Chapter 21: Electrochemistry

Electrochemistry deals with
(1) chemical changes produced by an electric current, and
(2) the production of electicity by chemical reactions

∴ it has provided much information about chemical reactions as we shall see.

In electrochemical reactions, there is ALWAYS a transfer of electrons.
∴ electrochemical reactions are REDOX reactions – a chemical species will be oxidized while a species is being reduced. The two half-reactions are separated physically in a cell and electrons flow between the two half-cells.

Note: Recall that current can flow in 2 ways
(1) metallic conduction: conduction of electical current by the flow of electrons along a metal wire or metal surface.
(2) ionic or electolytic conduction: conduction of electrical current by the motion of ions in a solution or a pure liquid (eg molten salt)

Both kinds of conduction occurs in electrochemical cells.

In the electrochemical cell, the oxidation and reduction half-reactions occur at electrodes, which may or may not participate in the reaction. If they do not participate, the electrodes are called INERT.

cathode: the electrode where reduction occurs + electrons are gained by a species
(hint: cations go to the cathode to get reduced)
anode: the electrode where oxidation occurs + electrons are lost by a species
(hint: anions go to the anode to get oxidized)

There are 2 types of electrochemical cells :

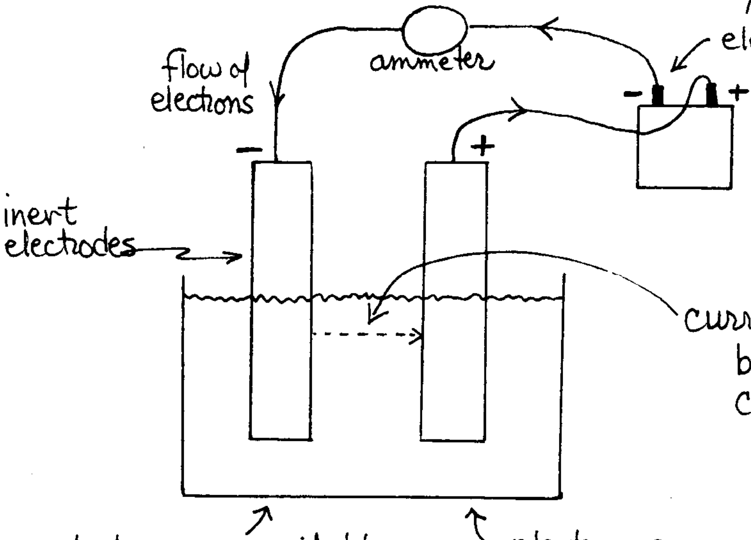
(1) electrolytic cell : cell in which electrical energy causes non-spontaneous chemical reactions to occur ($\Delta G > 0$).

(2) voltaic or galvanic cell : cell in which spontaneous chemical reactions produce electrical energy. ($\Delta G < 0$).

To restate, the electrolytic cell requires energy (from a battery) to go and the voltaic cell produces energy. Therefore a voltaic cell is a battery of sorts.

ELECTROLYTIC CELL

The process by which non-spontaneous reactions are forced to go in an electrochemical cell is called electrolysis.



electrons are produced at the negative terminal of the battery.

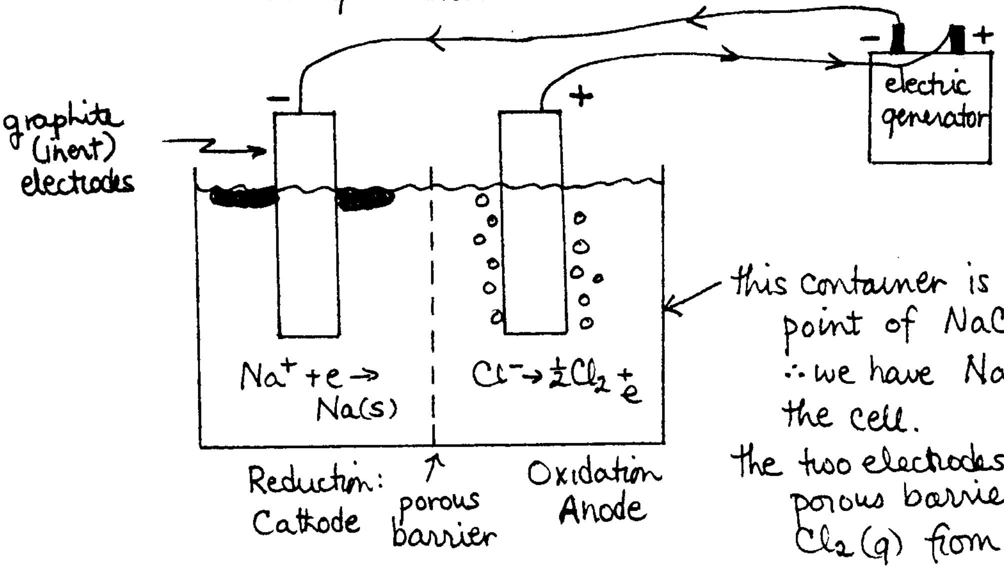
current is carried through the solution by the movement of ions, thereby completing the electrical circuit.

electrons are available at this electrode to participate in reactions
∴ e^- are a reactant
eg $M^+ + e \rightarrow M$
∴ reduction occurs here
∴ this is the
CATHODE

electrons are produced at this electrode and flow back to the battery
∴ reaction that occurs here produces e^-
eg $X^- \rightarrow X + e^-$
∴ oxidation occurs here
∴ this electrode is the ANODE

Examples: Electrolysis of Molten Sodium Chloride (Downs Cell)

This process is used for the commercial production of metallic sodium(s) – a very reactive metal.



this container is heated to T > melting point of NaCl (98.7°C)
∴ we have Na^+ ions and Cl^- ions in the cell.
the two electrodes are separated by a porous barrier to prevent Na(s) and $Cl_2(g)$ from combining + exploding.

Observations:

(1) a pale green gas, Cl_2, is liberated at one electrode
(2) molten, silvery white metallic Na forms at the other electrode and rises to the top

$$Na^+ + e \rightarrow Na(s) \qquad \text{reduction – cathode}$$
$$Cl^- \rightarrow \tfrac{1}{2}Cl_2(g) + e \qquad \text{oxidation – anode}$$
$$\underbrace{Na^+ + Cl^-}_{\text{molten NaCl}} \rightarrow Na(s) + \tfrac{1}{2}Cl_2(g) \qquad \text{overall reaction in the cell.}$$

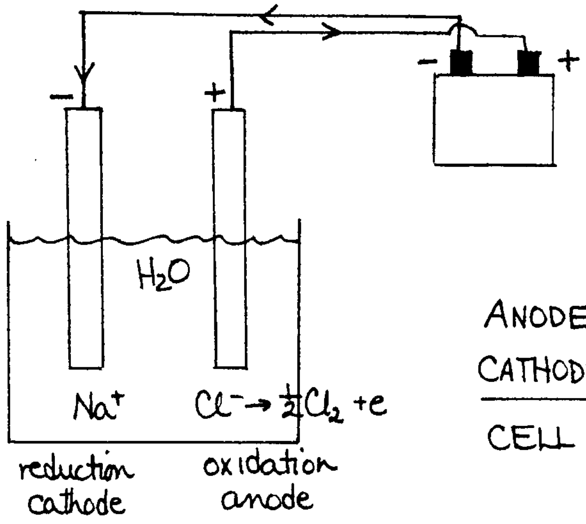
Electrolysis of Aqueous Sodium Chloride (Using Pt electrodes)

Observations:

(1) gaseous H_2 is evolved at one electrode and the solution becomes basic around the electrode
(2) gaseous Cl_2 is liberated at the other electrode

These are different observations from the electrolysis of molten NaCl. Why?

