

Electrochemistry



Electrochemistry

What is the chemical reaction?

❖ **Electrochemistry: Relation between chemical change and electrical energy**

❖ **Electrical energy can be used to bring chemical reaction \Rightarrow Electrolytic cell.**

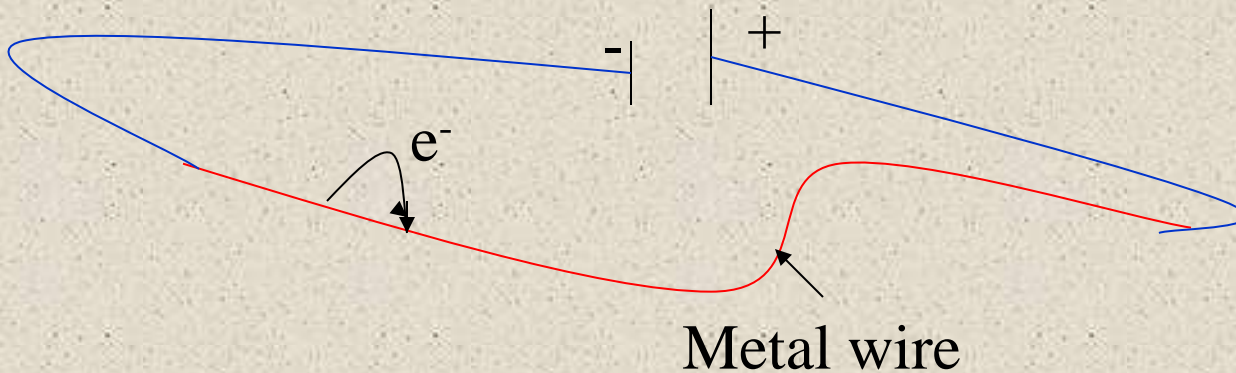
❖ **Chemical reaction leads to produce electric energy \Rightarrow galvanic cells.**

❖ **Through Electrochemistry we can understanding oxidization – reduction phenomena.**

Metallic conduction

❖ When electric current is flow through metals the, charge is carried by electrons .

❖ This type of conduction is called metallic conduction .



Notes

❖ Electric current is measured in amperes, A.

❖ Quantity of electricity is measured in coulombs, C.

$$\begin{aligned} C &= A \times \text{time (in second)} \\ &= A \times t(s) \end{aligned}$$

❖ **Electromotive force is measured in Volts, V .**

$$\mathbf{V = J/C}$$

$$\mathbf{V \times C = J}$$

Electrolytic conduction

❖ In electrolytic solution, the charge is carried by ions.

❖ What that means?

❖ Ions must be free to move.

❖ This is only occur at molten salts or aqueous solutions of electrolyte.

Electrolysis

❖ **Electrolytic cells - nonspontaneous RXNs which are driven by external source of electrical energy.**

❖ **Common example:**

➤ **Electrolysis of molten salts.**

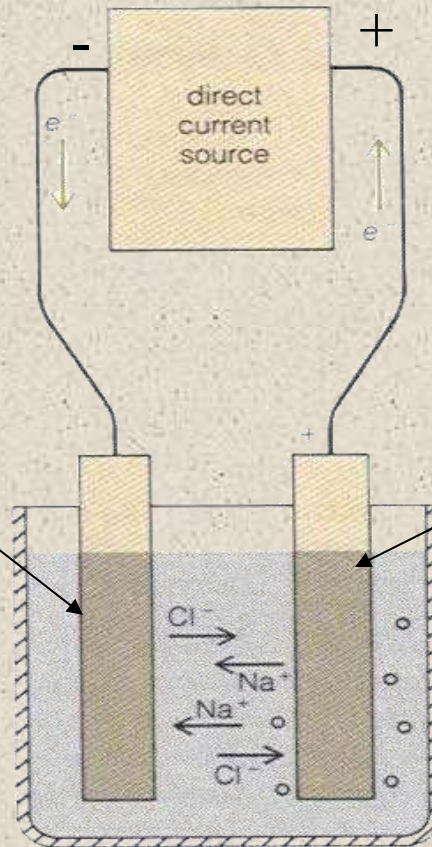
➤ **Electrolysis of aqueous solutions.**

➤ **Electroplating.**

Electrolysis of molten NaCl

cathode

anode



Battery pump
electrons into the left
hand electrode. (-ve)

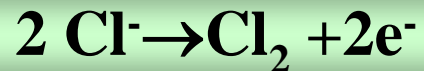
Electrons are drained
from the right-hand
electrode. (+ve)

Cathode reaction



Always reduction occurs at the cathode

Anode reaction

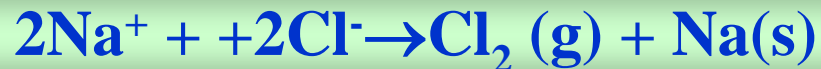
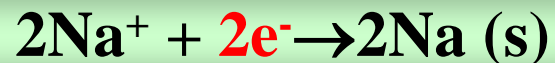


Always oxidization occurs at the anode

The cell reaction is the summation of the two half cell (reduction and oxidation)

Note:

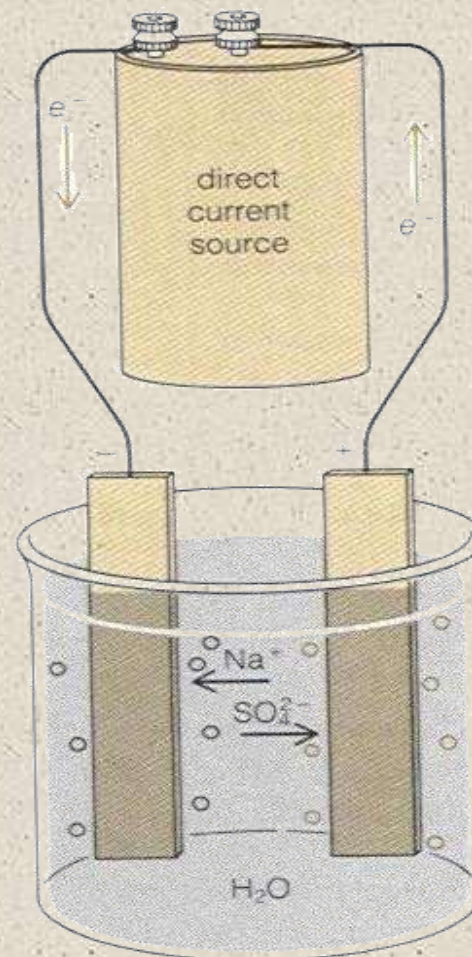
We have to balance the number of moles of electrons in the two half cell reactions.



Electrolysis of aqueous solutions of Na_2SO_4

In this electrolysis cell we have

Na^+ , SO_4^{2-} and H_2O

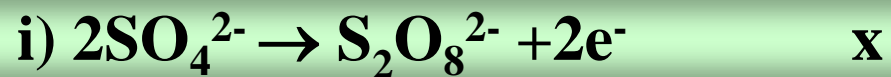


a). Cathode reaction ; (reduction)



at Cathode the reduction of water is occurs and H_2 (g) is evolved.

b). Anode reaction



Water is oxidized and \mathbf{O}_2 is evolved

Note :

In aqueous solution of Na_2SO_4

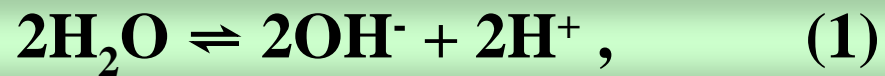
Na^+ is not reduced

SO_4^{--} is not oxidized

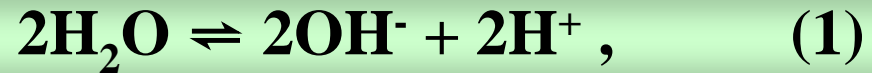
Water molecule are reduced and oxidized

How water is reduced and oxidized ?

