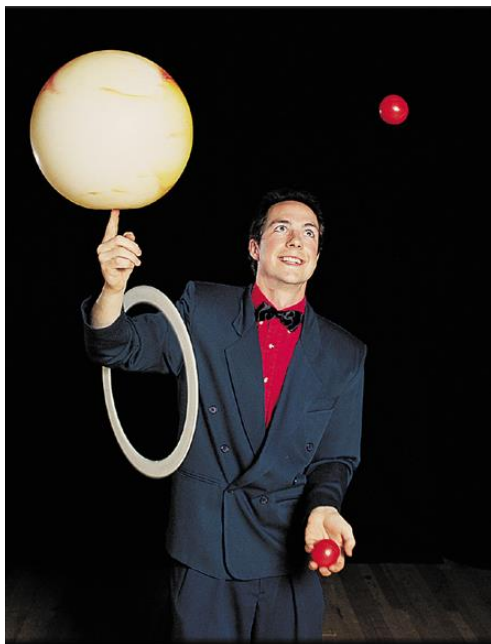
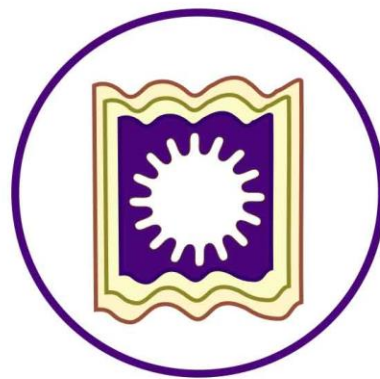


Section-A

2. Chemical Equilibrium and kinetics



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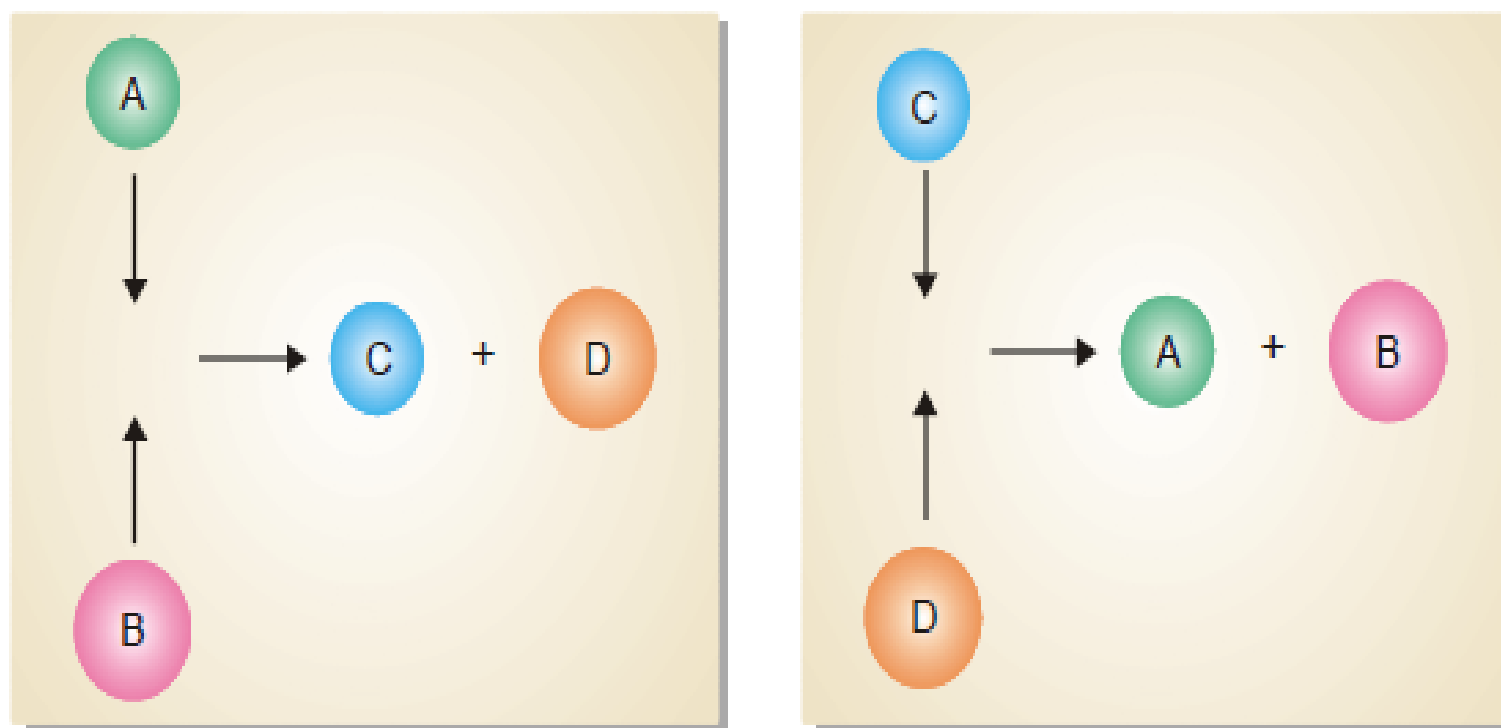
Rajshahi University

Equilibrium

- I. Dynamic Equilibrium
- II. Equilibrium Constant; K_c and K_p
- III. Homogenous vs. Heterogeneous Equilibrium
- IV. Calculation of K from Equilibrium Concentrations

Chemical Equilibrium is Dynamic Equilibrium

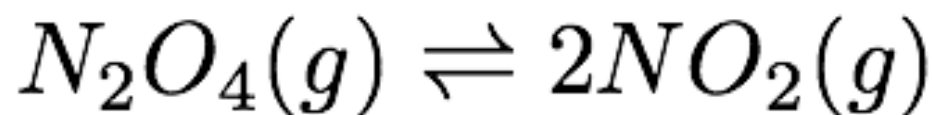
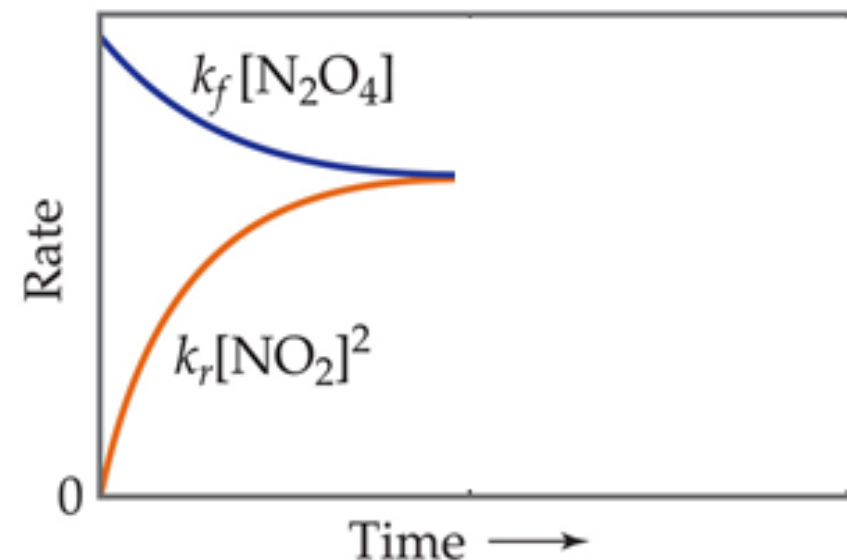
We have shown above that as the reaction $A + B \rightleftharpoons C + D$ attains equilibrium, the concentrations of A and B, as also of C and D remain constant with time. Apparently it appears that the equilibrium is dead. But it is not so. The equilibrium is dynamic. Actually, the forward and the reverse reactions are taking place at equilibrium but the concentrations remain unchanged.



■ **Figure 17.2**

Molecules of A and B colliding to give C and D, and those of C and D colliding to give A and B.