Ans. In electrochemistry, the most easily oxidized species is oxidized and the most easily reduced species is reduced.



$$\begin{array}{lcl} \text{ANODE}: & & Cl^- \rightarrow \frac{1}{2}Cl_2 + e \\ \text{CATHODE}: & & H_2O + e \rightarrow \frac{1}{2}H_2(g) + \dot{O}H^- \\ \hline \text{CELL}: & & H_2O + Cl^- \rightarrow \frac{1}{2}Cl_2 + \frac{1}{2}H_2 + OH^- \end{array}$$

OR

$$2H_2O + 2Cl^- \rightarrow Cl_2 + H_2 + 2OH^-$$

∵ water is more easily reduced than Na^+ ions

This is the commercial preparation for $H_2(g)$, $Cl_2(g)$ and $NaOH(s)$
The $NaOH(s)$ remains in solution until the H_2O is evaporated off.

<u>Electrolysis of Aqueous Sodium Sulphate</u> using Inert Electrodes (Pt)

Observations:

(1) gaseous H_2 is produced at one electrode; the solution becomes basic around the electrode.

(2) gaseous O_2 is produced at the other electrode; the solution becomes acidic around the electrode.

∴ water is the most easily reduced species <u>and</u> the most easily oxidized species. The ions of Na_2SO_4 only carry current in the solution. but take no part in the reaction.

$$\begin{array}{llcll} \text{CATHODE}: & 2\times(2H_2O + 2e & \rightarrow & H_2 + 2OH^-) & \text{reduction} \\ \text{ANODE}: & 2H_2O & \rightarrow & O_2 + 4H^+ + 4e & \text{oxidation} \\ \hline \text{OVERALL}: & 6H_2O & \rightarrow & 2H_2 + O_2 + \underbrace{4H^+ + 4OH^-}_{4H_2O} & \\ \text{NET REACTION}: & 2H_2O & \rightarrow & 2H_2 + O_2 & \end{array}$$

Recall: Electrolysis is the process by which non-spontaneous reactions are forced to go in an electrochemical cell.

Question: How much electrical charge must be supplied to cause a specified amount of reaction to occur?

Faraday's Law of Electrolysis

In 1832, Faraday observed that the amount of substances undergoing reactions at electrodes was proportional to the amount of electricity that passed through the cell.

Physics review

coulomb: amount of charge that passes a given point when 1 ampere flows for 1 second.

$$1 \text{ ampere} = \frac{1 \text{ coulomb}}{1 \text{ second}} \quad \text{or} \quad \boxed{\#\text{ coulombs} = \#\text{ amperes} \times \#\text{ s}}$$

faraday: a unit of charge that is larger than the coulomb

$$1 \text{ faraday} = 96487 \text{ coulombs} \qquad \text{or}$$

$$\boxed{\#\text{ faradays} = \frac{\#\text{ coulombs}}{96487}}$$

But how does a faraday relate to the process of electrolysis?

If 1 faraday of charge passed through an electrolytic cell, this means that 1 mole of electrons (6.023×10^{23} electrons) passed through the cell.

We remember that an equivalent weight of a (oxidizing or reducing agent) substance is the mass of a substance that produces or uses 1 mole of electrons.

∴ faraday is the amount of electricity that
(1) reduces 1 equivalent weight $\left(= \frac{\text{molecular weight}}{\#\,e^- \text{ in half reaction}}\right)$ of a species at the cathode
(2) oxidizes 1 equivalent weight $\left(= \frac{\text{molecular weight}}{\#\,e^- \text{ in half reaction}}\right)$ of a species at the anode

Each of these corresponds to the passage of 1 mole of electrons through the cell.

Example: Consider the half reaction

$$2\,Cl^-(aq) \rightarrow Cl_{2(g)} + 2e^- \qquad \text{oxidation} \quad \text{ANODE}$$

or

$$Cl^-(aq) \rightarrow \tfrac{1}{2}\,Cl_{2(g)} + e^-$$

∴ the equivalent weight of Cl_2 is $\frac{MW}{2} = \frac{70}{2} = 35$

∴ if 1 faraday passes through the electrolytic cell, only $\frac{1}{2}$ mole (35 g) of $Cl_2(g)$ is produced. Under standard temperature and pressure conditions (STP), the volume of Cl_2 gas produced $= 22.4\ L/mol \div 2$
$= 11.2\ L$

∴ moles of product formed in electrolysis $\propto$ amount of electricity passed through the cel

$$\boxed{\text{using faradays:} \quad \overset{\textbf{ACTUAL}}{\frac{\#\text{ moles of product formed}}{\#\text{ Faradays passed}}} = \overset{\textbf{HALF-REACTION}}{\frac{\#\text{ moles of product in half reaction}}{\#\text{ moles of electrons in half reaction}}}}$$

Example: Consider $2Cl^-(aq) \rightarrow Cl_2(g) + 2e$. How many moles of Cl_2 gas would be produced if 3 faradays of charge passed through the cell? How many grams? How many liters at STP?

$$\frac{\text{\# moles of } Cl_2 \text{ formed}}{\text{\# faradays passed}} = \frac{1 \text{ mole of } Cl_2}{2 \text{ moles of electrons} = 2 \text{ Faradays}}$$

$$\begin{aligned}
\therefore \text{ moles of } Cl_2 &= 3 \text{ faradays} \times \tfrac{1}{2} \\
&= 1.5 \text{ moles } Cl_2 \\
\text{mass of } Cl_2 &= 1.5 \text{ mol} \times 71 \text{ g/mol} \qquad 1 \text{ mole} = 71 \text{ g} \\
&= 1.1 \times 10^2 \text{ g} \\
\text{volume of } Cl_2 \text{ at STP} &= 1.5 \text{ mol} \times 22.4 \tfrac{\text{L}}{\text{mol}} \\
&= 34 \text{ L}
\end{aligned}$$

using coulombs : $$\frac{\text{\# moles of product formed}}{\text{\# coulombs passed}} = \frac{\text{\# mole of product in half reaction}}{\text{\# moles of } e^- \times 96487 \text{ coulombs/Far.}}$$

Example: Calculate the mass of palladium produced by the reduction of Pd(II) ions during the passage of 3.20 amperes of current through a solution of palladium(II) sulphate for 30.0 minutes. What if the electrode efficiency were only 65%?

$$Pd^{2+}_{(aq)} + 2e \rightarrow Pd_{(s)}$$

$$\frac{\text{\# moles Pd formed}}{\text{\# coulombs passed}} = \frac{1 \text{ mol of product}}{2 \times 96{,}487}$$

$$\begin{aligned}
\text{\# coulombs} &= \text{\#amperes} \times \text{\# seconds} \\
&= 3.20 \text{ amp} \times \left(30 \text{ min} \times \tfrac{60 \text{s}}{1 \text{ min}}\right) \\
&= 5760 \text{ coulombs}
\end{aligned}$$

$$\therefore \frac{\text{moles Pd}}{5760 \text{ coulombs}} = \frac{1 \text{ mole Pd}}{2 \times 96{,}500}$$

$$\begin{aligned}
\text{\# moles Pd} &= 0.0298 \text{ moles} \\
\text{mass of Pd} &= 0.0298 \text{ moles} \times 106.4 \text{ g/mol} \\
&= 3.18 \text{ g}
\end{aligned}$$

At 65% electrode efficiency, one could produce only 65% of 3.18 g of Pd or $3.18 \times 0.65 = 2.07$ g

Example: While Pd^{2+} is being reduced at the cathode, water is being oxidized at the anode:

$$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$$

For how many days would 3.00 amp of current have to flow to produce 45.0 L of O_2 gas at STP at 100% effeciency? at 65% efficiency?

