Module 11

Oxidation-Reduction & Electrochemistry

Session Slides with Notes

$$-C-\overset{H}{\underset{H^{+1}}{C^{-2}}}-C + \overset{0}{O_2} \longrightarrow \overset{-2}{O}=\underset{+4}{C}=O + H-\overset{-2}{O}-H^{+1}$$

ox #s

H 2.20																	He
Li 0.98	Be 1.57											B 2.04	C 2.55	N 3.04	O 3.44	F 3.98	Ne
Na 0.93	Mg 1.31											Al 1.61	Si 1.90	P 2.19	S 2.58	Cl 3.16	Ar
K 0.82	Ca 1.00	Sc 1.36	Ti 1.54	V 1.63	Cr 1.66	Mn 1.55	Fe 1.83	Co 1.88	Ni 1.91	Cu 1.90	Zn 1.65	Ga 1.81	Ge 2.01	As 2.18	Se 2.55	Br 2.96	Kr 3.00
Rb 0.82	Sr 0.95	Y 1.22	Zr 1.33	Nb 1.6	Mo 2.16	Tc 1.9	Ru 2.2	Rh 2.28	Pd 2.20	Ag 1.93	Cd 1.69	In 1.78	Sn 1.96	Sb 2.05	Te 2.1	I 2.66	Xe 2.60
Cs 0.79	Ba 0.89	*	Hf 1.3	Ta 1.5	W 2.36	Re 1.9	Os 2.2	Ir 2.20	Pt 2.28	Au 2.54	Hg 2.00	Tl 1.62	Pb 2.33	Bi 2.02	Po 2.0	At 2.2	Rn 2.2
Fr 0.7	Ra 0.9	**	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Uub	Uut	Uuq	Uup	Uuh	Uus	Uuo

*	La 1.1	Ce 1.12	Pr 1.13	Nd 1.14	Pm 1.13	Sm 1.17	Eu 1.2	Gd 1.2	Tb 1.1	Dy 1.22	Ho 1.23	Er 1.24	Tm 1.25	Yb 1.1	Lu 1.27
**	Ac 1.1	Th 1.3	Pa 1.5	U 1.38	Np 1.36	Pu 1.28	Am 1.13	Cm 1.28	Bk 1.3	Cf 1.3	Es 1.3	Fm 1.3	Md 1.3	No 1.3	Lr 1.3

$$CuSO_4 + 2NaOH \longrightarrow Cu(OH)_2 + Na_2SO_4$$

no oxidation #'s change

metathesis reaction

ox #

$$\overset{+3}{Fe_2}\overset{-2}{O_3} + 3\overset{+2}{C}\overset{-2}{O} \longrightarrow 2\overset{0}{Fe} + 3\overset{+4}{C}\overset{-2}{O_2}$$

oxidation-reduction reaction

Iron oxidized carbon.

Carbon reduced iron.

ox #s

$$2\,\overset{0}{Cu}(s) + \overset{0}{O_2}(g) \longrightarrow 2\,\overset{+2}{Cu}\overset{-2}{O}(s)$$

Oxygen oxidized copper.

$$\overset{+2}{Cu}\overset{-2}{O}(s) + \overset{0}{H_2}(g) \longrightarrow \overset{0}{Cu}(s) + \overset{+1}{H_2}\overset{-2}{O}(g)$$

Copper oxidized hydrogen.

Hydrogen reduced copper.

The oxidation number of an atom is zero in a neutral substance that contains atoms of only one element.

O_2 H_2 C *(graphite)*

The oxidation number of simple ions is equal to the charge on the ion.

Na^+ Cl^- Mg^{2+}

The oxidation number of hydrogen is +1 when it is combined with a nonmetal.

CH_4 NH_3 H_2O

The oxidation number of hydrogen is -1 when combined with a metal.

NaH MgH_2 $LiAlH_4$

Hydride

In compounds the metals in Group IA have an oxidation number of +1.

ox # $\underset{+1}{K}\underset{+3}{N}\overset{-2}{O_2}$

LiF

Na_2S

In compounds the metals in Group IIA have an oxidation number of +2.

MgH_2 $CaCO_3$ BeO

Oxygen usually has an oxidation number of -2.

