REDUCTION - OXIDATION TITRATION

REDOX TITRATION

References

1- Fundamentals of analytical chemistry, Skoog.

2- Analytical chemistry, Gary D. Christian.

3- الكيمياء التحليلية الجامعية تأليف د.هادي حسن جاسم

Oxidation is defined as a loss of electrons to give a higher oxidation state (more positive).

Reduction is defined as a gain of electrons to give a lower oxidation state (more negative).

OXIDATION NUMBERS The following rules predict the oxidation number for each of the atoms/ions in a compound or ion.

General Rules (Always applicable–No exceptions)

1. For any uncombined element, the oxidation number is zero.

Examples: Fe, Xe, O_2, H_2 (0 for all of these)

2. For any monatomic ion, the oxidation number is equal to the charge on the ion. Examples: Fe^{2+}, F^-, O^{2-}, H^+ (+2, -1, -2, and +1 respectively)

3. For any compound, the sum of the oxidation numbers must be zero.

Examples: $NaCl = Na^+ + Cl^- = +1 + (-1) = 0$

$MgF2 = Mg^{2+} + 2\ F^- = +2 + 2(-1) = 0$

$K_2(Cr_2O_7)_3 = 2\ K^+ + 6\ Cr + 21\ O^{2-}$

$= 2(+1) + 6(X) + 21(-2) = 0$ ---- $X = +6$

Special Rules These rules only apply to certain columns on the Periodic Table.

