CHEMISTRY GARDE 11
CHAPTER 4
CHEMICAL KINETICS
PART ONE

Chemical kinetics

- **Chemical kinetics** is the area of chemistry concerned with the speeds, or rates, at which reactions occur.
- The word “kinetic” suggests **movement** or **change**.
- Chemical kinetics refers to the rate of reaction, which is the change over times in the concentration of a reactant or a product.

RATE OF REACTION

- Rate of reaction is the change in concentration of a reactant or a product over a given period of time.
- The rate of a reaction is calculated by dividing the change in the concentrations of reactants or products by the time taken for the change to occur.
- Rate is the speed at which reactants disappear or products appear

RATE OF REACTION

❖For a simple reaction,

A —→B

❖the rate of reaction is expressed in terms of a reactant concentration as

$$r = -\frac{\Delta[A]}{\Delta t} = -\frac{[A]f - [A]i}{\Delta t}$$

❖Where r is rate of reaction,

A is a reactant, B is a product,

[A]i and [A]f are initial and final concentration of A respectively,

Δ[A] is change in concentration of A and Δt is the change in time.

cont.....

- The **negative(-)** indicate the final concentration of reactant is less than the initial concentration .This indicates that the reactant is being consumed
- Rate of reaction is positive quantity
- Note that concentration is usually expressed in **mole per liter.**
- The rate of a reaction can be expressed in units of **mol $L^{-1}s^{-1}$**

cont..

- In terms of product concentration, the rate of a reaction is given by:

$$\mathbf{r=}\ \frac{\Delta[B]}{\Delta t}\ \mathbf{=}\ \frac{[B]f-[B]i}{\Delta t}$$

- Where [B] is the molar concentration of a product
- For a given product, the final concentration of B, [B]f is greater than the initial concentration of B, [B]i.
- Thus, the difference, ΔB = [B]f– [B]i is **positive**, and the rate of a reaction is also positive.
- Therefore, there is no need to introduce a negative sign to the rate

expression when rate of a reaction is calculated by using product concentration.

cont....

Reaction Rate and Stoichiometry

- Consider, for example, the reaction

$$2A \longrightarrow B$$

- For two moles of A that disappear one mole of B is formed.
- That is, the rate of disappearance of A is twice as the rate of appearance of B. The reaction rate may be written as:

$$r = -\frac{1}{2}\frac{\Delta[A]}{\Delta t} = \frac{\Delta[B]}{\Delta t}$$

cont....

- In general, for the reaction

$$aA + bB \rightarrow cC + dD$$

- The rate of reaction is given by:

$$r = -\frac{1}{a}\frac{\Delta[A]}{\Delta t} = -\frac{1}{b}\frac{\Delta[B]}{\Delta t} = \frac{1}{c}\frac{\Delta[C]}{\Delta t} = \frac{1}{d}\frac{\Delta[D]}{\Delta t}$$

- Rate required $= \frac{coefficient\ of\ required}{coefficient\ of\ given} \times rate\ given$

Express the rate of reaction in terms of reactants and products

a) $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$

b) $4NH_3 + 7O_2 \rightarrow 4NO_2 + O_2$

Example: At some point in the reaction $2x \rightarrow 3y$ [x] is drops from 0.4 to 0.2M in 5min . What is the average rate of y during this time interval?

Example: From the synthesis of ammonia $N_2 + 3H_2 \rightarrow 2NH_3$, the rate of reaction was measured as $\frac{\Delta[NH_3]}{\Delta t} = 2 \times 10^{-4}$ molL^{-1}S^{-1}What is the rate of the reaction expressed in terms of H_2

Determination of Rate of Reaction

- The rate of reaction can be determined both **quantitatively** and **qualitatively**.
- quantitatively, to determine a rate of reaction we need to measure changes in concentration over time.
- An accurate quantitative estimate of the rate of reaction at any given moment during the reaction can be obtained from the slope of the tangent to the concentration time graph at that particular instant
- The rate of reaction is greatest at the beginning and slow down as the time proceeds

Determination of Rate of Reaction

- Some methods to determine the concentration of reactant or product

  Amount of precipitate(insoluble solid formed)

  Color change

  Gain or loss in weight

  Increase or decrease in volume or pressure particularly

Cont....

