CHAPTER TWELVE

THE RATE OF CHEMICAL REACTIONS:

INTRODUCTION:

- The rate of a chemical reaction is the amount of product which is formed per unit (within a limited) time, or the amount of reactant which is used per unit time.
- In order to measure it, we choose a property of the reaction which indicates how far the reaction has gone, and observe the way in which that property changes with time.
- For example, in a reaction in which colourless reactants change into coloured products, the rate of intensity of the colour increase will give us the rate of the reaction.
- Consider now the hypothetical reaction: A + B -> C + D.
- At the beginning of the reaction, there will be no C or D i.e. their concentration will be zero.
- As the reaction proceeds, C and D are formed and their concentrations increase.
- At the same time, the concentrations of A and B decrease.
- The rate may be defined as the decrease in the concentration of A or B with time, or the increase in the concentration of C or D with time.

Factors affecting the rate of a chemical reaction:

Factors which affect the rate of a chemical reaction are:

(1) The physical state of the reactants:

- The rate of a chemical reaction depends on whether the reactants are in the solid, liquid or the gaseous state.

(2) Concentration:

- According to the collision theory, for molecules of the reactants to form products, they must collide with each other. -
Also it is not all the collisions which lead to the formation of products, since it is only the effective ones which can lead to the formation of the products. - The rate of a reaction increases when the concentration of the reactants increases. - This is due to the fact when there is an increase in the concentration of the reactants, there will

be an increase in the molecular collisions of the reactants, and as such, there will be an increase in the number of effective collisions which can lead to the formation of products.

(3) Temperature:

- The rate of a chemical action increases with temperature or when the temperature increases.
- This is due to the fact that with increase in temperature, there will be an increase in the average kinetic energy of the molecules, leading to an increase in the number of molecular collisions, and as such an in increase in the number of effective collisions, which can lead to the formation of products.

(4) Catalyst:

- A catalyst is a substance which increases the rate of chemical reaction, but remains unchanged at the end of the reaction.
- The rate of a chemical reaction increases when an appropriate catalyst is used.
- For reactants to be able to react, the energy they possess must be more than the activation energy for that particular reaction.
- Since he work of the catalyst is to lower this activation energy, then more reactants can react to form products, leading to an increase in the rate of the reaction.

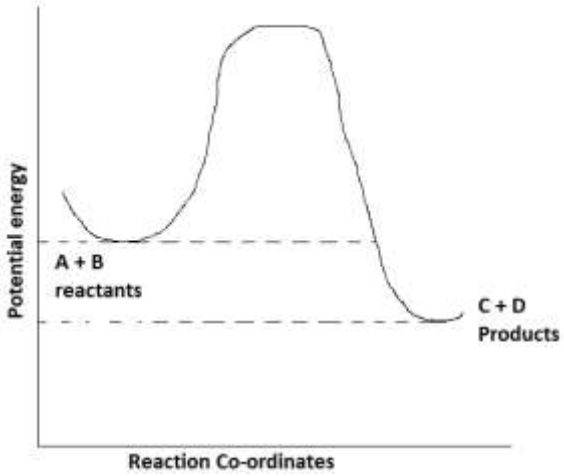
(5) The effect of medium:

- The medium in which a reaction occurs influences its rate.
- For example, there are certain reactions which occur at a faster rate, when the p.H of the medium increases.

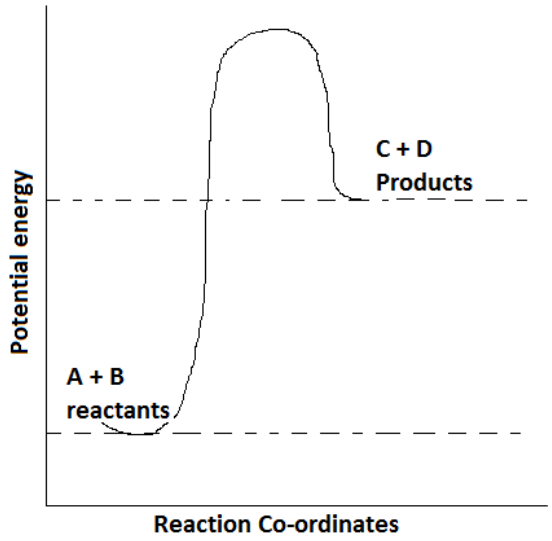
(6) The surface area:

- The rate increases when the surface area of the reactants is increased.

Exothermic reaction: This is the type of reaction in which the energy of the products is less than that of the reactants. In other words, the reaction proceeds with heat being lost to the surrounding.



<u>Endothermic reaction:</u> This is the type of reaction in which the energy possessed by the products, is greater than that possessed by the reactants. In other words, the reaction proceeds with the absorption of heat from the surrounding.



<u>Irreversible reaction:</u>

- This is the type of reaction in which the reactants can react to form products, but the products cannot react to form reactants.
- In other words, the reaction can only occur in the forward direction, but cannot occur in the backward direction.
- For example, consider the reaction A + B -> C + D. - If the reaction occurs in the forward direction, then A and B react to form C and D. - But if the reaction occurs in the backward direction, then C and D react to form A and B.

