oxidation reduction

Lesson Content

I. Definition

1. Oxidation: is a reaction during which there is loss of electrons.

Example

$Na \xrightarrow{\text{oxidation}} Na^{+} + 1e^{-}$

$Fe^{2+} \xrightarrow{\text{oxidation}} Fe^{3+} + 1e^{-}$

2. Reduction: is a reaction during which there is gain of delectons

Example

$F_2 + 2e^{-} \xrightarrow{\text{Reduction}} 2F^{-}$

3. Oxidation-reduction couple (redox)

Oxidation and reduction are two phenomena that occur simultaneously during the same reaction. They involve a reduced form and an oxidized form.

$a\ Red \rightleftharpoons b\ Oxyd + ne^{-}$

1: oxidation

2: reduction

Example

$\underline{Fe^{2+}} \rightleftharpoons \underline{Fe^{3+}} + 1e^{-}$

Reduced form oxidized form

Reduced form: **provides** electrons

Oxidized form: **captures** electrons

Redox couple: Ox/Red $\rightarrow$ Fe^{3+}/Fe^{2+}

Remark : To evry **oxidant** corresponds a **reductant** and vice versa.

4. Redox reaction

A redox reaction results from two redox half reactions.

In fact, the reduced Red_1 form of an Ox_1/Red_1 couple can only release electrons if it is in presence of an oxidized Ox_2 form of an Ox_2/Red_2 couple capable of capturing them.

$$Red_1 \rightleftarrows Ox_1 + n_1 e^- \ldots\ldots (1) \quad xn_2$$

$$Ox_2 + n_2 e^- \rightleftarrows Red_2 \ldots\ldots\ldots\ldots (2) \quad xn_1$$

$$\mathbf{n_2 Red_1 + n_1 Ox2 \rightleftarrows n_2Ox_1 + n_1Red_2} \ldots\ldots (3)$$

Reaction (3) represents the general form of a redox reaction.

Example :

The following Redox reaction:

$Fe^{2+} + 1/2Cl_2 \rightleftarrows Fe^{+3} + Cl^-$, results of 2 half-reactions:

$Fe^{2+} \overset{Oxy}{\rightleftarrows} Fe^{+3} + 1e^-$ $\qquad$ $1/2Cl_2 + 1e^- \overset{Red}{\rightleftarrows} Cl^-$

II. Oxidation degree or oxidation number

1. Definition

- Oxidation state of an element is characterized by an integer called the oxidation number which is denoted O.N .
- Oxidation number of an element is always indicated in Roman numerals.
- Oxidation number of an element represents the charge that the element would take if all the bonds in which it is involved were purely ionic.

Remark:

If x represents the number of external electrons of an element, its oxidation number varies between x - 8 and x.

Example

${}_1H$: 1external electron, O.N $\in$ {-I, O, +I }

$_7N$: 5 outer electrons, O.N ϵ {-III, -II, -I, O, I, II, III, IV, V}

2. Determination of the oxidation number

Oxidation number of an element is determined by the following rules:

- Oxidation number of isolated atoms is zero.

Example :

Na, Al, N: $\longrightarrow$ O.N(Na) = 0, O.N(Al) = 0, O.N (N) = 0

- Oxidation number of elements in neutral homonuclear molecules is zero.

Example :

O2,H2: $\longrightarrow$ O.N(O) = 0 ; O.N (H) = 0

- Oxidation number of charged elements is equal to their charges.

Example :

Al^{3+}, O^{2-}, H^{+}: $\longrightarrow$ O.N (Al) =+III ; N.O (O) =-II ; N.O (H) =+I

- Oxidation number of H is +I except in H_2 or O.N (H) = 0 and in hydrides (NaH, LiH) where O.N (H) = -I.

- Oxidation number of O is equal to –II except in peroxides (H_2O_2) where O.N (H) = -I.

- In a molecule the sum of oxidation numbers corresponding to different elements is equal to the charge of the molecule.

Example :

What is the oxidation number of Cr in the compound ion: $Cr_2O_7^{2-}$

Answer:

Let x be the oxidation number of C r, we have:

$2x + 7(-2) = -2 \longrightarrow x = +6 \longrightarrow$ O.N (Cr) = +VI

3. Variation of the oxidation number

During a redox reaction:

o The oxidation number of oxidant decreases.

o The oxidation number of reductant increases

Example :

soit la réaction redox :

$$2Fe^{3+} + Sn^{2+} \rightleftharpoons 2Fe^{2+} + Sn^{4+}$$

O.N (Fe) = +III O.N (Fe) = +II

Fe^{3+}: oxidant Fe^{2+} : réductant

O.N (Sn) = +II O.N(Sn) = +IV

Sn^{2+} :réductant Sn^{4+} :oxidant

4. Interest of the oxidation number:

The oxidation number makes it possible to:

- Recognize a redox reaction.

