Chapter 16. Chemical Kinetics and Reaction Mechanisms

Introduction

1. *Chemical Kinetics* is the study of

2. Why should we care about chemical kinetics?

3. Overview of this Chapter. In this chapter, we are concerned with two things:

   1)

   2)

4. Any “rate” can be described as

5. reaction rate =

   or, rate =

   where brackets, [A], represent:

6. What are the typical units of rate?

   Example: How could you describe the rate of the following reaction?

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

   Are these all equal?

   Which is fastest?

   Why the negative sign?

   How can these be equated?

7. For the reaction

   $aA + bB \rightarrow cC + dD$

   rate =

   Example: Express the rate in terms of each reactant and product below:

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

Example: In the reaction below, if hydrogen gas is being consumed at a rate of 2.7 M/s, how fast is ammonia being formed?

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$$

8. What are some of the things that influence the rates of reactions?

Instantaneous vs. Average Rates

• Consider a typical reaction:

• The rate can be expressed as:

• The reaction rate at a given time is equal to

• Note from the graph that when the concentrations of reactants *decrease*, the reaction rate ______________________.

Rate Laws

1. For the reaction: $aA + bB + cC \rightarrow$ products

   the rate law takes the form: rate =

   where k =

   and k is dependent only on a)

   b)

   The bigger the k the ________________ the reaction

2. Important: The rate law must be determined _________________________________.

   What is the relationship between the coefficients of the balanced equation and the exponents in the rate law?

3. The exponents in the rate law are referred to as the ______________________________.

The sum of the exponents is called the ____.

Examples: rate = k[A][B] ________ order in A, ______ order in B, ________ order overall

rate = $k[A]^2[B]$ ________ order in A, ______ order in B, ________ order overall

Example: The initial rate of a reaction A + B → C was measured for several different starting concentrations of A and B. The results were:

Exp #	$[A]_o$	$[B]_o$	Initial Rate, M/s
1	0.100	0.100	4.0×10^{-5}
2	0.100	0.200	4.0×10^{-5}
3	0.200	0.100	16×10^{-5}

Calculate 1) the rate law, 2) the magnitude of the rate constant, and 3) the rate of the reaction when [A] = 0.050 M and [B] = 0.100 M.

1) the rate law

2) the magnitude of the rate constant

3) the rate of the reaction when [A] = 0.050 M and [B] = 0.100 M.

Example: Consider the reaction: A + B → products

The initial rate of this reaction was measured for several different initial concentrations of A and B. Determine the rate law from the data below.

Exp #	$[A]_0$	$[B]_0$	Initial rate (M/s)
1	0.10	0.60	0.0120
2	0.30	0.60	0.108
3	0.10	0.30	0.00600

4.. Be careful not to confuse "*rate constant*" with "*reaction rate*" and "*rate law*":

rate law:

rate constant:

reaction rate:

5. *Remember*: You cannot determine the rate law just by looking at the balanced chemical equation! The rate law for a given reaction must be determined experimentally.

Example: For the reaction $CHCl_3(g) + Cl_2(g) \rightarrow CCl_4(g) + HCl(g)$
the experimentally determined rate law is: rate = $k[CHCl_3][Cl_2]^{½}$

6. First order reaction:

7. Second order reaction:

8. Zero order reaction:

9. Units of the rate constant, k:

Integrated Rate Laws

1. Suppose that the reaction $A \rightarrow$ products is first order.

rate =

rate =

equate:

integrate:

The first order integrated rate law is:

where

and

2. For a first order reaction, a plot of _________ vs. ___________ gives a straight line with a slope of

_________.

3. Half life of a first order reaction: $t_{1/2}$ =

Important: The half-life of a first order reaction is _____________________________________

4. The significance of the integrated rate law:

Example: The reaction $A \rightarrow$ products has been experimentally determined to be first order. If the rate constant for this reaction is 0.046 min^{-1} at a certain temperature, how long would it take 90.0% of A to react?

Example: If the half life of a certain first order reaction is 15 min, how long would it take for 87.5% of the reactant to react?

5. Other integrated rate laws:

zero order: rate = k

$[A] = -kt + [A]_0$

second order: rate = $k[A]^2$

$$\frac{1}{[A]} = kt + \frac{1}{[A]_0}$$

Reaction Mechanisms

1 The most important reason for studying chemical kinetics is in order to determine ____________ _________________.

2. A reaction mechanism is:

3. Think of an elementary step as

4. *Molecularity*:

unimolecular:

bimolecular:

termolecular:

5. Important: You *cannot* get the rate law from the ____,

but you *can* get the rate law from ____.

elementary step	molecularity	rate law
$A \rightarrow$ products		
$A+B \rightarrow$ products		
$A + A \rightarrow$ products		
$A + B + C \rightarrow$ products		
$A + A + B \rightarrow$ products		

6. **Multi-step mechanisms.** Reactions often occur in a series of elementary steps. These must satisfy two requirements:

Example:
Reaction: $NO(g) + O_3(g) \rightarrow NO_2(g) + O_2(g)$

Mechanism is believed to occur in one bimolecular step.

What is the mechanism, and what is the rate law?

Example:
Reaction: $NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$

Mechanism:

(1) $NO_2 + NO_2 \rightarrow NO_3 + NO$ slow, rate-determining step
(2) $NO_3 + CO \rightarrow NO_2 + CO_2$ fast

What is the rate law for this reaction?

In this reaction NO_3 is called:

Example:
For the reaction: $2Fe^{2+}(aq) + Cl_2(aq) \rightarrow 2Cl^{-}(aq) + 2Fe^{3+}(aq)$
the experimentally determined rate law is:
rate = k $[Fe^{2+}][Cl_2]$

Propose a Mechanism.

Example: What is the rate law for the following elementary reaction?

cyclopropane $\rightarrow$ propylene

The Collision Model

1. Two observations:

2. “Photographer’s Rule of Thumb”:

3. The Collision Model helps us understand why increasing the temperature increases the rate of reactions.

For the reaction: $A + BC \rightarrow AB + C$

Suppose this reaction occurs in one elementary step:

This model illustrates three principles:

Example: $Cl + NOCl \rightarrow NO + Cl_2$

but:

So it is not enough for molecules to collide, they must collide with sufficient __________________ and

with_____________________________________.

4. Draw a reaction energy profile for a one step endothermic reaction and a one step exothermic reaction.

5. Two important principles about E_a:

6. Boltzmann distribution:

7. How does a catalyst increase the rate of a reaction?

8. How does increasing the temperature increase the rate of a reaction?

9. Arrhenius Equation: $k = Ae^{-Ea/RT}$

where k = rate constant
E_a = activation energy (usually kJ/mol)
R = 8.3145 J/mol·K (WATCH UNITS!)
T = temperature (K)
A = frequency factor (has to do with the number of collisions with the proper orientation)

Easier form of the Arrhenius equation:

$$\ln\frac{k_2}{k_1} = -\frac{E_a}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)$$