✓ **NB: For balance basic condition → as acidic But once reaction balance But we may add OH to neutralize H & create water in its place which can be substracted from water in other side if present Ex:** $Cr_2O_7^{-2} + H2O2 \rightarrow Cr^{+3} + O_2$

Half Rxn (red): $6e^- + 14H^+ + Cr_2O_7^{-2}{}_{(aq)} \leftrightarrows 2Cr^{3+} + 7H_2O$

Half Rxn (oxid): $(H_2O_{2\,(aq)} \leftrightarrows O_2 + 2H^+ + 2e^-) \times 3$

after balanced $Cr_2O_7^{-2} + 8H^+ + 3H2O2 \rightarrow 2Cr^{+3} + 3O_2 + 7H2O$

add $8H2O \rightarrow 8H^+ + 8OH^-$

Net reaction: $Cr_2O_7^{-2} + H2O + 3H2O2 \rightarrow 2Cr^{+3} + 3O_2 + 8OH^-$

❖ **Question: Which of the following corrected balanced reduction half - Reaction**

a) $Fe^{+3} + e^- \rightarrow Fe^0$ b) $2Fe + 6HNO3 \rightarrow 2Fe(NO3)3 + 3H2$

c) $Mn^{+2} + 4H2O \rightarrow MnO4^- + 8H^+ + 5e^-$ d) $2O_2^{-2} \rightarrow O2 + 4e^-$ e) $Mg^{+2} + 2e^- \rightarrow Mg^0$

Equivalent weight (eq. wt) in redox reaction

Definition → weight of substance which react or produce or chemically equivalent to 1 mole of electrons transferred in reaction

So, Equivalent of any species = M.Wt / no. of e (form half reaction)

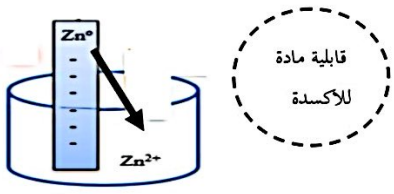
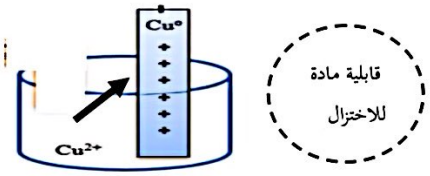
✓ *NB: some redox substance will have more than one equivalent weight ex:* $MnO4^{-1}$

(1) $MnO4^- + 8H^+ + 5e \rightarrow Mn^{+2} + 4H_2O$ *(in strong acidic medium) So, equivalent wt =M.wt /5*

(2) $MnO4^- + 4H^+ + 3e \rightarrow MnO_2$ *(solid) +* $2H_2O$ *(in alkaline medium) So, equivalent wt =M.wt / 3*

single electrode potential

** if we immerse M° rod in its* M^{+n} *solution, there are 2 process can occur depend on nature of metal*

Oxidation process (electron loss)	Reduction process (electron gain)
[depend on electrolytic solution pressure(ESP)	[depend on ionic pressure (IP)]
Ex: $Zn^0 \rightarrow Zn^{+2} + 2e$ 	Ex: $Cu^{+2} + 2e \rightarrow Cu^0$ 
* metal ion (M^o) tends to leave the rod So, the rod will be -vely charged	* metal ion (M^{+n}) tends to PPT on the rod So, the rod will be +vely charged

قراءة للفهم فقط

➢ ***which process will occur ? this depend on the nature of metal if***

(1) IP > ESP → metal will be reduced & deposited on rod (Ex: Cu ,Ag , Pt)

(2) ESP > IP → metal will be oxidized & go to solution (EX: Zn , Cd , Co, Ni)

