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

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

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

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

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

$$\boldsymbol{Ox + ne^- \leftrightharpoons Red}$$

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

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

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

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

Note: The name oxidation comes from the element oxygen. The first redox reaction studied involved involved the action of oxygen gas on metals, leading to the apparition of metal oxids. 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 renamed.

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 »:**

MnO_4^-/Mn^{2+}: $\boldsymbol{MnO_4^-} \leftrightharpoons \boldsymbol{Mn^{2+}}$.

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.

$MnO_4^- \leftrightharpoons Mn^{2+} + \boldsymbol{4H_2O}$.

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

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

$MnO_4^- + \boldsymbol{8H^+} \leftrightharpoons Mn^{2+} + 4H_2O$.

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.

$MnO^-_{4\,aq} + 8H^+_{aq} + \boldsymbol{5e^-} \leftrightharpoons Mn^{2+}_{aq} + 4H_2O$.

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, OF_2 ON(O) = +2
Peroxides (e.g. H_2O_2) 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: H_2SO_3 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: SO_4^{2-} 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 H_2SO_3 turns into SO_4^{2-}, the oxidation number of sulfur increases from +4 to +6. It has been oxidized. Whan SO_4^{2-} turns into H_2SO_3, the oxidation number of sulfur decreases from +6 to +4. It has been reduced.
SO_4^{2-} and H_2SO_3 form a redox couple: SO_4^{2-}/H_2SO_3: $SO_4{}^{2-}{}_{(aq)} + 4H^+{}_{(aq)} + 2e^- \leftrightharpoons H_2SO_3 + H_2O$

Redox reactions

1. Writing the equation of a redox reaction

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

$$MnO_4{}^-{}_{(aq)} + 8H^+{}_{(aq)} + 5e^- \leftrightharpoons Mn^{2+}{}_{(aq)} + 4H_2O$$
$$Cr_2O_7{}^{2-}{}_{(aq)} + 14H^+{}_{(aq)} + 6e^- \leftrightharpoons 2Cr^{3+}{}_{(aq)} + 7H_2O$$

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

$$\left(MnO_4{}^-{}_{(aq)} + 8H^+{}_{(aq)} + 5e^- \leftrightharpoons Mn^{2+}{}_{(aq)} + 4H_2O\right) \times 6$$
$$\left(Cr_2O_7{}^{2-}{}_{(aq)} + 14H^+{}_{(aq)} + 6e^- \leftrightharpoons 2Cr^{3+}{}_{(aq)} + 7H_2O\right) \times 5$$

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.

$$6MnO_4{}^-{}_{(aq)} + 48H^+{}_{(aq)} + 30e^- + 10Cr^{3+}{}_{(aq)} + 35H_2O \longrightarrow 6Mn^{2+}{}_{(aq)} + 24H_2O + 5Cr_2O_7{}^{2-}{}_{(aq)} + 70H^+{}_{(aq)} + 30e^-$$

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

$$6MnO_4{}^-{}_{(aq)} + \cancel{48H^+{}_{(aq)}} + \cancel{30e^-} + 10Cr^{3+}{}_{(aq)} + \underbrace{\cancel{35}}_{11}H_2O \longrightarrow 6Mn^{2+}{}_{(aq)} + \cancel{24H_2O} + 5Cr_2O_7{}^{2-}{}_{(aq)} + \underbrace{\cancel{70}}_{22}H^+{}_{(aq)} + \cancel{30e^-}$$

$$\Rightarrow \mathbf{6MnO_4{}^-{}_{(aq)} + 10Cr^{3+}{}_{(aq)} + 11H_2O \longrightarrow 6Mn^{2+}{}_{(aq)} + 5Cr_2O_7{}^{2-}{}_{(aq)} + 22H^+{}_{(aq)}}$$

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:

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

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

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

Ex: $E^0(MnO_4{}^-/Mn^{2+}) = 1.51\ V\ ;\ E^0(Cr_2O_7{}^{2-}/Cr^{3+}) = 1.23\ V$
$E^0{}_{Cr_2O_7{}^{2-}} - E^0{}_{Mn^{2+}} = 1.23 - 1.51 = -0.28\ V < 0 \Rightarrow$ non-spontaneous reaction
$E^0{}_{MnO_4{}^-} - E^0{}_{Cr^{3+}} = 1.51 - 1.23 = +0.28\ V > 0 \Rightarrow$ spontaneous reaction

$$\Rightarrow \mathbf{6MnO_4{}^-{}_{(aq)} + 10Cr^{3+}{}_{(aq)} + 11H_2O \longrightarrow 6Mn^{2+}{}_{(aq)} + 5Cr_2O_7{}^{2-}{}_{(aq)} + 22H^+{}_{(aq)}}$$