- o pH continues to increase rapidly past the endpoint, then once a basic solution is achieved, it will level off
- *Weak acid-strong base titration:*
  - o Initially an acidic pH, but not as low as a strong acid
  - o pH gradually increases as the strong base is added
  - o 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)
  - o As the endpoint is reached, pH increases rapidly → solution is basic
  - o After the endpoint, the pH will increase and level off until solution is strongly basic
- *Strong acid-weak base titration:*
  - o Initial pH is basic due to presence of weak base
  - o As strong acid is added, pH gradually decreases
  - o Once all of the weak base is consumed, the solution reaches equivalence point and only the conjugate base is present (pH rapidly decreases)
  - o 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:
  - o **Oxidation** – electrons are lost by the reducing agent
  - o **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:
  - o Fluorine is always -1, and other halogens are usually -1
  - o Group 1 metals are +1, and group 2 metals are +2
  - o Hydrogen is +1 (except when bonded to a metal, where it is -1)
  - o Oxygen is usually -2
- Increases when losing electrons, and decreases when gaining electrons
- Oxidation States of Carbon:
  - o May be determined by comparing the electronegativity of carbon to the electronegativity of each atom to which the carbon is bonded
  - o 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)
  - o 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 H_2O 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 H_2O
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: $Zn_{(s)} + Cu^{2+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$
  - To construct this cell, Zn and Cu bars are first immersed in separate beakers filled with aqueous $ZnSO_4$ and $CuSO_4$ 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 SO_4^{2-} ions in the Cu beaker to migrate to the Zn beaker
    - *Salt bridge* – filled with an aqueous solution of an inert salt (K_2SO_4)

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 → $Zn(s) \mid Zn^{2+} \parallel Cu^{2+} \mid Cu(s)$

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 → 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: $E^o_{cell} = E^o_{red} + E^o_{ox}$

Spontaneity of Redox Reactions

- $\Delta G^o = -nFE^o_{cell}$
    - n = # of electrons transferred between the electrodes
    - F = Faraday constant = 96485 C/mol e⁻
- If $E^o_{cell} > 0$, then the reaction is spontaneous from left to right
- If $E^o_{cell} < 0$, then the reverse reaction is spontaneous
- If $E^o_{cell} = 0$, 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 → $\Delta G = \Delta G^o + RT \ln Q$
- Can be rewritten as the Nernst Equation: $E_{cell} = E^o_{cell} - \left(\frac{RT}{nF}\right) \ln Q$
- 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^o_{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
      - $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$
    - While others are oxidized at the anode
      - $2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$
  - Overall reaction: $2H_2O(l) \rightarrow O_2(g) + H_2(g)$
  - 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: $E^o_{electrolysis} = -E^o_{cell}$
- ***Electrolysis of Water in Acidic Solution*** – abundance of H^+ ions in aqueous acid which can undergo reduction at the cathode ($E^o_{electrolysis}$ = +1.23 V)
- ***Electrolysis of Water in Basic Solution*** – abundance of OH^- ions in the solution which can undergo oxidation at the anode ($E^o_{electrolysis}$ = +1.23 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^o_{red} for all possible half-reactions)
- **For the reduction half-rxn at cathode:** the higher the E^o_{red}, the more favourable the reaction
- **For the oxidation half-rxn at anode:** the higher the E^o_{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: $\boldsymbol{Q = n_e F}$
- Electric current (I) is defined as the flow of charge per unit time: $\boldsymbol{Q = It}$

The Chlor-Alkali Process
- This is when an aqueous NaCl solution (brine) is electrolyzed to produce NaOH, $H_{2(g)}$ and $Cl_{2(g)}$
- 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

<u>Lead-Acid Battery</u>
- 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 PbO_2 in an electrolyte of H_2SO_4
- As the battery is discharged, both electrodes form $PbSO_4$ and the $[H_2SO_4]$ 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

<u>Other Rechargeable Batteries</u>
- **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
  - LiC_6 is at the anode and CoO_2 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

<u>Reaction Rates</u>
- 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: $Rate = -\frac{1}{a}\left(\frac{\Delta[A]}{\Delta t}\right) = -\frac{1}{b}\left(\frac{\Delta[B]}{\Delta t}\right) = \frac{1}{c}\left(\frac{\Delta[C]}{\Delta t}\right) = \frac{1}{d}\left(\frac{\Delta[D]}{\Delta t}\right)$