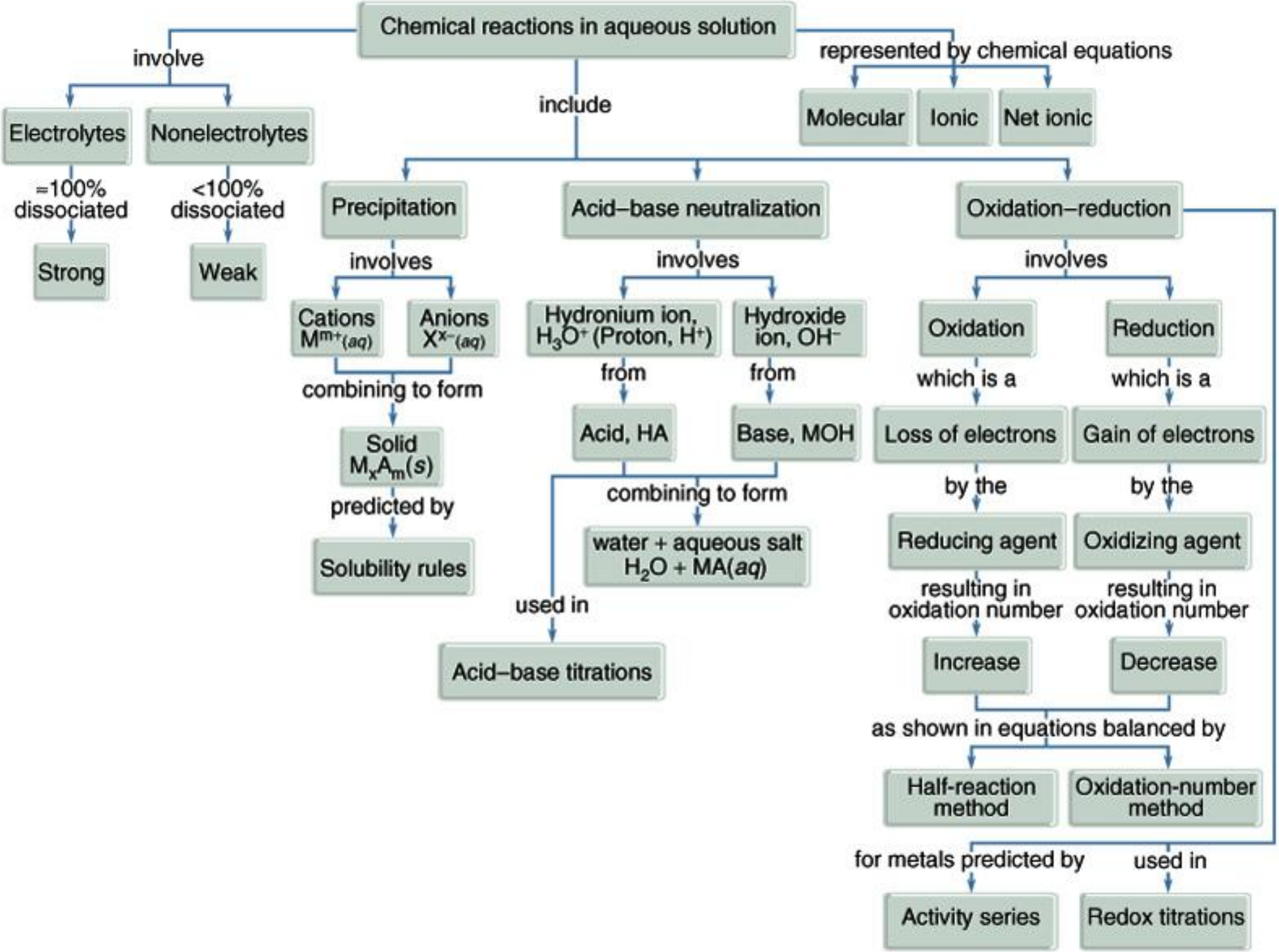
LECTURE № 10

Oxidation – Reduction Reaction

07.04.2017


Chemical reactions in aqueous solution
involve
Electrolytes
Nonelectrolytes
≈100% dissociated
<100% dissociated
Strong
Weak
include
Precipitation
involves
Cations $M^{m+}(aq)$
Anions $X^{x-}(aq)$
combining to form
Solid $M_xA_m(s)$
predicted by
Solubility rules
Acid–base neutralization
involves
Hydronium ion, H_3O^+ (Proton, H^+)
Hydroxide ion, OH^-
from
from
Acid, HA
Base, MOH
combining to form
water + aqueous salt $H_2O + MA(aq)$
used in
Acid–base titrations
Oxidation–reduction
involves
Oxidation
Reduction
which is a
which is a
Loss of electrons
Gain of electrons
by the
by the
Reducing agent
Oxidizing agent
resulting in oxidation number
resulting in oxidation number
Increase
Decrease
as shown in equations balanced by
Half-reaction method
Oxidation-number method
for metals predicted by
used in
Activity series
Redox titrations
represented by chemical equations
Molecular
Ionic
Net ionic

Electronegativity, symbol χ, is a chemical property that describes the tendency of an atom or a functional group to attract electrons (or electron density) towards itself. The higher the associated electronegativity number, the more an element or compound attracts electrons towards it. First proposed by Linus Pauling in 1932 as a development of valence bond theory:

$$\underset{2,1}{H}\,{*} \;\rightarrow\; {*}\overset{**}{\underset{**}{O}}{*} \;\leftarrow\; {*}\underset{2,1}{H}$$

$$\underset{3,5}{}$$

$$H^{+1}\ {**}\ O^{2-}\ {**}\ H^{+1} \quad (H_2^{+1}O^{2-})$$

ЭЛЕКТРООТРИЦАТЕЛЬНОСТЬ ЭЛЕМЕНТОВ

это способность одних атомов оттягивать на себя электроны от других атомов при взаимодействии

Шкала электроотрицательности элементов (Л. Полинг)

	I	II	III	IV	V	VI	VII
1	H 2,1						
2	Li 1,0	Be 1,5	B 2,0	C 2,5	N 3,0	O 3,5	F 4,0
3	Na 0,9	Mg 1,2	Al 1,5	Si 1,8	P 2,1	S 2,5	Cl 3,0
4	K 0,8						Br 2,8
5	Rb 0,8						I 2,5