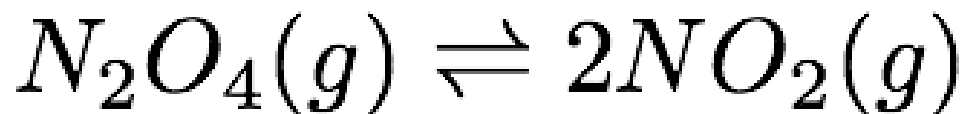
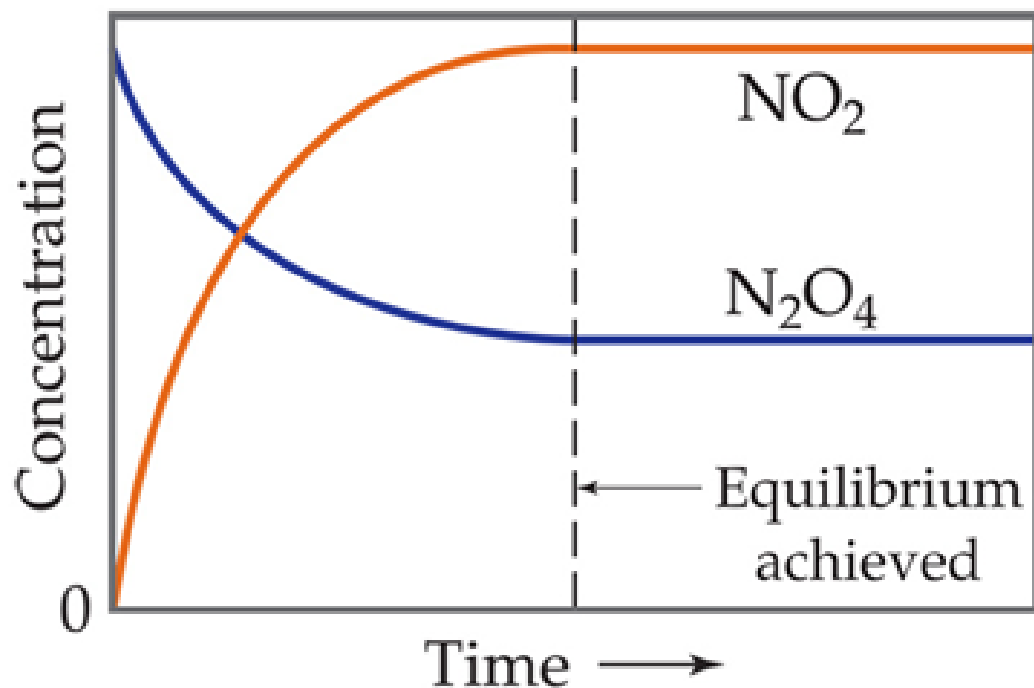
The Concept of Equilibrium



- As a system approaches equilibrium, both the forward and reverse reactions are occurring.
- At equilibrium, the forward and reverse reactions are proceeding at the same rate.

A System at Equilibrium

Once equilibrium is achieved, the *amount* of each reactant and product remains constant.

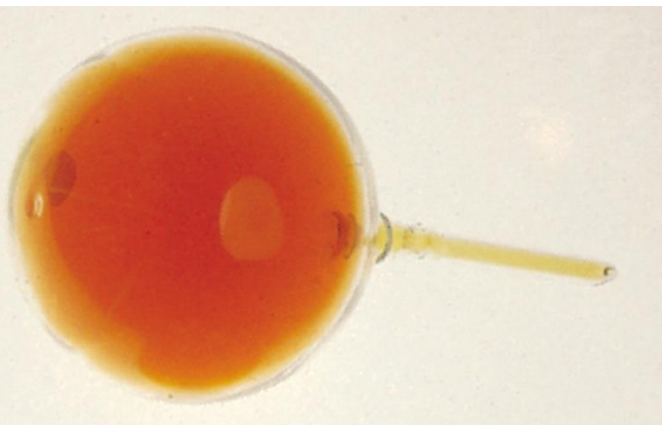
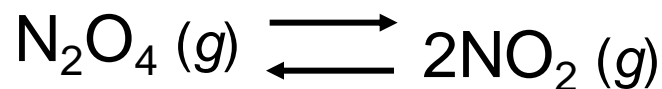


Equilibrium is a state in which there are no observable changes as time goes by.

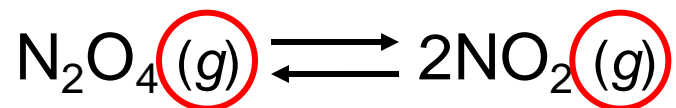
Chemical equilibrium is achieved when:

- the rates of the forward and reverse reactions are equal and they are not zero.
- the concentrations of the reactants and products remain constant

Chemical equilibrium



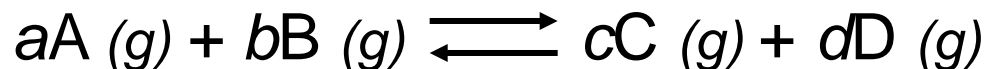
Homogenous equilibrium applies to reactions in which all reacting species **are in the same phase.**



$$K_c = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} \qquad K_p = \frac{P_{\text{NO}_2}^2}{P_{\text{N}_2\text{O}_4}}$$

In most cases

$$K_c \neq K_p$$



$$K_p = K_c(RT)^{\Delta n}$$

$$\begin{aligned} \Delta n &= \text{moles of gaseous products} - \text{moles of gaseous reactants} \\ &= (c + d) - (a + b) \end{aligned}$$

Heterogenous equilibrium applies to reactions in which reactants and products **are in different phases**.



$$K'_c = \frac{[\text{CaO}][\text{CO}_2]}{[\text{CaCO}_3]}$$

$$\begin{aligned} [\text{CaCO}_3] &= \text{constant} \\ [\text{CaO}] &= \text{constant} \end{aligned}$$

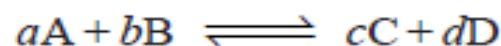
$$K_c = [\text{CO}_2] = K'_c \times \frac{[\text{CaCO}_3]}{[\text{CaO}]}$$

$$K_p = P_{\text{CO}_2}$$

The concentration of **solids** and **pure liquids** are not included in the expression for the equilibrium constant.

Equilibrium Constant Expression for a Reaction in General Terms

The general reaction may be written as



where a , b , c and d are numerical quotients of the substance, A, B, C and D respectively. The equilibrium constant expression is

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

where K_c is the **Equilibrium constant**. The general definition of the equilibrium constant may thus be stated as : **the product of the equilibrium concentrations of the products divided by the product of the equilibrium concentrations of the reactants, with each concentration term raised to a power equal to the coefficient of the substance in the balanced equation.**

How to Write the Equilibrium Constant Expression?

- (1) Write the balanced chemical equation for the equilibrium reaction. By convention, the substances on the left of the equation are called the **reactants** and those on the right, the **products**.
- (2) Write the product of concentrations of the 'products' and raise the concentrations of each substance to the power of its numerical quotient in the balanced equation.
- (3) Write the product of concentrations of 'reactants' and raise the concentration of each substance to the power of its numerical quotient in the balanced equation.
- (4) Write the equilibrium expression by placing the **product concentrations in the numerator** and **reactant concentrations in the denominator**. That is,

$$K_c = \frac{\text{Product of concentrations of 'products' from Step (2)}}{\text{Product of concentrations of 'reactants' from Step (3)}}$$

EQUILIBRIUM CONSTANT EXPRESSION IN TERMS OF PARTIAL PRESSURES

When all the reactants and products are gases, we can also formulate the equilibrium constant expression in terms of partial pressure. The relationship between the partial pressure (p) of any one gas in the equilibrium mixture and the molar concentration follows from the general ideal gas equation

$$pV = nRT \quad \text{or} \quad p = \left(\frac{n}{V} \right) RT$$

The quantity $\frac{n}{V}$ is the number of moles of the gas per unit volume and is simply the molar concentration. Thus,

$$p = (\text{Molar concentration}) \times RT$$

i.e., the partial pressure of a gas in the equilibrium mixture is directly proportional to its molar concentration at a given temperature. Therefore, we can write the equilibrium constant expression in terms of partial pressure instead of molar concentrations. For a general reaction



the equilibrium law or the equilibrium constant may be written as

$$K_p = \frac{(p_Y)^y (p_Z)^z}{(p_L)^l (p_M)^m}$$

Here K_p is the equilibrium constant, the subscript p referring to partial pressure. Partial pressures are expressed in atmospheres.

