№ 13. OXIDATION – REDUCTION REACTIONS. IMPORTANT DEFINITIONS. TYPES OF REDOX REACTIONS.

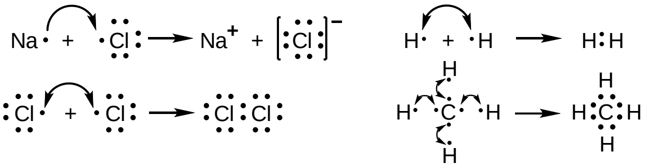
I. Valence and oxidation state

Introduction: It has long been known that some metals are more "active" than others in the sense that a more active metal can "displace" a less active one from a solution of its salt. The classic example is the reaction after immersing a zinc rod with clean surface into aqueous solution of copper (II) sulfate. Soon thereafter, the surface of the zinc rod becomes covered with a black coating of finely-divided copper, and the blue color of the hydrated copper (II) ions diminishes. The opposite reaction does not happen. Copper rod remains intact in solution of $ZnSO_4$. Zinc is more active than copper because it can displace (precipitate) copper from solution. The explanation of these facts is in the core of oxidation-reduction reactions or in short, redox reactions.

Before going into details of redox reactions let's review the basic concept in chemistry, that of valence.

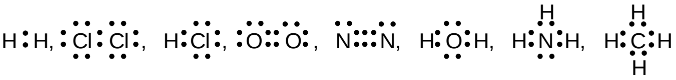
I.1. The property of atoms to combine with a definite number of atoms of another element is called valence. The IUPAC definition of valence is: **"The maximum number of univalent atoms (originally hydrogen or chlorine atoms) that may combine with an atom of the element under consideration, or with a fragment, or for which an atom of this element can be substituted"**. The combining power or affinity of an atom of an element was determined by the number of hydrogen atoms that it combined with. In methane, carbon has a valence of 4; in ammonia, nitrogen has a valence of 3; in water, oxygen has a valence of two; and in hydrogen chloride, chlorine has a valence of 1. The chemical bonds are formed through combining electrons. One covalent bond is described as sharing one electron pair between two atoms. We know through observations that eight electrons (an octet) in the outermost shell (called **valence shell**) impart special stability of the noble gas elements in group 8A, like Ne (2+8), Ar (2+8+8), etc. The chemistry of many elements is governed by a tendency for them to achieve an electron configuration of a noble gas through bonding with other elements.

Octet rule and Lewis structures: The atoms of reactive representative elements tend to undergo those chemical reactions that most directly give them electron configurations of the nearest noble gas.



The electron pairs of covalent bonds are counted with the other valence electrons in computing octets (remember: only the valence shell electrons are counted; the core are "understood").

In terms of Lewis description of a covalent bond as a shared electron pair, the following molecules are depicted as:



The number of shared electron pairs is different for various elements. A hydrogen atom participates in formation of one shared electron pair, the oxygen atom - in two, the nitrogen atom - in three, and the carbon atom - in four. The shared electron pairs are formed by providing from various atoms definite number of single electrons which in hydrogen is one, in oxygen - two, in nitrogen - three, etc. The number of electrons provided by an atom in formation of chemical bonds is numerically equal to the valence value. According to the atomic structure theory and the theory of chemical bonds, the valence of elements is determined by the number of electrons provided by certain atom in formation of its chemical bonds. Therefore, another expression for valence is: "The property of atoms of chemical elements to participate in formation of chemical bonds with definite number of electrons is called valence". **The number of electrons participating in formation of chemical bonds determines the valence state of an element, for instance:**

$\overset{1}{H}_2$ $\overset{1}{H}\overset{1}{Cl}$ $\overset{2}{Ca}\overset{1}{Cl}_2$ $\overset{3}{N}\overset{1}{H}_3$ $\overset{4}{C}\overset{1}{H}_4$ $\overset{1}{K}\overset{7}{Mn}\overset{2}{O}_4$

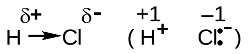
Some elements show only one valence state, like hydrogen, sodium, etc., whereas other elements possess several valence states, like iron, copper, etc.. Those atoms that participate in formation of chemical bonds with the same number of electrons have *constant valence*, whereas atoms that can form several numbers of bonds have *variable valence*. Constant valence is characteristic for atoms with small number of outer electrons, e.g. in groups IA, IIA, like Na, Ca. Variable valences have elements of IVA, VA, VIA, VIIA groups as well as B-groups of Periodic table. In some cases variable valence can be explained by splitting electron pairs in an outer shell, thus increasing the number of single electrons there and formation of more shared electron pairs. For instance, carbon has two single electrons and one pair in its outer shell. Carbon can form two or, in many organic compounds, four covalent bonds. Therefore carbon has valence of 2 or 4.

Quick review of Periodic table:

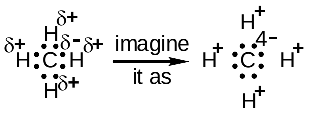
Type of Element	**Metal**	**Nonmetal**
Electronegativity (and what it means)	**Metals have LOW electronegativity, which means they do not attract electrons strongly in a chemical bond.**	**Nonmetals have HIGH electronegativity, which means they attract electrons strongly in a chemical bond.**
Ionization Energy (and what it means)	**Metals have LOW ionization energy, which means they can easily lose electrons when energy is added.**	**Nonmetals have HIGH ionization energy, which means they hold onto their valence electrons very strongly.**
How ions are formed	**Metal atoms LOSE their valence electrons (OXIDATION) to form POSITIVE charged ions (CATIONS).**	**Nonmetal atoms GAIN enough electrons (REDUCTION) to give themselves a stable octet of 8 valence electrons to form NEGATIVE charged ions (ANIONS).**

The most profound metallic properties have elements in lower left corner of Periodic table, whereas the strongest non-metals are located in the upper right corner.