1. Column IA +1 (Except H with a metal, then H = -1)

2. Column IIA +2

3. Column IIIA +3 (Normally, however +1 possible near the bottom of the table)

4. Column IVA +4

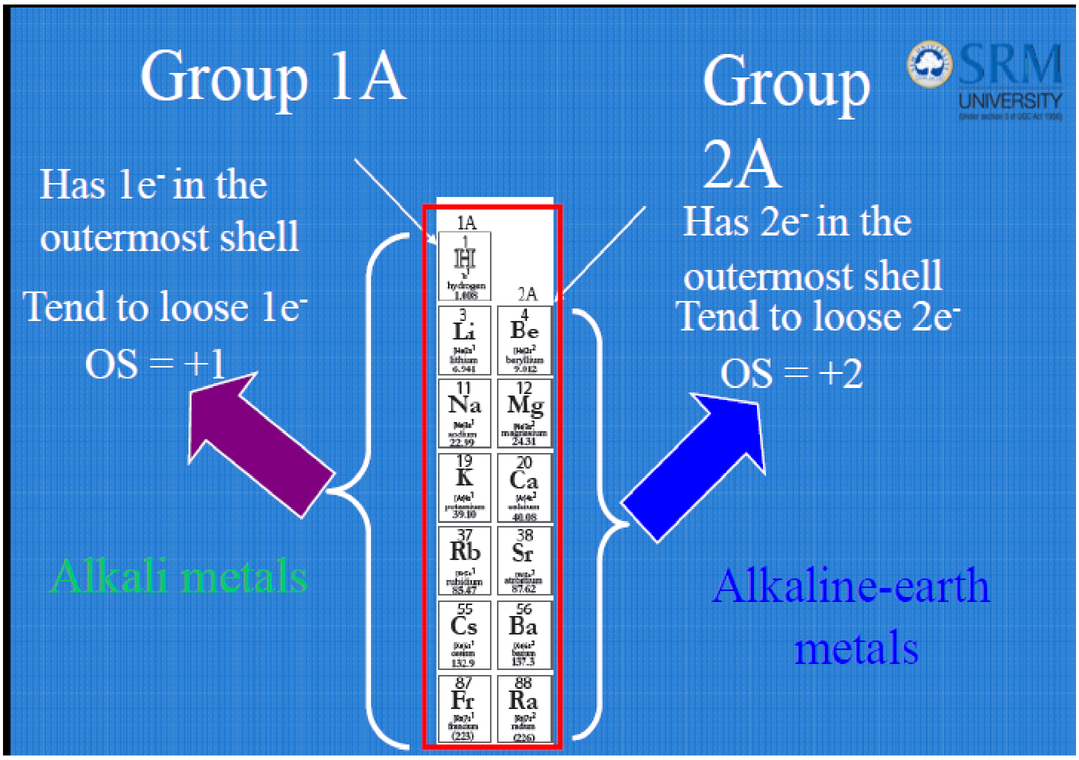
5. Column VA +5 to -3

6. Column VIA -2 (Oxygen is -2 except when combined with F, or in O_2^{2-})

7. Column VIIA -1 (Fluorine is -1 in compounds)

8. Column VIIIA (Usually only 0)

9. Transition Metals (3-12)



Group 1A

Has $1e^-$ in the outermost shell

Tend to loose $1e^-$

OS = +1

Alkali metals

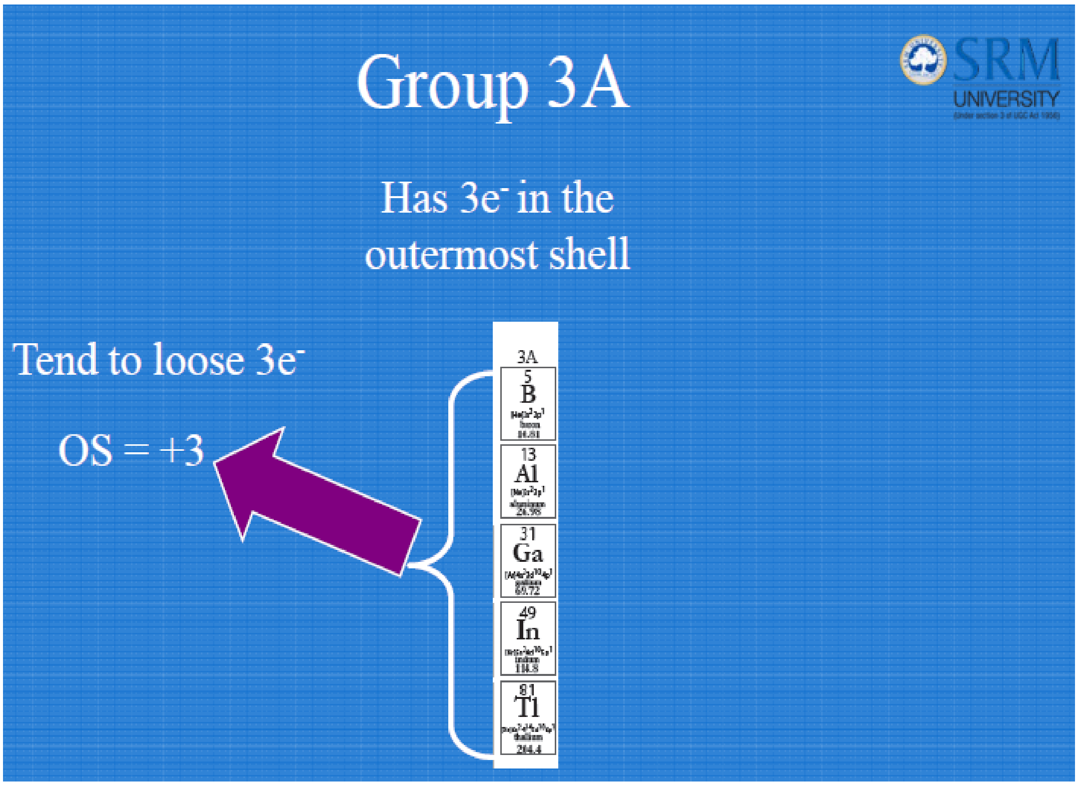
Group 2A

Has $2e^-$ in the outermost shell

Tend to loose $2e^-$

OS = +2

Alkaline-earth metals

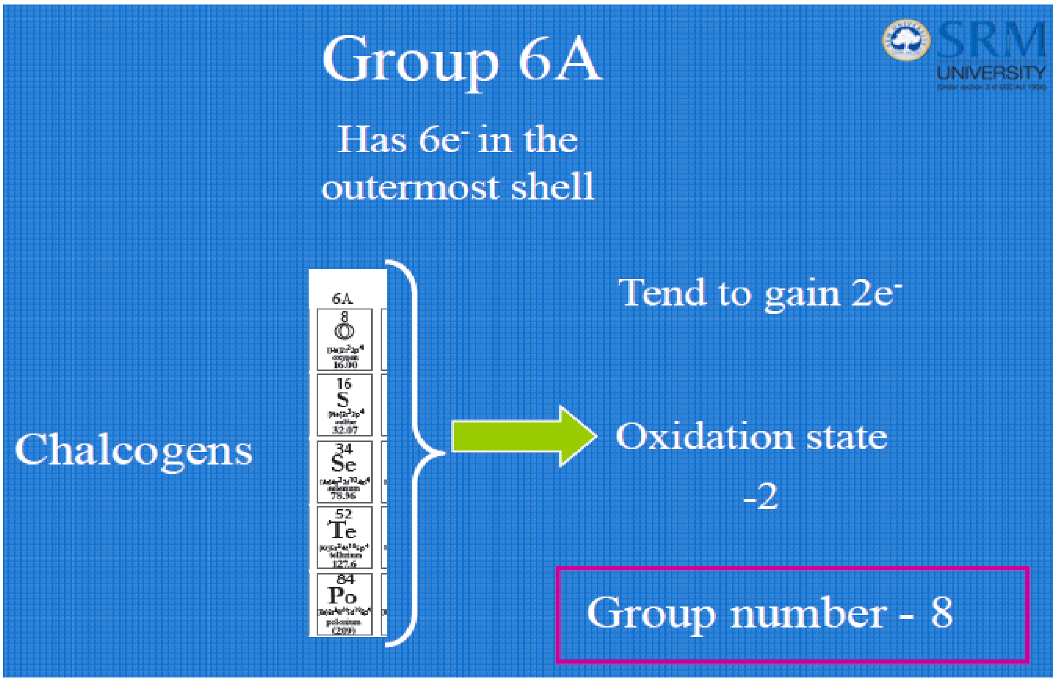


Group 3A

Has $3e^-$ in the outermost shell

Tend to loose $3e^-$

OS = +3



Group 6A

Has $6e^-$ in the outermost shell

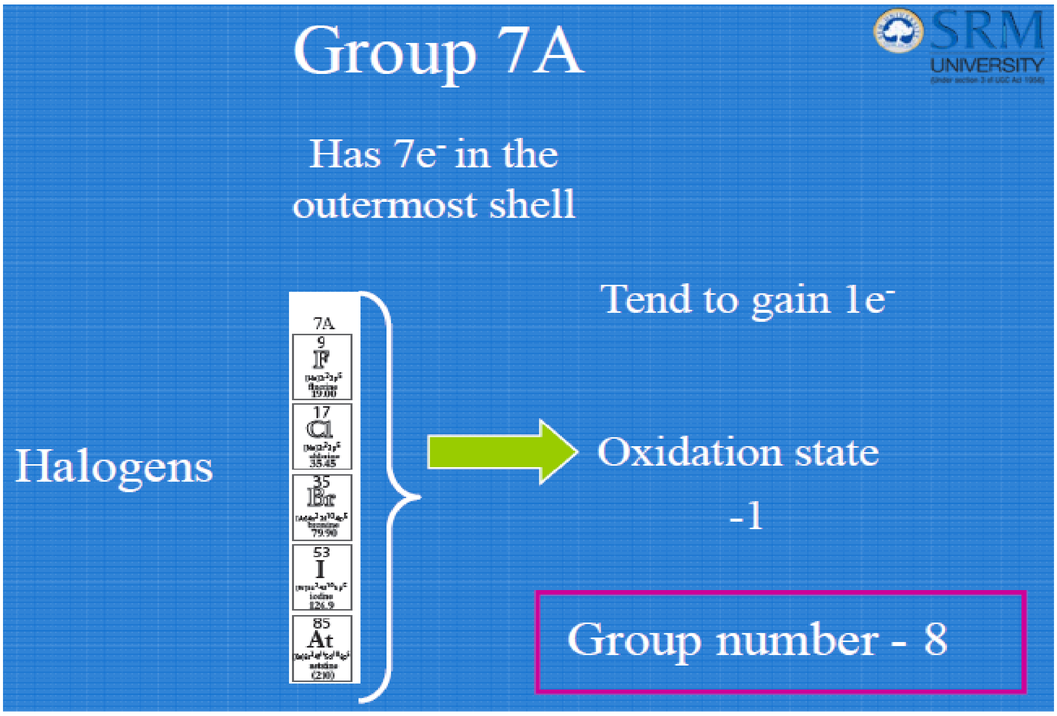
Chalcogens

Tend to gain $2e^-$

Oxidation state

-2

Group number - 8



Group 7A

Has $7e^-$ in the outermost shell

Halogens

Tend to gain $1e^-$

Oxidation state

-1

Group number - 8

Oxidizing agent an oxidizing substance which tend to take on an electron or electrons and be reduced to a lower oxidation state. For example - $\mathbf{M^{a+} + ne^- \longrightarrow M^{(a-n)+}}$

$$\mathbf{Ce^{4+} + e^- \longrightarrow Ce^{3+}}$$

- Oxidizing ability depends strongly on pH value.

$KMnO_4$ in presence of dil. H_2SO_4

$$\mathbf{MnO_4^{-1} + 8H^+ + 5e^- \longrightarrow Mn^{+2} + 4H_2O \qquad E^0_{red} = +1.52\ V}$$

Q – Calculate the oxidation number for the central atom in the following compounds.

$KMnO_4$, $K_2Cr_2O_7$, H_2O_2, HNO_3, H_2SO_4, KIO_3, $CdCl_2$.

H_2SO_4 : $(+1\times2)+(S)+(-2\times4) = 0 \longrightarrow S = +6$

Reducing agent an reducing substance which tend to give up an electron or electrons and be oxidized to a higher oxidation state. For example - $M^{a+} \longrightarrow M^{(a+n)+} + ne^-$

$$Fe^{2+} \longrightarrow Fe^{3+} + e^-$$

Oxalic acid $H_2C_2O_4{\bullet}2H_2O$ **:::** $C_2O_4^{2-} = CO_2 + 2e^-$

