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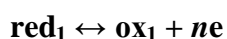
## Oxidation and reduction reactions

### 1. Oxidation and reduction reactions – definitions

Reactions in the acid-base system involve the exchange of a proton, and the reactions of formation of complexes - on the exchange of a ligand. The oxidation and reduction reaction consists in the exchange of an electron between the reducing agent (reducer), the electron donating, and the oxidizing agent (oxidizer), which takes up the electron



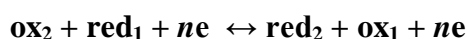
The oxidation reaction consists in giving up electrons and can be saved in general:



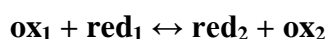
**The reduction reaction involves collecting electrons and can be saved in general:**



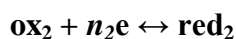
Because both *re*duction and *ox*idation are going on side-by-side, this is known as a *redox* reaction. None of these reactions can be run separately, only as a conjugated reaction of two redox systems. Only mixing the solutions or incorporating them into the circuit, allowing free migration of electrons, leads to the course of the oxidation-reduction reaction, called in short a redox reaction; this can be saved in the form of sums of equations by means of:



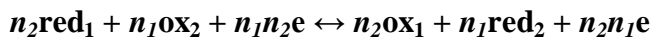
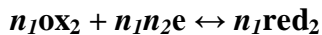
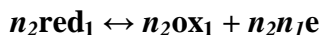
or



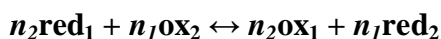
If each of the partial reactions takes place in separation or taking a different number of electrons:



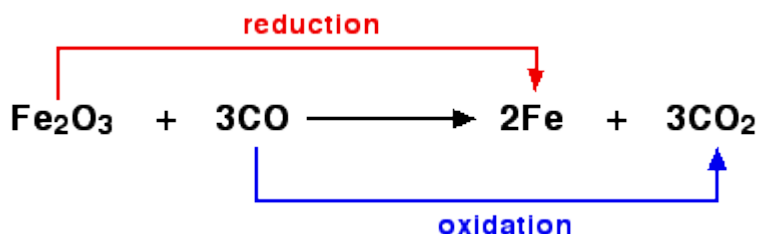
then adding up the equations, appropriate multipliers must be included so that the number of electrons on both sides remains equal to the smallest common multiple  $n_1$  and  $n_2$ . For this purpose, the first equation is multiplied by  $n_2$  and the second by  $n_1$ . By adding both equations, you get:



And finally, the general form of the coupled redox reaction is:



Example:



## 2. Assigning oxidation numbers

The following rules for assignment of oxidation numbers are listed in hierarchical order.

- Pure elements (in their natural, standard state): ox. state = 0.
- Monatomic ions: ox. state = ionic charge.
- The oxidation number of fluorine is always  $-1$ . Chlorine, bromine, and iodine usually have an oxidation number of  $-1$ , unless they're in combination with an oxygen or fluorine.
- Alkali metals (those in the 1st column of the periodic table): ox. number = 1.
- Alkaline-earth metals (those in the 2nd column of the periodic table): ox number = 2.

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- f) The oxidation state of hydrogen in a compound is usually +1. If the hydrogen is part of a *binary metal hydride* (compound of hydrogen and some metal), then the oxidation state of hydrogen is -1.
- g) The oxidation number of oxygen in a compound is usually -2. If, however, the oxygen is in a class of compounds called *peroxides* (for example, hydrogen peroxide), then the oxygen has an oxidation number of -1. If the oxygen is bonded to fluorine, the number is +1.
- h) The sum of all oxidation numbers in the species will equal the total charge of that species.

### 3. Guidelines for balancing redox equations:

1. Determine the oxidation states of each species.
2. Write each half reaction and for each:
  - a. Balance atoms that change oxidation state.
  - b. Determine number of electrons gained or lost
  - c. Balance charges by using  $H^+$  (in acidic solution) or  $OH^-$  (in basic solution).
  - d. Balance the rest of the atoms (H's and O's) using  $H_2O$ .
3. Balance the number of electrons transferred for each half reaction using the appropriate factor so that the electrons cancel.
4. Add the two half-reactions together and simplify if necessary.

