MOHAMED KHIDER UNIVERSITY OF BISKRA.

FACULTY OF EXACT SCIENCES AND NATURAL AND LIFE SCIENCES

DEPARTMENT OF BIOLOGY

Semester2: THERMODYNAMICS AND CHEMISTRY OF MINERAL SOLUTIONS

CHAPTER I
Part 4
Level: 1st year LMD

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5. Oxidation-reduction equilibrium:

5.1. Red-ox reaction: electron transfer:

A red-ox reaction is a reaction that involves electrons (**electron transfer**) between the governing species (molecules, ions and atoms). This reaction can be broken down into two half-reactions: oxidation reaction + reduction reaction).

5.2. Concept of oxidation, reduction and red-ox:

a. Oxidation: the oxidation of a compound corresponds to:

1- Loss of electrons (Example: $Cu \rightarrow Cu^{+2} + 2\,e^-$)

2- We call the element which loses the electrons reducing (Example: $Red \rightarrow Ox + n\,e^-$)

3- Increase in oxidation number (N.O).

b. A reduction: the reduction of a compound corresponds to:

1- Gain of electrons (Example: $Cu^{+2} + 2\,e^- \rightarrow Cu$)

2- We call the element which gains the oxidizing electrons (Example: $Ox + n\,e^- \rightarrow Red$)

3- Decrease in oxidation number (N.O).

5.3. Oxidation number (or degree of oxidation):

The oxidation number is an arbitrary charge. It consists of assigning the electrons of the bond to the most electronegative element or sharing them if the atoms are identical (The oxidation number is written in: the sign (+ or -) + Roman numeral.

a. The oxidation number of the oxygen atom is always –II except in the case: H_2O_2 and F_2O.

b. The oxidation number of the hydrogen atom is always +I except in the case of: hydrides (these are molecules made up of the hydrogen atom and a group IA atom).

c. The oxidation number of an isolated and neutral (uncharged) element (simple body) is zero. Example: Na, Fe, …

d. The oxidation number of an isolated and charged element (simple body) is the charge carried by this atom. Example: Cu^{+2} (O.N =+II), Al^{+3} (O.N=+III), …

e. The oxidation number of an element is found in an uncharged molecule:

Example: $CO_2 \Rightarrow x_c + 2x_o = 0 \Rightarrow x_c + 2\,(-2) = 0 \Rightarrow x_c = +IV$ ((O.N (C)=+IV).

f. The oxidation number of an element is found in a charged molecule:

Example: $MnO_4^- \Rightarrow x_{Mn} + 4x_o = -1 \Rightarrow x_{Mn} + 4\,(-2) = -1 \Rightarrow x_{Mn} = +VII$ ((O.N (Mn)= +VII).

g. Neutral combinations made up of a single element (diatom), the oxidation number is zero. Example: Cl_2, O_2, Br_2, N_2, ….

5.4. Writing red-ox reactions:

The red-ox reactions take place simultaneously, i.e. the electrons that are lost by the reducer are captured by the oxidant.

An oxidation-reduction reaction takes place by association of two red-ox couples:

Couple 1 (Ox1/Red1): Red1 $\rightleftharpoons$ Ox1 + ne- (Oxidation reaction)

Couple 2 (Ox2/Red2): Ox2 + ne- $\rightleftharpoons$ Red2 (Reduction Reaction)

$$\text{Red1} + \text{Ox2} \rightleftharpoons \text{Ox1} + \text{Red2}$$

5.5. Equilibrium an oxidation-reduction reaction:

There are several methods for equilibrating red-ox reactions, we cite here one of these methods:

To equilibrate an oxidation-reduction reaction, you must know the following steps (1-5):