H₂O is weak electrolyte



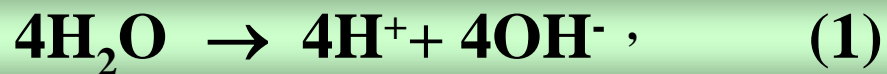
For reduction ,we have ;



By summation eqs. 1 and 2 ,we get



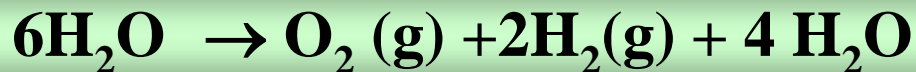
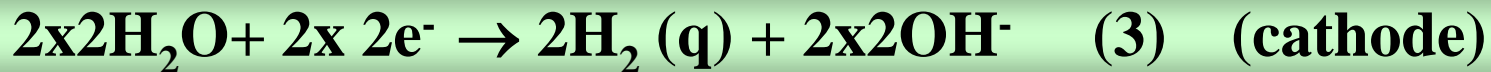
For oxidizes



The summation of eqs. 1 and 2, we get



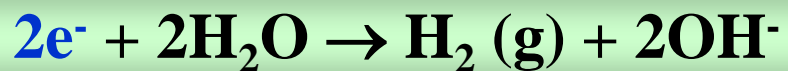
The cell reaction for Na_2SO_4



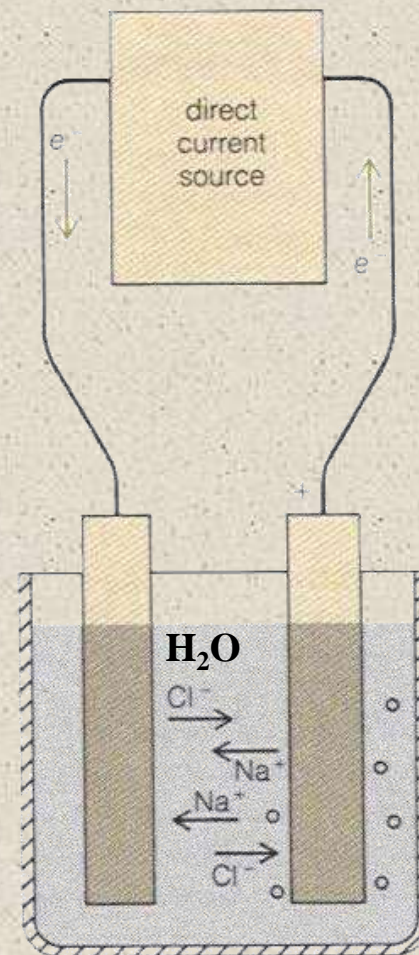
The net reaction is the oxidization and reduction of H_2O

Electrolysis of aqueous NaCl

Cathode reaction



Anode reaction



The cell reaction

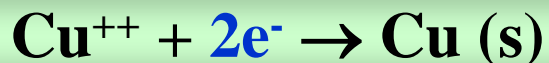


Note

This cell is the source of producing Sodium hydroxide.

Electrolysis of aqueous CuSO_4

Cathode:

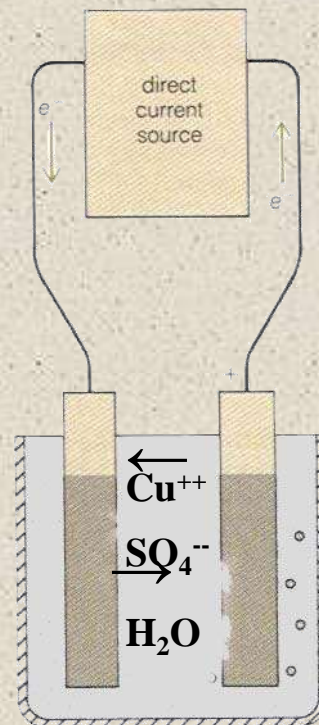
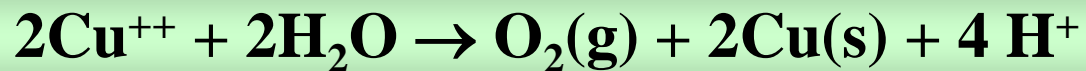


Anode:



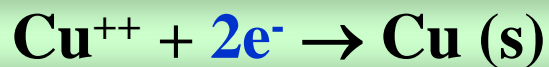
Cell reaction

Is the summation of cathode and anode reactions



Electrolysis of equation CuCl_2

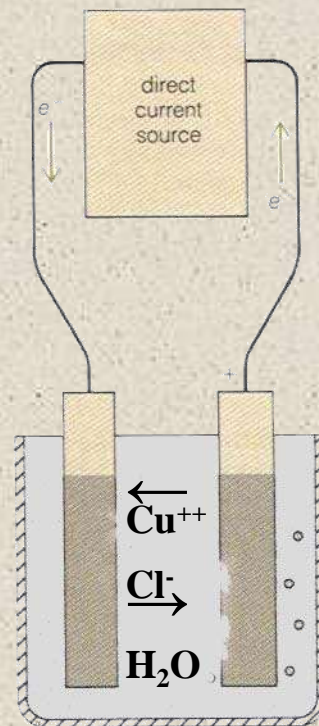
Cathode:



Anode:

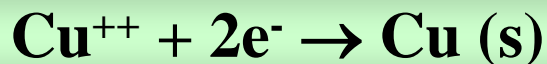


Cell reaction



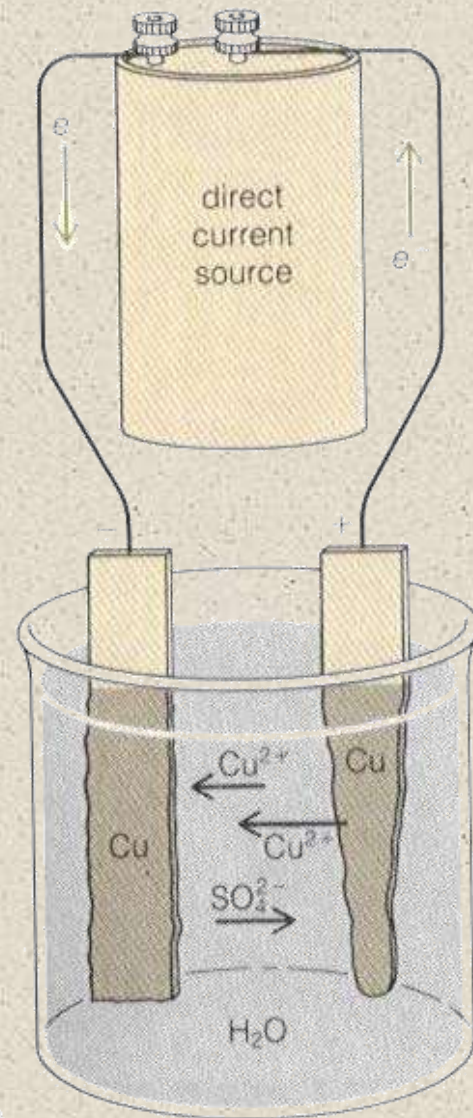
Electrolysis of equation CuSO_4 between Cu electrodes

Cathode reaction

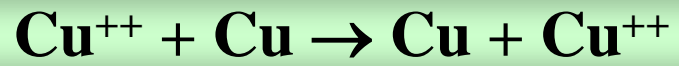


Anode reaction

We have three possible reactions :



Cell reaction



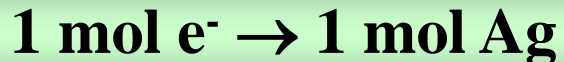
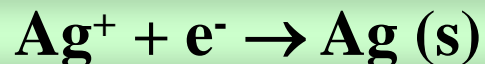
This is used as electroplating cell .



