

COLLEGE OF BASIC AND APPLIED SCIENCES
DEPARTMENT OF CHEMICAL SCIENCES (INDUSTRIAL CHEMISTRY OPTION)
CHM 413 (Advanced chemical kinetics and catalysis)
2units(R)
2017/2018 session/first semester
COURSE LECTURER: OGBEBOR, CLARA

THEORIES OF REACTION RATE

Reaction rate is the change in the concentration of a reactant or product with time. Reaction rate is obtained experimentally, to determine the rate of a reaction; the concentration of the reactant or product is monitored as a function of time. In chemical reactions, emphasis is placed more on speeding up the rate of reaction more than the maximum yield. Knowledge of reaction rate is useful in drug design, pollution control and food processing. There are two basic theories of reaction rates:

- i. Collision Theory
- ii. Absolute Theory

Collision Theory of reaction rate accounts for the kinetics of reaction in terms of kinetic molecular theory of gases; which postulates that gas molecules frequently collide with one another. According to collision theory, chemical reactions occur as a result of collisions between reacting molecules i.e. the rate of the reaction is directly proportional to the number of molecules or collisions per seconds. The implication of the theory is that reactions always occur when molecules collide. However not all collisions lead to reactions. In collision theory, the essential requirements for reaction to occur are:

- i. Collision between the reactant molecules
- ii. Activation of molecules
- iii. Proper orientation of reacting molecules

Limitations

The theory is applicable extensionally to gaseous reactants. According to collision theory, the rate of reaction is given by $-d[A]/dt = K[A] = Z_{11}q$

Where Z_{11} = Number of collision between the reacting molecules per second (mol/s) in dm^{-3}

q = Total number of molecules that are activated

Theory of absolute reaction rate/transition state assumes that equilibrium is established between the reactant and the activated complex. Activated complex is a temporary species formed by reactant molecules as a result of the collision before forming product. Activated complex has energy higher than the reactant or product. The rate of a reaction depends on the concentration of the activated complex and the rate of the decomposition of the activated complex. According to absolute reaction rate theory, the rate of the decomposition of the activated complex is given by :

$$k_2 = \frac{RT}{nAh} \left[\exp \frac{\Delta H}{RT} \exp \frac{\Delta S}{R} \right]$$

Where k = Rate constant

R = Gas constant

h = Plank constant

ΔH = Change in enthalpy

ΔS = change in entropy

T = Temperature

CHAIN REACTIONS

These are complex reactions with complex rate equations. In chain reaction the intermediate produced in one step generates an intermediate in another step. These intermediates are called chain carriers; some of them are radicals (species that possess unpaired electrons), ions or neutrons in nuclear fissions.

STEPS IN CHAIN REACTIONS

Chain Initiation: The reaction can be initiated by

- 1) Thermolysis (heating)
- 2) Photolysis (adsorption by light) which leads to bond breakage.

Chain propagation: During propagation the chain carrier produces another chain carrier.

Retardation: In retardation, the carrier reacts with the products to reduce the formation of the products. Retardation produces another chain carrier but the product concentration is reduced.

Chain termination: During this, the radical combine and the chain carriers are lost.

Inhibitors: These are the introduction of foreign radicals to remove carrier chains.

In chain reactions, three (3) major steps are formed;

- 1) Initiation

- 2) Propagation
- 3) Termination

RATE LAW OF CHAIN REACTIONS

Rate law expresses the relationship in the rate of the reactions, to the rate constant and the concentration of the reactant raised to some powers.

Mathematically the rate law is stated as;

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

Where x and y are the order of reaction which is the sum of powers.

The rate law of a chain reaction can be simple or complex. Rice- Herzfeld mechanisms enable complex chain reactions to give simple rate law in chemical kinetics. For Example the pyrolysis of acetaldehyde (pyrolysis is the decomposition of a substance in the absence air).



$$\text{Rate law } v = k (\text{CH}_3\text{CHO})$$

The Rice-Herzfeld mechanism for the decomposition of acetaldehyde is as follows:

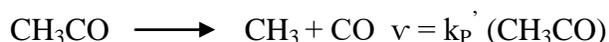
1. INITIATION



2. PROPAGATION



3. PROPAGATION



4. TERMINATION



The chain carrier (CH_3) and (CHO) (Aldehydes group) are formed in the initial step, the chain carrier attacks other reactant molecule in the propagation step and each attack gives rise to a new step. In termination step radicals combine in the end of the chain.