I.2. In some cases the valence does not coincide with the number of bonds, for instance, the stable ammonium cation, NH_4^+, has four bonds but the nitrogen is three-valent. In more complicated compounds the exact number of bonds if often difficult to determine and the valence of participating atoms is hard to define. Because of the ambiguity of the term valence, nowadays the notations of oxidation numbers or oxidation state are used. The terms oxidation state and oxidation number are often used interchangeably. The **oxidation state (OS)**, often called the **oxidation number**, is an indicator of the degree of loss of electrons (oxidation) of an atom in a chemical compound. **Conceptually, the oxidation state, which may be positive, negative or zero, 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. **In covalent compounds, this hypothetical charge is the electric charge an atom would have if the bonding electrons were assigned exclusively to the more electronegative atom.** Consider hydrogen chloride, HCl molecule in gas phase. The covalent bond hydrogen-chlorine is polar, as indicated because the electronegativity of chlorine is much higher than that of hydrogen.



The shared electron pair is shifted towards chlorine giving a partial negative charge on the chlorine atom and equal in size partial positive charge on hydrogen. Assuming that this shared electron pair belongs entirely to the chlorine atom, the bond will transform into ionic. Then, the charges of thus obtained imaginary ions are equal to the oxidation state: +1 for hydrogen, and -1 for chlorine. Similarly, methane can be viewed as consisting of 4 hydrogen cations and C^{4-} anion because $\chi_C > \chi_H$. Therefore, the oxidation state of carbon in methane is –4.



The atom with higher electronegativity, *typically a nonmetallic element*, is assigned negative oxidation number while the other atom, often a metallic element, is given positive oxidation number.

Oxidation number serves mainly as a tool for keeping track of electrons in reactions in which they are exchanged between reactants, and for characterizing the “combining power” of an atom in a molecule or ion.

Oxidation states are typically represented by small integers. In some cases, the average oxidation state of an element is a fraction, such as +8/3 for iron in magnetite (Fe_3O_4) or –8/3 for carbon in propane (C_3H_8). The highest known oxidation state is reported to be +9, while the lowest known oxidation state is –4 for some elements in the carbon group. The oxidation number is typically denoted on the top of a chemical symbol using sign “+” or “–” followed by the respective number, in contrast to ion charge where first is the number followed by a sign.

$\overset{+8/3}{Fe_3}\overset{-2}{O_4}$ $\overset{-8/3}{C_3}\overset{+1}{H_8}$

The oxidation state of an atom in any compound is determined by the following rules:

(1) the oxidation state of a free element (uncombined element) is zero (no charges): $\overset{0}{H_2}$ $\overset{0}{Cl_2}$ $\overset{0}{Na}$ $\overset{0}{C}$

(2) for a simple (monoatomic) ion, the oxidation state is equal to the net charge on the ion: (sodium cation +1, and chloride anion −1; usually are not indicated) $\overset{+1}{Na}\overset{-1}{Cl}$ $\overset{+2}{Zn}\overset{-2}{S}$

(3) hydrogen has an oxidation state of +1 (except in hydrides of active metals −1, e.g. NaH) and oxygen has an oxidation state of −2 (except in peroxides −1, e.g. H_2O_2).

(4) the algebraic sum of oxidation states of all atoms in a neutral molecule must be zero: $\overset{+1}{H_2}\overset{-2}{O}$ $\overset{+1}{Na_2}\overset{+6}{S}\overset{-2}{O_4}$ $\overset{+4}{C}\overset{-1}{Cl_4}$

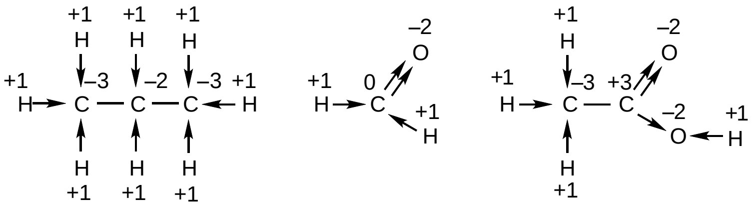
(5) for ions the algebraic sum of the oxidation states of the constituent atoms must be equal to the charge on the ion. $\overset{+6}{S}\overset{-2}{O_4^{2-}}$ $\overset{+5}{P}\overset{-2}{O_4^{3-}}$ $\overset{+5}{N}\overset{-2}{O_3^{-}}$

An example of nitrogen in ferrous nitrate OS calculation when not certain of its value: $Fe(\overset{x}{N}\overset{-2}{O_3})_2$

The nitrate anion has charge of 1−. There are two nitrate groups and the molecule is electrically neutral. Therefore, the iron charge is 2+. According to rule #2 the iron OS = charge = +2. From rule #4 follows that the sum of all OS in ferrous nitrate is: $(+2)_{Fe} + (2.x)_N + (6.\ -2)_O = 0$. Solving this equation gives x = +5; OS of N is +5. The sequence of steps is applicable for determination of unknown oxidation state.

