

## 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 PbO<sub>2</sub> in an electrolyte of H<sub>2</sub>SO<sub>4</sub>
- As the battery is discharged, both electrodes form PbSO<sub>4</sub> and the [H<sub>2</sub>SO<sub>4</sub>] 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
  - LiC<sub>6</sub> is at the anode and CoO<sub>2</sub> is at the cathode
  - Li<sup>+</sup> 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 ( $\Delta E$ ) 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 ( $\Delta H$ ) 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 ( $\Delta E_a$ ) 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 2<sup>nd</sup> order
  - **Proposal B** – reaction occurs in two steps
    - First step slow; second step fast
    - Rate law for overall reaction is based on RDS (1<sup>st</sup> 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