method is based on the assumption: redution patterns are determined by the medium and reaction partner
- In the reference book, you can find reduction half-reactions for different chemical species



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- Condition for the occurrence of a redox reaction: $E_{\text{ox}} > E_{\text{red}}$
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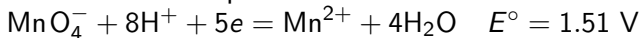


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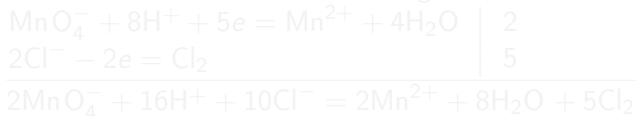


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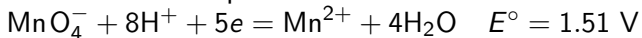


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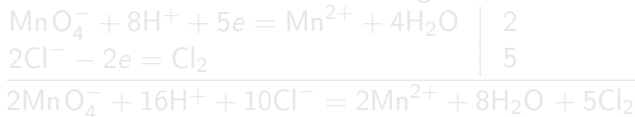


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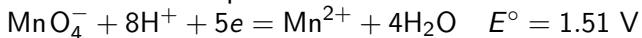


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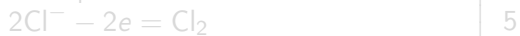


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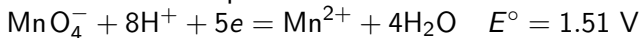


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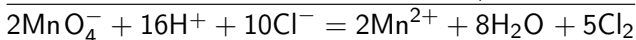
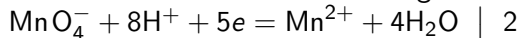


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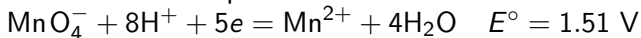


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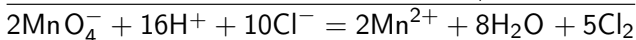
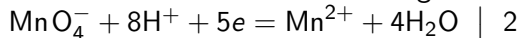


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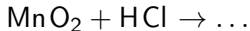


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ALGORITHM FOR WRITING THE REDOX EQUATION

- Assignment: for known reaction participants you need to write the redox equation

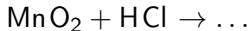


- The solution algorithm can be like this
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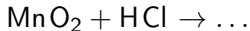


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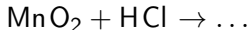


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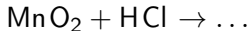


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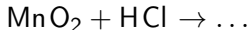


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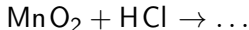


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- Writing transformation schemes requires knowledge of inorganic chemistry
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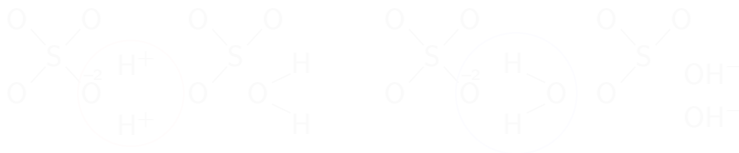
CHANGING CHEMICAL SPECIES COMPOSITION

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- Oxygen atoms number changes with H^+ , OH^- or H_2O depending on the pH of the medium

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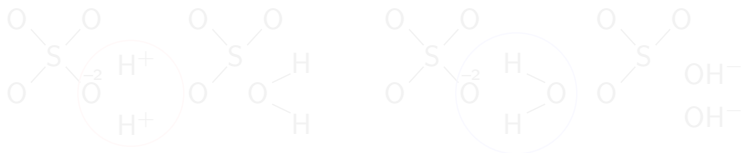


- Conclusion: in an acidic medium, O atoms are subtracted using H^+ , and in a neutral or alkaline medium – using H_2O



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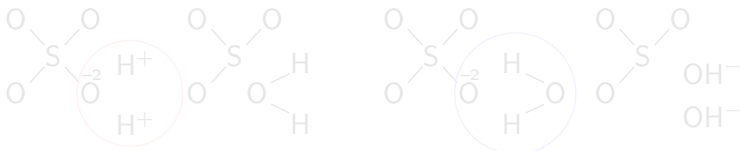