- Factor affecting the rate of reaction
  - Change in temperature
  - concentration,
  - nature of reactant,
  - surface area
  - catalyst

Cont.....

Nature of Reactants

- The rate of a reaction depends on the chemical nature of the substances participating in the reaction.
- The more reactive reactants have a faster rate of reaction
- Example i) $2Na + 2H_20 \rightarrow 2NaOH(g) + H_2(g)$,very fast

  ii) $Ca(s) + 2H_20 \rightarrow Ca(OH)_2(aq) + H_2$, slow
- Reaction i) is **fast** while reaction ii) is **slow** because sodium is more reactive than calcium

Cont.…

- The combination of two oppositely charged ions usually occurs very rapidly. For example, the reaction of an acid with a base
- Even similar reactions may have **different rates** under the same conditions.

Cont..

Surface Area of Reactants

- A reaction between substances that are in different physical phases (solid, liquid, gas) is called a heterogeneous reaction.

$$S(s) + O_2(g) \rightarrow SO_2(g)$$

- In this case, bringing the reacting molecules or ions together may be difficult.
- In general, the area of contact between the phases determines the rate of reaction in heterogeneous reaction
- When the size of particles is minimized, contact between the atoms, ions, or molecules in the solid state maximizes with those in a different phase.

Cont....

- A reaction of substances when both are in the gaseous or liquid phase, is referred to as a **homogeneous reaction**.

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

- The question of contact between the reactive molecules in a homogeneous reaction is not an important one, for the molecules and ions are free to move and collisions are frequent

Cont....

Concentration of Reactants

- When the concentration of one or more reactants increases, rate of reaction increases.
- This is because increasing the concentration produces more contacts between the reacting particles, which results in increasing the rate of reaction.



Cont....

Concentration of Reactants

- In the case of reactions that involve gaseous reactants, an increase in pressure increases the concentration of the gases which leads to an increase in the rate of reaction.
- However, pressure change has no effect on the rate of reaction if the reactants are either solids or liquids.

Cont....

Temperature of Reactants

- Temperature usually has a major effect on the rate of reaction.
- Molecules at higher temperatures have more thermal energy.
- Generally, an increase in the temperature of a reaction mixture increases the rate of reaction of chemical reactions.
- This is because as the temperature of the reaction mixture raises, the average kinetic energy of the reacting particles increases. So, they collide more frequently and with greater energy.

Cont.....

- The effect of temperature on rate of reaction can be experienced in our daily life. For example,
  - a. The food is kept in refrigerator to slow down the rate of decomposition of food; and
  - b. During heart surgery, the body of patient is cooled to slowdown the rates of biological reactions.
- Temperature not only affects the rate of reaction but can even change the course of a reaction

At 200°C,

$$NH_4NO_3(s) \rightarrow N_2O(g) + 2H_2O(g)$$

At even higher temperature,

$$2NH_4NO_3(s) \rightarrow N_2(g) + O_2(g) + 4H_2O(g)$$

Effect of Catalyst on Rate of Reaction

- A catalyst is a substance that changes reaction rate by providing a different reaction mechanism one with a lower activation energy,
- activation energy Ea, which is the minimum energy needed to start a chemical reaction.
- A catalyst may undergo intermediate physical changes and it may even form temporary chemical bonds with the reactants but it is recovered unchanged in original form at the end of the reaction.
- Although a catalyst speeds up the reaction, it does not alter the position of equilibrium.

Cont....

- Chemical catalysts can be either positive or negative.
- Positive Catalyst increases the rate of reaction by lowering the Activation Energy, Ea
- Negative Catalyst or Inhibitors decreases the rate of reaction by increasing the value of Ea
- A substance that catalyzes one reaction may have no effect on another reaction, even if that reaction is very similar.
- Many of the most highly specific catalysts are those designed by nature.
- The chemical reactions in living things are controlled by biochemical catalysts called enzymes.

THE END

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CHEMISTRY GARDE 11
CHAPTER 4
CHEMICAL KINETICS
PART TWO

THEORIES OF REACTION RATES

- Two important theories help us to explain why different reactions occur at different rates. These are

  The collision theory

  The transition-state theory

Cont.....