### 4. Nernst Equation

Nernst Equation can be used to find the cell potential at any moment in during a reaction or at conditions other than standard-state.

$$E = E^0 + \frac{RT}{nF} \ln \frac{a_{ox}}{a_{red}}$$

$E$  = cell potential (V) under specific conditions

$E^\circ$  = cell potential at standard-state conditions

$R$  = ideal gas constant = 8.314 J/mol-K

$T$  = temperature (kelvin), which is generally 25C (298 K)

$n$  = number of moles of electrons transferred in the balanced equation

$F$  = Faraday's constant, the charge on a mole of electrons = 95,484.56 C/mol

$a_{ox}$  and  $a_{red}$  – activity of the oxidizer and the conjugated reducer

Since the temperature is generally 25°C (298 K), three of the terms in the above Nernst equation can be considered constants:  $R$ ,  $T$ , and  $F$ . Substituting the values of these constants, results in the following equation:

$$E = E^\circ + \frac{0,059}{n} \log \frac{a_{ox}}{a_{red}}$$

If  $a_{ox} = a_{red}$ , then  $E = E^\circ$  and the system reaches the normal potential.

$a = fc$

$$E = E^\circ + \frac{0,059}{n} \log \frac{[ox]}{[red]} + \frac{0,059}{n} \log \frac{f_{ox}}{f_{red}}$$

Assuming that  $f_{ox} = f_{red}$  can be used in analyzes of systems, the last part of the equation will be equal to zero and the expression for the potential of the redox system, which is a function of the concentration ratio of oxidizer and reducer, will be obtained. This formula is usually used in practical analytical calculations.

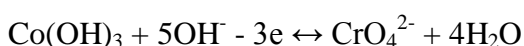
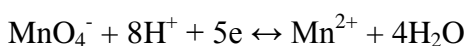
$$E = E^\circ + \frac{0,059}{n} \log \frac{[ox]}{[red]}$$

Table 1. Standard reduction potentials (at 298 K).

