Benha University **Advanced physical chemistry**
Faculty of agriculture **Time: 2 hours**
Biochemistry Dept. **January: 2020**
Post-graduate **Semester: 1**

Model Answer

First Question :- (Answer five only) (15 Marks)

1- What are adsorbate and adsorbent? Give an example?

Answer

Molecules (substances) that accumulates on the surface is called **adsorbate.**

The material on the surface of which adsorption takes place is called **adsorbent.**

Example: Ni adsorbs H_2. Ni is the adsorbate, H_2 is the adsorbent

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2- Give differences between adsorption and absorption?

Answer

Adsorption	Absorption
A substance gets concentrated on the surface liquid.	A substance gets uniformly distributed through the bulk of solid or liquid.
It increases with increase in surface area.	It remains unaffected by increase in surface area.
Example: adsorption of water by silica gel.	Example: Absorption of water by anhydrous $CaCl_2$.

3- Distinguish between physisorption and chemisorption.

Answer

Physiosorption (physical adsorption)	Chemisorption (chemical adsorption)
Accumulation of gas on a solid due to weak van der Waal's forces.	Accumulation of gas on a solid due to chemical bond (covalent or ionic)
This is not specific, as force between adsorbate and adsorbent is van der Waals forces which is universal.	It is highly specific as there is chemical bonding between adsorbate and adsorbent.
The process is reversible.	Process is irreversible.
Gases that can be easily liquefied (high critical temperature) are readily absorbed.	Gases that can form chemical compounds with adsorbent are specifically adsorbed.
Enthalpy of adsorption is low, as the forces involved are weak (ΔH is negative but low)	Enthalpy of adsorption is high, as the forces involved are strong (ΔH is negative, very high)
Adsorption decreases with increase in temperature. Low temperature favours better adsorption.	Adsorption process involves high energy of activation, therefore increases with increase in temperature.
Under high pressure, it leads to multimolecular layers of adsorption.	It leads to unimolecular layer of adsorption even at high pressure.

4- Write about Assumptions of Langmuir Adsorption Isotherm and BET.

Answer

The Langmuir Isotherm

Assumptions:

(1) Monolayer adsorption

(2) Localized adsorption (occur on specific sites)

(3) Heat of adsorption is constant. (Independent of the amount of material adsorbed)

(4) Based on kinetic model of adsorption-desorption process

The Brunauer-Emmett-Teller (BET) Isotherm

Assumptions:

(1) Multilayer adsorption;

(2) Adsorption of first layer has a heat of adsorption, ΔHA;

(3) The subsequent layers are controlled by heat of condensation, ΔHL.

5- What is a second order reaction and conclude the rate of reaction constant?

Answer

A reaction will be of the second order when the reaction rate would depend upon the product of two concentrations.

Second order reactions are of two types

(i) The rate is proportional to the square of the same reactant concentration

(ii) The rate is proportional to the product of the two reactant concentration

(i) The rate is proportional to the square of the same reactant concentration

Let say, 2A $\longrightarrow$ Products

6- Comment on half-life of a first order and second order reaction.

Answer

half-life of a first order

The time required for half the reactant to change can be easily evaluated. Let t1/2 Be the time required when x = a /2 .

Then $t1/2 = 1/K \ln a/ a-a/2$

$= 1 /K \ln a /a/2 = 2.303 \log2/ K = 0.693 /K$

The period of half decomposition is thus constant for a given reaction and is independent of initial concentration. The time required is called half value period or half life in case of radioactive changes.

second order reaction

In a second order reaction, where the two initial concentrations are the same then from 1.9 the half value period is given by

$t1/2 = x/ ak(a-a/ 2) = a/2 a.k .a/ 2 = 1 /ak$

Second Question :- (Answer five only) (15 Marks)

1- Conclude Langmuir Adsorption Isotherm Equation

Answer

Assumptions of Langmuir Isotherm

Langmuir proposed his theory by making following assumptions.