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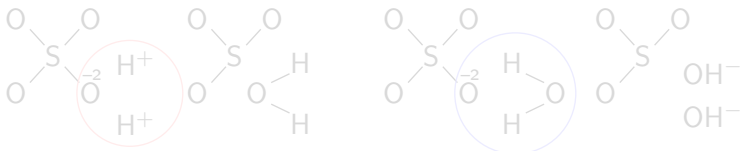


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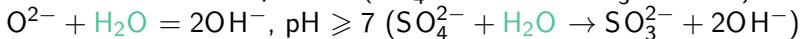
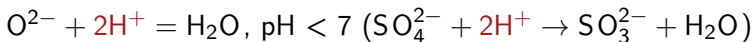
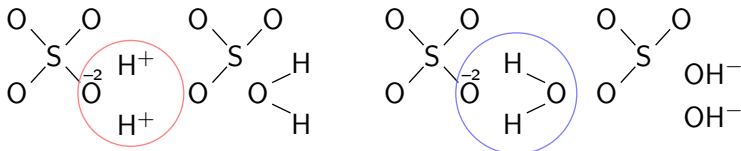


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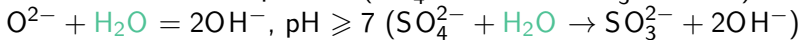
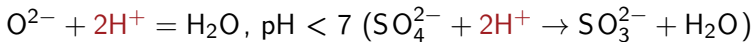
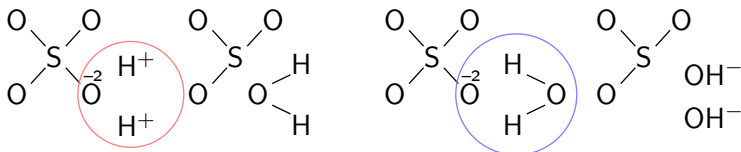


- Conclusion: in an acidic medium, O atoms are subtracted using H^+ , and in a neutral or alkaline medium – using H_2O



CHANGING CHEMICAL SPECIES COMPOSITION

- The number of atoms of an element that changes the oxidation state is balanced by multipliers
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 - $\text{Cr}_2\text{O}_7^{2-} \rightarrow 2\text{Cr}^{3+}$
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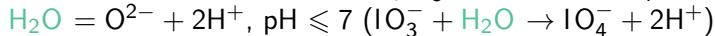
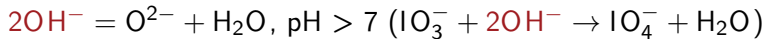
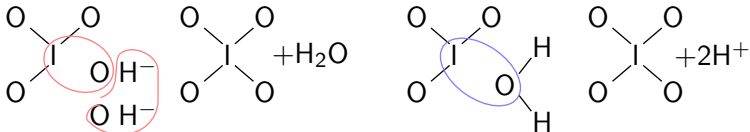


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CHANGING CHEMICAL SPECIES COMPOSITION

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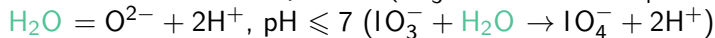
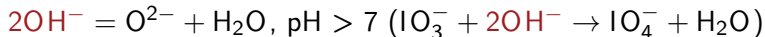
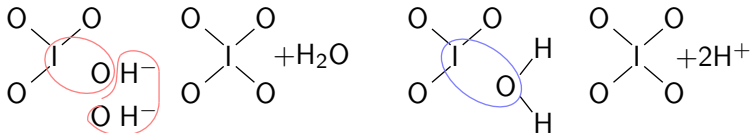


- In a non-aqueous medium, other particles are used, for example:

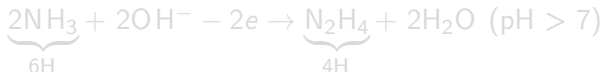


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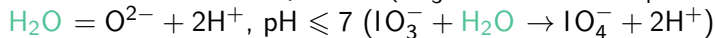
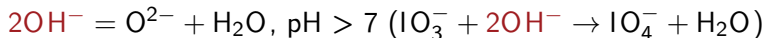
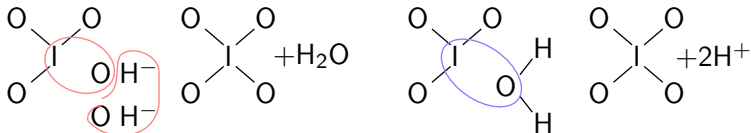


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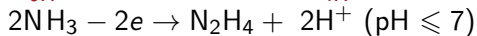
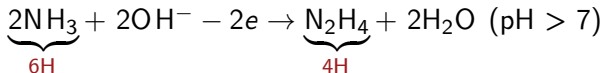


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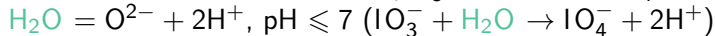
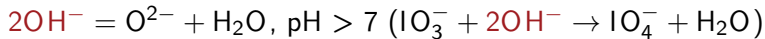
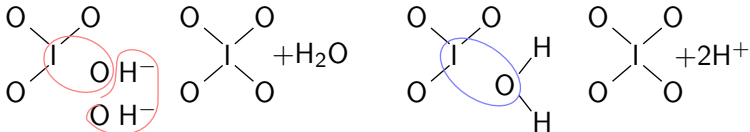


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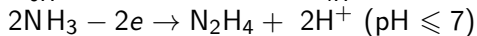
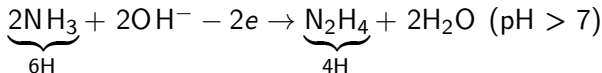


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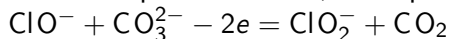
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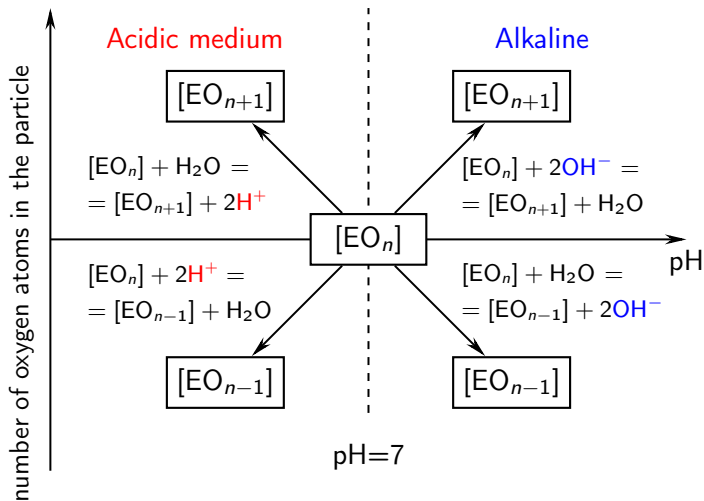
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SCHEME OF CHANGING THE NUMBER OF O ATOMS



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- Two half-reactions must be composed to obtain the ORR equation in ion-molecular form
- Key requirement: formal reduction of electrons according to the reaction equation

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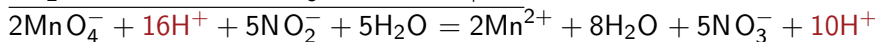
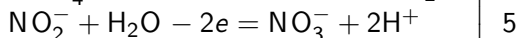
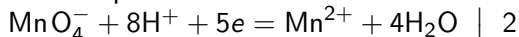
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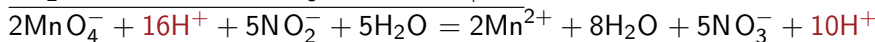
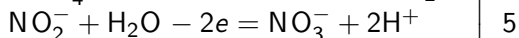
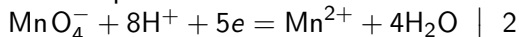
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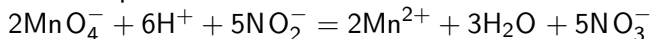
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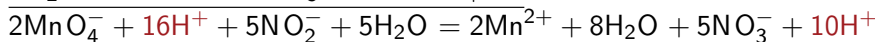
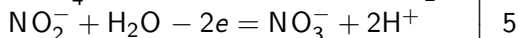
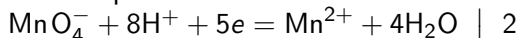
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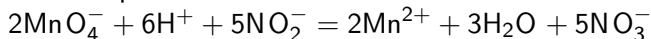
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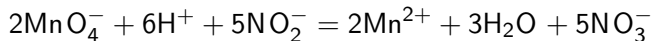


