

- pH continues to increase rapidly past the endpoint, then once a basic solution is achieved, it will level off
- Weak acid-strong base titration:
 - Initially an acidic pH, but not as low as a strong acid
 - pH gradually increases as the strong base is added
 - At midpoint of titration (half of volume needed to reach endpoint), the pH of the solution equals the pK_a of the acid ($K_a = H^+$, therefore $pK_a = pH$)
 - As the endpoint is reached, pH increases rapidly → solution is basic
 - After the endpoint, the pH will increase and level off until solution is strongly basic
- Strong acid-weak base titration:
 - Initial pH is basic due to presence of weak base
 - As strong acid is added, pH gradually decreases
 - Once all of the weak base is consumed, the solution reaches equivalence point and only the conjugate base is present (pH rapidly decreases)
 - After the endpoint, the pH will decrease and level off until solution is strongly acidic

Chapter 4.1 – Redox Reactions

Redox Half Reactions

- **Redox Reaction** – characterized by a change in the oxidation state of one or more elements in the reactants (net transfer of electrons from one reactant to another)
- Consist of 2 half reactions:
 - **Oxidation** – electrons are lost by the reducing agent
 - **Reduction** – electrons are gained by the oxidizing agent
- Oxidation and reduction always occur together (# of electrons lost = # of electrons gained)

Oxidation States

- Always zero in a pure element
- Is equal to the charge on a monatomic ion (e.g. $Na^+ = +1$)
- In a neutral species, the total must equal 0
- In a complex ion, the total must equal the charge on the ion
- When assigning oxidation states to the elements in a COMPOUND:
 - Fluorine is always -1, and other halogens are usually -1
 - Group 1 metals are +1, and group 2 metals are +2
 - Hydrogen is +1 (except when bonded to a metal, where it is -1)
 - Oxygen is usually -2
- Increases when losing electrons, and decreases when gaining electrons
- Oxidation States of Carbon:
 - May be determined by comparing the electronegativity of carbon to the electronegativity of each atom to which the carbon is bonded
 - If the carbon atom is bonded to an atom more electronegative than itself, that bond contributes +1 to the oxidation state of carbon (+1 for each bond)
 - If the carbon atom is bonded to an atom less electronegative than itself, that bond contributes -1 to the oxidation state of carbon

Steps for Balancing Redox Reactions

1. Write as two half-reactions
2. Balance the coefficients for all atoms except H and O
3. Add H₂O to the side deficient in O to balance O
4. Add H⁺ to the side deficient in H to balance H
5. For basic conditions → Add an equal # of OH⁻ to both sides to neutralize the H⁺, making H₂O
6. Balance charges by adding electrons to the side deficient in negative charge
7. If half-reactions have different # of electrons, multiply them in order to get same coefficients
8. Add the balanced half-reactions

Disproportionation Reactions

- These are reactions in which a substance in an intermediate oxidation state goes to higher and lower states by electron transfer
- To balance, separate into half-reactions and follow similar steps as above

Chapter 4.2 – Voltaic Cells

Electrochemical Cells

- **Electrochemical cell** (voltaic cell, galvanic cell) – the experimental setup that produces an electric current and does electric work through the use of a redox reaction
- The Daniell Cell:
 - Consisted of zinc and copper metals in oxidized form
 - Based on reaction: $Zn_{(s)} + Cu_{(aq)}^{2+} \rightarrow Zn_{(aq)}^{2+} + Cu_{(s)}$
 - To construct this cell, Zn and Cu bars are first immersed in separate beakers filled with aqueous ZnSO₄ and CuSO₄ solutions, and then connected with a wire
 - To compensate for the negative charge loss in the Zn beaker and negative charge gain in the Cu beaker, connect the two sulfate solutions with a **salt bridge**, allowing the negatively charged SO₄²⁻ ions in the Cu beaker to migrate to the Zn beaker
 - **Salt bridge** – filled with an aqueous solution of an inert salt (K₂SO₄)

Electrochemical Cell Notation

- **Half-cell** – the physically separated subsystem where each half-reaction occurs
- **Electrode** – where the half-reaction in each half-cell takes place on
 - The electrode is an electronic conductor that is in contact with an **electrolyte** – a solution or a molten salt
 - When none of the reactants is a solid conductor, a non-reactive metal is used as the electrode instead
 - **Cathode** – the electrode where reduction occurs
 - **Anode** – the electrode where oxidation occurs
- The current always flows from anode to cathode

Cell Diagram

- Anode is written first on the left, followed by other species in the order which they occur in the cell from the anode to cathode
- A phase boundary is represented by a single vertical bar
- The salt bridge is indicated by a double vertical bar
- If two or more reactants are in the same phase, separate them by a comma
- If inert electrodes are involved, they are placed on the anode or cathode end of the diagram as applicable, and separated by a single vertical bar
- Stoichiometric coefficients and species that aren't directly involved in the reaction aren't shown
- EXAMPLE $\rightarrow \text{Zn}(s) | \text{Zn}^{2+} || \text{Cu}^{2+} | \text{Cu}(s)$

