Chemistry 132 NT

We are what we repeatedly do. Excellence is, then, not an act, but a habit

Aristotle

Reaction Rates

The burning of steel wool

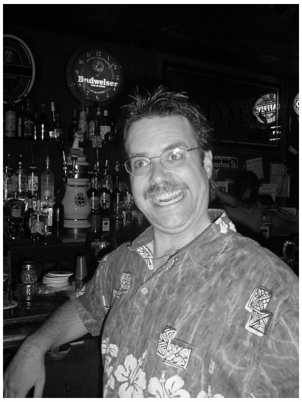
Module 1

Reaction Rates

- **Definition of Reaction Rate**
- **Experimental Determination of Rate**
- **Dependence of Rate on Concentration**

Chem 132 NT

- Chemistry 132 NT (First Exam)
  - Reaction Rates: Kinetics
  - Chemical Equilibrium
    - Each chapter broken into modules (3 or 4)
    - Tutorial quiz at end of each module
    - Homework assignment for each chapter



Tips

- Keep your text book handy.
- Take the tutorial quiz.
- Pace yourself.

Reasons for Studying Kinetics

- The production of chemicals.

Reasons for Studying Kinetics

- The production of chemicals.

Reaction Rates

- Chemical reactions require varying lengths of time for completion.
  - This "**reaction rate**" depends on the **characteristics of the reactants and products** and the **conditions under which the reaction is run.**
  - By understanding how the rate of a reaction is affected by changing conditions, one can learn the details of what is happening at the molecular level.

Reaction Rates

- The questions posed in this chapter will be:
  - **What conditions will affect the rate of a reaction?**
  - **How is the rate of a reaction measured?**
  - **How do you express the relationship of rate to the variables affecting the rate?**
  - **What happens on a molecular level during a chemical reaction?**

Reaction Rates

- **Chemical kinetics** is the study of reaction rates, how reaction rates change under varying conditions, and what molecular events occur during the overall reaction.
  - **What variables affect reaction rate?**

Concentration of reactants.

Reaction Rates

- **Chemical kinetics** is the study of reaction rates, how reaction rates change under varying conditions, and what molecular events occur during the overall reaction.
  - **What variables affect reaction rate?**

Concentration of a catalyst.

Reaction Rates

- **Chemical kinetics** is the study of reaction rates, how reaction rates change under varying conditions, and what molecular events occur during the overall reaction.
  - **What variables affect reaction rate?**

Temperature at which the reaction occurs.

Reaction Rates

- **Chemical kinetics** is the study of reaction rates, how reaction rates change under varying conditions, and what molecular events occur during the overall reaction.
  - **What variables affect reaction rate?**

Surface area of a solid reactant or catalyst.

Reaction Rates

- **Chemical kinetics** is the study of reaction rates, how reaction rates change under varying conditions, and what molecular events occur during the overall reaction.
  - **What variables affect reaction rate?**

Let’s look at each in more detail.

Factors Affecting Reaction Rates

- **Concentration of reactants**
  - More often than not, the rate of a reaction **increases** when the concentration of a reactant is increased.
  - Increasing the population of reactants increases the likelihood of a successful collision.
  - In some reactions, however, the rate is unaffected by the concentration of a particular reactant, as long as it is present at some concentration.

Factors Affecting Reaction Rates

- **Concentration of a catalyst.**
  - A **catalyst** is a **substance that increases the rate of a reaction <u>without being consumed</u> in the overall reaction.**
  - The catalyst, generally, does not appear in the overall balanced chemical equation (although its presence may be indicated by writing its formula over the arrow).

$$2H_2O_{2(aq)} \xrightarrow{HBr(aq)} 2H_2O_{(l)} + O_{2(g)}$$

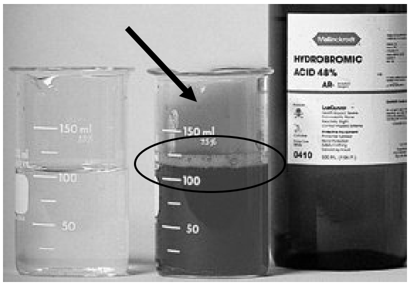
Factors Affecting Reaction Rates

- **Concentration of a catalyst.**
  - The next slide shows the HBr catalyzed decomposition of H_2O_2 to H_2O and O_2.

$$2H_2O_{2(aq)} \xrightarrow{HBr(aq)} 2H_2O_{(l)} + O_{2(g)}$$

  - A catalyst speeds up reactions by reducing the "activation energy" needed for successful reaction.
  - A catalyst may also provide an alternative mechanism, or pathway, that results in a faster rate.

