10(w)_Electrochemistry

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Competencies

1. Define oxidation-reduction (Redox) reactions
2. Balance oxidation-reduction reaction by the addition of H+ and OH-
3. Write and balance half-cell reactions
4. Describe:
   - Electrochemical cells
   - Voltaic cells
   - Electrolysis
   - Different industrial electrolytic processes
   - Different batteries
   - Fuel cells
5. Differentiate voltaic cell from electrolytic cell
6. Calculate cell under standard and non-standards conditions
7. Explain how to control corrosion

Introduction

- **Electrochemistry** is that branch of chemistry dealing with the relationship between chemical change and electrical work.


What is electrochemistry?

- Electrochemistry is the study of chemical reactions which take place at the interface of an electrode usually a solid, metal or semiconductor and an ionic conductor, the electrolyte.
- Electrochemistry deals with the interaction between electrical energy and chemical change.
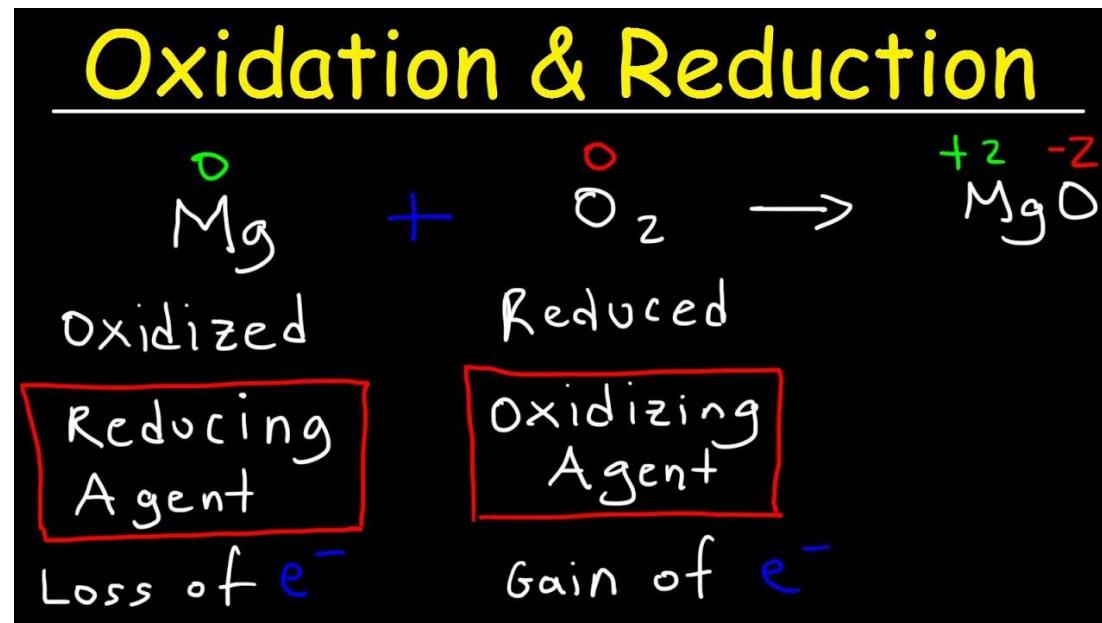
Balancing Oxidation-Reduction Equation – Oxidation-Reduction Reactions

- Chemical reactions in which the oxidation number of one or more substance changes is called as **redox**.

- **Oxidation** refers to the loss of electrons, on the other hand, **reduction** refers to the gain of electrons.

Zn(s) + 2H$^+$(aq)$\longrightarrow$ Zn^{+2}(aq) + H2(g)
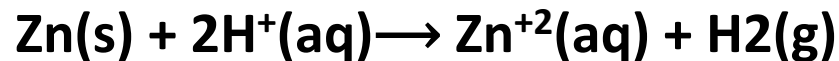
- The substance that makes it possible for another substance to be oxidized is called the **oxidizing agent**, or the **oxidant**.

- Similarly, a **reducing agent**, or **reductant**, is the substance that gives up electrons, thereby causing another substance to be reduced.

Half-Reactions

Example: $Sn^{+2}(aq) + 2Fe^{+3}(aq) \longrightarrow Sn^{+4}(aq) + 2Fe^{+2}(aq)$

2 processes:

1. The oxidation of Sn^{2+}

   Oxidation half-cell reaction: $Sn^{+2}(aq) \longrightarrow Sn^{+4}(aq) + \cancel{2e^-}$

2. The reduction of Fe^{+2}

   Reduction half-cell reaction: $2Fe^{+3}(aq) + \cancel{2e^-} \longrightarrow 2Fe^{+2}(aq)$

   Overall/Net reaction : $Sn^{+2}(aq) + 2Fe^{+3}(aq) \rightarrow Sn^{+4}(aq) + 2Fe^{+2}(aq)$

Equations that show either oxidation or reduction alone are called **half-reactions or partial equations.**

The Ion-Electron Method:
Steps in balancing redox reaction by ion-electron method

1. Divide the equation into two skeleton partial equations/half-cells/half-reactions. Balance the atoms other than O and H.

2. Balance the O and H atoms in each partial equation.
   a) For reactions in acid solution:
      i. For every O atom that is needed, add one H2O to the side of the partial skeleton that is deficient in oxygen,
      ii. ii. Add H+ where needed to balance the hydrogen.
   b) For reactions in alkaline solutions
      i. For every O atom that is needed, add one H2O to the side of the partial skeleton that is deficient in oxygen,
      ii. For every H atom that is needed, add one H2O to the side of the partial skeleton that is deficient in hydrogen, then add one OH- to the opposite side.

Steps in balancing redox reaction by ion-electron method:

3. Balance the net charge. Add electrons to the most positive side to balance the charges on both sides.

4. Multiply one or both partial equations by numbers that will make the number of electrons lost in one partial equation equal the number of electrons gained in the other partial equation.

5. Add the partial equations. In addition, cancel terms found at opposite sides of the final equation and add terms that are found in the side.

6. Check the net charges of both sides.

2 slightly different procedures employed in balancing the equation by the ion-electron method.

- One is for reactions taking place in acid solution, and

- the other one for reactions taking place in alkaline solution

Reactions Occurring in Acid Solution

Sample Problem 7.1	$Cr_2O_7^{-2} + Cl^- \longrightarrow Cr^{+3} + Cl_2$ occurring in acid solution
Two skeleton partial equation for the half-reactions: Let's take the case of partial equation 1 first:	**Half-cell reaction 1: $Cr_2O_7^{-2} \longrightarrow Cr^{+3}$** **Half-cell reaction 2: $Cl^- \longrightarrow Cl_2$**
The reaction is taking place in an acid solution, H_2O and H^+ can be added where needed.	
For half-cell reaction1, let us balance first atom other than H and O. In this case, we have Cr. (a) There are 2 Cr atoms in the reactant. (b) To balance Cr we need to add a coefficient of 2 to Cr in the product.	**$Cr_2O_7^{-2} \longrightarrow 2Cr^{+3}$**
To balance the O: (a) There are 7 atoms of O in the reactant. No O in the product. (b) For every O that is required, one water must be added to the side that requires O. We need to add 7 H2O to the product to balance the 7O in the reactant	**$Cr_2O_7^{-2} \longrightarrow 2Cr^{+3} + 7\ H_2O$**

Reactions Occurring in Acid Solution

Sample Problem 7.1	$Cr_2O_7^{-2} + Cl^- \longrightarrow Cr^{+3} + Cl_2$ occurring in acid solution
We have balanced the O atoms. We now have to balance the H. (a) For every H atom needed, add H+ to the side that requires H. (b) We have added 7H2O in the product, giving 14H atoms in the product. (c) So, 14H+ must be added to the reactant to balance the H atoms. (d) That balances both sides.	$14H^+ + Cr_2O_7^{-2} \rightarrow 2Cr^{+3} + 7H_2O$
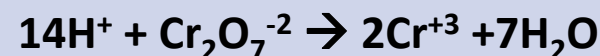
Let us now balance the net charge. Take note of the charges of the following: (a) H+ - has charge of +1 (monoatomic ion) (b) Cr2O7 -2 – has charge of -2 (polyatomic ion) (c) Cr+3 – has a charge of +3 (monoatomic ion) (d) H2O – has no charge at all (neutral compound) and its charge is zero (0)
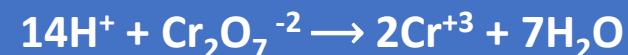
$14H^+ + Cr_2O_7^{-2} \longrightarrow 2Cr^{+3} + 7H_2O$			
14 (+1)	1 (-2)	2 (+3)	7 (0)
+14	-2	+6	0
+14 -2 = +12		+6 +0 = +6	
+12 ≠ +6			

(e) We need to add electrons to the most positive side. Take note that electrons have negative charges. (f) +12 (reactant) is more positive than +6 (product). Electrons must be added to the reactant.

