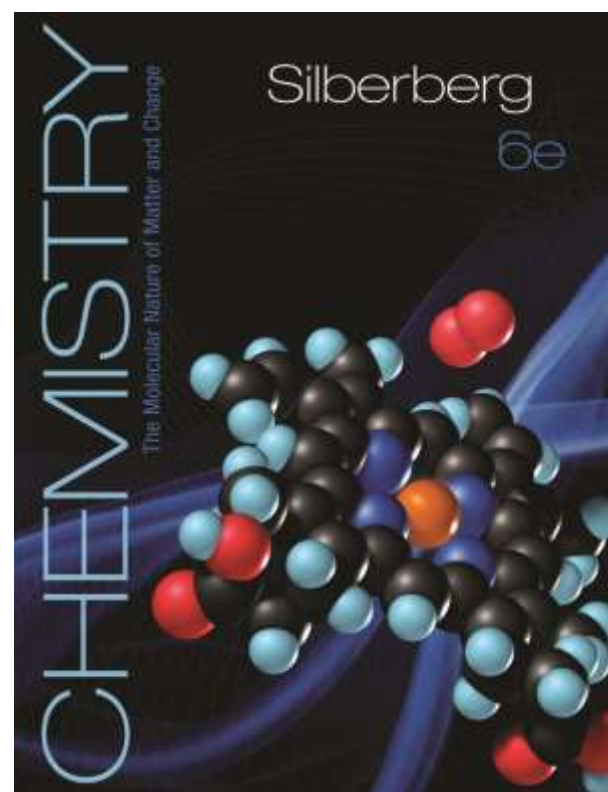


Lecture PowerPoint

Chemistry

The Molecular Nature of
Matter and Change
Sixth Edition

Martin S. Silberberg

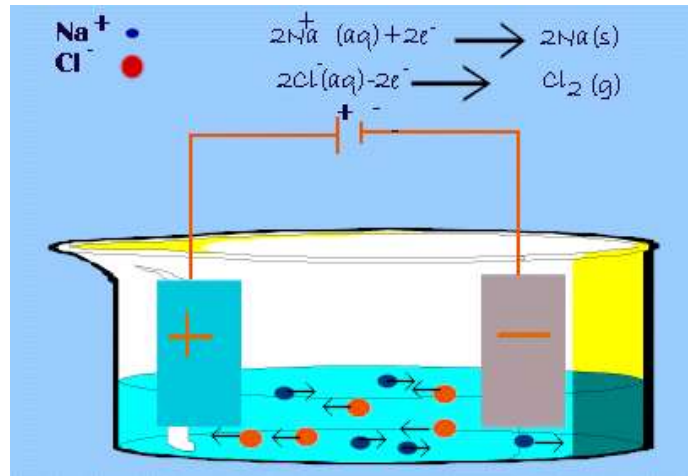


Electrochemistry: Chemical Change and Electrical Work



What is electrochemistry

- **Electrochemistry:** The science that deal with the conversion of electro energy to chemical energy and vice versa. Through oxidation- reduction reaction.



Overview of Redox Reactions

Oxidation is the **loss** of electrons and **reduction** is the **gain** of electrons. These processes occur **simultaneously**.

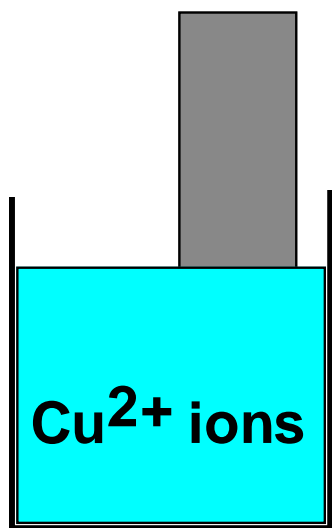
Oxidation results in an **increase** in O.N. while reduction results in a **decrease** in O.N.

The **oxidizing agent** takes electrons from the substance being oxidized. The oxidizing agent is therefore reduced.

The **reducing agent** takes electrons from the substance being oxidized. The reducing agent is therefore oxidized.



CHEMICAL CHANGE → ELECTRIC CURRENT



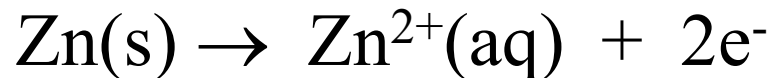
Zn metal

With time, Cu²⁺ precipitated on Zn metal strip.

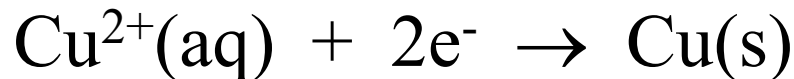
Zn strip “disappears.”

The color of CuSO₄ disappeared

- Zn is oxidized and is the reducing agent

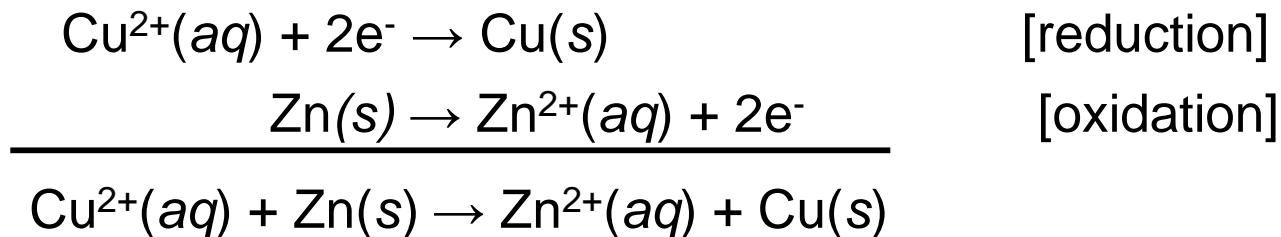


- Cu²⁺ is reduced and is the oxidizing agent



Spontaneous Redox Reactions

A strip of zinc metal in a solution of Cu^{2+} ions will react spontaneously:

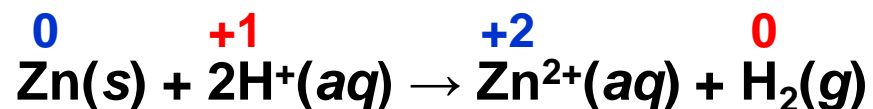


Zn is oxidized, and loses electrons to Cu^{2+} .


Although e^{-} are being transferred, electrical energy is not generated because the reacting substances are in the same container.



Figure 21.1 A summary of redox terminology, as applied to the reaction of zinc with hydrogen ion.



Copyright © The McGraw-Hill Companies, Inc. Permission required for reproduction or display.

<p>OXIDATION</p> <ul style="list-style-type: none"> • One reactant loses electrons. • Reducing agent is oxidized. • Oxidation number increases. 	<p>Zinc loses electrons. Zinc is the reducing agent and becomes oxidized. The oxidation number of Zn increases from 0 to +2.</p>	
<p>REDUCTION</p> <ul style="list-style-type: none"> • Other reactant gains electrons. • Oxidizing agent is reduced. • Oxidation number decreases. 	<p>Hydrogen ion gains electrons. Hydrogen ion is the oxidizing agent and becomes reduced. The oxidation number of H decreases from +1 to 0.</p>	

© The McGraw-Hill Companies, Inc./Stephen Frisch Photographer



What is Galvanic Cell?

An electrochemical cell that converts the chemical energy of spontaneous redox reactions into electrical energy is known as a galvanic cell or a voltaic cell.

▪ In oxidation-reduction reactions, electrons are moved from one species to another species. Energy is released if the reaction occurs spontaneously. Therefore, the released energy is used to do useful work. To tackle this energy, it is required to split the reaction into two separate half-reactions viz. oxidation and reduction. With the help of two different containers and wire, the reactions are put into them to drive the electrons from one end to the other end. This creates a voltaic cell.



Construction of a Voltaic Cell

Each half-reaction takes place in its own ***half-cell***, so that the reactions are physically separate.

Each half-cell consists of an electrode in an electrolyte solution.

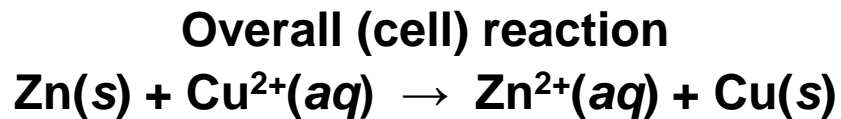
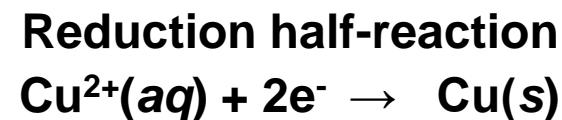
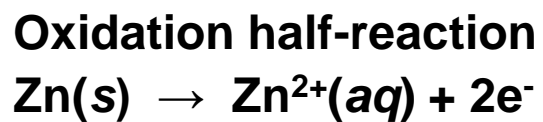
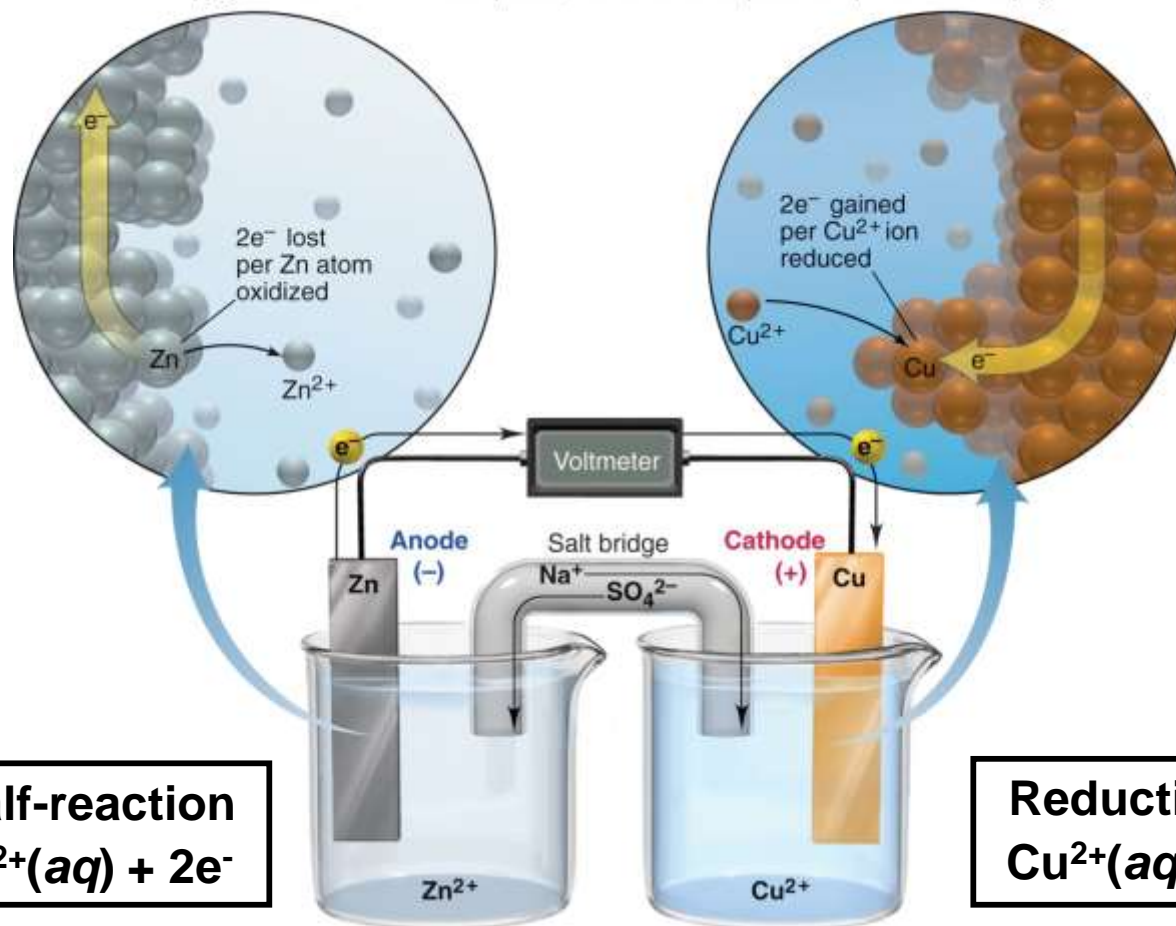
The half-cells are connected by the external circuit.