Collision Theory

- Collision theory is the theory of reaction rates that assumes that molecules must collide in order to react
- According to collision theory for a reaction to occur between reactants
- ✓ particle of reactant must be collide
- ✓ Particle of reactant must have a proper orientation
- ✓ The particle of reacting species must collide with the energy greater than or equal to the activation energy

Cont....

- The rate of reaction is directly proportional to the number of collisions per second (the frequency of collision)

$$\textbf{rate} \propto \frac{number\ of\ collision}{second}$$

- According to collision theory, the more collisions there are, the faster the rate of reaction would be.
- However, not all collisions between reacting species result in a reaction. This is because collisions between reactants can be either effective or ineffective.

cont....

- **Effective collisions** are collisions that result in a reaction to form the desired products.
- the reacting species must be in proper orientation to each other at the time of collision, they must collide with sufficient energy to break or rearrange bonds
- Ineffective collisions are collisions that do not result in a reaction to form the desired products.
- The reacting particle have no proper orientations

cont....

- According to collision theory, only collisions with proper orientation of reacting species possessing sufficient energy result in a reaction. The collision can either be linear or nonlinear (bent).

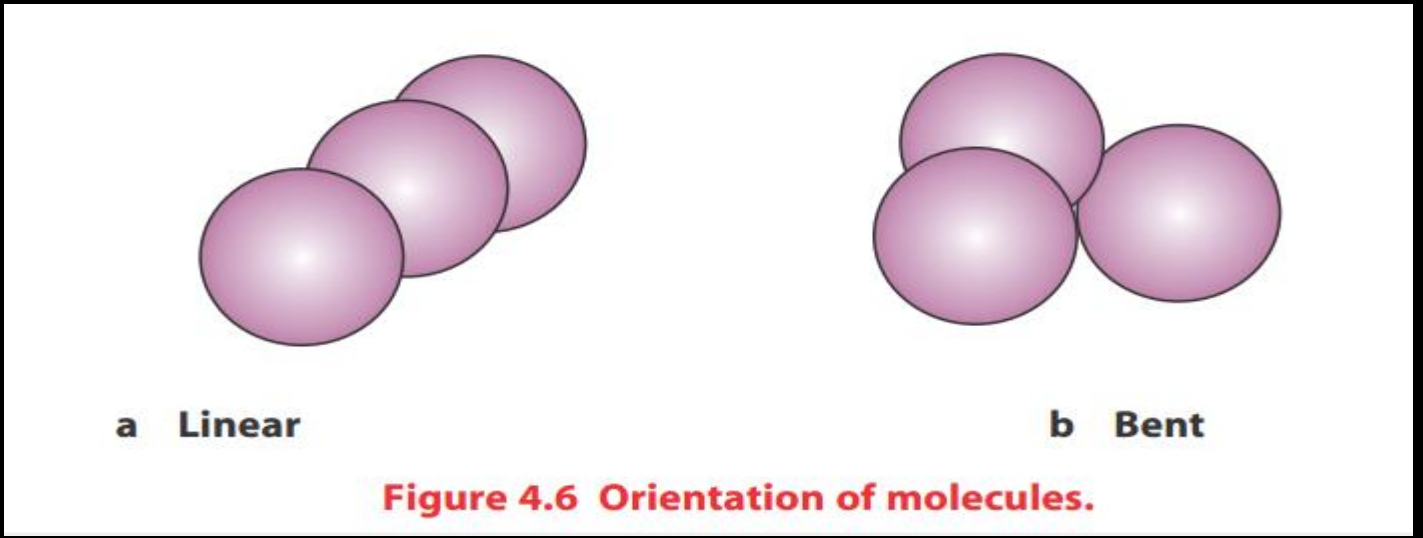


Figure 4.6 Orientation of molecules.

- Generally, Ea for activated complex formed in linear orientation is less than that is formed in bent orientation. Hence, orientation (a) is favored over orientation (b).

cont....

