CHAPTER III:

REDOX REACTIONS

This chapter introduces key concepts such as oxidants, reductants, oxidation, and reduction. It covers oxidation numbers, which help in identifying redox processes, and explores redox potentials using the Nernst equation. Additionally, the chapter discusses methods for writing balanced redox reactions and examines electrochemical cells, with a focus on the Daniell cell as a fundamental example.

1-General information.

1-1-Oxidant, reductant, oxidation, reduction.

- ✓ **An oxidant** is a compound capable of capturing electrons.

Example :

$Cu^{2+} + 2e^- \rightarrow Cu$ **Cu^{2+}** undergoes a reduction

- ✓ **An reductant** is a compound capable of yielding electrons.

Example :

$Cu \rightarrow Cu^{2+} + 2e^-$ **Cu** undergoes oxidation

Oxidant = e- acceptor , **Reducer** = e- donor

Oxidation = loss of e- , **Reduction** = gain of e-

Oxidation and reduction are reversible reactions:

oxidant + ne- <===> reducer

The species Ox is Red forms a redox couple: **Ox/Red**

Example: Ox/Red pair

$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$	Fe^{3+}/Fe^{2+}
$Fe^{2+} + 2e^- \rightleftharpoons Fe$	Fe^{2+}/Fe
$Cu^{2+} + 2e^- \rightleftharpoons Cu$	Cu^{2+}/Cu

1-2-Redox reaction

This involves two redox couples, as it consists in transferring electrons from the reducing agent of one couple to the oxidizing agent of the other:

$$Ox_1 + Red_2 <==> Red_1 + Ox_2$$

To equilibrate this reaction :

$$(Ox_1 + n1e^- <==> Red1) \times n_2 : \text{half-reaction 1}$$

$$(Red_2 <==> Ox2 + n2e^-) \times n_1 : \text{half-reaction 2}$$

Global reaction (1+2) :

$$n_2Ox_1 + n_2n_1e^- + n_1\ Red_2 <==> n_2Red_1 + n_1Ox_2 + n_1n_2e^-$$

Example: Fe^{+3}/Fe^{+2}, Sn^{+4}/Sn^{+2}

$$(Fe^{+3} + 1é <===> Fe^{+2})x2 \text{ (reduction)}$$

$$(Sn^{+2} <===> Sn^{+4} + 2é)x1 \text{(oxidation)}$$

Global reaction:

$$2Fe^{+3} + Sn^{+2} <===> Sn^{+4} + 2Fe^{+2}$$

2-Oxidation number (degree of oxidation)

2-1-Definition.

The oxidation number (O.N.) of an atom represents the apparent elementary charge assigned to it according to certain conventional rules:

a-The oxidation number of the atoms of an element in the Free State is zero.

Example : Fe : O.N = 0 ; Cu : O. N = 0.

b-The oxidation number of an atom in the monoatomic ion state is equal to the charge of the ion.

Example :

Element	Sn^{2+}	Fe^{3+}	Sn^{4+}	Fe^{2+}

O.N	**2**	**3**	**4**	**2**

c- When electrons are shared in covalent bonds between two atoms of different natures, they are allocated to the more electronegative atom.

Example :

	H-H	**Cl-Cl**	**CO**	**H_2S**	**2H-Cl**
O.N	0 0	0 0	+2 -2	+1 -2	+1 -1

d- The algebraic sum of the oxidation numbers of the atoms in a (neutral) molecule is zero.

Example : NH_3 : ΣO.N = O.N (N) + 3 ×O.N (H) = 0

When ; O . N (N) = -3 à partir de (O .N (H) = +1)

e- For a polyatomic ion, the sum of the O .N of the atoms in the ion is equal to the total charge of the ion.

Exemple:

CO_3^{2-} Σ O.N = -2 => O .N (C)+3× O .N (O)= -2 => O .N (C)=+4

SO_4^{2-} Σ O.N = -2 => O .N (S)+4× O .N (O)= -2 => O .N (S)=+6

PO_4^{3-} Σ O.N = -3 => O .N (P) +4× O .N (O)= -3 => O .N (P)=+5

2-2-Oxidation number of some elements.

-Fluorine: the most electronegative element: O .N = -1.

-Oxygen: the 2nd most electronegative element: O .N = -2, Sauf: OF_2 because F is more electronegative than O so O .N (O)=+2.