APPLICATION OF STEADY STATE APPLICATION

According to steady state approximation the rate of formation of the intermediate and its disappearance is equal.

1) Rate of Appearance

$$\frac{d[\text{CH}_3]}{dt} = k_i (\text{CH}_3\text{CHO}) + k_p (\text{CH}_3\text{CHO}) (\text{CH}_3) + k_p' (\text{CH}_3\text{CO}) + k_T (\text{CH}_3) (\text{CH}_3)$$

2) The Sum of the Equation

$$\frac{d[\text{CH}_3]}{dt} = k_i (\text{CH}_3\text{CHO}) + k_T (\text{CH}_3) (\text{CH}_3) = 0$$

The steady state approximation applies that the rate of chain initiation is equal to rate of chain termination.

ADSORPTION

Adsorption is the accumulation of a substance on the surface of a solid or liquid. In adsorption the gas or liquid surface is called adsorbate and the substance to which it is attached to is called adsorbent. Adsorption depends on the surface area of the adsorbent and the larger the surface area, the greater the extent of adsorption. Solids in the finely divided state, where the surface area is large are good adsorbent. Adsorption is an exothermic process and increases with the decrease in temperature. Adsorption isotherms are used to describe adsorption because temperature has a significant effect on the process. The amount of adsorbate bound to the adsorbent is expressed as a function of pressure or concentration at constant temperature. The various isotherms models are; linear, Freundlich, Langmuir etc. Examples of adsorbent are; silica gel, aluminum, activated carbon or charcoal, zeolite and biomaterials.

Adsorbent is classified into three:

1. Carbon based compounds.
2. Oxygen based compounds.
3. Polymer based compounds.

Types of Adsorption

Adsorption is classified based on the forces holding the solid molecules on the solid surface.

1. Physical adsorption or van der Waal's adsorption
2. Chemical adsorption or activated adsorption

When molecules are held by van der Waal's forces it is physical adsorption and when they are held by valence force they are called chemical adsorption.

Differences Between Chemical Adsorption and Physical Adsorption

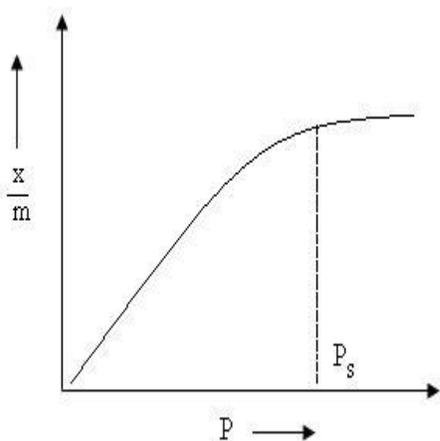
Physical Adsorption	Chemical Adsorption
It is characterized by low enthalpy of	It is accompanied by high enthalpy of

adsorption 20-40 kJ/mol. The adsorption equilibrium is reversible and it is established rapidly. There is a van der Waal's interaction between the adsorbate and adsorbent.	adsorption on H ₂ O order of 80- 200 kJ/mol. The attachment of the adsorbate on the adsorbent is stronger. The equilibrium is established slowly and is irreversible.
No appreciable amount of activated energy is involved.	Chemisorption usually occurs at high temperatures.
Physical adsorption is multilayer.	Chemisorption is unilayer or monolayer
Physical adsorption is more of a function of the adsorbent.	Chemisorption is characterized by both the adsorbent and the adsorbate.
The extent of the physical adsorption increases with an increase in pressure of the adsorbate and ultimately contains a limiting value.	Chemisorption decreases with the increase of pressure of the adsorbate.