A ***salt bridge*** completes the electrical circuit.



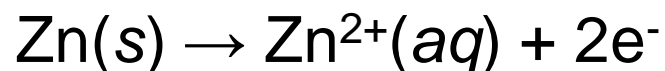
Figure 21.4A A voltaic cell based on the zinc-copper reaction.

Copyright © The McGraw-Hill Companies, Inc. Permission required for reproduction or display.



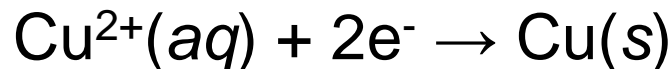
Operation of the Voltaic Cell

Oxidation (loss of e^-) occurs at the ***anode***, which is therefore the source of e^- .



Over time, the $\text{Zn}(s)$ anode decreases in mass and the $[\text{Zn}^{2+}]$ in the electrolyte solution increases.

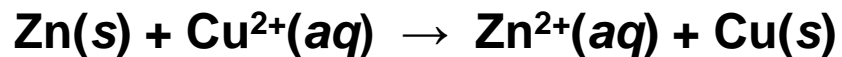
Reduction (gain of e^-) occurs at the ***cathode***, where the e^- are used up.



Over time, the $[\text{Cu}^{2+}]$ in this half-cell decreases and the mass of the $\text{Cu}(s)$ cathode increases.



Figure 21.4B A voltaic cell based on the zinc-copper reaction.



Oxidation half-reaction



After several hours, the Zn anode weighs less as Zn is oxidized to Zn^{2+} .



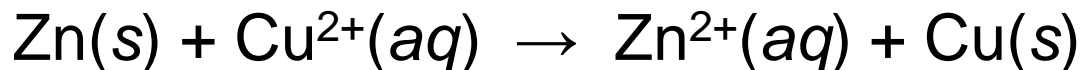
Reduction half-reaction



The Cu cathode gains mass over time as Cu^{2+} ions are reduced to Cu.



Charges of the Electrodes



The ***anode*** produces e^- by the oxidation of Zn(s) . The anode is the ***negative*** electrode in a voltaic cell.

Electrons flow through the external wire ***from the anode to the cathode***, where they are used to reduce Cu^{2+} ions.

The cathode is the ***positive*** electrode in a voltaic cell.



The Salt Bridge

- **Salt bridge – completes circuit between the two half cells**
- **Salt bridge is any medium through which ions can flow**
- **Contain strong electrolyte**
 1. **Allows electrical contact between two solutions without direct connection between two cell electrolyte**
 2. **Prevents mixing of electrode solutions**
 3. **Maintains electrical neutrality**



The Salt Bridge

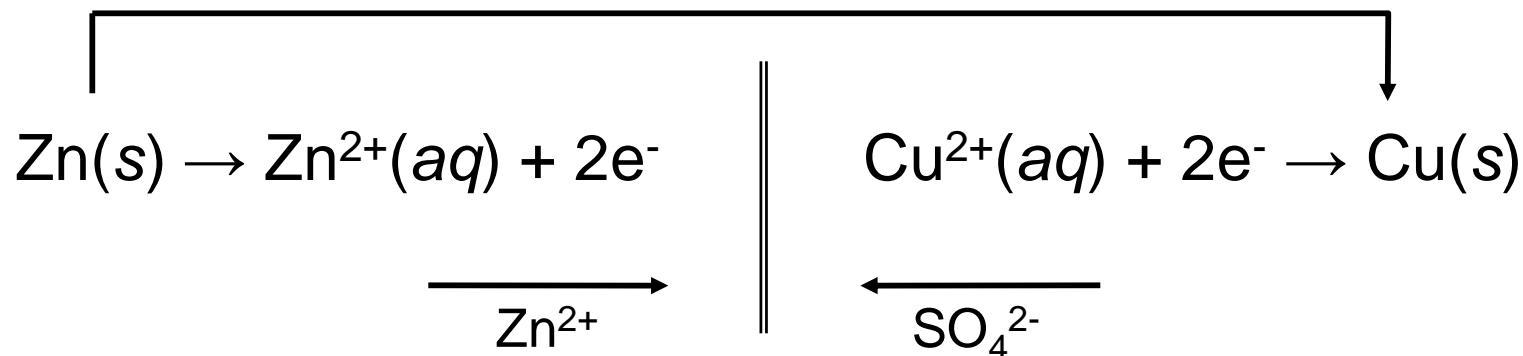
Salt bridge and its function. It's usually an inverted U-tube filled with concentrated solution of *inert electrolyte*. The essential requirements of electrolyte are:

- a) The mobility of the anion and cation of the electrolyte should be almost same.
- b) The ions of the electrolyte are not involved in electrochemical change.
- c) The ions do not react chemically with the species of the cell.



Flow of Charge in a Voltaic Cell

Electrons flow through the wire from anode to cathode.



Cations move through the salt bridge from the anode solution to the cathode solution.

Anions move through the salt bridge from the cathode solution to the anode solution.

By convention, a voltaic cell is shown with the anode on the left and the cathode on the right.

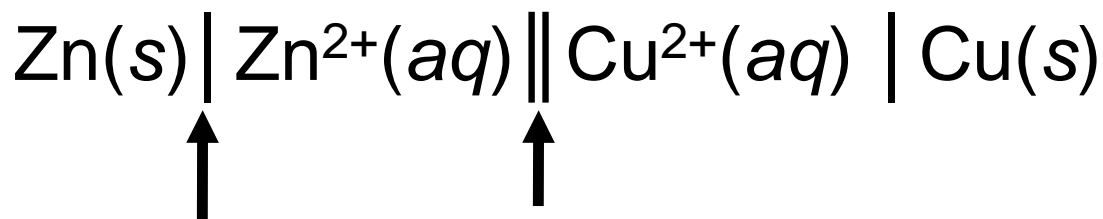


Notation for a Voltaic Cell

The components of each half-cell are written in the same order as in their half-reactions.

The anode components are written on the *left*.

The cathode components are written on the *right*.



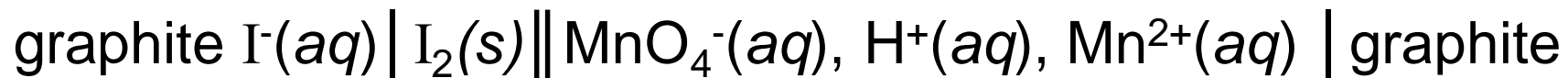
The single line shows a phase boundary between the components of a half-cell.

The double line shows that the half-cells are physically separated.

If needed, concentrations of dissolved components are given in parentheses. (If not stated, it is assumed that they are 1 *M*.)



Notation for a Voltaic Cell



The inert electrode is specified.



A comma is used to show components that are in the same phase.



Sample Problem 21.2

Describing a Voltaic Cell with Diagram and Notation

PROBLEM: Draw a diagram, show balanced equations, and write the notation for a voltaic cell that consists of one half-cell with a Cr bar in a $\text{Cr}(\text{NO}_3)_3$ solution, another half-cell with an Ag bar in an AgNO_3 solution, and a KNO_3 salt bridge. Measurement indicates that the Cr electrode is negative relative to the Ag electrode.

PLAN: From the given contents of the half-cells, we write the half-reactions. To determine which is the anode compartment (oxidation) and which is the cathode (reduction), we note the relative electrode charges. Electrons are released into the anode during oxidation, so it has a negative charge. Since Cr is negative, it must be the anode, and Ag is the cathode.



