Chapter 29

Electromotive Force

- ***The "pull," or driving force, inspiring the electron transfer.***
- ***The electrical energy permitting the transfer of a given charge.***

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HALF REACTIONS

- ***Electrochemical reactions involves the oxidation of a reducing agent simultaneously with the reduction of an oxidizing agent.***
- ***That is why they are always called Oxidation-Reduction or Redox reactions.***

$$2Na + Cl_2 \leftrightarrow 2Na^+ + 2Cl^-$$

$$2Na \leftrightarrow 2Na^+ + 2e^-$$

reducing agent ***oxidizing agent***

$\boxed{\textit{Oxidation= loss of } e^-}$

increase of oxidation state

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

oxidizing agent ***reducing agent***

$\boxed{\textit{Reduction= gaining } e^-}$

decrease of oxidation state

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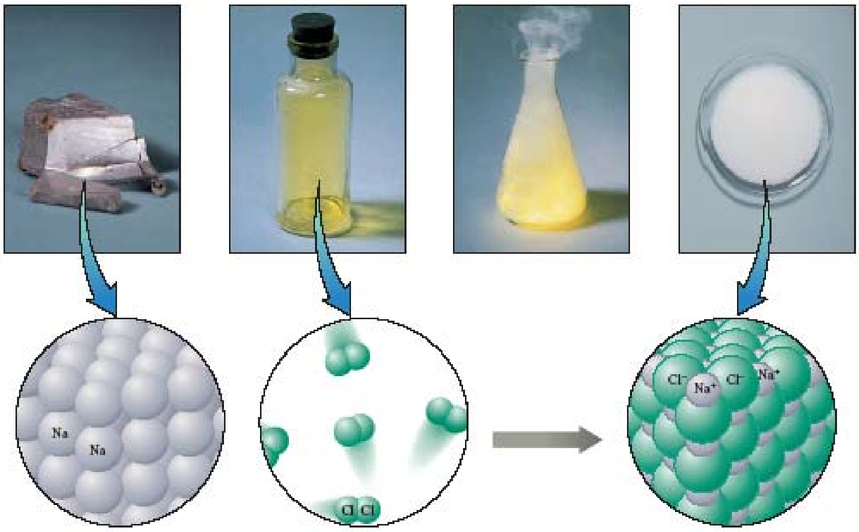

$$2Na + Cl_2 \leftrightarrow 2Na^+ + 2Cl^-$$

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Oxidation state (number) "ON:

- *is used to keep track of electron transfers.*

Simple binary ionic compound

- *is the number of e's gained or lost by an atom upon the formation of this compound.*
- *It corresponds to the actual charge on the ion.*

Molecular species *ON is assigned based on an arbitrary set of rules:*

- ***Generally**, The element farther to the right and higher up in the periodic table is assigned a **negative ON**, and the element farther to the left and lower down in the periodic table is assigned a **positive ON**.*

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Rules of ON

- **Keep first in mind that:**
  - ✓ ON are always assigned on a per atom basis ($K_2C_2O_7$).
  - ✓ Treat the rules in order of decreasing

Rules

1. The ON of the atoms in any free, uncombined element is zero. This includes polyatomic elements such as H_2, O_2, O_3, P_4, and S_8.

2. The ON of an element in a simple (monatomic) ion is equal to the charge on the ion.

3. Sum of ONs of all atoms in a compound is zero.

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Rules

1. The ON of the atoms in any free, uncombined element is zero. This includes polyatomic elements such as H_2, O_2, O_3, P_4, and S_8.

2. The ON of an element in a simple (monatomic) ion (Cl^-) equals the charge on the ion.

3. The sum of the ONs of all atoms in a compound is zero.

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4. *In a polyatomic ion, the sum of ONs of the constituent atoms is equal to the charge on the ion.*
5. *Fluorine has an ON of –1 in its compounds.*
6. *Hydrogen has an ON of 1 in compounds unless it is combined with metals, in which case it has an ON of –1. Examples of these exceptions are NaH and CaH_2.*
7. *Oxygen usually has an ON of –2 in its compounds. Exceptions:*
   a. *Oxygen has an ON of –1 in hydrogen peroxide, H_2O_2, and in peroxides, which contain the O_2^{2-} ion; e.g., CaO_2 and Na_2O_2.*
   b. *Oxygen has an ON of –1/2 in superoxides, which contain the O_2^- ion; examples are KO_2 and RbO_2.*
   c. *When combined with fluorine in OF_2, oxygen has an ON of +2.*