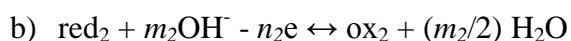
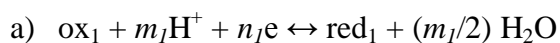
Half-reaction	$E^0$ (V)	Half-reaction	$E^0$ (V)
$F_2 + 2e^- \rightarrow 2F^-$	2.87	$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$	0.40
$Ag^{2+} + e^- \rightarrow Ag^+$	1.99	$Cu^{2+} + 2e^- \rightarrow Cu$	0.34
$Co^{3+} + e^- \rightarrow Co^{2+}$	1.82	$Hg_2Cl_2 + 2e^- \rightarrow 2Hg + 2Cl^-$	0.27
$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$	1.78	$AgCl + e^- \rightarrow Ag + Cl^-$	0.22
$Ce^{4+} + e^- \rightarrow Ce^{3+}$	1.70	$SO_4^{2-} + 4H^+ + 2e^- \rightarrow H_2SO_3 + H_2O$	0.20
$PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \rightarrow PbSO_4 + 2H_2O$	1.69	$Cu^{2+} + e^- \rightarrow Cu^+$	0.16
$MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O$	1.68	$2H^+ + 2e^- \rightarrow H_2$	0.00
$2e^- + 2H^+ + IO_4^- \rightarrow IO_3^- + H_2O$	1.60	$Fe^{3+} + 3e^- \rightarrow Fe$	-0.036
$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$	1.51	$Pb^{2+} + 2e^- \rightarrow Pb$	-0.13
$Au^{3+} + 3e^- \rightarrow Au$	1.50	$Sn^{2+} + 2e^- \rightarrow Sn$	-0.14
$PbO_2 + 4H^+ + 2e^- \rightarrow Pb^{2+} + 2H_2O$	1.46	$Ni^{2+} + 2e^- \rightarrow Ni$	-0.23
$Cl_2 + 2e^- \rightarrow 2Cl^-$	1.36	$PbSO_4 + 2e^- \rightarrow Pb + SO_4^{2-}$	-0.35
$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$	1.33	$Cd^{2+} + 2e^- \rightarrow Cd$	-0.40
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	1.23	$Fe^{2+} + 2e^- \rightarrow Fe$	-0.44
$MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$	1.21	$Cr^{3+} + e^- \rightarrow Cr^{2+}$	-0.50
$IO_3^- + 6H^+ + 5e^- \rightarrow \frac{1}{2}I_2 + 3H_2O$	1.20	$Cr^{3+} + 3e^- \rightarrow Cr$	-0.73
$Br_2 + 2e^- \rightarrow 2Br^-$	1.09	$Zn^{2+} + 2e^- \rightarrow Zn$	-0.76
$VO_2^+ + 2H^+ + e^- \rightarrow VO^{2+} + H_2O$	1.00	$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$	-0.83
$AuCl_4^- + 3e^- \rightarrow Au + 4Cl^-$	0.99	$Mn^{2+} + 2e^- \rightarrow Mn$	-1.18
$NO_3^- + 4H^+ + 3e^- \rightarrow NO + 2H_2O$	0.96	$Al^{3+} + 3e^- \rightarrow Al$	-1.66
$ClO_2 + e^- \rightarrow ClO_2^-$	0.954	$H_2 + 2e^- \rightarrow 2H^-$	-2.23
$2Hg^{2+} + 2e^- \rightarrow Hg_2^{2+}$	0.91	$Mg^{2+} + 2e^- \rightarrow Mg$	-2.37
$Ag^+ + e^- \rightarrow Ag$	0.80	$La^{3+} + 3e^- \rightarrow La$	-2.37
$Hg_2^{2+} + 2e^- \rightarrow 2Hg$	0.80	$Na^+ + e^- \rightarrow Na$	-2.71
$Fe^{3+} + e^- \rightarrow Fe^{2+}$	0.77	$Ca^{2+} + 2e^- \rightarrow Ca$	-2.76
$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$	0.68	$Ba^{2+} + 2e^- \rightarrow Ba$	-2.90
$MnO_4^- + e^- \rightarrow MnO_4^{2-}$	0.56	$K^+ + e^- \rightarrow K$	-2.92
$I_2 + 2e^- \rightarrow 2I^-$	0.54	$Li^+ + e^- \rightarrow Li$	-3.05
$Cu^+ + e^- \rightarrow Cu$	0.52		

### 5. Effect of change in oxidation-reducing properties on pH change.

In many reactions of oxidation and reduction,  $H^+$  and  $OH^-$  ions take part. Examples of such reactions are:



These reactions can be represented by general patterns:



Applying the Nernst formula to equation (a), an equation determining the potential of the system will be obtained:

$$E_1 = E_1^0 + \frac{0,059}{n_1} \log \frac{a_{ox1} a_{H^+}^{m_1}}{a_{red1}}$$

When converting a pattern, the dependence is obtained:

$$E_1 = E_1^0 - 0,059 \frac{m_1}{n_1} pH + \frac{0,059}{n_1} \log \frac{a_{ox1}}{a_{red1}}$$

The above dependence shows that when the redox reaction takes place with the participation of a proton (there is a decrease in pH, i.e. increased acidity of the environment), it increases the oxidation potential of the system.

Considering in a similar way the reaction (b), the corresponding Nernst equation can be written in the following way:

$$E_2 = E_2^0 + \frac{0,059}{n_2} \log \frac{a_{ox2} a_{OH^-}^{m_2}}{a_{red2}}$$

When converting a pattern, the dependence is obtained:

$$E_2 = E_2^0 + 0,059 \frac{m_2}{n_2} \log a_{OH^-} + \frac{0,059}{n_2} \log \frac{a_{ox2}}{a_{red2}}$$

And finally, considering that:  $\log(a_{OH^-}) = -pOH = pH-14$

$$E_2 = E_2^0 - 0,826 \frac{m_2}{n_2} + 0,059 \frac{m_2}{n_2} pH + \frac{0,059}{n_2} \log \frac{a_{ox2}}{a_{red2}}$$

In the case of a redox reaction involving OH<sup>-</sup> ions, the redox potential of the system increases as the pH increases; the system is therefore a stronger oxidant in more alkaline environments.