

# Unit V

## Part I-Chemical Kinetics

CHEMICAL KINETICS IS THE STUDY OF:

- 1)
- 2)

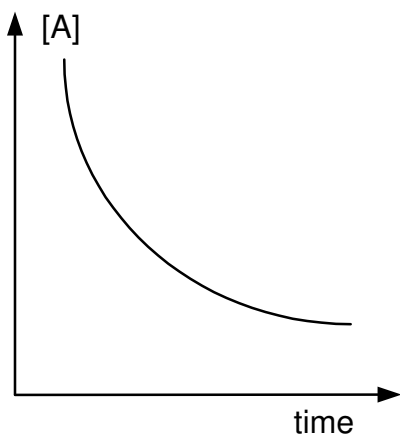
### I) RATE

FACTORS THAT CONTROL HOW RAPIDLY CHEMICAL CHANGES OCCUR:

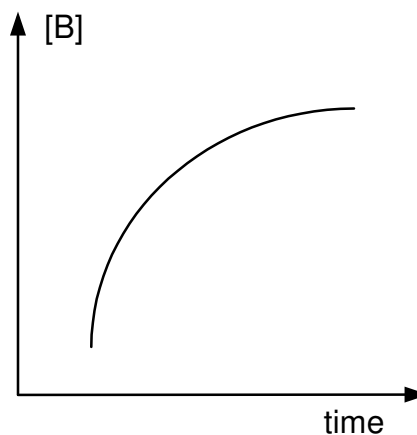
- 1) The nature of reactants and products
- 2) The concentration of reacting species
- 3) Temperature
- 4) Catalyst

REACTION RATES AND THEIR MEASUREMENTS:

$$\text{Rate of a chemical reaction} = \frac{\text{Change in concentration}}{\text{Change in time}}$$

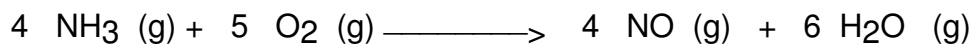


Rate of disappearance of A  
 $= - \frac{dA}{dt}$



Rate of formation of B  
 $= + \frac{dB}{dt}$

**Exercise:** Suppose that at a particular moment during the reaction, the oxygen is reacting at a rate of  $0.38 \text{ mole.liter}^{-1}.\text{sec}^{-1}$ :



a) What is the rate at which ammonia (g) is reacting?

b) What is the rate at which H<sub>2</sub>O is being formed?

**A) RATE LAW** To determine the rate law, you need to find the order of the reaction,  $x$ , with respect to each substance involved and the rate constant,  $k$ .



$$\text{Rate} \propto [\text{A}]^x$$

**1) ORDER OF A REACTION:** The rate is nearly always directly proportional to the concentration of the reactants raised to a power. The rate usually decreases as the reactants are consumed.

- $x = 1$ , first order
- $= 2$ , second order
- $= 3$ , third order
- $=$  higher order
- $=$  fraction
- $=$  negative value. That is, increasing the concentration of the reactant decreases the rate of the reaction.
- $=$  zero. That is the rate is constant and does not depend on the concentration of the reactant.

**A very important fact:** There is no necessarily any direct relationship between the coefficient in the overall balanced equation and the order of the reaction. Without doing experiments, we cannot predict for sure the “order “ of the reaction.

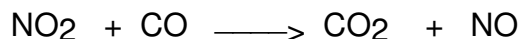
Let's consider a slightly more complex reaction:



$$\text{Rate} \propto [\text{A}]^x [\text{B}]^y$$

The overall order of the reaction = \_\_\_\_\_

**Example:** For the following reaction,



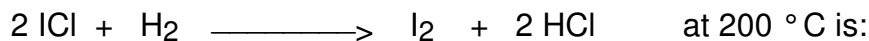
it has been found that:

$$\text{Rate} \propto [\text{NO}_2]^2 [\text{CO}]$$

Notice that there is no relationship between the coefficients and the exponents. The order can only be determined \_\_\_\_\_.

**2) RATE CONSTANT, k:** The value of k applies only for the particular reaction at a specific temperature. That is, different reactions have different values of k, which varies with temperature.

**Example:** The rate law for the reaction:

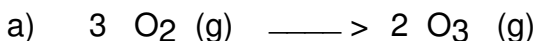


$$\text{Rate} = 0.163 \frac{\text{liter}}{\text{mol}\cdot\text{sec}} [\text{ICl}]^1 [\text{H}_2]^1$$

The above reaction is \_\_\_\_\_ order with respect to ICl, and \_\_\_\_\_ order with respect to H<sub>2</sub>.