Quantities Aspects of Electrochemistry

Relation between number of Faradays passed in the cell and the amount of substance deposit or evolved around anode or cathode .

Consider the half cell reaction



If we could measure the charge of moles of e^- , we could know the quantity of Ag formed .

But how to measure charge of mole of e^- ?

Current = charge passed / time (s)

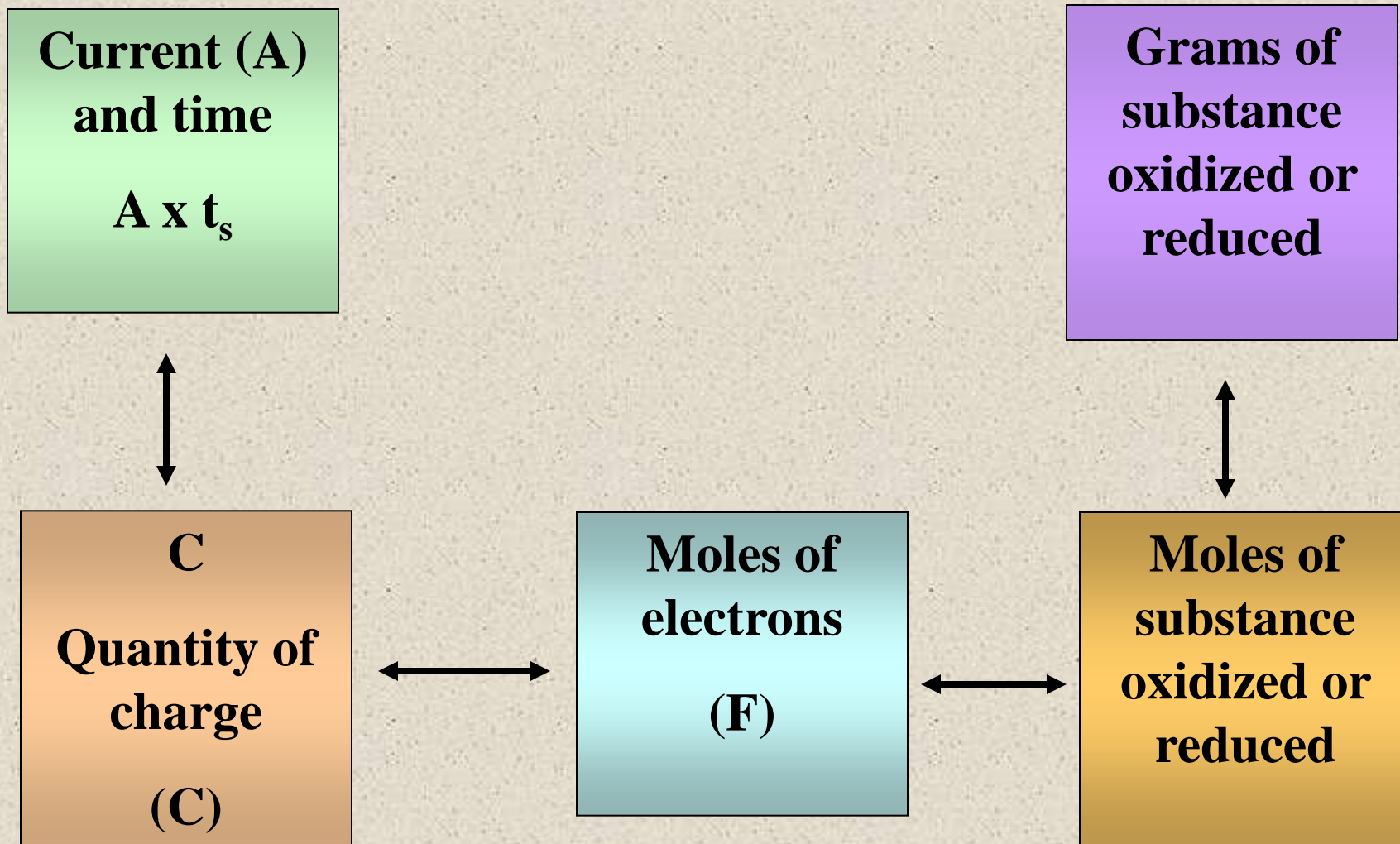
1 amp = Coulombs / second

Charge of 1 mol of e^- = Charge of e^- x A_v number

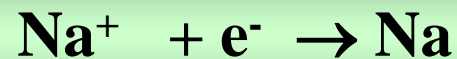
Charge of 1 mol of e^- = ($1.602 \times 10^{-19}C$) ($6.02 \times 10^{23} e^-/\text{mole}$)

= 96500 C/ mol = 1 Faraday

Electrolysis calculations



Ex :



From this half cell reaction we have

1 mole of $\text{e}^- \equiv 1 \text{ mol of Na}$

1 mole $\text{e}^- \equiv \text{mwt of Na}$

1 mole $\text{e}^- \equiv 23\text{g of Na} \equiv 96500\text{C}$

$\frac{1}{2}$ mole of e^- will ppt. $\frac{1}{2}$ mole of Na , $\frac{23}{2}$ g Na.

Ex :

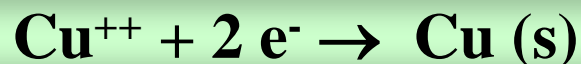
a) In the electrolysis of CuSO_4 , How much copper is plated out on the cathode by a current of 0.75 A in 10 min ?

b) What the volume of O_2 (g) at STP is librated ?

c) If 100 ml. of 1.0 M CuSO_4 is in the cell , what is the H^+ concentration ?

Solution :

$$\text{a) } C = A \times t_s = 0.75 \times 10 \times 60 = 450C$$



From the equation we have:

$$2 F = 2 \times 96500C \equiv 1 \text{ mol Cu} = 63.5g \text{ Cu}$$

450 C will ppt. Xg of Cu

$$X \text{ g of Cu} = 450 \times 63.5g / 2 \times 96500 = 0.148g \text{ Cu}$$

b) Anode reaction:



$$4\text{ F} \equiv 1 \text{ mole O}_2 \equiv 24.5 \text{ L}$$

$$450\text{C} \rightarrow \text{VL} ?$$

$$\text{VL} = 450 \times 24.5 / 4 \times 96500$$

$$= 2.83 \times 10^{-2} \text{ L O}_2 (\text{g})$$

c)