Catalytic decomposition of hydrogen peroxide



The hydrogen peroxide decomposes rapidly when hydrobromic acid is added to produce oxygen gas bubbles and the red color of Br_2.

Factors Affecting Reaction Rates

- **Temperature at which a reaction occurs.**
  - Usually reactions speed up when the temperature increases.
  - A good "rule of thumb" is that reactions approximately double in rate with a 10 ^oC rise in temperature.

Factors Affecting Reaction Rates

- **Surface area of a solid reactant or catalyst.**
  - Because the reaction occurs at the surface of the solid, the rate increases with increasing surface area.
  - The next slide shows the effect of surface area on reaction rate.

Effect of large surface area on the rate of reaction.

Very finely divided cellulose ignites easily to produce a yellow flame. The powder has a large surface area per volume and burns rapidly in air.

Summary

- Concentration of reactants
- Concentration of catalysts
- Temperature of reaction
- Surface area of solid reactants and catalysts

Definition of Reaction Rate

- The **reaction rate** is **the increase in molar concentration of a product of a reaction per unit time**.
  - It can also be expressed as the **decrease** in molar concentration of a **reactant** per unit time.

Definition of Reaction Rates

- Consider the gas phase decomposition of dintrogen pentoxide.

$$2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$$

  - If we denote molar concentrations using brackets, then the change in the molarity of O_2 would be represented as

$$\boxed{\Delta[O_2]}$$

where the symbol, Δ, (capital Greek delta) means the "change in".

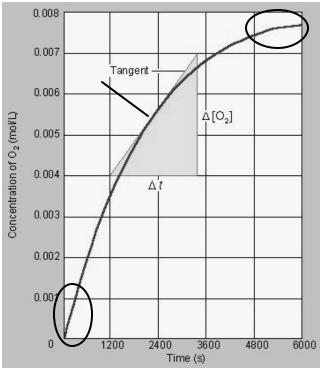
Definition of Reaction Rates

- Then, in a given time interval, Δt , the molar concentration of O_2 would increase by $\Delta[O_2]$.
  - The rate of the reaction is given by:

$$\textbf{Rate of formation of oxygen} = \frac{\Delta[O_2]}{\Delta t}$$

  - This equation gives the average rate over the time interval, Δt.
  - If Δt is short, you obtain an **instantaneous rate** , that is, the rate at a particular instant.

The instantaneous rate of reaction



In the reaction

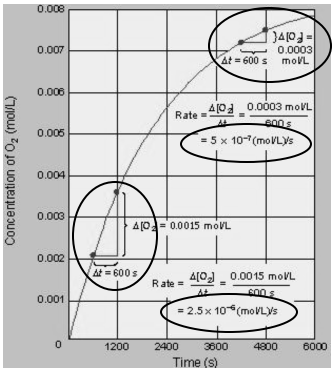
$$2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$$

The concentration of O_2 increases over time. You obtain the instantaneous rate from the slope of the tangent at the point of the curve corresponding to that time.

Definition of Reaction Rates

- The next slide shows the increase in concentration of O_2 during the decomposition of N_2O_5.
- Note that the **rate decreases** as the reaction proceeds.

Calculation of the average rate.



When the time changes from 600 s to 1200 s, the average rate is 2.5×10^{-6} mol/(L·s). Later when the time changes from 4200 s to 4800 s, the average rate has slowed to 5×10^{-7} mol/(L·s). Thus, the rate of a reaction decreases as the reaction proceeds.

Definition of Reaction Rates

- Because the amounts of products and reactants are related by **stoichiometry**, any substance in the reaction can be used to express the rate.

$$\textbf{Rate of decomposition of } N_2O_5 = \textcircled{-}\frac{\Delta[N_2O_5]}{\Delta t}$$

- Note the negative sign. This results in a positive rate as reactant concentrations decrease.