$+6e^- +14H^+ +Cr_2O_7^{-2} \rightarrow 2Cr^{+3} + 7H_2O$				
6 (-1)	14 (+1)	1 (-2)	2 (+3)	7 (0)
-6	+14	-2	+6	0
-6 +14 -2 = +6			+6 +0 = +6	
+6 = +6				

Reactions Occurring in Acid Solution

Sample Problem 7.1	$Cr_2O_7^{-2} + Cl^- \longrightarrow Cr^{+3} + Cl_2$ occurring in acid solution		
Next, we will balance half-cell reaction 2. (a) We only have Cl. No more other atoms to balance. (b) To balance Cl, a coefficient of 2 must be added to Cl-.	$Cl^- \longrightarrow Cl_2$ $2Cl^- \longrightarrow Cl_2$		
Proceed to net charge. (a) Cl^- - has a charge of -1. (b) Cl_2 – is a diatomic molecule and does not carry a charge. Its charge is zero (0).	$2Cl^- \longrightarrow Cl_2$		
	2 (-1)	1 (0)	
	-2 ≠ 0		
(c) The product is more positive (0) than the reactant (-2). Electrons must be added to the product to balance the net charge	$2Cl^- \longrightarrow Cl_2 + 2e^-$		
	2 (-1)	1 (0)	2 (-1)
	-2	0 -2	
	-2 = -2		

Reactions Occurring in Acid Solution

Sample Problem 7.1	$Cr_2O_7^{-2} + Cl^- \longrightarrow Cr^{+3} + Cl_2$ occurring in acid solution
Add the 2 half-cell reactions.	**Half-cell reaction 1:** $6e^- + 14H^+ + Cr_2O_7^{-2} \longrightarrow 2Cr^{+3} + 7H_2O$ **Half-cell reaction 2:** $2Cl^- \longrightarrow Cl_2 + 2e^-$
(a) We need to balance the electrons lost and gained to cancel them. (b) To balance, we need to multiply half-cell reaction 2 by 3 on both sides to bring the electrons lost to 6. Multiply half-cell reaction 1 by 1 on both sides considering that we have 6 electrons gained.	**Half-cell reaction 1:** $6e^- + 14H^+ + Cr_2O_7^{-2} \longrightarrow 2Cr^{+3} + 7H_2O$ **Half-cell reaction 2:** $6Cl^- \longrightarrow 3Cl_2 + 6e^-$
(c) Taking the algebraic sum, cancel common terms found opposite with each other. Add common terms	**Half-cell reaction 1:** $\cancel{6e^-} + 14H^+ + Cr_2O_7^{-2} \longrightarrow 2Cr^{+3} + 7H_2O$ **Half-cell reaction 2:** $6Cl^- \longrightarrow 3Cl_2 + \cancel{6e^-}$ --- **Overall/ net reaction: :** $6Cl^- + 14H^+ + Cr_2O_7^{-2} \longrightarrow 3Cl_2 + 2Cr^{+3} + 7H_2O$

Reactions Occurring in Acid Solution

Sample Problem 7.1	$Cr_2O_7^{-2} + Cl^- \longrightarrow Cr^{+3} + Cl_2$ occurring in acid solution				
Check the net charge.					
$6Cl^- + 14H^+ + Cr_2O_7^{-2} \longrightarrow 3Cl_2 + 2Cr^{+3} + 7H_2O$					
6 (-1)	14 (+1)	1 (-2)	3 (0)	2 (+3)	7 (0)
-6	+14	-2	0	+6	0
+6 = +6					

Sample 7.2. Balance the equation by ion-electron method. Reaction occurring in acid solution.

$$MnO_4^- + HCN + I^- \rightarrow Mn^{+2} + ICN$$

Reactions occurring in Alkaline or Basic Solution

Sample Problem 7.3	$MnO_4^- + N_2H_4 \longrightarrow MnO_2 + N_2$ in alkaline solution
Divide the equation to two half-cell reaction	**Half-cell reaction 1: $MnO_4^- \longrightarrow MnO_2$** **Half-cell reaction 2: $N_2H_4 \longrightarrow N_2$**
Half-cell reaction 1: (a) There are four O atoms in the reactant against only two O atoms in the product. We need to add 2 H2O molecules to the product to balance the O (b) We need to balance the H by adding 4H+ to the reactant to balance the H (c) We have balanced all species in the reaction. However, this is occurring in an alkaline or basic solution and we need to remove H+ from the equation. (d) To do this, we have added 4H+, so need to add OH- at both sides equivalent to the number of H+ added. In this particular example, we have added 4H+, therefore we must add 4OH- to both sides in order to remove H+ e. The 4OH- + 4H+ in the reactant combines to form 4H2O molecules. And the H2O molecules are subtracted.	**$MnO_4^- \longrightarrow MnO_2$** **$MnO_4^- \longrightarrow MnO_2 + 2H_2O$** **$4H^+ + MnO_4^- \longrightarrow MnO_2 + 2H_2O$** **$4OH^- + 4H^+ + MnO_4^- \longrightarrow MnO_2 + 2H_2O + 4OH^-$** **$(4H_2O - 2H_2O = 2H_2O)$** **$4H_2O + MnO_4^- \longrightarrow MnO_2 + 2H_2O + 4OH^-$** **$2H_2O + MnO_4^- \longrightarrow MnO_2 + 4OH^-$**

Reactions occurring in Alkaline or Basic Solution

Sample Problem 7.3	$MnO_4^- + N_2H_4 \longrightarrow MnO_2 + N_2$ in alkaline solution			
Balancing the net charge	$2H_2O + MnO_4^- \longrightarrow MnO_2 + 4OH^-$			
	2 (0)	1 (-1)	1 (0)	4 (-1)
	0	-1	0	-4
	$-1 \neq -4$			

-1 (reactant) is more positive than -4 (product). We must add 3e- to the reactant to balance the charge.

$3e^- + 2H_2O + MnO_4^- \longrightarrow MnO_2 + 4OH^-$				
3 (-1)	2 (0)	1 (-1)	1 (0)	4 (-1)
-3	0	-1	0	-4
$-4 = -4$				

Half-cell reaction 2
(a) No O atom only H atoms. We need to add 4H+ only to the product to balance H.
(b) We have added 4H+ to balance the H+, we must add the same number of OH- to both side to remove H+ added
(c) 4H+ + 4OH- combines to form 4H2O

$$N_2H_4 \longrightarrow N_2$$

$$N_2H_4 \longrightarrow N_2 + 4H^+$$

$$4OH^- + N_2H_4 \longrightarrow N2 + 4H^+ + 4OH^-$$

$$4OH^- + N_2H_4 \longrightarrow N_2 + 4H_2O$$

Reactions occurring in Alkaline or Basic Solution

Sample Problem 7.3	MnO_4^- + $N_2H_4 \longrightarrow MnO_2$ + N_2 in alkaline solution			
Balancing the net charge		**$4OH^-$ + $N_2H_4 \longrightarrow N_2$ + $4H_2O$**		
		4 (-1)	1 (0)	1 (0)	4 (0)
		-4	0	0	0
		$-4 \neq 0$			
O (product) is more positive than -4 (reactant). We must add 4e- to the product to balance the charge		**$4OH^-$ + $N_2H_4 \longrightarrow N_2$ + $4H_2O$ + $4e^-$**			
		4 (-1)	1 (0)	1 (0)	1 (0)	4 (-1)
		-4	0	0	0	-4
		-4 = -4				

Add the two half-cell reactions:

(a) 3e- gained against 4e- lost. Multiply both sides of half-cell reaction 1 by 4 & half-cell reaction 2 by 3 to balance number of electrons lost and gain

(b) get algebraic sum. Cancel electrons. Subtract H2O molecules (reactants & products) also OH- (reactants &products).

Half-cell reaction 1: 3e- + $2H_2O$ + $MnO_4^- \longrightarrow MnO_2$ + $4OH^-$ <u>Half-cell</u>
reaction 2: $4OH^-$ + $N_2H_4 \longrightarrow N_2$ + $4H_2O$ +$4e^-$
Half-cell reaction 1: 12e- + $8H_2O$ + $4MnO_4^- \longrightarrow 4MnO_2$ + $16OH^-$
Half-cell reaction 2: $12OH^-$ + $3N_2H_4 \longrightarrow 3N_2$ + $12H_2O$ + 12e-
Half-cell reaction 1: ~~12e-~~ + ~~$8H_2O$~~ + $4MnO_4^- \longrightarrow 4MnO_2$ + ~~$16OH^-$~~
Half-cell reaction 2: ~~$12OH^-$~~ + $3N_2H_4 \longrightarrow 3N_2$ + $12H_2O$ + ~~12e-~~
Overall/Net reaction:
    3N2H4 + $4MnO4^- \longrightarrow 4MnO2$ + $4OH^-$ + 3N2 + 4H2O

Reactions occurring in Alkaline or Basic Solution

Sample Problem 7.3			$MnO_4^- + N_2H_4 \longrightarrow MnO_2 + N_2$ in alkaline solution		
$3N2H4 + 4MnO4^- \longrightarrow 4MnO2 + 4OH^- + 3N2 + 4H2O$					
3 (0)	4 (-1)	4 (0)	4 (-1)	3 (0)	4 (0)
0	-4	0	-4	0	0
-4 = -4					

Sample Problem 7.4. Consider the following reaction: $Br_2 \rightarrow BrO_3^- + Br^-$ (alkaline solution)
In this type of reaction, Br_2 undergoes both oxidation (loss of electrons) and reduction (gain of electrons). This type of reaction is called **disproportionation or auto- oxidation-reduction reaction**.

Electrochemical Cell

- Oxidation-reduction or **redox reactions** take place in electrochemical cells.