H_2O CO_2 MgO

exceptions

$O=O$

$\overset{+2}{O}$

$F-O-F$

$R-O-\underset{-1}{O}-H$

ox #

peroxides

Halogens usually has an oxidation number of -1

AlF_3 HBr $ZnCl_2$

hypochlorite

The sum of the oxidation numbers in a neutral compound is zero, and the sum of the oxidation numbers in a polyatomic ion is equal to the charge on the ion.

SO_4^{-2}

H_2CO_3

+7

$KMnO_4$

+1 -2

ox # 0 0 +3 -1

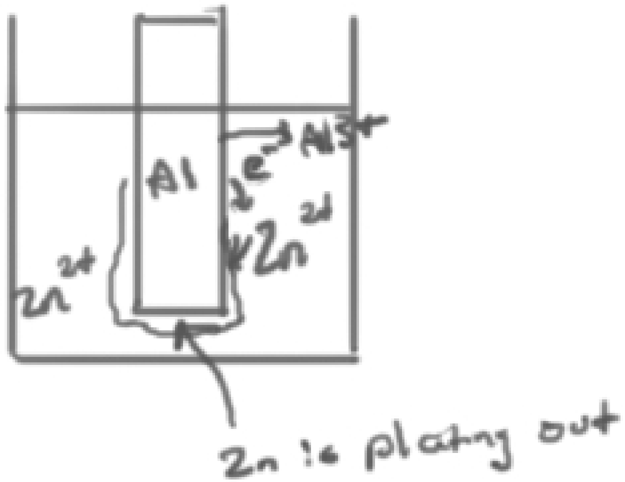
$$2\,Fe + 3\,Cl_2 \longrightarrow 2\,FeCl_3$$

ox #

$$4\,\overset{0}{Al} + 3\,\overset{0}{O_2} \longrightarrow 2\,\overset{+3}{Al_2}\overset{-2}{O_3}$$

$$2\,Al_2 + 3\,Zn^{2+} \longrightarrow 2\,Al^{3+} + 3\,Zn$$

Zinc is oxidizing aluminum.



ox #'s

$$\overset{0}{2\,Al} + \overset{+3\quad -2}{Fe_2O_3} \longrightarrow \overset{+3\quad -2}{Al_2O_3} + \overset{0}{2\,Fe}$$

Fe - oxidizing agent

Al - reducing agent

ox#

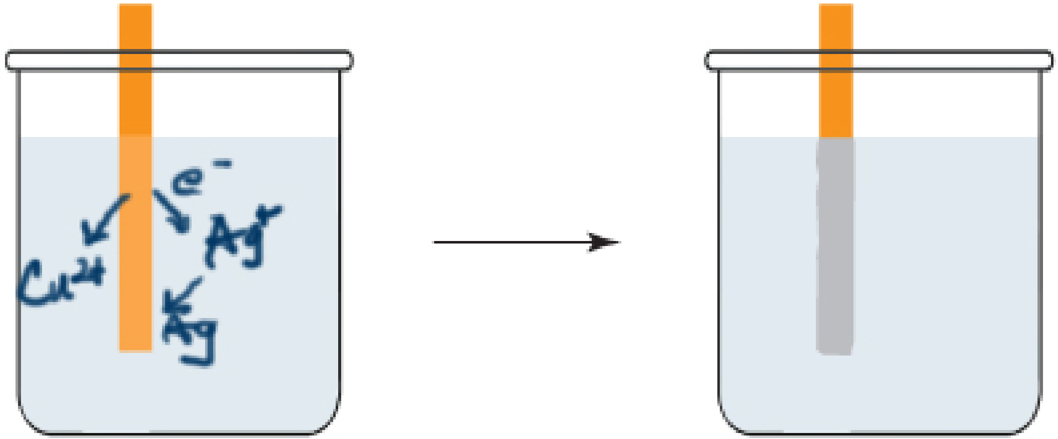
$$3\,\overset{0}{Ag} + 4\,\overset{+1}{H}\overset{+5}{N}\overset{-2}{O_3} \longrightarrow 3\,\overset{+1}{Ag}\overset{+5}{N}\overset{-2}{O_3} + 2\,H_2O + \overset{+2}{N}\overset{-2}{O}$$

