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RATES OF CHEMICAL REACTIONS

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Chemical kinetics is the study of rates of chemical reactions.

Reaction rate is the speed at which a chemical reaction proceeds. It is the measure of change in concentration of reactants over a given period of time. Or Rate of reaction is defined as the change in concentration of reactants or products in a given time. It is expressed as:.

Rate = change in amount/change in time

Reaction rate studies give useful information about the rates of chemical reactions. A deeper understanding of a chemical process includes knowing why a particular chemical reaction proceeds as fast or as slow. This is important in industrial processes in which time and the efficient use of resources are crucial. In industrial processes application of reaction rate enables the realization of maximum product from the minimum amount of raw material, using minimum fuel in the minimum possible time.

FACTORS AFFECTING RATE OF REACTION

The physical state of the reactants: the rate of a reaction can be affected whether the reactants are in solid, liquid, gas, aqueous or in solution form. If solid $AgNO_3$ is mixed with solid NaCl no reaction occurs but if the aqueous solutions of the two are mixed the reaction is instantaneous and a white precipitate occurs.

Effect of concentration: chemical reactions occur as a result of effective collusion between the reacting species. As the concentration of the reactant increases, the particles become more crowded and closer; which increases the chance of effective collision and hence the reaction rate. Therefore,if the concentration of the reactant increases, there rate of reaction also increases. Likewise, as the concentration of the reactant decreases the reaction rate decreases.

Effect of medium: the medium has influence on the reaction. Hydrolysis of tert-butyl chloride is 30,000 times faster in aqueous ethanol than in pure ethanol. Aqueous ethanol is more polar than pure ethanol. Salt and sugar do not dissolve in oil at room temperature but they do dissolve in water.

Effect of P^H: some reactions are affected or depend on the P^H value. If an aqueous solution of sucrose is left to stand for a long time, practically no detectable quantities of the hydrolysis product are obtained. However, if a small amount of mineral acid (acid derived from inorganic compounds) is added, the sucrose begins to break down and the rate of hydrolysis increases with increase in acidity of the medium.

Effect of temperature: the rate of reaction increases with increase in temperature. Certain reactions which would not occur at ordinary temperature do so when heated. E.g. standardization of oxalic acid solution using potassium permanganate solution occurs when the oxalic acid is heated to 333K. At high temperature, molecules are more energetic and have greater chances of colliding with each other.

Effect of catalyst: catalysts speed up chemical reactions without being used up.

EQUILIBRIUM

Equilibrium represents a balance between two opposing reactions. Few chemical reactions proceed in only one direction, most are reversible at least to some extent. Chemical equilibrium is achieved when the rates of the forward and reverse reactions are equal and the concentrations of the reactants and products remain constant. Chemical equilibrium is a dynamic process and it is also called dynamic equilibrium. As such, it can be likened to the movement of hikers at a busy hiking resort, where the number of hikers climbing the mountain is equal to the number coming down the slopes. Although there is a constant transfer of hikers, the number of people at the top and the number at the bottom of the slope do not change.

$H_2O(l) \rightleftharpoons H_2O(g)$

EQUILIBRIUM CONSTANT

We can generalize this phenomenon with the following reaction at equilibrium:

- In a reaction $aA + bB \rightleftharpoons cC + dD$, the equilibrium constant is expressed as:
- $Kc = \dfrac{[C]^c\,[D]^d}{[A]^a\,[B]^b}$

Equilibrium constant, Kc, is the ratio of the equilibrium concentrations of products over the equilibrium concentrations of reactants each raised to the power of their stoichiometric coefficients. Equilibrium constant is used in calculating equilibrium concentrations and predicting the direction of reactions.

Assumptions of reaction based on value of Kc:

- If Kc is > 1 then the reaction is product favored i.e. the mixture will contain more products than reactants
- If Kc is < 1, then the reaction is reactant favored i.e. the mixture will contain more reactants than products.
- If Kc = 1, the mixture will contain approximately equal amount of reactant and product.

Example 1

Gaseous nitrogen dioxide forms dinitrogen tetroxide according to this equation:

$2NO_2(g) \rightleftharpoons N_2O_4(g)$. $[NO_2] = 0.016$ M and $[N_2O_4] = 0.042$ M. What is the value of the equilibrium constant for the reaction?

LE CHÂTELIER'S PRINCIPLE

There is a general rule that helps us to predict the direction in which an equilibrium reaction will move when a change in concentration, pressure, volume, or temperature occurs. The rule, known as **Le Châtelier's principle**, states that if an external stress is applied to a system at equilibrium, the system adjusts in such a way that the stress is partially offset as the system reaches a new equilibrium position. The word "stress" here means a change in concentration, pressure, volume, or temperature that removes the system from the equilibrium state.

REACTION QUOTIENT

The reaction quotient, Q, for the general reaction is given as follows:

For $aA + bB \rightleftharpoons cC + dD$

$$Q = \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b}$$

The reaction quotient, Q, has the same form as the equilibrium constant, Kc, but it involves specific values that are not necessarily equilibrium concentrations.

$Q < Kc$ forward reaction predominates until equilibrium is established

$Q = Kc$ system is at equilibrium

$Q > Kc$ reverse reaction predominates until equilibrium is established

NB: The reaction quotient is sometimes called the mass action expression. When the forward reaction occurs to a greater extent than the reverse reaction, we say that a net forward reaction has occurred.

Example 2

$2NO_2(g) \rightleftharpoons N_2O_4(g)$

$$Q = \frac{[N_2O_4]}{[NO_2]^2}$$

Write the Reaction Quotient Expressions for these reactions:

i. $3O_2 \rightleftharpoons 2O_3$

ii. $N_2 + 3H_2 \rightleftharpoons 2NH_3$

iii. $4NH_3 + 7O_2 \rightleftharpoons 4NO_2 + 6H_2O$

EFFECT OF CONCENTRATION

Changing the concentrations of reactant and products in a chemical reaction does not change the equilibrium constant. Instead, the reaction shifts according to Le Chatelier's principle to establish a relative ratio of concentration. This technique is used frequently to obtain more products from a chemical reaction by adding more reactants and taking away more products.

EFFECT OF TEMPERATURE

This depends whether the reaction is endothermic or exothermic. For endothermic, the equilibrium constant increases causing forward shift with increase in temperature. In exothermic reaction, the equilibrium constant decreases causing backward shift with increase in temperature.

EFFECT OF PRESSURE

The pressure of gases is related to concentration. Changing the pressure by increasing or decreasing the volume of the container will disturb an equilibrium system.. If pressure increases and volume decreases, the system shifts to the side with a smaller number of gas molecules. This reestablishes equilibrium by decreasing the pressure. If pressure decreases and volume increases, the system shifts to the side with a greater number of gas molecules. Like in Haber process if the pressure is increased the equilibrium will shift to the right producing more ammonia.

EFFECT OF CATALYSTS

Catalysts do not change the value of the equilibrium constant. Catalysts change the rate of approach to equilibrium based on the activation energy of the slow step in the mechanism. Catalysts can make it faster for a system to reach equilibrium. The presence of a catalyst does not shift the equilibrium; it only causes the reaction to reach equilibrium faster. This is due to the fact that catalysts only lower activation energies.