Step	Example SO_4^{2-}
1. Determine and compare the electronegativity	$\chi_O > \chi_S$
2. Determine OS of more electronegative atom; use standard OS for oxygen and often – halogens	$\overset{x}{S}\overset{-2}{O_4^{2-}}$
3. Consider whether ion charge is present or molecule is neutral	
4. Apply rules #4 or #5 – write equation using the known OS of elements. Their sum must be equal to zero for neutral molecule or to the ionic charge	$(4.\ -2)_O + (x)_S = -2$ x = +6 The sulfur oxidation state in sulfate anion is +6.

Determination of OS in organic compounds is best achieved using structural formulae and considering each bond. Bonds between identical atoms are not assumed ionic (C−C or C=C, −N=N−, equal sharing of electrons) and multiple bonds are counted twice or three times. Examples where the arrow points to more electronegative atom that takes one for each bond imaginary negative charge:



Conclusion: **The bonding shared electron pairs are formally assigned as completely possessed by the more electronegative atom of the two bonded atoms**. Carbon has lowest −4 oxidation state in methane, and highest OS +4 in CO_2.

II. Oxidation-reduction reactions. Definitions. Oxidizing and reducing agents.

Some chemical reactions are NOT accompanied by changes of oxidation state of all participating atoms, for instance:

$H^+ + \overset{-2}{O}\overset{+1}{H}{}^- \longrightarrow \overset{+1}{H_2}\overset{-2}{O}$ $\underbrace{Cu^{2+} + SO_4^{2-}} + \underbrace{2\,Na^+ + 2\,OH^-} \longrightarrow Cu(OH)_2\downarrow + \underbrace{2\,Na^+ + SO_4^{2-}}$

Many others reactions proceed WITH changes of oxidation state:

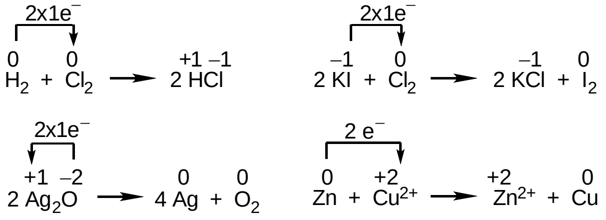
$\overset{0}{2\,Na} + \overset{0}{Cl_2} \longrightarrow \overset{+1\,-1}{2\,NaCl}$ $\qquad$ $\overset{0}{2\,Ca} + \overset{0}{O_2} \longrightarrow \overset{+2\,-2}{2\,CaO}$

$\overset{0}{Zn} + Cu^{2+} + SO_4^{2-} \longrightarrow \overset{0}{Cu} + Zn^{2+} + SO_4^{2-}$ The reaction described in the introduction goes with change of OS of Zn and Cu, the sulfate anion's constituent atoms do not change OS. Zn is more active metal than Cu. A more active metal (such as Zn) will donate electrons to the cation of a less active metal (Cu^{2+}, for example). Metals are arranged in order of descendent activity:

Displace H_2 from water, steam, or acids	**Li**	$2\,Li(s) + 2\,H_2O(\ell) \longrightarrow 2\,LiOH(aq) + H_2(g)$
	K	$2\,K(s) + 2\,H_2O(\ell) \longrightarrow 2\,KOH(aq) + H_2(g)$
	Ca	$Ca(s) + 2\,H_2O(\ell) \longrightarrow Ca(OH)_2(s) + H_2(g)$
	Na	$2\,Na(s) + 2\,H_2O(\ell) \longrightarrow 2\,NaOH(aq) + H_2(g)$
Displace H_2 from steam or acids	**Mg**	$Mg(s) + 2\,H_2O(g) \longrightarrow Mg(OH)_2(s) + H_2(g)$
	Al	$2\,Al(s) + 6\,H_2O(g) \longrightarrow 2\,Al(OH)_3(s) + 3\,H_2(g)$
	Mn	$Mn(s) + 2\,H_2O(g) \longrightarrow Mn(OH)_2(s) + H_2(g)$
	Zn	$Zn(s) + 2\,H_2O(g) \longrightarrow Zn(OH)_2(s) + H_2(g)$
	Fe	$Fe(s) + 2\,H_2O(g) \longrightarrow Fe(OH)_2(s) + H_2(g)$
Displace H_2 from acids only	**Ni**	$Ni(s) + 2\,H^+(aq) \longrightarrow Ni^{2+}(aq) + H_2(g)$
	Sn	$Sn(s) + 2\,H^+(aq) \longrightarrow Sn^{2+}(aq) + H_2(g)$
	Pb	$Pb(s) + 2\,H^+(aq) \longrightarrow Pb^{2+}(aq) + H_2(g)$
	H_2	
Can not displace H_2	**Cu**	
	Ag	
	Pt	
	Au	

The most active metals appear on top, and least active metals appear on the bottom. Note that the "active" metals are all "attacked by acids"; what this really means is that they are capable of donating electrons to H^+.

II.1. Reactions in which electrons transfer from one atom to another are called redox (or oxidation-reduction) reactions. The oxidation state of some atoms change in a redox reaction.



