Dr. Laxman Singh Department of Chemistry R.R.S. College (PPU) (Mokama, Patna) Email:laxmanrsearcher84@gmail.com

#### **Chemical Kinetics:** Rates and Mechanisms of Chemical Reactions

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- **4** Integrated rate laws: Concentration changes over time
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# Chemical Kinetics

The study of reaction rates, the changes in concentrations of reactants (or products) as a function of time

Quantitative relationships through the derivation of a rate law

Kinetics can reveal much about the mechanism of a reaction.

# **Chemical Kinetics**

#### **Chemical kinetics:**

study of *reaction rate*,  $\leftarrow$  a quantity conditions affecting it, the molecular events during a chemical reaction (mechanism), and presence of other components (catalysis).

**Factors Influencing Reaction Rates** 

**Reactant Concentration**: molecular collisions are required for reactions to occur

reaction rate  $\alpha$  collision frequency  $\alpha$  concentration

**Physical State**: molecules must mix to collide

When reactants are in different phases, the more finely divided a solid or liquid reactant, the greater the surface area per unit volume, the more contact it makes with other reactants, and the faster the reaction.

**Temperature**: molecules must collide with sufficient energy to react

Higher T translates into more collisions per unit time and into higher-energy collisions

reaction rate  $\alpha$  collision energy  $\alpha$  temperature

**Presence of a catalyst:** Catalysts speed up reactions by changing the mechanism of the reaction.

# **Reaction Rate**

 Change in concentration of a reactant or product per unit time

# $A \rightarrow B$

 $\frac{\text{Change in conc, A}}{\text{Change in time, t}} = \frac{[A]_t - [A]_0}{t_t - t_0} = \frac{\Delta[A]}{\Delta t}$ 

# **Expressing reaction rates**

For a chemical reaction, there are many ways to express the *reaction rate*. The relationships among expressions depend on the equation.

Note the expression and reasons for their relations for the reaction

$$2 \text{ NO} + \text{O}_2(\text{g}) = 2 \text{ NO}_2(\text{g})$$

$$\frac{\Delta[\text{O}_2]}{\Delta t} = \frac{1}{2} \frac{\Delta[\text{NO}]}{\Delta t} = \frac{1}{2} \frac{\Delta[\text{NO}_2]}{\Delta t}$$

# Determine reaction rate

The concentrations of  $N_2O_5$  are  $1.24e^{-2}$  and  $0.93e^{-2}$  M at 600 and 1200 s after the reactants are mixed at the appropriate temperature. Evaluate the *reaction rates* for

$$2 N_2 O_5 = 4 NO_2 + O_2$$
  
Solution:  
Decomposition rate of  $N_2 O_5 = -\frac{(0.93 - 1.24) e^{-2}}{1200 - 600} = -\frac{-0.31 e^{-2} M}{600 s}$ 

The reaction rates are expressed in 3 forms

Note however,

rate of formation of NO<sub>2</sub> =  $1.02^{e-5}$  M s<sup>-1</sup>. rate of formation of O<sub>2</sub> =  $2.6^{e-6}$  M s<sup>-1</sup>. To measure reaction rate, we measure the concentration of either a reactant or product at several time intervals.

The concentrations are measured using spectroscopic method or pressure (for a gas). For example, the total pressure increases for the reaction:

$$2 \operatorname{N}_2\operatorname{O}_5(g) \rightarrow 4 \operatorname{NO}_2(g) + \operatorname{O}_2(g)$$

Because 5 moles of gas products are produced from 2 moles of gas reactants. For the reaction

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$$

The increase in gas pressure is entirely due to  $CO_2$  formed.



# **Differential Rate Laws**

Dependence of reaction rate on the concentrations of reactants is called the rate law, which is unique for each reaction.