Definition of Reaction Rates

- The rate of decomposition of N_2O_5 and the formation of O_2 are easily related.

$$\frac{\Delta[O_2]}{\Delta t} = \frac{1}{2}\left(-\frac{\Delta[N_2O_5]}{\Delta t}\right)$$

- Since two moles of N_2O_5 decompose for each mole of O_2 formed, the rate of decomposition of N_2O_5 is twice the rate of the formation of O_2.

$$\textcircled{2}N_2O_5(g) \rightarrow 4NO_2(g) + \textcircled{}O_2(g)$$

A Problem to Consider

- Consider the reaction of nitrogen dioxide with fluorine to give nitryl fluoride.

$$2\,NO_2(g) + F_2(g)\ ®\ 2\,NO_2F(g)$$

- How is the rate of formation of NO_2F related to the rate of reaction of fluorine?

A Problem to Consider

- Consider the reaction of nitrogen dioxide with fluorine to give nitryl fluoride.

$$2\,NO_2(g) + F_2(g)\ ®\ 2\,NO_2F(g)$$

- The rate of disappearance of any reactant “X” is $-\Delta[X]/\Delta t$. So the rate of disappearance of the fluorine would be written:

$$\text{Rate of reactionof } F_2 = -\frac{D[F_2]}{Dt}$$

A Problem to Consider

- Consider the reaction of nitrogen dioxide with fluorine to give nitryl fluoride.

$$2\,NO_2(g) + F_2(g)\ ®\ 2\,NO_2F(g)$$

- The rate of appearance of any product “Y” is $\Delta[Y]/\Delta t$ (note that it’s positive). So the rate of appearance of the NO_2F would be written:

$$\text{Rate of reaction of } NO_2F = \frac{D[NO_2F]}{Dt}$$

A Problem to Consider

- Consider the reaction of nitrogen dioxide with fluorine to give nitryl fluoride.

$$2NO_2(g) + F_2(g) \rightarrow 2NO_2F(g)$$

- These rate expressions can be equated, if you divide each by the coefficient of the corresponding substance in the balanced chemical equation.

$$\frac{1}{2}\frac{\Delta[NO_2F]}{\Delta t} = -\frac{\Delta[F_2]}{\Delta t}$$

A Problem to Consider

- Calculate the average rate of decomposition of N_2O_5, $-\Delta[N_2O_5]/\Delta t$, by the reaction

$$2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$$

during the time interval from t = 600 sec to t = 1200 sec. Use the following data.

Time	**$[N_2O_5]$**
600 s	1.24×10^{-2} M
1200 s	0.93×10^{-2} M

A Problem to Consider

- Calculate the average rate of decomposition of N_2O_5, $-\Delta[N_2O_5]/\Delta t$, by the reaction

$$2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$$

during the time interval from t = 600 sec to t = 1200 sec.

The change in $[N_2O_5]$ is calculated by taking the final molarity minus the initial molarity. Therefore,

$$\text{Average rate} = -\frac{\Delta[N_2O_5]}{\Delta t}$$

A Problem to Consider

- Calculate the average rate of decomposition of N_2O_5, $-\Delta[N_2O_5]/\Delta t$, by the reaction

$$2\,N_2O_5(g) \rightarrow 4\,NO_2(g) + O_2(g)$$

during the time interval from t = 600 sec to t = 1200 sec.

The change in $[N_2O_5]$ is calculated by taking the final molarity minus the initial molarity. Therefore,

$$\text{Average rate} = -\frac{(0.93 - 1.24) \times 10^{-2}\,M}{(1200 - 600)\,sec}$$

A Problem to Consider

- Calculate the average rate of decomposition of N_2O_5, $-\Delta[N_2O_5]/\Delta t$, by the reaction

$$2\,N_2O_5(g) \rightarrow 4\,NO_2(g) + O_2(g)$$

during the time interval from t = 600 sec to t = 1200 sec.

The change in $[N_2O_5]$ is calculated by taking the final molarity minus the initial molarity. Therefore,

$$\text{Average rate} = \textcircled{-}\frac{\textcircled{-}0.31 \times 10^{-2}\,M}{600\,sec}$$

A Problem to Consider

- Calculate the average rate of decomposition of N_2O_5, $-\Delta[N_2O_5]/\Delta t$, by the reaction

$$2\,N_2O_5(g) \rightarrow 4\,NO_2(g) + O_2(g)$$

during the time interval from t = 600 sec to t = 1200 sec.

