

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: $\text{Rate} = -\frac{1}{a} \left(\frac{\Delta[A]}{\Delta t} \right) = -\frac{1}{b} \left(\frac{\Delta[B]}{\Delta t} \right) = \frac{1}{c} \left(\frac{\Delta[C]}{\Delta t} \right) = \frac{1}{d} \left(\frac{\Delta[D]}{\Delta t} \right)$

Concentration Effects and Rate Laws

- **Rate laws** – mathematical expressions that link the rate of a rxn with reactant concentration
- In the reaction: $aA + bB \rightarrow \text{products}$
 - The rate of the reaction (rate law) is: $\text{Rate} = k[A]^x[B]^y$
 - k is the specific rate constant for the reaction at a given temperature
 - x and y are the orders for each reactant and can only be found experimentally
- The “order” of a reaction defines how the rate of a reaction is affected by the concentration of the species involved in the reaction
- **Overall order of a reaction** – the sum of all the individual orders
- Experimental Determination of the Exponents
 - The initial rates are observed immediately after the reactants are mixed
 - If there is a graph, the initial slope = instantaneous rate at $t = 0$
 - Between any 2 runs, one of the reactant concentrations must be constant in order to determine the order of the second reactant

First-Order Reactions

- If $A \rightarrow \text{products}$ is a first-order reaction, $\text{Rate} = k[A] = -\left(\frac{\Delta[A]}{\Delta t}\right)$
- Integrated rate law: $\ln\left(\frac{\Delta[A]}{\Delta t}\right) = -k[t]$ or $[A]_t = [A]_0 e^{-kt}$ OR $\ln[A]_t = -kt + \ln[A]_0$
 - $[A]_t$ = concentration of A after time t has elapsed
 - $[A]_0$ = initial concentration
- A plot of $\ln[A]_t$ vs. time yields a straight line with a slope of $-k$ and y-intercept of $\ln[A]_0$
- **Half-life ($t_{1/2}$)** – the amount of time it takes to use up half of the reactant
 - $t_{1/2} = \frac{0.693}{k}$ (it only depends on the rate constant k in first-order reactions)
 - The half-life of a first-order reaction follows an exponential decay
 - Exponential decay plot is not a straight line ($[A]$ vs. time)
 - Graph approaches 0 but never reaches it; thus, the reaction is never complete
 - The fraction of reactant remaining after “ n ” half-lives can be expressed as:
 - $\text{Fraction remaining} = \frac{[A]_t}{[A]_0} = (0.05)^n$
 - $n = \text{number of elapsed half-lives} = \frac{\text{time elapsed}}{\text{length of half-life}}$

Zero-Order Reactions

- If $A \rightarrow \text{products}$ is a zero-order reaction, $\text{Rate} = -\left(\frac{\Delta[A]}{\Delta t}\right) = k[A]^0 = k$
- Integrated rate law: $[A]_t = -kt + [A]_0$
 - A plot of $[A]$ vs. time yields a straight line with a slope of $-k$ and y-intercept of $[A]_0$
- Half-life of zero-order reaction: $t_{1/2} = \frac{[A]_0}{2k}$

Second-Order Reactions

- If $A \rightarrow \text{products}$ is a second-order reaction, $\text{Rate} = -\left(\frac{\Delta[A]}{\Delta t}\right) = k[A]^2$
- Integrated rate law: $\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$
 - A plot of $1/[A]$ vs. time yields a straight line with a slope of k and y-intercept of $1/[A]_0$
- Half-life of a 2nd order reaction depends on the concentration of the reactant: $t_{1/2} = \frac{1}{k[A]_0}$

Chapter 5.2 – Reaction Mechanisms & the Arrhenius Equation

Thermodynamics and Kinetics

- **Thermodynamics** – net energy difference (ΔE) between reactants and products of a reaction
- **Kinetics** – the rate of the reaction depends on the size of the barrier
- Reaction coordinate diagrams illustrate the energy changes that occur on the route from reactants to products (represents progress along a reaction pathway)
- **Activation Energy** – the amount of energy required to overcome the activation barrier, in order to allow a reaction to proceed (this energy comes from heat, which is measured by temp.)
 - Temperature is a measure of the avg. kinetic energy of a collection of molecules
 - At any given temperature, there is a distribution of kinetic energies for molecules, as represented by a Boltzmann distribution graph
 - At low temperature, none of the reactants have enough energy to overcome barrier
 - As temperature increases, more of the molecules gain enough energy to overcome E_a
- **Collision Theory** – for a reaction to occur, reactants must collide in a proper orientation, with sufficient energy to overcome the activation barrier
- The rate of a reaction is affected by these factors:
 - Reactant concentration (higher concentration = more collisions)
 - Probability factor based on the probabilities of colliding in a particular geometry (steric factor) and continuing to the products at the transition state
 - E_a and temperature (higher temperature = more reactants able to overcome E_a)
- $\text{Rate} = \# \text{ of collisions} \times [\text{probability factor} \times \text{fraction of collisions with enough energy to overcome } E_a]$