Concentration and Collision Theory

- Concentration is one of the factors that influence the rate of reaction of a chemical reaction.
- Collision theory accounts for the observed increase in the rate of any reaction when the concentrations of reactants are increased.
- Increasing the concentrations of the reacting species results in higher number of collisions per unit time, and the reaction rate is correspondingly higher.

cont...

Temperature and Collision Theory

- According to the kinetic molecular theory, the average kinetic energy of the particles of a substance is directly proportional to the absolute temperature.
- As the temperature of the reacting species is raised, the average kinetic energy of the reacting particles increases considerably.
- This causes the particles of the reactants to collide more frequently and with greater energy. This results in an increase in reaction rate

cont...

- This can be summarized by Arrhenius equation

$$K = Ae^{-Ea/RT}$$

- Where K –reaction rate constant

  A- Frequency factor expressed in L/mol.S

  R-universal gas constant with value 8.314 J/mol.K

  T- Temperature in kelvin

Drive a formula for the above Arrhenius equation $\mathbf{K = Ae^{-Ea/RT}}$ at different temperature

Example calculate the activation energy for the decomposition of hydrogen iodide at different temperature

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

Where **$K_1 = 2.15 \times 10^{-8} \frac{L}{mol.s}$ at 377℃ and $K_2 = K_1 = 2.39 \times 10^{-7} \frac{L}{mol.s}$**

At 427℃

Example : The rate constant at $327℃$ is $2.7 \times 10^{-4} M^{-1} S^{-1}$. What is the temperature at which the rate constant increase to $3.2 \times 10^{-2} M^{-1} S^{-1}$ (energy activation for the reaction is $166.7 \frac{kj}{mol}$)

Cont.....

Transition State Theory

- It is also referred to as “activated-complex theory”.
- According to transition-state theory, the collision between two reacting species results in the formation of an activated complex or transition state.
- An activated complex or transition state is a short-lived, high energy state species that is temporarily formed by the collision of reactant molecules before they form products.

Cont.....

- According to transition-state theory, the rate of reaction depends on the rate at which reactants can climb to the top of the barrier and form an activated complex.
- On the other hand, the activation energy, Ea, is the energy that must be absorbed by the reactants to allow them to reach the transition state or the activated complex and cross the energy barrier.

RATE EQUATION OR RATE LAW

Order of Reaction and Rate Constant

- The rate law or rate equation for a chemical reaction is an equation which links the reaction rate with the concentrations or pressures of reactants and certain constant parameters (normally rate coefficients and partial reaction order).
- To determine the rate equation for a particular system, one combines the reaction rate with a mass balance for the system.

cont....

- For a simple reaction,

  $A \rightarrow B$

  Where A is reactant and B is the product.

- The rate law or rate equation for this reaction is written as:

  $Rate \ \alpha[A]^x$ or $Rate = K[A]^x$

- Where [A] expresses the concentration of A

  K is the rate constant of the reaction, and

  "x" is the order of the reaction.

cont...

- Note that “x” is not stoichiometric coefficient in the balanced equation and it is determined experimentally.
- The order of reaction is the power to which the reactant's concentration is raised in the rate law expression.

- For the general reaction.

$$aA + bB \rightarrow cC + Dd$$

- We can write the rate law expression as:

$$r = k[A]^m[B]^n$$

- The reaction is **m** the order in A,

n the order in B,

(m+ n) the order overall.

- m is determined by varying concentration of A while keeping constant concentration B
- n is determined by varying concentration of B while keeping constant concentration A

Example: The reaction $2NO + Cl_2 \rightarrow 2NOCl$ was studied at 263k and the following data were obtained

Experiment	[NO]M	[Cl2]	(Rate), M/min
1	0.1	0.1	0.18
2	0.1	0.2	0.36
3	0.2	0.2	1.44

Find the rate law and order of the reaction with respect to each reactant and the value of rate constant at 263k

cont...

- Note that the order of a reaction is not necessarily the same as the stoichiometric coefficients in the balanced equation for the reaction.
- The value of the rate constant, K, depends on conditions such as temperature, concentration and surface area of the adsorbent or light irradiation.

cont....