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8. *The position of the element in the periodic table helps to assign its oxidation number:*
   a. *Group IA elements have ONs of +1 in all compounds.*
   b. *Group IIA elements have ONs of +2 in all compounds.*
   c. *Group IIIA elements have ONs of +3 in all compounds, with a few rare exceptions.*
   d. *Group VA (N & P) elements have ONs of –3 in binary compounds with metals, with H, or with NH_4^+. Exceptions are compounds with a Group VA element combined with an element to its right in the periodic table; in this case, their ONs can be found by using rules 3 and 4.*
   e. *Group VIA (S & Se) elements below oxygen have ONs of –2 in binary compounds with metals, with H, or with NH_4^+. When these elements are combined with oxygen or with a lighter halogen, their ONs can be found by using rules 3 and 4.*

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TABLE 4-10 *Common Oxidation Numbers (States) for Group A Elements in Compounds and Ions*

Element(s)	Common Ox. Nos.	Examples	Other Ox. Nos.
H	+1	H_2O, CH_4, NH_4Cl	−1 in metal hydrides, e.g., NaH, CaH_2
Group IA	+1	KCl, NaH, $RbNO_3$, K_2SO_4	None
Group IIA	+2	$CaCl_2$, MgH_2, $Ba(NO_3)_2$, $SrSO_4$	None
Group IIIA	+3	$AlCl_3$, BF_3, $Al(NO_3)_3$, GaI_3	None in common compounds
Group IVA	+2 +4	CO, PbO, $SnCl_2$, $Pb(NO_3)_2$ CCl_4, SiO_2, SiO_3^{2-}, $SnCl_4$	Many others are also seen for C and Si
Group VA	−3 in binary compounds with metals −3 in NH_4^+, binary compounds with H	Mg_3N_2, Na_3P, Cs_3As NH_3, PH_3, AsH_3, NH_4^+	+3, e.g., NO_2^-, PCl_3 +5, e.g., NO_3^-, PO_4^{3-}, AsF_5, P_4O_{10}
O	−2	H_2O, P_4O_{10}, Fe_2O_3, CaO, ClO_3^-	+2 in OF_2 −1 in peroxides, e.g., H_2O_2, Na_2O_2 $-\frac{1}{2}$ in superoxides, e.g., KO_2, RbO_2
Group VIA (other than O)	−2 in binary compounds with metals and H −2 in binary compounds with NH_4^+	H_2S, CaS, Fe_2S_3, Na_2Se $(NH_4)_2S$, $(NH_4)_2Se$	+4 with O and the lighter halogens, e.g., SO_2, SeO_2, Na_2SO_3, SO_3^{2-}, SF_4 +6 with O and the lighter halogens, e.g., SO_3, TeO_3, H_2SO_4, SO_4^{2-}, SF_6
Group VIIA	−1 in binary compounds with metals and H −1 in binary compounds with NH_4^+	MgF_2, KI, $ZnCl_2$, $FeBr_3$ NH_4Cl, NH_4Br	Cl, Br, or I with O or with a lighter halogen +1, e.g., BrF, ClO^-, BrO^- +3, e.g., ICl_3, ClO_2^-, BrO_2^- +5, e.g., BrF_5, ClO_3^-, BrO_3^- +7, e.g., IF_7, ClO_4^-, BrO_4^-

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***9.** Group VIIA elements have ONs of –1 in binary compounds with metals, with H, with NH_4^+, or with a heavier halogen. When these elements except fluorine (i.e., Cl, Br, I) are combined with oxygen or with a lighter halogen, their oxidation numbers can be found by using rules 3 and 4.*

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Examples

Determine the oxidation numbers of nitrogen in the following species: (a) N_2O_4, (b) NH_3, (c) HNO_3, (d) NO_3, (e) N_2.