For a general reaction,  $aA + bB + cC \rightarrow products$ 

the rate law has the general form

reaction rate =  $(k)A \otimes [B] \otimes [C] \otimes [C]$ the rate constant

For example, the rate law is

*rate* = k [Br<sup>-</sup>] [BrO<sub>3</sub><sup>-</sup>] [H<sup>+</sup>] for

5 Br- + BrO<sub>3</sub><sup>-</sup> + 6 H<sup>+</sup> 
$$\rightarrow$$
 3Br<sub>2</sub> + 3 H<sub>2</sub>O

The reaction is 1<sup>st</sup> order wrt all three reactants, total order 3.

Expressing rate in terms of changes in [reactant] and [product]

$$H_2(g) + I_2(g) \rightarrow 2HI(g)$$

rate = -  $\Delta[H_2]/\Delta t$  = -  $\Delta[I_2]/\Delta t$  = 1/2  $\Delta[HI]/\Delta t$ 

or

### rate = $\Delta[HI]/\Delta t$ = -2 $\Delta[H_2]/\Delta t$ = -2 $\Delta[I_2]/\Delta t$

The mathematical expression for the rate, and the numerical value of the rate, depend on which substance is chosen as the reference.

For the general reaction: aA + bB cC + dD

rate =  $-1/a \Delta[A]/\Delta t = -1/b \Delta[B]/\Delta t = 1/c \Delta[C]/\Delta t = 1/d \Delta[D]/\Delta t$ 

# Integrated Rate Laws concentrations as functions of time

One reactant A decomposes in 1<sup>st</sup> or 2<sup>nd</sup> order rate law.

Differential rate law

Integrated rate law

$$-d[A] / dt = k$$

$$d[A] - - - - = k [A]$$

$$d[A] - - - - = k [A]^{2}$$

$$d[A] - - - = k [A]^{2}$$

$$[A] = [A]_{o} - k t$$

$$[A] = [A]_{o} e^{-kt} \text{ or } \ln [A] = \ln$$

$$\frac{1}{[A]} = \frac{1}{[A]_{o}} e^{-kt} [A] \text{ conc at } t$$

$$[A] = [A]_{o} \text{ [A]}_{o} \text{ conc at } t = 0$$

## 1<sup>st</sup> order reaction (Conc. Vs time)

Describe the features of plot of [A] vs. *t* and ln[A] vs. t for  $1^{st}$  order reactions. Apply the technique to evaluate *k* or [A] at various times.



### Half life & k of First Order Decomposition

The time required for half of A to decompose is called half life  $t_{1/2}$ .

- Since  $[A] = [A]_o e^{-kt}$  or  $\ln [A] = \ln [A]_o kt$
- When  $t = t_{1/2}$ ,  $[A] = \frac{1}{2} [A]_0$
- Thus  $\ln \frac{1}{2} [A]_{o} = \ln [A]_{o} k t_{1/2}$ 
  - $-\ln 2 = -k t_{1/2}$   $k t_{1/2} = \ln 2 = 0.693 \quad \leftarrow \text{ relationship between } k \text{ and } t_{1/2}$

Radioactive decay usually follow 1<sup>st</sup> order kinetics, and half life of an isotope is used to indicate its stability.

We can evaluate  $t_{1/2}$  from k or k from  $t_{1/2}$ 

# 1<sup>st</sup> order reaction calculation

 $N_2O_5$  decomposes according to 1<sup>st</sup> order kinetics, and 10% of it decomposed in 30 s. Estimate *k*,  $t_{\frac{1}{2}}$  and percent decomposed in 500 s.

