Electrochemistry Basics

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As the name suggests, electrochemistry is the study of changes that cause electrons to move. This movement of electrons is called electricity. In electrochemistry, electricity can be generated by movements of electrons from one element to another in a reaction known as a redox reaction or oxidation-reduction reaction.

Introduction

A redox reaction is a reaction which involves a change in oxidation state of one or more elements. When a substance loses its electron, its oxidation state increases, thus it is oxidized. When a substance gains an electron, its oxidation state decreases thus being reduced. For example, for the redox reaction:

$$H_2+F_2\longrightarrow 2HF$$

Rewrite it as

Oxidation: $H_2\longrightarrow 2H^++2e^-$

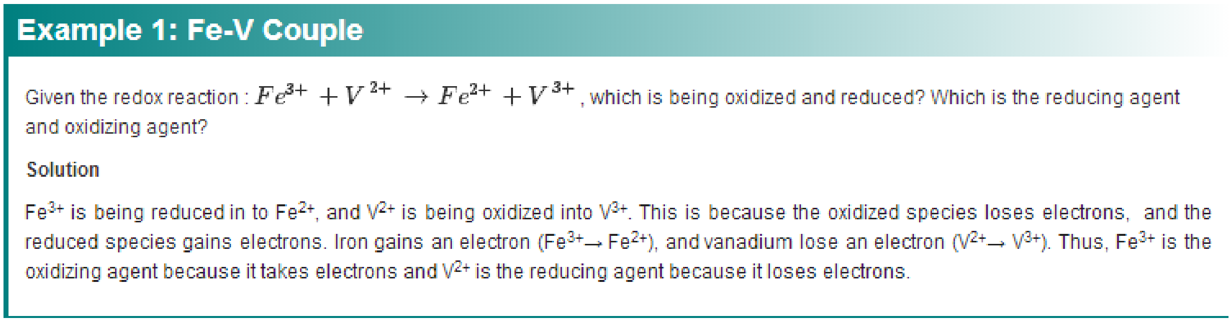
Reduction: $F_2+2e^-\longrightarrow 2F^-$

Overall Reaction : $H_2+F_2\longrightarrow 2H^++2F^-$

Oxidation reaction lose electrons thus they are being oxidized, while Reduction is gaining electrons thus they are being reduced. In this case, H_2 is being oxidized, while F_2 is being reduced.

OIL RIG

Oxidation **I**s **L**osing electrons **R**eduction **I**s **G**aining electrons



Example 1: Fe-V Couple

Given the redox reaction : $Fe^{3+} + V^{2+} \rightarrow Fe^{2+} + V^{3+}$, which is being oxidized and reduced? Which is the reducing agent and oxidizing agent?

Solution

Fe^{3+} is being reduced in to Fe^{2+}, and V^{2+} is being oxidized into V^{3+}. This is because the oxidized species loses electrons, and the reduced species gains electrons. Iron gains an electron ($Fe^{3+} \rightarrow Fe^{2+}$), and vanadium lose an electron ($V^{2+} \rightarrow V^{3+}$). Thus, Fe^{3+} is the oxidizing agent because it takes electrons and V^{2+} is the reducing agent because it loses electrons.

Voltaic Cells-Galvanic Cells

In 1793, Alessandro Volta discovered that electricity could be produced by placing different metals on the opposite sides of a wet paper or cloth. He made his first battery by placing Ag and Zn on the opposite sides of a moistened cloth with salt or weak acid solution. Therefore, these batteries got the name Voltaic Cells.

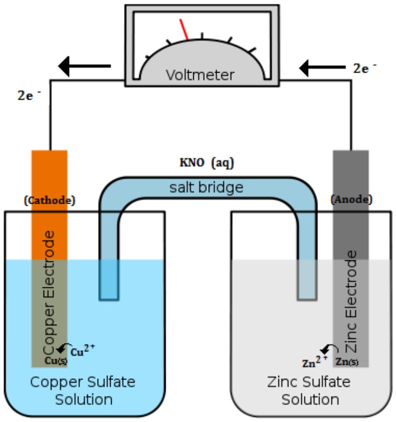
Voltaic (Galvanic) Cells are electrochemical cells which contain a spontaneous reaction, and always have a positive voltage. The electrical energy released during the reaction can be used to do work. A voltaic cell consists of two compartments called half-cells . The half-cell where oxidation occurs is called anode. The other half-cell where reduction occurs is called cathode. The Electrons in voltaic cells flow from the negative electrode to the positive electrode, which flows from anode to cathode.(See, figure below) (Note: electrodes=where the oxidation/reduction reactions occur).