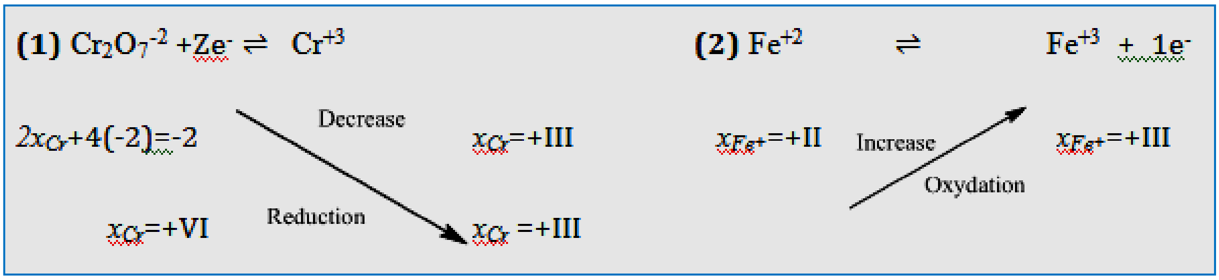
Consider the following example: equilibrium the following reaction in an acidic medium:

$$Cr_2O_7^{-2} + Fe^{+2} \rightleftharpoons Cr^{+3} + Fe^{+3}$$

Step 1: Separate between the two half-reactions

$$Cr_2O_7^{-2} \rightarrow Cr^{+3}$$
$$Fe^{+2} \rightarrow Fe^{+3}$$

Step 2: Calculate the oxidation number to see is an increase or decrease in O.N ⇒ type (oxidation or reduction) ⇒ the electrons on the left or on the right.



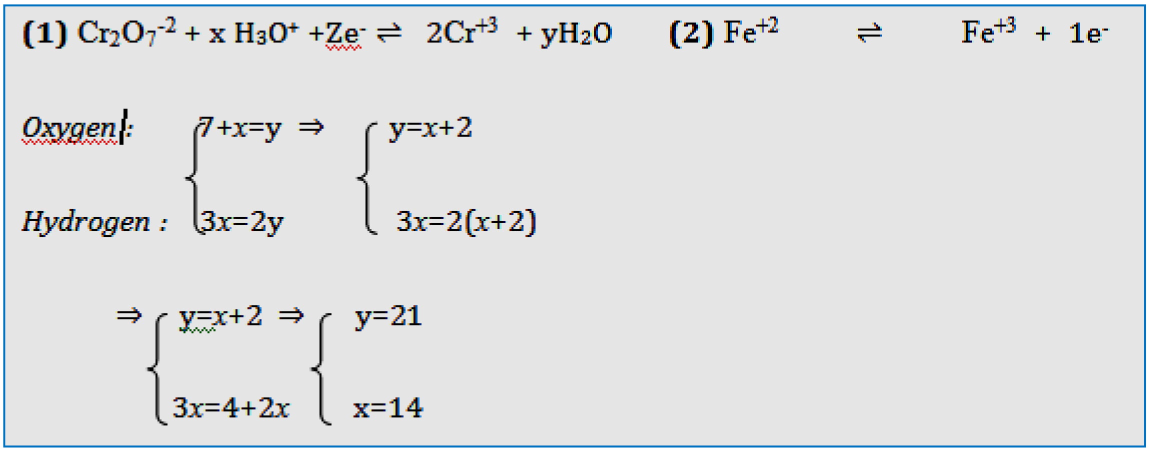
Step 3: Integrate the medium:

If we have an acidic environment: we must add H_3O^+ and H_2O.

If we have the basic medium: we must add the OH^- and H_2O.

Question: Do which side do we add the ions of: H_3O^+ and OH^-?

Answer: We must add the ions in H_3O^+ next to the electrons and the ions in OH^- the inverse of the position of the electrons.



(1) $Cr_2O_7^{-2} + x\,H_3O^+ + Ze^- \rightleftharpoons 2Cr^{+3} + yH_2O$ **(2)** $Fe^{+2} \rightleftharpoons Fe^{+3} + 1e^-$

Oxygen: / *Hydrogen :* $\begin{cases} 7+x=y \\ 3x=2y \end{cases} \Rightarrow \begin{cases} y=x+2 \\ 3x=2(x+2) \end{cases}$

$\Rightarrow \begin{cases} y=x+2 \\ 3x=4+2x \end{cases} \Rightarrow \begin{cases} y=21 \\ x=14 \end{cases}$

Step 4: Checking the conservation of the material and the conservation of the charge.