Относительная электроотрицательность подчиняется периодическому закону: в периоде она растет с увеличением номера элемента, в группе – уменьшается.

Not all atoms attract electrons with the same force. **The amount of "pull" an atom exerts on its electrons is called its electronegativity**. **Atoms with high electronegativities — such as fluorine (4,0), oxygen (3,5), and nitrogen (3,0) — exert a greater pull on electrons than atoms (metals have χ<1,5) with lower electronegativities**. In a bond, this leads to unequal sharing of electrons between the atoms, as electrons will be drawn closer to the atom with the higher electronegativity.

Because electrons have a negative charge, the unequal sharing of electrons within a bond leads to the formation of an electric dipole: a separation of positive and negative electric charge. Because the amount of charge separated in such dipoles is usually smaller than a fundamental charge, they are called partial charges, denoted as $\delta+$ (delta plus) and $\delta-$ (delta minus). These symbols were introduced by Christopher Ingold and his wife Hilda Usherwood in 1926. The bond dipole moment is calculated by multiplying the amount of charge separated and the distance between the charges.

These dipoles within molecules can interact with dipoles in other molecules, creating dipole-dipole intermolecular forces.

An amount of electrons which was lost or gained by the atom in a chemical compound is called the oxidation state, often called the oxidation number. Oxidation states are typically represented by small integers.

Conceptually, **the oxidation state, which may be positive (cations Na^{+1}, Mg^{2+}, Al^{3+}), negative (O^{2-}, Cl^{-}, NO_3^{-}, S^{2-}, SO_4^{2-}, PO_4^{3-}) or zero (free atoms Na°, H_2°, O_2°, P°), is the hypothetical charge** that an atom would have if all bonds to atoms of different elements were 100% ionic, with no covalent component. This is never exactly true for real bonds.