Plan

- *We first assign oxidation numbers to elements that exhibit a single common oxidation number.*
- *We recall that oxidation numbers are represented per atom and that the sum of the oxidation numbers in a compound is zero, and the sum of the oxidation numbers in an ion equals the charge on the ion.*

Solution

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(a) The ON of O is –2. The sum of ONs for all atoms in a compound must be zero: N_2O_4

total ox. no.: $2x + 4(-2) = 0$, *or* $x = +4$

(b) The ON of H is 1: NH_3

total ox. no.: $x + 3(+1) = 0$, *or* $x = -3$

(c) ON of H =1 and ON of O is 2. HNO_3

total ON= $1 + x + 3(-2) = 0$, *or* $x = +5$

(d) The sum of ONs for all atoms in an ion equals the charge on the ion: NO_3^-

total ON : $x + 3(-2) = -1$, *or* $x = +5$

(e) N_2 *: The ON of any free element is zero.*

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Characteristics of Redox Reactions

Consider the combustion of methane

$$\underset{-4\ \ +1\ (\text{each H})}{CH_4(g)} + \underset{0}{2O_2(g)} \longrightarrow \underset{+4\ \ -2\ (\text{each O})}{CO_2(g)} + \underset{+1\ (\text{each H})\ \ -2}{2H_2O(g)}$$

Oxidation state

Carbon undergoes a change in oxidation state from –4 in CH_4 to +4 in CO_2. Such a change can be accounted for by a loss of eight electrons (the symbol e stands for an electron):

$$\underset{-4}{CH_4} \longrightarrow \underset{+4}{CO_2} + 8e^-$$

$$\underset{0}{2O_2} + 8e^- \longrightarrow CO_2 + 2H_2O \qquad 4(-2) = -8$$

Oxygen changes from an oxidation state of 0 in O_2 to –2 in H_2O and CO_2, signifying a gain of two electrons per atom.

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Characteristics of Redox Reactions

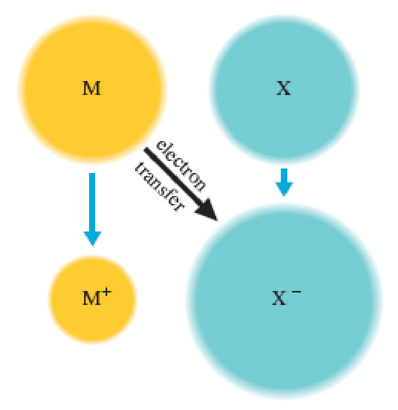
Oxidation is an ***increase*** in oxidation state (a loss of electrons).

Reduction is a ***decrease in oxidation state*** (a gain of electrons).

Thus in the reaction,

$$\underset{0}{2Na(s)} + \underset{0}{Cl_2(g)} \longrightarrow \underset{+1\ \ -1}{2NaCl(s)}$$

sodium is oxidized and chlorine is reduced. In addition, Cl_2 is called the ***oxidizing agent*** (**electron acceptor**), and Na is called the ***reducing agent*** (**electron donor**).



Oxidized	Reduced
loses electrons	*gains* electrons
oxidation state *increases*	oxidation state *decreases*
reducing agent	*oxidizing* agent

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Balancing Redox reactions

Two methods can be used:

- ✓ Oxidation States Method
- ✓ The Half-Reaction Method

Oxidation States Method

- Consider the reaction

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

- We can tell this is a redox reaction by assigning oxidation states

$$\begin{array}{ccccccc} & & \multicolumn{3}{c}{1\ e^{-}\ \text{gained}} & & \\ Cu & + & Ag^{+} & \longrightarrow & Ag & + & Cu^{2+} \\ 0 & & +1 & & 0 & & +2 \\ \multicolumn{7}{c}{2\ e^{-}\ \text{lost}} \end{array}$$

- The ***oxidation states method*** utilizes the principle that in a redox reaction, equal numbers of electrons gained and lost must ultimately match.

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

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Balancing Redox Reactions by Oxidation States

1) Write the unbalanced equation.
2) Determine the oxidation states of all atoms in the reactants and products.
3) Show electrons gained and lost using "tie lines."
4) Use coefficients to equalize the electrons gained and lost.
5) Balance the rest of the equation by inspection.
6) Add appropriate states.

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Example

Balance the reaction between solid lead(II) oxide and ammonia gas to produce nitrogen gas, liquid water, and solid lead.

Solution

We'll use the Problem-Solving Strategy for Balancing Oxidation–Reduction Reactions by Oxidation States.