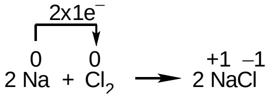
$\overset{0}{H_2} + \overset{0}{Cl_2} \longrightarrow \overset{+1\,-1}{2\,HCl}$ $\qquad$ $\overset{-1}{2\,KI} + \overset{0}{Cl_2} \longrightarrow \overset{-1}{2\,KCl} + \overset{0}{I_2}$

$\overset{+1\,-2}{2\,Ag_2O} \longrightarrow \overset{0}{4\,Ag} + \overset{0}{O_2}$ $\qquad$ $\overset{0}{Zn} + \overset{+2}{Cu^{2+}} \longrightarrow \overset{+2}{Zn^{2+}} + \overset{0}{Cu}$

The arrow on top of symbols indicates the direction of electron transfer.

The OS of the elements hydrogen and chlorine is zero, but the OS of hydrogen in HCl is +1, and of chlorine in HCl is −1. Each hydrogen transferred one electron to chlorine.

II.2. The process accompanied by loss of electrons is called oxidation. Any change that makes an oxidation state more positive is defined as an oxidation.



$\overset{0}{2\,Na} + \overset{0}{Cl_2} \longrightarrow \overset{+1\,-1}{2\,NaCl}$

When sodium transfers one electron to a Cl atom, the OS of Na changes from 0 to +1: We say that the sodium atom *is oxidized* to the sodium cation.

The reaction accompanied by gain of electrons is reduction. Any change that makes an oxidation state more negative is called reduction.

When a chlorine atom accepts an electron and goes to anion, the OS of Cl changes from 0 to −1: the chlorine atom *is reduced* to chloride ion.

OXIDATION	**Loss of electrons**	**Becomes more (+) charged**
REDUCTION	**Gain of electrons**	**Becomes more (−) charged**

II.3. A reduction cannot occur without oxidation of something else. Electrons don't just leave from or go to outer space: they transfer. A reaction that involves a reduction also must involve an oxidation, and any such reaction is redox reaction. **Oxidation and reduction are oppositely directed processes. They proceed always simultaneously**, i.e. if one substance is oxidized then another one is reduced.

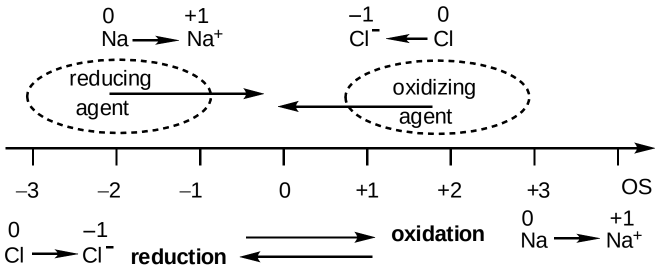
II.4. Oxidizing agent is the species that causes the oxidation. Oxidation is a loss of electrons, so **the oxidizing agent is the species that removes electrons from the reduced species. Atoms or ions that receive electrons are the oxidizing agents. Their oxidation state decreases.**

$$\underset{\text{reducing agent}}{\overset{0}{2\,Na}} + \underset{\text{oxidizing agent}}{\overset{0}{Cl_2}} \longrightarrow \overset{+1\;-1}{2\,NaCl}$$

Reducing agent: the species that causes the reduction. Reduction is a gain of electrons, so **the reducing agent is the species that gives electrons to the oxidized species. Atoms or ions that lose electrons are the reducing agents. Their oxidation state increases.**

In other words: **The species that is oxidized is called the reducing agent, the species that is reduced is called the oxidizing agent. Notice!** An oxidizing agent is always itself reduced in a redox reaction, and that a reducing agent is always itself oxidized.

How to identify which species is oxidized and which is reduced? If the OS becomes more positive going from left to right in a chemical equation, the species is oxidized and loses electrons. If the OS becomes more negative going from left to right, the species is reduced and gains electrons.



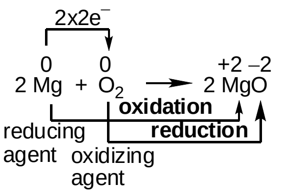
Spectator ions are called the ions that do not change oxidation state, e.g. sulfate in:

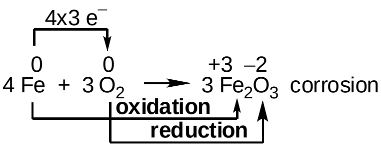
$$\underset{\text{reducing agent}}{\overset{0}{Zn}} + \underset{\text{oxidizing agent}}{Cu^{2+}} + SO_4^{2-} \longrightarrow \overset{0}{Cu} + Zn^{2+} + SO_4^{2-}$$

Atoms, ions, and molecules that have an unusually large affinity for electrons tend to be good oxidizing agents. Elemental fluorine, for example, is the strongest common oxidizing agent. F_2 is such a good oxidizing agent that metals, quartz, asbestos, and even water burst into flame in its presence. Other good oxidizing agents include O_2, O_3, and Cl_2, which are the elemental forms of the second and third most electronegative elements, respectively. Good reducing agents include the active metals, such as lithium, sodium, magnesium, aluminum, and zinc, which have relatively small ionization energies and low electronegativities. Metal hydrides, such as NaH, CaH_2, and $LiAlH_4$, which formally contain the H^- ion, are also good reducing agents.

Putting all definitions together:

For the left chemical equation, magnesium is oxidized (because Mg goes from 0 to +2) and oxygen is reduced (because O_2 goes from 0 to −2). The oxidizing agent is O_2 and the reducing agent is Mg.