Cell Potential

- **Cell potential/voltage** – the electrical energy difference between any two electrodes in an electrochemical cell (can be measured using a voltmeter)
- The voltage measured depends on the nature of the reactants in a cell, their concentrations (or pressures for gaseous reactants) and on the surrounding temperature
- Standard conditions for electrochemical cells \rightarrow 1.0 M and 25°C
- Only the potential of a complete cell can be measured with a voltmeter, not a half-cell
 - The potential for a half-cell can be measured relative to a commonly accepted reference half-cell (*standard hydrogen electrode*)
 - The standard electrode potential (E°) measures the tendency for a reduction process to occur at an electrode
- Stronger oxidizing agents are more easily reduced and have more positive E°_{red} values
- Stronger oxidizing agents form products that are more difficult to oxidize (weak reducing agent)
- To find E°_{cell} for a given redox reaction: $E^\circ_{\text{cell}} = E^\circ_{\text{red}} + E^\circ_{\text{ox}}$

Spontaneity of Redox Reactions

- $\Delta G^\circ = -nFE^\circ_{\text{cell}}$
 - n = # of electrons transferred between the electrodes
 - F = Faraday constant = 96485 C/mol e^-
- If $E^\circ_{\text{cell}} > 0$, then the reaction is spontaneous from left to right
- If $E^\circ_{\text{cell}} < 0$, then the reverse reaction is spontaneous
- If $E^\circ_{\text{cell}} = 0$, then the cell reaction is at equilibrium

Gibbs Free Energy and the Nernst Equation

- To determine the cell potential for a cell in which the reactants are in concentrations other than 1 M $\rightarrow \Delta G = \Delta G^\circ + RT \ln Q$
- Can be rewritten as the Nernst Equation: $E_{\text{cell}} = E^\circ_{\text{cell}} - \left(\frac{RT}{nF}\right) \ln Q$
- The Nernst equation can be used to predict the cell potential under non-standard conditions, and to predict the spontaneity of a redox reaction, or to calculate the unknown concentration of a reactant if a cell voltage is known
- It may be required to find the oxidation states of all involved species and take into account the number of moles of electrons involved in the balanced reaction

Chapter 4.3 – Electrolysis and Electrolytic Cells

Electrolysis

- **Electrolysis** – the process by which a non-spontaneous chemical reaction is forced to occur by the application of electrical energy from an external source
- The process of electrolysis is carried out in an **electrolytic cell**, which can be readily constructed from the corresponding voltaic cell
- If a voltage is applied to a voltaic cell from an external power source with an electromotive force greater than E°_{cell} , then the direction of electron flow in the cell will be reversed
 - The anodes and cathodes switch places (but the cell will still go from anode → cathode)
- You don't always have to place the electrodes in separate containers
 - Can have 2 electrodes in a single vessel filled with an electrolyte solution
 - The electrolyte filling can be a pure compound (e.g. water) or a molten salt (aqueous solution of a salt) or a mixture of pure compounds or aqueous solutions
 - A solid ionic compound that isn't melted or dissolved can't be electrolyzed because its ions are immobilized and cannot travel to the electrodes
- Electrolysis of Neutral Water
 - Pure water contains no ions to conduct electricity and so is very difficult to electrolyze
 - In order to decrease water's conductivity, you add a non-reacting, readily ionizing salt such as Na_2SO_4
 - Electrolysis of water is different from electrolysis of salts since individual H_2O molecules don't dissociate into cations and anions that migrate to the anode and cathode
 - Rather, some H_2O molecules are reduced at the cathode
 - $2\text{H}_2\text{O}(l) + 2e^- \rightarrow \text{H}_2(g) + 2\text{OH}^-(aq)$
 - While others are oxidized at the anode
 - $2\text{H}_2\text{O}(l) \rightarrow \text{O}_2(g) + 4\text{H}^+(aq) + 4e^-$
 - Overall reaction: $2\text{H}_2\text{O}(l) \rightarrow \text{O}_2(g) + \text{H}_2(g)$
 - Note that every time two moles of water react, 4 moles of electrons are involved

Voltage Needed for Electrolysis

- The minimum standard voltage required to force a non-spontaneous redox reaction to occur is:
 $E^\circ_{\text{electrolysis}} = -E^\circ_{\text{cell}}$
- **Electrolysis of Water in Acidic Solution** – abundance of H^+ ions in aqueous acid which can undergo reduction at the cathode ($E^\circ_{\text{electrolysis}} = +1.23 \text{ V}$)
- **Electrolysis of Water in Basic Solution** – abundance of OH^- ions in the solution which can undergo oxidation at the anode ($E^\circ_{\text{electrolysis}} = +1.23 \text{ V}$)
- **Overpotential** – the additional voltage required to force a non-spontaneous reaction to occur
 - Arises from kinetic factors such as the activation barrier for the reactions taking place at the surface of the electrode
 - This is why the voltage of a battery charger must be higher than the output voltage
 - The magnitude of the overpotential depends on the surface structure of the electrodes and the type of chemical reaction at the surface