Q – Calculate the oxidation number for the central atom in the following compounds.

$H_2C_2O_4{\bullet}2H_2O$, H_2S, $SnCl_2$

REDUCTION - OXIDATION REACTION

Is one that occurs between a reducing and an oxidizing agent,

For example $Ox_1 + Red_2 \longrightarrow Red_1 + Ox_2$

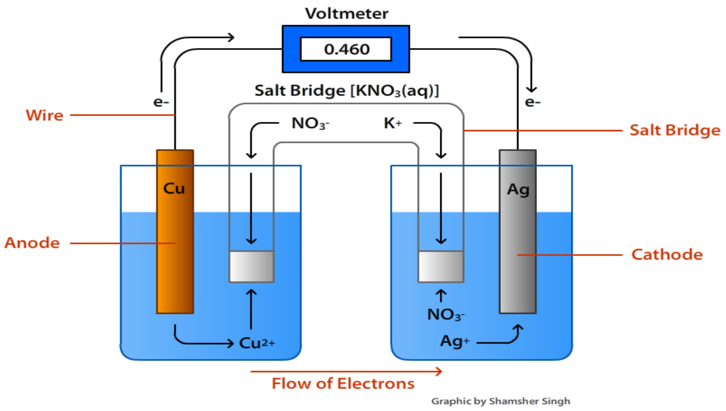
$$Ce^{4+} + Fe^{2+} \longrightarrow Ce^{3+} + Fe^{3+}$$

$$2H^+ + Zn_{(s)} \longrightarrow H_{2(g)} + Zn^{2+}$$

Electro chemical cells:

There are two kinds of electrochemical cells, galvanic (voltaic) and electrolytic cell.

1- galvanic cells In this type of cells the chemical reaction spontaneously occurs to produce electrical energy for example , zinc - copper cell, lead storage battery , copper - silver cell.



Copper - Silver cell

2- Electrolytic cell electrical energy is used to force a nonspontaneous chemical reaction to occur, that is to go in the reverse direction it would in a galvanic cell. An example is the electrolysis of water

$2H_2O \longrightarrow H_{2(g)} \uparrow + 2O_{2(g)} \uparrow$ (acid solution)

An electrochemical cell consists of two conductors called **electrodes** each of which is immersed in an electrolyte solution .

Anode is the electrode at which oxidation occurs.

Cathode is the electrode at which reduction occurs.

The solutions surrounding the two electrodes are different and must be separated to avoid direct reaction between the reactants.

The most common way of avoiding mixing is to insert a salt bridge.

Salt bridge allows charge transfer through the solution but prevent mixing of the solution .

Q- The equation that is not represented as a redox reaction is,

a- $AgNO_3 + NaCl \longrightarrow AgCl + NaNO_3$

b- $2H_2 + O_2 \longrightarrow 2H_2O$

c- $2H_2O_2 \longrightarrow 2H_2O + O_2\ (g)$

d- $Cu_{(s)} + 2\ AgNO_3 \longrightarrow Cu(NO_3)_2 + 2Ag_{(s)}$

Redox reaction as two half reaction As a redox reaction involves both oxidation and reduction components, it is possible to divide the total reaction , these clearly demonstrate which species gains electrons and which losses them .