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WRITING THE MOLECULAR REDOX EQUATION

- The ion-molecular equation describes the essence of the process



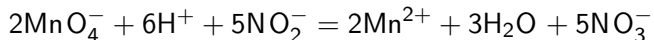
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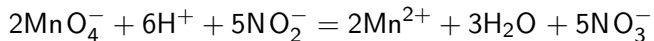
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- Compilation of half-reactions



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- Writing an equation in molecular form



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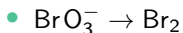
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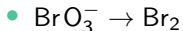
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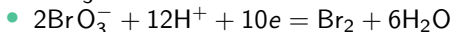
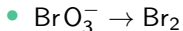
- Writing an equation in molecular form



EXAMPLE



- Reduction scheme:



- Oxidation scheme:



- Compilation of half-reactions



- Reducing the equation



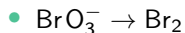
- Writing an equation in molecular form



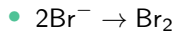
EXAMPLE



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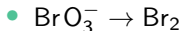
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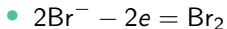
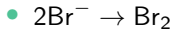
EXAMPLE



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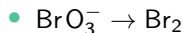
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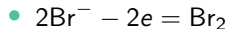
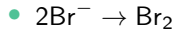
EXAMPLE



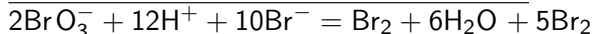
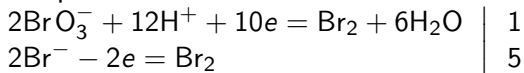
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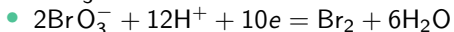
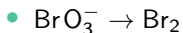
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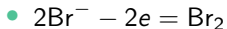
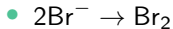
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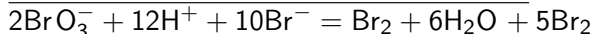
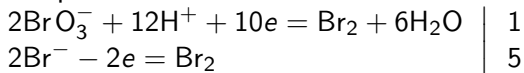
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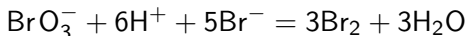
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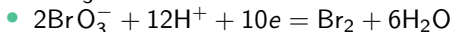
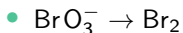
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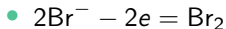
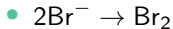
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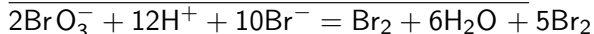
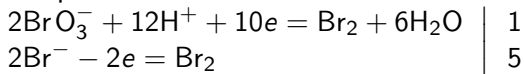
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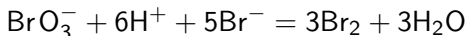
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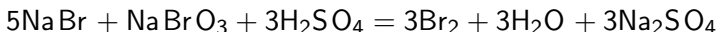
- Compilation of half-reactions



- Reducing the equation



- Writing an equation in molecular form





- Reduction scheme:

- $\text{SeO}_2 \rightarrow \text{Se}$
- $\text{SeO}_2 + 2\text{H}_2\text{O} \rightarrow \text{Se} + 4\text{OH}^-$
- $\text{SeO}_2 + 2\text{H}_2\text{O} + 4e = \text{Se} + 4\text{OH}^-$