-Alkali metals: highly electropositive : O .N = +1, Li^+, Na^+, K^+,...

-Alkaline earth metals: electropositive : O .N = +2, Mg^{2+}, Ba^{2+}, Ca^{2+}, ...

-Hydrogen: electropositive element : O .N = +1.

3-Redox potentials: Nernst equation

3-1-Normal (standard) potential

The oxidising or reducing power of a chemical species is characterized by its redox potential E°. E° is measured under normal conditions of temperature and pressure (P = 1 atm, T = 25°C). It is given as **E° (Ox/red).**

By convention: E° (H^+/H_2) = 0 V.

All **E°** values are then referenced to **E° (H^+/H_2).**

Example :

Redox pair	Fe^{2+}/Fe	MnO_4^-/Mn^{2+}	Fe^{3+}/Fe^{2+}	Zn^{2+}/Zn	Cu^{2+}/Cu
E° (V/ENH)	- 0,44	1,51	0,77	-0,76	0,34

3-2-Nernst equation :

The oxidising or reducing power of a species depends not only on E° but also on the concentrations in solution.

$$a\ Ox + n\acute{e} \Leftrightarrow b\ red$$

So ; $E_{ox/red} = E^{\circ}_{ox/red} + RT/nF\ ln\ ([ox]^a/[red]^b)$: Nernst equation

n: number of electrons involved at 25°C.

We can write:

$$E_{ox/red} = E^{\circ}_{ox/red} + 0,06/n\ log\ ([ox]^a/[red]^b)$$

Example :

1) **Fe^{2+}/Fe :** $Fe^{2+} + 2\acute{e} \Longleftrightarrow Fe$

$$E_{Fe^{2+}/Fe} = E^{\circ}_{Fe^{2+}/Fe} + 0,06/2\ log\ ([Fe^{2+}]/[Fe])\ ;\quad [Fe]=1$$

⇨ $E_{Fe^{2+}/Fe} = E°_{Fe2+/Fe} + 0/03 \ log [Fe^{2+}]$

2) MnO_4^-/Mn^{2+}

$$MnO_4^- + 8H^+ + 5é \Longleftrightarrow Mn^{2+} + 4H_2O$$

$$E_{MnO4^-/Mn^{2+}} = E°_{MnO4^-/Mn^{2+}} + 0,06/5 \ log ([MnO_4^-][H^+]^8 / [Mn^{2+}])$$

4-Writing redox reactions

-Let the redox couples be :

$$E°_{Fe^{3+}/Fe^{2+}} = 0,77 \text{ V/ENH and } E°_{MnO4^-/Mn^{2+}} = 1,51 \text{ V/ENH}$$

We note that: $E°_{MnO4^-/Mn^{2+}} > E°_{Fe^{3+}/Fe^{2+}}$

Possible half-reactions are:

$$(Fe^{+3}+1é \Longleftrightarrow Fe^{+2})x5 \quad \text{(oxidation)}$$

$$(MnO_4^- + 8H^+ + 5é \Longleftrightarrow Mn^{2+} + 4H_2O)x1 \quad \text{(reduction)}$$

Global reaction:

$$MnO_4^- + 8H^+ + 5Fe^{+3} \Longleftrightarrow Mn^{2+} + 5 Fe^{+2} + 4H_2O$$

4-1- Calculation of the equilibrium constant

Let the two redox couples (Ce^{4+}/Ce^{3+}) et (Fe^{3+}/Fe^{2+}):

$$E°(Ce^{4+}/Ce^{3+})=1,44 \text{ V /ENH et } E°(Fe^{3+}/Fe^{2+}) = 0,77 \text{ V/ENH}$$

We see that : $E°(Ce^{4+}/Ce^{3+}) > E°(Fe^{3+}/Fe^{2+})$

Possible half-reactions are :

$$Fe^{2+} \Longleftrightarrow Fe^{3+}+1é \text{ (oxidation).....1}$$

$$Ce^{4+}+1é \Longleftrightarrow Ce^{3+} \text{ (reduction)......2}$$

Global reaction :

$$Ce^{4+}+Fe^{2+} \Longleftrightarrow Fe^{3+}+ Ce^{3+}$$

Nersnt equations for the two redox couples :

