Redox Titrations. Permanganometry and iodometry methods

Practicum

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What will we study?

- The concept of a Oxidation-reduction reactions
- The main reaction of the Redox Titration

What does mean “Oxidation-reduction reactions”?

- **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

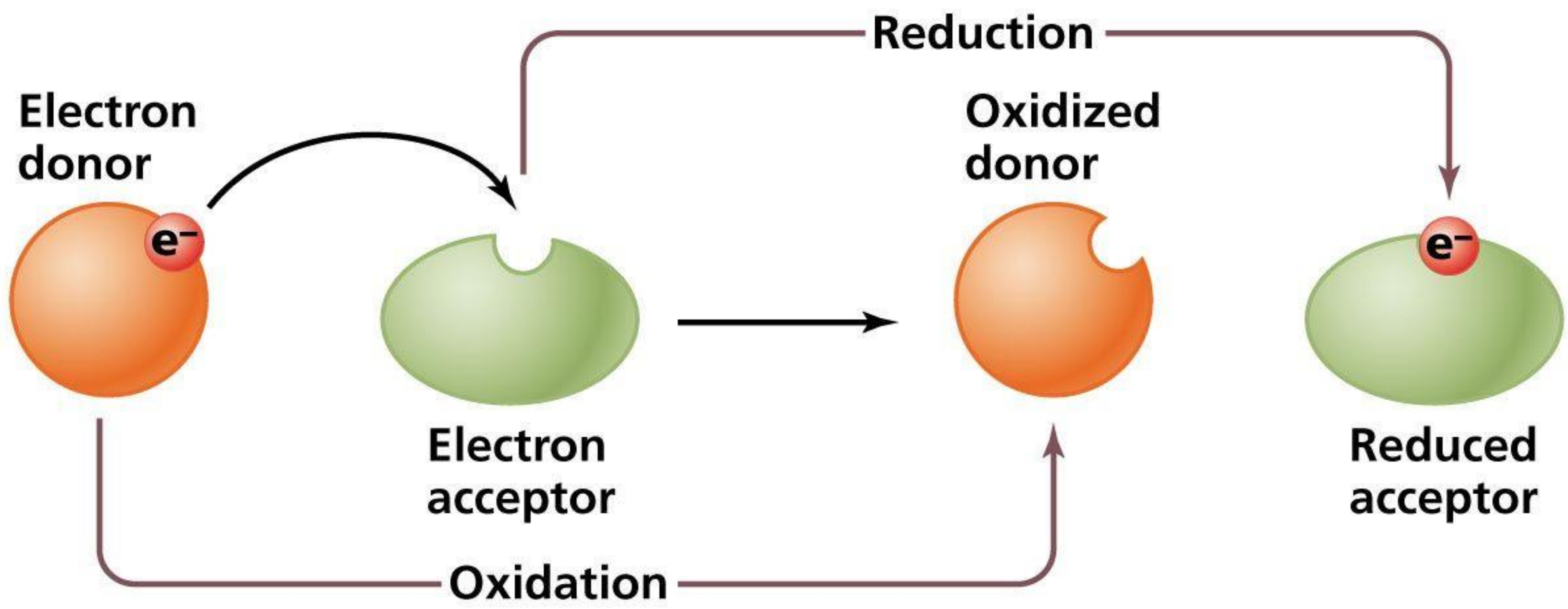
- **The oxidation state** is the conditional charge that an atom gets as a result of the donation or attachment of electrons. The process of giving an atom of electrons is called **oxidation** and the acceptance of electrons is called a **reduction**. The starting material containing the atom to be oxidized 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.

- **<u>Oxidizer + e = conjugate reductant</u>**

- **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.