- Consider a reaction with the rate equation,

$$r = k[A]^2[B]$$

- The reaction with the rate equation given above is described as "second-order in A" and "first-order in B."
- The overall reaction order is described as a third-order reaction overall, because the sum of the exponents on [A]and [B] is 3.

Table 4.2 Rate equation and reaction order for simple reaction rate

Rate equation	Overall reaction order
$k[A]^0$	zero
$k[A]$	first
$k[A]^2$	second
$k[A][B]$	second
$k[A]^3$	third
$k[A]^2[B]$	third
$k[A][B][C]$	third
$k[A]^{3/2}[B]$	5/2

cont....

- For hypothical reaction x → y what happens to the rate of reaction for the zero order reaction, **first order** and **second order** reaction if the concentration of x is doubled and tripled

cont....

Table 4.3 Change in initial rate with change in $[A]^o$ for rate = $k[A]^m$

For a reaction of	If $[A]^0$ is doubled	If $[A]^0$ is tripled
Zero-order (m = 0)	rate is unchanged	rate is unchanged
First-order (m = 1)	rate is doubled	rate is tripled
Second-order (m = 2)	rate is quadrupled (x 2^2)	rate is 9 times greater (x 3^2)

Concentration-Time Equation (Integrated Rate Law)

- A rate law tells us how the rate of reaction depends on the concentration of the reactants at a particular moment.
- A rate law can be transformed into a mathematical relationship between concentration and time using calculus.
- Therefore, an integrated law relates concentration to reaction time.

cont....

1. Zero Order Reaction

- A zero-order reaction is a reaction whose rate of reaction does not depend on the reactant concentration
- For the general reaction

$$A \rightarrow \text{Product}$$

the zero order rate law is written as the equation

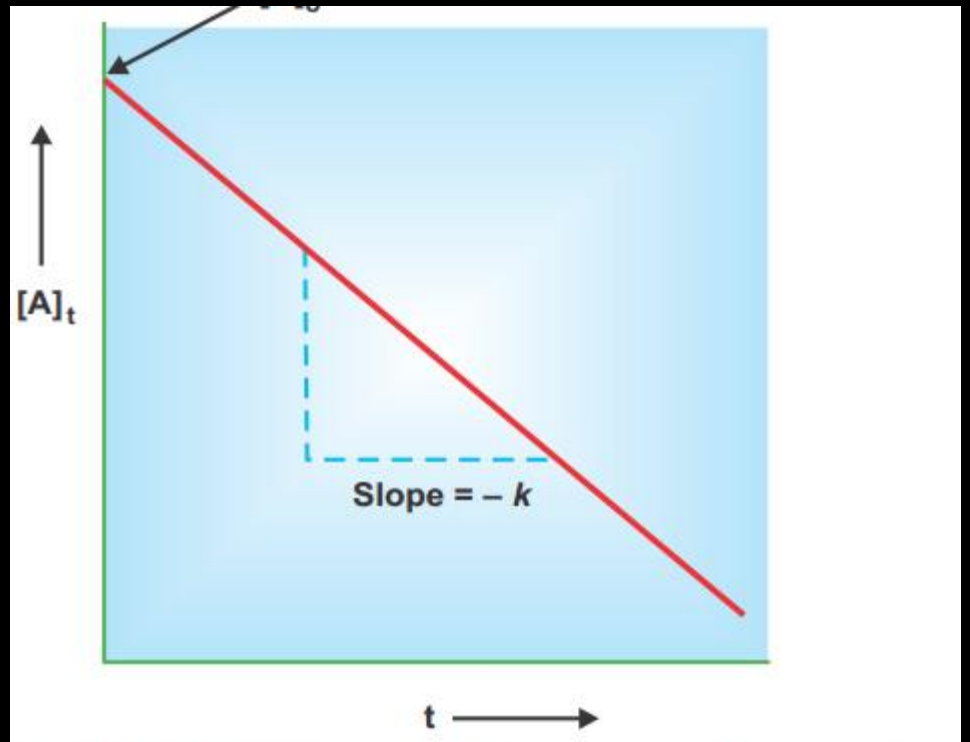
$$rate = -\frac{\Delta[A]}{\Delta t}$$

Using calculus, Integrated rate equation for 0^{th} order reaction

$$[A]_f = -kt + [A]_o$$

cont...

