

**The Rates of Chemical Reactions**

Time:

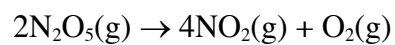
Rate:

Chemical Kinetics:

Reaction Rates:

Equations:

Some examples that date back to the early part of the last century:



Think of this graphically:

**Rate Laws**

The Rate Law

Rate Constant "k"

Reaction order is determined by experiment, not by stoichiometry or theory!

Two types of rate laws

**Method of Initial Rates**

Consider a reaction that is first order in 2.0 M A and 2.0 M B:

Double the concentration of A, what happens to the rate?

Consider a reaction that is second order in 2.0 M A and first order in 2.0 M B:

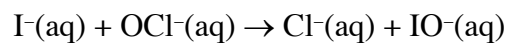
Double the concentration of A, what happens to the rate?

Triple the concentration of A, What happens to the rate?

Consider a reaction that is third order in 2.0 M A and first order in B:

Double the concentration of A, what happens to the rate?

1) Determine the rate law and the value of the rate constant for the following reaction, which depends on hydroxide ion as a catalyst:



$[\text{I}^{-}(\text{aq})] \times 10^{-3}$	$[\text{OCl}^{-}(\text{aq})] \times 10^{-3}$	$\text{OH}^{-}(\text{aq})$	Rate $\times 10^{-4}$ (M/s)
2.00	2.00	1.00	2.42
2.00	4.00	1.00	4.82
4.00	2.00	1.00	5.02
2.00	2.00	0.500	4.64

2) Consider a hypothetical reaction represented by the balanced equation below:



Experiment	[A]	[B]	[C]	Rate of formation of F $\times 10^{-2}$ (M/s)
1	0.10	0.10	0.10	1.50
2	0.20	0.10	0.10	3.00
3	0.20	0.20	0.10	12.0
4	0.20	0.20	0.20	12.0

Determine the order of the reaction with respect to each of the reactants.

Write the experimentally determined rate law for the reaction.

Calculate the value of the rate constant for experiment 2.

Determine the value of the rate of disappearance for A in experiment 4.

**Graphical Interpretation of Data**

What do plots of concentration versus time look like for first, second, and zero order reactions?

What type of a plot will give a straight line for each case?

Equation for a straight line in slope–intercept form

Let's put it all together:

	First	Second	Zeroth
Rate Law			
Integrated Rate Law			
Slope			
Half Life			

Half life

The half-life for a first order reaction does not depend on the concentration of the reactants!

First Order

Second Order

Zeroth Order



## **Energy Profiles**

Exothermic Reaction:

Endothermic Reaction:

Transition State/Activated Complex

Activation Energy



## Reaction Mechanisms

Reaction Mechanism:

Two restrictions!

1)

2)

Example:

Intermediate

Elementary Steps

Molecularity

Unimolecular

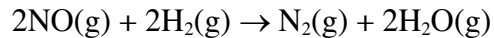
Bimolecular

Termolecular

## Rate Determining Step

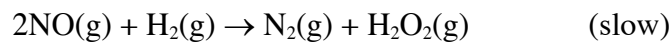
First we consider when step #1 is the slowest step in the reaction

For the reaction:



The experimentally determined rate law is:  $R = k[\text{NO}]^2 [\text{H}_2]$

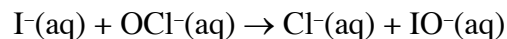
The mechanism is thought to be:



The molecularity (stoichiometry) of the overall balanced equation does not match the rate law, but it does match the molecularity of the *elementary step* in the mechanism.

## The Steady State Approximation

Now let's reconsider the reaction discussed on page 3.

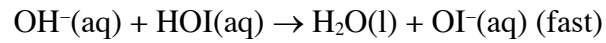
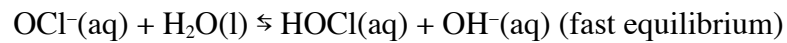


What was the experimentally determined rate law?

What does it mean to have a negative exponent?

This is an example of mechanism where the first step is a rapid equilibrium and a later step is the rate determining step.

Now consider the following proposed mechanism for the reaction:



The rate law for the slowest elementary step is:

But the HOCl is in equilibrium with the OCl<sup>-</sup> and OH<sup>-</sup>:

Solve this for HOCl:

Plug this back into the rate law:

Does this match the data? Does this give the overall balanced equation?

Why do we call it the steady state?

## **More About Energy**

The Ice Cream Graph

Catalyst

Catalyzed Reaction

How does it work?

Promoter/Inhibitor

Heterogeneous/Homogenous

Reaction at two different temperatures

## The Collision Model

What are the six factors affecting reaction rate?

- 1)
- 2)
- 3)
- 4)
- 5)
- 6)

If you increase the temperature, you will increase the velocity of the molecules. This will increase the number of collisions. BUT not all of the colliding molecules will produce a reaction!

Svante Arrhenius

How do you determine Activation Energy?

The Arrhenius Equation

1) Determine the activation energy of a reaction whose rate constant is  $5.54 \times 10^{-5} \text{ s}^{-1}$  at  $25^\circ\text{C}$  and  $9.30 \times 10^{-3} \text{ s}^{-1}$  at  $67^\circ\text{C}$ .

2) How much faster would a reaction happen at  $25^\circ\text{C}$  than at  $0^\circ\text{C}$  if the activation energy is 65 kJ/mole?

3) A reaction has a rate constant  $k = 2.00 \times 10^{-5} \text{ M}^{-1}\text{s}^{-1}$  at  $25^\circ\text{C}$ . Calculate the value of the rate constant at  $50^\circ\text{C}$  if the activation energy of the reaction is 85.0 kJ/mole.