(a)
$$\frac{\text{mol } O_2 \text{ produced}}{\#\text{ coulombs passed}} = \frac{1 \text{ mole } O_2}{4 \text{ mole } e^- \times 96500}$$

amp × seconds

$$\text{mol } O_2 \text{ produced} = \frac{45.0 \text{ L}}{22.4 \text{ L/mol}} = 2.01 \text{ moles}$$

(or use $PV = nRT$ at STP conditions: 1 atm and 273 K)

∴ substituting
$$\frac{2.01 \text{ mol } O_2}{3.00 \text{ amp} \times t(s)} = \frac{1 \text{ mol } O_2}{4 \text{ mole}^- \times 96500}$$

$$t(s) = 2.59 \times 10^5 \text{ s} \times$$

$$t(\text{days}) = 2.59 \times 10^5 \text{ s} \times \frac{1 \text{ min}}{60 \text{ s}} \times \frac{1 \text{ hr}}{60 \text{ min}} \times \frac{1 \text{ day}}{24 \text{ hr}} = 2.99 \text{ days}$$

(b) To produce the same volume of O_2 at a lower electrode efficiency, the electrolysis would have to continue for a longer period of time (reasonable!)

$$\therefore \text{ time at 65\% efficiency} = \frac{2.99 \text{ days}}{0.65} = 4.60 \text{ days}$$

Notes on Electrode Efficiency (or any % efficiency problem)

efficiency: amount of product made per unit time

$$\%\text{ efficiency} = \frac{\text{actual amount / actual time}}{\text{theoretical amt / theo. time}} \times 100 = \frac{\overset{\text{real cell}}{m/t}}{\underset{\text{perfect cell}}{m_o/t_o}} \times 100$$

Case 1: If a solution is electrolyzed in the real cell and perfect cell for the same time, $t = t_o$ and $\%\text{ efficiency} = \frac{m}{m_o} \times 100$ or $m = m_o \times \frac{\%\text{ efficiency}}{100}$

Case 2: If the same amount of product is made in real cell and perfect cell, $m = m_o$
$\%\text{ efficiency} = \frac{1/t}{1/t_o} \times 100 = \frac{t_o}{t} \times 100$ or $t = t_o \Big/ \frac{\%\text{ efficiency}}{100}$

Example: A 3.18 ampere current is passed for 0.431 hours through a solution containing a gold salt. If 3.36 g of gold plates out at the cathode, what is the charge on the gold ions in solution?

$$Au^{n+} + n e^- \rightarrow Au(s)$$

$$\frac{\text{moles of Au plated}}{\text{Coulombs passed}} = \frac{1 \text{ mol}}{n \times 96487}$$

$$\text{moles of Au} = \frac{3.36 \text{ g}}{197.0 \text{ g/mol}}$$ Atomic weight Au = 197

$$= 1.71 \times 10^{-2} \text{ moles}$$

$$\text{Coulombs passed} = i \text{ (amp)} \times t \text{ (s)}$$

$$= 3.18 \text{ amps} \times 0.431 \text{ hr} \times \frac{60 \text{ min}}{1 \text{ hr}} \times \frac{60 \text{ s}}{1 \text{ min}}$$

$$= 4.93 \times 10^3 \text{ coulombs}$$

$$\therefore \frac{1.71 \times 10^{-2} \text{ moles}}{4.93 \times 10^3 \text{ coulombs}} = \frac{1}{n \times 96487}$$

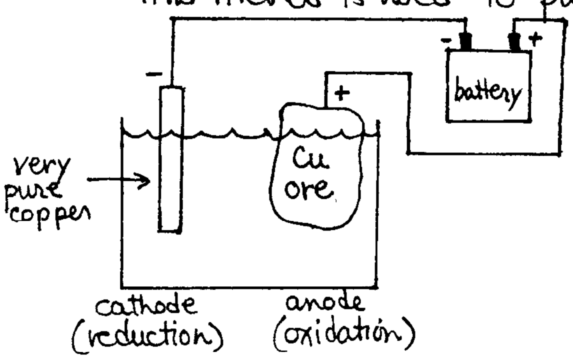
$$n = 2.99 = 3.0$$

∴ solution contained Au^{3+} ions.

For your information:

Electrolytic Refining and Electroplating

This method is used to purify metal ores (e.g. copper)



anode: $Cu(s) \rightarrow Cu^{2+} + 2e$

cathode: $Cu^{2+} + 2e \rightarrow Cu(s)$

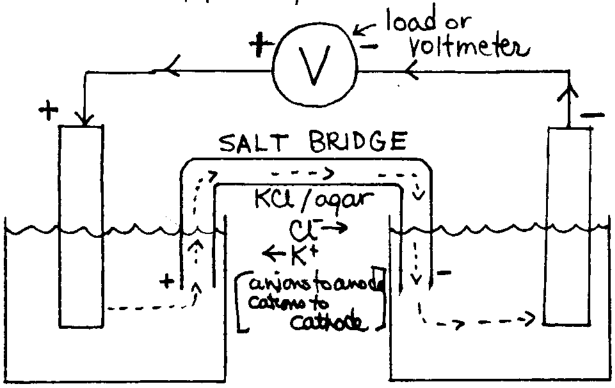
net: copper in ore dissolves & plates out as pure Cu

Electroplating with metal is similar – the object to be electroplated is made the cathode.

Voltaic (or Galvanic) Cells

voltaic or galvanic cell : an electrochemical cell in which spontaneous oxidation - reduction reactions produce electrical energy.

In this cell, the two half reactions (oxidation and reduction) are separated into half cells so that electron transfer is forced to occur by the passage of electrons through an external circuit. Therefore, useful electrical energy is produced.



$M^{2+} + 2e \rightarrow M$ reduction
cathode
electrons are consumed
Cathode is +(positive)

oxidation $M(s) \rightarrow M^{2+} + 2e$
∴ Anode
∴ electrons are produced here
∴ anode is − (negative)
and electrons flow away from the anode

Note : A salt bridge is used to ① complete the electrical circuit.
② avoid mixing the 2 solutions.
③ keep the solutions neutrally charged.

It is any medium through which ions will slowly pass, eg. sintered glas frit or KCl / 5% agar solution (a kind of gelatin material)

The negative ions (eg Cl^-) will move so as to complete the circuit.. Or in other words the ions will migrate in salt bridge to keep the two solutions neutrally charged - cations to cathode, anions to anode.

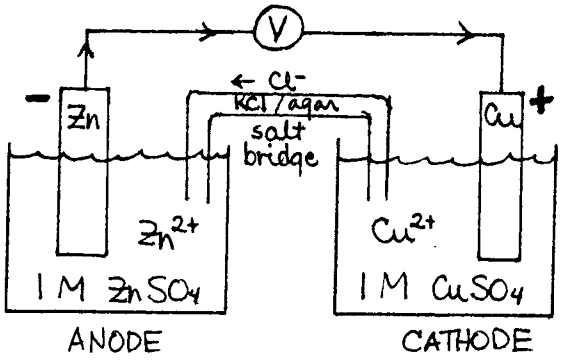
The most common half-cells contain a metal electrode in a solution of the salt of the metal:

e.g. Zn strip in a solution of $ZnSO_4(aq)$
Cu strip in a solution of $CuSO_4(aq)$.

but there are other kinds of half-cells as we shall see.

Standard cell : a cell in which the reactants are in their thermodynamic standard states. The electrodes are made of pure metals or platinum (if an inert electrode is required) in contact with a 1 M solution of its ions or 1 atm partial pressure of gas (reactant).

The Zn- Cu Standard Cell



Ⓥ voltmeter

*As 1 atom of Zn^{2+} is formed, 2 atoms of Cl^- must migrate into the solution from the salt bridge to keep the solution neutrally charged.