HOW K_c AND K_p ARE RELATED?

Let us consider a general reaction



where all reactants and products are gases. We can write the equilibrium constant expression in terms of partial pressures as

$$K_p = \frac{(p_C)^l (p_D)^m}{(p_A)^j (p_B)^k} \quad \dots(1)$$

Assuming that all these gases constituting the equilibrium mixture obey the ideal gas equation, the partial pressure (p) of a gas is

$$p = \left(\frac{n}{V} \right) RT$$

Where $\frac{n}{V}$ is the molar concentration. Thus the partial pressures of individual gases, A, B, C and D are:

$$p_A = [A] RT; p_B = [B] RT; p_C = [C] RT; p_D = [D] RT$$

Substituting these values in equation (1), we have

$$K_p = \frac{[C]^l (RT)^l [D]^m (RT)^m}{[A]^j (RT)^j [B]^k (RT)^k}$$

or

$$K_p = \frac{[C]^l [D]^m}{[A]^j [B]^k} \times \frac{(RT)^{l+m}}{(RT)^{j+k}}$$

$$K_p = K_c \times (RT)^{(l+m)-(j+k)}$$

\therefore

$$K_p = K_c \times (RT)^{\Delta n} \quad \dots(2)$$

where $\Delta n = (l+m) - (j+k)$, the difference in the sums of the coefficients for the gaseous products and reactants.

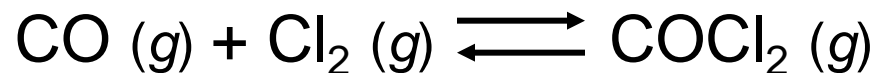
From the expression (2) it is clear that when $\Delta n = 0$, $K_p = K_c$.

Writing Equilibrium Constant Expressions

- The concentrations of the reacting species in the condensed phase are expressed in M . In the gaseous phase, the concentrations can be expressed in M or in atm.
- The concentrations of pure solids, pure liquids and solvents do not appear in the equilibrium constant expressions.
- The equilibrium constant is a dimensionless quantity.
- In quoting a value for the equilibrium constant, you must specify the balanced equation and the temperature.



The equilibrium concentrations for the reaction between carbon monoxide and molecular chlorine to form $\text{COCl}_2 (g)$ at 74°C are $[\text{CO}] = 0.012 \text{ M}$, $[\text{Cl}_2] = 0.054 \text{ M}$, and $[\text{COCl}_2] = 0.14 \text{ M}$. Calculate the equilibrium constants K_c and K_p .



$$K_c = \frac{[\text{COCl}_2]}{[\text{CO}][\text{Cl}_2]} = \frac{0.14}{0.012 \times 0.054} = 220$$

$$K_p = K_c(RT)^{\Delta n}$$

$$\Delta n = 1 - 2 = -1 \quad R = 0.0821 \quad T = 273 + 74 = 347 \text{ K}$$

$$K_p = 220 \times (0.0821 \times 347)^{-1} = 7.7$$

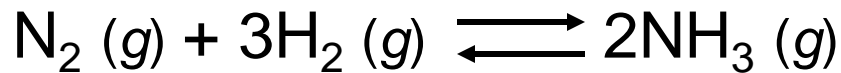
Le Châtelier's Principle

1. System starts at equilibrium.
2. A change/stress is then made to system at equilibrium.
 - Change in concentration
 - Change in volume
 - Change in pressure
 - Change in Temperature
 - Add Catalyst
3. System responds by shifting to reactant or product side to restore equilibrium.

Le Châtelier's Principle

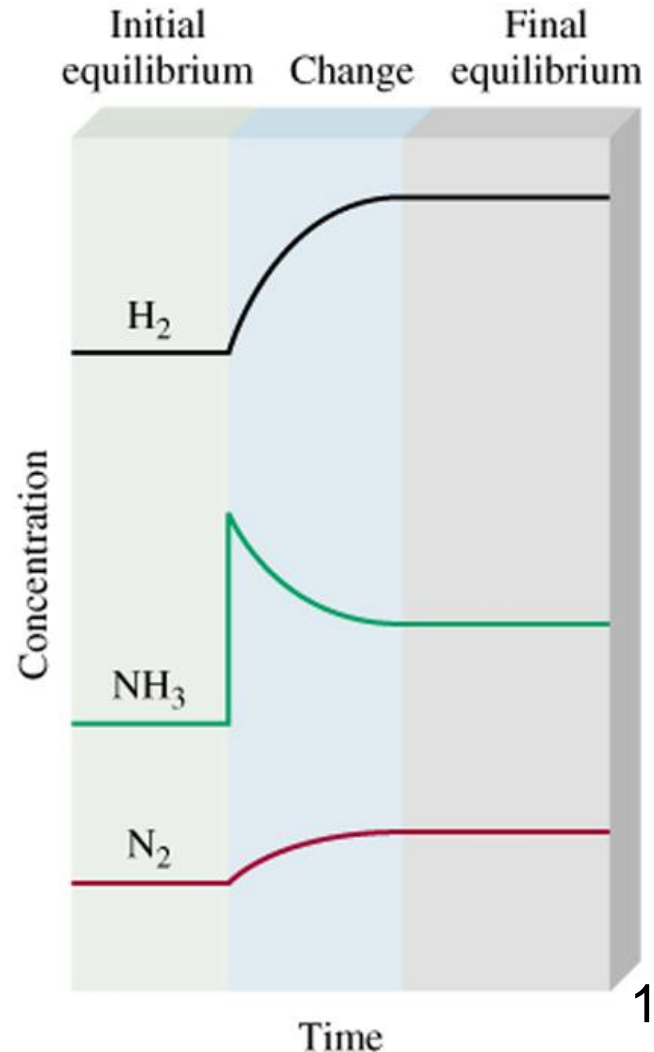
If an external stress is applied to a system at equilibrium, the system adjusts in such a way that the stress is partially offset as the system reaches a new equilibrium position.

- Changes in Concentration



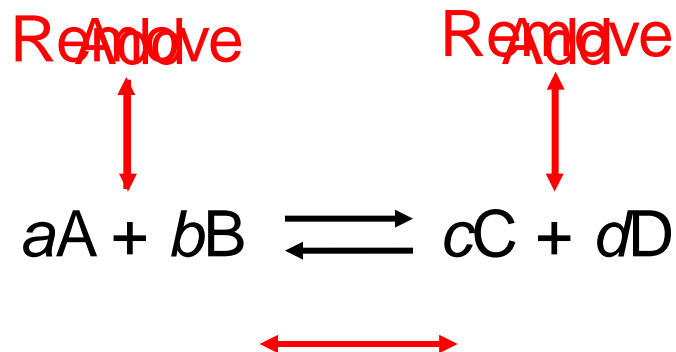
Equilibrium
shifts left to
offset stress