Example :

Let the chemical reaction:

$$CuO + H_2SO_4 \longrightarrow Cu\,SO_4 + H_2O$$

$$CuO + 2H^+ \longrightarrow Cu^{2+} + H_2O$$

O.N(Cu) = +II O.N(Cu) = +II

O.N(H) = +I O.N(H) = +I

The previous reaction is not a redox reaction.

- Allows a redox reaction to be balanced.

5. How to balance a redox reaction

Identify oxidized and reduced elements then calculate their O.N .In the same couple, the oxidizer is the one with the highest O.N and the reducer is the one with the lowest O.N.

- Write the redox half-reaction equations involved for each element.
- Balance the charges, if necessary, with H^+ (acidic medium) or OH^- (basic medium) ions and complete with H_2O.
- Adjust the multiplicative coefficients so that the number of electrons involved in each half-reaction is the same.
- Write the overall reaction by adding the two half-reaction equations (the electrons must disappear).

Example :

balance the following reaction, in an acidic medium.

$$MnO_4^- + Br^- \rightleftharpoons Mn^{2+} + Br_2$$

Answer :

Couple1: MnO^{4-}/Mn^{2+}: $MnO^{4-} + \mathbf{8}H^+ + \mathbf{5}e^- \rightleftharpoons Mn^{2+} + 4H2O$

+VII **+II** (O.N decreases $\rightarrow$ reduction)

$O.N(Mn) + 4O.N(O) = -1 \longrightarrow x + 4(-II) = -1 \longrightarrow x = +VII$

Couple2: Br^- / Br_2: $\mathbf{2}Br^- \rightleftharpoons Br_2 + \mathbf{2}e^-$

-I **0** (O.N increases $\rightarrow$ oxidation)

$$[MnO^{4-} + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O] \ldots\ldots\ x\ 2$$

$$[\quad 2Br^- \rightleftharpoons Br_2 + 2e^- \quad] \ldots\ldots\ x\ 5$$

$$\mathbf{2\,MnO^{4-} + 10Br^- + 16H^+ \rightleftharpoons 2\,Mn^{2+} + 5Br_2 + 8H_2O}$$

III. Oxidation-reduction potential

Also called redox potential or electrode potential

1. Concept of electrodes

A redox reaction is characterized by a transfer of electrons.

In order to be able to compare the oxidizing power (tendency to capture electrons) or the reducing power (tendency to give up electrons) of the different redox couples, we define a quantity called redox potential or electrode potential.

This last name reveals the way in which the magnitude is measured.

Indeed, the redox reaction:

$$n_1\, Ox_2 + n_2\, Red_1 \rightleftharpoons n_1\, Red_2 + n_2\, Ox_1$$

Which can take place chemically, can also be caused by the creation of a battery.

Each of the Ox_1/Red_1 and Ox_2/Red_2 couples intervenes at the level of a metal blade immersed in a solution and called an electrode.

Thus, an electrode is the site of oxidation: $Red_1 \longrightarrow Ox_1 + n_1 e^-$

the other is the site of reduction: $Ox_2 + n_2\, e^- \longrightarrow Red_2$

2.Expression of the electrode potential (Nernst formula)

Each of the electrodes has a certain potential E given by the relation:

$E = E_0 + 0.06/n \log ([ox]^a)/[Red]^b)$

For the reduction reaction: $aOx + ne- \longrightarrow bRed$

where E_0 represents the standard electrode potential.

3. Reference electrodes

Each of the 2 previous electrodes has a potential. E^+ highest and E^- lowest.

The problem is to reach each of the 2 potentials because the experience provides ΔE, $\Delta E = E^+ - E^-$.

To do this, we choose a reference electrode against which all the other electrode potentials are measured.

By convention, the standard potential of the reference electrode is zero.

Thus, we would have created a system composed of reference electrode and electrode whose potential we want to know and the difference $\Delta E°$ is directly equal to the unknown standard potential.

Noticed :

The most common reference electrode is the hydrogen electrode.

4. Prediction of redox reactions.

Let be the redox equilibrium:

$$n_2Red_1 + n_1\, Ox_2 \rightleftharpoons n_2\, Ox_1 + n_1Red_2$$

Depending on the oxidizing and reducing power of Ox_1/Red_1 and Ox_2/Red_2 couples, the balance will be shifted towards direction 1 or direction 2.