$$4F \equiv 4H^+ \text{ ions}$$

$$\text{number of } H^+ \text{ ions} = 4 \times 450 / 4 \times 96500$$

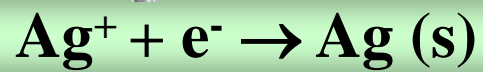
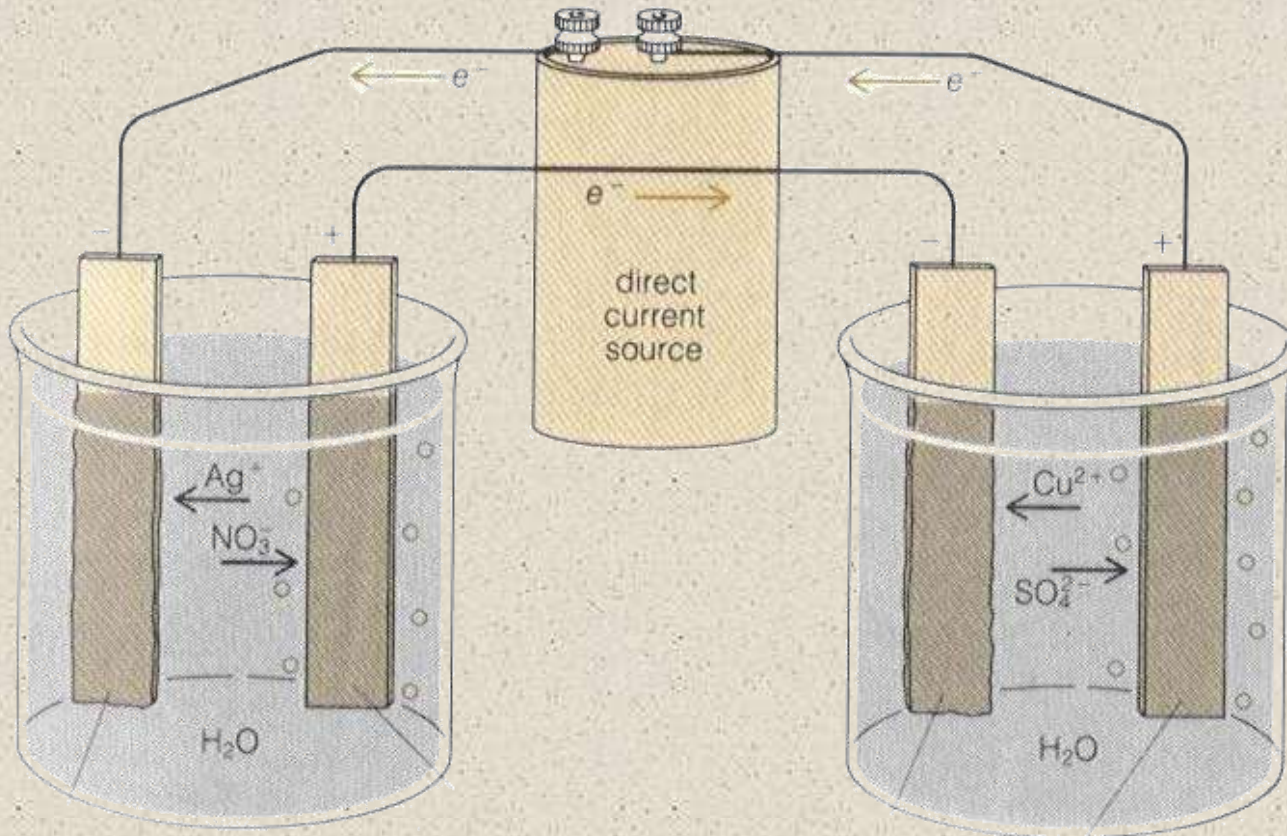
$$= 4.66 \times 10^{-3} \text{ moles}$$

$$[H^+] = n / VL$$

$$= 4.6 \times 10^{-3} \text{ moles} / 0.1$$

$$[H^+] = 4.66 \times 10^{-2} \text{ M}$$

Silver coulometer



Number of F in CuSO_4 cell = Number of F passed in AgNO_3

Example

a) What mass of copper is plated in the electrolysis of CuSO_4 in the same time 1.0g of Ag is plated in a silver coulometer that arranged in series with CuSO_4 cell ?

b) If 1.0 A is passed , how many minutes are required to plate this quantity ?

Solution



$$1 \text{ F} \equiv 96500 \quad \equiv \quad 107.868 \text{ g Ag}$$

If we have

$$\text{C} \quad \quad \quad 1.0 \text{ g}$$

$$\text{C} = 1 \times 96500 / 107.868$$

$$= 894.61 \text{ C}$$



$$2 \text{ F} \qquad 63.5 \text{ g}$$

$$894.61 \qquad \text{x g}$$

$$\text{xg/ Cu} = 894.61 \times 63.5 / 2 \times 96600 = 0.2948$$

$$\mathbf{b) C = A \times t_s}$$

$$\mathbf{894.61 \times 1.0 \times t_s}$$

$$\mathbf{t = 894.615 \text{ s} = 14.9 \text{ min}}$$

Voltaic cells

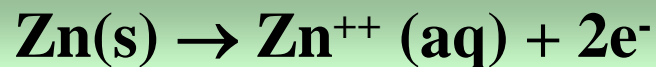
❖ Voltaic cell – device in which transfer of electrons takes place through an external circuit rather than directly between reactants .

❖ Voltaic cell = galvanic cell

❖ A spontaneous redox reaction generates an electric current

Basic concepts of Galvanic cells

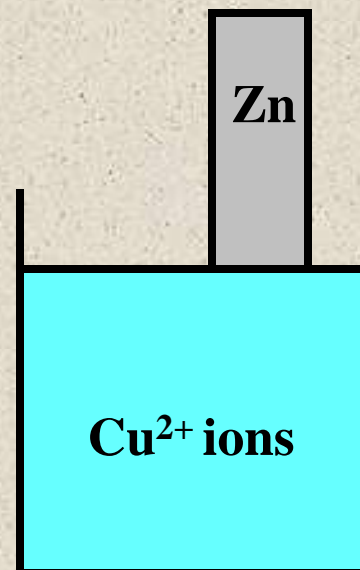
❖ With time , Cu plates out onto Zn ,Zn metal strip, disappears



Zn , oxidized



Cu⁺⁺ reduced

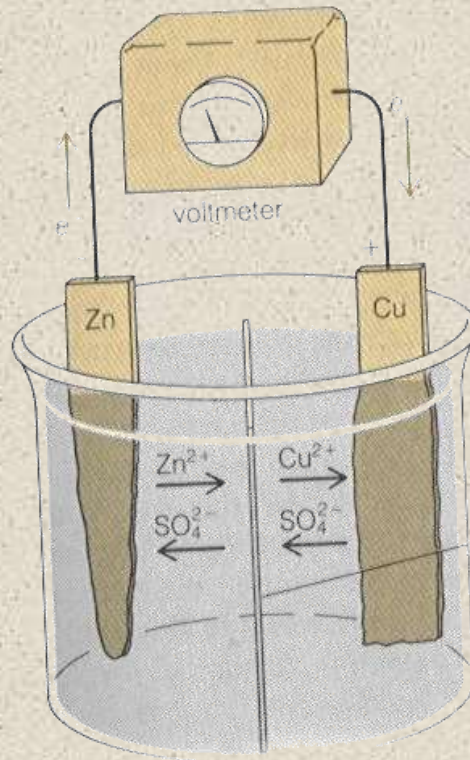


❖ Electrons are transferred from Zn to Cu⁺⁺ , but there is no useful electric current .