This can be suitably illustrated by the reaction between iron (III) and tin (II).

$$2Fe^{3+} + Sn^{2+} \longrightarrow Sn^{4+} + 2\,Fe^{2+}$$

This reaction can be divided into two half reactions show below

$$2Fe^{3+} + 2e^{-} \longrightarrow 2\,Fe^{2+} \quad \text{(reduction)}$$

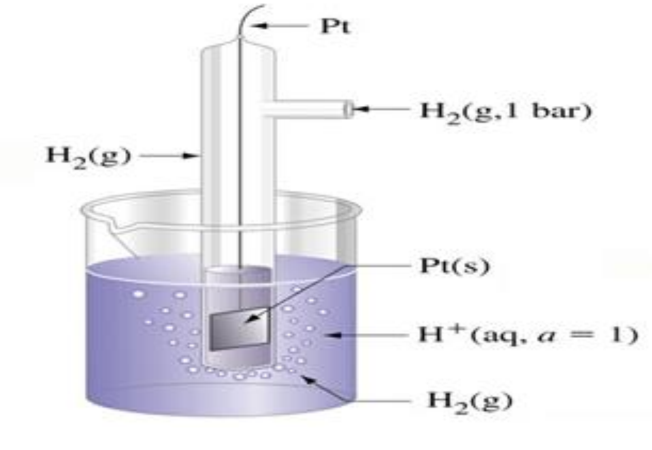
$$Sn^{2+} \longrightarrow Sn^{4+} + 2e^{-} \quad \text{(oxidation)}$$

Total $2Fe^{3+} + Sn^{2+} + \cancel{2e^{-}} \longrightarrow Sn^{4+} + 2\,Fe^{2+} + \cancel{2e^{-}}$

This method of expressing a redox reaction as two half reactions provide a kind of flexibility to the concept of redox reaction.

No half reaction occur by itself there must be an electron donor (reducing agent) and an electron accepter (an oxidizing agent) **Fe^{3+}** oxidizing agent **Sn^{2+}** reducing agent .

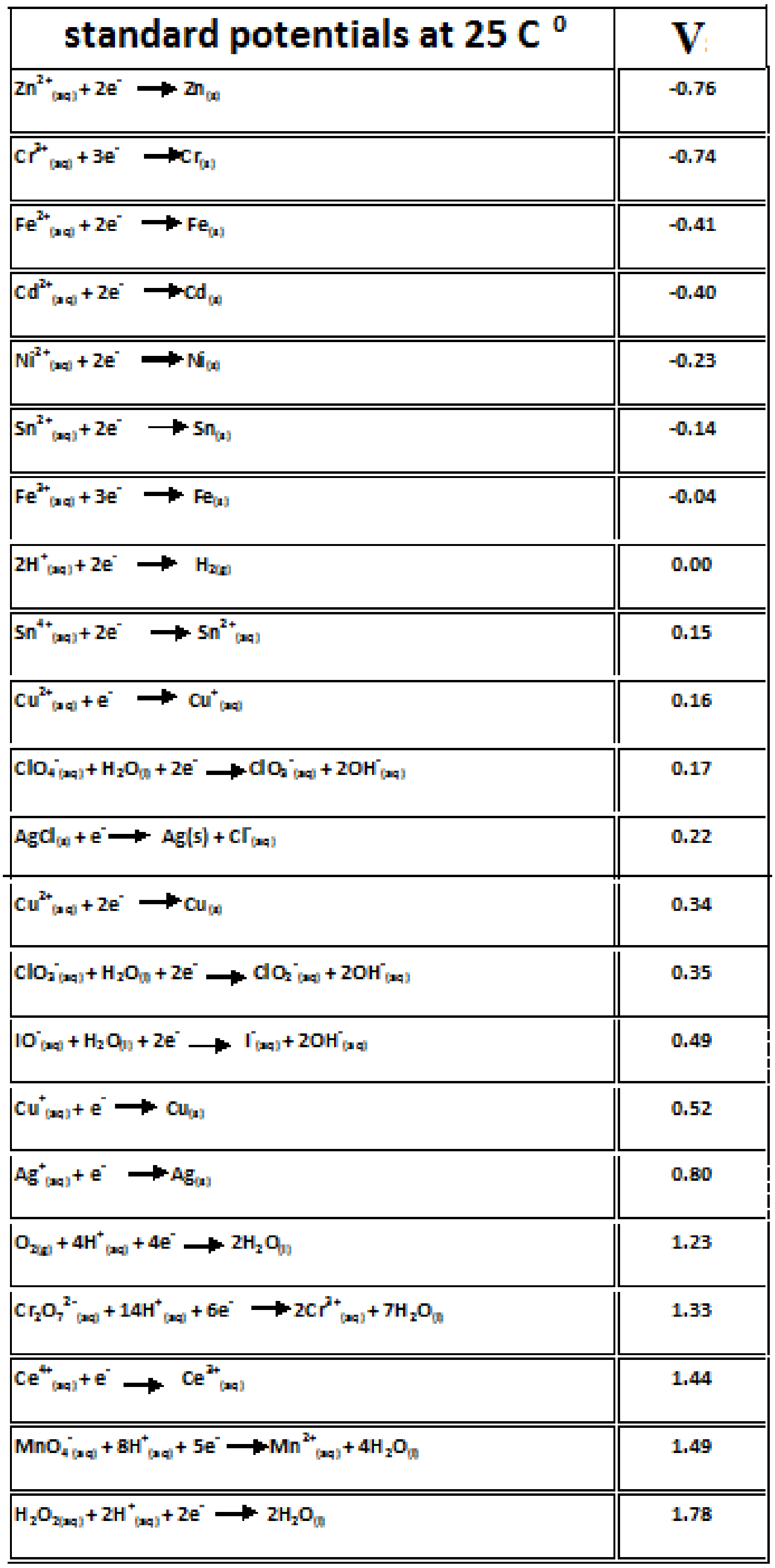
(SHE) standard hydraogen electrode: the electrode potential of the half reaction $2H^{+} + 2e^{-} \leftrightarrow H_2 \quad E^{0} = 0.00\ V$



This figure show the (SHE)

The potential have differences between this half reaction and other half reactions have been measured and arranged in increasing order.