- eq 1 : $E_{Fe^{+3}/Fe^{2+}} = E°_{Fe^{+3}/Fe^{2+}} + 0,06 \log([Fe^{3+}]/[Fe^{+2}])$
- eq 2 : $E_{Ce4+/Ce3+} = E°_{Ce4+/Ce3+} + 0,06 \log([Ce^{4+}]/[Ce^{3+}])$

When the reaction is complete **;**

$$\Delta E = 0 \implies E_{Ce4+/Ce3+} - E_{Fe^{+3}/Fe^{2+}} = 0$$

So ,

$$E°_{Fe^{+3}/Fe^{2+}} + 0,06 \log([Fe^{3+}]/[Fe^{+2}]) = E°_{Ce4+/Ce3+} + 0,06 \log([Ce^{4+}]/[Ce^{3+}])$$

$$\implies E°_{Ce4+/Ce3+} - E°_{Fe^{+3}/Fe^{2+}} = 0.06 \log k_c$$

$$\implies k_c = 10^{\Delta E°/0.06}$$

NA : $k_c = 1.47 \times 10^{11}$

Kc is very large, so the reaction is complete in direction (1).

4-2-Redox dosage

Oxidation-reduction reactions are often used to carry out assays. One of the solutions contains an oxidant and the other a reductant.

At equivalence the relation is : $N_{ox} \times V_{ox} = N_{red} \times V_{red}$

Example 1 :

-Determination of a solution of MnO_4^- by a solution of Fe^{2+} ions in an acid medium.

Dosage reactions:

$$(Fe^{+3} + 1é \Longleftrightarrow Fe^{+2}) \times 5 \text{ (oxidation)}$$

$$(MnO_4^- + 8H^+ + 5é \Longleftrightarrow Mn^{2+} + 4H_2O) \times 1 \text{(reduction)}$$

Global reaction: $MnO_4^- + 8H^+ + 5Fe^{+3} \Longleftrightarrow Mn^{2+} + 5 Fe^{+2} + 4H_2O$

At equivalence point:

$$N_{MnO4-} \times V_{MnO4-} = N_{Fe+2} \times V_{Fe+2} \text{........1}$$

Normality : $N = Z \times C_n$

C_n : concentration in mol/l. , Z: number of electrons exchanged.

For : MnO_4^- ==> Z = 5 donc ; $N_{MnO4-} = 5\ C_{MnO4-}$

For : Fe^{+2} ==> Z = 1 donc ; $N_{Fe+2} = C_{Fe+2}$

1 <===> $5C_{MnO4-} \times V_{MnO4-} = C_{Fe+2} \times V_{Fe+2}$

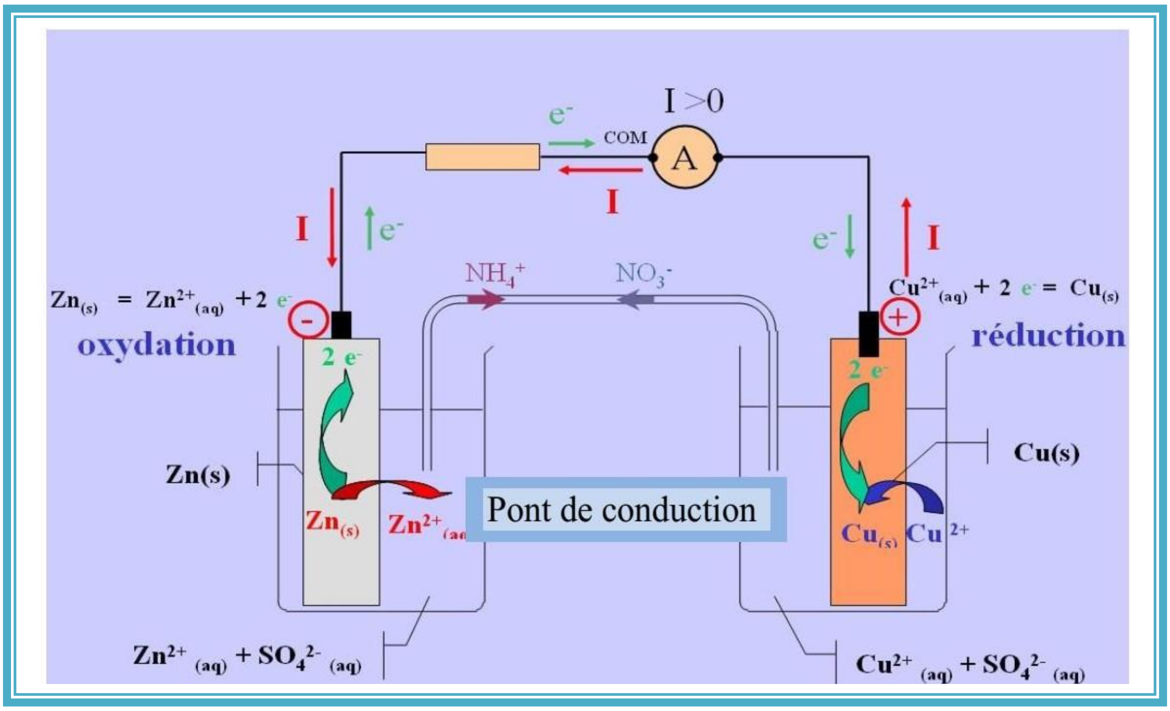
==> $C_{Fe+2} = 5C_{MnO4-} \times V_{MnO4-} / V_{Fe+2}$