Observations : (1) initial voltage = + 1.1 V
(2) mass of Cu electrode increases, $[Cu^{2+}]$ around the electrode decreases.
(3) mass of Zn electrode decreases, $[Zn^{2+}]$ around the electrode increases

∴ reduction $Cu^{2+} + 2e \rightarrow Cu$ CATHODE
oxidation $Zn \rightarrow Zn^{2+} + 2e$ ANODE
cell $Cu^{2+} + Zn \rightarrow Cu + Zn^{2+}$

Note : In a voltaic cell : cathode + anode −
In an electrolytic cell : cathode − anode +
} try to figure this out without memorizing it.

Note : If metallic zinc is dropped into a solution of $CuSO_4(aq)$, the zinc dissolves and Cu metal is formed. No electricity flows since the two half reactions are not separated into two beakers.

Note: Once the cell is running, it will continue until equilibrium is reached, for the reaction. At this time, the concentrations of ions present are the equilibrium concentrations – not zero concentration.

t equilibrium,
he battery
is dead !!

Last time, we investigated the Zn-Cu ~~voltaic~~ standard voltaic cell.

$Zn / Zn^{2+} (1M) \| Cu^{2+} (1M) / Cu$ initial potential = 1.1 V

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

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

overall $Cu^{2+} + Zn \rightarrow Zn^{2+} + Cu$

what is the oxidizing agent ? Cu^{2+}

what is the reducing agent? Zn

Here is another standard cell : $Cu / Cu^{2+} (1M) \| Ag^{+} (1M) / Ag$ initial pot. 0.46V

You can see that in this case,

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

cathode $2(Ag^{+} + e \rightarrow Ag)$

overall $2Ag^{+} + Cu \rightarrow Cu^{2+} + 2Ag$

oxidizing agent : Ag^{+}

reducing agent : Cu

Shorthand for writing a voltaic (or galvanic) cell is

$$\text{anode} \underset{\text{salt bridge}}{\overset{\uparrow}{||}} \text{cathode}$$

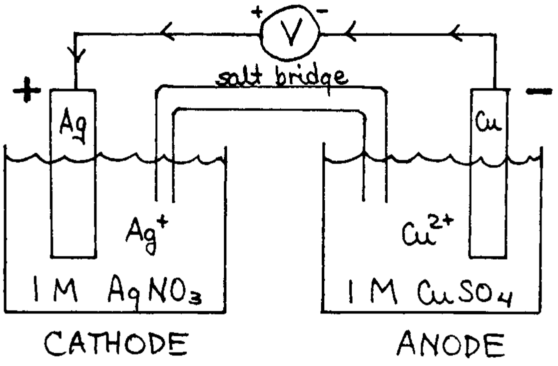
Example: Zn-Cu standard cell :

$$\underset{\text{electrode}}{Zn} \;\underset{\substack{\text{electrode}\\ \text{interface}\\ \text{(surface)}}}{/}\; \underbrace{Zn^{2+}(1M)}\; \overset{\substack{\text{salt}\\ \text{bridge}}}{||}\; \underbrace{Cu^{2+}(1M)}_{\substack{\text{solution species}\\ \text{and}\\ \text{concentration}}}\; \underset{\substack{\text{electrode}\\ \text{interface}}}{/}\; \underset{\text{electrode}}{Cu}$$

|← ANODE →|← CATHODE →|

OR $Zn / ZnSO_4\ (1M)\ ||\ CuSO_4\ (1M)\ / Cu$

The Cu-Ag Standard Cell



Note: in the laboratory, a voltmeter is connected to the two electrodes in order to get a positive reading. The electrode attached to the + terminal of voltmeter is the + electrode (cathode for galvanic cell). The electrode attached to - terminal of voltmeter is the - electrode (anode for a galvanic cell).

Observations :
(1) initial voltage of cell = +0.46 V
(2) mass of Cu electrode decreases, $[Cu^{2+}]$ around the electrode increases (Cu electrode is dissolving)
(3) mass of Ag electrode increases, $[Ag^+]$ around the electrode decreases (Ag metal is plating out)

∴ oxidation	$Cu \rightarrow Cu^{2+} + 2e$	ANODE
reduction	$2(Ag^+ + e \rightarrow Ag)$	CATHODE
cell	$2Ag^+ + Cu \rightarrow 2Ag + Cu^{2+}$	

Shorthand (anode || cathode) :

$$Cu \,/\, Cu^{2+}\ (1\,M)\ ||\ Ag^{+}\ (1\,M)\,/\,Ag$$

OR $$Cu\,/\,CuSO_4\ (1\,M)\ ||\ AgNO_3\ (1\,M)\,/\,Ag$$

Let us look at both of these standard cells again :

	Zn- Cu	Cu - Ag
anode (oxidation)	Zn $Zn \rightarrow Zn^{2+} + 2e$	Cu $Cu \rightarrow Cu^{2+} + 2e$
cathode (reduction)	Cu $Cu^{2+} + 2e \rightarrow Cu$	Ag $Ag^{+} + e \rightarrow Ag$

Recall: In a redox reaction, the oxidizing agent oxidizes other species; it itself gets reduced

Therefore what we discovered was that

Ag^{+} oxidizes Cu metal to Cu^{2+} (and Ag^{+} is reduced to Ag)

and Cu^{2+} oxidizes Zn metal to Zn^{2+} (and Cu^{2+} is reduced to Cu)

∴ relative strengths of oxidizing agents : $Ag^{+} > Cu^{2+} > Zn^{2+}$

∴ relative strengths of reducing agents : $Zn > Cu > Ag$

By combining different pairs of half cells and observing which is the cathode and which is the anode, we can derive an entire series of oxidizing agents (and reducing agents). This series is called the electromotive serie or activity series.

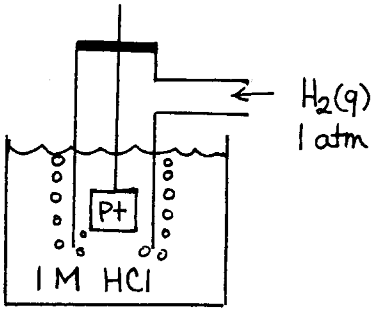
To quantify the differences in oxidizing ability between half cells, we use the potential difference between the half-cell pairs. [It is impossible to measure a single potential - we can only measure potential differences.

	potential difference (V)
Zn - Cu standard cell	+ 1.1 V
Cu - Ag standard cell	+0.46 V

* The <u>more positive</u> the voltage, the <u>greater the sponteneity</u> of the reaction.

∴ under standard conditions, the reaction in which Cu^{2+} oxidizes Zn metal has a greater tendency to go to $\overset{\text{(equilibrium)}}{\text{completion}}$ than the oxidation of Cu metal by Ag^+.

We can see that if we tabulated the standard potential differences between all the combinations of half cells, we would have a very long list. Instead, we put in a table the standard potential difference of each half cell paired up with a special half-cell which has a voltage set arbitrarily equal to zero. This is the <u>STANDARD HYDROGEN ELECTRODE</u> (SHE)

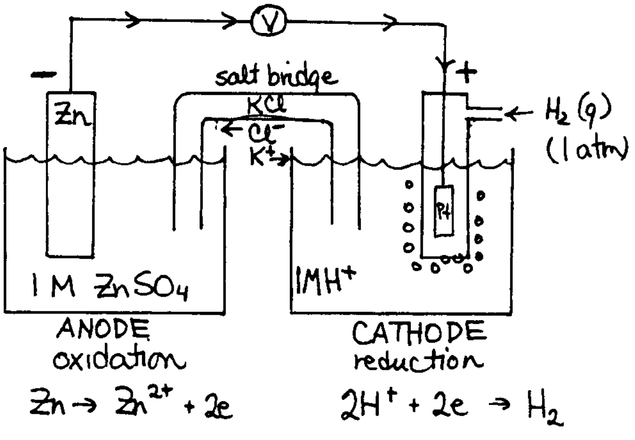


SHE is difficult to work with and so once each half cell is measured against it, we use the table to calculate the potential differences between all other combinations.