Table - standard potentials of some element



standard potentials at 25 C ^{0}	V
$Zn^{2+}_{(aq)} + 2e^- \rightarrow Zn_{(s)}$	-0.76
$Cr^{3+}_{(aq)} + 3e^- \rightarrow Cr_{(s)}$	-0.74
$Fe^{2+}_{(aq)} + 2e^- \rightarrow Fe_{(s)}$	-0.41
$Cd^{2+}_{(aq)} + 2e^- \rightarrow Cd_{(s)}$	-0.40
$Ni^{2+}_{(aq)} + 2e^- \rightarrow Ni_{(s)}$	-0.23
$Sn^{2+}_{(aq)} + 2e^- \rightarrow Sn_{(s)}$	-0.14
$Fe^{3+}_{(aq)} + 3e^- \rightarrow Fe_{(s)}$	-0.04
$2H^+_{(aq)} + 2e^- \rightarrow H_{2(g)}$	0.00
$Sn^{4+}_{(aq)} + 2e^- \rightarrow Sn^{2+}_{(aq)}$	0.15
$Cu^{2+}_{(aq)} + e^- \rightarrow Cu^+_{(aq)}$	0.16
$ClO_4^-{}_{(aq)} + H_2O_{(l)} + 2e^- \rightarrow ClO_3^-{}_{(aq)} + 2OH^-_{(aq)}$	0.17
$AgCl_{(s)} + e^- \rightarrow Ag(s) + Cl^-_{(aq)}$	0.22
$Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$	0.34
$ClO_3^-{}_{(aq)} + H_2O_{(l)} + 2e^- \rightarrow ClO_2^-{}_{(aq)} + 2OH^-_{(aq)}$	0.35
$IO^-_{(aq)} + H_2O_{(l)} + 2e^- \rightarrow I^-_{(aq)} + 2OH^-_{(aq)}$	0.49
$Cu^+_{(aq)} + e^- \rightarrow Cu_{(s)}$	0.52
$Ag^+_{(aq)} + e^- \rightarrow Ag_{(s)}$	0.80
$O_{2(g)} + 4H^+_{(aq)} + 4e^- \rightarrow 2H_2O_{(l)}$	1.23
$Cr_2O_7^{2-}{}_{(aq)} + 14H^+_{(aq)} + 6e^- \rightarrow 2Cr^{3+}_{(aq)} + 7H_2O_{(l)}$	1.33
$Ce^{4+}_{(aq)} + e^- \rightarrow Ce^{3+}_{(aq)}$	1.44
$MnO_4^-{}_{(aq)} + 8H^+_{(aq)} + 5e^- \rightarrow Mn^{2+}_{(aq)} + 4H_2O_{(l)}$	1.49
$H_2O_{2(aq)} + 2H^+_{(aq)} + 2e^- \rightarrow 2H_2O_{(l)}$	1.78

The electrochemical cell by convention a cell is written with the anode on the left

anode /solution /cathode

For example $\mathbf{C^{4+} + Fe^{2+} \longleftrightarrow Ce^{3+} + Fe^{3+}}$

$$\mathbf{Pt/\ Fe^{2+}(C_1)\ ,\ Fe^{3+}(C_2)\ //\ C^{4+}(C_3)\ ,\ Ce^{3+}(C_4)\ /Pt}$$

C_1 C_2 C_3 and C_4 represent the concentration of the different species , the double line represents the salt bridge.

Since oxidation occurs at the anode and reduction occurs at the cathode, the stronger reducing agent is placed on the left and the stronger oxidizing agent is placed on the right.

The potential of the cell is given by

$$\mathbf{E_{cell} = E_{cathode} - E_{anode}}$$

So a positive potential difference provides the necessary negative free energy. For example Electro chemical cells

$$\mathbf{Fe^{3+}} + e^- = \mathbf{Fe^{2+}} \qquad \mathbf{E^o_{red} = +0.771V}$$

$$\mathbf{Sn^{4+}}+2e^- = \mathbf{Sn^{2+}} \qquad \mathbf{E^o_{red} = +0.154V}$$

$$\mathbf{E^o_{cell} = E^o_{cathode} - E^o_{anode} = E^o_{Fe^{3+}/Fe^{2+}} - E^o_{Sn^{4+}/Sn^{2+}}}$$

$$\mathbf{= 0.771 - (0.154) = 0.617V}$$

Example - determine the reaction between the following half-reaction and calculate the corresponding cell voltage:

$$\mathbf{Fe^{3+}} + e^- = \mathbf{Fe^{2+}} \qquad \mathbf{E^o_{red} = +0.771V}$$

$$\mathbf{I_3^- + 2e^- = 3I^-} \qquad \mathbf{E^o_{red} = +0.5355V}$$

Solution: since the $\mathbf{Fe^{3+}/Fe^{2+}}$ potential is the more positive, $\mathbf{Fe^{3+}}$ is a better oxidizing agent than $\mathbf{I_3^-}$. $\mathbf{Fe^{3+}}$ will oxidize $\mathbf{I^-}$ and

$$\mathbf{E^o_{cell} = E^o_{cathode} - E^o_{anode}} = \mathbf{E^o_{cell} = E^o_{Fe^{3+}/Fe^{2+}} - E^o_{I_3^-/I^-}}$$

In the some fashion, the second half-reaction must be subtracted from the first (multiplied by 2) to give the overall cell reaction,

$\mathbf{2Fe^{3+} + 3I^{-} = 2Fe^{2+} + I_3^{-} \quad E^{o}_{cell} = 0.771\ V - 0.536\ V = +0.235\ V}$

* That multiplying a half-reaction by any number does not change its potential.

Balancing Redox Equations

Knowing how to balance oxidation- reduction reactions is essential to understanding all the concepts covered in this course .

Q- Complete and balance the following equation after adding H^+ OH^-, or H_2O as needed

$$\mathbf{MnO_4^- + NO_2^- \longleftrightarrow Mn^{2+} + NO_3^-}$$

1- We write and balance the two half-reaction involved.