Rules:	Examples	Exceptions:
Free elements (uncombined state) and pure compounds have an oxidation number of **zero**.	**Na°, H_2°, O_2°, P° $CaCl_2^{\circ}$, H_2O°, $H_3PO_4^{\circ}$**	
Fluorine always has a **-1** oxidation number within compounds	**$F_2^{-1}O$, HF^{-1}, CaF_2^{-1}**	
The oxidation number of oxygen in compound is usually **–2**	**CO_2^{2-}, Na_2O^{2-}**	**$H_2O_2^{-1}$, F_2O^{2+}**
The oxidation number of hydrogen in compound is usually **+1**	**$H^{+1}Cl$, $H_2^{+1}O$, NH_3^{+1}, CH_4^{+1}**	metal hydrides: **NaH^{-1}, CaH_2^{-1}, AlH_3^{-1}**
Alkali metal atoms (Group I) have an oxidation number equal to **+1** within compounds. Alkali earth atoms (Group II) have an oxidation number of **+2** within compounds.	**Li^{+}, Na^{+}, K^{+}, Rb^{+}, Cs^{+}** **Mg^{2+} , Ca^{+2} , Ba^{+2}, Sr^{+2}**	
The algebraic sum of oxidation states of all atoms in a neutral molecule must be zero	**$[K_2^{+1}Cr_2^{+6}O_7^{-2}]^{\circ}$** $2*(+1)+2*(+6)+7*(-2)=0$	
While in ions the algebraic sum of the oxidation states of the constituent atoms must be equal to the charge on the ion	**$[P^{+5}O_4^{-2}]^{3-}$** $1*(+5)+4*(-2)=-3$	

The increase in oxidation state of an atom through a chemical reaction is known as an <u>oxidation</u> (окисление):

$$Fe^{0} - 2\bar{e} \rightarrow Fe^{2+}$$

a decrease in oxidation state is known as a <u>reduction</u> (восстановление):

$$O_2^{0} + 2\bar{e} \cdot 2 \rightarrow 2O^{2-}$$

$$4\bar{e}$$

$$2Fe^{0} + O_2^{0} = 2[Fe^{2+}O^{2-}]^{0}$$

In 1st reaction no change of oxidation degrees of atoms:

$$Na^{+1}O^{-2}H^{+1} + H^{+1}Cl^{-1} = Na^{+1}Cl^{-1} + H_2^{-1}O^{-2}$$

In 2nd equation we see that Mn and N atoms change their oxidation states:

$$K^{+1}\underline{Mn^{+7}}O_4^{2-} + Na^{+1}\underline{N^{+3}}O_2^{2-} + H_2^{+1}S^{+6}O_4^{-2} =>$$

$$=> \underline{Mn^{+2}}S^{+6}O_4^{-2} + K_2^{+1}S^{+6}O_4^{2-} + Na^{+1}\underline{N^{+5}}O_3^{2-} + H_2^{+1}O^{2-}$$

Oxidation-Reduction Reactions are all reactions that involve the change of an oxidation number, and transfer of electrons among the reacting substances.

- **Oxidation** is the *loss of electrons* or an *increase in oxidation state* by a molecule, atom, or ion.

- **Reduction** is the *gain of electrons* or a *decrease in oxidation state* by a molecule, atom, or ion.

The chemical substance which loses electrons, is oxidised (as result increases its valency) and called the ***<u>reducing agent</u>*** (reductant).

