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:

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

$$2NO_2(g) \rightarrow 2NO(g) + O_2(g)$$

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) One of the reactions occurring in the ozone layer in the upper atmosphere is the combination of nitric oxide with ozone:

$$NO + O_3 \rightarrow NO_2 + O_2$$

The reaction has been extensively studied to produce the following data

[NO]	$[O_3]$	Reaction Rate (M/second or mole/liter sec)
1.00×10^{-6}	3.00×10^{-6}	0.660×10^{-4}
1.00×10^{-6}	6.00×10^{-6}	1.32×10^{-4}
1.00×10^{-6}	9.00×10^{-6}	1.98×10^{-4}
2.00×10^{-6}	9.00×10^{-6}	3.96×10^{-4}

What are the rate law and the rate constant for this reaction? What are the 4 values of k?

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

$$I^-(aq) + OCl^-(aq) \rightarrow Cl^-(aq) + IO^-(aq)$$

$[I^-(aq)]$ x10^{-3}	$[OCl^-(aq)]$ x10^{-3}	$OH^-(aq)$	Rate x10^{-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

3) The equation for the reaction between mercuric chloride and oxalate ion in hot aqueous solution is shown. The reaction rate may be determined by measuring the initial rate of formation of chloride ion, at constant temperature. Data is shown.

$$2HgCl_2 + C_2O_4^{2-} \rightarrow 2\ Cl^- + 2CO_2 + Hg_2Cl_2$$

Exp.	$HgCl_2$	$C_2O_4^{2-}$	Rate of Cl^- Formation (mol/lit min)
1.	0.0836 M	0.202 M	0.52×10^{-4}
2.	0.0836 M	0.404 M	2.08×10^{-4}
3.	0.0418 M	0.404 M	1.06×10^{-4}
4.	0.0316 M	?	1.27×10^{-4}

a. According to the data above what is the rate law for the reaction?

b. What is the specific rate constant? Specify the units!

c. What is the initial concentration of oxalate for experiment number four?

d. What is the value for the initial rate of disappearance of oxalate ion for experiment 1?

From the 1981 AP Exam

$$A_{(aq)} + 2\ B_{(aq)} \rightarrow 3\ C_{(aq)} + D_{(aq)}$$

For the reaction above, carried out in solution of 30°C, the following kinetic data were obtained:

Experiment	Initial Conc. of Reactants (mole·liter^{-1})		Initial Rate of Reaction (mole·liter^{-1}·hr^{-1})
	A_o	B_o	
1	0.240	0.480	8.00
2	0.240	0.120	2.00
3	0.360	0.240	9.00
4	0.120	0.120	0.500
5	0.240	0.0600	1.00
6	0.0140	1.35	?

(a) Write the rate-law expression for this reaction.

(b) Calculate the value of the specific rate constant k at 30°C and specify its units.

(c) Calculate the value of the initial rate of this reaction at 30°C for the initial concentrations shown in experiment 6.

(d) Assume that the reaction goes to completion. Under the conditions specified for experiment 2, what would be the final molar concentration of C?

Graphical Interpretation of Data

What do the 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?

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

Let's put it all together:

	Zero	First	Second
Rate Law			
Integrated Rate Law			
Linear Plot			
Slope			
Half Life			

Half life

1) The half-life for a first order reaction is 50 seconds. What is the rate constant for this reaction?

2) How much of a 10.0 gram sample will remain after 24 minutes if it decays by first order kinetics and has a half-life of 10.0 minutes?

3) If a reaction is first order and has a half-life of 30.00 minutes how long will it take for only 10% of the sample to remain?

4) A first order reaction has a rate constant of 0.500 per minute. How long will it take for 30% of the sample to be gone?

5) If a reaction is 37% complete in 37 seconds what is the rate constant and half-life of the reaction?

Reaction Profiles

Exothermic Reaction:

Endothermic Reaction:

Transition State/Activated Complex

Activation Energy

Reaction Mechanisms

Reaction Mechanism-

Example:

Intermediate

Elementary Steps

Molecularity

Unimolecular Bimolecular Termolecular

Reaction Mechanism

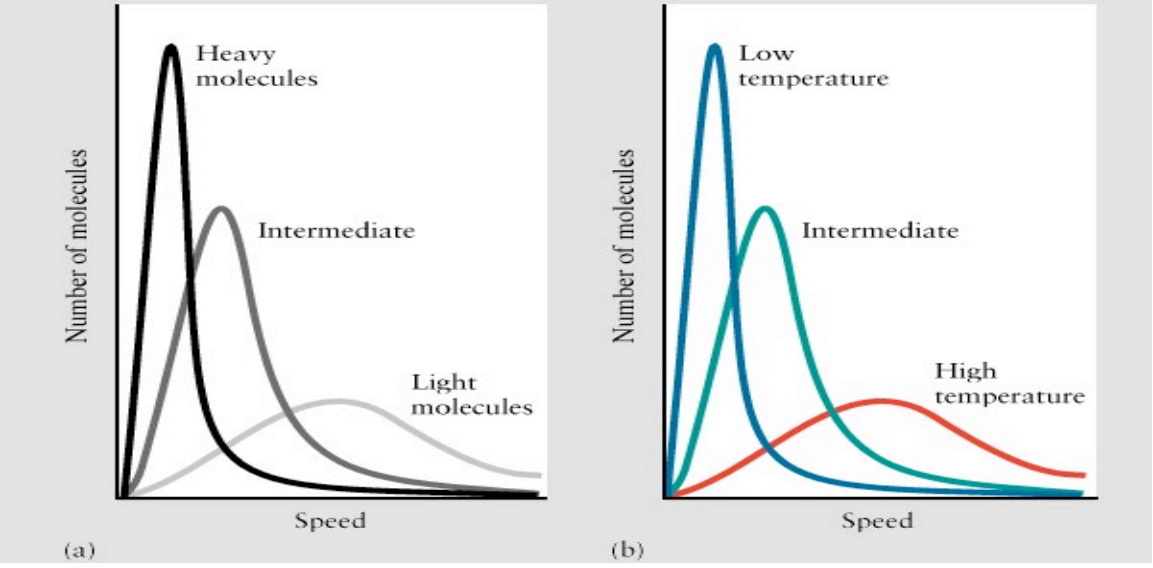
$$2A + B \rightarrow C \quad \text{(slow)}$$

$$C \rightarrow D \quad \text{(fast)}$$

$$D \rightarrow E + F \quad \text{(fast)}$$

More About Energy

The Ice Cream Graph



Catalyzed Reaction

Reaction at two different temperatures

The Collision Model

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?

How do you speed up a reaction?

Catalysis

Catalysts

How does it work?

Promoter

Inhibitor

Heterogeneous

Homogenous

Adsorption

Absorption

Sample Reaction:

Four steps

1.

2.

3.

4.

What are the six factors affecting reaction rate?

1.

2.

3.

4.

5.

6.