(i) Surface is energeticallyuniform. Fixed number ofvacant or adsorption sites are available on the surface of the solid.

(ii) All the vacant sites are of equal size and shape on the surface of adsorbent. Each site can hold maximum of one gaseous molecule and a constant amount of heat energy is released.

(iii) Heat of adsorption is constant throughout the surface and it ranges from 0 to 1.

(iv) Dynamic equilibrium exists between adsorbed gaseous molecules and the free gaseous molecules.

(v) Adsorption is monolayer or unilayer.

Derivation

Langmuir Equation depicts the relationship between the extent of adsorption and pressure.

Langmuir proposed that dynamic equilibrium exists between adsorbed gaseous molecules and the free gaseous molecules. Using the equilibrium equation, equilibrium constant can be calculated.

A (g)+B(s) Adsorption □ AB Desorption

Where A (g) − is unadsorbed gaseous molecule

B(s) − is unoccupied metal surface and

AB − is adsorbed gaseous molecule

According to Kinetic theory, Rate of forward reaction = K*a* [A] [B]

Rate of backward reaction = K*d* [AB]

At equilibrium, Rate of forward reaction is equal to Rate of backward reaction

K*a* [A] [B] = K*d* [AB]

A new parameter 'θ' is introduced.

Let θ be the number of sites of the surface which are covered with gaseous molecule and (1–è) be the fraction of surface unoccupied by gaseous molecule. Rate of forward direction depends upon two factors, number of sites available on the surface of adsorbent, (1 – θ) and pressure, P.

Rate of forward reaction $\propto$ P (1 − θ)

Rate of adsorption $\propto$ P (1 − θ) or

Rate of adsorption = K*a* P (1 − θ)

Rate of backward reaction or rate of desorption depends upon number of sites occupied by the gaseous molecules on the surface of adsorbent.

Rate of desorption $\propto$ θ (or)

Rate of desorption = K*d* θ

At equilibrium, rate of adsorption is equal to rate of desorption.

K*a* P (1 − θ) = K*d* θ

The above equation can be written in terms θ.

K*a* P − K*a* Pθ = K*d* θ

K*a* P = K*a* Pθ + K*d* θ

K*a* P = (K*d* + K*a* P)θ

θ = K*a* P

(K*d* + K*a* P)

Divide numerator and denominator on RHS by K*d* , we get

K*a* P θ =

But K = K*a* / K*d* K*d* K*d* + K*a* P K*d* K*d* KP

Substituting in the above equation we get

$\theta = Kp/1 + KP$

This is known as ***Langmuir Adsorption Equation***.

2- What are the factors that can change the rate of reaction?

Answer

Factors influencing the rate of reaction

Rate of a chemical reaction is influenced by the following factors

(i) Temperature (ii) Concentration of the reactants (iii) Nature of reactants (iv) Catalysts

(v) Radiation

(i) Temperature

In most cases, the rate of a reaction in a homogeneous reaction is approximately doubled or tripled by an increase in temperature of only 100 C. In some cases the rise in reaction rates are even higher.

(ii) Concentration of the reactants

At a fixed temperature and in the absence of catalyst, the rate of given reaction increases with increased concentration of reactants. With increasing concentration of the reactant the number of molecules per unit volume is increased, thus the collision frequency is increased, which ultimately causes increased reaction rate.

(iii) Nature of reactants

A chemical reaction involves the rearrangement of atoms between the reacting molecules to the product. Old bonds are broken and new bonds are formed. Consequently, the nature and the strength of the bonds in reactant molecules greatly influence the rate of its transformation into products. The reaction in which involve

lesser bond rearrangement proceeds much faster than those which involve larger bond rearrangement.

(iv) Catalysts

The rate of a chemical reaction is increased in presence of a catalyst which ultimately enhanced the speed of a chemical reaction.

