

Oxidation-reduction reactions

Redox couple

1. Definitions

An oxidizing agent (AKA oxidizer) is a chemical species (atom, ion or molecule) susceptible to gain at least one electron.

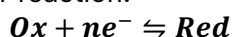
Ex: $\text{Cu}^{2+}_{\text{aq}}$ gains 2 electrons to form $\text{Cu}_{(\text{s})}$ and $\text{Ag}^{+}_{\text{aq}}$ gains 1 electron to form $\text{Ag}_{(\text{s})}$.

A reducing agent (AKA reductor) is a chemical species (atom, ion or molecule) susceptible to lose at least one electron.

Ex: $\text{Cu}_{(\text{s})}$ loses 2 electrons to form $\text{Cu}^{2+}_{\text{aq}}$ and $\text{Ag}_{(\text{s})}$ loses 1 electron to form $\text{Ag}^{+}_{\text{aq}}$.

$\text{Cu}_{(\text{s})}$ and $\text{Cu}^{2+}_{\text{aq}}$ constitute a redox couple: $\text{Cu}^{2+}_{\text{aq}}/\text{Cu}_{(\text{s})}$.

A redox couple can be defined by a redox half-reaction:



Ex: $\text{Cu}^{2+}_{(\text{aq})} + 2\text{e}^{-} \rightleftharpoons \text{Cu}_{(\text{s})}$

The oxidizer and the reductor are said to be conjugated: $\left\{ \begin{array}{l} \text{Oxidizer Ox has Red as his conjugated reductor} \\ \text{Reductor Red has Ox as his conjugated oxidizer} \end{array} \right.$

Ex: $\text{Cu}^{2+}_{\text{aq}}$ and $\text{Cu}_{(\text{s})}$ are conjugated

$\text{Cu}^{2+}_{\text{aq}}$ is the conjugated oxidizer of $\text{Cu}_{(\text{s})}$, and $\text{Cu}_{(\text{s})}$ is the conjugated reductor of $\text{Cu}^{2+}_{\text{aq}}$.

Note: The name oxidation comes from the element oxygen. The first redox reaction studied involved the action of oxygen gas on metals, leading to the apparition of metal oxides. An oxidation reaction was then defined as a reaction in which the ratio of oxygen atoms in a compound increased, and a reduction when it decreased.

Ex: Fe (0% oxygen) can be oxidized to Fe_3O_4 (57% oxygen), which can be oxidized to Fe_2O_3 (60% oxygen)
 Fe_2O_3 (60% oxygen) can be reduced to Fe_3O_4 (57% oxygen), which can be reduced to Fe (0% oxygen).

It was only later that the definition was enlarged to reactions not involving oxygen, but the names used remained.

Note: Some reduction reactions can also be identified via an increase of the ratio of hydrogen atoms in the compounds involved.

2. Writing the redox half-equation of a redox couple:

- i. Write the oxidizer and the reductor on both sides of a « double half arrow »:



- ii. Check the balance of heteroatoms (elements other than O or H):

1 Mn on the left, 1 Mn on the right => OK.

- iii. Check the balance of oxygen. It will be done with water molecules, H_2O .

4 O on the left => 4 H_2O on the right.



- iv. Check the balance of hydrogen. It will be done with aqueous protons, H^{+}_{aq} .

4 H_2O => 8 H have been added on the right => 8 H^{+} need to be added on the left.



- v. Check the balance of charges. It will be done with electrons, e^{-} .

8 « + » and 1 « - », meaning 7 « + » on the left. 2 « + » on the right => 5 « - » are missing on the left, therefore 5 electrons.



3. Oxidation state of an element

The **oxidation state**, or **oxidation number**, of an element is the hypothetical charge of the element if all of its bonds to other atoms were considered as fully ionic.

a. Determination of the oxidation number of an element:

- i. Free elements (chemicals made of 1 unique element): ON = 0

Ex: metallic iron, Fe ON(Fe) = 0

Chlorine gas, Cl_2 ON(Cl) = 0

- ii. Monoatomic ions: ON = their charge

Ex: Sodium ion, Na^{+} ON(Na) = +1

Note: This is the oxidizing number for all group 1 metals (it will be +2 for group 2 metals)