What is the unbalanced equation?

$$PbO(s) + NH_3(g) \longrightarrow N_2(g) + H_2O(l) + Pb(s)$$

What are the oxidation states for each atom?

$$\underset{+2}{\overset{-2}{PbO}} \quad + \quad \underset{+1}{\overset{-3}{NH_3}} \quad \longrightarrow \quad \overset{0}{N_2} \quad + \quad \underset{+1}{\overset{-2}{H_2O}} \quad + \quad \underset{0}{Pb}$$

How are electrons gained and lost?

$$\underbrace{\underset{+2}{PbO} + \overbrace{\overset{-3}{NH_3} \longrightarrow \overset{0}{N_2}}^{3\,e^-\text{ lost (each atom)}} + H_2O + \underset{0}{Pb}}_{2\,e^-\text{ gained}}$$

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The oxidation states of all other atoms are unchanged.

What coefficients are needed to equalize the electrons gained and lost?

$$\underbrace{\underset{+2}{PbO} + \overbrace{\overset{-3}{NH_3} \longrightarrow \overset{0}{N_2}}^{3\,e^-\text{ lost (each atom)} \quad \text{multiply by 2}} + H_2O + \underset{0}{Pb}}_{2\,e^-\text{ gained} \quad \text{multiply by 3}}$$

$$3PbO + 2NH_3 \longrightarrow N_2 + H_2O + 3Pb$$

What coefficients are needed to balance the remaining elements?

Balance O: $3PbO + 2NH_3 \longrightarrow N_2 + 3H_2O + 3Pb$

All the elements are now balanced. The balanced equation with states is: $3PbO(s) + 2NH_3(g) \longrightarrow N_2(g) + 3H_2O(l) + 3Pb(s)$

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Balancing Redox Reactions by Half-Reaction Method

- It separates the reaction into two ***half-reactions***: **one involving oxidation and the other involving reduction.**
- For example, consider the unbalanced equation for the oxidation–reduction reaction between cerium(IV) ion and tin(II) ion:

$$Ce^{4+}(aq) + Sn^{2+}(aq) \longrightarrow Ce^{3+}(aq) + Sn^{4+}(aq)$$

the substance being *reduced* $Ce^{4+}(aq) \longrightarrow Ce^{3+}(aq)$

the substance being *oxidized* $Sn^{2+}(aq) \longrightarrow Sn^{4+}(aq)$

- **The general procedure is to balance the equations for the half-reactions separately and then to add them to obtain the overall balanced equation.**
- The half-reaction method for balancing oxidation–reduction equations differs slightly depending on whether the reaction takes place in acidic or basic solution.

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Half-Reaction Method: Reactions Occurring in Acidic Solution

1) Write separate equations for the oxidation and reduction half-reactions.
2) **For each half-reaction**,
   a. Balance all the elements except hydrogen and oxygen.
   b. Balance oxygen using H_2O.
   c. Balance hydrogen using H^+.
   d. Balance the charge using electrons.
3) If necessary, multiply one or both balanced half-reactions by an integer to equalize the number of electrons transferred in the two half-reactions.
4) Add the half-reactions, and cancel identical species.
5) Check that the elements and charges are balanced.

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Example

Balance the reaction between permanganate and iron(II) ions in acidic solution using the half-reaction method

$$MnO_4^-(aq) + Fe^{2+}(aq) \xrightarrow{\text{Acid}} Fe^{3+}(aq) + Mn^{2+}(aq)$$

Solution

- **write equations for the half-reactions**

$$\underset{+7\ \ -2(\text{each O})}{MnO_4^-} \longrightarrow \underset{+2}{Mn^{2+}} \qquad \underset{+2}{Fe^{2+}} \longrightarrow \underset{+3}{Fe^{3+}}$$

- **Balance each half-reaction**
  a. The manganese is balanced.
  b. Balance oxygen by adding 4H2O to the right side of equation:

$$MnO_4^-(aq) \longrightarrow Mn^{2+}(aq) + 4H_2O(l)$$

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c. Next, we balance hydrogen by adding $8H^+$ to the left side:

$$8H^+(aq) + MnO_4^-(aq) \longrightarrow Mn^{2+}(aq) + 4H_2O(l)$$

d. Balance the charge using electrons

$$\underbrace{5e^- + 8H^+(aq) + MnO_4^-(aq)}_{2+} \longrightarrow \underbrace{Mn^{2+}(aq) + 4H_2O(l)}_{2+}$$

- **For the oxidation reaction** $\underbrace{Fe^{2+}(aq)}_{2+} \longrightarrow \underbrace{Fe^{3+}(aq) + e^-}_{2+}$
- **Equalize the electron transfer and add the half reactions**

$$5Fe^{2+}(aq) + MnO_4^-(aq) + 8H^+(aq) \longrightarrow 5Fe^{3+}(aq) + Mn^{2+}(aq) + 4H_2O(l)$$