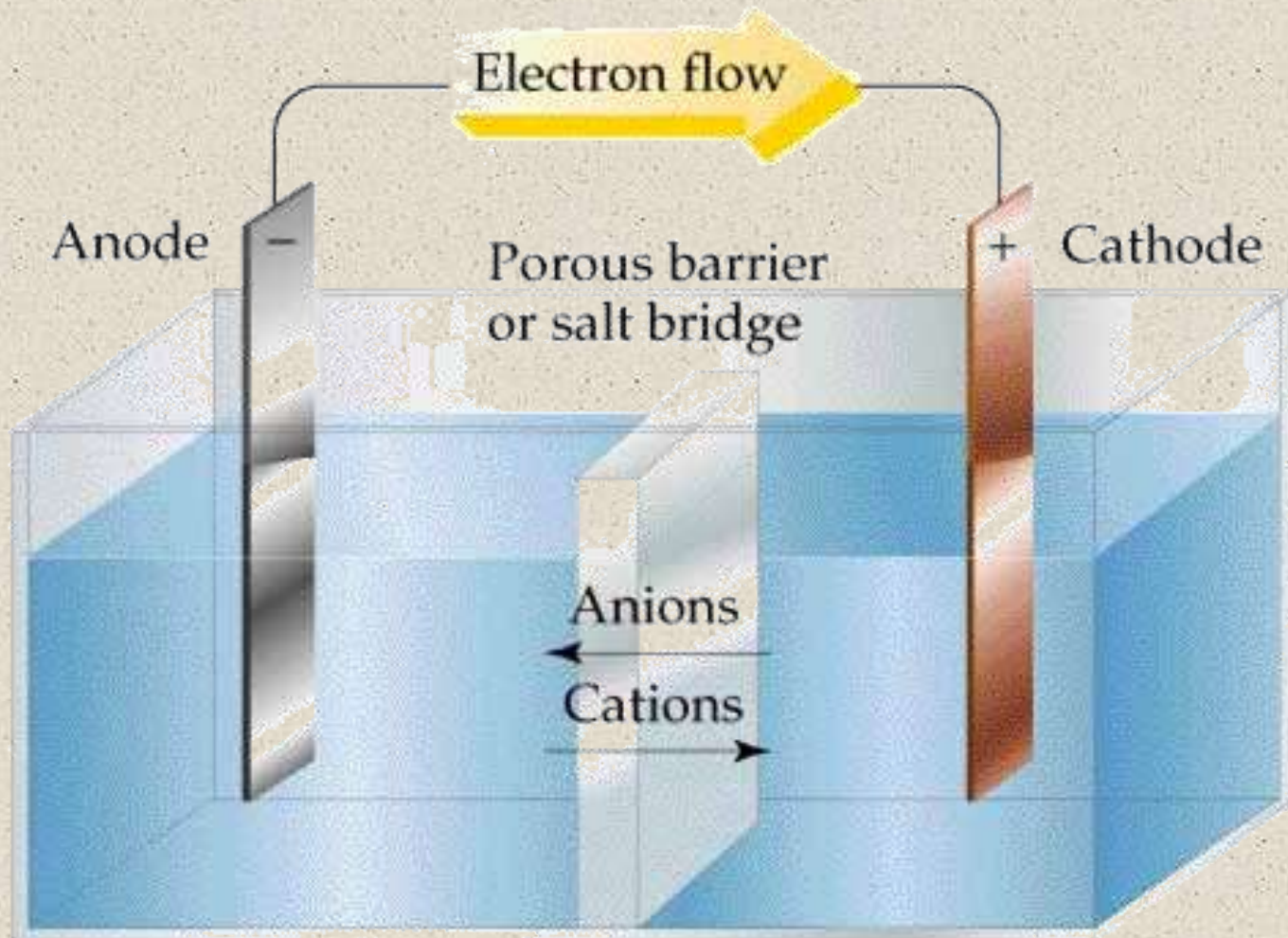
❖ To obtain a useful current , we separate the oxidizing and reducing agents so that electron transfer occurs though an external wire.

❖ This is accomplished in galvanic or voltaic cell .

Daniell cell



A general Voltaic cell



Anode compartment
Oxidation occurs

Cathode compartment
Reduction occurs

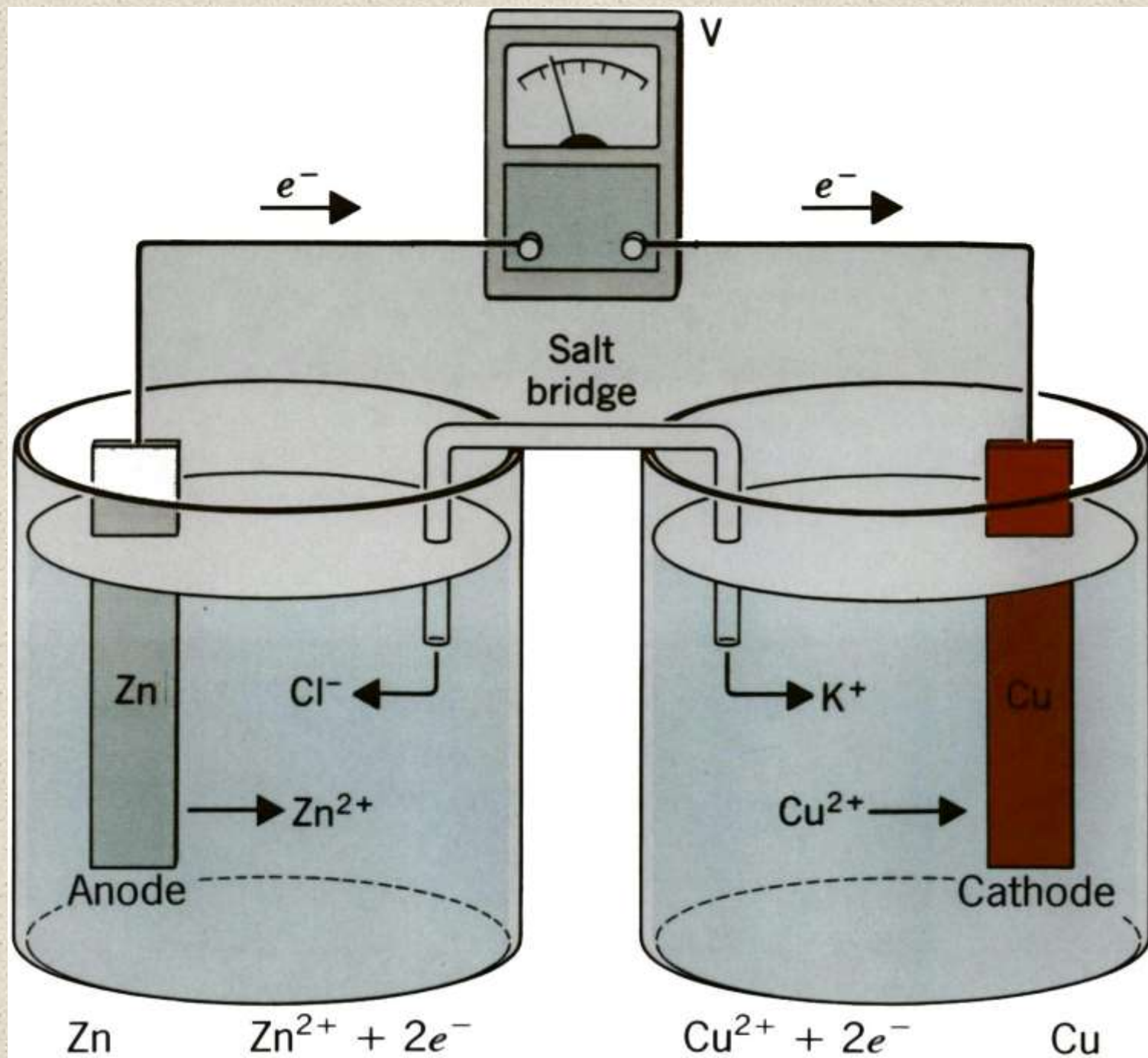
Voltaic cells (cont.)

Anode – electrode at which oxidation occurs

Cathode – electrode at which reduction occurs

Electrons always flow from anode to cathode

Salt bridge – tube that contains an electrolytes , maintains charge neutrality for a voltaic cell



EMF

= electromotive force

= E_{cell}

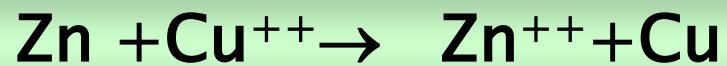
= Cell potential

= Cell voltage ($V = J/C$)

= driving force that moves electrons from anode to cathode

Cell Notation

For reaction



The anode



Cathode

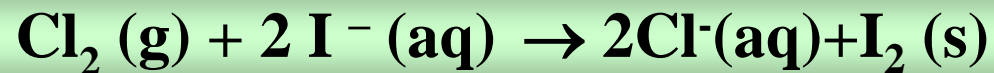


The cell notation is



Anode cathode

Ex.