Solution: Assume  $[A]_0 = [N_2O_5]_0 = 1.0$ , then [A] = 0.9 at t = 30 s or  $0.9 = 1.0 e^{-kt}$  apply [A]o = [A]  $e^{-kt}$  $\ln 0.9 = \ln 1.0 - k 30 \text{ s}$ -0.1054 = 0 - k \* 30 $k = 0.00351 \text{ s}^{-1}$  $t_{1/2} = \frac{0.693}{k} = 197 \text{ s}$  apply k t  $\frac{1}{2} = \ln 2$  $[A] = 1.0 e^{-0.00351*500} = 0.173$ Percent decomposed: 1.0 - 0.173 = 0.827 or 82.7 % After 2  $t_{\frac{1}{2}}$  (2\*197=394 s), [A] = ( $\frac{1}{2}$ )<sup>2</sup> = $\frac{1}{4}$ , 75% decomposed.

After 3  $t_{\frac{1}{2}}$  (3\*197=591 s), [A] = ( $\frac{1}{2}$ )<sup>3</sup> =1/8, 87.5% decomposed.

Apply integrated rate law to solve problems

# 2<sup>nd</sup> Order

Dimerization of butadiene is second order:

 $2 C_4 H_6(g) = C_8 H_{12}(g).$ 

The rate constant k at some temperature is 0.100 /min. The initial concentration of butadiene [B] is 2.0 M.

Calculate the time required for [B] = 1.0 and 0.5 M

Calculate concentration of butadiene when t = 1, 5, 10, and 30.

### Half life of 2<sup>nd</sup> Order Chemical Kinetics



How does half life vary in 2<sup>nd</sup> order reactions?

### Summary of the Kinetics of Zero-Order, First-Order and Second-Order Reactions

		<b>Concentration-Time</b>	
Order	Rate Law	Equation	Half-Life
0	rate = $k$	$[A] = [A]_0 - kt$	$t_{\frac{1}{2}} = \frac{[A]_0}{2k}$
1	rate = $k$ [A]	ln[A] = ln[A] <sub>0</sub> - <i>kt</i>	$t_{\frac{1}{2}} = \frac{\ln 2}{k}$
2	rate = $k [A]^2$	$\frac{1}{[A]} = \frac{1}{[A]_0} + kt$	$t_{\gamma_2} = \frac{1}{k[A]_0}$

### **Chemical Reaction and Molecular Collision**

Molecular collisions lead to chemical reactions. Thus, the reaction constant, k is determined by several factors.

k = Zfp

*Z*: collision frequency*p*, the fraction with proper orientation*f*, fraction of collision having sufficient energy for reaction

f is related to the potential energy barrier called activation energy,  $E_{\rm a}$ .

$$f \propto e^{-Ea/RT}$$
 or exp (–  $E_a/RT$ )

Thus, 
$$k = A e^{-Ea/RT}$$



### Energy involved in chemical reactions



**Progress of reaction** 

# Arrhenius Equation

The temperature dependence of the rate constant k is best described by the Arrhenius equation:

$$k = A e^{-Ea/RT}$$

or  $\ln k = \ln A - E_a / R T$ 

If  $k_1$  and  $k_2$  are the rate constants at  $T_1$  and  $T_2$  respectively, then

$$\ln \frac{k_1}{k_2} = -\frac{E_a}{R} \begin{pmatrix} 1 & 1 \\ -1 & -1 \\ T_1 & T_2 \end{pmatrix}$$



#### Graphical determination of the activation energy, $E_a$



# More about the Arrhenius Equation

The activation energy = the minimum energy that the molecules must possess in order for reaction to occur

The negative exponent suggests that, as T increases, the negative exponent becomes smaller (less negative), the value of k increases, and thus the reaction rate increases.

higher T 
$$\implies$$
 larger  $k \implies$  increased rate

# Effect of Temperature on Reaction Rates

Reaction rate =  $k [A]^x [B]^y [C]^z$  (Concentration effect at constant *T*)

 $k = A \exp(-E_a / RT)$  (Temperature effect)

Use graphic method to discuss the variation of k vs. T variation of k vs. 1 / T variation of  $\ln(k)$  vs T variation of  $\ln(k)$  vs. 1 / T