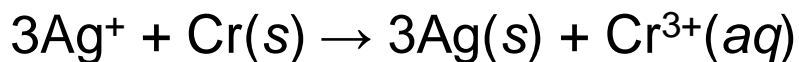
Sample Problem 21.2

SOLUTION:

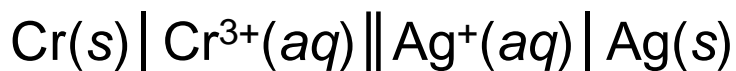
The half-reactions are:



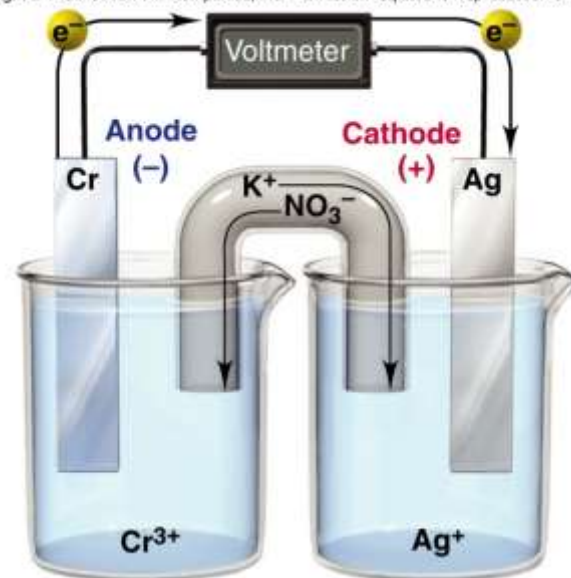
The balanced overall equation is:



The cell notation is given by:



Copyright © The McGraw-Hill Companies, Inc. Permission required for reproduction or display.

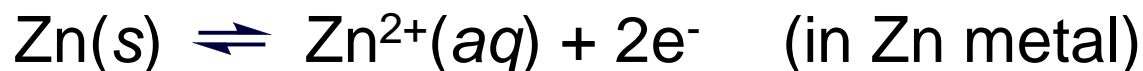


The cell diagram shows the anode on the left and the cathode on the right.



Electrical Potential and the Voltaic Cell

When the switch is closed and no reaction is occurring, each half-cell is in an equilibrium state:



Zn is a ***stronger reducing agent*** than Cu, so the position of the Zn equilibrium lies farther to the right.

Zn has a higher ***electrical potential*** than Cu. When the switch is closed, e^{-} flow from Zn to Cu to equalize the difference in electrical potential

The spontaneous reaction occurs as a result of the different abilities of these metals to give up their electrons.

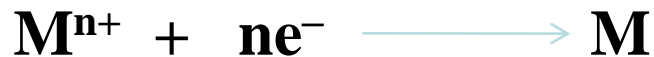


Electrode potential

- The tendency of a metal to get oxidised or reduced when it is placed in a solution of its own salt is called electrode potential.
- When a metal [M] is placed in a solution containing its own ions [Mⁿ⁺], then the metal may undergo either oxidation or reduction. If the metal undergoes oxidation, then the positive metal ions may pass into the solution



- If the metal undergoes reduction, then the negative ions may get deposited over the metal.



Electrode potential

- The tendency of metal to lose or gain electron is known as electrode potential.
- When it loses it is known as Oxidation potential and when it gains it is known as reduction potential.
- Nernst found that whenever any metal plate is in contact with its ions (electrolyte) two phenomenon are taking place simultaneously.

Explain the origin of single electrode potential

1. The metal starts dissolving producing ions. The ions go in the solution and electrons are shielding on plate.



This tendency of the metal to lose the electron and ions go in the solution shielding the electrons on the metal is known as solution pressure P_S of the metal and is also known as De-electronation.



Electrode potential

Explain the origin of single electrode potential?

2. When the metal is in contact with metal ions. In this case ions (cation) from the solution go and get deposited on the surface of metal plate.



This tendency of the ions of the solution to get deposited on the surface of plate as neutral product is known as Osmotic pressure P_0 of the solution. It is also known as Electronation.

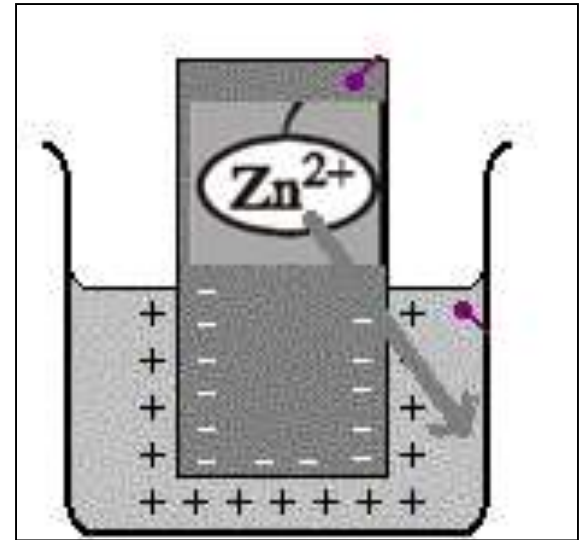


Now there are three possibilities.

1. $P_S > P_0$. It means solution pressure of ions of the metal is greater than the solution pressure of the ions. i.e. de-electronation phenomenon is greater than electronation, in that case the metal will be having -ve polarity and is written on LHS of the cell i.e. anode.
2. $P_S < P_0$. It means electronation phenomenon is greater than de-electronation. It will be having positive charge and is written on RHS of the cell and is having positive polarity and is called cathode.
3. $P_S = P_0$. It means the ability of loosing and gaining the electron is same for the metal. the metal in that case will not have polarity i.e. polarity is zero. such metals can not be used as the electrode in electrochemical cells and are known as Null electrode.

Zn in ZnSO₄

When Zn is placed in a solution of its own salt, zinc undergoes oxidation with the release of electrons. The electrons liberated in the process, accumulate over the surface of the metal and hence, the metal is negatively charged. Now, the negatively charged metal attracts the positive ions from the solution, and hence formation of a double layer takes place near the surface of the metal.



Single Electrode Potential:

It is a measure of tendency of a metallic electrode to lose or gain electrons when it is in contact with a solution of its own salt.

Standard Electrode Potential:

It is a measure of tendency of a metallic electrode to lose or gain electrons, when it is in contact with a solution of its own salt of 1 Molar concentration at 25°C.

The electrode potential depends upon :

- (i) the nature of the metal and its ions,*
- (ii) concentration of the ions in the solution, and*
- (iii) temperature.*

The electrode potential of an electrode can be determined by connecting this half cell with a standard hydrogen electrode.

The electrode potential of the standard hydrogen electrode is taken as zero.

The electrode potential of a metal electrode as determined with respect to a standard or normal hydrogen electrode is called **standard electrode potential (E^0)**. Standard electrode potentials are always associated with the reduction occurring at the electrodes.



Standard Electrode Potentials

The standard electrode potential ($E^\circ_{\text{half-cell}}$) is the potential of a given half-reaction when all components are in their standard states.

By convention, all standard electrode potentials refer to the half-reaction written as a **reduction**.

The standard cell potential depends on the **difference** between the abilities of the two electrodes to act as reducing agents.

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode (reduction)}} - E^\circ_{\text{anode (oxidation)}}$$



The Standard Hydrogen Electrode

Half-cell potentials are measured **relative** to a standard reference half-cell.

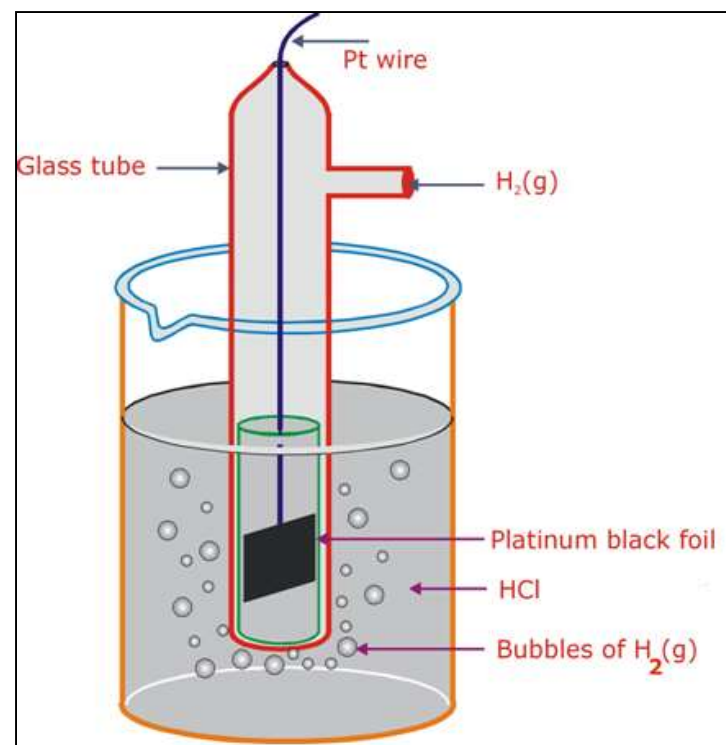
The standard hydrogen electrode has a standard electrode potential defined as **zero** ($E^\circ_{\text{reference}} = 0.00 \text{ V}$).

This standard electrode consists of a Pt electrode with H_2 gas at 1 atm bubbling through it. The Pt electrode is immersed in 1 *M* strong acid.



Standard hydrogen electrode(SHE)

It consists of a platinum wire in a inverted glass) tube(Jaket). Hydrogen gas is passed through the tube through small hole at 1 atm. A platinum foil (platinu Black) is attached at the end of the wire. The electrode is immersed in 1M H^+ ion solution at $25^{\circ}C$. The electrode potential of SHE is zero at all temperatures.



Standard hydrogen electrode(SHE)

It is represented as



In a cell when the standard hydrogen electrode acts as anode, the electrode reaction can be written as



When the standard hydrogen electrode acts as cathode, the electrode reaction can be written as



Based on the electrode potential obtained with reference to hydrogen, electrochemical series is obtained.