- Oxidation scheme:

- $\text{NH}_3 \rightarrow \text{N}_2$
- $\text{NH}_3 \rightarrow \text{N}_2 + 6\text{H}^+ + 6e$
- $2\text{NH}_3 - 6e = \text{N}_2 + 6\text{H}^+$

- Compilation of half-reactions



- Reducing the equation



- The equation obtained after reduction is molecular





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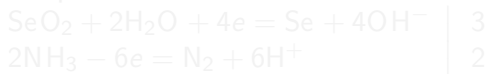
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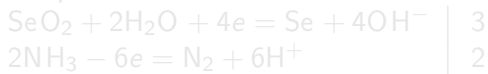
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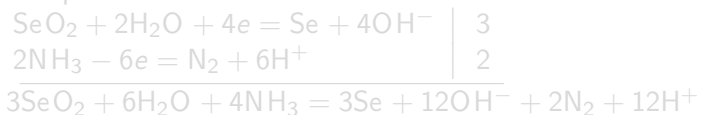
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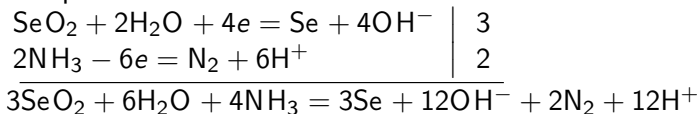
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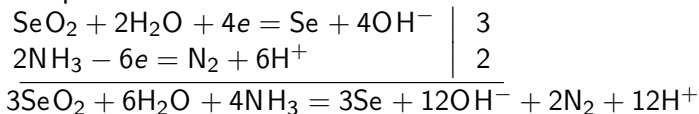
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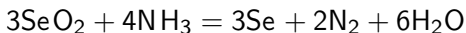
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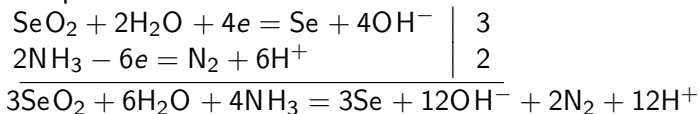
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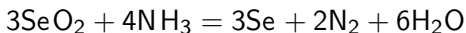
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- Reduction scheme:

- $\text{Br}_2 \rightarrow \text{Br}^-$
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- $\text{Br}_2 + 2e = 2\text{Br}^-$

- Oxidation scheme:

- Compilation of half-reactions



- Writing an equation in molecular form





- Reduction scheme:

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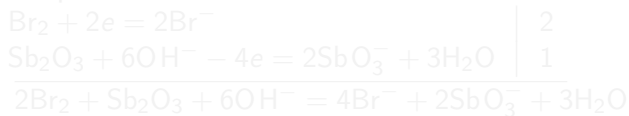
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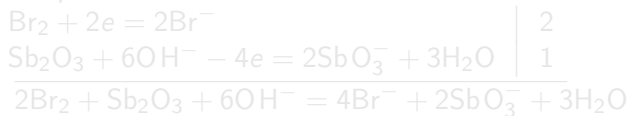
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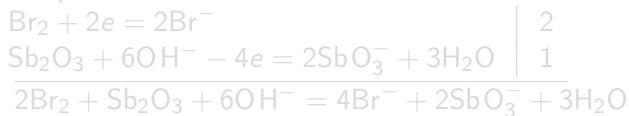
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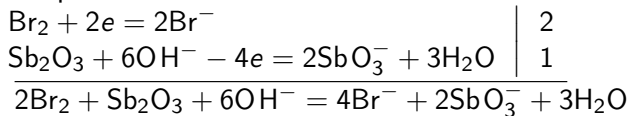
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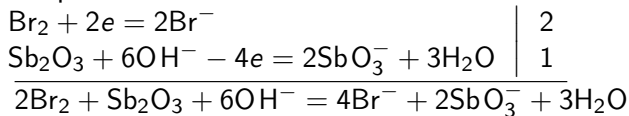
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