II.5. Half-Reactions A redox reaction may be split into two half-reactions, one signifying oxidation and the other signifying reduction. One such half-reaction shows the OS changes of either the reducing agent or the oxidizing agent. The half-reaction that includes loss of electrons is called "oxidation reaction"; the half-reaction that involves gain of electrons is "reduction reaction". Both occur simultaneously and are mutually connected. For the above example the first step is to indicate all changes of oxidation state:

$$\overset{0}{2\,Mg} + \overset{0}{O_2} \longrightarrow \overset{+2\;-2}{2\,MgO}$$

$$\overset{0}{Mg} - 2e^- \longrightarrow \overset{+2}{Mg} \quad \text{(also written as: } \overset{0}{Mg} \longrightarrow \overset{+2}{Mg} + 2.e^-\text{)}$$

The **oxidation half-reaction** is:

What this says is that Mg goes from 0 to +2 OS by losing 2 electrons (they can be put on the products side). The electron transfer in this half-reaction must: a) be **a loss** and b) satisfy the Law of conservation of charge.

The **reduction half-reaction** is:

$$2\,\overset{0}{O} + 2x2e^- \rightarrow 2\,\overset{-2}{O}$$

What this says is that O changes OS from 0 to –2 by gaining two electrons, each. The electrons are put on the reactants side to: a) show **a gain** and b) satisfy the Law of conservation of charge.

In general symbols, the half-reactions of a redox chemical transformation are expressed as:

$$\begin{array}{ll} \textbf{oxidation} & Red_1 - n.e^- \rightarrow Ox_1 \quad \text{(also as: } Red_1 \rightarrow Ox_1 + n.e^-\text{)} \\ \textbf{reduction} & Ox_2 + n.e^- \rightarrow Red_2 \end{array}$$

A half-reaction shows the number of electrons (**n**) that are transferred in oxidation or reduction. The number of exchanged electrons "**n**" is called **redox capacity**. It is used for calculating the equivalent mass of the reducing/oxidizing agent. **The number of lost electrons in the oxidation half-reaction must be equal to the number of gained electrons in the reduction half-reaction.** This statement is the same as to say: "the total increase of oxidation number due to oxidation must equal the total decrease in oxidation number due to reduction". Therefore, half-reactions are used for balancing redox reactions' equations. A powerful technique for balancing oxidation-reduction equations involves dividing these reactions into separate oxidation and reduction half-reactions. We then balance the half-reactions, one at a time, and combine them so that electrons are neither created nor destroyed in the reaction. There is an established sequence of steps, an algorithm in balancing redox reactions.

1) Write a skeleton equation for the reaction and assign oxidation numbers to atoms on both sides of the equation:

$$\overset{+7}{KMnO_4} + \overset{+3}{HNO_2} \rightarrow \overset{+2}{Mn}(\overset{+5}{NO_3})_2 + \overset{+5}{KNO_3} + \overset{+3}{KNO_2} + H_2O$$

2) Find all atoms or ions that change their OS and determine which atoms are oxidized and which are reduced.

3) Write the half-reactions for oxidation and reduction (inseparable and simultaneous). Balance these half-reactions one at a time using electron loss or gain:

$$\begin{array}{ll|c|l} \textbf{oxidation} & \underset{\text{reducing agent}}{\overset{+3}{N}} - 2e^- \rightarrow \overset{+5}{N} & & x5 \\ & & 10 & \\ \textbf{reduction} & \underset{\text{oxidizing agent}}{\overset{+7}{Mn}} + 5e^- \rightarrow \overset{+2}{Mn} & & x2 \end{array}$$

4) Combine these half-reactions so that electrons are neither created nor destroyed.

- find the smallest common multiple (smallest number divisible by) of the number of electrons given (2) and gained (5), that is 10;
- determine multipliers that will render equal number of electrons in both half-reactions − 10/2 = 5 for N and 10/5 = 2 for Mn;
- use them as coefficients for the reducing and oxidizing agent, respectively, in the chemical equation.

5) Calculate and write the remaining coefficients, according to the law of conservation of matter.

6) Check if the equation is balanced correctly by comparing the total number of the same kind of atoms on the left and on the right site.

- following generally the order of counting:
  - a. alkali metals, alkaline earth metals,
  - b. complex ions that do not change OS – sulfate, nitrate,
  - c. hydrogen atoms,
  - d. oxygen atoms – last.

In this particular reaction (rather complicated case), place first coefficients 2 for $KMnO_4$ and $Mn(NO_3)_2$ but do not hurry up with coefficients in front of N because some nitrogen atoms do not change OS of +3 on the right-hand side.

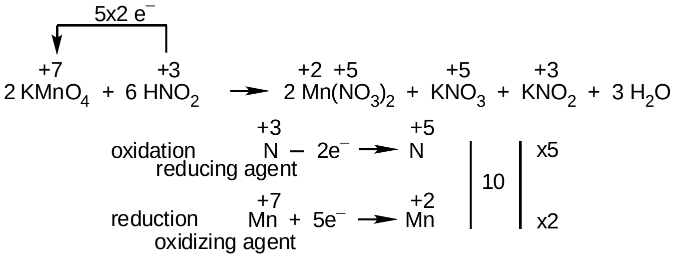
$$2\,KMnO_4 + HNO_2 \rightarrow 2\,Mn(NO_3)_2 + KNO_3 + KNO_2 + H_2O$$

At this stage of work, the oxidizing agent is balanced. Only Mn-containing molecule on the left has also potassium atoms. Compare their numbers on the left and on the right. They are equal, meaning potassium is also balanced. One molecule KNO_2 contains unchanged N (with OS of +3) and 5 more N atoms are necessary for electron balance. Four of these 5 are already in the balanced $Mn(NO_3)_2$ and one is in KNO_3, therefore place coefficient 6 for HNO_2 (coefficient 1 is not written for KNO_3).

$$2\,KMnO_4 + 6\,HNO_2 \rightarrow 2\,Mn(NO_3)_2 + KNO_3 + KNO_2 + H_2O$$

From the coefficient for nitrous acid follows that water coefficient is 3. Check the number of oxygen atoms: on the left 8 + 12 = 20; on the right 12 + 3 + 2 + 3 = 20. The equation is balanced correctly.