The chemical substance which gains electrons is reduced (as result decreases its valency) and called the ***<u>oxidising agent</u>*** (oxidant).

$$2Fe^{\square} + O_2^{\square} = 2FeO$$

reducing agent

oxidizing agent

IMPOTANT OXIDANTS

An oxidizing agent: contains an element whose oxidation state decreases in a redox reaction gains electrons:

1) Halogens in free state: $F_2 \rightarrow Cl_2 \rightarrow I_2 \rightarrow Br_2$
2) Oxigen O_2 and ozon O_3
3) Nitrogen N_2
4) Oxygen-containing mineral acids: nitric acid (HNO_3), perchloric acid ($HClO_4$), and sulfuric acid (H_2SO_4)
5) Permanganate (MnO_4^-), chromate (CrO_4^{2-}), and dichromate ($Cr_2O_7^{2-}$) ions in acidic solution
6) Oxides: CuO, PbO_2, Ag_2O
7) Compounds of Iron (III) ion (Fe^{3+}): $FeCl_3$

IMPOTANT REDUCTANTS

A reducing agent: contains an element whose oxidation state increases in a redox reation loses electrons:

1) Alkali metal atoms (Group I) and Alkali earth metal atoms (Group II): Na, K, Mg,Ca
2) Average activity metals: Zn, Al, Fe
3) Hydrogen H_2
4) Hydrides of alkali and alkaline earth metals: NaH, CaH_2
5) Some non-metals: P, Si, C (coal)
6) Hydrohalogen acids and their salts: HCl, HI, HBr
7) Compounds of Iron (II) ion (Fe^{2+}): $FeSO_4$ and $FeCl_2$
8) Metal cations in the lower oxidation state: $Sn^{2+} \rightarrow Sn^{4+}$
9) Nitrous acid HNO_2, ammonia NH_3
10) H_2S, CO, SO_2

Some substances containing elements in the intermediate oxidation may be oxidants or reductants:

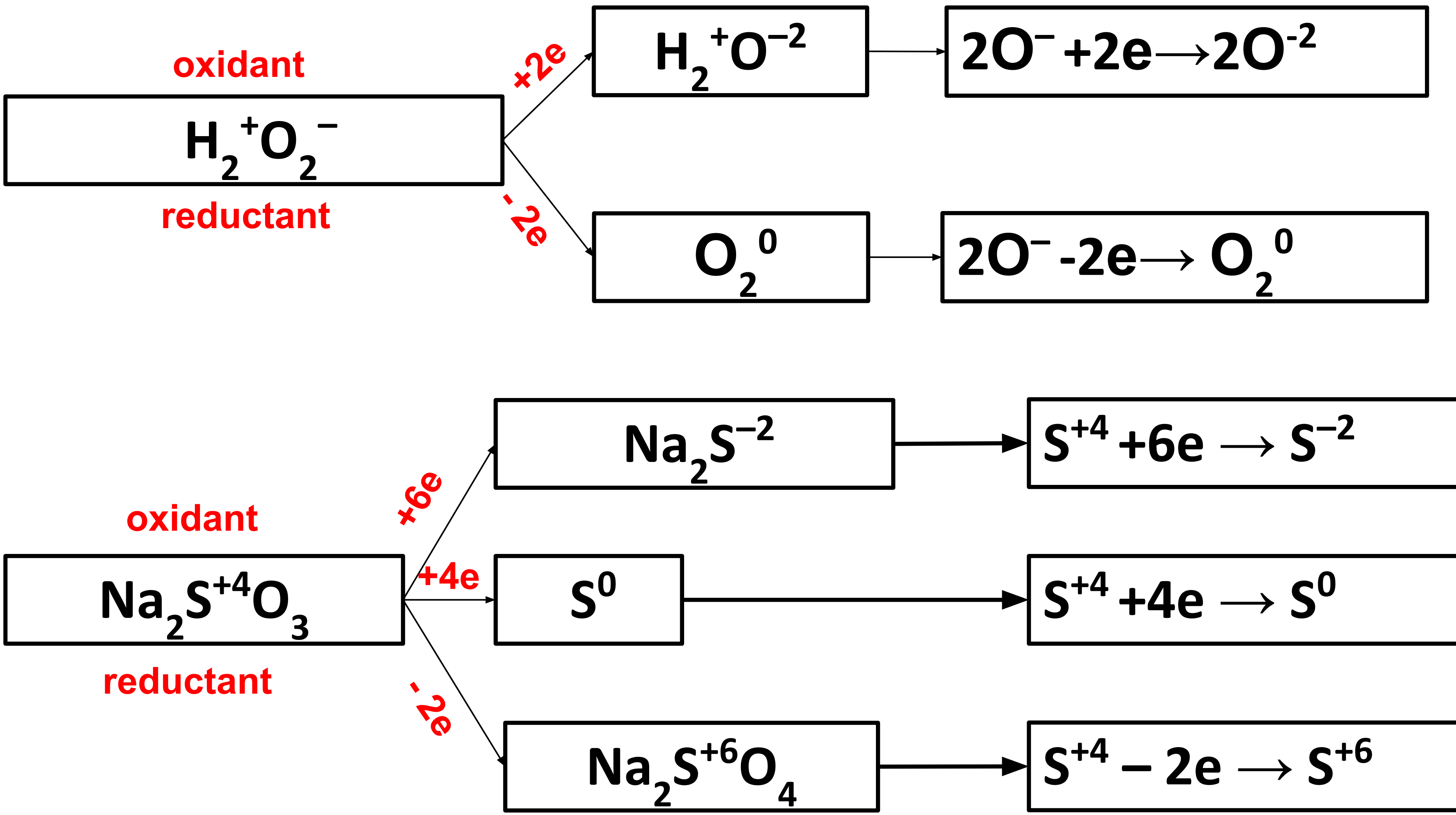
1) Halogens in basic solution (exception only F_2)