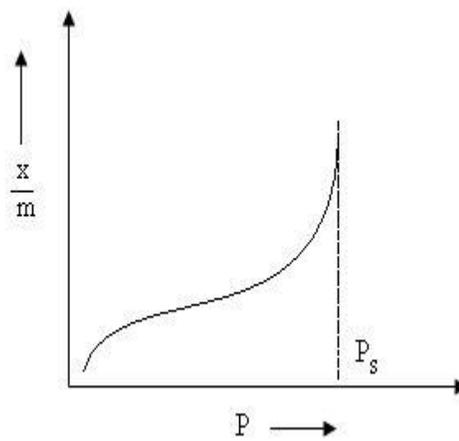
ADSORPTION ISOTHERMS

An adsorption isotherm is a plot between the amount of the adsorbate, substance adsorbed and the pressure of the adsorbate at constant temperature

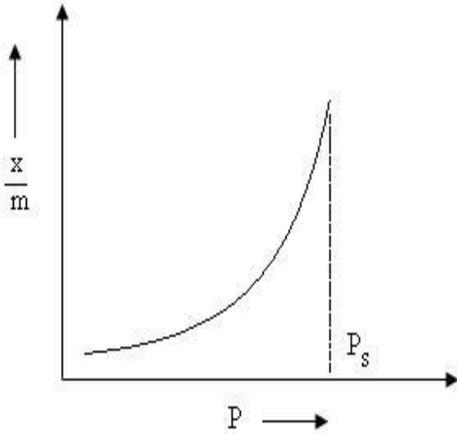
There are 5 (five) general types of isotherm in adsorption of gases on solid surfaces



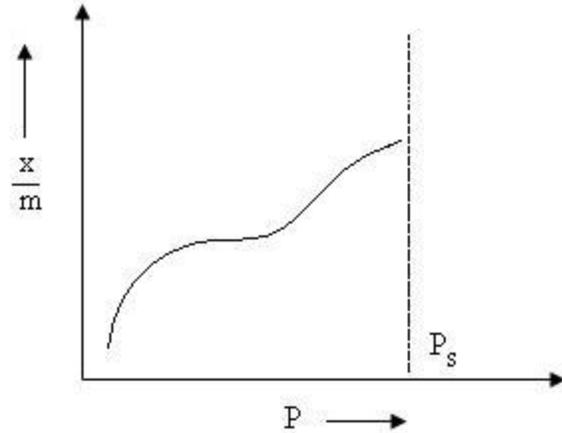
TYPE 1



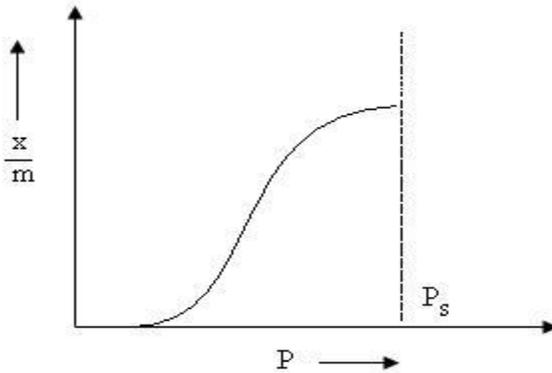
TYPE 2



TYPE4



TYPE3



TYPE5

Type I isotherm is obtained by chemisorption, while all other isotherms are observed in physical adsorption. In chemisorption, the amount of the gases absorbed per unit mass of the adsorbent increases linearly with pressure in initial stage and then more slowly attaining a limiting value as the surface becomes fully covered by the gas molecules.

FREUNDLICH ISOTHERM

This is used in measuring the extent of adsorption. The isotherm is only applicable in the limiting gases of low concentration because of the deviations of the linearity especially at low temperatures. Freundlich suggested an equation known as Freundlich adsorption isotherm

$$x/m = k(p)^n \text{ or } x/m = kp^{1/n}$$

Where x and m are masses of the substance absorbed and of the adsorbent respectively.