Cell notation

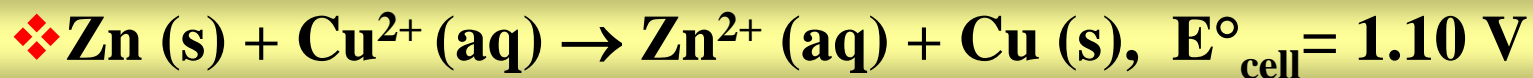


E_{cell}

$$\blacklozenge E_{\text{cell}} = E_{\text{rd.}} + E_{\text{ox.}} \text{ (potential difference)}$$

$$\blacklozenge E^{\circ}_{\text{cell}} = \text{standard cell potential}$$

$$\blacklozenge E^{\circ}_{\text{cell}} = E^{\circ}_{\text{re.}} + E^{\circ}_{\text{ox.}}$$



Note:

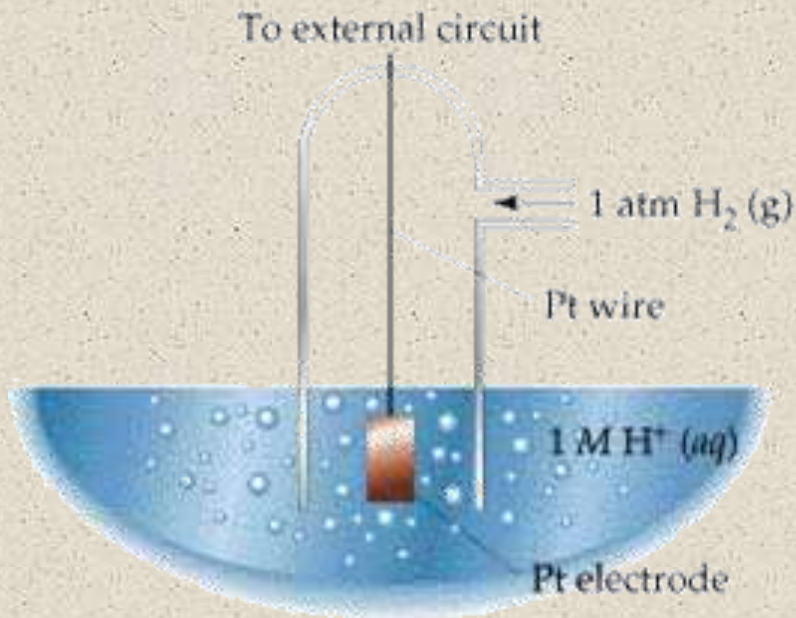
E°_{cell} must be +ve value for cell to operate, (spontaneous)

Electrode potential

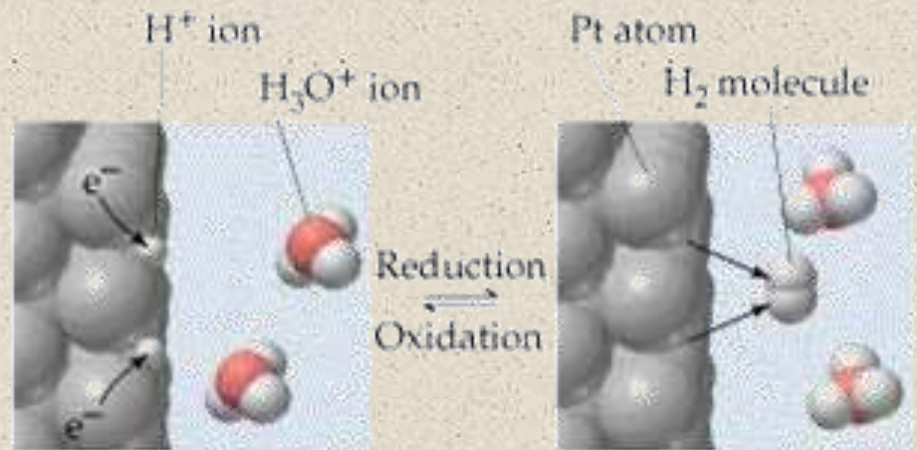
Standard Reduction Potentials, E°_{red}

Common half-reaction (half-cells) are tabulated as reductions.

The standard hydrogen electrode (SHE) is used as reference electrode.

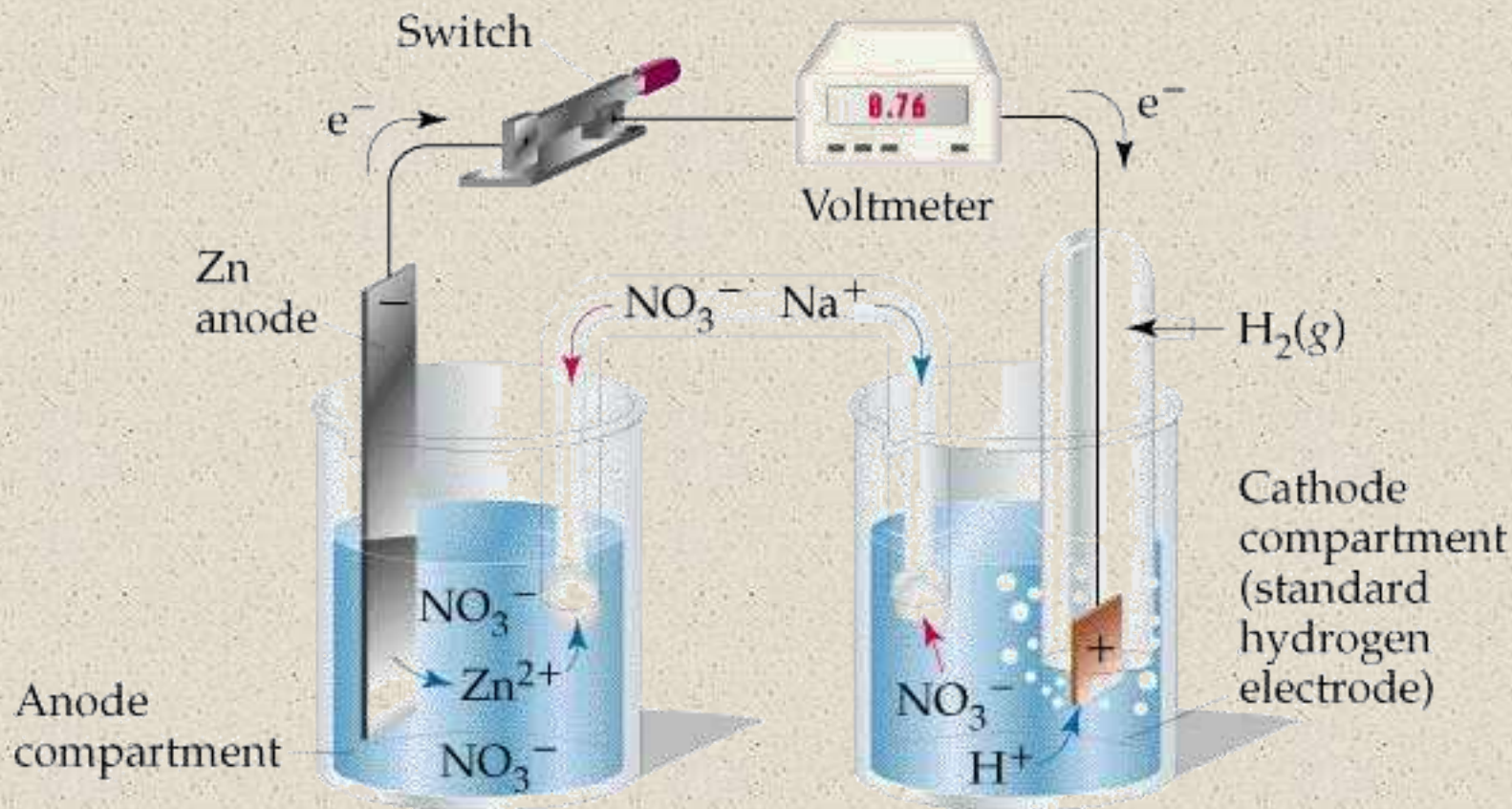


(a)