↑
Add
 NH_3



Le Châtelier's Principle

- Changes in Concentration continued



Change

Shifts the Equilibrium

Increase concentration of product(s)

left

Decrease concentration of product(s)

right

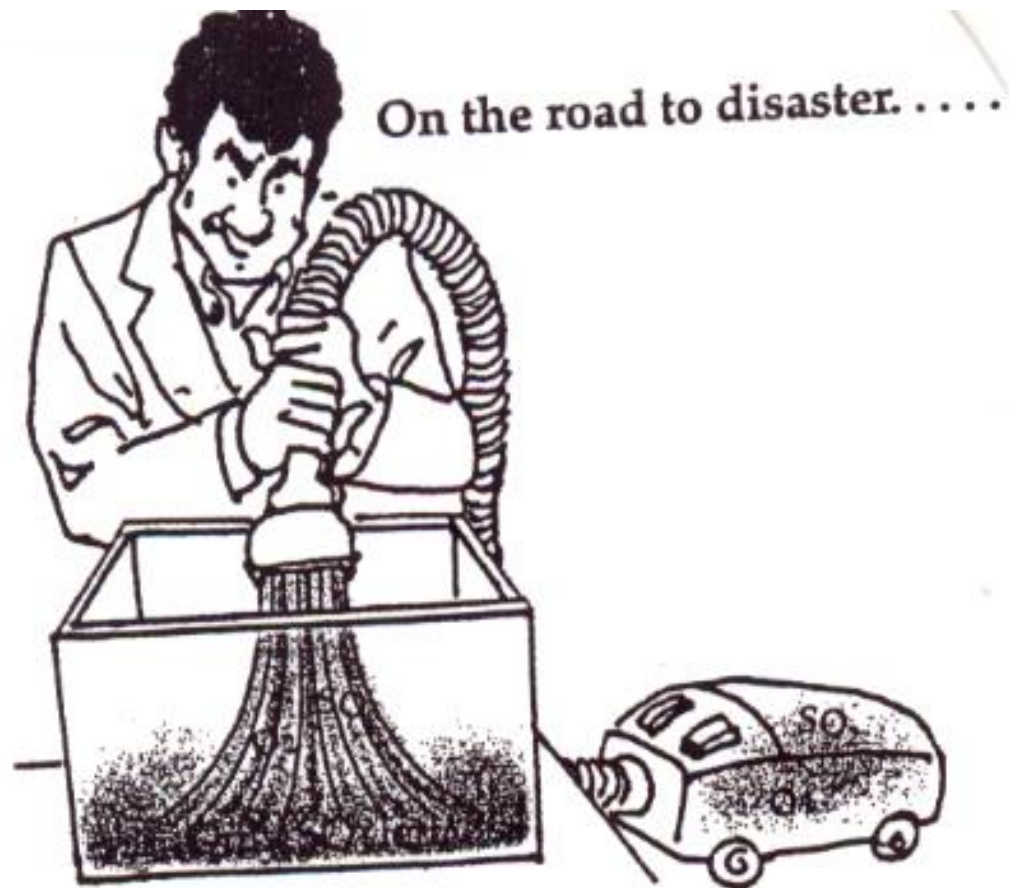
Increase concentration of reactant(s)

right

Decrease concentration of reactant(s)

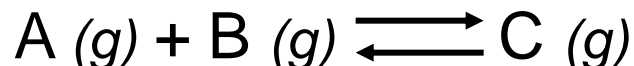
left

Le Chatelier's Principle



Le Châtelier's Principle

- Changes in Volume and Pressure
(Only a factor with gases)



Change

Shifts the Equilibrium

Increase pressure

Side with fewest moles of gas

Decrease pressure

Side with most moles of gas

Increase volume

Side with most moles of gas

Decrease volume

Side with fewest moles of gas

ORDER OF A REACTION

The order of a reaction is defined as the sum of the powers of concentrations in the rate law.

Let us consider the example of a reaction which has the rate law

$$\text{rate} = k [A]^m [B]^n \quad \dots(1)$$

The order of such a reaction is $(m + n)$.

The order of a reaction can also be defined with respect to a single reactant. Thus the reaction order with respect to A is m and with respect to B it is n . The overall order of reaction $(m + n)$ may range from 1 to 3 and can be fractional.

Examples of reaction order :

RATE LAW	REACTION ORDER
$\text{rate} = k [\text{N}_2\text{O}_5]$	1
$\text{rate} = k [\text{H}_2] [\text{I}_2]$	$1 + 1 = 2$
$\text{rate} = k [\text{NO}_2]^2$	2
$\text{rate} = k [[\text{H}_2] [\text{NO}]^2]$	$1 + 2 = 3$

The number of reactant molecules that involves in chemical reaction is called **molecularity** of a reaction.

Differences Between Order and Molecularity

Order of a Reaction

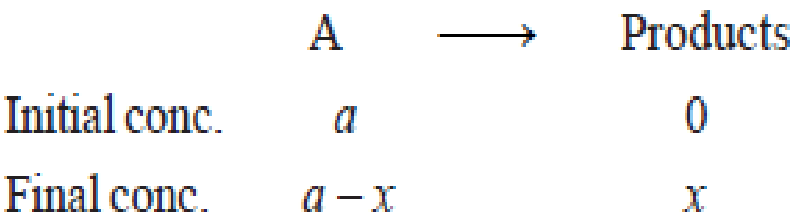
1. It is the **sum of powers** of the concentration terms in the rate law expression.
2. It is an **experimentally** determined value.
3. It can have **fractional** value.
4. It can assume **zero** value.
5. Order of a reaction can **change** with the conditions such as pressure, temperature, concentration.

Molecularity of a Reaction

1. It is number of **reacting species** undergoing simultaneous collision in the elementary or simple reaction.
2. It is a **theoretical** concept.
3. It is always a **whole number**.
4. It **can not** have zero value.
5. Molecularity is **invariant** for a chemical equation.

ZERO ORDER REACTIONS

In a zero order reaction, rate is independent of the concentration of the reactions. Let us consider a zero-order reaction of the type



$$\text{Rate of reaction} = \frac{-d[A]}{dt} = k_0[A]^0$$

or
$$\frac{dx}{dt} = \frac{-d(a - x)}{dt} = k_0(a - x)^0 = k_0$$

On integrating we get

$$k_0 = \frac{x}{t} \text{ or } x = k_0t$$

where k_0 is the rate constant of a zero-order reaction, the unit of which is concentration per unit time. In zero order reaction, the rate constant is equal to the rate of reaction at all concentrations.

FIRST ORDER REACTIONS

Let us consider a first order reaction



Suppose that at the beginning of the reaction ($t = 0$), the concentration of A is a moles litre⁻¹. If after time t , x moles of A have changed, the concentration of A is $a - x$. We know that for a first order reaction, the rate of reaction, dx/dt , is directly proportional to the concentration of the reactant. Thus,

$$\frac{dx}{dt} = k(a - x)$$

or
$$\frac{dx}{a - x} = k dt \quad \dots(1)$$

Integration of the expression (1) gives

$$\int \frac{dx}{a - x} = \int k dt$$

or
$$- \ln(a - x) = kt + I \quad \dots(2)$$

where I is the constant of integration. The constant k may be evaluated by putting $t = 0$ and $x = 0$.

Thus,

$$I = - \ln a$$

Substituting for I in equation (2)

$$\ln \frac{a}{a - x} = kt \quad \dots(3)$$

or
$$k = \frac{1}{t} \ln \frac{a}{a - x}$$

Changing into common logarithms

$$k = \frac{2.303}{t} \log \frac{a}{a-x} \quad \dots(4)$$

The value of k can be found by substituting the values of a and $(a-x)$ determined experimentally at time interval t during the course of the reaction.

Sometimes the integrated rate law in the following form is also used :

$$k = \frac{2.303}{t_2 - t_1} \log \frac{(a - x_1)}{(a - x_2)}$$

where x_1 and x_2 are the amounts decomposed at time intervals t_1 and t_2 respectively from the start.

SECOND ORDER REACTIONS

Let us take a second order reaction of the type



Suppose the initial concentration of A is a moles litre⁻¹. If after time t , x moles of A have reacted, the concentration of A is $(a - x)$. We know that for such a second order reaction, rate of reaction is proportional to the square of the concentration of the reactant. Thus,

$$\frac{dx}{dt} = k(a - x)^2 \quad \dots(1)$$

where k is the rate constant, Rearranging equation (1), we have

$$\frac{dx}{(a - x)^2} = k dt \quad \dots(2)$$

On integration, it gives

$$\frac{1}{a - x} = kt + I \quad \dots(3)$$

where I is integration constant. I can be evaluated by putting $x = 0$ and $t = 0$. Thus,

$$I = \frac{1}{a} \quad \dots(4)$$

Substituting for I in equation (3)

$$\begin{aligned} \frac{1}{a - x} &= kt + \frac{1}{a} \\ kt &= \frac{1}{a - x} - \frac{1}{a} \end{aligned}$$

Thus

$$k = \frac{1}{t} \cdot \frac{x}{a(a - x)}$$

This is the integrated rate equation for a second order reaction.

HALF-LIFE OF A REACTION

Reaction rates can also be expressed in terms of **half-life** or **half-life period**. It is defined as : the time required for the concentration of a reactant to decrease to **half its initial value**.

In other words, half-life is the time required for one-half of the reaction to be completed. It is represented by the symbol $t_{1/2}$ or $t_{0.5}$.

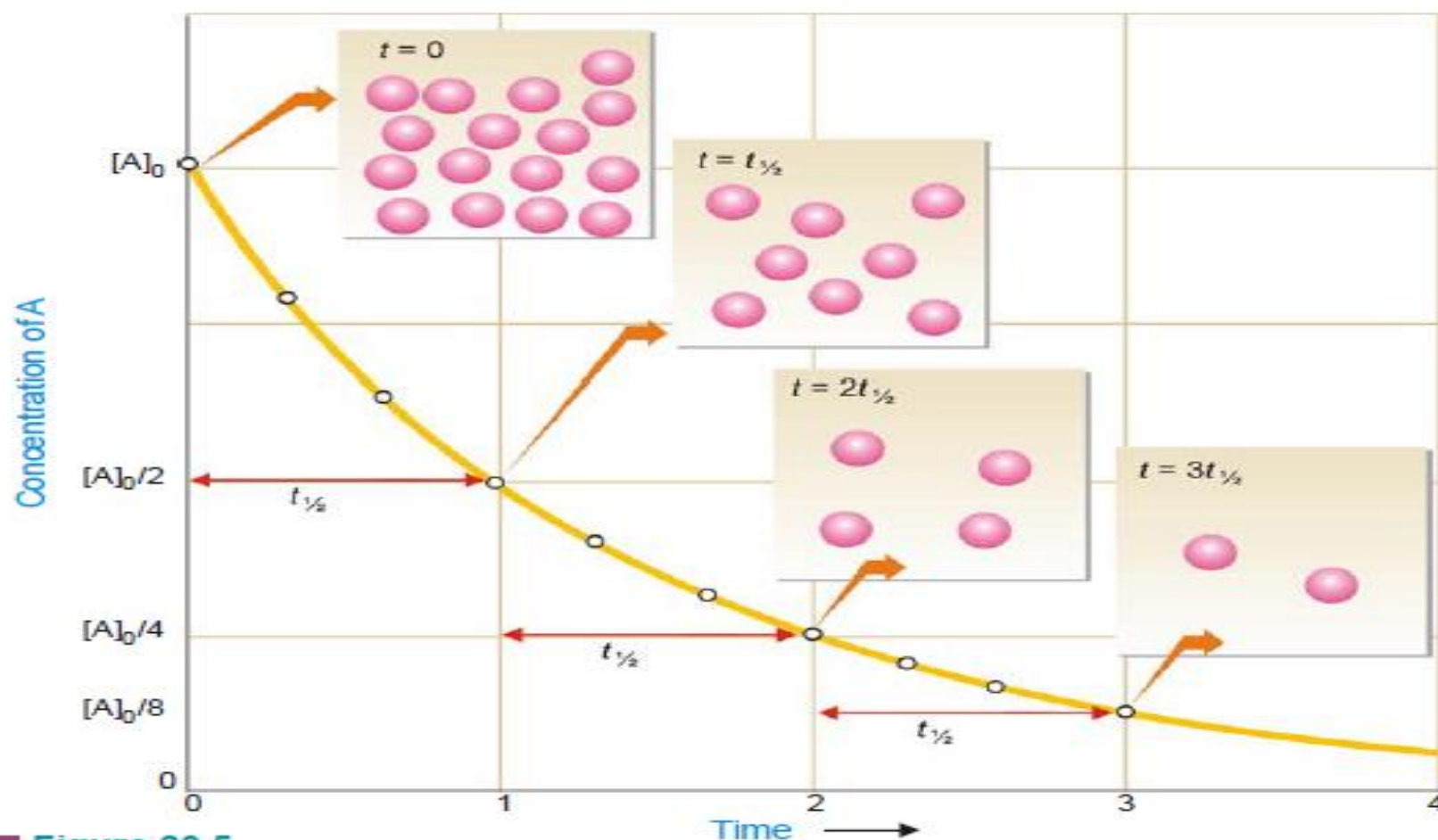


Figure 20.5

First-order half-life. Concentration of a reactant A as a function of time for a first-order reaction. The concentration falls from its initial value, $[A]_0$, to $[A]_0/2$ after one half-life, to $[A]_0/4$ after a second half-life, to $[A]_0/8$ after a third half-life, and so on. For a first-order reaction, each half-life represents an equal amount of time.

Calculation of Half-life of a First order Reaction

The integrated rate equation (4) for a first order reaction can be stated as :

$$k = \frac{2.303}{t} \log \frac{[A]_0}{[A]}$$

where $[A]_0$ is initial concentration and $[A]$ is concentration at any time t . Half-life, $t_{1/2}$, is time when initial concentration reduces to $\frac{1}{2}$ i.e.,

$$[A] = \frac{1}{2}[A]_0$$

Substituting values in the integrated rate equation, we have

$$k = \frac{2.303}{t_{1/2}} \log \frac{[A]_0}{1/2[A]_0} = \frac{2.303}{t_{1/2}} \log 2$$

or
$$t_{1/2} = \frac{2.303}{k} \log 2 = \frac{2.303}{k} \times 0.3010$$

or
$$t_{1/2} = \frac{0.693}{k}$$

It is clear from this relation that :

- (1) half-life for a first order reaction is independent of the initial concentration.
- (2) it is inversely proportional to k , the rate-constant.

HOW TO DETERMINE THE ORDER OF A REACTION

There are at least four different methods to determine the order of a reaction.

(1) Using integrated rate equations

The reaction under study is performed by taking different initial concentrations of the reactant (a) and noting the concentration ($a - x$) after regular time intervals (t). The experimental values of a ,

$(a - x)$ and t are then substituted into the integrated rate equations for the first, second and third order reactions. The rate equation which yields a constant value of k corresponds to the correct order of the reaction. This method of ascertaining the order of a reaction is essentially a method of hit-and-trial but was the first to be employed. It is still used extensively to find the order of simple reactions.

(2) Graphical method

For reactions of the type $A \rightarrow \text{products}$, we can determine the reaction order by seeing whether a graph of the data fits one of the integrated rate equations.

In case of First order

We have already derived the integrated rate equation for first order as

$$\ln \frac{a}{a - x} = kt$$

Simplifying, it becomes

$$\begin{array}{ccccc} \ln(a - x) & = & -kt & + & \ln a \\ \uparrow & & \uparrow & & \uparrow \\ y & = & mx & + & b \end{array}$$

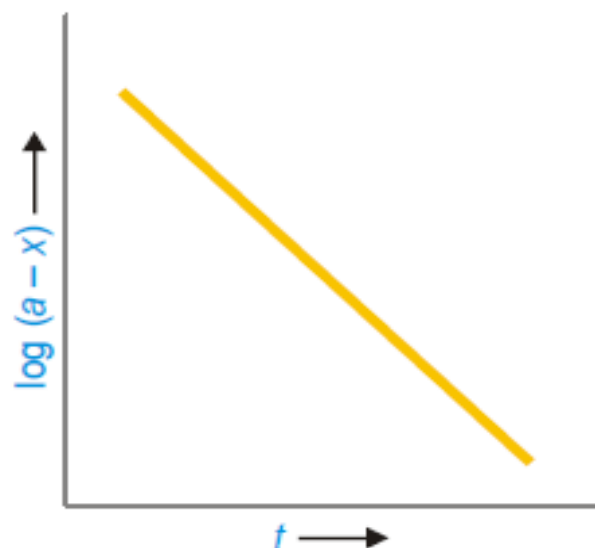
Thus the two variables in the first order rate equation are :

$$\ln \frac{a}{a - x} \text{ and } t$$

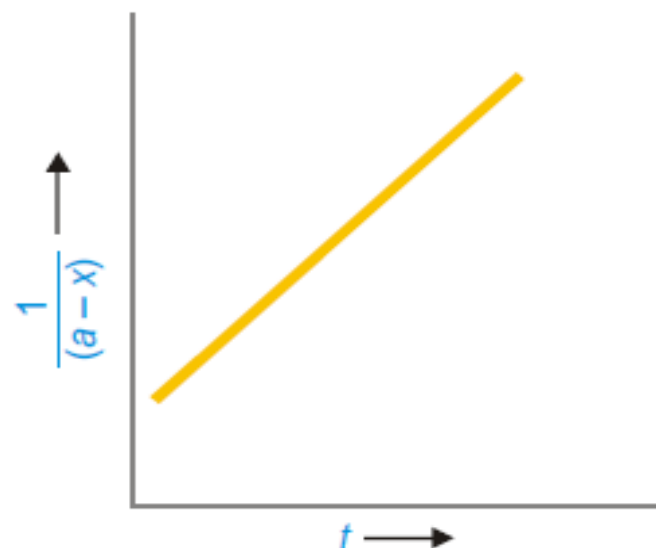
Hence, if $\ln \frac{a}{a - x}$ is plotted against t and straight line results (Fig. 20.7), the corresponding reaction is of the first order. However, if a curve is obtained, the reaction is not first order.

$$a - x$$

Hence, if $\ln \frac{a}{a-x}$ is plotted against t and straight line results (Fig. 20.7), the corresponding reaction is of the first order. However, if a curve is obtained, the reaction is not first order.



■ **Figure 20.7**
Plot of $\log(a - x)$ against t for a first order reaction.



■ **Figure 20.8**
Plot of $1/(a - x)$ against t for a second order reaction.

In case of Second order

We have already shown that second order rate equation can be written as

$$\begin{array}{ccccc} \frac{1}{a-x} & = & kt & + & \frac{1}{a} \\ \uparrow & & \uparrow & & \uparrow \\ y & = & mx & + & b \end{array}$$

This is the equation of a straight line, $y = mx + b$. Here the two variables are

$$\frac{1}{a-x} \text{ and } t$$

Thus when $\frac{1}{a-x}$ is plotted against t and we get a straight line (Fig. 20.8), the reaction is second order. In case a curve is obtained, the reaction is not second order.

(3) Using half-life period

Two separate experiments are performed by taking different initial concentrations of a reactant. The progress of the reaction in each case is recorded by analysis. When the initial concentration is reduced to one-half, the time is noted. Let the initial concentrations in the two experiments be $[A_1]$ and $[A_2]$, while times for completion of half change are t_1 and t_2 respectively.

Calculation of order of reaction. We know that half-life period for a first order reaction is independent of the initial concentration, $[A]$. We also know :

$$\text{half-life} \propto \frac{1}{[A]} \quad \text{for 2nd order reaction}$$

$$\text{half-life} \propto \frac{1}{[A]^2} \quad \text{for 3rd order reaction}$$

$$\text{half-life} \propto \frac{1}{[A]^{n-1}} \quad \text{for } n\text{th order reaction}$$

Substituting values of initial concentrations and half-life periods from the two experiments, we have

$$t_1 \propto \frac{1}{[A_1]^{n-1}} \quad t_2 \propto \frac{1}{[A_2]^{n-1}}$$

and

$$\frac{t_2}{t_1} = \left[\frac{A_1}{A_2} \right]^{n-1}$$

$$(n-1) \log \left[\frac{A_2}{A_1} \right] = \log \left[\frac{t_1}{t_2} \right]$$

Solving for n , the order of reaction

EFFECT OF INCREASE OF TEMPERATURE ON REACTION RATE

It has been found that generally an increase of temperature increases the rate of reaction. As a rule, an increase of temperature by 10°C doubles the reaction rate. Thus the ratio of rate constants of a reaction at two different temperatures differing by 10 degree is known as **Temperature Coefficient**.

$$\begin{aligned} \text{i.e., Temperature Coefficient} &= \frac{k_{35^{\circ}}}{k_{25^{\circ}}} = \frac{k_{308}}{k_{298}} \\ &= 2 \text{ to } 3 \end{aligned}$$

It has been found that **generally an increase of temperature increases the rate of reaction**. As a rule, an increase of temperature by 10°C doubles the reaction rate.

Temperature Dependence of Reaction Rate and Arrhenius Equation

We know that the kinetic energy of a gas is directly proportional to its temperature. Thus as the temperature of a system is increased, more and more molecules will acquire necessary energy greater than E_a to cause productive collisions. This increases the rate of the reaction.

In 1889, Arrhenius suggested a simple relationship between the rate constant, k , for a reaction and the temperature of the system.

$$k = A e^{-E_a/RT} \quad \dots(1)$$

This is called the **Arrhenius equation** in which A is an experimentally determined quantity, E_a is

the activation energy, R is the gas constant, and T is Kelvin temperature.

Taking natural logs of each side of the Arrhenius equation, it can be put in a more useful form :

$$\ln k = - \frac{E_a}{RT} + \ln A \quad \dots(2)$$

$$\log k = \frac{- E_a}{2.303 RT} + \log A \quad \dots(3)$$

If k_1 and k_2 are the values of rate constants at temperatures T_1 and T_2 respectively, we can derive

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303 R} \left[\frac{T_2 - T_1}{T_1 T_2} \right] \quad \dots(4)$$

Arrhenius equation is valuable because it can be used to calculate the activation energy, E_a if the experimental value of the rate constant, k , is known.

Calculation of E_a Using Arrhenius Equation

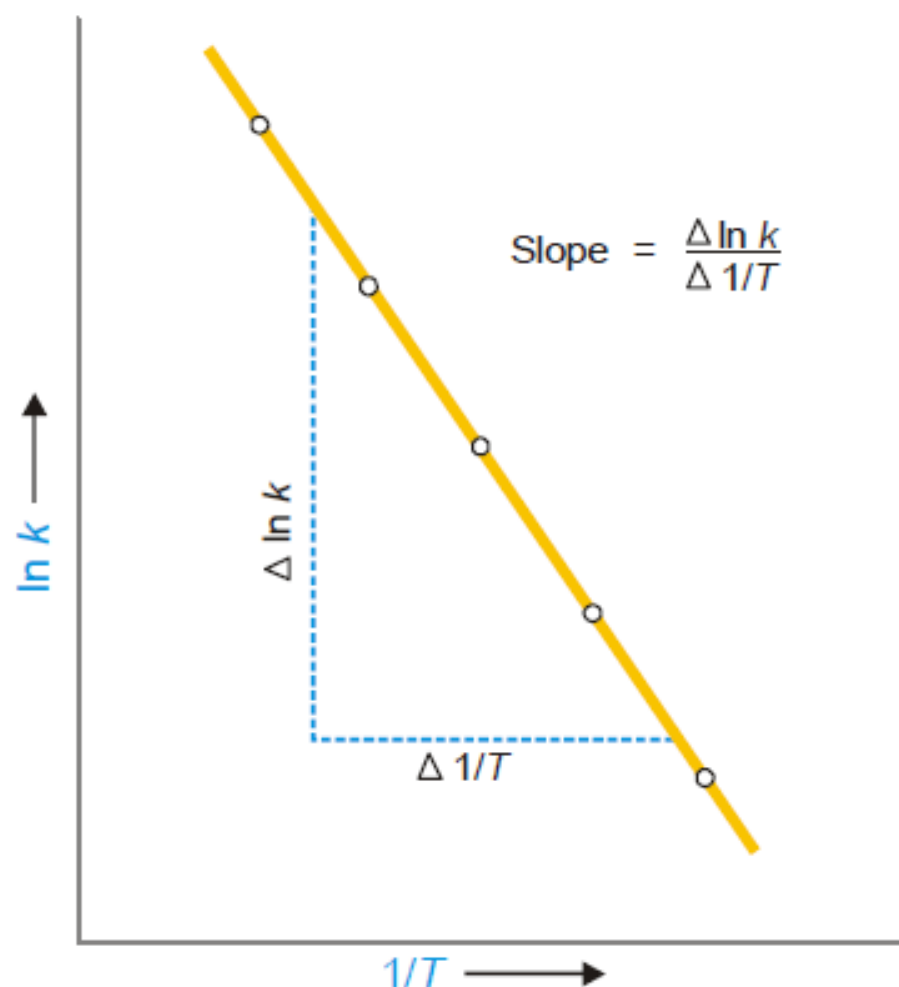
In slightly rearranged form Arrhenius equation (2) can be written as

$$\begin{array}{ccccccc} \ln k & = & - \frac{E_a}{R} \left(\frac{1}{T} \right) & + & \ln A & & \dots(3) \\ \uparrow & & \uparrow & & \uparrow & & \\ y & = & mx & + & b & & \end{array}$$

You can see that the equation (3) is that of a straight line, $y = mx + b$. The two variables in this equation are $\ln k$ and $1/T$.

Thus if we plot the natural logarithm of k against $1/T$, we get a straight line (Fig. 20.11). From the slope of the line, we can calculate the value of E_a .

$$\text{Slope} = -\frac{E_a}{R}$$



■ **Figure 20.11**

The plot of $\ln k$ versus $1/T$ gives a straight line. The slope of line $\Delta \ln k / \Delta 1/T$ gives E_a using the expression given above.

Calculation of E_a from the Values of k at Two Temperatures

The rate constant, k , is measured at two temperatures. E_a , is then calculated using the formula that can be derived as follows from equation (3) above.

At temperature T_1 , where the rate constant is k_1 ,

$$\ln k_1 = -\frac{E_a}{RT_1} + \ln A \quad \dots(1)$$

At temperature T_2 , where the rate constant is k_2 ,

$$\ln k_2 = -\frac{E_a}{RT_2} + \ln A \quad \dots(2)$$

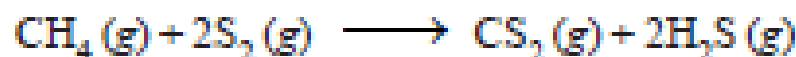
Subtracting the equation (1) from the equation (2), we have

$$\begin{aligned} \ln k_2 - \ln k_1 &= \left(-\frac{E_a}{RT_2} + \ln A \right) - \left(-\frac{E_a}{RT_1} + \ln A \right) \\ &= -\frac{E_a}{RT_2} + \frac{E_a}{RT_1} \end{aligned}$$

$$\text{or} \quad \ln \left(\frac{k_2}{k_1} \right) = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad \text{or} \quad \log \frac{k_2}{k_1} = \frac{E_a}{2.303 R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

Thus the values of k_1 and k_2 measured at T_1 and T_2 can be used to find E_a .

SOLVED PROBLEM. The gas-phase reaction between methane (CH_4) and diatomic sulphur (S_2) is given by the equation



At 550°C the rate constant for this reaction is $1.1 \text{ l mol}^{-1} \text{ sec}$ and at 625°C the rate constant is $6.4 \text{ l mol}^{-1} \text{ sec}$. Calculate E_a for this reaction.

SOLUTION

Here $k_1 = 1.1 \text{ litre mol}^{-1} \text{ sec.}$ $T_1 = 550 + 273 = 823 \text{ K}$
 $k_2 = 6.4 \text{ litre mol}^{-1} \text{ sec.}$ $T_2 = 625 + 273 = 898 \text{ K}$

Substituting the values in the equation

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\ln\left(\frac{6.4}{1.1}\right) = \frac{E_a}{8.3145 \text{ JK}^{-1} \text{ mol}^{-1}} \left(\frac{1}{823 \text{ K}} - \frac{1}{898 \text{ K}}\right)$$

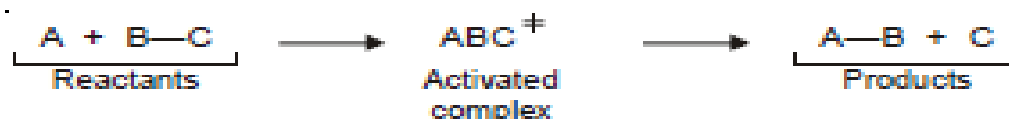
Solving for E_a , gives

$$\begin{aligned} E_a &= \frac{(8.3145 \text{ JK}^{-1} \text{ mol}^{-1}) \ln\left(\frac{6.4}{1.1}\right)}{\left(\frac{1}{823 \text{ K}} - \frac{1}{898 \text{ K}}\right)} \\ &= 1.4 \times 10^5 \text{ J/mol} \end{aligned}$$

TRANSITION STATE THEORY

The transition state or activated complex theory was developed by Henry Eyring (1935). This theory is also called the absolute rate theory because with its help it is possible to get the absolute value of the rate constant. The transition state theory assumes that simply a collision between the reactant molecules does not really cause a reaction. During the collision, the reactant molecules form a transition state or activated complex which decomposes to give the products.

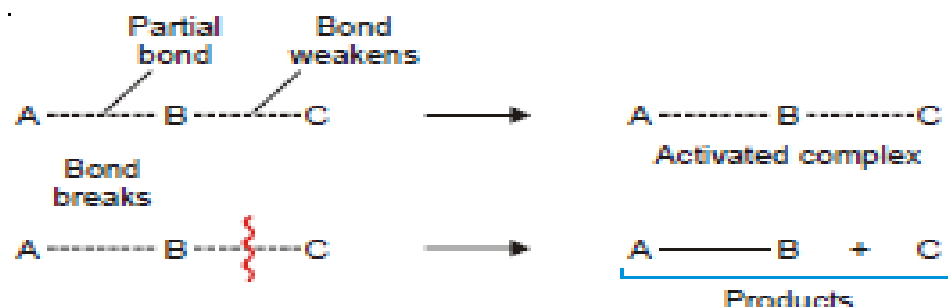
Thus,



The double dagger superscript (\ddagger) is used to identify the activated complex.

The transition state theory may be summarised as follows :

- (1) In a collision, the fast approaching reactant molecules (A and BC) slow down due to gradual repulsion between their electron clouds. In the process the kinetic energy of the two molecules is converted into potential energy.
- (2) As the molecules come close, the interpenetration of their electron clouds occurs which allows the rearrangement of valence electrons.
- (3) A partial bond is formed between the atoms A and B with corresponding weakening of B – C bond. This leads to formation of an activated complex or transition state. The activated complex is momentary and decomposes to give the products (A–B + C)



The activated complex theory may be illustrated by the reaction energy diagram (Fig. 20.13).

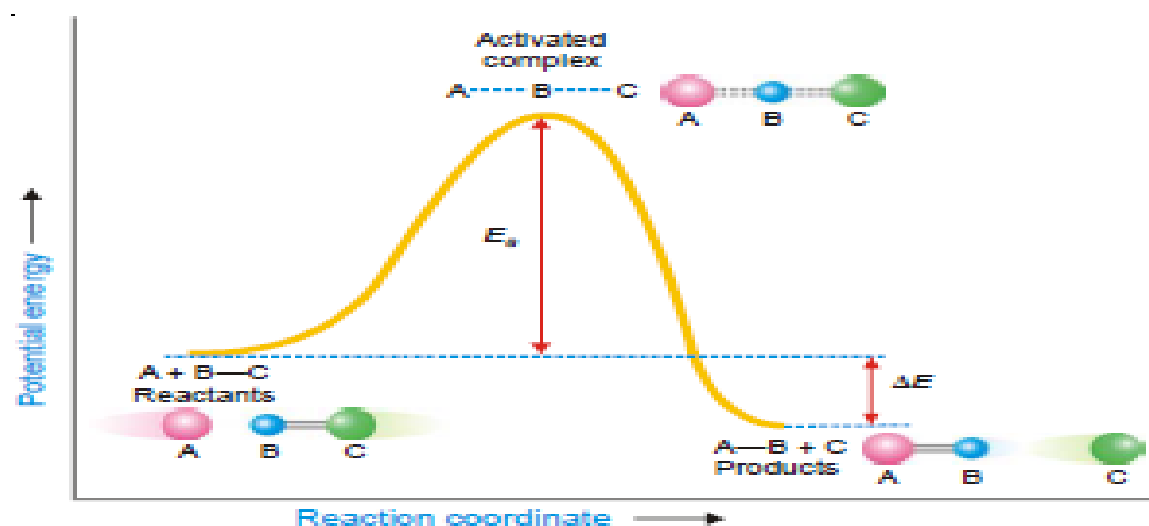


Figure 20.13
Change of potential energy during a collision between the reactant molecules for an exothermic reaction.

Here the potential energy of the system undergoing reaction is plotted against the **reaction coordinate** (the progress of the reaction). The difference in the potential energy between the reactants and the activated complex is the **activation energy**, E_a . The reactants must have this minimum energy to undergo the reaction through the transition state.

As evident from the energy diagram, energy is required by the reactants to reach the transition state. Also, the energy is obtained in passing from the transition state to the products. If the potential energy of the products is less than that of the reactants (Fig. 20.14) the energy obtained in going from the activated complex to products will be more than the activation energy (E_a). Thus such a reaction will be **exothermic**.

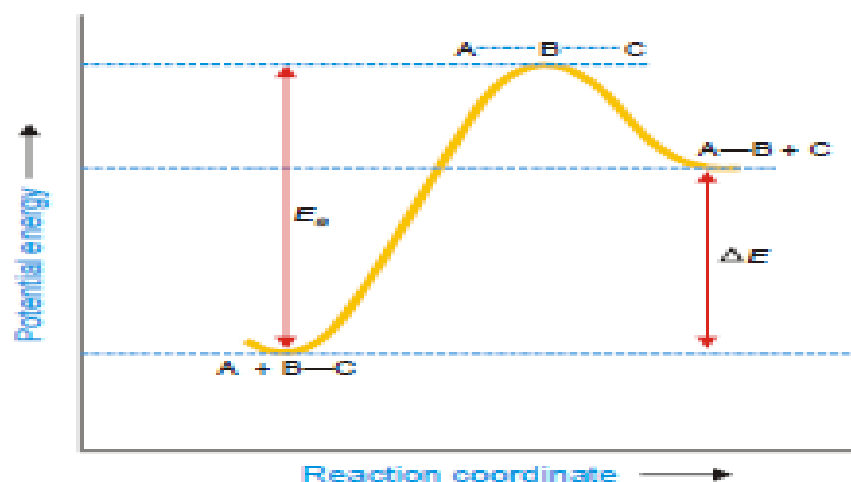
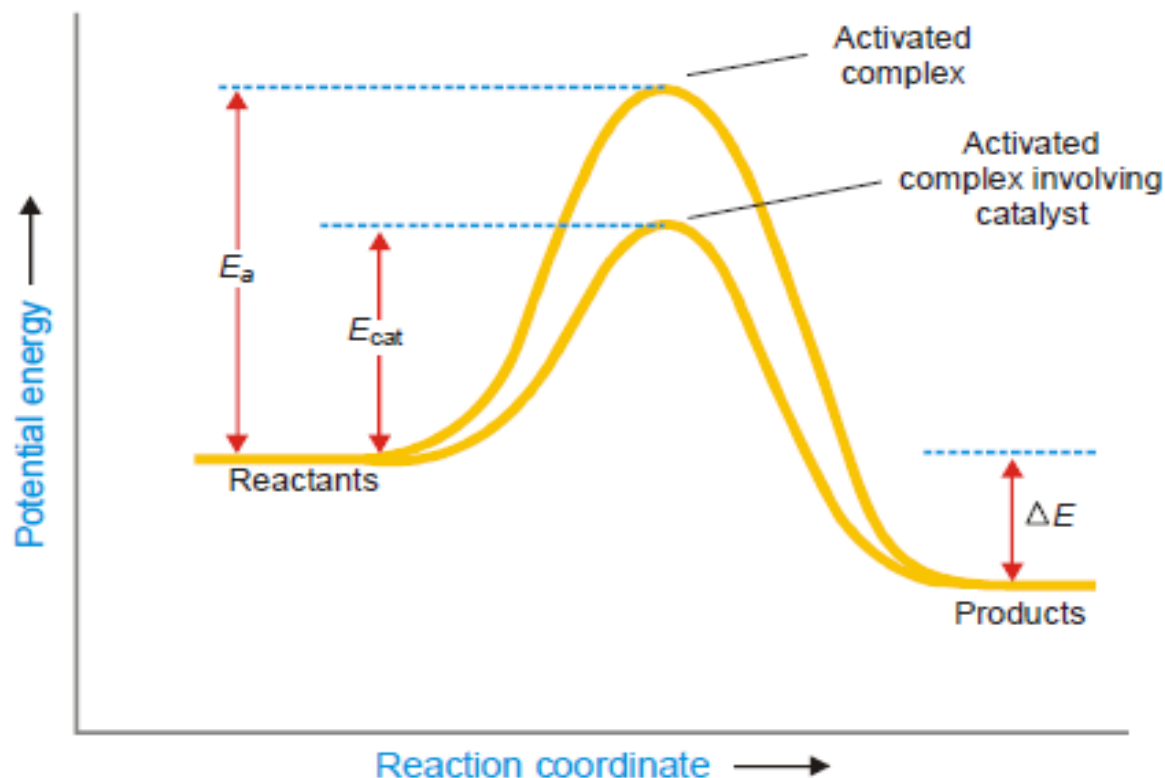


Figure 20.14
A potential energy diagram for an endothermic reaction.

ACTIVATION ENERGY AND CATALYSIS

We know that for each reaction a certain energy barrier must be surmounted. As shown in the energy diagram shown in Fig. 20.15, the reactant molecules must possess the activation energy, E_a , for the reaction to occur.



■ **Figure 20.15**

Energy diagram for a catalysed and uncatalysed reaction showing a lowering of activation energy by a catalyst.

The catalyst functions by providing another pathway with lower activation energy, E_{cat} . Thus a much large number of collisions becomes effective at a given temperature. Since the rate of reaction is proportional to effective collisions, the presence of a catalyst makes the reaction go faster, other conditions remaining the same. It may be noted from the above diagram that although a catalyst lowers the activation energy, the energy difference, ΔE , between products and reactants remains the same.