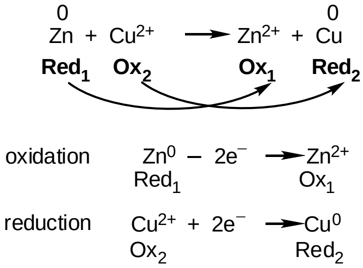
7) Final touch is to add arrow for the direction of electron transfer from the reducing agent to the oxidizing agent and indicate number of exchanged electrons considering the number of atoms that do this. The complete equation is:



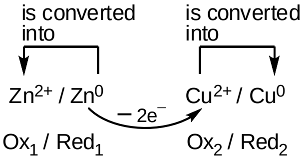
$$\overset{+7}{2\,KMnO_4} + \overset{+3}{6\,HNO_2} \rightarrow \overset{+2\;+5}{2\,Mn(NO_3)_2} + \overset{+5}{KNO_3} + \overset{+3}{KNO_2} + 3\,H_2O$$

$$\overset{+3}{N} - 2e^- \rightarrow \overset{+5}{N}$$

$$\overset{+7}{Mn} + 5e^- \rightarrow \overset{+2}{Mn}$$

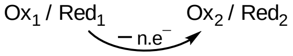


In the initial example, the oxidation and reduction half-reactions are shown as well as their representation using general symbols. Obviously, every half-reaction contains oxidized and reduced forms. The combination of an oxidizing and reducing agent that are involved in a particular (total) reaction is called a redox couple. **A redox couple is an oxidizing species and its corresponding reduced form, e.g. Zn^{2+}/Zn^0 and Cu^{2+}/Cu^0.** Conventionally, the redox couple is written for reduction reaction.



A redox reaction progresses when **two redox couples** are in contact – one is oxidized, the other - reduced (there is close similarity with acid/base reactions).

Redox reactions have always general form:



III. Types of redox reactions

III.1. Syntheses

$$A + B \rightarrow AB$$

Elements react with each other in redox reactions. Usually one or more reactants are of 0 OS. Some of these reactions are useful for humanity, like production of fertilizers from ammonia or generation of electricity from transfer of e⁻ from H_2 to O_2 in a fuel cell battery.

$$\overset{0}{2\,H_2} + \overset{0}{O_2} \rightarrow \overset{+1\,-2}{2\,H_2O} \qquad \overset{0}{N_2} + \overset{0}{3\,H_2} \rightarrow \overset{-3\,+1}{2\,NH_3}$$

$$\overset{0}{Fe} + \overset{0}{S} \rightarrow \overset{+2\,-2}{FeS}$$

III.2. Single displacement

$$A + BC \rightarrow AC + B$$

Reactions where an atom or an ion of one element is displaced from a compound by an atom of another element are typically redox reactions.

$$\overset{0}{2\,Na} + \overset{+1}{2\,H_2O} \rightarrow \overset{+1}{2\,NaOH} + \overset{0}{H_2} \qquad \overset{0}{Cl_2} + \overset{-1}{2\,KI} \rightarrow \overset{-1}{2\,KCl} + \overset{0}{I_2}$$

$$\overset{0}{Zn} + \overset{+2}{CuSO_4} \rightarrow \overset{+2}{ZnSO_4} + \overset{0}{Cu}$$

Synthesis and single replacement are intermolecular reactions. If the oxidizing and reducing agents are in the same molecule the redox reaction is intramolecular, such as:

III.3. Decomposition

$$AB \rightarrow A + B$$

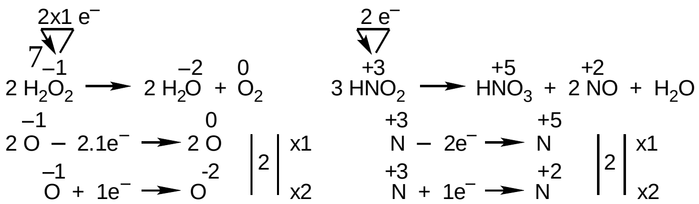
Breaking apart a compound thus producing one or more elements is a redox reaction. It usually needs external energy (electricity) to proceed.

$$\overset{+1\,-2}{2\,H_2O} \rightarrow \overset{0}{2\,H_2} + \overset{0}{O_2} \qquad \overset{+1\,-1}{2\,NaCl} \rightarrow \overset{0}{2\,Na} + \overset{0}{Cl_2}$$

$$\overset{+2\,-2}{2\,HgO} \rightarrow \overset{0}{2\,Hg} + \overset{0}{O_2}$$

III.4. Disproportionation

The reactant in disproportionation redox reaction contains an atom that can exist at least in three oxidation states. The reactant contains this atom in its



$$\overset{-1}{2\,H_2O_2} \rightarrow \overset{-2}{2\,H_2O} + \overset{0}{O_2} \qquad \overset{+3}{3\,HNO_2} \rightarrow \overset{+5}{HNO_3} + \overset{+2}{2\,NO} + H_2O$$

$$2\,\overset{-1}{O} - 2.1e^- \rightarrow 2\,\overset{0}{O} \qquad \overset{+3}{N} - 2e^- \rightarrow \overset{+5}{N}$$

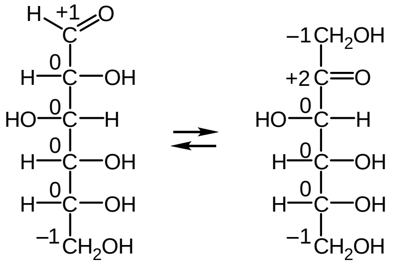
$$\overset{-1}{O} + 1e^- \rightarrow \overset{-2}{O} \qquad \overset{+3}{N} + 1e^- \rightarrow \overset{+2}{N}$$

intermediate oxidation state; the products have the same atom in lower and in higher OS. For instance, OS of oxygen in hydrogen peroxide is –1. After thermal decomposition of hydrogen peroxide, water is obtained with reduced oxygen (to lower OS, –2) and O_2 molecule with oxidized (to higher OS, 0) oxygen atom.

$$\overset{0}{Cl_2} + H_2O \longrightarrow H\overset{-1}{Cl} + H\overset{+1}{Cl}O$$

The above two examples are also decomposition reactions whereas the chlorine disproportionation in reaction with water is not decomposition.

Similar change of OS up and down of the same type atoms occurs in isomerization of glucose into fructose:



D-glucose D-fructose

III.5. Miscellaneous examples of redox reactions:

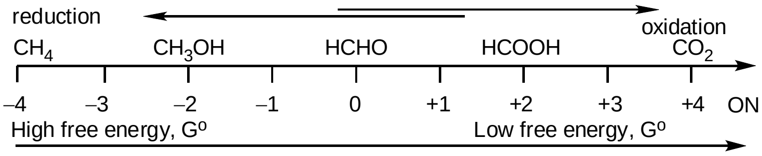
$$2\,K\overset{+7}{Mn}O_4 + 5\,H_2\overset{+3}{C_2}O_4 + 3\,H_2SO_4 \longrightarrow 2\,\overset{+2}{Mn}SO_4 + 10\,\overset{+4}{C}O_2 + K_2SO_4 + 8\,H_2O$$

$$\begin{array}{ll|c|l} \text{oxidation} & 2\,\overset{+3}{C} - 2.1e^- \longrightarrow 2\,\overset{+4}{C} & 10 & x5 \\ \text{reduction} & \overset{+7}{Mn} + 5e^- \longrightarrow \overset{+2}{Mn} & & x2 \end{array}$$

$$2\,Pb\overset{-2}{S} + 3\,\overset{0}{O_2} \longrightarrow 2\,Pb\overset{-2}{O} + \overset{+4}{S}\overset{-2}{O_2}$$

The distinguishing feature of all above described types of redox reactions is the change of the oxidation number realized by ***transfer of electrons***.

IV. Oxidation / reduction of organic molecules. Relationship with energy. Carbon in organic molecules can have OS ranging from –4 to +4. The most reduced C atoms are in methane and in higher hydrocarbons (–3 in CH_3 and –2 in CH_2 groups); the most oxidized C atoms are in carboxylic acid group (+3 in RCOOH) and in CO_2 (+4). In principal: free energy contents is higher in low OS carbon compounds, and lower in high OS organics or CO_2.



$$\xrightarrow{\text{oxidation}}$$

$$\overset{-4}{CH_4} \underset{+2e^-}{\overset{-2e^-}{\rightleftharpoons}} \overset{-2}{CH_3OH} \underset{+2e^-}{\overset{-2e^-}{\rightleftharpoons}} \overset{0}{HCHO} \underset{+2e^-}{\overset{-2e^-}{\rightleftharpoons}} \overset{+2}{HCOOH} \underset{+2e^-}{\overset{-2e^-}{\rightleftharpoons}} \overset{+4}{CO_2}$$

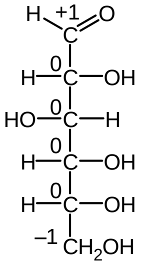
$$\xleftarrow[\text{reduction}]{}$$

Photosynthesis in plants produce compounds with higher free energy contents than the starting compounds. Such transformation is an endergonic reaction. Although photosynthesis is a complex set of reactions, the net free energy change of all steps is the difference of free energy of the starting reactants and the final products. The opposite reaction, e.g. oxidation of glucose by burning in air or catabolizing it in living organism, is an energy releasing reaction – an exergonic reaction.

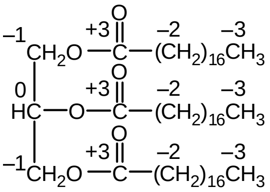
$$6\,CO_2 + 6\,H_2O \longrightarrow C_6H_{12}O_6 + 6\,O_2 \qquad \Delta G^o > 0$$

$$C_6H_{12}O_6 + 6\,O_2 \longrightarrow 6\,CO_2 + 6\,H_2O \qquad \Delta G^o < 0$$

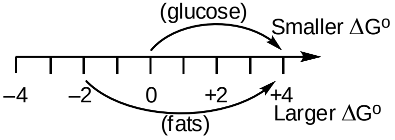
The concept of oxidation state provides another point of view at the bioenergetics. When carbon is oxidized in a biochemical reaction, the excess free energy is released to serve several purposes, like mobility, energy source for other biosynthetic reactions, storage of energy. Humans' *outside sources* of chemical energy are dietary carbohydrates and fatty acids. Our inside sources are other high-energy compounds, particularly triphosphates like APT. Photosynthesis yields carbon compounds in relatively reduced form. A glucose molecule (with relatively "reduced" carbon atoms) has more free energy contents than CO_2. Therefore, oxidation of glucose will release energy. Fats have more stored energy per gram than carbohydrates, although fat metabolism is slower. Why is so? Fats are esters of glycerol with long-chain fatty acids. These acids contain lots of $–CH_2–$ groups that have carbon in –2 OS. This oxidation state is lower than that of most carbon atoms in carbohydrates (0) – that is

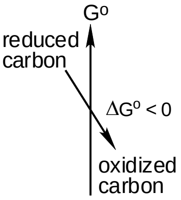


D-glucose



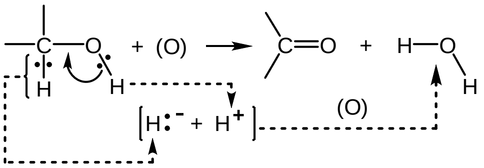
tristearine (tristearoyl glycerol)





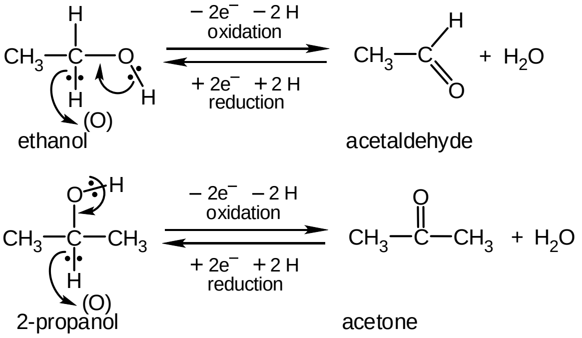
to say “fats are more reduced than carbohydrates”. Therefore free energy gain is higher after oxidation of fats than oxidation of carbohydrates.

It is well known that primary and secondary alcohols are oxidized to aldehydes and ketones, respectively. The reaction cannot be stopped to aldehyde when a strong oxidizing agent is used, *in vitro* (in a reaction vessel). Two oxidizing agents commonly used in the laboratory are $KMnO_4$ and $K_2Cr_2O_7$. The oxidation of an alcohol is an example of loss of 2 H, that’s why the reaction is called dehydrogenation. Enzymes with such action *in vivo* (in living cell) in organisms are dehydrogenases. These enzymes do not transfer 2 atoms H or molecule H_2 but hydrogen with one electron pair (hydride ion, H^-) and a proton (H^+). A general form of such biochemical oxidation is:



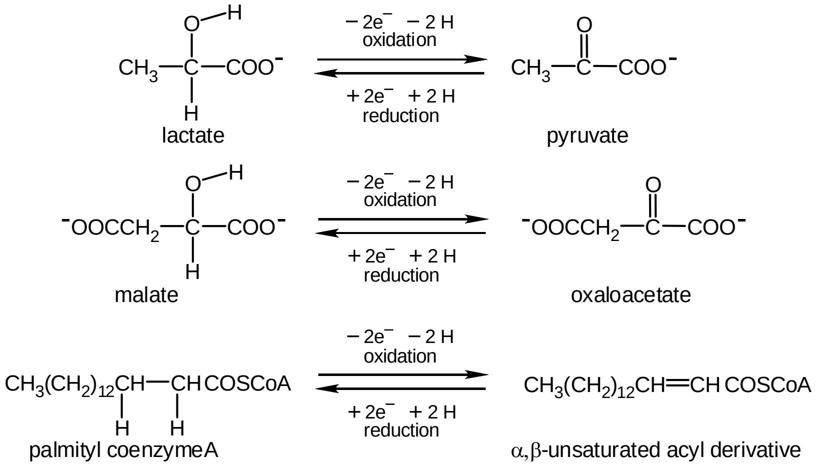
Symbol (O) designates any oxidizing agent that can accept electrons and bring about the oxidation in a reaction sequence. One hydrogen as H^+ is from the O–H bond, the other hydrogen as hydride **:**H^- is from the adjacent C–H bond. Specifically, the loss of the electron pair of the C–H bond in the alcohol makes this reaction oxidation. This electron pair, along with two H atoms ends up in a water molecule whose oxygen comes from the oxidizing agent. The general scheme describes well biochemical oxidation: in the body, when an alcohol is oxidized by a series of *in vivo* reactions, called the respiratory chain, the electron pair of the C–H bond is transferred from enzyme to enzyme until it finally does lodge in a water molecule.

Examples of oxidation-reduction reactions of organic molecules:



3^o alcohols can not be oxidized by dehydrogenation

Several more biochemically relevant and important dehydrogenation reactions are:



More on biochemical oxidation – in the next topic # 14.

The **importance** of redox reactions can be summarized by describing them in:

- ☐ DC sources; batteries
- ☐ Electrolysis (electrolytic decomposition), e.g. chloralkali process in the production of PVC
- ☐ Geochemistry; Earth’s oxidizing atmosphere and Earth’s crust is largely composed of metal oxides, oceans with oxide (H_2O)
- ☐ Biochemistry – life is based on redox, e.g. photosynthesis and citric acid cycle (Krebs’ cycle) producing H_2O, CO_2, and ATP (energy store)