The overall order of the reaction = \_\_\_\_\_

**Exercise:** Write the **rate expression** for the following:



**Exercise:** Consider the following reaction:  $\text{X} + \text{Y} \longrightarrow \text{Z}$   
The following data are obtained at 360 °C.

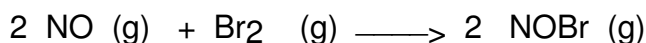
Initial rate of disappearance of X(M/sec)	[ X ]	[ Y ]
0.147	0.10	0.50
0.127	0.20	0.30
4.064	0.40	0.60
1.016	0.20	0.60
0.508	0.40	0.30

Determine the **order** of the reaction.

$$\text{Rate} = k [\text{X}]^{=?} [\text{Y}]^{=?}$$

The overall order of the reaction is \_\_\_\_\_

**Exercise:** Consider the following reaction

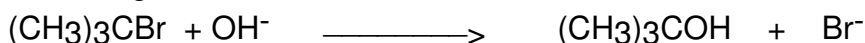


The following data were obtained.

Exp	Initial concentration of NO (mol/L)	Initial concentration of Br <sub>2</sub> (mol/L)	Initial rate (mol . liter <sup>-1</sup> .sec <sup>-1</sup> )
1	0.10	0.10	12
2	0.10	0.20	24
3	0.10	0.30	36
4	0.20	0.10	48
5	0.30	0.10	108

Determine the **rate law** of the reaction. Answer: \_\_\_\_\_

**Exercise:** The following data were collected at 60 °C for the reaction:



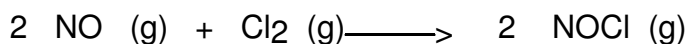
Find the **rate law** and the **value of the rate constant**.

Exp	Initial concentration of (CH <sub>3</sub> ) <sub>3</sub> CBr (mol/L)	Initial concentration of OH <sup>-</sup> (mol/L)	Initial rate of formation of (CH <sub>3</sub> ) <sub>3</sub> COH (M.sec <sup>-1</sup> )
1	0.10	0.10	0.0010
2	0.20	0.10	0.0020
3	0.30	0.10	0.0030
4	0.10	0.20	0.0010
5	0.10	0.30	0.0010

Answer:

Explain the fact that the OH<sup>-</sup> concentration does not show up in the above rate law. Answer: \_\_\_\_\_

**Exercise:** The reaction of NO with Cl<sub>2</sub> follows the equation:

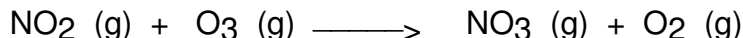


The following data were collected.

Initial NO concentration (mole/L)	Initial Cl <sub>2</sub> concentration(mol/L)	Initial rate (mol.L <sup>-1</sup> .sec <sup>-1</sup> )
0.10	0.10	2.53 x 10 <sup>-6</sup>
0.10	0.20	5.06 x 10 <sup>-6</sup>
0.20	0.10	10.1 x 10 <sup>-6</sup>
0.30	0.10	22.8 x 10 <sup>-6</sup>

- What is the rate law of the reaction
- What is the value of the rate constant ? Be sure to give the proper units.

**Exercise:** One of the reactions that can take place in polluted air is the reaction of NO<sub>2</sub> (g) with O<sub>3</sub> (g).



The following data were collected for the reaction given above at 25 °C.

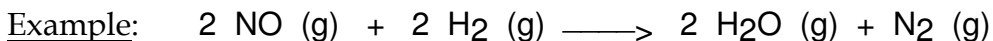
Initial NO <sub>2</sub> (mol/L)	Initial O <sub>3</sub> (mol/L)	Initial rate (M.sec <sup>-1</sup> )
5.0 × 10 <sup>-5</sup>	1.0 × 10 <sup>-5</sup>	0.022
5.0 × 10 <sup>-5</sup>	2.0 × 10 <sup>-5</sup>	0.044
2.5 × 10 <sup>-5</sup>	2.0 × 10 <sup>-5</sup>	0.022

a) What is the **rate law** for the reaction ?

b) What is the value of the **rate constant**?

## II) REACTION MECHANISM

The overall balanced equation for a reaction represents the net chemical change that occurs as the reaction proceeds to completion. The net change is the sum of a series of simple reactions, “elementary processes”. The sequence of elementary processes that leads to the formation of the products is called “reaction mechanism”.