Standard hydrogen electrode(SHE)

Advantages of standard hydrogen electrodes are as follows –

- If we use a standard hydrogen electrode as a reference to determine the electrode potential of another electrode of half cell connected to SHE then-unknown potential will be equal to the electromotive force of the cell.
- It can act as anode half cell and cathode half cell as well



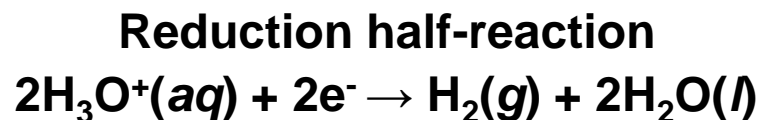
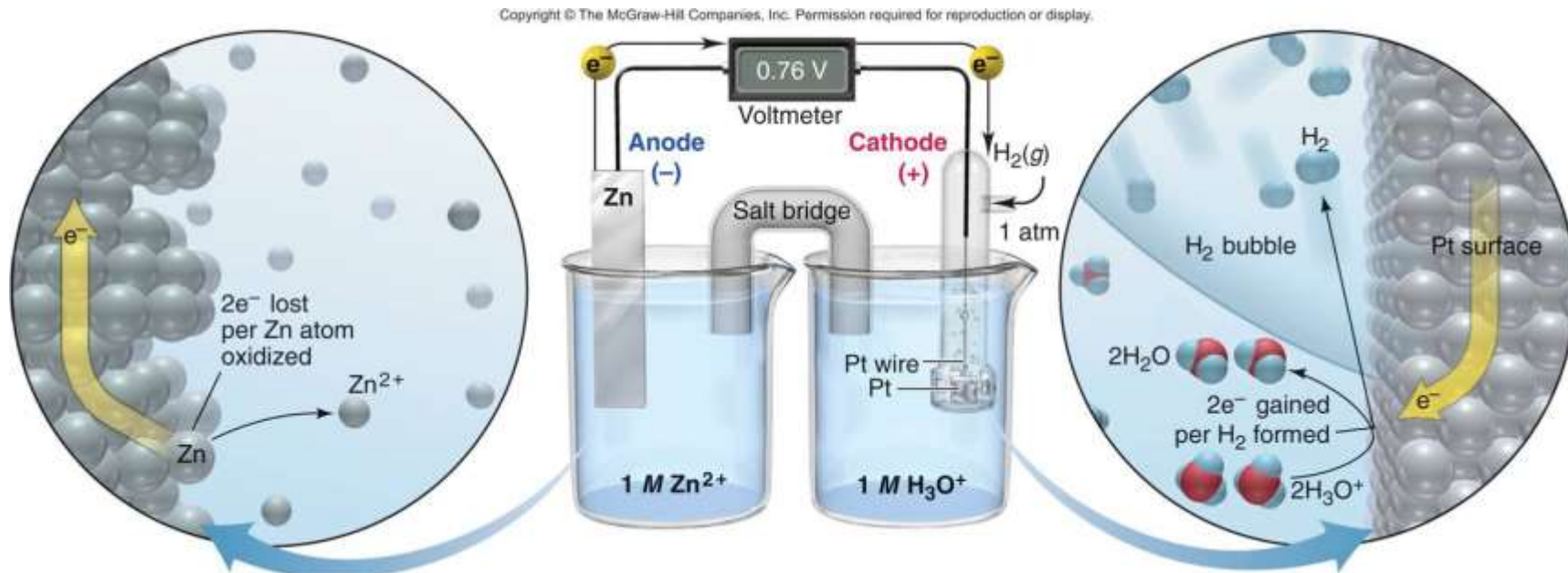
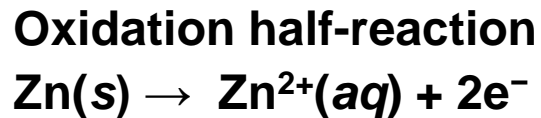
Standard hydrogen electrode(SHE)

Disadvantages of Standard Hydrogen Electrode

- It's difficult to transport.
- It's difficult to construct and maintain.
- It's difficult to maintain the pressure of hydrogen gas and concentration of the acid solution taken such as HCl. →
- It's difficult to get pure hydrogen gas.
- It's difficult to make an ideal platinum electrode.
- Platinum is expensive
- Generally, impurities in hydrogen and HCl spoil ideal platinum electrodes and reduce the life of standard hydrogen electrodes.



Figure 21.7 Determining an unknown $E^\circ_{\text{half-cell}}$ with the standard reference (hydrogen) electrode.



Overall (cell) reaction



Cell Potential

A voltaic cell converts the ΔG of a spontaneous redox reaction into the kinetic energy of electrons.

The **cell potential** (E_{cell}) of a voltaic cell depends on the **difference** in electrical potential between the two electrodes.

Cell potential is also called the **voltage** of the cell or the **electromotive forces (emf)**.

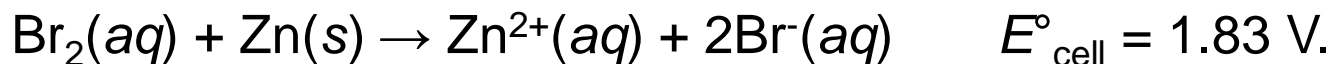
$E_{\text{cell}} > 0$ for a spontaneous process.



Sample Problem 21.3

Calculating an Unknown $E^\circ_{\text{half-cell}}$ from E°_{cell}

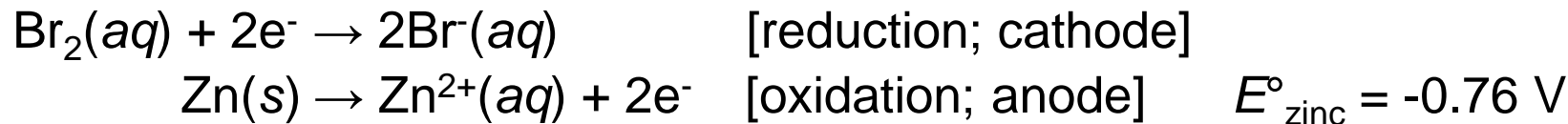
PROBLEM: A voltaic cell houses the reaction between aqueous bromine and zinc metal:



Calculate E°_{bromine} , given that $E^\circ_{\text{zinc}} = -0.76 \text{ V}$

PLAN: E°_{cell} is positive, so the reaction is spontaneous as written. By dividing the reaction into half-reactions, we see that Br_2 is reduced and Zn is oxidized; thus, the zinc half-cell contains the anode. We can use the equation for E°_{cell} to calculate E°_{bromine} .

SOLUTION:



Sample Problem 21.3

$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}}$$

$$1.83 = E^{\circ}_{\text{bromine}} - (-0.76)$$

$$1.83 + 0.76 = E^{\circ}_{\text{bromine}}$$

$$E^{\circ}_{\text{bromine}} = 1.07 \text{ V}$$



Electromotive series

Definition:

When the metals (electrodes) are arranged in the order of their increasing values of standard reduction potential on the hydrogen scale, then the arrangement is called electromotive series.



Comparing $E^\circ_{\text{half-cell}}$ values

Standard electrode potentials refer to the half-reaction as a reduction.

E° values therefore reflect the ability of the reactant to act as an ***oxidizing agent***.

The ***more positive*** the E° value, the more readily the ***reactant*** will act as an ***oxidizing agent***.

The ***more negative*** the E° value, the more readily the ***product*** will act as a ***reducing agent***.



Electromotive series

Electrode	Electrode Reaction	E°
Li^+/Li	$\text{Li}^+ + e \rightleftharpoons \text{Li}$	- 3.01
Zn^{2+}/Zn	$\text{Zn}^{2+} + 2e \rightleftharpoons \text{Zn}$	- 0.76
Fe^{2+}/Fe	$\text{Fe}^{2+} + 2e \rightleftharpoons \text{Fe}$	-0.44
H^+/H_2	$2\text{H}^+ + 2e \rightleftharpoons \text{H}_2$	0.00
Cu^{2+}/Cu	$\text{Cu}^{2+} + 2e \rightleftharpoons \text{Cu}$	+ 0.34
Ag^+/Ag	$\text{Ag}^+ + e \rightleftharpoons \text{Ag}$	+ 0.80
$1/2\text{F}_2/\text{F}^-$	$1/2 \text{F}_2 + e \rightleftharpoons \text{F}^-$	+ 2.87



Characteristics of Electrochemical Series

- The substances which are stronger reducing agents than hydrogen are placed above hydrogen in the series and have negative values of standard reduction potentials.
- All those substances which have positive values of reduction potentials and placed below hydrogen in the series are weaker reducing agents than hydrogen.
- The substances which are stronger oxidising agents than H^+ ion are placed below hydrogen in the series.
- The metals on the top (having high negative values of standard reduction potentials) have the tendency to lose electrons readily. These are active metals.
- The non-metals on the bottom (having high positive values of standard reduction potentials), have the tendency to accept electrons readily. These are active non-metals.



Applications of Electrochemical series :

Oxidizing and Reducing Strengths: The electrochemical series helps to identify the substances that are good oxidizing agents and reducing agents.

All the substances appearing on the top of the series behave as good reducing agents.

All the substances appearing at the bottom of the table are good oxidizing agents.

Displacement reactions: A metal higher in the series will displace the metal from its solution which is lower in the series. A metal higher in the series has a greater tendency to provide electrons to the cations of the metal to be precipitated.

The metal having low standard reduction potential will displace the metal from its salt's solution which has a higher value of standard reduction potential.

Predicting the Liberation of Hydrogen Gas from Acids by Metals: All metals having negative electrode potentials ($-E^\circ$) show a greater tendency of losing electrons as compared to hydrogen. So, when such a metal is placed in an acid solution, the metal gets oxidized, and H^+ ions get reduced to form hydrogen gas. Thus, the metals having $-E^\circ$ values liberate hydrogen from acids.

Predicting the Feasibility of a Redox Reaction: Depending on the E° values of the two electrodes feasibility of the given redox reaction can be found out. A redox reaction is feasible only if the species which has higher potential is reduced i.e., accepts the electrons and the species which has lower reduction potential is oxidized i.e., loses electrons.

Calculation of the EMF of the Cell: If the EMF of the cell is positive, the reaction is feasible in the given direction and the cell is correctly represented. If it is negative, the cell reaction is not feasible in the given direction and the cell is wrongly represented.

Comparison of Reactivities of Metals: The relative ease with which the various species of metals and ions may be oxidized or reduced is indicated by the reduction of potential values. The metals with lower reduction potential are not reduced easily but are easily oxidized to their ions losing electrons.

Writing Spontaneous Redox Reactions

Each half-reaction contains both a reducing agent and an oxidizing agent.

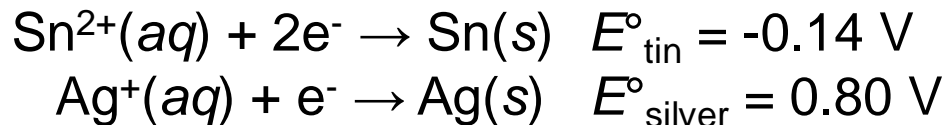
The **stronger** oxidizing and reducing agents react spontaneously to form the weaker ones.