		E°
If SHE is the anode (oxidation)	$H_2 \rightarrow 2H^+ + 2e$	0.000···
If SHE is the cathode (reduction)	$2H^+ + 2e \rightarrow H_2$	0.000···

where E° is the standard electrode potential $H_2(g)$ at 1atm
$[H^+]$ at 1M

Example: Zn - SHE standard cell.



Observations:

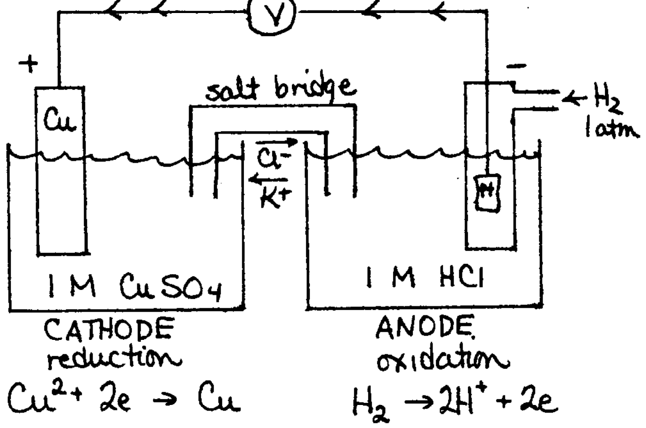
(1) mass of Zn electrode ↓, $[Zn^{2+}]$ ↑
(2) $[H^+]$ in SHE ↓ and $H_2(g)$ is produced.
(3) initial potential is + 0.763 V

		$E°$
standard half-cell: ANODE oxidation	$Zn(s) \rightarrow Zn^{2+}(aq) + 2e$	?
standard half-cell: CATHODE reduction	$2H^+(aq) + 2e \rightarrow H_2(g)$	0.000··· V
standard CELL	$2H^+(aq) + Zn(s) \rightarrow Zn^{2+}(aq) + H_2(g)$	0.763 V

∴ oxidation at ANODE : $Zn(s) \rightarrow Zn^{2+} + 2e$ = 0.763 − 0.000
= 0.763

Shortform : $Zn / Zn^{2+} (1M) \parallel H^+ (1M) ; H_2 (1 atm) / Pt$
ANODE CATHODE

Example: Cu- SHE standard cell



Observations
① mass of Cu electrode ↑
$[Cu^{2+}]$ around electrode ↓
② $H_2(g)$ is consumed , $[H^+]$ ↑
③ initial cell potential = +0.337

		$E°$
ANODE (oxidation)	$H_2(g) \rightarrow 2H^+(aq) + 2e$	0.0000
CATHODE (reduction)	$Cu^{2+}(aq) + 2e \rightarrow Cu(s)$	?
CELL	$Cu^{2+} + H_2(g) \rightarrow 2H^+ + Cu(s)$	+0.337

∴ potential of the half cell $Cu^{2+} + 2e \rightarrow Cu(s)$ = +0.337 V

Now we can build our table of data : Electromotive Series
Activity Series

This table is given in Appendix J p. A.21 . It is a list of standard potentials of half cells connected to the SHE. <u>But</u> the potentials are listed as REDUCTION potentials, only.

$M^{2+} + 2e \rightarrow M$ where all (aq) species : 1 M
all (g) species : 1 atm

Selected Standard Reduction Potentials (25°C)

Acidic Solution	Standard Reduction Potential, E°
oxidized form + ne^- → reduced form	-
$Zn^{2+} + 2e \rightarrow Zn$	-0.763 V
$2H^+ + 2e \rightarrow H_2$	0.000 V
$Cu^{2+} + 2e \rightarrow Cu$	+0.337 V
$Cu^+ + e \rightarrow Cu$	+0.521 V
$Ag^+ + e \rightarrow Ag$	0.7994 V
$Br_2 + 2e \rightarrow 2Br^-$	1.08 V
$MnO_4^- + 8H^+ + 5e \rightarrow Mn^{2+} + 4H_2O$	1.51 V

more powerful oxidizing agents ↓

more powerful reducing agents ↑

* the more positive is the standard reduction potential, the more the reduction reaction wants to go as written.

Which of the species in the table are oxidizing agents? (the oxidized forms)

ANS. all of the species on the left side of the reduction reactons

The most powerful oxidizing agent is MnO_4^-/H^+ since this species most want to be reduced.

Therefore,

$MnO_4^-/H^+ > Br_2 > Ag^+ > Cu^+ > Cu^{2+} > H^+ > Zn^{2+}$

strong oxidizing agent — weak oxidizing agent

Which of the species in the table are reducing agents? (the reduced forms)

ANS. all of the species on the right side of the reduction reactions.

$Zn > H_2 > Cu > Ag > Br^- > Mn^{2+}$

strong reducing agent — weak reducing agent

The stronger the reducing agent, the more it wants to be oxidized!

If you need the E° for the oxidation reaction eg $Zn \rightarrow Zn^{2+} + 2e$ (anode)

$$\boxed{E^\circ_{oxidation} = -E^\circ_{reduction}} \quad = +0.763\ V$$

We can use this standard reduction potential table to predict whether a reaction will occur under standard conditions (25°C, all aqueous species = 1 M, all gases at 1 atm partial pressure).

Example: Will Ag^+ oxidize metallic Zn(s) to Zn^{2+} <u>OR</u> will Zn^{2+} oxidize metallic Ag to Ag^+ under standard conditions?

		E° (V)
(1) look at table:	$Ag^+(aq) + e^- \rightarrow Ag(s)$	+ 0.7994
	$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$	−0.763

(2) The reduction reaction that is <u>more positive</u> will go as written and be the reduction reaction. The other half reaction will flip around and become the oxidation reaction.

		E° (V)
cathode (reduction)	$2\times[Ag^+(aq) + e^- \rightarrow Ag(s)]$	+ 0.7994
anode (oxidation)	$Zn \rightarrow Zn^{2+} + 2e$	+ 0.763
overall cell reaction	$2Ag^+ + Zn \rightarrow 2Ag + Zn^{2+}$	$+1.562\ V = E^\circ_{cell}$

Note: Do NOT multiply E° for Ag^+/Ag by 2!!!

The E° for half cell is controlled by the actual concentration in the cell; for a standard half cell, the concentration <u>is</u> 1 M; the concentration does not change when the coefficients change.

Shorthand notation: anode || cathode

$$Zn / Zn^{2+}(1M) \,||\, Ag^+(1M) / Ag$$

And so, Ag^+ oxidizes Zn(s) to Zn^{2+}

$$E^\circ_{cell} = E^\circ_{cathode} + E^\circ_{anode}$$
$$= 0.7994 + 0.763$$
$$= 1.562\ V$$

more simply, the reduction reaction that is more positive is the cathodic (reduction) reaction and has the oxidizing agent as the reactant.

Example: Will permanganate ions, MnO_4^- oxidize Fe^{2+} ions to Fe^{3+} ions? or will Fe^{3+} ions oxidize Mn^{2+} ions to MnO_4^- ions <u>under standard conditions</u>

↑ if concentrations are not given, this is assumed.

(1) From the table:

$$\begin{array}{lr} & E_0 \\ MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O & +1.5 \\ Fe^{3+}(aq) + e \rightarrow Fe^{2+}(aq) & +0.77 \end{array}$$

∴ MnO_4^- is being reduced

(2) The reduction reaction with more positive E° goes as written ∴ MnO_4^- is the oxidizing agent and will oxidize Fe^{2+} ions to Fe^{3+} ions.