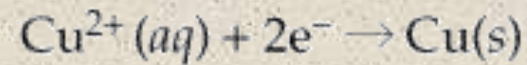
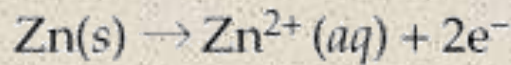
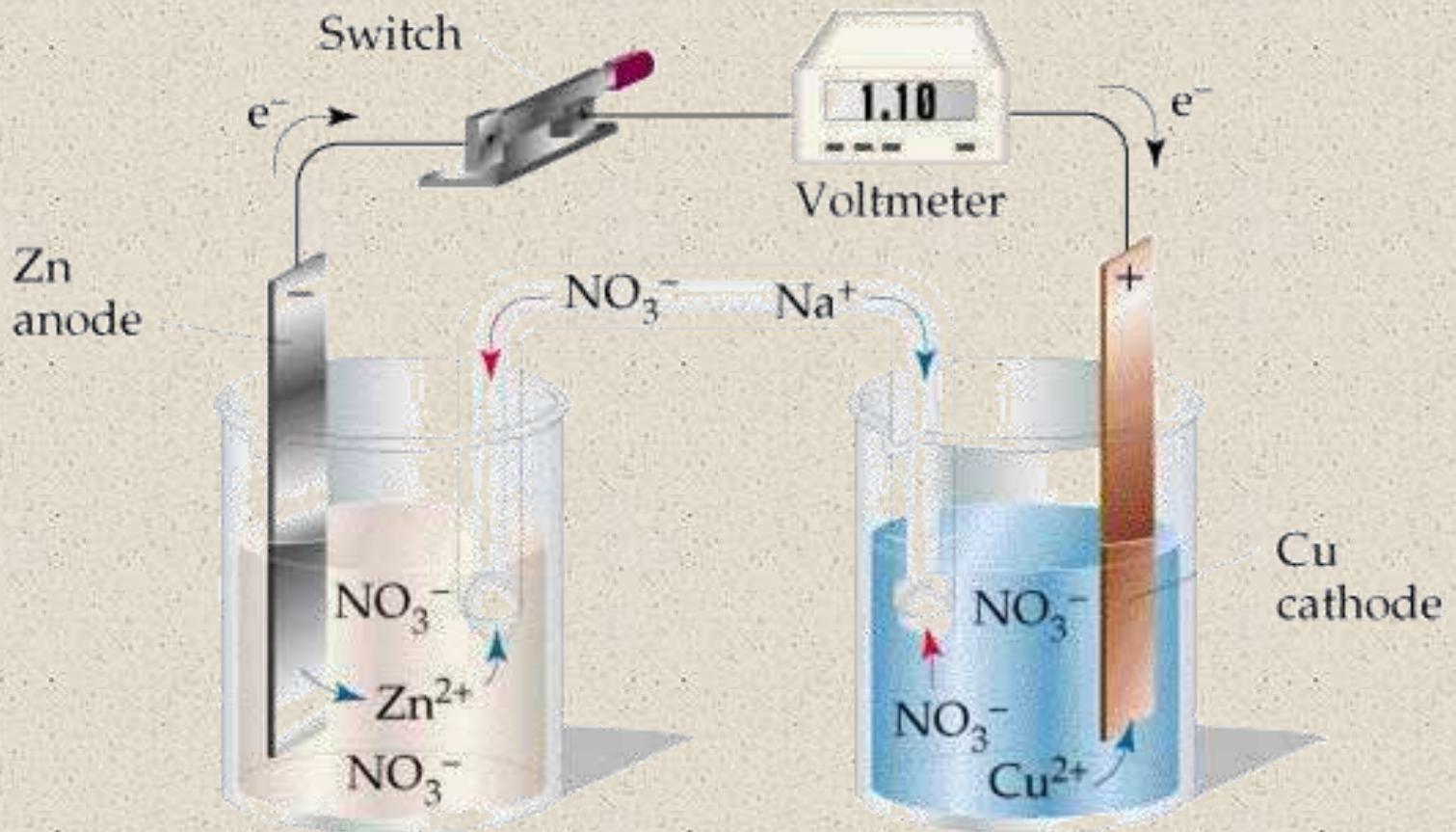


(b)

Voltaic cell using a SHE



Voltaic cell



Movement of cations \rightarrow

Movement of anions \leftarrow

Important Points about Standard Reduction Potentials

Changing the coefficients does not affect E°



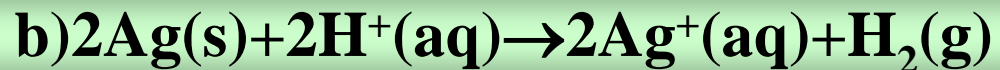
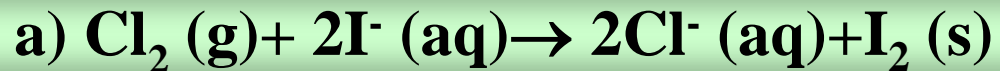
- Reversing the RXN reverses the sign of E°



- The more $\oplus E^\circ$ is,
the greater the driving force of the RXN

Example:

Use electrode potential to determine whether the following proposed reactions are spontaneous with all substances present at unit activity:



Solution

a) First we have to see who is reduced and who is oxidized .

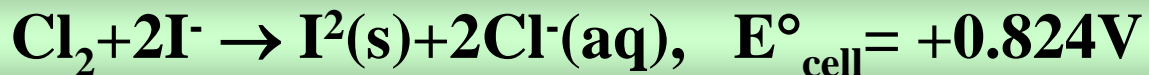
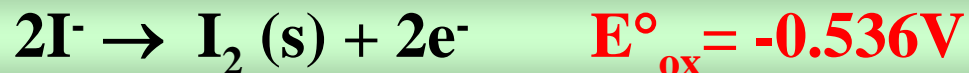
Cl_2 is reduced

I^- is oxidized

Cathode



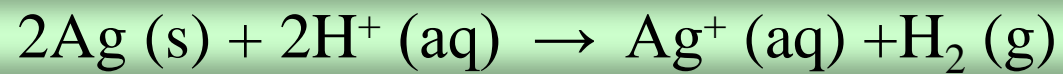
Anode reactor



Cell reaction

Since E°_{cell} is +ve the reaction is spontaneous

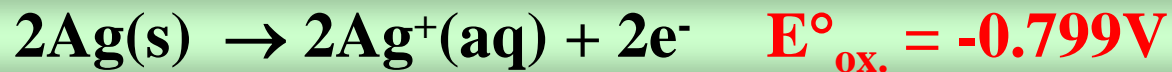
b:



H⁺ is reduced

Ag is oxidized

Anode reaction:



Cathode reaction:



The result is nonspontaneous, $E^\circ_{\text{cell}} = -\text{ve}$

Spontaneity of Redox RXNs

$E > 0$, spontaneous

$$\Delta G = -n F E$$

mol electrons

cell potential

Faraday's Constant
(96500 C/mol)

$$\Delta G^\circ = -n F E^\circ$$

E° and equilibrium constant

$$\Delta G^\circ = - RT \ln K \dots\dots\dots 1$$

$$\Delta G^\circ = - n F E^\circ \dots\dots\dots 2$$

From eqns. (1) and (2) we get

$$E^\circ = (RT/n F) \ln K$$

Example:

a) Use electrochemical data to calculate the value of ΔG° for the reaction



b) If $\Delta H^\circ = - 254.0 \text{ KS}$, calculate ΔS°

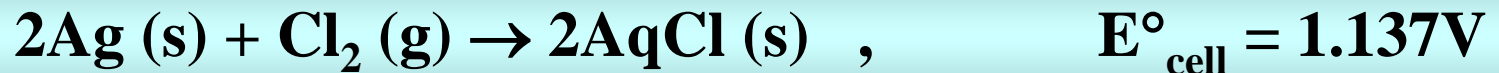
Solution

a) We have to calculate E°_{cell} from the two half cell reactions.