Sample Problem

### **Determining the energy of activation**

**PROBLEM:** The decomposition reaction of hydrogen iodide,  $2HI(g) \rightarrow H_2(g) +$ has rate constants of 9.51 x 10<sup>-9</sup> L/mol·s at 500. K and 1.10 x 10<sup>-5</sup> L/mol·s at 600. K. Find *E*<sub>2</sub>. **PLAN:** Use a modification of the Arrhenius equation to find E<sub>a</sub>. SOLUTIO N:  $\ln \frac{k_2}{k_1} = -\frac{E_a}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \frac{E_a}{R} = -\ln \frac{k_2}{k_1} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)^{-1}$   $E_a = -(8.314 \text{ J/mol} \cdot \left( \ln \frac{1.10 \times 10^{-5} \text{ L/mol} \cdot \text{s}}{9.51 \times 10^{-9} \text{ L/mol} \cdot \text{s}} \right) \left( \frac{1}{600.} - \frac{1}{500. \text{ K}} \right)^{-1}$  $E_a = 1.76 \times 10^5 \text{ J/mol} = 176$ kJ/mol

# **Elementary Reactions and Mechanism**

Elementary reactions are steps of molecular events showing how reactions proceed. This type of description is a mechanism.

The mechanism for the reaction between CO and  $NO_2$  is proposed to be

Step 1  $NO_2 + NO_2 \rightarrow NO_3 + NO$  (an elementary reaction)

Step 2  $NO_3 + CO \rightarrow NO_2 + CO_2$  (an elementary reaction)

Add these two equations led to the overall reaction

 $NO_2 + CO = NO + CO_2$  (overall reaction)

A mechanism is a proposal to explain the rate law, and it has to satisfy the rate law.

# Molecularity of Elementary Reactions

The total order of rate law in an elementary reaction is molecularity.

The rate law of elementary reaction is derived from the equation. The order is the number of reacting molecules because they must collide to react.

A molecule decomposes by itself is a unimolecular reaction (step); two molecules collide and react is a bimolecular reaction (step); & three molecules collide and react is a termolecular reaction (step).

$$O_{3} \rightarrow O_{2} + O \qquad rate = k [O_{3}]$$

$$NO_{2} + NO_{2} \rightarrow NO_{3} + NO \qquad rate = k [NO_{2}]^{2}$$

$$Br + Br + Ar \rightarrow Br_{2} + Ar^{*} \qquad rate = k [Br]^{2}[Ar]$$

### Rate Laws and Mechanisms

A mechanism is a collection of elementary steps devise to explain the the reaction in view of the observed rate law. You need the skill to derive a rate law from a mechanism, but proposing a mechanism is task after you have learned more chemistry

For the reaction,  $2 \operatorname{NO}_2(g) + F_2(g) \rightarrow 2 \operatorname{NO}_2F(g)$ , the rate law is,

 $rate = k [NO_2] [F_2]$ .

Can the elementary reaction be the same as the overall reaction?

If they were the same the rate law would have been

*rate* = k  $[NO_2]^2 [F_2]$ ,

Therefore, they the overall reaction is not an elementary reaction.

### **Correlating the Mechanism with the Rate Law**

Chemical mechanisms can never be proven unequivocally! But potential chemical mechanisms can be *eliminated* based on experimental data.

Three Key Criteria for Elementary Steps

1. The elementary steps must *add up* to the overall equation.

2. The elementary steps must be physically reasonable.

3. The mechanism must correlate with the rate law.

# Rate-determining Step in a Mechanism

The rate determining step is the slowest elementary step in a mechanism, and the rate law for this step is the rate law for the overall reaction.

The (determined) rate law is,  $rate = k [NO_2] [F_2],$ for the reaction,  $2 NO_2 (g) + F_2 (g) \rightarrow 2 NO_2 F (g),$ and a two-step mechanism is proposed:

- i  $\operatorname{NO}_2(g) + F_2(g) \rightarrow \operatorname{NO}_2F(g) + F(g)$
- ii  $NO_2(g) + F(g) \rightarrow NO_2F(g)$

Which is the rate determining step?