- **Check that elements and charges are balanced.**
  - **In each side we have** 5Fe, 1Mn, 4O, 8H and
  - charges of **17 +**

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Half-Reaction Method: Reactions Occurring in Basic Solution

1) Use the half-reaction method as specified for acidic solutions to obtain the final balanced equation *as if H^+ ions were present*.
2) To both sides of the equation obtained above, add a number of OH^- ions that is equal to the number of H^+ ions. (We want to eliminate H by forming H2O.)
3) Form H2O on the side containing both H^+ and OH^- ions, and eliminate the number of H2O molecules that appear on both sides of the equation.
4) Check that elements and charges are balanced.

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Example

Balance the reaction between permanganate and iron(II) ions in basic solution using the half-reaction method

$$Ag(s) + CN^-(aq) + O_2(g) \xrightarrow{\text{Base}} Ag(CN)_2^-(aq)$$

Solution

- **Balance the half-reactions as if H^+ ions were present**

$$2CN^-(aq) + Ag(s) \longrightarrow Ag(CN)_2^-(aq) + e^- \quad \boxed{x\ 4}$$

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

- **Addition of half reactions**

$$8CN^-(aq) + 4Ag(s) + O_2(g) + 4H^+(aq) \longrightarrow 4Ag(CN)_2^-(aq) + 2H_2O(l)$$

- **Add OH^- ions to both sides of the balanced equation to eliminate the H^+ ions**

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$$8CN^-(aq) + 4Ag(s) + O_2(g) + \underbrace{4H^+(aq) + 4OH^-(aq)}_{4H_2O(l)} \longrightarrow$$
$$4Ag(CN)_2^-(aq) + 2H_2O(l) + 4OH^-(aq)$$

- **Eliminate as many H2O molecules as possible:**

$$8CN^-(aq) + 4Ag(s) + O_2(g) + 2H_2O(l) \longrightarrow 4Ag(CN)_2^-(aq) + 4OH^-(aq)$$

- **Check that elements and charges are balanced.**
  - Elements balance: 8C, 8N, 4Ag, 4O, 4H
  - Charges balance: 8 –

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Homework

- Potassium dichromate ($K_2Cr_2O_7$) is a bright orange compound that can be reduced to a blue-violet solution of Cr^{3+} ions. Under certain conditions, $K_2Cr_2O_7$ reacts with ethyl alcohol (C_2H_5OH) as follows:

$$H^+(aq) + Cr_2O_7^{2-}(aq) + C_2H_5OH(l) \longrightarrow Cr^{3+}(aq) + CO_2(g) + H_2O(l)$$

Balance this equation in acidic solution using the half-reaction method.

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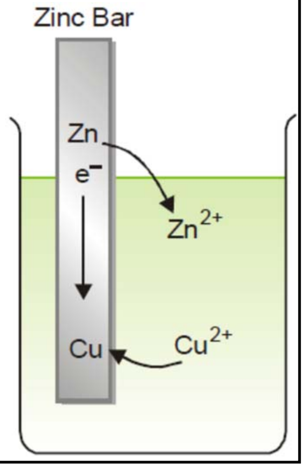
Production of electricity

- *When a bar of zinc is dipped in a solution of copper sulphate, Zn ions are dissolved and copper metal is deposited on the bar.*

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

$$Zn \leftrightarrow Zn^{2+} + 2e^{-} \quad \textit{Oxidation}$$

$$Cu^{2+} + 2e^{-} \leftrightarrow Cu \quad \textit{Reduction}$$



- *As both half-reactions occurred on the same electrode, no useful electricity can be obtained although it is a galvanic process.*
- *This is very similar to the case of corrosion*

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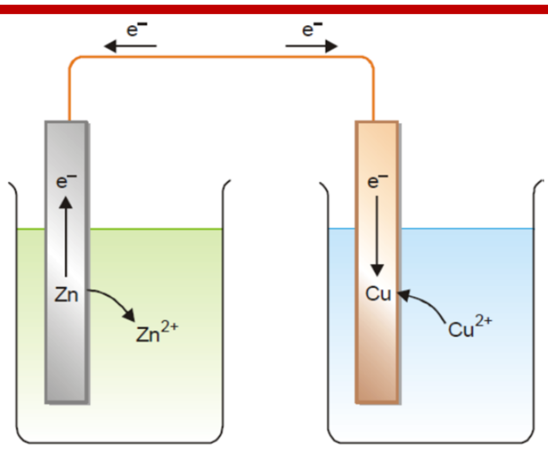
Two compartment cells /no salt bridge