5-Electrochemical batteries - DANIELL battery.

5-1-Description

When redox reactions are spontaneous, it is possible to transfer electrons from the reducing agent to the oxidising agent via an external electrical circuit.

This is illustrated by the principle of the **DANIELL cell:**



The Daniell cell has two compartments:

A left-hand compartment: containing a zinc strip immersed in a zinc(II) sulphate solution;

A right compartment: which contains a copper plate immersed in a copper(II) sulphate solution.

The two plates are linked by an electric wire that allows electrons to circulate. The two solutions are linked by a salt bridge (conductive bridge or junction) which allows ions to circulate.

We observe:

-the gradual dissolution of the zinc layer;

-the deposition of copper on the copper plate.

Copper strip: Cathode (Reduction) : $Cu^{2+} + 2e^- \Longleftrightarrow Cu$ (Reduction)

Zinc strip: Anode (Oxidation) : $Zn \Longleftrightarrow Zn^{2+} + 2e^-$ (Oxidation)

Global reaction: $Cu^{2+} + Zn \Longleftrightarrow Zn^{2+} + Cu$

The electrons therefore flow from the zinc plate to the copper plate.

The direction of the current is opposite to the direction of the electrons: Direction of the current from the copper plate (+ pole) to the zinc plate (- pole).

The sulphate ions flow from the right-hand compartment (excess SO_4^{2-}) to the left-hand compartment (lack of SO_4^{2-}).

Representation of the **DANIELL** battery : **(-) Zn /Zn²⁺(aq) // Cu²⁺(aq) / Cu (+)**

5-2- Calculating the e.m.f. of the battery

Potential of the cathode:

$$E_c = E_{Cu^{2+}/Cu} = E°_{Cu2+/Cu} + 0,03\ log\ ([Cu^{2+}] / [Cu])\ ; \quad [Cu]=1$$

Potential of the anode:

$$E_a = E_{Zn2+/Zn} = E°_{Zn2+/Zn} + 0,03\ log\ ([Zn^{2+}] / [Zn])\ ; \quad [Zn]=1$$

At equilibrium $\Delta E = 0$; So ;

$$\textbf{e.m.f} = 0 \Longrightarrow \textbf{e.m.f} = Ec - Ea = 0$$

$$E_{Cu^{2+}/Cu} - E°_{Zn2+/Zn} = 0,03\ log\ [Cu^{2+}]/ [Zn^{2+}]$$

$$E°_{Cu^{2+}/Cu} - E°_{Zn2+/Zn} = 0,03\ log\ 1/Kc \Longrightarrow Kc = 10^{\Delta E°/0.03}$$; (**Kc :** Equilibrium constant)

CHAPTER V :

COMPLEXATION REACTIONS

Complexation reactions involve the formation of coordination compounds where a central metal ion binds to surrounding ligands. These reactions are defined by key concepts such as coordination number and molecular geometry, which determine the structure of the resulting complex. The nomenclature of complexes follows standardized rules to describe their composition and charge. The formation of complexes is governed by a global stability constant, which quantifies the strength of metal-ligand interactions.

1-Definitions

A complex is a polyatomic **MLn** structure consisting of a central atom or cation **M** surrounded by n molecules or ions **L** called ligands or coordinates. The complex may or may not be charged.