Oxidizing agent = N (one of them)

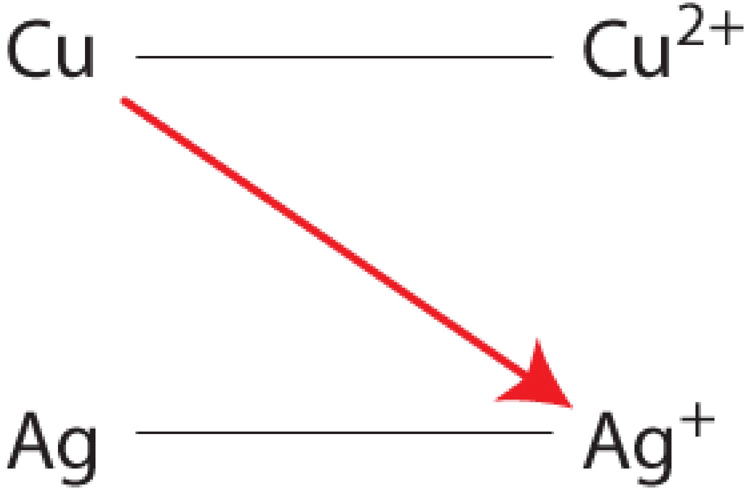
Reducing agent = Ag

$$Cu(s) + 2\,Ag^{+}(aq) \longrightarrow Cu^{2+}(aq) + 2\,Ag(s)$$

Ag^{+} oxidized Cu



$$Cu(s) + 2\,Ag^{+}(aq) \longrightarrow Cu^{2+}(aq) + 2\,Ag(s)$$



the fall of the electron

ΔG / mol e− transferred from H_2

$K^+ + e^- \rightarrow K$

$Na^+ + e^- \rightarrow Na$

good reducing agents

+ 300

+ 200

$Al^{3+} + 3e^- \rightarrow Al$

+ 100

$Zn^{2+} + 2e^- \rightarrow Zn$

$Fe^{2+} + 2e^- \rightarrow Fe$

$Ni^{2+} + 2e^- \rightarrow Ni$

$2H^+ + 2e^- \rightarrow H_2$

0

$Cu^{2+} + 2e^- \rightarrow Cu$

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

$Ag^+ + e^- \rightarrow Ag$

− 100

$O_2 + 4H^+ + 4e^- \rightarrow H_2O$

$Cl_2 + 2e^- \rightarrow Cl^-$

− 200

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

$O_3 + 2H^+ + 2e^- \rightarrow O_2 + 4H_2O$

$F_2 + 2e^- \rightarrow F^-$

− 300

good oxidizing agents

Reacting potassium metal with pure water produces

a. potassium oxide, K_2O
b. a basic solution
c. an acidic solution
d. oxygen gas

$$2K + 2H_2O \longrightarrow H_2 + 2OH^-$$

Reducing Agents

$LiAlH_4$
lithium aluminium hydride

$NaHg$
sodium amalgum

$NaBH_4$
sodiuim borohydride

H_2
hydrogen

Metals

Carbon

Hydrocarbons

Oxidizing Agents

O_2
oxygen

O_3
ozone

F_2
fluorine

Cl_2
chlorine

Br_2
bromine

I_2
iodine

OCl^-
hypochlorite

ClO_3^-
chlorate

HNO_3
nitric acid

CrO_3
chromium trioxide

CrO_4^{2-}
chromate

$Cr_2O_7^{2-}$
dichromate

H_2O_2
peroxides