A spontaneous redox reaction ($E^\circ_{\text{cell}} > 0$) will occur between an oxidizing agent and any reducing agent that lies **below** it in the emf series (i.e., one that has a less positive value for E°).

The oxidizing agent is the reactant from the half-reaction with the **more positive** $E^\circ_{\text{half-cell}}$.



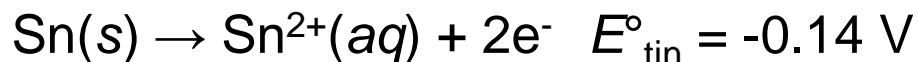
Using half-reactions to write a spontaneous redox reaction:



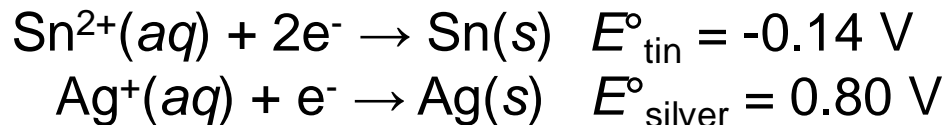
Step 1: Reverse one of the half-reactions into an oxidation step so that the difference between the E° values will be positive.

Here the Ag^{+}/Ag half-reaction has the more positive E° value, so it must be the reduction. This half-reaction remains as written.

We reverse the Sn^{2+}/Sn half-reaction, but we do **not** reverse the sign:



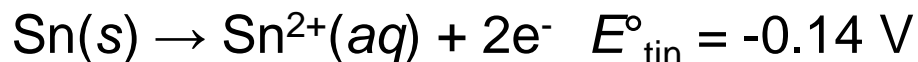
Using half-reactions to write a spontaneous redox reaction:



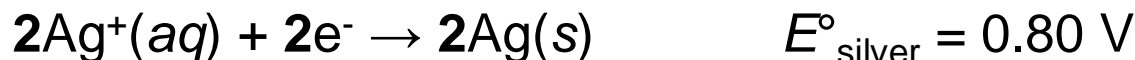
Step 1: Reverse one of the half-reactions into an oxidation step so that the difference between the E° values will be positive.

Here the Ag^{+}/Ag half-reaction has the more positive E° value, so it must be the reduction. This half-reaction remains as written.

We reverse the Sn^{2+}/Sn half-reaction, but we do **not** reverse the sign:



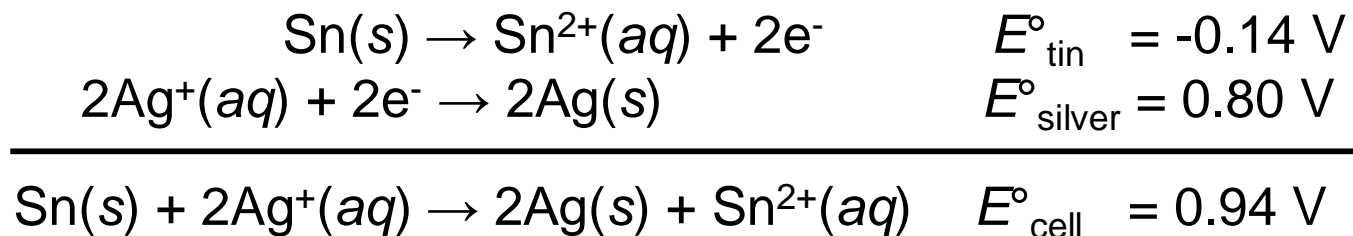
Step 2: Multiply the half-reactions if necessary so that the number of e^- lost is equal to the number of e^- gained.



Note that we multiply the equation but **not** the value for E° .

Step 3: Add the reactions together, cancelling common species.

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



$$E^\circ_{\text{cell}} = E^\circ_{\text{silver}} - E^\circ_{\text{tin}} = 0.80 - (-0.14) = 0.94 \text{ V}$$

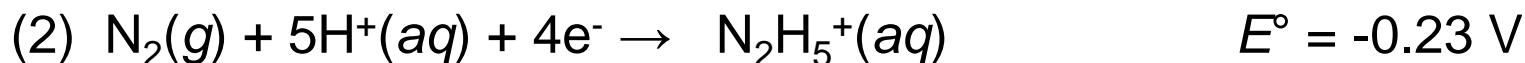
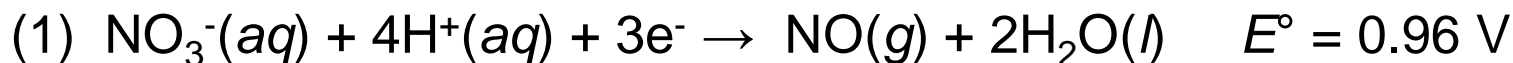


Sample Problem 21.4

Writing Spontaneous Redox Reactions and Ranking Oxidizing and Reducing Agents by Strength

PROBLEM: (a) Combine the following three half-reactions into three balanced equations for spontaneous reactions (A, B, and C), and calculate E°_{cell} for each.

(b) Rank the relative strengths of the oxidizing and reducing agents.



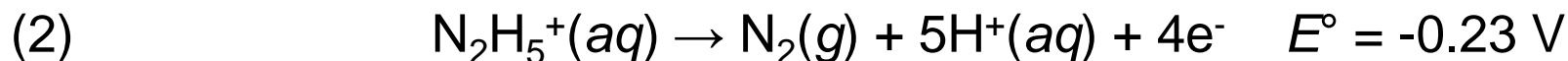
PLAN: To write the redox equations, we combine the possible pairs of half-reactions. In each case the half-reaction with the less positive value for E° will be reversed. We make e^- lost equal to e^- gained, add the half-reactions and calculate E°_{cell} . We can then rank the relative strengths of the oxidizing and reducing agents by comparing E° values.



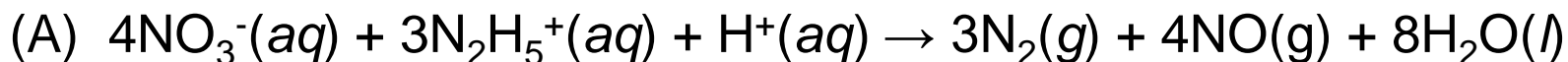
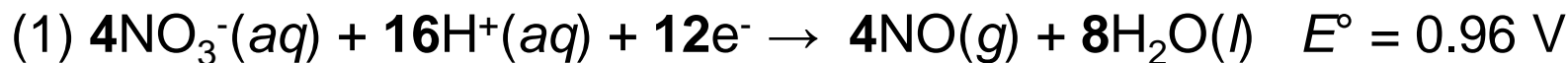
Sample Problem 21.4

SOLUTION: (a)

For (1) and (2), equation (2) has the smaller, less positive E° value:



We multiply equation (1) by 4 and equation (2) by 3:

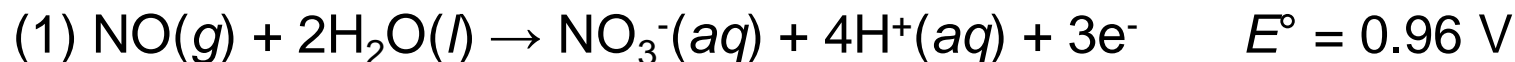


$$E^\circ_{\text{cell}} = 0.96 \text{ V} - (-0.23 \text{ V}) = 1.19 \text{ V}$$

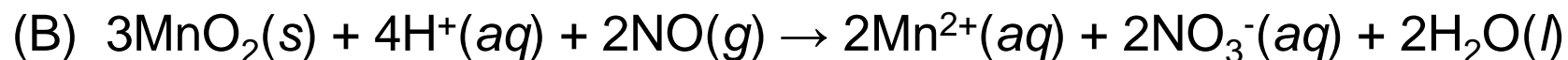
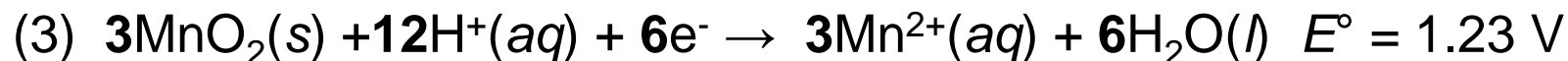
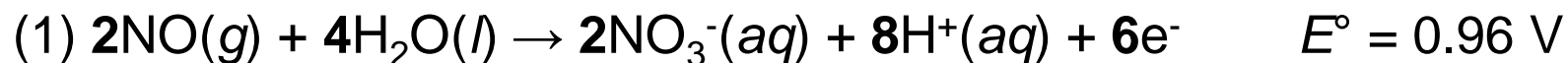


Sample Problem 21.4

For (1) and (3), equation (1) has the smaller, less positive E° value:



We multiply equation (1) by 2 and equation (3) by 3:

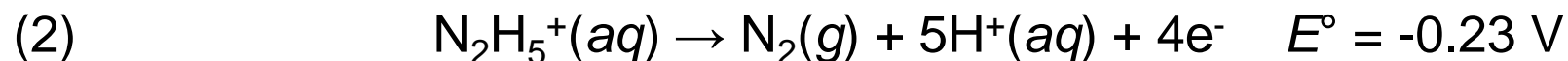


$$E^\circ_{\text{cell}} = 1.23 \text{ V} - (0.96 \text{ V}) = 0.27 \text{ V}$$

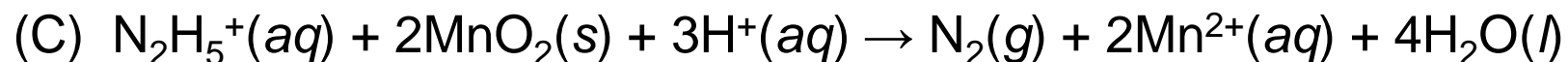
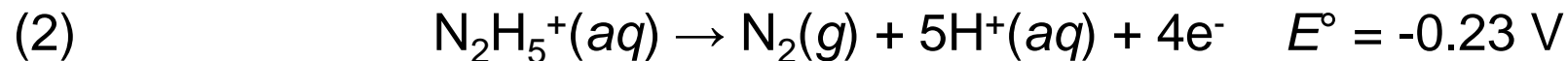


Sample Problem 21.4

For (2) and (3), equation (2) has the smaller, less positive E° value:



We multiply equation (3) by 2:



$$E^\circ_{\text{cell}} = 1.23 \text{ V} - (-0.23 \text{ V}) = 1.46 \text{ V}$$



Sample Problem 21.4:

(b) We first rank the oxidizing and reducing agents within each equation, then we can compare E°_{cell} values.