$$\overset{0}{I_2} + NaOH \xrightarrow{} Na\overset{-1}{I} + Na\overset{+5}{I}O_3 + H_2O$$

- 6e

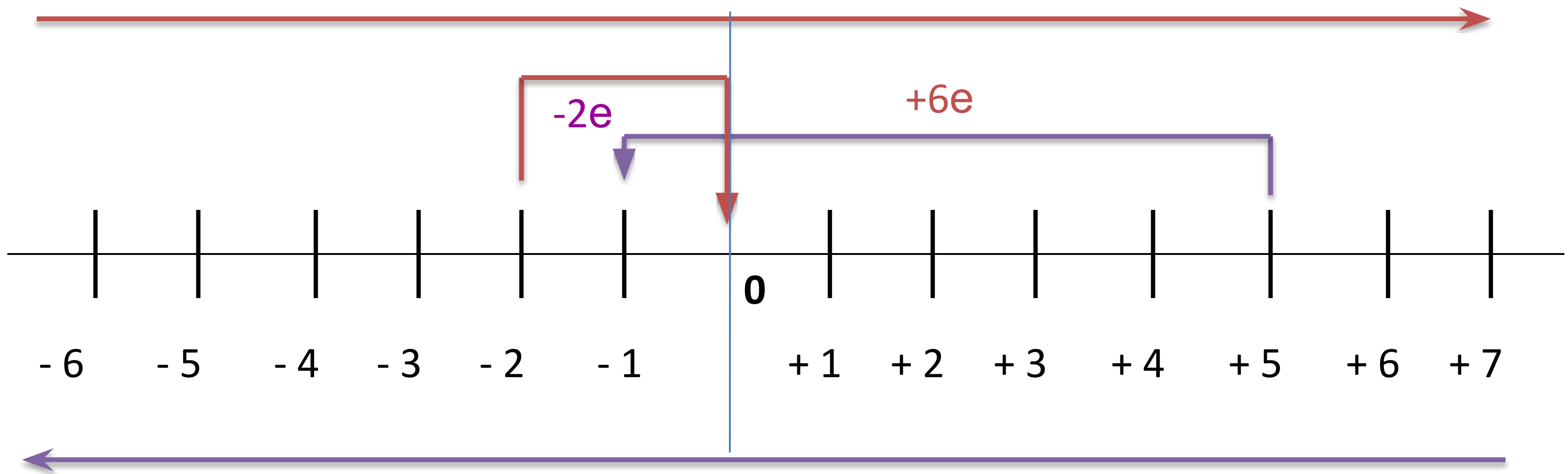
+2e

2) Hydrogen peroxide H_2O_2
3) Sulfurous acid and its salt H_2SO_3


oxidant
$H_2^{+}O_2^{-}$
reductant
+2e
- 2e
$H_2^{+}O^{-2}$
$2O^{-} + 2e \rightarrow 2O^{-2}$
O_2^{0}
$2O^{-} - 2e \rightarrow O_2^{0}$
oxidant
$Na_2S^{+4}O_3$
reductant
+6e
+4e
- 2e
Na_2S^{-2}
$S^{+4} + 6e \rightarrow S^{-2}$
S^{0}
$S^{+4} + 4e \rightarrow S^{0}$
$Na_2S^{+6}O_4$
$S^{+4} - 2e \rightarrow S^{+6}$

REDOX SCALE

Reducing agents are oxidised. Oxidation is the loss of electrons (-ne)



Oxidising agents are reduced. Reduction is the gain of electrons (+ne)

-2e

$$\overset{+1}{K}\,\overset{+5}{Cl}\,\overset{-2}{O_3} \rightarrow \overset{+1}{K}\,\overset{-1}{Cl} + \overset{0}{O_2}$$

+6e

REDOX REACTION TYPES

Intermolecular redox reactions in which the oxidant and reductant are part of different molecules

Intramolecular redox reactions in which the oxidant and reductant are composed into one molecule

$$H_2\overset{-2}{S} + \overset{0}{Cl_2} = \overset{0}{S} + 2H\overset{-1}{Cl}$$

$\overset{-2}{S} \xrightarrow{-2e} \overset{0}{S}$

$\overset{0}{Cl} \xrightarrow{+1e} \overset{-1}{Cl}$

reductant: H_2S

oxidant: Cl_2

$$K\overset{+5}{Cl}\overset{-2}{O_3} \rightarrow K\overset{-1}{Cl} + \overset{0}{O_2}$$

$\overset{-2}{O} \xrightarrow{-2e} \overset{0}{O}$

$\overset{+5}{Cl} \xrightarrow{+6e} \overset{-1}{Cl}$