MnO_4^-
permanganate

$Cu^{2+} + Zn \longrightarrow Cu + Zn^{2+}$

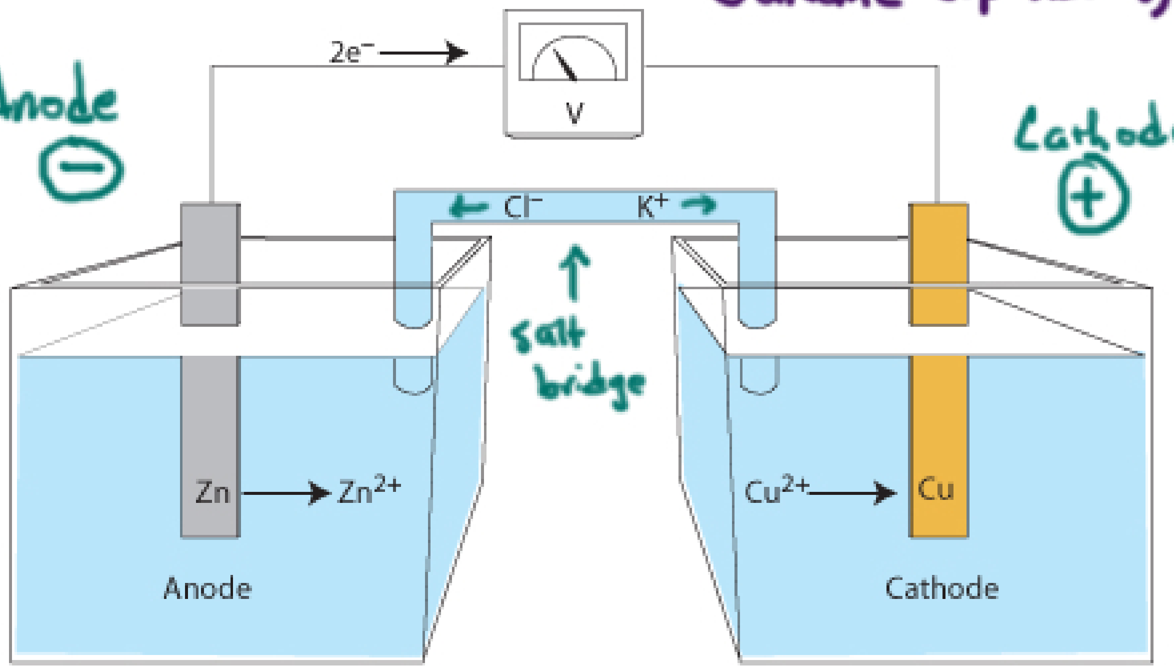
Electrochemistry

Galvanic (spontaneous)

Anode
$\ominus$

Cathode
$\oplus$

galvanic anode is $\ominus$



$Zn \longrightarrow Zn^{2+} + 2e^-$

oxidation half reaction

$Cu^{2+} + 2e^- \longrightarrow Cu$

reduction half reaction

$Zn \mid Zn^{2+}(1.0\ M) \parallel Cu^{2+}(1.0\ M) \mid Cu$

standard reduction potentials

$E°$ (V)	Half-reaction
−2.93	$K^+ + e^- \rightarrow K$
−2.71	$Na^+ + e^- \rightarrow Na$
−1.66	$Al^{3+} + 3\,e^- \rightarrow Al$
−0.76	$Zn^{2+} + 2\,e^- \rightarrow Zn$
−0.44	$Fe^{2+} + 2\,e^- \rightarrow Fe$
−0.25	$Ni^{2+} + 2\,e^- \rightarrow Ni$
0	$2\,H^+ + 2\,e^- \rightarrow H_2$
+0.16	$Cu^{2+} + 2\,e^- \rightarrow Cu$
+0.77	$Fe^{3+} + e^- \rightarrow Fe^{2+}$
+0.80	$Ag^+ + e^- \rightarrow Ag$
+1.23	$O_2 + 4\,H^+ + 4\,e^- \rightarrow H_2O$
+1.36	$Cl_2 + 2\,e^- \rightarrow Cl^-$
+1.51	$MnO_4^- + 8\,H^+ + 5\,e^- \rightarrow Mn^{2+} + 4\,H_2O$
+2.08	$O_3 + 2\,H^+ + 2\,e^- \rightarrow O_2 + 4\,H_2O$
+2.87	$F_2 + 2\,e^- \rightarrow F^-$

ΔG / mol e− transferred from H_2

+300

+200

+100

0

− 100

− 200

− 300

Faraday (F) = $\frac{96500\ C}{mol\ e^-}$

$\Delta G = -nFE$

$E = E°_{reduction} - E°_{oxidation}$

$1.23\ V - -0.76\ V \approx 2\ V$

The anode and cathode reactions for the silver oxide battery are respectively as follows:

$$Zn\,(s) + 2OH^-\,(aq) \longrightarrow Zn(OH)_2\,(s) + 2e^-$$
$$Ag_2O\,(s) + H_2O + 2e^- \longrightarrow 2Ag\,(s) + 2OH^-(aq)$$