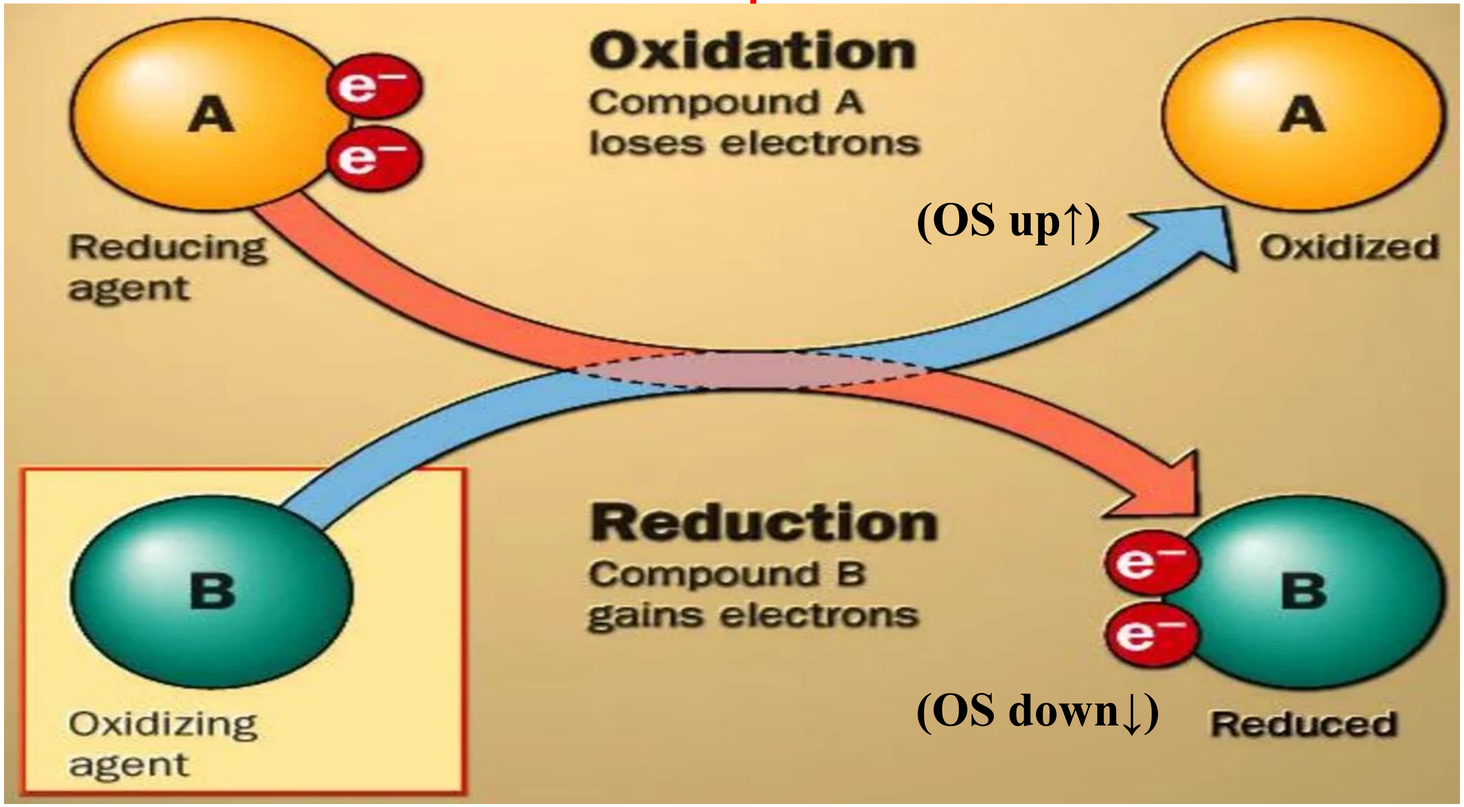
- **<u>Reductant – e = conjugate oxidizer</u>**



! Please, don’t confuse

- **-** the **oxidizing agent <u>takes</u> electrons (OS down↓)** from the reducing agent **and** therefore it is **reduced**

- - the **reducing agent <u>gives</u> electrons (OS up↑)** to the oxidizing agent **and** therefore it is **oxidizes**