- *e's flow (electricity) through the wire for an instant and then stop because of the charge build up in the two compartments. e's flow from the anode (becomes +Ve) to cathode (becomes –Ve)*

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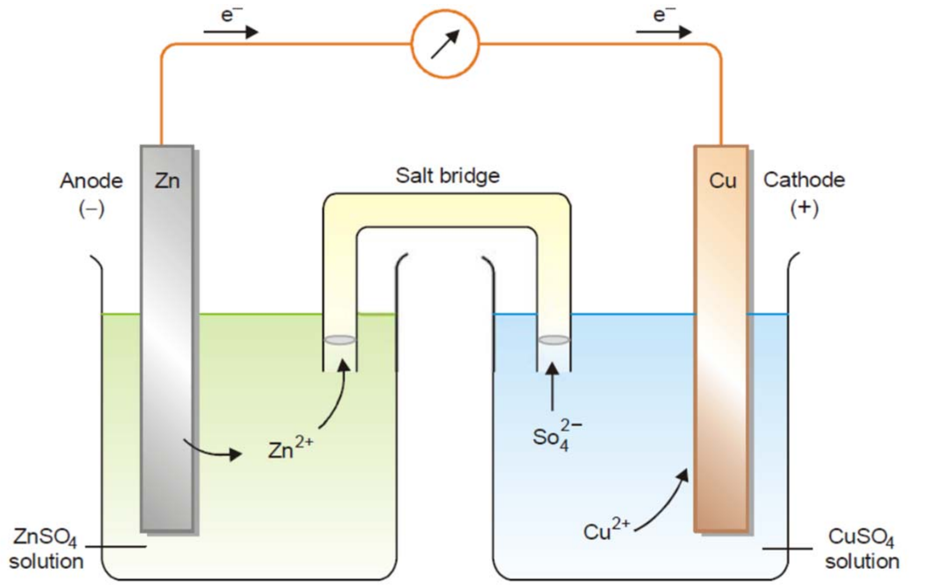
Voltaic/Galvanic Cells

- ***The cell operates till either Zn or Cu^{2+} is completely used up.***



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Example

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

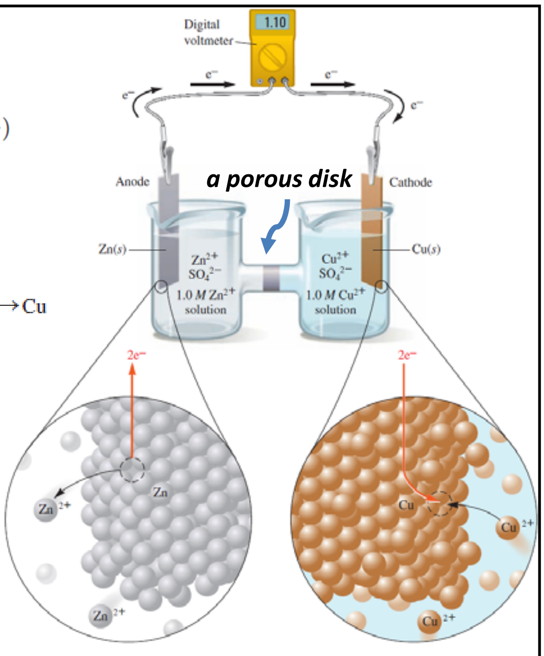
Anode: $Zn \longrightarrow Zn^{2+} + 2e^-$

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

$$\mathscr{E}^\circ_{cell} = \mathscr{E}^\circ_{Zn \longrightarrow Zn^{2+}} + \mathscr{E}^\circ_{Cu^{2+} \longrightarrow Cu}$$