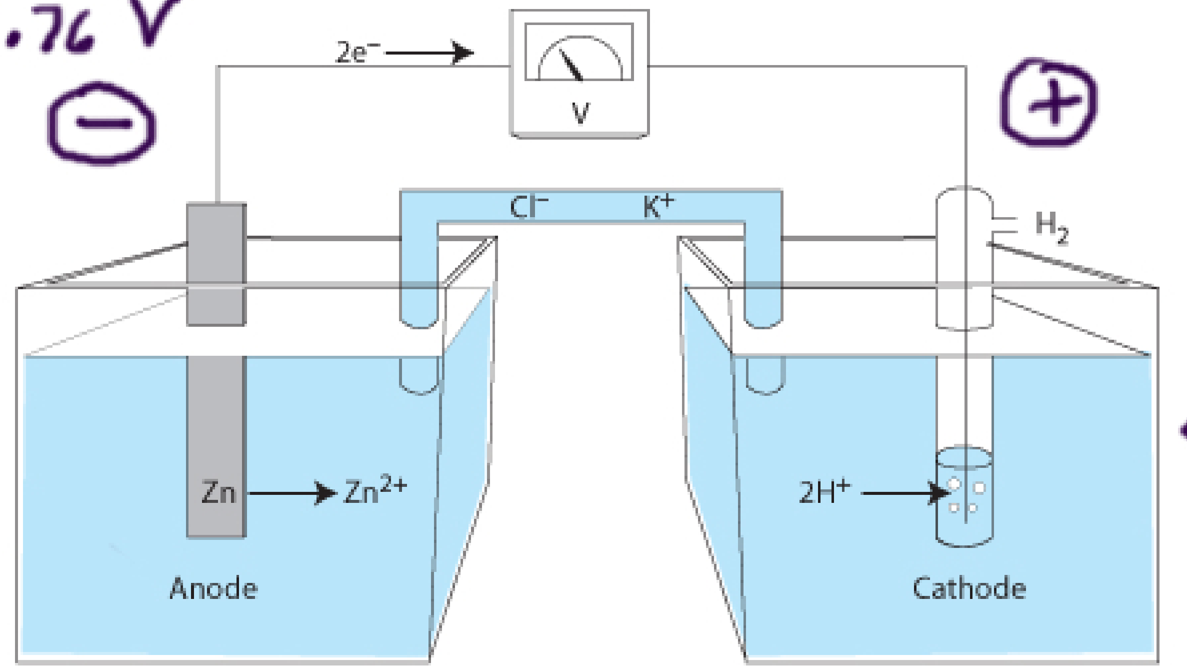
The standard reduction potential of Zn^{2+} is –0.762, and the standard reduction potential of Ag+ is 0.800 V. What is the approximate emf of the silver oxide battery?

a. 0.04 V
b. 0.8 V
c. 1.6 V
d. 2.4 V

-0.76 V

$\ominus$

$\oplus$



← standard hydrogen electrode

$$Zn \longrightarrow Zn^{2+} + 2e^- \qquad\qquad 2H^+ + 2e^- \longrightarrow H_2$$

Stoichiometry in electrochemistry often involves converting to DC current parameters.

Faraday = $\frac{96500\ C}{mol\ e^-}$

Commercial aluminum is formed electrolytically from aluminum oxide (Al_2O_3), which is reduced at the cathode. Approximately how long must a current of 965*A* be applied to form

1 mol → 27 g of aluminum?

