ELECTROCHEMISTRY
1: REDOX EQUATIONS

Dr. Sapna Gupta

INTRODUCTION

Electrochemistry is all about oxidation reduction (redox) reactions. These are electron transfer reactions which can result in producing energy.

To understand how energy is produced by electrochemistry, we need to learn the concepts below.

- Understand oxidation and reduction processes.
- Balance redox equations to know how many electrons have transferred.
- Learn the concept of standard electrode potential.
- Build a voltaic or galvanic cell.
- Calculate the electromotive force (EMF) of the voltaic cell.
- Predict spontaneity of a voltaic cell.

OXIDATION REDUCTION (*REDOX*) REACTIONS

The table below gives a good description of what is oxidation and reduction.

Oxidation	Reduction
Addition of oxygen	Removal of oxygen
Removal of hydrogen	Addition of hydrogen
Loss of electrons (LEO)	Gain of electrons (GER)
Metals lose electrons hence undergo oxidation.	Nonmetals gain electrons hence undergo reduction.
Reducing agents – an element that causes reduction of another element and gets oxidized (loses electrons) itself.	Oxidizing agent – an element that causes oxidation of another element and gets reduced (gains electrons) itself.

WRITING REDOX REACTIONS

Example:

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

gains 2 electrons, *reduction*

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

loses 2 electrons, *oxidation*

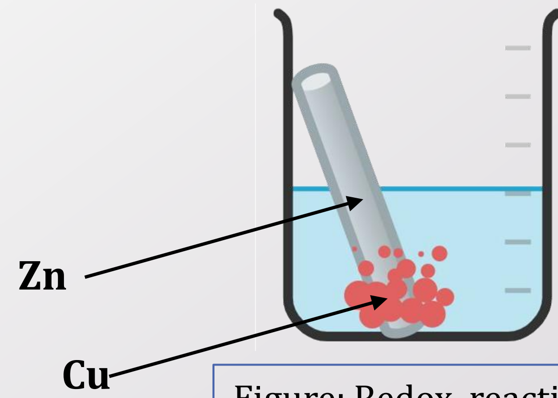

Figure: Redox reaction of Cu (II) (aq) to give Cu(s).

Another Example:

$$Mg_{(s)} + O_{2\ (g)} \longrightarrow MgO_{\ (s)}$$

Mg is adding oxygen hence getting oxidized; hence oxygen must be getting reduced. We can also do this with electrons using oxidation numbers (valencies or charges on any element or ion).

RULES FOR ASSIGNING OXIDATION NUMBERS

1. **Elements:** The oxidation number of an element in their natural state is zero e.g., Mg, Zn, Na, Cr etc. for metals. All diatomic gases (H_2, O_2, N_2 and halogens) are zero.
2. **Monatomic ions:** The oxidation number of a monatomic ion equals the charge on the ion e.g., Na^+ is +1, Mg^{2+} is +2, Fe^{3+} is +3 etc.
3. **Oxygen:** The oxidation number of oxygen is always −2 except in H_2O_2 and other peroxides, where the oxidation number of oxygen is −1.
4. **Hydrogen:** The oxidation number of hydrogen is +1 in most compounds. The oxidation number of hydrogen is −1 when combined with metals such as CaH_2.
5. **Halogens:** The oxidation number of fluorine is −1. Each of the other halogens (Cl, Br, I) has an oxidation number of −1 in binary compounds e.g., HCl, NaBr. When the other element is another halogen above it in the periodic table or the other element is oxygen e.g., $HClO_3$.
6. **Compounds and ions:** The sum of the oxidation numbers of a compound is *zero*. The sum of the oxidation numbers of the atoms in a polyatomic ion equals the charge on the ion.

A REDOX EQUATION

$$\underset{+2}{Fe^{2+}_{(aq)}} + \underset{+5}{NO_3^{-}{}_{(aq)}} \longrightarrow \underset{+3}{Fe^{3+}_{(aq)}} + \underset{+2}{NO_{(g)}} \text{ in acidic solution}$$

We determine the oxidation number of Fe and N in each substance.