(1) $Cr_2O_7^{-2} + 14\,H_3O^+ + 6e^- \rightleftharpoons 2Cr^{+3} + 21H_2O$ (Z=-6)

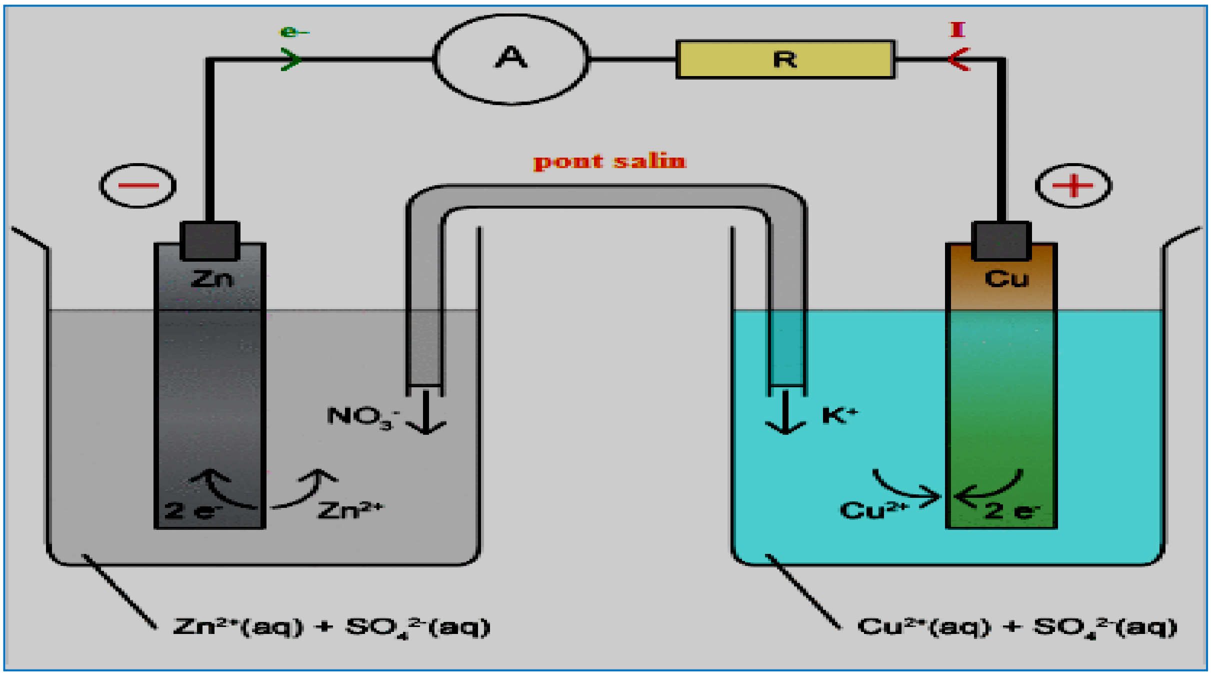
(2) $Fe^{+2} \rightleftharpoons Fe^{+3} + 1e^-$ /* 6

Step 5: Checking if the total reaction is balanced or not (see the loads)

Total Reaction: $Cr_2O_7^{-2} + 6\,Fe^{+2} + 14\,H_3O^+ + 6e^- \rightleftharpoons 2Cr^{+3} + 21H_2O$ (Z=-6)

5.6. Application of red-ox (Daniel battery):

A battery is a chemical device capable of providing electrical energy (circulation of electrons) to an external circuit. It is made up of two half-cells containing the two members of an oxidizing-reducing couple.



Two solutions connected by a saline conductive bridge (through which there is an ion exchange) between the two red-ox couples (Zn^{+2}/Zn) and (Cu^{+2}/Cu).

a. ***Concept of electrode:*** the electrode is the conductive part where an oxidation or reduction reaction will appear.

