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## Chapter 16. Chemical Kinetics and Reaction Mechanisms

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### 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

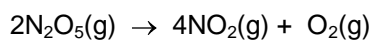
5. reaction rate =

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?



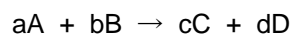
Are these all equal?

Which is fastest?

Why the negative sign?

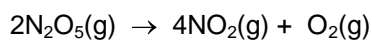
How can these be equated?

7. For the reaction

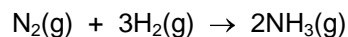


rate =

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



**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?

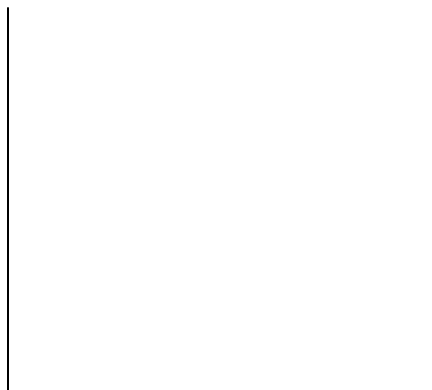


8. What are some of the things that influence the rates of reactions?

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### **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 \_\_\_\_\_.

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### **Rate Laws**

1. For the reaction:  $a\text{A} + b\text{B} + c\text{C} \rightarrow \text{products}$

the rate law takes the form:  $\text{rate} =$

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  $A + B \rightarrow C$  was measured for several different starting concentrations of A and B. The results were:

Exp #	$[A]_0$	$[B]_0$	Initial Rate, M/s
1	0.100	0.100	$4.0 \times 10^{-5}$
2	0.100	0.200	$4.0 \times 10^{-5}$
3	0.200	0.100	$16 \times 10^{-5}$

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:  $A + B \rightarrow \text{products}$

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  $\text{CHCl}_3(\text{g}) + \text{Cl}_2(\text{g}) \rightarrow \text{CCl}_4(\text{g}) + \text{HCl}(\text{g})$   
the experimentally determined rate law is:  $\text{rate} = k[\text{CHCl}_3][\text{Cl}_2]^{1/2}$

6. First order reaction:

7. Second order reaction:

8. Zero order reaction:

9. Units of the rate constant, k:

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### ***Integrated Rate Laws***

1. Suppose that the reaction  $\text{A} \rightarrow \text{products}$  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  $\text{A} \rightarrow \text{products}$  has been experimentally determined to be first order. If the rate constant for this reaction is  $0.046 \text{ min}^{-1}$  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 =  $k[A]^2$

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

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### **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

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$A \rightarrow$  products

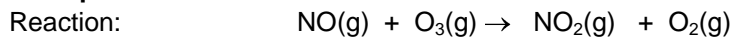
$A+B \rightarrow$  products

$A + A \rightarrow$  products

$A + B + C \rightarrow$  products

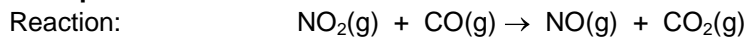
$A + A + B \rightarrow$  products

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

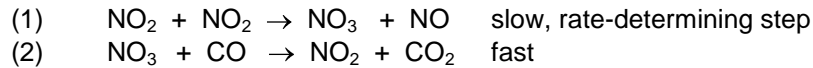
**Example:**

Mechanism is believed to occur in one bimolecular step.

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

**Example:**

Mechanism:



What is the rate law for this reaction?

In this reaction  $\text{NO}_3$  is called:

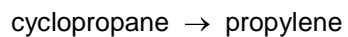
**Example:**

For the reaction:  $2\text{Fe}^{2+}\text{(aq)} + \text{Cl}_2\text{(aq)} \rightarrow 2\text{Cl}^-\text{(aq)} + 2\text{Fe}^{3+}\text{(aq)}$   
the experimentally determined rate law is:

$$\text{rate} = k [\text{Fe}^{2+}][\text{Cl}_2]$$

Propose a Mechanism.

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



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**The Collision Model**

1. Two observations:

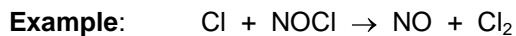
2. "Photographer's Rule of Thumb":

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



Suppose this reaction occurs in one elementary step:

**This model illustrates three principles:**



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:  $k = Ae^{-E_a/RT}$

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:

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