For MnO4, we write $\mathbf{MnO_4^- \longleftrightarrow Mn^{2+}}$

To account for the 4 oxygen atoms on the left-hand side of the equation we add **$4H_2O$** on the right-hand side of the equation, which means that we must provide **$8H^+$** on the left.

$$\mathbf{MnO_4^- + 8H^+ \longleftrightarrow Mn^{2+} + 4H_2O}$$

To balance the charge, we need to add 5 electrons to the left side of the equation. Thus

$$\mathbf{MnO_4^- + 8H^+ + 5e^- \longleftrightarrow Mn^{2+} + 4H_2O}$$

For the other half-reaction

$$\mathbf{NO_2^- \longleftrightarrow NO_3^-}$$

We add one H_2O to the left side of the equation to supply the needed oxygen and $2H^+$ on the right to balance hydrogen

$$\mathbf{NO_2^- + H_2O \longleftrightarrow NO_3^- + 2H^+}$$

Then we add two electrons to the right-hand side to balance the charge

$$\mathbf{NO_2^- + H_2O \longleftrightarrow NO_3^- + 2H^+ + 2e^-}$$

Before combining the two equation, we must multiply the first by 2 and the second by 5 so that the number of electrons lost will be equal to the number of electrons gained. We then add the two half-reactions to obtain

$$2MnO_4^- + 16H^+ + 10e^- + 5NO_2^- + 5\,H_2O \longleftrightarrow 2Mn^{2+} + 8H_2O + 5NO_3^- + 10\,H^+ + 10e^-$$

Which then rearranges to the balanced equation

$$2MnO_4^- + 6H^+ + 5NO_2^- \longleftrightarrow 2Mn^{2+} + 5NO_3^- + 8H_2O$$

Q - Complete and balance the following equation after adding H^+ OH^-, or H_2O as needed

$$MnO_4^- + Fe^{2+} \longleftrightarrow Mn^{2+} + Fe^{3+}$$

The effect of concentration on electrode potential

Nernst equation :

A mathematical expression that related the potential of an electrode to the activities of those species in solution that is responsible for potential. For a cell with the following general equation

$$aA + bB + \text{------} + ne \longleftrightarrow cC + dD + \text{-------}$$

The electrode potential for this reaction is given by the equation

$$\boxed{E = E^0 - \frac{RT}{nF}\, ln\, \frac{[C]^c[D]^d - -}{[A]^a[B]^b—}}$$

Where

E^0 = the standard electrode potential which is characteristic for each half-reaction, **R**= the gas constant **8.314** K^{-1} mol^{-1} ,T= temperature K, **n** = number of moles of electrons that appear in the half –reaction for the electrode process as written, **F** = faraday constant = 96485 C, **In** = natural logarithm = 2.303 log,

If we substitute numerical values for the constants convert to bas 10 logarithms and specify 25 ^{0}C for the temperature, we gat

$$\boxed{E = E^0 - \frac{0.0592}{n}\, log\, \frac{[C]^c[D]^d - -}{[A]^a[B]^b—}}$$

Examples : Typical half-cell reactions and their corresponding nernst expressions follow.

1- Zn^{2+} +2e $\longleftrightarrow$ $Zn_{(s)}$ $\quad E = E^0 - \frac{0.0592}{2}\log\frac{1}{[Zn^{2+}]}$ $\quad Zn_{(s)}$ is not included in the logarithmic because it is a pure solid. Thus, the electrode potential varies linearly with the logarithm of the reciprocal of the zinc ion concentration **$[Zn^{2+}]$**.

2- Fe^{3+} + e $\longleftrightarrow$ Fe^{2+} $\quad E = E^0 - \frac{0.0592}{1}\log\frac{[Fe^{2+}]}{[Fe^{3+}]}$

the potential for this couple can be measured with an inert metallic electrode immersed in a solution containing both iron species.
The potential depends on the logarithm of the ratio between the molar concentrations of these ions.

3- $2H^+$ + 2e $\longleftrightarrow$ $H_{2\,(g)}$ $\quad E = E^0 - \frac{0.0592}{2}\log\frac{pH_2}{[H^+]^2}$

ln this example PH_2 is the pressure of hydrogen (in atm) at the surface of the electrode.

4- MnO_4^- + 5e +$8H^+$ $\longleftrightarrow$ Mn^{2+} + $4H_2O$, $E = E^0 - \frac{0.0592}{5}\log\frac{[Mn^{2+}]}{[MnO_4{}^-][H^+]^8}$

Here, the potential depends not only on the concentration of manganese species but also on the pH of the solution.

5- $AgCl_{(s)}$ + e $\longleftrightarrow$ $Ag_{(s)}$ + Cl^- $\quad E = E^0 - \frac{0.0592}{1}\log[Cl^-]$

This half-cell reaction describes the behavior of silver electrode immersed in a chloride solution that is saturated with AgCl.
Example: calculate the electrode potential of a silver electrode immersed in a 0.05 M solution of NaCl using **(a) E^0 Ag+/Ag = 0.776 V**
(b) E^0 AgCl/Ag =0.222 V. $K_{sp\,(AgCl)}$ =1.82 x 10^{-10}.

Solution : **(a) Ag^+ + e $\longleftrightarrow$ $Ag_{(s)}$** $\quad$ **E^0 Ag+/Ag = 0.776** V

The **$[Ag^+]$** concentration of this solution is given by

$$[Ag^+] = \frac{K_{sp}}{[Cl^-]} = \frac{1.82 \times 10^{-10}}{0.05} = 3.64 \times 10^{-9} M$$

Substitution into nernst expression gives:

$$E = 0.776 - 0.0592 \log\frac{1}{3.64 \times 10^{-9}} = 0.299 \text{ V}$$ **(b)** Here we may write

$$E = 0.222 - 0.0592 \log[Cl^-] = 0.222 - 0.0952 \log 0.05 = 0.299 \text{ V}$$

Oxidation-reduction (redox) Titration: In redox titrations the concentration of the substances or ions involved in the reaction continuously keeps changing in the course of the titration. Hence the redox potential of the solution must also change (the phenomenon may be compared to the change of the pH of solution during acid-base titration) by plotting the redox potential corresponding to different points in the titration, a titration curve similar to the curve obtained in an acid-base method is obtained. The titration curve in redox reactions can be drawn by plotting the potential of half cell against the volume in millimeter of the titrant.