(v) Radiation

The rate of a number of chemical reactions increases when radiations of specific wave length are absorbed by the reacting molecules. Such reactions are called photochemical reactions.

For example, chlorine may be mixed safely with hydrogen in dark, since the reaction between the two is very slow. However when the mixture is exposed to light, the reaction is explosive.

3- What do you mean by chemical kinetics and rate of a reaction?

Answer

- **Chemical kinetics** is the branch of physical chemistry which deals with a study of the speed of chemical reactions. Such studies also enable us to understand the mechanism by which the reaction occurs. Thus, in chemical kinetics we can also determine the rate of chemical reaction.

- **The rate of reaction** i.e. the velocity of a reaction is the amount of a chemical change occurring per unit time.

The rate is generally expressed as the decrease in concentration of a reactant or as the increase in concentration of the product. If Cthe concentration of a reactant at

any time t is, the rate is dC / dt or if the concentration of a product be xat any time t, the rate would be dx /dt .

The time is usually expressed in seconds. The rate will have units of concentration divided by time.

4- Distinguish between order of a reaction and molecularity of a reaction?

Answer

- **The order** is the number of concentration terms on which reaction rates depends. Thus, if the rate of a reaction depends on the first power of the concentration of reactant, i.e. Rate = KC1

Thus the reaction is said to be of the first order. When the rate is proportional to the product of two reactant concentrations or the square of the concentration of a reactant, the reaction is of the second order.

- **The molecularity of a reaction** is defined as the number of molecules or atoms which take part in the process of a chemical change.

The reaction is said to be unimolecular, bimolecular, termolecular according to one, two, or three molecules are involved in the process of a chemical change.

The term unimolecular was used for all first order reactions, the term bimolecular for 2^{nd} order reactions etc.

5- What is first order reaction? Give examples of first order reaction and conclude the rate of reaction constant?

Answer

A reaction of the first order is represented as

$X \longrightarrow Y$

Where X is the reactant and Y the product. The rate of the reaction will be directly proportional to the concentration i.e.,

$-dc / dt = KC$

in which C is the concentration of the reactant at any time t and K is a constant, called the velocity constant or specific reaction rate.

Thus $-dc / C = Kdt$

On integration $-\int dc/ C = K \int dt$

$-\ln c = kt + Z$(Integration Constant).

If at the start of the reaction the initial concentration of the reactant is Co then we have

at $t = 0$; $C = Co$

Substituting $-\ln Co = Z$

$-\ln C = Kt - \ln Co$

$\ln Co / C = Kt$

Or $C / Co = e^{-Kt}$ Or

$C = Coe^{-Kt}$

The concentration C therefore diminishes exponentially with time.

We may also write

Co-C = Co(1-e-Kt)

The rate equation may also be conveniently expressed in an alternative form, by expressing the rate in terms of the product. When x moles per unit volume of product Y is formed from the reactant, the concentration of the reactant is(a-x), where a is the initial concentration of the reactants. So – d /dt (a-x) = K(a-x)

dx /dt = K(a-x)

dx /a-x = K dt

On integration

∫ dx a-x = K ∫ dt

or, -ln(a-x) = Kt +Z0 (Integration Constant)

When t = 0; x = 0; hence -lna = Z0

Characteristics

1) In a first order reactionC =Coe-Kt , the reaction cannot be complete because C would become zero at infinite time.

2) The quantity a / (a-x) or Co / C is a ratio of concentrations, so, its value will be the same whatever units are employed to express the concentrations e.g. moles/litre, gms/c.c etc.

It shows that the velocity constant K = 1t ln a a-x will have the dimension of reciprocal time, Sec-1 :

3) The equation is ln(a-x) = -Kt +lna

4) The time required for half the reactant to change can be easily evaluated.

6- What is the special characteristic of a zero order reaction?

Answer

A chemical reaction whose rate does not depend on concentration of reactants is called a zero order chemical reaction.