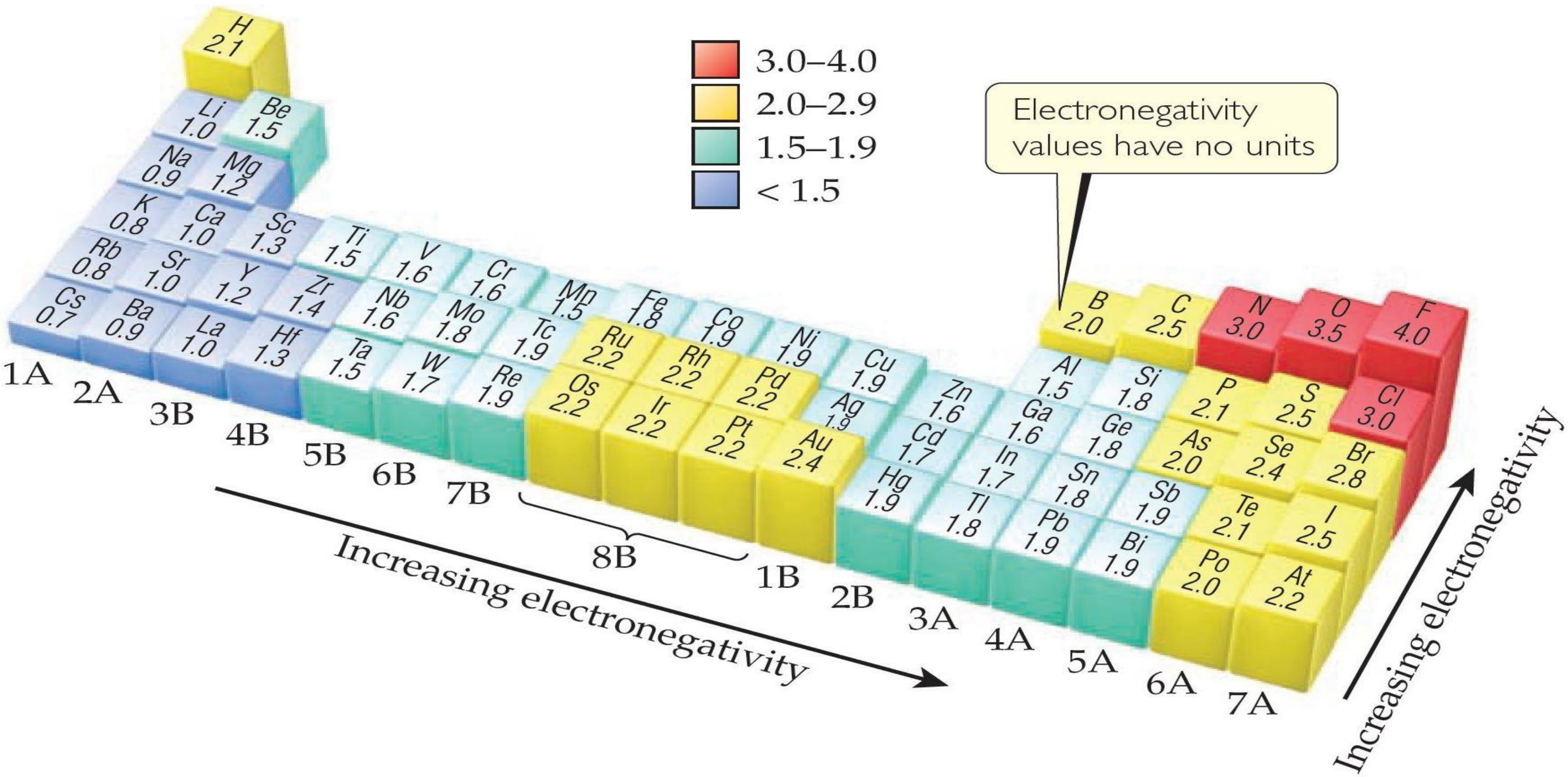


The most important oxidizing and reducing agents

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	

Electronegativity

- **Electronegativity** is the ability of atoms to attract common pairs of valence electrons to themselves during the formation of a covalent bond in a compound.



Rules for determining **the oxidation state** (OS) of atoms in compounds:

- Fluorine «F» always has OS = -1 in all complex connections.
- Oxygen «O» has OS = -2 (Exeption: oxygen fluoride $\overset{+2}{O}\overset{-1}{F_2}$, peroxides: $\overset{+1}{H_2}\overset{-1}{O_2}$, $\overset{+1}{Na_2}\overset{-1}{O_2}$).
- Metals in compounds always have positive OS.