Anode reaction:



Cathode reaction:



$$\Delta G^\circ = -nf E^\circ_{\text{cell}}$$

$$= -2 \times 96500 \times 1.137 \text{ J}$$

$$= -219.4 \text{ kJ}$$

$$\text{b) } \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$- 219.4 \times 1000\text{J} = - 254.0 \times 1000 \text{ J} - 298\Delta S^\circ$$

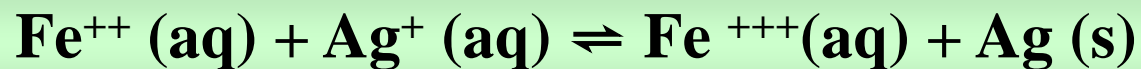
$$\Delta S^\circ = - \frac{(254.0 - 219.4) 1000\text{J}}{298 \text{ K}}$$

$$= - 116 \text{ J/K}$$

Is this agree with the 2nd. Law of thermodynamics?

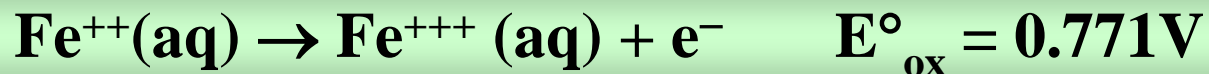
Example

Use electrochemical data to calculate the equilibrium constant K for the following reaction at 25°C



Solution

Anode reaction:



Cathode reaction



$$E^{\circ}_{\text{cell}} = - (RT / nF) \ln K$$

$$0.028 = - (8.314 \times 298 / 1 \times 96500) \ln K$$

$$\therefore \ln K = 1.091$$

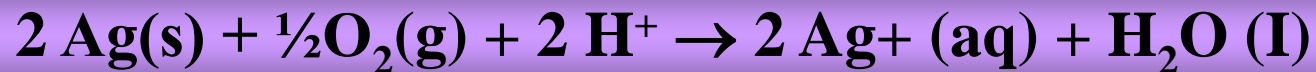
$$\therefore K = 2.98$$

Sample

Use Table 18.2 (or App.) to calculate ΔG° for:



b) Recalculate ΔG° , supposing the RXN were written as : (2)



Effect of concentration on cell potential

The Nernst Equation

$$\Delta G = \Delta G^\circ + RT \ln Q$$

$$-nFE = -nFE^\circ + RT \ln Q$$

$$E = E^\circ - RT \ln Q / nF$$

Nonstandard

standard

“correction term”

At equilibrium, $E^\circ = RT \ln K / nF$

Example

What is the electrode potential of Zn^{++}/Zn electrode in which the concentration of $\text{Zn}^{++} = 0.1\text{M}$.

Solution



$$E = E^\circ - \frac{RT}{nF} \ln Q$$

We have to calculate the value of Q as:

$$Q = \frac{(\text{Zn})}{(\text{Zn}^{++})} = \frac{1}{0.1}$$

$$E = -0.75 - \left(\frac{8.314 \times 298}{2 \times 96500} \ln(1/0.1) \right)$$

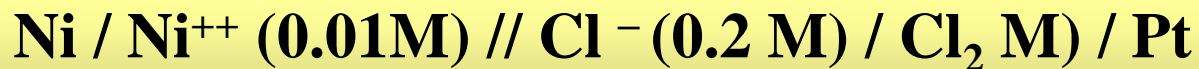
$$= -0.76 - 0.0128 (2.303)$$

$$= -0.76 - 0.0257$$

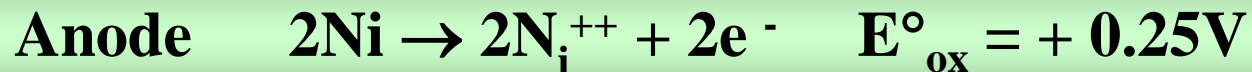
$$= -0.79V$$

Example

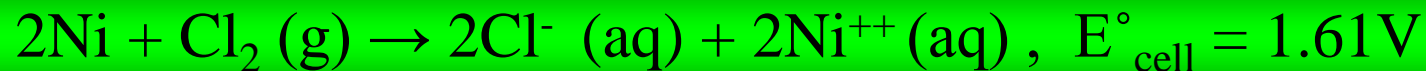
What is the potential for the cell :



Solution



Cathode



$$Q = [\text{Cl}^-]^2 [\text{Ni}^{++}] / P_{\text{Cl}_2}$$

Since $n = 2$

$$E = E^\circ - RT \ln Q / nF$$

$$= 1.61 - \frac{8.314 \times 298 \ln (0.2)^2 (0.01)}{2 \times 96500 \quad 1}$$

$$= 1.61 + 0.10$$

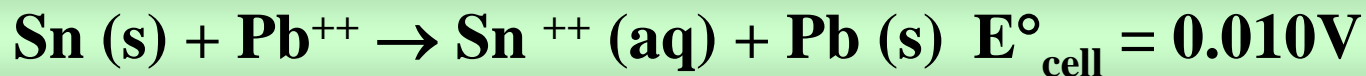
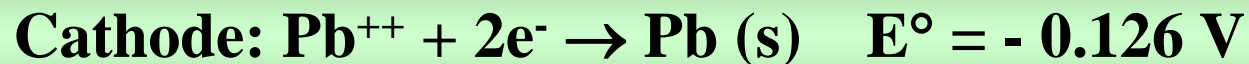
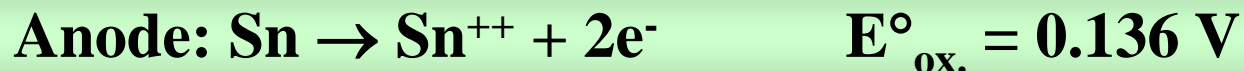
$$= 1.71\text{V}$$

Example

What is the E for the cell :



Solution



$$Q = [\text{Sn}^{++}] / [\text{pb}^{++}] = (1.0) / (0.001)$$

$$n = 2$$

$$E = E^\circ - (RT / nF) \ln Q$$

$$E = 0.01 - (8.314 \times 298 / 2 \times 96500) \ln (1.0 / 0.001)$$

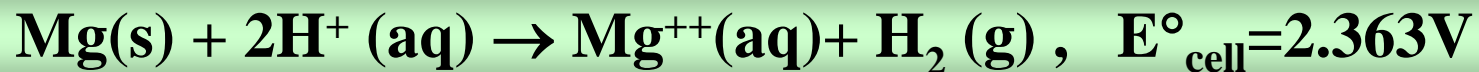
$$= 0.01 - 0.089$$

$$= -0.079 \text{ V}$$

What is this result mean?

Example

Consider a cell reaction



What is the concentration of $\text{H}^+(\text{aq})$ in a cell in which $[\text{Mg}^{++}] = 1.00\text{M}$ and $P_{\text{H}_2} = 1.0\text{atm}$, if the $E_{\text{cell}} = 2.099\text{V}$?

Solution

$$Q = [\text{Mg}^{++}] \text{PH}_2 / [\text{H}^2]$$

$$Q = 1 \times 1 / [\text{H}^+]^2$$

Since $n = 2$

$$E = E^\circ_{\text{cell}} - (RT / nF) \ln 1 / [\text{H}^+]^2$$

$$2.099 = 2.363 - \frac{8.314 \times 298}{2 \times 96500} \ln [\text{H}^+]^{-2}$$

$$2.099 - 2.363 = -0.0128 \ln [\text{H}^+]^{-2}$$

$$-0.264 = 0.0257 \ln [\text{H}^+]$$

$$\ln [\text{H}^+] = -10.272$$

$$[\text{H}^+] = 3.5 \times 10^{-5} \text{ M}$$