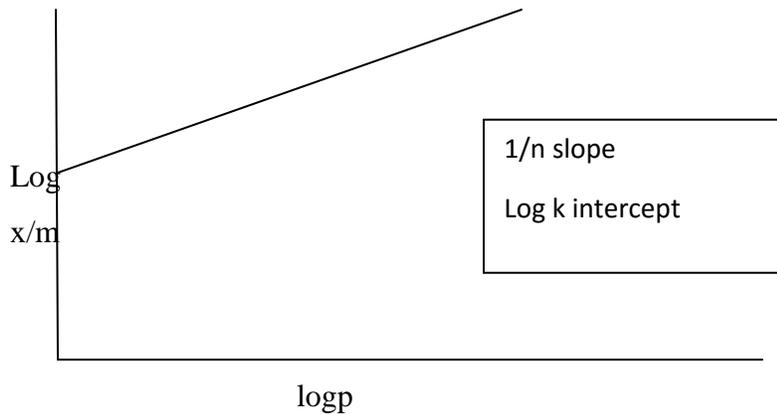
p = equilibrium concentration of the adsorbed substance.

k and n are constants.

Taking the logarithms of the above equation

$$\text{Log } x/m = \text{Log } k + \log^{1/2} np.$$

A plot of $\text{Log } x/m$ against $\text{Log } p$ gives a straight line graph with slope $1/n$ and intercept by k .



LANGMUIR ISOTHERM

Langmuir in 1966 proposed that adsorption process consist of two opposing actions

- 1) Condensation of molecules from the gas phase on the surface.
- 2) Evaporation of molecules from the surface bulk into the gaseous state. At equilibrium, these two rates become equal.

Langmuir derived an equation based on the following assumptions;

1. The solid surface is homogeneous and has fixed number of adsorption site.
2. Each site cannot absorb more than one molecule.
3. The adsorbed gas behaves ideally bin vapor phase.
4. Adsorption is considered as equilibrium
5. There is no interaction between the adsorbed molecules

Langmuir derived an equation for the types of isotherm

$$Y = \frac{ap}{1+ bp}$$

P = pressure of a gas

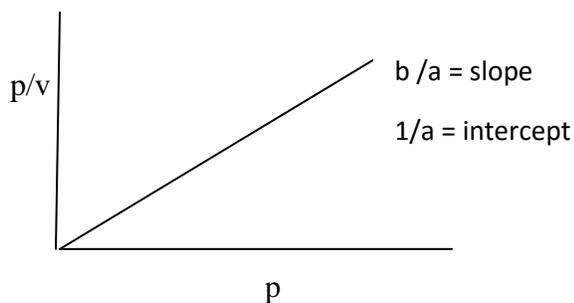
b = constant = k_1/k_2

Y = fraction of a solid surface covered by the adsorbate to the pressure of the gas at constant temperature and is known as Langmuir adsorption isotherm. The constant “a” and “b” depends on the system and temperature.

Arranging the above equation gives;

$$p/v = 1/a + (b/a)p$$

plot of p/v yields a straight line with slope (b/a) and intercepts $1/a$



Langmuir equation is application for smooth non-porous surface and low values of pressure.

CATALYSIS

A catalyst is a substance that increase the rate of chemical reaction without itself being used up and can be recovered unchanged chemically at the end of a chemical reaction. A catalyst provides an alternative part usually of lower activation energy for the reaction to proceed at an accelerated rate.

Examples of catalyst reaction

- 1) Iron in the manufacture of ammonia by Haber process
- 2) Platinum in contact process for the manufacture of sulphuric acids
- 3) Water vapour in the combination of hydrogen and chlorine.

In these examples, the catalyst accelerates the rate of reaction and is therefore sometimes termed as positive catalyst.

Examples of negative catalyst

- 1) Sulfur compounds in the auto- oxidation state of benzoadehdye.
- 2) Alcohol in the oxidation of chloroform.

CHARACTERISTICS OF A CATAYST

- 1) A catalyst remains chemically unaffected at the end of a chemical reaction.
- 2) The catalysts do not undergo any chemical changes although there may be change in its physical state such as the particle size or change in color.