The central atom or ion is often a transition (d-block) element: Cu^{2+}, Fe, Fe^{2+}, Fe^{3+}, Co, Co^{2+}, Ni, Ni^{2+}... but Ca^{2+} , Mg^{2+} and Ag^{+} ions can also form complexes.

The central metal cation is positively charged (it has electron vacancies) and acts as an attractor for ligands.

Ligands are molecules or ions with at least one non-bonding doublet (Lewis bases): Cl^-, CN^-, HO^-, H_2O, NH_3…

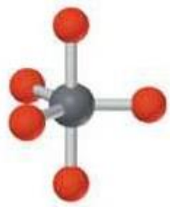
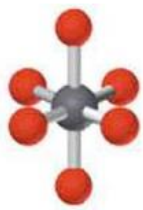
- n: Coordination number: number of bonds around the central atom.

-A ligand that can bind only once is monodentate.

-A ligand that can bind several times is polydentate.

2-Coordinance and geometry

Three main factors influence the coordination of a complex: the size of the central atom, steric interactions and electronic interactions.

Weak coordinations (1, 2 or 3) are rare. **2 coordinates** have a **linear** geometry, **3 coordinates** have a **trigonal planar** geometry.	 	
Coordinence 4 This is a very common coordination. Ligands can be organized in a **tetrahedral** or **square plane.**	**tetrahedral** 	**square plane** 
Coordinence 5 5 coordination complexes can be **square-based pyramid** or **trigonal bipyramid.**	**Trigonal bipyramid** 	**square based pyramid** 
Coordinence 6 Most coordination compounds are hexacoordinated. The structure adopted is generally an **octahedron**, more or less regular. Sometimes a triangular prism is formed.		

3-complex nomenclature :

The rules below are proposed by IUPAC (International Union of Pure and Applied Chemistry).3-1-Atome central.

Formulas:

the central atom is indicated first **M**, then, in order, the negative (**La**), neutral (**Ln**) and positive (**Lc**) ligands; the formula is bracketed [**M**(**La**)(**Ln**)(**Lc**)]charge.

Names: the central atom is named last; ligands appear in negative, neutral and positive order, or in alphabetical order.

-The oxidation number of the central atom is indicated by a Roman numeral to emphasize its formal character: Fe(II) or FeII.

-When the complex is anionic, the name of the central atom is suffixed with **-ate**:

3-2-Name of ligands :

- Anions: these are given the suffix "o":

H^-	hydruro	OH^-	hydroxo	OCN^-	cynato
O^{2-}	Oxo	S^{2-}	Thio	SCN^-	thiocyanato
I^-	Iodo	HS^-	mercapto	PO_4^{3-}	phosphato
Br^-	Bromo	CO_3^{2-}	carbonato	NO^{3-}	nitrato
Cl^-	Chloro	$C_2O_4^{2-}$	oxalato	NO^{2-}	nitrito
F^-	Fluoro	O_2^{2-}	peroxo	SO_4^{2-}	sulfato
CN^-	Cyano	HO^{2-}	hydrogénoperoxo	CH_3O^-	méthoxo
$S_2O_3^{2-}$	thiosulfato	SO_3^{2-}	sulfito	CH_3S^-	méthylthio

-Molecules, cations: name unchanged. Exceptions :

H_2O: aqua; NH_3: ammine; CO: carbonyl; NO: nitrosyl.

-The number of ligands is indicated by the prefixes di-, tri-, tetra-, penta-, hexa-, etc.

The total charge of the complex, also known as the EWING-BASSET number.

This is the load carried by the entire structure. It is noted after the end bracket, like the charge of a single ion or a complex ion.

Example :

-$[Al(H_2O)_6]^{3+}$: ion hexaaquaaluminium (III)

-$[Cu(NH_3)_4]^{2+}$: ion tétraamminecuivre (II)

-$[Fe(CN)_6]^{4-}$: ion hexacyanoferrate (II)

-$[CuCl_4]^{2-}$: ion tétrachlorocuprate (II)

-$[Fe(CO)_5]$: pentacarbonylefer ((NO(Fe) = 0, Les complexes neutres)

-$[CoCl(NH_3)_5]Cl_2$: chlorure de chloropentaaminecobalt (III)

-$[CoCl_3(NH_3)_3]$: trichlorotriaminecobalt (III)

-$[Cr(SCN)_4(NH_3)_2]^-$: ion tétrathiocyanatodiamminechromate (III)