Points in the redox titration

1- Before titration

2- Prior to the equivalence point

3- At the equivalence point

4- After the equivalence point

Example: consider the titration of **50.0 ml** of **0.05 M Fe^{2+}** with **0.10 M Ce^{4+}** in a medium that is **1.0 M in H_2SO_4** at all time.

$$\mathbf{Ce^{4+} + e^- \longleftrightarrow Ce^{3+} \quad E^o = 1.44\ V\ (1M\ H_2SO_4)}$$

$$\mathbf{Fe^{3+} + e^- \longleftrightarrow Fe^{2+} \quad E^o = 0.68\ V\ (1M\ H_2SO_4)}$$

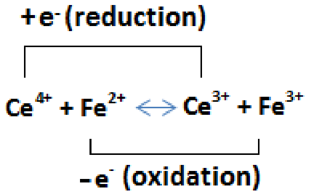
Solution:

At all times during the titration this reaction is rapid and reversible and in equilibrium hence

E_{system} is the potential of the titration and is the value plotted on the y-axis.

E_{system} represents the potential of the electrochemical cell:

$$\mathbf{Ce^{4+} + Fe^{2+} \longleftrightarrow Ce^{3+} + Fe^{3+}}$$



$$\mathbf{SHE//\ Ce^{4+},\ Ce^{3+},\ Fe^{3+},\ Fe^{2+}/Pt}$$

We can follow either $\mathbf{E_{Ce^{4+},Ce^{3+}}}$ or $\mathbf{E_{Fe^{3+},Fe^{2+}}}$

$\mathbf{E_{system}} = \mathbf{E_{Ce^{4+},Ce^{3+}}} = \mathbf{E_{Fe^{3+},Fe^{2+}}}$

(a) At Volume [Ce^{4+}]solution = 0 mL

In the beginning of the titration the solution would contain only **Fe^{2+}** ions and may have traces of **Fe^{3+}** due the aerial oxidation of the solution.

As the concentration of the **Fe^{3+}** ion is too small the calculation of the potential has no meaningful significance.

(b) At Volume [Ce^{4+}]solution = 5 mL

Excess of **Fe^{2+}** concentration of **(Fe^{2+} / Fe^{3+})** are measurable.

$$E_{system} = E_{Fe^{3+},Fe^{2+}} = E^o{}_{Fe^{3+},Fe^{2+}} - \frac{0.0592}{n} \log\frac{[Fe^{2+}]}{[Fe^{3+}]}$$

$$[Fe^{2+}] = \frac{50\times0.05-5\times0.1}{50+5} + [Ce^{4+}] \approx \frac{50\times0.05-5\times0.1}{50+5} = \frac{2.0}{55}\,M$$

$$[Fe^{3+}] = \frac{5\times0.1}{50+5} - [Ce^{4+}] \approx \frac{0.5}{50+5} = \frac{0.5}{55}\ M$$

$$E_{system} = E_{Fe^{3+},Fe^{2+}} = 0.68 - \frac{0.0592}{1} \log\frac{\left(\frac{2.0}{55}\right)}{\left(\frac{0.5}{55}\right)} = 0.64\ V$$

(c)- At Volume [Ce^{4+}]solution = 25 mL at the eq. point : no excess of [Fe^{2+}]

[Ce^{4+}]×V_{total} = [Fe^{2+}] ×V_{total} and [Ce^{3+}]×V_{total} = [Fe^{3+}] ×V_{total}

The reaction takes place in one vessel

[Ce^{4+}] = [Fe^{2+}] and [Ce^{3+}] = [Fe^{3+}]

$$E_{eq}=E_{Fe^{3+},Fe^{2+}} = E^o{}_{Fe^{3+},Fe^{2+}} - \frac{0.0592}{n} \log\frac{[Fe^{2+}]}{[Fe^{3+}]} \text{------(1)}$$

$$E_{eq}=E_{Ce^{4+},Ce^{3+}} = E^o{}_{Ce^{4+},Ce^{3+}} - \frac{0.0592}{n} \log\frac{[Ce^{3+}]}{[Ce^{4+}]} \text{------(2)}$$

Summation of eq(1) and eq(2)

$$2E_{eq} = E^o{}_{Fe^{3+},Fe^{2+}} + E^o{}_{Ce^{4+},Ce^{3+}} - \frac{0.0592}{n} \log\frac{[Fe^{2+}][Ce^{3+}]}{[Fe^{3+}][Ce^{4+}]}$$

$$= E^o{}_{Fe^{3+},Fe^{2+}} + E^o{}_{Ce^{4+},Ce^{3+}}$$

$$E_{eq} = \frac{E^o{}_{Fe^{3+},Fe^{2+}} + E^o{}_{Ce^{4+},Ce^{3+}}}{2} = \frac{0.68+1.44}{2} = 1.06\ V$$

(d)- At Volume [Ce^{4+}]solution = 25.10 mL > Veq = 25 mL

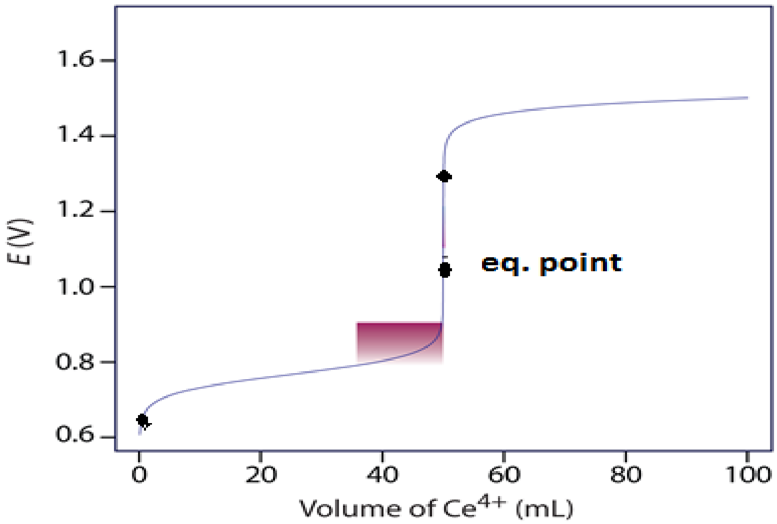
After the eq. point : excess of **[Ce^{4+}]** and concentration of **[Ce^{3+}]/ [Ce^{4+}]** Are measurable. Hence **E_{system}** post-eq = $\mathbf{E_{Ce^{4+},Ce^{3+}}}$