- 3) Small quantity of a catalyst is usually required to bring about a reaction to combine together. A very small amount of catalyst sufficient for reactants to combine together. This is because the catalyst is not used up in the reaction.
- 4) Presence of the catalyst does not affect the position of equilibrium in a reversible reaction. This is true when a small amount of a catalyst is used. The catalyst helps in attaining the equilibrium more quickly by increasing the rate of both forward and reverse reaction to some extent.
- 5) A catalyst does not initiate a reaction but only increases or decreases its speed, generally a catalyst speed up the reaction which is already occurring slowly in its absence.
- 6) The action of the catalyst is specific. A catalyst can only catalyse a specific reaction and cannot be used for any other reaction. For example, Manganese (IV) oxide can only catalyse the decomposition of potassium chlorate but not potassium nitrate or other substance. A change of catalyst also changes the nature of the reaction.
- 7) A catalyst has an optimum temperature at which the action of the catalyst is maximum
- 8) A catalyst is poisoned by the presence of other substances which destroys the catalytic activity and they are called catalytic poisons. Examples are arsenious oxides, carbon monoxide etc.

TYPES OF CATALYSIS

1. Heterogeneous catalysis
2. Homogeneous catalysis
3. Enzyme catalysis

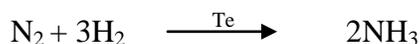
In heterogeneous catalysis, the catalyst is present in different phase from the reactant. In most cases, the catalyst is in the solid phase and the reactants are gases or liquids. The catalysts commonly used are metals like platinum, copper, nickel and iron and certain metal oxides; Such as ferric oxide, zinc oxide, molybdenum oxide etc.

Examples of heterogeneous catalysis

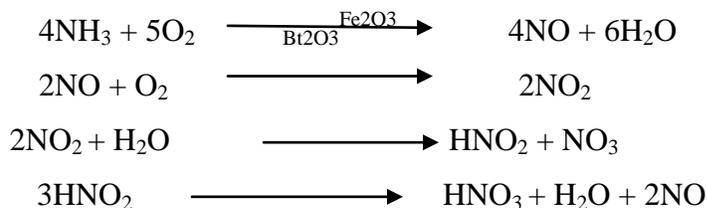
- 1) In contact process for the manufacture of sulphuric acids. Sulphur dioxide is directly oxidized into sulphur trioxide by atmospheric oxygen in the presence of platinum as catalyst.



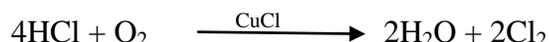
- 2) Haber's process for the manufacture of ammonia in which nitrogen and hydrogen in the ratio 1:3 are passed over heated iron which contains a promoter (molybdenum).



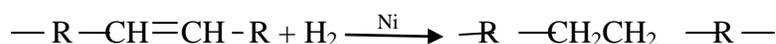
3) The oxidation of ammonia to nitric oxide and finally nitric acids in the presence of a mixture of ferric oxide and bismuth oxide.



4) a. Oxidation of hydrogen chlorine in the presence of copper II chloride as a catalyst.

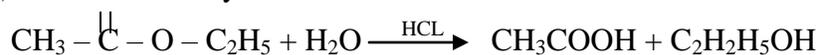


b. Hydrogenation of unsaturated hydrocarbons in the process of nickel as a catalyst.

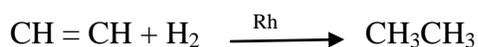


In homogeneous catalysis, the reactant and catalyst are disposed in single phase usually liquid. Some examples are:

a) Reaction of ethyl acetate with water to form acetic acids and ethanol in the presence of HCl



b) Conversion of carbon – carbon double bond to a carbon – carbon single in the presence of red violet compound rhodium.



Advantages of Homogeneous catalysis

- 1) It can be carried out under atmospheric condition thus, reducing production cost and minimizing the decomposition of the product at high temperature
- 2) Homogenous catalyst can be designed to function selectively for a particular type of reaction.