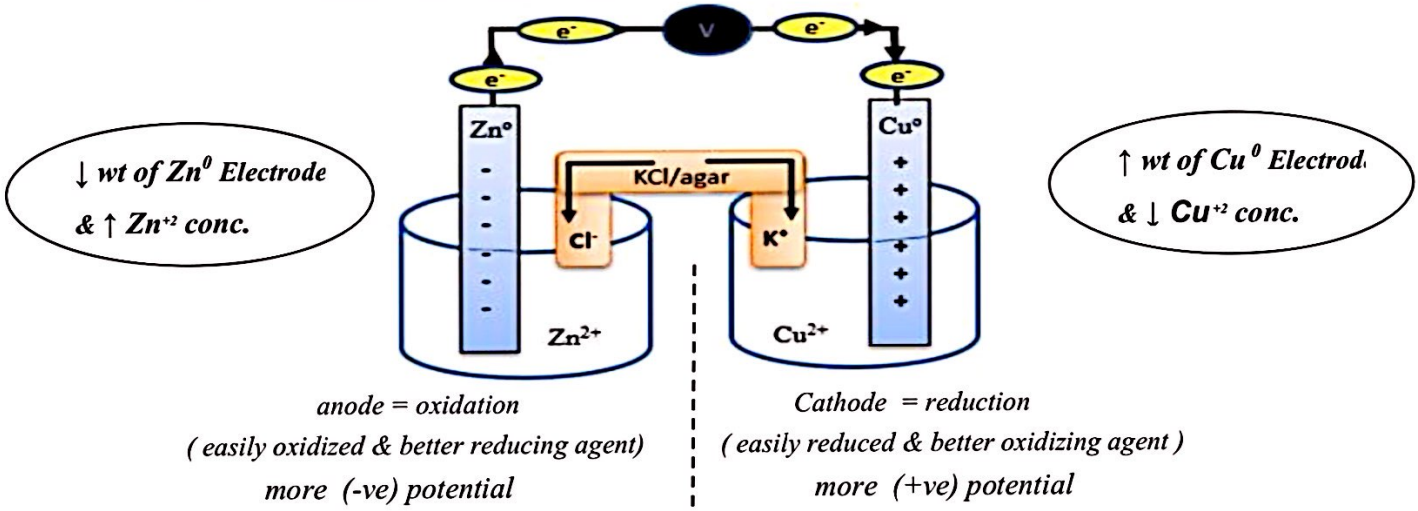
❖ *depend on **electrochemical activity series** of metal (topH → oxidized & down H → reduced)*

So, Cu below zinc in activity serious So, Zn^0 is easier to oxidize Zn^{+2} & Cu^{+2} easier to reduced to Cu^0

*NB: each electrode called **half - cell** &has its **single electrode potential** since each type of rod will be surrounded by equal amount of opposite charge called **electrical double layer***

- *when 2 electrode connected to each other → electrons **pass** from Zn electrode to Cu electrode creating **electrical current** & form complete **Electro-chemical cell (ECC)** called*

*[**Galvanic cell = volatic cell = Daniel cell**] where* ***→ chemical energy converted to electrical energy***



anode = oxidation
(easily oxidized & better reducing agent)
more (-ve) potential

Cathode = reduction
(easily reduced & better oxidizing agent)
more (+ve) potential

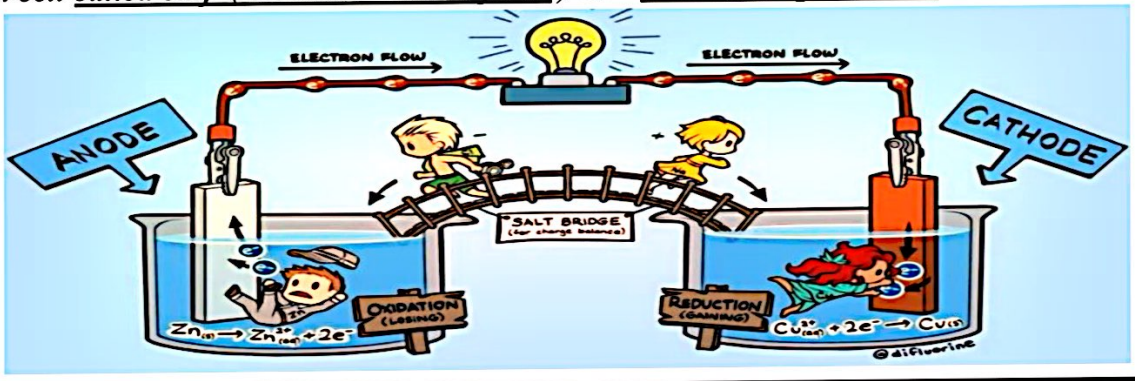
electrochemical cell : composed of 2 half cell connected

1- ***Externally by wire → used for electronic conduction***
2- ***internally by salt bridge (Kcl / agar)***

Salt bridge:

- ✓ ***KCl or KNO3 → where cation** Move to cathode & **anion** move to anode (in the same mobility)*
- ✓ ***Used for** → ionic contact without mixing of 2 solution + allow flow of ions to Keep charge balance & So maintain electron flow (if not present → prevent further electron flow)*

- *NB: Each electrode has its potential & potential difference between 2 half cell anode &cathode in cell **called emf (electron –motive force**) Or **E cell (cell potential)** in volt*



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Determination Potential of half cell (electrode potential)