Oxidation: $Fe^{2+}_{(aq)}$ is oxidized from +2 to +3 in $Fe^{3+}_{(aq)}$.

Reduction: N in $NO_3^{-}{}_{(aq)}$ is reduced from +5 to +2 in $NO_{(g)}$.

The reaction is in acidic conditions (HNO_3).

Then we proceed to balance the equation….next few slides.

EXAMPLE 1: DETERMINING OXIDATION STATES

Identify what is getting oxidized and reduced in the following reactions.

a) $FeI_{3(aq)} + Mg_{(s)} \longrightarrow Fe_{(s)} + MgI_{2(aq)}$

b) $6FeSO_{4\,(aq)} + K_2Cr_2O_{7\,(aq)} + 7H_2SO_{4\,(aq)} \longrightarrow$

$Cr_2(SO_4)_{3\,(aq)} + 3Fe_2(SO_4)_{3\,(aq)} + K_2SO_{4\,(aq)} + 7H_2O_{\,(l)}$

Answer:

The oxidation numbers are given below the reaction.

a) $FeI_{3\,(aq)} + Mg_{\,(s)} \longrightarrow Fe_{\,(s)} + MgI_{2\,(aq)}$

+3 −1 0 0 +2 −1

Mg is getting oxidized and Fe is getting reduced.

b) $6\underline{\mathbf{Fe}}SO_{4\,(aq)} + K_2\underline{\mathbf{Cr_2}}O_{7\,(aq)} + 7H_2SO_{4\,(aq)} \longrightarrow$

$\underline{\mathbf{Cr_2}}(SO_4)_{3\,(aq)} + 3\underline{\mathbf{Fe_2}}(SO_4)_{3\,(aq)} + K_2SO_{4\,(aq)} + 7H_2O_{\,(l)}$

Ignore H_2O and H_2SO_4 – focus on the transition metals.

Reactant Fe = +2 and Cr = +6; Product Fe = +3 and Cr = + 3

Fe is getting oxidized and Cr is getting reduced.

BALANCING REDOX REACTIONS – IN ACID

To balance a redox reaction, first separate the half reactions; oxidation and reduction (This is generally just separating by the same elements). Now for each do the following:

1) Balance all atoms other than H and O.
2) Balance O using H_2O on the opposite side.
3) Balance H using H^+ on the opposite side.
4) Balance the charges on both sides by using electrons on opposite sides. (remember for oxidation equation, electrons will be on the product side and for reduction equation, they will be on the reactant side).
5) Multiply the entire oxidation or reduction equation to have the same number of electrons for both half equations.
6) Add the two equations – that should nullify the electrons.

EXAMPLE 2: BALANCING REDOX EQUATION

Balance the redox reaction below in an acidic medium.

$$Fe^{2+}_{(aq)} + NO_3^{-}{}_{(aq)} \longrightarrow Fe^{3+}_{(aq)} + NO_{(g)}$$

Answer:

To find out the reduction and oxidation half reactions you can either write the oxidation numbers or in this equation separate it by the elements.

$$Fe^{2+}_{(aq)} + NO_3^{-}{}_{(aq)} \longrightarrow Fe^{3+}_{(aq)} + NO_{(g)}$$

+2 +7 +3 +2

Iron is getting oxidized and nitrogen is getting reduced.

Oxidation half–reaction

Fe is already balanced, there is no O to balance, so we need to add 1e⁻ on the product to have 2+ on both sides of the equation. (*Oxidation is loss of electrons, hence electrons are on the product side*).

$$Fe^{2+}_{(aq)} \longrightarrow Fe^{3+}_{(aq)} + e^{-}$$

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EXAMPLE 2: BALANCING REDOX EQUATION