An enzyme is a large protein molecule that contains one or more active site, where an interaction with substrate takes place. These sites are structurally compatible with specific substrate molecule. Enzyme catalysis is biochemical reactions. They increase the rate of biochemical reactions and are highly specific. An enzyme acts only on certain molecules called substrate (reactant) while leaving the rest of the system unaffected. Enzyme catalysts are usually homogeneous because the substrate and enzyme are present in aqueous solution. An enzyme molecule has a fair amount of structural flexibility and can modify its shape to accommodate more than one type of substrate. The mathematical treatment of enzyme kinetics is complex. A simplified scheme is given by the elementary step:



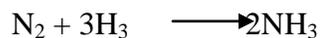
Where E, S and p represent enzymes, substrate, and products and ES is the enzyme – substrate complex.

CATALYST SURFACE

The total surface area of a catalyst has an important effect on the reaction rate, the smaller the catalyst particle size, the larger the surface area for a given mass of particles and the greater the activity of the catalyst. Catalyst has an active site which are the atoms or crystal faces where reaction takes place. Active site is where interaction with reactant molecules takes place. These sites are structurally compatible with reactant molecules.

ACTIVITIES AT SURFACES

The catalytic activities depend on the structure and the composition of a catalyst. In heterogeneous catalysis, production of Haber process, the surface of the solid catalyst serves as the site of the reaction. In Haber process the initial step involves the dissociation of nitrogen molecules N_2 on the metal surface. The dissociated species are bond to the metal surface because of their high reactivity. The two reactant molecules behave differently on the catalyst surface. Studies show that H_2 dissociates into atomic hydrogen and combine rapidly at high temperatures to produce the desired NH_3 molecule.



CATALYTIC CARRIERS AND PROMOTERS

Catalytic carrier is a neutral material used to support a catalyst. It serves as a medium for the delivery of catalyst substance and aid chemical process. This is achieved by coating the catalyst with substances which in turn will increase the number of catalytic site relievable. They initiate the reaction mechanism by providing a controlled surface area.

Mechanisms of a Catalytic Action

The action of a catalyst can only be explained by two mechanisms.

1. Intermediate compound formation
2. Adsorption theory

Intermediate compound formation theory was proposed in 1806. In this theory, two steps are involved;

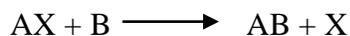
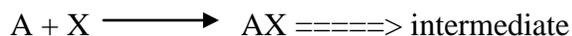
- 1) Combination of the catalyst with one or more of the reactants forming intermediate compound.

2) The decomposition of the intermediate compound or its combination with other reactants yielding the products and catalyst.

By illustration, a reaction between the reactant A and B giving the product AB



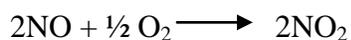
This reaction is very slow and it is catalyzed by X



The formation of an intermediate compound AX is an easy reaction and need low energy of activation there by accelerating the rate of the chemical reaction.

Examples of intermediate compound formation

1. In lead chamber process for the manufacture of sulfuric acid. The catalyst first forms an intermediate compound with oxygen



2. In the preparation of diethyl from ethanol using concentrated H_2SO_4 , ethyl hydrogen sulfate is first formed as an intermediate.



3. Formation of water by combination of hydrogen and oxygen in the presence of copper as catalyst.



Limitations of Intermediate Compound Formation Theory

- 1) The theory does not explain the cases of the heterogeneous catalysis in general.
- 2) The deactivation by a catalyst poison and the activation by a promoter.

Adsorption theory is applicable to reactions between gases in the presence of solid catalyst. The surfaces of a catalyst have a certain active center due to the unsaturation of valences. Appreciable quantities of the reactant are absorbed or retained by solids surface at these active centers and the reaction occurs at the surface of the solid. The absorbed molecules form salt of activated complex on the surface which then decomposes forming the products.

Steps in Catalytic Reactions

1. Diffusion of the reactant from the bulk into the surface.
2. Adsorption of the reactant on the surface of the catalyst.
3. Activation of the adsorbed reactant leading to a reaction on the adsorbed surface.
4. Desorption of the products from the surface of the catalyst.
5. Diffusion of the products away from the surface of the catalyst.

Reference materials: PETER ATKINS, GORDON M. BARROW, K.K SHARMA AND L.K SHARMA AND A.D NIGEL