- Oxidation occurs at the electrode termed the **anode** and reduction occurs at the electrode called the **cathode.**
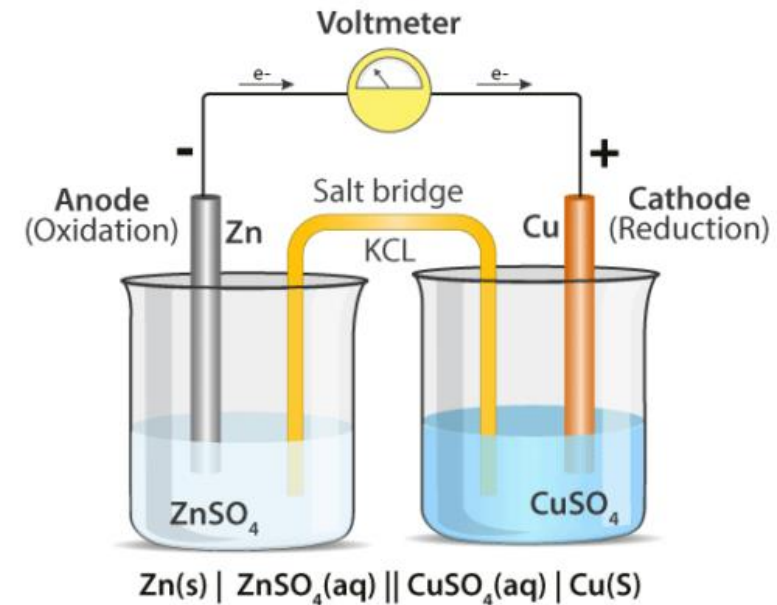
Electrodes and Charge
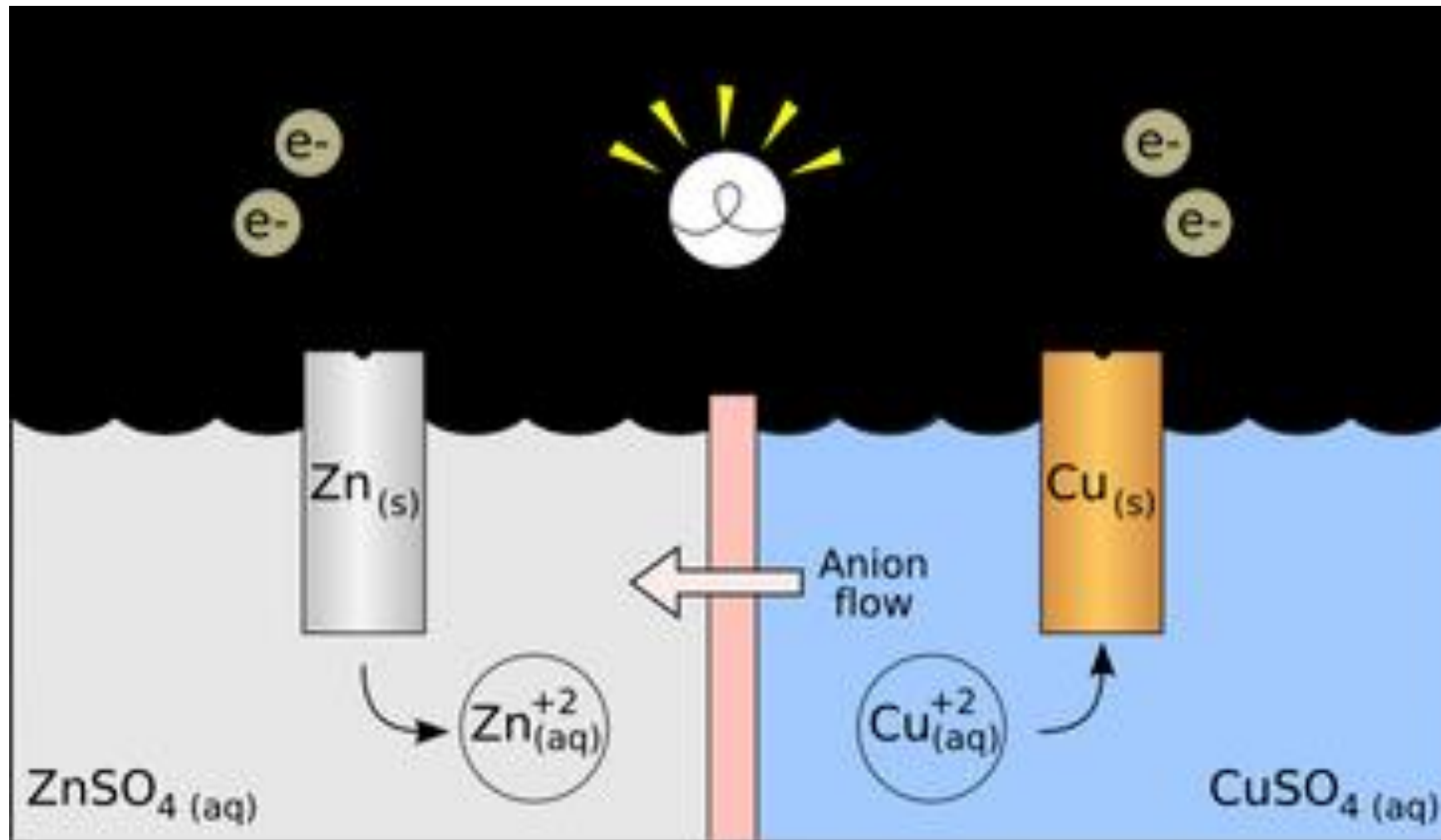
Galvanic or Voltaic C
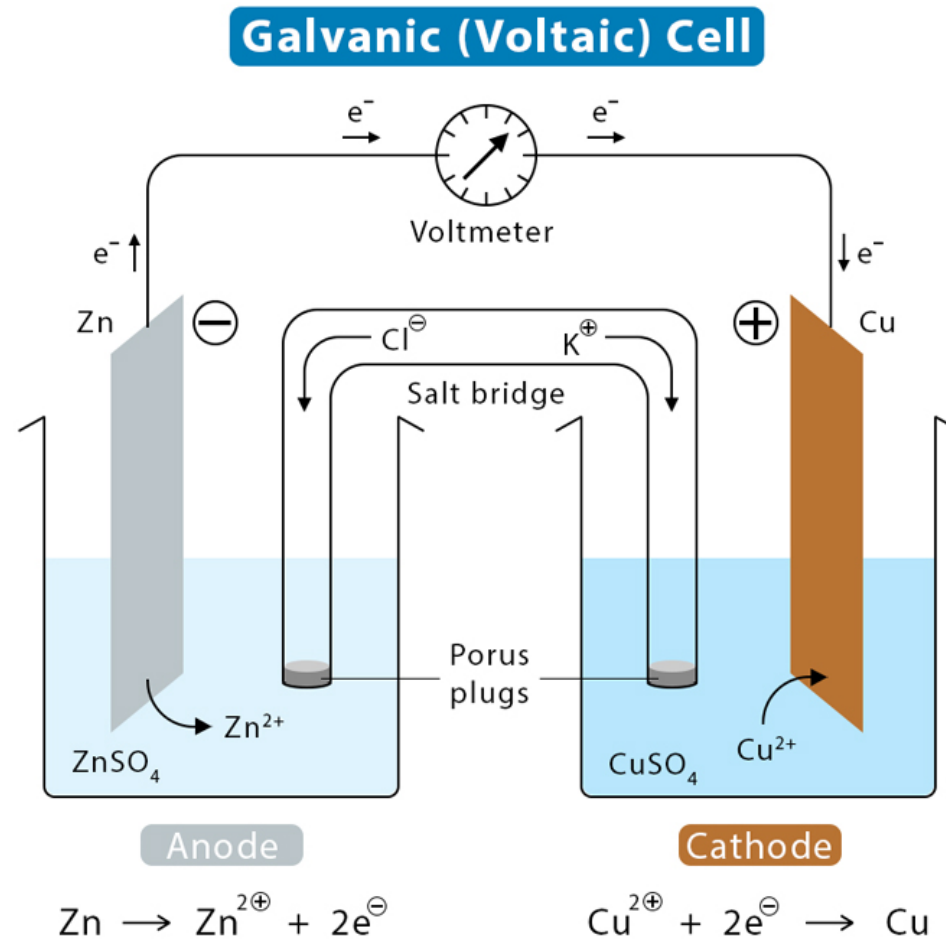
Types of Electrode