To find the potential of the standard cell:

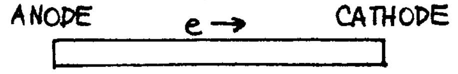
$$\begin{array}{llr} & & E^\circ(V) \\ \text{CATHODE} & MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+} + 4H_2O & +1.51 \\ \text{ANODE} & 5 \times (Fe^{2+} \rightarrow Fe^{3+} + e) & -0.771 \\ \hline \text{CELL} & MnO_4^-(aq) + 8H^+(aq) + 5Fe^{2+} \rightarrow Mn^{2+}(aq) + 4H_2O + 5Fe^{3+}(aq) & E^\circ_{cell} = +0.74 \end{array}$$

$$\boxed{\text{Shorthand: } Pt / Fe^{2+}(1M); Fe^{3+}(1M) \| MnO_4^-(1M); H^+(1M); Mn^{2+}(1M) / Pt}$$

Note: we are discussing voltaic cells - which concern only SPONTANEOUS reactions. E°_{cell} ∴ must be <u>POSITIVE</u> for a spontaneous reaction!

CORROSION

This is an example of redox reactions occurring in nature (eg your car) where a piece of metal is both the anode <u>and</u> the cathode.



$Fe \rightarrow Fe^{2+} + 2e$ $\qquad$ $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$

$\searrow \qquad \swarrow$

$Fe(OH)_2 \rightarrow Fe_2O_3$ <u>RUST</u>

Effect of Concentation (or Partial Pressure) on Electrode Potential

E° E°_{cell}

Up until now, we have only worked with standard half-cells and standard cells:
all solutions were 1 M with respect to the ions of interest and all gases were
at 1 atm partial pressure.

What if the concentrations and partial pressures are <u>not</u> at 1 M and 1 atm?
How does this affect the reduction potentials?

The Nernst Equation allows us to calculate

(1) the reduction potential of a half cell at non-standard conditions, E

(2) the potential of a voltaic cell at non-standard conditions, E_{cell}

$$\boxed{E = E^\circ - \frac{2.303\ RT}{n\,F} \log Q}$$

NERNST EQUATION

where Q = reaction quotient with aqueous species in M
gaseous species in atm

E = electrode reduction potential (or cell potential)

E° = electrode standard reduction potential (or cell standard potential)

R = 8.314 J/mol K

n = number of moles of electons involved in half reaction (or number of moles of electrons transferred in cell) for the reaction as written

$F = 96487 \ \frac{J}{V\ mol\ e^-}$

At 25°C, we can simplify the Nernst Equation

$$\boxed{E = E^\circ - \frac{0.0592}{n} \log Q \quad \text{at } 25^\circ C}$$

Consider the half-reaction

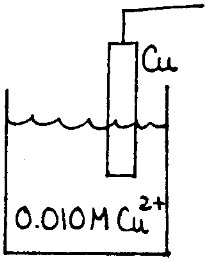
$$Cu^{2+} + 2e \rightarrow Cu \qquad E^\circ = +0.337\ V$$

$$E = E^\circ - \frac{0.0592}{2} \log \frac{1}{[Cu^{2+}]}$$

$E = E^\circ$ at standard conditions when $[Cu^{2+}] = 1\ M$ $\therefore \log \frac{1}{1} = 0$

Example: Calculate the reduction potential of Cu^{2+}/Cu electrode at 25°C when $[Cu^{2+}] = 0.010$ M.

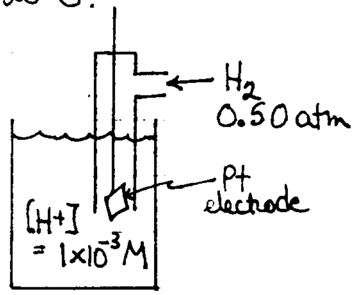
$$E = E^\circ - \frac{0.0592}{2} \log \frac{1}{(0.010)}$$
$$= +0.337 - 0.0592$$
$$= +0.278 \text{ V}$$



Example: Calculate the reduction potential of a hydrogen electrode H^+/H_2 in which pH = 3 and H_2 pressure is 0.50 atm at 25°C.

$$2H^+(aq) + 2e^- \rightarrow H_2(g) \qquad E^\circ = 0 \text{ V}$$

$$E = E^\circ - \frac{0.0592}{2} \log \frac{P_{H_2}}{[H^+]^2}$$
$$= 0.0 \text{ V} - \frac{0.0592}{2} \log \frac{0.50}{(1\times10^{-3})^2} \qquad \text{since pH} = 3$$
$$= 0.0 \text{ V} - (+0.169 \text{ V})$$
$$= -0.169 \text{ V}$$



The above examples were calculations of the reduction potentials of non-standard half cells.

<u>Calculation of E_{cell}</u> - the potential of a complete voltaic cell using non-standard halfcells (remember - the cell potential will be ⊕ for voltaic cel

There are 2 ways:

Method A: Calculate each half cell separately and add together
Method B: Calculate the cell potential directly.

Calculate the initial cell potential of a voltaic cell which consists of a Cu^{2+}/Cu electrode in which $[Cu^{2+}] = 0.010\ M$ connected to a hydrogen electrode in which pH = 3 and H_2 pressure is 0.50 atm. at 25°C

Method A

$Cu^{2+}\ (0.010\ M)/Cu$	$E = +0.278\ V$	cathode
$H^+\ (1\times10^{-3}\ M)/H_2\ (0.5\ atm)$	$E = -0.169\ V$	anode

The more positive half-cell goes as written ∴ it is reduction & occurs at cathod
∴ other half cell is the anode.

Shorthand: $Pt/H^+\ (1\times10^{-3} M);\ H_2\ (0.5\ atm)\ ||\ Cu^{2+}\ (0.010 M/Cu$

		E
cathode:	$Cu^{2+} + 2e^- \rightarrow Cu$	+0.278 V
anode:	$H_2 \rightarrow 2H^+ + 2e$	+0.169 V
overall:	$Cu^{2+} + H_2 \rightarrow Cu + 2H^+$	+0.447 V = E_{cell}

Method B: Calculate E_{cell} directly from Nernst Equation

$$E = E^\circ_{cell} - \frac{0.0592}{n} \log Q \qquad \text{at } 25^\circ C$$

		E°
We know	$Cu^{2+} + 2e^- \rightarrow Cu$	0.337 V
	$2H^+ + 2e^- \rightarrow H_2$	0.000 V

using standard potentials:

		E°
cathode	$Cu^{2+} + 2e^- \rightarrow Cu$	+0.337 V
anode	$H_2 \rightarrow 2H^+ + 2e^-$	0.000 V
overall	$Cu^{2+} + H_2 \rightarrow Cu + 2H^+$	+0.337 V = E°_{cell}

$$E_{cell} = E^\circ_{cell} - \frac{0.0592}{2} \log \frac{[H^+]^2}{[Cu^{2+}]\, pH_2}$$

$$= +0.337\ V - \frac{0.0592}{2} \log \frac{(1\times10^{-3})^2}{(0.010)(0.5)}$$

$$= +0.337\ V - (-0.109\ V)$$

$$= +0.446\ V$$

Example: Calculate the cell potential for

$$Pb \backslash Pb^{2+} (0.0010\,M) \parallel Au^{3+} (0.010\,M) / Au$$

From table:

	$E°$
$Pb^{2+} + 2e^- \rightarrow Pb$	$-0.126\,V$
$Au^{3+} + 3e^- \rightarrow Au$	$+1.50\,V$

Therefore

$2(Au^{3+} + 3e^- \rightarrow Au)$	$+1.50\,V$	cathode
$3(Pb \rightarrow Pb^{2+} + 2e^-)$	$+0.126\,V$	anode
$2Au^{3+} + 3Pb \rightarrow 2Au + 3Pb^{2+}$	$+1.63\,V$	overall

$$E_{cell} = E°_{cell} - \frac{0.0592}{6} \log \frac{[Pb^{2+}]^3}{[Au^{3+}]^2}$$

$$= +1.63\,V - \frac{0.0592}{6} \log \frac{(0.0010)^3}{(0.010)^2}$$

$$= +1.63\,V - (-0.049\,V)$$

$$= +1.68\,V$$

Relationship of $E°_{cell}$ to $\Delta G°$ and K

We recognize that it is important to know if a reaction is spontaneous or not.