(1) mathematically: *can be measured from* ***Nernest equation***

Redox couple $Ox. + n\,e^- = Red.$

Nernst Equation

$$E = E^0 + \frac{0.0591}{n} \log \frac{[Ox.]}{[Red.]}$$

- E: Electrode potential, volt.
- E^0: Standard electrode (reduction) potential, volt. (constant for every system)
- n: No. of electrons
- $[Ox.]$: Conc. of oxidized form (oxidant)
- $[Red.]$: Conc. of reduced form (reductant)

$$0.0591 = 2.303 \frac{RT}{F}$$

- R: Gas constant 8.314 J /K
- T: Temperature (K^0) = 298 K
- F: Faraday constant = 96500 coulomb

(1) $Zn^{+2} + 2\,e \rightarrow Zn^o$ (ion in metal)

$$E = E^0 (Zu^{+2}/Zn^o) + 0.059/2 \log [Zn^{+2}/Zn^0] = E^0 (Zu^{+2}/Zn^o) + 0.059/2 \log Zn^{+2}$$

So, the potential depend on Zn^{+2} conc.

(2) $Fe^{+3} + 1\,e \rightarrow Fe^{+2}$

$$E_{(Fe^{+3}/Fe^{+2})} = E^0_{(Fe^{+3}/Fe^{+2})} + 0.059/1 \log Fe^{+3}/Fe^{+2}$$

So, the potential depend on Both oxidant & reductant conc.

(3) $Ce^{+4} + e \rightarrow Ce^{+3}$ (ion in ion)

$$E_{(Ce+4/Ce+3)} = E^0_{(Ce+4/Ce+3)} + 0.059/1 \log Ce^{+4}/Ce^{+3}$$

So, the potential depend on Both oxidant & reductant conc.

(4) $Cr_2O_7^{-2} + 14\,H^+ + 6\,e \rightarrow 2\,Cr^{+3} + 7\,H_2O$

$$E_{(Cr_2O_7^{-2}/Cr^{+3})} = E^0_{(Cr_2O_7^{-2}/Cr^{+3})} + 0.059/6 \log \frac{(Cr_2O_7^{-2})^1 \times (H^+)^{14}}{(Cr^{+3})^2}$$

So, the potential depend on Both oxidant & reductant conc. & PH

(5) $MnO_4^- + 8\,H^+ + 5\,e \rightarrow Mn^{+2} + 4\,H_2O$ (in strong acidic medium)

$$*E_{(MnO_4^-/Mn^{+2})} = E^0_{(MnO_4^-/Mn^{+2})} + \frac{0.059}{5} \log \frac{(MnO_4^-)^1 \times (H^+)^8}{(Mn^{+2})^1 \times (H_2O)^4}$$

$$*E_{(MnO^-/Mn^{+2})} = E^0_{(MnO_4^-/Mn^{+2})} + \frac{0.059}{5} \log \frac{(MnO_4^-)^1 \times (H^+)^8}{(Mn^{+2})^1}$$

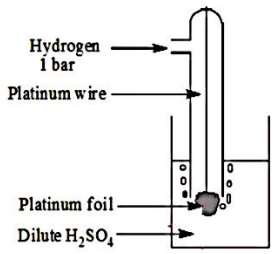
So, the potential depend on Both oxidant & reductant conc. & PH

2) practically : → *half-cell potential can't be determined But emf of whole cell can be determined So, we can measure it using standard hydrogen electrode half cell (SHE = NHE = RHE) which has Zero potential at all temperature (why ??????)*

❖ ***standard hydrogen electrode (SHE) / reference hydrogen electrode / Normal hydrogen electrod (NHE)***

pt (s) / H2 (gas) , (1atm) / H+ (1 M)

$$2H^+ + 2e \rightarrow H_2\,(gas)$$



$E_{(2H+/H2)} = E^0_{(2H+/H2)} + 0.059 / 2 \log (H^+)^2 / H_2\ gas$

So, if we use H^+ = 1 M & pss = 1 atmosphere & E^o = zero at all temperature

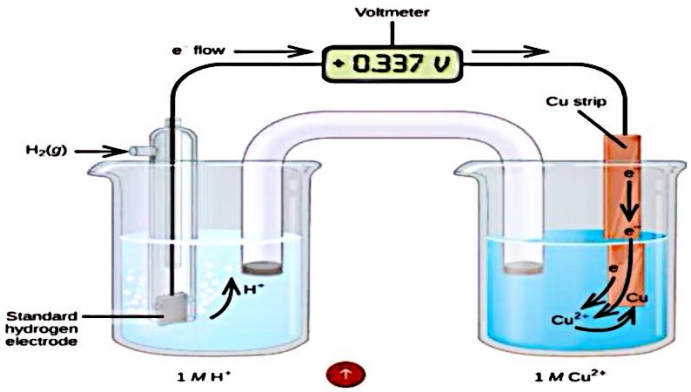
$E_{(2H+/H2)} = E^0_{(2H+/H2)} + 0.059 / 2 \log 1 = E^0_{(2H+/H2)}$ = Zero volt at all temp

➢ *Used as primary reference to determine potential E0 of any system .*

How to determine standard reduction potential experimentally ?