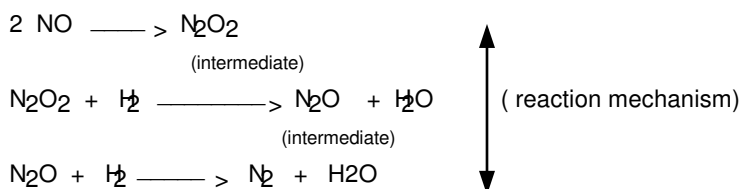
FIRST: We determine the rate law experimentally.

SECOND: We propose a mechanism that agrees with the rate law.

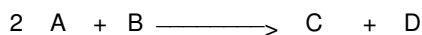
We can eliminate some mechanisms that do not agree with the rate law.

We cannot make sure that the proposed mechanism is the actual one, even though it agrees with the experimentally determined rate law.

The following mechanism was proposed for the above reaction:



**Example:** Suppose we wish to study the mechanism of the following:

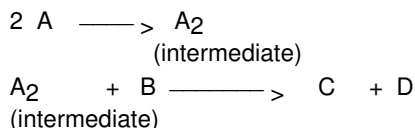


which has a rate law of:

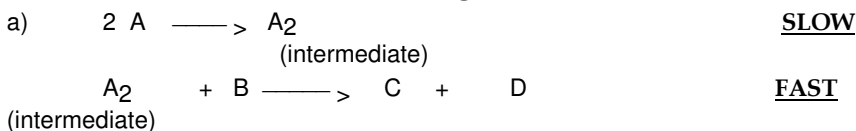
$$\text{Rate} = k [A]^2 [B] \quad (\text{Determined experimentally})$$

1) We might propose that two molecules of "A" and molecule of "B" come together simultaneously (three body-collision) termolecular collision. This process leads to the rate law above. (Here the exponents are equal to the coefficients.) But a three body collision is statistically unlikely.

2) Most probably the reaction is taking place through a series of simple **bimolecular** processes. A possible sequence:

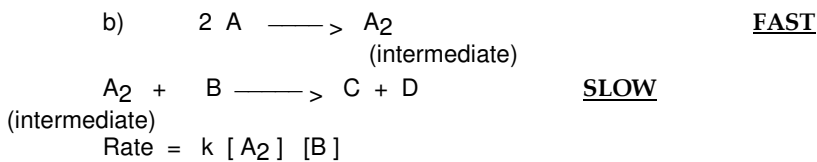


The sum of the above elementary processes gives us the net overall change. It is unlikely that these two elementary steps occur at the same time! Let us suppose that the first reaction is **slow**. The second step is **fast**. Therefore, the **first step** is the **rate determining step**.



$$\text{Rate} = k [A]^2$$

But this rate law does not agree with the experimentally determined rate law given above.

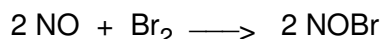


The rate law suggested above agrees with the rate law found experimentally.

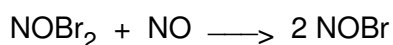
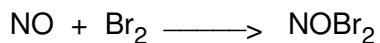
We can never be certain that we have truly discovered the actual path of the reaction, because there could be more than one mechanism that can be written to satisfy the experimentally determined rate law. However, studying the kinetics of a reaction allows to eliminate many alternatives.

EXERCISE:

A mechanism for the reaction



has been suggested to be:



a) What would be the rate law for the reaction if the first step in the mechanism were slow and the second step is fast?

b) What would be the rate law if the second step were slow, with the first reaction being a rapidly established dynamic equilibrium?

c) Experimentally, the rate law has been found to be:

$$\text{Rate} = k[\text{NO}]^2[\text{Br}_2]$$

What can we conclude about the relative rates of step (i) and (ii) ?

Answer: \_\_\_\_\_

d) Why do we not prefer a simple, one-step mechanism?

Answer: \_\_\_\_\_

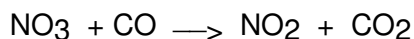
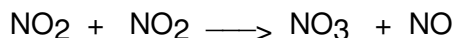
e) Can we on the basis of the experimental rate law, "definitely" exclude the one- step mechanism above?

Answer: \_\_\_\_\_

EXERCISE:



appears to have the mechanism:

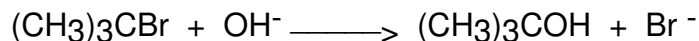


The rate law was found to be:  $\text{Rate} = k [\text{NO}_2]^2$

Explain why the reaction is zero-order with respect to CO.

EXERCISE:

The rate law for the reaction:



is  $\text{Rate} = k [(\text{CH}_3)_3\text{CBr}]$ . Try to propose a mechanism that can account for the rate law of the reaction.

