Chapter 20
Electrochemistry

Electrochemical Reactions

In electrochemical reactions, electrons are transferred from one species to another.

Oxidation Numbers

In order to keep track of what loses electrons and what gains them, we assign oxidation numbers.

Oxidation and Reduction

A species is oxidized when it loses electrons.

Here, zinc loses two electrons to go from neutral zinc metal to the Zn^{2+} ion.

Oxidation and Reduction

A species is reduced when it gains electrons.

Here, each of the H^+ gains an electron and they combine to form H_2.

Leo the lion goes ger

Oil rig

Oxidation and Reduction

What is reduced is the oxidizing agent.

H^+ oxidizes Zn by taking electrons from it.

What is oxidized is the reducing agent.

Zn reduces H^+ by giving it electrons.

Assigning Oxidation Numbers

1. Elements in their elemental form have an oxidation number of 0.
2. The oxidation number of a monatomic ion is the same as its charge.

Assigning Oxidation Numbers

3. Nonmetals tend to have negative oxidation numbers, although some are positive in certain compounds or ions.

Oxygen has an oxidation number of −2, except in the peroxide ion in which it has an oxidation number of −1.

Hydrogen is −1 when bonded to a metal, +1 when bonded to a nonmetal.

Assigning Oxidation Numbers

3. Nonmetals tend to have negative oxidation numbers, although some are positive in certain compounds or ions.

Fluorine always has an oxidation number of −1.

The other halogens have an oxidation number of −1 when they are negative; they can have positive oxidation numbers, however, most notably in oxyanions.

Assigning Oxidation Numbers

4. The sum of the oxidation numbers in a neutral compound is 0.
5. The sum of the oxidation numbers in a polyatomic ion is the charge on the ion.

Balancing Oxidation-Reduction Equations

Perhaps the easiest way to balance the equation of an oxidation-reduction reaction is via the half-reaction method.

Balancing Oxidation-Reduction Equations

This involves treating (on paper only) the oxidation and reduction as two separate processes, balancing these half reactions, and then combining them to attain the balanced equation for the overall reaction.

Half-Reaction Method

1. Assign oxidation numbers to determine what is oxidized and what is reduced.
2. Write the oxidation and reduction half-reactions.

Half-Reaction Method

3. Balance each half-reaction.
   a. Balance elements other than H and O.
   b. Balance O by adding H_2O.
   c. Balance H by adding H^+.
   d. Balance charge by adding electrons.

4. Multiply the half-reactions by integers so that the electrons gained and lost are the same.

Half-Reaction Method

5. Add the half-reactions, subtracting things that appear on both sides.
6. Make sure the equation is balanced according to mass.
7. Make sure the equation is balanced according to charge.

Half-Reaction Method

Consider the reaction between MnO_4^{-}(prmanganate) and $C_2O_4^{2-}$(oxalate) :

$MnO_4^{-}(aq) + C_2O_4^{2-}(aq) \longrightarrow Mn^{2+}(aq) + CO_2(aq)$

Half-Reaction Method

First, we assign oxidation numbers.

Oxidation Half-Reaction

$C_2O_4^{2-} \longrightarrow CO_2$

To balance the carbon, we add a coefficient of 2:

$C_2O_4^{2-} \longrightarrow 2\ CO_2$

Oxidation Half-Reaction

$C_2O_4^{2-} \longrightarrow 2\ CO_2$

The oxygen is now balanced as well. To balance the charge, we must add 2 electrons to the right side.

$C_2O_4^{2-} \longrightarrow 2\ CO_2$

Oxidation Half-Reaction

$C_2O_4^{2-} \longrightarrow 2\ CO_2$

The oxygen is now balanced as well. To balance the charge, we must add 2 electrons to the right side.

$C_2O_4^{2-} \longrightarrow 2\ CO_2 + 2\ e^{-}$

Reduction Half-Reaction

$MnO_4^{-} \longrightarrow Mn^{2+}$

The manganese is balanced; to balance the oxygen, we must add 4 waters to the right side.