The change in $[N_2O_5]$ is calculated by taking the final molarity minus the initial molarity. Therefore,

$$\text{Average rate} = 5.2 \times 10^{-6}\,M/s$$

Summary

- Using stoichiometry to relate the disappearance of reactants to the appearance of products.
- Calculating the average rate of a reaction over a given amount of time.

Experimental Determination of Reaction Rates

- To obtain the rate of a reaction you must determine the concentration of a reactant or product during the course of the reaction.
  - One method for slow reactions is to withdraw samples from the reaction vessel at various times and analyze them.
  - More convenient are techniques that continuously monitor the progress of a reaction based on some physical property of the system.

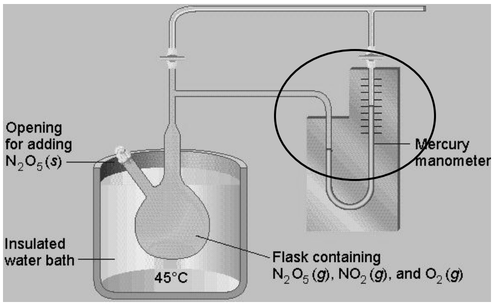
Experimental Determination of Reaction Rates

- **Gas-phase partial pressures.**
  - When dinitrogen pentoxide crystals are sealed in a vessel equipped with a manometer (see next slide) and heated to 45°C, the crystals vaporize and the $N_2O_5(g)$ decomposes.

$$\mathbf{2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)}$$

  - Manometer readings provide the concentration of N_2O_5 during the course of the reaction based on partial pressures

An experiment to follow the concentration of N_2O_5 as the decomposition proceeds



Experimental Determination of Reaction Rates

- **Colorimetry**
  - Consider the reaction of the hypochlorite ion with iodide.

$$\mathbf{ClO^-(aq) + I^-(aq) \rightarrow \boxed{IO^-}(aq) + Cl^-(aq)}$$

  - The hypoiodate ion, IO^{-1}, absorbs near 400 nm. The intensity of the absorbtion is proportional to $[IO^{-1}]$, and you can use the absorbtion to determine reaction rate.

Dependence of Rate on Concentration

- Experimentally, it has been found that the rate of a reaction depends on the concentration of certain reactants as well as catalysts.
  - Let's look at the reaction of nitrogen dioxide with fluorine to give nitryl fluoride.

    $2NO_2(g) + F_2(g)$ ® $2NO_2F(g)$
  - The rate of this reaction has been observed to be directly proportional to the concentration of nitrogen dioxide.

Dependence of Rate on Concentration

  - When the concentration of nitrogen dioxide is doubled, the reaction rate doubles.
  - The rate is also directly proportional to the concentration of fluorine; doubling the concentration of fluorine also doubles the rate.
  - **We need a mathematical expression** to relate the rate of the reaction to the concentrations of the reactants.

Dependence of Rate on Concentration

- A **rate law** is an **equation that relates the rate of a reaction to the concentration of reactants (and catalyst) raised to various powers**.

  Rate µ $[NO_2][F_2]$

Dependence of Rate on Concentration

- A **rate law** is an **equation that relates the rate of a reaction to the concentration of reactants (and catalyst) raised to various powers**.

$$\text{Rate} = \boxed{k}[NO_2][F_2]$$

  - The **rate constant**, **k**, is a proportionality constant in the relationship between rate and concentrations.

Dependence of Rate on Concentration

- A **rate law** is an **equation that relates the rate of a reaction to the concentration of reactants (and catalyst) raised to various powers**.

$$\underset{\mathbf{x\ 2}}{\text{Rate}} = k\underset{\mathbf{x\ 2}}{[NO_2]}[F_2]$$

Dependence of Rate on Concentration

- A **rate law** is an **equation that relates the rate of a reaction to the concentration of reactants (and catalyst) raised to various powers**.

$$\underset{\mathbf{x\ 2}}{\text{Rate}} = k[NO_2]\underset{\mathbf{x\ 2}}{[F_2]}$$

Dependence of Rate on Concentration

- A **rate law** is an **equation that relates the rate of a reaction to the concentration of reactants (and catalyst) raised to various powers**.