oxidant

reductant

DISPROPORTIONATION REACTIONS

In some redox reactions, called disproportionation reactions, the same substance is both oxidized and reduced.

Disproportionation reaction is a intramolecular reaction in which the atoms of one element is reduced and simultaneously increase the degree of oxidation state.

+2e

$$3Cl_2^0 + 6KOH = 5KCl^{-1} + KCl^{+5}O_3 + 3H_2O$$

- 5e

oxidant

reductant

DISPROPORTIONATION REACTIONS

-2e

$$4K\overset{+5}{Cl}O_3 \rightarrow 3K\overset{+7}{Cl}O_4 + K\overset{-1}{Cl}$$

+6e

+1e

$$\overset{0}{Br_2} + H_2O \rightarrow H\overset{-1}{Br} + H\overset{+1}{Br}O$$

-1e

METHODS OF BALANCING REDOX REACTIONS

1) **The Oxidation-Number Method (ionic balance)**: the key to this method is to realize that the net change in the total of all oxidation numbers must be zero. That is, any increase in oxidation number for the oxidized atoms must be match by the corresponding decrease in oxidation number for the reduced atoms.

$$Cu + HNO_3 = Cu(NO_3)_2 + NO_2 + H_2O$$

$$\underline{Cu^{0}} + H^{+1} + \underline{NO_3^{-1}} = \underline{Cu^{+2}} + 2\underline{NO_3^{-1}} + NO_2^{0} + H_2O^{0}$$

$$\begin{array}{l|cc|l} Cu^{0} - 2e \rightarrow Cu^{2+} & 2 & 1 & \text{oxidation, reductant} \\ \underbrace{NO_3^{-1} + 2H^{+1}}_{-1+2(+1)=+1} + 1e \rightarrow \underbrace{NO_2^{0} + H_2O^{0}}_{0+0=0} & 1 & 2 & \text{reduction, oxidant} \end{array}$$

2) Half Reactions Method (electronic balance):