Predicting Electrolysis Products of Aqueous Solutions

- If the electrolytic cell contains a mixture of compounds, then more than one variation is possible at each electrode (usually one reaction favoured over the others)

- We can predict the actual products of electrolysis based on the ability of reactants to give up or attract electrons (compare E°_{red} for all possible half-reactions)
- **For the reduction half-rxn at cathode:** the higher the E°_{red} , the more favourable the reaction
- **For the oxidation half-rxn at anode:** the higher the E°_{ox} , the more favourable the reaction

Quantitative Determination of Electrolysis Products

- **Faraday's Law** – the # of moles of products reduced or oxidized by the passage of an electric current through an electrolytic cell is stoichiometrically equivalent to the # of moles of electrons supplied
- The charge (Q) of n moles of electrons can be written as: $Q = n_e F$
- Electric current (I) is defined as the flow of charge per unit time: $Q = It$

The Chlor-Alkali Process

- This is when an aqueous NaCl solution (brine) is electrolyzed to produce NaOH, $\text{H}_{2(g)}$ and $\text{Cl}_{2(g)}$
- The current used in this process is extremely high, but the applied voltage is only a few volts
- An ion-exchange membrane allows Na^+ ions to flow through but not Cl^-

Chapter 4.4 – Batteries

Batteries

- **Battery** – device that converts the chemical energy stored in its active materials into electrical energy, thus providing a source of power
 - **PRIMARY** – can be used only once because the chemical reactions that supply the electrical current are irreversible
 - **SECONDARY** – can be used, recharged, and reused since the chemical reactions that supply electrical current are easily reversed so that the battery can regain its charge
- **Discharging** – electrons from the anode migrate through an external circuit to the cathode
 - This is a spontaneous process that can only continue until the cell is completely dead
 - Dead batteries have zero cell potential since its reactants and products have attained equilibrium (limiting reagent may still be present)

Electrolytic Cells

- If a dead cell can be recharged by an external source, it becomes an electrolytic cell
- The external voltage required to force this non-spontaneous cell reaction is greater than the voltaic cell voltage
- Since the negative terminal of the external voltage source is electron rich, electrons flow from this terminal to the cathode
 - The current is sustained by the oxidation at the anode, producing electrons that flow to the positive terminal of the voltage source
 - Note that the cathode and anode have switched places since the direction of the current is reverse of that in the voltaic cell

Lead-Acid Battery

- Comprised of six 2 V cells connected in series
- Overall voltage is the sum of the voltages produced by the individual cells (12 V)
- In the charged state, each cell contains electrodes of Pb and PbO₂ in an electrolyte of H₂SO₄
- As the battery is discharged, both electrodes form PbSO₄ and the [H₂SO₄] is reduced
- Large SA supplied by the plates allows high currents to be generated for short periods of time
- When it charges, an external current is used to provide the energy needed for the non-spontaneous reverse reaction in each of the battery's 6 cells

Other Rechargeable Batteries

- **Nickel-Cadmium (NiCd) Batteries:**
 - Cadmium at the anode and nickel oxide at the cathode
 - Gradually lose their max. energy capacity after repeated recharging ("memory effect")
- **Nickel-Metal Hydride (NiMH) Batteries:**
 - Most popular today, since they don't have any toxic cadmium or a "memory effect"
 - Also able to store more energy than NiCd on a weight-by-weight basis
 - Cheap to manufacture, reliable, and relatively safe
 - The metal hydride is at the anode and nickel oxyhydroxide is at the cathode
- **Lithium-Ion (Li-Ion) Batteries:**
 - Popular due to its high energy-to-weight ratio
 - LiC₆ is at the anode and CoO₂ is at the cathode
 - Li⁺ ions aren't oxidized or reduced to generate a voltage
 - Instead, they migrate to and from the anode and cathode in a process called *intercalation* (possible due to layered structure of electrodes)
 - Although more expensive than NiMH, Li-ion batteries are light, deliver more power and don't suffer from "memory effect"
 - However, they can rupture, ignite or explode when subjected to high temperature or overcharging, and also cannot deliver high currents
- **Lithium-Polymer (Li-Pol) Batteries:**
 - Uses a polymer (solid phase) electrolyte between the two electrodes
 - Electrode material are situated in a spiral inside a cylinder, which prevents electrodes from touching
 - Advantage over a liquid electrolyte is that it allows the materials in the Li-Pol battery to be stacked, with little chance of the two electrodes coming into contact
 - These batteries can therefore be manufactured in virtually any shape

Chapter 5.1 – Reaction Rates and Rate Laws

Reaction Rates

- The speed at which a reaction takes place depends on: what the reactants are and their concentrations, the temperature, and whether or not a catalyst is present
- For any reaction: $aA + bB \rightarrow cC + dD$
 - The rate is expressed as: $\text{Rate} = -\frac{1}{a} \left(\frac{\Delta[A]}{\Delta t} \right) = -\frac{1}{b} \left(\frac{\Delta[B]}{\Delta t} \right) = \frac{1}{c} \left(\frac{\Delta[C]}{\Delta t} \right) = \frac{1}{d} \left(\frac{\Delta[D]}{\Delta t} \right)$