Equation (A) Oxidizing agents: $\text{NO}_3^- > \text{N}_2$
Reducing Agents: $\text{N}_2\text{H}_5^+ > \text{NO}$

Equation (B) Oxidizing agents: $\text{MnO}_2 > \text{NO}_3^-$
Reducing Agents: $\text{N}_2\text{H}_5^+ > \text{NO}$

Equation (C) Oxidizing agents: $\text{MnO}_2 > \text{N}_2$
Reducing Agents: $\text{N}_2\text{H}_5^+ > \text{Mn}^{2+}$

Comparing the relative strengths from the E°_{cell} values:

Oxidizing agents: $\text{MnO}_2 > \text{NO}_3^- > \text{N}_2$
Reducing agents: $\text{N}_2\text{H}_5^+ > \text{NO} > \text{Mn}^{2+}$



Electrochemical cell and free energy

When a cell produces a current, the current can be used to do work - to run a motor, for instance.

The measured cell potential is the maximum potential the cell can produce and is related to the electrical work

Thermodynamic principles can be employed to derive a relation between electrical energy and the maximum amount of work, W_{\max} obtainable from the cell. The maximum amount of work obtainable from the cell is the product of charge flowing per mole and maximum potential difference, E , through which the charge is transferred.

$$W_{\max} = - n F E \quad (1)$$

where n is the number of moles of electrons transferred and is equal to the valence of the ion participating in the cell reaction. F stands for Faraday and is equal to 96500 coulombs and E is the emf of the cell. **The negative sign for the work indicates that the electrical work is done by the system (the galvanic cell)**

Electrochemical cell and free energy

The free energy was defined as the energy that was available to do work.

According to thermodynamics, the maximum work that can be derived from a chemical reaction is equal to the free energy (ΔG) for the reaction,

$$\Delta G = W_{\max} \quad (2)$$

A mount of energy transferred from anode to cathode and used to do useful work

A mount of free energy available to do useful work

Therefore, from (1) and (2), we can write

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

Thus only when E has a positive value, ΔG value will be negative and the cell reaction will be spontaneous and the **e.m.f.** of the cell can be measured.



Electrochemical cell and free energy

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

n = number of moles of electrons in reaction

$$\Delta G^{\circ} = -nFE_{\text{cell}}^{\circ} \quad F = 96,500 \frac{\text{J}}{\text{V} \cdot \text{mol}} = 96,500 \text{ C/mol}$$

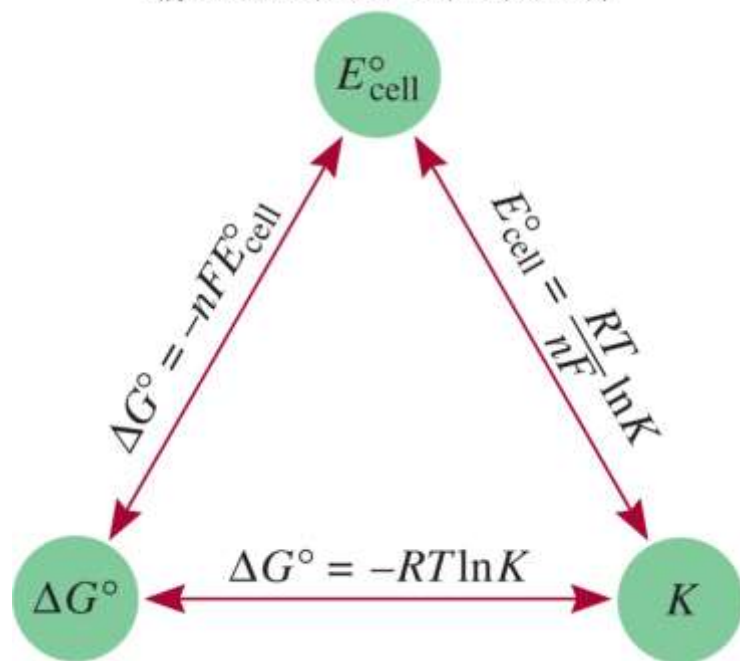
$$\Delta G^{\circ} = -RT \ln K = -nFE_{\text{cell}}^{\circ}$$

$$E_{\text{cell}}^{\circ} = \frac{RT}{nF} \ln K = \frac{(8.314 \text{ J/K} \cdot \text{mol})(298 \text{ K})}{n(96,500 \text{ J/V} \cdot \text{mol})} \ln K$$

Copyright © The McGraw-Hill Companies, Inc. Permission required for reproduction or display.

$$E_{\text{cell}}^{\circ} = \frac{0.0257 \text{ V}}{n} \ln K$$

$$E_{\text{cell}}^{\circ} = \frac{0.0592 \text{ V}}{n} \log K$$



The Effect of Concentration on Cell Emf

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

$$\Delta G = -nFE$$

$$\Delta G^{\circ} = -nFE^{\circ}$$

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

Nernst equation

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

At 298 K

$$E = E^{\circ} - \frac{0.0257 \text{ V}}{n} \ln K$$

$$E = E^{\circ} - \frac{0.0592 \text{ V}}{n} \log K$$



Predict whether the following reaction would proceed spontaneously as written at 298 K:

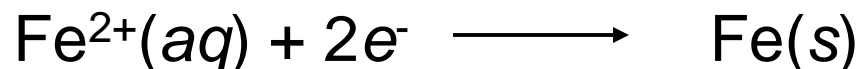


given that $[\text{Co}^{2+}] = 0.15 \text{ M}$ and $[\text{Fe}^{2+}] = 0.68 \text{ M}$.

The half-cell reactions are

Anode (oxidation): -0.28 V

Cathode (reduction): $-.44\text{V}$



$$\begin{aligned} E^{\circ}_{\text{cell}} &= E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}} \\ &= E^{\circ}_{\text{Fe}^{2+}/\text{Fe}} - E^{\circ}_{\text{Co}^{2+}/\text{Co}} \\ &= -0.44 \text{ V} - (-0.28 \text{ V}) \\ &= -0.16 \text{ V} \end{aligned}$$



$$\begin{aligned} E &= E^\circ - \frac{0.0257 \text{ V}}{n} \ln Q \\ &= E^\circ - \frac{0.0257 \text{ V}}{n} \ln \frac{[\text{Co}^{2+}]}{[\text{Fe}^{2+}]} \\ &= -0.16 \text{ V} - \frac{0.0257 \text{ V}}{2} \ln \frac{0.15}{0.68} \\ &= -0.16 \text{ V} + 0.019 \text{ V} \\ &= -0.14 \text{ V} \end{aligned}$$

Because E is negative, the reaction is not spontaneous in the direction written.



Cell Potential and Concentration

Nernst Equation

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{RT}{nF} \ln Q$$

- When $Q < 1$, [reactant] > [product], $\ln Q < 0$, so $E_{\text{cell}} > E^{\circ}_{\text{cell}}$
- When $Q = 1$, [reactant] = [product], $\ln Q = 0$, so $E_{\text{cell}} = E^{\circ}_{\text{cell}}$
- When $Q > 1$, [reactant] < [product], $\ln Q > 0$, so $E_{\text{cell}} < E^{\circ}_{\text{cell}}$

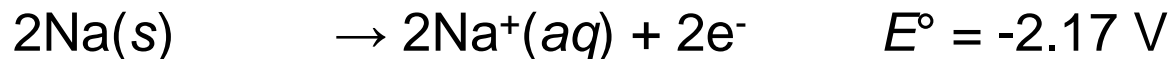
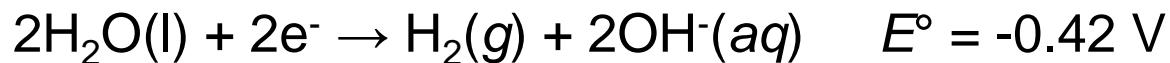
We can simplify the equation as before for $T = 298.15 \text{ K}$:

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0592 \text{ V}}{n} \log Q$$



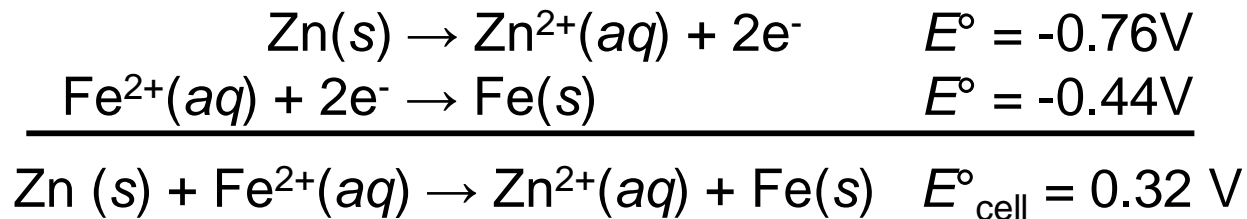
The Activity Series of the Metals

Metals that can displace H_2 from water are metals whose half-reactions lie below that of H_2O :



The Activity Series of the Metals

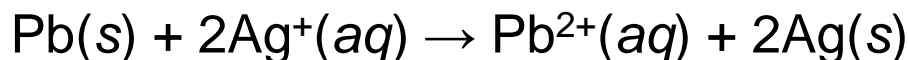
We can also predict whether one metal can displace another from solution. Any metal that is lower in the list of electrode potentials (i.e., has a larger E° value) will reduce the ion of a metal higher up the list.



Sample Problem 21.5

Calculating K and ΔG° from E°_{cell}

PROBLEM: Lead can displace silver from solution, and silver occurs in trace amounts in some ores of lead.

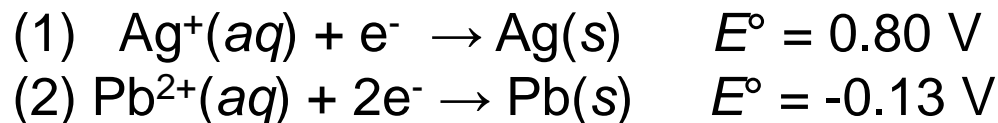


As a consequence, silver is a valuable byproduct in the industrial extraction of lead from its ore. Calculate K and ΔG° at 298.15 K for this reaction.