Red Cat and **An Ox**

Reduction **Cat**hode and **An**ode **Ox**idation is a helful way to remember which reaction occurs on which half cell.

In order for oxidation-reduction reaction to occur, the two substances in each respective half-cell are connected by closed circuit so that electrons can flow from the reducing agent to the oxidizing agent. It also needs a salt bridge so that reaction can keep proceeding.

Galvanic Cell Needs electrical current from outside for it to work:



Notice how there is a voltmeter. Galvanic cell take energy sources from outside to make itself work.

The figure above shows that Zn(s) is continuously oxidized, producing Zn^{2+} into the solution. Zn(s)--> Zn^{2+}(aq)+2e^{-}. Conversely, in the cathode, Cu^{2+} is reduced and continuously deposits on to the Cu(s) metal bar Cu^{2+}(aq)+2e^{-}-->Cu(s). As a result, the solution containing Zn(s) becomes more positively charged while the solution containing Cu(s) becomes more negatively charged. In order for the voltaic cell to work, the solutions in the two half-cells must remain electrically neutral. Therefore, a salt bridge containing KNO_3 is added to keep the solutions neutral by adding NO_3^-, an anion into the anode solution and K^{+}, a cation into the cathode solution. As oxidation and reduction proceed, ions from the salt bridge migrate to neutralize charge in the cell compartments.

The diagram of this electrical cell : $Zn_{(s)} \mid Zn^{2+}_{(aq)} \parallel Cu^{2+}_{(aq)} \mid Cu_{(s)}$

-use ‖ to separate anode(-) and cathode(+) and so represents the salt bridge in between.

-use │to separate different states of matter on the same side

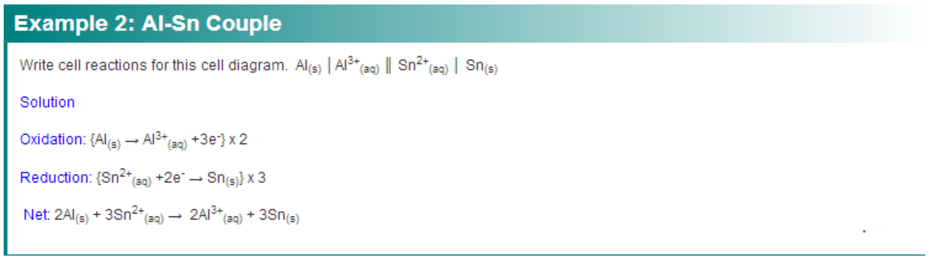
-use , to separate same states of matter on the same side. Example: $\mid Fe^{2+}_{(aq)}, Fe^{3+}_{(aq)} \parallel Ag^{+}_{(aq)} \mid Ag_{(s)}$

- The anode (where the oxidation occurs) is placed on the left side of the ‖
- The cathode (where reduction occurs) is placed on the right side of the ‖

Practice problem: Write out the Electrical cell diagram for this reaction:

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

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



Example 2: Al-Sn Couple

Write cell reactions for this cell diagram. $Al_{(s)} \mid Al^{3+}_{(aq)} \parallel Sn^{2+}_{(aq)} \mid Sn_{(s)}$

Solution

Oxidation: $\{Al_{(s)} \rightarrow Al^{3+}_{(aq)} + 3e^-\} \times 2$

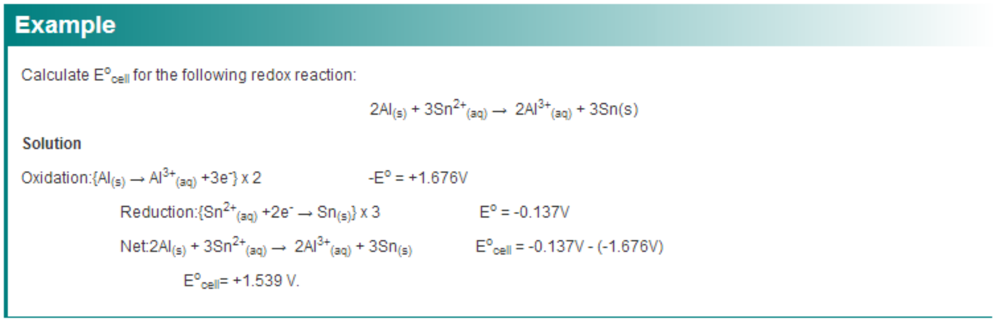
Reduction: $\{Sn^{2+}_{(aq)} + 2e^- \rightarrow Sn_{(s)}\} \times 3$