Liquid Junction

Liquid junction potentials

Galvanic cell without liquid junction.
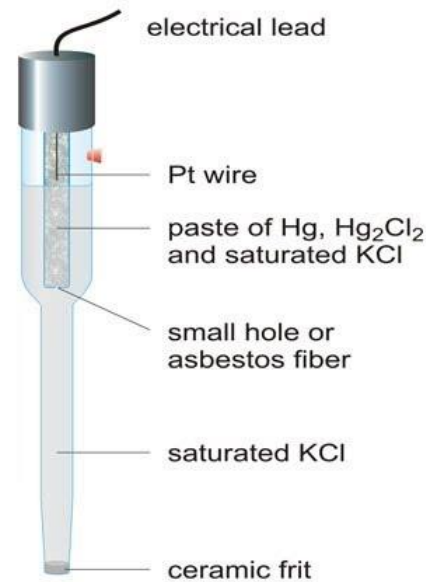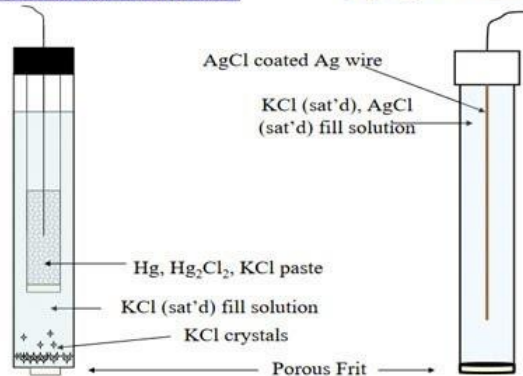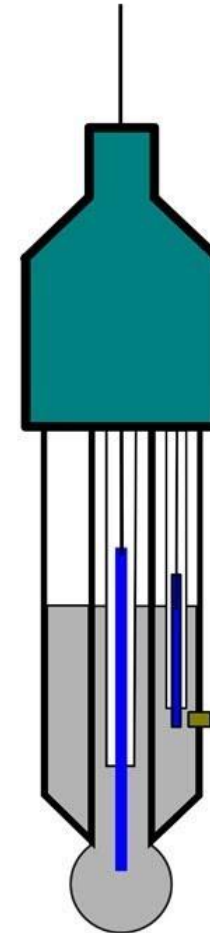
Galvanic cell with liquid junction.
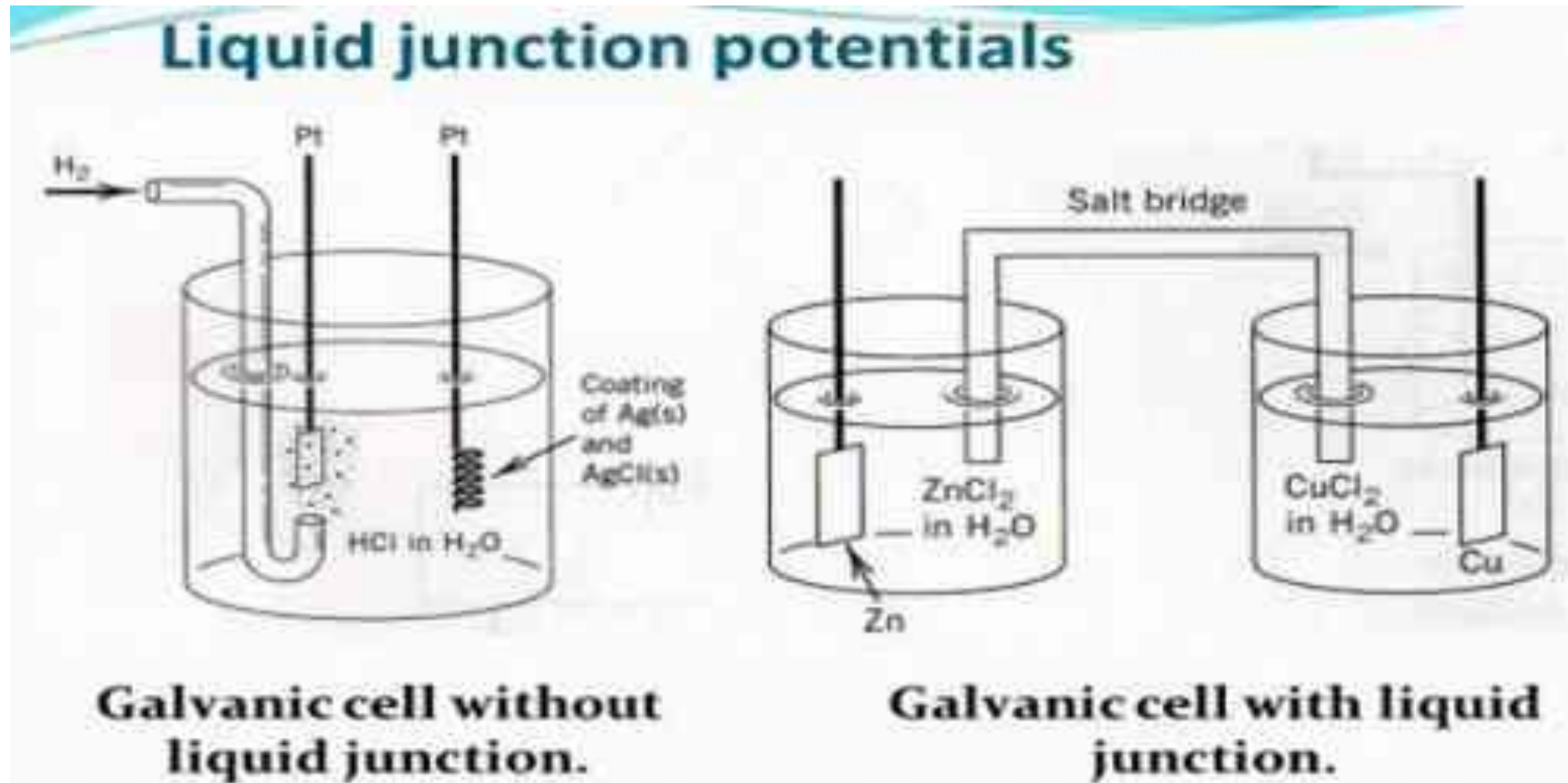
E^0 is Referenced to a Standard Hydrogen Electrode (Refer to figure below).
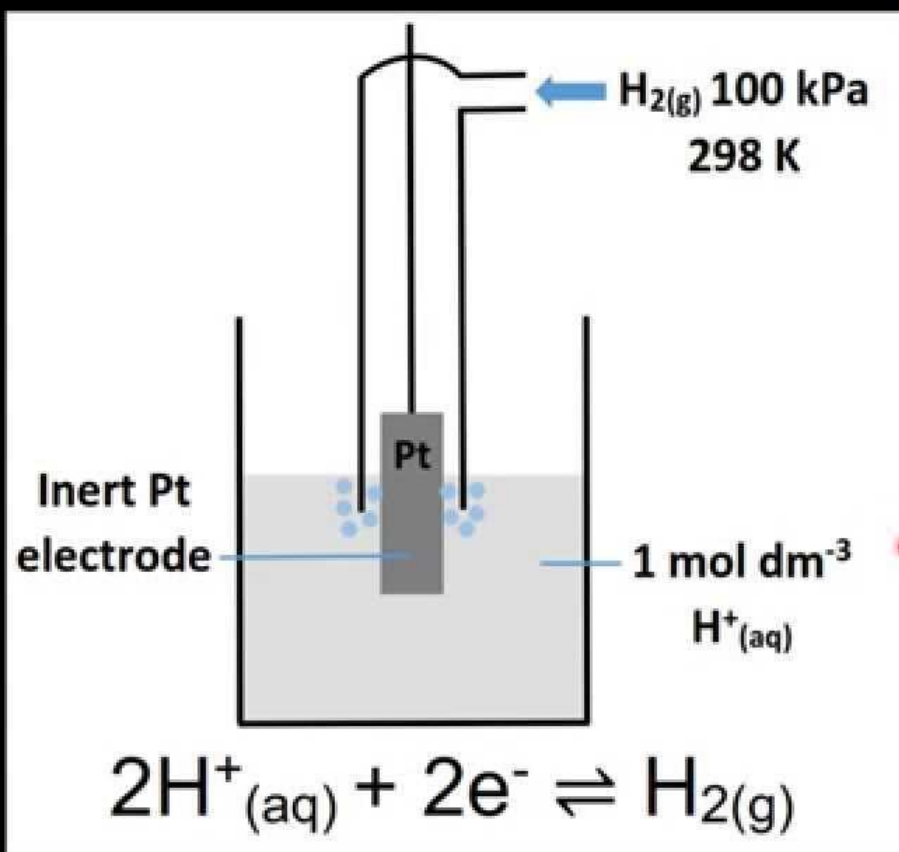
Types of electrochemical cells

GALVANIC CELL
VERSUS
ELECTROLYTIC CELL

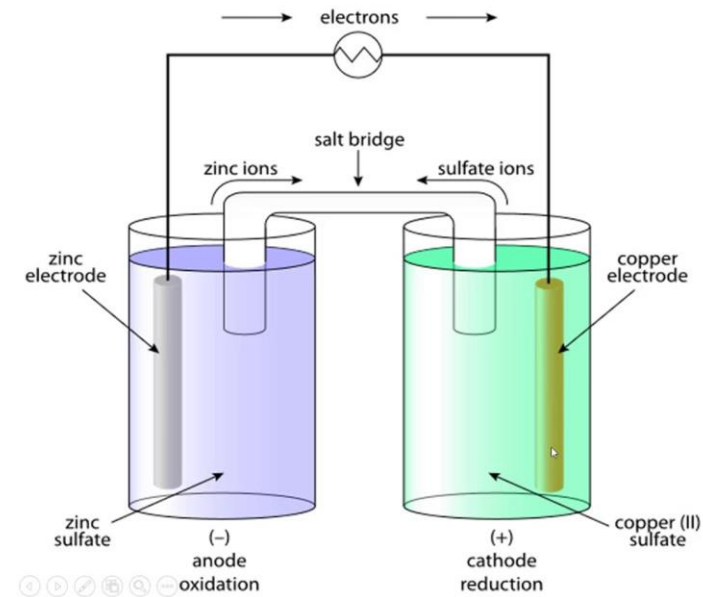|	
A Galvanic cell is an electrochemical cell that can produce electricity with the help of a chemical reaction	An electrolytic cell is a cell that uses an electric current for the progression of a chemical reaction
Converts chemical energy into electrical energy	Converts electrical energy into chemical energy
A spontaneous reaction occurs	A non-spontaneous reaction occurs
The anode is negatively charged, and the cathode is positively charged	The anode is positively charged, and the cathode is negatively charged