There are 3 ways to express the spontaneity of a reaction. For a reaction where all aqueous species are 1 M and all gaseous species 1 atm initially ($Q=1$), the reaction will be spontaneous – go in the forward direction when

(1) the standard Gibbs free energy change, $\Delta G° < 0$

(2) the thermodynamic equilibrium constant, $K > 1$

(3) the standard potential of a cell, $E°_{cell} > 0$

We have studied ΔG° and K in earlier chapters. The relationship between these thermodynamic quantities is :

$$\Delta G^\circ = -2.303\ RT \log K$$

where $R = 8.314\ J\ mol^{-1}\ K^{-}$
T = temperature (K)

Let's discuss E°_{cell} and its relationship to spontenecity :

In this chapter, we have discussed setting up of voltaic cells by combining two different half cells. The current flows, there is an initial voltage that can be measured (E_{cell} or E°_{cell} if all reactants and products are at 1 M and 1 atm partial pressure).

These cells are NOT at equilibrium. The current flows, reactants are used up and products are formed tying to reach a state of equilibrium Once equilibrium is reached, $E_{cell} = 0$ and no current flows (eg. the battery is dead).

This is why when a voltage is given for a cell, the problem states "the initial voltage is ..." Once the reaction begins, the concentrations are changing and the voltage of the cell approaches zero as the system goes to equilibrium.

In electrochemistry, $\boxed{\Delta G^\circ = -nFE^\circ_{cell}}$ for a reaction at standard conditions.

It is possible to relate K and E°_{cell} by equating the two reactions

$$\Delta G^\circ = -2.303\ RT \log K$$
$$\Delta G^\circ = -nFE^\circ_{cell}$$

$$\therefore\ -nFE^\circ_{cell} = -2.303\ RT \log K$$

$$E^\circ_{cell} = \frac{2.303\ RT}{nF} \log K$$

$$\boxed{E^\circ_{cell} = \frac{0.0592}{n} \log K \quad \text{at } 25^\circ C}$$

We can also derive this from the Nernst Equation:

$$E_{cell} = E^\circ_{cell} - \frac{0.0592}{n} \log Q \quad \text{at } 25°C$$

at equilibrium $Q = K$ and $E_{cell} = 0$

$$\therefore \quad E^\circ_{cell} = \frac{0.0592}{n} \log K$$

In a voltaic (galvanic) cell that is NOT at standard conditions, we can relate E_{cell} and ΔG. (we <u>cannot</u> determine K, though)

$$\boxed{\Delta G = -nFE_{cell}}$$

Example: Consider the following voltaic cell
Cr / Cr^{3+} (0.10 M) ‖ Sn^{4+} (0.05 M), Sn^{2+} (0.2M) / Pt

(a) Is the reaction spontaneous <u>under standard conditions</u>? Ans. calculate E°_{cell}. If $E^\circ > 0$, the reaction is spontaneous.

	E°
$Sn^{4+} + 2e \rightarrow Sn^{2+}$	+0.15 V
$Cr^{3+} + 3e \rightarrow Cr$	−0.74 V

cathode	$3(Sn^{4+} + 2e \rightarrow Sn^{2+})$	+0.15V
anode	$2(\quad Cr \rightarrow Cr^{3+} + 3e)$	+0.74V
cell	$3Sn^{4+} + 2Cr \rightarrow 3Sn^{2+} + 2Cr^{3+}$	+0.89V = E°_{cell}

Yes, the reaction under standard conditions is spontaneous.

(b) Calculate ΔG° and K for the reaction at 25°C
ANS. USE <u>E°_{cell}</u>:

(i) $\Delta G^\circ = -nFE^\circ_{cell}$

$= -6\left(\frac{96487\text{ coul}}{1\text{ mol}} \times \frac{1\text{ J}}{\text{V}\cdot\text{coul}}\right)(+0.89\text{V})$

$= -5.2 \times 10^5\text{ J}$

(ii) $E^\circ_{cell} = \frac{0.0592}{n}\log K$

rearranging

$K = \text{antilog}\ \frac{n}{0.0592}E^\circ_{cell}$

$= \text{antilog}\ \frac{6}{0.0592}(+0.89\text{V})$

$= 1.6 \times 10^{90}$

Note : what if E° cell was + 1.5 V ?

$K = \text{antilog}\ \frac{6}{0.0592} \times 1.5\text{ V}$

$= \text{antilog}\ 152$

voila - error on calculator !!

$K = 10^{152}$

(c) Is the reaction spontaneous under the conditions given? Calculate ΔG

$E_{cell} = E^\circ_{cell} - \frac{0.0592}{n}\log\frac{[Sn^{2+}]^3[Cr^{3+}]^2}{[Sn^{4+}]^3}$

$= +0.89\text{V} - \frac{0.0592}{6}\log\frac{(0.2)^3(0.1)^2}{(0.05)^3}$

$= +0.89\text{ V} - \frac{0.0592}{6}\log 0.64$

$= +0.89\text{ V} - (-0.002)$

$= +0.892\text{ V}$ Yes it is spontaneous :

$\Delta G = -nFE_{cell}$

$= -6 \times 96487 \times (+0.892\text{V})$

$= -5.2 \times 10^5\text{ J}$ similar to ΔG°

Final Note:

		E°
Example: Given	$Cr^{3+} + 3e \rightarrow Cr$	$-0.74\ V$
	$Ag^{+} + e \rightarrow Ag$	$+0.80\ V$

What is the E° for the reaction: $Cr^{3+} + 3Ag \rightarrow Cr + 3Ag^{+}$?

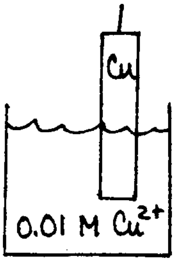
Solution: in this reaction:	$Cr^{3+} \rightarrow Cr$	$-0.74\ V$	cathode
	$Ag \rightarrow Ag^{+}$	$-0.80\ V$	anode

$$\therefore E^\circ_{cell} = E^\circ_{anode} + E^\circ_{cathode} = -0.74V - 0.80V = -1.54V$$

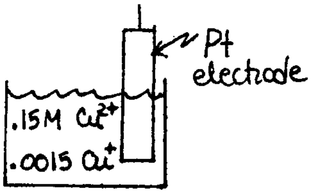
Can this be a voltaic (galvanic) cell? No!
Is this reaction spontaneous? No!