Net: $2Al_{(s)} + 3Sn^{2+}_{(aq)} \rightarrow 2Al^{3+}_{(aq)} + 3Sn_{(s)}$

Cell Potential

The oxidation of Zn(s) into Zn^{2+} and the reduction of Cu^{2+} to Cu(s) occur spontaneously. In other words, the redox reaction between Zn and Cu^{2+} is spontaneous. This is caused by the difference in potential energy between the two substances. The difference in potential energy between the anode and cathode dictates the direction of electrons movement. Electrons move from area of higher potential energy to area of lower potential energy. In this case, the anode has a higher potential energy so electrons move from anode to cathode. The potential difference between the two electrodes is measured in units of volts. One volt (V) is the potential difference necessary to generate a charge of 1 coulomb (C) from 1 Joule (J) of energy.

For a voltaic cell, this potential difference is called the **cell potential**, and is denoted $\mathbf{E_{cell}}$. For a spontaneous reaction, E_{cell} is positive and ΔG (Gibbs free energy that can be used to determine if a reaction occurs spontaneously) is negative. Thus, when ΔG is negative the reaction is spontaneous. By merging electrochemistry with thermodynamics we get this formula: $\Delta G = -n \times F \times E_{cell}$ *(or EMF). EMF= Electromotive Force.* Cell potential is different for each voltaic cell, its value depends upon the concentrations of specific reactants and products as well as temperature of the reaction. For **standard cell potential**, temperature of the reaction is assumed to be at 25° Celsius, the concentration of the reactants and products is 1M and reaction occurs at 1 atm pressure. The standard cell potential is denoted $\mathbf{E^o_{cell}}$. The can be written = oxidation potential + reduction potential. For Voltaic cells it will be $\mathbf{E^o_{cell}} = E^o(\text{cathode}) - E^o(\text{Anode})$



Example

Calculate E^o_{cell} for the following redox reaction:

$$2Al_{(s)} + 3Sn^{2+}_{(aq)} \rightarrow 2Al^{3+}_{(aq)} + 3Sn(s)$$

Solution

Oxidation: $\{Al_{(s)} \rightarrow Al^{3+}_{(aq)} + 3e^-\} \times 2$ $-E^o = +1.676V$

Reduction: $\{Sn^{2+}_{(aq)} + 2e^- \rightarrow Sn_{(s)}\} \times 3$ $E^o = -0.137V$

Net: $2Al_{(s)} + 3Sn^{2+}_{(aq)} \rightarrow 2Al^{3+}_{(aq)} + 3Sn_{(s)}$ $E^o_{cell} = -0.137V - (-1.676V)$

$E^o_{cell} = +1.539$ V.

Since the values of the standard potential are given in the form of standard reduction potential for each half-reaction, in order to calculate the standard cell potential E^o_{cell}, we need to find out which substance is being oxidized, then subtract the standard reduction potential of the oxidation reaction from the standard reduction potential of the reducing reaction. For example:

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

From the equation above, we know that Zn is being oxidized, and Cu is being reduced. For the redox reaction above, the potential for the two half reaction is given in the reduction form:

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

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

By looking at it's cell potential we can know which one is anode and cathode. Cathode has a more positive potential energy, thus

Cu is the cathode

Zn is the anode.

In order to calculate E^o_{cell}, subtract Zn of the oxdized species from the Cu of the reduced species, which is $E^o_{cell} =$(cathode)-E(Anode) (Note: Keep Cell potential in reduction form)

Oxidation: $Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + e^-$ - $E^o= +0.763V$

Reduction: $Cu^{2+}_{(aq)} + e^- \rightarrow Cu_{(s)}$ $E^o= +0.340V$

Or, you can rewrite the anode half reaction into it's oxidation form, then add to the reduction half reaction of cathode to find E^o_{cell}:

Oxidation: $Zn^{2+}_{(aq)} + e^- \rightarrow Zn_{(s)}$ $E^o= -0.763V$

Reduction: $Cu^{2+}_{(aq)} + e^- \rightarrow Cu_{(s)}$ $E^o= +0.340V$

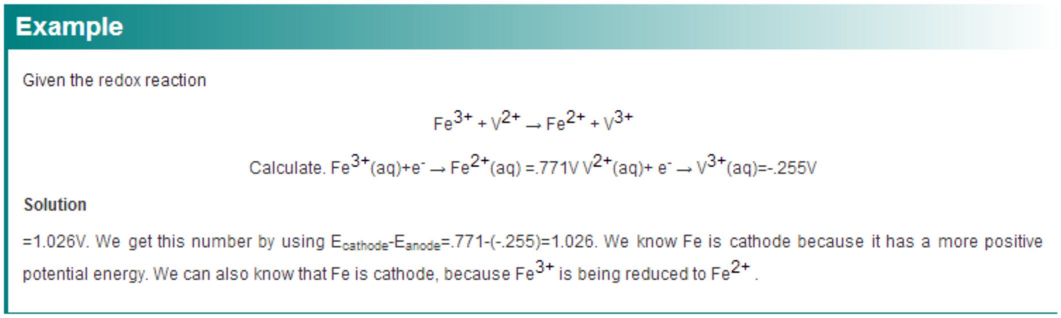
Net: $Zn_{(s)} + Cu^{2+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$
$E^o_{cell} = +0.340V + (-0.763V) = -.423V$

Since standard reduction potential have intensive properties, so changing the stoichiometric coefficient in a half reaction does not affect the value of the standard potential. For example,

Oxidation:$\{Al_{(s)} \rightarrow Al^{3+}_{(aq)} +3e^-\} \times 2$ is still $E^o= -1.676$

Reduction:$\{Sn^{2+}_{(aq)} +2e^- \rightarrow Sn_{(s)}\} \times 3$ is still $E^o= -0.137$

When multiplying the stoichiometric coefficient by 2, the standard potential does not change:



Example

Given the redox reaction

$$Fe^{3+} + V^{2+} \rightarrow Fe^{2+} + V^{3+}$$

Calculate. $Fe^{3+}(aq)+e^- \rightarrow Fe^{2+}(aq) = .771V$ $V^{2+}(aq)+ e^- \rightarrow V^{3+}(aq)=-.255V$

Solution

=1.026V. We get this number by using $E_{cathode}-E_{anode}=.771-(-.255)=1.026$. We know Fe is cathode because it has a more positive potential energy. We can also know that Fe is cathode, because Fe^{3+} is being reduced to Fe^{2+} .

Balancing Redox Reactions

Method 1: Oxidation Number Method

- Step 1: Assign oxidation numbers of each atom.
- Step 2: Determine the net change in charge to determine the ratio of atoms
- Step 3: Use the ratio to eliminate the net charge change
- Step 4: Use the ratio as coefficients for the elements
- Step 5: Use inspection to finish balancing of the equation

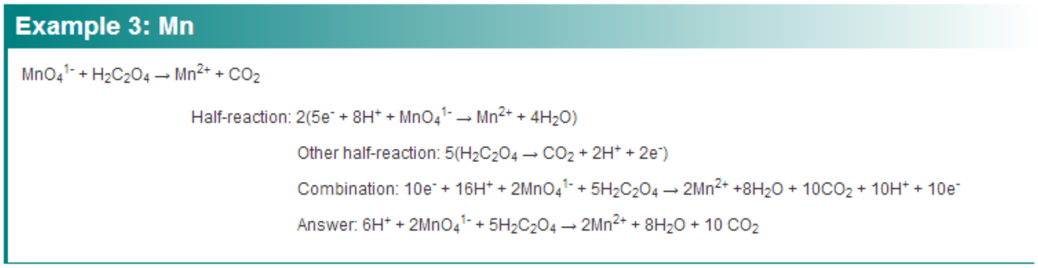
Method 2: Half-Reaction Method

- Step 1: Determine oxidation numbers for each atom
- Step 2: Use oxidation numbers to determine what's oxidized and what's reduced.
- Step 3: Write a half-reaction for reduction
- Step 4: Write a half-reaction for oxidation
- Step 5: Balance all elements except H and O

  \- **if have acid redox reaction:** Balance the O using $H_2$0, balance the H using protons

  - if have base redox reaction: Balance O using OH-

- Step 6: Sum up the charge in each side
- Step 7: Balance the charges by adding electrons
- Step 8: Multiply the half-reactions by factors that cancel out electrons
- Step 9: Add the two half-reactions back together to eliminate out intermediates