Reversible reaction:

- This is the type of reaction in which the reactants can react to form products, while the products can also react to form the reactants.
- In other words, the reaction can occur in both the forward and the backward directions,
- An example of such a reaction is A + B ⇌ C + D.
- While A and B can react to form C and D, C and D can also react to form A and B.

Equilibrium:

- Consider the reversible reaction A + B ⇌ C + D.
- At the beginning of the reaction, we only have A and B being present, while C and D are absent.
- In other words, the concentrations of C and D will be zero at the beginning of the reaction.
- As the reaction proceeds, little amounts of the products will be formed, i.e. the concentrations of C and D will start increasing and the reaction will occur in the forward direction. - As the reaction occurs in the forward direction, some of the products formed,, i.e. C and D will react to form A and B, which implies that the backward reaction will also occur.
- Since initially the rate of the forward reaction is greater than that of the backward reaction, more products will be formed than reactants.
- But with time, the rate of the backward reaction increases and the amount of reactants formed also increases.
- At a particular point, the rates of the forward and the backward reactions will become equal to each other, and the rate of formation of the products will be equal to that of the formation of the reactants.
- When the rates of the backward and the forward reactions become equal to each other, then the reaction is said of be in equilibrium or dynamic equilibrium, and the concentrations of the substances become constant over a time period.
- If the equilibrium shifts to the right or in the forward direction, then the forward reaction will be favoured more than the backward one, and more products will be formed than reactants.
- If the equilibrium shifts to the left or in the backward direction, then the backward reaction will be favoured more than the forward one, and more reactants will be formed than products.

The effect of concentration on equilibrium:

- Consider the reaction $A + B \rightleftharpoons C + D$.

(1) If the concentration of B is decreased, the equilibrium will shift to the left, so as to cause the necessary increase in the concentration of B, so as to maintain the equilibrium.

(2) If the concentration of A is decreased, the equilibrium will shift to the left, causing the necessary increase in the concentration of A, for the equilibrium to be maintained.

(3) If the concentration of B is increased, the equilibrium will shift to the right so that more products will be formed than the reactants.

- This will cause the necessary decrease in the concentration of B, in order for the equilibrium to be maintained.

(4) If the concentration A is increased, equilibrium shifts right in order for the concentration of A to decrease.

(5) If the concentration of C is decreased, equilibrium shifts to the right in order for more C to be formed, so as to cause an increase in its concentration, for the equilibrium to be maintained.

(6) On the other hand, if the equilibrium shifts left in order to cause a decrease in the concentration of C.

(7) If the concentration of D is increased, equilibrium shifts left.

(8) Lastly, if the concentration of D is decreased, then equilibrium shifts right.

(Q1) Assuming that reaction $2HCl + 2Na \rightleftharpoons 2NaCl + H_2$ is in equilibrium, explain what will happen if

(a) more HCl is added.

(b) more Na is added.

(c) NaoH solution is added.

(d) more NaCl is added.

Soln:

(a) If more HCl is added, then the concentration of HCl will be increased, causing the equilibrium to shift to the right so as to cause a decrease in the concentration of HCl.

- More products will be formed than the reactants.

(b) – If more Na is added, then the concentration of Na will b increased.

- The equilibrium will shift right, in order to cause a decrease in the concentration of Na.

(c) If NaoH is added, it will react with part of the HCl, since NaoH is a base.

- The concentration of HCl will therefore be decreased.
- Equilibrium therefore shifts left, causing more reactants to be formed than products, so as to increase the concentration of HCl.

(d) If more NaCl is added, then the concentration of NaCl will be increased.

- Equilibrium will therefore shift to the left, in order to cause a decrease in the concentration of the NaCl.

The effect of temperature:

- The effect of temperature will depend on whether the reaction is exothermic or endothermic.
- If a reversible reaction is exothermic, then the forward reaction proceeds with the liberation or the release of heat.
- On the other hand, if such a reaction is endothermic, then the forward reaction proceeds with the absorption of heat,
- If the $\triangle$H (the entropy change) of a reaction is negative, then the reaction is exothermic, and if $\triangle$H is positive, then the reaction is endothermic. - If a reaction is exothermic, then the reaction proceeds in the forward reaction within the liberation of heat (i.e. with reference to the forward direction, it does not like heat).
- Increasing temperature will not favour such a reaction in the forward direction, but rather it is the backward reaction which will be favoured. - With reference to the same exothermic reaction, decreasing temperature will rather favour the forward reaction. - With respect to an endothermic reaction, the forward reaction proceeds with the absorption of heat and increasing temperature will therefore favour the forward reaction.
- For such a reaction decreasing temperature will not favour the forward reaction, but rather it is the backward reaction which will be favoured.

N/B: (1) If a reaction is exothermic in the forward direction, then it will be endothermic in the backward direction.