- $[A]_f = -kt + [A]_o$ This is a linear equation with the form of **y= mx+b**. For a zero-order reaction, a plot of [A]versus-time is a straight line, whose slope is – k.



8 A plot of [A] versus t for a zero-order reaction.

Example : The decomposition reaction $2NO_2(g) \rightarrow 2N_2 + O_2$ is a zero order reaction that occur on the platinum surface . The concentration of N2O reduced from 0.4M to 0.1M in 20 seconds find the rate constant of the reaction

cont....

2. First-Order Reactions

❖A **first-order reaction** is a reaction whose rate of reaction depends on the reactant concentration raised to the first power.

In a first-order of the type

A → Product

$$rate = -\frac{\Delta[A]}{\Delta t}$$

r=k[A]

❖Using calculus, Integrated rate equation for 1^{th} order reaction

$$\ln[A]_t = -kt + ln[A]_o$$

Example : the decomposition of hydrogen peroxide is the first order in H_2O_2 and the rate constant is $\mathbf{1.06 \times 10^{-3} min^{-1}}$. If the initial concentration of H_2O_2 is 0.02M what is the concentration after exactly 100min

cont....

3. Second-Order Reactions

- A second order reaction is a reaction whose rate depends either on the concentration of one reactant raised to the second power or on the concentrations of two different reactants, each raised to the first power.
- The simpler type of reaction involves one kind of reactant molecule

$$2\,A \rightarrow \text{Product}$$

- Where $rate = -\frac{\Delta[A]}{\Delta t}$
- From the rate law **$r=k[A]^2$**

Using calculus, Integrated rate equation for 2th order reaction

$$\frac{\mathbf{1}}{[A]\mathrm{t}} = -\boldsymbol{kt} + \frac{\mathbf{1}}{[A]_o}$$

Example : **the decomposition of hydrogen iodide is the second order reaction with the rate constant is k=30** $\frac{L}{mol.min}$**.at 443**℃.calculate the time required for the concentration of **hydrogen iodide to fall from 0.02M to 0.01M at 443**℃?

The Half-life of a Reaction

- The half life of a reaction is defined as the time required for the concentration of a reactant to decrease to half of its initial concentration.
- This means that half-life is the time it takes for the concentration of A to fall from [A]o to ½[A]o, i.e. [A] = ½[A]o.
- The half-life of a reaction is designated by the symbol, t½

1. Half-life for zero order reaction

1. Half-life for first order reaction

3. Half-life for second order reaction

Example: For a first order reaction x → y, with k=0.02303s-1 what percent of x remain after 200 seconds?

Example If has a certain first order reaction has a half life of 40minutes

a) Calculate the rate constant for the reaction

b) How much time is required for this reaction to be 60% completed?

What Is half life of the irreversible reaction A $\rightarrow$ B if 75% of A converted to B in 60 minutes?

REACTION MECHANISM

- reaction mechanism is the sequence of bond making and bond breaking steps that occurs during the conversation of reactants in to product
- The term for the sequence of elementary steps that leads to product formation is **reaction mechanism**
- Each of the steps in the reaction sequence is called an **elementary reaction**
- Species that exist in elementary reaction but not in the overall reaction are called **intermediates**

cont....

Elementary process

The following are the characteristics of elementary processes

- Elementary processes are either unimolecular or bimolecular or termolecular
- **Unimolecular**-a process in involving a single molecules dissociates
- **Bimolecular** – a process in which involving the collision of two molecules
- **Termolecular**-a processes in which three molecules collide simultaneously
- Certain species are produced and consumed in the elementary process
- One elementary process may occur much more slowly than all other.such a process is called the **rate determining step**

Example the reaction NO2 (g) + CO(g) → NO(g) + CO2(g) can be thought of as occurring two elementary steps

i. $NO_2 + NO_2 \rightarrow NO + NO_3$ (slow step)

ii. $NO_3 + CO \rightarrow NO_2 + CO_2$ (fast step)

a) Identify the intermediate

b) Identify the rate determining step

c) Determine the molecularly of this reaction

THE END

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