Example: Calculate the reduction potential of Cu^{2+}/Cu electrode at 25°C when $[Cu^{2+}] = 0.01$ M.

$$E = E^\circ - \frac{0.0592}{2} \log \frac{1}{(0.01)}$$
$$= +0.337 - 0.0592$$
$$= +0.278 \text{ V}$$



Example: Calculate the reduction potential of Cu^{2+}/Cu^{+} electrode at 25°C when (a) $[Cu^{2+}] = 0.15$ M
$[Cu^{+}] = 0.0015$ M
(b) $[Cu^{+}] = 3[Cu^{2+}]$



For this electrode, we know $Cu^{2+} + e \rightarrow Cu^{+}$ $E^\circ = 0.153$ V

$$E = E^\circ - \frac{0.0592}{1} \log \frac{[Cu^{+}]}{[Cu^{2+}]}$$

Note: that whenever $[Cu^{+}] = [Cu^{2+}$
$\log 1 = 0$ and $E = E^\circ$

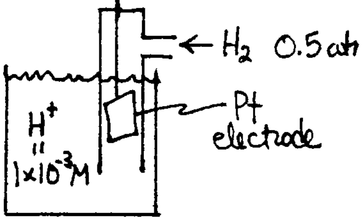
(a) $$E = 0.153\text{V} - \frac{0.0591}{1} \log \frac{0.0015}{0.15}$$
$$= 0.153\text{ V} - (-0.118)$$
$$= 0.271 \text{ V}$$

(b) $$E = 0.153\text{ V} - \frac{0.0591}{1} \log \frac{3[\cancel{Cu^{2+}}]}{[\cancel{Cu^{2+}}]}$$
$$= 0.153\text{V} - 0.028\text{V}$$
$$= 0.125\text{V}$$

substituting $3[Cu^{2+}]$ for $[Cu^{+}]$

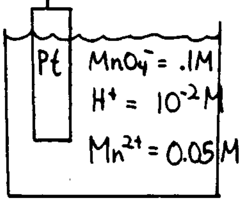
Example: Calculate the reduction potential of a hydrogen electrode H^{+}/H_2 in which $[H^{+}] = 1.0 \times 10^{-3}$ M and the H_2 pressure is 0.50 atm at 25°C
pH = 3

$$2H^{+} + 2e \rightarrow H_2(g) \qquad E^\circ = 0$$



$$E = E^\circ - \frac{0.0592}{2} \log \frac{P_{H_2}}{[H^{+}]^2}$$
$$= 0\text{ V} - \frac{0.0592}{2} \log \frac{0.5}{(1\times10^{-3})^2}$$
$$= 0 - (+0.169\text{ V})$$
$$= -0.169\text{V}$$

Example: Calculate the reduction potential of an electrode in which



$[MnO_4^-] = 0.200\,M$
$[Mn^{2+}] = 0.050\,M$
pH = 2.00 at 25°C

$$MnO_4^-(aq) + 8\,H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O \qquad E° = 1.51\,V$$

$$E = E° - \frac{0.0592}{5}\log\frac{[Mn^{2+}]}{[MnO_4^-][H^+]^8}$$

$$= +1.51\,V - \frac{0.0592}{5}\log\frac{(0.050)}{(0.200)(10^{-2})^8}$$

$$= +1.51\,V - 0.182\,V$$
$$= +1.33\,V$$

The above examples were calculations of the reduction potentials of non-standard half cells

<u>Calculation of E_{cell}, the potential of a complete voltaic cell</u> using non-standard half cells. (remember cell potential will be + for voltaic cell)

There are 2 ways: Method A : Calculate each half cell separately and add them together
Method B : Calculate the cell potential directly.

this is an example of a concentration cell

Example: Calculate the initial potential of a galvanic cell which consists of
(a) Cu^{2+}/Cu^+ electrode where $[Cu^{2+}] = 0.15\,M$ and $[Cu^+] = 0.0015\,M$
and (b) Cu^{2+}/Cu^+ electrode where $[Cu^+] = 3[Cu^{2+}]$ $[Cu^+] = 0.3\,M$ $[Cu^{2+}] = 0.1\,M$

CATHODE cell (a) $E = +0.271\,V$ $Cu^{2+} + e \rightarrow Cu^+$
ANODE cell (b) $E = +0.125\,V$

the more positive cell goes as written ∴ it is reduction ∴ it is cathode
∴ the other half cell is anode

Shorthand $Pt\,/\,Cu^{2+}\,(0.1\,M.);\,Cu^+(0.3\,M)\,||\,Cu^{2+}(.15\,M);\,Cu^+(0.0015\,M)/\,Pt$

			E
half cell (a)	CATHODE	$Cu^{2+} + e \rightarrow Cu^{+}$	+0.271 V
half cell (b)	ANODE	$Cu^{+} \rightarrow Cu^{2+} + e$	− 0.125 V
	CELL	$Cu^{2+} + Cu^{+} \rightarrow Cu^{2+} + Cu^{+}$	$E_{cell} = +0.146\ V$

Example : Calculate the initial potential of a cell that consists of permanganate half cell where $[MnO_4^-] = 0.200\ M$, $[Mn^{2+}] = 0.050\ M$, pH=2 and hydrogen electrode in which $[H^+] = 1.0 \times 10^{-3}\ M$ and $p_{H_2} = 0.5$ atm

Method A

we have already calculated E, the reduction potential, for each of these half cells

	E
$MnO_4^- + 8H^+ + 5e \rightarrow Mn^{2+} + 4H_2O$	+1.33 V
$2H^+ + 2e \rightarrow H_2$	−0.169 V

the half cell having the more positive reduction potential, E, goes as written ∴ is the CATHODE since reduction is occurring.

		E
cathode	∴ $2(MnO_4^- + 8H^+ + 5e \rightarrow Mn^{2+} + 4H_2O)$	+1.33 V
anode	$5(H_2 \rightarrow 2H^+ + 2e)$	+0.169 V

cell $2\ MnO_4^- + 16H^+ + 5H_2 \rightarrow 2\ Mn^{2+} + 10H^+ + 8\ H_2O$

do not cancel out $[H^+]$

$$E_{cell} = +1.33 + (+0.169)$$
$$= +1.50\ V$$

Shorthand

Pt/ H_2 (0.50 atm); H^+ (10^{-3} M) ‖ MnO_4^- (0.2M); H^+ (10^{-2}M); Mn^{2+} (0.050 M) / Pt

Method B : calculate Ecell directly from Nernst equation.

$$E_{cell} = E^\circ_{cell} - \frac{0.0592}{n} \log Q \quad \text{at } 25^\circ C$$

$$\begin{array}{lr} & E^\circ \\ MnO_4^- + 8H^+ + 5e \rightarrow Mn^{2+} + 4H_2O & 1.51 \\ 2H^+ + 2e \rightarrow H_2 & 0.000 \end{array}$$

$$\begin{array}{llr} \therefore \text{cathode} & 2(MnO_4^- + 8H^+ + 5e \rightarrow Mn^{2+} + 4H_2O) & +1.51 \\ \text{anode} & 5(H_2 \rightarrow 2H^+ + 2e) & 0.00 \\ \hline \text{cell} & 2MnO_4^- + 16H^+ + 5H_2 \rightarrow 2Mn^{2+} + 10H^+ + 8H_2O & E^\circ_{cell}\ +1.51 \end{array}$$

do not multipl by coeff.

$$E_{cell} = E^\circ_{cell} - \frac{0.0592}{10} \log \frac{[Mn^{2+}]^2 \overset{Hcell}{[H^+]^{10}}}{[MnO_4^-]^2 \underset{\uparrow \atop MnO_4^-\ cell}{[H^+]^{16}} (P_{H_2})^5}$$

$$= +1.51 - \frac{0.0592}{10} \log \frac{(0.050)^2 (10^{-3})^{10}}{(0.2)^2 (10^{-2})^{16} (0.5)^5}$$

$$= +1.51 - \frac{0.0592}{10} \log 200$$

$$= +1.51 - 0.01$$

$$= +1.50\ V$$

Relationship of E°_{cell} to ΔG° and K

We recognize that it is impotant to know if a reaction is spontaneous or not. There are three ways to express the sponteneity of a reaction (will a reaction go in the forward direction or in the reverse direction?)

For a reaction where all aqueous species are at 1 M, gaseous species 1atm

(1) the standard Gibbs free energy change, ΔG°
if $\Delta G^\circ < 0$, the reaction is spontaneous.

(2) the thermodynamic equilibrium constant, K
if $K > 1$, the reaction is spontaneous

(3) the standard potential of a cell, E°_{cell}
if $E^\circ_{cell} > 0$, the redox reaction is spontaneous.