EXERCISE:

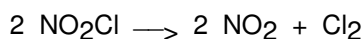
It is believed that a species with the formula  $\text{NO}_3$  is involved in the mechanism of the reaction:  $2 \text{NO}_2 + \text{O}_3 \rightarrow \text{N}_2\text{O}_5 + \text{O}_2$

The rate law for the reaction is:  $\text{Rate} = k [\text{NO}_2][\text{O}_3]$

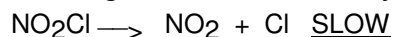
Propose a mechanism for the above reaction.

EXERCISE:

What would be the rate law for the reaction:



If the following are the elementary steps:



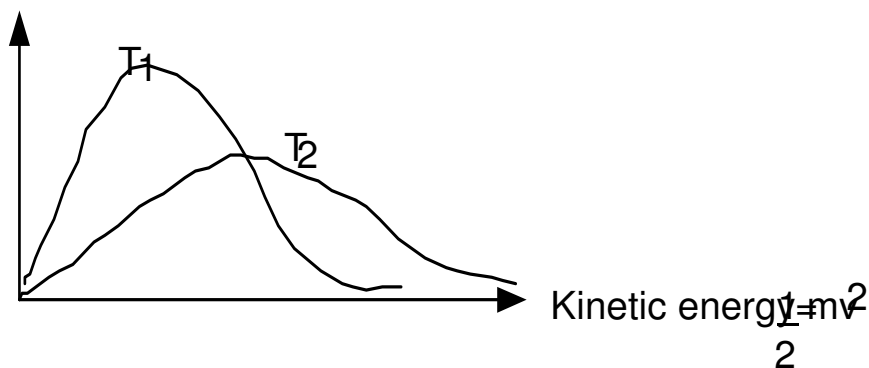
**THEORIES OF REACTION RATES**

A) Collision Theory:

Molecules must collide to react. The rate of reaction depends on:

- The frequency of collisions ( # of collisions/time).
- Fraction of these collisions that are strong ( effective collisions)

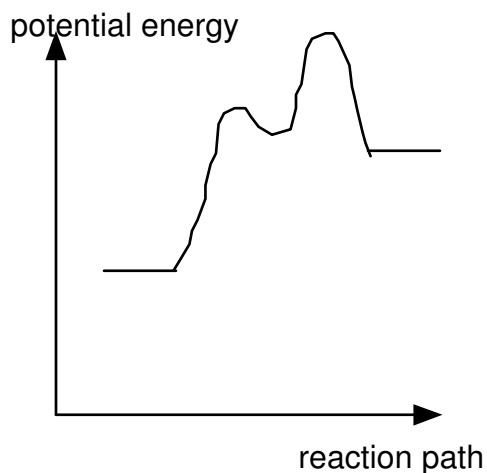
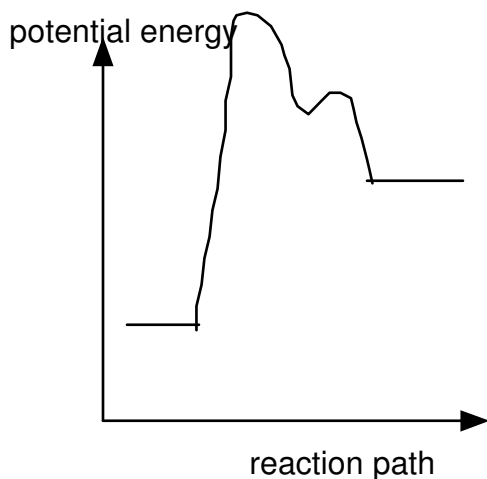
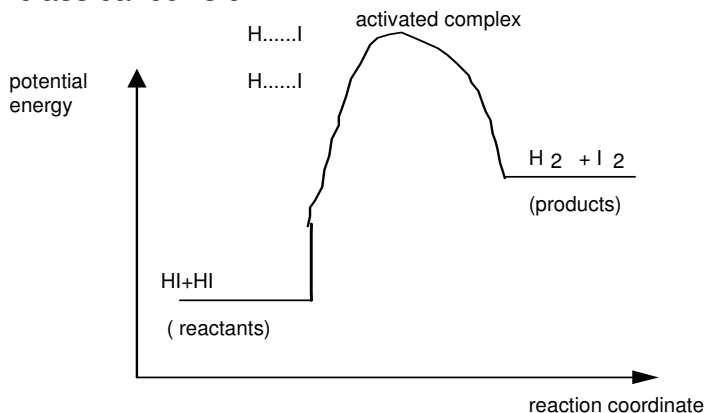
# of molecules



Increasing the temperature is required primarily for producing stronger effective collisions. (The frequency of collisions is high anyhow, even at room temperature!) Higher temperature is required to enhance the number of molecules exerting strong effective collisions.