(Note that 96500 *C* = 1 mole e^-)

$Al^{3+} + 3e^- \longrightarrow Al$

$\frac{1\ mol\ Al}{3\ mol\ e^-}$ $\frac{3\ mol\ e^-}{mol\ Al}$

a. 1 second

b. 1 1/2 minutes

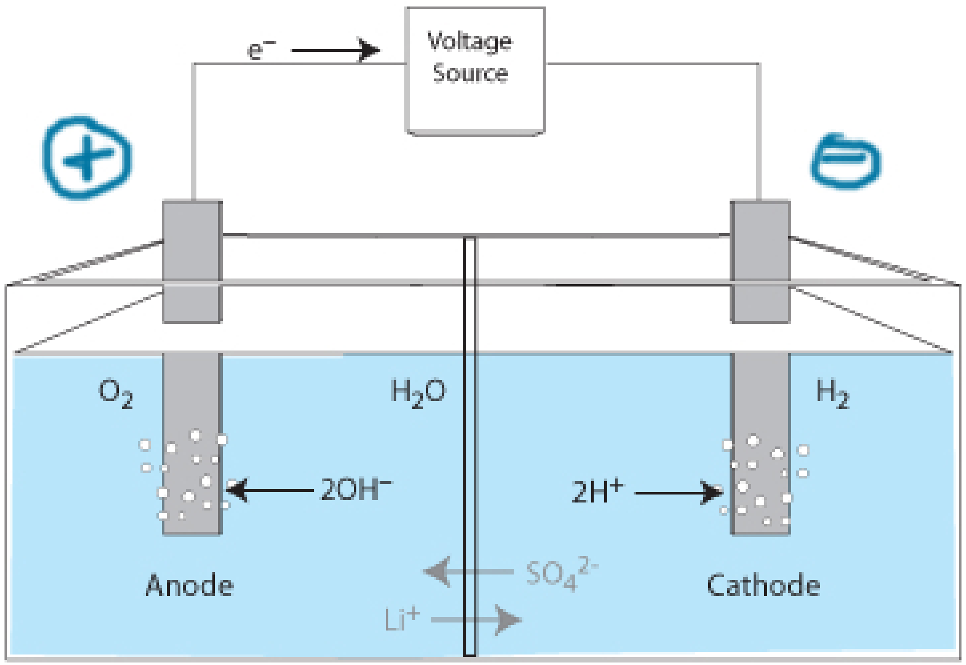
c. 5 minutes

d. 300,000 seconds

$\frac{3\ mol\ e^-}{mol\ Al} \cdot 1\ mol\ Al \cdot \frac{96500\ C}{mol\ e^-} \cdot \frac{1\ s}{965\ C} = 300\ s$

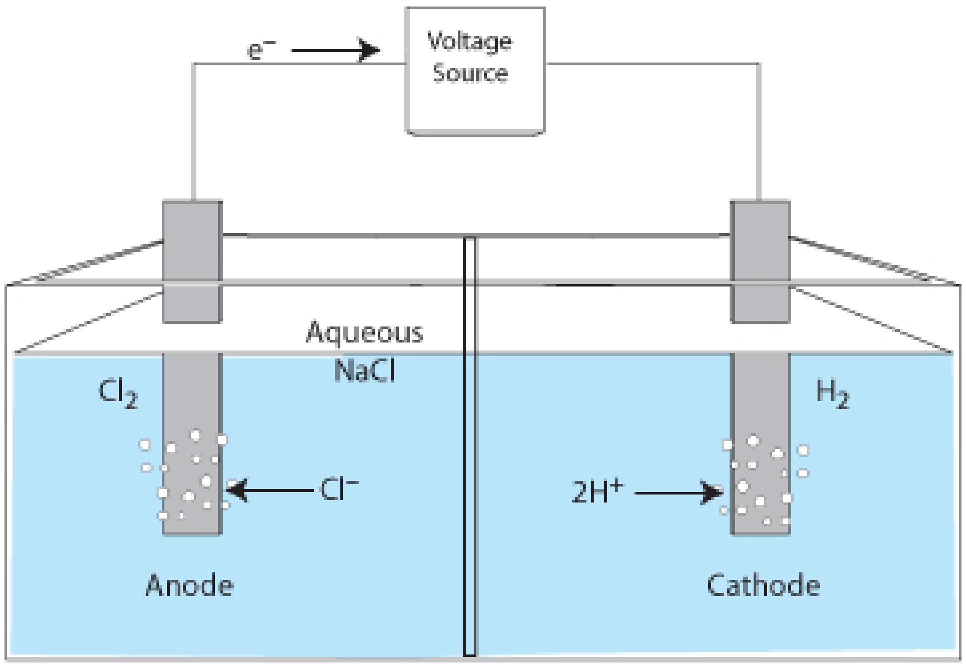
Electrolytic Cell

Anode is ⊕ in an electrolytic cell.



$$2H_2O \longrightarrow O_2 + 4H^+ + 4e^- \qquad\qquad 2H^+ + 2e^- \longrightarrow H_2$$

Electrolysis of brine (concentrated NaCl)



$2Cl^- \longrightarrow Cl_2 + 2e^-$

$2H^+ + 2e^- \longrightarrow H_2$

Nernst equation →

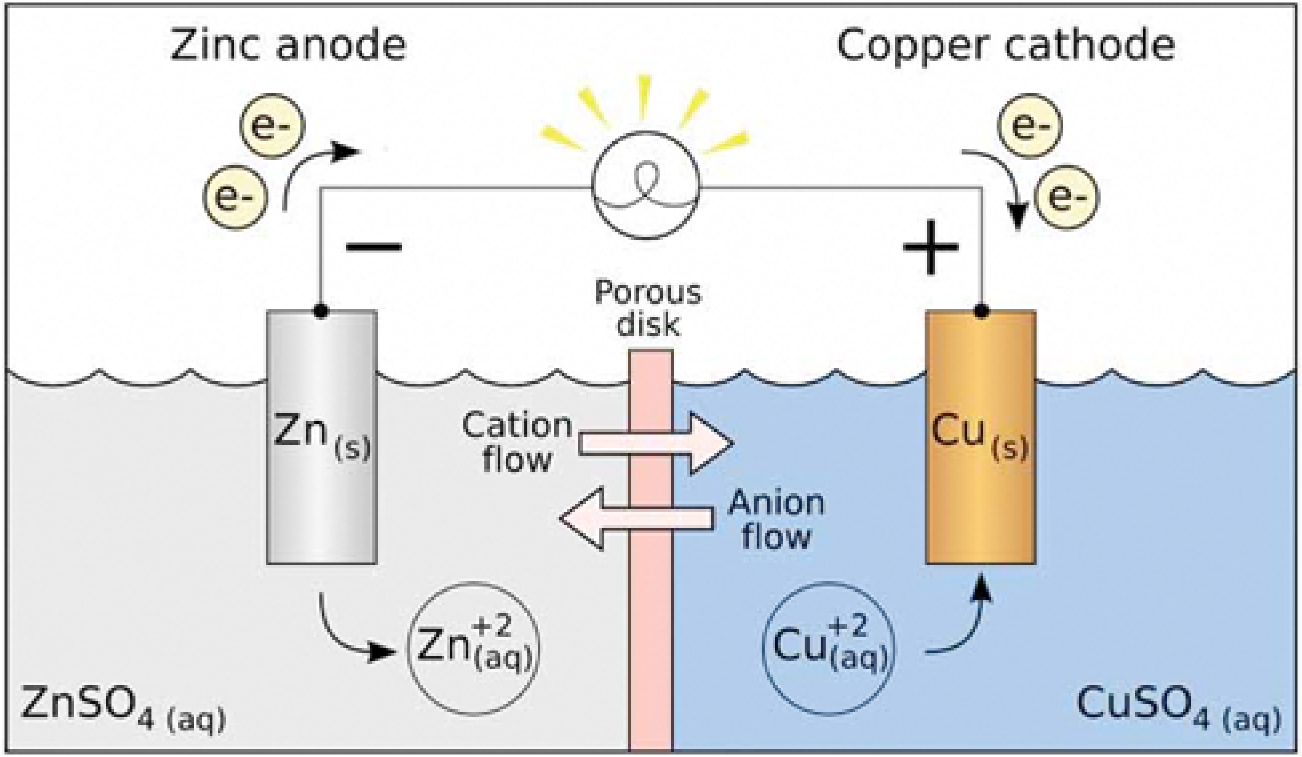
$$\Delta E = \Delta E^{o} - \frac{0.0592\ V}{n} \log Q$$

$\Delta G = \Delta G^{o} + 2.3 RT \log Q$

$Q = \frac{[B]}{[A]}$

as $\Delta G \rightarrow 0$

$Q \rightarrow K$



$Zn \longrightarrow Zn^{2+} + 2e^{-}$ $\qquad$ $Cu^{2+} + 2e^{-} \longrightarrow Cu$