OS coincides with the group number for metals of the main subgroups.

For metals of the **I group OS = +1**; for **II group OS = +2**; for **III group OS = +3**.

Beginning from the IV group OS of the metal can vary.

Rules for determining **the oxidation state** (OS) of atoms in compounds:

- Hydrogen «H» has OS = +1 (Exeption: metal hydrides: $\overset{+1}{Na}\overset{-1}{H}$, $\overset{+2}{Ca}\overset{-1}{H_2}$).
- In molecules of simple substances OS = 0 (Example: Cl_2^0; O_3^0; S_8^0).
- The molecule is electrically neutral as a whole: the sum of the products of the oxidation states of all atoms in the compound by the number of atoms is zero.

Example: $\boxed{\overset{+1}{H_2}\overset{+6}{S}\overset{-2}{O_4}}$ **(+1)·2 + (X)·1+ (–2)·4 = 0,**

X = +6

Redox Titration

- A **redox titration** is a titration of a reducing agent by an oxidizing agent or titration of an oxidizing agent by a reducing agent. Typically, this type of titration involves a redox indicator or a potentiometer.

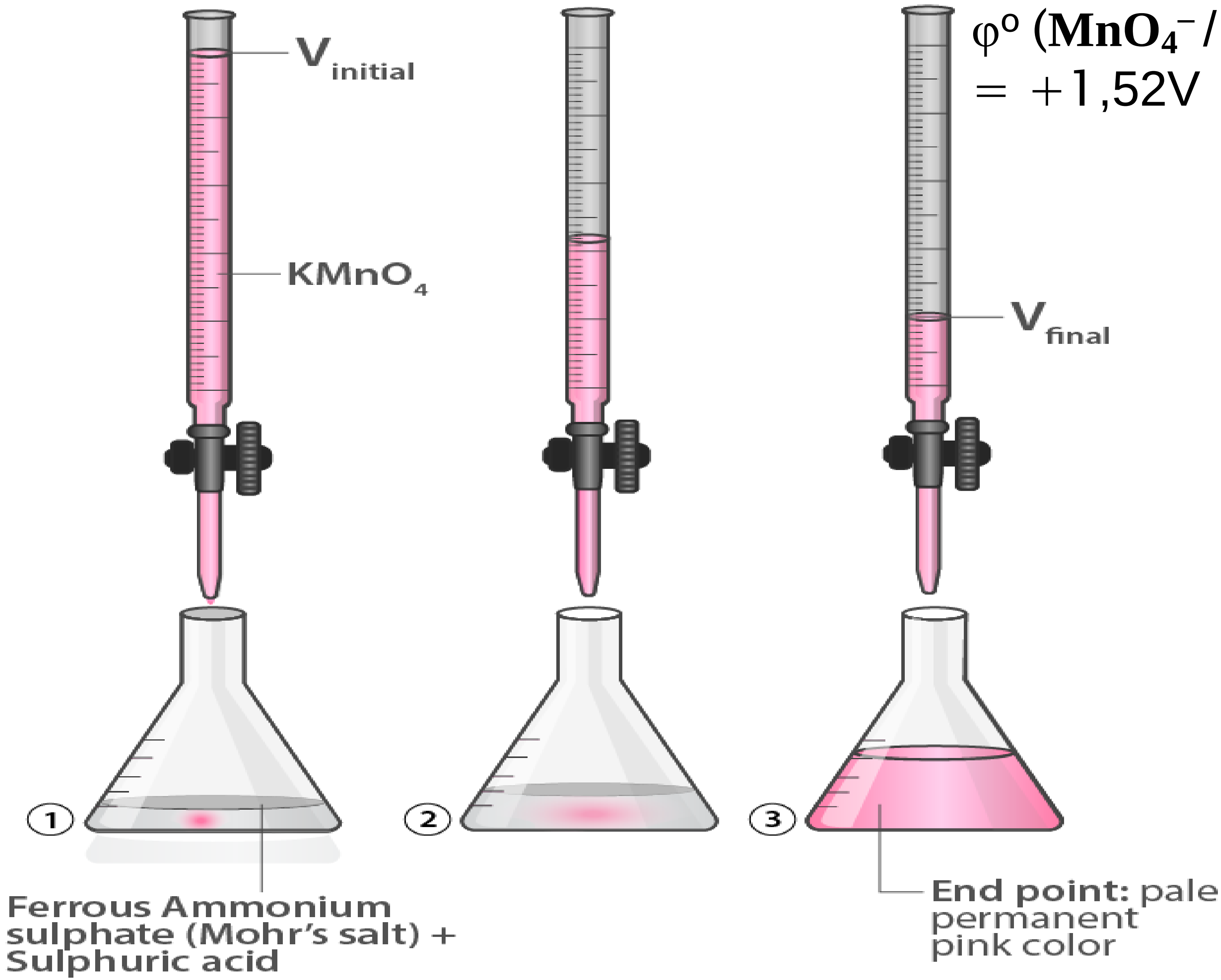
Types of Redox Titrations

Redox titrations are named according to the titrant that is used:

- *Bromometry* uses a bromine (Br_2) titrant.
- *Cerimetry* employs cerium(IV) salts.
- *Dichrometry* uses potassium dichromate ($K_2Cr_2O_7$).
- <u>*Iodometry*</u> uses iodine (I_2).
- <u>*Permanganometry*</u> uses potassium permanganate ($KMnO_4$).

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

$\varphi^o\ (\mathbf{MnO_4^- / Mn^{2+}}) = +1{,}52V$



Permanganatometry

Working reagents of the method are:

1. potassium permanganate 0.02e $KMnO_4$ is a titrant and an indicator
2. oxalic acid 0.02e $H_2C_2O_4 \cdot 2H_2O$ or its salt sodium oxalate $Na_2C_2O_4$ is used to set the titer
3. For the same purpose, you can use the Mora's salt $(NH_4)_2Fe(SO_4)_2$
4. H_2SO_4 is needed to create the necessary acidity of the reaction medium