$$\underset{\times 4}{\text{Rate}} = k[\underset{\times 2}{NO_2}][\underset{\times 2}{F_2}]$$

Dependence of Rate on Concentration

- As a more general example, consider the reaction of substances A and B to give D and E.

$$aA + bB \xrightarrow{C} dD + eE \qquad C = \text{catalyst}$$

  - You could write the rate law in the form

$$\text{Rate} = k[A]^{m}[B]^{n}[C]^{p}$$

  - The exponents m, n, and p are frequently, but not always, integers. <u>They must be determined experimentally</u> and cannot be obtained by simply looking at the balanced equation.

Dependence of Rate on Concentration

- Reaction Order
  - The **reaction order** with respect to a given reactant species **equals the exponent of the concentration of that species in the rate law, as determined experimentally.**
  - The **overall order** of the reaction **equals the sum of the orders of the reacting species in the rate law.**

Dependence of Rate on Concentration

- Reaction Order
  - Consider the reaction of nitric oxide with hydrogen according to the following equation.

$$2\text{NO(g)} + 2\text{H}_2\text{(g)} \text{ ® } \text{N}_2\text{(g)} + 2\text{H}_2\text{O(g)}$$

  - The experimentally determined rate law is

$$\text{Rate} = k[\text{NO}]^{\textcircled{2}}[\text{H}_2]^{\bigcirc}$$

  - Thus, the reaction is second order in NO, first order in H_2, and third order overall.

Dependence of Rate on Concentration

- Reaction Order
  - Consider the reaction of nitric oxide with hydrogen according to the following equation.

$$2\text{NO(g)} + 2\text{H}_2\text{(g)} \text{ ® } \text{N}_2\text{(g)} + 2\text{H}_2\text{O(g)}$$

  - The experimentally determined rate law is

$$\underset{\times 2}{\text{Rate}} = k[\text{NO}]^2\underset{\times 2}{[\text{H}_2]}$$

Dependence of Rate on Concentration

- Reaction Order
  - Consider the reaction of nitric oxide with hydrogen according to the following equation.

$$2\text{NO(g)} + 2\text{H}_2\text{(g)} \text{ ® } \text{N}_2\text{(g)} + 2\text{H}_2\text{O(g)}$$

  - The experimentally determined rate law is

$$\underset{\times 4}{\text{Rate}} = k\underset{(\times 2)^2}{[\text{NO}]^{\textcircled{2}}}[\text{H}_2]$$

Dependence of Rate on Concentration

- Reaction Order
  - Although reaction orders frequently have whole number values (particularly 1 and 2), they can be **fractional.**
  - **Negative** orders are also possible.
  - The concentration of a reactant with a **zero order** dependence has **no effect** on the rate of the reaction.

Dependence of Rate on Concentration

- Determining the Rate Law.
  - One method for determining the order of a reaction with respect to each reactant is the "**method of initial rates**".
  - This involves running the experiment multiple times, each time varying the concentration of only one reactant and measuring its initial rate..
  - The resulting change in rate indicates the order with respect to that reactant.

Dependence of Rate on Concentration

- Determining the Rate Law.
  - If **doubling the concentration** of a reactant has a **doubling** effect on the rate, then one would deduce it was a **first order dependence**.
  - If **doubling the concentration** had a **quadrupling** effect on the rate, one would deduce it was a **second order dependence**.
  - A **doubling of concentration** that results in an **eight-fold** increase in the rate would be a **third order dependence**.

A Problem To Consider

- Iodide ion is oxidized in acidic solution to triiodate ion, I_3^- , by hydrogen peroxide.

$$H_2O_2(aq) + 3I^-(aq) + 2H^+(aq) \rightarrow I_3^-(aq) + 2H_2O(aq)$$

- A series of four experiments was run at different concentrations, and the initial rates of I_3^- formation were determined.
- From the following data, obtain the **reaction orders** with respect to H_2O_2, I^-, and H^+.
- Calculate the numerical value of the **rate constant**

A Problem To Consider

	Initial Concentrations (mol/L)			
	H_2O_2	I^-	H^+	**Initial Rate [mol/(L·s)]**
Exp. 1	0.010	0.010	0.00050	1.15×10^{-6}
Exp. 2	0.020	0.010	0.00050	2.30×10^{-6}
Exp. 3	0.010	0.020	0.00050	2.30×10^{-6}
Exp. 4	0.010	0.010	0.00100	1.15×10^{-6}