$$E_{system} = E_{Ce^{4+},Ce^{3+}} = E^{o}_{Ce^{4+},Ce^{3+}} - \frac{0.0592}{n}\log\frac{[Ce^{3+}]}{[Ce^{4+}]}$$

$$[Ce^{4+}] = \frac{25.1\times0.1-50\times0.05}{50+25.1} + [Fe^{2+}] \approx \frac{25.1\times0.1-50\times0.05}{50+25.1} = \frac{0.01}{75.1}\text{M}$$

$$[Ce^{3+}] = \frac{25\times0.1}{50+25.1} - [Fe^{2+}] \approx \frac{2.5}{75.1} = \frac{2.5}{75.1}\text{M}$$

$$E_{system} = 1.44 - \frac{0.0592}{1}\log\frac{2.5}{0.01} = 1.3\text{ V}$$



Redox titration methods :

1- Permanganometry

2- Dichromatometry

3- Cerimetry

4- Iodometry and Iodimetry

5- Iodametry

6- Bromatometry

Permanganometrc Titration :

This method is based on reactions of oxidation by permanganate ion. Oxidation may proceed in acid or in alkaline or neutral solution. When KMnO4 acts as an oxidizing agent in acidic solution the septivalent Mn in it reduced to Mn^{2+} ions and a manganous salt of the acid used formed.

For example if $FeSO_4$ is the reducing agent and if it is oxidized in the presence of H_2SO_4 the reaction is represented by the equation;

$\mathbf{10FeSO_4 + 2KMnO_4 + 8H_2SO_4 = 5Fe_2(SO_4)_3 + 2MnSO_4 + K_2SO_4 + 8H_2O}$

Or in ionic form

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

The decrease of the valence of manganese by **5** shows that the $\mathbf{KMnO_4}$ molecule gains 5 electrons this is also very clear from the following equation:

$$\mathbf{MnO_4^- + 8H^+ + 5e^- = Mn^{2+} + 4H_2O}$$

It follows that in this case the gram-equivalent of $\mathbf{KMnO_4}$ is

$$\mathbf{g\text{-}eq = 158.03/5 = 31.61\ g}$$

during oxidation in alkaline or neutral solution the $\mathbf{Mn^{7+}}$ ion is reduced to $\mathbf{Mn^{4+}}$ with the formation of manganese oxide $\mathbf{MnO_2}$ in the form of a brown precipitate for example

$\mathbf{Cr_2(SO_4)_3 + 2KMnO_4 + 8KOH = 2K_2CrO_4 + 2MnO_2 + 2K_2SO_4 + 4H_2O}$

$$\mathbf{MnO_4^- + 4H^+ + 3e^- = MnO_2 + 2H_2O}$$

Therefore in this case the gram-equivalent of $\mathbf{KMnO_4}$ has a different value namly

$$\mathbf{g\text{-}eq = 158.03/3 = 52.68\ g}$$

A redox indicator

(Also called an **oxidation-reduction indicator**) is an indicator which undergoes a definite color change at a specific electrode potential. The requirement for fast and reversible color change means that the oxidation-reduction equilibrium for an indicator redox system needs to be established very quickly. Therefore, only a few classes of organic redox systems can be used for indicator purposes.

There are two common types of redox indicators:

- metal-organic complexes (Ex. phenanthroline)
- true organic redox systems (Ex. Methylene blue)

Sometimes colored inorganic oxidants or reductants (Ex. Potassium manganate, Potassium dichromate) are also *incorrectly* called redox indicators. They can’t be classified as **true** redox indicators because of their irreversibility. Almost all redox indicators with true organic redox systems involve a proton as a participant in their electrochemical reaction. Therefore, sometimes redox indicators are also divided into two general groups: independent or dependent on pH.

Questions:

1- What is an oxidizing agent? A reducing agent?

2- What is the Nernst equation?

3- What is the standard potential?

4- What is the redox indicator?

4- Complete and balance the following equation after adding H^+ OH^-, or H_2O as needed

(a) - $IO_3^- + I^- \longrightarrow I_2$

(b) - $MnO_4^- + H_2SO_3 \longrightarrow Mn^{2+} + SO_4^{2-}$

(c) - $MnO_4^- + H_2S \longrightarrow Mn^{2+} + S$

(d) – $Al + NO_3^- \longrightarrow AlO_2^- + NH_3$

5- What is the potential of a solution containing **10.0 ml** of **0.1 M Fe^{2+}** with **10 mL of 0.05 M Ce^{4+}** in a medium that is **1.0 M in H_2SO_4** at all time?

6- Prove the $-\frac{RT}{nF} \ln \frac{[C]^c[D]^d--}{[A]^a[B]^b—}$ equal $-\frac{0.0592}{n} \log \frac{[C]^c[D]^d--}{[A]^a[B]^b—}$

Knowing that **R** = **8.314** K^{-1} mol^{-1} and **F** = faraday constant = **96485 C**

7- Describe the types of electrolytic cells with examples.

8- What are the types of electrolytic cells and then explain the difference between them.

9- Determine the reaction between the following half-reaction and calculate the corresponding cell voltage:

$$Cu^{2+} + 2e^- = Cu \qquad E^o_{red} = +0.34V$$

$$Zn^{2+} + 2e^- = Zn \qquad E^o_{red} = -0.76V$$

10 - The element that undergoes oxidation is: $H_2 + O_2 \longrightarrow H_2O$

11- The element that undergoes reduction is: $N_2 + 3H_2 \longrightarrow 2NH_3$

$$Cu + 4HNO_3 \rightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$$