1) Write and balance separate half-equations for oxidation and reduction, and balance the equation.
2) Adjust coefficients in the two half-equation so that the same number of electrons appears in each half equation.
3) Add together the two half-equation, then cancel the species common to both side of the equation to obtain the balanced overall equation.

$$K^{+1}\underline{Cl^{+5}}\,\underline{O_3^{-2}} \rightarrow K^{+1}\underline{Cl^{-1}} + \underline{O_2}$$

$$\begin{array}{l|cc|l} Cl^{+5} + 6e \rightarrow Cl^{-1} & 6 & 4 = 2 & \text{reduction, oxidant} \\ 2O^{-2} - 2e \cdot 2 \rightarrow O_2 & 4 & 6 = 3 & \text{oxidation, reductant} \end{array}$$

$$2KClO_3 \rightarrow 2KCl + 3O_2$$

Oxidizing properties of potassium permanganate

$\overset{+7}{KMnO_4}$
permanganate ion
(purpule sln)

$KMnO_4 \xrightarrow{H^+\ (+5e)} Mn^{+2}$ colorless

$KMnO_4 \xrightarrow{H_2O\ (+3e)} \overset{+4}{MnO_2}$ yellow

$KMnO_4 \xrightarrow{OH^-\ (+1e)} \overset{+6}{K_2MnO_4}$ green

In acidic solution:

$$2KMnO_4 + 5Na_2SO_3 + 3H_2SO_4 = 2MnSO_4 + 5Na_2SO_4 + K_2SO_4 + 3H_2O$$

In neutral aqueous solution:

$$2\,KMnO_4 + 5Na_2SO_3 + H_2O = 2MnO_2 + 3\,Na_2SO_4 + 2KOH$$

In basic solution:

$$2\,KMnO_4 + Na_2SO_3 + 2KOH = 2\,K_2MnO_4 + Na_2SO_4 + H_2O$$

Влияние среды на изменение степеней окисления атомов химических элементов

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GLOSSARY

Oxidation Any chemical change in which at least one element loses electrons, either completely or partially.

Reduction Any chemical change in which at least one element gains electrons, either completely or partially.

Oxidation-reduction reactions The chemical reactions in which there is a complete or partial transfer of electrons, resulting in oxidation and reduction. These reactions are also called redox reactions.

Half-reactions Separate oxidation and reduction reaction equations in which electrons are shown as a reactant or product.

Reducing agent A substance that loses electrons, making it possible for another substance to gain electrons and be reduced.

Oxidizing agent A substance that gains electrons, making it possible for another substance to lose electrons and be oxidized.

Oxidation number A tool for keeping track of the flow of electrons in redox reactions (also called oxidation state).

Combination or synthesis reaction The joining of two or more elements or compounds into one product.

Decomposition reaction The conversion of one compound into two or more simpler substances.

Combustion reaction Rapid oxidation accompanied by heat and usually light.

Single-displacement reaction Chemical change in which atoms of one element displace (or replace) atoms of another element in a compound.

Loses electron : OXIDATION

LEO

GER

Gains Electron = REDUCTION

Oxidation - Reduction Reactions

Oxidation

$Zn \rightarrow Zn^{2+} + 2e^-$
- losing electron
- number of oxidation increase
- reducting agent

Reduction

$2H^+ + 2e^- \rightarrow H^2$
- gaining electrons
- number of oxidation decrease
- oxidaising agent

$$\overset{0}{Zn} + \underset{1+}{2H^+} \rightarrow \overset{2+}{Zn^{2+}} + \underset{0}{H_2}$$

The reaction is a **redox reaction.**

H_2SO_4 Hydrogen = +1 oxidation number Oxygen = -2 oxidation number	$(2 \times H) + S + (4 \times O) = 0$ $2 + S - 8 = 0$ $\mathbf{S = 6}$

Calculate the oxidation number of H_2SO_4

Uses of redox :

- Fuel
- Combustion
- Replacement
- Precipitation
- Electrochemical cell
- Electrolytic cell
- Respiration
- Rusting of iron