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$$

$$+0.34\ V = E^\circ_{Cu^{2+}/Cu} - E^\circ_{H^+/H_2}$$



General notes about electro-chemical activity serious نشاط السلسلة الكهروكيميائية

التفاعل الطبيعي يحصل بين
فوق شمال مع تحت يمين
يعني اللي فوق علي شمال
بياكسد تحت علي يمين

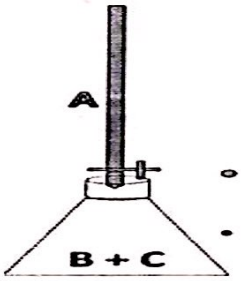
equilibrium			E° (volts)
$Li^+_{(aq)} + e^-$	⇌	$Li_{(s)}$	-3.03
$K^+_{(aq)} + e^-$	⇌	$K_{(s)}$	-2.92
$Ca^{2+}_{(aq)} + 2e^-$	⇌	$Ca_{(s)}$	-2.87
$Na^+_{(aq)} + e^-$	⇌	$Na_{(s)}$	-2.71
$Mg^{2+}_{(aq)} + 2e^-$	⇌	$Mg_{(s)}$	-2.37
$Al^{3+}_{(aq)} + 3e^-$	⇌	$Al_{(s)}$	-1.66
$Zn^{2+}_{(aq)} + 2e^-$	⇌	$Zn_{(s)}$	-0.76
$Fe^{2+}_{(aq)} + 2e^-$	⇌	$Fe_{(s)}$	-0.44
$Pb^{2+}_{(aq)} + 2e^-$	⇌	$Pb_{(s)}$	-0.13
$2H^+_{(aq)} + 2e^-$	⇌	$H_{2(g)}$	0
$Cu^{2+}_{(aq)} + 2e^-$	⇌	$Cu_{(s)}$	+0.34
$Ag^+_{(aq)} + e^-$	⇌	$Ag_{(s)}$	+0.80
$Au^{3+}_{(aq)} + 3e^-$	⇌	$Au_{(s)}$	+1.50

Substance is easily reduced (act as oxidizing agent)

NB:

- ***standard reduction potential → useful to determine direction of reaction***
- ***NB: standard reduction potential & standard oxidation potential are opposite in signs to each for the same chemical reaction.***
- ***<u>question1</u> : base on activity series which species will be oxidized & reduced Zn^{+2} or H^{+}***
- ***<u>question2</u>: the standard reduction potential of Fe+3 is + 0.77 what is standard oxidation potential ?***

<u>question 3</u>



Substance	Type	E^{o}
A	Titrant	+ 1.33
B	Sample	+ 0.771
C	Sample	+ 1.11

- A undergoes ....., A is .....
- Both B and C undergoes ..... By A.
  - ..... is more easily oxidized.
  - ..... is more oxidized first.

Dr. / shady sha3ban
Analytical king
01224544915

Factors affect oxidation potential of redox couple

(1) Common ion effect

EX: $MnO4^- + 8\,H^+ + 5\,e \rightarrow Mn^{+2} + 4\,H_2O$

$$E = E^o_{MnO_4^-/Mn^{+2}} + \frac{0.0591}{5} \log \frac{[MnO_4^-][H^+]^8}{[Mn^{2+}]}$$

NB: So ↑ Mn^{+2} conc. *by common ion* → ***↓ ratio*** → *↓ Potential of $MnO4^{-2}/Mn^{+2}$ system (**weaker**)*

- ***application**: used in **Zimmermann-Reinhardt reagent.** (MnSO4 + H3PO4 + H2SO4) during titration of **ferrous salt (FeCl2)** by **permanganate***

……

(2) PH effect :- ***for oxygenated oxidant [MnO4 – Cr2O7 – IO3 ,……]***

EX: ($MnO4^-/Mn^{+2}$ System) $MnO4^- + 8\,H^+ + 5\,e \rightarrow Mn^{+2} + 4\,H_2O$

$$E = E^o_{MnO_4^-/Mn^{+2}} + \frac{0.0591}{5} \log \frac{[MnO_4^-][H^+]^8}{[Mn^{2+}]}$$

So, ↑ PH → ↓ H → ↓ potential والعكس صحيح

Another example of PH effect امتحان:

$ASO4^{-3}$ arsnate / $ASO3^{-3}$ arsenite (E= +0.57) can be determined I_2 iodine / I^- iodide (E= +0.54)

$$AsO_4^{3-} + 2I^- + 2H^+ \underset{NaHCO_3}{\overset{H^+}{\rightleftharpoons}} AsO_3^{3-} + I_2 + H_2O$$

$$*E_{(ASO4^{-3}/ASO3^{-3})} = E^0_{(ASO4^{-3}/ASO3^{-3})} + \frac{0.059}{2} \log \frac{(ASO4)\ X\ (H)}{(ASO3)}$$

Direction of reaction is governed by PH of medium

1- in alkaline medium (NaHCO3) : arsnite ($ASO3^{-3}$) determined iodimetrically (left side)

2- in acidic medium : ↑ H^+ conc. → ↑ potential → arsnate $ASO4^{-3}$ is determined iodometrically (right side)

Question : according to the previous equation

- **in acidic medium;.....(1)..... is oxidized by.....(2)....**
- **In acidic medium;.....(3).....is an oxidizing agent.**
- **In alkaline medium;.....(4)..... is oxidized by.....(6).**
- **In alkaline medium;.....(7).....is an oxidizing agent.**

……

(3) complex agent effect $Fe^{+3} + 1\,e \rightarrow Fe^{+2}$

$$E_{Fe^{3+}/Fe^{2+}} = E^{\circ}_{Fe^{3+}/Fe^{2+}} + \frac{0.0591}{1} \log \frac{[Fe^{3+}]}{[Fe^{2+}]}$$

If we add F or $PO4^{-3}$ it will complex with Fe^{+3} → ↓ Ratio → ↓ Potential → easily oxidized

(4) PPT agent effect

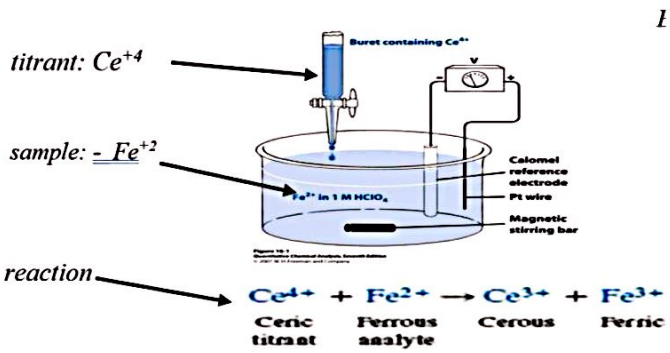
Ferri cyanide $Fe(CN)_6^{-3} + e \rightarrow Fe(CN)_6^{-4}$ *ferro cyanide*

$$E_{Ferri/ferro} = E^{o}_{Ferri/ferro} + \frac{0.059}{1} \log \frac{[Fe(CN)_6^{-3}]}{[Fe(CN)_6^{-4}]}$$

If we add Zn^{+2} ion will PPt ferro cyanide → ↑ Ratio → ↑Potential → ferricyanide easily reduced & can oxidize iodide into iodine

NB: $E\ (I2 / I^{-}) = 0.536\ V$ الاعلى & $E_{(ferri/ferro)} = 0.36V$ اقل

Redox titration curve



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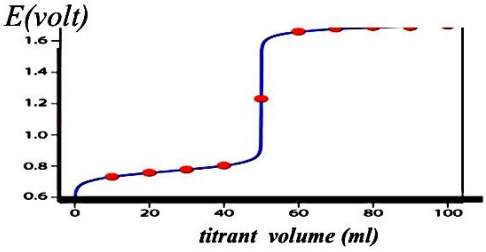

for the following system مسالة

Calculate the potential point of titration curve for ml 0.1N Fe^{+2} by 0.1 N Ce^{+4} calculate potential after 10 ml , 50 ml , 99.9 , after 100 ml , after 100.1 ml , after 200 ml

System	Fe^{+3} / Fe^{+2}	Ce^{+4} / Ce^{+3}
standard potential (E^0)	*+ 0.77 volt*	*+ 1.61 volt*

Calculate the potential point of titration curve for Fe^{+2} by Ce^{+4}

(1) at zero titration (0%) : ***potential can't be calculated***

(2) during titration (before 100 % titration) :

only Fe^{+3} / Fe^{+2} system present So, potential governed by sample redox pair (Fe^{+2} / Fe^{+3})

$$E_{Fe^{3+}/Fe^{2+}} = E^{\circ}_{Fe^{3+}/Fe^{2+}} + \frac{0.0591}{1} \log \frac{[Fe^{3+}]}{[Fe^{2+}]}$$