Permanganatometry

- Justification for using an acidic reaction condition: firstly, in an acidic condition, potassium permanganate is a strong oxidizer. Secondly, in an acidic condition, the equivalence point is well established because an extra drop of the pink permanganate ion MnO_4^- titrant is clearly visible against the background of the resulting colorless manganese Mn^{2+} ion . In neutral and alkaline conditions we have other reduction products with other colours.

Iodometry

The main reaction of the method:

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

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.

Task 1: determine the oxidation state of all elements in substances

OS = 0, because it's simple a substance

then find others: (+1)*1+(X)*1+(-2)*3 = 0, X=+5

$\overset{0}{Cu}$; $\overset{+1}{H}\overset{+5}{N}\overset{-2}{O_3}$; Fe; $CaCO_3$; $AlCl_3$; H_2SO_4;

first define constants OS (see the slides №8, 9)

Li_3N; $BaSO_4$; $CuSO_4$; NaOH; O_2; Zn;

H_2CO_3; O_3; OF_2; SO_3; KH; Na; K_2O;

KOH; BaH_2; H_2O; H_2O_2; NH_3

Task 2: determine the oxidizing agent and reducing agent in the reactions below

a) $2\overset{0}{Fe} + 3\overset{0}{Cl_2} = 2\overset{+3}{Fe}\overset{-1}{Cl_3}$

Firstly to find all OS

We can see that **OS (Fe)** was **0** and its conversion to **+3**. So **OS (Fe)** goes up ↑. This means that Fe donates electrons. So, Fe is a **reducing agent**

We can see that **OS (Cl_2)** was **0** and its conversion to **-1**. So **OS (Cl_2)** goes down↓. This means that Cl_2 accepts electrons. So, Cl_2 is a **oxidizng agent**

b) $2Al + 3S = Al_2S_3$

c) $4Li + O_2 = 2Li_2O$

d) $8HNO_3 + 3H_2S = 3H_2SO_4 + 8NO + 4H_2O$

e) $3Cl_2 + 6KOH = 5KCl + KClO_3 + 3H_2O$

f) $2KMnO_4 + 5KNO_2 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 5KNO_3 + 3H_2O$