- Comparing Experiment 1 and Experiment 2, you see that when the H_2O_2 concentration doubles (with other concentrations constant), the rate doubles.
- This implies a **first order dependence with respect to H_2O_2.**

A Problem To Consider

	Initial Concentrations (mol/L)			
	H_2O_2	I^-	H^+	**Initial Rate [mol/(L·s)]**
Exp. 1	0.010	0.010	0.00050	1.15×10^{-6}
Exp. 2	0.020	0.010	0.00050	2.30×10^{-6}
Exp. 3	0.010	0.020	0.00050	2.30×10^{-6}
Exp. 4	0.010	0.010	0.00100	1.15×10^{-6}

- Comparing Experiment 1 and Experiment 3, you see that when the I^- concentration doubles (with other concentrations constant), the rate doubles.
- This implies a **first order dependence with respect to I^-.**

A Problem To Consider

	Initial Concentrations (mol/L)			
	H_2O_2	I^-	H^+	**Initial Rate [mol/(L·s)]**
Exp. 1	0.010	0.010	0.00050	1.15×10^{-6}
Exp. 2	0.020	0.010	0.00050	2.30×10^{-6}
Exp. 3	0.010	0.020	0.00050	2.30×10^{-6}
Exp. 4	0.010	0.010	0.00100	1.15×10^{-6}

- Comparing Experiment 1 and Experiment 4, you see that when the H^+ concentration doubles (with other concentrations constant), the rate is unchanged.
- This implies a **<u>zero</u> order dependence with respect to H^+.**

A Problem To Consider

	Initial Concentrations (mol/L)			
	H_2O_2	I^-	H^+	**Initial Rate [mol/(L·s)]**
Exp. 1	0.010	0.010	0.00050	1.15×10^{-6}
Exp. 2	0.020	0.010	0.00050	2.30×10^{-6}
Exp. 3	0.010	0.020	0.00050	2.30×10^{-6}
Exp. 4	0.010	0.010	0.00100	1.15×10^{-6}

- Because $[H^+]^0 = 1$, the rate law is:

$$\text{Rate} = k[H_2O_2][I^-]$$

- The reaction orders with respect to H_2O_2, I^-, and H^+, are **1**, **1**, and **0**, respectively.

A Problem To Consider

	Initial Concentrations (mol/L)			
	H_2O_2	I^-	H^+	**Initial Rate [mol/(L·s)]**
Exp. 1	0.010	0.010	0.00050	1.15×10^{-6}
Exp. 2	0.020	0.010	0.00050	2.30×10^{-6}
Exp. 3	0.010	0.020	0.00050	2.30×10^{-6}
Exp. 4	0.010	0.010	0.00100	1.15×10^{-6}

- You can now calculate the rate constant by substituting values from any of the experiments. Using Experiment 1 you obtain:

$$1.15 \times 10^{-6} \frac{\cancel{\text{mol}}}{\cancel{\text{L}} \cdot \text{s}} = k \times 0.010 \frac{\cancel{\text{mol}}}{\cancel{\text{L}}} \times 0.010 \frac{\text{mol}}{\text{L}}$$

A Problem To Consider

	Initial Concentrations (mol/L)			
	H_2O_2	I^-	H^+	Initial Rate [mol/(L·s)]
Exp. 1	0.010	0.010	0.00050	1.15×10^{-6}
Exp. 2	0.020	0.010	0.00050	2.30×10^{-6}
Exp. 3	0.010	0.020	0.00050	2.30×10^{-6}
Exp. 4	0.010	0.010	0.00100	1.15×10^{-6}

- You can now calculate the rate constant by substituting values from any of the experiments. Using Experiment 1 you obtain:

$$k = \frac{1.15 \times 10^{-6}\,s^{-1}}{0.010 \times 0.010\ mol/L} = 1.2 \times 10^{-2}\ L/(mol \cdot s)$$

Operational Skills

- Relating the different ways of expressing reaction rates
- Calculating the average reaction rate
- Determining the order of reaction from the rate law
- Determining the rate law from initial rates

Time for a few review questions.