It is possible to predict the direction in which the equilibrium is shifted by comparing the values of the respective standard potentials of the pairs Ox_1/Red_1 and Ox_2/Red_2.

Indeed, if:

- $E° (Ox_1/Red_1) > E° (Ox_2/Red_2)$

The Ox_1/Red_1 couple is more oxidizing than the Ox_2/Red_2 couple, that is to say that Ox_1 has a greater tendency to capture electrons than Ox_2 and we will have:

$$Ox_1 + n_1e^- \rightleftharpoons Red_1 \;\ldots\ldots\ldots\ldots \quad \times\, n_1$$

$$Red_2 \rightleftharpoons Ox_2 + n_2e^- \;\ldots\ldots\ldots \quad \times\, n_2$$

So: $$n_2\, Ox_1 + n_1\, Red_2 \rightleftharpoons n_2Red_1 + n_1Ox_2$$

Thus the balance is shifted towards direction 2.

- E° (Ox$_1$/Red$_1$)< E° (Ox$_2$/Red$_2$)

The balance is shifted towards direction 1 (same reasoning as the previous one)

In general, a reduced form displaces an oxidized form if the latter has a greater standard potential.

Example :

$E°(Cu^{2+}/Cu) = +0.35V$

$E°(Ag^{+}/Ag) = +0.80V$

As: $E°(Ag^{+}/Ag) = +0.80V > E°(Cu^{2+}/Cu) = +0.35V$, Ag^{+}/Ag couple oxidizes Cu^{2+}/Cu couple and Ag^{+} is more oxidizing than cu^{2+}, then:

$$Cu \rightleftharpoons cu^{2+} + 2e^{-}$$

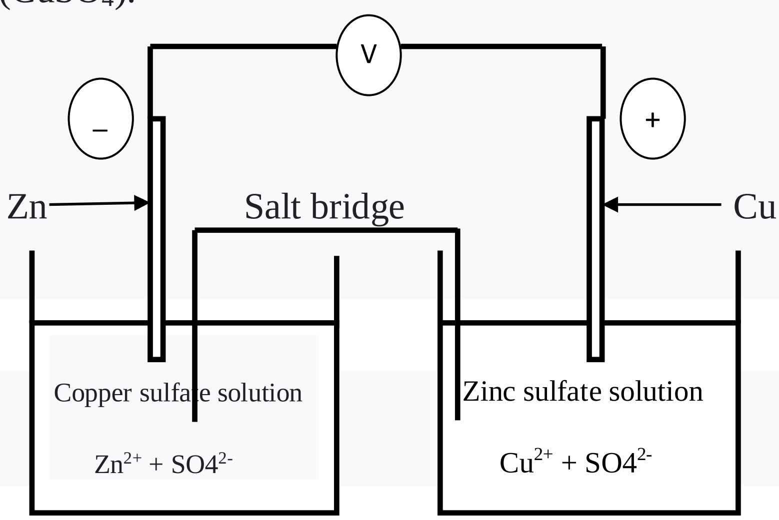
$$Ag^{+} + 1e^{-} \rightleftharpoons Ag$$

So the overall reaction is: $Cu(s) + 2Ag^{+} \rightleftharpoons Cu^{2+} + 2Ag(s)$

IV. Electrochemical battery: Danielle battery

1. Battery principle

Two metal electrodes: Zn and Cu respectively immersed in a solution of ($ZnSO_4$) and ($CuSO_4$).



Role of the salt bridge: the salt bridge ensures the passage of SO_4^{2-} ions from the cathode compartment to the anode compartment.

At the – pole :

- Oxidation (loss of electrons): $Zn \rightleftharpoons Zn^{2+} + 2e^-$
- The Zn^{2+} ions pass into solution, the $2e^-$ remain on the Zn plate, which dissolves.
- The Zn electrode is called anode because it is site of oxidation

At the + pole:

- Reduction (gain of electrons): $Cu^{2+} + 2e^- \rightleftharpoons Cu$
- The Cu^{2+} ions are deposited on the electrode in the form of metallic Cu.
- The Cu electrode, seat of a reduction, is called cathode.

Daniell Stack:

$$Zn \rightleftharpoons Zn^{2+} + 2e^-$$

$$Cu^{2+} + 2e^- \rightleftharpoons Cu$$

Overall reaction: $\mathbf{Zn(s) + Cu^{2+} \rightleftharpoons Zn^{2+} + Cu(s)}$