Reduction half–reaction

1) N is already balanced.
2) Balance O by adding $2H_2O$ on the right: $NO_3^-{}_{(aq)} \longrightarrow NO_{(aq)} + 2H_2O_{(l)}$
3) Balance H by adding $4H^+$ on the left:

$$4H^+_{(aq)} + NO_3^-{}_{(aq)} \longrightarrow NO_{(g)} + 2H_2O_{(l)}$$

4) Balance charges: There are 4+ and 1-, total 3+ on the left and 0 on the right. We need to add $3e^-$ on the left to have 0 charge on both sides of the equation.

$$3e^- + 4H^+_{(aq)} + NO_3^-{}_{(aq)} \longrightarrow NO_{(aq)} + 2H_2O_{(aq)}$$

Oxidation half reaction -

$$Fe^{2+}_{(aq)} \longrightarrow Fe^{3+}_{(aq)} + e^-$$

Multiply this equation by 3 to make sure the transfer of electrons is equal (3 e-)

$$3Fe^{2+}_{(aq)} \longrightarrow 3Fe^{3+}_{(aq)} + 3e^-$$

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EXAMPLE 2: BALANCING REDOX EQUATION

Combine the two equations

$$3Fe^{2+}{}_{(aq)} \longrightarrow 3Fe^{3+}{}_{(aq)} + \cancel{3e^-}$$

$$\cancel{3e^-} + 4H^+{}_{(aq)} + NO_3{}^-{}_{(aq)} \longrightarrow NO_{(g)} + 2H_2O_{(l)}$$

$$\boxed{4H^+{}_{(aq)} + 3Fe^{2+}{}_{(aq)} + NO_3{}^-{}_{(aq)} \longrightarrow 3Fe^{3+}{}_{(aq)} + NO_{(g)} + 2H_2O_{(l)}}$$

BALANCING REDOX REACTIONS – IN BASIC MEDIUM

All the rules are the same as in the acidic conditions. Once the equation is balanced and redox reactions are added to get the final reaction is obtained in the acidic medium, then we balance by adding hydroxides.

1. Add one OH^- to both sides for each H^+.
2. When H^+ and OH^- occur on the same side, combine them to form H_2O.
3. Cancel water molecules that occur on both sides and write the final equation.

The final equation should not have any protons left in the equation.

Balancing an equation in basic medium does not change the number of electrons transferred during the redox reaction.

EXAMPLE 3: BALANCING REDOX EQ IN A BASE

Balance the iron and nitrate equation from example 2 in the previous slides in a basic medium.

Answer:

The balance equation from previous slide:

$$4H^{+}{}_{(aq)} + 3Fe^{2+}{}_{(aq)} + NO_3^{-}{}_{(aq)} \longrightarrow 3Fe^{3}{}_{(aq)} + NO_{(g)} + 2H_2O_{(l)}$$

1) There are $4H^{+}$ on reactant side. We will add $4OH^{-}$ on both sides of the equation.

$$\mathbf{4H^{+}}{}_{(aq)} + 3Fe^{2+}{}_{(aq)} + NO_3^{-}{}_{(aq)} \longrightarrow 3Fe^{3+}{}_{(aq)} + NO_{(g)} + \mathbf{2H_2O}_{(l)}$$

$$\mathbf{+\ 4OH^{-}} \qquad\qquad\qquad\qquad + 4OH^{-}$$

2) $4H^{+}$ and $4OH^{-}$ form $4H_2O$ on the left. There are $2H_2O$ on the right, subtract them to get $2H_2O$ on the left.

$$3Fe^{2+}{}_{(aq)} + NO_3^{-}{}_{(aq)} + \mathbf{4H_2O}_{(l)} \longrightarrow 3Fe^{3+}{}_{(aq)} + NO_{(g)} + \cancel{\mathbf{2H_2O}}_{(l)} + 4OH^{-}{}_{(aq)}$$

$$\boxed{3Fe^{2+}{}_{(aq)} + NO_3^{-}{}_{(aq)} + 2H_2O_{(aq)} \longrightarrow 3Fe^{3+}{}_{(aq)} + NO_{(g)} + 4OH^{-}{}_{(aq)}}$$