$MnO_4^- \longrightarrow Mn^{2+} + 4\ H_2O$

Reduction Half-Reaction

$MnO_4^- \longrightarrow Mn^{2+} + 4\ H_2O$

To balance the hydrogen, we add 8 H^+ to the left side.

$8\ H^+ + MnO_4^- \longrightarrow Mn^{2+} + 4\ H_2O$

Reduction Half-Reaction

$8\ H^+ + MnO_4^- \longrightarrow Mn^{2+} + 4\ H_2O$

To balance the charge, we add 5 e^- to the left side.

$8\ H^+ + MnO_4^- \longrightarrow Mn^{2+} + 4\ H_2O$

Reduction Half-Reaction

$8\ H^+ + MnO_4^- \longrightarrow Mn^{2+} + 4\ H_2O$

To balance the charge, we add 5 e^- to the left side.

$5\ e^- + 8\ H^+ + MnO_4^- \longrightarrow Mn^{2+} + 4\ H_2O$

Combining the Half-Reactions

Now we evaluate the two half-reactions together:

$C_2O_4^{2-} \longrightarrow 2\ CO_2 + 2\ e^-$

$5\ e^- + 8\ H^+ + MnO_4^- \longrightarrow Mn^{2+} + 4\ H_2O$

To attain the same number of electrons on each side, we will multiply the first reaction by 5 and the second by 2.

Combining the Half-Reactions

$5\ C_2O_4^{2-} \longrightarrow 10\ CO_2 + 10\ e^-$

$10\ e^- + 16\ H^+ + 2\ MnO_4^- \longrightarrow 2\ Mn^{2+} + 8\ H_2O$

When we add these together, we get:

$10\ e^- + 16\ H^+ + 2\ MnO_4^- + 5\ C_2O_4^{2-} \longrightarrow$

$2\ Mn^{2+} + 8\ H_2O + 10\ CO_2 + 10\ e^-$

Combining the Half-Reactions

$10\ e^{-} + 16\ H^{+} + 2\ MnO_4^{-} + 5\ C_2O_4^{2-} \longrightarrow$

$2\ Mn^{2+} + 8\ H_2O + 10\ CO_2 + 10\ e^{-}$

The only thing that appears on both sides are the electrons. Subtracting them, we are left with:

$16\ H^{+} + 2\ MnO_4^{-} + 5\ C_2O_4^{2-} \longrightarrow$

$2\ Mn^{2+} + 8\ H_2O + 10\ CO_2$

Balancing in Basic Solution

If a reaction occurs in basic solution, one can balance it as if it occurred in acid.

Once the equation is balanced, add OH^{-} to each side to "neutralize" the H^{+} in the equation and create water in its place.

If this produces water on both sides, you might have to subtract water from each side.

SAMPLE EXERCISE 20.3 Balancing Redox Equations in Basic Solution

Homework question:

Practice exercise page 855 b

I will check for correctness.

Voltaic (Galvanic) Cells

In spontaneous oxidation-reduction (redox) reactions, electrons are transferred and energy is released.

Voltaic Cells

We can use that energy to do work if we make the electrons flow through an external device.

We call such a setup a voltaic cell.

Voltaic Cells

A typical cell looks like this.

The oxidation occurs at the anode.

The reduction occurs at the cathode.

Voltaic Cells

Once even one electron flows from the anode to the cathode, the charges in each beaker would not be balanced and the flow of electrons would stop.

Voltaic Cells

Therefore, we use a salt bridge, usually a U-shaped tube that contains a salt solution, to keep the charges balanced.

Cations move toward the cathode.

Anions move toward the anode.

Voltaic Cells

Remember-

Although anode and cathode are labeled with a – and + signs, this is not the charge on the electrode. The charges on electrodes are essentially zero.

The – and + label tells us the electrode at which electrons are released to the external circuit.

SAMPLE EXERCISE 20.4 Reactions in a Voltaic Cell

the electrons flow through the external circuit from the electrode immersed in the KI solution (the anode) to the electrode immersed in the $K_2Cr_2O_7$ – H_2SO_4 solution (the cathode).

The electrodes themselves do not react in any way; they merely provide a means of transferring electrons from or to the solutions

The cations move through the solutions toward the cathode, and the anions move toward the anode.