The Arrhenius Equation

- $k = Ae^{-\frac{E_a}{RT}}$, where A = Arrhenius probability factor for a specific reaction
- As the value of E_a increases (higher activation barrier), the value of k decreases
 - Therefore, fastest reactions have the smallest activation energy barrier
- **Effect of Temperature on Rate:**
 - For a given reaction, E_a is a constant and can be determined without knowing the probability factor by performing two experiments at different temperatures while maintaining the same reactant concentrations
 - $\text{Rate}_{T_1} = k_{T_1}[A][B]$ at temperature 1
 - $\text{Rate}_{T_2} = k_{T_2}[A][B]$ at temperature 2
 - Therefore, $\ln\left(\frac{\text{Rate}_{T_2}}{\text{Rate}_{T_1}}\right) = \ln\frac{k_2}{k_1} = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$
- **Determining Activation Energy Graphically:**
 - The Arrhenius equation can be rearranged as: $\ln k = \ln A - \frac{E_a}{R}\left(\frac{1}{T}\right)$
 - E_a can be determined experimentally by measuring a reaction rate at different temperatures, then plotting the graph of $\ln k$ vs. $1/T$
 - A straight line with a slope of $-\frac{E_a}{R}$ and a y-intercept of $\ln A$
- **Effect of a Catalyst on Activation Energy:**
 - A catalyst increases the rate of reaction but is not consumed in the reaction
 - It provides an alternative pathway with a lower E_a , that, in turn, increases k
 - Has no effect on the net enthalpy change (ΔH) of a reaction
 - **Rate enhancement factor** – the ratio of k values for the catalyzed and uncatalyzed reaction ($k_{\text{cat}} / k_{\text{uncat}}$)

- To determine that magnitude of the E_a reduction (ΔE_a) resulting from the introduction of a catalyst: $\ln\left(\frac{\text{Rate}_{cat}}{\text{Rate}_{uncat}}\right) = \ln\frac{k_{cat}}{k_{uncat}} = \frac{E_{a(uncat)} - E_{a(cat)}}{RT} = \frac{\Delta E_a}{RT}$

Reaction Mechanisms

- **Reaction Mechanism** – describes the sequence of steps that occur during a chemical reaction
- Each step is called an **elementary step**
 - Each elementary step has an E_a and a rate constant
 - # of steps = # of transition states
- Species formed and consumed within the reaction mechanism are **reaction intermediates**
 - Unlike transition states, these are real species that can be found in the reaction mixture as the reaction progresses (transition states are short-lived; cannot be found in mixture)
- **Molecularity** – refers to how many species react together in an elementary step
 - **Unimolecular process** – involves only one reactant species (first-order kinetics)
 - **Bimolecular process** – involves two species (second-order)
- ONLY in an elementary step, the coefficients of the reactants become exponents of the rate law
- The overall rate of a reaction is determined by the rate of the slowest or rate-determining step
- Determining Reaction Mechanisms
 - **Proposal A** – reaction occurs in one step
 - Overall reaction is therefore the elementary step
 - Reaction is bimolecular and rate law for the reaction is overall 2nd order
 - **Proposal B** – reaction occurs in two steps
 - First step slow; second step fast
 - Rate law for overall reaction is based on RDS (1st step)
 - Slower step has the higher transition rate
 - **Proposal C** – reaction occurs in two steps, but the slow/fast steps have been swapped
 - First step fast; second step slow
 - Rate law for overall reaction is based on step 2
 - However, since step 2 includes the intermediates (which cannot appear in overall rate law), step 1 must be rearranged and a substitute for the intermediate must be used in the step 2 (RDS) rate expression
- Guidelines for Deriving a Rate Law
 1. Look for the RDS
 2. Write a rate law in terms of concentrations of reactions in the RDS
 3. If there are intermediates, express their concentrations in terms of stable reactants appearing in the overall reaction equation
 - In an equilibrium reaction, forward and reverse rates are equal ($k_{if}[A] = k_{ir}[B]$)
 4. Substitute concentrations of stable reactants for concentrations of intermediates in the rate law
 5. Fast steps following the RDS in the mechanistic sequence may be ignored
 - NOTE: the RDS isn't always the one with the largest activation barrier
 - It is the step whose transition state has the highest overall energy