EXAMPLE 4: BALANCING REDOX EQ IN BASE

Lead(II) ion, Pb^{2+}, yields the plumbite ion, $Pb(OH)_3^-$, in basic solution. In turn, this ion is oxidized in basic hypochlorite solution, ClO^-, to lead(IV) oxide, PbO_2. Balance the equation for this reaction using the half–reaction method. The skeleton equation is

$$Pb(OH)_3^-{}_{(aq)} + ClO^-{}_{(aq)} \longrightarrow PbO_{2\,(s)} + Cl^-{}_{(aq)}$$

Answer:

First determine redox..

$$\begin{array}{ccccccc} Pb(OH)_3^-{}_{(aq)} & + & ClO^-{}_{(aq)} & \longrightarrow & PbO_{2\,(s)} & + & Cl^-{}_{(aq)} \\ +2 & & +1 & & +4 & & -1 \end{array}$$

Pb is oxidized from +2 to +4.

Cl is reduced from +1 to −1.

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EXAMPLE 3: REDOX EQ IN BASE..CONTD

Oxidation half–reaction

Balance Pb and O: $Pb(OH)_3^-{}_{(aq)} \longrightarrow PbO_{2(s)} + H_2O_{(l)}$

Balance H: $Pb(OH)_3^-{}_{(aq)} \longrightarrow PbO_{2\,(s)} + H_2O_{(l)} + H^+_{(aq)}$

Balance e⁻: $Pb(OH)_3^-{}_{(aq)} \longrightarrow PbO_{2\,(s)} + H_2O_{(l)} + H^+_{(aq)} \boxed{+ 2e^-}$

Reduction half–reaction

Balance Cl and O: $ClO^-_{(aq)} \longrightarrow Cl^-_{(aq)} + H_2O_{(l)}$

Balance H: $2H^+_{(aq)} + ClO^-_{(aq)} \longrightarrow Cl^-_{(aq)} + H_2O_{(l)}$

Balance e⁻: $\boxed{2e^-} + 2H^+_{(aq)} + ClO^-_{(aq)} \longrightarrow Cl^-_{(aq)} + H_2O_{(l)}$

Electrons are equal for oxidation and reduction.

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EXAMPLE 3: REDOX EQ IN BASE..CONTD

Combine the half–reactions.

$$Pb(OH)_3^-{}_{(aq)} \longrightarrow PbO_{2\,(s)} + H_2O(l) + \cancel{H^+}_{(aq)} + \cancel{2e^-}$$

$$\cancel{2e^-} + \cancel{2H^+}_{(aq)} + ClO^-{}_{(aq)} \longrightarrow Cl^-{}_{(aq)} + H_2O_{(l)}$$

$$Pb(OH)_3^-{}_{(aq)} + H^+{}_{(aq)} + ClO^-{}_{(aq)} \longrightarrow PbO_{2\,(s)} + Cl^-{}_{(aq)} + 2H_2O_{(l)}$$

To convert to basic solution, we add one OH^- to each side, converting H^+ to H_2O.

$$\underbrace{\mathbf{OH^-} + H^+{}_{(aq)}} + Pb(OH)_3^-{}_{(aq)} + ClO^-{}_{(aq)} \longrightarrow PbO_{2\,(s)} + Cl^-{}_{(aq)} + 2H_2O_{(l)} + \mathbf{OH^-}{}_{(aq)}$$

$$\cancel{H_2O}_{(l)} + Pb(OH)_3^-{}_{(aq)} + ClO^-{}_{(aq)} \longrightarrow PbO_{2\,(s)} + Cl^-{}_{(aq)} + 2H_2O_{(l)} + OH^-{}_{(aq)}$$

Finally, we cancel one H_2O that is on both sides.

$$\boxed{Pb(OH)_3^-{}_{(aq)} + ClO^-{}_{(aq)} \longrightarrow PbO_{2\,(s)} + Cl^-{}_{(aq)} + H_2O_{(l)} + OH^-{}_{(aq)}}$$

KEY CONCEPTS

- Define oxidation and reduction.
- Identify reducing and oxidizing agents.
- Balance redox equations in acid and base medium.