The anode (from which the electrons move) is the negative electrode, and the cathode (toward which the electrons move) is the positive electrode.

Voltaic Cells

In the cell, then, electrons leave the anode and flow through the wire to the cathode.

As the electrons leave the anode, the cations formed dissolve into the solution in the anode compartment.

Voltaic Cells

As the electrons reach the cathode, cations in the cathode are attracted to the now negative cathode.

The electrons are taken by the cation, and the neutral metal is deposited on the cathode.

Water only spontaneously flows one way in a waterfall.

Likewise, electrons only spontaneously flow one way in a redox reaction—from higher to lower potential energy.

Potential Difference

The energy that would be required to move a unit of electrical charge from one point to the other against the electrostatic field that is present.

As potential difference increases, the current increases as well

Potential Difference

It is measured in volts (V).

One volt is the potential difference required to impart one joule of energy to a charge of one coulomb.

One electron has the charge of

$$1.60 \times 10^{-19} C$$

Electromotive Force (emf)

The potential difference between the anode and cathode in a cell is the driving force for the electrons to move across the external circuit hence it is called the electromotive force (emf).

It is also called the cell potential, and is designated E_{cell}.

Because E_{cell} is measured in volts it is also called the cell voltage.

For any reaction in a cell that is spontaneous the cell potential will have to be positive.

The cell potential or emf or E_{cell}

depends on:

Specific reaction that occur at the cathode and anode,

Concentrations of the reactants and products

And the temperature, which we assume as 25^{o}C unless otherwise stated.

We are going to focus on cells that operate

under standard conditions of-

25^{o}C

1M concentration of reactants and products and 1 atm pressure for those that are gases.

Under these conditions the emf is called the standard emf or the standard cell potential

So for the Zn/Cu voltaic cell

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

The superscript ^{o} indicates standard state conditions

Standard Reduction (Half Cell) Potential

We can tabulate the standard cell potential for all the possible cathode / anode combinations.

But it is not really needed to do so.

The cell potential is the difference between two electrode potentials

By convention the potential associated with each electrode is the potential for reduction to occur at that electrode.

Thus standard electrode potentials are the standard reduction potentials denoted E^{o}_{red}

The cell potential is given by the standard reduction potential of the cathode reaction minus the standard reduction potential of the anode reaction

$$E^{o}_{Cell} = E^{o}_{red}(\text{cathode}) - E^{o}_{red}(\text{anode})$$

Standard Reduction Potentials

Reduction potentials for many electrodes have been measured and tabulated.

The standard

Hydrogen electrode (SHE) has a potential of 0

Standard Hydrogen Electrode

Their values are referenced to a standard hydrogen electrode (SHE).

By definition, the reduction potential for hydrogen is 0 V:

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

In the previous cell the reaction is

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

Zn^{2+} / Zn is the anode and SHE is the cathode

The EMF of the cell is +0.76V

$E^o_{Cell} = E^o_{red}$ (cathode)- E^o_{red} (anode)

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

E^o_{red} (anode) = - 0.76V

So a standard electrode potential of -0.76V can be assigned to the reduction of Zn^{2+} to Zn

Zn^{2+} (aq, 1M) + $2e^- \rightarrow$ Zn (s) E^o_{red} = 0.76V

Pay attention to the fact that the reaction is written in reverse even thought the actual reaction is an oxidation process in the mentioned cell.

Whenever we assign a potential to half reaction we write the reaction as a reduction.

Using a similar method the EMF of any electrode can be determined.

These standard reduction potentials can be combined to calculate the emf of a large variety of cells.

In the voltaic cell, Zn is oxidized and is therefore the anode. Thus, the given E_{red} for Zn^{2+} is E_{red} (anode). Because Cu^{2+} is reduced, it is in the cathode half-cell. Thus, the unknown reduction potential for Cu^{2+}

is E_{red} (cathode). Knowing E_{cell} and E_{red} (anode), we can use Equation solve for E_{red} (cathode).

As we have noted, the standard reduction potential is an intensive property, so it is independent of the specific stoichiometric coefficients.