Since $\mathscr{E}^\circ_{Zn \rightarrow Zn^{2+}}$ was earlier assigned a value of 0.76 V, the value of $\mathscr{E}^\circ_{Cu^{2+} \rightarrow Cu}$ must be 0.34 V

$$1.10\ V = 0.76\ V + 0.34\ V$$



Oxidation half-reaction   Reduction half-reaction

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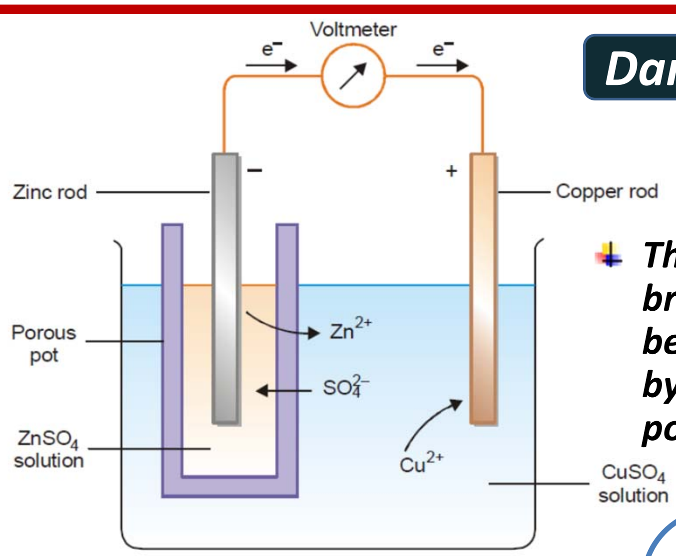
$$Zn + Cu^{2+} \longrightarrow Zn^{2+} + Cu \qquad E^0_{cell} = 1.1\ V$$

Daniel Cell



- *The salt-bridge has been replaced by a porous pot*

Cell diagram

$$Zn(s)|ZnSO_4(aq)||CuSO_4(aq)|Cu$$

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Cell diagram or Representation

- *is an abbreviated symbolic depiction of an electrochemical cell*
- *A single vertical line (|) represents a phase boundary between metal electrode and ion solution (electrolyte).*
- *The metal electrode in anode half-cell is on left, while in cathode half-cell is on right of metal ion.*
- *A double vertical line (||) represents the salt bridge, porous partition or any other means permitting ion flow while preventing the electrolyte from mixing.*
- *Anode half-cell is written on the left and cathode half-cell on the right.*

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Daniel Cell

$Zn\,|\,Zn^{2+}\,||\,Cu^{2+}\,|\,Cu$ (Salt Bridge at $||$)

Anode Half-Cell — Cathode Half-Cell

- *The symbol for an inert electrode, like the platinum electrode is often enclosed in a bracket.*

$Mg\,|\,Mg^{2+}\,||\,H^{+}\,|\,H_2(Pt)$ (Inert Electrode)

- *The value of emf of a cell is written on the right of the cell diagram. Thus a zinc-copper cell has emf 1.1V and is represented as*

$Zn\,|\,ZnSO_4\,||\,CuSO_4\,|\,Cu \qquad E = +1.1\ V$

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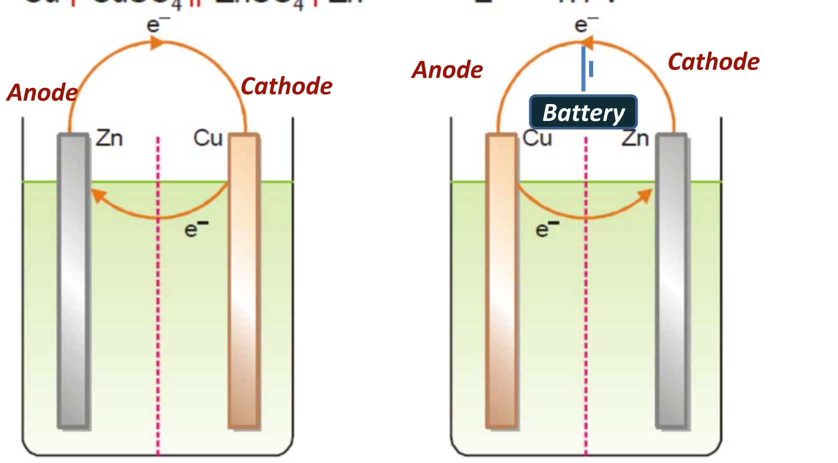
Convention in the sign of emf

$Zn\,|\,ZnSO_4\,||\,CuSO_4\,|\,Cu \qquad E = +1.1\ V$

$Cu\,|\,CuSO_4\,||\,ZnSO_4\,|\,Zn \qquad E = -1.1\ V$



E = + 1.1V *Spontaneous* — E = − 1.1V *Non-spontaneous*

The negative sign of E indicates the infeasibility of the given direction.

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