#### Answer:

The rate for step is rate = k [NO<sub>2</sub>] [F<sub>2</sub>], which is the rate law, this suggests that step is the rate-determining or the slow step.

### **Rate Laws for General Elementary Steps**

elementary	molecularity	rate
step A product	unimolecular	law rate = <i>k</i> [A]
→ 2A product	bimolecular	rate = <i>k</i> [A] <sup>2</sup>
→ A + B product	bimolecular	rate = <i>k</i> [A][B]
→ 2A + B product	termolecular	rate = <i>k</i> [A]²[B]

# **Catalysis: Enhancing Reaction Rates**

**Catalyst**: increases reaction rate but is *not consumed* in the reaction

A catalyst increases reaction rate (via increasing k) by lowering the activation energy (barrier) of the reaction.

Both forward and reverse reactions are catalyzed; reaction thermodynamics is unaffected!

The catalyzed reaction proceeds via a different mechanism than the uncatalyzed reaction.

# Catalysis

A catalyst is a substance that changes the y rate of a reaction by lowing the activation energy,  $E_a$ . It participates a reaction in forming an intermediate, but is regenerated.

Enzymes are marvelously selective catalysts.

A catalyzed reaction, NO (catalyst)  $2 \text{ SO}_2(g) + O_2 \longrightarrow 2 \text{ SO}_3(g)$ via the mechanism  $i \qquad 2 \text{ NO} + O_2 \implies 2 \text{ NO}_2(3^{rd} \text{ order})$  $ii \qquad \text{NO}_2 + \text{SO}_2 \implies \text{SO}_3 + \text{NO}$ 

#### Energ



# Activation Energy in the absence and presence of Catalyst



## Homogenous vs. heterogeneous catalysts

A catalyst in the same phase (gases and solutions) as the reactants is a homogeneous catalyst. It effective, but recovery is difficult.

When the catalyst is in a different phase than reactants (and products), the process involve heterogeneous catalysis. Chemisorption, absorption, and adsorption cause reactions to take place via different pathways.

Platinum is often used to catalyze hydrogenation

Catalytic converters reduce CO and NO emission.

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#### Table 16.7 Some Modern Processes Based on Catalysis

Reactants	Catalyst	Product	Use
Homogeneous			
Propylene, oxidizer	Mo(VI) complexes	Propylene oxide	Polyurethane foams; polyesters
Methanol, CO	$[Rh(CO)_2I_2]^-$	Acetic acid	Poly(vinyl acetate) coatings; poly(vinyl alcohol)
Butadiene, HCN	Ni/P compounds	Adiponitrile	Nylons (fibers, plastics)
$\alpha$ -Olefins, CO, H <sub>2</sub>	Rh/P compounds	Aldehydes	Plasticizers, lubricants
Heterogeneous			
Ethylene, O <sub>2</sub>	Silver, cesium chloride on alumina	Ethylene oxide	Polyesters, ethylene glycol, lubricants
Propylene, NH <sub>3</sub> , O <sub>2</sub>	Bismuth molybdates	Acrylonitrile	Plastics, fibers, resins
Ethylene	Organochromium and titanium halides on silica	High-density polyethylene	Molded products

# Enzymes – selective catalysts

**Enzymes** are a long protein molecules that fold into balls. They often have a metal coordinated to the O and N sites.

Molecules catalyzed by enzymes are called **substrates**. They are held by various sites (together called the **active site**) of the enzyme molecules and just before and during the reaction. After having reacted, the products  $P_1 \& P_2$  are released.

$$E_{nzyme} + S_{ubstrate} \otimes ES$$
 (activated complex)  
ES  $\otimes P_1 + P_2 + E$ 

Enzymes are biological catalysts for biological systems.