-$[CrCl_2(H_2O)_4]^+$: ion dichlorotétraaquachrome (III)

4-Complex formation equilibrium

Given the complex $[Ag(NH_3)_2]^+$, its equilibrium of formation is written :

$$Ag^+ + 2NH_3 \rightleftarrows [Ag(NH_3)_2]^+$$

So;

$$K_f = [Ag(NH_3)_2]^+ / [Ag^+][NH_3]^2$$

$\mathbf{K_f}$ is called the overall formation constant or stability constant; it is denoted β or $\mathbf{K_f}$. It characterizes the equilibrium of complex formation. The greater the $\mathbf{K_f}$, the more stable the complex.

We can also define the complex dissociation constant $\mathbf{K_d}$:

$$\mathbf{K_d = 1/k_f}$$

==> $\mathbf{K_d = 1/k_f} = [Ag^+][NH_3]^2 / [Ag(NH_3)_2]^+$

We also find that: $pK_d = -logK_d = logK_f$; These constants depend only on temperature. We note that the complex is more stable, the greater the **K_f** and the smaller the **K_d.**

Example :

$Fe^{2+} + 6CN^- \rightleftarrows [Fe(CN)_6]^{4-}$	$K_f = 10^{24}$	$K_d = 10^{-24}$
$Ag^+ + 2NH_3 \rightleftarrows [Ag(NH_3)_2]^+$	$K_f = 10^{7,1}$	$K_d = 10^{-7,1}$

$[Fe(CN)_6]^{4-}$ is more stable than $[Ag(NH_3)_2]^+$ because $K_f\,[Fe(CN)_6]^{4-} > K_f\,[Ag(NH_3)_2]^+$

5-Competitive complexations : reaction prediction

When there is competition between two metals for a ligand (or between two ligands for a metal), the complexation equilibrium constant depends on the formation constants of the complexes involved. The equilibrium is shifted towards the formation of the most stable complex, i.e. the one with the highest formation constant.

Example :

1- Thiocyanate ions SCN^- are added to a solution of Fe^{3+} and Cu^{2+} ions. What complex is formed?

2- To a solution of Fe^{3+} ions (orange in color), we add thiocyanate ions SCN^- and then oxalate ions $C_2O_4^{2-}$.

The solution changes color from orange to blood red, then to pale green. What happened?

Given at 25°C:

(1) $Cu^{2+} + SCN^- \rightleftharpoons Cu(SCN)^+$ $K_f(1) = 10^{1,7}$

(2) $Fe^{3+} + SCN^- \rightleftharpoons Fe(SCN)^{2+}$ $K_f(2) = 10^3$

(3) $Fe^{3+} + C_2O_4^{2-} \rightleftharpoons [Fe(C_2O_4)]^+$ $K_f(3) = 10^{9,4}$

1- Both complex-forming reactions take place, but since

K_f (2) > K_f(1), the **$[Fe(SCN)]^{2+}$** complex is more stable than the **$[Cu(SCN)]^{+}$** complex. Cu(SCN)]+ complex.

To compare their relative stability, we calculate the equilibrium constant between the two complexes:

$$Cu(SCN)^{+} + Fe^{3+} \rightleftharpoons Cu^{2+} + Fe(SCN)^{2+} \qquad K_c = K_f\ (2)/\ K_f\ (1)$$

$K_c = 10^{3-1,7} = 10^{1,3} = 20 > 1$, so the $Fe(SCN)^{2+}$ complex is in the majority, but the reaction between the two complexes is not complete.

When SCN^{-} ions are added to the Fe^{3+} solution, the blood-red complex $[Fe(SCN)]^{2+}$ is formed in an almost complete reaction(K_f (2)=10^3).

2- When $C_2O_4^{2-}$ ions are added, the equilibrium between the two complexes is established since K_f (3) > K_f(2)

$$[Fe(SCN)]^{2+} + C_2O_4^{2-} \rightleftharpoons [Fe(C_2O_4)]^{+} + Fe^{3+} \qquad K' = K_f\ (3)/\ K_f(2)$$

$K' = 10^{9,4-3} = 10^{6,4} >>1$

The blood red complex $[Fe(SCN)]^{2+}$ is destroyed and the pale green complex $[Fe(C_2O_4)]^{+}$ is formed, in a total reaction (K' >>1).