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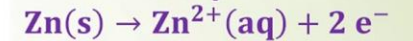# Electrodes (anode, cathode) in the presence of electrolyte
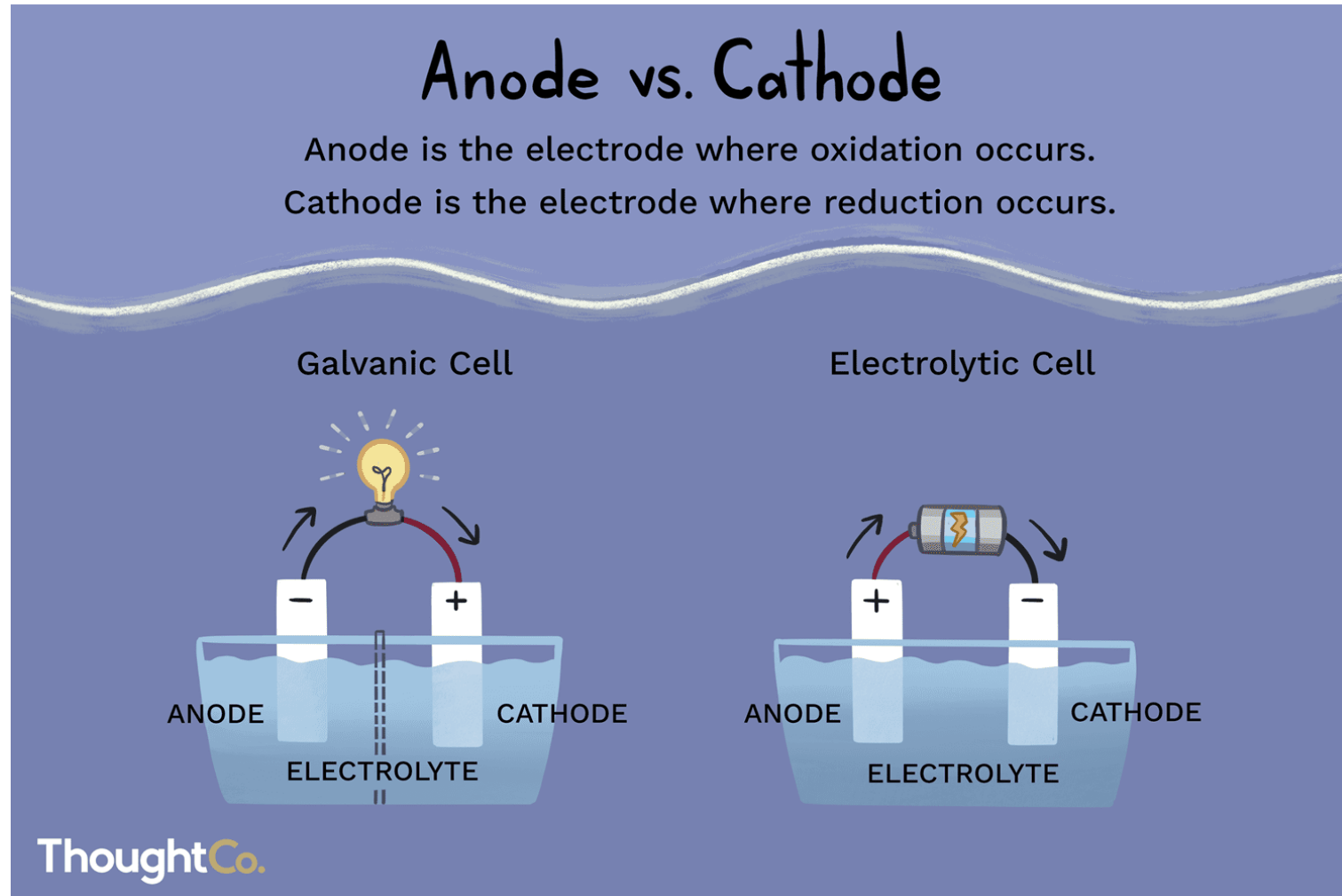
Daniel Cell

- **Daniel cell** is an example of a galvanic cell - contains zinc immersed in zinc sulfate solution and copper in copper sulfate solution separated by a diaphragm or salt bridge

electrons

salt bridge

zinc ions   sulfate ions

zinc electrode   copper electrode

zinc sulfate   copper (II) sulfate

(−)   (+)
anode   cathode
oxidation   reduction

The Daniell Cell

Anode compartment

$$Zn(s) \rightarrow Zn^{2+}(aq) + 2\,e^-$$

Cathode Compartment

$$Cu^{2+}(aq) + 2\,e^- \rightarrow Cu(s)$$

$E^{\circ}_{red}\left(Zn^{2+}(aq)/Zn(s)\right)$ **is** -0.7618 **V**

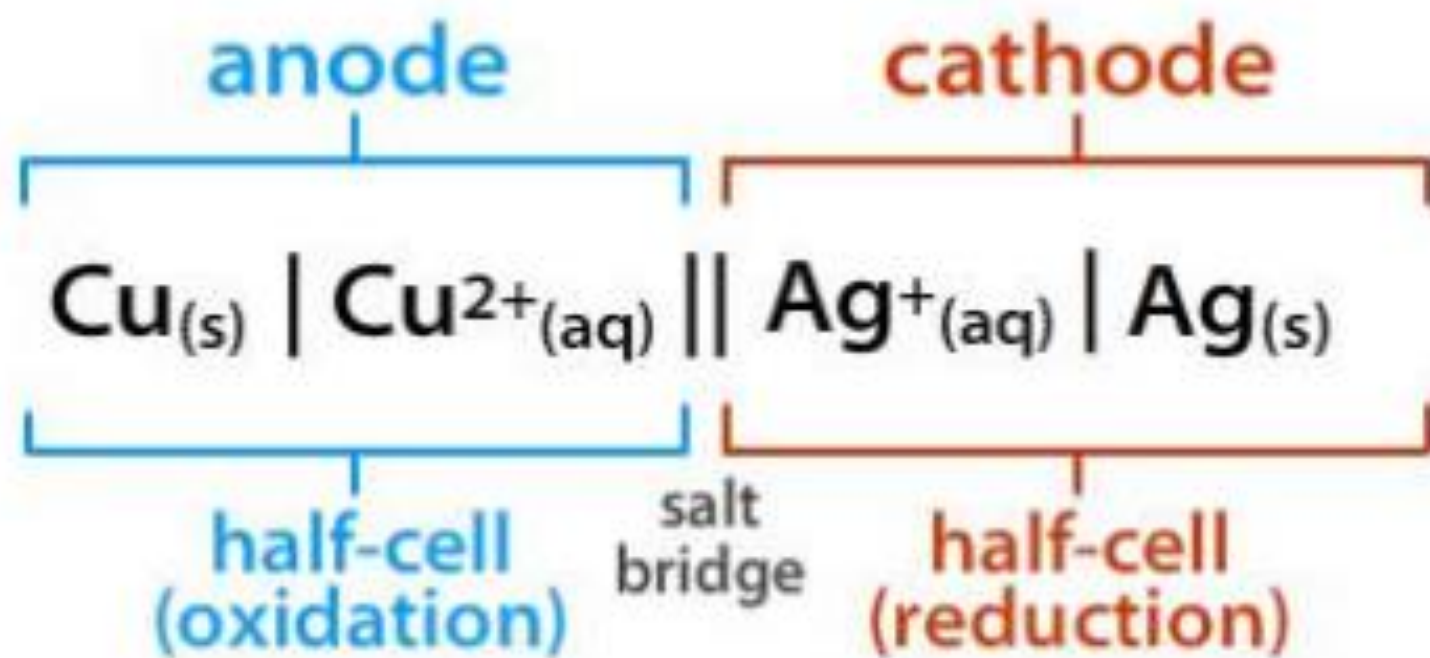$E^{\circ}_{red}\left(Cu^{2+}(aq)/Cu(s)\right)$ **is** $+0.34$ **V**

"Galvanic cell labeled" by Hazmat2 - Own work. Licensed under CC BY 3.0 via Wikimedia Commons - http://commons.wikimedia.org/wiki/File:Galvanic_cell_labeled.svg#/media/File:Galvanic_cell_labeled.svg

Voltaic Cell Notation
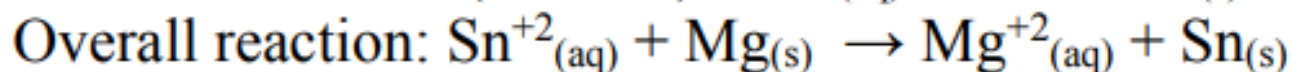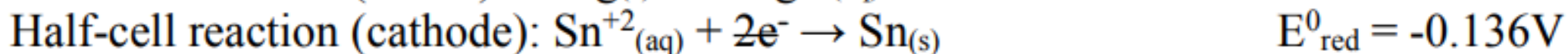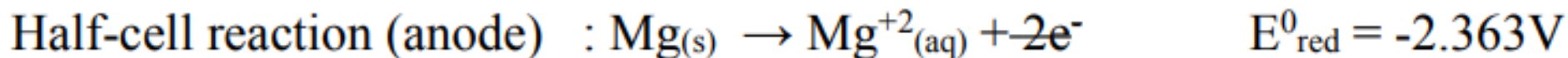
- The notation for the Zn/Cu+2 cell is

1. It is written in compartments. The anode (oxidation half-cell) and the cathode (reduction half-cell) compartments. A single vertical line represents a phase boundary within the compartment.	$Zn(s) \mid Zn^{+2}(aq)$ – anode and $Cu^{+2}(aq) \mid Cu(s)$
2. Combining the two compartments with the anode compartment to the left and the cathode compartment to the right, separated by a double vertical l	$Zn(s) \mid Zn^{+2}(aq) \mid\mid Cu^{+2}(aq) \mid Cu(s)$
3. If required, the concentrations of the dissolved components are enclosed in parentheses	$Zn(s) \mid Zn^{+2}(1\ M) \mid\mid Cu^{+2}(1\ M) \mid Cu(s)$
4. A comma separates the half-cell components that are in the same phase. Half-cell components usually appearing in the same order as in the half-cell reaction. Electrodes are at the far left for the anode and at the far right for the cathode separated by a single vertical line	$Graphite \mid I^{-}(aq) \mid I_2(s) \mid\mid MnO_4^{-}(aq), H^{+}(aq), Mn^{+2}(aq) \mid Graphite$

Cell Diagram

anode

cathode

$$Cu_{(s)} \mid Cu^{2+}_{(aq)} \parallel Ag^{+}_{(aq)} \mid Ag_{(s)}$$

half-cell
(oxidation)

salt
bridge

half-cell
(reduction)

Sample Problem 7.5. What is the E^0cell for the voltaic cell: Mg | Mg^{+2} || Sn^{+2} | Sn

Solution:

Half-cell reaction (anode)   : $Mg_{(s)} \rightarrow Mg^{+2}_{(aq)} + 2e^-$ $E^0_{red} = -2.363V$

Half-cell reaction (cathode): $Sn^{+2}_{(aq)} + 2e^- \rightarrow Sn_{(s)}$ $E^0_{red} = -0.136V$

Overall reaction: $Sn^{+2}_{(aq)} + Mg_{(s)} \rightarrow Mg^{+2}_{(aq)} + Sn_{(s)}$

$E^0_{cell} = E^0_{red}(\text{cathode}) - E^0_{red} (\text{anode}) = -0.136V - (-2.363V) = -0.136V + 2.363V = +2.227V$