Example 3: Mn

$MnO_4^{1-} + H_2C_2O_4 \rightarrow Mn^{2+} + CO_2$

Half-reaction: $2(5e^- + 8H^+ + MnO_4^{1-} \rightarrow Mn^{2+} + 4H_2O)$

Other half-reaction: $5(H_2C_2O_4 \rightarrow CO_2 + 2H^+ + 2e^-)$

Combination: $10e^- + 16H^+ + 2MnO_4^{1-} + 5H_2C_2O_4 \rightarrow 2Mn^{2+} + 8H_2O + 10CO_2 + 10H^+ + 10e^-$

Answer: $6H^+ + 2MnO_4^{1-} + 5H_2C_2O_4 \rightarrow 2Mn^{2+} + 8H_2O + 10\ CO_2$

Rules for Assigning Oxidation states

1. Free elements have an oxidation state of 0. (e.g., He, N_2, O_2 has an oxidation state of 0)
2. The oxidation state of one atom ion must equal to the net charge. (Ex: F^- oxidation state is -1, K^+ oxidation state is +1)

3. The sum of the oxidation state has to equal the total net charge for a compound. (Ex: MnO_4 has a net charge of -1, Mn(+7)O4(-8)= -1)
4. The Alkali metals (Group I elements) have an oxidation state of +1. (EX: Li_2O, Li= +1)
5. The Alkaline earth metals (Group II elements) always have an oxidation state of +2. (Ex: CaO, Ca=+2)
6. Oxygen has an oxidation state of -2 in a compound
7. Fluorine has an oxidation state of -1 in a compound
8. Hydrogen has an oxidation state of +1 in a compound.
9. Transition metals and other metals may have more than one common ionic charge. (EX: Chromium common ionic charge are Cr+2 and Cr+3)

Practice problem: What is the oxidation state for MgF_2

Answer key: MgF_2 total charge=0 Total Charge=(+2)+(-1*2)=0 Using rule 4 and 7.

Practice problem: What is the oxidation state of H_2O

Answer key: H_2O total charge=0 Total Charge=(+1*2)+(-2)=0 Using rule 6 and 8

Additional Materials

I. Conversion

1 amp (A) = 1 Coulomb/sec (C/s)

1 Faraday (F) = 1 mole of e-1

1 Faraday (1 mole of e-1) = 96475 Coulomb (C)

II. Free Energy & Cell Potential

-flow of electrons that the cell produces can do work

-free energy is the E available to do work or maximum work that can be done by system

-free energy equation: $\Delta G = -n \times F \times EMF$

ΔG = free energy (usually in J)

n = mole of electrons

F = 1 Faraday

EMF = cell potential.

-the negative sign in front of n ensures that the reaction will be spontaneous

III. Nernst equation

-equation: $EMF = EMF^o (-RT/nF) \ln Q$

EMF = cell potential at current conditions

EMF° = cell potential at standard state (usually at 25 degree Celsius)

R = 8.31 J/mole×K

T = Kelvin temperature

n = mole of electron

F = 1 Faraday

Q = reaction quotient (Product/Reactant)

-relates cell potential and reaction quotient

At Equilibrium

equation: $\ln K = (n)(F)(EMF^o)/(RT)$

EMF = 0, Q = K, K = equilibrium constant

-cell stops and remains at rest, and will continue to do so until something reactivate it

The cell reaction is spontaneous in the forward direction if $E_{cell}>0$, $\Delta G<0$

The cell reaction is not spontaneous in the forward direction if $E_{cell}<0$, $\Delta G>0$

Terminology

- Anode: Electrode in an electrochemical cell on which the oxidation reaction occurs.
- Cathode: Electrode in an electrochemical cell on which the reduction reaction occurs
- Electrochemistry: A field of chemistry that focuses on the inter-change between electrical and chemical energy
- Electricity: Flow of electrons over a wire that is affected by the presence and flow of electric charge.
- Electrolysis: The decomposition of a substance by means of electric current. This method pushes push a redox reaction toward the non-spontaneous side.
- Electrolytic cell: Electrochemical cell that is being pushed toward the non-spontaneous direction by electrolysis.
- Electromotive force, EMF (or Cell Potential): Difference of potential energy of electrons between the two electrodes.
- Oxidation number: Charge on an atom if shared electrons where assigned to the more electronegative atom.
- Oxidation: Lose of electrons, can occur only in combination with reduction. [remember: Oxidation Is Loss, Reduction Is Gain = OIL RIG]
- Reduction: Gain of electrons, can occur only in combination with oxidation. [remember: OIL RIG]
- Redox reaction: Short hand for reduction-oxidation reaction.
- Voltaic cell or Galvanic cell: An electrochemical cell that uses redox reaction to produce electricity spontaneously.

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