Chlorine ion, Cl^{-} ON(Cl) = -1

Note: This is the oxidizing number for all group 17 halogens

Aluminum ion, Al^{3+} ON(Al) = +3

Sulfure ion, S^{2-} ON(S) = -2

- iii. Fluorine is the element with the highest electronegativity.
Its oxidation number in a compound therefore will always be -1
- iv. Oxidation number of hydrogen in compounds can be considered as always be +1
Exception: metal hydrides (e.g. NaH) ON(H) = -1
- v. Oxidation number of oxygen in compounds can be considered as always be -2
*Exceptions: oxygen difluoride, OF₂ ON(O) = +2
Peroxides (e.g. H₂O₂) ON(O) = -1*
- vi. Oxidation number of nitrogen is mostly equal to -3
Exceptions: when nitrogen is bonded to oxygen, fluorine or chlorine
- vii. In polyatomic entities, the sum of oxidation numbers must be
 - equal to 0 in a molecule
*Ex: H₂SO₃ ON(O) = -2 and ON(H) = +1
ON(S) + 2ON(H) + 3ON(O) = 0 ⇒ ON(S) = -2ON(H) - 3ON(O) = -2x1 - 3x(-2) = +4*
 - equal to the ion's charge in an ion
*Ex: SO₄²⁻ ON(O) = -2
ON(S) + 4ON(O) = -2 ⇒ ON(S) = -4ON(O) - 2 = -4x(-2) - 2 = +6*

b. Redox reactions and oxidation state

An element is involved in a redox reaction when its oxidation number changes: it gets oxidized when its oxidation state increases and gets reduced when its oxidation state decreases.

*Ex: When H₂SO₃ turns into SO₄²⁻, the oxidation number of sulfur increases from +4 to +6. It has been oxidized. When SO₄²⁻ turns into H₂SO₃, the oxidation number of sulfur decreases from +6 to +4. It has been reduced.
SO₄²⁻ and H₂SO₃ form a redox couple: SO₄²⁻/H₂SO₃: SO₄²⁻(aq) + 4H⁺(aq) + 2e⁻ ⇌ H₂SO₃ + H₂O*

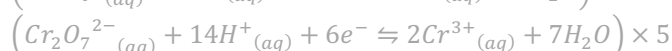
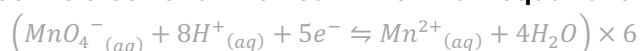
Redox reactions

1. Writing the equation of a redox reaction

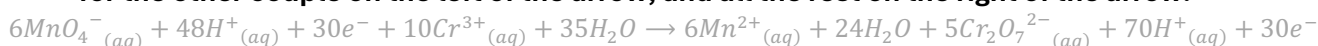
- i. Write the redox half-equation of each of the 2 couples



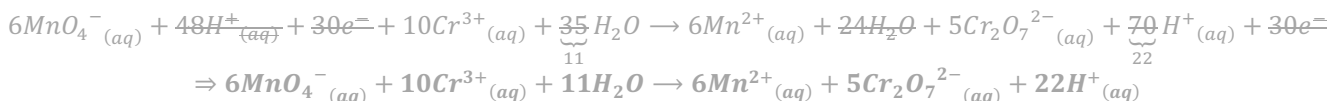
- ii. Balance the electrons involved in the 2 half-equations.



- iii. Add everything that is on the left side for 1 of the couples to everything what is on the right side for the other couple on the left of the arrow, and all the rest on the right of the arrow.



- iv. Cancel out what can be cancelled out. **Electrons should ALWAYS cancel out**



2. Spontaneous or non-spontaneous?

Usually, the reactants of a reaction can be guessed from the statements of the situation studied. However, this is not always the case, and the spontaneous reaction needs to be identified.

A redox couple can be characterized by a standard redox potential E^0 .

When 2 couples interact, the change in Gibbs energy of the system is related to the difference in standard redox potential between the 2 couples:

$$\Delta G^0 = -nF\Delta E^0 = -nF(E^0_{\text{oxidizer reactant}} - E^0_{\text{reductor reactant}})$$

Knowing the criterion for spontaneous reactions, this leads to the following conclusion:

$$\Delta E^0 < 0 \Rightarrow \Delta G^0 > 0 \Rightarrow \text{Non-spontaneous reaction}$$

$$\Delta E^0 > 0 \Rightarrow \Delta G^0 < 0 \Rightarrow \text{Spontaneous reaction}$$

Ex: $E^0(\text{MnO}_4^- / \text{Mn}^{2+}) = 1.51 \text{ V}$; $E^0(\text{Cr}_2\text{O}_7^{2-} / \text{Cr}^{3+}) = 1.23 \text{ V}$

$$E^0_{\text{Cr}_2\text{O}_7^{2-}} - E^0_{\text{Mn}^{2+}} = 1.23 - 1.51 = -0.28 \text{ V} < 0 \Rightarrow \text{non-spontaneous reaction}$$

$$E^0_{\text{MnO}_4^-} - E^0_{\text{Cr}^{3+}} = 1.51 - 1.23 = +0.28 \text{ V} > 0 \Rightarrow \text{spontaneous reaction}$$