Sample Problem 6.6

- Given the following:

$$PbSO_4 + 2e^- \leftrightarrow Pb(s) + SO_4^{-2} \qquad E^0red = -0.359V$$

$$Pb^{+2} + 2e^- \leftrightarrow Pb(s) \qquad E^0red = -0.126V$$
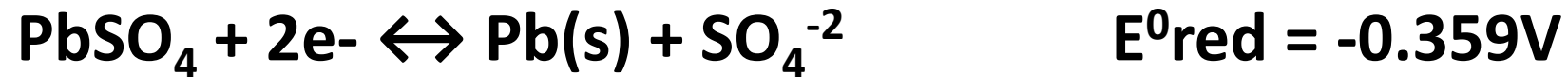
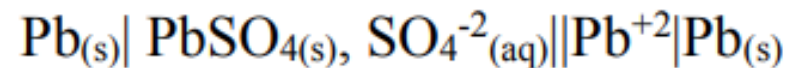a). Write the notation for a cell that uses these half-reactions

b). Write the equation for the cell reaction

Solution:

a). $Pb^{+2} + 2e^- \leftrightarrow Pb_{(s)}$, $E^0_{red} = -0.126V$ has the greater tendency for reduction and is the cathode

$$Pb_{(s)}| \; PbSO_{4(s)}, \; SO_4^{-2}{}_{(aq)}||Pb^{+2}|Pb_{(s)}$$

b). Half-cell reaction (anode): $\cancel{Pb_{(s)}} + SO_4^{-2} \leftrightarrow PbSO_4 + \cancel{2e^-} \qquad E^0_{red} = +0.359V$

Half-cell reaction (cathode) : $Pb^{+2} + \cancel{2e^-} \leftrightarrow \cancel{Pb_{(s)}} \qquad E^0_{red} = -0.126V$

Overall reaction: $\qquad\qquad Pb^{+2} + SO_4^{-2} \leftrightarrow PbSO_4 \qquad E^0_{red} = +0.233V$

Cell EMF Under Standard Condition

- The potential difference is called the **electromotive** (causing electron motion) **force, or emf.**

- The emf of the cell, denoted by E_{cell}, is called the **cell potential.**

- Under standard conditions, the emf is called the **standard emf**, or the **standard cell potential** and is denoted by E^0cell.

- For example, the Zn-Cu voltaic cell, the standard cell potential at 25^0C is +1.10V:

$Zn(s) + Cu^{+2}(aq, 1M) \longrightarrow Zn^{+2}(aq, 1M) + Cu(s)$ **$E^0cell = 1.10V$**
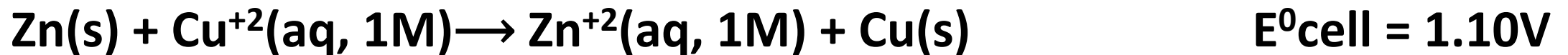
Standard Reduction (Half-Cell) Potential

- The **cell potential** is the difference between two electrode potentials, the first one is the one associated with the cathode and the other one is associated with the anode.

- **Standard electrode potentials** are tabulated for reduction reactions; they are referred to as standard reduction potentials denoted by **E^0red**

- The cell potential E^0cell, is given by the standard reduction potential of the cathode reaction, $E^0red(cathode)$, minus the standard reduction potential of the anode reaction, $E^0red(anode)$.

    $E^0cell = E^0red(cathode) - E^0red(anode)$

- The reference half-reaction is the reduction of $H^+(aq)$ to $H_2(gas)$ under standard conditions, which assigned a standard reduction potential of exactly 0V.

$2H^+(aq, 1M) + 2e^- \longrightarrow H_2(g, 1\ atm)$

$E^0cell = 0\ V$

- An electrode designed to produce this half-reaction is called as the **standard hydrogen electrode (SHE)** or the **normal hydrogen electrode (NHE).**
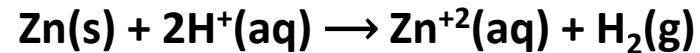
Standard Reduction (Half-Cell) Potential

- There are two suggested methods to determine the E^0cell:

1. Using the standard reduction potential as reduction process and solving the E^0cell using the formula:

E^0cell = E^0red(cathode) - E^0red(anode)

2. Identifying the half-cell reaction undergoing oxidation and the one undergoing reduction, then reversing the reduction potential in the table and taking the algebraic sum.

- For example, the oxidation of Zn and the reduction of H+ :

$Zn(s) + 2H^+(aq) \longrightarrow Zn^{+2}(aq) + H_2(g)$

- Zn^{+2}/Zn electrode is the anode and SHE is the cathode and cell voltage is +0.76 V.

- Standard potential of H+ (E^0red = 0).

- Standard reduction potential for the Zn^{+2}/Zn half-reaction:

E^0cell = E^0red(cathode) - E^0red (anode)

+0.76 V = 0 V - E^0red (anode)

E^0red (anode) = - 0.76 V

- Standard reduction potential of -0.76 V can be assigned to the reduction of Zn^{+2} to Zn.

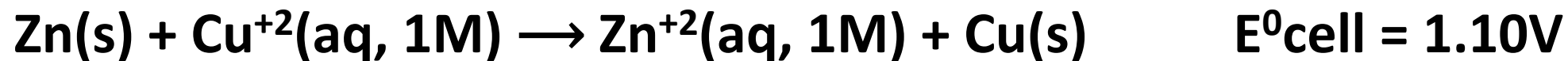**$Zn^{+2}(aq, 1M) + 2e- \longrightarrow Zn(s)$ E^0cell = -0.76 V**
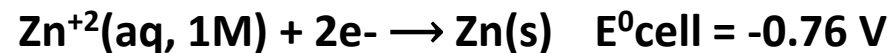
Standard Reduction (Half-Cell) Potential

- Changing the stoichiometric coefficient in a half-reaction does not affect the value of the standard reduction potential.
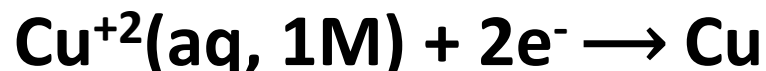
- For example:

10 mol Zn^{+2}(aq, 1M) + 20e^- ⟶ 10 Zn(s) E^0cell = -0.76V

Sample Problem 7.7.

- For the Zn-Cu^{+2} voltaic cell:

$Zn(s) + Cu^{+2}(aq, 1M) \longrightarrow Zn^{+2}(aq, 1M) + Cu(s)$ $E^0cell = 1.10V$

Given that the standard reduction potential of Zn^{+2} to $Zn(s)$ is -0.76 V, calculate the E^0cell for the reaction of Cu^{+2} to $Cu(s)$.

$Cu^{+2}(aq, 1M) + 2e^- \longrightarrow Cu$

Solution:

E^0_{cell} and E^0_{red} for Zn^{+2} are given and we are asked to calculate E^0_{red} for Cu^{+2}. Step: In the voltaic cell, Zn is oxidized (from 0 in the $Zn_{(s)}$ to +2 $Zn^{+2}_{(aq, 1M)}$) and is therefore the anode. Thus, the given E^0_{red} for Zn^{+2} is E^0_{red} (anode). Because Cu^{+2} is reduced (from +2 in the $Cu^{+2}_{(aq, 1M)}$ to 0 in the $Cu_{(s)}$, then it should be in the cathode half-cell. Thus, the unknown reduction potential for Cu+2 is E^0_{red}(cathode). Knowing E^0_{cell} and E^0_{red} (anode), we can solve for E^0_{red} (cathode).

Sample Problem 7.7

Using the first method:

Half-cell oxidation (anode) : $Zn_{(s)} \rightarrow Zn^{+2}_{(aq,\ 1M)} + 2e^-$ $E^0_{red} = -0.76V$
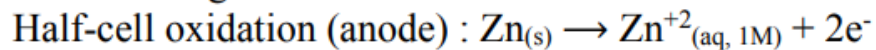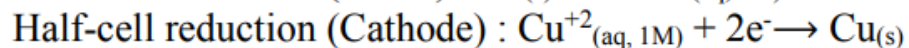
Half-cell reduction (Cathode) : $Cu^{+2}_{(aq,\ 1M)} + 2e^- \rightarrow Cu_{(s)}$ $E^0_{red} = ?$

$E^0_{cell} = 1.10V$

Solving for E^0_{red}(cathode):

$\qquad E^0_{cell} = E^0_{red}$(cathode) - E^0_{red} (anode)

$\qquad\quad 1.10\ V = E^0_{red}$(cathode) $- (-0.76\ V)$

E^0_{red}(cathode) $= 1.10\ V - 0.76\ V = 0.34\ V$
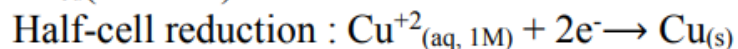
Half-cell reduction : $Cu^{+2}_{(aq,\ 1M)} + 2e^- \rightarrow Cu_{(s)}$ $E^0_{red} = 0.34\ V$

Checking:

This reduction potential agrees with the one listed in the appendix.

Note: The standard reduction potential for Cu^{+2} can be presented as $E^0_{Cu+2} = 0.34\ V$, and that for Zn^{+2} as $E^0_{Zn+2} = -0.76\ V$. The subscript identifies the ion that is reduced in the reduction half-cell.

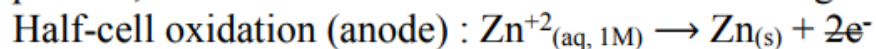Using the second method: (let us check whether the E^0_{cell} us 1.10V)

Half-cell reduction Cathode) : $Cu^{+2}_{(aq,\ 1M)} + 2e^- \rightarrow Cu_{(s)}$ $E^0_{red} = 0.34\ V$
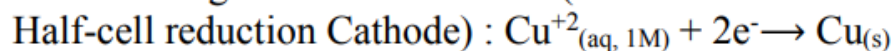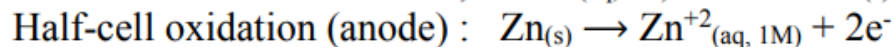
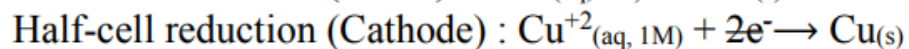Half-cell oxidation (anode) : $Zn_{(s)} \rightarrow Zn^{+2}_{(aq,\ 1M)} + 2e^-$ $E^0_{red} = -0.76V$
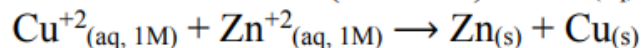
Since, the given data in the table are the reduction process and for the oxidation process, we need to reverse the reaction and the sign.