## B) ACTIVATED COMPLEX THEORY (TRANSITION STATE THEORY)

According to the activated complex theory, a chemical change is pictured as a continuous series of changes in bond distances accompanied by energy changes as reactant molecules approach each other. Changes in the arrangement of the atoms in molecules is taking place even when the distance between molecules is greater than the typical separation corresponding to a "classical collision".



Activated complex: It is the half-reacted state in an elementary reaction. It is the least stable arrangement of the system in going from reactants to products. The species that exists at the top of the potential energy barrier during an effective collision corresponds to neither the reactants nor the products, but instead, to some highly unstable combination of atoms that we speak of as "activated complex".

A catalyst may enter in one elementary step and exit in another elementary step during the mechanism.

## CONCENTRATION AND TIME RELATIONSHIP:

### A) FIRST-ORDER RATE LAW:

$$\text{Rate} = k [A]$$
$$-\frac{dA}{dt} = k [A]$$

Using calculus, the above rate law transforms into the following First-order rate equation:

$$\ln [A]_0 = k t$$

$$[A]_t$$

$\log \frac{[A]_0}{[A]_t} = \frac{k t}{2.303}$
--

Where  $[A]_0$  is the initial concentration, and  $[A]_t$  is the concentration at time,  $t$ .

By using the above first-order rate equation, we can calculate the concentration of the reactant,  $[A]_t$ , at any time,  $t$ .

### Graph of a First -ORDER Reaction:

At 400 °C, the first-order conversion of cyclopropane into propylene has a rate constant of  $1.16 \times 10^{-6} \text{ sec}^{-1}$ . If the initial concentration of cyclopropane is  $1.00 \times 10^{-2}$  mole/liter at 400 °C, what will its concentration be in 24.0 hrs after the reaction begins?

Setup:

Example:

a) Use the data given below to confirm that the decomposition of  $\text{N}_2\text{O}_5$  is a **first-order** reaction.

b) What is the value of the rate constant,  $k$ ?

Time(sec)	$[\text{N}_2\text{O}_5]$	Log $[\text{N}_2\text{O}_5]$
0	0.0200	-1.699
100	0.0169	-1.772
200	0.0142	-1.848
300	0.0120	-1.921
400	0.0101	-1.996
500	0.0086	-2.066
600	0.0072	-2.143
700	0.0061	-2.215

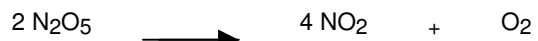
**Half-life of a first order- reaction:**

The half-life of a reaction,  $t_{1/2}$ , is the length of time required for the concentration of the reactant to be decreased to half of its original value.

$$t_{1/2} = \frac{0.693}{k}$$

**Example:**

The decomposition of  $\text{N}_2\text{O}_5$  is a first-order reaction.



At  $45^\circ\text{C}$ , the reaction began with an initial  $\text{N}_2\text{O}_5$  of 1.00 mole/liter. After 3.00 hrs. the  $\text{N}_2\text{O}_5$  concentration has decreased to  $1.21 \times 10^{-3}$  mole/liter. What is the half-life of  $\text{N}_2\text{O}_5$  expressed in minutes at  $45^\circ\text{C}$  ?

Setup:

**The equation relating concentration to time is different for different reaction orders!**

**B) SECOND-ORDER RATE LAW:**

$$\text{Rate} = k [B]^2$$

$$\frac{-dB}{dt} = k [B]^2$$

Using calculus, the above rate law transforms into the following Second-order rate equation:

$$\frac{1}{[B]_t} - \frac{1}{[B]_0} = k t$$

**Graph of a second-order reaction:**

**Example:**

The decomposition of  $\text{NO}_2$  is a second-order reaction. The concentration -time data for this reaction at 300 °C is given:

Time, sec	$[\text{NO}_2]$ , M	Time, sec	$[\text{NO}_2]$ , M
0	$8.00 \times 10^{-3}$	200	$4.29 \times 10^{-3}$
50	$6.58 \times 10^{-3}$	300	$3.48 \times 10^{-3}$
100	$5.59 \times 10^{-3}$	400	$2.93 \times 10^{-3}$
150	$4.85 \times 10^{-3}$	500	$2.53 \times 10^{-3}$

a) How could you confirm that the reaction is really second-order?

b) Calculate the value of the rate constant.

Setup:

c) What is the concentration of  $\text{NO}_2$  at  $t = 20.0$  min ?

Setup:

