

## CHAPTER NOTES – CHAPTER 19

### Reaction Rates and Equilibrium

#### Goals : To gain an understanding of :

1. Collision theory and Rate laws.
2. Reaction mechanisms.
3. Entropy changes.
4. Equilibrium and Le Chatelier's Principle.

#### NOTES:

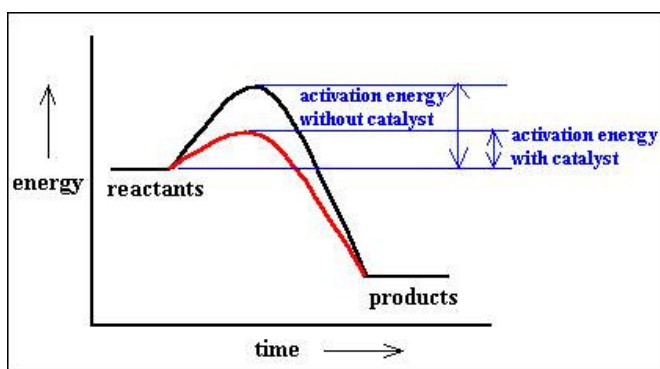
Reaction rate is the number of reactant particles that react to form product particles per unit of time. Four factors which affect reaction rate are :

a. Temperature - the higher the temperature, the faster the particles move and the more likely the reactant particles will have enough energy to overcome the energy barrier to form products. A general rule is that for every 10 °C rise in temperature the reaction rate doubles.

b. Concentration - the higher the concentration the higher the reaction rate. The more particles present, the more likely they are going to collide with each other and react.

c. Particle size - the smaller the particle size, the greater the surface area. The increase in surface area makes it more likely that reactant particles will collide to react to form product particles. The best way to increase the surface area of a solid reactant is to dissolve it. This breaks down the solid into very small particles (atoms, ions or molecules). For this reason homogeneous mixtures (solutions) react faster than heterogeneous mixtures.

d. Catalysts - catalysts reduce the activation energy needed for a reaction to occur and so increase the number of effective collisions. Catalysts speed up reaction rate but do not enter into the reaction and are therefore not changed or used up. This makes them very effective molecules for creating change. Our body has many enzymes (organic catalysts) which speed up reaction rates allowing the body to control its metabolism.

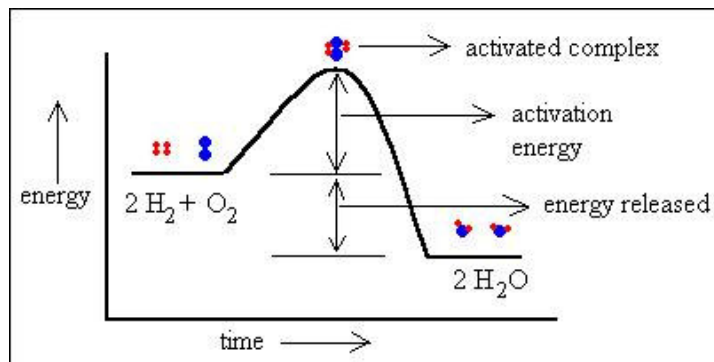


The collision theory states that in order for reactants to react (change into products) they must collide or come into contact with each other. In order for a collision to be effective (cause the change) it must have two things:

a. Enough energy to overcome the energy barrier to break the bonds of the reactant particles and to form the bonds of the product particles. This is called activation energy.

b. Proper orientation - reactant particles must collide in the correct positions to break and reform bonds

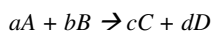
An activated complex is the temporary combination of reactant particles formed as they collide with each other with enough energy to overcome the energy barrier.



Reactions involving homogeneous mixtures of reactants are faster than reactions involving heterogeneous mixtures of reactants because of the smaller size and therefore greater surface area of reactants as explained in 1c above.

Inhibitors are substances which slow or stop chemical reactions

The rate law is a mathematical expression relating the rate of a reaction to the concentrations of reactants. It involves a specific rate constant ( $k$ ) which is a proportionality constant relating the concentrations of reactants to their respective concentrations. For example, in the reaction



where  $a$ ,  $b$ ,  $c$  and  $d$  represent the coefficients of the balanced equation and  $A$  and  $B$  and  $C$  and  $D$  represent the reactants and products respectively. The rate law for this reaction can be written as

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

The brackets  $[ ]$  indicate the molar concentration of the reactant. The exponents  $x$  and  $y$  are determined experimentally.

Determining order of reaction :

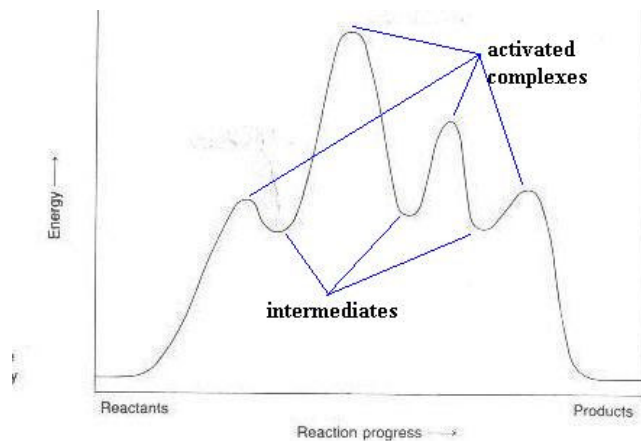
The order of a reactant is the power to which the concentration of the reactant must be raised to produce the amount of product indicated by the reaction. observe the following data for the above reaction :

<i>Initial [A]</i>	<i>Initial [B]</i>	<i>Initial rate(mol/L-s)</i>
0.02	0.01	0.003
0.04	0.01	0.012
0.04	0.02	0.024

Comparing the first two lines of data we see that  $[A]$  is doubled (.02 to .04) and the reaction rate is increased by a factor of four(.003 to .012). The order of reactant A is therefore 2, or second order ( $2^2=4$ ). If  $[B]$  is doubled the reaction rate is doubled and it is therefore a first order reactant ( $2^1=2$ ). the overall reaction order is the sum of each of the orders of the reactants and is therefore a third order reaction. The rate law equation for this reaction can then be written as

$$\text{rate} = k[A]^2[B]$$

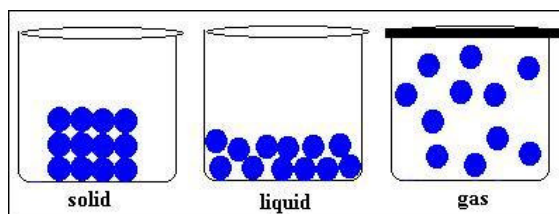
A reaction mechanism is the pathway that a reaction takes as the reactants change into the products. Elementary reactions are reactions in which the reaction mechanism is a single step. Fig 4-1 above shows a reaction progress curve for an elementary reaction. Complex reactions involve two or more steps or elementary reactions and have one or more intermediates and two or more activated complexes.



Intermediates are the temporary products of elementary reactions within a complex reaction. They correspond to the valleys in the reaction progress curve of a complex reaction (see above diagram).

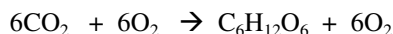
Entropy is a measure of the disorder of a system. The law of disorder states that things move spontaneously in the direction of maximum chaos or disorder. For a practical example just think of your locker. It does not spontaneously neaten itself (that takes work), it spontaneously becomes chaotic (messy).

In general solids have the least amount of entropy (are often well ordered and crystalline). Liquids have less order as the molecules can move more freely about, and gases have the most entropy. Therefore the entropy of a substance will increase as it changes from a solid to a liquid to a gas.



As temperature of a substance increases entropy will also increase due to the increased motion and chaotic movement of the particles of the substance.

Entropy will also increase when a substance is divided into more parts. Think of a jigsaw puzzle. The puzzle in the box (many individual pieces) has much more entropy than the assembled puzzle (one "piece"). In chemical equations there is more entropy on the side that has a greater number of pieces. In the equation for photosynthesis



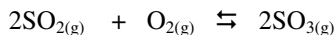
There is more entropy in the reactants (12 molecules) and less entropy in the products (7 molecules).

Two factors which determine the spontaneity of chemical reactions are the changes in entropy and the changes in enthalpy. An increase (positive value for  $S^\circ$ ) in entropy favors a spontaneous reaction and a decrease in enthalpy (negative  $H^\circ$  value) favors a spontaneous reaction.

Enthalpy ( $H$ ) is a measure of the heat content of a substance at a given temperature and pressure. Standard enthalpy ( $H^\circ$ ) is the enthalpy of a substance at  $25^\circ\text{C}$  and 1 atm of pressure. The equation for the change in standard enthalpy is

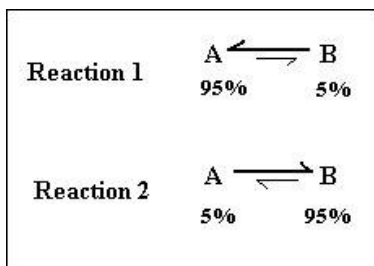
$$\Delta H^\circ = H^\circ(\text{products}) - H^\circ(\text{reactants})$$

Reversible reactions are reactions in which the reactants change into the products and the products change into the reactants simultaneously. reversible reactions are indicated by a double yields sign between reactants and products as follows :



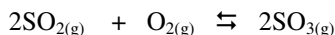
Chemical equilibrium is the condition in which the forward and backward rates of a reversible reaction occur at the same rate causing no net change in the amounts of reactants and products present. This condition is dependent on the reaction environment. A change in conditions such as temperature or pressure may cause the reaction to shift its equilibrium position towards the reactants or products.

The equilibrium position of a reaction is determined by the relative amounts of reactants and products at equilibrium. The equilibrium position is said to favor the reactants if at equilibrium there is more of the reactant chemicals than the product chemicals as shown in reaction 1 below. The equilibrium position is said to favor the products if at equilibrium there is more products than reactants as show in reaction 2 below.



Catalysts speed up both the forward and the reverse direction of a reversible reaction and so do not affect equilibrium position. The reaction may get to equilibrium faster with a catalyst present than absent, but the equilibrium position would be the same.

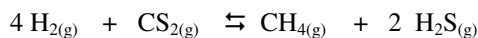
The equilibrium constant ( $K_{eq}$ ) for a reaction at equilibrium is the ratio of the product concentrations to reactant concentrations, each raised to the power of the number of moles there are in the balanced equation. For example the equation



would have the equilibrium expression of :

$$K_{eq} = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2 \times [\text{O}_2]}$$

To show another example, the equation



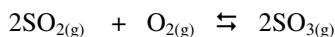
would have the equilibrium expression of :

$$K_{eq} = \frac{[\text{CH}_4] \times [\text{H}_2\text{S}]^2}{[\text{H}_2]^4 \times [\text{CS}_2]}$$

Le Châtelier's principle states that if a stress is applied to a system at equilibrium, the system will shift its equilibrium position to relieve the stress.

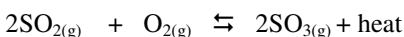
Factors which can create stress on a system at equilibrium are :

- Changes in concentration : changing the concentration of reactants or products by the addition or removal of reactants or products will shift the equilibrium position. For example if more SO<sub>2</sub> is added to the following reaction



the equilibrium position would shift to the right (products) causing more SO<sub>3</sub> to form and removing some of the added SO<sub>2</sub>. If SO<sub>3</sub> were added, the equilibrium position would shift to the left removing some of the added SO<sub>3</sub> and forming more SO<sub>2</sub> and O<sub>2</sub>. Or, if SO<sub>3</sub> were removed, the equilibrium position would shift to the right to replace the removed SO<sub>3</sub> and reduce the concentrations of the reactants. Chemists can use this to increase the amount of product formed by removing the product of a reversible reaction.

- Changes in temperature : changing the temperature of a reaction at equilibrium will shift the equilibrium position to undo the stress of the temperature change. You can treat temperature just like a reactant or product. In the following exothermic reaction the heat energy (may be given in units of calories or joules) can be treated like a product.



If heat is added (temperature raised) the equilibrium position will shift to the left to remove the added heat and favor the formation of more of the reactants. If heat were removed (temperature lowered) the equilibrium position would shift to the right of favor the formation of the products.

- Changes in pressure : changing the pressure on a system at equilibrium will change the equilibrium position of reversible reactions with unequal numbers of moles of gaseous reactants and products. It will not affect nongaseous reactants or products. This is really the same as changing the concentrations of the gaseous reactants or products. Increasing the pressure on a gas compresses it increasing the density or concentration of the gas. In the equation above there are 3 moles of gaseous reactants and 2 moles of gaseous products. An increase in pressure will then increase the concentrations of the reactants more than the products and the system will shift to the right and the opposite for a decrease in pressure. For the following reaction a change in pressure would not affect the equilibrium position. The reason is that there are equal numbers of moles of gaseous reactants and products.



## The Reaction Process

### I. Reaction Mechanisms

#### A. Reaction Mechanism

1. The step-by-step sequence of reactions by which the overall chemical change occurs
2. Reactions proceed by a series of simple steps called the reaction pathway

#### B. Intermediates

1. Species that appear in some steps but not in the net equation

### II. The Two Principals of Collision Theory

- A. Particles must collide while favorably oriented
- B. Particles must collide with enough energy to disrupt the bonds of the molecules

### III. Activation Energy and the Activated Complex

#### A. Activated Complex

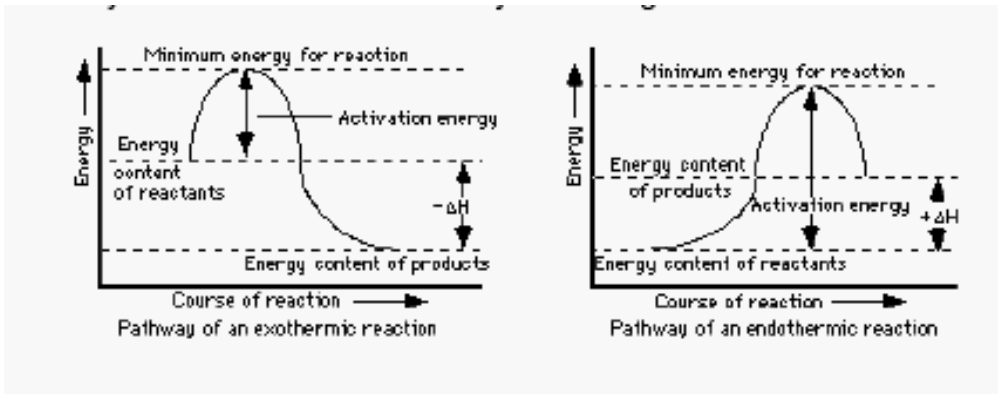
1. A transitional structure resulting from an effective collision that persists while old bonds are breaking and new bonds are forming

#### B. Activation Energy

1. The minimum energy required to transform reactants into the activated complex

#### C. Sources of Activation Energy

1. Flame, spark, high temperature, radiation
2. Once an exothermic rxn is activated (reaches the top) the energy released by the rxn sustains the rxn by activating other molecules



## Reaction Rate

### I. Rate Influencing Factors

#### A. Nature of the Reactants

1. Rate depends on the particular bonds involved

#### B. Amount of Surface

1. The more surface area of a solid exposed, the faster the rxn

#### C. Temperature

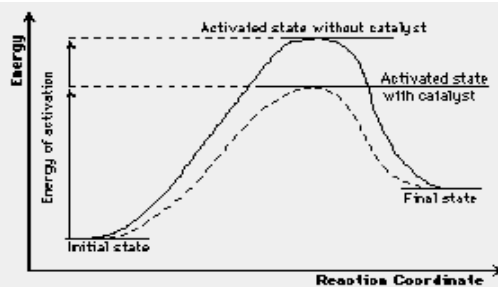
1. Rates of rxns are roughly doubled for every  $10^\circ\text{C}$  increase in temperature
  - a. increase in collision energy
  - b. increase in collision frequency

#### D. Effect of Concentration

1. Increasing concentrations of liquid or gaseous solutions usually increases rates of rxns

#### E. Presence of Catalysts

1. A catalyst is a substance of substances that increase the rate of a chemical by lowering the activation energy needed for the reaction without itself being changed
  - a. Homogeneous catalyst
    - (1) Catalyst is in the same phase as the reactants
  - b. Heterogeneous catalyst
    - (1) Catalyst in different phase from reactants



2. Catalysts provide an alternate reaction mechanism or pathway with a lower activation energy

## Le Chatelier's Principle

### A. Statement of Le Chatelier's Principle (very important!)

1. If a change is imposed on a system at equilibrium, the position of the equilibrium will shift in a direction that tends to reduce that change

### B. The Effect of Change in Concentration

1. If a reactant or product is added to a system at equilibrium, the system will shift away from the added component (it will attempt to "use up" the added component)
2. If a reactant or product is removed from a system at equilibrium, the system will shift toward the removed component (it will attempt to "replace" the removed component)

### C. The Effect of a Change in Pressure

#### 1. Ways to change pressure

- a. Add or remove a gaseous reactant or product

(1) covered above ↑

- b. Add an inert gas (one not involved in the reaction)

(1) An inert gas increases the total pressure but has no effect on the concentrations or partial pressures of the reactants or products

- c. Change the volume of the container

(1) When the volume of the container holding a gaseous system is reduced, the system responds by reducing its own volume. This is done by decreasing the total number of gaseous molecules in the system

$\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$  shifts to the right to decrease the total molecules of gas present

(2) When the container volume is increased, the system will shift so as to increase its volume

$\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$  shifts to the left to increase the total number of molecules of gas present