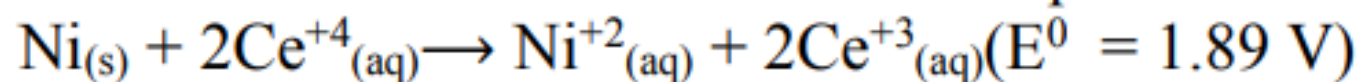Half-cell oxidation (anode) : $Zn^{+2}_{(aq,\ 1M)} \rightarrow Zn_{(s)} + \cancel{2e^-}$ $E^0_{red} = +0.76V$

Half-cell reduction (Cathode) : $Cu^{+2}_{(aq,\ 1M)} + \cancel{2e^-} \rightarrow Cu_{(s)}$ $E^0_{red} = +0.34\ V$

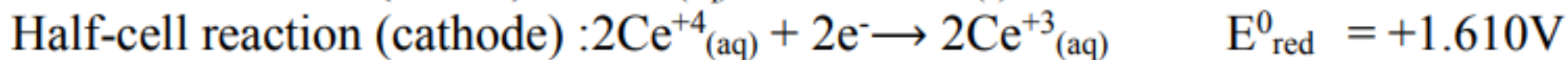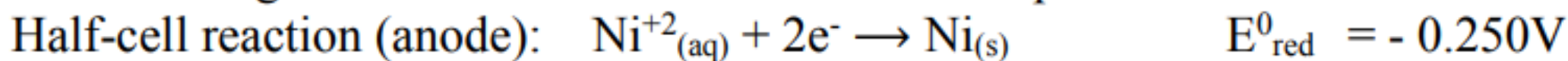$Cu^{+2}_{(aq,\ 1M)} + Zn^{+2}_{(aq,\ 1M)} \rightarrow Zn_{(s)} + Cu_{(s)}$ $E^0_{cell} = +1.10V$

Sample Problem 7.8. Using standard reduction potentials, calculate the standard emf for each of the following reaction decide whether the reaction is spontaneous.
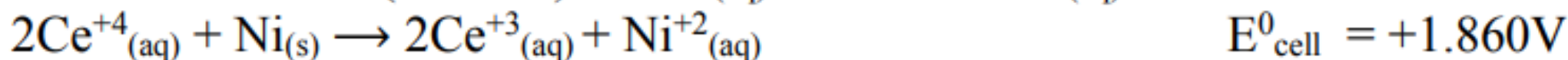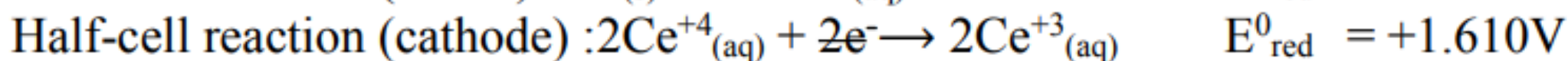
$$Ni_{(s)} + 2Ce^{+4}_{(aq)} \longrightarrow Ni^{+2}_{(aq)} + 2Ce^{+3}_{(aq)}(E^0 = 1.89 \text{ V})$$

Solution:

Using the first method: From the reduction potential table

Half-cell reaction (anode): $Ni^{+2}_{(aq)} + 2e^- \longrightarrow Ni_{(s)}$ $E^0_{red} = -0.250V$

Half-cell reaction (cathode) : $2Ce^{+4}_{(aq)} + 2e^- \longrightarrow 2Ce^{+3}_{(aq)}$ $E^0_{red} = +1.610V$

$E^0_{cell} = E^0_{red}(cathode) - E^0_{red} (anode) = +1.610V - (-0.250 \text{ V}) = 1.610V + 0.250V = 1.860V$

Using the second method (reversing the anode and its sign):

Half-cell reaction (anode): $Ni_{(s)} \longrightarrow Ni^{+2}_{(aq)} + 2e^-$ $E^0_{red} = +0.250V$

Half-cell reaction (cathode) : $2Ce^{+4}_{(aq)} + 2e^- \longrightarrow 2Ce^{+3}_{(aq)}$ $E^0_{red} = +1.610V$

$2Ce^{+4}_{(aq)} + Ni_{(s)} \longrightarrow 2Ce^{+3}_{(aq)} + Ni^{+2}_{(aq)}$ $E^0_{cell} = +1.860V$

Since the overall emf is positive, the reaction is spontaneous.

The problems can be solved using either first or second method.

Sample Problem 7.9. Using the standard reduction potential based in the appendix, calculate the standard emf for the voltaic cell based on the reaction:

$$Cr_2O_7^{-2}{}_{(aq)} + 14H^+{}_{(aq)} + 16I^-{}_{(aq)} \longrightarrow 2Cr_2^{+3}{}_{(aq)} + 3I_{2(s)} + 7H_2O_{(l)}$$
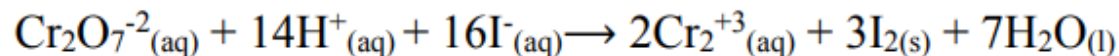
Solution:

We are given the equation for the redox reaction and asked to use data in the appendix to calculate that standard emf (standard potential) for the associated voltaic cell.

Step 1: Identify the two half reactions (cathode and anode).

     a. Let us determine first the oxidation numbers of all the species present.

     b. Oxygen has -2 and hydrogen has +1 in the reactant and in the product.

     c. I from -1 in the reactant to 0 ($I_{2(s)}$) - oxidized (oxidation).

     d. For Cr, we have: $Cr_2O_7^{-2}$

$Cr_2O_7^{-2} = -2$, solving for Cr;

$2\,(Cr) + 7(-2) = -2$

$2Cr - 14 = -2$

$2Cr = -2 + 14$

$Cr = \dfrac{12}{2} = +6$

     e. Cr from +6 in the reactant to +3 in the product – reduced (reduction).

$$Cr_2O_7^{-2}{}_{(aq)} + 14H^+{}_{(aq)} + 6I^-{}_{(aq)} \longrightarrow 2Cr_2^{+3}{}_{(aq)} + 3I_{2(s)} + 7H_2O_{(l)}$$
     +6 -2   +1   -1   +3   0   +1 -2
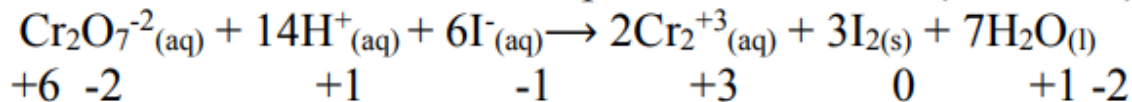
Step 2. $Cr_2O_7^{-2}{}_{(aq)}$ and $14H^+{}_{(aq)}$ produces $2Cr_2^{+3}{}_{(aq)}$ and $7H_2O_{(l)}$ as reduction. $16I^-{}_{(aq)}$ is oxidized to $3I_{2(s)}$.

Step3. Half-cell reaction (anode) : $6I^-{}_{(aq)} \longrightarrow 3I_{2(s)}$

     Half-cell reaction (cathode): $Cr_2O_7^{-2}{}_{(aq)} + 14H^+{}_{(aq)} \longrightarrow 2Cr_2^{+3}{}_{(aq)} + 7H_2O_{(l)}$

Step 4. To determine the number of electrons lost/gained, we need to balance the charges.
Half-cell reaction (anode) : $2I^-_{(aq)} \longrightarrow I_{2(s)}$ (
    a. Taking the net charge.

$6I^-_{(aq)} \longrightarrow$	$3I_{2(s)}$
6(-1)	3(0)
-6	0

    b. Balancing the net charge by adding electrons to the most positive side.
    c.

$6I^-_{(aq)} \longrightarrow$	$3I_{2(s)}$	+	$6e^-$
6(-1)	3(0)		6(-1)
-6	0		-6
	-6 = -6		

Half-cell reaction (cathode): $Cr_2O_7^{-2}{}_{(aq)} + 14H^+_{(aq)} \longrightarrow 2Cr_2^{+3}{}_{(aq)} + 7H_2O_{(l)}$
    a. Taking the net charge.

$Cr_2O_7^{-2}{}_{(aq)}$	+	$14H^+_{(aq)} \longrightarrow$	$2Cr_2^{+3}{}_{(aq)}$	+	$7H_2O_{(l)}$
2(-1)		14(+1)	2(+3)		7(0)
-2		+14	+6		0
		+12 > +6			

    b. Balancing the net charge by adding electrons to the most positive side.