There is a passage of current from Cu to Zn.

The Anode: is the electrode where oxidation occurs; it corresponds to the negative pole of the battery.

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

We then observe the progressive dissolution of the Zn layer.

The Cathode: is the electrode where the reduction occurs; it corresponds to the positive pole of the battery.

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

A deposit of Cu is observed on the copper blade.

The total reaction will be:

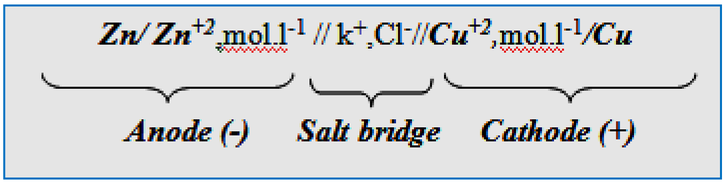
Couple 1 (Zn^{+2}/Zn): $Zn \rightleftharpoons Zn^{+2} + 2e^-$ (Oxidation reaction)

Couple 2 (Cu^{+2}/Cu): $Cu^{+2} + 2e^- \rightleftharpoons Cu$ (Reduction reaction)

$$\mathbf{Zn + Cu^{+2} \rightleftharpoons Zn^{+2} + Cu}$$

b. General writing of a battery:

By convention we write the battery as follows:



$$\underbrace{Zn/Zn^{+2},mol.l^{-1}}_{\textit{Anode (-)}}\ \underbrace{//\ k^{+},Cl^{-}//}_{\textit{Salt bridge}}\ \underbrace{Cu^{+2},mol.l^{-1}/Cu}_{\textit{Cathode (+)}}$$

Summary:

The Anode: negative pole (-): Oxidation: Loses electrons

The Cathode: positive pole (+): Reduction: gain of electrons

Salt bridge: ensured the circulation of ions (equilibrium between the two electrodes).

5.7. Electrode potential:

This is the difference in potential between the electrode and the solution in which it is immersed; we will see that the electromotive force (e.m.f) of the battery is directly linked to the values of the two electrode potentials.

a. Normal hydrogen electrode (ENH)

Couple : H_3O^+/H_2 *(or* H^+/H_2 *or* H_2O/H_2*)*

$2\,H_3O^+ + 2\,e^- \rightleftharpoons H_2 + 2H_2O$

$E°_{H+/H2} = 0$ at 25°C

b. NERNST relation (1889): Electrode or electrochemical potential

This relation applies to a red-ox couple (ox/red):

$$E = E^0 + \frac{RT}{nF}\ \mathrm{Ln}\,\frac{[\mathrm{Ox}]}{[\mathrm{Red}]}$$

E: Red-ox potential of the ox/red couple or electrochemical potential

E°: Standard electrode potential.

R: Ideal gas constant (8.31 J/mol.K)

n: Number of electrons involved

F: Faraday (=96500 C)

T: Temperature (298 K)

Ln: Natural logarithm: 2.3 log

$$E = E^0 + \frac{0.059}{n}\ \mathrm{Log}\,\frac{[\mathrm{Ox}]}{[\mathrm{Red}]}$$

$$E = E^0 + \frac{0.006}{n}\ \mathrm{Log}\,\frac{[\mathrm{Ox}]}{[\mathrm{Red}]}$$

5.8. Relationship between the standard potential and the equilibrium constant (K):

Or two red-ox couples: (Ox1/Red1) and (Ox2/Red2)

Red1 ⇌ Ox1 + ne$^-$ $\qquad E_1 = E_1^{\circ} + \frac{0.06}{n}\,log\frac{[Ox_1]}{[Red_1]}$

Ox2 + ne$^-$ ⇌ Red2 $\qquad E_2 = E_2^{\circ} + \frac{0.06}{n}\,log\frac{[Ox_2]}{[Red_2]}$

Red1 + Ox2 ⇌ Ox1 + Red2 $\qquad K = \frac{[Ox_1][Red_2]}{[Red_1][Ox_2]}$

But in equilibrium we have: ΔE= 0 , i.e. : $E_1=E_2$

$$E_1^{\circ} + \frac{0.06}{n}\, log\frac{[Ox_1]}{[Red_1]} = E_2^{\circ} + \frac{0.06}{n}\, log\frac{[Ox_2]}{[Red_2]}$$

$$E_1^{\circ} - E_2^{\circ} = \frac{0.06}{n}\, log\frac{[Ox_2]}{[Red_2]} - \frac{0.06}{n}\, log\frac{[Ox_1]}{[Red_1]}$$

$$E_1^{\circ} - E_2^{\circ} = \frac{0.06}{n}\, log\frac{[Ox_1][Red_2]}{[Red_1][Ox_2]} = \frac{0.06}{n}\, logK$$

$$logK = \frac{n(E_1^{\circ} - E_2^{\circ})}{0.06}$$

$$With:\ E_1^{\circ} > E_2^{\circ}$$

<u>Note:</u> the couple with the highest potential will undergo reduction; the other couple (lower potential) will undergo oxidation.

5.9. Influence of pH on electrode potential (Relationship between E and pH):

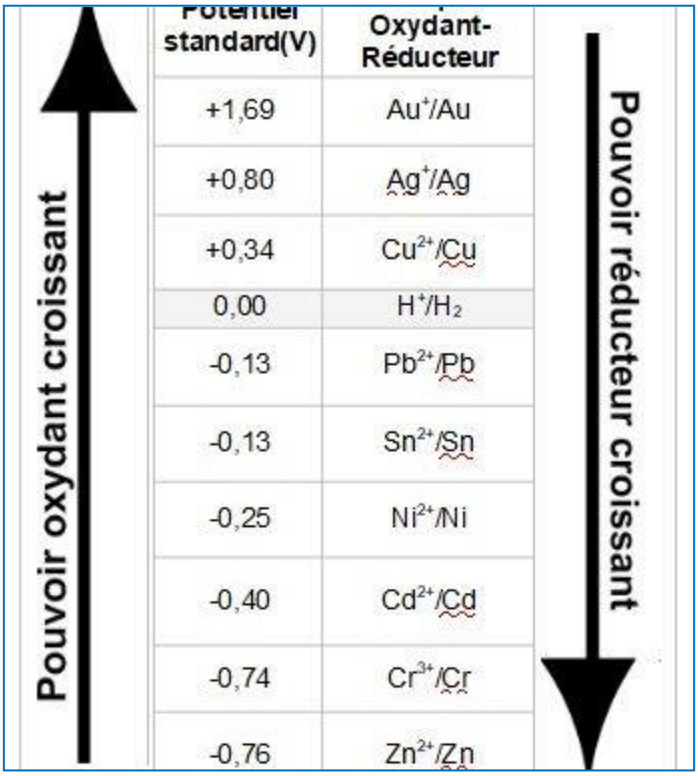
Consider the following reaction: Ox + X H_3O^+ + ne- ⇌ Red + X H_2O

$$E = E^0 + \frac{0.06}{n} \log \frac{[\mathrm{Ox}][H_3O^+]^x}{[\mathrm{Red}]}$$

$$E = E^0 - \frac{0.06}{n}(-\log[H_3O^+]^x) - \frac{0.06}{n} \log \frac{[\mathrm{Ox}]}{[\mathrm{Red}]}$$

$$E = E^0 - \frac{0.06}{n} x\, pH + \frac{0.06}{n} \log \frac{[\mathrm{Ox}]}{[\mathrm{Red}]}$$

E°: Standard electrode potential.



Potentiel standard(V)	Oxydant-Réducteur
+1,69	Au^+/Au
+0,80	Ag^+/Ag
+0,34	Cu^{2+}/Cu
0,00	H^+/H_2
-0,13	Pb^{2+}/Pb
-0,13	Sn^{2+}/Sn
-0,25	Ni^{2+}/Ni
-0,40	Cd^{2+}/Cd
-0,74	Cr^{3+}/Cr
-0,76	Zn^{2+}/Zn