PLAN: We divide the spontaneous redox reaction into the half-reactions and use values from Appendix D to calculate E°_{cell} . From this we can find K and ΔG° .

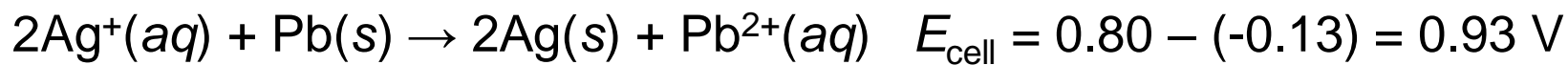
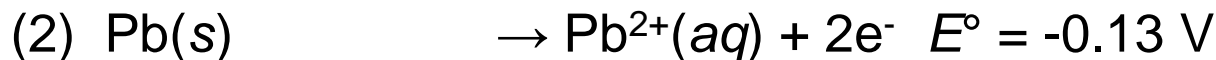
SOLUTION:

Writing the half-reactions with their E° values:



Sample Problem 21.5

We need to reverse equation (2) and multiply equation (1) by 2:



$$E_{\text{cell}}^\circ = \frac{RT}{nF} \ln K = \frac{0.0592 \text{ V}}{2} \log K = 0.93 \text{ V}$$

$$\log K = \frac{0.93 \text{ V} \times 2}{0.0592 \text{ V}} = 31.42$$

$$\boxed{K = 2.6 \times 10^{31}}$$

$$\Delta G^\circ = -nFE_{\text{cell}}^\circ = -\frac{2 \text{ mol e}^-}{\text{mol rxn}} \times \frac{96.5 \text{ kJ}}{\text{V} \cdot \text{mol e}^-} \times 0.93 \text{ V}$$

$$= -1.8 \times 10^2 \text{ kJ/mol rxn}$$



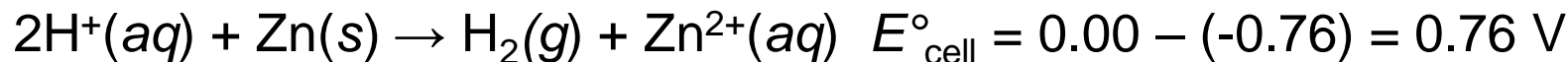
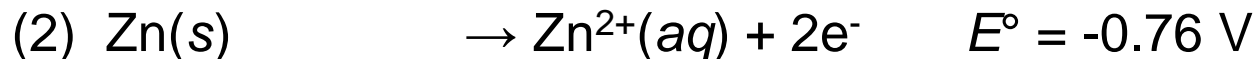
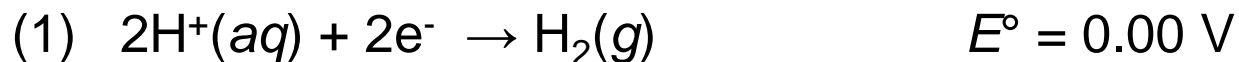
Sample Problem 21.6**Using the Nernst Equation to Calculate E_{cell}**

PROBLEM: In a test of a new reference electrode, a chemist constructs a voltaic cell consisting of a Zn/Zn²⁺ half-cell and an H₂/H⁺ half-cell under the following conditions:

$$[\text{Zn}^{2+}] = 0.010 \text{ M} \quad [\text{H}^+] = 2.5 \text{ M} \quad P_{\text{H}_2} = 0.30 \text{ atm}$$

Calculate E_{cell} at 298 K.

PLAN: To apply the Nernst equation and determine E_{cell} , we must know E°_{cell} and Q . We write the equation for the spontaneous reaction and calculate E°_{cell} from standard electrode potentials. We must convert the given pressure to molarity in order to have consistent units.

SOLUTION:

Sample Problem 21.6

Converting pressure to molarity:

$$\frac{n}{V} = \frac{P}{RT} = \frac{0.30 \text{ atm}}{0.0821 \frac{\text{atm}\cdot\text{L}}{\text{mol}\cdot\text{K}} \times 298.15 \text{ K}} = 1.2 \times 10^{-2} \text{ M}$$

$$Q = \frac{[\text{H}_2][\text{Zn}^{2+}]}{[\text{H}^+]^2} = \frac{0.012 \times 0.010}{(2.5)^2} = 1.9 \times 10^{-5}$$

Solving for E_{cell} at 25°C (298.15 K), with $n = 2$:

$$\begin{aligned} E_{\text{cell}} &= E_{\text{cell}}^{\circ} - \frac{0.0592 \text{ V}}{n} \log Q \\ &= 1.10 \text{ V} - \left(\frac{0.0592 \text{ V}}{2} \log(1.9 \times 10^{-5}) \right) = 0.76 - (-0.14 \text{ V}) = \mathbf{0.90 \text{ V}} \end{aligned}$$



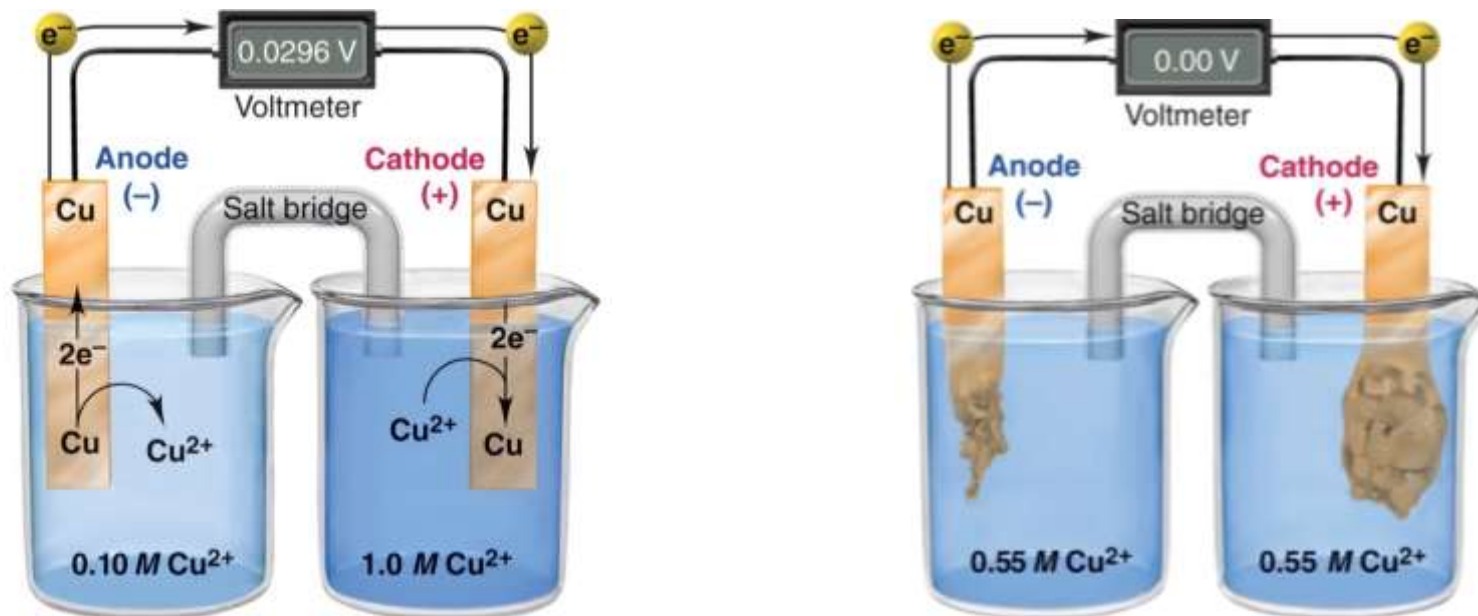
Concentration Cells

- It is possible to get a spontaneous reaction when the oxidation and reduction reactions are the same, as long as the electrolyte concentrations are different.
- Concentration cells consist of identical electrodes dipped in the solutions of the same electrolytes but with varying concentrations. In these type cells, the electrolyte tries to diffuse from higher concentration solutions towards lower concentration solutions.
- **Electrons will flow from the electrode in the less concentrated solution to the electrode in the more concentrated solution.**
 - Oxidation of the electrode in the less concentrated solution will increase the ion concentration in the solution; the less concentrated solution has the anode.
 - Reduction of the solution ions at the electrode in the more concentrated solution reduces the ion concentration; the more concentrated solution has the cathode.

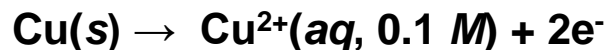


Figure 21.12 A concentration cell based on the Cu/Cu²⁺ half-reaction.

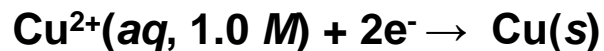
Copyright © The McGraw-Hill Companies, Inc. Permission required for reproduction or display.



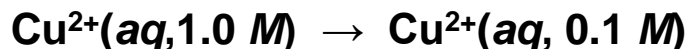
Oxidation half-reaction



Reduction half-reaction



Overall (cell) reaction



$E_{\text{cell}} > 0$ as long as the half-cell concentrations are different.

The cell is no longer able to do work once the concentrations are equal.



Sample Problem 21.7

Calculating the Potential of a Concentration Cell

PROBLEM: A concentration cell consists of two Ag/Ag⁺ half-cells. In half-cell A, the electrolyte is 0.0100 M AgNO₃; in half-cell B, it is 4.0x10⁻⁴ M AgNO₃. What is the cell potential at 298.15 K?

PLAN: The standard half-cell potentials are identical, so E°_{cell} is zero, and we find E_{cell} from the Nernst equation. Half-cell A has a higher [Ag⁺], so Ag⁺ ions are reduced and plate out on electrode A, which is therefore the cathode. In half-cell B, Ag atoms of the electrode are oxidized and Ag⁺ ions enter the solution. Electrode B is thus the anode. As for all voltaic cells, the cathode is positive and the anode is negative.