$6e^-$	+	$Cr_2O_7^{-2}{}_{(aq)}$	+	$14H^+_{(aq)} \longrightarrow$	$2Cr_2^{+3}{}_{(aq)}$	+	$7H_2O_{(l)}$
6(-1)		2(-1)		14(+1)	2(+3)		7(0)
-6		-2		+14	+6		0
				+6 > +6			

Step 5. Adding the two half-reactions:
Cathode: $Cr_2O_7^{-2}{}_{(aq)} + 14H^+_{(aq)} + 6e^- \longrightarrow 2Cr^{+3}{}_{(aq)} + 7H_2O_{(l)}$ Anode: $6I^-_{(aq)} \longrightarrow 3I_{2(s)} + 6e^-$

$Cr_2O_7^{-2}{}_{(aq)} + 14H^+_{(aq)} + 6I^-_{(aq)} \longrightarrow 3I_{2(s)} + 2Cr^{+3}{}_{(aq)} + 7H_2O_{(l)}$

Step 6. We can use these values then for the calculations:

Cathode: $Cr_2O_7^{-2}{}_{(aq)} + 14H^+{}_{(aq)} \rightarrow 2Cr^{+3}{}_{(aq)} + 7H_2O_{(l)}$ $E^0_{red} = 1.330V$

Anode: $6I^-{}_{(aq)} \rightarrow 3I_{2(s)}$ $E^0_{red} = 0.536V$
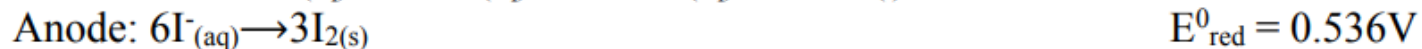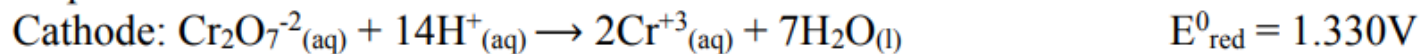
$E^0_{cell} = E^0_{red}(\text{cathode}) - E^0_{red}(\text{anode}) = 1.33\ V - 0.536\ V = 0.794\ V.$

   Using method two (reversing the sign of the anode):

Cathode: $Cr_2O_7^{-2}{}_{(aq)} + 14H^+{}_{(aq)} \rightarrow 2Cr^{+3}{}_{(aq)} + 7H_2O_{(l)}$ $E^0_{red} = 1.330V$

Anode: $6I^-{}_{(aq)} \rightarrow 3I_{2(s)}$ $E^0_{red} = -0.536V$

$Cr_2O_7^{-2}{}_{(aq)} + 14H^+{}_{(aq)} + 6I^-{}_{(aq)} \rightarrow 3I_{2(s)} + 2Cr^{+3}{}_{(aq)} + 7H_2O_{(l)}$ $E^0_{cell} = +0.794V.$
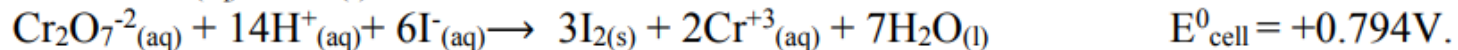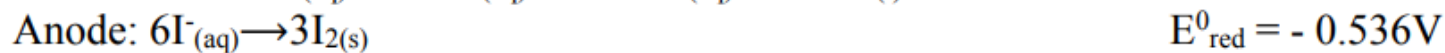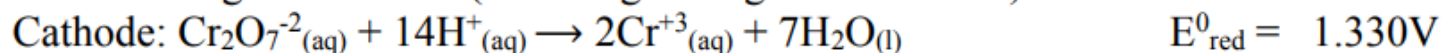
- Although we have different coefficients, the value of E^0cell is not multiplied by the coefficients.
- As we have noted the standard reduction potential is an intensive property, so it is not dependent of the specific stoichiometric coefficients.
- The cell potential, 0.794V, is a positive number.
- As noted earlier, a voltaic cell must have a positive emf (spontaneous) in order to operate.
- For each of the half-cells in a voltaic cell, the standard reduction potential provides a measure of the driving force for the reaction to occur.
- The more positive the value of E 0 red, the greater the driving force for reduction under standard conditions.
- In any voltaic cell operating under standard conditions, the reaction at the cathode has a more positive value of E^0red than does the reaction at the anode

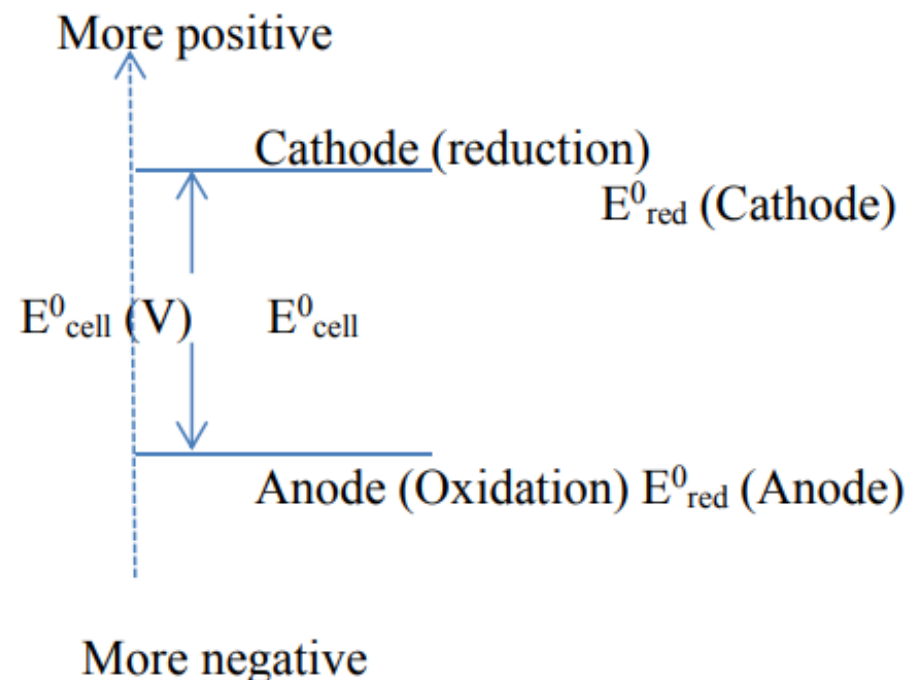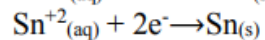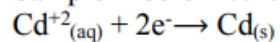| Standard Cell Potential of a Voltaic Cell	
The cell potential measures the difference in the standard reduction potentials of the cathode and the anode reactions: $E0cell = E^0_{red}(cathode) - E^0_{red}(anode)$. In a voltaic cell, the cathode reaction is always the one that has the more positive (or less negative) value for E^0_{red}.	More positive ↑ Cathode (reduction) E^0_{red} (Cathode) E^0_{cell} (V) E^0_{cell} Anode (Oxidation) E^0_{red} (Anode) More negative

Figure 7.2. The Standard Potential of a Voltaic Cell

Sample Problem 7.10: A voltaic cell is based on the following two standard half-reactions:
$Cd^{+2}_{(aq)} + 2e^- \rightarrow Cd_{(s)}$
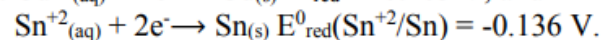$Sn^{+2}_{(aq)} + 2e^- \rightarrow Sn_{(s)}$
   By using the data in the appendix, determine a) the half reactions that occur at the cathode, and b) the standard cell potential

Solution:
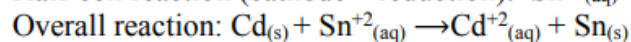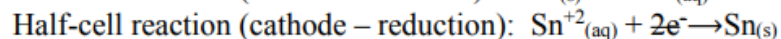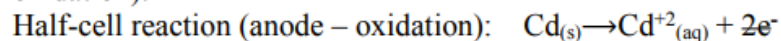a). Determining the half-reaction taking place at the cathode.
Step 1: Refer to the E^0_{red} for two half-reactions in the appendix and use these values to compare and to predict the cathode and anode of the cell and to calculate its standard cell potential, E^0_{cell}. The cathode will have the reduction with the more positive E^0_{red} value. The anode will have the less positive E^0_{red}. To write the half-reaction at the anode, we reverse the half-reaction written for the reduction, so that the half-reaction is written as an oxidation.
Step 2. $Cd^{+2}_{(aq)} + 2e^- \rightarrow Cd_{(s)}$ $E^0_{red} = -0.403$ V, and
       $Sn^{+2}_{(aq)} + 2e^- \rightarrow Sn_{(s)}$ $E^0_{red}(Sn^{+2}/Sn) = -0.136$ V.
Step 3. $E^0_{red}(Sn^{+2}/Sn) = -0.136$ V has more positive (less negative) E^0_{red} value, and is the cathode.
Step 4. Writing the cathode (half-cell reaction – reduction) and the anode (half-cell reaction – oxidation):
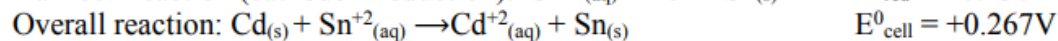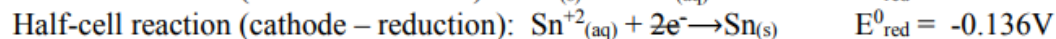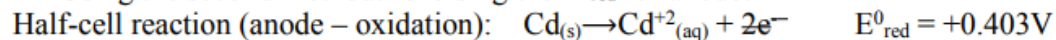Half-cell reaction (anode – oxidation): $Cd_{(s)} \rightarrow Cd^{+2}_{(aq)} + 2e^-$
Half-cell reaction (cathode – reduction): $Sn^{+2}_{(aq)} + 2e^- \rightarrow Sn_{(s)}$
Overall reaction: $Cd_{(s)} + Sn^{+2}_{(aq)} \rightarrow Cd^{+2}_{(aq)} + Sn_{(s)}$
b). The cell potential is:
       $E^0_{cell} = E^0_{red}(cathode) - E^0_{red} (anode)$
       $E^0_{cell} = (-0.136V) - (-0.403V) = 0.267$ V
   Using the second method: reversing the E^0_{red} for anode:
Half-cell reaction (anode – oxidation): $Cd_{(s)} \rightarrow Cd^{+2}_{(aq)} + 2e^-$ $E^0_{red} = +0.403V$
Half-cell reaction (cathode – reduction): $Sn^{+2}_{(aq)} + 2e^- \rightarrow Sn_{(s)}$ $E^0_{red} = -0.136V$
Overall reaction: $Cd_{(s)} + Sn^{+2}_{(aq)} \rightarrow Cd^{+2}_{(aq)} + Sn_{(s)}$ $E^0_{cell} = +0.267V$

Note: That it is important that the E^0red values of both half-reactions are negative; the negative values merely indicate how these reductions compare to the reference reaction, the reduction of H+ (aq). Yet the cell potential for the reaction is positive, as it must be for a voltaic cell

10(w)_Electrochemistry

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Mar.08.2023

TBC