Standard Cell Potentials

The cell potential at standard conditions can be found through this equation:

Cell Potentials

For the oxidation in this cell,

For the reduction,

Cell Potentials

If we use Hess's Law

In any voltaic cell the reaction at the cathode has more positive value of E^o_{red} than does the reaction at the anode.

Oxidizing and Reducing Agents

The greater the difference between the two, the greater the voltage of the cell.

Strengths of Oxidizing and Reducing Agents

The more positive the E^o_{red} value of the half reaction, the greater is the tendency of the reactant of the half reaction to be reduced and therefore to oxidize other species.

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

The E^o_{red} value for Cu^{2+} is 0.34 V and for Zn is -0.76V

Frequently used Oxidizing Agents

Halogens

O_2

Oxianions whose central atoms have high oxidation states

MnO_4^-

$Cr_2O_7^{2-}$

NO_3^-

All these undergo reduction with

Large positive values of E^o_{red}

Frequently used Reducing Agents

H_2

Active metals

Alkali and Alkaline earth metals

Zn and Iron – the metals with negative E^o_{red} values.

Oxidizing and Reducing Agents

The strongest oxidizers have the most positive reduction potentials.

The strongest reducers have the most negative reduction potentials.

Standard Reduction Potentials

Reduction potentials for many electrodes have been measured and tabulated.

The standard

Hydrogen electrode (SHE) has a potential of 0

Free Energy and Redox Reactions

We know by now that Voltaic Cells use redox reactions that occur spontaneously

How do we find out if a redox reaction will be spontaneous

Do you remember the reaction:

We can rewrite this equation more generally as:

A positive value of E indicates a spontaneous process and a negative value indicates a nonspontaneous process

a. Now find out which one is the oxidation and which one is the reduction reaction
b. Then find the E^o_{red} valus from a table
c. Now fill these values in the formula

Now remember that a positive value means a spontaneous process.

If the value is negative the reverse reaction will be spotaneous.

Do you remember the activity series from chapter 4?

Do you remember the activity series from chapter 4?

You do not !!!!?????

How could you

Activity Series

Decreasing ease of oxidation

Active metals to noble metals

Any metal on the list can be oxidized by the ions of elements below it

$2Li + Cu^{2+} \rightarrow 2Li^{+} + Cu$

LEO GER

$2Li + Cu^{2+} \rightarrow 2Li^{+} + Cu$

LEO GER

$E^{o} = (+0.34V) - (-3.05V) = 0.34\ V + 3.05\ V = +3.39\ V$

Because cell potential is based on the potential energy per unit of charge, it is an intensive property.

So even if the ions are doubled in the reaction the reduction potential is not.

Gibbs Free Energy

$\Delta G = \Delta H + T\Delta S$ Δ H= Change in enthalpy

Δ S= Change in entropy

The change in Gibbs Energy (free energy change) is a measure of the spontaneity of a process at constant temperature and pressure.

Because emf, E of a redox reaction is an indication of the spontaneity of the reaction there is a relationship between ΔG and E

Free Energy

ΔG for a redox reaction can be found by using the equation

$\Delta G = -nFE$

where *n* is the number of moles of electrons transferred, and *F* is a constant, the Faraday.

1 *F* = 96,485 C/mol = 96,485 J/V-mol

Free Energy

As n and F are both positive values a positive value of E leads to a negative value of ΔG.

Therefore

A positive value of E and a negative value of ΔG both represent a spontaneous reaction

Under standard conditions,

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

This is an important equation which relates the standard emf E° to the standard free energy change ΔG°

ΔG° is related to the equilibrium constant K

$$\Delta G^\circ = - RT \ln K$$

the E° can be related to the K too.

Problem

Nernst Equation

Remember that

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

This means

$-n FE = -nFE^\circ + RT \ln Q$

Nernst Equation

Dividing both sides by $-nF$, we get the Nernst equation:

Nernst Equation

At room temperature (298 K),

Concentration Cells

Notice that the Nernst equation implies that a cell could be created that has the same substance at both electrodes.

Applications of Oxidation-Reduction Reactions

Batteries

Alkaline Batteries

Hydrogen Fuel Cells

Corrosion and…

…Corrosion Prevention