Types of indicator electrodes

Classification of Electrodes

The general electrode reaction:



Electrodes of
the first type

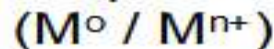
Electrodes of
the second type

Electrodes of
the third type

A) According to the type:

1) First type (kind or order):

In this type electrode potential depends on equilibrium between element and its ions (i.e. two phase electrode).



$$E_{25^\circ\text{C}} = E_0 - 0.059/n \log 1 / [\text{M}^{n+}]$$

From Nernst equation $E \propto [\text{M}^{n+}]$

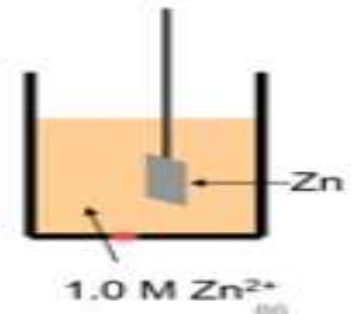
1. Metal-metal ion electrodes

Line notation $\text{Zn}^{2+} | \text{Zn}$

reaction $\text{Zn}^{2+} + 2\text{e} \rightleftharpoons \text{Zn}$

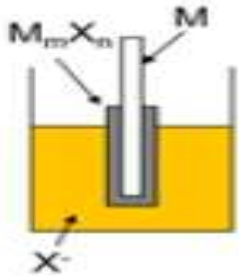
$$e_{\text{Zn}^{2+}|\text{Zn}} = e_{\text{Zn}^{2+}|\text{Zn}}^\circ - \frac{0.059}{2} \log \left(\frac{1}{[\text{Zn}^{2+}]} \right)$$

$$e_{\text{M}^{n+}|\text{M}} = e_{\text{M}^{n+}|\text{M}}^\circ - \frac{0.059}{n} \log \left(\frac{1}{[\text{M}^{n+}]} \right)$$



Types of indicator electrodes

Electrodes of the second kind



- These electrodes consist of three phases.
- The metal is covered by a layer of its sparingly soluble salt and is immersed in a solution containing the anions of this salt.



- Because of the two interfaces, equilibrium is established between the metal atoms and the anions in solution through two partial equilibria:

1. between the metal and its cation of the sparingly soluble salt



2. between the anion in the solid phase of the sparingly soluble salt and the anion in solution

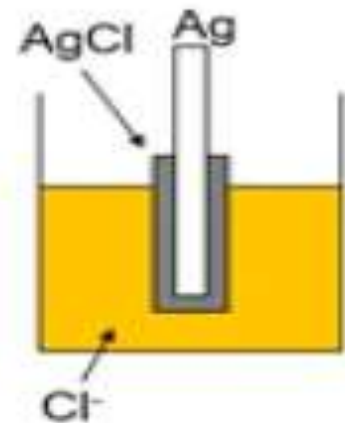


1. Silver-silver chloride electrode

- $Ag^{+} + e \rightleftharpoons Ag(s)$
- $AgCl(s) \rightleftharpoons Ag^{+} + Cl^{-}$



$$e_{AgCl|Ag} = e_{AgCl|Ag}^{\circ} - \frac{0.059}{1} \log ([Cl^{-}])$$



Types of indicator electrodes

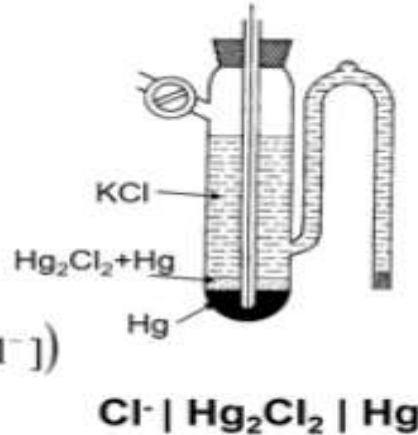
2. Calomel electrode

- $(\text{Hg}_2^{2+}) + 2e \rightleftharpoons 2\text{Hg}(l)$
 - $\text{Hg}_2\text{Cl}_2(s) \rightleftharpoons (\text{Hg}_2^{2+}) + 2\text{Cl}^-$
- $$\text{Hg}_2\text{Cl}_2(s) + 2e \rightleftharpoons 2\text{Hg}(l) + 2\text{Cl}^-$$

$$e_{\text{Hg}_2\text{Cl}_2|\text{Hg}} = e_{\text{Hg}_2\text{Cl}_2|\text{Hg}}^{\circ} - \frac{0.059}{1} \log([\text{Cl}^-])$$

For $[\text{Cl}^-] = 0.001$

$$\begin{aligned} e_{\text{Calomel}} &= 0.268 - 0.059 \times (-3) \\ &= 0.268 + 0.177 \\ &= 0.445 \text{ V} \end{aligned}$$



3) Electrode of Third type:

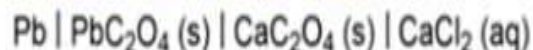
This type of electrodes relates for potentiometric determination of cations. Which the electrode of 1st order are unavailable for determination this cation e.g Ca^{2+} . In this case the electrode involves two slightly soluble salts with common anions as shown



Types of indicator electrodes

Metal Indicator Electrodes of 3rd kind

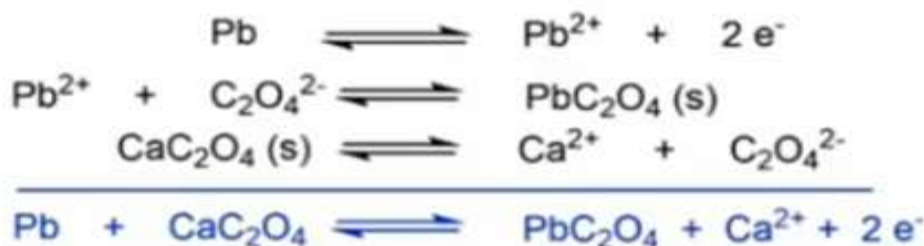
- This type of electrode consists of a metal, one of its insoluble salts, another insoluble salt of another metal having same anion and solution of any soluble salt of the latter having same cation



- Lead 1st dissolves to form Pb^{2+} ions with the liberation of 2 electrons. The lead ions then combine with $\text{C}_2\text{O}_4^{2-}$ ions to form insoluble lead oxalate



- The removal of $\text{C}_2\text{O}_4^{2-}$ ions from solution results in dissolution of calcium oxalate that ionises to maintain the equilibrium



these calcium ions are used to maintain

equilibrium in overall process



Saturated Calomel Electrode

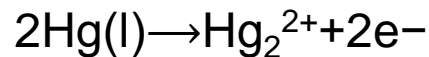
Consist of glass container containing some mercury at the bottom covered by a paste of mixed $\text{Hg}+\text{HgCl}_2+\text{KCl}$ and solution of saturated KCl and shown as a following (المذكورة).

Hence, three types of Calomel electrodes are available, viz., normal (1N), decinormal (0.1N) and saturated.

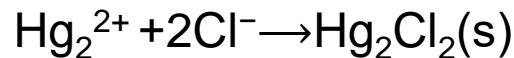
Working : The potential of the calomel electrode depends upon the concentration of the chloride ions in solution. The electrode is represented as :



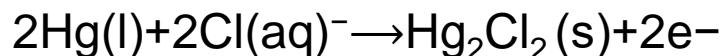
Oxidation : If the electrode serves as anode, then half reaction that occurs on it will be oxidation. Mercury is first oxidised to mercuric ions.



The chloride ions supplied by KCl solution combine with mercuric ions $[\text{Hg}_2^{2+}]$ to form insoluble mercurous chloride. Thus,

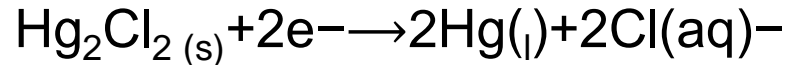


Overall reaction is,



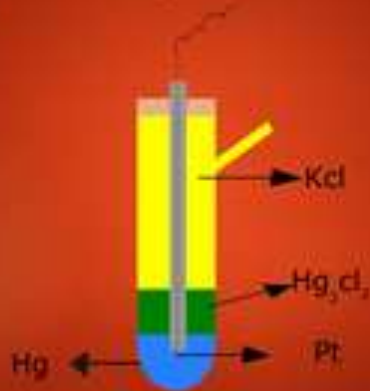
Saturated Calomel Electrode

Reduction : If the electrode is cathode (+) in the galvanic cell, the half reaction that occurs on it will be reduction :



The potential of calomel electrode decreases with increase in the concentration of chloride ions at a given temperature. Thus, electrode is reversible with respect to concentration of chloride ions

Construction & working of Calomel Electrode



From Above equation it is evident that potential of calomel electrode depends on concentration of Cl⁻

For 0.1N KCl

$$E_{\text{calomel}} = 0.334 \text{ V}$$

For 1N KCl

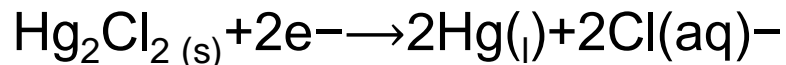
$$E_{\text{calomel}} = 0.28 \text{ V}$$

For Saturated KCl

$$E_{\text{calomel}} = 0.2422 \text{ V}$$

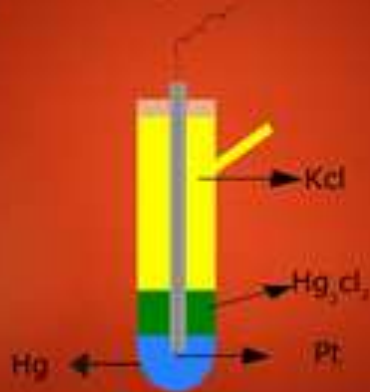
Saturated Calomel Electrode

Reduction : If the electrode is cathode (+) in the galvanic cell, the half reaction that occurs on it will be reduction :



The potential of calomel electrode decreases with increase in the concentration of chloride ions at a given temperature. Thus, electrode is reversible with respect to concentration of chloride ions

Construction & working of Calomel Electrode



From Above equation it is evident that potential of calomel electrode depends on concentration of Cl^-

For 0.1N KCl

$$E_{\text{calomel}} = 0.334 \text{ V}$$

For 1N KCl

$$E_{\text{calomel}} = 0.28 \text{ V}$$

For Saturated KCl

$$E_{\text{calomel}} = 0.2422 \text{ V}$$